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Architecting a Stable High-Energy Aqueous Al-Ion Battery

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ABSTRACT: Aqueous Al-ion batteries (AAIBs) are the subject of great interest due to the inherent safety and high theoretical capacity of aluminum. The high abundance and easy accessibility of aluminum raw materials further make AAIBs appealing for grid-scale energy storage. However, the passivating oxide film formation and hydrogen side reactions at the aluminum anode, as well as limited availability of cathode lead to low discharge voltage and poor cycling stability. Here, we proposed a new AAIB system consisting of Al_xMnO_2 cathode, zinc substrate supported Zn-Al alloy anode and an $\text{Al}(\text{OTF})_3$ aqueous electrolyte. Through the in-situ electrochemical activation of MnO, the cathode was synthesized to incorporate a two-electron reaction, thus enabling its highest theoretical capacity (755 mAh g^{-1}) among all manganese oxides. The anode was realized by a simple deposition process of Al^{3+} onto Zn foil substrate. The featured alloy interface layer can effectively alleviate the passivation and suppress the dendrite growth, ensuring ultralong-term stable aluminum stripping/plating. The architected cell delivers a record-high discharge voltage plateau near 1.6 V and specific capacity of 460 mAh g^{-1} for over 80 cycles. This work provides new opportunities for the development of high-performance and low-cost AAIBs for practical applications.

INTRODUCTION

Conventional Li-ion batteries (LIBs) have revolutionized energy storage and been used as a major power source in portable electronic and electric vehicles.¹ In light of the concerns over the cost, safety, and the availability of lithium reserves, the ‘beyond Li-ion’ batteries have emerged as potential candidates, such as Zn-ion, Mg-ion, and Al-ion batteries.²⁻⁴ Among them, rechargeable Al-ion batteries (AIBs) can offer the considerable advantages of cost-effectiveness and high anode capacity due to the high-abundance and three-electron redox properties of aluminum.⁵⁻⁷ Recently, AIBs receive more attention than ever because Dai’s group made a breakthrough in AIBs relying on an ionic liquid (IL) electrolyte.⁴ Nevertheless, the high cost, severe corrosiveness, $\text{H}_2\text{O}/\text{O}_2$ sensitivity of IL electrolyte limit the practical application of ILs-based AIBs.⁸ Alternatively, the development of aqueous AIBs (AAIBs) is highly desirable, but it still faces scientific challenges associated with designing suitable cathode materials and achieving reversible aluminum stripping/plating.

Recent progress revealed that manganese-based cathodes possess higher energy density than that of other kinds of cathodes (V-based oxides,^{9,10} Ti-based oxides,¹¹⁻¹³ Prussian blue analogs,^{14,15} etc.).⁸⁻¹⁸ For example, the cryptomelane and birnessite MnO_2 were used as cathodes, showing the acceptable discharge capacities.^{17,18} Impressively, the $\text{Al}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$ cathode synthesized via the

in-situ electrochemical transformation of Mn_2O_3 precursor delivers a record high energy density in all rechargeable AIBs.⁸ Thus, the strategy of electrochemical transformation is expected to explore more cathode materials with high energy density for AAIBs. However, the reaction mechanism utilizes only one electron redox of $\text{Mn}^{4+}/\text{Mn}^{3+}$ in the $\text{Al}_x\text{MnO}_2 \cdot n\text{H}_2\text{O}$ cathode (with a theoretical capacity of 462 mAh g^{-1}), limiting its capacity and voltage. The two-electron redox of $\text{Mn}^{4+}/\text{Mn}^{2+}$ in principle can offer higher theoretical capacity and voltage.^{19,20} It is therefore postulated that the Al_xMnO_2 cathode prepared by the transformation of MnO can lead to the highest theoretical capacity of 755 mAh g^{-1} , as summarized in **Figure 1a**.

Despite these efforts to cathode development, owing to the low standard potential of aluminum anode, there are several intrinsic drawbacks rendering AAIBs over past 30 years hard to compete with other aqueous battery systems, such as passivating oxide film formation, notorious hydrogen side reactions and rapid self-discharge.²¹ To date, extensive efforts have focused on developing the anodes comprising of other materials rather than metal aluminum.²¹ For instance, the feasibility of TiO_2 as anode in aluminum storage has been validated.¹¹⁻¹³ Albeit the utilization of alternative anode enhances the longevity of the cell, the overall reachable energy density is very low due to Al^{3+} ions intercalation/de-intercalation mechanism in TiO_2 . Generally, metal anode based on the metal stripping/plating mechanism enables high energy storage.²² Previous researches indicated that using

various Al-based alloys as anodes can circumvent the above-mentioned thorny issues.²³⁻²⁵ To date, no aluminum alloys-based AAIBs system has been reported yet. Theoretically, the alloying elements need to satisfy the following criteria: (a) high redox potential in aqueous system and (b) similar reaction activities with aluminum. Therefore, engineering for the suitable Al-based alloys is a pivotal gateway to achieve the AAIBs with high reversibility.

Herein, we tackled these limitations by architecting a new AAIBs in the form of Zn-Al/2 M Al(OTF)₃/Al_kMnO₂. The Al_kMnO₂ cathode was synthesized via an in-situ electrochemical transformation from MnO precursor. According to our DFT calculation, the Al³⁺ with strong electrostatic force can compete with other ions to arouse the extraordinary two-electron redox of Mn⁴⁺/Mn²⁺. This leads to a theoretical capacity of up to 755 mAh g⁻¹, which is the highest among all manganese oxide-based cathodes (Figure 1a, the corresponding calculation details are shown in Methods of Supporting Information). Moreover, Zn-Al alloy anode with excellent metal plating/stripping electrochemistry was achieved by depositing Al³⁺ onto Zn foil substrate. Particularly, the addition of alloying element Zn can mitigate the passivation and self-discharge behavior, and improve the Coulombic efficiency (CE)

by inhibiting H₂ evolution side reaction. Meanwhile, compared with Zn²⁺ ions, Al³⁺ ions have the lower electrochemical redox potential in aqueous media. Thus, during Zn²⁺/Al³⁺ deposition, Al³⁺ can form a positively charge electrostatic shield to suppress the metal dendrite growth. As a consequence, the as-designed cell delivers a superior rate performance, high discharge voltage 1.6 V and an unprecedented high capacity of 460 mAh g⁻¹ at 100 mA g⁻¹ after 80 cycles. As per our knowledge, the achieved specific capacity and voltage are the highest values among all the reported AAIBs.

RESULTS AND DISCUSSION

Structural Characterization of Designed Cathode. In 'beyond Li'-Mn battery, MnO is electrochemically inactive for ions storage because of the absence of tunnel structure.²⁶ To capitalize on its high theoretical capacity, we adopt a conventional charging process to enable MnO activation (Figure S1). In detail, MnO was used as cathode and assembled into a cell with the aqueous electrolyte of aluminum trifluoromethanesulfonate (Al(OTF)₃) (2 M). The crystal structure and phase information of the as-prepared cathode was first examined by X-ray diffraction (XRD). After electrochemical activation, all the characteristic peaks are weakened (Figure 1b), which might be related to the formation of

Figure 1. Formation of Al_kMnO₂ cathode. (a) Theoretical capacity of various manganese oxide cathodes. (b) XRD patterns of MnO and Al_kMnO₂ at the range of 15-80° and 30-50°. (c) HRTEM image of MnO. (d) HRTEM image of Al_kMnO₂. (e) A masked lattice fringe image of MnO obtained by auto-correlation of HRTEM, showing the MnO crystal structure with Mn (yellow) element. (f) A masked lattice fringe image of Al_kMnO₂ obtained by auto-correlation of HRTEM, showing the Al_kMnO₂ crystal structure. (g) STEM images and element mappings of Al_kMnO₂. (h) EXAFS spectra of MnO and Al_kMnO₂. (i) Schematic of the crystal structure transformation from MnO into Al_kMnO₂. The balls with yellow, purple and blue colors represent Mn, O and Al atoms. Scale bars: (c, d) 2 nm.

amorphous phases.⁸ In the magnified view of **Figure 1b**, there are peaks from a new MnO_2 phase observed in the XRD pattern of the activated cathode. To achieve a better resolution, we collected high-energy synchrotron XRD patterns from MnO and the activated cathode. In addition to the peak weakening, the arrows indicate the appearance of new diffraction peaks, which can be indexed to the cubic phased MnO_2 (**Figure S2**). The structural evolution was further detected by scanning electron microscopy (SEM) and transmission electron microscopy (TEM). **Figure S3** shows that the pristine MnO is observed as nanoparticles with a size range of 100-150 nm. As displayed in the high-resolution TEM (HRTEM) images, the two lattice fringes of 0.26 and 0.16 nm can be assignable to the (111) and (022) planes of MnO , respectively (**Figure 1c**). After activation, there is no obvious change of the particle morphology (**Figure S4a**). The observed lattice fringes correspond to the (022) and (111) planes of MnO_2 and (111) plane of MnO (**Figure 1d** and **Figure S4b-d**), respectively. The contrastive lattice fringe images obtained by auto-correlation (**Figure 1e,f**) offer a view of the atomic arrangement, as schematically projected along the $[0\bar{1}1]$ direction of cubic phased MnO and MnO_2 . The activation concurrently induces the formation of abundant amorphous phases along the phase boundaries between MnO_2 and MnO (**Figure S4e,f**). Energy-dispersive spectroscopy (EDS) mappings on an activated particle, using TEM, reveal the homogeneous distribution of Al element in the cathode (**Figure 1g**). According to the above results, we hereafter refer to the activated cathode as Al_xMnO_2 . **Figure 1h** displays the corresponding Fourier transform of phase-uncorrected extended X-ray absorption fine structure (FT-EXAFS) spectra. The spectrum of Al_xMnO_2 resembles that of MnO_2 , further confirming the XRD and TEM observations. Notably, the relative intensity of Mn-O peak decrease, which is related to the intercalation of Al^{3+} ions on activation.²⁷ **Figure 1i** illustrates the crystal structure evolution from MnO into Al_xMnO_2 . MnO has a rock-salt crystal structure and each atom has six neighbors of the opposite type, which are at the vertices of a regular octahedron.²⁸ Thus, each translational cell is arrayed as Mn_4O_4 cubes. In the process of charging, partial Mn^{2+} ions dissolve out and other Mn^{2+} ions are oxidized into Mn^{4+} to balance the charges. The cubic Mn_4O_4 subunits in MnO are topologically similar to Mn_4O_4 subunits in MnO_2 .²⁹ Moreover, with the Mn^{4+} rearranged into MnO_2 phase, trivalent Al^{3+} ions would be able to insert into the phase boundaries with the presence of strains and defects.⁸ As a result, cubic structure Al_xMnO_2 is generated.

X-ray photoelectron spectroscopy (XPS) spectra reveal the variation of chemical composition and elemental state of electrode material after activation. In Mn $2p_{3/2}$ XPS spectra (**Figure 2a**), the dominant peak centred at around 642.6 eV is characteristic of Mn^{4+} ,³⁰ suggesting the $\text{Mn}^{2+}/\text{Mn}^{4+}$ oxidation on charging. Correspondingly, the peak of Mn-O bond in O 1s spectra shifts toward a higher binding energy due to the oxidation state change of Mn (**Figure S5**). The presence of Al signals in Al 2p and full spectra (**Figure 2b** and **Figure S6**) confirms the intercalation of Al^{3+} ions into host. The Mn oxidation state was further investigated using synchrotron X-ray absorption spectroscopy (XAS). **Figure 2c** shows the normalized Mn K-edge X-ray absorption near-edge spectroscopy (XANES) of pristine MnO and Al_xMnO_2 . Clearly, compared with MnO , the entire edge shifts to higher energy for

Al_xMnO_2 , indicating an increase of the Mn oxidation state.³¹ To determine the average valence of Mn, the first-order derivative of Mn-K XANES was conducted. As shown in **Figure 2d**, the absorption edge energy of Al_xMnO_2 is about 6550 eV, which is slightly less than that of MnO_2 , but is higher than that of Mn_2O_3 .^{32,33} This result implies that, on full activation, Mn^{2+} is partially oxidized to Mn^{4+} and Mn^{3+} . Thus, the average Mn oxidation state of Al_xMnO_2 is estimated to be between +3 and +4. Based on above measurements, the facile electrochemical charging approach successfully produces Al_xMnO_2 , which can serve as a high-capacity cathode material for AAIBs.

Figure 2. Structure analysis of Al_xMnO_2 cathode. (a) Mn 2p and (b) Al 2p XPS spectra of MnO and Al_xMnO_2 . (c) Mn K-edge XANES spectra and (d) First derivative spectra of MnO and Al_xMnO_2 .

Structural Characterization of Designed Anode. Metal Zn foil was employed as substrate to form a Zn supported Zn-Al alloy anode. Briefly, a symmetric cell was assembled by using Zn foils as electrodes and aqueous $\text{Al}(\text{OTf})_3$ (2 M) solutions as electrolyte. On charging, Al^{3+} in electrolyte were deposited on and reacted with the metal Zn substrate to form Zn-Al alloy. The morphology and elemental distribution of the as-designed anode were characterized by SEM, EDS and Scanning Kelvin probe microscopy (SKPM). In sharp contrast with the smooth surface of the initial Zn substrate, the rough surface manifests the uniform coverage of the deposited coating onto substrate after charging (**Figure 3a,b** and **Figure S7, 8**). The big Volta potential difference in SKPM image suggests the formation of other phases on the substrate (**Figure 8d**). The deposition layer with thickness on the order of 30 μm is composed of integrated nanoparticles of 15–30 nm in size (**Figure 3b, c**). The backscatter SEM image shows the obvious phase boundary between Zn substrate and deposition layer (**Figure S9**). The co-existence of Zn and Al elements in the deposition layer suggests the generation of Zn-Al alloy (**Figure S10**). To further ascertain the structure of Zn-Al alloy anode, XRD, XPS and XAS were employed. XRD was carried out to identify the crystal structure of the alloy anode (**Figure 3d**). After charging, only diffraction peaks belonging to hexagonal Zn are observed without detectable metallic Al or aluminum oxide phases, indicating the complete alloying of Al with Zn. Compared to Zn foil, the peak positions of

Figure 3. Formation of Zn-Al alloy anode. (a, b) SEM images of the top view of Zn foil (a) and Zn-Al alloy (b). (c) SEM image of the cross section of Zn-Al alloy. (d) XRD patterns of Zn foil and Zn-Al. (e) High energy synchrotron XRD pattern of Zn-Al. (f) Zn 2p XPS spectra of Zn foil and Zn-Al. (g) Al 2p XPS spectrum of Zn-Al. (h) XANES spectra and (i) EXAFS spectra of Zn foil and Zn-Al. Scale bars: (a) 1 μm , (b) 500 nm, (c) 30 μm

Zn-Al anode shift to a lower angle due to the alloying effect.³⁴⁻³⁶ The distinct change in relative peak intensity, $I_{(002)}/I_{(100)}$, further attests the alloying of Al with Zn substrate.³⁶ The diffraction pattern at a higher resolution is used to detect the as-prepared alloy owing to the much lower content of Al than Zn. As evidenced by the high-energy synchrotron XRD pattern of Zn-Al (Figure 3e), all characteristic peaks could be attributed to the hexagonal Zn phase, which verifies the successful alloying process.

XPS and XAS analyses were conducted to capture in-depth information about the electronic and structural properties of the alloy layer. XPS spectra in Figure 3f,g explicitly validate the existence of metallic states of Zn and Al, revealing the formation of Zn-Al alloy.³⁷⁻³⁹ In Al 2p spectrum, the minor peak at 74.0 eV is ascribed to the inevitable oxidation of Al at room temperature.^{38,39} The Zn 2p peaks of Zn-Al shift to a lower binding energy than that of Zn foil. This is because the electronic states of Zn in Zn-Al alloy are modified by alloying with Al³⁷. As reflected in the XANES curves at the Zn k-edge (Figure 3h), Zn-Al alloy has a lower energy of the adsorption edge than Zn foil, suggesting the electron

richness of Zn atoms and electron deficiency of Al atoms.⁴⁰ In the FT-EXAFS spectra (Figure 3i), an obvious decrease in the main peak intensity of Zn-Al anode is observed relative to Zn foil. This phenomenon indicates the variation in local coordination of Zn species after alloying, which is in accordance with the XANES and XPS results.^{34,40} Theoretically, the above variation of electronic structure would increase the overpotential of Al for hydrogen evolution to improve the cycle life of AAIBs.²³

Study of Dendrite Growth and Al Deposition on Various Substrates. The electrochemical behaviors of Al plating/stripping on various metal substrates were investigated by comparing the voltage profiles in symmetric cells. Al(OTF)₃ electrolyte was used in all symmetric and full cells, unless otherwise stated. Specifically, Al-based alloy interface layers form during the cycling process. As demonstrated in Figure 4a, the cell using Al substrate runs for only few cycles and suffers from large voltage hysteresis (>2 V). An abrupt voltage change occurs and renders the cell failure after the continuous voltage increase due to an uneven ion transport through the passivated oxide interface.¹⁶ The large voltage

Figure 4. Electrochemical performance for symmetric cells. (a) Voltage profiles for symmetric cells based on Zn and Al substrates in 2 M Al(OTF)₃ electrolyte at 0.2 mA cm⁻². (b) Voltage profiles for symmetric cells based on Zn substrate in 2 M Al(OTF)₃ and 2 M Zn(OTF)₂ electrolytes at 0.2 mA cm⁻². Each cycle contains the discharge process for 0.5 h and the charge process for 0.5 h. Inset in a and b, the magnification of selected periods. Illustration of (c) dendrite suppression and (d) dendrite growth. (e, f) SEM images of Zn substrates after 100 stripping/plating cycles in (e) 2 M Al(OTF)₃ and (f) 2 M Zn(OTF)₂ electrolytes. (g) The comparative Nyquist plots. Scale bars: (e) 4 μm, (f) 2 μm.

polarization makes the bare Al electrode unviable as anode for AAIBs. In striking contrast, the charge and discharge of cell based on Zn-Al electrode can proceed under a significantly low overpotential. Even after cycling for 1000 h, the voltage polarization still remains less than 25 mV and no short-circuit is observed, exhibiting remarkably stable metal plating/stripping behaviors on Zn-Al electrode. However, bare Zn electrode using Zn(OTF)₂ electrolyte suffers the irreversible process during Zn plating/ stripping, which leads to low CE and cell short-circuit (**Figure 4b** and **Figure S11,12**). Furthermore, metal Zn presents a better corrosion resistance in Al(OTF)₃ than in Zn(OTF)₂ electrolyte (**Figure S13-15**). These results imply the improvement in Al-based anode stability realized by the assistance of alloying element Zn. Meanwhile, Al can inhibit the accompanying negative effect (dendrite growth) from Zn, which can be explained via an electrostatic shield mechanism.^{41,42} Theoretically, on plating, Zn²⁺ deposits more easily than Al³⁺ because of its higher electrochemical redox potential⁶⁷. That is, Al³⁺ will form a positively electrostatic shield to suppress the growth of metal dendrites (**Figure 4c, d**). As observed in **Figure S4e,f**, the alloy plating layer after 100 cycles is relatively smooth under the shield of Al³⁺ in contrast to the massive growth of metal dendrite in Zn(OTF)₂ electrolyte. In low-concentration Al(OTF)₃ electrolyte, it lacks sufficient Al³⁺ to prevent the growth of metal dendrite or the resultant micro-shortening (**Figure S16**). As for high-concentration Al(OTF)₃ electrolyte, although short-circuit is not observed, the symmetric

cells exhibit large polarization potentials (**Figure S17**). These observations confirm that a proper concentration of Al(OTF)₃ electrolyte (2 M) is needed to enable the superior reversibility of metal plating/stripping. Electrochemical impedance spectroscopy (EIS) measurements were further performed on the symmetric cells to examine the interfacial resistance (**Figure 4g**). The charge transfer resistances of cells using bare Al and Zn electrodes are enormous, as high as 4500 and 1300 Ω, respectively. Dramatically, the corresponding value for Zn-Al electrode decreases to 150 Ω in 2 M Al(OTF)₃ electrolyte (**Figure 14**), underscoring the importance of alloy layer on improving charge transfer kinetics. To highlight the key role of Zn-Al alloy, various metal foils that can form alloy with Al are tested as substrates in such electrochemical process. By contrast, Zn-Al anode displays the best cycling stability with the smallest polarization and lowest interfacial resistance (**Figure S18** and **S19**). The cycling is still very stable with the polarization voltage below 30 mV even after resting for 9 days (**Figure S20**). Based on the above discussion, the high stability and reversibility of Zn-Al anode make it the most promising candidate for new-type AAIBs, which rely on a combination of plating and alloying processes for achieving stable, long-term operation.

Electrochemical Performance of Full Cell. Building on the success of Zn-Al anode in facilitating reversibility, we then explore its practical application in coin-type full cell by coupling with the Al_xMnO₂ cathode we made. As expected, the cell using Zn-Al anode demonstrates better cycling performance and higher CE

Figure 5. Electrochemical performance comparison of metal/ Al_xMnO_2 full cells using different anodes in 2 M $\text{Al}(\text{OTf})_3$ electrolyte. (a) Cycling performance at a current density of 100 mA g^{-1} . (b) Rate performance of full cell using Zn-Al anode. (c) The first galvanostatic discharge/charge curves. (d) CV curves at the scan rate of 0.1 mV s^{-1} . (e) Nyquist plots of fresh full cells. (f) Time dependence of the OCP decay. (g) Comparison of voltage and capacity in the reported AAIBs.

than that using bare Al anode (Figure 5a). Specifically, the cell with bare Al anode experiences a fast decay in capacity and stops discharging after 47 cycles. This phenomenon, namely battery broken circuit, can be attributed to the quick accumulation of passivated film and generation of hydrogen gas on the surface of Al foil.^{16,21} In contrast, the Zn-Al/ Al_xMnO_2 cell delivers a superior cycling capacity of 460 mAh g^{-1} at 100 mA g^{-1} after 80 cycles, which is the highest value so far reported for AAIBs (Figure 5g, corresponding detailed parameters are listed in Table S1 and S2). Even at a high current density of 1 A g^{-1} , the cell still exhibits an excellent stability with only a minimal increase of overpotential (Figure S21). Superior to the cell using bare Al and Zn anode, smaller voltage polarization and higher discharge plateau are achieved for cells using Zn-Al anode (Figure 5c,d and Figure S22), which could originate from the fast reaction kinetics enabled by alloying of Al with Zn.⁴³⁻⁴⁵ The potential higher than that from either individual constituent further verifies the assistance of Zn to Al in alloy anode. Moreover, we characterized the CV of cell using the concentration-gradient hybrid electrolyte. As seen in Figure S23, the discharge plateau gradually decreases with the increase of the $\text{Zn}(\text{OTf})_2$ content. This indicates that the dominated trapping aluminum is responsible for the high-potential of

Zn-Al/ $\text{Al}(\text{OTf})_3/\text{Al}_x\text{MnO}_2$ cell. Most notably, the discharge plateau of Zn-Al/ Al_xMnO_2 cell is as high as 1.6 V, which is a record-high value among all reported AAIBs (Figure 5g). The advantages of such cell are further evidenced by the attractive rate capability (Figure S24), realizing a capacity close to 100 mAh g^{-1} at an extremely high current density of 3 A g^{-1} (Figure 5b). When the rate switches back to 1 A g^{-1} , a discharge capacity of 230 mAh g^{-1} can be completely recovered. Confirmed by EIS and the galvanostatic intermittent titration technique (GITT), the alloy interphase layer is highly conductive for ions transfer (Figure 5e and Figure S25). The effects of other Al-based alloy anodes, electrolyte type and concentration on the full cell performance are also investigated and the results are shown in Supplementary Figure S26-32. The full cell based on Zn-Al anode in 2 M $\text{Al}(\text{OTf})_3$ electrolyte exhibits the best electrochemical performance in terms of specific capacity and voltage plateau, which is highly consistent with the results of the symmetric cells. Considering the intermittent nature of large scale grid-storage batteries, a low self-discharge is essential for practical applications. We first monitored the decay of open circuit voltage (OCV), as shown in Figure 5f. The initial OCV of Zn-Al/ Al_xMnO_2 fresh cell (1.58 V) is higher than that of Al/ Al_xMnO_2 cell (1.22 V), and

displays a negligible voltage change after 10 h. However, the Al/Al_xMnO₂ fresh cell presents a sharp reduction and can only retain at 0.9 V after 10 h. Furthermore, a delayed discharge test is conducted after resting for 12 h following the fully charge. The capacity loss of Zn-Al/Al_xMnO₂ is the lowest between charge and discharge cycles, manifesting its remarkable application potential with extremely low self-discharging (Figure S33-35).

Mechanism Investigation. The reaction mechanism was investigated to uncover the origin of the exceptional performance of the Zn-Al/2 M Al(OTF)₃/Al_xMnO₂ cell. CV measurements at different scan rates were carried out. The peak current increases linearly with the square root of the scan rate, indicating that the Al³⁺ transport at the Al_xMnO₂ cathode is under diffusion control (Figure S36).¹⁶ This can be reflected in the formation of more amorphous component due to the deep intercalation of more Al³⁺ into Al_xMnO₂ during discharge (Figure S37 and Table S3). The emergence of amorphous phase ignores the concentration of Al(OTF)₃ electrolyte (Figure S38). However, when using other manganese oxides as cathode precursors, no obvious phase transformation or weakened peaks arises after cycling (Figure 39). This might be stemmed from the incomplete Al³⁺ intercalation reactions, causing the inferior battery performance (Figure 40-42). To gain a deep insight into the reversibility, ex-situ XANES, XRD and TEM were performed to probe the structural evolution of electrode materials during the cycling process. In Figure 6a, the Mn K-edge shifts towards lower energy during Al³⁺ insertion and moves back to the high-energy position during Al³⁺ extraction. After full discharge and charge, the close edge positions as compared to those of precursor MnO and Al_xMnO₂ imply that the redox process is highly reversible. Ex-situ XPS spectra also provide the evidence of the reversible valence variation during the Al³⁺ insertion/extraction (Figure S43). Ex-situ XRD of Al_xMnO₂ indicates a reversible change in phase structure (Figure 6b). The

(311) peak intensity of MnO₂ is weakened as the discharge proceeds. At the end of the discharge, the (311) peak completely disappears but recovers during the charging process. Correspondingly, the atomic ratio of Al/Mn gradually increases during discharge, while decreases for charging process (Table S4). This suggests a reversible Al³⁺ storage for Al_xMnO₂ derived from MnO. The topological conversion relationship between MnO and MnO₂ might be the reason of delivering a reversible charge-discharge process. Besides, the formation of the abundant amorphous phase might induce the simultaneous process of intercalation and conversion, which conduces to the achievement of the reversible process.⁴⁶ Notably, except for Al³⁺, the Zn²⁺ released by anode may also intercalate into cathode. Nevertheless, Al_xMnO₂ cathode stores a negligible amount of Zn²⁺ compared to that of Al³⁺ after 1st- and even 80th-cycle discharge (Table S3). To suppress the diffusion of Zn²⁺ ions, a Celgard separator with smaller pore size is employed. As seen in Figure S44, the cell displays similar discharge capacity, eliminating the possibility of the contribution from Zn²⁺ ions. The contribution of Al³⁺ in capacity is further identified by comparing the cases when employing pure Zn(OTF)₂ and hybrid (Zn(OTF)₂ and Al(OTF)₃) as aqueous electrolytes. In the cell using pure Zn(OTF)₂ electrolyte, the capacity is totally attributed to Zn²⁺ and H₃O⁺ because neither the Zn(OTF)₂ nor Zn anode provide any Al³⁺. The discharge/charge profiles and cycling performance are shown in Figure S45, which displays a very low and negligible discharge capacity of 15 mA h g⁻¹. Indeed, no phase conversion occurs and only a small amount of ions can be stored in MnO during the cycling process (Figure S46 and S47 and Table S5). When using hybrid electrolyte, with the increased of Al(OTF)₃ content, the gradual increase in capacity manifests that Al³⁺ plays an important role for phase conversion from MnO to MnO₂ (Figure S48). As obtained from the theoretical computation, obviously, Al_xMnO₂ is the most thermodynamically stable species, implying the trivalent Al³⁺ ions

Figure 6. Proof of excellent cycling stability and high capacity. a Mn K-edge XANES spectra of Al_xMnO₂ cathodes after fully discharge and charge. b XRD patterns of Al_xMnO₂ cathodes at selected states during the first cycle and typical charge/discharge curves at 100 mA g⁻¹. c CV curves of Zn-Al/2 M Al(OTF)₃/Al_xMnO₂ cell at a scan rate of 0.1 mV s⁻¹. d EXAFS spectra of Zn-Al anodes before and after cycling. e SEM image of Zn-Al anode after cycling. Scale bar: (e) 500 nm.

are more likely to induce the phase conversion (**Figure S49**). Therefore, other cations including Zn^{2+} and H_3O^+ in Zn-Al/2 M $\text{Al}(\text{OTf})_3/\text{Al}_x\text{MnO}_2$ cell hardly contribute to the discharge capacity. **Figure 6c** shows the CV curves for Zn-Al/2 M $\text{Al}(\text{OTf})_3/\text{Al}_x\text{MnO}_2$ cell scanned at 0.1 mV s^{-1} . One pair of redox peaks can be clearly observed, which are assignable to the intercalation/extraction of Al^{3+} . Besides, there is no obvious change of CV curves in the first three cycles, demonstrating a low polarization and high stability of Al_xMnO_2 cathode.

On the anode side, ex-situ XAS, XPS and SEM were employed to track of Al stripping/plating and investigate the structural stability of alloy anode in the full cell. As observed in the FT-EXAFS spectra (**Figure 6d**), more Zn-Zn bonds recover due to the stripping of Al after the 1st- and even 80th- discharge. The Zn 2p XPS spectra in **Figure S50** show the peak shift towards higher binding energy due to the release of Al during the discharging process. In the following deposition, the aluminum re-alloys with Zn, which is reflected in the peak shift towards lower binding energy. EDS analysis collected on the discharged anode shows a decreased ratio of Al compared with pristine anode (**Figure S51**). Conversely, the ratio of Al increases on charging. The above results prove the effectiveness of Al stripping/plating in improving the cell potential under the assistance of Zn, similar as in other alloys.⁴⁷⁻⁴⁹ In the high-energy synchrotron XRD pattern, the pure alloy phase can be observed after cycling without the formation of byproducts (**Figure S52**), elucidating that alloying can effectively prevent the corrosion of metal anode. The morphological evolution of Zn-Al anode in full cell was recorded, as shown in **Figure 6e**. Owing to the electrostatic shield effect of Al^{3+} , alloy anode presents a dendrite-free flat surface after cycling. In comparison, large amounts of dendrites and complex products appear on the surface of the bare Zn anode (**Figure S53**). These results demonstrate the excellent stability of alloy anode during electrochemical cycling. Although a small amount of Zn^{2+} ions involve in the stripping/plating to assist the formation of alloy layer on the anode side, they do not contribute to the capacity on the cathode side. All the above results suggest that Al^{3+} ions dominate the overall electrochemical reaction.

CONCLUSIONS

In conclusion, we have developed a new aqueous Al-ion battery configuration using Al_xMnO_2 as the cathode combined with Zn-Al alloy anode in a 2 M $\text{Al}(\text{OTf})_3$ electrolyte. The cathode material was successfully prepared via in-situ topological transformation from cubic MnO in the trivalent Al^{3+} aqueous solution. Theoretical calculations and comparative experiments reveal that the two-electron reaction aroused by Al^{3+} intercalation plays the key role in achieving high capacity. An oxidation-resistant and dendrite-suppressed Zn-Al alloy anode was fabricated through depositing Al^{3+} onto Zn substrate. The alloy anode with high-reversibility exhibits an ultralong cycling life of over 1500 h. As a result, the Zn-Al/ $\text{Al}(\text{OTf})_3/\text{Al}_x\text{MnO}_2$ cell delivers a high reversible capacity (460 mAh g^{-1} at 100 mA g^{-1} after 80 cycles), high discharge voltage plateau (1.6 V) and high rate capability (100 mAh g^{-1} at 3 A g^{-1}), which are the highest values to date reported for AAIBs. This work therefore represents an important step towards developing high-capacity AAIBs and opens up a promising prospect for practical application.

ASSOCIATED CONTENT

The Supporting Information is available free of charge at <http://pubs.acs.org>.

Materials and methods; Figures S1-S47 and Tables S1-S5.

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Notes

The authors declare no competing financial interest.

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