Review

From aqueous Zn-ion battery to Zn-MnO_2 flow battery: A brief story

Tong Xue[a], Hong Jin Fan[b, *]

[a] *School of Materials Science and Engineering, North Minzu University, Yinchuan 750021, Ningxia, P.R. China*

[b] *School of Physical and Mathematical Sciences, and Innovative Centre for Flexible Devices, Nanyang Technological University, Singapore 637371, Singapore*

[*] Corresponding author. *Email address*: fanhj@ntu.edu.sg (H. J. Fan)

Abstract

Aqueous Zn-ion battery (AZIB) has become an attractive technology because of its unique features of low cost, high safety and the eco-friendliness. MnO_2 is the model cathode material for AZIB since the first report on reversible Zn-MnO_2 battery, but recent studies have unveiled different charge storage mechanisms. Because of revamping of the electrochemistry and redesigning of the electrolyte and interface, there is tremendous performance enhancement in AZIB. This mini Review will first give a brief introduction of ZIB, including fundamentals of materials and components, and the progress in recent years. Then, a general classification of working mechanisms related to MnO_2 in neutral and mildly acidic electrolyte is elaborated. Our focus is put on the recent blossoming Zn-MnO_2 electrolytic mechanism, which has given birth to the Zn-MnO_2 redox flow batteries that are highly promising for large-scale static energy storage.

Keywords: Aqueous zinc-ion battery; Deposition/dissolution; Electrolytic battery; Zn-MnO_2 flow battery

Tong Xue is currently an Associate Professor at North Minzu University. She received her Bachelor and Master degree from Lanzhou University, followed by Ph.D. from Nanyang Technological University (NTU) in 2013. She is working in Prof. Fan's group as a Visiting Scholar from 2019 to 2020. Her research interests are metal oxides-based nanocomposites for electrochemical energy storage and conversion (including supercapacitors, metal-ion and metal-air batteries).

Hong Jin Fan received his Ph.D from the National University of Singapore, followed by postdoc study at Max Planck Institute of Microstructure Physics and University of Cambridge. He joined in Nanyang Technological University since 2008. His research interests include flexible energy storage, cost-effective nanomaterial electrocatalysts for hydrogen generation and metal-air batteries. His group uses atomic layer deposition and plasma techniques in energy research.

1. **Introduction**

To meet the energy needs in the not far future, tremendous efforts have been made to formulate the global strategies for energy storage. It is urgent to seek an efficient way to store the intermittent energy, such as wind, tidal and solar power. Currently, lead-acid batteries and lithium-ion batteries (LIBs) occupy the principal market of energy storage [1]. However, due to the low energy density of 75 Wh kg^{-1} and the toxic lead usage, the lead-acid battery is not favored for the large volumetric occupation and the harmfully environmental consideration [2]. The LIBs are progressing in terms of energy density, but the main bottleneck is the safety issue due to the usage of organic electrolyte [3, 4] Hence, the aqueous secondary batteries based on economical and safe metals, and the environmental friendly electrolytes with high ionic conductivity, are very important to revolutionize the battery market [5, 6] .

Aqueous zinc-ion battery (AZIB) is one of excellent choices for the above purpose. All the components of an AZIB can be from economical materials, including oxide cathode, Zn metal anode, and aqueous electrolyte containing Zn salts [7]. The fabrication can be conducted in ambient condition without glove box environment. Zn has a high theoretical capacity of 820 mAh g^{-1}, a low redox potential of -0.76 V (vs SHE) and the favorable reversibility of Zn^{2+}/Zn [8]. As MnO_2 is a non-toxic and low-cost material compared to other oxide cathodes, the Zn-MnO_2 AZIB has become a model system in the field of aqueous batteries with a high potential for large-scale static energy storage. A comparison of Zn-MnO_2 AZIBs [9] with other AZIBs [10], LIBs [11-13] and sodium ion batteries (SIBs) [14, 15] is shown in Table 1 to further demonstrate the advantage of Zn-MnO_2 AZIBs.

There are also pitfalls. First, the one electron redox reaction limits the capacity and the voltage of the device [9]. If we can design the two-electron reaction of Mn^{4+}/Mn^{2+}, the theoretical capacity will be increased to 616 mAh g^{-1}, and the voltage will also be improved. Second, the inferior kinetics of Zn ion intercalation and chemical instability of typical layered oxides also limit the electrochemical performance. Furthermore, the importance of Zn anode should not be overlooked, and could become the main obstacle for large-scale commercialization. The zinc dendrite growth occurs during the plating/stripping process, especially at high currents and alkaline electrolytes. The mild acidic aqueous electrolyte is useful to suppress dendrite growth and unwanted oxides formation, but it is still not fully effective. Other approaches, such as the surface coating or replacement of the anode current collector, have been attempted to eliminate the dendrites [16].

Table 1 Comparison of Zn-MnO_2 AZIBs, other AZIBs, LIBs and SIBs

	Zn-MnO_2 AZIBs	Other AZIBs	LIBs	SIBs
Cathode	MnO_2	Vanadium-based $MFe(CN)_6 \cdot nH_2O$ Co_3O_4	$LiCoO_2$ $LiNi_{1-x}M_xO_2$ $LiNi_xMn_yCo_zO_2$	$NaCoO_2$ $NaNi_{1-x}M_xO_2$ $NaNi_xCo_yMn_zO_2$
Anode	Zn	Zn	graphite	hard carbon
Electrolyte	inorganic	inorganic	organic	organic
Voltage (V)	1.2–2.8	0.6–1.8	3–5	2.5–4
Capacity (mAh g^{-1})	100–600	65–400	80–200	80–180
Energy density (Wh kg^{-1})	70–400	100–200	150–260	120–220
Power density (W kg^{-1})	100–10000	10–20000	150–2000	40–500
Safety	×	××	×××	××××
Stability	√√√√	√√√	√√	√
Costs (¥ (kWh)$^{-1}$)	<70	450	<1530	16.8

The redox flow batteries (RFBs) can satisfy the scale-up requirements [17]. The electrolytes with the redox active materials are stored in the external container. The battery capacity is totally independent from the battery basic unit (cathode, anode and separator). Among many types of aqueous flow battery systems, Zn-based RFBs recently emerge as a new star [18]. In particular, the new electrolytic mechanism associated with MnO_2/Mn^{2+} gives rise to the advert of Zn-MnO_2 flow battery (ZMFB) [19]. With very high theoretical voltage and energy density, ZMFB can help to boost the commercialization of Zn-based aqueous flow batteries.

In recent years, there has been rapid increase in research about aqueous AZIBs and ZMFBs. To provide a snap view for the reader, we pick up some representative papers in recent years (see Fig. 1). These include the pioneering study on the Mn-based AZIB [20], the V-based AZIB [21], the Prussian blue analog (PBA)-based AZIB [22], the flexible AZIB [23, 24], the MnO_2/Mn^{2+} electrolytic mechanism and birth of ZMFB [9], decoupled electrolytes design of ZMFB [25, 26], and some important papers about high voltage realization [26-28]. This chart may not be complete or precise; The readers can refer to some comprehensive review articles on AZIB [7, 10, 29, 30]. In this mini review, we attempt to tell a short story about MnO_2-based AZIB, covering the evolution of charge storage mechanism, performance enhancement, and possible commercialization of flow batteries. Alkaline and "water-in-salt" electrolyte based ZIBs are beyond our discussion.

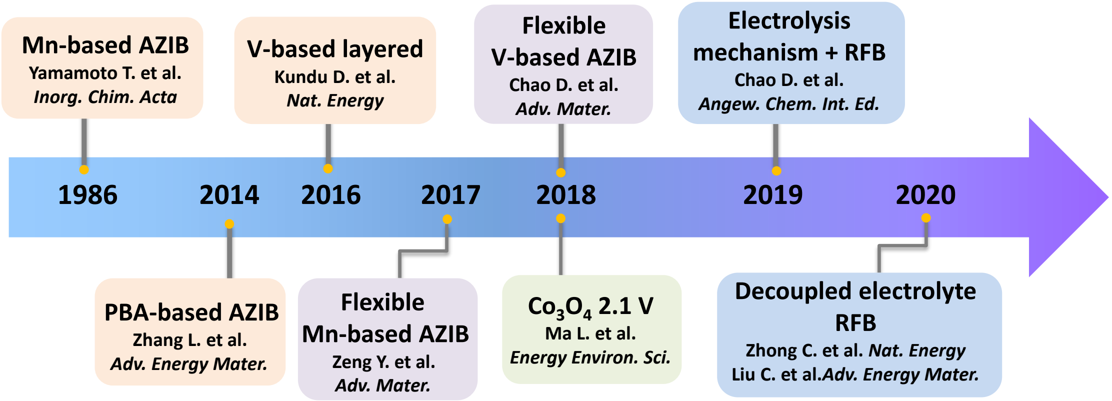


Fig. 1. Representative milestones of aqueous Zn-ion batteries.

2. The zinc anode

For all metal-ion batteries, electron transfer occurs via redox reactions in both electrodes with electrolyte as media. Various metal ions are being studied recently in their (de)intercalation electrochemistry with cathodes and/or anode for emerging batteries. We made a comparison among all these metal ions from monovalent, divalent, to trivalent (Fig. 2). Zinc is a cheap, safe and non-toxic metal. The cation radius of Zn is just slightly larger than that of Li ion, and the (de)intercalation kinetics might not be a serious issue compared to other multivalent cations. The two-electron transfer character of Zn/Zn^{2+} offers high theoretical gravimetric and volumetric capacities of 820 mAh g^{-1} and 5851 mAh cm^{-3}, respectively. Additionally, zinc has theoretical redox potential of -0.763 V vs. standard hydrogen electrode (SHE), and relatively high hydrogen evolution reaction (HER) overpotential (–1.06 V). Therefore, the aqueous electrolytes are less easy to decompose via water splitting reactions, making the AZIB more stable than aqueous Li-metal batteries for long cycles.

While Zn foil is commonly used as the anode, it has a low utilization ratio and causes reduction of the specific capacity on the total device. Normally, the neutral and mildly acidic electrolytes are preferable to achieve higher columbic efficiency and cycling stability as compared to alkaline ones. Dendrite formation has been an issue for Zn foil anode which is particularly severe in alkaline electrolytes [8]. Three-dimensional (3D) Zn is shown beneficial to mitigate the dendrite problem. For example, 3D monolithic Zn sponge electrode can maintain longer cycles than powder-composite Zn electrodes and even increase the depth of discharge (DOD) of Zn [31]. The reason was claimed to be a reduction in local current density on the 3D anode. Electrodeposited Zn flakes on carbon scaffolds are also effective for the same purpose [23, 32]. It has been discovered that the dendrite formation is also dependent on current density; a small current density can lead to dissolution of the formed Zn dendrites, giving an indirect approach to recover the anode [33]. Additional method is to coat the surface of Zn foil with an inorganic [34] or polymer layer [35], or in-situ formed SEI layer [36]. It is uncertain if these methods are equally effective when going to large scale or long cycles. On top of dendrites, a change in local pH value due to hydrogen evolution reactions next to the Zn anode can lead to self-corrosion of Zn, especially in mild acid solution. The challenges of dendrite and corrosion, and perspective solutions are recently reviewed by Liang group [8] and Choi group [37].

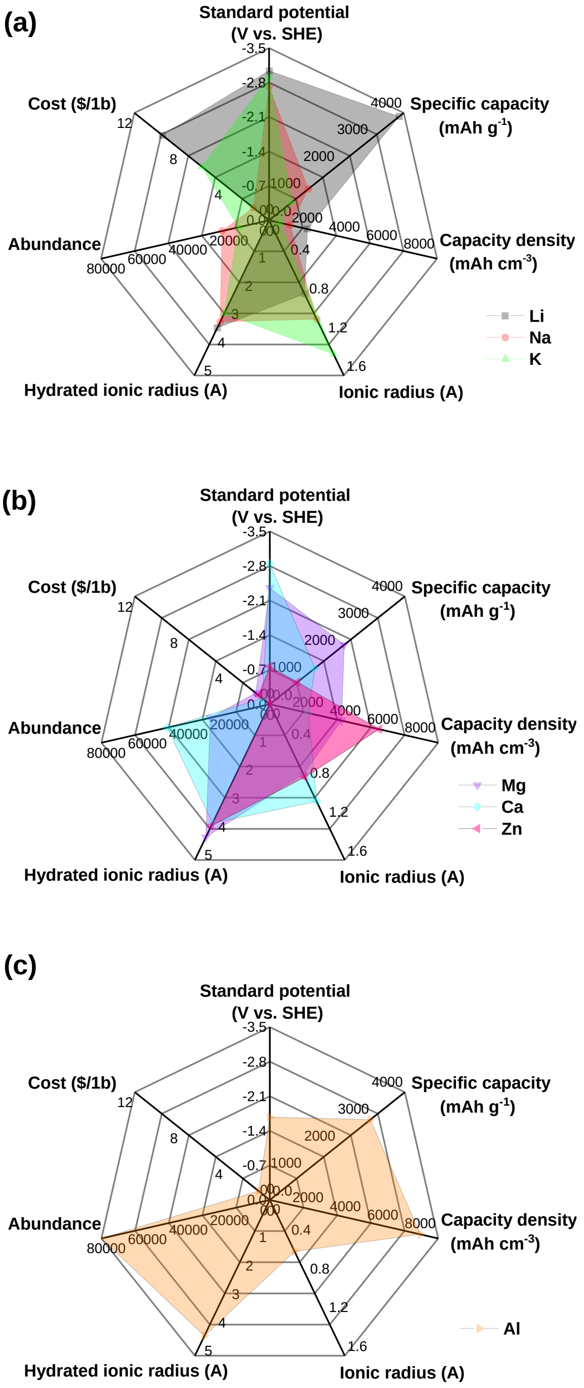


Fig. 2. Comparison of various metals in metal-ion batteries. (a) Monovalent, (b) divalent, and (c) trivalent ions.

3. Cathode materials

As the anode is Zn metal, the choice of cathode is important to the whole battery. The electrochemical performance, for example, specific capacity, open circuit voltage, ionic and electronic transport ability, cyclic stability of an AZIB is mainly determined by the cathode materials (in addition to electrolyte, see discussion below). The cathode materials can be roughly classified to three main categories, namely, manganese-based, vanadium-based, and Prussian blue analogue-based materials. The others are organic ones, which are beyond our discussion. There are already quite a number of review papers on the cathode materials used in AZIBs [10, 29, 38]. In the following, we just make a brief summary.

According to the statistics in Fig. 3(a), the Mn-based materials are the priority choice in AZIBs. MnO_2 has obvious advantages; it is non-toxic, low cost, environment friendly, and easy to obtain, especially nanostructures. However, the drawbacks are also obvious: low electrical conductivity and instability (dissolution and detachment from current collector during the charge/discharge cycles). the Mn-based cathode materials present better overall energy storage performance as compared with the other two types [39-41]. The theoretical specific capacity of MnO_2 is 308 mAh g^{-1} calculated by the one-electron transfer in redox reaction. The MnO_2 has a diversity of crystalline polymorphs due to the different connecting ways of the MnO_6 (octahedron) basic unit. Normally, the crystal structure of MnO_2 is divided into three types: tunnel structure (α-, β-, γ-, λ-, *R*- and *T*-MnO_2), layered structure (δ-MnO_2) and dense stacked structure (ε-MnO_2). Hence, the redox chemistry of MnO_2 can be very different depending on the salt and pH value of the aqueous electrolyte (see schematic in Fig. 3b). In an alkaline electrolyte system, the zinc anode reacts with OH^- to form $[Zn(OH)_4]^{2-}$, which may further dehydrate into ZnO. However, in neutral or mild acid electrolytes, the reversible Zn/Zn^{2+} deposition/dissolution mechanism dominates on the Zn anode side. More precisely, in the electrolyte, Zn^{2+} will form hexaaquo complexes of $[Zn(H_2O)_6]^{2+}$ which serves as proton donors. Because of this, the $ZnSO_4$ solution exhibits weak-acid character. During the reaction, the Zn^{2+} will be desolvated from the complexes and form Zn metal at the anode. The cathode reactions in both electrolytes are similar, namely, the MnO_2 is converted into MnOOH and $ZnMn_2O_4$ when H^+ and Zn^{2+} are intercalated, respectively, accompanied by one electron transfer during the discharging process. But formation of the zinc hydroxide sulfate nanoflakes on MnO_2 has been commonly observed in both alkaline or neutral electrolytes [7, 42].

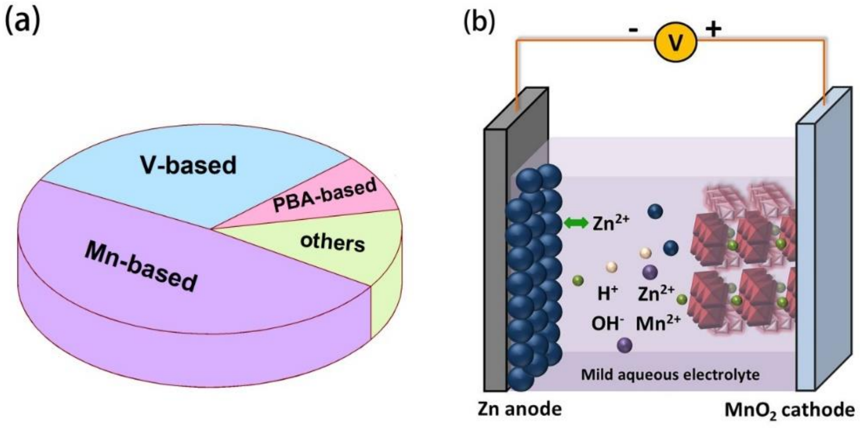


Fig. 3. (a) Relative proportion of journal publications of different cathode materials in AZIBs (data from web of knowledge as per Apr 2020); (b) Schematic of AZIB exemplified by MnO_2 cathode in different types of electrolytes.

The next most popular candidate is V-based materials. The vanadium-based oxides as the cathode materials firstly appeared in 2016 to solve the low cycling stability of Mn-based AZIB [21]. Similar to Mn-based oxides, V-based compounds (including vanadium oxides, vanadate, vanadium phosphates and vanadium sulfides) also have the layered or tunnel crystalline structures. A large number of Review articles are dedicated to vanadium-based cathodes for AZIB [43-46]. Layered vanadium oxides, such as vanadium oxide bronze [21], VO_2, zinc orthovanadate[23], can provide long-cycle stable capacities, especially when they are pillared by water molecules or metal cations. Another method to boost the rate performance of vanadium oxide is to create oxygen vacancies which are helpful to increase the channel width and improve high conductivity [47]. However, the relatively low operating voltage of V-based cathode limits the development for AZIB.

The Prussian blue analogues (PBAs) have a general formula of $MFe(CN)_6 \cdot nH_2O$ (M = Fe, Co, Ni, Cu, Mn, Zn) with face-centered cubic (fcc) structure [22]. The PBAs generally gives a high operating voltage. The stable open-framework structure guarantees the rapid migration of the guest ions. In addition, the two-mole electron transfer per mole PBA with two redox-active sites contributes to higher theoretical specific capacities than other common oxides. However, because of a large amount of vacancies, lattice defects, and water in the PBA crystalline structure, the experimentally obtained specific capacity is lower than the theoretical value.

4. On mechanisms of Zn-MnO_2 battery

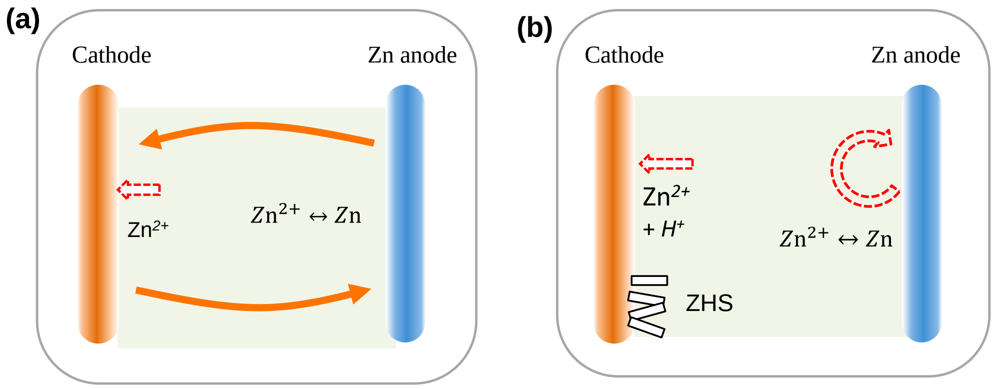
The reversible Zn-MnO_2 battery using alkaline electrolyte originates from the old-styled primary alkaline battery, which suffers from formation of (hydro)oxide byproducts on both cathode and anode, making the battery irreversible. Current AZIB mainly utilizes non-alkaline electrolyte solutions. Despite the wealth publication on MnO_2 based AZIB [38, 48-50] since the pioneering paper on γ-MnO_2−Zn full cell by the Japanese group [20], there has been debate on the mechanisms underlying their electrochemical performance. New insights to the electrochemistry of MnO_2 are revealed by subsequent more careful studies of intermediate states. In a nutshell, the mechanism spans from the original mere Zn ion (de)insertion, Zn^{2+}/H^+ co-(de)insertion, conversion reaction accompanied by H^+ intercalation, to the recent electrolytic dissolution/deposition. In the following, we would like to highlight them in four categories (see also schematic in Fig. 4).

4.1 Zn^{2+} intercalation/extraction

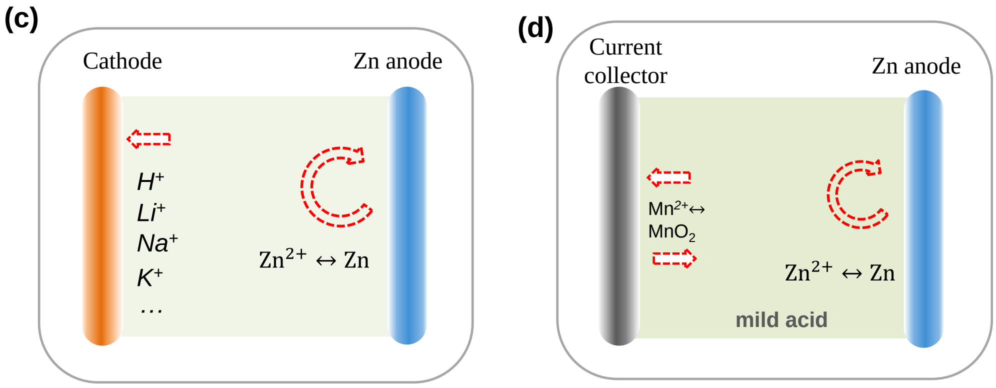
The reversible Zn^{2+} intercalation/extraction has been long regarded the charge storage mechanism for MnO_2 because of its channeled structure [51], and the Zn^{2+} shuttle between the cathode and anode pretty much like conventional Li-ion batteries (Fig. 4a). The MnO_2 transfers into $ZnMn_2O_4$ due to Zn^{2+} insertion [52-55] as shown in Reaction 1:

$$Zn^{2+} + 2e^- + 2MnO_2 \leftrightarrow ZnMn_2O_4 \qquad (1)$$

The process occurs mainly in neutral aqueous electrolyte with associated reversible redox reaction of Mn^{4+}/Mn^{3+}. This mechanism is no longer true in a wide range of pH electrolytes, and capacity calculation based on Reaction (1) may lead to significant discrepancy from the experimental value.



Zn^{2+} insertion/extraction Zn^{2+}/H^{+} co insertion/extraction



Hybrid process, dual ions Electrolytic process

Fig. 4. A general classification of working mechanisms of MnO_2-based AZIBs.

4.2 Proton/Zn^{2+} co-intercalation and conversion

In the recent literature of MnO_2-based AZIB, it is believed that H^{+} plays an important role in the cathode reaction and may be the major source of the capacity. This mechanism has been evidenced by the increase of Mn^{2+} and pH value in the electrolyte during discharge. It now becomes a consensus that Zn^{2+}/H^{+} may co-(de)intercalate with MnO_2 (as well as with V-based and organic cathode materials). The reactions for both electrodes are traditional redox ones which can be expressed in a simple way as follows (see Fig. 4b):

$$MnO_2 + H_2O + e^- \leftrightarrow MnOOH + OH^- \tag{2}$$

$$Zn^{2+} + 2e^- + 2MnO_2 \leftrightarrow ZnMn_2O_4 \tag{3}$$

In this process, the MnO_2 is converted into MnOOH with one electron transfer during the discharging process, and simultaneously, there may still have a small portion of capacity coming from Zn^{2+} intercalation [56, 57]. Additionally, there is a formation of byproduct $[Zn(OH)_4]SO_4$ (ZHS) in the form of nanosheets anchored on the surface of MnO_2 cathode [42, 56]. Such a growth of ZHS occurs in both neutral as well as mildly acidic electrolytes and can be accelerated by the local increase in pH due to Reaction (2). Obviously, the ZHS is a nuisance because it does not contribute to reversible capacity, and the non-conductive ZHS reduces the kinetics and the capacity. Hence, to eliminate this unwanted byproduct, one approach is to maintain the mild acid environment of the solution using, for example, buffered electrolyte.

4.3 Dual-ions hybrid battery

Another type of hybrid Zn aqueous battery is also possible, although the available reports are scarce. Such a hybrid battery has two types of separated cations: Zn^{2+} follows the traditional stripping/plating mechanism on the anode side, while $H^+/Li^+/Na^+/K^+$ obeys the (de)insertion mechanism on the cathode side (see Fig. 4c). For example, reversible proton (or more generally, hydronium ion) intercalation/extraction can be the dominating process in Zn-MnO_2 battery through the reaction of $MnO_2 + H^+ + e^- \leftrightarrow MnOOH$, especially in the case that pure aqueous H_2SO_4 electrolyte is used without addition of Zn salt. There are relatively less reports on intercalation/extraction of other metal ions, but it is foreseen that such dual-ion batteries are feasible.

4.4 MnO_2 electrodeposition/electrolysis

The three mechanisms mentioned above effectively have only one electron transfer in the Mn^{4+}/Mn^{3+} redox process. The theoretical capacity and the output voltage are limited to 308 mAh g^{-1} and 1.4 V, respectively. The Mn^{4+}/Mn^{2+} redox reaction with a two-electron process gives a theoretical capacity of 616 mAh g^{-1} and electrode potential of 1.228 V (versus SHE). A new type of Zn-MnO_2 battery based on the reversible MnO_2 electrodeposition/electrolysis mechanism (see schematic in Fig. 4d) was recently reported first by the Qiao group [9], followed immediately by the Zhi group [58] and Xia group [59], and more recently also by the Liang group [60]. And more reports are being published since after. This new mechanism pushes the working voltage far beyond the thermodynamic window (~1.23 V) of the aqueous electrolyte. Herein, the Zn^{2+} does not participate the (de)insertion reaction in the cathode at all, instead, the two reactions on the two electrodes are decoupled. Hence, it might be controversial if this type of battery should be called AZIB; it is more like a flow battery. The MnO_2 electrodeposition/electrolysis mechanism on the cathode side is shown in Reaction (4).

$$Mn^{2+} + 2H_2O \leftrightarrow MnO_2 + 4H^+ + 2e^- \qquad (4)$$

The beauty of this new battery mechanism lies in a delicate engineering of electrolyte. First, it uses a mildly acidic electrolyte with suitable pH values, which suppresses the formation of ZHS byproduct but not to destroy the Zn anode (note: membrane free). Second, the unwanted dissolution of MnO_2 is utilized effectively. As a result, it gives birth to a completely new battery configuration. Last, it further simplifies the battery design, so that active material is not required to be pre-deposited on the current collector. This new electrolytic mechanism provides an opportunity to develop Zn-Mn flow batteries that are discussed below.

In fact, the electrolytic process should widely exist in all other types of aqueous Zn-MnO_2 battery systems in neutral electrolyte, which has not been aware of by researchers. In the past, it has been regarded that the $MnSO_4$ added into electrolyte can help suppress the dissolution of MnO_2. However, with the discovery of electrolysis process, it is now realized that is a misinterpretation; the truth could be that the addition of $MnSO_4$ actually enhances the reversibility of MnO_2/Mn^{2+} deposition/dissolution reaction, leading to improved cyclic stability and specific capacity.

5. The advent of Zn-MnO_2 flow batteries

Different from traditional batteries, redox flow batteries (RFBs) have the separated power generation part (including two electrodes and membrane) and energy storage part (including externally flowing electrolytes with electro-active species). Notably, both cathode (carbon cloth) and anode (metal plate) are active material-free before utilization [17]. It means the pre-synthesis of active materials becomes redundant. During the discharging process, the electrode materials are dissolved into the electrolyte with electron transfer from anode to cathode. It is indeed a reversible process with mass and electron transfer between electrolyte and anodic/cathodic materials. The RFBs is more like fuel cells rather than batteries due to their intrinsic property of heterogeneous electron transfer (not ion intercalation). The full cell is separated from electrolyte, and the electrolyte enters the cell via continuously pumping. Aqueous Zn-ion RFB is becoming a very competitive technology due to their high safety, low cost, and long lifespan.

The development of traditional RFBs including Fe/Cr and all-vanadium-based flow batteries is limited by low energy density, low system efficiency and narrow operating temperature window [61]. Many efforts have been made to design the RFBs such as S_x/Br_2, Zn/Br_2, Zn/Fe and V/Ce systems to further improve the energy density, but the progress has been marginal because of the relatively low cell voltage (<1.7 V). Recently, the Zn-I RFB system [17, 62] with the relatively high open circuit voltage of ~1.7 V and energy density of 330.5 Wh L^{-1} has been designed. A comprehensive Review is also available on zinc-based hybrid flow batteries [18]. However, the working voltages of all these systems are still lower as compared with non-aqueous systems. To develop a new-typed RFB is in urgent need to satisfy the energy requirement.

The proposed MnO_2 electrodeposition/electrolysis mechanism opens a new door for the RFBs. The MnO_2 electrode with two electron transfer (Mn^{4+}/Mn^{2+}) has the electrode potential of 1.228 V. Zn metal plate as anode in neutral or mild acid aqueous solution has the electrode potential of –0.763 V. So the theoretical voltage window of a Zn-MnO_2 battery can reach 1.991 V [9]. The mechanisms are shown in Reaction (5 – 7).

$$\text{Cathode:}\quad Mn^{2+} + 2H_2O \leftrightarrow MnO_2 + 4H^+ + 2e^- \quad E^{\emptyset} = 1.228\,V \tag{5}$$

$$\text{Anode:}\quad Zn^{2+} + 2e^- \leftrightarrow Zn \quad E^{\emptyset} = -0.763\,V \tag{6}$$

$$\text{Full cell:}\quad Zn^{2+} + Mn^{2+} + 2H_2O \leftrightarrow Zn + MnO_2 + 4H^+ \quad E = 1.991\,V \tag{7}$$

The schematic and charging/discharging mechanism is shown in Fig. 5a. In the charging process, the Zn^{2+} and Mn^{2+} are deposited to the current collectors and become Zn and MnO_2, respectively. As the battery starts to discharge, both the Zn anode and MnO_2 cathode dissolve into the electrolytes with the electrons transfer from anode to cathode. In the pioneering work by the Adelaide group, Chao and coworkers used an mildly acidic sulfate electrolyte containing 1 mol L^{-1} $ZnSO_4$/1 mol L^{-1} $MnSO_4$ /0.1 mol L^{-1} H_2SO_4 was used in order to improve the deposition efficiency and avoid the water splitting [9]. The related energy diagram indicates that the charging voltage should be less than 2.41 V to ensure the stability of water molecules, and higher than 2.00 V to confirm the effective electrodeposition of both electrodes. An output voltage of 1.95 V can be demonstrated. Based on the above process, the authors for the first time demonstrated a prototype Zn-MnO_2 RFB stack that can be changed to 2 Ah. This result is impressive and opens the door towards new-generation Zn-MnO_2 RFB. Following this, the group led by Li at Dalian also demonstrated high-performance Zn-MnO_2

RFBs by using $Mn(Ac)_2$ salt as the electrolyte and carbon fiber cloth as the current collector [19]. The configuration (Fig. 5b) is quite close to the very mature vanadium RFB for the storage of renewable energy.

The Qiao group [9] first constructed a single Zn-MnO_2 RFB with the discharging voltage of ~2.0 V (Fig. 5c, left) and demonstrated cell phone charging. Cui group at Stanford [63] designed a Zn-MnO_2 RFB without separator, and further scaled up the battery into the 10 packed cell (Fig. 5c, right). The storage capacity of this bench-scale cell can be charged to 1.2 Ah with the discharging capacity of 1.10 Ah at current rate of 500 mA. Nevertheless, in this study, the selected charging voltage is relatively low so that the discharge voltage of single battery is just ~1.78 V. This may scarify the energy storage ability of the battery.

Analogous to the decoupled water splitting reactions by bi-polar membrane, a better choice in Zn-MnO_2 RFB is to decouple the electrolyte. In this way, the subtle balance of the cathode stability and anode stability in the same electrolyte is no longer needed. This was very recently realized by three groups, viz., Liu [25], Hu [26], Qiao [64] and their coworkers independently. The Liu group [25] employed a bipolar membrane to separate the redox reactions on the cathode and anode side in two independent chambers. In this way, both sides can have their full reactions and stabilities without crosstalk. A widened working voltage of 2.40 V was achieved, and the maximum energy density was claimed to be 1503 Wh kg^{-1} (based on only cathode material). The Hu group [26] developed a similar system but utilized two membranes to separate the electrolytes, namely, acidic electrolyte on MnO_2 side and basic on the Zn side, with a neutral buffer zone in between. This design is pretty much like the previously reported three-compartments Zn/Fe flow battery, which has an output voltage of 1.99 V [65]. As such, they further extended the discharge voltage to 2.71 V. Nonetheless, the use of two separators could increase the resistance and the polarization of the battery, resulting in unsatisfactory rate capability and power density. In order to solve the kinetics issues in the decoupled systems, recently, Qiao group [64] made another breakthrough by designing a catalyzed MnO_2/Mn^{2+} electrolysis system, in which a trace amount of Ni^{2+} was introduced to the electrolyte solution. The designed Zn-Mn hybrid aqueous battery is endowed with fast reaction kinetics (50 C, discharge in 60 s), a large electrochemical stability window over 3.40 V, a record high power density of 19 kW kg^{-1} and energy density of ca.

650 Wh kg^{-1} (both anode and cathode active materials are taken into consideration). This highest voltage is certainly striking and brings the ZIB to the cutting edge of aqueous batteries.

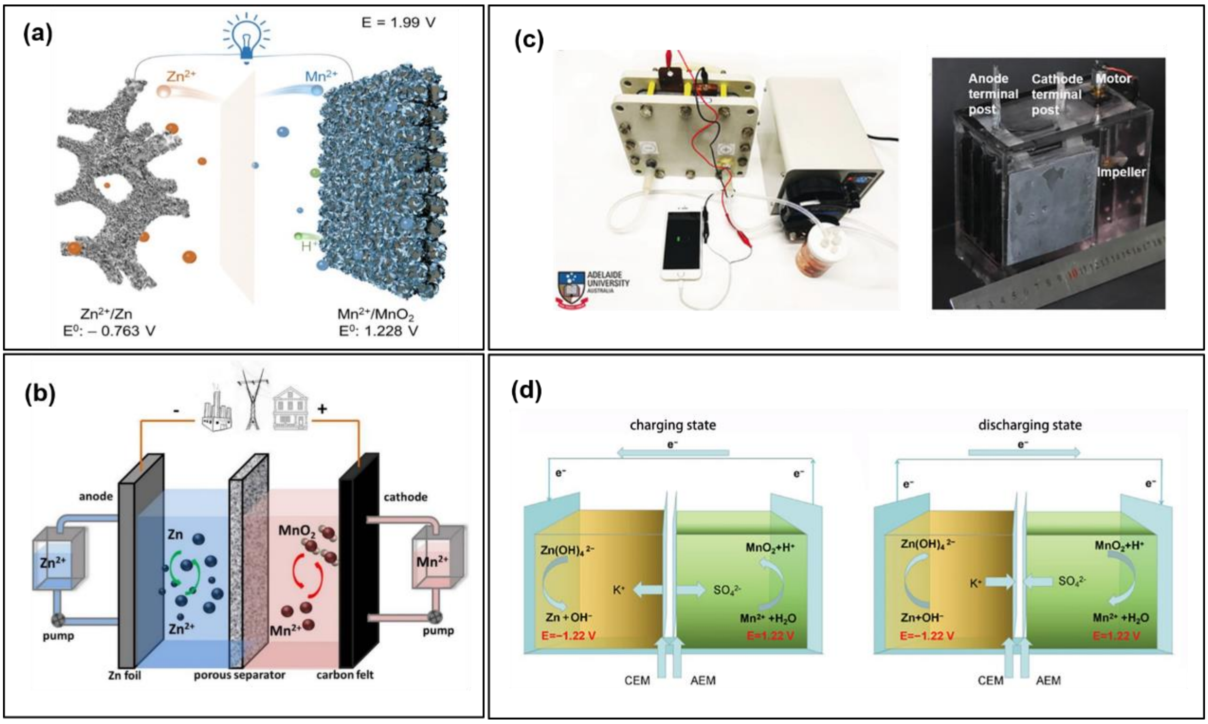


Fig. 5. Zn-MnO_2 flow battery based on the electrolytic mechanism: (a) Electrolytic process (deposition/dissolution) on both sides. Reprinted with permission from Ref. [9]. (b) Schematic of the working process of a ZMFB, and (c) Digital photos of prototype Zn-MnO_2 RFB (left part) and large-scale stack (right part) based on the electrolytic mechanism. Reprinted with permission from Ref. [9] and Ref. [63]. (d) Decoupled electrolyte battery in which the redox reactions on the cathode side and anode side are in acidic and basic electrolytes, respectively. Reprinted with permission from Ref. [25].

The dendrite formation in zinc anode is another barrier in the development of Zn-based RFBs. The zinc dendrite will result in dead Zn, low coulombic efficiency, and short circuit of the battery. To restrict the growth of Zn dendrite, additives including organics, inorganics and polymers, are proposed to add into the electrolytes [66-68]. However, the additives could be toxic and expensive. Structure engineering of the current collector is another effective approach. Recently, tin-modified 3D carbon felt was fabricated as the current collector of anode [16]. This design is not only effective in suppressing the Zn dendrite during charging/discharging process, but also enhances the coulombic efficiency and the cycle life of the flow battery. In short, Zn-MnO_2 RFB is a very promising technology, but certainly more efforts are still needed to mitigate the Zn dendrite issue by e.g., redesigning the electrolyte, engineering the electrode and current collectors.

6. **Conclusions**

Redox flow battery may be an ideal choice for stationary energy storage in the future. In the past ten years, rechargeable ZIBs are under the research focus of new batteries and its operation voltage window has been increased by implementing new charge storage mechanism and battery configurations. We have highlighted some Zn-MnO_2 AZIB systems to expound the different mechanisms, which is hopefully useful to young researchers who are interested in ZIBs. The discovery of the MnO_2 deposition/dissolution mechanism supplies a perfect connection between the AZIBs and RFBs. The Zn-MnO_2 RFB has the very high output voltage and energy density, thus very promising for near future commercialization of RFBs. To achieve high volumetric energy density, power density and life span of Zn-MnO_2 AZIB and RFB, it is necessary to achieve a delicate balance by rationally designing the electrolyte and its interaction with electrode surface. The inhibition of Zn dendrite growth in large-scale devices needs enormous research preferably from close collaboration between physicists, material scientists, and organic chemists. There is a long way to go, but it is a highway.

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9681-9687.

TOC Abstract

Aqueous Zn-ion batteries are currently under the spotlight. New mechanisms and unconventional battery configurations have pushed the performance. In this review, we briefly summarize the recent advance of AZIB and explain how Zn-MnO_2 batteries are evolving to redox flow battery.