



Short communication

Characteristics of a mercury substituent inhibitor in alkaline manganese dioxide/zinc batteries

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1. Introduction

Manganese dioxide/zinc batteries are the most widely used portable electrochemical power source. Such cells cause serious environmental pollution due to the fact that mercury is used as an anode additive for inhibiting zinc corrosion and extending shelf life [1, 2]. The disposal of large quantity of used cells inevitably results in mercury pollution.

So far there have been two approaches to achieving inhibition of zinc corrosion under the mercury-free condition [3–7]. One is to alter the properties of the zinc by alloying it with other elements, the other is to modify the property of the electrolyte by introducing additives. Research has been carried out in our laboratory where approximately one hundred kinds of additive have been tried, some of which are effective in inhibiting zinc corrosion in alkaline solutions [8, 9]. But since few have proved successful as complete substitutes for mercury, emphasis has been placed on the search for a composite addition agent. We have now found a nonpoisonous composite inhibitor (designated as HSJ) that has proved suitable as a substitute for mercury. The composite inhibitor is a mixture of a polyoxyethylene ether and a quarternary ammonium salt. The characteristics of HSJ as a substitute for mercury in alkaline manganese cells are described in this paper.

2. Experimental details

2.1. Gas evolution test

The sample used was pure zinc powder (purity 99.995%) with 90% of the particles within the range 0.075–0.425 mm. Amalgamated zinc powder of the same particle size was used for comparison. The apparatus for the measurement of gas evolution rate was described previously [4]. The sample was immersed in 8 M KOH solution containing 0.75 M zincate with or without the inhibitor HSJ. The apparatus was immersed in a constant temperature bath at 50 ± 0.5 °C.

2.2. Electrochemical test

A three-electrode system was used with a working electrode of ingot zinc (purity 99.995%). 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 surface was polished with emery paper (800 grade), degreased with acetone and rinsed with distilled water. The electrolyte was purged with nitrogen for 1 h to remove oxygen. The temperature was 20 ± 1 °C.

The polarization curves were measured using a PAR model 342 system at a scanning rate of 0.2 mV s^{-1} . A PAR model 378 system was used to obtain the electrochemical impedance spectra (EIS). The frequency ranged from 0.003 Hz to 100 kHz, and the amplitude of the a.c. signal was 5 mV.

2.3. Battery assembly and measurement

Batches of LR6 (AA-size) mercury-free alkaline MnO_2/Zn batteries were assembled in several battery factories using a technique similar to that used for conventional mercury-containing alkaline manganese batteries, except that mercury in zinc paste was substituted by HSJ and brass collectors were plated with tin. The discharge performance of the batteries were measured according to [10].

3. Results and discussion

3.1. Inhibition behaviour

Figure 1(a) shows the volume of hydrogen evolved from zinc powder in alkaline solution with and without HSJ. The volume of hydrogen in the presence of HSJ is greatly reduced, that is, the corrosion of zinc powder in the alkaline solution is strongly inhibited. The inhibition is due to surface adsorption of the inhibitor. The corrosion rate of the amalgamated zinc powder in alkaline solution is low since the hydrogen evolution

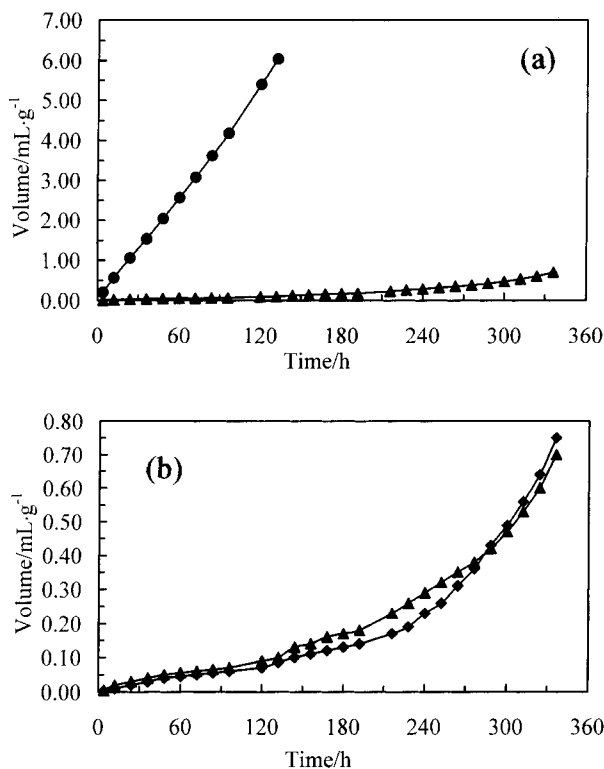


Fig. 1. Plots for volume of hydrogen evolution against time ($T = 323$ K). Key for (a): (●) KOH and zincate; (▲) KOH, zincate and Hg. Key for (b): (▲) KOH, zincate and Hg; (◆) KOH, zincate and Hg.

overpotential on zinc is increased by the addition of mercury. Figure 1(b) indicates that the inhibition efficiency of Hg is about the same as that of 4% Hg added to the zinc powder. A mercury content of 3.6% in the zinc is the minimum amount necessary for maintaining an acceptable battery quality as regards storage life, service hours, field of application and other properties without having to resort to other measures [11]. Therefore, the inhibition performance of the composite inhibitor Hg can meet the requirements of a mercury-free zinc anode in alkaline batteries.

3.2. Electrochemical characteristics

The polarization behaviour of zinc in alkaline solution with and without Hg is shown in Figure 2. In the low polarization potential region both anode and cathode reactions are inhibited in the Hg-containing system by the surface adsorption of the inhibitor. In the potential region AB on curve 2, the inhibitor quickly desorbs from the surface, and the anodic current density increases rapidly as the electrode potential becomes more positive [8]. In the region BC the inhibitor has completely desorbed from the electrode surface and the two polarization curves overlap. Another polarization test was carried out for the same electrode system after the preceding polarization test had been finished for ten minutes. The anodic desorption of the inhibitor is again observed on the polarization curve (Figure 3). This

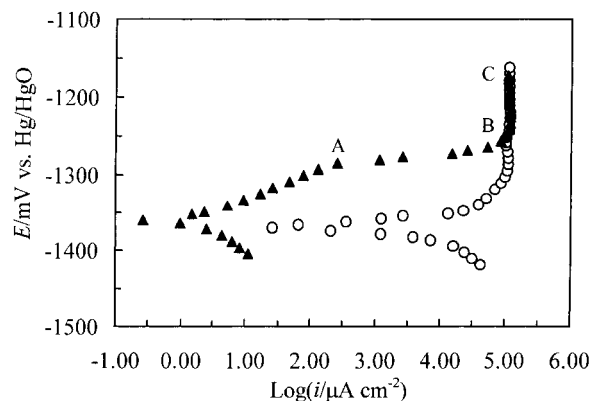


Fig. 2. Polarization curves of zinc in 8 M KOH solutions containing 0.75 M zincate with (▲) and without (○) Hg at a scanning rate of 0.2 mV s^{-1} .

shows that the adsorption/desorption processes are reversible with variation of electrode potential. The phenomenon of adsorption/desorption of Hg with changing electrode potential allows its use as an inhibitor in place of mercury in alkaline manganese dioxide/zinc batteries. When the cell is in the open-circuit state, the inhibitor can suppress the self-discharge of the zinc anode by adsorbing on its surface. Meanwhile, the inhibitor may also desorb from the surface of a discharging zinc anode, so the discharge performance of the cells containing Hg will not be influenced.

The electrochemical impedance spectra (EIS) of zinc in alkaline solution with and without Hg are shown in Figure 4. The high-frequency capacitive loops are due to the charge transfer resistance in parallel with the double layer capacitance [12]. Comparing the EIS data in Figure 4(a) and (b) reveals that the addition of Hg remarkably increases the charge transfer resistance of the electrochemical reactions, that is, the cathode and anode processes are inhibited. The low-frequency loop in Figure 4(a) is attributable to transport processes of the zinc electrode [13]. With the addition of Hg, a large capacitive loop occurs in the low-frequency region in the complex plane impedance plot (Figure 4(b)), which is possibly due to the inhibitor adsorbing on the zinc electrode [14].

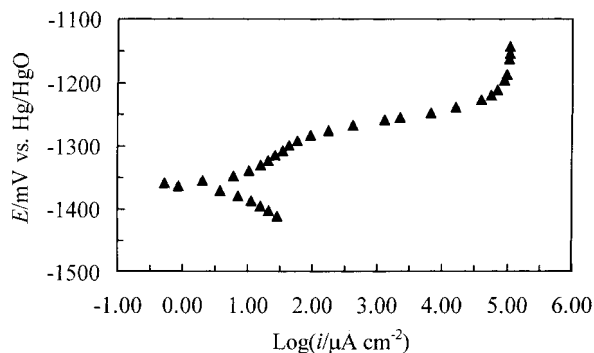


Fig. 3. Polarization curve of zinc in 8 M KOH solution containing 0.75 M zincate and Hg (No. 2 polarization) at a scanning rate of 0.2 mV s^{-1} .

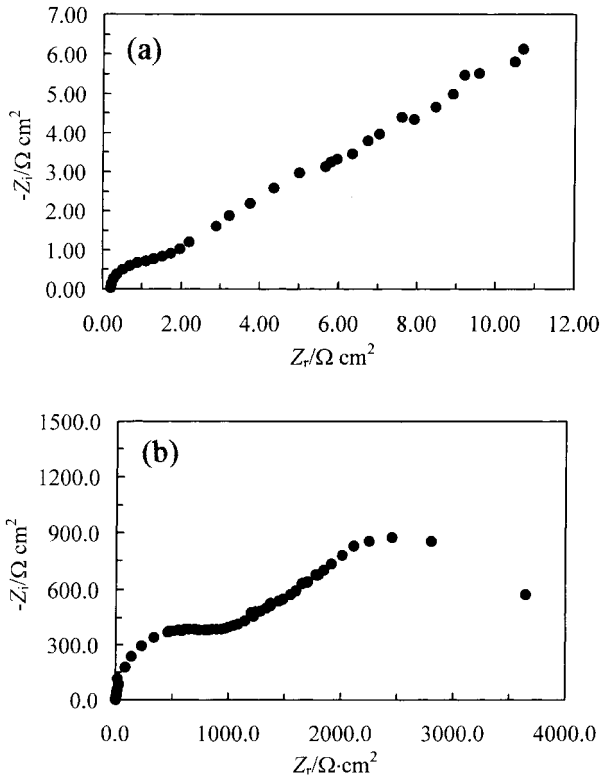


Fig. 4. EIS of zinc in 8 M KOH solution containing 0.75 M zincate with (b) and without (a) HSJ.

3.3. Performance of mercury-free alkaline manganese dioxide/zinc batteries assembled with HSJ

Figures 5 and 6 give, respectively, the continuous medium-rate discharge (on 10 Ω load) and high-rate discharge (on 1 Ω load) curves for mercury-free batteries and conventional mercury-containing batteries assembled under the same conditions. The mercury-free batteries resemble the mercury-containing batteries in both the medium-rate and high-rate discharge characteristics. This shows that the addition of HSJ hardly influences the discharge performance of the batteries as expected from the results of the preceding polarization test.

To obtain a thorough understanding of the performance of the mercury-free batteries, a number of sample cells were measured according to [10]. Some results are

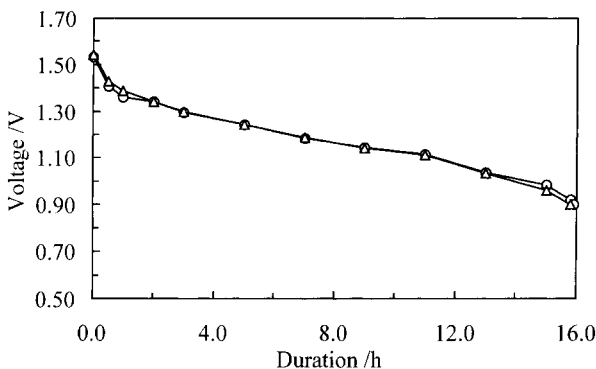


Fig. 5. Continuous discharge curves on 10 Ω load for new AA-size cells. Key: (○) cells with HSJ; (△) cells with Hg.

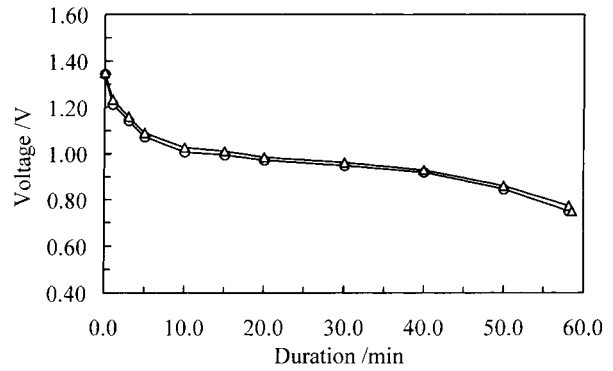


Fig. 6. Continuous discharge curves on 1 Ω load for new AA-size cells. Key: (○) cells with HSJ; (△) cells with Hg.

Table 1. Performance of LR6 (AA size) alkaline zinc-manganese cells

Addition agent	Continuous discharge time on 1.0 Ω load/min		Continuous discharge time on 10.0 Ω load/h	
	New cells	Cells stored for 6 months	New cells	Cells stored for 6 months
HSJ	58.2	56.2	15.9	15.5
Hg	58.6	56.4	15.8	15.4

listed in Table 1 which indicates that the continuous discharge performance of the mercury-free cells in both the initial stage and stored stage is almost identical to that of the mercury-containing cells.

4. Summary

The inhibition efficiency of the composite addition agent HSJ for zinc in alkaline solution almost is identical with that of 4% Hg. Moreover the adsorption and desorption processes of HSJ on the zinc surface are reversible with variation of electrode potential, which allows its use as an inhibitor in the cells. Mercury-free alkaline manganese dioxide/zinc batteries with HSJ resemble mercury-containing ones in their discharge performance. The composite inhibitor HSJ has proved to perform well as a corrosion inhibitor in place of mercury in alkaline manganese dioxide/zinc batteries.

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