Binder-free stainless steel@Mn$_3$O$_4$ nanoflower composite: a high-activity aqueous zinc-ion battery cathode with high-capacity and long-cycle-life†

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Rechargeable aqueous zinc-ion batteries (ZIBs) are highly desirable for large-scale energy storage to meet the increasing demand for safe and sustainable energy storage devices. Herein, we report a binder-free stainless steel welded mesh@flower-like Mn$_3$O$_4$ (SSWM@Mn$_3$O$_4$) composite with high zinc storage capability for aqueous ZIBs. Chemical conversion reaction mechanism is proposed for this material. The hierarchical nanoflower structure composed of ultrathin nanosheets facilitates electrolytic infiltration and diffusion of Zn$^{2+}$. Benefiting from the binder-free conductive substrate, SSWM@Mn$_3$O$_4$ exhibits lower electrode reaction resistance and smaller slope of Warburg diffusion element, which contributes to the excellent electrochemical performances, including high specific capacity of 296 mA h g$^{-1}$ at 100 mA g$^{-1}$ and long-term cyclic stability up to 500 cycles at 500 mA g$^{-1}$, thus demonstrating a promising cathode for aqueous ZIBs.

1. Introduction

Lithium ion batteries (LIBs) have been a great success in the global battery market due to their high energy density. However, the cost, limited terrestrial lithium reserves, and safety concerns make it hard to scale up LIBs, thus leading to the urgent exploration of alternate materials for novel batteries. Recently, rechargeable aqueous zinc-ion batteries (ZIBs) in a neutral or mildly acidic electrolyte have held particular promise because of safety, low-cost and eco-friendliness.

Aqueous ZIBs have attracted great attention because they can deliver higher storage capacity with divalent charge transport and employ ecofriendly aqueous electrolytes with ionic conductivity two orders of magnitude higher than that in organic electrolytes. In addition, ZIBs can be assembled in air, demonstrating facile fabrication.

Many materials such as MnO$_2$,$^7$–$^8$ Zn$_{0.25}$V$_2$O$_5$·nH$_2$O,$^9$ LiV$_5$O$_{11}$,$^{10,11}$ Na$_3$V$_2$(PO$_4$)$_3$,$^{12,13}$ V$_2$S$_3$,$^{14}$ MnS,$^{15}$ and Prussian blue,$^{16}$ have been explored as cathodes for aqueous ZIBs. Among these cathode materials, manganese-based oxides are considered the most suitable as cathodes for aqueous ZIBs due to their natural abundance, low-cost, low toxicity and multiple valence states of Mn.$^8,^{21}$–$^{25}$ Chen et al.$^7$ reported a high-performance reversible β-manganese dioxide cathode, which exhibited high reversible capacity of 225 mA h g$^{-1}$ and long-term cyclability with 94% capacity retention over 2000 cycles. Manganese sesquioxide (Mn$_3$O$_4$) also exhibited excellent zinc-ion storage performance.$^{22}$ Despite significant advances in electrochemical performance, these materials suffer from poor electrical and ionic conductivities, which limit their practical application. Therefore, it is urgent to explore new materials or construct composites that facilitate the storage/release of divalent Zn$^{2+}$ ions.

Most previous reports focused on Mn-based cathodes for ZIBs with a single Mn valence. Inspired by the knowledge that the Mn vacancy in ZnMn$_2$O$_4$ spinel with multiple Mn valences contributed to the diffusivity and migration of Zn$^{2+}$ ions,$^{26}$ exploring mixed-valent Mn-based cathodes for ZIBs would be a feasible idea. Mn$_3$O$_4$ with Mn valences of 2+ and 3+ (ref. 27) has been confirmed to have high activity in metal-air batteries (ORR) due to the facile formation of defects (vacancies, electrons and holes) and may have promising application as cathodes in aqueous ZIBs.$^{28,29}$ Moreover, combining Mn$_3$O$_4$ with three-dimensional (3D) substrates, such as titanium foam, carbon fiber, and stainless steel welded mesh, is also an
effective way to improve electrochemical performance of manganese-based oxides.\(^{21}\) For instance, Wang et al. reported a composite of MnO\(_2\) coated on carbon fiber paper, which delivered excellent cycling performance with a low capacity decay rate of 0.007% per cycle for 10 000 cycles at a high rate of 6.5C.\(^{21}\) The 3D substrates not only provide stable support for materials, but also possess highly efficient electrical conductivity for electron transfer.\(^{32} - ^{34}\) However, to the best of our knowledge, Mn\(_3\)O\(_4\)/3D substrate composite as a binder-free cathode has not yet been reported as an electrode for aqueous ZIBs, but has the potential to greatly improve their performance.

Herein, we report the facile synthesis of SSWM@Mn\(_3\)O\(_4\) composite and evaluate it as a new cathode for aqueous ZIBs. The SSWM@Mn\(_3\)O\(_4\) demonstrates a chemical conversion reaction mechanism with high zinc storage capability. Compared to Mn\(_3\)O\(_4\) powder, SSWM@Mn\(_3\)O\(_4\) delivered higher specific capacity of 296 mA h g\(^{-1}\) at 100 mA g\(^{-1}\) and better long-term cycling performance without capacity fading after 500 cycles at 500 mA g\(^{-1}\). These results demonstrate a high-activity aqueous ZIBs cathode of SSWM@Mn\(_3\)O\(_4\).

2. Experimental section

2.1. Synthesis of SSWM@Mn\(_3\)O\(_4\)

SSWM@Mn\(_3\)O\(_4\) was synthesized via a one-step hydrothermal method. In a typical synthesis, 1 mmol KMnO\(_4\) was dissolved in 40 mL deionized water to form a dark violet solution. Then, the solution was transferred to a 50 mL Teflon-lined stainless steel autoclave with the addition of a piece of stainless steel mesh (2 × 3 cm\(^2\)) into the solution. The hydrothermal reaction was heated at 160 °C for 24 h. After cooling, the stainless steel mesh was removed and washed with deionized water several times and dried at 60 °C. For comparison, Mn\(_3\)O\(_4\) powders were also prepared by a similar method without stainless steel mesh.

2.2. Materials characterization

XRD patterns were obtained using a Rigaku D/Max-2500 diffractometer (Cu K\(_\alpha\), \(\lambda = 0.15405\) nm). X-ray photoelectron spectroscopy (XPS) spectra were recorded on an ESCALAB 250Xi X-ray photoelectron spectrometer (Thermo Fisher). Morphological features were observed with a field-emission scanning electron microscope (FEI Quanta FEG250) and field-emission transmission electron microscope (JEOL JEM-2100F).

2.3. Electrochemical test

Electrochemical coin cells were assembled with SSWM@Mn\(_3\)O\(_4\) as the cathode, metallic zinc foils as the anode and glass fiber membrane as the separator. An aqueous solution containing 2 M ZnSO\(_4\) and 0.1 M MnSO\(_4\) was used as the electrolyte. Moreover, for comparison, a cell with stainless steel mesh as the anode was assembled. The electrochemical tests were carried out between 1.0 and 1.8 V vs. Zn\(^{2+}\)/Zn by cyclic voltammetry, electrochemical impedance spectroscopy, and charge-discharge tests.

3. Results and discussion

SSWM@Mn\(_3\)O\(_4\) was synthesized via a one-step hydrothermal method, as shown in Fig. 1a. Mn\(_3\)O\(_4\) nanoflowers were coated on SSWM by decomposition and deposition of KMnO\(_4\) (1 mmol) in 40 mL deionized water at 160 °C; compactness of the as-obtained nanoflowers can be controlled by adjusting the hydrothermal time (Fig. S1†). Reaction time of 24 hours led to the formation of a compact and uniform Mn\(_3\)O\(_4\) nanoflowers layer and each nanoflower is composed of ultrathin nanosheets (Fig. 1b). Without adding SSWM, Mn\(_3\)O\(_4\) powders also demonstrate nanoflower morphology (Fig. S2†). Elemental mapping images clearly show uniform distribution of Mn and O elements (Fig. 1c). The X-ray diffraction (XRD) pattern of the composite (Fig. 2a) indicates that the diffraction peaks, except for the peaks of stainless steel, are similar to those of Mn\(_3\)O\(_4\) powders.

![Fig. 1](image-url) (a) Synthesis schematic, (b) SEM image, and (c) elemental mapping images of Mn and O elements of SSWM@Mn\(_3\)O\(_4\).
and can be well indexed to the tetragonal phase of Mn$_3$O$_4$ [space group $I4_1/amd$ (141), ICSD card 00-24-0734]. Elemental mapping analysis and EDS results of the nanoflower from the composite (Fig. S3†) show that the atomic ratio of Mn : O is $\sim$3 : 4, which confirms the stoichiometric value of Mn : O in Mn$_3$O$_4$. Inset of Fig. 2a shows the crystal structure of Mn$_3$O$_4$, in which Mn(II) occupies the tetrahedral gap (blue polyhedron) and Mn(III) occupies the octahedral gap (green polyhedron). X-ray photoelectron spectroscopy (XPS) analysis was carried out to investigate the Mn valence, revealing peak positions of Mn 2p$^{3/2}$ and Mn 2p$^{1/2}$ at 642.2 and 654.0 eV, respectively (Fig. 2b). The fitting peaks of Mn 2p$^{3/2}$ confirmed the mixed valences, with

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Fig. 2  (a) XRD patterns of Mn$_3$O$_4$ powders and SSWM@Mn$_3$O$_4$; inset: crystal structure of Mn$_3$O$_4$, (b) Mn 2p XPS spectrum, (c) TEM image and (d) HRTEM image and inset: corresponding FFT pattern of SSWM@Mn$_3$O$_4$.

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Fig. 3  (a) Schematic of aqueous Zn//SSWM@Mn$_3$O$_4$ cell, (b) CV curves at 0.1 mV s$^{-1}$ and (c) cycle performance at 100 mA g$^{-1}$ and inset: discharge/charge profiles of SSWM@Mn$_3$O$_4$. Performance comparison of SSWM@Mn$_3$O$_4$ and Mn$_3$O$_4$: (d) capacity at different current densities and (e) cycle performance at 500 mA g$^{-1}$.
peaks at 640.9 and 642.2 eV corresponding to Mn(II) and Mn(III), respectively. The peak at 643.5 eV ascribed to Mn(IV) may be derived from surface oxidation of Mn$_3$O$_4$. For Mn 2p$_{1/2}$, three fitting peaks were observed at 653.1, 654.0 and 654.9 eV, corresponding to Mn(II), Mn(III) and Mn(IV), respectively. The flower structure of Mn$_3$O$_4$ was further confirmed by transmission electron microscopy (TEM) image (Fig. 2c); this hierarchical framework facilitates permeation of electrolyte and diffusion of Zn$^{2+}$. As indicated in Fig. 1d, high-resolution TEM (HRTEM) shows clear lattice fringes, indicating an ultrathin nanosheet and high crystallinity of Mn$_3$O$_4$. The d-spacing of 0.61 nm and 0.33 nm correspond to
(101) and (211) crystal planes of Mn$_3$O$_4$, respectively, which were also confirmed by the corresponding FFT pattern (inset of Fig. 1d).

Electrochemical coin cells were assembled with SSWM@Mn$_3$O$_4$ as the cathode, metallic zinc foils as the anode and glass fiber membrane as the separator in an aqueous solution containing 2 M ZnSO$_4$ and 0.1 M MnSO$_4$, as shown in Fig. 3a. The electrochemical tests were carried out between 1.0 and 1.8 V vs. Zn$^{2+}$/Zn. Fig. 3b shows the cyclic voltammetry (CV) curves at a scan rate of 0.1 mV s$^{-1}$, revealing one reduction peak at 1.24 V for the 1$^{st}$ cathodic scan, which may represent the reduction of Mn(III) to Mn(II). One oxidation peak at 1.62 V with a weak shoulder peak at 1.65 V in the 1$^{st}$ anodic scan corresponds to the oxidation of Mn(II) to Mn(III). During the 2$^{nd}$ cathodic scan, two reduction peaks at 1.23 V and 1.36 V correspond to the successive reduction of Mn(III) to Mn(II), which is similar to the electrochemical behaviors of other manganese oxides. The Zn/SSWM@Mn$_3$O$_4$ cell delivered a high specific capacity of 296 mA h g$^{-1}$ with capacity retention of 98% after 50 cycles at 100 mA g$^{-1}$ (Fig. 3c), which was superior to those obtained using Mn$_3$O$_4$ as the cathode (Fig. S4,† showing a capacity retention of 48% after 30 cycles). Inset in Fig. 3c shows a nontrivial overpotential of ~196 mV (100 mA g$^{-1}$) for SSWM@Mn$_3$O$_4$ in the initial cycle. The different discharge curves for the initial two cycles may be related to the change in surface energy caused by the morphology evolution.† The bare SSWM electrode delivers negligible capacity compared to that of the SSWM@Mn$_3$O$_4$ electrode (Fig. S5†), suggesting that Mn$_3$O$_4$ nanoflowers contribute to nearly the entire capacity. SSWM@Mn$_3$O$_4$ electrode also showed higher rate capacities than Mn$_3$O$_4$ electrode [Fig. 3d]. Specifically, the SSWM@Mn$_3$O$_4$ electrode also exhibited good long-cycle-life stability at 500 mA g$^{-1}$ without capacity fading even after 500 cycles (Fig. 3e).

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$$i = av^b$$

where $i$ is current, $v$ is scan rate, and $a$ and $b$ are adjustable parameters. Fig. 4a shows CV curves at different scanning rates. The $b$ value is determined by the slope of log($i$) vs. log($v$) plot and provides insight into the charge storage mechanism: $b$ value of 0.5 indicates a diffusion-controlled process, whereas 1.0 represents a surface capacitive-controlled process. By plotting log($i$) versus log($v$) (Fig. 4b), the $b$ values of peaks 1 and 2 are found to be 0.55748 and 0.56584, respectively. This result implies that the corresponding redox reactions in SSWM@Mn$_3$O$_4$ electrode are mainly diffusion-controlled processes. The diffusion coefficient was determined by the galvanostatic intermittent titration technique (GITT) measurements (Fig. S6†); the SSWM@Mn$_3$O$_4$ electrode showed a high diffusion coefficient of $10^{-12}$ to $10^{-7}$ cm$^2$ s$^{-1}$. The EIS spectra (Fig. 4c) indicate that the SSWM@Mn$_3$O$_4$ electrode possesses lower electrode reaction resistance and smaller slope of Warburg diffusion element than the bare Mn$_3$O$_4$ electrode, suggesting that the 3D substrate effectively enhances the kinetics of electron transfer in the electrode.

![Fig. 6](image-url) SEM images of (a and b) pristine Zn anode and (c and d) Zn anode after recharging to 1.8 V.

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electrodes. In addition, the hierarchical nanoflower structure composed of ultrathin nanosheets facilitates electrolytic infiltration and diffusion of Zn$^{2+}$. The \textit{ex situ} XRD, \textit{ex situ} SEM and \textit{ex situ} XPS at full discharge/charge states were conducted to reveal the structure and morphology evolution of the SSWM@Mn$_3$O$_4$ electrode. In our case, the MnO phase [PDF# 78-0424] and ZnSO$_4$[Zn(OH)$_2$)$_3$·5H$_2$O phase [PDF# 39-0688] appear at the 1$^{\text{st}}$ full discharge state (Fig. 5a). It is very likely to be a chemical conversion reaction mechanism. On the one hand, Mn(ni) in Mn$_3$O$_4$ electrode was reduced to Mn(ni) and exists in the form of MnO after discharge. On the other hand, ZnSO$_4$ and H$_2$O in the aqueous electrolyte react with the sequent OH$^-$ ions to form large flake-like ZnSO$_4$[Zn(OH)$_2$)$_3$·5H$_2$O, which is clearly observed in the \textit{ex situ} SEM image of the 1$^{\text{st}}$ D 1.0 V electrode (Fig. 5b). The nanoflower structure was also well maintained after the first discharge process. Elemental mapping images of 1$^{\text{st}}$ D 1.0 V electrode show uniform distribution of Mn, O, and Zn elements (Fig. 5c). At 1$^{\text{st}}$ full charge state, the diffraction peaks of ZnSO$_4$[Zn(OH)$_2$)$_3$·5H$_2$O phase disappeared and the Mn$_3$O$_4$ phase emerged again, suggesting good reversibility of the electrode, which was also confirmed by a SEM image with the absence of most of the flake-like morphology (Fig. 5d). It should be noted that partial Mn$_3$O$_4$ nanoflowers aggregated after the initial cycle, which was also observed in the MnO$_2$ electrode reported by Liu \textit{et al.} The morphology evolution could release strain and reduce surface energy of the electrode, which would facilitate the structural stability of the electrodes and help improve the cycling performance. The survey XPS spectrum of the first discharged electrode shows clear Zn 2p and Zn LM2 peaks (Fig. 5e), indicating the existence of Zn element in the electrode, which is further confirmed by the high-resolution Mn 3s XPS spectra (Fig. 5f). At the discharged state, a new Zn 3p peak appears at 92.09 eV, which is consistent with the previous report on Mn$_3$O$_4$ nanoflowers. The surface of Zn anode is neat and smooth before cycling. After the 1$^{\text{st}}$ cycle, a dense and dendrite-free surface of Zn electrode can be observed (Fig. 6), which was proved to be caused by the highly reversible plating/stripping of Zn metal and would be important for long-term cycling stability. The above observation in this study greatly contributes to understanding the charge storage mechanism of SSWM@Mn$_3$O$_4$ as cathode for aqueous ZIBs. The mechanisms should be explored detail in future studies. As discussed above, the excellent electrochemical performance for SSWM@Mn$_3$O$_4$ should be ascribed to the following reasons: first, the hierarchical structure of Mn$_3$O$_4$ reduces the ion diffusion path and facilitates electrolytic infiltration; second, SSWM provides a stable support for materials, which contributes to structural stability and long-term cycling performance; third, the SSWM@Mn$_3$O$_4$ composite possess higher electrical conductivity than bare Mn$_3$O$_4$.

4. Conclusion

In summary, SSWM@Mn$_3$O$_4$ was successfully synthesized via a one-step hydrothermal method. This composite was employed for the first time as a cathode for aqueous ZIBs in this study and demonstrated a chemical conversion reaction mechanism. Compared to Mn$_3$O$_4$ powder, the binder-free SSWM@Mn$_3$O$_4$ electrode exhibits lower electrode reaction resistance and smaller slope of Warburg diffusion element, contributing to excellent electrochemical performance. In addition, the hierarchical nanoflower structure composed of ultrathin nanosheets facilitates electrolytic infiltration and diffusion of Zn$^{2+}$.

As a result, SSWM@Mn$_3$O$_4$ composite demonstrates high zinc storage capability, high specific capacity of 296 mA h g$^{-1}$ at 100 mA g$^{-1}$ and long-term cyclic stability up to 500 cycles at 500 mA g$^{-1}$. These results suggest that SSWM@Mn$_3$O$_4$ is a promising cathode material for aqueous ZIBs.

Conflicts of interest

There are no conflicts to declare.

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Notes and references