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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, $[Zn_3(H_2PO_4)_6(H_2O)_3]$(1,2,3-benzotriazole), that exhibited a low melting temperature (114 °C) and a high anhydrous single-ion proton conductivity (8.0×10^{-3} S cm^{-1} at 120 °C). Converting crystalline CPs to their glassy-state counterparts *via* melt-quenching not only initiated an isotropic disordered domain that enhanced H^+ 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^+ battery utilizing the new glassy-state CP, which exhibited a wide operating-temperature range of 25 to 110 °C.

Introduction

The proton (H^+) has a diameter of 0.84 fm and is easily localized in the solid state.[1] Fast-moving protons in solids are difficult to achieve, whereas solid-state H^+ conductors are widely used in various electrochemical applications, including fuel cells, electrochemical catalysis, and sensors.[2] Proton batteries are a new class of secondary batteries employing protons instead of metal ions as charge carriers.[3,4] They consist of faradaic electrodes and acidic electrolytes. Since the H^+ charge radius is significantly smaller than that of other ions, faster ion migration and negligible volume changes upon H^+ insertion/desertion are expected. Additionally, replacing high-cost Li^+ with cheaper and more abundant H^+ provides a promising platform for environmentally benign and intrinsically safe energy storage.[5–7] Redox-active organic molecules, such as quinone-functionalized conductive polymers,[4,8] and metal oxides, including MoO_3, WO_3, and H_xIrO_4, are available as H^+ electrodes.[9–11] 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^{-1}) and extends cycling stability to over 0.5 million charge–discharge cycles, which is a unique advantage of aqueous proton batteries.[6,12,13] In spite of various choices of electrodes, electrolytes are mostly limited to aqueous H_2SO_4 or H_3PO_4, which dictates the operating-temperature window and selection of usable electrodes.[8,13–15]

Safely extending the operating-temperature window to ~100 °C is essential for H^+ 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.[16] As employing a conventional aqueous electrolyte is not possible at these high temperatures, solid-state H^+ batteries with anhydrous solid electrolytes would be more suitable. There are no reports of solid-state H^+ batteries working near or above 100 °C due to the difficulties in achieving high anhydrous H^+ conductivity, high-temperature stability, and moldability required for H^+ conductors.[17] Apart from achieving a high H^+ conductivity value (near 10^{-2} S cm^{-1}), 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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† Electronic supplementary information (ESI) available: Experimental details, PXRD, solid PXRD, ^{31}P MAS NMR, TG, and FTIR results, Nyquist plots, long-term conductivity measurements, transport number measurements, cross-sectional SEM images, and a solid state H^+ battery. CCDC 2044808. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/d1sc00392e

solid-state electrolytes is a core factor that promotes charge-transport efficiency and prevents anion polarization.[18,19] Discontinuities along the electrode–electrolyte interfaces and grain boundaries are primary bottlenecks for efficient utilization of solid electrolytes.[17,20,21] 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).[22–25]

Coordination polymers (CPs) and metal–organic frameworks (MOFs) exhibiting high H^+ conductivity over a wide temperature regime (∼200 °C) represent a new class of solid-state H^+ conductors.[26–29] Despite their remarkable H^+ conductivity, their crystalline nature hinders their processing ability, thus limiting their practicality.[30] 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.[31–34] Some of these glassy-state CPs show anhydrous H^+ conductivity superior to that of their crystalline counterparts by several orders of magnitude.[35,36] Moreover, the vitrifying/melting behavior provides these CPs with processing capabilities and forms a grain-boundary free monolith and a flawless heterogeneous interface.[31–34,37–41]

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 (8.0×10^{-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),[38] and it is expected that the dynamics of the phosphates bridging the Zn^{2+} ions (through a single bridging oxygen atom (μ_2)) and the non-coordinating BTA could facilitate an anhydrous H^+ migration.[2,38,42,43]

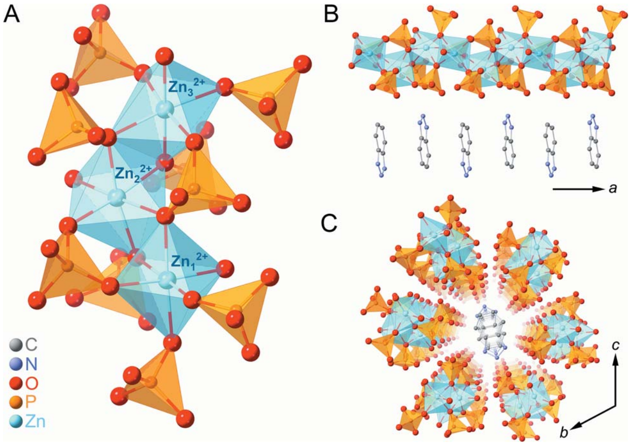

Fig. 1 (A) Local coordination geometry in **1a**. (B) Crystal structure of the one-dimensional (1D) chain along the *a*-axis. (C) Packing structure of **1a** on the *bc*-plane. Zn, P, O, C, and N atoms are represented by light blue, orange, red, grey, and blue spheres, respectively. H atoms are omitted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

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†).[44] 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.[45–47] 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†).[48–50] 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.[38]

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.[33] 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

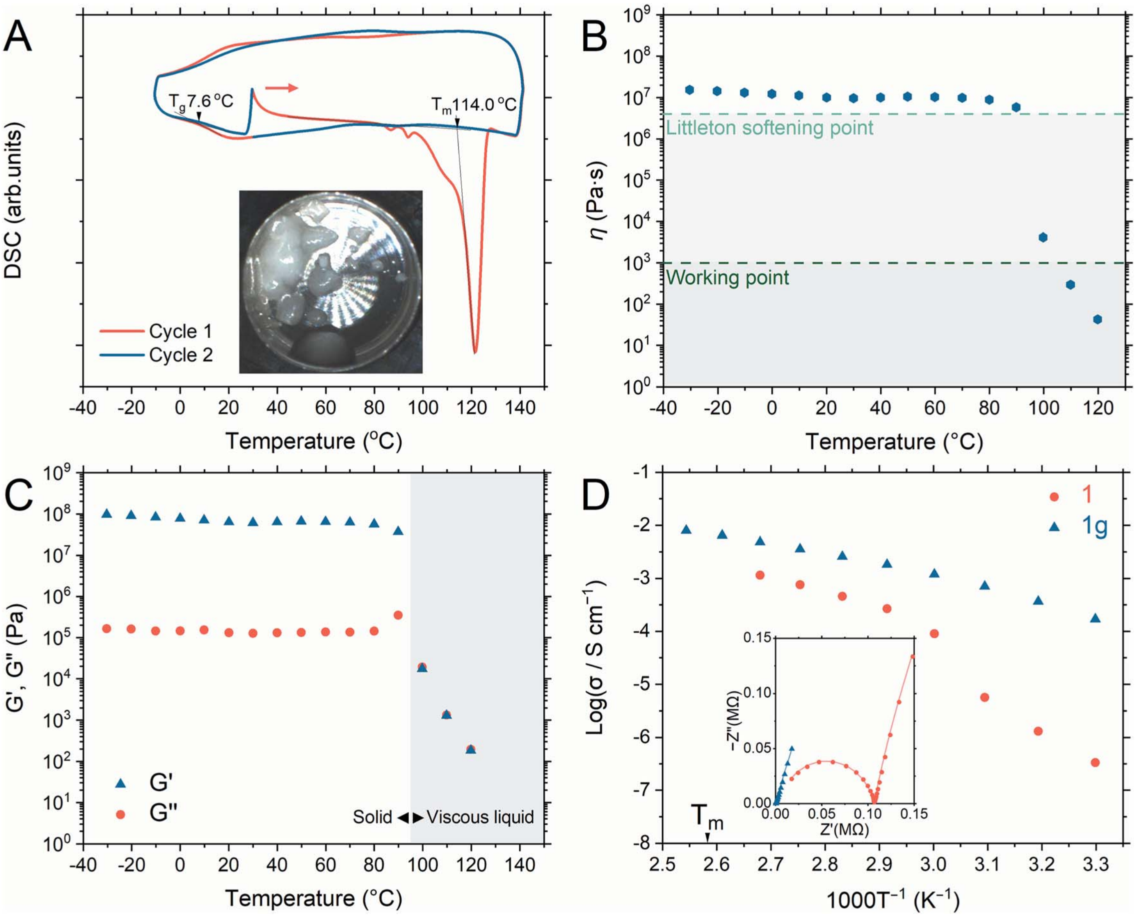

Fig. 2 (A) First- (blue) and second-cycle (red) DSC profiles of 1 from −10 to 140 °C (begin with a heating step from 30 °C). The inset shows a photo of **1m** at 140 °C. (B) Temperature-dependent viscosity of **1g**. (C) DMA of **1g** from −30 to 120 °C (heating rate of 2 °C min^{-1}). The storage (G′) 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.[31,33] 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†).[34]

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).[51] 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.[31,52]

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.[52,53] The conductivity of **1** was measured from 30 to 100 °C, where the crystalline phase of **1** was preserved. We observed conductivity values of 3.3×10^{-7} S cm^{-1} and 9.0×10^{-5} S cm^{-1} at 30 and 60 °C, respectively. The conductivity value increased rapidly upon heating, reaching 1.2×10^{-3} S 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 $[Zn_3(H_2PO_4)_6](HBim)$ at 30 °C (1.2×10^{-7} S cm^{-1}) and 60 °C (1.5×10^{-5} S cm^{-1}).[38]

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 3.3×10^{-4} S cm^{-1}, which increased to 4.9×10^{-3} S cm^{-1} and 6.5×10^{-3} S cm^{-1} at 100 and 110 °C, respectively. A conductivity value of 8.0×10^{-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 H^+ transport number (transference number) measurements.[52,54] The transport numbers of most aqueous and ionic liquid electrolytes are lower than 0.6.[54–56] 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†).[57] According to eqn S1 (ESI),† the H^+ transference number of **1g** is 1.0, indicating an ideal single-ion H^+ conductivity. The absence of anion mobility suggests that the coordination networks are retained even in the molten state.[31,58]

Proton dynamics in 1 and 1g

The H^+ conductivity would be dominated by either the phosphate or BTA dynamics; therefore, we utilized variable-temperature ^{1}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 H^+, respectively.[44,52] 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).[38] The 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 H^+ mobility than that of **1** (Fig. 3B). This higher degree of 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.[59]

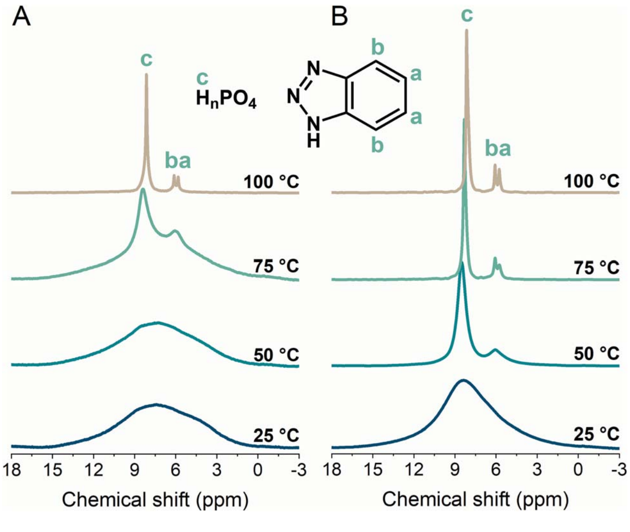

Fig. 3 Variable-temperature ^{1}H magic-angle spinning (MAS) solid-state NMR spectra (MAS 8 kHz) of (A) **1** and (B) **1g** from 25 to 100 °C.

Electrode–electrolyte interface

Discontinuities along the heterogeneous interface inhibit practical applications of solid-state electrolytes.[17] Therefore, we are interested in the 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.[8,9,12,13] 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.[60] 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 H^+ battery under anhydrous conditions

Adequately high H^+ conductivity, single-ion conductivity, low processing temperatures, and thermal/electrochemical stabilities motivated us to apply **1g** as a solid electrolyte for H^+ batteries. MoO_3 and $Cu^{II}[Fe^{III}(CN)_6]_{2/3}\cdot 4H_2O$ (CuFe-TBA) were selected as a model cathode and anode, respectively.[10,12] As a reference, we also evaluated a full-cell configuration in 2 M H_2SO_4 solution at 25 °C. It exhibited a discharge capacity of 35.8 mA h g^{-1} at 100 mA g^{-1} (Fig. S14†). The specific capacity was calculated based on the cathode mass. The distance between the electrodes was *ca.* 1 cm.[12] The solid-state 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 H^+ batteries under an Ar atmosphere utilizing the **1g** electrolyte at 25 °C. The

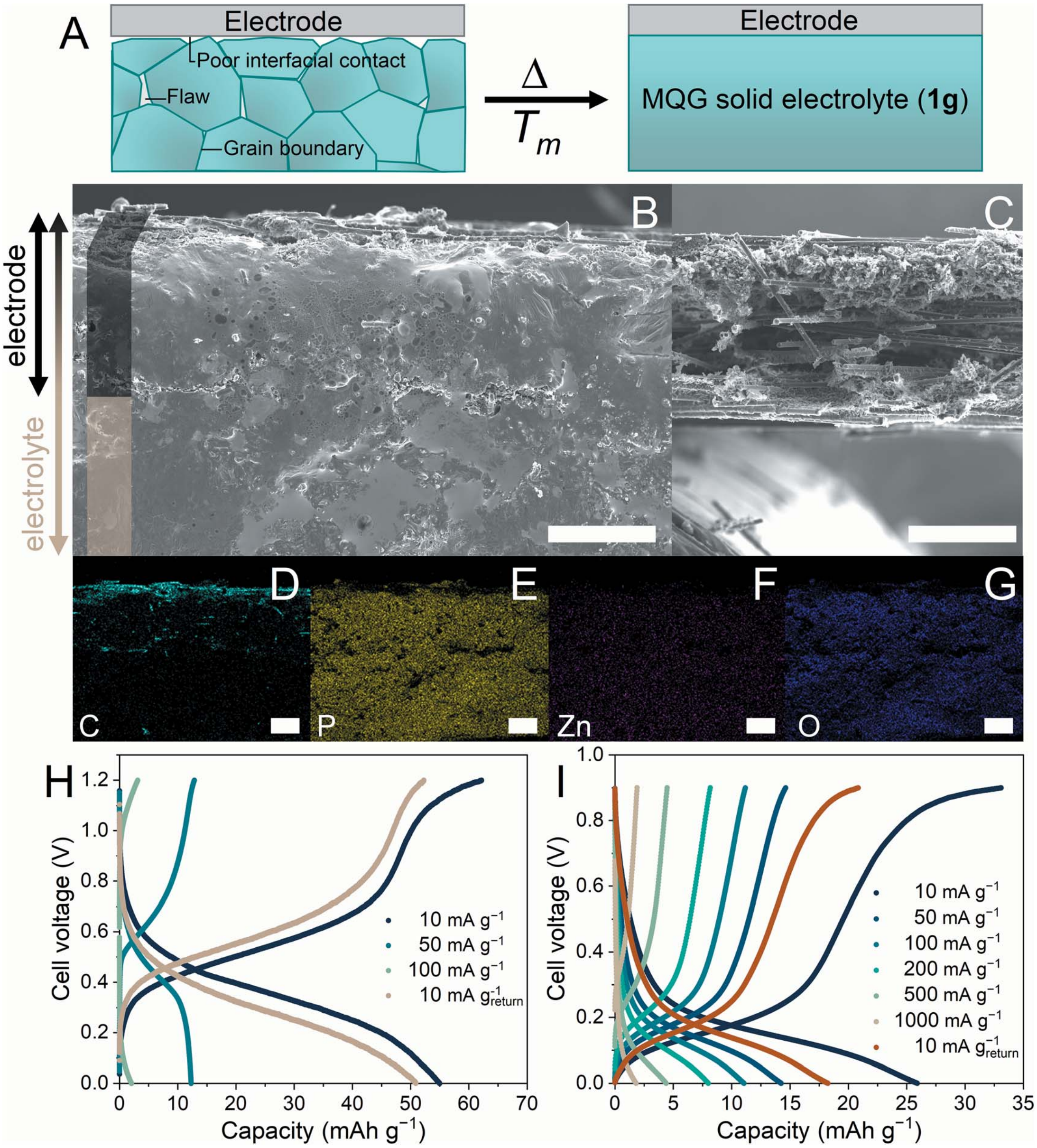

Fig. 4 (A) Schematic representation of the interfaces/flaws within the polycrystalline solid electrolyte (left) and MQG solid electrolyte proposed in this work (**1g**). Cross-sectional scanning electron microscopy (SEM) images (×150 magnification) of (B) the electrode–solid-state electrolyte interface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

highest discharge capacity was 55.4 mA h g^{-1} at 10 mA g^{-1}. Another advantage the **1g**-electrolyte system has over the aqueous system is its large operating-temperature range. The elevated-temperature H$^+$ battery was evaluated at 100 and 110 °C under an Ar atmosphere (Fig. 4I and S15C†) and the redox potentials of both electrodes reduced, corresponding to the change in free energy.[61,62] As shown in Fig. S15B and D,† rate performances improved significantly as the ionic conductivity of **1g** was enhanced.[2] 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 $Li_3V_2(PO_4)_3$ as elevated temperature promotes a larger structural distortion between $Li_3V_2(PO_4)_3$ and $V_2(PO_4)_3$ limiting the re-insertion of Li$^+$.[63] Additionally, 76% of the original capacity was retained after 1000 cycles of the charge–discharge process at 110 °C (Fig. S16†). We also attempted to demonstrate a solid-state 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 °C nor under low-current (10 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 H$^+$ conductivity and moldability.[17,20,21]

Conclusions

We synthesized a new H^+ conductive CP, $[Zn_3(H_2PO_4)_6(H_2O)_3](BTA)$, where the dehydrated state (**1**) integrated promising anhydrous H^+ conductivity (1.2×10^{-3} S cm^{-1} at 100 °C) and relatively low melting point (114 °C). The melt-quenched glass of **1** (**1g**) enhanced the H^+ dynamics of both phosphate and BTA, resulting in a H^+ conductivity value of 8.0×10^{-3} S cm^{-1}, a H^+ 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^+ battery applications. A solid-state H^+ 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^+ conductivity, working temperature, and softness could provide H^+ 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.

Acknowledgements

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