



Rechargeable Zn-ion batteries (RZIBs) are considered to be promising energy storage systems for large-scale applications owing to their relatively high energy densities and inherently low costs, environmental benignity, as well as safety. With increasing interest and effort being devoted to this field, RZIBs are being tremendously advanced and are very likely to be commercialized in the near future. However, some challenges remain that need to be addressed. Moreover, reported results are quite often overstated through artificial exaggeration and

cannot be translated to industrial applications as they were obtained under ideal testing conditions. Therefore, in this perspective, we discuss key parameters that need to be carefully considered when translating laboratory-developed RZIBs into commercial reality. We also present a critical mini-review on RZIBs and devote effort to issues that are overlooked in academic research. We believe that this perspective provides new or seldom-discussed insight for future work and bridges the gap between academia and industry.

## 1. Introduction

Owing to their high energy densities and long lifespans, lithium-ion batteries (LIBs) have conquered and dominated electrification markets, from portable smart electronics to emerging electric vehicles (EVs).<sup>[1]</sup> This flourishing scene is becoming gloomier as LIBs approach their energy density limit (250 Wh kg<sup>-1</sup>).<sup>[2]</sup> they are also unfavorably priced (about US \$300 per kWh) for large-scale applications.<sup>[3]</sup> Furthermore, LIBs use toxic and flammable organic electrolytes, which have led to several catastrophic accidental explosions (i.e., Tesla cars and Samsung smart phones).<sup>[4]</sup> To circumvent these issues, rechargeable Zn-ion batteries (RZIBs) that employ mild aqueous electrolytes (i.e., ZnSO<sub>4</sub>) rather than alkaline electrolytes have aroused considerable recent interest,<sup>[5]</sup> which is partly due to the ability of an RZIB to simply use a Zn metal anode and take advantage of its merits, such as its high capacity (820 mAh g<sup>-1</sup>), resource abundance, eco-friendliness, and low redox potential (−0.76 V vs. the standard hydrogen electrode (SHE)).<sup>[6]</sup> Moreover, as a century-old battery system, the mature and less stringent process used to manufacture alkaline Zn/MnO<sub>2</sub> batteries can be directly translated to the preparation of RZIBs.<sup>[4b,7]</sup> All of these features endow RZIBs with cost-effectiveness, environmental benignity, a lack of toxicity, and

superior safety, which are particularly attractive for large-scale applications.<sup>[8]</sup>

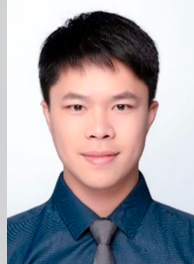
However, RZIB development is plagued by its somewhat inferior cycling stability and low energy density compared to those of commercial LIBs.<sup>[9]</sup> As a consequence, there is tremendous enthusiasm for exploring effective strategies that overcome these obstacles. Despite recent immense academic advancements in RZIB technology, several challenges still block the pathway to commercialization and need to be further addressed, including low Coulombic efficiency (CE),<sup>[10]</sup> inevitable Zn dendrite growth,<sup>[11]</sup> limited choice of cathode materials, and their insufficient performance<sup>[12]</sup> and low operating voltages,<sup>[3a,13]</sup> among others. Meanwhile, unlike the well-established lithiation/delithiation chemistry that operates in a LIB, the RZIB reaction mechanism remains disputed and unclear,<sup>[9b,14]</sup> which is another key constraint for advancing RZIBs in a significant way. Moreover, the substantially promising performance reported in the literature is quite often overstated for a variety of reasons. For example, the energy density of as-prepared RZIBs is generally calculated on the basis of the active materials not the practical weight of the system. In addition, considering the ideal testing environment of the laboratory from which very convincing improvements are reported, the data provided do not guarantee translation and scale-up for commercialization.

Inspired by these observations, rather than providing a systematic review on recent RZIB progress, herein we devote our effort to issues that are overlooked in academic research. Taking a commercial LIB with an energy density of ~250 Wh/kg as a benchmark, we first highlight key parameters that need to be considered in order to transform laboratory-based RZIBs into real commercial products. We then provide a critical mini-review on cathode materials and RZIB reaction mechanisms. Issues beyond the cathode are also discussed, such as Zn dendrite growth, electrolyte modification, and flexible RZIBs. We believe that this perspective will offer some new or seldom-discussed insight for future academic studies, and will draw the attentions of more researchers to key battery parameter requirements, thereby bridging the gap between academic studies and industrial applications.

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## 2. Key Parameters for Commercializing RZIBs

Commercial batteries can be presented in various shapes, such as cylinders, prisms, coins, and pouches.<sup>[2b]</sup> The use of light-weight packaging materials can maximize the energy density of a battery, with the pouch battery adopted as the main commercial LIB format for electronics applications, such as in a smartphone, where LiCoO<sub>2</sub> and graphite are used as the cathode and anode, respectively.<sup>[15]</sup> Consequently, such a LIB is used to discuss key parameters that need to be deeply considered in order to commercialize RZIBs. Table 1 shows typical values of the key parameters of such a LIB, with its energy density limit (~250 Wh kg<sup>-1</sup> per cm<sup>2</sup>) calculated using Equation (1):

$$\text{Energy density}_{\text{battery}} = \frac{\text{Voltage}_{\text{battery}} \times \text{Capacity}_{\text{battery}}}{\text{Weight}_{\text{battery}}} \quad (1)$$

According to Equation (1), increasing the voltage and capacity of a battery, or reducing its weight, can improve its energy density. Therefore, intensive effort has focused on exploring cathode candidates for RZIBs that have high capacities and operate at high voltages. Interestingly, many researchers claim that as-synthesized novel cathodes can engender RZIBs with exceptional energy densities; however, upon close inspection, such impressive energy densities are mostly overstated since only the active materials are counted under the precondition of low mass loading (i.e., 1–

5 mg cm<sup>-2</sup>).<sup>[9a,16]</sup> This strategy appears to be increasing in popularity, as such high energy densities are very attractive for readers. In addition, such a calculation criterion is imprecise and will lead to a misunderstanding of the research status of RZIBs for practical applications. Consequently, we suggest that researchers should at least provide the energy densities of as-prepared RZIBs based on the active materials, binder, conductive materials, current collector, and electrolyte.

The negative capacity/positive capacity (N/P)<sup>[1a,17–18]</sup> and the electrolyte-weight/capacity (E/C)<sup>[17]</sup> ratios are key parameters that need to be considered when assembling a commercial battery, as they play vital roles in determining the energy density and cycling performance of the battery. As the specific capacity of the cathode (i.e., 308 mAh g<sup>-1</sup> for MnO<sub>2</sub>,<sup>[3a,19]</sup> single-electron-transfer) is much lower than that of Zn (820 mAh g<sup>-1</sup>),<sup>[8b,20]</sup> the energy density of an RZIB is largely limited by cathode selection and its loading. According to the low loading in the literature (i.e., 5 mg cm<sup>-2</sup> for MnO<sub>2</sub>) and an N/P value of 1.3,<sup>[17]</sup> the matched Zn foil should be 2.8 μm thick. To be consistent with a commercial LIB,<sup>[2b,17]</sup> the Zn foil will need to be 12.3 μm thick to achieve a loading of 22 mg cm<sup>-2</sup>. Furthermore, given the inferior dischargeable depth of Zn and its side reactions with acidic electrolytes (i.e., pH=4 for 1 M ZnSO<sub>4</sub>),<sup>[7a,21]</sup> more Zn is required. The analogous situation can also be observed in concept rechargeable LIBs based on Li-metal anodes, where N/P is suggested to be three.<sup>[2b,17]</sup> Following this logic, the Zn foil in an RZIB should be approximately 50 μm thick by further considering that Zn foil can concurrently act as the current collector. Even so, the thickness of the Zn foil (200 μm) that is used in a laboratory button-type RZIB is still remarkably larger than this value. An E/C ratio of 3 g Ah<sup>-1</sup> is recommended in order to realize an energy density of 350 Wh Kg<sup>-1</sup>, taking the aforementioned concept LIB as the benchmark.<sup>[17]</sup> When this value is applied to current laboratory RZIBs, only 4.6 mg of electrolyte is required (based on a 1 cm<sup>2</sup> MnO<sub>2</sub> cathode with a loading of 5 mg cm<sup>-2</sup>), which corresponds to maximum ZnSO<sub>4</sub> electrolyte volume of 4.6 μL. It is highly likely that the electrode cannot even be sufficiently wetted with such a small amount of electrolyte, resulting in huge resistance at the electrolyte/electrode interface, which is disadvantageous for ion and electron transfer. Whereas, the superior cycling performance (i.e., 2000 cycles with 94% capacity retention at 6.5 C)<sup>[22]</sup> of RZIBs reported to date are always obtained with a large excess of Zn (200 μm) and with electrolyte flooding (75–100 μL). The reported RZIBs may not have long lifespans if cycling stability testing was required to be conducted under the strict conditions mentioned above. Let alone the abundant inactive materials would at the very least dramatically decrease the practically energy density of the RZIB.

Rate performance is another key parameter for commercial batteries.<sup>[23]</sup> It is quite common to see compelling RZIBs with high rate capacities in the literature. For example, Kang and coauthors declared that their as-synthesized flower-like MnO<sub>2</sub> cathode exhibits high rate performance as it can deliver 358 mAh g<sup>-1</sup> and 124 mAh g<sup>-1</sup> at 0.3 Ag<sup>-1</sup> and 3 Ag<sup>-1</sup>, respectively.<sup>[19a]</sup> However, according to the requirements of

**Table 1.** Key data for a commercial LIB with an energy density of ~250 Wh kg<sup>-1</sup> cm<sup>-2</sup> based on a LiCoO<sub>2</sub> cathode and a graphite anode.<sup>[a]</sup>

Battery component	Battery parameter	Value
LiCoO <sub>2</sub> cathode	Capacity [mAh g <sup>-1</sup> ]	150
	Active material loading [mg cm <sup>-2</sup> ]	22
	Active material ratio [%]	96
	Cathode areal capacity [mAh cm <sup>-2</sup> ]	3.3
	Al foil thickness [μm]	15
	Al foil areal weight [mg cm <sup>-2</sup> ]	4.05
Graphite anode	Negative capacity/positive capacity ratio (N/P ratio)	1.1
	Capacity [mAh g <sup>-1</sup> ]	360
	Active material loading [mg cm <sup>-2</sup> ]	10
	Active material ratio [%]	95
	Cu foil thickness [μm]	8
	Cu foil areal weight [mg cm <sup>-2</sup> ]	7.12
Electrolyte	Electrolyte weight/capacity ratio (E/C ratio) [g Ah <sup>-1</sup> ]	1.3
	Areal weight [mg cm <sup>-2</sup> ]	4.29
Celgard separator (2325)	Thickness [μm]	25
	Areal weight [mg cm <sup>-2</sup> ]	–
Packing materials Battery	Thickness [μm]	–
	Areal weight [mg cm <sup>-2</sup> ]	–
	Capacity per cm <sup>2</sup> [mAh]	3.3
	Operating voltage [V]	3.7
	Areal energy per cm <sup>2</sup> [mW]	12.2
	Active material weight per cm <sup>2</sup> [mg]	32
	Inactive material weight per cm <sup>2</sup> (without separator and packing) [mg]	16.86
	Energy density per cm <sup>2</sup> [Wh Kg <sup>-1</sup> ]	250

[a] Values were obtained from the reports of Liu *et al.*<sup>[2b,17]</sup> and Li.<sup>[18]</sup>

industrial batteries, if the battery can hold 80% of its capacity at one rate, then we can assert that the battery can cycle at this rate.<sup>[18,24]</sup> Based on this criterion, most of the claims about high rate performance are inaccurate to certain extents. Furthermore, the rate performance of a current laboratory RZIB is normally examined at low loads, typically 2–5 mg cm<sup>-2</sup>. Such low loadings are suggestive of short diffusion distances and low electrode polarization, which are particularly favorable for capturing high rate performance, but unfavorable for achieving high energy densities. Moreover, there are other key parameters that need to be deeply considered when commercializing RZIBs, which include but are not limited to: 1) The Coulombic efficiency (CE). Although the utilization of mild electrolyte (i.e., pH=4 for 1 M ZnSO<sub>4</sub>) can endow ZIBs with enhanced CE as compared to conventional alkaline Zn batteries, the uneven Zn plating/stripping associated with Zn corrosion cannot be eradicated completely. Accordingly, the ZIBs usually possess lower CE than commercial LIBs. Whereas, the most references present high CE approaching 100%, which are comparable to commercial LIBs. This is mainly derived from the reported data were obtained under excessive Zn and electrolyte. The additional consumption of Zn and electrolyte were not taken into consideration when calculating CE. Therefore, the reported attractive CE is not accurate to some extent and will give readers a mislead. 2) The slurry composition. As shown in Table 1, an active material ratio of 95–96% is required for a commercial LIB, while it drops to 80% or even 70% for RZIBs. More binder and conductive additive are indicative of stronger adhesion and better electrode conductivity, as well as higher cycling stability, whereas, more inactive materials also lead to a larger decrease in energy density. 3) The selection of the current collector. Carbon paper is usually employed to load active materials in current studies; however, its brittle nature provides challenges for maintaining integrity in continuous industrial production. 4) The separator. As the essential part and inactive materials of batteries, separators play crucial function in ensuring batteries' normal operation. Due to its excellent absorption capacity and commercially available, glass fiber mat with thickness of few hundred microns is widely employed in the reported ZIBs.<sup>[4b,25]</sup> This is significantly thicker than the Celgard separator (i.e., 25 μm thick) being used in commercial LIBs. Thicker separator means more inactive materials, leading to larger loss of energy density inevitably. Furthermore, Zn dendrites with Young's modulus of 108 GPa can readily pierce the glass fiber mat and invalid the ZIBs.<sup>[26]</sup> As a consequence, exploring much thinner and robust enough separators for ZIBs deserves more attention.

On the basis of the above discussion, the most compelling achievements reported in the literature cannot be translated to the preparation of commercial RZIBs. One can argue that the values listed in Table 1 are not suitable for RZIBs, which begs the question: what specific values should be used when commercializing RZIBs? Clearly, since RZIBs are still at an early stage of development, testing using the coin-cell model under less rigorous conditions is very necessary for revealing fundamental mechanisms and evaluating RZIB performance. However, researchers need to understand the key parameters that drive a commercial battery and be clearly aware that significant differences between academia and industry exist. In addition, if a standard laboratory-based testing protocol can be established, it would sharply improve research efficiency and boost the development of RZIBs as well as their progress toward commercialization.

### 3. Scientific Issues Concerning the Cathode

Divalent Zn<sup>2+</sup> has a similar ionic radius to monovalent Li<sup>+</sup> (0.74 Å vs. 0.76 Å).<sup>[16c,27]</sup> Theoretically, host materials with promising lithiation/delithiation capacity are also able to accommodate Zn<sup>2+</sup>. However, the high charge density of Zn<sup>2+</sup> would lead to the following issues: 1) A strong electrostatic interaction between Zn<sup>2+</sup> and the host, which impedes insertion and diffusion within the solid phase.<sup>[13,28]</sup> 2) The formation of Zn(H<sub>2</sub>O)<sub>6</sub><sup>2+</sup> with a large radius of 4.3 Å imposes further insertion and diffusion barriers for Zn species.<sup>[16b,28c]</sup> 3) The redistribution of charge upon insertion/extraction promotes gradual structural collapse and the irreversible phase transformation of the host, resulting in poor cycling stability.<sup>[4b,7b]</sup> All of these issues challenge the exploration of high-performance cathode candidates for RZIB applications, making their development lagging far behind expectation.

So far, only three main types of cathode material have been used in RZIBs, namely Mn-based oxides, V-based composites, and Prussian blue analogues (PBAs). They all feature open frameworks, including tunnel structures with various channel sizes, and layer structures with adjustable interlayer distances. The typical characteristics of these cathodes are provided in Table 2, which reveals that each candidate holds its own specific concurrent merits and drawbacks; indeed, it is hard to determine which cathode is more competitive. In addition, the specific shortcomings of these candidates still inhibit their large-scale applications. With this in mind, elucidating the microstructures of cathode candidates and probing the corre-

**Table 2.** Comparisons of Mn-based oxides, V-based composites, and PBAs.

	Mn-based oxide	V-based composite	PBAs
Advantages	Moderate operating voltage (1.3 V) Moderate specific capacity (308 mAh g <sup>-1</sup> ) Eco-friendly	High specific capacity (~400 mAh g <sup>-1</sup> ) High rate performance Good cycling stability	High operating voltage (1.7 V) High rate properties Good cycling stability
Disadvantages	Inferior rate properties Inferior cycling stability	Low operating voltage (~0.8 V) Toxicity	Low specific capacity (~100 mAh g <sup>-1</sup> )

sponding reaction mechanisms that operate in RZIBs are essential.

### 3.1. Crystallographic Structures of Cathode Candidates

Tunnel-structured materials that possess one-dimensional (1D) open channels are regarded to be promising Zn-storage candidates. Thus, diverse crystallographic  $\text{MnO}_2$  ( $\alpha$ -,  $\beta$ -,  $\gamma$ - and todorokite-) [14,22,29] polymorphs and monoclinic  $\text{VO}_2$  [30] that feature such structure have drawn considerable attention for RZIB applications. These materials are often constructed of  $[\text{MO}_6]$  ( $\text{M}=\text{Mn}^{4+}$ ,  $\text{V}^{5+}$ ) octahedrons, [29–31] with a theoretical model structure shown in Figure 1a. The size of the  $\text{MnO}_2$  channel can be tailored according to the arrangement of  $[\text{MnO}_6]$  units. For example,  $\beta$ - $\text{MnO}_2$  has a 2.3 Å  $[1 \times 1]$  channel,  $\alpha$ - $\text{MnO}_2$  has a 4.6 Å  $[2 \times 2]$  channel, while todorokite- $\text{MnO}_2$  has a 6.9 Å  $[3 \times 3]$  channel. [31b,32] Different from tetragonal  $\text{MnO}_2$ , monoclinic  $\text{VO}_2$  is built with distorted  $[\text{VO}_6]$  octahedrons; hence it contains two 8.2 Å and 0.5 Å channels along the  $b$ - and  $c$ -axes, respectively. [30,31c]

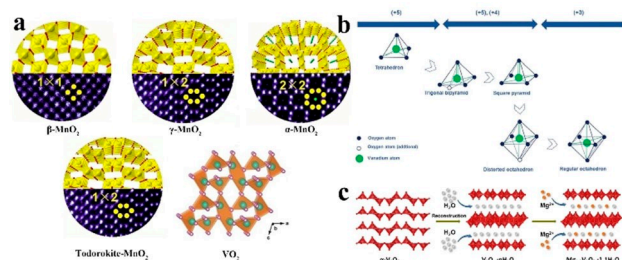
Same as the widespread application of layer-structured materials in LIBs, such materials also show notable potential for RZIB applications due to their large and adjustable interlayer distances. Among them,  $\delta$ - $\text{MnO}_2$  (simply constructed from  $[\text{MnO}_6]$  octahedrons) [11a,33] and V-based composites with  $\text{V}_2\text{O}_5$  [34] and  $\text{M}_x\text{V}_3\text{O}_8$  formulas ( $\text{M}=\text{H}$  or metal) [16c,35] have demonstrated attractive Zn storage capacities. Due to the distinct valence states of V ( $\text{V}^{3+}$ – $\text{V}^{5+}$ ), V–O coordination is significantly diverse (Figure 1b). [7a] Consequently, the crystal structures of V-based composites are more complex than those of  $\delta$ - $\text{MnO}_2$  and tunnel-structured  $\text{MnO}_2$ , especially when V exists in mixed valence states in a composite. [7a,27,36] For example,  $\text{H}_2\text{V}_3\text{O}_8$  and  $\text{M}_x\text{V}_3\text{O}_8$  ( $\text{M}$  is a metal) can both be considered as composed of  $\text{V}_3\text{O}_8$  layered skeletons; however their unit compositions are slightly different. The former is built with  $[\text{VO}_6]$  octahedrons and  $[\text{VO}_5]$  trigonal bipyramids, whereas the latter is formed by  $[\text{VO}_6]$  octahedrons and  $[\text{V}_2\text{O}_8]$  square pyramids. [16c,35c,37] Furthermore, the addition of polar water molecules and/or metal ions

into the layers also changes the arrangement and structure of the intrinsic unit, which generates a new structure. As shown in Figure 1c,  $\alpha$ - $\text{V}_2\text{O}_5$  is typically composed of  $[\text{VO}_5]$  square pyramids. [8a] However, the structural units and the layer structure of the formed  $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$  is quite different to that of  $\alpha$ - $\text{V}_2\text{O}_5$ . [38]

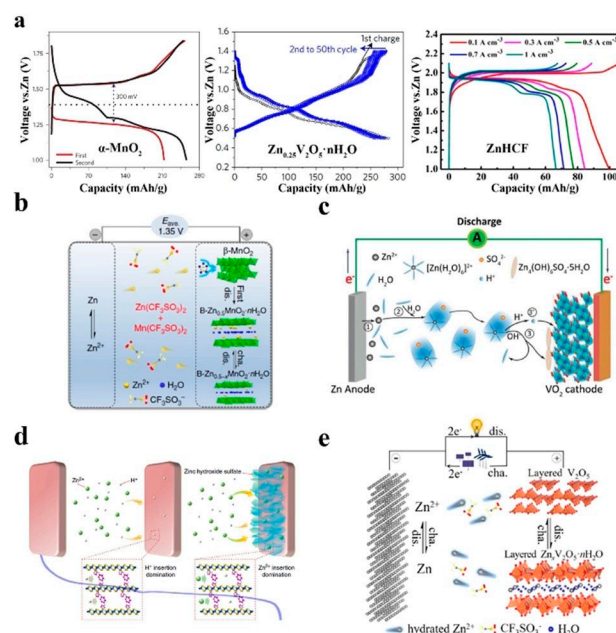
In addition to the open frameworks discussed above, other open structures, such as the Na super-ionic conductor (NASICON) [40], Li super-ionic conductor [13] and PBAs [41] exist and are profitable for  $\text{Zn}^{2+}$  insertion/extraction. Undoubtedly, the channel type and size of the host profoundly influence their capacities and diffusion rates for  $\text{Zn}^{2+}$ , since larger and stable 1D/2D channels are beneficial for reversible  $\text{Zn}^{2+}$  insertion/extraction. As a consequence, we suggest that researchers need to devote more attention to accurately deciphering the microstructures of their as-prepared materials and determining the corresponding relationships with  $\text{Zn}^{2+}$ -storage capacities.

### 3.2. RZIB Reaction Mechanisms

Representative RZIB discharge-charge profiles are displayed in Figure 2a, which show typical ion insertion/extraction characteristics. However, unlike the well-established lithiation/delithiation chemistry in a LIB, the RZIB reaction mechanism is still



**Figure 1.** a) The theoretically model structure for various crystallographic polymorphs  $\text{MnO}_2$  [39] and monoclinic  $\text{VO}_2$ . [31c] Reprinted with permission from Ref. [39]. Copyright (2019) Elsevier. Reprinted with permission from Ref. [31c]. Copyright (2019) Wiley-VCH. b) The schematic illustration of vanadium coordination polyhedras. [7a] Reprinted with permission from Ref. [7a]. Copyright (2018) Wiley-VCH. c) The structural units difference between  $\alpha$ - $\text{V}_2\text{O}_5$  and  $\text{Mg}_{0.3}\text{V}_2\text{O}_5 \cdot 1.1\text{H}_2\text{O}$ . [38] Reprinted with permission from Ref. [38]. Copyright (2019) Elsevier.



**Figure 2.** a) The representative discharge-charge profiles of RZIBs based on  $\alpha$ - $\text{MnO}_2$ , [9a]  $\text{Zn}_{0.3}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ , [12] and zinc hexacyanoferrate (ZnHCF). [47] Reprinted with permission from Ref. [9a]. Copyright (2016) Springer Nature. Reprinted with permission from Ref. [12]. Copyright (2016) Springer Nature. Reprinted with permission from Ref. [47]. Copyright (2019) American Chemical Society. The schematic illustration of various reaction mechanisms for RZIBs: b)  $\text{Zn}^{2+}$  insertion/extraction. [22] Reprinted with permission from Ref. [22]. Copyright (2017) The Authors. c)  $\text{H}^+$  insertion/extraction. [43] Reprinted with permission from Ref. [43]. Copyright (2019) Wiley-VCH. d)  $\text{Zn}^{2+}$  and  $\text{H}^+$  co-insertion/extraction. [42] Reprinted with permission from Ref. [42]. Copyright (2018) The Authors. e)  $\text{Zn}^{2+}$  and  $\text{H}_2\text{O}$  co-insertion/extraction. [21] Reprinted with permission from Ref. [21]. Copyright (2018) American Chemical Society.

controversial and under debate, which hinders the design and fabrication of compelling cathode candidates for RZIBs. Based on a literature review, the following three mechanisms exist.

Firstly, inspired by the lithiation/delithiation chemistry in LIBs, a mechanism in which  $\text{Zn}^{2+}$  reversibly inserts into and is extracted from the original host structure has naturally been proposed by some investigators. Interestingly, the insertion of  $\text{Zn}^{2+}$  during the first cycle had been found to trigger a phase transformation in the initial material in some reports.<sup>[7b,42]</sup> When compared to the preliminary structure, the new structure generated is more stable and favorable for the reversible intercalation/deintercalation of  $\text{Zn}^{2+}$ ; therefore, it acts as the new host for  $\text{Zn}^{2+}$  in subsequent cycles. For example, as shown in Figure 2b, Chen *et al.*<sup>[22]</sup> found that  $\beta\text{-MnO}_2$  is converted into a layer-structured Zn-buserite phase with the  $\text{B-Zn}_x\text{MnO}_2\cdot\text{H}_2\text{O}$  formula after the first discharge, which guarantees reversible and stable  $\text{Zn}^{2+}$  insertion/extraction in subsequent cycles. Secondly, considering the high charge state and large radius of  $\text{Zn}^{2+}$  (0.74 Å), most of the aforementioned hosts cannot accommodate substantial amounts of  $\text{Zn}^{2+}$ .<sup>[31c]</sup> However, the capacities of some reported materials are approaching their single-electron-transfer limits. It is also noteworthy that the insertion/extraction of  $\text{H}^+$  generates an identical specific capacity for  $\text{MnO}_2$  ( $\text{MnOOH}$  vs.  $\text{Zn}_{0.5}\text{MnO}_2$ ), especially noting that  $\text{H}^+$  is significantly smaller than  $\text{Zn}^{2+}$ . Consequently, a  $\text{H}^+$  insertion/extraction mechanism accompanied by the formation of zinc hydroxide sulfates on the cathode surface was proposed by Liu *et al.*<sup>[9a]</sup> These researchers characterized the cathode after the first discharge by scanning transmission electron microscopy (STEM), and could not detect elemental Zn in the  $\alpha\text{-MnO}_2$  nanorods. Wagemaker and coworkers<sup>[43]</sup> also support this chemistry on the basis of their as-prepared Zn/ $\text{VO}_2$  system. Figure 2c shows the corresponding discharge-charge process of this kind of battery. In addition, the discharge curves of RZIBs (Figure 2a) are observed to always exhibit multiple platforms that correspond to different thermodynamic and kinetic processes.<sup>[14,19a]</sup> As a consequence, Wang and coauthors<sup>[14]</sup> proposed a  $\text{Zn}^{2+}$  and  $\text{H}^+$  co-insertion/extraction mechanism based on electrodeposition involving a  $\text{MnO}_2$  cathode. Interestingly, this mechanism was also separately proposed by Xia *et al.*<sup>[42]</sup> and Chen *et al.*<sup>[35c]</sup> using layer-structured  $\text{MnO}_2$  and  $\text{NaV}_3\text{O}_8\cdot 1.5\text{H}_2\text{O}$  nanobelt hosts. This mechanism is well described in Figure 2d. Thirdly, as  $\text{H}_2\text{O}$  can act as a “charge shield” or “lubricant” that facilitates the insertion and diffusion of  $\text{Zn}^{2+}$ , some researchers considered that  $\text{Zn}^{2+}$  and  $\text{H}_2\text{O}$  concurrently insert into and are extracted from the host (Figure 2e).<sup>[10b,12,21,31c,44]</sup> Based on XRD and scanning electron microscopy (SEM) elemental maps, they observed the transformation of pristine  $\text{V}_2\text{O}_5$  into  $\text{Zn}_x\text{V}_2\text{O}_5\cdot n\text{H}_2\text{O}$  during discharge, which is entirely absent when fully charged.<sup>[21]</sup>

The variety of reaction mechanisms proposed for RZIBs are ascribable to many factors. Firstly, as discussed above, the co-existence of  $\text{H}^+$ ,  $\text{H}_2\text{O}$ , and  $\text{Zn}^{2+}$  in a mildly acidic electrolyte results in a more complicated reaction process for an RZIB than a LIB, which is possibly the main reason. The diversity of cathode material types, crystallographic structures, particle sizes, as well as micromorphologies will lead to a variety of ion

insertion/extraction thermodynamics and kinetics.<sup>[14,35c,45]</sup> Therefore, unveiling the practical redox chemistry that operates in an RZIB is difficult. Moreover, XRD is usually used to determine the phase compositions of an as-prepared host;<sup>[46]</sup> however, the collected data cannot describe local microstructural differences in the host well. For example, using aberration-corrected STEM, Lu and coauthors<sup>[29b]</sup> found that even a pure  $\alpha\text{-MnO}_2$  phase still contains heterogeneous  $[2\times 3]$  and  $[2\times 4]$  tunnels, which are different from its pristine  $[2\times 2]$  tunnels. All of these factors impose significant challenges for expounding the RZIB reaction mechanism. Hence, in order to establish the precise reaction mechanism, researchers need to first unveil the host structure using more-visual characterization techniques, after which an accurate structure-performance relationship can be established. In addition, the characterization techniques employed, including *ex situ*/in situ XRD, X-ray photoelectron spectroscopy (XPS), and the galvanostatic intermittent titration technique (GITT), cannot provide direct evidence for the  $\text{Zn}^{2+}$  or  $\text{H}^+$  ( $\text{H}_2\text{O}$ ) insertion process. Despite STEM elemental maps clearly revealing the existence of Zn in the cathode, the corresponding mechanisms discussed are still not convincing to some extent as the Zn source is ambiguous. As a consequence, an effective characterization tool that can provide first-hand information on ion insertion is urgently required. Perhaps *in situ* aberration-corrected liquid-STEM is a promising solution, since it can monitor local structures and/or compositional changes; however, the high energy and high flux of the electron beam is likely to induce new side reactions. Ways of rebuilding a reaction environment similar to that of a practical RZIB in such equipment need to be carefully considered. Additionally, designing a proper control experiment is very helpful in probing the reaction mechanisms of ZIBs. Accordingly, how to design a facile control experiment to exclude the influence of multiple insertion species (i.e.,  $\text{Zn}^{2+}$ ,  $\text{H}^+$  and  $\text{H}_2\text{O}$ ) also deserves more attention.

### 3.3. Strategies for Improving RZIB Performance

Although the RZIB reaction mechanism is still unclear, it does not restrict investigators from using various approaches to enhance RZIB performance. Generally speaking, cathodes suffer from low rate performance and rapid capacity fading upon cycling.<sup>[48]</sup> Several approaches have been adopted for optimizing performance, with tremendous advancements reported. Firstly, the rapid capacity degradation of the host is partly due to its dissolution in the electrolyte. More specifically, the  $\text{Mn}^{3+} \leftrightarrow \text{Mn}^{2+} + \text{Mn}^{4+}$  disproportionation reaction induced by the Jahn-Teller effect causes the  $\text{MnO}_2$  cathode to dissolve, which adversely affects the capacity retention of the corresponding RZIB.<sup>[19a,22]</sup> To solve this problem, the addition of a small amount of  $\text{MnSO}_4$  into the electrolyte has been demonstrated to suppress the dissolution of  $\text{MnO}_2$  and is an effective strategy. For example, Liu *et al.*<sup>[9a]</sup> prepared an outstanding Zn/ $\alpha\text{-MnO}_2$  battery based on a 0.1 M  $\text{MnSO}_4 + 2$  M  $\text{ZnSO}_4$  electrolyte, which is stable and retains exceptional capacity (92%) over 5000 cycles. Moreover, coating the host with a particular



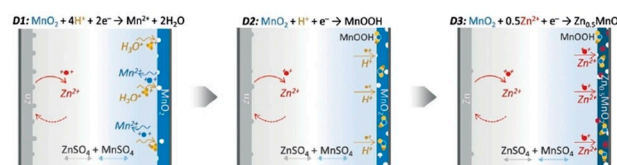
functional material that confines the redox reaction area and restrains  $\text{Mn}^{3+}$  transportation may provide an alternative solution.

In addition, structural collapse and the irreversible transformation to an inactive phase caused by continuous  $\text{Zn}^{2+}$  insertion/extraction are also responsible for the capacity fading of the host.<sup>[7b,22,42]</sup> It is well known that larger channels are favorable for reversible ion insertion/extraction and rapid ion diffusion, which are suggestive of higher cycling stability and better rate performance, respectively. However, hosts that feature such characteristics are inherently unstable and require specific agents to support their open frameworks. For example, cations (i.e.,  $\text{K}^+$ ) are always present in the tunnels of  $\alpha\text{-MnO}_2$  and todorokite- $\text{MnO}_2$ , and act as tunnel supporters.<sup>[49]</sup> Similarly, layer-structured hosts, such as  $\delta\text{-MnO}_2$  and various V-based composites (i.e.,  $\text{V}_2\text{O}_5$ , NASICON), also experience this effect. Specifically, the layer-structured  $\delta\text{-MnO}_2$  will convert into other crystalline structure in the repeated  $\text{Zn}^{2+}$  insertion/extraction, inducing a large volume variation and eventually causing its structure collapse.<sup>[50]</sup> Therefore, exploring light-weight and appropriate agents for enlarging the channels of the host while concurrently maintaining its pristine structure is a promising strategy.  $\text{H}_2\text{O}$  and various cations (i.e.,  $\text{H}^+$ ,  $\text{NH}_4^+$ ,  $\text{K}^+$ ,  $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{Zn}^{2+}$ , and  $\text{Mg}^{2+}$ ) are considered to be good choices in this regard.<sup>[8a,12,36,38,51]</sup> For instance, the use of a  $\text{Zn}_{0.25}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  cathode formed through zinc hydrate pre-insertion led to an RZIB with a high energy density of  $450 \text{ Wh L}^{-1}$  and long cycling stability (1000 cycles).<sup>[12]</sup> Similarly, Zhi and coauthors<sup>[50]</sup> employed  $\delta\text{-Na}_{0.44}\text{Mn}_2\text{O}_4 \cdot 1.5\text{H}_2\text{O}$  as the host of  $\text{Zn}^{2+}$ , which could cycling up to 10000 cycles with 98% capacity retention. Such performance improvements are ascribable to the pre-intercalated mediums that serve as robust pillars and expand the interlayer distance while supporting the layer structure.<sup>[8b,35c]</sup> In addition, a conductive polymer may be an alternative channel holder and expander. One representative case involves layer-structured  $\text{MnO}_2$  modified by intercalation with polyaniline, which exhibited exceptional stability over 200 cycles.<sup>[42]</sup> Compared to the tremendous achievements reported for layer-structured cathodes, strengthening the tunnel-structured host using such a strategy, for example by replacing heavy  $\text{K}^+$  with  $\text{H}^+$  or  $\text{NH}_4^+$ , has not been well developed and deserves more attention.

Since cathode candidates are mostly oxides or vanadates, their low inherent conductivities are detrimental for ion and electron transfer, which leads to large electrode/electrolyte resistance that adversely influences the rate performance and energy density of the battery. Naturally, coupling hosts with conductivity species (i.e., graphene, carbon nanotubes, carbon fibers, stain steel) can efficiently improve their conductivities.<sup>[16a,c,52]</sup> Furthermore, coating the cathode with carbon materials also plays a profound role in inhibiting its dissolution. Consequently, this strategy has been widely employed, especially the *in situ* growth of active materials on conductive substrates to form integrated electrodes.<sup>[10b,53]</sup> It is worth noting that the *in situ* synthesis method does not promise high loadings, and yields are relatively low, which are not suitable for large-scale applications. However, considering

that no binder is needed in the fabrication process, the as-prepared integrated cathode may be a good option for studying the fundamental RZIB mechanism. Moreover, as discussed above, the crystal structure and water molecules seem quite important to the cathode candidates. However, whether the coupling process between cathode candidates and carbon-based materials will destroy the crystal structure and affect the condition of water molecules are generally overlooked, which need to be considered carefully.

Apart from the detailed approaches discussed above, other promising measures for improving the properties of cathodes exist, including crystallographic control (i.e., orientation regulation and amorphism<sup>[54]</sup>), morphological engineering (i.e., porous,<sup>[31b]</sup> hollow,<sup>[55]</sup> and 1D/2D morphologies), and defect engineering (i.e., oxygen vacancies<sup>[49,56]</sup> and cation/anion doping<sup>[28b,49]</sup>). For instance, Wang and coauthors<sup>[54]</sup> studied the effect of crystallographic structure and found that the ZIB with a self-healing bi-layered  $\text{NH}_4\text{V}_4\text{O}_{10}$  exhibits superior capacity of  $147 \text{ mAh g}^{-1}$  at a current density of  $200 \text{ mA g}^{-1}$ . It is much better than the ZIB with monolayered vanadium oxides. Deng and coauthors<sup>[55]</sup> designed a bubble-encapsulated double-shelled hollow spheres cathode material ( $\text{Zn}_2\text{V}_2\text{O}_7$ ) and studied its  $\text{Zn}^{2+}$  capacity, which holds superior capacity retention than its counterpart with a random shape morphology (96.5% vs. 84.5% over 300 cycles at  $0.5 \text{ A g}^{-1}$ ). Additionally, Xue and coauthors<sup>[56]</sup> focused on the influence of oxygen vacancies to the  $\text{Zn}^{2+}$  capacity of  $\text{MnO}_2$ . Interestingly, the  $\text{MnO}_2$  cathode with abundant oxygen vacancies delivers capacity of  $345 \text{ mAh g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ . It is much higher than the pristine  $\text{MnO}_2$  cathode without oxygen vacancies ( $270 \text{ mAh g}^{-1}$  at  $0.2 \text{ A g}^{-1}$ ). All of these approaches can endow a host with a modified electronic structure, thereby facilitating the absorption-insertion-diffusion processes of ions or other species. In particular, the current energy densities of RZIBs are rooted in single-electron-transfer redox processes. Interestingly, the specific capacity of a cathode will double if a  $2\text{e}^-$  transfer process can be accomplished, which would lead to a density of  $616 \text{ mAh g}^{-1}$  for  $\text{MnO}_2$ . This would endow RZIBs with much higher energy densities, further reinforcing their LIB competitiveness. For example, Qiao and coauthors<sup>[3a]</sup> introduced an electrocatalytic mechanism into a traditional Zn/ $\text{MnO}_2$  battery, which led to a higher operating voltage of  $1.95 \text{ V}$  and an impressive cathode capacity of  $570 \text{ mAh g}^{-1}$ ; the corresponding reaction process is shown in Figure 3. Although the  $2\text{e}^-$  transfer process is extraordinarily attractive, it will result in additional issues that will need to be well considered. For example, how



**Figure 3.** The reaction mechanism of Zn/ $\text{MnO}_2$  battery based on  $2\text{e}^-$  transferring process.<sup>[3a]</sup> Reprinted with permission from Ref. [3a]. Copyright (2019) Wiley-VCH.



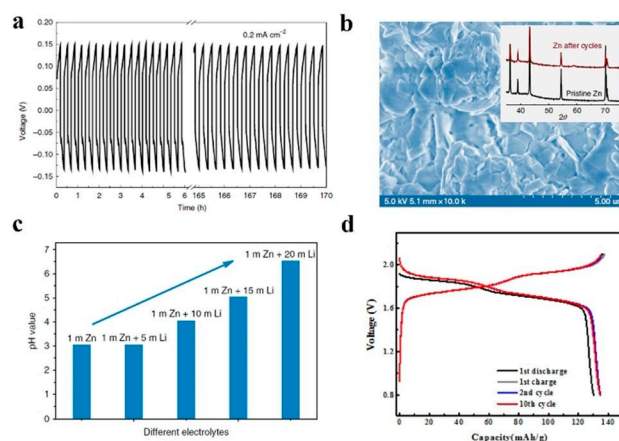
will electrocatalysis and insertion/extraction chemistry be balanced?

#### 4. Zn Dendrite Growth and Electrolyte Modification

Although the emergence of mild electrolytes has significantly advanced the rechargeability of Zn, it cannot radically eliminate the growth of Zn dendrites that are derived from uneven Zn plating/stripping processes.<sup>[2b]</sup> Moreover, the hydrogen evolution reaction (HER) will inevitably occur in such an electrolyte. Apparently, the low-depth chargeability and CE of the Zn metal anode are other obstacles that need to be overcome before RZIB performance can be further improved.<sup>[10a,57]</sup> In addition, the H<sub>2</sub> bubbles generated by the HER will very likely affect Zn<sup>2+</sup> diffusion. To our best knowledge, work focusing on the influence of the HER and the corresponding evolution of local pH in the electrolyte has rarely been reported, which is very necessary in the case of the H<sup>+</sup> insertion/extraction reaction mechanism.

Tremendous effort has been devoted to addressing the above-mentioned issues. Among them, designing a novelty configured Zn anode may be a powerful strategy for inhibiting dendrite growth. For example, inspired by the confined reaction mechanism, a 3D porous sponge Zn anode that delivered an impressive deep Zn dischargeability (90%) in an alkaline electrolyte was constructed.<sup>[58]</sup> However, this novel anode is not applicable for use in an acidic environment, since its higher specific surface area may promote the parasitic reaction between Zn and H<sup>+</sup>, resulting in more severe H<sub>2</sub> evolution and capacity degradation. Consequently, elucidating the dendrite-growth mechanism of Zn metal in a mild electrolyte is highly desirable in order to build novelty constructed anodes that are favorable for use in RZIBs. The use of advanced characterization techniques can help researchers efficiently conquer this challenge.<sup>[59]</sup> For example, coupling high-resolution *in situ* TEM with synchrotron X-ray computed tomography (SXCT) provides concurrent quantitative real-time information. Moreover, exploring more robust separators or solid-state electrolytes with higher shear moduli is another alternative method for overcoming dendrite growth.

Alternatively, optimizing the electrolyte composition is another method for overcoming the above-mentioned challenges that has immense potential.<sup>[60]</sup> For example, a “water-in-salt” electrolyte, composed of 1 M Zn(N(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>)<sub>2</sub> + 20 M LiN(SO<sub>2</sub>CF<sub>3</sub>)<sub>2</sub> (1 M Zn(TFSI)<sub>2</sub> + 20 M LiTFSI), has been developed by Wang and coauthors.<sup>[61]</sup> As shown in Figure 4a and b, the as-prepared Zn/Zn symmetrical cell operated for more than 500 cycles at 0.2 mA cm<sup>-2</sup> without exhibiting Zn dendrite growth. More impressively, such a neutral electrolyte (Figure 4c) dramatically inhibited the dissolution of Zn and endowed it with an extremely high CE of 99.7% over 200 cycles. Furthermore, the narrow electrochemical potential windows of current electrolytes are remarkably restraints on the operating voltage of an RZIB, which is typically low (1.3 V) for a Zn/MnO<sub>2</sub>



**Figure 4.** a) The galvanostatic cycling profiles of Zn/Zn symmetrical cell at 0.2 mA cm<sup>-2</sup>, b) SEM image and XRD pattern of the Zn anode after 500 stripping/plating cycles, c) the difference of pH values of the electrolyte with 1 M Zn(TFSI)<sub>2</sub> and different LiTFSI concentrations, d) the discharge-charge profiles of the Zn/MnO<sub>2</sub> battery with (0.2 M Zn(TFSI)<sub>2</sub> + 20 M LiTFSI) at 0.2 C.<sup>[61]</sup> Reprinted with permission from Ref. [61]. Copyright (2018) Springer Nature.

battery.<sup>[19a]</sup> This value is considerably lower than that of a LIB (3.7 V) and results in a relatively low RZIB energy density. Interestingly, as shown in Figure 4, the “water-in-salt” electrolyte also provides a higher operating voltage (up to 1.8 V); such an electrolyte is also very viscous, which is not suitable for rapid charge-transport kinetics. Furthermore, the super-expensive price of the “water-in-salt” electrolyte, which 500-times higher than that of the ZnSO<sub>4</sub> electrolyte, definitely undermines the low-cost advantage of an RZIB.<sup>[7a]</sup> Therefore, we expect that a novel electrolyte system that not only exploits the advantages of the “water-in-salt” electrolyte but also circumvents its disadvantages for RZIB use, will be developed.

#### 5. Flexible RZIBs

Portable, wearable, and implantable electronics driven by flexible energy storage system form the mainstream of future digital life.<sup>[62]</sup> Surprisingly, flexible RZIBs with high volumetric energy densities induced by Zn (5854.8 mAh cm<sup>-3</sup>) are the most promising candidates, as they satisfy almost all the requirements of flexible electronics.<sup>[57]</sup> For instance, an ultrathin (0.5 mm thick) primary Zn/MnO<sub>2</sub> battery capable of delivering an energy density of 300 Wh L<sup>-1</sup> has been successfully commercialized.<sup>[57]</sup> In addition to the obstacles mentioned above for traditional RZIBs, flexible RZIBs suffer from some further challenges. Firstly, the choice of flexible electrolyte is limited. Currently, flexible electrolytes are fabricated by adding suitable polymer agents (i.e., polyvinyl alcohol<sup>[63]</sup> and polyacrylamide<sup>[64]</sup>) to a traditional liquid electrolyte. Indeed, such a gel endows a traditional electrolyte with a certain degree of flexibility; however, the low conductivities of these flexible electrolytes further compromise the low rate capacities of RZIBs. To overcome this, it is particularly important to explore appropriate gels for constructing specific 3D networks

that can absorb more Zn salts and guarantee the rapid transportation of ions and electrons. In addition, flexible electrolytes with multiple functions, such as ultra-tough electrolytes and self-healing electrolytes, are attracting intense interest for a variety of applications.<sup>[65]</sup> Therefore, unveiling the cross-linking mechanisms of polymer gels and determining the deep relationship between the polymer gel and the performance of the flexible electrolyte is essential.

Secondly, compared to glass fibers that are used in traditional RZIBs, currently available flexible electrolytes are much thicker. As electrolytes are inactive materials, excess electrolyte is detrimental to the energy density of a flexible RZIB. However, fabricating a flexible electrolyte with a thickness comparable to that of a glass fiber without compromising its performance represents a significant challenge. Furthermore, very limited configurations exist for current flexible RZIBs. RZIBs with 2D film structures are attractive, but they are only flexible in a limited number of specific directions. Alternatively, 1D fiber-shaped RZIBs are more compelling, since they can be tied, twisted, and knitted into fabrics, but they also come with additional challenges. Furthermore, as discussed above for RZIBs in general, there is also a lack of evaluation standards for flexible capacity. For example, the electrochemical performance of a flexible RZIB in the laboratory is examined in a few specific static stress states, while the practical stress environment is much more complicated and dynamic. As a consequence, all of these challenges need to be deeply considered and more research needs to be conducted.

## 6. Conclusions and Outlook

RZIBs are regarded to be among the most compelling energy-storage devices for large-scale applications, especially for stationary grid storage. As was observed during the commercialization of LIBs, advances in RZIB technology has been sluggish due to its infancy, a lack of appropriate hosts for  $\text{Zn}^{2+}$ , as well as suitable electrolyte systems. Although tremendous improvements have been reported for laboratory-based RZIBs, especially following the introduction of mild electrolytes, their development is still impeded with further challenges that need to be overcome. Furthermore, the data reported in the literature to date are often acquired under ideal testing conditions, such as with a large excess of Zn, abundant electrolyte, and a low active material loading. While these achievements appear to be significant, they are only of limited value for industrial production, where much stricter conditions are required. As a consequence, in this perspective, with a commercial LIB as a reference point, we emphasize key commercial battery parameters in order to highlight the differences between industrial and academic practices. To shorten the commercialization pathway for laboratory-based RZIBs, we recommend that a standard testing and evaluation protocol for laboratory RZIBs, one that is close to that required for practical applications, be adopted. Given that the RZIB reaction mechanism is unclear, we provide a critical mini-review on cathode candidates and corresponding reaction mecha-

nisms. In order to achieve a high-performance cathode, more effort that focuses on deciphering host microstructures is required, especially local microstructures, using more-visual characterization techniques. Establishing a deep relationship between structure and electrochemical performance is favorable for the design and synthesis of novel cathode materials. Furthermore, special attention has been given to issues that have been overlooked in research work, such as Zn dendrite growth, electrolyte modification, and flexible RZIBs. We believe that this article offers new or seldom-discussed insight for future academic endeavors, and bridges the gap between academic studies and industrial applications.

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## Conflict of Interest

The authors declare no conflict of interest.

**Keywords:** rechargeable batteries · zinc-ion batteries · cathode materials · reaction mechanisms

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