

Tailoring the *OH-mediated manganese deposition chemistry via fluorine-doped carbon for reversible aqueous zinc batteries

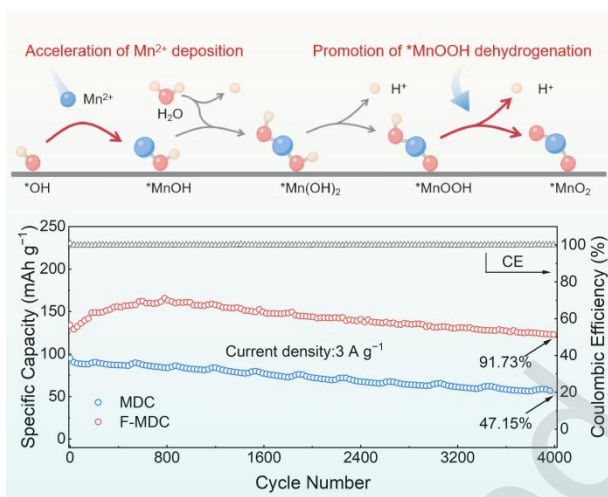
Haiyan Sun[§], Shijie Chen[§], Hao Wang, Chu Zhang, Ju Zhao, Weihao Xu, Chade Lv(✉), Chunshuang Yan(✉)
MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China
[§] Haiyan Sun and Shijie Chen contributed equally to this work.

Nano Res., **Just Accepted Manuscript** • <https://doi.org/10.26599/NR.2026.94909104>
<https://www.sciopen.com/journal/1998-0124> on Aug. 10, 2026

© The Authors(s)

Just Accepted

This is a “Just Accepted” manuscript, which has been examined by the peer-review process and has been accepted for publication. A “Just Accepted” manuscript is published online shortly after its acceptance, which is prior to technical editing and formatting and author proofing. Tsinghua University Press (TUP) provides “Just Accepted” as an optional and free service which allows authors to make their results available to the research community as soon as possible after acceptance. After a manuscript has been technically edited and formatted, and the page proofs have been corrected, it will be removed from the “Just Accepted” web site and published officially with volume and article number (e.g., *Nano Research*, **2025**, *18*, 94906990). Please note that technical editing may introduce minor changes to the manuscript text and/or graphics which may affect the content, and all legal disclaimers that apply to the journal pertain. In no event shall TUP be held responsible for errors or consequences arising from the use of any information contained in these “Just Accepted” manuscripts. To cite this manuscript please use its Digital Object Identifier (DOI®), which is identical for all formats of publication.



The high electronegativity of F in the as-designed cathode could strengthen the binding between Mn²⁺ and *OH as well as lower the ΔG of the MnOOH dehydrogenation step, thereby suppressing Mn³⁺ generation and disproportionation to prevent “dead MnO₂” formation and enhance reversibility.

Tailoring the *OH-mediated manganese deposition chemistry via fluorine-doped carbon for reversible aqueous zinc batteries

Haiyan Sun[§], Shijie Chen[§], Hao Wang, Chu Zhang, Ju Zhao, Weihao Xu, Chade Lv[✉], and Chunshuang Yan[✉]

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

[§] Haiyan Sun and Shijie Chen contributed equally to this work.

Received: 30 May 2026; Revised: 9 August 2026; Accepted: 10 August 2026

✉ Address correspondence to Chade Lv, lv.chade@hit.edu.cn; Chunshuang Yan, csyan@hit.edu.cn

 Cite this article: Nano Research, 2026, 19, 94909104 <https://doi.org/10.26599/NR.2026.94909104>

ABSTRACT: Aqueous zinc-manganese batteries face the critical issue of irreversible dissolution/deposition of manganese dioxide (MnO₂) stemmed from the disproportionation of Mn³⁺. Herein, the fluorine-doped manganese acetylacetonate-derived carbon (F-MDC) was designed as the cathode substrate to realize reversible dissolution/deposition of MnO₂. An *OH-mediated deposition pathway of MnO₂ was elucidated as follows: *OH → *MnOH → *Mn(OH)₂ → *MnOOH → *MnO₂. Attributed to the high electronegativity of fluorine on F-MDC, such pathway was promoted by accelerating the MnOOH dehydrogenation and strengthening the binding between Mn²⁺ and *OH, which could effectively avoid the disproportionation of Mn³⁺ and the formation of “dead MnO₂”. The Zn-Mn battery based on F-MDC delivered a capacity retention rate of 91.7% after 4000 cycles at 3 A g⁻¹ and still retained the specific capacity of 87.5 mAh g⁻¹ even at a high current density of 10 A g⁻¹. In addition, the assembled pouch cell also displayed standout rate capability, cycling stability and power supply performance.

KEYWORDS: aqueous zinc-manganese battery • cathode • deposition mechanism • reversibility • disproportionation of Mn³⁺

1 Introduction

Aqueous zinc-ion batteries (AZIBs) are highly promising for large-scale energy storage, due to their inherent safety, environmental friendliness, and cost-effectiveness, coupled with the high theoretical capacity and low redox potential of the zinc metal anode [1–8]. Manganese dioxide (MnO₂) has emerged as a prominent candidate for aqueous zinc-ion battery (AZIB) cathodes, owing to its diverse manganese oxidation states, high open-circuit voltage, and environmental friendliness [9–11]. The theoretical specific capacity of MnO₂ is 308 mAh g⁻¹, originating from the Mn⁴⁺/Mn³⁺ redox reaction coupled with ion insertion/extraction processes [12–15]. However, the strong Coulombic interaction between Zn²⁺ ions and the MnO₂ matrix triggers irreversible phase transformations concomitant with Mn dissolution, leading to the loss of active materials and subsequent capacity fading [16–20]. Conversely, the dissolution/deposition mechanism involving a two-electron Mn⁴⁺/Mn²⁺ redox process facilitates a higher theoretical capacity of 616 mAh g⁻¹ while mitigating capacity degradation associated with structural collapse [21–25]. Nevertheless, achieving fully reversible dissolution/deposition of MnO₂ remains a significant challenge [26–28].

Owing to the sluggish deposition kinetics and poor intrinsic conductivity of MnO₂, the deposition process is highly susceptible to inhomogeneity and structural

delamination [29, 30]. This is further exacerbated by the diffusion of interfacial Mn³⁺ intermediates into the electrolyte, where they undergo disproportionation (2Mn³⁺ + 2H₂O → Mn²⁺ + MnO₂ + 4H⁺) [31–35]. This results in the accumulation of “dead MnO₂” outside the active region, causing the loss of electrical contact [36–41]. Therefore, precise regulation of MnO₂ deposition is essential for achieving a highly reversible Mn²⁺/MnO₂ chemistry [42]. To improve the MnO₂ dissolution/deposition reversibility, Liu et al. modified pristine carbon felt with a carbon nanotube framework [43]. This structure induced the growth of porous MnO₂, effectively suppressing material cracking and exfoliation. Lan et al. prepared the Zn/Mn co-doped Prussian blue analog (ZnMn-PBA) with an abundant specific surface area and strong Mn-affinity [44]. These features regulate the Mn²⁺ deposition kinetics, thereby establishing a highly reversible dissolution/deposition mechanism. Zhou et al. immobilized Mn³⁺ ions at the carbon felt interface using electronegatively charged SiO₂ colloidal particles [45]. This strategy effectively suppressed the diffusion of Mn³⁺ into the bulk electrolyte, enhancing the long-term cycling stability of aqueous zinc-manganese batteries. Based on the aforementioned studies, current research primarily focuses on enhancing Mn²⁺ deposition through strengthened adsorption or physical confinement. However, the critical role of Mn³⁺ disproportionation and the fundamental dehydrogenation process during Mn²⁺ oxidation (Mn²⁺ + 2H₂O → MnO₂ + 4 H⁺ + 2e⁻) remains under-explored [46]. To

circumvent the above issue, decoding the manganese deposition chemistry is imperative to develop reversible aqueous Zn-Mn battery.

Herein, we unveiled that the deposition process proceeds via the following pathway: $*OH \rightarrow *MnOH \rightarrow *Mn(OH)_2 \rightarrow *MnOOH \rightarrow *MnO_2$ (**Fig. 1**), mediated by $*OH$ intermediates derived from water dissociation. To promote the kinetics of Mn^{2+} binding with $*OH$ and dehydrogenation, F-doped manganese acetylacetonate-derived carbon (F-MDC) was employed as a substrate to host Mn^{2+} deposition. Leveraging the high electronegativity of fluorine, F-MDC promotes the kinetics of the Mn^{2+} hydroxylation step ($Mn^{2+} +$

$*OH \rightarrow *MnOH$) and diminishes the activation energy required for the dehydrogenation of $*MnOOH$ to MnO_2 . This effectively mitigated Mn^{3+} accumulation by simultaneously hampering the one-electron oxidation of Mn^{2+} and the protonation-driven conversion of interfacial $*MnOOH$. Benefiting from the aforementioned attributes, the zinc-manganese battery achieves an impressive rate capability (87.5 mAh g^{-1} at 10 A g^{-1}) and outstanding long-term durability (91.73% retention after 4000 cycles at 3 A g^{-1}). Beyond performance, this study sheds light on the underlying dissolution/deposition mechanisms and paves the way for the design of highly reversible aqueous zinc-ion batteries using MnO_2 -based cathodes.

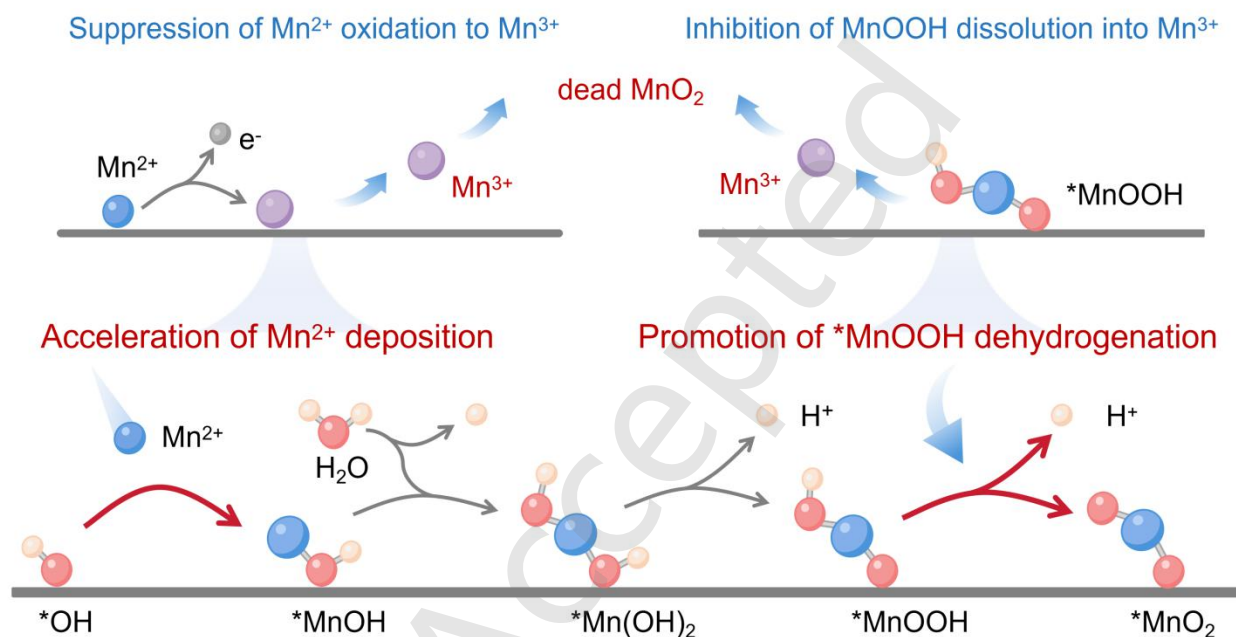


Figure 1 Schematic diagram illustrating the $*OH$ -mediated MnO_2 deposition pathway facilitated by F-MDC.

2 Results and discussion

Firstly, a fluorine-doped MnO-loaded carbon substrate derived from manganese acetylacetonate (F-MDC@F-MnO) was synthesized. F-MDC@F-MnO was fabricated into a working electrode and then assembled into a coin cell, galvanostatically charged to 1.9 V (referred to as F-MDC@F-MnO-1.9) and then discharged to 0.4 V to yield the fluorine-doped manganese acetylacetonate-derived carbon substrate (F-MDC). The F-MDC@F-MnO was synthesized via a molten salt method using ammonium fluoride and manganese acetylacetonate. The F content in F-MDC@F-MnO is tunable by varying the dosage of ammonium fluoride (NH_4F) (**Fig. S1**). Thermogravimetric (TG) analysis shows that F-MDC@F-MnO has a carbon mass fraction of 74.79% (**Fig. S2**). The scanning electron microscopy (SEM) image of MDC@MnO reveals the nanosheet morphology (**Fig. S3a**). In contrast, F-MDC@F-MnO exhibits a porous nanosheet morphology (**Fig. S3c and S4**) triggered by gas release from precursor decomposition and the porosity of this morphology increases with the amount of NH_4F added (**Fig. S3b-d**). Nitrogen adsorption/desorption isotherms were recorded to characterize the textural properties of F-MDC@F-MnO and MDC@MnO (**Fig. S5**). Based on Brunauer-Emmett-Teller (BET) calculations, F-MDC@F-MnO possesses a significantly

higher specific surface area ($463.46 \text{ m}^2/\text{g}$) than MDC@MnO ($220.06 \text{ m}^2/\text{g}$), which potentially facilitates the exposure of more active sites for MnO_2 deposition. **Figure. S6** displays the Raman spectra of F-MDC@F-MnO and MDC@MnO, where the G-band ($\sim 1590 \text{ cm}^{-1}$) and D-band ($\sim 1350 \text{ cm}^{-1}$) represent the ordered graphitic carbon and structural defects [47]. The corresponding ID/IG values were determined to be 1.21 for F-MDC@F-MnO and 1.09 for MDC@MnO, respectively. This suggests that F doping increases the defect density [48], which may endow the electrode with more active sites for Mn^{2+} adsorption. Transmission electron microscopy (TEM) image of F-MDC@F-MnO (**Fig. S7a**) exhibits a carbon matrix anchored with MnO nanoparticles. This architecture is further validated through a combination of high-resolution TEM (HRTEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) characterizations (**Fig. S7-S9**) [49]. Specifically, the F 1s XPS spectra (**Fig. S10**) confirm the presence of C-F (688.57 eV) and F-Mn (684.67 eV) bonds [50, 51]. Owing to the high electronegativity of fluorine, the charge density is redistributed around the carbon defects, which likely facilitates the nucleation and deposition of MnO_2 on the electrode surface during the charging process. Meanwhile, the F-Mn bonds on the MnO surface may alter the surface energy and electronic structure of MnO,

potentially lowering the overpotential for its electrochemical oxidation to MnO_2 .

To activate the electrochemical activity of MnO and preliminarily evaluate the deposition behavior on the cathode [49], the galvanostatic charging was conducted to 1.9 V (**Fig. S11**). As illustrated in **Fig. S12a**, MDC@ MnO -1.9 appears uneven and aggregated, whereas F-MDC@F- MnO -1.9 is uniform and fine-grained (**Fig. S12b**). The distinct morphological difference between MDC@ MnO -1.9 and F-MDC@F- MnO -1.9 suggests that F-doping plays a pivotal role in regulating the nucleation and growth kinetics of MnO_2 . The MnO_2 forms via both the electrochemical oxidation of pre-existing MnO and the electrodeposition of Mn^{2+} from the electrolyte [49]. Elemental mappings reveal a homogeneous distribution of C, O, Mn, and F within the F-MDC@F- MnO -1.9 (**Fig. S13**). The absence of diffraction peaks in the XRD pattern suggests that the as-formed MnO_2 is amorphous (**Fig. S14**) [52, 53]. XPS analysis confirms the +4 oxidation state of

Mn, identifying the product obtained after charging to 1.9 V as MnO_2 (**Fig. S15**) [54, 55].

Upon galvanostatic discharging to 0.4 V, the MnO_2 almost completely dissolved, as evidenced by the extreme weakness of the Mn 2p signal (**Fig. 2a**) and the complete disappearance of the F-Mn bond (**Fig. 2c**), ultimately yielding the F-MDC substrate. The fluorine in this substrate is primarily incorporated into the carbon framework through covalent C-F bonds. With a bond energy of approximately 485 kJ/mol and chemical inertness within the electrochemical window of this study (0.4–1.8 V vs. Zn^{2+}/Zn), the C-F configuration is expected to remain structurally stable during prolonged cycling. This ensures that the doping effect of fluorine is sustained over extended operation without significant leaching. Similarly, upon galvanostatic discharging of MDC@ MnO -1.9 to 0.4 V, the MDC substrate was obtained.

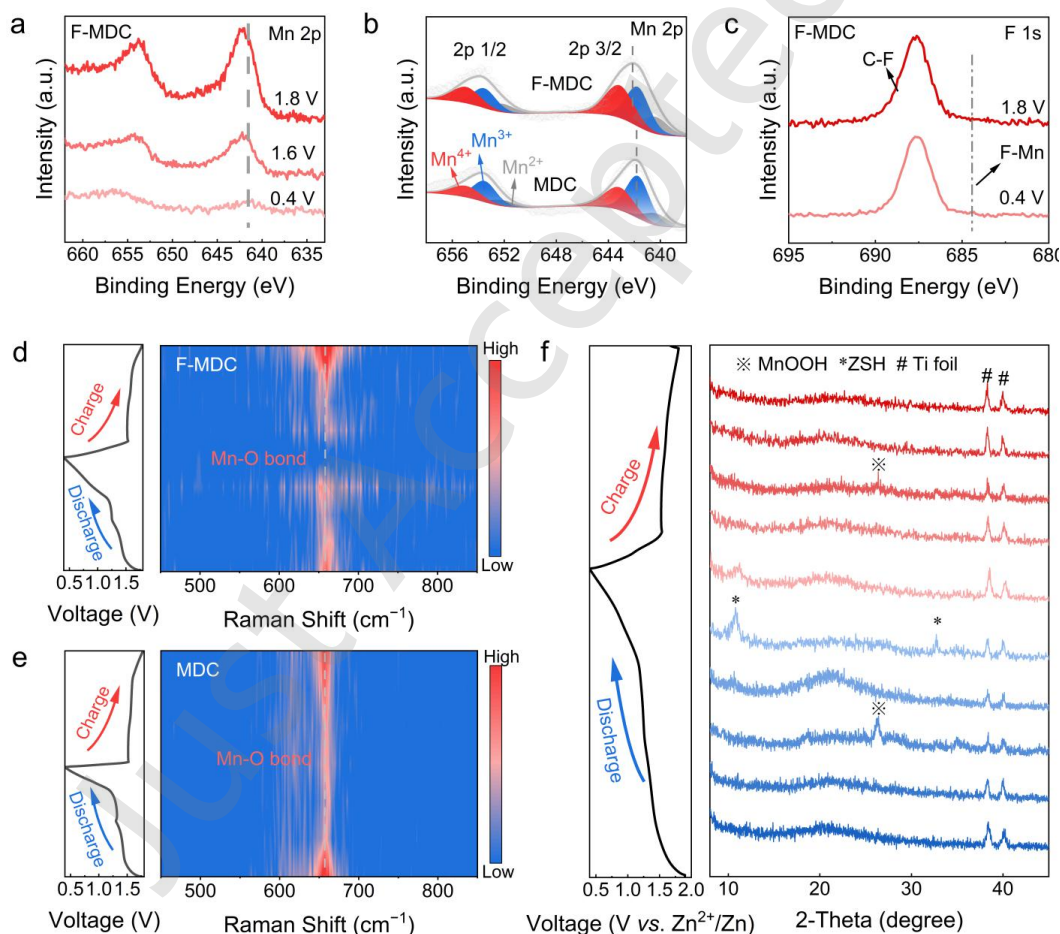


Figure 2 (a) Ex situ XPS spectra of Mn 2p for F-MDC electrode at various states of charge. (b) Ex situ XPS spectra of Mn 2p for the F-MDC and MDC electrodes at the fully charged state. (c) Ex situ XPS spectra of F 1s for the F-MDC electrode at fully charged and fully discharged states. Electrochemical discharge/charge profiles and the corresponding operando Raman spectral contour maps of Zn- MnO_2 batteries using F-MDC (d) and MDC (e) substrates. (f) Electrochemical discharge/charge profiles and ex situ XRD patterns of the F-MDC electrode at various electrochemical states.

To further elucidate the deposition behavior of F-MDC and MDC during cycling, a combination of in situ and ex situ characterizations was conducted on electrodes at various states of charge. The Mn 2p XPS spectra (**Fig. 2a and S16a**) exhibit a significant increase in peak intensity and a discernible shift toward higher binding energy upon charging, implying the oxidation of Mn species and the subsequent deposition of MnO_2 [37, 56]. Compared with

MDC, the drastically enhanced Mn 2p signal in F-MDC confirms that F-incorporation accelerates the deposition kinetics (**Fig. S16b**). Moreover, the higher Mn valence state observed in F-MDC at the fully charged state (**Fig. 2b**) suggests a more complete oxidation of Mn^{2+} to Mn^{4+} [42]. Interestingly, the absence of Mn-F bonds in the F 1s spectra (**Fig. 2c**) indicates that MnO_2 nucleation and growth preferentially occur at carbon active sites instead of direct

bonding with fluorine species. In situ Raman spectroscopy (setup illustrated in **Fig. S17**) was employed to monitor the real-time deposition processes on F-MDC and MDC substrates during a full galvanostatic charge-discharge cycle. **Figure. 2d** presents the Raman heat map of F-MDC, where the characteristic peak at 680 cm^{-1} is assigned to the Mn-O stretching vibration of MnO_2 [57, 58]. During the discharging process, the intensity of this peak gradually diminishes until it completely vanishes. Upon charging process, the peak intensity progressively recovers to its initial level, confirming the reversible dissolution/deposition behavior of MnO_2 on F-MDC. Although the MDC substrate exhibits a similar trend (**Fig. 2e**), its peak intensity only partially weakens during discharging and fails to return to its original value after charging. This discrepancy clearly reflects the superior electrochemical reversibility of F-MDC over MDC.

To investigate the dynamic phase evolution, ex situ XRD measurements were conducted on F-MDC and MDC electrodes. When discharged to 1.3 V, a diffraction peak appears at 26.1° (**Fig. 2f and S18**), corresponding to the MnOOH phase (JCPDS No. 41-1379). As discharge proceeds to 0.4 V, the MnOOH peak gradually diminishes, accompanied by the appearance of a characteristic peak at 12.4° , assigned to $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot 0.5\text{H}_2\text{O}$ (ZSH, JCPDS No. 44-0674). The formation of ZSH is attributed to the continuous consumption of H^+ during discharge, which leads to the gradual accumulation of OH^- reacting with Zn^{2+} and SO_4^{2-} in the electrolyte. During the subsequent charging process, the release of H^+ causes the ZSH peak to progressively weaken, while the MnOOH reappears at 1.6 V. Upon reaching full charge, the MnOOH peak disappears, replaced by the formation of amorphous MnO_2 . This evolution aligns well with the reported dissolution/deposition processes

involving a two-step reaction pathway ($\text{Mn}^{2+} \leftrightarrow \text{MnOOH} \leftrightarrow \text{MnO}_2$) [59–61]. The typical processes are further corroborated by additional experimental results (detailed discussions are provided in Electronic Supplementary Material, **Fig. S19–S21**) [62].

To uncover the underlying mechanism by F doping in governing dissolution/deposition reversibility, we performed in situ differential electrochemical mass spectrometry (DEMS) measurements (**Fig. 3a**) [63, 64]. In a MnSO_4 -free 2 M Na_2SO_4 electrolyte, a prominent $^*\text{OH}$ signal ($m/z = 17$) is captured during the charging process for both F-MDC and MDC electrodes, whereas the $^*\text{O}$ signal ($m/z = 16$) is weak and the $^*\text{OOH}$ signal ($m/z = 33$) is nearly undetectable (**Fig. S22**). This indicates that $^*\text{OH}$ is the predominant intermediate involved in Mn^{2+} coordination for deposition. Specifically, the F-MDC electrode exhibits a significantly stronger $^*\text{OH}$ signal compared to the MDC electrode (**Fig. 3b**), suggesting that F doping effectively facilitates water dissociation to generate $^*\text{OH}$. Upon the introduction of MnSO_4 , a marked attenuation in the signal was observed (**Fig. 3c**), implying that $^*\text{OH}$ participates in Mn^{2+} electrodeposition via the following pathway: $^*\text{OH} \rightarrow ^*\text{MnOH} \rightarrow ^*\text{Mn}(\text{OH})_2 \rightarrow ^*\text{MnOOH} \rightarrow ^*\text{MnO}_2$. Notably, the more pronounced signal decay for F-MDC than for MDC suggests that F doping significantly enhances the binding affinity between Mn^{2+} and $^*\text{OH}$. This pathway effectively suppresses the one-electron oxidation of Mn^{2+} to soluble Mn^{3+} ($\text{Mn}^{2+} - e^- \rightarrow \text{Mn}^{3+}$), thereby inhibiting the formation of “dead MnO_2 ” and ultimately enhancing the dissolution/deposition reversibility. As reflected in the weaker O_2 signal ($m/z = 32$) on F-MDC, the O–O coupling is inhibited towards oxygen evolution, which further affirms the promoted binding between Mn^{2+} and $^*\text{OH}$ (**Fig. 3d**).

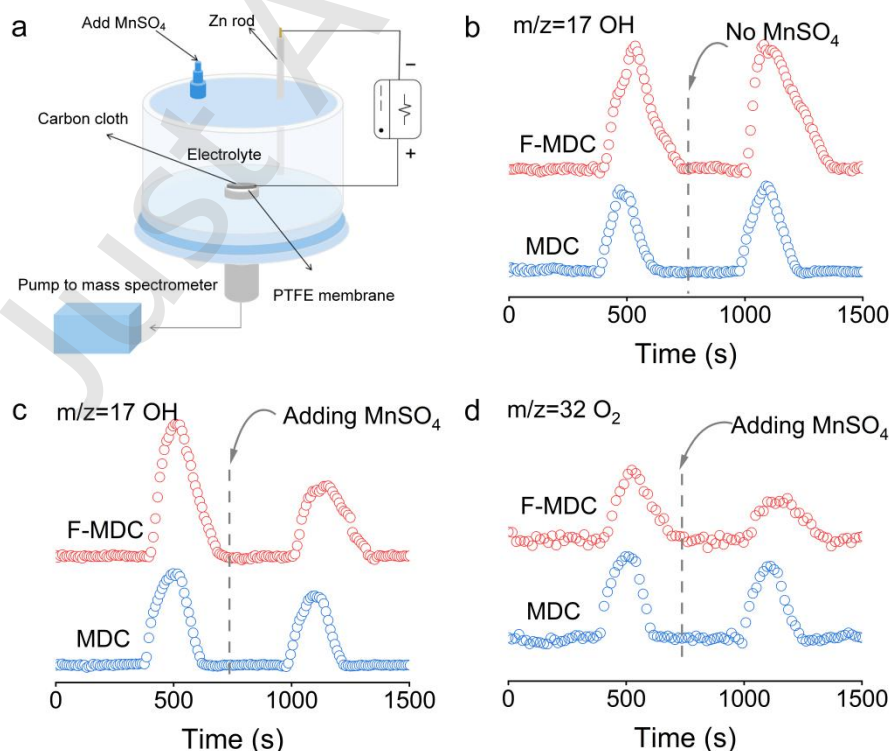


Figure 3 (a) Schematic diagram of in situ DEMS technique. $m/z = 17$ signals for F-MDC and MDC during charging without (b) and with (c) adding MnSO_4 , respectively. (d) $m/z = 32$ signals for F-MDC and MDC during charging with adding MnSO_4 .

Density functional theory (DFT) calculations were performed to determine the critical role of F in regulating

the free energy of the reaction pathway and corresponding intermediate configurations are displayed in **Fig. S23 and S24** [65]. Compared with MDC, the binding energy between Mn^{2+} and *OH intermediate is significantly enhanced on F-MDC, as evidenced by the lower ΔG (**Fig. 4a**), which promotes the formation of *MnOH . Furthermore, F-incorporation markedly reduces the ΔG for the dehydrogenation of *MnOOH , facilitating the oxidative conversion of MnOOH to MnO_2 . This process effectively suppresses the disproportionation of MnOOH in acidic media, thereby preventing the formation of “dead MnO_2 ”. Concurrently, the ΔG for the dehydrogenation of *OH to *O intermediate on F-MDC is considerably higher than that on MDC (**Fig. 4b**), which effectively suppresses the *OH decomposition. This theoretical finding is consistent with the intensified *OH signals detected on the F-MDC electrode during the charging process. To elucidate the origin of this phenomenon, the projected density of states (PDOS) calculations were further performed. As shown in **Fig. 4c**, only limited peak overlap is observed among the C 2p

orbitals, the Mn 3d orbitals of Mn^{2+} , and the O 2p orbitals of *OH in MDC. In contrast, F-MDC exhibits pronounced peak overlap among these three orbitals (**Fig. 4d**), indicating the strong electronic coupling between them. Manifested by this result, the presence of fluorine can modify the electronic configuration of carbon, thereby enhancing charge transfer between carbon atoms and $\text{Mn}^{2+}/\text{*OH}$ and promoting the formation of *MnOH intermediates. To gain further insight into the dehydrogenation of *MnOOH , which was the rate-determining step (RDS) for the overall deposition process, the density of states of the H 1s orbital and its adjacent O 2p orbital in *MnOOH was calculated. In MDC, a pronounced overlap is observed between the O 2p and H 1s orbitals (**Fig. 4e**), indicating strong O–H bond in *MnOOH [3]. In contrast, F-MDC exhibits a weak O–H bond as reflected in the remarkably low degree of hybridization between these two orbitals (**Fig. 4f**). Consequently, the ΔG for *MnOOH dehydrogenation is significantly reduced to facilitate the formation of MnO_2 .

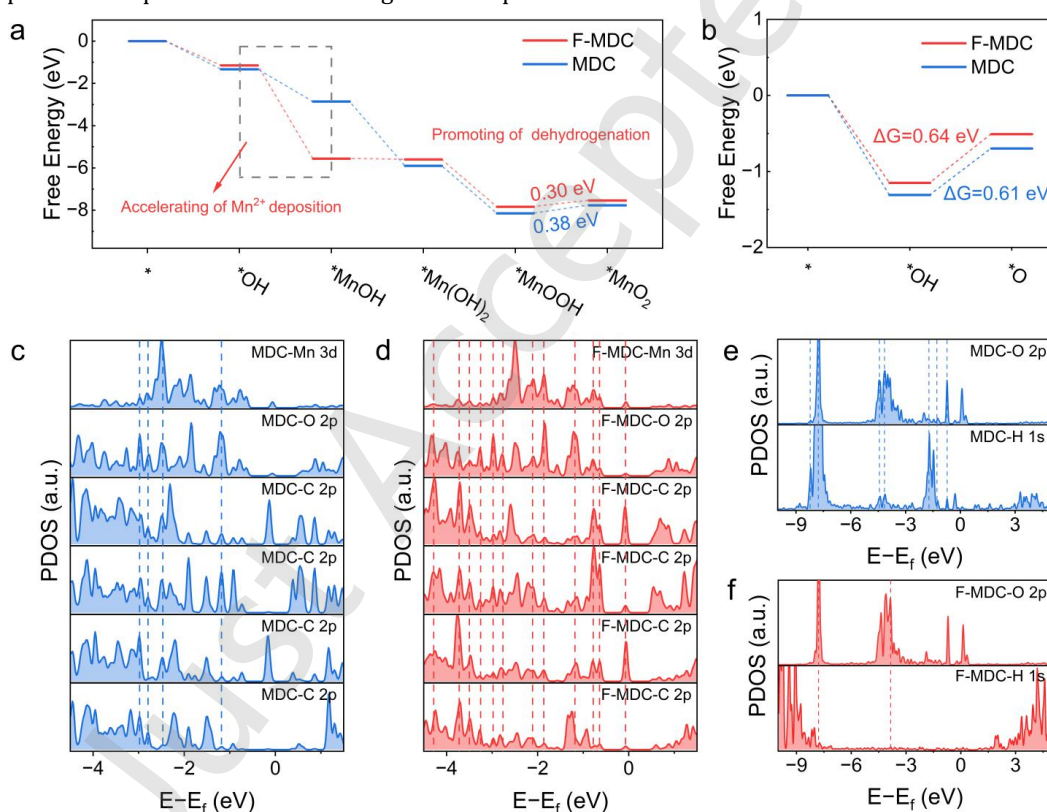


Figure 4 (a) Free energy diagram of the MnO_2 deposition process on F-MDC and MDC substrates. (b) Free energy diagram for further dehydrogenation of the *OH intermediate on F-MDC and MDC substrates. PDOS of C 2p, O 2p, and Mn 3d for *MnOH on MDC (c) and F-MDC (d). PDOS of O 2p and H 1s for *MnOOH on MDC (e) and F-MDC (f).

Intrigued by the above merits, the Zn- MnO_2 battery utilizing F-MDC substrate is expected to facilitate reversible dissolution/deposition chemistry. Its electrochemical behavior was systematically investigated via galvanostatic charge-discharge (GCD), cyclic voltammetry (CV), galvanostatic intermittent titration technique (GITT), and electrochemical impedance spectroscopy (EIS) measurements. The optimal NH_4F dosage was identified as 0.4 g according to the capacity and stability performance (**Fig. S25**). Unless otherwise specified, the F-MDC substrate prepared with 0.4 g was employed in all full-cell tests. **Figure. 5a** presents the GCD curves of F-MDC and MDC at a

current density of 0.05 A g^{-1} . During the charging process, two distinct voltage plateaus at 1.53 V and 1.60 V are observed, corresponding to the stepwise oxidation of Mn. In the subsequent discharging process, the battery exhibits two plateaus at 1.26 V and 1.36 V, attributed to the reversible reduction of Mn species [66]. Notably, the F-MDC cathode demonstrates a narrower voltage hysteresis and a significantly enhanced specific capacity compared to MDC, which can be attributed to its high specific surface area and abundant defect sites that provide more active nucleation sites for MnO_2 . This is further supported by the CV analysis at 1 mV s^{-1} (**Fig. S26**), where the F-MDC battery shows a

larger integrated area, consistent with the GCD results. Furthermore, the nearly overlapping CV curves during the initial three cycles (Fig. S27) signify the excellent electrochemical reversibility of the F-MDC electrode [67]. Rate performance tests were conducted to further evaluate the dissolution/deposition reversibility (Fig. 5b and S28). A gradual capacity-activation phenomenon can be observed in the coin-cell rate test (Fig. 5b), originating from progressive electrolyte infiltration into the electrode and step-by-step exposure of active sites on F-MDC, which requires several cycles to reach electrochemical equilibrium. Similarly, such capacity activation behavior is also detected in the long-term cycling of coin cells (Fig. 5d). The Zn-

MnO₂ battery featuring the F-MDC substrate exhibits a high specific capacity of 340.3 mAh g⁻¹ at 0.1 A g⁻¹ and retains 87.5 mAh g⁻¹ even at a stringent current density of 10 A g⁻¹, underscoring its rapid deposition kinetics. Conversely, the MDC substrate shows significant capacity decay from 293.3 to 23.3 mAh g⁻¹ under the same conditions. Upon returning the current density to 0.1 A g⁻¹, the F-MDC electrode recovers a capacity of 300.8 mAh g⁻¹, whereas the MDC electrode only manages 172.9 mAh g⁻¹, confirming the enhanced electrochemical activity and reversibility afforded by fluorine doping. Furthermore, the Coulombic efficiencies (CEs) of F-MDC

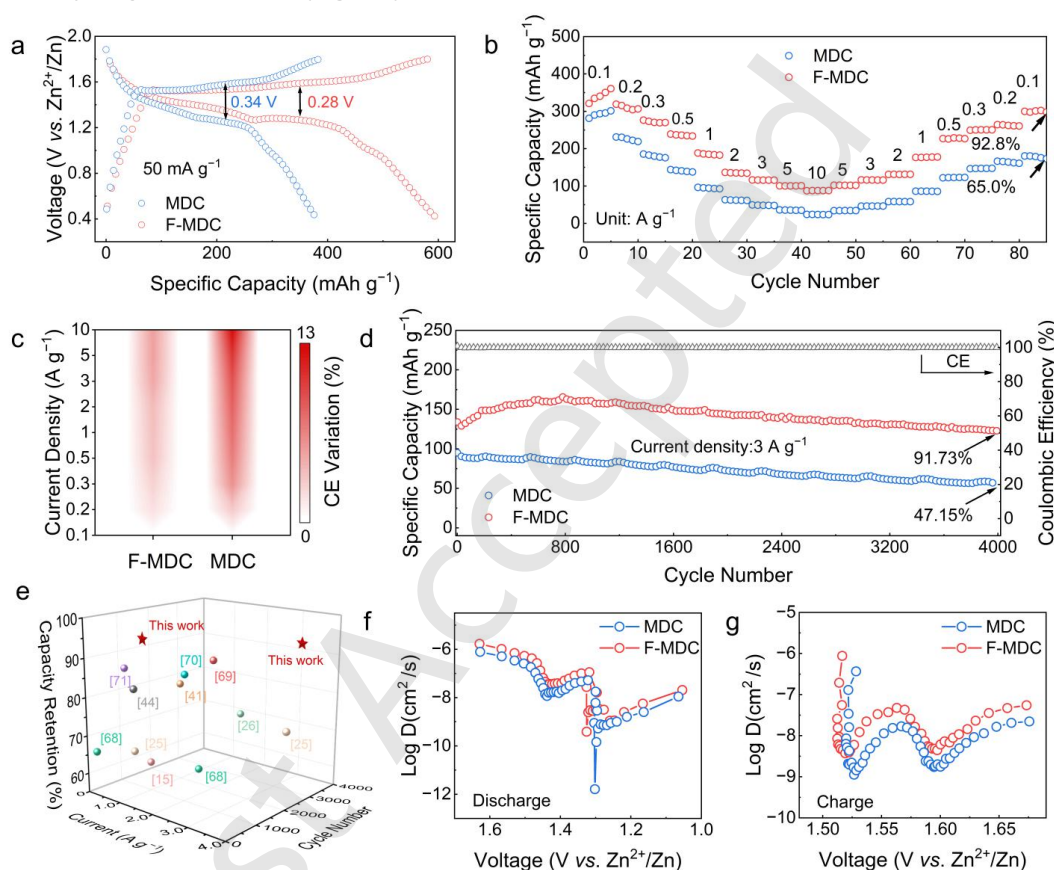


Figure 5 The electrochemical performance: (a) GCD curves of F-MDC and MDC at 50 mA g⁻¹. (b) Rate performance of F-MDC and MDC. (c) Coulombic efficiencies variation contour map of F-MDC and MDC at varied current densities. (d) Long-cycle stability of Zn-MnO₂ batteries with F-MDC and MDC substrates at 3 A g⁻¹. (e) Comparison of cycling stability for this work versus previously reported Zn-MnO₂ batteries based on the dissolution-deposition mechanism. Diffusion coefficients of F-MDC and MDC during discharge (f) and charge processes (g).

remain stable across varying current densities, while those of MDC fluctuate significantly (Fig. 5c). The result validates that the F-MDC substrate facilitates fast conversion kinetics for the reversible Mn²⁺-MnOOH-MnO₂ redox process. Long-term cycling stability was further assessed at 3.0 A g⁻¹ (Fig. 5d). The F-MDC-based battery maintains a reversible capacity of 123.2 mAh g⁻¹ after 4000 cycles, corresponding to an impressive retention of 91.7%. Under identical conditions, the MDC-based battery only retains 58.4 mAh g⁻¹ (47.1% retention, Fig. S29). Such outstanding cycling performance outperforms most reported Zn-MnO₂ batteries based on the dissolution/deposition mechanism (Fig. 5e) [15, 25, 26, 41, 44, 68–71]. The superior durability of F-MDC is further corroborated by cycling tests at 1.0 A g⁻¹ (Fig. S30 and S31) and disassembly-reassembly experiments (see

Electronic Supplementary Material and Table S1 for details). The GITT curves of F-MDC and MDC display two distinct charge-discharge plateaus (Fig. S32), which resemble their corresponding GCD profiles. F-MDC exhibits a higher diffusion coefficient (D_{GITT}) than MDC during the discharging process (Fig. 5f). Similarly, during the charging process (Fig. 5g), F-MDC maintains a superior D_{GITT} compared to MDC. This enhanced diffusion coefficient suggests that fluorine doping not only facilitates the reversible deposition/dissolution of MnO₂ but also improves charge transfer within the active material. Furthermore, as the potential corresponding to the minimum identifies the dominant reaction potential, the lower charging potential of F-MDC confirms the accelerated deposition kinetics induced by fluorine doping [72].

CV tests at various scan rates ($0.1\text{--}0.5\text{ mV s}^{-1}$) were performed to evaluate the impact of fluorine on reaction kinetics. Both F-MDC and MDC exhibit one oxidation peak and two reduction peaks (**Fig. S33a and S33c**). Although the redox peaks shift slightly toward higher potentials as the scan rate increases, the overall CV profiles remain well-preserved, suggesting good reversibility. This peak shift is primarily ascribed to inherent kinetic barriers associated with the MnO_2 deposition/dissolution process. To quantify the reaction mechanism, the relationship between peak current (i) and scan rate (v) was analyzed using the power-law equation: $i = a v^b$. The b -value was obtained by linear regression of $\log(i)$ vs. $\log(v)$. A b -value of 0.5 indicates a diffusion-controlled Faradaic process, while a b -value of 1.0 represents a surface-controlled capacitive process [73]. As shown in **Fig. S33b**, the b -values for the oxidation peak (b_{O1}) and reduction peaks (b_{R1} , b_{R2}) of F-MDC are 0.68, 0.75, and 0.86, respectively. These values indicate a hybrid mechanism involving both diffusion and capacitive processes. Notably, the higher values of F-MDC compared to MDC (**Fig. S33d**) demonstrate that fluorine doping effectively accelerates the electrode reaction kinetics. The capacitive and diffusion-controlled contributions to total capacity were quantitatively analyzed. **Fig. S34** shows the capacitive contribution analysis for Zn-MnO₂ battery at various scan rates. As the scan rate increases from 0.1 to 0.5 mV s^{-1} , the capacitive contribution of F-MDC rises from 54% to 72%, which is significantly higher than that of MDC. This result confirms that fluorine doping effectively enhances

electrochemical reactivity and reaction kinetics. Furthermore, EIS analysis reveals that the charge-transfer resistance (R_{ct}) of F-MDC in the high-frequency region is markedly lower than that of MDC (**Fig. S35**), indicating the improved interfacial charge transport. In the low-frequency region, F-MDC exhibits a steeper slope than MDC, implying a reduced Warburg diffusion resistance. These results collectively demonstrate that fluorine doping reduces interfacial resistance and promotes ion diffusion kinetics, thereby boosting overall electrochemical performance.

To further assess the practical viability of F-MDC, a Zn-MnO₂ pouch cell ($3 \times 3\text{ cm}^2$) was assembled with an areal loading of $\sim 1.2\text{ mg cm}^{-2}$ (**Fig. 6a**). The CV curve at 0.1 mV s^{-1} (**Fig. 6b**) displays well-defined redox peaks, aligning well with the electrochemical behavior observed in coin cells. As depicted in **Fig. 6c and 6d**, the pouch cell yields a high specific capacity of 313 mAh g^{-1} at 0.3 A g^{-1} and retains 149 mAh g^{-1} at a high current density of 1.2 A g^{-1} . Furthermore, the device demonstrates robust cycling stability, retaining 77% of its initial capacity after 3000 cycles at 1.2 A g^{-1} (**Fig. 6e**). Different from coin cells, no obvious capacity activation phenomenon is observed for the pouch cell. The larger electrode area and sufficient electrolyte dosage guarantee sufficient ion transport, thus enabling effective MnO_2 deposition/dissolution even in initial cycles. To showcase its real-world utility, three parallel-connected pouch cells successfully energized a 4 V LED indicator, confirming its promising potential for practical applications.

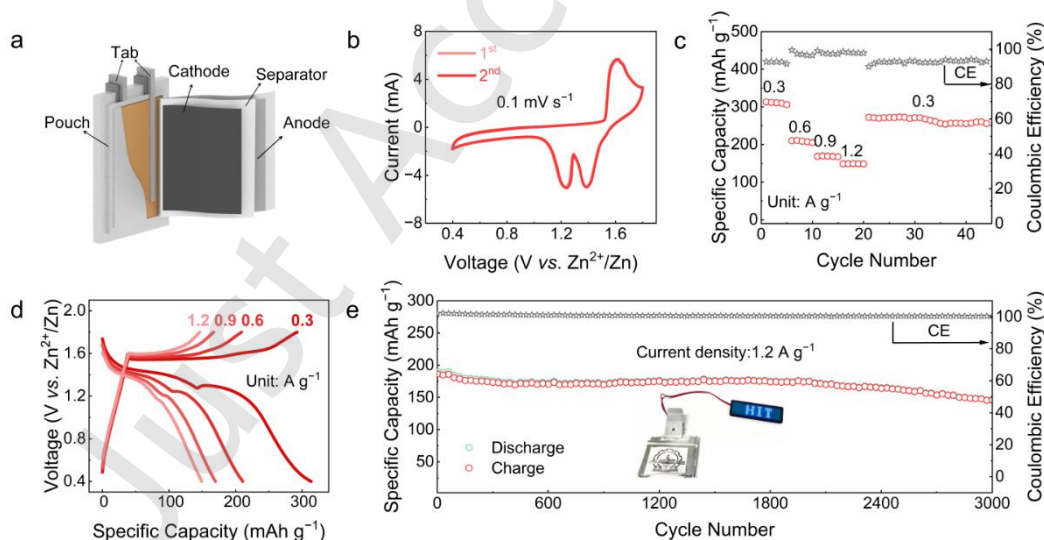


Figure 6 Electrochemical performance of the soft-packaged Zn-Mn battery with F-MDC, using $2.0\text{ mol/L ZnSO}_4 + 0.1\text{ mol/L MnSO}_4$ aqueous solution as the electrolyte and zinc foil as the anode: (a) Schematic configuration of the soft-packaged battery. (b) CV curves. (c) Rate performance. (d) GCD curves at various current densities. (e) Cyclic stability and (inset) photograph of a 4 V LED indicator powered by the soft-packaged battery.

3 Conclusions

To summarize, fluorine-doped manganese acetylacetonate-derived carbon (F-MDC) was developed as the cathode substrate, which enabled reversible MnO_2 dissolution/deposition in aqueous zinc-manganese batteries. Based on the in situ DEMS analysis and DFT calculations, the $^*\text{OH}$ -mediated MnO_2 deposition mechanism was elucidated as $^*\text{OH} \rightarrow ^*\text{MnOH} \rightarrow ^*\text{Mn}(\text{OH})_2 \rightarrow ^*\text{MnOOH} \rightarrow ^*\text{MnO}_2$. The high electronegativity of F in the as-designed cathode could strengthen the binding between Mn^{2+} and $^*\text{OH}$ as well as

decrease the ΔG of the MnOOH dehydrogenation step. Thanks to the above merits, the generation and disproportionation of Mn^{3+} could be inhibited to fundamentally prevent the formation of “dead MnO_2 ”. The zinc-manganese battery with F-MDC substrate exhibited excellent electrochemical performance, in terms of the high specific capacities of 340.3 mAh g^{-1} at 0.1 A g^{-1} and 87.5 mAh g^{-1} even at a high current density of 10 A g^{-1} . A capacity retention rate of 91.7% after 4000 cycles at 3 A g^{-1} was also realized to highlight the superior reversibility, outperforming most reported Zn-MnO₂ batteries. The

assembled pouch cell also showed superior rate and cycling performance. This study not only provides a feasible strategy for regulating the reversible MnO_2 deposition behavior in aqueous zinc-manganese batteries, but also offers new insights into the manganese deposition chemistry.

4 Experimental

4.1 Materials

All chemical reagents were used without additional purification. Sodium chloride (NaCl , 99%), potassium chloride (KCl , 99%), ammonium fluoride (NH_4F , 99%), and N-methylpyrrolidone (NMP, 99%) were purchased from Aladdin Reagents (Shanghai) Co., Ltd.; manganese(III) acetylacetonate ($\text{C}_{15}\text{H}_{21}\text{MnO}_6$, 98%) was purchased from Shanghai Titan Technology Co., Ltd.; zinc sulfate heptahydrate ($\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$, 98%) was purchased from Sinopharm Chemical Reagent Co., Ltd.; polyvinylidene fluoride (PVDF) was purchased from Tianjin Kemiou Chemical Reagent Co., Ltd.; and acetylene black was purchased from Shanghai Haotian Chemical Co., Ltd.

4.2 Preparation of F-MDC@F-MnO

Fluorine-doped MnO-loaded carbon substrate derived from manganese acetylacetonate (F-MDC@F-MnO) was synthesized in one step by the molten salt method. 0.5 g of $\text{C}_{15}\text{H}_{21}\text{MnO}_6$, a certain amount of NH_4F (0.2 g, 0.4 g, 0.6 g), and 2.5 g of mixed salts ($n\text{NaCl}$: $n\text{KCl}$ = 1:1) were weighed and fully ground in an agate mortar for 60 min until the powder was uniform. The ground mixture was transferred to an alumina crucible and heated to 700 °C at a heating rate of 2 °C min^{-1} in a tube furnace, with a holding time of 5 h, and the whole process was protected under an inert atmosphere (N_2). After the reaction, the furnace body was naturally cooled to room temperature, and the product was washed 3 times with distilled water and absolute ethanol respectively to remove residual molten salts and unreacted impurities. Finally, it was dried overnight at 60 °C to obtain F-MDC@F-MnO samples with different fluorine doping amounts, which were denoted as F-MDC@F-MnO-0.2, F-MDC@F-MnO-0.4, and F-MDC@F-MnO-0.6 respectively. As a control sample, pure manganese acetylacetonate-derived carbon (MDC@MnO) without adding NH_4F was prepared by the same process.

4.3 Fabrication of Electrodes and Assembly of Cells.

70% (mass fraction) of F-MDC@F-MnO, 20% of conductive carbon black, and 10% of PVDF were fully mixed in NMP to form a uniform slurry. Subsequently, the slurry was uniformly coated on a carbon cloth/titanium foil current collector and dried in a vacuum oven at 60 °C for 12 h. After drying, a puncher was used to punch the electrode sheet into a circular sheet with a diameter of 12 mm, and the loading amount of the active material was controlled in the range of 1~2 mg cm^{-2} . Electrochemical tests were conducted using CR2025 coin cells. The electrode loaded with active material served as the positive electrode, zinc foil (≈ 0.1 mm thick) as the negative electrode, Whatman glass fiber as the separator, and a mixed aqueous solution of 2.0 mol/L ZnSO_4 and 0.1 mol/L MnSO_4 as the electrolyte. Approximately 100 μL of electrolyte was injected into each cell. The cells were assembled in air and tested at room temperature. Before

charging, all cells were rested for 8 h to ensure sufficient electrolyte wetting.

4.4 Preparation of F-MDC

F-MDC@F-MnO was fabricated into a working electrode and then assembled into a coin cell, galvanostatically charged to 1.9 V (referred to as F-MDC@F-MnO-1.9) and then discharged to 0.4 V to yield the fluorine-doped manganese acetylacetonate-derived carbon substrate (F-MDC).

For clarity, F-MDC@F-MnO and F-MDC are defined throughout this work. F-MDC@F-MnO denotes the as-synthesized product containing MnO nanoparticles loaded on the fluorine-doped carbon framework. F-MDC refers to the bare carbon substrate obtained by electrochemically activating F-MDC@F-MnO (charging to 1.9 V followed by discharging to 0.4 V) to completely remove manganese species. F-MDC serves as the working electrode substrate for all subsequent MnO_2 deposition/dissolution studies.

Electronic Supplementary Material: Supplementary material (including detailed material characterizations, electrochemical measurements, in situ/ex situ characterizations, DFT calculation details, supplementary figures and table) is available in the online version of this article at <https://doi.org/10.26599/NR.2026.94909104>.

Data availability

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

Acknowledgements

C.L. acknowledges the National Natural Science Foundation of China (22479034 and 52302231), and Key Research & Development Plan of Heilongjiang Province (2024ZXJ03C06). C.Y. acknowledges the Natural Science Foundation of Heilongjiang Province, China (YQ2022B006). All the authors thank sci-go (www.sci-go.com) for the TEM, BET and TG analysis.

Declaration of competing interest

All the contributing authors report no conflict of interests in this work.

Author contribution statement

Haiyan Sun: Data Curation, Formal Analysis, Methodology, Visualization, Writing-Original Draft, Investigation. Shijie Chen: Software, Methodology, Visualization, Validation, Formal Analysis, Investigation. Chunshuang Yan: Funding Acquisition, Methodology, Supervision, Writing-Review & Editing. Chade Lv: Funding Acquisition, Methodology, Supervision, Writing-Review & Editing. Hao Wang: Software, Methodology, Visualization. Chu Zhang: Software, Methodology, Visualization. Jv Zhao : Software, Methodology, Visualization. Weihao Xu : Methodology, Visualization. All the authors have approved the final manuscript.

Informed consent

Not applicable

Ethics statement

Not applicable

Use of AI statement

None.

References

- [1] Lv, W.; Liu, J.; Shen, Z.; Li, X.; Xu, C. Novel approaches to aqueous zinc-ion batteries: Challenges, strategies, and prospects. *eScience* **2025**, *5*, 100410.
- [2] Zhao, Y.; Zhou, R.; Song, Z.; Zhang, X.; Zhang, T.; Zhou, A.; Wu, F.; Chen, R.; Li, L. Interfacial designing of MnO₂ half-wrapped by aromatic polymers for high-performance aqueous zinc-ion batteries. *Angew. Chem. Int. Ed.* **2022**, *61*, e202212231.
- [3] Wang, Y.; Zhou, H.; Wei, S.; Chen, S.; Cao, D.; Zhou, Q.; Wu, X.; Song, L. Boosting ion transport in manganese dioxide cathodes through electronically tuned molecular intercalants. *J. Am. Chem. Soc.* **2025**, *147*, 41297–41307.
- [4] Du, K.; Qi, H.; Zhang, C.; Xu, W.; Chen, D.; Zhou, X.; Lv, C.; Yan, C. Halogenated organic acid additive rendered highly reversible four-electron transfer zinc-iodine batteries by strengthened interhalogen interaction and protons supply. *Adv. Funct. Mater.* **2026**, *36*, e27634.
- [5] Kim, Y.; Park, Y.; Kim, M.; Lee, J.; Kim, K. J.; Choi, J. W. Corrosion as the origin of limited lifetime of vanadium oxide-based aqueous zinc ion batteries. *Nat. Commun.* **2022**, *13*, 2371.
- [6] Meng, S.; Liu, D.; Feng, J.; Zeng, Z.; Wu, F.; Liu, W.; Shi, W.; Cao, X. Prussian blue analogs for zinc hybrid ion batteries: A promising and competitive alternative to aqueous zinc-ion batteries. *Exploration* **2025**, *5*, 20240180.
- [7] Jing, F.; Xu, L.; Shang, Y.; Chen, G.; Lv, C.; Yan, C. Interface engineering enabled by sodium dodecyl sulfonate surfactant for stable Zn metal batteries. *J. Colloid Interface Sci.* **2024**, *669*, 984–991.
- [8] Chen, D.; Xu, W.; Yan, C.; Lyu, P.; Zhu, Q.; Yu, H.; Gao, Z.; Lv, C. Disrupting hydrogen bond network connectivity with a double-site additive for long-life aqueous zinc metal batteries. *Exploration* **2025**, *5*, e20240007.
- [9] Yao, H.; Yu, H.; Zheng, Y.; Li, N. W.; Li, S.; Luan, D.; Lou, X. W.; Yu, L. Pre-intercalation of ammonium ions in layered δ -MnO₂ nanosheets for high-performance aqueous zinc-ion batteries. *Angew. Chem. Int. Ed.* **2023**, *62*, e202315257.
- [10] Becknell, N.; Lopes, P. P.; Hatsukade, T.; Zhou, X.; Liu, Y.; Fisher, B.; Chung, D. Y.; Kanatzidis, M. G.; Markovic, N. M.; Tepavcevic, S.; Stamenkovic, V. R. Employing the dynamics of the electrochemical interface in aqueous zinc-ion battery cathodes. *Adv. Funct. Mater.* **2021**, *31*, 2102135.
- [11] Soundharajan, V.; Sambandam, B.; Kim, S.; Islam, S.; Jo, J.; Kim, S.; Mathew, V.; Sun, Y. K.; Kim, J. The dominant role of Mn²⁺ additive on the electrochemical reaction in ZnMn₂O₄ cathode for aqueous zinc-ion batteries. *Energy Storage Mater.* **2020**, *28*, 407–417.
- [12] Ye, J. J.; Li, P. H.; Hou, Z.; Zhang, W.; Zhu, W.; Jin, S.; Ji, H. Se-dopant modulated selective co-insertion of H⁺ and Zn²⁺ in MnO₂ for high-capacity and durable aqueous Zn-ion batteries. *Angew. Chem. Int. Ed.* **2024**, *63*, e202410900.
- [13] Chacón-Borrero, J.; Chang, X.; Min, Z.; Yu, J.; Montaña-Mora, G.; Mejía-Centeno, K. V.; Sun, Y.; Zhou, X.; Tunmee, S.; Kidkhunthod, P.; Li, J.; Llorca, J.; Arbiol, J.; Cabot, A. Boosting high-loading zinc-ion battery performance: Zn-Doped δ -MnO₂ cathodes to promote Zn²⁺ storage. *Energy Storage Mater.* **2025**, *81*, 104486.
- [14] Kankanallu, V. R.; Zheng, X.; Leschev, D.; Zmich, N.; Clark, C.; Lin, C. H.; Zhong, H.; Ghose, S.; Kiss, A. M.; Nykypanchuk, D.; Stavitski, E.; Takeuchi, E. S.; Marschilok, A. C.; Takeuchi, K. J.; Bai, J.; Ge, M.; Chen-Wiegar, Y. C. K. Elucidating a dissolution–deposition reaction mechanism by multimodal synchrotron X-ray characterization in aqueous Zn/MnO₂ batteries. *Energy Environ. Sci.* **2023**, *16*, 2464–2482.
- [15] Li, Y.; Zhang, N.; Wang, J. Y.; Wang, P.; Liu, Z.; Zhu, Y. R.; Shu, J.; Yi, T. F. Construction of high-voltage aqueous Zn-MnO₂ batteries based on polar small-molecule organic acid-induced MnO₂/Mn²⁺ reactions. *Chem. Eng. J.* **2025**, *507*, 160415.
- [16] Jing, F.; Liu, Y.; Shang, Y.; Lv, C.; Xu, L.; Pei, J.; Liu, J.; Chen, G.; Yan, C. Dual ions intercalation drives high-performance aqueous Zn-ion storage on birnessite-type manganese oxides cathode. *Energy Storage Mater.* **2022**, *49*, 164–171.
- [17] Wang, S.; Guo, X.; Huang, K.; Achari, A.; Safaei, J.; Lei, Y.; Li, D.; Gu, Q.; Sun, C.; Gloag, L.; Langford, S.; Geim, A.; Nair, R. R.; Wang, G. Cooperative Jahn-Teller effect and engineered long-range strain in manganese oxide/graphene superlattice for aqueous zinc-ion batteries. *Nat. Commun.* **2025**, *16*, 5191.
- [18] Zhang, A.; Chen, T.; Zhao, R.; Wang, Y.; Yang, J.; Han, X.; Wang, X.; Wu, C.; Bai, Y. Tunable organic-inorganic p- π -d electron conjugation triggers d- π hybridization in quinonized MnO₂ superlattice toward ultrastable and high-rate Zn-MnO₂ batteries. *Angew. Chem. Int. Ed.* **2025**, *64*, e202423824.
- [19] Selvakumaran, D.; Pan, A.; Liang, S.; Cao, G. A review on recent developments and challenges of cathode materials for rechargeable aqueous Zn-ion batteries. *J. Mater. Chem. A* **2019**, *7*, 18209–18236.
- [20] Zheng, X.; Han, B.; Cheng, S.; Liu, S.; Wang, F.; Wu, Y. Molecular armor encapsulation of practical layered cathode empowers energetic Ah-level Zn-MnO₂ pouch and prismatic cells. *JACS Au* **2025**, *5*, 4904–4915.
- [21] Son, J.; Zhanadilov, O.; Aniskevich, Y.; Shin, H. J.; Jung, H. G.; Park, J.; Heo, K.; Ihm, K.; Lee, K. S.; Lim, J. H.; Myung, S. T. Manganophilic surface formation aided by alkaline-earth metal element for long lasting manganese based zinc aqueous batteries. *Chem. Eng. J.* **2025**, *519*, 164966.
- [22] Xue, X.; Liu, Z.; Chandrasekaran, S.; Eisenberg, S.; Althaus, C.; Freyman, M. C.; Pinongcos, A.; Ren, Q.; Valdovinos, L.; Hsieh, C.; Hu, B.; Dunn, B.; Orme, C. A.; Wang, X.; Worsley, M. A.; Li, Y. Interface-controlled redox chemistry in aqueous Mn²⁺/MnO₂ batteries. *Adv. Mater.* **2025**, *37*, 2419505.
- [23] Sambandam, B.; Mathew, V.; Kim, S.; Lee, S.; Kim, S.; Hwang, J. Y.; Fan, H. J.; Kim, J. An analysis of the electrochemical mechanism of manganese oxides in aqueous zinc batteries. *Chem* **2022**, *8*, 924–946.
- [24] Liu, Y.; Wang, K.; Yang, X.; Liu, J.; Liu, X. X.; Sun, X. Enhancing two-electron reaction contribution in MnO₂ cathode material by structural engineering for stable cycling in aqueous Zn batteries. *ACS Nano* **2023**, *17*, 14792–14799.
- [25] Wu, T. H.; Huang, J. X.; Liao, S. J. Ammonium-preintercalated layered manganese oxide with single-phase intercalation chemistry and enhanced two-electron reaction in aqueous zinc-ion batteries. *J. Mater. Chem. A* **2025**, *13*, 9737–9746.
- [26] Liu, Y.; Zhi, J.; Sedighi, M.; Han, M.; Shi, Q.; Wu, Y.; Chen, P. Mn²⁺ ions confined by electrode microskin for aqueous battery beyond intercalation capacity. *Adv. Energy Mater.* **2020**, *10*, 2002578.
- [27] Yang, Z.; Zhang, Q.; Hu, C.; Tang, Y.; Li, J.; Wang, Q.; Zhou, W.; Chao, D.; Wang, H. Unlocking reversible Mn²⁺/MnO₂ chemistry in semisolid slurry electrodes for high-performance aqueous Zn-Mn batteries. *Nano-Micro Lett.* **2026**, *18*, 148.
- [28] Chuai, M.; Tong, H.; Yang, Z.; Deng, S.; Wu, M.; Xing, J.; Chai, G. Design of a P-O-M (M = Mn, Zn) d- π backbonding electrolyte additive for 40 Ah electrolytic Zn-MnO₂ batteries. *J. Am. Chem. Soc.* **2025**, *147*, 31591–31602.
- [29] Xie, K.; Zhu, P.; Han, D.; Zhang, B.; Wang, X.; Wu, Z. S.; Weng, Z.; Yang, Q. H. Decoding ‘Dead Mn’ in MnO₂ deposition/dissolution

- chemistry for energetic aqueous batteries: A perspective. *Energy Mater. Devices* **2025**, *3*, 9370071.
- [30] Wang, X.; Liu, R.; Li, Z.; Gao, H.; Zhao, T.; Jiang, H. Unlocking MnO₂ electrolysis kinetics via dynamic chromium doping for efficient and stable zinc-manganese flow batteries. *J. Colloid Interface Sci.* **2026**, *702*, 138983.
- [31] Ren, Y.; Li, H.; Rao, H.; Zhou, H.; Guo, S. Aqueous MnO₂/Mn²⁺ electrochemistry in batteries: progress, challenges, and perspectives. *Energy Environ. Sci.* **2024**, *17*, 425–441.
- [32] Ye, X.; Han, D.; Jiang, G.; Cui, C.; Guo, Y.; Wang, Y.; Zhang, Z.; Weng, Z.; Yang, Q. H. Unraveling the deposition/dissolution chemistry of MnO₂ for high-energy aqueous batteries. *Energy Environ. Sci.* **2023**, *16*, 1016–1023.
- [33] Wang, Y.; Hong, Z.; Wei, Z.; Li, D.; Yang, X.; Zhu, J.; Li, P.; Wang, S.; Zhi, C. Cation-regulated MnO₂ reduction reaction enabling long-term stable zinc-manganese flow batteries with high energy density. *Energy Environ. Sci.* **2025**, *18*, 1524–1532.
- [34] Wang, H.; Wang, T.; Stevenson, G.; Chamoun, M.; Lindström, R. W. MnO₂ /Mn²⁺ chemistry: Charging protocol and electrolyte regulation. *Energy Storage Mater.* **2023**, *63*, 103008.
- [35] Siamionau, U.; Siamkevich, Y.; Mazanik, A.; Kokits, O.; Ragoisha, G.; Jo, J. H.; Myung, S. T.; Streltsov, E. Rechargeable zinc-ion batteries with manganese dioxide cathode: How critical is choice of manganese dioxide polymorphs in aqueous solutions? *J. Power Sources* **2022**, *523*, 231023.
- [36] Li, X.; Qi, K.; Qin, Z.; Ding, X.; Zhu, Y.; Hou, Z.; Qian, Y. Ion-anchored strategy for MnO₂/Mn²⁺ chemistry without ‘Dead Mn’ and corrosion. *ACS Nano* **2024**, *18*, 27016–27025.
- [37] Fan, W.; Tian, S.; Qin, L.; Alomar, T. S.; Ruan, P.; El-Bahy, Z. M.; AlMasoud, N.; Lu, B.; Zhou, J. Inner-sphere electron transfer enabling highly reversible Mn²⁺/MnO₂ conversion toward energy-dense electrolytic zinc-manganese batteries. *J. Am. Chem. Soc.* **2025**, *147*, 18694–18703.
- [38] Wu, S.; Guo, H.; Su, Z.; Jia, C.; Zhang, X.; Wang, S.; Zhao, T.; Meyer, Q.; Zhao, C. Suppressed manganese oxides shuttling in acidic electrolytes extends shelf-life of electrolytic proton batteries. *Adv. Funct. Mater.* **2024**, *34*, 2315706.
- [39] Qin, Z.; Song, Y.; Yang, D.; Zhang, M. Y.; Shi, H. Y.; Li, C.; Sun, X.; Liu, X. X. Enabling reversible MnO₂/Mn²⁺ transformation by Al³⁺ addition for aqueous Zn-MnO₂ hybrid batteries. *ACS Appl. Mater. Interfaces* **2022**, *14*, 10526–10534.
- [40] Liu, Z.; Qin, L.; Lu, B.; Wu, X.; Liang, S.; Zhou, J. Issues and opportunities facing aqueous Mn²⁺/MnO₂-based batteries. *ChemSusChem* **2022**, *15*, e202200348.
- [41] Zhang, G.; Zhu, J.; Lin, L.; Liu, Y.; Li, S.; Li, Q.; Liu, X. X.; Sun, X. A polydopamine coating enabling the stable cycling of MnO₂ cathode materials in aqueous zinc batteries. *Chem. Sci.* **2024**, *15*, 3545–3551.
- [42] Xian, C.; He, R.; Chen, Q.; Li, Q.; Ma, Y.; Bao, S. J.; Sun, W.; Chen, H.; Xu, M. Cobalt-catalyzed reversible deposition/dissolution of MnO₂ for enhancing the long-cycle stability of aqueous Zn-Mn batteries. *Chem. Eng. J.* **2025**, *512*, 162576.
- [43] Liu, Y.; Xie, C.; Li, X. Carbon nanotube network induces porous deposited MnO₂ for high-area capacity Zn/Mn batteries. *Small* **2024**, *20*, 2402026.
- [44] Qi, Y.; Li, F.; Sheng, H.; Zhang, H.; Yuan, J.; Ma, L.; Bi, H.; Ma, Y.; Li, W.; Lan, W. Seed-assisted reversible dissolution/deposition of MnO₂ for long-cyclic and green aqueous zinc-ion batteries. *Small* **2024**, *20*, 2404312.
- [45] Chen, H.; Ruan, P.; Zhang, H.; El-Bahy, Z. M.; Ibrahim, M. M.; Lu, B.; Zhou, J. Achieving highly reversible Mn²⁺/MnO₂ conversion reaction in electrolytic Zn-MnO₂ batteries via electrochemical-chemical process regulation. *Angew. Chem. Int. Ed.* **2025**, *64*, e202423999.
- [46] Guo, J.; Wang, R.; Li, J.; Ma, R.; Wang, Q.; Lv, Z.; Jin, H.; Wei, W.; Han, L.; Ling, T. Water dissociation: A new dimension for understanding and designing aqueous electrocatalysts. *Adv. Mater.* **2026**, *0*, e72916.
- [47] He, B.; Feng, L.; Hong, G.; Yang, L.; Zhao, Q.; Yang, X.; Yin, S.; Meng, Y.; Xiao, D.; Wang, Y.; Ai, J. A generic F-doped strategy for biomass hard carbon to achieve fast and stable kinetics in sodium/potassium-ion batteries. *Chem. Eng. J.* **2024**, *490*, 151636.
- [48] Samartzis, N.; Bhorkar, K.; Sygellou, L.; Bellou, E.; Boukos, N.; Chrissanthopoulos, A.; Yannopoulos, S. N. Dry laser-assisted fabrication of F-doped graphene electrodes: Boosting performance of Zn-ion hybrid capacitors. *Chem. Eng. J.* **2025**, *507*, 160505.
- [49] Wang, J.; Wang, J. G.; Liu, H.; You, Z.; Wei, C.; Kang, F. Electrochemical activation of commercial MnO micro-sized particles for high-performance aqueous zinc-ion batteries. *J. Power Sources* **2019**, *438*, 226951.
- [50] Yang, C.; Zhong, W.; Liu, Y.; Deng, Q.; Cheng, Q.; Liu, X.; Yang, C. Regulating solid electrolyte interphase film on fluorine-doped hard carbon anode for sodium-ion battery. *Carbon Energy* **2024**, *6*, e503.
- [51] Xiong, L.; Kim, Y.; Fu, H.; Han, W.; Yang, W.; Liu, G. F-Doped carbon nanoparticles-based nucleation assistance for fast and uniform three-dimensional Zn deposition. *Adv. Sci.* **2023**, *10*, 2300398.
- [52] Zhang, C.; Wang, Q.; Li, Z.; Liu, H.; Zhong, L.; Liu, J.; Wang, Z.; Wu, R.; Song, P.; Chen, W. J.; Qi, Z.; Yan, C.; Song, L.; Yan, Q.; Lv, C. Enabling unconventional ‘Alternating-Distal’ N₂ reduction pathway for efficient ammonia electrolysis. *Angew. Chem. Int. Ed.* **2025**, *64*, e202502957.
- [53] Zhang, X.; Ma, X.; Bi, H.; Zhang, Y.; Mi, P.; Liu, F.; Jin, X.; Chen, Y.; Zhang, K.; Wang, J.; Dong, Y. Carboxymethylcellulose induced the formation of amorphous MnO₂ nanosheets with abundant oxygen vacancies for fast ion diffusion in aqueous zinc-ion batteries. *Adv. Funct. Mater.* **2024**, *35*, 2411990.
- [54] Wang, H.; Guo, R.; Ma, Y.; Zhou, F. Core-shell cross-doped Mn/Mo oxide heterojunction for high-performance aqueous zinc ion batteries. *Adv. Funct. Mater.* **2023**, *33*, 2301351.
- [55] Li, S.; Chen, D.; Tian, S.; Zhang, C.; He, W.; Lv, C.; Yan, C. Breaking low-strain and rapid-kinetics trade-off in heterostructured prussian blue cathode toward robust sodium storage. *J. Colloid Interface Sci.* **2025**, *698*, 138106.
- [56] Chao, D.; Ye, C.; Xie, F.; Zhou, W.; Zhang, Q.; Gu, Q.; Davey, K.; Gu, L.; Qiao, S. Z. Atomic engineering catalyzed MnO₂ electrolysis kinetics for a hybrid aqueous battery with high power and energy density. *Adv. Mater.* **2020**, *32*, 2001894.
- [57] Zhao, S.; Lu, W.; Dai, W.; Hou, Z.; Li, S.; Tang, J.; Zhang, D.; Wang, Y.; Jiang, H.; Du, F. In situ formation of lattice-distorted Mn-based catalysts boosting high energy-efficiency aqueous metal-air batteries. *Adv. Mater.* **2026**, *38*, e17696.
- [58] Li, Y.; Li, Y.; Liu, Q.; Liu, Y.; Wang, T.; Cui, M.; Ding, H.; Li, H.; Yu, G. Revealing the dominance of the dissolution-deposition mechanism in aqueous Zn-MnO₂ batteries. *Angew. Chem. Int. Ed.* **2024**, *63*, e202318444.
- [59] Cui, S.; Zhang, D.; Gan, Y. Traditional electrochemical Zn²⁺ intercalation/extraction mechanism revisited: Unveiling ion-exchange mediated irreversible Zn²⁺ intercalation for the δ-MnO₂ cathode in aqueous Zn ion batteries. *Adv. Energy Mater.* **2024**, *14*, 2302655.
- [60] Chen, H.; Dai, C.; Xiao, F.; Yang, Q.; Cai, S.; Xu, M.; Fan, H. J.; Bao, S. J. Reunderstanding the reaction mechanism of aqueous Zn-Mn batteries with sulfate electrolytes: Role of the zinc sulfate hydroxide. *Adv. Mater.* **2022**, *34*, 2109092.
- [61] Li, X.; Xu, Z.; Qian, Y.; Hou, Z. In-situ regulated competitive proton intercalation and deposition/dissolution reaction of MnO₂ for high-performance flexible zinc-manganese batteries. *Energy Storage Mater.*, **2022**,

53, 72–78.

- [62] Guo, D.; Sun, J.; Wang, C.; Quan, H.; Lu, H.; Wei, Y.; Sun, C.; Wang, S. To make a painstaking investigation: Revealing the electrochemical reactions in aqueous Zn-Mn batteries. *Angew. Chem. Int. Ed.* **2025**, *64*, e202505102.
- [63] Tian, S.; Wu, R.; Liu, H.; Yan, C.; Qi, Z.; Song, P.; Chen, W. J.; Song, L.; Wang, Z.; Lv, C. Realizing unconventional tandem nitrate reduction for efficient ammonia electrosynthesis enabled by Co, Fe dual-site conjugated metal organic framework. *Angew. Chem. Int. Ed.* **2025**, *64*, e202510665.
- [64] Qian, F.; Cao, D.; Chen, S.; Yuan, Y.; Chen, K.; Chintali, P. J.; Liu, H.; Jiang, W.; Sheng, B.; Yi, L.; Huang, J.; Hu, C.; Lei, H.; Wu, X.; Wen, Z.; Chen, Q.; Song, L. High-entropy RuO₂ catalyst with dual-site oxide path for durable acidic oxygen evolution reaction. *Nat. Commun.* **2025**, *16*, 6894.
- [65] Zhong, Z.; Li, J.; Li, L.; Xi, X.; Luo, Z.; Fang, G.; Liang, S.; Wang, X. Improving performance of zinc-manganese battery via efficient deposition/dissolution chemistry. *Energy Storage Mater.* **2022**, *46*, 165–174.
- [66] Moon, H.; Ha, K. H.; Park, Y.; Lee, J.; Kwon, M. S.; Lim, J.; Lee, M. H.; Kim, D. H.; Choi, J. H.; Choi, J. H.; Lee, K. T. Direct proof of the reversible dissolution/deposition of Mn²⁺/Mn⁴⁺ for mild-acid Zn-MnO₂ batteries with porous carbon interlayers. *Adv. Sci.* **2021**, *8*, 2003714.
- [67] Xu, Y.; Zhang, G.; Wang, X.; Zhang, J.; Wen, H.; Wang, D.; Yuan, Y.; Jiang, Q.; Qian, H.; Xi, Y.; Zuo, J.; Li, M.; Liu, J.; Yang, H.; Luo, J.; Wang, W.; Li, X. Efficient modulation d/p-band center proximity in birnessite-type MnO₂ by cation/anion co-doping for enhanced dual-ion storage. *Adv. Funct. Mater.* **2025**, *35*, 2500137.
- [68] Li, G.; Huang, Z.; Chen, J.; Yao, F.; Liu, J.; Li, O. L.; Sun, S.; Shi, Z. Rechargeable Zn-ion batteries with high power and energy densities: a two-electron reaction pathway in birnessite MnO₂ cathode materials. *J. Mater. Chem. A* **2020**, *8*, 1975–1985.
- [69] Liu, Y.; Ma, Y.; Yang, W.; Bao, S.; Chen, H.; Xu, M. Spontaneously dissolved MnO: A better cathode material for rechargeable aqueous zinc-manganese batteries. *Chem. Eng. J.* **2023**, *473*, 145490.
- [70] Zhao, Y.; Xia, X.; Li, Q.; Wang, Y.; Fan, Y.; Zhao, Y.; Liu, W.; Sun, X. Activating the redox chemistry of MnO₂/Mn²⁺ in aqueous Zn batteries based on multi-ions doping regulation. *Energy Storage Mater.* **2024**, *67*, 103268.
- [71] Zhang, L.; Yang, S.; Fu, W.; Cui, J.; Wang, D.; Zhao, C.; Yang, X.; Wang, B.; Cao, B. Plasma-induced ε-MnO₂-based aqueous zinc-ion batteries and their dissolution-deposition mechanism. *J. Mater. Sci. Technol.* **2022**, *127*, 206–213.
- [72] Li, X.; He, D.; Zhou, Q.; Zhou, X.; Wang, Z.; Wei, C.; Shi, Y.; Hu, X.; Huang, B.; Yang, Z.; Han, X.; Lin, Y.; Yu, Y. Deciphering anomalous zinc ion storage in intermediate-state MnO₂ during layer-to-tunnel structural transition. *Energy Environ. Sci.* **2024**, *17*, 9195–9204.
- [73] Xie, D.; Wang, Y.; Tian, L.; Huang, H.; Sun, J.; Kim, D. W.; Zhao, J.; Mao, J. Dual-functional Ca-ion-doped layered δ-MnO₂ cathode for high-performance aqueous zinc-ion batteries. *Adv. Funct. Mater.* **2024**, *35*, 2413993.

© The Author(s) 2026. Nano Research published by Tsinghua University Press. The articles published in this open access journal are distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits use, distribution and reproduction in any medium, provided the original work is properly cited.

Tailoring the *OH-mediated manganese deposition chemistry via fluorine-doped carbon for reversible aqueous zinc batteries

Haiyan Sun[§], Shijie Chen[§], Hao Wang, Chu Zhang, Ju Zhao, Weihao Xu, Chade Lv[✉], and Chunshuang Yan[✉]

MIIT Key Laboratory of Critical Materials Technology for New Energy Conversion and Storage, School of Chemistry and Chemical Engineering, Harbin Institute of Technology, Harbin 150001, China

[§] Haiyan Sun and Shijie Chen contributed equally to this work.

✉ Address correspondence to Chade Lv, lv.chade@hit.edu.cn; Chunshuang Yan, csyan@hit.edu.cn

Supporting information to <https://doi.org/10.26599/NR.2026.94909104>

Material Characterization. The morphology of the samples was characterized using a Zeiss Supra55 field-emission scanning electron microscope (SEM) equipped with energy-dispersive X-ray spectroscopy (EDS) for elemental mapping. The microstructure and crystal structure were further analyzed using an FEI Talos F200X transmission electron microscope (TEM) and high-resolution TEM (HRTEM). X-ray diffraction (XRD) patterns were collected on a D8 ADVANCE diffractometer with Cu K α radiation ($\lambda = 0.154$ nm) over a 2θ range of 8–80°. X-ray photoelectron spectroscopy (XPS) measurements were performed on an ESCALAB 250Xi spectrometer using monochromatic Al K α radiation (1486.6 eV), and the binding energies were calibrated against the C 1s peak at 284.6 eV. Thermogravimetric analysis (TGA) was conducted on a STA4 analyzer under air atmosphere from 3 to 800 °C at a heating rate of 10 °C min⁻¹ to determine the carbon content of the as-prepared material. Nitrogen adsorption-desorption measurements were carried out to determine the specific surface area and pore size distribution; the specific surface area was calculated using the Brunauer-Emmett-Teller (BET) method. Prior to measurement, the sample was degassed under vacuum at 120 °C for 8 h, followed by measurement under liquid nitrogen in full-pore mode. The composition of the electrolyte was quantitatively analyzed using an iCAP 7400 inductively coupled plasma (ICP) spectrometer. In situ monitoring of material characterization and electrochemical processes was performed using a MODEL BX41TF Raman spectrometer.

Electrochemical Measurements. Galvanostatic charge-discharge tests and galvanostatic intermittent titration technique (GITT) tests were performed on a BTS-5V/2-50mA battery testing system with a voltage window of 0.4–1.8 V (vs. Zn²⁺/Zn). Cyclic voltammetry (CV) tests were conducted in the range of 0.4–1.8 V, and electrochemical impedance spectroscopy (EIS) tests were carried out in the frequency range of 0.01 Hz to 100 kHz; both measurements were performed using an Autolab electrochemical workstation.

In situ Raman measurements. In situ Raman spectroscopy was conducted using Renishaw's 500 inVia Raman microscopes with a 532 nm laser source in a custom cell. Carbon cloth loaded with the active material was used as the cathode, and zinc foil as the anode. The two electrodes were immersed in an electrolyte of 2 mol/L ZnSO₄ + 0.1 mol/L MnSO₄. Galvanostatic charge-discharge tests were carried out in the voltage range of 0.4–1.8 V (vs. Zn²⁺/Zn), and in situ Raman spectroscopic measurements were performed synchronously throughout the entire test process.

Online DEMS measurements. Online differential electrochemical mass spectrometry (DEMS) measurements were performed using a PM-DEMS spectrometer (Shanghai Jing-protech Co., Ltd.) in a home-made electrochemical cell with 2 mL of 2 mol/L Na₂SO₄ as the electrolyte. Carbon cloth loaded with the active material was used as the cathode and zinc foil as the anode. The electrolyte was degassed and purged until the mass spectral baseline was stabilized. Potentiostatic measurements were conducted intermittently at 2.0 V (vs. Zn²⁺/Zn), and each test was terminated when the mass spectral signal returned to the baseline.

Computational details. All density functional theory (DFT) [1] calculations were performed using the Vienna Ab initio Simulation Package (VASP) [2, 3] with the projector-augmented wave (PAW) method to describe the ion-electron interactions. The exchange-correlation functional was approximated by the generalized gradient approximation (GGA) with the Perdew-Burke-Ernzerhof (PBE) [4] parameterization. A plane-wave cutoff energy of 450 eV was adopted for the basis set. The convergence criteria for the total energy and atomic force were set to 10⁻⁵ eV and 0.03 eV Å⁻¹, respectively. The Brillouin zone was sampled with a 2×2×1 Monkhorst-Pack k-point mesh for geometry optimization, and a 2×2×1 k-point mesh was used for the density of states (DOS) calculations. The van der Waals (vdW) interaction was corrected using the DFT-D3 method to accurately describe the weak interaction between the carbon substrate and Mn-based intermediates.

The free energy change (ΔG) for each elementary step in the *MnO₂ formation process was calculated using the computational hydrogen electrode (CHE) model, as follows: $\Delta G = \Delta E + \Delta ZPE - T\Delta S$, where ΔE is the electronic energy difference obtained from DFT calculations, ΔZPE is the zero-point energy correction, T is the temperature (298.15 K), and ΔS is the entropy change. The zero-point energy and entropy of adsorbed species were calculated from the vibrational frequencies of the

adsorbed species, while the gas-phase entropy of H₂O was taken from the standard thermodynamic database. According to the computational hydrogen electrode (CHE) model proposed by Nørskov et al., the free energy of the (H⁺ + e⁻) pair is defined as 1/2 G(H₂, g) at standard conditions (298.15 K, 1 bar, pH = 0, U = 0 V vs. SHE) [5].

The partial density of states (PDOS) was calculated to analyze the electronic structure of MDC and F-MDC substrates, as well as the adsorbed Mn-based intermediates. The PDOS was calculated using the tetrahedron method (ISMEAR = -5) with LORBIT = 11, and the energy was aligned by setting the Fermi level to 0 eV. The PDOS of C 2p, F 2p, Mn 3d, and O 2p orbitals were plotted to investigate the orbital hybridization and charge transfer at the substrate-intermediate interface.

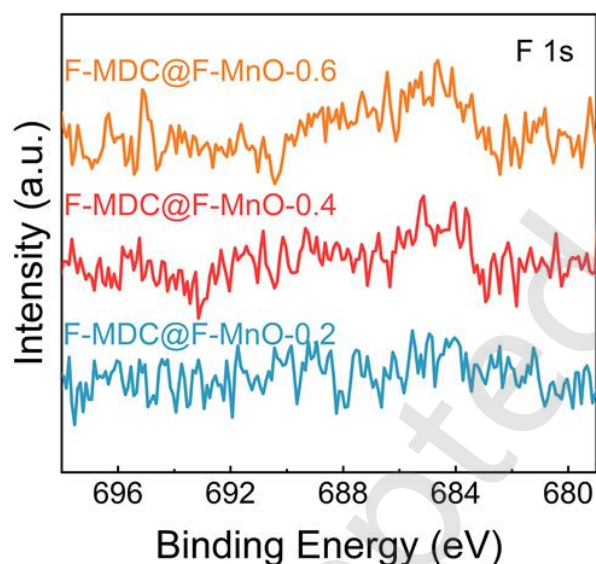


Figure S1 F 1s XPS spectra of F-MDC@F-MnO prepared with varying NH₄F addition amounts.

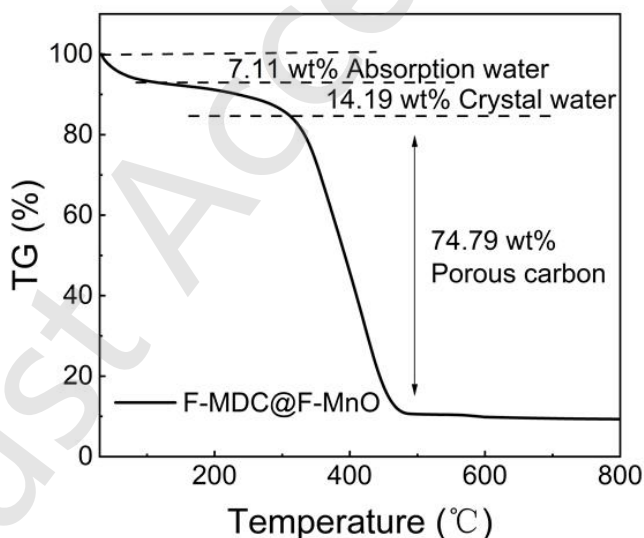


Figure S2 Thermogravimetric (TG) curve of F-MDC@F-MnO.

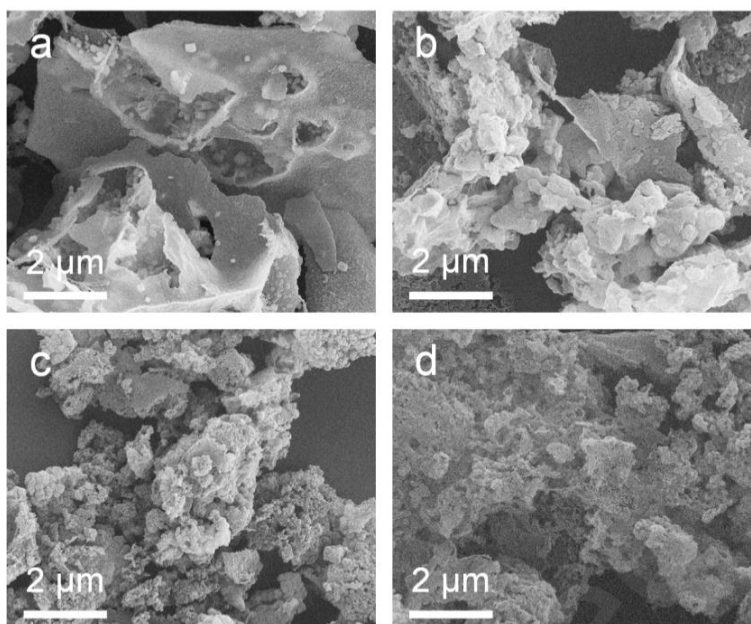


Figure S3 SEM images of F-MDC@F-MnO prepared with different NH_4F addition amounts. (a) MDC@MnO, (b) F-MDC@F-MnO-0.2, (c) F-MDC@F-MnO-0.4, (d) F-MDC@F-MnO-0.6.

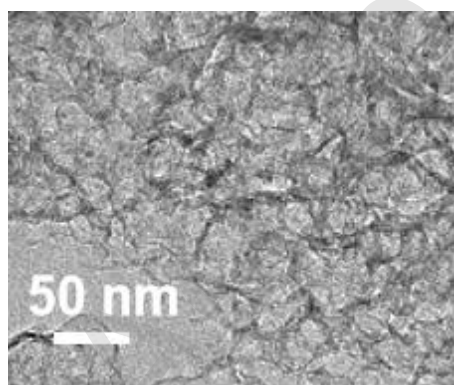


Figure S4 TEM image of F-MDC@F-MnO.

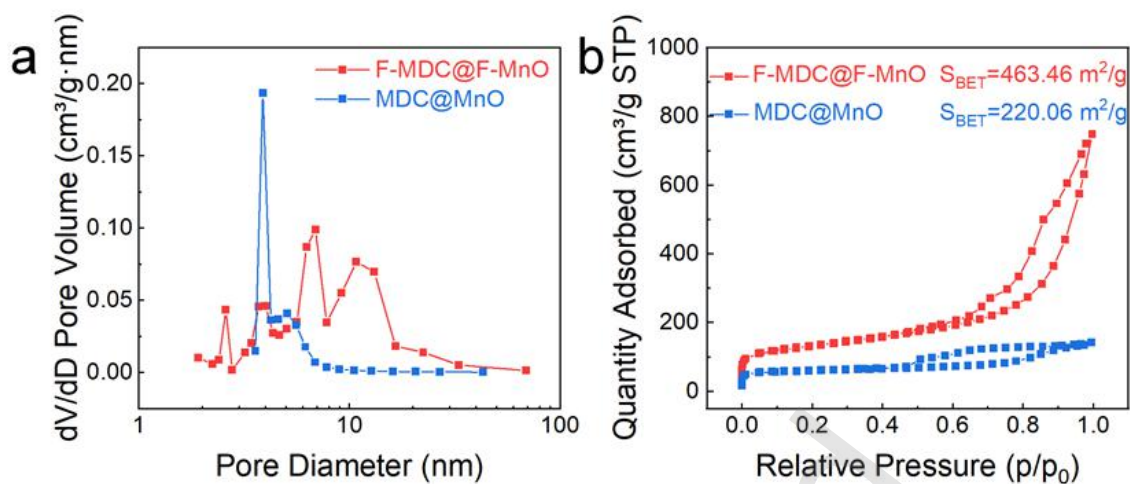


Figure S5 Nitrogen adsorption-desorption measurements of F-MDC@F-MnO and MDC@MnO. (a) Nitrogen adsorption-desorption isotherms, (b) Pore size distribution curves.

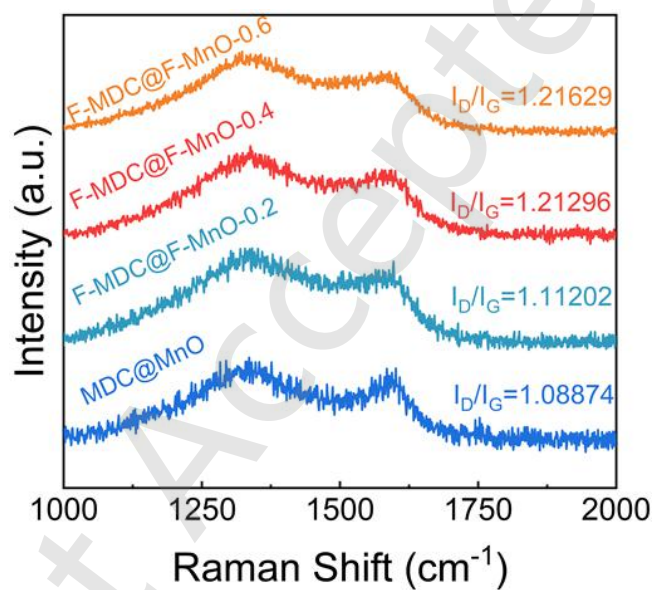


Figure S6 Raman spectra of F-MDC@F-MnO prepared with different NH_4F addition amounts.

High-resolution transmission electron microscopy (HRTEM) revealed (Figure S7b) that these nanoparticles exhibit clear lattice fringes. The measured interplanar spacing is approximately 0.256 nm, which is in good agreement with the standard value of the MnO (111) plane, confirming that the nanoparticles are MnO.

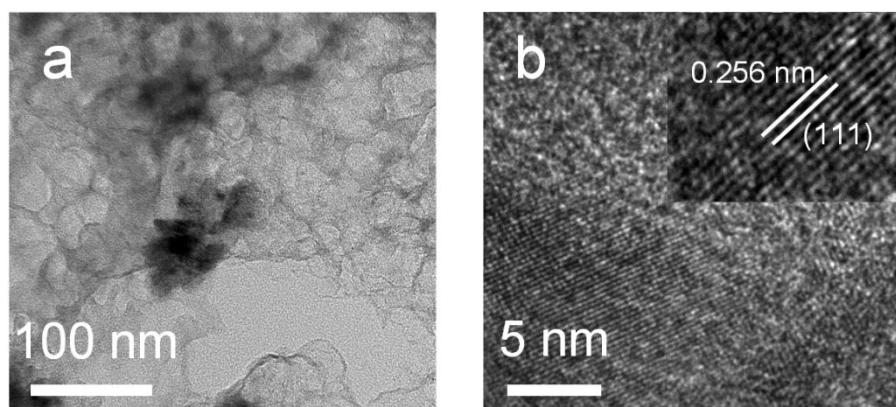


Figure S7 TEM characterization of F-MDC@F-MnO. (a) TEM image, (b) HRTEM image.

In the X-ray diffraction (XRD) pattern (Figure S8), besides the broad diffraction peak typical of carbon materials, the MDC@MnO sample exhibits characteristic diffraction peaks of MnO. The peaks at 34.9°, 40.5°, 58.7°, 70.1°, and 73.8° correspond to the (110), (200), (220), (311), and (222) planes of MnO (JCPDS No. 75-1090), respectively, consistent with the nanoparticles observed by TEM and further confirming their identification as MnO. The weak intensity of the MnO diffraction peaks in F-MDC@F-MnO is mainly attributed to the lattice distortion induced by the addition of NH₄F, which reduces the crystallinity of MnO.

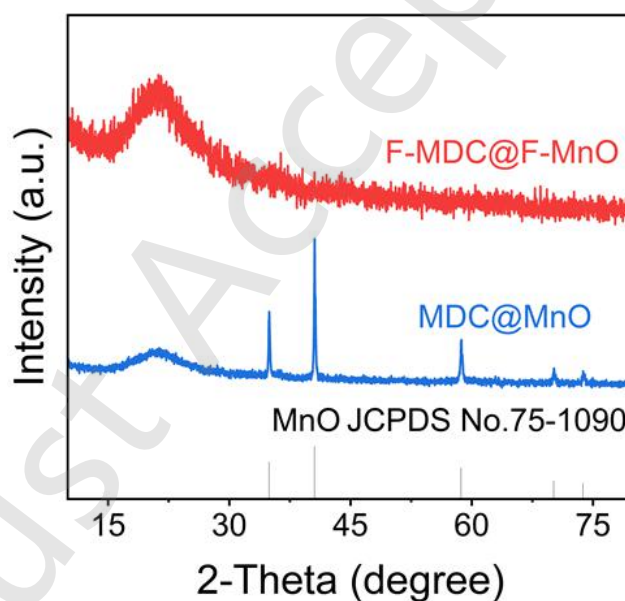


Figure S8 XRD patterns of F-MDC@F-MnO and MDC@MnO.

The surface elemental composition and chemical states of the F-MDC@F-MnO and MDC@MnO samples were analyzed by X-ray photoelectron spectroscopy (XPS). All spectra were charge-corrected using the C 1s peak at 284.6 eV as a reference, and the high-resolution core-level spectra were deconvoluted using Gaussian fitting. Figure S9a shows the high-resolution C 1s XPS spectra and their corresponding fitting curves for the two samples. The C 1s spectra can be deconvoluted into three characteristic peaks: the intense peak at 284.6 eV is assigned to C-C bonds, the shoulder peak at 285.9 eV corresponds to C-O bonds, and the weak peak at 288.4 eV is attributed to C=O bonds. The O 1s spectra (Figure S9b) are fitted into three peaks, corresponding to Mn-O bonds (530.2 eV), C-Mn-O bonds (531.7 eV), and C-O bonds (533.4 eV), respectively. In the high-resolution Mn 2p spectra of both samples (Figure S9c), two distinct spin-orbit doublets are observed. The peak at approximately 641.5 eV corresponds to the Mn 2p_{3/2} signal, while the peak at approximately 653.0 eV corresponds to Mn 2p_{1/2}. The fitting results indicate that Mn predominantly exists in the +2 oxidation state, further confirming that the nanoparticles are MnO.

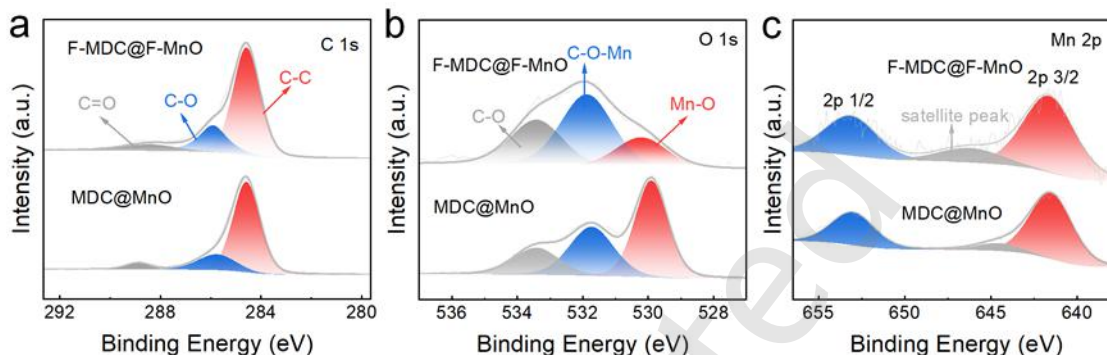


Figure S9 XPS spectra of F-MDC@F-MnO and MDC@MnO. (a) C 1s, (b) O 1s, (c) Mn 2p.

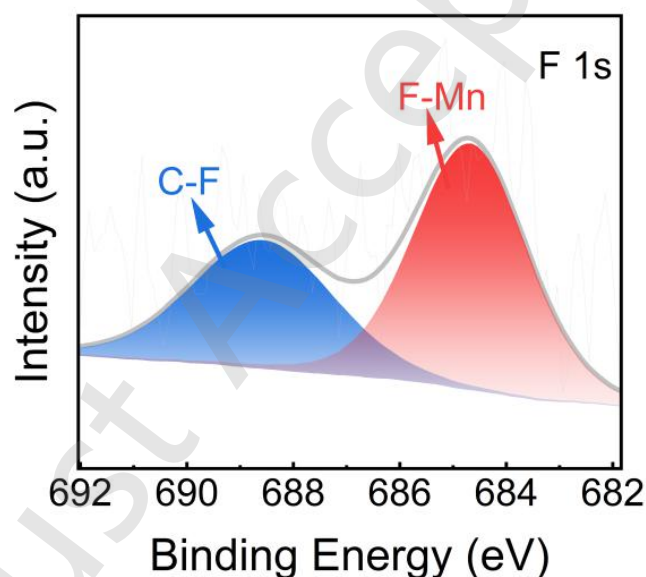


Figure S10 XPS spectrum of F-MDC@F-MnO.

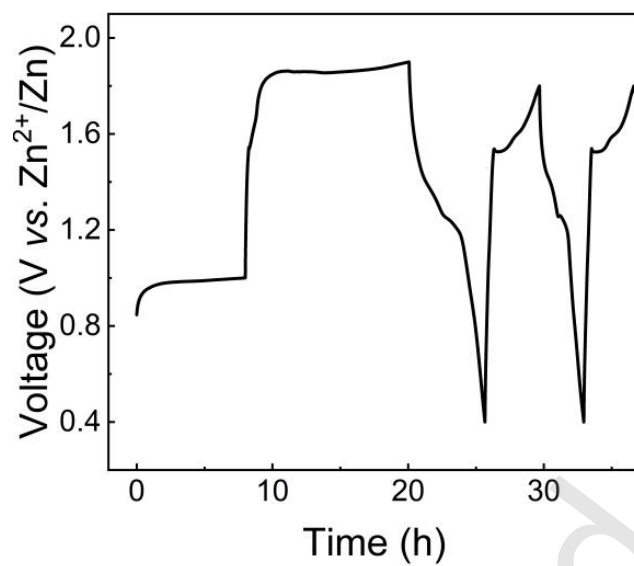


Figure S11 GCD curve of F-MDC@F-MnO during the initial cycles.

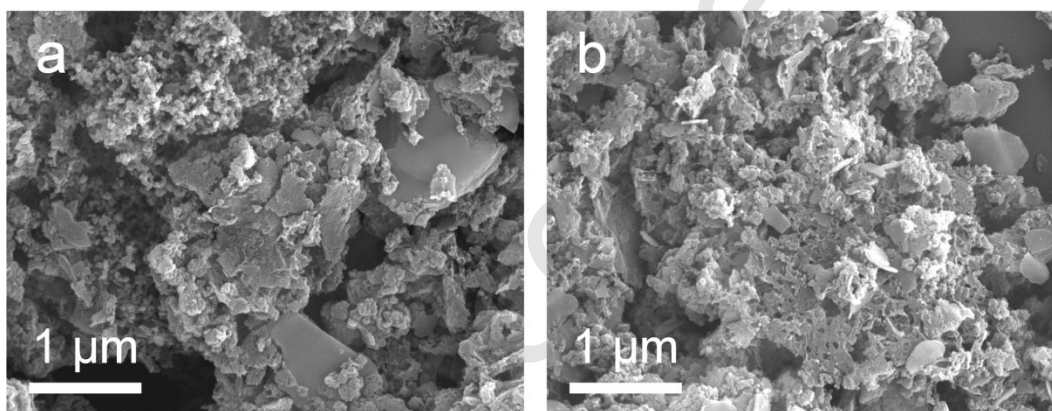


Figure S12 SEM images of (a) MDC@MnO-1.9 and (b) F-MDC@F-MnO-1.9.

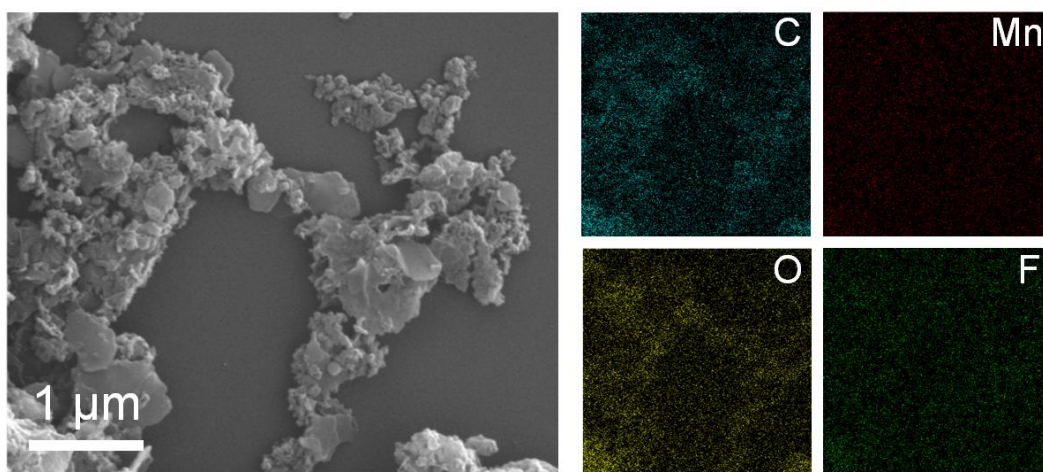


Figure S13 SEM and corresponding EDS elemental mapping images of F-MDC@F-MnO-1.9.

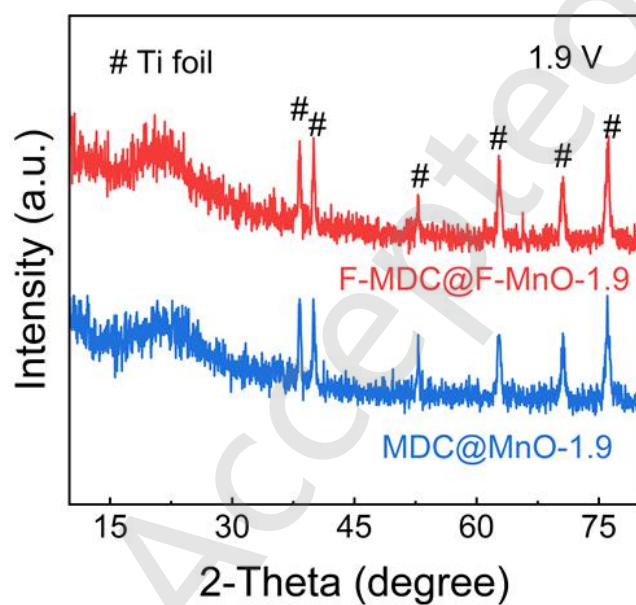


Figure S14 XRD patterns of F-MDC@F-MnO-1.9 and MDC@MnO-1.9.

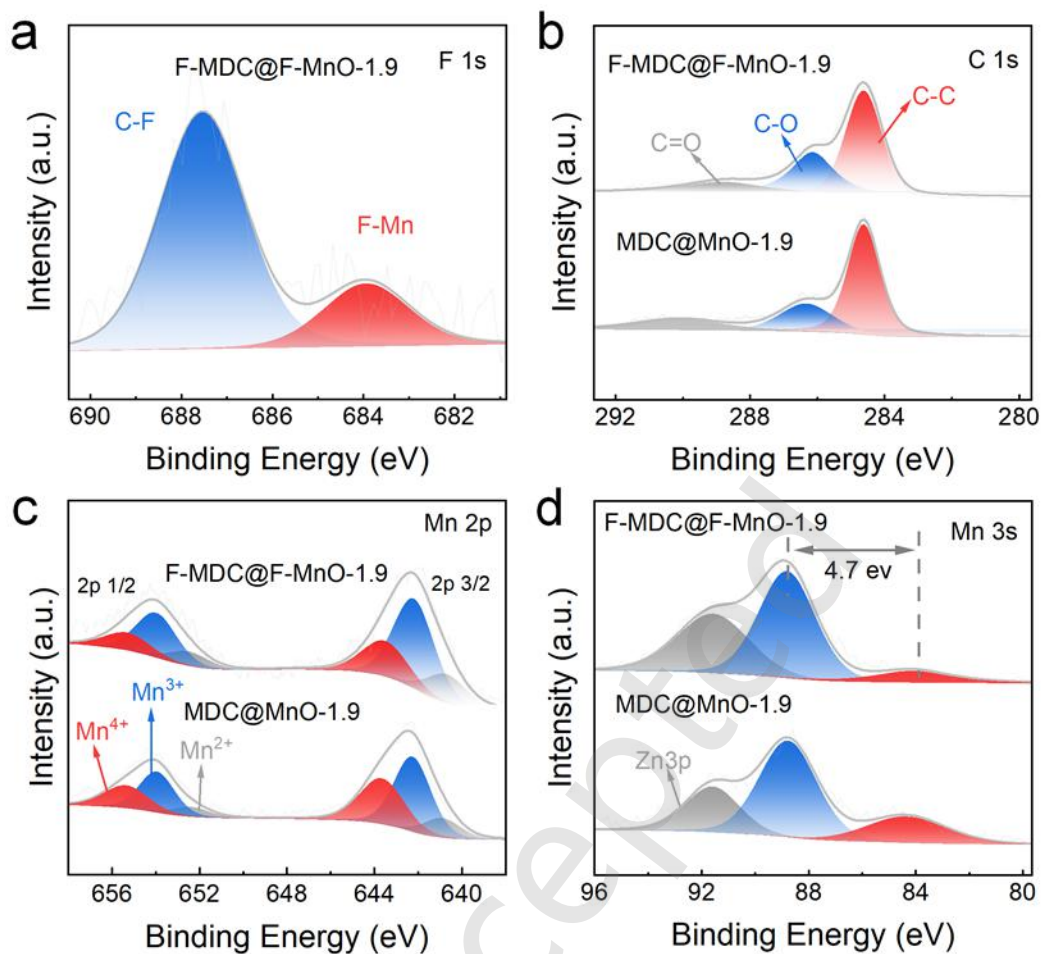


Figure S15 XPS spectra of F-MDC@F-MnO-1.9 and MDC@MnO-1.9 electrodes. (a) F 1s, (b) C 1s, (c) Mn 2p, (d) Mn 3s.

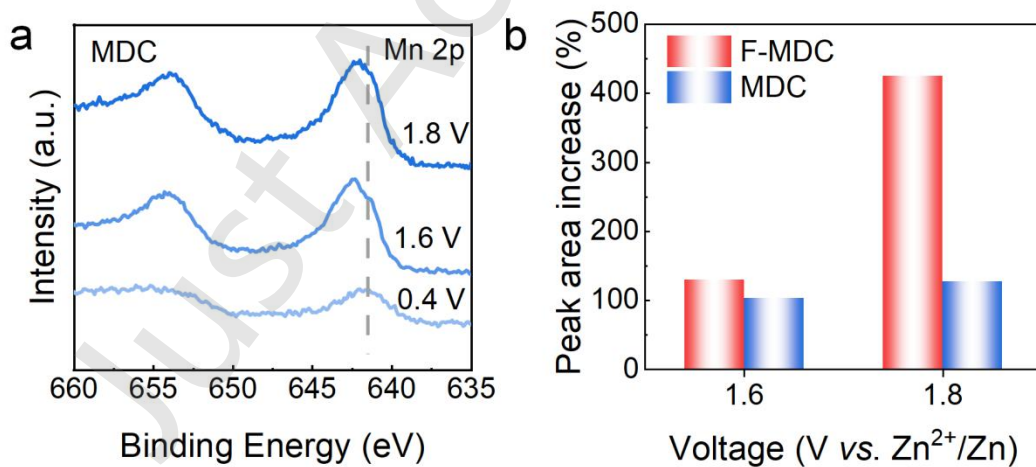


Figure S16 (a) Ex situ XPS spectra of Mn 2p for the MDC electrode at various states of charge, (b) Comparison of the relative Mn 2p peak area increase for F-MDC and MDC electrodes, normalized to the peak area at 0.4 V.

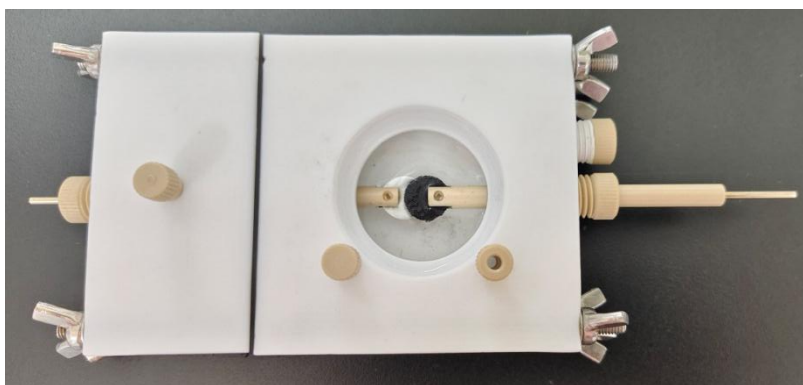


Figure S17 In situ Raman setup diagram.

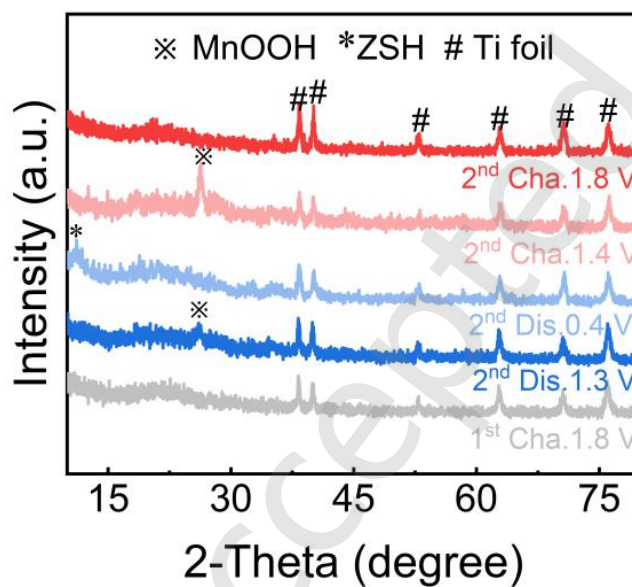


Figure S18 Ex situ XRD patterns of MDC at different electrochemical states.

To further verify the reaction mechanism, a series of control experiments were designed with a focus on the role of Mn^{2+} and Zn^{2+} in the electrolyte.

1.Role of Zn^{2+} : After fully charging a standard cell to 1.8 V in a 0.1 M MnSO_4 + 2 M ZnSO_4 electrolyte, the cathode was carefully rinsed with ultrapure water, dried, and then reassembled into new cells with three different electrolytes: (i) 0.1 M MnSO_4 + 2 M ZnSO_4 , (ii) 2 M ZnSO_4 only, and (iii) water + buffer solution. The cell with the Mn^{2+} -containing electrolyte delivered a slightly lower capacity than the one with 2 M ZnSO_4 only (Figure S19a). This suggests that the presence of Mn^{2+} in the electrolyte marginally suppresses the dissolution of Mn^{2+} from the electrode. The cell with the water + buffer electrolyte showed a normal capacity, confirming that Zn^{2+} does not participate in the redox reaction and therefore does not contribute to the capacity.

2.Necessity of Mn^{2+} for the Charging Process: To determine whether Mn^{2+} from the electrolyte is essential for recharging, a separate cell was first fully discharged to 0.4 V in the standard 0.1 M MnSO_4 + 2 M ZnSO_4 electrolyte. The cathode was then rinsed, dried, and reassembled with either the standard 0.1 M MnSO_4 + 2 M ZnSO_4 electrolyte or the 2 M ZnSO_4 -only electrolyte (Figure S19b). The cell with the ZnSO_4 -only electrolyte exhibited a dramatic capacity drop, in contrast to the stable performance of the cell with the Mn^{2+} -containing electrolyte. This finding demonstrates that Mn^{2+} from the electrolyte is indispensable for the subsequent charging process, as it is the primary species being oxidized to MnO_2 .

3.Capacity Preservation Mechanism: The cathode obtained after full charging to 1.8 V (rinsed and dried) was reassembled into a cell using only 2 M ZnSO_4 as the electrolyte (Figure S19a). Even without any external Mn^{2+} source, after an initial discharge followed by charging, no capacity loss was observed. This striking result indicates that once a MnO_2 deposit is formed on the cathode during the initial charge, the Mn^{2+} ions generated from its subsequent dissolution are sufficient to sustain reversible capacity in the following cycles.

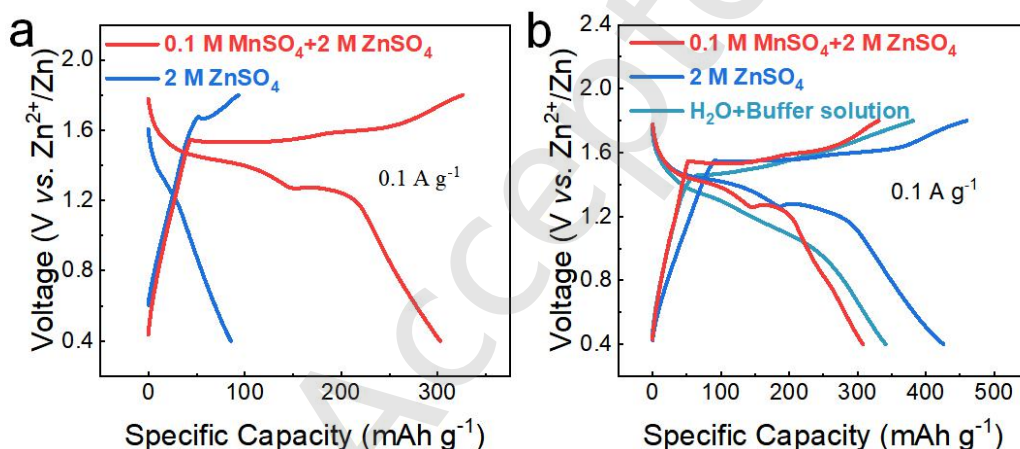


Figure S19 GCD curves at 0.1 A g⁻¹ after the cell was fully (a) charged to 1.8 V and (b) discharged to 0.4 V, then disassembled, with the electrodes washed, dried, and the cell reassembled using different electrolytes.

To further verify the reaction mechanism, the concentrations of H^+ and Mn^{2+} in the electrolyte were experimentally manipulated, and the corresponding open-circuit voltage (OCV) data were recorded, as shown in Figures S20a and b. The OCV increased with increasing H^+ concentration and decreased with increasing Mn^{2+} concentration. According to the Nernst equation, this indicates that Mn^{2+} is generated and H^+ is consumed during the discharge process.

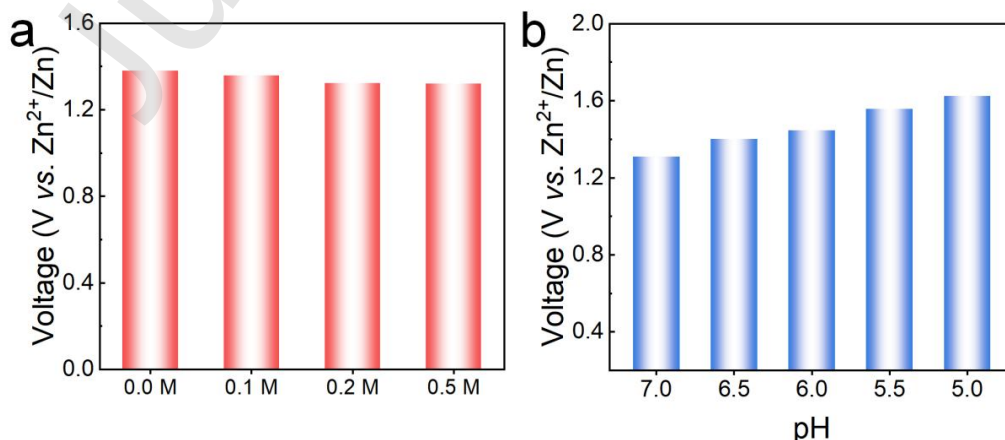


Figure S20 Open-circuit voltages of batteries with different concentrations of (a) Mn^{2+} and (b) H^+ in the electrolyte.

As shown in Figure S21, the pH gradually increases during discharge, providing additional evidence for H^+ consumption. Collectively, these findings indicate that the discharge process involves H^+ consumption and Mn^{2+} dissolution, whereas the charge process corresponds to Mn^{2+} deposition.

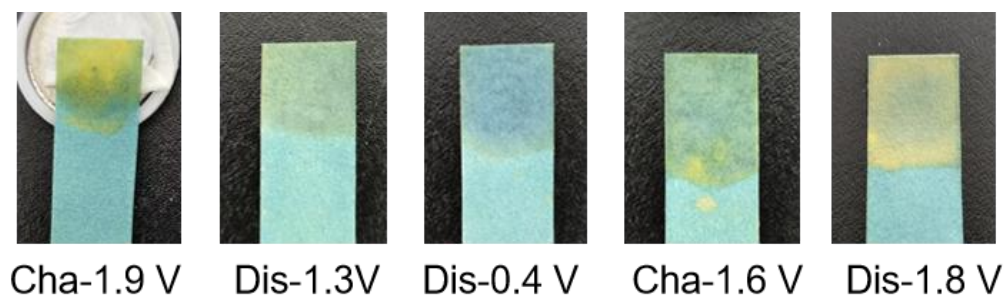


Figure S21 The pH measurements under different charge–discharge states.

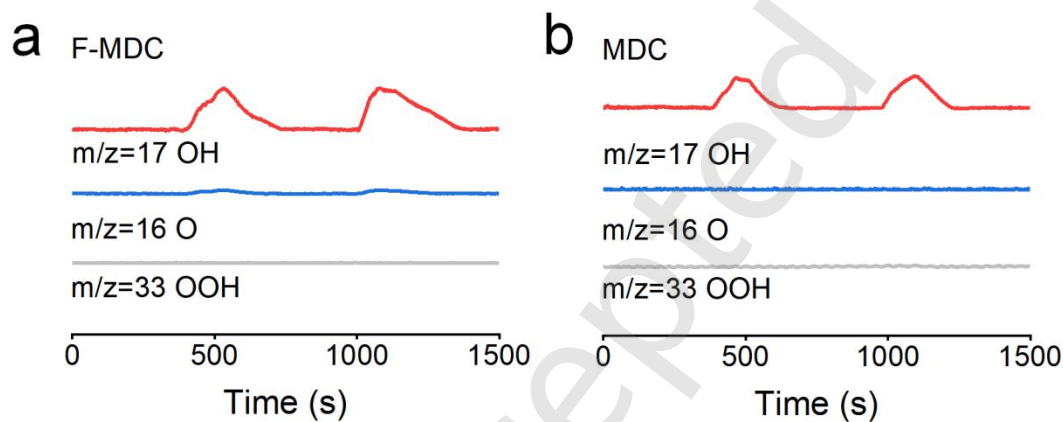


Figure S22 In situ DEMS signals of OH, O, and OOH intermediates on (a) F-MDC and (b) MDC during $MnSO_4$ -free charging in 2 M Na_2SO_4 .

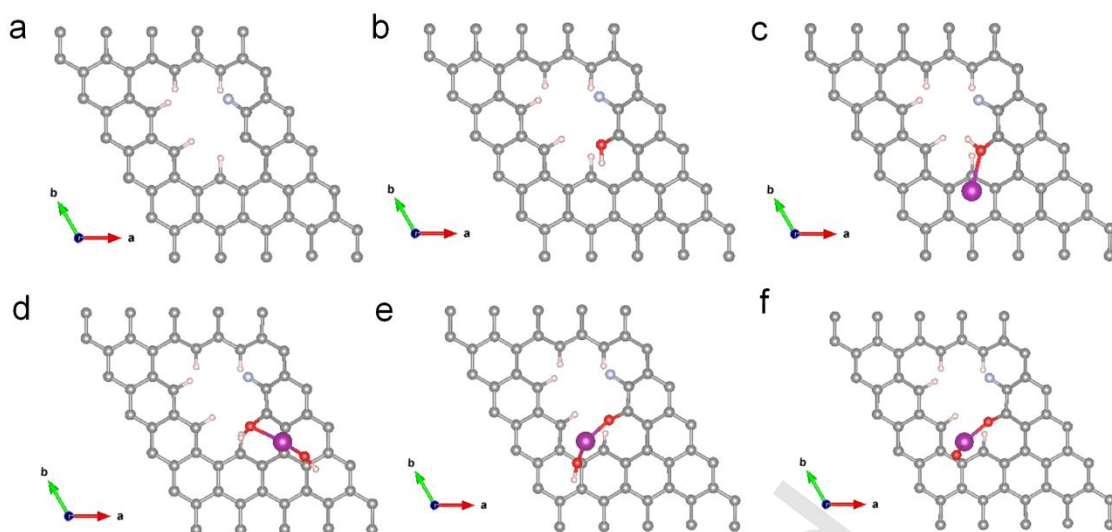


Figure S23 Optimized adsorption configurations of the intermediates at each step during the deposition of Mn^{2+} to MnO_2 on the F-MDC substrate. (a) F-MDC substrate, (b) *OH , (c) *MnOH , (d) *Mn(OH)_2 , (e) *MnOOH , (f) *MnO_2 .

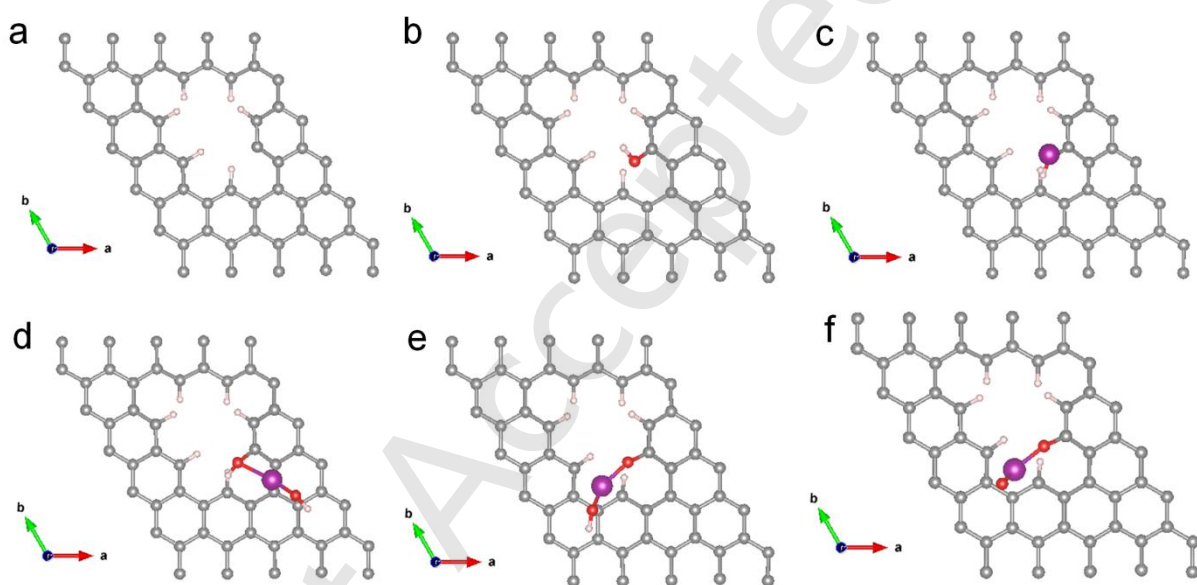


Figure S24 Optimized adsorption configurations of the intermediates at each step during the deposition of Mn^{2+} to MnO_2 on the MDC substrate. (a) MDC substrate, (b) *OH , (c) *MnOH , (d) *Mn(OH)_2 , (e) *MnOOH , (f) *MnO_2 .

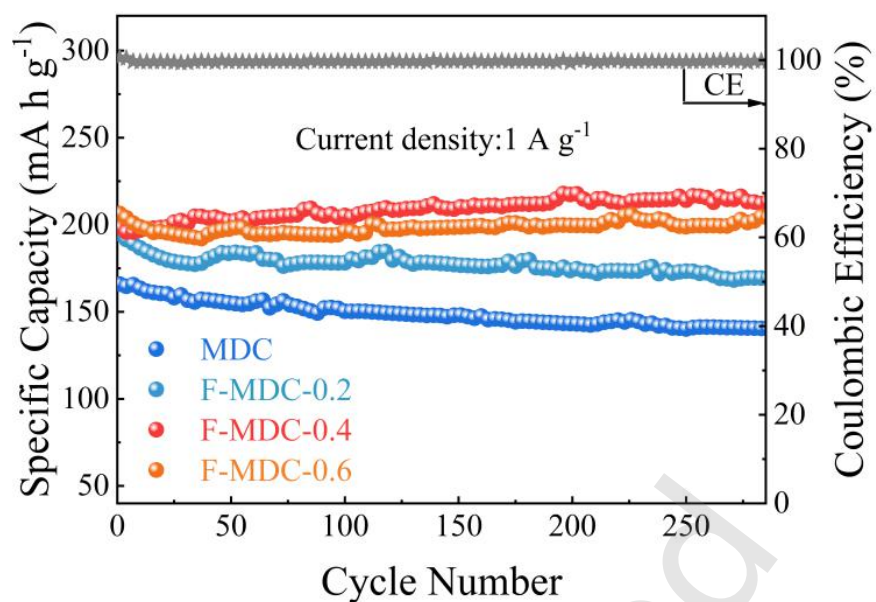


Figure S25 Cycling performance of F-MDC prepared with different NH_4F addition amounts.

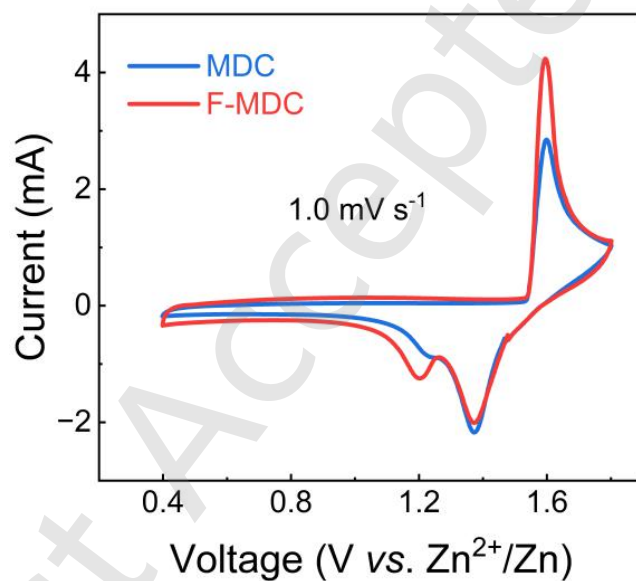


Figure S26 CV curves of F-MDC and MDC at a scan rate of 1 mV s^{-1} .

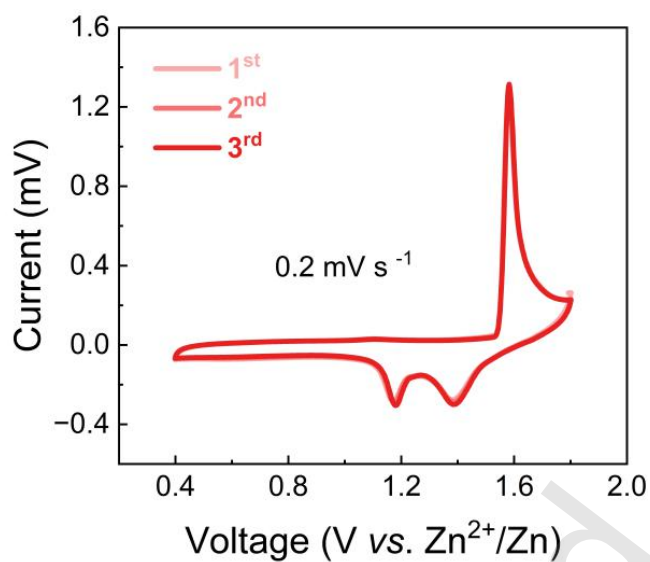


Figure S27 CV curves of F-MDC for the first three cycles at a scan rate of 0.2 mV s⁻¹.

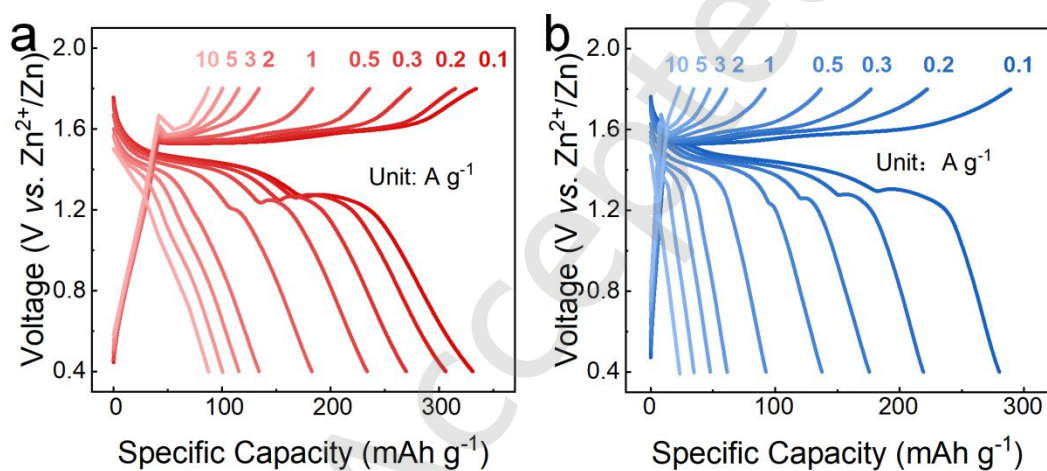


Figure S28 GCD curves of (a) F-MDC and (b) MDC at different current densities.

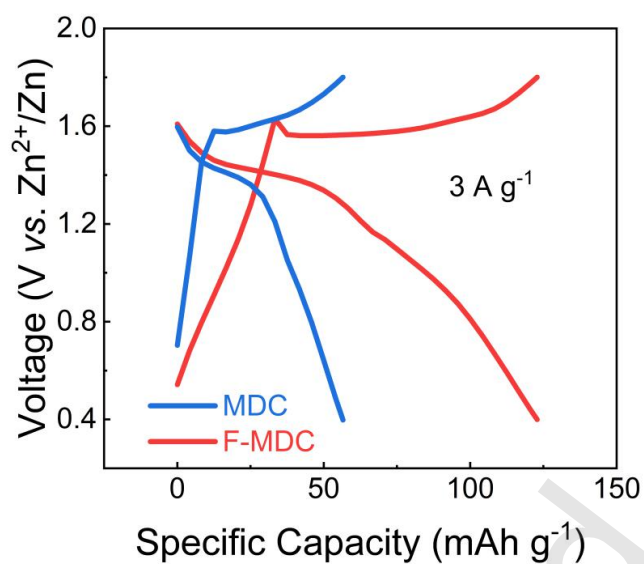


Figure S29. GCD curves of F-MDC and MDC after 4000 cycles at 3 A g^{-1} .

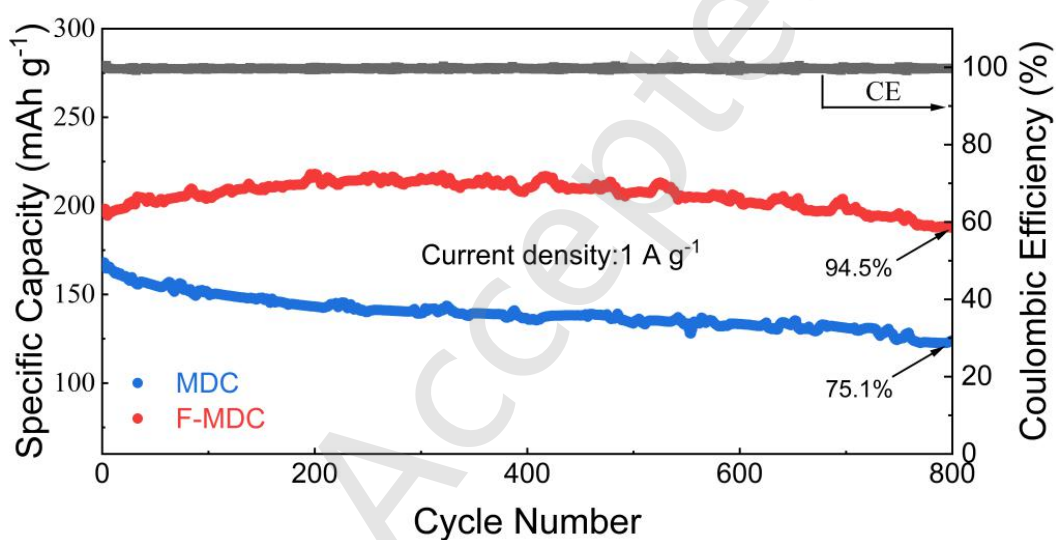


Figure S30 Cycling performance of F-MDC and MDC at 1 A g^{-1} .

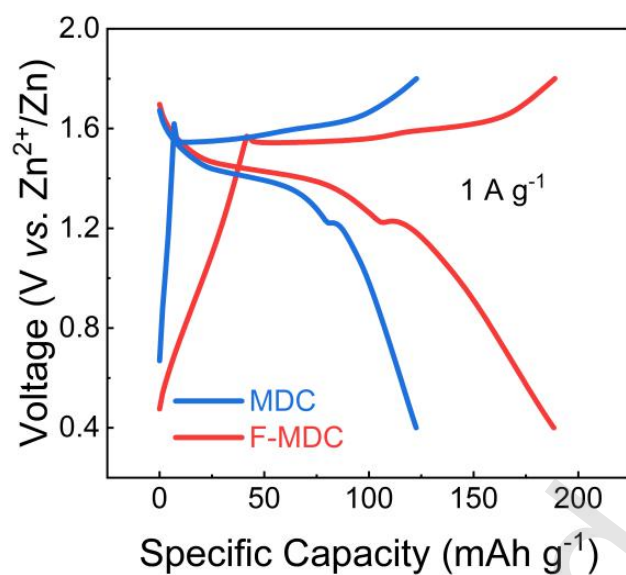


Figure S31 GCD curves of F-MDC and MDC after 800 cycles at 1 A g⁻¹.

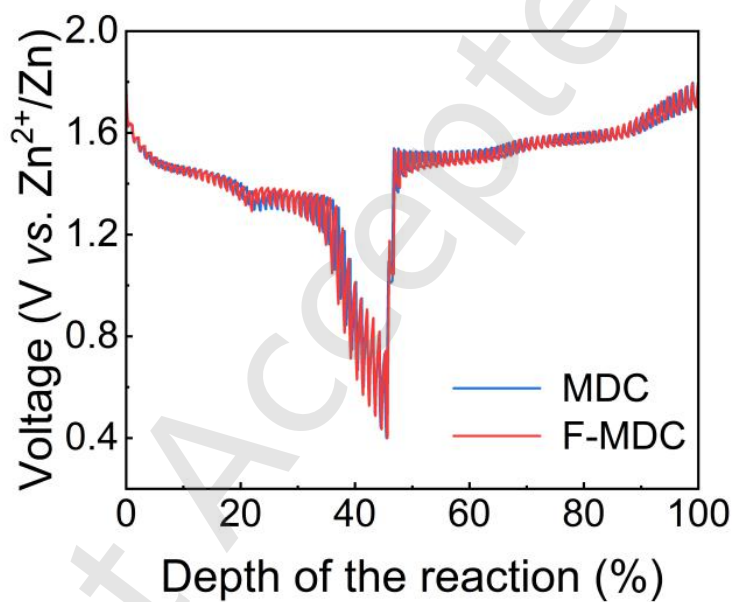


Figure S32 GITT curves of F-MDC and MDC.

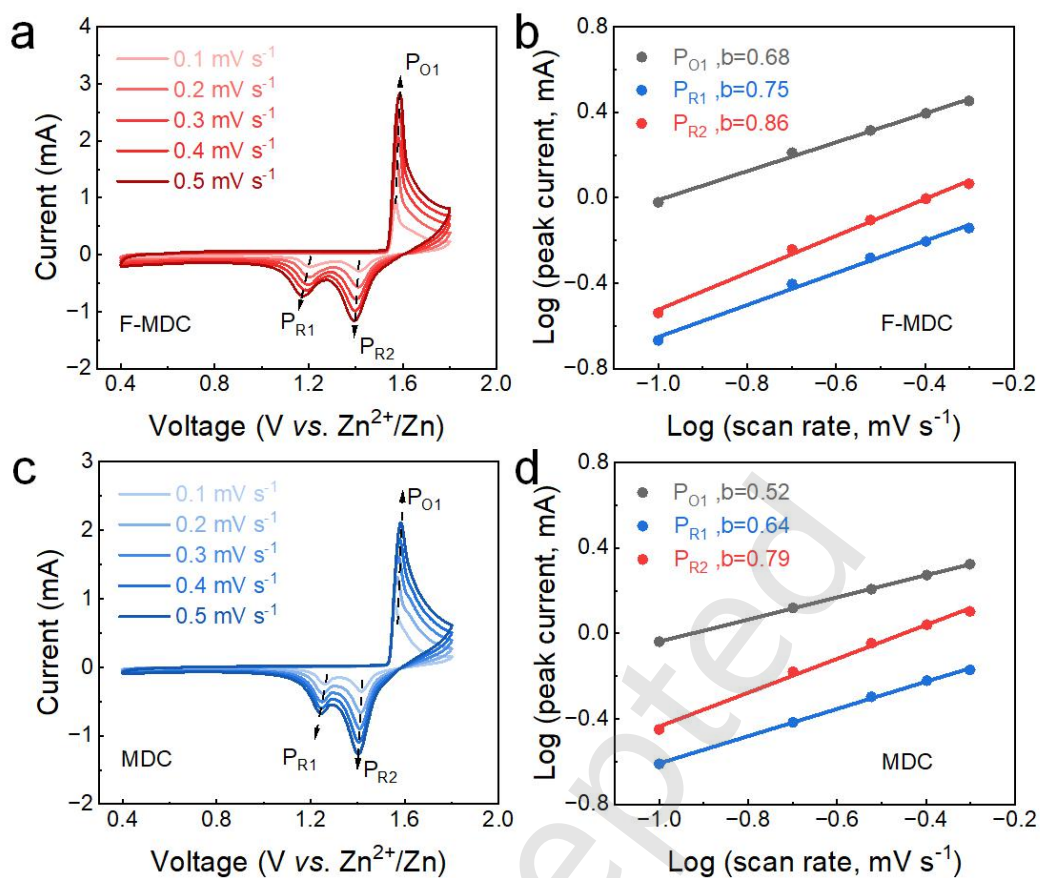


Figure S33 Kinetic analysis of F-MDC and MDC. (a) CV curves of F-MDC at various scan rates, (b) Log i vs. Log v plots of F-MDC, (c) CV curves of MDC, (d) Log i vs. Log v plots of MDC.

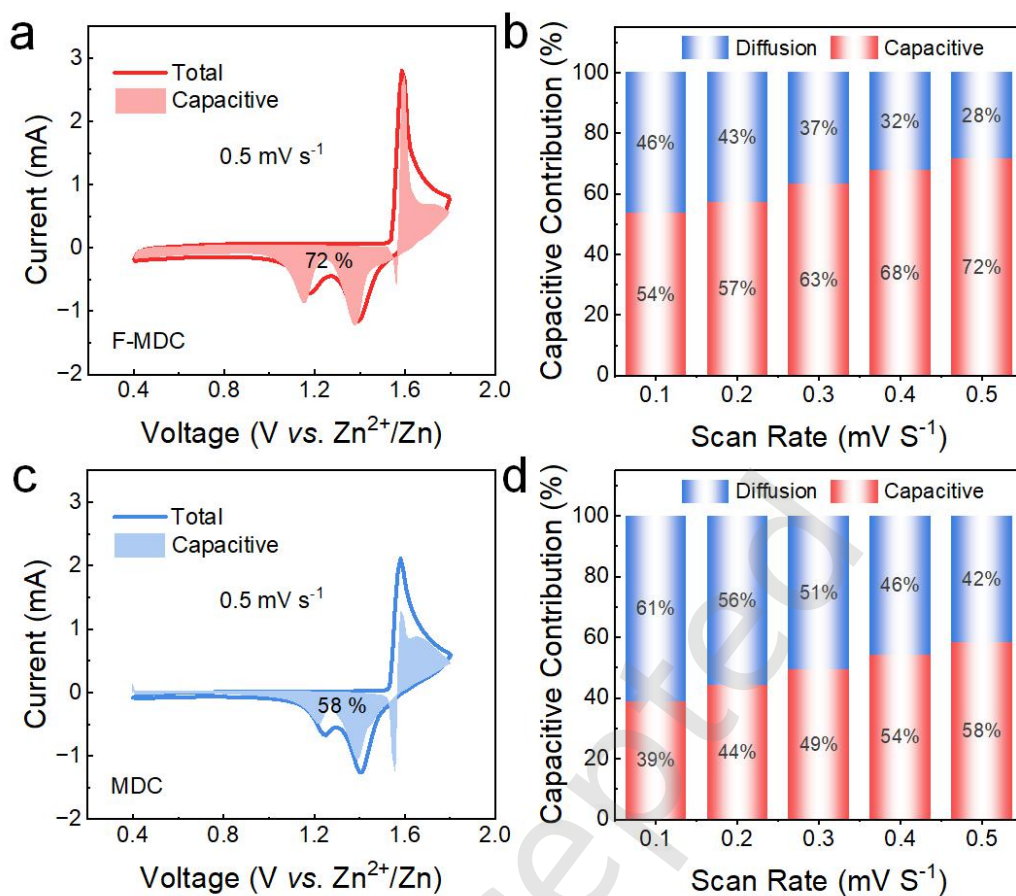


Figure S34. Pseudocapacitive behavior analysis of F-MDC and MDC. (a) Pseudocapacitive contribution of F-MDC at a scan rate of 0.3 mV s^{-1} , (b) Pseudocapacitive contribution ratio of F-MDC at different scan rates, (c) Pseudocapacitive contribution of MDC at 0.3 mV s^{-1} , (d) Pseudocapacitive contribution ratio of MDC at various scan rates.

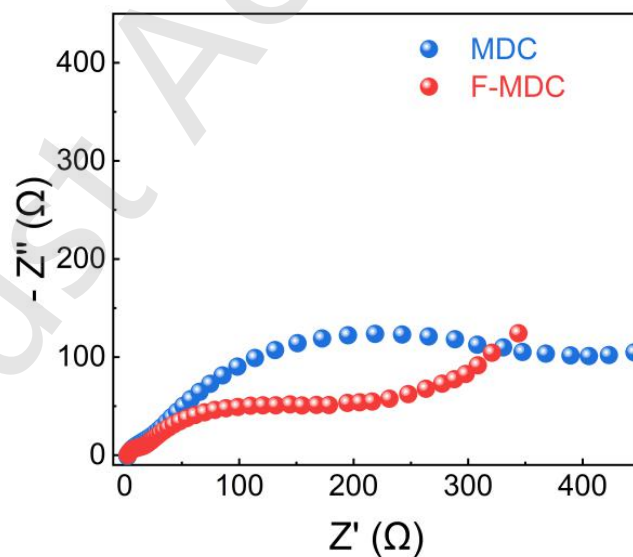


Figure S35 EIS plots of F-MDC and MDC.

After 100 cycles, the battery was disassembled and the electrode was thoroughly rinsed with ultrapure water and dried. The electrode was reassembled with 0.1 M MnSO_4 + 2 M ZnSO_4 as the electrolyte. Following full charging, the battery was disassembled again, and the Mn^{2+} concentration in the electrolyte was measured by ICP-OES (Table S1). The Mn^{2+} concentration in the F-MDC electrolyte was 0.025 mol L^{-1} , which is markedly lower than that of MDC (0.031 mol L^{-1}), demonstrating that fluorine doping effectively facilitates manganese deposition. This further confirms that the F-MDC substrate improves the reversibility of MnO_2 deposition/dissolution.

Table S1. ICP-OES results of the electrolytes after charging for F-MDC and MDC.

	F-MDC (mol/L)	MDC (mol/L)
Concentration of Mn^{2+}		
ions	0.025	0.031
in the electrolyte		

References

- [1]W. Kohn, L. Sham, Self-Consistent Equations Including Exchange and Correlation Effects, Phys. Rev. 140 (1965) A1133–A1138. <https://doi.org/10.1103/PhysRev.140.A1133>.
- [2]G. Kresse, J. Furthmüller, Efficiency of Ab-Initio Total Energy Calculations for Metals and Semiconductors Using a Plane-Wave Basis Set, Comput. Mater. Sci. 6 (1996) 15–50. [https://doi.org/10.1016/0927-0256\(96\)00008-0](https://doi.org/10.1016/0927-0256(96)00008-0).
- [3]G. Kresse, J. Furthmüller, Efficient Iterative Schemes for Ab Initio Total-Energy Calculations Using a Plane-Wave Basis Set, Phys. Rev. B. 54 (1996) 11169–11186. <https://doi.org/10.1103/PhysRevB.54.11169>.
- [4]S. Grimme, J. Antony, S. Ehrlich, H. Krieg, A Consistent and Accurate Ab Initio Parametrization of Density Functional Dispersion Correction (DFT-D) for the 94 Elements H-Pu, J. Chem. Phys. 132 (2010) 154104. <https://doi.org/10.1063/1.3382344>.
- [5]J.K. Nørskov, J. Rossmeisl, A. Logadottir, L. Lindqvist, J.R. Kitchin, T. Bligaard, H. Jónsson, Origin of the Overpotential for Oxygen Reduction at a Fuel-Cell Cathode, J. Phys. Chem. B 108 (2004) 17886–17892. <https://doi.org/10.1021/jp047349j>.