ANL/CHM/CP-93252

*Submitted to: **Proceedings of the Materials Research Using Cold Neutrons at Pulsed Neutron Sources**, Intense Pulsed Neutron Source, Argonne National Laboratory, August 25-26, 1997*.

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# SMALL ANGLE NEUTRON SCATTERING ANALYSIS OF NOVEL CARBONS FOR LITHIUM SECONDARY BATTERIES

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This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

# SMALL ANGLE NEUTRON SCATTERING ANALYSIS OF NOVEL CARBONS FOR LITHIUM SECONDARY BATTERIES

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Small angle neutron scattering analyses of carbonaceous materials used as anodes in lithium ion cells have been performed. The carbons have been synthesized using pillared clays (PILCs) as inorganic templates. Pillared clays are layered silicates whose sheets have been permanently propped open by sets of thermally stable molecular props. The calcined PILC was loaded with five different organic precursors and heated at 700 °C under nitrogen. When the inorganic pillars were removed by acid treatment, carbon sheets are produced with holes. The fitting of the data in the high q region suggested that the carbon sheets have voids with radii ranging from 4 to 8 Å. Similar radii were obtained for the PILC and PILC/organic precursor, which suggests that the carbon was well distributed in the clay prior to pyrolysis.

## 1. Introduction

The application of carbonaceous materials for the negative electrode of lithium ion batteries has been investigated intensively in recent years, since the dendritic growth of metallic lithium on charging can be avoided and so the use of carbon anodes can be expected to prolong the cycle life of a whole cell and to improve the safety reliability. On the other hand, the use of a carbon anode may lower the specific energy density of a cell because of a high reversible potential and the limited amount of lithium accommodation in a carbon matrix. These two factors can vary with the type of carbon material. So far, a wide variety of carbon materials such as natural graphite, cokes, carbon fibers, non-graphitizable carbon, and pyrolitic carbon have been investigated [1,5], but in all these cases there is no predictable knowledge of surface area and porosity.

The main objective of this work is to synthesize carbon with predictable porosity and surface area characteristics that would be useful for battery applications. This is accomplished by employing pillared clays (PILCs). PILCs are layered silicates whose sheets have been permanently propped open by sets of thermally stable molecular props. Several organic precursors are loaded in to the PILC layers and subsequently pyrolyzed. After elimination of the inorganic matrix via conventional demineralization, the layered carbons show holes due to the pillaring $Al_{13}$ cluster where lithium diffusion occurs.

In these studies, small angle neutron scattering is used to obtain information concerning the hole radius, fractal dimension, cutoff length and density of carbons and their organic precursors, prepared using inorganic PILC 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 (6,7). Preliminary results suggested that these carbons contain holes whose diameter is approximately the same as the $Al_{13}$ pillar, thus enhancing 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.

An important feature of SANS 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 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 (8). 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:

$$M(r) \propto r^{d_f} \qquad (1)$$

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 $q^{-d_f}$.

## 2. Experimental Part

The synthesis of the calcined pillared clays (PILCs) and the carbonaceous materials has been described in detail elsewhere (6,7).

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 Å, binned into 67 wavelength channels with 5% wavelength spread in each channel. This instrument uses a $BF_3$ detector, and the scattered neutrons are detected by a 20 x 20 $cm^2$ $^3He$ area detector with 64 x 64 spatial channels. The $q$ range covered is 0.005-0.35 $Å^{-1}$ . The measurements took about two hours per sample.

## 3. Results

Figure 1 shows SANS data for PILC, PILC loaded with pyrene before pyrolysis and the carbon obtained after pyrolysis at 700 °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.

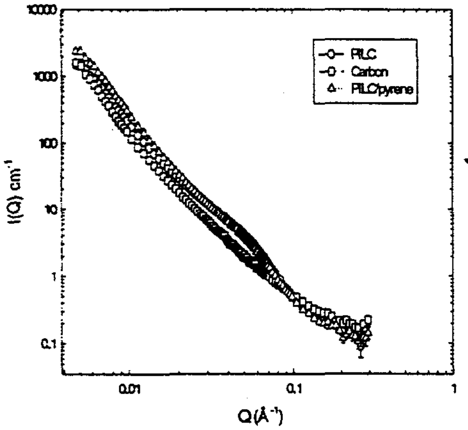

Figure 1: log $I$ vs log $q$ plot of the small- angle neutron scattering for (○) PILC, (△) PILC/pyrene, and (□) carbon obtained after pyrolysis and clay removal.

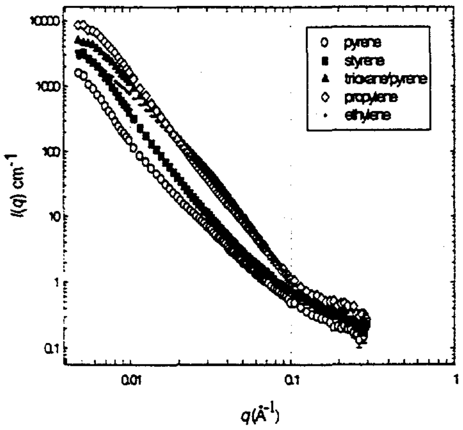

Figure 2: log $I$ vs log $q$ plot of the small-angle neutron scattering for samples prepared using PILC and different organic precursors. (○) pyrene, (■) styrene, (▲) trioxane/pyrene, (◇) propylene and (*) ethylene.

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.* (9) 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. 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.

Table 1: Experimental parameters calculated from SANS data.

| Sample | $r_0$/Å | $\xi$/Å | $d_f$ |
|---|---|---|---|
| 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 |

## Conclusions

Analysis of SANS 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 places 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.

## Acknowledgments

The help in acquiring SANS data from Mr. D. Wozniak and Dr. V. Urban, from the Intense Pulsed Neutron Source at Argonne National Laboratory, is greatly appreciated. This work was performed under the auspices of the Office of Basic Energy Sciences, Division of Chemical Sciences, U.S. Department of Energy, under contract number W-31-109-ENG-38.

## References

1. J. R. Dahn, A. K. Sligh, H. Shi, B. W. Way, W. J. Weydanz, J. N. Reimers, Q. Zhong, and U. von Sacken, in *Lithium Batteries-New Materials, Developments and Perspectives*, G. Pistoia, Editor, p. 1, Elsevier, Amsterdam (1994).
2. D. Aurbach, I. Weissman, A. Zaban, and O. Chusid, *Electrochim. Acta*, **39**, 5 (1994).
3. J. R. Dahn, A. K. Sleigh, H. Shi, J. N. Reimers, Q. Zhong, and B. M. Way, *Electrochim. Acta*, **38**, 1179 (1993).
4. K. Tatsumi, N. Iwashita, H. Sakaebe, H. Shioyama, and S. Higuchi, *J. Electrochem. Soc.*, **143**, 716 (1995).
5. A. M. Wilson, and J. R. Dahn, *J. Electrochem. Soc.*, **142**, 326 (1995).
6. G. Sandí, R. E. Winans, and K. A. Carrado, *J. Electrochem. Soc.*, **143**, L95 (1996).
7. G. Sandí, K. A. Carrado, R. E. Winans, J. R. Brenner and G. W. Zajac, Mater. Res. Soc. Symp.Proc., *Macroporous and Microporous Materials* **431**, 39 (1996).
8. C. Windsor, J. Appl. Cryst., **21**, 582 (1988).
9. T. Freltoft, J. K. Kjems, and S. K. Sinha, *Physical Review B* **33**, 269 (1986).