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# NH<sub>4</sub><sup>+</sup>-mediated interfacial chemistry for collaborative dual-pathway high-mass-loading energy storage

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The deposition/dissolution mechanism of MnO<sub>2</sub> with two-electron transfer is promising for high-energy aqueous energy storage. However, this reaction is severely limited by the kinetically unfavorable dissolution step, a challenge that is greatly exacerbated as the deposit thickens. Herein, by refining NH<sub>4</sub><sup>+</sup>-mediated interface chemistry, we achieve the precise configuration of MnO<sub>2</sub> with controlled hydroxylation, which guides the reversible MnO<sub>2</sub>/Mn<sup>2+</sup> conversion under high-mass-loading conditions. The partially hydroxylated surface further creates a kinetically favorable microenvironment for NH<sub>4</sub><sup>+</sup> storage, ultimately leading to energetic dual-pathway storage behaviors. This enables a remarkable areal capacitance of 13.8 F cm<sup>-2</sup> and sound cycling stability over 6000 cycles under high-mass-loading conditions (27.1 mg cm<sup>-2</sup>). Theoretical calculations reveal that the controlled partial hydroxylation of MnO<sub>2</sub> promotes electronic conduction and lowers the adsorption energy of NH<sub>4</sub><sup>+</sup>, outperforming both highly hydroxylated and pure MnO<sub>2</sub>. The adsorbed NH<sub>4</sub><sup>+</sup> delivers intimate interfacial electronic interaction with partially hydroxylated MnO<sub>2</sub> to trigger local charge redistribution, substantially lowering the MnO<sub>2</sub>/Mn<sup>2+</sup> conversion energy barrier of the nonspontaneous rate-determining step at the NH<sub>4</sub><sup>+</sup>-proximal site. Our findings highlight the significance of the interfacial microenvironment governing the collaborative dual-pathway storage chemistry, which provides guidance for boosting high-mass-loading energy storage.

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## Introduction

The escalating global energy crisis and climate change highlight the great demand for developing clean and sustainable energy techniques,<sup>1–3</sup> e.g., aqueous electrochemical energy storage with inherent safety, environmental friendliness, and cost-effectiveness.<sup>4,5</sup> MnO<sub>2</sub> has been widely considered as an economic and highly promising cathode alternative in a near-neutral environment, featuring a wide operating voltage and high theoretical capacitance.<sup>6,7</sup> However, the sluggish kinetics and the poor stability occur under commercial-level mass loading (≥10 mg cm<sup>-2</sup>), posing significant challenges for sustaining efficient practical applications of MnO<sub>2</sub> electrodes so far.<sup>8,9</sup>

Tremendous efforts have been made to tailor the reactivity and kinetics behaviors of the electrode materials by controlling the microstructure and local reaction environment toward optimal carrier-intercalation/diffusion and interface behaviors.<sup>7,9–13</sup> For instance, it was reported that the structural

stability issue can be partially relieved by harnessing the physical confinement effect and abundant interfacial interactions.<sup>13,14</sup> In another case, robust electronic coupling between the heteroatom and the Mn atom was developed to suppress the structure deformation and Jahn–Teller effect during cycling.<sup>15,16</sup> Despite the progress, under practical scenarios with substantially increased electrode thickness and non-active substances, significant kinetics limitations still exist to compromise the storage capability, stemming from the super-long diffusion distance and complicated interfacial redox process.<sup>17–19</sup> Beyond that, the dynamic reconstruction of the surface/interface happens with deactivation and dissolution, creating a varied local reaction microenvironment over time that requires better control.

In contrast to intercalation chemistry, the MnO<sub>2</sub>/Mn<sup>2+</sup> deposition/dissolution chemistry provides a new opportunity for highly efficient energy storage. The *in situ* formation and interface reset during the charge/discharge process can bypass the undesired compositional/structural evolution and considerable local strain accumulation, responsible for breaking the limitations for energetic and sustainable high-mass-loading applications. Moreover, the topological structure and the spatial arrangement of MnO<sub>2</sub> can be tailored by refining the cation environment and the reactivity. For better practice, the

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high concentration of  $\text{Mn}^{2+}$  is preferred to boost the deposition behaviors and thereby the charges stored. However, a high-concentration pure  $\text{Mn}^{2+}$  electrolyte leads to the suppressed dissolution of  $\text{MnO}_2$  according to Le Chatelier's principle. At the same time, the deposited thick  $\text{MnO}_2$  features highly compromised mass/charge-transfer rates with an inferior utilization rate of active species. An open question appears regarding how to enable better control of the deposition/dissolution chemistry with enhanced conversion kinetics under high  $\text{Mn}^{2+}$  concentration conditions. Besides, it is predicted that synergistically coupling the cation storage with the  $\text{MnO}_2/\text{Mn}^{2+}$  conversion chemistry may potentially boost high-mass-loading energy storage with ultra-efficient utilization of active species. The mechanistic insights can help the step-forward optimization of high-mass-loading energy storage techniques for better applications.

Herein, by introducing  $\text{NH}_4^+$  into a dynamic environment, we overcome the kinetics limitation of  $\text{MnO}_2/\text{Mn}^{2+}$  conversion and trigger its synergistic coupling with  $\text{NH}_4^+$  (de)intercalation chemistry toward an optimal integrated reaction system. This dual-pathway storage mechanism enables a high areal capacitance of  $13.8 \text{ F cm}^{-2}$  for electrodes with a superhigh mass loading of  $27.1 \text{ mg cm}^{-2}$ , along with a good capacitance retention of 80% after 6000 cycles. The theoretical and experimental results indicate that  $\text{NH}_4^+$  acts as the modulator at the reaction interface to precisely control the hydroxylation degree of  $\text{MnO}_2$ , creating a kinetically favorable reaction microenvironment with fast electronic conduction and enhanced interfacial  $\text{NH}_4^+$  adsorption. Furthermore, the adsorption of  $\text{NH}_4^+$  on the reconstructed interface triggers a local charge redistribution, which substantially reduces the energy barrier of the nonspontaneous rate-determining step during dissolution of  $\text{MnO}_2$ , thereby promoting an energetic dual-pathway storage mechanism. This work offers novel insights into cationic environment engineering for mutual manipulation of deposition/dissolution and intercalation chemistry, and provides

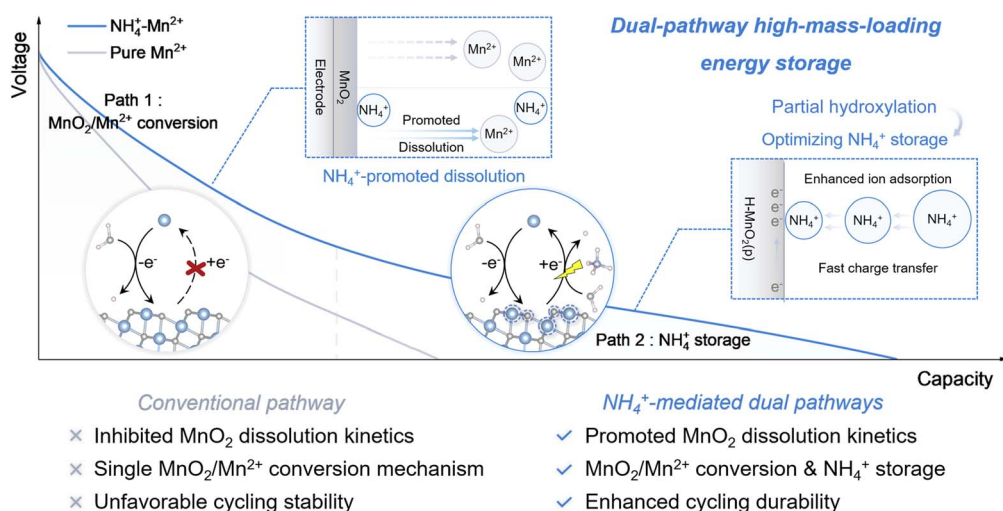
a promising avenue for tailoring better high-mass-loading energy storage.

## Results

### Refining the interfacial microenvironment for favoring $\text{MnO}_2/\text{Mn}^{2+}$ conversion

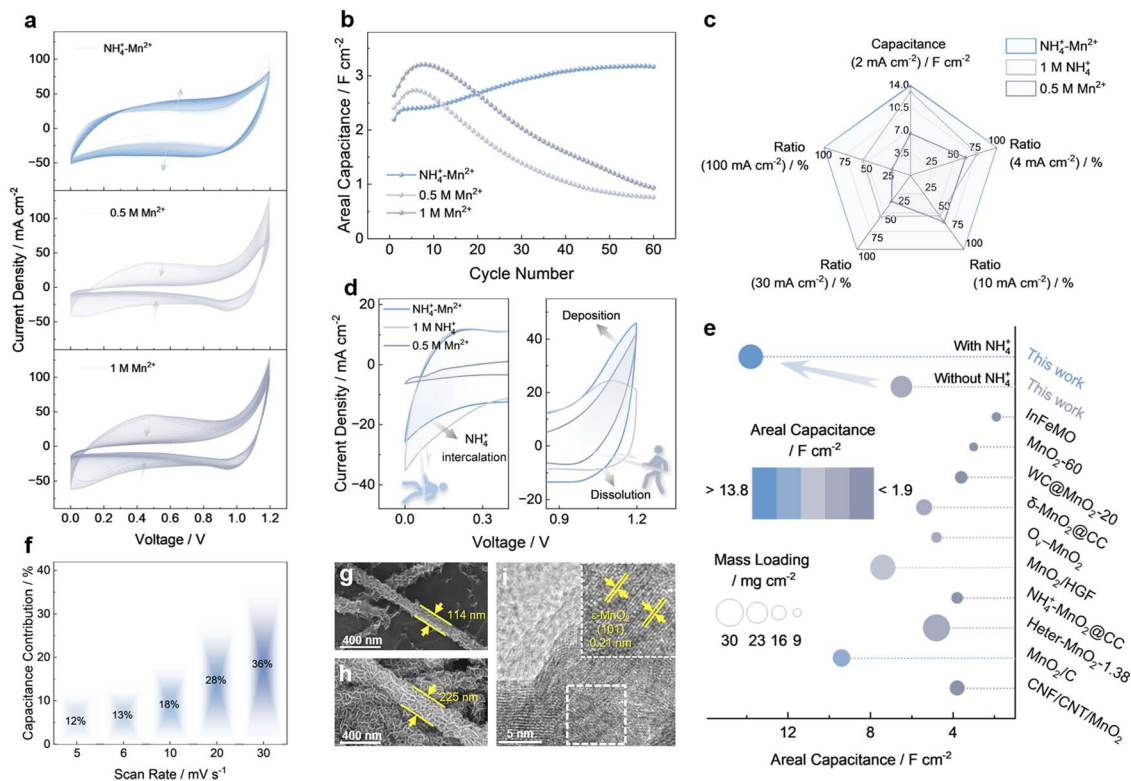
Our previous study has demonstrated that dissolved  $\text{Mn}^{x+}$  assists in the progressive formation of the electrode–electrolyte interphase, providing the energetic dual-cation storage mechanisms.<sup>20</sup> We herein demonstrate the key role of  $\text{NH}_4^+$  in regulating the hydroxylation degree of the derived high-mass-loading  $\text{MnO}_2$ , which is responsible for enhanced intrinsic capability of  $\text{NH}_4^+$  storage (Scheme 1). More importantly, optimized  $\text{MnO}_2$  dissolution chemistry is revealed with  $\text{NH}_4^+$  in the electrode–electrolyte interface, leading to the collaborative dual-pathway energy storage. The reaction system and the new concept in the collaborative interface chemistry can help break the bottleneck toward energetic high-mass-loading energy storage (Scheme 1).

We start with the formation of an active  $\text{MnO}_2$  substrate through phosphate-assisted *in situ* reconstruction.<sup>20</sup> By studying its charge/discharge properties in  $0.5 \text{ M Mn}^{2+}$  electrolyte, we found an increase of the CV curve area and thereby the areal capacitance value for the first 10 cycles (Fig. 1a and b), along with the increased active mass with cycling (SI Fig. 1). However, further cycling leads to a significant performance decline, indicating an unstable storage interface derived from poorly controlled deposition/dissolution chemistry. Increasing the  $\text{Mn}^{2+}$  concentration to  $1 \text{ M}$  leads to an increment of the areal capacitance, but the poor sustainability of the reaction system remains unsolved. In sharp contrast, we discovered that the areal capacitance exhibits a continuous increment during electrochemical cycling in the  $\text{NH}_4^+-\text{Mn}^{2+}$  mixed electrolyte, which achieves the highest value after 60 CV cycles (Fig. 1a and b). The derived 60-cycled electrode in  $\text{NH}_4^+-\text{Mn}^{2+}$  mixed electrolyte was denoted as Rec-NM- $\text{MnO}_2$  for further study.



Scheme 1 Schematics of collaborative dual-pathway high-mass-loading energy storage.





**Fig. 1** Regulation of electrolytes and substrates. (a) CV curves of the activated MnO<sub>2</sub> substrate in different electrolytes. (b) Performance evolution of the active MnO<sub>2</sub> substrate with cycling in different electrolyte environments. (c) Comparison of areal capacitance for Rec-NM-MnO<sub>2</sub> in different electrolytes and the ratio of the capacitance measured in different electrolytes to that measured in NH<sub>4</sub><sup>+</sup>-Mn<sup>2+</sup> mixed electrolyte. (d) Comparison of CV curves at a scan rate of 2 mV s<sup>-1</sup> for the Rec-NM-MnO<sub>2</sub> electrode in different electrolytes. (e) Comparison of the areal capacitance for the Rec-NM-MnO<sub>2</sub> electrode with previously reported high-mass-loading MnO<sub>2</sub>-based electrodes. (f) Capacitive contributions for Rec-NM-MnO<sub>2</sub>. (g and h) SEM images of Rec-NM-MnO<sub>2</sub> (g) before and (h) after electrochemical cycling. (i) HRTEM image of Rec-NM-MnO<sub>2</sub>.

To further test the superiority of the mixed electrolyte system, we applied the bare carbon substrate (electrochemically exfoliated graphene, EG) to eliminate the influence of active MnO<sub>2</sub>. A fast increase of areal capacitance with cycling was observed by using the pure EG substrate, ultimately achieving a decent areal capacitance of 9.3 F cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> (SI Fig. 5). This result reflects the superiority of NH<sub>4</sub><sup>+</sup>-Mn<sup>2+</sup> mixed electrolyte to sustain the deposition/dissolution behaviors of MnO<sub>2</sub>. Of note, a highly improved capacitance was demonstrated by applying the active MnO<sub>2</sub> electrode as the substrate (SI Fig. 5), attributed to more abundant nucleation sites and a larger accessible area for better deposition/dissolution chemistry. It delivers an appealing areal capacitance with a high value of 13.8 F cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> and maintains an areal capacitance of 2.9 F cm<sup>-2</sup> at 50 mA cm<sup>-2</sup> (Fig. 1c and SI 3d), superior to many state-of-the-art high-mass-loading electrodes (Fig. 1e and SI Table S1).<sup>6,21-29</sup> Moreover, it displays good cycling stability with a retention of 80% after 6000 cycles (SI Fig. 3i).

The analysis of capacitive contribution and the *b* value by Dunn's method indicates a diffusion-controlled behavior during the charge-storage process (Fig. 1f and SI 2b). An asymmetric supercapacitor (Rec-NM-MnO<sub>2</sub>//active carbon) was configured and investigated in the NH<sub>4</sub><sup>+</sup>-Mn<sup>2+</sup> mixed electrolyte. It delivers a high areal capacitance of 3.1 F cm<sup>-2</sup> at 4 mA

cm<sup>-2</sup> (SI Fig. 6d), alongside a maximum energy density of 1070 μWh cm<sup>-2</sup>, which is superior to many previously reported results (SI Fig. 6e).<sup>30-36</sup> Besides, it can operate stably for 500 cycles at a current density of 120 mA cm<sup>-2</sup> (SI Fig. 6f). Please refer to SI Note 2 for details.

### Revealing the reconstructed high-mass-loading electrode structure

To reveal the reconstructed structure, we first collected scanning electron microscopy (SEM) and high-resolution transmission electron microscopy (HRTEM) images. Before cycling, it demonstrates a core-shell heterostructure with ultra-thin nanosheets uniformly distributed (Fig. 1g and SI 7). It is noted that the unique structure with a large active area creates rich nucleation sites for the energetic MnO<sub>2</sub> deposition process, in good agreement with our electrochemical results (SI Fig. 5).<sup>20</sup> After 60 cycles in the NH<sub>4</sub><sup>+</sup>-Mn<sup>2+</sup> mixed electrolyte, the Rec-NM-MnO<sub>2</sub> microstructure features the dense stacking of nanosheets with an enlarged size and thickness compared to before, causing an increase of the overall diameter of the heterostructure from 114 nm to 225 nm and thereby an increment of mass loading from 7.4 mg cm<sup>-2</sup> to 27.1 mg cm<sup>-2</sup> (Fig. 1g, h, SI 7a and b and 8a-d). The accumulation of mass loading is further indicated by an increase of the charge transfer



resistance ( $R_{ct}$ ) from 1.10  $\Omega$  to 6.12  $\Omega$  (SI Fig. 9a–c and Table S2). Notably, the system ohmic impedance ( $R_s$ ) of the Rec-NM-MnO<sub>2</sub> electrode is as low as 0.61  $\Omega$  (SI Fig. 9a–c and Table S2), compared to the pristine electrode (0.49  $\Omega$ ). Meanwhile, the Warburg factor ( $\sigma$ ) of the samples after different cycles exhibits slight variation in the range of 3.6 to 5.55 (SI Fig. 9d), demonstrating a favorable ion diffusion capability in the thick electrode. The lattice spacing of 0.21 nm in HRTEM images can be indexed to the (101) plane of  $\epsilon$ -MnO<sub>2</sub> (Fig. 1i and SI 8e).<sup>37</sup> One detail is the uniform distribution of N elements on the pristine active substrate, as shown by elemental mapping, which might come from intercalated NH<sub>4</sub><sup>+</sup> and the dopamine-derived N-doped carbon layer (SI Fig. 8f).

*Ex situ* X-ray diffraction (XRD) measurements were carried out to further reveal the structural evolution with cycling. As shown in Fig. 2a, the pristine active substrate shows diffraction peaks located at 36.2, 43.0, and 65.6°, indexed to the (110), (11-2), and (020) planes of  $\delta$ -MnO<sub>2</sub> (JCPDS card no. 43-1456).<sup>20,22,38</sup> However, after cycling, the as-made Rec-NM-MnO<sub>2</sub> electrode

exhibits diffraction peaks at 37.1, 42.4, and 66.2°, which are matched well with the (100), (101), and (110) planes of  $\epsilon$ -MnO<sub>2</sub> (JCPDS card no. 30-0820), in good accordance with the HRTEM results.<sup>39,40</sup> The transformation of the main structure of the material is further reflected by the gradual shift of diffraction peaks with cycling (SI Fig. 10). Of note, there is an increase in the relative peak intensity of MnO<sub>2</sub> compared with that of the EG substrate, attributed to the gradual accumulation of  $\epsilon$ -MnO<sub>2</sub> upon electrochemical cycling. These results indicate that, despite the enhanced kinetics, the active substrate features a higher deposition rate than that of the dissolution one during the early stage of cycling. The reconstructed reaction interface modulated by the accumulated  $\epsilon$ -MnO<sub>2</sub> might play a key role in the highly improved electrochemical energy storage behaviors.

*Ex situ* X-ray photoelectron spectroscopy (XPS) measurement was conducted to study the evolution of the interfacial electronic structure. The peak separation energy ( $\Delta E$ ) of Mn 3s increases from 4.91 eV for pristine MnO<sub>2</sub> to 5.13 eV after the first two cycles (Fig. 2b and SI 11a), suggesting the decrease of

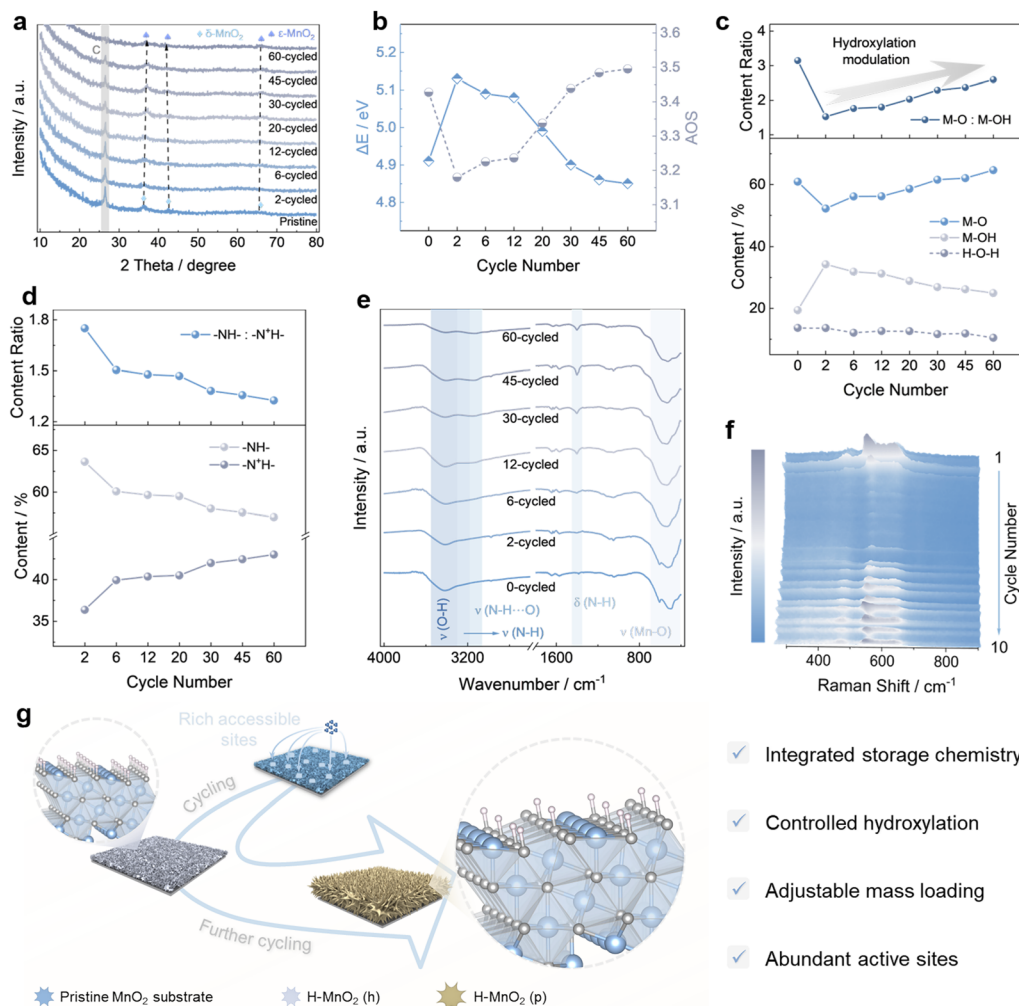


Fig. 2 Structure and composite analysis during electrochemical cycling. (a–e) *Ex situ* investigations of the active MnO<sub>2</sub> substrate: (a) XRD patterns; (b)  $\Delta E$  value of Mn 3s peaks and the AOS of Mn; characteristic content analysis based on (c) the O 1s spectra and (d) the N 1s spectra; (e) FTIR spectra. (f) *Operando* Raman contour maps of the active MnO<sub>2</sub> substrate during electrochemical cycling. (g) Schematic illustration of the development of the high-mass-loading partially hydroxylated  $\epsilon$ -MnO<sub>2</sub> electrode.



the average oxidation state (AOS) of Mn from 3.42 to 3.18 with the accumulation of  $\varepsilon$ -MnO<sub>2</sub>. Subsequently, the AOS of Mn increases to 3.49, demonstrating that surface oxidation happens with further cycling. This is also the case in the pure 0.5 M Mn(NO<sub>3</sub>)<sub>2</sub> electrolyte (SI Fig. 12). The O 1s fine spectra can be decoupled and fitted into three components at 530.1, 531.6, and 533.2 eV, assigned to M–O–M, M–OH, and H–O–H, respectively (Fig. 2c and SI 11b).<sup>41</sup> The content ratio between M–O–M and M–OH bonds exhibits a reduction after the first two cycles and a gradual increase in the subsequent cycles. This suggests the initial formation of MnO<sub>2</sub> with a high hydroxylation degree (H-MnO<sub>2</sub>(h)), but the hydroxylation degree shows a slight decrease with further cycling, yielding the partially hydroxylated MnO<sub>2</sub> (H-MnO<sub>2</sub>(p)) for the Rec-NM-MnO<sub>2</sub> electrode. In the early stage, it is believed that a considerable amount of H<sup>+</sup> was produced with the hydrolysis of Mn<sup>2+</sup> and the deprotonation effect of NH<sub>4</sub><sup>+</sup>, which promotes the transformation from M–O–M to M–O–H bonds with discharging.<sup>42</sup> The similar evolution of M–O–M and M–O–H bonds is found during deposition in the pure 0.5 M Mn<sup>2+</sup> electrolyte (SI Fig. 13). However, a relatively low hydroxylation degree was demonstrated, attributed to the inferior H<sup>+</sup> supply during hydroxylation.

The N 1s spectra of the pristine active substrate show two main peaks at 400.2 and 407.3 eV, attributed to the –NH– bond derived from dopamine (PDA)-derived carbon and NO<sub>3</sub><sup>–</sup> from the NaNO<sub>3</sub> electrolyte, respectively (SI Fig. 11c).<sup>20,43,44</sup> Note that a new peak located at 401.4 eV, ascribed to the –N<sup>+</sup>H– bond, appears at the second cycle, which originates from the NH<sub>4</sub><sup>+</sup> intercalated in MnO<sub>2</sub>. Besides, the content ratio between –NH– and –N<sup>+</sup>H– bonds gradually decreases with cycling (Fig. 2d and SI 11c), indicative of the varied main N source and the gradual accumulation of NH<sub>4</sub><sup>+</sup>-intercalated MnO<sub>2</sub>, which is also evidenced by XPS full-spectra (SI Fig. 11d and e). Moreover, it is also demonstrated by the *ex situ* Fourier transform infrared spectra (FTIR), where the characteristic absorptions indexed to the N–H bending vibration (1400 cm<sup>–1</sup>), N–H⋯O bending vibration (3100–3180 cm<sup>–1</sup>) and N–H stretching vibration (3180–3300 cm<sup>–1</sup>) show an increase in intensity, while the peak indexed to the O–H stretching vibration (3300–3600 cm<sup>–1</sup>) decays with cycling (Fig. 2e and SI 11f), which is consistent with the O 1s results (Fig. 2c).<sup>23,45</sup>

We focused on the first two cycles to study the structural evolution of the active substrate by *ex situ* characterization (SI Fig. 14–16). XRD results show periodic changes in the characteristic diffraction peaks (SI Fig. 14). There is a dynamic increase/decrease for the ratio of M–O–M/M–OH with reversible oxidation/reduction (SI Fig. 16), indicating H<sup>+</sup> participation in the early stage (please refer to SI Fig. 14–16 for details).

To gain more insights into the microstructure transformation, *operando* Raman characterization was performed. The pristine active substrate demonstrates three main peaks at 645 cm<sup>–1</sup> ( $\nu_1$ ), 571 cm<sup>–1</sup> ( $\nu_2$ ), and 497 cm<sup>–1</sup> ( $\nu_3$ ), associated with the symmetric stretching vibration of the Mn–O bond along the d<sub>z<sup>2</sup></sub> orbital within [MnO<sub>6</sub>] octahedra, the stretching vibration in the basal plane along the d<sub>x<sup>2</sup>–y<sup>2</sup></sub> orbital, as well as the weak Mn–O vibration mode, respectively (SI Fig. 17a).<sup>46,47</sup> The intensity of

these major peaks ( $\nu_1$ ,  $\nu_2$ , and  $\nu_3$ ) weakened during the first several cycles of deposition (Fig. 2f and SI 17b). This phenomenon might originate from the generation and accumulation of new substances, *i.e.*, hydroxylated MnO<sub>2</sub> on the surface of the original MnO<sub>2</sub> as discussed (Fig. 2c and SI 11b). As the hydroxylation degree slightly decreases with cycling, the characteristic peaks of MnO<sub>2</sub> demonstrate increasing intensity (Fig. 2f and SI 17b). We further focus on the *operando* Raman spectra during the 10th cycle with the well-defined characteristic peaks. As shown in Fig. 2f and SI 17d, with charging,  $\nu_1$  and  $\nu_2$  shift negatively and positively, respectively, and both of them shift back to the original locations upon discharging, indicating a highly reversible lattice deformation with NH<sub>4</sub><sup>+</sup> insertion/extraction.<sup>8,23,47–52</sup> A similar evolution trend was observed during the 1st cycle, except for the spectra in the potential range from 0 to 0.19 V. This unique oscillation phenomenon indicates a significant change in the surface chemical environment with the voltage applied (Fig. 2f and SI 17c).

XPS depth profiles were collected to gain more insights into the surface-accumulated hydroxylated  $\varepsilon$ -MnO<sub>2</sub> of the derived Rec-NM-MnO<sub>2</sub> electrode. A high content of Mn–OH (>20%) was found after different etching times, indicative of the considerable hydroxylation degree in the bulk structure upon cycling (Fig. 3f and SI 18b). It is further found that the outermost surface of the electrode demonstrates a higher hydroxylation degree.

The above results have evidenced the interface reconstruction with the accumulation of H-MnO<sub>2</sub>(p) with high mass loading when cycling in the mixed NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> electrolyte (Fig. 2g), responsible for a significant increase in electrochemical performance (Fig. 1e and SI Table S1).

### Understanding the role of NH<sub>4</sub><sup>+</sup> in the reconstructed interface

After understanding the promising nature of H-MnO<sub>2</sub>(p), we further performed a series of electrochemical analyses and *in situ/ex situ* characterization experiments to gain insights into two questions: (1) what is the key role of NH<sub>4</sub><sup>+</sup> in boosting high-mass-loading energy storage? (2) How does NH<sub>4</sub><sup>+</sup> help overcome the inherent dissolution kinetics limitations?

We first studied the electrochemical behaviors of the Rec-NM-MnO<sub>2</sub> electrode in the pure 0.5 M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub> or 0.5 M Mn(NO<sub>3</sub>)<sub>2</sub> electrolyte. The electrode exhibits a higher areal capacitance value in the mixed electrolyte than its counterparts, reinforcing an effective collaborative storage mechanism (Fig. 1c, SI 3a–d and 4). It displays a pronounced oxidation current by using the NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> or 0.5 M Mn(NO<sub>3</sub>)<sub>2</sub> electrolyte (Fig. 1d and SI 3e), attributed to Mn<sup>2+</sup>-to-MnO<sub>2</sub> deposition in the Mn<sup>2+</sup> rich reaction environment.<sup>53,54</sup> In contrast, the reduction current from 1.2 V to 0.9 V increases a lot with NH<sub>4</sub><sup>+</sup> introduction (Fig. 1d and SI 3e), suggesting a unique role of NH<sub>4</sub><sup>+</sup> in promoting MnO<sub>2</sub> dissolution, which contributes to an increased discharge capacitance.<sup>53,54</sup>

This is also demonstrated by the charge evolution analysis of the Rec-NM-MnO<sub>2</sub> electrode (SI Fig. 3f and g), wherein an obvious charge accumulation was observed in the pure Mn<sup>2+</sup> electrolyte, indicative of inadequate dissolution dynamics. In





Fig. 3 Study of the energy storage mechanism of Rec-NM-MnO<sub>2</sub>. (a–e) *Ex situ* characterization of the Rec-NM-MnO<sub>2</sub> electrode at different voltages: (a) XRD patterns; (b)  $\Delta E$  value of Mn 3s peaks and the AOS of Mn; (c) N 1s spectra and position variation of the peak relative to the  $-N^+H$ -bond; (d) O 1s spectra and corresponding content analysis; (e) FTIR spectra. (f) The content analysis of the O 1s spectra for Rec-NM-MnO<sub>2</sub> with different etching times. (g and h) *Operando* characterization of Rec-NM-MnO<sub>2</sub>: (g) Raman contour map and (h) EIS spectra.

contrast, gradual charge consumption was found when cycling in the pure  $NH_4^+$  electrolyte, implying promoted  $MnO_2$  dissolution with  $NH_4^+$  introduction. This is further evidenced by significantly weakened charge accumulation in  $NH_4^+-Mn^{2+}$  mixed electrolyte in comparison to that in the pure  $Mn^{2+}$  electrolyte.<sup>55</sup> In addition, with further discharging, an obvious reduction peak was observed in  $NH_4^+-Mn^{2+}$  or 0.5 M  $(NH_4)_2SO_4$  electrolyte (Fig. 1d and SI 3e), which might originate from the extensive intercalation of  $NH_4^+$  in the  $NH_4^+$ -rich environments.<sup>23,54</sup> We have further studied the electrochemical behaviors in a series of mixed electrolyte environments, evidencing the unique role of  $NH_4^+$  in boosting charge-storage capability of the reaction system (SI Fig. 3h).

Then, we studied the energy storage mechanism of the Rec-NM-MnO<sub>2</sub> electrode in the  $NH_4^+-Mn^{2+}$  mixed electrolyte. According to *ex situ* XRD patterns, the diffraction peaks, relative to the (110) and (020) planes of  $\epsilon$ -MnO<sub>2</sub>, demonstrate a positive shift of 0.6° and 0.5° with charging, respectively, and return to

the original locations upon discharging, which might originate from the interaction between  $NH_4^+$  and  $\epsilon$ -MnO<sub>2</sub> (Fig. 3a).<sup>56</sup> This is accompanied by the reversible change of the average oxidation state (AOS) of Mn (Fig. 3b and SI 18a). The characteristic peak indexed to the  $-NH^+$  bond displays a negative shift of  $\sim 0.3$  eV with charging (Fig. 3c), and shifts back upon discharging, implying the reversible deintercalation/intercalation of  $NH_4^+$  and its potential interaction with MnO<sub>2</sub>. Another detail is the negligible change of Mn–O–H content upon discharging, indicative of the negligible contribution of  $H^+$  storage after interface reconstruction, which is responsible for the enhanced cycling stability (Fig. 3d).<sup>57</sup> This phenomenon is attributed to the accumulation of  $\epsilon$ -MnO<sub>2</sub> with partial hydroxylation during cycling, which leads to the fast consumption of free  $H^+$  in the electrolyte environment. Moreover, the FTIR spectra demonstrate the reversible decrease/increase of peak intensity for the N–H/N–H $\cdots$ O bending vibration and N–H stretching vibration during charging/discharging, while the peak indexed to the O–



H stretching vibration shows a negligible change, reinforcing that  $\text{NH}_4^+$  serves as the charge carrier during the energy storage process (Fig. 3e and SI 18c).

We further collected the *operando* Raman spectra of the Rec-NM-MnO<sub>2</sub> electrode for tracking the  $\text{NH}_4^+$  storage behaviors. With charging,  $\nu_1$  shifts positively from 639  $\text{cm}^{-1}$  to 650  $\text{cm}^{-1}$  (Fig. 3g and SI 19), ascribed to the oxidation of the Mn element and enhancement of the Mn–O stretching vibration along the  $d_{z^2}$  orbital of  $[\text{MnO}_6]$  octahedra due to the extraction of  $\text{NH}_4^+$ .<sup>23,47–50</sup> Moreover, the  $\nu_2$  peak shows an enhanced intensity and a negative shift of 8  $\text{cm}^{-1}$  from 580  $\text{cm}^{-1}$  to 572  $\text{cm}^{-1}$  during charging, originating from the increase of Mn(IV) in the  $[\text{MnO}_6]$  framework and reduced Jahn–Teller disorder, accompanied by  $\text{NH}_4^+$  deintercalation.<sup>8,47,52</sup> Both of them shift back to the pristine locations upon discharging, indicative of the reversible structural change with charge carrier deintercalation/intercalation. *Operando* electrochemical impedance spectra (EIS) of the Rec-NM-MnO<sub>2</sub> electrode demonstrate that the semicircle diameter indexed to the charge transfer resistance

( $R_{\text{ct}}$ ) decreases with charging, while the slope in the low-frequency region relative to the ionic diffusion process increases (Fig. 3h and SI 2a). The reversed changes were observed with discharging, further confirming the highly reversible evolution of reaction dynamics.

The above results indicated that  $\text{NH}_4^+$  serves as the charge carrier during the charge/discharge process of the Rec-NM-MnO<sub>2</sub> electrode. To further study the effect of  $\text{NH}_4^+$  in the mixed reaction system, the electrochemical behaviors of Rec-NM-MnO<sub>2</sub> were further studied in the pure  $\text{Mn}^{2+}$  electrolyte. In this case, the capacitance gradually falls behind that in the  $\text{NH}_4^+$ – $\text{Mn}^{2+}$  mixed electrolyte with cycling (Fig. 4a). *Ex situ* XPS results demonstrate the irreversible change of the AOS of Mn after one charge/discharge cycle in the pure  $\text{Mn}^{2+}$  electrolyte, resulting in a higher oxidation state of Mn (SI Fig. 20), indicative of an unsatisfactory dissolution dynamics. The fast MnO<sub>2</sub> accumulation but unfavorable dissolution kinetics, *i.e.*, an irreversible deposition/dissolution process, serve as the main cause of a fast discharge capacitance decay. The inconspicuous variation in



Fig. 4 Understanding the MnO<sub>2</sub> dissolution behavior assisted by  $\text{NH}_4^+$ . (a) The capacitance ratio of the Rec-NM-MnO<sub>2</sub> electrode in the 0.5 M  $\text{Mn}(\text{NO}_3)_2$  or 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  electrolyte to that in the  $\text{NH}_4^+$ – $\text{Mn}^{2+}$  mixed electrolyte at 2  $\text{mA cm}^{-2}$ . (b) The digital images of  $(\text{NH}_4)_2\text{SO}_4$  electrolyte before and after cycling. (c) *Operando* Raman contour map of Rec-NM-MnO<sub>2</sub> in 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  electrolyte. (d–f) *Ex situ* XPS characterization of the Rec-NM-MnO<sub>2</sub> electrode during the first two GCD cycles in the pure 0.5 M  $(\text{NH}_4)_2\text{SO}_4$  electrolyte: (d) O 1s spectra; (e) content analysis of the O 1s spectra; (f) Mn 3s spectra. (g) Schematic diagram of the electrochemical behavior for Rec-NM-MnO<sub>2</sub> in the  $\text{NH}_4^+$ – $\text{Mn}^{2+}$  mixed electrolyte.



the content of the Mn–O–H bond also manifests the negligible contribution of H<sup>+</sup> storage in the pure Mn<sup>2+</sup> electrolyte (SI Fig. 21).

Of particular note, the capacitance of Rec-NM-MnO<sub>2</sub> in the pure NH<sub>4</sub><sup>+</sup> electrolyte displays a dramatic decline, with only 52% of the capacitance retained compared with that in the mixed electrolyte after 8 cycles (Fig. 4a). At the same time, we noticed the significantly darkened brown color of the electrolyte (Fig. 4b). This detail indicates the fast dissolution of active Mn species into Mn ions, accompanied by the irreversible disproportionation of Mn<sup>3+</sup> in the pure NH<sub>4</sub><sup>+</sup> electrolyte, which triggers the sharp decrease of capacitance. *Operando* Raman characterization was employed to further study the microstructure evolution after adopting the pure NH<sub>4</sub><sup>+</sup> electrolyte.  $\nu_1$  demonstrates a positive shift of 15 cm<sup>-1</sup> during charging (Fig. 4c and SI 22), analogous to the scenario in the mixed electrolyte, suggesting the extraction of NH<sub>4</sub><sup>+</sup> and the oxidation of Mn centers.<sup>23,47–50</sup> Nevertheless, no reverse shift is observed for the  $\nu_1$  peak in the discharge stage (Fig. 4c and SI 22), indicating the emergence of irreversible oxidation/dissolution processes, in good accordance with our discussion, as shown in Fig. 4a. This is in good agreement with our electrochemical results in the pure NH<sub>4</sub><sup>+</sup> electrolyte, *e.g.*, the considerable increase of the reduction current (Fig. 1d), the variation of charge accumulation (SI Fig. 3f and g), and the decreased discharge capacitance (Fig. 4a), which concurrently evidence an NH<sub>4</sub><sup>+</sup>-promoted dissolution dynamics.<sup>58,59</sup>

Through the *ex situ* XPS measurement, we noticed a considerable change in the content of the Mn–O–H bond during charging/discharging (Fig. 4d and e), indicating a significant proton-storage process along with local structural distortion, which destabilizes the structure and facilitates the dissolution of MnO<sub>2</sub> during electrochemical processes. Besides, the most significant variation range of the AOS of Mn (0.47) was found in the pure NH<sub>4</sub><sup>+</sup> electrolyte (Fig. 4f and SI 23a). The periodic shifts of the –N<sup>+</sup>H– peak are associated with the intercalation and deintercalation of NH<sub>4</sub><sup>+</sup> during the cycles (SI Fig. 23b and c). The intercalated NH<sub>4</sub><sup>+</sup> could also increase local structural disorder, facilitating the interaction of MnO<sub>2</sub> with H<sup>+</sup> for enhanced dissolution kinetics.<sup>47</sup>

In addition, in the NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> mixed electrolyte system, NH<sub>4</sub><sup>+</sup> competes with Mn<sup>2+</sup> for weakly bound water molecules in the outer solvation sheath through hydrogen bonds and ion-dipole interactions (with solvated H<sub>2</sub>O), which breaks the compact and ordered solvation configuration of [Mn(H<sub>2</sub>O)<sub>6</sub>]<sup>2+</sup> in the pure Mn<sup>2+</sup> electrolyte.<sup>60,61</sup> This reconstruction increases the diversity and weakens the aggregation of solvation structures, thereby elevating the solvation-configurational entropy.<sup>62,63</sup> It has been reported that high solvation-configurational entropy can effectively reduce the desolvation energy barrier and accelerate interfacial charge-transfer kinetics.<sup>64,65</sup> Meanwhile, the optimized solvation environment is expected to facilitate fast and reversible transport of both NH<sub>4</sub><sup>+</sup> and Mn<sup>2+</sup> by reducing the desolvation energy barrier and weakening the electrostatic aggregation between cationic solvation clusters.<sup>64,66</sup> Additionally, the weakly aggregated solvation clusters can also suppress local ion concentration polarization and the subsequent severe

interfacial side reactions, thus stabilizing the electrode/electrolyte interface and maintaining the structural integrity of partially hydroxylated MnO<sub>2</sub>, contributing to good cycling stability.<sup>67,68</sup>

Therefore, with NH<sub>4</sub><sup>+</sup> introduced into the reconstructed reaction interface, a synergistic energy storage mechanism integrating the MnO<sub>2</sub> deposition/dissolution process coupled with NH<sub>4</sub><sup>+</sup> storage was enabled (Fig. 4g). This NH<sub>4</sub><sup>+</sup>-assisted cationic environment not only overcomes the dissolution kinetics limitation but also brings additional capacitance contribution through NH<sub>4</sub><sup>+</sup> storage, leading to sustainable and collaborative dual-pathway high-mass-loading energy storage.

### Deciphering the dual-pathway storage mechanism

The X-ray absorption near-edge structure (XANES) characterization was conducted to gain more insights into the evolution of active Mn species. In the Mn K-edge spectra, the absorption edge energy of Rec-NM-MnO<sub>2</sub> shows a positive shift to higher energy upon charging (Fig. 5a), indicating the increased oxidation state. Of particular note, the Mn species fabricated by 60 CV cycling in the pure Mn<sup>2+</sup> system exhibits a higher valence at 0 V, which is even closer to that in the NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> mixed system at 1.2 V (Fig. 5a, SI 24a and b). This is mainly attributed to the sluggish dissolution dynamics for MnO<sub>2</sub> in the pure Mn<sup>2+</sup> system, resulting in a higher oxidation state at the same discharged state, in good accordance with the *ex situ* XPS analysis. As shown in the Fourier-transformed (FT) *k*<sup>3</sup>-weighted extended XAFS (FT-EXAFS) spectra in Fig. 5b, the peaks located at 1.42 and 2.43 Å indexed to Mn–O and Mn–Mn bonds, respectively, exhibit almost no change in shifts after charging to 1.2 V in NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> mixed electrolyte, implying the structural stability of Rec-NM-MnO<sub>2</sub> during cycling, in good accordance with the results of the *ex situ* O 1s spectra (Fig. 3d).<sup>69,70</sup> The wavelet transform (WT) analysis further corroborates that the intensity of the Mn–Mn bond experiences a slight increase as the operating voltage ascends (Fig. 5c). In the NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> mixed system, the slightly lower intensity of peaks at 0 V than that at 1.2 V is ascribed to insertion of NH<sub>4</sub><sup>+</sup> and the structural distortion derived from the decline of Mn valence (SI Fig. 24c). Furthermore, the R-space curve in the pure Mn<sup>2+</sup> electrolyte shows a high similarity to that in NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> mixed electrolyte (SI Fig. 24d), demonstrating the same coordination environment of MnO<sub>2</sub> generated, consistent with the XRD analysis (SI Fig. 14c).

Our study has demonstrated the formation of partially hydroxylated MnO<sub>2</sub> (H-MnO<sub>2</sub>(p)) as the true active species in the NH<sub>4</sub><sup>+</sup>–Mn<sup>2+</sup> mixed system to guide the deposition/dissolution process. For further clarification of the working mechanisms, density functional theory (DFT) simulations were conducted to study the influence of the hydroxylation degree on the interfacial reaction dynamics. As shown in SI Fig. 25, we chose pure  $\epsilon$ -MnO<sub>2</sub> (named pure MnO<sub>2</sub>), H-MnO<sub>2</sub>(p), and H-MnO<sub>2</sub>(h) (highly hydroxylated MnO<sub>2</sub>) as models for the calculations. The H-MnO<sub>2</sub>(p) and H-MnO<sub>2</sub>(h) structures are modelled as  $\epsilon$ -MnO<sub>2</sub> with small and large amounts of hydroxyl groups adsorbed on the (101) plane, respectively, according to our aforementioned experimental results. The density of states (DOS) calculation





Fig. 5 Fine structure characterization and theoretical calculations for understanding the integrated storage mechanism. (a) Mn K-edge XANES spectra of the Rec-NM-MnO<sub>2</sub> electrode in NH<sub>4</sub><sup>+</sup>-Mn<sup>2+</sup> mixed electrolyte and the counterpart electrode derived in pure 0.5 M Mn(NO<sub>3</sub>)<sub>2</sub> electrolyte at different states. (b) The  $k^3$ -weighted Fourier transformation of the Mn K-edge EXAFS spectra. (c) Wavelet transformation of the  $k^3$ -weighted Mn K-edge EXAFS signals. (d) Density of states for pure MnO<sub>2</sub>, H-MnO<sub>2</sub>(h), and H-MnO<sub>2</sub>(p). (e) Differential charge density of NH<sub>4</sub><sup>+</sup> adsorbed on H-MnO<sub>2</sub>(p) (the cyan and yellow colors correspond to charge depletion and accumulation, respectively). (f) Adsorption energies of NH<sub>4</sub><sup>+</sup> on the surface of pure MnO<sub>2</sub>, H-MnO<sub>2</sub>(h), and H-MnO<sub>2</sub>(p). (g) Relative energy profile of the dissolution processes for the sites near (below) and far (above) from the adsorbed NH<sub>4</sub><sup>+</sup>.

results demonstrate that the band gap decreases in the following sequence: pure MnO<sub>2</sub> > H-MnO<sub>2</sub>(h) > H-MnO<sub>2</sub>(p) (Fig. 5d), indicating the enhanced electron transfer capability of H-MnO<sub>2</sub>(p).

To gain more information on the superiority of the storage capacitance of H-MnO<sub>2</sub>(p) in the NH<sub>4</sub><sup>+</sup>-Mn<sup>2+</sup> mixed system, the charge density difference (CDD) analysis and adsorption energy for NH<sub>4</sub><sup>+</sup> on pure MnO<sub>2</sub>, H-MnO<sub>2</sub>(h), and H-MnO<sub>2</sub>(p) were studied. As depicted in Fig. 5e, at an isosurface level of 0.002 e

Å<sup>-3</sup>, a pronounced charge-transfer behavior appears from the NH<sub>4</sub><sup>+</sup> side to the MnO<sub>2</sub> side, implying an intimate interfacial electronic interaction between NH<sub>4</sub><sup>+</sup> and H-MnO<sub>2</sub>(p). In addition, the calculated NH<sub>4</sub><sup>+</sup> adsorption energy of H-MnO<sub>2</sub>(p) was considerably lower than that of pure MnO<sub>2</sub> and H-MnO<sub>2</sub>(h) (Fig. 5f), suggesting its kinetically favorable NH<sub>4</sub><sup>+</sup> adsorption stemming from the tailored interface microenvironment. We further calculated the Gibbs free energy to identify the synergistic modulation mechanism of NH<sub>4</sub><sup>+</sup> ions during the MnO<sub>2</sub>



discharge process. As demonstrated in Fig. 5g, this process begins with a proton binding to a lattice oxygen atom on the MnO<sub>2</sub> surface, followed by an attack from a second proton. Remarkably, the second proton attack is more favorable at the nearby site, with an energy of  $-3.03$  eV compared to  $-2.22$  eV at the distal site (Fig. 5g). This is followed by the *in situ* formation of a structural H<sub>2</sub>O molecule, which is a nonspontaneous process serving as the rate-determining step (RDS). Of note, the energy barrier for this RDS is markedly lower at the NH<sub>4</sub><sup>+</sup>-proximal site (0.51 eV) compared to the distal site (1.13 eV), underscoring the critical role of NH<sub>4</sub><sup>+</sup> in promoting dissolution kinetics. Also, the proximal site demonstrates a low energy barrier for H<sub>2</sub>O molecule release from the MnO<sub>2</sub> surface, signifying the facilitated dissolution behavior along with the interfacial proton/electron transfer.

## Conclusions

In summary, we discovered NH<sub>4</sub><sup>+</sup>-mediated interface chemistry for dynamically reshaping the hydroxylation degree of MnO<sub>2</sub> toward an optimal reconstructed interface, which ensures fast Mn<sup>2+</sup>/MnO<sub>2</sub> conversion chemistry, and at the same time, creates a kinetically favorable microenvironment for efficient NH<sub>4</sub><sup>+</sup> storage. The as-enabled dual-pathway storage mechanism triggers a superior areal capacitance of 13.8 F cm<sup>-2</sup> and good cycling stability at a superhigh mass loading of 27.1 mg cm<sup>-2</sup>. Theoretical calculations indicate that local partial hydroxyl groups help strengthen the electronic conduction and facilitate the interfacial adsorption for NH<sub>4</sub><sup>+</sup> storage. The adsorbed NH<sub>4</sub><sup>+</sup> triggers the redistribution of local electrons and thereby results in a considerably reduced uphill energy barrier of the nonspontaneous rate-determining step of the dissolution process, enabling a collaborative dual-pathway storage behavior. This research establishes a study paradigm focusing on the synergistic dual-pathway mechanism by refining the interfacial microenvironment for better high-mass-loading energy storage.

## Author contributions

W. G. and Q. Z. supervised the research. J. W. and W. G. designed the experimental routes. J. W. carried out the material fabrication and most of the characterization experiments. J. W. and W. G. conducted the main data analysis and the paper writing. J. W., M. S., N. H., and Y. Y. carried out electrochemical measurements. J. W., W. G., G. Z., M. C., and W. X. performed *operando* Raman characterization. All co-authors contributed to discussions on the relative results and improving the paper.

## Conflicts of interest

There are no conflicts to declare.

## Data availability

The data supporting this article have been included as part of the supplementary information (SI). Supplementary information: the detailed experimental procedures for electrode

fabrication, materials characterization, electrochemical measurements, and density functional theory (DFT) computational methods, mass variation data, charge storage dynamics analysis, electrochemical performance comparisons across different electrolytes and substrates, characterization of asymmetric supercapacitors, scanning and transmission electron microscopy images, *operando* electrochemical impedance spectroscopy, *ex situ* X-ray diffraction patterns, X-ray photoelectron spectra, Fourier-transform infrared spectra, *operando* Raman spectra, X-ray absorption near-edge structure data, additional interpretive analysis, performance comparisons with literature reports, and fitted equivalent circuit parameters from impedance measurements. See DOI: <https://doi.org/10.1039/d6sc02038k>.

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