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# Boosting the capacity and stability of a MoO<sub>3</sub> cathode *via* valence regulation and polypyrrole coating for a rechargeable Zn ion battery†

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Molybdenum trioxide (MoO<sub>3</sub>) is emerging as a hugely competitive cathode material for aqueous zinc ion batteries (ZIBs) for its high theoretical capacity and electrochemical activity. Nevertheless, owing to its undesirable electronic transport capability and poor structural stability, the practical capacity and cycling performance of MoO<sub>3</sub> are yet unsatisfactory, which greatly blocks its commercial use. In this work, we report an effective approach to first synthesise nanosized MoO<sub>3-x</sub> materials to provide more active specific surface areas, while improving the capacity and cycle life of MoO<sub>3</sub> by introducing low valence Mo and coated polypyrrole (PPy). MoO<sub>3</sub> nanoparticles with low-valence-state Mo and PPy coating (denoted as MoO<sub>3-x</sub>@PPy) are synthesized *via* a solvothermal method and subsequent electrodeposition process. The as-prepared MoO<sub>3-x</sub>@PPy cathode delivers a high reversible capacity of 212.4 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup> with good cycling life (more than 75% capacity retention after 500 cycles). In contrast, the original commercial MoO<sub>3</sub> sample only obtains a capacity of 99.3 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup>, and a cycling stability of 10% capacity retention over 500 cycles. Additionally, the fabricated Zn//MoO<sub>3-x</sub>@PPy battery obtains a maximum energy density of 233.6 W h kg<sup>-1</sup> and a power density of 11.2 kW kg<sup>-1</sup>. Our results provide an efficient and practical approach to enhance commercial MoO<sub>3</sub> materials as high-performance cathodes for AZIBs.

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## Introduction

With the rapid development of wind, water, and solar energy, along with other forms of clean energy, the need for corresponding electrochemical energy storage technology has become extremely urgent.<sup>1,2</sup> Additionally, increased demands for the development of this technology have been raised due to the electrification of transportation tools and the growing intelligence of electronic devices.<sup>3</sup> Rechargeable lithium-ion batteries are already extensively utilized in energy storage devices on account of the advantages of their high energy density.<sup>4</sup> Nevertheless, the limited resources of lithium elements, as well as safety concerns associated with the use of high-cost organic electrolytes, have restricted the further development of lithium-ion batteries.<sup>5</sup> Compared with organic batteries, aqueous batteries use an aqueous solution as the electrolyte,<sup>6</sup> which have remarkable merits of high safety,

inexpensive, eco-friendly, and simple packaging.<sup>7</sup> The superior ionic conductivity of aqueous solutions gives them excellent rate performance.<sup>8</sup> In recent years, aqueous secondary batteries, including monovalent ion (Li<sup>+</sup>, Na<sup>+</sup>, K<sup>+</sup>) and multivalent ion (Ca<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, Al<sup>3+</sup>) batteries, have attracted a lot of attention.<sup>9,10</sup> Among them, aqueous zinc ion batteries (AZIBs) are growing rapidly for the advantages of inexpensive,<sup>11</sup> low potential (−0.76 V *vs.* SHE),<sup>12,13</sup> high capacity (820 mA h g<sup>-1</sup>),<sup>14</sup> and good stability in aqueous solutions of zinc anode,<sup>15</sup> making them suitable for the broad scope of use in large-scale grid energy storage as well as flexible and wearable electronic devices.<sup>16</sup>

As an innovative energy storage device, AZIBs currently have limited range of materials suitable as cathode materials for zinc ion storage.<sup>17</sup> They are mainly consist of manganese-based oxides,<sup>18</sup> vanadium-based oxides,<sup>19</sup> molybdenum-based oxides,<sup>1</sup> Prussian blue and its analogues,<sup>20</sup> and organic oxides.<sup>21</sup> Among them, molybdenum trioxide (MoO<sub>3</sub>) has the advantages of high abundance,<sup>22</sup> low toxicity and easy recovery,<sup>23</sup> as well as its multivalent states and two-dimensional layered structure.<sup>24</sup> Nevertheless, MoO<sub>3</sub> suffers from a serious drawback that it tends to dissolve in neutral or weakly acidic electrolytes to destroy its structure,<sup>25</sup> resulting in low actual capacity and poor cycling stability.<sup>26</sup> In previous studies, the electrochemical performance of electrode materials have been

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generally boosted by means of modifications such as morphology modulation,<sup>27</sup> interfacial engineering,<sup>28</sup> valence modulation,<sup>29</sup> doping and coating,<sup>30</sup> and composites.<sup>31</sup> As an instance, Liu *et al.* reported that MoO<sub>3</sub> can exhibit an initial discharge capacity of 120 mA h g<sup>-1</sup>, but its capacity decreases sharply over 5 cycles of charging/discharging, mainly due to the structure damage.<sup>26</sup> Liu *et al.* used a surface engineering to avoid the structure damage of electrode material through coating a layer of Al<sub>2</sub>O<sub>3</sub> on the surface of MoO<sub>3</sub>. Through the DFT calculations, MoO<sub>3-x</sub> obtain a lower Gibbs free energy of Zn<sup>2+</sup> adsorption on the surface of MoO<sub>3-x</sub>, indicating that the desorption of Zn<sup>2+</sup> on MoO<sub>3-x</sub> is thermodynamically more beneficial and its adsorption/desorption of Zn<sup>2+</sup> is more reversibility. In addition, it leads to a narrower of the band gap between the valence band and the conduction band, which facilitates the excitation of charge carriers to the conduction band and thus improves the electrical conductivity of MoO<sub>3-x</sub>.<sup>32</sup> The assembled Zn//P-MoO<sub>3-x</sub>@Al<sub>2</sub>O<sub>3</sub> battery shows improved cycling stability. The capacity retention of Zn//P-MoO<sub>3-x</sub>@Al<sub>2</sub>O<sub>3</sub> battery was 69.2% over 100 cycles, which is better than that of that of Zn//P-MoO<sub>3-x</sub> battery (only 40.8%).<sup>32</sup> He *et al.* developed an effective strategy for quasi-solid PVA/ZnCl<sub>2</sub> gel electrolyte to stabilize MoO<sub>3</sub> nanowires instead of aqueous electrolyte, and the capacity retention of the assembled MoO<sub>3</sub>//Zn battery reach to 70.4% in gel electrolyte over 400 cycles, but only 27.1% in aqueous electrolyte.<sup>33</sup> In addition, Zhang *et al.* developed WP-MoO<sub>3</sub> electrodes by a water-proton co-pre-insertion strategy. WP-MoO<sub>3</sub> electrode achieve selective hydrated proton insertion by using water molecules between the layers to increase the insertion energy barrier of zinc ions by blocking the transport path of zinc ions. Based on the above merits, the capacity retention of the prepared battery is 83% after 1000 cycles.<sup>34</sup> Despite the impressive progress of these works, there is still room to enhance the capacity and cycle stability of MoO<sub>3</sub>. Moreover, exploring simpler and practical ways to boost the electrochemical performance of MoO<sub>3</sub> electrodes remains a meaningful challenge.<sup>35</sup>

In this work, we focus on improving the capacity and cycling stability of commercial MoO<sub>3</sub> through a simple and effective approach. Low-valent state enriched and polymer coated MoO<sub>3</sub> electrode materials (MoO<sub>3-x</sub>@PPy) are synthesized by a simple solvothermal method and subsequent electrodeposition process. The reactivity and structural stability of MoO<sub>3-x</sub>@PPy electrodes are boosted with the help of low-valence-state Mo introduction and coating strategies. Firstly, the solvothermal reaction allows the MoO<sub>3</sub> particles to be nanosized to obtain more active sites, while the introduction of low-valent molybdenum improves the reactivity of the electrode material. Secondly, the coated PPy layer improves the stability of the electrode material in the electrolyte. Combining the above advantages, the assembled Zn//MoO<sub>3-x</sub>@PPy battery obtain a high reversible capacity of 212.4 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup> and favorable cycle life of 75% capacity retention over 500 cycles, while that of Zn//MoO<sub>3</sub> battery is only 99.3 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup> and 10% capacity retention over 500 cycles. Moreover, the fabricated Zn//MoO<sub>3-x</sub>@PPy battery exhibits a maximum

energy density of 233.6 W h kg<sup>-1</sup> and power density of 11.2 kW kg<sup>-1</sup>.

## Experimental section

### Preparation of MoO<sub>3-x</sub> electrode

All chemicals in this work were utilized without any purification (the chemicals were 99% pure). 0.3 g of commercial MoO<sub>3</sub> powder was added to a mixed solution of 10 ml of water and 10 ml of ethylene glycol. After stirring magnetically for 30 min at room temperature, the homogeneous mixed solution was poured into an autoclave lined with polytetrafluoroethylene and then placed in a blast drying oven at 180 °C for 12 h. After it cooled down, the powder was washed repeatedly with deionized water and anhydrous ethanol after centrifugation, and then set it in an oven at 60 °C for 6 h to obtain black MoO<sub>3-x</sub> powder. After that, the obtained MoO<sub>3-x</sub> powder, acetylene black and polyvinylidene fluoride (PVDF) were mixed and ground in the ratio of 8 : 1 : 1 by mass. Then, the above mixture powder was added to *N*-methylpyrrolidone (NMP) solution to form a uniform slurry. Then the obtained slurry was homogeneously coated on carbon paper and dried in a vacuum oven for 6 h to obtain MoO<sub>3-x</sub> electrode.

### Preparation of MoO<sub>3-x</sub>@PPy electrode

The above prepared MoO<sub>3-x</sub> electrode (1 × 2 cm) was electro-deposited in a homogeneous electrolyte formed by mixing and stirring 0.1 M sodium sulfate and 0.145 M pyrrole. The deposition process was performed using cyclic voltammetry with a voltage window of -0.5 to 0.8 V for 4 segments at 50 mV s<sup>-1</sup>, resulting in the electrodeposition of PPy coating on the surface of the MoO<sub>3-x</sub> electrode material (MoO<sub>3-x</sub>@PPy).

### Characterization of the material

The surface morphology, microstructure, and elemental distribution of electrode materials are characterized by Scanning electron microscopy (SEM, Sigma500, ZEISS) equipped with X-ray energy spectrometry (EDS, INCA 300, Oxford Instruments) and transmission electron microscope (TEM, JEM-F200, JEOL) analysis. The crystal structure of the prepared electrode materials is measured by X-ray diffraction analysers (XRD, Bruker Germany) equipped with a Cu-Kα radiation source. X-ray photoelectron spectroscopy (XPS, NEXSA, Thermo VG) and Fourier Transform infrared spectroscopy (FTIR, NICOLET 6700) were utilized to investigate the elemental composition and functional groups of prepared electrode materials.

### Electrochemical tests

The cathode material has an active substance loading of about 2 mg cm<sup>-2</sup>. Electrochemical characterization techniques such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and galvanostatic charge/discharge (GCD) tests were conducted on an electrochemical workstation (CHI660E) with a potential window of 0.2–1.3 V using AZIBs packed in air with pure MoO<sub>3</sub>, fabricated MoO<sub>3-x</sub>, and fabricated



$\text{MoO}_{3-x}\text{@PPy}$  as cathodes, zinc plates as anodes, and 2 M  $\text{ZnSO}_4$  as the electrolyte.

## Results and discussion

The synthesis of  $\text{MoO}_{3-x}\text{@PPy}$  electrode consists of a two-step synthesis process as shown in Fig. 1a. Firstly, the  $\text{MoO}_{3-x}$  electrode material enriched in the low-valence-state Mo was synthesized by solvothermal reaction of commercial  $\text{MoO}_3$  with ethylene glycol. The free molybdenum produced by the dissolving of commercial  $\text{MoO}_3$  is partially reduced by ethylene glycol in solution, which resulted in the synthesis of  $\text{MoO}_{3-x}$  electrode material. Subsequently, it was coated with acetylene black and PVDF in the ratio of 8:1:1 on carbon paper to produce  $\text{MoO}_{3-x}$  electrode. A comparison of SEM image of commercial  $\text{MoO}_3$  electrode (Fig. S1†) and  $\text{MoO}_{3-x}$  electrode (Fig. 1b and d) shows that the particles of  $\text{MoO}_{3-x}$  electrode materials become smaller after the solvent heat treatment. Secondly, the conducting polymer PPy was deposited on the surface of the  $\text{MoO}_{3-x}$  electrode with an electrodeposition process. As shown in Fig. 1c and e, the morphology of the electrode material is almost unchanged after PPy deposition, implying that the polymer coating has not changes the microscopic morphology of the  $\text{MoO}_{3-x}$  electrode material.

To further investigate the microstructure and crystal type of the material, the synthesized material was characterized by TEM and XRD. Fig. S2† shows a TEM image of commercial  $\text{MoO}_3$  showing a particle size of approximately 150 nm. In addition, a lattice stripe of 0.133 nm is visible in the HRTEM image of  $\text{MoO}_3$ , which corresponds to the (202) crystal plane of  $\text{MoO}_3$  (JCPDF # 05-0508), while the calibrated diffraction points in selected electron diffraction (SAED) pattern of the  $\text{MoO}_3$  material correspond to the (150), (210) and (110) crystal

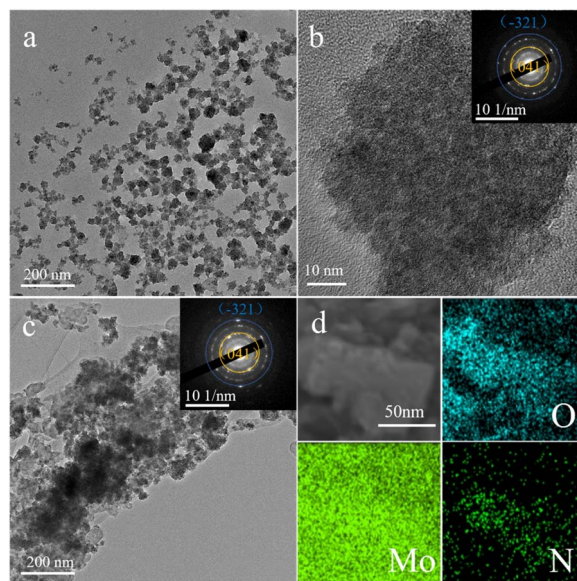


Fig. 2 (a) TEM and (b) HRTEM images of  $\text{MoO}_{3-x}$  material (inset the SAED pattern). (c) TEM image of  $\text{MoO}_{3-x}\text{@PPy}$  material (inset the SAED pattern). (d) The corresponding area EDS mapping.

planes of  $\text{MoO}_3$  (JCPDF # 05-0508). Fig. 2a and b shows a TEM image of  $\text{MoO}_{3-x}$ , showing a particle size of approximately 50 nm, which is much smaller than the commercial  $\text{MoO}_3$  material and in line with the SEM results. However, SAED pattern of the  $\text{MoO}_{3-x}$  material shows two distinct diffraction rings corresponding to the  $(-321)$  crystal plane of  $\text{MoO}_2$  (JCPDS # 32-0671) and the (041) crystal plane of  $\text{MoO}_3$  (JCPDF # 05-0508), indicating the introduction of low-valent-state Mo after solvothermal reaction. Fig. 2c shows a TEM image of  $\text{MoO}_{3-x}\text{@PPy}$  showing a thin film outside the  $\text{MoO}_{3-x}$  material, demonstrating that PPy is encapsulated on the surface of the  $\text{MoO}_{3-x}$  electrode material. Subsequently, the elemental distribution in the  $\text{MoO}_{3-x}\text{@PPy}$  material was analyzed by energy density spectroscopy (EDS). The results display that the O, Mo and N elements are evenly dispersed on the electrode material, again proving that PPy is evenly coated on the  $\text{MoO}_{3-x}$  electrode material. The crystallization pattern of the prepared materials was investigated more thoroughly by XRD test. Fig. 3a shows the XRD patterns of commercial  $\text{MoO}_3$ ,  $\text{MoO}_{3-x}$ , and  $\text{MoO}_{3-x}\text{@PPy}$  materials. It is noteworthy that the  $\text{MoO}_{3-x}$  sample synthesized after the solvothermal reaction contains a large number of characteristic peaks  $(-111)$ , (200), and (211) of  $\text{MoO}_2$  (JCPDS # 32-0671) peaks and a small number of characteristic peaks (110), (040), and (112) of  $\text{MoO}_3$ , while only characteristic peaks of  $\text{MoO}_3$  (JCPDF # 05-0508) are present in the commercial  $\text{MoO}_3$ , which implies the successful introduction of low-valent-state Mo in the commercial  $\text{MoO}_3$  by the solvothermal reaction. In addition, the XRD pattern of  $\text{MoO}_{3-x}\text{@PPy}$  material after electrodeposition of PPy shows a decrease in peak intensity, but characteristic peaks of  $\text{MoO}_2$   $(-111)$ , (200), (211) and  $\text{MoO}_3$  (112) still can be found in the sample, which indicates that the coated amorphous PPy do not change the crystal structure, which is in line with the results of

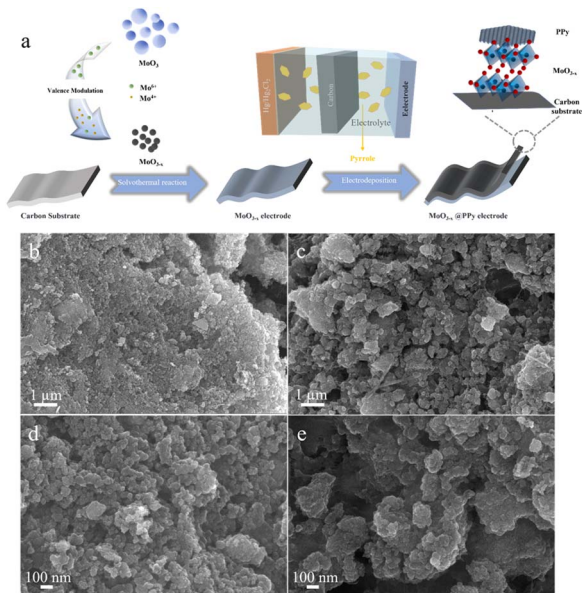


Fig. 1 (a) Schematic illustration of the synthesis of  $\text{MoO}_{3-x}\text{@PPy}$  electrode material. (b and d) SEM images of  $\text{MoO}_{3-x}$  electrode material. (c and e) SEM images of  $\text{MoO}_{3-x}\text{@PPy}$  electrode material.





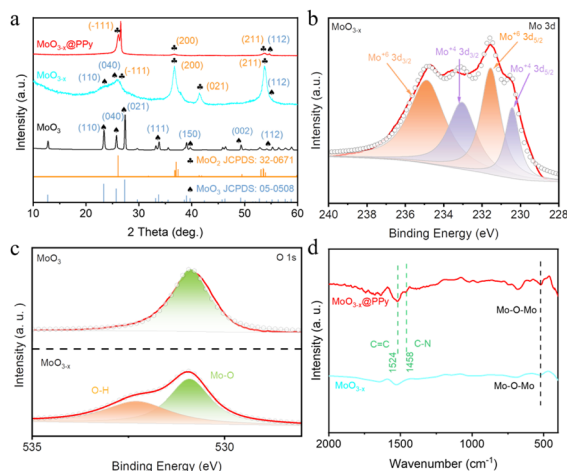


Fig. 3 (a) XRD patterns corresponding to MoO<sub>3</sub>, MoO<sub>3-x</sub> and MoO<sub>3-x</sub>@PPy samples. (b) Mo 3d spectra of the synthesized MoO<sub>3-x</sub> sample. (c) O 1s spectra of MoO<sub>3</sub> and MoO<sub>3-x</sub> samples. (d) FT-IR of MoO<sub>3-x</sub> and MoO<sub>3-x</sub>@PPy samples.

TEM test. Furthermore, XPS was utilized to analyse the valence and elemental composition of the material. As shown in Fig. 3b and S3b,<sup>†</sup> the Mo 3d spectrum of commercial MoO<sub>3</sub> matches the two characteristic peaks of 3d<sub>5/2</sub> and 3d<sub>3/2</sub> of Mo<sup>6+</sup> at 232.75 and 235.93 eV respectively,<sup>36</sup> indicating that molybdenum is predominantly present in commercial MoO<sub>3</sub> at +6 valence. However, the MoO<sub>3-x</sub> sample produced by solvothermal reduction with ethylene glycol showed two additional peaks in its Mo 3d spectrum. Of these, 230.43 and 233.13 eV correspond to the 3d<sub>3/2</sub> and 3d<sub>5/2</sub> characteristic peaks of Mo<sup>4+</sup>.<sup>37</sup> The presence of Mo<sup>4+</sup> indicates the introduction of low-valence-state Mo into the material. Furthermore, according to the analysis of the XPS test, the two characteristic peaks of Mo<sup>6+</sup> are still found at 232.64 and 235.41 eV, which implies that the commercial MoO<sub>3</sub> has not been completely reduced to MoO<sub>2</sub>. Fig. S3a<sup>†</sup> displays the XPS survey spectra of MoO<sub>3</sub> and MoO<sub>3-x</sub>@PPy electrode material, which shows that only the material of MoO<sub>3</sub>@PPy contains N elements, indicating the successful coating of PPy.<sup>38</sup> Also Fig. S3c<sup>†</sup> shows the Mo 3p spectra of MoO<sub>3</sub> and MoO<sub>3-x</sub>@PPy. The Mo 3p peak is sharper for MoO<sub>3</sub>, while the distinct hump at 397.5 eV in the Mo 3p XPS spectrum of MoO<sub>3-x</sub>@PPy further confirms the presence of N on the MoO<sub>3-x</sub>@PPy surface.<sup>39</sup> The O 1s spectra of the MoO<sub>3</sub> and MoO<sub>3-x</sub> samples in Fig. 3c show that for 530.8 ± 0.1 eV (green area fraction) the binding energy component is derived from the lattice oxygen (O<sub>a</sub>) of MoO<sub>3</sub>, for the MoO<sub>3-x</sub> sample the peak at 532.2 ± 0.1 eV (yellow area fraction) is associated with a chemically absorbed oxygen site (O<sub>c</sub>).<sup>38</sup> Fig. 3d shows the Fourier transform infrared spectra (FT-IR) of MoO<sub>3-x</sub> and MoO<sub>3-x</sub>@PPy electrode materials. The FT-IR spectra of both electrode materials show the core characteristic peaks of molybdenum oxide (Mo-O-Mo), while the main characteristic peaks of PPy (C=C and C-N) are also observed in the MoO<sub>3-x</sub>@PPy electrode,<sup>40</sup> again demonstrating that PPy was successfully coated on the surface of the MoO<sub>3-x</sub> material.

To further investigate the effects of low-valence-state Mo introduction and PPy coating strategies on the zinc storage property of commercial MoO<sub>3</sub> materials, a series of AZIBs based on the synthesized MoO<sub>3</sub>, MoO<sub>3-x</sub>, and MoO<sub>3-x</sub>@PPy materials MoO<sub>3</sub> as cathode, zinc plate as anode and 2 M ZnSO<sub>4</sub> as electrolyte were assembled. First, we optimised the thickness of the electrodeposition PPy layers. As shown in Fig. S4,<sup>†</sup> its electrochemical property decreases as the number of deposition cycles increases, indicating that too thick PPy will hinder MoO<sub>3-x</sub> from participating in the electrochemical reaction. However, PPy layer with appropriate thickness (2 cycles of electrodeposition) can not only stabilize the structural stability of MoO<sub>3-x</sub> in electrolyte, but also provide additional zinc storage performance. Fig. 4a shows the CV curves of assembled Zn//MoO<sub>3</sub>, Zn//MoO<sub>3-x</sub>, and Zn//MoO<sub>3-x</sub>@PPy batteries at 20 mV s<sup>-1</sup> within the operating window of 0.2–1.3 V.

The graph clearly shows that the CV curves of the three batteries are almost identical in shape, but the current response signal gradually enlarges as the introduction of the low-valence-state Mo and the PPy coating, indicating that their zinc storage performance gradually enhanced. Then, the GCD curves in Fig. 4b shows more clearly that the Zn//MoO<sub>3-x</sub>@PPy battery achieves a highest discharge capacity of 212.4 mA h g<sup>-1</sup> (based on the mass of the cathode active material) at 1 A g<sup>-1</sup>, while that of Zn//MoO<sub>3-x</sub> and Zn//MoO<sub>3</sub> batteries are only 181.7 mA h g<sup>-1</sup> and 99.3 mA h g<sup>-1</sup>, respectively. These results demonstrate that

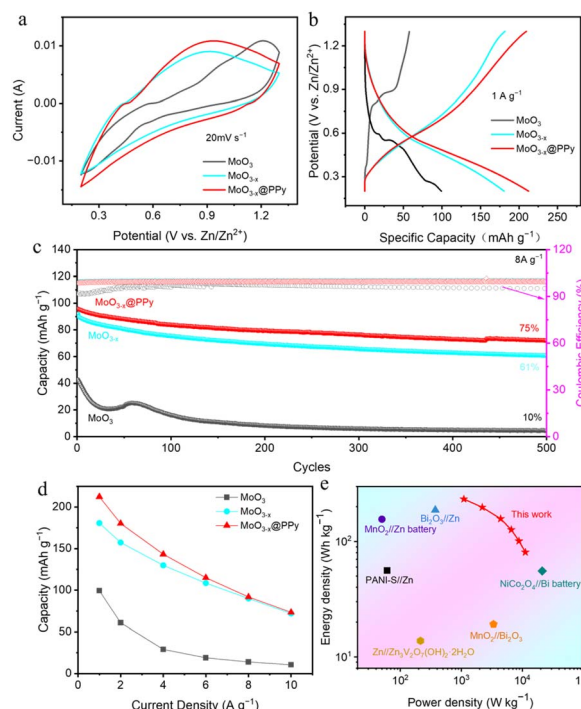


Fig. 4 (a) CV curves of Zn//MoO<sub>3</sub>, Zn//MoO<sub>3-x</sub> and Zn//MoO<sub>3-x</sub>@PPy batteries at 20 mV s<sup>-1</sup>. (b) GCD curves of Zn//MoO<sub>3</sub>, Zn//MoO<sub>3-x</sub> and Zn//MoO<sub>3-x</sub>@PPy batteries at 1 A g<sup>-1</sup>. (c) Cycle performance of Zn//MoO<sub>3</sub>, Zn//MoO<sub>3-x</sub> and Zn//MoO<sub>3-x</sub>@PPy batteries at 8 A g<sup>-1</sup>. (d) Rate performance of Zn//MoO<sub>3</sub>, Zn//MoO<sub>3-x</sub> and Zn//MoO<sub>3-x</sub>@PPy batteries. (e) Ragone plots of the fabricated Zn//MoO<sub>3-x</sub>@PPy battery in this work compared to other reported batteries.

the introduce of low-valence-state Mo and PPy coating strategies can boost the Zn storage capacity of commercial  $\text{MoO}_3$ . Furthermore, the rate performance of the fabricated three kinds of batteries was characterized at different current densities, illustrated in Fig. 4d, where the  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  shown highest capacities at all currents. The reversible specific capacities of  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  battery can reach  $212.4 \text{ mA h g}^{-1}$  to  $73.3 \text{ mA h g}^{-1}$  at the current density of  $1$  to  $10 \text{ A g}^{-1}$ , respectively. In particular,  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  battery exhibited 35% capacitance retention even at a high current density of  $10 \text{ A g}^{-1}$ . By contrast,  $\text{Zn}/\text{MoO}_3$  battery achieved specific capacities of  $99.3 \text{ mA h g}^{-1}$  to  $10.5 \text{ mA h g}^{-1}$  at  $1$  to  $10 \text{ A g}^{-1}$ , respectively. Its rate property is only 10.6%, again indicating that the low-valence-state Mo introduction and PPy coating strategies can boost the capacity and rate property of commercial  $\text{MoO}_3$  for zinc storage. Much encouragingly, the  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  battery maintained 75% capacity retention over 500 cycles, while that of  $\text{Zn}/\text{MoO}_3$  and  $\text{Zn}/\text{MoO}_{3-x}$  batteries were not high, 61% and 10%, respectively, indicating that coating with a corrosion resistant polymer coating is a very simple and practical way to enhance the stability of electrode materials (Fig. 4c). It is worth noting that the specific capacity of  $\text{MoO}_3$  is improved over the first 100 cycles, which might attribute to the continuous activation of the electrode due to the surface chemical reactions between  $\text{MoO}_3$  and the  $\text{ZnSO}_4$  electrolyte.<sup>41</sup> Energy density and power density are the two vital parameters for evaluating the energy storage capacity of batteries. As shown in Fig. 4e, the fabricated  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  battery obtained an energy density of up to  $233.6 \text{ W h kg}^{-1}$  (power density of  $1.1 \text{ kW kg}^{-1}$ ) and the maximum power density of  $11.2 \text{ kW kg}^{-1}$  (energy density of  $80.6 \text{ W h kg}^{-1}$ ), exceed those of some newly published aqueous batteries, as shown in Table 1. This satisfactory energy density and power density are expected to enable our designed  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  battery to become a more practical alternative power source.

The electrochemical kinetics of the fabricated electrode were further investigated by conducting CV measurements at various scan rates ranging from  $1$  to  $10 \text{ mV s}^{-1}$  (displayed in Fig. 5a and S5†). As can clearly be seen the figure of the CV curve at any scan rates is essentially the same, but the peaks are slightly shifted. The diffusion and pseudocapacitance behaviour of the battery during the charge/discharge cycle was distinguished by adjusting the scan rate to correspond to the response of the

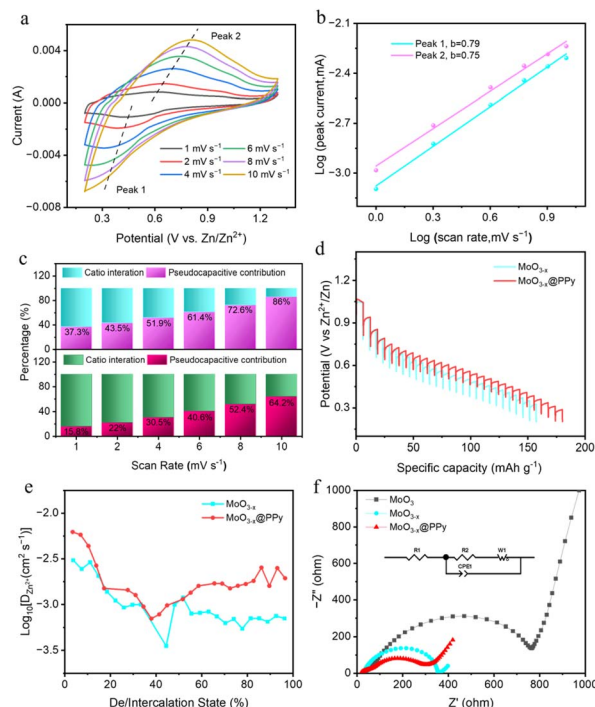


Fig. 5 (a) CV curves for  $\text{MoO}_{3-x}\text{@PPy}$  at a range of scan rates of  $1, 2, 4, 6, 8$  and  $10 \text{ mV s}^{-1}$ . (b)  $\log(i)$  vs.  $\log(v)$  plots of the two peaks in the CV curve for  $\text{MoO}_{3-x}\text{@PPy}$ . (c) Ratio of diffusion contribution to capacitance contribution for  $\text{Zn}/\text{MoO}_{3-x}$  and  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$ . (d) Discharge GITT curves for  $\text{Zn}/\text{MoO}_{3-x}$  and  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  at a current density of  $2 \text{ A g}^{-1}$  and (e) corresponding  $\text{Zn}^{2+}$  coefficients  $D_{\text{Zn}^{2+}}$ . (f) Nyquist plots of  $\text{MoO}_3$ ,  $\text{MoO}_{3-x}$  and  $\text{MoO}_{3-x}\text{@PPy}$ .

peak current. In the case of a dominant battery behaviour, the relationship between peak current  $i$  and scan voltage  $v$  follows a power function of  $0.5$ , indicating that diffusion plays an important role throughout the process. When analyzing battery behavior during charge/discharge cycles, it is possible to distinguish between diffusive and pseudo-capacitive behavior by adjusting the scan rate to match peak current response. In cases where the process is dominated by capacitance, peak current  $i$  varies linearly with scanning voltage  $v$ . To determine the presence of pseudo-capacitive behavior, researchers can calculate the  $b$  value using the equation  $i = av^b$ . This allows for a more accurate understanding of electrode material behavior during charging and discharging. When the value of  $b$  equals  $0.5$ , the electrode material displays battery characteristics. If the value of  $b$  falls among  $0.5$  to  $1$ , both battery and pseudocapacitive properties can be observed in the electrode material. When  $b$  is greater than or equal to  $1$ , the electrode material mainly displays pseudocapacitive behavior. Fig. 5b displays the fitted CV curves for the  $\text{MoO}_{3-x}\text{@PPy}$  samples at different scan rates. It is noteworthy that the calculated  $b$  value of the reduction peak is  $0.79$ , suggesting that a blend of both diffusion-controlled and capacity-based kinetic phenomena occurred. To determine the pseudo-capacitance contribution of  $\text{MoO}_{3-x}\text{@PPy}$  at various scan rates, the pseudo-capacitance equation was utilized:  $i = k_1v + k_2v^{1/2}$ . This equation takes into account  $k_1$  and  $k_2$  as constants, with  $k_1v$  representing the

Table 1 The energy density and power density of the  $\text{Zn}/\text{MoO}_{3-x}\text{@PPy}$  battery and other reported batteries

ZIBs	Power density ( $\text{W kg}^{-1}$ )	Energy density ( $\text{W h kg}^{-1}$ )	Ref.
$\text{MnO}_2/\text{Zn}$ battery	50	156.1	42
$\text{Bi}_2\text{O}_3/\text{Zn}$ battery	375	187.5	43
$\text{PANI-S}/\text{Zn}$ battery	61	56	44
$\text{Ni}/\text{Fe}$ battery	3370	19.1	45
$\text{NiCo}_2\text{O}_4/\text{Bi}$ battery	21 200	55.4	46
$\text{Zn}/\text{Zn}_3\text{V}_2\text{O}_7(\text{OH})_2 \cdot 2\text{H}_2\text{O}$ battery	214	13.8	47
This work	11 000	233.6	

theoretical value of the pseudo-capacitance contribution. Fig. 5c and S5† showcase the outcomes of this calculation for Zn//MoO<sub>3</sub>, Zn//MoO<sub>3-x</sub>, and Zn//MoO<sub>3-x</sub>@PPy batteries with varying scan rates ranging from 1 to 10 mV s<sup>-1</sup>. Upon comparison of the pseudocapacitance contribution at a scan rate of 10 mV s<sup>-1</sup>, it is evident that the Zn//MoO<sub>3-x</sub>@PPy battery exhibits the highest pseudocapacitance contribution, indicating superior rate performance. This finding corroborates with the data presented in Fig. 4d. Additionally, it is worth noting that the Zn//MoO<sub>3-x</sub>@PPy battery achieves a significant capacitance contribution of 86% at 10 mV s<sup>-1</sup>, further highlighting the dominance of pseudocapacitance in determining its performance (Fig. S6†). Notably, this observation is consistent with the outcomes obtained from our experiments and analysis. The MoO<sub>3-x</sub>@PPy active material possesses a pseudo-capacitive nature that facilitates selective storage of Zn<sup>2+</sup> ions at the electrode surface. This results in a shortened ion transport distance and an enhanced electron transport rate, ultimately leading to improved rate capabilities and longer cycle life of the electrode material. Zn<sup>2+</sup> diffusion coefficients  $D_{\text{Zn}^{2+}}$  in the MoO<sub>3</sub>, MoO<sub>3-x</sub> and MoO<sub>3-x</sub>@PPy cathodes were also investigated through the galvanostatic intermittent titration technique (GITT). From Fig. 5d and S7,† all three electrodes exhibit a curve shape similar to the GCD curve (Fig. 4b). The ion diffusion coefficient of the MoO<sub>3-x</sub>@PPy electrode consistently surpasses that of the MoO<sub>3</sub> and MoO<sub>3-x</sub> electrode, indicating that the ion diffusion rate is enhanced by coating it with PPy and low-valence-state Mo introduction (Fig. 5e and S7†). The electrochemical impedance spectroscopy (EIS) data for all electrode materials is presented in Fig. 5f. This figure clearly illustrates that the MoO<sub>3-x</sub>@PPy electrode exhibits a smaller semicircle in the high frequency region, which indicates a lower charge transfer resistance ( $R_{\text{ct}}$ ). The  $R_{\text{ct}}$  of MoO<sub>3-x</sub>@PPy is approximately 278.3  $\Omega$ , lower than that of MoO<sub>3-x</sub> (357.5  $\Omega$ ) and commercial MoO<sub>3</sub> (769.9  $\Omega$ ), demonstrating that the  $R_{\text{ct}}$  of the MoO<sub>3-x</sub>@PPy electrode material can be greatly boosted by the low-valence-state Mo introduction and PPy coating strategies. Furthermore, in the low frequency region, the MoO<sub>3-x</sub>@PPy electrode demonstrates a steep linear slope, implying efficient electron diffusion capability. This is in contrast to the other electrode materials tested, which exhibit a lower and less steep slope in this region.

## Conclusions

In this work, we synthesized high capacity, long cycle life PPy coated low-valent-state Mo enriched composites MoO<sub>3-x</sub>@PPy as cathode materials for AZIBs by a simple and effective solvothermal and electrodeposition method in two steps. With the help of low-valence-state Mo introduction and PPy coating to synergistically enhanced the capacity and cycling life of commercial MoO<sub>3</sub>. The Zn//MoO<sub>3-x</sub>@PPy battery assembled based on MoO<sub>3-x</sub>@PPy as the cathode material exhibited a high capacity of 212.4 mA h g<sup>-1</sup> at 1 A g<sup>-1</sup> and outstanding rate performance (73.3 mA h g<sup>-1</sup> capacity even at 10 A g<sup>-1</sup>). Encouragingly, the Zn//MoO<sub>3-x</sub>@PPy battery exhibits excellent cycling life with a capacity retention rate of 75% after 500 cycles.

Meanwhile, the Zn//MoO<sub>3</sub> battery assembled based on commercial MoO<sub>3</sub> has only 99.3 mA h g<sup>-1</sup> capacity at 1 A g<sup>-1</sup> and 10% capacitance retention (after 500 cycles). Moreover, the prepared battery exhibited favorable energy density of 233.6 W h kg<sup>-1</sup>. This work shows practical strategies to boost the zinc storage property of commercial MoO<sub>3</sub>, providing new ideas and approaches for its commercialization.

## Conflicts of interest

There are no conflicts to declare.

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