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Electric Double Layer Capacitors on Hierarchical Porous Carbons

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Introduction

Electric double layer capacitors (EDLCs) have attracted great interests for their potential application to auxiliary power sources of hybrid electric vehicles, owing to their high power density and long cycle life. In order to increase EDLCs energy density, porous carbons with large surface areas are widely used as electrodes. Capacitance, however, does not proportionally increase with surface area, especially for micropores (< 2 nm in diameter), resulting from poor accessibility of micropores to electrolytes. Micropores also increase electrolyte resistance that causes potential loss. It is of importance to design and fabricate pore structures of porous carbons. Porous carbons that are prepared by colloidal crystal templating method provide promising pore structure, i.e., large meso/macropore surface area (typically > 500 m^2 g^{-1}) and interconnected meso/macropores with mono-dispersed diameters.[1,2] In this paper, we report dependence of EDLC performance on pore structures of porous carbons fabricated by colloidal crystal templating method.

Experimental

Porous carbons were prepared by following the reported process.[1,2] First, colloidal crystals of monodispersed SiO$_2$ colloidal solutions (with diameters ranging 8 – 80 nm) were fabricated by centrifugation and subsequent drying. Then, the colloidal crystals were immersed in a mixed solution of phenol, aqueous formaldehyde, and a small amount of concentrated hydrochloric acid. Next phenol and formaldehyde underwent polymerization (at 400 K for 12 h) and carbonization (at 1073 – 1273 K for 5 h in Ar). On the carbonization, heating rate was varied in the range of 1 – 5 K min^{-1}. Finally, SiO$_2$ templates were removed from the carbon/SiO$_2$ composites by an aqueous HF solution and the resultant porous carbons were dried under vacuum for 1 day. The carbons thus obtained are referred to as C[d_{SiO2}], where d_{SiO2} is the average diameter of the template SiO$_2$ particles. Porous structure of the obtained porous carbons was investigated by transmission electron microscopy (TEM) and the analysis of nitrogen adsorption-desorption isotherms recorded at 77 K. EDLC performance was examined in both aqueous solution (1 M H$_2$SO$_4$) and organic electrolyte solution (1 M LiClO$_4$ in PC+DME) by cyclic voltammetry, galvanostatic charge/discharge test, and electrochemical impedance spectroscopy.

Results and Discussions

The obtained porous carbons exhibited meso/macropores originated from template SiO$_2$ particles and micropores resulting from carbonization of the phenolic resin. TEM images (Fig. 1) revealed that meso/macropores were highly ordered for $d_{SiO2} \geq 80$ nm and were disordered with decreasing d_{SiO2}. As summarized in table 1, the total surface

areas (S_{total}) of the C[d_{SiO2}] ranged $1,000 - 2,000 \text{ m}^2 \text{ g}^{-1}$. Note that very large meso/macropore surface area (S_{meso}) of more than $1,000 \text{ m}^2 \text{ g}^{-1}$ was obtained.

For smaller d_{SiO2}, cyclic voltammograms exhibited humps around potential of zero charge ($0.3 \sim 0.4$ V), which may be explained by potential drop in micropores. Table 1 also lists diffe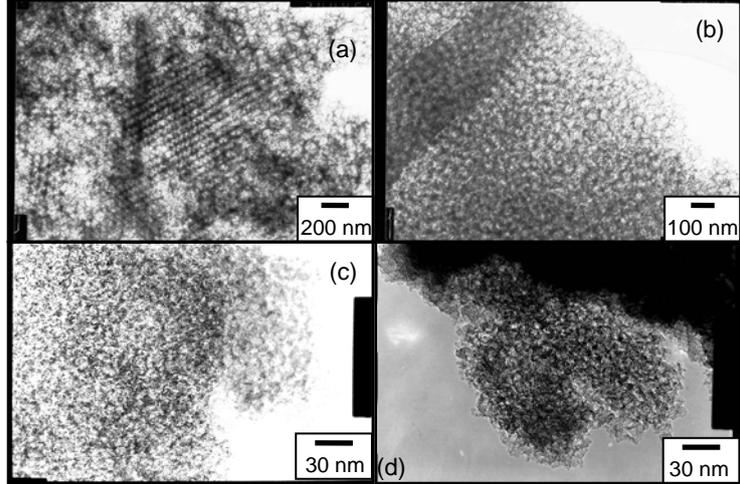rential capacitance obtained from cyclic voltammograms. For C[8], very large capacitance of greater than 250 F g^{-1} were obtained, resulting from the large surface area and good electrolyte accessibility through mesopores.

Figure 1. TEM images of porous carbons C[d_{SiO2}] ((a) $d_{SiO2} = 80$, (b) 45, (c) 11.5, and (d) 8 nm).

Surface area dependence of double layer capacitance, C_{DL}, indicated that C_{DL} is affected not only S_{meso} but also micropore surface area (S_{micro}). Therefore, C_{DL} was analyzed by the following equation:

$$C_{DL} = C_{DL,meso} + C_{DL,micro} = c_{meso} \cdot S_{meso} + c_{micro} \cdot S_{micro} \qquad (1)$$

Figure 2 plots C_{DL}/S_{micro} as a function of S_{meso}/S_{micro} based on Eq. (1). The plot exhibited linear relationship for small S_{meso}/S_{micro}, and specific capacitance on mesopores (c_{meso}) and micropores (c_{micro}) were obtained from the slope and the intercept, respectively. c_{micro} was less than 5 μF cm^{-2}, while cmeso was dependent on potential: 22 and 29 μF cm^{-2} for 0.6 and 0.3 V (vs. Ag/AgCl), respectively. With the fact that double layer capacitance on carbon electrodes in aqueous electrolyte are typically 20 μF cm^{-2}, these results imply that micropore contribution to double layer capacitance depends on electrode potential.

References

[1] I. Moriguchi, F. Nakahara, H. Yamada, T. Kudo, *Electrochem. Solid-State Lett.*, 7, A221 (2004). [2] H. Yamada, H. Nakamura, F. Nakahara, I. Moriguchi, T. Kudo, *J. Phys. Chem. C*, 111, 227 (2007).

Table 1. Specific surface area and specific capacitance (in 1 M H$_2$SO$_4$) of porous carbons.

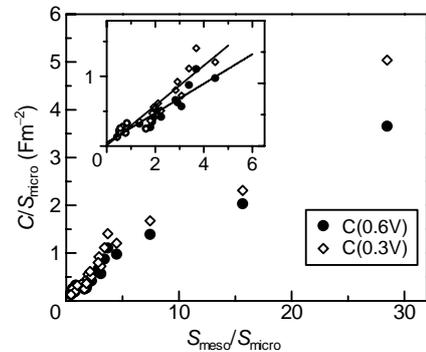| sample	specific surface area			capacitance	
	S_{total} (m^{2}g^{-1})	S_{meso} (m^{2}g^{-1})	S_{micro} (m^{2}g^{-1})	$C(0.3 \text{ V})$ (F g^{-1})	$C(0.6 \text{ V})$ (F g^{-1})
C[80]	1508	520	988	223	203
C[45]	1399	1041	358	330	224
C[16]	1656	1079	577	271	200
C[11.5]	1214	1070	144	241	200
C[8]	2090	1964	125	290	255

Figure 2. Relationship between C/S_{micro} and S_{meso}/S_{micro}.