



Unveiling the action mechanism of synergistic d/p-band center modulation on the zinc storage capability of industrial-grade MnO_2 cathode

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ABSTRACT

Sluggish reaction kinetic, high-energy barrier and poor structural stability lead to rapid capacity decay and terrible self-charging properties, becoming major obstacles in using industrial-grade manganese dioxide (MnO_2) as a cathode in aqueous zinc-ion batteries (AZIBs). To address this challenge, we herein report a d/p-band center-modulated MnO_2 via a facile mechanical ball-milling method using industrial-grade MnO_2 as the precursor. Systematic characterization and theoretical calculations reveal that oxygen vacancy (O_v) serves as favorable adsorption sites, synergistically strengthening the interfacial stability for both Zn^{2+} and H^+ ions. Critically, the structural defect substantially reduces migration barriers, facilitating solid-state Zn^{2+} diffusion within the MnO_2 lattice and enabling ultrafast Grotthuss-type proton transport. Furthermore, the modified electronic structure around O_v effectively suppresses Jahn-Teller distortions and mitigates cyclic lattice strain, thereby inhibiting irreversible phase transformation. The d/p-band center modulated MnO_2 delivers a high initial discharge capacity of $339.7 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C. Remarkably, it achieves a capacity retention of 98.7% after 700 cycles at 2 C, substantially outperforming its pristine counterpart. This work provides atomic-level insights into the role of O_v in enhancing electrochemical performance, thereby establishing a rational design principle for transforming industrial-grade MnO_2 into high-performance AZIBs cathodes.

KEYWORDS

zinc-ion batteries, manganese dioxide, d/p-band center, oxygen vacancy, scalable application

1 Introduction

The growing global demand for safe and sustainable energy storage has spurred intensive researches into post-lithium battery technologies [1]. Aqueous zinc-ion batteries (AZIBs) stand out as promising options owing to the inherent benefits of metallic zinc anodes, including a remarkable theoretical capacity of $820 \text{ mAh}\cdot\text{g}^{-1}$, a negative redox potential (-0.76 V vs. SHE), exceptional abundance, and the intrinsic safety of aqueous electrolytes [2]. Researchers have explored numerous materials for AZIBs cathodes, including Prussian blue analogs, manganese oxides, vanadium compounds, and polyanionic compounds [3].

Manganese-based oxides, particularly manganese dioxide (MnO_2), have attracted significant attention due to their diverse crystal structures, high voltage operation, and environmental friendliness [4]. Nonetheless, practical deployment of MnO_2 cathodes remains hindered by two critical challenges. Firstly, the sluggish solid-state diffusion kinetics of divalent Zn^{2+} ions within the MnO_2 lattice often result in unsatisfactory rate capability and inadequate power density. Secondly, repeated Zn^{2+} (de)interaction induces structural instability, resulting in rapid capacity decay. The underlying degradation mechanisms are primarily associated with irreversible phase transitions and the dissolution of Mn^{3+} species, the latter generated via the detrimental Jahn-Teller distortion upon H^+ co-

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insertion, which causes severe lattice strain and eventual structural collapse [5].

In recent years, multiple strategies have been proposed, including defect engineering, doping engineering, pre-intercalating, etc. [6]. Notably, the incorporation of oxygen vacancy (O_v) has emerged as an effective method to enhance the rate performance of MnO_2 electrodes. Prior investigations have suggested that O_v not only improve electronic conductivity but also generate under-coordinated Mn ions, which can create more efficient pathways for ionic transport [7]. However, a thorough and mechanistic understanding of the precise role of O_v in modulating the co-insertion behavior of Zn^{2+} and H^+ ions, controlling their transport kinetics, and ultimately stabilizing the host structure during prolonged cycling remains lacking. Moreover, the synergistic effects that span from electronic-level charge redistribution to macroscopic electrochemical performance warrant further detailed investigation.

The advancement of sustainable energy storage systems critically relies on the development of cathode materials that are simultaneously high-performing, cost-efficient, and scalable. Although various sophisticated nanostructured polymorphs of MnO_2 , such as δ - MnO_2 , have exhibited outstanding electrochemical characteristics under laboratory conditions, their intricate synthesis procedures and elevated production costs significantly hinder their large-scale commercial deployment [8]. In contrast, industrially manufactured electrolytic MnO_2 (EMD) offers a promising alternative due to its inherent scalability and remarkable cost-effectiveness, stemming from well-established mass production processes primarily predominantly utilized in the alkaline battery industry [9]. However, the practical application of industrial EMD is hampered by its poor intrinsic conductivity, which slows reaction kinetics, and its structural instability during cycling. The latter leads to irreversible phase transitions, structural degradation, and consequent manganese dissolution, causing irreversible capacity loss [10]. Therefore, the exploration of EMD cathodes represents a critical step in bridging the gap between fundamental research and the practical implementation of AZIBs, thereby offering a pragmatic route toward developing commercially viable grid-scale energy storage solutions.

Mechanical ball milling is a scalable and industrially viable technique, capable of generating hundreds of tons of materials in commercial applications [11]. In this study, we demonstrate that ball milling provides a facile yet effective route to engineer oxygen defects in commercial EMD by mechano-alloying explosion of oxygen atoms from its crystal structure. To elucidate the underlying mechanisms, first-principles calculations were employed to examine the thermodynamic preferences, as indicated by adsorption energies, and kinetic barriers, reflected in migration energies, for Zn^{2+} and H^+ ions in both pristine MnO_2 and oxygen-deficient (BM- MnO_2) models. Further insights into ion-host interactions were obtained through analyses of the electronic structure, band edge position, electron localization function (ELF) and charge density difference (CDD). These theoretical findings are substantiated by experimental data, including *ex-situ* and *in-situ* Raman spectroscopy, which directly reveals the alleviation of lattice strain and suppression of phase transitions in the BM- MnO_2 sample. Notably, BM- MnO_2 shows much larger capacity of $339.7 \text{ mAh}\cdot\text{g}^{-1}$ in contrast to the pristine MnO_2 ($168.2 \text{ mAh}\cdot\text{g}^{-1}$) at 0.2 C. This work provides a novel perspective for the rational design of superior performance commercial manganese dioxide cathode materials tailored for advanced AZIBs and makes the large-scale commercial application a viable reality.

2 Results and discussion

2.1 Structural evolution of MnO_2 during the mechanical ball milling process

Unlike the methods previously reported, we hereby adopted a facile mechanical alloying route simply by ball-milling to introduce abundant O_v . The synthesis procedure is illustrated in Fig. 1(a). During the mechanical alloying by ball-milling, mechanical shear force and compressive stress are applied on the MnO_2 , which induces a significant amount of lattice distortion, thereby removing oxygen atoms from their original lattice positions and leaving oxygen defects behind within the lattice [12]. Scanning electron microscopy (SEM) analysis demonstrates that mechanical pulverization effectively reduces the particle size of the materials, yielding micro- to nano-scale particles (Fig. S1 in the Electronic Supplementary Material (ESM)). As illustrated in Fig. S2(a) in the ESM, the textural properties of MnO_2 and BM- MnO_2 were evaluated via N_2 adsorption/desorption isotherms. Both samples exhibit type-IV isotherms with a prominent H3-type hysteresis loop, which confirms the mesoporous nature of MnO_2 [13]. An increase in the Brunauer–Emmett–Teller (BET) surface area from $34.2 \text{ m}^2\cdot\text{g}^{-1}$ to $43.2 \text{ m}^2\cdot\text{g}^{-1}$ was observed, which is due to the decreased particle size resulting from the mechanical action during ball milling. Furthermore, particle size analysis via laser particle size analyzer also corroborates these findings, showing a decrease in the median particle size from $26.158 \mu\text{m}$ to $0.736 \mu\text{m}$ (Fig. S3 and Table S1 in the ESM). The synergistic effects of a higher specific surface area, larger pores, and smaller particle sizes favor the creation of additional active sites and facilitate the transport of Zn^{2+} and H^+ ions to the MnO_2 surface.

To elucidate the crystalline structure, samples were characterized by X-ray diffraction (XRD). The obtained patterns, shown in Fig. 1(c), correspond well to the characteristic reflections of γ - MnO_2 (JCPDS: 14-0644). The prominent peaks observed at 22.4° , 37.1° , 42.6° , 56.1° and 65.6° are indexed to the (120), (131), (300), (160) and (421) planes, respectively [14]. The XRD pattern of the BM- MnO_2 sample exhibits a distinct shift of diffraction peaks toward lower angles. According to Bragg's law, this shift indicates an expansion of the MnO_2 crystal lattice, which is likely attributable to the introduction of O_v during the ball-milling process [15]. The lattice fringe analysis indicates an expansion of the (300) plane spacing from 0.210 nm to 0.216 nm , in good agreement with the XRD results (Fig. S4 in the ESM). This lattice expansion effectively increases the interplanar spacing, which is favorable for ion mass transfer. High-angle annular dark field transmission electron microscopy (HAADF-TEM) images presented in Fig. 1(b) and Fig. S5 in the ESM reveal that both MnO_2 and BM- MnO_2 consist of irregularly shaped, stacked plate-like structures. The similarity in morphology indicates that the ball milling process does not induce changes in the microscopic architecture of the material. The energy dispersive X-ray spectroscopy (EDS) elemental mapping images demonstrate a uniform spatial distribution of both manganese (Mn) and oxygen (O) in pristine MnO_2 or BM- MnO_2 (Fig. 1(b) and Fig. S5 in the ESM). Following ball milling treatment, the oxygen content decreases from $68.93 \text{ at.}\%$ to $61.17 \text{ at.}\%$, while the manganese content correspondingly increases from $31.07 \text{ at.}\%$ to $38.83 \text{ at.}\%$. This compositional shift indicates the formation of O_v within the MnO_2 structure. This inference is further proved by inductively coupled plasma optical emission spectroscopy (ICP-OES), as shown in Fig. S6 in the ESM, which reveals a corresponding

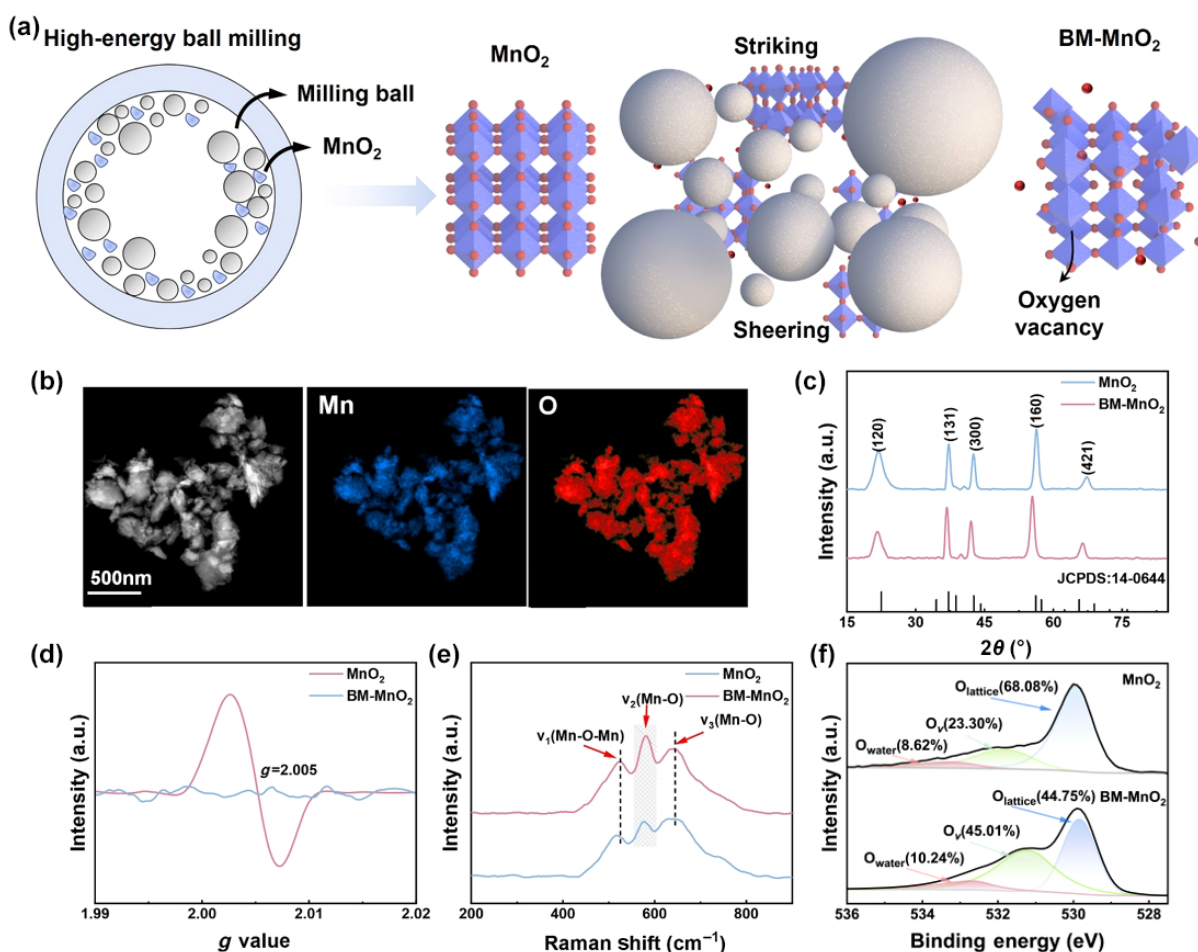


Figure 1 (a) Schematic diagram of the synthesis process of BM-MnO₂. (b) HAADF-TEM and EDS element mapping images of BM-MnO₂. (c) XRD, (d) EPR spectra, (e) Raman spectra and (f) high-resolution O 1s XPS spectra of MnO₂ and BM-MnO₂.

increase in Mn content consistent with the EDS results. In Fig. S7 in the ESM, the O₂ temperature-programmed desorption (O₂-TPD) spectrum provides additional spectroscopic evidence for O content, which can be categorized into three parts: surface-adsorbed active oxygen species (below 300 °C), sub-surface lattice oxygen (300–600 °C), and bulk lattice oxygen (over 600 °C) [16]. Compared to pristine MnO₂, BM-MnO₂ exhibits a larger amount of labile oxygen species but a lower content of both sub-surface lattice oxygen and bulk lattice oxygen. The surface-adsorbed oxygen possesses greater mobility than lattice oxygen, which could effectively shuttle charge from electrolyte ions into the MnO₂ framework, boosting its charge-transfer capacity [17]. Collectively, the ICP-OES and O₂-TPD results confirm that the ball-milling process successfully introduces abundant surface oxygen species, which are strongly correlated with the presence of O_v. To verify the existence of O_v and quantify their relative concentrations across the samples, electron paramagnetic resonance (EPR) spectroscopy was employed. As shown in Fig. 1(d), a pronounced EPR signal is observed at a *g*-factor of 2.005, which is the canonical fingerprint of unpaired electrons trapped at O_v sites, offering unambiguous confirmation of their presence [18]. The presence of O_v promotes electron transport via the induced half-metallicity that improves conductivity, which can improve the electrochemical performance [19].

Raman spectroscopy was utilized to examine the structural distortions and the coordination environment of Mn cations within the [MnO₆] octahedra, as presented in Fig. 1(e). The

Raman shifts at ~520 cm⁻¹ and 580 cm⁻¹ are attributed to the Mn–O–Mn stretching and the in-plane Mn–O stretching vibrations, with the latter being correlated with Mn⁴⁺ content [20]. The attenuation of the 580 cm⁻¹ signal following ball milling implies a gradual decrease in Mn⁴⁺. Ball milling treatment markedly reduces the intensity of the 643 cm⁻¹ Raman peak, assigned to the symmetric Mn–O stretching vibration of [MnO₆] groups [21]. This reduction correlates with a decrease in the Mn–O bond force constant (*k*), a metric for bond strength derived from Hooke's law [22]. The observed decrease in vibrational frequency intensity is indicative of a weakened Mn–O bond strength, stemming from localized interactions between manganese and O_v. This structural weakening promotes manganese dissolution and concurrently generates a high density of active sites. These sites effectively lower the activation energy required for Zn²⁺ intercalation, thereby enhancing ionic diffusion kinetics.

The surface chemical states were characterized by X-ray photoelectron spectroscopy (XPS), revealing distinct signals corresponding to Mn and O elements, as shown in Fig. 1(f), Figs. S8 and S9 in the ESM. Semiquantitative analysis of O 1s XPS spectra (using the RSF-based peak area method) shows a decrease in oxygen atomic content from 74.75% (MnO₂) to 69.54% (BM-MnO₂), evidencing increased O_v. This result aligns with EPR and O₂-TPD findings (Fig. 1(d), Fig. S7 in the ESM). In Fig. 1(f), the high-resolution O 1s spectra reveal three discernible peaks, which can be attributed to tetra-valent Mn–O–Mn bond (529.8 eV),

defective oxide (531.2 eV), and surface hydroxyl species (532.6 eV) [23]. The significantly larger integral peak area corresponding to defective oxide in BM-MnO₂ directly reveals the successful incorporation of defects via ball milling, which is consistent with EPR analysis. These defects play a crucial role by providing additional active sites. They promote interfacial Zn²⁺ ion kinetics, which in turn enhances the electronic conductivity and improve faradaic pseudo-capacitance. The average oxidation state (AOS) of Mn was determined from the Mn 3s splitting energy (ΔE), using the equation: $AOS = 8.956 - 1.123 \times \Delta E$ [24]. The Mn 3s spectra shows that the AOS value of Mn decreases from 5.06 to 4.92 after ball milling, indicating more low-valence Mn species (Fig. S8 in the ESM) [25]. In the high-resolution Mn 2p spectrum, two peaks are observed at approximately 642.4 eV and 654.0 eV, assigned to Mn 2p_{3/2} and Mn 2p_{1/2}, respectively (Fig. S9 in the ESM) [26]. The ratio of Mn³⁺/Mn⁴⁺ shown in Fig. S9(c) in the ESM was calculated from the peak area. According to previous studies, the introduction of oxygen defects leads to an intensification of the Mn³⁺ signal alongside a corresponding decrease in the Mn⁴⁺ signal, consistent with prior reports [27]. Notably, BM-MnO₂ displays a higher Mn³⁺/Mn⁴⁺ ratio than the untreated sample, implying an increased concentration of O_v to maintain electrostatic balance.

2.2 The effect of structural defects on the d/p-band of MnO₂

To understand how the structural modification influences the electronic properties, the electronic structure of MnO₂ and BM-

MnO₂ was investigated using Ultraviolet visible spectroscopy (UV-vis) (Fig. 2(a), Fig. S10 in the ESM). For metal oxides acting as semiconductors, the band gap is a critical parameter governing carrier mobility and electrical conductivity. A Tauc plot was constructed, and the band gap was evaluated by extrapolating the linear region near the absorption edge to its intersection with the energy ($h\nu$) axis [28]. The Tauc plot analysis yields direct band gap values of 1.373 eV for MnO₂ and 1.293 eV for BM-MnO₂, indicating a reduction in the band gap following the ball-milling treatment. This is further substantiated through theoretical calculations by constructing models of pristine MnO₂ and BM-MnO₂ (Fig. S11 in the ESM). As shown in Fig. S12 in the ESM, pristine MnO₂ possesses a broad band gap of 1.130 eV, which validates its intrinsically the poor conductivity and in agreement with the electrochemical behavior. Notably, the MnO₂ with oxygen defects exhibits a greatly reduced band gap of 0.316 eV, which indicates that O_v can greatly boost the conductivity of the MnO₂. The band gap reduction originates from electronic structure adjustments, including a downward shift in band positions and the introduction of defect levels within the band gap. These mid-gap states heighten carrier density and promote faster charge transport kinetics [29]. Four-point probe measurements reveal a significant enhancement in electrical conductivity, with BM-MnO₂ exhibiting a value of 92.01 Ω cm compared to 908.25 Ω cm for pristine MnO₂, directly corroborating the improved charge transport capability (Fig. S13 in the ESM). As shown in Fig. 2(b), the calculated band gap from the TDOS is 1.130 eV for pristine MnO₂. The introduction of O_v creates defect

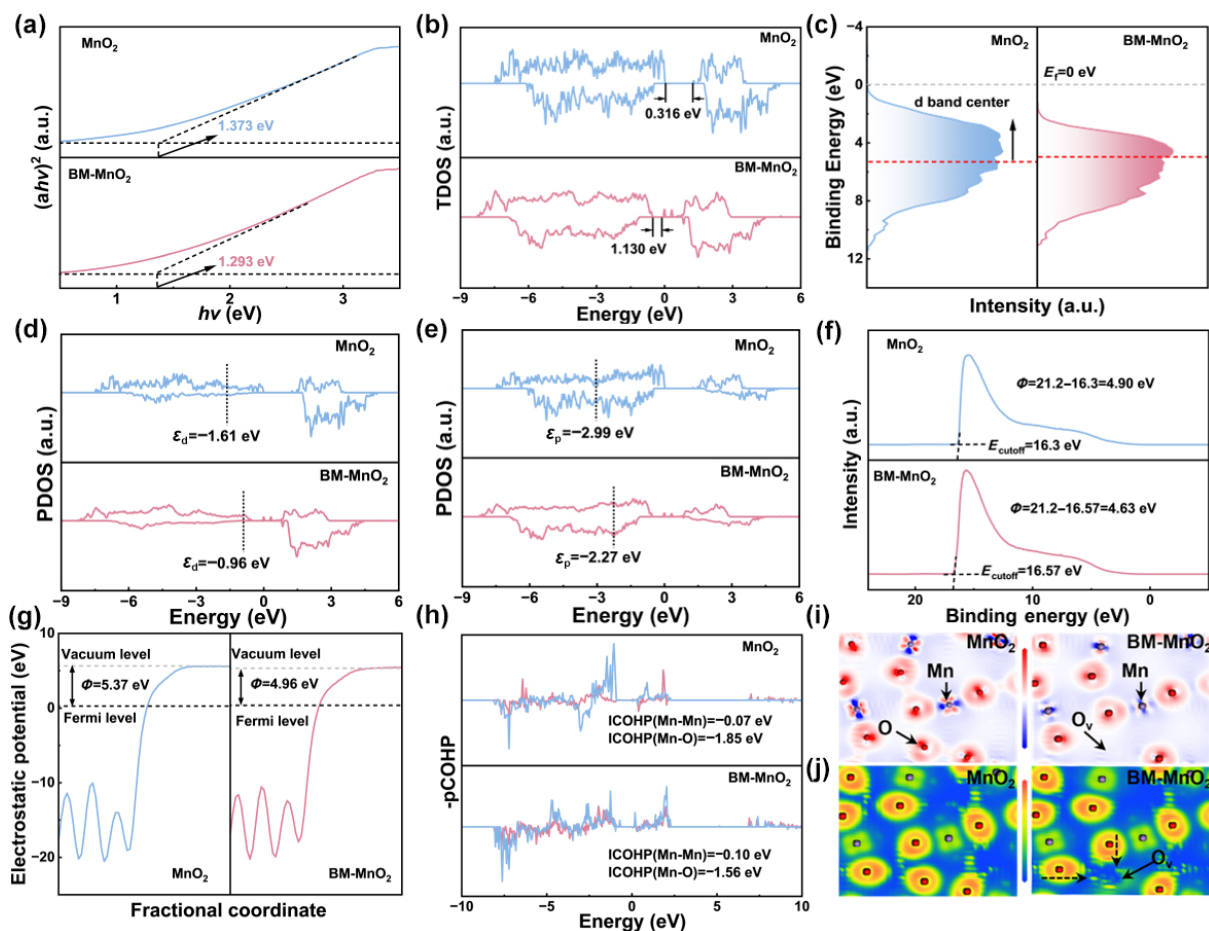


Figure 2 (a) UV-vis spectra, (b) TDOS, (c) XPS valence band spectra, (d) Mn 3d PDOS, (e) O 2p PDOS, (f) UPS, (g) work function, (h) ICOHP analysis, (i) charge density difference plots, and (j) electron localization function plots of MnO₂ and BM-MnO₂.

energy levels within the band gap of BM-MnO₂, which effectively reduce the band gap to 0.316 eV. These defect states serve as intermediate stepping stones for electron transitions, lowering the activation energy and thereby significantly improving the electrical conductivity. The enhanced conductivity originates from the synergistic modulation of the electronic structure by O_v. Primarily, the formation of each vacancy leaves behind two highly delocalized electrons, which are readily excited from the valence to the conduction band [30]. Concurrently, the coexisting Mn³⁺ ions and vacancies reduce the crystal field splitting energy of the Mn 3d orbitals. This dual effect collectively facilitates charge carrier generation and transport, leading to significantly improved conductivity in BM-MnO₂ [31]. The valence band spectra demonstrate that ball-milling attenuates the valence band maximum (VBM) of BM-MnO₂ to 1.179 eV, relative to 1.271 eV for pristine MnO₂ (Fig. S14 in the ESM). This downward shift signifies that the VBM moves closer to the Fermi level upon the introduction of O_v. Moreover, the observed shift in the d-band center (ϵ_d) suggests a substantial modulation of the MnO₂ electronic structure induced by these defects (Fig. 2(c)). This experimental observation is further corroborated by theoretical calculations of the Mn 3d partial density of states (PDOS), which verify that O_v upshifts the ϵ_d towards the Fermi level, consequently boosting electronic conductivity. Given the covalency of Mn–O bonds, the interaction between Zn²⁺ ions and O active sites is also governed by the ϵ_d of Mn (Fig. 2(d)). The upshifted ϵ_d in BM-MnO₂ suggests a stronger adsorption strength, which is theoretically favorable for faster ion transport [32]. Furthermore, the p-band center (ϵ_p) level of O sites is widely regarded as an effective descriptor for the balance of adsorption and desorption of Zn²⁺/H⁺ ions [32]. PDOS was utilized to calculate the ϵ_p of O atom in two cathodes, aiming for further insights into the enhanced rate capacity observed in the BM-MnO₂ cathode (Fig. 2(e)). The BM-MnO₂ cathode exhibits significantly upshifted ϵ_p , indicating that O_v can effectively regulate charge redistribution and modify the electronic structure of O elements. Therefore, an optimal d/p-band center separation ($\Delta\epsilon_{d-p}$) is crucial in alleviating interlayer stress and electrostatic repulsion during ion intercalation, while accelerating reaction kinetics. PDOS analysis reveals that the $\Delta\epsilon_{d-p}$ values for MnO₂ and BM-MnO₂ are 1.38 eV and 1.31 eV, respectively. The significant reduction in $\Delta\epsilon_{d-p}$ for BM-MnO₂ suggests superior energy alignment of d- and p-orbitals and intensified orbital hybridization, promoting electron delocalization and rapid transport for enhanced conductivity. To elucidate the influence of defect-induced d- and p-band center shifts on the electron transfer kinetics of BM-MnO₂, ultraviolet photoelectron spectroscopy (UPS) was utilized to measure the work functions (Φ). As Fig. 2(f) depicted, BM-MnO₂ exhibits a reduced work function of 4.63 eV compared to 4.90 eV for pristine MnO₂, suggesting a lowered energy barrier that facilitates electron transfer. These experimental findings are further corroborated by the theoretical work function values shown in Fig. 2(g), which align well with the observed trends. Furthermore, the Fermi level reveals a shift from 0.27 eV (pristine MnO₂) to 0.37 eV (BM-MnO₂). This upward shift reduces the electron-transfer barrier at the electrode/electrolyte interface, which, combined with altered d- and p-band centers, contributes to the enhanced kinetics and reversibility of the BM-MnO₂ electrode.

Crystal Orbital Hamilton Population (COHP) calculations reveal the bond strength evolution around O_v (Fig. 2(h)). The absolute ICOHP values of adjacent Mn–O bonds decrease from –1.85 eV (MnO₂) to –1.56 eV (BM-MnO₂) due to the upshifted d-

band center filling antibonding states, thereby weakening the bonds and mitigating Jahn-Teller distortion. Conversely, the radial expansion of wave functions associated with this d-band upshift induces direct d-orbital overlap between neighboring Mn atoms. This generates new bonding states and increases the absolute Mn–Mn ICOHP values from –0.07 eV (MnO₂) to –0.10 eV (BM-MnO₂), creating channels for electron transport. The influence of O_v on the electronic structure of manganese dioxide was further investigated via charge density difference and electron localization function theoretical calculations. As depicted in the CDD plot, the introduction of O_v induces local charge redistribution, characterized by a fraction of electrons on neighboring Mn atoms remains non-bonding, which enhances the filling of Mn 3d orbitals and causes an upshift in the d-band center (Fig. 2(i)). Regarding the ELF analysis, the defective region displays a more extensive blue delocalization zone compared to the pristine structure (Fig. 2(j)). Furthermore, electron density around O atoms adjacent to the defect extends asymmetrically toward the vacancy, indicating weakened electronic interactions between the remaining O and Mn atoms, and a transition from localized Mn–O covalent bonding to a delocalized state with a diffuse electron cloud. This delocalization promotes d-p orbital hybridization, consistent with the increased overlap of Mn 3d and O 2p states near the Fermi level in the PDOS. These results underscore the key role of O_v in tailoring the d/p-band centers of MnO₂. This electronic structure adjustment thereby optimizes ion adsorption, increases active site availability, and improves electrical conductivity. Therefore, a comprehensive improvement in electrochemical properties is theoretically predicted for the BM-MnO₂.

2.3 The effect of structural evolution on the electrochemical performance of MnO₂

To test the electrochemical performance, Zn||MnO₂ batteries were constructed in CR2032 coin cells, employing zinc foil as the anode and 2 M ZnSO₄ + 0.1 M MnSO₄ aqueous solution as the electrolyte. The CV curve in Fig. 3(a) reveals the redox mechanisms. For the BM-MnO₂ cathode, two cathodic peaks at 1.40 V and 1.25 V correspond to the concurrent insertion of Zn²⁺/H⁺ and the reduction of MnO₂, while the anodic peaks at 1.55 V and 1.60 V are attributed to their extraction [33]. Notably, the BM-MnO₂ cathode exhibits significantly higher current intensities for both redox couples. Furthermore, its smaller voltage gaps (0.20 V and 0.30 V) compared to those of pristine MnO₂ (0.21 V and 0.31 V) indicate faster reaction kinetics and enhanced electrochemical activity, attributable to the introduced O_v [27].

To elucidate the enhanced reaction kinetics of BM-MnO₂, CV curves were measured at various scan rates (Fig. 3(b), Fig. S15 in the ESM). The peak current (i) and the scan rate (ν) obey a power law: $i = a\nu^b$, where a and b are constants. Typically, the b -value approaching 1 signifies a capacitive-controlled process, whereas the b value near 0.5 indicates a diffusion-limited reaction [34]. In Fig. 3(c), the calculated b values for the four redox peaks of the BM-MnO₂ are 0.59, 0.61, 0.81, and 0.63 respectively, which point to a dominant contribution from pseudocapacitive processes to the overall charge storage. The total capacity is quantitatively separated into capacitive and diffusion-controlled contribution, as analyzed through the equation: $i = k_1\nu + k_2\nu^{1/2}$, where i is the current density at a given potential (V), k_1 and k_2 are constants, ν is the scan rate. The term $k_1\nu$ corresponds to the capacitive-controlled current, while $k_2\nu^{1/2}$ represents the diffusion-limited

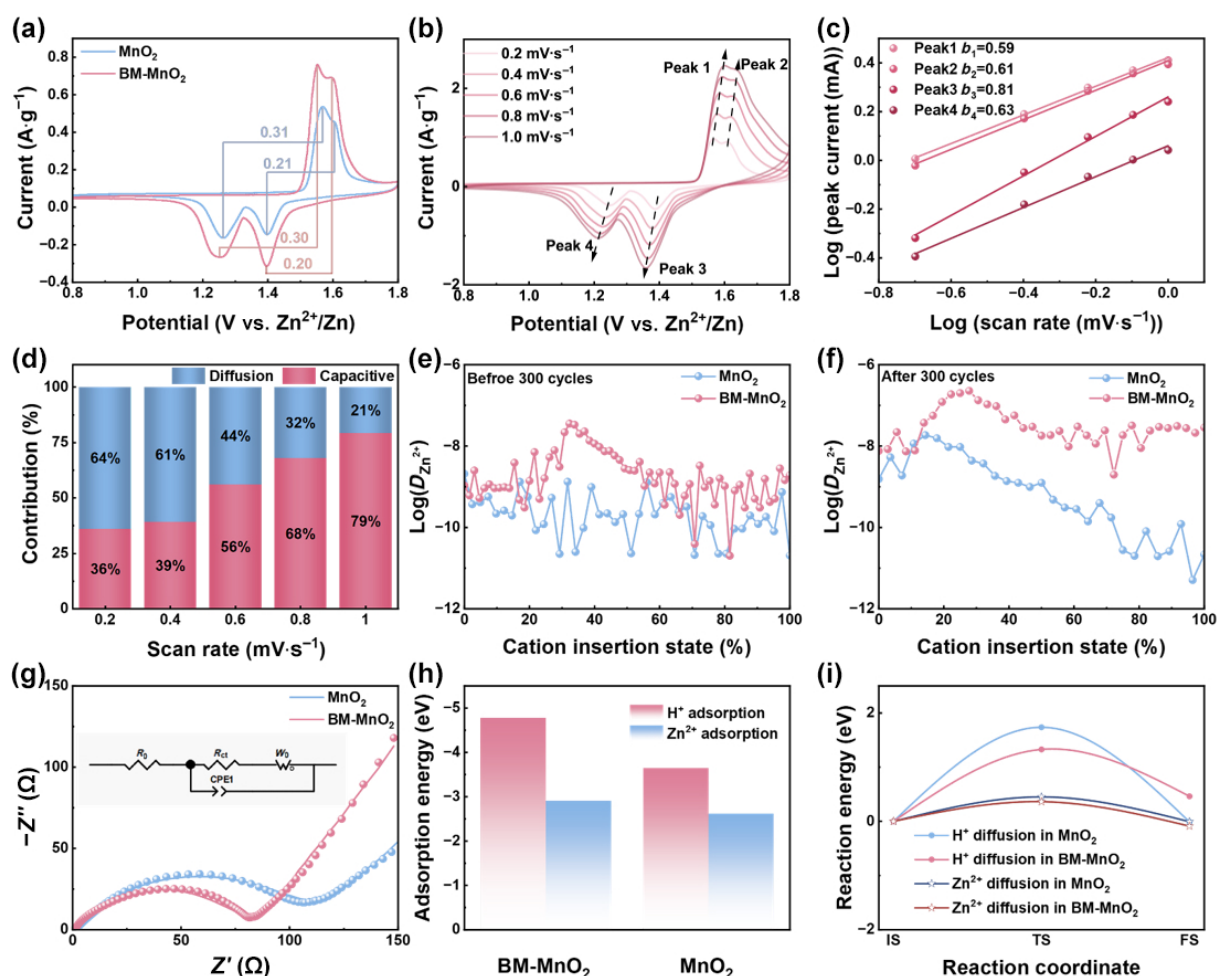


Figure 3 (a) CV curves of MnO₂ and BM-MnO₂ at 0.1 mV·s⁻¹. (b) CV curves of BM-MnO₂ at different scan rates. (c) Capacitive and diffusion contribution and (d) log *i* vs. log *v* plots of four peaks in the CV curves of BM-MnO₂. Zn²⁺ ion diffusion coefficients (e) before 300 cycles and (f) after 300 cycles. (g) Nyquist plots (the inset is the equivalent circuit), (h) the adsorption energies of Zn²⁺ and H⁺, (i) Zn²⁺ and H⁺ migration pathways of MnO₂ and BM-MnO₂.

component [35]. From Fig. 3(d) and Fig. S15(b) in the ESM, BM-MnO₂ exhibits significantly higher capacitive contributions (36%–79%) than MnO₂ across scan rates (0.2–1.0 mV·s⁻¹). This reveals that O_v enhances ion release/storage kinetics, thereby promoting a greater capacitive storage capacity.

The galvanostatic intermittent titration technique (GITT) measurements were performed to gain deeper insights into the ion diffusion kinetics in MnO₂ and BM-MnO₂. The diffusion coefficient of ions in discharging was determined based on GITT measurement and the following equation:

$$D = 4(m_B V_M \Delta E_s) / \pi \tau (M_B S \Delta E_\tau)^2$$

where *D* is the ion diffusion coefficient; *m_B*, *V_M*, and *M_B* refer to the diffusion molar mass, and molar volume; *τ* means the relaxing time; *S* is the surface area of the electrode; *ΔE_s* represents the voltage change eliminating the *i_R* drop during the pulse process; *ΔE_τ* denote the voltage difference between the voltages before the pulse process and after relaxing [36]. The Zn²⁺ diffusion coefficients (*D_{Zn²⁺}*) derived from GITT are significantly higher for BM-MnO₂ than that for MnO₂ (Figs. 3(e) and 3(f)). This enhancement correlates with a moderate rise in the d-band center of BM-MnO₂, thereby promoting more efficient Zn²⁺ ion adsorption/desorption during cycling. The limited mobility of Zn²⁺ ions in the MnO₂ structure can be attributed to their strong affinity for the electronegative oxygen atoms, which creates a significant diffusion barrier. The reaction kinetics of the cathodes were further characterized by electrochemical impedance

spectroscopy (EIS), as displayed in Fig. 3(g). The obtained Nyquist plots were fitted using the equivalent circuit model played in the inset, which comprises the solution resistance (*R_s*), a constant phase element (CPE1), charge-transfer resistance (*R_{ct}*), and the Warburg impedance (*W₀*). Obviously, the BM-MnO₂ cathode shows a smaller semicircle in the Nyquist plots compared to the other. The *R_{ct}* for the semicircle are 108.9 Ω and 71.6 Ω for pristine MnO₂ and BM-MnO₂ cathodes, respectively. Additionally, BM-MnO₂ cathode has the steeper slope, which illustrates a lower Warburg diffusion resistance. This is evidenced by a smaller fitted slope value of BM-MnO₂ (20.03) versus that of MnO₂ (34.33) in the *Z'* ~ *ω*^{-1/2} plot, confirming its enhanced ion diffusivity (Fig. S16 in the ESM) [37]. Additionally, the adsorption energy barriers and migration energy barriers for Zn²⁺ ions and H⁺ ions in MnO₂ and BM-MnO₂ were calculated using DFT (Figs. S17 and S18 in the ESM). As shown in Fig. 3(h), adsorption energy calculations confirm that oxygen vacancies provide substantially enhanced adsorption stability. The calculated values are -2.91 eV for Zn²⁺ and -4.78 eV for H⁺, both significantly more favorable than those on the pristine material. The more negative adsorption energy of H⁺ reveals its thermodynamic preference over Zn²⁺ in competing for the limited vacancy sites [38]. In Fig. 3(i), the markedly reduced H⁺ migration barrier in the oxygen-deficient structure (1.32 eV vs. 1.73 eV in the pristine structure) provides atomic-scale validation for the ultrafast proton conduction via the Grotthuss mechanism, a key contributor to the

superior rate capability [39]. Furthermore, acting as an “expanded node”, the O_v facilitates Zn^{2+} diffusion by lowering its migration barrier from 0.45 eV to 0.36 eV. This further highlights the important role played by the improved proximity of the d/p-band center due to the introduction of O_v in facilitating ion migration rates.

Figure S19 in the ESM presents the GCD curves at 0.5 C, revealing that both cathode materials feature two discernible charge/discharge plateaus across the voltage from 0.8 V to 1.8 V. The BM-MnO₂ cathode outperforms its counterpart with lower polarization and higher capacity, concomitant with increased H^+/Zn^{2+} insertion capacity. This is attributed to the expanded specific surface area and introduced O_v , which supply a greater density of active sites for ion storage. Figure 4(a) presents GCD profiles of MnO₂ and BM-MnO₂ cathodes, as the discharge/charge current densities incrementally increased from 0.2 C to 1.5 C. The less plateau change upon elevated current density can be observed in the BM-MnO₂ cathode, along with a relatively higher specific capacity under each current density compared with the MnO₂ cathode. Figure 4(b) compares the rate performance of samples. The BM-MnO₂ cathode delivers high discharge capacities of 316, 215, 152, and 94 mAh·g⁻¹ at 0.2 C, 0.5 C, 1 C, and 1.5 C, all exceeding those of the pristine MnO₂. Notably, when the rate returns to 0.2 C, a high capacity of 327 mAh·g⁻¹ is recovered, demonstrating excellent rate capability and reversibility. This performance starkly contrasts with the rapid capacity fade observed for MnO₂ at increasing rates, directly verifying the enhanced conductivity and kinetics imparted by ball milling. Furthermore, Fig. 4(c) illustrates the superior cycling performance of BM-MnO₂ at a 1 C, demonstrating a capacity retention of 95.4% after 650 cycles. In Fig. 4(d), BM-MnO₂ exhibits outstanding cycling stability at 1.5 C, retaining 97.9% of its capacity after 650 cycles with a Coulombic efficiency near 100%. Figure 4(e) manifests the exceptional durability of BM-MnO₂ at 2 C, where the electrode sustains a discharge capacity of 88.5 mAh·g⁻¹ and a capacity retention of 98.7% over 700 cycles. This remarkable stability is attributed to the engineered O_v . The practical potential is confirmed by a Zn||BM-MnO₂ pouch cell, which has a high capacity of 86.5 mAh·g⁻¹ after 80 cycles at 1 C, highlighting its promise for grid-scale aqueous zinc-ion storage (Fig. 4(f)).

2.4 The charge storage and structural evolution mechanisms of MnO₂

To gain fundamental insights into the exceptional performance, the charge storage mechanism and structural evolution of the BM-MnO₂ cathode were systematically probed using *in-situ* Raman spectroscopy, *ex-situ* XRD and SEM characterizations. As shown in Figs. 5(a) and 5(b), the major regions can be recognized at 370–410 cm⁻¹ (v_1 band), 430–470 cm⁻¹ (v_2 band) and 560–620 cm⁻¹ (v_3 band). The appearance of a new Raman peak around 700 cm⁻¹ in the pristine MnO₂ during cycling suggests irreversible phase transformation (such as to ZnMn₂O₄), whereas its effective suppression in BM-MnO₂ confirms enhanced structural reversibility afforded by the ball-milling modification [40]. The v_2 band and v_3 band are characteristic of the symmetric Mn–O stretching and the [MnO₆] octahedral stretching vibrations, respectively [24]. Thus, Zn^{2+} insertion/extraction is able to influence the v_1 band largely. In addition, a weak Mn–O vibration mode (v_1 band), induced by interlayer coupling, reflects variations in the interlayer spacing [41]. It is evident that the intensity of the v_3 peak increases upon charging can be directly attributed to the Zn^{2+} ions extraction process. Simultaneously, the v_2 peak becomes more intense due to the increased Mn³⁺ and the shortening of the Mn–O bond [42]. The extraction process of Zn^{2+} requires a significant amount of energy, resulting in an enhanced Raman signal during charging. Notably, the vibration of the v_3 peak coincides with the pristine state when it is fully charged to 1.8 V, revealing a reversible change in the local coordination of the [MnO₆] octahedra. On the contrary, a reverse change can be observed upon discharging. Additionally, the subtle changes in the intensity of the v_1 peak imply no significant alteration in the atomic interaction within the layer during cycling [43]. Furthermore, *in-situ* Raman spectra at pristine, 0.8 V, and 1.8 V reveal that upon discharge, both samples show a slight v_1 downshift due to lattice expansion from ion insertion (Fig. S20 in the ESM). Upon charging, BM-MnO₂ fully recovers its v_1 position, whereas pristine MnO₂ retains a residual shift, confirming that oxygen vacancies effectively suppress Jahn-Teller distortion and stabilize the MnO₂ framework, consistent with literature reports [44–46]. As a result, the well-maintained Raman peak profiles after a full charging cycle indicates outstanding structural

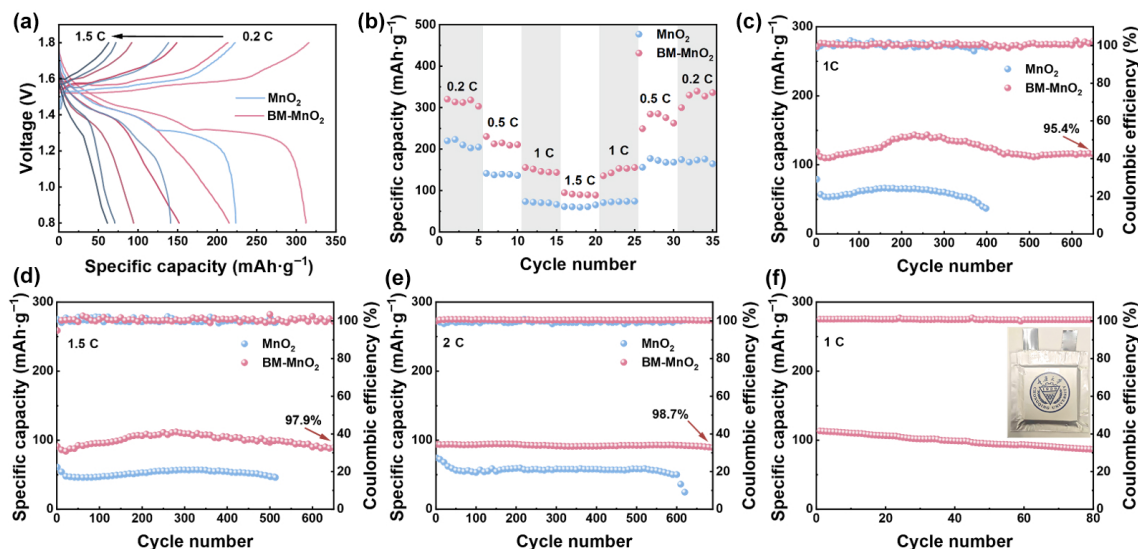


Figure 4 (a) GCD curves of MnO₂ and BM-MnO₂ at 0.2–1.5 C. (b) Corresponding rate performance. (c) Cycling performance at 1 C, (d) at 1.5 C and (e) at 2 C. (f) Cycling performance of BM-MnO₂ pouch battery at 1 C.

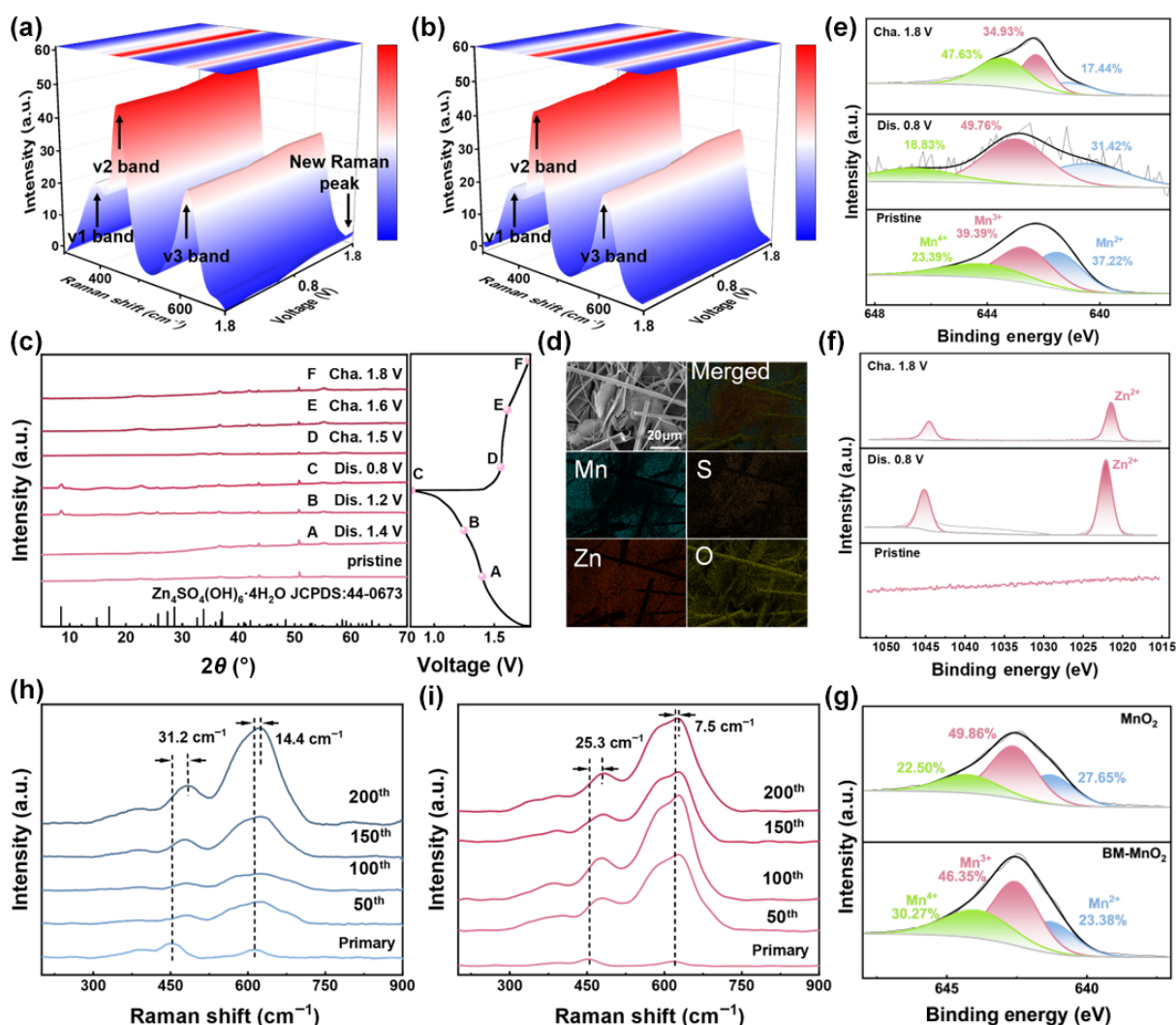


Figure 5 *In-situ* Raman operated at different states of the charge against the voltage during a cycle of (a) MnO_2 and (b) BM-MnO_2 . (c) *Ex-situ* XRD patterns of BM-MnO_2 at selected voltage states. (d) SEM images and mappings of BM-MnO_2 after discharged to 0.8 V. *Ex-situ* XPS of (e) Mn 2p of BM-MnO_2 during one cycle, (f) Zn 2p of BM-MnO_2 during one cycle, and (g) Mn 2p spectra of MnO_2 and BM-MnO_2 after 200 cycles. *Ex-situ* Raman spectra of (h) MnO_2 and (i) BM-MnO_2 .

reversibility and stability of the MnO_2 framework. Figure 5(c) presents the *ex-situ* XRD patterns of the BM-MnO_2 electrode obtained at different states of charge and discharge at 0.1 C in the second cycle. As the discharge process proceeds a new phase appears at 8.07° , 16.22° , 24.43° , 27.59° , 28.49° , and 58.48° are observed clearly in the discharge process, which can be well indexed to $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 5\text{H}_2\text{O}$ (denoted as ZSH, JCPDS: 44-0673). The peak intensity of ZSH increased with the deep discharging to 0.8 V, confirming a growing structure of ZSH. However, the ZSH phase disappear when charging to 1.8 V, suggesting that the ZSH formation is highly reversible and does not accumulate in the electrode. Furthermore, *ex-situ* XRD patterns of the pristine MnO_2 reveal that the peak intensities of the ZSH byproduct at 1.2 V and 0.8 V are significantly higher than those of BM-MnO_2 (Fig. S21 in the ESM). This indicates that the introduction of defects effectively suppresses the formation of ZSH. SEM images are consistent with the previous results, revealing the reversible surface morphology evolution (Figs. S22 and S23 in the ESM). During the discharge process, the electrode exhibits the formation of flake-like products, which are clearly identified as ZSH ultrathin nanosheets (Fig. 5(d)). The reversibility of ZSH stems from the cyclic insertion and extraction of $\text{H}^+/\text{Zn}^{2+}$ ions [47]. Discharge (ion insertion) elevates pH, leading to ZSH

formation. The discharge process (ion insertion) drives local deacidification and ZSH deposition, while charging (H^+ extraction) induces reacidification and ZSH dissolution. This mechanism enables the electrode to alternate between ZSH-deposited and ZSH-free states [48]. Comparative SEM images of the cathodes discharged to 1.2 V and 0.8 V reveal that the surface of the pristine MnO_2 is densely covered with flaky ZSH, whereas BM-MnO_2 exhibits only localized ZSH growth. These morphological observations are highly consistent with the *ex-situ* XRD results.

The evolution of surface chemical states in BM-MnO_2 and MnO_2 was probed via *ex-situ* XPS. As shown in the Mn $2p_{3/2}$ spectra, discharging to 0.8 V leads to a marked enrichment of low-valence Mn species (Fig. 5(e)). This is ascribed to the reduction of high-valence Mn driven by the co-insertion of Zn^{2+} and H^+ . Upon recharging to 1.8 V, the Mn^{4+} content recovers accompanied by a decline in low-valence Mn, corresponding to ion extraction and corroborating the reversible Mn redox kinetics. Figure 5(f) illustrates the Zn 2p spectra. No Zn signal was detected in the pristine state. However, distinct Zn 2p peaks appeared upon discharging to 0.8 V, verifying the incorporation of Zn^{2+} into the MnO_2 host. The signal intensity weakened upon charging to 1.8 V, indicative of Zn^{2+} deintercalation, with the remaining weak

signal attributed to surface-adsorbed species from the electrolyte. Pristine MnO_2 shows a similar trend but suffers from worse reaction reversibility than the modified samples, with a higher fraction of lower-valence Mn at 1.8 V (Fig. S24 in the ESM). As illustrated in Fig. 5(g), the Mn 2p spectra after 200 cycles demonstrate that BM- MnO_2 maintains a dominant Mn^{4+} state, signifying effective suppression of Mn dissolution. This enhanced stability is attributed to the incorporation of O_v , which alleviates lattice stress caused by repetitive ion (de)intercalation. ICP analysis of the electrolyte after 10 cycles reveals that the Mn dissolution in the BM- MnO_2 sample is significantly lower than that in the pristine sample (Fig. S25 in the ESM). This demonstrates that the introduction of O_v effectively mitigates the Jahn-Teller effect, thereby suppressing Mn dissolution. *Ex-situ* Raman spectroscopy after multiple cycles reveals a substantial peak shift for the pristine MnO_2 , indicating severe lattice micro-strain and alterations in bonding strength during the repetitive $\text{Zn}^{2+}/\text{H}^+$ intercalation/deintercalation (Fig. 5(h)) [49]. In contrast, the oxygen-deficient sample exhibits a markedly smaller peak shift (Fig. 5(i)). This demonstrates that the pre-existing lattice distortions around the O_v effectively acts as stress-buffering centers, accommodating the volumetric changes and thereby helping to preserve the initial crystal structure. The vacancies enhance structural stability by suppressing the onset of long-range, destructive phase transitions.

3 Conclusion

In conclusion, this work has successfully demonstrated a facile and scalable strategy for introducing defect engineering into MnO_2 via a straightforward ball-milling process, which modulates the proximity of the d/p-band center and optimizes the adsorption and desorption behavior of $\text{Zn}^{2+}/\text{H}^+$ ions. The incorporation of O_v serves as a multifaceted strategy to address the key challenges of sluggish kinetics and structural instability. O_v serves as high-affinity adsorption sites that strengthen the interfacial stabilization of $\text{Zn}^{2+}/\text{H}^+$, synergistically facilitate solid-state Zn^{2+} diffusion and Grotthuss-type ultrafast proton conduction by reducing ion migration barriers, and effectively suppress Jahn-Teller distortions and irreversible phase transitions via localized electronic structure modulation. Thus, the BM- MnO_2 exhibits a high specific capacity of $339.7 \text{ mAh}\cdot\text{g}^{-1}$ at 0.2 C and maintains outstanding cycling stability (98.7% capacity retention after 700 cycles at 2 C). This study not only provides a high-performance electrode material for advanced ZIBs but also offers profound mechanistic insights into the critical role of defect chemistry in regulating reaction kinetics, presenting a promising and scalable pathway for the development of next-generation energy storage materials.

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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.

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