

Effects of bismuth ion and tetrabutylammonium bromide on the dendritic growth of zinc in alkaline zincate solutions

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Abstract

The effectiveness of bismuth ion and tetrabutylammonium bromide (TBAB) as deposit-enhancing additives of zinc electrode has been investigated by means of current–time technique, potentiodynamic polarization and scanning electron microscopy. The experimental results showed that the dendritic growth of zinc in alkaline zincate solution was inhibited by the addition of Bi^{3+} and TBAB, respectively. However, at a higher cathodic overpotential TBAB produced little effective suppression on zinc dendrites. Obvious synergistic effect of Bi^{3+} and TBAB on the dendrite inhibition of zinc electrode was also found. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Zinc electrodes; Alkaline solutions; Dendrite inhibition; Bismuth ion; Tetrabutylammonium bromide

1. Introduction

As an anode material, zinc is widely used in Zn–Mn, Zn–Ag and Zn–Ni batteries [1,2]. These secondary zinc based cells are usually limited in their performance and widespread commercialization by poor cycling characteristics of zinc anode [3]. The dendritic growth of zinc electrode, which results from the high solubility of zinc discharge products in the electrolyte [4], is one of the main problems that are responsible for the short cycle life of the zinc electrode [5]. Dendritic growth leads to eventual cell failure due to short circuiting [4]. In order to inhibit or eliminate zinc dendrite formation, many attempts including the use of additives in either the electrode [6–8] or the electrolyte [9–11] have been undertaken. McBreen et al. [8] reported that bismuth oxide as an electrode additive had the beneficial effect on the performance of zinc electrode. The addition of bismuth ion to the electrolyte can make bismuth well-distributed on the surface of zinc anode, by which the dendritic growth of zinc may be more effectively inhibited. However, very few studies on the use of Bi^{3+} in alkaline solutions are reported. Quaternary ammonium compounds have been found to be effective in inhibiting zinc dendrite [10]. However, their effectiveness

in high cathodic overpotential region remains to be investigated.

In the present work, the influences of bismuth chloride (BiCl_3) and tetrabutylammonium bromide (TBAB) as electrolyte additives on the dendritic growth of zinc electrode was studied, and their synergistic effect was also investigated.

2. Experimental

2.1. Electrochemical test

A three-electrode system was used with working electrode of planar zinc (99.995% pure; area: 0.75 cm^2). A platinum foil served as counter-electrode and a Hg/HgO electrode as reference. The working electrode was insulated with epoxy resin except for the surface to be tested. Before each experiment the electrode was polished emery paper (800 grade), degreased with acetone and rinsed with distilled water. An 8 M KOH electrolyte containing $40 \text{ g l}^{-1} \text{ ZnO}$ was used. To this solution the additives were added. The electrolytes were prepared from A.R. grade reagent with deionized water. The experimental temperature was $25 \pm 1^\circ\text{C}$.

Electrochemical data were obtained with a potentiogalvanostat (Solartron, SI 1287). The current–time curves were measured at a pre-determined cathodic overpotential. The polarization curves were obtained by potentiodynamic method, at a sweep rate of 0.5 mV s^{-1} .

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2.2. Scanning electron microscopy (SEM)

After measuring the current–time curves, the zinc electrodes were washed repeatedly in deionized water and then rinsed in methanol and air-dried. The dried electrodes were soaked in a 10 M NH_4OH + 1 M $(\text{NH}_4)_2\text{SO}_4$ solution at 25°C for 3 h to remove zinc oxide [12]. The electrodes were again repeatedly washed in deionized water, rinsed in methanol and air-dried prior to the electron microscopy studies.

3. Results and discussion

3.1. The effect of Bi^{3+} on the dendritic growth of zinc

The current–time curves of zinc in the alkaline zincate solutions with and without BiCl_3 at a cathodic overpotential $\eta = -100$ mV are shown in Fig. 1. At this potential zinc deposition is the only significant cathodic reaction [9]. Since the cathodic deposition of zinc is controlled by mass transport, any rise in cathodic current during a potential-controlled electrodeposition can be assumed to be due to an increase in true electrode surface area (often dendritic growth). Therefore, the effect of additives on the dendritic growth of zinc can be readily assessed by their effect on the current. A flat current–time profile, exhibiting current values similar to the ‘blank’ solution (no additive) before the onset of dendritic growth, would be optimal [9].

Fig. 1 indicates that the rise in the cathodic deposition current of zinc in the blank solution during the test is large (from about 19–107 mA), which shows that a lot of zinc dendrites are produced on the electrode surface. Visual observation did find heavy dendrites on the zinc electrode surface. The addition of BiCl_3 in the electrolyte produced flatter current–time responses, and with the concentration of the additive increasing, the rise in the deposition current during the test decreased. When the content of Bi^{3+} in the electrolyte was 0.16 g l^{-1} , the cathodic deposition current was similar to the initial current in the blank solution and

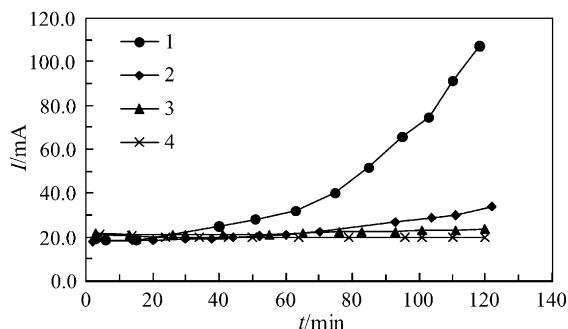


Fig. 1. Current–time curves of zinc in the alkaline solutions with and without Bi^{3+} at the cathodic overpotential $\eta = -100$ mV. (1) Blank solution; (2) $0.04 \text{ g l}^{-1} \text{ Bi}^{3+}$; (3) $0.08 \text{ g l}^{-1} \text{ Bi}^{3+}$; (4) $0.16 \text{ g l}^{-1} \text{ Bi}^{3+}$ (Blank solution: 8 M KOH electrolyte containing $40 \text{ g l}^{-1} \text{ ZnO}$).

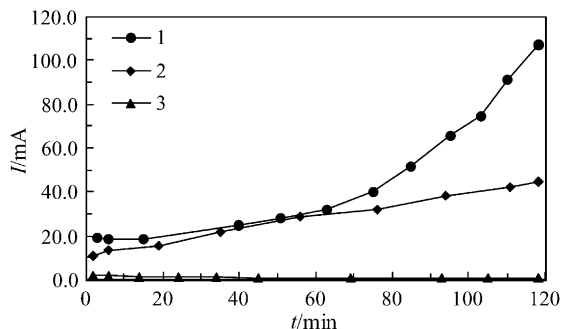


Fig. 2. Current–time curves of zinc in the alkaline solutions with and without TBAB at $\eta = -100$ mV. (1) Blank solution; (2) $0.02 \text{ g l}^{-1} \text{ TBAB}$; (3) $0.1 \text{ g l}^{-1} \text{ TBAB}$.

almost kept constant in the experimental duration. Few zinc dendrites were visually found on the electrode surface. The experimental results indicate that the formation of zinc dendrites is effectively inhibited by the addition of BiCl_3 , and the charging efficiency of the zinc electrode will not be decreased obviously. Bismuth has a more positive electrode potential than zinc, so bismuth ion is reduced to bismuth prior to zinc deposition. The beneficial effect of Bi^{3+} is attributed to substrate effect [13].

3.2. The effect of TBAB on the behavior of zinc deposition

Fig. 2 illustrates the current–time data for the electrolytes containing TBAB at the cathodic overpotential $\eta = -100$ mV. Clearly, the addition of TBAB produced effective dendrite inhibition. The lower concentration (0.02 g l^{-1}) brought about obvious improvement for zinc deposition. At higher concentration (0.1 g l^{-1}) the electrodeposition from this electrolyte produced no discernible deposit, which is in general agreement with other investigators [10].

Fig. 3 provides the current–time profiles of zinc electrodes in the alkaline solutions with and without TBAB at the cathodic overpotential $\eta = -200$ mV. Comparing the current–time data in Figs. 2 and 3 reveals that the rate of the cathodic deposition in the blank solution increases more

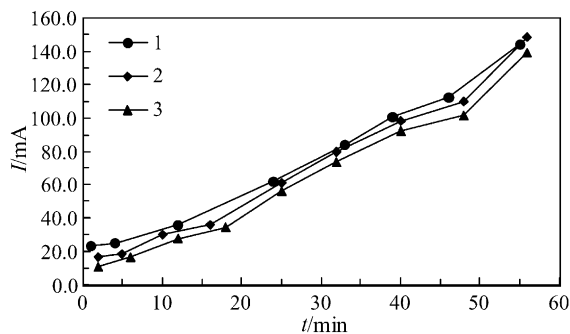


Fig. 3. Current–time curves of zinc in the alkaline solutions with and without TBAB at $\eta = -200$ mV. (1) Blank solution; (2) $0.02 \text{ g l}^{-1} \text{ TBAB}$; (3) $0.1 \text{ g l}^{-1} \text{ TBAB}$.

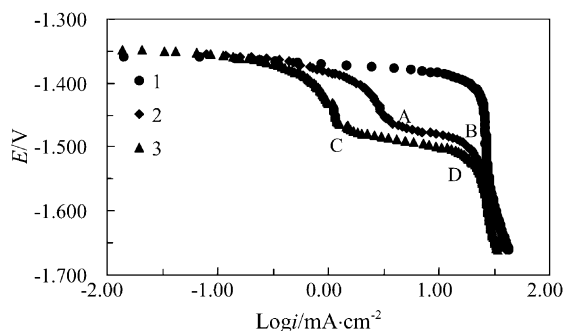


Fig. 4. Cathodic polarization curves of zinc in the alkaline solutions with different amounts of TBAB. (1) Blank solution; (2) 0.02 g l^{-1} TBAB; (3) 0.1 g l^{-1} TBAB.

rapidly at $\eta = -200 \text{ mV}$ than $\eta = -100 \text{ mV}$, which shows that zinc dendrites are prone to growth at higher cathodic overpotential. At $\eta = -200 \text{ mV}$ TBAB brought about little effective dendrite inhibition in the concentrations examined.

Fig. 4 displays the cathodic polarization curves of the zinc electrode in the alkaline solutions with different amounts of TBAB. In the low cathodic polarization region the zinc deposition reaction is inhibited in the TBAB-containing solutions due to the surface adsorption of the additive, and TBAB in high concentration (0.1 g l^{-1}) produces larger inhibition effect. The adsorption effect of H_2O on the zinc surface increases as the electrode potential becomes more negative, thus the desorption of TBAB occurs in the certain potential regions on curves 2 and 3 in Fig. 4 (AB for curve 2 and CD for curve 3) [14]. At higher cathodic overpotential (e.g. $\eta = -200 \text{ mV}$) TBAB has completely desorbed from the electrode surface, therefore, the additive produces little inhibition on the dendritic growth of zinc electrode. The above-mentioned results can well interpret the current–time data in Figs. 2 and 3.

3.3. Synergistic effect of Bi^{3+} and TBAB

The current–time curves of zinc in the alkaline solutions with and without the additives at the cathodic overpotential $\eta = -200 \text{ mV}$ are represented in Fig. 5. The addition of

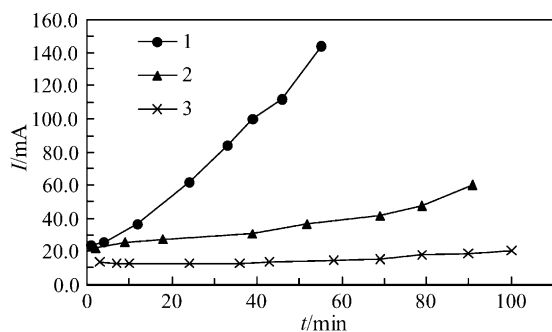


Fig. 5. Current–time curves of zinc in the alkaline solutions with and without the additives at $\eta = -200 \text{ mV}$. (1) Blank solution; (2) 0.1 g l^{-1} Bi^{3+} ; (3) 0.1 g l^{-1} Bi^{3+} and 0.02 g l^{-1} TBAB.

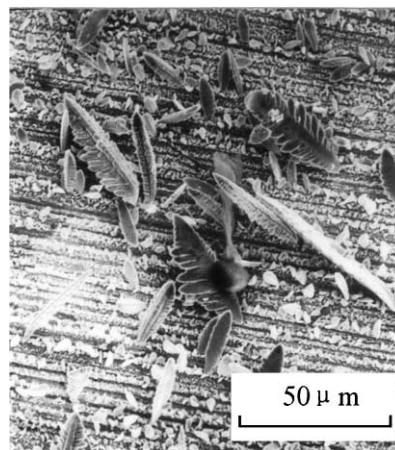


Fig. 6. Zinc electrodeposit at $\eta = -200 \text{ mV}$ from the blank solution.

0.1 g l^{-1} Bi^{3+} in the electrolyte produced flatter current–time response, which indicates that the dendritic growth of zinc at higher cathodic overpotential is inhibited by substrate effect of bismuth. But the rise of the cathodic current in this system was still observed during the test (from 22–60 mA), which showed that some zinc dendrites were produced. Visual observation found a few dendrites at the edges of the zinc electrode. The cathodic deposition current of zinc in the electrolyte containing 0.1 g l^{-1} Bi^{3+} and 0.02 g l^{-1} TBAB (curve 3) almost kept constant during the test. This shows that the dendritic growth of zinc is greatly suppressed by joint addition of Bi^{3+} and TBAB in the electrolyte.

The electrodeposited zinc surfaces at the cathodic overpotential $\eta = -200 \text{ mV}$ were examined by SEM. Figs. 6–8 are a selection of micrographs. An additive-free solution produced dendritic deposits (Fig. 6). The deposition morphologies of the electrodes in additive-containing electrolytes are completely different from the one of the electrodes in additive-free electrolytes. Bi^{3+} (0.1 g l^{-1}) brought about a less open, granular deposit except for the edges of

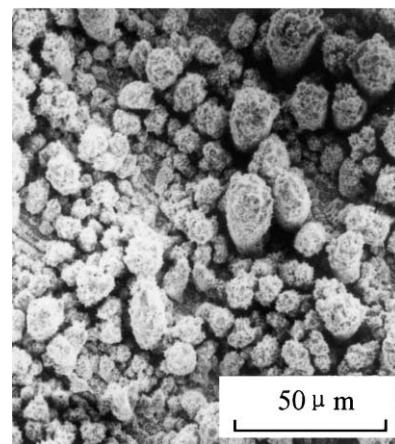


Fig. 7. Zinc electrodeposit at $\eta = -200 \text{ mV}$ from the alkaline solution containing 0.1 g l^{-1} Bi^{3+} .

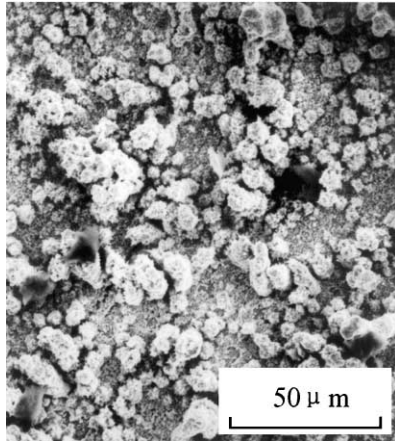


Fig. 8. Zinc electrodeposit at $\eta = -200$ mV from the alkaline solution containing $0.1 \text{ g l}^{-1} \text{ Bi}^{3+}$ and $0.02 \text{ g l}^{-1} \text{ TBAB}$.

the electrode (Fig. 7). The addition of Bi^{3+} and TBAB produced a dense, smooth and granular deposit, which consisted of small crystallites (Fig. 8). The finer deposition grains are possibly due to the cathodic overpotential increased by synergistic effect of Bi^{3+} and TBAB.

The cathodic polarization curves of the zinc electrodes in the alkaline solutions with and without the additives are displayed in Fig. 9. Comparing curves 2 and 3 shows that the joint addition of Bi^{3+} and TBAB produces much larger cathodic polarization than individual addition of TBAB, and the desorption potential of the additive becomes more negative. The configuration of the outer-shell electrons of elemental bismuth is $6s^2 6p^3$, there are some vacant p-shells which may be filled by the lone pairs of electrons of nitrogen atom in TBAB, while the configuration of outer-shell electrons of elemental zinc is $4s^2$, and there is no shell vacancy. Therefore, the adsorption of TBAB is much stronger on bismuth than on zinc. This possibly is the reason why the desorption potential of TBAB becomes more negative in Bi-containing system. It can be seen that point H on curve 3 in Fig. 9 (the cathodic overpotential of this point is -200 mV) is within the desorption potential region of TBAB (EF), i.e. a portion of TBAB still adsorbs on the electrode surface.

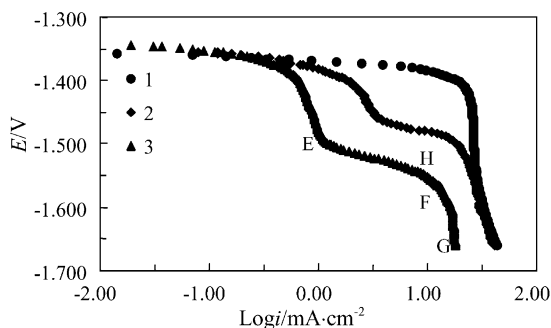


Fig. 9. Cathodic polarization curves of zinc in the alkaline solutions with and without the additives. (1) Blank solution; (2) $0.02 \text{ g l}^{-1} \text{ TBAB}$; (3) $0.1 \text{ g l}^{-1} \text{ Bi}^{3+}$ and $0.02 \text{ g l}^{-1} \text{ TBAB}$.

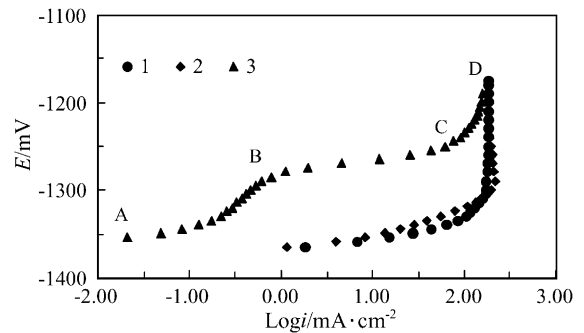


Fig. 10. Anodic polarization curves of zinc in the alkaline solutions with and without the additives. (1) Blank solution; (2) $0.1 \text{ g l}^{-1} \text{ Bi}^{3+}$; (3) $0.1 \text{ g l}^{-1} \text{ Bi}^{3+}$ and $0.02 \text{ g l}^{-1} \text{ TBAB}$.

Therefore, the growth of zinc dendrites is effectively inhibited at the cathodic overpotential $\eta = -200$ mV by the synergistic effect of Bi^{3+} and TBAB.

3.4. The influences of additives on the anodic dissolution behavior of zinc electrode

The anodic polarization curves of zinc electrodes in the alkaline solution with and without additives are shown in Fig. 10. It can be seen that the anodic dissolution behavior of zinc is not almost influenced by the addition of Bi^{3+} , however, it is greatly changed by synergistic effect of Bi^{3+} and TBAB. At the low anodic polarization region (marked as AB on curve 3) the dissolution of zinc is inhibited due to TBAB adsorbing on electrode surface. In the potential region BC on curve 3 the additive quickly desorbs from the electrode surface [14], and the anodic current density increases rapidly as the electrode potential becomes more positive than one at point B. In the region CD the additive has completely desorbed from the electrode surface and curves 1 and 3 almost overlaps. The phenomenon of adsorption and desorption of the additive with changing electrode potential allows its use as an additive in secondary zinc based cells. When the cells are charged, zinc dendrites will be inhibited by the adsorption of the additive on zinc surface. Meanwhile, the additive may desorb from the surface of a discharging zinc anode, so the zinc electrode will have acceptable discharge performance.

4. Conclusions

The effectiveness of bismuth ion and TBAB on the dendrite inhibition of zinc electrodes has been investigated. The addition of Bi^{3+} inhibits the dendritic growth of zinc electrodes in the alkaline solution by substrate effect both at $\eta = -100$ mV and at $\eta = -200$ mV. At lower cathodic overpotential ($\eta = -100$ mV) the zinc dendrites can be effectively inhibited by the adsorption of TBAB on electrode surface, however, at higher cathodic overpotential

($\eta = -200$ mV) TBAB produces little effective dendrite inhibition due to its desorption from electrode surface. The dendritic growth of zinc is greatly suppressed by synergistic effect of Bi^{3+} and TBAB at higher cathodic overpotential ($\eta = -200$ mV). A dense and granular deposit is obtained from the electrolyte containing Bi^{3+} and TBAB. Since the additive may desorb from the surface of a discharging zinc anode, it is acceptable in terms of the discharge performance of zinc electrodes.

Further work must be carried out before the additives are applied to secondary zinc technology. The investigation on the stability of the additives to prolonged cycling is in progress, and their influences on the behavior of positive electrodes will be also undertaken soon in our laboratory.

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