Effects of stannous ions on the electrochemical performance of the alkaline zinc electrode

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Abstract

The effect of stannous ions as an electrolyte additive on the electrodeposition characteristics of Zn was investigated by chronoamperometry, the potential-step method and cyclic voltammetry. The chronoamperometry measurements showed that the addition of stannous ions inhibited the dendritic growth of Zn deposits. SEM observation also revealed that the Zn deposit was in the form of compact cylinders with rounded tops that consist of many small crystallites, rather than the classical dendrites with side branches. The inhibition effect of Sn^{2+} on the very initial electrocrystallization of Zn was not a substrate effect. The 0.17 V difference in reduction potential between Zn and Sn resulted in the codeposition of Sn and Zn. An interruption effect was proposed to illuminate the inhibition effect of Sn^{2+} on the formation of Zn dendrites. Furthermore, Sn^{2+} additive was found to suppress the corrosion reaction of Zn by 87% in the Sn^{2+}-containing zincate electrolyte, comparing to that in the blank zincate electrolyte.

1. Introduction

Secondary alkaline Zn batteries show the advantages of high specific energy, non-toxicity, and low cost. However, the widespread commercialization of this kind of Zn-based battery is limited due to its poor cycling characteristics. This problem has been traced to the shape change of the Zn electrode, dendritic growth of Zn deposit, self-discharge and formation of H_2 [1–3]. There is an extensive literature on the effect of metallic ions, e.g. Bi^{3+}, Pb^{2+}, on Zn deposition in the alkaline electrolyte [3–7]. Even though it is known that Bi^{3+} and Pb^{2+} additives effectively inhibit Zn dendritic growth and extend the cycle life of the Zn electrode, no systematic study has been carried out on the effects of these metallic ions on other aspects of the electrochemical behavior of the Zn electrode, e.g. the electrocrystallization process of Zn from the alkaline zincate electrolyte and formation of H_2. Essentially, both dendritic growth and shape change are the results of Zn electrocrystallization. Self-discharge can result in a decline in the capacity of the battery. It is now well established that detailed information about the kinetics of electrocrystallization can be obtained readily from the initial stages of potentiostatic deposition on a foreign substrate [8]. Detailed analysis of the very initial stages of the deposition of Zn can elucidate the effect of metallic ions on the electrochemical characteristics of the electrode. The purpose of the present work was to investigate the effects of Sn^{2+} ions on the morphology, dissolution and deposition behavior of Zn deposits in alkaline electrolytes. As a potential dendrite-inhibiting additive for secondary Zn battery application, Sn offers advantages over Pb and Bi, because (1) Sn is non-toxicity; (2) its oxidation potential is much lower than that of Pb or Bi and favorable for secondary Zn batteries.

2. Experimental

Chronoamperometry measurements were made in a conventional three-compartment cell at 25 °C, using a potentio-galvanostat (EG& G Princeton Applied Research, M273A). The current-time curves were obtained at a predetermined cathodic overpotential $\eta = -200$ mV. The three-compartment cell consisted of an Hg/HgO electrode as reference, a foam Ni electrode as the counter electrode and the working electrode. The working electrode was a Zn rod of purity 99.9% and 1.5 cm in diameter, embedded in epoxy resin. The working electrode was polished with successively 400# and 600# sandpapers, then washed with distilled water. The electrolyte was a ZnO-saturated 6 M KOH solution and $SnCl_2$ additive was added to the electrolyte.

After the measurements, the Zn electrode was immediately removed from the electrolyte, washed repeatedly in distilled water, rinsed with ethanol and air-dried. The morphology of the surface was analyzed by scanning electron microscopy (SEM, SIRION-100).

Investigations were carried out into the electrodeposition of Zn on Ag substrate. The electrolyte was prepared by adding excess $SnCl_2$ to the zincate electrolyte, stirring overnight and then filtering the electrolyte. Measurements were made in a similar three-compartment cell at 25 °C, using a CHI 640B Electrochemical Workstation. The cyclic voltammetry was recorded. The voltage envelope was -1.4 V to 0 V (versus Hg/HgO electrode) and the scan rate was 100 mV s^{-1}. The cell and experimental procedures were identical with the aforementioned experiments, but the working electrode was a flag type Ag electrode (1.5×1.5 cm^2) embedded in epoxy resin.

Potential-step measurements were performed to elucidate the effect of Sn on Zn using the same potentiogalvanostat and the current transients were recorded. A similar three-compartment cell was used, but the working electrode was a tin rod electrode of purity 99.9% and 1.5 cm in diameter embedded in epoxy resin. The electrolyte was a ZnO-saturated KOH solution. Other treatments were identical with that of the aforementioned Zn electrode.

3. Results and discussion

3.1. Effect of Sn^{2+} on dendritic growth of Zn deposit

The chronoamperometry measurements of Zn in alkaline zincate electrolyte with and without $SnCl_2$ are shown in Figure 1. Zn electrodeposition is significant at charging due to the high solubility of ZnO in the alkaline electrolyte. The unfavorable electrocrystallization that occurs during the Zn electrodeposition process, namely dendritic growth, is the main cause of the short
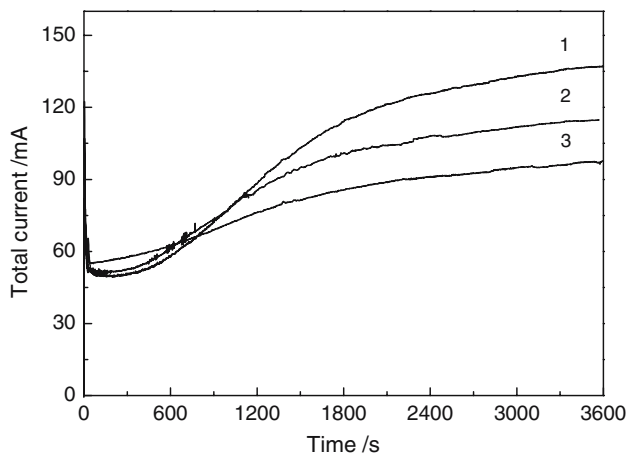
cycle life of secondary Zn batteries. Chronoamperometry measurements under cathodic overpotential can reflect the effect of Sn^{2+} on the electrocrystallization process of Zn, because Zn electrodeposition is the only significant cathodic reaction [9], and the cathodic deposition of Zn is controlled by mass transport. Any increase in cathodic current during the potential-controlled electrodeposition can be generally considered as an increase in true electrode surface area. Thereby, the effect of the additive on the electrocrystallization of Zn can be readily assessed by analyzing the current response. From Figure 1, it is clear that the cathodic current of the Zn electrode is much greater in the blank electrolyte (without the Sn^{2+} additive), indicating significant formation of dendritic Zn. Visual observation confirms the presence of dendrites on the electrode surface. The addition of Sn^{2+} decreases the current-time responses. The higher the concentration of Sn^{2+}, the lower the cathodic deposition current. The above results indicate that the formation of Zn dendrites is effectively inhibited by the addition of Sn^{2+}.

After the chronoamperometry measurement, the electrode surface was examined by SEM. As shown in Figure 2(a), the typical dendritic Zn deposits were
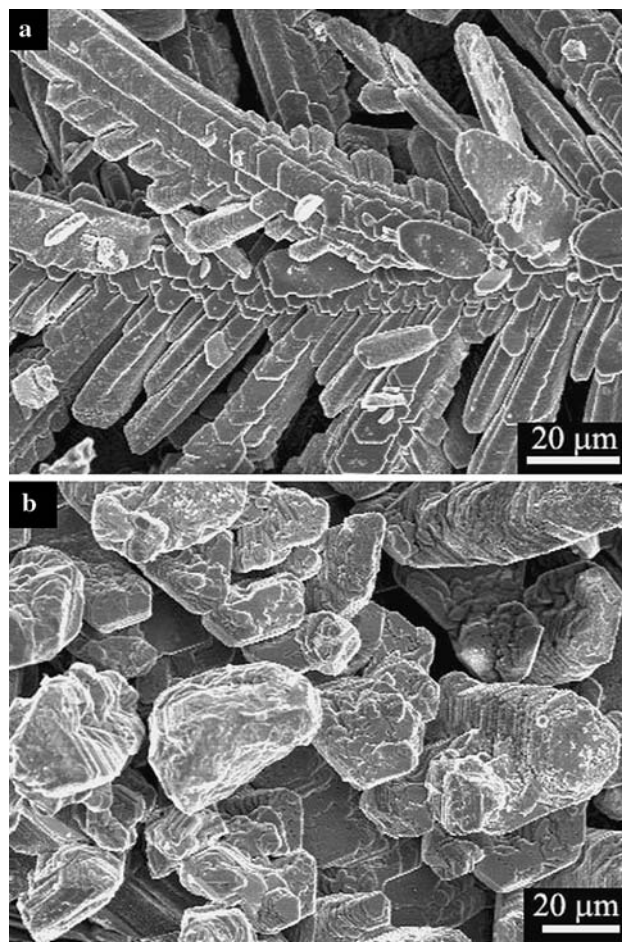

Fig. 1. Current-time curves of Zn in alkaline zincate electrolyte with and without Sn^{2+} at the cathodic overpotential $\eta = -200$ mV. (1) blank electrolyte; (2) 0.12 g L^{-1} Sn^{2+}; (3) 0.24 g L^{-1} Sn^{2+}. (blank solution: 6 M KOH solution saturated with ZnO).

Fig. 2. Electrodeposit morphology on the surface of Zn electrode from (a) the blank electrolyte and (b) the electrolyte containing 0.12 g L^{-1} Sn^{2+}.

evident when the electrolyte did not contain the Sn^{2+} additive, whereas the addition of Sn^{2+} ions modified the morphology. From Figure 2(b), the deposit is converted from classical dendrites with side branches to compact cylinders with rounded tops consisting of small crystallites, which mitigates the possibility of interior short circuit caused by dendrites penetrating separator of battery.

3.2. Effect of Sn^{2+} on the initial electrocrystallization and corrosion of Zn

Figure 3(a) shows the transient current-time curves at the initial stage of electrocrystallization of Zn from an alkaline zincate electrolyte onto a Zn electrode. The very initial stage of electrocrystallization includes the initial nucleation, three-dimensional growth of centers and the initial formation of monolayers [8]. Therefore, the transient current at the very initial stage can reflect the holistic influence of Sn^{2+} on the initial nucleation, three-dimensional growth and the initial formation of monolayers. The transient current of the Zn electrode in the electrolyte containing Sn^{2+} is about half of that in the blank electrolyte, which indicates that the addition of
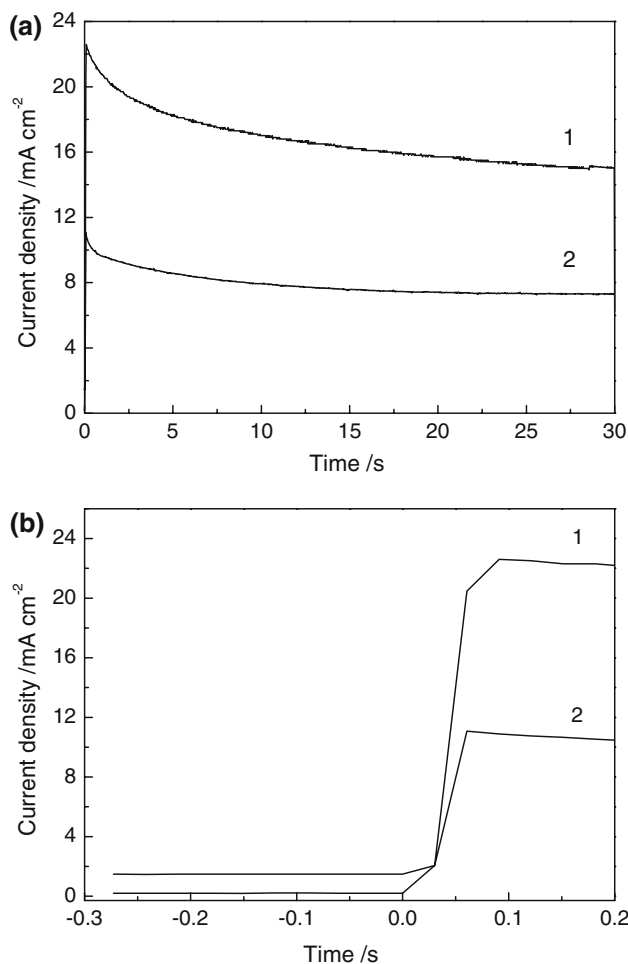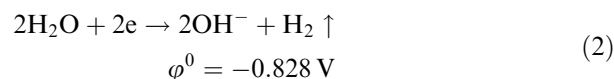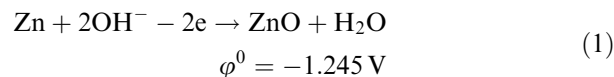

Fig. 3. Current transients-time curves for Zn deposition on a Zn electrode. (1) overpotential 40 mV, blank electrolyte; (2) overpotential 40 mV, 0.12 g L^{-1} Sn^{2+}.

Sn^{2+} inhibits the initial nucleation, three-dimensional growth and formation of monolayers. The reason why dendritic growth of Zn deposit is suppressed by metallic ion additives has been considered as a substrate effect [10]. The metallic ion additives are reduced to the corresponding metals prior to Zn electrodeposition, and then the formed metallic substrate influences the Zn electrodeposition. The inhibition effect of Sn^{2+} on the Zn electrocrystallization can also occur even in the very initial stages. Since the amount of Sn deposition is trivial few at the very initial electrodeposition stage, the substrate effect of the Sn deposit is negligible. Therefore, the inhibition effect is not simply attributable to the substrate effect and may be related to codeposition of Sn and Zn. The electrodeposited Sn is expected to deposit on the preferred growth sites, interrupting further Zn deposition on the particular crystallite and leading to nucleation of new Zn grains. The electrodeposited Sn shows an interrupting effect.

The initial parts of the transient current-time curves are amplified further and shown in Figure 3(b). The Zn electrode shows a stable initial non-zero current. This initial currents results from hydrogen evolution since the electrodeposition does not occur at this time [11]. The hydrogen evolution results from the corrosion of Zn in alkaline solutions. The corrosion reactions are:

$$Zn + 2OH^- - 2e \rightarrow ZnO + H_2O$$
$$\varphi^0 = -1.245\,V \tag{1}$$

$$2H_2O + 2e \rightarrow 2OH^- + H_2 \uparrow$$
$$\varphi^0 = -0.828\,V \tag{2}$$

The corrosion of Zn is the main cause for self-discharge of secondary alkaline Zn batteries. A fully charged Ni–Zn battery loses about 0.8% of its original capacity per day at open-circuit at 25 °C [3]. The capacity retention is an important parameter for the rechargeable battery. The initial non-zero current of the Zn electrode in electrolyte containing Sn^{2+} is just 13% of that in blank electrolyte. This indicates that Sn^{2+} has an intensive suppressive effect on the corrosion of Zn. The corrosion reaction makes the Zn electrode electronegative. Tin ions are attracted to the Zn surface. Tin ions around the surface of Zn electrode form a barrier that prevents H_2O from obtaining electrons to produce H_2. Consequently, corrosion is suppressed.

In order to study further the interaction of Zn and Sn in the electrodeposition, cyclic voltammetry measurements for a silver electrode in the alkaline zincate electrolyte with and without Sn^{2+} were carried out and are shown in Figure 4. Ag was used as the substrate due to the stability of Ag in the sweep potential range. From Figure 4(a), the reduction potential of ZnO is about −1.25 V. The anodic peak at −1.32 V corresponds to the oxidation of Zn. The anodic peak at −1.08 V and the cathodic peak at −1.0 V in Fig. 4(b) belong to the oxidation/reduction reactions of tin. The difference in
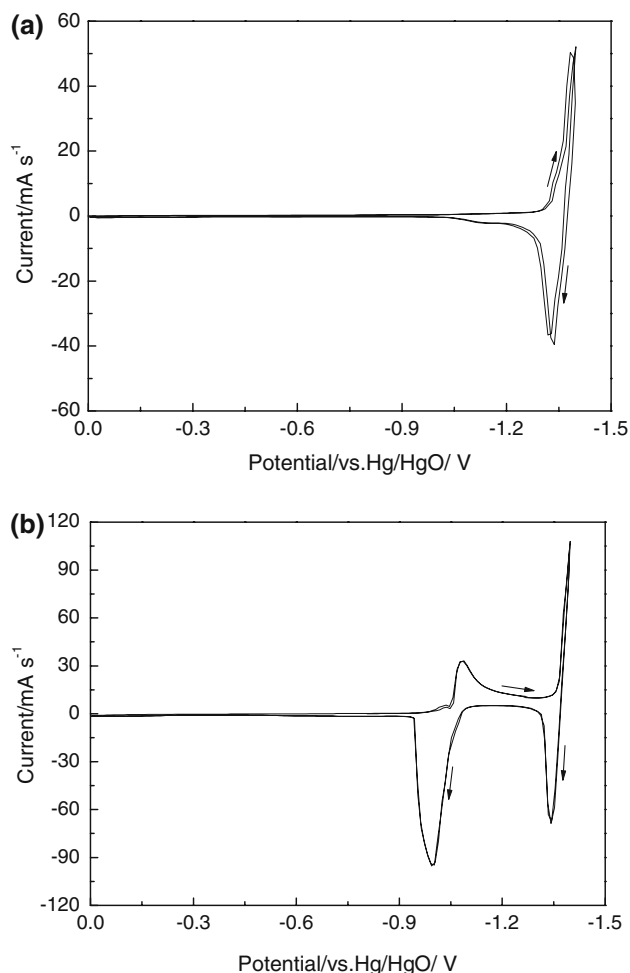
(a)

(b)

Fig. 4. Cyclic voltammograms for Ag electrodes from (**a**) the blank electrolyte and (**b**) the electrolyte containing 5.6 g L^{-1} Sn^{2+}.

reduction potential between Zn and Sn is only about 0.17 V. For most electrode reactions, since the diffusion migration rate is generally less than the electrochemical reaction rate, the polarization is inevitable and the electrode potential changes remarkably, increase or decrease. When the current density is relatively large, the phenomenon is more significant. The electrode potential decreases gradually in electrodeposition. Due to the polarization and the relatively large current, the electrode potential falls more quickly. Because the difference in reduction potential between Zn and Sn is relatively small, the electrode potential can get across rapidly the potential difference and reach the electrodeposition potential of zincate, thus the co-deposition of Zn and Sn occurs in electrodeposition.

3.3. Nucleation overpotential of Zn on Sn

According to the mechanism of interrupting effect, the electrodeposited Sn is expected to deposit on the preferred growth sites, blocking Zn deposition on the particular crystallite and leading to nucleation of Zn grains. According to the growth mechanism of a crystal, impurities can promote non-uniform nucleation. How-

ever, it is clear that the electrodeposited Sn does not promote the nucleation and growth of new Zn grains since the electrodeposition current that reflects the nucleation and growth of Zn grains decreases, as shown in Figure 1. The likely reason is that the deposited Sn increases the nucleation overpotential of new Zn grains. Overpotential is a very important parameter in electrodeposition. If the overpotential exceeds a threshold value dendritic deposition ceases. Studies with Ag dendrites indicated that a critical overpotential, η_{crit}, was necessary for dendrite formation, and this overpotential was related to a sharp increase at η_{crit} of the dendrite radius for maximal growth [12]. The critical nucleation overpotential of Zn on Sn was investigated by a potential-step method as shown in Figure 5.

The transient current in Figure 5 can be fitted to a simple electrocrystallization model that assumes instantaneous nucleation of Zn and growth of the nuclei under kinetic control [8]. When the deposition time is relatively short and the second deposition current maximum does not appear, the total current (i) is

$$i = i_b + i_p \tag{3}$$

$$i_b = i'_b \exp\left(\frac{-\pi M^2 k_p^2 N_0 t^2}{\rho^2}\right) \tag{4}$$

$$i_p = zFk'_p\left[1 - \exp\left(\frac{-2 K_p^2 N_0}{\rho^2}t^2\right)\right] \tag{5}$$

where M is the molecular weight of Zn; ρ is the Zn density; N_0 is the instantaneous nucleation rate; and t is the elapsed time from application of the potential step, i_b' is the value of current observed at $t = 0$, k_p' and k_p are the respective rates (mol cm^{-2} s^{-1}) of crystal growth of the nuclei in the directions perpendicular and parallel to the substrate; subscript p denotes that the rates belong to the nucleation and growth of primary centers;
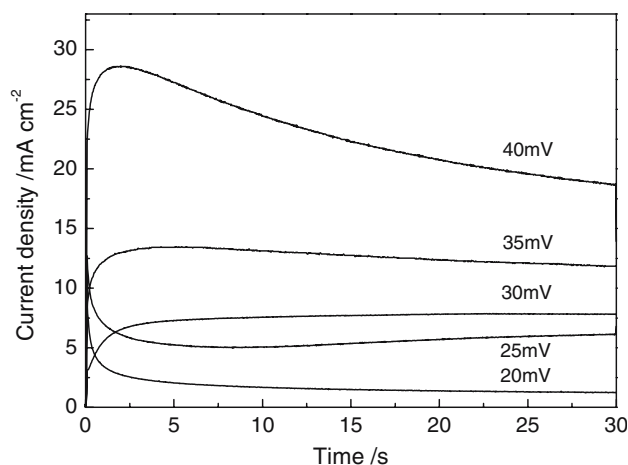

Fig. 5. Current transients for Zn deposition on single-crystal Sn.

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subscript b denotes that the current belongs to the background current. The background current tends to diminish gradually at the initial stage of electrodepos- ition, and the fall is generally related to the coverage of the primary growth centers.

According to Eqs. 3–5, when the overpotential is less than the nucleation overpotential of Zn on Sn, i_b is predominant in the total current. The total current is small and diminishes gradually since i_b is relatively small and declines. When the overpotential approaches the nucleation overpotential, the deposition current i_p increases gradually, and as a result, the total current stops declining and then increases gradually. Once the overpotential exceeds the nucleation overpotential, a maximum appears. If the overpotential keeps on increasing, the total current will rise rapidly and a current peak will appear. At a potential of 20 mV, the decrease in total current indicates that the overpotential is less than the nucleation overpotential of Zn. At 25 mV, the total current initially decreases and then increases somewhat, indicating that the overpotential begins to approach the nucleation overpotential. The current transient shows a slight peak at 35 mV and a clear peak at 40 mV, which shows that the overpotential is already higher than the nucleation potential of Zn. Thus the nucleation overpotential of Zn on Sn is about 30 mV. The high nucleation overpotential of Zn on Sn makes it causes the nucleation and growth of new Zn grains to be inhibited by the electrodeposited Sn. Therefore, the growth of Zn dendrites is suppressed.

4. Conclusions

Sn^{2+} as an electrolyte additive in secondary Zn batteries can inhibit the dendritic growth of the Zn deposit and therefore change the morphology of the deposit. The corrosion of Zn is also suppressed to a certain extent. The beneficial effect of Sn^{2+} additive is not a substrate effect, since the very initial electrocrystallization of Zn was also inhibited by Sn^{2+}. Cyclic voltammetry shows that the difference in reduction potential between Zn and Sn is only 0.17 V, which may explain the codepos- tion of Zn and Sn. An interrupting effect is put forward to explain the inhibition effect of Sn^{2+} on Zn dendrites. Because of the high nucleation overpotential of Zn on Sn (about 30 mV), the pre- electrodeposited Sn can interrupt the growth of Zn dendrites and suppress the nucleation of new Zn grains, thus inhibiting Zn dendrite formation.

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