



# Recent Advances in Aqueous Zn||MnO<sub>2</sub> Batteries

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## Abstract

Recently, rechargeable aqueous zinc-based batteries using manganese oxide as the cathode (e.g., MnO<sub>2</sub>) have gained attention due to their inherent safety, environmental friendliness, and low cost. Despite their potential, achieving high energy density in Zn||MnO<sub>2</sub> batteries remains challenging, highlighting the need to understand the electrochemical reaction mechanisms underlying these batteries more deeply and optimize battery components, including electrodes and electrolytes. This review comprehensively summarizes the latest advancements for understanding the electrochemistry reaction mechanisms and designing electrodes and electrolytes for Zn||MnO<sub>2</sub> batteries in mildly and strongly acidic environments. Furthermore, we highlight the key challenges hindering the extensive application of Zn||MnO<sub>2</sub> batteries, including high-voltage requirements and areal capacity, and propose innovative solutions to overcome these challenges. We suggest that MnO<sub>2</sub>/Mn<sup>2+</sup> conversion in neutral electrolytes is a crucial aspect that needs to be addressed to achieve high-performance Zn||MnO<sub>2</sub> batteries. These approaches could lead to breakthroughs in the future development of Zn||MnO<sub>2</sub> batteries, offering a more sustainable, cost-effective, and high-performance alternative to traditional batteries.

**Keywords** Aqueous Zn||MnO<sub>2</sub> batteries · Zinc-ion batteries · Zinc batteries · MnO<sub>2</sub>

## Introduction

Rechargeable aqueous zinc-based (Zn-based) batteries have recently garnered considerable attention due to their safety, sustainability, and cost-effectiveness [1–6]. Aqueous Zn||MnO<sub>2</sub> batteries, in particular, have been extensively studied since the early 1860s [7]. To unlock their full potential, advancing our understanding of electrochemical reaction mechanisms (ERMs) and achieving high energy density are crucial [8–10]. However, ERM diversity and the resulting conflicting views hinder further development [7, 11–13].

Moreover, the challenge of achieving high-energy-density pouch cells for Zn||MnO<sub>2</sub> batteries remains a considerable obstacle to commercialization [9, 14].

According to previous studies, six typical ERMs are revealed in aqueous Zn||MnO<sub>2</sub> batteries, contributing to the rational design of high-energy-density Zn batteries. They include (1) insertion/extraction of main Zn<sup>2+</sup> [15–17], (2) primary conversion of H<sup>+</sup> into MnOOH [18], (3) co-intercalation of H<sup>+</sup> and Zn<sup>2+</sup> [19–23], (4) main MnO<sub>2</sub>/Mn<sup>2+</sup> redox conversion in neutral environments [24, 25], (5) combination of MnO<sub>2</sub>/Mn<sup>2+</sup> redox conversion with H<sup>+</sup> and Zn<sup>2+</sup> co-intercalation in neutral environments [26], and (6) redox conversion of only MnO<sub>2</sub>/Mn<sup>2+</sup> in strong acid environments [27, 28]. These ERMs were reported based on the experimental results and/or characterization of the charge–discharge products by employing MnO<sub>2</sub> polymorphs as cathodes [7]. To achieve high-energy-density Zn batteries, two key factors must be considered: the areal capacity and discharge voltage of the battery. Therefore, the direction for achieving high energy density is to maximize the areal capacity and discharge voltage.

In this review, we comprehensively introduce different ERMs of aqueous Zn||MnO<sub>2</sub> batteries based on recently reported results. Further, we discuss the developments of

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electrolyte materials and innovative cell configurations for achieving high-energy-density Zn batteries. In addition, we compare the performance of various Zn||MnO<sub>2</sub> batteries to clearly state promising directions, remaining challenges, and prospective alternatives. Furthermore, we highlight various practical application scenarios of the recently reported flexible Zn||MnO<sub>2</sub> batteries. Finally, we clarify the key scientific problems limiting the further development of Zn||MnO<sub>2</sub> batteries and propose their solutions.

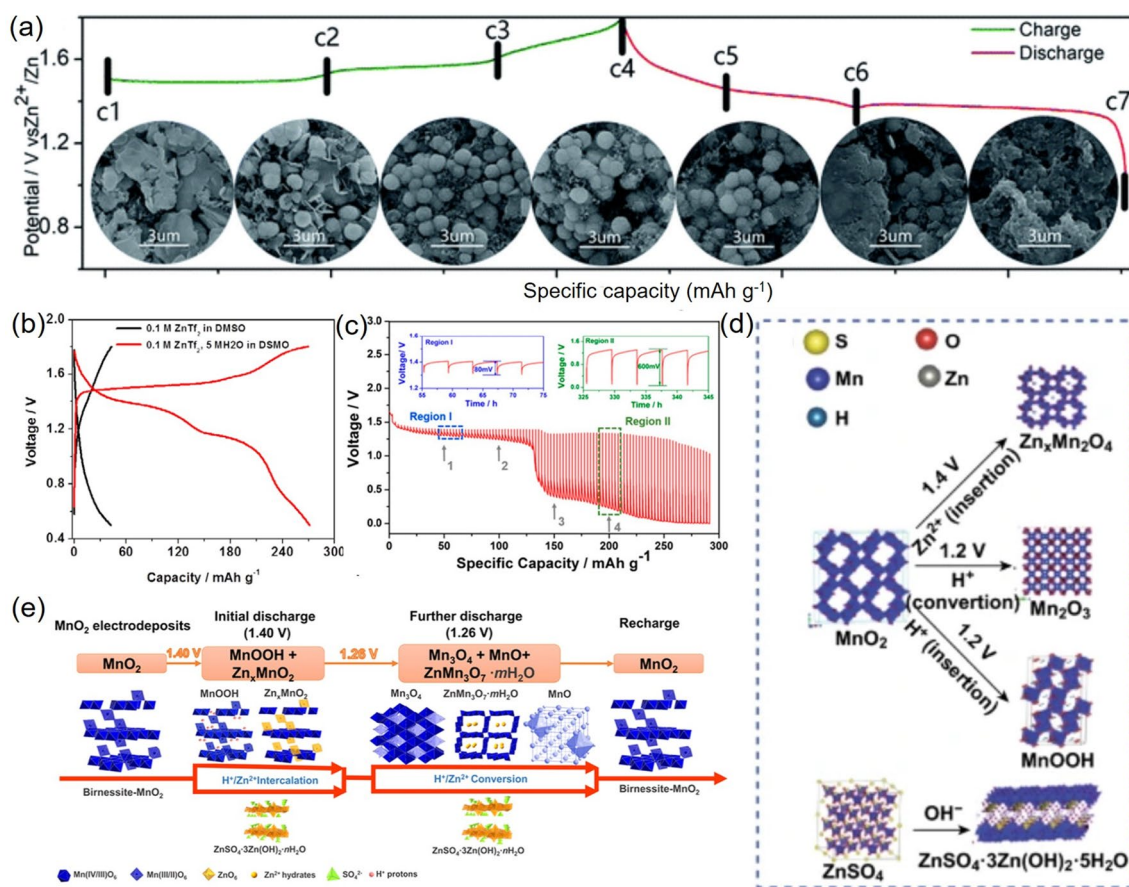
## ERMs of Zn||MnO<sub>2</sub> Batteries

Alkaline Zn–Mn batteries, with a well-established reaction mechanism, have been commercially available for a long time [29–31]. However, aqueous Zn||MnO<sub>2</sub> batteries, which can operate in mildly and strongly acidic conditions, exhibit various ERMs, posing challenges for researchers and

hindering the development of this battery system. Herein, we summarize the typical ERMs of aqueous Zn||MnO<sub>2</sub> batteries in detail, including the Zn<sup>2+</sup>/H<sup>+</sup> intercalation chemistry and MnO<sub>2</sub>/Mn<sup>2+</sup> conversion reaction mechanism.

## Zn<sup>2+</sup>/H<sup>+</sup> Intercalation Chemistry in Mildly Acidic Electrolytes

Aqueous Zn||MnO<sub>2</sub> batteries exhibit diverse ERMs. Zhao et al. [32] reported the dissolution and redeposition of Zn<sub>4</sub>(OH)<sub>6</sub>SO<sub>4</sub>·5H<sub>2</sub>O accompanied by the formation and dissolution of ZnMn<sub>2</sub>O<sub>4</sub> during the charge–discharge process of an aqueous Zn||MnO<sub>2</sub> battery (Fig. 1a), suggesting that only Zn<sup>2+</sup> intercalation/deintercalation occurs in the MnO<sub>2</sub> cathode. However, Pan et al. [18] found that Zn<sup>2+</sup> cannot be inserted into the MnO<sub>2</sub> crystal in the presence of an organic electrolyte unless water is introduced into the electrolyte during cycling (Fig. 1b), indicating that only H<sup>+</sup>



**Fig. 1** **a** Charge–discharge profile of an aqueous Zn||MnO<sub>2</sub> battery and the corresponding scanning electron microscopy images. Adopted with permission from Ref. [32]. Copyright 2018, Royal Society of Chemistry. **b** Charge–discharge profiles of an aqueous Zn||MnO<sub>2</sub> battery assembling by different electrolytes. Adopted with permission from Ref. [18]. Copyright 2016, Springer Nature. **c** Discharge galvanostatic intermittent titration technique profiles. Adopted

with permission from Ref. [19]. Copyright 2017, American Chemical Society. **d** Schematic of the phase transformation of a cathode. Adopted with permission from Ref. [20]. Copyright 2019, Springer Nature. **e**, Schematic of the crystal structures and redox reactions. Adopted with permission from Ref. [21]. Copyright 2019, American Chemical Society

intercalation occurs in aqueous Zn||MnO<sub>2</sub> batteries. Interestingly, Sun et al. [19] observed the phenomenon of Zn<sup>2+</sup>/H<sup>+</sup> co-insertion; however, they first observed H<sup>+</sup> intercalation (1.4 V) followed by Zn<sup>2+</sup> insertion (1.2 V) based on the discharge galvanostatic intermittent titration technique results (Fig. 1c). Notably, Ma et al. [33] reported that MnO<sub>2</sub> formed from L-Zn<sub>x</sub>MnO<sub>2</sub> acted as the host for H<sup>+</sup>, which was observed at 1.9–1.44 V after the occurrence of Zn<sup>2+</sup> intercalation (1.44–0.8 V). Conversely, Huang et al. [20] believed that Zn<sup>2+</sup> insertion occurred at a discharge plateau voltage of 1.4 V during the first discharge process (Zn<sub>x</sub>Mn<sub>2</sub>O<sub>4</sub> formation) rather than H<sup>+</sup> intercalation (occurred at 1.2 V based on monitoring XRD characteristic signal peaks of Mn<sub>2</sub>O<sub>3</sub> and MnOOH) (Fig. 1d). In fact, the occurrence of H<sup>+</sup>/Zn<sup>2+</sup> co-intercalation at 1.4 V and H<sup>+</sup>/Zn<sup>2+</sup> conversion at 1.26 V are more reasonable due to observe the appearance of byproducts at these discharge plateaus. Li et al. [21] supported this assumption by detecting Zn<sub>x</sub>MnO<sub>2</sub> + MnOOH at 1.4 V and Mn<sub>3</sub>O<sub>4</sub> + MnO + ZnMn<sub>3</sub>O<sub>7</sub> at 1.26 V (Fig. 1e). Obviously, unclear explanations regarding ERMs hinder the development of aqueous Zn||MnO<sub>2</sub> batteries. Accordingly, H<sup>+</sup>/Zn<sup>2+</sup> intercalation and conversion chemistry need to be revealed clearly in future explorations.

### Reaction Mechanism for MnO<sub>2</sub>/Mn<sup>2+</sup> Conversion

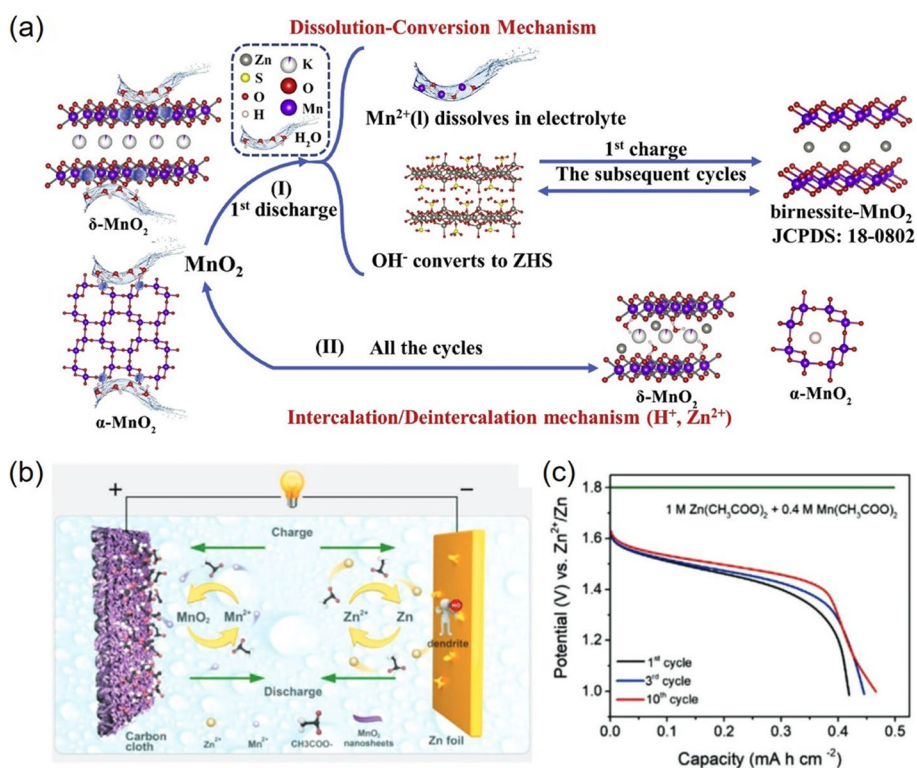
In addition to exploring genuine conditions for H<sup>+</sup>/Zn<sup>2+</sup> intercalation and conversion chemistry, new ERMs for

MnO<sub>2</sub>/Mn<sup>2+</sup> conversion offer the potential for obtaining high-performance aqueous Zn||MnO<sub>2</sub> batteries. We discuss the MnO<sub>2</sub>/Mn<sup>2+</sup> conversion chemistry in neutral or mildly acidic environments and strong acidic conditions separately. By doing so, we aim to better understand the involved chemical processes and identify optimal conditions for achieving high battery performance.

### Neutral and Mildly Acidic Environments

The low discharge plateau (< 1.5 V) of the Zn||MnO<sub>2</sub> battery involves the redox conversion of MnO<sub>2</sub>/Mn<sup>2+</sup>, complicating the understanding of electrode reaction mechanisms. Some studies have suggested that the primary reaction mechanism is the MnO<sub>2</sub>/Mn<sup>2+</sup> dissolution–deposition reaction, while the classical cation intercalation/deintercalation mechanism plays a negligible role (Fig. 2a) [24]. This suggestion is explained by the fact that MnO<sub>2</sub> reacts with active H<sub>2</sub>O, leading to subsequent appearance of Zn<sub>4</sub>SO<sub>4</sub>(OH)<sub>6</sub>·4H<sub>2</sub>O (ZHS) in the discharge process. Furthermore, the newly generated ZHS is converted to birnessite-MnO<sub>2</sub> with the help of Mn<sup>2+</sup> in the electrolyte in the charging process. Additionally, Bao et al. [34, 35] further elaborated on the role of ZHS in aqueous Zn||MnO<sub>2</sub> batteries. In detail, the main reversible capacity and improved cycle performance of this battery resulted from the conversion process occurring between

**Fig. 2** **a** Schematic of electro-chemical reaction mechanism in a Zn||MnO<sub>2</sub> battery. Adopted with permission from Ref. [24]. Copyright 2020, Elsevier. **b** Schematic of an aqueous Zn||MnO<sub>2</sub> battery in an acetate-based electrolyte and **c** the corresponding charge–discharge profiles of an aqueous Zn||MnO<sub>2</sub> battery in an acetate-based electrolyte. Adopted with permission from Ref. [25]. Copyright 2020, Wiley-VCH Verlag





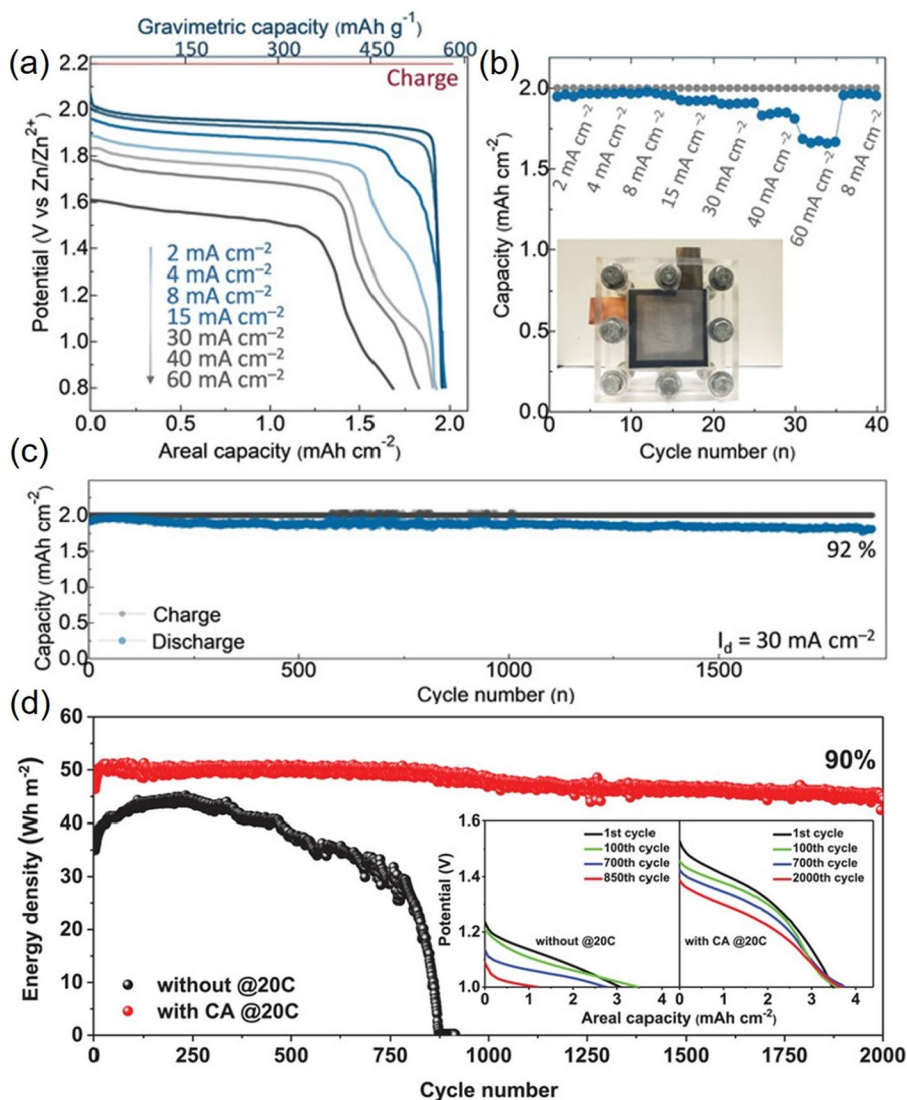
ZSH and  $\text{Zn}_x\text{MnO}(\text{OH})_2$  nanosheets at a sweeping voltage of  $> 1.6$  V. Here,  $\text{MnO}_2$  initiated ZSH formation but contributed negligibly to the apparent capacity.

In an acetate-based electrolyte, aqueous  $\text{Zn}||\text{MnO}_2$  batteries exhibited typical  $\text{MnO}_2/\text{Mn}^{2+}$  conversion chemistry, but a discharge plateau was obtained at approximately 1.4 V (Fig. 2b) [25]. According to the Nernst equation, the novel acetate-based electrolyte comprising 0.5 mol/L  $\text{ZnCl}_2$ , 0.5 mol/L  $\text{Mn}(\text{Ac})_2$ , 2 mol/L KCl, and 1.75 mol/L HAc enhanced the discharge plateau of an aqueous  $\text{Zn}||\text{MnO}_2$  battery to approximately 1.5 V because of the small decrease in pH compared to neutral electrolytes [36]. This enhancement is because  $\text{MnO}_2/\text{Mn}^{2+}$  conversion chemistry occurs at relatively low potentials in a mildly acidic environment. Additionally, with a further decrease in pH, the discharge plateau of the aqueous  $\text{Zn}||\text{MnO}_2$  battery increased slightly.

### Strong Acidic Environment

The potential for  $\text{MnO}_2/\text{Mn}^{2+}$  conversion depends on the pH value of the electrolyte. Chao et al. [27] revealed that adding 0.1 mol/L  $\text{H}_2\text{SO}_4$  to 1 mol/L  $\text{ZnSO}_4 + 1$  mol/L  $\text{MnSO}_4$  electrolyte solution resulted in a discharge plateau of 1.95 V based on  $\text{MnO}_2/\text{Mn}^{2+}$  conversion during chronoamperometric charging at 2.2 V vs.  $\text{Zn}/\text{Zn}^{2+}$  (Fig. 3a). The electrolytic  $\text{Zn}||\text{MnO}_2$  battery exhibited a superior rate performance of up to  $60 \text{ mA}/\text{cm}^2$  (Fig. 3b) and cycling stability for 1800 cycles at  $30 \text{ mA}/\text{cm}^2$  (Fig. 3c). Furthermore, Chuai et al. [28] modified the strong acid electrolyte of 0.1 mol/L  $\text{H}_2\text{SO}_4 + 1$  mol/L  $\text{ZnSO}_4 + 1$  mol/L  $\text{MnSO}_4$  by introducing 0.07 mmol/L polyvinylpyrrolidone as a cationic accelerator (CA). The assembled  $\text{Zn}||\text{MnO}_2$  battery demonstrated an energy density of  $50 \text{ W h}/\text{m}^2$  over 2000 cycles (Fig. 3d, e) because of efficient cation migration in the electrolyte and effective charge transfer at the electrode–electrolyte

**Fig. 3** **a** Galvanostatic discharge curves and **b** the rate capability at various rates and **c** long-cycle performance of an aqueous  $\text{Zn}||\text{MnO}_2$  battery in a modified strong acid electrolyte. Adopted with permission from Ref. [27]. Copyright 2019, Wiley-VCH Verlag. **d** Long-cycle performance of an aqueous  $\text{Zn}||\text{MnO}_2$  battery in a modified strong acid electrolyte. Adopted with permission from Ref. [28]. Copyright 2022, Wiley-VCH Verlag



interface, facilitated by CA introduction. H<sup>+</sup> concentration considerably influences the potential of MnO<sub>2</sub>/Mn<sup>2+</sup> conversion. Although the high discharge plateau (1.95 V) of the aqueous Zn||MnO<sub>2</sub> battery was achieved under strong acid conditions, anode corrosion limits the further development of this system. Therefore, developing high-voltage MnO<sub>2</sub>/Mn<sup>2+</sup> conversion reactions in neutral or mildly acidic environments is urgently needed.

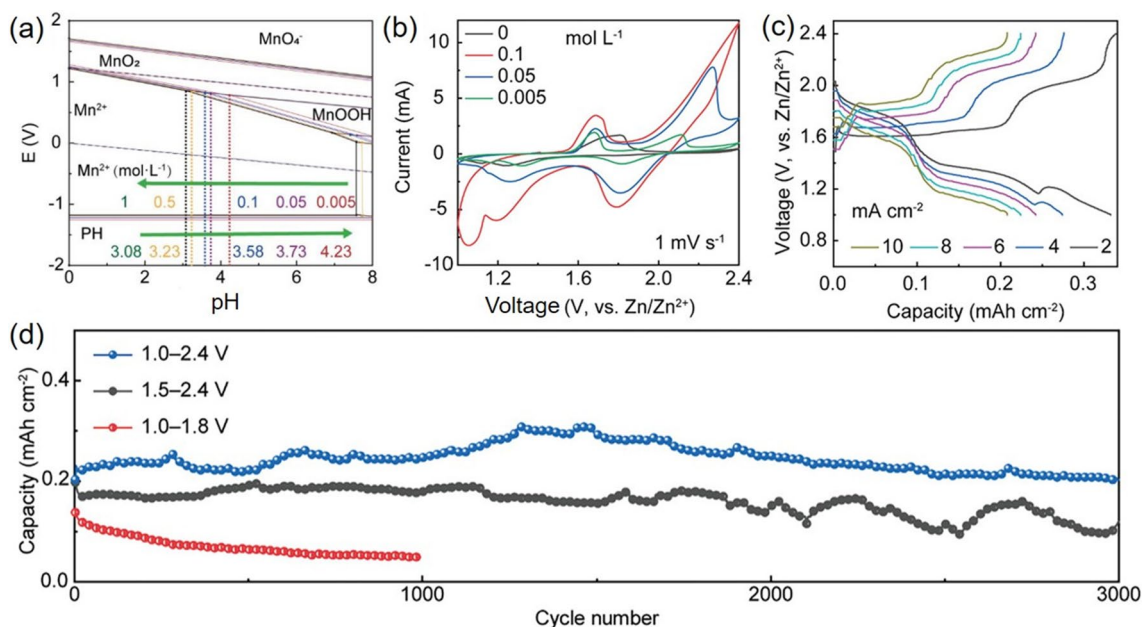
### Zn<sup>2+</sup>/H<sup>+</sup> Intercalation Chemistry and MnO<sub>2</sub>/Mn<sup>2+</sup> Conversion

The development of high-voltage Zn||MnO<sub>2</sub> batteries in neutral and mildly acidic environments can promote their practical application. On the one hand, these conditions help realize high discharge plateaus, resulting in high energy densities. On the other hand, it can alleviate the issue of anode corrosion in strong acids. Shen et al. [26] calculated the critical concentration of Mn<sup>2+</sup> in an electrolyte for tuning the triple point (MnO<sub>2</sub>-MnOOH-Mn<sup>2+</sup>) from low to high pH values based on thermodynamic calculations. As shown in Fig. 4c, 0.005 mol/L Mn<sup>2+</sup> allowed for MnO<sub>2</sub>/Mn<sup>2+</sup> conversion. The cyclic voltammetry curve of the Zn||MnO<sub>2</sub> battery using 0.005 mol/L Mn<sup>2+</sup> exhibited excellent redox peaks corresponding to MnO<sub>2</sub>/Mn<sup>2+</sup> conversion (Fig. 4b). Note that the redox potential for MnO<sub>2</sub>/Mn<sup>2+</sup> conversion in a neutral environment exhibited a

large variation, namely, from 1.4 to 1.8 V (vs. Zn/Zn<sup>2+</sup>), which could be attributed to differences in Mn<sup>2+</sup> activity in different electrolytes. Furthermore, H<sup>+</sup> increases the activity of Mn<sup>2+</sup> and the reaction potential of Mn<sup>2+</sup>/MnO<sub>2</sub> redox reactions. In neutral electrolytes, by tuning the activity of Mn<sup>2+</sup> (e.g., coordination with water molecules or additives, desolvation, and so on), the reaction potential for MnO<sub>2</sub>/Mn<sup>2+</sup> conversion can also be tuned. Additionally, the rate performance of the Zn||MnO<sub>2</sub> battery using 0.005 mol/L Mn<sup>2+</sup> displayed a distinct 1.75 V discharge plateau resulting from MnO<sub>2</sub>/Mn<sup>2+</sup> conversion (Fig. 4c). In addition, the cyclic stability of Zn||MnO<sub>2</sub> batteries over 3000 cycles demonstrated considerable potential for practical application. However, the low areal capacity and harsh reaction conditions of this strategy challenge its further development. To overcome these limitations, future research should focus on exploring new electrolytes for achieving a large-scale, high-voltage aqueous Zn||MnO<sub>2</sub> battery in neutral or mildly acidic environments.

### High-Energy-Density Zn||MnO<sub>2</sub> Batteries

The development of high-energy-density Zn||MnO<sub>2</sub> batteries is crucial for their commercialization. To achieve this goal, two key factors must be realized: high areal capacity and discharge voltage plateau.



**Fig. 4** **a** E–pH diagram of MnO<sub>2</sub> for different Mn<sup>2+</sup> concentrations. **b** Cyclic voltammetry curves of Zn||MnO<sub>2</sub> batteries performed at 1 mV/s in electrolytes with MnSO<sub>4</sub> concentrations of 0, 0.005, 0.05,

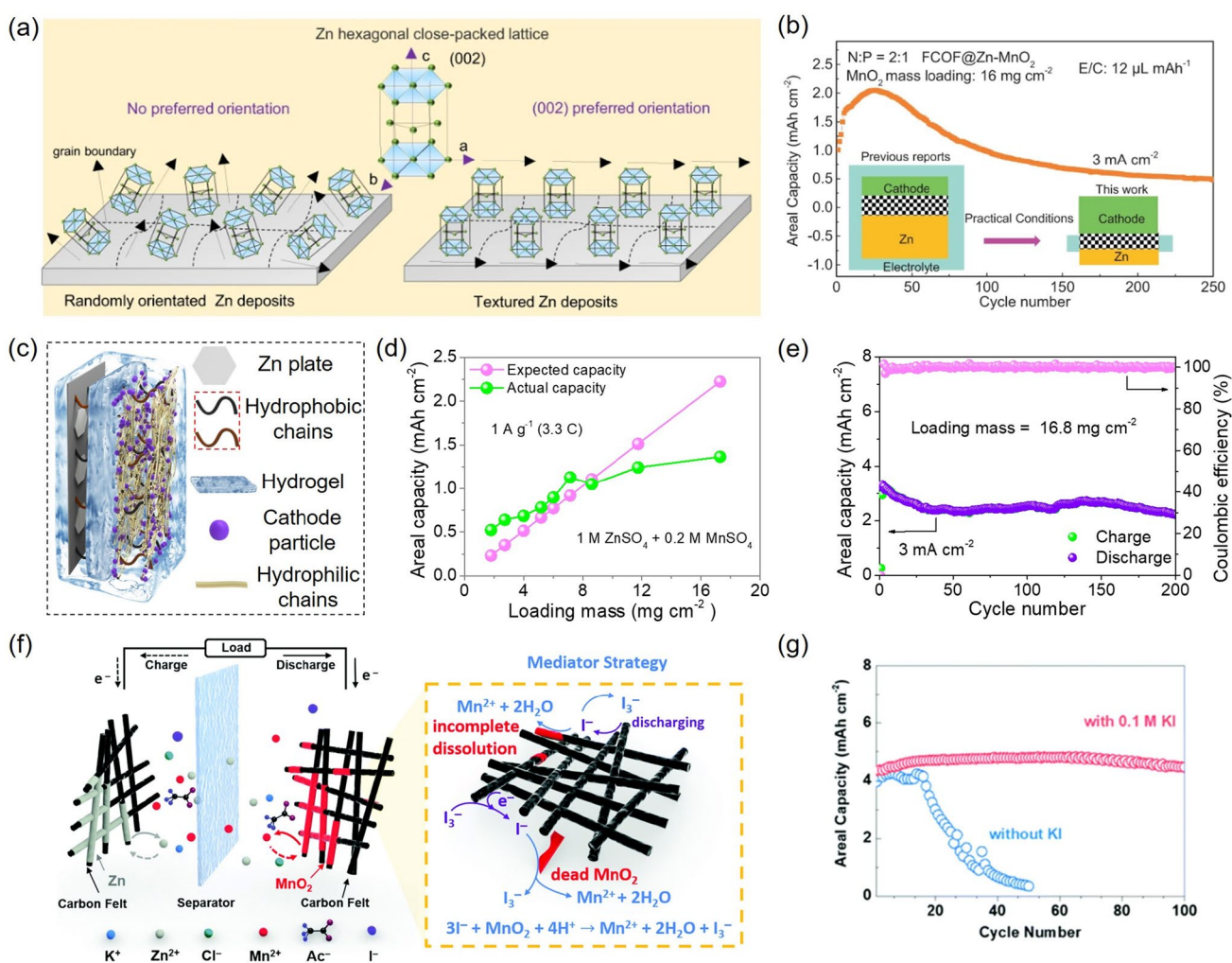
and 0.1 mol/L. **c** Charge–discharge curves at different current densities. **d** Cycle stability of Zn||MnO<sub>2</sub> batteries. Adopted with permission from Ref. [26]. Copyright 2021, Wiley-VCH Verlag

## High Areal Capacity

### Electrolyte Designs

Two major challenges hinder the practical implementation of Zn||MnO<sub>2</sub> batteries: the underutilization of high-loading materials at the cathode side and Zn dendrite growth at the anode side. To address these issues, researchers have turned to electrolyte engineering. Zhao et al. [37] developed and fabricated a two-dimensional fluorinated-porous covalent organic framework (FCOF) film as a protective layer on the Zn surface. The strong interaction between fluorine (F) in FCOF and Zn reduces the surface energy of the Zn (002) crystal plane, enabling its preferential growth during

the electrodeposition process. Consequently, Zn deposits exhibited a horizontally arranged platelet morphology with the preferred (002) orientations (Fig. 5a). The pouch cell assembled using a modified Zn anode demonstrated an areal capacity of > 0.5 mA h/cm<sup>2</sup> for 250 cycles (Fig. 5b). Furthermore, Li et al. [38] designed an amphiphilic hydrogel electrolyte that effectively used cathode materials and regulated Zn (002) plate deposits (Fig. 5c). At a high loading of MnO<sub>2</sub> of 17.3 mg/cm<sup>2</sup>, the utilization rate of cathode materials remained high at 62.7% with a remarkable peak areal capacity of approximately 1.40 mA h/cm<sup>2</sup> at 3.3 C (Fig. 5d). Hence, the assembled Zn||MnO<sub>2</sub> battery exhibited an areal capacity of > 2 mA h/cm<sup>2</sup> for 200 cycles (Fig. 5e). Notably, with an increase in the MnO<sub>2</sub> loading mass, cathode material



**Fig. 5** **a** Schematic of the preferred orientations of Zn deposits. **b** Schematic of a flexible transparent battery assembly. Adopted with permission from Ref. [37]. Copyright 2021, Springer Nature. **c** Targeted permeation of cathodes and horizontally controlled Zn deposition using amphiphilic hydrogel electrolytes with brush-like structures in a water environment. **d** Expected and actual areal capacities when loading different masses of MnO<sub>2</sub>. **e** Cycle performance of

Zn||MnO<sub>2</sub> batteries assembled using an amphiphilic hydrogel electrolyte with 16.8 mg/cm<sup>2</sup> of MnO<sub>2</sub> loading mass at 3 mA/cm<sup>2</sup>. Adopted with permission from Ref. [38]. Copyright 2023, Elsevier. **f** Schematic of a Zn-manganese battery and a conceptual diagram of KI promoting the MnO<sub>2</sub> dissolution process. **g** Cycling performance of aqueous Zn||MnO<sub>2</sub> batteries. Adopted with permission from Ref. [39]. Copyright 2021, Royal Society of Chemistry



utilization and cycle stability decreased rapidly. In general, a Zn||MnO<sub>2</sub> battery will achieve thousands of cycles and 100% utilization of cathode materials when the loading mass ranges between 0 and 3 mg/cm<sup>2</sup>. Therefore, this performance level does not meet the standard of commercialization. When mass loading reached > 16.8 mg/cm<sup>2</sup>, cycle stability and cathode utilization rapidly decreased to < 200 cycles and < 62.7%, indicating the need to improve these factors further in future studies employing high-loading mass. In addition, introducing redox mediators, such as I<sup>-</sup> [39, 40] or Br<sup>-</sup> [41], promoted MnO<sub>2</sub> dissolution, achieving high areal capacity. Lei et al. [39] proposed that when KI was added to the electrolyte, it formed I<sub>3</sub><sup>-</sup>, activating inactive MnO<sub>2</sub> (Fig. 5f). The assembled Zn||MnO<sub>2</sub> battery exhibited an areal capacity of > 4 mA h/cm<sup>2</sup> for 100 cycles (Fig. 5g).

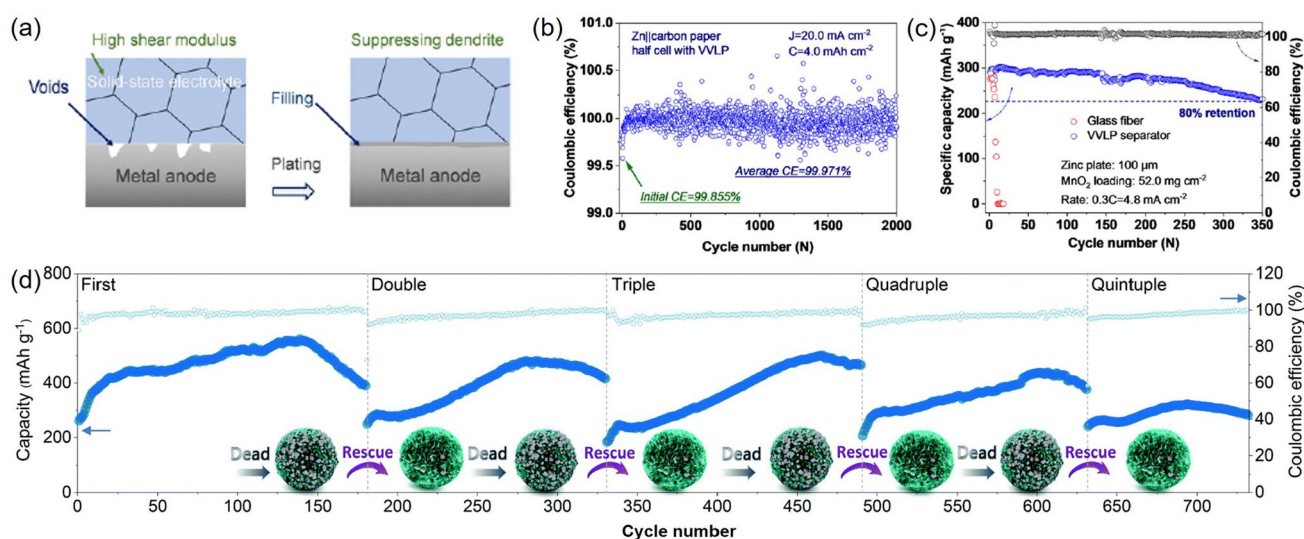
### New Configuration

In addition to electrolyte engineering, innovative cell configurations have also enhanced the electrochemical performance of aqueous Zn||MnO<sub>2</sub> batteries. Yang et al. [42] developed sustainable high-energy aqueous Zn||MnO<sub>2</sub> batteries by exploiting stress-governed metal electrodeposition and fast Zn<sup>2+</sup> diffusivity. Figure 6a shows schematics of an entire Zn-based battery under external mechanical stress, leading to improved electrochemical performance. Specifically, its half-cell delivered an initial coulombic efficiency (CE) of 99.86% and an average CE of 99.97% at an aggressive current density of 20.0 mA/cm<sup>2</sup> and areal capacity of 4.0 mA h/cm<sup>2</sup>, with negligible Zn loss during repeated

cycles (Fig. 6b). Furthermore, full cells exhibited a specific capacity of 300 mA h/g even when loading 52 mg/cm<sup>2</sup> of MnO<sub>2</sub>, demonstrating the substantial benefits of stress (Fig. 6c). In another novel configuration of Zn||MnO<sub>2</sub> batteries, the repeated addition of new electrolytes activated inactive MnO<sub>2</sub>, promoting their long-term cycling performance (Fig. 6d) [43].

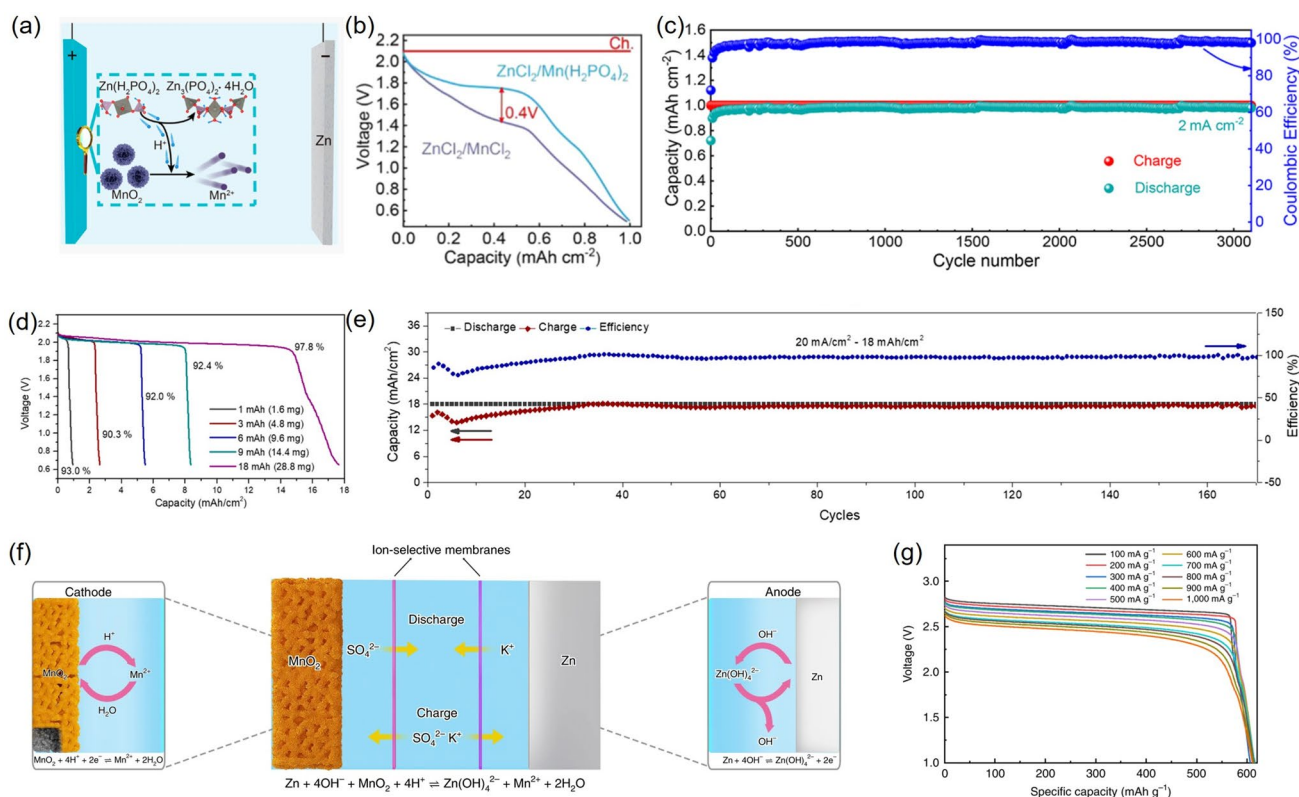
### High Voltage

Improving the high discharge plateau of aqueous Zn||MnO<sub>2</sub> batteries is crucial for developing high-energy-density cells. However, MnO<sub>2</sub>/Mn<sup>2+</sup> conversion heavily depends on proton concentrations, causing corrosion issues in the Zn anode. To address this challenge, a strategy is urgently needed to facilitate the interaction of protons with the cathode without affecting the Zn anode. To address this issue, Mateos et al. [44] first proposed the use of weak Brønsted acids to achieve a highly reversible conversion of MnO<sub>2</sub>/Mn<sup>2+</sup> in a mild environment. This approach was further developed by Liu et al. [45], who created a phosphate proton reservoir that only provided protons to the MnO<sub>2</sub> cathode without affecting the Zn anode (Fig. 7a). This innovative design yielded a high discharge plateau of 1.75 V (Fig. 7b) and maintained cycling stability over 3000 cycles (Fig. 7c). In addition to electrolyte innovations, exploiting new cell configurations is another important development direction for commercializing aqueous Zn||MnO<sub>2</sub> batteries. Cui et al. [46, 47] designed a proton-shuttle-shielding and hydrophobic-ion-conducting membrane to separate the neutral anode and acidic cathode,



**Fig. 6** **a** Schematic of an entire Zn-based battery under mechanical strength. **b** Coulombic efficiency (CE) profiles with the initial and average CE values for Zn electrodeposited on a carbon paper current collector. **c** High-capacity cycle performance of Zn||MnO<sub>2</sub> coin cells (MnO<sub>2</sub> loading: 52 mg/cm<sup>2</sup>). Adopted with permission from Ref.

[42]. Copyright 2023, Royal Society of Chemistry. **d** Electrochemical performance of rescued Ba<sup>2+</sup>-pillared  $\delta$ -MnO<sub>2</sub> at a current density of 0.3 A/g with rescue for five recycles. Adopted with permission from Ref. [43]. Copyright 2021, Royal Society of Chemistry



**Fig. 7** **a** Schematic of a phosphate proton reservoir in aqueous Zn||MnO<sub>2</sub> batteries. **b** Electrochemical performance of aqueous Zn||MnO<sub>2</sub> cells. **c** Cycling stability of an aqueous Zn||MnO<sub>2</sub> battery. Adopted with permission from Ref. [45]. Copyright 2022, American Chemical Society. **d** Discharge profiles of an aqueous Zn||MnO<sub>2</sub> battery. **e** Long-term cycling performance of an aqueous Zn||MnO<sub>2</sub> bat-

tery at 20 mA/cm<sup>2</sup> and a charge capacity of 18 mA h/cm<sup>2</sup>. Adopted with permission from Ref. [47]. Copyright 2022, American Chemical Society. **f** Schematic of the cell structure and chemical reactions at the cathode and anode. **g** Discharge curves for DZMB at various discharge current densities. Adopted with permission from Ref. [48]. Copyright 2020, Springer Nature

resulting in a hybrid Zn||MnO<sub>2</sub> battery, exhibiting a high discharge plateau of 2.05 V and an areal capacity of 18 mA h/cm<sup>2</sup> over 160 cycles (Fig. 7d, e). Similarly, Zhong et al. [48] employed ion-selective membranes to develop an innovative cell configuration, resulting in a higher discharge plateau of 2.83 V than all previous reports (Fig. 7g). These advancements in cell configurations have considerably improved the performance of aqueous Zn||MnO<sub>2</sub> batteries. Moreover, as shown in Table 1, we compare the performance of various aqueous Zn||MnO<sub>2</sub> batteries with high areal capacity and voltage [25, 27, 28, 37–39, 42, 45, 47–56].

## Others

Flexibility in constructing Zn||MnO<sub>2</sub> batteries is crucial for their use in various real-world scenarios. To address this issue, researchers have explored the use of flexible hydrogel electrolytes to assemble flexible cells [57–62]. Li et al. [63] proposed a double-network strategy to achieve excellent compression performance in acidic, alkaline, and mild

environments (Fig. 8a). The resulting Zn||MnO<sub>2</sub> batteries exhibited exceptional electrochemical performance, even under 50% compression (Fig. 8b). In addition, An et al. [64] developed a freestanding, lightweight, and zincophilic MXene/nanoporous oxide heterostructure-engineered separator for fabricating flexible Zn||MnO<sub>2</sub> batteries (Fig. 8c). The flexible full cell with a modified separator showed stable cycling stability with a high capacity of 224.0 mA h/g and a high-capacity retention of 99.03% (Fig. 8d). Furthermore, Zn||MnO<sub>2</sub> microbatteries (MBs) were fully developed by integrating flexible electrodes and hydrogel electrolytes. However, the key issue with the MBs is the flexibility of current collectors. Wang et al. [65] designed and fabricated a new flexible current collector based on Au/Ni (Fig. 8e). MBs were successfully fabricated by electrodepositing active electrode materials (e.g., Zn and MnO<sub>2</sub>) on the surface of Au/Ni and the coating of a hydrogel electrolyte between them (Fig. 8f). It is also very crucial to develop flexible Zn||MnO<sub>2</sub> batteries in the future by employing different schemes, including modified hydrogel electrolytes or innovative electrode designations (e.g., new binder design



**Table 1** Performance comparison of aqueous Zn||MnO<sub>2</sub> batteries

Battery configuration	Electrolyte	Plateau (V)	Capacity (mA h/cm <sup>2</sup> )	Cycle	References
Coin cell	1 mol/L Zn(CH <sub>3</sub> COO) <sub>2</sub> + 0.4 mol/L Mn(CH <sub>3</sub> COO) <sub>2</sub>	1.43	1.0	1000	[25]
Coin cell	2 mol/L ZnSO <sub>4</sub>	1.30	0.9	1000	[37]
Coin cell	2 mol/L ZnSO <sub>4</sub> + 0.1 mol/L MnSO <sub>4</sub>	1.30	15.6	350	[42]
Coin cell	1 mol/L Al(CF <sub>3</sub> SO <sub>3</sub> ) <sub>3</sub> + 1 mol/L Zn(CF <sub>3</sub> SO <sub>3</sub> ) <sub>2</sub>	1.70	0.26	1000	[49]
Teflon cell	1 mol/L MnSO <sub>4</sub> + 1 mol/L ZnSO <sub>4</sub> + 0.1 mol/L H <sub>2</sub> SO <sub>4</sub>	1.95	2.0	1800	[27]
Teflon cell	1 mol/L MnSO <sub>4</sub> + 1 mol/L ZnSO <sub>4</sub> + 0.1 mol/L H <sub>2</sub> SO <sub>4</sub> + 0.07 mmol/L PVP	1.40	3.5	2000	[28]
Teflon cell	2 mol/L ZnCl <sub>2</sub> + 0.07 mol/L Mn(H <sub>2</sub> PO <sub>4</sub> ) <sub>2</sub>	1.75	1.0	> 3000	[45]
Pouch cell	1 mol/L ZnSO <sub>4</sub> + 0.2 mol/L MnSO <sub>4</sub>	1.30	0.8	1800	[38]
			> 2	200	
Flow cell	1 mol/L Mn(Ac) <sub>2</sub> + 1 mol/L Zn(Ac) <sub>2</sub> + 2 mol/L KCl + 0.1 mol/L KI	1.30	15.0	225	[39]
Flow cell	0.5 mol/L Mn(Ac) <sub>2</sub> + 0.5 mol/L Zn(Ac) <sub>2</sub> + 2 mol/L KCl	1.58	13.0	100	[50]
Flow cell	1 mol/L MnSO <sub>4</sub> + 1 mol/L ZnSO <sub>4</sub>	1.72	1.0	500	[51]
Decoupled cell	Cathode: 0.5 mol/L ZnSO <sub>4</sub> + 1 mol/L LiTFSI Anode: 1 mol/L MnSO <sub>4</sub> + 1 mol/L HTFSI	2.05	1.0	2000	[47]
			18.0	> 160	
Decoupled cell	Cathode: 3 mol/L H <sub>2</sub> SO <sub>4</sub> + 0.1 mol/L MnSO <sub>4</sub> Middle chamber: 0.1 mol/L K <sub>2</sub> SO <sub>4</sub> Anode: 6 mol/L KOH + 0.2 mol/L ZnO + 5 m mol/L vanillin	2.71	3.3	200	[48]
Decoupled cell	Cathode: 3 mol/L MnSO <sub>4</sub> + 0.3 mol/L H <sub>2</sub> SO <sub>4</sub> + 0.06 mol/L NiSO <sub>4</sub> Anode: 3 mol/L NaOH + 0.3 mol/L ZnO	2.44	1.0	450	[52]
Decoupled cell	Cathode: 1 mol/L MnSO <sub>4</sub> + 1 mol/L H <sub>2</sub> SO <sub>4</sub> + 0.3 mol/L CuSO <sub>4</sub> BPE: Cu Anode: 2.4 mol/L KOH + 0.1 mol/L Zn(Ac) <sub>2</sub>	1.84	0.5	3500	[53]
Decoupled cell	Cathode: 1 mol/L MnSO <sub>4</sub> + 1 mol/L ZnSO <sub>4</sub> /PAM Anode: 2 mol/L ZnSO <sub>4</sub> /PAM	1.90	0.225	500	[54]
Decoupled cell	Cathode: 1 mol/L MnSO <sub>4</sub> + 0.5 mol/L H <sub>2</sub> SO <sub>4</sub> or 0.5 mol/L KMnO <sub>4</sub> + 0.5 mol/L H <sub>2</sub> SO <sub>4</sub> Anode: 45 wt% KOH/PAA	2.20 or 2.65	< or = 0.6	35 or 120	[55]
Decoupled cell	Cathode: 2 mol/L MnSO <sub>4</sub> + 0.5 mol/L H <sub>2</sub> SO <sub>4</sub> Anode: alkaline electrolyte	2.4	1.88	100	[56]

[66], electrode material innovation [67], or optimized Zn anodes [68, 69]).

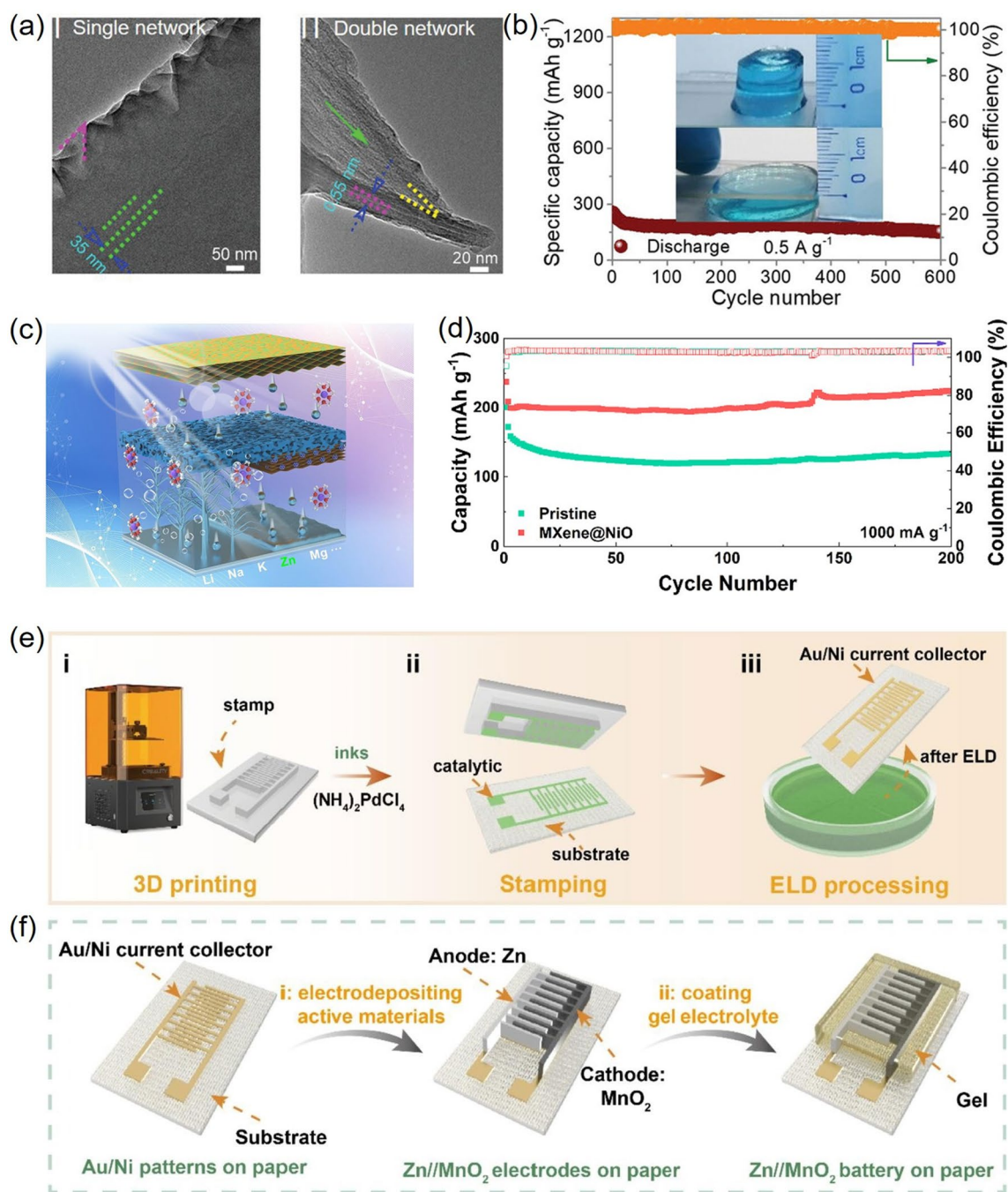
## Challenges and Perspectives

Based on this review, aqueous Zn||MnO<sub>2</sub> batteries have exhibited promising electrochemical properties and revealed their electrochemical reaction mechanism, accompanied by the achievements of ideal specific/areal capacity, cyclic stability, and a high discharge plateau. Despite these advancements, the practical application of aqueous Zn||MnO<sub>2</sub> batteries has not yet been achieved because of several challenges and issues. To develop commercial aqueous Zn||MnO<sub>2</sub> batteries that can be fabricated on a large scale, the following challenges must be addressed:

(1) ERM clarity. Diverse ERMs in aqueous Zn||MnO<sub>2</sub> batteries have caused controversy and hindered their com-

mercialization. ERMs involve Mn<sup>2+</sup>, Zn<sup>2+</sup>, and H<sup>+</sup> cations, with MnO<sub>2</sub>/Mn<sup>2+</sup> redox conversion dependent on proton concentration. However, the complex interplay between Zn<sup>2+</sup> intercalation and H<sup>+</sup> conversion chemistry complicates ERMs. To clarify ERMs, it is essential to separate MnO<sub>2</sub>/Mn<sup>2+</sup> conversion, Zn<sup>2+</sup> intercalation, and H<sup>+</sup> conversion chemistry. By artificially fixing MnO<sub>2</sub>/Mn<sup>2+</sup> conversion at high voltage (> 1.5 V), the ERM of Zn<sup>2+</sup> intercalation and/or H<sup>+</sup> conversion can be revealed at low voltage (< 1.5 V). Nevertheless, ERMs at low voltage remain unclear, and exploring these mechanisms is crucial for the rapid development of aqueous Zn||MnO<sub>2</sub> batteries.

(2) High-areal-capacity and high-voltage Zn||MnO<sub>2</sub> batteries. To commercialize Zn||MnO<sub>2</sub> batteries, improving their energy density is crucial and can be achieved by enhancing their high areal capacity and voltage. Current challenges in this aspect include the insufficient use of high-loading cathode materials and Zn dendrite



**Fig. 8** **a** Transmission electron microscopy images of hydrogels consisting of polyacrylamide and betaine methacrylate sulfonate. **b** Cycle performance under compression. Adopted with permission from Ref. [63]. Copyright 2023, Wiley-VCH Verlag. **c** Schematics of a flexible Zn||MnO<sub>2</sub> battery and **d** its cycle performance. Adopted with permis-

sion from Ref. [64]. Copyright 2022, American Chemical Society. **e** Fabrication process of two-dimensional metal patterns transformed from a three-dimensional-printed stamp. **f** Fabrication of a Zn||MnO<sub>2</sub> microbattery on a filter paper. Adopted with permission from Ref. [65]. Copyright 2023, Elsevier

growth at the anode. To address these issues, researchers must optimize various measures, such as electrolyte engineering and innovative cell configurations, for improving cathode utilization and inhibiting dendrite growth. Moreover, MnO<sub>2</sub>/Mn<sup>2+</sup> conversion in strong

acid environments occurs at relatively high voltage (vs. Zn<sup>2+</sup>/Zn), resulting in Zn anode corrosion. Therefore, the development of a neutral or mildly acid electrolyte that can activate MnO<sub>2</sub>/Mn<sup>2+</sup> conversion at a high voltage is essential.

## Conclusion

The development of aqueous Zn||MnO<sub>2</sub> batteries has been hindered by a lack of deep understanding of their ERMs. Despite substantial progress, their real reaction mechanisms remain unclear. Suppose the reaction potentials for MnO<sub>2</sub>/Mn<sup>2+</sup> conversion (> 1.75 V vs. Zn<sup>2+/Zn</sup>), Zn<sup>2+</sup> intercalation (approximately 1.40 V vs. Zn<sup>2+/Zn</sup>), and H<sup>+</sup> intercalation/conversion (approximately 1.20 V vs. Zn<sup>2+/Zn</sup>) can be fixed at a specific reaction potential. Then, their natural reaction mechanism will be revealed. In addition, high energy density and superior stability are prerequisites for aqueous Zn||MnO<sub>2</sub> battery commercialization. Therefore, research efforts must be intensified to develop high-areal-capacity and high-voltage aqueous Zn||MnO<sub>2</sub> batteries with excellent electrochemical features. To yield high areal capacity, a profound exploration of the relationship between the mass loading of cathode materials and cycle stability or utilization is highly important. Development in this area should focus on fully utilizing the high-loading mass of MnO<sub>2</sub> and reducing the degree of irreversible reactions. For high voltage, developing the high reaction potential of MnO<sub>2</sub>/Mn<sup>2+</sup> conversion (> 1.75 V vs. Zn<sup>2+/Zn</sup>) in neutral electrolytes is challenging. The key factor for achieving high voltage of MnO<sub>2</sub>/Mn<sup>2+</sup> conversion is to tune Mn<sup>2+</sup> activity. Overall, these advancements will enable their use in future electric vehicle and stationary storage applications.

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## Declarations

**Conflict of interest** All authors declare that there is no competing interest.

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