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Three-Dimensionally Arrayed and Mutually Connected 1.2-nm Nanopores for High-Performance Electric Double Layer Capacitor

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Supporting Information

ABSTRACT: Zeolite-templated carbon is a promising candidate as an electrode material for constructing an electric double layer capacitor with both high-power and high-energy densities, due to its three-dimensionally arrayed and mutually connected 1.2-nm nanopores. This carbon exhibits both very high gravimetric (140−190 F g^{-1}) and volumetric (75−83 F cm^{-3}) capacitances in an organic electrolyte solution. Moreover, such a high capacitance can be well retained even at a very high current up to 20 A g^{-1}. This extraordinary high performance is attributed to the unique pore structure.

Electric double layer capacitor (EDLC) is one of the key energy storage devices for the development of clean energy technology including next-generation electric vehicles.[1] EDLC is charged in principle through the physisorption of electrolyte ions onto nanopore surfaces of a carbon electrode. Before the ions are adsorbed, they need to migrate from a bulk solution to the electrode surface through the narrow nanopores. Thus, the reduction of the ion-transfer resistance in the nanopores is one of the key issues to realize a high-power density EDLC.[2,3] Thus far, great efforts have been made to produce nanostructured electrode materials that possess efficient paths for ion diffusion. The successful examples are single-walled carbon nanotubes (SWCNT),[4] templated mesoporous carbons (TMC),[2] and hierarchical porous carbons (HPC).[5] These high-rate materials are characterized with large diffusion paths, the sizes of which are much larger than the size of solvated ions (∼0.5 to 1.4 nm),[6] allowing the ions to move very rapidly during the charge/discharge processes. Consequently, these materials can retain their capacitance even at an ultrahigh current, i.e., exhibiting a high rate performance, which is essential to construct a high-power density EDLC. However, paths too large make the electrode density significantly low and thus seriously decrease the volumetric capacitance, eventually resulting in the low volumetric energy density of the final EDLC device.[5] To avoid this problem, the size of the diffusion path should be as small as possible, but the fast ion transport has to be retained. In the present work, we demonstrate that it is possible to meet the two seemingly contradictory requirements with zeolite-templated carbon (ZTC),[7] an ordered microporous carbon obtained as a negative replica of zeolite template, which can be clearly distinguished from TMCs with narrow pore size distributions in the mesopore range (>2 nm) and therefore with the low volumetric capacitance.[2]

We have recently revealed that ion-transfer resistance inside ZTC is extremely low despite its small nanopore size (∼1.2 nm), due to the regularly arrayed and three-dimensionally (3D)-linked pore network structure.[3] In addition, ZTC is promising as an electrode material with high gravimetric and volumetric capacitances. Table 1 summarizes gravimetric (S_g) and volumetric (S_v) surface areas for several high-rate materials reported so far. In principle, S_g and S_v have directly to do with the gravimetric and the volumetric capacities, respectively. It is clear that ZTC has a great potential for higher capacity, especially for the volumetric one, compared with the others. In this work, we report not only a high volumetric capacitance of ZTC but also its surprisingly high rate performance (the capacitance was measured up to an ultralarge discharge current of 20 A g^{-1}). Moreover, we propose a general direction to achieve high rate performance together with high volumetric capacitance in a nanoporous carbon electrode.

Table 1. Gravimetric (S_g) and Volumetric (S_v) Surface Areas of the High-Rate Materials Reported so Far

carbon	S_g [m^2 g^{-1}]	S_v [m^2 cm^{-3}] [a]	reference
SWCNT	∼1000	∼600	4
TMC	∼1700	∼900	2
HPC	∼2060	<510 [b]	5
ZTC	∼3040	∼1460	3

[a] $S_v = S_g \rho$, where ρ is the particle density of carbon. ρ was calculated by $\rho = \{V_{total} + 1/\rho_{carbon}\}^{-1}$, where V_{total} is the total pore volume estimated from N_2 isotherm (77 K) and ρ_{carbon} is the true density of carbon (2 g cm^{-3}). [b] ρ of HPC was calculated without considering the total macropore volume because of a lack of the data in the reference. Therefore, S_v of HPC could actually be much less than 510 m^2 cm^{-3}.

The inorganic template used in this work is FAU zeolite, whose porosity consists of a diamond-like framework of spherical cavities (supercage, ∼1.3 nm in diameter). By changing the carbon-filling amount into the zeolite nanopores (38.9 and 46.2 carbon atoms per one supercage on average), the two types of ZTCs with the same ordered structure but with different sizes of carbon framework were synthesized (see the Supporting Information for preparation methods, the possible molecular structures of these two ZTCs, and the difference between ZTC and TMC). ZTCs with smaller and larger frameworks are referred to as ZTC-S and ZTC-L, respectively. ZTC-L has a higher electrical conductivity than ZTC-S as we will discuss later.

For comparison, two commercial activated carbons were used: A20 (Unitika, Ltd.) and MSC30 (Kansai Coke and Chemicals Co., Ltd.). The framework morphologies of ZTCs and the activated carbons are intrinsically different, as evident from their transmission

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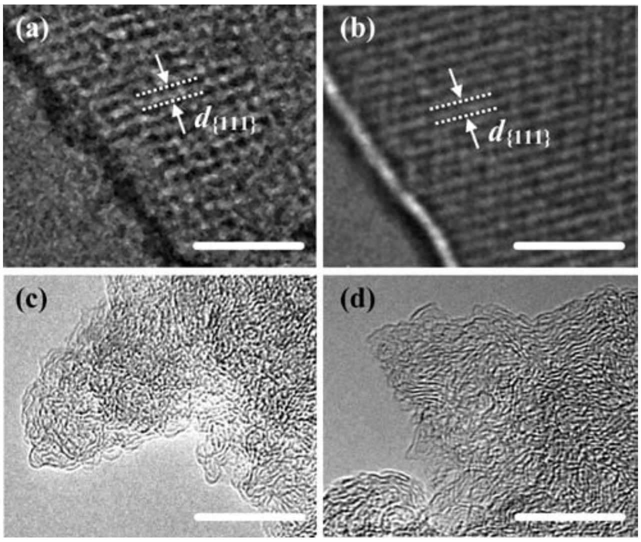

Figure 1. TEM images of (a,b) zeolite-templated carbons and (c,d) activated carbons. (a) ZTC-L, (b) ZTC-S, (c) MSC30, and (d) A20. Scale bars are 10 nm.

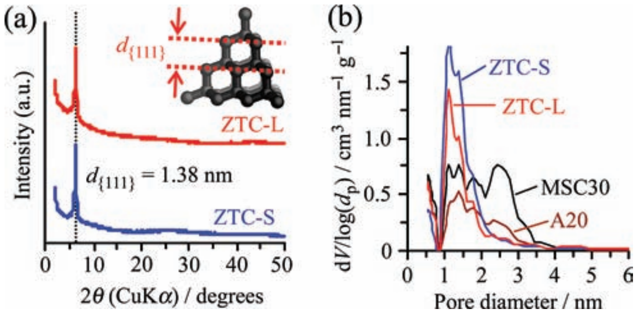

Figure 2. (a) XRD patterns of ZTCs and (b) pore size distributions of all the samples. Inset of (a) is the model of ZTC-framework morphology (space group is $Fd\bar{3}m$).[8]

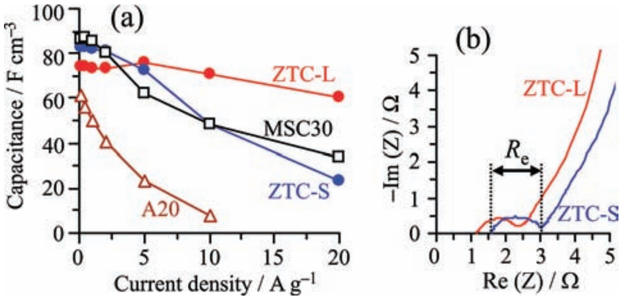

Figure 3. (a) Volumetric capacitance (C_v) versus current density. C_v was calculated by $C_v = C_s\,\rho$, where C_s is a gravimetric capacitance obtained by Galvanostatic charge−discharge cycling, and ρ is the particle density (see Table 1). (b) Nyquist plots for the two ZTCs. The size of the semicircle (R_e) is shown for ZTC-S.

electron microscope (TEM) images (Figure 1). Since ZTC is a negative replica of the zeolite template, the nanopores of ZTC correspond to the pore walls of zeolite, thereby being 3D-arrayed and linked to each other (see the white cavities in a and b of Figure 1). On the other hand, the activated carbon comprises disordered, defective, and curved graphene layers (c and d of Figure 1), making the resulting nanopores complex and random. In the X-ray diffraction (XRD) patterns of ZTCs (Figure 2a), both of them show a sharp peak at $2\theta = 6.4°$, corresponding to {111} planes of the ordered framework that is shown in the inset of Figure 2a.[8] Another important feature of the ZTCs is the absence of the carbon (002) peak in their XRD patterns (Figure 2a), indicating that there is no carbon stacking structure that is sometimes formed outside zeolite particles if the carbon-deposition conditions are not appropriate.[7] Figure 2b shows pore size distributions that were calculated by density functional theory. As expected from the TEM images, ZTCs have very sharp distributions around 1.2 nm, while the activated carbons show broader distributions. MSC30 has especially larger nanopores than the others. The volumetric surface areas (S_v) of ZTC-S and ZTC-L are 1693 and 1590 m^2 cm^{-3}, respectively, which are extremely high compared with those of the other high-rate materials (Table 1). Such extremely high volumetric surface areas can be ascribed to the following two reasons. First, ZTC comprises a single graphene[8] and is free from the graphene stacking structure that is commonly included in other conventional porous carbons. The stacking structure is a nonporous wall and becomes a dead volume that decreases the volumetric surface area. Second, the nanopore size of ZTC is only 1.2 nm, much smaller than those of other high-rate materials (>2−50 nm). A smaller nanopore size is effective in increasing the particle density of carbon, resulting in a high volumetric surface area. The values of S_v for MSC30 and A20 are 1191 and 1170 m^2 cm^{-3}, respectively (see the Supporting Information for the experimental details on N_2 isotherms, how to calculate the surface areas and the pore size distributions, and the resulting textural properties).

Figure 3a shows the change of the volumetric capacitances with the current density in 1 M Et_4NBF_4/propylene carbonate (PC) electrolyte solution at 25 °C. Note that a larger current density corresponds to a faster discharge rate. To obtain reproducible and meaningful data under such an ultrahigh current region, all the experiments were carried out in a very careful manner and without any artificial errors (see the Supporting Information for details). In the low-current region below 2 A g^{-1}, all the ZTCs and the activated carbons show larger volumetric capacities than those of the high-rate materials (SWCNT[4] shows 22 F cm^{-3} at 10 A g^{-1}, and HPC[5] shows 39 F cm^{-3} at 4 A g^{-1}) due to their high volumetric surface areas. However, A20, an activated carbon with smaller nanopores (Figure 2b), cannot retain the capacitance, which decreases rapidly with increasing the current. MSC30, a carbon with larger nanopores (Figure 2b), retains 40% of its initial capacitance even at an ultrahigh current density of 20 A g^{-1}. These results are in accord with the general tendency in the references,[2,3,5] i.e. larger nanopores can accelerate ion transfer, and as a result, a better rate performance is achieved. On the other hand, ZTCs can well retain the capacitance in the ultrahigh current region, although their nanopore sizes (∼1.2 nm) are less than those of MSC30. This high rate performance can be ascribed to their 3D and mutually connected nanopore arrangement. According to the simulation work, Et_4N^+ and BF_4^- ions are solvated to form the corresponding clusters of $Et_4N^+\cdot 4PC$ (1.35 nm) and $BF_4^-\cdot 8PC$ (1.40 nm).[6] These sizes are, however, larger than the ZTC nanopore size (∼1.2 nm). This means that the solvation shells have to be deformed[9] when the solvated ions enter the nanopores of ZTCs, and such deformation could increase the ion-transfer resistance. On the other hand, Ue reported that these ions do not form solvation shells in PC solution and can move as naked ions in the sea of

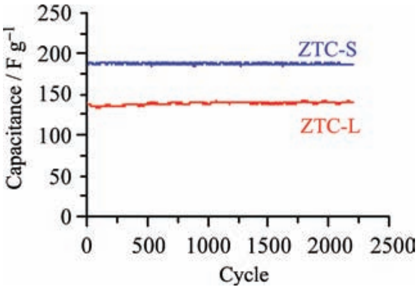

Figure 4. Gravimetric capacitances of ZTCs versus cycle number measured at 1 A g^{-1} in 1 M Et_4NBF_4/PC at 25 °C.

solvent molecules (the mean ion sizes of Et_4N^+ and BF_4^- are estimated to be 0.686 and 0.458 nm, respectively), from the minute molar conductivity measurements.[10] The ultrahigh rate performance of ZTC-L suggests that Ue's report is more probable, but more work is necessary for further understanding the mechanism of the motions of the ions and solvent molecules in carbon micropores upon charging. We have previously shown that a ZTC with nanopores smaller than 1.2 nm cannot exhibit high rate performance.[3] The pore size of 1.2 nm could thus be the best nanopore size which well balances high volumetric capacitance and high rate performance in the present electrolyte solution.

It should be noted that ZTC-L exhibits much higher rate performance than ZTC-S, although they have the same ordered framework structure as shown in Figure 1a and b and Figure 2a. The reason for the better performance of ZTC-L can be ascribed to its better electrical conductivity and due to its larger framework size (see the Supporting Information for the molecular structures of ZTC-S and ZTC-L). By using a four-probe method, we measured electrical conductivity of each working electrode sheet that was prepared by mixing ZTC-S or ZTC-L with binder polymer: the sheets from ZTC-S and ZTC-L show 71.0 and 37.5 Ω cm, respectively. The better conductivity of ZTC-L was further confirmed from the Nyquist plots (Figure 3b). The size of the semicircle (R_e) is smaller in ZTC-L, indicating that the electrode cell made by ZTC-L actually has the lower inner resistance. Note that the semicircle can also be attributed to the contact resistance between carbon particles or between carbon and current collector. However, these resistance components should be almost the same in the two three-electrode cells constructed with ZTC-S and ZTC-L, because the particle sizes of the two ZTCs are the same and their electrode sheets were prepared and then attached to the Pt mesh (current collector) in the exactly the same manner.[3] The size of the semicircle can be increased also by the appearance of a pseudocapacitance; however, this possibility can be ruled out because ZTC is a pure carbon material and does not contain nitrogen or boron atoms that exhibit large pseudocapacitances.[11] Though several groups have also reported the capacitor performances of microporous carbons synthesized by the template method,[12] their capacitances and rate performances are much lower than those of ZTC-L. In addition to its superior EDLC performances, ZTC-L retains its original capacitance over 2000 charge−discharge cycles, exhibiting its excellent life cycle (Figure 4).

In conclusion, 3D-arrayed and mutually connected 1.2-nm nanopores are effective to achieve high volumetric capacitance together with high rate performance in a nanoporous carbon electrode. In addition, the high electrical conductivity of the carbon framework is another key for obtaining high rate performance. With these superior performances, zeolite-templated carbon is a promising candidate as an electrode material for constructing an electric double layer capacitor with both high-power and high-energy densities.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information. Detailed experimental procedures, possible molecular structures of ZTCs, explanation for the difference between ZTC and TMC, and N_2 physisorption isotherms. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ REFERENCES

(1) (a) Kotz, R.; Carlen, M. *Electrochim. Acta* **2000**, *45*, 2483. (b) Arico, A. S.; Bruce, P.; Scrosati, B.; Tarascon, J. M.; Van Schalkwijk, W. *Nat. Mater.* **2005**, *4*, 366.

(2) (a) Jurewicz, K.; Vix-Guterl, C.; Frackowiak, E.; Saadallah, S.; Reda, A.; Parmentier, J.; Patarin, J.; Beguin, F. *J. Phys. Chem. Solids* **2004**, *65*, 287. (b) Xing, W.; Qiao, S. Z.; Ding, R. G.; Li, F.; Lu, G. Q.; Yan, Z. F.; Cheng, H. M. *Carbon* **2006**, *44*, 216.

(3) Nishihara, H.; Itoi, H.; Kogure, T.; Hou, P. X.; Touhara, H.; Okino, F.; Kyotani, T. *Chem—Eur. J.* **2009**, *15*, 5355.

(4) (a) Futaba, D. N.; Hata, K.; Yamada, T.; Hiraoka, T.; Hayamizu, Y.; Kakudate, Y.; Tanaike, O.; Hatori, H.; Yumura, M.; Iijima, S. *Nat. Mater.* **2006**, *5*, 987. (b) An, K. H.; Kim, W. S.; Park, Y. S.; Moon, J. M.; Bae, D. J.; Lim, S. C.; Lee, Y. S.; Lee, Y. H. *Adv. Funct. Mater.* **2001**, *11*, 387. (c) Niu, C. M.; Sichel, E. K.; Hoch, R.; Moy, D.; Tennent, H. *Appl. Phys. Lett.* **1997**, *70*, 1480.

(5) (a) Woo, S. W.; Dokko, K.; Nakano, H.; Kanamura, K. *J. Mater. Chem.* **2008**, *18*, 1674. (b) Yamada, H.; Nakamura, H.; Nakahara, F.; Moriguchi, I.; Kudo, T. *J. Phys. Chem. C* **2007**, *111*, 227.

(6) Yang, C. M.; Kim, Y. J.; Endo, M.; Kanoh, H.; Yudasaka, M.; Iijima, S.; Kaneko, K. *J. Am. Chem. Soc.* **2007**, *129*, 20.

(7) (a) Ma, Z. X.; Kyotani, T.; Tomita, A. *Chem. Commun.* **2000**, 2365. (b) Hou, P. X.; Yamazaki, T.; Orikasa, H.; Kyotani, T. *Carbon* **2005**, *43*, 2624.

(8) Nishihara, H.; Yang, Q. H.; Hou, P. X.; Unno, M.; Yamauchi, S.; Saito, R.; Paredes, J. I.; Martinez-Alonso, A.; Tascon, J. M. D.; Sato, Y.; Terauchi, M.; Kyotani, T. *Carbon* **2009**, *47*, 1220.

(9) (a) Tanaka, A.; Iiyama, T.; Ohba, T.; Ozeki, S.; Unta, K.; Fujimori, T.; Kanoh, H.; Kaneko, K. *J. Am. Chem. Soc.* **2010**, *132*, 2112. (b) Chmiola, J.; Largeot, C.; Taberna, P. L.; Simon, P.; Gogotsi, Y. *Angew. Chem., Int. Ed.* **2008**, *47*, 3392. (c) Chmiola, J.; Yushin, G.; Gogotsi, Y.; Portet, C.; Simon, P.; Taberna, P. L. *Science* **2006**, *313*, 1760.

(10) Ue, M. *J. Electrochem. Soc.* **1994**, *141*, 3336.

(11) Kwon, T.; Nishihara, H.; Itoi, H.; Yang., Q. H.; Kyotani, T. *Langmuir* **2009**, *25*, 11961.

(12) (a) Ania, C. O.; Khomenko, V.; Raymundo-Pinero, E.; Parra, J. B.; Beguin, F. *Adv. Funct. Mater.* **2007**, *17*, 1828. (b) Portet, C.; Yang, Z.; Korenblit, Y.; Gogotsi, Y.; Mokaya, R.; Yushin, G. *J. Electrochem. Soc.* **2009**, *156*, A1.