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Journal Article as: peer-reviewed accepted version (Postprint)

DOI of this document*(secondary publication): https://doi.org/10.26092/elib/3696

Publication date of this document: 26/02/2025

Recommended Citation (primary publication/Version of Record) incl. DOI:

Michele Tribbia, Giorgia Zampardi, Fabio La Mantia,
Towards the commercialization of rechargeable aqueous zinc ion batteries: The challenge of the zinc electrodeposition at the anode,
Current Opinion in Electrochemistry, Volume 38, 2023, 101230, ISSN 2451-9103,
https://doi.org/10.1016/j.coelec.2023.101230.

Review Article

Towards the commercialization of rechargeable aqueous zinc ion batteries: The challenge of the zinc electrodeposition at the anode

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Abstract

The low efficiency of the electrodeposition of metallic zinc from mild-acidic electrolytes in realistic operating conditions currently represents the main challenge hindering the commercialization of aqueous Zn-ion batteries (ZIBs). These devices offer good environmental compatibility, low production costs, and high powder densities, thus are considered as a viable energy storage solution for stationary applications. The electrodeposition of metallic zinc is generally affected by dendrites, spontaneous evolution of gaseous hydrogen, and precipitation of insulating passivation products on the electrode surface. The recent scientific literature has provided many strategies addressing the zinc electrodeposition through the optimization of the electrode, of the aqueous electrolyte, or of the electrode–electrolyte interface. However, industrially relevant requirements such as *realistic* values of anode usage, current densities, and capacity limits, must be implemented in the future research studies.

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Keywords

Aqueous zinc-ion batteries, Zinc electrodeposition efficiency, Dendrites, Hydrogen evolution, Depth of discharge.

Abbreviations

ZIB, Zinc-Ion Battery; D.O.D., Depth of Discharge.

Introduction

The development of efficient and cost-effective stationary energy storage systems has become now an impellent requirement for the envisaged massive implementation of renewable energy sources in the power production sector [1,2]. Modern rechargeable batteries (such as organic-based Li-ion or Na-ion systems) are characterized by high efficiencies and power densities, suitable for this application. Nevertheless, their use on a large scale is discouraged because of their high materials, production and handling costs, practical safety concerns, and low environmental compatibility [3,4]. In contrast, metal-ion batteries employing Zn in a quasi-neutral aqueous electrolyte ($5 < pH < 7$) require lower investments due to the wide availability of their components and their simpler manufacturing process that can be carried out in open air. Also, both electrodes and electrolytes are generally cheap and non-toxic, hence optimal for stationary applications [5].

Aqueous ZIBs, usually constituted of a Zn^{2+} (de)insertion positive electrode (often referred to as cathode) coupled with a Zn-based negative electrode (often referred to as anode), have raised significant interests in the last decade. The reasons for this lays within the higher plating/stripping reversibility of the metallic zinc anode compared to other reactive metals, together with its high theoretical capacity (820 mAh g^{-1} or 5855 mAh cm^{-3}) and low standard redox potential (-0.76 V vs SHE) [6,7]. During cycling, Zn plating and stripping occurs at stable potentials at the zinc electrode. However, due to the low redox potential of metallic Zn, also the thermodynamically favoured hydrogen evolution reaction occurs, being its equilibrium redox potential at pH = 5 equal to -0.29 V vs SHE.

The hydrogen evolution reaction always results in the loss of active zinc and in the accumulation of gaseous H_2 inside the cell, which can lead to dangerous pressure build-ups. Moreover, the depletion of H^+ ions nearby the electrode surface causes a local alkalinization, thus leading to the precipitation of insulating layered Zn hydroxides [8,9]. The accumulation of these passivation products, in addition to the formation and growth of hydrogen bubbles on the zinc electrode, decreases the active surface area on which zinc can be plated. On the other side, upon the zinc deposition sharp and stiff dendrites may form, which can easily punch through the cell separator and cause internal short circuits, other than lead to the formation of isolated zinc pieces with no electric contact with the electrode. All these phenomena lead to full Zn-ion cells with short lifespans, regardless of the performance of the active material on the cathode side.

All the factors affecting the Zn electrodeposition are discussed in Section 2 of this review. Particular attention had been devoted to the definition of the Zn electrodeposition efficiency and the ambiguity behind its determination. Section 3 provides a concise, but comprehensive insight into the various strategies proposed in the most recent literature to improve the Zn electrodeposition in aqueous ZIBs. Every strategy is discussed in terms of general mechanism, major advantages, and weaknesses.

The ambiguity behind the determination of the Zn electrodeposition efficiency

The development of highly performant cathode materials is useful to make aqueous ZIBs ever more competitive over other energy-storage systems. Nevertheless, the optimization of the electrodeposition of zinc from quasi-neutral aqueous environment is crucial to enable their *actual rechargeability* and consequently their commercialization [6,10]. It is worth noticing that optimizing the zinc electrodeposition for battery applications means not only to achieve smooth Zn deposits, but also (and primarily) to minimize the charge loss due to unwanted sub-reactions.

The zinc electrodeposition efficiency (Eff_{Zn}) can be defined as the ratio between the electric capacity retrieved during the zinc-stripping step (Q_s) and the one related to the zinc-plating step (Q_p):

$$Eff_{Zn} = \frac{Q_s}{Q_p} \qquad (1)$$

In general, the Zn electrodeposition efficiency is affected by Refs. [10,11].

(I) the parasitic hydrogen evolution rate (thus the current employed, indirectly);
(II) the utilization degree of the zinc anode with respect to the total electrode capacity (i.e., with respect to the total amount of zinc);
(III) the Zn dendrite growth.

It is crucial to clarify at first the effect of all these factors in order to evaluate the *real* improvement to the zinc electrodeposition due to any strategy reported in the literature.

Parasitic hydrogen evolution reaction

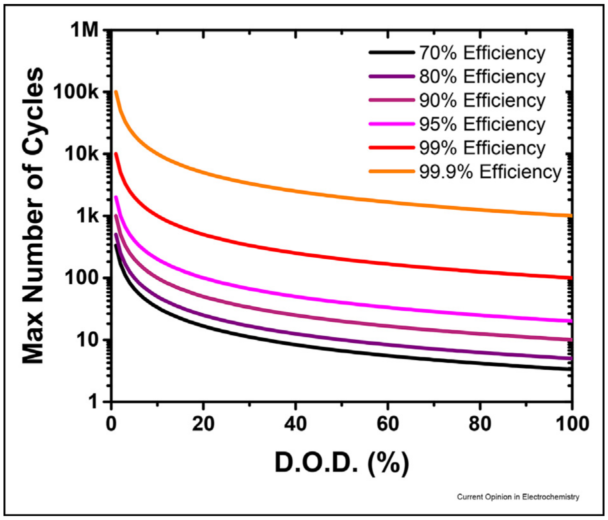
The parasitic hydrogen evolution is indirectly affected by the current density and the deposition time employed during the zinc stripping/plating cycles. For instance, high current densities (i.e. > 2 mA cm^{-2}) lead to more negative deposition overpotentials, thus to a higher percentage of the total current lost due to the unwanted H_2 gas evolution, in accordance with the Tafel equation [12]. Most works reported in the literature lack of a discussion on the occurrence of the hydrogen evolution reaction, even if this reaction can never be really suppressed in water-based electrolyte [13–15]. On the other side, ultrahigh (>5 mA cm^{-2}) current densities are at times used in combination with very short times for stripping/plating cycles, which are unrealistic in terms of the envisaged working conditions of ZIBs. This generally leads to higher electrodeposition efficiencies just because there is simply not enough time for side reactions to happen [15].

Some papers report an estimation of the hydrogen evolution and of the stability of the aqueous electrolyte by means of linear sweep voltammetry (LSV) [16–18]. However, attempting an estimation of the electrolyte stability by LSV can be misleading for two reasons: (I) zinc electrodes for ZIBs have to be cycled using galvanostatic protocols. This implies a fixed current intensity and therefore a different hydrogen evolution rate from the one that is observed when a potentiodynamic protocol is used [19,20]. (II) The hydrogen evolution rate changes at every stripping/plating cycle in galvanostatic tests (because of the changes in the electrode surface), while LSV measurements are carried out only one time for the anodic and the cathodic branch. Also, it is worth noticing that a reliable determination of the cathodic stability limit of the aqueous electrolyte (meant as the detection and the quantification of the H_2 evolved during the Zn plating/stripping cycles) is possible only through differential electrochemical mass spectrometry (DEMS [21,22]) or employing scanning electrochemical microscopy (SECM [23]).

Utilization degree of the zinc electrode

The use of a reservoir of metallic zinc on the negative electrode side is commonly adopted to compensate the inevitable loss of electric charge occurring during every cycle because of the irreversible side reactions. Nevertheless, the amount of excess metallic zinc should be carefully reduced as much as possible in order to match the requirements of realistic ZIBs prototypes [4,6,19]. Unfortunately, the utilization degree of all the zinc mass that is present on the negative electrode (often referred to as the depth of discharge, or D.O.D.) is highly variable among all the recent publications on zinc anodes. In most cases, when a metallic zinc foil is employed as negative electrode (anode), the D.O.D. is around only 1%–10% [15], taking into account that its areal capacity per unit thickness is equal to ≈ 0.58 mAh cm^{-2} μm^{-1}. In order to understand the deep inter-relation among the D.O.D., the Zn electrodeposition efficiency, and the performance of a Zn-based anode, an estimation can be

Figure 1



Current Opinion in Electrochemistry

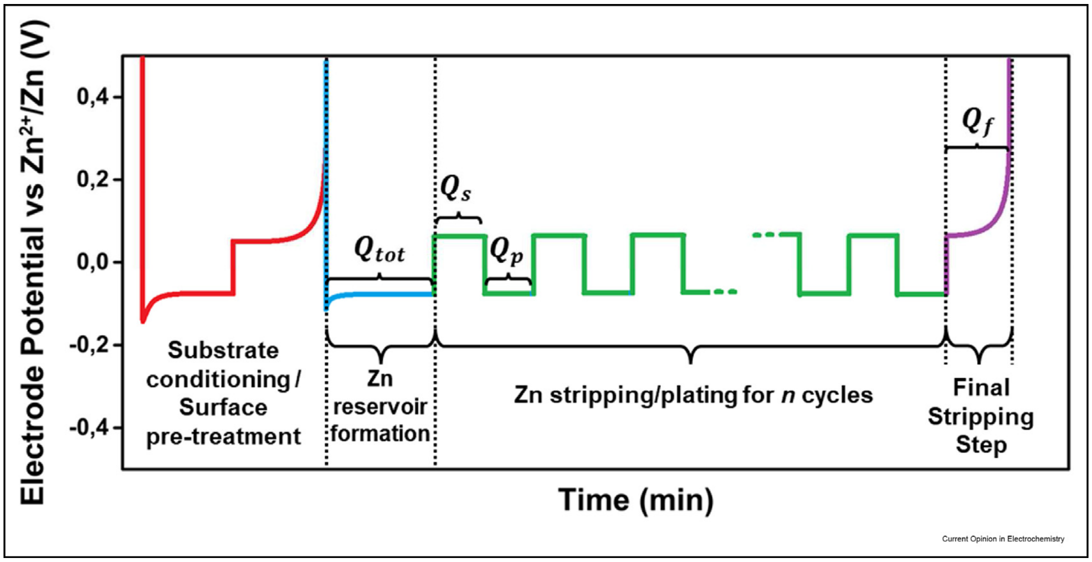
Maximum number of stripping/plating cycles that can be achieved before consuming the whole Zn reservoir that is present on the negative electrode as a function of the depth of discharge (D.O.D.).

made of the maximum number of stripping/plating cycles that a zinc electrode can undertake before consuming entirely its zinc reservoir, given a D.O.D. value and an average electrodeposition efficiency, as graphically represented in Figure 1 (see Supporting Information, S1). It is evident that longer cycling can be achieved even with low electrodeposition efficiencies if the D.O.D. is low enough. However, such operating conditions should be always avoided, as it is *unrealistic* from a practical point of view. A minimum value of 50% of D.O.D. should be always employed in the research works oriented toward the development of practical ZIB devices [6]. In most papers the zinc electrodeposition efficiency is discussed by reporting potential—time profiles of electrodes cycled at very low D.O.D. in half-cell configurations [24—33]. However, such experimental conditions often lead to misleading conclusions because the influence of the actual electrodeposition efficiency and of the D.O.D. value on the cell lifespan is undistinguishable. In 2020, Ma et al. proposed an alternative protocol for the determination of the average zinc electrodeposition efficiency ($\overline{Eff_{Zn}}$) on a generic metal substrate. It consists of an initial plating step of a certain amount of zinc reservoir followed by several stripping/plating cycles at a certain D.O.D. [19], as illustrated in Figure 2. We suggest implementing analogue protocols in future research works by using realistic values of current ($\geq$2 mA cm^{-2}) and D.O.D. ($\geq$50%), possibly together with an appropriate *operando* evaluation of the hydrogen evolution measured quantitatively through DEMS. Also, a maximum upper potential of 0.2 V vs Zn^{2+}/Zn should be adopted in order to resemble realistic discharge conditions of ZIBs.

Dendrite growth

Low currents and low D.O.D. values imply low amounts of zinc stripped/plated at every cycle, which is unrealistic when compared to the operating conditions envisaged for a real ZIB, as discussed in the previous paragraphs [4]. Also, this induces an apparent extension of the cell lifespan due to an artificial control of the dendrite growth and the zinc consumption [34,35]. The dendrite formation is, in truth, a common feature of the deposition of most metals. One of the main reasons for

Figure 2



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Cycling protocol for the determination of the average zinc electrodeposition efficiency proposed by Ma et al.. The figure was drawn according to the protocol described in Ref. [19].

this phenomenon is the “tip effect”, that is, the preferential growth of metal deposits onto the protrusions of the electrode surface [36]. The dendrite growth is influenced by the parameters employed in the galvanostatic experiments: when low deposition times and low currents are used, small zinc deposits accumulate at every cycle on the electrode surface and vice versa [34].

As regards the electrodeposition efficiency of zinc, the dendritic deposition causes the electrode surface area to grow at every cycle, thus increasing the number of active sites for the parasitic H_2 evolution. Moreover, the dissolution of uneven dendrites during the stripping step leads to an additional, irreversible loss of active metallic zinc from the electrode.

Strategies for the Zn electrodeposition improvement

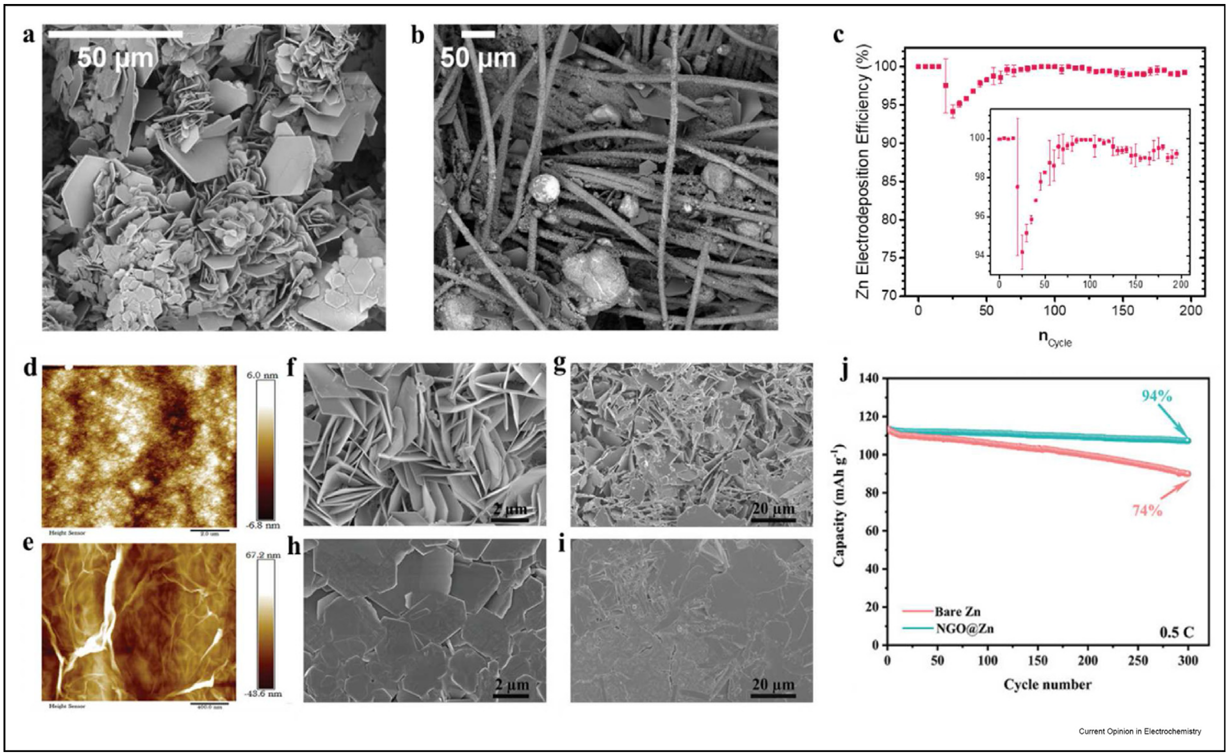
Within the recent scientific literature on ZIBs, different strategies have been developed to overcome the inefficient zinc electrodeposition by working on plating substrates, electrode coatings, and/or electrolyte composition.

In general, when working on the optimization of the zinc electrodeposition for battery applications it is of paramount importance to carefully consider the anode usage, which influences costs, manufacture, and safety of the total device. Experimental proofs of the real effectiveness of the various strategies are often obtained by tests in half-cell using a Zn plate as a counter electrode and in full-cell configurations. Unfortunately, it should be underlined that the Zn anodes usage (D.O.D.) is often negligible in both cases (i.e. usually <10%) [4,6]. In full cells, in particular, this is due to the very low mass loading of the positive electrodes ($\approx 2-3$ mg cm^{-2}) with respect to the negative electrode.

Substrates for Zn electrodeposition

Strategies involving the development of optimized substrates as ZIBs anodes focus mostly on accelerating the Zn electrodeposition kinetics over the hydrogen reduction one. The Zn plating efficiency can be improved using metals and composites having high binding energies with zinc [25,36–42] or slowing down the hydrogen reduction reaction [22,43,44] (Figure 3a–c). Since these substrates are effective as long as they are in

Figure 3



SEM images of (**a**) a Zn-powder electrode after 90 galvanostatic cycles and of a Bi–In powder electrode after 200 galvanostatic cycles in 500 mM $ZnSO_4$. (**c**) Average zinc electrodeposition efficiency of a Bi–In powder electrode in 500 mM $ZnSO_4$. Reprinted with permission from Ref. [22] Copyright (2022) the Authors. (**d**,**e**) AFM images of the initial Zn foil (**d**) and the NGO@Zn electrode (**e**), respectively. (**f**,**g**) Top-view SEM images of bare Zn foil electrode after plating of 1 mAh cm^{-2} (**f**), and plating/stripping 100 cycles at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2} (**g**), respectively. h) Top-view SEM images of NGO@Zn electrode after plating of 1 mAh cm^{-2}, and i) plating/stripping 100 cycles at a current density of 1 mA cm^{-2} with a capacity of 1 mAh cm^{-2}, respectively. (**j**) Long-term cycling performance at a rate of 0.5 C of LMO//bare Zn and LMO//NGO@Zn full cells. Reprinted with permission from Ref. [49] Copyright (2021) Wiley.

contact with the electrolyte, the effects of the zinc mass loading and of the morphology of the Zn deposits on the electrodeposition efficiency must be carefully evaluated.

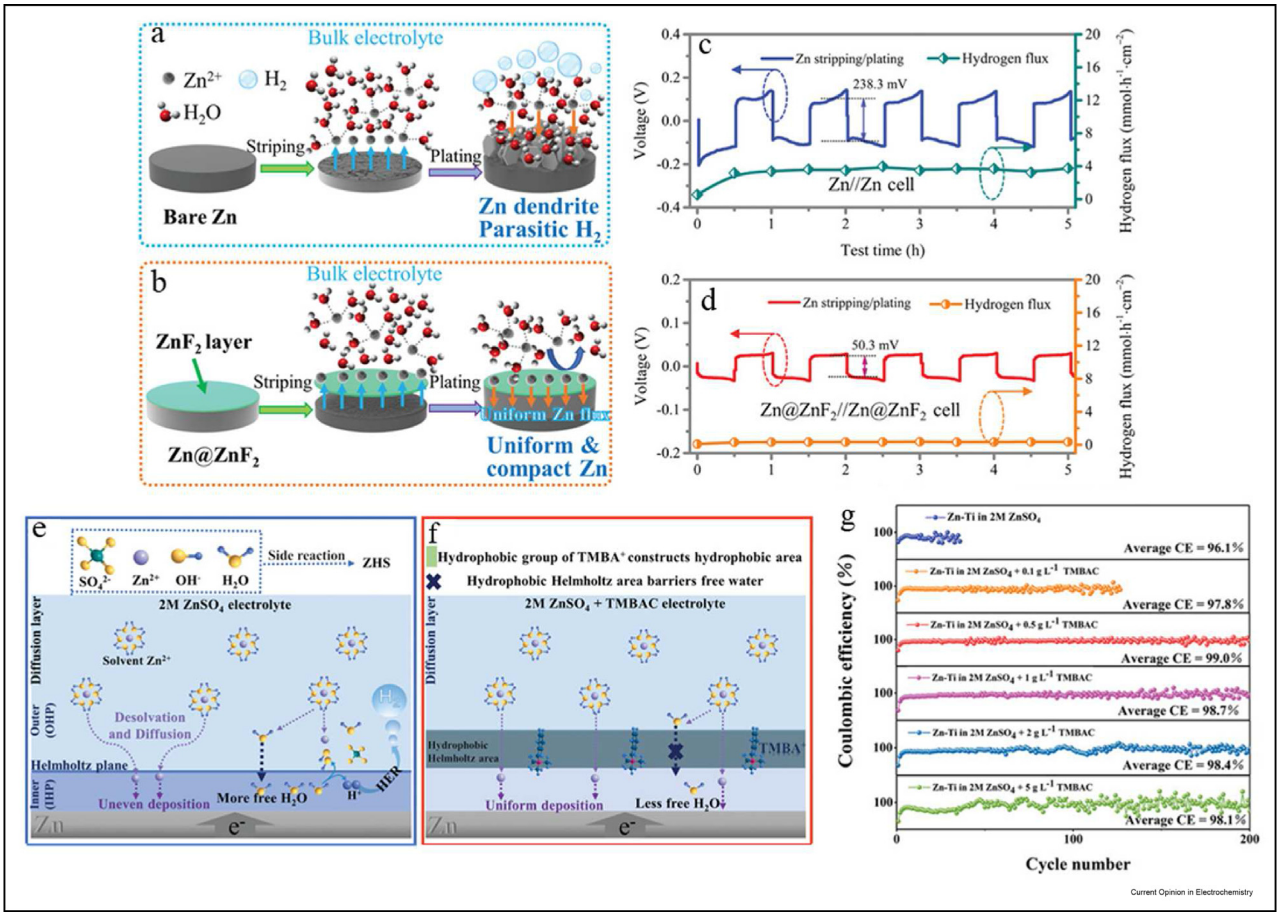
Moreover, as side reactions can be only kinetically and not thermodynamically hindered, a quantitative evaluation of the amount of H_2 gas evolved during the electrode cycling through DEMS is always necessary. In fact, although some metals may have good affinity for zinc, they could at the same time promote the hydrogen evolution reaction as well [45].

It is worth mentioning that some works report microstructured or porous substrates in order to mitigate the effect of the dendrite growth, hence avoiding short-circuits in compact cell designs [39–42]. Even if this has been proved a successful strategy for avoiding internal-short circuits, extended surfaces generally lead to higher amounts of gaseous hydrogen evolved during cycling.

Functional coatings

Functional coatings for Zn anodes mostly consist of porous non-conductive scaffolds [42,46–48], carbonaceous materials [49,50] (Figure 3d–j), and ion-conductive polymers or composites [21,24,46,51–56] (Figure 4a–d). The main aim of these coatings is to decrease the electric contact between the zinc electrode and the aqueous electrolyte, thus suppressing the decomposition of the latter by acting as an artificial SEI (namely an electronic insulator and an ion conductor [57]) [21,49]. On the other side, porous scaffolds generally provide smoother zinc deposits by promoting their oriented growth [47]. A preferential growth of zinc deposits along the (002) Zn crystal plane has been reported when using carbonaceous coatings [49]. Such

Figure 4



(**a**) Schematic illustration of Zn deposition on bare Zn foil. The corrosion, abundant “dead” Zn, and dendrite are observed due to 2D Zn^{2+} diffusion and thermodynamically instability of Zn metal in aqueous electrolyte. (**b**) Schematic illustration of Zn deposition on Zn@ZnF_2 foil. The ZnF_2 layer endows a dense and dendrite-free Zn deposition by regulating Zn^{2+} diffusion, controlling nucleation, and prohibiting the permeation of H_2O and O_2. In situ monitoring of hydrogen evolution flux for a Zn//Zn symmetric cell (**c**) and a Zn@ZnF_2//Zn@ZnF_2 symmetric cell (**d**). Reprinted with permission from Ref. [21] Copyright (2021) Wiley. Schematic illustration of reaction process of Zn deposition for Zn surface evolution in (**e**) 2 m $ZnSO_4$ and (**f**) 2 m $ZnSO_4$ with TMBA + electrolyte. (**g**) CE measurements of Zn–Ti batteries in different electrolytes. Reprinted with permission from Ref. [64] Copyright (2022) Wiley.

oriented Zn deposits appear to be less prone to corrosion in aqueous media [58]; however, the mechanism causing such behaviour remains unclear.

When using protective coatings for Zn anodes, particular attention must be paid in ensuring a good adhesion of the coating to the whole Zn metal substrate also during its cycling, which causes changes in the electrode surface. At the same time, optimal coatings should not increase excessively the overall reaction resistance in order to reach the high-power density expected from ZIBs.

Optimized electrolytes

The strategies involving the electrolyte optimization for improving the zinc electrodeposition efficiency include the development of: (I) mixed aqueous-organic electrolytes [59], (II) concentrated water-based solutions [60–62], (III) gel electrolytes [63], and (IV) the employment of low concentrations of surfactants and salts designed to enhance the metals electrodeposition [64–67] (Figure 4e–g). Recent works on mixed solvents and concentrated electrolytes report promising electrodeposition performances because of the strong suppression of the water decomposition. This is explained by a lower activity of water itself (i.e. a thermodynamic effect of stabilization, rather than kinetic) and thus by a more extended electrochemical stability window of the electrolyte. However, the use of high amounts of alcohol-based or other flammable organic cosolvents can lead to serious safety issues on large-scale devices [66]. On the other side, concentrated electrolytes can be a promising alternative for extending the electrolyte stability.

However, the employment of massive quantities of some salts, such as 20 m Li (TFSI) + 1 m Zn $(TFSI)_2$ [62], can lead to a great increase in the costs of the final ZIB prototype. So far, the employment of surfactants is among the most successful strategies to improve the zinc electrodeposition. These compounds can improve the zinc electrodeposition by strongly adsorbing onto the zinc negative electrode surface: on one side, the 2D planar movement of Zn^{2+} ions towards the surface protrusions is hindered (and therefore the dendrite growth is suppressed) [66], while on the other side, a mobile ad-layer protects the metal substrate from corrosion [64,65]. However, since high additive concentrations lead to a significant increase of the solution resistance, the electrolyte formulation remains yet to be optimized to reach a good balance between zinc protection and increase in the total impedance of the electrodeposition process [64].

Outlooks and future developments

The research on rechargeable aqueous ZIBs has drawn increasing attention from the scientific community in the last few years. The low environmental impact and the cheap production process of mildly acidic aqueous Zn-ion energy storage systems make them a realistic alternative to the Li-ion technology for large-scale stationary application. However, the low electrodeposition efficiency of zinc remains the main issue to overcome in order to market *actually rechargeable* ZIB prototypes.

Several strategies have been proposed to increase the Zn electrodeposition efficiency in aqueous media, such as the optimization of the electrode, the electrolyte, and/or the interface between them. The excellent results often claimed in the literature would suggest a quick introduction to ZIBs in the energy storage market in the near future. However, most reports result unfortunately misleading due to their lack of a quantitative measurement of side reactions. In addition, the discussion on the claimed improvement in the electrodeposition performance often fails to consider some requirements that are fundamental for realistic batteries [4]. This leads to misleading conclusions and considerations on the strategies adopted.

The zinc electrodeposition could be effectively improved by strategies (such as the use of electrolyte additives) that address the electrode–electrolyte interface continuously during cycling. However, one single strategy is often not enough to meet the electrodeposition efficiency required in ZIBs and therefore the use of combined strategies is highly recommended in future research [42,68]. Despite this approach means introducing a multivariable study on zinc electrodeposition, it seems to be a successful path for the development of realistic Zn-ion prototypes in the near future [15].

In addition, future efforts should focus on improving the zinc electrodeposition and matching at the same time the experimental strategies with the industrial requirements for ZIBs [4,19,35]. This implies on one side using high D.O.D. values (at least of 50%, if not higher) and high current densities and capacity limits (>2 mA cm^{-2} and >2 mAh cm^{-2}, respectively), while on the other side, making the economic and environmental sustainability of the chosen strategies a priority.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Cleis Santos reports financial support was provided by European Union.

Data availability

No data was used for the research described in the article.

Acknowledgements

This work was supported by the Federal Ministry of Education and Research (BMBF) in the framework of the project "ZIB" (FKZ 03XP0204A).

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.coelec.2023.101230.

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