A Nanostructured Honeycomb Carbon Anode

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We have been investigating a general template-based method for preparing nanostructured Li-ion battery electrodes. We have shown that these nanostructured electrodes have improved rate capabilities relative to thin-film control electrodes composed of the same material. Improved rate capabilities are observed because the high-rate capacity obtained from Li+-insertion materials is limited by slow solid-state Li+ transport in the electrode material, and the nanostructured electrodes decrease the distance that Li+ must diffuse in the solid state. We describe here an alternative type of nanostructured electrode material, a honeycomb carbon anode that consists of a thin carbon film containing an ordered array of monodispersed nanoscopic pores. This honeycomb carbon anode shows a low-rate discharge capacity of 325 mA h g⁻¹, close to that of graphite. At high discharge rates (10 C), the honeycomb anode, delivers 50 times the capacity of a thin-film control anode that did not contain the honeycomb of nanopores. Improved rate capabilities are obtained because penetration of solvent and Li⁺ electrolyte into the pore structure of the honeycomb anode insures that the distance Li⁺ must diffuse in the solid state is smaller than in the thin-film control electrode.

Experimental

Materials.—Aluminum foil (100 × 500 × 0.5 mm, purity 99.99%, Alfa Aesar), quartz slides (75 × 25 × 1 mm, ChemGlass), Li ribbon (1.5 mm thick, 100 mm wide. 99.9%, Aldrich), oxalic acid (Fisher), lithium perchlorate (99.99%, Aldrich), diethyl carbonate (99+% Aldrich), ethylene carbonate (Aldrich), and ethylene (30% balanced with He, Praxair) were used as received.

Preparation of the nanopore alumina membrane.—We have used Masuda’s two-step method for preparing high quality nanopore alumina membranes.25 Briefly, the Al foil was first degreased using acetone and then annealed in air at 400°C for 1 h. A 42 cm² section of foil was then electropolished at 15 V in a solution that was 95 wt % H₃PO₄, 5 wt % H₂SO₄, and was 0.20 M in CrO₃; the cathode was a Pb plate. After rinsing with distilled water, the polished Al foil was anodized at 50 V in 5 wt % aqueous oxalic acid at 1.5°C for 1 h; the cathode was a stainless steel plate. This resulted in the formation of a thin nanopore alumina film on the surface of the Al foil. This precursor film was dissolved away in an aqueous solution that was 0.2 M in CrO₃ and 0.4 M in H₃PO₄ at 80°C. As discussed by Masuda and Satoh,26 this leaves a highly ordered pattern of scallops on the Al substrate.

In the second step, this textured Al substrate was anodized for 15 min at 50 V in the 5 wt % oxalic acid solution. This yields the desired ordered nanopore alumina film. The voltage reduction technique was then used to detach this film from the underlying Al surface.26 This entails gradually (over a period of 1 h) reducing the anodizing voltage to 15 V, followed by detachment by immersion in 10 wt % H₃PO₄ solution. The resulting free-standing nanopore alumina membrane (1.2 μm thick) has two distinct surfaces, the barrier-layer surface, which faced the substrate Al foil during the anodization process, and the solution surface.

Preparation of the carbon films.—The carbon films were prepared using a chemical vapor deposition (CVD) method described previously.27 A quartz slide was inserted into the center of a quartz tube reactor housed in a high-temperature tube furnace. The furnace was heated at 30°C/min to 970°C in flowing Ar gas (90 sccm). The Ar gas stream was then replaced by ethylene (20.7 sccm), which decomposed on the quartz surface to yield the CVD graphitic carbon film.27 After 2 h of CVD reaction, the ethylene was replaced by Ar, and the furnace was allowed to cool to room temperature. This yielded carbon films that were 1 μm in thickness.

Preparation of the honeycomb carbon film.—The nanopore alumina membranes were used as masks, in conjunction with an O₂ plasma etching method, to prepare the honeycomb carbon films. First, however, the barrier-layer surface of the alumina membrane...
was etched in an Ar plasma to widen the pores at this surface. The alumina membrane was placed, barrier-layer surface up, on top of the CVD carbon film. This assembly was then inserted into the center of the vacuum chamber of a reactive ion etching apparatus (Plasma-Therm 790 series), and an Ar plasma was used to etch the barrier-layer surface. This was accomplished using a plasma with radio frequency (rf) power of 200 W and inductively coupled plasma (ICP) power of 300 W. The plasma pressure was 2 mTorr Ar, the Ar flow rate was 15 sccm, and the etch time was 14 min.

After the Ar-plasma etch, the rf power was switched to 300 W, and the Ar was replaced by a mixture of O\textsubscript{2} (10 sccm) and Ar (5 sccm). The alumina membrane/carbon film assembly was exposed to this O\textsubscript{2} plasma for 2 min. During this time, the O\textsubscript{2} plasma propagated into the pores of the alumina membrane and etched away the portions of the underlying carbon film beneath the pores. This led to a honeycomb carbon film that is a replica of the pore structure in the alumina membrane mask.

**Preparation of surface-oxidized nonhoneycomb carbon films.**—These films were prepared in order to explore the effect of surface oxidation on the Li\textsuperscript{+} intercalation electrochemistry of the carbon films. A nonhoneycombed carbon film was placed in the center of the vacuum chamber of a bench-top plasma system (Micro-RIE Series 85, Technics International), and O\textsubscript{2} plasma etching was conducted for 1 min (150 W, 300 mTorr O\textsubscript{2}).

**X-ray diffraction.**—X-ray diffraction (XRD) studies were conducted on a MRD X’Pert XRD system (Phillips) using Cu K\textalpha\textsubscript{r} radiation in a glancing angle reflection mode. The data were collected between 10° and 80° 2\theta at a scanning step of 0.01° with a 1 s interval between each step. As is shown below, the diffraction pattern for the carbon film overlapped with the pattern for the underlying quartz substrate. The deconvolution software package provided with the diffractometer was used to correct the carbon data for the contribution from the quartz.

**Scanning electron microscopy (SEM).**—The sample was attached to an SEM sample stub using a piece of copper foil tape. To improve the quality of the SEM image, the surface of this sample assembly was then sputtered with a very thin (<10 nm) Au film using a Hummer 6.2 (Anatech, Ltd.) sputtering system. Samples were im-

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**Figure 1.** Electron micrographs of the nanopore alumina membrane. Solution surface (A), barrier-layer surface (B), and cross section (C) before Ar-plasma etching. Cross section and barrier layer surface after Ar-plasma etching (D).
aged using a JEOL 6330 cold field emission scanning electron microscope. For quantitative evaluations of the film thickness, pore diameter, porosity, and pore-depth, data from three different SEM images were averaged.

Constant-current charge/discharge experiments.—The Li\textsuperscript{+} intercalation electrochemistry of three different carbon electrodes were investigated, the as-synthesized (AS) CVD thin-film electrode, the AS electrode whose surface had been O\textsubscript{2}-plasma etched (this non-honeycombed material is designated the PE electrode), and the honeycomb (HC) electrode. Electrochemical experiments were run on an EG&G PAR model 263 potentiostat/galvanostat in conjunction with a Gateway 2000 computer. A three-electrode cell, AS, PE, or HC working electrode and Li foil counter and reference electrodes, was used. The electrolyte was 1 M LiClO\textsubscript{4} in a 30:70 (vol %) mixture of ethylene carbonate and diethyl carbonate. All electrochemical experiments were conducted at room temperature in a glove box filled with argon. All potentials reported in this paper are vs. the Li\textsuperscript{+}/Li reference electrode. Constant-current experiments were performed between 0 and 3 V at currents ranging from 10 to 600 μA. The charge/discharge capacity was calculated from the charge/discharge times, the mass of the carbon anode and the currents used.\textsuperscript{7,11} The masses of the carbon electrodes were obtained by measuring the mass difference between the bare quartz substrate and the carbon-covered substrate. The balance used was a Mettler model AX205DR (±0.01 mg).

Results and Discussion

Scanning electron microscopy (SEM).—Figure 1a shows that the solution surface (vide supra) of the nanopore alumina membrane has an array of pores that are on average 66 nm in diameter with a porosity of 36.9%. In contrast, prior to Ar-plasma etching, it is difficult to see open pores on the barrier-layer surface (Fig. 1b). The cross-sectional image (Fig. 1c) shows that the barrier layer surface is covered with a disordered matt of Al\textsubscript{2}O\textsubscript{3}, the remnants of the barrier layer that was present on this surface prior to voltage reduction and detachment. Figure 1c also shows that the as-prepared membrane is 1.2 μm thick, and −0.2 μm of this thickness is the barrier-layer

<table>
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<th>Type</th>
<th>Mass (mg)</th>
<th>Area (cm\textsuperscript{2})</th>
<th>Pore diameter (nm)</th>
<th>Pore Depth (nm)</th>
<th>Porosity (%)</th>
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<td>As-synthesized (AS)</td>
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<td>0.85</td>
<td>75</td>
<td>420</td>
<td>50</td>
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Figure 2. Electron micrographs of (A, top) the as-synthesized (AS) CVD carbon film, and the surface (B, center), and cross section (C, bottom) of the honeycomb (HC) film.

Figure 3. XRD patterns for the quartz substrate and the as-synthesized CVD carbon film on this substrate.
matt. Figure 1d shows that Ar-plasma etching removes the disordered matt from the barrier layer surface and opens the pores at this surface. Ar-plasma etching also decreases the membrane thickness to 0.4 \mu m.

Figure 2a shows a cross-sectional and surface image of an as-synthesized (AS) CVD carbon film. Images of this type indicate that these films are defect-free and spacing filling with smooth surfaces; the film thickness is 1 \mu m. Figure 2b shows that the surface of the honeycomb carbon (HC) film has a high density of monodisperse pores with pore diameter \approx 75 \text{ nm}, slightly larger than that of the alumina mask; the porosity is 50%. The cross-sectional image (Fig. 2c) shows that these pores do not extend all the way through the thickness of the carbon film. Rather, the pore depth is \approx 420 \text{ nm} and there is a base layer of unetched (nonporous) carbon that is \approx 370 \text{ nm} thick. This unetched portion of the carbon film allows for good electrical contact to the overlying etched portion of the film. The characteristics of the various carbon electrodes studied here are summarized in Table I.

X-ray diffraction (XRD).—Figure 3 shows X-ray diffraction (XRD) data for the quartz substrate and for the AS carbon film on this substrate. The peak in the AS carbon-film data is due to the diffraction from the d_{002} plane, and the breadth of this peak shows that the film is disordered. After correcting for the contribution from the quartz we find that the d_{002} peak of the carbon thin film occurs at lower angles than in graphite (2\theta = 25.402^\circ \text{ vs. } 26.381^\circ \text{ for graphite}). Furthermore, the interlayer distance is expanded from 3.376 \text{ Å (graphite)} to 3.497 \text{ Å}. These features are typically of turbostatically disordered carbon films prepared by the CVD method.

Constant current charge/discharge experiments.—The AS, HC, and PE electrodes were charged from the open circuit (\approx 3 \text{ V}) to 0 V (Fig. 4). The charging curve for the HC film is distinctly different from those of the AS and PE films. In particular, much longer times are required before the potential of the HC film reaches the negative limit of 0 V. The corresponding discharge curve (Fig. 5) shows that a large portion of this first-charge capacity is irreversible. This indicates that the irreversible capacity of the HC electrode is larger than for either the AS or PE electrodes. Because the surface area of the HC electrode is much higher than the nonhoneycombed AS and PE
electrodes, this result is not surprising. We are currently studying the surface chemistry changes associated with this irreversible capacity, and we will report on these results soon.

Low-rate (0.2 C) discharge curves for the HC, AS, and PE electrodes are shown in Fig. 5. There are no potential plateaus, which corroborates the conclusion that these electrodes are composed of disordered carbon.29 Gnanaraj et al. have explained that the small size of the elementary graphene flake fragments and the lack of long-range order in the c lattice direction in disordered carbon preclude staging phenomenon during Li⁺ insertion/extraction.29 Figure 5 also shows that the reversible capacity of the HC electrode is significantly higher than the reversible capacities of the AS and PE electrodes. The reversible capacity of the HC electrode at this low discharge rate is almost 90% of the maximum theoretical capacity of graphite.

Figure 6 shows the discharge capacity vs. discharge rate data for the AS, PE, and HC electrodes. As is typically observed for Li-ion battery electrodes, capacity falls off with increasing discharge rate.3-12 As noted earlier, this is because the rate of discharge is limited by slow solid-state Li⁺ diffusion in the electrode material.3-12 The consequence of this slow Li⁺ transport is that at high discharge rates, the surface of the electrode material becomes depleted in Li⁺ causing the electrode potential to reach the positive cutoff value before Li⁺ in the interior of the material can be deintercalated (i.e., concentration polarization).

In our previous papers we have shown that electrodes composed of monodisperse nanotubes and nanoﬁbers of the electrode material are much less susceptible to the deleterious effects of concentration polarization than thin-film control electrodes composed of the same material.3-12 This is because the distance Li⁺ must be transported in the solid state is dramatically reduced in the nanostructured electrodes. As a result, the nanostructured electrode retains a much larger fraction of its theoretical capacity at high discharge rates than the corresponding thin-film control electrode.3-12

Like the nanotuber and nanotube electrodes described previously, the HC electrode also shows dramatically higher discharge capacities at high C rates than the two nonhoneycombed thin-film control electrodes (Fig. 6). This shows, as might be expected, that the HC carbon is another form of nanostructured electrode in this case, penetration of solvent and Li⁺ electrolyte into the pore structure of the HC anode insures that the distance Li⁺ must diffuse in the solid state is dramatically lower than in the AS or PE electrodes. This rate capability advantage of the HC electrode can be shown more clearly by plotting the ratio of the discharge capacities of the HC and AS electrode vs. C rate (curve labeled HC/AS in Fig. 7). At the highest C rate, the HC electrode delivers 50 times higher capacity than the AS electrode.

It is also of interest to compare the capacities of the HC vs. PE electrodes as a function of the C rate (Fig. 7). The HC electrode shows better rate capabilities than the PE electrode, but the advantage is not as large as the HC vs. AS case. Put another way, the thin-film control electrode whose surface had been O₂ plasma etched (PE) shows better rate capabilities than the nonplasma-etched AS control electrode. There have been a number of recent studies of the effect of surface oxidation on the discharge properties of carbon electrode materials.31,32 Peled et al.31 showed that mild oxidation (burning) of synthetic graphite resulted in electrodes that showed higher discharge capacities and longer cycle lives than the corresponding nonoxidized electrode. Ein-Eli et al.32 chemically oxidized the surfaces of graphite electrodes and obtained similar benefits. The key point to make here is that since the pores in the HC electrode are made by an oxygen-plasma method, the benefits of surface oxidation are inherent in the HC fabrication process.

Figure 8 compares the cycle lives of the HC, PE, and AS electrodes. In agreement with the above conclusions, the two O₂ plasma-etched electrodes (HC and PE) show better cycle life than the AS electrode. For example, the ratios of the capacities obtained after the 50th cycle to that obtained for the first cycle for the HC, PE, and AS electrodes are 0.75, 0.77, and 0.53, respectively. Finally, Fig. 9 shows that the HC electrode delivers usable capacity even after 700 cycles.

Conclusions

We have shown that a new type of nanostructured honeycomb carbon anode can be prepared using an O₂ plasma etch method in conjunction with a nanopore alumina mask. These honeycomb carbon anodes show low-rate discharge capacities of 325 mA h g⁻¹, and at high discharge rates (10 C), delivery 50 times the capacity of a thin-film control anode that did not contain the honeycomb of nanoopes.

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