Electrochemical Properties of Pillared Carbons for the Electrode of Electric Double Layer Capacitor

Yoshiaki MATSUO, Takuma KINO, Junichi INAMOTO, Osamu KIMIZUKA, Motoaki NISHIJIMA, and Hajime KINOSHITA

Abstract

Microporous pillared carbon prepared from graphite oxide silylated with methyltrichlorosilane for three times was tested for the electrode of electric double layer capacitor. The capacitance gradually increased as the applied potential increased and reached 74 F/g at an initial stage of cycling in 1 M triethylmethylammonium tetrafluoroborate (TEMABF4) -propylene carbonate (PC) when it is used as a positive electrode, independent of the counter cations or existence of solvent molecules. This value indicated that two BF4− ions were accommodated in a micropore of it. On the other hand, only one ion per micropore was stored when larger ions such as TEMA+, bis(trifluoromethanesulfone) imide (TFSI−) and ethylmethylimidazolium (EMI+) ions were used. These results indicated that two larger ions cannot be accommodated in a micropore of pillared carbon.

Keywords : Pillared Carbon, Electric Double Layer Capacitor, Micropores, Size of Ions

1. Introduction

Carbon materials with controlled pore structure such as mesoporous carbons, carbon nanotubes, carbide derived carbons, template carbons, etc. are attracting much attention for the electrode materials of electric double layer capacitor (EDLC) to replace activated carbons. As novel carbon based porous materials, we have recently introduced pillared carbons in which adjacent graphene layers are connected with each other by silsesquioxane pillars.1-3 They are obtained by the thermal reduction of silylated graphite oxide (hereafter GO) and possess micro- or meso-pores between the graphene layers and pillars. We have developed three methods for the preparation of pillared carbons, which are to use silylated GO with (i) 2-aminopropylmethyldiethoxysilane for long time,1 first alkyltrichlorosilane and then (ii) with methyltrichlorosilane for one time or more2-4 or (iii) 3-aminopropyltriethoxysilane5 as starting materials. Yoo, et al. reported the EDLC properties of one of the pillared carbons prepared from graphite oxide silylated by the method (i), however, the capacity was not so high (27 F/g),6 which could be due to the low surface area of it. On the other hand, we have found that a pillared carbon prepared by the method (ii) possesses higher surface area and they possess micropores with the size of between 0.70 and 0.87 nm within its interlayer space.4 This size seems more suitable for the adsorption of smaller ions such as BF4− used in EDLC,7 though the entrance for the micropores of less than 0.40 nm is rather narrow.8 Therefore, it is worth investigating the EDLC properties of this type of pillared carbon. Moreover, the maximum c-axis repeat distance of it upon the intercalation of various electrolyte solutions containing different ions.8-11

2. Experimental

Natural graphite powder (Z-5F, Ito graphite, ca. 5 µm) was oxidized in a fuming nitric acid with potassium chlorate at 60°C for 3 h, based on the Brodie’s method and GO was obtained. It was silylated with methyltrichlorosilane for 3 times at 60°C for 3 h, based on the Brodie method and GO was obtained. It was silylated with methyltrichlorosilane for one time or more2-4 or (iii) 3-aminopropyltriethoxysilane5 as starting materials. Yoo, et al. reported the EDLC properties of one of the pillared carbons prepared from graphite oxide silylated by the method (i), however, the capacity was not so high (27 F/g),6 which could be due to the low surface area of it. On the other hand, we have found that a pillared carbon prepared by the method (ii) possesses higher surface area and they possess micropores with the size of between 0.70 and 0.87 nm within its interlayer space.4 This size seems more suitable for the adsorption of smaller ions such as BF4− used in EDLC,7 though the entrance for the micropores of less than 0.40 nm is rather narrow.8 Therefore, it is worth investigating the EDLC properties of this type of pillared carbon. Moreover, the maximum c-axis repeat distance of it upon the intercalation of various electrolyte solutions containing different ions.8-11

The interlayer spacing and Si content of the resulting pillared carbon were 1.31 nm and 21.1%, respectively. The X-ray diffraction patterns of GO, silylated GO and pillared carbon are shown in Fig. S1. The X-ray diffraction patterns of pillared carbons before and after electrochemical measurements were performed using RINT-2100 diffractometer (Rigaku, CuKα). The pillared carbon powders are mixed with acetylene black and polytetraethylene as a conducting additive and binder, respectively with a weight ratio of 85:10:5. The mixture was pressed onto aluminum mesh and the resulting pellet was used as a working electrode. Activated carbon (MSC-30, Kansai Coke and Chemicals Co. Ltd., 3200 m²/g) and Ag/Ag+ (0.1 M AgClO4 solution of acetonitrile) couple were used as counter and reference electrodes. The capacitance of the activated carbon was 142 F/g. Charge-discharge measurement was performed in 1 M triethylmethylammonium tetrafluoroborate-propylene carbonate (TEMABF4-PC), ethylmethylimidazolium tetrafluoroborate (EMIBF4) or 1 M triethylmethylammonium bis(trifluoromethanesulfone) imide -propylene carbonate (1 M TEMATFSI-PC) by a
constant current method of 80 mA/g at 50°C. The upper cutoff potentials were increased every 5 cycles from 1.0 to 1.75 V.

3. Results and Discussion

Figure 1 shows the charge-discharge curves of pillared carbon positive or negative electrodes in various electrolyte solutions of 1 M TEMABF4-PC, 1 M TEMATFSI-PC and EMIBF4. The potential of pillared carbon electrode during charge changed linearly at the beginning and then a plateau was observed. The plateau mostly became longer as the upper/lower limit potentials increased/decreased and was apparently observed only at the first cycle after the upper/lower limit potentials changed as shown in Fig. S2. The potential during discharge almost linearly, which is the typical behavior of the electrode of EDLC. This phenomenon that the capacitance increases after showing potential plateau by applying high potential is commonly observed for some soft carbons or thermally reduced graphite oxide with large interlayer spacings. It is considered that they are electrochemically “activated” as the result of some structural change and large amounts of ions are adsorbed after “activation”. The present result shows that pillared carbon was also electrochemically activated and it occurred gradually as the increase in the applied potential. The capacitance increased as the increase/decrease in the upper/lower limit potentials as shown in Fig. 2. It reached 68 F/g at the initial stage of cycling at 1.75 V of polarization when pillared carbon was used as a positive electrode in 1 M TEMABF4-PC. However, it greatly decreased to 57 F/g at the fifth cycle. Considering the plateau at 1.7 V observed at the initial stage of cycling at 1.75 V and relatively large polarization during discharge (Fig. S2(A)), one possible explanation for this phenomenon could be that the decomposition of electrolyte occurred and the resulting products were deposited on the surface of electrode, providing additional but degrading capacitance. On the other hand, the capacitances of pillared carbon positive electrode in EMIBF4 and negative electrodes in 1 M TEMABF4-PC and 1 M TEMATFSI-PC were about 40 F/g. In 1 M TEMATFSI-PC, a plateau at 0.9 V was clearly observed (Fig. S2(B)). This suggests that relatively large energy was needed to “activate” pillared carbon in order to store larger TFSI⁻ ions in it. The capacitance of pillared carbon negative electrode in EMIBF4 was extraordinarily low, however, as shown in Fig. 3, as the increase in the cycle number the capacitance gradually increased and reached almost constant value of 34 F/g, which was similar to those observed above. This indicates that it takes long
time to “activate” pillared carbon especially when larger ions were used in a viscose electrolyte solution without solvent molecules. Figure 4 shows the cycling properties of pillared carbon positive electrodes after cycling as negative electrodes in 1 M TEMABF₄-PC and EMIBF₄. In both cases, the capacitance reached 50 F/g even when the polarization was 1.0 V and it increased as the polarization increased to 70 F/g at 1.75 V. These cycling behaviors were almost identical to that observed for pillared carbon positive electrode in 1 M TEMABF₄-PC shown in Fig. 2, which indicates that the amount of adsorbed BF₄⁻ ions was constant independent of the counter cations or the presence of solvent molecules. The capacitance of 66 F/g was obtained even in the fifth cycle at 1.75 V of polarization and this value corresponds to 17 μF/cm², based on the BET surface area of about 380 m²/g obtained for pillared carbons with similar Si contents (Fig. S3). This value seems reasonable considering the cylindrical pores of pillared carbon with a diameter of 0.87–0.76 nm and 1.9 nm of height⁴ and the reported values in Ref. 8.

Figure 5 shows the X-ray diffraction patterns of pillared carbon before and after a polarization of 1.75 V in 1 M TEMABF₄-PC. The diffraction peaks at 2θ = 13.86° (d = 0.639 nm) and 20.36° (d = 0.436 nm) which were indexed as (002) and (003) lines were observed for the pristine pillared carbon electrode (Fig. 5(A)). The latter three peaks are indexed as (001), (004) and (006) lines and the interlayer spacing was calculated to be 2.27 nm. This value was almost the same as that observed for pillared carbon after insertion of alkylamines with long alkyl chain lengths,⁴ meaning that some chemical species (BF₄⁻ ions and/or PC molecules) entered the interlayer space of pillared carbon and the pillars took almost perpendicular orientation against the carbon layers. In IR spectrum of the polarized sample, absorption peaks at 1085 and 1124 cm⁻¹ due to BF₄⁻ were observed, indicating that it was electrochemically intercalated into pillared carbon. As shown in Fig. 5(D), the diffraction pattern of the discharged sample became almost identical to that observed before polarization. This means that BF₄⁻ ions and/or PC molecules were removed from the interlayer space of pillared carbon and the structure of the resulting sample was almost identical to that of the pristine one. These results strongly indicate that the entrance to the interlayer space of pillared carbon existing between pillars “opens” when the pillared carbon was electrochemically polarized and BF₄⁻ ions and/or PC molecules entered the interlayer space of it. As shown in Fig. 5(E) the diffraction peak shifted to lower angle of 2θ = 8.22° (d = 1.08 nm) when the electrode after polarization was immersed in PC, indicating the penetration of PC molecules into the interlayer space of pillared carbon. This means that the entrance to the interlayer space of pillared carbon existing between pillars remained open for PC molecules. However, the unchanged interlayer spacing of pillared carbon even after cycling suggests that the structure of it was not greatly changed. On the other hand, as shown in Fig. 6, the diffraction peak of pillared carbon negative electrode after polarization at −1.75 V in 1 M TEMABF₄-PC was observed at 2θ = 9.1° (d = 0.97 nm). The indicates that TEM⁺ ions were also intercalated into pillared carbon, however, the smaller interlayer spacings
suggests that the number of adsorbed TEMA$^+$ ions was smaller, reflecting the smaller capacitances.

We have previously proposed that pillared carbon contains silesquioxane type pillars with a composition of Si$_{12}$O$_{20}$(CH$_3$)$_{12}$ which was proposed based on various spectroscopic data of it and the intercalation behaviors of organic molecules into it. The composition of the present pillared carbon is, therefore, calculated to be C$_{64}$Si$_{12}$O$_{20}$(CH$_3$)$_{12}$, based on the Si content of 21.1%. The amount of BF$_4^-$ ions adsorbed in pillared carbon can be also estimated from the capacitance of 68 F/g, and the composition of C$_{64}$Si$_{12}$O$_{20}$(CH$_3$)$_{12}$.1.9BF$_4^-$ was obtained for fully charged pillared carbons in 1 M TEMABF$_4$-PC. Considering the size of the cylindrical pores of pillared carbon with a diameter of 0.87–0.76 nm and 1.9 nm of height, the above composition indicates that two BF$_4^-$ ions were accommodated in one micropore of it. On the other hand, only one ion was stored per one micropore of pillared carbon in the case of the adsorption of larger TEMA$^+$ ions. As schematically illustrated in Fig. 7, there is not enough space for two of it to be accommodated in the same micropore of pillared carbon. This is also the case for the ions of larger TFSI$^-$ and EMI$^+$ shown in Fig. 7 for comparison.

In conclusion, we have investigated the electrochemical properties of pillared carbon as the positive and negative electrodes of EDLC. The capacitance of pillared carbon positive electrode reached 74 F/g in 1 M TEMABF$_4$-PC, otherwise it was about 40 F/g. These values were not large enough, though the capacitance normalized by BET surface area was large as expected. This is because pillared carbons contain considerable amounts of heavier Si. However, the present study has shown that the number of adsorbed ions per micropore of pillared carbon is greatly influenced by the size of ions in the electrolyte solution and this would provide important insight to design the pore of carbon-based electrode materials for EDLC. For example, the capacitance can increase if we can prepare pillared carbons with pillars consisting of lighter elements.

Supporting Information

The Supporting Information is available on the website at DOI: https://doi.org/10.5796/electrochemistry.19-63085.

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References

1. Y. Matsuo, Y. Sakai, T. Fukutsuka, and Y. Sugie, Chem. Lett., 36, 1050 (2007).
2. Y. Matsuo, T. Komiya, and Y. Sugie, Carbon, 47, 2782 (2009).
3. Y. Matsuo and K. Konishi, Chem. Commun., 47, 4409 (2011).
4. Y. Matsuo and K. Konishi, Carbon, 50, 2280 (2012).
5. Y. Matsuo, T. Komiya, and Y. Sugie, J. Phys. Chem. Solids, 73, 1424 (2012).
6. H. D. Yoo, Y. Park, J. H. Ryu, and S. M. Oh, Electrochim. Acta, 56, 9931 (2011).
7. M. Takeuchi, K. Koike, T. Maruyama, A. Mogami, and M. Okamura, Denki Kagaku (presently Electrochemistry), 66, 1311 (1998).
8. J. Chmiola, G. Yoshi, Y. Gogotsi, C. Portet, P. Simon, and P. L. Taberna, Science, 313, 1760 (2006).
9. N. Jickel, P. Simon, Y. Gogotsi, and V. Presser, ACS Energy Lett., 1, 1262 (2016).
10. K. Urita, N. Ide, K. Isobe, H. Furukawa, and I. Moriguchi, ACS Nano, 8, 3614 (2014).
11. K. Urita, C. Urita, K. Fujita, K. Horio, M. Yoshida, and I. Moriguchi, Nanoscale, 9, 15643 (2017).
12. M. M. Hantel, T. Kaspar, R. Nesper, A. Wokaun, and R. Kötz, Electrochem. Commun., 13, 90 (2011).
13. M. Ue, J. Electrochem. Soc., 141, 3336 (1994).
14. H. D. B. Jenkins and K. R. Thakur, J. Chem. Educ., 56, 576 (1979).