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## Al-doped $\alpha$ -MnO<sub>2</sub> coated by lignin for high-performance rechargeable aqueous zinc-ion batteries†

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Zn/MnO<sub>2</sub> batteries, one of the most widely studied rechargeable aqueous zinc-ion batteries, suffer from poor cyclability because the structure of MnO<sub>2</sub> is labile with cycling. Herein, the structural stability of  $\alpha$ -MnO<sub>2</sub> is enhanced by simultaneous Al<sup>3+</sup> doping and lignin coating during the formation of  $\alpha$ -MnO<sub>2</sub> crystals in a hydrothermal process. Al<sup>3+</sup> enters the [MnO<sub>6</sub>] octahedron accompanied by producing oxygen vacancies, and lignin further stabilizes the doped Al<sup>3+</sup> via strong interaction in the prepared material, Al-doped  $\alpha$ -MnO<sub>2</sub> coated by lignin (L + Al@ $\alpha$ -MnO<sub>2</sub>). Meanwhile, the conductivity of L + Al@ $\alpha$ -MnO<sub>2</sub> improves due to Al<sup>3+</sup> doping, and the surface area of L + Al@ $\alpha$ -MnO<sub>2</sub> increases because of the production of nanorod structures after Al<sup>3+</sup> doping and lignin coating. Compared with the reference  $\alpha$ -MnO<sub>2</sub> cathode, the L + Al@ $\alpha$ -MnO<sub>2</sub> cathode achieves superior performance with durably high reversible capacity ( $\sim$ 180 mA h g<sup>-1</sup> at 1.5 A g<sup>-1</sup>) and good cycle stability. In addition, *ex situ* X-ray diffraction characterization of the cathode at different voltages in the first cycle is employed to study the related mechanism on improving battery performance. This study may provide ideas of designing advanced cathode materials for other aqueous metal-ion batteries.

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## 1. Introduction

With the rapid development of the utilization of renewable energy (e.g., solar, wind, tide, and biomass), advanced batteries for energy storage have attracted extensive consideration.<sup>1–3</sup> Aqueous metal-ion batteries with the advantages of good safety and high ion conductivity are considered to be the next generation of large-scale energy storage devices.<sup>4,5</sup> Among numerous contenders of rechargeable aqueous metal-ion batteries,<sup>6,7</sup> aqueous Zn-ion batteries (AZIBs) appear to be tremendously promising because of their superior attributes,<sup>8</sup> including high theoretical capacitance of the Zn anode (820 mA h g<sup>-1</sup>), low electrochemical potential of Zn<sup>2+</sup>/Zn ( $-0.763$  V, SHE), low cost, and environmental friendliness.<sup>9–11</sup>

As for AZIBs, the commonly used cathode materials include Mn-based oxides,<sup>12,13</sup> V-based compounds,<sup>14,15</sup> Prussian blue analogs,<sup>16,17</sup> spinel ZnCo<sub>2</sub>O<sub>4</sub> materials,<sup>18</sup> transition metal

dichalcogenides,<sup>19</sup> and quinone and ketone compounds.<sup>20</sup> MnO<sub>2</sub> with various polymorphs is the most explored material in the family of cathode materials due to its advantages, such as high theoretical capacity (308 mA h g<sup>-1</sup> based on single-electron transfer or 616 mA h g<sup>-1</sup> based on two-electron transfer), low toxicity, scalable industrial manufacturing, and abundance.<sup>21–23</sup>  $\alpha$ -MnO<sub>2</sub> with a typical  $2 \times 2$  tunnel structure made of [MnO<sub>6</sub>] octahedral units are more beneficial for playing theoretical capacity than MnO<sub>2</sub> with other crystal forms.<sup>24–26</sup>

However,  $\alpha$ -MnO<sub>2</sub> electrodes still suffer from severe capacity fading because of structure collapse, which is caused by the formation of Zn<sub>4</sub>(OH)<sub>6</sub>(SO<sub>4</sub>)<sub>2</sub>·5H<sub>2</sub>O (ZHS)<sup>27</sup> and the dissolution of Mn<sup>2+</sup> in the electrolyte during charge–discharge process.<sup>28–30</sup> Thus far, some mitigation strategies focusing on the optimization of crystal structure of MnO<sub>2</sub> have been proposed.<sup>31–35</sup> For example, Cao's group prepared  $\alpha$ -MnO<sub>2</sub>/graphite nanosheet hybrids *via* ball milling method. The chemical bonding between MnO<sub>2</sub> and graphite nanosheets strengthened the internal stability and interfacial adhesion and enhanced wettability and conductivity, thereby promoting charge transfer rate.<sup>36</sup> Fang *et al.* studied a hypoxic  $\alpha$ -MnO<sub>2</sub> (K<sub>0.8</sub>Mn<sub>8</sub>O<sub>16</sub>) with potassium ions inserted into the tunnel as a highly active cathode for Zn-ion batteries. They showed that oxygen defects promoted conductivity and opened the polyhedral wall of [MnO<sub>6</sub>] to enhance ion diffusion, which is beneficial to accelerate the reaction kinetics and increase the capacity of K<sub>0.8</sub>Mn<sub>8</sub>O<sub>16</sub>.<sup>37</sup> In particular, Xu *et al.* reported a new nanocomposite material, which was implemented *via* pre-

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intercalation of  $\text{Fe}^{3+}$  during the formation of  $\alpha\text{-MnO}_2$  crystals and the coating of a polypyrrole layer on the surface of  $\alpha\text{-MnO}_2$ .  $\text{Fe}^{3+}$  enlarged the lattice spacing and decreased the hindrance for  $\text{Zn}^{2+}$  insertion/extraction. Meanwhile, polypyrrole prevented the dissolution of  $\alpha\text{-MnO}_2$  during charge-discharge process.<sup>38</sup> These meaningful studies led to the study of the link between polymer coating and metal doping for the modification of  $\text{MnO}_2$ .

Herein, Al-doped  $\alpha\text{-MnO}_2$  coated by lignin ( $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ ) was prepared *via* hydrothermal method to stabilize the structure of  $\alpha\text{-MnO}_2$ . Lignin, a renewable and abundant natural material, was selected as the target polymer because of its strong interaction with various metal ions for the electrostatic and cation- $\pi$  interaction.<sup>39,40</sup>  $\text{Al}^{3+}$  doping combined with lignin coating effectively inhibited the production of ZHS on the electrode surface and prevented rapid collapse of the  $\text{MnO}_2$  structure.  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  displayed better electrical conductivity and structural stability than  $\alpha\text{-MnO}_2$ . In particular, the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  cathode achieved a durably higher reversible capacity of 188  $\text{mA h g}^{-1}$  at 1.5  $\text{A g}^{-1}$  and good cycle stability with lower fluctuations. Changes in doping and coating on the surface compositions of materials were analyzed by X-ray photoelectron spectroscopy (XPS). The synergistic effect of lignin on metal ions allowed  $\text{Al}^{3+}$  to enter the  $\text{MnO}_2$  lattice more fully. In addition, the reason behind the stability of the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  electrode was clarified by studying the evolution of electrodes during charge-discharge process.

## 2. Experimental section

### 2.1. Materials

$\text{NH}_4\text{F}$  ( $\geq 99.99\%$  metal basis) was purchased from Shanghai Macklin Biochemical Co., Ltd (Shanghai, China).  $\text{KMnO}_4$  (GR) was purchased from Nanjing Chemical Reagent Co., Ltd (Nanjing, China). Sodium lignosulfonate (Vanisperse A, battery-grade) was provided by Shandong Jinkeli Power Sources Technology Co., Ltd (Zibo, China).  $\text{Al}_2(\text{SO}_4)_3$  (AR) was purchased from Shanghai Yien Chemical Technology Co., Ltd (Shanghai, China).  $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$  (AR) and  $\text{MnSO}_4 \cdot \text{H}_2\text{O}$  (AR) were purchased from Shanghai Aladdin Bio-Chem Technology Co., Ltd (Shanghai, China).

### 2.2. Synthesis of $\alpha\text{-MnO}_2$ , $\text{Al}@\alpha\text{-MnO}_2$ , $\text{L}@\alpha\text{-MnO}_2$ and $\text{L} + \text{Al}@\alpha\text{-MnO}_2$

$\alpha\text{-MnO}_2$  was synthesized *via* a hydrothermal method.<sup>41</sup> Typically, 3.6 g of  $\text{NH}_4\text{F}$  was dissolved in 160 mL of deionized water, with continuous stirring. Then, 0.4 g  $\text{KMnO}_4$  was added to the obtained aqueous solution of  $\text{NH}_4\text{F}$ . After mixing was conducted by magnetic stirring for 15 min at room temperature, the prepared reaction mixture was transferred into a Teflon-lined autoclave with an inner volume of 200 mL. Finally, the autoclave was sealed, slowly heated to 200 °C, maintained at 200 °C for 24 h, and cooled to room temperature. The prepared brown flocculent precipitates were filtered, sufficiently rinsed with deionized water, and then dried at 80 °C for 12 h.

$\text{Al}@\alpha\text{-MnO}_2$  was synthesized using the same method as that of  $\alpha\text{-MnO}_2$ . All the reaction conditions were the same except

that the reaction mixture was changed to an aqueous solution containing 3.6 g  $\text{NH}_4\text{F}$ , 0.2164 g  $\text{Al}_2(\text{SO}_4)_3$  and 0.4 g  $\text{KMnO}_4$ .

$\text{L}@\alpha\text{-MnO}_2$  was synthesized using the same method as that of  $\alpha\text{-MnO}_2$ . All the reaction conditions were the same except that the reaction mixture was changed to an aqueous solution containing 3.6 g  $\text{NH}_4\text{F}$ , 0.022 g sodium lignosulfonate, and 0.4 g  $\text{KMnO}_4$ .

$\text{L} + \text{Al}@\alpha\text{-MnO}_2$  was also synthesized using the same method as that of  $\alpha\text{-MnO}_2$ . All the reaction conditions were the same except that the reaction mixture was changed to an aqueous solution containing 3.6 g  $\text{NH}_4\text{F}$ , 0.2164 g  $\text{Al}_2(\text{SO}_4)_3$ , 0.022 g sodium lignosulfonate, and 0.4 g  $\text{KMnO}_4$ . The preparation process for  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  is shown in Fig. 1.

### 2.3. Material characterizations

The  $\alpha\text{-MnO}_2$  based materials were characterized by X-ray diffraction (XRD, Empyrean, Netherlands) equipped with a  $\text{Cu K}\alpha$  radiation source ( $\lambda = 1.5406 \text{ \AA}$ ). The scanning was conducted within the range of  $2\theta = 5\text{--}90^\circ$  with intervals of 0.02°.

A vacuum coater (Leica EM ACE600, Germany) was used to enhance the conductivity of  $\alpha\text{-MnO}_2$ -based materials *via* gold coating. Then, morphologies were characterized by field-emission scanning electron microscopy (SEM, Zeiss/Auriga-bu, Germany).

High-resolution transmission electron microscopy (HRTEM, FEI TalosF200S, Czech Republic) and energy dispersive X-ray spectroscopy (EDX) mapping were used to investigate the microstructures and element distribution of the materials.

The composition and surface element state of the material samples were analyzed by XPS (AXIS Supra, UK).

Inductively coupled plasma emission spectrum (ICP-OES, Agilent 5110, USA) was used to measure the element content in the sample.

A Fourier transform infrared spectrometer (Bruker, Tensor II, USA) and STA8000 Synchronous Thermal Analyzer (PerkinElmer, USA) were used to evaluate the effect of doping and coating on the  $\alpha\text{-MnO}_2$  based materials.

Raman spectroscopy was conducted on a Raman spectrometer (LabRAM HR Evo, France).

### 2.4. Electrochemical measurements

A homogeneous slurry consisted of active material ( $\alpha\text{-MnO}_2$ ,  $\text{Al}@\alpha\text{-MnO}_2$ , or  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ ), acetylene black, and polyvinylidene fluoride was prepared by adequately mixing them at a mass ratio of 70 : 20 : 10 in *N*-methyl-2-pyrrolidone. The prepared slurry was coated on a conductive polyethylene film, subsequently dried in a vacuum oven at 60 °C, and finally cut to

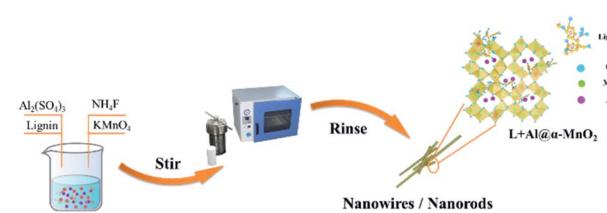


Fig. 1 Schematic diagram of the preparation of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ .



a 12 mm-diameter disc to be used as the cathode. The mass loading of the active material in the cathode was approximately  $1\text{--}2\text{ mg cm}^{-2}$ . A polished Zn metal foil with a diameter of 12 mm and a thickness of 0.3 mm was used as the anode. The battery was assembled by packing the cathode, anode, separator (absorbed glass mat), and aqueous electrolyte (2 M  $\text{ZnSO}_4$  + 0.2 M  $\text{MnSO}_4$ ) in a CR 2025-type coin cell base.

Electrochemical impedance spectroscopy (EIS, from 100 kHz to 0.01 Hz) and cyclic voltammetry (CV) were performed on the CHI604E electrochemical workstation (Shanghai Chenhua Instrument Co., Ltd., China). The CV scanning voltage was 1–1.9 V. The cycle performance of the battery was tested using the NEWARE battery tester (Neware Co. Ltd., China) at room temperature, and the current density was  $1.5\text{ A g}^{-1}$ . The rate performance of the battery was tested under the same instrument and environmental conditions as the cycle performance test, and the constant current charge and discharge current density was set to 0.1, 0.2, 0.5, 1, 2, 3, and  $5\text{ A g}^{-1}$ .

The evolution of cathode during the first charge–discharge process was characterized by *ex situ* XRD. Before characterization, the tested cathodes were fully rinsed with deionized water to remove the residual electrolyte.

### 3. Results and discussion

#### 3.1. Structural analysis of materials

The microstructure and morphology of the as-prepared  $\alpha\text{-MnO}_2$ -based materials were characterized by XRD, SEM, TEM,

and energy-dispersive spectroscopy (EDS) mapping. Fig. 2a shows the XRD patterns of the as-prepared  $\alpha\text{-MnO}_2$ -based materials. The diffraction peaks clearly revealed that  $\alpha\text{-MnO}_2$  (JCPDS 44-0141) was successfully synthesized, and  $\text{Al}^{3+}$  doping and lignin coating did not change the major crystalline phase of  $\alpha\text{-MnO}_2$ . SEM was used to observe the morphology of  $\alpha\text{-MnO}_2$ ,  $\text{Al}@\alpha\text{-MnO}_2$ , and  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ . The SEM image in Fig. 2b presents a major one-dimensional (1D) nanowire structure of  $\alpha\text{-MnO}_2$ . Single  $\text{Al}^{3+}$  doping slightly changed the morphology of  $\alpha\text{-MnO}_2$  according to the SEM images displayed in Fig. 2b and c, in which a small amount of 1D nanorod structures appeared. However, more 1D nanorod structures also appeared in the SEM image (Fig. 2d) of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ . This finding indicated that more  $\alpha\text{-MnO}_2$  transformed from 1D nanowire structure to 1D nanorod structure during the formation process participated by  $\text{Al}^{3+}$  and lignin. The possible reason is because in the synthesis process of  $\alpha\text{-MnO}_2$ , lignin accelerates the crystal nucleation rate (Fig. S1a†), and the force between  $\text{Al}^{3+}$  and lignin further accelerates the crystallization process of the material, thereby limiting the growth of  $\text{MnO}_2$  particles, eventually resulting in a shortened length of the nanowire. Even when the  $\text{Al}^{3+}$  doping amount was doubled, the  $\text{Al}@\alpha\text{-MnO}_2$  doped alone still only had few nanorods (Fig. S1b†), and the electrochemical performance worsened. The shorter rod structure effectively increased the specific surface area of the material, thus providing more electrochemically active sites for redox reactions. Examination of the diffraction rings obtained from SAED analysis (Fig. S2b†) showed the polycrystalline nature of the sample. According to the EDS mappings (Fig. 2f), except for the obvious Mn and O elements in the region, the distribution of Al elements reflected that  $\text{Al}^{3+}$  was uniformly doped in  $\alpha\text{-MnO}_2$  and lignin coating caused C to overlap with  $\text{MnO}_2$  in the region. The content of C atom in  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  was 4.42% based on the EDS mappings. The results of ICP-OES showed that the contents of Al and Mn element in  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  were 1.41 wt% and 63.27 wt%. Thus, the atomic ratio of Mn to Al (22 : 1) was calculated. Although the ratio of Mn : Al used to prepare the material was 1 : 0.5, the amount of  $\text{Al}^{3+}$  that could enter  $\text{MnO}_2$  was limited due to the limitation of the number of active sites of  $\text{MnO}_2$ .<sup>33</sup> In addition, the  $\alpha\text{-MnO}_2$  based materials were investigated using Raman spectroscopy (Fig. S3†) and FT-IR spectroscopy (Fig. S4†) to confirm the change of crystal lattice. The Mn–O vibration of the crystal caused peaks shift under the effect of doping, further indicating that  $\text{Al}^{3+}$  had entered the  $\text{MnO}_2$  crystal.<sup>38,42</sup>

Fig. 3 depicts the wide-scan XPS spectrum of the  $\text{MnO}_2$ -based materials, in which the positions of all peaks were obtained after calibrating the position peak of C 1s (284.8 eV). XPS detection of the material surface could analyze the structural composition and element states. The Mn 2p of  $\text{MnO}_2$  spectrum is shown in Fig. 3a. The peak positions were 642.1 and 653.8 eV, which were assigned to  $\text{Mn} 2p_{3/2}$  and  $\text{Mn} 2p_{1/2}$ , respectively.<sup>43</sup> In addition, the occurrence of multiple splitting led to several contributions to the spectra of  $\text{MnO}_2$  (Mn 2p), caused by the presence of multiple oxidation states of Mn. For the Mn 2p peak of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  in Fig. 3b, the peak position of  $\text{Mn} 2p_{3/2}$  was 641.75 eV, and the peak position of  $\text{Mn} 2p_{1/2}$  was 653.5 eV. The peak position of Mn 2p obviously shifted to low binding energy,

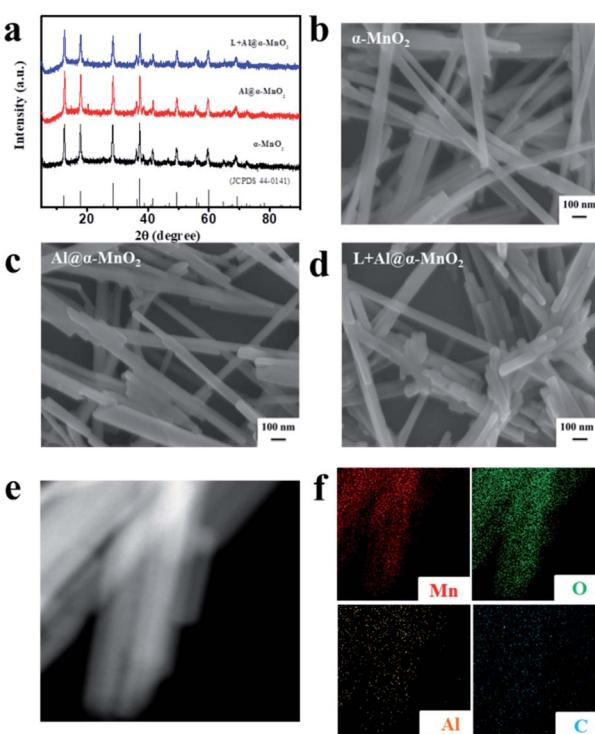


Fig. 2 Structural analyses of as-prepared  $\alpha\text{-MnO}_2$ -based materials. (a) XRD patterns of  $\alpha\text{-MnO}_2$ ,  $\text{Al}@\alpha\text{-MnO}_2$ , and  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ . (b–d) SEM images of  $\alpha\text{-MnO}_2$ ,  $\text{Al}@\alpha\text{-MnO}_2$ , and  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ . (e and f) EDS elemental mapping images of Mn, O, Al, and C elements of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ .



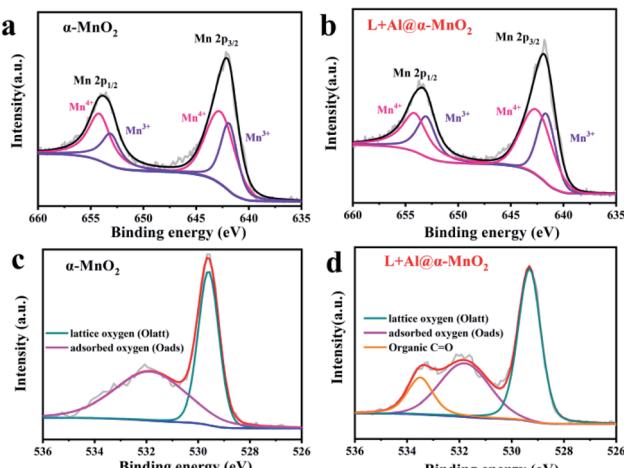


Fig. 3 XPS spectra of as-prepared  $\alpha$ -MnO<sub>2</sub>-based materials. (a and b) Mn 2p spectrum of  $\alpha$ -MnO<sub>2</sub> and L + Al@ $\alpha$ -MnO<sub>2</sub>. (c and d) O 1s spectrum of  $\alpha$ -MnO<sub>2</sub> and L + Al@ $\alpha$ -MnO<sub>2</sub>.

indicating that the average oxidation state of Mn is lower than that of  $\alpha$ -MnO<sub>2</sub>. This situation was due to the fact that a part of Al<sup>3+</sup> replaced Mn<sup>4+</sup> in [MnO<sub>6</sub>] units, resulting in the generation of oxygen vacancies. The introduction of oxygen defects in MnO<sub>2</sub> reduces the Gibbs free energy of ion intercalation,<sup>44</sup> which enhances the structural stability in repeated cycles, thereby improving electrochemical reversibility.

As shown in Fig. 3c, the O 1s of the MnO<sub>2</sub> spectrum exhibited two fractional peaks. The peak position of lattice oxygen (Mn–O–Mn) was 529.6 eV, and the peak position of surface-adsorbed oxygen (H–O–H) was 531.7 eV. However, with the coating of lignin, L + Al@MnO<sub>2</sub> showed a new type of fractional peak, which was organic carbon–oxygen double bond oxygen (O=C) at 533.6 eV.<sup>45</sup> Compared with L + Al@MnO<sub>2</sub>, the new peak does not exist in the O 1s spectrum of Al@MnO<sub>2</sub> (Fig. S5e†). Thus, the XPS spectrum proved that lignin was successfully coated on the surface of MnO<sub>2</sub>. Thermogravimetric analysis (Fig. S6†) of  $\alpha$ -MnO<sub>2</sub> based materials further indicated that the average oxidation state of Mn decreased and the existence of lignin in L + Al@ $\alpha$ -MnO<sub>2</sub>. In addition, the weight loss of L + Al@ $\alpha$ -MnO<sub>2</sub> was more than  $\alpha$ -MnO<sub>2</sub> within 100–300 °C, which indicated that the content of structural water in L + Al@ $\alpha$ -MnO<sub>2</sub> increased significantly. This was probably due to the hydrophilic groups of sodium lignosulfonate adsorbed more water molecules into L + Al@ $\alpha$ -MnO<sub>2</sub>. The rich of structural water in the material effectively improved the interfacial kinetics of ions, which led to that the battery using L + Al@ $\alpha$ -MnO<sub>2</sub> presented superior cyclability than that of the battery using  $\alpha$ -MnO<sub>2</sub> after activation.<sup>46</sup>

### 3.2. Electrochemical performance and behavior

Fig. 4 shows the electrochemical performance of the  $\alpha$ -MnO<sub>2</sub>-based batteries. The change in the structure of  $\alpha$ -MnO<sub>2</sub> improved the electrochemical performance. Fig. 4a and b show the CV data of two electrodes. The  $\alpha$ -MnO<sub>2</sub> electrode exhibited an obvious cathodic peak near 1.17 V during the first cathodic sweep. However, the reduction peak disappeared in the second

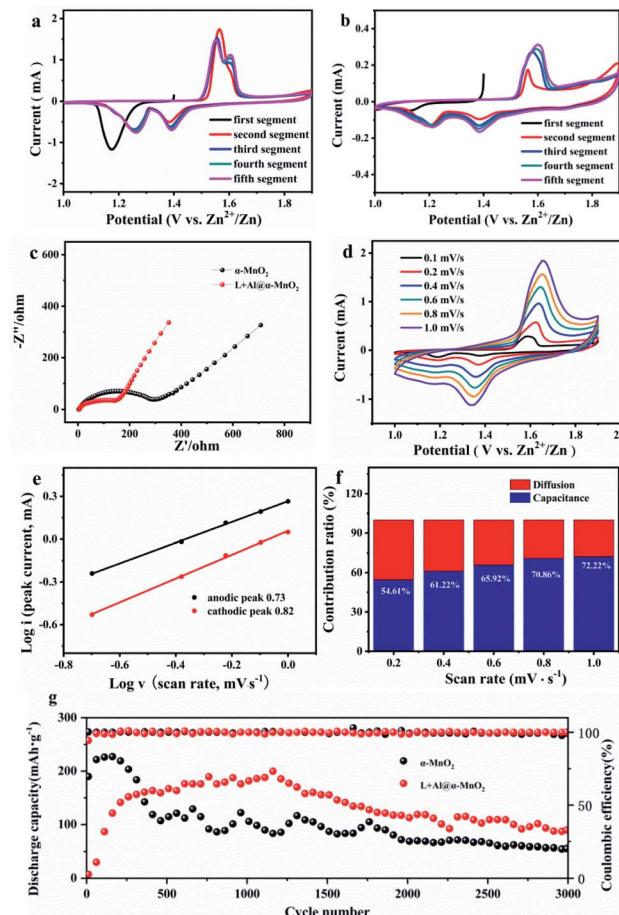


Fig. 4 Electrochemical performance of MnO<sub>2</sub> and L + Al@ $\alpha$ -MnO<sub>2</sub> electrodes. (a and b) Cyclic voltammetry curves of  $\alpha$ -MnO<sub>2</sub> and L + Al@ $\alpha$ -MnO<sub>2</sub> at 0.1 mV s<sup>-1</sup>. (c) Electrochemical impedance spectroscopy plots of  $\alpha$ -MnO<sub>2</sub> and L + Al@ $\alpha$ -MnO<sub>2</sub>. (d) CV curves of L + Al@ $\alpha$ -MnO<sub>2</sub> at different sweep rates. (e) Log (*i*, peak current) versus log (*v*, scan rate) plots of two peaks in the CV curves of L + Al@ $\alpha$ -MnO<sub>2</sub>. (f) Percentage of capacitance of L + Al@ $\alpha$ -MnO<sub>2</sub> electrode. (g) Cycling performance of  $\alpha$ -MnO<sub>2</sub> and L + Al@ $\alpha$ -MnO<sub>2</sub> and corresponding coulombic efficiency at a current density of 1.5 A g<sup>-1</sup>.

sweep. New reduction peaks appeared near 1.26 and 1.38 V, while the anode sweep had corresponding anode peaks near 1.57 and 1.61 V. The appearance of two peaks in the working window from 1 V to 1.9 V implied a two-step insertion process. In the following sweeps, the strengths of the redox peak at 1.57 V decreased, while the oxidation peak at 1.61 V gradually increased. Unlike in  $\alpha$ -MnO<sub>2</sub>, with the following sweep, the reaction at higher voltage (1.38/1.61 V) occupied the dominant position in the charge–discharge process of L + Al@ $\alpha$ -MnO<sub>2</sub>. By studying the evolution of the electrode, this phenomenon was determined to correspond to the insertion/extraction of H<sup>+</sup>. According to the CV curves, the battery using L + Al@ $\alpha$ -MnO<sub>2</sub> had much lower current responses than that of the battery using  $\alpha$ -MnO<sub>2</sub>. This was because L + Al@ $\alpha$ -MnO<sub>2</sub> underwent an activation process. The peak at ~1.57 V was related to the insertion of Zn<sup>2+</sup>,<sup>47</sup> which was hindered by Al<sup>3+</sup> in the tunnel of  $\alpha$ -MnO<sub>2</sub>. Hence, the peak at ~1.57 V presented attenuation trend incipiently. H<sup>+</sup> was not as much affected as that of Zn<sup>2+</sup> due to its

small ion radius. The same trend appeared in the battery using  $\text{Al}@\alpha\text{-MnO}_2$  (Fig. S7a†), showing the dominated insertion/extraction of  $\text{H}^+$  at the beginning. The CV curve of battery using  $\text{L}@\alpha\text{-MnO}_2$  (Fig. S7b†) was similar to that of battery using  $\alpha\text{-MnO}_2$ . These phenomena illustrated that the activation process of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  was due to the  $\text{Al}^{3+}$  doping.

The resistance and conductivity of  $\alpha\text{-MnO}_2$  and  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  were obtained by EIS to further explore the resistance and diffusion behavior of the electrode. Fig. 4c illustrates the Nyquist plots of two electrodes. The semicircle of the charge transfer resistance ( $R_{ct}$ ) was located in the high frequency region, and the oblique line in the low frequency region was associated with the Warburg-type impedance of diffusion process. The semicircle of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  was smaller than that of  $\alpha\text{-MnO}_2$ , indicating the improvement of electron transfer kinetics after doping, resulting in lower  $R_{ct}$  of the material. In the low frequency region, the line slope of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  was higher than that of  $\alpha\text{-MnO}_2$ , indicating that the diffusion rate of ions in  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  was faster. The short nanorod tunnel structure of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  shortened the electron transport path effectively and promoted the diffusion of active materials. In addition, the oxygen defects produced by  $\text{Al}^{3+}$  doping improved the conductivity and reversibility of the material, increasing the rate of ions transmission effectively.<sup>44,48</sup> Thus, the reaction kinetics was enhanced.

The CV profiles of  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  electrode at various scan rates from  $0.1 \text{ mV s}^{-1}$  to  $1.0 \text{ mV s}^{-1}$  are shown in Fig. 4d. As the scanning speed increased, the cathode and anode peaks shifted to higher and lower potentials, respectively, due to the increased polarization at higher scan rates. The pair of reduction and oxidation peaks gradually disappeared in the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  electrode compared with that in the  $\alpha\text{-MnO}_2$  electrode (Fig. S7c†). The linear relationship was calculated using the following equation:<sup>38</sup>

$$i = av^b \quad (1)$$

$$\lg(i) = b \lg(v) + \lg(a) \quad (2)$$

where  $a$  and  $b$  are constants. In general, the range of  $b$  is from 0.5 to 1. In addition,  $b = 0.5$  means a diffusion-controlled process, and  $b = 1$  indicates a surface capacitive-controlled process. As displayed in Fig. 4e, the  $b$  values of the peaks were 0.73 and 0.82, suggesting two capacity contributions in the charge storage process. When the scanning speed was  $1.0 \text{ mV s}^{-1}$ , the capacitance contribution in the electrode increased to 72.22% (Fig. 4f), which is the dominant capacity contribution at high current densities. The percentage was calculated using the following equation:<sup>43</sup>

$$i(v) = k_1 v + k_2 v^{1/2} \quad (3)$$

Fig. 4g shows that the  $\alpha\text{-MnO}_2$ -based battery delivered  $225 \text{ mA h g}^{-1}$  at the current density of  $1.5 \text{ A g}^{-1}$  in the first 100 cycles. However, this capacity was only maintained for about 300 cycles, and soon began to decline significantly. After approximately 500 cycles the capacity only remained around  $107 \text{ mA h g}^{-1}$  and gradually decreased to  $54 \text{ mA h g}^{-1}$  after 3000

cycles. In addition, the capacity fading of  $\alpha\text{-MnO}_2$ -based-battery was accompanied by obvious fluctuations, indicating that the structure of  $\alpha\text{-MnO}_2$  was unstable. When tested at the same current density,  $\text{Al}^{3+}$  doped electrodes showed better stability. After undergoing an activation process about 400 cycles, the  $\text{Al}@\alpha\text{-MnO}_2$ -based battery (Fig. S8a†) showed a stable discharge capacity of  $140 \text{ mA h g}^{-1}$ . After 1400 cycles, the capacity began to decline slowly. The  $\text{L}@\alpha\text{-MnO}_2$ -based battery (Fig. S8a†) began to decay after 50 cycles when the capacity reached a peak of  $230 \text{ mA h g}^{-1}$ , and showed a capacity platform of  $155 \text{ mA h g}^{-1}$  at 200 cycles. The capacity faded after 1300 cycles, and only remained at  $47 \text{ mA h g}^{-1}$  after 3000 cycles. On the basis of  $\text{Al}^{3+}$  doping and lignin coating, lignin did not change the cycle trend of the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$ -based battery, which presented the similar trend with the  $\text{Al}@\alpha\text{-MnO}_2$ -based battery. Specifically, although the capacity before 300 cycles was not as high as that of  $\alpha\text{-MnO}_2$ -based battery, the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  based battery showed highest capacity of  $188 \text{ mA h g}^{-1}$  after 400 cycles of activation process. After 1400 cycles, battery using the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  also showed capacity fading, but the process was much more stable than that of battery using the  $\alpha\text{-MnO}_2$ . After 3000 cycles, battery using the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  still maintained a higher capacity ( $\sim 90 \text{ mA h g}^{-1}$ ) than the other batteries, and the capacity was 66.7% more than that of battery using the  $\alpha\text{-MnO}_2$ . This finding is largely attributable to the synergistic effect of lignin and metal ions, which made  $\text{Al}^{3+}$  better doped and enhances the reversibility of ion insertion/extraction, thus avoiding collapse of the  $\text{MnO}_2$  structure during charge-discharge process.

Compared with  $\alpha\text{-MnO}_2$ , the materials after doping needed to undergo an activation process. The reason for this trend may be that the ionic radius of  $\text{Al}^{3+}$  is similar to that of  $\text{Mn}^{4+}$ , which replaces part of  $\text{Mn}^{4+}$  in the  $[\text{MnO}_6]$  octahedron. The result of doping strengthened the structure of the  $\text{MnO}_2$  host; however, a part of  $\text{Al}^{3+}$  entered the tunnel.<sup>49</sup> Thus, the insertion of ions into the main body of  $\text{MnO}_2$  was hindered, particularly the  $\text{Zn}^{2+}$  with a large ion radius. This was consistent with the CV curves of battery using the  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  cathode (Fig. 4b), which presented low current responses of the insertion/extraction of  $\text{Zn}^{2+}$  and  $\text{H}^+$ . Moreover, the current response of  $\text{Zn}^{2+}$  was much lower than that of  $\text{H}^+$ . As the reversible insertion/extraction of ions ( $\text{H}^+$  and a small amount  $\text{Zn}^{2+}$ ) in the cathode material, the  $\text{Al}^{3+}$  in the tunnel was gradually released. Therefore, the amounts of  $\text{Zn}^{2+}$  and  $\text{H}^+$  that entered the cathode material rose, resulting in an increase in capacity over cycle number.

The charge-discharge curve is shown in Fig. 5a and d to explore the transformation of  $\alpha\text{-MnO}_2$  and  $\text{L} + \text{Al}@\alpha\text{-MnO}_2$  in the charge-discharge process. The voltage corresponding to the obvious change in the curve was recorded, and the *ex situ* XRD patterns of cathode were tested at selected voltage states. Fig. 5b shows the XRD patterns of  $\alpha\text{-MnO}_2$  during the discharge process. A notable detail that the strong diffraction peak at  $21\text{--}24^\circ$ , which belongs to the current collector made of PE material, was shielded. In the following discharge process, the characteristic peaks of  $\alpha\text{-MnO}_2$  were unchanged. However, a new phase was generated when the electrode was discharged from the initial voltage to  $1.25 \text{ V}$ , because the insertion of  $\text{H}^+$  increased the pH in the electrolyte, and more  $\text{OH}^-$  combined



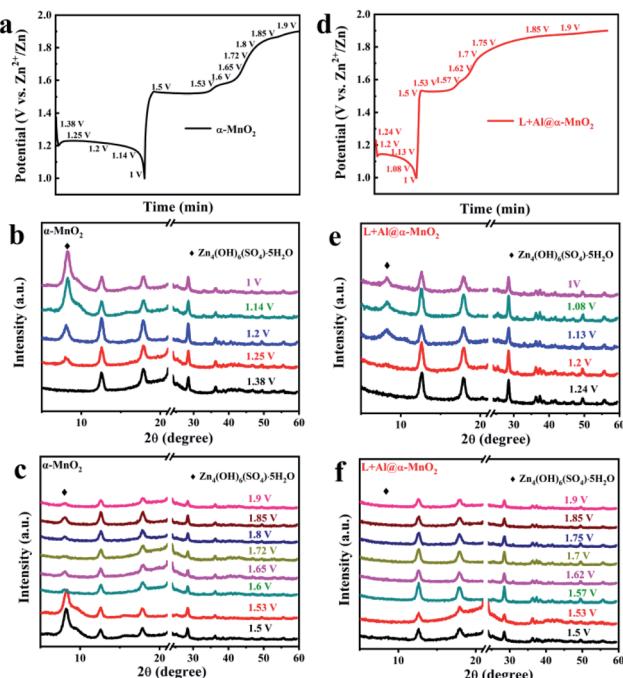


Fig. 5 Structure evolution of cathodes in *ex situ* X-ray diffraction patterns during charge-discharge process at 100 mA g<sup>-1</sup>. (a-c) Charge-discharge curve of  $\alpha$ -MnO<sub>2</sub> and XRD patterns at selected voltage. (d-f) Charge-discharge curve of L + Al@ $\alpha$ -MnO<sub>2</sub> and XRD patterns at selected voltage.

with other components to form this sheet-like ZHS,<sup>50</sup> which adheres to the surface of the electrode. Fig. 5c shows the evolution of  $\alpha$ -MnO<sub>2</sub> during the charge process. Except the still unchanged characteristic peaks of  $\alpha$ -MnO<sub>2</sub>, the diffraction peak of ZHS weakened rapidly at the first charging platform, and a small amount of the product remained on the cathode of  $\alpha$ -MnO<sub>2</sub> when charged to 1.9 V. However, as shown in Fig. 5e, the generation of ZHS was significantly suppressed during the discharge process of L + Al@ $\alpha$ -MnO<sub>2</sub>. In the charge process, ZHS basically disappeared when charged to 1.5 V, and its diffraction peak completely disappeared after charging to 1.6 V.

In a word, a new phase was formed during the discharge process, and it disappeared during the charge process. The CV data and XRD pattern showed that the behavior of H<sup>+</sup> and Zn<sup>2+</sup> during the initial electrochemical process could be determined. After the electrode was discharged from the initial voltage, ZHS did not appear immediately. Subsequently, during the charge process, the ZHS on the electrode surface did not decrease significantly at first but began to disappear rapidly when the voltage reached 1.6 V, indicating the extraction of H<sup>+</sup>. Thus, the higher peak at 1.38/1.61 V corresponded to H<sup>+</sup> insertion/extraction and the lower peak at 1.26/1.57 V was assigned to Zn<sup>2+</sup> insertion/extraction. However, after charging to 1.9 V, visible ZHS still remained on the electrode surface. The presence of ZHS was accompanied by the disproportionation of a part of Mn<sup>3+</sup> into Mn<sup>2+</sup> causing the dissolution of Mn,<sup>51</sup> leading to the collapse of the MnO<sub>2</sub> host structure. According to previous reports, these residual sulfates gradually recombine into ZnMn<sub>2</sub>O<sub>4</sub>,<sup>23</sup> which reduces the electrochemical activity of

the electrode. ZHS obviously showed better reversibility of L + Al@ $\alpha$ -MnO<sub>2</sub> than  $\alpha$ -MnO<sub>2</sub> due to the effect of lignin on Al<sup>3+</sup> during the doping process, which accelerated the nucleation of MnO<sub>2</sub> and promoted the entry of Al<sup>3+</sup> into the crystal lattice. H<sup>+</sup> was highly related to the formation of ZHS in the electrolyte, and the good reversibility was due to the enhancement of H<sup>+</sup> diffusion in the host material after ion doping and lignin coating.<sup>52</sup> At the same time, the oxygen vacancies generated with Al<sup>3+</sup> substitution in L + Al@ $\alpha$ -MnO<sub>2</sub> further reduced the resistance of H<sup>+</sup> insertion/extraction.<sup>35</sup> Therefore, almost no ZHS was attached to the electrode surface after charging, further protecting the electrode structure and improves the cycle stability.

## 4. Conclusions

In summary, L + Al@ $\alpha$ -MnO<sub>2</sub> was successfully fabricated as high-performance cathode materials through Al<sup>3+</sup> doping and lignin coating *via* hydrothermal route. The resulting material presented a morphology of short nanorod, which had a larger specific surface area and could provide more active sites. The lignin coating could allow Al<sup>3+</sup> to be fully doped into the MnO<sub>2</sub> lattice during the synthesis process. The doping of Al<sup>3+</sup> improved the insertion/extraction of H<sup>+</sup> to reduce the residue of zinc hydroxide sulfate in the electrode during the charge-discharge process. The related spectroscopic analysis was consistent with the results of local structural changes in the material and theoretical assumptions. The results showed that L + Al@ $\alpha$ -MnO<sub>2</sub> by Al<sup>3+</sup> doping and lignin coating effectively alleviated the structural collapse caused by Mn dissolution, thus stabilizing the electrochemical performance of the electrode. These positive effects made the Zn/MnO<sub>2</sub> battery operate in high specific capacity (66.7% higher than  $\alpha$ -MnO<sub>2</sub> after 3000 cycles). The synergistic effect of lignin and Al<sup>3+</sup> could provide a reference for the synthesis of next-generation electrode materials with using the modification method of polymers and metal ions.

## Conflicts of interest

There are no conflicts to declare.

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