Preparation and Characterization of Activated Carbon Tablets for Electric Double Layer Capacitors

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Two types of activated carbon tablets (AC tablets) were prepared and characterized by adsorption methods for electric double-layer capacitors. The tablets were prepared from either the activation or carbonization of molded mixtures comprising phenolic resin-based activated carbon powders and phenolic resins. The specific surface area of the tablets (a) prepared from activation was 2010 m^2g^{-1} and the bulk density was 0.45 $g\,cm^{-3}$. The area of tablets (b) from carbonization was 1400 m^2g^{-1} with a yield of 83% (weight of obtained tablets/weight of molded mixtures). The capacitance of the capacitors with tablets (a) showed 7.3—12.5 F/(cm^3 of AC tablets). The reliability of the capacitors with AC tablets (a) and (b) was improved in comparison with that of capacitors with polarizable electrodes comprising activated carbon powders and binders.

Electric double-layer capacitors have been used as memory back-up devices. Various types of polarizable electrodes for the capacitors have been developed, such as a paste type,[1] a clay-carbon composite type,[2] an activated-carbon fiber cloths (ACFC) type,[3-7] and an activated-carbon fiber sheet (ACF sheets) type.[8]

We have previously reported that phenolic resin-based activated carbon fibers (ACF) are suitable materials for polarizable electrodes.[3-8] The ACF showed a large specific surface area, a large electric conductivity, and high strength without binders. The bulk density, however, is small (at most 0.2 $g\,cm^{-3}$). Though polarizable electrodes with a large bulk density are easily prepared using binders, the binders, themselves, deteriorate during the charge-discharge process of capacitors. It is thus necessary to develop polarizable electrodes with a large specific surface area and a large bulk density without using binders.

In the present paper we report: (1) the specific surface area and pore size distribution of activated carbon tablets (AC tablets) prepared by either the activation or carbonization of molded mixtures comprising activated carbon powders and phenolic resins, and (2) the capacitance and reliability of capacitors with AC tablets and an organic electrolyte.

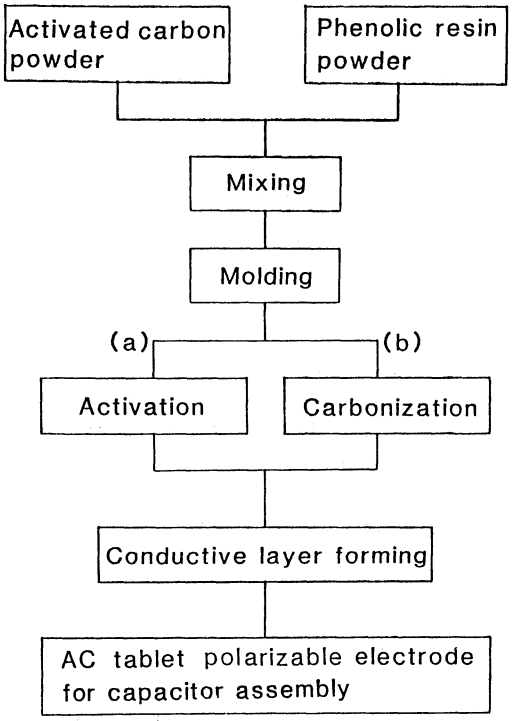


Fig. 1. Fabrication process of two types of activated carbon tablets (AC tablets) polarizable electrodes. a); AC tablets (a), b); AC tablets (b).

Experimental

Sample Preparation. Two types of activated carbon tablets, AC tablets (a) and (b), were prepared by changing the fabrication processes: AC tablets (a) and (b) were, respectively, prepared by the activation and carbonization of molded mixtures (the density of 0.75 $g\,cm^{-3}$ consisted of 70% phenolic resin-based activated-carbon powders and 30% phenolic resins).

Figure 1 shows the fabrication process of tablets (a) and (b) as polarizable electrodes. Phenolic resin-based activated-carbon powders (diameter of less than 20 μm) and the phenolic resin powders (diameter of less than 20 μm, the specific gravity of 1.24, Kanebo Ltd., Bell-pearl-S) were mixed. The mixed powders were molded under a pressure of 220 $kg\,cm^{-2}$ at 160 °C for 10 min. The molded mixtures comprising activated carbon powders and phenolic resins as binders were, thus, formed. The phenolic resin-based activated carbon powders used in the molded mixtures were prepared by the activation of phenolic resin powders (Kanebo Ltd., Bell-pearl-R) in a nitrogen atmosphere at 1000 °C while supplying water vapor as an activation gas. AC tablets (a) and (b) were prepared by changing the fabrication processes, as shown by (a) and (b) in Fig. 1. AC tablets (a) were prepared by the activation of molded mixtures at 1000 °C while supplying water vapor. AC tablets (b) were prepared by the carbonization of mixtures while heating (from room temperature up to 1000 °C at a rate of 80 $°C\,h^{-1}$). After the activation or carbonization of molded mixtures, an aluminum layer (100—150 μm) was formed by a plasma-spraying method on one side of the AC tablets.

A propylene carbonate (PC) solution containing 0.51

mol dm^{-3} of tetraethyl ammonium fluoroborate (Et_4NBF_4) was used as the electrolyte.

Analysis of AC Tablets. It is well known that the pore size distributions is determined from the adsorption isotherm and the statistical thickness of the adsorbed layer.[9] The specific surface area is calculated from the pore-size distribution based on the assumption of cylindrical micropores. In this experiment the pore size distributions of the molded mixtures and AC tablets were obtained by a methanol vapor adsorption isotherm.[10] Details of the measurements were described previously.[8]

Characteristics Measurements. The capacitance of coin-type electric double-layer capacitors with AC tablets (6 mm in diameter and 0.65 mm in thickness) was measured at 25 °C. Details of the construction and the measurement of the capacitance of the capacitors were described previously.[8] The capacitors were charged at 2.8 V dc, and the capacitance, C, in F was calculated according to,

$$C=(i\times t)/V,$$

where i is the constant discharge current of 1.0 mA, t the time for a discharge in s, and V the potential change of the capacitors (from 1.5 to 0.5 V) caused by the discharge (in volts).

The stability of the capacitors during dc voltage loading tested during charging at a constant dc voltage of 2.8 V at a constant temperature of 70 °C for 1000 h.

Results and Discussion

Characterization of AC Tablets. Figure 2 shows the relation of the yield (weight of obtained activated carbon powders/weight of phenolic resin powders) or the specific surface area of AC powders with the activation time. Upon increasing the activation time, the yield decreases and the specific surface area increases. The AC powders show a specific surface area of 1700 m^{2}g^{-1} with a 25% yield for an activation time of 15 min. AC powders with an area of 1700 m^{2}g^{-1} were used in this experiment. Under the same activation condition, the area was twice as large as that of conventional activated carbons; the yield was also large. This is because the phenolic resins contained 75.8% carbon.

Figure 3 shows the adsorption isotherms of the molded mixtures and AC tablets (a). The adsorption amount of AC tablets (a) increased 1.7-times as much as that of molded mixtures. Although the mechanical strength of tablets (a) was smaller than that of the molded mixtures, they did not deteriorate during plasma spraying.

Figure 4 shows the relation between the accumulated pore volume and the pore diameter for the molded mixtures and AC tablets (a). From this figure the specific surface area of the molded mixtures and tablets (a) is seen to be 1360 and 2010 m^{2}g^{-1}, respectively. The specific surface area of tablet (a) was more than 2-times larger than that of conventional activated carbon powders. The pore-size dis-

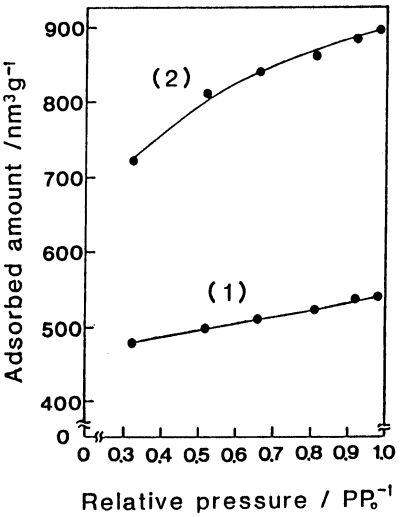


Fig. 3. Adsorption isotherm of molded mixtures and AC tablets (a). 1); molded mixtures composed of 70% AC powders and 30% phenolic resins, 2); AC tablets (a).

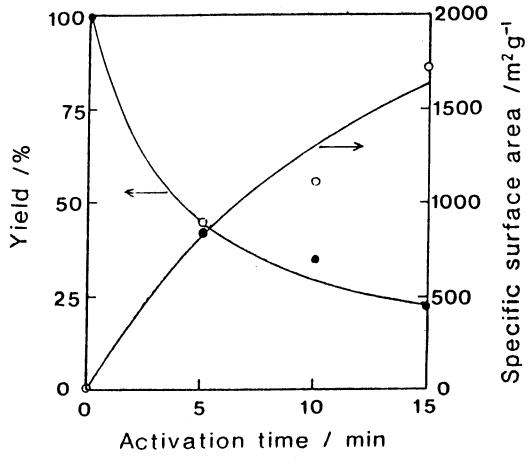


Fig. 2. Yield and specific surface area of AC powders vs. the activation time.

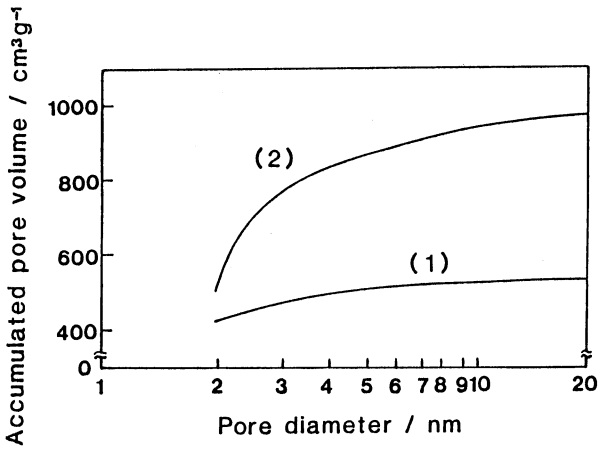
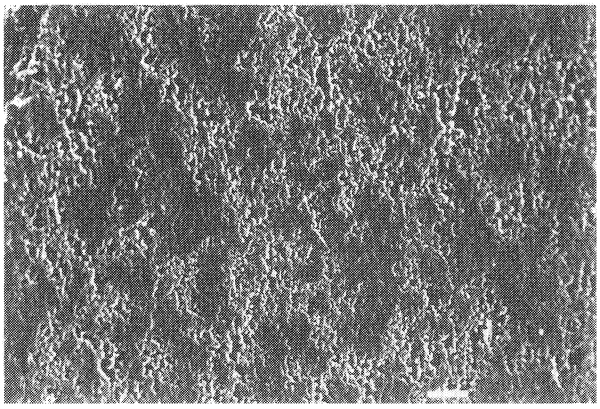


Fig. 4. Accumulated pore volume of molded mixtures and AC tablets (a). 1); molded mixtures composed of 70% AC powders and 30% phenolic resins, 2); AC tablets (a).

tribution was estimated from the ratio of the pore volume of large pores with diameters larger than 2 nm to the total pore volume. The above-defined ratios of the molded mixtures and tablets (a) were 20.5 and 43.5%, respectively.

Figures 5a) and b) show SEM photographs of the molded mixtures and tablets (a), respectively. The pore-size distribution of these are shown in Fig. 4. In Fig. 5, the surface of the molded mixtures is more smooth than that of tablets (a). Their surface was etched by activation. From the SEM observations, the AC powders seem to be mixed uniformly in molded mixtures.

Figure 6 shows an SEM photograph of AC tablets (a). Although tablets (a) are porous with a density of 0.45 g cm^{-3}, this value is 2-times larger than that of activated-carbon fiber cloth. From the SEM observations, the activated-carbon particles seem to remain in tablets (a). Tablets (a) were uniformly activated according to an observation of the cross section.



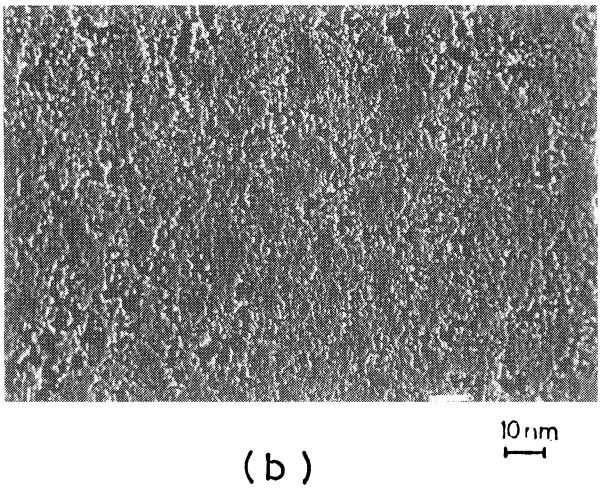


Fig. 5. SEM photographs of molded mixtures and AC tablets (a). a); molded mixtures composed of 70% AC powders and 30% phenolic resins, b); AC tablets (a).

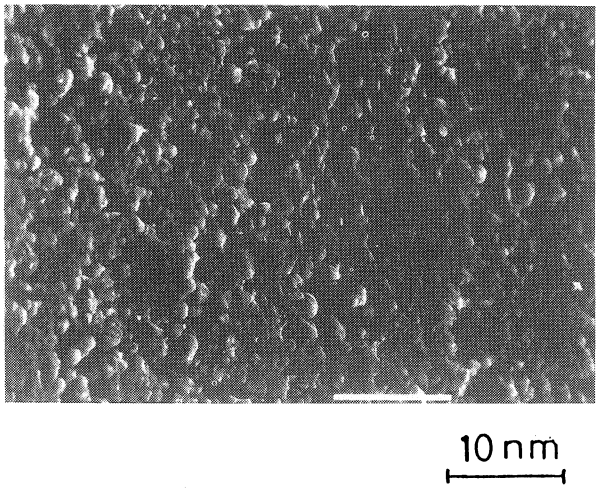


Fig. 6. SEM photograph of AC tablets (a).

Since activation gas entered the mixtures easily, they were activated uniformly.

For molded mixtures containing more than 50% phenolic resins, it was difficult to activate them uniformly since most of the AC powders were covered by resins. On the other hand, molded mixtures with more than 90% AC powders are very fragile after activation. Molded mixtures with 30% phenolic resins are of suitable composition to obtain AC tablets (a) with a large specific surface area and a high mechanical strength.

AC tablets (b) were prepared by the carbonization of molded mixtures which comprising 70% AC powders and 30% resins. The specific surface area and the density of tablets (b) were 1400 $m^2 g^{-1}$ and 0.61 g cm^{-3}, respectively. The phenolic resin in the mixtures was carbonized and the yield (weight of obtained AC tablets/weight of molded mixtures) was 83%. The yield was 1.3—2.1 times larger than that of

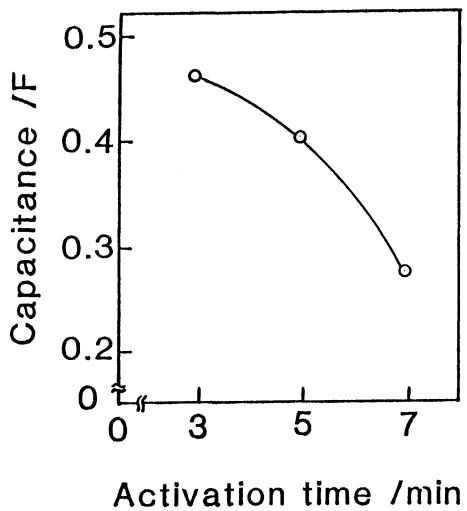


Fig. 7. Capacitance of the capacitors with AC tablets (a) vs. activation time.

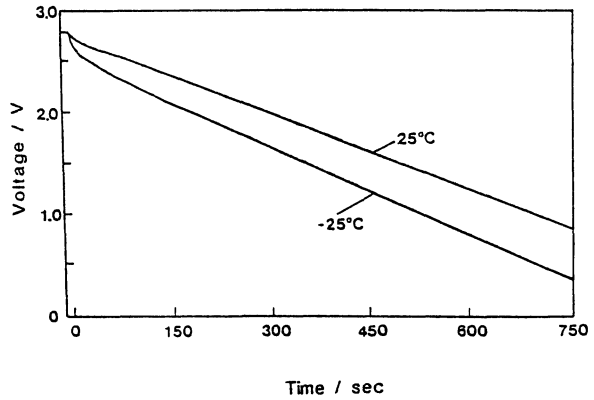


Fig. 8. Discharge curves of the coin type electric double layer capacitors with AC tablets (b) under a 100 μA discharge current at 25 and −25 °C.

tablets (a). Tablets (b) showed a smaller specific surface area and a higher density compared with those of tablets (a).

Characteristics of Capacitors. Figure 7 shows the relation between the capacitance of capacitors with AC tablets (a) and the activation time of the molded mixtures used in capacitors. The capacitance was 7.3—12.5 F/(cm^3 of AC tablets). These values were 1.4—2.3 times larger than those of activated-carbon fiber cloth previously reported.[6] Although the specific surface area of AC tablets (a) increased with increasing activation time, the yield decreased. Therefore, the capacitance of capacitors decreased with increasing activation time.

After a load life test of capacitors with AC tablets (a) and (b), the capacitance decreased by 5 and 7%, respectively. In the case of a capacitor with polarizable electrodes comprising 80% AC powders and 20% fluorocarbon polymers as a binder, however, the capacitance decreased by 36.5%. The reliability of the capacitors was, thus, improved by using polarizable electrodes without using binders.

The discharge curves of the capacitors with AC tablets (b) at different temperatures under a current of 100 μA are shown in Fig. 8. The capacitance of the capacitors was 9.5 F/(cm^3 of AC tablets) at 25 °C.

Capacitors with AC tablets are suitable for memory back-up devices under a small discharge current.

Conclusion

1) AC tablets without using binders were prepared from the activation or carbonization of molded mixtures comprising AC powders and phenolic resin. The specific surface area of tablets (a) prepared from activation was 2010 $m^2 g^{-1}$ with a density of 0.45 $g cm^{-3}$. The area of tablets (a) was more than 2-times larger than that of conventional activated carbons. The area of tablets (b) prepared from carbonization was 1400 $m^2 g^{-1}$ with a yield of 83%. Both types of AC tablets were suitable materials for the polarizable electrodes of capacitors.

2) In accordance with the results regarding the bulk density and the specific surface area of the tablets, the capacitance of capacitors with AC tablets was 1.4—2.3 times larger than that of capacitors with the previously reported activated-carbon fiber cloth. The reliability of capacitors with AC tablets was improved in comparison with that of capacitors with polarizable electrodes containing binders.

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