

## SMALL ANGLE NEUTRON AND X-RAY SCATTERING STUDIES OF CARBONS PREPARED USING INORGANIC TEMPLATES

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### ABSTRACT

Small angle neutron (SANS) and X-ray (SAXS) scattering analyses of carbons derived from organic-loaded inorganic template materials, used as anodes in lithium ion cells, have been performed. Two clays were used as templates to load the organic precursors, pillared montmorillonite (PILC), a layered silicate clay whose sheets have been permanently propped open by sets of thermally stable molecular props, and sepiolite, a natural channeled clay. Five different organic precursors were used to load the PILC: pyrene, styrene, pyrene/trioxane copolymer, ethylene and propylene, whereas only propylene and ethylene were used to load sepiolite. Pyrolysis took place at 700 °C under nitrogen. Values such as hole radius, fractal dimension, cutoff length and density of the final carbons will be compared as a function of the clay and carbon precursors.

### INTRODUCTION

In these studies, SANS and SAXS scattering techniques are used to obtain information concerning the hole radius, fractal dimension, cutoff length and density of carbons and their precursors, prepared using inorganic pillared templates. These carbons have been tested in electrochemical cells as anodes in lithium secondary batteries and proved to deliver high specific capacity (a measure of the power in mAh/g) and excellent performance in terms of the number of cycles runs (1,2). Preliminary results suggested that these carbons contain holes whose diameter is approximately the same as the Al<sub>13</sub> pillar, thus facilitating the lithium ion diffusion. It is one of our goals to determine the distribution of the carbon within the pillared clay before and after the heating process and upon removal of the pillared clay by acid treatment.

A critical feature of SANS and SAXS scattering methods is their potential for analyzing the inner structure of disordered systems. Their application is a unique way of obtaining direct information on systems with a random arrangement of density inhomogeneities in a colloid-size range. The signal measured in SANS is the intensity of scattered neutrons as a function of the scattering angle. Since the scattering angle  $\theta$  is related to the wave vector of the scattered radiation according to:

$$q = \frac{2\pi}{\lambda} |s - s_0| = \frac{4\pi}{\lambda} \sin \frac{\theta}{2} \quad (1)$$

where  $s$  and  $s_0$  are the unit vectors in the direction of the incident and scattered radiation, it is customary to express the scattering intensity as a function of the wave vector  $q$ .

The amplitude of the scattered radiation is given by:

$$A(q) = b \sum_{k,l} e^{-iq \cdot r_{kl}} \quad (2)$$

where  $b$  is the scattering length of one atom and  $r_{kl}$  is a vector describing the distance between atom  $k$  and  $l$ . The intensity of the scattered radiation  $I(q)$  is proportional to the square of this amplitude. The product of wave vector  $q$  and the distance between two scattering centers  $r_{kl}$  determines the phase difference between two scattered waves. The smaller the scattering angle, i.e., the smaller the  $q$  value, the larger the particle size can be from which emanates scattered radiation before a phase difference that leads to destructive interference is established. The total scattering signal reflects an average measure of the particle size and geometry (3). Since the high- $q$  range of the scattering function results from the smallest features of the scattering particles, the inverse power terms describe the external surface of the particles, and the exponent depends entirely on the structure of this surface.

For porous materials, depending on the geometrical arrangement of the filled or the void space, the power law that describes the mass scaling may have an exponent of less than three. In the most general case the scaling law is given by:

$$M(r) \propto r^{d_f} \quad (3)$$

where the  $d_f$  is called the Hausdorff dimension or fractal dimension and can assume noninteger values. It describes how the mass of the cluster increases with its linear dimension  $r$ . While a material may appear perfectly regular and three dimensional on the scale of a centimeter it may scale in a fractal way on the scale of a nanometer. Diffraction experiments probe the density correlations on length scales that correspond to the inverse momentum transfer  $q^{-1}$ , and since the intensity per particle scales with the correlated mass in the probing volume, it is expected that the intensity scales as  $q^{-d_f}$ .

SAXS probes scattered wave vectors  $q$  ranging from  $10^{-4}$  to  $10^1 \text{ \AA}^{-1}$ , where the scattered wave vector is defined as in equation 1. Scattered intensities reflect a correlation in X-ray scattering length density on length scales between 10 and  $10^4 \text{ \AA}$ . For porous materials consisting of a void and a solid phase, the difference in scattering length density is approximately equal to the scattering length density of the solid phase.

## EXPERIMENTAL

The synthesis of the calcined pillared clays (PILCs) has been described in detail elsewhere (1,2). The calcined PILC was loaded with five different organic precursors using the procedures summarized as follows. For pyrene, the pillared clay is stirred in a 0.1 M solution of pyrene in benzene at room temperature overnight. Liquid styrene was heated under a nitrogen flow in a vacuum system. The styrene vapor was carried to a round bottom flask containing the PILC. The PILC was stirred as a solid phase and heated to  $150^\circ\text{C}$ . Trioxane was heated to  $70^\circ\text{C}$ . Pyrene was added to the reaction vessel once the trioxane was completely melted. PILC was then added to the solution and stirred. The reaction was catalyzed by addition of few drops of 0.1 M HCl. The excess trioxane and pyrene mixture was washed away with toluene before pyrolysis. The pyrolysis of the above samples took place in stainless steel tubes purged with nitrogen for several minutes. The tubes were sealed and heated to  $700^\circ\text{C}$  for 4 hours. Ethylene and propylene were loaded in the gas phase, where the loading and the pyrolysis processes were done in one step. Here, a three-zone furnace was used. Quartz boats containing PILC or sepiolite were placed within a quartz tube. The tube was initially flushed with nitrogen for about 3 hours. After that period of time, the gas was switched to propylene or ethylene and the gas flow was kept about  $5 \text{ cm}^3/\text{min}$ . The temperature of the oven was gradually increased from room temperature (about  $5^\circ\text{C}/\text{min}$ ) to  $700^\circ\text{C}$ . The oven was then held at that target temperature for 4 hours.

The clay from the loaded/pyrolyzed PILC or sepiolite was removed using HF, rinsed to neutral pH and refluxed with concentrated HCl for 2 hours. The sample was washed with distilled water until the pH was  $> 5$  to ensure that there was no acid left. The resultant carbon was oven dried overnight at  $120^\circ\text{C}$ .

X-ray powder diffraction (XRD) patterns of clay precursors and carbons were determined using a Rigaku Miniflex, with  $\text{Cu K}_\alpha$  radiation and a beryllium solid-state detector at a scan rate of  $0.5^\circ 2\theta/\text{min}$ .

SANS experiments were conducted at the Intense Pulsed Neutron Source at Argonne National Laboratory. The powders were held in 1mm path quartz cells. The incident neutron spectrum is supplied by a cold moderator. The wavelength of the scattered neutrons range between 0.5 and  $14 \text{ \AA}$ , binned into 67 wavelength channels with 5% wavelength spread in each channel. This instrument uses a  $\text{BF}_3$  detector, and the scattered neutrons are detected by a  $20 \times 20 \text{ cm}^2$   $^3\text{He}$  area detector with  $64 \times 64$  spatial channels. The  $q$  range covered is  $0.005\text{-}0.35 \text{ \AA}^{-1}$ . The measurements took about two hours per sample. SAXS data were obtained at the Center for Micro-Engineered Materials, University of New Mexico. Both a Bonse-Hart and pin-hole instrument were used, resulting in a  $q$  range of  $0.0002\text{-}0.8 \text{ \AA}^{-1}$ .

## RESULTS AND DISCUSSION

Figure 1 shows SANS data for PILC, PILC loaded with pyrene before pyrolysis and the carbon obtained after pyrolysis at  $700^\circ\text{C}$  and removal of the clay matrix. Scattering curves are nearly identical for the PILC and the loaded clay, indicating no appreciable structural changes of the pillared clay upon organic incorporation. Both the pillared clay and the loaded pillared clay exhibit a hump in the middle- $q$  region that suggests a high degree of aggregation. The scattering

in the middle- $q$  region of the carbon sample did not show the aggregation feature observed in the PILC and PILC/pyrene.

Figure 2 shows SANS data for five carbons derived from PILC and different organic precursors. Note that for the carbons derived from trioxane/pyrene copolymer, ethylene and propylene, a certain degree of aggregation is observed at the middle- $q$  region. The low and high  $q$  regions are very similar. These data were evaluated as described by Freltoft *et al.* (4) to fit the experimental data in terms of the adjustable parameters  $d_f$  (fractal dimension),  $r_0$  (cluster size) and  $\xi$  (cutoff length). It is not possible to discriminate between voids and clusters, thus,  $r_0$  represents an average of both voids and clusters.  $\xi$  is related to the macroscopic density of the material, and  $d_f$  represents the particle distribution; it is a description of the geometrical arrangement of the particles in a cluster. A perfectly layered material such as graphite under well dispersed, conditions would exhibit  $d_f=2$ .

Table I summarizes the above parameters calculated for carbons and their precursors. The fractal dimensions for the carbon are similar to those calculated for the PILC, indicating that there is some layering in these disordered systems. Furthermore,  $r_0$  of the holes for the carbonaceous materials range from about 4 to 8 Å, the largest radius corresponding to the carbon derived from PILC/pyrene. SAXS data of a carbon sample prepared from PILC/pyrene is shown in Figure 3. In the middle- $q$  range the scattering intensity is characterized by a fractal dimension of 2.56, whereas at low  $q$  the fractal dimension corresponds to 3.88, which suggest that they have a small amount of roughness.

Another clay template used in the preparation of holey carbons is called sepiolite. It has the general structure  $\text{Si}_{12}\text{Mg}_9\text{O}_{30}(\text{OH})_6(\text{OH}_2)_4 \cdot 6\text{H}_2\text{O}$  (5). It is a clay that does not have to be pillared since it contains a channeled structure. Preliminary results using pyrene as the organic precursor demonstrated that some carbon is incorporated into the clay. However, smaller molecules such as propylene or ethylene may be incorporated at a faster rate. Figure 5 shows an X-ray powder diffraction (XRD) of the carbon synthesized by incorporating propylene within sepiolite in the gas phase. The broad peak corresponds to the 002 reflection and is indicative of a disordered system. Further characterization of this carbon by SANS, SAXS and electrochemical testing is in progress.

## CONCLUSIONS

Analysis of SANS and SAXS data of carbons synthesized using clays as templates show that they contain holes with a radius range from 4 to 8 Å. These holes are accessible to lithium ions when the intercalation process takes place in a lithium secondary battery. The values of the fractal dimension for the carbons are similar to those found for the clays, suggesting that there is some layering in the disordered system.

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Table I: Experimental parameters calculated from SANS data.

Sample	$r_g/\text{\AA}$	$\xi/\text{\AA}$	$d_f$
PILC	3.70	876	2.469
Carbon from PILC/pyrene	7.66	1080	2.660
Carbon from PILC/styrene	6.60	148	2.650
Carbon from PILC/ethylene	4.00	143	2.690
Carbon from PILC/propylene	4.30	534	2.880
Carbon from PILC/trioxane/pyrene	1.40	NA	2.930

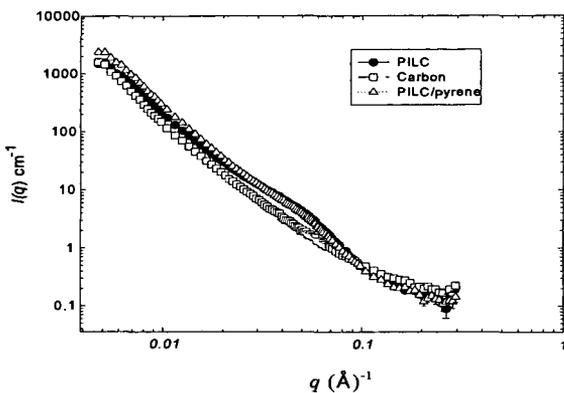


Figure 1:  $\log I$  vs  $\log q$  plot of the small-angle neutron scattering for (●) PILC, (Δ) PILC/pyrene and (□) carbon obtained after pyrolysis and clay removal.

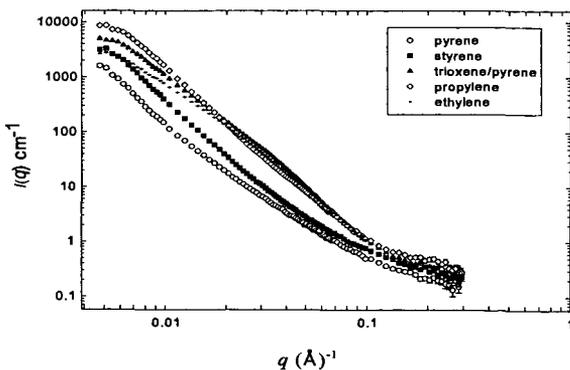


Figure 2:  $\log I$  vs  $\log q$  plot of the small-angle neutron scattering for carbon samples prepared using PILC and different organic precursors. (○) pyrene, (■) styrene, (▲) trioxane/pyrene, (◇) propylene and (·) ethylene.

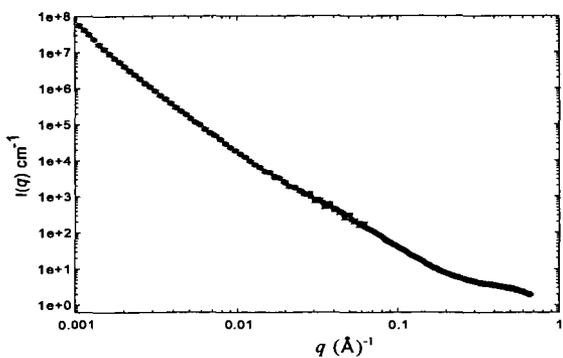


Figure 3:  $\log I$  vs  $\log q$  of the small angle X-ray scattering of a carbon sample derived from PILC/pyrene.

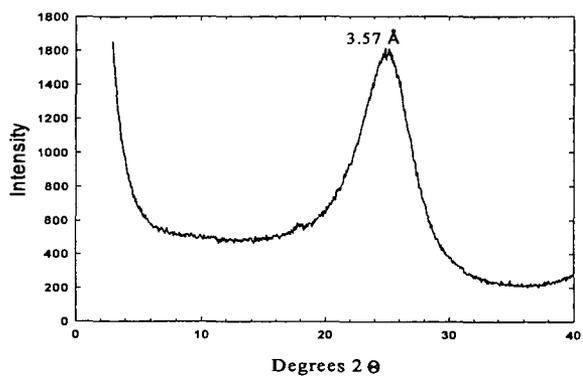


Figure 4: XRD of a carbon derived from sepiolite/propylene.