Effect of Tin Ion Additive on Zinc Electrode in Alkaline Solution*

YUAN Yong feng, TU Jiang ping, WU Hui ming, LI Yang, ZHAO Xin bing
(Department of Materials Science and Engineering, Zhejiang University, Hangzhou 310027, China)

Abstract: Co-deposition of zincate and tin ion on zinc electrode were conducted to investigate the effect of tin ion on electro-deposition of zincate. The results showed that the deposit morphology of zincate changed from dendrite to many small compact crystallites in a spongy array. With increasing tin ion additive, zinc dendrite was dramatically inhibited. The precise mechanism of inhibition was discussed. In addition to the deposition of tin on preferred growth sites blocking further zinc deposition, the high deposition over-potential on tin is an important factor.

Key words: zinc electrodes; dendrite inhibition; tin ion
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The secondary alkaline zinc batteries have advantages of high specific energy, non-toxicity and low cost. However, the widespread development of cells with zinc anodes has been limited due to shape change and dendrite growth with zinc electrode. So far, many attempts have been undertaken to overcome these difficulties. Various additives, such as Bi_2O_3, In(OH)3, PbO, etc., were added to the electrode to minimize these problems[1-6]. The beneficial effect of the electrode additives is creation of a metallic substrate that is more conductive to the electrodeposition of compact Zn. The effect of corresponding ion additive is prior deposition to block zinc preferred deposition locations[7-9]. The effect of tin ion additive should not be prior deposition, but co—deposition, due to the potential of tin is not much higher than that of zinc, which was investigated primarily in this work.

1 Experimental

Co-deposition of zinc and tin was performed on cylindrical zinc electrode (99.99% purity, 1.5 cm in diameter, 0.5 cm in length). Prior to deposition, the lead and the back of the electrode were masked with epoxy, and the front of the electrode was polished and degreased in acetone. After deposition, the zinc electrodes were washed repeatedly in distilled water, rinsed with ethanol, and then air-dried. Nickel electrodes served as counter-electrode and the Hg/HgO electrode as reference. A 6 mol/L KOH electrolyte saturated with ZnO containing tin ion additive was used.

The potential-step measurements and the current-time techniques with a Potentio-Galvanostat (EG&G priston applied research, M273A) were conducted at room temperature to study the dendrite-inhibiting effect. The morphology of zinc deposition was examined using scanning electron microscope (SEM, Hitachi, S4700).

2 Results and discussion

The current-time curves of zinc in the alkaline zincate solution with and without $SnCl_4$ at a cathodic over-potential $\eta = 200$ mV are shown in Fig. 1. At this potential zinc deposition is the only significant cathodic reaction[10]. Because the cathodic deposition of zinc is controlled by mass transport, any rise in cathodic current during a potential-controlled electrodeposition can be assumed to arise from an increase in true electrode surface area (due to dendrite growth usually). Thereby, the influence of additives on the dendrite growth of zinc can be readily estimated by their effect on the current.

From Fig. 1, it is obvious that the rise in the cathodic deposition current of zinc in the blank solution during the test is largest, which indicates that a great deal of zinc dendrites is produced on the electrode surface. Visual observation did find heavy dendrites on the zinc electrode surface. The addition of $SnCl_4$ in the electrolyte made lower current-time responses. With increasing the concentration of $SnCl_4$, the rise in the deposition current decreased, and the morphology of zinc deposits changed at the same time. The morphology of deposits is changed from dendrite to structure consisting of many small crystallites arranged in a spongy array, as shown in Fig. 3a and

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作者简介: 袁永锋 (1979 年生), 博士生; 通讯联系人: 涂江平, E-mail: tujp@cmsce.zju.edu.cn

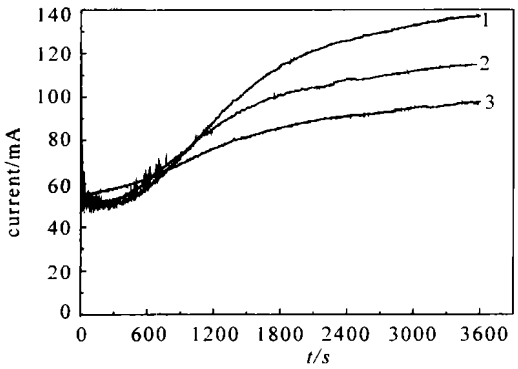

Fig 1　Current-time curves of zinc in the alkaline solution with and without Sn^{4+} at the cathodic over-potential $\eta = -200$ mV. (1) **Blank solution;** (2) 0.12 **g** l^{-1} Sn^{4+}; (3) 0.24 **g** l^{-1} Sn^{4+} (**Blank solution:** 6 **mol** l^{-1} **KOH electrolyte saturated with ZnO**)

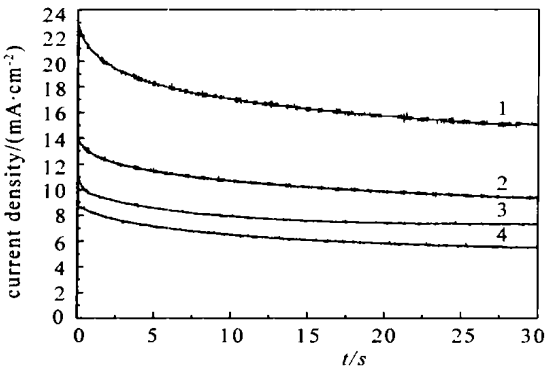

Fig 2　Current transients for zinc deposition on zinc electrodes. (1) **over-voltage** 40 **mV, blank electrolyte;** (2) **over-voltage** 30 **mV, blank electrolyte;** (3) **over-voltage** 40 **mV,** 0.12 **g/L** Sn^{4+}; (4) **over-voltage** 30 **mV,** 0.12 **g/L** Sn^{4+}

Fig. 3b. The whole structure is more compact than that in the blank solution. These results indicate that the formation of zinc dendrite is partially suppressed by the addition of $SnCl_4$, and the charging efficiency of the zinc electrode does not be decreased evidently. The effect of tin ion additive must more logically be attributed to co-deposition of tin ion and zinc[11]. In the course of charging, tin deposit blocked zinc deposition on the particular crystallite and led to nucleation of new grains since tin was expected to deposit on preferred growth sites. Second, because mass transmission velocity was usually less than electrochemical reaction velocity, the electrochemical polarization of tin ion additive occurred, so the zinc electrode potential kept on decreasing. When the potential approached the zinc deposit potential, co-deposition occurred and changed the crystal structure of deposits and then influenced the crystal preferential growth direction, which resulted in changing the deposit morphology. For the deposition over-voltage of zinc on tin was high relatively, the deposition velocity of zincate was low relatively, which made the beneficial co-deposition effect cooperating with slow tin ion transmission.

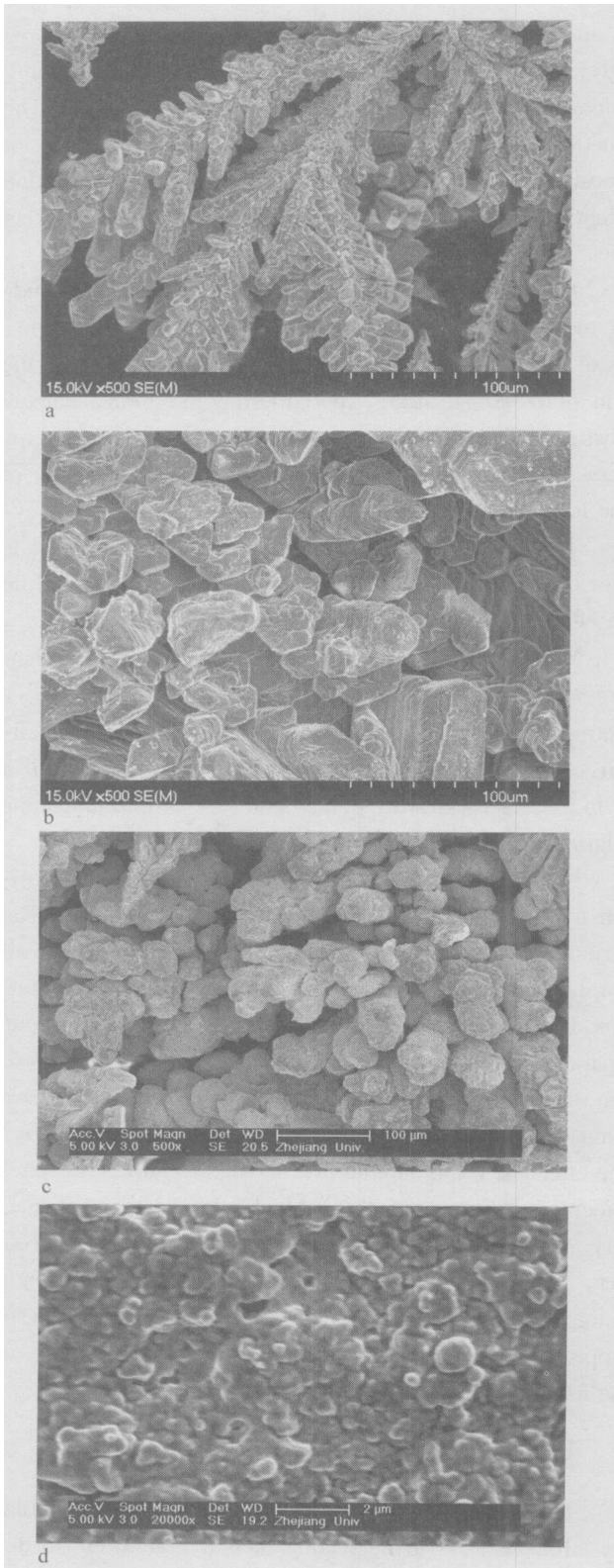

Fig 3　Electron micrographs of morphology of zinc deposits from alkaline electrolyte containing various additives after 1 800 **s.** (**a**) **blank;** (**b**) 0.12 **g/L** Sn^{4+}; (**c**) **Bi** $(NO_3)_3$**-saturated;** (**d**) 0.12 **g/L** Pb^{2+}

Additionally, the oxidation potential of tin is not much higher than that of zinc, which results in that both

tin and zinc ionize simultaneously on discharge. Accordingly, tin ion is available for the recharge process again, which markedly distinguishes from bismuth and lead. The beneficial effect of bismuth and lead is attributed to prior deposition effect and substrate effect[7—9]. The oxidation potential of these additives is much higher than that of zinc, which results in that these

additives are irreversible reduced to the corresponding metals prior to zinc deposition during charging first. These bismuth and lead additives exist stationary in the form of metal substrate, not altering the form, namely substrate effect. Thereby, the dendrite growth is just suppressed to some extent and the deposition morphology of zinc is modified partially, which not occurs after many cycles. In short, the effect of bismuth, lead and so on is prior deposition and substrate effect and irreversible while the effect of tin is co-deposition and reversible effect.

Moreover, the potential-step results in Fig. 2 show decreasing current transients in electrolyte with $SnCl_4$, contrasted with blank electrolyte under the same condition. A slight decrease in the deposition rate is helpful a lot to inhibit the growth of zinc dendrite due to diminishing polarization.

Fig. 3 illustrates the SEM morphology of zinc deposition in the alkaline zincate solution containing tin, lead bismuth ion and blank electrolyte respectively. The all morphology of zinc deposits consists of many small crystallites arranged in a spongy array and hardly penetrating separator, which lead to increase cycle life of batteries. The over-all structure in the presence of lead is the most compact, and its microstructure can be observed clearly. The effect of tin is similar to that of bismuth. The phenomenon of zinc dendrite in blank electrolyte is obvious very much. As a whole, the effect of lead ion is excellent, which basing on plentiful electrolyte and single charging. Considering toxicity of lead and repetition of suppression effect, tin ion additive is a better choice to use as dendrite inhibition agent.

3 Conclusions

Tin deposit blocked zinc deposition on the particular crystallite and led to nucleation of new grains due to depositing on preferred growth sites. High deposition over-voltage on tin decreased the zincate deposition velocity. The polarization prolonged the deposition course of tin ion additive. By the effective co-deposition of zincate and tin, the morphology of deposits was changed from dendrite to many small compact crystallites. Considering non-toxicity and repetition of suppression effect, tin ion additive is a better choice to use as dendrite inhibition agent in comparison with lead and bismuth electrolyte additives.

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锡离子添加剂在碱性溶液中对锌电极的作用

袁永锋，涂江平，吴惠明，黎　阳，赵新兵

（浙江大学材料科学与工程系，浙江 杭州 310027）

摘　要：通过对锌酸盐和锡离子的共沉积研究了锡离子对锌酸的电沉积作用。实验结果表明锌酸盐的沉积形态从枝晶转变为的紧凑的小晶粒。随着锡离子添加剂含量的增加，锌枝晶被显著抑制。讨论了抑制机理。除了锡沉积在最优生长位置阻塞锌沉积外，锡上的高沉积过电位也是一个重要因素。

关键词：锌电极；抑制枝晶；锡离子

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