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Effect of Supporting Carbon Particles on Electric and Electrochemical Properties of Polarizable Electrodes Using Activated Carbon Fiber Sheets in Electric Double Layer Capacitors

Ichiro TANAHASHI,* Akihiko YOSHIDA, and Atsushi NISHINO
Central Research Laboratories, Matsushita Electric Industrial Co., Ltd., Yagumo-Nakamachi, Moriguchi, Osaka 570
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The effect of supporting carbon particles on the electric and electrochemical properties of polarizable electrodes in electric double layer capacitors have been studied. The polarizable electrodes examined were activated carbon fiber sheets (ACF sheets) composed of phenolic resin-based activated carbon fibers, carbon fibers, and pulps. The sheets with supporting carbon particles have been prepared by impregnation of the sheets with suspension of submicron carbons. The electric resistance of the sheets with supporting carbon particles of 18.7 $g\,m^{-2}$ decreased by 53% and the differential electric double layer capacitance in an organic electrolyte increased by 12%. In accordance with these results, the impedance of the capacitors composed of ACF sheets with supporting carbon particles decreased by 33% and the capacitance increased by 11% in comparison with those of the capacitors composed of the sheets without supporting ones.

Electric double layer capacitors have widely been used as memory back-up devices. The polarizable electrodes in electric double layer capacitors prepared from phenolic resin-based activated carbon fiber cloths and activated carbon fiber sheets (ACF sheets) previously developed showed advantages of high capacitance, high working voltage, and high reliability.[1—6] We have reported that the electric resistance of ACF sheets was drastically decreased with the addition of pitch-based carbon fibers.[6] The capacitors with lower impedance and higher reliability have strongly been required in the devices. The impedance of the capacitors is largely influenced by the conductivity of electrolytes and polarizable electrodes.

There are two ways to decrease the impedance of the capacitors. One is to use aqueous electrolytes which show two orders of magnitude larger conductivity than that of organic electrolytes. However, the decomposition voltage of aqueous electrolyte (theoretical decomposition voltage=1.23 V) is lower than that of organic electrolytes. It is thus necessary to use organic electrolytes to obtain the capacitors with high working voltage (more than 2.0 V dc). The other is to decrease the electric resistance of polarizable electrodes. We have tried to reduce the electric resistance of ACF sheets and found that the sheets with supporting carbon particles showed the lower electric resistance with the larger electric double layer capacitance compared with that of the sheets without supporting ones.

In this paper, we report that the specific surface area, electric resistance, and differential electric double layer capacitance of ACF sheets with and without supporting carbon particles. The impedance, capacitance, and reliability of the capacitors with the sheets have been investigated.

Experimental

Preparation of ACF Sheets with Supporting Carbon Particles. The activated carbon fiber sheets (ACF sheets) were composed of phenolic resin-based activated carbon fibers (ACF), pitch-based carbon fibers (CF), and natural pulps. The sheets were prepared by the conventional paper-making method. The details of the production process of the sheets were described previously.[6] Two types of ACF sheets were prepared. One showed 790—850 μm thick with the specific weight of 140 $g\,m^{-2}$ and the other showed 550—600 μm with 130 $g\,m^{-2}$. The ACF sheets with supporting carbon particles were prepared by impregnation of the sheets with suspension of submicron carbons (Acheson Japan Ltd., Aguadag). The specific gravity of the suspension was 1.05. After impregnation, the sheets were dried at 110 °C for more than 3 h. The specific surface area of the sheets was obtained from the methanol vapor adsorption isotherm at 50 °C. The details of the measurement were described previously.[4]

The aluminum layer (100—150 μm) was formed by a plasma spraying method on the side of the sheets as a collector electrode.

The propylene carbonate solution(PC) containing 0.51 $mol\,dm^{-3}$ of tetraethylammonium fluoroborate (Et_4NBF_4) was used as the electrolyte.

Characteristics Measurement. The electric resistance of ACF sheets was measured with a digital multimeter (Takeda Riken, TR 6843). The size of ACF sheets was 1 cm in width and 5 cm in length. Both ends of the specimens were in contact with metal clips to obtain an enough electric contact with leads.

The triangular voltage sweep cyclic voltammetric experiments were carried out using a potentiostat (Hokuto Denko, Model HA-303) and a function generator (Hokuto Denko, Model HB-104) at 25 °C in a dry box. The ACF sheets (6 mm in diameter) with plasma sprayed aluminum layer were used as a working electrode. The measurement was carried out between −1.5 and 1.5 V vs. SCE at 25 °C with the sweep rate of 5 mV sec^{-1}. The details of the experiments were described previously.[5]

Capacitance of coin type electric double layer capacitors was measured at 25 °C. The details of the constructions and the measurements of the capacitance of the capacitors were described in a previous paper.[4] The impedance of the capacitors was measured at 1 kHz with an LCR meter (Yokogawa Hewllet Packard, 4261A).

The stability of the capacitors during dc voltage load was tested with charging at a constant dc voltage of 2.0 V at a constant temperature of 70 °C for 1000 h.

Results and Discussion

Properties of ACF sheets with supporting carbon particles. Figure 1 shows the adsorption isotherms of ACF sheets with supporting carbon particles of 18.7 $g\,m^{-2}$ and without supporting ones. The sheets examined were composed of 54% ACF, 31% pitch-based carbon fiber (CF), and 15% pulps, whose specific weight and thickness are 140 $g\,m^{-2}$ and 820 μm, respectively. From the figure, the specific surface area of ACF sheets with and without supporting carbon particles were found to be 970 and 906 $m^2 g^{-1}$, respectively. With supporting ones, the specific surface area increased by 7%. The area of supported carbon particles was estimated to be 1450 $m^2\,g^{-1}$.

The electric resistance of the sheets decreased from 40.9 to 19.2 Ω with supporting carbon particles of 18.7 $g\,m^{-2}$. We have previously reported that the electric resistance of the sheets was largely influenced by the electric resistance of the pulps in the sheets.[6] Therefore, it is important to develop the pulps with electric conductivity. In order to clarify the effects of supported carbon particles on the electric resistance of the sheets, the electric resistance of papers made of natural pulps (50 μm in thickness) with supporting carbon particles of 2.3 $g\,m^{-2}$ was measured. The papers with supporting ones showed electric resistance of 2.56 kΩ. As the electric resistance of the films of the carbon particles examined (25μm in thickness) was 15 Ω, the electric resistance of the papers was expected to be decreased with increasing the amount of supporting carbon particles. The electric resistance of the pulps in the sheets thus decreased with supporting carbon particles.

Figures 2 and 3 show microscopic photograph and SEM micrograph of the sheets, respectively. In Fig. 2, the carbon particles cover the sheets like a film. In Fig. 3, the carbon particles are attached on the surface of ACF, CF, and pulps. Since pulps are easy to absorb

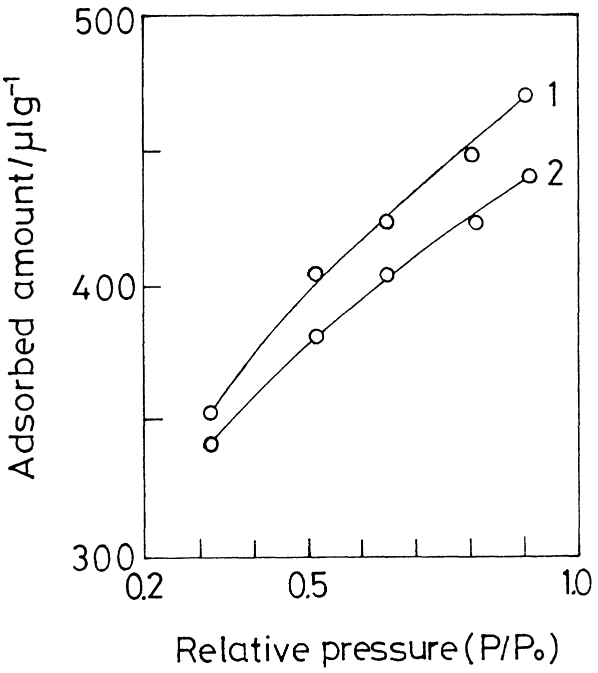

Fig. 1. Adsorption isotherm of ACF sheets with and without supporting carbon particles. (1) With supporting carbon particles, (2) without ones.

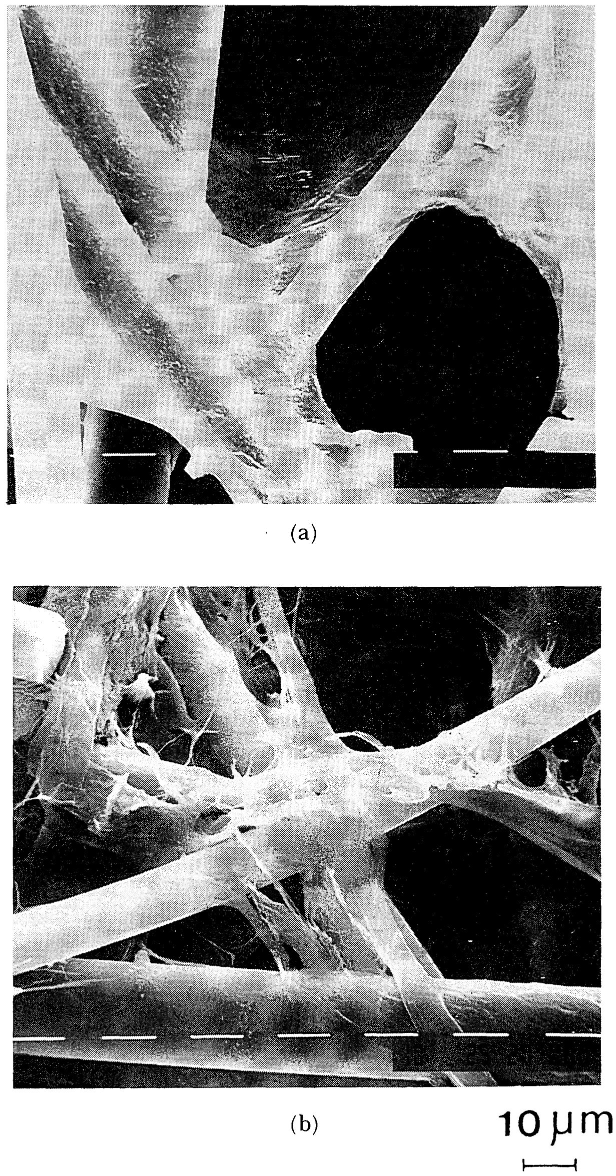

Fig. 2. Microscopic photograph of ACF sheets with and without supporting carbon particles. (a) With supporting carbon particles, (b) without ones.

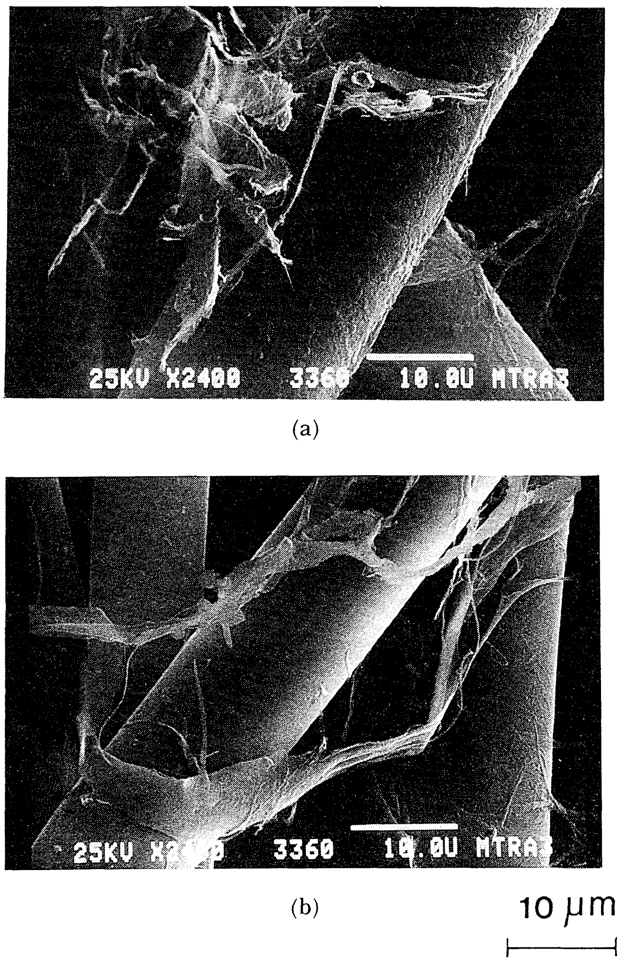

Fig. 3. SEM micrographs of ACF sheets with and without supporting carbon particles. (a) With supporting carbon particles, (b) without ones.

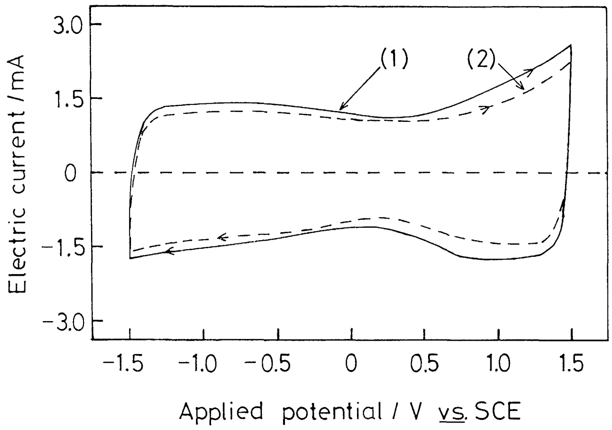

Fig. 4. Cyclic voltammograms of ACF sheets (6 mm in diameter) with plasma sprayed aluminum layer at $5\ \mathrm{mV\ s^{-1}}$. (1) With supporting carbon particles, (2) without ones.

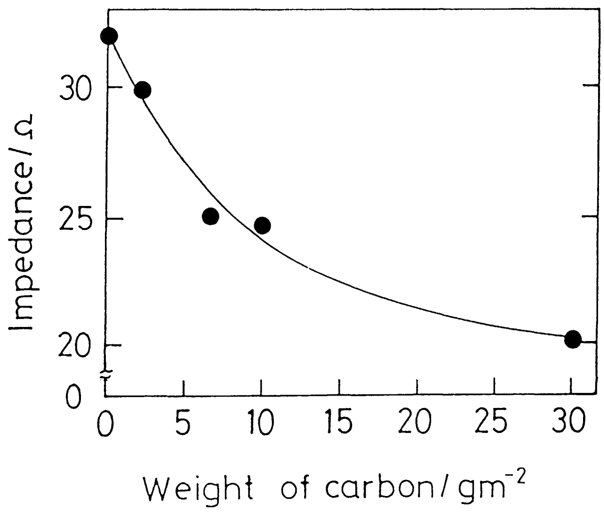

Fig. 5. Impedance vs. weight of supporting carbon particles.

the suspension of carbon particles, carbon particles seem to be supported inside the pulps. The suspension of submicron carbons examined is mainly used for the electrostatic screening. The submicron carbons used are suitable materials to form conductive layer on the insulators. To test the stability of the supported carbons, the sheets with carbon particles were dipped in the organic electrolyte of PC containing 0.51 mol of Et_4NBF_4 for 24 h at 70°C. The carbon particles on the sheets did not change after dipping. The carbon particles are thus firmly supported on the sheets.

Cyclic voltammometry is a useful technique to investigate the electrochemical properties of activated carbon electrodes.[8] Figure 4 shows cyclic voltamogram of the sheets with and without supporing carbon particles in the organic electrolyte of PC containing 0.51 mol of Et_4NBF_4. Since most of the electric double layer capacitors essentially operated in the 0.8—2.8 V dc range, we have carried out electrochemical experiments in this range. From the minimum capacitive current at 0.1 V vs. SCE in Fig. 4, the differential double layer capacitance of ACF sheets with and without supporting carbon particles was found to be 63.6 and 57.3 $\mathrm{F\ g^{-1}}$, respectively. In accordance with the increase in the capacitance of 11%, the surface area of the sheets increased by 12% with supporting carbon particles. The surface area was calculated using the value of specific surface area of the sheets with and without supporting carbon particles obtained from Fig. 1.

Characteristics of Capacitors. The characteristics of two types of capacitors, capacitor A and B, have been investigated. The polarizable electrodes used for capacitor A and B were the sheets with and without supporting carbon particles, respectively. The sheets used were composed of 54% ACF, 31% CF, and 15% pulps. With supporting 18.7 $\mathrm{g\ m^{-2}}$ carbon particles on the sheets, the impedance of the capacitors decreased by 33% and the capacitance increased by 11%.

These results were attributed to the decrease in the electric resistance and the increase in differential double layer capacitance of ACF sheets with supporting carbon particles.

After the load life test of the capacitors composed of the sheets with carbon particles of $18.7\ \text{g m}^{-2}$, the capacitance decreased by 13%, while in the case of capacitors composed of the sheets without supporting one, the capacitance decreased by 37%. The reliability of the capacitors were thus considerably improved by supporting carbon particles on the sheets.

Figure 5 shows the relation between the impedance of the capacitors and the weight of supported carbon particles on the sheets. The sheets examined were composed of 29% ACF, 56% CF, and 15% pulps, whose specific weight was $130\ \text{g m}^{-2}$. The impedance is gradually decreased with increasing weight of suppoirting carbon particles. It seems that the space in ACF sheets is filled with carbon particles and the electric resistance of the sheets is decreased. With supporting carbon particles of $10—30\ \text{g m}^{-2}$, the impedance of the capacitors decreased effectively. The capacitors composed of the sheets with supporting carbon particles thus showed low impedance and the suitable amount of supporting carbon particles was $10—30\ \text{g m}^{-2}$.

Conclusion

(1) The electric resistance of ACF sheets with supporting carbon particles became less than half in comparison with that of the sheets without supporting ones. This is mainly attributed to the pulps containing carbon particles with electric conductivity.

(2) The surface area of the sheets with supporting carbon particles increased by 11%. In accordance with this increse, the differential electric double layer capacitance of the sheets increased by 12%.

(3) Using ACF sheets with supporting carbon particles for polarizable electrodes, the impedance of the capacitors decreased by 33%, while the capacitance increased by 11% and the reliability of the capacitors was considerably improved.

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