STRUCTURE OF CARBONS PREPARED WITH PILLARED CLAY TEMPLATES

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Introduction

Based on results from X-ray diffraction, small-angle neutron (SANS) and X-ray (SAXS) scattering, and elemental analysis, we have developed a model for a disordered carbon produced with pillared clays as a template. The carbon sheets within the crystallites appear to have holes due to the pillaring units, and there are no dangling ends on the periphery of these holes. Multiple layers of carbon are formed between the inorganic layers. These carbons are being tested as anodes for lithium secondary batteries.

Experimental

The carbons described here were prepared by heating pyrene imbibed within pillared clays at 700 °C; a complete description of the procedure has been published [1-3]. Characterization of SANS has been described [4]. Recently, SAXS data have been obtained at the Center for Micro-Engineered Materials, University of New Mexico [5]. Both a Bonse-Hart and pin-hole instrument were used, resulting in a q range of 0.0002 - 0.8 $Å^{-1}$.

Results and Discussion

Carbons produced from pillared clay templates contain very low concentrations of hydrogen, for a 700 °C carbon the H/C = 0.04 [3]. This value is on the same order of magnitude to carbons produced at 1000 °C by other precursors and heating methods [6-7]. We have attributed this result to enhanced carbonization due to the acidic nature of the inorganic template. Also, the carbon sheets are produced with holes where the inorganic pillars were removed. SANS results [4] strongly suggest that this is the case, resulting in structures as depicted in Figure 1. The SAXS data also support these results. Analysis of the data shown in Figure 2 in the high q region shows that the carbons have small voids with radii varying from 3 to 6 Å. From SANS data a radius of 7.6 Å was derived, and it was shown in a solvent contrast study that the voids are accessible to perdeuterobenzene. Therefore, they are without question accessible for lithium which is important for Li battery applications. In the mid-q range the scattering intensity exhibits a power law of $q^{-2.56}$ for SAXS and $q^{-2.66}$ for SANS. A perfectly

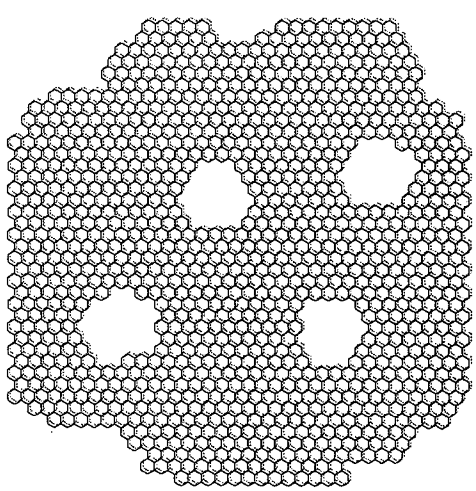

Figure 1. Representation of carbon layers.

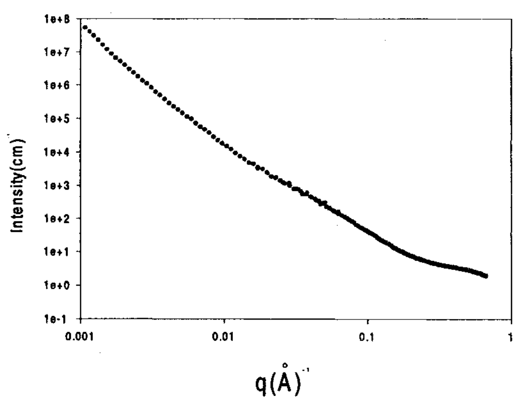

Figure 2. SAXS data from pyrene-clay derive carbon.

layered material such as graphite under well dispersed conditions would be at $q^{-2.0}$. The values for the carbon are similar to those found for clays, suggesting some layering in a disordered system. At low q we see the surface scattering of the particles with a fractal dimension of -3.88 which suggest that they have a small amount of roughness.

Because of the very low hydrogen content, it is not likely that these holes in the carbon sheets can be terminated with hydrogens. Also, the interlayer spacing between the clays will allow for at least two layers of carbon to form per layer of clay. Questions arise about how these holes are terminated and whether the multiple sheets are connected together. The hole would have to occur in the same place through both sheets of carbons in such a scenario.

It is known from the study of nanotubes that a combination of pentagon and heptagon rings can be used to bend tubes and also cap them at the ends [8]. More recently it has been claimed, based on high resolution electron microscopy, that the curves are due to fractures or bends in the planes [9]. They suggest that sp^3 carbons may be responsible for this result. Data from single pulse ^{13}C NMR on our samples demonstrated that only sp^2 carbons are found in these samples.

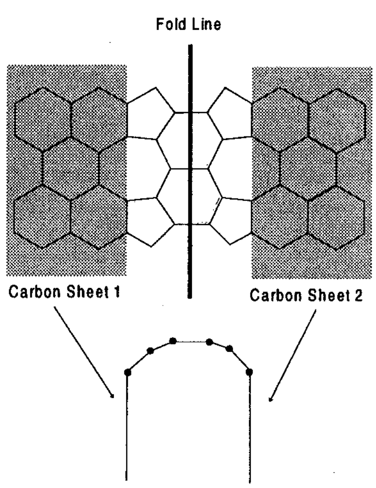

Figure 3. An unfolded partial edge at a hole with two carbon sheets.

A model for connecting two layers of carbons at the holes left by the pillars is shown in Figure 3. For clarity, only a portion of the connection is shown. These carbons have a very high reversible capacity of 800-825 mAh/g. Part of this capacity may be the result of Li uptake by the edges of these holes. Buckyballs, C_{60}, have been shown to take up twelve lithiums [10-11] which is greater than the 1/6 Li/C found in graphite and may be connected with the pentagon rings. Ethylene links ($-CH_2-CH_2-$) would be a more stable connection between the carbon layers such as is found in cyclophanes, however the hydrogen content and the NMR data eliminate this possibility.

Conclusions

Small angle scattering data are consistent with the predicted structure for these carbons. How the layers of carbon are connected at the holes produced by the pillars in the clays is still an unresolved question.

Acknowledgments

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