

Preparation of polyaniline coated activated carbon and their electrode performance for supercapacitor

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Abstract Polyaniline coated mesoporous and microporous activated carbons were prepared by chemical oxidation polymerization of aniline adsorbed on activated carbons. BET and mesopore specific surface areas of the obtained activated carbons decreased by coating with polyaniline. The electrode performance of the polyaniline coated activated carbons for supercapacitor was investigated. The electrochemical pseudo-capacitances increased with increasing polyaniline content in activated carbons. The capacitances due to polyaniline in the mesoporous activated carbon are much higher than those in the microporous activated carbon. The uniform coating of polyaniline on mesopores of activated carbon plays an important role in pseudo-capacitance due to polyaniline.

Introduction

Recently supercapacitors, especially electric double layer capacitors (EDLCs), have attracted much attention as clean energy storage systems. One of the advantages of supercapacitors such as EDLCs is that they can provide high power density, compared with other conventional rechargeable batteries such as lithium ion secondary battery. As typical EDLC

electrodes, porous carbon materials, e.g., activated carbons are frequently used. However, a disadvantage of EDLCs is that their energy densities are much lower than those of batteries. Therefore, the improvement of energy density of EDLCs is important for their wide practical applications. On the other hand, it is known that some metal oxides [1–6] such as RuO_2 and MnO_2 or electroconductive polymers [7–9] such as polyaniline and polypyrrole provide high electrochemical capacitances, namely, pseudo-capacitances as electrodes materials for supercapacitors. From these points of view, the preparation of porous carbon/metal oxide or electroconductive polymer composites and their performances as supercapacitor electrodes have been investigated [10–13]. However, there are few reports considering the influence of pore structures of porous carbons on capacitance.

In this work, we investigated the introduction of polyaniline in mesoporous and microporous activated carbons to enhance EDLC capacitance of activated carbon. The introduction of polyaniline was carried out by adsorption of aniline on pores of activated carbons, followed by chemical oxidation polymerization. By applying both a highly mesoporous activated carbon and a microporous activated carbon, the influence of pore characteristics of these activated carbons on the introduction of polyaniline and the electrode performance for supercapacitor were investigated.

Experimental methods

Vinylidene chloride-co-methyl acrylate copolymer [Poly(VDC/MA)] was purchased from Aldrich. The copolymer composition was $\text{VDC/MA} = 9/1$. Tris(acetyl

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acetato) yttrium *n*-hydrate (Wako Chemical) [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. Aniline (Kanto Chemical) was purchased commercially and distilled before use. Ammonium peroxodisulfate (Kanto Chemical) was purchased commercially and recrystallized twice before use.

The microporous activated carbon and the mesoporous one were prepared by carbonization followed by activation of Poly(VDC/MA) and Poly(VDC/MA) containing Y(acac)₃, respectively [14]. 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 °C for 2 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 N₂ containing H₂O was flowing at 900 °C, for the prescribed time.

The polyaniline coated activated carbons were prepared by adsorption of aniline followed by polymerization with ammonium peroxodisulfate. The adsorption of aniline on activated carbons was conducted by stirring 0.2 g of activated carbon in 40 mL of EtOH solution of aniline for 24 h under 5 °C. The adsorption was carried out in various concentrations of aniline. The aniline-loaded activated carbon was separated from the solution by centrifugation. The polymerization of aniline adsorbed on activated carbon was carried out by dispersing and stirring aniline-loaded activated carbon in 50 mL of 0.18 M ammonium peroxodisulfate aqueous solution for 3 h under 5 °C. The dispersion was filtrated and the separated activated carbons were washed with 1 N HCl and 0.1 N NH₃ aqueous solution several times. Eventually, polyaniline coated activated carbons were obtained by washing with deionized water. The polyaniline coated activated carbons were dried under vacuum for one night. The amounts of polyaniline introduced into activated carbons, namely polyaniline contents in activated carbons, were determined by elemental analysis.

BET specific surface areas were determined from N₂ adsorption/desorption isotherms, which were obtained by a Quantachrome NOVA 3200. The estimations of mesopore specific surface areas and pore size distributions were carried out according to BJH method [15].

The EDLC performance of polyaniline coated 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. The activated carbons were mixed with poly(tetrafluoroethylene) (PTFE) binder (activated carbon/PTFE weight ratio = 95/5) and molded to a disk (diameter:10 mm, thickness: 150–200 μm) for electrochemical measurements. 1 M H₂SO₄ solution was used as an electrolyte solution. We used these electrodes after impregnation in 1 M H₂SO₄ for 1 h in vacuum. All measurements were performed at room temperature, by filling the cells by 1 M H₂SO₄ solution. The charge and discharge cycling tests were carried out under constant current conditions. The cut-off voltages were 0.8 V for charging and 0 V for discharging. The specific capacitance (*C*) was calculated by the following equation,

$$C = (I)(t)/(E_1 - E_2)(m)$$

where *E*₁ and *E*₂ are discharge voltages, *I* is discharge current, *t* is discharge time from *E*₁ to *E*₂ and *m* is the weight of the two electrodes. These measurements were carried out with a Charge/Discharge Unit HJ-201B (Hokuto Denko).

Results and discussion

The mesoporous activated carbon was prepared from Poly(VDC/MA) containing Y(acac)₃ by steam activation [14]. The pores of the obtained mesoporous activated carbon were coated with polyaniline by adsorption of aniline followed by chemical oxidation polymerization. The pore characteristics of the obtained polyaniline coated activated carbons and their pore size distributions are shown in Table 1 and Fig. 1, respectively. Both BET and mesopore specific surface areas decreased by coating with polyaniline and these values decreased with increasing polyaniline content in activated carbons, that is, aniline concentration used in adsorption of aniline. This result indicates that the inner parts of pores of activated carbon are coated with polyaniline. On the other hand, mesopore surface ratios are unchanged in spite of the increase in polyaniline content of activated carbons. As shown in Fig. 1, pore volumes decrease in all pore sizes by coating with polyaniline. These results suggest that both micropores and mesopores are coated with polyaniline.

Similarly, the microporous activated carbon, which was obtained from Poly(VDC/MA) without Y(acac)₃, was coated with polyaniline. The pore characteristics of the obtained polyaniline coated microporous activated

Table 1 Pore characteristics of polyaniline coated mesoporous activated carbons

	Aniline concentration cm ³ /cm ³ -EtOH	BET-SSA m ² g ⁻¹	MP-SSA ^a m ² g ⁻¹	MP ratio %	Pore volume cm ³ g ⁻¹	Polyaniline content ^b wt%
AC _{meso}	–	2122	1273	60	1.61	–
AC _{meso} -PA-1	1/40	1428	748	52	1.022	11.9
AC _{meso} -PA-2	5/40	1235	676	55	0.888	14.5
AC _{meso} -PA-3	10/40	1129	660	58	0.835	24.2
AC _{meso} -PA-4	20/40	875	517	59	0.639	25.7

^a Mesopore specific surface area (MP-SSA) evaluated by BJH method

^b Polyaniline content calculated from elemental analysis data

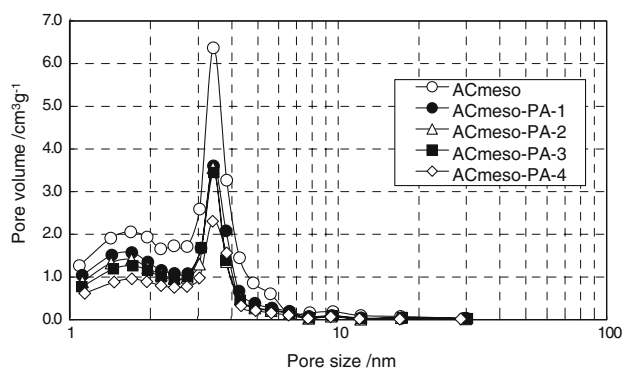


Fig. 1 Pore size distributions of polyaniline coated mesoporous activated carbons

carbons and their pore size distributions are shown in Table 2 and Fig. 2, respectively. BET specific surface areas steeply decreased by coating with polyaniline. However, in the case of the microporous activated carbon, polyaniline contents scarcely increased for increasing aniline concentration in high aniline concentrations. The adsorption of aniline on micropores is supposed to be saturated with high aniline concentrations.

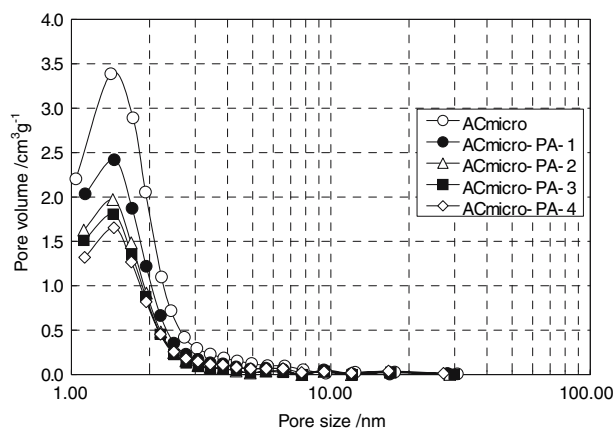


Fig. 2 Pore size distributions of polyaniline coated microporous activated carbons

The morphologies of activated carbon powders before and after coating with polyaniline were observed by scanning electron microscopy (SEM). SEM images of both polyaniline coated mesoporous and microporous activated carbons are shown in Fig. 3. The morphology of the mesoporous activated carbon is almost unchanged with polyaniline coating.

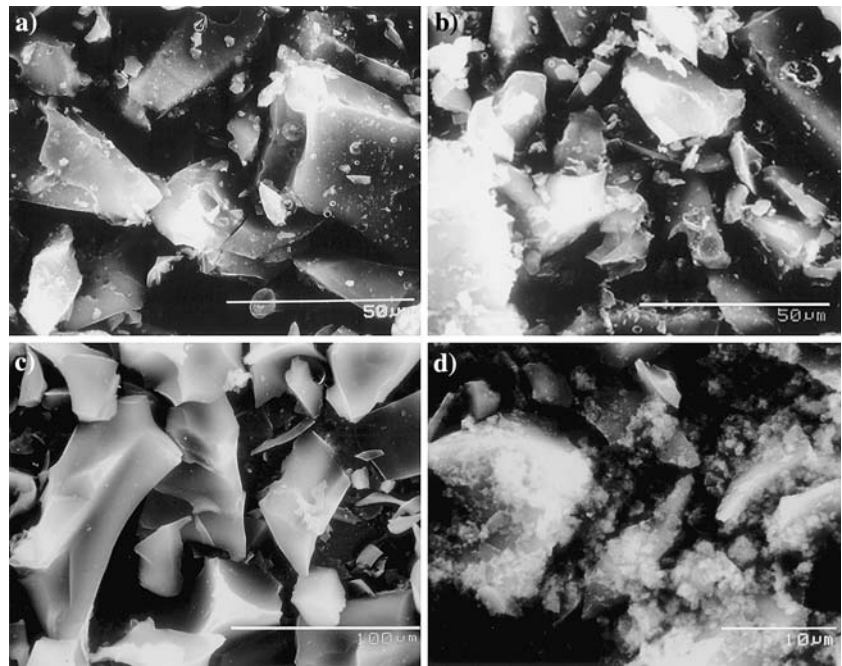
Table 2 Pore characteristics of polyaniline coated microporous activated carbons

	Aniline concentration cm ³ /cm ³ -EtOH	BET-SSA m ² g ⁻¹	MP-SSA ^a m ² g ⁻¹	MP ratio %	Pore volume cm ³ g ⁻¹	Polyaniline content ^b wt%
AC _{micro}	–	2312	321	14	1.1	–
AC _{micro} -PA-1	1/40	1638	151	9	0.769	13.3
AC _{micro} -PA-2	5/40	1287	99	8	0.603	20.0
AC _{micro} -PA-3	10/40	1178	97	8	0.561	18.3
AC _{micro} -PA-4	20/40	1067	117	11	0.543	21.0

^a Mesopore specific surface area (MP-SSA) evaluated by BJH method

^b Polyaniline content calculated from elemental analysis data

Fig. 3 Scanning electron microscope images of polyaniline coated activated carbons (a) mesoporous activated carbon (AC_{meso}), (b) polyaniline coated mesoporous activated carbon ($AC_{\text{meso-PA-4}}$), (c) microporous activated carbon (AC_{micro}), (d) polyaniline coated microporous activated carbon ($AC_{\text{micro-PA-4}}$)



It is supposed that polyaniline was introduced into mesopores of the activated carbon and the inner surface of mesopores was uniformly coated with polyaniline. On the other hand, in the case of the microporous activated carbon, many aggregates of small particulates in addition to activated carbon particles were observed on the activated carbon after polymerization of aniline adsorbed. This suggests that the polymerization of adsorbed aniline largely takes place out of micropores of the activated carbon.

Electrochemical capacitances were measured as a function of discharge current density. Figure 4 shows the specific discharge capacitances of the polyaniline coated mesoporous activated carbons as a function of

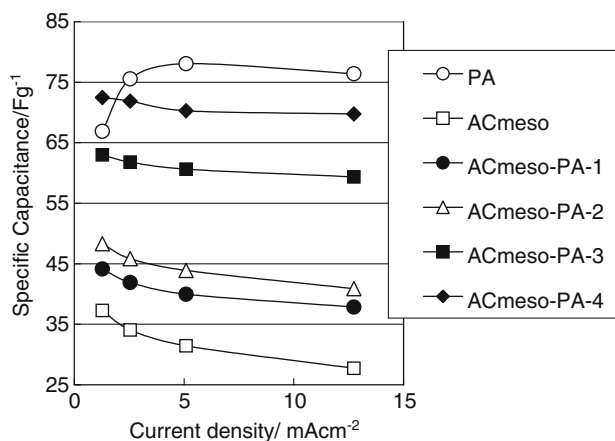


Fig. 4 Discharge capacitances of polyaniline coated mesoporous activated carbon as a function of current density

discharge current density. The capacitances increased with polyaniline content in activated carbons, that is, in the order of $AC_{\text{meso}} < AC_{\text{meso-PA-1}} < AC_{\text{meso-PA-2}} < AC_{\text{meso-PA-3}} < AC_{\text{meso-PA-4}}$, and reached the value of about 70 Fg^{-1} . This is due to pseudo-capacitance based on polyaniline oxidation–reduction in addition to electric double layer capacitances of the activated carbon. As shown in Fig. 4, polyaniline itself exhibited high capacitance.

Figure 5 shows the specific discharge capacitances of the polyaniline coated microporous activated carbons. Although the discharge capacitances increase with increasing polyaniline content of the activated carbon, they do not necessarily provide large capacitances,

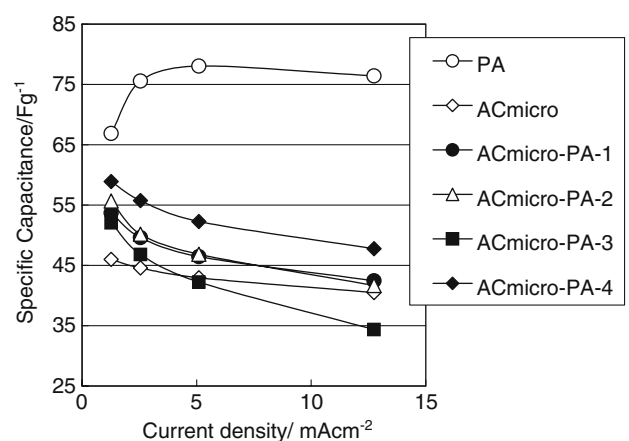


Fig. 5 Discharge capacitances of polyaniline coated microporous activated carbon as a function of current density

compared with those of the mesoporous activated carbon. In addition, the decrease of capacitance with increase in discharge current density is larger than those of the mesoporous activated carbon. It is supposed that this behavior depends on two factors. The first is the amount of polyaniline coated on activated carbons and the second is the morphology of polyaniline coated. The amounts of polyaniline introduced in the mesoporous activated carbon are on the whole higher than those in the microporous activated carbon, as shown in Tables 1 and 2. Regarding the morphology of polyaniline coated on the microporous activated carbon, many aggregates were observed as shown in SEM image (Fig. 3D). Considering these results, we compared the capacitances per unit weight of polyaniline. These capacitances per unit weight of polyaniline were calculated by reducing the EDLC capacitances of activated carbons, namely, the capacitances of AC_{meso} or AC_{micro} , from those of polyaniline coated activated carbons and dividing the reduced capacitances by the amounts of polyaniline. Figures 6 and 7 show the capacitances per unit weight of polyaniline coated on the mesoporous activated carbon and the microporous one, respectively, as a function of discharge current density. The capacitances of polyaniline on the mesoporous activated carbon are much higher than those on the microporous activated carbon, and their values increased with increasing polyaniline content. On the other hand, in the case of the microporous activated carbon, the capacitances do not necessarily depend on polyaniline content. In addition, as shown in Fig. 6, the capacitances per unit weight of polyaniline on the mesoporous activated carbon increase with increase in discharge current density. On the other hand, the capacitances of polyaniline on the microporous activated carbon decreased with discharge current density. From these

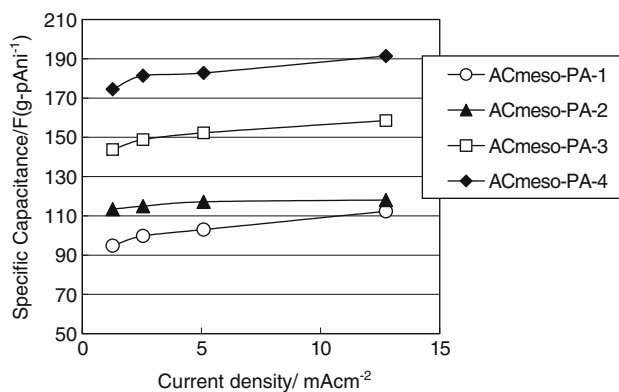


Fig. 6 Discharge capacitances per polyaniline unit weight of polyaniline coated mesoporous activated carbon as a function of current density

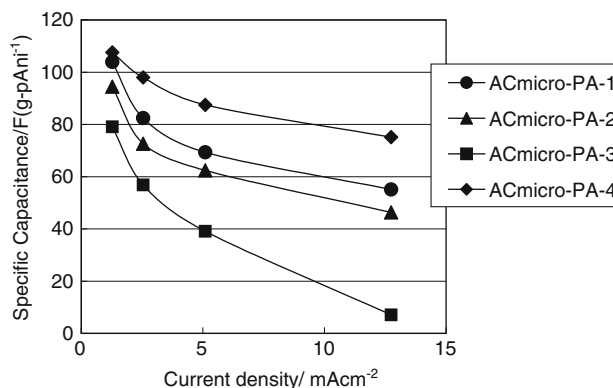


Fig. 7 Discharge capacitances per polyaniline unit weight of polyaniline coated microporous activated carbon as a function of current density

results, it is supposed that the uniform coating of polyaniline on pores of activated carbons, that is, effective coating of polyaniline plays an important role in pseudo-capacitance due to polyaniline.

The cycling stability upon charge/discharge was tested at constant charge/discharge current density. Figure 8 shows the variations of capacitances of both polyaniline and the polyaniline coated mesoporous activated carbon (AC_{meso} -PA-4) at current density of 1.27 mA/cm². During the first 100 cycles of AC_{meso} -PA-4, an increase of capacitance was observed. After 200 cycles, the capacitance was stabilized at about 70 Fg⁻¹.

Conclusion

Polyaniline coated mesoporous and microporous activated carbons were prepared by chemical polymerization of adsorbed aniline. BET and mesopore specific

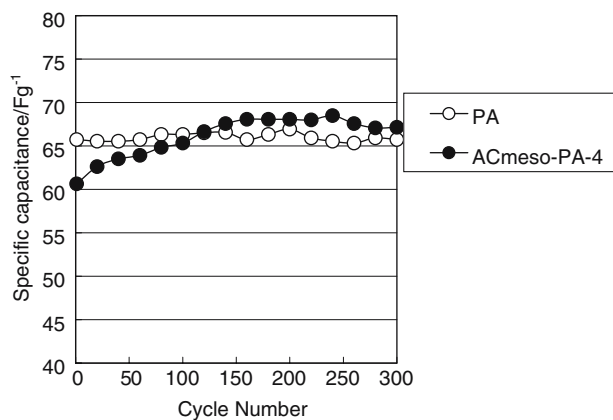


Fig. 8 Cyclic stabilities of polyaniline and polyaniline coated mesoporous activated carbon. Discharge current density: 1.27 mA cm⁻²

surface areas of the activated carbons decreased by coating with polyaniline. The morphologies of the activated carbons observed by SEM suggested that polyaniline coating is uniform in the case of the mesoporous activated carbon, compared with the microporous activated carbon. The electrochemical capacitances increased with increasing polyaniline content. The capacitances due to polyaniline coated on the mesoporous activated carbon are much higher than that on the microporous activated carbon. The uniform coating of polyaniline is important for pseudo-capacitance due to polyaniline.

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