Supporting Information for

Coordination Polymer Glass from Protic Ionic Liquid: Proton Conductivity and Mechanical Property as Electrolyte

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References
EXPERIMENTAL

Materials and methods: ZnO (99.99% trace metals basis) and diethylmethylamine were purchased from Aldrich, and phosphoric acid (85% in H₂O) was purchased from Wako pure chemical industries. All reagents were used without further purification process. The reported ionic liquid (dema)(H₂PO₄) (2) was synthesized according to the literature method.¹

Synthesis: Synthesis of Zn-dema-H₂PO₄ (1): ZnO (3.25 g, 0.04 mol) and 3 equimolar of phosphoric acid (85%) (8.18 mL, 0.12 mol) were mixed and grinded in a mortar until form transparent colorless liquid, then, excess H₃PO₄ was neutralized by addition of 1 equimolar diethylmethylamine (4.84 mL, 0.04 mol) and grinding for 30 min. Then resulting transparent colorless liquid was transferred to a round bottom flask and dried under reduced pressure at room temperature for 8 h and then at 120 °C for 2 h. After cooling to room temperature, transparent high viscoelastic colorless material was obtained (13.9 g). The chemical composition of 1 was determined by solid-state NMR and elemental analysis. (dema)₀.₃₅[Zn(H₂PO₄)₂.₃₅(H₃PO₄)₀.₆₅]. Elemental analysis calcd for C₁.₇₅H₁₁.₅₅N₀.₃₅O₁₂P₂Zn: C, 5.42; H, 3.00; N, 1.26, found C, 5.64; H, 3.36; N, 1.30. Density = 1.87 g cm⁻³.

Thermogravimetric analysis (TGA) were recorded using Rigaku TG8120 instrument under flowing N₂ with 10 K min⁻¹ scan rate. Differential Scanning Calorimetry (DSC) experiments were measured using Hitachi DSC 7020 instrument in an inert argon atmosphere. The sample was placed in an aluminum sample folder and a lid.

Impedance spectra from 30 °C to 120 °C under Ar atmosphere were collected using a BioLogic VSP-300 with an EC Frontier sample cell (SB1A, φ = 13 mm, d = 5 mm). The frequency ranges from 0.1 Hz to 1.0 MHz with a sinus voltage (10 mV) was collected at each temperature. The measurements were performed at thermal equilibrium after holding 30 min at each temperature. Collected impedance data were treated and analyzed by a ZView software. The VFT (eq. 1) fitting (Levenberg-Marquardt Method) was performed using an Origin 2018 software.

\[ \sigma(T) = A \exp\left(\frac{-B}{T-T_0}\right) \]  
(eq. 1)

A is proportional to the concentration of the carrier ions, B is the pseudo activation energy for the ion conduction, while T₀ is the ideal glass transition temperature.
Proton Transport number \( (t_{H^+}) \) was determined by the electromotive force (EMF) measurements using a BioLogic VSP-300. A membrane filter (Omnipore\textsuperscript{TM} Merck, 10.0 uM, 2 X 2 cm) was impregnated with 1 or 2 at 120 °C or at room temperature, respectively. The membrane was then sandwiched between Pt loaded carbon papers (1.5 mg cm\(^{-2}\), \( \phi = 5 \) mm, Chemix Co. Ltd.) and placed into a single cell with straight gas flow channels. On one side \( \text{H}_2/\text{Ar} \) (3.99 vol%) was fed continuously while on the other side the \( \text{H}_2/\text{Ar} \) gas was diluted with \( \text{N}_2 \) (99.99995 vol%) gas to achieve variable partial pressures. The \( \text{H}_2 \) concentration was precisely controlled by mass flow controllers (SEC-E40, Horiba, ltd.) while maintaining total gas flow rate of 100 mL/min on both the sides. The assembly was maintained at desired temperature using Oven and stabilized for ~10 min before measurement. The EMF generated between the sensing and counter electrodes were measured under different \( \text{H}_2 \) partial pressures \( (P_2) \) on equilibrating for 3 min. The proton transport number \( (t_{H^+}) \) is calculated using following equation

\[
E = \frac{RT}{2F} \ln \left( \frac{P_1}{P_2} \right) \quad \text{(eq. 2)}
\]

where, \( E, T, R, F, P_1, P_2, \) and \( t \) denote EMF, temperature, the gas constant, Faraday constant, partial pressure of \( \text{H}_2 \) gas, and transport number, respectively.

The polarization curves of a \( \text{H}_2/\text{O}_2 \) fuel cell were recorded using a Solartron SI 1287. Gas diffusion electrodes (0.3 mg/cm\(^2\), 46.5 wt% Pt/C) for both cathode and anode were fabricated by spray coating of 46.5wt% Pt/C (TEC10E50E, Tanaka Kikinzoku, ltd.) onto the carbon paper gas diffusion layer (Sigracet\textsuperscript{®} 29 BC, SGL Carbon, GmbH.). A membrane electrode assembly (MEA) was prepared by sandwiching the electrolyte membrane between two gas diffusion electrodes, and the contact area between electrode and electrolyte were \( \phi = 7 \) mm. The resulting MEA was installed into a single cell with straight gas flow channels, and the dry \( \text{H}_2 \) (>99.999vol%) and \( \text{O}_2 \) (>99.999vol%) gases were supplied to the single cell at a flow rate of both 100mL/min under anhydrous conditions. The flow rate was controlled by mass flow controllers (SEC-E40, Horiba, ltd.). The polarization curves of the single cell were measured at 120 °C.

Extended X-ray Absorption Fine-Structure Spectroscopy were collected on beamline BL14B2 at SPring-8. X-ray absorption spectra in the energy region of the Zn K-edge were measured in transmission mode. Fourier transformation was \( k^3 \)-weighted in the \( k \) range from 3.0 to 12.5 Å\(^{-1} \). The data processing and coordination number fitting were performed with Athena and Artemis software, respectively. All samples were measured under Ar atmosphere. The resulting \( k^3 \)-weighted radial distribution function of 1 was fitted by a FEFF calculation using first Zn-O single scattering path of Zn(SO\(_4\))·7H\(_2\)O.
X-ray total scattering data were collected with four CdTe and two Ge detectors covering the $Q$ range up to 25 Å$^{-1}$ at SPring-8 on beamline BL04B2 (61.377 keV; $\lambda = 0.2020$ Å). The collected scattering data was applied absorption, background, and Compton scattering corrections, and then normalized to give the Faber–Ziman total structure factor $S(Q)$. Then, the pair distribution function was calculated by Fourier transforming the $S(Q)$ with a Lorch modification function. Reverse Monte Carlo structural modeling of amorphous state of 1 (a cubic cell; $a = b = c = 27.44$ Å) was performed using the RMC++ program. The initial structure was generated by random command. The initial configuration was converted by hard-sphere Monte Carlo simulations with constraints applied to avoid unrealistic structures. The closest distance, bond angles and bond length constraints were performed to form reasonable diethylmethylammonium cations and H$_2$PO$_4$/$\text{H}_3$PO$_4$ structures (the constraints were listed below). The closest atom–atom distance was chosen based on the information from related crystal structures of TBA(H$_2$PO$_4$) and Zn$_3$(PO$_4$)$_2$$\cdot$4H$_2$O. After the hard-sphere Monte Carlo simulations, RMC simulations containing X-ray $S(Q)$ and $k^3\chi(k)$ EXAFS data were performed with the constraint of averaged coordination number of Zn-O = 4.6. The EXAFS back scattering tables were prepared by the FEFF calculations. The reported atomic scattering factors and anomalous scattering factors of each atoms were used for these calculations. The protons were put using constraints and RMC simulations, although the X-ray $S(Q)$ experimental data does not include much information from protons. Therefore, the position of protons from RMC structure was not used for discussion of proton conducting mechanism.

The list of constraints applied in RMC structural modeling is listed as follows

| Bond constraints | distance (Å) | Angle constraints | degree (°) |
|-----------------|-------------|------------------|------------|
| N-C             | 1.45-1.60   | C-N-C            | 110        |
| C-C             | 1.45-1.60   | C-C-N            | 110        |
| C-H             | 0.80-1.00   | C-N-H            | 110        |
| N-H             | 0.80-1.00   | C-C-H            | 110        |
| P-O             | 1.45-1.70   | H-C-H            | 110        |
| O-H             | 0.80-1.00   | O-P-O            | 110        |
| Zn-O            | 1.80-2.20   | P-O-H            | 110        |
|                 |             | O-Zn-O          | 105        |
Solid-state NMR experiments were performed on JNM-ECZ600R spectrometer (JEOL RESONANCE Inc., Japan) at 14.01 T with a $^1$H resonance frequency of 599.7 MHz, equipped with a 2.0 mm double resonance MAS probe (JEOL RESONANCE Inc, Japan). 1D $^1$H and $^{31}$P spectra, and $^1$H T$_2$ relaxation time were measured by single pulse and spin-echo pulse sequence, respectively, at 20 kHz spinning rate in the temperature range of 0-100 °C. RF field strength of $^1$H and $^{31}$P nuclei was 121.95 kHz at the $\pi/2$ pulse width of 1.98 µs and 131.58 kHz at the $\pi/2$ pulse width of 1.9 µs, respectively. The spectra were processed with the Delta software (JEOL RESONANCE Inc).

Laboratory scale powder X-ray radiation diffraction patterns were collected on a Rigaku SmartLab multipurpose diffractometer (CuKα; $\lambda = 1.540598$ Å).

FT-IR spectra were measured with a Thermo Scientific Nicolet Summit FT-IR equipped with a diamond ATR accessory.

Variable-temperature viscoelastic measurement was performed by using a rotational parallel-plate rheometer (Rheosol-G5000, UBM Co., Ltd.) under dry N$_2$ flow with applying oscillatory strain of 1 Hz. The sample-holding gap was set to 1.0 mm.
Scheme S1. Synthetic scheme of 1 (top) and 2 (bottom).

Table S1. VFT fitting parameters of H⁺ conductivity using eq. 1.

|   | A (S cm⁻¹) | B (K)      | T₀ (K)  | R²   |
|---|------------|------------|---------|------|
| 1 | 4.8 (±3.3) | 1400 (±294)| 155 (±21)| 0.999|
| 2 | 8.2 (±1.6) | 1600 (±74) | 179 (±4.4)| 0.999|
**Fig. S1.** Solid-state $^1$H NMR spectra of 1 (black) and 2 (red) at 20 °C. The assignments and integration values are also shown.
Fig. S2. Solid-state $^{31}$P NMR spectra of 1 (black) and 2 (red) at 20 °C.
Fig. S3. IR spectra of 1 (black) and 2 (red) at room temperature.
Fig. S4. (A) TGA curve of 1 under N₂ atmosphere (scan rate = 10 °C min⁻¹) and (B) DSC curves of first (blue) and second (purple) cooling, second (red) and third (orange) heating scans of 1 after initial first heating from room temperature under Ar atmosphere (scan rate = 10 °C min⁻¹). The viscoelastic 1 exhibited glass transition during cooling scan. Then, we determine the glass transition point in following heating scan ($T_g = 22 ^\circ C$). There is no peak assignable to crystallization up to 120 °C. However, continuous base line change around 60-100 °C cannot be assigned at this time. While the DMA properties at this temperature range exhibited similar complicated shape, this DSC baseline change is probably due to the change of coordination structures in Zn coordination polymer.
Fig. S5. DMA of 1 (black) and 2 (red) from −20 °C to 120 °C. The storage modulus and loss modulus were marked by circles (●) and squares (■), respectively.
**Fig. S6.** XAFS spectra of Zn K-edge of 1 (black) and references with known coordination structures: Zn(SO₄)·7H₂O (blue), Zn₃(PO₄)₂·4H₂O (green) and ZnO (red).
Fig. S7. Nyquist plots of (A) 1 and (B) 2 from 1.0 MHz to 0.2 Hz measured at 30-120 °C. The enlarged low resistance regions of (C) 1 and (D) 2 are also shown.
Fig. S8. Nyquist plots of 1 (black) and 2 (red) at 120 °C. The solid lines represent the fitted curves obtained by an equivalent circuit model (Fig. S8). Inset showed enlarged plot around low resistance region.
**Fig. S9.** Equivalent circuit for the fitting of impedance measurements. R1, R2 and Q1 represent the bulk resistance of 1 or 2, resistance and constant phase element of the interface between electrodes and electrolytes, respectively.
Fig. S10. Bode plots for the impedance measurements. $|Z|$ vs frequency plots for (A) 1 and (B) 2. Impedance phase angle vs frequency plots for (C) 1 and (D) 2. The fitted curves are plotted as blue lines by an equivalent circuit model shown in Fig. S8.
**Fig. S11.** OCV of a H₂/O₂ fuel cell using 1 as an electrolyte with PTFE (black) or without PTFE (red) at 120 °C without humidification.
| Atom | X      | Y      | Z     |
|------|--------|--------|-------|
| Zn44 | 0.2448261 | 0.8333216 | 0.4454987 |
| Zn43 | 0.5149518 | 0.1841990 | 0.20016481 |
| Zn42 | 0.4079465 | 0.7064724 | 0.7599793 |
| Zn41 | 0.5176467 | 0.3874308 | 0.9025062 |
| Zn40 | 0.7682691 | 0.1725405 | 0.25351639 |
| Zn39 | 0.145660 | 0.7602948 | 0.95890053 |
| Zn38 | 0.3980832 | 0.6960161 | 0.54316285 |
| Zn37 | 0.7682691 | 0.1725405 | 0.25351639 |
| Zn36 | 0.5176467 | 0.3874308 | 0.9025062 |
| Zn35 | 0.145660 | 0.7602948 | 0.95890053 |
| Zn34 | 0.3980832 | 0.6960161 | 0.54316285 |
| Zn33 | 0.7682691 | 0.1725405 | 0.25351639 |
| Zn32 | 0.5176467 | 0.3874308 | 0.9025062 |
| Zn31 | 0.145660 | 0.7602948 | 0.95890053 |
| Zn30 | 0.3980832 | 0.6960161 | 0.54316285 |

**Table S2.** Simulated RMC structure in cif format. This text file can be opened in a visualization software for crystal structures.
| H685 | H | 0.95452487 | 0.903893908 | 0.947136794 | H690 | H | 0.915046539 | 0.730285888 | 0.715606555 |
|------|---|------------|--------------|-------------|------|---|------------|--------------|-------------|
| H686 | H | 0.287921371 | 0.820085226 | 0.582261244 | H691 | H | 0.946464754 | 0.905288896 | 0.111585889 |
|------|---|------------|--------------|-------------|------|---|------------|--------------|-------------|
| H687 | H | 0.762441909 | 0.18794007 | 0.033956624 | H692 | H | 0.964101566 | 0.7060215558 | 0.6099284465 |
|------|---|------------|--------------|-------------|------|---|------------|--------------|-------------|
| H688 | H | 0.79711176 | 0.491412283 | 0.901094908 | H693 | H | 0.0082669354 | 0.436393057 | 0.478727548 |
|------|---|------------|--------------|-------------|------|---|------------|--------------|-------------|
| H689 | H | 0.99396116 | 0.521313391 | 0.867440322 |       |   |            |              |             |
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