Synthesis of a new mesoporous carbon and its application to electrochemical double-layer capacitors

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A mesoporous carbon with regular three-dimensionally interconnected 2 nm pore arrays using AlMCM-48 as a template has been synthesised; the mesoporous carbon exhibited excellent performance as an electrochemical double layer capacitor.

The development of mesoporous silica materials by Mobil Oil researchers in 1992 stimulated explosive research on the preparation of porous materials through template approaches.[1] Various types of organic templates including surfactant self-assemblies, block copolymers and polymer lattices have been utilized to synthesize such mesoporous inorganic materials.[2] Recently many types of nanostructured carbons have been produced through templating approaches.[3] Electrochemical double-layer capacitors (EDLCs) find new promising applications as pulse power sources for digital communication devices and electric vehicles.[4] The popularity of these devices is derived from their higher energy density relative to conventional capacitors and their longer cycle life and higher power density relative to batteries. Here, we report the first synthesis of a mesoporous carbon material with regular three-dimensionally interconnected pore channels. We also present preliminary results on the EDLC performance of the mesoporous carbon. In our approach, a mesoporous MCM-48 aluminosilicate with three-dimensional channel structure has been utilized as a template. Mesoporous silica MCM-48 was prepared by the reported method.[1] Aluminium was implanted onto MCM-48 to generate strong acid catalytic sites for the polymerization of phenol and formaldehyde. Phenol and formaldehyde were incorporated into the pores of aluminium-implanted MCM-48 (AlMCM-48) by heating for 12 h at 90 °C under reduced pressure. The polymerization of phenol and formaldehyde to obtain the phenol resin inside AlMCM-48 was carried out by heating the mixture under a nitrogen atmosphere at 125 °C for 5 h.[5] The resulting AlMCM-48–phenol resin composite was heated under an N_2 flow at a heating rate of 5 °C min^{-1} to 700 °C and held there for 7 h to carbonize phenol resin inside the MCM-48 channels. The dissolution of MCM-48 frameworks using 48% aqueous hydrofluoric acid (HF) generated mesoporous carbon, designated SNU-1 (Seoul National University).

The ordered mesoporous structure of SNU-1 was investigated by X-ray diffraction (XRD), transmission electron microscopy (TEM) and gas adsorption measurements. XRD patterns were obtained at various times during the course of the synthesis. Fig. 1(a) shows the characteristic pattern of the AlMCM-48 template with a *d* spacing value of 3.37 nm.[6] To our surprise, intense peaks at $2\theta = 1.6$ and 2.7° from the long-range ordering of mesopores is clearly shown in the XRD pattern of SNU-1 carbon [Fig. 1(b)]. This result revealed that the carbon networks formed inside the mesopores of AlMCM-48 are strong enough to survive even after the removal of the aluminosilicate framework by HF etching. Elemental analysis (EA) revealed a high C/H molar ratio of 9.3 and <1 mol% aluminosilicate residue in the SNU-1 carbon material (EA result: 93.24% C, 0.84% H, 0.09% N, 2.56% O). TEM studies of mesoporous SNU-1 carbon showed a regular array of 2 nm diameter holes separated by 2 nm thick carbon walls (Fig. 2). The specific surface area of SNU-1 was found to be 1257 $\mathrm{m}^2\ \mathrm{g}^{-1}$ from nitrogen BET adsorption measurements. This is comparable to values reported for other mesoporous inorganic materials. Nitrogen adsorption–desorption curves showed hysteresis at high relative pressure characteristic of mesopores. The pore size distribution data calculated from the adsorption branch of the nitrogen isotherm by the BJH (Barrett–Joyner–Halenda) method showed that pores are uniform with an average pore size of 2.3 nm (Fig. 3).

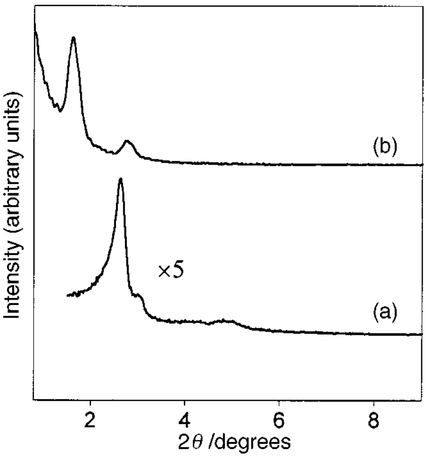

Fig. 1 X-Ray diffraction (XRD) patterns of AlMCM-48 template (a) and mesoporous SNU-1 carbon (b). Trace (a) was obtained with a Rigaku D/Max-3C diffractometer equipped with a rotating anode and Cu-Kα radiation ($\lambda = 0.15418$ nm) and trace (b) was acquired on a Bruker GADDS small-angle X-ray scattering diffractometer with a general area detector.

The EDLC performance of SNU-1 was compared to the most popularly applied activated carbon, MSC-25. Fig. 4 shows the cyclic voltammograms of two carbon electrodes that were obtained in organic electrolyte (1 M $\mathrm{NEt_4BF_4}$ in propylene carbonate). An immediately apparent feature is that SNU-1 shows a more ideal capacitor behavior than MSC-25 with a steeper current change at the switching potentials (0.0 and 3.0 V), resulting in a more rectangular-shaped (mirror-imaged) *i*–*V* curve. An important characteristic of electrical energy storage in a capacitor is that energy is retrievable in discharge over the same potential range as that required to store the energy on charging, otherwise the energy storage is limited. The slow changes at the switching potentials in the cyclic voltammogram (CV) of MSC-25 electrode stem from the slow re-organization

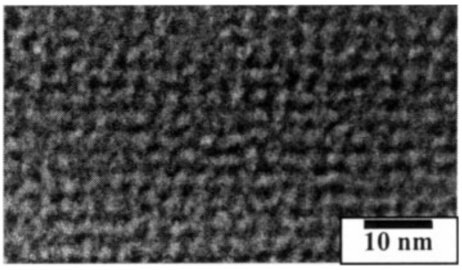

Fig. 2 Transmission electron micrograph (TEM) of mesoporous SNU-1 carbon. The image was obtained with a Phillips CM-20 instrument.

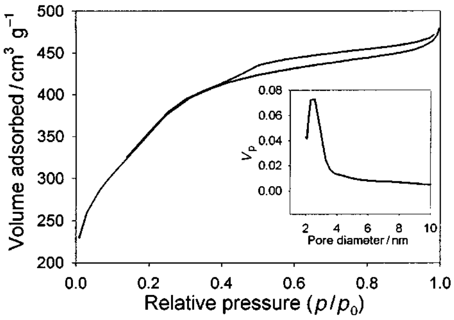

Fig. 3 N_2 adsorption and desorption isotherms of mesoporous SNU-1 carbon. (Inset) The corresponding pore size distribution curve calculated from the adsorption branch of the nitrogen isotherm by the BJH method. V_p is the incremental pore volume. The isotherms were collected at 77 K on a Micrometrics ASAP2010 Gas Adsorption Analyzer after the carbon material was degassed at 250 °C at 30 μTorr for 5 h.

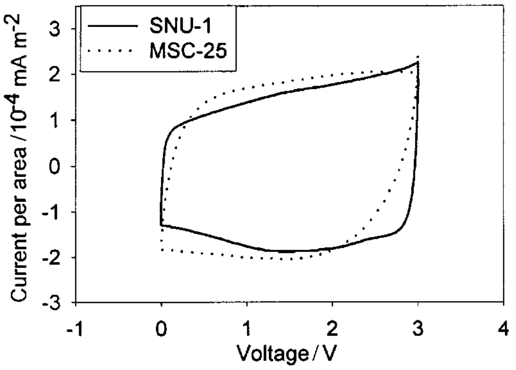

Fig. 4 Cyclic voltammograms of SNU-1 and MSC-25 activated carbon in organic electrolyte (1 M NEt_4BF_4 in propylene carbonate). A two-electrode system consisting of working and counter electrodes was used. These two electrodes were fabricated with equal amounts of the carbon materials. CV measurements were made in the potential range 0–3 V with a scan rate of 5 mV s^{-1}.

of the double layer owing to slow ionic motions in micropores. The steep changes in the CV of the SNU-1 electrode in turn reflect the dominance of regular interconnected mesopores among electrochemically usable pores.

When cyclic voltammetry of SNU-1 carbon was performed in an aqueous electrolyte solution (2 M H_2SO_4), a similar rectangular-shaped pattern was obtained. Rectangular-shaped cyclic voltammograms over a wide range of scan rates is the ultimate goal in EDLC. This behavior is very important for practical applications. First, a higher energy density is expected, because the usable potential range is wide. Second, a higher power density is expected as the critical scan rate is increased. SNU-1 carbon is much closer to this behavior than MSC-25. When cyclic voltammograms were recorded for these two carbons in an aqueous electrolyte solution by varying the scan rate from 5 to 50 mV s^{-1}, SNU-1 carbon retained a rectangular shape up to a scan rate of 20 mV s^{-1}. By contrast, MSC-25 carbon showed a deformed cyclic voltammogram at a scan rate of 10 mV s^{-1} and a completely collapsed one at a scan rate of 20 mV s^{-1}.

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