**Electrochemical Performance of Hybrid Cationic Aqueous-Based Rechargeable Battery with Different Current Collectors and Electrolytes**

**Shang Chen,1 Fang Tang,1 Ting He,1 Huanhuan Zhang,1 Shanshan Deng,1 Yukang Li,1 Xianwen Wu①,1 Qiaobao Zhang,2,3 Yanhong Xiang②,4 and Wenbin Yan①**

1School of Chemistry and Chemical Engineering, Jishou University, Jishou Hunan 416000, China  
2Key Laboratory of Testing Technology for Manufacturing Process, Southwest University of Science and Technology, Mianyang 621010, China  
3Department of Materials Science and Engineering, College of Materials, Xiamen University, Xiamen 361005, China  
4School of Physics, Mechanical and Electrical Engineering, Jishou University, Jishou 416000, China

Correspondence should be addressed to Xianwen Wu; wxwcsu2011@163.com, Yanhong Xiang; 420228446@qq.com, and Wenbin Yan; jishouyanwenbin@163.com

Received 14 August 2019; Accepted 5 November 2019; Published 23 December 2019

Guest Editor: Yi Long

Copyright © 2019 Shang Chen et al. This is an open access article distributed under the Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited.

Different zinc foils as anode current collectors by electrowinning in various electrolytes with additives were prepared, which were evaluated through X-ray diffraction (XRD), scanning electron microscopy (SEM), float charge, and Tafel curve tests. The effect of different cathode current collectors, electrolytes, and the as-prepared zinc foils as the anode on the coulombic efficiency and the cycling performance of aqueous batteries were investigated. The results indicate that the initial coulombic efficiency and discharge capacity of the battery with 1 mol/L ZnSO₄ and 2 mol/L Li₂SO₄ are 94.31% and 105.7 mAh/g using graphite as the current collector, which are much higher than 68.20% and 71.0 mAh/g using conductive polyethylene, respectively, attributed to the smaller polarization and electrochemical transfer impedance ($R_{ct}$) of the former. However, the capacity retention of the latter is much higher than that of the former, especially using the high-concentration-lithium-based hybrid electrolyte, of which it is up to 74.63% even after 500 cycles. Moreover, the cycling performance of a battery with as-prepared zinc foil adding thiourea and gelatin into electrolyte during electrowinning is much better than that without additives, which is due to the smaller corrosion rate and side reaction.

1. Introduction

The energy problems have been paid more and more attention recently. All kinds of energy including solar energy have been developed [1–4]. Although lithium ion batteries (LIBs) based on organic electrolyte have gained great improvement as one of the most competitive energy conversion and storage systems with high energy/power density [5–7], their cost, safety, and large-rate charge/discharge characteristics are still the challenging issues which need to be solved in view of their large-scale use in electric vehicles and smart grids [8–13].

On the contrary, the aqueous rechargeable batteries are much safer and cheaper than LIBs since it was first proposed by Dahn’s group in 1994 [14]. Many efforts have been made to improve the electrochemical performance, and a series of aqueous rechargeable battery systems have been constructed and investigated [15–18]. However, the aqueous rechargeable batteries at present still suffer from very poor cycling and rate performance due to the side reactions such as the serious oxygen evolution and so on. The main bottleneck for the practical application is associated with selection about the electrode materials.

In recent years, many studies have showed that zinc as the anode exhibits excellent reversibility, high overpotential for hydrogen evolution in a weak acidic environment. Based on the defects and limitations of aqueous rechargeable...
lithium ion batteries (ARLIBs), a hybrid cationic aqueous-based rechargeable battery system based on lithium intercalation cathode with undoped LiMnO$_2$ and low equilibrium potential and low-cost zinc anode was first reported by Chen’s group [19]. Since then, they have attracted increasing concerns about aqueous batteries [20, 21] and the similar systems such as Na$_{0.44}$MnO$_2$/Zn [22], LiMnPO$_4$/Zn [23], LiCo$_{1/3}$Mn$_{1/3}$Ni$_{1/3}$PO$_4$/Zn [24], and so on [25–28].

However, the hydrogen evolution, zinc corrosion, and zinc dendrite could not be ignored in the hybrid cationic aqueous-based rechargeable battery, which takes place as the side reaction in the anode. Wu et al. [29] studied the effect of different zinc anodes on the electrochemical performance in the previous report and found that the surface morphology of zinc anode could affect the cycling performance.

In this paper, the different zinc foils were prepared by adding different additives into the electrolyte during electrowinning. The structure, morphology, and corrosion performance of the zinc anodes were compared, and the float charge and the cycling performance of batteries were discussed. Meanwhile, the effect of different cathode current collectors and electrolytes on the coulombic efficiency and the cycling performance of the battery were studied systematically.

2. Experimental

Zinc foil was prepared by electrowinning under the following conditions, aluminum plate and lead plate were used as the cathode and anode, respectively, and 58 g/L Zn$^{2+}$ and 150 g/L H$_2$SO$_4$ were used as the electrolyte, including some additives like thiourea (TU) and getatin (GL) in order to improve the morphology and the electrodeposition process of zinc.

The cathode electrode was prepared by casting slurries of LiMn$_2$O$_4$ (MTI Co.), KS-6 (Alfa Aesar Co.), and polyvinylidene fluoride (PVDF, Arkema Inc.) (86:7:7 wt.% ) in N-methyl-2-pyrrolidinone (NMP, Sigma-Aldrich Co.) on graphite or conductive polyethylene (abbreviated for PE) foil (SGL Group Co.) and dried in a vacuum oven at 60°C for 6 h. The cathode electrode with disks of 14 mm diameter was cut and then soaked in electrolyte under vacuum for 10–15 min. The electrolyte was prepared by dissolving zinc sulfate and lithium sulfate (analytical grade from Aldrich) in deionized water and adjusting the solution of pH to 4. Similarly, the zinc foil was used as an anode current collector, and AGM (Absorbed Glass Mat, NSG Corporation) wet with the above electrolyte was used as a separator. Lastly, the galvanostatic charge-discharge test for coin-type batteries was performed with a battery tester (Land in China) in the potential range of 1.4–2.1 V at room temperature at 4 C-rate. The float charge performance was measured to investigate the side reaction based on the result of float charge current density. First, the battery was cycled for 3 times at 0.2 C-rate between 1.4 and 2.1 V and then charged to 2.1 V and the last charged at 2.1 V with the constant voltage for 24 h at 60°C.

The Tafel curve was used to evaluate the corrosion performance in a three-electrode system. The working electrode is zinc anode after electrowinning (d = 5 mm), the counter electrode is platinum wire (d = 8 mm), and the reference electrode is Hg/Hg$_2$SO$_4$.

To identify the phase constitutions, the as-prepared zinc foils were characterized by X-ray diffraction (XRD, D8 Discover, Bruker) employing Cu Kα ($\lambda = 0.15406$ nm) radiation from 20° to 90°. Field emission scanning electron microscopy (FE-SEM, Leo-1530, Zeiss) with an accelerating voltage of 20 kV was conducted to investigate the morphology of zinc foil after electrowinning.

3. Results and Discussion

3.1. Effect of Different Cathode Current Collectors and Electrolyte on the Electrochemical Performances. The charge/discharge performance of LiMn$_2$O$_4$/Zn at 4 C-rate with two different cathode current collectors was evaluated between 1.4 and 2.1 V at room temperature. Obviously, with the cycle number increasing as shown in Figure 1, the discharge capacity of the battery with the same electrolytes using graphite as the cathode current collector fades gradually, while the capacity of the battery using PE increases at the beginning and then decreases correspondingly. Meanwhile, the battery using graphite shows higher charge/discharge capacities than that with PE, and the initial charge/discharge capacities of the former with 1 mol/L ZnSO$_4$ and 2 mol/L Li$_2$SO$_4$ are 112.1 mAh/g and 105.7 mAh/g, respectively, with a capacity retention of 67.22% even after 500 cycles, while that of the latter delivers 104.0 mAh/g and 71.0 mAh/g, respectively, and the capacity retention is up to 74.63% after 500 cycles compared to the initial discharge capacity, indicating a much better cycling stability than the battery with graphite as the current collector. However, from Figure 2(a), it can be seen that the charge capacities of both batteries using graphite and PE with the same electrolyte are nearly the same, while the initial coulombic efficiencies are 94.31% and 68.20%,
respectively. That is to say, the increased coulombic efficiency is due to the higher discharge capacity of the battery with graphite. In addition, the charge/discharge plateau was compared to each other in Figure 2(a). The charge plateau of the battery using PE is much higher, while the discharge plateau is much lower than that using graphite, indicating the larger polarization for the former with PE. In order to further confirm this, the electrochemical impedance spectroscopy (EIS) measurements simulated by Zview 2.0 were performed for the batteries before cycling with 1 mol/L ZnSO₄ and 2 mol/L Li₂SO₄, and the parameter results are listed in Table 1. As can be seen from Figure 2(c), the curve consists of two parts, a semicircle at high frequency and a sloping line at low frequency. The semicircle corresponds to the charge transfer resistance ($R_{ct}$) and double layer capacitance ($C_{dl}$). The sloping line represents the Warburg impedance ($Z_{w}$), which is related to the diffusion coefficient of Li⁺ in the solid phase.

<table>
<thead>
<tr>
<th>Current collector</th>
<th>$R_s$ (Ω)</th>
<th>$R_{ct}$ (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite</td>
<td>4.787</td>
<td>74.57</td>
</tr>
<tr>
<td>PE</td>
<td>8.613</td>
<td>347.7</td>
</tr>
</tbody>
</table>

However, the $R_{ct}$ is only 74.57 Ω for the battery with graphite, which is much smaller than that of 347.7 Ω with PE. The smaller polarization for the battery with graphite is mainly attributed to the smaller charge transfer resistance ($R_{ct}$) than that with PE.

Furthermore, the cycling performance and the charge-discharge curves of the batteries with different electrolytes are compared in Figures 1 and 2(b). When using the same cathode current collectors of PE, it delivers the higher initial
discharge capacity with high-concentration zinc-based electrolyte than that with high-concentration lithium-based electrolyte although the charge capacity is nearly the same, while the capacity retention of the former is much worse than the latter after 300 cycles, demonstrating the worse cycling stability, which is attributed to the high polarization with high-concentration zinc-based electrolyte. However, the coulombic efficiency of the former with 77.72% is much higher than the latter with 68.20%; the reason should be further investigated.

In fact, the charge-discharge mechanism is different from the traditional “rocking-chair” type battery [30, 31]. During the charge/discharge process, the hybrid lithium and zinc coexist in the electrolyte, and the lithium ions are deintercalated from the cathode of LiMn₂O₄ first and dissolved into the weak acid electrolyte, accompanied by releasing electrons. While zinc ions accept electrons from the external circuit, depositing onto the surface of a zinc current collector, of which the opposite process will take place during the discharge process. We note that the deposited material composition in the charge process is the same as the zinc current collector in the anode side. Previous research [29] indicates that it is easy for zinc to be corroded by acid electrolyte and the cycling performance of the battery with different surface morphologies of zinc is different. Herein, we prepared different zinc anodes by electrowinning below.

3.2. The XRD and SEM of Zinc during Electrowinning. Organic additives are most widely investigated for controlling the various qualities of electrowinning metal. It can usually reduce the grain size and change the morphology of deposited metals and the orientation growth of lattice plane using different additives. The reduction of grain size by different organic additives is mainly related to the synergistic effect [21]. Considering these, TU and GL have been used in this paper.

Figure 3 shows the XRD patterns of zinc foils. As can be seen, all peaks are indexed with that of the JCPDS 87-0713, and no impurity peaks can be found. However, compared with the electrowinning zinc from a sulfate solution containing 58 g/L Zn²⁺ and 150 g/L H₂SO₄ without additives, the (002), (100), and (101) peak intensity of zinc adding TU in the electrolyte has been increased a lot, which means that the preferred orientation of zinc particles happens in these planes after adding TU. Furthermore, XRD patterns of electrowinning zinc adding TU and GL have been characterized. To our surprise, the (002) plane has been inhibited to a certain extent, while the peak intensity of (100) and (101) has been increased continually. In order to find out the differences, SEM images of the electrowinning zinc have been tested, as indicated in Figure 4. The deposited zinc without additives is furry in Figure 4(a), which is due to the hydrogen evolution probably during the electrowinning. However, the zinc surface is very compact after adding the single GL in Figure 4(b), while the finest particles like leaves are formed due to the addition of GL in the electrolyte in Figure 4(c). As the mixture of TU and GL is added into the electrolyte in Figure 4(d), it shows a similar synergistic effect on the morphology, resulting in the smooth and compact zinc.

3.3. The Electrochemical Performance of Battery with Electrowinning Zinc. To further compare the difference of the zinc foils by electrowinning with or without mixed additives, galvanostatic charge/discharge was conducted between 1.4 and 2.1 V at 4 C-rate. As shown in Figure 5(a), there are two distinguished plateaus using the electrowinning zinc adding TU and GL that reflect two-stage Li-ion extraction/insertion behavior and are consistent with the previous reports [27]. In Figure 5(b), the capacity retentions after 300 cycles are 1.62%, 34.88%, and 45.63%, respectively, for three parallel batteries, of which the zinc current collectors were cut from the same piece of zinc foil by electrowinning from a sulfate solution containing 58 g/L Zn²⁺ and 150 g/L H₂SO₄ without additives in the electrolyte, and the consistency of the zinc is very bad. However, it is noted that the specific discharge capacity of the battery using electrowinning zinc adding TU and GL delivers 78.5 mAh/g after 300 cycles and the capacity retention is up to 70.88% with a much better stability.

A float charge test is used here for evaluating the side reactions of the battery; the float charge measurement with different electrowinning zinc was performed with 1 mol/L ZnSO₄ and 2 mol/L Li₂SO₄ as illustrated in Figure 6(a). Obviously, the float charge current densities are 13.0 and 9.5 mA/g for the battery using electrowinning zinc adding TU and GL compared with that without additives. Furthermore, the Tafel curves of different zinc current collectors were tested as shown in Figure 6(b). The corrosion potential (-1.427 V) of electrowinning zinc with mixed additives in the electrolyte in Table 2 is a little higher than that (-1.434 V) without additives, indicating that it is easy to be dissolved into the electrolyte for the former zinc, while the corrosion current (79.926 μA) of the former is much lower than the latter (2173.021 μA), which is consistent with the float charge result, demonstrating the smaller side reaction.
4. Conclusions

The hybrid cationic aqueous battery based on Li\(^+\) insertion/extraction at cathode and Zn\(^{2+}\) dissolution/deposition at anode is built up. It is found that graphite as the cathode current collector increases the initial coulombic efficiency and discharge capacity compared to that with PE, while high-concentration lithium-based hybrid electrolyte improve the cycling performance of the battery compared to that with high-concentration zinc-based hybrid electrolyte. The hybrid electrolyte additives improve the morphology of the zinc foil, furtherly improving the cycling performance of the battery.

Figure 4: SEM images of zinc foils by electrowinning (a) without additives; (b) gelatin; (c) thiourea; (d) gelatin+thiourea.

Figure 5: The cycling performance of LiMn\(_2\)O\(_4\)//Zn at 4 C-rate with different zinc foils by electrowinning as the anode.
The excellent reversibility and good cycling properties indicate that LiMn$_2$O$_4$//Zn based on hybrid aqueous electrolyte is a promising battery system for large-scale energy storage/conversion devices.

Data Availability

The data used to support the findings of this study are available from the corresponding author upon request. All of the data used to support the findings of this study are included within the article.

Conflicts of Interest

The authors declare that they have no conflicts of interest.

Authors’ Contributions

Shang Chen and Fang Tang contributed equally to this work.

Acknowledgments

This research was financially supported by the Undergraduate Innovation Project of Hunan Province (No. S201910531033), the Opening Project of the Key Laboratory of Testing Technology for Manufacturing Process, Southwest University of Science and Technology (Grant No. 16kjzk02), the Natural Science Foundation of Hunan Province (Nos. 2018JJ3415 and 2018JJ34157), the Key Project of Hunan Province Education Department (No. 18A285), the Key Planned Science and Technology Project of Xiangxi Tujia and Miao Autonomous Prefecture (No. 2018GX2001), the Program of Young Talent Support of Huxiang in Hunan Province (2018RS3098), and the National Natural Science Foundation of China (Nos. 21566010, 51704124, and 51762017), which were greatly appreciated.

References


