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PREPARATION OF ACTIVATED CARBONS FROM POLYMER/CARBON BLACK COMPOSITES AS AN EDLC ELECTRODE

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Abstract

The influence of addition of an electro-conductive substance in carbon precursors on the performance of electric double layer capacitor (EDLC) was investigated. As activated carbon precursors, vinylidene chloride/vinyl chloride copolymer [Poly(VDC-co-VC)], phenol resin(Novolac), and polydivinylbenzene[Poly(DVB)] were applied and carbon black was used as an electro-conductive substance. The activated carbons prepared from these precursors/carbon black composites were microporous and have high BET surface area more than $1800 \mathrm{m}^2/\mathrm{g}$. The EDLC capacitance of the activated carbon obtained from Novolac/carbon black composite was increased by addition of carbon black, whereas the capacitances of activated carbons from Poly(VDC-co-VC) and Poly (DVB) were decreased. The decrease of EDLC capacitance of the activated carbon from Novolac/carbon black composite with increase in discharge current was smaller, compared with those of activated carbons from Poly(VDC-co-VC) and Poly (DVB). It was observed by TEM that, the smaller aggregates of carbon black primary particles were dispersed in activated carbon from Novolac/carbon black composite, compared with those in activated carbons from Poly(VDC-co-VC) and Poly (DVB). These results suggested that, the uniform dispersing of electro-conductive substance such as carbon black in carbon matrix is effective for EDLC capacitance.

Keywords and phrases: activated carbons, electro-conductive substance, EDLC capacitance.

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1. Introduction

Electric double layer capacitors (EDLCs) are receiving a considerable attention as a clean energy storage system. EDLCs have high power density compared with conventional rechargeable batteries, e.g., lithium ion secondary battery, and long life cycle [5, 19]. A disadvantage of EDLC as an energy storage system is low energy density compared with rechargeable battery systems. Because electric energy in EDLCs is stored at the interface between surface of electrodes and electrolyte solution, it has been supposed that surface area of electrodes plays an important role in amount of electric energy stored, that is, EDLCs capacitance. In general, activated carbons (ACs) are applied as electrodes for EDLCs. Various ACs have been investigated for the electrodes of EDLCs [3, 4, 8, 10-13, 15-18, 20, 21]. Actually, in the case of ACs below about $1000 \mathrm{m}^2/\mathrm{g}$ of specific surface area, EDLC capacitance increases with increasing surface area of ACs. However, it has been reported that in the case of ACs with high surface area more than $1500 \mathrm{m}^2/\mathrm{g}$, EDLC capacitance is not necessarily proportional to surface area of ACs [1, 6, 7, 14].

On the other hand, it is supposed that in addition to surface area, electric conductivity of AC electrode influences on EDLC capacitance. The influence of electric conductivity on EDLC capacitance was investigated by using activated carbon fiber as EDLC electrodes [9]. Their results indicated that, the increase in electric conductivity increases the EDLC capacitance. However, there have been few investigations for ACs having high surface area more than $1500 \mathrm{m}^2/\mathrm{g}$. From these points of view, in this work, the influence of addition of carbon black (CB) as an electro-conductive substance in polymeric carbon precursors on EDLC capacitance was investigated. ACs with high surface area more than $1800 \mathrm{m}^2/\mathrm{g}$ were applied as electrodes of EDLCs.

2. Experimental

Vinylidene chloride/vinyl chloride copolymer[Poly(VDC-co-VC)] was purchased from Aldrich. Phenol and formaldehyde aqueous solution were purchased from Kanto Chemical and used without further purification. Divinylbenzene (Melk) was purchased commercially and distilled before use. Potassium peroxodisulphate and 2, 2-azobisisobutyronitrile were from Kanto Chemical and recrystalized twice before. Acetylene black (strem chemicals) was used as a CB.

Poly(VDC-co-VC) dissolved in THF was mixed with CB dispersed in THF. THF was removed by flash distillation after mixing for 24h. Poly (VDC-co-VC)/CB composites were dried under vacuum.

Phenol resin [Novolac] was prepared by addition condensation. 250g of phenol was dissolved in 185ml of 37% formaldehyde solution, and then 0.25ml of 35% HCl solution was added. After reacting the mixture at 85°C for 2h, Novolac was obtained by flash distillation. The obtained Novolac was dissolved in methanol and to this solution CB in methanol was added. After mixing for 24h, to this mixture methanol solution of hexamethylene tetramine was added. Novolac/CB composites were obtained by removing methanol by flash distillation.

CB dispersed in toluene was added to 270ml of divinylbenzene(30ml) toluene solution. After to this mixture, 2.5g of 2, 2-azobisisobutyronitrile was added as an initiator, polymerization of divinylbenzene was carried out at 75°C for 24h. Polydivinylbenzene [Poly(DVB)]/carbon black composites were obtained by removing toluene by flash distillation.

ACs were prepared by carbonization followed by activation of polymer/CB composites. The carbonization was carried out at 800°C for 2h under Ar atmosphere. The activation was conducted with a cylindrical furnace by N_2 flow containing H_2O at 900°C.

BET specific surface area was determined from N_2 adsorption /desorption isotherms obtained by using a Quantachrome NOVA 3200. Mesopore specific surface areas and size distributions were estimated by Barett-Joyner-Halenda (BJH) method [2].

Capacitances of the ACs for EDLC electrode were evaluated by a two electrode system. Propylene non-woven sheet was used as a separator. ACs were mixed with poly(tetrafluoroethylene) binder and molded to a disk (10mm, about $150 \sim 200\mu\,\mathrm{m}$) for electrochemical measurements. 1M Et_4NBF_4/ propylene carbonate solution was used as an electrolyte solution. The specific capacitance C was calculated by the following equation: $C = (I \times t)/(\Delta V \times m)$, where I is the constant discharge current, t is the time for discharge, ΔV is the potential change by discharge, and m is the sum of weight of two electrodes. The charge and discharge cycling tests were carried out under constant current conditions ($12\mathrm{mA/cm^2}$). The cut off voltages were 3.0V for charging and 0V for discharge.

3. Results and Discussion

3.1. Activated carbon

In order to obtain the ACs with high surface area, steam activations were carried out for 50min for carbonized Poly(VDC-co-VC) and Novolac, and for 75min for Poly(DVB), based on the preliminary activation experiments. The ACs were prepared from these polymer composites with different contents of CB. Figure 1 shows N_2 adsorption/desorption isotherms of the ACs prepared from Novolac/CB composites at 77K. The contents of CB in Novolac/CB composites were 0, 0.1, 0.5, and 1.0 wt % for AC-N, AC-N-1, AC-N-2, and AC-N-3, respectively. The major uptake of N_2 in the adsorption/desorption isotherms of the ACs obtained occurs at relatively low relative pressure (< 0.2) and reaches the plateau at high relative pressure. These results indicate that the ACs were microporous. The amounts of N_2 adsorbed on these ACs are almost same, although AC-N-2 shows slightly higher amounts of N_2 adsorbed than AC-N-1 and AC-N-3. In the cases of Poly(VDC-co-VC)/CB and Poly(DVB)/CB composites, the similar N_2 adsorption isotherms to these isotherms were obtained. The pore size distributions of the ACs obtained from Novolac/CB composites, estimated by BJH method, are shown in Figure 2. The ACs indicated the maximum pore volume at about 1.4 ~ 1.5 nm of pore width. Similarly, in the cases of the ACs from Poly(VDC-co-VC)/CB and Poly(DVB)/CB composites, the maximum pore volumes were observed at about 1.4 ~ 1.5nm in spite of with or without CB.

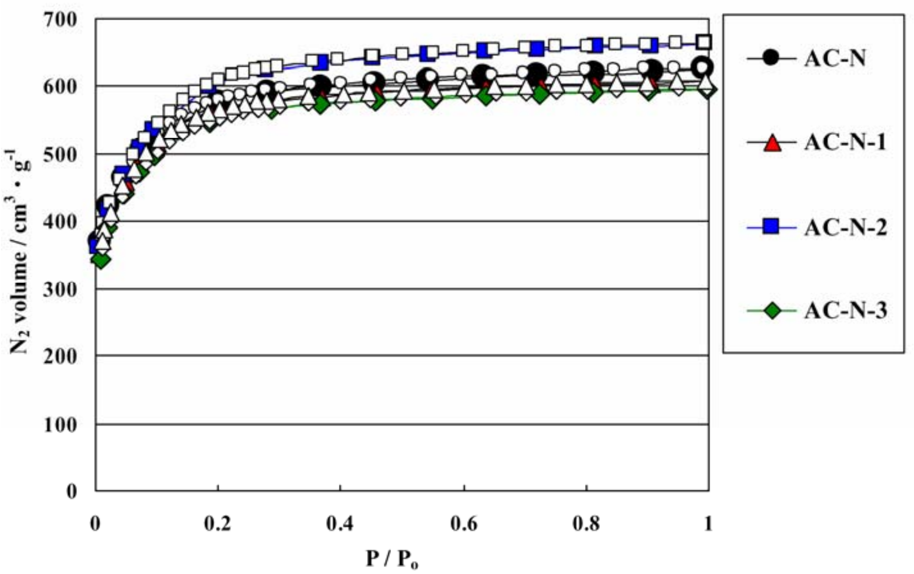

Figure 1. N_2 adsorption/desorption isotherms of ACs prepared from Novolac/CB composites. AC-N: CB content in Novolac 0 wt%, AC-N-1: 0.1 wt%, AC-N-2: 0.5 wt%, and AC-N-3: 1.0 wt%, closed: adsorption, open: desorption.

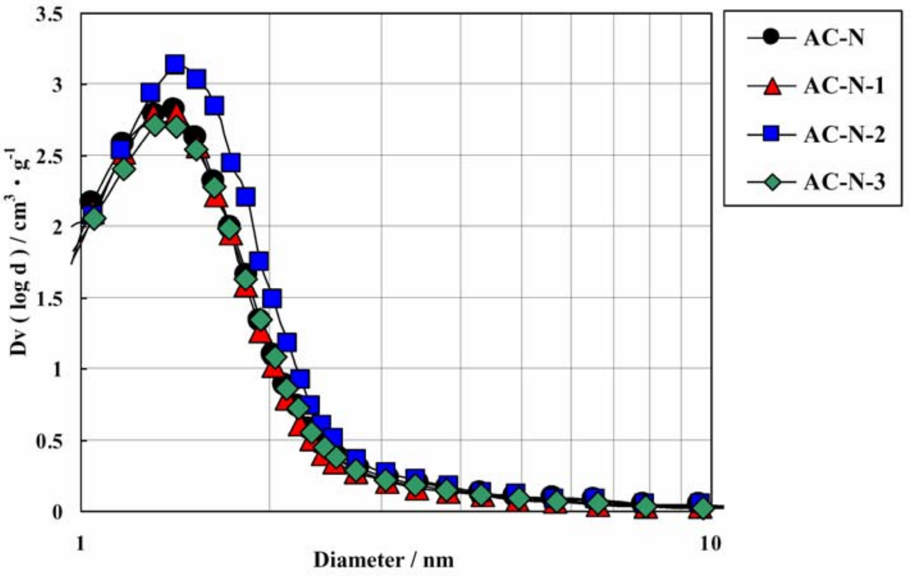

Figure 2. Pore size distributions of ACs prepared from Novolac/CB composites. AC-N: CB content in Novolac 0 wt%, AC-N-1: 0.1 wt%, AC-N-2: 0.5 wt%, and AC-N-3: 1.0 wt%.

The pore characteristics of ACs estimated based on N_2 adsorption/desorption isotherms are shown in Table 1. All ACs prepared from Poly(VDC-co-VC), Novolac, and Poly(DVB) without CB are microporous, and have high BET specific surface area more than $2100\text{m}^2/\text{g}$. Although, the BET surface areas of these ACs as a whole decreased with increasing content of CB, they have still high BET surface areas of more than $1800\text{m}^2/\text{g}$. As shown in Table 1, mesopore surface area slightly increased with increasing content of CB in these polymers. The CB contents were calculated from the carbon yields and the contents of CB in precursor polymers, as the amounts of CB contained in polymers are kept in ACs throughout carbonization and activation. The CB contents in the ACs from Poly(DVB)/CB composites were higher than those from other polymers/CB composites, because the carbon yields after activation are lower.

Table 1. Pore characteristics of ACs

Sample	CB in Polymer /%	CB in AC /%	BET-SSA[a)] / $m^2 \bullet g^{-1}$	MP-SSA[b)] / $m^2 \bullet g^{-1}$	Total pore volume / $cm^3 \bullet g^{-1}$	Average pore size /nm
AC-P	0	-	2248	231	1.05	1.87
AC-P-1	0.1	1.5	2281	293	1.12	1.96
AC-P-2	0.5	6.4	2137	232	1.02	1.90
AC-P-3	1.0	12.5	1950	305	0.98	2.00
AC-N	0	-	2113	138	0.97	1.83
AC-N-1	0.1	0.6	2061	162	0.94	1.82
AC-N-2	0.5	3.3	2157	225	1.03	1.90
AC-N-3	1.0	5.7	2004	172	0.92	1.84
AC-D	0	-	2340	381	1.19	2.03
AC-D-1	0.1	2.5	2172	401	1.13	2.09
AC-D-2	0.5	11.0	1979	371	1.02	2.07
AC-D-3	1.0	22.5	1820	440	1.00	2.19

(a) BET-specific surface area.

(b) Mesopore specific surface area estimated by BJH.

CB particles in the AC were observed by transmission electron microscopy (TEM). Figure 3 shows TEM images of (a) AC-P-2, (b and c) AC-N-2, and (d) AC-DCB-1. As shown in Figure 3 (b), small aggregates of primary CB particles were observed in the AC (AC-N-2) prepared from Novolac/CB composite. On the other hand, as shown in Figure 3 (a) and (d), larger blocks or aggregates (50 ~ 200nm) of CB particles were observed around AC powders in the ACs (AC-P-2 and AC-DCB-1) prepared from Poly(VDC-co-VC)/CB and Poly(DVB)/CB composites. These sizes are much larger than those of small aggregates in AC-N-2. This suggests that, CB particles are more uniformly dispersed in the AC from Novolac/CB composite than those from Poly(VDC-co-VC) and Poly(DVB) composites.

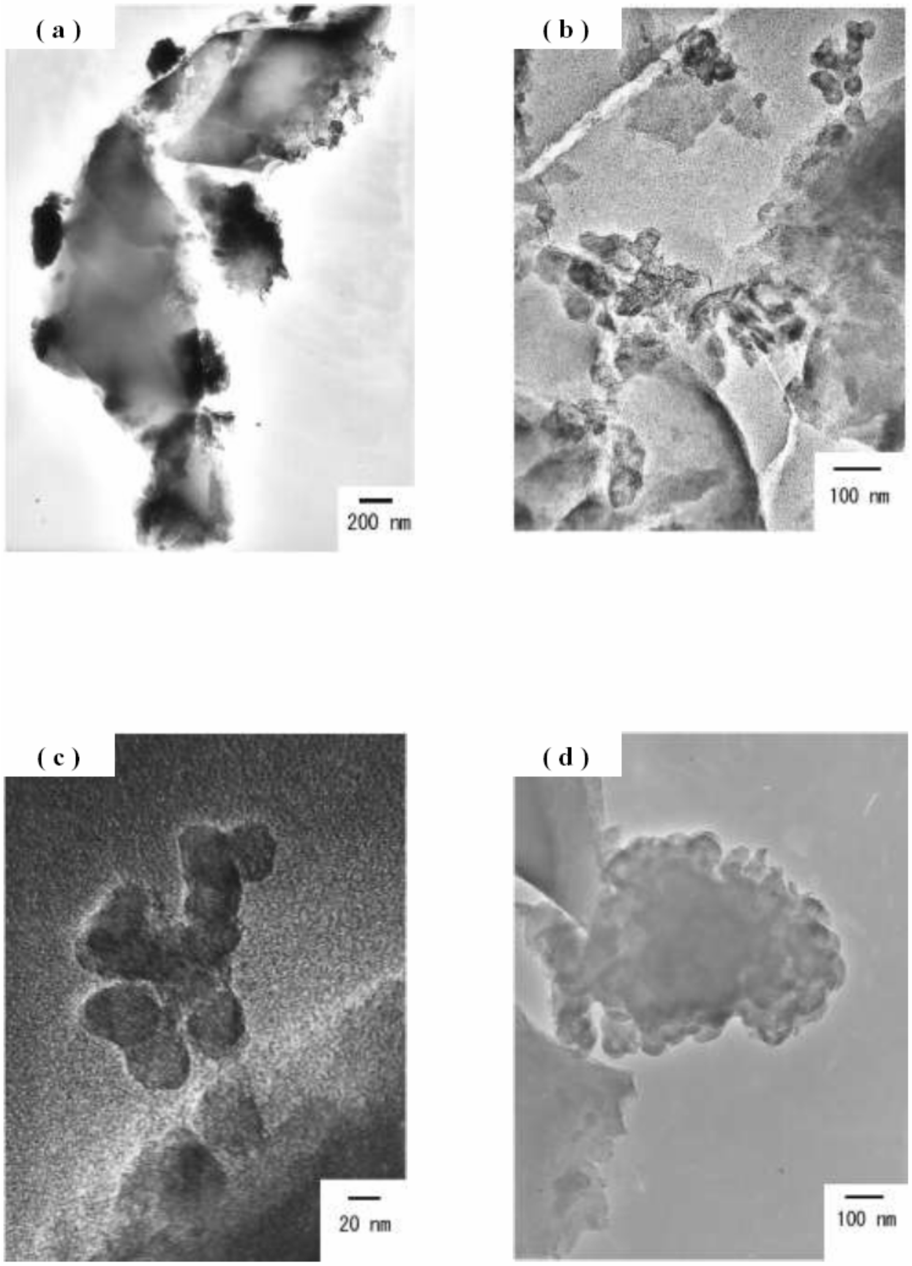

Figure 3. TEM images of ACs prepared from polymer/ CB composites, (a) AC-P-2, (b) and (c) AC-N-2, and (d) AC-DVB-2.

3.2. EDLC performance

EDLC capacitances were measured as a function of discharge current density. Figures 4, 5, and 6 show the specific discharge capacitances of the ACs from Poly(VDC-co-VC), Novolac, and Poly(DVB)/ composites, respectively, in 1M Et_4NBF_4/ propylene carbonate solution as a function of discharge current density. As shown in these figures, at low discharge current $(1.27 mA/cm^2)$, the capacitances of the ACs with and without CB are the almost same value of about $30 \sim 35\,F/g$. That is, the addition of CB to precursor polymers scarcely influences the capacitance at low discharge current density. The capacitances of these ACs decreased with increasing discharge current. This lowering of capacitance for the AC from Novolac/CB composites is lower than those for the ACs from Poly(VDC-co-VC) and Poly(DVB) composites. As a result, the capacitances of the ACs (AC-N series) from Novolac/CB composite increased with addition of CB. This effect was large in the AC from 2 wt% of CB added composite (AC-N-2) and was lowered with additional amount of CB added. This improvement in EDLC capacitance against discharge current is supposed to be due to the contribution of increase in electric conductivity by addition of CB. In the cases of AC-N-2 and AC-N-3, the decrease in BET surface area is supposed to decrease the capacitance compared with AC-N-1. On the other hand, the capacitances of the ACs from Poly(VDC-co-VC) and Poly (DVB) decreased with addition of CB. This is due to the dispersion of CB in AC. That is, as shown in Figure 3, because the aggregate sizes of CB particles in these ACs are larger than those in ACs from Novolac/CB composites, the effect of addition of CB is limited. It is supposed that EDLC capacitance decreased by addition of CB, because the decrease in effective surface area by addition of CB are larger than the contribution to electric conductivity.

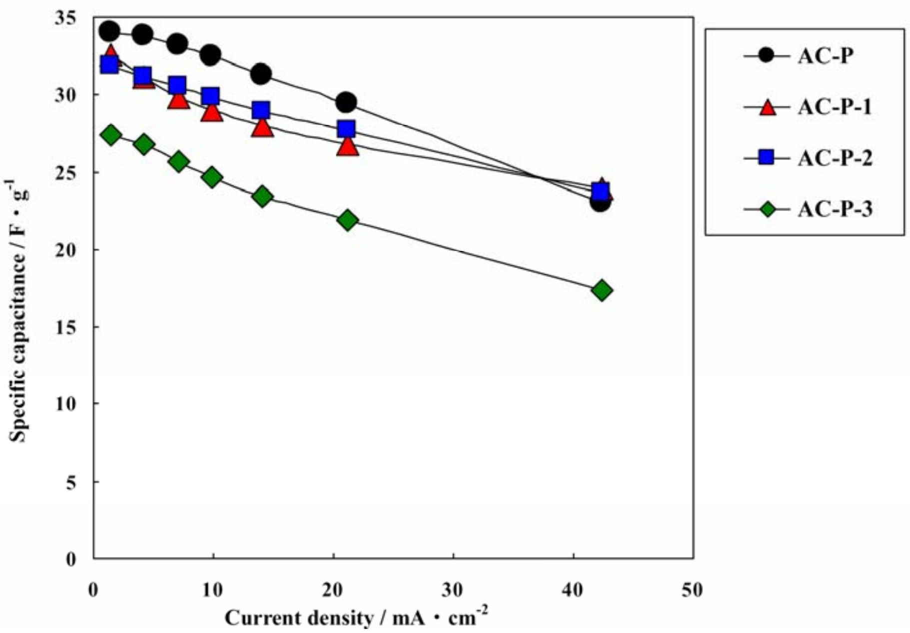

Figure 4. EDLC capacitance per weight of ACs prepared from Poly(VDV-co-VC)/CB composites as a function of discharge current in 1M Et_4NBF_4/ propylene carbonate.

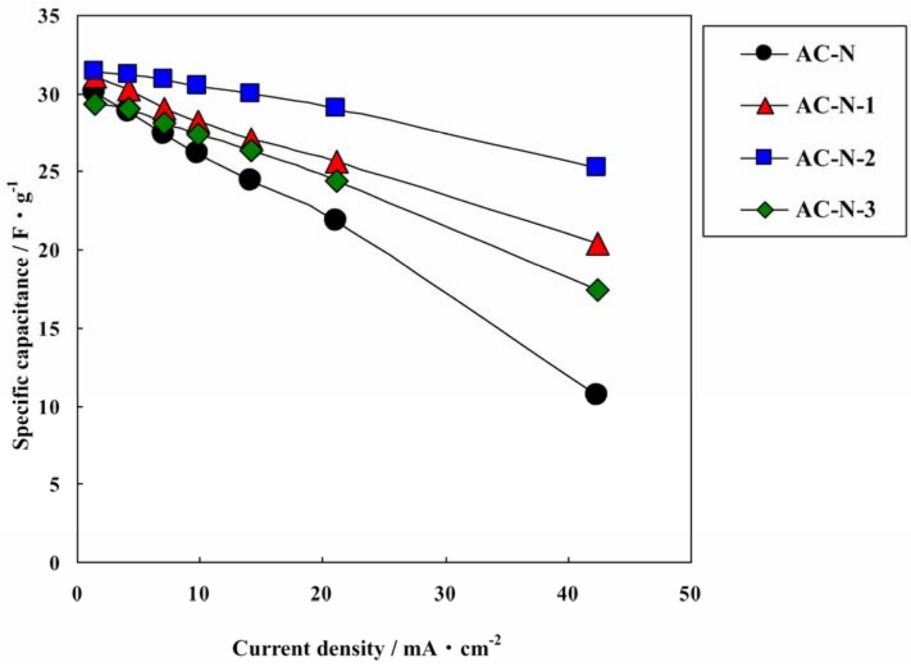

Figure 5. EDLC capacitance per weight of ACs prepared from Novolac /CB composites as a function of discharge current in 1M Et_4NBF_4/ propylene carbonate.

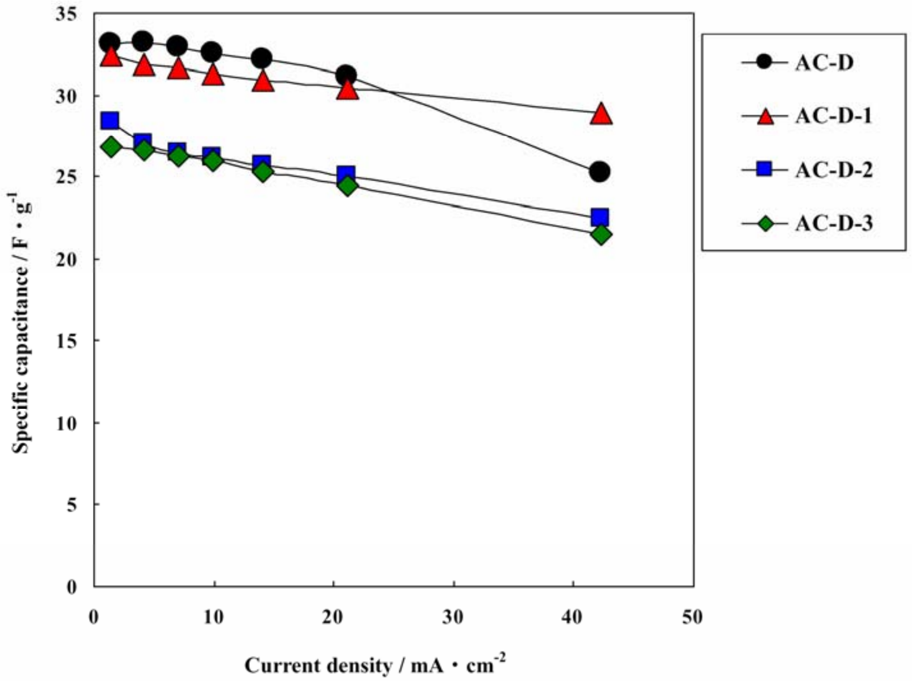

Figure 6. EDLC capacitance per weight of ACs prepared from Poly(DVB) /CB composites as a function of discharge current in 1M Et_4NBF_4/ propylene carbonate.

The cycling stability upon charge/discharge was tested at constant charge/ discharge current density. Figure 7 shows the variations of EDLC capacitances for the ACs with and without CB (AC-N-2 and AC-N) at current density of 1.27mA/cm^2 . Both capacitances of the ACs prepared from CB-free Novolac and Novolac/CB composite gradually decreased with repetition of cycles. However, regarding until 100 cycles, the decrease in capacitance of AC (AC-N-2) from Novolac/CB composite was lower than that of AC (AC-N) from CB-free Novolac. This suggests that, the cycling stability is improved by addition of CB into polymeric carbon precursors.

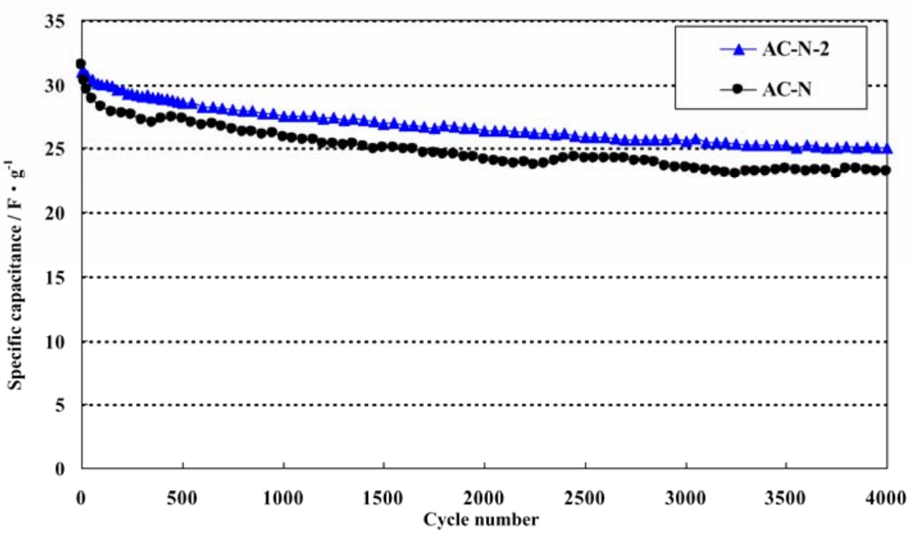

Figure 7. Cyclic stabilities of AC-N and AC-N-2. Charge and discharge current density: 1.27mAcm^{-2}.

4. Conclusion

ACs with high surface area were prepared from polymers/CB composites, e.g., Poly(VDC-co-VC), Novolac, and Poly (DVB) composites. The EDLC capacitance of the AC obtained from Novolac/CB composite increased compared with that of the AC from Novolac without CB, and the lowering of EDLC capacitance by increase in discharge current density was small. The capacitances of the ACs from Poly(VDC-co-VC) and Poly (DVB) decreased with addition of CB into polymers. TEM observation of the ACs prepared suggested that, the uniformly dispersing of CB in carbon matrix is effective for increase in EDLC capacitance.

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