



## An overview of progress in electrolytes for secondary zinc-air batteries and other storage systems based on zinc



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### ABSTRACT

The revived interest and research on the development of novel energy storage systems with exceptional inherent safety, environmentally benign and low cost for integration in large scale electricity grid and electric vehicles is now driven by the global energy policies. Within various technical challenges yet to be resolved and despite extensive studies, the low cycle life of the zinc anode is still hindering the implementation of rechargeable zinc batteries at industrial scale. This review presents an extensive overview of electrolytes for rechargeable zinc batteries in relation to the anode issues which are closely affected by the electrolyte nature. Widely studied aqueous electrolytes, from alkaline to acidic pH, as well as non-aqueous systems including polymeric and room temperature ionic liquids are reported. References from early rechargeable Zn-air research to recent results on novel Zn hybrid systems have been analyzed. The ambition is to identify the challenges of the electrolyte system and to compile the proposed improvements and solutions. Ultimately, all the technologies based on zinc, including the more recently proposed novel zinc hybrid batteries combining the strong points of lithium-ion, redox-flow and metal-air systems, can benefit from this compilation in order to improve secondary zinc based batteries performance.

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## 1. Introduction

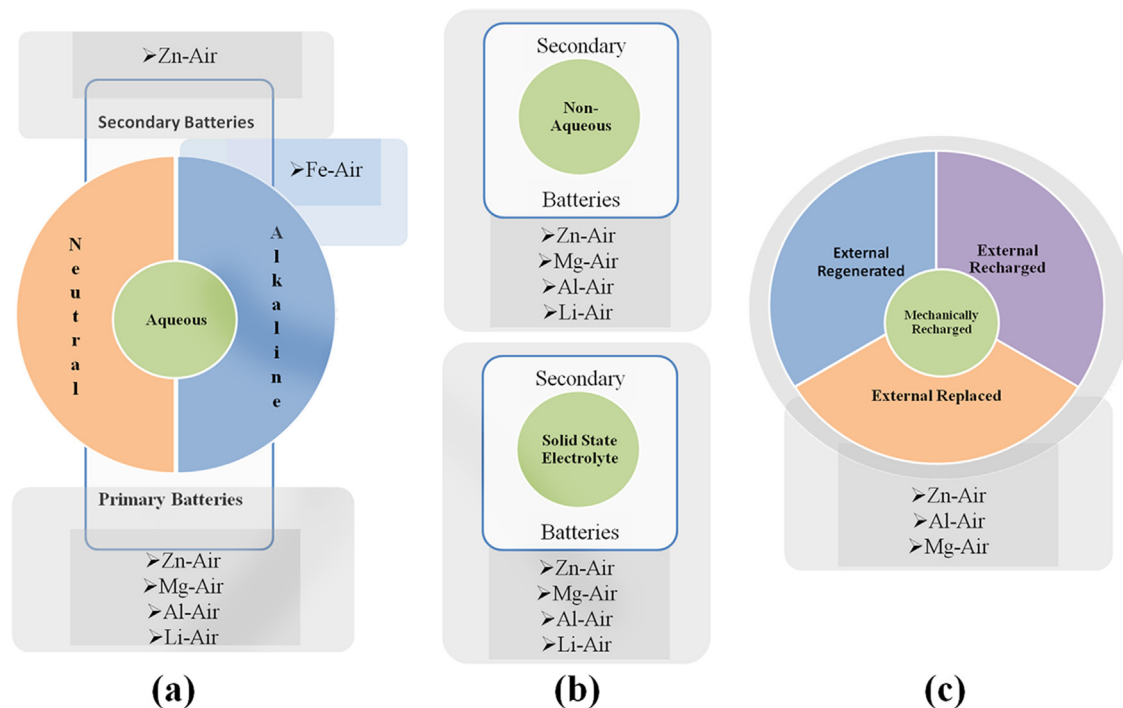
Nowadays, lithium-ion batteries are the most widely used secondary batteries for portable consumer electronics. However, its low theoretical energy density ( $100\text{--}200\text{ Wh kg}^{-1}$ ) is insufficient to meet the demands of large-scale applications [1]. The potentialities for high performance power sources demand a system which efficiently stores and/or generates more energy. In this context, the energy storage requires the development of sustainable, inexpensive, and high energy density electrochemical storage devices.

Batteries traditionally have not widely been used for large scale energy storage, they are mainly used for energy and power applications. Energy applications involve the storage system discharge over periods of hours with correspondingly long charging periods. Power applications involve comparatively short periods of discharge, short recharging periods and often require many cycles per day [2]. On the other hand, battery technologies can be distinguished in the way they store the energy; namely, static, flowing and fuel cells. The static cells store energy within the electrode structure and the electrolyte is static and it is hold into the cell, whereas redox flow batteries store the energy in the reduced and oxidized electroactive species in the electrolyte system which is recirculated through the cell [3–5]. There are various types of developed flow cells, namely (1) Redox flow battery (e.g. zinc-halide); (2) Hybrid flow battery, where one or more electroactive components deposited as a solid layer (e.g. zinc-bromide, zinc-cerium [6] or zinc ferro-ferricyanide [7]); and (3) Membrane-less flow battery, in which two liquids are pumped through a channel where the flow naturally separates the liquids, eliminating the need for a membrane (e.g. zinc-quinone [8]). Other

type of battery is the fuel cell. In this type the energy is stored in reactants external to the cell such as hydrogen, alcohol or even zinc-slurries (zinc-air fuel battery cell) [9–11].

Classical secondary batteries, such as lead-acid, nickel-cadmium or lithium-ion can be deployed for stationary energy storage applications. However, such current technologies cannot fully satisfy the requirements for this application in terms of e.g. performance, economic issues, environment regulations, etc. In this context, flow batteries become attractive as stationary storage device [10] (viz. aqueous zinc based flow batteries like zinc-bromide, zinc-cerium, nickel-zinc or zinc-air [12,13]) in spite of the high size and low energy density in comparison to other electrochemical devices. Unfortunately, insufficient consideration of redox flow battery design and engineering has limited their performance and hindered their scale-up resulting in restricted confidence in large-scale, long-term, low-maintenance operation [14].

On the other hand, among emerging battery technologies, metal-air batteries are being considered as preferable technologies with regards to energy density needs, while e.g. redox flow batteries are favorable with respect to power density requirements [15]. An advantage implementing metal-air batteries is the fact that the active material at the cathode is oxygen from the air which is abundant, free, and does not require a heavy casing (simple design provide significant cost advantages [16]) to keep it inside which increases the energy density of the system. This fact has supported an increasing interest of companies and researchers in developing further this technology as an energy storage system [17–25]. Furthermore, metal-air batteries offer a promising alternative because of their theoretical energy densities; typically flat discharge voltages; very long shelf lives (when properly



**Fig. 1.** Classification of metal-air batteries and electrolyte types used: (a) aqueous electrolytes (neutral and alkaline), (b) non-aqueous electrolytes, and (c) mechanically recharged.

sealed); minimal or no ecological problems; low cost; and capacity typically independent of load and temperature [26]. However, this emerging technology has its own limitations preventing it from having a significant impact; such is the case of being in long-term electrically rechargeable to become a sustainable and cost-effective solution when it is implemented.

The electrochemistry of the metal-air batteries is mainly related to the metal-anode. Several metals have been considered for the development of metal-air batteries (*viz.* Li; Ca; Mg; Al; Zn; Fe), and hence diverse nature and composition of the electrolyte system is needed for each individual technology in order to reach the required electrochemical reactions [26,27]. Fig. 1 illustrates the classification of the metal-air batteries according to the nature of their electrolyte and chargeability; *i.e.* primary (no rechargeable), secondary (electrically rechargeable) and mechanically recharged (based on the replacement of one component (metal-anode) by fresh one) [17,28].

Despite the fact that Li-air; Al-air and Mg-air cells have the highest theoretical energy densities (13.0; 8.1 and 6.8 kWh kg<sup>-1</sup>, respectively) Zn-air battery has received the attention because besides of having a higher theoretical energy density (1.3 kWh kg<sup>-1</sup>) compare to the current energy storage systems [29–31], zinc is abundant in nature, environmentally safe, and can be handled safely in oxygen and humid atmosphere. Mg-air and Al-air batteries are considered promising technologies, but in spite of that they are still in an early development stage due to several remaining scientific and technical challenges such as corrosion, cell irreversibility, low shelf life, etc. [28 and refs. therein]. Therefore, the scientific community has been mainly focused on Zn-air and Li-air technologies. Although both of them present challenges which limit their performance, nowadays these technologies are more viable than those based on Al-air or Mg-air [Ref. [32] and refs. therein]. However, the high cost and the potential safety issues associated with lithium, including thermal instability and reactive oxygen discharge products have become the main disadvantages of this technology [26,32] in comparison with Zn-air batteries. Unlike lithium metal, zinc has very low reactivity making it a great candidate for an environmentally safe product which can be handled safely in oxygen and humid conditions.

The secondary Zn-air battery by itself offers also other distinct advantages over the Li-air batteries. Firstly, zinc is a low cost metal that is readily available being the 24th most abundant element in the Earth's crust. Secondly, zinc is the most active metal that can be electrodeposited from an aqueous electrolyte making it highly favorable for secondary batteries [21,27,33–36]. In addition, the primary Zn-air battery is a mature technology besides to be among the metal-air batteries the most worldwide commercially available. This achievement provides a fundamental and technical basis for developing further this technology as a secondary system. These matters of facts make Zn-air technology economically more feasible than the other electrically rechargeable metal-air technologies [18,37,38]. However, as any emerging technology, achieving a rechargeable Zn-air battery is not exempted from challenges mainly due to the degradation of the electrodes during cycling, which might result in a rapid reduction in (storage) capacity.

It is well known that zinc has been a favorable anode material for electrochemical power sources since the invention of the battery more than 200 years ago [23]. Traditionally, secondary zinc-based energy storage systems have been developed employing aqueous alkaline electrolyte (*e.g.* rechargeable alkaline manganese (RAM) or Ni-Zn type batteries). The improvements and learnings related to the zinc electrode in these batteries can be used to progress towards electrically rechargeable aqueous alkaline Zn-air batteries because of the reaction at the zinc electrode are basically the same [39]. The zinc electrode and the electrolyte limitations are closely related because of zinc reactivity varies as a function of the electrolyte or in other words as a function of the solution's pH (*i.e.* aqueous alkaline, neutral, or acid as it can be seen in Table 1).

Consequently, for the traditionally aqueous alkaline electrolytes the principal problems are the high dissolution and corrosion of zinc [40 and Refs. cited therein]. The high dissolution of zinc results in the growth of dendrites which cause **cell shorting**, as well as electrode shape change (the migration of zinc) which causes gradual **capacity loss** due to the redistribution of active material, and, therefore, **curtails cycle life** [41]. On the other hand, the corrosion of zinc electrode is related to the Hydrogen Evolution Reaction (HER) on the surface of the zinc which **deteriorates the efficient utilization of the zinc**. All these phenomena occur during battery charging. Therefore, as it has been recognized, the commercialization of secondary Zn-air battery is still difficult due to the low charge/discharge cycle life of its both electrodes; zinc and the bi-functional air electrode (active towards both the oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER)). In contrast to the initial regenerative zinc-air fuel cell industrial prototypes where a zinc slurry was pumped through the cell [42], the current strategies invest their effort in developing robust electrical rechargeable zinc-electrodes and/or a stable bi-functional catalyst, which should decrease the over-potential at the cathode, and as a consequence will increase the coulomb efficiency beside to diminish the damage of the air electrode during charging (OER). In this sense, companies such as EnZinc (formal CarV3), EDF, EOS Energy Storage, ZAF Energy Systems, Fluidic Energy or start-ups like ZnR Batteries (EDF filial) have recently reported advances in designing and manufacturing commercial available zinc-based/air batteries.

Since the electrolyte governs the battery electrochemistry, a key feature to achieve the long cycle life of zinc-anode is the selection of the proper electrolyte system, and hence effectively improves its rechargeability. The approaches done in the state of the art to mitigate zinc-electrode major challenges have been mainly focused on the use of additives in the electrolyte and/or negative electrode itself [41,43]. However, recently, the scientific community is more interested in developing alternative electrolyte systems, such as **aqueous neutral** [44] or **non-aqueous electrolytes** [45], to minimize or skip the zinc-electrode problems associated to aqueous alkaline electrolytes [46].

As it is shown in Fig. 1, the electrolyte system can be divided according to its nature: aqueous (Fig. 1a; incl. neutral and alkaline) or non-aqueous (Fig. 1b; incl. organic and solid-state) [19,28]. Comparing both types, the advantages of aqueous electrolyte with regards to non-aqueous electrolytes include its non-flammability,

**Table 1**  
Examples of zinc-air reactions in different aqueous electrolytes at different pH.

Aqueous electrolyte	Reaction on zinc electrode	E <sup>0</sup> (V)	Reaction on air electrode	E <sup>0</sup> (V)
Alkaline	$\text{Zn} + 2\text{OH}^- \leftrightarrow \text{ZnO} + \text{H}_2\text{O} + 2\text{e}^-$	1.250	$\text{O}_2 + 2\text{H}_2\text{O} + 4\text{e}^- \leftrightarrow 4\text{OH}^-$	0.401
Neutral	$\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^-$	-0.762	$2\text{H}^+ + 1/2\text{O}_2 + 2\text{e}^- \leftrightarrow \text{H}_2\text{O}$	1.229
Acid	$\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^-$	-0.762	$\text{O}_2 + 4\text{H}^+ + 2\text{e}^- \leftrightarrow 2\text{H}_2\text{O}$	1.229

less toxicity, cheaper, higher ionic conductivity, their demand is simpler and their manufacturing environment is less stringent. However, for aqueous electrolyte system the principal issues which limit the battery's shelf life comprise the electrolyte evaporation, the ambient moisture uptake, the narrow electrochemical stability window and the low thermodynamic stability of the metal-anode [47–52]. In contrast, the principal advantage of organic electrolytes is the elimination of corrosion processes, but the air cathode electrode does not perform properly in aprotic organic electrolytes [48]. In spite of that non-aqueous zinc ion-conducting electrolytes might offer some advantages over current Zn-air batteries that use aqueous alkaline electrolytes [52].

It has been published interesting reviews dedicated to secondary zinc-air batteries [32,53–55] covering in general all the aspects (*meaning* anode; cathode; electrolyte; cell design; etc.) of this technology. However, more dedicated overview includes one exclusively about aqueous alkaline electrolytes [40] used in zinc-based batteries. In the same line with the latter, the current review pretends to go further and provide a synopsis of the progress done in the development of suitable aqueous and non-aqueous electrolytes for rechargeable zinc-based systems, especially for secondary zinc-air technology. To achieve this goal, this present overview will use the basic knowledge of the zinc electrochemistry as a function of the electrolyte pH as the vector to sum up and define the requirements of the zinc-based system. With that in mind, alternative electrolytes systems will be compared against the typically aqueous alkaline system used in primary zinc-air batteries, and hence provide a better understanding of those and the means to improve the performance of the emerging secondary zinc-air technology.

## 2. Aqueous electrolytes

Looking back to the basis given by the zinc's Pourbaix diagram, which is a representation of the reactions of zinc in aqueous solutions and equilibrium conditions (see Ref. [56] or Table 2.1 and Fig. 2.2 in Ref. [57]), it shows that Zn is thermodynamically unstable in water and aqueous solutions as well as it tends to dissolve with the evolution of hydrogen over the whole pH range. From this diagram it can be interpreted that no surface oxides of zinc are stable under acidic conditions, and thus under this conditions zinc has high solubility and dissolves with formation of  $Zn^{2+}$  ions. Nevertheless, oxide films may occur in the pH range of 3.8 to 5.8, but this oxide film is porous and not passivating [58]. However, since the solubility of zinc decreases with increasing pH in acidic solutions, under neutral or slightly alkaline conditions more stable Zn corrosion products are generated (like e.g. Zn(OH)<sub>2</sub>). In solutions with pH values higher than 9, zinc solubility rise again with pH, and hence in the high-pH-range zincate ions ( $Zn(OH)_4^{2-}$ ) formation is favored since zinc oxide and hydroxides tend to dissolve [40,56].

It should be note that Pourbaix diagram for zinc is well justifiable for those aqueous systems with the absence of chemical species with which Zn may form more soluble or insoluble compounds as it is the case in neutral or acidic electrolyte systems (e.g. chloride or ammonium based electrolytes like in Leclanché battery) [59].

Beyond those equilibrium conditions represented by Pourbaix diagram, one should also take into consideration the ion diffusion processes and the dynamic operating conditions (fast or slow charge/discharge cycling) to which the zinc-anode electrode is exposed. Such process may be governed by the applied current density (high or low) which affects the electrode kinetics and might also promote high over-potentials especially at the air-cathode (sluggish electrochemical kinetics). Such conditions provoke as well at the anode the well-known dendrite growth,

shape-change, Zn-corrosion (represented by evolution of hydrogen) or Zn-passivation.

Having that knowledge in mind, Zn-based-batteries researchers have investigated all kind of additive to modify the electrochemical respond of Zn [40,60], and hence mitigate its corrosion (in term of HER). Nevertheless, in spite of the achievements reached with the zinc electrode (and electrolyte), there remain challenges that may prevent its large scale commercialization. Among those challenges battery manufacturing is also one of high relevance. There highly clean processes are required to minimize any kind of impurity that catalyzes the self-discharge (corrosion) of the battery affecting its shelf life. Self-discharge can also be accelerated in partially discharge aqueous alkaline batteries. In this case, an excess of generated ZnO can catalyze the evolution of hydrogen as it has been pointed out by [61]. In the following, dedicated sections will further highlight the corrosion issues (in term of HER) in zinc-based batteries.

Since zinc's electrochemistry is different as function of the solution's pH, aqueous electrolytes are then classified accordingly in alkaline (*where*:  $Zn + 2OH^- \leftrightarrow ZnO + H_2O + 2e^-$ ), neutral (*where*:  $Zn \leftrightarrow Zn^{2+} + 2e^-$ ) and acid (*where*:  $Zn \leftrightarrow Zn^{2+} + 2e^-$ ). As it is well known, alkaline aqueous electrolytes are more widely used for secondary Zn-air batteries than acid or neutral electrolytes [62,63]. However, the use of zinc electrodes in secondary batteries has limitations with all electrolytes systems [64] because each system has its own advantages and disadvantages which would generally define the characteristics of the resultant Zn-based system.

It is worth to mention that manganese dioxide catalyst is one of the most used positive electrodes in zinc-based batteries regardless of the electrolyte. The reason is its versatility to work as catalyst for the oxidation and reduction of water (e.g. zinc-air system) or as host material for the insertion/disinsertion of zinc-ions or/and protons (e.g. zin-ion or zinc-hybrid systems). The latter is debatable since the 60's when A. Kozawa and J.F. Yeager [65] proposed that electrolytic manganese dioxide (EMD;  $\gamma$ -MnO<sub>2</sub>) undergoes reduction based on concerted electron-proton insertion into the host  $\gamma$ -MnO<sub>2</sub> structure. Latter A. Kozawa and R.A Powers [66] pointed out a sequential mechanism where initially electron-proton insertion occurs and then  $Zn^{2+}$  intercalation takes place. More recent publications confirm such consequent proton and Zn-ion insertion/extraction process in Zn/MnO<sub>2</sub> (Zn-ion) reversible batteries [67–77]. However, other publication highlights the critical role of the electrolyte pH over the intercalation of zinc-ions [78]. These discrepancies show how relevant is to understand the mechanisms that govern the reversibility in Zn-based battery systems and hence, to develop more suitable materials including appropriate electrolytes.

In the following the main characteristics of alkaline, neutral and acidic aqueous electrolyte system will be assessed.

### 2.1. Alkaline electrolytes

Traditionally, a battery having an alkaline electrolyte with a zinc anode has been desirable due to the inherent electrochemical reversibility and fast electrochemical kinetics (low overpotential) of the zinc; high ionic conductivity of the electrolyte; good performance at low temperature; high solubility of zinc salts; and the availability of rugged, compact, nontoxic, and long-lived positive electrodes (e.g., NiOOH and MnO<sub>2</sub>) [64,79].

The electrolytes most used in Zn-based batteries (e.g. RAM; Ni-Zn; or Zn-Air) have been alkaline aqueous solutions containing potassium hydroxide (KOH) [40,64,80–86], sodium hydroxide (NaOH) [87–89], and lithium hydroxide (LiOH) [52]. Nonetheless, among them, KOH has been the most extensively used due to the fast electrochemical kinetics and high solubility of zinc salts [64,80–86] besides the superior ionic conductivity given by K<sup>+</sup>

(73.50  $\Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) compared to  $\text{Na}^+$  (50.11  $\Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) or  $\text{Li}^+$  (38.7  $\Omega^{-1} \text{ cm}^2 \text{ equiv}^{-1}$ ) [19,64,90–94].

On the other hand, disadvantages correlate to the use of aqueous alkaline electrolytes include the dissolution of zinc (associated to intermediate species, zinc corrosion, shape changes, and dendrite growth), precipitation of insoluble carbonates, electrolyte evaporation or ambient moisture uptake, and hydrogen evolution. In the following, a brief summary of these unfavorable aspects related to the use of alkaline aqueous electrolyte will be given. However, for a more extensive description of those see ref. [40].

### 2.1.1. Detrimental phenomena in alkaline systems

**2.1.1.1. Dissolution of zinc.** The high solubility of zinc in strong alkaline media plays one of the most important roles in secondary zinc-air batteries. It causes the formation of saturated or supersaturated zincate solution ( $\text{Zn}(\text{OH})_4^{2-}$ ) which is strongly associated with dendrite formation and zinc shape-change process. In these negative situations, the system performance is reduced and, at worst, an internal short circuit could occur due to the excessive growth of dendrite. In that sense, it is necessary to control zincate diffusion within the bulk electrolyte and hence maintain a homogeneous deposition of zinc upon the electrode surface. This is one of the main challenges in the development of rechargeable zinc batteries [95–100].

Several assumptions about zinc dissolution mechanism have been discussed in the literature [89,97,98,101–118], however the most accepted one for alkaline electrolytes takes place in two steps: firstly the oxidation of zinc to zincate takes place (reaction (1)). Second, when the solution near the surface becomes saturated with the dissolved zinc species (*viz.*  $\text{Zn}(\text{OH})_4^{2-}$ ), precipitation of zinc oxide may occur according to reaction (2). Thus, in overall the Zn-dissolution is expressed according to reaction (3) as shown below.



In general, zinc dissolution-deposition process is known to occur mainly from  $\text{Zn}(\text{OH})_4^{2-}$ , but other zinc dissolved species have been identified [119,120–132]. In this process, the pH of the electrolyte has a considerable influence on the resulting intermediate zinc specie. In strong alkaline solutions (pH  $\geq$  13),  $\text{Zn}(\text{OH})_4^{2-}$  is the principal specie. In those electrolytes with a pH in the range of *e.g.* 9.3 to 12.3, intermediate species such as  $\text{Zn}(\text{OH})_y^{2-y}$  (*where* “*y*” varies from 0 to 4) are formed. Among the identified species,  $\text{Zn}(\text{OH})_3^-$  and  $\text{Zn}(\text{OH})_4^{2-}$  have been reported as being the predominant ones, although, only  $\text{Zn}(\text{OH})_4^{2-}$  appears to determine the electromotive force of the zinc electrode [101,133]. One must keep in mind that the type and concentration of zinc intermediate species is also influenced by other parameters besides pH such as the scan rate, zinc electrode position, and accessible water near the surface [48,64,90,95,97,102,119,134–140].

As it was pointed out, from the dissolution of zinc detrimental mechanism may take place during the re-deposition of zinc. Among them, passivation, dendrite formation and shape change are the most recognized ones. In the following they will be briefly outlined.

**Zinc passivation** is the formation of a layer which inactivates the metal surface. It occurs when the dissolution of the metal

causes an excess of the solubility of a solid zinc salt or hydroxide in the electrolyte near the electrode surface forming a compact solid film. The stability and continuity of this film determine the degree of passivation. The passivating film serves as a diffusion barrier to the  $\text{OH}^-$  ion, with the result that the discharge capacity and power capability of the zinc anode decrease [89,97,105,141–160].

In general terms, there are two types of zinc oxide layers. Type I which is proposed to be formed according to the dissolution-precipitation model. This Type I zinc oxide layer is usually porous, limiting the diffusion of  $\text{OH}^-$  to the metal surface and hence, depleting the concentration of  $\text{OH}^-$  at the interface electrode/electrolyte. The latter induces changes in the interfacial pH allowing the formation of a more compact/thick irreversible layer known as Type II zinc oxide. This type of zinc oxide may proceed *via* the nucleation and growth model [161] and/or *via* the adsorption model [161–164]. This compact ZnO layer passivates the zinc electrode, although, its formation can be partially controlled by means of adjusting the discharge cell cut-off voltage or the depth of discharge (DoD) [162,165].

It is also suggested that Type II zinc oxide can be formed directly by the combination of low  $\text{OH}^-$  concentration and electrolyte saturated by zincate ions. The formation mechanism of ZnO has been deep investigated on planar zinc surface [166–170]; however, Q. Horn et al. [171] extended such studies to commercial porous zinc-anode. The authors concluded that solution-precipitation mechanism is the main responsible of ZnO formation in porous electrodes. The morphology, size and spatial distribution are driven by the applied drain rate (current density), *i.e.* low rate promote uniform distribution of ZnO whereas high rate provokes segregation of ZnO near the current collector. J.-Y. Huot et al. [172] investigated by transient studies the electrochemical aspects of high-power discharge conditions limiting commercial alkaline primary cells. Among their findings, they identified from color pictures three type of zinc, namely gray-fresh zinc, blueish-discharged zinc (identified as ZnO by Raman spectroscopy), and white-very-discharged zinc. At high rate discharge (2 W) blueish color was found at the anode-separator interface, while gray (undischarged) was observed at the bulk of the anode-electrode. In contrast, when the rate discharge was lower (100 mW) the blueish color expanded but with a white-very-discharge layer formed within the bluish layer. The rest of the electrode keeps undischarged (gray color). A fully zinc utilization was achieved just at very low discharge power (10 mW). They also pointed out that increasing the discharge time will drive the discharge layers towards the current collector, while formation of ZnO near the separator could limit the cell life under increasing discharge rates.

Recently, J. Stamm et al. [162], modeled for a Zn-air primary battery the nucleation and growth of Zn oxide and its effect on Zn dissolution. They modeled a commercial Zn-air button cell and used it for experimentally validating their model. In the model they have taken into account the electrolyte diffusion, migration and convection as well as galvanostatic discharge and their effect on ZnO nucleation, crystallization, growth and passivation. They pointed out that the passivating nature of the discharge product is the responsible of the limited cell performance. They also model the kinetics of  $\text{CO}_2$  adsorption into the electrolyte and how it limits the cell lifetime.

On the other hand, the use of very concentrated alkaline solutions reduces zinc passivation due to the dissolution of the passivating film. However, this mitigation strategy induces shape-changes when solubility becomes too high. Another way to suppress the surface passivation is the use of an electrolyte with additives that modify the electrode surface and reduce the blocking effect of the passivating layer on the diffusion of the discharged zinc ions [63,153]. Additives such as silicate ( $\text{SiO}_3^{2-}$ ) have been studied in alkaline electrolytes [96,173,174]. The

mechanism for enhanced zinc solubility appears to be silicate adsorption on ZnO particles, which blocks further zinc precipitation [64,154]. Yang et al. [153] showed that the surfactant sodium dodecyl benzene sulfonate (SDBS) in an alkaline electrolyte can effectively depress the surface passivation and greatly improve the discharge capacity of the zinc anode, particularly in a diluted alkaline solution [63,175]. On the other hand, since passivation mainly occurs during high discharge (scan) rate, a slow discharge (scan) rate can also reduce zinc passivation because more time is allowed for the cathodic scan, which leads to the dissolution of a larger amount of the passive layer [97].

**Shape changes and dendrite growth:** the high solubility of zinc [176] manifests itself mainly as two failure mechanisms, namely (i) shape changes and (ii) unwanted zinc electrode morphologies such as dendrites [63,79,137,177]. Shape-change in alkaline zinc batteries is defined as the migration of zinc, usually from the top and sides of the electrode to the bottom, due to gravitational forces. This redistribution of active material results in an irreversible loss of capacity and triggers the formation of dendrites, which can easily penetrate into the separators and result in an internal short circuit [63,79,96,99,134,137,178–183]. There are five principal types of zinc deposits in an aqueous alkaline electrolyte under battery conditions: mossy, heavy spongy, layered, boulder, and dendrite [38,134,184–186].

Anode shape change and redistribution of zinc can be mitigated by the addition of special compounds that reduce or inhibit the dissolution of zinc in alkaline electrolytes [48,64,93,96,178,187–193]. Such compounds can be classified as chemicals that form insoluble complexes with zinc and those that lower the pH of the electrolyte [79,110,194]. For example, compounds containing fluoride (KF), borate ( $K_3BO_3$ ), phosphate ( $K_3PO_4$ ), arsenate ( $K_3AsO_4$ ), and carbonate ( $K_2CO_3$ ) can be used because they have been shown to exhibit reduced zinc species solubility. Another type of electrolyte could be a mixture of organic-inorganic electrolytes such as  $CH_3OH-KOH$  [64,96,181,195–197]. Surfactants are believed to be effective additives for alkaline zinc batteries because the introduction of small amounts affects the growth of zinc moss and dendrites through the control of electrode passivation [187,198–202].

**2.1.1.2. Precipitation of insoluble carbonates.** From the moment that an alkaline zinc-air battery is exposed to the air, the electrolyte gets in contact with the carbon dioxide ( $CO_2$ ), which reacts with the hydroxyl groups ( $OH^-$ ) producing carbonate/bicarbonate anions ( $HCO_3^-/CO_3^{2-}$ ) (reactions (4), (5)).



The carbonation process originates [19,26,63,91,203–209]:

1. Decline in the ionic conductivity because the mobility of  $HCO_3^-/CO_3^{2-}$  is lower than that of  $OH^-$ . However, this is not a fatal issue because the carbonated electrolyte is still conductive and even more than other electrolytes such as acidic ones.
2. Air electrode micropore blocking due to the low solubility of the carbonates impeding oxygen access with subsequent deterioration of the cathode performance.
3. An increase in electrolyte viscosity which complicates the oxygen diffusion into the electrolyte, resulting in a worse oxygen reduction reaction (ORR) of the bifunctional air electrode.

It is possible to achieve suitable cycle-life performance of the bifunctional air electrode by removing or reducing the amount of  $CO_2$  from the air by filters composed of  $CO_2$  absorbents via chemical and/or physical absorption [189,210,211]. Drillet et al. [212] used solid adsorbents based on physisorption and chemisorption processes ( $LiOH$  and  $LiOH-Ca(OH)_2$ ) to remove  $CO_2$  from a feed gas in alkaline zinc-air batteries [189,212,213]. Chen et al. [189] used a chemisorption process involving piperazine (PZ), 2-(2-aminoethylamino) ethanol (AEEA), and monoethanolamine (MEA). The success of these solvents is due to the high rate of reaction of the primary or secondary amine with carbon dioxide [189,214–217]. On the other hand, companies like ReVolt Technology describes the addition of ionic liquids and/or deep eutectic solvents to the aqueous alkaline electrolyte in order to mitigate the  $CO_2$  transport [218], while other compounds have been reported in the bibliography [48,189].

Alternative to abovementioned strategies to control the  $CO_2$  absorption by the alkaline electrolyte, some authors have suggested the incorporation of  $K_2CO_3$  to the electrolyte [219,220]. The idea of this approach is to reduce the kinetics of carbonate species formation as it was pointed out by Kucka et al. [221]. Following this approach, Schröder et al. [222] concluded that it is acceptable to add about 30 mol% potassium carbonate to high molar KOH electrolyte to extend the lifetime of the zinc air battery, although with the penalty of marginal battery performance loss.

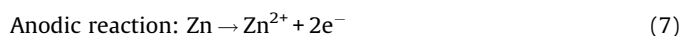
**2.1.1.3. Effect of water.** Electrolyte evaporation and ambient moisture uptake are another process responsible of the long-term fail of aqueous metal-air batteries. In environment with high relative humidity the accumulation of water might induce the flooding of the air electrode affecting the transport of oxygen to the catalyst active sites. Since oxygen cannot readily diffuse through water, this restriction causes losses in the electrochemical activity of the cathode. In addition, as the electrolyte becomes diluted, the ionic conductivity might reduce over the time inducing higher internal resistances. On the other hand, excessive water loss via e.g. evaporation increases the electrolyte concentration affecting negatively the discharge reaction [26].

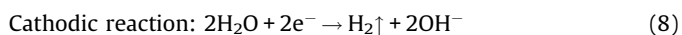
Taking into account the volume and composition of the electrolyte, the amount of zinc, and the gas diffusion degree, a suitable battery design might help to optimize the internal balance of water [26,63]. For example, ReVolt's approach to manage the water evaporation involved the modification of the electrolyte by polymerizing and hence the water was trapped into the electrolyte reducing the loss of humidity and/or modification of the electrode. A siloxane membrane was also used because of its beneficial protections against dry out and flooding. With this improvements implemented in the ReVolt's modified system, no weight loss was observed due to water evaporation after several thousand hours of testing [218].

**2.1.1.4. Hydrogen evolution.** The hydrogen evolution reaction (HER) at the anode-zinc-surface in counterpart to the water electrolysis at the cathode side results in an increase of internal pressure during the charging battery mode. This side reaction (HER) decreases the cycle life of a zinc-air battery generating hydrogen gas according to reaction (6) [19,64,106,223–226] and thus the capacity retention is directly affected over long-term due to corrosion of Zn anode.



Two simultaneous reactions (7), (8) occur at the zinc electrode surface during the corrosion process.





As it known, Zn corrosion is cathodic controlled, thus the cathodic hydrogen evolution rate limits the Zn corrosion rate. In this sense, the best way to mitigate the corrosion of zinc is then to slow down the rate of HER. K. Wippermann et al. [227] built in a Pourbaix diagram (Zn/H<sub>2</sub>O with Zn<sup>2+</sup> in the electrolyte and ZnO as solid product) the potential of the HER referring to a current density of  $-1 \text{ mA cm}^{-2}$ . Thus, a high cathodic over-potential for the HER is found when the pH becomes alkaline (e.g. higher than  $-1.6 \text{ V}_{\text{SHE}}$  at pH above 12). However, the authors have pointed out that hydrogen evolution is mainly important only in strongly acid solutions. When the pH increases becoming the electrolyte alkaline, oxygen reduction is the dominating cathodic corrosion reaction. Similar conclusions were presented by S. Thomas and co-workers [228]. In their studies of Zn corrosion as function of pH they concluded that in the pH range 1 to 4 the kinetics of HER dominates the overall corrosion rates. Nevertheless, in the pH range 4 to 11, the corrosion rate of Zn does not change significantly because of a change from HER to ORR in the cathodic reaction. Finally a protective Zn-oxide layer is formed when the local pH is between 11 and 12 and electrode potential about  $-1.15 \text{ V}_{\text{SCE}}$ . In the latter the Zn corrosion rate are minimum.

To retard HER, some additives can be incorporated in alkaline electrolytes [64], such as compounds containing lead, antimony, bismuth, cadmium, and gallium [48,229], whose use is limited due to their toxicity. In this context, organic compounds as surfactants are also proposed as alternative inhibiting compounds. Lee et al. [190] studied ZnO anodes in presence of phosphoric acid, tartaric acid, succinic acid, and citric acid as additives to alkaline solutions. These acids induced an increase in the hydrogen overpotential of the ZnO electrode because during cathodic polarization the surface of the zinc electrode is partially covered by absorbed molecules which block some of the active sites of the electrode surface. Lee et al. reported that while the highest number of polar groups is believed to resist dendrite formation, for reduced HER, the molecules with the least number of polar groups are highly effective. Fluorosurfactants have also been reported as additives that raise the hydrogen overpotential [199].

In accordance with reaction (9), some researchers have added ZnO into the alkaline electrolyte with the aim of reducing the activity of water and consequently the HER [105,110].



If water activity is reduced, then the reaction (9) will expected to proceed in the right side suppressing the solubility of zincate ions and promoting the formation of zinc active material (ZnO) in the vicinity of electrode surface preserving thus the electrode morphology and promoting cell rechargeability. On the other hand, reduction of the water activity would also restrict the HER during battery charging (reaction (8)).

## 2.2. Neutral electrolytes

Recently, the interest of scientific community is focusing on the development of secondary zinc-air battery based on aqueous neutral electrolytes [230,231]. Although the reported aqueous neutral composition for secondary zinc-air batteries is based on the well-known Leclanché battery electrolyte system (ZnCl<sub>2</sub>/NH<sub>4</sub>Cl), the electrochemical performance of the bifunctional air electrode and also, the zinc electrode reversibility behavior under this electrolyte system is not well understood and it requires an extensive work in this field.

The neutral electrolyte has two principal advantages in comparison to an alkaline electrolyte: (i) avoid the carbonization of the electrolyte and (ii) reduces dendrite formation. Both factors

might improve cycle life of the secondary zinc-air batteries. These advantages are due to the “neutral” pH of the electrolyte, which reduces zinc solubility and makes CO<sub>2</sub> absorption very low or almost non-existent [63,95]. The pH of the electrolyte can be tuned either around 7 with solutions such as KCl, KNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, and K<sub>2</sub>SO<sub>4</sub> or around 5 with ammonium salts. The latter is considered as near-neutral electrolyte in comparison with solutions of H<sub>2</sub>SO<sub>4</sub> (acid) or KOH (alkaline) [203,232].

Johnson and co-workers [233,234] proposed the reactions (10)–(12) to explain the dissolution mechanism of zinc in neutral solutions containing various anion species that are not reducible by zinc.

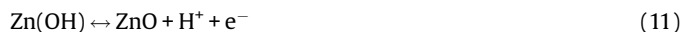


Table 2 compiles the precursor salts used for the neutral electrolytes described in the bibliography, which are grouped as chloride-based electrolytes and those based on other soluble salts. It should be pointed out that an aqueous neutral electrolyte can be composed of one or more of the chemicals listed in Table 2.

In certain electrolyte systems, Zn<sup>2+</sup> might form Zn-complex with those reducible anion species. An example of such kind of system is found in chlorine or ammonium-based electrolytes such as in Leclanché batteries where different studies have shown the possible formation of zinc-complex in the Zn<sup>2+</sup>-Cl<sup>-</sup>-NH<sub>4</sub><sup>+</sup>-H<sub>2</sub>O system. Part of these findings will be summarized in the following section.

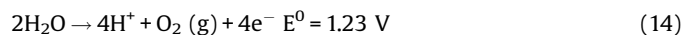
**Table 2**  
Table 2. Reported aqueous neutral electrolytes.

Chloride based electrolyte	References
KCl	[203]
NaCl	[203]
NH <sub>4</sub> Cl	[203,235,236]
PbCl <sub>2</sub> , PbCl <sub>4</sub> <sup>a</sup>	[63]
HgCl <sub>2</sub> , Hg <sub>2</sub> Cl <sub>2</sub> <sup>a</sup>	[63]
CdCl <sub>2</sub> <sup>a</sup>	[63]
BiCl <sub>3</sub> <sup>a</sup>	[63]
SnCl <sub>2</sub> , SnCl <sub>4</sub> <sup>a</sup>	[63]
LiCl	[63]
MgCl <sub>2</sub>	[203]
ZnCl <sub>2</sub>	[203,235]
Electrolyte based on other soluble salts	References
BF <sub>4</sub> <sup>-</sup>	[63,95]
BO <sub>3</sub> <sup>3-</sup>	[63,95]
CH <sub>3</sub> SO <sub>3</sub> <sup>-</sup>	[63,95]
CO <sub>3</sub> <sup>2-</sup>	[63,95]
MnO <sub>4</sub> <sup>-</sup>	[63,95]
NO <sub>3</sub> <sup>-</sup>	[63,95,203]
PF <sub>6</sub> <sup>-</sup>	[63,95]
PO <sub>4</sub> <sup>3-</sup>	[63,95]
SO <sub>4</sub> <sup>2-</sup>	[63,95,203]
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	[203]
ClO <sub>4</sub> <sup>-</sup>	[139,237,238]
Additives to minimize chlorine evolution	References
CoCl <sub>2</sub>	[63]
IrO <sub>2</sub>	[63]
(NH <sub>2</sub> ) <sub>2</sub> CO	[63]
Soluble manganese salts	[63]

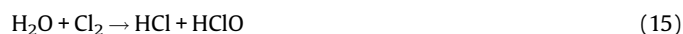
<sup>a</sup> Increase HER overpotential.

### 2.2.1. Chloride-based electrolytes

Jindra and co-workers confirmed that for zinc-air primary cells, the most suitable quasi-neutral electrolyte was 5 M  $\text{NH}_4\text{Cl}$  [203]. However, battery developers have not considered until the recent years the use of aqueous chloride-based electrolytes in rechargeable metal-air battery systems due to corrosion issues when anodic potentials are applied. Reaction (13) is the unwanted side reaction involving chlorine evolution during cell charging, which disfavors oxygen evolution (reaction (14)) and reduces overall cell charging efficiencies [63,236].



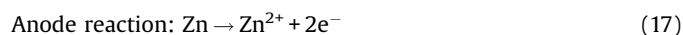
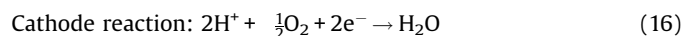
Chlorine gas generation is a simple chemical reaction. For this reason, undesirable chlorine evolution becomes more likely to occur than oxygen evolution in chloride environments. The generation of chlorine leads to the formation of acids such as  $\text{HClO}$  and  $\text{HCl}$  (reaction (15)). In addition, hypochlorite ions can decompose into chloride, oxidized chlorine species, or even free dissolved chlorine gas, depending on the conditions [63].



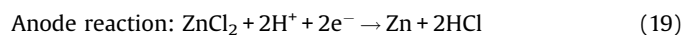
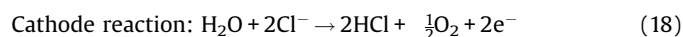
Some inorganic additives such as cobalt chloride ( $\text{CoCl}_2$ ), iridium oxide ( $\text{IrO}_2$ ), or soluble manganese salts could be used to minimize chlorine evolution. Among organic compounds, urea can be used because it prevents chlorine and/or hypochlorite evolution during recharge, since it reacts with chlorine to produce benign gaseous products such as  $\text{N}_2$ ,  $\text{CO}_2$ , and  $\text{H}_2$ . However, the main drawback is that it has to be replenished to prevent its depletion [63,236].

Aqueous chloride-based electrolytes have a cation suitable for yielding a soluble chloride salt in an aqueous solution such as zinc, ammonium [203], sodium, or others. On the other hand, some chloride salts such as tin chloride ( $\text{SnCl}_2$ ), lead chloride ( $\text{PbCl}_2$ ), mercury chloride ( $\text{HgCl}_2$ ), cadmium chloride ( $\text{CdCl}_2$ ), or bismuth chloride ( $\text{BiCl}_3$ ) can improve the HER overpotential in secondary zinc-air batteries [63]. Reactions (16)–(19) describe the discharge/charge processes in a zinc-air battery using chloride electrolyte (at pH 6) [63].

#### During Cell Discharge



#### During Cell Charge



The composition of resulted zinc complexes during the battery discharge should be highly sensitive to several conditions. It has to be taking into account, that the electrowinning of zinc from ammoniacal leaching solution is a currently used technology [239] and the zinc complexes formed at different conditions have been previously studied.

The  $\text{Zn}^{2+}$  ions can be complexed by many forms and the dominating one strongly depends on the solution composition [240]. Thermodynamic calculations have been reported for predicting speciation of zinc in  $\text{Zn(II)} - \text{NH}_3 - \text{Cl}^- - \text{H}_2\text{O}$  system as a function of pH, ammonia concentration and chlorine concentration. In this context, the zinc anode product of the

discharge reaction could be  $\text{ZnCl}_2$ ,  $4\text{Zn(OH)}_2$ ,  $\text{ZnCl}_2 \cdot 2\text{NH}_3$  [58],  $\text{ZnO}$  [241] and  $\text{Zn(OH)}_2$  [241] depending on the  $\text{NH}_4\text{Cl}$  concentration [242], water amount, temperature [241], and pH [243] where the solubility of zinc chloride complex changes [244].

A horizontal configuration cell helps zinc chloride particles settle back onto the horizontally positioned zinc metal electrode. In this way, zinc is deposited back on or near the zinc electrode and less zinc will be lost to other locations in the cell [63,245].

EOS Energy Storage LLC has patented a neutral aqueous electrolyte that contains amounts of zinc chloride ( $\text{ZnCl}_2$ ) and ammonium chloride ( $\text{NH}_4\text{Cl}$ ) in the range of 10–20% in mass for each or other salts such as  $\text{LiCl}$  (5% mass). EOS Energy Storage suggested that other materials can be also added to buffer the electrolyte such as ammonium citrate, ammonium acetate, or ammonium hydroxide in 1–2% mass [63]. The mixture of  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  proposed by EOS Energy Storage is based on the Leclanché battery electrolyte and is already reported in the bibliography. For example, Abdallah et al. [235] reported on the combined effect of  $\text{ZnCl}_2$  and  $\text{NH}_4\text{Cl}$  in reducing the corrosion of the zinc electrode.

F. W. Thomas Goh et al. [230] reported for first time in a scientific article a secondary zinc-air battery working in aqueous neutral electrolyte systems. They obtained more than 1000 h and hundreds of discharge-charge cycles with minimized zinc dendrite formation and no carbonate formation problem. The optimal electrolyte formulation was based on 0.51 M of  $\text{ZnCl}_2$ , 2.34 M  $\text{NH}_4\text{Cl}$ , 1000 ppm of PEG and 1000 ppm of thiourea with pH value of 6. The PEG and thiourea were added as additives to the aqueous neutral electrolyte system. In a further work at the same group, A. Sumboja et al. [231] reported 90 days running secondary zinc-air battery and the electrochemical performance was compared with aqueous alkaline based secondary zinc-air battery where 36 days running time were obtained. The electrolyte formulation was composed by 5 M  $\text{NH}_4\text{Cl}$ ,  $35 \text{ g L}^{-1}$  of  $\text{ZnCl}_2$  and 1000 ppm of thiourea with pH value of 7. In this context, the state of the art of secondary zinc-air battery based on aqueous neutral electrolyte system is composed by  $\text{ZnCl}_2/\text{NH}_4\text{Cl}$  electrolyte, metallic zinc as secondary anode and a bifunctional air electrode loaded with  $\text{MnO}_x$  as catalyst. Nevertheless, more work is still required in order to understand in details the electrochemistry of this system, as well as to evaluate its potential for real applications.

In that way, Clark and co-worker [243] developed a model considering the thermodynamics stability of aqueous species in continuum simulations. They were able to investigate in the near-neutral  $\text{ZnCl}_2\text{-NH}_4\text{Cl}$  system how the stability of the aqueous Zn-ligand complexes shifts significantly with small changes in concentration. They found how this complex stability affects the ionic conductivity of the electrolyte, the composition of the final discharge product, and the pH stability. Their simulations show that under conditions reported in the literature [230,231], the pH may become strongly acidic, which affects the performance and stability of the bifunctional air catalyst ( $\text{Mn}_x\text{O}_y$ -based). Thus, the authors were able to show how the composition of the electrolyte and the architecture of the cell can be adjusted to maintain a stable, near neutral pH over lifecycle.

Other aqueous neutral electrolytes based on chloride have been used by some researchers such as Bennett [246], who potentiostatically polarized pure zinc in an air-saturated unbuffered 3%  $\text{NaCl}$  solution, and Jackovitz [247], who patented a primary cell with zinc as the anode and oxygen as the cathode that operates in seawater (a salinity between 2.2 and 3.5%) [246–248].

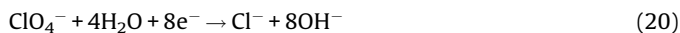
In addition, Larothenko and Shteyman reported a reduction of hydrogen corrosion with a neutral pH electrolyte for metal-air systems based on saline salt (5%wt.), alcohol (7.5% wt.), glycerin (7.5% wt.), and starch (2–3% wt.) [88].



### 2.2.2. Neutral electrolytes based on other soluble salts

Aqueous neutral electrolytes composed of other soluble salts have also been reported, such as those based on sulfates, nitrates, carbonates, tetrafluoroborates, methane sulfonates, permanganate, hexafluoro-phosphates, borates, or phosphates, either alone or mixed together [63,95].

Perchlorates are another neutral media widely used as supporting electrolytes in electrochemical and corrosion studies [139].  $\text{ClO}_4^-$  ions are reduced to  $\text{Cl}^-$  and  $\text{OH}^-$  during spontaneous dissolution (reaction (20)) on a variety of metal surfaces. Such reduction during zinc corrosion represents an alternative source of  $\text{OH}^-$  production [237].



Reaction (20) is expected to be very complicated, as eight electrons are involved in the overall reaction, so it is believed that any stable intermediate or product of side reactions can be formed. Reported possible intermediates formed during perchlorate reduction are chlorate  $\text{Zn}(\text{ClO}_3)_2$ , chlorite  $\text{Zn}(\text{ClO}_2)_2$ , and hypochlorite  $\text{Zn}(\text{ClO})_2$ , which are all soluble species and do not contribute in the passivating layer [139]. The principal issue is that the perchlorate ion shows aggressive behavior toward metals. For example, Hassan [238] studied the aggressiveness of  $\text{NaClO}_4$  with  $\text{pH} \approx 7 \pm 2$  toward the passivated zinc electrode. The data revealed that for higher concentrations of  $\text{ClO}_4^-$  ions ( $>0.01$  M) the passive layer breaks down and cause pitting corrosion at a certain anodic potential.

### 2.2.3. Aqueous neutral electrolytes in novel reversible zinc-based energy storage systems

Recently, in other reversible systems, aqueous neutral electrolytes were reported: zinc hybrid and zinc ion batteries with  $\text{LiCl-ZnCl}_2$  and  $\text{ZnSO}_4\text{-Zn}(\text{NO}_3)_2$ , respectively. The zinc anode in these media has shown a good reversibility, low redox potential, large specific capacity, and high over-potential for hydrogen evolution [74,249].

The difference between them is that the electrolyte of the zinc ion batteries is based on the migration of  $\text{Zn}^{2+}$  ions between the cathode and the anode. The ionic radii of  $\text{Zn}^{2+}$  (74 pm) were comparable with that of  $\text{Li}^+$  (68 pm); hence, insertion compounds used for lithium could be used for  $\text{Zn}^{2+}$  [35], whereas the zinc hybrid electrolyte involved two types of chemistries: zinc dissolution/deposition and lithium extraction/intercalation, as shown in Fig. 2 [74,249].

A zinc ion battery with near 100% discharge capacity retention after 100 cycles (Fig. 3a) was reported by Xu et al. [74]. On the other hand, Yan et al. have published up to 95% capacity retention after 4000 cycles for a zinc hybrid cell using doped  $\text{LiMn}_2\text{O}_4$ . For the undoped cathode, nearly 90% of the initial capacity is retained after 1000 cycles (Fig. 3b) [249].

### 2.3. Acid electrolytes

Acid electrolytes have barely been utilized in rechargeable zinc-air batteries because they require a suitable catalyst and support [203] to overcome problems related to the catalytic activity of the air electrode and their low life times.

Acid electrolytes include sulfuric, phosphoric, nitric, and hydrochloric acids [250] or methanesulfonic acid electrolytes [251,252] proposed for other zinc based technologies like zinc-cerium flow batteries [253]. Their electrochemical behaviors differ from those of alkaline electrolytes. The current densities at which dendrite formation begins in aqueous acid electrolytes are generally somewhat higher than in alkaline solutions [254]. In addition, in acid media, the passivation of a zinc surface does not occur without the presence of film-forming agents [105].

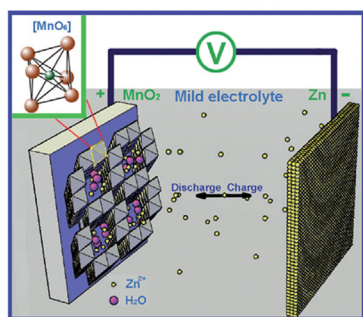
The mechanism of dissolution is different for acidic and alkaline solutions and for complexing and non-complexing solutions. In acidic and non-complexing neutral solutions, the  $\text{Zn}/\text{Zn}^{2+}$  electrode reaction appears to occur in two consecutive charge-transfer steps (reactions (21), (22)) with the intermediate product  $\text{Zn}_{\text{ad}}^+$  being adsorbed on the metal surface [255–257].



Reaction (21) is very fast, while reaction (22) is slower, and it determines the anodic dissolution or cathodic deposition [105,258]. Wiart [259–262] proposed a more complicated mechanism of zinc dissolution and deposition in the sulphate medium. The model consists of parallel paths for dissolution in which three adsorbed intermediates ( $\text{Zn}_{\text{ad}}^+$ ,  $\text{Zn}_{\text{ad}}^{2+}$ , and  $\text{ZnOH}_{\text{ad}}$ ) participate. A similar but simpler model was previously proposed by Deslouis et al. [263]. This dissolution model involves two parallel processes in which two adsorbed intermediates,  $\text{Zn}_{\text{ad}}^+$  and  $\text{Zn}_{\text{ad}}^{2+}$ , are formed [258].

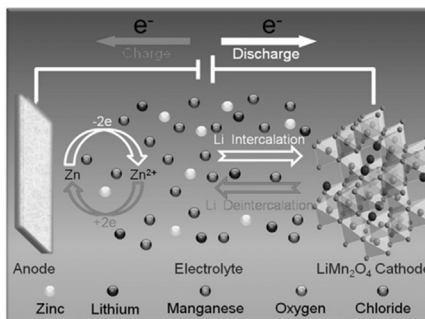
#### (a) ZINC ION BATTERY

1. Dissolution/deposition of zinc  
 $\text{Zn} \leftrightarrow \text{Zn}^{2+} + 2\text{e}^-$
2.  $\text{Zn}^{2+}$  intercalation into tunnels of  $\alpha\text{-MnO}_2$

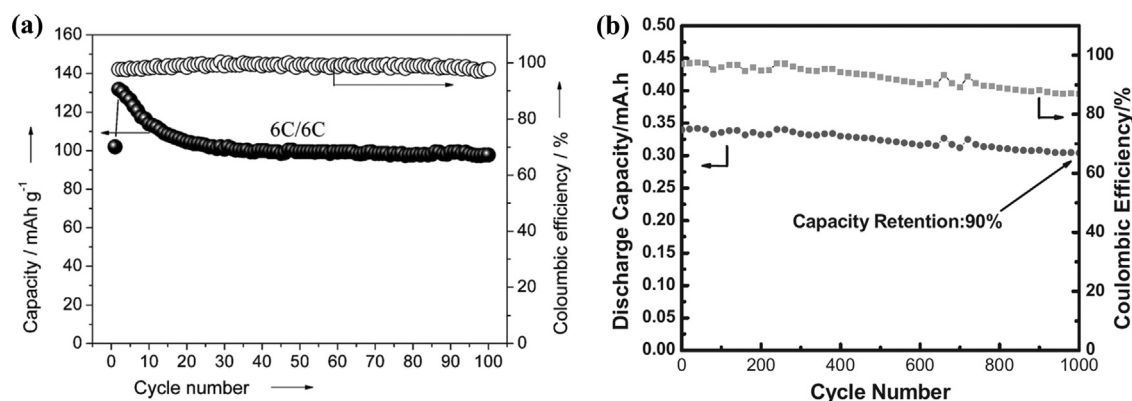


#### (b) ZINC HYBRID BATTERY

1. Dissolution/deposition of zinc
2. Lithium extraction/intercalation in spinel  $\text{LiMn}_2\text{O}_4$

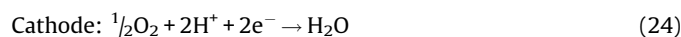
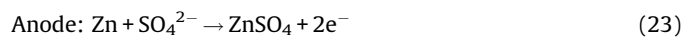


**Fig. 2.** Left: Schematic representation of zinc ion battery. Reprinted from [74], with permission from Elsevier. Right: Schematic representation of zinc hybrid battery. Reprinted from [249], with permission from Elsevier.



**Fig. 3.** (A) Zinc ion system at continuous charge/discharge (6C/6C) cycling test (reprinted from [74], with permission from Elsevier). (B) Zinc hybrid cell using undoped  $\text{LiMn}_2\text{O}_4$  (4C rate) (reprinted from [249], with permission from Elsevier).

Blurton et al. [62] patented an aqueous acid electrochemical cell for zinc-oxygen. The electrolyte was selected from a group consisting of sulfuric acid ( $\text{H}_2\text{SO}_4$ ), phosphoric acid ( $\text{H}_3\text{PO}_4$ ), boric acid ( $\text{H}_3\text{BO}_3$ ), and mixtures thereof. They reported that their electrolyte avoids dendrite formation and carbon dioxide adsorption problems experienced with alkaline electrolytes. The aqueous sulfuric acid electrolyte exhibits the following overall reactions (23), (24) upon production of electricity:



HER on zinc is largely independent of pH except in concentrated acid or alkaline solutions. In acid solution, the hydrogen evolution reaction can be expressed by reaction (25), while reaction (26) takes place in alkaline electrolyte [105].



Quaternary ammonium ions have been used as an inhibitor of HER for zinc batteries in aqueous electrolytes; for example, in Leclanché-type batteries containing  $\text{NH}_4\text{Cl}/\text{ZnCl}_2$  salts. In this way, it could be possible to use a quaternary ammonium compound as an additive in acidic electrolyte, as done for lead-anode, lead-oxide cathode, and sulfuric electrolyte systems. This additive concentrates along the interface between the anode and the electrolyte, altering the potential at which the hydrogen evolution reaction takes place [264]. Although the authors wanted to point out here the mitigation strategies related to corrosion and electroplating of zinc; it is worthy to mention that corrosion inhibitors and electrolyte additives to mitigate the zinc loss and zinc change morphology during deposition are well documented in the corresponding literature. In this sense, the authors refer the reader to [40,60,105] and references therein for a better understanding in this specific topic.

Considering several parameters, the corrosion of zinc in flow battery systems was investigated by P.K. Leung et al. [251,252]. They concluded that dominant hydrogen evolution and faster corrosion rate was observed at higher acid concentration, lower Zn (II) methanesulfonate concentration and higher temperature. Regarding the electrolytic inorganic additives the indium and lead are suitable for zinc-based redox flow battery due to its large hydrogen over-potential, and as organic inhibitors CTAB and BTPC are preferred due to the retarded rate of zinc corrosion.

### 3. Non-aqueous electrolytes

The problems associated with zinc-air batteries having conventional aqueous electrolytes, such as water evaporation or ambient moisture uptake, bicarbonate formation [18], limited electrochemical window (which causes cells to behave poorly or become non-rechargeable because the open-circuit voltage is higher than the stability window of the aqueous electrolyte: 1.65 V vs. 1.23 V [52,265]), or battery short shelf life, have caused non-aqueous electrolytes to be investigated as an alternative [266,267]. Organic electrolytes can potentially offset a number of shortcomings such as hydrogen evolution [268], dendrite formation, dry-out of the electrolyte due to water evaporation, and carbonation of the alkaline electrolyte. They provide a higher temperature range [52] and present a relatively broad electrochemical window.

On the other hand, it is necessary to select the appropriate composition to avoid potential problems in non-aqueous metal-air batteries such as volatility, flammability, and toxicity [269]. This is why traditionally the metal-air battery's electrolyte has been a liquid solution (normally water-based), which allows ionic transport between the metal electrode and the air electrode [63].

Unfortunately, while extensive work has been done on organic electrolytes for lithium ion batteries, relative little has been devoted to secondary zinc-air batteries. The secondary zinc anode performance in non-aqueous electrolytes is very promising. A. Guerfi et al. [270] selected an organic electrolyte based on PC and 0.3 M fluoro-based salt reaching more than 1700 cycles at 99.8% efficiency at 1C charge/discharge rate.

In general, a new secondary zinc-air system should have the following desirable properties [52,271]

- Non-aqueous electrolytes conduct  $\text{Zn}^{2+}$  ions with high conductivity.
- Non-volatile solvents.
- Low-toxicity compounds.

In aqueous zinc-air batteries, the known three-phase boundary reaction (solid-liquid-gas) takes place at the air cathode. The reaction zone consists of two interpenetrating sub-systems: a hydrophobic sub-system in which oxygen diffuses and hydrophilic micro-channels in which metal ions are transported and reaction sites are formed, enabling the oxygen reduction reaction (ORR). Non-aqueous electrolytes present a significant challenge to the operation of air cathodes, because most electrolytes easily wet all electrode pores, flooding the air channels. Hence, only dissolved oxygen participates in the ORR occurring in a two-phase boundary reaction zone. The mobility of dissolved oxygen is at least one order

of magnitude lower than that of gaseous oxygen. One way to reduce this issue (improving specific capacity) is to increase oxygen pressure, which results firstly in a higher solubility and concentration in the electrolyte solution and, secondly, in a dewetting of some cathode pores, achieving the formation of desirable three-phase reaction zones throughout the air electrode [272–275]. Alternatively, increased oxygen solubility can be achieved using patented fluorinated compounds as co-solvents of the non-aqueous electrolytes for metal-air cells [276].

The mechanism of zinc dissolution in anhydrous organic solvents is similar to that in aqueous media [277–279]. However, the stabilities of monovalent cations and adsorbed intermediate products in these solvents are much better than in an aqueous environment [279–281]. Therefore, in organic solvents, the solubility of corrosion products is also lower than in aqueous solutions. The stability of surface species and the mechanism of desorption or dissolution, both play very important roles in the electrochemical processes occurring on zinc electrodes in organic environments.

Since non-aqueous electrolytes have not been yet widely studied for zinc-air batteries, the purpose of this section is to identify the different types of non-aqueous electrolytes and assess the possibility of their use in secondary zinc-air systems.

### 3.1. Solid polymer electrolytes

Solid polymer electrolytes (SPEs), or thin-film electrolytes, could offer numerous advantages over current electrolytes in zinc-air batteries. This kind of electrolyte enhances the energy, operating temperature range, shelf life, and electrical rechargeability [47,52,175,271,282–287]. SPEs are ionic conductive solids based on macromolecules containing heteroatoms that allow the dissolution of one or several salts and enable their diffusion under an applied electric field. Furthermore, SPEs offer several advantages over conventional liquid or solid electrolytes, such as [288]:

1. Good mechanical strength with some ability to deform.
2. Ease of handling, which allows the fabrication of thin films.
3. Low convection, which reduces the problems of electrode corrosion and increases battery life.
4. Elimination of the problem of battery leakage.

The principal problems associated with this type of electrolyte are its low ionic conductivity [47] (not exceeding  $1 \mu\text{S cm}^{-1}$  under ambient conditions [52]), its low solubility of zinc salts [52,175,271,285,286,289,290], and the formation of passive layers between the SPE and the electrode [291].

One important requirement of solid non-aqueous electrolytes is their adhesion with the electrode, as Stone [292] reported for lithium metal batteries. This means that the solid electrolyte has to be able to adhere to the electrode while the electrode volume increases or reduces during charging and discharging, respectively.

Among the polymer electrolytes reported, poly(ethylene oxide) (PEO)-based electrolytes are the most widely studied [290,293], such as PEO- $\text{ZnX}_2$  (where  $\text{X} = \text{Cl}, \text{Br}, \text{I}, \text{ClO}_4, \text{and } \text{CF}_3\text{SO}_3$ ), PEO-KOH [294], or polyvinyl alcohol (PVA)-proton/iodide systems [52,175,271,295], as well as combinations with various zinc salts. However, in spite of being zinc ion-conducting polymer electrolytes, they are unsuited for battery applications because of low conductivities [282–284,296].

### 3.2. Gel polymer electrolytes

Gel polymer electrolytes (GPEs) are interesting [297] due to their practically acceptable ionic conductivity. A GPE contains a liquid electrolyte retained in the polymer gel, which enhances the

ionic conductivity [273,293] in the range of  $10^{-4}$  to  $10^{-3} \text{ S cm}^{-1}$  at ambient temperature, which may be sufficient for many battery applications [182,271,285,286,298,299].

Conventionally, gel-type polymer electrolytes are fabricated by phase-inversion methods followed by immersion in liquid electrolytes [300], solvent-casting steps [301,302], and in situ polymerization [303–305].

Various polymers, such as poly(ethylene oxide) (PEO) [306], poly(methyl methacrylate) (PMMA) [307], poly(acrylonitrile) (PAN) [308], and poly(vinylidene fluoride) (PVDF) [301,309], have been widely used as polymer matrices for GPEs.

Propylene carbonate (PC), ethylene carbonate (EC), and dimethylsulfoxide (DMSO) have been proposed as aprotic solvents [175,273,289]. Ikeda et al. [285,286] reported a GPE of PAN and zinc triflate ( $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ ), obtaining a conductivity of  $2.67 \times 10^{-3} \text{ S cm}^{-1}$  at  $25^\circ\text{C}$ . By using PVDF instead of PAN [175], a maximum ionic conductivity of  $3.94 \times 10^{-3} \text{ S cm}^{-1}$  was attained at ambient temperature. Kumar et al. [271] optimized the GPE to have the minimum amount of liquid component (PC and EC) required for gel formation.

In spite of being zinc ion conductors and having acceptable ionic conductivity, organic solvents such as PC, EC, and DMSO are inapplicable for open systems such as secondary zinc-air systems due to their volatility [47,52,265].

Therefore, oligomeric polyethers such as poly(ethylene glycol) dimethyl ether (PEGDME) having a molecular weight 250 or 400 have been proposed. They have boiling points over  $300^\circ\text{C}$  [293] and a lower vapor pressure than organic solvents such as PC [310].

Ye et al. [265] found that PEGDME has unusually strong capabilities for dissolving zinc salts in large amounts that are an order of magnitude higher than PC [311]. The combined use of a PEGDME solvent and a zinc salt with a very large anion such as  $\text{Zn}(\text{TFSI})_2$  or  $\text{Zn}[\text{N}(\text{SO}_2\text{CF}_3)_2]_2$  provide high solubility and high ionic conductivity. Coupled with its very low vapor pressure and the fact that it blends exceptionally well with a range of polymers, such as poly(vinylidene fluoride-co-hexafluoropropylene) (PVDF-HFP) [312] and PMMA, PEGDME appears to be a suitable solvent for zinc ion-conducting polymer electrolytes for potential applications in zinc-air cells. Furthermore, Ye et al. [265] reported that blending PEGDME with a small amount of EC has beneficial effects on the ionic conductivity without affecting the volatility of the electrolyte system.

Finally, Xu et al. [52] reported novel zinc ion-conducting GPE based on room temperature ionic liquids having an ionic conductivity on the order of  $10^{-3} \text{ S cm}^{-1}$  at room temperature. This electrolyte was composed of 1-ethyl-3-methylimidazolium trifluoromethanesulfate (EMITf) and 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide (EMITFSI) ionic liquids, which are capable of dissolving significant amounts of zinc salts and blending particularly well with PVDF-HFP polymer. Xu et al. reported stability up to 2.8 V vs.  $\text{Zn}^{2+}/\text{Zn}$ , which is high enough for primary cells but would also enable its use for secondary cells.

Unfortunately, nowadays the use of GPEs in real applications for secondary zinc-air batteries is still not feasible due to the poor solubility of zinc salts [52,313] and other issues such as the flammability and/or volatility of organic solvents [52,299,313].

### 3.3. Room temperature ionic liquids

Room temperature ionic liquids (RTILs) have been increasingly recognized as promising electrolyte candidates to replace the traditional alkaline aqueous electrolyte system and volatile organic solvents (starting from catalysis [314,315] to electrochemistry [316]) [52,317–319]. Information about RTILs can be found in the literature using keywords such as “room temperature molten salt,”

“low-temperature molten salt,” “ambient-temperature molten salt,” “liquid organic salt,” or simply “ionic liquid” [320].

RTILs are salts with low melting temperatures at or below room temperature, which are composed exclusively of ions, usually organic cations and an organic/inorganic anion [51,52,136,189,313,317,321–324].

Ionic liquids (ILs) are classified primarily by considering the anion and its ease of reactivity with water, although nowadays, they can be classified into other categories such as aprotic ionic liquids [325] and protic ionic liquids [326,327].

- First generation ILs. Based on haloaluminate anions such as  $[\text{AlCl}_4]^-$ , they are sensible to moisture, which requires that they be handled under anhydrous conditions [328].
- Second generation ILs. Based on anions such as tetrafluoroborate or hexafluorophosphate ( $[\text{BF}_4]^-$ ,  $[\text{PF}_6]^-$ , respectively), they are less reactive with water but they do absorb moisture, which changes the physical and chemical properties of the liquids [329,330].
- Modern generation ILs. Composed of more hydrophobic anions such as bis(trifluoromethanesulfonyl) imide ([TFSI]) or perfluoroalkyl phosphate ([FAP]), they are less moisture sensitive than first and second generation ILs [315,331].

The physicochemical properties of RTILs depend strongly on the nature of the ions. For example, the zinc redox reaction in [MPP][TFSI] and [BMP][TFSI] shows better reversibility than in either [EMI][TFSI] or [BMP][DCA] [18,332]. On the other hand, the reported potential for zinc deposition is different for  $\text{Zn}^{2+}$  salts varying the anion. This is because complex anions ( $\text{Zn}(\text{X})_a^{b-}$ ) are involved, and they will affect the thermodynamics of  $\text{Zn}/\text{Zn}^{2+}$ , where “X” can be a mixture of anions,  $a$  is the number of anions coordinated with the zinc, and  $b$  is the resulting charge on the complex [267].

The advantages RTILs offer include low vapor pressure, high thermal stability (300 °C or above), high ionic conductivity (0.1–30  $\text{mS cm}^{-1}$  [333,334]) with respect to other non-aqueous electrolytes, and wide electrochemical stability windows [25,52,189,268,313,317,321–324,335–339] (usually in the range of 4.5–5.5 V [331,340–344]). Furthermore, aprotic RTILs exhibit the capacity to eliminate hydrogen evolution [345] and modify metal deposit morphology [346,347].

A disadvantage for the ILs is the high-purity required, since impurities, even in trace amounts, affect their physical properties.

For example, the quantification and electrochemical properties of halides in ILs (particularly chloride) have attracted significant interest because chloride can be present as an impurity that influences the physicochemical properties of ILs such as viscosity, melting point, electrochemical window, and even catalytic activity [315,344,348,349].

Additionally, their synthesis is far from environmentally friendly, since it generally requires anion exchange. These drawbacks together with the high price of common ILs hamper their industrial emergence, and new concepts are now strongly needed in order to utilize these systems in a more rational way [51,322,350]. In addition, due to the large size of ionic species, their viscosity is high [351] (1–3 orders of magnitude higher than conventional solvents [352]); consequently, their ionic conductivity is lower. One way to alleviate this problem is to include oxygen in the alkyl chain of an IL [18,353] or to incorporate water as diluent to reduce the viscosity of the electrolyte [354], which also improves reversible cycling [18] and the deposition morphology of zinc [347]. As shown in Fig. 4, water bonds with anions and the general effect is the improvement of  $\text{Zn}/\text{Zn}^{2+}$  reversibility as well as the diffusion coefficient of the zinc species. The principal inconvenience is that an excess amount of water decreases the electrochemical window and interferes with the zinc redox reaction [354].

The information on ion-based properties serves as a powerful guide for selection of RTILs in battery applications. Table 3 displays some cations and anions commonly used for the preparation of RTILs [355].

Dicyanamide [DCA] anion has provided highly fluid and conductive ionic liquids made by combining hetero cations such as 1,3-dimethylimidazolium (MMIm) [356], 1-ethyl-3-methylimidazolium (EMIm) [356–359], and diethyl-methyl sulfonium [333,360]. [DCA] has been a major focus of recent studies involving  $\text{Zn}^{2+}$  electrochemistry due to the fact that it provides some of the lowest viscosities and highest conductivities of any of the major families of aprotic ILs [347].

Deng et al. [361] reported that [DCA] anion-based ILs are good solvents for metal ions resulting from the high complexing ability of [DCA]. While zinc could not be electrodeposited from most Lewis basic or neutral ILs reported in literature, it can be obtained from the [DCA]-based ILs. Simons et al. [267,347] reported [EMIm][DCA] ILs as being a potential electrolyte for secondary zinc-air batteries offering high charge and discharge capabilities and good efficiency in the presence of a significant amount of water. But

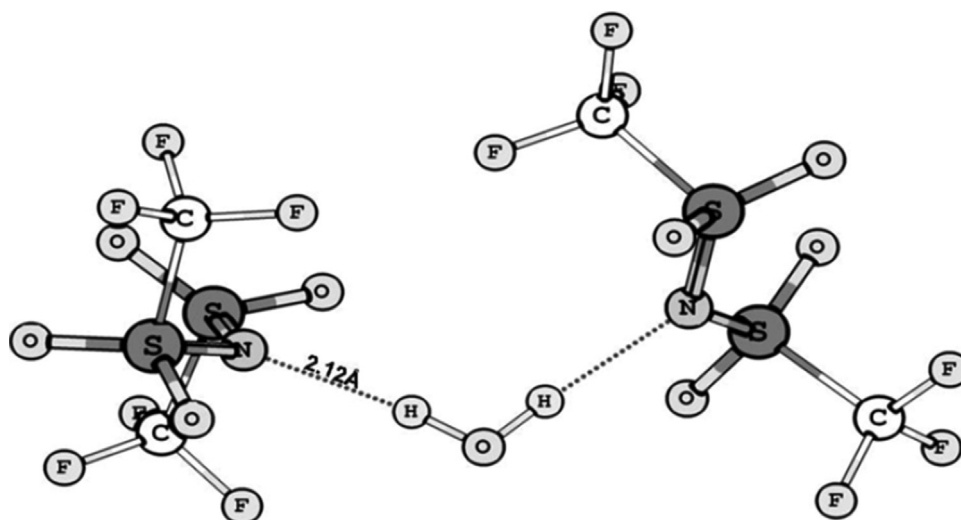


Fig. 4. One water molecule bonded to two [TFSI] anions. Reprinted from [354], with permission from Elsevier.

**Table 3**

Structures and abbreviations for commonly occurring cations and anions. Adapted with permission from [334]. Copyright 2008 American Chemical Society.

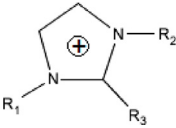
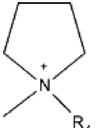
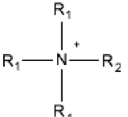
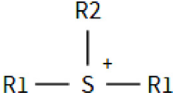
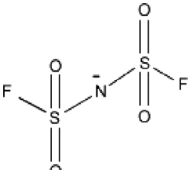
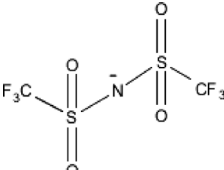
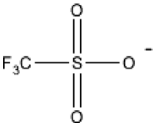
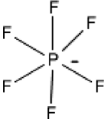
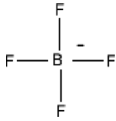
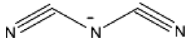
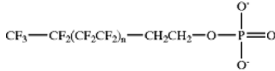
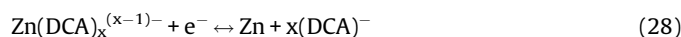
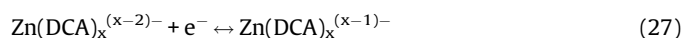
Structure	Abbreviation	R1	R2	R3
	[HmIm]	H	CH <sub>3</sub>	H
	[MmIm]	CH <sub>3</sub>	CH <sub>3</sub>	H
	[EmIm]	CH <sub>3</sub>	C <sub>2</sub> H <sub>5</sub>	H
	[PmIm]	CH <sub>3</sub>	C <sub>3</sub> H <sub>7</sub>	H
	[BmIm]	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	H
	[HexMIm]	CH <sub>3</sub>	C <sub>6</sub> H <sub>13</sub>	H
	[BEIm]	C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	H
	[EMMIm]	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	[BMMIm]	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	[HexMMIm]	C <sub>6</sub> H <sub>11</sub>	CH <sub>3</sub>	CH <sub>3</sub>
	[MPhMIm]	CH <sub>3</sub>	C <sub>6</sub> H <sub>6</sub>	CH <sub>3</sub>
	[EtP]	C <sub>2</sub> H <sub>5</sub>		
	[BuP]	C <sub>4</sub> H <sub>9</sub>		
[PenP]	C <sub>5</sub> H <sub>11</sub>			
[HexP]	C <sub>6</sub> H <sub>13</sub>			
	[Pyr <sub>2</sub> ]	C <sub>2</sub> H <sub>5</sub>		
	[Pyr <sub>3</sub> ]	C <sub>3</sub> H <sub>7</sub>		
	[Pyr <sub>4</sub> ] or [BMP]	C <sub>4</sub> H <sub>9</sub>		
	[Pyr <sub>5</sub> ] or [MPP]	C <sub>5</sub> H <sub>11</sub>		
	[Pyr <sub>6</sub> ]	C <sub>6</sub> H <sub>13</sub>		
	[Me <sub>3</sub> BuN]	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	
	[Et <sub>3</sub> BuN]	C <sub>2</sub> H <sub>5</sub>	C <sub>4</sub> H <sub>9</sub>	
	[MeBu <sub>3</sub> ]	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	
	[Et <sub>3</sub> HexN]	C <sub>2</sub> H <sub>5</sub>	C <sub>6</sub> H <sub>13</sub>	
	[Et <sub>3</sub> OctN]	C <sub>2</sub> H <sub>5</sub>	C <sub>8</sub> H <sub>17</sub>	
	Diethyl-methyl sulfonium	C <sub>2</sub> H <sub>5</sub>	CH <sub>3</sub>	
	[FSI]			
	[TFSI]			
	[OTf]			
	[PF <sub>6</sub> ]			
	[BF <sub>4</sub> ]			

Table 3 (Continued)

Structure	Abbreviation	R1	R2	R3
				
	[DCA]			
	[FAP]			
CH <sub>3</sub> COO <sup>-</sup>	[AcO]			

further development is needed to know if the air cathode can be supported in the ionic liquid [267].

The ability to deposit and strip zinc from ILs depends on the anion; hence, its nature is critical to the electrochemical cycling of zinc [18,267,362]. Xu et al. [332] reported that in [TFSI] anion-based RTILs, Zn<sup>2+</sup> ions are present in the electrode reaction occurring in a single-step, two-electron transfer process. Whereas in [DCA] anion-based RTIL, a complex ion between Zn<sup>2+</sup> and [DCA] forms, turning the electrode reaction into a two-step, single-electron process (reactions (27), (28)).



The presence of metal ion in an anionic complex is, in principle, undesirable for facile reduction electrochemistry, but if the IL cation contains a coordinating functional group that is able to participate in the formation of metal complexes, then this issue would be ameliorated [18].

Metal-air batteries are exposed to the atmosphere, and thus H<sub>2</sub>O may be absorbed by hygroscopic electrolytes [347,363]. Hence, hydrophobic compounds are desirable for achieving a stable electrolyte system under open-air conditions [354].

For this reason, the incorporation of small amounts of water has been studied in order to emulate its effect. Kar et al. [18] increased the concentration of water from 5 mol% to 20 mol% with respect to the IL. Higher rates of deposition were obtained from the IL as the water concentration was increased. Kar et al. concluded that the [TFSI] anion has more favorable properties for metal-air battery applications. In the same manner, Xu et al. [354] added water to [BMP][TFSI] to improve the ionic conductivity of RTIL, and they reported that 2 wt% was an optimal amount of water in terms of the kinetic properties of Zn/Zn(II) redox for rechargeable zinc-air batteries.

In conclusion, a fundamental understanding of the influence of water addition on the physical and electrochemical behavior of electrode reactions is necessary for selecting potential RTIL candidates as electrolytes for secondary zinc-air batteries.

### 3.4. Room temperature deep eutectic solvents

Room temperature deep eutectic solvents (DESs) developed by Abbot and co-workers at the beginning of this century [322,351,364,365] are expected to be cheaper and greener alternatives to RTILs. A DES is an ionic solvent that is composed of a mixture of solid salt and a complexing agent that forms a

eutectic system with a melting point much lower than that of either of the individual components [350,366,367]. Preparation is very simple because the mixed components are stirred under heating (~80 °C) until homogeneous, clear liquid forms [368–370].

The mechanism of a DES is the interaction of the complexing agent (typically a hydrogen-bond donor – HBD) with the anion. Thereby, its effective size increases and its interaction with the cation is shielded, in turn inducing a depression in the melting point of the mixture [370,371]. It has been reported that the melting point decreases with increasing asymmetry of the cation, and that the freezing points are influenced by the hydrogen bond strength of the different negatively charged counter ions [370,372].

Abbot and co-workers defined DESs using the R<sub>1</sub>R<sub>2</sub>R<sub>3</sub>R<sub>4</sub>N<sup>+</sup>X<sup>-</sup>Y<sup>-</sup> general formula, where Y can be different depending on the type of eutectic system [350,351,373]:

1. Type I DES: Y = MCl<sub>x</sub>, M = Zn, Sn, Fe, Al, Ga
2. Type II DES: Y = MCl<sub>x</sub>, yH<sub>2</sub>O, M = Cr, Co, Cu, Ni, Fe
3. Type III DES: Y = R<sub>5</sub>Z, Z = -CONH<sub>2</sub>, -COOH, -OH

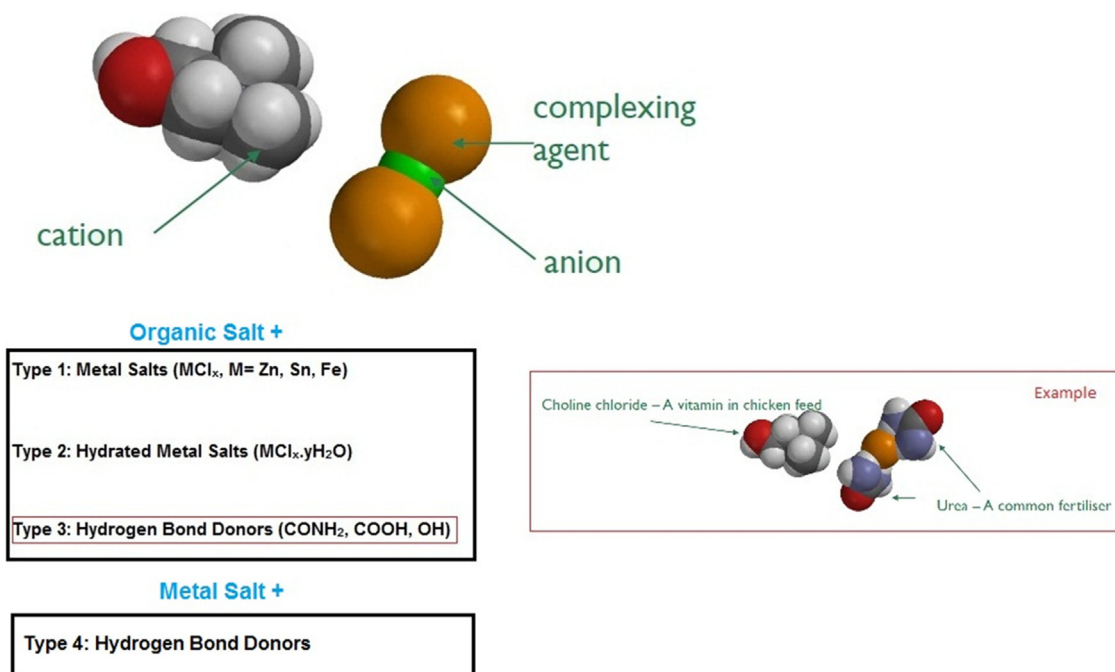
A fourth type of DES has been defined as a mixture of metal chlorides and HBD [370]. Fig. 5 summarizes the different DEPs. The first three types are mixed with an organic salt such as choline chloride (ChCl) and the last type is mixed with a metal salt such as ZnCl<sub>2</sub> [322,371,374].

DESs are capable of dissolving various metal oxides [322,350] because they donate or accept electrons or protons to form hydrogen bonds, which confer excellent dissolution properties [375].

Deep eutectic solvents have many of the characteristics of conventional ILs such as high thermal stability. In addition, they offer certain additional advantages as they are more synthetically accessible, nontoxic, less expensive, and biodegradable [322,350,351,364–366,370,372,376–378]. Table 4 displays the similarities and differences among DESs and ILs.

Viscosity is one of the disadvantages of DESs. While the viscosities of ILs vary from 10 cP to 500 cP, the viscosities of DESs can vary from 50 to 8500 cP [370]. These values depend on the chemical nature of DES components, the temperature, and water content [350]. Table 5 gives some examples of DES viscosities [370].

In just a few years, different (uncharged) HBD of natural and synthetic origin have been used in combination with choline chloride (ChCl) [322,368–370,381,382]. Some examples of different compounds utilized as HBD in DESs are showed in Fig. 6 [332,350,373].



**Fig. 5.** Types of deep eutectic solvents (DESs) and one example of an eutectic mixture between choline chloride ( $ChCl$ ; m.p.  $302^\circ C$ ) and urea (m.p.  $133^\circ C$ ) forming a DES with a melting point of  $12^\circ C$ .

**Table 4**

Similarities and differences between ionic liquids (IL) and deep eutectic solvents (DES).

Similarities	DES differences in comparison to ILs
Wide electrochemical window	Low price
High thermal stability	Easy to prepare
Low vapor pressure	Biodegradable
Non-volatility	Not entirely composed of ionic species
Chemical inertness	

**Table 5**

Viscosities of some deep eutectic solvents (DESs).

Mixture	Viscosity (cP)	Reference
Chloride with carboxylic acids	50–5000	[322]
Choline with carboxylates	650–8500	[379]
Choline-amino acid	121–5640	[380]

An acetamide based eutectic solvent has been reported as an alternative to be used in developing zinc ion-conducting DES electrolytes [313,383–385] due to its good donor and acceptor abilities, large dipole moment, and large dielectric permittivity [386]. Venkata et al. [313,383] reported room temperature binary molten electrolytes for secondary zinc batteries based on acetamide and zinc perchlorate and a ternary mixture of acetamide, urea, and zinc salt.

The use of small cations or fluorinated HBD can lead to the formation of DESs with low viscosity [350,381]. The most representative DESs described to date are shown in Table 6; depending on their properties, some of them may be applicable for secondary zinc-air batteries [370,387].

#### 4. Potential of Zn-based batteries as energy storage systems

As abovementioned, the materials for large-scale battery energy storage systems (BESS) have to be robust, environmental friendly, safe and low cost. Zinc-based batteries, principally

secondary Zn-air, are one of the candidates to fulfil these requirements. However, there remain challenges to overcome and limitations like abridged cycle life and low efficiency (Table 7). Therefore secondary Zn-air technology is still considered under development [395,396], although few companies started to offer their BESS based on this technology. The reason is that in spite of its drawbacks this technology provides high energy density, abundant raw materials, and low toxicity, easy to scale up and it is considered to be the cheapest BESS (readers are referred to more dedicated publications supporting this statement) [26,395–401]. These advantages make this battery chemistry a potential competitor in comparison to those batteries technologies considered as mature or developed like Pb-acid, NiMH or Li-ion. Nevertheless, such comparison should be carefully done according to a specific scenario, where operating characteristics, performance and capital cost must be taken into account.

Among the Zn-based battery technologies, Zn hybrid (incl. Zn-ion) batteries seem to be more suitable to compete against other battery technologies for high power applications owing to its high C-rate capability, cost and extended cycle life (Table 7). In comparison, secondary Zn-air presents limited rate capability and cycle life. However, it does not mean that it cannot be implemented as BEES. Since low C-rate should be applied its discharge time is relatively long (from seconds to over long periods of hours, 24+ h, [395–397]) with a power rating of 1 MW (5.4 MWh) [395]. These capabilities make this technology suitable for bridging power applications (less cycling requirements) like Pb-acid, Li-ion or NiMH may do [396,397,400]. Nevertheless, on the other hand, owing to its low self-discharge loss, this technology can be employed for long storage time (hours to months) in contrast to Pb-acid or Li-ion which are suitable for storage duration in the range of minutes to days. Furthermore, based on its higher energy density in comparison to that for these other technologies, rechargeable Zn-air battery has worldwide a grand potential as BEES. The latter is further support when capital lifetime investment cost ( $\epsilon$  per kWh per cycle) assessments are also taken into account. These analysis have demonstrated that this technology is called to compete in cost with other BESS but with the add value of

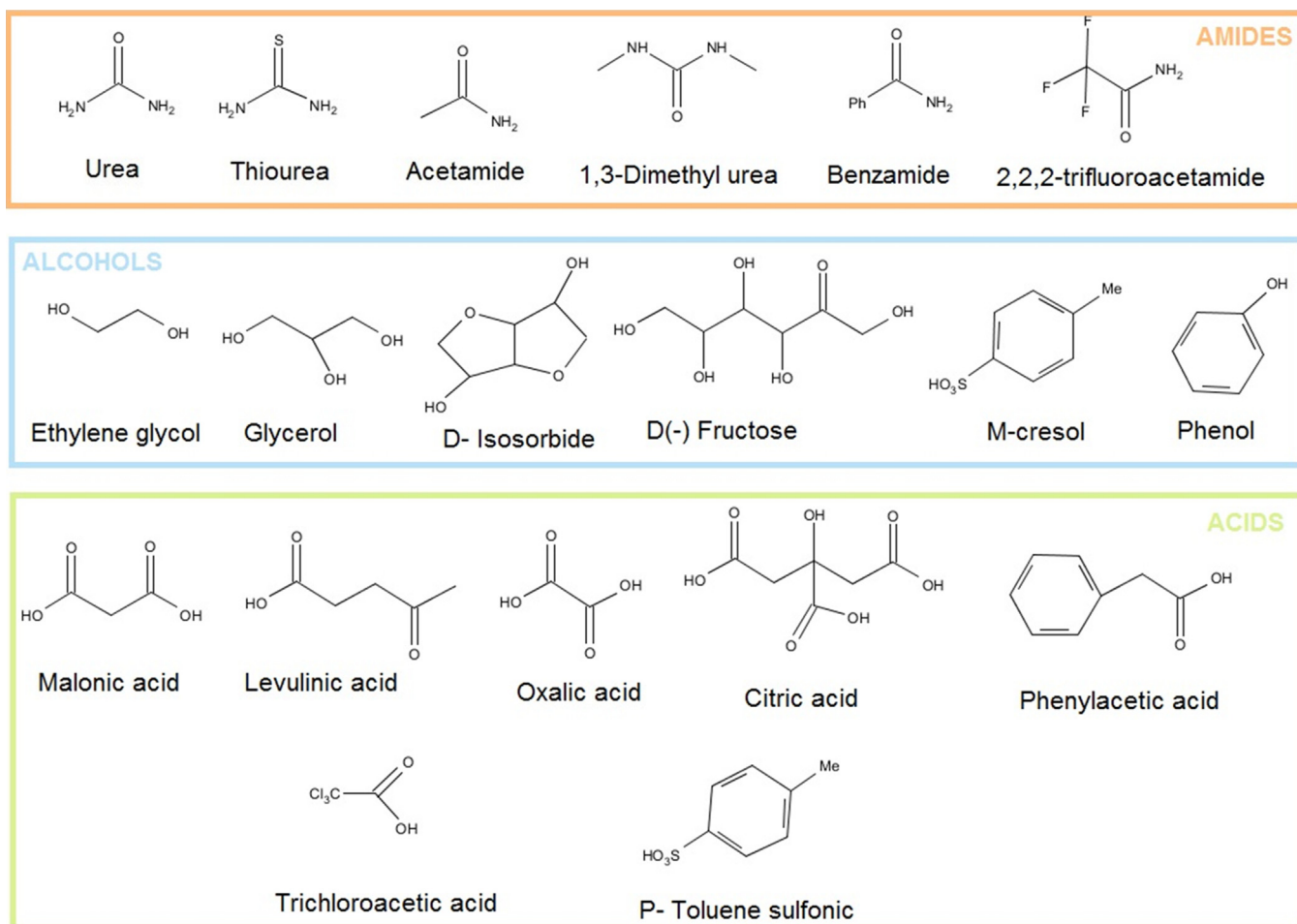


Fig. 6. Hydrogen-bond donors (HBD) utilized in deep eutectic solvents (DESs).

negligible environmental impact [397,401]. N.D. Ingale et al. [399] evaluated a reversible alkaline Zn/MnO<sub>2</sub> cell for large scale energy storage application. They determined a projected cost of 100 to 150 \$/kWh (delivered) as a function of shallow depths of discharge (DOD) at specific C-rates. The final estimation of cost was 5 ¢ per kWh per cycle (lifetime investment cost). This estimation was far below those showed by other secondary battery technologies [397,399,401], making this battery chemistry very attractive and competitive as alternative electrical energy storage system.

## 5. Summary

Rechargeable zinc-air batteries have been considered as promising systems for high energy and higher power but the technology has not achieved commercial success due to the low cycle life of the zinc electrode and in addition the large over-potential of the bifunctional air electrode (BAE) which already determined its low power density and low round-trip efficiency. In the last years, many efforts have been focused on the development of high-performance non-precious metal based bifunctional electrocatalysts, mainly based on metal oxides (spinel, perovskite, or pyrochlore structures). Nevertheless, due to the semiconducting nature of the metal oxide materials the use of carbon as conductive media is spread used to promote the electron transfer [411]. Although high corrosion resistant carbon materials have been synthesized, the electrochemical corrosion of carbon during battery charging also contributes to the low long-term stability of the BAE. In this sense, replacement of carbon by alternative

conductive media like for example silver, nickel or others is one milestone to achieve in the development of advanced BAE [412–414]. Other approaches include the doping of the metal oxide itself to increase its electrical conductivity; however stability of those dopants under charging/discharging cycle conditions is still questionable. Other promising catalysts for BAE including NiCo<sub>2</sub>O<sub>4</sub> or LaNiO<sub>3</sub> display good electrical conductivity without the need of a conductive additive. The readers are referred to [415–418] and reference therein for a deeper overview on the topic of BAE.

In spite of the improvements towards BAE development, the challenge of low reversibility of zinc electrode still remains, although it can be mostly alleviated with the selection of proper electrolyte system; composition and nature.

Since the electrochemistry of the zinc is close associated to the nature of the electrolyte to which it is exposed, the main strategy from older approaches until recent developments have been focused on the improvement of zinc anode reversibility by means of tuning the electrode characteristics, and electrolyte alkalinity adjusting its properties to zinc requirements, and at the end to battery specifications.

As it is summarized in Table 8, there is any electrolyte system without challenges to overcome when it is implemented for secondary zinc-air batteries or other systems based on zinc. In this sense, researcher should make a compromise among the zinc electrode characteristics and electrolyte properties as function of the requested battery specification and/or application. For example, if long run time between charges is requested, then high-energy battery is demanded based on a stable discharge voltage



**Table 6**

List of some deep eutectic solvents (DESS) obtained by complexation between hydrogen acceptor and hydrogen-bond donor molecules.

Hydrogen acceptor	Hydrogen-bond donor	Molar ratio	Reference
1,8-Cineole	Ibuprofen	From 4:1 to 2:1	[386]
Antimony chloride	Acetamide	From 0:1 to 0.9:0.1	[384]
Benzoic acid	Urea	2:1	[387]
Benzyltriphenylphosphonium chloride	2,2,2-Trifluoroacetamide	3:1	[374]
Benzyltriphenylphosphonium chloride	Ethylene glycol	1:3	[374]
Benzyltriphenylphosphonium chloride	Glycerine	1:5	[374]
Choline acetate	Glycerol	1:1 to 1:2	[371]
Choline chloride	1,3-Dimethylurea	2:1	[372]
Choline chloride	1,4- Butanediol	1:2	[382]
Choline chloride	1-Methylurea	2:1	[372]
Choline chloride	4- Hydroxybenzoic acid	2:1, 1:2	[388]
Choline chloride	Acetamide	2:1	[372]
Choline chloride	Aconitic acid	1:1	[389]
Choline chloride	Adiptic acid	1:1	[322,376]
Choline chloride	Benzamide	2:1	[372]
Choline chloride	Benzoic acid	1:2	[322]
Choline chloride	Citric acid	2:1	[322,376]
Choline chloride	Citric acid	1:2, 1:3	[389]
Choline chloride	Ethylene glycol	1:2	[382]
Choline chloride	Fructose: water	1:2 (1 + 1)	[389]
Choline chloride	Gallic acid	2:1	[388]
Choline chloride	Glucose: water	1: (1 + 1)	[389]
Choline chloride	Glycerol	1:2	[368,382]
Choline chloride	Levulinic acid	1:2	[368]
Choline chloride	Maleic acid	1:1, 1:2, 1:3	[389]
Choline chloride	Malic acid	1:1, 1:2, 1:3	[389]
Choline chloride	Malonic acid	1:1	[322,376]
Choline chloride	Mandelic acid	1:2	[388]
Choline chloride	Oxalic acid	1:1	[322]
Choline chloride	Phenyl acetic acid	1:2	[322,376]
Choline chloride	Phenylpropionic acid	1:2	[322,376]
Choline chloride	Succinic acid	1:1	[322,376]
Choline chloride	Sucrose: water	1:2 (1 + 1)	[389]
Choline chloride	Thiourea	2:1	[372]
Choline chloride	Tricarballic acid	2:1	[322,376]
Choline chloride	Trifluoroacetamide	1:2	[376]
Choline chloride	Urea	2:1	[372]
Choline chloride	Valeric acid	1:2	[388]
Citric acid	1,3-Dimethylurea	1:3.5	[390]
D- (-)- Fructose	1,3-Dimethylurea	1:1	[390]
D- (+)- Mannose	1,3-Dimethylurea	1:5	[390]
Ethylammonium chloride	Acetamide	1:1.5	[381]
Ethylammonium chloride	Trifluoroacetamide	1:1.5	[381]
Ethylammonium chloride	Urea	1:1.5	[381]
Fructose	Malic acid	1:1	[389]
Fructose	Sucrose	1:1	[389]
Fructose	Sucrose: glucose	1:2 (1+ 1)	[389]
Glucose	Citric acid	1:2	[389]
Glucose	Fructose	1:1	[389]
Glucose	Maleic acid	1:4	[389]
Glucose	Malic acid	1:1	[389]
Glucose	Sucrose	1:1	[389]
Iron (III) chloride	Choline chloride	2:1	[391]
L- (+)- Tartaric acid	1,3-Dimethylurea	1:7	[390]
L- Menthol	Ibuprofen	3:1	[386]
Magnesium perchlorate	Acetamide	1:5	[392]
Magnesium perchlorate	Acetamide: urea	0.5:9.5 (5.5 + 4)	[393]
Magnesium triflate	Acetamide: urea	0.5:9.5 (5.5 + 4)	[393]
Menthone	Ibuprofen	From 4:1 to 2:1	[386]
Methyltriphenylphosphonium bromide	2,2,2- Trifluoroacetamide	1:8	[374]
Methyl triphenil phosphonium bromide	2,2,2-Trifluoroacetamide	1:8	[394]
Methyl triphenil phosphonium bromide	Ethylene glycol	1:4	[394]
Methyltriphenylphosphonium bromide	Ethylene glycol	1:4	[374]
Methyltriphenylphosphonium bromide	Glycerine	1:1.75	[374]
Methyl triphenil phosphonium bromide	Glycerol	1:2	[394]
N,N-Diethyl ethanol ammonium chloride	2,2,2-Trifluoroacetamide	1:2	[394]
N,N-Diethyl ethanol ammonium chloride	Ethylene glycol	1:3	[394]
N,N-Diethyl ethanol ammonium chloride	Glycerol	1:2	[394]
Proline	Citric acid	1:1, 1:2, 1:3	[389]
Sorbitol	1,3-Dimethylurea: NH <sub>4</sub> Cl	1:1 (0.5 + 0.5)	[390]
Sucrose	Citric acid	1:1	[389]
Sucrose	Maleic acid	1:1	[389]
Tellurium chloride	Acetamide	From 0:1 to 0.4:0.6	[384]
Thymol	Ibuprofen	2:1	[386]
Tin (II) chloride	Choline chloride	2:1	[391]
Trehalose	Citric acid	1:2	[389]

**Table 6** (Continued)

Hydrogen acceptor	Hydrogen-bond donor	Molar ratio	Reference
Zinc Bromide	Choline chloride	2:1	[391]
Zinc chloride	Acetamide	1:4	[351]
Zinc chloride	Ethylene glycol	1:4	[351]
Zinc chloride	Hexanediol	1:3	[351]
Zinc chloride	Urea	1:3.5, 7:2	[351]
Zinc perchlorate	Acetamide	1:4	[383]
$\alpha$ -Naphthol	Urea	3:1	[387]

Adapted from [387] with permission of The Royal Society of Chemistry.

**Table 7**

Comparison of technical characteristics of mature, developed and developing BEES [44,54,74,95,236,249,396,397,402–410].

	Ni-Zn	Hybrid-Zn	Zn-ion	Zn-air	Pb-acid <sup>a</sup>	Ni-Cd	Ni-MH	Li-ion	
Anode	ZnO/Zn	Zn	Zn	Zn	ZnO/Zn	Pb	Cd	MH	C
Cathode	NiOOH	LiMn <sub>2</sub> O <sub>4</sub>	LiFePO <sub>4</sub>	$\alpha$ -MnO <sub>2</sub>	EMD	PbO <sub>2</sub>	NiOOH	NiOOH	LiCoO <sub>2</sub>
Electrolyte	alkaline (KOH)	mild (ZnCl <sub>2</sub> /LiCl)	mild (ZnCl <sub>2</sub> /LiCl)	mild (ZnSO <sub>4</sub> )	alkaline (KOH)	acid (H <sub>2</sub> SO <sub>4</sub> )	alkaline (KOH)	alkaline (KOH)	organic (-)
Efficiency (% , average)	95	>95	>95	>95	50	75–90	65–90	70	>95
Wh kg <sup>-1</sup>	60–80	50–80	–	50–80	180–200	30–50	10–75	80	160
W/kg	1000–2000	–	>1000	1450	200	75–300	150–300	200–1000	400
Cycle life (C-rate)	200–1000	4000 (4C)	>500 (6C)	100 (6C)	200 (C/15)	200–2500	300–2500	300–600	>1000+
Discharge time (ms–h)	s–h	–	–	–	s–24 h + <sup>(b)</sup>	s–h	s–h	–	m–h
Storage durability	–	–	–	–	h–months <sup>b</sup>	min–days	min–days	–	min–days
Cost (\$/kWh)	303–500	200	–	–	10–400	200–700	400–1500	400	500–2500
Cost (¢/kWh/cycle)	~70 <sup>d</sup>	~5 <sup>d</sup>	~40 <sup>d</sup>	–	3–5 <sup>c</sup>	20–107	20–115	~90 <sup>d</sup>	15–100

<sup>a</sup> Ranking based on different type of lead-acid batteries.

<sup>b</sup> Determined for Metal-Air batteries in general.

<sup>c</sup> Estimated for alkaline Zn/MnO<sub>2</sub> secondary battery.

<sup>d</sup> Estimated based on data reported in the table.

**Table 8**

Summary of the issues to handle (depending on the compound and/or additive) with the selected electrolyte for secondary zinc-based battery applications.

Electrolyte	AQUEOUS			NON-AQUEOUS			
	Alkaline	Neutral	Acid	SPE	GPE	RTILs	DES
Formation of carbonates	X						
Hydrogen evolution reaction	X	X	X				
Dendrite formation	X		X				
Low solubility of zinc salt				X	X		
Ionic conductivity (S cm <sup>-1</sup> ) <sup>a</sup>	0.5–0.6	0.2–0.3	0.5–0.7	10 <sup>-8</sup> –10 <sup>-6</sup>	10 <sup>-4</sup> –10 <sup>-3</sup>	10 <sup>-5</sup> –10 <sup>-2</sup>	10 <sup>-5</sup> –10 <sup>-3</sup>
Sensitive to impurities – high purity and expensive products are required –						X	
Lower temperature range	X	X	X				
High viscosity				X	X	X	X
Limited electrochemical window	X	X	X				
Water evaporation or ambient moisture uptake	X	X	X			X	

profile and capacity. On the other hand, if the demand is bursts energy, accelerated process, then high-power density battery is requested. In this case, fast discharge capability in short period of time is mandatory. Common to both cases is how frequent is such demand required which will impact the lifecycle of the battery and at the end the electrode integrity/robustness.

Aqueous alkaline electrolytes have been commonly used in zinc-air batteries. The aqueous nature as well as the alkalinity of this electrolyte system promotes the precipitation of insoluble carbonate, dendrite growth, and zinc shape change process or zinc corrosion, all of them limiting the performance of secondary zinc-air batteries.

Although a great effort has been done to mitigate these detrimental issues since the invention of secondary zinc-based technologies, there is any unique solution to overcome all these aqueous alkaline limitations. *From the authors competences and experience it seems to be that an aqueous alkaline electrolyte with additives is necessary in order to improve the cycle life of zinc anode having in some cases the penalty of losing capacity.* However, as it

was pointed out above, all in all depends on the requirement and application of the battery. If the demand is to provide a stable energy density for long period of time, then the loss of capacity by the adapted electrolyte properties via additives is well compensated meanwhile the battery can provide the such energy over an extended cycle of life.

The aqueous alkaline electrolyte composed by *carbonate and fluoride ions in KOH environment saturated with ZnO* is as promising starting point to minimize the zinc dissolution, maintain the shape of the anode during the cycling, polarize the HER and therefore, to enhance the zinc electrode performance in aqueous alkaline electrolyte, however a systematic research should be done in order to defined the optimal composition (perhaps, additive concentration and ratio among them) as function of the end-user requirements.

On the other hand, an *alternative approach* to improve for example the lifecycle of the electrically rechargeable zinc-air battery is the use of *non-alkaline electrolyte*. In this case the pH of the electrolyte is in the range of slight acidic to slight alkaline. This

type of electrolyte minimizes or skips some of the issues associated to the common used alkaline electrolyte being the principal evidence of extended cycle life. However, issues such as HER and/or chlorine evolution (for those electrolytes based on chloride salts) should still carefully handle. The use of additives such as urea can polarize the hydrogen evolution reaction to more negative voltage, as well as the *implementation of buffers to regulate any drastic pH change* especially at the interface electrode/electrolyte. On the other hand, alternative salts to chloride ones might be used as sources of zinc ions.

In general, the *aqueous based electrolyte systems are preferred* because they are environmentally benign and cheaper. But the *hydrogen evolution is still an issue to overcome* since it is close to zinc deposition and consequently the battery performance is reduced. In order to avoid this problem, and as an *alternative approach, the development of non-aqueous electrolytes for secondary zinc-air battery* has been started in the past years. During this review it has been identified four types of non-aqueous electrolyte systems. Among them, SPEs due to its low conductivity and some flammable and volatile GPEs are not feasible for secondary zinc-air batteries. The RTILs based electrolyte systems present low vapor pressure, high thermal stability and high ionic conductivity among the other non-aqueous electrolyte systems. Unfortunately, their industrial application is limited because they require high purity besides to be expensive. Thereby, *from the authors point view, alternative DESs based electrolyte are the most interesting ones to be incorporated in an non-aqueous based secondary zinc-air battery because they are cheaper and greener than e.g. RTILs.*

All in all, *the electrolyte selection will mainly depend on the end-user battery specifications and application.* Thus, although zinc-based batteries based on alkaline aqueous electrolytes are a mature technology for primary application, its implementation in secondary systems is still in process to achieve a commercial level. So far alkaline reversible zinc-air battery can be considered as a system that has been demonstrated under realistic operational environment (perhaps TRLs 6–8), but with relevant limitations (like cycle life) that avoid its extended commercialization. In this sense, the scientific community should focus on what have to be done in order to improve the zinc utilization and keep over the battery lifecycle a homogeneous current distribution through the electrode. It would help to improve the rate (power) capability as well as will minimize the formation of dendrites and passive layers due to local high current densities. Additive to the electrolyte is just a mitigation strategy.

On the other size, rechargeable zinc-based batteries using acid or near-neutral electrolyte formulations is an emerging technology (TRLs 4–5) with high potential of application, although relevant improvement must be implemented at all level. Attention should be pay on the development of proper zinc-electrode structure and *buffer systems to minimize the drastic pH changes* happening at the electrode/electrolyte interface as a function of the charging/discharging time as well as to *reduce the passivation processes from discharge products. Additive to avoid size reactions like evolution of hydrogen and chlorine should be systematically investigated.*

Finally, the non-aqueous based electrolyte zinc-air batteries is considered a technology at TRLs around 2–3, although companies like Fluidic Energy has sold several units claiming its technology based on one type of these electrolytes. Development of non-aqueous electrolyte should address good zinc dissolution, good ionic conductivity, minimize or avoid the use of volatile and toxic solvents and compounds, improved the contact (in case of solid polymer electrolytes) electrode/electrolyte during charge/discharge. In addition, the electrolyte should assure good oxygen diffusion, although in the latter cell design may help by increasing the oxygen partial pressure. From the different kind of non-aqueous electrolytes, *deep eutectic solvents seem to be a promising*

*candidate to be further investigated owing to their properties similar to IL in addition to their non-toxicity, non-volatility and easy handling/accessibility.*

It is worth to point out that further progress on any of these zinc-based technologies goes through an *effective development of the cathode electrode*, which beyond the challenges itself associated to the anode/electrolyte, can be considered as the lesser capacity electrode and thus one of the major limiting factors. Therefore, *scientific community dedicate to the development and improvement of cathode catalysts should take into account relevant environment testing conditions [419], as for example realistic electrolytes compositions ideally designed to protect and improve the zinc electrode capabilities, but in some cases detrimental to the cathode performance or stability.*

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