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### ARTICLE

## Boosting Zn-ion Storage Capability of Birnessite Manganese Oxide Nanoflorets by La<sup>3+</sup> Intercalation

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The development of aqueous rechargeable Zn-ion batteries (ZIBs) with high-capacity and good rate capability has turned the effort on the cathode limit. Herein, birnessite  $\delta$ -MnO<sub>2</sub> nanoflorets with La<sup>3+</sup> intercalation (LMO) are reported as a highenergy and high-rate cathode for ZIBs. The intercalation La<sup>3+</sup> within  $\delta$ -MnO<sub>2</sub> nanoflorets is readily achieved by a simple, scalable and effective precipitation process. Benifiting from the larger interlamellar spacing, reduced Zn<sup>2+</sup> (de)insertion resistance and increased surface area after La<sup>3+</sup> intercalation, the Zn-ion storage capability of  $\delta$ -MnO<sub>2</sub> nanoflorets is significantly boosted, achieving a high reversible capacity of 278.5 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup> and a superb rate capability of 121.8 mAh g<sup>-1</sup> at 16 times higher current density (only 3.4 mAh g<sup>-1</sup> for the pristine  $\delta$ -MnO<sub>2</sub> nanoflorets), as well as a good durability. Moreover, the maximum energy and power densities of the as-obtained Zn//LMO battery reach 375.9 Wh kg<sup>-1</sup> and 4.8 kW kg<sup>-1</sup> (based on the cathode mass). Considering the new design of La<sup>3+</sup> intercalation, this study is hoped to provide insightful guide for exploring next-generation Mn-based cathode materials for ZIBs.

#### Introduction

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The exploration of aqueous rechargeable batteries is essential for realizing the high-efficient utilization of renewable energies.<sup>1-7</sup> As a promising multivalent ion battery technology, aqueous Zn-ion batteries (ZIBs) have drawn increasing attention as grid-scale energy storage device in recent years.<sup>8-13</sup> Among various ZIBs, Zn-MnO<sub>2</sub> battery employing mild neutral electrolytes are of particular research interest because of its excellent safety, large capacity, high output voltage, environmental friendliness and low cost.14-16 Although significant achievements having been made, the biggest bottleneck of the current Zn-MnO<sub>2</sub> batteries for widespread application is their unsatisfactory energy density and rechargeable ability.<sup>17</sup> Firstly, the substantially poor conductivity of  $MnO_2$  (10<sup>-5</sup> – 10<sup>-6</sup> S cm<sup>-1</sup>) renders the practical capacity of those MnO<sub>2</sub> cathodes far behind its theoretical capacity (307.7 mAh g<sup>-1</sup>, based on single electron transfer reaction), <sup>18, 19</sup> especially under high current densities, which is much lower than the Zn anode (820 mAh g<sup>-1</sup>). Secondly, the chemical dissolution and structure pulverization of the MnO<sub>2</sub> during charging/discharging process also results in a poor cyclic

stability. To figure out these issues, some approaches including nano-structuring,<sup>20</sup> conductive polymer coating,<sup>21</sup> have been reported and exhibited improved electrochemical properties. For example, Qu and his coworkers developed a kind of amorphous MnO<sub>2</sub> nanoparticle film as a cathode of ZIBs, exhibiting a maximum specific capacity of 253.8 mAh g<sup>-1</sup> (at a current density of 0.5 A g<sup>-1</sup>), and a capacity retention of 57.6% after 200 cycles.<sup>22</sup> A hexagonal ε-MnO<sub>2</sub> cathode with improved cycling performance by adding Mn<sup>2+</sup> ions into the electrolyte was demonstrated to own a high capacity of 233 mAh g<sup>-1</sup> at a current density of 0.03 A g<sup>-1</sup> and 75 mAh g<sup>-1</sup> at a current density of 1.5 A g<sup>-1,23</sup> Zeng et al. designed a MnO<sub>2</sub>@poly(3,4ethylenedioxythiophene) core shell cathode by a two-step electrodeposition process, achieving a good cycling retention of 83.7% after 300 charge-discharge cycles. While the current density increased by five folds, it could still keep 49.1% of its capacity.<sup>24</sup> Zhang *et al.* synthesized a nanorod-like pyrolusite  $\beta$ -MnO<sub>2</sub>, which exhibited a high reversible capacity of 225 mAh g<sup>-1</sup> and a maximum energy density of 254 Wh kg<sup>-1</sup> at 197 W kg<sup>-1</sup> and 110 Wh kg<sup>-1</sup> at 5.9 kW kg<sup>-1</sup> in 3 M Zn( $CF_3SO_3$ )<sub>2</sub> and 0.1 M  $Mn(CF_3SO_3)_2$  electrolyte.<sup>25</sup> Although those advanced processes have been made, it still remains huge challenge to explore facile and efficient strategies to synthesize new stable MnO<sub>2</sub>-based cathodes with large capacity and high rate performance for ZIBs.

In this work, we demonstrate the first example of using La<sup>3+</sup> inserted birnessite  $\delta$ -MnO<sub>2</sub> (LMO) nanoflorets as highperformance cathode in ZIBs. The LMO is easily realized via a simple, scalable and effective precipitation approach, which endows them with porous structure, high accessible surface area, superior electron and ion transport rates. Moreover, the intercalation of La<sup>3+</sup> into  $\delta$ -MnO<sub>2</sub> could enlarge the interlamellar spacing and reduce the resistance of Zn<sup>2+</sup> (de)insertion.<sup>26-29</sup> La<sup>3+</sup>

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facile

transmission

liquid

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**Results and discussion** 

is also able to be the support species to prevent the structural collapse during cycling. As a consequence, the Zn<sup>2+</sup> storage performance of the LMO electrode is remarkably enhanced compared to the pristine  $\delta$ -MnO<sub>2</sub> (MO) nanoflorets. The optimized LMO cathode is able to reach an admirable capacity of 278.5 mAh g<sup>-1</sup> at 100 mA g<sup>-1</sup>, an excellent rate capability (more than 43.7% capacity retention at 1600 mA g<sup>-1</sup> when only 0.02% for MO), and good cycling stability. Moreover, the maximum energy and power densities of the Zn-MnO<sub>2</sub> battery by employing this LMO electrode as cathode are up to 375.9 Wh kg<sup>-1</sup> and 4.8 kW kg<sup>-1</sup> (based on the mass of cathode), outperforming most of current MnO<sub>2</sub>-based cathodes in Zn-MnO<sub>2</sub> batteries.

#### Experimental

Preparation of birnessite  $\delta\text{-MnO}_2$  with  $La^{3+}$  intercalation (LMO): All the chemicals are directly used after purchase without further purification. First, 5 mmol of MnSO<sub>4</sub>·H<sub>2</sub>O was dissolved into 150 mL of H<sub>2</sub>O at room temperature to form a transparent pink solution, and then add 2 mmol of La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O. After 5 min of magnetic agitation, 12.5 mmol of KMnO<sub>4</sub> was dissolved into the as-obtained homogeneous solution. Then the solution was stirred at room temperature for 3 hours. After that, the solution was filtered and the resulting powder was centrifuged and washed for 3 times with deionized water. Finally, the powder was air-dried overnight at 60 °C.

Fabrication of LMO Electrodes: LMO electrodes were fabricated by mixing carbon black (AR, Sigma-Aldrich) and polyvinylidene fluoride (PVDF) binder (AR, Sigma-Aldrich) with LMO powder. The weight ratio was 8 : 1 : 1 and 1-methyl-2pyrrolidinone (NMP, AR, Sigma-Aldrich) was used as a solvent. The mixture was coated on carbon paper (Shanghai Hesen Electric Company), and the coated sample was then dried overnight in vacuum at 60 °C. Total mass loading of the electrode was 2.5 mg cm<sup>-2</sup>.

Materials Characterization and Electrochemical Measurements: The morphology structure and composition of the electrode materials were characterized scanning electron microscopy (FE-SEM, JSM-6330F), X-ray diffraction (XRD, D-MAX 2200 VPC, RIGAKU), transmission electron microscope (FEI Tecnai G<sup>2</sup> F30). The functional group distribution was measured through photoelectron spectroscopy (XPS, NEXSA, Thermo VG), Raman Spectroscopy (Renishaw inVia), The surface area of the sample was obtained by N<sub>2</sub> adsorption/desorption isotherms at  $77\ \text{K}$  that were conducted on an ASAP 2020 PLUS HD88 instrument.

Galvanostatic charge/discharge measurements, cyclic voltammetry measurements, and electrochemical impedance spectroscopy were collected by using an electrochemical workstation (CHI760). All the electrochemical performance of LMO based electrodes was characterized by employing a twoelectrode cell with commercial Zn foil as counter electrode and 1 M ZnSO<sub>4</sub> and 0.4 M MnSO<sub>4</sub> mixed solution as electrolyte. The addition of MnSO<sub>4</sub> to the electrolyte can suppresses Mn<sup>2+</sup> dissolution into the electrolyte and improve the stability. The used area of working electrode is 0.5 cm<sup>2</sup>.

#### View Article Online DOI: 10.1039/C9TA08418E $La^{3+}$ inserted $\delta$ -MnO<sub>2</sub> (Denote as LMO) was synthesized by a precipitation method based on comproportionation reaction between MnO<sub>4</sub><sup>-</sup> and Mn<sup>2+</sup> in the aqueous phase environment with La<sup>3+</sup>. For comparison, pure $\delta$ -MnO<sub>2</sub> (Denote as MO) was also synthesized by the same way without the addition of La<sup>3+</sup>. The scanning electron microscopy (SEM) images of MO and LMO are shown in Fig. 1a and 1b. Both of the samples exhibit a similar floret-like structure, indicating that the insertion of La<sup>3+</sup> has no obvious effect on the morphology. The representative transmission electron microscopy (TEM) image of the LMO is shown in Fig. 1c,

corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping in Fig. 1e-1h. The elements of Mn, O and La are uniformly distributed through this nanofloret material. The crystalline phases of the MO and LMO samples were examined by X-ray diffraction (XRD). As shown in Fig. 2a, the MO sample has a good agreement with the structure of layered birnessite  $\delta$ -MnO<sub>2</sub> (JCPDS#13-0105). After the insertion of La<sup>3+</sup>, four main diffraction peaks of LMO slightly shift toward lower angles compared with MO, especially the (001) plane. This suggests the layer spacing of LMO became broader. According to Bragg's law, the layer thickness calculated from the angle of (001) plane is increased from 6.9 Å to 7.6 Å, confirming the introduction of  ${\rm La}^{\rm 3+}$  is able to expand the interlayer spacing. Larger the interlamellar spacing can reduce the resistance of Zn<sup>2+</sup> (de)insertion, further to improve the Zn-ion storage ability. The nitrogen adsorption-desorption isotherms of MO and LMO samples are displayed in Fig. 2b. The Brunauer-Emmett-Teller



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**Fig. 2** (a) XRD patterns; (b) The nitrogen adsorption–desorption isotherms analysis; (c) XPS La 3d spectra and (d) The element percentage results of the MO and LMO samples.

(BET) surface area of LMO (145.1 m<sup>2</sup> g<sup>-1</sup>) is nearly 1.63 times higher than that of MO (88.9 m<sup>2</sup> g<sup>-1</sup>). Larger surface area can bring about more active sites and better contact with electrolyte, further to improve the electrochemical activity of LMO sample.

To examine the influence of the La<sup>3+</sup> insertion process, X-ray photoelectron spectroscopy (XPS) measurements of MO and LMO samples were carried out. In comparison with MO sample, the La 3d spectra of LMO shown in Fig. 3c could be split into two satellite peaks and a doublet peak at 834.5 eV and 850.8 eV, which respectively correspond to the La  $3d_{3/2}$  and La  $3d_{5/2}$ , indicating the existence of La<sup>3+</sup>.<sup>30</sup> Mn 2p and O 1s spectra of the LMO are also exhibited in Fig. S2. There are two peaks of Mn  $2p_{3/2}$  and Mn  $2p_{1/2}$  at the binding energy 642.2 and 654.0 eV with an energy separation of 11.8 eV (Fig. S2a), which is in consist with MnO<sub>2</sub>. In O 1s spectra (Fig. S2b), the peaks at 530.1 and 531.4 eV are respectively attributed to the lattice oxygen and hydroxyl functional group. There are no significantly difference of Mn and O between MO and LMO (Fig. S3), revealing the La<sup>3+</sup> was only inserted into the interlayers of MO without causing further influence, which is consist with the Raman analysis results in Fig. S4. The element percentage calculated by XPS spectrum of MO and LMO samples is illustrated in Fig. 2d. The Mn : O ratio of MO is nearly 1: 2, indicated the mainly existence form of the sample was MnO<sub>2</sub>. The Mn : O ratio of LMO sample (0.968 : 2) is little lower than the MO, and the atom% of La is calculated to be 1.5%.

The effect of  $La^{3+}$  intercalation on the electrochemical properties of  $\delta$ -MnO<sub>2</sub> was firstly evaluated by cyclic voltammetry (CV) measurements with a commercial Zn metal plate as anode in 1 M ZnSO<sub>4</sub> and 0.4 M MnSO<sub>4</sub> electrolyte. Fig. 3a presents the CV curves of the pristine MO and LMO sample at a scan rate of 1 mV s<sup>-1</sup>. The LMO electrode exhibited much higher peak current densities than those of the MO electrode, clearly demonstrating that the electrochemical reactivity of the MO electrode is obviously enhanced after La<sup>3+</sup> intercalation.

Additionally, in comparison with the MO electrode, the overpotential gap of redox peaks for LMO ହାର୍ଡ୍ଟୋଡିଡିଅଟେ ନିମିବିଶ୍ୱାହନ୍ showing the smaller polarization of the LMO electrode. Fig. 3b displays the typical galvanostatic charge/discharge (GCD) curves of the MO and LMO electrodes collected at 100 mA g<sup>-1</sup>. The much obvious voltage plateaus and longer discharge time of the LMO electrode than the MO electrode further confirm its superior electrochemical properties. The GCD curves of the LMO electrode collected at various current densities are shown in Fig. 3c, indicating its typical charge/discharge plateaus and high coulombic efficiency. Fig. 3d compares the discharge capacities of the MO and LMO electrodes at different current densities. All these capacities for the LMO electrode are considerably higher than the MO electrode at the same current density. Specifically, the LMO electrode reached a large capacity of 278.5 mAh g<sup>-1</sup> at the current density of 100 mA g<sup>-1</sup>, greatly higher than that of the MO electrode (199.7 mAh g<sup>-1</sup>) and most of recently reported MnO2 cathodes at similar current density such as  $\delta$ -MnO<sub>2</sub> (123 mAh g<sup>-1</sup>),<sup>31</sup>  $\delta$ -MnO<sub>2</sub> (238 mAh g<sup>-1</sup>),<sup>16</sup>  $\gamma$ -MnO<sub>2</sub> (128.3 mAh g<sup>-1</sup>) and  $\alpha$ -MnO<sub>2</sub> (233 mAh g<sup>-1</sup>).<sup>32, 33</sup> In addition, our LMO cathode owns a superb maximum energy density of 375.9 Wh kg<sup>-1</sup> and a maximum power density of 4.8 kW kg<sup>-1</sup>. The superior rate performance can also be viewed in LMO. Even the current density increases 16 times at a high current density of 1600 mA g<sup>-1</sup>, a remarkable capacity retention of 43.7% (121.8 mAh g<sup>-1</sup>) is achieved by this LMO electrode, when only 0.02% (3.4 mAh g<sup>-1</sup>) is delivered by MO electrode. All these results fully prove that the intercalation of La<sup>3+</sup> can significantly boost the energy storage performance of MnO<sub>2</sub> and ameliorate the Zn<sup>2+</sup> intercalation/deintercalation kinetics. We also studied the influence of the La<sup>3+</sup> intercalation content on the electrochemical performance of the LMO sample. As the EDS results in Fig. S5 shown, the La atom% of LMO samples is gradually increased from 0% to 1.7% by adjusting the number of moles of lanthanum nitrate. The morphology of these LMO samples is almost the same (Fig. S6). However, the layer thickness calculated from the XRD patterns in Fig. S7 is



**Fig. 3** (a) CV curves at 1 mV s<sup>-1</sup>; (b) GCD curves at 100 mA g<sup>-1</sup> of the MO and LMO electrodes. (c) GCD curves of LMO electrode at different current densities. (d) Discharge capacity of MO and LMO electrodes at different current densities. (e) Capacity of electrodes with different La content at different current densities.

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aggrandized with the increased of the La<sup>3+</sup> intercalation contents, which is consistent with the previous results. Fig. S8 presents the GCD curves of these LMO samples at various current densities and Fig. 3e compare the discharge capacity of LMO samples as a function of La atom%. Significantly, all these LMO samples deliver substantially higher capacity than the pristine MO sample at each discharge current density, supporting that the intercalation of La<sup>3+</sup> into MO can dramatically boost its electrochemical activity. The capacity of the LMO increases with the increased amount of La<sup>3+</sup> and achieves the largest when the introduced La atom% is 1.5%.

The reaction kinetics of the MO and the LMO cathodes were further evaluated. Fig. 4a shows the first four CV curves of the LMO electrode in the voltage range from 0.8 to 1.9 V vs.  $\text{Zn}^{2+}/\text{Zn}$ . Here are two distinct peaks centered at 1.32 and 1.19 V are observed on cathodic sweeping, indicating a two-step intercalation. This two-step process was previously explained as stepwise H<sup>+</sup> and Zn<sup>2+</sup> intercalation, which was verified by the GCD curves tested in different electrolyte (Fig. 4b).<sup>31</sup> While the electrolyte contained both H<sup>+</sup> and Zn<sup>2+</sup>, the GCD curve exhibits two discharge plateaus at 1.37 V and 1.24 V, respectively, which consists with the CV results. After changing the electrolyte to 1 M  $H_2SO_4$  and 0.4 M MnSO<sub>4</sub> (without Zn<sup>2+</sup>), the lower plateau is totally disappeared and the higher plateau is virtually retained. The result demonstrated that the plateau at 1.37 V corresponds to the insertion of  $H^{\scriptscriptstyle +}\!,$  and the other corresponds to the insertion of Zn<sup>2+</sup>. During the initial cathodic cycle of the CV curves, only zinc ions are embedded to form the Zn<sub>x</sub>MnO<sub>2</sub>. After that, the Zn<sup>2+</sup> insertion is still dominated up to the third cycle and the curve shape was almost keep afterwards. In addition, it also can be seen that the area of the CV curves remains invariable after the initial cycle, proving the good reversibility. To analyse the charge transport and electrode kinetics of MO



**Fig. 4** (a) First for CV curves of the LMO electrode at the scan rate of 1 mV s<sup>-1</sup>. (b) GCD curves of the LMO electrode at 200 mA  $g^{-1}$  in different electrolyte. (c) Nyquist plots and (d) cycling performance for the MO and LMO electrodes and the coulombic efficiency of the LMO during the cycling test.

#### and LMO, the electrochemical impedance spectroscopy (EIS) was employed. As shown in Fig. 4c, both the curves contains semicircle in the high frequency region and an inclined line in the low frequency region, categories correspond to the charge transfer resistance $(R_{ct})$ and the semi-infinite Warburg impedance resulting from the diffusion limited electrontransfer process.<sup>34, 35</sup> From the plots, the LMO electrode possesses a much smaller diameter than MO at high frequency orientating, which means a less charge transfer resistance, suggesting the electron transportation is markedly facilitated by La<sup>3+</sup> intercalation. In addition to this, the LMO electrode also exhibits a larger slope of the straight line in the low-frequency region, reflecting a faster transfer/diffusion kinetics at the electrode-electrolyte interface. Moreover, the cycling performance of the MO and LMO electrodes was evaluated at a current density of 800 mA g<sup>-1</sup> for 200 cycles (Fig. 4d). The LMO electrode yields an excellent cycling stability retention of 71.0% with an ultraslow capacity decay rate of only 0.14% per cycle and the coulombic efficiency of LMO was nearly 100%. As a contrast, the MO electrode displays a retention of 52.1% with far larger capacity decay rate of 0.24% per cycle, which confirms the improvement of the circular reversibility by La3+

#### Conclusions

intercalation.

In summary, we developed a La<sup>3+</sup> intercalation strategy to markedly enhancing Zn-ion storage ability of layered birnessite $\delta$ -MnO<sub>2</sub> as high energy density cathode for aqueous ZIBs. With the expanded interlamellar spacing and promoted Zn<sup>2+</sup> intercalation/deintercalation kinetics which caused by La<sup>3+</sup> intercalation, the advanced LMO owned larger Zn storage capacity, better rate capability and more reversible redox reaction. While capitalizing on the LMO cathode, the aqueous LMO//Zn battery possessed both a remarkable capacity of 278.5 mAh g<sup>-1</sup>, a superior rate performance of 43.7% capacity retention at a 16-times fold current density and good electrochemical durability of 71.0% initial capacity after 200 cycles. Furthermore, the advanced aqueous ZIB with a LMO cathode exhibited not only a superb high energy density of 375.9 Wh kg<sup>-1</sup> at a current density of 100 mA g<sup>-1</sup>, but also an outstanding peak power density of 4.8 kW kg<sup>-1</sup> with an ultrafast charge-discharge ability in two minutes. The successful concept about La<sup>3+</sup> intercalation structure and the understanding about the Zn-ion storage kinetics of aqueous ZIBs light on the optimization of advanced systems to fulfill the requirement of the renewable energy storage.

#### Conflicts of interest

The authors declare no competing financial interest.

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