Electric Double Layer Capacitors Based on Polyacrylonitrile-derived Porous Carbon Beads: Effects of Particle Size and Composite

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ABSTRACT
Two sizes of polyacrylonitrile beads were prepared as precursors of carbon beads by varying the reaction solvent ratio of \( N,N \)-dimethylformamide to methanol for dispersion polymerization reaction. The spherical structure of the carbon beads were maintained after carbonization and activation. Charge-discharge tests and AC-impedance analyses revealed that the electric resistance between the particles is low without conducting supplements. In addition, an appropriate pore size brought by the KOH activation of smaller carbon beads lead to a better capacitor performance at high current conditions.

Keywords: Electric Double Layer Capacitor, Polyacrylonitrile, Porous Carbon Beads, Activation by KOH

1. Introduction
Electric double layer capacitors (EDLCs) are energy storage devices that store electric energy by the charge separation at an electrode/electrolyte solution interface. Since any kinds of chemical reactions are not involved in the charge-discharge processes, EDLCs possess some advantages to secondary batteries, such as a longer cycle life and a higher power density.1–3 Activated carbons (ACs) have been widely used as electrode materials for EDLCs due to large specific surface that is favorable for large capacitance.4–11 Electrodes comprised of ACs usually need conductive supports such as acetylene black (AB) because the electric conductivity of the AC is relatively low. The introduction of AB, however, causes a decrease in volumetric energy density since the specific capacitance of the AB is comparatively low.12 The conventional capacitors are inevitably fabricated to balance the capacitance and conductivity of electrodes.

The present study aims to develop a new carbon material that have both capacitance like AC and conductivity like AB. So far, we have reported that polyacrylonitrile (PAN)-derived carbon beads showed a good capacitor properties without the addition of conductive supports.13 The size and shape of the carbon beads were quite regular, whereas those of commercial AC, usually made from plants, were irregular. The size of the PAN beads, as a precursor of carbon beads, is controlled by adjusting the rich/poor solvent ratio for the dispersion polymerization reactions.14 In the present study, we synthesized the carbon beads with two different sizes, and evaluated the effect of carbon materials, i.e., size and shape, on their properties as capacitor materials.

2. Experimental
The typical procedure for the synthesis of PAN beads is described in our previous report.13 The size of the PAN beads became smaller with the increase in the mixing ratio of methanol to \( N,N \)-dimethylformamide (DMF). Carbonization (sintering at 1,000°C in Ar atmosphere) and KOH activation (sintering at the maximum temperature of 800°C in the presence of 4 times the amount of KOH under N2 atmosphere) for PAN beads were also executed, to produce carbonized PAN (PANC) and PANC activated by KOH (KOH-PANC), respectively. The resulting KOH-PANC had average diameter of 270 nm and 820 nm, for the samples polymerized in the solution of DMF/methanol = 10/90 and 75/25, respectively.

The morphology of PAN and PANC was investigated with a scanning electron microscope (SEM; Hitachi S-3400N). Nitrogen adsorption/desorption isotherms at \(-196°C\) were measured by using Nova 4200e systems. The specific surface area of the samples was calculated from the isotherms based on the Brunauer-Emmett-Teller equation. The pore size distribution was analyzed by applying the isotherms to the density functional theory (DFT) model.

The KOH-PANC beads (95 wt%) were mixed with 5 wt% of poly(tetrafluoroethylene) binder (PTFE; DuPont-Mitsui Fluorochemicals Company, LTD., Japan), and the mixture was well-kneaded and was formed into a sheet. It was then cut into a 5 mm disk, the thickness of which was ca. 0.10 mm. The prepared disk was dried under vacuum at 80°C, and was pressed onto a platinum mesh (7 mm × 7 mm). The weight of electrode materials (including the binder) per unit area was 5.81 mg cm\(^{-2}\) for the KOH-PANC (270 nm) and 5.79 mg cm\(^{-2}\) for the KOH-PANC (820 nm) electrodes. The KOH-PANC beads-based electrode with a conducting supplement were also prepared by mixing KOH-PANC beads (85 wt%), PTFE (5 wt%), and AB (10 wt%). For comparison, commercially available palm shell-derived activated carbon (YP50F; Kuraray Chemical) was formed into an electrode with a mixing ratio of YP50F (85 wt%), PTFE (5 wt%), and AB (10 wt%), the weight of which (5.19 mg cm\(^{-2}\)) was smaller than KOH-PANC beads-based electrodes.

Constant-current charge-discharge tests were performed by a 2-electrode cell equipped with two parallel disk electrodes and a glass filter as a separator. An acetonitrile solution containing tetraethylammonium tetrafluoroborate (TEABF\(_4\)) in 1 M (TEABF\(_4\)/AN) was used as an electrolyte and the electrochemical operations were...
conducted using a VarsaSTAT4 (Princeton Applied Research). The electrochemical impedance spectra were recorded by ALS660A (BAS). All the electrochemical measurements were carried out at room temperature.

3. Results and Discussion

The diameter of the KOH-PANC beads polymerized in less polar solution (DMF/methanol = 75/25) was ca. 3 times larger than those prepared in polar solution (DMF/methanol = 10/90). Their SEM images are shown in Fig. 1(c) and (d). It is obvious that the spherical shape and uniform size of the original PAN beads were almost kept during carbonization and activation (Fig. 1(a), (b), and (c)). The specific surface area of KOH-PANC (270 nm) and KOH-PANC (820 nm) reached 2148 m² g⁻¹ and 2158 m² g⁻¹, respectively, whereas that of YP50F was 1404 m² g⁻¹.

Although the surface areas of the two types of KOH-PANC beads were almost same, their pore size distributions were obviously different (Fig. 2). Both samples show pore volume maxima at a similar pore width (1.5 nm), however, the pore volume at the maximum was smaller for the KOH-PANC (270 nm) than for the KOH-PANC (820 nm). Considering the measurable increase in the pore volume at around 2 nm pore width for the KOH-PANC (270 nm), the coalescence of pores occurred during the activation by KOH, probably because the activation was proceeded more efficiently due to the small size of the 270 nm carbon beads.

Figure 3 shows the charge-discharge profiles and their specific capacitances are summarized in Table 1. The specific capacitances ($C_s$) were calculated by the following equation.

$$C_s = \frac{I_{ds} \Delta t}{\Delta V m}$$

where $I_{ds}$ is the discharge current, $\Delta t$ is the discharge time, $\Delta V$ is the cell voltage difference in discharge, and $m$ is the weight of carbon material in a single electrode (excluding the weight of the conducting supplement). Obviously, the KOH-PANC based electrodes exhibited higher capacitance than the YP50F-AB electrode irrelevant to their size, which is due to the larger specific surface area obtained by the KOH activation. The advantage of the KOH-PANC electrode becomes more remarkable when they are compared in terms of specific capacitance per unit volume because the packing densities of the KOH-PANC electrodes were ca. 12% higher than the YB50F-AB electrode (Table 1). When the two sizes of KOH-PANC were compared, the specific capacitances of the KOH-PANC (820 nm) electrode was about 10% higher than that of the KOH-PANC (270 nm) electrode at low current density (0.5 A g⁻¹) in spite of their nearly same specific surface area. This can be explained by the difference in micro pore (1.5 nm) volume that is known to contribute to the capacitance and obviously larger for the KOH-PANC (820 nm) sample. Even if the current density was increased 100-fold (50 A g⁻¹), the specific capacitances of the KOH-PANC electrodes were well-maintained. Remarkably, the electrodes without AB showed almost same retention ratios as the electrodes with AB, indicating the high electron conductivity of KOH-PANC that are comparable to AB, and the merit of their intricately folded morphology facilitating an electric contact between the particles. Especially, the KOH-PANC (270 nm) electrode exhibited a markedly high retention ratio (54.4%) even if a substantial effect of IR drop is seen in the charge-discharge profiles. When the specific capacitances were estimated from the linear region of the discharge profiles (in order to remove the effect of IR drop), the retention ratio of KOH-PANC (270 nm) electrode was 84.8%, even higher than that of KOH-PANC (820 nm) electrode (70.6%) and YP50F-AB electrode (71.7%). The larger pore width of the KOH-PANC (270 nm) is not advantageous in terms of specific capacitance at low current condition, but rather favorable for the use at high current condition due to the smooth ionic diffusion in the pores and the resulting increase in pore availability.

Figure 4 shows the Nyquist plots of AC impedance for each electrode. The semicircles were assigned to the grain boundary
resistance ($R_{gb}$) between the carbon particles. The linear regions with a slope of ca. 45° were assignable to the ionic diffusion resistance ($R_{dif}$). The values of each resistance component are given in Table 1. In accord with the charge-discharge experiments, the addition of AB to the two types of KOH-PANC beads-based electrodes had little effects on the $R_{gb}$ values and these tendencies were independent of the size of the KOH-PANC beads. The increase in $R_{dif}$ was observed by addition of AB to KOH-PANC beads. Probably, the presence of AB might be obstacle for ionic species to come in and out of the pore because KOH-PANC beads-based electrodes had little effects on the $R_{gb}$ values and these tendencies were independent of the size of the KOH-PANC beads. The increase in $R_{dif}$ was observed by addition of AB to KOH-PANC beads. Probably, the presence of AB might be obstacle for ionic species to come in and out of the pore because KOH-PANC beads-based

| Sample                      | Specific capacitance per unit weight $a$ | Specific capacitance per unit volume | Retention ratio $c$ | $R_{gb}$ $b$ [Ω] | $R_{dif}$ $b$ [Ω] |
|-----------------------------|-----------------------------------------|-------------------------------------|---------------------|------------------|------------------|
| KOH-PANC (270 nm)-AB $a$    | 60 [F g$^{-1}$]                         | 25 [F cm$^{-3}$]                    | 56.7%               | 2.0              | 12.3             |
| KOH-PANC (270 nm)           | 57 [F g$^{-1}$]                         | 32 [F cm$^{-3}$]                    | 54.4%               | 1.4              | 9.1              |
| KOH-PANC (820 nm)-AB $a$    | 67 [F g$^{-1}$]                         | 35 [F cm$^{-3}$]                    | 37.3%               | 2.0              | 17.7             |
| KOH-PANC (820 nm)           | 63 [F g$^{-1}$]                         | 34 [F cm$^{-3}$]                    | 38.1%               | 2.0              | 15.1             |
| YP50F-AB $a$                | 47 [F g$^{-1}$]                         | 21 [F cm$^{-3}$]                    | 40.4%               | 2.3              | 14.5             |

$a$The capacitance was calculated excluding the weight of the conducting supplement (AB).

$b$ $R_{dif}$ was estimated as the real-part difference between the right edge of semicircle and the point of lowest frequency.

$c$The retention ratio was calculated using specific capacitance per unit weight.

Figure 3. Charge-discharge profiles of (a) KOH-PANC (270 nm), (b) KOH-PANC (820 nm) and (c) YP50F measured with 2-electrode cell using 1M acetonitrile solution of TEBF$_4$ at current density of 0.5 A g$^{-1}$ (solid line) and 50 A g$^{-1}$ (dashed line). Black lines show the profiles for the electrode assembly with AB, and red lines do without AB.

Figure 4. Nyquist plots of (a) KOH-PANC (270 nm), (b) KOH-PANC (820 nm) and (c) YP50F measured using 2-electrode cell in 1M acetonitrile solution of TEBF$_4$. 

Table 1. Specific capacitances and resistance components of YP50F and two KOH-PANC beads electrodes.
electrodes were already in a close-packed condition (Fig. 1(c) and (d)). Notably, $R_{\text{diff}}$ of the KOH-PANC (270 nm) was apparently smaller than those of the KOH-PANC (820 nm) and YP50F electrodes. This is consistent with a good capacitance retention of the KOH-PANC (270 nm) electrode presumably due to the high availability of coalesced, larger pores at high current condition. In addition, the smaller beads size itself is also contributing to shorten the diffusion distance of ionic species to move around in the pores and decrease the $R_{\text{diff}}$.

4. Conclusion

Two types of carbon beads with different diameters were successfully synthesized using the dispersion polymerization. Unlike the common ACs (YP50F), the specific capacitances of the electrode assemblies with and without AB was similar for the KOH-PAN beads over a wide current density range due to their good electric conductivity. Interestingly, the KOH-PANC (820 nm) electrode recorded highest specific capacitance (67 F g$^{-1}$), while KOH-PANC (270 nm) possessed a good retention ratios (54.4% and 84.8% including and excluding IR drops, respectively) when the current density was switched from 0.5 A g$^{-1}$ to 50 A g$^{-1}$. The AC-impedance measurements revealed the low $R_{\text{gb}}$ values even in the absence of AB, and instead, it revealed that the value of $R_{\text{diff}}$ determined an overall performance of KOH-PANC beads electrodes. The $R_{\text{diff}}$ value was smallest for the KOH-PANC (270 nm) and it contributed to the good retention ratio when the current density was increased 100-fold. These results were explained in relation to the smooth ionic diffusion in large pores of KOH-PANC (270 nm) formed by the coalescence during the KOH activation, as well as the small size of the carbon beads. An entire effect, including the increased surface area by KOH activation, demonstrated specific capacity 1.5–2 fold superior than commercial materials.

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