Preparation of Fast Proton-Conducting Zinc Metaphosphate Hydrogel and Its Potential Application to Electric Double-layer Capacitors

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A novel highly viscous hydrogel electrolyte with high proton conductivity was prepared via hydration of zinc metaphosphate glass powders. The hydrogel showed a high electrical conductivity of $\approx 5\,\mathrm{mS\,cm^{-1}}$ at room temperature due to proton hopping between P–OH groups and water molecules. The hydrogel exhibited a low self-discharge rate. Chronoamperometric measurements indicated that the hydrogel has fast charge-discharge capability.

A great deal of attention has been paid to high proton-conducting materials because of their practical use in fuel cells,[1] capacitors,[2] and chemical sensors.[3] Such proton-based energy systems are clean and can produce high energy around room temperature without the emission of harmful pollutants. Liquid electrolytes (e.g., sulfuric acid, phosphoric acid) and solid-state electrolytes (e.g., Nafion®) have been investigated.[2] However, these materials still have problems. Although liquid electrolytes have an advantage in that they allow most electrode surfaces to be used, they may experience dangerous leakage. In contrast, solid-state electrolytes may develop contact resistance at electrode/electrolyte interfaces.

Recently, we found a highly viscous calcium metaphosphate hydrogel, which is derived from a mixture of distilled water and melt-quenched calcium metaphosphate glass powders.[4] Metaphosphate glass powders crushed below 10 μm have high surface chemical potentials, i.e., the high reactivity with water molecules. The hydrogel includes large numbers of P–OH groups and water molecules, and its conductivity is as high as 4–5 $\mathrm{mS\,cm^{-1}}$ around room temperature.[5] The proton dissociation energy is related to the strength of the hydroxy bonds. A P–OH bond, which is strongly hydrogen-bonded with water molecules, is appropriate for promoting proton conduction. Phosphate hydrogels also have advantages such as their ability to be shaped or formed as thin films. Their fluidity may reduce the tendency for the contact resistance.

Calcium metaphosphate glasses consist of long phosphate chains. Calcium ions serve as ionic crosslinks between the non-bridging oxygens of two different chains. It is known that $MO{\cdot}P_2O_5$ (e.g., M = Ca, Mg, Zn, Ba, Sr, etc.) glasses are materials with phosphate chains. In the hard–soft acid-base (HSAB) theory, Zn^{2+} ion is classified as a "borderline" and is more polarizable than Ca^{2+}, Mg^{2+}, Ba^{2+}, or Sr^{2+} ions which are classified as a "hard acid.[6]" We anticipated that polarizable hydrogels is applicable to energy-storage devices, such as electric double-layer capacitors (EDLCs). In the present letter, we report the hydrogelation of the zinc metaphosphate glass and its potential in use as an EDLC electrolyte.

Nominal compositions of $MO{\cdot}P_2O_5$ (M = Ca, Zn) metaphosphate glasses were prepared by a conventional melt-quenching technique using reagent grade $CaCO_3$ or ZnO and H_3PO_4 (85% liquid).[4] These glasses were crushed using an alumina mortar to below 10 μm in diameter. One gram of the glass powders and 1 mL of distilled water (DW) were mixed and held in tightly sealed vessels for 3 days at room temperature to form a viscous transparent hydrogel. Hereafter, calcium or zinc metaphosphate is denoted as either CP or ZP.

We have previously reported that CP gels have high viscosities.[4] Likewise, ZP gel have high viscosity of 1.5 Pa s at room temperature. X-ray diffraction analysis revealed no peaks due to crystalline phases.

^{31}P magic-angle spinning nuclear magnetic resonance (MAS-NMR) was used to determine structural changes through the gelation of ZP glass powders. Figure 1 shows the NMR spectra of the samples before and after DW addition to the ZP glass powders. The bonding of the PO_4 tetrahedra is described in terms of Q^n groups, where n represents the number of oxygens bonded to phosphorus.[7] A broad Q^2 signal around −20 ppm is seen for as-prepared ZP glass powders, indicating that the glass consists of long phosphate chains. On the other hand, after DW was added to the glass powders, Q^0 and Q^1 groups appear along with Q^2 groups in 10 min. The surfaces of glass powders are rapidly hydrolyzed. However, there are only slight differences of intensities of Q^0 and Q^1 groups between the samples after 10 min and 3 days, suggesting that the phosphate chains remain under hydrogelation of the glass powders.

Three signals in the Q^2 band from −20 to −28 ppm are assigned to ring or linear phosphates, phosphate chains connected to protons, and phosphate chains connected to M^{2+} ions (M =

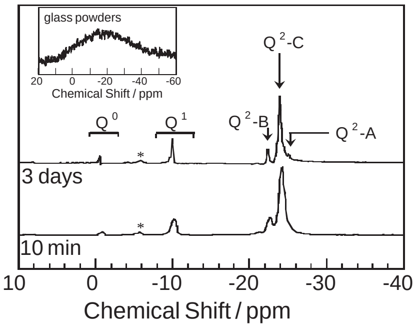

Figure 1. ^{31}P MAS-NMR spectra before and after DW addition to the zinc metaphosphate glass powders. The inset shows the spectrum of as-prepared $ZnO{\cdot}P_2O_5$ glass powders. The mixture of the glass powders and distilled water were held at room temperature for 10 min and 3 days. Q^2-A, Q^2-B, and Q^2-C are assigned to ring or linear phosphates, phosphate chains connected to protons, and phosphate chains connected to Zn^{2+} ions, respectively.[4] (*: unassigned group)

Zn for ZP glasses).[4] Zn^{2+} ions in the ZP glass have been suggested from the electric field strength, F,[8,9] to be more strongly crosslinking with phosphate chains to make a stronger bond between P and O than Ca^{2+} ion in the CP glass. When DW was added to ZP glass powders, hydration occurred with a stronger exothermic reaction in comparison with that of CP glass. This reaction is believed to be related to bonding strengths of the phosphate chains in the glasses.

The electrical conductivities of the hydrogels were determined from Cole–Cole plot by an ac method at 30 °C under relative humidity of 70% to prevent drying of hydrogels. A Solartron SI-1260 impedance analyzer was used with frequencies ranging from 1 to 10^7 Hz. For electrical measurements, hydrogels were placed in a silica glass tube. The hydrogels exhibited high proton conductivities of 4.8 and 6.6 mS cm^{-1} for CP and ZP gel, respectively. The activation energies of proton conduction estimated from Arrhenius plot ($\log(\sigma)$ vs T^{-1}) ranging from 30 to 60 °C are around 0.2 eV. The proton conduction is suggested to be related to the hopping between hydroxy P–OH groups and water molecules.[10] Since Zn^{2+} ions in ZP gel are connected to phosphate chains and the gel contains no carriers other than protons, the protons act as electrical charge carriers.

Self-discharge curves of CP and ZP gels after charging at 1 V for 24 h were measured. In the ZP gel, open-circuit potentials were 0.75 and 0.58 V after 5 and 24 h, respectively, whereas those of CP gel were 0.65 and 0.47 V. The ZP gel retained higher potentials than CP gel within the experimental period. As mentioned above, Zn^{2+} ion is supposed to be polarized more easily as compared to a "hard acid" such as Ca^{2+} ion. These results indicate that Zn^{2+} ion plays an important role in reduction of self-discharge of hydrogel electrolytes.

Cyclic voltammetry measurements were carried out at a scan rate of 1 mV s^{-1} in the potential window of 0 to 1 V at room temperature. Carbon papers (specific surface area of 10 m^2 g^{-1}, total pore volume of 0.1 cm^3 g^{-1}, average pore diameter of 3.8 nm) were used as polarizable electrodes. Figure 2a shows cyclic voltammograms of CP and ZP gels. Both CP and ZP gels show an ideal capacitor behavior with a steep current change at the switching potentials (0 and 1 V), resulting in a rectangular-shaped *i*–V curve. This indicates that the hydrogels are electrochemically stable within the potential range from 0 to 1 V. The discharge capacitances calculated from voltammograms are 18 and 63 mF g^{-1} for CP and ZP gels, respectively. This difference results from the fact that the ZP gel shows higher open-circuit potentials than those of CP gel.

Chronoamperometry measurements were carried out under switching potentials of 0 and 1 V with pulse width of 10 s. The same carbon papers were used as electrodes. Figure 2b shows the chronoamperometric plot of the ZP gel. Note that charge-discharge currents of ZP gel settle to ≈0 A within 5 s, suggesting that the ZP gel has fast charge–discharge capability.

Table 1 summarized viscosity, conductivity, and capacitance of ZP and CP gels. The differences in the values may be closely related to bonding strengths of phosphate-chains in the glasses. Further investigation is in progress.

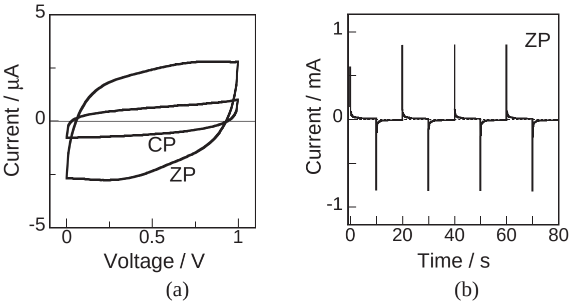

Figure 2. (a) Cyclic voltammograms of the ZP and CP gels, and (b) chronoamperogram of the ZP gel.

Table 1. Viscosities, conductivities, and capacitances of CP and ZP gels measured at room temperature

Gel	Viscosity /Pa s	Conductivity /mS cm^{-1}	Capacitance /mF g^{-1}
CP	0.36	4.8	18
ZP	1.5	6.6	63

EDLCs operate on the principle that double-layers form at electrode/electrolyte interfaces, where electric charges are accumulated on the electrode surfaces. Granular or fibrous carbons are widely used for EDLC electrodes because of their high specific surface areas as well as their relatively high electric conductivities.[11] Although the specific capacitance and the charge–discharge currents of the ZP gel in the present work are not large enough at this stage, we expect that they can be improved through the use in a composite with high-specific-surface-area carbon electrodes.

In summary, a novel viscous gel material, derived via hydration of the metaphosphate glass powders, exhibited a low self-discharge rate and fast charge–discharge capability. The material is expected to be applied to an EDLC electrolyte.

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