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Interlayer engineering-induced charge redistribution in Bi_2Te_3 toward efficient Zn^{2+} and NH_4^+ storage†

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Bismuth-based materials show promise for aqueous energy storage systems due to their unique layered structures and high storage capacity. Some bismuth-based materials have been applied to store Zn^{2+} or NH_4^+ , indicating that one bismuth-based compound may be innovatively used in both zinc-ion and ammonium-ion batteries (ZIBs and AIBs). Herein, we successfully design a poly(3,4-ethylenedioxythiophene) (PEDOT) coated and embedded Bi_2Te_3 ($\text{Bi}_2\text{Te}_3@\text{PEDOT}$). Theoretical calculations and experimental studies demonstrate that the PEDOT coating and its intercalation into the interlayer enhance the structural stability of Bi_2Te_3 and significantly improve the storage capacities for Zn^{2+} and NH_4^+ . The PEDOT intercalation results in an increased interlayer spacing and a charge redistribution in the interlayer, facilitating charge transfer. Additionally, the insertion-type mechanism of Zn^{2+} and NH_4^+ in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ is revealed through *ex situ* tests. The optimized electrode (5 mg cm⁻²) exhibits high discharge capacities of 385 mA h g⁻¹ in ZIBs and 235 mA h g⁻¹ in AIBs at 0.2 A g⁻¹ and long-term cycle stability. $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ performs robustly even at a high mass loading of 10 mg cm⁻². $\text{Bi}_2\text{Te}_3@\text{PEDOT}@\text{MnO}_2$ (ZIBs) and $\text{Bi}_2\text{Te}_3@\text{PEDOT}@\text{ZnMn}_2\text{O}_4$ (AIBs) full cells offer high reversible capacities. This work provides a reference for designing bifunctional energy storage materials.

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Introduction

Aqueous batteries (ABs) are a new type of promising energy storage device due to their abundant raw materials, inherent safety, and high cost-effectiveness.^{1–5} Various types of ABs have been developed such as Na^+ , K^+ , Al^{3+} , Zn^{2+} , Ca^{2+} , H^+ and NH_4^+ ion batteries.^{6–9} Among them, zinc-ion and ammonium-ion batteries (ZIBs and AIBs) have gained significant attention owing to the high theoretical specific capacity (5855 mA h cm⁻³)

of Zn anodes and the small hydrated ion size (0.331 nm) of NH_4^+ .^{10–13} Though some materials have been reported to show good electrochemical performances in ZIBs and AIBs, such as MoO_3 and CuS , two different modification methods are essential to separately obtain high storage capacities for Zn^{2+} and NH_4^+ .^{14–16}

Recently, the design of bifunctional materials has been drawing more and more attention. For instance, Yu *et al.* synthesized a heterostructural VS_2/VO_x by an *in situ* electrochemical method; the VS_2/VO_x cathode displayed a high specific capacity of 156 mA h g⁻¹ at 10 A g⁻¹ in ZIBs and maintained a reversible capacity of 150 mA h g⁻¹ over more than 1000 cycles in AIBs.¹⁷ Li and coworkers designed a layered $\text{NH}_4\text{V}_4\text{O}_{10}$ cathode with an adjustable interlayer distance through an *in situ* electrochemical strategy, and the optimized electrode exhibited good electrochemical performances for both Zn^{2+} and NH_4^+ storage.¹⁸ However, there are few reports on bifunctional anodes for both ZIBs and AIBs.

In previous works, layered bismuth-based materials such as BiOXs , $\text{Bi}_2\text{O}_2\text{CO}_3$, and Bi_2SeO_5 exhibited good Zn^{2+} or NH_4^+ storage properties due to their large interlayer spacings and robust crystal structures.^{19–21} Therefore, bismuth-based materials show great potential for both Zn^{2+} and NH_4^+ storage. To achieve excellent electrochemical properties in bismuth-based materials, it is very important to improve electronic/ionic

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conductivity.^{22,23} Doping/defect engineering is often used to promote electronic rearrangement and therefore enhances ion/electron transfer, such as Co-doped BiOBr and Se vacancy-activated Bi₂Se₃.^{20,24} However, localized or uneven doping and defects result in their restricted enhancement. For instance, excessive Co doping increases the diffusion barrier in a local area.²⁰ Moreover, the designs of the coating and composite can only improve electron or ion transfer. Fortunately, interlayer engineering is a good choice for layered materials. Benefiting from the existence of structural pillars (cations, graphene, polymers and so on), the interlamellar spacing is increased and the electrostatic interaction between layers is decreased, enabling fast reversible ion diffusion/intercalation and high structural stability.^{25–27}

In this study, we prepare a PEDOT-coated/embedded Bi₂Te₃ (Bi₂Te₃@PEDOT) as a bifunctional anode material for efficient Zn²⁺ and NH₄⁺ storage. The coating of PEDOT improves the stability and electronic conductivity of Bi₂Te₃, and the embedded PEDOT changes the interlayer spacing and charge distribution of Bi₂Te₃ and thus enhances Zn²⁺/NH₄⁺ transport kinetics. The Bi₂Te₃@PEDOT electrode shows superior capacity for Zn²⁺ and NH₄⁺ storage at mass loadings of 5 and 10 mg cm⁻². Remarkably, Zn²⁺ and NH₄⁺ full cells also display satisfactory discharge capacity and cycling stability.

Results and discussion

The preparation processes of Bi₂Te₃ and Bi₂Te₃@PEDOT are schematically displayed in Fig. 1a. Firstly, hexagonal Bi₂Te₃ nanosheets are synthesized *via* a solvothermal method, and then PEDOT is coated on and embedded in Bi₂Te₃ during the polymerization process of EDOT. The compositions and distinctions of Bi₂Te₃ and Bi₂Te₃@PEDOT are characterized by various tests. The X-ray diffraction (XRD) patterns reveal that both samples exhibit similar characteristic peaks which are consistent with Bi₂Te₃ (JCPDS no. 15-0863), suggesting that the crystal structure of Bi₂Te₃ remains unchanged after the incorporation of PEDOT (Fig. 1b). Significantly, the (006) crystal plane in Bi₂Te₃@PEDOT (17.22°) shifts to a low angle compared to Bi₂Te₃ (17.48°), indicating that the lattice spacing increases from 0.507 to 0.515 nm due to the insertion of PEDOT (inset of Fig. 1b). The pure PEDOT is characterized by means of multiple methods (Fig. S1†). Raman spectra further confirm the presence of both Bi₂Te₃ and PEDOT in Bi₂Te₃@PEDOT (Fig. 1c). The peaks at 62, 102, and 134 cm⁻¹ arise from the A¹_{1g}, E²_g, and A²_{1g} modes of Bi₂Te₃, while the characteristic peaks of PEDOT are located at 990, 1263, 1365, 1435, 1510, and 1566 cm⁻¹.^{27–29} Additionally, the peaks in Bi₂Te₃@PEDOT exhibit a visible red shift (inset in Fig. 1c). X-ray photoelectron spectroscopy (XPS) is employed to analyze the chemical state of Bi₂Te₃ and Bi₂Te₃@PEDOT. In the Te 3d XPS spectra (Fig. 1d), the peaks at 571.8 and 582.2 eV in Bi₂Te₃ originate from the Te–Bi bonds, and the Te–O bonds at 572.5 and 586.0 eV are attributed to surface oxidation.³⁰ Similarly, the peaks at 157.2/162.5 eV and 158.6/164.0 eV in the Bi 4f XPS spectra correspond to the Te–Bi and O–Bi bonds, respectively (Fig. S2a†).^{31,32} However, those peaks in Bi₂Te₃@PEDOT shift towards higher binding energies,

indicating the change in the chemical environment due to the introduction of PEDOT. Further evidence for the successful synthesis of Bi₂Te₃@PEDOT is provided by the C 1s and S 2p XPS spectra and the Fourier-transform infrared (FT-IR) spectroscopy spectra (Fig. S2b–d†).^{33,34} Nitrogen adsorption/desorption isotherms and pore size distribution curves reveal that the cumulative pore volume of Bi₂Te₃ rises from 0.0395 to 0.1201 cm³ g⁻¹, and the specific surface area grows from 7.54 to 19.66 m² g⁻¹ after the introduction of PEDOT (Fig. S3†).

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images provide insights into the microstructure and morphology of the samples. The SEM image reveals that Bi₂Te₃ exhibits a smooth hexagonal nanosheet structure (Fig. 1e). Conversely, Bi₂Te₃@PEDOT displays a rough surface, due to the PEDOT coating layer (Fig. 1f). This explains the increased specific surface area in Bi₂Te₃@PEDOT and enhances the charge transfer between Bi₂Te₃@PEDOT and electrolyte. The TEM images reveal a PEDOT coating layer with a thickness of approximately 10 nm in Bi₂Te₃@PEDOT (Fig. S4a and b†). The high-resolution TEM (HRTEM) image exhibits the lattice fringes (0.383 nm) which corresponds to the (101) crystal plane of Bi₂Te₃ (greater than 0.377 nm for pure Bi₂Te₃) (Fig. 1g).³⁵ This result corresponds to the shift in the XRD test. Simultaneously, the polycrystalline nature of Bi₂Te₃@PEDOT is confirmed by the selected area electron diffraction (SAED) test (Fig. S4c†). Elemental mapping illustrates that Bi, Te, S, O, and C elements are evenly distributed across the nanosheet (Fig. 1h). The above results demonstrate the successful synthesis of Bi₂Te₃ and Bi₂Te₃@PEDOT.

Density functional theory (DFT) calculations are used to investigate the role of the embedded PEDOT in the Bi₂Te₃ structure. The optimized crystal structures of Bi₂Te₃ (8.87 × 15.38 × 30.55 Å, $\alpha = 90.15^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$) and PEDOT-Bi₂Te₃ (8.94 × 15.44 × 37.96 Å, $\alpha = 90.09^\circ$, $\beta = 90.03^\circ$, $\gamma = 89.98^\circ$) are presented in Fig. S5.† The insertion of PEDOT results in an expanded interlayer distance and a slight lattice distortion, which is consistent with the experimental results. Differential charge distribution diagrams reveal significant interlamellar electron exchange in the Bi₂Te₃, reflecting a strong interaction in the interlayer (Fig. 1i). PEDOT intercalation reduces such electron exchange, weakening the interlayer interaction (Fig. 1j). Bader charge analysis further supports this finding. Specifically, the average electron count of Te atoms adjacent to PEDOT decreases from 0.37 (without PEDOT) to 0.06 e, indicating that more electron transfer occurs between PEDOT and its neighboring Te atoms. The density of states (DOS) is simulated for both Bi₂Te₃ and PEDOT-Bi₂Te₃ (Fig. S6†). The Bi₂Te₃ model exhibits typical semiconductor properties. The downward shift of the DOS peaks in the PEDOT-Bi₂Te₃ model along with the significant DOS at the Fermi level indicates a transformation from semiconductor to conductor, suggesting that the insertion of PEDOT significantly improves the electrical conductivity of PEDOT-Bi₂Te₃.³⁶ The reduced interlayer electronic interactions and improved electrical conductivity are expected to facilitate ion diffusion in the interlayer, therefore enhancing the electrochemical performances of Bi₂Te₃@PEDOT.



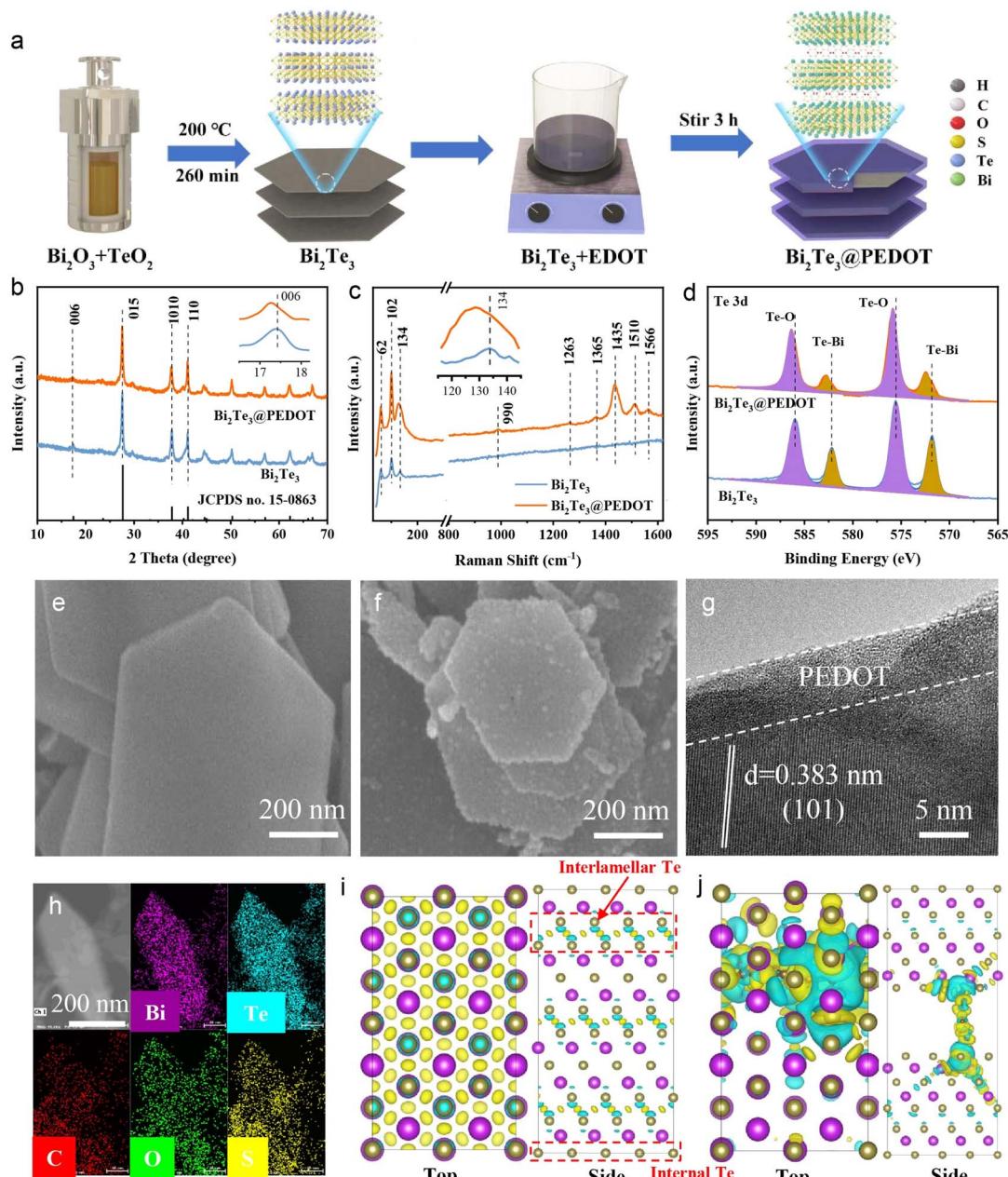


Fig. 1 (a) Schematic diagram of the preparation of Bi₂Te₃ and Bi₂Te₃@PEDOT. (b) XRD patterns, (c) Raman spectra, and (d) Te 3d XPS spectra of Bi₂Te₃ and Bi₂Te₃@PEDOT. SEM images of (e) Bi₂Te₃ and (f) Bi₂Te₃@PEDOT. (g) TEM images of Bi₂Te₃@PEDOT. (h) Elemental mapping of Bi₂Te₃@PEDOT. Charge density distributions of (i) Bi₂Te₃ and (j) PEDOT-Bi₂Te₃ (the purple and brown colors represent Bi and Te atoms, and the yellow and blue regions reflect electron accumulation and electron depletion, respectively).

The electrochemical properties of Bi₂Te₃ and Bi₂Te₃@PEDOT in ZIBs are evaluated firstly. In cyclic voltammetry (CV) tests, Bi₂Te₃ exhibits two redox peaks at 0.62, 0.68, 1.15, and 1.20 V, suggesting the multi-step insertion/deinsertion of Zn²⁺ in Bi₂Te₃. Meanwhile, Bi₂Te₃@PEDOT shows a pair of redox peaks at ~0.6/1.2 V, reflecting a variation in the insertion/deinsertion process of Zn²⁺ after the introduction of PEDOT (Fig. S7†).³⁷ This change is explored in the subsequent studies. Meanwhile, the first three CV curves of Bi₂Te₃@PEDOT overlap better than those of Bi₂Te₃, indicating its improved reversibility.

The first three galvanostatic charge-discharge (GCD) curves show an average discharge plateau at about 0.69 V in Bi₂Te₃ and 0.67 V in Bi₂Te₃@PEDOT, implying their suitability as anodes in full cells (Fig. S8†). The rate performances and cycling properties are further explored. At current densities of 0.2, 0.5, 1.0, 2.0, 3.0, 5.0, and 10 A g⁻¹, Bi₂Te₃@PEDOT offers specific capacities of 378, 340, 320, 312, 310, 300, and 253 mA h g⁻¹, significantly higher than those of Bi₂Te₃ (195, 180, 152, 123, 110, 97, and 80 mA h g⁻¹) and PEDOT (Fig. 2a and S9†). Fig. 2b and c shows the GCD curves at different current densities, in which

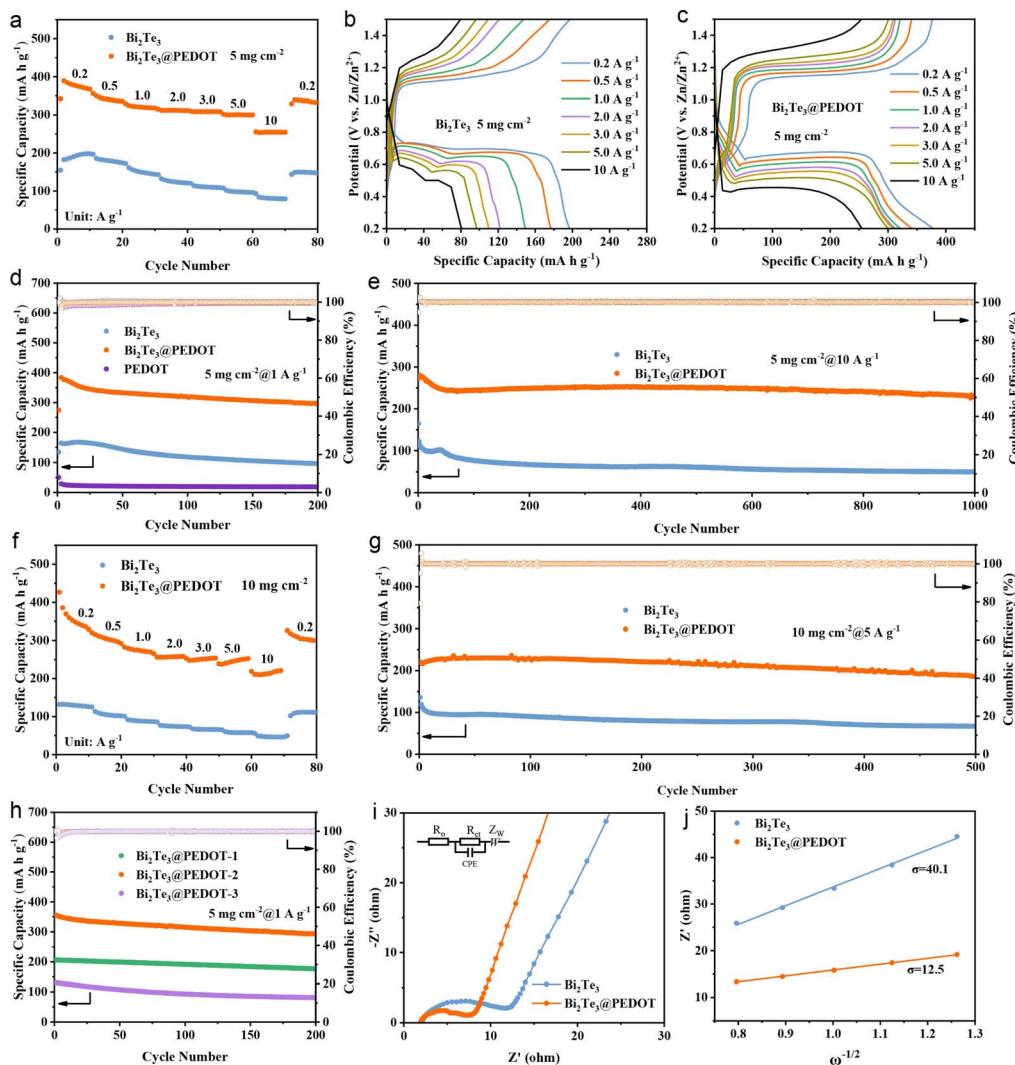


Fig. 2 (a) Rate performances and (b and c) corresponding GCD curves of Bi₂Te₃ and Bi₂Te₃@PEDOT. (d) Cycle life of Bi₂Te₃, Bi₂Te₃@PEDOT, and PEDOT at 1 A g⁻¹. (e) Cyclic performances of Bi₂Te₃ and Bi₂Te₃@PEDOT at 10 A g⁻¹ (5 mg cm⁻²). (f) Rate capabilities and (g) cyclic performances of Bi₂Te₃ and Bi₂Te₃@PEDOT at 5 A g⁻¹ (10 mg cm⁻²). (h) Cycle life of Bi₂Te₃@PEDOT-x at 1 A g⁻¹. (i) EIS spectra and (j) relationship between $\omega^{-1/2}$ and Z' of Bi₂Te₃ and Bi₂Te₃@PEDOT.

Bi₂Te₃@PEDOT exhibits more stable charging and discharging plateaus. In the cycle life test, Bi₂Te₃@PEDOT maintains a discharge capacity of 295 mA h g⁻¹ after 200 cycles at 1 A g⁻¹, which is significantly higher than that of Bi₂Te₃ (96 mA h g⁻¹) (Fig. 2d). Significantly, PEDOT exhibits a negligible Zn²⁺ storage capacity (18 mA h g⁻¹), reflecting its low capacity contribution to Bi₂Te₃@PEDOT. After 1000 cycles at 10 A g⁻¹, Bi₂Te₃@PEDOT retains 82% of its initial capacity, while Bi₂Te₃ retains only 40% (Fig. 2e). Additionally, the high mass loading Bi₂Te₃@PEDOT electrodes (10 mg cm⁻²) are further tested. The discharge capacities of Bi₂Te₃@PEDOT are 325, 290, 263, 257, 253, 251, and 219 mA h g⁻¹ at current densities from 0.2 to 10 A g⁻¹, much higher than those of Bi₂Te₃ (125, 99, 85, 75, 64, 56, and 49 mA h g⁻¹) (Fig. 2f). After 500 cycles at 5 A g⁻¹, Bi₂Te₃@PEDOT maintains a discharge capacity of 187 mA h g⁻¹, while Bi₂Te₃ retains only 68 mA h g⁻¹ (Fig. 2g). The rate and cycling performances of Bi₂Te₃@PEDOT-x are compared (Fig. 2h and S10†). It

is clear that Bi₂Te₃@PEDOT-2 (Bi₂Te₃@PEDOT) outperforms Bi₂Te₃@PEDOT-1 and Bi₂Te₃@PEDOT-3, reflecting that a suitable amount of PEDOT is critical to battery performance.

The electrochemical kinetics of Bi₂Te₃ and Bi₂Te₃@PEDOT is analyzed by CV tests at different sweep rates (Fig. S11a and b†). Fitting the slopes of the $\log(i)$ versus $\log(v)$ curves (Fig. S11c†), the *b*-values of the redox peaks R1, O1, R2, and O2 are 0.72, 0.98, 0.62, and 0.67, respectively. This suggests the enhanced diffusion-controlled behavior of Bi₂Te₃@PEDOT due to its fast ion diffusion.^{38,39} The electrochemical impedance spectra (EIS) show that the ohmic resistance ($R_o = 2.13 \Omega$), charge transfer resistance ($R_{ct} = 9.9 \Omega$), and Warburg factor ($\sigma = 40.1$) of Bi₂Te₃ are larger than those of Bi₂Te₃@PEDOT ($R_o = 1.94 \Omega$, $R_{ct} = 4.56 \Omega$, and $\sigma = 16.8$), thereby indicating an improved reaction kinetics in Bi₂Te₃@PEDOT (Fig. 2i and j). To further demonstrate the superiority of Bi₂Te₃@PEDOT, the Zn²⁺ diffusion coefficient is calculated by the galvanostatic intermittent

titration technique (GITT) test and Fick's second law. As shown in Fig. S12,† the ion diffusion rate in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ is larger than that in Bi_2Te_3 . This result is attributed to the interlayer expansion and reduced electrostatic interaction of Bi_2Te_3 and thus the improved ion diffusion rate.⁴⁰

To explore the storage mechanism in Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$, *ex situ* XRD, XPS, and SEM are conducted. *Ex situ* XRD profiles of Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ are displayed in Fig. 3a–d. Both materials maintain similar XRD patterns during the charge and discharge processes, indicating their intercalation/deintercalation mechanism. The (006) crystal plane in Bi_2Te_3 shifts to a higher angle after the electrode is discharged to 0.2 V, which results from strong electrostatic interactions between the embedded Zn^{2+} and Bi_2Te_3 layers (Fig. 3b).⁴¹ In contrast, the (006) crystal plane of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ shifts to a lower angle at the fully discharged state. This opposite result is attributed to the insertion of PEDOT and the enlarged interlayer spacing which reduces the interaction forces between Zn^{2+} and Bi_2Te_3 layers (this is proved by DFT calculations).⁴² Meanwhile, the by-product of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 4\text{H}_2\text{O}$ (ZSH) is generated in both Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$, though the intensity of ZSH peaks is weak in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. To assess the stability of the materials, Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ are soaked in 2 mol L⁻¹ ZnSO_4 electrolyte for 2 h. As shown in Fig. S13a,† numerous bubbles

are clearly observed on the surface of Bi_2Te_3 , and some white by-products appear on Bi_2Te_3 after drying. In contrast, there is no obvious change for $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. In addition, the XRD pattern of Bi_2Te_3 shows the peaks of Bi_2TeO_5 and $\text{Zn}(\text{SO}_4)(\text{H}_2\text{O})_6$, whereas no obvious new phase is detected in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (Fig. S13b†).

The energy storage mechanism is further investigated using *ex situ* XPS spectra. In the Bi 4f spectra of Bi_2Te_3 (Fig. 3e), the peaks of the Bi–O and Bi–Te bonds irreversibly shift to high binding energy during the first cycle, and the Bi–Te peaks almost disappear at the fully charged state. Moreover, Te–O and Te–Bi peaks in the Te 3d XPS spectra also exhibit similar change, implying the poor reversibility and stability of Bi_2Te_3 (Fig. 3f). For comparison, those peaks in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ do not change significantly during the reaction, highlighting its enhanced stability due to the coating and insertion of PEDOT (Fig. 3g and h). In the Zn 2p XPS spectra, no Zn signal is observed at the original state (Fig. S14†). Zn 2p peaks emerge when the electrode is discharged to 0.2 V and become weak at the fully charged state, indicating the Zn^{2+} intercalation/deintercalation.^{37,43} The O 1s XPS spectra can be divided into two peaks: the O–H peak at 532.0 eV and the O–Bi/O–Te peak at 530.5 eV (Fig. S15†).⁴⁴ The area ratios of O–H and O–Bi/O–Te peaks increase and decrease in the discharge and charge

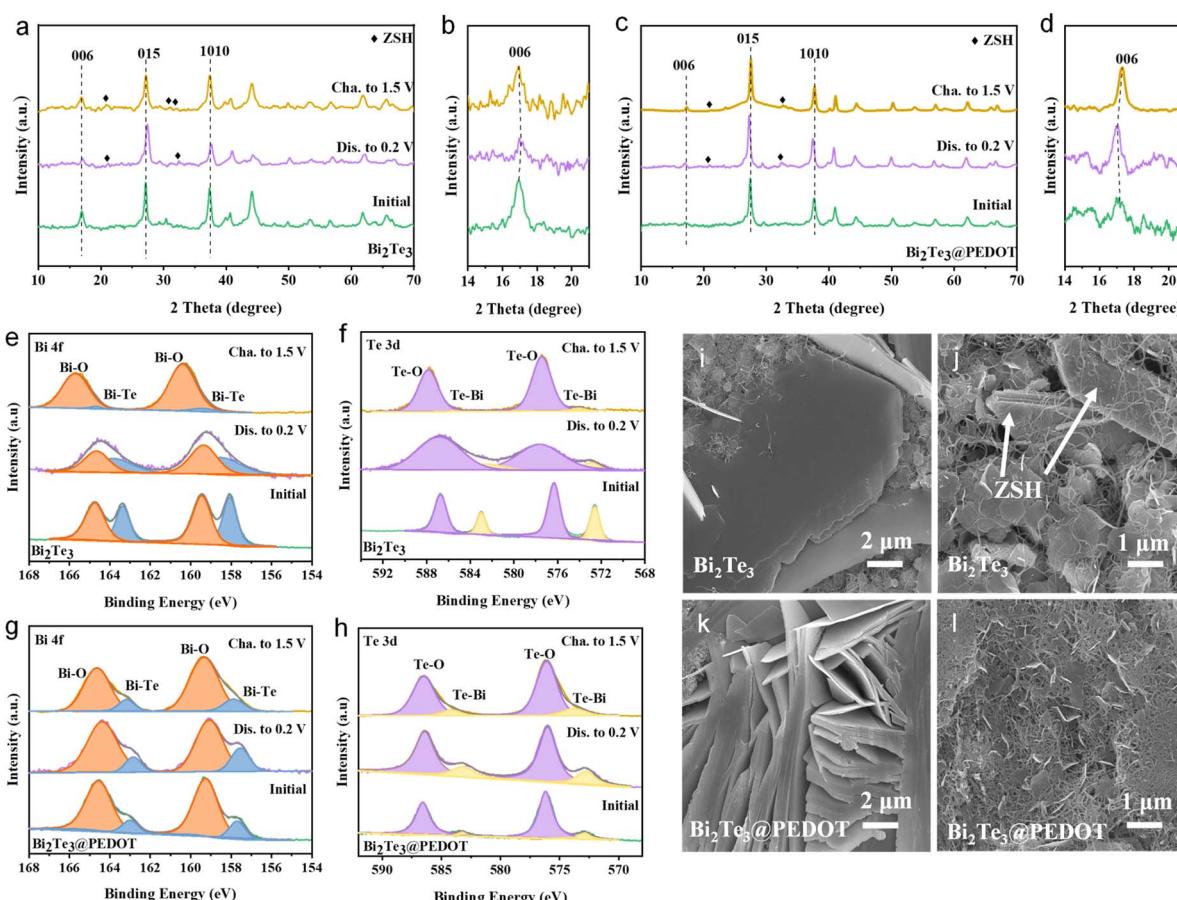


Fig. 3 (a–d) *Ex situ* XRD patterns, (e and g) Bi 4f XPS spectra, and (f and h) Te 3d XPS spectra of Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. SEM images of (i and j) Bi_2Te_3 and (k and l) $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ at the fully discharged/charged states.



processes, respectively, indicating the insertion/extraction of H^+ . The discharge capacities of H^+ and Zn^{2+} in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ are studied in $\text{ZnSO}_4/\text{DMSO}$ and H_2SO_4 ($\text{pH} = 5$) electrolytes, respectively (Fig. S16†). The specific discharge capacity of H^+ (194 mA h g^{-1}) is higher than that of Zn^{2+} (103 mA h g^{-1}), indicating dominant H^+ storage. Additionally, the morphology changes of the electrodes at different charge states are observed by *ex situ* SEM. Many large-sized ZSH flakes are observed in both Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ at 0.2 V (Fig. 3i and k). The ZSH flakes are still visible in Bi_2Te_3 at the fully charged state (Fig. 3j). Meanwhile, the ZSH almost disappears in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$, implying its enhanced reaction reversibility (Fig. 3l). The above study demonstrates the co-insertion mechanism of Zn^{2+} and H^+ in both Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ shows high stability and reversibility in the $\text{Zn}^{2+}/\text{H}^+$ insertion/deinsertion processes.

The remarkable performances of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ in ZIBs prompt an exploration of its electrochemical properties in AIBs. $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ exhibits good rate performance with specific capacities of $266, 235, 200, 164$, and 113 mA h g^{-1} at $0.1, 0.2, 0.5, 1.0$, and 2.0 A g^{-1} , respectively, which is higher than those of Bi_2Te_3 ($245, 212, 168, 120$, and 71 mA h g^{-1}) (Fig. 4a). The corresponding GCD curves are displayed in Fig. S17,† and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ exhibits more obvious discharge plateaus at all current densities. $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ and Bi_2Te_3 deliver the

discharge capacities of 156 and 113 mA h g^{-1} with capacity retentions of 72% and 67% , respectively, after 700 cycles at 1 A g^{-1} (Fig. 4b). Notably, PEDOT shows a low NH_4^+ storage capacity, suggesting its low capacity contribution to $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (Fig. S18†). Additionally, Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ electrodes are tested under a high mass loading of 10 mg cm^{-2} . The discharge capacities of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ are $257, 219, 169, 112$, and 50 mA h g^{-1} at current densities from 0.1 to 2.0 A g^{-1} , while Bi_2Te_3 exhibits lower discharge capacities (Fig. 4c). After 300 cycles at 1.0 A g^{-1} , $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ exhibits a significantly higher discharge capacity of 115 mA h g^{-1} than that of Bi_2Te_3 (66 mA h g^{-1}) (Fig. 4d). Evidently, $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ is well suited for use as a host material for NH_4^+ storage.

The reaction kinetics of Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ is further investigated through CV, EIS, and GITT tests. In the first five CV curves, the redox peaks of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ are more obvious, suggesting its higher capacity for NH_4^+ storage (Fig. S19†). The corresponding b -values for peaks R1, O1, R2, and O2 are $0.67, 0.77, 0.83$, and 0.74 respectively, suggesting an increased capacitive contribution of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (Fig. S20†). The R_{ct} and Warburg factor of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (68Ω and 38.2) are significantly lower than those of Bi_2Te_3 (108Ω and 57.6), implying its enhanced charge transport (Fig. 4e and f). The GITT results also reveal the fast insertion and extraction rates of NH_4^+ in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (Fig. S21†). The above results suggest the

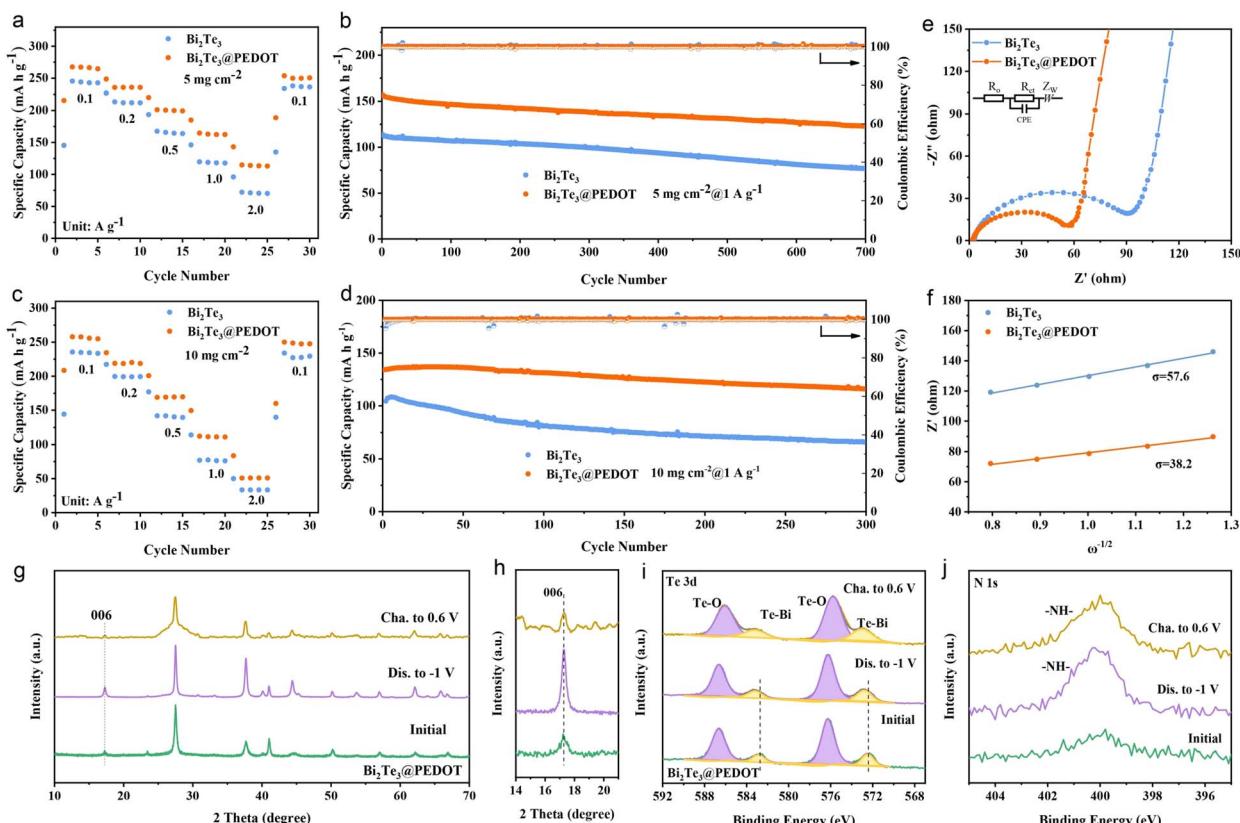


Fig. 4 (a) Rate performances and (b) cycle life of Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (5 mg cm^{-2}) at 1 A g^{-1} . (c) Rate capabilities and (d) cycle life of Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (10 mg cm^{-2}) at 1 A g^{-1} . (e) EIS spectra and (f) relationship between Z' and $\omega^{-1/2}$ of Bi_2Te_3 and $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. (g and h) *Ex situ* XRD patterns, (i) Te 3d XPS spectra, and (j) N 1s XPS spectra of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$.



improved charge transfer of Bi_2Te_3 after the introduction of PEDOT.

To study the NH_4^+ storage mechanism in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$, *ex situ* XRD and XPS tests are conducted. The XRD test reveals that no new phase appears after the electrode is fully discharged/charged (Fig. 4g). The partial enlargement of the XRD pattern is shown in Fig. 4h, in which the (006) crystal plane remains

stable, implying that the insertion and extraction of NH_4^+ do not affect the structure of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. This good stability is due to the protective layer of PEDOT and the increased interlayer spacing in $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. As exhibited in Bi 4f and Te 3d XPS spectra, the Bi–Te peaks shift to higher binding energies after discharging, while the peak positions remain unchanged after charging, indicating a degree of irreversible reaction in the first

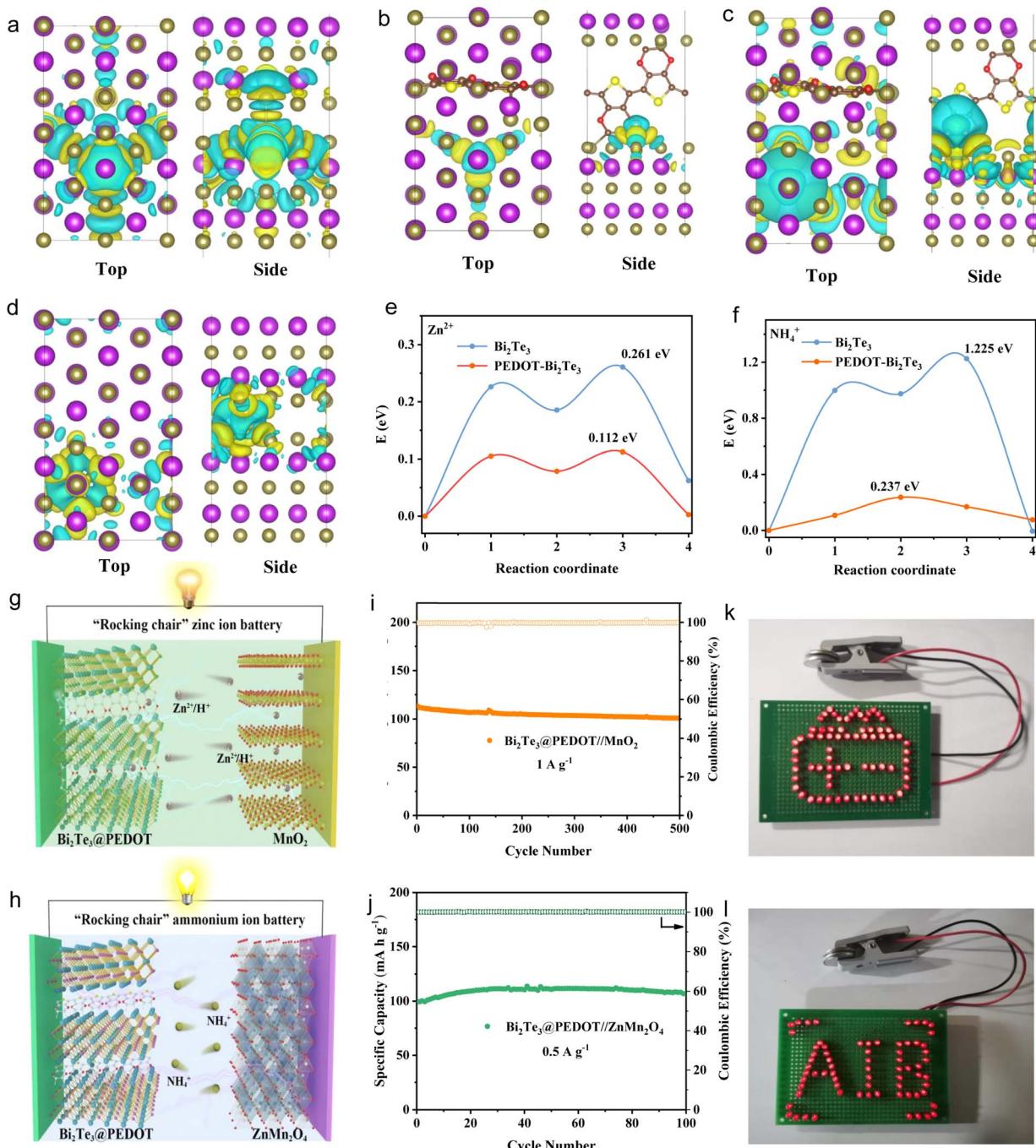


Fig. 5 Charge density distributions of (a) $\text{Bi}_2\text{Te}_3 + \text{Zn}^{2+}$, (b) $\text{PEDOT-Bi}_2\text{Te}_3 + \text{Zn}^{2+}$, (c) $\text{Bi}_2\text{Te}_3 + \text{NH}_4^+$, and (d) $\text{PEDOT-Bi}_2\text{Te}_3 + \text{NH}_4^+$ (the purple and brown colors represent Bi and Te atoms, and the yellow and blue regions reflect electron accumulation and electron depletion, respectively). (e) Zn^{2+} and (f) NH_4^+ diffusion barriers of Bi_2Te_3 and $\text{PEDOT-Bi}_2\text{Te}_3$. (g and h) Structural illustration and (i and j) cycle life of $\text{Bi}_2\text{Te}_3@\text{PEDOT}/\text{MnO}_2$ and $\text{Bi}_2\text{Te}_3@\text{PEDOT}/\text{ZnMn}_2\text{O}_4$ full cells. Digital photos of two (k) $\text{Bi}_2\text{Te}_3@\text{PEDOT}/\text{MnO}_2$ and (l) $\text{Bi}_2\text{Te}_3@\text{PEDOT}/\text{ZnMn}_2\text{O}_4$ full cells lighting up red LEDs.



cycle (Fig. 4i and S22a†). In the N 1s spectra, a strong peak of $\text{NH}_\text{—}$ appears at the fully discharged state, providing evidence that NH_4^+ inserts into $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ (Fig. 4j). However, a weakened peak can still be seen after charging, reflecting the incomplete extraction of NH_4^+ .^{17,45} The intensity of O-H bonds in the O 1s spectra is enhanced after discharging and decreased after charging, demonstrating the co-insertion of H_2O along with NH_4^+ (Fig. S22b†).^{45,46} The above results prove the insertion of NH_4^+ into $\text{Bi}_2\text{Te}_3@\text{PEDOT}$. Significantly, $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ outperforms most of the reported anodes in both ZIBs and AIBs (Tables S1 and S2†). Moreover, the high mass loading anode has been reported rarely.

The Zn^{2+} and NH_4^+ storage properties of Bi_2Te_3 , as well as the function of the embedded PEDOT, are further validated by DFT calculations. The ionic transport is affected by adsorption energy and lattice distortion. The charge density distributions are used to reveal the effect of PEDOT insertion on Zn^{2+} and NH_4^+ adsorption. In the PEDOT- Bi_2Te_3 model, the charge transfer between Zn^{2+} and surrounding Te atoms is reduced, leading to a change in adsorption energy from -0.547 (Bi_2Te_3) to -0.492 eV (PEDOT- Bi_2Te_3) (Fig. 5a and b). This is beneficial to Zn^{2+} diffusion. According to Bader charge analysis, when Zn^{2+} is inserted into Bi_2Te_3 , the Zn transfers a charge of 0.428 e to Bi_2Te_3 , and it drops to 0.089 e in PEDOT- Bi_2Te_3 . Meanwhile, the three neighboring Te atoms obtain an average electron number of 0.046 e before PEDOT intercalation, and it decreases to 0.009 e after PEDOT intercalation. This is consistent with the charge density distributions. By contrast, the adsorption energy between NH_4^+ and Te atoms increases from -0.735 (Bi_2Te_3) to -2.204 eV (PEDOT- Bi_2Te_3) (Fig. 5c and d). Bader charge analysis shows that NH_4^+ transfers 0.53 e before PEDOT insertion and 0.73 e after PEDOT insertion, while the average electron numbers gained by the three neighboring Te atoms are 0.028 and 0.131 e, respectively, indicating the formation of strong covalent interactions between NH_4^+ and Bi_2Te_3 after the PEDOT insertion and the adverse NH_4^+ diffusion. On the other hand, the average bond length of Te-Bi near the adsorption site of Bi_2Te_3 is 3.08 Å and increases to 3.15 and 3.27 Å after Zn^{2+} and NH_4^+ insertion. This change shows a decrease from 3.07 Å to 3.07 and 3.10 Å with the help of interlayer engineering, facilitating Zn^{2+} and NH_4^+ diffusion. Further analysis of the $\text{Zn}^{2+}/\text{NH}_4^+$ diffusion barriers in Bi_2Te_3 and PEDOT- Bi_2Te_3 reveals a significant reduction in diffusion barriers with the insertion of PEDOT. The diffusion pathways of $\text{Zn}^{2+}/\text{NH}_4^+$ are illustrated in Fig. S23.† Specifically, the $\text{Zn}^{2+}/\text{NH}_4^+$ diffusion barrier in Bi_2Te_3 ($1.225/0.237$ eV) declines to $0.261/0.112$ eV with the help of PEDOT (Fig. 5e and f). This reflects that the insertion of PEDOT improves the diffusion of $\text{Zn}^{2+}/\text{NH}_4^+$ due to the combined influence of adsorption energy and lattice distortion.

Finally, full cells are assembled to investigate the practical application of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ in both “rocking-chair” ZIBs and AIBs, respectively. Commercial MnO_2 and ZnMn_2O_4 are used as cathodes due to their low cost and high operating voltages. The schematics of $\text{Bi}_2\text{Te}_3@\text{PEDOT}/\text{MnO}_2$ and $\text{Bi}_2\text{Te}_3@\text{PEDOT}/\text{ZnMn}_2\text{O}_4$ full cells are shown in Fig. 5g and h, where $\text{Zn}^{2+}/\text{H}^+$ or NH_4^+ shuttles between the anode and cathode through the electrolyte. The zinc-ion full battery exhibits a high capacity of

110 mA h g^{-1} at 1 A g^{-1} and a capacity retention of 88% after 500 cycles (Fig. 5i). The ammonium-ion full battery delivers a discharge capacity of 110 mA h g^{-1} at 0.5 A g^{-1} and good cycling stability over 100 cycles (Fig. 5j). The GCD curves of the ZIB and AIB full cells are displayed in Fig. S24.† In addition, both full cells drive the self-assembled red LED logos (Fig. 5k and l).

Conclusions

In summary, a PEDOT-coated/embedded Bi_2Te_3 is successfully fabricated through a hydrothermal method followed by the polymerization of EDOT. Various characterizations and DFT calculations demonstrate that the embedded PEDOT enlarges the interlayer spacing and reduces the interlamellar interaction, thus improving the reaction kinetics of Bi_2Te_3 . Meanwhile, the coating of PEDOT enhances structural stability, suppresses side reactions with the aqueous solution, and increases electronic conductivity. *Ex situ* tests demonstrate the insertion-type mechanism of $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ in both ZIBs and AIBs. The $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ electrode exhibits high discharge capacities of 385 and 235 mA h g^{-1} at 0.2 A g^{-1} in ZIBs and AIBs, respectively. Even at a high mass loading of 10 mg cm^{-2} , $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ shows satisfactory rate performances and cycling stability. Furthermore, “rocking-chair” ZIBs and AIBs with the $\text{Bi}_2\text{Te}_3@\text{PEDOT}$ anode offer high reversible capacities of 110 mA h g^{-1} at 1.0 A g^{-1} (ZIBs) and 110 mA h g^{-1} at 0.5 A g^{-1} (AIBs), respectively. This work extends the utilizing scope of layered bismuth-based materials and serves as a reference for bifunctional energy storage electrodes.

Data availability

The data supporting this article have been included in the main text and ESI.†

Author contributions

X. L.: writing – original draft, data curation; F. L.: writing – original draft, data curation; H. Y.: data curation, investigation; Y. D.: formal analysis, resources, software; L. C.: investigation; T. S.: investigation; Y. P.: resources, software; X. W.: project administration, funding acquisition; B. L.: writing – review & editing, conceptualization, supervision; Y. X.: writing – review & editing, conceptualization, supervision; X. W.: writing – review & editing, project administration, funding acquisition. X. L. and F. L. contributed equally to this work.

Conflicts of interest

There are no conflicts to declare.

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