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Broader context

Manganese buffer induced high-performance disordered MnVO cathodes in zinc batteries†

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Buffer reactions can prevent changes induced by external causes. Here, we demonstrate the significant buffer role of a very small amount of Mn in a self-optimized cathode for an aqueous Zn-ion battery. Our operando X-ray characterization studies reveal that the dissolution of most of the Mn in MnV_2O_4 during the first charging cycle induces atomic re-arrangement to form a disordered vanadium oxide phase with 0.88 at% Mn. Interestingly, the residual Mn ions exhibit voluntary migration between tetrahedral and octahedral sites during Zn^{2+} de/intercalation. This Mn migration not only stabilizes the main structure of the vanadium-based electrode, but also modulates the Fermi surface of V 3d against excessive drift. As result, the optimized cathode delivers an excellent capacity of 610.2 mA h g⁻¹ at 0.2 A g⁻¹ and long-term cycling stability over 4000 cycles. This buffer contribution *via* tunable metal ions exhibits high potential for applications in long-life metal-ion batteries and related fields.

The stability of battery systems is considered to be crucial for large-scale energy storage. However, systems will experience huge fluctuations during the conversion of chemical energy and electrical energy, which results in poor lifespans, especially for multivalent metal-ion batteries and under aqueous conditions. In this situation, a buffer reaction is imperative to minimize the structure and valence mutations during ion-storage electrochemistry. Here, in an aqueous zinc battery, we uncover the *in situ* electrochemical reconstruction of the structure of the MnV_2O_4 spinel during the first charging cycle using *operando* synchrotron radiation X-ray diffraction (SXRD). We demonstrate that the structure reconstruction *via* the dissolution of most of the Mn generates a site enriched disordered phase in which the residual Mn ions in the host play a significant buffering role on both the structure and the valence of V based on X-ray absorption spectroscopy (XAS) and DFT calculations. The corresponding results indicate ultra-high capacity and long-term cycling stability. These findings underline the significance of the buffer role for the stability of batteries and the advantages of synchrotron radiation X-ray characterization.

Introduction

Buffer reactions are ubiquitously used for preventing great changes from the initial state when external forces are imposed on a system.^{1,2} It has long been considered that buffers are mainly for regulation of the concentration of hydronium ions and other metal ions in chemistry.^{3,4} For example, acid-base buffers can maintain a constant concentration of hydrated hydrogen ions (*i.e.*, pH) in solution.² It is worthwhile to investigate buffering in electrochemical systems, which exhibit fluctuations during the conversion of chemical energy and electrical energy. However, to date, few efforts have been made to discover and understand the buffer phenomenon in electrochemistry. The most compelling reason is that buffer reactions in electrochemical systems are so inconspicuous and the contents of the buffering agents are so relatively low that there is a lack of compatible characterization methods to probe them. In particular, it is known that structure and valence changes are closely correlated to the lifespan of a battery system during the operating process.5,6 In this scenario, a buffer

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reaction might be of paramount importance to the stability of electrochemical batteries. Hence, it is imperative to select a promising representative battery and utilize an appropriate electrode model to unravel the vital but often-overlooked buffer reactions in battery systems.

Among the various electrochemical storage systems, the rechargeable aqueous Zn-ion battery (AZIB) has emerged as a very close complement to the commercial lithium-ion battery (LIB) for future large-scale energy storage technology in virtue of its low cost, the abundance of its raw materials, and environmental friendliness.⁷⁻¹¹ However, it is worth noting that the development of AZIB has been blocked by the scarcity of suitable cathodes and limited cycle life.^{12,13} The intrinsic cause is the instability of the Zn²⁺ storage system due to the enormous fluctuations of large Zn^{2+} and hydrated ions during the de/ intercalation process.¹⁴ Consequently, it is essential to tackle these limitations via exploring new cathodes and designing structural models that can cushion these volume changes for ZIBs. Up to the present, Mn and V-based oxides have tended to be the prevailing cathode materials for ZIBs, in which Mn-based oxides have a voltage window of 0.8-1.8 and V-based oxides have a window of 0.1–1.4, typically.^{13,15–20} Observing the history of the shift from conventional oxide cathodes to ternary cathodes in LIBs, which produce a high energy density,^{21,22} it is reasonable to combine Mn and V-based oxides to achieve a wider voltage window in hopes of achieving a synergistic effect, as shown in Fig. 1a. Furthermore, we note that dissolution and Jahn-Teller distortion of Mn are unavoidable in Mn-based compounds,²³ and a fraction of the Mn ions will remain inside the electrode or the battery system. Actually, even very small amounts of metal ions have been found to exert considerable influence on the structure and electronic state of electrodes.^{24,25} Thus, it is inferred that the vestigial Mn ions might have a domino effect during the electrochemical process.

Based on these ideas, we have rationally designed a structural model of MnV_2O_4 (denoted as MnVO), in which structural self-optimization *via* the dissolution of the majority of the Mn occurs. Interestingly, it is noting that 0.88 at% Mn ions reversibly migrate between tetrahedral and octahedral sites with the entrance and exit of Zn^{2+} , simultaneously acting as significant buffers to the electrode structure and modulating the Fermi surface of V 3d. As a result, a recorded specific capacity of 610.2 mA h g⁻¹ is achieved, as well as outstanding rate properties, long-term cycling stability over 4000 cycles with 73% retention and a remarkable energy density of 469.3 W h kg⁻¹ at 215 W kg⁻¹. The results highlight the highly effective buffering phenomenon of a very small amount of metal ions, which cannot be ignored in AZIBs and other metal-ion batteries.

Results and discussion

Structural characterization of the MnVO spinel model

MnVO spinel was prepared *via* calcination of a precursor acquired from a sol–gel solution, as detailed in Fig. S1, ESI[†] and Methods. The phase and crystal structure of the as-prepared

sample were determined by Rietveld refinement of the powder X-ray diffraction (PXRD) data (Fig. 1b). The results show that all the diffraction peaks are well indexed to the space group $Fd\bar{3}m$ with lattice parameters of a = 8.521 Å, b = 8.521 Å, and c = 8.521 Å, indicating the success in synthesizing a high-quality and pure MnVO sample. A typical scanning electron microscope (SEM) image shows the nanoparticulate morphology of MnVO (Fig. S2, ESI⁺). The transmission electron microscope (TEM) image further shows that these nanoparticles are uniform with a size of about 30 nm (Fig. 1c). Fig. 1d shows the atomic-resolution HAADF-STEM image used to examine the detailed structure of MnVO. Compared to the structure of the standard MnVO spinel model, which consists of Mn²⁺ in tetrahedral sites and V³⁺ ions in octahedral sites along the (110) zone axis, the theoretical positions of Mn and V atoms are superimposed in the HAADF-STEM image, indicating that the elements and positions in the standard model closely fit the observed ones in the STEM image. Additionally, a crystalline interplanar spacing of 4.94 Å is related to the (111) crystallographic planes. The perfectly ordered arrangement of the atoms is revealed in Fig. S3, ESI,† demonstrating the high crystallinity and defect-free features of the MnVO spinel. For the sake of improving the electrical conductivity of the MnVO spinel, the raw materials of MnVO were fortified with an additional carbon source to produce a carbon-coated sample (MnVO@C), similarly to the method used for raising the conductivity of spinels in Li/Na batteries.^{26,27} After carbon coating, the MnVO phase is maintained without additional diffraction peaks corresponding to carbon, illustrating the amorphous nature of the coated carbon (Fig. S4, ESI[†]). It is obvious that carbon is uniformly coated on the MnVO, as observed in the TEM image (Fig. S5, ESI⁺) and the even distribution of the elements Mn, V, O and C (Fig. S6, ESI†).

Electrochemistry

In the interest of investigating the Zn²⁺ storage behaviour in the aforementioned spinel model, the electrochemistry of MnVO@C was examined using coin-type half-cells, which comprise a MnVO@C cathode, a Zn foil anode and 3 M Zn(CF₃SO₃)₂ electrolyte. Cyclic voltammogram (CV) curves of the first three cycles in the range of 0.2-1.8 V were recorded at a scan rate of 0.1 mV s^{-1} , as shown in Fig. 2a. The experimental results indicate that an aberrantly intense redox peak at 1.53 V is unexpectedly detected during the initial charging and vanishes in the 2nd and 3rd cycles, indicating that an irreversible process took place at 1.53 V. In the 2nd and 3rd cycles, it should be noted that two redox peak couples at 0.586/0.72 V and 0.90/1.01 V were significantly enhanced and coincided well, clearly demonstrating enhanced and reversible electrochemical activity. An identical conclusion could be drawn from the galvanostatic chargedischarge (GCD) curves (Fig. 2b). In addition to that, the capacities of 1st and 10th cycles are 66.1 and 610.2 mA h g^{-1} , respectively. This means that the Zn²⁺ storage property rises steeply, increasing over nine-fold after the initial charging process. The elevated capacity might be attributed to the irreversible transformation during the initial charging, which introduces a more suitable structure for Zn²⁺ storage. Additionally,



Fig. 1 Structural characterization of the MnVO spinel. (a) A sketch of the design of the MnVO sample. (b) Rietveld refinement of the PXRD (Cu K α) data of the MnVO sample. (c) A low-magnification TEM image of MnVO. (d) An atomic-resolution HAADF-STEM image of the MnVO spinel. The bright balls correspond to Mn and V atoms. The inset is the projection of the structure of the MnVO spinel along the $\langle 110 \rangle$ zone axis; oxygen has been removed for clarity.

the high-performance of MnVO@C may be due to the significant role of Mn, as evidenced by its superior specific capacity at 0.2 to 5 A g⁻¹ compared to that of ZnVO@C and V₃O₇ electrodes without Mn (Fig. 2c and Fig. S7, ESI⁺). The variation of capacity and coulombic efficiency caused by the test environment are analyzed in Fig. S8, ESI.† The Zn-ion device is capable of delivering a maximum energy density of 469.3 W h kg⁻¹ at a power density of 215 W kg⁻¹ based on the active mass of the MnVO@C electrode, which is an improvement over recently reported AZIBs. The stability of energy storage devices is assumed to be of enormous importance to practical applications. As shown in Fig. 2e, the MnVO@C-based device possesses long-term cycling stability (91% retention after 1000 cycles, 73% retention after 4000 cycles at 5.0 A g^{-1}) and exhibits stable cycling with a high specific capacity of 375 mA h g^{-1} at 1.0 A g^{-1} after 100 cycles (Fig. S9, ESI^{\dagger}), which is superior to those without Mn. The ultimate capacity of 610.2 mA h g^{-1} at 0.2 Ag^{-1} and long cycle life of 4000 cycles exceed those of the stateof-the-art cathodes reported in the literature for AZIB (Fig. 2d and Tables S1 and S2, ESI[†]). The results suggest that the MnVO@ C-based AZIB electrode has great application potential on account of its high capacity, excellent energy and power density and long cycling stability.

Structure self-optimization

The question of the mechanism responsible for dramatic increase in the discharge capacity value from 66.1 to 528.9 mA h g^{-1} for the first and second cycles, respectively was considered. The preliminary electrochemistry research showed that an irreversible phase transition had arisen during the 1st charging process, after which the electrochemical activity was markedly enhanced. That is to say, a phase transition introduced a more favorable structure for Zn²⁺ storage. Therefore, operando synchrotron radiation X-ray diffraction (SXRD) was utilized to constantly monitor the phase evolution of MnVO@C during the operating condition (Fig. 3a). A hole-opening coin cell was used for the operando SXRD test (Fig. S10 and S11, ESI⁺). It is critical for a hole to be bored in the center of the zinc wafer in order to avoid the strong X-ray adsorption of Zn. The results demonstrate that there is no noticeable transformation in any of the diffraction peaks in terms of either position or intensity during the 1st discharging process (Fig. 3b). On the contrary, during the 1st charging process, the intensity of all the peaks begins to decrease at a voltage of 1.5 V. Finally, all the peaks are blurred after charging to 1.8 V, and only a faint peak is observed at 34.8° in the subsequent electrochemical process, indicating that



Fig. 2 Electrochemistry measurements of MnVO@C in Zn-ion cells. (a) CV curves of the 1st, 2nd, and 3rd cycles at a scan rate of 0.1 mV s⁻¹ for MnVO@C. (b) Galvanostatic charge–discharge curves during different cycles at a current density of 200 mA g⁻¹ for MnVO@C. (c) The rate performance at current densities from 200 to 5000 mA g⁻¹ of MnVO@C, ZnVO@C, and V₃O₇. (d) A comparison of the specific capacity of MnVO@C and other cathodes, including V-based and Mn-based oxides and other compounds. More extensive tabulation is available in Table S1 (ESI†). (e) The long-term cycling properties of MnVO@C, ZnVO@C, and V₃O₇ at a current density of 5000 mA g⁻¹.

phase transition has taken place to produce a disordered microcrystalline phase. The conclusion could be drawn from the *operando* SXRD measurement that the phase transition is a transition towards an amorphous phase.

To investigate what had occurred inside, the coin cells were unfolded after being subjected to different cut-off voltage cycles. From an intuitive observation of the separators under different voltage states (Fig. S12, ESI[†]), it can be seen that the separators began to blacken after the 1st charging process, indicating the dissolution of the elements caused by phase transition. Thus, electron probe macroanalysis (EPMA), an accurate element content analysis technique, was performed to detect the element content variation. As shown in Fig. 3c, the initial element ratio of Mn was 21.32 at%, while it was only 0.88 at% after the 1st charging to 1.8 V, indicating that the vast majority of the Mn had dissolved, leaving only 0.88 at% Mn in the final structure. Thus, the MnV_2O_4 phase was converted into a disordered vanadium oxide phase with 0.88 at% Mn *via* the dissolution of most of the Mn due to the oxidization of Mn^{2+} (electronic configuration $3d^5$) to unstable Mn^{3+} (electronic configuration $3d^4$) during the 1st charging process.²⁸ To emphasize, no dissolved Mn ions reach the cathode again,



Fig. 3 The structural self-optimization of MnVO@C during the electrochemical process. (a) A schematic diagram of the *operando* SXRD measurement environment. (b) *Operando* SXRD spectra of MnVO@C during the first and second charging and discharging cycles at a current density of 0.2 A g⁻¹. (c) EPMA spectra of the element content levels of Mn, V, and Zn in different states. (d) The contact angle of the MnVO@C model before and after structural self-optimization.

and the electrolyte containing Mn ions does not affect the performance, as discovered by element contents of Mn at different states. The phenomenon of Mn dissolution is of widespread significance, suggesting that the Mn in Mn-based oxides or Prussian blue could dissolve out as the result of the disproportionation reaction of manganese and the Jahn–Teller effect.^{28–30}

This phase transformation is a peculiar self-optimization process, in which Mn dissolution, which has previously been regarded as a dilemma for ion storage chemistry,^{7,28,31} becomes a favorable direction for Zn²⁺ electrochemistry. We attribute this phase transition to a structure self-optimization process in which the structure is modified to improve the internal structure of the electrodes for Zn²⁺ intercalation without changing the overall framework. In fact, structure self-optimization exists in many electrochemical processes, such as electrocatalysis, which has a tendency to expose more active sites, and ion storage processes that tend to reconstruct a more favorable embedded structure.^{32,33} In our MnVO@C spinel model, the structure is compact and highly crystalline, so that there are finite sites for Zn²⁺ occupation and only a small amount of Zn²⁺ will be intercalated or adsorbed on the surface. This explains why a low discharging capacity and unchanged XRD diffraction peaks were detected in the 1st discharging process (before structure self-optimization). Different results appear after the structure self-optimization since a substantial fraction of the Mn is removed, creating more sites and more favorable structure for Zn²⁺ entry and movement. The final MVO@C is a microcrystalline phase with amorphous features that would enhance the electrochemical performance due to more active sites, abundant defects, porosity and improved ion diffusion. As shown in Fig. 3d and Fig. S13, ESI,† the hydrophilicity and specific surface were greatly improved after structure selfoptimization. Additionally, the much higher conductivity of the final MVO@C significantly contributes to the excellent Zn²⁺ storage ability as well (Fig. S14, ESI[†]). These features would be propitious in terms of the contact between the electrode and electrolyte and would make for the electrolyte transport, which results in a surface-dominated process. As indicated in Fig. S15, ESI, \dagger the *b* values calculated from the CV curves are more pertinent to a pseudocapacitance process, which as a corollary, leads to high power performance.

Spatial migration of the Mn dopant

As discussed above, the dissolution of most Mn in MnVO@C cathode produces a self-optimized electrode with a great deal of conducive characters to Zn^{2+} electrochemistry. Additionally, the performance of the Mn-doped disordered vanadium oxide is superior to that without Mn. To obtain a deeper understanding, it is certainly worth examining the true role of the residual very

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small amount of Mn on the conformational changes of the optimized electrode structure during Zn²⁺ storage. XRD is a technology based on long-range ordered structure, but is incapable of furnishing local structure information; therefore, another technique that is highly capable of characterizing local electronic structures should be used. X-Ray absorption spectroscopy (XAS), which is a bulk technique but can probe local structure precisely, was performed to detect the local structure

evolution of the restructured MnVO@C during cycling. Three takeaways can be drawn from the V K-edge X-ray absorption near-edge spectra (XANES) and the corresponding EXAFS refinements of MnVO@C at various states (Fig. 4a). First, after structure self-optimization (1st-C1.8 V), the final overall framework was converted into a vanadium oxide structure and did not revert to the initial spinel structure (Fig. S16, ESI†). The final overall framework of MnVO@C is mainly composed



Fig. 4 The local electronic structure of MnVO@C and the role of Mn in Zn ion intercalation. (a) V K-edge XANES spectra of MnVO@C in various states. (b) Mn K-edge XANES spectra of MnVO@C in various states. (c) Mn EXAFS spectra of MnVO@C in different states. (d) Zn EXAFS spectra of MnVO@C in different states. (e) A schematic diagram of the electronic structure in the vanadium oxide electrode without Mn doping. (f) A schematic diagram of the electronic structure in the vanadium oxide electrode without Mn doping.

of V and O, considering that the majority of the Mn has dissolved. Second, the intensity of pre-edge peaks at 5470 eV is strengthened after the derangement of the atoms, hinting at a diverse local coordination environment of V due a fraction of the V atoms having slipped to tetrahedral sites. The final structure is a disordered vanadium oxide that has both tetrahedral and octahedral sites. The fitting results of the V K-edge EXAFS indicate that the disordered vanadium oxide after the first optimization has two V-O paths with coordination numbers of 2.9 and 1.5 and bond lengths of 1.52 and 1.99 (Table S3, ESI[†]). Finally, the position of the V K-edge absorption threshold moved to lower energy while discharging and shifted to the initial position while charging, which indicated the reduced valence during discharging and the increased valence of V during charging. Additionally, the exact average chemical valence variation of V is from 4.73 to 4.87 as determined from the linear fitting of the first-order derivative (Fig. S17, ESI[†]).

In general, the structure self-optimization engendered an overall vanadium oxide framework, but there was a very small amount of Mn in this host. The retained Mn also exhibited mean valence changes from 2.39 to 2.55 during the process of discharging and charging as uncovered using Mn K-edge XANES (Fig. 4b and Fig. S18, ESI[†]). It should be emphasized that the Mn participated in the electrode reaction along with V, which is attributable to the high capacity of Zn-ion devices. Furthermore, the structure information related to the XANES spectra of Mn supports an interesting phenomenon, namely, that there are two types of local structures at the fully discharged and charged states. More specifically, the structure of Mn reverts to the initial structure at full discharge, suggesting that most of the Mn is located at tetrahedral sites when Zn ions are embedded. On the contrary, most of the Mn glides to octahedral sites in the fully charged state as confirmed by the shape of the spectral lines, which is similar to that observed for octahedral coordination, such as the octahedral coordination of Mn and Fe ions reported in the literature.³² There was no change in the Zn valence, which was constant at +2 during the whole process, compared to that of the reference ZnO (Fig. S19, ESI[†]). Fig. 4c and d exhibit the corresponding EXAFS spectra of Mn and Zn, which provide the coordination numbers and the type of the neighboring atoms. The Mn and Zn K-edge EXAFS refinements were further fitted to confirm the sites of Zn²⁺ and Mn²⁺ upon cycling (Fig. S20 and Table S4, ESI[†]). It was found that the length of the Mn-O bond at full discharge (2.00 and 2.01 Å) is shorter than the bond at full charge (2.08 and 2.09 Å). It has been shown in the literature that the chemical bonds between metal atoms in tetrahedra and oxygen ions are slightly shorter than their counterparts in octahedra.^{33,34} Additionally, the Mn-Mn bond lengths at full discharge are 3.74 and 3.72 Å, which are longer than the Mn-Mn bonds of 3.08 and 3.07 Å at full charge, conforming to the law that the distance between two octahedral sites is typically shorter than the bonds between two tetrahedral sites. The fitting results of the Zn K-edge EXAFS show a near six-coordinated environment of Zn²⁺ in the intercalated state, which indicates that the Zn²⁺ is present in octahedral sites after full discharge (Fig. S21 and Table S5, ESI⁺). Therefore, it can be concluded that the remaining very small amount of Mn enters the tetrahedral site when the zinc ion is embedded, and enters the octahedral site when the zinc ion leaves. This means that both Mn and Zn are more likely to occupy octahedral sites, but there is a competitive relationship between them. When zinc ions are embedded into octahedral sites during discharging, Mn ions are forced to abdicate to another tetrahedral position (as shown in the discharging cartoon movie, ESI⁺). Our theoretical calculations further verified that the structure with Zn²⁺ occupying the tetrahedral site and Mn²⁺ occupying the octahedral site has a decreased system energy (Fig. S22, ESI⁺). During charging, the zinc ions leave, and Mn²⁺ moves back to the octahedral sites, becoming Mn³⁺ (as shown in the charging cartoon movie, ESI[†]). Accordingly, we can conclude that the insertion and extraction of Zn^{2+} are accompanied by the spatial migration of a very small amount of Mn, which simultaneously induces a valence change in Mn.

A very small amount of Mn as a highly effective buffer to assist Zn ion intercalation

In the overall electrochemistry process of Zn²⁺, Mn plays a momentous role as a buffer via spatial migration between two sites. Above all, the role of Mn as a buffer is responsible for the abatement of the Fermi surface shift of V 3d during Zn²⁺ electrochemistry. Previous works have stated that the redox voltage is determined by the energy gap between the electron states involved in the redox reaction and the Zn⁰/Zn²⁺ energy level.35 In our self-optimized model, the Fermi surface would shift up and down with the loss and the gain of electrons, whether the 3d electrons of the V ions, or the 3d electrons of the Mn ions. As shown in Fig. 4e, if Mn ions do not participate in the redox reaction of the electrode (i.e., in the case of vanadium oxide without Mn-doping), the Fermi surface shift of the V 3d is $\Delta 1$ during the discharge and charge process. In contrast, when Mn ions share part of the variation of the electrons as shown in Fig. 4f, the Fermi surface shift of V 3d is $\Delta 2$ in A-MnVO (Mn doped vanadium oxide). As observed in the XANES spectrograms of V and Mn, the V ions and a very small amount of Mn ions co-participated in the electrochemical reaction of Zn²⁺ (Fig. 4a and b). Consequently, the value of $\Delta 2$ is less than $\Delta 1$ due to the co-involvement of the Mn and V valence changes, which ensures that V is not oxidized to pentavalent during charging. Certainly, the average valence of V does not reach pentavalence in the fully charged condition, in contrast with the standard sample of V_2O_5 (Fig. S17, ESI^{\dagger}). The theoretical calculations of the local DOS further confirm that the manganese makes a great contribution to the valence band of the MnVO model (Fig. S23, ESI[†]). Analysis of the Zn²⁺ behavior of the MnVO@C electrode using the dQ/dV curves of MnVO@C and ZnVO@C electrodes shows higher reduction potential, lower oxidation potential, and lower overpotential and polarization, which further demonstrate that the manganese buffer not only modulates the Fermi surface of V 3d against excessive drift, but also stabilizes the main structure of the vanadium-based electrode (Fig. S24, ESI[†]). It should be noted that the framework of

vanadium oxide with both tetrahedral and octahedral sites of A-MnVO may not be retained without Mn inside.

Secondly, the Mn ions act as a buffer against dramatic structure changes during Zn ion de/intercalation. The accepted wisdom is that insertion electrodes for AZIBs face large stability penalties because of the high hydrated ionic radius of Zn^{2+} (4.04–4.30 Å).^{14,36} In this situation, it is little wonder that the most suitable cathodes for AZIB in the literature are layered and large channel structures.^{18,37–39} Our "occupied sites"-type model is stable for more than 4000 cycles, which is superior to the ones without Mn buffer. This stability is credited to the spatial migration of the Mn ions, which move back and forth between the tetrahedral and the octahedral sites during the de/ intercalation of Zn^{2+} , as mentioned above and shown in the cartoon movie. This spatial migration helps to protect the main structure of vanadium oxide against collapse at the fully charged state.

The role of the buffer in the main structure in the optimized electrode was further evidenced by high resolution X-ray photoelectron spectroscopy (XPS) and the soft X-ray absorption spectrum (sXAS). With the insertion and extraction of Zn^{2+} (Fig. 5a), no significant changes are observed in the V L-edge and O K-edge (Fig. 5b), suggesting the stability of the main frame of our optimized electrodes. The V L-edge can be segmented to two main parts including an L₃-edge and L₂-edge, which correspond to the V $2p_{3/2}$ to V 3d and V $2p_{1/2}$ to V 3d transitions,⁴⁰ respectively. The O K-edge located above 527 eV corresponds to the transition from O 1s to hybridized states between the V 3d and O 2p orbitals.⁴⁰ There are only two slight perturbations in the V L-edge and O K-edge. The first is the structure response for Zn^{2+} insertion and extraction characterized by the peaks occurring at 516.4 eV. According to previous studies, this peak is considered to be the $2p_{3/2}$ to $b_2 (d_{xy})$ transition.²⁴ Upon discharge, the intensity of the b_2 peaks becomes much weaker, indicating the higher electron filled density compared with the initial and charged samples. The second is the blue-shift of the L₃-edge in the discharged state, which is induced by the intercalation of Zn²⁺, suggesting the reduction of V to lower valence with the intercalation of Zn²⁺. The findings further reflect the small degree of structural change and limited valence variation during Zn²⁺ electrochemistry, consistent with the previous XANES results for V. Importantly, the Mn buffer is durable during subsequent cycles (Fig. S25, ESI⁺).

In general, the buffer role of Mn ions in Zn^{2+} electrochemistry includes the processes presented in Fig. 5c: (i) the selfoptimization process, which is favorable for the spatial migration of the very small amount of Mn via structure reconstruction. After the first charging to 1.8 V, most of the Mn has exited the MnVO@C, resulting in an amorphous Mn-doped vanadium oxide (A-MnVO), which contains tetrahedral and octahedral sites. At this moment, the very small amount of Mn is in the octahedral position. (ii) The buffer action process via the spatial migration of the very small amount of Mn. The dissolution of most of the Mn provides substantial sites for Zn²⁺ intercalation. Zn²⁺ and Mn ions both tend to embed in octahedral sites, but Zn²⁺ is more competitive; hence, when Zn²⁺ enters, the very small amount of Mn ions is forced into tetrahedral sites. When the Zn²⁺ departs the A-MnVO@C skeleton, Mn returns to the octahedral sites. In subsequent cycles, Mn makes a round-trip between the tetrahedral and octahedral sites in synchronization with Zn²⁺ to minimize the structural strains and the shift of the Fermi surface, thus assisting Zn²⁺ intercalation.



Fig. 5 The use of a very small amount of Mn as a buffer to assist Zn ion intercalation. (a) High-resolution XPS spectra of Zn in different states. (b) V Ledge and O K-edge sXAS spectra of MnVO@C in different states. (c) The process by which Mn ions act as a buffer to assist Zn^{2+} de/intercalation.

Conclusions

In summary, we present the electrochemical rearrangement of structure as a result of the dissolution of most of the Mn in MnV₂O₄ spinel during the first charging cycle to produce a new disordered phase, which enables the reversible intercalation of Zn²⁺, as observed using SXRD. XAS and DFT calculations demonstrated the significant role of the residual very small amount of Mn ions as a buffer via spatial migration, buffering both the principal structure and the Fermi level of V 3d to assist in Zn ion intercalation. As a result, the self-optimized electrode delivers a high capacity, outstanding energy density, and longterm cycling performance, suggesting that it will find extremely impressive applications in the future. The discovery suggests the possibility of engineering electrodes via designs that cushion volume changes, which demonstrates promise for guiding the rational design of high-performance electrodes for metal-ion batteries.

Experimental

Preparation of MnVO spinel and MnVO@C

The MnVO sample was synthesized using a sol-gel solution, followed by crystallization through a calcination process. Concretely, 0.245 g of manganese acetate tetrahydrate and 0.53 g of vanadium oxide bis(2,4-pentanedionate) were evenly blended with 100 mL absolute ethanol by ultrasonication. Afterwards, the mixed solution was heated at 80 °C and stirred at 300 rpm until the absolute ethanol was fully evaporated, and then dried for further use in an electric oven. Finally, the collected precipitates were crystallized at 800 °C for 12 h at a heating rate of 2 °C min⁻¹ under an argon atmosphere. The MnVO@C sample was prepared following the same procedure except that 0.3 g of glucose (30%) was added during the initial procedure. The ZnVO@C sample was prepared using the same procedure as MnVO@C, except that the manganese acetate tetrahydrate was replaced with zinc acetate tetrahydrate.

Characterization

Powder XRD measurements were performed using an X-ray diffractometer (D/Max2500V; Rigaku, Tokyo, Japan) with Cu Ka radiation (1.5418 Å). Rietveld refinement was performed using the program GSAS, in which the parameters of scale factor, heat factor, background, lattice parameters, and zero point were trimmed until convergence. The apparent morphology and EDS mapping were obtained using a cold field emission scanning electron microscope (SU8220). The detailed structure was further visualized using TEM (JEOL JEM2010) and high-angle annular dark field transmission electron microscopy (HAADF-STEM: Talos F200X) with a spherical aberration corrector. Analysis of the content of the elements Mn, V and Zn was carried out using an X-ray electron probe microanalyzer (EPMA: 8050G). The contact angles of MnVO@C before and after structure self-optimization were obtained using a contact angle tester (Theta Flex). XPS tests were conducted using an X-ray photoelectron spectrometer (ESCALAB 250Xi) with an Al Ka $(h\nu = 1486.6 \text{ eV})$ X-ray source.

Electrochemical measurements

Zn-ion cells were assembled with a positive shell, a negative shell, a gasket, a shrapnel, a MnVO or MnVO@C cathode, a filter paper separator, aqueous 3 M Zn(CF₃SO₃)₂ electrolyte (130 µL) and a Zn foil anode in the air with a calendering pressure of 50 kg cm^{-2} . Specifically, the cathodic electrodes were fabricated by grinding a mixture of MnVO or MnVO@C, Ketjen Black and PVDF in a weight ratio of 70:20:10 in the solvent N-methyl-2-pyrrolidone (NMP), after which the paste was evenly spread on stencil wafers. The wafers were dried in a vacuum drying oven at 100 °C for subsequent use. The mass loading of the cathode electrodes is based on the pristine MnVO@C. After the initial charging, the actual mass of the self-optimized electrodes decreased by 10.4 wt% due to the dissolution of Mn, as analyzed in Fig. S26, ESI.[†] All electrochemical tests were conducted at room temperature (25 °C) with a suitable voltage window of 0.2-1.8 V. The electrochemical performance tests, including galvanostatic charge/discharge (GCD), rate and cycling stability, were carried out using a Land CT2001A cell test system. The CV was measured using an electrochemical workstation (CHI660D, Shanghai CH Instrument Company, China). The EIS spectra were acquired in the frequency range from 0.01 to 10⁵ Hz using the same electrochemical workstation. Calculations, such as the specific capacity, specific energy density and power density were based on the active mass of the cathode. The energy density (E: W h kg⁻¹) and power density (P: W kg⁻¹) were calculated based on the following equations:

$$E = \int I V \mathrm{d}t \tag{1}$$

$$P = \frac{3600 \times E}{t} \tag{2}$$

where *I* is the discharge current density (A g^{-1}), *V* is the discharge voltage (V), and *t* is the discharge time (s).

Operando XRD measurements

The electrode for the *operando* XRD measurement was prepared using the same approach as the electrodes for electrochemical tests, excepting that the slurry was coated on carbon paper in order to attenuate the assimilation of X-rays. The electrode was incorporated into a coin cell in which a small circular hole had been opened in the center of the stainless-steel gasket, Zn foil, anodic and cathodic shells. In order to maintain the hermetic seal of the cell, Kapton adhesive tape was glued on the surface of anodic and cathodic shells. The *operando* XRD was carried out at beamline BL14B1 in the Shanghai Synchrotron Radiation Facility (SSRF) with a synchrotron radiation X-ray wavelength of 0.8857 Å, and the cell was operated using a Land CT2001A cell test system at 0.2 A g⁻¹ at the same time.

XAS measurements

The electrodes for XAFS measurements were the same as for the operando XRD test. The electrodes were charged and discharged to different cut-off voltages in coin cells at 0.2 A g^{-1} , and subsequently disassembled and recycled by washing with deionized water and anhydrous ethanol for further XAFS testing. The XAFS measurements were undertaken at beamline 1W1B of the Beijing Synchrotron Radiation Facility (BSRF) using a Si(111) double-crystal monochromator. The Mn, V and Zn K-edge XAFS measurements were carried out in transmission or fluorescence mode based on the optimal signal and the energy was calibrated using a Mn, V or Zn metal foil, respectively. The XAFS data were analyzed with the program WinXAS3.1.41 The theoretical amplitudes and phase-shift functions of Zn-O, Zn-V, V-O, V-V, Mn-O, Mn-V/O, and Mn-Mn were calculated with the FEFF8.2 code42 using the crystal structural parameters of the V₂O₃, MnO₂, and 1 M ZnSO₄. The electrodes for the soft XAS tests were prepared using the same procedure as for the XAFS measurements. The soft X-ray absorption spectroscopy (sXAS) measurements were carried out at beamline BL12B (CMD) at the National Synchrotron Radiation Laboratory (NSRL).

Computational methods

All density functional theory (DFT) calculations in this study were performed using the Vienna Ab initio Simulation Package (VASP) within the projector augmented-wave approach. The Perdew–Burke–Ernzerhof (PBE) generalized-gradient approximation functional was used. The cutoff energy for the plane waves was set to 500 eV, and the convergence for the total energy was 10^{-5} eV. The $5 \times 5 \times 5$ Monkhorst–Pack (MP) *k*-points sampling with gamma point centered was used for the full geometry relaxation including the cells. All atoms in the unit cell were fully relaxed until the force on each atom was less than 0.02 eV Å⁻¹.

Author contributions

L. S. supervised the project. S. Q. W. and S. M. C. carried out most of the experiments and data analysis. P. M. A. and B. G. gave useful proposals for the manuscript. X. Z. S. helped to analyze the energy band structure. Z. H. Q. performed DFT calculations and X. J. W. gave useful proposals for the DFT results. C. D. W. and Q. H. revised the manuscript and provided helpful discussion. P. J. Z., K. F. Z., G. X., and Y. Y. C. helped to do some sample characterization. D. F. C. helped to characterize the samples with TEM. W. W. guided the *operando* XRD measurements and helped to analyze the XRD results. All the authors discussed the results and assisted during the manuscript preparation.

Conflicts of interest

The authors declare no competing financial interests.

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