

Short communication

Novel alloys to improve the electrochemical behavior of zinc anodes for zinc/air battery

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Received 21 October 2005; received in revised form 6 February 2006; accepted 6 February 2006

Available online 2 May 2006

Abstract

In our continued efforts for improving the performance of zinc anodes for a Zn/air battery, we now report the preparation of three alloys and improved performances of anodes made up with these alloys. The alloys contained zinc, nickel, and indium with different weight percentages and were calcined at two different temperatures. Out of the six alloys, the alloy which has a composition of zinc 90%, nickel 7.5% and Indium 2.5% and fired at 500 °C is found to be the best. In the case of the hydrogen evolution reaction, this alloy had its potential shifted to a more negative potential. As far as the cyclic voltammograms were concerned, the difference between the anodic and cathodic part was minimal when compared with other alloys. Surprisingly, this alloy had reversibility even after 100 cycles of the cyclic voltammogram. This is a clear indication that dendrite formation was reduced to a considerable extent. Images taken with a scanning electron microscope also indicated reduced dendrite formation. © 2006 Elsevier B.V. All rights reserved.

Keywords: Zn alloys; Hydrogen overpotential; Dendrite formation; Electrochemical behavior; Morphology

1. Introduction

High specific energy, low cost and environmental friendliness are some of the merits of the Zn/air battery system. It has been classified as a primary or a secondary battery according to its electrical rechargeability. Even though the Zn/air system is a promising power source and energy storage device [1,2], the full potential cannot not be utilized because of dendrite formation during recharging in the case of an electrically rechargeable system. Means and ways are to be found to avoid dendrite formation. This field is still in its infancy, even though some work has already been done [3–8]. However, the majority of the work done so far is on the zinc oxide anode rather than on zinc itself. The main reason for this is the irreversibility of the zinc electrode. Hence it was thought of interest to study the electrochemical behavior of alloys with various compositions to make zinc anodes more reversible. Specifically, it is believed that alloys with nickel and indium will reduce the zinc dendrite formation to a considerable extent. In our previous studies we

added additives to the electrode material [7] and additives to the electrolyte [8]. However, zinc oxide was the electrode material in both cases.

Now, the electrochemical behavior of the alloys have been studied. We have newly prepared six alloys as shown in Table 1. In all the alloys, the weight percentage of zinc was maintained at 90.

The electrochemical behavior of these alloys was studied using cyclic voltammetry. Physical characterization was done by analysis of the XRD pattern. The surface morphology of the alloy materials was studied by recording the images taken by a scanning electron microscope (SEM) before and after the reactions.

2. Experimental

2.1. Materials

The alloys were prepared as follows.

The metals were taken in the form of acetate salts in the required quantities. Then 3 g of citric acid, acrylamide and *N,N'*-Methylene bisacrylamide were, respectively, added followed by a small amount (less than 0.5 g) of ammonium peroxodisulphate. The mixtures in water were then heated. The resulting gels were

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Table 1
Summary of the synthesized alloys

Prepared alloys	Weight percentage (wt.%)	Calcination temperature (°C)	Time (h)
ZNI-1	Zn90 Ni5 In5	500	6
ZNI-2	Zn90 Ni5 In5	750	3
ZNI-3	Zn90 Ni7.5 In 2.5	500	6
ZNI-4	Zn90 Ni7.5 In 2.5	750	3
ZNI-5	Zn90 Ni2.5 In 7.5	500	6
ZNI-6	Zn90 Ni2.5 In 7.5	750	3

kept at 100 °C overnight. Then these were fired at the required temperature in an argon atmosphere for the desired time as indicated in Table 1. The resulting alloys were ground into powders.

Similarly, for pure zinc, metallic zinc powder was taken as such without treatment. The alloys and pure metallic powder were made into pellets using a copper mesh and hydraulic press purchased from Greaseby, Specac Company, England. A pellet was placed in an electrochemical cell with a platinum electrode as the counter electrode and a Hg/HgO electrode was used as the reference electrode. The electrolytes were prepared by dissolving 476.94 g of KOH (8.5 M), 25 g of ZnO, and 3000 ppm of polyethylene glycol in one liter of distilled water. The preparatory work was done in a dry room.

2.2. Measuring techniques

The cyclic voltammograms were taken by using an impedance measurement unit (IM6, Zahner Elektrik) and the same unit was used to investigate the hydrogen evolution reaction. Also, a potential of -1.3 V versus Hg/HgO was applied to study the corrosion of the electrode. This potential was selected since all the alloys were showing this potential after hydrogen evolution reaction. The XRD patterns of all the alloys were determined to characterize them by using a X-ray diffractometer (1830 X-ray diffractometer, Philips) with Ni filtered Cu K α radiation ($\lambda = 1.5406$ Å) in the 2θ range of 20–120° at a scan rate of $0.02^\circ \text{ s}^{-1}$. The surface morphologies of all the alloys before and after carrying out the current-time studies were examined to study the dendrite formation by SEM (S-3000H, JEOL).

3. Results and discussion

3.1. Hydrogen evolution reactions (HER) on the alloys

Suppression of hydrogen evolution is necessary for a Zn/air battery system. In order to replace mercury with environmentally friendlier materials, the suitability of all the six alloys was tested for the hydrogen evolution reaction. These values were compared with that of pure zinc. Cathodic polarization curves at 1 mV s^{-1} from the rest potential in 8.5 M KOH against Hg/HgO reference electrode for both pure zinc and alloys are shown in Fig. 1. For pure zinc the hydrogen overpotential was found to be -1.609 V. When compared with pure zinc, the hydrogen overpotentials for the four alloys were shifted to more negative values indicating postponement of the hydrogen evolution reaction. As

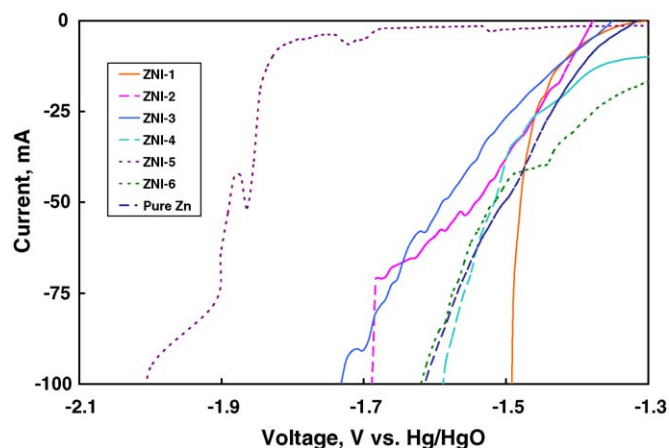


Fig. 1. Cathodic polarization curves for both zinc and alloys at 1 mV s^{-1} from the rest potential in 8.5 M KOH vs. Hg/HgO reference electrodes.

a result, the corrosion of the zinc electrode would be reduced to a great extent. The hydrogen overpotentials of the alloys are presented in Table 2. From the table it is clear that the alloy with the composition: Zn90% Ni2.5% In7.5% and fired at 500 °C had the hydrogen overpotential shifted to the most negative value of -2.009 V. For controlling the hydrogen overpotential, both the composition of the alloy and the firing temperature had a major role to play. The shifting of the hydrogen overpotential may be due to the covering of zinc by both nickel and indium. However, it seems that indium may have a better covering power than nickel. This is because when the indium percentage is 7.5, it has a hydrogen overpotential shifted to -2.009 V from -1.725 at 2.5 wt.% of indium. Similarly when the firing temperature is 500 °C the hydrogen overpotential is shifted to the more negative side, the only exception being Zn90% Ni5% In5% at 500 °C.

3.2. Cyclic voltammograms of the alloys

Cyclic voltammograms for the electrodes made of pure zinc as well as the Zn alloys were studied between 0.1 and -0.5 V versus Hg/HgO in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol and are shown in Fig. 2. The cyclic voltammogram of pure zinc was also recorded under the same conditions and is shown in Fig. 3. It was found to be irreversible and hence pure zinc metal may not be useful in rechargeable systems. Moreover, in case of pure zinc, the anodic activity is also reduced when compared with the alloys.

Table 2
Hydrogen overpotentials of alloys and pure zinc

Alloy	Hydrogen overpotential, V vs. Hg/HgO
ZNI-1	-1.490
ZNI-2	-1.683
ZNI-3	-1.725
ZNI-4	-1.594
ZNI-5	-2.009
ZNI-6	-1.621
Pure zinc	-1.609

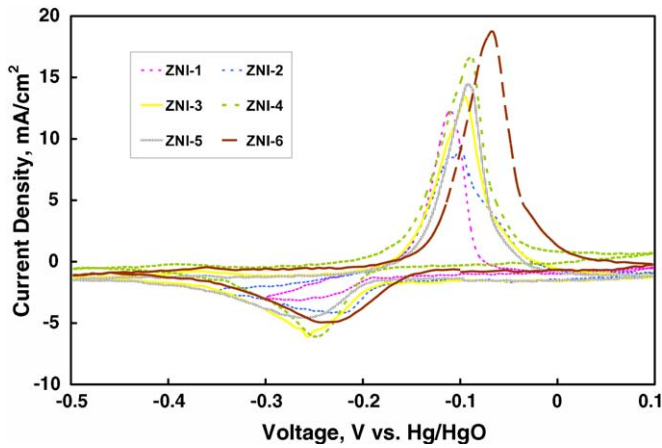


Fig. 2. Cyclic voltammograms for the alloy electrodes between 0.1 and -0.5 V vs. Hg/HgO in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol.

On comparing the cyclic voltammograms of all the six alloys, the firing temperature plays a major role than the composition. The alloys which were fired at 750°C had enhanced anodic activity and also an enhanced cathodic activity, the only exception being Zn90% Ni5% In5%. From Fig. 2, it is clear that the alloy containing Zn90% Ni5% In5% shows less reversibility. A higher reversibility is shown by all the other alloys. Since the difference in the currents between the anodic and cathodic regions is less in the case of alloy containing Zn90% Ni7.5% In2.5% fired at 500°C , this alloy was chosen to study the reversibility. We have studied the reversibility by recording cyclic voltammograms, and it is surprisingly reversible even after 100 cycles. Each first cycle produced enlarged anodic and cathodic regions and then almost the same sized anodic and cathodic regions. This may be due to the time taken by the electrode to attain equilibrium as shown in Fig. 4.

3.3. Analysis of the XRD data

We have recorded the XRD patterns for all the alloys which are given in Fig. 5. It is clear from the figure that alloys were

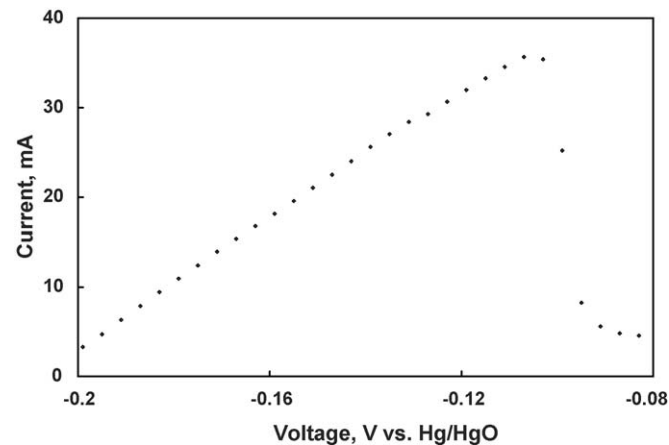


Fig. 3. Cyclic voltammogram of pure zinc vs. Hg/HgO in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol.

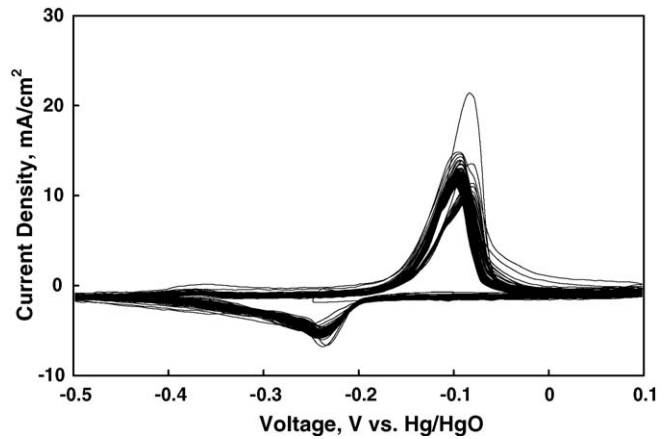


Fig. 4. Cyclic voltammograms for the electrodes made up of the alloy ZNI-3 between 0.1 and -0.5 V vs. Hg/HgO in 8.5 M KOH containing 25 g l^{-1} of zinc oxide and 3000 ppm of polyethylene glycol during 100 cycles.

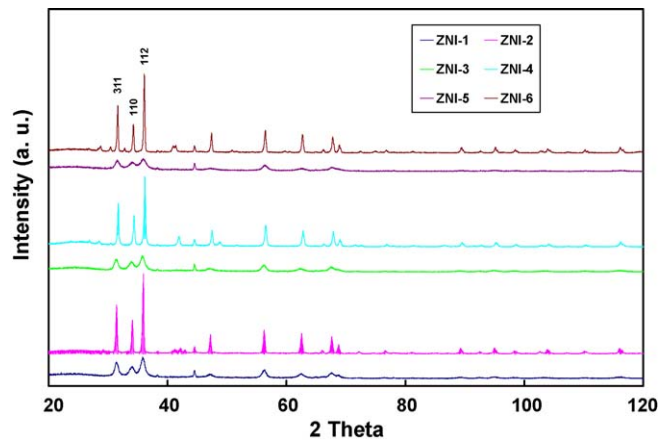


Fig. 5. The XRD patterns for all the alloys.

formed as a single phase and were well crystallized even at 500°C , but at 750°C an improvement in the degree of crystallinity was observed. Therefore, it is believed that a temperature of as low as 500°C is the minimum temperature required for the formation of a single-phase product. Though the crystallization of the product has been well initiated at 500°C , it is felt

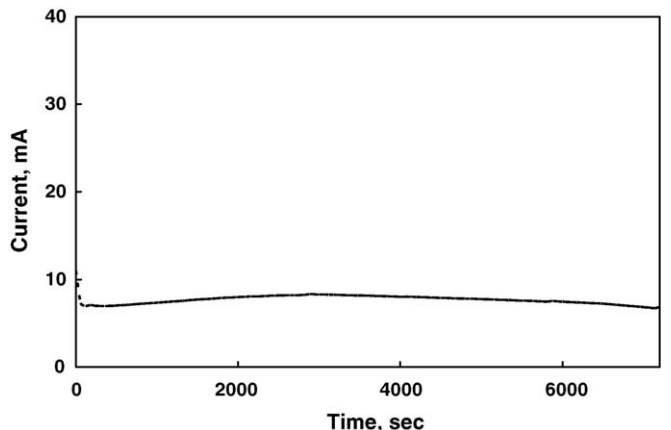
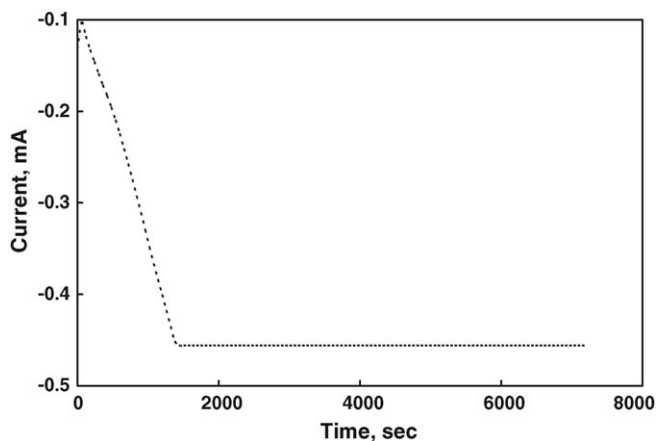
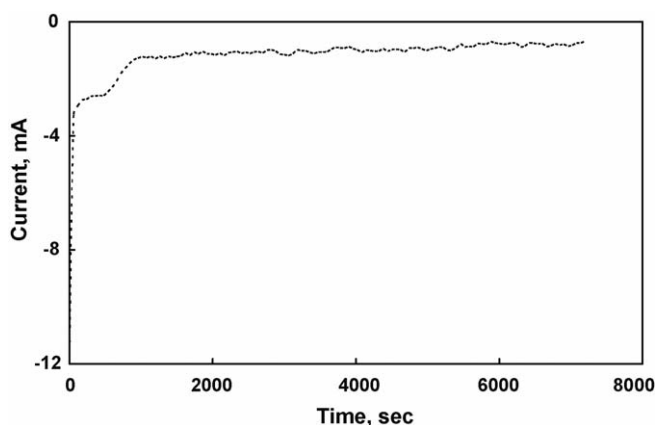
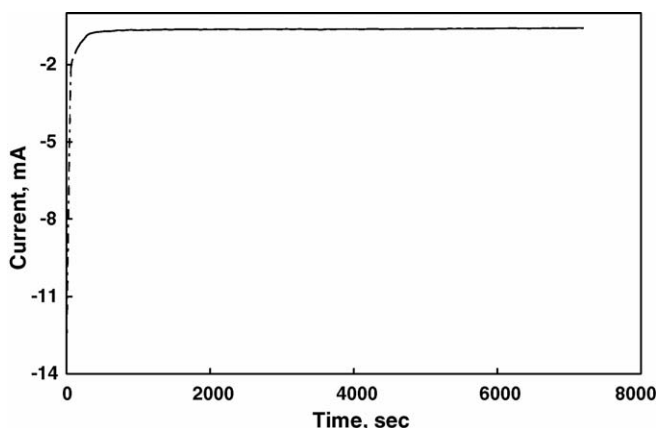
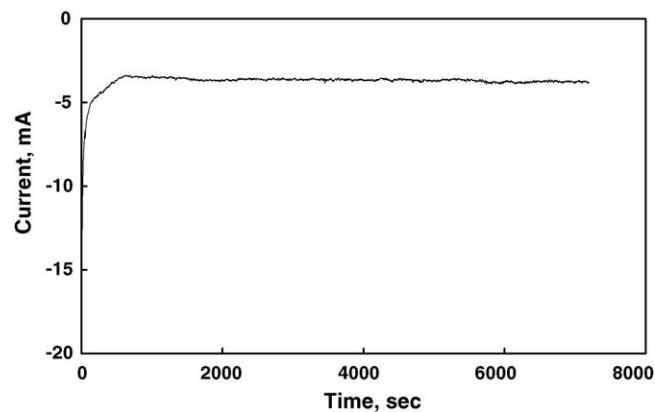
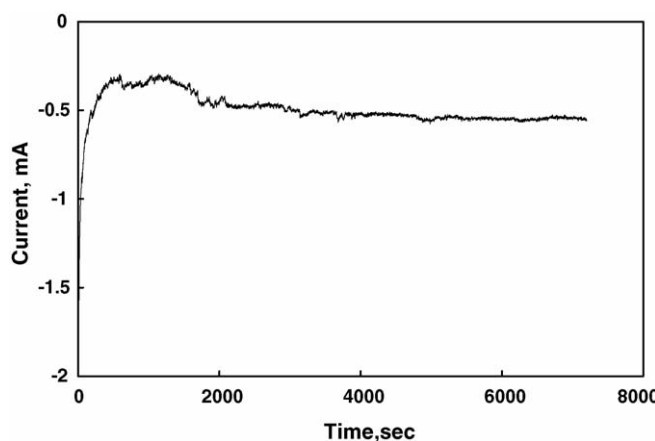


Fig. 6. Current behavior for pure zinc at -1.3 V vs. Hg/HgO for 120 min.

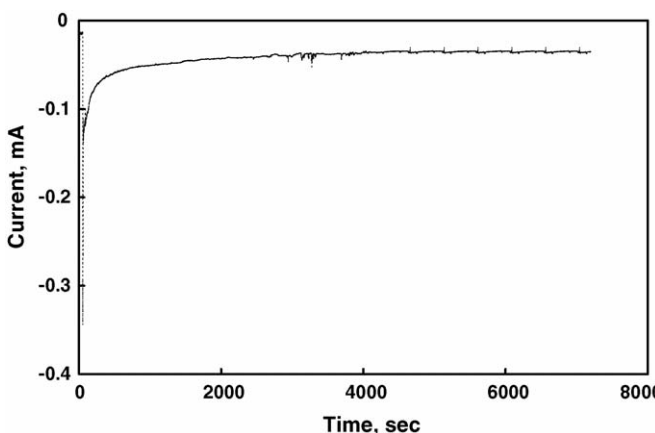
Fig. 7. Current behavior for the alloy ZNI-1 at -1.3 V vs. Hg/HgO for 120 min.Fig. 8. Current behavior for the alloy ZNI-2 at -1.3 V vs. Hg/HgO for 120 min.

that the improved crystallinity is expected for the samples prepared at a high temperature say 750°C . There is no considerable change in the position of the peaks in the XRD pattern for the samples fired at 500 and 750°C . The peaks around 31.77 , 34.43 and 36.25 correspond to zinc. In addition to this, we had peaks for Ni and In at 56.83 and 29.49 , respectively.

Fig. 9. Current behavior for the alloy ZNI-3 at -1.3 V vs. Hg/HgO for 120 min.Fig. 10. Current behavior for the alloy ZNI-4 at -1.3 V vs. Hg/HgO for 120 min.Fig. 11. Current behavior for the alloy ZNI-5 at -1.3 V vs. Hg/HgO for 120 min.

3.4. Linear polarization measurements

In order to examine the corrosion of the electrodes, a linear polarization technique was applied [9] and the electrodes were potentiostatically polarized to -1.3 V versus Hg/HgO. The behavior of the pure zinc and all the alloys we synthesized were monitored at -1.3 V versus Hg/HgO for 120 min and are shown

Fig. 12. Current behavior for the alloy ZNI-6 at -1.3 V vs. Hg/HgO for 120 min.

in Figs. 6–12. This potential was selected since the electrodes reached this potential on open circuit voltage after the hydrogen evolution reaction. The potential was applied for 2 h. From Fig. 6, it is clear that in the case of pure zinc, the corrosion is the severest since the current value was around +6 mA for the entire 2 h. However, this value was greatly reduced in the case of all the alloys. The order of the corrosion currents is ZNI-4 < ZNI-2 < ZNI-3 < ZNI-1 < ZNI-5 < ZNI-6. This is a clear indication that corrosion is very much reduced in the case of all the alloys except for two alloys. These two alloys had hydrogen overpotential values slightly positive compared to pure zinc. However, the alloys showing a high corrosion current had the hydrogen overpotential shifted to more positive values than pure zinc.

3.5. Effect on electrodeposition of zinc

Indium and nickel were added to zinc to reduce dendrite formation during the electrodeposition of zinc, i.e., during recharging. The inherent problem of dendrite formation is almost overcome by using the alloys. This is confirmed by two ways: one is by testing for reversibility in the cyclic voltammetry and the other is by comparing the scanning electron microscope (SEM) images of the alloys as well as pure zinc before and after the current–time studies. The SEM images are given in Fig. 13. The SEM images of all the alloys were recorded after the preparation of the electrode and after a cathodic potential of -1.3 V for 120 min. From the images it is clear that the inherent property of dendrite formation is very much reduced in the alloys. The

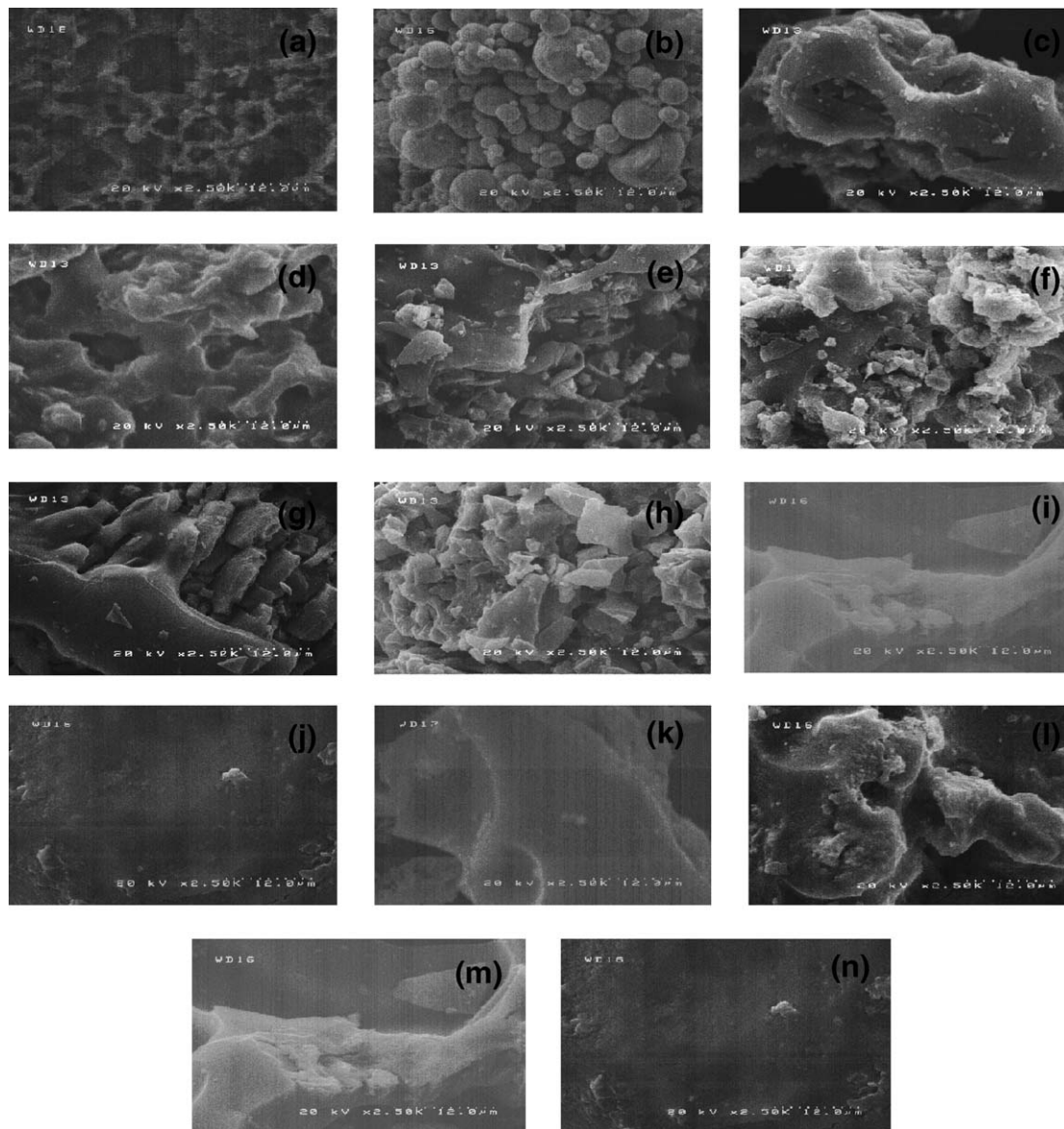


Fig. 13. Scanning electron microscope images of pure zinc and alloy materials. (a) Pure zinc before reaction; (b) Pure zinc after reaction; (c) ZNI-1 before reaction; (d) ZNI-1 after reaction; (e) ZNI-2 before reaction; (f) ZNI-2 after reaction; (g) ZNI-3 before reaction; (h) ZNI-3 after reaction; (i) ZNI-4 before reaction; (j) ZNI-4 after reaction; (k) ZNI-5 before reaction; (l) ZNI-5 after reaction; (m) ZNI-6 before reaction; (n) ZNI-6 after reaction.

images before the reaction and after the reaction are almost the same indicating that less dendrite formation is occurring during the supply of cathodic potential of -1.3 V for 120 min.

4. Conclusions

The effectiveness of the alloys of Zn in reducing dendrite formation and raising the hydrogen overpotential was studied. Dendrite formation was almost completely removed and the hydrogen overpotential was raised to some extent. From the hydrogen evolution reaction, all the alloys except ZNI-1 and ZNI-4 were clearly having their hydrogen overpotentials shifted to more negative values. Hence these alloy materials could be used as anode materials in Zn/air batteries.

Acknowledgements

This work was supported by the Core Technology Development Program of the Ministry of Commerce, Industry and

Energy (MOCIE). One of the authors (K.S.) thanks the management of Vellore Institute of Technology, India for providing sabbatical leave to carry out this work.

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