RESEARCH ARTICLE

Systematic cycle life assessment of a secondary zinc–air battery as a function of the alkaline electrolyte composition

Aroa R. Mainar[1,2] (iD) , Elena Iruin[1], Luis C. Colmenares[1], J. Alberto Blázquez[1] & Hans-Jürgen Grande[1,2]

[1]CIDETEC Energy Storage, Pº Miramón, 196, Donostia-San Sebastián 20014, Spain
[2]Departamento de Ciencia y Tecnología de Polímeros, Facultad de Química, UPV/EHU, Pº Manuel de Lardizábal 3, Donostia-San Sebastián (Guipúzcoa) 20018, Spain

Abstract

Development of secondary zinc–air batteries goes through a proper specification of the electrolyte formulation adapted to extend the cycle life of the battery. However, defining an optimal formulation is not a trivial work due to the specific requirements for each electrode. At half-cell level, it has been determined that ZnO-saturated 4 mol L^{-1} KOH with 2 mol L^{-1} KF and 2 mol L^{-1} K_2CO_3 (4s-2) is the most suitable formulation to increase the cycle life of secondary zinc electrode, whereas additive-free 8 mol L^{-1} KOH (8-0) formulation is more beneficial for the bifunctional air electrode (BAE). Through this systematic cycle life assessment, it has been found that the most suitable electrolyte formulation for the full cell system is a compendium for both electrodes requirements. It has determined an optimal electrolyte formulation for the full system consisting of ZnO-saturated 7 mol L^{-1} KOH with 1.4 mol L^{-1} KF and 1.4 mol L^{-1} K_2CO_3 (7s-1.4). This electrolyte composition increases at least 2.5 times the reversibility of the secondary zinc–air battery in comparison with that employing the traditional formulation for primary zinc–air batteries (additive-free 8 mol L^{-1} KOH). In addition, the development of a proper cell design or separator is also necessary to further enhance the secondary zinc–air cycle life.

Introduction

The current changes in the society energy consumption habits have requested modifications of the worldwide policies to promote the use of renewals as sustainable energy sources. The promotion of solar and wind energy sources has boosted the development of effective technologies able to store and deliver in a stable manner their intermittent energy supply. Among such technologies, the electrochemical energy storage systems (EESS) are one out the promising. These facts drive the development and implementation of secondary batteries for load-leveling applications. This development requests safety, long-cycle life, cheap, abundant, and environmental friendly materials.

Zinc–air is one out the suitable battery technologies to fulfill such requirements. Although the primary version is a worldwide well-established technology, its conversion to secondary system is still a challenge owning to the several issues related to zinc and its electrochemistry in high concentrated aqueous alkaline electrolyte. Therefore, since the electrochemistry of the zinc is closely associated to the nature of the electrolyte to which it is exposed, a key feature to achieve the long-cycle life of zinc is the selection and optimization of the proper electrolyte formulation.

The reversibility of the zinc has been intensively investigated having as starting point the traditional materials and the electrolyte formulation of the primary zinc–air

system, that is, 32 wt.% KOH (~8 mol L^{-1}). This electrolyte concentration has been usually selected owning to its high ionic conductivity. However, under such conditions, the solubility of zinc is also high. This fact increases the irreversibility of Zn/Zincate (zinc discharge product; $Zn(OH)_4^{2-}$) redox couple during extended charge/discharge (C/D) cycling, promoting the formation of dendrites and being the reason of zinc shape changes (non-uniform ZnO deposition). Thus, over battery cycle life these processes trigger the battery capacity fading. In this sense, and in order to develop secondary zinc–air batteries, researchers should better understand and properly deal with the electrolyte properties. From authors viewpoint, a good starting point is to analyze what it has learnt in other already established alkaline reversible zinc-based systems as, for example, secondary nickel-zinc technology.

One out of different strategies implemented over years to improve the reversibility of zinc electrode is the use of additives in the electrode [1–4] and/or electrolyte [5, 6] formulations [7, 8]. At electrode level, a variety of inorganic or organic compounds (readers are referred to ref. [1] for a detailed overview about this topic) have been used in the zinc paste to mitigate negative electrode harmful issues. Furthermore, due to the high zinc dissolution rate into the aqueous alkaline electrolyte forced by concentration gradients (viz. migration of zincate ions into bulk electrolyte), the use of ZnO in the electrode paste composition could be also an effective approach to assure a good reservoir of Zn. On the other hand, ZnO is also dissolved in KOH electrolyte (till zincate saturation, investigated since more than half a century ago [9] in strongly alkaline solutions) to reduce the zinc dissolution rate and to minimize the migration of $Zn(OH)_4^{2-}$ from the negative electrode. This approach will promote a uniform zincate concentration in the electrode/electrolyte interlayer, and hence, it induces during charging homogeneous deposition of ZnO upon zinc electrode.

On the other hand, electrolyte additives [10] are also used to increase or to maintain electrolyte's ionic strength (especially in less alkaline electrolytes), as well as to promote uniform deposition of zinc [5]. This approach was one of the procedures implemented in secondary zinc-based technologies such as nickel-zinc [7, 11–13]. For this technology, advanced electrolyte formulations containing a set of additives have been developed to suppress the problems associated with the reversibility of the zinc. Since early 1980s, a series of investigations have been done in this field; the ZnO, KF, and K_2CO_3 have been reported as effective electrolyte additives [7, 11, 13]. Such systematic research reached an suggested optimized electrolyte formulations (viz. ZnO-saturated 3.2–4.5 mol L^{-1} KOH with 2.0 mol L^{-1} of either additive) which allowed the nickel-zinc system to increase the number of C/D
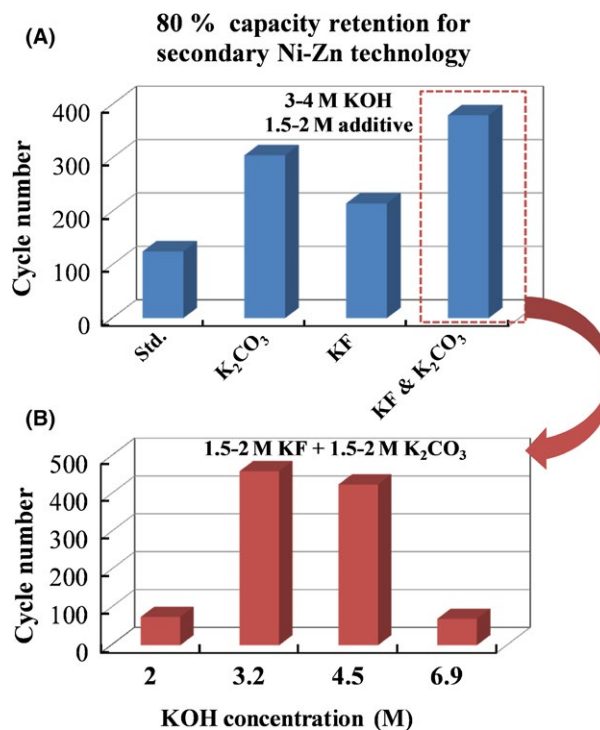

Figure 1. Cycle performance of nickel-zinc batteries based on aqueous alkaline electrolyte formulations saturated with ZnO. (A) Effect of 1.5–2 mol L^{-1} K_2CO_3 and KF additives in 3–4 mol L^{-1} KOH aqueous alkaline electrolyte, and (B) effect of KOH concentration for the optimal additive approach (red dotted line). Adapted from [7, 11, 14].

cycles (before declining below 80% of initial capacity) from 75 to 100 (in 6.8 mol L^{-1} KOH) to 425–460 cycles (in KOH-based electrolytes containing additives) as it is summarized in Figure 1 [11]. Following such electrolyte formulation progress, Bonnick and Dahn [12] employed this optimal electrolyte composition (viz. 4 mol L^{-1} KOH with 2 mol L^{-1} KF and 2 mol L^{-1} K_2CO_3, saturated with ZnO) during their implementation of coin cells as a reliable nickel-zinc battery tester vehicle. They suggested adapting this methodology to assess other alkaline zinc-based technologies such as under development rechargeable zinc–air batteries.

Hwang et al. [15] have investigated the electrochemical reactions at the negative electrode in zinc–air batteries. They highlighted the importance of selecting properly the concentration of hydroxide ions (OH-) to suppress the zinc corrosion and to minimize the hydrogen evolution reaction (HER). They concluded that KOH molarities between 4 and 6 are optimal to get the highest current for cell operation. Whereas 4 mol L^{-1} KOH is better to suppress the HER (although the selection of suitable cut-off voltage will also contribute to withhold the HER), 6 mol L^{-1} is better for cell performance based on its lower resistance. Nevertheless, it was clearly pointed out

that when additives are intended to be used, higher KOH concentrations are preferable. Li et al. [16] have also shown for a zinc–air fuel cell that the best performance was reached using 7 mol L^{-1} KOH electrolyte resulting in the highest current density (ca. 100 mA cm^{-2} at 1.0 V vs. Zn).

As it is known, zinc as negative electrode material has diverse application in systems like manganese–zinc, silver–zinc, nickel–zinc, and zinc–air. As noticed, all these systems are alkaline based, and hence, the electrochemistry of the zinc is basically the same. In that sense, the incorporation of additives has been defined as strategy to preserve a long-lasting reversible zinc electrode. However, the positive electrode plays also a crucial role in the final battery performance. Therefore, the strategy may be totally different than those applied for zinc electrode. Although it is still not a common practice in the scientific community focused on developing advanced bifunctional air electrodes, some authors have investigated whether electrolyte additives have a benefit or not on the positive electrode characteristics. For example, in nickel-zinc system, Adler et al. [7] have found Zn (eventually ZnO) on the NiOOH electrode. The presence of ZnO might block some electrode active areas affecting its capacity retention. Chen et al. [17] in silver-zinc batteries found that F$^-$ and CO_3^{2-} ions reduced the capacity of the battery due to the formation of AgF and Ag_2CO_3 upon silver electrode. In this context, high concentrations of KOH are preferred to avoid the precipitation of additive species into the porous structure of the electrode. On the other hand, Schröder et al. [18] suggested that for extending the lifetime of the zinc–air battery, it is acceptable to add about 30 mol% potassium carbonate (which reduces the carbonation reaction [19]) to high molar KOH electrolyte, although it slightly impacts the battery performance. Hwang et al. [20] determined that fluoride ion (specifically from KF precursor salt) is a good additive to reduce the overpotential toward both ORR and OER at α-MnO_2-positive electrode. They found that there is an optimal concentration of F$_-$ for each reaction.

In this order of ideas and to elucidate to what extent the electrolyte formulation (KOH-KF-K_2CO_3 saturated with ZnO) affects the electrochemical performance of a homemade secondary zinc–air battery, the present study intents to systematically achieve an optimal electrolyte composition that assures the best full cell reversibility under here proposed testing conditions. The impact on each electrode (half-cell testing) of the given electrolyte formulations will be analyzed by means of an accelerated protocol taking into account the cycle number with 100% of initial capacity retention. At the end, the full cell rechargeable zinc–air battery will be tested under more realistic operating conditions (viz. higher depth of discharge [DoD]) contrasting the number of cycles achieved by the traditional electrolyte against the defined electrolyte formulation.

Experimental Section

Aqueous alkaline electrolyte systems

The different electrolyte systems were prepared from KOH (Sigma-Aldrich, 85% purity), ZnO (Sigma-Aldrich, Madrid, Spain, 99% purity), KF (Sigma-Aldrich, 99% purity), and K_2CO_3 (Sigma-Aldrich, 99% purity) dissolved in deionized water. All chemical were used as-received. Each electrolyte system has been labeled as Xs-Y where "X" is the molarity of KOH, "s" reflects that the electrolyte system is saturated with ZnO, and "Y" represents the molarity of both KF and K_2CO_3 additives (a 1:1 molarity ratio between both was kept [7, 11–13]).

Electrolyte properties such as ionic conductivity, viscosity, and electrochemical potential window were determined. The ionic conductivity was measured at room temperature using a Crison conductimeter EC-meter GPL 31 (Hach Lange Spain SLU, Barcelona, Spain), while the viscosity was analyzed at different temperatures with a rheometer TA Instruments model AR2000EX (Waters Cromatografia SA, TA Instruments Division, Barcelona, Spain). Determination of the electrochemical potential window was performed in a standard three-electrode cell were the working electrode was a glassy carbon, the counter electrode a platinum wire and a zinc foil (Alfa, Aesar, Karlsruhe, Germany, 99.98%, 100 μm thickness), previously cleaned and treated, as pseudo-reference electrode (OCV$_{2 h}$: -1.27 V$_{RHE}$). A Biologic Multichannel Potentiostat Galvanostat (MPG) was used to sweep lineally the potential at 1 mV sec^{-1}.

Electrodes preparation and electrochemical characterization

Zinc electrodes were prepared from commercial (Umicore) powders with battery specification grade. The zinc paste was composed of 49.28 wt.% of zinc BIA, 21.12 wt.% of ZnO, 28.2 wt.% of the corresponding aqueous alkaline electrolyte formulation, and 1.4 wt.% of gelling agent carboxymethyl cellulose (CMC, Cekol, Grossenbrode, Germany). The zinc paste was properly mixed, and then, it was stored in a syringe before using. Electrodes based on Zn-paste (45 mg$_{Zn}$ cm^{-2}) with a geometric surface area of 1.3 cm^2 were prepared. The paste was deposited on copper mesh (Copper Net Foil for Battery Anode Substrate, MTI Corporation, Richmond, California, USA, 55 μm thickness) as current collector. The cycle life assessment of the zinc was evaluated in a symmetric two electrodes Zn/Zn homemade cell containing a cavity to place the zinc paste. A zinc foil (Alfa Aesar, 99.98%,

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250 μm thickness) was used as counter electrode. A glass fiber separator (Whatman Grade GF/D, Whatman plc. Maidstone, England) was embedded in the electrolyte system and placed between both electrodes. When the cell was closed, the separator presented around 370 μm thickness and 300 μL electrolyte volume. Cyclic voltammetry (CV) at 5 mV sec^{-1} was conducted using a Biologic MPG starting from OCV. The cycling potential range was defined between 0.16 V and -0.16 V $\pm$ 0.04 V depending on the sample to minimize corrosion issues.

The bifunctional air electrode (BAE) consisted of a monolayer prepared by mixing 20 wt.% of α-MnO$_2$-13 catalyst (see ref. [21] for more details), 70 wt.% carbon nanotube (CNT, Arkema, Barcelona, Spain), and 10 wt.% PTFE (Dyneon TF 5032 PTFE, 3M Germany GmbH, Neuss, Germany). The mixture was pressed against a carbon gas diffusion layer (Freudenberg H2315) applying twice 20 bar during 1 min. The resulting catalyst loading was ca. 5.5 mg cm^{-2} based on active material. BAE were electrochemically characterized employing a commercial ECC-Air cell (EL-CELL GmbH, Hamburg, Germany) with an active area of 2.5 cm^2. A zinc foil (Alfa Aesar, 99.98%, 250 μm thickness) was used as counter electrode, whereas a glass fiber filter (Whatman, GF/D) was placed as separator. The separator was embedded with 400 μL of the aqueous alkaline electrolyte system, and oxygen (Air Liquide, ALPHAGAZ 99.999% oxygen) was flowed (40 mL min^{-1}) at the BAE. The cycle life of the bifunctional air electrode was determined by each electrolyte system under accelerated testing conditions applying a constant current density of $\pm$10 mA cm^{-2} during 5-min charge and 5-min discharge cycling using a BaSyTec Battery Test System.

Zinc–air full cell characterization

The secondary zinc–air battery performance was analyzed in a homemade cell design. It consisted of zinc paste as negative electrode (45 mg$_{Zn}$ cm^{-2}), a glass fiber separator embedded with 300 μL of given electrolyte systems, and the BAE as positive electrode. The optimal electrolyte formulation was identified as function of the most lasting cycle life by means of an accelerated charge/discharge (C/D) cycling test at 2.5 mA cm^{-2} requiring 100% retention of initial 5 mAh g$_{Zn}$$^{-1}$. Once the aqueous alkaline electrolyte formulation was defined, a more realistic testing protocol was defined through a full discharge (Fig. S1) and galvanostatic pulse cycling procedure at different currents densities (Fig. S2). Based on these preliminary results, the homemade rechargeable zinc–air battery was evaluated by C/D cycling at 2 mA cm^{-2} and 100 mAh g$_{Zn}$$^{-1}$, where the effect on the cell cycle life of developed electrolyte formulation was contrasted with the additive-free 8 mol L^{-1} KOH electrolyte formulation.

Results and Discussion

Electrolyte basic specifications

The reversibility of zinc is closely related to the electrolyte nature. Traditionally, secondary zinc-based energy storage systems have been developed with aqueous alkaline electrolyte. In this medium, as mentioned, the zinc dissolution is too high, presenting problems associated with morphology change, dendrite growth, and corrosion ([5] and refs. cited therein).

The strategy followed in this work has been based on the modification of the traditional electrolyte formulation (6–8 mol L^{-1} KOH) by the addition of specific additives, such as ZnO to mitigate or reduce the zinc dissolution; and potassium fluoride (KF) and potassium carbonate (K$_2$CO$_3$) to reduce the zinc dissolution and/or to delay the HER onset. The combinations of additives can improve their benefits such as it has been demonstrated for nickel-zinc system. The mixture of alkaline-fluoride and alkaline-carbonate electrolytes reduces the zinc shape change, and it results in a more uniform distribution of zinc [11]. However, the determination of the optimal electrolyte formulations is nontrivial work. There is not a fix formulation to be implemented for all the needs. Therefore, it is necessary to assume the penalties in benefit of cell characteristics that are sought. Consequently, in this work, the optimal electrolyte formulations are provided for each electrode, and finally, for the full cell system. This section compresses a systematic study done on different electrolyte formulations based on KOH and selected additives. The electrolyte specifications were outlined as a function of the ionic conductivity, viscosity, and electrochemical stability window (electrolyte potential window – from H$_2$ to O$_2$ evolution onset potentials).

The ionic conductivity (IC) has been determined for each electrolyte formulation as shown in Figure 2(A). As noticed, 6–8 mol L^{-1} KOH (6-0; 8-0) have the highest IC. However, this value drops when the electrolyte is saturated with zincate ions (about 17% for ZnO-saturated 8 mol L^{-1} KOH: 8s-0). This decay is mainly due to the consumption of [OH$^-$] (viz. ZnO + H$_2$O + 2OH$^-$ $\leftrightarrow$ Zn(OH)$_4$$^{2-}$) instead of an increase in the viscosity (Table 1). Thus, the highest IC of ZnO-saturated electrolyte is 6 mol L^{-1} KOH (6s-0). The addition of KF and K$_2$CO$_3$ further induces a decrease of the ionic conductivity (up to 306 mS cm^{-1} for 8s-2) owning to an increment of its viscosity (Fig. S3), which reduces the mobility of the ions. However, the incorporation of these additives improves the physicochemical stability of the electrolyte at low temperature (-10°C) and at lower KOH concentrations where the zinc is less soluble (Fig. S4). This characteristic is relevant for real applications where the battery may be exposed to a range of temperatures.
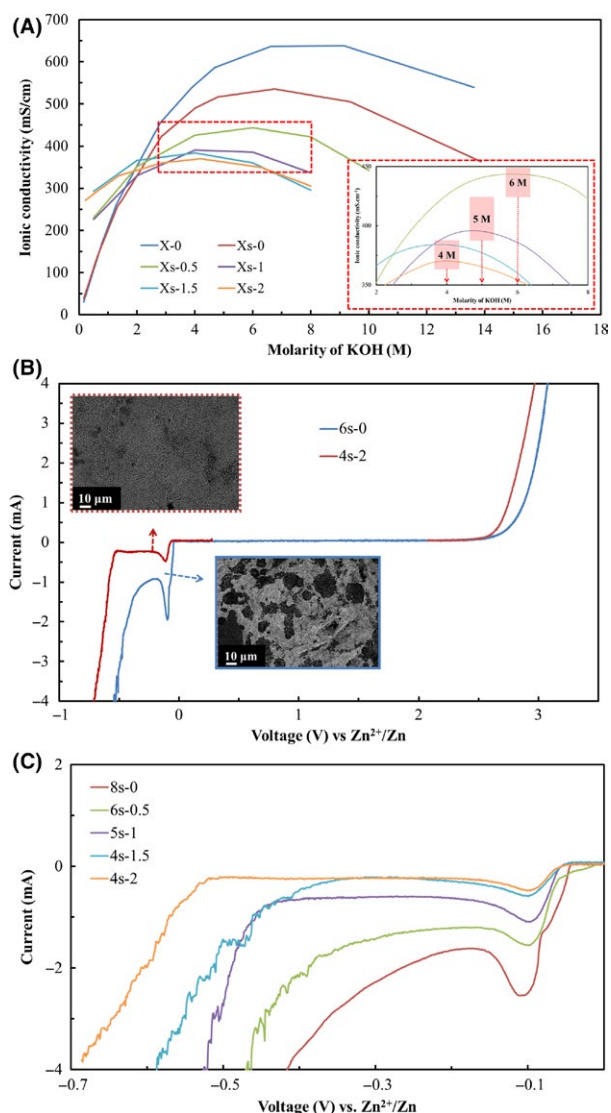
Figure 2. (A) Ionic conductivity of different electrolyte formulations, (B) effect of electrolyte additives on the electrochemical stability window and zinc deposition (FE-SEM pictures inserted), and (C) polarization of HER on different electrolyte systems. LSV at 1 mV sec^{-1}.

In order to investigate the electrochemical influence of additives (KF and K_2CO_3), ZnO-saturated electrolyte system (6s-0, blue line in Fig. 2B) has been defined as blank sample, where the $Zn(OH)_4^{2-}$ in the solution are the source of zinc for its electrodeposition upon glassy carbon surface. In this way, it is possible to distinguish the zinc deposition potential and the onset potential for the hydrogen evolution reaction (HER). Figure 2(B) illustrates the expansion of the electrochemical stability window when the additives (4s-2, red line) are incorporated in the aqueous ZnO-saturated KOH electrolyte. Additives delay around 394 mV the HER, whereas the system without additives (6s-0, blue line) showed a voltage difference between the

zinc deposition and HER of ca. 81 mV. The overpotential for hydrogen reduction is strongly affected by the ions present in the solution owing to their specific adsorption on the zinc electrode and their interaction with water [22]. The presence of $Zn(OH)_4^{2-}$ ions generally results in a reduction of the hydrogen reduction rate [23–26], and as it has explained before, the added ZnO reacts with OH$^-$ and water forming $Zn(OH)_4^{2-}$. The KOH-based electrolyte containing KF and K_2CO_3 additives reduce the solubility of discharged zincate ions contrary to the traditional additive-free KOH electrolyte. The rate of zinc active material redistribution is found to decline dramatically [27] leading a more uniform and substantial zinc deposition as shown in Figure 2(B) where the hydrogen evolution current is very small [28]. In this way, both formed zincates and KF-K_2CO_3 additives included in 4s-2 electrolyte delay the higher HER contribution to more negative potentials.

The FE-SEM pictures inserted in Figure 2(B) highlight that the KF-K_2CO_3 additives promote a homogeneous zinc deposition (red marked picture) in comparison with the less uniform zinc deposition obtained from the additive-free 6s-0 electrolyte formulation (blue marked picture). On the other hand, meanwhile allowing the zinc deposition, higher concentration of additives induces an effective suppression/delay of H_2 evolution reaction as shown in Figure 2(C). Furthermore, as a function of the composition of the electrolyte (8-0 vs. 4s-2), the corrosion rate of 1 g of zinc sample was measured by a standard gassing test at 70°C, in which the volume of evolved hydrogen was collected during a period of 24 h. The results have shown that effectively the electrolyte 4s-2 suppresses the generation of H_2 by 30% in comparison to additive-free 8 mol L^{-1} KOH electrolyte formulation (0.250 μL (h·g$_{Zn}$)$^{-1}$ for 4s-2 in contrast to 0.375 μL (h·g$_{Zn}$)$^{-1}$ for 8-0).

Taken into account the ionic conductivity and the electrochemical stability window, electrolytes 8-0 (KOH solution without any additive) and 4s-2 (ZnO-saturated 4 mol L^{-1} KOH with 2 mol L^{-1} KF and 2 mol L^{-1} K_2CO_3) have been selected as baselines due to the highest ionic conductivity (8-0) and the highest electrochemical stability (4s-2). These formulations have been used as references to evaluate the systematic electrolyte development proposed in this work.

Reversibility of zinc anode electrode

Taking as basis the primary zinc–air system, the zinc paste composition has been based on the formulation proposed by Malone et al. [29]. In brief, it is constituted by 70.4 wt.% of zinc active material, 28.2 wt.% of alkaline electrolyte system, and 1.4 wt.% of Carboxymethyl cellulose (CMC) as gelling agent. However, Malone et al. studied

Table 1. Properties of baseline aqueous alkaline electrolyte formulations.

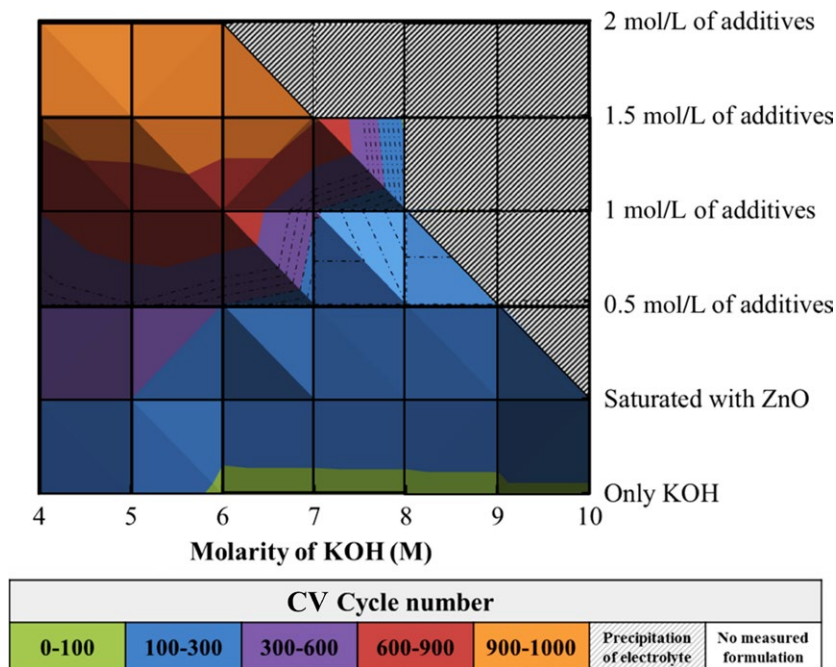| Electrolyte formulation	Ionic conductivity (mS cm^{-1}) at 25°C	Viscosity (Pa sec) at 25°C	HER onset (V)
8-0	638	0.00166	−0.160
6s-0	536	0.00168	−0.180
4s-2	370	0.00229	−0.518

Figure 3. Reversibility map of zinc anode electrode as a function of KOH and additives concentration.

a primary zinc–air battery where ZnO was not used in the zinc anode formulation. Nevertheless, for reversible zinc electrodes, ZnO is recommended to be added to the electrode formulation in order to deal with electrode volume changes (and hence, the variation of the battery internal pressure) during C/D cycling tests [ref. [1] and references cited therein]. In this context, the present work has implemented a relation of 70:30 of Zn to ZnO as active material in the paste. This relation is based on the patent of Kainthla and Manko [30] who suggested to use between 33 and 40 wt.% of ZnO respect to Zn. This ratio was preliminary confirmed by C/D cycling test performed in 8-0 electrolyte using p625 cell tester (results not shown and performed under specific protocol at Varta Microbattery GmbH). The ratio of 70 to 30 (Zn:ZnO) is later corroborated in full cell with the selected electrolyte formulation (*Determination of full cell cycle life by accelerated test*).

The effect of the electrolyte formulation on the reversibility of the zinc–paste electrode is determined by cyclic voltammetry (CV) at 5 mV sec^{-1}. The electrode is cycled

until typical zinc features CV (anodic and cathodic peaks as pointed in Fig. S5) are not more appreciable. A wide range of electrolyte formulations are analyzed and the CV cycle number for each case determined. Based on these results, a secondary zinc electrode reversibility map is constructed as a function of KOH and additives concentration (Fig. 3).

As expected, the lowest zinc reversibility (between 0 and 100 CV cycles) is observed for those electrolytes without additives and with high concentrations of KOH (above 6 mol L^{-1}) where the solubility of zinc is higher. Decreasing the KOH concentration (viz. 4 and 5 mol L^{-1}), and thus zinc dissolution, the CV cycle number increases close to 300. Hence, lower KOH concentrations are preferred to extend the cycle life of secondary zinc electrodes.

The reversibility of zinc is enhanced by the saturation of electrolyte with ZnO at any KOH concentration. This result is due to the fact that more uniform concentration of zincate ions in the near of the electrode surface is obtained. Thus, the dissolution of zinc species through
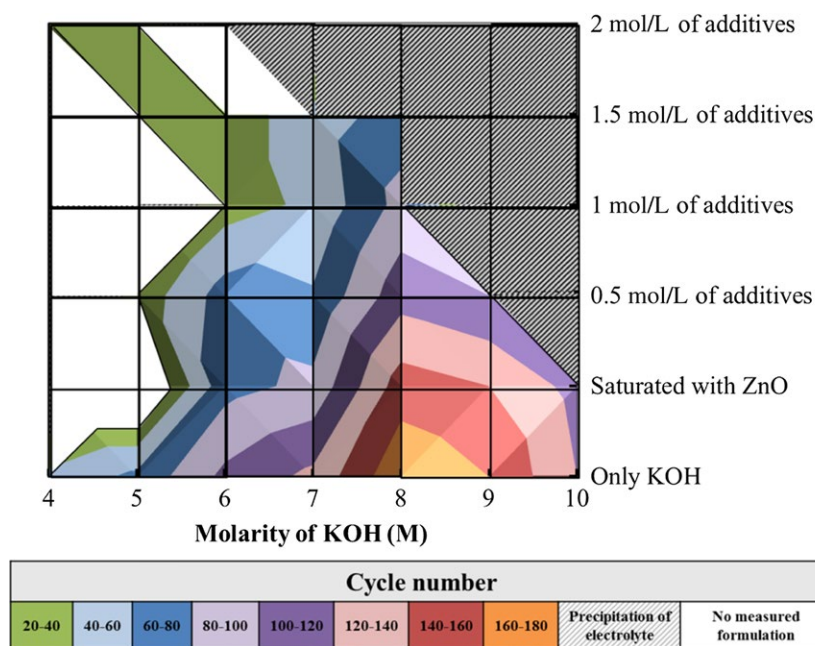
Figure 4. Cycle life map of bifunctional air electrode as a function of KOH and additives concentration.

the electrolyte system is reduced and the reversibility improved. Furthermore, water activity decreases by its consumption via reaction with ZnO (see above in *Electrolyte basic specifications*), and hence, saturation with ZnO promotes as well a reduction of the HER rate.

Finally, as it is shown in Figure 3 for a given concentration of KOH, the electrochemical performance of secondary zinc electrode increases at higher concentrations of additives. Thus, the maximal zinc cycle life is achieved with ZnO-saturated low KOH concentration in the range of 4–7 mol L^{-1} and high concentration of additives in the range of 1.5–2 mol L^{-1}. In these cases, the system is able to reach close to 1000 CV cycles being the optimal electrolyte formulation defined as 4 mol L^{-1} KOH, 2 mol L^{-1} KF, and 2 mol L^{-1} K_2CO_3 (4s-2). This formulation is in good agreement with the alkaline electrolyte compositions reported for secondary zinc electrodes working in nickel-zinc batteries [7, 11–13]. Furthermore, for secondary zinc–air batteries, 4 mol L^{-1} of KOH was also found by Hwang et al. [15] as an optimal concentration to reduce effectively zinc corrosion (via HER) and to enhance the reversibility of zinc electrode.

Bifunctional air electrode (BAE) cycle life

The reactivity of novel materials toward the ORR and OER in advanced BAE is usually investigated in additive-free KOH electrolytes with concentrations ranking, in general, from 0.1 to 1.0 mol L^{-1} (see, e.g., Table 1 in [31] and [32] for a quick overview). However, for

industrial applications and as it is already demonstrated in *Reversibility of zinc anode electrode*, the secondary zinc electrode needs specific additives to increase its reversibility. In this context, it is the first time that a BAE (MnO$_2$-based) cycle life is evaluated under specific electrolyte formulations for the secondary zinc electrode. The criterion used for the quantification of the BAE cycle number is based on 100% retention of the initial cell capacity. Figure S6(A) illustrates an example of this criterion where the full cell with the electrolyte 4s-2 does not achieve 100% of the initial cell capacity retention after 50 C/D cycles while 8-0 electrolyte formulation does. Based on this criterion, the cycle life mapping achieved by the BAE as a function of the electrolyte formulation is shown in Figure 4.

As observed, the maximal cycle life range (160–180 cycles) of the BAE is found for 8-0 electrolyte formulation, which is an electrolyte with high alkalinity, good ionic conductivity, and without any additives. The latter is rationalized with the fact that ORR and OER are surface sensitive reactions where any "surface contaminant" may be detrimental for the catalyst activity. Generally, this matter could be associated to active surface blocking effects.

During discharge, ORR takes place on the BAE, thus oxygen from the atmosphere diffuses into the cathode and it is reduced to OH$^-$ which migrates to the zinc anode generating zincate ions $(Zn(OH)_4^{2-})$ and releasing electrons from the negative electrode to the BAE through an external circuit. The BAE configuration should then allow O$_2$ diffusion and good electrical conductivity. These two properties can be disturbed by the clogging of its porous structure

and/or the formation of less conductive materials (e.g., $ZnMn_2O_4$) [33–36]. As Figure 4 illustrates, it could be the case when the 8 mol L^{-1} KOH-based electrolyte is saturated with zincate ions (e.g., 8s-0 allows 140–160 cycles).

Whereas zinc anode cycle life is enhanced by saturating the electrolyte with ZnO and in the presence of additives (Fig. 3) in contrast, the BAE cycle life is negatively affected using the same strategy. It is rationalized by means of precipitation of additive-containing species on BAE surface or porous structure. A similar effect was reported by Chen et al. [17] for silver-zinc batteries in the presence of fluoride and carbonate ions.

Oxygenated solid zinc species as $Zn(OH)_2$ or ZnO can be generated upon BAE surface and/or electrode porous structure where the oxygen and/or the concentration gradients of water could promote the dissolution-precipitation processes of zinc species due to changes in their solubility at the near electrode surface (ref. [37] and refs. therein). For example, $Zn(OH)_2$ or ZnO could be generated when $Zn(OH)_4^{2-}$ reacts with the oxygen from the air or with that generated from the OER during cell charging. On the other hand, the ZnO precipitation is also favored by water depletion in the near electrode surface. The consumption of water occurs during OER or during the conversion of MnO_2 into MnOOH (viz. $MnO_2 + H_2O + e^- \leftrightarrow MnOOH + OH^-$, battery discharging mode). In this sense, the lower water content to solvate zincate ions favors the $Zn(OH)_4^{2-}$ decomposition and hence, ZnO precipitation could take place (viz $Zn(OH)_4^{2-} \leftrightarrow ZnO + H_2O + 2OH^-$ proceeds to the right such as with water consumption during OER).

There are other species which can limit the BAE performance. For example, highly resistive $ZnMn_2O_4$ might be formed at the cathode surface by the interaction of Zn ions with MnO_2 [33–36]. The formation of this spinel-type compound depends on zincate concentration [38]. Hertzberg et al. [39] prevented the "Zn-poisoning" of the cathode by implementing a mixed electrolyte (KOH-LiOH in ratio 1:3) promoting the intercalation of protons and Li-ions instead of Zn.

Altogether, as observed in Figure S6(B), the additives (ZnO, KF, and K_2CO_3) trigger higher cell overvoltage during discharging (211 mV, 8s-1 vs. 8-0) than during charging (136 mV, 8s-1 vs. 8-0). This result indicates that the ORR is more affected by the additives than OER. This fact could be related to (1) an increment of the electrode resistance (not determined, although readers are referred to [17, 36–38] for a more dedicate study on the effect of additives on Zn-MnO_2 batteries), (2) slower ORR kinetics associated to lower O_2 diffusion/solubility in higher viscose electrolytes (Fig. S3), (3) surface poisoning which limits the electrode active catalytic sides, and/or (4) the precipitation of species in the BAE porous structure blocking the oxygen crossing.

A deeper understanding on this interesting topic should be done to elucidate the real effect of each electrolyte additives on BAE reactivity. Unfortunately, this is beyond the goal of this publication. However, on this topic, other authors have found benefits of specific concentrations of KF and K_2CO_3 on the cell performing. For example, Schröder et al. [18] analyzed the electrochemical performance of zinc–air battery with a KOH electrolyte and potassium carbonate as additive. They determined that there is a maximal concentration of carbonates which might enhance the ORR kinetics through a consumption of OH^- with added carbonates. However, beyond this specific K_2CO_3 concentration, extra added carbonates will decrease the solubility of O_2 in the electrolyte being this effect predominant, and thus, reducing the ORR kinetics due to less accessible oxygen. They concluded that the variation of the hydroxide concentration is more crucial for the performance of zinc–air battery than increasing up to 50 mol% the carbonate concentration. On the other hand, Hwang et al. [20] concluded that fluoride (specifically from KF as precursor) is a very efficient additive to promote ORR and OER on α-MnO_2 bifunctional air electrode. Nevertheless, similar to carbonate additive, there is a maximal concentration of F^- that promotes such reactions. They found 4 m mol L^{-1} F^- and 8 m mol L^{-1} F^- in 1 mol L^{-1} KOH as optimal concentration to catalyze the ORR and OER, respectively. They rationalized the positive effect of fluoride anions as promotor of fast charge transfer rate for ORR by changing the oxidation state of Mn(IV) to Mn(III) in α-MnO_2. Yan et al. [40] confirmed also the beneficial effect of KF (similar to ref. [20] having F^- as proton carrier) as additive of KOH electrolyte in Ni/MH batteries.

The results of this section suggest that zincate anions are the main responsible of the higher cell overvoltage. In that sense, from authors' point of view, cell engineering strategies should be also implemented such as the development of selective membranes able to suppress or to reduce the crossover of zincate ions from the anode to cathode but allowing hydroxide ions pass through [37, 38].

In general, the results at half-cell level suggest that the optimal formulation for secondary zinc anode and BAE is opposite in nature. However, anything is known about what will be the case in the full cell system. In this context, in the following section, the cycle life of the full cell system will be investigated as a function of the electrolyte formulation.

Determination of full cell cycle life by accelerated test

As previously determined by half-cell testing, the optimal electrolyte formulations for zinc anode and bifunctional air electrodes are 4s-2 and 8-0, respectively. As notice,
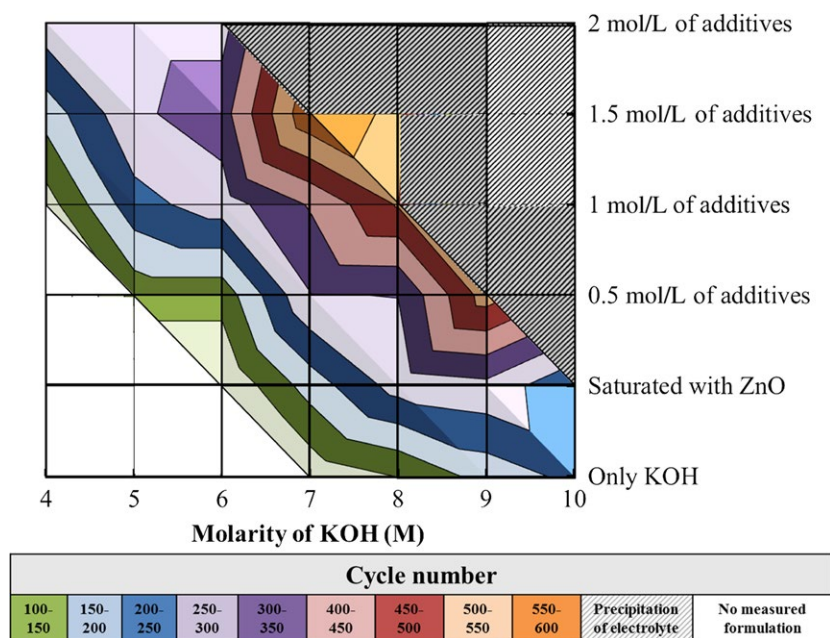
Figure 5. Cycle life mapping of zinc–air full cell system as a function of KOH and additives concentration.

zinc cycle life is enhanced by low KOH concentration and high KF-K_2CO_3 additives concentration. In contrast, BAE cycle life needs additive-free high alkaline KOH electrolyte to promote long life cycling. Hence, the development of an optimal electrolyte formulation for the full system is proposed in the present section to reach practical application of reversible zinc–air batteries.

Both electrodes are simultaneously tested in a homemade zinc–air cell which allows a working time of ca. 120 h before cell drying get irreversible. In this context, the assessment of the full cell is done under an accelerated protocol (cycled at 2.5 mA cm^{-2}) with symmetric charge/discharge capacities (5 mAh g$_{Zn}$$^{-1}$). Figure 5 shows the cycle life mapping for the homemade zinc–air full cell. The determined cycle number of the secondary zinc–air battery has been based on the 100% capacity retention for each system.

The results suggest that under the accelerated test conditions, the optimal electrolyte formulation for the full system is based on ZnO-saturated 7–7.5 mol L^{-1} KOH and 1.2–1.5 mol L^{-1} of each KF and K_2CO_3 additives. Concretely, the 7s-1.4 aqueous alkaline electrolyte is selected as the optimal composition to enhance the secondary zinc–air battery cycle life. As observed, the suitable electrolyte composition establishes a balance between what is needed for extending the cycle life of the anode and cathode. This means high concentration of KF-K_2CO_3 additives (beneficial for zinc, including good zinc deposition and lower HER rate) and high KOH concentration (appropriate for BAE, comprising good ionic conductivity

and favorable ZnO solubility). Thus, whereas 250–300 cycles is achieved with 4s-2 electrolyte formulation (optimal for the zinc electrode), in contrast, just up to 150 cycles is reached when 8-0 (suitable for BAE) electrolyte is implemented (Fig. S7). However, the electrolyte system based on 7s-1.4 enhances the cycle number close to 600 cycles (i.e., two and four times more cycles than those reported for zinc electrode (4s-2) and BAE (8-0), respectively).

It has to be indicated that the given formulation could be different if a selective separator (as proposed in [37] and [38]) is implemented. As pointed out in *Bifunctional air electrode (BAE) cycle life*, the separator used in this work is based on a macro-porous structure in order to avoid a fast drying of the cell. However, this characteristic might disfavors the BAE performance due to detrimental effects of zincates and/or additives ions on BAE reactivity. Even though, the defined full cell optimal electrolyte system (viz. 7s-1.4) is used to corroborate the effect of different Zn:ZnO ratios on the cell cycle life. It is confirmed that a ratio of 70 to 30 of metallic zinc to ZnO powder provides the highest reversibility (ranking from 400 to 600 cycles) of the system as shown in Figure S8.

As next step, the secondary zinc–air cycle life will be contrasted between the optimized (7s-1.4) and traditional (8-0) electrolyte formulations by C/D cycling the homemade zinc–air full cell under more realistic operating conditions (viz. higher DoD). The results and the proposed testing conditions (i.e., applied current density and
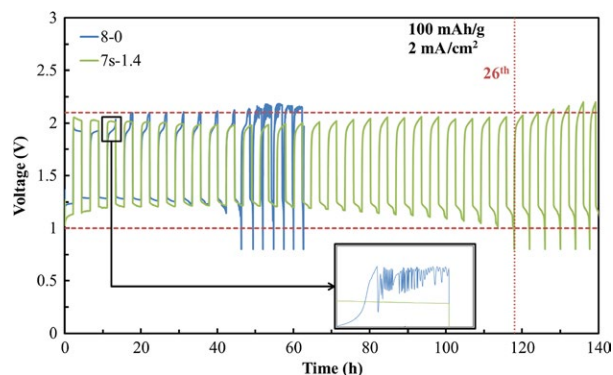
Figure 6. Charge/discharge cycling profile of rechargeable zinc–air batteries based on 8-0 (blue-line) and 7s-1.4 (green-line) electrolyte formulations.

practical capacity) are justified and shown in *Full cell cycle life assessment under close realistic operating conditions*.

Full cell cycle life assessment under close realistic operating conditions

The cycle life assessment of a homemade secondary zinc–air full cell based on 7s-1.4 electrolyte formulation is analyzed at 2 mA cm^{-2} by charge/discharge cycling capacity of 100 mAh g$^{-1}_{Zn}$ (approx. 20% DoD of the nominal capacity of our system – 515 mAh g$^{-1}_{Zn}$ as shown in Fig. S1). As noticed in Figure S2, the applied current density (2 mA cm^{-2}) is the most suitable to evaluate the cycle life of the homemade secondary zinc–air full cell. This fact is based on the criterion of safer potential window (1.05–1.95 V; black-dotted lines in Fig. S2) assigned to minimize side reactions such as zinc passivation and HER, respectively. Therefore, both processes can be partially controlled by means of adjusting the charge (HER) and discharge (passivation) cut-off voltages [1, 15, 41, 42].

With the proposed current density, the full secondary zinc–air battery presents an overvoltage ($\Delta V = V_{OER} - V_{ORR}$) of 0.77 V (Fig. S2), whereas the effective cell operating voltage window at 20% DoD comprised between 1.18 V (discharge) and 1.95 V (charge) which represents ca. 60.5% of round-efficiency. In spite of knowing the limitations of our system concerning cathode cycle life (see *Bifunctional air electrode (BAE) cycle life*) and cell design, these initial results allow contrasting the cell's cycle life between the traditional additive-free KOH electrolyte (8-0) and the developed advanced electrolyte formulation (7s-1.4). This systematic cycle life assessment wants to demonstrate that the reversibility of the secondary zinc–air batteries can be improved by tuning the electrolyte composition, although both cathode development and proper

cell design (including the separator) are needed to further develop the technology.

Figure 6 shows the corresponding 100 mAh g$^{-1}_{Zn}$ C/D cycling profiles of two rechargeable zinc–air batteries based on different electrolyte formulation (8-0 and 7s-1.4) at 2 mA cm^{-2}. The battery using 8-0 electrolyte works during 10 cycles before discharging and charging cell voltages go beyond the safe voltage limits implemented to prevent/minimize passivation and hydrogen evolution. In spite of the applied safety voltage range, in the 3rd cycle, the contribution of HER starts to be appreciable during the battery charging (see magnification in Fig. 6) in agreement with previously reported behavior in Figure 2 (*Electrolyte basic specifications*) for those electrolytes without additives.

The secondary zinc–air battery based on 8-0 electrolyte formulation presents a maximal round-efficiency of 65% (1st cycle) which decreases to 54% after 10 cycles (ca. 45 h). Correspondingly, the overvoltage increased from 0.68 V at the first cycle to 0.97 V at 10th cycle. In contrast, the cell using the advanced 7s-1.4 electrolyte formulation reaches 26 cycles (ca. 116 h) before discharging voltage suddenly dropped off beyond 1.0 V. This result represents ca. 2.5 times enhancement in the cycle life of the zinc–air cell by tuning accordingly the electrolyte formulation. This cell showed a maximal round-efficiency of 62% with an overvoltage of 0.76 V.

Overall, the secondary zinc–air battery based on novel electrolyte formulation which includes a combination of ZnO, KF, and K$_2$CO$_3$ as additives demonstrates a better reversibility than that based on the traditional electrolyte formulation for primary zinc–air batteries. This fact highlights that secondary zinc–air cell should be developed taking into account the compromises existing between the conditions of either high performing and reversible positive and negative electrodes. This compromise is somehow handled by mean of a corresponding electrolyte formulation. It cannot be ruled out that cell design will play a significant role in the further development of the technology. This includes optimal or custom-made separators which can even allow implementing hybrid electrolyte systems owning to the benefits for each electrode.

Summary

It has reported the impact of the electrolyte formulation on the cycle life of the negative (zinc) and positive (BAE) electrodes, as well as on the secondary zinc–air full cell. From this systematic cycle life assessment, it has found that zinc cycle life is enhanced by low KOH concentrations and high KF-K$_2$CO$_3$ additives concentrations, whereas BAE cycle life needs high alkaline additive-free KOH-based electrolyte to enhance its cycle life. Thus, the most

favorable electrolyte formulations for zinc and bifunctional air electrodes were found to be 4s-2 (ZnO-saturated 4 mol L^{-1} KOH with 2 mol L^{-1} KF and 2 mol L^{-1} K$_2$CO$_3$) and 8-0 (8 mol L^{-1} KOH), respectively. Optimal electrolyte formulation for zinc electrode is in good agreement with those reported for alkaline secondary nickel-zinc batteries, whereas it is the first time that a BAE (MnO$_2$-based) cycle life is evaluated under specific electrolyte formulations for zinc electrodes. On the other hand, although in principle the results suggest that zincate anions have a major impact on the BAE, a more dedicated research on the influence of additives on BAE performance should be carried out.

Through this systematic cycle life assessment, it has demonstrated that the cycle life of the secondary zinc–air batteries is improved by adjusting the electrolyte composition, and hence, satisfying both anode and cathode electrodes requirements. In this context, it has determined that 7s-1.4 (ZnO-saturated 7 mol L^{-1} KOH, 1.4 mol L^{-1} KF, and 1.4 mol L^{-1} K$_2$CO$_3$) was the most suitable electrolyte formulation. This electrolyte has allowed enhancing 2.5 times the battery cycle life in comparison to a battery using the traditional 8 mol L^{-1} KOH electrolyte. The homemade battery showed a maximal round-efficiency of 62% with an overvoltage of 0.76 V.

All in all, it suggests that while cycle life of zinc electrode is optimized, impact of the chosen strategy (namely, KOH concentration, additives types, operating conditions, or a combination of all them) on the others cell components (specifically on positive electrode) and on the full cell performance and cycle life has to be also carefully assessed. In this analysis, of course, the cell design or battery tester vehicle may also be a key factor to take into account. As it has been shown, in spite of the benefits obtaining from the additives on the negative zinc electrode, some penalties in the system might be paid such as electrolytes with lower conductivity (and thus a battery with lower power) or less performing cathode catalysts. In this case, key factors like cell engineering strategies may be implemented (e.g., custom-made separators, shorter distance anode-cathode, etc.) or depending on the battery application a balance between the benefit (e.g., extended cycle life) and the penalty (lower nominal capacity) should be faced.

Acknowledgments

Conflict of Interest

The authors declare no conflict of interest.

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Supporting Information

Additional supporting information may be found in the online version of this article:

Figure S1. Nominal capacity determination (5 mA cm^{-2}) of the homemade secondary zinc–air battery.

Figure S2. Determination of the cell overvoltage of homemade secondary zinc–air battery as function of applied current density.

Figure S3. Viscosity of different aqueous alkaline electrolyte formulations at different temperatures.

Figure S4. Ionic conductivity at low temperatures for different aqueous alkaline formulations.

Figure S5. Cyclic voltammetry of secondary zinc electrode composed by 4s-2 electrolyte system.

Figure S6. (A) Charge and discharge profile of bifunctional air electrodes working with 8-0 and 4s-2 aqueous alkaline electrolyte systems and (B) comparison of the C/D voltage behavior between 8 M KOH-based electrolyte and 8 M KOH with additives (ZnO, KF and K$_2$CO$_3$).

Figure S7. Cycle life of homemade secondary zinc–air batteries with different electrolyte formulations.

Figure S8. Cycle life of secondary zinc–air battery composed by different Zn:ZnO ratios with the optimal aqueous alkaline electrolyte formulation 7s-1.4.