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Fabrication of inorganic@organic V₂O₅@PEDOT nanocomposite cathode for advanced aqueous manganese-ion batteries†

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Aqueous manganese-ion batteries (AMIBs) show promise for energy storage because Mn anodes exhibit high capacity (976 mAh g^{-1}) and low potential (-1.18 V vs. SHE). However, cathode development faces challenges due to solvated Mn²⁺ with a large radius, resulting in slow ion diffusion, structural instability and limited capacity. Herein, we synthesized inorganic@organic V_2O_5 @PEDOT nanocomposite via a facile in situ polymerization method by combining the EDOT monomer with V_2O_5 . The resulting PEDOT coating exhibited strong adhesion to the V_2O_5 substrate owing to the redox reaction at the organic–inorganic interface, creating a unique hybrid architecture with enhanced charge transfer properties. Furthermore, the PEDOT composite significantly enhanced electrochemical performance by simultaneously suppressing vanadium dissolution and improving electronic conductivity, resulting in exceptionally high specific capacity (340.3 mAh g^{-1} at 0.5 A g^{-1}) and rate capability (211.8 mAh g^{-1} at 5 A g^{-1}). Systematic mechanism characterization confirmed the structural stability and high reversibility of Mn²⁺ insertion/extraction. The practical applicability of the nanocomposite was further demonstrated in a full-cell configuration (Mn|| V_2O_5 @PEDOT), demonstrating high capacity. This study presents a high-performance cathode material for advanced AMIBs and provides new insights into design principles.

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1. Introduction

Aqueous battery systems have emerged as promising candidates for large-scale energy storage applications primarily because of their inherent safety features and environmental advantages. Among the various aqueous battery technologies, manganese (Mn) metal stands out because of its low redox potential (-1.18 V vs. standard hydrogen electrode), suggesting that aqueous manganese-ion batteries (AMIBs) can achieve higher operating voltages. Furthermore, Mn anodes offer additional advantages, including abundant natural reserves, low costs, nontoxicity, and high capacity (976 mAh g⁻¹ based on the Mn/Mn²⁺ redox couple), positioning AMIBs as highly competitive candidates for next-generation aqueous rechargeable batteries. The electrochemical performance of AMIBs is largely governed by their cathode materials. Current research has focused on three major categories of cathode materials:

Among these cathode materials, vanadium-based materials have attracted particular attention owing to their costeffectiveness, multivalent oxidation states, and high theoretical capacities. 10,11 Nevertheless, the practical application of V₂O₅-based cathodes is limited by sluggish reaction kinetics and rapid capacity fading due to poor electrical conductivity, strong Mn²⁺ electrostatic interactions, and material dissolution issues.12-14 To address these technical challenges, research efforts have been devoted to developing effective modification strategies, which primarily focus on defect engineering,15 heteroatom doping,16,17 conductive network construction18,19 optimization.20,21 electrolyte These approaches synergistically enhance electrochemical performance by simultaneously improving charge transfer kinetics, structural stability, and interfacial compatibility.22 For instance, Al3+ was introduced as a pillar in layered V2O5 to develop an AlVO cathode via facile one-step hydrothermal synthesis, demonstrating exceptional compatibility with AMIBs. This cathode material exhibited remarkable electrochemical properties and rapid reaction kinetics.5 However, metal-ionintercalated V₂O₅ electrodes typically exhibit poor electronic conductivity, which significantly limits their electrochemical performance. Moreover, conducting ethylenedioxythiophene) (PEDOT) has been widely employed

vanadium-based compounds, manganese-based oxides and organic materials. $^{7-9}$

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host structures.

as an electrode material in energy storage systems because of its relatively high conductivity. 23,24 PEDOT has emerged as an ideal candidate for enhancing the electrical conductivity of composite materials because of its excellent compatibility with inorganic materials. The incorporation of PEDOT can significantly improve the overall performance of electrode materials by optimizing electron conduction pathways. 25,26 PEDOT polymers can be incorporated into $\rm V_2O_5$ to fabricate inorganic@organic nanocomposites, significantly enhancing the stable

In this study, we develop an inorganic@organic V_2O_5 @-PEDOT nanocomposite via an in situ polymerization approach utilizing the interfacial redox reaction between V_2O_5 and the EDOT monomer at room temperature. The in situ formed PEDOT chains form conductive networks and mixed V^{5+}/V^{4+} valences, which significantly improve the electronic conductivity and ionic diffusion coefficients for AMIBs. Benefiting from these synergistic effects, the as-prepared inorganic@organic V_2O_5 @PEDOT nanocomposite manifests exceptional electrochemical performance, including a high capacity of 340 mAh g^{-1} at 0.5 A g^{-1} , a remarkable rate capability (maintaining 211.8 mAh g^{-1} at 5 A g^{-1}) and outstanding cycling stability after 1000 cycles in an MnSO₄ electrolyte. This approach demonstrates exceptional potential for practical applications, combining facile synthesis with outstanding electrochemical performance.

2. Experimental section

2.1 Material preparation

Initially, 7 g of a V_2O_5 powder was dispersed in 70 mL of deionized water under continuous stirring at room temperature to form a homogeneous suspension. Subsequently, 3 mL of the EDOT monomer was added to the system drop-wise, followed by continuous stirring for 144 h at room temperature. During this process, a distinct color transition from yellow to green was observed, indicating the occurrence of polymerization. The resultant V_2O_5 @PEDOT products were obtained *via* vacuum-drying at 80 °C for 15 h.

2.2 Material characterization

The crystalline phases and structural properties of the synthe-sized $V_2O_5@PEDOT$ were characterized by X-ray diffraction (XRD) using a Rigaku D-Max-3A diffractometer with Cu K α radiation ($\lambda=1.5418~\mbox{\normalfont\AA}$). Morphological analysis was performed by scanning electron microscopy (SEM; Zeiss SUPRA 55 SAPPHIRE) and transmission electron microscopy (TEM; JEM2100F). The chemical compositions and surface electronic states were investigated by X-ray photoelectron spectroscopy (XPS) on a PerkinElmer PHI 1600 ESCA system equipped with an Al K α X-ray source.

2.3 Electrochemical measurement

The carbon anodes were prepared by formulating uniform slurries containing activated carbon (AC), conductive carbon, and a PVDF binder in an optimized weight ratio (8:1:1) using NMP as the processing solvent. These slurries were precisely

coated onto a carbon felt, followed by drying at 80 °C, achieving controlled active material loadings of $\sim 20 \text{ mg cm}^{-2}$. The cathodes were prepared by combining V2O5@PEDOT composites with carbon nanotubes (CNTs) at a ratio of 7:3 and dispersed in DMF. The mixed solution underwent ultrasonic treatment for 30 min to ensure homogeneous dispersion. Then, the V₂O₅(a)-PEDOT composites were obtained via filtration. The weight loading of V_2O_5 @PEDOT was ~1.5 mg cm⁻². For the cell assembly, 2032-type coin cells were configured using either polished Mn metal sheets or carbon felt as anodes, with multiple filter paper separators (diameter = 16 mm) and an aqueous MnSO₄ electrolyte (3 M). The electrochemical performance was comprehensively evaluated via cyclic voltammetry (0.5-2.5 mV s⁻¹ scan rates) and galvanostatic charge-discharge tests within appropriate voltage windows (-1.4 to 0.8 V for $AC||V_2O_5|$; 0.4-1.9 V for $Mn||V_2O_5|$ PEDOT) using analysis equipment (CHI 660E workstation and LAND CT2001A system, respectively).

Results and discussion

To elucidate the structure-property relationship of the V₂O₅@-PEDOT composite, SEM and TEM were employed for morphological investigations. As evidenced in Fig. 1a-c, the composite maintains a well-defined nanorod-like architecture, exhibiting uniform widths of approximately 30 nm with longitudinal dimensions extending to several micrometers. After composting with CNTs, V2O5@PEDOT is embedded within the 3D interconnected CNT network (Fig. 1d-f). The CNT matrix fully encapsulates V₂O₅ nanorods, forming a robust conductive framework that ensures stable interfacial contact between the active material and conductive substrate. This hierarchical architecture facilitates efficient charge transfer pathways, thereby optimizing electrochemical kinetics.27 Further SEM-EDS mapping (Fig. S1a and b†) reveals the homogeneous distribution of C, V, O, and S, confirming the uniform incorporation of PEDOT across the composite. The oxidative polymerization process is initiated when EDOT monomers come into contact with V₂O₅ in the aqueous medium, leading to the in situ formation of a conductive PEDOT layer on the V₂O₅ surface. As shown in Fig. S2,† the content of PEDOT is \sim 16.3%. This interfacial reaction occurs via a well-defined redox mechanism, in which V2O5 serves as the oxidizing agent and structural template. Thus, bulk V2O5 is exfoliated into the nanorod-like morphology.28 XRD analysis was performed to investigate the structural evolution of the V₂O₅@PEDOT composite (Fig. 2a). The diffraction patterns confirm that the phase of V_2O_5 (JCPDS no. 41-1426) remains intact after PEDOT modification (Fig. S3†). Importantly, the (200) diffraction peak exhibits a notable shift from 15.3° in pristine V₂O₅ to 9.1° in the V₂-O₅@PEDOT composite, accompanied by peak broadening and intensity reduction. According to Bragg's law calculations, this shift corresponds to an interlayer spacing expansion from 5.8 Å to 9.7 Å, providing direct evidence of the successful PEDOT intercalation and the resulting interlayer expansion effect.24 Furthermore, intercalated PEDOT molecules serve as structural

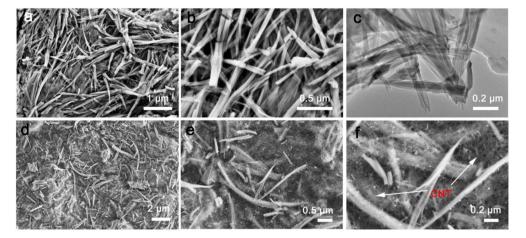


Fig. 1 (a and b) SEM image and (c) TEM image of V₂O₅@PEDOT. (d-f) SEM images of V₂O₅@PEDOT composites with CNTs.

pillars that effectively prevent the collapse of the layered structure during electrochemical cycling.²⁹

The XPS spectrum of the V_2O_5 @PEDOT composite is presented in Fig. 2b. Survey scan analysis reveals distinct characteristic peaks corresponding to C 1s, S 2p, V 2p, and O 1s core levels, confirming the successful incorporation of PEDOT into the composite. The high-resolution V 2p spectrum (Fig. 2c) exhibits a doublet structure with binding energies of 516.2 eV (V 2p_{3/2}) and 525.0 eV (V 2p_{1/2}), which demonstrates the coexistence of V⁵⁺/V⁴⁺ mixed valence states in the composite.²⁵ This valence state analysis indicates that the interfacial interaction between V_2O_5 and PEDOT induces the partial reduction of V⁵⁺ to

 ${
m V^{4^+}}$, and the resulting mixed valence configuration significantly enhances the ${
m Mn^{2^+}}$ transport kinetics during electrochemical processes. The S 2p spectrum (Fig. 2d) displays characteristic features of the thiophene-based PEDOT polymer. These spectroscopic signatures provide compelling evidence of the successful polymerization of EDOT and its effective integration into the ${
m V_2O_5}$ matrix. Based on the XRD and XPS results of the ${
m V_2O_5}$ @PEDOT composite, the reaction mechanism between ${
m V_2O_5}$ and PEDOT is discussed in detail. This study proposes a simple *in situ* polymerization method based on the redox reaction between ${
m V_2O_5}$ and the EDOT monomer. ${
m V_2O_5}$ acts as an oxidizing agent, initiating electron transfer and the

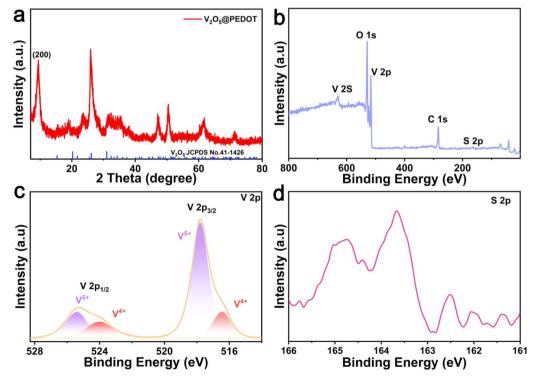


Fig. 2 (a) XRD pattern, (b) XPS spectrum, (c) V 2p spectrum and (d) S 2p spectrum of the V₂O₅@PEDOT composite.

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deprotonation of EDOT monomers. This redox process involves oxygen extraction from the V₂O₅ lattice at the interface, leading to the reduction of V⁵⁺ to V⁴⁺ (as confirmed by XPS V 2p analysis in Fig. 2c) while simultaneously promoting EDOT polymerization into PEDOT on V₂O₅. After PEDOT polymerization, the (200) diffraction peak exhibits a notable shift to a high degree in the V₂O₅@PEDOT composite (Fig. 2a), providing direct evidence of the successful PEDOT intercalation and the resulting interlayer expansion effect.24 The resulting PEDOT coating exhibits strong adhesion to the V2O5 substrate at the organic-inorganic interface, creating a unique hybrid architecture with enhanced charge transfer properties.31

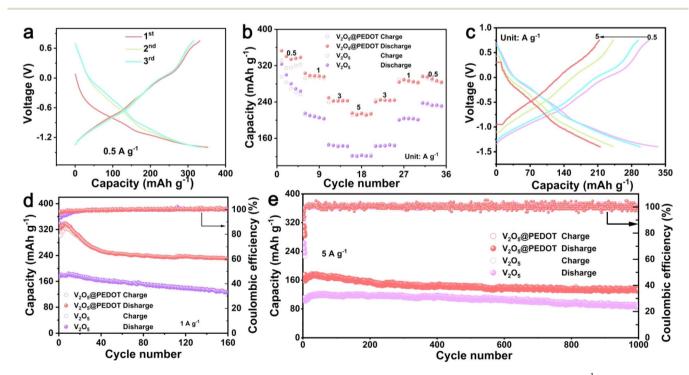
Coin cells were assembled using the AC anodes and 3 M MnSO₄ electrolyte for comparing the performance of V₂O₅@-PEDOT composite cathodes. As shown in Fig. 3a, the composite cathode exhibits similar charge-discharge voltage plateaus at 0.5 A g⁻¹, demonstrating excellent electrochemical reversibility. Rate capability analysis (Fig. 3b) reveals that the optimized V₂-O5@PEDOT cathode delivers superior specific capacities of 340.3, 297.4, 242.3, and 211.8 mAh g^{-1} at various current densities. The capacity significantly outperforms unmodified V_2O_5 (143.1 mAh g^{-1} at 5 A g^{-1}). Remarkably, when the current density is returned to 0.5 A g⁻¹ after high-rate testing, V₂O₅@-PEDOT maintains 291.2 mAh g⁻¹, demonstrating exceptional Mn²⁺ storage reversibility and rapid ion transport kinetics. This was further confirmed by the well-defined charge-discharge plateaus and reduced polarization observed at various current densities (Fig. 3c). Long-term cycling tests at 1 A g⁻¹ (Fig. 3d) show that the V₂O₅@PEDOT nanocomposite cathode achieves an initial capacity of 328.9 mAh g^{-1} , which is much higher than that of V₂O₅. Furthermore, the V₂O₅@PEDOT nanocomposite

maintains 176.4 mAh g^{-1} at 5 A g^{-1} after 1000 cycles (Fig. 3e), demonstrating outstanding structural stability in the MnSO₄ electrolyte. The stable cycle performance can also be proven by EIS measurements. After 100 cycles at 1.0 A g^{-1} , the R_{ct} of the V_2O_5 @PEDOT electrodes is 7.2 Ω (Fig. S4†). The R_{ct} after cycling is similar to that before cycling (7.5 Ω). This means that ion transport is stable during cycling.

To elucidate the electrochemical kinetics of the V₂O₅(a)-PEDOT composite, CV measurements were systematically performed across a range of scan rates (0.5-2.5 mV s⁻¹), as presented in Fig. 4a and S5.† The CV profiles exhibit welldefined redox peaks with maintained shape integrity across scan rates, demonstrating the electrochemical reversibility of the V₂O₅@PEDOT nanocomposite. The kinetic behavior was quantitatively analyzed using the relationship between the peak current (i) and scan rate (ν) :^{32,33}

$$i = av^b$$

where the b-value serves as a critical indicator of the charge storage mechanism. b = 0.5 suggests a diffusion-controlled process. b = 1.0 indicates surface-controlled capacitive storage. The kinetic analysis of the V2O5@PEDOT nanocomposite cathode reveals a mixed charge storage mechanism, as evidenced by the calculated b-values of 0.85 (peak I), 0.71 (peak II), 0.81 (peak III), and 0.88 (peak IV) derived from scanrate-dependent CV measurements (Fig. 4b). These intermediate b-values between 0.5 and 1.0 suggest that the electrochemical reactions are governed by a combination of diffusioncontrolled intercalation and surface-mediated capacitive processes.



(a) Initial three charge-discharge cycles, (b) rate performance, (c) charge-discharge curves, (d) cycle life at 1 A g^{-1} and (e) cycle life at 5 A $\rm g^{-1}$ of the $\rm V_2O_5$ @PEDOT composite.

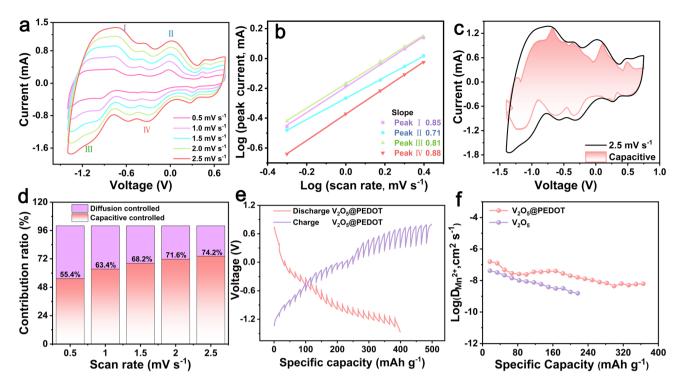


Fig. 4 (a) CV curves, (b) $\log(i)$ vs. $\log(\nu)$, (c) capacitive contribution, (d) capacitive contribution at 2.5 mV s⁻¹, (e) the GCD curve of GITT, and (f) the relevant Mn²⁺ ion diffusion coefficient of the V₂O₅@PEDOT composite.

The quantitative separation of capacitive- and diffusion-controlled contributions can be achieved using the following equation:^{34,35}

$$i = k_1 \nu + k_2 \nu^{\frac{1}{2}}$$

Electrochemical kinetic analysis reveals a distinct evolution in the charge storage behavior of the V2O5@PEDOT cathode with increasing scan rates $(0.5-2.5 \text{ mV s}^{-1})$. As shown in Fig. 4c, the capacitive contribution percentage demonstrates a progressive increase from 55.4% to 74.2%, reaching its maximum at a scan rate of 2.5 mV s⁻¹ (Fig. 4d). This trend contrasts markedly with the V₂O₅ cathode, which exhibits low b-values (Fig. S6†) and decreased capacitive contributions (Fig. S7†). These findings demonstrate that the inorganic@organic V2O5@PEDOT nanocomposite architecture effectively promotes surfacecontrolled charge storage processes. The Mn²⁺ diffusion coefficient was quantitatively analyzed using the galvanostatic intermittent titration technique (GITT). As illustrated in Fig. 4e, the linear correlation between the voltage change (ΔE_{τ}) and $\tau^{1/2}$, where τ is pulse duration, enabled the calculation of Mn²⁺ diffusion coefficients $(D_{Mn^{2+}})$ using the equation:

$$D_{
m Mn^{2+}} = rac{4}{ au\pi} igg(rac{m_{
m B} V_{
m m}}{M_{
m B} S}igg)^2 igg[rac{\Delta E_{
m s}}{\Delta E_{
m \tau}}igg]^2 ig(au \ll L^2/D_{
m Mn}ig)$$

The GITT parameters are defined as follows: τ is the pulse time, $m_{\rm B}$ is the active mass, $M_{\rm B}$ is the molar mass, $V_{\rm m}$ is the molar volume, and $\Delta E_{\rm s}$ is the equilibrium voltage change. The V₂-O₅@PEDOT cathode demonstrates significantly enhanced kinetics, with $D_{\rm Mn^{2+}}$ values between 1.56 \times 10⁻⁷ cm² s⁻¹ and

 4.46×10^{-9} cm 2 s $^{-1}$ (Fig. 4f), which are better than those of pristine V_2O_5 (4.21 \times 10^{-8} cm 2 s $^{-1}$ to 1.55 \times 10^{-9} cm 2 s $^{-1}$).

Using a combination of ex situ XRD and XPS analyses, the structural dynamics and charge storage mechanism of the V2-O₅@PEDOT cathode during the electrochemical process were systematically elucidated (Fig. 5a). As depicted in Fig. 5b, the (200) diffraction peak shifts toward lower angles during the discharging process, corresponding to an interlayer expansion induced by Mn²⁺ intercalation. Notably, the peak fully reverts to its initial position upon charging to 0.8 V, demonstrating exceptional structural reversibility and lattice stability (Fig. 5c).³⁶ Complementary XPS analysis (Fig. 5d) reveals the redox chemistry underlying this process: the pristine electrode exhibits mixed V⁵⁺ (517.6/525.2 eV) and V⁴⁺ (516.2/523.6 eV) states due to partial reduction during PEDOT polymerization. Upon discharging to -1.4 V, the emergence of V^{3+} species and the enhancement of V4+ signals confirm Mn2+ intercalation, while recharging restores the dominant V⁵⁺ state, verifying the presence of the highly reversible vanadium redox (Fig. 5e). Concurrently, the Mn 2p spectra show clear Mn²⁺ signals in the discharged state, with residual intensity persisting in the charged state, corroborating the XRD observations of incomplete Mn2+ extraction. These findings collectively establish a Mn²⁺ intercalation/deintercalation mechanism with minor irreversibility (Fig. 5f). The spatial distribution and electrochemical evolution of elemental constituents in the V2O5@-PEDOT cathode were thoroughly investigated using SEM-EDS. As illustrated in Fig. S8,† EDS elemental mapping demonstrates that V, O, and S exhibit nearly identical spatial distribution patterns in discharged (Fig. S8a†) and charged (Fig. S8b†)

states, confirming exceptional structural stability during electrochemical cycling. Mn exhibits pronounced state-dependent behavior, with strong characteristic signals appearing during discharging and a significantly attenuated intensity appearing upon charging, which provides direct evidence of the Mn²⁺ Mn^{2+} intercalation/deintercalation mechanism. intercalation/deintercalation mechanism is schematically shown in Fig. 6. According to ex situ XRD and XPS analyses, Mn²⁺ ions are intercalated into the V₂O₅@PEDOT electrodes in the discharged state. After the charging process, Mn²⁺ ions are deintercalated from the V₂O₅@PEDOT electrodes.

Building on the outstanding performance of AC||V2O5@-PEDOT cells, we further investigated the practical application potential of V2O5@PEDOT cathodes in manganese-ion full battery systems by pairing them directly with Mn metal anodes. The Mn||V₂O₅@PEDOT full cell demonstrates remarkable electrochemical properties, delivering an exceptional specific capacity of 424.3 mAh g⁻¹ at 0.2 A g⁻¹, which is a significant improvement compared to V₂O₅ cathodes (Fig. 7a). More importantly, the cell maintains superior rate capability, exhibiting 122.5 mAh g⁻¹ even at a high current density of 1.0 A g⁻¹ (Fig. 7a). The galvanostatic charge-discharge profiles (Fig. 7b) reveal distinct voltage plateaus, indicating well-defined redox

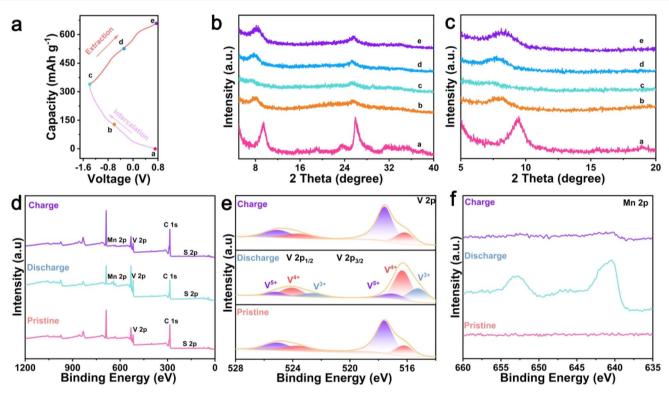


Fig. 5 (a) Charge-discharge profiles, (b) XRD curves, (c) magnified XRD curves, (d) XPS spectra, (e) V 2p spectra and (f) Mn 2p spectra of the V₂O₅@PEDOT composite at different discharged-charged states.

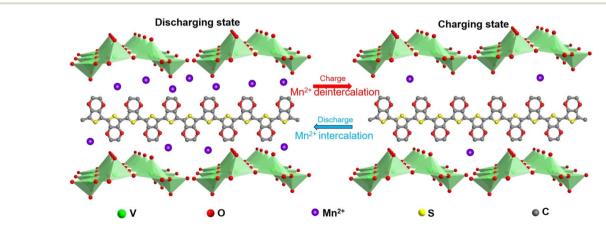


Fig. 6 Schematic of the storage mechanism of Mn²⁺ ions.

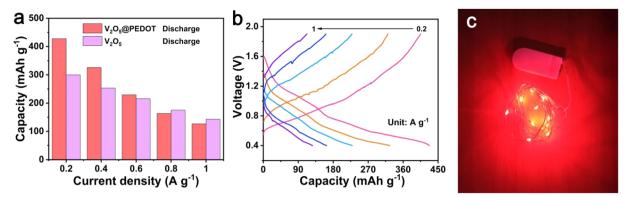


Fig. 7 (a) Capacity and (b) discharge—charge curves of the Mn $\|V_2O_5$ @PEDOT full cell at different current densities. (c) Optical image of the red LED lighted using two Mn $\|V_2O_5$ @PEDOT cells.

reactions during Mn^{2+} insertion/extraction processes. To validate practical applicability, we successfully powered light-emitting diodes (LEDs) using two serially connected $Mn\|V_2-O_5$ @PEDOT cells (Fig. 7c), demonstrating the real-world viability of this battery configuration. These results collectively highlight that the inorganic@organic V_2O_5 @PEDOT nanocomposite is a promising cathode material for high-performance AMIBs.

4. Conclusions

The inorganic@organic V₂O₅@PEDOT nanocomposite was successfully synthesized via a facile in situ polymerization method by simply introducing the EDOT monomer into a V₂O₅ solution at room temperature, eliminating the need for additional oxidants or complex processing steps. The conformal PEDOT coating significantly enhanced the electrochemical performance by simultaneously suppressing vanadium dissolution and improving electronic conductivity, resulting in exceptional cycling stability after 1000 cycles at 5 A g⁻¹ in the MnSO₄ electrolyte and an exceptional rate capability (211.8 mAh g^{-1} at 5 A g^{-1}). Systematic mechanism characterization confirmed the structural stability and high reversibility of Mn²⁺ insertion/extraction. The practical applicability was further demonstrated in a full-cell configuration (Mn||V2O5@PEDOT), which maintained high capacity. This study not only presents a high-performance cathode material but also provides new insights into the design principles for advanced AMIBs, potentially expanding the research scope in sustainable energy storage systems.

Data availability

All data supporting this research are included in the main article and ESI.†

Author contributions

Xianyu Liu: conceptualization, writing original draft, and funding acquisition. Jianan Zhao: methodology, data curation,

and validation. Zhigang Fan: writing – review & editing. Ying-chun Xiao: supervision, investigation, and funding acquisition. Yande Zhao: formal analysis and resources. Qing Guo: investigation and validation.

Conflicts of interest

The authors declare that they have no conflict of interest.

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