Zinc regeneration in rechargeable zinc-air fuel cells—A review

Aaron L. Zhu\textsuperscript{a}, David P. Wilkinson\textsuperscript{b}, Xinge Zhang\textsuperscript{c,\textsuperscript{**}}, Yalan Xing\textsuperscript{d}, Alex G. Rozhin\textsuperscript{e}, Sergei A. Kulinin\textsuperscript{e,\textsuperscript{f,\textsuperscript{*}}}

\textsuperscript{a}Department of Chemistry, University of British Columbia, 2036 Main Mall, Vancouver, BC V6T 1Z1, Canada
\textsuperscript{b}Department of Chemical and Biological Engineering, University of British Columbia, 2350 East Mall, Vancouver, BC V6T 1Z4, Canada
\textsuperscript{c}Energy, Mining and Environment, National Research Council, 4250 Wesbrook Mall, Vancouver, BC V6T 1W5, Canada
\textsuperscript{d}School of Materials Science and Engineering, Beihang University, 37 Xueyuan Road, Beijing 100191, China
\textsuperscript{e}Nanoscience Research Group, School of Engineering and Applied Science, Aston University, Birmingham, B4 7ET, UK
\textsuperscript{f}Institute of Innovative Science and Technology, Tokai University, Hiratsuka, Kanagawa, 259-1292, Japan

ARTICLE INFO

Article history:
Received 23 May 2016
Received in revised form 8 September 2016
Accepted 20 September 2016
Available online xxx

Keywords:
Zinc-air fuel cell
Rechargeable alkaline fuel cell
Zinc regeneration
Zinc deposition
Metal-air cell
Zinc deposition additives

ABSTRACT

Zinc-air fuel cells (ZAFCs) present a promising energy source with a competing potential with the lithium-ion battery and even with proton-exchange membrane fuel cells (PEMFCs) for applications in next generation electrified transport and energy storage. The regeneration of zinc is essential for developing the next-generation, i.e., electrochemically rechargeable ZAFCs. This review aims to provide a comprehensive view on both theoretical and industrial platforms already built hitherto, with focus on electrode materials, electrode and electrolyte additives, solution chemistry, zinc deposition reaction mechanisms and kinetics, and electrochemical zinc regeneration systems. The related technological challenges and their possible solutions are described and discussed. A summary of important R&D patents published within the recent 10 years is also presented.
© 2016 The Author(s). Published by Elsevier Ltd. This is an open access article under the CC BY license (http://creativecommons.org/licenses/by/4.0/).

Contents

1. Introduction .......................................................... 35
2. Electrochemical fundamentals of zinc regeneration .......................................................... 37
3. Zinc regeneration .......................................................... 38
  3.1. Negative and positive electrode materials .......................................................... 39
  3.2. Separator .......................................................... 40
  3.3. Znatec electrolyte .................................................. 40
  3.4. Additives to electrode and electrolyte .......................................................... 41
  3.5. Zinc deposition .......................................................... 42
    3.5.1. Thermodynamics of zinc deposition .................................................. 42
    3.5.2. Kinetics and reaction mechanisms of zinc deposition .................................. 42
    3.5.3. Zinc deposition and morphology control ................................................. 44
4. Latest progress in zinc regeneration .................................................. 46
5. Concluding remarks .......................................................... 48
Acknowledgements .......................................................... 49
References .......................................................... 49

1. Introduction

The concepts of “metal–air fuel cell” and “metal–air battery” are normally defined as follows. If both metallic fuel and oxidant, such as oxygen or air, are added to the system from outside the cell, the system should be referred to as a “metal–air fuel cell”. If the
chemical energy from metallic fuel is still confined within the cell, the system should be regarded as a “metal-air battery”. Recently, the research on metal-air has gradually emerged as a hot-topic, which is attributed to their remarkably high theoretical specific energy densities [1–4]. The theoretical specific energy density of the available metal-air batteries reaches 13,300 Wh/kg for Li/O2 [5], 8140 Wh/kg for Al/O2 [6], 6462 Wh/kg for Mg/O2 [7] and 1084 Wh/kg for Zn/O2 [1]. A comparison of the specific energy densities of some representative types of primary/rechargeable batteries, metal–air batteries, H2–air fuel cell with gasoline is shown in Fig. 1 [2]. Clearly, the H2–air fuel cell, i.e. proton-exchange membrane fuel cell (PEMFC), possesses the best theoretical specific energy density. This is one of key factors explaining why all car manufacturing companies in the world have their strong interest and have invested heavily into the PEMFC vehicle for future clean transportation.

However, in reality, due to respective technical barriers, the difference in practical specific energy density between PEMFC and metal-air batteries, as shown in Figs. 1 and 2, is not very striking. Although it is difficult to compare directly a “PEM fuel cell” with a “metal-air battery”, the Ragone plot [8] in Fig. 2 shows candidly that the advanced metal-air batteries have equivalent (or even slightly higher) power values than PEMFCs do. In comparison with the primary/rechargeable batteries presented in Fig. 1, metal-air fuel cells also have attractive energy densities, which results from the high ratio of valence electrons to atomic nuclei of anodic metals while cathodic oxygen is virtually unlimited (as oxygen is not stored in the cell but comes from the air) [2,3,9,10].

Among the metal-air fuel cells and batteries, alkaline-based cell systems, such as Zn-air, are well balanced with respect to energy density, kinetics, stability and reversibility, as illustrated in Fig. 3. The Zn-air battery system was intensively developed in the past, as it is relatively simple, easy to operate, inexpensive to manufacture, and has excellent reliability, cycle-ability, and recharge-ability [10]. Thus far, the practical specific energy density of the Zn-air system has reached 350 Wh/kg in industry (MetAir) [11] and 580–750 Wh/kg in academia (data published sporadically from 2013 till now). Compared with the market dominating Li-ion battery, the Zn-air system exhibits certain advantages. Firstly, it is more cost efficient, going for less than a third of its Li-ion counterpart [12]. Secondly, it is constructed using safer materials, while Li-ion batteries are vulnerable to catch fire [13,14]. Thirdly, the currently achieved specific energy density of the Zn-air system is superior to that of its Li-ion competitors (typically within 100–250 Wh/kg) [15]. Compared with other high-energy battery systems such as the sodium-sulfur or sodium-metal chloride, which work at elevated operating temperatures (300 °C) and contain highly reactive and potentially polluting components, the Zn-air system is environmentally friendly and has a low safety risk [16]. The widespread accessibility, recyclability and abundant natural resources of raw zinc materials further guarantee its long-term use on the mass market. Therefore, these days the Zn-air system is considered as one of the most promising metal-air power sources.

At present, Zn-air batteries already have certain applications, for example, in hearing-aids and miniature medical devices [5,17,18]. However, certain technological challenges are still hindering their success on the competing market. The main obstacles can be briefly summarized as follows: (i) poor rechargeability, (ii) low utilization of the anode, (ii) sluggish kinetics of the cathode, (iii) longevity challenge. Compared with the Zn-air battery, the Zn-air fuel cell (ZAFC) offers several benefits, such as higher specific energy density, more attractive costs, better environmental compatibility and faster on-site refueling which requires only a standard electrical supply [1–4,19,20]. It also has
the potential of achieving the performance of the state-of-art H2-air fuel cells used as energy converters [1]. Of all the metal-air fuel cells being developed nowadays, the ZAFC has the most promising potential in terms of technical and commercial availability.

The principle of the Zn-air system was discovered in 1868 by Leclanché who noticed that the electrochemical performance of his cell significantly improved when its carbon cathode with a depolarizer of manganese dioxide was moist by only half-filling of the cell with electrolyte [5]. However, the commercialization of the Zn-air battery only started in 1932 when Heise and Schumcher proposed a porous carbon air cathode impregnated with wax to prevent the air cathode flooding. Large-sized low-drain batteries were then built for radio and railway-signal applications. The first example of mechanically rechargeable Zn-air batteries was shown in the 1950s when the cell design permitted to replace the consumed zinc anode with a new one. It was well realized in the 1960s that such batteries could have a high potential and wide applications if a low-cost zinc anode was available. Then the use of hydrophobic Teflon film made the high-energy Zn-air button cell come to being, which has since become a dominant power source for hearing aids [5,19,20].

Recently, technologies based on mechanical recharging have demonstrated significant progress [16,19,20], which led to practical availability of Zn-air systems with power from 170 to 350 Wh/kg. With further consistent development, power levels of 500–600 Wh/kg can be expected in the near future [16]. The latest mechanically rechargeable Zn-air fuel cells (ZAFCs) can be indeed regarded as a 1.5th generation of ZAFCs in which a discharged zinc anode and spent potassium hydroxide electrolyte are quickly replaced by fresh ones in a changing-printer-cartridge way, making continuous refuel/discharge process possible [21]. The significant improvements obtained in the development of mechanically rechargeable ZAFCs have driven much more research and industrial interests to reach the electrochemically rechargeable ZAFC in the near future. Therefore, Zinc regeneration becomes of the highest importance, both fundamentally and technologically. This review provides an overview of electrochemical zinc regeneration systems, with focus on electrode materials, electrode and electrolyte additives, solution chemistry, and zinc deposition reaction kinetics. The related technological challenges and their possible solutions are also mentioned and discussed. A concise patent summary of progress in R&D achieved both in academia and industry within the recent ten years is also provided.

2. Electrochemical fundamentals of zinc regeneration

A rechargeable zinc-air fuel cell (RZAFc) consists of two subsidiary electrochemical systems. The first is a typical ZAFc power generation system. It consists mainly of a zinc anode, an air cathode and a concentrated potassium hydroxide electrolyte (above 30 wt.%) which is circulated with pumps. The electrochemical reactions in such a galvanic cell are as follows. At the anode, zinc will dissolve in potassium hydroxide electrolyte, thus, Zn + 4OH\(^-\) → Zn(OH)\(_4\)^2\(^-\) + 2e\(^-\) \(E^0 = -1.199\) V vs. NHE (1)

(2)

Zn(OH)\(_4\)^2\(^-\) → ZnO + H\(_2\)O + 2OH\(^-\)

In parallel, the reaction can also proceed as:

Zn + 2H\(_2\)O → Zn(OH)\(_2\) + H\(_2\)

At the cathode, the reduction reaction of oxygen from ambient atmosphere occurs, leading to the following cathodic reactions:

\(1/2\) O\(_2\) + H\(_2\)O + 2e\(^-\) → 2OH\(^-\) \(E^0 = 0.401\) V vs. NHE

O\(_2\) + H\(_2\)O + 2e\(^-\) → (H\(_2\)O\(_2\))\(^+\) + OH\(^-\) \(E^0 = -0.076\) V vs. NHE

The overall reaction can be generally written as [23]:

\[ Zn + 1/2 O_2 → ZnO E^0 = 1.667\) V vs. NHE

It should be noted that the real reaction processes at both the anode and cathode are much more complex. The reaction processes undergo several steps, and the electrolyte with dissolved zinc can form a saturated, or even supersaturated solution containing various anionic species derived from the basic form of Zn(OH)\(_4\)^2\(^-\), the mixture being called the ‘spent solution’ or ‘zincate solution’. The term ‘zincate’, in the context of ZAFCs, generally refers to a salt containing the tetrahydroxozincate ion Zn(OH)\(_4\)^2\(^-\), such as K\(_2\)Zn(OH)\(_4\), or an oxide containing zinc and a less electronegative element, e.g. K\(_2\)ZnO\(_2\). The reaction processes and the formation of the saturated electrolyte will be described in greater detail in the related sections below.

The second subsidiary system is an electrolytic cell for the zinc regeneration. In the electrolytic cell, at the negative electrode zinc will be re-deposited from zincate solution produced by the electrochemical reactions occurred in the power generation system mentioned above, while oxygen will be produced at the positive electrode. The general electrolysis reactions can be summarized as follows:

At the negative electrode:

\[ ZnO + H_2O + 2OH^- → Zn(OH)_4^{2-} \]

(7)

Zn(OH)\(_4\)^2\(^-\) + 2e\(^-\) → Zn + 4OH\(^-\)

At the positive electrode:

\[ 2H_2O + 2e^- \rightarrow H_2 + 2OH^- \]

\(E^0 = -0.828\) V

\[ 2OH^- \rightarrow 1/2 O_2 + H_2O + 2e^- \]

Overall reaction:

\[ ZnO → Zn + 1/2 O_2 \]

(11)

Fig. 4a,b show, respectively, a schematic drawing of a rechargeable ZAFC system (a) and a picture of an industrial single-cell-modeled ZAFC system (b). Fig. 5 presents a potential (E)-current (I) polarization curve to explain explicitly the major origin of potential loss in rechargeable zinc-air electrochemical. cell. In Fig. 5 the theoretical electrochemical equilibrium and the practical potential windows of a reactive cell in the course of discharging are represented by the black vertical lines and red polarization curves for both electrodes, respectively. At zinc anode, the zinc oxidation reaction just needs a minor energy to overcome the resistance stemmed from the chemical potential state at the anode surface and then initiate the reaction. Thus, the over-potential needed to activate the anodic reaction is low. However, the over-potential at the air cathode is much larger than that in an equilibrium state, which is owing to the sluggish kinetics of oxygen reduction reaction (ORR) at the cathode.

A large potential (green arrow line) is needed to generate hydroxyl ions via ORR, which results in the working voltage of the actual zinc-air cell (E\(_s\), red line) being significantly lower than 1.65 V, i.e. the open-circuit potential (OCV, i.e., E\(_{eq}\), see the black vertical lines) of the ZAFC using air during the discharging course. Subsequently, in the charging course the polarization curves (blue lines in Fig. 5) clearly indicate that a larger potential is still needed at the positive electrode for the oxygen evolution reaction (OER). Compared with that at the zinc anode in discharging course, a
The zincate intermediates, as well as ZnO, are thermodynamically stable, and therefore more energy is required to initiate the reverse reactions and regain zinc in the charging processes. The overall effect resulted from both negative and positive electrode reactions taking place during the charging course generates two over-potentials. One is a radically higher over-potential than the equilibrium potential for the OER occurring at the positive electrode. The other is a noticeably lower over-potential than the potential for zinc deposition occurring at negative electrode. This leads to a larger potential window (the gap between the two vertical blue lines in Fig. 5) in the course of charging of ZAFC (or Zn regeneration). Nevertheless, when it comes to a primary Zn-air cell, it is not necessary to consider any challenge sit the zinc anode. However, to develop electrically rechargeable batteries, it requires the studies on how to improve the electrochemical behavior of zinc in both charging and discharging courses.

3. Zinc regeneration

For both discharging and charging courses, a major obstacle is the unpredictable nature of zinc electro-crystallization and related longevity issues, which can be associated with the redistribution of zinc active area (causing Zn electrode shape change) and formation of zinc crystals with various undesirable morphologies such as dendrite and spongy forms (Fig. 6). Although the formation mechanisms of various-formed zinc crystals in electrochemical courses are different, the forms of such crystals do reflect the common characteristics of zinc in nature, i.e., its high solubility in alkaline media and its rapid electrochemical reaction kinetics [19]. In the electrochemically rechargeable ZAFC, granular zinc is expected to be deposited from the spent electrolyte containing zincate. Therefore, the morphology control of zinc deposit plays a critical role in determining the reusability of the regenerated zinc in discharging process. The zinc morphology is a function of electrode materials, electrochemical deposition dynamics and kinetics, solution chemistry, additives and system engineering design [23]. It should be pointed out that after the selection of electrode couple, a dynamic polarization plot must be acquired prior to performing zinc regeneration because different electrode couples demonstrate different kinetic behavior during deposition. The obtained dynamic polarization plot then should be used as a guidance for the rate control during zinc deposition.

![Fig. 4](image1.png)

**Fig. 4.** (a) Rechargeable zine-air fuel cell system [23] (Reprint with permission from Academic Press). (b) An industrial single-cell-modeled zine-air fuel cell system (Power Air). The actual dimensions of the unit cell are 18 cm (L) × 20 cm (H) × 5 cm (W), with serpentine flow channels, while the actual reactive area is 12 cm × 14 cm, electrolyte is 37% KOH spent solution, Zn is supplied in pellet form, electrolyte flowing rate is 5 mL/s.

considerably larger over-potential is required for regenerating zinc from spent electrolyte. This is because the metastable zincate forms several intermediates, and even ZnO, via different saturation, supersaturation and dimerization steps [24,25].

![Fig. 5](image2.png)

**Fig. 5.** Schematic polarization curves of zine-air fuel cell. The equilibrium potential of the zinc-air cell [1] (Reprint with permission from Wiley Press). The equilibrium potential of ZAFC (black line) is 1.65 V, while the practical voltage (red line) in discharge is lower than 1.65 V due to the sluggish oxygen reduction reaction. A large potential is needed to charge zinc-air, higher than the equilibrium potential (blue line). For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)
3.1. Negative and positive electrode materials

The first important issue to be considered in respect of electrochemical zinc regeneration is the nature of substrate employed for metallic zinc deposition, i.e., the negative electrode. While choosing the electrode material, the possibility of side reactions on its surface should be taken into account, as such reactions would decrease the current efficiency during zinc deposition and result in impurities, as well as decrease oxidation and reduction potentials of the material and thus influence its longevity. The cost of the material is another aspect. From the thermodynamic and engineering points of view, it is ideal to use zinc as the negative electrode for zinc regeneration. Fig. 7 shows a typical potential-current curve of a zinc electrode performance [23]. When the potential is swept from the open-circuit potential towards more negative values, zinc deposition initially governs the reduction reaction until the potential reaches a zone where hydrogen release commences. When the potential ramps to positive values, accordingly, the current resulted from zinc dissolution increases exponentially and eventually reaches a peak, after which it decreases drastically at a certain narrow potential range, indicating the occurrence of zinc electrode passivation. After that, the current increases slightly and then reaches a plateau. With continuous zinc dissolution, ZnO begins to precipitate even at
a relatively low current. The initial ZnO precipitates are normally loose, but then they tend to agglomerate and thicken over time, eventually forming a compact layer causing conductivity problems at electrode surface.

Previously, various negative electrodes, such as Zn plate, sheet, cylinder, strip, or Zn amalgam, were applied to study zinc deposition from zincate solutions or Zn/ZnO phase equilibria in the Zn/ZnO system [26–32]. A porous electrode made of spherical 0.2-cm-sized zinc particles was also tested to study the electro-winning of zinc with simultaneous hydrogen evolution [33]. The mechanism of dendrite formation was also studied during zinc film deposition on Pt [34]. Nevertheless, all the above mentioned studies did not permit to solve the inherent problem of the zinc electrode, i.e., its shape changing upon Zn deposition (which results in uneven current density distribution on the electrode surface). Therefore, alternative electrode materials were examined afterwards. Copper electrodes were tested in experiments where pulse was used to control zinc deposition [35]. Steel-based materials were selected to study the properties of zinc deposit [36]. Aluminum was also utilized in studies involving zincate reaction processes [37] and zinc nucleation and growth [38]. Inspired by its use in the treatment of cast alloys, Al-Si was studied in its relation to zincate chemistry and the precipitation sequence of Cu, Fe, Ni, and Zn in zincate solution [39]. McBreen et al. have systematically investigated the possibility of Cu, Au, U, Pb, Ti, Sn and In as negative electrodes and their effect on the morphology of zinc deposits [40,41]. The nucleation and growth of zinc deposit on glassy carbon electrode was studied in order to mitigate the emergence of dendrite and other unhealthy deposit forms [42]. Based on the reported results, Zn pellet [43,44], stainless steel, and oxide-coated steel [45] were the main electrode materials chosen for industrial applications. Apart from these, a pasted insoluble zinc electrode was developed by the Scherrer Institute in Switzerland [21]. An original approach was proposed by Binder and co-authors who reported on a series of electrodes with different combination of Zn/ZnO/Zn(CN)₂/Na-CMC/Cu/HgO in gel form for alkaline cells [46].

At the same time, the selection of materials for the positive electrode in zinc regeneration systems is very simple. While in laboratory, conventional Au and Pt are primarily chosen, steel, stainless steel, and recently developed Ni based electrodes are typically used for industrial applications. Although glassy carbon electrodes are frequently selected for zinc plating in acidic bath, they are seldom used for the regeneration of zinc from alkaline zincate solution, being prone to the formation of mossy zinc deposits [42] and CO₂ generation whose content should be strictly limited since it reacts with the KOH electrolyte [21].

3.2. Separator

The separator is a porous membrane placed between electrodes of opposite polarity, permeable to ionic flow but preventing any electric contact between them. In batteries, separators play a key role, keeping the cathode and anode apart and preventing electrical short circuits, simultaneously allowing for rapid transport of ionic charge carriers, which is necessary to complete the circuit during the passage of current in an electrochemical cell. They should be very good electric insulators and have the capability of conducting ions via either their intrinsic ionic conductivity or soaking electrolyte, thus minimizing any processes that adversely affect the electrochemical energy efficiency of the battery [5,47,48]. Apart from playing a major role in preventing electric short circuit and conducting ion transport, separators are also utilized in electrolysis cells as physical barriers for impurities. For example, they stop solid by-products of the negative electrode from moving to the positive electrode or vice versa. In addition, they also help maintain the concentration gradient of the bulk electrolyte adjacent to the reaction zones of the electrodes. Compared to the tremendous research efforts dedicated to electrode materials and electrolytes, very little work has been conducted towards developing and characterizing new separators for both batteries and electrolytic cells for metal plating. Moreover, mathematical models that reflect the influence of separator’s resistance, thickness, pore size, shrinkage, tortuosity, and mechanical strength on the final performance and safety of electrochemical cells need to be further studied and developed.

In a traditional zinc plating system, Agar-sort polymer membrane has been typically used to prevent electrical short circuit caused by the fast growth of zinc dendrites and to trap ZnO particles. In the lately-developed zinc battery systems, polyolefin separators, e.g., Freudenberg FS 2227, were often used for both laboratory and industrial applications [49]. Currently, the requirements dictate the membranes be fairly resistant to oxidation, relatively stable in cells at high potentials, and chemically inert to KOH at high temperatures. They should also have a fine porous capillary structure to hold the electrolyte in the pores (and limit the diffusion of oxygen gas) and a high bubble pressure, as well as to exhibit low electrical resistance [49]. Since Celgard LLC succeeded in developing separator materials used in Zn-air batteries, such as Celgard 4500 and Celgard 5550 which have a microporous membrane laminated with a nonwoven fiber that is a textile product manufactured directly from fibers, the commercial laminated Celgard membrane has become the first choice in rechargeable ZAFCs with zinc regeneration.

Recently, Schubert et al. [50,51] developed a new polymeric separator membrane which is composed of a water-soluble copolymer of acrylic acid and sodium styrene-sulfonate monomers (PAASS). This new polymer has been further developed for alkaline electrochemical systems (e.g., metal/air, Zn/Na, Zn/MnO₂, Zn/HgO, etc.). The monomer ratio is tuned to manipulate both the electrolyte absorption and ionic resistivity of the copolymer. Processes have been developed to coat PAASS onto conventional nonwoven separator paper, thus fabricating composite membranes. The monomer ratio and the coating weight can be adjusted to balance ionic resistivity and short-circuit protection, providing adequate overall performance. PAASS-coated separators demonstrate good barrier properties to soluble zincate species. Preliminary use of PAASS-based separator materials in a rechargeable Zn-air system demonstrated a significant improvement in short-circuit protection over microporous materials such as Celgard 3401. The separators used in the future are expected not only to demonstrate good insulation and mechanical filtration, but are also required to have unique electrochemical properties [49].

3.3. Zincate electrolyte

In general, zinc electrochemistry in alkaline electrolytes seems rather simple. The zinc/air chemistry is normally described by the following simple reactions [19,21]:

Anodic reaction: \[ \text{Zn} + 2\text{OH}^- \rightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^- \] \hspace{1cm} (12)

Cathodic reaction: \[ \frac{1}{2} \text{O}_2 + \text{H}_2\text{O} + 2\text{e}^- \rightarrow 2\text{OH}^- \] \hspace{1cm} (13)

Overall reaction: \[ \text{Zn} + \frac{1}{2} \text{O}_2 \rightarrow \text{ZnO} \] \hspace{1cm} (14)

Accordingly, ZnO precipitation may seem favorable. When ZnO precipitates, the overall reaction is given by Reaction (14). If it is the case, the electrolyte composition does not change during the cell operation. However, the zincate concentration in the spent
solution produced via electrochemical oxidation was often reported to be much higher than those in the electrolytes prepared by dissolving zinc oxide into aqueous KOH based on the ZnO/KOH reaction equilibrium. This suggests that the spent solution generated via electrochemical oxidation of zinc is highly saturated and/or supersaturated with zincate and zincate-like species. In reality, the above presented simple reactions now are known to hide numerous complex reactions involving intermediates. Debiemme-Chouvy et al. have systematically studied the precipitation reactions and solution forms by means of conductometry, nephelometry, complexometric titration, nuclear magnetic resonance (NMR) and extended x-ray absorption fine structure (EXAFS) analysis [24,25]. Apart from zincate species Zn(OH)₄²⁻, zinc oxidation produces other soluble species, such as oxodihydroxy-zincate anion [ZnO(OH)₂]²⁻ and ZnO₂²⁻, depending on water activity in the KOH solution. In less concentrated alkaline solutions, the final products are [ZnO(OH)₂]²⁻ and Zn(OH)₄²⁻ (Reactions [15] and [16]), while in very concentrated basic solutions, such as with 45% KOH, the final species formed is ZnO₂²⁻ (Reaction [17]). In addition, Zn(OH)₂ can slowly form short-living species having a dimer [24].

\[
\text{Zn} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{2-} + 2\text{e}^- \quad (15)
\]

\[
\text{Zn(OH)}_2^{2-} \rightarrow \text{Zn(OH)}(\text{OH})_2^{2-} + \text{H}_2\text{O} \quad (16)
\]

\[
[\text{ZnO(OH)}_2]^{2-} \rightarrow [\text{ZnO}]^{2-} + \text{H}_2\text{O} \quad (17)
\]

Light scattering was applied to fresh and supersaturated zincate solutions [52,53], revealing that colloids are not involved in the formation of such species. The different zinc-hydroxide zincate species being present in the spent solution can demonstrate different kinetics in the course of zinc deposition [25,52]. This can be supported by the finding that regenerated zinc has very different morphologies even under the same galvanostatic control conditions [23,45]. It should also be noted that oxodihydroxy-zincate species are known to evolve easily into ZnO, the latter being an insulator causes problems in electrochemical cells. Therefore, the best way to eliminate its negative effect would be dissolving oxodihydroxy-zincate species by slowly adding water into the spent solution, which is recently realized in practice and called the “concentration fine-tuning” of the spent solution [53].

### 3.4. Additives to electrode and electrolyte

The role of additives is primarily important owing to their essential effect on the crystal growth, structure and glossiness of zinc deposits. Such additives can be classified into two categories: those to modify the electrode and those to modify the solution. Some additives are able to have a dual function. CaO, SrO, BaO, BeO, MgO, SnO, Ni(OH)₂ and Co(OH)₂ were described by Renuka et al. [54] as zinc electrode additives for the dissolution and deposition of zinc from zincate using practical 5.3 M KOH electrolyte in actual batteries. The effect of the above alkaline-earth oxides was compared with those of the already-established battery additives such as Bi₂O₃, LiOH, CdO and Na₂CO₃. Each of the alkaline-earth oxides was found to exhibit a distinct behavior towards zincate. In the presence of CaO, the electrochemical behavior of zinc electrode was not observed to show any remarkable change. Barium and strontium oxides were found to form respectively two types of solid solutions with zincate and ZnO, i.e., Ba[Zn(OH)₄]₂, Ba₂[Zn (OH)₆], Sr₂[Zn(OH)₄]·H₂O, and Sr₂[Zn(OH)₆] [55–57], whereas calcium oxide demonstrated only one type of solid solution with zincate, Ca[Zn(OH)₃]·2H₂O [58,59]. Therefore, adding Ca(OH)₂ into a zincate medium is expected to reduce the initial content of active zincate species at the electrode surface, thus lowering the specific energy of zincate [60–63]. Recently, it was shown that Ca(OH)₂ efficiently scavenges zincate in KOH solution, forming calcium zincate solid solution with a chemical formula of Ca(OH)₂·2Zn(OH)₂·2H₂O [53].

Lanthanum and neodymium hydroxides coated on zinc electrode were found to be effective in impeding the shape change of zinc electrode [64]. The additives of BeO, MgO, SnO, CdO, Ni(OH)₂ and Co(OH)₂ all have the capability of forming solid solutions with ZnO [65]. Ni(OH)₂ and Co(OH)₂ are also known to provide excellent host lattice for zincate [65]. The effect of LiOH was found to be the formation of two possible compounds, KLiZnO₂ and Li₂ZnO₄ [65]. The oxo-zincate compounds like KLiZnO₂ are expected to leach OH⁻ ions, leading to a higher solubility of Zn ions and thus preventing the unhealthy precipitation of ZnO [65]. LiOH and Na₂CO₃ can be more effective if they are used as electrolyte additives rather than electrode additives [65]. The functional effect of some metal oxide additives can be summarized roughly as CdO = Bi₂O₃ > BeO = [Co(OH)₂ + SnO] > MgO > CaO > BaO > SrO [65]. Since zinc can be deposited on bimuth and/or bismuth oxide during electrochemical processes, and Bi₂O₃ is easily soluble in KOH electrolyte, it can be used as both electrode and electrolyte additive [66,67]. The addition of Bi ions into the electrolyte can also result in a more homogeneous distribution of Bi on the Zn electrode surface and thus effectively inhibit the dendrite growth [66,67].

The effect of Pb and Na₂WO₄ was investigated by Wen et al. [68] who showed that both additives could suppress the initiation and propagation of spongy zinc, yielding more uniform and compact deposits [68]. However, Zn deposition can also be largely blocked by adding excess PbO and Na₂WO₄ in addition. Co-deposition of lead with zinc may occur if the amount of added PbO is not properly controlled. Therefore, the concentration ranges for PbO and Na₂WO₄ were recommended to be between 10⁻³ and 10⁻⁴ M and around 0.6 M, respectively [68]. The oxides and hydroxides of Cd, Pb, Sn, In, Ga, Tl and Bi have received the most attention as those mitigating the shape change of zinc electrodes [21]. All of them have two common features. First, their metals of these chemicals have a more noble potential than Zn does, and as such they can be deposited on zinc and change its surface properties. Second, they all have high hydrogen over-potentials and hence suppress hydrogen evolution at the zinc electrode surface [21].

Recently, a new approach was proposed in which conducting polymers, such as polypyrrole and zinc-ionomer derived from styrot-acrylic acid copolymer, were used as a direct contact additive on zinc electrode [69,70]. Ionomer types, typically with hydrocarbon backbones, initially aggregate as micro-domains at the interface between the electrode and the electrolyte. After that they act as physical cross-links into the electrode material and eventually affect the kinetics of zinc deposition, resulting in mitigating the shape change of the zinc electrode. Regarding the solution additives, tetrabutyl ammonium bromide (TBAB) has also shown promise for limiting dendrite formation in repeated charge/discharge cycles at lower cathodic over-potentials [21,67,71,72]. Its large organic cationic species were suggested to undergo specific adsorption at high-charge-density sites of the electrode where zinc–dendrite growth centers were active. This blocked the deposition at such sites, while it continued at other, less favorable, sites with lower and even more surface charge densities, thereby producing a smoother distribution of coherent Zn deposits [28,67,71,72]. The solution additives, e.g., fluorinated surfactants such as Atochem F1110 (C₁₅H₃₀–C₆F₁₄H₂(CH₂)₁₀–OH) have the advantage of being chemically stable in strong basic electrolytes and can stabilize the grain structure of zinc deposits, hindering the formation of mossy and dendrite deposits through the absorption
at rapid-growth sites on the negative electrode surface [73–76]. Impedance measurements revealed that during discharging/charging of the Zn electrode in a rechargeable battery system, the additive F1110 helps maintain the compactness of Zn deposits, also eliminates the deleterious effect of spongy Zn formation induced by anodically dissolved zinc [76]. Tetra-alkyl ammonium hydroxide and tetra-alkyl ammonium ethoxide were tested. The former was proven to provide a better effect than the latter at deposition temperatures above 30°C because it enhances or catalyzes Zn deposition from a mono-valent zinc complex [27].

Minor concentrations of Pb ions (10−3–10−5 M) presented in the electrolyte were found to increase the compactness of zinc deposits [68]. It should be mentioned that ZnO itself was reported to be a favorable electrode additive in zinc battery for its positive effect in reducing the electrode corrosion, discouraging the passivation of the electrode in alkaline electrolyte and increasing both the discharge capability and the cycle life [77]. However, it minimizes the reversibility of Zn ion to be Zn metal because it lowers the reduction capacity of zincate to metallic zinc [77]. Though no details on how to use ZnO in the most efficient way were reported, studies on this subject look worth conducting since ZnO is naturally present in all spent zincate electrolytes. Therefore, by controlling ZnO concentration in such electrolytes, it might be possible to take advantage of this inherent state-of-the-art additive. Moreover, the potential additives which have already been considered for non-rechargeable ZAFCs for the discharging process, such as HgO, Tl2O3, CdO, In2O3, In(OH), In and Ga2O3 [78], are also worth testing in zinc deposition in rechargeable ZAFCs.

During electrochemical regeneration of Zn from spent zincate electrolytes, the processes are always accompanied by hydrogen evolution as Zn has a lower standard potential. The quantity of H2 produced due to hydrogen evolution is dependent on several factors, such as electrode and electrolyte inhibitor concentrations in spent solution, electrode material’s type, form and crystal structure, water and ZnO contents in spent electrolyte, zincate saturation level, applied deposition potential/current densities, the designs of zinc-regeneration cell and spent-solution flow system, etc. According to Ravindran and Muralidharan [30], the hydrogen evolution rate is about 5 mL/s/m2 in 6 M KOH spent electrolyte containing 0.02 M ZnO at 20 mA/cm2 of applied deposition current density and room temperature. Hydrogen evolution decreases with an increase of zincate concentration. The co-deposited hydrogen can diffuse along three directions: to air, to electrode substrate and to the deposited Zn matrix, not only resulting in decreased current efficiency, but also producing mechanical problems to the electrode, such as surface embrittlement or plating blister (Fig. 8) [79]. Thus, in principle, any hydrogen inhibitors which sluggish the kinetics of hydrogen evolution should be re-examined for zinc regeneration.

An elaborative list of hydrogen inhibitors potentially applicable in the discharging process of ZAFCs can be found in the reports of Haas et al. [21], Yoshizawa et al. [80] and the patents of Goldstein and coworkers [80–82]. Among those additives, the effectiveness of indium, tetrabutyl ammonium bromide and PbO was already proven by industry, though no comprehensive reports were published thus far. In addition, brighteners which may either enhance hydrogen evolution or inhibit it are also used to prevent hydrogen diffusion into both deposited Zn layers and the negative electrode [79]. In this context, anis-aldehyde bisulfate and Na-N-benzyl nicotinate have been examined on stainless steel as the electrode [79]. Na-N-benzylnicotinate was concluded to enhance hydrogenation processes on such electrodes causing blisters to appear in Zn deposits, whereas anis-aldehyde bisulfate dissipates generated hydrogen into air. A summary of industrially developed patents on such additives can be found in the review of Basset al. [83].

3.5. Zinc deposition

3.5.1. Thermodynamics of zinc deposition

The thermodynamics of zinc regeneration is known to be very complex. Metallic zinc (Zn0) is not directly and simply deposited from freely mobile Zn2+ ions in the used alkaline electrolyte, but it is regained from different zincate complexes with different composition and charges. When it comes to discussing the thermodynamics of electrochemical Zn deposition, the Pourbaix diagram should be used as the foundation [84]. The activity coefficients for all common alkaline electrolytes used with zinc electrode were previously reported by Pound et al. [85]. Nevertheless, the surface state of electrode and the zincate/ZnO equilibrium in a spent electrolyte are dependent on both the charge/discharge running conditions (temperature, running time, KOH concentration, additives, zinc feeding rate, and so on) and the cell design. Moreover, since zincate undergoes a few intermediate formation steps when aging (Fig. 9), the conventional Pourbaix diagram published in the “Atlas of Electrochemical Equilibria in Aqueous Solution” may not provide a sufficient accuracy. A more practical Pourbaix diagram guiding Zn regeneration, including industrial on-site zinc deposition, can be constructed by using the HYDRA program database [86] and updated equilibrium constants published sporadically in the journal “Hydrometallurgy”, the “Handbook of Chemical Equilibria in Analytical Chemistry” (Halsted Press), “Stability of Metal-Ion Complex” (Royal Chemical Society) and “Critical Stability Constants” (Plenum Press). Since there is a wide variety of values and conditions for these equilibrium constants, the ion strength index should be used as the first criterion for the selection of other values. In this way, the variables can be much simplified as electrolytes used in zinc-regeneration systems are highly concentrated [87]. The thermodynamic data of hydroxyl-zinc complexes are listed in Table 1.

3.5.2. Kinetics and reaction mechanisms of zinc deposition

During zinc regeneration, metallic Zn deposition from Zn (OH)22− based zincate complex ions and the release of OH− ions are expected [88]. The mechanisms for the discharge of Zn2+ ions are still remaining controversial and disputed. One of the two most realistic mechanisms was proposed by Hampson and coworkers [89–91] who used galvanostatic and double-impulse methods to perform transient measurements and thus to evaluate exchange current densities at zinc electrodes in the potential ranges near the equilibrium value. The mechanism can be described by the below Reactions (18)–(21):

Fig. 8. Appearance of blister formation assigned to hydrogen diffusion into the deposits [79]. (Reprint with permission from Springer Press).
Zn(OH)\textsubscript{2} + OH\textsuperscript{−} \rightleftharpoons Zn(OH)\textsubscript{3}\textsuperscript{−} + OH\textsuperscript{−}  \hfill (23)

Zn(OH)\textsubscript{3}\textsuperscript{−} \rightarrow ZnOH + OH\textsuperscript{−}  \hfill (24)

ZnOH + e\textsuperscript{−} \rightarrow Zn + OH\textsuperscript{−}  \hfill (25)

In this approach, it is the Reaction (23) that is considered as the rate-determining step. The two mechanisms mainly debate about which reaction is the rate determining step and whether Zn(OH)\textsubscript{3}\textsuperscript{−} is truly present as a species, since the comprehensive electrolyte studies accomplished by Debiemme-Chouvy et al. using NMR and extended X-ray absorption fine structure (EXAFS), in conjunction with conductometric, nephelometric and complexometric analyses, did not support fully the appearance of such a species [24,25]. A more recent quantum-chemical study demonstrated that the activation energy of the [Zn(OH)\textsubscript{3}\textsuperscript{−}] discharge is much higher than those for the [Zn(OH)\textsubscript{2}\textsuperscript{−}] and [ZnOH\textsuperscript{−}] species [92]. This suggests no direct charge transfer onto this species, while there are possibly some preceding chemical stages of OH\textsuperscript{−} ligand abstraction reaction, which is supported by the experimental results of Maslii et al. [92] and Debiemme-Chouvy and coworkers [24,25]. As a result, it is the [Zn(OH)\textsubscript{2}\textsuperscript{−}] that seems to be the preferred electroactive species since it requires the lowest energy for activation.

The two aforementioned kinetic mechanisms have some vulnerability because the proposed reactions listed in the mechanisms are mostly deduced from results obtained in the transient pseudo-equilibrium rather than steady-state measurements, and the steady-state behaviors of the zinc electrolyte are not predicted sufficiently. Epelboin et al. [93] and Cachet et al. [28,76,94] applied electrochemical impedance spectroscopy (EIS) to investigate zinc electrocrystallization at steady state and observed the occurrence of the following autocatalytic reaction step: Zn\textsuperscript{2+} + Zn\textsubscript{ads} + e\textsuperscript{−} \rightarrow 2Zn\textsuperscript{ads} which was accompanied by the adsorption of hydrogen, OH\textsuperscript{−} and Zn\textsuperscript{+} at the electrolyte/electrode interface. Moreover, at least four adsorbed species were shown to be involved in zinc electrocrystallization at the electrolyte/electrode interface [93]. In order to avoid measurement errors associated with the shape changes of zinc electrode, Despić et al. used a zinc amalgam electrode to investigate the reaction mechanism and the exchange-current density in a full range of alkaline hydroxide concentrations (1–14N) that are of interest for practical applications [31]. While the rate determining step at the pure zinc electrode is the first-electron-transfer step towards the cathode [88], it was found to be the chemical step between the two electrochemical steps at a zinc-amalgam electrode [31]. Based on the obtained experimental data, the reaction mechanism was proposed to be chemical-electrochemical-chemical-electrochemical type, i.e., the deposition of zinc proceeds as follows [31]:

\[\text{[Zn(OH)\textsubscript{2}]_2 + 2H\textsubscript{2}O \rightarrow [Zn(OH)\textsubscript{2}]\textsubscript{2}H\textsubscript{2}O + 2OH\textsuperscript{−} + 2H\textsuperscript{+}}\]  \hfill (26)

\[\text{[Zn(OH)\textsubscript{2}]_2 - 2H\textsubscript{2}O \rightarrow [ZnOH] + OH\textsuperscript{−} + 2H\textsuperscript{2}O}\]  \hfill (27)

\[\text{[ZnOH] + e\textsuperscript{−} \rightarrow Zn + OH\textsuperscript{−}}\]  \hfill (29)

Although this mechanism is deduced from experimental results obtained with zinc-amalgam electrode, it supports the earlier

\[
\begin{array}{|c|c|c|}
\hline
\text{Equilibrium} & \text{Log K} & \text{Ionic strength} \\
\hline
\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{ZnOH}^+ & 5 & 0 \\
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2^- & 8.3 & 3 \\
\text{Zn}^{2+} + 3\text{OH}^- \rightarrow \text{Zn(OH)}_3^{2−} & 13.7 & 3 \\
\text{Zn}^{2+} + 4\text{OH}^- \rightarrow \text{Zn(OH)}_4^{3−} & 18 & 3 \\
\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{ZnOH}^{2+} & 5.5 & 1 \\
\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn(OH)}_2\text{O} & 30.5 (±0.4) & / \\
\text{Zn}^{2+} + \text{OH}^- \rightarrow \text{Zn(OH)}_2\text{O}_2 & 17 & 2 \\
\text{Zn}^{2+} + 2\text{OH}^- \rightarrow \text{Zn(OH)}_2\text{O} & 16.8 & / \\
\text{Zn}^{2+} + \text{H}_2\text{O} + \text{OH}^- \rightarrow \text{Zn(OH)}_2\text{O} & −11.2 & / \\
\hline
\end{array}
\]
3.5.3. Zinc deposition and morphology control

The morphology of zinc deposits is closely related to the quality of regenerated zinc product. Hence, its control plays a vital role, affecting significantly the performance of the ZAFC system upon zinc regeneration and during re-use. Ideally, the regenerated zinc deposit should be granular. A long-lasting challenge encountered by the rechargeable ZAFCs consists in the formation of non-granular forms of zinc deposit during charging reactions, i.e., those commonly termed as “dendrites”. Hence, studies on the morphology control of zinc deposited from zincate electrolyte, which have been carried out for decades, are still of high importance for the battery/fuel cell field [31,76,88–91].

Detailed information on the kinetics of early-stage zinc deposition can be acquired from the derivation of electro-crystallization equations established on current-time transient curves easily measured experimentally using a potentiostat and a traditional three-electrode cell containing zincate electrolyte with different concentrations. The equations cover two restraining modes for instantaneous and progressive nucleation [100]. A model for the electro-crystallization kinetics of zinc deposition that involves an autocatalytic step expressed by the reaction: $\text{Zn}^{2+} + \text{Zn}^{2+} + 2\text{e}^- \rightarrow 2\text{Zn}^{0}$ in its reaction scheme was also proposed, being in good agreement with experimental current-potential polarization and impedance results [102–104]. It is clear that the presence of such an autocatalytic reaction step and the interaction of its product, i.e., the intermediate zinc complex ion, with hydrogen and anions such as $\text{OH}^-$ can lead to multiple steady states of zinc ion thus resulting in instabilities and continuous oscillations of the system. Using this autocatalysis step and interactions between hydrogen and zinc (both cations and anions), the oscillation of the zinc electrode potential observed during zinc deposition at high current densities could be partially explained [76,103,105]. The oscillation was further proved to be caused by a local transient alternating depletion of such electroactive species as zinc and zinc hydroxide ions at the electrode/electrolyte interface. As a result, the concentration-overpotential generated by these electroactive species triggers hydrogen evolution and stirs the electrolyte, thus replenishing the local concentration of electroactive zinc species and leading to a periodic over-potential oscillation [106–108].

The values of reaction order in the linear Tafel and the other over-potential regions were determined by Dirkse [109–111]. The concentrations of $\text{Zn}^{2+}$ and $\text{OH}^-$ were shown to affect the values of the Tafel slope while the changes in ionic strength have little effect in its linear region. However, in other over-potential regions, solutions with different ionic strength (attributed to different concentrations) were found to demonstrate inconsistent polarization results [109–111]. The values of exchange-current density measured by several reputable groups were found to scatter over a range of three orders of magnitude, which was presumably assigned to the consecutive shape change of the zinc electrode during zinc deposition [19]. A study using electrochemical impedance spectroscopy combined with steady-state polarization measurements revealed that the Faradic relaxation processes of zinc deposition not only proceeded via a series of reduction reactions of zinc ions but also involved reactions with the four above mentioned adsorbents occurring in parallel paths [28].

There are three ranges of KOH electrolyte concentration (3–6 M, 7–10 M, and 10–14 M) in which the relationships among the over-potential, electrode activation and deposition rate are remarkably different [28,31]. The effect of OH$^-$ ions is also important for zinc deposition because the convection between zincate ions and OH$^-$ during the zinc deposition exists, as pointed out by Bockris et al. [88]. However, the effect is hard to elucidate as it is closely related to all the complexity of zincate species in the solution, its kinetics and diffusion. Electrochemical Impedance Spectroscopy (EIS) analysis performed in magnetic field by Devos and collaborators demonstrated that the differentiation of OH$^-$ diffusion from that of zincate species was possible, which also permitted to conclude that zinc deposition was governed by OH$^-$ [112].

The EIS results obtained by Cachet et al. showed that the steady state of zinc electrode was controlled by the presence of interfacial layers whose geometric properties and conductivity depended upon the electrode polarization [76]. There exists an oxide-containing layer at electrode surface whose ionic and electronic conducting performances are potential activated. The discharge of zincate ions is controlled by ion diffusion through this porous layer [76]. The existence of this layered structure was also confirmed by means of in-situ Raman spectroscopy [113]. Rogers and Taylor used a rotating disk electrode, aiming at separating the reaction from other related electrochemical processes and from hydrogen evolution, and showed that it is always controlled by mass transport [114]. This implies that the formation of dendrite deposits is in the nature of the element [114]. In contrast, hydrogen evolution was found to be very strongly dependent on over-potentials or current densities provided by the deposition system [114]. At low current densities, long dendrites start to grow preferentially along not one but two facets of zinc deposit tip and then amplify the growth differences at the two facets when the long dendrites grow further, eventually result in function failure of the cell. At high current densities, short dendrites grow only on one developed facet of zinc deposit tip due to the dominance of nucleation over growth. Hydrogen evolution may affect positively through stirring, leading to neither dense nor long deposits of zinc dendrites [114]. The over-potential of hydrogen evolution on zinc electrode was measured, and corresponding calculation formulas were established [115].

The water activity in the electrolyte is also a key parameter to obtain accurate enough results. It should be noted that the solution chemistry of zincate species is rather complex [53], which brings more challenges in getting correct values of activity, and therefore manipulating concentrations during deposition in such solutions is rather hard. Still, all information necessary for finding functional relationships between the alkaline electrolyte concentration, ZnO solubility, electrode potential, solution conductivity and the limiting current of zinc electrode is presented in Fig. 10. The electrode potential decreases with increasing KOH concentration. By contrast, the solution conductivity and the reaction kinetics (in terms of exchange current) increase with KOH concentration up to about 30% and then decrease at higher concentrations. Therefore, to get a good conductivity and kinetic behavior of the reaction, the best KOH concentration range is between 20 and 40%. ZnO solubility increases with increase in KOH concentration up to 30%, leading to the formation of supersaturated electrolyte, then decreases at KOH concentrations between 30 and 50% (Fig. 10). The rate of hydrogen evolution in zincate solutions was studied at different current densities ranging from 20 to 500 A/m$^2$ and at different zincate concentrations [116]. The results permitted to conclude that: (i) the type of the electrode (materials, binders and additives) determines the hydrogen evolution rate; (ii) the hydrogen evolution mainly results from zinc electrode corrosion,
(iii) the hydrogen evolution rate is higher at higher current densities or at lower KOH (or zinicate) concentrations [116]. Further studies based on the gasometric method [30] showed that increasing ZnO content in zinicate solutions significantly lowered the hydrogen evolution rate.

In industry, dendrite formations with mossy and spongy morphologies have been regarded as an inherent challenge in zinc recovery, since zinc in this form will decrease power efficiency when reused in the power-generation compartment of the fuel cell or battery system. While some efforts were made on using different additives and electrode substrates to improve the situation, kinetic studies were also undertaken aiming at better understanding and control of deposition processes. The morphology of Zn deposits is known to depend on over-potential during deposition, as well as on current density, electrode substrate, and electrolyte chemistry. Up to date, four major types of zinc deposits have been reported and described in the literature: (i) dendrite, (ii) mossy, (iii) spongy and layer-like mixed with boulder, and (iv) filamentous forms (Fig. 6) [34,117,118].

The effect of over-potential on the deposit morphology is generally known. Mossy forms, layer mixed with boulder forms and dendrite forms are deposited respectively at low, medium and high over-potential values. Although there are no clear criteria for defining the over-potential ranges, the equilibrium potential of zinc electrode should depend primarily on the potential of Zn/Zn (OH)₂ and subsequently the OH⁻ contribution to the potential composition [119]. In their classic work using freshly deposited zinc as both working and reference electrodes, Diggle et al. [34] reported that the critical potential for dendrite initiation was between −75 and −85 mV versus pure Zn (in this case, the freshly deposited zinc is used as the reference electrode). Positively below this critical over-potential, e.g., at −50 mV vs. Zn, spongy morphology was formed, while negatively above it, between −85 and −160 mV vs. Zn, dendrite mixed with spongy or dendrite forms were obtained [34]. A valid model for dendrite-crystal growth over time at different over-potential and current density values, solution concentrations, and temperatures was proposed by the same researchers [34]. The dendrite initiation and growth were shown to be controlled by mass transport and activation, respectively [34]. However, a more recent report suggested again that the dendrite growth might be controlled by mass transfer [118]. In addition, direct development of dendrite forms from the electrode surface rather than from the tips of precedent nuclei was also observed. It has never been found that a dendrite initiated at the top of a pyramid of nucleus. The imaging evidence does not support the dendrite initiation and growth model of Bockris et al. [120]. Moshtev and Zlatilova demonstrated that it was the over-potential rather than the current density to be the critical variable for deposited forms [121]. It should be mentioned that the critical over-potential value for zinc dendrite growth was found to be −173 mV when pure zinc was used as the reference electrode in zinc deposition [122].

The use of zinc electrodes with different crystallinity and orientations at varied current densities permitted to conclude that spongy dendrites formed at high current densities (100 mA/cm² and above), layers mixed with granules grew at moderate current densities (between 4 and 20 mA/cm²), and mossy morphology appeared at low current densities (less than 4 mA/cm²) [117]. It was also found that, compared with polycrystalline zinc substrates, the use of single-crystal substrates resulted in lower (up to 2 orders of magnitude) nucleation densities of dendrites observed at initial stages of growth, while later on, the dendrite density was observed to be identical (10⁸/cm²) on all electrodes used irrespective of their crystallinity and orientation [117]. Therefore, the effect of electrode substrate has to be seriously considered for the morphology control of zinc deposit. Dendrite deposition was investigated on glassy carbon [42], carbon [123], porous carbon foam [32], Ni [124], zinc powder [26], aluminum [38], Cu, Au, Cd, Pb, Ti, Sn, In [40,41], Al-Si [39], Ag [125,126] and steel [36]. Lead and cadmium substrates were also reported as those facilitating dramatically zinc dendrite formation [40,41]. The effect of different factors, such as electrode surface preparation, grit size of sandpaper during polishing, electrolyte impurities and so on, on the morphology of zinc deposited on different high-purity zinc electrodes was categorized and well-documented in the report of Wang et al. [118].

The solution chemistry and electrolyte composition were demonstrated to have a decisive effect on the dendrite formation [127–132]. Among other factors, probably one of the most long-lasting and not-fully-understood yet is the role of ZnO and its reduction mechanisms, since it is a thermodynamically stable compound that tends to precipitate from concentrated zinicate solutions [54]. As such, ZnO can be used as an additive to change the electrode surface structure and subsequently modify the morphology of zinc deposit (see Section 3.4 above). Two distinct mechanisms explaining the influence of ZnO on zinc deposit morphology were proposed: the dissolution-precipitation [133–135] and the direct solid-state reduction [136]. A way to trace the activity of ZnO by measuring the potential of Zn/ZnO versus HgO/Hg was proposed and developed by Sharma [29]. A later study conducted by Debiemme-Chouvy et al. [24,25] proposed a new insight on the understanding of ZnO forms existing in solution. The presented conclusions may stimulate new ideas and approaches to find a fully satisfactory solution for this issue in the future.

The observations reported by different groups over years suggest that the dendrite growth occurs under the diffusion-limited current conditions, and it is the growth rate rather than the nucleation rate that is the controlling factor, although the nucleus dimension (1D, 2D or 3D) may also affect the morphology when zinc deposition is carried out via tuning the over-potential [137,138]. Different approaches were tested to control the morphology of zinc deposits, among which: restricting the charging current density below the limiting current density, adjusting the over-potential range, and employing half-wave or square-wave potential pulsing [137,138]. Nonetheless, substantial progress in understanding the above phenomena was achieved by now, permitting to conclude that if the diffusion-depleted layer close to the electrode surface could be minimized, or even prevented from forming via some hydrodynamic-control means such as stirring, the morphology of zinc deposit would be more or less under control. Using rotating-disc electrode might be a good approach for this, while at industrial scale, controlling the electrolyte flow rate might be attractive. By studying a wide range of Reynolds’s numbers (from 0 to 14,000) coupled with different
current densities (2–1600 mA/cm²) in a short period of time (1–3 min). Naybour reported on the morphology control over zinc deposits and proposed a formation phase diagram for dendrite, bulbous and flat zinc deposits [137].

4. Latest progress in zinc regeneration

Finding how to effectively control and remove the dendrites of zinc deposit has been a constant industrial demand since the 1960s. It was concluded that smooth zinc deposits cannot be obtained from alkaline zincate solution at constant over-potential or current rate [34,139], which implies that conventionally used constant current or potential does not allow for zinc deposits with smooth surfaces. More recent work demonstrated that using pulsing over-potentials with square-shaped profiles led to a reduced fraction of dendrites in deposits [35,140]. Ultrasonic agitation was found to increase remarkably the cathodic current efficiency [141], suggesting that it could also reduce the formation of dendrite forms. In recent years, organic electrochemical industry is regarded as very innovative, green and rapidly developing, which in part is because many organic products are obtained through the reduction or oxidation of organic compounds via electron transfer on electrodes. However, the drawback is that products can only be obtained on one electrode while energy has to be wasted on the other. Wen et al. hybridized the electrochemical propanol oxidation system with a traditional ZAFC and used cadmium-coated nickel plate as the electrode substrate, which permitted to restrict considerably both the dendrite growth and hydrogen evolution [142].

Chiba et al. proposed to use magnetic field, reporting on remarkably inhibited dendrite growth in highly-concentrated alkaline electrolytes [143]. The suppression effect was found to be more pronounced at magnetic flux density above 0.11T, leading to an increase in cathodic efficiency as high as 5–10% [143]. Devos et al. also used magnetic field to improve the quality of zinc deposit. Their results also confirmed that dendrite appearance can be ameliorated by performing the deposition in a magnetic field [112]. Modeling zinc deposition from zincate solution has constantly encountered a number of challenges. An illustrative model for the equilibrium behavior of ZnO in alkaline zincate solution was proposed by Kriengsman and Cheh [144], whose results may be useful for the control of ZnO content in zincate electrolytes. Another significant progress was made by Wang and coworkers [145] who established a 3D model via a three-dimensional-kinetics-Monte-Carlo method to analyze the mechanism of shape change and morphology control in zinc regeneration. Combining some findings obtained in their experiments designed to complement their simulation results, they concluded that the morphological evolution is a function of the flowing electrolyte, surface roughness, electrode structure and charging current. The uniform morphology of deposited zinc can be attained via the manipulations of low current, pulsating current or hydrodynamic electrolyte. To achieve a granular morphology, an electrode with discrete columnar structure, in conjunction with high current and electrolyte flowing, has to be applied [145]. In light of new operation system for zinc regeneration, following the original work of Jirinc and coworkers [146], a unique system with a spouted-bed electro-plating regenerator and a pin-array patterned cathode was designed [147]. This system permits to conduct zinc deposition at a high current density, so that the regenerated zinc particles could reach a desired size of 0.5 mm (Fig. 11) [147]. A DOE-funded company, Fluidic Energy, focuses on developing metal–air batteries that rely on ionic liquids as electrolytes instead of aqueous solution.

While the alkaline–polymer based technology is still in its infancy, using ionic liquid to replace alkaline electrolyte may bring a new breakthrough in developing ZAFCs with compact size. ReVolt introduced a concept of new cell design for flow-zinc/air battery [148]. The design exploits a closed circuit in which zinc suspended in KOH is pumped from a storage tank to pass the tubular electrodes, while the diffusion electrode is bi-functionally constructed so that oxygen can be either absorbed or released. This structure offers a number of advantages, one of which being the possibility to charge the ZAFC either electrically or via refueling [148]. More recently, a novel electrochemical cell constructed with three distinctive sections for energy absorption, storage and delivery has been developed [149]. In this system, energy absorbed in metal zinc through electro-deposition in the top section is then delivered through zinc dissolution in the bottom section, while metal zinc is contained in the middle section between the sections for deposition and dissolution. This leads to simultaneous zinc deposition and dissolution occurring in separate spaces, thus allowing for independent charging and discharging processes [149]. This dual-power-cell prototype could be a good basis for further innovative designs of electrochemically rechargeable ZAFCs in the future.

To mitigate the situation of the historically poor electrochemical rechargeability of zinc in alkaline electrolyte, quite lately, two attempts were made towards electrode design [150] and new electrolyte development [151], showing promise in the Zn-Ni battery system. Following the prevailing trend and focusing on incorporation of additives into the electrode structure for enhancing the cycle life of zinc-based batteries, a 3D sponge-like architectured electrode was designed and then tested in both additive-free and additive-added alkaline electrolytes. The sponge-structured electrode was made by mixing zinc powder with trace amounts of In and Bi (to suppress H₂ evolution), then emulsified in carboxymethyl-cellulose and sodium dodecyl sulfate, and finally heat-treated. This not only resulted in a long-range conductivity in the 3D metal framework (which was maintained throughout charge-discharge even to deep theoretical depth-of-discharge at zinc, DOD₂₋), but also allowed the 3D-interconnected pores to attain the confined volume effect. The approach has led to modest success, though long-cycle-life tests are still needed [150]. The results have demonstrated no dendrite formation, also indicating that adding electrolyte and electrode additives in the battery cell is indispensable to retain effectively the cycled sponge structure in its pre-cycled condition [150].

In Japanese society related to battery-manufacturing there is a consensus that the dissolution of zinc electrode and formation of zincate is a continuous process which never stops until the electrode surface is fully covered by ZnO. Such a degradation of
zinc electrode is primarily assigned to the soluble nature of zincate ions, especially Zn(OH)₄²⁻, which form prior to ZnO [151]. Therefore, Nakata and coworkers suggested that reducing the electrolyte water activity would suppress the solubility of zincate anions, storing active-zinc in the vicinity of the electrode, and thus helping preserve the initial electrode morphology and enhance the system rechargeability [151]. For this purpose, propylene carbonate (PC), an organic solvent commonly used in the early stage of lithium-ion battery development, was added into KOH to prepare a mixed electrolyte [151]. The results demonstrated that when using highly-concentrated PC (up to 1.8 M), no dendrite formation was observed after as many as 500 charge-discharge cycles, and the morphology of zinc electrode remained close to its initial electrochemical state [151].

Two general reviews on ZAFCs [152,153], as well as three reviews focused on materials [154], oxygen catalysis [3] and electrolytes [4] related to ZAFCs, were published very recently. Although the development of electrochemically rechargeable ZAFCs is not much discussed in the above reports, the reviews suggest the following directions for the future research: (i) The continuous development of the new-typed cycle-able zinc electrode composed by a mixture of zinc, ceramic electronic conductor and polymer binder. This new electrode should allow for uniform zinc deposition on charge and keep the longevity of the electrode up to 1500 cycles without degradation and changes in electrode shape. (ii) Searching for the optimal recipes for the currently used additives and finding novel metal oxides and organic compounds as additives to the electrolyte seem to be of

---

**Table 2**

<table>
<thead>
<tr>
<th>Patent Number</th>
<th>Patent Title and Approved Year</th>
<th>Brief Comments</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>US 20150056524 A1</td>
<td>Electrochemical system for storing electricity in metals (2015)</td>
<td>An electrochemical system for storing electrical energy in metallic material comprises a charging assembly with one or more cathode and anode couples for metal deposition.</td>
<td>e-Zn [Canada]</td>
</tr>
<tr>
<td>US 20140162145 A1</td>
<td>Operating a metal-air battery (2014)</td>
<td>Methods for operating open electrochemical cells are disclosed.</td>
<td>Battelle Memorial Institute [USA]</td>
</tr>
<tr>
<td>US20140266055 A1, WO2014160087 A2, WO2014160087 A3</td>
<td>Hetero-ionic aromatic additives for electrochemical cells comprising a metal fuel (2014)</td>
<td>An ioni-conductive medium is used for communicating the electrodes. The medium comprises hetero-ionic aromatic additives.</td>
<td>Fluidic, Inc. [USA]</td>
</tr>
<tr>
<td>US 8877391 B2, CN102844932 A, EP2537205A1, EP2537205B1, US20110200893, WO201103142 A1, WO201103142 A8</td>
<td>Electrochemical cell, and particularly a cell with electrodeposited fuel (2014)</td>
<td>The present invention relates to an electrochemical cell for generating electrical power that includes an anode, a cathode, a charging electrode and an ioni-conductive medium containing at least metal fuel ions and poly (ethylene glycol) tetrahydrofurfuryl. It also relates to a method for charging the cell by electrodeposition of metal fuel on the anode thereof.</td>
<td>Fluidic, Inc. [USA]</td>
</tr>
<tr>
<td>KR20120104709</td>
<td>Manufacturing method for zinc-air battery anode using zinc with high-specific surface area by electrolysis in zinc oxide (2012).</td>
<td>Regeneration of zinc with large surface area from zinc oxide.</td>
<td>Hyundai Heavy Industry, and UNIST Academy Industry Research [South Korea]</td>
</tr>
<tr>
<td>CN102270777</td>
<td>Method for recovering and electrolyzing zinc electrode of insert-block-type zinc air battery (2010).</td>
<td>Restoration method for zinc oxide from ZAFC.</td>
<td>Beijing Zhonghang Changli Energy Technology [China]</td>
</tr>
<tr>
<td>TW201121134</td>
<td>Reduction method for ZnO of zinc air fuel cell (2009).</td>
<td>A reduction method for ZnO from ZAFC. The recycled ZnO is fed into a solar reactor and then reduced into gaseous zinc by using CO as reductant. Electrolyte treatment method for increasing the solution capacity using calcium hydroxide.</td>
<td>University of Science and Technology [Taiwan]</td>
</tr>
<tr>
<td>US20040053132</td>
<td>Improved fuel for zinc-based fuel cell and regeneration of (2004)</td>
<td>Improved fuel compositions have improved flow properties for use in ZAFC systems. Due to the presence of a non-zinc metal and other additives, the improved regeneration solution can be used to generate an improved fuel, zinc.</td>
<td>Metallic Power [USA]</td>
</tr>
<tr>
<td>ZA200204013</td>
<td>Method and device for regenerating zinc electrodes (2002).</td>
<td>The invention relates to a method for regenerating zinc. ZnO is introduced into an electrolyte received in a dissolving chamber to produce zinc ions, then at least partially converted into zincate ions. The electrolyte containing the zincate ions dissolved therein is then supplied to a reactor vessel and the zincate ions in the reactor vessel are at least partially electrolytically converted into zinc.</td>
<td>Gartner Rolf Zoxy Energy Systems [South Africa]</td>
</tr>
<tr>
<td>WO200210877</td>
<td>System of and method for power management (2002)</td>
<td>System and method for power management are provided for monitoring and controlling a regenerative fuel cell, allowing electricity generated by the regenerative fuel cell to power at least one powered device.</td>
<td>Teck Metals [Canada]</td>
</tr>
<tr>
<td>WO9635830</td>
<td>Production of zinc fuel pellets (1996)</td>
<td>Zinc in a spent Zn-alkali slurry of zinc-air batteries is produced in the form of pellet on a non-zinc-adherent cathode for reuse in the zinc-air batteries.</td>
<td>Lawrence Livermore National Lab, and US Department of Energy [USA]</td>
</tr>
</tbody>
</table>
high importance. (iii) Using the hybrid electrolyte, i.e., a mixture of a traditional aqueous alkaline solution and new organic electrolyte candidates may be very promising. (iv) The design of new chargeable ZAFCs systems employing elements of already well-developed architectures of other zinc-related battery systems such as redox-flow batteries [155].

Apart from the above, it should be added that the importance of hydrodynamic control in zinc deposition/regeneration has not been fully realized yet, although it certainly plays a vital role in increasing the deposition efficiency and controlling the morphology of zinc deposit. A profound understanding of its role in zinc morphology control may need new attempts in both academia and industry-oriented research.

There is no doubt that the majority of the recent advances related to the development of rechargeable ZAFCs comes from the various companies and are reflected in their numerous patents, most representative of which being shown and summarized in Table 2 with a brief explanation.

5. Concluding remarks

The combination of a number of attractive characteristics, such as, high energy density (associated with high electrochemical performance), low costs of components, inherent safety and environmental benignity, draws a lot of attention to zinc-air fuel cells as a novel class of power sources, which may have the shortest path required to catch up for energy-storage devices. Based on the progress achieved during several past decades, zinc-air power systems have been proved to be promising and become an irresistibly outdoing choice. However, there are three major challenges faced by researchers and engineers on the way of the realization of commercially affordable rechargeable zinc-air products: (i) the sluggish oxygen reduction reaction which needs developing a new dually-functional catalyst; (ii) the capacity loss assigned to the migration of Zn(II) ions from anode to cathode for which new separators or gas diffusion layers with optimized pore sizes are demanded; and (iii) the morphology control of zinc deposit regenerated from the spent alkaline electrolyte. In this review, we have made an effort to provide a reasonable coverage of the progress recently achieved in zinc regeneration as related to the fields of zinc-air fuel cells.

While the rechargeable zinc-air fuel cell system appears to be a very promising candidate as a future power source, a number of scientific and technological issues need to be resolved before the extensive application of such fuel cells on a large scale can be realized. Of the highest priority in this context are: (i) better understanding of the formation mechanisms of zinc deposits and the correlation between the deposition product and its electrochemical performance; (ii) screening of industrially applicable electrode materials; (iii) unraveling of the kinetics of electrochemical deposition and reaction mechanisms in presence/absence of additives; (iv) understanding of the chemistry of alkaline electrolyte with and without additives; (v) realization of a simple but highly-effective engineering approach to the design of the electrochemical cell for zinc regeneration; and (vi) the development of simple computational models allowing for adjusting the electrolyte, accounting for additives and concentration control, fine-tuning of over-potential for the hydrogen and oxygen evolution improvements.

In addition to complex and complete fundamental studies in all related fields, it is also important to develop highly-efficient, inexpensive, and environment-friendly electrode materials that promote zinc deposition in desired forms (e.g., granular form), while also providing high energy efficiency for fuel cells and lowest possible hydrogen and oxygen evolution. Thus far, there are only three materials, Pt, Au and carbon, which have been proved to be inert, durable and reliable as electrodes. It is therefore of critical importance to find new materials for new-generation electrodes with improved performance. For this, all possible means, combining both experimental approaches (conventionally used in solid state physics, physical chemistry, surface science, and materials science) and theoretical approaches (such as estimation of chemical/electrochemical potential changes or accurate estimation of new “electrochemical phase diagrams”, or so-called the Pourbaix diagrams) should be widely applied. New stainless steel and Ni-based alloys might be attractive as durable candidates with catalytic properties which are already used in plating or fuel-cell industry. Zinc alloys or other materials with coatings capable of suppressing hydrogen evolution and dendrite formation are another choice worth considering and developing.

Although using alkaline polymers can lead to the replacement of liquid electrolytes with solid electrolyzers, currently the development of solid alkaline polymer electrolyzers is still in its infancy. The use of ionic solutions or gels is believed to widen the flexibility and application of ZAFCs, but such a cell system suffers from having a low power density and low energy efficiency. The directions for future research activities on electrolyte chemistry might, predictably, focus on: (i) better understanding of zincate species (their forms occurring in saturated and supersaturated alkaline solution and in the zinc metal deposition mechanisms involved); (ii) ZnO solubility limits in alkaline electrolytes with and without various additives; and (iii) more detailed knowledge on the reduction mechanisms of ZnO in alkaline media.

The utilization of in-situ electrochemical scanning tunneling microscopy, in a combination with electrochemical atomic force microscopy, is seen as a potentially very powerful means for understanding deeper the formation mechanisms of zinc dendrites during deposition. In turn, this may help in developing new-generation electrodes and additives that minimize the deposition of dendrite zinc. Finally, the potential of rationally designed structure of both the cell itself and its electrodes, taking into account all knowledge on reaction kinetics in the system and optimizing its performance, still needs to be realized. Thus far, many aspects of such optimal designs have not been openly available in the literature, even though they may contribute significantly, or even boost the progress of rechargeable Zn-air systems. Very recently, significant progress was achieved in developing redox flow batteries. The concepts and technology used in such flow-battery cells and their electrode design can also be considered as important references when working on zinc regeneration for ZAFCs.

At the current state of technology, only up to 1000 cycles with energy efficiency as much as 40–50% can be achieved with on-trial designs of rechargeable Zn-air fuel cells. However, to achieve a breakthrough, new technologies in the following four aspects: (i) decoupling engineering of loading from unloading, (ii) adequate integration and optimization applied in cell design along with functioning water management, (iii) transferring successful concepts and techniques developed in other zinc-related batteries, such as zinc-flow battery, to zinc regeneration in rechargeable ZAFCs, (iv) suppressing the carbonate formation, and (v) increasing the cycle stability, require highly pursued for developing the rechargeable Zn-air fuel cells.

Indisputably, the realization of the rechargeable zinc-air fuel cells will require new research efforts in multiple disciplines to address the tough challenges which both scientists and engineers are facing now. However, both the theoretical and industrial platforms for further advances in the field are already provided, while commercial demands keep fueling and stimulating any breakthroughs in this direction.