Tailoring the Pore Alignment for Rapid Ion Transport in Microporous Carbons

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The success of a future energy-efficient economy largely depends on our ability to develop novel materials with greatly improved characteristics for electrical energy storage and delivery. The development of electrical double layer capacitors (EDLC) has attracted much attention[1−4] because of the increasing importance of EDLC for industrial equipment, electric vehicles, and smart grid applications.[5,6] The outstanding operational life of EDLC in excess of 500 000 charge−discharge cycles and charging within tens of seconds are unattainable in Li-ion batteries.[5,6] Improving the charge−discharge rate of EDLC by an order of magnitude or more without sacrificing their energy storage characteristics is critical for many peak-power hungry applications, including the leveling of subsecond disturbances in power lines.

The power storage and the charge−discharge time of EDLC are determined by how fast the ions can travel within the electrodes.[7] The straight pores of carbon nanotube (CNT) arrays have demonstrated the potential for ultrafast transport of ions.[8−10] However, CNT electrodes offer only moderate specific capacitance owing to their small surface area. The high surface area of activated carbon electrodes results in higher specific capacitance,[7] but at the expense of slow discharge, presumably due to the presence of irregular curved pores,[11−13] which may dramatically slow down the ion transport. The large mesopores (5−50 nm) introduced in some activated carbon may also allow for rapid ion transport,[14] but they lead to significant lowering of the volumetric capacitance. The effect of the pore tortuosity, particularly in the case of micropores (<2 nm), remains unclear. At the same time, a novel class of porous carbons synthesized in the ordered and uniform micropores of zeolite templates[15] offers a very high specific surface area as well as a great potential for the formation of aligned pore channels that enable an unobstructed transportation of electrolyte ions.

Several zeolite-templated carbons demonstrated high capacitance and attractive energy storage characteristics in EDLC using both organic[16] and aqueous[17] electrolytes due to the well developed surface area and, in the later case, N dopant-induced pseudocapacitance. Here we report a systematic study of the effects of tailored micropore alignment on electrolyte ion adsorption and transport.

In contrast to other studies, where oxygen- or nitrogen-containing precursors were introduced into the zeolite via impregnation[15,17,18] and/or atmospheric-pressure chemical vapor deposition (CVD),[15,16,19] we employed a low-pressure (1−10 Torr) CVD using a simple hydrocarbon precursor (acetylene, C_2H_2) to minimize the incorporation of carbon dopants, avoid the influence of the operator, and improve sample uniformity. After C deposition at 700 °C, the sacrificial zeolite template was etched away using a concentrated HF solution. Since HF treatment was found to leave small cryolite

(Na_3AlF_6) residues at the end of the process, we introduced additional treatment in a concentrated H_2SO_4 solution to dissolve them. Selected samples were annealed at 800 °C for 4 h prior to zeolite etching.
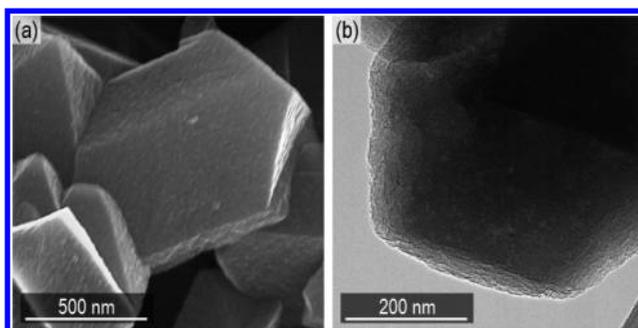

Figure 1. Electron microscopy of zeolite Y-templated carbons: (a) scanning and (b) transmission electron microscopy (SEM and TEM) images of synthesized porous carbon particles produced at 700 °C.

In contrast to highly nonuniform porous carbon with large voids and dense carbon shells observed in samples produced using atmospheric-pressure CVD[16] (Figure S1 in the Supporting Information (SI)), templated carbons synthesized in this work not only retained the zeolite shape (Figure 1a) but also showed very uniform structure (Figure 1b), suggesting that under low pressure conditions the mean free path of acetylene diffusing into the zeolite micropores prior to decomposition exceeds the size of zeolite particles.
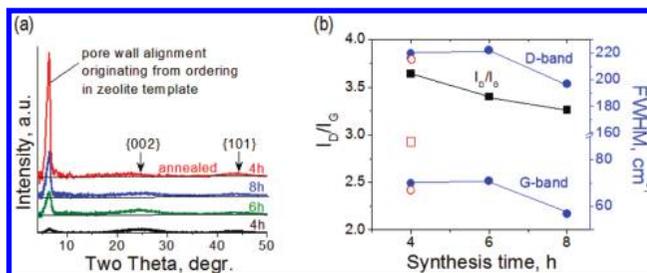

Figure 2. Microstructure of zeolite Y-templated carbons synthesized at 700 °C for 4, 6 and 8h: (a) XRD and (b) Raman analyses. The background in panel a was removed. Values in panel b for the annealed sample are shown by unfilled symbols.

X-ray diffraction (XRD) studies (Figure 2a) showed the strong influence of synthesis conditions on the carbon structure. Increasing the synthesis time from 4 to 8 h increases the amount of carbon deposited onto the zeolite template and the surface area of the carbons obtained only moderately, by less than 30% (Tables S1 and S2, SI). However, it significantly increases the relative intensity of the low angle peak at ∼6° (Figure 2a), which corresponds to carbon walls regularly spaced at ∼1.3 nm and originates from the

ordering of the {111} planes of the zeolite Y template. Annealing the 4 h sample at 800 °C for 4 h prior to zeolite etching improved the pore alignment to an even greater extent (Figure 2a). The broad peaks at ~26° and ~44° correspond to scattering on the {002} and {101} planes of graphitic carbon. The very low intensity of these peaks indicates the low percentage of multiwalled structures in the sample. The lower intensity of the 6° peak observed at lower synthesis time indicates the absence of well-aligned graphene pore walls and thus the absence of straight pores. In fact, synthesis at 700 °C for 2 h or less resulted in the collapse of the carbon structure during HF etching (not shown).

The pore size distributions of all the synthesized carbons were very similar, with the majority of pores smaller than 2 nm (Figure S2, SI). All carbons demonstrated Raman spectra typical for disordered carbons (Figure 2b) with broad D- and G-bands.[20] The full width at half-maximum (FWHM) of both bands showed small variations with synthesis time (within 10 and 17%, respectively). The ratio of the integrated intensities of the bands (I_D/I_G) showed a decrease of ~10% and 20% with increasing synthesis time from 4 to 8 h or with postannealing, respectively (Figure 2b), suggesting a slightly higher number of defects in the graphene walls of the carbons synthesized for shorter times, which did not contain well-aligned pores.
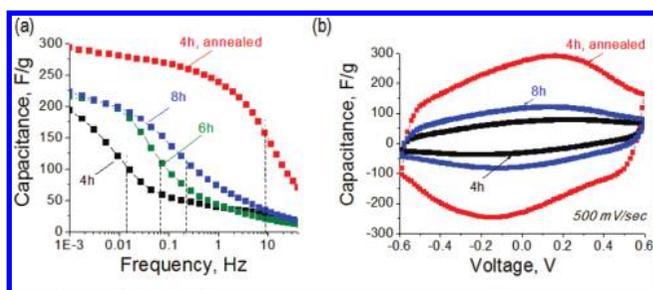

Figure 3. Effect of pore alignment in zeolite Y-templated carbons on ion transport in EDLC: (a) estimated capacitance retention with increasing operating frequency, (b) cyclic voltammetry recorded at ultrafast sweep rate of 500 mV/s; 1 M H_2SO_4 was selected as electrolyte.

Electrochemical impedance spectroscopy (EIS) at zero bias of the ~250 μm carbon electrodes in a symmetric EDLC showed the major influence of pore alignment on the rate of ion transport (Figure 3). The capacitance of carbon synthesized at 700 °C for 4 h does not show signs of saturation at a frequency as low as 0.001 Hz, suggesting that tortuous diffusion paths for electrolyte ions prevent the achievement of the equilibrium ion adsorption within ~17 min. Increasing deposition time or performing post-deposition annealing results in a major improvement in the frequency response. Similarly fast response was also observed in zeolite-templated carbon synthesized at a higher temperature of 800 °C (Figure S3, SI). If we approximate the highest operating frequency as the frequency at which the capacitance is 50% of its maximum value, then tuning the carbon synthesis conditions allowed for an improvement in the frequency response by more than 2 orders of magnitude (Figure 3a). Since all the carbons have very similar pore size distributions, compositions, and particle sizes, we conclude that pore alignment and the absence of obstacles for ion diffusion are responsible for the observed phenomenon.

Figure 3b compares the cyclic voltammograms of the carbon electrodes in a symmetric EDLC recorded at an ultrafast sweep rate of 500 mV/s. While the capacitance of all the carbons at a low sweep rate of 1 mV/s (not shown) or a frequency of 1 mHz (Figure 3a) has similar values (200−300 F/g), the aligned pores of the

postannealed sample allow for significantly better capacitance retention and ~5 times higher capacitance at the increased sweep rate (Figure 3b). The broad peak at zero bias is likely related to the pseudocapacitance, which originates from surface oxides unintentionally introduced at room temperature. Interestingly, in contrast to nitrogen-related pseudocapacitance, which shows significant fading after 10000 cycles, our carbons showed excellent stability as well as 5% increase in capacitance after 10000 cycles (Figure S4, SI).

Note that while the size of the initial zeolite crystallites is submicrometer (Figure 1), they are commonly sintered into dense 2−10 μm aggregates. Therefore, the overall size of most of our carbon particles is in the 2−10 μm range, similar to or higher than that of most activated carbons. Yet, our selected samples demonstrated the unique combination of extremely high specific capacitance of up to ~300 F/g, excellent stability and an outstanding frequency response, which is superior even to that of activated carbons with large mesopores.[14] This combination leads to a combination of high energy and high power density that is desirable in EDLC.

In summary, atomic-level micropore alignment control in carbons, achieved by exploiting the robust zeolite lattice as a template, permitted us to experimentally demonstrate the greatly enhanced rate of ion transport in porous carbons with aligned pore channels, consistent with earlier theoretical prediction.[8] This conclusion is not affected by the type of functional groups present on the carbon surface. Our findings not only prove that mesopores are not required for rapid ion diffusion but also provide guidance for the optimal design of porous carbons with improved power storage characteristics.

Supporting Information Available: Experimental details for porous carbon and electrode fabrication; additional structural and porosity characterization. This material is available free of charge via the Internet at http://pubs.acs.org.

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