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Effect of inhibitors on Zn-dendrite formation for zinc-polyaniline secondary battery

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Abstract

The effects of Pb^{2+}, sodium lauryl sulfate and Triton X-100 on inhibition of Zn-dendrite growth in Zn-polyaniline batteries were studied by scanning electron micrograph and cyclic voltammetry. The results show that Triton X-100 in the region of 0.02–500 ppm in the electrolyte containing 2.5 M $ZnCl_2$ and 2.0 M NH_4Cl with pH 4.40 can effectively inhibit zinc-dendrite growth during charge–discharge cycles of the battery and yield longer cycles.

Keywords: Zinc dendrite; Triton X-100; Lead chloride; Sodium lauryl sulfate; Zinc-polyaniline battery; Inhibitor

1. Introduction

As an electrode material, zinc is widely used in Zn-Mn, Zn-Ag and/or Zn-Ni batteries [1–5]. Zn-electrodes form Zn-dendrites during charge–discharge cycles in these batteries. It results in decreased coulombic efficiency of batteries and charge life [6]. In order to inhibit or eliminate Zn-dendrite formation on zinc electrode during charge–discharge cycles for secondary batteries, many methods have been described, for example, Renuka et al. reported that the growth of zinc dendrites was reduced in the presence of CdO for a Zn/NiOOH battery [3]; Chiba and Takahashi showed that battery containing zinc and an anionic polymer electrolyte can suppress dendrite growth and give long cycle life for Zn/MnO_2 battery [7]. These methods effectively inhibited formation of Zn-dendrite during charge–discharge processes for many of the alkaline batteries.

Polyaniline (PAn) has a high conductivity, sufficiently electrochemical reversibility, and a high environmental stability. It can be used as a cathode in aqueous and lithium batteries [8–12]. Polyaniline used as electrode material is neither soluble nor passive during the oxidation process, and there is no precipitate on the polyaniline electrode during the reduction process. These characteristics are very important for rechargeable batteries. A metal electrode does not display such behavior. However, polyaniline easily hydrolyzed in an alkaline medium [13], zinc-dendrite also formed on zinc electrode in aqueous acidic batteries without any additives during charge–discharge processes [6,14]. However there have been very few studies on how to overcome the shortcomings of the Zn-polyaniline battery [6].

In this paper we will report on a low acid medium, the effect of Pb^{2+}, sodium lauryl sulfate and Triton X-100 on the charge–discharge cycles of Zn-polyaniline batteries, and the results of scanning electron micrograph (SEM) and cyclic voltammetry in the systems containing different additives.

2. Experimental

The battery is represented by $Zn/ZnCl_2$, NH_4Cl/PAn. The zinc-negative electrodes were polished with emery paper (Nos. 600 and 800) before use. Polyaniline was polymerized on a graphite flake by electrolysis in a solution containing 0.2 M aniline and 1.0 M hydrochloric acid [15]. The electrolyte in batteries was an aqueous solution of 2.5 M $ZnCl_2$ and 2.0 M NH_4Cl with different additives (pH 4.4). Those additives were used to inhibit or eliminate Zn-dendrite formation during charge–discharge cycles. The batteries were assembled by extrusion molding of a zinc-negative electrode, a polyaniline-positive electrode and a piece of polypropylene separator with above electrolyte.

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The DH-1 potentiostat–galvanostat was used for electrolysis of aniline and cyclic voltammetry. The instruments for the charge and discharge of the battery were an automatic battery charge–discharge unit (HJ-201B, Japan) and a pen recorder (YEW3036). The batteries were charged and discharged between 0.75 and 1.50 V at a constant current density of 20 mA/cm^2 for the zinc electrode. Total charge–discharge time varied between 1.3–2.2 h for each cycle at various tests. Scanning electron micrographs were taken on a transmission electron microscope H-300 with a scanner (Japan).

3. Results and discussion

3.1. Effect of additives on SEM of zinc electrodes

The SEMs of zinc electrodes are shown in Fig. 1a–d. Those zinc electrodes used for determining SEMs are obtained by charge to 1.50 V at the third charge–discharge cycle in the electrolyte containing 2.5 M $ZnCl_2$ + 2.0 M NH_4Cl with no additive (a) and with additives of 15 ppm $PbCl_2$ (b), 2 ppb sodium lauryl sulfate (c) or 0.01% Triton X-100 (d), respectively. From the SEMs, we can see that the particles on the zinc electrode surface in the electrolyte containing 0.01% Triton X-100 are the most well-distributed and the finest, in contrast, the zinc electrode surface without any additives is uneven and the particles are the roughest among all zinc electrodes. This is due to the fact that additives improved the dispersion and cathodic polarization of the electrolyte, which lead to the finer zinc particles of deposition on the zinc electrode. The fine zinc particles formed during the charging process are advantageous in prolonging charge–discharge life of the batteries and raising the current efficiency of the batteries [6].

Table 1
The effective concentration ranges of three kinds of additives

Additives	$PbCl_2$	Sodium lauryl sulfate	Triton X-100
Effective concentration (ppm)	10–20	0.01–100	0.02–500

We found that the inhibition of the three kinds of additives for zinc-dendrite formation are different and their effective concentration ranges are different (see Table 1), but all of them can improve charge–discharge character of the zinc electrodes in the batteries.

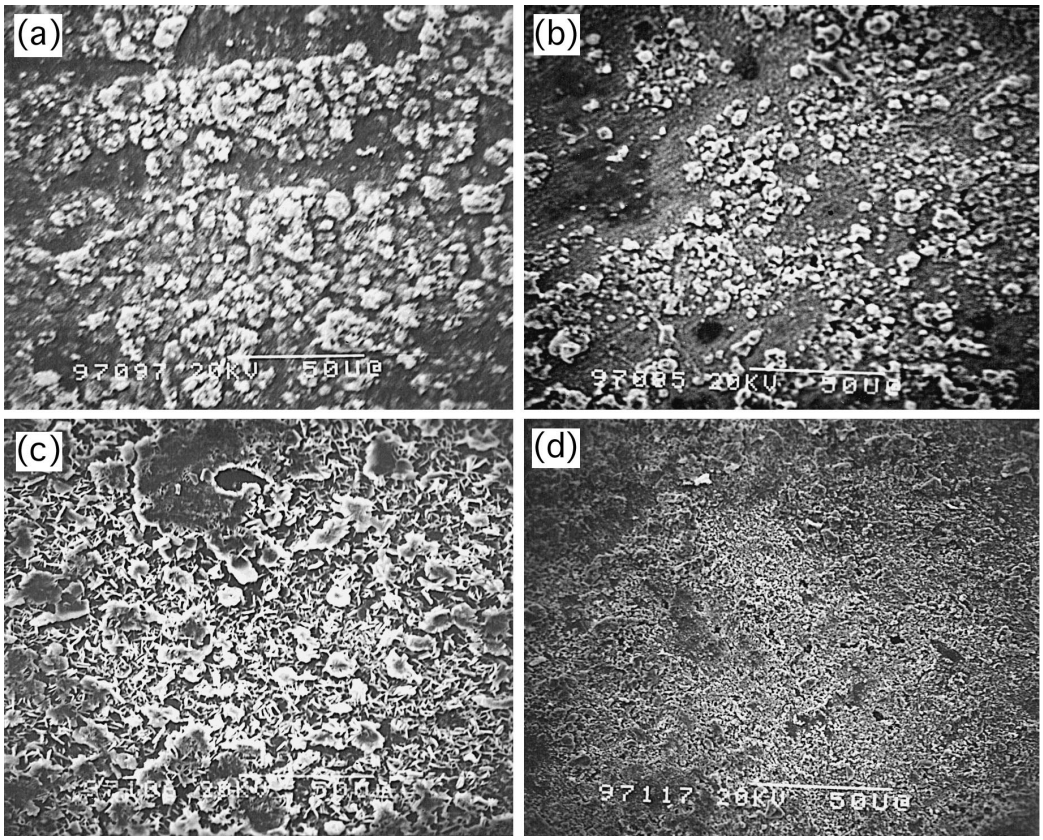

Fig. 1. Scanning electron micrographs of zinc electrodes surface charged to 1.50 V at the third charge–discharge cycle in the solution containing 2.5 M $ZnCl_2$ and 2.0 M NH_4Cl with different additive (pH 4.40): (a) with no additive; (b) with 15 ppm $PbCl_2$; (c) with 2 ppb sodium lauryl sulfate; (d) with 0.01% Triton X-100.

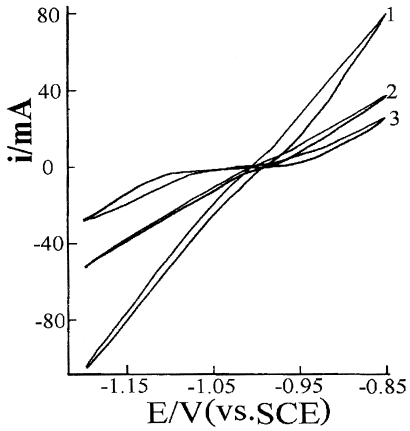

Fig. 2. The cyclic voltammograms of zinc electrodes in the solution containing 2.5 M $ZnCl_2$ and 2.0 M NH_4Cl with different additive (pH 4.4): (1) 15 ppm $PbCl_2$; (2) 2 ppb sodium lauryl sulfate; (3) 0.01% Triton X-100.

The cyclic voltammograms of zinc electrodes in 2.5 M $ZnCl_2$ + 2.0 M NH_4Cl + the additive are shown in Fig. 2. Comparing Fig. 1 with Fig. 2, we can conclude that the broader potential range of the zero current in cyclic voltammograms, the finer are the particles formed on zinc electrode. These results show that the addition of suitable surface-active agents often leads to improved deposits [16].

Based on the results of SEMs and voltammograms we can see that the solution containing 0.01% Triton X-100 is better than those containing other two kinds of additives for inhibiting zinc dendrite formation on zinc electrodes during charge process.

In order to study surface morphology change of the zinc-negative electrode during charge–discharge cycles, the SEMs of zinc electrodes charged to 1.50 V and discharged to 0.75 V were recorded in Fig. 3a,b for the third charge–discharge cycle in the electrolyte containing 2.5 M $ZnCl_2$ + 2.0 M NH_4Cl with pH 4.40. From them we can see that the zinc electrode surface at 1.50 V is rougher than that at 0.75 V. The former is caused by nonuniform distribution of zinc particles deposited on zinc electrode, the latter is attributed to the oxidation of the newborn zinc, which is easier than substrate zinc. Evidence for the latter is that SEM displays the surface morphology of substrate zinc (Fig. 3b).

Table 2
Relationship between additives of different kinds and cycle numbers

	Additives			
	None	$PbCl_2$	Sodium lauryl sulfate	Triton X-100
Cycle number	23	36	38	79
Initial discharge capacity (mAh)	19.5	21.7	20.1	21.5
Final discharge capacity (mAh)	15.6	17.4	16.1	17.2

3.2. Effect of additives of different kinds on charge–discharge cycles

Table 2 shows the change in cycle number, which is defined as the value when the capacity of a battery decreased to 80% of the initial capacity, with additives of different kinds in the electrolyte containing 2.5 M $ZnCl_2$ and 2.0 M NH_4Cl with the optimum additive concentration and pH 4.4.

Recharge cycles are very important in battery operation. The life of a Zn/PAn battery without any additives was less than 23 cycles. The life-limiting factor was due to the development of dendrites of the zinc-negative electrode. After several cycles of charge and discharge, these crystals may penetrate the separator, thereby, make direct contact with the positive electrode and short out the battery, which leads to the droop of battery capacity. By contrast, 79 recharge cycles were recorded for a battery containing 0.01% Triton X-100. Comparing the effects of the three kinds of additives on inhibition of Zn-dendrite formation, we see that the solution containing 0.01% Triton X-100 is more effective than those containing the other two kinds of additives for inhibition of zinc dendrite.

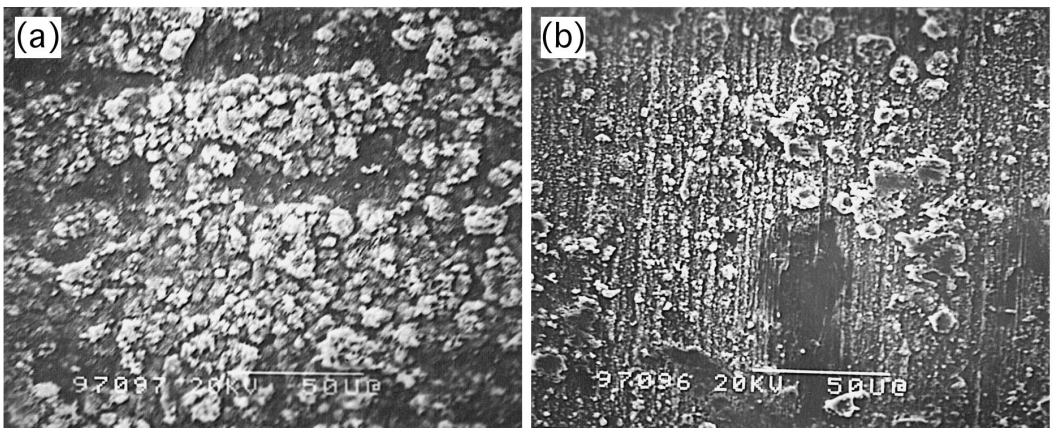

Fig. 3. Scanning electron micrographs of zinc electrodes surface at the third charge–discharge cycle in the solution containing 2.5 M $ZnCl_2$ and 2.0 M NH_4Cl (pH 4.4): (a) charged to 1.50 V, (b) discharged at 0.75 V.

4. Conclusions

The above results show that Triton X-100 can effectively inhibit zinc-dendrite growth during charge–discharge cycles of the Zn-polyaniline battery with an acid medium and give longer cycles. It is possible that Triton X-100 can be employed as an effective additive in the rechargeable Zn-polyaniline batteries.

Acknowledgements

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