ELECTRIC DOUBLE LAYER capacitors based on PHOSPHATE GLASS-Derived HYDROGELS prepared by a CHEMICOVECTORIAL METHOD

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Abstract: New types of proton-conducting phosphate hydrogels were prepared utilizing a chemicovectorial effect. Fine-sized magnesium metaphosphate, calcium metaphosphate, or zinc metaphosphate glass powders reacted with distilled water to hydrate immediately, resulting in formation of the hydrogels with high viscosity. $^{31}$P MAS-NMR spectra showed that the hydrogels include orthophosphates and long-chain phosphates coordinated to $\text{H}^+$ or $\text{M}^{2+}$ (M=Mg, Ca, Zn) ions; no significant differences in their structures among the hydrogels were shown. Electric double layer capacitors (EDLCs) with electrolytes consisting of the hydrogels showed no oxidation-reduction processes in the range of 0–1 V and high rate charge-discharge capabilities. The EDLCs showed excellent self-discharge behaviors; they retained high open circuit potentials of the EDLCs after charging. EDLC consisting of zinc phosphate hydrogel showed much higher (3–6 times higher) specific capacity than those of magnesium phosphate and calcium phosphate hydrogels under the present condition. The possibility as an EDLC electrolyte may be related to polarizability of the hydrogels.

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INTRODUCTION

Some high performance ceramic-based materials can be prepared by physical, chemical, or biological supplies of some external energies and/or chemical substances. The typical example is seen in the fact that bioactivity of hydroxyapatite ceramics is enhanced after an electrical polarizing treatment.1-3 Yamashita designated the enhancement as an "electrovectorial" effect.4 Such materials having "vectorial" effects are expected to bring numerous benefits in various applications.

Recently, we succeeded in formation of a viscous gel material by means of reaction of calcium metaphosphate glass powders, whose surface chemical potentials were enhanced by crush of the glass, with distilled water.5 We consider that this phenomenon is "chemicovectorial" effect.6 At this stage, hydrogelation of magnesium metaphosphate, calcium metaphosphate, and zinc metaphosphate glass powders were found.7 It was reported that these gel materials have numerous protons and show the high conductivities of $10^{-3}$–$10^{-2}$ S/cm.7,8

We are now discussing fuel cells and hydrogen gas sensors using the metaphosphate glass-derived hydrogels. In the present work, the possibility for a new application to an electric double layer capacitor (EDLC) electrolyte will be discussed utilizing high ionic conductivities of the hydrogels. A typical EDLC includes an electrolyte sandwiched with two electrodes. In general, acids, bases, or salts dissolved in aqueous or organic solvents are used for the electrolytes. The aqueous liquid electrolytes (e.g., sulfuric acid) have been applied to EDLC because of their high conductivity at around room temperature. However, the corrosive aqueous liquid electrolytes may induce dangerous leakage, resulting in degradation in safety and lifetime of EDLC. To solve the problem, EDLC using a solid electrolyte such as Nafion® membrane is investigated, but it is not easy to prepare the excellent contact of the electrolyte with the electrodes.10 EDLC consisting of the glass-derived hydrogels which show relatively high viscosity, may have an advantage in preparation of EDLC since good handling and safety due to no leakage of liquid components are expected.

EXPERIMENTAL PROCEDURE

A glass having a nominal composition of $\text{MO}_2\text{P}_2\text{O}_7$ (M=Mg, Ca, Zn) in molar ratio was prepared by melting a batch mixture of reagent-grade chemicals such as $\text{MgO}$, $\text{CaCO}_3$, $\text{ZnO}$, and $\text{H}_3\text{PO}_4$ (85% liquid) under air in a Pt crucible at 1300 °C for 0.5 h. The melt was poured onto an iron plate and quenched by pressing. The resulting glasses were crushed using an alumina mortar below 10 µm in diameter. A mixture of the glass powders and distilled water (DW) was placed on a polystyrene dish. The dish was shielded with a polystyrene cover using vinyl tape for prevention from serious drying and then the sample was held at room temperature for 3 days to prepare metaphosphate glass-derived hydrogels. The weight ratio of a mixture of the glass powders and DW is 1:1 (in this work, 2 g : 2 g). Magnesium metaphosphate,
calcium metaphosphate, and zinc metaphosphate glass-derived hydrogels are denoted as MP, CP, and ZP gels, respectively.

$^{31}$P magic angle spinning nuclear magnetic resonance (MAS-NMR) spectrum of the mixture was recorded on a Varian Unity 400 plus NMR spectrometer operating at 161.906 MHz, with a spinning speed of 3 kHz, a delay time of 10 sec, and pulse length of 8.8 μsec.

The hydrogel was filled in silica glass tube of 6-mm inner diameter and 0.5-mm height. The glass tube filled with the hydrogel was sandwiched with carbon papers (specific surface area 10 m$^2$/g) as electrodes of EDLC cell. Electrochemical properties of the hydrogel-based EDLC cell was examined by cyclic voltammetry, chronoamperometry using ALS electrochemical analyzer Model 630A, and charge-discharge test using Solartron SI-1287 electrochemical interface, and self-discharge test using Keithley 199 system DMM/scanner in an ambient atmosphere at room temperature. The cyclic voltammetry was carried out the scan rate of 1 mV/s in the potential window of 0–1 V up to 35 cycles. The charge-discharge test was carried out the fixed current of +2 and −2 μA in the potential window of 0–1 V up to 50 cycles. The self-discharge curve was recorded after constant-voltage charging at 1 V for 24 h.

RESULTS AND DISCUSSION

When MO$_2$P$_2$O$_7$ (M=Mg, Ca, Zn) glass powders are placed in contact with DW, they were converted into viscous products within 10 min. The mixture of their glass powders and DW was completely converted into a transparent gel product with high viscosity after 2 days. These hydrogels seem to be similar, in term of viscosity, to coagervation derived from mixed solutions of sodium polyphosphate and CaCl$_2$ under appropriate conditions.

Figure 1 shows $^{31}$P MAS-NMR spectra of MP, CP, and ZP gels. Generally, for the metaphosphate glasses consisting of long-chain phosphate structure, an isotropic peak with the broad width around −25 ppm for the $Q^0$ group (the bonding of PO$_4$ tetrahedron is described as $Q^n$ units, where $n$ is the number of bridging oxygens to neighboring tetrahedra) is seen. The three hydrogels have $Q^0$ and $Q^1$ peaks, due to the orthophosphate group and the end phosphate group, respectively, which are not seen for the metaphosphate glasses. The glasses are

FIGURE 1. $^{31}$P MAS-NMR spectra of (a) MP gel, (b) CP gel, and (c) ZP gel. Chemical shifts were measured relative to 85%H$_3$PO$_4$. 

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suggested to be immediately hydrolyzed to break the phosphate chains, resulting in formation of the \( Q^0 \) and \( Q^1 \) groups.

In case of MP and CP gels, small three peaks in the \( Q^2 \) band of \(-20 \text{ to } -28 \) ppm were reported to be observed.\(^5,7\) These peaks are suggested to be due to \( \text{H}^+ \)-coordinated \( \text{PO}_4 \), \( \text{Mg}^{2+} \) or \( \text{Ca}^{2+} \)-coordinated \( \text{PO}_4 \), and long polyphosphate in order of the increasing magnetic field. Similarly, the peaks are also observed in ZP gel. This result shows that these hydrogels are based on the long-chain phosphate structure. The peak widths of ZP gel is narrower than those of MP and CP gels. The origin is not clear yet at this stage. Further investigation to clarify the structure of ZP gel is in progress.

Figure 2 shows cyclic voltammograms at the 35th cycle of the EDLC cells with electrolytes consisting of (a) MP gel, (b) CP gel, and (c) ZP gel. Three cyclic voltammograms show no peaks of oxidation-reduction processes in the range of 0–1 V; their almost rectangular shapes imply that they are possible capacitors. Charge and discharge curves are symmetrically drawn; the charge/discharge processes are reversible. Charge amounts were estimated by integrating the charge and discharge curves, and the amounts were converted to specific capacities; specific charge capacities were 12, 20, and 66 mF/g, specific discharge capacities were 11, 18, and 63 mF/g for MP, CP, and ZP gels, respectively. The hydrogels have no differences of capacities and high-rate capabilities between charge and discharge.

Figure 3 shows charge-discharge curves at the 50th cycle of the EDLC cells with electrolytes consisting of MP, CP, and ZP gels. Three charge-discharge curves are almost linear triangular shapes such as a typical EDLC, but the charge and discharge curves are distorted slightly by overvoltage due to high internal resistance of EDLC cells.\(^10\) The internal resistance of EDLC cell is expected to decrease with decreasing the thickness of the cell. Specific charge and discharge capacities were estimated to be 7, 19, and 52 mF/g for MP, CP, and ZP gels, respectively. These specific capacities are corresponding to those obtained from cyclic voltammogram.
Figure 4 shows self-discharge curves of the EDLC cells with electrolytes consisting of MP, CP, and ZP gels. Each cell with electrolyte consisting of the hydrogel shows a slow self-discharge curve; open circuit potentials after 24 hours are 0.36, 0.47, and 0.58 V for MP, CP, and ZP gels, respectively. Two-step discharge process, that is, a fast discharge in the initial 6 hours and a slow discharge after 6–24 hours, are observed in the curves of the hydrogels.

The EDLC cell consisting of ZP gel shows much higher capacity than that consisting of MP or CP gel and the most excellent self-discharge behavior. This is suggested to originate from differences among properties of bivalent metal ions in the hydrogels. The hard-soft acid-base (HSAB) principle gives a definition that central metal ions; ligands of complex are classified into Lewis acids and Lewis bases, respectively. Its bold Lewis acid/base statement "soft likes soft; hard likes hard" may be widely used.14 In the HSAB principle, Zn2+ ion is classified as a "borderline" and Mg2+ and Ca2+ ions are classified as "hard acids".15 H2O, OH−, and PO43− ions in the hydrogels are classified as "hard bases". Zn2+ ion may be more polarizable in the hydrogel than Mg2+ and Ca2+ ions; ZP gel has an high ability to store an electric charge. ZP gel is the most promising candidate as an EDLC electrolyte for storage of the electric charge in the present hydrogels.

Figure 5 shows chronoamperogram of an EDLC cell with electrolyte consisting of ZP gel. Charge-discharge currents settle to ~0 A within a few seconds; ZP gel has fast charge-discharge ability, which is one of the essential properties as an EDLC electrolyte. Maximum charge-discharge currents slightly increase with increasing the measurement time. ZP gel may infiltrate into pores of the electrodes to form fine contacts at the electrode-electrolyte interfaces.

**SUMMARY**

When magnesium metaphosphate, calcium metaphosphate, or zinc metaphosphate glass powders were contacted with water, their hydration started immediately, resulting in formation of high viscous hydrogels including orthophosphates and long-chain phosphates coordinated to H+ or M2+ (M=Mg, Ca, Zn) ions. Since the hydrogels show high proton conductivities, their possibility as EDLC electrolytes was discussed. EDLCs consisting of metaphosphate glass-derived hydrogels have no oxidation-reduction
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processes in the range of 0–1 V. They showed high rate charge-discharge capabilities and excellent self-discharge behaviors. The EDLC cell consisting of ZP gel showed much higher capacity than that of MP or CP gel and fast charge-discharge ability. Although the specific capacities of the hydrogels in the present work are not large at this stage, we expect that they can be improved after optimizing the cell structure, especially, the electrode structure.

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