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# Proton-conductive coordination polymer glass for solid-state anhydrous proton batteries†

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Designing solid-state electrolytes for proton batteries at moderate temperatures is challenging as most solid-state proton conductors suffer from poor moldability and thermal stability. Crystal–glass transformation of coordination polymers (CPs) and metal–organic frameworks (MOFs) *via* melt-quenching offers diverse accessibility to unique properties as well as processing abilities. Here, we synthesized a glassy-state CP, [Zn<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>6</sub>(H<sub>2</sub>O)<sub>3</sub>](1,2,3-benzotriazole), that exhibited a low melting temperature (114 °C) and a high anhydrous single-ion proton conductivity (8.0 × 10<sup>−3</sup> S cm<sup>−1</sup> at 120 °C). Converting crystalline CPs to their glassy-state counterparts *via* melt-quenching not only initiated an isotropic disordered domain that enhanced H<sup>+</sup> dynamics, but also generated an immersive interface that was beneficial for solid electrolyte applications. Finally, we demonstrated the first example of a rechargeable all-solid-state H<sup>+</sup> battery utilizing the new glassy-state CP, which exhibited a wide operating-temperature range of 25 to 110 °C.

## Introduction

The proton (H<sup>+</sup>) has a diameter of 0.84 fm and is easily localized in the solid state.<sup>1</sup> Fast-moving protons in solids are difficult to achieve, whereas solid-state H<sup>+</sup> conductors are widely used in various electrochemical applications, including fuel cells, electrochemical catalysis, and sensors.<sup>2</sup> Proton batteries are a new class of secondary batteries employing protons instead of metal ions as charge carriers.<sup>3,4</sup> They consist of faradaic electrodes and acidic electrolytes. Since the H<sup>+</sup> charge radius is significantly smaller than that of other ions, faster ion migration and negligible volume changes upon H<sup>+</sup> insertion/desertion are expected. Additionally, replacing high-cost Li<sup>+</sup> with cheaper and

more abundant H<sup>+</sup> provides a promising platform for environmentally benign and intrinsically safe energy storage.<sup>5–7</sup> Redox-active organic molecules, such as quinone-functionalized conductive polymers,<sup>4,8</sup> and metal oxides, including MoO<sub>3</sub>, WO<sub>3</sub>, and H<sub>x</sub>IrO<sub>4</sub>, are available as H<sup>+</sup> electrodes.<sup>9–11</sup> Though proton batteries show a smaller specific capacity with a limited number of applications, as compared to their metallic counterparts, diffusion-free charge transport *via* the Grotthuss mechanism in a defective, Prussian blue analog establishes a high-rate capability (380 A g<sup>−1</sup>) and extends cycling stability to over 0.5 million charge–discharge cycles, which is a unique advantage of aqueous proton batteries.<sup>6,12,13</sup> In spite of various choices of electrodes, electrolytes are mostly limited to aqueous H<sub>2</sub>SO<sub>4</sub> or H<sub>3</sub>PO<sub>4</sub>, which dictates the operating-temperature window and selection of usable electrodes.<sup>8,13–15</sup>

Safely extending the operating-temperature window to ~100 °C is essential for H<sup>+</sup> batteries to tolerate internal/external heat generation so that they can be used in various high-temperature applications, such as rescue/inspection robots, space exploration, and measure-while-drilling (MWD) equipment in the oil and gas industries.<sup>16</sup> As employing a conventional aqueous electrolyte is not possible at these high temperatures, solid-state H<sup>+</sup> batteries with anhydrous solid electrolytes would be more suitable. There are no reports of solid-state H<sup>+</sup> batteries working near or above 100 °C due to the difficulties in achieving high anhydrous H<sup>+</sup> conductivity, high-temperature stability, and moldability required for H<sup>+</sup> conductors.<sup>17</sup> Apart from achieving a high H<sup>+</sup> conductivity value (near 10<sup>−2</sup> S cm<sup>−1</sup>), high thermal/chemical stability, processing ability, and ion selectivity are also needed to expand the practicality of solid-state electrolytes. Single-ion conductivity in

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solid-state electrolytes is a core factor that promotes charge-transport efficiency and prevents anion polarization.<sup>18,19</sup> Discontinuities along the electrode–electrolyte interfaces and grain boundaries are primary bottlenecks for efficient utilization of solid electrolytes.<sup>17,20,21</sup>  $H^+$  conductivity at the grain boundary of most crystalline compounds requires a higher migration activation energy than that required by  $H^+$  conductivity through the bulk crystal (grain boundaries contribute up to 40–50% of the overall resistance for  $Li^+$  conductors).<sup>22–25</sup>

Coordination polymers (CPs) and metal–organic frameworks (MOFs) exhibiting high  $H^+$  conductivity over a wide temperature regime ( $\sim 200$  °C) represent a new class of solid-state  $H^+$  conductors.<sup>26–29</sup> Despite their remarkable  $H^+$  conductivity, their crystalline nature hinders their processing ability, thus limiting their practicality.<sup>30</sup> The glassy state of CP/MOFs is a strong platform to tackle these issues, and there have been increasing numbers of glassy-state CPs recently made from crystalline-state CPs.<sup>31–34</sup> Some of these glassy-state CPs show anhydrous  $H^+$  conductivity superior to that of their crystalline counterparts by several orders of magnitude.<sup>35,36</sup> Moreover, the vitrifying/melting behavior provides these CPs with processing capabilities and forms a grain-boundary free monolith and a flawless heterogeneous interface.<sup>31–34,37–41</sup>

To address this issue, we have developed a new  $H^+$ -conductive CP glass suitable for high-temperature anhydrous solid-state  $H^+$  batteries. By optimizing the  $pK_a$  value of the component with 1,2,3-benzotriazole (BTA,  $pK_a$  1.6) and the extended hydrogen-bonding network in  $Zn^{2+}$ -based CPs, the material demonstrated high anhydrous  $H^+$  conductivity ( $8.0 \times 10^{-3}$  S  $cm^{-1}$  at 120 °C), relatively low melting point (114 °C), and mechanical softness (42.8 Pa s at 120 °C), which are suitable for electrolytes. The structure and properties were characterized by single-crystal X-ray diffraction (SC-XRD), thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), impedance spectroscopy, electromotive force measurements, and solid-state NMR. We also demonstrated a full-cell evaluation of the anhydrous solid-state  $H^+$  batteries at 25, 100, and 110 °C.

## Results and discussion

### Crystal structure of $[Zn_3(H_2PO_4)_6(H_2O)_3](BTA)$ (**1a**)

Zinc oxide, phosphoric acid, and BTA were subjected to mechanical milling to form the CP (**1a**) as a white crystalline powder. SC-XRD analysis of **1a** provided its chemical formula,  $[Zn_3(H_2PO_4)_6(H_2O)_3](BTA)$ , and it was found to exist as a one-dimensional (1D) chain along the  $a$ -axis (Fig. 1). Three crystallographically independent octahedral  $Zn^{2+}$  ions were identified, each with six bridging  $H_2PO_4^-$  anions and one water molecule coordinated to them (Fig. 1A). BTA was stacked in a 1D fashion along the  $a$ -axis and surrounded by six chains of  $ZnO_6$  octahedra, which orderly arranged in the  $bc$  plane due to hydrogen-bonding interactions (Fig. 1B and C). Furthermore, **1a** is an isostructure of previously reported  $[Zn_3(H_2PO_4)_6(H_2O)_3](benzimidazole)$ ,<sup>38</sup> and it is expected that the dynamics of the phosphates bridging the  $Zn^{2+}$  ions (through a single

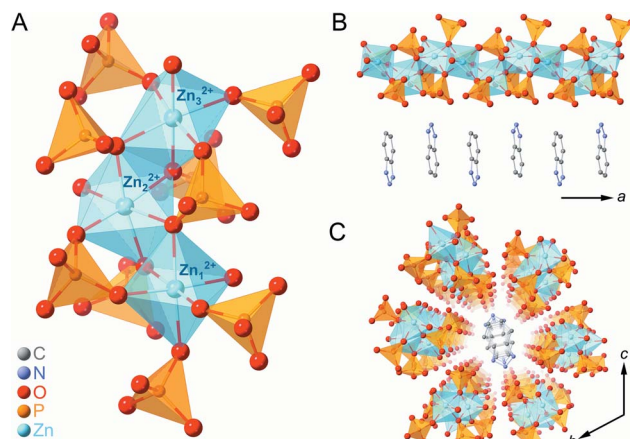


Fig. 1 (A) Local coordination geometry in **1a**. (B) Crystal structure of the one-dimensional (1D) chain along the  $a$ -axis. (C) Packing structure of **1a** on the  $bc$ -plane. Zn, P, O, C, and N atoms are represented by light blue, orange, red, grey, and blue spheres, respectively. H atoms are omitted for clarity.

bridging oxygen atom ( $\mu_2$ ) and the non-coordinating BTA could facilitate an anhydrous  $H^+$  migration.<sup>2,38,42,43</sup>

The gram-scale synthesis of **1a** was feasible *via* mechanical milling for 1 h followed by vacuum drying for 3.5 h to remove excess water molecules. Powder X-ray diffraction (PXRD) of **1a** (Fig. S1†) demonstrated a pattern identical to the simulated SC-XRD pattern. The absence of residual free phosphoric acid in **1a** was confirmed using both inductively coupled plasma emission spectroscopy (ICP-ES) and  $^{31}P$  magic-angle spinning (MAS) solid-state NMR (Fig. S2†).<sup>44</sup> A P to Zn ratio (1 : 1.97) slightly lower than the theoretical ratio (1 : 2) suggested the presence of a small amount of structural defects. All peaks in  $^{31}P$  NMR were located in the range of orthophosphate, suggesting that no condensation occurs during the mechanical synthesis.<sup>45–47</sup> TGA of **1a** showed a gradual weight loss due to the release of coordinated water at 100 °C (Fig. S4†). The total weight loss of dehydrated **1a** is equivalent to the release of three coordinated water molecules (5.7 wt%). This dehydrated state is henceforth denoted as **1**. A reversible structural change between **1a** and **1** upon water adsorption and desorption was observed by PXRD (Fig. S5†).<sup>48–50</sup> The release of each water molecule from the octahedral ( $O_h$ ) coordination sphere caused the 1D chain structure to deform around the  $Zn^{2+}$  ion. Under ambient air, **1** converted to **1a** by capturing atmospheric moisture.<sup>38</sup>

### Crystal melting and glass formation

Differential thermal analysis of **1a** by TGA (Fig. S4†) showed two endothermic peaks due to the release of coordinated water and crystal-to-liquid transformation and only the latter peak was observed in **1**. DSC of **1** (Fig. 2A) showed an endothermic peak with an onset melting point ( $T_m$ ) of 114 °C. Two minor endothermic peaks before that of the  $T_m$  were assigned to the dehydration of adsorbed water during the measurement setup.<sup>33</sup> The  $T_m$  of **1** was 50 °C lower than that of the isostructure,  $[Zn_3(H_2PO_4)_6(H_2O)_3](benzimidazole)$ , as BTA exhibits





Fig. 2 (A) First- (blue) and second-cycle (red) DSC profiles of **1** from  $-10$  to  $140$  °C (begin with a heating step from  $30$  °C). The inset shows a photo of **1m** at  $140$  °C. (B) Temperature-dependent viscosity of **1g**. (C) DMA of **1g** from  $-30$  to  $120$  °C (heating rate of  $2$  °C  $\text{min}^{-1}$ ). The storage ( $G'$ ) and loss ( $G''$ ) moduli were marked as (▲) and (●), respectively. (D) Arrhenius plots of the anhydrous conductivity of **1** (●) and **1g** (▲) under an Ar atmosphere. The inset shows the Nyquist plot of **1** (●) and **1g** (▲) at  $50$  °C.

lower  $T_m$  and  $pK_a$  values than those of benzimidazole.<sup>31,33</sup> Additionally, no significant weight loss was seen at  $120$  °C after 12 h, confirming a stable liquid state (Fig. S6†). The liquid/molten state of **1** is henceforth referred to as **1m**. The first cooling process in DSC confirmed the vitrification of **1m** to a glassy state of **1** (denoted as **1g**) that demonstrated a glass transition temperature ( $T_g$ ) of  $7.6$  °C, exhibiting no Bragg diffraction, and was categorized as melt-quenched glass (MGQ) (Fig. S7†).<sup>34</sup>

DMA and viscosity evaluation of **1g** further determined its processing ability, where its viscosity (Fig. 2B) was observed above the Littleton softening point ( $10^{6.6}$  Pa s) from  $-30$  to  $90$  °C until it sharply decreased below the working point regime ( $10^3$  Pa s) above  $100$  °C. The working point defines the viscosity regime in which the viscosity of a substance is equivalent to that of soda-lime-silica glass above  $1100$  °C (suitable for industrial forming processes).<sup>51</sup> The storage modulus ( $G'$ ) dominated the loss modulus ( $G''$ ) from  $-30$  to  $90$  °C, verifying the solid character of **1g** (Fig. 2C). Immediate reduction of  $G'$  at  $100$  °C represents the softening of **1g**, and the  $G'/G''$  crossover indicates the range in which **1g** starts to behave like a viscous liquid.<sup>31,52</sup>

### Anhydrous $H^+$ conductivity

We measured the  $H^+$  conductivity of **1** and **1g** via variable-temperature alternating current (AC) impedance under an Ar atmosphere to exclude the influence of water molecules (Fig. 2D and S9†). The Nyquist plots were fitted with a single impedance response corresponding to the bulk resistance without the grain-boundary region.<sup>52,53</sup> The conductivity of **1** was measured from  $30$  to  $100$  °C, where the crystalline phase of **1** was preserved. We observed conductivity values of  $3.3 \times 10^{-7}$  S  $\text{cm}^{-1}$  and  $9.0 \times 10^{-5}$  S  $\text{cm}^{-1}$  at  $30$  and  $60$  °C, respectively. The conductivity value increased rapidly upon heating, reaching  $1.2 \times 10^{-3}$  S  $\text{cm}^{-1}$  at  $100$  °C. The activation energy of **1** from  $30$  to  $60$  °C was  $1.22$  eV. Above  $60$  °C, the Arrhenius plot flattened and the activation energy reduced to  $0.57$  eV. Utilizing BTA with its low  $pK_a$  in **1** provided higher conductivity values than those of the isostructure  $[\text{Zn}_3(\text{H}_2\text{PO}_4)_6](\text{HBim})$  at  $30$  °C ( $1.2 \times 10^{-7}$  S  $\text{cm}^{-1}$ ) and  $60$  °C ( $1.5 \times 10^{-5}$  S  $\text{cm}^{-1}$ ).<sup>38</sup>

To highlight the advantage of glass transformation on ionic conductivity, we prepared a monolith (**1g**) via melt-quenching directly into the electrochemical cell for impedance analysis. Upon the crystalline-to-glassy state transformation, only the



bulk impedance response pattern was obtained (Fig. S9†) and it was identical to that of **1a** in the higher temperature range. The Arrhenius plot (Fig. 2D) shows two different activation energy regimes: 0.59 eV between 30 and 60 °C and 0.39 eV from 60 to 120 °C. At 30 °C, **1g** exhibited a conductivity value of  $3.3 \times 10^{-4} \text{ S cm}^{-1}$ , which increased to  $4.9 \times 10^{-3} \text{ S cm}^{-1}$  and  $6.5 \times 10^{-3} \text{ S cm}^{-1}$  at 100 and 110 °C, respectively. A conductivity value of  $8.0 \times 10^{-3}$  was achieved at 120 °C (molten state, **1m**). Long-term conductivity retention was also evaluated. After 12 h, less than 4% and 10% loss in conductivity was observed at 100 and 120 °C, respectively (Fig. S10†). The contribution of the ions of interest to the total current can be distinguished *via* the  $\text{H}^+$  transport number (transference number) measurements.<sup>52,54</sup> The transport numbers of most aqueous and ionic liquid electrolytes are lower than 0.6.<sup>54–56</sup> The transport number of **1m** was elucidated *via* electromotive force (EMF) measurements, which were conducted for different hydrogen partial pressure ( $-\ln(P_1/P_2)$ ) values of 0.22, 0.51, 0.69, 0.92, and 1.61) at 120 °C (Fig. S11†).<sup>57</sup> According to eqn S1 (ESI),† the  $\text{H}^+$  transference number of **1g** is 1.0, indicating an ideal single-ion  $\text{H}^+$  conductivity. The absence of anion mobility suggests that the coordination networks are retained even in the molten state.<sup>31,58</sup>

### Proton dynamics in **1** and **1g**

The  $\text{H}^+$  conductivity would be dominated by either the phosphate or BTA dynamics; therefore, we utilized variable-temperature  $^1\text{H}$  MAS solid-state NMR to study their mobilities (Fig. 3). The peaks from 8.1–8.5 and 5.8–6.1 ppm were assigned to the phosphate and BTA  $\text{H}^+$ , respectively.<sup>44,52</sup> The substantial narrowing and intensifying of the peaks between 50 and 75 °C suggested a significant increase in both the phosphate and BTA dynamics. The molecular motion of BTA initiates at the temperature above 50 °C as the BTA peaks are barely distinguishable at 25 and 50 °C (Fig. 3A).<sup>38</sup> The  $\text{H}^+$  mobilities of **1g** and **1** were compared at 25 and 50 °C as well as at 50 and 75 °C,

where the narrower and more intense peaks of **1g** demonstrated its higher  $\text{H}^+$  mobility than that of **1** (Fig. 3B). This higher degree of  $\text{H}^+$  mobility was promoted by a disordered structure formed in **1g**. Furthermore, the BTA dynamics were observable in **1g** even at temperatures lower than 60 °C, which agrees with the impedance response and lower activation energy of **1g**. Additionally, hydrogen-bond formations are indicated by downfield shifts.<sup>59</sup>

### Electrode–electrolyte interface

Discontinuities along the heterogeneous interface inhibit practical applications of solid-state electrolytes.<sup>17</sup> Therefore, we are interested in the  $\text{H}^+$ -conductivity integration and moldability of **1g** as a grain boundary-free immersive solid electrolyte (Fig. 4A). Additionally, the lower  $T_m$  of **1** would prevent the anode/cathode materials from degrading during the fabrication process.<sup>8,9,12,13</sup> A carbon fiber (CF) electrode was pressed to **1m** at 120 °C and quenched to room temperature to provide the electrode–electrolyte interface (CF–**1g**). Cross-sectional scanning electron microscopy (SEM) images of CF–**1g** were collected (Fig. 4B, S12A, and B†), where neither a distinguishable solid–electrolyte interface nor grain boundaries were observed.<sup>60</sup> Optimum contact between the CF layer and **1g** domain was achieved as **1m** can penetrate the CF, generating a fully immersed environment. Fig. 4C shows a cross-sectional SEM reference image of the pristine CF. Energy-dispersive X-ray (EDX) mapping (Fig. 4D–G) further elucidated the position of the CF electrode (intense C) with homogeneously distributed Zn, P, and O signals. To amplify the benefits of melt-quenching glass, we re-examined the morphological alteration of CF–**1g** after recrystallization. **1g** undergoes the recrystallization process upon humidity exposure and transforms back to **1a**. As confirmed by PXRD (Fig. S13†), atmospheric humidity (65% relative humidity) at room temperature (25 °C) is sufficient for the recrystallization to occur within 4 h. Fig. S12C and D† revealed grain boundaries and fractures formed throughout the recrystallized **1g** matrix, especially in the region where the CF and **1g** co-exist.

### Solid-state $\text{H}^+$ battery under anhydrous conditions

Adequately high  $\text{H}^+$  conductivity, single-ion conductivity, low processing temperatures, and thermal/electrochemical stabilities motivated us to apply **1g** as a solid electrolyte for  $\text{H}^+$  batteries.  $\text{MoO}_3$  and  $\text{Cu}^{\text{II}}[\text{Fe}^{\text{III}}(\text{CN})_6]_{2/3} \cdot 4\text{H}_2\text{O}$  (CuFe-TBA) were selected as a model cathode and anode, respectively.<sup>10,12</sup> As a reference, we also evaluated a full-cell configuration in 2 M  $\text{H}_2\text{SO}_4$  solution at 25 °C. It exhibited a discharge capacity of  $35.8 \text{ mA h g}^{-1}$  at  $100 \text{ mA g}^{-1}$  (Fig. S14†). The specific capacity was calculated based on the cathode mass. The distance between the electrodes was *ca.* 1 cm.<sup>12</sup> The solid-state  $\text{H}^+$  battery was prepared by immersing both electrodes (1 cm separations) in **1m** at 120 °C under an Ar atmosphere, where subsequent quenching to room temperature gave the **1g** electrolyte. Fig. 4H and S15A† show the charge–discharge profiles (from 0 to 1.2 V) and rate performance evaluation of solid-state  $\text{H}^+$  batteries under an Ar atmosphere utilizing the **1g** electrolyte at 25 °C. The

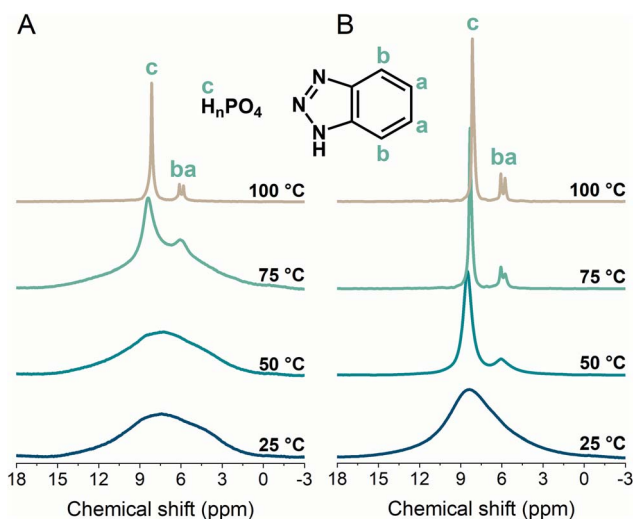


Fig. 3 Variable-temperature  $^1\text{H}$  magic-angle spinning (MAS) solid-state NMR spectra (MAS 8 kHz) of (A) **1** and (B) **1g** from 25 to 100 °C.





Fig. 4 (A) Schematic representation of the interfaces/flaws within the polycrystalline solid electrolyte (left) and MQG solid electrolyte proposed in this work (**1g**). Cross-sectional scanning electron microscopy (SEM) images ( $\times 150$  magnification) of (B) the electrode–solid-state electrolyte interface (CF–**1g**) and (C) CF electrode. Scale bar = 150  $\mu\text{m}$ . Energy-dispersive X-ray (EDX) mapping for (D) C, (E) P, (F) Zn, and (G) O. Scale bar = 100  $\mu\text{m}$ . Full-cell charge–discharge profiles utilizing **1g** as a solid-state electrolyte at (H) 25  $^{\circ}\text{C}$  and (I) 100  $^{\circ}\text{C}$ .

highest discharge capacity was 55.4  $\text{mA h g}^{-1}$  at 10  $\text{mA g}^{-1}$ . Another advantage the **1g**-electrolyte system has over the aqueous system is its large operating-temperature range. The elevated-temperature  $\text{H}^+$  battery was evaluated at 100 and 110  $^{\circ}\text{C}$  under an Ar atmosphere (Fig. 4I and S15C†) and the redox potentials of both electrodes reduced, corresponding to the change in free energy.<sup>61,62</sup> As shown in Fig. S15B and D,† rate performances improved significantly as the ionic conductivity of **1g** was enhanced.<sup>2</sup> In a high-temperature regime, electrodes would show an excessive self-discharge as well as a thermal structural distortion limiting the protonation/deprotonation processes, causing a net loss of capacity. For instance, in a Li-ion battery, capacity fading was observed in  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  as

elevated temperature promotes a larger structural distortion between  $\text{Li}_3\text{V}_2(\text{PO}_4)_3$  and  $\text{V}_2(\text{PO}_4)_3$  limiting the re-insertion of  $\text{Li}^+$ .<sup>63</sup> Additionally, 76% of the original capacity was retained after 1000 cycles of the charge–discharge process at 110  $^{\circ}\text{C}$  (Fig. S16†). We also attempted to demonstrate a solid-state  $\text{H}^+$  battery using crystalline **1** with a similar configuration and an identical anode and cathode. However, charging and discharging processes were not possible at 25  $^{\circ}\text{C}$  nor under low-current (10  $\text{mA g}^{-1}$ ) conditions, even though the thickness of this electrolyte was ten times smaller than that of the **1g** electrolyte. This emphasizes the importance of interface engineering that endows soft glass materials with high  $\text{H}^+$  conductivity and moldability.<sup>17,20,21</sup>



## Conclusions

We synthesized a new H<sup>+</sup> conductive CP, [Zn<sub>3</sub>(H<sub>2</sub>PO<sub>4</sub>)<sub>6</sub>(-H<sub>2</sub>O)<sub>3</sub>](BTA), where the dehydrated state (**1**) integrated promising anhydrous H<sup>+</sup> conductivity (1.2 × 10<sup>-3</sup> S cm<sup>-1</sup> at 100 °C) and relatively low melting point (114 °C). The melt-quenched glass of **1** (**1g**) enhanced the H<sup>+</sup> dynamics of both phosphate and BTA, resulting in a H<sup>+</sup> conductivity value of 8.0 × 10<sup>-3</sup> S cm<sup>-1</sup>, a H<sup>+</sup> transference number of 1.0, and a viscosity of 42.8 Pa s at 120 °C. The coexistence of high conductivity, transport number, and moldability of **1g**, as well as its flawless interface, encouraged us to implement it in solid-state H<sup>+</sup> battery applications. A solid-state H<sup>+</sup> battery with an operating temperature range above room temperature (25–110 °C) was demonstrated for the first time. The tuning capability of the CP glass H<sup>+</sup> conductivity, working temperature, and softness could provide H<sup>+</sup> batteries with wider applications.

## Author contributions

S. H. designed the project, and N. M. and A. Y. synthesized the compounds. S. K. collected and analyzed solid-state NMR measurements. N. M. collected and analyzed SC-XRD, PXRD, TGA, SEM, DSC, ICP-ES, DMA, FTIR, conductivity and transport number measurements and battery evaluation. S. H. and N. M. wrote the paper.

## Conflicts of interest

There are no conflicts to declare.

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