Preparation of Polyaniline-coated Composite Aerogel of MnO$_2$ and Reduced Graphene Oxide for High-performance Zinc-ion Battery

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Abstract Aqueous zinc-ion batteries, especially Zn-MnO$_2$ battery, have attracted intensive attention owing to their unique features of high capacity, environmental friendliness, and safety. However, the problem of Mn dissolution hinders the development of zinc-ion batteries with long-term usage and high-rate performance. In this work, a novel preparation method for the polyaniline (PANI)-coated composite aerogel of MnO$_2$ and rGO (MnO$_2$/rGO/PANI) electrode is reported. The obtained composite possesses high electrical conductivity, and also effectively suppresses the dissolution of Mn. The fabricated MnO$_2$/rGO/PANI//Zn battery exhibits a high capacity of 241.1 mAh·g$^{-1}$ at 0.1 A·g$^{-1}$, and an excellent capacity retention of 82.7% after 600 charge/discharge cycles. In addition, the rapid diffusion coefficient of the MnO$_2$/rGO/PANI electrode was further examined by galvanostatic intermittent titration technique. This work provides new insights into the development of high-performance Zn-MnO$_2$ battery with a better understanding of its diffusion kinetics.

Keywords MnO$_2$; Polyaniline; Composite aerogels; Aqueous zinc-ion batteries; Galvanostatic intermittent titration techniques

INTRODUCTION

With the rapid development of industry and increasing demand for energy from the human society, the construction of high-performance energy storage systems with low cost, long cycling life, and environmental friendliness is of great importance nowadays.[1–3] Recently, aqueous zinc-ion batteries (ZIBs) have been attracting increasing attention.[6–10] ZIBs utilize Zn as the anode, which possess the advantages of low redox potential (−0.76 V versus standard hydrogen electrode), high theoretical capacity (820 mAh·g$^{-1}$), and good compatibility with water.[11–14] Such unique features make ZIBs promising for large-scale and safe energy storage applications.

Manganese dioxide is one of the most widely used cathode materials for ZIBs due to its high theoretical capacity (308 mAh·g$^{-1}$), earth abundance, and environmental friendliness.[15–20] However, MnO$_2$-based electrode materials suffer from low electrical conductivity, poor rate performance, and inferior cycling sustainability.[21–23] Most importantly, the gradual dissolution of MnO$_2$ in the electrolyte during the insertion of Zn$^{2+}$ decreases the capacity and cycling performance.[24–27] Up to now, several approaches have been attempted to deal with the aforementioned problems and to improve the performance of Zn-MnO$_2$ batteries. For instance, Mai and coworkers combined MnO$_2$ nanowires with reduced graphene oxide to fabricate the electrode with improved electrical conductivity.[28] Liu and coworkers used MnSO$_4$ additive to pre-balance Mn between the MnO$_2$ electrodes and the electrolyte so as to improve the cycling performance of resultant Zn-MnO$_2$ batteries.[29] Chen and coworkers reported a Zn-insertion cathode material of ZnMn$_2$O$_4$/carbon composite in aqueous Zn(CF$_3$SO$_2$)$_2$ electrolyte that could suppress Mn dissolution effectively.[30] Although these reports have demonstrated improved performance of Zn-MnO$_2$ batteries, the following challenges are still existing. First, the MnSO$_4$ additive may lead to side reactions, such as deposition of Mn compounds in the charge/discharge process, which makes the composition of active material complicate. Second, large-scale and practical applications of ZIBs may be hindered by the extra cost from additives and the use of expensive electrolyte (e.g. Zn(CF$_3$SO$_2$)$_2$). Third, for micro energy storage devices, additives increase the weight of the whole device and decrease energy density.

Herein, a novel strategy to achieve high-performance ZIBs...
by the construction of polyaniline (PANI)-coated composite aerogel of MnO$_2$ and rGO (MnO$_2$/rGO/PANI) was reported. On the one hand, the dense skeleton composed of interconnecting graphene nanosheets can effectively improve the conductivity and diffusion rate.[18] On the other hand, MnO$_2$ tightly coated by rGO and PANI can inhibit the dissolution of Mn to improve rate performance and cycling stability of the electrode materials for ZIBs.[12] Benefiting from the compositional and structural features, the performance of the aqueous MnO$_2$/rGO/PANI/Zn battery was obviously enhanced to 241.1 mAh·g$^{-1}$ at 0.1 A·g$^{-1}$, which is much higher than those of the control samples (178.8 mAh·g$^{-1}$ for MnO$_2$/rGO and 177.4 mAh·g$^{-1}$ for MnO$_2$ electrodes). More importantly, the aqueous MnO$_2$/rGO/PANI/Zn battery demonstrated a highly reversible performance even after 600 cycles with 82.7% capacity retention. Furthermore, galvanostatic intermittent titration technique (GITT) measurements were conducted to illustrate the reaction kinetics of these fabricated electrodes.

**EXPERIMENTAL**

**Preparation of MnO$_2$/rGO Composite Hydrogel**

Firstly, MnO$_2$ particles with smaller size of ~2 μm were obtained by ball-milling the commercial MnO$_2$ powders (Shanghai Meixing, 99.9%) at 400 r·min$^{-1}$ for 24 h. Secondly, the obtained MnO$_2$ particles were added into an aqueous dispersion of graphene oxide (GO, 20 mL with a concentration of 2 mg·mL$^{-1}$, Hangzhou Gaoxi Technology Co., Ltd.), and mixed by vigorously stirring for 30 min to form a uniform solution. After that, the homogeneous mixture was transferred to a Teflon-lined stainless autoclave (50 mL) and heated at 150 °C for 6 h to obtain a cylindrical MnO$_2$/GO hydrogel. The hydrogel prepared was then immersed into 20 mL deionized water (DI water) and added with 1.0 g of ascorbic acid (AA) as the reductant. The mixture was transferred to a Teflon-lined stainless autoclave and heated at 120 °C for 3 h. After cooling down to room temperature naturally, the resultant precipitates (MnO$_2$/rGO composite hydrogel) were collected by centrifugation and washed with distilled water and ethanol for 5 times.

**Preparation of MnO$_2$/rGO/PANI Composite Aerogel**

The MnO$_2$/rGO/PANI composite hydrogel was prepared by an *in situ* polymerization process. Briefly, the as-prepared MnO$_2$/rGO composite hydrogel was placed into a reaction vessel kept in an ice bath, which contains a 20 mL aqueous solution of 0.16 mol·L$^{-1}$ aniline monomer and 1 mol·L$^{-1}$ HCl. Then, 20 mL (1 mol·L$^{-1}$) HCl of aqueous solution containing ammonium persulfate (APS) and aniline monomers with a molar ratio of 1:1 was added into the above reaction vessel. The polymerization was conducted at 0 °C for 1 h. The resultant product was washed for 3–5 times with DI water and dried in a vacuum oven at 60 °C for 24 h to give a MnO$_2$/rGO/PANI composite aerogel (MnO$_2$/rGO/PANI). For comparison, the MnO$_2$/rGO composite aerogel (MnO$_2$/rGO) was prepared by the aforementioned same method.

**Material Characterization**

The morphology and composition of samples were characterized by field-emission SEM (FE-SEM, HITACHI S-4700) and TEM (JEM-100CX II). Brunauer-Emmett-Teller (BET) adsorption isotherm was conducted by ASAP 2020M+e (Micromeritics, USA). XRD (D/max-Ultima IV, X’Pert PRO) with a Cu Kα irradiation (λ = 0.154 nm). Raman spectra were collected by a LabRAM HR800 spectrometer (Horiba JobinYvon, laser wavelength of 325 nm). Fourier transform infrared spectroscopy (FTIR) was conducted by a Nicolet6700 (Thermo fisher, USA) instrument. X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra-DLD system (Shimadzu Co., Ltd. Hongkong).

**Electrochemical Measurements**

Electrochemical characterizations were performed with 2032 coin-type cells, which were assembled in ambient condition. The cathode was fabricated by mixing active materials, acetylene black, and poly(vinylidene difluoride) (PVDF) with a weight ratio of 8:1:1 in N-methyl pyrrolidone (NMP). The slurry was evenly coated on a carbon paper and vacuum dried at 65 °C for 18 h.[20] The loading content of active materials on carbon paper was about 1.0–1.2 mg·cm$^{-2}$. Commercial zinc foil, 2 mol·L$^{-1}$ ZnSO$_4$ aqueous solution, and glass fiber membrane were used as the anode, electrolyte, and separator, respectively. Cyclic voltammetry (CV) measurements were performed in the voltage range of 0.8–1.8 V versus Zn/Zn$^{2+}$ and electrochemical impedance spectroscopy (EIS) was measured within 0.1–10 kHz by using an electrochemical workstation (Chenhua, CHI 760E). Galvanostatic charge/discharge (GCD) measurements and galvanostatic intermittent titration technique (GITT) were carried out on a battery test system (Land, CT2001A). Before GITT measurement, the assembled cells were charged and discharged at 20 mA·g$^{-1}$ for two cycles for stabilization. The current pulse was lasted for 20 min at 20 mA·g$^{-1}$, and then the cell was relaxed for 2 h to make the cell voltage reach equilibrium. These procedures were repeatedly applied to the cell in the entire charge/discharge process. All tests were performed at room temperature.

**RESULTS AND DISCUSSION**

The preparation process of MnO$_2$/rGO/PANI is schematically shown in Fig. 1. First, commercial MnO$_2$ powders (Fig. S1a in the electronic supplementary information, ESI) were subjected to ball milling to obtain MnO$_2$ particles with smaller size of ~2 μm (Fig. S1b in ESI). The obtained MnO$_2$ particles were mixed with GO suspension, subjected to hydrothermal treatment to form a hydrogel cylinder, and then reduced by ascorbic acid. Next, the obtained hydrogel was coated with PANI by *in situ* polymerization to form a MnO$_2$/rGO/PANI composite hydrogel (Fig. S2a in ESI), which then underwent a mild vacuum-drying process to afford the MnO$_2$/rGO/PANI composite aerogel (Fig. S2b in ESI). For comparison, MnO$_2$/rGO aerogel was also prepared from MnO$_2$/rGO composite hydrogel by the same vacuum-drying process.

The morphologies of the obtained MnO$_2$/rGO and MnO$_2$/rGO/PANI aerogels as well as the rGO aerogel (Fig. S3 in ESI) were investigated by scanning electron microscopy (SEM). As shown in Fig. 2(a), the MnO$_2$/rGO aerogel had a compact and dense structure, in which MnO$_2$ spheres were tightly wrapped with rGO nanosheets and uniformly distributed in the graphene networks. After coated with a uniform and thin layer of PANI, the original morphology and microstructure of MnO$_2$/rGO were well preserved, and the ob-

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**Fig. 1**  Schematic illustration of the preparation process of MnO$_2$/rGO/PANI.

**Fig. 2**  (a) SEM images and (b) corresponding EDX elemental mappings of MnO$_2$/rGO; (c) SEM images and (d) corresponding EDX elemental mappings of MnO$_2$/rGO/PANI. Insets in (a) and (c) are high-magnification SEM images.

Treated MnO$_2$/rGO/PANI aerogel remained highly compact with a density of 1.42 g·cm$^{-3}$ (Fig. 2c). Besides, the elemental mappings in Figs. 2(b) and 2(d) clearly indicate the uniform distribution of Mn, O, and C elements in MnO$_2$/rGO sample and Mn, O, C, and N elements in MnO$_2$/rGO/PANI sample. The presence of N element indicates the MnO$_2$/rGO composite monoliths were successfully coated by PANI. TEM image in Fig. S4(a) (in ESI) further indicates that the MnO$_2$ particle was surrounded by rGO and PANI. High-resolution transmission electron microscopy (HRTEM) image of a MnO$_2$ particle displays the lattice distances of 0.30 and 0.32 nm (Fig. S4b in ESI), corresponding to the (220) and (211) planes of MnO$_2$, respectively. Furthermore, Fig. S5 (in ESI) indicates that the resultant MnO$_2$/rGO/PANI aerogel possessed a specific surface area of ~142.1 m$^2$·g$^{-1}$.

X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy (XPS) were performed to further investigate the
crystal structure and composition of the obtained MnO₂/rGO/PANI aerogel. The typical XRD patterns of MnO₂, MnO₂/rGO, and MnO₂/rGO/PANI are shown in Fig. 3(a). The XRD patterns of as-synthesized MnO₂/rGO/PANI aerogel display the characteristic peaks of (101), (111), (211), (220), and (301) planes, which are consistent with that of pristine MnO₂ (JCPDS No. 24-0735). An additional broad peak at ~26° in XRD patterns of both MnO₂/rGO and MnO₂/rGO/PANI samples can be ascribed to rGO. Raman spectra of MnO₂/rGO, MnO₂/rGO, and MnO₂/rGO/PANI samples are illustrated in Fig. 3(b). There are two prominent bands located at ~1351 and 1602 cm⁻¹, corresponding to D band and G band of GO or rGO, respectively. The I_D/I_G ratios were 1.04 for MnO₂/rGO/PANI, 1.04 for MnO₂/rGO, and 0.85 for MnO₂/rGO, suggesting the successful reduction of graphene oxide. The PANI networks coated on MnO₂/rGO composite hydrogel were further characterized by FTIR (Fig. 3c). The bands at 1476 and 1557 cm⁻¹ are assigned to benzenoid rings and C—C stretching vibrations of quinoid, respectively. The bands of aromatic C—H, C=N, and C=N stretching vibration located at 798, 1118, and 1300 cm⁻¹, respectively, can be also clearly identified. The survey spectrum of XPS reveals the presence of Mn, O, C, and N elements in the MnO₂/rGO/PANI sample (Fig. S6a in ESI). In the high-resolution spectrum of Mn 2p shown in Fig. 3(d), the two peaks at the binding energies of 642.4 and 654.1 eV can be assigned to Mn 2p₃/2 and Mn 2p₁/2, respectively. The high-resolution C 1s spectrum in Fig. 3(d) reveals four obvious peaks corresponding to binding energies of 284.6 eV (C—C), 285.5 eV (C—N), 286.2 eV (C—O), and 288.6 eV (O—C=O). The N 1s spectrum (Fig. 3e) exhibits three peaks centered at 399.5 eV (~NH—), 400.4 eV (polaron), and 401.1 eV (~NH+=), which is to improve the conductivity of PANI largely. In addition, the O 1s spectrum further demonstrates the formation of MnO₂ (Fig. 3d in ESI).

The electrochemical performances of the obtained samples were examined with coin cells using 2 mol·L⁻¹ ZnSO₄ as the aqueous electrolyte and a Zn foil as the anode. Fig. 4(a) shows the first three cycles of cyclic voltammetry (CV) curves of the MnO₂/rGO/PANI electrode at a scan rate of 1 mV·s⁻¹ between 0.8–1.8 V versus Zn/Zn⁺. The two pairs of reversible redox peaks can be clearly observed, corresponding to a two-step reaction. Fig. 4(b) shows the charge/discharge profiles of MnO₂/rGO/PANI electrode at different rates, which is consistent with CV curves. Rate performance is an important parameter for evaluating battery property. Fig. 4(c) shows the rate performance at various current densities ranging from 0.1 A·g⁻¹ to 1 A·g⁻¹ for the MnO₂, MnO₂/rGO, and MnO₂/rGO/PANI electrodes. The capacity of MnO₂/rGO/PANI electrode could reach 241.1 mAh·g⁻¹ at 0.1 A·g⁻¹ based on the weight of MnO₂/rGO/PANI sample, which is much higher than those of MnO₂/rGO (178.8 mAh·g⁻¹) and MnO₂ electrodes.

Fig. 3  (a) XRD patterns of MnO₂, MnO₂/rGO, and MnO₂/rGO/PANI; (b) Raman spectra of MnO₂/rGO, MnO₂/rGO, and MnO₂/rGO/PANI; (c) FTIR spectrum of MnO₂/rGO/PANI; (d) High-resolution XPS spectrum of Mn 2p in MnO₂/rGO/PANI.

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Even at a high current density of 1 A·g⁻¹, MnO₂/rGO/PANI delivered a reversible capacity of 111.7 mAh·g⁻¹ (47.9% of the capacity at 0.1 A·g⁻¹), which is higher than those of the MnO₂/rGO electrode (84.6 mAh·g⁻¹, 47.3%) and MnO₂ electrode (80.3 mAh·g⁻¹, 45.2%), suggesting the improved rate capability of MnO₂/rGO/PANI electrode. More importantly, the superior and enduring cycling performance of MnO₂/rGO/PANI is displayed in Fig. 4(d), where a discharge capacity of 100.6 mAh·g⁻¹ (82.7% capacity retention) could be achieved after 600 charge/discharge cycles at 1 A·g⁻¹. In comparison, only 58.6 and 31.4 mAh·g⁻¹ remained for the MnO₂/rGO and MnO₂ electrodes, respectively, which further demonstrated the excellent long-term cycling stability of MnO₂/rGO/PANI.

GITT was conducted to further investigate the kinetics of Zn²⁺ diffusion coefficient (D) in the MnO₂/rGO/PANI electrode during cycling. The calculation formula is manifested in the ESI. Charge/discharge curves and the corresponding D of Zn²⁺ in GITT measurement for MnO₂/rGO/PANI, MnO₂/rGO, and MnO₂ electrodes are shown in Fig. 5(a). The D values of MnO₂/rGO/PANI ranged from 4.9 × 10⁻⁹ cm²·s⁻¹ to 4.1 × 10⁻¹¹ cm²·s⁻¹ in the charge process and 3.7 × 10⁻⁹ cm²·s⁻¹ to 1.1 × 10⁻¹⁰ cm²·s⁻¹ in the discharge process (Fig. 5b), which are much higher than the corresponding D values of MnO₂/rGO (from 9.6 × 10⁻¹⁰ cm²·s⁻¹ to 6.1 × 10⁻¹² cm²·s⁻¹ during cycling) and MnO₂ (from 9.7 × 10⁻¹¹ cm²·s⁻¹ to 2.9 × 10⁻¹² cm²·s⁻¹ during cycling). The higher Zn²⁺ diffusion coefficient suggests faster reaction kinetics for the MnO₂/rGO/PANI electrode. The analysis based on electrochemical impedance spectroscopy (EIS) further reveals that the compact structure of MnO₂/rGO/PANI electrode ensures smaller charge-transfer resistance (Fig. S7 in ESI).

Based on the above results, the high performance of MnO₂/rGO/PANI could be attributed to the following factors: (1) The dense and compact structure improves not only the structural stability of the composite but also the interaction among components; (2) The coated layer of PANI contributes to high conductivity and additional Zn storage capacity, which also inhibits the dissolution of Mn.

CONCLUSIONS

In summary, a facile and convenient preparation method for MnO₂/rGO/PANI aerogel was demonstrated, which was then used as high-performance cathode for ZIB. Different from the commonly used method with extra addition of MnSO₄ to pre-balance Mn in electrolyte, we offer a new insight into suppressing the dissolution of Mn via coating the MnO₂/rGO composite hydrogel with PANI layer. Benefiting from the high electrical conductivity of PANI and the unique micro-/nano-
structure of MnO$_2$/rGO/PANI, as-fabricated MnO$_2$/rGO/PANI/Zn battery exhibited a superior capacity of 241.1 mAh·g$^{-1}$ at 0.1 A·g$^{-1}$, and a long-term cycling stability with 82.7% capacity retention after 600 cycles. Furthermore, the GITT result suggests the MnO$_2$/rGO/PANI cathode possessed a faster diffusion kinetics. This strategy provides an effective solution to the current problem of Mn dissolution, and contributes to the development of high-performance zinc-ion batteries.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at https://doi.org/10.1007/s10118-020-2353-6.

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