



Electrostatic co-assembly derived mesoporous polyoxometalate-intercalated polyaniline hybrid nanospheres for stable zinc-ion batteries

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ABSTRACT

Aqueous zinc-ion batteries (AZIBs) are promising large-scale energy storage devices, yet their practical application is severely restricted by cathode materials suffering from sluggish ion transport kinetics and poor cyclic stability. Organic polyaniline cathodes feature tunable redox sites and mechanical flexibility, but dense chain stacking and drastic volume expansion degrade their capacity and lifespan. Herein, we propose an electrostatic co-assembly and confined template polymerization strategy to fabricate mesoporous vanadium-manganese polyoxometalate-intercalated polyaniline hybrid nanospheres (mPANI@POM). Negatively charged colloidal silica (SiO_2) serves as sacrificial templates to guide uniform adsorption of protonated aniline, while anionic polyoxometalate (POM) clusters are electrostatically intercalated into polyaniline chains to form an organic-inorganic hybrid after template etching. The interconnected mesoporous framework shortens $\text{Zn}^{2+}/\text{H}^+$ diffusion paths, and the synergistic dual redox centers of conjugated polyaniline and multi-electron vanadium-manganese polyoxometalate greatly accelerate charge transfer. The mPANI@POM cathode achieves $264 \text{ mAh}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$, retains $147 \text{ mAh}\cdot\text{g}^{-1}$ at $3.0 \text{ A}\cdot\text{g}^{-1}$, and exhibits good cycling stability with 90.6% capacity retention after 1000 cycles at $5.0 \text{ A}\cdot\text{g}^{-1}$. Combined *in-situ* characterizations verify that energy storage relies on synergistic reversible benzenoid-quinoid transformation and reversible V/Mn-O coordination evolution. This electrostatic co-assembly strategy offers a universal route to design high-performance organic-inorganic hybrid cathodes for durable AZIBs.

KEYWORDS

electrostatic co-assembly, hybrid mesoporous nanospheres, polyoxometalate, zinc-ion batteries

1 Introduction

Amid global carbon neutrality initiatives and the shift to sustainable energy, the exploration of safe, affordable and environmentally friendly electrochemical energy storage technologies has emerged as a core research direction for energy materials [1–3]. Featuring high theoretical capacity ($820 \text{ mAh}\cdot\text{g}^{-1}$), low redox potential (-0.76 V vs. SHE), inherent safety and low cost, aqueous zinc-ion batteries (AZIBs) show great competitiveness for large-scale energy storage [4–6]. Nevertheless, the practical implementation of AZIBs remains constrained by the absence of ideal cathode materials that concurrently deliver excellent structural stability [7], fast reaction kinetics and high capacity. The mainstream cathode materials extensively investigated for AZIBs primarily include manganese-based compounds [8], vanadium-based compounds [9], Prussian blue analogues [10], and organic materials [11]. Their charge-storage of mechanism depends on the reversible insertion/extraction of $\text{Zn}^{2+}/\text{H}^+$. However, this electrochemical process inevitably suffers

from sluggish ion diffusion kinetics, severe lattice distortion, active material dissolution, and irreversible phase evolution during long-term cycling [12–14]. Accordingly, the rational design of advanced cathode materials with fast ion transport, abundant accessible active sites, and robust structural frameworks is critically important for promoting the development of high-performance AZIBs.

Organic polymer cathodes have been regarded as appealing candidates by virtue of their tailorable molecular structures, rich accessible redox-active sites, environmental sustainability, and superior mechanical flexibility [15, 16]. In particular, aromatic conjugated polymers possess delocalized π -electron skeletons for efficient electron conduction, while functional redox sites enable reversible $\text{Zn}^{2+}/\text{H}^+$ accommodation and doped-state structural regulation, achieving fast and highly reversible charge-storage properties [17, 18]. Despite these merits, pristine conjugated polymers still face intrinsic drawbacks, including dense molecular chain stacking, insufficient exposure of active sites, irreversible

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deprotonation, and drastic volume changes during cycling, which greatly impair their electrochemical capacity and cycling durability [19, 20]. Hybridizing organic polymers with inorganic functional components has proven effective in resolving these bottlenecks [21]. Mesoporous construction can effectively expand the electrode-electrolyte contact area and shorten ion diffusion paths [22], while polyoxometalates (POMs), as typical multi-metallic oxygen clusters, possess abundant redox-active centers, intrinsic multi-electron reaction capability, and excellent structural stability [23]. The integration of conductive polymer skeletons, mesoporous ion-transport channels, and multielectron POM redox centers is expected to simultaneously address the insufficient active site utilization [24], sluggish kinetics, and structural instability of pure organic cathodes. However, the controllable fabrication of high-quality organic inorganic POM-hybridized electrodes remains challenging due to inherent structural mismatching, poor template compatibility, and weak interfacial interaction between POM clusters and organic polymer units [25].

Herein, we propose an interfacial electrostatic coupling-driven approach integrated with *in-situ* polymerization-induced co-assembly to construct ordered mesoporous organic-inorganic hybrid nanospheres. Specifically, the negatively charged colloidal SiO_2 acts as a template and enables the directional adsorption of protonated aniline monomers. Meanwhile, negatively charged POM clusters serving as guest molecules intercalate into the polyaniline (PANI) molecular chains. Polymerization proceeds under the driving force of surface energy minimization, which directs the spontaneous co-assembly of building blocks into well-ordered mesoporous spherical architectures (mPANI@POM). The hybrid structure synergistically integrates the fast $\text{Zn}^{2+}/\text{H}^+$ diffusion pathways, abundant redox sites, efficient ion diffusion of mesoporous frameworks, and superior multi-electron redox activity derived from V/Mn-O moieties. Benefiting from the structural and electronic synergies, the mPANI@POM delivers a high capacity of $264 \text{ mAh}\cdot\text{g}^{-1}$ at $0.5 \text{ A}\cdot\text{g}^{-1}$, retains a capacity of $147 \text{ mAh}\cdot\text{g}^{-1}$ at $3.0 \text{ A}\cdot\text{g}^{-1}$, and exhibits stable cycling performance with 90.6% capacity retention after 1000 cycles at $5.0 \text{ A}\cdot\text{g}^{-1}$. Moreover, combined *in-situ* characterizations and theoretical calculations demonstrate that the superior $\text{Zn}^{2+}/\text{H}^+$ storage properties of mPANI@POM originate from the synergistic reversible redox reactions of the PANI benzenoid-quinoid transformation and V/Mn-O coordination evolution mechanisms. This work provides a new design strategy for developing high-capacity, high-rate and long-life organic-inorganic hybrid cathodes for AZIBs.

2 Experimental

2.1 Chemicals and materials

Colloidal SiO_2 suspension was purchased from Guangdong Heli Industrial Co., Ltd. Aniline hydrochloride was obtained from Adamas-beta. Hydrochloric acid and nitric acid solutions were purchased from Kunshan Jincheng Reagent Co., Ltd. Hydrofluoric acid, ammonium persulfate and sodium bicarbonate were purchased from Aladdin. Sodium vanadate, sodium acetate, sodium persulfate, manganese sulfate and acetic acid were obtained from Macklin. Anhydrous ethanol was purchased from Shanghai Honghuanxin Biochemical Technology Co., Ltd. All chemicals were used without further purification. Deionized water was supplied by a Millipore Autopure system for all experiments.

2.2 Preparation of the mPANI@POM

Typically, 1 mL of colloidal SiO_2 suspension was dispersed in 5 mL of 1 M HCl solution by ultrasonication and stirring for 5–10 min. Aniline hydrochloride (0.2 g) was then added to the above suspension under an ice bath, followed by continuous stirring to ensure homogeneous dispersion. Subsequently, VMnPOM (0.1 g, dissolved in 2 mL of deionized water) and ammonium persulfate (APS) (0.5 g, dissolved in 2 mL of 1 M HCl) were introduced into the mixture. The reaction was maintained for 24 h under continuous stirring. After removing SiO_2 and excess ions through repeated washing with hydrofluoric acid (HF), water and ethanol, the resulting product is further transferred to a 40°C dryer and dried for 24 h until completely dry. mPANI@POM is obtained. The large-scale preparation of the mPANI@POM is achieved through scaling up from small batch preparations.

2.3 Material characterizations

The phase compositions of mPANI@POM, PANI@POM and mPANI were examined by powder X-ray diffraction (XRD, D/MAX/2500PC) with $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$) over the range of 3° – 90° (2θ) at room temperature. Field emission scanning electron microscopy (FESEM, JSM-6700F), transmission electron microscopy (TEM) and high-resolution transmission electron microscopy (HRTEM, JEM-F200) tests were carried out to characterize the morphologies and microstructures of these samples. Energy dispersive X-ray spectrometry (EDS) was conducted to understand the distribution of elements using JEM-F200. The Brunauer-Emmett-Teller (BET) method was applied to evaluate the specific surface area of the mPANI@POM. The pore-size distribution (PSD) curves were obtained from N_2 adsorption data. X-ray photoelectron spectroscopy (XPS) analysis was performed to reveal the chemical states of elements. Fourier transform infrared (FTIR) spectra were performed on Nicolet iS50 spectrometer (Thermo Fisher) ranging from 4000 cm^{-1} to 500 cm^{-1} . The Raman spectra were conducted with Horiba LabRAM HR Evolution. Zeta potential values were conducted on Zetasizer Nano ZS analyzer.

3 Results and discussion

3.1 Synthesis and characterizations of mPANI@POM nanospheres

Microscale electrostatic interactions serve as a key driving force that controls the aggregation, assembly and bonding of various building units. Leveraging this inherent electrostatic modulation effect enables precise regulation of interfacial assembly and structural evolution, offering a reliable pathway for the rational design of multi-component hybrid architectures. An ordered mesoporous spherical architecture of polyaniline@vanadium-manganese polyoxometalate ammonium composite (mPANI@POM) was successfully constructed through a confined templating and electrostatic co-assembly approach (Fig. S1 in the Electronic Supplementary Material (ESM)). As illustrated in Fig. 1, under acidic conditions, the aniline monomers are fully protonated and uniformly anchored onto the negatively charged colloidal SiO_2 surface through electrostatic attraction. Subsequently, negatively charged VMnPOM clusters derived from the pre-synthesized sodium vanadium manganese oxide are introduced (Figs. S2–S4 in the ESM), which formed stable ionic

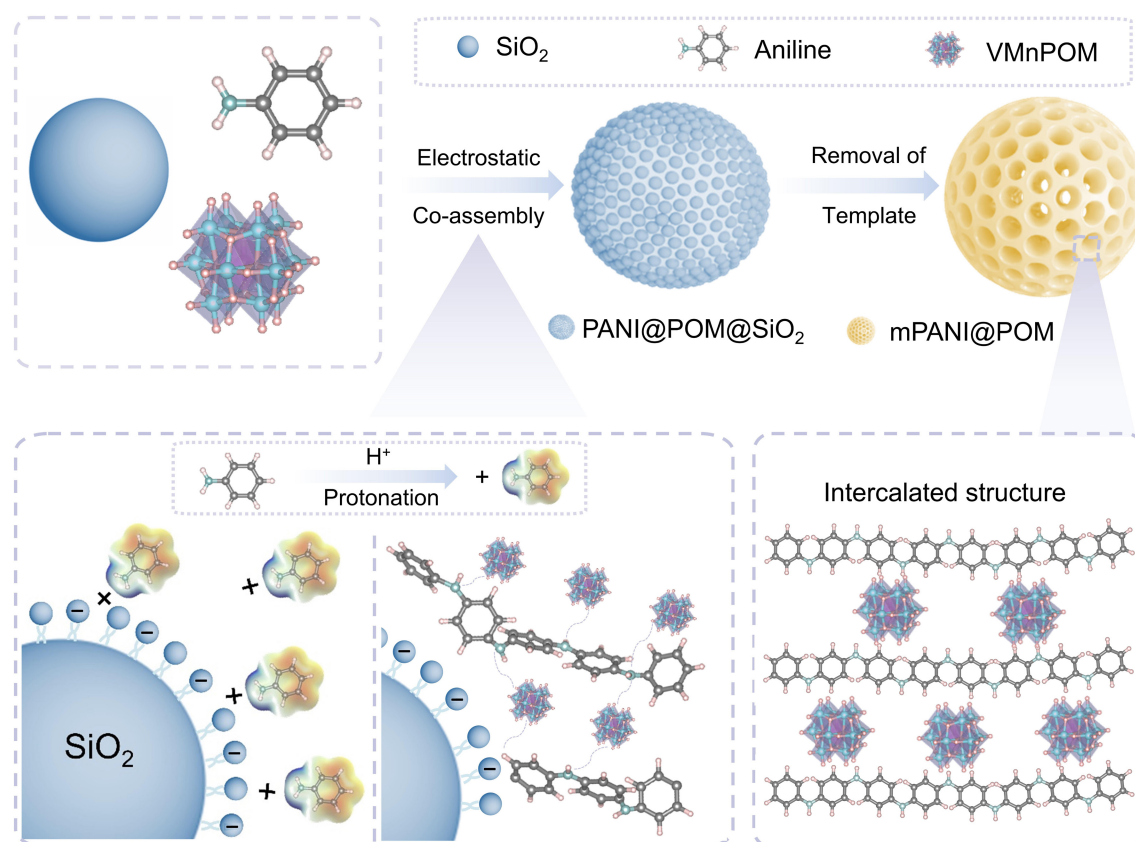


Figure 1 Schematic illustration on electrostatic co-assembly synthesis of mPANI@POM nanospheres.

associates with the protonated aniline species through electrostatic interactions (Figs. S5 and S6 in the ESM). Subsequent addition of ammonium persulfate initiates the *in-situ* oxidative polymerization of aniline, which triggers polymerization-induced assembly: ongoing aniline polymerization drives the ordered rearrangement and directional assembly of PANI molecular chains, while VMnPOM clusters are homogeneously embedded and fixed within the growing conjugated conductive framework. Finally, the SiO₂ template is substantially removed through an etching process, yielding mPANI@POM hybrid nanospheres.

Notably, the formation mechanism of mPANI@POM is closely associated with the confined assembly behaviour induced by colloidal SiO₂. Beyond serving as rigid sacrificial scaffolds for generating interconnected mesoporous channels, the SiO₂ nanospheres provide spatially confined reactive interfaces that effectively suppress the disordered agglomeration of polyaniline chains, guaranteeing the uniform spherical morphology driven by the tendency to minimize surface energy. Specifically, when protonated aniline was introduced into the colloidal SiO₂ suspension, the positively charged aniline molecules were uniformly adsorbed onto the negatively charged SiO₂ surface by robust electrostatic interaction, leading to the formation of well-defined aniline/SiO₂ assemblies with homogeneous surface coverage. In addition, pronounced electrostatic coupling and electronic interactions between the VMnPOM anionic clusters and protonated aniline facilitated the uniform intercalation of VMnPOM active clusters within the conjugated PANI chains, resulting in a robust organic-inorganic hybrid framework. This unique intercalated structure effectively promotes charge redistribution via electron delocalization across the PANI backbone and VMnPOM clusters, thereby enhancing the overall electronic transport capability. More importantly, the uniformly

dispersed POM active clusters effectively mitigate the structural collapse and volume expansion of PANI during repeated redox cycling, further improving the structural stability and reversibility of the electrode.

The introduction of SiO₂ nanoparticles provides an effective route to tailor the mesoporous architecture of PANI@POM. To verify the formation of the SiO₂-confined hybrid intermediate before template removal, the unetched PANI@POM@SiO₂ sample was characterized. As shown in Fig. S7 in the ESM, the high-angle annular dark-field-scanning transmission electron microscopy (HAADF-STEM) image and corresponding energy dispersive spectroscopy (EDS) elemental mapping reveals the coexistence of C, N, O, V, Mn and Si within the hybrid particles. In addition, the X-ray diffraction (XRD) pattern exhibits a distinct diffraction peak in the low-angle region, which can be attributed to the intercalation-induced structural ordering between VMnPOM clusters and PANI chains (Fig. S8 in the ESM). After etching of the SiO₂ template, scanning electron microscopy (SEM) reveals that mPANI@POM consists of uniform mesoporous (Fig. 2(a)), and the corresponding size statistics further confirm a relatively narrow particle-size distribution with an average diameter of approximately 250 nm (Fig. S9 in the ESM). Moreover, the generality of the electrostatic co-assembly and confined template polymerization strategy was further demonstrated by the successful synthesis of a mesoporous polypyrrole-based analogue, mPPy@POM (Fig. S10 in the ESM). Well-defined mesopores are clearly observed, and the particles are loosely packed. For comparison, the SEM images of pure mesoporous PANI (mPANI) and PANI@POM are shown in Fig. S11 in the ESM. Transmission electron microscopy (TEM) further confirms the presence of interconnected mesoporous structure (Fig. 2(b) and Figs. S12 and S13 in the ESM). Such an open mesoporous

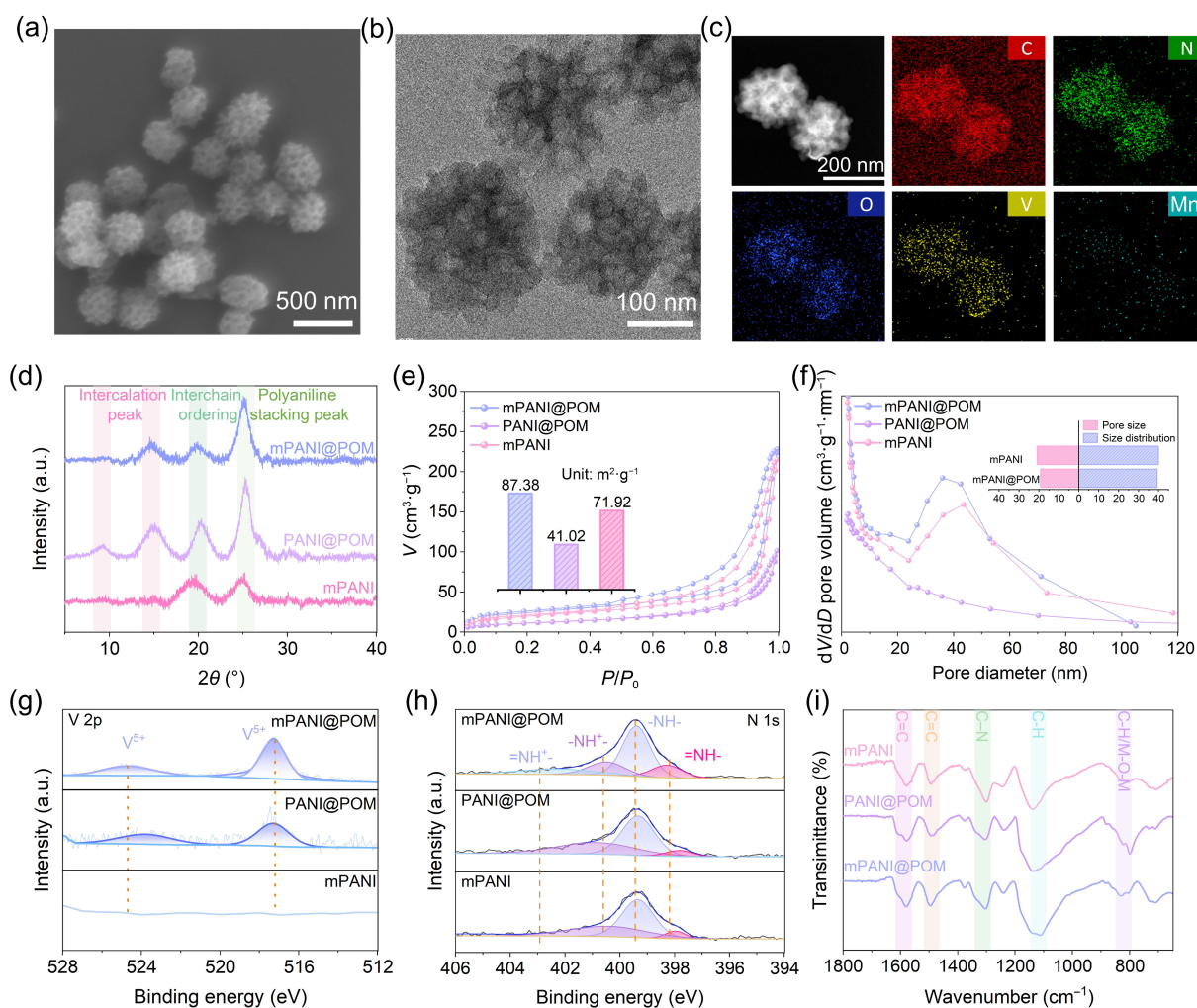


Figure 2 Structural and chemical characterizations of mPANI@POM. (a) SEM image and (b) TEM image of mPANI@POM. (c) HAADF-STEM image with corresponding EDS elemental mapping images of mPANI@POM. (d) XRD patterns of mPANI, PANI@POM and mPANI@POM. (e) N₂ adsorption-desorption isotherms and BET surface-area comparison of mPANI, PANI@POM and mPANI@POM. (f) Pore-size distributions and dominant pore-size ranges of mPANI, PANI@POM and mPANI@POM. (g) High-resolution XPS analysis of V 2p in mPANI, PANI@POM and mPANI@POM. (h) High-resolution XPS analysis of N 1s in mPANI, PANI@POM and mPANI@POM. (i) FTIR spectra of mPANI, PANI@POM and mPANI@POM.

architecture can enlarge the electrode-electrolyte contact area and shorten ion-diffusion pathways, thereby facilitating the rapid transport of Zn²⁺/H⁺ within the cathode.

In addition, EDS elemental mapping images show that C, N, O, V and Mn are uniformly distributed throughout the mPANI@POM framework (Fig. 2(c)), confirming that VMnPOM is effectively embedded and confined within the mPANI network. In contrast, the elemental mapping images of PANI@POM without the mesoporous template also confirm the presence of V and Mn, but its irregular aggregated morphology is less favorable for exposing active sites and forming continuous ion-transport channels (Fig. S14 in the ESM). XRD was then performed to investigate the structural evolution of mPANI@POM. As depicted in Fig. 2(d), mPANI mainly exhibits broad diffraction features, indicating its intrinsic low-crystallinity polymeric feature. The peak at around 20° can be assigned to the periodic ordering between PANI chains, whereas the diffraction peak near 25° corresponds to π - π stacking between conjugated PANI segments [26]. Compared with mPANI, PANI@POM displays a more pronounced diffraction signal in the low-angle region, suggesting an intercalation formation between VMnPOM and the PANI chains, which induces local structural ordering of the polymer skeleton [27]. Notably, mPANI@POM inherits the characteristic

diffraction features of PANI@POM, while its diffraction peaks become broader and weaker, which is mainly ascribed to the successful introduction of mesoporous structure and the uniform dispersion of VMnPOM species. This observation is consistent with the SEM, TEM and EDS mapping results, confirming the mesoporous and highly dispersed organic-inorganic hybrid nature of mPANI@POM.

N₂ adsorption-desorption measurements further verify the mesoporous structure of mPANI@POM. Fig. 2(e) compares the adsorption-desorption isotherms of mPANI, PANI@POM and mPANI@POM. All three samples exhibit type-IV isotherm characteristics with obvious hysteresis loops, indicating the presence of mesoporous structures [22]. Compared with PANI@POM, both mPANI and mPANI@POM show a sharper increase in adsorption at medium-to-high relative pressures, suggesting more open mesoporous channels. Notably, mPANI@POM delivers a specific surface area of 87.38 m²·g⁻¹ which is higher than those of PANI@POM (41.02 m²·g⁻¹) and mPANI (71.92 m²·g⁻¹) respectively. The corresponding pore-size distribution (Fig. 2(f)) shows a broad peak in the range of 35–45 nm for mPANI@POM, further confirming the formation of mesopores. This result agrees well with the SEM and TEM observations. In contrast, PANI@POM exhibits a much lower

pore volume. These results suggest that the introduction of VMnPOM does not block the pore channels. Instead, interfacial electrostatic interactions between VMnPOM and PANI regulate the polymer assembly process, leading to a more open mesoporous structure. Such a porous framework is beneficial for rapid $\text{Zn}^{2+}/\text{H}^+$ diffusion and for improving the accessibility of V/Mn redox-active sites.

X-ray photoelectron spectroscopy (XPS) provides further insight into the composition and valence states of mPANI@POM. As shown in Fig. 2(g), the high-resolution V 2p spectra display characteristic V^{5+} signals [28], indicating that VMnPOM is successfully incorporated into the PANI framework. The high-resolution Mn 2p spectra further reveal the presence of Mn species with mixed valence states, including Mn^{2+} and Mn^{3+} (Fig. S15(c) in the ESM) [29]. In addition, the C 1s spectra of mPANI, PANI@POM and mPANI@POM show typical C=C, C=N and C-N components associated with the conjugated PANI backbone (Fig. S15(a) in the ESM). The variation of O 1s components after hybridization further indicates that the local oxygen coordination environment of VMnPOM is affected by its interaction with the PANI (Fig. S15(b) in the ESM). The high-resolution N 1s spectra can be deconvoluted into four components located at approximately 398.2, 399.5, 400.7 and 402.8 eV, corresponding to imine nitrogen (=N), amine nitrogen (-NH-), protonated amine nitrogen (-NH⁺) and protonated imine nitrogen (=NH⁺) [30], respectively (Fig. 2(h)). The presence of these nitrogen species indicates that the PANI framework is partially protonated. Fourier-transform infrared spectroscopy (FTIR) further elucidates the structural features of mPANI@POM (Fig. 2(i)). The reference spectra of pristine VMnPOM and PANI are provided in Fig. S16 in the ESM. The absorption bands at 1580 cm^{-1} and 1490 cm^{-1} are assigned to the skeletal vibrations of quinoid and benzenoid rings in PANI, respectively [31]. The band near 1300 cm^{-1} corresponds to C-N stretching, while the signals in the 1100–1150 cm^{-1} region are associated with the doped, protonated state of PANI [31]. These features indicate that the PANI frameworks in mPANI, PANI@POM and mPANI@POM are partially protonated. Meanwhile, absorption signals in the low-wavenumber region related to M-O-M (M = V/Mn) vibrations in VMnPOM further confirm the successful incorporation and confinement of VMnPOM within the mPANI network. Raman spectroscopy was also conducted to probe the structural modulation of the PANI framework after VMnPOM incorporation. As shown in Fig. S17 in the ESM, the Raman bands at approximately 1320–1360, 1470–1500, and 1570–1600 cm^{-1} are attributed to polaron-associated C-N⁺ stretching, quinonoid C=N stretching, and conjugated C=C stretching of the PANI backbone, respectively. The additional bands at low-wavenumber region can be associated with the characteristic metal-oxygen vibrations of the polyoxometalate [32]. Taken together, these results demonstrate that electrostatic co-assembly strategy successfully constructs mPANI@POM cathodes with an open mesoporous architecture. Rather than being a simple physical mixture of PANI and VMnPOM, mPANI@POM is a mesoporous organic-inorganic hybrid formed through POM-induced interchain modulation, interfacial coupling and template-directed confinement.

3.2 Electrochemical properties and kinetics

The synergistic interplay between the continuous conjugated conductive network and the multielectron redox-active polyoxometalate clusters in mPANI@POM markedly enhances electron delocalization and charge-transport kinetics within the

electrode framework. Motivated by these structural advantages, the electrochemical energy-storage behavior of mPANI@POM in aqueous zinc-ion batteries was systematically investigated. Coin-type cells were assembled using a Zn metal anode and 2 M $\text{Zn}(\text{OTf})_2$ electrolyte to evaluate the electrochemical performances of mPANI@POM, mPANI, and PANI@POM cathodes. As revealed by the galvanostatic charge/discharge (GCD) profiles at 0.5 $\text{A}\cdot\text{g}^{-1}$ (Fig. 3(a)), the mPANI@POM electrode exhibits more distinct voltage plateaus, a higher discharge specific capacity, and a smaller polarization voltage than those of mPANI and PANI@POM.

The rate capability further highlights the superior electrochemical kinetics of the composite electrode (Fig. 3(b)). At current densities ranging from 0.5, 1.0, 1.5, 2.0, 2.5 to 3.0 $\text{A}\cdot\text{g}^{-1}$, the mPANI@POM electrode delivers specific capacities of 193, 178, 168, 160, 153, and 147 $\text{mAh}\cdot\text{g}^{-1}$, respectively. Notably, when the current density returns to 0.5 $\text{A}\cdot\text{g}^{-1}$, 98% of the initial capacity is recovered, accompanied by a significantly higher Coulombic efficiency than those of the mPANI and PANI@POM electrodes. These results demonstrate the outstanding rate performance and good reversibility of the mPANI@POM cathode. Such enhanced rate behavior can be attributed to the interconnected mesoporous architecture, which effectively shortens the Zn^{2+} diffusion pathways and accelerates charge transfer. Meanwhile, the V/Mn redox-active centers within the polyoxometalate clusters provide additional electrochemically active sites, thereby further boosting the overall charge-storage capability. Importantly, the rate performance of mPANI@POM surpasses that of most previously reported polyaniline-based and other organic cathode materials (Fig. 3(c)) [33–38], highlighting its considerable potential for high-power energy-storage applications.

Before assessing the long-term cycling stability, we first investigated the effect of electrolyte chemistry on the electrochemical behavior of mPANI@POM. Owing to its better compatibility with the mPANI@POM cathode, $\text{Zn}(\text{OTf})_2$ was selected as the optimized electrolyte system for subsequent electrochemical tests (Fig. S18 in the ESM). The cycling stability of the mPANI@POM cathode was further evaluated. Impressively, the mPANI@POM electrode retains a high specific capacity of 199.88 $\text{mAh}\cdot\text{g}^{-1}$ after 50 cycles at 0.5 $\text{A}\cdot\text{g}^{-1}$, substantially outperforming both mPANI and PANI@POM (Fig. S19 in the ESM). Moreover, mPANI@POM, mPANI and PANI@POM all show improved cycling stability compared with pristine PANI, suggesting that both VMnPOM incorporation and mesoporous structural engineering contribute to enhanced electrochemical reversibility. Meanwhile, SEM-EDS mapping before and after cycling shows that the main elemental components of mPANI@POM are well preserved and remain relatively homogeneous (Fig. S20 in the ESM), demonstrating the structural and compositional stability of the cathode. The emergence of Zn signals after cycling further indicates the participation of Zn^{2+} during the charge-storage process. Even at a higher current density of 2.0 $\text{A}\cdot\text{g}^{-1}$, the mPANI@POM cathode still maintains a considerably higher capacity than the comparison electrodes after 800 cycles, despite a moderate decline in capacity retention. This enhanced capacity stability can be attributed to the synergistic coupling between the highly conductive mesoporous polyaniline framework and the redox-active sites of vanadium-manganese polyoxometalate clusters, thereby effectively boosting the reversibility and reaction kinetics of charge storage and ion transformation. Meanwhile, the Coulombic efficiency remains consistently close to 100% throughout prolonged cycling,

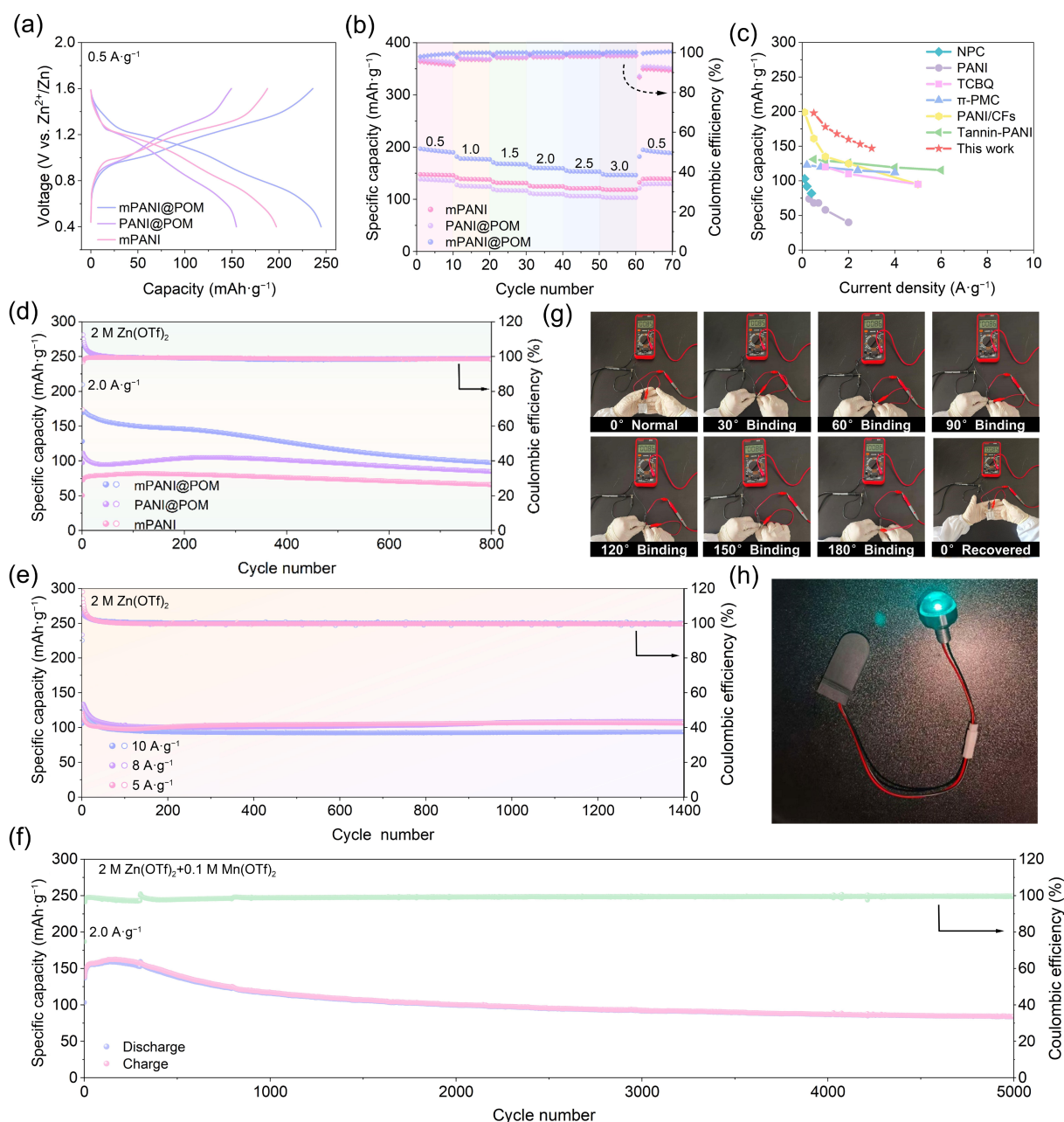


Figure 3 Electrochemical performances. (a) Galvanostatic charge/discharge profiles of mPANI, PANI@POM and mPANI@POM at 0.5 A·g⁻¹ in 2 M Zn(OTf)₂. (b) Rate capability of mPANI, PANI@POM and mPANI@POM electrodes in 2 M Zn(OTf)₂. (c) Comparison of the rate performances between the mPANI@POM electrode and recently reported organic cathodes. (d) Cycling performance of mPANI, PANI@POM and mPANI@POM at 2.0 A·g⁻¹ in 2 M Zn(OTf)₂. (e) Cycling performance of mPANI@POM at 5, 8 and 10 A·g⁻¹. (f) Cycling performance of mPANI@POM at 2.0 A·g⁻¹ in 2 M Zn(OTf)₂ + 0.1 M Mn(OTf)₂. (g) Bending test of the belt-shaped Zn//mPANI@POM battery at different angles. (h) Zn//mPANI@POM battery driving an LED lamp.

indicating good reaction reversibility and interfacial stability of the electrode (Fig. 3(d)).

Under more demanding high-rate conditions (Fig. 3(e)), the mPANI@POM electrode maintains stable cycling performance for over 1400 cycles at 5.0, 8.0, and 10.0 A·g⁻¹ with nearly 100% Coulombic efficiency. Moreover, 90.6% capacity retention is achieved after 1000 cycles at 5.0 A·g⁻¹ demonstrating its robust cycling stability under high-rate conditions. Furthermore, to suppress manganese dissolution and enhance interfacial stability, a Zn(OTf)₂ electrolyte containing Mn²⁺ additive was employed. As shown in Fig. 3(f), the cycling durability was further improved, enabling the mPANI@POM electrode to achieve ultralong cycling stability over 5000 cycles at 2 A·g⁻¹. The introduction of Mn²⁺

effectively mitigates cathode dissolution and structural collapse while suppressing parasitic side reactions, thereby significantly prolonging cycle life and enhancing interfacial stability [39].

To further evaluate the practical applicability of mPANI@POM, a higher-mass-loading cathode was assembled into a coin cell. The electrode with a mass loading of 3.38 mg·cm⁻² delivers stable cycling behavior at 0.5 A·g⁻¹ and retains 91.1% of its capacity after cycling (Fig. S21 in the ESM). Building upon these results, flexible pouch cells were assembled to further evaluate the potential for flexible energy-storage applications in wearable electronics. As shown in Fig. 3(g), the pouch-type Zn//mPANI@POM battery operates steadily under various bending states (0°, 30°, 60°, 90°, 120°, 150°, 180° and recovered to 0°) with almost no fluctuation in

output voltage, demonstrating excellent mechanical flexibility [40]. In addition, the charge/discharge curves of the pouch cell from the 2nd to 6th cycles show good overlap and good cycling stability at 0.5 A·g⁻¹ (Fig. S22 in the ESM). Finally, the Zn//mPANI@POM device successfully powers an LED lamp (Fig. 3(h)), further evidencing the promising application prospects of the mPANI@POM cathode in wearable energy-storage systems.

To gain deeper insight into the charge-storage kinetics of the mPANI@POM cathode, a series of electrochemical characterizations, including cyclic voltammetry (CV), pseudocapacitive contribution analysis, galvanostatic intermittent titration technique (GITT), and electrochemical impedance spectroscopy (EIS), were systematically conducted. CV measurements of mPANI@POM, mPANI, and PANI@POM electrodes were first performed within a voltage window of 0.4–1.6 V at a scan rate of 0.1 mV·s⁻¹. As shown in Fig. 4(a), the CV profiles of the mPANI@POM cathode from the second to sixth cycles exhibit highly overlapped redox peaks, indicative of excellent structural stability and highly reversible Zn²⁺ insertion/extraction behavior. In contrast, although the mPANI electrode displays discernible redox responses, pronounced peak shifts are observed during cycling (Fig. S23(a) in the ESM), suggesting inferior electrochemical reversibility. The PANI@POM electrode shows

moderately improved cycling stability. However, both the peak current intensity and reversibility remain inferior to the mPANI@POM (Fig. S23(b) in the ESM). These results demonstrate that the synergistic coupling between the mesoporous architecture and VMnPOM active centers enhances reaction stability and charge-storage reversibility.

The charge-storage kinetics of the mPANI@POM electrode were investigated by CV measurements at various scan rates. As illustrated in Fig. 4(b) and Fig. S24 in the ESM, the CV curves collected at scan rates ranging from 0.1 to 0.5 mV·s⁻¹ retain nearly identical shapes. Compared with mPANI and PANI@POM (Fig. S25 in the ESM), mPANI@POM exhibits more stable redox peaks, suggesting enhanced reaction reversibility arising from the synergistic coupling between the mesoporous PANI framework and VMnPOM redox clusters. According to the power-law relationship between peak current (*i*) and scan rate (*v*) expressed as $i = avb$, the calculated *b* values for the oxidation peaks are 0.99 and 0.89, while those for the reduction peaks are 0.93 and 0.82 (Fig. 4(c)). These values are all close to 1, suggesting the surface-controlled pseudocapacitive behavior rather than conventional diffusion-limited intercalation. The large *b* values indicate that mPANI@POM can rapidly undergo redox reactions at the electrode surface, thereby facilitating excellent rate capability.

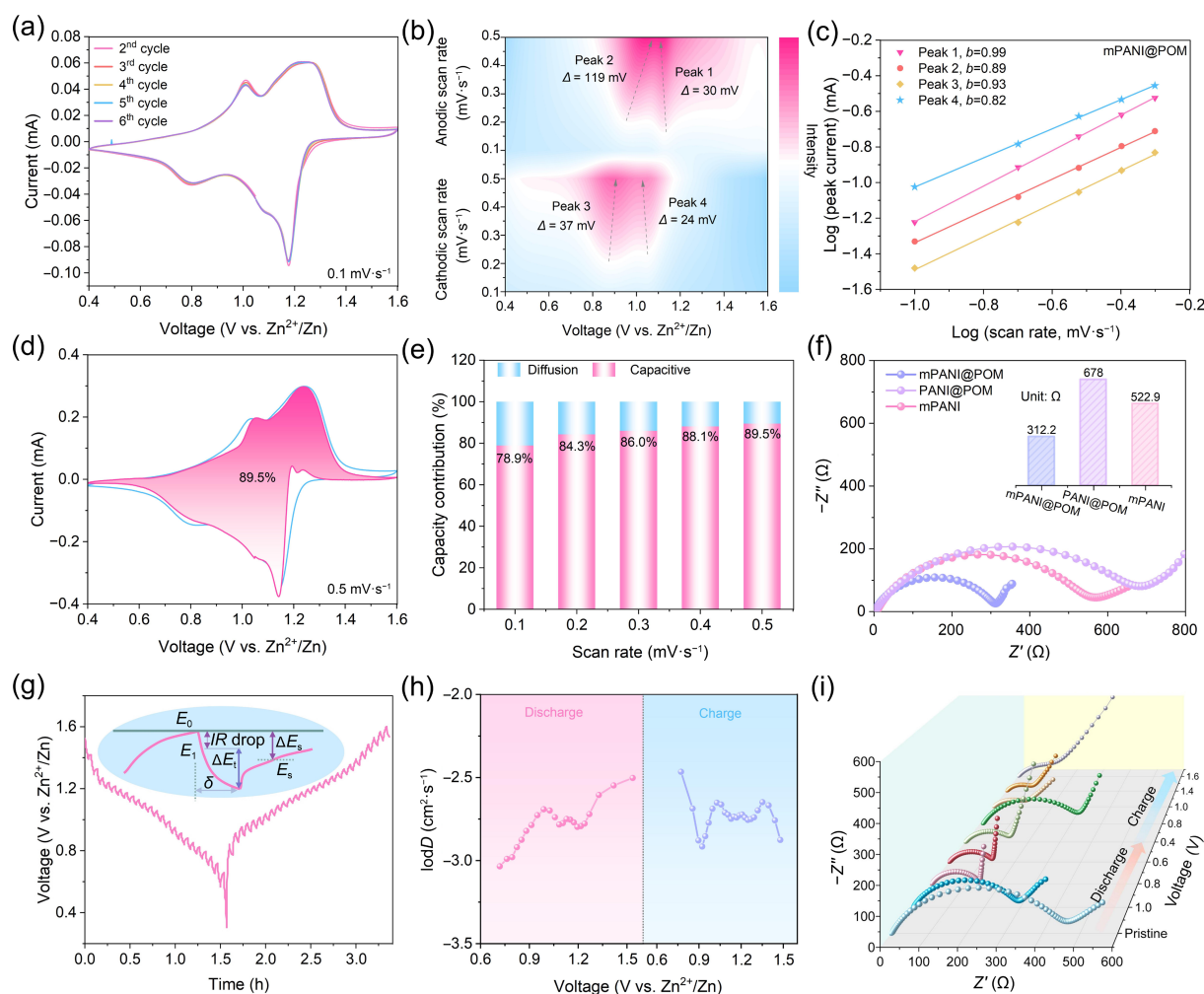


Figure 4 Electrochemical kinetics analyses. (a) CV curves of mPANI@POM from the 2nd to 6th cycles at 0.1 mV·s⁻¹. (b) CV curves of mPANI@POM at various scan rates. (c) "log(*i*_p)" versus "log(*v*)" curves for the cathodic and anodic peaks. (d) Capacitive contribution of mPANI@POM at 0.5 mV·s⁻¹. (e) Capacitive contribution at the scan rate of 0.1–0.5 mV·s⁻¹. (f) Nyquist plots of mPANI, PANI@POM and mPANI@POM, with the calculated charge-transfer resistance (*R*_{ct}) values shown in the inset. (g) GITT curves at the current density of 0.2 A·g⁻¹. (h) Corresponding zinc ion diffusion coefficients obtained from the corresponding GITT curves. (i) EIS spectra of mPANI@POM collected at selected electrochemical states during discharge/charge.

To quantitatively evaluate the pseudocapacitive contribution, the CV response was further analyzed using the equation $i(v) = k_1v + k_2v^{1/2}$, k_1v and $k_2v^{1/2}$ represent the current contributions of the surface-controlled and diffusion-controlled capacity, respectively. As shown in Figs. 4(d) and 4(e) and Fig. S26 in the ESM, the pseudocapacitive contributions reach 78.9%, 84.3%, 86.0%, 88.1% and 89.5% at 0.1 mV·s⁻¹, 0.2 mV·s⁻¹, 0.3 mV·s⁻¹, 0.4 mV·s⁻¹, 0.5 mV·s⁻¹, respectively. In general, a higher capacitive contribution reflects faster ion-transport kinetics. Even at elevated scan rates, the mPANI@POM electrode maintains a dominant pseudocapacitive contribution, highlighting its rapid surface redox kinetics. Such superior pseudocapacitive behavior is typically associated with efficient interfacial electron/ion transport.

To further elucidate the charge-transfer characteristics and interfacial reaction kinetics, EIS and GITT measurements were carried out on different electrodes. The equivalent circuit fitting based on EIS is shown in Fig. S27 in the ESM, confirming that the Zn//mPANI@POM battery exhibits a substantially lower charge-transfer resistance than the Zn//mPANI and Zn//PANI@POM counterparts (Fig. 4(f)). It is noteworthy that the mPANI@POM electrode exhibits a significant reduction in interfacial resistance after cycling (Fig. S28 in the ESM), which suggests an electrochemical activation process and improved charge-transfer kinetics during repeated charge/discharge. As shown in Fig. 4(g), the mPANI@POM electrode displays relatively smooth voltage plateaus and a small IR drop during the galvanostatic pulse process, indicative of reduced polarization and enhanced Zn²⁺ diffusion capability. The Zn²⁺ diffusion coefficients calculated from the GITT results (Fig. 4(h)) show an average value of 1.32×10^{-3} cm²·s⁻¹ throughout the charge/discharge process, markedly higher than those of mPANI (7.41×10^{-4} cm²·s⁻¹) and PANI@POM (2.63×10^{-4} cm²·s⁻¹), revealing rapid Zn²⁺ migration within the electrode matrix. Meanwhile, comparative GITT profiles of the mPANI and PANI@POM electrodes (Fig. S29 in the ESM) further demonstrate that mPANI@POM exhibits smaller voltage polarization and faster voltage recovery, whereas both pristine mPANI and PANI@POM show more pronounced voltage fluctuations during current pulses. These observations further verify the accelerated ion-diffusion kinetics of the mPANI@POM electrode.

To further probe the dynamic evolution of interfacial reaction kinetics during Zn²⁺ insertion/extraction, *ex-situ* EIS measurements were conducted at different charge/discharge states. As shown in Fig. 4(i), the semicircle diameter in the Nyquist plots gradually decreases during discharge, indicating that continuous Zn²⁺ insertion progressively lowers the interfacial charge-transfer resistance and enhances the electrode reaction kinetics. During the subsequent charging process, the impedance gradually recovers to a state close to the initial condition, suggesting excellent electrode reversibility and robust structural stability upon repeated Zn²⁺ insertion/extraction.

3.3 Mechanistic investigation

To further elucidate the charge-storage mechanism and structural evolution of the mPANI@POM during cycling in aqueous zinc-ion batteries, a series of *in-situ* and *ex-situ* characterizations were carried out. As shown in Figs. 5(a) and 5(b), the FTIR bands located at approximately 1580 and 1490 cm⁻¹ are assigned to the quinoid C=C and benzenoid C=C stretching vibrations of PANI, respectively [32, 41–42]. During discharge, the decreased intensity ratio of the quinoid/benzenoid bands (1580/1490 cm⁻¹) indicates that PANI accepts electrons and undergoes a transition from a

relatively oxidized state to a reduced state, accompanied by the partial conversion of quinoid units into benzenoid units. Meanwhile, the reversible evolution of the C-N vibration around 1300 cm⁻¹ further reflects the modulation of the local electronic environment of the PANI backbone during the Zn²⁺/H⁺ coupled electrochemical process. Upon subsequent charging, the recovery of the quinoid/benzenoid ratio together with the reversible variation of the C-N vibration suggests the restoration of the electronic structure and oxidation state of PANI. These results demonstrate that the PANI framework undergoes reversible electronic and structural evolution during the charge/discharge process, contributing to the reversible charge storage of mPANI@POM. In the low-wavenumber region of 1000–700 cm⁻¹, the M=O and M-O-M (M = V/Mn) vibrations of VMnPOM also exhibit reversible variations [43], suggesting that Zn²⁺/H⁺ insertion and extraction are associated with reversible modulation of the local coordination environment of the VMnPOM.

The structural evolution of mPANI@POM during cycling was further examined by *ex-situ* XRD. As shown in Figs. 5(c) and 5(d), states 1–5 correspond to the discharge process, while states 5–10 represent the subsequent charge process. The broad diffraction feature at 20°–21° can be assigned to the periodic ordering between PANI chains [44]. During discharge, both the intensity and position of this peak change markedly. In the early discharge stage, the peak becomes stronger, suggesting that the initial insertion of a small amount of H⁺ promotes local ordering through electrostatic interactions. The proton insertion may also strengthen hydrogen-bonding interactions between adjacent PANI chains, reducing the interchain spacing and shifting the peak toward higher angles. As discharge proceeds, the continuous insertion of Zn²⁺/H⁺ causes structural distortion within the mPANI@POM framework, leading to decreased ordering and weakened diffraction intensity. During charging, Zn²⁺/H⁺ extraction releases the insertion-induced distortion, and the diffraction feature gradually returns towards its original position. At intermediate charge states, extensive H⁺ extraction reduces hydrogen-bonding interactions between the chains, resulting in a temporary decrease in ordering and peak intensity. At the fully charged state, the PANI framework is largely restored, and the peak intensity increases again, confirming the reversibility of the structural modulation. The broad feature at 24°–27° is mainly related to π - π stacking between conjugated PANI segments [45]. Its periodic evolution during discharge and charge further suggests that the π - π stacking of the PANI backbone is highly reversible during the redox process, in agreement with the *in-situ* FTIR results.

The *in-situ* Raman spectra provide additional evidence for the cooperative involvement of PANI and VMnPOM. The baseline spectrum of the pristine mPANI@POM cathode collected in an *operando* electrochemical Raman cell (Fig. S30 in the ESM) displays distinct vibrational fingerprints assigned to the mPANI backbone and VMnPOM clusters, verifying preserved structural integrity under measurement conditions. The Raman bands in the 1250–1350 cm⁻¹ region are mainly associated with the C-N stretching vibration of the protonated polaronic structure of PANI, reflecting the evolution of the local electronic environment and oxidation state of the polymer backbone (Fig. 5(e) and Fig. S31 in the ESM) [46]. During the initial discharge stage, the interaction between H⁺ and nitrogen sites of PANI may contribute to the enhancement of the C-N related Raman response. With further discharge, Zn²⁺/H⁺ insertion and electron injection further reduce the PANI backbone, decreasing the concentration of C-N

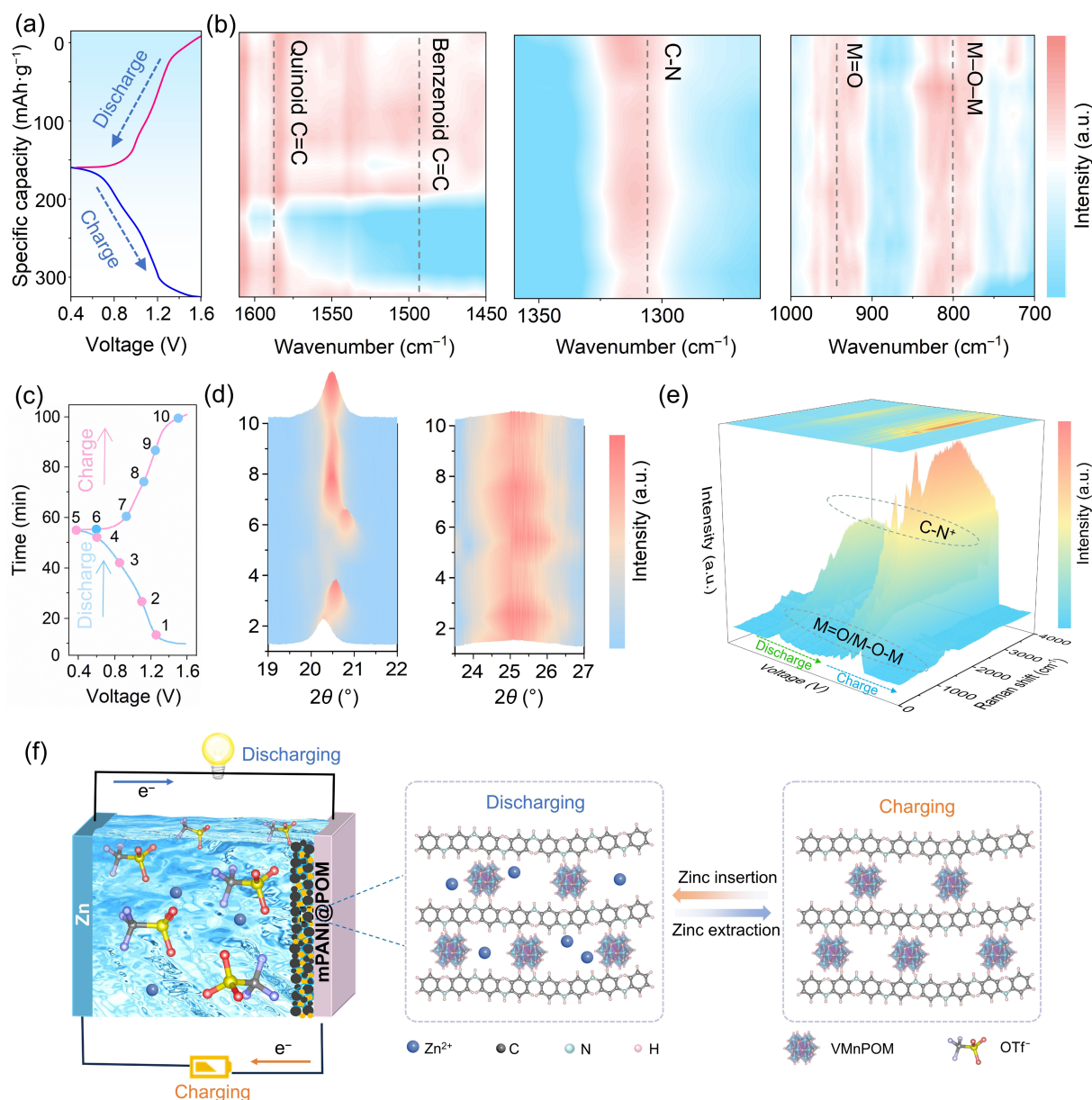


Figure 5 In/ex-situ characterizations. (a) GCD curve of mPANI@POM. (b) In-situ FTIR spectra of mPANI@POM. (c) Selected electrochemical states for ex-situ XRD measurements. (d) Ex-situ XRD patterns of mPANI@POM. (e) In-situ Raman spectra of mPANI@POM. (f) Schematic diagram of the energy storage mechanism of mPANI@POM.

species and weakening the corresponding Raman signal. During charging, the reversible oxidation process of PANI restores the corresponding Raman features [47]. At higher potentials, the continuous oxidation of PANI during charging further modifies the distribution of charge carriers within the polymer backbone, leading to changes in the C-N related Raman response.

In parallel, the low-wavenumber Raman signals associated with M=O and M-O-M vibrations also evolve reversibly. In the early discharge stage, a small amount of $\text{Zn}^{2+}/\text{H}^{+}$ enters the cathode and interacts with oxygen sites in VMnPOM, enhancing the Raman response. Upon deep discharge, more extensive $\text{Zn}^{2+}/\text{H}^{+}$ insertion perturbs the M-O coordination environment and weakens the terminal M=O and bridging M-O-M vibrations [48]. During charging, $\text{Zn}^{2+}/\text{H}^{+}$ is extracted from the POM oxygen sites, and the M-O environment recovers, giving rise to the restored Raman signal. This reversible response further demonstrates the robustness of the VMnPOM coordination environment.

Moreover, the ex-situ XPS results provide additional evidence that the VMnPOM component actively participates in the charge-storage process through reversible redox and coordination evolution (Fig. S32 in the ESM). This observation is consistent with the ex-situ EIS results (Fig. 4(i)), which further reveal the reversible changes in interfacial charge-transfer kinetics during cycling.

Overall, the charge-storage mechanism of mPANI@POM is illustrated in Fig. 5(f). During discharge, PANI participates through the redox conversion of quinoid/imine units, while VMnPOM contributes through reversible coordination interactions between $\text{Zn}^{2+}/\text{H}^{+}$ and V/Mn-O sites. During charging, these processes proceed in reverse: PANI is re-oxidized, $\text{Zn}^{2+}/\text{H}^{+}$ is extracted from the POM framework, and the local M-O coordination environment is restored. These results demonstrate that charge-storage in mPANI@POM arises from the synergistic coupling of reversible PANI redox modulation and VMnPOM-

based coordination chemistry, rather than from a simple ion-intercalation process.

Finite-element simulations and density functional theory (DFT) calculations were further conducted to elucidate the structural mechanism underlying the rapid reaction kinetics and stable charge-storage behavior of mPANI@POM. A flower-like structure model was established to simulate the mesoporous mPANI@POM (Fig. 6(a)). Simulation results demonstrate that the volume fraction of Zn^{2+} fluid within the model gradually increases with simulation duration and finally reaches ~95%, which verifies the thorough penetration of Zn^{2+} into the interior of the mPANI@POM architecture. These simulation results provide direct evidence that the mesoporous architecture plays a pivotal role in promoting ion diffusion and supporting the fast charge-storage kinetics of mPANI@POM.

Furthermore, the optimized aniline/POM adsorption

configuration yields a negative adsorption energy of -2.38 eV (Fig. 6(b)), indicative of thermodynamically favorable coupling between PANI and VMnPOM. Such favorable interfacial adsorption establishes a molecular foundation for electrostatic co-assembly and enables stable incorporation of VMnPOM into the growing PANI framework. Differential charge density and electron localization function (ELF) analyses were further conducted to probe the interfacial interaction and charge distribution characteristics. As presented in Fig. 6(c) and Fig. S33 in the ESM, distinct charge accumulation and depletion regions emerge around the oxygen-enriched POM cluster and nitrogen-containing PANI segment, verifying strong interfacial electronic interactions during interface construction. The ELF results further confirm localized electronic interactions near the POM framework, where the oxygen active sites of VMnPOM act as efficient coordination and charge-transfer centers. This unique

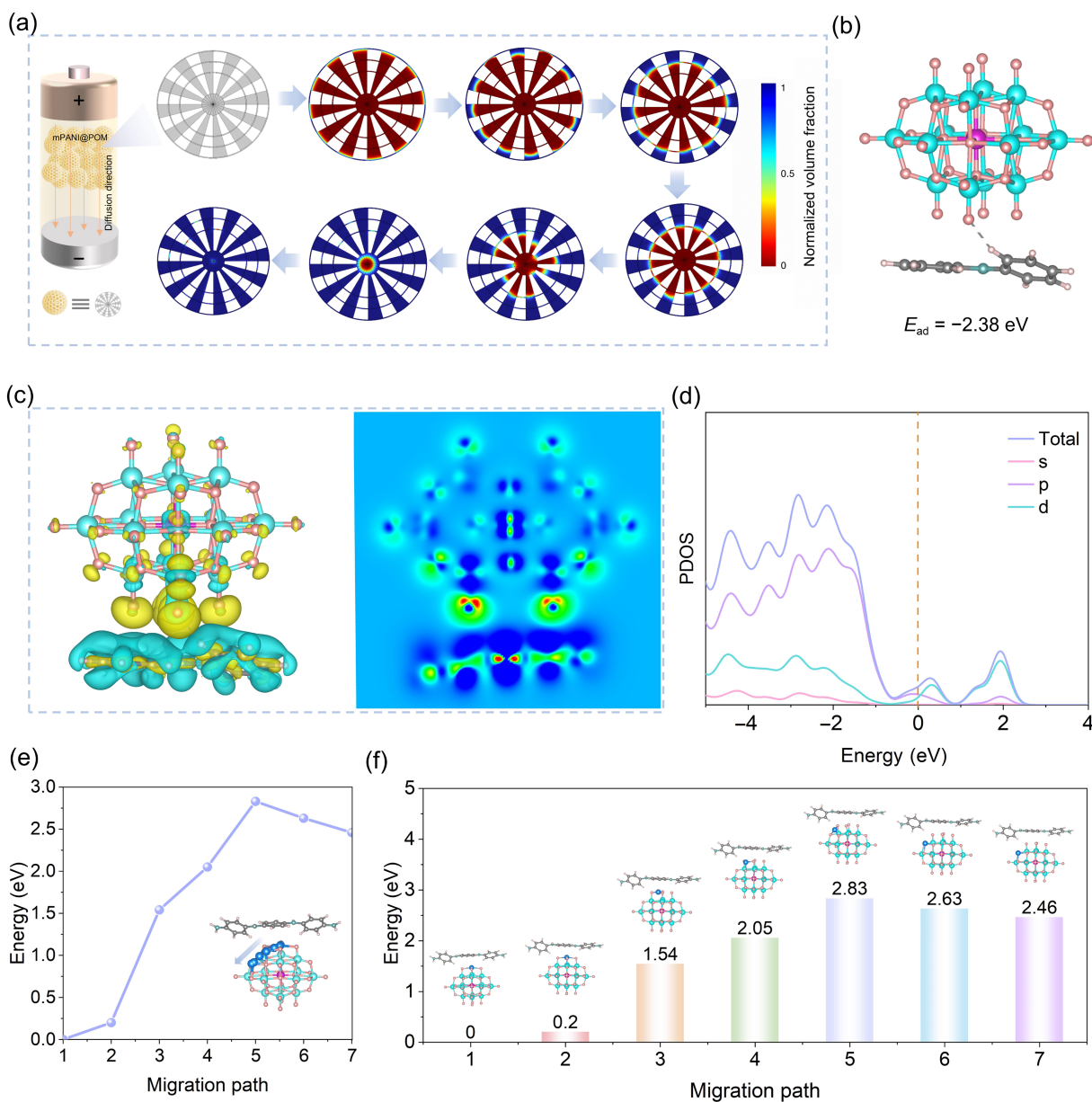


Figure 6 Theoretical simulation and calculation of mPANI@POM. (a) Computational fluid dynamics simulations for mPANI@POM based on a 2D model. (b) Optimized polyaniline/POM adsorption configuration and the corresponding adsorption energy. (c) Differential charge density and electron localization function (ELF) of mPANI@POM. (d) PDOS of mPANI@POM. (e) Schematic illustration of Zn^{2+} migration along the pathway and the corresponding migration barrier curve. (f) Representative configurations and relative energies at selected Zn^{2+} migration states.

interfacial electronic coupling bridges the conjugated PANI skeleton and V/Mn-O redox centers, substantially promoting electron transport during reversible $\text{Zn}^{2+}/\text{H}^+$ insertion/extraction reactions. In addition, the electronic structure of mPANI@POM was further examined by partial density of states (PDOS) calculations (Fig. 6(d)). The pronounced density of electronic states at the Fermi level indicates that mPANI@POM possesses an electronic structure favorable for charge transport. In the occupied region, the total density of states is dominated by p-orbital contributions, which can be mainly ascribed to the conjugated PANI backbone and the oxygen-rich POM framework. Notably, mPANI@POM exhibits more pronounced electronic states near the Fermi level (Fig. S34 in the ESM), discernible d-orbital states are also present near the Fermi level, suggesting that the incorporation of VMnPOM effectively modulates the electronic structure of the PANI framework and promotes interfacial charge transfer. These PDOS results further reveal the electronic-structure synergy between PANI and VMnPOM, providing theoretical support for the fast reaction kinetics of mPANI@POM.

Subsequently, the Zn^{2+} migration behavior was investigated to clarify the ion-transfer process within the mPANI@POM framework. The relative energy evolution along a possible Zn^{2+} migration pathway was calculated, as shown in Figs. 6(e) and 6(f). Along the selected pathway, Zn^{2+} migrates through successive interactions with the oxygen-rich POM region, accompanied by a pronounced variation in relative energy. The energy increases from 0 eV at the initial state to a maximum of 2.83 eV, and then slightly decreases to 2.46 eV at the final state, suggesting that Zn^{2+} can be restabilized by adjacent oxygen-rich coordination sites after passing through the highest-energy configuration. This energy evolution indicates that Zn^{2+} transport in mPANI@POM is closely associated with continuous coordination rearrangement rather than simple free diffusion. Therefore, the mesoporous PANI framework provides accessible ion-transport channels, while the embedded VMnPOM clusters offer abundant oxygen coordination sites for Zn^{2+} migration and storage. The synergistic integration of open ion pathways and POM-regulated coordination sites accounts for the rapid reaction kinetics and durable electrochemical behavior of mPANI@POM.

4 Conclusions

In summary, we developed an interfacial electrostatic coupling-driven, *in-situ* polymerization-induced co-assembly strategy, in which colloidal SiO_2 -directed confined polymerization was combined with the electrostatic incorporation of VMnPOM clusters to construct mesoporous PANI/VMnPOM hybrid nanospheres as a cathode material for aqueous zinc-ion batteries. This integrated hybrid architecture synergistically combines rapid $\text{Zn}^{2+}/\text{H}^+$ diffusion pathways, abundant redox-active sites, efficient ion transport through the mesoporous framework, and multielectron redox activity arising from the V/Mn-O moieties. Benefiting from the synergistic structural and electronic effects, mPANI@POM delivered a high specific capacity of 264 $\text{mAh}\cdot\text{g}^{-1}$ at 0.5 $\text{A}\cdot\text{g}^{-1}$, retained 147 $\text{mAh}\cdot\text{g}^{-1}$ at 3.0 $\text{A}\cdot\text{g}^{-1}$, and excellent cycling stability with 90.6% capacity retention after 1000 cycles at 5.0 $\text{A}\cdot\text{g}^{-1}$. Mechanistic investigations revealed that $\text{Zn}^{2+}/\text{H}^+$ storage in mPANI@POM originates from the coupled reversible redox processes involving the benzenoid-quinoid conversion of PANI, together with the coordination evolution of V/Mn-O sites. Furthermore, a flexible Zn/mPANI@POM pouch cell demonstrated the practical potential of the hybrid cathode. This

work provides a new design strategy for developing high-capacity, high-rate and long-life hybrid cathodes for aqueous zinc-ion batteries.

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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 (further details of the preparation of materials, battery assembling and electrochemical measurement, theoretical calculations and dynamics simulation, Zeta potential measurement, electrochemical performances, electrochemical kinetic analysis, SEM and TEM imaging, XRD, XPS, FTIR and Raman spectroscopy measurements) is available in the online version of this article at <https://doi.org/10.26599/NRE.2026.9120271>.

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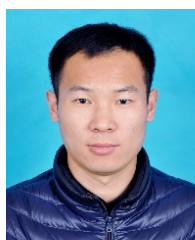
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