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Mesoporous activated carbon as electrode for electric double layer capacitor

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Mesoporous activated carbon with high surface area (AC-Y-A) was prepared by carbonization followed by activation of vinylidene chloride copolymer containing yttrium acetylacetonate. Their performances as electrodes for electric double layer capacitor (EDLC) in tetraalkylammonium tetrafluoroborate (R_4NBF_4)/propylene carbonate (PC) or acetonitrile (AN) solutions were evaluated and compared with those of microporous activated carbons [AC and AC(CO_2)]. The specific EDLC capacitances of the mesoporous AC-Y-A are almost the same as those of microporous AC at low discharge current. However, at high discharge current, the specific capacitance of AC-Y-A is much higher than those of both AC and AC(CO_2) in PC and AN solutions. The capacitances decreased with increasing alkyl chain length of R_4 N^+ ions and discharge current. These results suggest that EDLC capacitance depends on pore size of activated carbons and smooth movement of R_4 N^+ ions in pores.

1. Introduction

Electric double layer capacitors (EDLCs), where the charge and discharge of electric energy are carried out without faradaic reaction, are receiving considerable attention as a clean energy storage system. Additionally EDLCs have longer cycle life and higher power density compared with conventional rechargeable batteries. As electrodes for EDLCs, porous carbons, especially, activated carbons have been widely applied.

EDLCs generally can be divided into two types, aqueous system EDLC and nonaqueous system EDLC. In aqueous system EDLCs, aqueous electrolyte solutions such as H_2SO_4 or KOH/H_2O are used. On the other hand, in nonaqueous system EDLCs, organic electrolyte solutions such as tetraethylammonium tetrafluoroborate (Et_4NBF_4)/propylene carbonate (PC) solution are used. Regarding these electrolyte solutions, it is supposed that nonaqueous system EDLC is more effective from the point of its higher charge voltage compared with that of aqueous system EDLC.

As electrodes of nonaqueous system EDLCs, various activated carbons have been investigated [1–8]. In general, electric energy in EDLC is stored up by electric double layer formed at the interface between carbon and electrolyte solution. According to this storage mechanism, specific surface area of activated carbons plays an important role. That is, it is supposed that the higher the specific surface area, the higher the specific EDLC capacitance. However, the electrodes prepared with activated carbons of high BET surface area do not necessarily exhibit the high capacitance [5]. This might be attributed to the size of electrolyte ions, e.g., Et_4 N^+ and BF_4^- whose sizes are presumed to be 2.0 and 1.7 nm, respectively, due to solvation [9], because the movements of these ions in micropores are restricted. However, there are only a few investigations dealing with the relation between pore characteristics of activated carbon and EDLC capacitance [10–12]. From these points of view, in this work, we prepared highly mesoporous activated carbon and investigated the EDLC performances of mesoporous activated carbons and microporous activated carbons in various tetraalkylammonium tetrafluoroborate (R_4NBF_4)/propylenecarbonate (PC) or acetonitrile (AN) solutions. Additionally the discharge capacitances of mesoporous activated carbons were compared with those of microporous activated carbons.

2. Experimental

Vinylidene chloride-co-methyl acrylate copolymer [Poly(VDC/MA)] was purchased from Aldrich. The copolymer composition was VDC/MA = 9/1.

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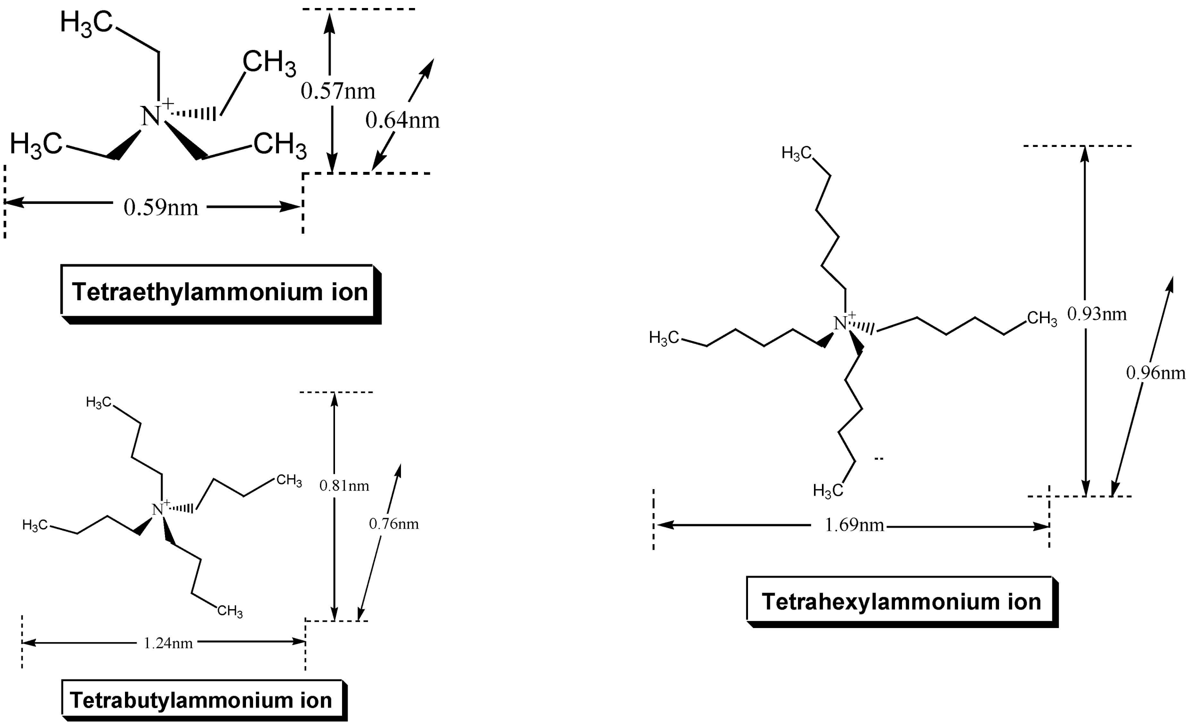

Tetraethylammonium ion

Tetrabutylammonium ion

Tetrahexylammonium ion

Figure 1 Structures of tetraalkylammonium ions.

Yttrium acetylacetonate [Y(acac)$_3$] was purchased from Wako Pure Chemicals and used without further purification. Tetrahydrofuran (THF) (Kanto Chemical) was dried over Na/K alloy and distilled before use. 1 M Et_4NBF_4/PC solution was purchased from Nacalai. Tetrabutylammonium tetrtafluoroborate (Bu_4NBF_4) and tetrahexylammonium terafluoroborate (Hex_4NBF_4) were purchased from Aldrich and were used without further purification. The molecular structures and sizes of R_4N^+ ions were estimated with molecular modeling system CAChe. The estimated molecular structures and sizes in three dimensions of these ions are shown in Fig. 1. As shown in Fig. 1, the sizes of Et_4N^+, Bu_4N^+, and Hex_4N^+ ions are $0.57 \times 0.59 \times 0.64$ nm, $0.81 \times 1.24 \times 0.76$ nm, and $0.93 \times 1.69 \times 0.96$ nm, respectively and these sizes are smaller than the size of micropore of the activated carbons (~2.0 nm). PC and AN were distilled before use.

Mesoporous activated carbon was prepared by carbonization followed by activation of Poly(VDC/MA) containing Y(acac)$_3$ (Y content in polymer: 2 wt%) [13]. Poly(VDC/MA) containing Y(acac)$_3$ was obtained by mixing a THF solution of Poly (VDC/MA) with a THF solution of Y(acac)$_3$. The mixture was stirred for 2 h, and then THF was removed by flash distillation. Poly(VDC/MA) containing Y(acac)$_3$ were carbonized at 600°C for 1 h under an Ar atmosphere. Activation was conducted with steam. The carbonized sample was directly put into the furnace (Motoyama MTKW-11-1040), in which N_2 containing H_2O was flowing at 900°C, for the prescribed time.

BET specific surface area was determined from N_2 adsorption/desorption isotherms, which were obtained by a Quantachrome NOVA 3200. The estimations of specific surface area of mesopores and size distribution were carried out by postulating pores as cylinders from mesopore volume determined by BJH method [14].

EDLC performances of activated carbons were evaluated by a two-electrode system. The experimental capacitor was composed of two activated carbon electrodes and a propylene non-woven separator impregnating the electrolyte solution with a fluororesin cell case. Activated carbons were mixed with poly(tetrafluoroethylene) (PTFE) binder and molded to a disk (10 mm diameter and about 150–200 μm thickness) for electrochemical measurements. 1 M R_4NBF_4/PC or AN solutions were used as electrolyte solutions. The charge and discharge cycling tests were carried out under constant current conditions (2–160 mA). The cut-off voltages were 3.0 V for charging and 0 V for discharge.

3. Results and discussion

EDLC capacitance in R_4NBF_4 solution is influenced by various properties of activated carbons constructing electrodes, e.g., pore size, surface area, surface property of pores, and electric conductivity, etc. In these factors, pore size and its distribution are supposed to play an important role, because the ion sizes of R_4N^+ are relatively large as shown in Fig. 1. Ta-

TABLE I Surface characteristics of activated carbons

	Yttrium content (%)	Carbonization temp.-time (°C - h)	Activation temp.-time (°C - min)	BET-SSA ($m^2 \cdot g^{-1}$)	MP-SSA ($m^2 \cdot g^{-1}$)
AC[a]	0	600–1	900–35	2384	155
AC-Y[a]	2	600–1	900–25	1033	780
AC-Y-A[a,c]	2	600–1	900–25	1477	979
AC(CO_2)[b]	0	600–1	900–840	2923	411

[a] H_2 activation, [b] CO_2 activation, [c] AC-Y was treated with 1 M HNO_3.

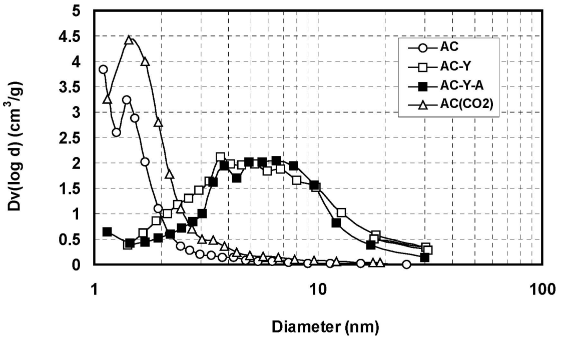

Figure 2 Pore size distributions of activated carbons.

ble I summarizes BET specific surface area (BET-SSA) and mesopore specific surface area (MP-SSA). The activated carbons, AC and AC(CO_2), obtained from Y(acac)$_3$-free Poly(VDC/MA) by H_2O and CO_2 activations were microporous and exhibited high BET surface areas of about 2400 and 2900 m^2/g, respectively. On the other hand, the activated carbon (AC-Y) obtained from Poly(VDC/MA) containing Y(acac)$_3$ was mesoporous. This indicates that the addition of a small amount of Y(acac)$_3$ accelerated the formation of mesopore without large disappearance of micropores by burn-off of carbon. Additionally, the activated carbon (AC-Y-A) obtained by treatment of AC-Y with 1 M HNO_3 has high BET and mesopore surface areas of 1477 and 979 m^2/g, respectively. The increase in BET and mesopore surface areas with HNO_3 treatment seems to be due to the dissolving of yttrium oxide (Y_2O_3) particles, which were formed from Y(acac)$_3$ with carbonization and steam activation [15], and the generation of new pores.

Mesopore size distributions of the activated carbons, determined by BJH method [14], are shown in Fig. 2. Fig. 2 shows pore volume changes (Dv) against pore diameter. The pore sizes of mesoporous AC-Y and AC-Y-A are in the region of about 2–30 nm. Mesoporous carbons with narrow pore size distribution (average pore size: about 3 nm), which are prepared by a template method with a mesoporous silica, have been reported [16, 17]. The pore sizes and their distributions of the mesoporous carbons obtained in this work are larger and wider, respectively, compared with those of mesoporous carbons prepared by a template method. It is supposed that the pores are formed throughout the dehydrochlorination of Poly(VDC/MA) polymer and degassing process in the course of carbonization and activation. Y(acac)$_3$ decomposes itself during carbonization and activation to result in the formation of Y_2O_3 particles [17]. In addition, Y_2O_3 particles catalytically promote the exhaustion of carbon by H_2O activation. That is, it is supposed that Y_2O_3 particles catalytically accelerates the reaction of carbon with H_2O to result in the enlargement of pore size. The pore sizes of microporous AC and AC(CO_2) are below about 3 nm and most pores are below 2 nm. Considering the three dimensional sizes of R_4N^+ ions shown in Fig. 1, it is presumed that all the electrolyte ions used, Et_4N^+ Bu_4N^+, and Hex_4N^+ can be introduced into micropores(pore diameter <2 nm) besides mesopores (2 nm < pore diameter < 50 nm).

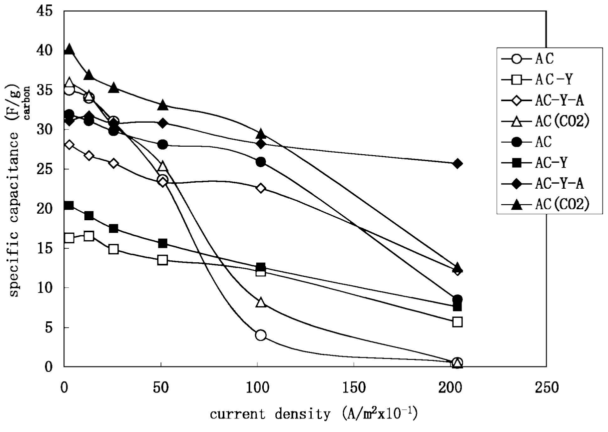

Figure 3 Discharge capacitances of activated carbons in 1 M Et_4NBF_4/propylene carbonate (open symbol) and acetonitrile (closed symbol) solutions as a function of current density.

EDLC capacitances were measured as a function of discharge current density. Fig. 3 exemplifies the specific discharge capacitances of the activated carbons in 1 M Et_4NBF_4/propylene carbonate(PC) and cetonitrile (AN) solutions as a function of discharge current density. At low current density of 10 mA/cm^2, the specific capacitances of microporous activated carbons (AC and AC(CO_2)) are higher than those of mesoporous activated carbons (AC-Y and AC-Y-A). However, the capacitances of microporous activated carbons rapidly decreased with increasing discharge current density and no capacitance was observed at high discharge current density of 200 mA/cm^2 in PC solution. On the other hand, the decrease of capacitances of the mesoporous AC-Y and AC-Y-A with current density is low and still high at high current density. Consequently, at high discharge current density of 200 mA/cm^2, the mesoporous AC-Y-A exhibited higher capacitances than microporous carbons. The changes of capacitances for discharge current in AN solution are on the whole similar to those in PC solution, whereas the capacitances in AN solution are higher than those in PC solution except AC. The lower viscosity of AN (0.3 mPa s [18]) than that of PC(2.5 mPa s [18]) is supposed to give higher EDLC capacitances. That is, AN solutions seems to easily penetrate into pores because of its lower viscosity. It is noted that the decrease of capacitances of mesoporous AC-Y and AC-Y-A with current density is very small in AN solution, although the capacitances of AC-Y are lower than those of AC-Y-A. Y_2O_3 particles are dissolved out from activated carbon by HNO_3 treatment and the surface of activated carbon becomes lyophilic. As a result, AC-Y-A may exhibit higher capacitances than AC-Y, because the movement of Et_4N^+ ion in pores of AC-Y-A is easier than that in pores of AC-Y.

Fig. 4 shows the specific discharge capacitances of microporous AC and mesoporous AC-Y-A in various R_4NBF_4/PC solutions as a function of discharge current. The capacitances decreased with increase in alkyl chain length of R_4N^+ ions. This behavior is apparent in microporous AC and the capacitances of microporous AC in Bu_4NBF_4 and Hex_4NBF_4/PC solutions was not detected at high current density of 100 mA/cm^2. On the other hand, the capacitances of mesoporous AC-Y-A in Bu_4NBF_4 and Hex_4NBF_4/PC solutions are higher

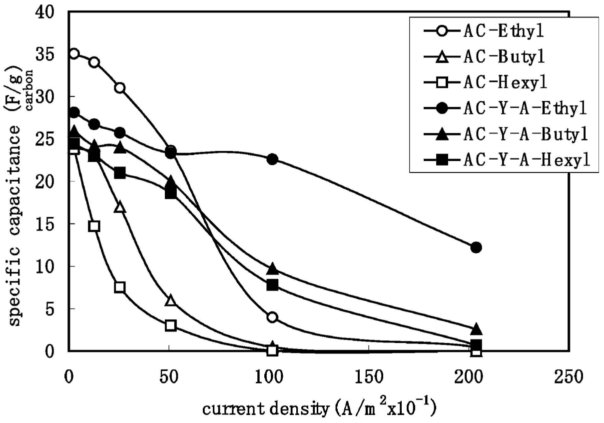

Figure 4 Discharge capacitances of microporous activated carbon (AC) and mesoporous activated carbon (AC-Y-A) in R_4NBF_4/propylene carbonate solutions as a function of current density.

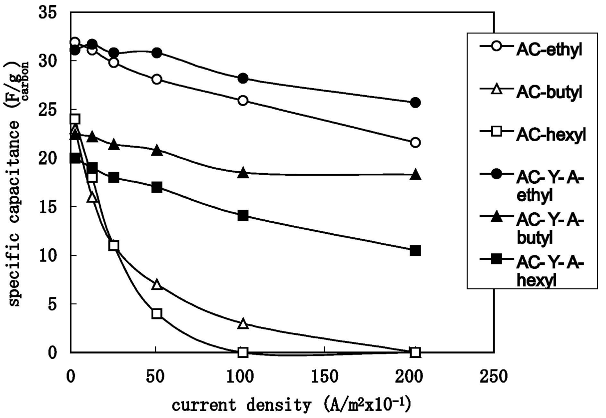

Figure 5 Discharge capacitances of microporous activated carbon (AC) and mesoporous activated carbon (AC-Y-A) in R_4NBF_4/acetonitrile solutions as a function of current density.

than those of AC. Fig. 5 shows the specific discharge capacitances of AC and AC-Y-A in R_4NBF_4/AN solutions as a function of discharge current. The capacitances of mesoporous AC-Y-A are high compared with those of AC and scarcely decreased with increase in discharge current density. The capacitance of AC-Y-A in Et_4NBF_4/AN solution is still more than 25 F/g even at 200 mA/cm^2. In addition, from the point that the capacitances of microporous AC in Bu_4NBF_4 and Hex_4NBF_4/AN solutions rapidly decreased with increase in discharge current density, the dependence of EDLC capacitance on pore size is noticeable in Bu_4N^+ and Hex_4N^+ ions. From the results shown in Figs 3–5, it is suggested that at low discharge current, both microporous and mesoporous activated carbons exhibit high EDLC capacitances because the introduction and the release of electrolytes ions such as Et_4N^+ in and from micropores in addition to mesopores readily take place. On the other hand, at high discharge current, because the rapid movement of electrolyte ions is capable only in mesopores, mesoporous activated carbons exhibit high EDLC capacitances. In this mean, mesoporous activated carbons are useful as an EDLC electrode material at high discharge current.

Fig. 6 shows the relation between power density and energy density of mesoporous AC-Y-A and microporous AC (Ragone plot), which were calculated from the curves of capacitances with discharge current density. The energy density was obtained by 1/2 CV^2, whereas C is capacitance and V is charged voltage. The power density was calculated from IV (I: discharge current density). As expecting from the capacitance curves shown in Fig. 3, both AC-Y-A and AC exhibit high maximum energy densities of about 40 Wh/kg. Additionally, it is noted that mesoporous AC-Y-A gives very high energy densities of about 30 Wh/kg even at high power density of 5 × 105 W/kg.

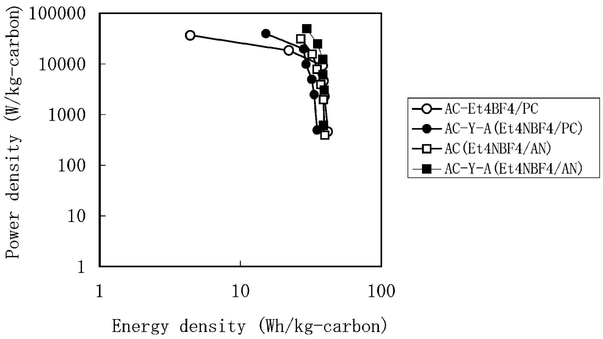

Figure 6 Ragone plots of microporous activated carbon (AC) and mesoporous activated carbon (AC-Y-A) in Et_4NBF_4/propylene carbonate (PC) and acetonitrile (AN) solutions.

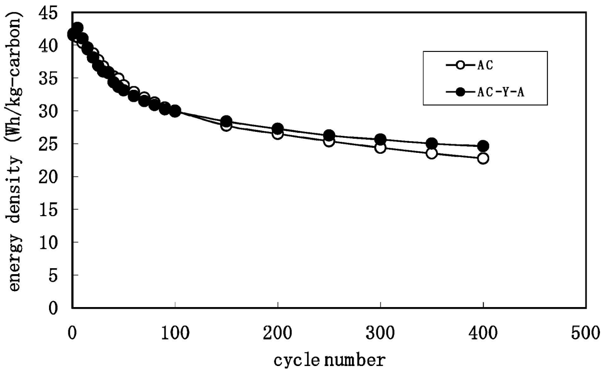

Figure 7 Cycle performances of microporous activated carbons (AC) and mesoporous activated carbon (AC-Y-A) in Et_4NBF_4/propylene carbonate solution.

The cycling stability upon charge/discharge was tested at constant charge/discharge current density. Fig. 7 shows the variations of energy densities of AC and AC-Y-A in Et_4NBF_4/PC solution at current density of 10 mA/cm^2. An initial energy loss of 38% was observed during the first 200 cycles. This initial energy loss is large and the improvement of cycle efficiency will be investigated in future work. However, the energy density of AC-Y-A was about 26 Wh/kg after 200 cycles. This energy density is still high. The energy density of AC continues to decrease slightly after 200 cycles. The lowering of discharge capacitance with cycling seems to be due to the remaining of Et_4N^+ and BF_4^- ions introduced into pores by charging.

4. Conclusion

The EDLC capacitances of mesoporous activated carbon (AC-Y-A) prepared by H2O activation of vinylidene chloride copolymer containing yttrium acetylacetonate and microporous activatrd carbons [AC and

$AC(CO_2)$] in various tetraalkylammonium tetrafluoroborates (R_4NBF_4)/propylene carbonate (PC) and acetonitrile (AN) solutions were investigated as a function of discharge current. The specific EDLC capacitances of the mesoporous AC-Y-A are almost the same as those of microporous AC at low discharge current. However, the specific capacitances of mesoporous AC-Y-A are much higher than those of both AC and $AC(CO_2)$ in PC and AN solutions at high discharge current. The capacitances decreased with increasing alkyl chain length of R_4N^+ ions. The EDLC capacitances depend on pore sizes of activated carbons at high discharge current.

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