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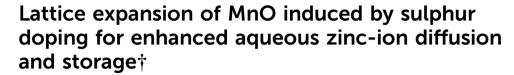


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Zixiang Cui, Luwei Shi, Yan Lin, Shiliu Yang, Shiliu Yang, Shengyi Wu, An Tao Hu,

Lattice engineering is reported to enhance Zn2+ storage capability of MnO via anionic doping, which effectively lowers the Zn2+ diffusion barrier and boosts Zn2+ diffusion kinetics. The optimized MnOS_{0.3}@rGO exhibits superior rate capability and reversible capacity of 115.1 mA h g^{-1} at 0.5 A g^{-1} for 350 cycles.

In recent years, aqueous zinc-ion batteries (ZIBs) have emerged as a promising candidate for next-generation energy storage systems due to their high energy density, low cost, and environmental friendliness. However, the slow kinetics of zinc ions (Zn²⁺) during charge-discharge processes has been a major challenge limiting the rate capability and high-power performance of ZIBs.^{2,3} To address this issue, various strategies have been explored, including the design of novel electrode materials and the optimization of electrolyte composition.⁴

Manganese-based materials are widely applied as cathode materials in ZIBs due to their high theoretical capacity, abundant availability, and relatively low cost.5 However, the application of manganese-based materials in ZIBs faces some challenges.^{6,7} Additionally, structural changes may occur during charge-discharge cycles, leading to capacity fading and reduced cycling stability.8 To overcome these challenges, researchers have been exploring various strategies to improve the electrochemical performance of manganese-based materials. 9,10 For instance, nanostructure design, doping with other elements, and composites with conductive materials have been attempted to enhance the con-

In recent years, researchers have made certain progress on MnO-based materials. A typical example is that Tang et al.

reported the application of metal-organic framework (MOF)derived manganese oxide (MnO) composites with active functional groups in aqueous ZIBs. 12 Moreover, Shen et al. added multi-wall carbon nanotubes (MWCNTs) to form 3D ternary MnO/rGO/MWCNTs (MPGC) with a high specific capacity of 267.4 mA h g^{-1} at 0.2 A g^{-1} and good stability with retention rate of 96.2% after 200 cycles at 0.5 A g⁻¹. 13

Among these strategies for modulating the Zn²⁺ storage capability of MnO, intrinsic regulation of lattice could be especially effective for improving the electrochemical performance, owing to the fundamental structure-property relationship. 14 Herein, we dope anionic sulphur into the lattice of MnO (MnOS_x) from Mn-based MOF to regulate the property of MnO, and further wrap MnOS_x spheres outside by reduced graphene oxide (rGO) with good conductivity. Specifically, the doping of S intrinsically contributes more density of states (DOS) of electrons around the Fermi level, which promotes the electron transport. Moreover, sulphur doping-induced lattice expansion boosts the zinc-ion insertion/extraction kinetics. These two factors lead to improved rate performance and long-term reversible capacity. Therefore, when used as a cathode in ZIBs, MnOS_{0.3}(a) rGO exhibits a reversible specific capacity of 115.1 mA h g⁻¹ after 350 cycles at a high rate of $0.5 \,\mathrm{A\,g^{-1}}$, much better than the pristine MnO. This enhanced performance demonstrates the potential of MnOS_{0.3}@rGO as a cathode material for ZIBs. 15

A typical synthesis of MnOS_{0.3}@rGO is schematically illustrated in Fig. 1a. Namely, a certain amount of graphene oxide (GO) was added into the solution containing manganese acetate, polyvinyl pyrrolidone (PVP) and 1,3,5-benzenetricarboxylic (BTC) acid. After reaction for 24 hours at 60 °C, the product (Mn-BTC MOF) was formed. Subsequently, Mn-BTC@GO was annealed at 700 °C in an argon atmosphere for 3 hours at a heating rate of 5 °C min⁻¹ to obtain MnO@rGO. Then a certain amount of sulphur powder was mixed with MnO@rGO and underwent secondary annealing at 400 °C in an argon atmosphere for 2 hours at a heating rate of 5 °C min⁻¹ to obtain MnOS_{0.3}@rGO. The control samples, such as pristine MnO and MnOS_{0,3} were also synthesized by using the similar method, except the addition of sulphur powder and/or GO.

ductivity and structural stability of manganese-based materials. 11

^a School of Materials Science and Engineering, Suzhou University of Science and Technology, Suzhou 215009, China. E-mail: ruguangma@usts.edu.cn

^b Research Unit of Sustainable Chemistry, University of Oulu, Oulu 90570, Finland. E-mail: ulla.lassi@oulu.fi

^c School of Chemistry and Materials Engineering, New Energy Materials and Technology Research Centre, Huainan Normal University, Huainan 232038, Anhui,

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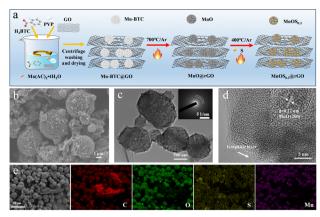


Fig. 1 (a) Scheme of synthetic process of MnOS_{0.3}@rGO. (b) SEM image, (c) TEM image and SAED image (inset), (d) HRTEM image with clear lattice fringes (inset), and (e) EDS and element mapping images of MnOS_{0.3}@rGO.

Scanning electron microscopy (SEM) image shows that the morphology of MnOS_{0,3}@rGO is hierarchical spheres consisting of many nanoparticles (Fig. 1b and Fig. S1, ESI†). Transmission electron microscopy (TEM) clearly reveals that some nanospheres assigned to MnOS_{0.3} are wrapped by rGO layers (Fig. 1c). The selected area electron diffraction (SAED) shows concentric rings, indicating the polycrystallinity of MnOS_{0,3} nanoparticle (inset of Fig. 1c). The enlarged TEM image shows that a typical nanoparticle with the size of 8 nm is wrapped by a few graphitic layers. Such microstructure is beneficial for the improvement of electrical conductivity. High-resolution TEM (HRTEM) image (inset of Fig. 1d) shows obvious lattice fringes, which also demonstrates the good crystallinity of MnOS_{0.3}. The lattice spacing is 0.22 nm, corresponding to the (200) facet of MnO. Energy-dispersive X-ray spectroscopy (EDS) image (Fig. 1e) and the corresponding elemental mapping images, reveal the existence of Mn, S, C and O elements uniformly distributing throughout the entire MnOS_{0.3}@rGO. SEM image and the corresponding elemental mapping images of MnOS_{0,3} also confirm the uniform distribution (Fig. S2 in ESI†).

X-ray diffraction (XRD) patterns as shown in Fig. 2a and Fig. S3 (ESI†), clearly show the crystal structure of MnOS_{0.3}@ rGO, which match well with MnO (JCPDS no. 07-0230), confirming the successful synthesis. Compared to the pattern of pristine MnO, the peaks of MnOS_{0.3} and MnOS_{0.3}@rGO show a little shift toward low angle due to S doping, especially for the peaks corresponding to (200) and (220). In Raman spectra (Fig. 2b), the typical peak at 646.5 cm⁻¹ is ascribed to Mn-O vibration, which also indicates the formation of MnO.¹⁶ Two prominent peaks at 1342 and 1591 cm⁻¹ are assigned to the D band and G band, respectively, which is caused by the rGO and carbonization of Mn-BTC. The intensity ratio (I_D/I_G) of MnOS_{0.3}@rGO is about 0.95, which is a little lower than that of MnO (1.07). This could be caused by the good graphitization of rGO, which is beneficial for the electrical conductivity.¹⁷

To analyse the surface chemical state of different elements in MnOS_{0.3}@rGO, X-ray photoemission spectroscopy (XPS) was conducted. The peaks in the C 1s XPS spectrum (Fig. 2c) located at 284.3, 288.6, and 285.4 eV, correspond to C-C, C=O, and

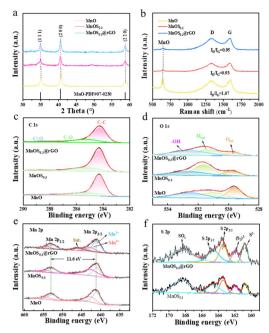


Fig. 2 (a) XRD patterns, (b) Raman spectra, (c) C 1s XPS spectra, (d) O 1s XPS spectra; (e) Mn 2p XPS spectra of MnO, MnOS_{0.3}, and MnOS_{0.3}@rGO; and (f) S 2p XPS spectra $MnOS_{0.3}$, and $MnOS_{0.3}$ @rGO

C-O bonds, respectively. The peaks in the O 1s spectrum (Fig. 2d) located at 529.8, 531.4, and 532.8 eV, correspond to Olat (Mn-O), Ovac, and -OH bonds, respectively. The relative intensity of Ovac peak to Olat peak increases in both MnOS_{0.3} and MnOS_{0.3}@rGO can be attributed to the reaction between O in MnO and carbon derived from MOF at the high temperature. In addition, the addition of rGO also affects the intensity of O 1s peaks due to the interaction between residual oxygen-containing functional groups and MnOS_{0.3}. The Mn 2p spectrum shows two main peaks at about 641.3 and 652.9 eV (Fig. 2e), corresponding to Mn 2p_{1/2} and Mn 2p_{3/2}, respectively. 18 The spin energy separation is 11.6 eV, which is typical of MnO phase.19 The S 2p XPS spectrum shows five main peaks of SO_x , $S 2p_{1/2}$, $S 2p_{3/2}$, $(S_2)^{2-}$, and S^{2-} located at 168.3, 161.9, 163.4, 164.6, and 160.9 eV (Fig. 2f), respectively, indicating the presence of S-O and S-Mn bonds. 15,20 The nitrogen sorption isotherm shows (Fig. S4a, ESI†) that the Brunauer-Emmett-Teller (BET) specific surface area of MnOS_{0.3}@rGO is 82.6 m² g⁻¹, much lower than that of MnO (235.8 $\text{m}^2\text{ g}^{-1}$) and MnOS_{0.3} (115.6 $\text{m}^2\text{ g}^{-1}$). But MnOS_{0.3}@rGO shows abundant micropores (Fig. S4b, ESI†) rather than mesopores compared to MnO and MnOS_{0.3}, which provide rapid transport channels for the storage of H⁺ and Zn²⁺, thus remarkably facilitating the diffusion kinetics of guest ions. The carbon content of MnO, MnOS_{0.3} and MnOS_{0.3}@rGO was analysed through the thermal gravimetric analysis (TGA) as shown in Fig. S5 (ESI†). The mass loss before 200 °C is attributed to the reduction of crystal water. The subsequent mass decrease after 200 °C is caused by the loss of carbon. Based on the TGA curve, the calculated carbon content of MnO, MnOS_{0.3} and MnOS_{0.3}@rGO in the material is about 24.57%, 18.99%, and 20.17%, respectively.

The electrochemical performance of MnOS_{0.3}@rGO material as a cathode for ZIBs was evaluated in a half cell by using zinc foil ChemComm Communication

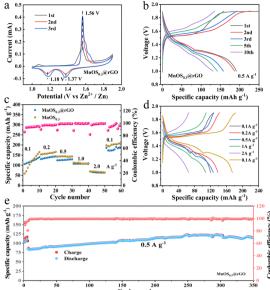


Fig. 3 (a) CV curves of MnOS_{0.3}@rGO at a scanning rate of 0.1 mV s⁻¹; (b) charging and discharging curves of different cycle number at a current density of 0.5 A g^{-1} ; (c) rate capabilities; (d) charge/discharge curves of MnOS_{0.7}@rGO at different current densities; and (e) cycling performance at 0.5 A g^{-1} for the MnOS_{0.3}@rGO electrodes.

as anode. The cyclic voltammetry (CV) curves of MnO, MnOS_{0.3}, and MnOS $_{0.3}$ @rGO at 0.1 mV s $^{-1}$ are shown in Fig. 3a and Fig. S6 (ESI†). They show the similar redox peaks due to the same reaction mechanism. But the positions of redox peaks show a little difference. MnOS_{0.3}@rGO shows two cathodic peaks at 1.37 and 1.18 V, corresponding to H⁺ insertion and Zn²⁺ insertion, respectively. The cathodic reduction peak of MnOS_{0.3} shifts slightly to the high potential (i.e., 1.21 V). In addition, MnOS_{0.3} and MnOS_{0.3}@rGO show similar curve areas, much larger than the area of MnO, indicating the improved capacity. Fig. 3b shows the capacity of MnOS_{0,3}@rGO after different cycles. Two plateaus become remarkable during the discharge/charge process, which corresponds to intercalation/deintercalation of H⁺ and Zn²⁺, respectively.²¹ Fig. 3c shows the rate performance of MnOS_{0.3}(a) rGO at different current densities. The reversible capacity is about 165.3, 144, 129.7, 109.2, and 64.6 mA h g^{-1} at 0.1, 0.2, 0.5, 1.0, and 2.0 A g⁻¹, respectively, much higher than that of MnO (40.7, 36.9, 45.2, 45, and 40.6 mA h g⁻¹). Fig. 3d shows the charge-discharge curves of MnOS_{0.3}@rGO at 0.1, 0.2, 0.5, 1.0, and 2.0 A g^{-1} . At the current density higher than 0.2 A g⁻¹, the capacity approaches to be stable, indicating good reaction kinetics. In addition, when the current returns to 0.1 A g⁻¹, the capacity increases compared to the initial value, which is caused by the activation required by the electrode material itself. The enhanced electrochemical performance of MnOS_{0.3}(arGO can be attributed to the excellent conductivity of rGO and graphitic layer, which enables higher electrochemical activity and faster electron/ion diffusion in the cathode.

Fig. 3e shows the cycling performance of MnOS_{0.3}@rGO at 0.5 A g^{-1} after five-cycle activation at 0.1 A g^{-1} . It can be seen that MnOS_{0,3}@rGO initially exhibits the capacity of about 85.8 mA h g^{-1} . With the increase of cycling number, the

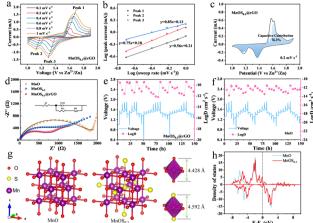


Fig. 4 (a) CV curves measured at different scan rates from 0.2 to 0.8 mV s⁻¹; (b) b value according to the relationship of log(i) and log(v) at different peaks; (c) pseudocapacitive contributions (shaded area) at a scan rate of 0.2 mV s^{-1} ; (d) EIS of the MnO, MnOS $_{0.3}$, and MnOS $_{0.3}$ @rGO; (e) and (f) charge/discharge profiles of MnOS $_{0.3}$ @rGO electrode in GITT test and the Zn $^{2+}$ diffusivity coefficient; (g) structure model and (h) projected DOS of MnO, and MnOS_{0.3}.

capacity gradually increases up to 100.6 mA h g^{-1} , much higher than that of MnOS_{0.3} (Fig. S7, ESI†). The initial increase of specific capacity could be attributed to an electrochemical activation process. In this process, incomplete deintercalated zinc ions act as "pillars" between layers to improve the structural stability and contribute to the enhanced capacity.²² After activation, the specific capacity of about 115.1 mA h g⁻¹ remains relatively stable over 350 cycles. In addition, the Coulombic efficiency of MnOS_{0,3}@rGO almost keeps 100% at 0.5 A g^{-1} , demonstrating good reversibility. The more stable cycle performance and higher capacity of MnOS_{0.3}@rGO, could be attributed to the synergistic effect of S doping and rGO.

In order to further understand the advantages of S doping and rGO wrap, the electrochemical reaction kinetics was analyzed based on CV curves at different scanning rates (0.1-1 mV s⁻¹) in Fig. 4a. The CV curves illustrate similar shapes and peaks at different scanning rates. The CV curve can be divided into diffusion-controlled and capacitive processes. And the measured peak current (i) and scanning rate (v) follow eqn (1) and (2):²³

$$i = av^b \tag{1}$$

$$\log(i) = b\log(v) + \log(a) \tag{2}$$

where the b value close to 1 indicates that the capacity of the material is controlled by the capacitive process, while a value close to 0.5 indicates the diffusion-controlled process. As shown in Fig. 4b, the b value of MnOS_{0.3}@rGO indicates that the capacity of MnOS_{0.3}@rGO is controlled by diffusion and surface capacitance processes.

$$i(\nu) = k_1 \nu + k_2^{\frac{1}{2}} \tag{3}$$

The ratio of capacitance to diffusion-controlled capacity can be quantified using eqn (3), where $i(\nu)$, $k_1\nu$, and $k_2^{\frac{1}{2}}$ correspond Communication ChemComm

to the measured current, the current contributed by the capacitance, and the current contributed by diffusion-controlled process, respectively.24 As shown in Fig. 4c and Fig. S8 and S9 (ESI†), the capacitance contribution of MnOS_{0.3}@rGO electrode at the scanning rate of 0.2, 0.4, 0.6 and 0.8 mV s⁻¹ is 79.3%, 79.5%, 79.6% and 79.2%, which is higher than the corresponding value of MnO. Due to S doping, the diffusion efficiency is improved, which is conducive to the transport of Zn²⁺ ions and electrons during the insertion/extraction process. Fig. 4d shows the electrochemical impedance spectroscopy (EIS) results of MnO, MnOS_{0.3}, and MnOS_{0.3}@rGO. Nyquist plot of each sample shows a typical semicircle, corresponding to the charge-transfer resistance (R_{ct}) in the high-frequency region. Compared to MnO and MnOS_{0.3}, MnOS_{0.3}@rGO has the smallest radius, with an $R_{\rm ct}$ of about 728.4 Ω , much lower than that of MnO (1559 Ω) and MnOS_{0.3} (917 Ω).

Galvanostatic intermittent titration technique (GITT) was also employed to measure the diffusion coefficient of Zn²⁺ $(D_{\rm Zn}^{2+})$ according to eqn (4):²⁵

$$D_{\rm Zn}^{2+} = \frac{4}{\pi\tau} \left(\frac{n_{\rm M} V_{\rm M}}{s}\right)^2 \left(\frac{\Delta E_{\rm s}}{\Delta E_{\tau}}\right)^2 \tag{4}$$

where $n_{\rm M}$ and $V_{\rm M}$ are the molar mass and molar volume of the samples, respectively, S stands for the active surface area of the electrode, t is the relaxation time, and ΔE_s and ΔE_τ represent the potential change between steps and during the current pulse, respectively. Under different charging and discharging states (Fig. 4e and f), the $D_{\rm Zn}^{2+}$ (10^{-12} – 10^{-9} cm² s⁻¹) of MnOS_{0.3}@rGO is relatively larger than that of $\rm MnOS_{0.3}\,(10^{-14}\text{--}10^{-12}\,cm^2\,s^{-1})$ and MnO $(10^{-13}-10^{-12} \text{ cm}^2 \text{ s}^{-1})$, which means that S doping and rGO wrap accelerate the diffusion kinetics.

To gain insights into the underlying mechanism, density functional theory (DFT) calculations were conducted by constructing MnO and S-doped MnO models (Fig. 4g). After the construction optimization, it is found the lattice constant is expanded from 4.428 to 4.592 Å, which is consistent with the low-angle shift of XRD peaks. The expanded lattice with large pathway for the Zn²⁺ diffusion endows MnOS_{0.3} with good rate performance. The projected density of states (DOS) of electrons in Fig. 4h increases around Fermi level after S doping, which suggests that the substitution of O atom with S atom improves the electrical conductivity of MnO. Coupling with the external rGO wrap, MnOS_{0.3}@rGO demonstrates good cycling stability and rate capability.

In conclusion, MnOS_{0.3}@rGO has been successfully synthesized by doping S into MnO@rGO at high temperature. S doping into MnO expands the lattice of MnO, providing larger pathways for ion transport, while the increased DOS around Fermi level improves the electrical conductivity of MnOS_{0.3}, boosting the electron transport. The synergistical improvement of ion/electron transport effectively lowers the Zn²⁺ diffusion barrier, enabling faster Zn²⁺ insertion/ extraction kinetics. Coupling the external rGO wrap, MnOS_{0.3}@rGO demonstrates superior Zn2+ storage capability and good rate performance in ZIBs. This work opens a new avenue for the development of next-generation aqueous ZIBs.

Z. C. and L. S. carried out the synthesis and characterization. Y. L., S. Y., Z. W. and T. H. performed partial characterization. U. L. and R. M. supervised the project. All authors contributed to writing the manuscript.

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Data availability

The data that supports the findings of this study are available in the manuscript and ESI† of this article.

Conflicts of interest

There are no conflicts to declare.

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