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An Artificial MnWO_4 Cathode Electrolyte Interphase Enabling Enhanced Electrochemical Performance of $\delta\text{-MnO}_2$ Cathode for Aqueous Zinc Ion Battery

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Abstract: The dissolution of active material in aqueous batteries can lead to a rapid deterioration in capacity, and the presence of free water can also accelerate the dissolution and trigger some side reactions that affect the service life of aqueous batteries. In this study, a MnWO_4 cathode electrolyte interphase (CEI) layer is constructed on a $\delta\text{-MnO}_2$ cathode by cyclic voltammetry, which is effective in inhibiting the dissolution of Mn and improving the reaction kinetics. As a result, the CEI layer enables the $\delta\text{-MnO}_2$ cathode to produce a better cycling performance, with the capacity maintained at 98.2% (vs. activated capacity at 500 cycles) after 2000 cycles at 10 A g^{-1} . In comparison, the capacity retention rate is merely 33.4% for pristine samples in the same state, indicating that this MnWO_4 CEI layer constructed by using a simple and general electrochemical method can promote the development of MnO_2 cathodes for aqueous zinc ion batteries.

Keywords: cathode electrolyte interphase; Mn dissolution; $\delta\text{-MnO}_2$ cathode; electrochemical performance; aqueous zinc ion battery



Citation: Tian, H.; Zhang, H.; Zuo, Y.; Ling, L.; Meng, T.; Zhang, H.; Sun, X.; Cai, S. An Artificial MnWO_4 Cathode Electrolyte Interphase Enabling Enhanced Electrochemical Performance of $\delta\text{-MnO}_2$ Cathode for Aqueous Zinc Ion Battery. *Materials* **2023**, *16*, 3228. <https://doi.org/10.3390/ma16083228>

Academic Editors: Huang Zhang and Yuan Ma

Received: 23 March 2023

Revised: 12 April 2023

Accepted: 15 April 2023

Published: 19 April 2023



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1. Introduction

At present, aqueous zinc ion batteries (AZIBs) have been widely studied for energy storage due to various advantages such as low cost, environmental benignity, and high safety performance [1–10]. So far, there have been various materials reported to be suitable as cathodes for AZIBs, including manganese-based materials [11–15], vanadium-based materials [16–20], and Prussian blue analogs [21–24]. Among them, manganese oxide has attracted widespread attention because of its abundance, low toxicity, high energy density, and structural diversity [25]. However, Mn dissolution issues still limit the cycling stability of manganese-based materials for AZIBs [26].

In the past decades, there has been some progress made in the research on how to improve the performance of electrode materials [27] and electrolytes [28] in resisting the dissolution of cathodes. Apart from the existing strategies, researchers have also discovered that the construction of an electrode-electrolyte interphase (EEI), including anode electrolyte interphase and cathode electrolyte interphase, can also help improve the energy density, cycling performance, and power density of batteries [29]. Therefore, building the cathode electrolyte interphase (CEI) surface protection layer is considered a feasible solution to the dissolution of cathodes. However, the research on CEI is still limited now due to the complexity of the cathode energy storage mechanism for AZIBs and the difficulty in characterizing various interfacial reactions [30].

Typically, the methods of CEI construction are divided into two categories: in situ formation and artificial synthesis. In recent years, some studies have reportedly been conducted on the in situ formation of CEI. Liang et al. proposed to perform electrochemical synthesis of the $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ layer in situ on a Ca_2MnO_4 cathode, which significantly improved the stability and service life of the battery [31]. Cao et al. also built an in situ CEI

layer of BaSO₄ on the Ba_{0.26}V₂O₅·0.92H₂O cathode of AZIBs, which reduced the dissolution of cathodes, thus leading to an excellent cycling performance [32]. Compared with the synthesis of CEI in situ, the artificial construction of CEI is much easier to manipulate. Xiong et al. synthesized a reduced graphene oxide (rGO) layer coated with α-MnO₂ powder, which improved both rate performance and cycling stability [33]. For different coating materials, powder coating may cause hindrances to ion transport to some extent. Unlike the powder coating as described above, the artificial CEI is more similar to cathode coating, where a layer is formed between the cathode and the electrolyte. Guo et al. reported a HfO₂ layer formed on a Zn₃V₂O₇(OH)₂·2H₂O electrode as an artificial solid electrolyte interphase. The HfO₂ layer was built by means of atomic layer deposition and is capable of isolating the electrode from the electrolyte, thereby reducing the dissolution of the cathode in the electrolyte and inhibiting the formation of insulated by-products. As a result, the capacity retention rate was considerably improved from 45% to 90% after 100 cycles at 0.1 A g⁻¹ [34]. Based on the construction of the CEI layer and its effect on cycling performance, there have been many studies carried out. For example, Paraffin [35], (Zn(OH)₂)₃(ZnSO₄)(H₂O)₅ [36], and SrCO₃ [37] have been reported as a kind of CEI layer. All these results demonstrate that the construction of CEI is effective in significantly enhancing the electrochemical performance of AZIBs.

For the manganese-based material used in AZIBs, the CEI layer can help prevent the cathode from direct exposure to the electrolyte, which suppresses Mn dissolution, thus maintaining high cycling performance and capacity. However, the strategy of CEI layer construction on manganese-based materials is not universal, and the economic benefits are unsatisfactory. In this study, a CEI layer of MnWO₄ is constructed on a δ-MnO₂ cathode through a facile electrochemical method (cyclic voltammetry), which not only inhibits the Mn dissolution but also improves the reaction kinetics. The key to this economical and efficient strategy lies in the dissolution of the Mn-based cathode in solutions that do not co-exist with Mn²⁺ ions. The prepared MnWO₄-coated δ-MnO₂ (denoted as W-MnO₂) shows an outstanding cycling performance (98.2% capacity retention vs. activated capacity at 500 cycles, after 2000 cycles at 10 A g⁻¹), indicating the effectiveness of the CEI construction strategy. In addition, the low-cost strategy of the CEI layer can be applied to other manganese-based AZIBs.

2. Experimental Section

2.1. Materials Preparation

The synthesis of the cubic MnCO₃ precursor was performed in the way as reported by others [38]. Firstly, 25 mL of 0.8 M NH₄HCO₃ aqueous solution, 25 mL of n-butanol, and 500 mL of cyclohexane were thoroughly mixed. Then, 20 g of cetyltrimethylammonium bromide (CTAB) was added into the mixed solution and stirred until it became clear. Next, 25 mL of 0.4 M MnSO₄ aqueous solution was added dropwise into the solution, which led to a white precipitate. Afterwards, the precipitate was collected through centrifugation, washed clean with alcohol and distilled water, respectively, and dried under vacuum at 100 °C to obtain white MnCO₃. To further oxidize MnCO₃ into MnO₂ [39,40], 1 g of the synthesized MnCO₃ precursor was added into 0.032 M of KMnO₄ aqueous solution. Then, the mixed solution was subjected to ultrasonic treatment for 30 min and stirred for 1 day. The δ-MnO₂ precursor was collected by centrifugation, washed (three times) with alcohol and distilled water, and finally dried at 75 °C.

The δ-MnO₂ cathode was produced by using N-methylpyrrolidone (NMP) as a solvent to disperse the precursor powder (δ-MnO₂, 70 wt%), conductive additive (Super P, 20 wt%), and binder (PVDF, 10 wt%), and was coated on carbon fiber paper. The loading density of the cathode was set to about 1.5 mg cm⁻².

The MnWO₄-coated δ-MnO₂ (W-MnO₂) was constructed in a conventional three-electrode configuration by cyclic voltammetry (CV) at a scan rate of 50 mV/s (negative scan from -0.6 to 0.6 V for 100 segments). The electrolyte was 0.1 mol/L Na₂WO₄ solution, and the pH value was adjusted to 7 by using H₂SO₄. The pristine δ-MnO₂ cathode was

treated as the working electrode of the three-electrode system, while Ag/AgCl and graphite were taken as the reference and counter electrodes, respectively. Finally, W-MnO₂ was obtained by washing it thoroughly with distilled water (three times) and drying it at 75 °C. The loading density of the W-MnO₂ cathode was approximately 0.5–1% higher than the pristine cathode.

2.2. Materials Characterization

X-ray diffraction (XRD, D8 Advance, Bruker, Cu K α) data were collected at a scan range of 5–70° (2 θ) and a step size of 0.02°. Both SEM (Sigma 300, Zeiss, operating voltage 5 kV) and HR-TEM (JEM-2100F, JEOL) were employed to examine the morphology and microstructure of the samples. X-ray photoelectron spectroscopy (XPS, PHI-1600, PerkinElmer) was performed to record the valence states of the samples loaded with Cu. The C 1s peak with a binding energy of 284.8 eV was used to calibrate all XPS spectra. Nitrogen adsorption measurements for Brunauer–Emmett–Teller (BET) analysis were tested at 77 K using an ASAP 2460.

2.3. Electrochemical Measurements

The 2032-type coin cells were assembled with prepared W-MnO₂ as the cathode, a Zn foil as the counter electrode, and an aqueous ZnSO₄ (3 M) solution with a MnSO₄ additive (0.2 M) as the electrolyte. The CV and EIS (100 kHz to 10 mHz) were measured on a CHI 660E electrochemical workstation. To conduct the CV tests at different scan rates, the peak current (*i*) and scan rate (ν) were determined through Equation (1) [41]:

$$i = a\nu^b, \quad (1)$$

where *a* and *b* represent variable parameters, and the *b*-value is obtained through the slope of log(*i*) vs. log(ν). Furthermore, the current contribution is divided into capacitive and diffusion contributions according to Equation (2) [42]:

$$i = k_1\nu + k_2\nu^{\frac{1}{2}}, \quad (2)$$

where *k*₁ and *k*₂ refer to the coefficients of proportionality for capacitive and diffusion contributions, respectively. The GCD curves, cycling performance, and GITT measurements were achieved by using the LAND CT2001A battery test system at room temperature. Moreover, the pause and rest time of GITT at 0.2 A g^{−1} lasted 10 min and 180 min, respectively. The diffusion coefficient can be determined through the following equation [43]:

$$D = \frac{4l^2}{\pi\tau}, \quad (3)$$

where *D* represents the diffusion coefficient, *l* indicates the diffusion length (cm) of active materials, and τ refers to the duration of the current pause (s). ΔE_s and ΔE_t represent the voltage difference by the current pulse and the voltage difference during the constant current pulse, respectively.

3. Results and Discussion

The MnWO₄-coated δ -MnO₂ (W-MnO₂) was obtained by means of the electrochemical treatment (cyclic voltammetry) conducted in a three-electrode system, as shown in Figure 1a. The working electrode was the δ -MnO₂ cathode. Figures S1 and S2 show the XRD and BET results of δ -MnO₂ powder, respectively. According to the N₂ adsorption isotherm, the specific area of δ -MnO₂ is 20 m² g^{−1}. To confirm the chemical composition of the CEI layer on the δ -MnO₂ cathode, XRD was performed for the W-MnO₂ cathode, as shown in Figure 1b. In addition to the weak characteristic peaks of δ -MnO₂, a peak appears at 18° corresponding to MnWO₄ (JCPDS No. 72-0478) after the CV process. Moreover, there are some other characteristic peaks of MnWO₄ observed at around 37° and 52°, indicating the

presence of the MnWO_4 after the CV process. It is suspected that the absence of the $\delta\text{-MnO}_2$ characteristic peaks may result from the limited crystallinity of $\delta\text{-MnO}_2$ and the strong diffraction peak of the carbon fiber paper. XPS was performed to determine the Mn valence during the CV process. As shown in Figure 1c, the splitting magnitude of two splitting components for the Mn 3s peak increases to 6.13 eV from 4.87 eV after the electrochemical treatment. In general, the Mn 3s peak consists of two multiple splitting components [11,44], with the oxidation state of Mn determined by the splitting magnitude ΔE , which is 6.0 eV and 4.7 eV for Mn^{2+} and MnO_2 (Mn^{4+}), respectively [45]. It can be found that the valence state of Mn shifted from +4 in $\delta\text{-MnO}_2$ to +2 in W-MnO_2 , indicating the formation of the MnWO_4 on the $\delta\text{-MnO}_2$ cathode. To determine the effect of MnWO_4 formation on the morphology of $\delta\text{-MnO}_2$ and the area of MnWO_4 distribution, SEM and TEM tests were performed. As shown in Figure 1d, the size of $\delta\text{-MnO}_2$ cubes is approximately 500 nm, and the morphology of the $\delta\text{-MnO}_2$ cubes is barely changed during the formation of MnWO_4 (Figure 1e). The EDS element mapping of W-MnO_2 (Figure 1f) shows a uniform distribution of element W on the surface of the MnO_2 cube, indicating that the MnWO_4 is formed uniformly on the surface of the $\delta\text{-MnO}_2$ cathode. Moreover, the HRTEM (Figure 1g) images of the W-MnO_2 surface show that lattice fringes are 0.22 nm and 0.249 nm, which correspond to the (121) and (002) crystal planes of MnWO_4 , respectively. Meanwhile, the (121), (002), and (-113) crystal planes of MnWO_4 are also observable in the results of selected area electron diffraction (SAED). Judging from the image of TEM (Figure 1f), it can be concluded that MnWO_4 was formed on the surface of $\delta\text{-MnO}_2$ cathodes as a CEI layer. Thus, it can be inferred that during the CV process, the $\delta\text{-MnO}_2$ surface is partially dissolved and rapidly reacts with WO_4^{2-} to form MnWO_4 during the CV process. Finally, the MnWO_4 CEI layer is successfully constructed on the $\delta\text{-MnO}_2$ cathode.

To examine the effect of the MnWO_4 CEI layer on the electrochemical performance of the $\delta\text{-MnO}_2$ cathode, a number of coin cells were assembled with 3 M ZnSO_4 + 0.2 M MnSO_4 as the electrolyte and zinc foil as the anode. Figure 2a presents the CV curves drawn for the W-MnO_2 cathode in the initial five CV cycles. The peak of the CV curves almost overlap, and their intensity increases at a slow pace after the second cycle, indicating that the W-MnO_2 cathode maintains excellent performance in electrochemical activity and reversibility after the construction of the CEI layer. For the W-MnO_2 cathode, the two cathodic peaks at 1.2 V and 1.4 V correspond to different stages of charge carrier insertion [15,46]. By drawing a comparison with the CV curves of the $\delta\text{-MnO}_2$ cathode (Figure S3), the increased intensity of cathodic peak shown by W-MnO_2 near 1.4 V is suspected to result from the improvement of reaction kinetics by the MnWO_4 CEI layer. The galvanostatic charge and discharge (GCD) curve of the W-MnO_2 cathode at 0.2 A g^{-1} (Figure 2b) shows a slow-paced improvement of capacity during cycling, suggesting the activation of the W-MnO_2 cathode. Afterwards, the W-MnO_2 cathode exhibits two-stage charge carrier intercalation, which is coherent with the CV results. In comparison with the GCD curves of the $\delta\text{-MnO}_2$ cathode (Figure S4) and W-MnO_2 cathode, there is almost no difference found between them, indicating that the CEI layer did not change the characteristics of the two-stage charge carrier intercalation. As confirmed by the cycling test conducted at 0.2 A g^{-1} (Figure 2c), the W-MnO_2 cathode is slowly activated by the MnWO_4 CEI layer. In the first 100 cycles, the capacity of the W-MnO_2 cathode improves slowly and stabilizes gradually at around 301.2 mAh g^{-1} , which is close to the initial capacity of the $\delta\text{-MnO}_2$ cathode. However, the capacity of the $\delta\text{-MnO}_2$ cathode declines continuously, which indicates that the MnWO_4 CEI layer improves the cycling stability significantly. As shown in Figure 2d, the rate capability of the W-MnO_2 cathode was evaluated after the activation process. To be specific, the W-MnO_2 cathode achieves a specific discharge capacity of 295.2, 260.5, 237.4, 210.3, 158.1, and 105.5 mAh g^{-1} at the current density of 0.2, 0.5, 1, 2, 5, and 10 A g^{-1} , respectively. The corresponding GCD curves of W-MnO_2 and $\delta\text{-MnO}_2$ cathodes at various current densities are presented in Figures S5 and S6, respectively. Compared with the corresponding values of the $\delta\text{-MnO}_2$ cathode that vary from 0.2 to 10 A g^{-1} , the capacity rate of W-MnO_2 and $\delta\text{-MnO}_2$ cathodes reaches 35.7% and 26.9%, respectively. It implies that the MnWO_4 CEI layer is conducive

to improving rate performance. Notably, the W-MnO₂ cathode achieves an outstanding performance in cycling stability at 10 A g⁻¹, as shown in Figure 2e, from which it can be seen that the capacity of the W-MnO₂ cathode slowly increases to 98.6 mAh g⁻¹ during activation (initial 500 cycles). After 2000 cycles, the W-MnO₂ cathode maintains a capacity retention rate of 98.2% (vs. the activated capacity at 500 cycles). However, the cycling capacity of the δ -MnO₂ cathode without the MnWO₄ CEI layer decreases rapidly after the initial 100 cycles. Subsequently, the capacity is gradually reduced to 35 mAh g⁻¹ after 2000 cycles. At this point, the capacity retention rate is merely 33.4%. This result confirms that the electrochemical cycling performance can be improved by the MnWO₄ CEI layer on the δ -MnO₂ cathode. Without any significant change in the structure and morphology of the cathode material, a thin layer constructed on the cathode surface is sufficient to improve the electrochemical performance significantly. The construction of the CEI layer is more universal than the adjustment for electrodes [12] and electrolytes [13]. In comparison with other reported CEI or SEI layers (Table S1, Supporting Information) [31–37], the MnWO₄ CEI layer, as constructed in this paper, leads to a significant improvement of high current cycle performance.

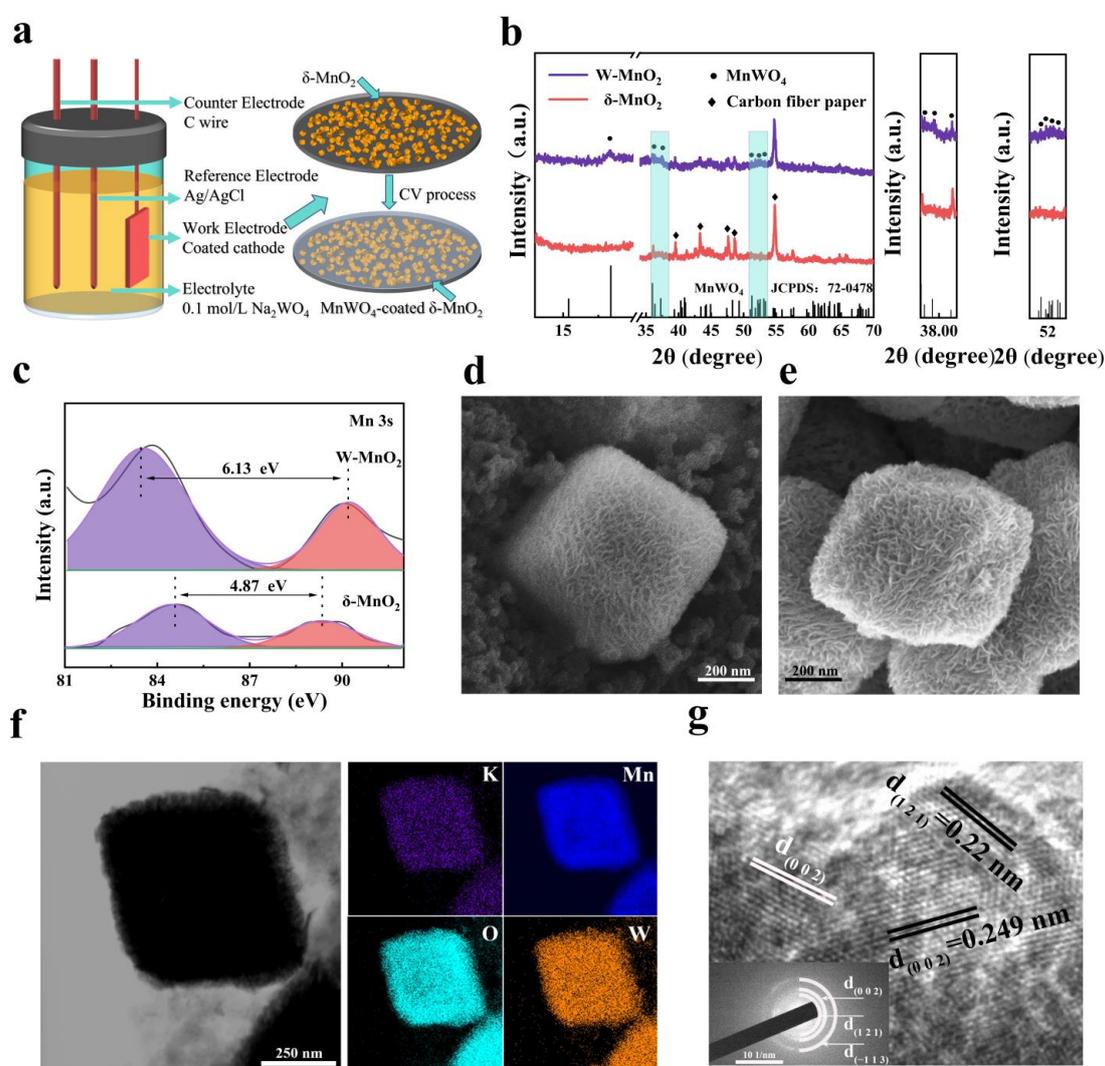


Figure 1. (a) Schematic illustration of the preparation process of MnWO₄ CEI layer. (b) XRD patterns of δ -MnO₂ and W-MnO₂. (c) High-resolution XPS spectra of Mn 3s region in δ -MnO₂ and W-MnO₂. (d,e) The morphology of (d) δ -MnO₂ and (e) W-MnO₂. (f) TEM image and the elemental mappings of W-MnO₂. (g) HRTEM image of MnWO₄ on the surface of W-MnO₂ and the corresponding SAED pattern (inset).

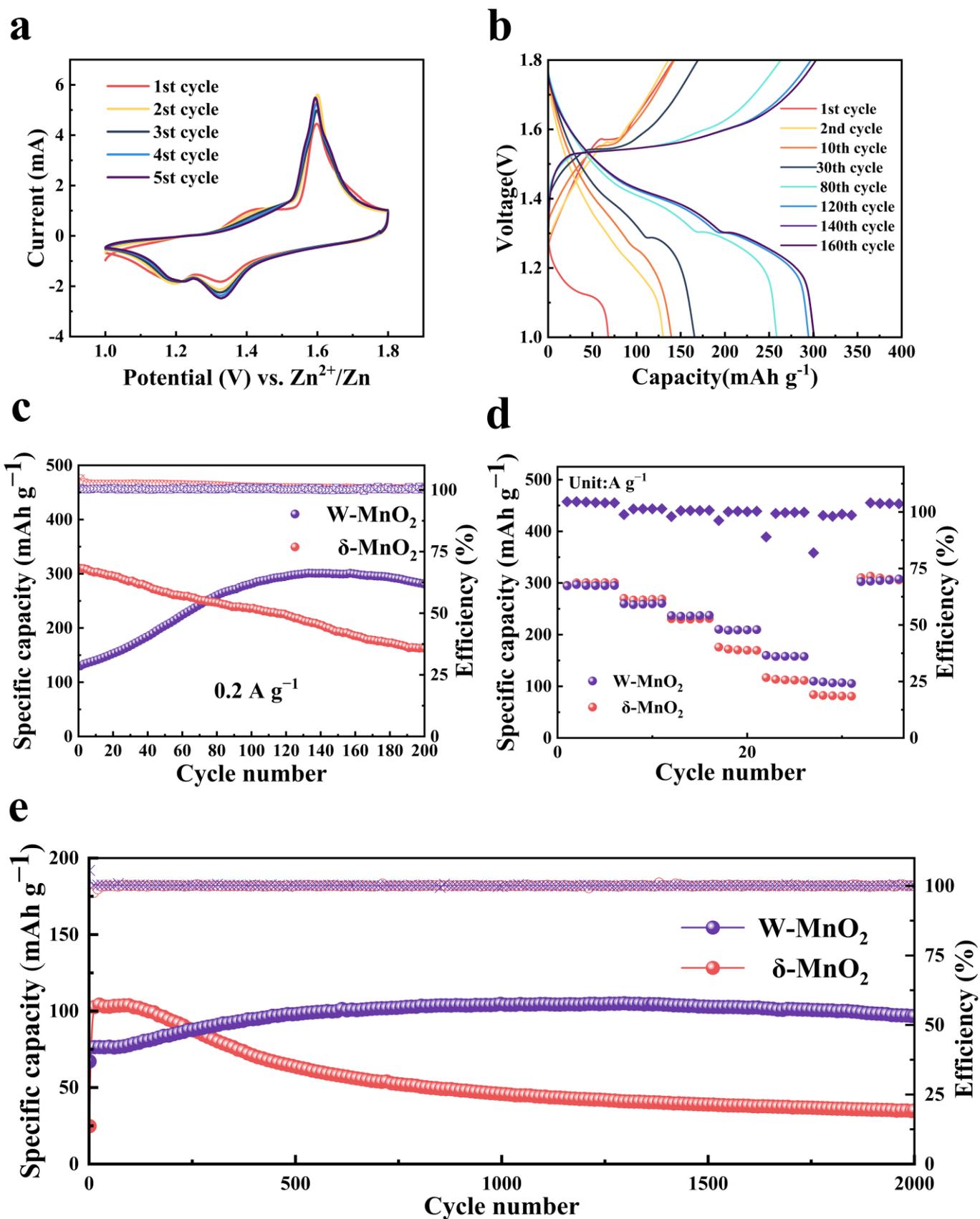


Figure 2. Electrochemical performance of δ -MnO₂ and W-MnO₂ cathodes. (a) CV curves of W-MnO₂ cathode at 1 mV s⁻¹. (b,c) Galvanostatic charge and discharge curves of the W-MnO₂ cathode and corresponding cycling performance at 0.2 A g⁻¹. (d) Rate capacity of δ -MnO₂ and W-MnO₂ cathodes with current density from 0.2 to 10 A g⁻¹. (e) Cycling performance at 10 A g⁻¹.

To explore the effect of the CEI layer on the mechanism of energy storage, the structure evolution of the W-MnO₂ cathode was analyzed by means of ex situ XRD, XPS, and TEM. Taking into account the BET result of δ -MnO₂ and the morphology change of the W-MnO₂ cathode, the storage mechanism was analyzed through bulk diffusion rather than surface adsorption. The ex situ XRD of the W-MnO₂ cathode (Figure 3a) reveals the incremental increase of characteristic peaks (around 10° and 33°) corresponding to Zn₄SO₄(OH)₆·xH₂O upon the entire discharge process, which evidences the occurrence of H⁺ insertion. This is consistent with the findings of previous research [47–50]. In addition, the formation of Zn₄SO₄(OH)₆·xH₂O nanosheet at the discharge stage is revealed by ex situ TEM (Figure S7). The results of TEM mapping show the presence of S, Zn, and O elements. Moreover, it can be seen from the SAED pattern (Figure S7) that the nanosheet is Zn₄SO₄(OH)₆·xH₂O. In contrast, H⁺ is gradually released from the W-MnO₂ cathode during the subsequent charge to 1.8 V, which is accompanied by the disappearance of Zn₄SO₄(OH)₆·xH₂O, as shown in Figure 3c. That is to say, reversible (de)insertion occurs to H⁺ throughout the storage process. The reversible storage of Zn²⁺ in the W-MnO₂ host is confirmed by the ex situ XPS performed on the acid-washed cathodes (Figure 3b). When the cathode is discharged to 1.3 V, there are two strong peaks emerging at 1045.8 and 1022.7 eV, which can be considered evidence of Zn²⁺ intercalation [51,52]. The peak strength of the Zn 2p further increases when the cathode is fully discharged (1 V), indicating the occurrence of Zn²⁺ intercalation throughout the discharge process. In addition, the stability of the MnWO₄ CEI film during the cycle process is indicated by TEM, HRTEM, and corresponding SAED (Figure S8) in full charge and discharge states. Therefore, H⁺/Zn²⁺ co-insertion is confirmed as the storage mechanism of the W-MnO₂ cathode during the discharge process.

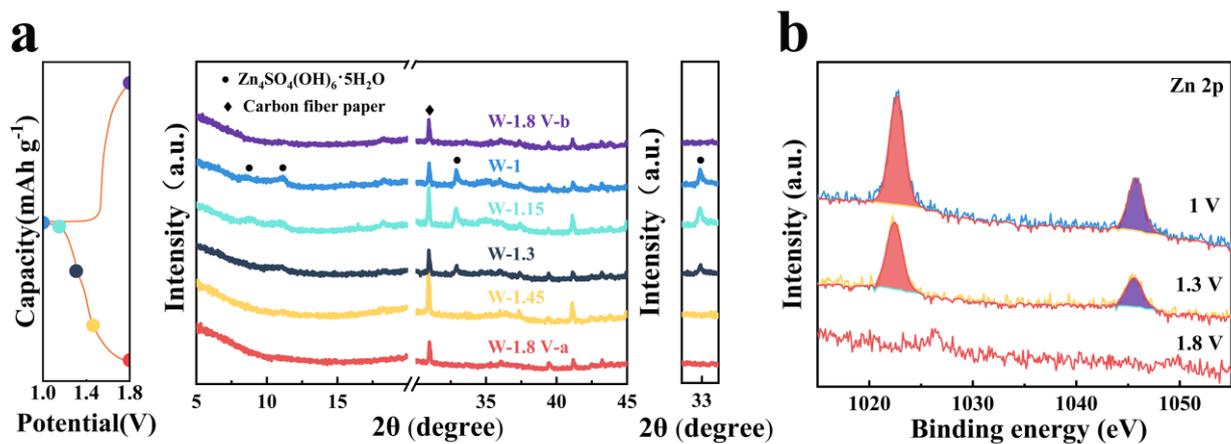


Figure 3. (a) Ex situ XRD analysis of W-MnO₂ cathode at various voltages. (b) XPS spectra of Zn 2p at different discharge stages.

When the mechanism of energy storage is investigated, the reversible formation of the by-product (Zn₄SO₄(OH)₆·xH₂O) on the cathode is worth noting. During the discharge process, the formation of Zn₄SO₄(OH)₆·xH₂O nanosheets could inhibit the electrochemical reaction in the cathode to some extent, as reported in other studies [34]. To demonstrate the impact of the by-product (Zn₄SO₄(OH)₆·xH₂O) on the charge transfer resistance, the EIS test was performed during the discharge process. The EIS data (Figure S9) of the W-MnO₂ cathode were fitted with the equivalent circuit template, as indicated by two semicircles in the medium and high-frequency regions. The semicircle at a high frequency is considered as the constructed MnWO₄ CEI layer and the Zn₄SO₄(OH)₆·xH₂O formed during the discharge process, while that at a medium frequency is attributed to the charge transfer resistance (R_{ct}). Figure 4a shows the variation and comparison of the R_{ct} during different stages of discharge for both W-MnO₂ and δ -MnO₂ cathodes. Apparently, the R_{ct} of δ -MnO₂ cathode increases rapidly (from 12.62 to 201 Ω), which suggests that the existence of Zn₄SO₄(OH)₆·xH₂O nanosheet plays a part in insulating the active material, which

impedes electron transport and increases internal resistance. For the W-MnO₂ cathode, the incremental of R_{ct} is more significant compared to the δ -MnO₂ cathode, indicating that the impact of Zn₄SO₄(OH)₆·xH₂O is mitigated by the presence of the MnWO₄ CEI layer. Moreover, the R_{ct} of the W-MnO₂ cathode is higher than that of the δ -MnO₂ cathode in the initial state, which is due to the relatively low conductivity of the MnWO₄ CEI layer.

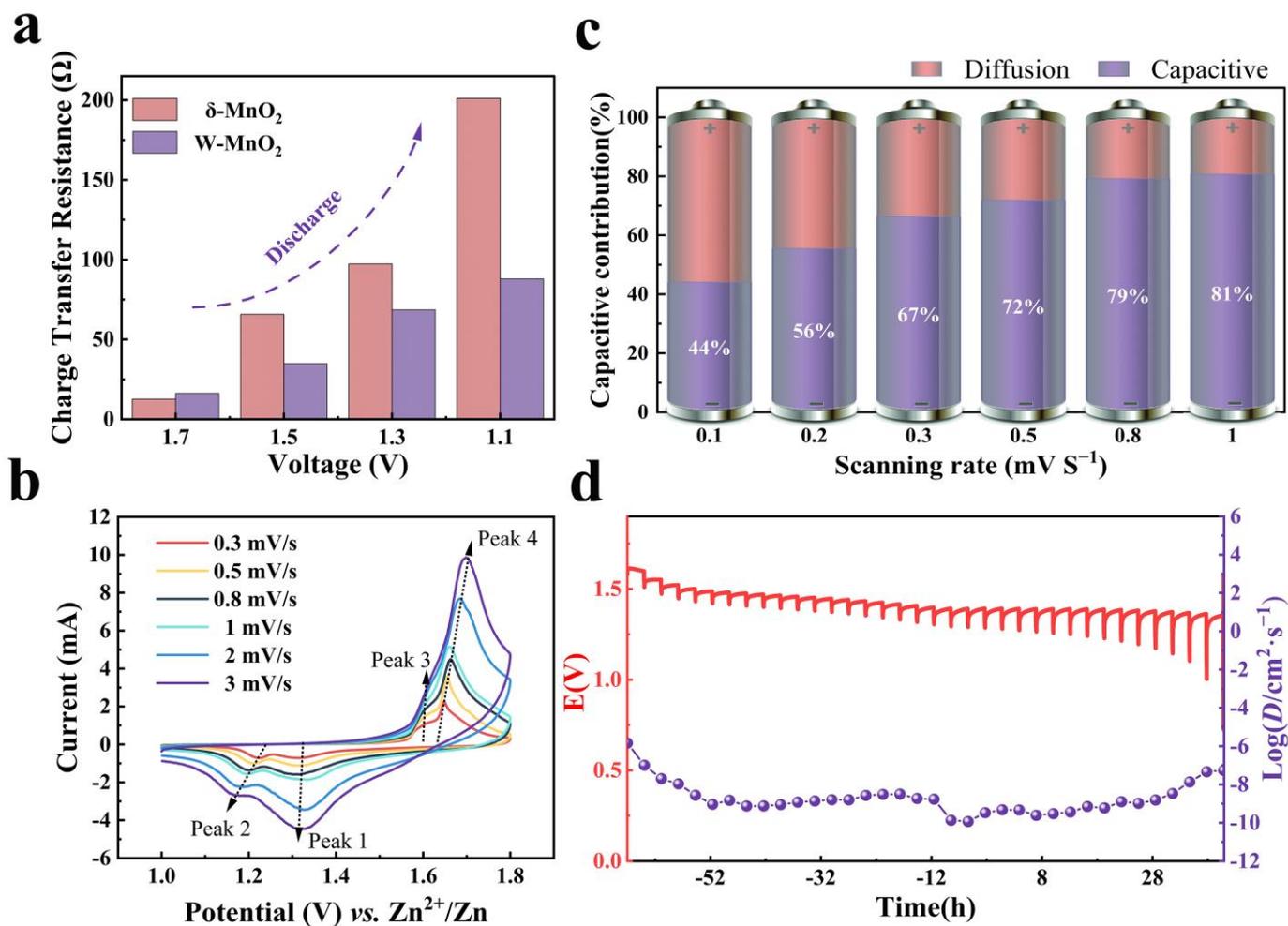


Figure 4. (a) The charge transfer resistance of W-MnO₂ and δ -MnO₂ cathodes at the discharge stage. (b) CV tests at various scan rates from 0.3 to 3 mV s⁻¹. (c) The proportion of capacitive contributions at different scan rates for W-MnO₂. (d) GITT curves of the W-MnO₂ cathode after activation during the discharge process.

To reveal the effect of the MnWO₄ CEI layer and Zn₄SO₄(OH)₆·xH₂O intermediate on the reaction kinetics of the W-MnO₂ cathode, the kinetics behaviors were analyzed by carrying out CV (cyclic voltammetric curve) tests at varying scan rates (0.3 to 3.0 mV s⁻¹), as shown in Figure 4b. For the W-MnO₂ cathode, the b-value (Figure S11a) of the three different peaks is calculated to be 0.80, 0.58, and 0.62 for peaks 1, 2, and 4, respectively. As for δ -MnO₂ cathode (Figures S10 and S11b), the b-value of peaks 1, 2, and 4 is 0.6, 0.41, and 0.53, respectively. The rise in the b-value of the W-MnO₂ cathode indicates that the improvement of reaction kinetics contributes to an excellent rate performance [53]. Furthermore, the capacitive-controlled contribution for the W-MnO₂ cathode is calculated to be 44.1%, 55.5%, 66.5%, 71.9%, 79.2%, and 80.7% at a scan rate of 0.1, 0.2, 0.3, 0.5, 0.8, and 1 mV s⁻¹, respectively (Figure 4c). The proportion of capacitive contribution to the whole capacity for the W-MnO₂ cathode at 1 mV s⁻¹ is 80.7%, suggesting that the pseudocapacitive behavior dominates the storage mechanism. Compared with the δ -MnO₂ cathode, the capacitive contributions of the δ -MnO₂ cathode (Figure S12) is less

significant at different scan rates, which reaffirms the improvement of reaction kinetics by the construction of the MnWO_4 CEI layer. Finally, to gain an insight into the diffusion dynamics, the galvanostatic intermittent titration technique (GITT) was applied to calculate the diffusion coefficient (D) at different stages of discharge (Figures 4d and S13). It can be found that the W-MnO_2 and $\delta\text{-MnO}_2$ cathodes experience two stages of discharge according to the D value. In the first one, D is between 10^{-8} and 10^{-9} . In the second one, D decreases to the range of 10^{-9} – 10^{-10} . It is noteworthy that the MnWO_4 CEI layer causes the diffusion coefficient of the W-MnO_2 cathode to be relatively more stable, which is always above 10^{-10} . To sum up, the MnWO_4 CEI layer of $\delta\text{-MnO}_2$ can mitigate the impact of $\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$ on the cathode and ensure sufficient reaction kinetics, which explains the better electrochemical performance.

4. Conclusions

In the present study, a MnWO_4 CEI layer was constructed on the $\delta\text{-MnO}_2$ surface by following a facile cyclic voltammetry method, which significantly reduced the impact of by-product ($\text{Zn}_4\text{SO}_4(\text{OH})_6 \cdot x\text{H}_2\text{O}$) on the cathode and improved the reaction kinetics during the process of $\text{H}^+/\text{Zn}^{2+}$ co-intercalation, thus enhancing the rate performance (295.2 mA at 0.1 A g^{-1} and 105.5 mA at 10 A g^{-1}). More importantly, the dissolution of Mn was inhibited in the AZIBs by the MnWO_4 CEI layer, thus ensuring its long cycling lifespan. Compared to the activated capacity at 500 cycles, the capacity retention rate at 10 A g^{-1} was maintained at 98.2% after 2000 cycles, which is much higher than the retention rate of 33.4% for the pristine MnO_2 cathode. This CEI construction strategy could contribute to exploring the stable Mn-based cathode of AZIBS.

Supplementary Materials: The following supporting information can be downloaded at: <https://www.mdpi.com/article/10.3390/ma16083228/s1>, Figure S1: XRD pattern of synthetic $\delta\text{-MnO}_2$ pristine powder; Figure S2: N_2 adsorption isotherms of $\delta\text{-MnO}_2$; Figure S3: CV curves of the $\delta\text{-MnO}_2$ electrode at 1 mV/s ; Figure S4: Galvanostatic charge and discharge curves of the $\delta\text{-MnO}_2$ cathode at 0.2 A g^{-1} ; Figure S5: Galvanostatic charge and discharge curves of W-MnO_2 cathode at various current densities ranging from 0.2 A g^{-1} to 10 A g^{-1} ; Figure S6: Galvanostatic charge and discharge curves of the $\delta\text{-MnO}_2$ cathode at various current densities ranging from 0.2 A g^{-1} to 10 A g^{-1} ; Figure S7: High-angle annular bright-field scanning TEM (HAABF-STEM) image and the corresponding elemental mappings, respectively; Figure S8: (a,b) TEM, HR-TEM and SAED pattern of W-MnO_2 : (a,c) charged (1.8 V). (b,d) discharged (1 V); Figure S9: EIS of (a) the W-MnO_2 and (b) $\delta\text{-MnO}_2$ cathodes at different stages during the discharge process. The equivalent circuit model for (c) the W-MnO_2 and (d) the $\delta\text{-MnO}_2$ electrode; Figure S10: CV tests for $\delta\text{-MnO}_2$ cathode at various scan rates ranging from 0.3 to 3 mV/s ; Figure S11: (a,b) b values of different peaks in CV curves for W-MnO_2 and $\delta\text{-MnO}_2$ cathodes: (a) W-MnO_2 . (b) $\delta\text{-MnO}_2$; Figure S12: The proportion of capacitive and diffusion contributions at various scan rates for $\delta\text{-MnO}_2$; Figure S13: GITT test of the $\delta\text{-MnO}_2$ cathode; Table S1: Comparison of cycling performance with other recent studies [31–37].

Author Contributions: Conceptualization, H.T. and S.C.; methodology, H.Z. (Huanlin Zhang), Y.Z. and X.S.; software, L.L. and T.M.; validation, H.T., H.Z. (Hang Zhang) and Y.Z.; investigation, H.T. and Y.Z.; resources, X.S. and S.C.; data curation, H.T.; writing—original draft preparation, H.T.; writing—review and editing, S.C.; supervision, S.C.; funding acquisition, S.C. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the National Natural Science Foundation of China (Nos. 51872197 and 52271246). This study was additionally funded by Tianjin Research Innovation Project for Postgraduate Students (Project No. 2021YJSB171).

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author.

Conflicts of Interest: The authors declare no conflict of interest.

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