Small Angle X-Ray Scattering Studies of Carbon Anodes Used in Lithium Rechargeable Batteries

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SMALL ANGLE X-RAY SCATTERING STUDIES OF CARBON ANODES USED IN LITHIUM RECHARGEABLE BATTERIES

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ABSTRACT

In our laboratories, disordered carbons with predictable surface area and porosity properties have been prepared using inorganic templates containing well-defined pore sizes. The carbons have been tested in electrochemical cells as anodes in lithium secondary batteries. They deliver high specific capacity and display excellent performance in terms of the number of cycles run. In situ small angle X-ray scattering (SAXS) during electrochemical cycling was carried out at the Advanced Photon Source, at ANL. In order to monitor the carbon electrode structural changes upon cycling, an electrochemical cell was specially designed to allow for the application of electrical current and the collection of SAXS data at the same time. Results show that upon cycling the structure of the carbon remains unchanged, which is desirable in reversible systems.

KEYWORDS: SAXS, carbon anodes, lithium secondary batteries

INTRODUCTION

Carbonaceous materials have received considerable interest for use as anodes ever since Sony introduced the lithium-ion battery [1,2]. Carbon containing systems are noted for potential safety and reliability advantages because the carbon anodes are less prone to form dendrites than metallic lithium anodes. Most investigations have utilized carbon materials that are available from existing sources such as natural graphite, cokes, carbon fibers, non-graphitizable carbon, and pyrolitic carbon [3,4]. In these studies, high lithium capacities have been found to be associated with either disorder [5] or the presence of hydrogens [6].

An alternative avenue is the custom synthesis of carbons specifically tailored for use as anodes in lithium-ion batteries. This latter approach provides predictable control over critical properties such as the surface area or the porosity. Previously, Sandi and coworkers employed pillared clays with known interplanar spacing as templates for the synthesis of custom carbon anode materials [7-9]. More recently, they have focused on the concept that carbons with curved lattices can exhibit enhanced lithium capacity over that of graphite [10].

Our latest approach focuses on the use of sepiolite clay to tailor the synthesis of carbonaceous materials. Sepiolite is a phyllosilicate clay insofar as it contains a continuous two-dimensional tetrahedral silicate sheet. However, it differs from other clays in that it lacks a continuous octahedral sheet structure. Instead, its structure can be considered to contain ribbons of 2:1 phyllosilicate structure, with each ribbon linked to the next by inversion of Si-O-Si bonds. In this framework, rectangular channels run parallel to the x-axis between opposing 2:1 ribbons, which results in a fibrous morphology with channels running parallel to the fiber length. Channels are 3.7 x 10.6 Å in sepiolite (they are 3.7 x 6.4 Å in palygorskite). Individual fibers generally range from about 100 Å to 4-5 microns in length, 100-300 Å width, and 50-100 Å thickness. Inside the channels are protons, coordinated water, a small number of exchangeable cations, and zeolitic water. There are three sorption sites in sepiolite: (a) oxygen ions on the tetrahedral sheets, (b) a small amount of cation exchange sites (0.1-0.15 meq/100gm), and (c) SiOH groups along the fiber axis. Adsorption is also influenced by the size, shape, and polarity of the molecules involved. The SiOH groups act as neutral adsorption sites suitable for organic species. These factors are all important to our goal of loading the clay with certain organic
monomers that will polymerize on the surface and, following a pyrolysis step, carbonize to a material suitable for use as a carbonaceous anode in secondary lithium batteries.

Our main objective is to synthesize carbon with pore sizes capable of Li⁺ diffusion in a rechargeable battery. The carbonaceous materials are derived from ethylene or propylene upon incorporation in the vapor phase in the channels of sepiolite, taking advantage of the Brønsted acidity in the channels to polymerize olefins. In order to monitor the carbon electrode structural changes upon cycling, an electrochemical cell was specially designed to allow for the application of electrical current and the collection of SAXS data at the same time.

EXPERIMENTAL

Details about the synthesis of the carbonaceous materials can be found in reference [11]. In summary, ethylene and propylene (AGA, 99.95%) were loaded and pyrolyzed in the gas phase in one step. A three-zone furnace was used. Quartz boats containing sepiolite were placed within a quartz tube. The temperature of the oven was gradually increased from room temperature (about 5 °C/min) to 700 °C. The oven was then held at that target temperature for 4 hours. The clay from the loaded/pyrolyzed sepiolite sample was removed using HF. It was then 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 °C.

X-ray powder diffraction (XRD) patterns of sepiolite, sepiolite/organic composite and carbons were determined using a Rigaku Miniflex, with Cu Kα radiation and a NaI detector at a scan rate of 0.5° 2θ/min.

Transmission electron microscopy (TEM) was performed in a JEOL 100CXII Transmission Electron Microscope operating at 100kV. Approximately 0.01 g of the powder sample was placed into a vial containing about 10 ml of methanol. After sonicating for 30 seconds, copper grids with "holey" carbon films were then dipped into the resulting slurry. The Cu grids were allowed to dry for 2 hours in a vacuum oven at 100 °C. Once dry, the grids were inserted into non-tilt holders and loaded into the instrument. Only regions overlapping holes in the carbon grid were used. Scale markers placed on the micrographs are accurate to within three percent.

In situ small angle X-ray scattering (SAXS) during electrochemical cycling was carried out at the Advanced Photon Source, (Basic Energy Sciences Synchrotron Research Center CAT), Argonne National Laboratory. Monochromatic X-rays (8.5 - 23.0 keV) are scattered off the sample and collected on a 19 x 19 cm² position sensitive two-dimensional gas detector. The scattered intensity has been corrected for absorption and instrument background. The differential scattering cross section has been expressed as a function of the scattering vector Q, which is defined as: Q = (4 π/λ) sin θ, where λ is the wavelength of the X-rays and θ is the scattering half angle. The value of Q is proportional to the inverse of the length scale (Å⁻¹). The instrument was operated with two different sample-to-detector distances, 68.5 cm to obtain data at 0.04 < Q < 0.7 Å⁻¹ and 3740 cm to measure at 0.006 < Q < 0.1 Å⁻¹. For these studies, a specially designed sample cell was used to record both the electrochemical response and SAXS data at the same time. The carbon sample was mixed with a teflon binder suspension (80/20 % w/w). The sample was oven dried and pressed against a Cu mesh. The electrode was then dried out in a vacuum oven at 80 °C overnight. A piece of lithium foil (0.008"; 0.203 mm from FMC Lithium Division, Gastonia, NC) with the same dimensions as the carbon composite was also pressed against Cu mesh. A propylene membrane (Hoechst-Celanese, Charlotte NC) was used as the separator. The electrodes were held together by using kapton tape along the edges. The electrolyte was 1 M LiPF₆ in a mixture of 50% v/v ethylcarbonate and 50 % v/v diethylcarbonate (Merck, Germany). A control experiment was performed using commercial graphite (Aldrich). The cell was discharged from the open circuit voltage (OCV) to 0 V and back to 2.5 V at a scan rate of 0.1 mV/s using a EG&G 273A potentiostat.
RESULTS AND DISCUSSION

Figure 1 shows XRD patterns of a) pure sepiolite, b) a sepiolite/propylene composite already heated to 700 °C, and c) the pure carbon derived from the sample b. As evidenced by the disappearance of the 110 peak of sepiolite in 1(b), there is marked loss of crystallinity upon heating the clay in the presence of propylene at 700 °C. This was expected, and other clay peaks are still apparent, albeit shifted somewhat from pristine clay. The incorporation of carbonaceous precursor is indicated by a new broad peak at about 24° 2θ (figure 1b). Upon removal of the inorganic matrix, there is only a broad peak at 3.57 Å (figure 1c), which corresponds to the 002 reflection of a disordered graphite. In a pure graphite sample, the 002 reflection appears at 3.35 Å and the peak is very sharp, unlike the disordered carbon obtained in our synthesis. No peaks related to the clay structure remain after the acid removal, which is an indication of the purity of the carbon sample. The percentage organic loading in the sepiolite, calculated by TGA, corresponded to 47.0 %. The yield of carbon with respect to the initial clay weight was 53%, which is a 25 fold increase compared to our previous methods (7-9).

In order to monitor the carbon electrode structural changes upon cycling, an electrochemical cell was specially designed to allow for the application of electrical current and the collection of SAXS data at the same time. The availability of very intense X-rays from synchrotron sources enables the use of SAXS to study the meso and micropore size distributions of many materials. Small-angle scattering from x-rays arises due to the presence of discontinuities in the density of a material. Thus, the particles and pores in the carbons can produce strong small angle scattering signals in a wide momentum-transfer range. The small angle scattering data can be modeled to obtain information on the microstructure of the porous network. In battery applications, if the liquid organic electrolyte penetrates the pores of the carbon anode, it leads to irreversible electrolyte decomposition during the first electrochemical reaction of lithium with the carbon, and hence a large irreversible capacity. If the pores are small (of the order of 15 Å or less), and the structure remains intact, the liquid electrolyte cannot penetrate, so excellent reversible behavior should be expected. Figure 3 shows time resolution studies of a lithium ion cell made with carbon derived from sepiolite/propylene composite. A spectrum was taken of the cell at the open circuit voltage (OCV = 2.99 V) and used as the background correction for the subsequent measurements. Upon application of voltage, a spectrum was taken every 60 mV (every 5 minutes). The results indicated that during cycling there are no structural changes upon lithium intercalation as is evidenced by the near overlap of all curves. This means that solvent penetration into the carbon anode, which causes irreversible capacity, is avoided and so excellent reversibility is attained. A control experiment was performed using commercial graphite as the carbonaceous material and is shown in figure 4. It is very clear from figure 4 that there are changes in the structure of graphite and these changes are not reversible. Overall, the performance of the sepiolite-derived carbon anode is satisfactory for lithium-ion applications.

CONCLUSIONS

Based on the electrochemical performance and much higher structural stability compared to graphite, carbon anodes derived from sepiolite as templates are demonstrated as good candidates for lithium ion cells. The synthetic approach described here yielded well defined carbon tubes with little or no graphitic character as evidenced by TEM. The yield of carbon based on the amount of inorganic template is about 25 times higher than our previous synthetic method, which makes it viable for commercial applications.
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REFERENCES


Figure 1: X-ray powder diffraction of a) sepiolite clay, b) sepiolite/propylene composite after heated at 700 °C, and c) carbon sample derived from the composite.
Figure 2: TEM of a carbon sample derived from sepiolite/propylene composite. A JEOL 100CXII Transmission Electron Microscope operating at 100kV was used.

Figure 3: SAXS of carbon electrode derived from sepiolite/propylene composite.

Figure 4: SAXS of a graphite sample upon cycling.