γ-MnO₂ nanorods/graphene composite as efficient cathode for advanced rechargeable aqueous zinc-ion battery

Chao Wang¹, Yinxiang Zeng², Xiang Xiao³, Shijia Wu⁴, Guobin Zhong⁴, Kaiqi Xu⁴, Zengfu Wei⁴, Wei Su⁴, Xihong Lu⁴,∗

¹Electric Power Research Institute of Guangdong Power Grid Co., Ltd., Guangzhou 510080, Guangdong, China
²MOE of the Key Laboratory of Bioinorganic and Synthetic Chemistry, The Key Lab of Low-Carbon Chem & Energy Conservation of Guangdong Province, School of Chemistry, Sun Yat-Sen University, Guangzhou 510275, Guangdong, China

ARTICLE INFO

Article history:
Received 3 July 2019
Revised 10 August 2019
Accepted 13 August 2019
Available online 3 September 2019

Keywords:
γ-MnO₂
Graphene
Zinc-ion battery
High-capacity cathode

ABSTRACT

Aqueous Zn//MnO₂ batteries are emerging as promising large-scale energy storage devices owing to their cost-effectiveness, high safety, high output voltage, and energy density. However, the MnO₂ cathode suffers from intrinsically poor rate performance and rapid capacity deterioration. Here, we remove the roadblock by compositing MnO₂ nanorods with highly conductive graphene, which remarkably enhances the electrochemical properties of the MnO₂ cathode. Benefiting from the boosted electric conductivity and ion diffusion rate as well as the structural protection of graphene, the Zn/MnO₂–graphene battery presents an admirable capacity of 301 mAh g⁻¹ at 0.5 A g⁻¹, corresponding to a high energy density of 411.6 Wh kg⁻¹. Even at a high current density of 10 A g⁻¹, a decent capacity of 95.8 mAh g⁻¹ is still obtained, manifesting its excellent rate property. Furthermore, an impressive power density of 15 kW kg⁻¹ is achieved by the Zn/MnO₂–graphene battery.

© 2019 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.

1. Introduction

The overconsuming fossil fuels and rising energy demands have encouraged the global exploration of energy storage devices, which play an important role in next-generation renewable energy systems [1–5]. Although Li-ion batteries with high energy density are protagonists in the commercial battery market, the potential safety issues, limited availability of Li resources, and environmental concerns impede their large-scale deployment. Thus, enormous efforts have been devoted to exploring alternative aqueous rechargeable batteries [6–10]. In particular, aqueous Zn-ion batteries (ZIBs) have been regarded as showing the most prospect among aqueous rechargeable batteries as Zn features earth-abundance, good water compatibility, and high theoretical capacity (820 mAh g⁻¹) [11–15]. In addition, the attractiveness of ZIBs resides in the low negative potential (−0.762 V vs. SHE) and multivalent charge transfer reactions of Zn [16–19]. At present, Prussian blue analogs, metal oxides and sulfides, and even organic materials have been proposed as cathodes for Zn storage [20–24]. Among them, MnO₂ has attracted particular interest in view of its favorable theoretical capacity, cost-efficiency, eco-friendliness, and matched voltage versus Zn in the construction of Zn//MnO₂ batteries with a high output voltage [25–28]. Considering the advantages of low cost, high safety, and easy manufacturing process, Zn//MnO₂ batteries have been commercialized as primary batteries for a very long time. However, the development of rechargeable Zn//MnO₂ batteries is severely restricted by the limited specific capacity and poor cycling stability arising from the inherently poor electrical conductivity and structural damage of MnO₂ cathodes during the charge-discharge process [28,29].

To tackle these problems, great attention has been focused on developing MnO₂ materials with a wide variety of crystallographic polymorphs (such as α-, β-, γ-, R-, δ-, λ-, romanechite, and todorokite type MnO₂) [30–32]. It has been reported that different crystal structures greatly affect the Zn²⁺ storage performance of MnO₂. Among them, γ-MnO₂ is comprised of randomly arranged 1 × 1 (size ~2.3 × 2.3 Å, pyrolusite) and 1 × 2 (size ~2.3 × 4.6 Å, ramsdellite) tunnels, which are beneficial for Zn²⁺ intercalation/deintercalation [16,32]. Furthermore, combining MnO₂ with highly conductive materials is a good strategy for compensating its conductivity and accommodating the structural change during the cycling process. In this regard, various MnO₂/conductive material composites such as MnO₂/poly(3,4-ethylenedioxythiophene) (PEDOT) [33], MnO₂/polyaniline (PANI) [29], MnO₂/carbon nanotube

https://doi.org/10.1016/j.jechem.2019.08.011
2055-4956/© 2019 Science Press and Dalian Institute of Chemical Physics, Chinese Academy of Sciences. Published by Elsevier B.V. and Science Press. All rights reserved.
Finally, the sample was further thermally annealed at a temperature of 300 °C in air for 1 h.

2.2. Preparation of MnO₂

The MnO₂ sample was prepared by a similar procedure but without graphene. Firstly, 0.02 mol/L of potassium permanganate (KMnO₄) and 0.06 mol/L of MnCl₂ were dissolved in 40 mL of distilled water. The as-prepared suspension was transferred into a 50-mL Teflon-lined autoclave and heated at 120 °C for 6 h. The precipitates obtained were gathered and washed with water three times. Finally, the sample was further thermally annealed at a temperature of 300 °C in air for 1 h.

2.3. Material characterization

The microstructures and compositions of the electrode materials were analyzed by field-emission SEM (FE-SEM, JSM-6330F), transmission electron microscopy (TEM, FEI Tecnai G² F30), Raman spectroscopy (Renishaw inVia), XPS (XPS, ESCALab250, Thermo VG), and X-ray diffractometry (XRD, D8 ADVANCE). The TGA was conducted using a TG209F1 Libra (Netzsch, Germany) analyzer with samples of approximately 2–4 mg, at a scan rate of 10 °C/min from 25 to 800 °C in air.

2.4. Electrochemical measurement

All electrochemical tests were performed at room temperature. Cyclic voltammetry (CV), galvanostatic charge/discharge measurements, and electrochemical impedance spectroscopy were conducted on an electrochemical workstation (CHI 760E). The as-prepared MnO₂ and MnO₂-graphene samples were mixed with carbon and polyvinylidene fluoride in a ratio of 7:2:1 with N-methyl-2-pyrrolidone. The mixture was hand-ground for at least 30 min to obtain a slurry. The slurry was later coated onto carbon paper, which served as a current collector, after which it was heated at 80 °C overnight for further use. A Zn foil was used as the anode, and 2 M ZnSO₄ and 0.4 M MnSO₄ solutions were employed as the electrolyte. The thickness of the Zn anode was 0.25 mm, and the mass loading of the MnO₂/graphene cathode was ∼2 mg cm⁻². The electrochemical tests of the aqueous Zn-MnO₂ battery were performed in a two-electrode cell with a voltage ranging from 0.8–1.8 V.

3. Results and discussion

The MnO₂-graphene sample is synthesized by a facile hydrothermal method with the reduction of KMnO₄ by graphene (Supporting Information, Experimental Section). As a comparison, the bare MnO₂ sample is also prepared by a hydrothermal reaction between KMnO₄ and MnCl₂ (Supporting Information, Experimental Section). Scanning electron microscopy (SEM) images reveal that the MnO₂ sample shows an agglomerated morphology (Fig. 1(a)). From Fig. 1(b), notable graphene wrinkles can be noticed for the MnO₂ sample prepared with graphene. To obtain further insights into the microstructure, TEM examination was carried out. As depicted in Fig. S1, the MnO₂ sample shows a nanosheet structure with the clear lattice fringes of 0.242 nm assigned to the (131) plane of γ-MnO₂ (JCPDS 14-0644). For the MnO₂-graphene sample, MnO₂ nanorods with diameters ranging from 10 to 20 nm have closely adhered to the ultrathin graphene nanosheet (Figs. 1c, S2). The thickness of the graphene is about 4–6 layers. The high magnification TEM image in Fig. 1(d) indicates that the interplanar spacings of 0.163 nm and 0.242 nm are well indexed to the (160) and (131) lattice planes of γ-MnO₂ (JCPDS 14-0644), respectively. The corresponding selected area electron diffraction (SAED)
pattern indicates that the MnO₂ nanorod has a single-crystalline structure, and graphene is amorphous (Figs. 1e, f). The energy-dispersive spectroscopy mapping of Mn, O, and C clearly verifies that the MnO₂ nanorods are dispersed on the graphene nanosheets (Fig. 1g).

To discover the structures and chemical compositions of the MnO₂ and MnO₂-graphene sample, XRD, Raman, and XPS measurements were conducted. As shown in Fig. 2(a), all the XRD peaks for the bare MnO₂ sample are indexed well to the layered γ-MnO₂ [JCPDS 14–0644]. While the XRD pattern for the MnO₂-graphene sample presents less noticeable peaks for γ-MnO₂ [JCPDS 14–0644] and a high peak for carbon, unveiling the combination of MnO₂ and carbon. The Raman spectra in Fig. 2(b) displays a similar result, where both samples depict a sharp peak at 636 cm⁻¹, which can be attributed to the symmetric Mn–O stretching vibrations of the MnO₂ octahedron in MnO₂ [33]. Except that, another peak at 298 cm⁻¹ assigned to γ-MnO₂ can be observed for the bare MnO₂ sample [37]. Conversely, the MnO₂-graphene sample shows the existence of the D band (1328 cm⁻¹) and G band (1585 cm⁻¹) from graphene besides typical MnO₂ peaks [38]. By calculation, the ratio of I₆/I₇C reaching 1.47 for the MnO₂-graphene sample, suggesting its enriched structure defective sites and edge plane exposure [39]. From the full X-ray photoelectron spectroscopy (XPS) results of the MnO₂ and MnO₂-graphene samples shown in Fig. S3(a), both samples show the presence of Mn, O, and C without other impurities, which is in good agreement with the XRD result. The two peaks in the Mn 2p spectra correspond to the Mn 2p₃/2 and 2p₁/2 binding energies (Fig. S3(b)). In addition, the spin-energy separation of 4.8 eV in the Mn 3 s spectra for both samples reveals that Mn⁴⁺ is the dominant valence state in the MnO₂ and MnO₂-graphene samples [33]. Subsequently, TG was used to study the content of graphene in the MnO₂-graphene sample. As illustrated in Fig. 2(d), the weight loss below 240 °C is derived from the removal of adsorbed water, and subsequent decrease originates from the combustion of graphene to CO₂. For MnO₂, a weight loss of about 8% is observed in the range of 500–600 °C, which is attributed to the transformation of MnO₂ into MnO₂. By calculation, we estimated that the mass percentage of graphene in the MnO₂-graphene sample is ~16.3%.

Next, we evaluate the electrochemical performance of the MnO₂ and MnO₂-graphene electrodes using a Zn foil anode and 2 M ZnSO₄ + 0.4 M MnSO₄ electrolyte. Firstly, we studied the effect of the KMnO₄ concentration on the electrochemical properties of the MnO₂-graphene electrodes. The graphene content in the MnO₂-graphene samples with different concentrations of KMnO₄ was determined by TG (Fig. S4). By calculation, we estimated that the mass percentages of graphene in the MnO₂-graphene samples with different concentrations of KMnO₄ (7.5, 12.5, 17.5, and 25 mM) are about 37%, 16.3%, 8.5%, and 5.4%, respectively. Moreover, the discharge time (normalized by the content of MnO₂ in the samples) of the MnO₂-graphene electrodes increases with the increment of the KMnO₄ concentration from 7.5 to 12.5 mmol/L and then decreases (Fig. 3(a)), indicating that 12.5 mmol/L KMnO₄ is the optimum concentration for the preparation of the MnO₂-graphene electrode. Additionally, the relationship between the performance and the hydrothermal temperature was investigated, and the MnO₂-graphene electrode synthesized at 120 °C exhibited the highest capacity (Fig. S5).

Fig. 3(b) compares the CV profiles of the MnO₂ and MnO₂-graphene electrodes at a scan rate of 1 mV s⁻¹ with a voltage range of 0.8–1.8 V. In the cathodic scans, two distinct peaks are observed for both electrodes, probably ascribed to the two-step intercalation. Evidently, the polarization between the cathodic and anodic peaks for the MnO₂-graphene electrode is visibly lower than that for
the bare MnO$_2$ electrode, indicating the improved reversibility of the MnO$_2$-graphene electrode. Furthermore, the galvanostatic charge/discharge curves of the MnO$_2$ and MnO$_2$-graphene electrodes at a current density of 1 mA cm$^{-2}$ are illustrated in Fig. 3(c), where two noticeable discharge plateaus located at around 1.35 and 1.23 V are consistent with the CV curves. In comparison with those of the bare MnO$_2$ electrode, a longer discharge platform with a relatively smaller voltage hysteresis is noticed for the MnO$_2$-graphene electrode, evidencing the enhanced energy storage properties. Specifically, the MnO$_2$-graphene electrode exhibits a remarkable capacity of 301 mAh g$^{-1}$ at 1 mA cm$^{-2}$ (0.5 A g$^{-1}$), which is more than twice that for the bare MnO$_2$ electrode (147 mAh g$^{-1}$) at the same current density. Encouragingly, a favorable capacity of 95.8 mAh g$^{-1}$ is still obtained as the current density increases to 20 mA cm$^{-2}$ (10 A g$^{-1}$), corresponding to the capacity retention of 31.8% (Fig. 3(d), Fig. 56). Such a high rate capability is superior to those of the bare MnO$_2$ electrode (only 14.2%) and most reported Zn-ion batteries, including MnO$_2$@CNT (51 mAh g$^{-1}$ at 2 A g$^{-1}$) [34], oxygen-deficient ZnMn$_2$O$_4$@PEDOT (62.5 mAh g$^{-1}$ at 1.66 A g$^{-1}$) [40], MnO$_2$@PEDOT (76 mAh g$^{-1}$ at 5.58 A g$^{-1}$) [33], PANI-intercalated MnO$_2$ ($\sim$110 mAh g$^{-1}$ at 3 A g$^{-1}$) [29], and MnO$_2$ (113 mAh g$^{-1}$ at 3.08 A g$^{-1}$) [36].

To investigate the improved electrochemical performance of the MnO$_2$-graphene electrode, electrochemical impedance spectroscopy measurement was carried out. Fig. 4(a) presents the Nyquist plot of the MnO$_2$ and MnO$_2$-graphene electrodes, and the corresponding equivalent circuit diagram. Here, $R_h$ is the bulk solution resistance; $R_{ct}$ is the interfacial charge-transfer resistance; CPE represents the constant phase element accounting for a double-layer capacitance, and $Z_W$ is the Warburg impedance. It is well-known that the diameter of the semicircle in a high-frequency range is related to the $R_{ct}$ value of the electrode, and the slope in the low-frequency region has a positive correlation with the diffusion rate of the electrolyte. By simulation, the $R_{ct}$ value of the Zn//MnO$_2$ battery with the MnO$_2$-graphene cathode is determined as 457 $\Omega$, which is dramatically smaller than that based on the bare MnO$_2$ cathode (1148 $\Omega$). This confirms the boosted electric conductivity of the MnO$_2$-graphene electrode. In addition, the significantly higher straight slope in the low-frequency region for the MnO$_2$-graphene electrode also indicates its faster ion-diffusion rate compared to the case of the bare MnO$_2$ electrode. Moreover, the cyclic durability of the MnO$_2$ and MnO$_2$-graphene electrodes were evaluated at 20 mA cm$^{-2}$ for 300 cycles (Fig. 4(b)). The MnO$_2$-graphene electrode exhibits decent cycling stability and retains 64.1% of the initial capacity with an ultralow capacity decay rate of 0.12% per cycle. In contrast, the bare MnO$_2$ electrode delivers a relatively low cycling stability with only 5.1% capacity retention after 300 cycles. Except for the first cycle, the Coulombic efficiency for the Zn/MnO$_2$-graphene battery reached nearly 100%, indicating its good reversibility during the charging/discharging process.

To confirm the charge storage mechanism, the evolution of Mn valence states and Zn contents during the charge-discharge process was investigated by ex-situ XPS. As shown in Fig. 4(c), the peaks of Mn 2p move toward low energy at the full discharge state, suggesting the decrease of the Mn valence due to the insertion of Zn$^{2+}$. On the contrary, the peaks of Mn 2p return to the high energy region accompanied by the extraction of Zn$^{2+}$ after the charged state, thereby revealing the reversible phase transformation during the discharge and charging processes. Correspondingly, the intensities of the Zn 2p peaks increase gradually in the discharge process (from point A to C in Fig. 4(d)) and then decrease when charged to 1.8 V, confirming the insertion/extraction of Zn$^{2+}$ into/from the MnO$_2$-graphene electrode (Fig. 4(e)). The partial residue of the detected Zn in the fully charged state may indicate that Zn$^{2+}$ has not been completely extracted from the MnO$_2$ framework, which might be the reason for the capacity decay during cycling.
Energy density and power density are two crucial factors for assessing the energy storage properties of batteries. Fig. 5 presents the Ragone plot comparing the specific energy and power densities of the present Zn//MnO$_2$-graphene battery with other reported aqueous rechargeable batteries. Impressively, the present Zn//MnO$_2$-graphene battery exhibits a maximum energy density of 411.6 Wh kg$^{-1}$ (11.7 mWh cm$^{-2}$) at a power density of 0.57 kW kg$^{-1}$. Even at a high power density of 15 kW kg$^{-1}$ (0.43 W cm$^{-2}$), an energy density of 95.8 Wh kg$^{-1}$ is still obtained for the Zn//MnO$_2$-graphene battery. Such an excellent performance is better than those of most recently reported aqueous batteries, including the Zn//Na$_2$V$_2$(PO$_4$)$_2$F$_2$ battery (44.7 Wh kg$^{-1}$; 4.47 kW kg$^{-1}$) [41], Ni//Bi battery (85.8 Wh kg$^{-1}$; 1.02 kW kg$^{-1}$) [42], Ni//Fe battery (141 Wh kg$^{-1}$; 1.6 kW kg$^{-1}$) [43], Zn//MnO$_2$ battery (250 Wh kg$^{-1}$; 0.75 kW kg$^{-1}$) [44], Zn//ZnMn$_2$O$_4$ battery (273.4 Wh kg$^{-1}$; 0.15 kW kg$^{-1}$) [40], and Ni//Zn battery (355.7 Wh kg$^{-1}$; 0.48 kW kg$^{-1}$) [45].

4. Conclusions

In conclusion, the γ-MnO$_2$-graphene composite prepared by a facile hydrothermal method has proven to be a high-performance cathode for aqueous Zn//MnO$_2$ batteries. The incorporation of graphene could not only improve the conductivity of MnO$_2$ but also endow the electrode with the ability to accommodate the structural damage and dissolution of MnO$_2$ during the discharge/charge process, contributing to an enhanced rate property and cyclic stability. Consequently, the battery utilizing this MnO$_2$-graphene cathode delivers an impressive discharge capacity (301 mAh g$^{-1}$ at 0.5 A g$^{-1}$), high-rate capability (95.8 mAh g$^{-1}$ at 10 A g$^{-1}$), as well as decent cycling durability (64.1% after 300 cycles), exhibiting its superiority to the bare MnO$_2$ electrode. Additionally, the Zn//MnO$_2$-graphene battery yields a high energy density of 411.6 Wh kg$^{-1}$ and a maximum power density of 15 kW kg$^{-1}$. This work may shed light on the design of MnO$_2$-based cathodes for high-performance aqueous Zn//MnO$_2$ batteries.

Declaration of Competing Interest

There are no conflicts to declare.

Acknowledgments

This work was financially supported by the Guangdong Power Grid Co., Ltd. (Grant No. GDKJXM20160000).

Supplementary material

Supplementary material associated with this article can be found, in the online version, at doi:10.1016/j.jechem.2019.08.011.

References
