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Energy Materials

Review

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Zn-based batteries for energy storage

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Abstract

Zn-based electrochemistry is considered to be the most promising alternative to Li-ion batteries due to its abundant reserves and cost-effectiveness. In addition, aqueous electrolytes are more convenient to be used in Zn-based batteries due to their good compatibility with Zn-chemistry, thereby reducing cost and improving safety. Furthermore, Zn^{2+}/Zn couples involve two-electron redox chemistry, which can provide higher theoretical energy capacity and energy density. Based on this, a series of Zn-based battery systems, including Zn-ion batteries, Zn-air batteries, and Zn-based redox flow batteries, have received more and more research attention. Here, the fundamentals and recent advances in Zn-based rechargeable batteries are presented, along with perspectives on further research directions.

Keywords: Batteries, Zn-based batteries, energy storage

INTRODUCTION

Since the first commercial lithium-ion battery (LIBs) developed by Yoshio Nishi in 1991, LIBs have dominated the market for portable electronic devices and electric vehicles[1-3]. However, for LIBs, limited lithium resources, soaring costs and safety hazards still inevitably hinder their development. Therefore,

some alternative energy storage battery systems with lower cost, such as sodium-ion batteries (SIBs) and potassium-ion batteries (PIBs), are put on the agenda for replacing LIBs[4,5]. At the same time, some metal-based batteries with high theoretical energy density, such as lithium-oxygen batteries and lithium-sulfur batteries, have also been proposed to cope with the increasing demand for high-energy-density batteries[6,7]. Nonetheless, the electrolytes used in those metal-based batteries are usually both water and air sensitive, posing safety and environmental concerns. In contrast, aqueous batteries (Zn^{2+}, Fe^{2+}, Mg^{2+}, Al^{3+}, and so forth) are considered promising next-generation battery systems due to their safety and environmental friendliness[8,9]. Among them, rechargeable Zn-based batteries are gaining increasing attention for replacing Li-ion batteries due to their high theoretical energy density, good stability, low cost and environmental friendliness[10].

Aqueous Zn-based batteries are built on reversible Zn^{2+}/Zn dissolution/deposition reactions with a redox potential of 0.76 V *vs.* standard hydrogen electrode (SHE)[11-16]. Depending on the battery system, the electrolyte can be neutral, acidic or alkaline solution. According to the electrochemistry of cathode materials, Zn-based batteries mainly consist of the following battery systems: Zn-ion batteries, Zn-based redox flow batteries and Zn-air batteries. Besides, some modified batteries, such as flexible devices, have also been proposed [Figure 1]. Despite the rapid development of Zn-based batteries in recent years, more efforts are still needed to drive them toward commercialization. In this focused review, recent progress on aqueous Zn-based battery systems is outlined. The operating mechanisms of each battery system are briefly introduced, followed by their existing challenges and research directions. Perspectives are also provided for the future development of Zn-based battery systems.

ZN BASED BATTERIES

Zn anode

As an important part of Zn-based battery systems, Zn anodes usually exist in the form of Zn foils in the battery system. When discharging, Zn loses two electrons to form Zn^{2+} and dissolves into the electrolyte; when charging, it regains two electrons and is plated onto the Zn flakes[17,18]. Zn anodes undergo side reactions during electrochemical processes, especially the hydrogen evolution reaction (HER) due to its poor thermodynamic stability in aqueous electrolytes, leading to severe self-discharge reactions[19-23]. There are two main solutions to this problem: surface engineering and electrolyte additives. Surface engineering strategies usually employ a layer of artificial SEI, such as inorganic passivation layers, carbon coating layers or polymer membranes, to prevent the electrolyte from directly contacting the Zn metal anode[24,25]. For example, Li *et al.* adopted graphite-modified Zn anode, a mitigated corrosion reaction was obtained and a high Coulombic efficiency was achieved[26]. Additionally, some organic additives, such as thiourea, diethyl ether (Et_2O), sodium dodecyl sulfate (SDS), or cetyltrimethylammonium bromide (CTAB), contribute to alleviating the corrosion of Zn metal anode[27].

Another major problem is the growth of dendrites in developing alkaline rechargeable batteries. The growth of dendrites will not only lead to the growth of "dead Zn" which degrades the coulombic efficiency of the battery, but also may pierce the separator and cause the battery to short circuit. One of the most direct solutions is to modify the surface of the Zn anode to form a stable solid-electrolyte interface (SEI). Higashi *et al.* used polypropylene to modify the surface of the Zn anode to ensure the stable operation of the Zn-Ni battery 800 times [Figure 2A and B][28]. Besides surface engineering, an epitaxial electrodeposition technique was also developed by Yu *et al.* to suppress dendrite growth[29]. Using graphene with a low lattice mismatch with metallic Zn as the substrate, highly reversible Zn metal reversible deposition was achieved[29]. In addition, salt concentration electrolytes are also employed to regulate the deposition of Zn metal anode. A high-concentration electrolyte containing 1 M $Zn(TFSI)_2$ and 20 M LiTFSI was proposed by

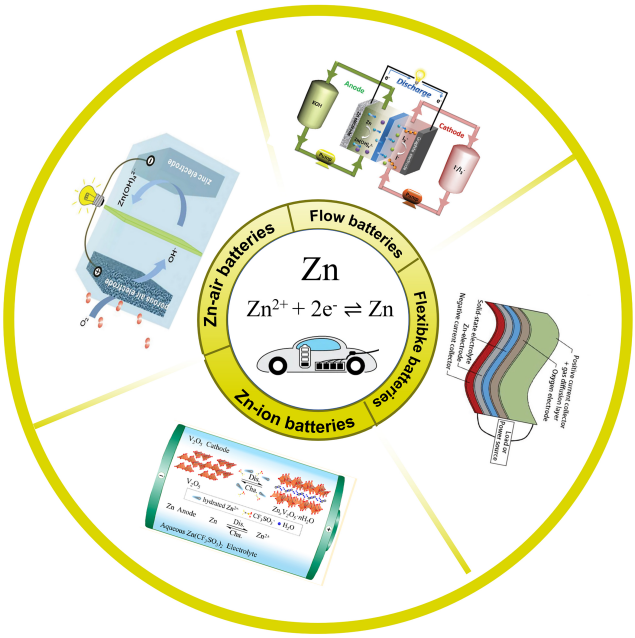

Figure 1. Schematic illustration of various types of Zn-based battery configurations.

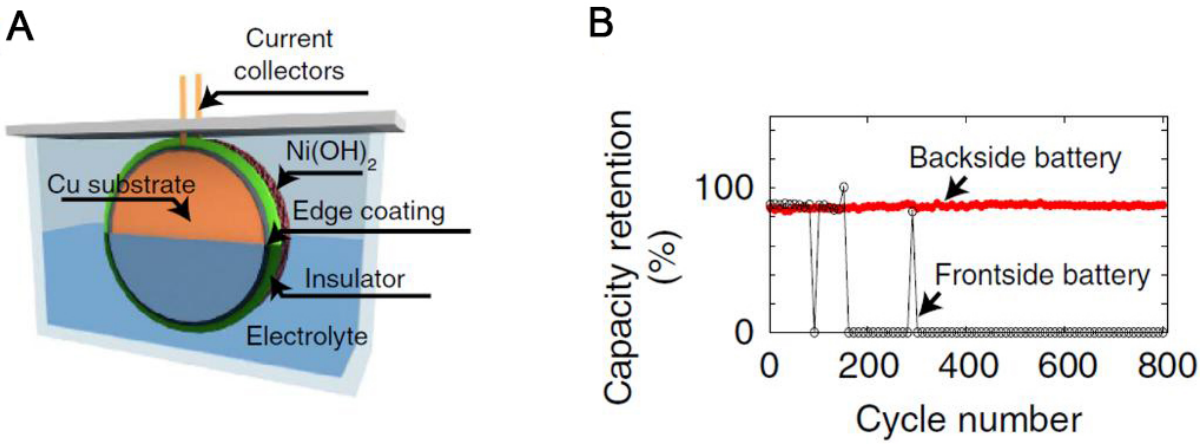

Figure 2. (A) Schematic diagram of the backside-plating configuration full-cell battery. (B) Cycling stability curves of Ni-Zn battery with the conventional frontside and backside battery cells[28]. Reproduced with permission from Ref.[28]. Copyright 2016 Nature Publishing Group.

Wang *et al.* Spectroscopic analysis combined with molecular simulation analysis revealed that high concentrations of $TFSI^-$ could effectively inhibit the formation of by-product $(Zn\text{-}[H_2O]_6)^{2+}$, thereby contributing to the deposition of Zn with near 100% Coulombic efficiency[30].

Zn-ion batteries

A Zn-ion battery consists of four components, a Zn metal anode, an metal oxides cathode, a separator, and an electrolyte. Generally, metal oxides are used as cathode materials in Zn-ion batteries, including manganese-based, vanadium-based, and Prussian blue analogs and organic cathode materials[12,31]. The characteristics of some cathode materials are listed in Table 1 below[32-37]. The characteristics of some cathode materials are listed in Table 1 below. Depending on how they store Zn ions, these materials can be

Table 1. The characteristics of some cathode materials in the Zn-ion batteries

Cathode materials	Output voltage [V]	Capacity [mAh g^{-1}]/energy Density [Wh kg^{-1}]	Capacity retention/cycle numbers/current density	Mechanism	Ref.
Ni-doped Mn_2O_3	1.2	252 (0.1 A g^{-1})/327.6	85.6%/2500/1.0 A g^{-1}	H^+ and Zn^{2+} coinsertion	[32]
MnO_2	1.35	365 (0.5 A g^{-1})/486	93.3%/4000/4 A g^{-1}	H^+ and NH_4^+ coinsertion	[33]
V^{4+}-doped V_2O_5	0.6	430 (0.5 A g^{-1})/258	86%/1000/10 A g^{-1}	Zn^{2+} insertion	[34]
$K_2MnFe(CN)_6$	1.6	138 (0.2 A g^{-1})/221	72.4%/400/0.2 A g^{-1}	Zn^{2+} insertion	[35]
m-TAPA	1.1 V	210.7 (0.5 A g^{-1})/236	87.6%/1000/6 A g^{-1}	Cl^- coordination	[36]
π-PMC	0.4	122.5 (0.2 A g^{-1})/49	68.2%/1000/8 A g^{-1}	Zn^{2+} coordination	[37]

broadly divided into two categories: intercalation chemistry or conversion chemistry. For intercalation-type materials, Zn^{2+} undergoes reversible intercalation/deintercalation reactions between the electrolyte and the cathode material during the charge-discharge process. One of the most serious problems in those cathode materials is structural collapse during charge and discharge. Defect engineering (cation vacancy or oxygen vacancy) is widely adopted to deal with this problem. A cation-deficient $ZnMn_2O_4$ spinel structure was proposed as a cathode material by Cai *et al.*, demonstrating the positive effect of defects on the structural stability of the material [Figure 3A and B][38]. They believed that the migration of Zn^{2+} in this special structure was not affected by the large electrostatic repulsion, thus contributing to the improvement of the electrode kinetics. In addition, an oxygen-deficient β-MnO_2 structure was introduced as a cathode by Cai *et al.*, which exhibited enhanced Zn^{2+} intercalation/deintercalation kinetics and achieved striking electrochemical stability[39].

As for the cathode materials based on the conversion reaction, they are usually based on the redox conversion between metal oxides and metal hydroxides, which can also be accompanied by the co-intercalation reaction of hydrogen ions. Zhang *et al.* found that α-MnO_2 would bind a H^+ during charging, and would further react with $ZnSO_4$ and H_2O to form $ZnSO_4[Zn(OH)_2]_3$ in order to achieve charge balance[38]. In addition, some researchers found that the intercalation reaction of Zn^{2+} also triggers the structural transformation of the cathode material into layered Zn_xMnO_2 and/or $ZnMn_2O_4$ with the depth of discharge[28,40,41]. Besides inorganic materials, organic materials, such as quinone, have also been proposed as conversion reaction-based cathode materials, which can reversibly bind and release Zn ions. Organic cathode materials are getting more and more attention, and some compounds are gradually being reported, such as poly(pyrene-4,5,9,10-tetraone) (PPTO), quinone (C_4Q), and polyaniline (PANI)[30,42]. A crystalline 3,4,9,10-perylenetetracarboxylic dianhydride (PTCDA) was introduced by Rodriguez-Perez *et al.* to adhere dimethyl metal ions in aqueous electrolytes, demonstrating an internal structural stability and superior electrochemical performance[43].

Neither of the above two methodes can effectively solve the inherent limitations regarding the voltage window and energy density of Zn-ion batteries. Obviously, the low electrochemical potential window of aqueous electrolytes with a redox potential of 1.23 V *vs.* SHE, severely limits the choice of high-voltage electrode materials. Therefore, widening the electrochemical cell window of aqueous electrolytes is crucial for high-pressure aqueous Zn-ion batteries. An effective method is to effectively prevent the water molecules of the electrolyte from contacting the Zn anode. For example, the NaCl/sodium alginate (SA) gel electrolyte exhibited an electrochemical window of 2.72 V due to the confinement of water molecules in the gel electrolyte through hydrogen bonding[44]. Consequently, the direct contact between the water molecules and the electrode material is largely alleviated. Another effective way is to form a salt concentration electrolyte. In the electrolyte with ultra-high salt concentration, the free water molecules will disappear due to the lack of water solvent, avoiding direct contact between the water molecules and electrodes. At the

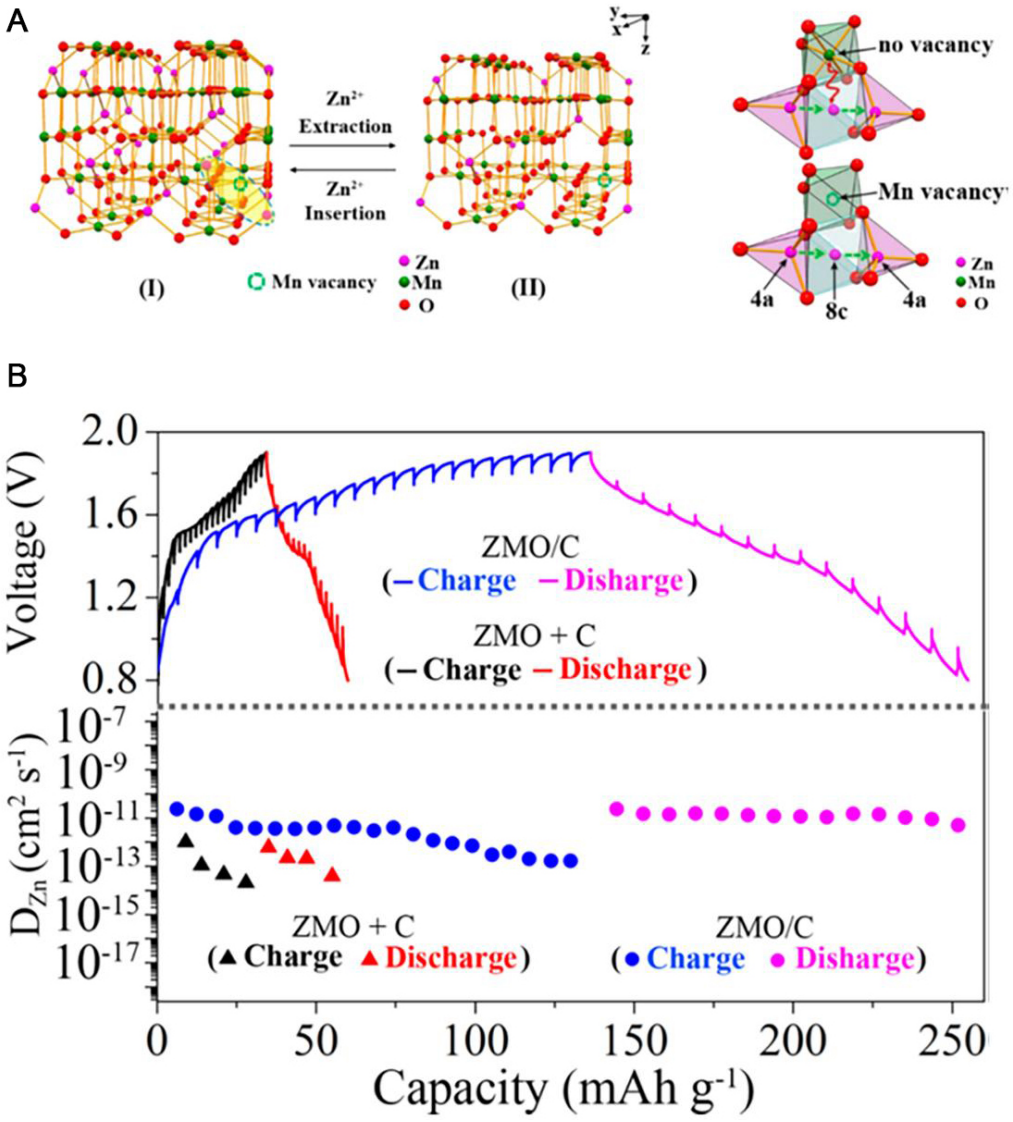

Figure 3. (A) Schematic description of Zn^{2+} insertion/extraction in a three-dimensional ZMO spinel framework; (B) Zn^{2+} diffusion coefficient of ZMO/C and ZMO + C electrodes by GITT technique[38]. Reproduced with permission from Ref.[38]. Copyright 2016, American Chemical Society.

same time, the anions will enter into the solvated structure and induce the generation of anion-derived SEI, improving the stability of the electrode interface[45-47]. Therefore, some typical salt concentration electrolytes for high voltage batteries have been reported, including 21 m LiTFSI + 0.5 m $ZnSO_4$[48], 1 m $Zn(CH_3COO)_2$ + 31 m KCH_3COO[49], 30 m $ZnCl_2$[50]. However, the cost factor brought by the high concentration of salt prevents their practical application. The development of localized high-concentration electrolytes with diluents may be an effective approach for practical applications[51-54].

Zn-air batteries

Generally speaking, a Zn-air battery consists of four components, a Zn metal anode, an air cathode, a separator, and an electrolyte. Generally, a high-concentration aqueous alkaline solution (NaOH or KOH) is used as the electrolyte, which can not only provide an alkaline environment, but also sufficient ionic conductivity[10,11,55-58]. The membrane is usually an anion exchange membrane, which allows the free

movement of the anion OH^- and prevents the passage of the cation Zn^{2+}. The redox reactions occurring at the air cathode and the Zn anode are shown below[59-61]:

Air cathode reaction:

$$O_2 + 2H_2O + 4e^- \rightarrow 4OH^- \quad (1)$$

Zn anode reaction:

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^- \quad (2)$$

Overall reaction:

$$O_2 + 2Zn \rightarrow 2ZnO \quad (3)$$

As the core part of the air electrode, the activity and durability of the catalyst are the most important considerations in determining the performance of ZABs[62,63]. Although platinum (Pt) is considered to be one of the best catalysts for ORR, its scarcity and high price hinder its commercial application. Similarly, other noble metal catalysts such as iridium oxide (IrO_2) and ruthenium oxide (RuO_2) also face the same dilemma as Pt-based catalysts[64-66]. To reduce cost, transition metal compounds have been reported as promising ORR and OER electrocatalysts[65,67-69]. Although most of them do not perform as well as Pt-based catalysts for ORR, their acceptable OER activity makes them better choices for ZABs.

Besides metal-based catalysts, carbon-based materials are also widely used as catalysts in ZABs. They generally exhibit good chemical stability and electrical conductivity, which facilitates long-term electron transport during electrochemical processes, while the porous structure with high specific surface area facilitates the exposure of catalyst active sites and efficient mass transport[70-72]. Therefore, carbon-based catalysts have gained a lot of attention for developing reversible ZABs. Unfortunately, carbon corrosion inevitably occurs in alkaline electrolytes, and those catalysts are often prone to loss of structural stability, leading to a widening of the voltage gap[72,73]. In contrast, metal oxide-based catalysts usually have good durability, such as excellent durability of 600 h when using Co_3O_4 nanowire arrays as catalysts [Figure 4][74-76]. Therefore, the rational design of composites of carbon materials and oxides has attracted a lot of research attention when a pioneering work on N-doped CNT-supported $LaNiO_3$ was developed for ZABs[77].

Flow batteries

Zn-based redox flow batteries usually use Zn as the anode and redox pairs as electrodes, including Zn-Fe, Zn-Ce, Zn-halogen (Cl_2, Br_2, and I_2), and Zn-organic couples [Figure 5][78-86]. Although substantial progress has been made in Zn-based flow batteries, more efforts are still needed to improve some important parameters to achieve the goal of commercialization. Current efforts mainly focus on optimization of the electrolyte, membrane and electrode[87]. This review focuses on the Zn-I_2 flow battery as an example.

The typical structure of Zn-I_2 is shown in Figure 5B[85]. Basically, repeated Zn^{2+}/Zn deposition/dissolution reactions occur on the negative side of Zn in acidic or alkaline electrolytes, while conversion reactions between iodide anions (I^-) and triiodide anions (I_3^-) occur on the positive side. Despite the advantages of I^-/I_3^-couples in terms of cost and water solubility, the low utilization of iodine originates from the formation of insoluble I_2 during charging and discharging severely hinders the application of Zn-I_2 batteries[88].

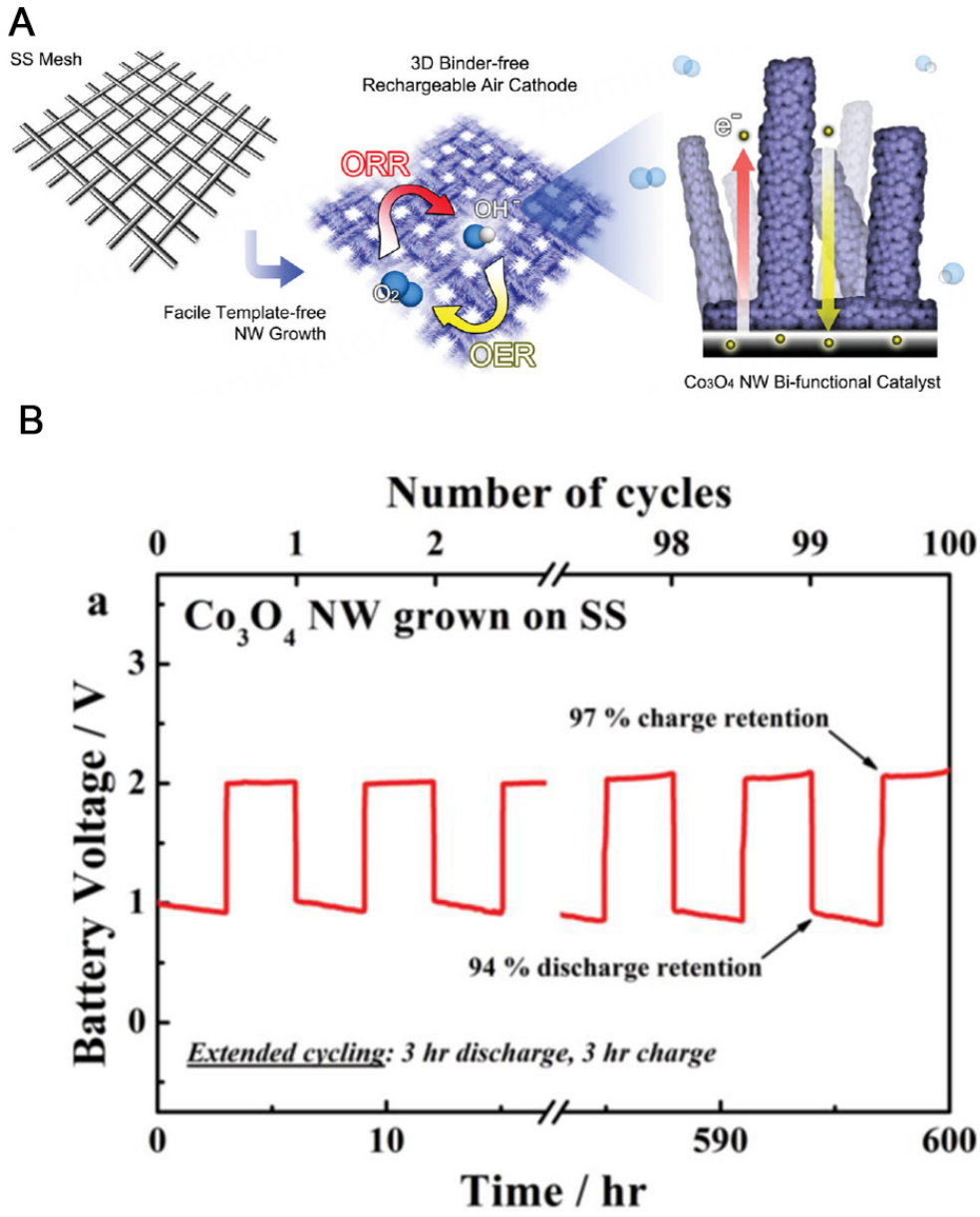

Figure 4. (A) Schematic illustration of the growth of 3D Co_3O_4 nanowires as bifunctional catalyst; (B) The Zn-air battery cycling tests based on Co_3O_4 nanowires bifunctional catalyst[74]. Reproduced with permission from Ref.[74]. Copyright 2013 John Wiley & Sons, Inc.

Furthermore, the "shuttle effect" of soluble iodine species is another factor limiting the development of Zn-I_2 flow batteries[85]. The usual way to address the above issues is through electrode structure design, electrolyte formation or membrane modification. For electrode material design, one of the most effective methods is to prepare catalyst/carbon material composites as cathode hosts to improve the electrochemical reaction of Zn-I_2 flow batteries. Li *et al.* reported two metal-organic frameworks (MOFs), MIL-125-NH_2 and Uio-66-CH_3, as catalysts to improve the utilization of iodine during electrochemical reactions and alleviate the "shuttle reaction" of soluble iodine[89]. For electrolyte modification, additives may be one of the most feasible and effective methods to improve the environment of polyanions present in electrolytes. Weng *et al.* introduced bromide ions (Br^-) to form bromo-iodine complex for stabilizing iodine in the electrolyte, which greatly improved the utilization of iodine[90]. In addition, an alkaline anolyte was reported by Weng *et al.*,

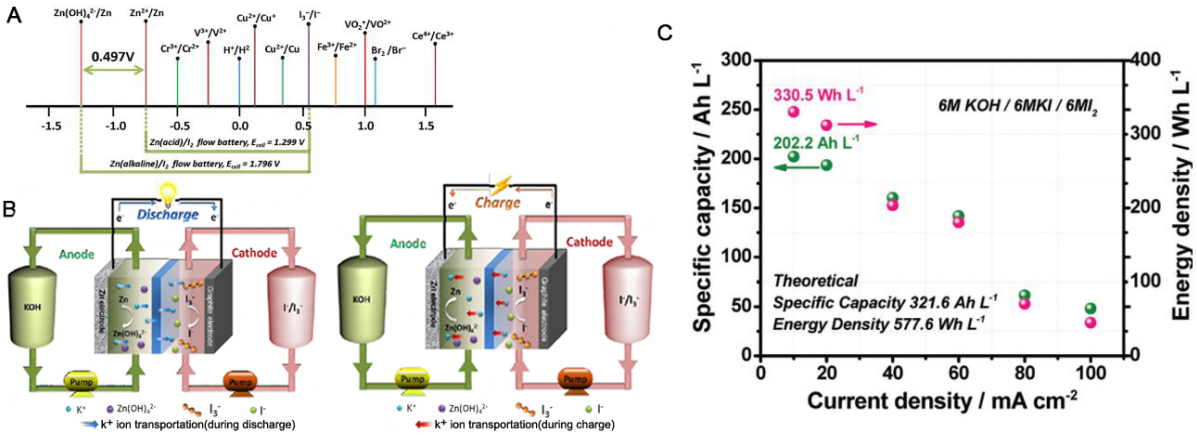

Figure 5. (A) Redox couples commonly adapted in flow batteries and corresponding standard reduction potentials; (B) schematic illustration of the charging and discharging mechanisms in alkaline Zn-I_2 flow batteries; (C) specific capacity and energy density at different current densities of alkaline Zn-I_2 flow batteries[85]. Reproduced with permission from Ref.[85]. Copyright 2018 Royal Society of Chemistry.

which broadened the potential window of the cell by 0.497 V and obtained an improved energy density of 330.5 W h L^{-1}[85]. For battery membranes, apart from the commercial cation-selective Nafion membranes, polyolefin-based membranes have also been used in the Zn-I_2 flow batteries[91,92].

Flexible batteries

The adoption of flexible Zn-based batteries for wearable devices has gained increased attention due to their environmental friendliness and cost-effectiveness[18]. Flexible Zn-based batteries usually consist of flexible electrode materials and polymer electrolytes. Flexible cathode materials are usually integrated active electrode materials on flexible substrates, such as carbon cloth, nickel foam, stainless-steel mesh, *etc.*[93-95]. As shown in Figure 6, a typical fabrication process of flexible Zn-air battery cathodes was presented [Figure 6A][96]. A chemical vapor deposition was employed with ZnCo-Hexamine (HMT) as the gas source to obtain cobalt-decorated carbon arrays with a nickel foam substrate as the flexible cathode. Gel electrolytes, usually synthesized by polymer membranes absorbing aqueous electrolytes, have been explored and widely used in flexible Zn-air batteries. In general, the performance of gelled electrolytes is mainly determined by the properties of the chosen gelling agent. Polyvinyl alcohol (PVA) is generally considered to be a perfect gelling agent due to its abundant hydroxyl functional groups and good water solubility[96]. However, its relatively low ion conductivity severely limits its commercial application. To address this challenge, a modified cellulose membrane was prepared as a promising alternative[97]. Fu *et al.* used a functionalized cellulose membrane with a rich hydrogen-bonded network structure by tetraammonium salt treatment [Figure 6B], demonstrating excellent electrochemical performance in a flexible Zn-air battery[98].

Although the Zn-air battery has an ultra-high specific energy density, 6070 Wh L^{-1}, it is not a suitable flexible battery system because its semi-open structure that ensures easy access of atmospheric oxygen to the battery system would lead to continuous water loss in the electrolyte and then causes the battery to fail[11]. Therefore, seeking a new cathode material that also has the characteristics of high specific energy density, but rarely suffers from the adverse effects of half-cells, may be the future direction. For example, Wang *et al.* developed a Zn-Co_3O_4 flexible battery with an energy density of 2807 Wh L^{-1}[99]. In addition, Zn-ion batteries have also been adopted as flexible batteries due to their better rechargeability. For example, a Zn-MnO_2 battery, with α-MnO_2 nanofiber as the positive electrode, Zn sheets as the negative electrode and $ZnSO_4$/$MnSO_4$ solution as the electrolyte, was successfully demonstrated. This battery exhibited excellent

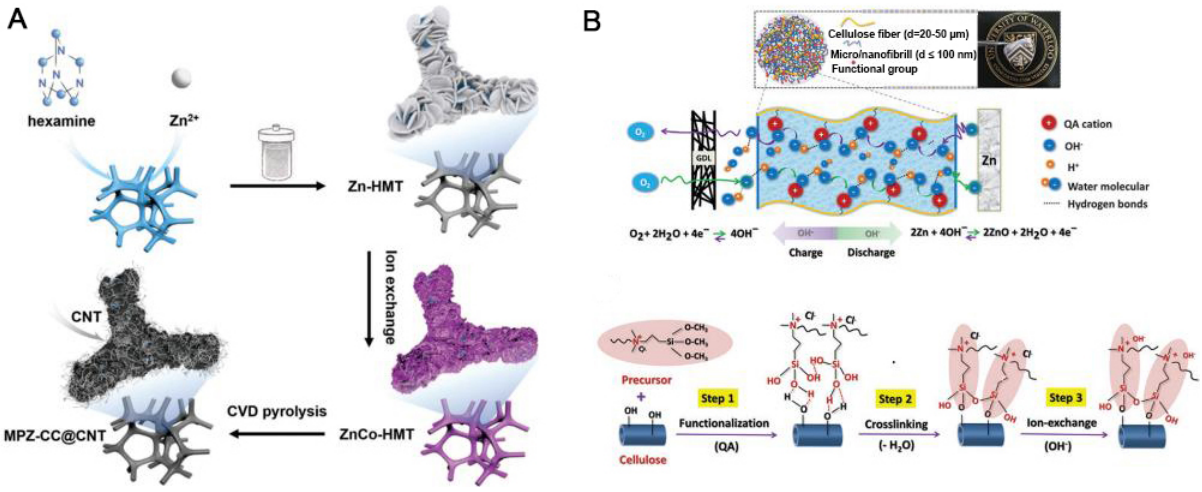

Figure 6. (A) Schematic illustration of ordered arrays on nickel foam as self-supported for flexible Zn-air battery[96] Reproduced with permission from Ref.[96]. Copyright 2019 John Wiley & Sons, Inc.; (B) Schematic presentation of nanocellulose membrane functionalization and demonstration of flexible Zn-air battery[98]. Reproduced with permission from Ref.[98]. Copyright 2015 Royal Society of Chemistry.

cycling stability, maintaining a capacity retention rate of 92% after 5000 cycles at a current density of 5C[100]. This work opens a direction for the development of long-lived flexible Zn-MnO_2.

PERSPECTIVES

This review describes the overall landscape of aqueous Zn-based batteries, including Zn-ion batteries, Zn-air batteries, redox flow batteries, and flexible batteries. Within each classification, the basic working principle and recent research progress are summarized. Currently, there are still many obstacles that need to be removed on the road to the commercialization of Zn-based batteries. Therefore, two main perspectives related to battery material design and intrinsic mechanism exploration are given as follows:

(1) Material design and optimization to improve electrochemical performance is still a challenge for various types of Zn-based battery configurations. For Zn-ion batteries, the search for materials that can withstand sustained multi-electron transfer while maintaining structural stability is strongly needed for both the intercalation and conversion cathodes. Electrocatalysts, with sufficient active sites, high activity and sufficient durability, are required in Zn-air batteries. The development of highly active cathode materials and cost-effective, stable and ion-conducting membranes is crucial for redox flow batteries. For flexible batteries, the mechanical flexibility and structural stability of battery materials are prerequisites for flexible devices, while the hydroxyl conductivity, water-holding ability, and alkali tolerance of gel electrolytes determine the performance of Zn-air batteries.

(2) Apart from material design, the electrochemical behavior of electrode materials is still not well understood. Deeper mechanistic studies are desperately needed to further improve the electrochemical performance of Zn-based batteries. Taking Zn-air batteries as an example, although metal-based materials are widely used as bifunctional catalysts in Zn-air batteries, it was only recently revealed that their derived metal hydroxides are the real active sites for OER. A metal hydroxide layer was found on the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_3$-δ surface during the OER reaction. This phenomenon was also found when spinel $CoFe_{0.25}Al_{1.75}O_4$ was used as a catalyst. Therefore, further mechanistic understanding through in situ probing methods is strongly demanded to aid the search for better catalyst materials.

DECLARATIONS

Authors' contributions

Contributed to this review: Xiao D, Lv X, Fan J
Revised this review: Li Q, Chen Z

Availability of data and materials

Not applicable.

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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