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Carbons for Lithium Ion Cells Prepared Using Sepiolite as an Inorganic Template

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DISCLAIMER

CARBONS FOR LITHIUM ION CELLS PREPARED USING SEPIOLITE AS INORGANIC TEMPLATE

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ABSTRACT

Carbon anodes for Li ion cells have been prepared by the *in situ* polymerization of olefins such as propylene and ethylene in the channels of sepiolite clay mineral. Upon dissolution of the inorganic framework, a disordered carbon was obtained. The carbon was tested as anode in coin cells, yielding a reversible capacity of 633 mAh/g, 1.70 times higher than the capacity delivered by graphitic carbon, assuming 100 % efficiency. The coulombic efficiency was higher than 90%.

INTRODUCTION

The lithium-ion battery market has been in a period of dynamic growth ever since Sony introduced the first commercial cell in 1991 (1). The lithium-ion battery system has become increasingly popular in applications such as portable computers, camcorders and cellular phones. As new materials are developed, cost reduction should spur growth in new applications. Carbonaceous materials have been used as anode electrodes, thus avoiding the dendritic growth of metallic lithium upon charging, prolonging the cycle life of a whole cell and improving the reliability. On the other hand, a carbon anode may lower the specific energy density of a cell due to both a high reversible potential and a limited amount of lithium accommodation in the carbon matrix. These two factors vary with the type of carbon material. Thus far, carbon materials such as natural graphite, cokes, carbon fibers, non-graphitizable carbon, and pyrolitic carbon have been investigated (2-6), but critical parameters such as of surface area and porosity are not predictable for these materials.

In our laboratories, disordered carbons with more predictable properties have been prepared using inorganic templates containing well-defined pore sizes (7, 8). 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 runs (9). Although the performance of the clay-derived carbons is excellent, there is still a need to improve the efficiency of the synthetic process without sacrificing electrochemical performance of the resulting carbons.

The inorganic templates that we have used thus far consist of pillared clays. The specific clays for pillaring are so-called 2:1 smectites, in which two tetrahedral silicate layers sandwich a central octahedral aluminum layer. These 2:1 layered units are separated by interlayers containing hydrated metal cations. In pillared clays, the interlayers have been permanently propped apart by polyvalent aluminion oxy-hydroxy clusters that condense, in a heating step, to aluminum oxide clusters. These provide thermally stable templates of a desirable pore size and structure for specialty carbon production, but they are time-consuming to make and the overall carbon yields are low. Therefore a more desirable template in terms of ease-of-use and yield is of interest.

The palygorskite-sepiolite group of clay minerals has a wide range of technological applications derived from its sorptive, rheological, and catalytic properties which are based on their fabric, surface area, porosity, crystal morphology, structure, and compositon. While commercial deposits are rare, these two clays occur relatively frequently in sediments and soils; over 90% of commercially available sepiolite is from Spain (10). 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 SiO_4 tetrahedra along a set 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. The BET surface area of Vallecas sepiolite from Spain is reported to be 230 m^2/gm (11) which can be modified by heating (which drives out zeolitic water) and acid treatment. Sepiolite is a magnesium silicate since the octahedral sites contain Mg(II) rather than the Al(III) that is present in aluminosilicate clays. Figure 1 shows a structural representation of sepiolite.

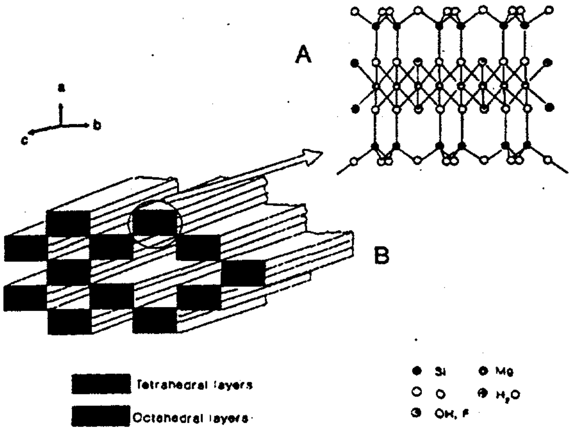

Figure 1: Structure of sepiolite. A: structural block composed of two tetrahedral sheets and a central octahedral magnesium sheet. B. cross-section of an assembly of structural blocks forming an ideal sepiolite fiber.

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. Neither large molecules nor those of low polarity can penetrate into channels, though they can be adsorbed on the external surface, which accounts for 40-50% of the total surface area (10). Between 200-400°C a sharp decrease in surface area is observed for pure sepiolites that is due to crystal folding (10,11). The SiOH groups act as neutral adsorption sites suitable for organic species, and the content for the Vallecas sepiolite is about 0.60 mmol/g (12). 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.

There have been several recent references concerning the sorption of organics by sepiolite that relate to our interest in adsorbing carbonaceous precursors. Most relevant are those involving sorption of monomers with subsequent polymerization. For example, isoprene was sorbed or loaded not only on the outer surface but also in the channels of sepiolite (13). Strong Brønsted acid sites on the inner and outer surfaces of the sepiolite initiated polymerization at 25 °C. When the sepiolite was heated to 300 °C prior to loading, after crystal collapse and folding occurred, the isoprene loaded only on the outer surfaces. There was also evidence of styrene polymerization within the channels, whereas thiophene and pyrrole had only slight polymerization on the external surfaces (13). Others have had more success with pyrrole, however. When Kitayama et al.(14) pre-adsorbed a small amount of I_2 within the channels of sepiolite, they found that polymerization of pyrolle took place in the tunnels. Other related studies include: (a) external surface loading of rhodamine 6G (15) and of methylene blue and crystal violet dyes together with model calculations (12), (b) internal channel loading of pyridine (16 and references therein], and (c) the crystallization nucleating effect of sepiolite on certain polymer blends (17). Our main objective is to synthesize carbon with pores 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 our previous method (7-9) we employed pillared clays (PILCs), in which after elimination of the inorganic matrix, the layered carbons showed holes due to the pillaring Al_{13} cluster where lithium diffusion may be able to occur. In the present work, due to the presence of channels in the structure of sepiolite, the pillaring process can be eliminated and the carbon loading enhanced. To the best of our knowledge, there have not been any reports on the preparation of carbonaceous materials derived from sepiolite and used as anodes in lithium-ion cells.

EXPERIMENTAL

Carbon Synthesis

Sepiolite was from Yunclillos (Toledo, Spain), provided by TOLSA, S.A. 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 tube was initially flushed with nitrogen for about 3 hours. The gas was then switched to propylene or ethylene and the gas flow was kept about 5 cm^3/min. 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, previously cooled at 0°C to passivate the exothermic reaction. The resulting slurry was 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.

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

Electrochemical Testing

The electrolyte was 1M $LiPF_6$ dissolved in 50 vol.% ethylene carbonate (EC) & 50 vol.% dimethylcarbonate (DMC) obtained as a solution from FMC Lithium Division (Gastonia, NC). The cell hardware used in the galvanostatic cycling studies was obtained from either Ray-O-Vac or Eveready Battery Company. The button cells were 1225, nickel-plated stainless steel and assembled in a dry room. Carbon electrode pellets were dried at 80 °C in a vacuum oven inside the dry room prior to assembly. All cell hardware and separator materials were also rigorously dried.

Electrodes were prepared using 90% by weight of the carbonaceous materials, and a binder solution made of polyvinylidene fluoride (PVDF, Aldrich, 99+%) dissolved in N-methyl-pyrrolidinone (NMP, Aldrich, 99+%). An excess of NMP was added to make a slurry. The slurry was oven-dried at 120 °C overnight. This resulting powder is used to make pellets in carbon-steel dies. About 20-30 milligrams of carbon is put into the die and evened-out with the plunger. The die and plunger are put into the press and are pressed at about 5000 psi. The dual electrode configuration in these cells uses metallic lithium as the anode. Cells fabricated are cathode capacity limiting and contain metallic lithium (FMC) foil (0.008"; 0.203 mm) as the anode. To help wet the lithium surface with the electrolyte one drop of 1,2-dimethoxyethane (DME, 99.9+%, Aldrich) was added to the cell. Two Celgard 2400 separators (Hoechst-Celanese, Charlotte NC) were placed on top of the wetted lithium foil. More drops of electrolyte and only one drop of DME was added. The cells were allowed to sit undisturbed for about 15 minutes to let the DME evaporate. The carbon electrode pellet was placed against the separator, and a copper-foil spacer was situated on top of the carbon electrode pellet. The spacer acts as both a current collector and also fills the button cell space, depending on the thickness of the pellet. The button cell can was placed over the rest of the cell and against the grommet. The cell was loaded onto the die spot for crimp-sealing, and was subsequently pressed to a stack height of 0.061" and 2000 psi (Figure 2). After crimping, the cell voltage was immediately checked for shorts. Those sealed button cells which displayed a

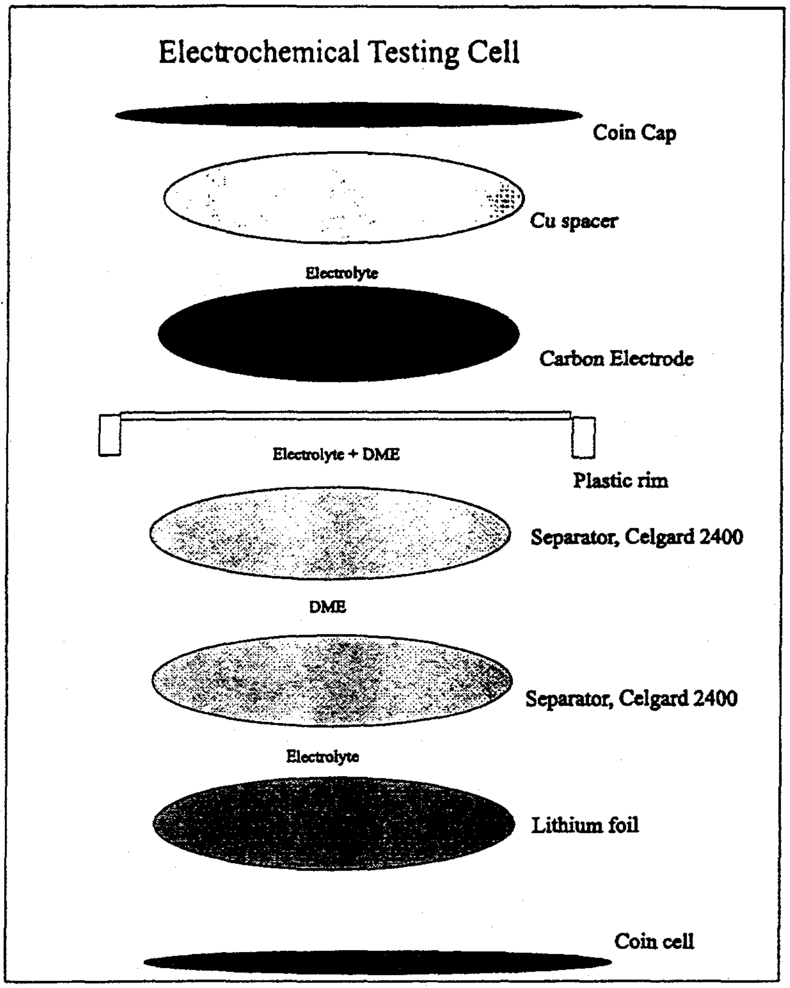

Figure 2: Coin cell hardware and assembly

good voltage were transported out for electrochemical testing on an Arbin 2400 station.

RESULTS AND DISCUSSION

X-ray powder diffraction (XRD) patterns of sepiolite, sepiolite/organic composite and carbons were determined using a Rigaku Miniflex, with Cu K_α radiation and a NaI detector at a scan rate of 0.5° 2Θ/min. Figure 3 shows an XRD of the carbon synthesized by incorporating propylene within sepiolite in the gas phase. The broad peak at 3.57 Å corresponds to the 002 reflection of graphite and is indicative of a disordered system. The percentage organic loading in the sepiolite, calculated by TGA, corresponds to 47.0 %. The yield of carbon with respect to the initial clay weight is 53%.

Figure 4 shows a voltage performance plot of fourteen cycles of a carbon electrode prepared as described earlier. Both the discharging and the charging cycles were run at a constant current rate C/20 or 18.6 mA/g. The first discharge capacity is higher than the subsequent cycles because lithium foil is used as the negative electrode, but the coulombic efficiency for the remaining cycles is higher than 90%. The specific discharge capacity at the end of the 14th cycle corresponds to 633 mAh/g, 1.70 times higher than the

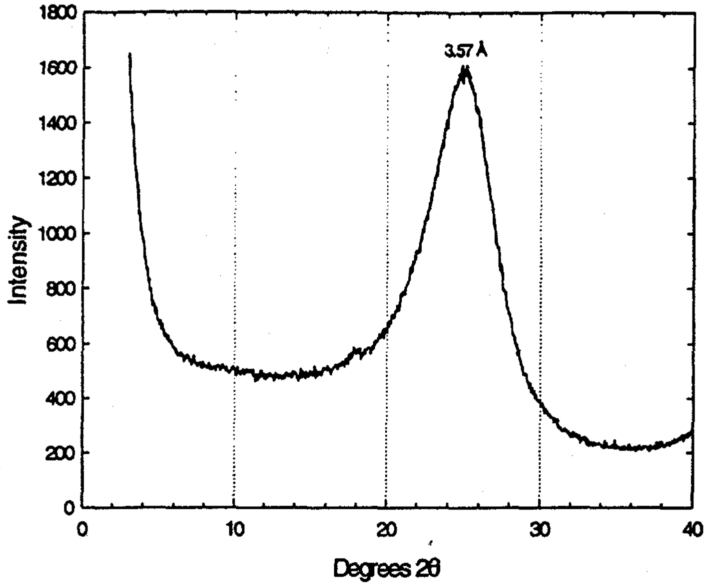

Figure 3: XRD of a carbon sample derived from sepiolite/propylene.

capacity delivered by graphitic carbon, assuming 100 % efficiency. There is some hysteresis in voltage. Figure 5 shows the capacity performance as a function of cycle number. There is not a significant capacity fade upon cycling and the irreversible capacity (discarding the first cycle) corresponds to 115 mAh/g. The performance of the carbon anodes from the present work is satisfactory for lithium-ion applications, taken into account the specific capacity delivered and stability of the cells upon cycling.

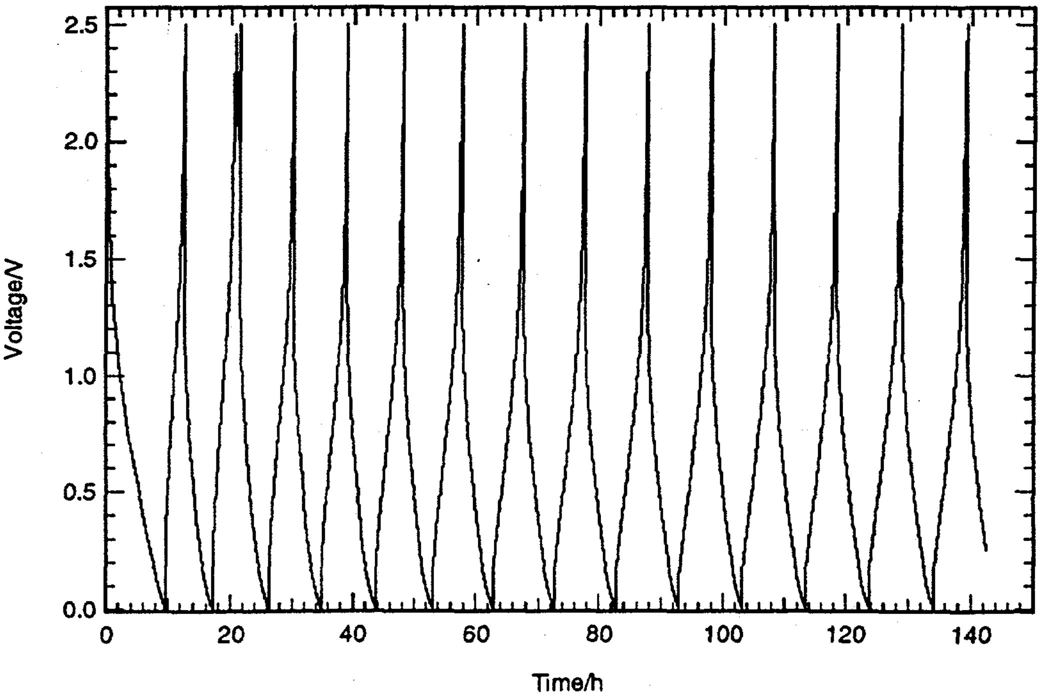

Figure 4: Voltage profile of a carbon electrode derived from sepiolite/propylene. Voltage limit: 0 to 2.5 V; current rate: C/20.

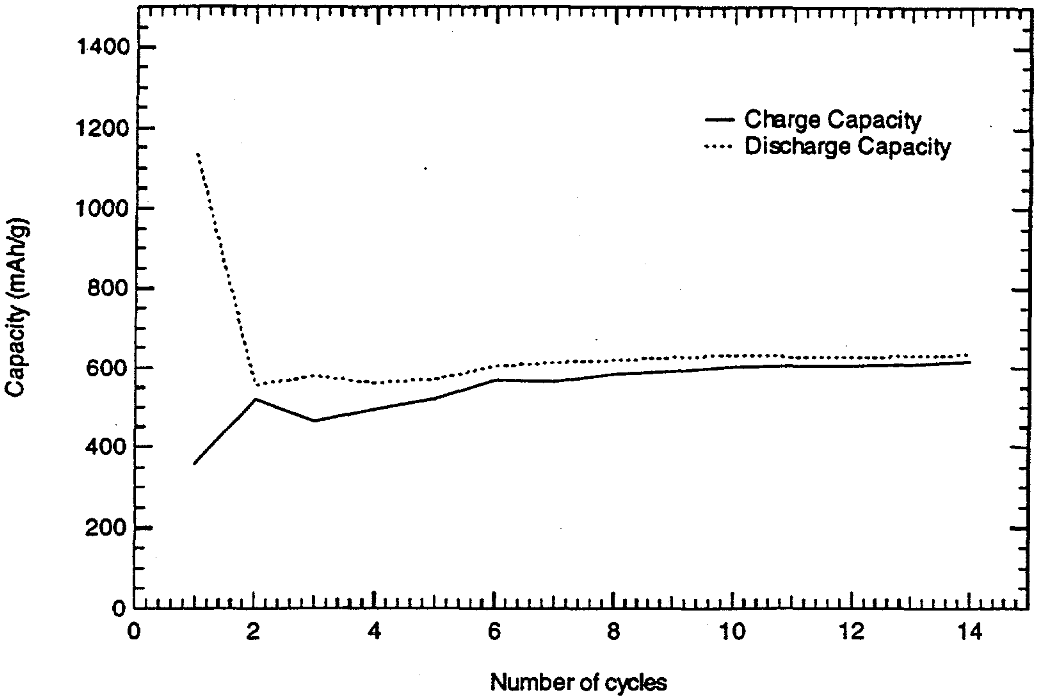

Figure 5: Capacity performance as a function of cycle number of a carbon electrode derived from sepiolite/propylene. Voltage limit: 0 to 2.5 V; current rate: C/20.

ACKNOWLEDGMENTS

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