

ELECTRIC DOUBLE-LAYER CAPACITORS USING POROUS AND ELECTRICALLY CONDUCTING CLAY-CARBON COMPOSITES AS ELECTRODES

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(Received January 8, 1990)

Summary

Porous and electrically conducting clay-carbon composites, which are prepared by firing mixtures of clay minerals and porous carbon powder, show large electrostatic capacitance ($10 - 14 \text{ F cm}^{-3}$; the value assigned to the surface area of the composite is about $6 - 7 \mu\text{F cm}^{-2}$) in aqueous and organic solutions. The composites have been used as polarizable electrodes of double-layer capacitors and characterization of the capacitors has been carried out. A capacitor using the composites as both the positive and negative electrodes gives a capacitance of 3.4 F (per cm^3 of capacitor) at about 20 wt.% of carbon content in the composite. Electrolytic salts and solvents influence the internal electrical resistance of the cell, but scarcely affect the capacitance at room temperature. These results indicate that ions can move smoothly into micropores of the clay-carbon composites due to the wettability of the clay minerals to both the aqueous and the organic solutions employed in the present work.

Introduction

With increasing demands for miniaturization of electric equipment and the use of semiconductor memories in association with microcomputers, several types of small energy storage systems, such as secondary lithium batteries and rechargeable polymer batteries, have been developed. Carbon black, with a large specific surface area, has been used for the positive electrodes of secondary lithium batteries that give long-term charging and discharging times [1].

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On the other hand, a new type of capacitor with a large capacitance has been developed recently by Nishino *et al.* [2]. This capacitor has been commercialized as a maintenance-free power source. The large capacitance is assigned to an electric double-layer formed at the interface of the activated carbon fibre electrode with the liquid electrolyte [2 - 4]. In this capacitor, a Faradaic reaction does not contribute to the charging and discharging cycles.

We have previously reported the preparation of porous, mechanically strong, electrically conducting, clay-carbon composites. These are useful as electrodes for Zn/I₂, Zn/O₂ and lithium secondary cells [5 - 7]. The composites exhibit a large surface area of 240 m² g⁻¹ (or 168 m² cm⁻³) but the value per unit weight is lower than that of the activated carbon fibres (700 - 1500 m² g⁻¹) used in industrialized electric double-layer capacitors [2 - 4]. The surface area per unit volume of the composite is, however, larger, or comparable to that of the activated carbon fibres, since the latter have a considerably lower bulk density (0.1 - 0.05 g cm⁻³) [4, 8]. Moreover, the clay-carbon composite has a higher mechanical strength, and appears to be a suitable material for constructing electrodes for a double-layer capacitor.

We now report properties of electric double-layer capacitors using the clay-carbon composites as polarizable electrodes for the capacitor. The present capacitor shows large electrostatic capacitance per volume over a wide temperature range. Some of results in this paper have been communicated previously [9].

Experimental

The clay-carbon composites, with carbon contents of 5 - 20 wt.%, were prepared by firing mixtures of clay mineral (Kibushi clay) powder and a porous carbon black (Ketjen black ECDJ-600) as reported previously [5]. The bulk density of the composite was calculated from its weight and size. The specific surface area was measured by the BET method [10].

Cyclic voltammetry was carried out using a beaker-type cell with a small piece (0.012 - 0.015 cm³) of the composite serving as the working electrode, a platinum plate (2 × 2 cm) as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode. All potentials are reported with respect to the SCE. A Hokuto-Denko HB-301 potentiostat/galvanostat and a Hokuto-Denko HB-104 function generator were used to obtain the cyclic voltammograms.

Figure 1 shows a diagram of the electric double-layer capacitor. The capacitor comprised a pair of clay-carbon composite (10 mm diam. and 2.3 mm thickness) polarizable electrodes, platinum-plate collectors, and a separator (glass fibre mat). The clay-carbon composites and the separator were impregnated with an electrolytic solution. All the solvents (water, γ -butyrolactone, *N,N*-dimethylformamide, sulfolane, methyl formate and chlorobenzene) were distilled, and the electrolytic salts were dried under

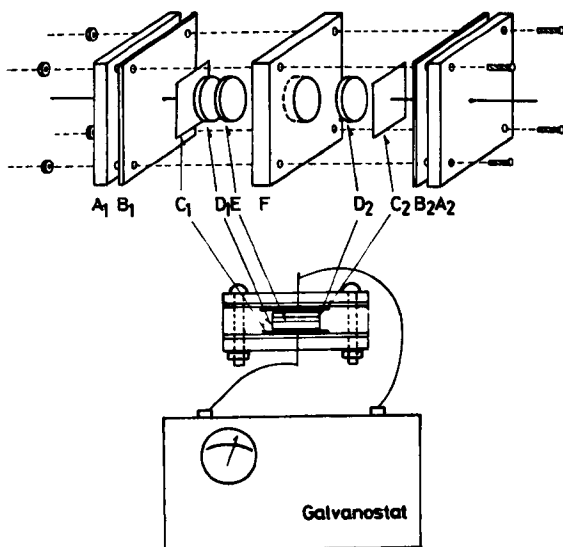


Fig. 1. Diagram of electric double-layer capacitor: A, end board made of glass-epoxy resin; B, silicone rubber board; C, platinum plate (collector); D, clay-carbon composite-polarizable electrode, dia. = 10 mm, thickness = 2.3 mm; E, glass fibre mat separator.

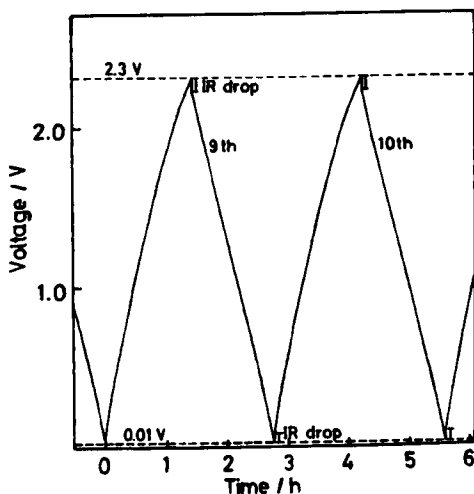


Fig. 2. Charge/discharge profile of electric double-layer capacitor at 25 °C in a γ -butyrolactone solution of Bu_4NClO_4 (1.5 M).

vacuum. The electrical conductivity of the electrolytic solution was measured using a Toa-Denpa CM-5B electrical conductivity meter.

Figure 2 shows a typical charge/discharge profile of the capacitor at a constant electric current of 0.5 mA. The capacitor was charged to 1.2 V for aqueous solution and *N,N*-dimethylformamide solution, and to 2.3 V for the other organic solutions; it was discharged to 0.01 V in all cases. The

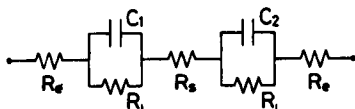


Fig. 3. Equivalent circuit for capacitor. C_1 , C_2 : electric double layer capacitance; R_e : resistance of electrode; R_s : resistance of electrolyte and separator; R_1 : insulating resistance.

discharge capacity of the cell was calculated from the electric current and the discharge time. As shown in Fig. 2, the discharging voltage dropped linearly with time over a given voltage range (e.g., 0.6–1.8 V, Fig. 2). The electrostatic capacitance of the cell was estimated from this linear relationship. In order to estimate the electrostatic capacitance assigned to each composite electrode, an equivalent circuit (as shown in Fig. 3) was devised. In this calculation, the two capacitors are assumed to have the same capacitance (i.e., $C_1 = C_2$). The internal electrical resistance of the cell, corresponding to total resistance of the equivalent circuit (R_e , R_s and R_1 , Fig. 3), was calculated from the IR drop of the charge/discharge profile, see Fig. 2.

Results and discussion

Cyclic voltammetry and determination of electrostatic capacitance

The electrostatic capacitance of the clay-carbon composite electrode was determined by two methods, i.e., from the charge/discharge data of the capacitor (e.g., Fig. 2) and from the cyclic voltammograms of the clay-carbon electrode.

Figure 4 shows typical cyclic voltammograms of the clay-carbon electrode dipped in a γ -butyrolactone solution of LiClO_4 at various potential sweep rates. Potential scans over the range from 0.5 to -0.7 V gave similar flat I - E curves. No oxidation-reduction peaks were observed and the cyclic voltammogram was approximately symmetrical. A Δi value obtained at the flat region (Fig. 4) is related to the sweep rate, dE/dt , according to:

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

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 evaluated from the slope of the linear plot between $(1/2)\Delta i$ and dE/dt . The C values of the capacitance in different types of electrolytic solution are listed in Table 1.

As shown in Table 1, the clay-carbon composites showed large electrostatic capacitances. A porous and electrically conductive nylon-6-carbon composite (commercialized from Spacy Chemical Co., Ltd.) also showed a large electrostatic capacitance in electrolytic solution, but its value is less

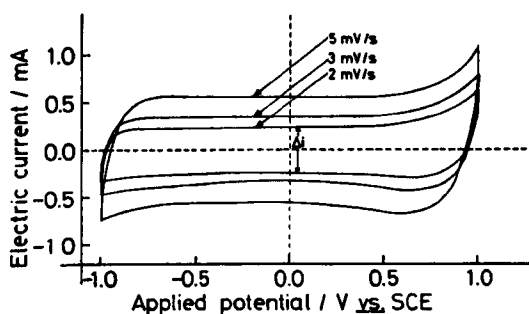


Fig. 4. Cyclic voltammograms in γ -butyrolactone solution of LiClO_4 (1.5 M) at 25 °C. Working electrode: clay-carbon (15 wt.%) composite (volume = 0.012 cm³); counter electrode: platinum plate. Sweep rates as shown.

TABLE 1

Electrostatic capacitance of a clay-carbon composite^a

No.	Solvent ^b	Electrolytic salt	Concentration (mol dm ⁻³)	Electrostatic capacitance per unit volume of electrode (F cm ⁻³)
1	H ₂ O	KCl	2.5	9.8
2	H ₂ O	NaCl	2.5	9.8
3	γ -BL	NaClO ₄	1.5	12.6
4	γ -BL	LiClO ₄	1.5	11.0
5	γ -BL	Bu ₄ NClO ₄	1.5	11.8
6	S/CB(50/50)	Bu ₄ NClO ₄	1.5	9.9
7	DMF	NaClO ₄	1.0	9.1
8	DMF	LiClO ₄	1.0	9.0
9 ^c	H ₂ O	KCl	2.5	3.1

^aObtained by cyclic voltammetry; clay-carbon composite contained 15 wt.% of carbon black (Nos. 1 - 8).

^b γ -BL, DMF and S/CB(50/50) represent γ -butyrolactone, *N,N*-dimethylformamide and 1:1 mixture of sulfolane and chlorobenzene, respectively.

^cData for a nylon-6-carbon (Ketjen black EC, 20 wt.%) composite (see text).

than half the values obtained for the clay-carbon composites. The electrostatic capacitance of the clay-carbon composite is slightly influenced by the type of electrolyte, indicating that all the electrolytic solutions can penetrate the pores of the clay-carbon composite to form the electric double-layer efficiently.

Properties of electric double-layer capacitor

Effect of composite composition

Charging and discharging tests of the double-layer capacitors using the composites as the positive and negative electrodes were carried out. Typical

charge/discharge curves are shown in Fig. 2. All the capacitors gave good rechargeability, *i.e.*, more than 100 times with 90 - 100% current efficiency and without any observable change in the charge/discharge curves.

The electrostatic capacitance of the capacitor was determined from the charge/discharge curve (*e.g.*, Fig. 2). Figure 5 shows the dependence of the electrostatic capacitance on the carbon content of the composite (over the range 3 - 20 wt.%). A 2.5 M KCl aqueous solution was selected as the electrolytic solution. As seen from the data in Fig. 5, the electrostatic capacitance at first increases steeply with increase in the carbon content (*i.e.*, from about 5 wt.%) and then increases linearly at contents above 10 wt.%. The electrostatic capacitance reaches a value of 3.4 F (per cm^3 of the capacitor cell) at about 20 wt.% of carbon. This value corresponds to 14 F (per cm^3 of the clay-carbon composite), which is calculated from the equivalent circuit ($C_1 = C_2$ in Fig. 3). The electrostatic capacitance per surface area of the composite was estimated as 6 - 7 $\mu\text{F cm}^{-2}$ over the range of 10 - 20 wt.% carbon content. The value was larger than those obtained for the activated carbon fibres used in industrialized electric double-layer capacitors [2 - 4]. This appears to result from the hydrophilic nature of the clay-carbon composite, and most of the surface of the composite seems to be able to participate in the formation of the electric double-layer.

Figure 6 shows the relationship between the internal electrical resistance of the cell and the carbon content of the clay-carbon composite electrode. It can be seen that the resistance decreases with increasing carbon content, and becomes almost constant (10 Ω) above about 10 wt.% carbon.

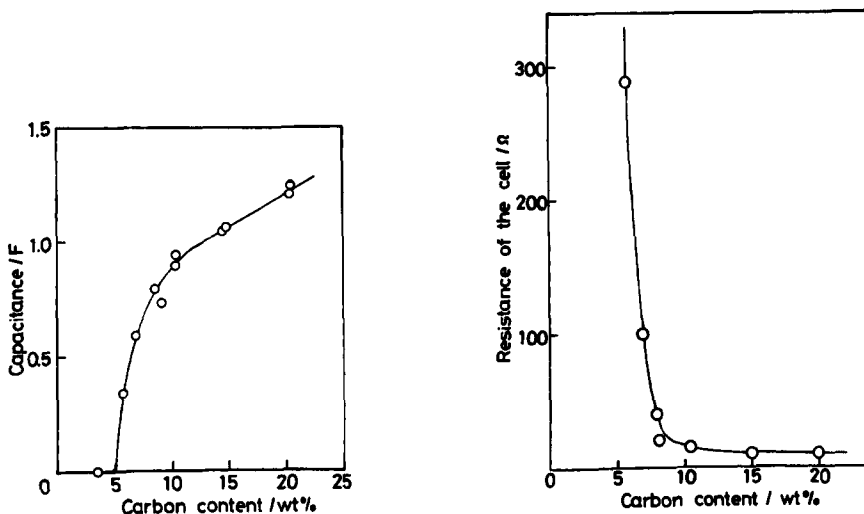


Fig. 5. Dependence of electrostatic capacitance of carbon content of composite electrode. Electrolytic solution: 2.5 M KCl aqueous solution. Inner volume of capacitor: 0.38 cm^3 .

Fig. 6. Internal electrical resistance of cell as a function of carbon content of composite electrode. Electrolytic solution: 2.5 M KCl aqueous solution.

This result corresponded to the electrical conductivity of the composites [5]; the latter was $1.8 \times 10^{-2} \text{ S cm}^{-1}$ and 2 S cm^{-1} for carbon contents of 5 wt.% and 20 wt.%, respectively, whereas 2.5 M KCl aqueous solution gave a moderate conductivity ($\sim 0.25 \text{ S cm}^{-1}$). These findings indicate that the resistance of the cell at high carbon contents is mainly affected by the resistance of the electrolyte and separator (R_s in Fig. 3) rather than by the resistance of the electrode (R_e in Fig. 3).

As shown in Figs. 5 and 6, high carbon contents impart better charge/discharge characteristics to the capacitor. Increase in the carbon content to values above 20 wt.%, however, causes a decrease in the mechanical strength of the composite [5]. From these features, a composite with about 15 - 20 wt.% carbon seems to be most suitable for use in electric double-layer capacitors.

Effect of electrolytic solution

The charging and discharging tests were carried out by using various electrolytic solutions. Table 2 summarizes the electrical conductivity values of the electrolytic solutions and the characteristics of the capacitor in the various electrolytic solutions. As shown in Table 2, the internal electrical resistance of the cell corresponds well with the electrical conductivity of the electrolytic solution. The KCl aqueous solution has the highest conductivity of the solutions used and gives the lowest electrical resistance for the cell. On the other hand, the organic electrolytes exhibit higher electrical resistances. The organic solvents listed in Table 2 (nos. 4 - 9), however, showed high resistivities against electrochemical oxidation/reduction. In contrast to the relatively low charging voltage (up to 1.2 V) of the capacitor in aqueous medium, use of the organic electrolytic solution gave good rechargeability up to 2.3 V. The capacitor employing the organic electrolyte was also rechargeable for more than 100 times.

It should also be noted that the electrostatic capacitance of the capacitors listed in Table 2 remains almost constant with variation of the electrolytic solution. This reveals that properties of the electrolytic solution, such as the viscosity of the solvent and the ionic radius of the electrolytic salt, influence only slightly the final formation of the electric double-layer. The same conclusion was obtained from cyclic voltammetric studies (see above).

The value of the capacitance estimated from the charge/discharge profile (Fig. 2) agreed approximately with that estimated from the cyclic voltammogram (Fig. 4), although the latter value was obtained with a much smaller specimen (about 1/15) than that used for the electrode in the capacitor. This result indicates that the electrolytic solution thoroughly penetrates the micropores of the clay-carbon composite and that the ions can move smoothly in the porous electrode. These properties of the electrode might result from a suitable combination of the inherent hydrophilic and lyophilic properties in the clay-carbon composites; it appears that each type of elec-

TABLE 2
 Characteristics of capacitor^a and electrical conductivity of electrolytic solution

No.	Electrolytic ^b solution	Electrical conductivity (mS cm ⁻¹)	Discharging capacity (mA h)	Internal electrical resistance (Ω)	Capacitance ^c per unit cell volume (F cm ⁻³)	Capacitance ^d assigned to each composite (F cm ⁻³)
1	KCl (2.5 M) in H ₂ O	250	0.34	10	2.8	11.6
2	NaClO ₄ (1 M) in DMF	19.0	0.27	95	2.4	9.7
3	LiClO ₄ (1 M) in DMF	20.0	0.24	88	2.2	9.0
4	LiClO ₄ (1.5 M) in γ -BL	12.2	0.66	110	3.0	12.2
5	Bu ₄ NClO ₄ (1.5 M) in γ -BL	7.6	0.65	116	2.9	12.0
6	Bu ₄ NPF ₆ (1.5 M) in γ -BL	8.2	0.57	122	2.8	11.4
7	Bu ₄ NSO ₃ C ₆ H ₄ CH ₃ (1.5 M) in γ -BL	3.3	0.75	200	3.1	12.6
8	Bu ₄ NClO ₄ (1.5 M) in S/MF (50/50)	6.9	0.62	184	3.2	13.2
9	Bu ₄ NClO ₄ (1.5 M) in S/CB (50/50)	2.8	0.55	292	2.7	11.4

^aCapacitor was charged to 1.2 V (Nos. 1 - 3) or 2.3 V (Nos. 4 - 9) and discharged to 0.01 V at 0.5 mA constant electric current (at 25 °C); polarizable electrode: clay-carbon (15 wt.%) composite.

^bAs in Table 1, and S/MF(50/50) represents 1:1 mixture of sulfolane and methyl formate.

^cObtained with a capacitor having an inner volume of 0.38 cm³ (Fig. 1).

^dCalculated from equivalent circuit (Fig. 2).

trolytic solution is able to come into intimate contact with most of the surface of the carbon black.

Temperature effect

Figure 7 shows the dependence of the electrostatic capacitance on temperature. For a 2.5 M KCl aqueous electrolyte, the variation of electrostatic capacitance on temperature is almost negligible ($< 3\%$) in the range 5 - 75 °C. With an organic electrolytic solution, data were obtained over a wider range of temperature (*viz.*, -25 to 75 °C). Since the viscosity and electrical resistivity of the organic electrolyte become higher at low temperatures, lowering the temperature might suppress the formation of the electric double-layer in the micropores of the clay-carbon composite. The effect of temperature was, however, found to be small. Among the organic electrolytes tested, γ -butyrolactone solution containing tetrabutylammonium perchlorate (Bu_4NClO_4) displayed the smallest variation in electrical resistivity with temperature ($\sim 20\%$ over the wide temperature range of -25 to 75 °C).

From these results, the clay-carbon composite with 15 - 20 wt.% carbon and KCl aqueous solution and/or γ -butyrolactone solution of Bu_4NClO_4 is considered to be most suitable for the preparation of electric double-layer capacitors. Since the porous and electrically conducting clay-carbon composite is easily prepared, has large specific surface area with both hydrophilic and lyophilic properties, and has a good handleability due to its high mechanical strength, the present capacitor promises advantages from a practical standpoint.

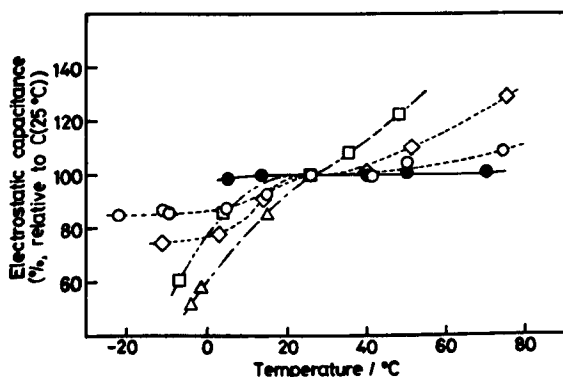


Fig. 7. Dependence of electrostatic capacitance of capacitor on temperature. (●) KCl (2.5 M) aqueous solution; (○) γ -butyrolactone solution of Bu_4NClO_4 (1.5 M); (◇) γ -butyrolactone solution of $\text{Bu}_4\text{NSO}_3\text{C}_6\text{H}_4\text{CH}_3$ (1.5 M); (△) sulfolane/methyl formate (50/50) solution of Bu_4NClO_4 (1.5 M); (□) sulfolane/chlorobenzene (50/50) solution of Bu_4NClO_4 .

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