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Inverse Opal Manganese Dioxide Constructed by Few-Layered Ultrathin Nanosheets as High-Performance Cathodes for Aqueous Zinc-Ion Batteries

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ABSTRACT

Considering the high safety, low-cost and high capacity, aqueous zinc ion batteries have been a potential candidate for energy storage ensuring smooth electricity supply. Herein, we have synthesized inverse opal manganese dioxide constructed by few-layered ultrathin nanosheets by a solution template method at mild temperature. The ultrathin nanosheets with the thickness as small as 1 nm are well separated without obvious aggregation. Used as cathode material for aqueous zinc ion batteries, the few-layered ultrathin nanosheets combined with the inverse opal structure guarantee excellent performance. A high specific discharge capacity of 262.9 mAh g⁻¹ is retained for the 100th cycle at a current density of 300 mA g⁻¹ with a high capacity retention of 95.6%. A high specific discharge capacity of 121 mAh g⁻¹ at a high current density of 2000 mA g⁻¹ is achieved even after 5000 long-term cycles. The ex-situ X-ray diffraction patterns, selected-area electron diffraction patterns and high-resolution transmission electron microscopy results demonstrate that the discharge/charge processes involve the reversible formation of zinc sulfate hydroxide hydrate on the cathode while in-plane crystal structure of the layered birnessite MnO₂ could be maintained. This unique structured MnO₂ is a promising candidate as cathode material for high capacity, high rate capability and long-term aqueous zinc-ion batteries.

KEYWORDS

Inverse opal, ultrathin, few-layered nanosheets, MnO₂, zinc ion batteries

1 Introduction

Considering the pollution and limited reserves of fossil fuels, sustainable sources like wind and solar energy have drawn much attention nowadays [1-4]. Regarding the intermittency nature of green energy sources, rechargeable batteries are one of the most effective media for energy storage guaranteeing smooth electricity supply [5-10]. Although lithium-ion batteries (LIBs) have been acting well in general for about three decades, they still suffer from safety and high-cost issues [5,11-13]. Recently, emerging rechargeable Li⁺ and Na⁺ batteries using aqueous-based electrolytes have been a research hotspot due to the advantages of aqueous electrolytes including low cost, high safety and better ionic conductivity [14-19]. However, the low capacity of aqueous Li⁺ and Na⁺ batteries (ALIBs and ASIBs) is an obstacle for large-scale application. Compared to the monovalent ALIBs and ASIBs, multivalent cations can transfer more electrons, resulting in higher capacities [20]. To date, a series of aqueous multivalent-ion batteries including Mg²⁺, Al³⁺, Ca²⁺, Ni²⁺ and Zn²⁺ have been investigated, among which aqueous Zn²⁺ batteries (AZIBs) in mild electrolyte are more promising benefiting from high abundance, low cost, low redox potential and high theoretical capacity of Zn metal [20-23]. Up to now, several groups of cathodes for AZIBs have been investigated and led to positive progress.

Vanadium-based cathodes such as V₂O₅·nH₂O, Zn_{0.25}V₂O₅·nH₂O, Na₂V₆O₁₆·1.63H₂O, V₁₀O₂₄·12H₂O and Ca_{0.25}V₂O₅·nH₂O, show high discharge capacities and decent cycle stability [24-28]. However, the discharge voltage plateau is quite low (< 1 V vs. Zn²⁺/Zn) which will hinder the energy density. On the contrary, zinc hexacyanoferrate and copper hexacyanoferrate cathodes show high voltage up to 1.73 V vs. Zn²⁺/Zn, whereas the capacities are very low and they may suffer from oxygen evolution problem [29,30]. Compared with the above cathodes, manganese-based cathodes including ZnMn₂O₄, Mn₃O₄ and MnO₂ show high discharge voltages around 1.4 V vs. Zn²⁺/Zn and decent capacities, especially MnO₂ [31-35].

For low-cost and high-abundant MnO₂, different polymorphs including α-, β- and γ-MnO₂ as cathodes for AZIBs have been investigated and the high capacity is reported to be contributed from Zn²⁺ and H⁺ co-insertion [33,34,36]. However, different MnO₂ polymorphs suffer from phase transformation to layered phase with interlayered crystal water [36-38]. Although the interlayered water could expand the interspace and reduce the electrostatic interactions between Zn²⁺ and the oxide framework thus promoting cation carrier diffusion, the large volume change during the phase transformation is too severe to maintain the crystal structure resulting in vital capacity fading [24,39]. Directly using layered MnO₂ as cathode materials for AZIBs can increase

the discharge capacity and cycling stability to some extent [40]. However, the capacity is still much lower than the theoretical one, and the high rate performance is not satisfying. Further effort has been made by expanding the interlayer space of the layered MnO_2 by polyaniline-intercalation, resulting in excellent performance, which is similar to some vanadium-based cathodes with expanded interlayer space [24,28,39]. Here, instead of expanding the interlayer space of layered MnO_2 , we propose to use mono-layered or few-layered MnO_2 directly as the cathode material for AZIBs, hence the space between monolayers or few-layered nanosheets should be much larger and more surface sites can be provided as compared with the interlayer space of thick layered MnO_2 , facilitating cation carrier diffusion. Unfortunately, mono-layered or few-layered MnO_2 is easy to stack or aggregate forming thicker nanosheets and causing loss of surface sites. To synthesize few-layered MnO_2 without stacking or aggregation as cathode material for AZIBs is promising while challenging.

Herein, we have synthesized inverse opal manganese dioxide constructed by few-layered ultrathin nanosheets (IO- MnO_2) by a solution template method at mild temperature. The templates can effectively separate the nanosheets in case of aggregation, forming few-layered birnessite $\text{MnO}_2 \cdot 0.44\text{H}_2\text{O}$. The thickness of the ultrathin nanosheets is as small as 1 nm. As a cathode material for AZIB, a high discharge capacity of 275.1 mAh g^{-1} is acquired at a current density of 300 mA g^{-1} . After 100 cycles at the current density of 300 mA g^{-1} , a high discharge capacity of 262.9 mAh g^{-1} is still retained, leading to a high capacity retention of 95.6%. In addition, the ultrathin nanosheets combined with the inverse opal structure ensure excellent high rate performance. A high specific discharge capacity of 121 mAh g^{-1} at a high current density of 2000 mA g^{-1} is achieved even after 5000 long-term cycles. Furthermore, ex-situ X-ray diffraction (XRD) patterns, selected-area electron diffraction (SAED) patterns and high resolution transmission electron microscopy (HRTEM) results of fully discharged IO- MnO_2 show that the layered crystal structure could be maintained. This cathode material by a solution method at mild temperature is promising for low-cost and long-term AZIBs.

2 Experimental

2.1 Chemicals

Potassium permanganate (KMnO_4 , $\geq 99.0\%$), sodium dodecyl sulfate ($(\text{CH}_3(\text{CH}_2)_{11}\text{OSO}_3\text{Na}$, $\geq 99.0\%$, SDS), 1-methyl-2-pyrrolidinone ($\text{C}_5\text{H}_9\text{NO}$, $\geq 99.0\%$, NMP), tetrahydrofuran ($\text{C}_4\text{H}_8\text{O}$, $\geq 99.0\%$, THF), polyvinylpyrrolidone (average M.W.=40000, PVP) and sulfuric acid (H_2SO_4 , 95.0–98.0%) were purchased from Sigma-Aldrich. Carbon black (Super P@Conductive, $>99\%$), polystyrene latex microsphere (2.5 wt% dispersion in H_2O , 200 nm, PS) and polyvinylidene fluoride (PVDF) were purchased from Alfa Aesar.

2.2 Synthesis

0.5 g of PVP was dissolved into 20 mL of de-ionized (DI) water (18.2 M Ω) to form a uniform solution, after which 1 mL of PS solution was added. The solution was kept overnight under stirring condition. The PVP-treated PS was collected by centrifuge, followed by DI water washing and another round of centrifuge. The collected PS was dispersed into 315 mL of DI water. 0.9 g of SDS was dissolved into the PS suspension under stirring, after which 1.6 mL of pre-made H_2SO_4 (0.1 M) was added to form a

weak acidic solution. The solution was heated to 70°C under stirring and 3.2 mL of KMnO_4 (0.05 M) was added. The solution was maintained at 70°C for 30 min with stirring. The sample was collected by centrifuge and washed 5 times by DI water and 3 times by ethanol. The PS templates were removed by stirring the collected powder in tetrahydrofuran overnight followed by washing by ethanol. The final IO- MnO_2 product was dried at ambient condition for 12 h followed by vacuum-drying at 60°C for 6 h.

Similar to the synthesis of IO- MnO_2 , the aggregated MnO_2 nanosheets were synthesized without PS templates.

2.3 Material characterization

The XRD patterns were recorded by a Bruker D8 Advance X-ray diffractometer equipped with a Cu-K α radiation source ($\lambda=1.5406 \text{ \AA}$) operated at 40 kV and 40 mA in a 2-theta range of $10\text{--}80^\circ$. The thermal gravimetric analysis (TGA) was conducted by a Q500 thermal gravimetric analyser (TA Instruments) to record the weight loss in air from room temperature to 500°C at a ramp of $10^\circ\text{C min}^{-1}$. The elemental analysis was performed using PerkinElmer Optima 8300 inductively coupled plasma optical emission spectrometry (ICP-OES) spectrometer. The X-ray photoelectron spectroscopy (XPS) spectra were collected using a Kratos AXIS Supra equipped with an automated dual anode (Al/Ag K α) X-ray monochromatic source. The C 1s peak at 284.6 eV was used to calibrate the binding energies. A field emission scanning electron microscope (FESEM, JEOL JSM 7600F) was used to investigate the surface morphology of the samples with an accelerating voltage of 5 kV. A JEOL JEM 2010UHR was used to take transmission electron microscopy (TEM) images, SAED patterns at an accelerating voltage of 200 kV. A JEOL JEM 2100F transmission electron microscope equipped with high-angle annular dark-field (HAADF) detector and energy dispersive X-ray spectrometry (EDS) was used to take high resolution TEM, scanning TEM (STEM) images and to analyze the STEM-EDS elemental distribution at an accelerating voltage of 200 kV. An Asylum Research Cypher S atomic force microscope (AFM) was used to take the AFM micrograph and to measure the thickness of the nanosheets in alternating current mode.

2.4 Electrochemical characterization

The electrochemical measurements of the samples were conducted with CR2032 coin cells using Solartron electrochemical station. The full cells were assembled with MnO_2 as cathode material, zinc metal foil as anode, aqueous 2 M ZnSO_4 + 0.1 M MnSO_4 as electrolyte, and glass fiber paper as separator. The amount of the electrolyte for each coin cell was fixed to 50 μL . The mass of the Zn foil anode used for each cell was excess as compared to that of the cathode in order to eliminate the influence of the anode part. The slurry was made by mixing MnO_2 , carbon black and PVDF binder together in a weight ratio of 7:2:1, with NMP as solvent. The working cathode electrode was prepared by pasting the slurry onto a stainless steel mesh substrate followed by vacuum-drying at 100°C overnight. The mass loading of the active material is around 1.5 mg cm^{-2} . The cyclic voltammetry (CV) measurements were conducted in a potential window of 1.0 V – 1.8 V vs. Zn^{2+}/Zn at a scan rate of 0.1 mV s^{-1} . The CV measurements at various scan rates from 0.2 mV s^{-1} to 2.4 mV s^{-1} were conducted to investigate the charge storage behavior. The electrochemical impedance

spectroscopy (EIS) was conducted at the open circuit potential with an amplitude of 5 mV in a frequency ranging from 1 MHz to 0.1 Hz. The galvanostatic discharge/charge performances were recorded with a Neware BTS 4000 battery test system. The materials for characterization after cycling performance were collected by opening the coin cells, rinsing the working electrodes with abundant DI water, penetrating the rinsed working electrodes in DI water overnight followed by another round of rinsing by DI water.

3 Results and discussion

The IO-MnO₂ was synthesized by a solution method using polystyrene (PS) as templates. With the assistance of sodium dodecyl sulfate (SDS) in weak acidic aqueous solution, single-layered or few-layered MnO₂ nanosheets can be produced from KMnO₄ [41]. However, without templates, the nanosheets tend to stack together as characterized by SEM (Fig. S1(a) in the Electronic Supplementary Material (ESM)). The nanosheets can be indexed to layered birnessite MnO₂ (JCPDS No. 042-1317) as revealed by the XRD pattern (Fig. S1(b) in the ESM) [42]. The stacked nanosheets lead to a strong peak at 12.31°, which corresponds to an interlayer space of 0.719 nm between the stacked interlayers [43]. By introducing the PS templates, heterogeneous nucleation and growth of MnO₂ occurs on the PS template surface [44]. Simultaneously, the templates could separate the generated nanosheets effectively, preventing stacking or aggregation. Inverse opal structured MnO₂ composed of ultrathin few-layered nanosheets can be obtained after removal of PS templates by dissolution in tetrahydrofuran. The XRD pattern of the IO-MnO₂ in Fig. S2 in the ESM shows that it is layered birnessite MnO₂ phase with weak peaks. Especially, the weak peak at around 12.3° indicates the separation of the nanosheets without obvious re-stacking. The interlayered crystal water amount is determined by TGA in air. The weight loss of the TGA curve (Fig. S3 in the ESM) could be divided into three parts. The weight loss from room temperature to around 100 °C is attributed to the loss of physically adsorbed water on the sample surface. The next 8.41% weight loss between 100 and 300 °C is ascribed to the crystal water loss. The rest weight loss at above 300 °C results from the transformation from MnO₂ to Mn₂O₃ [45]. The K, Mn, O and adventitious C elements are detected by XPS, as shown by the survey spectrum in Fig. 1(a). The K element originates from the K⁺ in the solution from the KMnO₄ reagents, which intercalates into the interlayers of the birnessite. The elemental ratio of K to Mn is 0.058:1, as determined by the ICP-OES results shown in Table S1 in the ESM, which is negligible in the molecular formula. The molecular formula is determined to be MnO₂·0.44H₂O. The high resolution XPS spectra of K, Mn and O are presented in Figs. 1(b)–1(d). The peaks located at 653.98 eV and 642.24 eV correspond to the Mn 2p_{1/2} and Mn 2p_{3/2} for the Mn spectrum in Fig. 1(b) [46]. The Mn 2p_{3/2} peak could be fitted to multi-peaks. The peak at 642.05 eV is ascribed to Mn⁴⁺ binding with oxygen, accompanied by two shoulder peaks around 643 eV and a satellite peak around 645 eV [47,48]. A small peak located at 640.95 eV indicates the existence of Mn³⁺ [49]. Besides, a small peak at 640.09 eV may be from Mn²⁺, which may be ascribed to MnO [47]. The high resolution spectrum of Mn 3s doublet shows a spin-energy separation of 4.78 eV (Fig. S4 in the ESM), which indicates the Mn charge state is approximately 4.0. The spectrum of O 1s (Fig. 1(c)) could be fitted into three peaks at 529.9, 531.0 and 532.2 eV, which are ascribed

to Mn–O, Mn–OH and H–O–H bonds, respectively [49]. The peaks at 292.4 and 295.2 eV for K spectrum presented in Fig. 1(d) are assigned to the K 2p_{1/2} and K 2p_{3/2}, respectively [50].

The inverse opal structure of the IO-MnO₂ is illustrated in the SEM image as shown in Fig. 2(a). The diameters of the hollow parts are about 200 nm, consistent with that of the PS templates (Fig. S5 in the ESM). The magnified SEM micrograph (Fig. 2(b)) clearly shows that it is composed of thin nanosheets with the thickness of less than 10 nm (including the thickness of platinum coatings when preparing the sample for SEM). The inverse opal structure is further confirmed by TEM micrograph as presented in Fig. 2(c), from which the hollow parts encompassed by thin nanosheets could be observed. The TEM micrograph in Fig. 2(d) shows that the thin nanosheets are composed of few atomic layers. The zoomed-in TEM micrograph (Fig. 2(e)) displays the thickness of the nanosheets is as thin as only 1–1.5 nm, which is also confirmed by the HAADF-STEM observation (Figs. S6(a)–S6(d) in the ESM). The statistical thickness of the ultrathin nanosheets shows that the main thickness is 1–4 nm (Fig. S7 in the ESM). More precise thickness is measured by AFM. The thickness of the nanosheets from the IO-MnO₂ sample is approximately 1 nm (Figs. S8(a) and S8(b) in the ESM). The elemental composition and distribution of the IO-MnO₂ are collected by STEM-EDS. The STEM-EDS mapping images (Figs. S9(a)–S9(d) in the ESM) of the K, Mn and O show the uniformly distributed elements. The IO-MnO₂ is polycrystalline as demonstrated by the ring pattern in the SAED (Fig. S10 in the ESM) [51]. The HRTEM micrograph in Fig. 2(f) shows the lattice fringes of 0.247 nm corresponding to the lattice spacing of birnessite MnO₂ (110) planes [52].

Figure 1 XPS spectra of the synthesized IO-MnO₂ powder. (a) Survey spectrum. High-resolution spectra of (b) Mn 2p, (c) O 1s and (d) K 2p.

The performance of the IO-MnO₂ as cathode material for AZIBs have been investigated by using CR2032 type coin cells, where excess zinc metal foil is used as anode. A 2 M ZnSO₄ + 0.1 M MnSO₄ aqueous solution is used as electrolyte. The electrochemical behavior is investigated by CV in a potential window ranging from 1.0 V to 1.8 V vs. Zn²⁺/Zn at a scan rate of 0.1 mV s⁻¹. During the first scan, a reduction peak at around 1.21 V and an oxidation peak at 1.56 V occur, as shown in Fig. 3(a), corresponding to the Zn²⁺ insertion and extraction processes [33]. For the subsequent scan, a new pair of redox peaks occur at around 1.36 and 1.62 V, which are assigned to H⁺ insertion and extraction

according to previous reports [33,34]. The redox peaks are reversible in the third scan. The CV results at various scan rates are used to determine the charge storage behavior for the IO-MnO₂ based AZIB. The redox peaks shift slightly when the scan rate is increased as shown by the CV results (Fig. S11(a) in the ESM), which is caused by kinetic limitations related to the cation carrier diffusion [53]. The current at different scan rates follows a power

law relationship with the scan rate v , based on $i = av^b$, where a and b are adjustable parameters [54,55]. The value of b can be determined from the slope of the linear $\log(i) - \log(v)$ plot. Here for the IO-MnO₂ based AZIB, the resulted b values of all the four redox peaks are close to 0.5 as shown in Fig. S11(b) in the ESM, indicating the charge storage is assigned to faradaic intercalation contributions.

Figure 2 (a)-(b) SEM and (c)-(f) TEM micrographs of the IO-MnO₂ sample.

Figure 3 Electrochemical performance of the IO-MnO₂ based AZIB. (a) CV at a scan rate of 0.1 mV s⁻¹ in the potential window of 1.0 – 1.8 V vs. Zn²⁺/Zn, (b) discharge-charge profile at a current density of 300 mA g⁻¹, (c) cycling performance at different current densities from 300 to 3000 mA g⁻¹ and (d) corresponding discharge-charge profile at various current densities.

The galvanostatic discharge/charge profiles for the primary three cycles are record at a current density of 300 mA g⁻¹ as shown in Fig. 3(b). For the first discharge process, only one voltage plateau at about 1.3 V is observed, leading to a specific capacity of 148.4 mAh g⁻¹. The first charge capacity is 225.2 mAh g⁻¹. For the second discharge, a new voltage plateau around 1.4 V presents, which corresponds to the proton insertion [33]. The second specific discharge capacity is up to 275.1 mAh g⁻¹, and the capacity is highly reversible for the following cycles. The discharge/charge results are well consistent with the CV results. The AZIB

performance at various discharge/charge current densities from 300 mA g⁻¹ to 3000 mA g⁻¹ are presented in Fig. 3(c) with the corresponding discharge/charge profiles presented in Fig. 3(d). The specific discharge capacities are summarized in Table S2. High discharge capacities of 101 and 75 mAh g⁻¹ are achieved even at high current rates of 2000 and 3000 mA g⁻¹, respectively. At high current densities, the discharge capacity is mainly contributed from the first voltage plateau related to the proton insertion as shown by the discharge/charge profiles (Fig. 3(d)), which is mainly due to that the proton insertion process is much faster than that of Zn²⁺

[39].

In order to determine the crystal structure evolution during the discharge/charge processes, ex-situ XRD is conducted for the first fully discharged and fully charged IO-MnO₂ electrodes at a current density of 300 mA g⁻¹, as presented in Fig. S12 in the ESM. The initial electrode before discharge process shows no obvious peaks besides strong peaks related to the stainless steel mesh substrate, which makes the ex-situ XRD analysis difficult. However, there are some new peaks for the first fully discharged electrode, which locate at similar positions to that of the bare IO-MnO₂ powder (Fig. S2 in the ESM). Whereas all the peaks could be well indexed to zinc sulfate hydroxide hydrate (Zn₄SO₄(OH)₆·H₂O, JCPDS No. 39-690). When the battery is fully charged back to 1.8 V, no obvious peak is observed besides that from stainless steel mesh. The discharge/charge profiles of the aggregated MnO₂ nanosheet

electrodes at a current density of 50 mA g⁻¹ are presented in Fig. S13(a) in the ESM. The discharge/charge states of the electrodes for ex-situ XRD characterization are labeled accordingly. As shown in Fig. S13(b) in the ESM, for the first fully discharged electrode, a series of peaks are observed besides the ones assigned to MnO₂ and stainless steel mesh. The peaks could be well indexed to Zn₄SO₄(OH)₆·5H₂O (JCPDS No. 39-688) and Zn₄SO₄(OH)₆·4H₂O (JCPDS No. 44-673). The peaks of the zinc sulfate hydroxide hydrates diminish when the AZIBs are gradually charged to 1.8 V. These peaks re-appear when the sample is discharged to 1.0 V (Fig. S13(c) in the ESM), demonstrating the reversible formation of the zinc sulfate hydroxide hydrates. Interestingly, there is no obvious change for the MnO₂ peaks, which means there may be no crystal structure change for the layered birnessite MnO₂ during the discharge/charge processes.

Figure 4 (a) TEM micrograph of the fully discharged IO-MnO₂. (b) SAED patterns of the fully discharged IO-MnO₂ (right side) in comparison with that of the initial IO-MnO₂ (left side). HRTEM micrographs of the (c) fully discharged IO-MnO₂ and (d) the initial IO-MnO₂.

To determine the crystal structure, the fully discharged IO-MnO₂ cathode material is characterized by TEM. The inverse opal structure can be well maintained as shown in Fig. 4(a). The STEM-EDS mapping images (Figs. S14(a)-S14(f) in the ESM) and the corresponding EDS spectrum (Fig. S15 in the ESM) confirm that Zn²⁺ is inserted into the IO-MnO₂ cathode material after the discharge process. However, the SAED pattern taken from the discharged IO-MnO₂ shows no obvious change as compared with the initial electrode (Fig. 4(b)), indicating the layered MnO₂ crystal structure is sustained. The only difference is that the rings of the SAED pattern become a little diffusive, which should result from the inserted Zn²⁺ between or on the surface of the ultrathin

few-layered nanosheets. Additionally, atomic resolution HRTEM micrograph of the discharged IO-MnO₂ shows hexagonal arranged atoms as presented in Fig. 4(c). The spacing of the in-plane adjacent atom lines is 0.26 nm, which is unchanged as compared with that of the initial IO-MnO₂ as shown in Fig. 4(d) [56]. This result and the spots of the corresponding fast Fourier transform (FFT) images (Insets of Figs. 4(c) and 4(d)) indicate that the in-plane crystal structure shows no obvious change. Besides the IO-MnO₂, some large plates separate from the IO-MnO₂ are observed (Figs. S16(a) and S16(b) in the ESM). The STEM-EDS mapping images (Figs. S16(c)-S16(f) in the ESM) and the corresponding EDS spectrum (Fig. S17 in the ESM) show the

existence of Zn, O and S elements without any Mn element. Combined with the XRD patterns of the fully discharged IO-MnO₂ electrode in Fig. S12 in the ESM, the plates should be pure zinc sulfate hydroxide hydrate. The rings of the SAED pattern for the plate (Inset of Fig. S16(a) in the ESM) corresponds well with zinc sulfate hydroxide hydrate, Zn₄SO₄(OH)₆·H₂O, confirming the crystal information.

The cycling stability of the IO-MnO₂ is carried out at a current density of 300 mA g⁻¹ for 100 cycles, as shown in Fig. 5(a). After 100 cycles, a high discharge capacity of 262.9 mAh g⁻¹ can be maintained. This shows excellent cycling stability and high Coulombic efficiency close to 100%. This result is much better compared to that of the aggregated MnO₂ nanosheets synthesized without using PS templates (73.6 mAh g⁻¹ after 50 cycles as shown in Fig. S18 in the ESM), and it is also competitive compared with other excellent cathode materials (Table S3 in the ESM) [57–59]. The inverse opal structure after the cycling performance have been characterized by SEM. Figs. S19(a) and S19(b) in the ESM show that the structure can be well retained for both charged and discharged states. On the other hand, the excess Zn foil anode (Fig. S20(a) in the ESM) shows obvious plates on the surface after the cycling performance at the discharged state, as shown in Figs. S20(b) and S20(c) in the ESM. The Zn foil anode in the charged state could recover relatively smooth indicating good reversibility (Fig. S20(d) in the ESM). Even though, it should be noted that the coulombic efficiency of Zn anode is usually poor for Zn-ion batteries, which is due to irreversible side reactions such as metal corrosion and hydrogen evolution [60]. According to previous reports, the MnSO₄ additive in the ZnSO₄ electrolyte leads to decent efficiency [33–39]. However, more improvements on the Zn anode topic are still required to achieve better performance of AZIBs. The EIS was used to investigate the impedance change before and after the cycling performance. Fig. 5(b) shows the Nyquist plots and the corresponding equivalent circuits, where the typical semicircles in the high frequency region are related to the charge transfer resistance R_{ct} at the electrode/electrolyte interface, and the sloping lines in the low frequency region are assigned to the finite Warburg element Z_w for diffusion of ions in the

electrodes. The smaller semicircle after the cycling performance means smaller charge transfer impedance as compared to the initial state [61]. This should be ascribed to the activation process and better contact with the electrolyte upon cycling. In addition, the cycling performance at a current density of 500 mA g⁻¹ is also evaluated as presented in Fig. S21 in the ESM. A high discharge capacity of 232.0 mAh g⁻¹ is achieved during the 200th cycle with a high coulombic efficiency of 98.53%. The long-term cycling stability is investigated by the cycling performance at a high current density of 2000 mA g⁻¹ (Fig. 5(c)). At this high current density, it takes about 30 cycles to activate the high discharge capacity. A high specific discharge capacity of 121 mAh g⁻¹ can be maintained even after 5000 cycles. The cycling performance at a higher current density of 3000 mA g⁻¹ is further conducted for 2000 cycles. Prior to the measurement, an activation process at 300 mA g⁻¹ for 3 cycles is conducted. There is no capacity fading observed and a high discharge capacity of 75 mAh g⁻¹ is acquired after 2000 cycles (Fig. S22 in the ESM). The high rate performance is promising for high power applications. The excellent performance is ascribed to the well-separated ultrathin few-layered nanosheets ensuring good contact with the electrolyte and more active sites for fast cation insertion/extraction processes. In addition, the few-layered ultrathin birnessite IO-MnO₂ nanosheets have good structural stability, preventing the capacity fading.

It should be noted that the MnSO₄ additive in the ZnSO₄ electrolyte plays an important role for the sustainable cycling performance. It was reported that the pre-added Mn²⁺ likely provides an appropriate equilibrium between Mn²⁺ dissolution and the re-oxidation of the Mn²⁺ in the electrolyte [33,34]. In our observation, the electrodeposited MnO₂ is vital for the cycling performance. An electrodeposition method in the same electrolyte used for AZIB was even used to synthesize MnO₂ as cathode material for AZIB [34]. We have investigated the effect of the MnSO₄ additive concentration in the ZnSO₄ electrolyte on the cycling performance of AZIBs. Without using MnSO₄ additive, the cycling performance of the IO-MnO₂ is relatively poor (Fig. S23 in the ESM). With the increasing of the MnSO₄ additive concentration, the cycling stability is improved. Especially, when

Figure 5 AZIB performance of the IO-MnO₂ sample. (a) cycling performance at a current density of 300 mA g⁻¹ for 100 cycles, (b) The Nyquist plots and the corresponding equivalent circuits in the inset before and after cycling performance. The R_s is the Ohmic resistance. The R_{ct} is the charge transfer resistance at the electrode/electrolyte interface. The C_{dl} represents double layer capacitance, and the Z_w stands for the finite Warburg element for diffusion of ions in the electrode. (c) long-term cycling performance at a high current density of 2000 mA g⁻¹.

the concentration is set to be 0.1 M, stable cycling discharge capacity can be maintained. However, when the concentration is increased to 0.2 M, the specific discharge capacity increases upon cycling. The corresponding IO-MnO₂ electrodes after cycling performance have been examined by SEM (Figs. S24(a)-S24(d) in the ESM). Without MnSO₄ additive, severe dissolution of the IO-MnO₂ occurs (Fig. S24(a) in the ESM), which is responsible for the poor cycling stability. When 0.05 M MnSO₄ is added, some of the IO-MnO₂ structures could be maintained (Fig. S24(b) in the ESM). The inverse opal morphology could be well maintained when the concentration is 0.1 M, whereas some deposited aggregates are observed (Fig. S24(c) in the ESM). However, the high stability infers that the dissolution and electrodeposition should reach an equilibrium during the discharge/charge processes. Large amount of aggregated nanosheets form on the IO-MnO₂ electrode when the concentration is increased to 0.2 M (Fig. S24(d) in the ESM). The aggregated nanosheets will increase the amount of the cathode material. This should be the reason for the increased specific discharge capacity upon cycling. Consequently, the concentration of the MnSO₄ additive in the ZnSO₄ electrolyte should be carefully taken into consideration when assemble AZIBs.

4 Conclusions

In summary, inverse opal layered birnessite MnO₂ constructed by few-layered ultrathin nanosheets were prepared by a solution template method at mild conditions. The ultrathin nanosheets are effectively separated to form mono or few layers as thin as 1 nm without stacking or aggregation. This unique structured material as cathode material for AZIBs shows excellent performance. A high specific discharge capacity of 262.9 mAh g⁻¹ is maintained after 100 cycles at a current density of 300 mA g⁻¹. The long-term cycling performance at a high current density of 2000 mA g⁻¹ shows high stability with a high discharge capacity of 121 mAh g⁻¹ even after 5000 cycles. The ex-situ XRD, SAED and HRTEM results demonstrate that the discharge/charge processes involve the reversible formation of zinc sulfate hydroxide hydrate on the cathode while the in-plane crystal structure of the layered birnessite MnO₂ could be maintained. The IO-MnO₂ is a promising candidate as cathode material for high capacity, high rate capability and long-term AZIBs.

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Electronic Supplementary Material

Inverse Opal Manganese Dioxide Constructed by Few-Layered Ultrathin Nanosheets as High-Performance Cathodes for Aqueous Zinc-Ion Batteries

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Supplementary Figures and Tables

Figure S1 (a) SEM micrograph and (b) XRD pattern of the synthesized aggregated MnO_2 nanosheets.

Figure S2 XRD pattern of the synthesized IO- MnO_2 powder.

Figure S3 TGA curve of the synthesized IO-MnO₂ powder in air.

Figure S4 High resolution XPS spectrum of the Mn 3s for the IO-MnO₂ powder.

Figure S5 SEM micrograph of the PS templates.

Figure S6 (a)-(d) HAADF-STEM images of the IO-MnO₂ sample.

Figure S7 The statistical thickness of the ultrathin nanosheets in the IO-MnO₂ sample.

Figure S8 (a) AFM micrograph and (b) the corresponding height profiles of the nanosheets from the IO-MnO₂ sample.

Figure S9 STEM-EDS mapping images of the IO-MnO₂ sample. (a) HAADF-STEM image. (b) K Kα, (c) Mn Kα and (d) O Kα.

Figure S10 SAED pattern of the IO-MnO₂ sample.

Figure S11 (a) CV of the IO-MnO₂ based AZIB at various scan rates from 0.2 mV s⁻¹ to 2.4 mV s⁻¹ in a potential window of 1.0 V to 1.8 V vs. Zn²⁺/Zn. (b) Linearly fitted log(*i*) – log(*v*) plots of the current response at the four redox peaks labeled in (a).

Figure S12 Ex-situ XRD patterns of the IO-MnO₂ electrodes on stainless steel mesh.

Figure S13 Ex-situ XRD patterns of the aggregated MnO_2 electrodes on stainless steel mesh. (a) discharge/charge profile at a current density of 50 mA g^{-1} , where the samples for XRD are collected as labeled accordingly. A: initial electrode before discharge process, B: first fully discharged, C: first fully charged, D: second half discharged, E: second fully discharged, and F: second half charged. (b) XRD of the first fully discharged electrode as compared with the standard JCPDS cards. (c) XRD of electrodes at different discharge/charge states corresponding to the states labeled in (a). The star marks (*) are indexed to the stainless steel mesh.

Figure S14 STEM-EDS mapping images of the IO- MnO_2 after fully discharged to 1.0 V. (a) HAADF-STEM, (b) K K α , (c) Mn K α , (d) O K α , (e) Zn K α , and (f) overlay images.

Figure S15 STEM-EDS spectrum of the fully discharged IO-MnO₂ corresponding to the STEM-EDS mapping results in Fig. S14.

Figure S16 (a) TEM micrograph of the large plate for the discharged IO-MnO₂ electrode sample. (b)-(f) STEM-EDS mapping micrographs of the plate. (b) HAADF-STEM, (c) Zn K α , (d) S K α , (e) O K α , and (f) overlay images.

Figure S17 STEM-EDS spectrum of the sheet-like particles in the discharged IO-MnO₂ electrode sample, corresponding to the STEM-EDS mapping results in Figs. S16(c)-S16(f).

Figure S18 Cycling performance of the aggregated MnO_2 based AZIB at a current density of 300 mA g^{-1} .

Figure S19 SEM micrographs of the IO- MnO_2 electrodes after cycling performance, (a) charged and (b) discharged state. The fibers are from the glass fiber paper separator.

Figure S20 SEM micrographs of the Zn foil anode before and after 100 cycles at a current density of 300 mA g^{-1} . (a) Initial state before cycling performance. (b) and (c) Discharged state after 100 cycles. (d) Charged state after 100 cycles.

Figure S21 Cycling performance of the IO-MnO₂ based AZIB at a current density of 500 mA g⁻¹.

Figure S22 Long-term cycling performance of the IO-MnO₂ based AZIB at a high current density of 3 A g⁻¹.

Figure S23 Effect of the MnSO₄ additive concentration of the electrolyte on the cycling performance of the IO-MnO₂ based AZIBs at the current density of 300 mA g⁻¹.

Figure S24 SEM micrographs of the IO-MnO₂ electrodes after cycling performance using different concentration of MnSO₄ additive in the ZnSO₄ electrolyte. (a) 0 M, (b) 0.05 M, (c) 0.1 M, and (d) 0.2 M.

Table S1 Elemental composition of K and Mn elements in the IO-MnO₂ sample by ICP-OES.

element	Weight concentration (mg L ⁻¹)	Molar Concentration (mmol L ⁻¹)
K	7.49	0.19
Mn	181.56	3.30

Table S2 Specific discharge capacities of the IO-MnO₂ based AZIB at various current densities from 300 to 3000 mA g⁻¹.

Current Density (mA g ⁻¹)	300	500	1000	1500	2000	2500	3000
Specific Capacity (mAh g ⁻¹)	262	226	172	123	101	86	75

Table S3 Comparison of the IO-MnO₂ based AZIB performance with other reported cathode materials for AZIBs.

Material	Electrolyte	Current Density (mA g ⁻¹)	Cycle Number	Capacity (mAh g ⁻¹)	Reference
δ-MnO ₂	1 M ZnSO ₄	83	100	112	[1]
α-MnO ₂	Polyacrylamide-based hydrogel	308	60	260	[2]
ε-MnO ₂	2 M ZnSO ₄ + 0.2 M MnSO ₄	377	300	150	[3]
β-MnO ₂	3 M Zn(CF ₃ SO ₃) ₂ + 0.1 M Mn(CF ₃ SO ₃) ₂	200	150	225	[4]
γ-MnO ₂	1 M ZnSO ₄	0.5 mA cm ⁻²	40	158	[5]
Co ₃ O _{4-x}	Polyacrylamide-based hydrogel	500	75	176	[6]
Co ₃ O ₄	2 M ZnSO ₄ + 0.2 M CoSO ₄	1000	500	158	[7]
α-MnO ₂	1 M ZnSO ₄	150	100	130	[8]
α-MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	300	45	260	[9]
Todorokite MnO ₂	1 M ZnSO ₄	50	50	98	[10]
ZnMn ₂ O ₄	3 M Zn(CF ₃ SO ₃) ₂	50	50	150	[11]
α-Mn ₂ O ₃	2 M ZnSO ₄	100	30	117.2	[12]
δ-MnO ₂	2 M ZnSO ₄ + 0.1 M MnSO ₄	300	100	262.9	This work

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