DESIGNER CARBONS TEMPLATED BY PILLARED CLAYS: LITHIUM SECONDARY BATTERY ANODES

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ABSTRACT

This work describes the designed synthesis and physical characterization of carbons containing predictable microporosity. The approach is to pyrolyze aromatic hydrocarbons such as pyrene within a pillared clay. The pillared clay serves two functions. It performs as the inorganic template around which the designer carbon can be formed, and it acts as an acid catalyst to promote condensation of the aromatics similar to the Schöll reaction. These precursors then undergo thermal polymerization and carbonization at 700 °C. Removal of the pillared clay template is accomplished by standard acid demineralization techniques, leaving behind carbons with 15 to 50 Å holes.

INTRODUCTION

The application of carbonaceous materials for the negative electrode of lithium ion batteries has been investigated intensively in recent years, where the reversible insertion/extraction of lithium into/from a carbon matrix occurs upon charge/discharge instead of the deposition/dissolution of metallic lithium. The dendritic growth of lithium on charging can be avoided and hence 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. Tomita *et al.* [6] have reported the formation of carbon using inorganic templates, where polyacrylonitrile was carbonized at 700 °C yielding thin films with relatively low surface area. In the present work 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. Pyrene, the organic precursor for these studies, is dispersed in benzene between 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 may be able to occur. In a previous study of these materials using small angle neutron scattering (SANS), Winans and Carrado [7] showed that the diameter of the holes was about 15 Å, which is the approximate size of the Al_{13} pillar [8,9]. Lithium should be able to diffuse rapidly through such a molecular porous carbon.

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EXPERIMENTAL

Synthesis

Details about the synthesis of the PILC can be found elsewhere [7,10]. The calcined clay was loaded with organic using either a "solvent" method or a "diffusion" method. In the solvent method, the pillared clay is stirred in a 0.1 M solution of pyrene (Aldrich) in benzene (J. T. Baker) at room temperature overnight. After filtration, the samples were dark green. The diffusion method involved loading of the clay and pyrolysis in a one step process. In this case a three-zone furnace was used. Five grams of pyrene were placed inside a 18 in long quartz tube (½ in O.D.) in the first zone. Three grams of the pillared clay were placed on the second zone at 700 °C. The temperature of the first and third zones was set to 200°C. Quartz wool was used to avoid mixing of pyrene and pillared clay at the beginning of the experiment. The opened end of the quartz tube was connected to a diffusion pump to accelerate the loading process. Both furnace and pump were on for 3 hours.

For pyrolysis, the loaded sample was put in stainless steel tubes with a nitrogen purge for several minutes. The tubes were sealed and heated to 700 °C for 4 hours. Before opening the tubes, pressure was released by cooling the tubes in liquid nitrogen for approximately 30 minutes. The clay was removed using conventional demineralization methods. The loaded/pyrolyzed PILC wa: placed in HF, previously cooled at 0 °C to passivate the exothermic reaction, and stirred for about one hour. 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.

Characterization

N_2 BET surface areas, pore size distributions and thermal isotherms were obtained in an Autosorb 6, instrument from QuantaChrome. Approximately 0.10 g of material was weighed into a pyrex tube and evacuated at 80 mTorr overnight at room temperature. After backfilling with He, the carbon was briefly exposed to air prior to analysis. The static physisorption experiments consisted of determining the amount of liquid nitrogen (LN_2) adsorbing to or desorbing from the material as a function of pressure (P/P_0 = 0.025-0.999, increments of 0.025).

Transmission electron microscopy (TEM) was carried out in a JEOL 4000EX II (line-to-line resolution = 0.14 nm, point-to-point resolution = 0.17 nm). Approximately 0.01 g of carbonaceous material was placed into a vial containing ~ 10 ml of isopropanol. After sonicating for 30 minutes, several drops of the resulting slurry were pipetted onto 3 mm holey carbon on Cu grids. Once dry, the grids were inserted into non-tilt holders and loaded into the instrument. Only regions overhanging holes in the carbon grid were used. The micrographs were in all cases taken at magnifications of either 150,000x or 500,000x. Scale markers placed on the micrographs are accurate to within three percent.

Near-edge absorption fine structure (NEXAFS) experiments were carried out at the U1 beamline of the National Synchrotron Light Source, Brookhaven National Laboratory. Information concerning the optics on the beamline and the UHV chamber with capabilities for high pressure reactions, has been reported elsewhere [11,12]. NEXAFS spectra were obtained by measuring the intensity of electron yield, recorded by a channeltron electron multiplier located near the sample holder. The spectra were measured as a function of the incident X-ray photon energy in the vicinity of the carbon K-edge (275-325 eV) and oxygen K-edge (510-590 eV). The data were recorded with the photon beam at a normal incident angle with respect to the sample surface. The carbonaceous

materials were pressed into stainless steel sample holders of about 1.3 cm in diameter and 0.1 cm in depth.

X-ray powder diffraction (XRD) patterns of clay precursors and carbons were determined using a Scintag PAD-V instrument, with Cu K_α radiation and a germanium solid-state detector at a scan rate of 0.5° 2Θ/min. Laser desorption mass spectroscopy (LDMS) was performed on a Kratos Maldi III. Scanning tunneling microscopy (STM) was performed at Amoco, using a Digital Instrument Nanoscope II, at -1.0 V with respect to the tip. CHN elemental analysis was performed in the Analytical Chemistry Laboratory in order to calculate the H/C ratio of these materials.

RESULTS AND DISCUSSION

The surface areas of the carbonaceous materials range from 10 to 100 m^2/g (Table I). There was some microporosity ($r < 1$ nm) in the highest surface area carbons. Most of the surface area, however, came from mesopores with radii of 1-5 nm (information obtained from the adsorption isotherm).

Table I. Comparison of d_{002} spacing, surface area and synthetic conditions of carbon samples prepared by using PILCs.

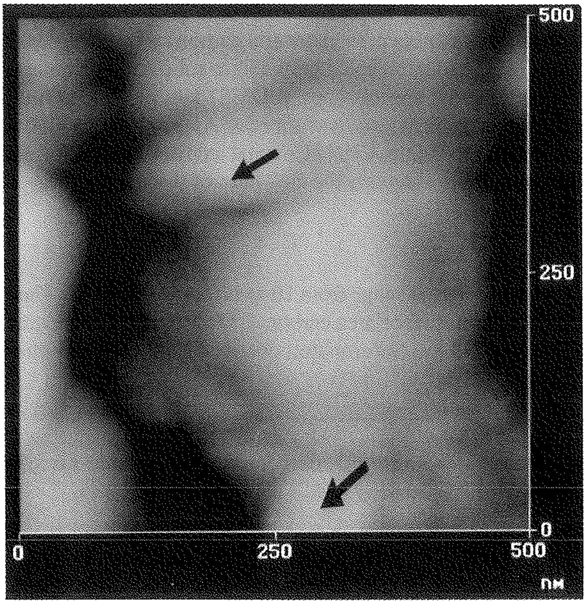
Loading Method	Pyrolysis ° C	H/C ratio	d_{002} spacing Å	Surface area m^2/g
diffusion	700	0.027 ± 0.004	3.40	84.5
solvent	500	0.039 ± 0.004	3.42	101
solvent	700	0.040 ± 0.004	3.45	10.8

The pore size distributions determined from isotherm desorption all had a sharp pore size peak at a radius (r) of 1.9 nm. This peak at 1.9 nm is characteristic of layered and pillared materials [13] and is not reflective of actual surface area. Thus, only the adsorption isotherms were used to calculate surface areas and pore size distributions.

As discussed by Kinoshita [14], the XRD pattern of disordered carbons contains only a few diffraction peaks. For cokes and soft carbons heated to near 1000 °C, only the (002) and (004) peaks due to the stacking of the layers and the (100) and (110) two dimensional peaks due to in-plane order can be readily observed. The broad d_{002} peak (see Table I) in this diffraction pattern is then indicative of a disordered or turbostratic system.

Because LN_2 physisorption does not effectively probe the macroporosity, we also employed scanning tunneling microscopy (STM). The black channels ($50 \text{ nm} < r < 100$ nm) in the STM micrograph of a carbon sample prepared by using PILC/pyrene/benzene and pyrolyzed at 700 °C correspond to the pore structure network (Figure 1). Denoted by black arrows are several of the mesopores already characterized by LN_2 physisorption. The concentration of these mesopores is much lower in the lower surface area materials (~ $10 m^2/g$).

Transmission electron microscopy (TEM) of the carbons indicated that the carbon formed agglomerates of 1-10 μm, which were composed of a broad range (5-500 nm) of many overlapping



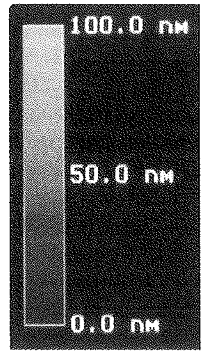


Figure 1. STM of a carbon sample prepared by using PILC pyrene/benzene at 700 °C. Scan size = 500 nm; setpoint = -1.0 V; scan rate = 5 Hz.

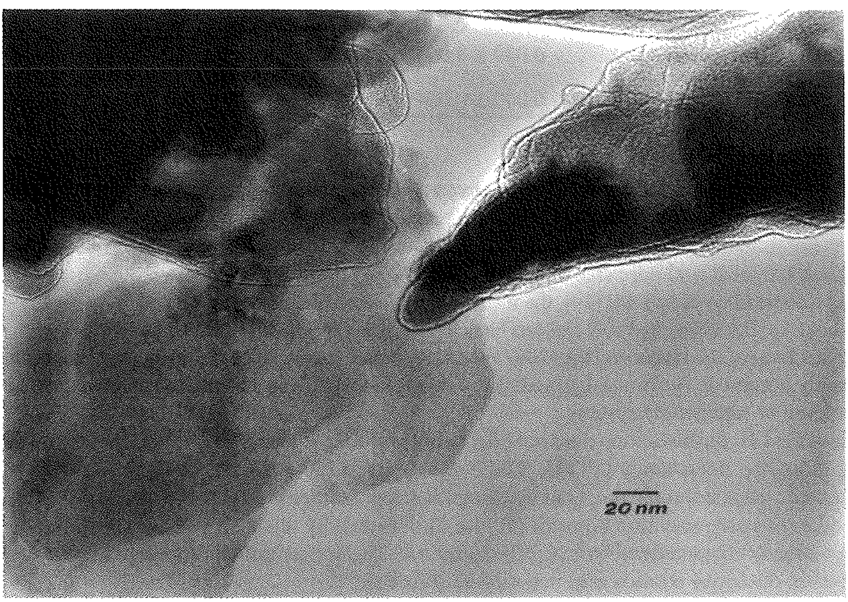


Figure 2. TEM of same sample as in Figure 1.

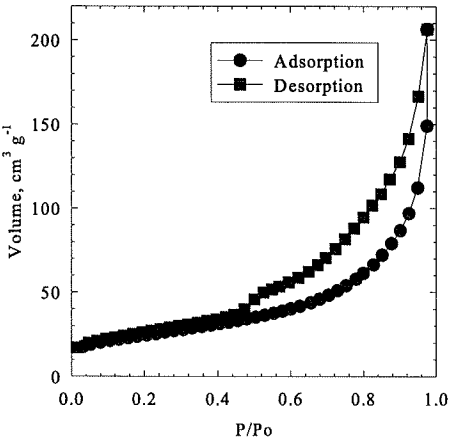


Figure 3. Isotherm of a carbon sample prepared by the templated method at 700 °C as in Table I.

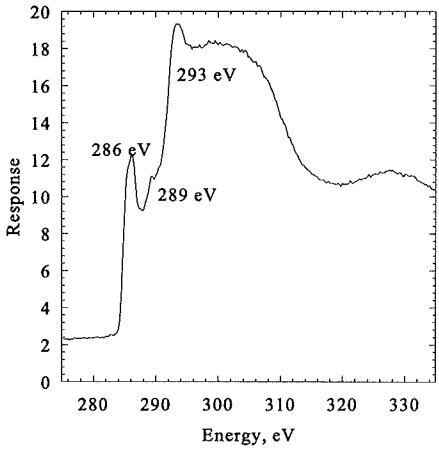


Figure 4. Carbon K-edge features of a amorphous carbon sample as in Figure 3.

particles. The vast majority of these particles were completely amorphous (Figure 2).

Figure 3 shows the adsorption-desorption isotherm for a carbon sample with a surface area of 10.8 m^2/g (see Table I). According to Gregg and Sing [15], this isotherm is identified as Type V, which is characterized by being convex to the pressure axis. This suggests that the adsorption is cooperative in nature, which means that the more molecules that are already adsorbed, the easier for further molecules to become adsorbed. Type V isotherms are expected for those systems for which the differential heat of desorption is close to the value of the latent heat of evaporation, thus the net heat of adsorption is not far from zero. Hysteresis is observed here, which is evidence of the presence of porous materials.

Figure 4 shows the electron-yield NEXAFS spectrum of the carbon K-edge features of a carbon sample pyrolyzed at 700 °C. Three transitions can be observed: a π^* resonance at 286 eV, C-H* resonance at 289 eV and a broad σ^* region between 291 and 315 eV. The peak position and the lineshapes of the carbon K-edge of this carbon is very different from those of graphite, as reported by Rosenberg *et al.* [16]. This is another indication of the amorphous nature of this material. Furthermore, the intensity of the peak at 289 eV indicates the relatively low amount of hydrogen in these carbons. Hydrogen is detrimental in the performance of the anodes, as discussed by Sandí *et al.* [10].

Laser desorption mass spectrometry showed that these materials contain carbon clusters, C_n, n= 4-40. No peaks were seen for C_nO, which suggests that no oxygen was taken from the clay minerals.

CONCLUSIONS

Amorphous carbon with desirable porosity and characteristic surface area have been

produced by the new synthesis-by-design method previously described. The dendritic growth of lithium on charging can be diminished by decreasing the surface area of the carbon. The amount of hydrogen in these samples is minimum, as shown by carbon K-edge NEXAFS measurements and the low H/C ratios, which is an advantage for the performance of these carbons as anodes in lithium secondary batteries.

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