



Surface treatment of zinc anodes to improve discharge capacity and suppress hydrogen gas evolution

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ABSTRACT

The shape change and redistribution of zinc anode material over the electrode during repeated cycling have been identified as the main factors that can limit the life of alkaline zinc-air batteries. $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ (lithium boron oxide, LBO) glass with high Li^+ conductivity and stability can be coated on the surface of zinc powders. The structures of the surface-treated and pristine zinc powders were characterized by XRD, SEM, TEM, ESCA and BET analyses. XRD patterns of LBO-coated zinc powders revealed that the coating did not affect the crystal structure. TEM images of LBO-coated on the zinc particles were compact with an average passivation layer of about 250 nm. The LBO layer can prevent zinc from coming into direct contact with the KOH electrolyte and minimize the side reactions within the batteries. The 0.1 wt.% LBO-coated zinc anode material provided an initial discharge capacity of 1.70 Ah at 0.5 V, while the pristine zinc electrode delivered only 1.57 Ah. A surface-treated zinc electrode can increase discharge capacity, decrease hydrogen evolution reaction, and reduce self-discharge. The results indicated that surface treatment should be effective for improving the comprehensive properties of anode materials for zinc-air batteries.

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1. Introduction

The zinc-air battery provides the highest available energy density for any primary battery system [1] and is commonly used for hearing aids and mobile applications. Furthermore, the zinc-air secondary battery has a flat discharge voltage, long shelf life and safety features. It is low cost, non-toxic, more environmentally friendly than many other battery systems, and it can be used within a wide temperature range [1].

The main disadvantage of both primary and secondary zinc-air batteries is their limited cycle life due to degradation of the zinc anode material and carbonation of the KOH electrolyte. Shape change, dendrite shorting, passivation or zinc densification, and hydrogen evolution reaction (HER) of the zinc electrode, have been identified as the principal causes for its poor cycle life [2]. Shape change refers to the reduction of the electrochemically active surface area of the zinc electrode during repeated cycling of the battery, as a result of the redistribution of zinc material over the electrode. These problems have largely been solved by improving separators [3,4] or by using various additives like Bi_2O_3 [5,6], $\text{Ca}(\text{OH})_2$ [7,8], Ga_2O_3 [9], $\text{In}(\text{OH})_3$ [10,11], PbO [12,13], SnO_2 [13], Ti_2O_3 [11,14], CdO [14], $\text{Mg}(\text{OH})_2$ [15], and $\text{Ba}(\text{OH})_2$ [15] with the zinc electrode. In

some cases, additives like KF [16] or LiOH [17] were added directly into the electrolyte to minimize zinc degradation. The final solution to these problems must come from a thorough understanding of the fundamental phenomena involved in the redistribution of zinc material over the electrode [18–20].

Zinc has a more negative reduction potential than hydrogen, which consequently creates the problem of a hydrogen evolution reaction [21]. This disadvantage makes it difficult for zinc secondary batteries to be commercialized. Many attempts have been made to suppress hydrogen gas evolution. Mercury has been found to be the most effective additive for suppressing HER, but is prohibited from use due to environmental concerns [22–26]. Other additives such as zincate [27], ZnO , V_2O_5 , PbO , $(\text{NH}_4)_2\text{CS}$ [28], and surfactant [29,30] have also been proposed. Yano et al. [31] reported that using zinc particles alloyed with bismuth and lead, and modified with indium, also suppressed hydrogen gas evolution.

In this paper, the surface of zinc particles modified with various wt.% of $\text{Li}_2\text{O}-2\text{B}_2\text{O}_3$ (lithium boron oxide, LBO) by a solution process was investigated to clarify its effect on suppressing the hydrogen evolution reaction. In addition, we examined the electrochemical performance of the surface modified zinc electrodes.

2. Experimental

Zinc anode particles were coated with 0.05, 0.1, 1.0, and 2.0 wt.% of LBO by a solution process. LBO was synthesized according to a described procedure from 5.97×10^{-4} mol ethanolic $\text{LiOH}\cdot\text{H}_2\text{O}$

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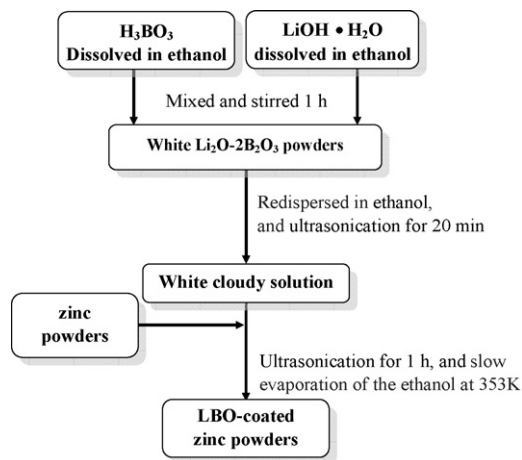


Fig. 1. Schematic of the LBO-coated zinc powders by solution process.

(99%, Aldrich) and 1.19×10^{-3} mol ethanolic H_3BO_3 (98.5%, Aldrich) with constant stirring at 333 K for 1 h to remove excess solvent and form a white LBO powder. The LBO powders were re-dispersed in ethanol and ultrasonicated for 20 min. The 5 g zinc powders (purity: 99.9%, Merck) were added to the above solution and ultrasonicated for 1 h. A subsequent slow evaporation of the ethanol at 353 K resulted in a dark dry mass of the LBO-coated zinc powders. The complete procedure for the synthesis of LBO-coated zinc particles is illustrated in Fig. 1. Zinc electrodes were composed of 95 wt.% LBO-coated zinc powders, 5 wt.% Polytetrafluoro ethylene (PTFE). Electrodes were cast as a slurry in 99% ethanol onto copper current collectors and dried at 60 °C for at least 1 h, the dried coated electrodes roller-pressed with 3 tons pressure for use as anodes.

The corrosion rate can be investigated by volumetric measurement of the hydrogen evolution reaction as a function of time. In this work, a volumetric measurement was used to investigate the hydrogen evolution rate. The apparatus used consisted of a glass vial with airtight cap and a cylindrical graduated Teflon tube fed with paraffin, as shown in Fig. 2 [31]. The volumetric measurement was performed at 323 K. The as-prepared LBO-coated zinc anode active material was packed in a 1.6 cm² separator bag, which was placed into a glass vial filled with 25 wt.% KOH. The vial was sealed airtight and connected to a capillary tube containing 10 ml of paraffin. Levels of paraffin were monitored during an 18-day period. As corrosion occurs with subsequent hydrogen evolution, the paraffin level rose as a function of the corrosion rate.

Structural properties of the LBO-coated zinc materials were studied by the X-ray diffraction method (Siemens D5000). Diffraction

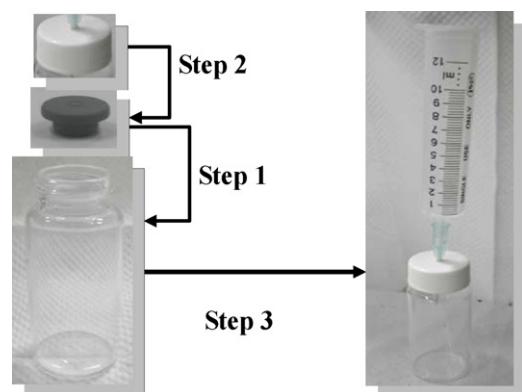


Fig. 2. Apparatus for measuring hydrogen gas evolution.

patterns were acquired with nickel-filtered $\text{Cu K}\alpha$ radiation between scattering angles of 15° and 80° in increments of 4°. The depth profiles of lithium, boron, oxygen and zinc were recorded by an electron spectroscopy for chemical analysis (ESCA) instrument (VG Scientific ESCALAB 250) with monochromatic $\text{Al K}\alpha$ radiation of 1486.6 eV. The morphology and size of the particles were examined by scanning electron microscopy (Hitachi model S-3500V) and transmission electron microscopy (JEOL JEM-200FXII). The LBO coating was confirmed with energy dispersive spectroscopy (energy dispersive X-ray spectrometry). BET surface area was measured by the nitrogen adsorption–desorption method (Micromeritics ASAP 2010).

The alkaline zinc-air cell was assembled in a nitrogen-filled glove box. Fig. 3 is the apparatus of the alkaline zinc-air cell. The cell consisted of two rectangular shaped Teflon casing containers, 5 cm in length and 3.5 cm in breadth, that sandwiched the components of the cell in the order: a LBO-coated zinc electrode functioning as an anode (2.6 cm × 1.5 cm × 0.3 cm), a Celgard 2216 separator microporous polypropylene membrane (2.6 cm × 1.5 cm × 0.01 cm) being soaked in a 25 wt.% KOH solution, and a carbon-based commercial air cathode (2.6 cm × 1.5 cm × 0.15 cm) that was sufficiently porous and permeable to air. Furthermore, an acrylic plate, which had a volume of 4.45 cm³ (3.3 cm × 1.5 cm × 0.9 cm) with 18 small holes (diameter 0.3 cm), was placed next to the cathode to allow limited air passing. To avoid self-discharge of zinc in contact with air, the acrylic plate was kept closed until the cell was ready to discharge. The alkaline zinc-air cell was operated at an applied current of 0.64 A and a discharge cut-off voltage of 0.5 V in a multi-channel battery tester (Arbin, BT 2000) at 298 K.

3. Results and discussion

3.1. Gassing testing

The need to suppress hydrogen formation is critical for both primary and secondary zinc-air batteries. Although mercury has been an effective additive for this purpose, it is prohibited due to its environmental toxicity. Other less-toxic alternative additives such as ZnO and sodium dodecyl sulfate (SDS) have been proposed [27,30]. In general, the rate of hydrogen evolution reaction (HER) greatly depends on the hydrogen overpotential of the zinc anode materials. In order to study the additive effect on HER, the hydrogen volume evolved from the as-prepared LBO-coated zinc particles were measured by a volumetric method. Fig. 4 shows the results of the measurements of hydrogen evolution volume during zinc corrosion. Fig. 4 displays a significant difference in gassing behavior between the bare zinc and various LBO-coated zinc powders. It is evident that zinc corrosion was quite intensive without the use of any additive and the volume of hydrogen evolution was approximately 3.75 times higher than that for the optimal coating composition of 0.1 wt.% LBO-coated zinc powders. The remarkable effect of suppressing HER by LBO coating on zinc powders was due to the fact that the surface of the zinc particles was protected by the LBO layer which provided a passivation layer to prevent direct contact of zinc with the electrolyte. At higher coating levels of 1.0 and 2.0 wt.% LBO, it is difficult to form a homogeneous coating layer, as can be observed from TEM analysis. However, the hydrogen evolution of 0.1 wt.% LBO added zinc reached almost 10 ml after 16 days which is about 80 % of the bare zinc sample. It might cause the easy dissolution of the $\text{Li}_2\text{O}\cdot 2\text{B}_2\text{O}_3$ coating layer in high concentration KOH solution. Table 3 which shows the ICP-AES results of 25 wt.% KOH electrolyte after discharge testing. There were some Li and B components in the electrolyte and a LiOH composition could have formed which stabilized the supersaturated discharge product

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