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Polypyrrole Film Decorated Manganese Oxide Electrode Materials for High-Efficient Aqueous Zinc Ion Battery

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Abstract: Aqueous zinc-ion batteries (AZIBs) have raised wide concern as a new generation energy storage device due to their high capacity, low cost, and environmental friendliness. It is a crucial step to develop the ideal cathode materials that match well with the Zn anode. In this work, we report polypyrrole-(PPy)-encapsulated MnO$_2$ nanowires as cathode materials for AZIBs. The assembled Zn//MnO$_2$@PPy batteries deliver a reversible capacity of 385.7 mAh g$^{-1}$ at a current density of 0.1 A g$^{-1}$. Also, they possess an energy density of 192 Wh kg$^{-1}$ at a power density of 50 W kg$^{-1}$. The cells show long-term cycling stability, with a retention rate of 96% after 1000 cycles. The outstanding electrochemical performance indicates their potential applications in large-scale energy storage.

Keywords: zinc ion battery; manganese oxide; nanowires; electrode materials; cycling stability

1. Introduction

With increasing climatic deterioration and environmental pollution, it is imperative to build a low-carbon society. Many renewable energy sources arose in the last decade, including wind, tidal, and nuclear energy [1]. Nevertheless, their intrinsic unsustainability hampers their further applications in energy capture [2]. Recently, the research focus has shifted to developing sustainable energy storage technology [3]. Lithium-ion batteries (LIBs) are widely applied in power grids, smart homes, and electronic devices due to their high energy density [4,5]. Their future application is restricted by the scarcity of lithium resources and thermal safety problems. Aqueous zinc ion batteries (ZIBs) are expected to be the alternatives to LIBs due to their high Zn theoretical capacity of 819 mAh g$^{-1}$ and nontoxicity [6–9]. It is still a challenge to explore the desired electrodes for Zn$^{2+}$ storage owing to their sluggish reaction kinetics [10].

So far, some cathode materials have entered the spotlight [11,12]. Manganese oxides possess the characteristic of a wide work voltage, and multiple valences (Mn$^{2+}$, Mn$^{3+}$, and Mn$^{4+}$) [13]. In effect, the connection pattern of MnO$_6$ octahedrons controls the type of MnO$_2$ crystal structure (e.g., α-, δ-, γ-, β-, λ-, ε-MnO$_2$) [14]. β-MnO$_2$: materials show strong stability due to their tunnel structure. In the literature, Huang et al. synthesized β-MnO$_2$: nanorods by doping the N element to enhance the overall performance of the battery [15]. They effectively improved the conductivity of MnO$_2$: materials. Zhou’s group designed β-MnO$_2$: with oxygen defects (302 mAh g$^{-1}$ at 0.05 A g$^{-1}$) [16]. Ding and co-workers constructed β-MnO$_2$: with a graphene oxide coating layer [17]. They achieved a capacity of 129.6 mAh g$^{-1}$ after 2000 times cycle at 4 C. However, it is still unsatisfactory in terms of the dissolution of the Mn ion. It can reduce the contact between MnO$_2$: and the electrolyte by coating the conducting polymer on the surface of the active material [18]. Polypyrrole (PPy) is a common conductive polymer due to its highly conductive, non-toxic, and low price. It can be used as a coating to improve the structural stability and conductivity of the cathode in various energy storage devices [19,20].
Herein, we prepare PPy-encapsulated MnO₂ nanowires by a one-step hydrothermal avenue. The strategy of the coating layer improves the conductivity and cycling stability of the batteries. Their zinc storage mechanism (H⁺ and Zn²⁺ co-intercalation) not only prevents the dilapidation of the materials during the long cycle but also improves the transfer rate of Zn²⁺. The assembled Zn//MnO₂@PPy battery possesses a discharge specific capacity of 385.7 mAh g⁻¹ at 0.1 A g⁻¹. It still shows a specific capacity of 169.04 mAh g⁻¹ with a capacity retention rate of 96% after 1000 times cycle at 1 A g⁻¹.

2. Experimental Section

2.1. Materials Synthesis

In a typical experiment, 5 mmol MnSO₄·H₂O, 5 mmol (NH₄)₂S₄O₆, and 10 mmol (NH₄)₂SO₄ were dissolved in 70 mL of deionized water (DI). Then, the mixture was stirred for 30 min at room temperature until it formed a uniform solution. Finally, they were put into a 100 mL Teflon-lined autoclave and heated at 180 °C for 12 h. The obtained black powder was washed with DI and alcohol and kept at 60 °C for 12 h. The collected sample was labeled as β-MnO₂. The MnO₂@PPy product was prepared by the following procedure: 0.3 g of MnO₂ was put into a beaker with 50 mL of DI and sonicated for 30 min. After that, one adjusted pH ~ 3 with 1 M HCl is added, and 20 µL of pyrrole is added under the condition of magnetic stirring. Finally, the samples were obtained by centrifuging several times and dried at 60 °C overnight.

2.2. Morphology and Structural Characterization

The crystallographic information of the samples was researched by X-Ray diffraction (XRD, Shimadzu-7000, Cu Kα radiation, λ = 0.1541 nm, 40 KV) and X-Ray photoelectron spectrometer (XPS, Thermo Scientific K-Alpha, Waltham, MA, USA). Fourier transformed infrared (FTIR) spectroscopy spectra were studied using the Nicolet Nexus 470 spectrometer. N₂ absorption and desorption isotherms (JW-TB200) were used to study their specific surface area and pore size by the Brunauer-Emmett-Teller (BET) method. The scanning electron microscope (SEM, Gemini 300-71-31) equipped with energy dispersive spectroscopy (EDS) was used to analyze the microscopic morphology and elements of the samples.

2.3. Electrochemical Characterization

The electrodes were fabricated by grinding the active material (70 wt%), acetylene black (20 wt%), and polyvinylidene fluoride (PVDF, 10 wt%) in N-methyl-2-pyrrolidone (NMP). Then the above slurry was applied to graphite paper (0.05 mm thickness) and kept in a vacuum oven at 60 °C overnight. The strategy of the coating layer improves the conductivity and cycling stability of the batteries. Their zinc storage mechanism (H⁺ and Zn²⁺ co-intercalation) not only prevents the dilapidation of the materials during the long cycle but also improves the transfer rate of Zn²⁺. The assembled Zn//MnO₂@PPy battery possesses a discharge specific capacity of 385.7 mAh g⁻¹ at 0.1 A g⁻¹. It still shows a specific capacity of 169.04 mAh g⁻¹ with a capacity retention rate of 96% after 1000 times cycle at 1 A g⁻¹.

3. Result and Discussion

XRD is first employed to characterize the crystallinity and structural information of the obtained samples. As shown in Figure 1a, the diffraction peaks of the two samples can be matched as tetragonal β-MnO₂ phases with a P42/mmm(136) space group (JCPDs no. 24-0735). Their lattice parameters are a = 4.4 Å, b = 4.4 Å, and c = 2.874 Å. The diffraction peaks at 28.7, 37.3, 41.0, 42.8, 46.1, 56.7, 59.4, 64.8, 67.2, and 72.3° correspond to the (110), (101), (200), (111), (210), (211), (220), (002), (310), and (301) planes, respectively. MnO₂ and MnO₂@PPy samples possess diffraction peaks at the same angle, indicating that the coating method does not change the crystal structure of the materials. In addition, the latter
shows a slightly lower peak intensity, which is caused by the coating of the amorphous PPy layer on the surface of \( \beta \)-MnO\(_2\). In order to verify the encapsulation of the PPy, the FTIR test is conducted with a wavelength range of 500–4000 cm\(^{-1}\) (Figure 1b). The peaks at 1460 and 1550 cm\(^{-1}\) can be attributed to the symmetric and antisymmetric vibrations of the pyrrole ring [21], respectively. The peak at 1168 cm\(^{-1}\) derives from the C-N stretching vibration between the two pyrrole rings [22]. Meanwhile, the bending vibration of the N-H stretching mode is found at a peak of 3450 cm\(^{-1}\) [23]. The results confirm the successful synthesis of composites.

As shown in Figure 1c from the XPS spectra, the Mn 2p3/2 and Mn 2p1/2 peaks are located at 654.88 and 643.38 eV, respectively, which correspond to Mn\(^{4+}\). Also, Mn\(^{3+}\) peaks are found at 642.28 and 653.88 eV [24]. The O 1s spectra (Figure 1d) are de-convoluted into three peaks, including the Mn-O-Mn bond at 529.18 eV, and oxygen defects at 530.88 eV, and Mn-OH at 531.98 eV [25]. For C elements in Figure 1e, they are split into three peaks at 284.8 eV, 286.08 eV, and 288.28 eV, which correspond to C-C, C-N, and C=O bonds, respectively [26]. In Figure 1f, the peaks at 398.78, 400.18, and 401.68 eV can be attributed to the \(-N=\), \(-NH_2\), and \(-NH_-\) bonds in polypyrrole [27], respectively. The presence of C and N elements further indicates that \( \beta \)-MnO\(_2\) is coated by PPy.

![Figure 1](https://crystals.baselibrary.org/13/1445/1.png)

**Figure 1.** Structural and compositional characterization of as-prepared samples (a) XRD patterns (b) FTIR spectrum (c-f) XPS spectra of Mn 2p, O 1s, C 1s and N 1s of MnO\(_2\)@PPy samples.

The N\(_2\) adsorption-desorption isotherms of the samples are presented in Figure 2. They present typical IV hysteresis loops, indicating their mesoporous feature. Mesoporous materials possess the characteristics of moderate pore size and interconnected pore channels. It serves as an electrolyte and ion storage tank, facilitating ion transport and alleviating volume changes during cycling. In Table 1, the specific surface areas of the MnO\(_2\) and MnO\(_2\)@PPy samples are 18.1 cm\(^2\) g\(^{-1}\) and 23.7 cm\(^2\) g\(^{-1}\), respectively. In addition, the total pore volume (0.069 cm\(^3\) g\(^{-1}\)) of the latter is larger than that of the former (0.053 cm\(^3\) g\(^{-1}\)). The large specific surface area and pore volume provide a wide distribution of zinc storage sites.
Table 1. Specific surface areas, total pore volumes and average pore diameter of MnO\(_2\) and MnO\(_2\)@PPy samples.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Specific Surface Area (m(^2)/g)</th>
<th>Total Pore Volume (cm(^3)/g)</th>
<th>Average Pore Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MnO(_2)</td>
<td>18.1</td>
<td>0.053</td>
<td>11.595</td>
</tr>
<tr>
<td>MnO(_2)@PPy</td>
<td>23.7</td>
<td>0.069</td>
<td>11.699</td>
</tr>
</tbody>
</table>

Figure 2. N\(_2\) adsorption-desorption isotherm and pore size distribution curve (inset) of (a) MnO\(_2\) and (b) MnO\(_2\)@PPy samples.

Two kinds of samples show the shape of nanowires with a length of ~5 µm and a width of 100 nm (Figure 3a–f). These suggest that the coating of PPY does not change the morphology of the samples. This is related to the amount of pyrrole used during the experiment. The generation of nanowires in the longitudinal direction originates from the preferential growth of corresponding high-energy crystal planes. This is attributed to the growth mechanism of recrystallization after dissolution. MnO\(_2\) materials exhibit strong oxidizing properties under acidic conditions, and pyrrole monomers are in-situ oxidized on the surface of manganese dioxide to form polypyrrrole. Compared with MnO\(_2\) samples, the MnO\(_2\)@PPy nanowires are more dispersed. Also, the nanowires in MnO\(_2\) samples underwent slight aggregation. This phenomenon is attributed to the ultrasonic dispersion step in the experimental process of coating PPY, which results in a uniform distribution of nanowires. Figure 3g shows the EDS images of MVO samples. The element mappings prove the uniform distribution of Mn, O, N, and C in MnO\(_2\)@PPy nanowires.
Subsequently, we explore the effect of PPy coating on the electrochemical properties of MnO₂ samples. Figure 4a shows the CV curves of the two electrodes at a scan rate of 0.1 mV s⁻¹. There are two pairs of redox peaks; oxidation peaks appeared in the potential range of 0.8–1.8 V (vs. Zn²⁺/Zn). The O1/R1 (1.6/1.38 V) and O2/R2 (1.55/1.26 V) peaks correspond to the intercalation/de-intercalation behaviors of H⁺ and Zn²⁺, respectively. This phenomenon suggests the transfer of Mn⁴⁺→Mn²⁺ and Mn²⁺→Mn⁴⁺. Compared with the CV curve of MnO₂ electrodes, the MnO₂@PPy samples possess a larger CV curve envelope area. It indicates that the latter presents superior electrochemical activity and capacity. Notably, when carbon paper without active substances is used as the cathode material for batteries, the area of the CV curve is about 13% of MnO₂ and 7% of MnO₂@PPy. This shows that carbon paper possesses a certain contribution to the electrochemical performance of batteries. Moreover, MnO₂@PPy electrodes show a low peak potential interval (0.232 V). It may be attributed to the increased conductivity of the PPy coating, thereby accelerating the transfer rate of ions and electrons [28].

The cycle capacity of Zn//MnO₂/MnO₂@PPy cells at 0.1 A g⁻¹ is also studied in Figure 4b. In the initial cycle, the Zn//MnO₂@PPy batteries deliver a specific capacity of 281.2 mAh g⁻¹. The capacity reaches 385.7 mAh g⁻¹ after 80 times cycling. The MnO₂ materials show the same capacity increase phenomenon (129.0 → 214.0 mAh g⁻¹). It still needs further investigation into the complex activation process of manganese-based materials. The possible reasons are as follows: First, the added Mn²⁺ in the electrolyte can be converted into MnO₂ active materials during the redox process, resulting in an increase in capacity. Moreover, the cathode material can only be fully wetted in the electrolyte after several times cycling. Finally, the MnO₂ materials may undergo structural phase transitions during the first few cycles [29]. The coulomb efficiency of the Zn//MnO₂@PPy battery is always maintained at near 100% during the cycle. It proves that Zn²⁺ and H⁺ possess excellent reversibility during the process of intercalation/de-intercalation. Two obvious charge-discharge plateaus appear in the GCD curves of the batteries (Figure 4c), which are consistent with the CV curves. For the MnO₂@PPy electrodes, two platforms provide a specific capacity of ~150 and 140 mAh g⁻¹, respectively.

Rate capability is also an essential parameter in assessing their commercial applications. In Figure 4d, the Zn//MnO₂@PPy cells work at 0.1, 0.2, 0.4, 0.8, 1.6, and 3.2 A g⁻¹; they can reach the specific capacities of 304.1, 300.1, 294.0, 236.9, 174.4, and 137.0 mAh g⁻¹.
respectively. The specific capacities are 336.2 (0.2 A g⁻¹) and 350.9 mA h g⁻¹ (0.1 A g⁻¹). It is advantageous that they achieve a recovery rate of 115.4% at 0.1 A g⁻¹. The Zn/MnO₂ batteries possess specific capacities of 168.0, 170.0, 159.3, 133.3, 101.4, 72.8, 197.3, and 224.6 mAh g⁻¹ at the above current densities. Figure 4e shows the corresponding charge/discharge profiles of MnO₂@PPy electrodes. It can be found that capacity decreases with an increase in current density. And the platforms still exist at the current density of 3.2 A g⁻¹, revealing the reversible intercalation process of Zn species.

We further explore the cycling stability of two kinds of cells at 1 A g⁻¹. In Figure 4f, the Zn/MnO₂@PPy battery reaches a specific capacity of 174.5 mA h g⁻¹ after a short activation process (80 cycles). It maintains a specific capacity of 169.1 mA h g⁻¹ with a recovery rate of 96.4% after 1000 cycles. As a comparison, the MnO₂ electrode shows a capacity of 107.6 mA h g⁻¹ after 50 times cycling. And the reversible discharge capacity decreases to 88.0 mA h g⁻¹ after 1000 cycles. The results demonstrate that electrochemical performance and cycle stability can be optimized by using the PPy coating optimization strategy. The PPy coating on the surface of MnO₂ improves the conductivity of the sample and accelerates the charge transfer rate, thereby enhancing the electrochemical activity. Also, it avoids direct contact between the electrode and the electrolyte, which weakens the dissolution of active materials in aqueous electrolytes. Therefore, the host materials enhance structural stability and achieve excellent cycle performance. Table 2 summarizes the electrochemical properties of some previously reported manganese oxide electrode materials [18,30–33].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Discharge Capacity (Current Density)</th>
<th>Cyclic Stability (Cycles, Current Density)</th>
<th>Electrolyte</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>β-MnO₂</td>
<td>288 mAh g⁻¹ (0.1 C)</td>
<td>84.3% (1000, 4 C)</td>
<td>3 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>[28]</td>
</tr>
<tr>
<td>O₂-O₂-MnO₂</td>
<td>345 mAh g⁻¹ (0.2 A g⁻¹)</td>
<td>80% (2000, 5 A g⁻¹)</td>
<td>1 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>[18]</td>
</tr>
<tr>
<td>(Na, H₂O) δ-MnO₂</td>
<td>389 mAh g⁻¹ (0.2 A g⁻¹)</td>
<td>70% (700, 0.5 A g⁻¹)</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>[29]</td>
</tr>
<tr>
<td>HxMnO₂</td>
<td>281 mAh g⁻¹ (0.1 A g⁻¹)</td>
<td>93% (1000, 1 A g⁻¹)</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>[30]</td>
</tr>
<tr>
<td>MnO₂</td>
<td>148 mAh g⁻¹ (0.1 A g⁻¹)</td>
<td>91% (1000, 2 A g⁻¹)</td>
<td>2 M ZnSO₄ + 0.1 M MnSO₄</td>
<td>[31]</td>
</tr>
<tr>
<td>β-MnO₂@PPy</td>
<td>386 mAh g⁻¹ (0.1 A g⁻¹)</td>
<td>96% (1000, 1 A g⁻¹)</td>
<td>2 M ZnSO₄ + 0.2 M MnSO₄</td>
<td>This work</td>
</tr>
</tbody>
</table>

Figure 4. Electrochemical performance of the samples (a) CV curves at 0.1 mV s⁻¹ (b) Cycling performance at 0.1 A g⁻¹ (c) GCD curves (d) rate capability at different current densities (e) specific capacity at various current densities (f) long-term cycles at 1 A g⁻¹.

Table 2. Comparison of the recently reported manganese oxides materials in capacity and cycle performance.
After that, CV tests are conducted at various sweep speeds (0.1–0.5 mV s\(^{-1}\)) to study the reaction kinetics (Figure 5a). They possess similar shapes with an increase in the sweep speed. The relationship between the peak current (\(i\)) and scan rate (\(v\)) in the CV curves is governed by the following equation [34]:

\[
i = a v^b
\]

where \(a\) and \(b\) are adjustable parameters. When the \(b\) value approaches 0.5, the reaction belongs to a diffusion-controlled process. The \(b\) value close to 1 indicates a surface capacitive behavior [35]. The fitted \(b\) values are 0.51 (Peak 1), 0.56 (Peak 3), and 0.50 (Peak 4) (Figure 5b). It indicates that the capacity is mainly controlled by the diffusion process. In addition, it can be found that the \(b\) value of Peak 3 is higher than that of Peak 4. They represent the reduction reactions of H\(^+\) and Zn\(^{2+}\) intercalation, respectively. This means that the H\(^+\) intercalation process is more affected than Zn\(^{2+}\) by the surface capacitance effect [36]. Meanwhile, the capacitive contribution is calculated in Equation (2) [37]:

\[
i (V) = k_1 v + k_2 v^{1/2}
\]

As shown in Figure 5c, the diffusion behavior is hindered as the scanning speed increases. Therefore, the proportion of diffusion behavior decreases in charge storage.

The zinc ion diffusion coefficient (\(D_{\text{Zn}}\)) is also employed to study the capacity of Zn\(^{2+}\) storage by GITT curves. In Figure 5d, the discharge process is divided into two regions. Regions I and II correspond to the intercalation of H\(^+\) and Zn\(^{2+}\), respectively. Thereinto, the \(D_{\text{Zn}}\) of Region I is calculated to be \(10^{-9}\) to \(10^{-7}\) cm\(^2\) s\(^{-1}\). The \(D_{\text{Zn}}\) of H\(^+\) is two orders of magnitude higher than that of Zn\(^{2+}\) (Region II: \(10^{-10}\) cm\(^2\) s\(^{-1}\)). It accords with the above study on the redox reaction kinetics of MnO\(_2@\)PPy electrodes. Figure 5e shows the Nyquist curves of MnO\(_2\) and MnO\(_2@\)PPy batteries. The linear slope of MnO\(_2@\)PPy samples is higher than that of MnO\(_2\) materials in the low-frequency region. The result demonstrates that the electrical conductivity is significantly improved through the PPy coating strategy. The Ragone plot (Figure 5f) calculates the energy density of the MnO\(_2@\)PPy cells based on the following equation:

\[
E = QU/2m
\]
\[
P = iU/2m
\]

The Zn//MnO\(_2@\)PPy batteries possess an energy density of 192 Wh kg\(^{-1}\) at a power density of 50 W kg\(^{-1}\). It is superior to some Mn-based electrodes [25,38–40].
Finally, we use ex-suit XRD to investigate the electrochemical reaction mechanism of the MnO\textsubscript{2}@PPy electrodes. Figure 6a shows the different potential sites of the Zn/MnO\textsubscript{2}@PPy batteries during the first two cycles. In Figure 6b, multiple diffraction peaks appear at XRD patterns located at 28.7, 37.3, 41.0, 46.1, and 59.4°. They correspond to the (110), (101), (200), (210), and (220) planes, respectively. It indicates the electrodes maintain β-MnO\textsubscript{2} crystal structure. Some peaks are observed at 21.52°, 34.14°, and 58.68° in a fully discharged state. They correspond with MnOOH [41], ZnOH\textsubscript{6}·ZnSO\textsubscript{4}·xH\textsubscript{2}O [42], and ZnMn\textsubscript{2}O\textsubscript{4} materials [43], respectively. Moreover, the diffraction peaks of the new phases disappear when charged to 1.8 V. The results prove that the energy storage mechanism is a reversible co-insertion/extraction of H\textsuperscript{+} and Zn\textsuperscript{2+}.

Figure 6. (a) GCD curves (b) Ex-situ XRD patterns at various charge/discharge states.
4. Conclusions

In summary, we have prepared MnO@PPy nanowires by a simple hydrothermal route. Benefiting from the PPy-encapsulated strategy, the as-prepared samples possess excellent structural stability and conductivity. Moreover, the large specific surface area and pore volume provide a wide distribution of active sites and rapid ion transport channels. It improves the capability of Zn\(^{2+}\) insertion/extraction. Therefore, Zn/MnO@PPy batteries realize favorable specific capacity and fast reaction kinetics. Also, they possess high energy density and power density. It indicates that PPy coating is an effective method to enhance electrochemical performance. This work provides a prospective approach for designing AZIBs with practical applications.

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