Flexible high energy density zinc-ion batteries enabled by binder-free MnO$_2$/reduced graphene oxide electrode

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We demonstrate a rechargeable zinc-ion battery with high energy density and cyclability using MnO$_2$ and reduced graphene oxide (MnO$_2$/rGO) electrode. The flexible and binder free electrode, with high MnO$_2$ mass ratio (80 wt% of MnO$_2$), is fabricated using vacuum filtration without any additional additives other than rGO. Compared to batteries with conventional MnO$_2$ electrodes, the Zn–MnO$_2$/rGO battery shows a significant enhanced capacity (332.2 mAh g$^{-1}$ at 0.3 A g$^{-1}$), improved rate capability (172.3 mAh g$^{-1}$ at 6 A g$^{-1}$) and cyclability. The capacity retention remains 96% after 500 charge/discharge cycles at 6 A g$^{-1}$. The high MnO$_2$ mass ratio makes MnO$_2$/rGO electrode advantageous when the capacity is normalized to the whole electrode, particularly at high rates. The calculated gravimetric energy density of Zn–MnO$_2$/rGO battery is 33.17 Wh kg$^{-1}$, which is comparable to the existing commercial lead-acid batteries (30–40 Wh kg$^{-1}$). Furthermore, the discharge profile and capacity of our Zn–MnO$_2$/rGO battery shows no deterioration during bending test, indicating good flexibility. As a result, zinc-ion battery is believed to be a promising technology for powering next generation flexible electronics.

**INTRODUCTION**

There is an increasing demand of high safety, high energy density, and low cost energy storage device for wearable or flexible electronics. In this aspect, aqueous zinc-ion batteries (ZIBs) have received incremental attention because of their high safety, abundance of Zn source, and environmental friendliness. MnO$_2$ is a most common low cost cathode material for ZIBs, which provides high capacity, large voltage window (~2 V) and high output voltage (~1.3 V). While the exact reaction mechanism of MnO$_2$ in ZIBs remains to be explored, it is generally believed that, similar to other types of ion batteries, the Zn-insertion process into MnO$_2$ is an important step. In this regard, the phase, powder structure and conductivity of MnO$_2$ are critical for realizing high energy density ZIBs. Nonetheless, MnO$_2$ suffers from low electronic conductivity ($10^{-5}$–$10^{-6}$ S cm$^{-1}$), which leads to unsatisfactory performance, such as low capacity and low rate capability. Many attempts have been made to tackle this problem, including doping of MnO$_2$, coating conductive surface layer, and adding conductive additives, etc. Among them, adding conductive additives (with mass ratio ranging from 20 to 33%) to the MnO$_2$ cathode has been frequently employed in preparing the MnO$_2$-based cathode. Due to its ease of fabrication. Examples include depositing poly(3,4-ethylenedioxythiophene) (PEDOT) layer on the surface of MnO$_2$ and forming MnO$_2$/acid-treated carbon nanotube nanocomposites. These electrodes exhibited high reversible capacity (310 mA h g$^{-1}$) at 1.11 A g$^{-1}$ (see ref. 9), fast charging and discharging capability (143.3 mA h g$^{-1}$ at 7.43 A g$^{-1}$) (see ref. 9), and good cycling stability (100 mA h g$^{-1}$ at 5 A g$^{-1}$ up to 500 cycles). Usually, binders (such as polytetrafluoroethylene (PTFE), polyvinylidene fluoride (PVDF), or carboxymethyl cellulose with mass ratio around 10%) are required to construct a workable cell. This is done at the expense of reduced active material content. Therefore, finding efficient additives that enhance the electronic conductivity of MnO$_2$, while at the same time minimizing the content of both additives and binders, become an attractive approach for achieving high mass loading of active material in the battery.

There are several requirements for screening the optimum conducting additives for MnO$_2$. First of all, the additives should not react with electrolyte or cathode materials. Second, the adopted materials should be light weight, and also possess high surface area. Ideally, the additives should be able to wrap up the MnO$_2$ nanopowders and form a percolating conducting network. Finally, the additives should also facilitate ion transportation in the composite matrix. Taking all these into account, reduced graphene oxide (rGO), due to its light weight, excellent electrical conductivity and high specific surface area, is considered as an ideal additive candidate for the MnO$_2$ electrode. The benefits of rGO additives in battery electrodes have been previously demonstrated in lithium-ion batteries and supercapacitors. The MnO$_2$/rGO composite structure with high specific surface area and mesopores has been noted to be favorable for improving both the main pseudocapacitance of MnO$_2$ and the electric double-layer capacitance of rGO. In addition, the use of nanostructured MnO$_2$/rGO composites as a Faradic electrode can also improve the electrical conductivity of the electrode.

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Similarly to supercapacitors, the electrodes for the lithium ion batteries application required easy transportation of electrons through the highly conductive rGO channels. MnO$_2$/rGO composites with high specific surface area afford more active sites for lithium redox reactions and better access to Li ions, leading to increased capacity and improved rate capability. Moreover, the mesopores in the composite accommodates the volume expansion of MnO$_2$ during the process of charge/discharge, resulting in superior cycling stability. Here, we adopt vacuum filtration, a simple experimental method, to deposit MnO$_2$ nanosheets and rGO sheets onto the carbon cloth. The vacuum filtration method is a simple fabrication process to prepare MnO$_2$/rGO electrode. In fact, vacuum filtration is known to deposit densely packed active materials. It is capable of producing uniform deposits with an intimate interface between active materials (MnO$_2$/rGO in the present case) and current collector (carbon cloth in this case). It has the additional advantage of producing samples free of binders and other additives, which increases the packing density of the active material. In this manner, we have obtained a flexible, binder free MnO$_2$/rGO cathode with high MnO$_2$ mass ratio (80 wt% of MnO$_2$). ZIBs with MnO$_2$/rGO electrode (Fig. 1) demonstrate enhanced capacity, improved rate capability and cycling performance, when compared to a control sample with the conventional MnO$_2$ electrodes. More importantly, the high MnO$_2$ mass ratio makes MnO$_2$/rGO electrode advantageous when the capacity is normalized to the whole electrode, particularly at high rates.

RESULTS AND DISCUSSION

General characterizations of the MnO$_2$ and MnO$_2$/rGO samples The MnO$_2$ samples were synthesized by a hydrothermal method. XRD result of MnO$_2$ samples is shown in Fig. 2a. All Bragg peaks can be indexed to the crystalline phase of α-MnO$_2$ (JCPDS: 44–0141). The SEM image shown in Fig. 2b discloses the nanosheet structure of α-MnO$_2$ with lengths/width in micrometer scale and thickness in less than tens of nanometers. The MnO$_2$ nanosheets were believed to provide high surface area as well, and were intentionally grown for this study. Fig. 2c gives the typical TEM image of the α-MnO$_2$ sample, showing a crumpled surface. The α-MnO$_2$ is further revealed in the HRTEM (the inset of Fig. 2c) with an interlayer spacing between the MnO$_2$ sheets estimated to be 0.69 nm, which can be ascribed to the (110) planes of α-MnO$_2$. The α-MnO$_2$ is featuring for its (2 × 2) + (1 × 1) tunnel structure, which would facilitate Zn insertion. It is highly possible that the Zn-insertion/extraction occurs in the (2 × 2) tunnels of the α-MnO$_2$ since the geometric dimension of the tunnels (size ~4.6 Å) in α-MnO$_2$ is sufficiently wide to accommodate guest Zn$^{2+}$ (size ~0.74 Å) ion-insertion/extraction.

The MnO$_2$/rGO electrodes were prepared using a vacuum filtration method (Fig. 2d). Fig. 2e–j shows the representative structural characterization results taken from the MnO$_2$/rGO sample. The SEM image shown in Fig. 2e provides a general view of the morphology. The MnO$_2$/rGO sample presents a loose structure that comprises numerous highly wrinkled MnO$_2$ nanosheets with the size of 100–200 nm, and rGO nanosheets with slightly larger dimensions. The overall thickness of the MnO$_2$/rGO film lying over carbon cloth is ~130 µm, measured from the cross-sectional SEM image (Fig. 2f). EDX elemental mapping gives the spatial distribution of the compositional elements (Fig. 2g–j). It confirms the existence of MnO$_2$ nanosheets and the rGO sheets. The structure of rGO has been examined using Raman spectroscopy, which data displays the degree of graphitization of carbon. As shown in Fig. S1, Raman spectrum of rGO shows two typical peaks of graphene, centered at 1351 and 1598 cm$^{-1}$, corresponding to its D and G bands. The D band is attributed to defects and disordered portions of carbon (sp$^3$), whereas the G band is indicative of ordered graphitic crystallites of carbon (sp$^2$). As a comparison, additional peaks centered at 555 and 645 cm$^{-1}$ are observed in the Raman spectrum of the MnO$_2$/rGO sample. They are related to the $v_3$ (Mn–O) stretching vibrations and $v_2$ (Mn–O) symmetric stretching vibrations of MnO$_2$ groups, respectively. The BET surface area of MnO$_2$/rGO sample is 201.6 vs. 63.74 m$^2$ g$^{-1}$ for conventional MnO$_2$. The nitrogen adsorption–desorption isotherms of MnO$_2$/rGO sample (Fig. S2) appear to be type IV curves with the H3 hysteresis loops that can be linked to slit-shaped pores.

Comparison between MnO$_2$/rGO and conventional MnO$_2$ electrodes The electrochemical properties of MnO$_2$/rGO electrode are fairly sensitive to the amount of rGO. Insufficient amount of rGO additives would not be able to enhance conductivity of the mixture, whereas overloading of rGO additives would reduce the capacity of the electrode. In experiments, specific capacities of the MnO$_2$/rGO electrodes with different MnO$_2$/rGO ratios (15, 20, and 25 wt% rGO) have been investigated, and the results are presented in Fig. S3. The optimum MnO$_2$/rGO ratio has been identified to be 8:2 in experiments. The electrochemical properties of the MnO$_2$/rGO electrodes with a mass ratio of 8:2 have been compared to those of the conventional MnO$_2$ electrode (70 wt% MnO$_2$ nanosheets, 20 wt% Super P, and 10 wt% PVDF binder). To make the samples more comparable, the same mass ratio of conductive additive was introduced to the conventional MnO$_2$ electrode. Electroplated Zn on carbon cloth was used as counter electrode. More details of the electrodes preparation can be found in the Experimental section. The morphology of electroplated Zn on carbon cloth is presented in Fig. S4.

Fig. 3a shows cyclic voltammograms (CV) of the MnO$_2$/rGO and conventional MnO$_2$ electrodes at a scan rate of 0.2 mV s$^{-1}$ in voltage range of 1.0–1.9 V vs. Zn$^{2+}$/Zn. For conventional MnO$_2$ cathode, two separated reversible redox peaks (reduction peaks: 1.26 and 1.39 V, oxidation peak: 1.55 and 1.60 V) can be clearly observed, corresponding to a two-step reaction. The reaction mechanism for MnO$_2$ has been reported previously that the MnO$_2$ cathode experiences a consequent H$^+$ and Zn$^{2+}$ insertion/ extraction process during the discharging/charging. The MnO$_2$/rGO sample shows similar oxidation/reduction peaks during the anodic/cathodic scan, indicating that the rGO additive did not affect the redox reactions in the MnO$_2$ electrode. Nevertheless, the
magnitudes of their current density of peaks are different. The MnO$_2$/rGO electrodes show much higher peaks than the conventional MnO$_2$ electrodes, indicating its higher capacity than the conventional MnO$_2$ electrodes. Figure 3b and Fig. S5 compare the charging and discharging profiles of the samples at the current density of 0.3 A g$^{-1}$. Both batteries present two similar discharge plateaus, which are attributed to subsequent H$^+$ and Zn$^{2+}$ insertion process. However, the discharging capacity of the MnO$_2$/rGO electrodes at 0.3 A g$^{-1}$ is significantly higher (~332.2 mAh g$^{-1}$) than that of the conventional MnO$_2$ electrode (~259.1 mAh g$^{-1}$). This result is consistent with the CV profiles in Fig. 3a. Figure 3c shows comparison of the rate performance of the MnO$_2$/rGO and conventional MnO$_2$ electrodes. It is obvious that the MnO$_2$/rGO electrode exhibits superior rate capability when compared to the conventional MnO$_2$ electrode. For example, the MnO$_2$/rGO sample can deliver discharging capacity of ~332.2 mAh g$^{-1}$ at low rate of 0.3 A g$^{-1}$. A Little decrease in the discharging capacity is observed when the rate is increased to 0.6 A g$^{-1}$, and is kept at ~227.5 and ~172.3 mAh g$^{-1}$ at further rate increase to 3, and 6 A g$^{-1}$, respectively. As a comparison, the conventional MnO$_2$ electrodes exhibits much lower discharge capacity, that is, ~259.1 mAh g$^{-1}$ even at low discharge rate of 0.3 A g$^{-1}$, and further drops to ~82.7 mA h g$^{-1}$ at 6 A g$^{-1}$. The capacity of pure rGO electrode is also studied to check whether rGO contributes to the capacity of MnO$_2$/rGO electrode. As shown in Fig. 5d, in contrast, the pure rGO electrode exhibits extremely low capacity, indicating the negligible contribution to overall capacity of the examined MnO$_2$/rGO electrodes by employing rGO as the conductive additive.

Similar to the specific capacity, the capacity retention would improve when rGO is incorporated. It is worth to note that the binder free MnO$_2$/rGO maintains much higher capacity retention when discharged at large current density. As shown in Fig. 3c, the MnO$_2$/rGO sample shows ~51.9% capacity retention (at 6 A g$^{-1}$) of the first discharging capacity at 0.3 A g$^{-1}$, which is about twice higher than that of the conventional MnO$_2$ sample (~31.9% at 6 A g$^{-1}$).

To obtain a better understanding on the difference between the ZIB samples with different electrodes, the electrochemical impedance spectroscopy (EIS) measurements were carried out on the ZIBs after charging to ~1.9 V vs. Zn$^{2+}$/Zn. The corresponding Nyquist plots (dot) and fitting results (line) are shown in Fig. 3d. An appropriate equivalent circuit model (inset in Fig. 3d) is established to fit the Nyquist curves. The electrical parameters
(e.g., $R_s$: solution resistance; $R_{ct}$: charge-transfer resistance; $Z_w$: Warburg diffusion process) in this model can be calculated, as shown in Table S1†. The charge-transfer resistance of MnO$_2$/rGO sample is 1.2 Ω, which is lower than that of conventional MnO$_2$ sample (3.1 Ω). The large $R_s$ difference of MnO$_2$/rGO and conventional MnO$_2$ electrodes can be ascribed to the reduction of internal resistance due to the rGO additive, which is conductive and reduces the resistance contribution of the electrode. MnO$_2$ by itself is a very poor conductor, and the addition of binder (PVDF) in conventional MnO$_2$ electrode also increases the internal resistance of the electrodes. Overall, the binder-free structure of MnO$_2$/rGO electrode leads to the reduction of internal resistance.

The cycling performance of the MnO$_2$/rGO sample is also improved especially at high rates when compared to conventional MnO$_2$ samples (Fig. 3e). More than 96% of its initial capacity and high Coulombic efficiency (>99.7%) still remained even the cyclic number extended to 500 cycles at high current density of 6.0 A g$^{-1}$, indicating the excellent cycling stability of the MnO$_2$/rGO sample. As a comparison, the capacity retention of the conventional MnO$_2$ sample at 6.0 A g$^{-1}$ (after 500 cycles) is 79%. To examine the structure stability of the MnO$_2$/rGO cathode and electroplated Zn anode, the morphological changes were characterized after the 300 cycles. For the cathode, as shown in Fig. S4c, MnO$_2$/rGO structure after cycling remains nearly unchanged as compared to

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**Fig. 3** Electrochemical performance of MnO$_2$/rGO and conventional MnO$_2$ electrodes. a Cyclic voltammogram of the MnO$_2$/rGO and conventional MnO$_2$ electrodes at a scan rate of 0.2 mV s$^{-1}$ in 1.0–1.9 V vs. Zn$^{2+}$/Zn. b Comparison of the charging and discharging profiles of the samples at the current density of 0.3 A g$^{-1}$. c Specific capacities (normalized over the mass of MnO$_2$) of the samples at various current density. Inset in Fig. c: comparison of the specific capacity retention of the samples. d Nyquist plots of the samples after charging to ~1.9 V vs. Zn$^{2+}$/Zn. e Cycling stability of the samples (MnO$_2$/rGO and conventional MnO$_2$ electrodes) cycled at 6.0 A g$^{-1}$ and corresponding Coulombic efficiency of MnO$_2$/rGO electrode. f A summary graph of the specific capacity (based on the total mass of the whole electrode material, including MnO$_2$, additive and binder) of our MnO$_2$/rGO electrode and other reported MnO$_2$-based electrodes for ZIB at different current densities.
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Flexible Zn–MnO$_2$/rGO battery

For wearable applications, energy storage devices are required to be highly flexible. Herein, we tested the flexibility of the Zn–MnO$_2$/rGO battery by bending the devices around a radius of 1 cm. The batteries can be bent without deteriorating the discharge profile and capacity (Fig. 4a). The highest bending angle of Zn–MnO$_2$/rGO battery approaches 180°, as shown in Fig. 4b. The flexibility of Zn–MnO$_2$/rGO battery was tested by bending a Zn–MnO$_2$/rGO battery for 500 times with a bending angle of 180°. Ninety percent capacity was retained after 500 times bending cycles (Fig. 4b). These observations demonstrate a good mechanical stability of the electrodes. Moreover, the battery successfully powered a quantum-dot light emitting diodes display, a timer and light-emitting diodes under bending condition, demonstrating its promising potential in personalized wearable electronics (Fig. 4b and Fig. S8).

CONCLUSION

In summary, MnO$_2$/rGO electrode has been successfully fabricated by a vacuum filtration process, which results in a flexible and binder/additive free cathode for ZIBs. When compared to conventional MnO$_2$ cell, the MnO$_2$/rGO cathode shows largely enhanced capacity, excellent rate capability and cycling stability. The presence of rGO effectively enhances the charge transport and increase the specific surface area in the electrode, resulting in large capacity and outstanding rate performance. The results strengthen our hypothesis that rGO is ideally suited for good ionic transport into the electrode and electronic transport from the electrode. Furthermore, the removal of an extra component (the binder) should help reduce production cost and ease manufacture of the electrode paste. Our work demonstrates that the MnO$_2$/rGO electrodes are one of the most attractive cathodes in zinc storage applications. With the excellent device performance, the ease of fabrication, such Zn–MnO$_2$/rGO batteries are very promising for use as wearable energy storage devices.

METHODS

Preparation of MnO$_2$/rGO electrode

The MnO$_2$ nanosheets were synthesized by a hydrothermal method.\textsuperscript{23} 0.1264 g KMnO$_4$ and 0.0428 g (NH$_4$)$_2$SO$_4$ were homogeneously mixed with 40 mL distilled water. The solution was then poured into a Teflon-lined reactor and was subjected to hydrothermal condition at 140 °C for 24 h. Then, the resulting powder was filtered and washed with plenty of distilled water. Finally, the filtered powder was dried in a vacuum oven at 60 °C for

The vacuum filtration method is a simple fabrication process to prepare MnO$_2$/rGO electrode. When compared with reported filtration methods in the literature using conventional filtration membranes (e.g., filter papers), the use of carbon cloth as filtration membranes allows the one-step fabrication of the electrode, as it avoids the transfer process. Moreover, this method is capable of producing samples free of binders and other additives, which increases the packing density of the MnO$_2$. The advantage of high packing density of the active material in the MnO$_2$/rGO electrode can be further justified when the capacity is normalized to the whole electrode. As shown in Fig. 3f, when the specific capacity is normalized over the total mass of the whole electrode material (including MnO$_2$, additive and binders), the MnO$_2$/rGO electrode is comparable to the best reported results, presenting the highest specific capacity at high current density (~138 mAh g$^{-1}$ at 6 A g$^{-1}$) among the MnO$_2$-based electrodes for ZIBs reported to date.\textsuperscript{1,8,10,11,18–20} We also calculated the specific capacity based on the whole weight of MnO$_2$/rGO electrode (including carbon cloth). The specific capacity based on the whole electrode (including carbon cloth) is around 44 mAh g$^{-1}$ at 0.3 A g$^{-1}$.

The energy and power densities of our Zn–MnO$_2$/rGO battery are shown in Fig. S7. The maximum energy density is 456.2 Wh kg$^{-1}$ and peak power density is 7.9 kW kg$^{-1}$. Taking the total mass of the cell (including active materials, additive, binders and current collectors of both anode and cathode) into consideration, the gravimetric energy density of Zn–MnO$_2$/rGO battery is 33.17 Wh kg$^{-1}$, which is much higher than that of typical commercial supercapacitors (5–10 WH kg$^{-1}$) and comparable to the existing commercial lead-acid batteries (30–40 WH kg$^{-1}$).\textsuperscript{21,22}

Flexible Zn–MnO$_2$/rGO battery

Flexible Zn–MnO$_2$/rGO battery powers a timer under normal and 180 degrees of bending conditions.
2 h, following an annealing process at 300 °C for 1 h under air atmosphere. The mass of the MnO2 is ~3 mg cm−2.

The MnO2/rGO electrodes were prepared using a vacuum filtration method. Twelve milligram MnO2 nanosheets and 3 mg rGO were dispersed in 3 mL isopropl alcohol (IPA) by sonication for 2 h, and then mixed to form a uniform suspension. The suspension was filtered through carbon cloth on the top of a filter paper (with a pore size of 450 nm), via vacuum filtration. Finally, the electrode was dried in a vacuum oven at 60 °C for 2 h.

Structure and morphology characterization

The morphologies and elemental analyses were characterized by a field-emission scanning electron microscope (FESEM, Zeiss SUPRA-55). Transmission electron microscopy (TEM) measurements were also carried out with a Tecnai F20 (FEI) microscope operating at 200 kV. The crystallinity and phases of the samples were examined by X-ray diffraction (XRD, D8 Advance). Raman analysis was performed using a Raman spectrometer (Jobin-Yvon Horiba Evolution) with an Ar+ laser at 514 nm. A Brunauer–Emmett–Teller (BET) analyser (Micromeritics Tristar II 3020 v1.03 analyzer) was used to study the surface area by nitrogen gas absorption–desorption.

Electrochemical characterization

The electrochemical properties of the MnO2/rGO electrode were characterized by using electroplated Zn on carbon cloth as a counter electrode. Zn was deposited on carbon cloth by an electrodeposition method. The electrolyte used was 2 M ZnSO4 with 0.1 M MnSO4 as an additive in H2O. A conventional MnO2 electrode is composed of 70 wt% MnO2 nanosheet, 20 wt% Super P, and 10 wt% PVDF, which were coated on carbon cloth. CV was measured on an electrochemical station (CHI660, Shanghai CH Instrument Co., Ltd.) with potential range from 1.0 to 1.9 V vs. Zn+/Zn. The assembled cells were cycled at a constant current mode using a CT2001A multichannel battery test system (Wuhan Kingnuo Electronic Co., Ltd.). The EIS of the batteries was measured on an electrochemical station (CH660, Shanghai CH Instrument Co., Ltd.) under an alternating current (AC) signal with 5 mV amplitude. The frequency ranges from 100 kHz to 0.1 Hz.

Data availability

All data generated or analysed during this study are included in this published article and its supplementary information files.

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AUTHOR CONTRIBUTIONS

Y.H. and J.L. contributed equally to this work. Y.H., H.Z. and Z.Z. conceived the idea. Y. H., J.L., and Q.H. designed the work. S.S and S.C. carried out the fabrication of the batteries. P.H.T. provided Raman data. J.L. provided the rest of the experimental data. F.Z., D.O., and Z.S. participate in the data analysis and interpretation. Y.H. drafted the article. H.Z., P.H., and Z.Z. revised the article.

ADDITIONAL INFORMATION

Supplementary information accompanies the paper on the npj Flexible Electronics website (https://doi.org/10.1038/s41528-018-0034-0).

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