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Electric double-layer capacitor using composites composed of phosphoric acid-doped silica gel and styrene–ethylene–butylene–styrene elastomer as a solid electrolyte

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Abstract

Solid state electric double-layer capacitors have been fabricated using a composite composed of H_3PO_4-doped silica gel and styrene–ethylene–butylene–styrene elastomer as the electrolyte. A composite hybridized with activated carbon powders (ACP) was the polarizable electrode. The cyclic voltammogram of the electric double-layer capacitor fabricated demonstrated that electric charge was stored in the electric double-layer at the interface between the polarizable electrode and the electrolyte. Resistance of the capacitor obtained from impedance plots in ambient air was smaller by three orders of magnitude than that of the capacitor in a dry Ar atmosphere. The drastic decrease in the resistance should be ascribed to the increase in the proton conductivity of the composite due to the water adsorption in H_3PO_4-doped silica gel in an ambient atmosphere. The value of capacitance of the capacitor in an ambient atmosphere was 10 F/(gram of total ACP), which was 10 times larger than that of the capacitor in a dry Ar atmosphere. The large capacitance of the capacitor in an ambient atmosphere is attributable to the formation of electric double-layer with large electric charge at the interface between the composite and ACP in the capacitor due to the water adsorption. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Capacitor; Elastomer; Proton conduction; Molding property; Sol–gel ionics; Acid

1. Introduction

In recent years, there has been much interest in electric double-layer capacitors because of their practical applications as power storage devices for memory back-up of computers and electric vehicles [1]. Such capacitors are composed of a pair of polarizable electrodes and an electrolyte. Activated carbons, which exhibit large specific surface area and high electrical conductivity, have been used as a polarizable electrode of the capacitors [2,3]. Electric charge is stored in the electric double-layer at the interface between the polarizable electrode and the electrolyte when DC voltage is applied. Liquid electrolytes like aqueous electrolyte solution and organic electrolyte solution have been used so far in the electric double-layer capacitors [4–7]. By replacing the liquid electrolytes with the solid electrolytes like organic polymer electrolytes [8–11] or inorganic silica gel electrolytes [12] the reliability of the capacitors is expected to improve markedly from several practical viewpoints such as leakage of liquids, corrosion, etc.

We have fabricated a totally solid state electric double-layer capacitor using acid-doped silica gels as an electrolyte and the gels hybridized with activated carbon powders (ACP) as a polarizable electrode, the capacitance of which was comparable to that of capacitors using liquid electrolytes [13]. The excellent feature of the newly fabricated capacitor is ascribed to a good contact achieved via sol–gel processes at the interface between acid-doped silica gel and ACP. For the practical application of the acid-doped silica gel as a solid electrolyte for the electric double-layer capacitor, the improvement of the molding property of the gel is desired. Recently we have also successfully prepared highly proton-conductive elastic composites composed of H_3PO_4-doped silica gel and a styrene–ethylene–butylene–styrene (SEBS) block elastic copolymer and found that the composites are promising as a solid electrolyte for electric double-layer capacitors [14].

In the present work, solid state electric double-layer capacitors have been fabricated using the composite composed of H_3PO_4-doped silica gel and SEBS elastomer as

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an electrolyte and the composite hybridized with ACP as a polarizable electrode. Characteristics of the capacitors are evaluated by the cyclic voltammograms and discharge properties. The influence of water adsorption to the composites in an ambient atmosphere on the characteristics of the capacitors was also investigated.

2. Experimental

Fig. 1 shows the preparation procedure of two kinds of composites for the electrolyte part and the polarizable electrode part of electric double-layer capacitors. One for the electrolyte part is an ion-conductive composite composed of H_3PO_4-doped silica gel and SEBS elastomer. The other for the polarizable electrode part is a mixed conductive composite hybridized with ACP. Silica sol was prepared from tetraethoxysilane, $Si(OEt)_4$, ethanol, EtOH, H_2O containing HCl as a catalyst and $[(C_2H_5)_4N]BF_4$ in a molar ratio of $Si(OEt)_4$:EtOH:H_2O:HCl:$[(C_2H_5)_4N]BF_4$ = 1:4:8:0.01:0.01. $[(C_2H_5)_4N]BF_4$ was used to shorten the gelation time. The molar ratio of H_3PO_4 to SiO_2 was fixed to be 0.5. Only in the case of preparation of the composite for the polarizable electrode part, a mixture of ACP (Kanto Chemical) and acetylene black, AB, (Denki Kagaku Kogyo) as an electric collector was added to the hydrolyzed H_3PO_4-doped silica sol, where the weight ratio of $Si(OEt)_4$:ACP:AB was 1:0.5:0.075. Each H_3PO_4-doped silica sol with or without an addition of ACP and AB was then stirred at room temperature until gelation occurred. ACP consisted of granules of 20–100 μm in grain size; the diameter of their dominant pores was less than 10 Å and the specific surface area was 1240 m^2 g^{-1}. Each composite with or without the addition of ACP and AB obtained was dried in vacuo at 60–80°C for 8 h.

The average molecular weight of the SEBS elastomer (Kraton G®, Shell Chemical) used was 150 000 and the content of styrene in the elastomer was 15 mass%. The SEBS elastomer was dissolved in toluene and mixed with H_3PO_4-doped silica gel powder, where the weight ratio of SEBS elastomer: H_3PO_4-doped silica gel was fixed to be 5:95. The electric double-layer capacitor fabricated in the present study has a three layered cell structure of polarizable electrode/electrolyte/polarizable electrode, which is almost the same as that reported in our previous paper [13]. The electrolyte and electrode parts were prepared by separately grinding to powders and pressing them together at 4×10^8 N m^{-2} to be a three layered pellet of 13 mm in diameter and 1–2 mm in thickness.

The evaluation of the electric double-layer capacitors fabricated was carried out in a dry Ar atmosphere and an ambient atmosphere using a pair of platinum disks as the blocking electrodes at room temperature. The resistivities of the capacitors fabricated were determined by the impedance data obtained using an impedance analyzer (Solartron SI 1260) in a frequency range from 10 Hz to 10 MHz. Cyclic voltammetry of the capacitors was carried out to evaluate the capacitor performance using a potentiostat (Hokuto Denko, HA-501) and a function generator (Hokuto Denko, HB-301). The DC resistance of the capacitors fabricated was calculated from an initial voltage drop when the capacitors were discharged. Discharge properties of the capacitors fabricated were also investigated and the capacitance was determined from the discharge curves.

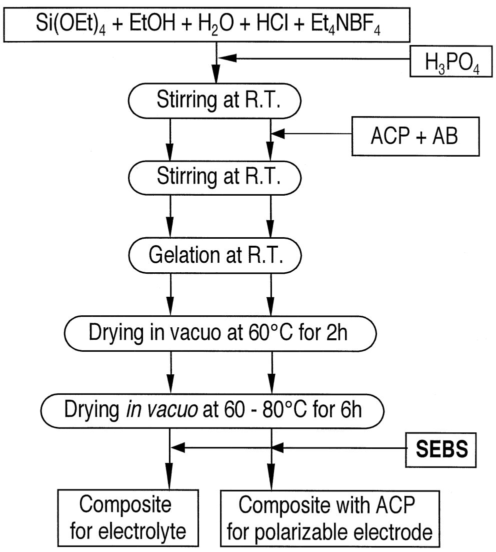

Fig. 1. Preparation procedure of two kinds of composites for the electrolyte part and the polarizable electrode part of electric double-layer capacitors. The ion-conductive composite composed of H_3PO_4-doped silica gel and SEBS elastomer is for the electrolyte part and the mixed conductive composite hybridized with ACP is for the polarizable electrode.

3. Results and discussion

3.1. Molding properties of composites

Each composite composed of H_3PO_4-doped silica gel and SEBS elastomer with or without the addition of ACP showed rubber-like elasticity and good molding properties due to the excellent elasticity of the SEBS elastomer and is promising as a polarizable electrode or an electrolyte for totally solid state electric double-layer capacitors. The fabrication process of the capacitors in the present study is simple; high productivity is expected due to the good molding properties of the composite materials.

Fig. 2 shows SEM photographs of the surface of the pellets of H_3PO_4-doped silica gel (a) and a composite composed of H_3PO_4-doped silica gel and SEBS elastomer (b). Both samples were prepared by pelletizing the powders under a pressure of 4×10^8 N m^{-2}. In Fig. 2(a), H_3PO_4-doped silica gel powders consist of grains of 5 to 20 μm in size and the voids among the grains are observable. On the other hand, the voids among the grains are clearly diminished in Fig. 2(b), indicating that the gel

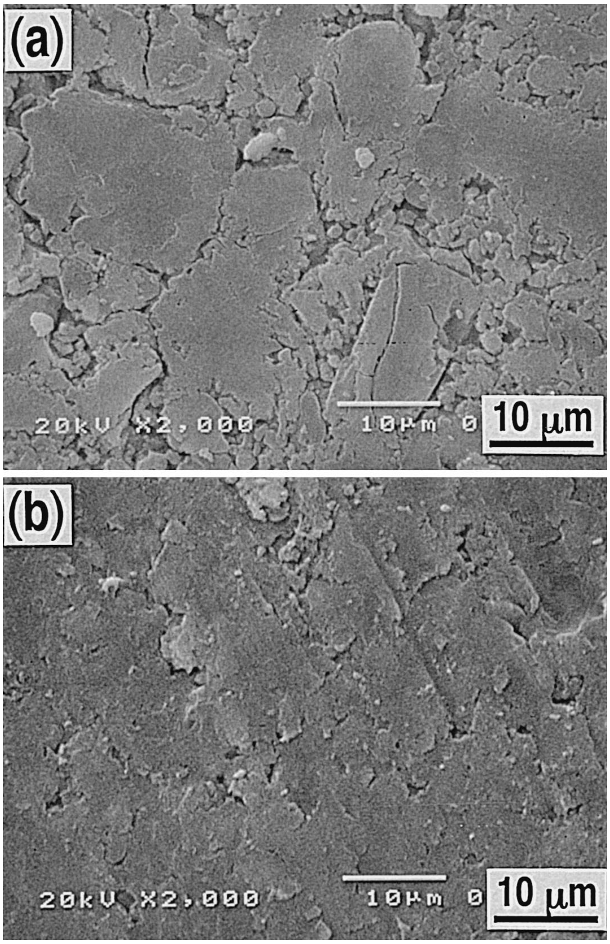

Fig. 2. SEM photographs of the surface of the pellets of H_3PO_4-doped silica gel (a) and a composite composed of H_3PO_4-doped silica gel in 95 mass% and SEBS elastomer in 5% without the addition of ACP (b). Both samples were prepared by pelletizing the powders under a pressure of 4×10^8 N m^{-2}.

powders are homogeneously hybridized with SEBS elastomer and the voids among the grains are filled with the SEBS elastomer.

3.2. Cyclic voltammogram of electric double-layer capacitor

Fig. 3 shows the cyclic voltammogram of a totally solid state electric double-layer capacitor fabricated using the composite composed of H_3PO_4-doped silica gel and SEBS elastomer as an electrolyte and the composite hybridized with ACP as a polarizable electrode. The sweep rate was 0.5 mV/s. The capacitive current curve is smooth and varies from +0.62 to −0.62 mA in a sweep region of 0.4 to −0.4 V. This result demonstrates that electric charge is stored in the electric double-layer at the interface between the polarizable electrode and the electrolyte in spite of its totally solid state structure. No redox is observed in the sweep region and the cyclic voltammogram was unchanged on repeated runs.

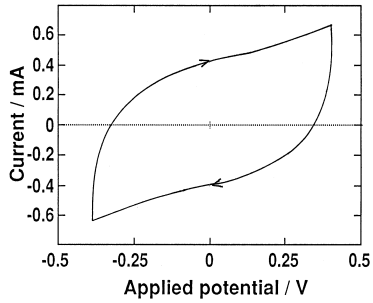

Fig. 3. Cyclic voltammogram of a totally solid state electric double-layer capacitor fabricated. The measurement was carried out in an ambient atmosphere at room temperature under a sweep rate of 0.5 mV/s.

3.3. Complex impedance analysis

Fig. 4 shows the comparison of complex impedance plots measured in dry Ar (a) and ambient air (b) atmospheres at room temperature for an electric double layer capacitor fabricated. Before the measurement in a dry Ar atmosphere, the electric double-layer capacitor was dried in vacuo at room temperature for 2 h. In the plots obtained in a dry Ar atmosphere (a), not a semicircle but an arc of a circle and a straight line are observed. The arc should be caused by the heterogeneity of the capacitor, i.e., overlapping of several impedances due to the multiphase in the capacitor. The total impedance of the capacitor is attributed to the arc in high frequency range. The resistance from impedance plots, R_{imp} in dry Ar was identified to be 3.2×10^4 Ω from the intersecting point of the arc with the real axis. On the other hand, a straight line is only observed for the plots obtained in an ambient air atmosphere

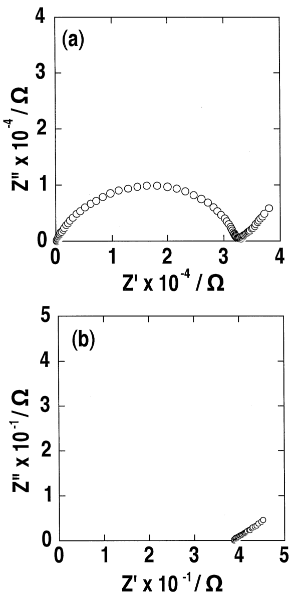

Fig. 4. Comparison of complex impedance plots measured in dry Ar (a) and ambient air (b) atmospheres at room temperature for the electric double-layer capacitor fabricated.

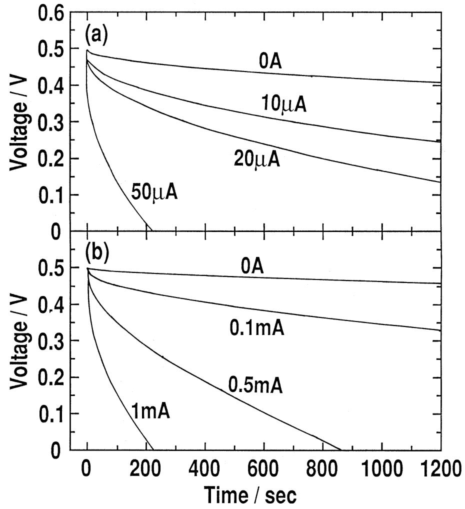

Fig. 5. Comparison of discharge curves measured in dry Ar (a) and ambient air (b) atmospheres at room temperature for the electric double layer capacitor fabricated. The capacitor was charged by applying a constant DC voltage of 0.5 V for 30 min at room temperature before the measurement.

(b) in the present frequency range, indicating that internal resistance of the capacitor is very small. R_{imp} in an ambient air was identified to be 38 Ω from the intersecting point of the line with the real axis, which is smaller by three orders of magnitude than that of the resistance in dry Ar. The drastic decrease in the resistance should be ascribed to a decrease in the interfacial resistance between the composite and ACP and an increase in the proton conductivity of the composite due to the water adsorption in the H_3PO_4-doped silica gel in an ambient atmosphere.

3.4. Discharge properties of electric double-layer capacitor

Fig. 5 shows the comparison of discharge curves measured in dry Ar (a) and ambient air (b) atmospheres at room temperature for an electric double layer capacitor fabricated. The capacitor was charged by applying a constant DC voltage of 0.5 V for 30 min at room temperature before the measurement. Both in dry Ar (a) and ambient air (b) atmospheres the voltage drop during discharge of the capacitor increases with an increase in the discharge current. It can be seen that the capacitor has a capacitance in an ambient atmosphere to discharge a larger current by two orders of magnitude than that in a dry Ar atmosphere. This result corresponds to the drastic decrease in the resistance of the capacitors due to the water adsorption to the composite in an ambient atmosphere as shown in Fig. 4 and suggests that the capacitance of the capacitor greatly depends on the interfacial resistance of the capacitor and the ionic conductivity of the composite as an electrolyte. Small voltage drops by around 10% in 1200 s under a discharge current of 0 A are observed in both dry Ar (a) and ambient air (b) atmospheres. One of the most important factors which cause these voltage drops should be a leak current through the side area of the three layered tablet capacitor. Perfect insulation between a pair of polarizable electrode layers in capacitors is, thus, required to diminish the current leakage. The difference of voltage drop during discharge in dry Ar and ambient air atmospheres should be also ascribed to the fact that the capacitor has a much smaller capacitance in a dry Ar atmosphere than in an ambient atmosphere.

3.5. Internal resistance and capacitance of electric double-layer capacitor

The DC resistance of capacitor can be estimated by voltage drop, IR-drop, at the beginning of discharge process of the capacitors. Since the IR-drop was proportional to the discharge current, I the DC resistance, $R_{IR\text{-drop}}$, of the capacitor can be obtained. The capacitance, C, of capacitors can be also given by $(It)/V$, where I is the constant discharge current, t is the time for discharge, and V is the potential change of the capacitor caused by discharge [8]. The values of $R_{IR\text{-drop}}$ and C calculated are listed in Table 1 together with R_{imp} estimated from Fig. 4 in a dry Ar atmosphere and in an ambient air atmosphere at room temperature. The value of R_{imp} is comparable to that of $R_{IR\text{-drop}}$ in an ambient air. On the other hand, the value of R_{imp} is 20 times as large as that of $R_{IR\text{-drop}}$ in dry Ar. This result suggests that R_{imp} includes not only the intrinsic resistance of the capacitors but also the resistance at the interface between the capacitor and platinum blocking electrodes of the cell. The values of C and $C/$(gram of total ACP) of the capacitor in an ambient atmosphere are 10 times larger than those of the capacitor in dry Ar and these phenomena correspond to the fact that the value of $R_{IR\text{-drop}}$ in a dry Ar atmosphere is twenty five times as large as that in an ambient atmosphere. The large C value in an ambient atmosphere should be attributable to the formation of the electric double-layer with large electric charge at the interface between the composite and ACP in the capacitor due to the water adsorption. The adsorption gives a good contact between the composite and ACP, which should achieve the paths suitable for fast proton transport.

It has been found that the capacitance of the capacitor in the present work is a little smaller than that of the capacitor using a PVA-containing silica gel doped with $HClO_4$ [13]. However the present composite has shown

Table 1
Resistance from impedence plots (R_{imp}), DC resistance ($R_{IR\text{-drop}}$), and capacitance (C and $C/$(gram of total ACP)) of the electric-double layer capacitor measured in dry Ar and in an ambient air at room temperature

Atmosphere	R_{imp} (Ω)	$R_{IR\text{-drop}}$ (Ω)	C (F)	C (F g^{-1})
Ar	32 000	1400	0.16	1.0
Air	38	56	1.61	10.3

much better molding properties and relatively higher temperature stability than the PVA-containing silica gel due to the inclusion of SEBS elastomer and H_3PO_4, so that the composite composed of H_3PO_4-doped silica gel and SEBS elastomer is promising as an electrolyte for practical application to the solid electric double-layer capacitor.

4. Conclusions

The cyclic voltammogram of a totally solid state electric double-layer capacitor fabricated using the composite composed of H_3PO_4-doped silica gel and SEBS elastomer as an electrolyte and the composite hybridized with ACP as a polarizable electrode demonstrated that electric charge was stored in the electric double-layer at the interface between the polarizable electrode and the electrolyte. The resistance of the capacitor obtained from impedance plots in ambient air was 38 Ω, which was smaller by three orders of magnitude than that of the capacitor in dry Ar. The drastic decrease in the resistance should be ascribed to a decrease in the interfacial resistance between the composite and ACP and to an increase in the proton conductivity of the composite due to the water adsorption in an ambient atmosphere. The value of capacitance of the capacitor in an ambient atmosphere was 10 F/(gram of total ACP), which was 10 times larger than that of the capacitor in dry Ar. The large capacitance in an ambient atmosphere should be attributable to the formation of electric double-layer with sufficient electricity at the interface between the composite and ACP due to the water adsorption, which allowed the interface to form paths suitable for fast proton transport.

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