

Short communication

Effect of additives on the electrochemical behaviour of zinc anodes for zinc/air fuel cells

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Abstract

Due to its low cost and high power density, the Zn/air energy system is considered to be a promising power energy source. Furthermore, Zn/air technology could be used as either an electrically or a mechanically rechargeable system. Electrical recharging is problematic, however, due to the formation of zinc dendrites. Similarly, hydrogen overpotential plays a major role. The present study attempts to reduce dendrite formation and raise hydrogen overpotential through the addition of cellulose and lead oxide, respectively. It is concluded that cellulose reduces dendrite formation to some extent. It also works well to raise the hydrogen overpotential even in the absence of lead oxide.

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1. Introduction

The Zn/air energy system has the attributes of high specific energy, low cost and environmental friendliness. According to its electrical rechargeability, it has been classified as either a fuel cell or a secondary battery. Although the Zn/air energy system is a promising power source and energy-storage device [1,2], but its full potential has not been utilized due to zinc dendrite formation during recharging when used as an electrically rechargeable battery. Accordingly, ways and means must be found to avoid this problem. Even though some work had already been done in this direction [3–6], little progress has been made. Thus, it is considered to be of interest to examine the behaviour of zinc anodes in the presence of cellulose. Cellulose is expected to function as an additive that can cover the electrode area and thereby reduce the growth of dendrites. Similar studies have been reported in the literature [7]. The investigation reported here is the first time that the additive has been added to the electrode material rather than to the electrolyte.

Cellulose had an excellent chemical stability in the alkaline solution. Lead oxide is added to raise the hydrogen overpotential. The effect of cellulose and lead oxide on the electrochemical behaviour of zinc oxide anodes is examined by means of cyclic voltammetry and X-ray diffraction (XRD) analysis. The surface morphologies of the zinc oxide electrodes after the deposition reaction are comparatively studied.

2. Experimental

2.1. Electrode materials

In order to prepare zinc oxide electrodes as anodes, zinc oxide, lead oxide, cellulose and PTFE were taken in a ratio of 89, 2, 5 and 4 wt.%, respectively. For a 10 g batch 100 ml of distilled water was added to the mixture and stirred for 24 h. The mixture was dried in an oven at 100 °C for 4 h and then dried at 90 °C under vacuum. The resulting powder was made into pellet using a copper mesh and hydraulic press (Graseby, Specac). For lead oxide free material, lead oxide was replaced by zinc oxide. Also for both cellulose and lead oxide free material, only zinc oxide was taken. Details of the prepared anodes are summarized in Table 1.

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Table 1
Anode samples

Sample name	Contents	Composition ratio
ZOPO	Zinc oxide:lead oxide:PTFE	94:2:4
ZOPOC	Zinc oxide:lead oxide:cellulose:PTFE	89:2:5:4
ZOC	Zinc oxide:cellulose:PTFE	91:5:4
ZO	Zinc oxide only	100

2.2. Electrolytic cell

The pellet was placed in an electrochemical cell with a platinum counter electrode and a Hg/HgO reference electrode. All potential are reported with respected to this reference electrode.

2.3. Electrolyte

The electrolyte was prepared by dissolving 476.94 g of KOH (8.5 M), 25 g of ZnO and 3000 ppm of polyethylene glycol in 1 l of distilled water.

Cyclic voltammograms were taken with an impedance measurement unit (IM6, Zahner elektrik). X-ray diffraction patterns of used powders were determined with a philips 1830 X-ray diffractometer that used Ni filtered Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$) in a 2θ range of $10\text{--}110^\circ$ at a scan rate of 0.1° s^{-1} . The surface morphology of zinc electrodes was examined with a scanning electron microscope (S-3000H, Jeol).

3. Results and discussion

3.1. Effect of cellulose and lead oxide on hydrogen evolution reaction (HER) on zinc oxide electrode

Suppression of hydrogen evolution is very much necessary for both primary and secondary zinc solidus air batteries. In order to replace mercury, lead oxide and cellulose have been used as additives. Cathodic curves from the rest potential of the zinc electrodes at $500 \mu\text{V s}^{-1}$ in an electrolyte of 8.5 M of KOH, 25 g of ZnO and 3000 ppm of polyethylene glycol in 1 l of distilled water are shown in Fig. 1. The hydrogen overpotential in the

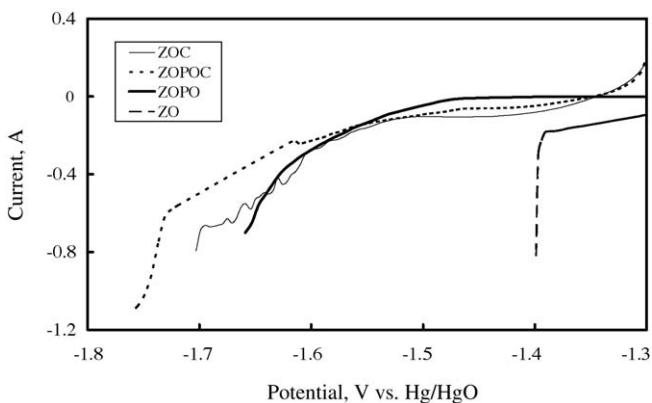


Fig. 1. Effect of additives to a zinc oxide electrode on hydrogen evolution reaction in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol as electrolyte.

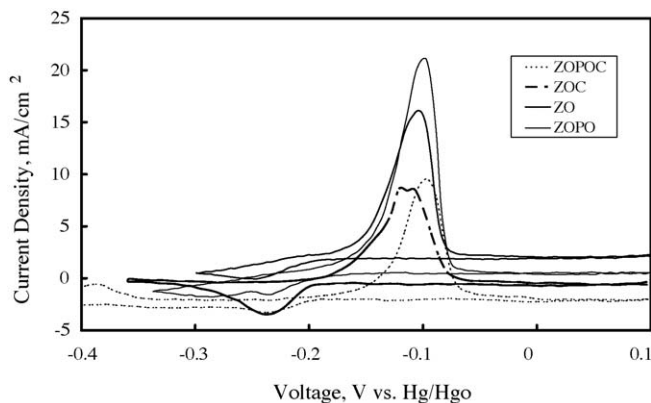


Fig. 2. Cyclic voltammograms for the zinc oxide electrodes between 0 and -0.3 V vs. Hg/HgO in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol in the presence of cellulose and lead oxide.

case of a pure zinc oxide electrode is -1.399 V . It is increased to -1.66 V when lead oxide is added and to -1.71 V when cellulose is added. Thus, cellulose serves as a more effective additive. When both cellulose and lead oxide are added, the hydrogen overpotential is shifted to the most negative potential, viz., -1.76 V .

The hydrogen overpotential is shifted to a more negative value because of the building of electrolyte channels that act as an internal wick through the electrode and thereby improve the transport of the electrolyte [7]. This behaviour is entirely different from that of the adsorption phenomenon that has been reported for additives that are added directly to the electrolyte [8]. In other words, the charge–discharge may be more significantly affected if the additives are added to the electrolyte. This does not apply to the present study, however, as the additives are added during preparation of the electrode itself.

3.2. Effect on cyclic voltammetric curves of zinc oxide electrodes

Cyclic voltammograms for the zinc oxide electrodes between 0 and -0.3 V vs. Hg/HgO in an electrolyte of 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol in the presence of cellulose and lead oxide were studied. The findings are given in Fig. 2. The lead oxide and cellulose influence the cyclic voltammetric behaviour of the zinc electrode, i.e. both the cathodic and the anodic curves.

On comparing the cyclic voltammogram of zinc oxide with that of a mixture of zinc and lead oxides, the oxidation part is enhanced and there is a slight suppression in the reduction reaction. With cellulose, however the trend is reversed, i.e. the oxidation reaction is suppressed whereas the cathodic reaction is considerably increased. Surprisingly, on the addition of both cellulose and lead oxide, both the oxidation and reduction reactions are reduced. A possible explanation for this behaviour is as follows. Zinc oxide and lead oxide in the electrode are both exposed to oxygen introduced in through a hole and is intended for the counter electrode. Also, lead oxide cannot function as a corrosion inhibitor as long as it is added to the electrode and not

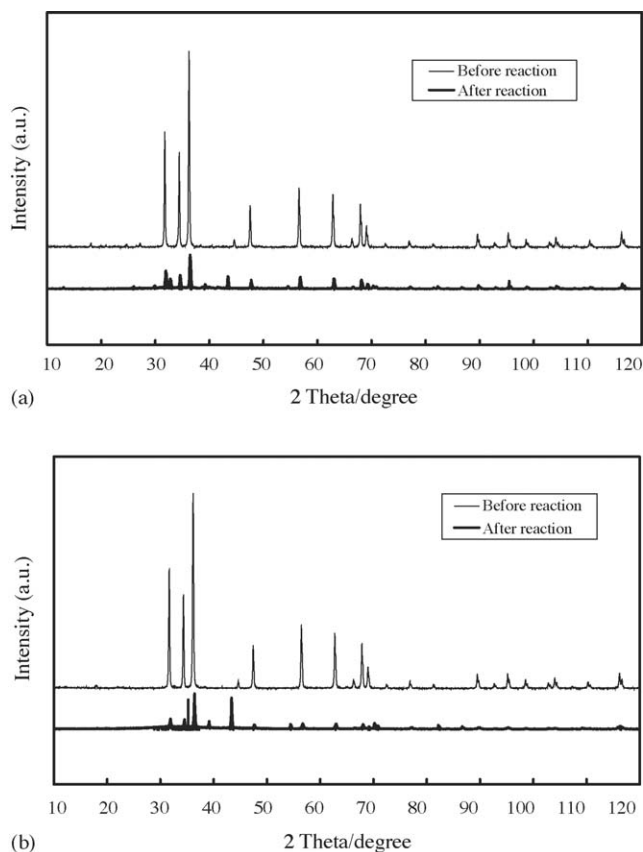


Fig. 3. XRD patterns of anodes before and after hydrogen evolution reaction: (a) ZOPOC; (b) ZOC.

to the electrolyte. Hence, the oxidation is enhanced, and thus the reduction reaction is slightly suppressed. With cellulose, the condition is entirely different. Being an organic substance, it is less susceptible to oxidation. Hence, the oxidation reaction of zinc is reduced and reduction reaction is increased. On adding both lead oxide and cellulose, however, there is less of an effect on both oxidation and reduction.

3.3. Analysis of XRD data

X-ray diffraction patterns were obtained for electrodes of zinc oxide and cellulose, and for electrodes of zinc oxide, lead oxide and cellulose, both before and after the hydrogen evolution reaction (Fig. 3). From the data, it is clear that no major changes occur during the reaction. There is, however, a new peak at the $2\theta = 43^\circ$ in electrodes either with or without lead oxide after the hydrogen evolution reaction. This may be due to the formation of zincate in both cases.

3.4. Effect on electrodeposition of zinc

Current–time curves for all the electrodes in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol in the presence of cellulose and lead oxide were recorded at a cathodic overpotential of 100 mV, as shown in

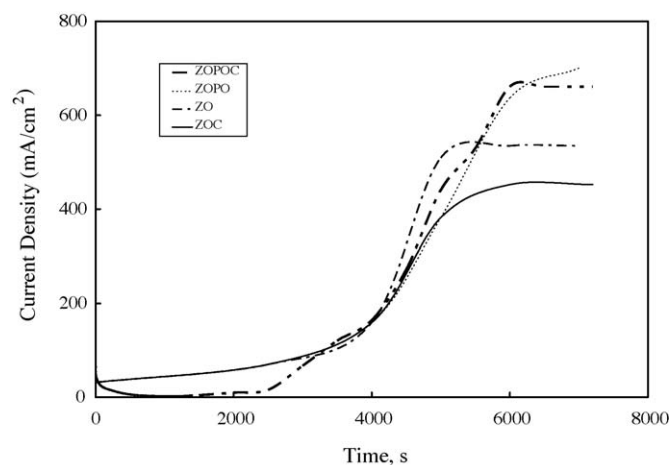


Fig. 4. Current–time curves for zinc oxide electrodes at cathodic overpotential of 100 mV in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol in presence of cellulose and lead oxide.

Fig. 4. Current–time data can be considered to be representative of the change in surface structure during a potential-controlled electrodeposition [9] because electrodeposition at this potential of 100 mV is regarded as the only significant cathodic reaction, while oxygen reduction is a very minor reaction at this KOH concentration [8,9]. If the deposition of zinc is completely uniform and compact, the current flow through the electrode will not increase as the real surface area of the electrode remains the same. Conversely, if zinc deposition takes place with dendrite formation, the current passing through the electrode will increase due to an increase in the effective surface area. As shown in Fig. 4, it is found that all electrodes display a sharp rise in current starting from around 4000 s. Notably, ZOPOC and ZOC electrodes that contain cellulose exhibit a suppression of current density, which indicates a change in the surface structure compared with other ZO and ZOPO electrodes. This behaviour agrees with the results of an earlier study [7] that showed a decrease in the porosity of electrodes with high cellulose content [7]. From Fig. 3, it is also clear that dendrite formation is more or less the same for pure zinc oxide alone and a mixture of zinc oxide and lead oxide only. It is least, however, in the case of a zinc oxide–cellulose mixture although it is not significantly eliminated. When lead oxide is added, dendrite formation is not effectively reduced. This trend is clearly illustrated in Figs. 3 and 4.

For all the potential-controlled electrodes, the change in surface morphology corresponding to the deposition of zinc during the 120 min test has been investigated by means of scanning electron microscopy, as shown in Fig. 5. The deposit from a blank solution containing only zinc oxide is shown in Fig. 5(a). There is a large quantity of dendrite crystallites and the deposition is uneven. The situation remains the same after the addition of lead oxide, as displayed in Fig. 5(b). On the other hand, the addition of cellulose improves the morphology and a somewhat uniform deposition is obtained, as shown in Fig. 5(c). On adding lead oxide, there is a deterioration in morphology, as illustrated in Fig. 5(d). In summary, these surface morphological investiga-

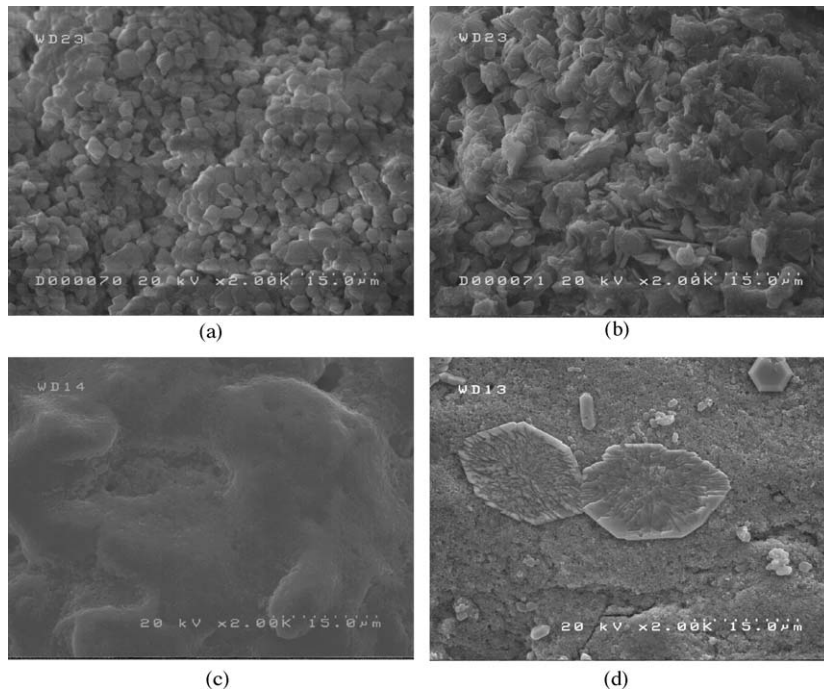


Fig. 5. Scanning electron micrographs of anodes of zinc electrodeposits from 8.5 M KOH containing 25 g l^{-1} of ZnO and 3000 ppm of polyethylene glycol: (a) ZO; (b) ZOPO; (c) ZOC; (d) ZOPOC.

tions for all electrodes strongly support current–time behaviour under potential-controlled electrodeposition.

4. Conclusions

The efficacy of lead oxide and cellulose as inhibitors of zinc corrosion and dendrite growth has been examined. The additives are added not to the electrolyte but to the electrode during its preparation. Cellulose is more effective than lead oxide, but both additives can be used as a substitute for mercury to decrease the electrode corrosion reaction in an alkaline zinc/air fuel cell. Nevertheless, there is limited improvement in both the surface morphology of the zinc deposit and in reduction of dendrite growth.

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