



Ion expressways directed by vertically aligned TiO₂ nanotubes in quasi-solid electrolyte for flexible zinc-ion batteries

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ABSTRACT

Flexible zinc-ion batteries are promising power sources for wearable devices, but are hindered by zinc dendrite growth and limited cycle life, due to limited ionic transport and poor mechanical strength of electrolyte. This work presents a quasi-solid polymer gel (PG) electrolyte incorporating vertically aligned TiO₂ nanotubes (PATG) in a crosslinked polyvinyl alcohol matrix. PATG exhibited a compressive Young's modulus of 56.7 MPa (vs. 21.9 MPa for PG), and especially much higher Zn²⁺ conductivity of 0.26 mS·cm⁻¹ than that of PG (0.056 mS·cm⁻¹) and PPTG (0.074 mS·cm⁻¹) and larger Zn²⁺ transference number of 0.71 than those of PPTG film (0.61) and PG film (0.43). PATG electrolyte exhibited stable cycling performance over 3000 hours with low polarization and effectively suppressed zinc dendrite growth. In full batteries, Zn|PATG|α-MnO₂ delivered an initial capacity of 301.2 mAh·g⁻¹ at 0.1 C and 212.9 mAh·g⁻¹ at 0.5 C. Moreover, the flexible Zn|PATG|α-MnO₂ can work at different bending states and power electronic devices well. This work underscores that the directed ion-transport strategy is feasible and promising for safe, flexible, and durable zinc-ion batteries.

KEYWORDS

ionic conductivity, TiO₂ nanotubes, quasi-solid electrolyte, zinc-ion batteries

1 Introduction

Rapid development of wearable electronic devices, including smartwatches, bendable electronics, health monitors, and soft microrobots, has intensified the demand for flexible power modules [1, 2]. Lithium-ion batteries (LIBs) represent the state-of-the-art technology, but intrinsic safety issues and cost concerns, which stem from flammable nonaqueous electrolytes and limited lithium resources, are still critical bottlenecks [3, 4]. Aqueous zinc-ion batteries (AZIBs) are emerging as a promising alternative for energy storage [5, 6], owing to many advantages, such as high theoretical capacity of zinc anode (820 mAh·g⁻¹), inherent safety of nonflammable electrolyte, cost-effectiveness, environment compatibility, and natural abundance of Zn reserves (over 300 times greater than lithium) [7]. Despite these merits, flexible AZIBs face significant challenges common to metal-anode batteries, including zinc dendrite growth, parasitic side reactions (e.g., hydrogen evolution, zinc corrosion and passivation), and limited power density [8]. Consequently, significant innovation efforts [9] are focused on optimizing structure design and enhancing functional properties of flexible anodes, cathodes [10], and electrolytes [11].

As a critical component of flexible AZIBs, the electrolyte is expected to possess fast ionic conductivity between cathode and anode, good interfacial compatibility, mechanical integrity, and

suppression for growth of zinc dendrites [12]. Among various options, polymer electrolytes have garnered significant research interests due to their leakage-free nature and suppression for dendrites [13]. For instance, solid polymer electrolytes (SPEs) based on polyethylene oxide (PEO) [14], with a Young's modulus of 50–800 MPa, combined with zinc salts (e.g., ZnCl₂ or Zn(TFSI)₂), have shown great promise for flexible AZIBs. However, these SPEs often suffer from low room-temperature ionic conductivity (10⁻⁶–10⁻⁸ S·cm⁻¹) [15] and low Zn²⁺ transference number (*t*_{Zn²⁺}).

Hydrogel electrolytes, typically based on poly(vinyl alcohol) (PVA), polyacrylamide (PAM) [16, 17], or cellulose derivatives, leverage non-covalent interactions with zinc salts to achieve high ionic conductivity (>10⁻² S·cm⁻¹), enabling superior rate performance. For example, Chen et al., reported an inducement of crystallographic (002) orientation of Zn anode in AZIBs with PVA coating [18]. However, the quasi-solid nature often results in poor mechanical strength (20 kPa–5 MPa). Chemical crosslinking of the polymer matrix (e.g., PVA, PAM, or cellulose) has been proved to be effective in enhancing the mechanical properties [19]. Notably, a polyelectrolyte hydrogel electrolyte was applied in dual-ion Zn batteries with high performance, due to its regulated anion/cation transportation and dendrite suppression [20]. Thus, the poor

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performance is likely caused by low ionic conductivity in SPEs and the difficulty of balancing mechanical properties between overly rigid SPEs and excessively soft hydrogel electrolytes [21, 22].

Nanostructured fillers incorporating into the polymer matrices to form composite electrolyte is effective to enhance the performance of polymer electrolytes [13, 23–25]. This strategy has been significantly developed in LIBs [26, 27], but rarely reported in ZIBs. Zero-dimensional (0D) nanoparticles, such as SiO_2 [17], TiO_2 , Al_2O_3 , ZnO [28], $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZO), and carbon dots, are randomly dispersed to create additional ion transport pathways along their interfaces and disrupt polymer crystallinity, thereby enhancing conductivity. One-dimensional (1D) nanostructures, including electrospun polymer fibers, inorganic nanowires, nanorods establish interconnected conductive networks while reinforcing the mechanical integrity of the electrolyte membrane. Notably, aligned 1D nanowires, as demonstrated by Cui et al. in LIBs, can guide directional Li^+ ion transport [29]. Two-dimensional (2D) nanosheets with high surface area, such as reduced graphene oxide (rGO or GO) [30], Mxenes [31], and layered double hydroxides (LDHs), can enhance interfacial interactions and create tortuous ionic pathways. However, the orientation of these anisotropic fillers is often misaligned with the ion-transport direction. In addition, increasing the nanofiller content or membrane thickness to enhance mechanical properties further impedes vertical ion conduction. Therefore, the mismatch between mechanical stress and ionic conductivity perpendicular to the electrolyte membrane remains a critical problem.

Herein, a PVA-based composite electrolyte reinforced with vertically aligned titanium dioxide nanotubes (TiO_2NTs) is reported to boost ion transport and mechanical strength in flexible ZIBs. This electrolyte is crosslinked using glutaraldehyde. A quasi-solid electrolyte crosslinked by glutaraldehyde is formed, which displays improved tensile and compressive modulus. The presence of aligned TiO_2NTs within polymer matrix remarkably enhances the Zn^{2+} conductivity from 0.056 to 0.26 $\text{mS}\cdot\text{cm}^{-1}$, resulting in improved power and cycling performance in $\text{Zn}||\alpha\text{-MnO}_2$ batteries. Flexible $\text{Zn}||\text{PATG}||\alpha\text{-MnO}_2$ cell works well at different bending states and exhibits an initial capacity of 188.2 $\text{mAh}\cdot\text{g}^{-1}$ with a capacity retention of 82.1% after 30 cycles. This superior performance can be attributed to the uniform zinc-ion diffusion perpendicular to the anode surface, which is beneficial for Zn plating, thus effectively suppressing Zn dendrite growth.

2 Experimental

2.1 Materials

Poly(vinyl alcohol) (PVA, $M_w=75,000$) was obtained from Shanghai Macklin Biochemical Technology Co., Ltd.. Ti foil, Zn foil (99.9%), ammonium fluoride solution (NH_4F , 40%), potassium permanganate (KMnO_4 , A.R.) and zinc sulfate heptahydrate ($\text{ZnSO}_4\cdot 7\text{H}_2\text{O}$, A.R.) were purchased from Sinopharm (Shanghai). TiO_2 , glutaraldehyde solution (GA, 50%), hydrogen chloride (HCl, 37%), NaOH (98%), ethylene glycol (A.R.), sulfuric acid (98.3%), and manganese sulfate hydrate ($\text{MnSO}_4\cdot \text{H}_2\text{O}$, A.R.) were bought from Aladdin (Shanghai). N-methylpyrrolidone (99.9%) polyvinylidene fluoride (PVDF, A.R.) and conductive carbon (Super P) were available from Chemische Werke Kluthe GmbH. The dispersed and arrayed TiO_2NTs were prepared through hydrothermal conversion [32] and anodic oxidation [33] of Ti foil (see the Electronic Supplementary Material (ESM)), respectively.

2.2 Crosslinked quasi-solid PVA membrane

PVA solution (5 mL, 10 wt.%) was blended with varying amounts of TiO_2NTs fillers (0–7 wt.%) under magnetic stirring at 90 °C for 4 hours. The resulting dispersion was adjusted to pH=2 using 1 M HCl, followed by the addition of glutaraldehyde (GA, 0–150 μL) to ensure a homogeneous mixture. This PVA dispersion with random TiO_2NTs fillers was then cast onto a clean glass substrate using a doctor blade and then was air-dried at ambient condition for 12 hours, forming crosslinked opaque PVA films (designated PPTG). Notably, the PVA with aligned TiO_2NTs arrays (designated PATG) was prepared by directly casting PVA onto the TiO_2NTs and crosslinked by GA. Similarly, PVA solution (5 mL) mixed with varying GA amounts, but without TiO_2NTs fillers, was cast directly onto either a glass substrate or a $\text{TiO}_2\text{NT}/\text{Ti}$ substrate, yielding crosslinked transparent PVA films without fillers (named as PG). For accurate comparison, the mass of the randomly oriented TiO_2NTs was kept strictly identical to that of the TiO_2NTs arrays.

2.3 Symmetric cells

Zinc foil discs (12 mm in diameter, 80 μm in thickness) were polished and cleaned prior to utilization. PG, PPTG, and PATG films were soaked in a 2 M ZnSO_4 solution. And the swollen films were employed as quasi-solid electrolytes. Symmetric $\text{Zn}||\text{PG}||\text{Zn}$ coin cells (2032 type) were assembled using the swollen PG film with Zn^{2+} between two Zn discs, while $\text{Zn}||\text{PPTG}||\text{Zn}$ and $\text{Zn}||\text{PATG}||\text{Zn}$ cells were prepared by replacing PG with the corresponding film and different concentration of ZnSO_4 .

2.4 Full cells and flexible battery

To assemble the full battery, $\alpha\text{-MnO}_2$ nanowires were synthesized via a hydrothermal method [34] using a $\text{MnSO}_4\text{-H}_2\text{SO}_4\text{-KMnO}_4$ system at 120 °C for 12 h. The cathode was prepared by coating a slurry of $\alpha\text{-MnO}_2$, Super P carbon, and PVDF (7:2:1 weight ratio) in N-methyl-2-pyrrolidone (NMP) onto graphite carbon paper, followed by drying. $\text{Zn}||\text{PATG}||\alpha\text{-MnO}_2$ full cell (CR2032 type) was assembled with a zinc foil disc as the anode, $\alpha\text{-MnO}_2$ electrode as the cathode [35], and a PATG film saturated with 100 μL 2 M ZnSO_4 (0.2 M MnSO_4) as an electrolyte. Control cells were also constructed using PG and PPTG electrolyte films for comparison.

In a bendable device construction, electrodes were scaled to 1 cm $\times$ 3 cm, where a $\alpha\text{-MnO}_2$ cathode was placed on the flexible substrate followed by the placement of PATG (or PG, PPTG) electrolyte soaked with Zn^{2+} ions and anode plate. The sandwich structures were sealed by thermo-pressing.

2.5 Electrochemical measurement

The electrolytes were electrochemically characterized using a two-electrode coin cell on a CH Instruments 760 potentiostat. Cyclic voltammetry (CV) was conducted at scan rates from 0.1 to 1 $\text{mV}\cdot\text{s}^{-1}$ for symmetric zinc cells with PG, PPTG, or PATG as electrolyte, respectively. The zinc ion transference number ($t_{\text{Zn}^{2+}}$) was determined via the Bruce-Vincent method [36], applying a constant DC voltage of 0.01 V for 1200 s. Electrochemical impedance spectroscopy (EIS) was performed at 0 V before and after DC polarization to measure interfacial charge transfer resistance (R_{ct}), using a 5 mV AC amplitude over a frequency range of 100 kHz to 0.1 Hz. The ionic conductivity of the PG, PPTG and PATG electrolytes were measured by using EIS on the symmetric stainless-steel electrodes in coin cells, accordingly. Galvanostatic cycling of the quasi-solid electrolytes was performed

in symmetric Zn cells at a current density of $0.1 \text{ mA}\cdot\text{cm}^{-2}$ and a capacity of $0.1 \text{ mAh}\cdot\text{cm}^{-2}$, within a voltage window of -0.2 to 0.2 V .

For full cells, Warburg impedance and diffusion coefficients were derived from EIS analysis of full Zn|PATG|| α -MnO₂ batteries at 1.4 V , using a 5 mV AC amplitude across 100 kHz to 0.1 Hz . Zn²⁺ diffusion coefficients in Zn|PATG|| α -MnO₂ batteries were measured using the galvanostatic intermittent titration technique (GITT), applying constant current pulses (0.1 C , 30 min) followed by 3-hour open-circuit relaxation periods to reach near steady state. Diffusion coefficients were calculated from the voltage response during pulses and relaxation steps. CV curves were acquired at scan rates of 0.1 to $1.0 \text{ mV}\cdot\text{s}^{-1}$ within a potential window from 1.0 to 1.8 V . Rate capability was assessed through five cycles at constant current rates of 0.1 C , 0.2 C , 0.5 C , 1 C , 2 C , and back to 0.1 C (1 C : $308 \text{ mA}\cdot\text{g}^{-1}$ for α -MnO₂) in the same voltage range. Long-term capacity retention was evaluated at 0.5 C between 1.0 and 1.8 V .

Other characterization details including scanning electron microscopy (SEM) and atomic force microscopy (AFM) can be found in the ESM.

3 Results and discussion

Figure 1(a) illustrates the formation of a chemically crosslinked PVA hydrogel by glutaraldehyde (PG). Moreover, a hybrid composite with random TiO₂NTs embedded in the PG matrix (PPTG) is formed (Fig. 1(b)), while PATG is obtained by incorporating vertically aligned TiO₂NTs arrays within the crosslinked PG matrix (Fig. 1(c)). This crosslinking process involves a condensation reaction between hydroxyl groups ($-\text{OH}$) on PVA polymer chains and aldehyde groups ($-\text{CHO}$) from a crosslinking agent, typically facilitated by acidic catalysis. The resulting acetal linkages ($-\text{C}-\text{O}-\text{C}-\text{O}-\text{C}-$) form covalent bonds

between polymer chains, establishing a three-dimensional (3D) hydrogel network that encapsulates water. The random or aligned nanotubes are expected to enhance the mechanical and electrochemical properties of hydrogel. Figs. S1(a)–S1(c) in the ESM presents cross-section SEM images of PG, PPTG, and PATG films, which hold the thickness of $30\text{--}50 \mu\text{m}$. Correspondingly, Figs. 1(d)–1(f) demonstrate the enlarged cross-section SEM images. It is obvious that powdered TiO₂ nanotubes were dispersed randomly in PPTG (Fig. 1(e)) and the TiO₂ nanotubes were well aligned in PATG (Fig. 1(f)). The optical images of PG, PPTG, and PATG films with the size of $2 \text{ cm}\times 2 \text{ cm}$ in the insets of Figs. 1(d)–1(f) also shows obvious difference. The incorporation of nanofillers, e.g., TiO₂ nanotubes and TiO₂ arrays, rather than differences in film thickness, causes slight color variation. To ensure a highly uniform and identical thickness across all three polymer gel films, a professional stainless-steel doctor blade was utilized to cast the pure PVA solution and the mixture solutions containing TiO₂ nanotube under identical blade gap and processing conditions. When a laser traverses the films (Fig. S2 in the ESM), PATG film shows an ellipse ($a/b=2.5$) spot in Fig. S2(c) in the ESM, which is different from a small round green spot of PG film in Fig. S2(a) in the ESM, and a large round spot of PPTG film in Fig. S2(b) in the ESM. This difference also indicates that there is an ordered structure in PATG film, analogous to Laue diffraction patterns. The top surface of the three films displayed super flat nature (roughness factor $R_q < 0.4 \text{ nm}$) as shown in the atomic force microscopy (AFM) images (Fig. S3 in the ESM).

Random TiO₂NTs and aligned TiO₂NTs annealed at 500°C show similar Raman spectra with tiny difference (Fig. 2(a)). The random TiO₂NTs displayed four unique scatter peaks at 147.1 , 400.3 , 521.3 and 642.8 cm^{-1} , corresponding to the E_g , B_{1g} , $A_{1g}+B_{1g}$, and E_g modes of anatase, respectively. The TiO₂NTs array showed

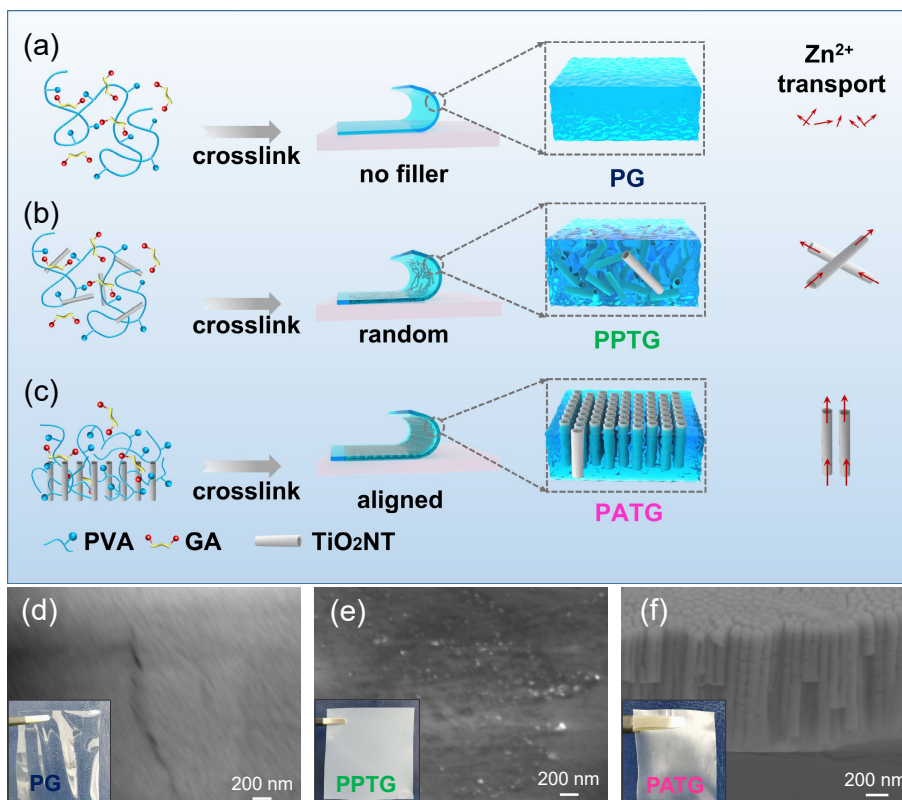


Figure 1 Scheme of synthetic process of (a) PG, (b) PPTG and (c) PATG; Enlarged cross-sectional SEM images and corresponding optical images (inset) of (d) PG, (e) PPTG and (f) PATG.

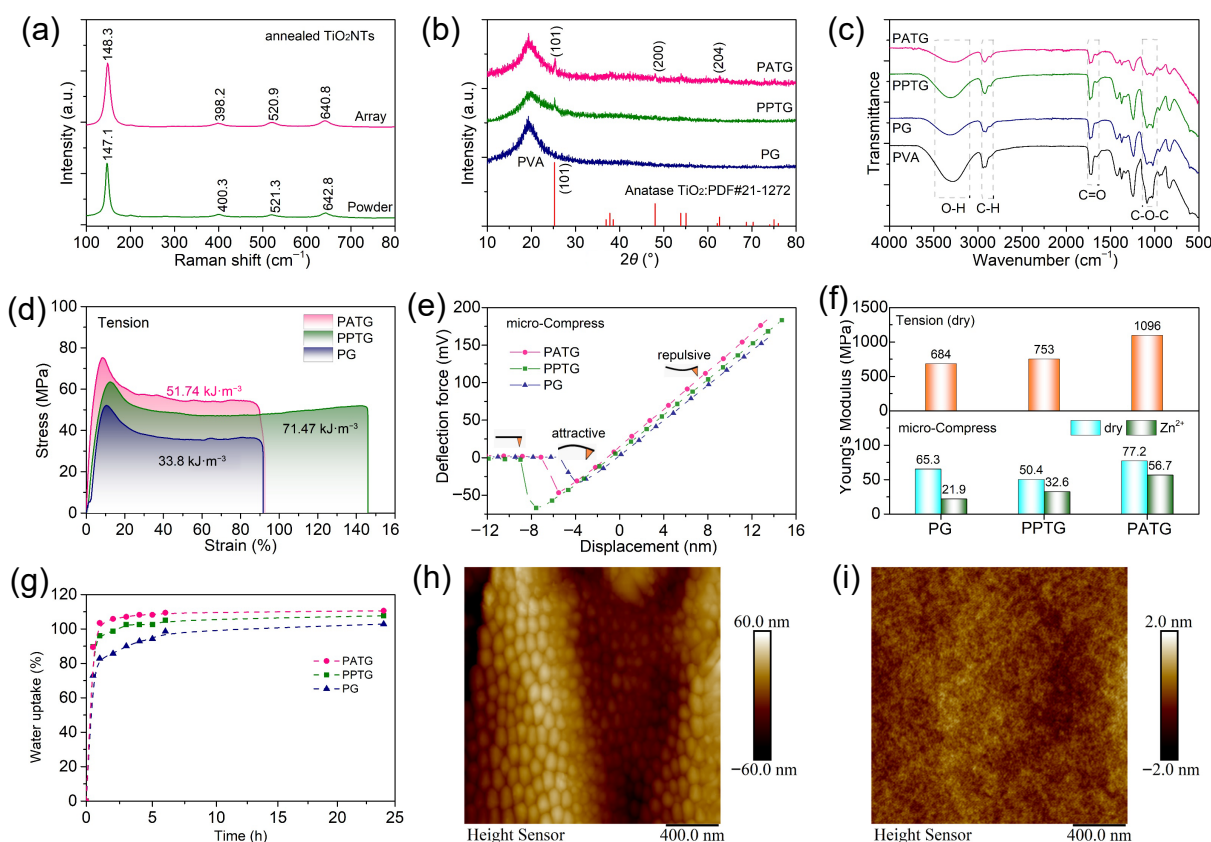


Figure 2 (a) Raman spectra of TiO₂NTs powder and aligned TiO₂NTs, respectively. (b) XRD patterns of PG, PPTG and PATG (c) FT-IR spectra of PVA, PG, PPTG and PATG. (d) Tensile stress-strain curves, (e) compressive properties (f) Modulus of PG, PPTG and PATG and (g) water uptake percentage. AFM images of (h) interface between TiO₂NTs and polymer matrix of PATG, and (i) bottom surface of PATG.

scattering peaks at 148.3, 398.2, 520.9, and 640.8 cm⁻¹, corresponding to the four scatter modes mentioned above. The blueshift of E_g corresponding to the Ti-O-Ti bending vibration, is caused by a stiffening of the Ti-O vibrational modes (from the quantum confinement of nanoscale crystallites or compressive stress in arrayed structure). Scanning electron microscopy (SEM) images of random TiO₂NTs (Fig. S4(a) in the ESM) and aligned TiO₂NTs (Fig. S4(b) in the ESM) clearly show the 1D feature and the hollow nanotubes clearly observed from the surface of aligned TiO₂NTs. XRD pattern of PG film only demonstrate a hump, indicating the PVA amorphous nature as shown in Fig. 2(b). For PPTG and PATG, in addition to one broad diffraction peak close to 20° arising from amorphous PVA, three smaller diffraction peaks corresponding to (101), (200) and (204) of anatase were observed, which is consistent with the pattern of pure random TiO₂NTs (Fig. S5(a) in the ESM) and aligned TiO₂NTs (Fig. S5(b) in the ESM).

Fourier transform infrared (FT-IR) spectra for PVA films were shown in Fig. 2(c). The hydroxyl group (-OH) absorption peaks locating at ~3200 and ~3450 cm⁻¹, significantly decrease after crosslinking (PG, PPTG and PATG). The broadening in the region of 1000–1100 (~1020–1050) cm⁻¹ is a manifestation of the formation of new C-O-C linkages within the more rigid and heterogeneous crosslinked network [37]. TGA curves suggest that TiO₂NTs loading amount in both PPTG and PATG was about 3.2–3.7 wt.% (Fig. S6 in the ESM). The incorporation of TiO₂NTs significantly enhanced the mechanical properties of the cross-linked PG films, as illustrated by the tensile stress-strain curves in Fig. 2(d). All films initially exhibited a sharp and linear increase in stress at low strains, indicating an elastic behavior. Following the

yield point and the neck formation region, strain hardening effect was observed. It is shown that the PATG film displays strain >90% and modulus 50% larger than the PG film. PPTG film displays a moderate improvement of the tension modulus (10% increase), but could withstand strain resistant to >140%. In Fig. 2(e), the compressive properties of the crosslinked films were investigated by using AFM in ScanAsyst mode and probed with Si₃N₄ cantilever (calibrated with Si wafer in Fig. S7 in the ESM), by employing ramp curves for nanoindentation analysis. Within a small compressive strain region (<200 nm), all three films exhibited elastic behavior. The deflection force-displacement slopes (corresponding to stiffness) show a trend of PATG > PPTG > PG. Using a Hertzian contact model (detailed in the ESM), the Young's modulus of three films are presented in Fig. 2(f). Notably, PATG film demonstrates the highest modulus of 56.7 MPa and 77.2 MPa with/without swollen state. All the crosslinked PG, PPTG and PATG films possess modulus much larger than the PVA hydrogel.

All three films exhibit substantial water uptake upon swelling, ranging from approximately 90% to 110% (Fig. 2(g)). Among them, PATG film shows the highest absorption capability. AFM investigation of the swollen films reveals distinct surface morphologies. PATG film displays spherical patterns on the surface, connecting TiO₂NTs and polymer matrix of PATG (Fig. 2(h)), potentially attributable to the TiO₂NTs fillers, while the opposing surface exhibits exceptional flatness (Fig. 2(i)) with a root-mean-square roughness (R_q) of less than 2 nm as PPTG and PG films. The combination of controlled mechanical properties, significant electrolyte uptake capability, and ultra-flat surface morphology on one side suggests that these flat and TiO₂NTs-

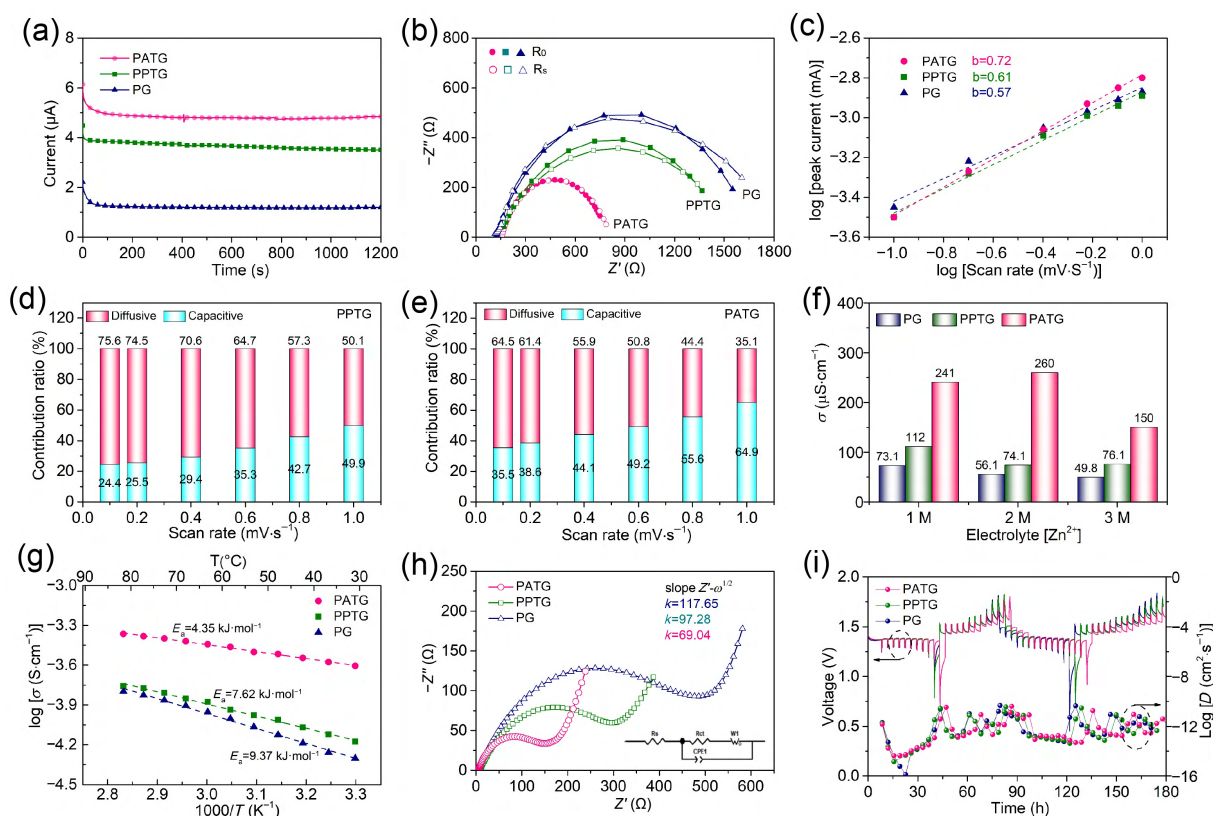


Figure 3 (a) Current-time curves, (b) EIS and (c) plots of $\log(i_p)$ vs. $\log(\nu)$ of Zn|PG|Zn, Zn|PPTG|Zn and Zn|PATG|Zn, respectively. Capacitive contribution ratio in (d) PPTG and (e) PATG. (f) Ionic conductivity of PG, PPTG and PATG under different Zn^{2+} concentrations from 1 M to 3 M. (g) Activation energies for ionic conductivity, (h) Nyquist plots at the open circuit voltage and (i) GITT curves and diffusion coefficients of Zn|PG| α -MnO₂, Zn|PPTG| α -MnO₂ and Zn|PATG| α -MnO₂, respectively.

reinforced PG films hold promising application as high-performance electrolytes in AZIB devices.

Electrochemical characterization of the symmetric cells incorporating the crosslinked PG, PPTG and PATG films as electrolytes (e.g., Zn|PATG|Zn) provides insights into ionic transport properties and performance. As shown in Fig. 3(a), the zinc transference number ($t_{\text{Zn}^{2+}}$) was evaluated by using I - t curves to quantify the contribution of zinc cations to the total ionic conductivity. It is known that the larger Zn^{2+} transference number in SPEs would suppress the dendrites formation [13]. The $t_{\text{Zn}^{2+}}$ of PATG film was found to be 0.71, significantly higher than those of PPTG film (0.61) and PG film (0.43). The largest $t_{\text{Zn}^{2+}}$ of PATG can be attributed to facile diffusion pathways for Zn^{2+} ions provided by the well-aligned TiO₂NTs. Notably, the obtained transference numbers for all three films were higher than those typically reported values of conventional hydrogel electrolytes (e.g., PVA-PAN [38]). As revealed by the EIS spectra in Fig. 3(b), both the initial total cell resistance (R_0) and the steady-state total cell resistance (R_s) decrease significantly from pure PG film, PPTG to PATG. In the high-to-medium frequency range, the semicircle diameter reflects the charge-transfer resistance (R_{ct}) at the electrode-electrolyte interfaces. Nyquist plots of EIS in Fig. 3(b) demonstrate that PATG possesses much lower R_{ct} (623.9 Ω) than PPTG (1364 Ω) and PG (1539 Ω) in the symmetric cells.

Cyclic voltammetry (CV) was performed on the Zn|| α -MnO₂ full cells with different films to further probe the electrochemical behavior. Figure S8 in the ESM shows the XRD pattern and morphology of α -MnO₂. The CV profiles display characteristic peaks associated with zinc stripping/plating, and MnO₂ redox reactions, typically one anodic peak and two cathodic current

peaks (Fig. S9 in the ESM). Consistent with the transference number analysis, PATG exhibits larger current than PPTG and PG, indicating enhanced electrochemical activity and faster ion transport kinetics. Analysis of the relationship between current density and sweeping rate, as presented in Fig. 3(c), yields slope values (b -values) of 0.72, 0.61, and 0.57 for PATG, PPTG, and PG electrolytes, respectively. A b -value approaching 1.0 suggests a capacitive-controlled process, while a value closer to 0.5 indicates a diffusion-controlled process. The higher b -value for PATG (0.72) compared to PPTG (0.61) and PG (0.57) suggests a greater contribution of capacitive current to the total current response in the PATG electrolyte (Fig. 3(c), Fig. S10 in the ESM). This increased capacitive behavior was further quantified by analyzing the contribution of capacitive current from the CV curves (Figs. S11 and S12 in the ESM). For PPTG, the capacitive contribution increases from 24.4% to 49.1% as the scanning rate increases from 0.1 to 1 mV·s⁻¹ (Fig. 3(d)). Interestingly, PATG demonstrates an even more pronounced increase in capacitive contribution, rising from 35.5% to 64.9% over the same scanning rate range (Fig. 3(e)). This higher capacitive contribution and more rapidly increasing value with increasing scan rate in PATG indicates its potential to support higher charge/discharge rates.

EIS measurements further support these findings, revealing a smaller impedance for the PATG electrolyte compared to PPTG and PG. At 30 °C, the ionic conductivity of PG, PPTG and PATG was measured under different Zn^{2+} concentrations from 1 M to 3 M (Fig. 3(f)). The PATG-2M composition demonstrates a significant improvement in ionic conductivity of 0.26 mS·cm⁻¹, showing an approximately 5-fold increase compared to PG-2M film (0.056 mS·cm⁻¹) and PPTG-2M film (0.074 mS·cm⁻¹).

Furthermore, the ionic conductivity of PG, PPTG and PATG was found to increase with increasing temperature in the range of 30–80 °C (Fig. S13 in the ESM), consistent with thermally activated ion transport. The activation energies for ionic conductivity, calculated from the temperature-dependent data shown in Fig. 3(g), are determined to be 9.37 kJ·mol⁻¹ for PG, 7.82 kJ·mol⁻¹ for PPTG, and 4.35 kJ·mol⁻¹ for PATG, respectively, under 2 M and other concentrations (1 M and 3 M in Fig. S14 in the ESM). The lower activation energy for PATG indicates that ion transport in this film requires less thermal energy, contributing to its higher ionic conductivity and superior electrochemical performance.

EIS was further performed on the full Zn|| α -MnO₂ batteries to further investigate the interfacial charge transfer and ionic diffusion kinetics. Figure 3(h) shows the EIS Nyquist plots collected at the open circuit voltage (OCV, 1.3 to 1.5 V). The PATG cell exhibits a significantly smaller semicircle, indicating a lower charge-transfer resistance compared to full cells employing PPTG and PG as electrolytes. In the low-frequency region, the linear behavior corresponds to the Warburg impedance, characteristic of diffusion-controlled processes. The slopes obtained from the linear fitting of Warburg impedance (Z' versus $\omega^{-1/2}$) can be represented by the k values. The k values are determined to be 117.65, 97.28, and 69.04 ($\Omega \cdot s^{-1/2}$) for PG, PPTG, and PATG electrolytes, respectively. A smaller Warburg slope indicates faster ion diffusion within the electrolyte and potentially at the interfaces. From the Warburg impedance analysis, the Zn²⁺ diffusion coefficients ($D_{Zn^{2+}}$) were calculated to be 1.48×10^{-13} , 2.16×10^{-13} , and 4.29×10^{-13} cm²·s⁻¹ for PG, PPTG, and PATG,

respectively (Fig. S15 in the ESM). These results quantitatively confirm that Zn²⁺ diffusion is the fastest in the PATG electrolyte among the three tested films. Furthermore, the galvanostatic intermittent titration technique (GITT) was applied to assess the Zn²⁺ diffusion kinetics during the charge and discharge cycles (Fig. 3(i)). Consistent with the EIS findings, the diffusion coefficients obtained *via* GITT for PATG were slightly higher than those for PPTG and PG in a logarithmic scale. These collective results from both EIS and GITT strongly suggest that the PATG film offers superior Zn²⁺ transport kinetics.

The performance of the full cells assembled with the different PG-based electrolytes was thoroughly evaluated by CV and rate capability tests. Figure 4(a) presents the CV curves of Zn|PATG|Zn full cell. The anodic peak at ~1.5 V versus Zn²⁺/Zn corresponds to the Zn plating coupled with the extraction of Zn²⁺ ions from the Zn_xMnO₂ during charging. Conversely, the cathodic peaks located between 1.2 and 1.3 V versus Zn²⁺/Zn are attributed to the Zn²⁺ insertion into the α -MnO₂ lattice during discharge. The rate capability of full cells is shown in Fig. 4(b). The Zn|PATG| α -MnO₂ full cell demonstrates superior specific capacities across all the tested C-rates, delivering 301.2, 267, 219.3, 179.4, and 133.9 mAh·g⁻¹ at 0.1 C, 0.2 C, 0.5 C, 1 C, and 2 C, respectively. The Zn|PPTG| α -MnO₂ full cell shows moderate capacities of 227.8, 217.7, 193.5, 156.5, and 111.5 mAh·g⁻¹ at the corresponding rates, while the Zn|PG| α -MnO₂ cell exhibits the lowest capacities of 204.5, 172.6, 154.1, 125.6, and 93.7 mAh·g⁻¹. The high specific capacity achieved with the PATG electrolyte at 0.1 C (approximately 97% of the theoretical capacity) confirms the efficient utilization of the active material, which is facilitated by the

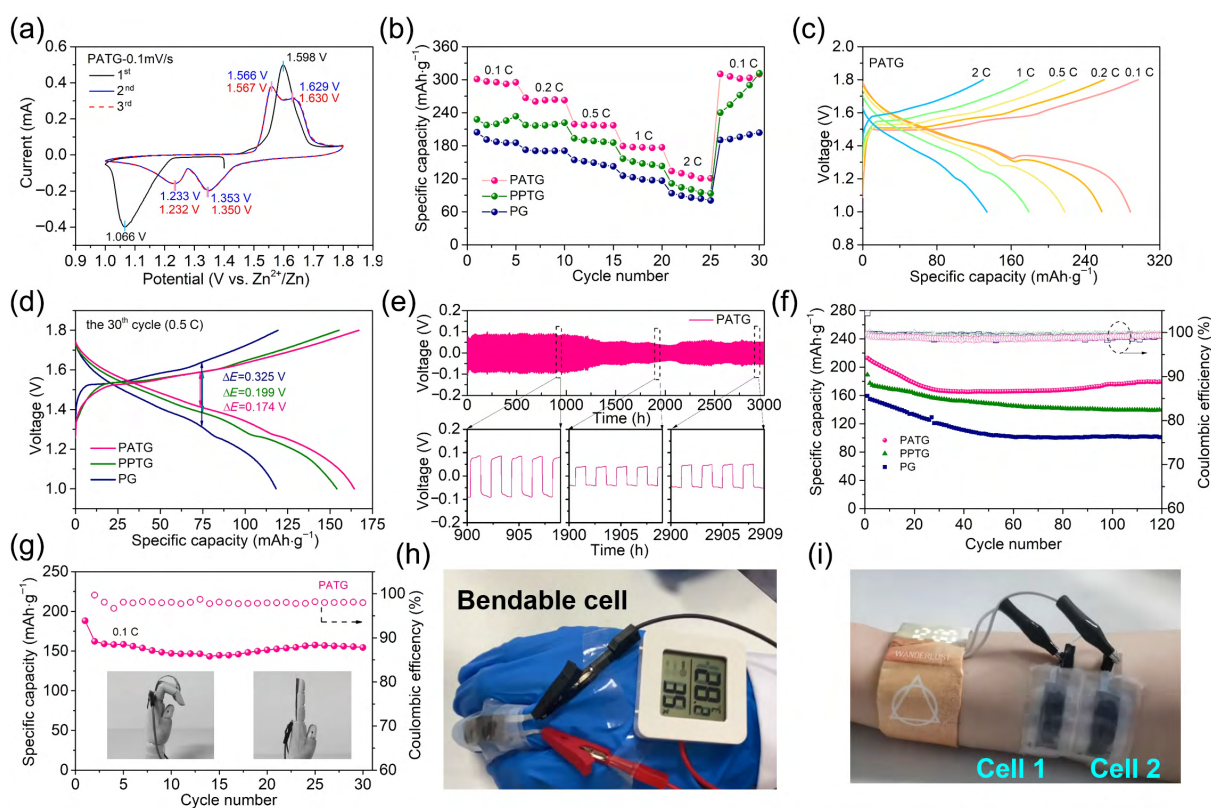


Figure 4 (a) CV curves of Zn|PATG| α -MnO₂ at 0.1 mV·s⁻¹. (b) Rate capability of Zn|| α -MnO₂ cells with PG, PPTG and PATG as the electrolyte. (c) GCD curves of Zn|PATG| α -MnO₂ at different rates. (d) Polarization of full Zn|| α -MnO₂ cells with PG, PPTG and PATG as the electrolyte in the 30th cycle at 0.5C. (e) Voltage profiles of the symmetric Zn|PATG|Zn cell for 3000 hours and (f) Cycling performance of full Zn|| α -MnO₂ cells with PG, PPTG and PATG as the electrolyte. (g) Flexible Zn|PATG| α -MnO₂ cell and (inset) its photos at different bending states. (h) photo of flexible cell working at a bendable state and (i) serial circuit of Zn|PATG| α -MnO₂ cells for powering an electronic watch.

high ionic conductivity and favorable transport kinetics of aligned TiO₂NTs in electrolyte. Figure 4(c) presents the discharge/charge profiles at different rates. It is noted that there are two plateaus corresponding to the insertion of Zn²⁺ and H⁺ into α -MnO₂ lattice during the discharge process, which is consistent with the two cathodic peaks in the CV curves (Fig. 4(a)). Even at the high rates (e.g., 1 C and 2 C), the plateaus are still remarkable, which suggests the good Zn²⁺/H⁺ transport in the PATG. The distinct voltage drop between the two plateaus is attributed to both thermodynamic differences and kinetic transitions during the sequential ion insertion processes of H⁺ and Zn²⁺ [39].

A smaller voltage difference or gap between the charge and discharge curves at a given current density indicates lower overpotential and faster reaction kinetics. As shown in Fig. 4(d), at a constant discharge capacity of 75 mAh·g⁻¹, the voltage polarization significantly decreases from 0.325 V for Zn|PG| α -MnO₂ to 0.199 V for Zn|PPTG| α -MnO₂ and further to 0.174 V for Zn|PATG| α -MnO₂. This lower voltage polarization in the Zn|PATG| α -MnO₂ cell directly correlates with the smaller Zn²⁺ resistance through the optimized electrolyte structure, highlighting its effectiveness in facilitating efficient charge/discharge processes even at higher current densities. The symmetric Zn|PATG|Zn exhibits excellent cycling stability with lower potential hysteresis over 3000 h (Fig. 4(e)), which also proves the low polarization and highly reversible Zn deposition/stripping behavior. The initially higher polarization of *circa* 0.08 V is attributed to an activation process, where the PATG gel electrolyte gradually achieves conformal wetness at the zinc metal interface. And the tiny fluctuations during extended cycling are attributed to the continuous rearrangement of local zinc stripping/plating active sites. This reduced voltage polarization during the prolonged cycling underscores the enhanced kinetics and lower internal resistance provided by the PATG electrolyte. The cycling performance of Zn|PATG| α -MnO₂ batteries was evaluated at a rate of 0.5 C as shown in Fig. 4(f). The initial specific capacities for Zn|PATG| α -MnO₂, Zn|PPTG| α -MnO₂, and Zn|PG| α -MnO₂ were recorded to be 212.9, 189.1, and 159.4 mAh·g⁻¹ at 0.5 C, respectively, demonstrating the advantage of the PATG electrolyte. The initial capacity decrease followed by subsequent stabilization of the PATG electrode is a typical activation process. During the first few discharge cycles, the preferential insertion of H⁺ possibly triggers localized irreversible phase transitions within the α -MnO₂ framework, accompanied by minor lattice water loss and trace manganese dissolution. This leads to a slight loss of initially accessible active material. After 120 cycles, the discharge capacities retain 179.3 mAh·g⁻¹ for Zn|PATG| α -MnO₂, 139.4 mAh·g⁻¹ for Zn|PPTG| α -MnO₂, and 100.8 mAh·g⁻¹ for Zn|PG| α -MnO₂, corresponding to capacity retentions of 84.2%, 73.7%, and 63.6%, respectively. After replacing cycled α -MnO₂ cathodes with new ones, the batteries exhibited capacities ranged from 155.5 mAh·g⁻¹ to 150 mAh·g⁻¹ over 200 cycles (Fig. S16 in the ESM). This demonstrates the excellent cycling stability performance of the quasi-solid PATG electrolyte.

Flexible Zn|PATG| α -MnO₂ cells were assembled in a sandwich structure (in Fig. 4(g)). The cycling performance was slightly inferior to that of coin cells, with an initial capacity of 188.2 mAh·g⁻¹, which decreased to 154.5 mAh·g⁻¹ after 30 cycles, with a capacity retention of 82.1%. Moreover, the flexible Zn|PATG| α -MnO₂ can work well at different bending states (inset of Fig. 4(g)). When worn on a ring finger, the flexible cell powered an electronic display screen (Fig. 4(h)). Additionally, connecting two full cells enabled an electronic watch to work normally (Fig. 4(i)). Supporting videos are available in the ESM.

The post-cycling surface morphology of the zinc anodes provides insights into the crucial role of electrolyte in suppressing dendrite formation. As shown in Fig. 5(a), XRD patterns of the cycled anodes (insets of Fig. 5(a)) provide solid evidence of dendrites prevention. Strong diffraction peaks (with blue index) corresponding to basic zinc sulfate byproduct, ZnSO₄(OH)₆(H₂O), were observed and normalized for comparison. Notably, when using PPTG and PATG as electrolytes, a significant enhancement in the intensity of (002) plane relative to (101) plane of the deposited Zn phase is evident. The increased intensity ratio of (002)/(101) indicates a preferred crystallographic orientation or texture in the deposited layer. This change in preferred orientation and the observed morphology directly correlate with the presence and functionality of the TiO₂NTs incorporated in the PPTG and PATG films. These results fully confirm the critical role of vertically aligned TiO₂NTs in mediating the zinc plating process and byproduct formation towards a more favorable and dendrite-resistant morphology.

The cycled anode surface exhibits increasing roughness in the order of PATG, PPTG and PG, where the anode coupled with the PATG electrolyte yields the smoothest surface. The roughness is particularly severe for the cycled Zn anode coupled with glass fiber separator (Fig. S17 in the ESM). AFM further reveals the nanoscale morphology of the cycled anodes (Figs. 5(b)–5(g)). The cycled Zn anode coupled with the PG electrolyte displayed the formation of irregular worm-like features with the heights around 500 nm (Figs. 5(b) and 5(c)). For the PPTG electrolyte, there are obvious features resembling hexagonal discs (R_q =300 nm) on the surface of cycled Zn anode (Figs. 5(d) and 5(e)). In contrast, the cycled Zn anode coupled with the PATG electrolyte exhibits a remarkably flat surface in Figs. 5(f) and 5(g), with R_q typically less than a few tens of nanometers. SEM images in Figs. 5(h)–5(j) and Fig. S18 in the ESM reveal the same trend as AFM results. It is obvious that the surface of cycled zinc contacting with PG (Fig. 5(h)) exhibits small, loosely organized plate-like deposits. The zinc surface contacting with PPTG (Fig. 5(i)) shows larger, thick, and randomly oriented platelet aggregates. Remarkably, the surface of cycled zinc contacting with PATG is very flat and smooth (Fig. 5(j)). This smooth morphology strongly suggests that the PATG electrolyte effectively regulates the electric field and ion flux, suppresses the formation of detrimental zinc dendrites, and promotes a more uniform deposition layer [40, 41].

To clearly understand the mechanisms behind the different dendrite suppression, a scheme is illustrated in Figs. 5(k)–5(m). In the control PG electrolyte without TiO₂NTs fillers, the crosslinked PVA hydrogel effectively swells in the zinc sulfate solution, providing pathways for ionic conduction. But the deposition process at the zinc surface is less controlled (Fig. 5(k)). Unrestricted in-plane diffusion of Zn²⁺ near the metal surface leads to heterogeneous nucleation and uncontrolled outward growth, resulting in significant dendrite formation and a very rough anode surface after cycling (Figs. 5(b), 5(c), and 5(h)). The incorporation of randomly dispersed TiO₂NTs in the PPTG electrolyte leads to improved bulk Zn²⁺ diffusion compared to PG. The presence of these fillers helps to distribute the ionic current somewhat uniformly within the polymer film (Fig. 5(l)). However, the random dispersion provides less precise control over the Zn²⁺ ions flux directly at the anode-electrolyte interface. So, the deposition on the Zn anode coupled with PPTG is still non-uniform, which is characterized by the formation of distinct hexagonal disc-like features on the surface (Figs. 5(d), 5(e), and 5(i)). But the surface is smoother than that coupled with PG, and rougher than that coupled with PATG (Figs. 5(f), 5(g), and 5(j)).

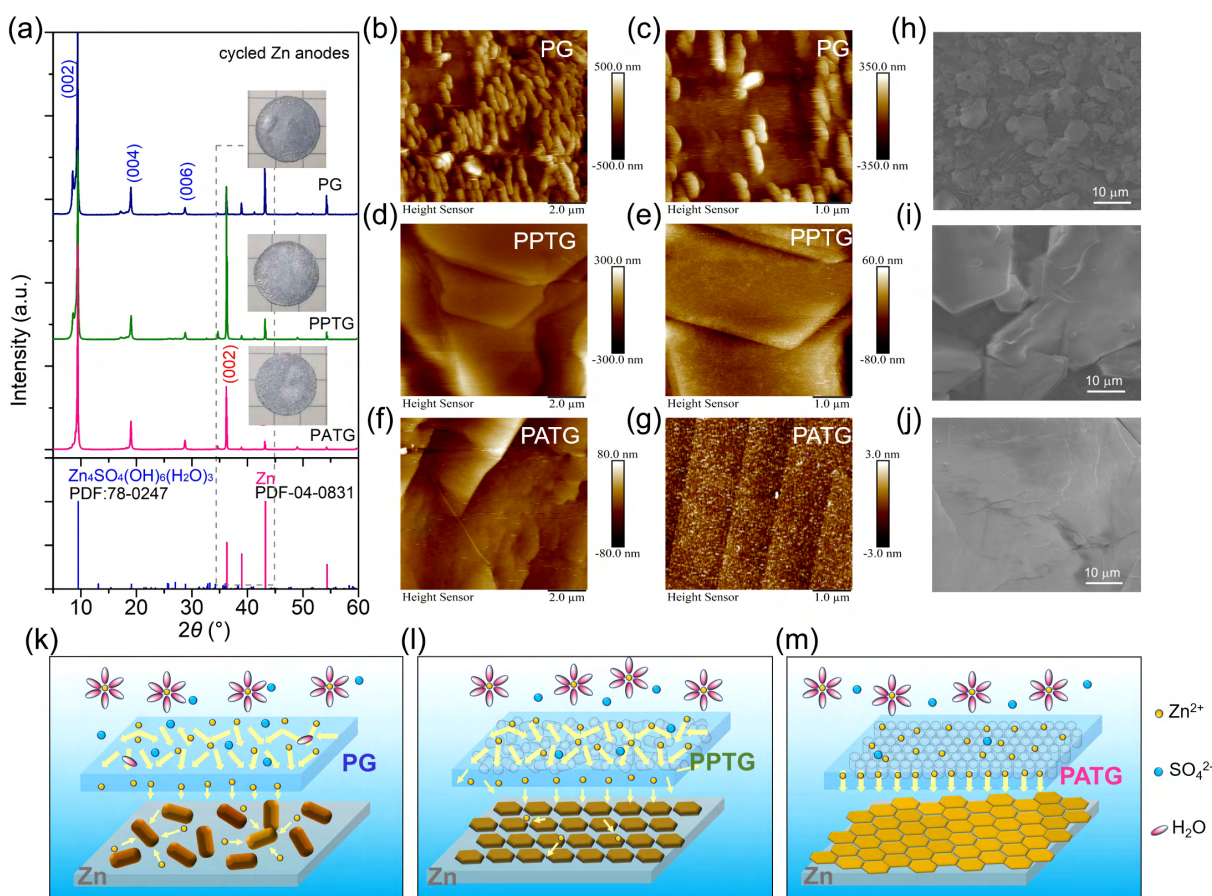


Figure 5 (a) XRD patterns of cycled Zn anodes coupled with PG, PPTG and PATG. AFM images with low and high magnification of (b, c) Zn-PG, (d, e) Zn-PPTG and (f, g) Zn-PATG, respectively. SEM images of (h) Zn-PG, (i) Zn-PPTG and (j) Zn-PATG, respectively. Scheme of Zn²⁺ ions diffusion and Zn growth of dendrites in Zn||α-MnO₂ cells with (k) PG, (l) PPTG, and (m) PATG as electrolyte, respectively.

The mechanism here appears to involve some mediation of nucleation and growth by the randomly distributed fillers (Figs. 5(k) and 5(l)), but without fully suppressing localized growth. The PATG electrolyte, with aligned TiO₂NTs perpendicular to the basal plane, offers a significantly directed pathways (Fig. 5(m)). These aligned nanotubes function as uniform nanochannels that effectively guide the Zn²⁺ cation diffusion directly and evenly towards the zinc anode surface. This directed and uniform ionic flux minimizes local concentration gradient and suppresses heterogeneous nucleation, thereby promoting more even zinc deposition. Furthermore, these rigid, aligned inorganic nanotubes act as mechanical pillars embedded within the softer polymer matrix to provide substantial mechanical reinforcement, and increase the stiffness of the electrolyte layer. These synergistic effects of guided diffusion and mechanical suppression in PATG are key to achieving the superior dendrite-free cycling performance.

4 Conclusion

Vertically aligned TiO₂ nanotubes were successfully integrated into a crosslinked PVA matrix, creating a robust, quasi-solid Zn²⁺-conductive polymer electrolyte. These oriented TiO₂NTs significantly enhanced the mechanical strength of electrolyte and facilitated directed transport of Zn²⁺ ions, outperforming PVA matrices containing randomly dispersed fillers or no fillers. Specifically, the electrolyte with vertically aligned TiO₂NTs exhibited a higher Young's modulus of 56.7 MPa, superior to the randomly dispersed counterpart (32.6 MPa) and the control

without fillers (21.9 MPa). This polymer electrolyte also demonstrated high Zn²⁺ conductivity of 0.26 mS·cm⁻¹, along with the lowest ion activation energy. When incorporated into Zn|PATG|α-MnO₂ full batteries, these vertically aligned TiO₂NT fillers delivered an initial discharge capacity of 301.2 mAh·g⁻¹ at 0.1 C, demonstrating distinctly improved cycling stability, and effectively suppressed zinc dendrite growth. Moreover, the batteries can work at different bending states and power portable electronics well, which highlights the potential application in wearable devices. This work highlights that the strategy of directed ion flux is promising for long-life, flexible aqueous zinc-ion batteries.

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Author contributions

Z. D. and X. Y. conceived and designed this work. Z. D. and Q. L. performed the experiments. J. H., J. Q., R. M., and X. Y. analyzed the results. X. Y. wrote the manuscript. R. M. and X. Y. supervised the project and revised the manuscript. All authors contributed to the discussion of the results.

Declaration of conflicting interests

The authors declare no conflicting interests regarding the content of this article.

Data availability

All data needed to support the conclusions in the paper are presented in the manuscript and/or the Supplementary Materials. Additional data related to this paper may be requested from the corresponding author upon request.

Electronic Supplementary Material: Supplementary material (experimental details, including TiO₂ nanotubes preparation, water uptake test, structure characterization, and some additional results) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120251>.

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