

## Optimized zinc electrode for rechargeable zinc-air batteries

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In this study, two different approaches to improve the zinc anode cyclic stability are discussed: (i) optimization of the active zinc mass composition by adding different metal oxides, which aims to prevent the formation of dendrites and thus to inhibit the degradation processes and (ii) optimization of the current collector by replacing the most commonly applied tinned copper mesh with a galvanized one which aims to prevent the copper dissolution during operation of the battery. Zinc electrodes, prepared by mixing of Zn and ZnO with a binder, were pasted on both sides of the current collector and examined by charge/discharge tests in a half-cell configuration with stainless steel mesh counter electrode and reference reversible hydrogen electrode (RHE) in alkaline electrolyte. The effects of different oxides ( $\text{Bi}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ) addition to the Zn paste and copper mesh galvanization on the electrode performance were evaluated. The results show that additives significantly influence the Zn electrode capacity (about 30% improvement) and the replacement of copper mesh with a galvanized one increases its stability and cyclic efficiency.

**Keywords:** reversible Zn electrode, ZnO additives, optimized Zn/ZnO paste, current collector

### INTRODUCTION

Zinc-air batteries stand as some of the best successfully commercialized primary metal-air batteries [1]. They have been considered to be potentially attractive as power sources for various applications such as electric vehicles and renewable energy sources. Their many advantages include: high energy density, high capacity, and operation in humid environments, aqueous electrolytes with low self-discharge and low-cost materials. In the last decades major efforts have been made especially in the development of alkaline Zn-air batteries [2-5]. However, electrically rechargeable alkaline zinc-air cells still suffer from low efficiency and insufficient cyclability, partially related to anodic passivation of the zinc electrode [6, 7]. The challenge for science and industry is the development of rechargeable Zn-air batteries for accumulation of solar energy and peak shaving with load displacement [8].

The main issue for the commercialization of zinc-air batteries is their lifetime (number of discharge/charge cycles) which is related to the degradation of the electrodes during cycling and leads to a rapid decrease of their capacity [9]. Concerning the Zn-electrode, the main reasons for degradation are dissolution of Zn and passivation of the electrode with ZnO. This leads to a rapid decrease in capacity and limits the lifetime of the batteries. For a Zn electrode, zinc particle morphology is of great importance for better

interparticle contact and lower internal resistance which improves electrochemical performance [10-12].

Nowadays, Zn electrode in state-of-the-art primary Zn-air batteries consists of tinned copper mesh as current collector [8] and metal Zn electrode with ppm doping levels of In, Bi and Al [13]. Bismuth is used to improve conductivity of the zinc particles [14, 15]. Indium is shown to segregate to grain boundaries of Zn and decrease dendrite formation [16]. The co-doping of both In and Bi was observed to decrease the HER dramatically [17, 18]. Aluminum minimizes the corrosion rate of the Zn electrode and provides more than 50% longer discharging time over pristine zinc in 6 M KOH [19]. The aim of this study is to investigate the effect of: i) addition of various metal oxides ( $\text{Bi}_2\text{O}_3$ ,  $\text{In}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ ) to the initial zinc paste in order to prevent the formation of dendrites and thus, inhibit the degradation processes and ii) replacement of the tinned copper current collector with a galvanized one.

### EXPERIMENTAL

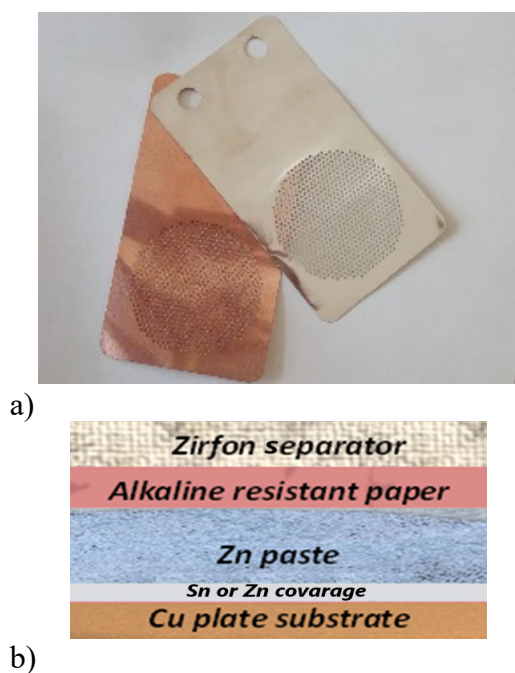
The basic Zn anode was prepared from zinc paste made of ZnO (Pharma B-D48230) and Zn (UMICORE 100 BIA) at a ratio of 70/30 wt. %. As a binder a mixture of carboxymethylcellulose (CAS:9004-32-4), polyvinyl alcohol (Chimspectar-EC №209-183-3) and polytetrafluoroethylene

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emulsion (Sigma Aldrich – CAS 9002-84-0) was applied. The active Zn mass was deposited on both sides of the current collectors: tinned copper mesh (TCM) and galvanized copper mesh (GCM). After drying in air, the electrodes were pressed at  $300 \text{ kg}\cdot\text{cm}^{-2}$  for 3 min. Before use, the electrodes were covered with alkali-resistant paper and a separator (Zirfon) (AGFA-Zirfon Perl UTP 500). The schematic view of anode construction and a photograph of both, CM and GCM current collectors are presented on Figure 1.

Thus prepared Zn electrode was used as a starting point for electrode behavior and will be further named BL (Baseline) electrode. As the proposed zinc electrode contains an increased amount of ZnO (70 wt.%), the following additives:  $\text{Bi}_2\text{O}_3$  (0.0113 wt.%),  $\text{In}_2\text{O}_3$  (0.0238 wt.%) and  $\text{Al}_2\text{O}_3$  (0.0439 wt.%), commonly used with the Zn powder, were added to the ZnO. After fine homogenization of the initial ZnO powder with the above-mentioned additives, the optimized Zn electrode was obtained by the same procedure as the BL electrode and will be further named BIA.

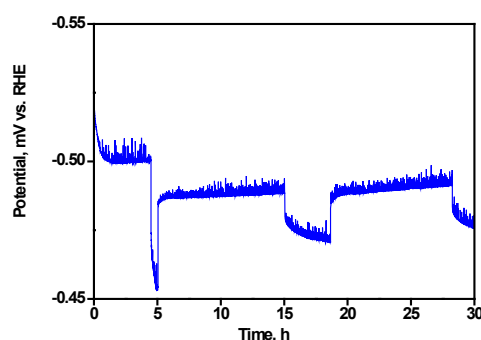


**Fig. 1.** Zn electrode composition: a) different current collectors, b) schematic view.

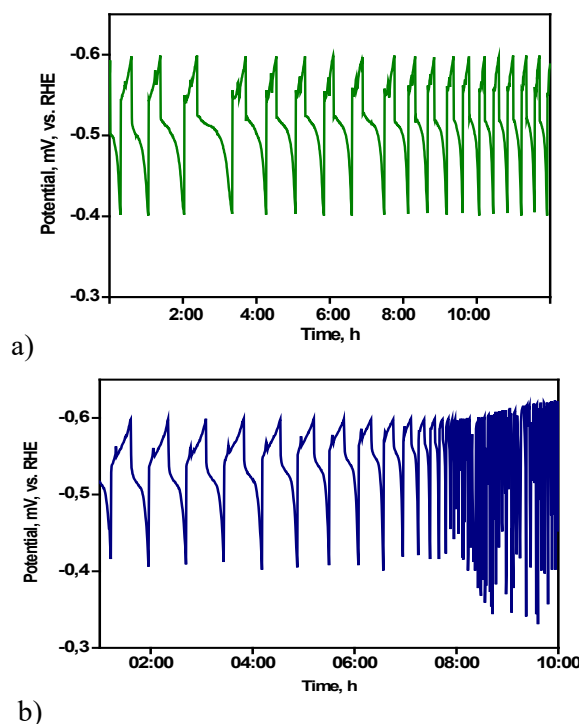
The charge/discharge tests were done in a half cell configuration in 6M KOH electrolyte using RHE, HydroFlex (Gaskatel) and stainless-steel counter electrode in a specially designed three-electrode cell with  $10 \text{ cm}^2$  working surface area. The electrodes were loaded with  $I_{\text{Zn}} \pm 15 \text{ mA}\cdot\text{cm}^{-2}$  at  $C_{\text{rate}} = C/5$ . The charge/discharge potential limit for Zn electrode was chosen  $-0.6 \text{ V}$  and  $-0.4 \text{ V}$  with time of 4:30 and 3:30 hours, respectively.

## RESULTS AND DISCUSSION

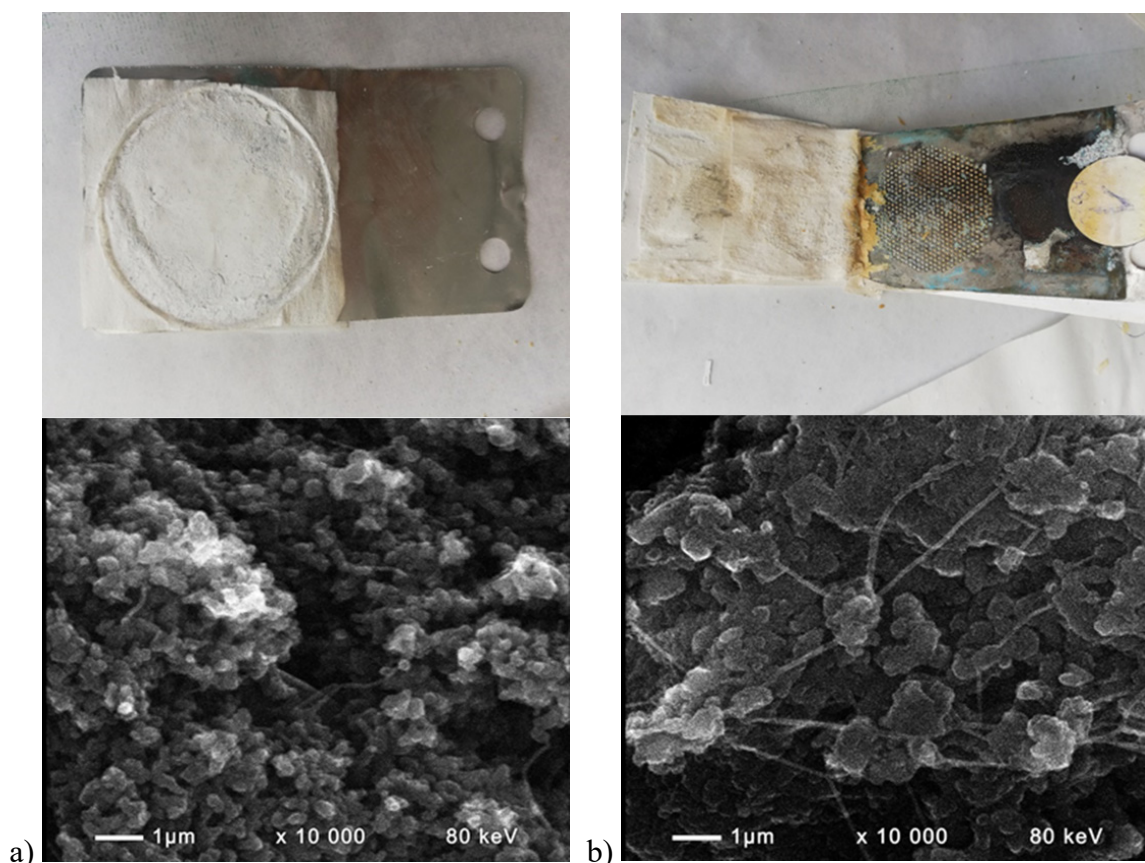
The first generation of zinc electrodes was made by applying zinc paste to a galvanized copper mesh. Two series of electrodes were fabricated, (1) ZnO without additives (BL), and (2) ZnO with additives (BIA). Considering the bigger initial ZnO quantity a special procedure for reduction of ZnO to Zn was introduced. It involves 3 charge/discharge cycles at very low current densities. An example of BIA electrode activation is given on Figure 2. After activation, both electrodes, BL and BIA stay stable for more than 8 hours operation at  $C/5$  rate, the results are very similar, as it can be seen on Figure 3.



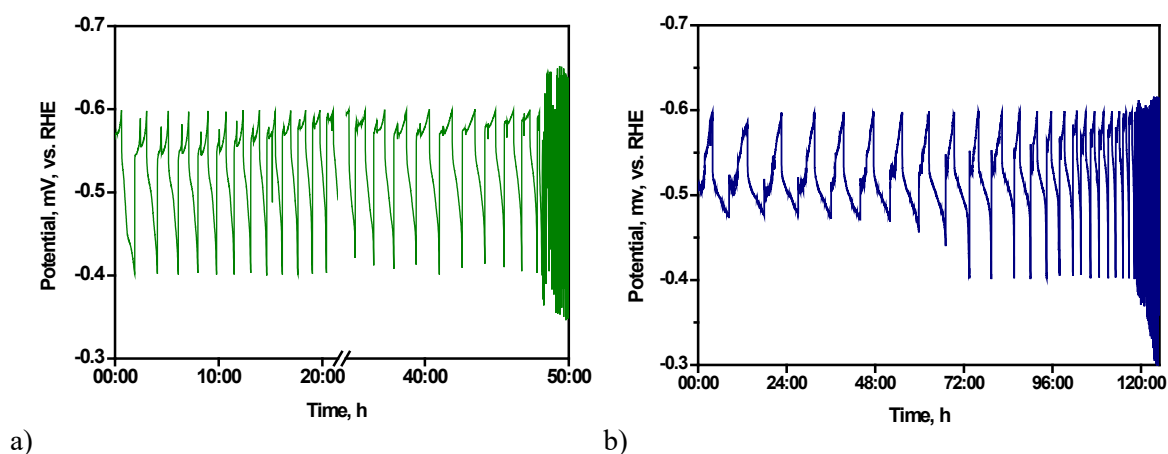
**Fig. 2.** Zn electrode activation procedure: first charge/discharge cycle at  $10 \text{ mA}\cdot\text{cm}^{-2}$  ( $C/15$  rate) followed by 2 charge/discharge cycles at  $5 \text{ mA}\cdot\text{cm}^{-2}$  ( $C/10$  rate).



**Fig. 3.** Charge/discharge cycling tests of the first-generation Zn electrodes BL (a) and BIA (b) with tinned copper mesh (TCM) current collector.



**Fig. 4.** Photographs and SEM micrographs of the BL electrode with GCM current collector before work (a) and after work (b).

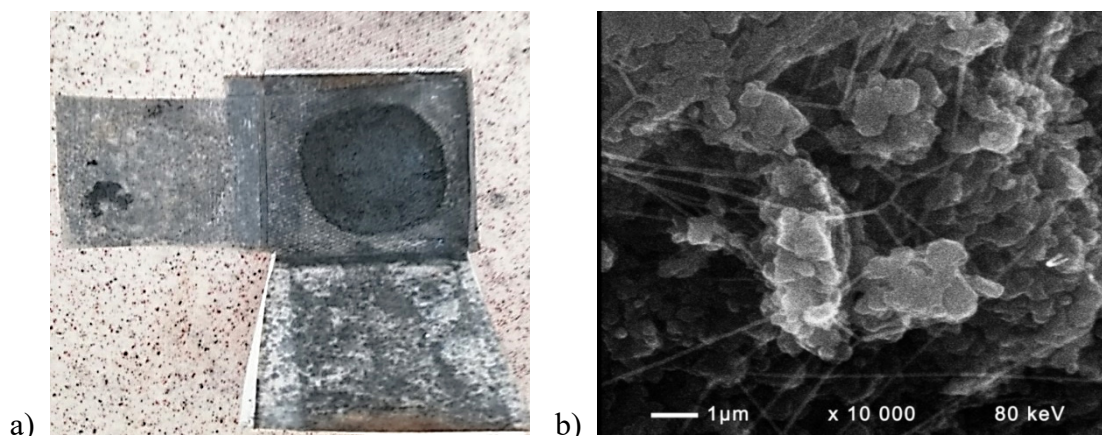


**Fig. 5.** Charge/discharge cycling tests of the second-generation Zn electrodes BL (a) and BIA (b) with galvanized copper mesh (GCM) current collector.

Obviously, the whole Zn paste fell out from the tinned copper mesh as a result of bad adhesion between the zinc and the tin coating, which leads to total zinc anode destruction. Therefore, the second-generation zinc electrodes were fabricated with replacement of the tinned copper mesh with galvanized copper mesh. The cycling results are presented on Figure 5. They show a significant increase in the lifetime of the zinc electrode. The BIA electrode (Fig. 5b) operated for more than 115

hours, which is twice as long as the results obtained for BL electrode.

The discharge process in the first 70 hours of operation of the BIA electrode with GCM current collector (Fig. 5b) stops when the time limit is reached. After that the zinc electrode polarization increases and the electrode reaches the set discharge potential limit. The electrode is fully discharged after 115 hours of operation and active zinc mass dissolution is observed (Fig. 6).



**Fig. 6.** Photograph (a) and SEM micrograph (b) of the BIA electrode with GCM current collector after work.

The presented *post-mortem* analysis shows the electrode surface after cyclization. The GCM current collector holds a small amount of the active mass, and it is visibly greater than that on the TCM current collector (Fig. 6a, Fig. 4b). The SEM observation (Fig. 6b) does not significantly differ from that of the BL electrode (Fig. 4b), zinc dendrite formation and characteristic polytetrafluoroethylene threads appear.

### CONCLUSIONS

The increase in the lifetime of rechargeable zinc–air batteries is a challenge and its overcoming depends on a lot of obstacles, for instance, passivation and corrosion of the zinc anode leading to fast zinc degradation. A complex approach should be used to optimize several directions related to the main breakdown process observed in the original zinc electrode. The method we reported in this study is focused on the improvement of (i) the active zinc mass composition and (ii) the current collector which aims to further enhance the reversibility of the zinc anode. The obtained results showed that the addition of Bi-, In- and Al- oxides to the initial zinc paste, rather than to the ZnO which quantity is twice and half larger (70 wt.%) than the Zn content (30 wt.%), as well as the replacement of copper mesh current collector with a galvanized one, improved the electrochemical behavior of the zinc anode. The additives inhibit the Zn degradation processes and substantially improve the electrode capacity (by about 30%) over a larger number of cycles. More than 115 hours of charge/discharge operation at C/5 rate were achieved with BIA electrode and galvanized copper mesh, which fully meets the requirements for a reversible zinc anode.

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