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Short communication

Novel electrochemical behavior of zinc anodes in zinc/air batteries in the presence of additives

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Abstract

In our continued efforts to find an electrically rechargeable zn/air secondary battery, we report the unique behavior of a zinc oxide anode in the presence of additives such as phosphoric acid, tartaric acid, succinic acid and citric acid. These additives were added to the electrolyte, which is an 8.5 M KOH solution containing 25 g of ZnO and 3000 ppm of polyethylene glycol in 1 l of water. In zn/air systems there are two main problems namely the hydrogen overpotential and dendrite formation during recharging. Investigations have studied in detail both of the problems in order to overcome them. The results obtained in presence of additives are compared with the behavior of the electrolyte 8.5 M KOH in the absence of additives. It has been concluded that the hydrogen overpotential is raised enormously while dendrite formation is reduced to some extent. Out of the four acids studied, the order of increase in hydrogen overpotential is: tartaric acid > succinic acid > phosphoric acid > citric acid. The prevention of dendrite formation follows the order: citric acid > succinic acid > tartaric acid > phosphoric acid.
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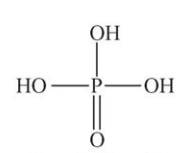
Keywords: Zn/air secondary battery; Hydrogen overpotential; Dendrite formation; Morphology; Electrochemical behavior

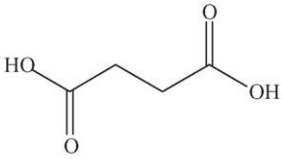
1. Introduction

High specific energy, low cost and environmental friendliness are some of the merits of the Zn/air energy system. It has been classified as a fuel cell or secondary battery according to its electrical rechargeability. Even though the Zn/air system is a promising power source and an energy storage device [1,2], the full potential cannot be utilized because of dendrite formation during recharging in the case of an electrically rechargeable system. This field is still in its infancy, even though some work has already been done [3–7]. Hence it was thought of interest to study the electrochemical behavior of zinc oxide anodes in the presence of certain additives. In the present study we have analyzed the electrochemical behavior of zinc oxide anodes in the presence of phosphoric acid, tartaric acid, succinic acid, and citric acid as additives to 8.5 M KOH solutions and the results have been compared with the behavior of 8.5 M KOH in the absence of these additives.

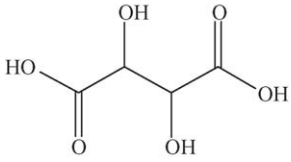
The four acids are chosen for the following reasons. Phosphoric acid is an inorganic acid whereas the other three are organic acids. Out of these three acids, succinic acid is a dicarboxylic acid, tartaric acid has two hydroxyl and two carboxyl groups and citric acid has three carboxyl groups and one hydroxyl group. The structures of the acids are as follows.



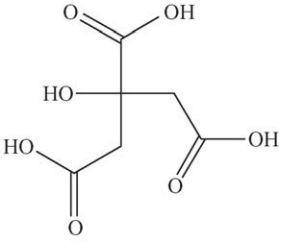
Phosphoric acid



succinic acid



Tartaric acid



Citric acid

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The effect of these additives on the electrochemical behavior of zinc oxide anode was studied using cyclic voltammetry. The surface morphology of zinc oxide electrode was studied using a scanning electron microscope (SEM).

2. Experimental

2.1. Materials

Zinc oxide powder was made into pellets using a copper mesh and hydraulic press provided by Graseby, Specac, England. The pellet was placed in an electrochemical cell with a platinum electrode as the counter electrode and an Hg/HgO electrode was used as the reference electrode. In the Hg/HgO electrode, the concentration of the KOH was 6 M. The electrolytes were prepared by dissolving 476.94 g of KOH (8.5 M), 25 g of ZnO, 3000 ppm of polyethylene glycol, and 4000 ppm of respective additives into 1 l of distilled water. An alkaline solution with no additives was used as the base electrolyte.

2.2. Measuring techniques

The cyclic voltammograms were taken using an impedance measurement unit (IM6, Zahner Electrik) and the same unit was used to investigate the hydrogen evolution reaction. Also, a cathodic overpotential of 100 mV was applied to the zinc oxide electrode to study the surface morphology of the zinc deposition over the electrode. Then the surface morphologies of the zinc deposition on the surface of the zinc oxide electrodes were examined by SEM (S-3000H, JEOL). All of the electrochemical measurements were carried out at a temperature of 25 °C.

3. Results and discussion

3.1. Effect of additives on the hydrogen evolution reaction (HER) on zinc oxide electrodes

Suppression of hydrogen evolution is necessary for both primary and secondary zinc air batteries. The hydrogen overpotential is the potential at which hydrogen is evolved and the electrode undergoes corrosion because of hydrogen evolution. Mercury is an important additive, which is being added to suppress hydrogen evolution. In order to replace mercury by more environmentally friendly materials, the four different acids were added. A cathodic polarization curve taken at 1 mV s^{-1} from the rest potential of the zinc oxide electrode in 8.5 M KOH electrolyte in the absence of additives is shown in Fig. 1. The hydrogen overpotential in the case of the zinc oxide electrode is −1.399 V versus Hg/HgO. In order to investigate the hydrogen evolution reaction on addition of additives to the 8.5 M KOH electrolyte, cathodic polarization curves were taken at 1 mV s^{-1} from the rest potential of the zinc oxide electrode in 8.5 M KOH electrolyte in presence of additives at 4000 ppm level and are shown in Fig. 2. The overpotential is greatly raised in presence of the additives. On adding citric, phosphoric, succinic, and tartaric acids the hydrogen overpotential was raised to −4.17, −4.18, −4.19, and −4.23 V versus Hg/HgO, respectively. These acids may suppress the hydrogen evolution due to the adsorption of their molecules on the surface of the zinc oxide electrode. These adsorbed molecules block some of the active sites of the electrode surface [8]. During cathodic polarization, there are negative charges on the surface of the zinc oxide electrode. However, these acids induce an increase in hydrogen overpotential of the zinc oxide electrode. Hence adsorption of these molecules may not be caused by electrostatic attraction but by the organic group present in the acid. It is very clear from the fact that all the organic acids except the citric acid are suppressing the hydrogen evolution more effectively than the phosphoric acid. The following conclusions may be drawn from the above discussions:

(i) By adding additives to the electrolytes the hydrogen overpotential of the zinc oxide electrode is raised.
(ii) In the case of tartaric acid the increase of hydrogen overpotential is the greatest and it is the least for citric acid.
(iii) In the case of organic acids the increase is more if the number of polar groups is less. This is in consequence of adsorption of these acids onto the surface of the zinc and is not caused by electrostatic attraction.

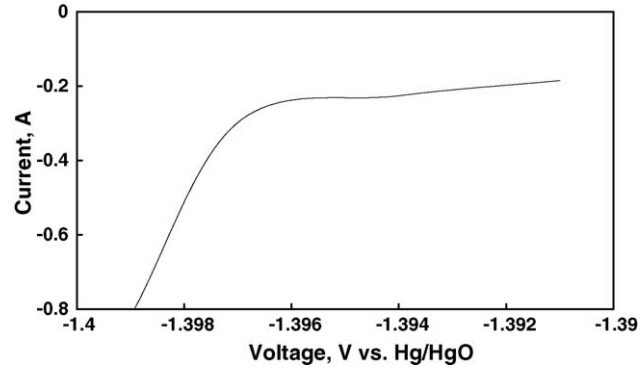

Fig. 1. A cathodic polarization curve at 1 mV s^{-1} from the rest potential of the zinc oxide electrode in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol in presence of no additives to electrolytes.

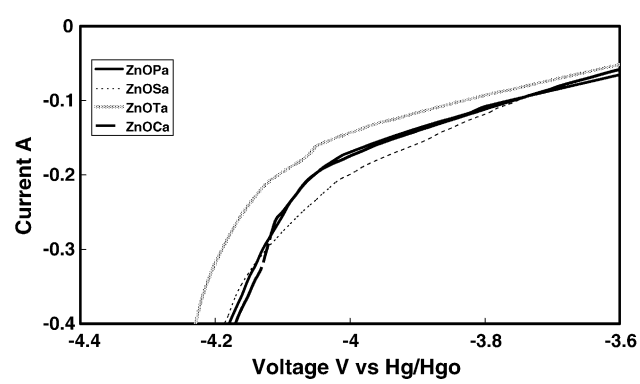

Fig. 2. Cathodic polarization curves of the zinc oxide electrodes at 1 mV s^{-1} with addition of 4000 ppm level of additives into the 8.5 M KOH-based alkaline electrolytes; ZnOPA, phosphoric acid; ZnOSA, succinic acid; ZnOTA, tartaric acid; ZnOCA, citric acid.

3.2. Effects on cyclic voltammetric curves of zinc oxide electrode

To study the reversible behavior of zinc oxide electrodes in the presence and absence of additives, the cyclic voltammograms for zinc oxide electrodes between 0.1 and −0.35 V at 1 mV s^{-1} in 8.5 M KOH containing 25 g l^{-1} zinc oxide and 3000 ppm polyethylene glycol as the base electrolyte in presence and absence of additives were taken and are presented in Fig. 3. The additives affect both the cathodic and anodic part of the cyclic voltammogram. The increase is greater in the anodic part in the case of tartaric acid and it is least in the case of phosphoric acid. In the case of succinic acid it is less than that of the base electrode even without additives. These shifts of the onset potential of deposition and the potential at the cathodic current maximum indicate that the deposition of zinc from zincate electrolyte is inhibited to a certain degree in the presence of the additives. The possible explanation of this may be that the adsorbed molecules of additives may form a layer, which prevents the electro-reduction process of zincate [9].

The inductive loop occurs because of the nucleation process of the zinc [10]. The inductive loop occurs at a negative overpotential. This is due to the formation of mature nuclei under the conditions of overpotential deposition. A possible explanation for this may be that the adsorbed molecules of the additives on the active sites of the electrode surface may block the deposition of zinc on these active sites. Hence the formation of new nuclei would probably require a higher potential. As a result,

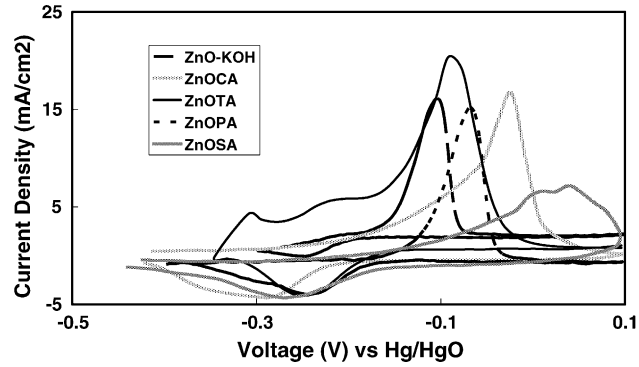

Fig. 3. Cyclic votammograms for a zinc oxide electrode between 0.1 and −0.35 V at 1 mV s^{-1} in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm polyethylene glycol as the base electrolyte in presence and absence of 4000 ppm level of additives, ZnO–KOH, in the absence of additives; ZnOCA, in the presence of citric acid; ZnOTA, in the presence of tartaric acid; ZnOPA, in the presence of phosphoric acid; ZnOSA, in the presence of succinic acid.

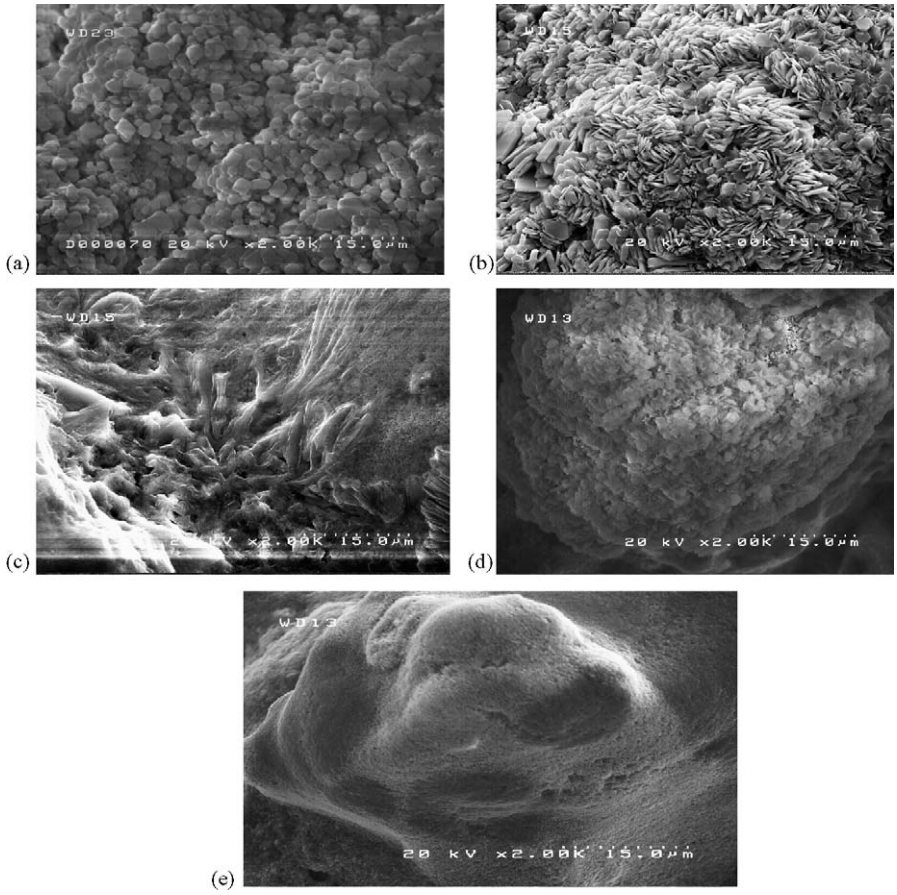

Fig. 4. The surface morphologies of the deposited zinc after the potential-controlled electro-deposition with −100 mV over the zinc oxide electrode for 120 min in the absence and the presence of additives to the base electrolyte: (a) no additives, (b) in presence of phosphoric acid, (c) in presence of tartaric acid, (d) in presence of succinic acid, and (e) in presence of citric acid.

the zinc deposition from zincate solution is suppressed and shifted to more negative potentials. Similarly the anodic part is also slightly affected, but the effect is more in case of succinic acid. Hence, we suggest that reversibility of the reaction for the zinc oxide electrode is increased on adding the acids as additives.

3.3. Studies on surface morphology

The surface morphologies of the deposited zinc, after the potential controlled electro-deposition with −100 mV over the zinc oxide electrode for 120 min, were investigated using a scanning electron microscope and are shown in Fig. 4. The deposition from a blank solution containing only the base electrolyte with no additives is shown in Fig. 4(a). Fig. 4(b)–(e) shows the surface morphology of the deposit in the presence of additives: phosphoric acid, tartaric acid, succinic acid and citric acid, respectively. It appears that the prevention of the dendrite formation follows the order: citric acid > succinic acid > tartaric acid > phosphoric acid. Dendrite formation is due to the uneven deposition of zinc over the zinc oxide electrode. This deposition is purely electrostatic in nature. Hence the molecule, which has the highest number of polar groups, is believed to be acting as a helpful resistor of dendrite formation. From this point of view it is clear that for the hydrogen evolution reaction, among the organic molecules added, the molecules with least number of polar groups are highly effective. However, in the case of prevention of dendrite formation, the molecules with the highest number of polar groups are most effective. Scanning electron microscope images clearly show that the deposition of zinc in the absence of additives is in the form of bunches with dendrite formation. More or less the same condition prevails in the case of phosphoric acid as the additive. But with the other three acids, the condition is much improved and in the case of citric acid deposition, neither needle like nor dendrites are formed. The deposition is very compact.

4. Conclusions

The effectiveness of four additives namely phosphoric acid, tartaric acid, succinic acid and citric acid to the electrolyte to suppress the hydrogen evolution and to prevent dendrite formation were studied. In the case of suppression of hydrogen evolution, the order is tartaric acid > succinic acid > phosphoric acid > citric acid. In the case of prevention of dendrite formation, the order is citric acid > succinic acid > tartaric acid > phosphoric acid. Above all, the postponing of hydrogen evolution is very remarkable by shifting from −1.3 to around −4.1 V versus Hg/HgO. Hence these additives can be used in a Zn/air electrically rechargeable battery, which can replace the existing primary/mechanically rechargeable batteries as electrical recharging is easier than mechanical recharging.

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