# Effect of Carbon Source on the Textural and Electrochemical Properties of Novel Cage-type Mesoporous Carbon as a Replica of KIT-5 Mesoporous Silica

Satoshi Inagaki,*[1,2] Koji Oikawa,[1] and Yoshihiro Kubota[1]
[1]*Division of Materials Science and Chemical Engineering, Yokohama National University,*
*79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501*
[2]*Interdisciplinary Research Center, Yokohama National University,*
*79-5 Tokiwadai, Hodogaya-ku, Yokohama 240-8501*

(Received June 1, 2009; CL-090531; E-mail: sinagaki@ynu.ac.jp)

Novel cage-type mesoporous carbon "carbon nanocage (CNC)," which is prepared as a carbon replica of KIT-5 mesoporous silica, showed a high electrochemical performance as an electrode material, due to the high specific surface area and mesopore volume as well as the sparse carbon network.

Electric double-layer capacitors (EDLCs) have been extensively studied in order to find new promising applications as pulse power sources for digital communication devices and electric vehicles.[1–3] For an ideal EDLC electrode material, it is necessary to have a large surface area for charge accumulation, an appropriate pore structure for electrolyte wetting, and rapid ionic motion.[1–3]

Rechargeable lithium ion ($Li^+$) secondary batteries also have been widely investigated as a compact energy-storage system for portable electronics and hybrid electric vehicles.[4–6] Among a variety of possible anode materials, graphite is commonly used for the fabrication of $Li^+$ batteries and provides a theoretical specific capacity of 372 mA h $g^{-1}$. Improving the performance of $Li^+$ batteries requires novel carbonaceous anode materials with higher discharge capacity.

Over the past decade, a wide variety of ordered mesoporous carbons as replicas of mesoporous silica materials has been developed. The successful synthesis of highly ordered mesoporous carbon using mesoporous silica templates was simultaneously achieved by two groups: Lee et al. (designated as SNU series)[7] and Ryoo et al. (designated as CMK series).[8] Lee and co-workers[7] presented the preliminary results on the EDLC performance of the self-ordered mesoporous carbons SNU-1 and SNU-2, which are replicas of Al-MCM-48 and 2D-hexagonal mesoporous aluminosilicate (HMAS), respectively. As these SNU-*x* carbons have relatively narrow pores (less than 2 nm), which are not accessible by larger electrolyte ions, the surface area corresponding to such narrow pores hardly contributes to the total electrochemical double-layer capacitance. Recently, CMK-3, a carbon replica of SBA-15 mesoporous silica, has been applied to EDLC electrodes and $Li^+$ batteries and showed a higher discharge capacity than microporous carbons.[8–13] The good capacitive behavior of CMK-3 could be attributed to high surface area as well as large mesopore volume. In addition, an inverse opal carbon as a replica of a three-dimensionally ordered assembly of monodispered colloidal silica has been developed and showed high EDLC performance.[14]

Recently, "carbon nanocage (CNC)"[15] has been synthesized as a replica of KIT-5 mesoporous silica, which is highly ordered three-dimensional close-packed cage-type mesoporous silica with the face-centered cubic *Fm*3*m* symmetry.[15] CNC possessing the same symmetry as KIT-5 has extremely high surface area (ca. 1500 $m^2\,g^{-1}$) and large mesopore volume (ca. 2.0 $cm^3\,g^{-1}$).

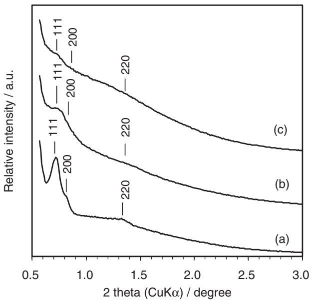

**Figure 1.** XRD patterns of (a) KIT-5, (b) $CNC_{suc}$, and (c) $CNC_{FA}$.

These notable textural properties of CNC allow us to expect a great possibility of high discharge capacity. Very recently, it was reported that CNC showed a high electric capacitance (ca. 200 F $g^{-1}$) using tetraethylammonium tetrafluoroborate ($TEABF_4$) as an electrolyte.[16]

In this study, we investigated both the electric double-layer capacitance and $Li^+$ discharge capacity of CNC prepared from two different carbon sources: sucrose ($C_{12}H_{22}O_{11}$) and furfuryl alcohol (FA, $C_5H_6O_2$). The CNCs prepared from sucrose and FA were designated as $CNC_{suc}$ and $CNC_{FA}$, respectively. For comparison, CMK-3 materials were prepared from sucrose and FA, which were designated as CMK-$3_{suc}$ and CMK-$3_{FA}$. The synthetic procedures and characterization techniques of mesoporous carbons are shown in Supporting Information (SI) 1.[17]

Figure 1 shows XRD patterns of KIT-5, $CNC_{suc}$, and $CNC_{FA}$. The reflections of all three samples are indexed to the 111, 200, and 220 reflections of the cubic group *Fm*3*m*. These XRD measurements indicate that the CNC materials obtained are indeed replicas of KIT-5. CMK-$3_{suc}$ and CMK-$3_{FA}$ were also obtained as replicas of SBA-15 (Figure S1).[17] Table 1 lists the textural properties of KIT-5, SBA-15, CNC, and CMK-3 materials, determined from nitrogen adsorption–desorption isotherms (Figure S2).[17] Mesoporous silica materials, KIT-5 and SBA-15, showed general textural properties. CNC materials were found to have a higher BET surface area and mesopore volume than CMK-3 materials, due to the three-dimensional mesoporosity with internal large cavities therein.

The BET surface area and mesopore volume of $CNC_{suc}$ were larger than those of $CNC_{FA}$, probably because the sparse carbon network containing many defects are formed by the removal of a large amount of oxygen atoms in sucrose molecules during the carbonization process.

The EDLC performances of these four types of carbon materials were investigated. Figure 2 shows the EDLC cyclic performances of the CNC and CMK-3 materials at a current density of 2000 mA $g^{-1}$ during discharge on the positive voltages, esti-

**Table 1.** Textural properties of mesoporous materials

| Sample | Mesopore volume /cm$^3$ g$^{-1}$ | Pore diameter (BJH) /nm | BET surface area /m$^2$ g$^{-1}$ |
|---|---|---|---|
| KIT-5 | 0.95 | 9.2 | 590 |
| CNC$_{suc}$ | 2.02 | 3.0 | 1760 |
| CNC$_{FA}$ | 1.64 | 3.7 | 1257 |
| SBA-15 | 1.01 | 7.1 | 831 |
| CMK-3$_{suc}$ | 1.11 | 3.0 | 1509 |
| CMK-3$_{FA}$ | 0.69 | 3.0 | 933 |

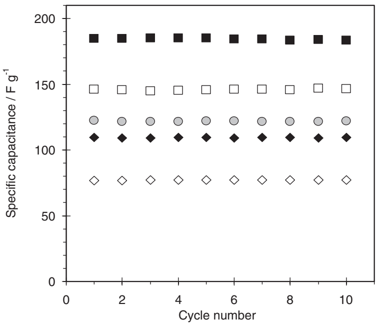

**Figure 2.** The EDLC cyclic performance of CNC and CMK-3 materials as an EDLC negative electrode. The current density was 2000 mA g$^{-1}$. ■, CNC$_{suc}$; □, CNC$_{FA}$; ◆, CMK-3$_{suc}$; ◇, CMK-3$_{FA}$; ●, activated carbon purchased from Housen.

mated from the potential–time curves (Figure S3).[17] For comparison, activated carbon (1700 m$^2$ g$^{-1}$, made from phenol polymer, Housen), which is used as a counter electrode in this study (see SI 1),[17] was also tested as a negative electrode in the EDLC measurement. CNC materials showed a higher specific capacitance than CMK-3 materials and activated carbon in the range of 2000–10000 mA g$^{-1}$ (Figure S4)[17] without any decreases in the capacitance. It should be noted that CNC$_{suc}$ showed an extremely high specific capacitance as high as 180 F g$^{-1}$ in every cycle, being consistent with a very recent publication.[16] Each value of CNC$_{suc}$ is always higher than that of CNC$_{FA}$. Such a high electrochemical performance of CNC$_{suc}$ is probably due to high BET surface area and mesopore volume caused by the three-dimensional character of its pore system and also a sparse carbon network originating from the nature of sucrose molecules.

The electrochemical properties of mesoporous carbons and activated carbon (RP-20, 1750 m$^2$ g$^{-1}$, made by phenol polymer, Kuraray Chemical) were characterized in LiPF$_6$-containing electrolyte. Figure 3 shows discharge capacities of CNC$_{suc}$, CNC$_{FA}$, CMK-3$_{suc}$, CMK-3$_{FA}$, and RP-20, estimated from the discharge-charge profiles (Figure S5).[17] The discharge capacities of both CNC and CMK-3 were higher than the theoretical discharge capacity of graphite (372 mA h g$^{-1}$), probably due to ordered mesoporosity and mesopore volume of CNC and CMK-3. Surprisingly, the initial Li$^+$ capacity of CNC$_{suc}$ and CNC$_{FA}$ reached 1600 and 1450 mA h g$^{-1}$, respectively, whereas those of CMK-3$_{suc}$ and CMK-3$_{FA}$ were 1150 and 900 mA h g$^{-1}$, respectively. The high discharge capacities of the CNC materials remained over 1000 mA h g$^{-1}$ even at the tenth cycle, as shown in Figure 3. All the porous carbon materials exhibited a relatively low Coulombic efficiency of 35–45% at the first cycle (Figure S6),[17] caused by the formation of solid electrolyte interface.[18] At the second cycle, their Coulombic efficiencies increased and the values remained over 90% after the fourth cycle. Such behavior of their Coulombic efficiency is quite common in most carboneous materials.[5]

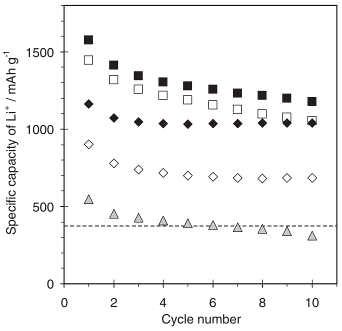

**Figure 3.** The cyclic performance of activated carbon, CNC and CMK-3 materials in discharge capacity of LiPF$_6$ at a current density of 100 mA h g$^{-1}$. ■, CNC$_{suc}$; □, CNC$_{FA}$; ◆, CMK-3$_{suc}$; ◇, CMK-3$_{FA}$; △, RP-20. The dash line means the specific capacity of graphite (372 mA h g$^{-1}$).

In conclusion, novel cage-type mesoporous carbons, especially CNC$_{suc}$, showed much higher electric double-layer capacitance and Li-accumulation capacity than CMK-3 and conventional activated carbon. Such an astonishing high performance of CNC$_{suc}$ as an electrode material is probably caused by high BET surface area and mesopore volume as well as the sparse carbon network. The findings in this work would be useful in the development of electrochemically applicable new porous materials.

This work was supported by Project of Development of High-performance Battery System for Next-generation Vehicles (NEDO). We thank Profs. M. Watanabe and K. Dokko for helpful discussion.

### References and Notes

1 B. E. Conway, *Electrochemical Superconductors, Scientific Fundamental and Technological Application*, Kluwer Academic, New York, **1999**.

2 A. Burke, *J. Power Sources* **2000**, *91*, 37.

3 E. Frackowiak, F. Béguin, *Carbon* **2001**, *39*, 937.

4 J.-M. Tarascon, M. Armand, *Nature* **2001**, *414*, 359.

5 K. Xu, *Chem. Rev.* **2004**, *104*, 4303.

6 M. Winter, R. J. Brodd, *Chem. Rev.* **2004**, *104*, 4245.

7 J. Lee, S. Yoon, T. Hyeon, S. M. Oh, K. B. Kim, *Chem. Commun.* **1999**, 2177; S. Yoon, J. Lee, T. Hyeo, S. M. Oh, *J. Electrochem. Soc.* **2000**, *147*, 2507.

8 R. Ryoo, S. Hoon, S. Jun, *J. Phys. Chem. B* **1999**, *103*, 7743.

9 H. Zhou, S. Zhu, M. Hibino, I. Honma, M. Ichihara, *Adv. Mater.* **2003**, *15*, 2107; H. Zhou, S. Zhu, M. Hibino, I. Honma, *J. Power Sources* **2003**, *122*, 219.

10 H. Li, H. Xi, S. Zhu, Z. Wen, R. Wang, *Microporous Mesoporous Mater.* **2006**, *96*, 357.

11 K. Jurewicz, C. Vix-Guterl, E. Frackowiak, S. Saadallah, M. Reda, J. Parmentier, J. Patarin, F. Béguin, *J. Phys. Chem. Solids* **2004**, *65*, 287.

12 K. Xia, Q. Gao, J. Jiang, J. Hu, *Carbon* **2008**, *46*, 1718.

13 T. Wang, X. Liu, D. Zhao, Z. Jiang, *Chem. Phys. Lett.* **2004**, *389*, 327.

14 S. Tabata, Y. Isshiki, M. Watanabe, *J. Electrochem. Soc.* **2008**, *155*, K42.

15 A. Vinu, M. Miyahara, V. Sivamurugan, T. Mori, K. Ariga, *J. Mater. Chem.* **2005**, *15*, 5122; A. Vinu, M. Miyahara, T. Mori, K. Ariga, *J. Porous Mater.* **2006**, *13*, 379.

16 M. Tadokoro, S. Tsumeda, N. Tsuhara, H. Nakayama, Y. Miyazato, K. Tamamitsu, A. Vinu, K. Ariga, *J. Nanosci. Nanotechnol.* **2009**, *9*, 391.

17 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

18 J. O. Besenhard, M. Winter, J. Yang, W. Biberacher, *J. Power Sources* **1995**, *54*, 228.

Published on the web (Advance View) August 22, 2009; doi:10.1246/cl.2009.918