Anhydrous Fast Proton Transport Boosted by the Hydrogen Bond Network in a Dense Oxide-Ion Array of \(\alpha\)-MoO\(_3\)

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1. Introduction

The increasing concern given to the global environment and energy sustainability is driving the research and development of electrochemical energy storage devices that provide power supply with more resilience and flexibility. Currently, lithium-ion batteries dominate the power-source market for portable devices and electric vehicles due to their high energy density, high energy efficiency, and long lifetime.[1,2] However, the global maldistribution of lithium resources has impeded their further widespread use.[3] In particular, flammable organic electrolytes in lithium-ion batteries result in a low safety level and high fabrication/maintenance costs, both of which are unacceptable for grid-scale use.[4] Therefore, aqueous rechargeable batteries that contain safe and less expensive aqueous electrolytes are an important future alternative for sustainable development.[5]

Developing high-power battery chemistry is an urgent task to buffer fluctuating renewable energies and achieve a sustainable and flexible power supply. Owing to the small size of the proton and its ultrahigh mobility in water via the Grotthuss mechanism, aqueous proton batteries are an attractive candidate for high-power energy storage devices. Grotthuss proton transfer is ultrafast owing to the hydrogen-bonded networks of water molecules. In this work, similar continuous hydrogen bond networks in a dense oxide-ion array of solid \(\alpha\)-MoO\(_3\) are discovered, which facilitate the anhydrous proton transport even without structural water. The fast proton transfer and accumulation that occurs during (de)intercalation in \(\alpha\)-MoO\(_3\) is unveiled using both experiments and first-principles calculations. Coupled with a zinc anode and a superconcentrated \(\text{Zn}^{2+}/\text{H}^+\) electrolyte, the proton-transport mechanism in anhydrous hydrogen-bonded networks realizes an aqueous MoO\(_3\)–Zn battery with large capacity, long life, and fast charge–discharge abilities.
dissolution in aqueous electrolytes; therefore, the capacity decays gradually upon cycling, making it difficult to study the detailed H\(^+\) intercalation mechanism. Although many attempts have been made to solve this issue, for example, the use of concentrated electrolytes, gel-type or quasi-solid-state electrolytes with polymer additives, and electrode surface coating with polymers or ceramics, the ideally reversible and stable H\(^+\) (de)intercalation in α-MoO\(_3\) has yet to be accomplished. Herein, we stabilized the cycling of α-MoO\(_3\) with a superconcentrated aqueous Zn\(^{2+}/H^+\) electrolyte and achieved a fully reversible 2.5 proton (de)intercalation (Figure 1). Based on the electrochemical performances and density functional theory (DFT) calculations, we decoded the mechanism of H\(^+\) intercalation and transportation in α-MoO\(_3\) as a cathode host material. Facile anhydrous H\(^+\) transfer in α-MoO\(_3\) through a dense anhydrous hydrogen bonded network having similar features and comparable kinetic barriers with Grotthuss topochromy realizes aqueous batteries with large capacity, high rates, and long life.

2. Electrochemical Properties of MoO\(_3\) in Aqueous Zn\(^{2+}/H^+\) Electrolytes

α-MoO\(_3\) was synthesized by a previously reported hydrothermal method and the synchrotron X-ray diffraction (XRD) pattern confirmed the successful synthesis of a pure α-MoO\(_3\) phase with a morphology of micro-sized rods (Figure S1, Supporting Information). To study the H\(^+\) intercalation mechanism in α-MoO\(_3\), ZnCl\(_2\) was selected as an electrolyte salt. In addition to its compatibility with a Zn anode, the high solubility of ZnCl\(_2\) enabled the formation of a superconcentrated liquid structure with limited amount of free water molecules, while its Brønsted acidity generated a low pH environment with a high H\(^+\) concentration. Therefore, the electrochemical properties of α-MoO\(_3\) were evaluated using three aqueous electrolytes: conventional Zn\(^{2+}\) electrolyte (3 mol kg\(^{-1}\) ZnCl\(_2)/H_2O\), superconcentrated Zn\(^{2+}\) electrolyte (32 mol kg\(^{-1}\) ZnCl\(_2)/H_2O\), and superconcentrated dual-ion (Zn\(^{2+}/H^+\)) electrolytes (32 mol kg\(^{-1}\) ZnCl\(_2\) + 1 mol kg\(^{-1}\) P_2O_5/H_2O\). Note that P_2O_5 in a dual-ion electrolyte generates H\(^+\) through hydrolysis (P_2O_5 + 3H_2O → 2H_3PO_4). The Raman spectra for the superconcentrated electrolytes indicate that most water molecules are coordinated to Zn\(^{2+}\) (Figure S2, Supporting Information).

Before testing the electrochemical properties of α-MoO\(_3\), we evaluated the negative electrode, namely, Zn stripping and plating on a Ti current collector using the three electrolytes (Figure 2a; Figures S3, Supporting Information). The average coulombic efficiency in the aqueous Zn\(^{2+}/H^+\) dual-ion electrolyte is 99.0% over 200 cycles (Figure S3, Supporting Information), largely outperforming the superconcentrated Zn\(^{2+}\) electrolyte (95.0% over 200 cycles) and conventional Zn\(^{2+}\) electrolyte (82.2% over 100 cycles). The improved zinc reversibility after the addition of P_2O_5 may result from the formation of a Zn\(_4\)(PO_4)_2-based solid electrolyte interphase (SEI) layer. This reversible Zn stripping and plating was used as the counter electrode in this work.

Figure 2b shows the cyclic voltammetry (CV) curves measured for α-MoO\(_3\) using the three electrolytes at a scan rate of 0.5 mV s\(^{-1}\). To suppress the hydrogen evolution and chlorine evolution reactions on the α-MoO\(_3\) electrode, the cutoff voltages were set at 0.45 and 1.3 V for the aqueous Zn\(^{2+}/H^+\) dual-ion electrolyte (Figure 2a) and 0.25 and 1.1 V for the Zn\(^{2+}\) aqueous electrolytes. In the first CV cycle (Figure 2b inset), the α-MoO\(_3\) electrode shows identical asymmetric-shaped CV curves for all three electrolytes, in which there are four cathodic and two anodic current flows. However, in the subsequent cycles, the CV curves become symmetric, showing two pairs of redox peaks. Note that the redox potentials using the aqueous Zn\(^{2+}/H^+\) dual-ion electrolyte are centered at ≈0.6 and 0.95 V vs Zn/Zn\(^{2+}\), which shift by +0.2 V from those using Zn\(^{2+}\) aqueous electrolytes presumably owing to the potential shift of the Zn/Zn\(^{2+}\) counter electrode and/or the change in the activity of H\(^+\). The shapes of the CV curves for all three electrolytes resemble those reported for H\(^+\) (de)intercalation in α-MoO\(_3\) using a 9.5 m H_3PO_4 aqueous electrolyte, suggesting dominant H\(^+\) (de)intercalation even when using the Zn\(^{2+}\) aqueous electrolytes. In earlier studies, Zn\(^{2+}\) ion was considered naturally as the only charge carrier in ZnCl\(_2\)-based aqueous electrolytes. However, the importance of proton intercalation in aqueous electrolytes of multivalent cations was realized recently and the true charge carriers in such systems should be reevaluated. Indeed, the X-ray fluorescence (XRF) elemental analysis of the electrodes after a cathodic scan shows no evident increase in the peak intensity of Zn compared to that of the pristine electrode (Figure S4, Supporting Information). Also, MoO\(_3\) electrode showed limited capacity (<10 mAh g\(^{-1}\)) in an H\(^+\)-free Zn-based electrolyte (1 m ZnCl\(_2\) in triethyl phosphate (TEP), Figure S5, Supporting Information), indicating the inactivity of bare Zn\(^{2+}\) intercalation in MoO\(_3\) structure. Considering that the aqua Zn\(^{2+}\) complex is a Brønsted acid to generate H\(^+\), it is most likely that H\(^+\) (de)intercalation occurs even when using the aqueous Zn\(^{2+}\) electrolytes. Importantly, while 3 and 32 mol kg\(^{-1}\) ZnCl\(_2\) aqueous electrolytes exhibit steep redox peak degradation upon repeated CV cycling, the 32 mol kg\(^{-1}\) ZnCl\(_2\) + 1 mol kg\(^{-1}\) P_2O_5 aqueous dual-ion electrolyte exhibits stable CV curves (Figure 2b). The improved cycle stability should be ascribed...
to the suppression of $\alpha$-MoO$_3$ dissolution and the formation of effective SEI.[43] Indeed, the X-ray photoelectron spectroscopy (XPS) analysis of the Zn metal anode after cycling in the 3 m ZnCl$_2$ electrolyte evidences the Mo deposition from the Mo ions dissolved in the electrolyte (Figure S6, Supporting Information).

Figure 2c shows the charge/discharge curves of the $\alpha$-MoO$_3$ electrode with galvanostatic charging followed by 3 h of potentiostatic charging in the aqueous Zn$^{2+}$/H$^+$ dual-ion electrolyte. The $\alpha$-MoO$_3$ electrode delivers a large capacity of 465 mAh g$^{-1}$ at a rate of 0.5 A g$^{-1}$ during the first discharge, corresponding to 2.5 H$^+$ intercalation per formula unit of MoO$_3$ with an average voltage of -0.9 V. Note that “discharge” and “charge” of the $\alpha$-MoO$_3$ electrode are defined as H$^+$ intercalation (cathodic process) and deintercalation (anodic process), respectively. Although the galvanostatic charge at 0.5 A g$^{-1}$ can extract only 1.5 H$^+$, the remaining 1.0 H$^+$ can be extracted when applying a constant voltage of 1.3 V for 3 h (Figures S7,S8, Supporting Information). The diffusion coefficient determined by the potentiostatic intermittent titration technique (PITT) shows a significant 4.9-fold deceleration in H$^+$ diffusion during the deprotonation from H$_{1.1}$MoO$_3$ to MoO$_3$, confirming the trapped nature of $\approx$1.0 H$^+$ in MoO$_3$ (Figure S9, Supporting Information).

Under galvanostatic charging (without a potentiostatic step), the $\alpha$-MoO$_3$ electrode in an aqueous Zn$^{2+}$/H$^+$ dual-ion electrolyte retains 98% of its initial capacity after 1000 cycles at a rate of 2 A g$^{-1}$ (Figure 3a). Furthermore, 62% of the specific capacity at 1 A g$^{-1}$ is available at the fast discharge rate of 16 A g$^{-1}$ (Figure 3b; Figure S10, Supporting Information). These performance results indicate the stability of the MoO$_3$ framework against (de)protonation as well as the fast proton diffusion therein H$_x$MoO$_3$ (1.0 $\leq$ x $\leq$ 2.5). In contrast, the $\alpha$-MoO$_3$ electrodes in the aqueous Zn$^{2+}$/H$^+$ dual-ion electrolyte outperform those reported previously.
for α-MoO₃ electrodes using aqueous electrolytes, including quasi-solid-state Zn²⁺ electrolytes[37,38] and concentrated acid electrolytes[29,35] (Table S1, Supporting Information).

3. MoO₃ Host-Lattice Response to Anhydrous Proton Intercalation

To clarify the structural evolution of the α-MoO₃ electrode in the aqueous Zn²⁺/H⁺ dual-ion electrolyte, in situ XRD was performed during the 1st cycle (Figure 4a). The interlayer distance of α-MoO₃ remains nearly constant (∼70 Å) during the entire protonation process, while it increases from 70 to 75 Å and then decreases to 70 Å during deprotonation. This asymmetric lattice response is consistent with the asymmetric CV and charge/discharge curves, which also highly resemble those reported in a 6 m H₂SO₄ electrolyte[29] and in a 4.4 m H₂SO₄ electrolyte.[27] However, despite the asymmetric structural evolution, the α-MoO₃ structure recovers to the pristine state after a constant voltage is applied. The structure of the fully protonated phase was clarified using ex situ synchrotron XRD and Rietveld refinement (Figure 4b,c; Figure S13, Tables S2–S4, Supporting Information). Although it is difficult to determine proton positions using X-rays, the MoO₃ framework only exhibits a slight monoclinic distortion after protonation, which is consistent with a previous report on H₁.₆₈MoO₃[43] and the in situ XRD results. The Mo–O bond length of the terminating O (pointed to the interlayer space) is increases by ∼23% after full protonation, which might be caused by the formation of O–H bond.

Importantly, no water cointercalation occurs in the protonated HₓMoO₃, as evidenced by the absence of water in the refined structure. Also, when a small amount of water (one water or hydronium intercalation in 16 formula units of MoO₃) is intercalated, the DFT calculation predicts that the interlayer

Figure 3. Cycle stability and rate capability of HₓMoO₃ (1.0 ≤ x ≤ 2.5) in galvanostatic charge mode. a) Discharge capacity and coulombic efficiency at 2 A g⁻¹, b) rate performance at discharge rates from 1 to 16 A g⁻¹. Inset: the corresponding discharge curves.
distance expands by 13.8\% (H_2O intercalation) and 17.2\% (H_3O^+ intercalation) (Figure S14, Supporting Information), which are considerably larger than those observed experimentally. Additionally, the interlayer distance after water cointercalation in a 1 m H_2SO_4 electrolyte has been reported to show an expansion of 11\% upon protonation,\cite{34} another report on MoO_{2.92}·0.07 H_2O sample prepared by chemical water insertion approach also suggests an expansion of \textgreater 8\%,\cite{44} in contrast to the negligible change observed in the protonation process in our experiment. Although Ji. et al. evidenced the water intercalation in MoO_3 in a concentrated H_3PO_4 aqueous electrolyte via in situ electrochemical quartz crystal microbalance (EQCM) method,\cite{35} another EQCM study of MoO_3 in a 4.4 m H_2SO_4 electrolyte attributed the mass change to the adsorption of the solvation shell of protons on electrode surface.\cite{27} This phenomenon was also reported especially on porous structures and matrices with carbon additive.\cite{45,46} Therefore, to further rule out the water insertion in bulk MoO_3 in the aqueous Zn^{2+}/H^+ electrolyte, we cycled the MoO_3 electrode (dried at 160 °C overnight under vacuum) with an anhydrous proton electrolyte (HTFSI acid in an ionic liquid, water content < 300 ppm) in an Ar filled glovebox. As expected, identical CV curves were obtained with those in aqueous Zn^{2+}/H^+ electrolyte with similar capacity, which excluded the possibility of both water intercalation and Zn^{2+} intercalation (Figure S15, Supporting Information). This result is also in agreement with another work of Ji. et al. reporting a non-aqueous proton electrolyte (1 m H_3PO_4 in acetonitrile),\cite{28} where an identical-shaped charge-discharge curve of MoO_3 electrode in such water-free electrolyte was shown. Therefore, bare H^+ (de)intercalation occurs in the bulk of α-MoO_3 electrode with the aqueous Zn^{2+}/H^+ electrolyte.

4. Solid-State Anhydrous Proton Transfer in Dense Hydrogen Bond Network

The above experimental results indicate asymmetric bare-H^+ (de)intercalation in the α-MoO_3 electrode. To clarify the origin
of this asymmetry, we conducted DFT calculations on the H⁺ dynamics in α-MoO₃. The stable sites for H⁺ were determined by the structural optimization of the protonated phases. The three most stable H⁺ absorption sites are labeled as site A (O2-H···O2), site B (O1-H···O1/O2), and site C (O1-H···O1), where O1 and O2 are the terminating oxygen coordinated to one Mo and the bridging oxygen coordinated to two Mo, respectively (Figure S16, Supporting Information). The remaining edge-sharing oxygen (O3) coordinated to three Mo atoms is not favorable for H⁺ adsorption because all O 2p orbitals (2pₓ, 2pᵧ, and 2pₜ) participate in the Mo 4d–O 2p bonds. Site A is located within the MoO₃ layer, while sites B and C are located in the MoO₃ interlayer space.

The most favorable site for H⁺ changes as a function of x in HₓMoO₃. At low H⁺ concentrations during protonation (0 < x ≤ 0.5 in HₓMoO₃), intralayer site A is the most favorable for H⁺ adsorption. However, after 0.5 H⁺ intercalation (0.5 < x ≤ 2.5 in HₓMoO₃), interlayer sites B and then C become more favorable than site A, leading to the final formula of H₂.₅MoO₃ (site A (0.5 H⁺) → site B (1.₅ H⁺) → site C (0.₅ H⁺), Figure 5a; Figure S17, Supporting Information). Further protonation of site B (H₃MoO₃) is not thermodynamically favored, as it causes structural decomposition. The protonation on site B would weaken the Mo–O bond, consistent with that observed in the synchrotron XRD result (Figure 3c; Table S4, Supporting Information).

On the other hand, at the early stage of deprotonation (2.₅ > x ≥ 2.₂₅ in HₓMoO₃), the DFT calculations suggest that H⁻ is extracted from interlayer site C. Then, for 2.₂₅ > x ≥ 1.₅ in HₓMoO₃, 0.₅ H⁺ at site A is predominantly deintercalated in addition to the simultaneous partial deintercalation of H⁺ at site B. After completing H⁺ deintercalation from site A, the H⁻ at site B is deintercalated (1.₅ > x ≥ 0 in HₓMoO₃). In parallel, the remaining 0.₂₅ H⁺ at site C is deintercalated at the end of deprotonation. Notably, the deprotonation order (site C (0.₂₅ H⁻) → site A (0.₅ H⁻) → site B (0.₇₅ H⁻) → site B + site C (1.₀H⁻)) (Figure 5b) does not follow the protonation order (site A (0.₅ H⁺) → site A (0.₅ H⁺) → site B (1.₅ H⁺) → site C (0.₅ H⁺)), which explains the asymmetric charge/discharge profile. Experimentally, complete deprotonation is possible only when a constant voltage is applied (Figure 2c). The sluggish deprotonation at the end of charging may arise from the slow kinetics of the

Figure 5. Solid-state anhydrous proton transport in dense oxide-ion array via hydrogen bond network. a,b) The occupancy of each site in protonation with an order of site A (0.₅ H⁺) → site B (1.₅ H⁺) → site C (0.₅ H⁺) (a), and deprotonation with an order of site C (0.₂₅ H⁻) → site A (0.₅ H⁺) → site B (0.₇₅ H⁻) → site B + site C (1.₀H⁻) (b). c,d) Anhydrous proton transport via hydrogen bond network and corresponding energy barriers at the early stages of protonation (c) and deprotonation (d).
remaining H⁺ at sites B and C. The calculated voltage profile agrees well with the experimental results, confirming the validity of the asymmetric (de)protonation processes (Figure S18, Supporting Information).

To unveil the origin of the facile (de)protonation in the 1.0 < x ≤ 2.5 range of HₓMoO₃ and the sluggish deprotonation in the 1.0 ≥ x ≥ 0 range of HₓMoO₃, climbing image nudged elastic band (CI-NEB) calculations were conducted, and the energy profile of H⁺ diffusion in MoO₃ was visualized (Figure 5c). At the beginning of protonation, H⁺ rotates and hops consecutively between site A with a low energy barrier of 0.13 eV. The dense, zigzagged O₂ (bridging oxygen) and hops consecutively between site A with a low energy barrier of 0.26 eV with an O₁–O₁/ O₂ distance of 2.71 Å (Figure S19, Supporting Information), confirming the high mobility of H⁺ at site B.

As shown in Figure 5d, the deprotonation from site C of H₂.₅MoO₃ also involves a small energy barrier of 0.29 eV through the interlayer diffusion channel containing sites B and C (O–O distance of 2.86 Å). The H⁺ transfer in the dense oxide-ion array is explained by the solid-state anhydrous proton-transfer mechanism in hydrogen-bonded networks (Figure S17b, Supporting Information), whose kinetics highly rely on the distance between two adjacent lattice oxide ions. Figure S20, Supporting Information summarizes the statistics of O–O distances in all possible deprotonation channels of the charged structures. As expected, during deprotonation from H₂.₅MoO₃ to HMoO₃, short O–O distances of <2.9 Å exist to enable fast solid-state anhydrous H⁺ transfer. This value is consistent with the average molecular distance (O–O distance) in water (3.1 Å at room temperature), where a dense and continuous hydrogen-bonded network enables fast proton transfer via Grotthuss mechanism. Indeed, the required O–O distance in Grotthuss proton transfer is reported to be around 2.6–2.9 Å,[16,47] that is coincident with those in the diffusion channels of MoO₃ discussed above. Similar discussions have also been made in solid-state proton-conduction materials.[48,49] The similarity of proton- transfer mechanism in MoO₃ with that in water reveals the origin of fast proton kinetics in MoO₃ even without structural water. However, after extracting 0.25 H⁺ from site C in H₂.₅MoO₃, the O–O distances in the diffusion channel consisting of sites B and C increase drastically (>3.1 Å); meanwhile, the energy barrier therein for H⁺ diffusion becomes remarkably high (0.98 eV; Figure S21, Supporting Information). Therefore, further deprotonation from site C is unfavorable, instead, protons in site A are deintercalated, resulting in asymmetric (de)protonation (Figure 5b). A summary of the calculated proton hopping activation energies with the corresponding O–O distances is plotted in Figure S22, Supporting Information. Indeed, after deprotonation to HMoO₃, all the long-range 1D channels are disrupted so that fast H⁺ transfer through hydrogen-bonded network is no longer applicable (Figure S23, Supporting Information). The remaining H⁺ can be removed only under long relaxation times, such as potentiostatic charging and PITT (Figures S24,S25, Supporting Information). However, except for the trapped H⁺ at site C, HₓMoO₃ (1.0 ≤ x ≤ 2.5) exhibits fast H⁺ transport through the diffusion channels upon charge/discharge, providing a remarkably high capacity and high-rate capability, as demonstrated in Figure 3.

5. Conclusion
The fast proton transfer mechanism in MoO₃ was studied with both experiments and theoretical calculations. Contrary to conventional intercalation chemistry, which requires a porous host that accommodates ion diffusion and storage, the solid-state anhydrous proton transfer in hydrogen-bonded networks demonstrated in this work enables fast H⁺ transfer and accumulated H⁺ storage in dense oxide-ion arrays, which highly resembles that of Grotthuss mechanism in water only that the formation of hydrogen bond network is based on lattice oxygen arrays and intercalated protons instead of water molecule. Indeed, the proton transfer energy barrier is comparable to that of Grotthuss mechanism (<0.4 V).[8] Coupled with a zinc anode and a concentrated Zn²⁺/H⁺ electrolyte, this prototype cell successfully outperforms most aqueous zinc-ion batteries and proton batteries (Figure S26, Supporting Information). Therefore, further exploration for other host materials with dense and continuous oxygen arrays and thus capable of fast H⁺ intercalation and transfer will be an important challenge for not only fabrication of high-power aqueous H⁺ batteries but also other solid-state ionics applications using protons.

6. Experimental Section
α-MoO₃ was synthesized via a simple hydrothermal synthesis approach,[39] where 1 g of (NH₄)₂MoO₄·4H₂O (Wako) was dissolved in 25 mL of water, followed by the addition of 10 mL of HNO₃ solution (3 M). After stirring for 10 min, the transparent colorless solution was poured into a 50 mL Teflon-lined Parr autoclave and heated at 180 °C for 12 h. After filtration, the white-colored powder was washed with water and ethanol and then dried in an oven at 80 °C in an overnight.

The aqueous electrolytes were prepared by weighing ZnCl₂ and P₂O₅ in an argon-filled glovebox to prevent the absorption of water. After weighing, ultrapure water (Wako) was mixed with salts to form a solution in open air. The non-aqueous zinc electrolyte was prepared and stored in an argon-filled glovebox by dissolving vacuum dried ZnCl₂ in TEPI (Wako). The non-aqueous proton electrolyte was prepared and stored in an argon-filled glovebox by dissolving vacuum dried HTFSI solid in 1-ethyl-3-methylimidazolium bis(trifloromethanesulfonyl) ionic liquid (TCI).

The working electrode for electrochemical characterization was formulated by slurry casting 70 wt% MoO₃, active material, 20 wt% Ketjenblack (ECF-600JD, Lion Corp.), and 10 wt% polyvinylidene difluoride binder on Ti foil or carbon paper (for in situ XRD) using prompt amounts of N-methyl-2-pyrrolidone (Kanto, 99%) as the solvent. The loading level of the electrodes was controlled to ~1 mg cm⁻².

The electrochemical performance was tested in PTFE three-electrode beaker cells with Ag/AgCl (in a saturated KCl aqueous solution) as the reference electrode and activated carbon as the counter electrode. The reference electrode used in non-aqueous proton electrolyte was Ag/Ag⁺ in 0.01 M AgNO₃ and 0.1 M tetrabutylammonium perchlorate dissolved in acetonitrile. In the two-electrode cell tests, zinc foil was attached to a titanium wire, working as both the reference and counter electrode. The zinc stripping and plating tests were conducted in a 2032-type coin cell where a titanium foil and a zinc foil were separated with a glass fiber separator (Fisher) presoaked with an electrolyte. The in situ XRD studies...
were conducted in a custom cell with a Kapton membrane window on the cathode side.

The electrochemical performance was studied via CV and galvanostatic charge and discharge, the galvanostatic intermittent titration technique and the PITT using a VMP3 potentiostat (BioLogic) at room temperature.

Powder XRD and in situ XRD studies were conducted with a Bruker AXS D8 ADVANCE diffractometer using a Co sealed tube (operating at 35 kV, 40 mA) and a linear position-sensitive detector (LYNX-EYE). VESTA[50] software was used to illustrate the crystal structure. For crystal structure refinement, a powder diffractometer was used at a synchrotron radiation beamline 522 of Aichi Synchrotron Radiation Center, Japan. The wavelength used was calibrated by refining a powder diffraction pattern of the ceria powder, and the value was 0.700072(9) Å.

Elemental analysis of the MoO3 electrodes by energy dispersive XRF spectroscopy was performed with a JSX-3400RII instrument (JEOL).

The surface chemistry of the Zn electrodes was analyzed via XPS (PHI5000 VersaProbe II, ULVAC-PHI) with a monochromatic Al Kα-X-ray source. The Zn electrode samples were rinsed with pure water and acetone after being extracted from cycled cells.

The coordination states of the water molecules were investigated by Raman spectroscopy (NRS-5100, JASCO). A 532 nm excitation laser was used. The electrolyte solution was sealed in a quartz cell, and the laser was directed through the quartz crystal window.

Spin-polarized DFT calculations were carried out using the Vienna ab initio simulation package.[51,52] The projector-augmented wave pseudopotential and a plane-wave basis set with an energy cutoff of 520 eV were used.[53] The Perdew–Burke–Ernzerhof functional[54,55] with the Grimme scheme D2[56] described the exchange-correlation energy, and the Hubbard U correction was applied to the d electrons of the Mo atoms (UMo = 3.5 eV). A k-point separation of ~0.04 Å−1 was used in all calculations.

Based on a 2×1×2 supercell (MoO3)2, a series of H-intercalated structures of H2MoO3 (0 ≤ x ≤ 3.0) was calculated. Each proton was placed between two nearby O atoms where one covalent bond (∼1 Å) and one hydrogen bond (1.6–2.3 Å) were formed. All possible configurations were calculated by optimizing both the lattice and ion positions, and then a convex hull was constructed to identify the stable phases in the discharge and charge processes. The formation energies (at 0 K) were calculated as:

\[ \Delta E(H_2 MoO_3) = E(H_2 MoO_3) - \left( \frac{3-x}{3} \right) E(MoO_3) - \frac{x}{3} E(H_3 MoO_3) \]  

where \( E(H_2 MoO_3) \), \( E(MoO_3) \), and \( E(H_3 MoO_3) \) are the total energies of \( H_2 MoO_3 \), pristine MoO3, and \( H_3 MoO_3 \), respectively. The determined structures are shown in Figure S19, Supporting Information. The voltage profile was then evaluated, with the average voltage of the reaction between two adjacent stable phases calculated as:

\[ U(x_1, x_2) = \frac{-[E(H_2 MoO_3) - E(H_3 MoO_3) - (x_1 - x_2) \mu_H]}{(x_1 - x_2) F} \]  

where \( F \) is the Faraday constant, \( \mu_H \) is the chemical potential of hydrogen gas at atmospheric pressure, and \( T = 298.15 \) K.

\[ \mu_H = E(H_2) + \frac{1}{2} k_B T - \Delta S \]  

where \( E(H_2) \) is the total calculated energy of a hydrogen molecule, \( k_B \) is the Boltzmann constant, and \( \Delta S \) is obtained from the JANAF thermochemistry tables.[57]

The CI-NEB method was used to calculate proton diffusion pathways in a 2×2×1×2 supercell.[58] For the stable structures in the discharge process, an extra proton was added to migrate between two neighboring adsorption sites. In the charge process, a proton was removed from the stable structures to construct a vacancy site for the migration of other protons.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Author Contributions

Z.M. and X.-M.S. contributed equally to this work. M.O. and A.Y. conceived and directed the project. Z.M. conducted material synthesis and theoretical calculations. S.-i.N. conducted the structural analysis. Z.M. and X.-M.S. contributed equally to this work. M.O. and A.Y. designed the experiments. All authors wrote the manuscript.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aqueous batteries, high-rate batteries, proton intercalation, proton transfer

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