Synthesis and Characterization of Nanoporous Carbon

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Abstract
A method for the construction of highly-ordered, nanoporous carbon was adopted. The method utilized evaporation induced self-assembly of amphiphilic triblock copolymers in a phenolic resin carbon precursor. A variety of pore sizes with diameters around 4 nm were obtained and a representative subset is presented here. The material is characterized with Transmission Electron Microscopy (TEM) and gas adsorption isotherms. TEM image simulation was done for a variety of focus settings in attempt to offer constraints on size measurements made on real images.

Introduction
Lithium borohydride (LiBH$_4$) as a hydrogen storage material has been an active area of research$^{1,2}$. Although LiBH$_4$ has a high capacity for hydrogen storage, the pressure and temperature requirements of the cycling process make it an impractical solution for widespread adoption in hydrogen fueled vehicles$^3$. As part of a larger project that aimed to study the effects of nano-confinement on these parameters, it was necessary to construct a nanoporous carbon (NPC) framework. This manuscript will focus on the preparation and characterization of the NPC.

To provide motivation for working with these materials, a summary of results from the work our group has published will be given$^{4,5}$. First, by confining the LiBH$_4$ into pores with a diameter of a few nanometers in a carbon framework, the particle size was substantially limited and the behavior significantly changed from its bulk material counterpart. Once melted into the nanopores, the LiBH$_4$ lost its crystalline structure and remained amorphous despite re-cooling. As a result, the typical structural transition from orthorhombic to hexagonal at 115ºC was not observed in calorimetry, nor a defining melting point. Most importantly, whereas the bulk material begins to only melt at around 284ºC, our nano-confined material begins to release its hydrogen and decompose at 220ºC. For comparison, the bulk material decomposes around 460ºC. The effects of nano-confining the material in a NPC framework can lead to drastic changes in behavior. Whether the effects are caused by the size-limitation due to nano-confinement, interactions with the carbon, or some combination is not clear. To systematically study the effects of pore size on the system, it was necessary to make nanoporous materials with a variety of average pore sizes but with a narrow size distribution for a given batch.

Outline of Preparation Techniques
We want to create a well-controlled, solid structure on the nano-scale. Specifically, we want long and narrow, hollow tubes of a diameter around a few nanometers in an otherwise solid framework. This is accomplished through the self-assembly of molecules in a background framework. Once this is done, thermopolymerization locks the structure of the framework. Next, one removes the self-assembling molecules.

Following a well established method$^6$, we use a phenolic resin/resol as our template. Under particular ratios of phenol to formaldehyde, cross-linking is possible to a high degree, which results in high thermal stability. Amphiphilic (parts hydrophilic, others hydrophobic) polymers are used as the self-assembly molecules. They also strongly react with the template, so it's expected to form
highly-ordered polymer nano-structures.

Self-assembly is achieved using a technique called Evaporation-Induced Self-Assembly (EISA). The resol/polymer mixture is in an ethanol solvent. The solvent is then allowed to evaporate. This process gives a changing concentration of the amphiphilic polymer, resulting in clustering and eventually the creation of liquid-crystalline mesophases. The final structure is determined by the ratio of resol to polymer and the ratios used here result in hexagonally ordered columnar tubes of polymer.

Once self-assembly is undergone and the structures are formed, the material is then heated to allow cross-linking of the template, essentially locking in the structure. Once cross-linked, the material can now be annealed at an even higher temperature so that the molecules used for self-assembly are removed and only the nanoporous framework is left behind. Finally, annealing at an even higher temperature removes all but the carbon atoms.

**Transmission Electron Microscope (TEM) Analysis**

Images were taken using a Philips EM430 High-Resolution TEM. A small amount of NPC powder was mixed with ethanol solution. Then a few drops were placed onto a lacy carbon coated copper TEM grid. Once the ethanol is evaporated, small particles of NPC remain.

![Figure 1. TEM image of NPC looking (a) parallel and (b) perpendicular to pore channels](image)

Figure 1 shows two different views of the NPC; 1a looks downward into the pores and 1b is perpendicular to the pores, showing a stripe-like pattern. Under bright field and under-focus imaging conditions, holes and low-density regions reveal themselves as bright on the image and dense regions as dark. The hexagonal packing structure and long-range order are clearly observed.

Obtaining and interpreting images like those shown above is non-trivial. Keeping in mind that these images are obtained by transmission, the only way to observe features like those seen in the figure is if the particle is aligned in a very particular way. In the case of Fig. 1a, the pore channels must be parallel to the beam direction. Since a sample holder with a single-axis tilt was used, one must rely on luck and perseverance. To obtain the stripe-like pattern seen in Fig. 1b, the columnar pores must be stacked in the direction of the beam, like turning one's hand sideways so that the fingers are aligned. This is necessary to provide a region of consistent low-density to allow contrast in electron penetration of the sample. If the particle is tilted off the ideal alignment, the features can appear elongated in the direction of tilt or disappear completely beyond a certain tilt.
Returning to the hand analogy for the stripe pattern, if the hand were rotated somewhere between flat and sideways, the fingers are no longer aligned and the transmitting electrons would face a region of more uniform density, acting to diminish contrast. These features not only make it difficult to observe the relevant properties of the sample, but also force one to be careful about drawing conclusions from measurements due to elongation effects.

A further complication arises from focus settings. There is a give-and-take between image clarity and contrast. At perfect Gaussian focus, very little contrast exists in TEM images for flat and thin particles. As one goes under-focus, contrast is gained at the expense of clarity; a typical standard is at Scherzer defocus. To obtain images like those shown above, it was necessary to go significantly below this standard setting. As the image is brought deeper under-focus, features like the bright Fresnel fringes become wider. This means that when we measure the diameter of bright spots on the image, we must be careful about calling it the pore size since it might be significantly altered by changing focus settings.

To try and quantify this effect, some image simulation work was done. A digital sample of amorphous carbon atoms was constructed with different sized holes, representative of the pores. This sample was then used in a TEM image simulator at different defocus settings. The real pore sizes defined by the digital sample were then compared to measured pore sizes on the resulting image.

![Figure 2. Simulated TEM images with defocus settings of (a) Gaussian: 0 Å, (b) Scherzer: -571 Å, and (c) Deep defocus: -3000 Å.](image)

Figure 2 demonstrates the effects of different defocus settings. Going left to right, the focus starts at zero and gets progressively more under-focused. While we gain contrast, the pore edge becomes less well-defined. The bottom-right corner of each image contains a hole with a diameter of 1 nm. In the case of deep under-focus (Fig. 2c), the bright ring is large enough to fill the entire pore, making it very bright. This may explain why real pores are more easily imaged at deep under-focus, as in Figure 1a.

When the measured pore sizes in the simulated images were compared to the real ones defined in the sample, it was found that they were larger; as the amount of defocus increased, the size discrepancy also increased. However, even when going nearly a factor of 20 below Scherzer, the average pore size measurement discrepancy was only about 0.5 nm. This provides error-bars on our pore size measurements. These results should be taken with caution, however. The actual values of defocus used in obtaining the real images are only approximately known. Further, the approximations made in the simulated image calculation may not be valid under such imaging...
conditions. Further work must be done in this area.

**Gas Adsorption**

![Figure 3. Pore Size Distribution of a NPC Sample](image)

Pore size was also measured via the BJH model using nitrogen adsorption isotherms at 77 K in a SA3100 analyzer (Coulter). The results from gas adsorption experiments agree well with pore size determination from TEM imaging.

**Discussion and Conclusions**

In sum, a reliable method outlined in the literature for creating highly-ordered NPC was successfully implemented. TEM imaging was successful in confirming the hexagonally packed nanopores and offered information on pore size. Some of the complications with pore-size measurement and defocus settings were explored with image simulation and may provide error bars on obtained values. More work needs to be done in this area to draw hard conclusions. Gas adsorption data was used as an independent measure on pore size and agreed well with values obtained from TEM analysis.

**Preparation Details**

For the synthesis of our resol precursor, the typical molar ratios of phenol/formaldehyde/NaOH was 1:2:0.1. Phenol is first melted by submerging it’s holding flask in water heated to 42ºC and stirring. Next, the NaOH catalyst is slowly dripped into the solution and allowed to stir for 10 minutes. The formaldehyde is now added by slowly dripping it into the stirring solution while maintaining a temperature below 50ºC. Once added, the solution is brought up to about 75ºC and allowed to stir for 70 minutes. Next, the resol is neutralized with diluted HCl and water is evaporated using a cold trap. Ethanol is then used as the solvent. In a typical batch, a resol with 6.1 g of phenol would be dissolved in 40 g of ethanol.

Our triblock copolymer, F127 (M_w=12 600, EO_{106}-PO_{70}-EO_{106}, Aldrich), was then dissolved in ethanol. For a typical batch that used 6.1 g of phenol for the resol, 10 g of F127 would be dissolved
in 200 g of ethanol. Next, the resol and polymer solutions would be mixed. After the addition of ethanol, there is an NaCl precipitate in the resol solution. Care was taken to minimize the amount of NaCl allowed in the mix with the polymer. Once the mixture is stirred for about 20 minutes, the solution is pored into many clean petri dishes and the ethanol is allowed to evaporate. In a typical batch that contained 10 g of polymer, between 8 to 10 petri dishes were used. The system then undergoes evaporation-induced self-assembly by allowing the petri dishes to sit at least five hours, but typically over night, in a fume hood.

Once formed, the films are thermopolymerized at 100ºC for 24 hours. The resulting hard, thin films on the petri dishes were then scraped using glass slides. This yielded a yellowish powder that was then crushed further by hand using a mortar and pestle. The next goal was to remove the self-assembled polymers, resulting in only a framework with hollowed out nanotubes in a highly-ordered, hexagonal pattern. This was achieved by heating a tubular furnace under an argon flow to 350ºC at a rate of 1 deg/min and then keeping this temperature for 4 hours. Once removed, it was desired to remove all but the carbon atoms. This was done by further heating to 900ºC at a rate of 1 deg/min and left for 5 hours. Now we have a carbon structure with highly-ordered, hollow nanotubes. Finally, the nanoporous carbon (NPC) is dried at 900ºC first for 5 hours under an argon flow, and then at 400ºC under vacuum.

The process just described produces pore diameters of around 2 nm. If an O2/N2 (O2: 2.5 % vol) flow is introduced during the calcination process, the pore size is increased to about 4 nm. The maximum heating temperature now becomes about 600ºC. Less drastic effects on pore size can result from maximum temperature control; see the literature for details6.

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**References**


**Biography**

The author is finishing his last semester in pursuit of a Masters in Physics at the University of Missouri-St. Louis. Originally from Troy, Missouri, he currently resides in St. Louis.