The Korean Journal of Ceramics, **5**[4] 353-356 (1999)

Application of Composites Composed of Phosphoric Acid-Doped Silica Gel and Styrene-Ethylene-Butylene-Styrene Elastomer to Electric Double-Layer Capacitors

Atsunori Matsuda, Hiroshi Honjo, Kazuki Hirata, Masahiro Tatsumisago and Tsutomu Minami

Department of Applied Materials Science, Graduate School of Engineering Osaka Prefecture University, Sakai, Osaka 599-8531, Japan

(Received September 23, 1998)

Highly proton-conductive elastic composites have been successfully prepared from H_3PO_4-doped silica gel and styrene-ethylene-butylene-styrene block elastic copolymer. In addition solid state electric double-layer capacitors have been fabricated using the composite as an electrolyte and activated carbon powders (ACP) hybridized with the composite as a 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. The value of capacitance of the capacitor was 10 *F/(gram of total ACP)*, which was comparable to that of the capacitors using conventional liquid electrolytes.

Key words: *Sol-gel method, Proton conductivity, Heat-treatment temperature, Rubber elasticity*

I. Introduction

The electric double-layer capacitors have been attracting much interest as rechargeable devices because they have an excellent charge/discharge property with high rate and a high energy density comparable to that of the conventional rechargeable batteries. These capacitors are applied as power sources for memory back-up of computers and as complements to batteries in electric vehicles.[1] As the polarizable electrodes for the electric double-layer capacitor, activated carbons, which exhibit large specific surface area and high electrical conductivity, have been used.[2,3] As to the electrolytes for the capacitors, liquid electrolytes like aqueous electrolyte solution and organic electrolyte solution have so far been used.[4-7] By replacing the liquid electrolytes with the solid electrolytes like organic polymer electrolytes[8-10] or inorganic silica gel electrolytes[11] the reliability of the capacitors is expected to improve markedly from several practical viewpoints like 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 activated carbon powders (ACP) hybridized with the gels as a polarizable electrode, the capacitance of which was comparable to that of capacitors using liquid electrolytes.[12] 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 a molding property of the gel is desired.

Very recently, we have successfully prepared highly proton-conductive elastic composites from H_3PO_4-doped silica gel and styrene-ethylene-butylene-styrene (SEBS) block elastic copolymer[13] and fabricated solid state electric double-layer capacitors using the composite as an electrolyte and ACP hybridized with the composite as a polarizable electrode.[14] This paper reports the ionic conductivity and elasticity of the composites and also the characteristics of the capacitors on the bases of cyclic voltammograms and discharge properties.

II. Experimental Procedure

1. Preparation of electric double-layer capacitors

The electric double-layer capacitor fabricated in the present study has a three-layer pelletized structure of polarizable electrode/electrolyte/polarizable electrode. The electrolyte part is an ion-conductive composite composed of H_3PO_4-doped silica gel and styrene-ethylene-butylene-styrene (SEBS) elastomer. On the other hand, the polarizable electrode part is a mixed conductive composite composed of ACP hybridized with the H_3PO_4-doped silica gel and SEBS elastomer. 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, x, was varied from 0.25 to 1.0. 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 the mixture 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 and the specific surface area was 1240 m^2g^{-1}. Each composite with or without the addition of the mixture 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 1.5×10^5 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. The electorolyte and electrode parts were prepared by separately grinding to fine powders and pressing them together at 4×10^8 Nm^{-2} to be a three layered pellet of 13 mm in diameter and 1-2 mm in thickness.

2. *Characterization of composites*

The ionic conductivity was measured for the pelletized composites using a pair of platinum plates as the electrodes. The conductivity was determined by the impedance data obtained using an impedance analyzer (Solartron, SI 1260) in a frequency range of 10 Hz-8 MHz The elastic modulus of the composites and SEBS elastomer was determined by a thermo-mechanical analyzer, TMA (MAC Science, TMA 4000), at a frequency of 0.125 Hz and a heating rate of 5 C min^{-1}.

3. *Evaluation of electric double-layer capacitors*

The evaluation of the electric double-layer capacitors fabricated was carried out in an ambient atmosphere at room temperature using a pair of platinum disks as the blocking electrodes. 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 investigated and then the capacitance was determined from the discharge curves.

III. Results and Discussion

1. *Proton conductivity of composites*

Fig. 1 shows the temperature dependence of ionic conductivities of composites composed of the H_3PO_4-doped silica gel with different H_3PO_4/SiO_2 mole ratios, x, and SEBS elastomer. All the H_3PO_4-doped silica gels used were dried *in vacuo* at 60-80 °C for 8 h. The mass percentage of the SEBS elastomer added was 5 for all the composites in Fig. 1. The conductivity of composites was measured in a dry N_2 atmosphere during both heating and cooling processes in a temperature range from room temperature to 100 °C. Before the measurement, the composites were dried *in vacuo* at room temperature for 1 h. The conductivities of the composites increase significantly with an increase in x. The temperature dependence of conductivity of the composites is not the Arrhenius type but the Vogel-Tamman-Fulcher type.[15] Such a temperature dependence of the conductivity indicates that proton is transferred through a liquid-like phase formed in micropores of the H_3PO_4-doped silica gel. The temperature dependence of conductivity was found to be almost the same in both heating and cooling processes. The H_3PO_4-doped silica gel with x=1.0 was, however, unstable against humidity and deliquescent. We chose x to be 0.5, since the composite of this composition has a high conductivity and proper humidity resistance.

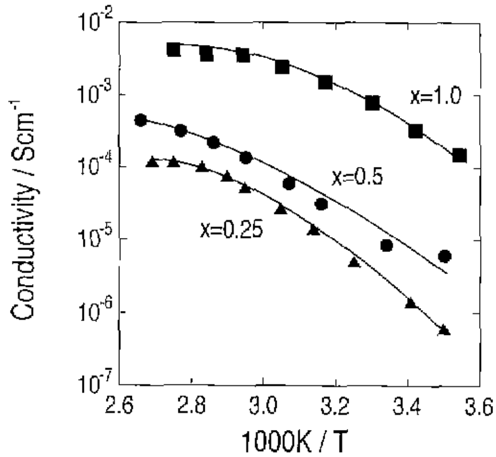

Fig. 1. Temperature dependence of ionic conductivities of the composites composed of H_3PO_4-doped silica gel with different H_3PO_4/SiO_2 mole ratios, x, and SEBS elastomer in 5 mass%.

2. *The rubber elasticity of the composites*

The H_3PO_4-doped silica gel without elastomer was brittle and thus the molding character was poor. On the other hand, the composite composed of the H_3PO_4-doped silica gel and SEBS elastomer exhibited a good molding property due to its rubber-like elasticity. The elastic modulus of the composites was measured to discuss the influence of the addition of the elastomer to the H_3PO_4-doped silica gel. Fig. 2 shows a typical example of temperature dependence of the elastic moduli of the composite composed of H_3PO_4-doped silica gel with x=0.5 and SEBS elastomer in 20 mass% and of the SEBS elastomer itself. Closed and open circles represent the composite and SEBS elastomer itself, respectively. The elastic modulus of the composite is larger by about one order of magnitude than that of the SEBS elastomer. The temperature dependence of the modulus of the composite was similar to that of the SEBS elastomer. In the elastic modulus of SEBS elastomer, a bending is seen around 70 ° C, which corresponds to the thermoplastically deforming temperature of the elastomer. The bending is observed around 100 °C in the composite, indicating that the thermoplasti-

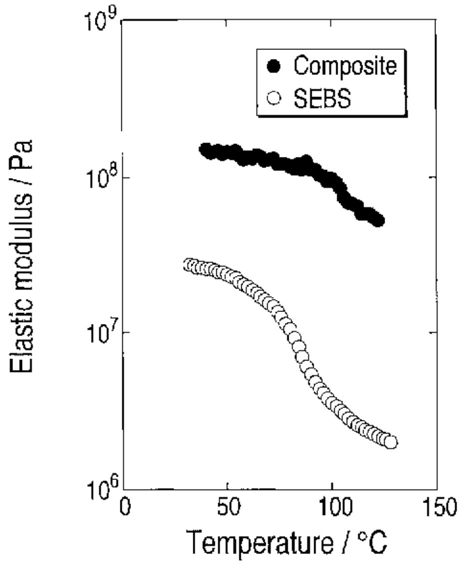

Fig. 2. Temperature dependence of elastic moduli of the composite composed of H_3PO_4-doped silica gel with x=0.5 and SEBS elastomer in 20 mass% and of the SEBS elastomer itself. Closed and open circles represent the composite and SEBS elastomer, respectively.

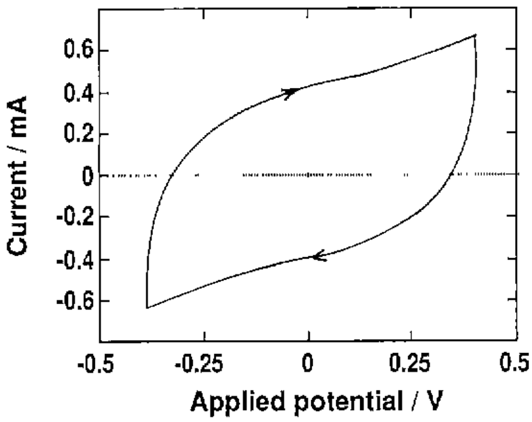

Fig. 3. Cyclic voltammogram of a totally solid state electric double-layer capacitor fabricated. The measurement was carried out in an ambient atmosphere at room temperature under a sweep rate of 0.5 mV/s.

cally deforming temperature becomes higher by 30 °C due to the hybridization of the SEBS elastomer with the gel.

3. Cyclic voltammogram of electric double-layer cap-acitor

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 ACP hybridized with the composite 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 −0.4V. 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.

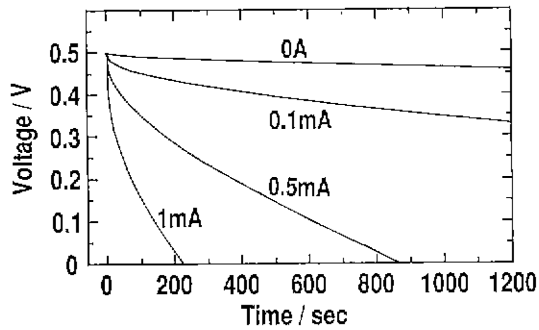

Fig. 4. Discharge curves measured in an ambient atmosphere at room temperature for the electric double layer capacitor fabricated. The capacitor was charged by applying a constant dc voltage of 0.5V for 30 min at room temperature before the measurement.

4. Discharge properties of electric double-layer cap-acitor

Fig. 4 shows the discharge curves measured in an ambient atmos-phere at room temperature for an electric double layer capacitor fabricated. The capacitor was charged by applying a constant dc voltage of 0.5V for 30 min at room temperature before the measurement. The voltage drop during discharge of the capacitor increases with an increase in the discharge current. A small voltage drop by around 10% in 1200 sec under a discharge current of 0 A is observed. One of the factors which cause the voltage drops should be the leak current at the side area of the three layered tablet capacitor. From the voltage drop during the constant discharge, the value of capacitance of the capacitor was calculated to be about 10 F/*(gram of total ACP)*, which was comparable to that of conventional capacitor with a liquid electrolyte.[5] The large capacitance of the solid state capacitor fabricated can be ascribed to the good molding property of the composite and formation of the sufficient electric double-layer at the interface between the composite and ACP. The dc resistance of the capacitor was estimated to be as low as 56 Ω by voltage drop at the beginning of discharge process. The low dc resistance is attributable to the high electric conductivity of the composite.

IV. Conclusions

The conductivities of the composites composed of H_3PO_4-doped silica gel and SEBS elastomer increased significantly with an increase in the H_3PO_4 content. The temperature dependence of conductivity of the composites is not the Arrhenius type but the Vogel-Tamman-Fulcher type, indicating that proton is transferred through a liquid-like phase formed in micropores of the H_3PO_4-doped silica gel. The composite composed of the H_3PO_4-doped silica gel and

SEBS elastomer exhibited a good molding property due to its rubber-like elasticity. The elastic modulus of the composite was larger by about one order of magnitude than that of the SEBS elastomer and the thermoplastically deforming temperature was improved by 30 °C. The cyclic voltammograms showed that the electric charge was stored in the electric double-layer at the interface between the polarizable electrode and the electrolyte in spite of its totally solid state structure. From the voltage drop during the constant discharge, the values of capacitance and dc resistance of the capacitor were calculated to be about 10 F/*(gram of total ACP)* and 56 Ω, respectively. The large capacitance of the capacitor fabricated was attributable to the formation of the sufficient electric double-layer at the interface between the composite and ACP.

Acknowledgment

This work was supported by the "Research for the Future Program" from the Japan Society for the Promotion of Science and also partly supported by a Grant-in-Aid from the Ministry of Education, Science, Sports and Culture of Japan. We thank Dr. I. Tanahashi of Matsushita Electric Industrial Company for valuable discussion and Mr. Y. Takeuchi of JSR Co. Ltd., for supply of SEBS elastomer.

References

1. A. Nishino, "Capacitors: Operating Principles, Current Market and Technical Trends," *J. Power Sources*, **60**, 137-147 (1996).
2. I. Tanahashi, A. Yoshida, and A. Nishino, "Activated Carbon Fiber Sheets as Polarizable Electrodes of Electric Double Layer Capacitor," *Carbon*, **28**(4), 477-482 (1990).
3. I. Tanahashi, A. Yoshida, and A. Nishino, "Characterization of Activated Carbon Fiber Cloths for Electric Double-Layer Capacitor by Adsorption Method," *Carbon*, **29**(7), 1033-1037 (1991).
4. S. Sekido, Y. Yoshino, T. Muranaka, and M. Mori, "An Electric Double-Layer Capacitor Using Organic Electrolyte," *Denki Kagaku*, **48**(1), 40-45 (1980).
5. I. Tanahashi, A. Yoshida, and A. Nishino, "Comparison of the Electrochemical Properties of Electric Double-Layer Capacitors with an Aqueous Electrolyte and with a Non-aqueous Electrolyte," *Bull. Chem. Soc. Japan*, **63**(12), 3611-3614 (1990).
6. I. Tanahashi, A. Yoshida, and A. Nishino, "Electrochemical Characterization of Activated Carbon-Fiber Cloth Polarizable Electrodes for Electric Double-Layer Capacitor," *J. Electrochem. Soc.*, **137**(10), 3052-3057 (1990).
7. Y. Sanada, K. Hiratsuka, T. Morimoto, and K. Kurihara, "Electric Double Layer Capacitor Using Sulfolane-Based Electrolytic Solution," *Denki Kagaku*, **61**(4), 448-450 (1993).
8. Y. Matsuda, M. Morita, M. Ishikawa, and M. Ihara, "New Electric Double-Layer Capacitors Using Polymer Solid Electrolytes Containing Tetraalkylammonium Salts," *J. Electrochem. Soc.*, **140**(7), L109-110 (1993).
9. M. Ishikawa, M. Morita, M. Ihara, and Y. Matsuda, "Electric Double-Layer Capacitor Composed of Activated Carbon Fiber Cloth Electrodes and Solid Polymer Electrolytes Containing Alkylammonium Salts," *J. Electrochem. Soc.*, **141**(7), 1730-1734 (1994).
10. X. Liu and T. Osaka, "All-Solid-State Electric Double-Layer Capacitor with Isotropic High-Density Graphite Electrode and Polyethylene Oxide/$LiClO_4$ Polymer Electrolyte," J. *Electrochem. Soc.*, **143**(12), 3982-3986 (1996).
11. M. Tatsumisago, H. Honjo Y. Sakai, and T Minami, "Proton-Conducting Silica-Gel Films Doped with a Variety of Electrolytes," *Solid State Ionics*, **74**, 105-108 (1994).
12. A. Matsuda, H. Honjo, M. Tatsumisago and T. Minami, "Electric Double-Layer Capacitor Using $HClO_4$-Doped Silica Gels as a Solid Electrolyte," *Solid State Ionics*, **113-115**, 97-102 (1998).
13. K. Hirata, A. Matsuda, H. Hirata, M Tatsumisago and T. Minami, "Preparation and Characterization of Highly Proton-Conductive Composites Composed of Phosphoric Acid-Doped Silica Gel and Styrene-Ethylene-Butylene-Styrene Elastomer," *J Sol-Gel Sci. Tech.*, in press.
14. A. Matsuda, H. Honjo, K. Hirata, M. Tatsumisago, and T. Minami, "Electric Double-Layer Capacitor Using Composites Composed of Phosphoric Acid-Doped Silica Gel and Styrene-Ethylene-Butylene-Styrene Elastomer as a Solid Electrolyte," *J. Power Sources*, **77**, 12-16 (1999).
15. F.M. Gray, J R. MacCallum, C.A. Vincent and J.R.M Giles, "Novel Polymer Electrolytes Based on ABA Block Copolymer," *Macromolecules*, **21**(2), 392-397 (1988).