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Porous and Electrically Conducting Clay-Carbon Composite as Electrode of Electric Double-Layer Capacitor

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Porous and electrically conducting clay-carbon composite, which is produced by sintering of mixtures of clay and porous carbon, shows large electrostatic capacitance (ca. 10 F cm^{-3}). By using the composites, electric double-layer capacitors with capacitance of 2.3-3.4 F/(cm^3 of the capacitor) have been prepared.

Preparation and utilization of various porous electrode materials have been reported.[1-3] We now report use of a new porous and electrically conducting clay-carbon composite, which is prepared by sintering mixtures of clay and porous carbon, as an excellent electrode of electric double-layer capacitor. Although clay-modified electrodes have been recently reported to show interesting electrochemical properties,[4,5] use of clay based materials as electrode of capacitor has no precedent.

The clay-carbon composite was prepared by sintering mixtures of clay (Kibushi (Sanage) clay mainly composed of kaolinite) and porous carbon powder (Ketjen black EC-DJ600 having surface area of 1200 m^2 g^{-1}). When a 85:15 mixture of the clay and porous carbon was sintered at 800 °C for 1 h, the composite showed high mechanical strength with compressive strength of 200 kg cm^{-2}, good electrical conductivity (1 S cm^{-1}), large surface area of 210 m^2 g^{-1} or 177 m^2 cm^{-3} (measured by BET method), bulk density of 0.84 g cm^{-3}, and high porosity of 61%. Increase in carbon content gave a composite with higher surface area and higher porosity (e.g., 240 m^2 g^{-1} or 168 m^2 cm^{-3} and 67% porosity at 20 wt% of carbon), but it showd lower mechanical strength (compressive strength = 100 kg cm^{-2}) and the composite with 15 wt% of carbon seemed to be best suitable for preparation of the electric double-layer capacitors. The surface area per weight of the composite is lower than those of activated carbon fiber (700-2500 m^2 g^{-1}) used in reported and commercialized electric double-layer capacitors.[6-8] However, the surface area per volume of the composite is larger or comparable to those of the activated carbon fibers, since the activated carbon fibers have considerably low bulk density (0.1-0.05 g cm^{-3}).[8,9] Consequently the electric double-layer capacitor using the clay-carbon composite showed higher or comparable charging and discharging capacity per volume to those of the commercialized electric double-layer capacitor.

The electric double-layer capacitance of the clay-carbon composite in electrolytic solutions was measured by cyclic voltammetry. A small piece (0.012-0.015 cm^3) of the composite (working electrode) and a platinum plate (2 cm x 2 cm, counter electrode) were dipped in an electrolytic solution, and working electrode potential was swept against a reference electrode (SCE).

Figure 1 shows current-potential (I-E) curves at various potential sweep rates. Sweep in a range from 0 to +1.2 V gave similar I-E curves. As shown in Fig.1, the I-E curve was almost flat in some sweep range, and the Δi value obtained at the flat region (Fig. 1) is related to the sweep rate, dE/dt, by the following equation,

$$\Delta i = 2C(dE/dt) \quad (1)$$

where C represents the electric double-layer capacitance. The Δi value was proportional to the sweep rate, indicating that the composite served as a stable electric double-layer capacitor. The capacitance of the composite was estimated from the slope of a linear line obtained by plotting 1/2 Δi against dE/dt and the value is summarized in Table 1.

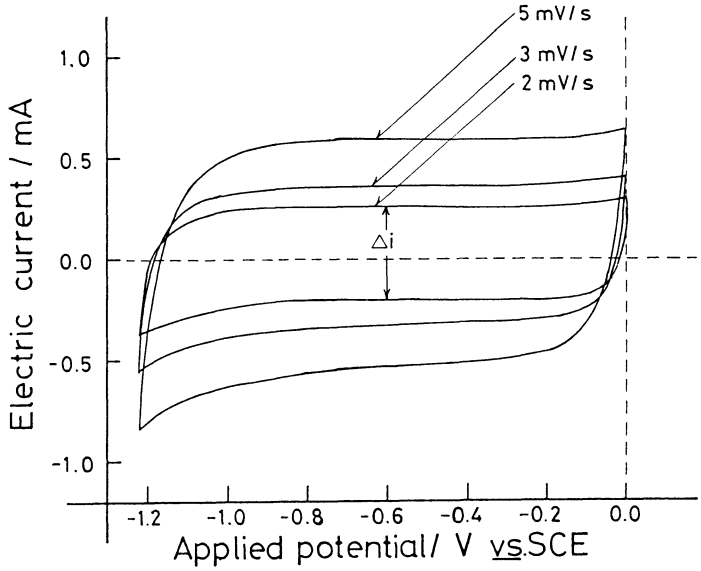

Fig. 1. Cyclic voltammograms in γ-butyrolactone solution of $LiClO_4$ (1 M) at 5 °C. Volume of the composite = 0.012 cm^3. The sweep rate is shown in the figure.

Table 1. Electrostatic capacitance of the clay-carbon composite

No.	Solvent[a)]	Electrolyte	Concentration mol dm^{-3}	Capacitance divided by volume of the electrode F cm^{-3}
1	H_2O	KCl	2.5	9.8
2	H_2O	NaCl	2.5	9.8
3	γ-BL	$NaClO_4$	1.0	13.1
4	γ-BL	$LiClO_4$	1.0	11.0
5	DMF	$NaClO_4$	1.0	9.1
6	DMF	$LiClO_4$	1.0	9.0

a) γ-BL and DMF represent γ-butyrolactone and N,N-dimethylformamide, respectively.

As shown in Table 1, the clay-carbon composite showed large electric capacitance. The capacitance per the surface area of the composite was about 6 μF cm^{-2}, the value being reasonable for the electric double layer capacitor[6,7)] and indicating that most of the surface area of the composite participated to form the electric double layer. A nylon-6-carbon (Ketjen black-EC, 20 wt%) composite (commerciallized from Spacy Chemical Co. Ltd.) is also porous and showed large electrostatic capacitance in electrolytic solutions, but its value is about half of the value obtained for the clay-carbon composite.

Figure 2 shows a sketch of the electric double-layer capacitor using the clay-carbon composite. The clay-carbon composites and separator were impregnated with the electrolytic solution, and charging and discharging was carried out at a constant electric current. Figure 3 shows the charging and dicharging curves of thr capacitor at 20th and 21st charging and discharging cycles. In Fig. 3, the capacitor was charged to 2.0 V and discharged to 0.2 V. The capacitor was rechargeable more than 100 times without any observable change of the charging and discharging curves. The data shown in Fig. 3 gives capacity of 0.52 mA h/(0.38 cm^3 of the capacitor inner volume) corresponding to 1.4 mA h/(cm^3 of the capacitor). The discharging voltage dropped linearly with time in a certain voltage range (e.g., 1.7-0.2 V in Fig. 3), and from this linear part, electrostatic capacitance of the cell was estimated. Table 2 summarizes the discharging capacity and the electrostatic capacitance of the capacitor.

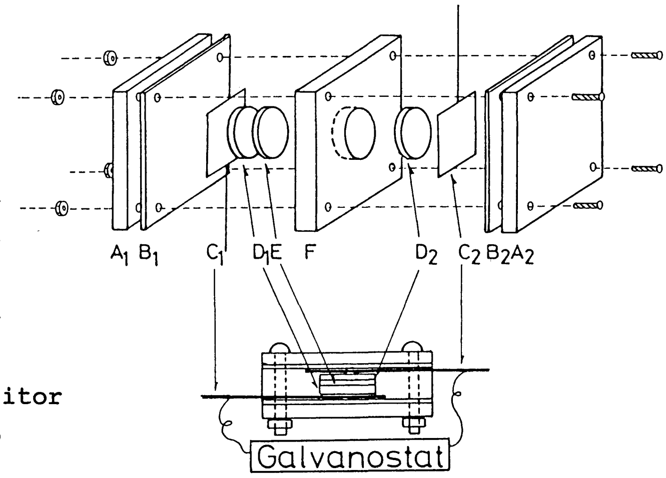

Fig. 2. Sketch of the capacitor. A: end board made of glass-epxy resin, B: silicone rubber board, C: platinum plate (collector), D: clay-carbon composite (ϕ = 10 mm, thickness = 2.5 mm), E: separator (filter paper), F: spacer.

As shwon in Table 2, the capacitor has large discharging capacity and electrostatic capacitance, the value of the electrostatic capacitance being even larger than that of the commerciallized electric double-layer capacitor using the active carbon fiber.[6,7] The electrostatic capacitance assigned to the each

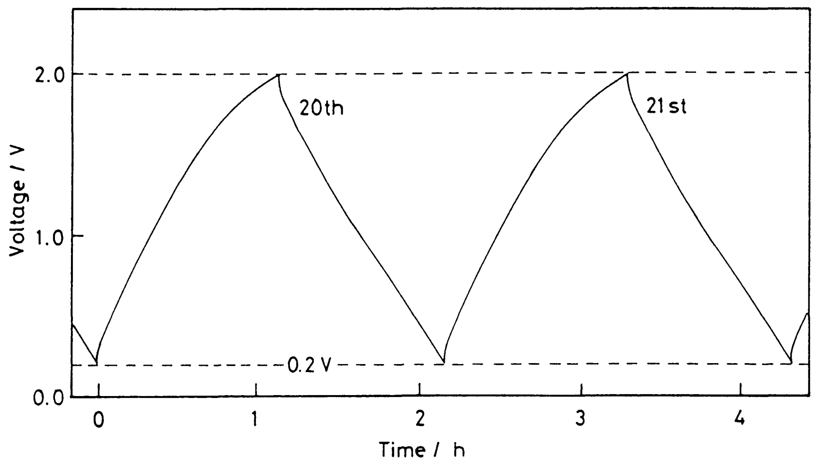

Fig. 3. Charging and discharging profile of the capacitor at 25 °C in a γ-butyrolactone solution of $LiClO_4$ (1 M). Electric current = 0.50 mA

Table 2. Discharging capacity and electrostatic capacitance of the capacitor[a)]

No.	Electrolytic[b)] solution	Discharging capacity mA h	Capacitance per cell volume[c)] F cm^{-3}	Capacitance Assingned to each composite[d)] F cm^{-3}
1	$NaClO_4$ (1 M) in γ-BL	0.51	3.0	11.6
2	$LiClO_4$ (1 M) in γ-BL	0.52	3.1	12.9
3	$LiBF_4$ (1 M) in γ-BL	0.56	3.4	13.1
4	$NaClO_4$ (1 M) in DMF	0.23	2.4	9.1
5	$LiClO_4$ (1 M) in DMF	0.20	2.3	9.0
6	KCl (2.5 M) in H_2O	0.44	2.8	11.0

a) The capacitor was charged to 2.0 V (Nos. 1-3) or 1.2 V (Nos. 4-6) and discharged to 0.2 V.
b) As in Table 1. c) Per 0.38 cm^3 of the inner volume of the capacitor (Fig. 2).
d) The capacitor shown in Fig. 2 is regarded to be composed of two capacitors arranged in series (each composite, D_1 or D_2, corresponds to the each capacitor), and this value was estimated by assuming that the two capacitors (D_1 and D_2) had the same capacitance.

clay-carbon composite capacitor (see last column in Table 2) of the two capacitors, D_1 and D_2, in Fig. 2 is about 11 F cm^{-3}, the value roughly agrees with those shown in Table 1 which were obtained with much smaller specimen. This indicates that ions can move smoothly in the porous clay-carbon composite. Due to the high mechanical strength of the clay-carbon composite, handling of the composite is easy; consequently the present capacitor seems to have advantages from a viewpoint of practical use.

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