

Short Communication

New solid-state electric double-layer capacitor using poly(vinyl alcohol)-based polymer solid electrolyte

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(Received March 1, 1991; in revised form April 9, 1991)

Abstract

Poly vinyl alcohol (PVA) dissolves large amounts of lithium salts (up to about 1.5 g/g of PVA) such as LiCF_3SO_3 , LiClO_4 and LiBF_4 in its polymer matrix. The composites obtained show good ionic conductivity. When the PVA–lithium salt composites are used as the solid electrolyte in solid-state electric double-layer capacitors with porous and electrically conducting clay–carbon composites as polarizable electrodes, the solid-state electric double-layer capacitors show good charge/discharge behavior with large capacitance of 2.5–3.5 F/cm³ of the capacitor).

Introduction

With increasing demand for miniaturization of electric equipment, new electric double-layer type capacitors with large capacitance have been developed [1–3].

It has been previously reported that firing of clay–carbon composites affords porous and mechanically strong composite materials with good electrical conductivity (2 S cm^{-1}) and large surface area ($180 \text{ m}^2 \text{ cm}^{-3}$ of the composite materials) [4]. Due to these properties, the clay–carbon composites showed large electrostatic capacitance (*c.* 14 F cm^{-3}) in electrolytic solutions and were suitable to be used as the polarizable electrodes of electric double-layer capacitors employing conventional aqueous and organic electrolytic solutions [5].

On the other hand, recently, polymeric solid electrolytes have also attracted strong interest, because of their great potentiality in applications to devices such as solid-state batteries, fuel cells and novel chemical sensors [6]. However, use of polymer solid electrolytes as the electrolyte in electric double-layer capacitors has been limited, probably owing to the relatively low solubility of the electrolytic salt in the polymer matrix (e.g. 0.05–0.42

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g/g of polymer) [6–10]. Polymer solid electrolytes usually show crystallized domains of the electrolytic salt at high concentrations of the electrolytic salt [11], whereas charging of the double-layer capacitor requires the presence of a large amount of ions around the polarizable electrode.

We recently reported that poly vinyl alcohol (PVA) formed transparent and homogeneous composites with lithium salts (LiCF_3SO_3 , LiClO_4 and LiBF_4) up to a very high concentration (1.0–1.5 g/g of PVA), and the composites showed good ionic conductivity of $2 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature and about $1 \times 10^{-3} \text{ S cm}^{-1}$ at 50 °C [12]. Moreover, the PVA–lithium salt composite thin film has high mechanical strength, and seems to be suitable as the solid electrolyte of an electric double-layer capacitor. Actually the capacitor prepared using the PVA–lithium salt solid electrolyte shows large electrostatic capacitance and good rechargeability.

We now report preparation of a new solid-state electric double-layer capacitor consisting of the PVA–lithium salt composite as electrolyte and clay–carbon composites as polarizable electrodes.

Experimental

The clay–carbon composite electrodes with carbon content of 15 wt.% were prepared by firing an 85:15 mixture of clay minerals (Kibushi clay) powder and a porous carbon black (Ketjen black ECDJ-600) in the same way as reported previously [4].

The clay–carbon composite electrode ($\phi = 10 \text{ mm}$, thickness = 1.7 mm) was impregnated with a dimethyl sulfoxide (DMSO) solution containing PVA (average molecular weight = 25 000, 88% hydrolyzed, 1 g/30 ml of DMSO) and LiCF_3SO_3 (1.5 g/30 ml of DMSO) under reduced pressure. This electrode was placed on a glass plate, and most of the DMSO was removed by evaporation under vacuum at room temperature for 12 h. Repetition of the impregnation–evaporation process three times produced an electrode containing a sufficient amount of the PVA– LiCF_3SO_3 composite.

The electrode thus obtained has excess PVA– LiCF_3SO_3 composite on its surface, and consequently, joining a pair of the electrodes to each other was possible through the excess PVA– LiCF_3SO_3 . After joining the pair of the electrodes, the solid-state capacitor thus prepared was treated at 70 °C under vacuum for 20 h to remove DMSO. The thickness of the PVA– LiCF_3SO_3 polymer electrode film between the pair of electrodes was *c.* 250 μm . By using LiClO_4 and LiBF_4 as the electrolytic salt, similar capacitors were obtained. In charge/discharge tests, we used a cell similar to that reported in our previous paper [5]. The construction of the capacitors and measurement were carried out under argon or dry N_2 atmosphere. The charge/discharge test was carried out at a constant electric current by using a Hokuto-Denko HJ-201B auto-control galvanostat. For comparison, a similar capacitor using a γ -butyrolactone solution of LiClO_4 (1.0 M) was also constructed. When the γ -butyrolactone solution of LiClO_4 (1.0 M) was used as electrolytic

solution, both the clay-carbon composite electrodes and separator (glass fiber mat) were impregnated with the electrolytic solution [5].

Results and discussion

Since the PVA-lithium salt solid electrolyte shows relatively high electric resistance below room temperature compared with conventional aqueous and organic electrolytic solutions, the capacitor using the PVA-lithium salt and the clay-carbon composite electrode is best suited for use at (i) relatively low electric current ($<c. 10 \mu\text{A}$) below room temperature; or (ii) somewhat larger electric current (e.g. $50 \mu\text{A}$) at higher temperature, to minimize the IR drop due to the large internal resistance.

Figure 1(a) shows the repeated charge/discharge profile of the capacitor at $50 \mu\text{A}$ (current density = $64 \mu\text{A cm}^{-2}$) at 50°C . The capacitor was charged to 1.0 V and discharged to 0.01 V; the charging limit voltage was set to avoid decomposition of the electrolyte. Comparison of the charge/discharge profile with that of a capacitor using the clay-carbon composite electrode and a 1 M γ -butyrolactone solution of LiClO_4 (Fig. 1(b)) reveals that the clay-carbon composite electrode essentially serves as a good electrode not only for the conventional electrolytic solution but also for the polymer solid electrolyte, although the capacitor using the conventional electrolytic solution can be charged and discharged up to higher voltage limit (2.0 V) at larger electric current ($500 \mu\text{A}$) at lower temperature (25°C).

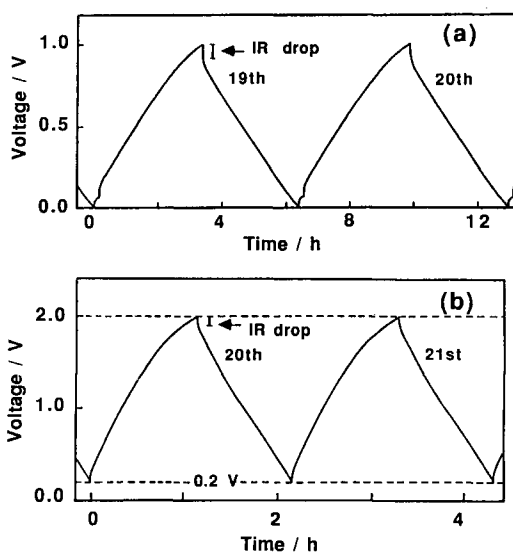


Fig. 1. Charge/discharge profile of electric double-layer capacitor: (a) electrolyte = PVA- LiCF_3SO_3 (1.5 g of LiCF_3SO_3 /1 g of PVA) polymer solid electrolyte at 50°C , electric current = $50 \mu\text{A}$; (b) electrolyte = γ -butyrolactone solution of LiClO_4 (1.0 M) at 25°C , electric current = 0.5 mA.

The capacitance ($2.3\text{--}2.7\text{ F cm}^{-3}$) of the capacitor using the polymer solid electrolyte calculated from the linear part of the charge/discharge curves ($0.7\text{--}0.2\text{ V}$ in Fig. 1(a)) is comparable to that ($2.2\text{--}3.2\text{ F cm}^{-3}$ [5]) of the capacitor using the conventional electrolytic solution. The capacitance of the capacitor using the polymer solid electrolyte remained virtually constant over a current density range of $25\text{--}100\text{ }\mu\text{A}$ ($30\text{--}130\text{ }\mu\text{A cm}^{-2}$) at $50\text{ }^\circ\text{C}$. Both types of capacitor were cycled more than 50 cycles without any observable change of the charge/discharge curves. These results indicate that the PVA-LiCF₃SO₃ composite serves as an excellent solid electrolyte for the electric double-layer capacitor.

Characteristics of solid-state electric double-layer capacitors using various PVA-lithium salts are summarized in Table 1. All the capacitors summarized in Table 1 gave good rechargeability for, at least, 50 cycles with 90–100% current efficiency and without any observable change in the charge/discharge curves. It is seen that the capacitors listed in Table 1 show almost the same electrostatic capacitance in spite of the change of the electrolytic salt. This indicates that the electrostatic capacitance is essentially determined by the surface area of the clay-carbon composite electrode. The high solubility of the lithium salts in PVA is considered to be a crucial factor for affording the excellent characteristic of the capacitor. The fact that both the negative and positive electrodes can be polarized in charging indicates that not only Li⁺ ion but also anions (CF₃SO₃⁻, ClO₄⁻ and BF₄⁻) can move to the respective electrodes to polarize the electrodes efficiently.

Figure 2 shows a dependence of the electrostatic capacitance on temperature. The data at 50 and 70 °C were taken at 50 μA charge/discharge current, whereas the data at 17 and 27 °C were obtained at 20 μA. The electrostatic capacitance increases somewhat with temperature. However, over a temperature range 15–70 °C, the change of electrostatic capacitance is less than 20%. Similar results were obtained for the capacitors using

TABLE 1

Characteristics of the solid-state electric double-layer capacitor^a

No.	Polymer solid electrolyte (wt. wt.)	Discharge capacity (mA h)	Internal electrical resistance (Ω)	Capacitance per unit cell volume (F cm ⁻³)	Current efficiency (%)
1	PVA-LiCF ₃ SO ₃ (1:1.5)	0.16	500	2.7	90
2	PVA-LiClO ₄ (1:1)	0.16	1100	2.7	92
3	PVA-LiBF ₄ (1:1)	0.10	4700	2.3	90

^aCapacitance was charged to 1.0 V and discharged to 0.01 V at 50 μA constant electric current (at 50 °C) obtained with a capacitor with an inner volume of 0.26 cm³.

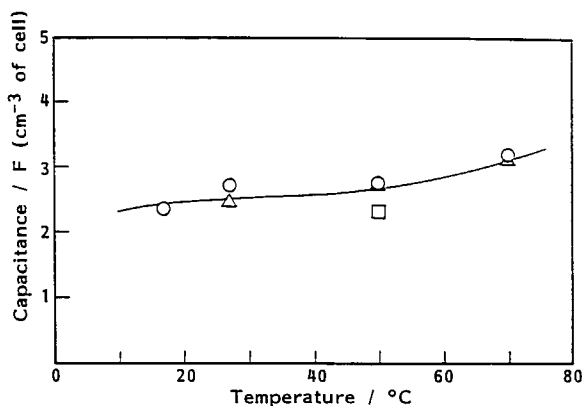


Fig. 2. Dependence of electrostatic capacitance on temperature: ○, PVA-LiCF₃SO₃ (1:1.5 wt./wt.); △, PVA-LiClO₄ (1:1 wt./wt.); □, PVA-LiBF₄ (1:1 wt./wt.) polymer electrolyte.

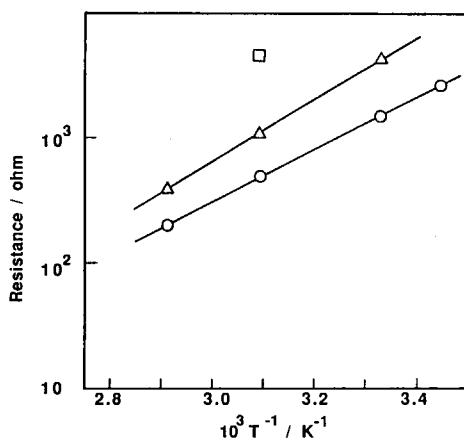


Fig. 3. Temperature dependence of internal electrical resistance: ○, PVA-LiCF₃SO₃ (1:1.5 wt./wt.); △, PVA-LiClO₄ (1:1 wt./wt.); □, PVA-LiBF₄ (1:1 wt./wt.) polymer electrolyte.

conventional electrolytic solutions [5]. Temperature dependence of the electrostatic capacitance is almost independent of the anion species.

Figure 3 shows the temperature dependence of the internal electrical resistance of the cell (r). The internal electrical resistance was calculated from the IR drop in the charge/discharge profile as shown in Fig. 1. As shown in Fig. 3, the temperature dependence of the internal electrical resistance obeys an Arrhenius type equation.

$$r = r_0 \exp(E_a/RT) \quad (1)$$

Table 2 summarizes an apparent activation energy value (E_a) obtained from the slope of the line shown in Fig. 3. It was reported elsewhere that the temperature dependence of the electrical conductivity of the PVA-LiCF₃SO₃, -LiBF₄ and -LiClO₄ composites also obeys an Arrhenius type equation [12].

TABLE 2

Apparent activation energy (E_a) for the internal resistance of the solid-state capacitor and PVA–lithium salt polymer solid electrolyte film

	Run	Composition of polymer electrolyte	E_a^a (eV)
Capacitor	1	PVA–LiCF ₃ SO ₃ (60 wt.%)	0.43
	2	PVA–LiClO ₄ (50 wt.%)	0.51
	3	PVA–LiBF ₄ (50 wt.%)	
Polymer electrolyte film	4	PVA–LiCF ₃ SO ₃ (60 wt.%) ^b	0.76
	5	PVA–LiClO ₄ (50 wt.%)	0.99
	6	PVA–LiBF ₄ (50 wt.%) ^b	0.58

^a E_a value was calculated for a temperature range of 15–70 °C (runs 1–3), –20 to 80 °C (runs 4, 5), and –20 to 25 °C (run 6).

^bData from ref. 12.

The E_a values of the PVA–lithium salt polymer solid electrolytes are also listed in Table 2. As shown in Table 2, the E_a values obtained from the internal resistance of the capacitors are the same order as those of the PVA–lithium salt composite, suggesting that the resistance of the polymer electrolyte is the main factor of the internal resistance of the capacitors. Though the present capacitor has a relatively high resistance, preparation of thinner polymer solid electrolyte films between the electrodes seems to be able to improve the internal resistance of the cell.

In summary, the PVA–lithium salt composite has been found to be a useful solid electrolyte for the electric double-layer capacitor. The present solid-state capacitor, for which one need not worry about leakage of the electrolytic solution, shows large capacitance comparable to that of the capacitor using the conventional electrolytic solution.

Acknowledgements

This research was partially supported by a Grant-in-Aid (No. 02750627) from the Ministry of Education, Science and Culture, Japan.

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