Mesoporous Carbon Electrodes for Electric Double Layer Capacitor

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Introduction

Electric double layer capacitors (EDLCs) are clean energy storage systems because the charge and discharge of electric energy are carried out without faradaic reaction. Activated carbons are receiving considerable attention in the applications as electrodes for EDLCs. Various activated carbons have been investigated for the electrodes of EDLCs. In general, electric energy in EDLC is stored up by electric double layer formed at the interface between carbon and electrolyte solution, and consequently the pore characteristics of activated carbons, e.g., specific surface area and pore size play an important role. From these points of view, in this work, we investigated the EDLC performance of highly mesoporous activated carbons in tetraalkylammonium tetrafluoroborate (R_4NBF_4) / propylenecarbonate(PC) or acetonitrile(AN) solutions and compared their discharge capacitances with those of microporous activated carbon.

Experimental

Mesoporous activated carbons were prepared by carbonization followed by activation of vinylidene chloride-co-methyl acrylate copolymer(Poly(VDC/MA)) containing yttrium acetylacetonate ($Y(acac)_3$).[1,2] 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 $Y(acac)_3$ was carbonized at 800℃ for 2h under an Ar atmosphere. Activation was conducted with steam or CO_2. BET specific surface area was determined from N_2 adsorption/desorption isotherms, which were obtained by a Quantachrome NOVA 3200. The estimations of mesopore specific surface area and size distribution were carried out according to BJH method.[3]

The EDLC performance of activated carbons was 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 fluoro-resin cell case. Activated carbons were mixed with poly(tetrafluoroethylene) (PTFE) binder and molded to a disk (10nm, about 150~200 μm) for electrochemical measurements.

Results and Discussion

The activated carbons (AC and AC(CO_2)) obtained from Y(acac)$_3$-free Poly(VDC/MA) are microporous and exhibited high BET surface areas. On the other hand, the activated carbons (AC-Y and AC-Y-A) obtained from Poly(VDC/MA) containing Y(acac)$_3$ were mesoporous. Fig. 1 shows pore volume changes (Dv) against pore diameter. The activated carbons (AC-Y and AC-Y-A) obtained from Poly(VDC/MA) containing Y(acac)$_3$ possess the pore size in the region of about 2~20 nm and these mesopore size distributions are narrow.

Figure 2 shows the specific discharge capacitances of the microporous (AC) and

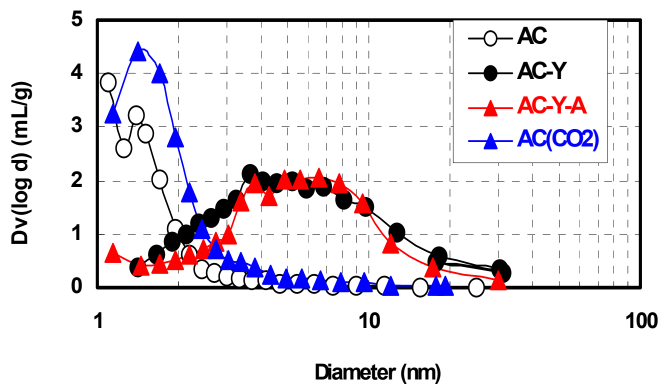

Fig.1 Pore size distributions of the activated carbons

mesoporous activated carbons (AC-Y-A) with various R_4NBF_4 in PC solutions, as a function of discharge current. Both specific capacitances of microporous activated carbon(AC) and mesoporous activated carbon(AC-Y-A) are high at low discharge current with tetraethylammonium tetrafluoroborate (Et_4NBF_4) solutions. The

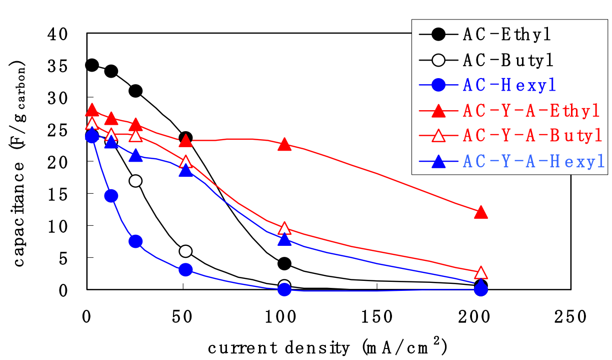

Fig.2 Capacitances of mesoporous (AC-Y-A) and microporous (AC) carbons in R_4NBF_4/propylenecarbonate(PC) solutions

microporous carbon with high BET surface area exhibited higher capacitance than mesoporous carbons. These capacitances decreased with increasing discharge current. This behavior is remarkable for the microporous carbons. Consequently, at high discharge currents of 100 and 200 mA/cm^2, the mesoporous activated carbon exhibited higher capacitance than microporous carbons. The capacitances of microporous AC deceased rapidly with increasing alkyl chain length of R_4N^+ ions. These results indicate that the pore sizes of activated carbons play an important role for high capacitances at high discharge current.

Figure 3 shows the specific discharge capacitances of the microporous and mesoporous activated carbons with various R_4NBF_4 in AN solutions, as a function of discharge current. Both specific capacitances of microporous activated carbon(AC) and mesoporous activated carbon(AC-Y-A) are high, compared with those in PC solutions. Especially, mesoporous carbons (AC-Y-A) exhibited the high capacitances even at high discharge current and with large R_4N^+ ion (Hex_4N^+). This result suggests that the EDLC capacitances are influenced by diffusion of solvents into pores of activated carbons

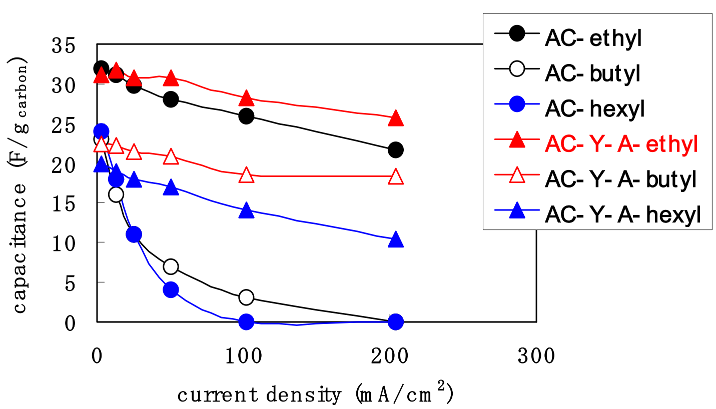

Fig.3 Capacitances of mesoporous (AC-Y-A) and microporous (AC) carbons in R_4NBF_4/acetonitrile(AN) solutions

References

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