

Influence of the binder on the mechanical stability and electrochemical properties of Zn electrode for rechargeable zinc-air batteries

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The development of electrically rechargeable zinc-air batteries is a challenge to the efforts of many scientists for decades. The optimization of a zinc electrode as a function of its reversibility and mechanical stability is a key factor for battery efficiency improving and approaching to the Zn-air system commercialization. The present investigation is focused on the improvement of the zinc electrode with regard to its wettability and with aim to reduce the volume change caused by the density difference between the charged zinc and discharged ZnO electrode, respectively. Originally, the Zn-paste is made of a mixture of Zn powder, ZnO, additives and binding agents (usually carboxymethyl cellulose, CMC). However, the use of CMC as a gelling agent is not appropriate as it tends to swell in aqueous solution and reduce the capacity of cells over long-term reversibility tests. Our results showed that the replacement of CMC with polymer-type gelling agents such as polytetrafluoroethylene (PTFE) or teflonized Vulcan XC-72 carbon blacks with 35 wt% PTFE (TV35) binders significantly improved the electrochemical performance of the electrode resulting in higher specific discharge capacity and also in good durability and stability. Different contents of PTFE and TV35 on a zinc electrode in 6 M KOH were examined. Maximum initial discharge capacity of 498 mAh.g⁻¹ was registered by the addition of 13 wt% TV35 to the pasted zinc electrode.

Keywords: Zn electrode, PTFE, Teflonized carbon blacks, Discharge capacity

INTRODUCTION

Nowadays, there is an urgent need to develop efficient, safe and affordable energy storage devices for both electric vehicles and stationary grid storage. Rechargeable metal-air batteries have the potential to store and release high amounts of energy in a short time when required. From the group of metals used Mg, Zn, Al, Fe, Ca, Li, zinc is the most active one in aqueous electrolytes. Zn electrode is cheaper and non-toxic. It operates well in humid environment and has low self-discharge, and can also be recharged *via* ZnO. Due to the oxygen supply from the atmosphere, Zn-air batteries have drastically higher theoretical energy density than traditional Ni-MH and lithium-ion batteries, which have had practical applications for a long time. Although the rechargeable Zn-air batteries are in a very mature state, there are many barriers towards their commercialization, the main is the lifetime (number of charge/discharge cycles) which is related to the degradation of the electrodes during cycling and leads to a rapid decrease of their capacity. Despite the numerous studies that problem is still not solved.

The problems associated with the zinc electrode can be structured in three main groups: (1) corrosion (release of hydrogen as a parasitic reaction) and dissolution, (2) dendritic formation at charge, combined with electrode change due to no uniform dissolution of zinc; (3) passivation of zinc

electrode with ZnO layer formation due to zinc ions saturation [1-12]. The increase of the specific electrode surface [13-15] (standard battery optimization approach) by regulating the morphology of the starting material and the process conditions that provide a porous structure with good contact between the grain boundaries activates also the corrosion and passivation processes. The classical zinc reversible electrodes operate with a Zn/ZnO mixture [16-18]. For inhibition of the degradation processes several approaches, based on introduction of additives which modify the electrode, reduce self-corrosion, prevent passivation, dendritic formation and change in electrode shape, such as zinc alloys formation (Pb, Bi, Sn, In) [13, 19-21] oxide additives (Al₂O₃, Bi₂O₃, In₂O₃, TiO₂, [13, 20, 22-25] or gelling agents or binders such as carboxymethyl cellulose [16, 17, 26, 27] are used. The current work is focused on the investigation of the influence of different binders on the mechanical stability and electrical properties of the Zn electrode for rechargeable zinc-air batteries. The replacement of carboxymethyl cellulose (CMC) with polytetrafluoroethylene (PTFE) and teflonized Vulcan XC-72 carbon blacks (TV35) of different contents in Zn/ZnO paste electrodes were examined by charge/discharge tests using a KOH-based electrolyte in half-cell configuration. The discharge capacity of the first cycle was chosen as the criterion to define the optimum amount of binder.

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EXPERIMENTAL

Electrode preparation

The zinc electrode was prepared as a mixture of zinc and zinc oxide (UMICORE). The initial powders were in the micrometric range (particle size of 100–300 μm) and metallic traces (*viz.* In, Bi, Al) were present. The active Zn paste was deposited on 9 cm^2 of stainless steel mesh (counter electrode) and pressed for 3 min with 300 $\text{kg}\cdot\text{cm}^{-2}$ at 300°C. The quantity of gelling agent was varied in the range of 40 mg to 150 mg keeping the amount of Zn/ZnO constant: *Binder 1* - PTFE (Sigma Aldrich, emulsion); *Binder 2* - teflonized (35 wt%) carbon blacks (Vulcan XC-72, Cabot corp.).

Experimental conditions

The charge/discharge tests were conducted using six-channels Galvanostat 54 (PMC) testing system with custom software developed at IIES-BAS [28–30]. The cell discharge was controlled by limiting time or voltage. The charge was defined by time with the voltage limit reaching up to +2.5 V. The testing was done in a half cell configuration in 6M KOH-based electrolyte using HydroFlex hydrogen reference electrode (Gaskatel) and stainless steel counter electrode (CE) in a specially designed three-electrode cell (Fig. 1). The electrodes were loaded with 5 $\text{mA}\cdot\text{cm}^{-2}$ (440 min charge and 400 min discharge).



Fig. 1. General view of the experimental set up.

RESULTS AND DISCUSSION

The preliminary investigation of pasted Zn electrode prepared as most commonly used for secondary alkaline zinc-air battery was conducted. The performed charge/discharge test presented in Fig. 2 shows that the fabricated zinc electrode (with 1.4 wt% CMC) withstands up to 20 cycles. Better results with respect to the discharge capacity (240 $\text{mAh}\cdot\text{g}^{-1}$) were obtained while utilizing lower current densities (5 $\text{mA}\cdot\text{cm}^{-2}$). However, the obtained Zn electrode has low mechanical and

electrochemical stability and needs further improvements.

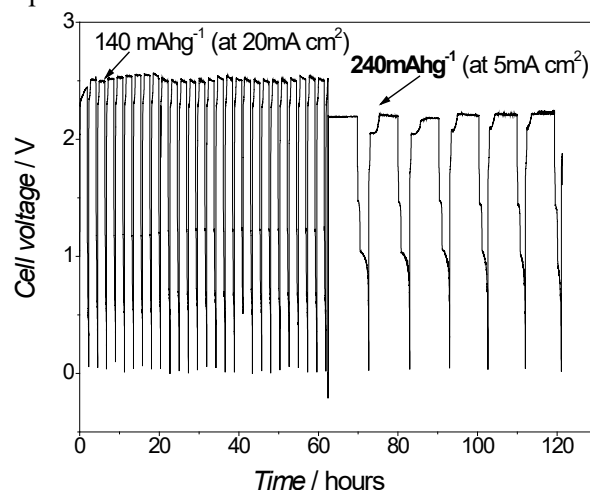


Fig. 2. Initial exploratory charge/discharge battery cycling test. The electrode is loaded with 20 $\text{mA}\cdot\text{cm}^{-2}$ (110 min charge/100 min discharge) and then with 5 $\text{mA}\cdot\text{cm}^{-2}$ (440 min charge /400 min discharge). The cell voltage is measured *versus* RHE. The Zn electrode contains 1.4 wt.% carboxymethyl cellulose (CMC).

The replacement of CMC with PTFE during the preparation of the Zn electrode brings an increase of the initial nominal discharge capacity (Fig. 3).

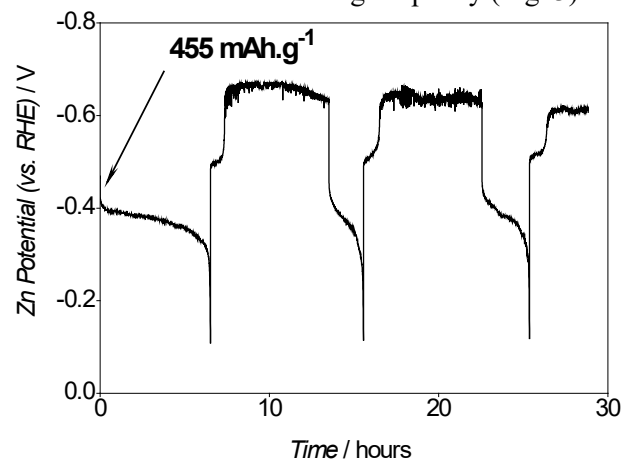


Fig. 3. Charge/discharge performance of the Zn electrode with 150 mg PTFE.

The best results were obtained after the addition of 150 mg PTFE (Fig. 3). To reach this capacity, the amount of PTFE was changed in the range of 40 mg to 200 mg keeping Zn/ZnO constant. The results presented on Figure 4 show that the optimal ratio PTFE:Zn-paste is 1:5.

In order to achieve comparatively high nominal capacity, the pure PTFE binder was replaced with TV35. Keeping the proportion of active Zn/ZnO paste constant, the TV35 amount was varied in the same proportions as PTFE binder - from 40 mg up to 200 mg (Fig. 5). The optimum ratio of TV35 to Zn/ZnO was found to be 1:7 (Fig. 6).

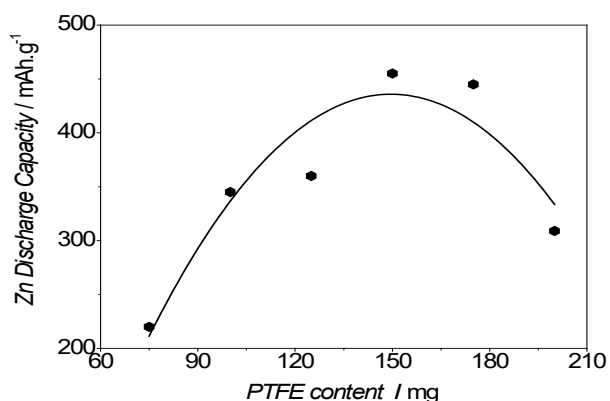


Fig. 4. Dependence of the Zn electrode capacity on the PTFE content.

The maximum initial discharge capacity reaches *ca.* 500 mAh.g⁻¹, i.e. it is 100% for the active zinc electrode (nominal *vs.* calculated mAh.g⁻¹_{Zn}). However, this capacity gradually decreased to 80 mAh.g⁻¹ during the cycling test. The high specific surface area of the added TV35 decreases the density of the Zn electrode and it even shows a capacity improvement.

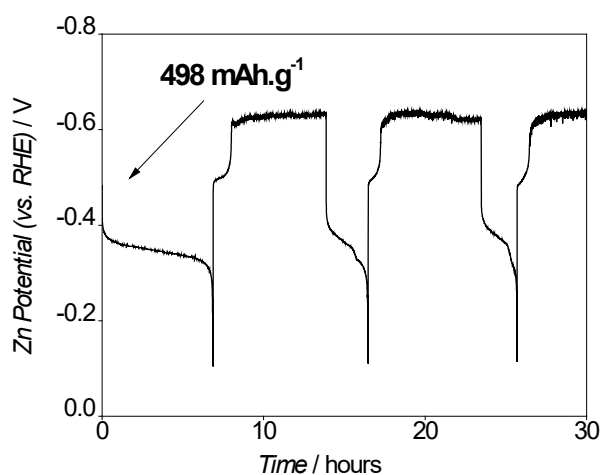


Fig. 5. Charge/discharge performance of the Zn electrode with 100 mg TV35.

In respect to the discharge capacity, the cycle life of the as prepared zinc electrode drastically decreases with the increase of TV35 amount (Fig. 7). The maximum numbers of charge/discharge cycles were obtained for a sample containing 50 mg TV35, but only 430 mAh.g⁻¹ capacity was reached. The high specific surface area of the added Vulcan carbon blacks decreased the density of the Zn electrode and it even showed a capacity improvement at the beginning; the further increment of carbon content decreasing the electric conductivity of Zn electrode.

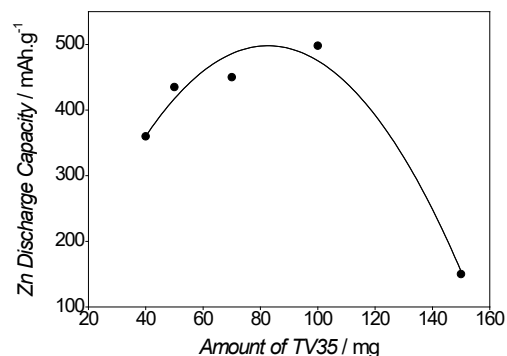


Fig. 6. Dependence of the Zn electrode capacity on the TV35 content.

Finding the right dependence binder amount *vs.* durability *vs.* high discharge rate capability is a very complex gathering, as the cell performance is mostly dependent from the Zn electrode degradation.

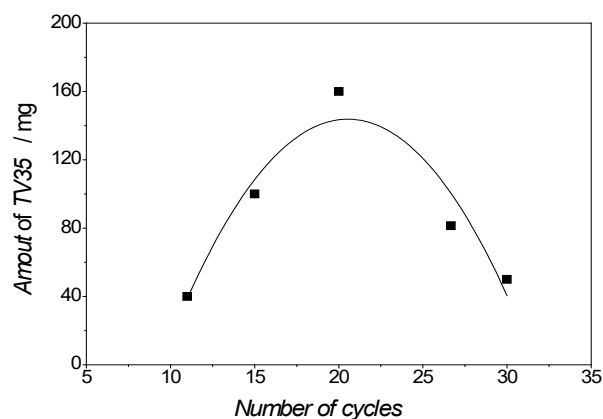


Fig. 7. Dependence of the Zn electrode life cycles on the TV35 content

CONCLUSIONS

In order to improve the discharge performance of the Zn anode, different binders were applied to the initial Zn-paste composition. The impact of using PTFE or teflonized carbon blacks (TV35) instead of carboxymethyl cellulose was examined by electrochemical charge/discharge tests. The obtained results showed that the porous zinc electrode is sufficiently prevented from the side of passivation during the operation of the cell in both, PTFE and TV35, but in search of high initial capacity, TV35 gives better results. A solution to improve the stability of electrode could be found through the combination of the three binders, achieving good balance of their capacity, charge-discharge cycling life and rate capability.

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