Proton Conductive Silica Gels Doped with Several Acids and Their Application to Electric Double-Layer Capacitor

Atsunori Matsuda, Hiroshi Honjo, Masahiro Tatsumisago, and Tsutomu Minami
Department of Applied Materials Science, Osaka Prefecture University, Sakai, Osaka 599-8531

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Polyvinyl alcohol-containing silica gels doped with $HClO_4$, H_2SO_4, or H_3PO_4 prepared by the sol-gel method exhibited high proton conductivities of 10^{-5}-10^{-2} S cm^{-1} at room temperature. Totally solid state electric double-layer capacitors fabricated using the gels as an electrolyte and activated carbon powder, ACP, as a polarizable electrode showed large capacitances of 31-44 F/(gram of total ACP), which were comparable to those of the capacitors with liquid electrolytes.

The sol-gel method is one of the most promising techniques to design high ion-conducting materials, which are applicable for electrochemical devices in solid state.[1,2] In the sol-gel method, metal alkoxides are often used as a starting material and are hydrolyzed and polymerized in an alcohol solution with water containing acids, bases or salts. The wet gel obtained from the method consists of interpenetrating inorganic solid and liquid phases, so that the liquid phases are regarded as paths for fast proton transport and the interface between the inorganic solid and the liquid is expected to enhance the ionic conductivity. We have developed the bulk silica gels and films containing $HClO_4$ by the sol-gel method and found that the conductivities of the silica gels are as high as 10^{-2} S cm^{-1} at room temperature.[3,4] Recently we have successfully fabricated the totally solid electric double-layer capacitors using the polyvinyl alcohol, PVA,-containing silica gels doped with $HClO_4$ as an electrolyte and activated carbon powder, ACP, hybridized with the gels as a polarizable electrode aiming at the improvement of the reliability of the capacitors from several practical viewpoints like leakage of the liquids, corrosion, etc.[5]

In the present paper, we report the comparison of electric properties of the PVA-containing silica gels doped with $HClO_4$, H_2SO_4, or H_3PO_4 and characteristics of the capacitors fabricated using the silica gels as an electrolyte.

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 a PVA-containing silica gel doped with acid and the polarizable electrode part is ACP hybridized with the gel.

Distilled water, HCl, and $(C_2H_5)_4NBF_4$, were mixed with an aqueous solution of PVA (10 mass%). $HClO_4$, H_2SO_4, or H_3PO_4 was added to the mixture and then stirred at 0 °C. Tetraethoxysilane, TEOS, diluted with ethanol was added to the mixture with stirring at 0 °C, where the mole ratio of $HClO_4$, H_2SO_4, or H_3PO_4 to silica was fixed to be 0.5. Two kinds of silica sols without and with an addition of the mixture of ACP and acetylene black, AB, as an electric collector were prepared and then stirred at room temperature until gelation occurred. The gels without and with the addition of the mixture are for the electrolyte part and polarizable electrode part, respectively. Both gels were dried *in vacuo* at 60 °C for 2 h. The molar ratio of TEOS / ethanol / H_2O / HCl / $(C_2H_5)_4NBF_4$ was fixed to be 1 / 4 / 20 / 0.01 / 0.01 and the mass ratio of TEOS / PVA / ACP / AB was 1 / 0.5 / 0.5 / 0.075. The two kinds of silica gels prepared were separately ground to powders and subsequently pressed at 400 MPa to be a three-layered pellet of 13 mm in diameter and 1-2 mm in thickness.

The conductivities of the PVA-containing silica gels doped with several acids for an electrolyte part were determined by the impedance data obtained using an impedance analyzer (Solartron SI 1260). The measurement was carried out in a dry N_2 atmosphere using a couple of platinum disks as the electrodes in a temperature range from -80 to 30 °C. Cyclic voltammetry of the electric double-layer capacitor fabricated was carried out to evaluate the capacitor performance at room temperature using a potentiostat (Hokuto Denko, HA-501) and a function generator (Hokuto Denko, HB-301). The dc resistance, R_{dc}, of capacitors can be estimated by voltage drop, IR drop, at the beginning of discharge process of the capacitors from the following equation:

$$R_{dc} = V_{drop} / i, \quad (1)$$

where V_{drop} is the observed IR drop and i is the discharge current. The capacitance was calculated from the following equation:

$$C = (i \times \Delta t) / \Delta V, \quad (2)$$

where C is the capacitance, i is the constant discharge current, Δt is the time for discharge and ΔV is the potential change of the capacitor caused by discharge.

It was found from preliminary experiments that ionic conductivity of the silica gel doped with $HClO_4$, H_2SO_4, or H_3PO_4 increased with an increase in the amounts of the acid added and attained 10^{-1} to 10^{-2} S cm^{-1} in an ambient atmosphere at room temperature although that of the silica gel doped with HCl or HNO_3 was about 10^{-5} S cm^{-1} independent of the amounts of the acid added. Protonic acids with hydrated water such as $HClO_4$, H_2SO_4 and H_3PO_4 are, thus, considered to act as an effective proton donor and increase the proton conductivity of the resultant acid-doped silica gel.

Figure 1 shows the temperature dependence of the ionic conductivity in dry N_2 atmosphere for PVA-containing silica gels doped with $HClO_4$, H_2SO_4, or H_3PO_4. It can be seen that conductivities of all the acid-doped silica gels exponentially

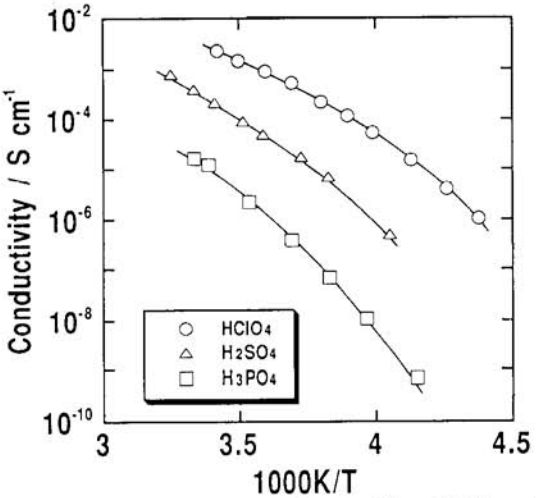

Figure 1. Temperature dependence of conductivities of PVA-containing silica gels doped with $HClO_4$, H_2SO_4, or H_3PO_4.

increase with an increase in temperature. The temperature dependence of conductivity of the gels is not the Arrhenius type but the Vogel-Tamman-Fulcher (VTF) type,[6] suggesting that proton is transferred through a liquid path formed in micropores of the PVA-containing silica gels which are macroscopically solid. The curves in Figure 1 are the results obtained by fitting the following VTF equation to the experimental measurements:

$$\sigma = \sigma_0 \exp (-B / (T - T_0)), \qquad (3)$$

where σ and T are respectively the ionic conductivity and the absolute temperature, and σ_0, B and T_0 are empirical constants. The constant B is related to free energy barrier.[6] The curves obtained by fitting are in good agreement with the experimental values of conductivities for the PVA-containing silica gels doped with the acid. The values of T_0, RB, where R is the gas constant, σ_0, and the conductivity at 25 °C, σ_{25}, obtained by fitting are listed in Table 1. The conductivities of silica gels

Table 1. VTF parameters of a pre-exponential factor (σ_0), the apparent activation energy (RB) and the identical glass transition temperature (T_0) obtained from the fitting of temperature dependence of conductivities of the PVA-containing silica gels doped with $HClO_4$, H_2SO_4, or H_3PO_4. The conductivities of the gels at 25 °C (σ_{25}) are also listed

Dopant	T_0 / K	RB / kJmol^{-1}	σ_0 / Scm^{-1}	σ_{25} / Scm^{-1}
$HClO_4$	168	7.6	3.3×10^{0}	3.0×10^{-3}
H_2SO_4	160	12.6	2.0×10^{1}	3.4×10^{-4}
H_3PO_4	147	20.7	2.2×10^{2}	1.5×10^{-5}

doped with $HClO_4$, H_2SO_4, and H_3PO_4 decreased in this order. It can be found that the PVA-containing silica gel doped with $HClO_4$ shows the lowest value of RB. The lowest value of B should be responsible for the highest ionic conductivity of the resultant silica gel. The conductivities of acid-doped silica gel can be related to the property of the acid on the basis of acid dissociation constant, K_a,. The values of K_a of $HClO_4$, H_2SO_4, and H_3PO_4 are respectively 1×10^{10}, 1×10^{2} and 8×10^{-8}; namely acidity drastically decreases in this order.[7] The acid with hydrated water and larger K_a provides the resultant acid-doped silica gel with higher proton conductivity.

Figure 2 shows the cyclic voltammograms of a totally solid state electric double-layer capacitors fabricated; (a), (b) and (c) are for the capacitors using PVA-containing silica gels doped with $HClO_4$, H_2SO_4 and H_3PO_4 as an electrolyte, respectively. The measurements were carried out in an ambient atmosphere at room temperature. All the capacitive current curves are smooth and vary from +4 to -4 mA in a sweep region of 0.4 to -0.4V. This result demonstrates that electric charge is effectively stored in all the electric double-layers at the interface between the polarizable electrode and the electrolyte.[8] Very broad peaks are observed at 0.05 and -0.05 V in the cyclic voltammograms of (a) and (b), which are probably attributable to a redox of the surface functional groups of ACP with $HClO_4$ and H_2SO_4.

The values of R_{dc} obtained from IR drop using equation

Table 2. The values of R_{dc} obtained from IR drop and the values of C calculated from the discharge curves of the PVA-containing silica gels doped with $HClO_4$, H_2SO_4, or H_3PO_4

Dopant	R_{dc} / Ω	C / F g^{-1}
None	526	–
$HClO_4$	1.3	44
H_2SO_4	2.6	40
H_3PO_4	5.6	31

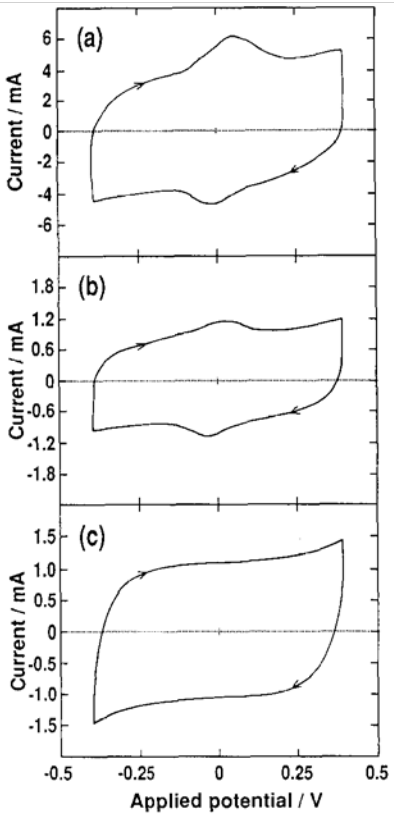

Figure 2. Cyclic voltammograms of totally solid state electric double-layer capacitors fabricated; (a), (b) and (c) are for the capacitors used PVA-containing silica gels doped with $HClO_4$, H_2SO_4 and H_3PO_4 as an electrolyte, respectively. The sweep rates are (a) 1, (b) 0.2 and (c) 0.5 mV/sec.

(1) and the values of C calculated from the discharge curves using equation (2) are listed in Table 2. The capacitance of the capacitors using PVA-containing silica gels without acid is too small to be estimated. The values of C of the capacitors doped with $HClO_4$, H_2SO_4 and H_3PO_4 are 44, 40 and 31 F/(gram of APC), respectively, which are comparable to those of the conventional capacitors with liquid electrolytes.[9] The large capacitance of the totally solid electric double-layer capacitors fabricated is attributable to the sufficient formation of electric double-layer at the interface between the highly proton conductive silica gel and ACP.

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