Crossroads in the renaissance of rechargeable aqueous zinc batteries

Junhua Song¹,2, Kang Xu³*, Nian Liu⁴*, David Reed¹, Xiaolin Li¹*

¹Pacific Northwest National Laboratory, Richland, WA 99354, United States
²Storagenergy Technologies Inc., Salt Lake City, UT 84104, United States
³Energy Storage Branch, Energy and Biomaterials Division, Sensor and Electronics Directorate, U.S. Army Research Laboratory, 2800 Powder Mill Road, Adelphi, MD 20783-1197, United States
⁴School of Chemical and Biomolecular Engineering, Georgia Institute of Technology, Atlanta, GA 30332, United States

Aqueous zinc batteries dominate the primary battery market with alkaline chemistries and recently have been rejuvenated as rechargeable devices to compete for grid-scale energy storage applications. Tremendous effort has been made in the past few years and improved cyclability has been demonstrated in both alkaline, neutral, and mild acidic systems. In this review/perspective, we will elucidate the merits of rechargeable aqueous zinc batteries through side-by-side comparison to Li-ion batteries, examine the challenges and progress made in the pursuit of highly rechargeable alkaline and mild acidic batteries, and finally provide a holistic forward look at the technology. The focus is placed on static closed cell designs, while flow batteries and open systems like zinc-air batteries will not be included due to space constraint.

Introduction

Electrification has become a global megatrend as we move into an era that the world runs on clean and sustainable energy and mankind is forced to adapt to a society of virtual interactions. The core technology of the process is a secure, flexible, and resilient electric power system to harness and store intermittent renewable energy resources in large scale, to flatten the peaks and valleys induced by electricity consumption surge/decrease with numerous electric cars plugging in/out simultaneously, and to satisfy unexpected national/regional catastrophes. Reversible energy storage plays an essential role in accomplishing these missions as it matches perfectly with the intrinsic nature of the electrical grid, which requires a bi-directional electron movement. Highly efficient, safe and low-cost rechargeable batteries with the advantage of high portability and little geographic restrictions present one of the most important candidates for grid-scale energy storage applications. Lithium-ion batteries (LIBs) with their high energy density and long cycle life have been a drop-in option for this purpose owing to the mature industry, but the flammable nature of the organic electrolyte used therein induces undeniably high risk on safety, particularly at a mega/gigawatt hour scale deployment. Moreover, the high cost of LIBs, the non-uniform geographical distribution of the raw materials as well as the geopolitical risks in supply chain have made it an imminent interest to look for alternative battery chemistries. Aqueous zinc batteries (AZBs) using water-based electrolyte, Zn metal anode and usually earth-abundant cathode materials, if made highly rechargeable, would provide a highly attractive solution to all these challenges mentioned above.

AZB is believed to be a more appropriate terminology than Zn-ion battery for our discussion below. First, for a similar concept to Li-ion battery, Zn-ion battery will exclude alkaline and other batteries that do not have Zn²⁺ ions as charge carriers, particularly on the cathode side. Second, the mild acid Zn battery systems (pH ~4–6) still have controversial storage mechanisms. Third, it highlights the importance of aqueous electrolyte and Zn anodes, which literally are the foundation of all the goods and the bads. Last, as implied by the term of “Li-ion battery”, Zn-ion battery
would carry the misleading hint of a dual-ion intercalation chemistry, which by definition excludes Zn metal as anode.

AZBs have a long history of development and commercialization. In 1799, the first AZB, also the first electrochemical battery, was demonstrated by Alessandro Volta, who paired zinc metal and copper plates in brine electrolyte [1]. Early aqueous zinc-manganese oxide (Zn–MnO2) batteries can be dated back to 1866, when Georges Leclanche invented the Leclanche cell [2]. In 1886, Carl Gassner developed Dry Cell based on the technology [3]. The battery was also known as zinc-carbon battery for the use of carbon rod as cathode current collector, while the electrochemical redox reactions at cathode and anode actually were from MnO2 and Zn. Mild acidic solution of ammonium chloride (NH4Cl) with/without zinc chloride (ZnCl2)-gel materials was used as electrolyte.

Alkaline Zn–MnO2 batteries that currently dominate the primary battery market were developed by Lewis Urry in 1950s, which was almost 6 decades after Waldemar Jungner and Thomas Edison first introduced alkaline electrolyte to batteries [4]. The Zn–MnO2 cells with alkaline electrolyte have similar voltage to those with mild acid electrolyte. Alkaline batteries have almost 5 times greater capacity and energy density than an equal-sized battery with mild acid electrolyte because of the high ionic conductivity in denser electrode made of MnO2. The market over the years has voted the alkaline system as a better route for primary aqueous Zn–MnO2 batteries for its advantageous overall performance at similarly low cost.

It has also been a-century-long endeavor to make AZBs rechargeable, starting with Edison’s invention on the rechargeable zinc-nickel (Zn–Ni) battery system in 1901 [4–7]. Early Zn–Ni batteries provided very limited number of discharge/recharge cycles and were not of much interest. The first renaissance of rechargeable AZBs began with dealing the oil crisis in early 1970s. Back then, rechargeable Zn–Ni batteries were developed for electric vehicles. In the 1970s and 1980s, a lot of research were reported on understanding the battery degradation mechanism and developing electrode/electrolyte additives to improve the reversibility of Zn anode and various cathodes [8–11]. These efforts did not eventually made alkaline batteries rechargeable in practical sense, but they did start the fundamental understanding of the complicated chemistries and materials involved. The accessible cell capacity by then was only around two-thirds of that of primary cells and died within 20 deep-discharge cycles. Attempts were also made to recharge the mild acid Zn–MnO2 cells by exploiting aqueous ZnSO4 electrolyte and different types of MnO2 cathodes [12,13]. The charge/discharge reactions on both the Zn anode and the MnO2 cathode were reversible in mild acid electrolyte. Improved cycling stability have been obtained by using electrolyte additive of MnSO4 to alleviate the MnO2 cathode degradation from Mn2+ dissolution [14,15].

Recently, rechargeable AZBs started gaining new momentum by leveraging the technical advances in material nanoeengineering, electrolyte development as well as breakthroughs in fundamental understanding of the electrochemistry at the interphase or bulk electrodes. Zn–Ni batteries and Zn–MnO2 batteries with alkaline and mild acid electrolyte have been reported to have long cycle life [15–17]. With the advantage of lower cost comparing to other rechargeable batteries, AZBs have been rejuvenated as a competitive energy storage candidate to enable secure, flexible, and resilient electrical grid. There have been many research papers and several reviews on rechargeable Zn batteries with focuses on Zn anode, cathode materials and Zn-air systems [11,18–25]. In this review/perspective paper, we use Zn–MnO2 as the model chemistry to compare the energy density and cost of AZBs to typical LIBs. We also provide a systematic view on challenges and progresses on different Zn battery development routes and holistic forward look at the AZB technologies. As aqueous Zn battery is a field with a lot of exciting research going on and the review is not attempted for a comprehensive coverage but a reflection of the authors’ perspective or personal viewpoint on current research, we will not try to exhaustively cover every aspect in the selection of references.

The essential merits of aqueous Zn batteries
AZBs, like all other batteries, are composed of common components, including cathodes, anodes, current collectors, electrolyte, separators, and packing cases etc. However, the Zn metal anodes and aqueous-based electrolyte bring significant advantages on energy, power, safety, environment, cost, and other aspects.

High degree of safety
Cell failure due to thermal runaway has been a heated topic around LIBs and incited many discussions and studies on developing safety/abuse tests and prevention mechanisms. One of the major safety concerns of LIBs comes from the flammable organic electrolyte vapor that escapes from failed cells and the heat released from internal and localized short. The combustible nature and low heat capacity of liquid aprotic solvents require little energy input to move them to their ignitable gas phase. For instance, the latent heat of vaporization of dimethyl carbonate (DMC), a typical LIB electrolyte solvent, is only 8.38 kJ/mol [26], while the heat to vaporize water is 40.8 kJ/mol, ~5 times of that of DMC’s [26,27]. This enables the cells containing aqueous electrolyte to tolerate a wider temperature swing before critically pressurizing the cell case. Also, steam would be generated even if the batteries ended up in the worst-case scenario of a thermal runaway, which would rapidly cool down the cell by taking away tremendous amount of energy. On the contrary, the heated aprotic electrolyte vapor from LIBs is susceptible to combustion after mixing with oxygen in air, which could lead to chain reactions with adjacent cells.

In addition to the above discussion, the aqueous electrolyte interaction with electrode materials used in AZBs is often much safer than that in LIBs. On the cathode side, the most studied cathode material in AZBs, MnO2, for example, has very low chemical reactivity at charged state and remains resilient to structural breakdown up to 500 °C [28]. In contrast, many LIB cathode materials such as lithium cobalt oxide (LiCoO2), lithium nickel manganese oxide (LiNi1/3Mn1/3Co1/3O2, NMC), are physicochemically unstable when heated to elevated temperatures with the electrolyte. These cathodes are prone to decompose by releasing oxygen at relatively low temperature of ~200–300 °C, which accelerates electrolyte decomposition and cell pressurization [29,25]. Carbonaceous anode in LIBs is a relatively inert component by itself. However, carbon anodes, such as graphite, are
highly reactive with electrolyte at fully lithiated states [30,31]. The residual Li metal film formed on the carbon anode surface after prolonged cell operation or high rate charging is also susceptible to ignition when exposed to air and moisture. The safety risk becomes notoriously high when Li foil is directly used as anode for high-energy Li metal batteries [32]. Considering the Li metal battery history, safety presented a much bigger challenge than improving the energy density and cycle life. Metallic Zn used in AZBs, is much more stable than Li, making Zn anode easy to handle and relatively less obstacles to be used as a legitimate anode for cell manufacturing and operation.

AZBs have Zn dendrite formation and H₂ release under abuse conditions and potentially can be of safety concern. However, without a large amount of synergetic heat generation, the cell safety is relatively easier to handle by monitoring the cell voltage, installing H₂ sensor in the room and building ventilation. The experience from dealing with lead acid batteries can also be leveraged for safe operation of AZBs.

**High specific energy**

As one of the main parameters in performance evaluation and driving forces behind new battery chemistries, the specific energy of AZBs at the material-level is by no means comparable with LIBs in most scenarios. Yet, for practical use, the specific energy value at pack-level can come very close or even higher than LIB chemistries. Fig. 1 gives our own exemplary specific energy analysis of AZBs and LIB chemistries of graphite (Gr)- and Gr/silicon (Si, ~5wt.%)-NMC622 using BatPaC 4.0, which is a well-accepted model developed by Argonne National Laboratory. Our analysis was done under the assumption that they have similar cell and pack designs, except the AZBs have less inactive components at pack-level (Fig. 1a). The assumption is reasonable as LIBs have very successful architectures to follow in designing rechargeable devices and the “safe” nature of AZBs enables them to pay less toll on the inactive components, such as thermal and other management systems.

Fig. 1b shows the comparative analysis result of the cell- and pack-level specific energy (SE) of Gr-NMC622, Gr/Si-NMC622, and Zn–MnO₂ batteries using BatPac 4.0 (see Supporting Tables S1–S6 for detail cell parameters used in the calculation). The Gr-NMC622, Gr/Si-NMC622 have specific energy of 289 Wh/kg and 304 Wh/kg at the cell level. The specific energy of Zn–MnO₂ cells were estimated based on the percentage of Zn utilization and the number of electron transfer in MnO₂ cathode redox reactions. We have chosen two representative scenarios of 50% and 90% of Zn anode utilization, corresponding to the negative to positive electrode capacity ratio (N/P ratio) of 2 and 1.1, respectively. According to the general consensuses, the specific capacity of MnO₂ cathode with one and two electron transfer were fixed at 290 mAh/g and 616 mAh/g [17,33–35]. With one electron redox reaction of MnO₂, the cell-level SE of Zn–MnO₂ battery is between ~120 and 109 Wh/kg (50% to 90% Zn utilization). It is ~180 Wh/kg lower than that of the Gr- or Gr/Si-NMC622 cells. Only when two electrons are utilized in the MnO₂ redox reaction, the cell-level SE can reach 374 Wh/kg (50% Zn utilization) and 449 Wh/kg (90% Zn utilization), sur-
passing the Li-ion rivals. When assembled into 20 kWh/120 kW packs, the SE decreases for all chemistries due to the addition of extra component such as series of circuit board and thermal responsive regulation components. The specific energy of Gr-NMC622, Gr/Si-NMC622 pack drops to 201 Wh/kg and 209 Wh/kg. While for Zn–MnO2 packs, the elimination of the cooling components (liquid/air cooling) and simplified battery management system (BMS) can reduce the pack weight by ~10 kg (~10–14 wt. %). Even with the pack structure specifically designed for LiBs, the SE gap between Zn–MnO2 with one electron transfer and Gr-/Gr/Si-NMC622 shrinks to ~121 Wh/kg at pack-level. The Zn–MnO2 battery with two-electron transfer remain advantageous with SE of 232–288 Wh/kg. Although coupling high nickel NMC cathode (e.g. NMC811) and Li metal anode can reach a cell-level SE over 500 Wh/kg [36], AZBs can still compete if two-electron transfer of MnO2 is stably achieved.

The nature of aqueous electrolyte in AZBs enables them to have large heat specific capacity and “relatively low flammable/explosive risk” for use in confined spaces and deployment at large-scale. Furthermore, AZBs, benefit from the safer nature, have much more simplified pack architecture with the elimination of temperature-regulating system, such as coolant circuit and associated mounting accessories [37]. This enables them a rather competitive system with comparable specific energy to LIB chemistries at the pack level, which after all, is the basic energy storage unit in practical use scenarios. It lights up the path for implementing AZBs in grid-scale storage applications and low/medium speed electrified transportation. It has to be noted that AZB is a wonderful example to demonstrate that battery-pack energy is the parameter that matters in practical use. The value is not only determined by the fundamental redox chemistry, but also a natural outcome of the system-level design based on the intrinsic safety features, which has been often overlooked in previous literature.

**Low cost**

Cost usually is not considered much in the academic research aiming mostly for understanding the fundamental science of batteries. However, “the cost-performance correlation” is extremely important for a new battery technology to have its market success. Many AZBs use low-cost and widely available raw materials, which can have a substantially lowered cost than lithium-based batteries. Currently, the market price of zinc carbonate, a typical precursor for zinc metal production, is only $110/ton, 10 times cheaper than that of lithium carbonate’s $17,000/ton [38,39]. Zinc cathode materials, such as MnO2 and its different phase derivatives, are much cheaper than lithium battery cathodes, which usually contain cobalt and/or large amount of nickel and suffer from a vulnerable supply chain and continuously increasing production cost [40]. In addition, the electrolyte using water and zinc sulfate salt is also low cost comparing to the aprotic solvents and lithium hexafluorophosphate salt used in LiBs [41,42]. According to our cost estimation using BatPaC 4.0, the material cost of a 20kWh/120 kW battery pack of Gr- or Gr/Si-NMC622 is between ~$1600–$1800/pack, which is around ~$110–$1467/pack higher than that of the rivals of Zn–MnO2 batteries (Fig. 1c, Table S7). The material cost per kWh is ~$91–$18–$76 for LiBs and ~$91–$18–$76 for Zn–MnO2 batteries (Fig. 1d, Table S7).

As the total pack cost includes materials, processing, labor and capital equipment, the material cost being ~40% for LiBs translates to a total pack cost per kWh of ~$206/kWh–$218/kWh for the selected LiB chemistries. According to the BatPaC 4.0 simulation, the conventional LiB manufacturing cost includes operational expenditure associated with dry room processing, use of NMP solvent, labor with air/moisture sensitive materials and so on. These processes are unique to LiBs but not all necessary in making AZBs. There are significant room for reducing the manufacturing cost of AZBs. For example, solvent used for slurry and electrolyte can be completely replaced by water; MnO2 cathode storage and handling can happen in ambient environment; cell assembly does not require low moisture condition as in a “dry-room” and simplified pack architecture would lower the labor intensity. Zn–MnO2 battery will have a total pack cost per kWh significantly lower than ~$45/kWh–$188/kWh (values obtained assuming the material cost in Zn–MnO2 battery pack also is 40% of the total cost), while having better safety rating and comparable energy density with LiBs [43,44].

With the bright future of lower cost, higher safety, comparable specific pack energy to LiBs, the renaissance of rechargeable AZBs, particularly Zn–MnO2 batteries, is entirely feasible. The AZBs benefit from the high conductivity of the aqueous electrolyte and can have high power density too.

**Aqueous vs. non-aqueous electrolyte**

The above discussion has demonstrated the advantages of AZBs, which we would like to elucidate further by comparing AZBs and Zn-based batteries using non-aqueous electrolytes (Fig. 2). Aqueous and non-aqueous electrolyte have different limitations due to different parasitic reactions within the operation voltage window: the H2 and O2 evolution for aqueous electrolytes and the reduction/oxidization of organic solvents for non-aqueous electrolytes. LiBs benefit from the use of non-aqueous solvents, which decompose at the anode and cathode surface and form interphase essential to the stable battery performance. LiBs with appropriate aprotic electrolyte stably encompass the operation voltage of carbon anodes and metal oxide cathodes that expand from 0.2 V to 4.4 V vs. Li/Li+ enabling an average cell voltage of ~3.8 V and subsequently high specific energy. In the case of Zn-based batteries, Zn metal has a potential of ~2.28 V vs Li/Li+ (~0.76 V vs. standard hydrogen electrode), while the majority of suitable cathode materials falls in a similar voltage range (~0.2 V–2 V vs. standard hydrogen electrode). There is not much voltage disadvantage of AZBs over non-aqueous Zn batteries for regular cathodes. Solvent-in-salt electrolytes can further boost the voltage window of both aqueous and non-aqueous Zn batteries [45–47]. It is a relatively new research area and the voltage effect and energy density of these systems would request more work to utilize their potential to the fullest. The non-aqueous electrolyte can have wider electrochemical stability window over aqueous electrolyte. Electrolyte made of Zn(TFSI)2 in acetonitrile has been demonstrated to have anodic stability potential up to ~3.8 V vs Zn2+/Zn [48]. However, lack of compatible high voltage
cathode materials (e.g. NiOOH@~1.6 V, MnO2@~1.3 V) makes the organic electrolyte an overkill. The highest open circuit potential of oxide cathodes reported so far was the zinc alum-

inium cobalt oxide spinel cathode (ZnAl<sub>x</sub>Co<sub>2-x</sub>O<sub>4</sub>) which showed an open circuit potential of ~1.95 V vs Zn<sup>2+</sup>/Zn and achieved steady cycling at 114 mAh g<sup>-1</sup> over 100 cycles [49]. Recently, Zn-graphite-based dual-ion batteries (anions intercalate into the cathode while the Zn<sup>2+</sup> redox reactions happen at the Zn anode side) enabled high voltage output of 2.2 V and some hybrid designs showed promising cycling stability [50,51]. Some non-flammable aprotic electrolytes, such as, trimethyl phosphate-based electrolyte also can be used to address the safety concern [52]. While all the innovative research keeps a high hope for non-aqueous Zn batteries, further validation of the technologies at close-to-practical testing conditions and side-by-side comparison of the performance and cost to water-based chemistries are needed.

Because of the fundamental difference of Zn<sup>2+</sup> ion solvation structure in aqueous and non-aqueous electrolyte (Fig. 2) and subsequent solvation/desolvation energy in electrochemical processes, non-aqueous Zn batteries can suffer from poor transport kinetics. Kundu et al., have systematically compared the electrochemical performance of layered V<sub>3</sub>O<sub>7</sub>/H<sub>2</sub>O materials in aqueous and non-aqueous electrolytes [53]. When assembled into a full cell against a Zn anode in ZnSO<sub>4</sub>/H<sub>2</sub>O aqueous electrolyte, the cathode was able to deliver high capacity of 375 mAh/g at 1 C and 275 mAh/g at 8 C with close to 100% Coulombic efficiency. While a sharp contrast was displayed in non-aqueous counterpart: only 50 mAh/g capacity was accessed in the initial cycle at low current density of 5 mA/g in Zn(TFSI)<sub>2</sub>/acetonitrile electrolyte. The poor rate performance and large voltage hysteresis were attributed to the high charge transfer resistance and associated activation energies for both anode and cathode in non-aqueous systems. The slow activation of metallic Zn anode was ascribed to the native oxide layer on Zn metal that could be readily removed in alkaline or acidic aqueous electrolyte, while multiple cycles were needed to completely clean out the passivation layer in non-aqueous systems [53]. This drawback can be circumvented by pretreating the anode surface before cell assembly, such as polishing or acid itching. Another penalty paid by the non-aqueous Zn batteries was the high desolvation energy of Zn<sup>2+</sup> ions in aprotic electrolyte due to the strong coordination of bivalent Zn<sup>2+</sup> and solvent molecules. Hydroxyl groups and the existence of H<sub>2</sub>O molecules usually are required to form a coordination environment beneficial for Zn<sup>2+</sup> transport in non-aqueous electrolyte. Although the recent work on bilayer hydrated V<sub>2</sub>O<sub>5</sub> showed high discharge capacity and high power for non-aqueous Zn batteries [54], more works are required to understand the solid-electrolyte-interphase (SEI) composition, ion solvation/desolvation behaviors, high voltage cathode material development and ion-host interaction in order to take advantage of the oxidatively resistant aprotic electrolytes and counterbalance their higher cost and safety risk than AZBs. To sum up the above discussion, non-aqueous Zn chemistries require more
fundamental research and practical validation to match the attractiveness of the aqueous rivals for rechargeable zinc batteries.

**Challenges and progresses in AZB development**

AZBs have great potentials while also facing big challenges from the cathode, Zn metal anode and electrolyte. The integration of these components together leads to poor cycling stability. For the convenience of discussion and clear outlining of future research directions, we systematically analyze the alkaline and mild acid Zn battery chemistries in a side-by-side comparison manner.

We show the basic reaction mechanisms and summarizes the major challenges of these battery systems in Fig. 3. For the alkaline system, electrolyte usually consists of lithium hydroxide (LiOH), sodium hydroxide (NaOH) or potassium hydroxide (KOH) in water (H2O) with pH >12. KOH electrolyte, because of the larger cation radius and hence reduced interaction between cation and water molecules, has higher ion conductivity and better transportation kinetics than the others [55,56]. In a typical alkaline AZB set-up, the general consensus is that the metallic Zn anode goes through a dissolution/deposition process through zincate ions, Zn(OH)4^2− and cathode undergoes proton insertion and conversion reactions (MnO2 as an example) as shown by the Eqs. (1)–(6) in Table 1. For the mild acid system, various kinds of salts ranging from conventional inorganic salts, such as ZnCl2, zinc fluoride (ZnF2), zinc nitrate (Zn(NO3)2), zinccarbonate (ZnCO3)2, zinc perchlorate (Zn(ClO4)2) and organic compounds, including zinc trifluoromethanesulfonate (Zn(CF3SO3)2), Trifluoromethanesulfonic anhydride (Zn(N(CF3SO2)2)2), zinc di[bis(trifluoromethylsulfonyl)imide]. (Zn(TFSI)2), zinc acetate (Zn(CH3COO)2) and zinc tetrafluoroborate (Zn(BF4)2) in water have been used as electrolytes [11]. ZnSO4 is less oxidizing than Zn(ClO4)2 and Zn(NO3)2, which leads to less local pH change and more stable Zn stripping/plating and thus has been the most common electrolyte [15,57]. The Zn metal dissolution/deposition process is through Zn^{2+} ions and the MnO2 cathode reaction mechanism, highly debatable, is believed to involve proton intercalation, Zn^{2+} ion intercalation or both (Table 1, Eqs. (7)–(10)) [11,58].

Zn, as an amphoteric metal, is able to react with both OH− and H+ species. This is the foundation for alkaline and mild acid Zn batteries to work, but at the same time the origin of all their challenges too. First, both alkaline and mild acid Zn batteries pro-

---

**FIGURE 3**

Reaction mechanisms and summary of the challenges of aqueous zinc batteries.

**TABLE 1**

Reactions in alkaline and mild acid systems using MnO2 as the example cathode.

<table>
<thead>
<tr>
<th>Alkaline system (MnO2 as the example cathode)</th>
<th>Mild acid system (MnO2 as the example cathode)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Anode reactions</strong></td>
<td><strong>Anode reactions</strong></td>
</tr>
<tr>
<td>Zn^{0} (s) → Zn^{2+} + 2e− - Eq. (1)</td>
<td>Zn^{0} (s) → Zn^{2+} (aq.) + 2e− (aq.) - Eq. (7)</td>
</tr>
<tr>
<td>Zn^{2+} (aq.) + 4OH− (aq.) → Zn(OH)4^{2−} (aq.) - Eq. (2)</td>
<td></td>
</tr>
<tr>
<td>Zn(OH)4^{2−} (aq.) → ZnO (s) + H2O (aq.) + 2OH− (aq.) - Eq. (3)</td>
<td></td>
</tr>
<tr>
<td><strong>Cathode reactions</strong></td>
<td><strong>Cathode reactions</strong></td>
</tr>
<tr>
<td>H2O (aq.) → H^{+} (aq.) + OH− (aq.) - Eq. (4)</td>
<td>H2O (aq.) → H^{+} (aq.) + OH− - Eq. (8)</td>
</tr>
<tr>
<td>MnO2 (s) + H^{+} (aq.) + e− → MnOOH (s) - Eq. (5)</td>
<td>MnO2 (s) + H^{+} (aq.) + e− → MnOOH (s) - Eq. (9)</td>
</tr>
<tr>
<td>MnOOH (s) + H2O (aq.) + e− → Mn(OH)2 (s) + OH− (aq.) - Eq. (6)</td>
<td>2MnO2 (s) + Zn^{2+} (aq.) + 2e− → ZnMn2O4 (s) - Eq. (10)</td>
</tr>
</tbody>
</table>

Please cite this article in press as: J. Song et al., Materials Today, (2021), https://doi.org/10.1016/j.mattod.2020.12.003
duce H₂ gas because of the reaction between Zn metal anode and electrolyte. The repeated dissolution/deposition of Zn metal during charge and discharge processes make the H₂ evolution worse because of the high reactivity of freshly formed Zn nanocrystals (Fig. 3). The cycling also leads to Zn anode morphology change and dendrite formation in both systems, even though the detail mechanisms are slightly different. In alkaline electrolyte, the process of dendrite formation is through the solvated divalent Zn (OH)₂⁻ ions, the passivation of ZnO precipitation and loss of Zn from zincate condensation at the cathode surface. In the mild acid system (ZnSO₄ electrolyte), it is through the Zn metal corrosion and Zn²⁺ ion loss via ZnSO₄[Zn(OH)₂]₃ precipitation at the cathode side (Fig. 3) [15,57,59].

Various types of cathode materials can be used in alkaline and mild acid systems, respectively. For example, the NiOOH cathode for alkaline Zn–Ni batteries and vanadium oxides for mild acid Zn batteries [18]. If not counting air or some organic material cathodes, MnO₂ probably is the most attractive one in terms of balancing the capacity and the cost. Yet, both alkaline and mild acid systems have similar Mn²⁺ dissolution problems and hence quick capacity fade at the anode side in deep charge and discharge cycles (using full capacity of MnO₂ through Mn⁴⁺/Mn²⁺ redox).

There has been quite a lot of effort trying to understand and address the challenges in the two AZB systems. For the Zn metal anode, direct observation of dendrite growth has been carried out in both alkaline and mild acid electrolytes. Nucleation control, nanostructure design and surface treatment have been developed to impede dendrite formation and growth. For cathodes, different MnO₂ structures and various kinds of other cathode materials have been explored. Electrolyte and electrolyte additives have also been investigated to mitigate the cross communication between the cathode and anode in both systems. In the following part, recent progress will be discussed in detail.

**Zinc metal anode**

Zinc is an exemplary metal that forms dendrite. Its nucleation and dendrite growth are easily observable for understanding the crystal growth mechanism at heterogenous interfaces. The short cycle-life of AZBs, partially originated from zinc dendrite formation, remains a daunting challenge. Maintaining uniform ion flux and stable Zn deposition/stripping at the electrolyte/Zn metal interface are key to delay nucleation and growth of dendrites, but presently out of reach using conventional materials and aqueous electrolyte at reasonably fast charging conditions. In this section, we compare the Zn dendrite growth fundamentals in acidic and alkaline conditions and discuss the possible remedies to alter the negative outcomes in these corresponding systems (Fig. 4). Some exemplary solutions that control, mitigate, and suppress the dendrite formation will be discussed in detail, while the improvement of cyclability by limiting capacity utilization is not included.

**Fundamentals of dendrite growth**

Zinc dendrite propagation in acidic electrolyte has long been known to depend on Zn²⁺-ion concentration, current density and local pH value [67,68]. According to Kim et al., the film roughness was determined by (1) hydrodynamic conditions at appreciable fraction of the limiting current and (2) microthrowing power at well below the limiting current [58]. The concomitant presence of dendrite and local current density increment was explained in terms of the hydrodynamic flow and the level of Zn²⁺-ion concentration. Oren et al., analyzed the pH effect on the current density of dendrite tip by adjusting the hydrochloric acid (HCl) content in ZnCl₂ electrolyte [68]. The critical overpotential for dendrite formation slightly decreased and tip current density increased when pH was decreased. However, lowering pH to <4 greatly increases the likelihood of hydrogen evolution and electrode corrosion, which is not welcome in battery with confined enclosure and causes additional safety concerns [69]. The propagation of Zn dendrite in acidic condition was also documented recently by Banik, et al. using in situ optical microscopy [60]. Needle-like Zn dendrites growth in 0.1 M ZnCl₂ electrolyte happened within 10 minutes of plating at the voltage of −1.25 V and rapidly grew to several hundred microns in length (Fig. 4a). The growth of dendritic structures was faster and more ramifying with a lower deposition voltage. Fig. 4b showed the more severe Zn dendrites obtained at −1.30 V over the same period of deposition time.

When Zn(OH)₂⁻ instead of Zn²⁺ ions are present in the alkaline electrolyte, it is a general consensus that dendritic zinc formation takes different routes [70]. Historically, Diggle et al. attributed the dendrite initiation as the result of pyramidal growth under bulk diffusion control [71], and elucidated the growth by modelling the radius of the curvature of dendrite tip area with time and overpotential: a critical overpotential was needed to drive the change in tip radius of the dendrite; once the dendrite was initiated, its growth was linear with time due to simultaneously increasing electrode area; the dendrite growth will be terminated when a required radius of curvature of dendrite tip was reached. The protrusion of dendrite tip and its relationship with applied current and time were recorded by Moshtev et al. [72]. The study by Wang et al. has shown a relatively complicated mechanism: that most dendrite morphologies were either under diffusion or activation control, except heavy spongy and boulder-shaped deposits that were controlled by both diffusion and activation [63]. Recently, Yuft et al. directly visualized the dendritic zinc development using multi-scale tomography analysis in operating cells (Fig. 4c and d) and provided more insight into the dendrite growth process in alkaline conditions [61]. The surface dendrites formation was inhomogeneous, and the dendrite size increased with higher current density. The initially deposited dendrite underwent dissolution and regrowth and formed a porous metal network ramified on the anode. The dendritic growth could not be blocked by the presence of separator and once the dendritic network started constructing on top of the separator, the dendrites could not be re-dissolved back into the electrolyte, leading to permanent loss the active ions and short-circuit of the battery.

The mechanism study and visualization of the growth process, in spite of being done with model substrates or systems, provided various angles for controlling Zn platting and stripping. Below we will discuss the mitigation of dendrite growth by nucleation control of Zn deposition, nanostructure design and surface treatment of Zn metal.
Nucleation control of Zn deposition by tuning the current

Zinc metal has been used for protecting steel from corrosion, via an electrochemical mechanism [73]. The electrochemical deposition conditions under which zinc is plated has tremendous effect on Zn nucleation and subsequent film growth rate and morphology. Similarly, zinc crystal growth in battery applications can be controlled at the beginning stage, that is, the nucleation step. For example, pulse-current charging was used to tune the electron flow that contributes to dendrite formation (It controls the electron in the Zn deposition reactions, Zn^{2+} + 2e = Zn, Table 1, Eqs. (1) and (7)). The high instantaneous current flux in pulse electrodeposition can produce ultrafine-grained, homogenous surface nucleation when Zn^{2+} concentration/diffusion remains similar. While the period with no current flux provides time for Zn^{2+} diffusion to repeat the process for a relatively uniform Zn film growth. Lin et al. has shown the morphology of zinc deposits can be regulated using different pulse frequencies in mild acid electrolyte containing ZnSO_4 [62]. The electrodeposited Zn film using continuous direct current showed a rough film with densely packed nano-flaked crystals (Fig. 4e), while high frequency pulse current introduced porous structure to the zinc nano-flakes (Fig. 4f). The different morphologies also were correlated to battery performance. The porous zinc nano-flakes obtained from high frequency pulse current deposition showed higher capacity utilization under high power operation. This is ascribed to the greatly reduced local current density and inhibited anode passivation, which therefore results in higher anode utilization. A variation of electrochemical nucleation control can be achieved by programming the current-on and -off time. Depending on the correlation to the Zn^{2+} concentration/
diffusion in the electrolyte, the dimension of Zn deposit is affected by the resting step between adjacent current pulses. Prolonging the time interval could increase the particle size and direct crystal growth in preferential orientation [74].

Similarly, Zn nucleation also can be controlled by tuning the electron flow in alkaline electrolyte. Fig. 4g and h showed the zinc deposit morphologies as layer-like and filamentous mossy (Fig. 4g) and heavy spongy (Fig. 4h) at different current densities [63]. At very low current density, mossy initiation was determined by the nucleation process and thus was highly site-selective. In contrast, the formation of heavy spongy deposits were large boulder agglomerates was under diffusion control (high electron flux, low ion diffusion and after long deposition time). The morphology of zinc was not merely controlled by a universal overpotential or current density [63,75]. Any conditions driving the reaction into diffusion control can trigger dendritic initiation, including low temperature, low zincate, or high KOH concentration, no stirring, and high electrolyte viscosity. Garcia et al. also found that the pulsing protocol such as 2 s On/1s Off pulsed charging step can lead to significantly longer cycle life for a commercially available Zn–Ni cylindrical battery [75].

Zinc nano/micro-structure design

The local current density based on the charge per surface area of Zn metal has profound influence on the Zn nucleation and growth in both alkaline and acidic media. Designing and harnessing nano/microstructured Zn anode with high surface area can greatly reduce the local current density and keep zinc deposition outside the diffusion-controlled region for uniform metal plating. Zn fibers of ~200 micrometers in diameter have been used in alkaline and Zn-air batteries >15 years ago. These sheets/rods of Zn fibers have demonstrated tremendous advantages over regular foils because of the high porosity, effective surface area and structural flexibility [76].

Recently, three-dimensional (3D) Zn anodes have been widely adopted for alkaline and mild acid Zn batteries. 3D Zn coated carbon fiber anodes using electrodeposition method demonstrated surface area of 121.2 m²/g. 5 orders of magnitude higher than Zn foil, leading to an increased electroactive area, lower charge transfer resistance and areal current density [64]. As a result, the symmetric cell using 3D nanostructured Zn anodes in mild acid electrolyte (2 M ZnSO₄ and 0.1 M MnSO₄) showed ultralow overpotential of 30 mV (1 mA/cm², 1 mA/cm) over 150 h and smooth Zn plating (Fig. 4i and j). While under similar conditions, planetary Zn plate failed shortly after 50 h operation with the average overpotential as high as ~1 V.

Recent representative Zn nano/micro-structure design for alkaline Zn batteries is the monolithic sponge anode developed by Parker et al. [16]. With simple pore-generation techniques, metallic Zn powders formed interconnected networks providing long-range continuous electronic pathway and more uniform current distribution. In addition, the void space of the 3D structure accommodated the products of Zn anode redox reaction and dendrite formation (Fig. 4k and l). The structural advantages make a compelling case for adopting spongy Zn anode in alkaline battery for a variety of applications, including (1) deep depth of discharge for Zn primary cells, (2) high-rate cycling of Zn–Ni cells at 40% Zn utilization with comparable specific energy to LIBs, and (3) long-life and power-demanding start-stop Zn–Ni cells for hybrid vehicles. Inspired by the work of other rechargeable batteries, nanostructure design, including nanoparticles, nanorods and hierarchical Zn anodes have also been developed [77]. These novel nano/microstructures with surface functionalization or modification suppressed dendrite formation and hence substantially boost the cycling performance.

Surface treatment

Surface factors do not appear directly in the electrochemical reactions of Zn plating/striping (Table 1, Eqs. (1) and (7)). Yet, as the Zn surface (interface between Zn anode and electrolyte) is where the reactions happen, it is extremely important to control the electrochemical redox reaction dynamics through affecting the overpotential and local current density. In this regard, the above nano/micro-structure design can also be categorized as a kind of surface treatment.

Zn is reactive in alkaline and acid conditions and so as in the air. The Zn metal forms a layer of ZnO on the surface. The formation of dendritic Zn is known to be promoted by the ununiform distribution of ZnO. Surface modification that blocks direct contact between electrode and electrolyte is considered an effective method to mitigate surface parasitic reactions. Fig. 4m and n show the pristine and cycled Zn anodes with a thin layer (8 nm) of TiO₂ coating [65]. With a thin TiO₂ coating from atomic layer deposition, the Zn anode corrosion and gas evolution in acidic electrolyte can be greatly suppressed. The symmetric cell with coated Zn anodes was able to achieve low stripping/deposition overpotential of 72.5 mV at 1 mA/cm² and improved Coulombic efficiency. The acidic Zn–MnO₂ battery offered 1000 stable cycles with 85% capacity retention at the current density of 3 mA/cm² without excessive dendrite formation [65]. Similar coating strategy has also been explored with different TiO₂ crystal orientations, which show distinct cycling performance of Zn metal [78].

Polymer coating is also a promising approach in directing Zn²⁺ diffusion and regulating surface film formation. Recently, a polyamide coating, which quarantined Zn metal from contacting bulk electrolyte, was developed to advert H₂O and O₂ induced electrode corrosion and passivation [79]. The amide groups on the polymer back chain provided coordination site with Zn²⁺ and hence altered the electrochemical deposition potential.

In alkaline electrolyte, ZnO passivation of Zn anode is much more severe due to the reprecipitation from Zn(OH)₂⁺ species. To tackle these problems, Wu et al., leveraged the fact that hydroxide anions (OH⁻) is more mobile than zinicate species (Zn(OH)₂⁺) diffusing through the nanoropes, applied a carbon nanoshell with ion-sieving capability on ZnO nanoparticle-based anode [66]. The pristine sample of ZnO nanoparticles with uniform ion-sieve carbon coating (Fig. 4o) showed unchanged electrode morphology after cycling (Fig. 4p), while a holey structure was observed for control sample with uncoated ZnO particles. As a result, the battery with the carbon protected anode showed 1.6 and 6 times longer cycle life than bare ZnO and Zn foil under harsh testing conditions, respectively [66]. Other coating layers also have been demonstrated to increase zinc utiliza-
tion and/or negate ZnO passivation in alkaline electrolyte [80]. Leveraging the silicon dioxide (SiO₂) to Si(OH)₄ gel reaction in aqueous KOH electrolyte, Zn anodes with SiO₂ coating of ~10-20 nm thick can have the hydrogen evolution reduced by 40% and hence zinc utilization increased up to 69% from the 57% of the unmodified Zn. Similar approach was shown in Zhang et al.’s work, in which a Ti₅N₇O₄ layer was conformally coated on ZnO nanorods and provided dual functions of mitigating Zn dissolution and mechanically retaining the nanostructure of Zn particles [81].

In addition to the above approaches, alloying or metal doping/mixing also are widely acknowledged to be helpful in Zn metal plating/stripping [82-86]. Mercury and lead were added into zinc anodes in the early days of alkaline batteries, while the commercial Zn powders nowadays usually contain bismuth and/or indium [87,88]. These metals usually are known to have a high overpotential for H₂ evolution and provide conductive scaffold or active sites for Zn nucleation and growth in the repeatable plating/stripping. These approaches can be considered as nucleation control, structure design or surface treatment. We considered the alloying or metal doping/mixing as a common approach and thus did not list it as a specific strategy. We do believe the alloying and metal doping/mixing method holds great potential on controlling Zn metal dendrite growth if appropriately combined with nanoengineering.

Challenge still remains to obtain dendrite free, highly reversible Zn anodes despite all the progress made above. The pulse current charging method mitigates the problem by limiting the battery running conditions. It also increases the total charging duration and thus not suitable for fast-charging applications. The approach of nano/micro-structure design and surface treatment often will lead to the increase of cost, reduce of the electrode packing density, and subsequent specific energy. Future research along these approaches should also consider the scalability and compatibility with existing manufacturing process. Another aspect of future Zn metal research involves the accurate measurement of Coulombic efficiency, which has not been well-documented in aqueous Zn batteries. Coulombic efficiency has been investigated thoroughly in Li-ion and other non-aqueous Zn batteries as an important parameter to evaluate the reversibility and predict cycle life. A standard testing protocol needs to be developed for AZBs. We would like to further emphasize that a consistent methodology has to be used to obtain meaningful comparison of the Zn metal cycling efficiency between labs, which includes apply thin Zn metal (~30 μm), higher depth of discharge and limited electrolyte volume [21].

**Cathode materials**

Although limited by the electrochemical stability window of conventional aqueous electrolytes, there are still copious amount of cathode materials suitable to pair with Zn anodes. Well-known cathode materials used in alkaline zinc batteries include NiOOH, silver (Ag), and MnO₂, which all show reversible reactions towards proton insertion. In acidic or near neutral electrolyte, a more diverse cathode options, such as layered metal oxide cathodes, Prussian blue analogues, and organic compounds have been explored. There have been many dedicated review articles on zinc battery cathodes, where the readers are encouraged to explore [11,18,58]. Here, we mainly focus on side-by-side comparison of some of the most representative cathode materials in acid and alkaline electrolytes and highlight their unique characteristics.

**Phase transformation and reversibility comparison of MnO₂-based cathodes**

Manganese oxides are the most studied cathode materials for AZBs. On the one hand, manganese is highly abundant and low-cost: it is one of the most abundant elements in the earth crust, and has been studied and used for steel making, molecular sieves, catalysts, and battery materials. On the other hand, it has various oxidation states and structures when accommodating a wide range of metal cations, which brings tremendous complexity for research.

Various kinds of MnO₂ polymorphs, including different tunnel structure (α, γ-MnO₂), layer structure (δ and birnessite MnO₂), and 3D structure (β-MnO₂) have been used in Zn–MnO₂ batteries with acid/near neutral electrolytes. Because of the number of ways to assemble MnO₆ octahedra units in the MnO₂ materials, the proton or Zn²⁺ storage mechanism differs correspondingly with the crystallographic structure. Furthermore, the electrolyte composition and different charge-discharge conditions make the ion storage mechanism even more complicated. Up to the point of writing this review, there is limited consensus made regarding the reversible charge storage mechanism in different manganese oxides.

Typical spinel structured Mn₃O₄ is electrochemically inactive in alkaline Zn–MnO₂ batteries. In mild acid electrolyte (2 M ZnSO₄), however, Mn₁O₄ can be electrochemically activated to deliver a high specific capacity of ~240 mAh/g at low current density [89]. Investigation showed that (1) the spinel Mn₃O₄ underwent a phase transition during charge to form layer structured birnessite (Fig. 5a) through an intermediate phase of Mn₁O₄ (Fig. 5b); (2) a mix phase of birnessite and Mn₁O₄ were present in the following charge states; (3) Proton and Zn²⁺ intercalation happened during the discharge process forming MnOOH, Zn₃SO₄(OH)₆·5H₂O and Zn-birnessite with large interlayer distance of 6.93 Å (Fig. 5c). Fig. 5d illustrated the phase evolution process and the accompanied Mn⁴⁺/Mn³⁺ redox. The fact that spinel Mn₃O₄ can be used as the cathode material in acidic electrolyte is a unique discovery even though Mn²⁺ dissolution, water decomposition-proton intercalation and electrolyte pH change are still responsible for the capacity fade. It shows more distinction between acidic and alkaline Zn batteries and opens new routes for searching of cathode materials for acidic Zn batteries.

MnO₂ with α and δ/birnessite polymorphs have attracted quite some attention as Zn battery cathodes due to their relatively large tunnel or layer structure. S. Kim and S. Oh first reported the mechanism of H⁺ intercalation and precipitation of ZnSO₄·3Zn(OH)₂·nH₂O on δ-MnO₂ or naturally occurring birnessite-related MnO₂ in 1998 [14]. The addition of MnSO₄ solution to improve the battery cycling stability also was demonstrated. Subsequently, a high specific capacity of ~350 mAh/g with stable cycling over 100 cycles were obtained. While the results were re-elucidated with α-MnO₂ [15], a different mechanism of Zn²⁺ intercalation was reported by several research
FIGURE 5

Side-by-side comparison of MnO₂-based cathodes in acidic and alkaline electrolytes. In acidic electrolyte: (a–d) TEM images of birnessite (a) Mn₅O₈ (b) and Zn-birnessite (c) from spinel Mn₃O₄ cathode cycling and the corresponding schematic illustration of the structural evolution (d). Reproduced with permission [89]. Copyright 2018 Elsevier Inc. (e and f) X-ray absorption near-edge spectroscopy of α-MnO₂ electrodes in discharged (e) and charged (f) states. Reproduced with permission [90]. Copyright 2018 Elsevier Inc. (g) Schematic illustration of the phase evolution of γ-MnO₂ at various charged states. Reproduced with permission [33]. Copyright 2015 American Chemical Society. In alkaline electrolyte: (h) Schematic illustration of the structure evolution process of the Cu²⁺-intercalated Bi-birnessite upon charge–discharge cycles. Reproduced with permission [17]. Copyright 2017 Springer Nature. (i) Schematic illustration of phase change mechanism of Cu²⁺ intercalated birnessite. Reproduced with permission [91]. Copyright 2017 Royal Society of Chemistry.

Please cite this article in press as: J. Song et al., Materials Today, (2021), https://doi.org/10.1016/j.mattod.2020.12.003
groups [90,92,93]. With advanced characterization techniques, such as the ex-situ synchrotron X-ray absorption near-edge structure analysis (Fig. 5e and f), the one-electron-transfer redox reaction between Mn$^{4+}$ and Mn$^{3+}$ has been clearly confirmed. However, the characterization did not help much on reaching a consensus on the reaction mechanism. It is still under debate whether it is mainly proton intercalation forming MnOOH and Zn$_2$SO$_4$(OH)$_x$SH$_2$O or real Zn$^{2+}$ insertion and reversible formation of ZnMn$_2$O$_4$. The controversial results have aroused some interest on the mechanism study. Recently, Sun et al., used electrochemically deposited MnO$_2$ (Akhthenskite, ε-MnO$_2$) as the material platform and demonstrated the two-region reaction mechanism in acidic electrolyte [34]. The galvanostatic intermittent titration technique (GITT) experiment linked the slope region to H$^+$ intercalation into the tunnel structure of the MnO$_2$ to form MnOOH, and the plateau region to the Zn$^{2+}$ intercalation to form ZnMn$_2$O$_4$ phase. Besides the new insight into the storage mechanism, the cathode demonstrated extraordinary cycling stability with negligible capacity decay over 10,000 cycles at 6.5C.

As the most common polymorph used commercially, electrolytic manganese dioxide (EMD) is primarily γ-MnO$_2$. Its phase transition mechanism is also of particular interest in acidic and alkaline electrolytes. Alfaruqi et al., have systematically studied the phase transition of tunnel-type MnO$_2$ in 1 M ZnSO$_4$ (pH = 4.0) aqueous solution and summarized the phase transition roadmap [33]. Instead of forming MnOOH, the tunnel structure transitions to spinel-type MnMnO$_4$ and two intermediary tunnel-type γ-Zn$_{1/2}$MnO$_4$ and layered-type L-Zn$_{1/2}$MnO$_4$ in battery cycling. Table 2 shows the reaction mechanism and Fig. 5g shows the schematic of crystal structures. The phase transition was believed to be reversible with 158 mAh/g retained over 40 cycles according to the electrochemical tests and extensive characterization results. The phase transition was quite different from the two-step reaction process of γ-MnO$_2$ in alkaline electrolyte consists of 9 M KOH salt [94,95].

Different from the complicated and controversial results in acidic electrolyte, the fading mechanism of MnO$_2$ cathodes in alkaline electrolyte is straightforward. In the one electron reaction region, the fading is mainly due to the formation of Mn$_3$O$_4$ phase [94]. Meanwhile, the overpotential and disproportional reaction of Mn$^{3+}$ lead to Mn$^{2+}$ dissolution resulting in further capacity fade [95]. MnO$_2$ cathode has been known to deliver only 60–80% of the theoretical capacity of 617 mAh g$^{-1}$ (2-electron transfer) and is not able to retain capacity over long cycles in alkaline environment [91]. Recently, Birnessite δ-MnO$_2$ cathode came in the spotlight as Yadav et al. found that the 2-electron reaction pathways can be stabilized by intercalating/doping some heteroatoms or ions such as Bi and Cu into the layered structure without changing the basic crystal structure over long term cycling [17,91]. The authors claimed that the introduction of Cu reduced the charge transfer resistance of the δ-MnO$_2$, which enabled complete regeneration of the materials from the dissolved state during each cycle (Fig. 5h) [17]. In a separate work, the same group showed that Cu$^{2+}$-intercalated birnessite MnO$_2$ can stably deliver a near-theoretical 2-electron capacity reversibly for 1000 cycles [91]. The cathode degradation in full cell was ascribed to the loss of Mn$^{3+}$ and formation of irreversible ZnMn$_2$O$_4$ phase due to the increase of pH zincate concentration upon electrolyte evaporation (Fig. 5i). Nevertheless, this set of study has completely changed the impression that MnO$_2$ in alkaline electrolyte cannot deliver >60–80% of theoretical capacity or long cycle life. The excellent cell performance injects fresh life into the half a century old battery technology and put it back to the race for low cost energy storage development.

**TABLE 2**

Representative γ-MnO$_2$ cathode reaction mechanism.

<table>
<thead>
<tr>
<th>γ-MnO$_2$ in 1 M ZnSO$_4$</th>
<th>γ-MnO$_2$ → Spinel ZnMn$_2$O$_4$ + γ-MnO$_2$ → Spinel ZnMn$_2$O$<em>4$ + γ-Zn$</em>{1/2}$MnO$_4$ (Tunnel-type) → Spinel ZnMn$_2$O$<em>4$ + γ-Zn$</em>{1/2}$MnO$<em>4$ (Tunnel-type) + L-Zn$</em>{1/2}$MnO$_4$ (Layered-type)</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-MnO$_2$ in 9 M KOH</td>
<td>γ-MnO$_2$ + xH$^+$ + xe$^-$ ↔ γ-Mn$_1$...Mn$_y$O$_2$...O(OH)$_x$</td>
</tr>
</tbody>
</table>

**Other cathodes materials**

Other cathode materials, including layered oxides, Prussian blue analogues, conversion materials, and polyanion-type cathodes, also have been developed for acidic or base zinc batteries. Vanadium oxides, with their open framework crystal structure, allow reversible and fast Zn$^{2+}$ intercalation/deintercalation and thus are one of the most widely used cathodes in mild acid zinc batteries.

In acidic electrolyte, the interstitial water insertion is a critical factor affecting the Zn$^{2+}$ ion uptake upon reversible layer expansion and contraction. Kundu et al., through systematic study of the behavior bilayer Zn$_{0.25}$V$_2$O$_5$.nH$_2$O in aqueous and non-aqueous electrolyte, demonstrated the importance roles of water co-intercalation and the indigenous Zn ions in stabilizing the layered structure, which therefore ensure high rate performance and long-term cycling stability [43]. Fig. 6a showed the operando XRD of the intercalation process at different charge states. Water insertion was reversible and caused increased interlayer distance of Zn$_{0.25}$V$_2$O$_5$. The Zn$^{2+}$ intercalation. Compared to H$^+$ intercalation into MnO$_2$ as a likely intercalation mechanism in acidic environments, vanadium oxide-based compounds are truly Zn$^{2+}$ intercalation cathodes even though it formed ternary intercalation compounds with hydrolyzed Zn$^{2+}$ rather than binary compounds. The reversible process was illustrated in Fig. 6b. Even with the co-intercalation of H$_2$O, the AZB system delivers a specific energy of 250 Wh/kg (based on cathode), a capacity of 220 mAh/g at a 15C rate, and a capacity retention of more than 80% after 1 similar charge storage mechanism with core-intercalation of water also has been observed with V$_2$O$_5$.nH$_2$O cathode [96]. Fig. 6c and d shows the signal gain in NMR spectra with the intercalation of water, CF$_3$SO$_3$ and Zn$^{2+}$ together into the layered structure. The participation of water during charge-discharge significantly increased the power output, which was even better than Zn$_{0.25}$V$_2$O$_5$.nH$_2$O and δ-MnO$_2$ (Fig. 6e). In addition to the cost and toxicity, the potential dissolution of vanadium species in water also posed concern for the future of the technology. The ability of V$_2$O$_5$ to react with strong alkali to form polyoxovanadates might destroy the layered structure and hence, to the best our knowledge, metal vanadium oxide-based
Other representative cathodes for acidic and alkaline Zn batteries. In acidic electrolyte. (a) Ex-situ XRD spectra of Zn$_{0.25}$V$_2$O$_5$ cathode at different state of charges and cycle numbers. (b) Schematic illustration of Zn$_{0.25}$V$_2$O$_5$ reaction mechanism. Reproduced with permission [43]. Copyright 2016 Springer Nature. (c and d) MAS NMR spectra of various V$_2$O$_5$·nH$_2$O for $^1$H (c) and $^{13}$C (d). (e) Ragone plot Zn/V$_2$O$_5$·H$_2$O cell. Reproduced with permission [96]. Copyright 2018, John Wiley & Sons. In alkaline electrolyte. (f) Schematic illustration of the synthesis method of NiCo-LDH. (g) SEM image of the NiCo-LDH. (h) Charge–discharge curves of NiCo-LDH and its derivatives. Reproduced with permission [97]. Copyright 2019, John Wiley & Sons. (i) TEM image of NiAlCo-LDH/CNT composite. (j) XRD spectra of various Ni-based LDH compositions. (k) Comparison of charge–discharge curves of Ni(OH)$_2$/CNT and Ni-based LDH/CNT composites. Reproduced with permission [98]. Copyright 2014, Royal Society of Chemistry.
cathodes have not been reported for use in alkaline electrolyte [99]. Similarly, Prussian blue, conversion-type materials, and organic cathodes have only been reported with near neutral and mild acid electrolytes [100,101]. The stability of these cathode materials in high pH environment remain to be tested.

Transition metal oxides other than manganese oxides have been explored as cathodes for Zn batteries with alkaline electrolyte. For example, nickel-based double hydroxides (Ni-DH) have been studied as a class of high-performance cathodes. H. Chen et al. developed a NiCo-DH using an etching-deposition-growth process (Fig. 6f) [97]. The synthesis method rendered a unique hierarchical structure with interlocked NiCo-DH nanosheets vertically standing on the supporting skeleton of Ni form (Fig. 6g). The optimized NiCo-DH composition tripled the discharge capacity compared to the single element (Ni or Co) hydroxide as well as conventional NiCo hydroxide (Fig. 6h). Other Ni-based double hydroxide compounds and their composite materials also have been explored [98]. The cathode performance varies greatly with different metal composition and the structure of composite or electrodes. With well controlled particle dispersion (Fig. 6i), composting carbon nanotube (CNT) with Al or Co-Al co-doped Ni-based layered double hydroxide (LDH) could boost the electrical conductivity of the active material. The LDH materials are mostly amorphous and have altered crystal structure compared to the baseline Ni(OH)₂ (Fig. 6j). While the Ni-based LDH materials generally have improved capacity utilization compared to α-Ni(OH)₂, the binary NiAl-LDH system delivered the highest average voltage and discharge capacity (Fig. 6k).

Cobalt oxides also have good performance in alkaline electrolyte, even though the practicality may be limited by the cost. Wang et al., showed an alkaline AZB with an average voltage of 1.78 V by coupling carbon fiber supported Zn anode with cobalt oxide (Co₃O₄) cathode and achieved good cycling performance [102]. During discharge, the Co₃O₄ cathode underwent phase transition by a two-step-reaction with OH⁻ from alkaline electrolyte to finally form CoO₂. Reversibly, Co₃O₄ was regenerated upon the removal of oxygen from CoO₂ together with H₂O to produce CoO₄ and OH⁻. Such reversible phase transition was highly stable and can be sustained for over 2000 cycles at current density of 1 A/g.

Another emerging family of cathodes are organic materials, which have already demonstrated impressive performance and cost-effectiveness in mild acidic electrolyte [103,104]. Although we do not have a dedicated section of organic cathodes due to the early development status and space constraint, several works with promising results are worth of mentioning. For example, a sulfur heterocyclic quinone dibenzo[b,j]thian-threne-5,7,12,14-tetraone (DTT) cathode in near-neutral electrolyte (2 M ZnSO₄) has demonstrated a high specific capacity of ~200 mAh/g and ultra-long cycle life of 23,000 cycles with 83.8% capacity retention [105]. A low-cost calix[4]quinone cathode also has been developed to deliver a high capacity of 335 mAh/g and the pouch zinc battery can have a specific energy of 220 Wh/kg with the average discharge voltage of ~1 V [106]. Organic cathodes have the advantage of tuning the electrochemical performance by rational design of molecular structures and also malleable crystal lattice to enable molecular reorientation for reversible intercalation. P-chloranil was found to allow low volume change upon Zn²⁺ intake and delivers high specific capacity >200 mAh/g at ~1.1 V [107]. Despite these encouraging electrochemical results, the intrinsic downsides of organic cathodes, such as, low voltage, low electronic conductivity, low material density, and high solubility in electrolyte, remain to be solved to compete with inorganic rivals.

**Electrolyte and electrolyte additives**

Electrolyte is essential to a battery just like blood is essential to a human body. The interphase, which is highly dependent on the electrolyte and the electrodes (cathodes/Zn metal anodes) interaction and experiences constant dynamic change during cycling, is a real devil complicating the stability of the bulk electrolyte and electrodes. As we briefly mentioned before, a lot of research efforts have been made on the development of electrolyte at the beginning of the zinc battery technology. The salt has evolved from NH₄Cl to ZnCl₂, ZnSO₄, KOH etc. of various concentrations [108]. For example, increasing the concentration of KOH (>7 M) can facilitate the transformation of ZnO to Zn(OH)₂, which has been developed to address the zincate formation and subsequent ZnO condensation reaction in alkaline electrolyte [48]. However, this was achieved at the expense of reduced ionic conductivity, promoted dendrite formation, and corrosion of cathode materials and current collectors [109]. Recently, organic zinc salts, mixed salts and water-in-salt electrolytes opened new research directions and have attracted quite a lot of attention for mild acid AZB development. In most cases, these systems present a better case for avoiding side reactions and stabilizing anode. The presence of bulky anions, such as, FSI⁻ and TFSI⁻, or the extremely high salt concentration improves Zn²⁺ transport kinetics by reducing the coordination number of water molecules with the cation [110,111].

Inorganic and organic electrolyte additives are very diverse and have been extensively explored to tune the bulk electrolyte properties (e.g. viscosity, ion coordination/solubility) or provide modification of the electrode/membrane surface. In this section, we will highlight some of the recent developments in both acidic and alkaline electrolyte systems.

**Mixed salts/additive salt**

One early example of mixing salts was the addition of ZnCl₂ into the NH₄Cl electrolyte for heavy duty cells [112]. Along the way, mixing salts or adding salt additives have been one of the most effective approaches to achieve control on Zn deposition or cathode fading. In addition to the notable example of adding MnSO₄ salt to ZnSO₄ electrolyte to mitigate the Mn²⁺ dissolution [14], organic anions have also been used to further tune the electrolyte properties. Zhang et al. investigated the Zn metal cycled in three different electrolytes and discovered that the FSI⁻ anion was very beneficial for Zn plating [110]. The post-mortem analysis of the cycled Zn anode in Fig. 7a revealed that (1) dense and dendrite-free surface morphology can be formed in 3 M ZnFSI + 0.1 M MnFSI electrolyte, neither dendritic morphology nor formation of byproducts, such as ZnO and Zn(OH)₂, was evidenced in Zn–MnO₂ full cell tests; (2) Zn plate with lots of cracks formed in 3 M ZnSO₄ + 0.1 M MnSO₄ electrolyte; (3) ZnO nanorods were observed in KOH electrolyte, which would deteriorate the cyclability of Zn anodes. The electrochemical performance was consis-
tent with the different Zn metal structures in different electrolytes: among all the cells, the one with ZnFSI and MnFSI-based mild acid electrolyte showed the least capacity fading over 100 cycles (Fig. 7b).

Electrolyte using mixed salts has also been demonstrated in alkaline conditions. Parker et al., have investigated several salt blends consisting of lithium hydroxide (LiOH), potassium silicate (K₂SiO₃), potassium fluoride (KF), potassium carbonate (K₂CO₃), calcium hydroxide (Ca(OH)₂) and reported their determining effect on the morphology and reversibility of sponge Zn anodes (Fig. 7c) [113]. Two salt combinations have shown promise for Zn morphology control: (1) 4 M KOH + 2 M KF + 1 M K₂CO₃ and (2) 6 M KOH + 1 M LiOH + 8 wt. % Ca(OH)₂. The sponge cycled in (1) maintained their mechanical robustness, exhibited the least discoloration, and retained most of the starting morphology. Similarly, if not better, they found the cycled sponge with salt combination (2) was rigid and monolithic with the presence of Ca(OH)₂ at the surfaces of the Zn electrode (Fig. 7c), which was possibly due to the precipitation of calcium zincate at early stages of discharge, minimizing zincate dissolution and anode shape change [64]. Although Ca(OH)₂ has very low solubility in the electrolyte, the ability to react with zincate makes it an appropriate electrolyte component for anode modification. These salt combinations led to smaller voltage hysteresis at different stages of a cycle compared to other electrolyte formulations (Fig. 7d). Mixed salts strategy has also been used to improve the MnO₂ cathode stability. Minakshi et al. have shown that the addition of LiOH into KOH electrolyte suppressed Mn dissolution by intercalating Li⁺ into the tunnel structure of γ-MnO₂ and forming LiₓMnO₂ spinel phase. It is at the expense of lower cathode capacity utilization [116].

Electrolyte additive

Many organic chemicals or ligands absorbed on the electrode surfaces can alter the surface overpotential and reaction dynamics and thus affect the Zn morphology and battery performance. Sun et al., evaluated zinc deposition and cell cycling with different organic electrolyte additives, including cetyltrimethylammonium bromide (CTAB), sodium dodecyl sulfate (SDS),

FIGURE 7
Electrolyte composition and additive effect on the fading of acidic and alkaline AZBs. Mixed salt. (a and b) Zn anode morphology change (a) and cycling performance of Zn–MnO₂ cells in in various acidic electrolytes. Reproduced with permission [110]. Copyright 2016, American Chemical Society. (c and d) Zn anode morphology change in various alkaline electrolytes (c) and corresponding voltage hysteresis of the Zn–Ni cells (d). The green, blue and red bars corresponds to the voltages in the early, middle, and ending stages of a cycle. Reproduced with permission [113]. Copyright 2016, IOP Publishing.
polyethylene-glycol (PEG-8000), and thiourea (TU) in acidic electrolyte (1 M ZnSO₄ + 1 M Li₂SO₄) [114]. The zinc morphology with CTAB was porous needle-like crystals, while dense zinc deposition forms in various directions perpendicular to the substrate with SDS, PEG or TU additive (Fig. 8a). The change in Zn morphology with CTAB was attributed to the strong blocking effect of the large additive molecule that intensified the competition between nucleation and crystal growth and facilitated dendrite growth. In comparison, the absorption of SDS, PEG or TU on Zn anode reduced the nucleation and produced more uniform Zn deposits. As a result, anode with denser surface in the presence of SDS, PEG, or TU additives showed capacity retention of 79%, 76%, and 80%, respectively, after 1000 cycles. These were much higher than that of the cell without additive (67%) or with CTAB additive (sudden cell failure after 350 cycles) (Fig. 8b).

Many organic additives also show compatibility and effectiveness in alkaline electrolyte. Xiao et al., evaluated the organic additives such as benzotriazole (BTA), thiourea (CH₄N₂S) and sodium dodecyl benzene sulfonate (SDBS) in 6 M KOH electrolyte [115]. Either of the single electrolyte additives can inhibit corrosion and reduce charge transfer resistance of zinc-bismuth electrode, whereas combining the anionic and cationic surfactants (BTA and SDBS) was more effective for corrosion resistance and dendrite suppression (Fig. 8c). The benefits of the organic additives were further shown in the cycling test, where the electrode performance was improved in the order of BTA > SDBS > CH₄N₂S > blank electrode (Fig. 8d).

The use of electrolyte additive usually leads to the change of overpotential of the cell. Recently, novel additive to suppress Zn dendrite in alkaline electrolyte has been reported without affecting the voltage hysteresis [117]. The additive presented a unique hysteresis effect. That is, the Zn surface was rendered either polarizer or depolarized depending on the relative rates of additive’s transport, adsorption and deactivation at the Zn surface as well as the scan direction of potential sweep. Under certain conditions, it can suppress the accelerated growth of
micro-scale dendrite tips. This opens the possibility for “localized” suppression of dendrites, even though it is still a challenge to maintain the effect from electrolyte additive over long term cycling.

Salt concentration effect
Increasing Zn battery electrolyte concentration (>3M for acidic electrolyte and >6 M for alkaline electrolyte) has been proven to be effective in achieving higher performance than that with conventional electrolyte of dilute salt concentration [94]. Recently, there is a trend to use extremely high concentration electrolyte or water-in-salt electrolyte for “extreme battery” performance. From the fundamental point of view, electrolyte with ultra-high concentration can change the ion coordination structure, the solvent accessibility to the reactive interphase, the interphase chemistry and hence enable new electrolyte properties or enhancement of existing ones [118]. It opens a new research regime, even though the potential for industrial implementation requires further investigation.

One notable example of the water-in-salt electrolyte application in the near neutral aqueous Zn battery was the use of mixed salt of 1/0.5 M Zn(TFSI)2 and 20/21 M LiTFSI [119]. The electrolyte not only greatly expanded the electrochemical stability window, but also suppressed dendrite formation in Zn metal plating. Fig. 9A demonstrated the Zn2+-solvation structures at various electrolyte concentrations and the dense Zn film obtained after long term cycling in 20 m electrolyte. Zn dendrite formation can be greatly mitigated when the water hydrolysis is effectively suppressed and the reduction potential of the Zn(TFSI)2 solvate is increased [46]. The Coulombic efficiency for Zn plating/stripping can achieve nearly 100% and the AZB full cell using high voltage LiMn2O4 cathode delivered a specific energy of 180 Wh/kg with 80% capacity retention for >4000 cycles (Fig. 9b). Further attempts have been made on different electrolyte recipes for performance optimization and economic consideration. Ji et al. developed the ZnCl2 salt, intending to provide high stripping/plating efficiency of Zn anode, while keeping the electrolyte cost low [120]. In a separate work from the same group, the compatibility of water-in-salt ZnCl2 electrolyte with a CaO0.20-V2O5-0.80H2O cathode has been demonstrated. The cathode capacity utilization was raised from 296 mAh/g to 496 mAh/g with electrolyte concentration increased from 1 M to 30 M [45].

Extremely high concentration alkaline electrolyte also has profound effect on promoting the performance of AZBs. For example, Yadav et al. showed that the tendency of ZnO rods formation was highly dependent on the KOH concentration, where the rod-shape characteristics become more pronounced with longer length at higher electrolyte concentration (Fig. 9c, 1st row) [91]. Although bismuth MnO2 cathode showed similar microscopic morphology retained after cycling (Fig. 9c, 2nd row), the cell with 45 wt% (~14.6 M) KOH had more zincate cross-over and lost more of the Cu-dopant during the formation of inactive heteroclite ZnMn2O4 phase. The synergistic effect of KOH concentration on anode and cathode led to different reversibility of Zn–MnO2 cells, where 30 wt% (~7.6 M) KOH electrolyte seemed to enable more stable cycling than electrolytes of other concentrations (Fig. 9d).

Hybrid design using solid membranes/separators
Membranes and separators are inactive yet essential components to battery performance. In the development of AZBs, various kinds of separators have been developed, including glass fibers, polyolefin, and ion-exchange/selective polymers etc. [121]. Due to the wettability and stability considerations, glass fiber and polyolefin separators are typical in lab set-ups. However, their inability to prevent zinc dendrite penetration, zincate and transition metal crossover, especially in a high areal loading scenario, are undesirable for use in practical AZBs. It is vital to develop new technology to improve the membrane/separators’ electrolyte wettability/permeability, ion transfer properties, chemical stability, and mechanical properties etc. Recently, two layers of ion-selective membranes have been demonstrated to decouple acidic-neutral-alkaline electrolytes to mitigate the Mn2+ dissolution from the cathode side and zincate cross-over from the anode side [35]. It enabled two-electron redox reaction of MnO2 cathode in acidic electrolyte, leading to a high specific energy of 1621.7 Wh/kg (based on cathode). A prototype cell of 3.33 Ah capacity was demonstrated with Zn anode and delivered an impressive 90 Wh/kg cell energy density. However, the cell configuration inevitably uses more electrolytes and expensive ion-selective membranes as separators, which could decrease gravimetric/volumetric energy and increase cost compared to insertion/conversion-based MnO2 system.

A different approach using solid membranes/separators also has been investigated. The physical blocking property of solid separator is considered an effective strategy to reduce ion crossover and prevent dendrite penetration. Duay et al., reported the use of sodium super ion conducting ceramic (NASICON) separator as a physical blocking layer in Zn–MnO2 cells [122]. Encouraging results were demonstrated using a 0.5 mm thick NASICON membrane in Zn–MnO2 battery with 30% KOH as electrolyte. The cell showed a 22% increase of cycle lifetime when compared to a traditional Celgard/Cellophane layered separator. The improved performance was attributed to the blocking effect of the ceramic membrane that was impermeable to Zn (OH)2− crossover. The cell performance, however, was very sensitive to the ceramic separator thickness. As shown in Fig. 10a, applying a thinner NASICON separator (0.5 mm) helped increase the discharge capacity and lower the polarization related to the separator resistance. The dQ/dV plots derived from the galvanostatic charge curves showed that the discharge potential peaks decreased from 1.22 V to 1.17 V as the resistance of the separator decreased from 1.0 mm thick NASICON separator in Zn–MnO2 battery to the most resistive 1.0 mm thick NASICON separator. This indicated that the resistance of the separator could greatly affect the discharge voltage and hence overall battery energy (Fig. 10b-d).

Ca(OH)2 is well-known to react with zincate ions in alkaline AZBs [123,124]. Recently, separators with Ca(OH)2 interlayer have also been developed to alleviate the shuttle effect of zincate [125]. Utilizing the zincate trapping ability of Ca(OH)2, the separator effectively avoided the undesirable spinel phase transition of MnO2 cathode, and retained over 90mAh/g capacity after 60 cycles at 100% depth of discharge, which was almost three times better than the control cell.
Solid-state electrolyte, which is known to have fast conduction of certain ions, has also been introduced to aqueous Zn battery development [127]. The solid-state electrolyte separator/membrane can selectively control the ion transport between the positive and negative electrodes and mitigate the challenges from dendrite penetration. It is an ideal feature for alkaline Zn batteries to have because (1) the reactions at the cathode and the anode are linked together only by the water media and \( \text{OH}^- \) anions (Table 1); (2) there are many ceramic oxides stable in alkaline conditions and have good conductivity for \( \text{OH}^- \) anions; (3) there is big size difference for \( \text{OH}^- \) and zincate \( \text{Zn(OH)}_4^{2-} \). Fig. 10e and f present the layered double hydroxide-ion-conductive ceramic separator for Zn–Ni secondary batteries to prevent short-circuit by Zn dendrites [128]. By controlling the thickness, crystal orientation and polymer component of the separator, it is possible to achieve low cell impedance and comparable energy density to the cells with conventional porous separator. The ceramic separator design opens a new research direction in the development of alkaline aqueous zinc batteries.

Polymer-based ion conductors not only can block the undesirable ion cross-talking, but also provide good electrolyte/electrode contact due to its soft nature. Unlike ceramic separators that have to use a solid–liquid hybrid design, polymer-based ion conductors can either be used as gel polymers or pure solid-state polymer electrolyte for all solid-state batteries. Li et al., has reported a novel hierarchical polymer electrolyte (HPE) for AZBs (Fig. 10g) [126]. Despite it is called solid-state electrolyte, the polymer layer was in fact gelled in aqueous ZnSO\(_4\) and MnSO\(_4\) solution to incorporate ion conducting media. The Zn/MnO\(_2\) cells with HPE showed good capacity utilization of 306 mAh/g with 1-electron transfer (Fig. 10h). Benefiting from the polymer nature, the flexible HPE enabled stable cycling even under 800 repeated bending cycles with over 93% capacity retention (Fig. 10i). Cell failure due to short-circuit and quick loss of liquid.

![Salt concentration—acidic and alkaline](image.png)
Hybrid AZBs using solid membranes/separators. Ceramic separator. (a) Comparison of discharge curves of Zn–MnO$_2$ with Celgard + Cellophane, 0.5 mm NaSICON and 1.0 mm NaSICON separators. (b–d) dQ/dV curves derived from the cells in (a). Hybrid design with layered hydroxide separator. Reproduced with permission [122]. Copyright 2018, Elsevier. (e and f) Schematic illustration of a Ni-Zn battery with hydroxide-ion-conducting ceramic separator (e) and cross section SEM image of the separator (f) [128]. Gel polymer separator. (g) Cross section SEM image of HPE. (h) Charge-discharge curves of Zn/HPE/MnO$_2$ battery. (i) Cycling performance with bending cycles. (j) Capacity retention with pouch holes. Reproduced with permission [126]. Copyright 2018, Royal Society of Chemistry.
electrolyte after puncture were also improved with the HPE membrane. Fig. 10j shows that even with four penetrated holes on the electrode, the cell can still retain 90% of the capacity. Gel-like polymer electrolyte also enables the design of flexible Zn batteries. A composite separator made of branched aramid nanofibers and PEO-based polymer electrolyte has been developed for Zn–MnO₂ battery, which was able to cycle with 96% capacity retention over 50 cycles at room temperature [129]. More impressively, a prototype pouch cell has successfully powered a small drone under low ambient temperature of 0°C.

**Perspective**

Aqueous zinc batteries are not one of the new “beyond” Li-ion technologies. They predated LIBs and have been part of our life for centuries. In the rechargeable world, however, the antique AZBs deserve revisit as the new materials and techniques developed in recent decades might provide avenues to solve the problems that have been regarded too challenging to be addressed before. In this review, we have presented to the readers how much progress have been made on the understanding and development of rechargeable AZBs by integrating advanced postmodern analyses, in-situ/operando characterizations, and nanomaterials design. As we discussed, recent progress on the porous Zn anode, Ca(OH)₂ separator and the solid-state ion conductor etc. have brought promising signs for commercial deployment of some alkaline-based AZBs such as Zn–Ni batteries. Mild acid electrolyte, compared to alkaline counterpart, enables a relatively more stable anode, and wider choice of cathode materials. Yet, no trace of acidic AZBs prototype has been spotted so far even though significant progress on the fundamental research has been achieved and excellent electrochemical performance has been demonstrated in lab-settings (Several examples of high performance AZBs in different electrolyte systems are summarized in Table S8.). For the future of AZB research, it is more important to take a systematic approach and evaluate these achievements in both alkaline and mild acid electrolyte under more practical conditions, such as high loading of active materials on electrodes, reasonable cell size with controlled electrolyte amount and high cell-level energy density etc. We believe it will be more efficient in finding out the potential drawbacks (e.g. pH swing, hydrogen evolution and electrode corrosion) that may not be obvious in lab-scale cell testing and quickly narrow down the technology routes for the renaissance of rechargeable aque-
ous zinc batteries. Leveraging the tremendous knowledge and technologies mankind has gained, we are optimistic that the challenges on the path to highly rechargeable and low cost AZBs will be overcome. A path (Fig. 11) through using either alkaline, acidic or some new routes will emerge when the time comes.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgement

XL would like to thank the support from the U.S Department of Energy (DOE) Office of Electricity (Contract No. 70247A). Pacific Northwest National Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the DOE under Contract DE-AC05-76RL01830. KX acknowledges the support from DOE BES via Joint Center of Energy Storage Research under funds to this article can be found online at https://doi.org/10.1016/j.mattod.2020.12.003.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mattod.2020.12.003.

References

[37] T.A. Edison, Alkaline battery, (1906).
[38] T.A. Edison, Reversible galvanic battery, (1901).
[57] C. Gassner, Galvanic Battery, Publication of US373064A, 1887.
[58] T.A. Edison, Alkaline battery, (1906).
[64] C. Gassner, Galvanic Battery, Publication of US373064A, 1887.