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Comparison of the Electrochemical Properties of Electric Double-Layer Capacitors with an Aqueous Electrolyte and with a Nonaqueous Electrolyte

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The electrochemical properties of phenolic resin-based activated carbon fiber cloth (ACFC) in an aqueous electrolyte and in a nonaqueous organic electrolyte have been investigated. The differential electric double-layer capacitance of ACFC with the specific surface area of 1630 $m^2 g^{-1}$ in the aqueous electrolyte was 1.50-times larger than that of the ACFC in the organic electrolyte. In accordance with the result, the capacitance of capacitors consisted of the ACFC and the aqueous electrolyte was 1.47-times larger than that of capacitors comprising ACFC and the organic electrolyte. The IR drop of capacitors with the aqueous electrolyte was smaller by one order of magnitude than that of capacitors with the organic electrolyte.

Electric double-layer capacitors with activated carbon and electrolytes have been widely used as memory back-up devices. We have previously reported that capacitors with phenolic resin based activated carbon fiber cloth (ACFC) and organic electrolytes showed advantages of high capacitance, high working voltage, and high reliability.[1-6] Capacitors with a higher capacitance and a lower internal resistance have strongly been required for devices. The capacitance of capacitors is determined by the electric double-layer capacitance between ACFC and electrolytes. The IR drop (the voltage drop at the beginning of the discharge of the capacitors) is largely influenced by the conductivity of the electrolytes. Although the decomposition voltage of aqueous electrolytes (theoretical decomposition voltage=1.23 V) is lower than that of organic electrolytes, the electric conductivity of aqueous electrolytes is larger by one order of magnitude than that of organic electrolytes. Thus, the comparison of the electrochemical properties of ACFC in aqueous electrolytes and in organic electrolytes is important for clarifying the mechanism of capacitors.

In this paper we report: (1) the electrochemical properties of three types of ACFC in an aqueous electrolyte and in an organic electrolyte, and (2) the capacitance and IR drop of the two types of capacitors (capacitors (A) comprising ACFC and aqueous electrolytes and capacitors (B) comprising ACFC and organic electrolytes).

Experimental

Sample Preparation. ACFC were prepared by the carbonization and activation of phenolic resin-based fiber cloth (Nippon Kynol Inc.) in a nitrogen atmosphere at 1000 °C while supplying water vapor as an activation gas. Three types of ACFC (ACFC (a), (b), and (c)) were prepared by changing the activation time.

An aluminum layer or a nickel layer (100—150 μm) was formed by a plasma-spraying method on one side of ACFC as a collector electrode.

The 5.35 mol dm^{-3} of KOH and the propylene carbonate solution (PC) containing 0.51 mol dm^{-3} of tetraethylammonium fluoroborate (Et_4NBF_4) were used as an aqueous electrolyte and an organic electrolyte, respectively.

Analysis of ACFC. The specific surface area and pore size distribution of ACFC was obtained from methanol vapor adsorption. Details of the measurements were described previously.[4] The crystallity of ACFC was examined by X-ray diffraction.

Electric Measurements. A schematic diagram of the triangular voltage sweep cyclic voltammetry was shown in a previous paper.[5] The measurement was carried out using a potentiostat (Hokuto Denko, Model HA-303) and a function generator (Hokuto Denko , Model HB-104) at 25 °C. The ACFC (3—5.3 mg, 6 mm in diameter) with a plasma-sprayed aluminum or nickel layer was prepared as a working electrode. An ACFC with glassy carbon plates and a saturated calomel electrode (SCE) were used as a counter and a reference electrode, respectively. The voltage sweep of the cyclic voltammetric experiments started from the rest potential of the specimens.

The differential capacitance, C_d, in F is calculated simply from

$$C_d = i/k,$$

where i is the capacitive current (mA) at 0.1 V vs. SCE and k the sweep rate (mV s^{-1}).

The capacitance of coin-type electric double-layer capacitors was measured at 25 and −25 °C. Details of the construction and the measurement of the capacitance of capacitors were described previously.[4]

Results and Discussion

Properties of ACFC. Figure 1 shows the relation between the accumulated pore volume and the pore diameter of ACFC (a), (b), and (c), calculated from the adsorption isotherm using a modified version of Kelvin's equation.[7] Upon increasing the activation time, the accumulated pore volume increases. From the figure, the specific surface area of ACFC (a) was 1630 $m^2 g^{-1}$, ACFC (b) 1290 $m^2 g^{-1}$, and ACFC (c) 850 $m^2 g^{-1}$. The pore-size distribution was estimated from the ratio of the pore volume of large pores with diameters larger than 2 nm to the total pore volume.

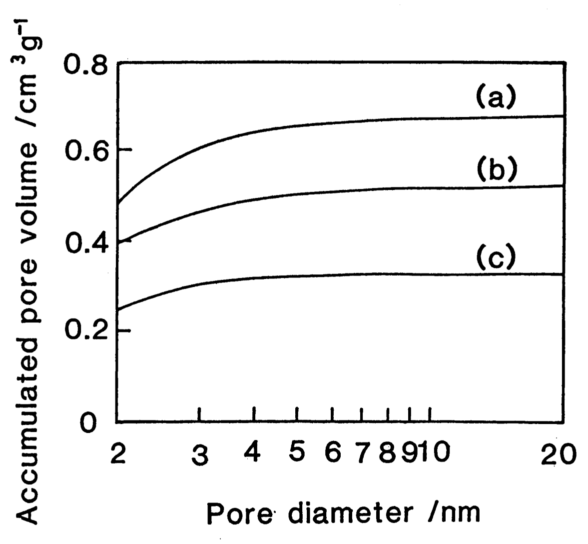

Fig. 1. Accumulated pore volume vs. pore diameter of ACFC.

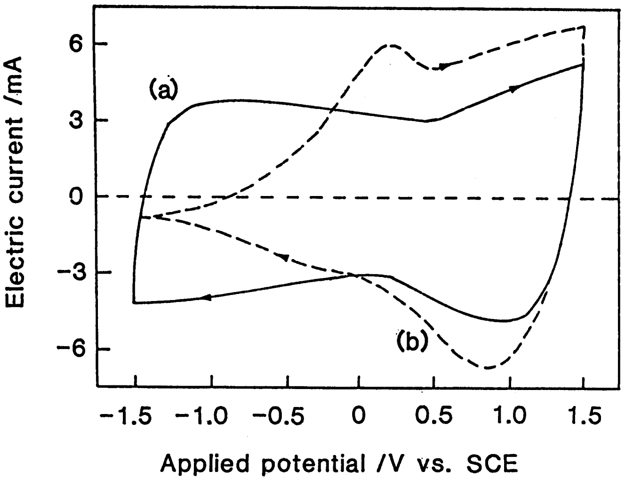

Fig. 3. Cyclic voltammogram of ACFC (a) and (b) with a sprayed aluminum in the organic electrolyte of PC containing 0.51 mol dm^{-3} of Et_4NBF_4 at 10 mV s^{-1}.

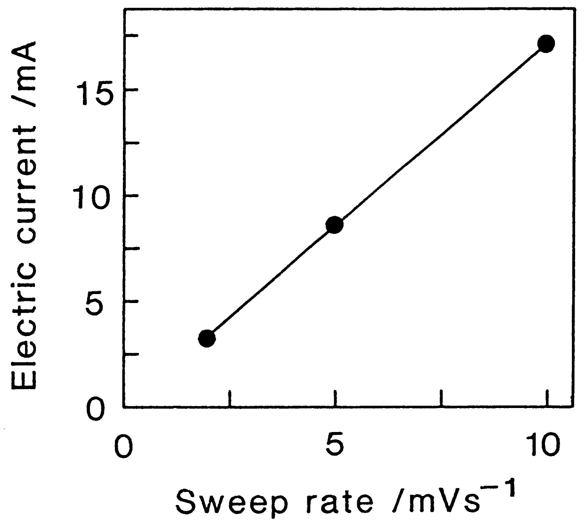

Fig. 2. Sweep rate dependence of ACFC with a sprayed nickel in the aqueous electrolyte of 5.35 mol dm^{-3} of KOH.

The above-defined ratio of ACFC (a) was 35%, ACFC (b) 23%, and ACFC (c) 20%. The specific surface area and pore size distribution of ACFC were, thus, easily controlled by changing the activation conditions.

The X-ray diffraction patterns of ACFC (a), (b), and (c) were broad. Therefore, the ACFC examined maintained an amorphous structure in the specific surface area of 850—1630 m^2 g^{-1}.

Cyclic voltammometry is a useful technique to investigate the electrochemical properties of activated carbon electrodes.[8–10]

The cyclic voltammogram was measured for ACFC (b) with a sprayed nickel layer in 5.35 mol dm^{-3} of KOH at 25 °C in the voltage range between −0.6 and 0.6 V vs. SCE. The capacitive electric currents were almost constant in this region. The relation between the electric currents at 0.1 V vs. SCE and the sweep rate is shown in Fig. 2. The currents are proportional to the sweep rates. Therefore, the electric double-layer of ACFC (b) in 5.35 mol dm^{-3} of KOH was stable. From the currents at 0.1 V vs. SCE, the differential capacitance of ACFC (b) was seen to be 140 F g^{-1}. Similar to the case of ACFC (b), the currents at 0.1 V vs. SCE were proportional to the sweep rates in the voltammograms of ACFC (a) and (c). The differential capacitance of ACFC (a) and (c) was 169 and 108 F g^{-1}, respectively.

Figure 3 shows cyclic voltammograms of ACFC (a) and (b) with aluminum layer in the organic electrolyte of PC containing 0.51 mol dm^{-3} of Et_4NBF_4. We carried out experiments between −1.5 and 1.5 V vs. SCE. In this region, the aluminum was stable in the organic electrolyte.[5] Although, the capacitive electric current of ACFC (a) is almost constant within this voltage region, that of ACFC (b) decreases at the cathodic polarization. This is probably because the electric double-layer between the ACFC (b) with rather small pores and solvated Et_4N^+ cations in the organic electrolytes was unstable. From the electric current at 0.1 V vs. SCE in the figure, the differential electric double-layer capacitance of ACFC (a) was 113 F g^{-1}. Since the electric double-layer of ACFC (b) and (c) in the organic electrolyte was unstable, the differential capacitance was not calculated from the voltammogram correctly.

Compared with the voltammograms of ACFC (a) in the aqueous electrolyte and in the organic electrolyte, the differential capacitance of ACFC (a) in the aqueous electrolyte was 1.50-times larger than that of ACFC (a) in the organic electrolyte. This is because the diameter of solvated Et_4N^+ and BF_4^- in PC is larger than that of K^+ and OH^- in water and the permeability of the PC (viscosity of 2.53 cp at 25 °C) is lower than that of water (viscosity of 0.895 cp at 25 °C). In conclusion, the difference in the size of solvated electrolytes and permeability of electrolytic solution affect the properties of the electric double-layer on ACFC. Further investigation is necessary in order to clarify the nature of the electric double-layer between ACFC and electrolytes.

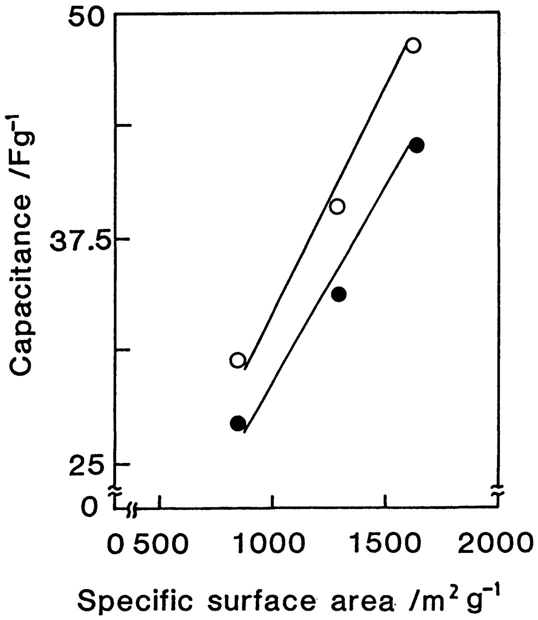

Fig. 4. Temperature dependence of the capacitors with 5.35 mol dm^{-3} of KOH, ○; capacitance at 25 °C, ●; capacitance at −25 °C.

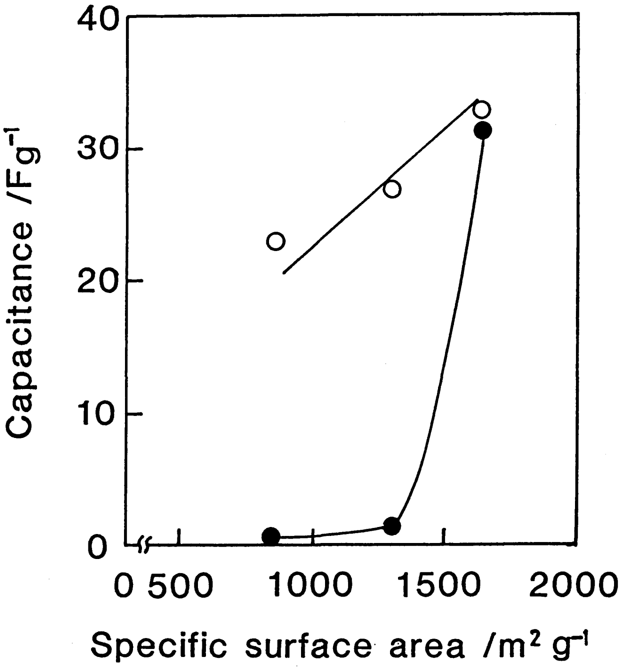

Fig. 5. Temperature dependence of the capacitors with the organic electrolyte of PC containing 0.51 mol dm^{-3} of Et_4NBF_4, ○; capacitance at 25 °C, ●; capacitance at −25 °C.

Characteristics of Capacitors. The characteristics of two types of capacitors have been investigated: capacitors (A) consisted of ACFC and 5.35 mol dm^{-3} of KOH and capacitors (B) consisted of ACFC and the organic electrolyte of PC containing 0.51 mol dm^{-3} of Et_4NBF_4.

Figures 4 and 5 show the temperature dependence of capacitors (A) and (B), respectively. In the case of capacitors (A), the capacitance at −25 and 25 °C is proportional to the specific surface area of ACFC used in the capacitors. The capacitance at −25 °C decreased by about 12% in comparison with that at 25 °C. This is because the electric conductivity of the aqueous electrolyte of KOH decreased at −25 °C and IR drop became larger with decreasing temperature. The capacitance of capacitors (A) with ACFC (a) at 25 °C is 48 F/(gram of total ACFC in the capacitor), ACFC (b) 39 F, and ACFC (c) 30.5 F.

In the case of capacitors (B), the capacitance at 25 °C is proportional to the specific surface area of ACFC, while the capacitance at −25 °C of capacitors with ACFC (b) and (c) is small. This is because the pore-size of ACFC (b) and (c) was smaller than that of ACFC (a). Since the resistance in micropores of ACFC (b) and (c) becomes large at low temperatures, the apparent capacitance becomes small.[4] The capacitance of capacitors (B) with ACFC (a) at 25 °C is 32.6 F/(gram of total ACFC in the capacitor), ACFC (b) 24.6 F, and ACFC (c) 22.6 F. The capacitance of capacitors (A) with ACFC (a) was 1.47-times larger than that of capacitors (B) with ACFC (a).

Figure 6 shows the relation between the leak current of capacitors (B) with ACFC (a) and the app-

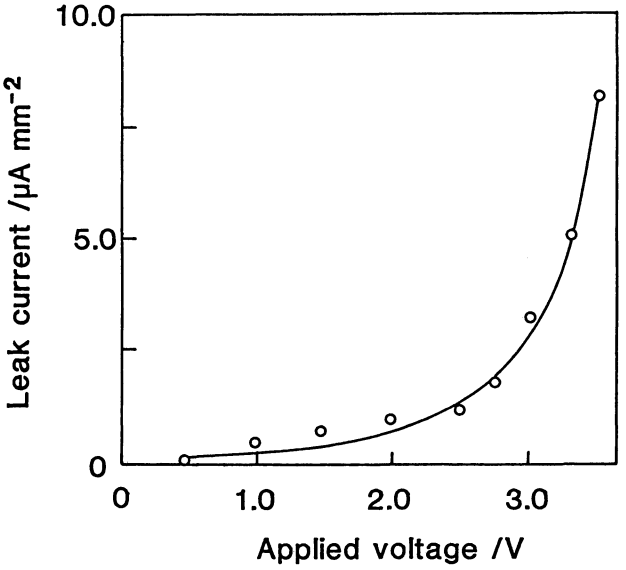

Fig. 6. Leak current vs. applied voltage of the capacitors with the organic electrolyte.

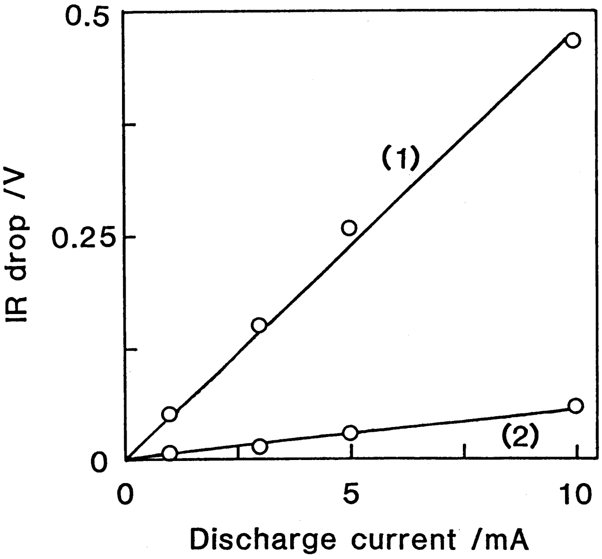

Fig. 7. IR drop vs. discharge current of the capacitors, (1); the capacitors with the organic electrolyte, (2); the capacitors with the aqueous electrolyte.

lied voltage. In the voltage range between 0.5 and 2.8 V dc, the leak current gradually increases with increasing applied voltage, and the current increases abruptly above 3.0 V dc. In conclusion, the working voltage of capacitors (B) was less than 2.8 V dc. The working voltage of capacitors (A) was limited by the decomposition voltage of aqueous electrolytes. Thus, the working voltage of capacitors (A) was less than half than that of capacitors (B).

Figure 7 shows the IR drop (the voltage drop at the beginning of discharge of the capacitors) of capacitors (A) and (B) and the discharge current of capacitors. The ACFC used in capacitors (A) and (B) were ACFC (a). The IR drop is proportional to the discharge current. The IR drop of capacitors (A) is smaller by one order of magnitude than that of capacitors (B) at a discharge current of 10 mA. Thus, capacitors (A) using a large discharge current were more suitable devices than capacitors (B).

Conclusion

1) In the aqueous electrolyte, the differential capacitance of ACFC with the specific surface area of 1630, 1250, and 850 $m^2 g^{-1}$ was stable. On the other hand in the organic electrolyte, only the ACFC with the area of 1630 $m^2 g^{-1}$ was stable. The differential capacitance of ACFC with 1630 $m^2 g^{-1}$ in the aqueous electrolyte at 25 °C was 1.50-times larger than that of the ACFC in the organic electrolyte.

2) The capacitance of capacitors (A) with the aqueous electrolyte at 25 °C was 1.48-times larger than that of capacitors (B) with the organic electrolyte. The working voltage of capacitors (A) was less than half compared with that of capacitors (B) and the IR drop of capacitors (A) was smaller by one order of magnitude than that of capacitors (B).

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