SURFACE TREATMENT OF Zn ANODES FOR ZINC-AIR BATTERIES

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The shape change and redistribution of zinc anode material over the electrode during repeated cycling and self-discharge have been identified as the main life-limiting factors for alkaline zinc-air batteries. The Li$_2$O-2B$_2$O$_3$ (LBO) glass with high Li$^+$ conductivity and stability can be coated on the surface of Zn powders. The structures of the surface-treated and pristine Zn powders were characterized by XRD, SEM, TEM, ESCA and BET analysis. XRD patterns of LBO-coated Zn powders revealed that the coating did not affect the crystal structure. TEM images of LBO-coated on the Zn particles were compact with an average passivation layer of about 250 nm. The LBO layer can prevent Zn from coming into direct contact with the KOH electrolyte and minimize the side reactions within the batteries. The discharge studies indicated that the 0.1 wt.% LBO coated sample had the best electrochemical performance with an initial discharge capacity of 1.70 Ah at 0.5 V and discharge depth was 89%. The initial discharge capacity and discharge depth of the pristine Zn electrode was 1.57 Ah and 82%, respectively. A surface-treated Zn electrode can increase discharge capacity, decrease hydrogen evolution, 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.

1. Introduction

Zinc-air batteries are still the most promising candidates for electric propulsion purposes. They have a relatively high operating voltage, high energy and high power density. Furthermore, they can be used within a wide temperature range, are relatively cheap and are more environmentally friendly than many other battery systems. The main disadvantages of zinc-air batteries is their limited cycle life, due to the degradation of the zinc anode material. Self-discharge, shape change, dendrite shorting, and, to a lesser extent, passivation and densification of the zinc electrode have been identified as the principal causes for the poor cycle life of the zinc electrode. Zn has a more negative redox potential than hydrogen and thus promotes hydrogen gas evolution. This condition makes it difficult for batteries to be scaled. In this paper, the structure of zinc particles modified with various wt.% of Li$_2$O-2B$_2$O$_3$ (LBO) by a solution process was investigated to clarify its effect in suppressing hydrogen gas evolution. In addition, we examined the electrochemical performance of the surface modified zinc particles.

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 procedure described from LiOH·H$_2$O (5.97×10$^{-4}$mol) and H$_3$BO$_3$ (1.19×10$^{-3}$mol). The white powder LBO was redispersed in water, and sonicated with 5 g zinc powders. A subsequent slow evaporation of the water at 323K resulted in a dark dry mass of the LBO-coated zinc powders.

The alkaline zinc-air cells were assembled in a nitrogen-filled VAC MO40-1 glove box. The cell was constituted of two rectangular shaped teflon casing containers, 5 cm in length and 3.5 cm in breadth, that sandwiched the components of the cell. The electrochemical cell performance was carried out at 0.64A and 0.5V discharge cutoff voltages in a multi-channel battery tester (Arbin, BT 2000) at 298 K.
3. Results and discussion
3.1 Gassing testing

In Fig. 1, it is clear that the 0.1 wt.% LBO-coated zinc particles have efficient compositions, which reduce hydrogen gas evolution and decrease corrosion rate, because the surface of the zinc particles is protected by the LBO which imparts some corrosion resistance on the metal particles and reduces gassing.

3.2 XRD

The XRD diffraction patterns (Fig. 2) conform to the hexagonal structure of the core material and show no basic change in the lattice parameters, which indicate that LBO forms a thin layer on the surface of the core materials and does not form a solid solution by interacting with core material.

3.3 Morphology

Fig. 3 shows the surface morphology of a TEM image of 0.1 wt.% LBO-coated particles. The 0.1 wt.% LBO-coating formed a uniform and translucent compact layer over the zinc particles (dark opaque region) and the thickness of the kernel is around 250 nm.

3.4 Electrochemical properties

The discharge studies (Table 1) indicated that the 0.1 wt.% LBO coated sample had the best electrochemical performance with an initial discharge capacity of 1.70 Ah at 0.5 V and discharge depth was 89%. The initial discharge capacity and discharge depth of the pristine Zn electrode was 1.57 Ah and 82%, respectively.

![Figure 1. The hydrogen gassing vs time for the different wt.% of LBO-coated zinc anode.](image)

![Figure 2. Typical TEM images of the LBO-coated zinc particles (a) 0.1 wt.% Li2O-2B2O3; (b) 2.0 wt.% Li2O-2B2O3](image)

| Table 1. The capacity vs time for the different wt.% LBO-coated zinc anode. |
|---------------------------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
|                                | Initial voltage of discharge (V) | Discharge energy (Wb) | Discharge capacity (Ah) | Work voltage Wh / Ah (V) | Time of discharge (min) | Depth of discharge (%) |
| Blank-Zn                       | 1.42             | 1.48            | 1.57           | 0.94            | 147             | 82              |
| 0.1 wt.% LBO-coated           | 1.44             | 1.59            | 1.70           | 0.94            | 159             | 89              |
| 1.0 wt.% LBO-coated           | 1.43             | 0.33            | 0.35           | 0.94            | 33              | 18              |
| 2.0 wt.% LBO-coated           | 1.43             | 0.25            | 0.29           | 0.93            | 21              | 11              |

![Figure 3. Typical TEM images of the 0.1 wt.% LBO-coated zinc particles.](image)