

Short Communication

Possibility and advantages of an anodic-type inhibitor for Zn/MnO₂ dry batteries

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Abstract

In developing mercury-substituting inhibitors for zinc/manganese dry batteries, the authors have discovered an anodic-type composite organic inhibitor (designated as PA) which is quite effective in suppressing the corrosion of zinc during cell storage, yet will not impede the dissolution of zinc during cell discharge. Moreover, the inhibitor PA has a unique advantage in that the corrosion of zinc is inhibited irrespective of the conjugate cathodic process.

Keywords: Dry batteries; Zinc corrosion; Anodic-type inhibitors; Non-mercurization

1. Introduction

With increasing public concern on mercury pollution of the environment, the use of soluble mercury salts as inhibitors in zinc/manganese dioxide battery electrolytes (leading to the deposition of mercury on zinc surface and the amalgamation of the latter), a long tradition of the battery industry, is no longer considered a suitable practice. For maintaining the performance of the battery, the corrosion of the zinc electrode has to be suppressed by other means. In searching for mercury-substituting inhibitors, attention is naturally focused on inhibitors of the cathodic type, because mercury salts are prime examples of this category in that the amalgamated zinc with high hydrogen overpotential mainly impedes the cathodic evolution of hydrogen, the conjugate reaction of anodic zinc dissolution. Few cathodic-type inhibitors other than mercury salts have been found to be satisfactory. The work reported here broadens the scope of inhibitor studies. Eventually, a composite organic additive (designated as PA) was found to be quite suited for use in Zn/MnO₂ dry batteries as a corrosion inhibitor instead of mercury salt [1]. An organic additive of this category is characterized by its capability to shift the rest potential of zinc to a more positive value and, hence, according to principles of electrochemical corrosion, is an anodic-type inhibitor. The inhibiting effect of PA is so good that Zn/MnO₂ batteries made with PA instead of mercury salt meet all the technical requirements specified by the International Electrochemical Commission (ICE). Moreover, as an anodic-type inhibitor, PA has a unique

advantage in that the corrosion of zinc is inhibited irrespective of the conjugate cathodic process. Here arises a question: how can an anodic-type inhibitor such as PA suppress the corrosion of zinc during cell storage yet does not impede the dissolution of zinc during cell discharge? As there are few reports of the working mechanism of anodic-type inhibitors, attempts are made in this paper to examine this matter in detail.

2. Experimental

2.1. A.c. impedance and d.c. polarization measurements

In order to observe the variation of surface state and polarization behaviour of zinc electrodes in the presence of PA, a.c. impedance and d.c. polarization measurements were performed on sample zinc/manganese cells assembled in the factory, or on sample zinc plates placed in electrolyte solution. In the former case, each sample cell was pierced to make a small hole in order to accommodate a Lugging capillary via which the zinc electrode was connected electrolytically to a saturated calomel reference electrode to form a three-electrode system. Polarization curves were measured with a computer-controlled PAR Model 273 potentiostat. The bidirectional polarization curves were processed by the computer using special software to obtain the corrosion parameters of zinc in NH₄Cl solutions that contained different inhibitors. The a.c. impedance of the zinc electrode at differ-

ent potentials was measured with a Solatron Model 1172 frequency response analyzer equipped with an electrochemical interface and controlled by a microcomputer to run automatically the frequency sweep from 0.1 Hz to 10 kHz. The impedance spectra were computer-analyzed using a special curve-fitting software with reference to a simplified equivalent circuit.

2.2. Immersion test

Zinc samples of dimension 3 cm×5 cm were cut from sheet zinc of cell grade. After degreasing, cleaning and weighing, the samples were immersed separately in 26% NH₄Cl solutions that contained different inhibitors for periods of up to several weeks. The temperature was maintained at 45 °C in order to accelerate the reaction. Corrosion of the immersed zinc is accompanied by evolution of hydrogen gas which is collected in a burette. Both the loss of sample weight after immersion and the volume of hydrogen evolved during immersion served as a rough indication of the rate of zinc corrosion.

3. Results and discussion

In previous work [1] it was shown that PA manifests itself as an anodic-type inhibitor in that the addition of PA to pure NH₄Cl solution causes a marked decrease in the zinc corrosion rate i_{corr} while shifting the corrosion potential E_{corr} in the positive direction. This proposition is based on the results of bi-directional polarization measurements of pure zinc in pure NH₄Cl electrolyte. In an actual Zn/MnO₂ cell, the conditions are not all the same: the zinc anode is not so pure (it contains impurities such as Pb, Cd, Fe, etc.), and there are other ingredients in the electrolyte (e.g. starch and other additives). Thus, it is important to examine the polarization behaviour of zinc electrodes under actual cell conditions. Polarization characteristics for R6P cells with different inhibitors are given in Fig. 1. The open-circuit potential (i.e. the corrosion potential E_{corr} of zinc) of a cell with PA as an inhibitor is about 30 mV more positive than that in a conventional cell with mercury chloride. The difference between the two polarization curves gradually diminishes, however, with the advancement of anodic polarization. This suggests that the influence of PA is weaker at higher potentials due to desorption.

The variation of the differential double-layer capacity, C , of a zinc electrode in an R6P cell containing PA is shown in Fig. 2. The C values were calculated from impedance data. At open circuit, C assumes a minimum value. When the potential is made to deviate from E_{corr} in either a positive or negative direction, C gradually increases and two peak values occur within a narrow range of potential. This phenomenon is quite similar to that mentioned by Frumkin [2] in the case of specific adsorption of organic molecules on a mercury surface. The double-layer capacity of the electrode may be seen as that for a plain plate capacitor, for which $C = \epsilon/4\pi d$

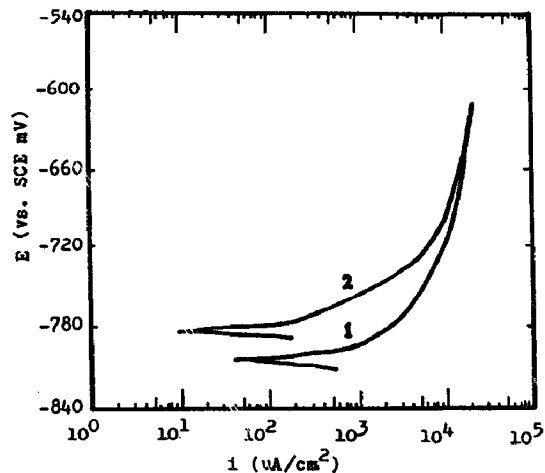


Fig. 1. Anodic polarization curves of zinc electrode in an R6P cell: (1) cell with HgCl₂, and (2) cell with PA.

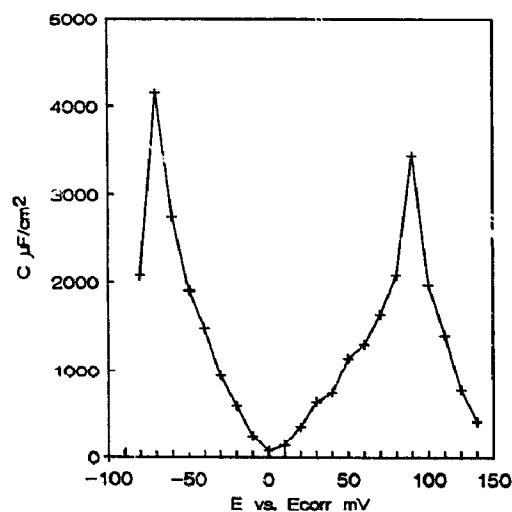


Fig. 2. Dependence of zinc electrode capacity on potential for an R6P cell with PA.

where ϵ denotes the dielectric constant of the medium and d the distance between the plates. The decrease of double-layer capacity is attributed to the displacement of small water molecules of high dielectric constant in the double-layer region by large organic molecules of low dielectric constant. Hence, the data implies that PA is adsorbed on the zinc surface at open-circuit potential. They also indicate that desorption of PA takes place when zinc is polarized to some extent. From the above experimental results, it is believed that at an open-circuit condition, PA is adsorbed on the zinc surface and the corrosion of zinc is inhibited. Once the cell is discharged in a closed circuit, the potential of zinc undergoes a positive shift. This leads to the desorption of PA from the surface and the anodic dissolution process can proceed without hindrance.

Since anodic-type inhibitors owe their inhibiting effect to the suppression of the anodic reaction of metal dissolution, they should remain effective irrespective of any variation in

Table 1
Corrosion parameters of zinc in 26% NH_4Cl solution

Inhibitor	E_{corr} vs. saturated calomel electrode (V)		i_{corr} ($\mu\text{A cm}^{-2}$)	
	Solution de-aerated	Solution aerated	Solution de-aerated	Solution aerated
Hg	-1.204	-1.018	15	191
Bi	-1.151	-1.102	4	1398
None	-1.106	-1.059	110	1212
PA	-0.922	-0.858	7	20

the conjugate cathodic reaction. The following experiments were performed in order to verify this hypothesis.

3.1. Inhibition of zinc corrosion in an aerated NH_4Cl solution

The effect of aeration of zinc corrosion in the presence of different inhibitors was examined by determining the bi-directional polarization curves in aerated NH_4Cl solutions, as well as in de-aerated NH_4Cl solutions. The results are given in Table 1. It is seen that in aerated NH_4Cl solution, the corrosion of zinc is accelerated greatly and can no longer be suppressed by a traditional cathodic inhibitor, i.e. a mercury (or bismuth) salt. This is because with oxygen present in the system, the conjugate cathodic reaction of zinc corrosion changes from hydrogen evolution to oxygen. Nevertheless, PA is found to remain effective under such conditions.

3.2. Inhibition of zinc corrosion in an NH_4Cl solution containing Fe^{3+} ions

Fe^{3+} ions are known to be a very harmful impurity to zinc cell electrolyte, they tend to increase the zinc corrosion rate. Immersion tests of zinc in NH_4Cl solution containing 10 ppm Fe^{3+} showed considerable hydrogen evolution even in the presence of HgCl_2 or BiCl_3 at optimum concentrations. By contrast, with PA as inhibitor, there was practically no hydrogen evolution during prolonged immersion, as illustrated in Fig. 3. This feature of an anodic-type inhibitor is of significance, since it is difficult to eliminate completely impurities such as oxygen and iron during battery production.

4. Conclusions

Electrochemical studies reveal that anodic-type inhibitors, such as PA, may be used as substitutes for the mercury salts used in Zn/MnO_2 dry batteries with satisfactory results. It is

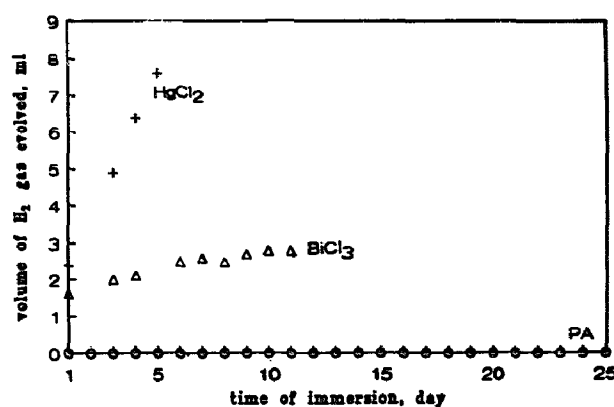


Fig. 3. Zinc immersed in 26% NH_4Cl solution with 10 ppm Fe^{3+} , and different inhibitors at their optimum conditions.

believed that the working mechanism of PA is closely related to the adsorption of PA on the zinc surface at open-circuit potential. But once the cell is discharged in a closed circuit, PA is desorbed from the surface by the positive shift of the zinc electrode potential, and the anodic dissolution process can proceed without hindrance. Moreover, as an anodic-type inhibitor, PA has a unique advantage over cathodic-type inhibitors in that it is effective in inhibiting zinc corrosion, irrespective of the conjugate cathodic process.

Acknowledgements

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References

- [1] C.B. Huang, N.F. Yang, X.J. Cao and P.H. Shi, *J. Power Sources*, 45 (1993) 169–175.
- [2] A.N. Frumkin, *Nova Acta Leopoldina. Neue Folge*, 19 (1957) 1–19.