# A new type of nonpoisonous addition agent for substituting mercury in zinc/manganese dry cells

Chubao Huang, Naifeng Yang, Xuejing Cao and Peihua Shi
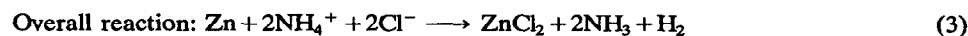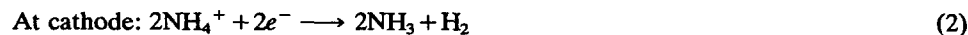*Department of Chemistry, Jilin University, Changchun 130023 (China)*

## Abstract

By means of immersion test, a.c. impedance measurements and a bidirectional polarization study, a new type of composite addition agent has been developed for completely substituting mercury (compound) in zinc/manganese dry cells. Type R6P (AA-size, high power) mercury-free dry cells assembled with pasted electrolyte paper that contains this addition agent instead of mercuric chloride have showed satisfactory performance. For example, 95% of the original discharge capacity is still retained after storage for one year.

## Introduction

Zinc/manganese dry cells are the most widely used portable chemical sources of electricity. For example, billions of zinc dry cells are manufactured and consumed in China each year. While such cells offer much convenience to modern human life, they also cause serious pollution problems. This is because, hitherto, mercury has been used as an anode inhibitor for suppressing zinc corrosion and extending shelf life. The disposal of large quantity of consumed cells will inevitably result in a scattering and accumulation of significant amounts of mercury that is very harmful to live. It has been estimated that about 30%, or more, of mercury pollution comes from abandoned dry cells [1]. With increasing awareness of the importance of environmental protection, it has therefore become an urgent and important task to reduce, or better still to eliminate completely, the mercury from zinc dry cells. The present work is aimed at solving this problem by substituting the mercury with a suitable nonpoisonous addition agent.

It is well known that the zinc anode in dry cells tends to undergo electrochemical corrosion with simultaneous evolution of hydrogen as represented by the following reactions [12]:

At anode: $Zn + 2Cl^- \longrightarrow ZnCl_2 + 2e^-$                              (1)

At cathode: $2NH_4^+ + 2e^- \longrightarrow 2NH_3 + H_2$                      (2)

Overall reaction: $Zn + 2NH_4^+ + 2Cl^- \longrightarrow ZnCl_2 + 2NH_3 + H_2$         (3)

The standard Gibbs free-energy change of reaction (3) is calculated to be $-191.426$ kJ and the standard potential of the $Zn/Zn^{2+}$ electrode is $-0.763$ V. Thus, thermodynamically, the zinc corrosion accompanied by hydrogen evolution in this system is spontaneous and unavoidable. The only way to impede the corrosion rate is to set up a suitable kinetic barrier. Mercury has long time been used for this purpose.

On introducing a mercuric salt into the cell electrolyte, the surface of the zinc anode will be amalgamated with mercury that is produced by a chemical displacement reaction. The effect of mercury in the cell can be attributed to the following factors:

(i) the amalgamation of zinc renders its surface more uniform with elimination of micro local cells;

(ii) the high hydrogen overvoltage of mercury greatly impedes the hydrogen evolution reaction with which the zinc dissolution is conjugated, and

(iii) the amalgam does not impede zinc dissolution during cell discharge.

Many substitutes have been tried, but few have proved successful as it is hard to find a single substance that also possesses all the above three features.

So far, there have been two approaches to reaching the goal of impeding the zinc corrosion rate. One is to alter the property of zinc by alloying it with some other elements, the other is to modify the properties of the electrolyte by introducing some additives. We have been working on the second approach because it is more conducive to industrialization. Since a single substance is unlikely to be effective, we lay particular stress on searching for a composite addition agent. Following a large amount of experimental research, we have found a nonpoisonous composite organic addition agent that is quite effective. We designate it as PA. The effect of PA as a substitute for mercury in zinc dry cells is illustrated in the following experiments.

## Experimental

### Immersion test

Zinc samples of dimensions 3 cm × 5 cm were cut from sheet zinc of cell grade. After degreasing, cleaning and weighing, they were immersed separately in $NH_4Cl$ or $NH_4Cl + ZnCl_2$ that contained different addition agents. The glass containers used were equipped with a graduated tube for collecting and measuring the hydrogen gas that was evolved during the immersion via displacement of liquid. The temperature was maintained at 45 °C in order to accelerate the reaction. The immersion period usually lasted for 40 days. After that, the samples were taken out, washed, dried and weighed again. The corrosion rates of the samples were then evaluated from their weight loss and the quantity of the $H_2$ evolved. Visual or microscopic examination of the samples was also expected to give qualitative information about the nature and extent of the corrosion.

The results of the immersion test, listed in Table 1, show that the corrosion rate of zinc in the presence of the composite addition agent PA is greatly reduced, i.e., in a manner similar to that observed in presence of mercuric chloride. Note that there is a weight increase, instead of weight loss, of the zinc sample after immersion in a solution containing mercuric chloride. This is due to deposition of mercury.

### Polarization resistance

The sample electrodes were made from pure zinc rod (purity 99.999% and diameter 0.64 cm) and were tightly inserted in a Teflon sleeve. Before each experiment, the section area exposed to the electrolyte was finely polished to a mirror-like surface, thoroughly washed, and ultrasonically cleaned. The counter electrode was a platinum foil. The two electrode compartments of the measuring cell were separated by a glass frit. A reference electrode of Ag/AgCl was led to the working electrode compartment via a Luggin capillary. All potentials are reported with respect to this electrode. Measurements of the polarization characteristics of zinc in the linear polarization

TABLE 1

Results of immersion test

| Addition agent | Electrolyte | Immersion period (days) | Total gas evolved (cm$^3$) | Weight change of sample (g) |
|---|---|---|---|---|
| None | 26% NH$_4$Cl | 4 | 5.00 | −0.0342 |
| PA | 26% NH$_4$Cl | 40 | 0.20 | −0.0012 |
| 0.8% HgCl$_2$ | 26% NH$_4$Cl | 40 | 0.40 | +0.4185 |

TABLE 2

Corrosion parameters from polarization resistance measurements

| Sample electrode | Addition agent in 26% NH$_4$Cl | $E_{corr}$ (mV) | $R_p$ k$\Omega$ cm$^{-2}$ | $i_{corr}$ $\mu$A cm$^{-2}$ |
|---|---|---|---|---|
| Pure Zn | None | −979 | 0.3639 | 59.7 |
| Pure Zn | PA | −980 | 2.8195 | 7.7 |
| Zn, surface amalgamated | None | −1185 | 4.2154 | 6.2 |

region were carried out in electrolytes containing different addition agents with a PAR model 273 potentiostat that was controlled by an electronic computer. At open circuit, the rest electrode potential corresponds to $E_{corr}$, which is usually stabilized within 10 min. A special operating programme enabled the electrode potential $E$ to be automatically swept from −6 to +6 mV with respect to $E_{corr}$. The polarization resistance, $R_p$, was calculated from the slope $dE/di$. Then, the corrosion current $i_{corr}$ was computed using the Stern and Geary equation [3, 4]:

$$i_{corr} = \frac{1}{2.3R_p} \frac{b_a \times b_c}{b_a + b_c} \qquad (4)$$

with appropriate values of the anodic and cathodic Tafel slopes $b_a$ and $b_c$.

Table 2 lists some of the corrosion parameters obtained from the polarization resistance measurements. In the presence of PA, the $R_p$ of zinc in 26% NH$_4$Cl is markedly increased and the $i_{corr}$ is markedly decreased. This indicates that PA is effective in inhibiting the corrosion of zinc.

*Bidirectional polarization characteristics over a strong polarization region*

The measurements were similar to the preceeding experiments, except they were extended to high polarization regions (i.e., from −250 to +160 mV with respect to $E_{corr}$) while the electrode was constantly rotated at 900 rpm to drive away any adhered hydrogen bubbles. The results are shown in Fig. 1.

It is of interest to note that although PA and amalgamation both exhibit a great retarding effect on zinc corrosion, their mechanisms are quite different. While amalgamation mainly retards the cathodic reaction of hydrogen evolution, the PA seems
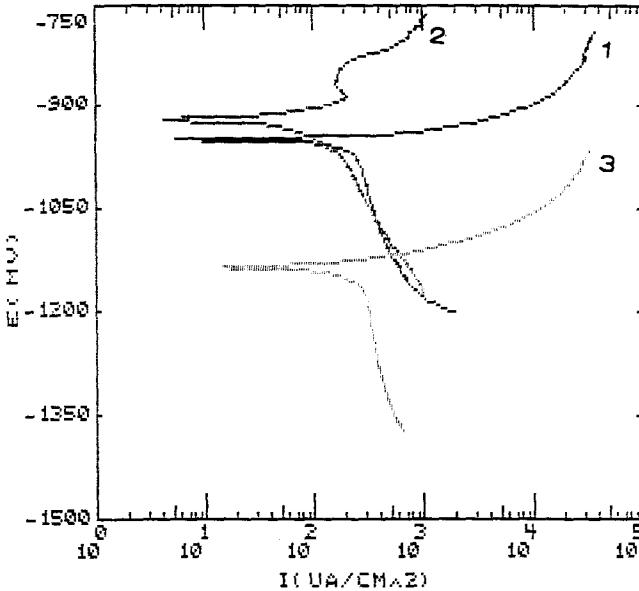
Fig. 1. Polarization characteristics of zinc in 26% NH₄Cl solution: curve (1) pure Zn, no addition agent in solution; curve (2) pure Zn, solution with PA, and curve (3) amalgamated zinc, no addition agent in solution.

to exert a greater influence on the anodic dissolution of zinc than on the cathodic evolution of hydrogen. As seen from curve 2 in Fig. 1, the anodic polarization curve of zinc in the presence of PA suggests slight passivation at relatively low current densities with the normal anodic course reassumed later. Would this behaviour influence the performance of zinc cell under normal discharge conditions? This question can only be answered by making an on-the-spot investigation on cells assembled with the addition agent PA.

*Investigation of test cells assembled with PA*

Batches of R6P (AA-size, high power) mercury-free test cells were assembled in several cell factories with technology similar to that used for conventional mercury-containing cells, except that mercury-free pasted electrolyte paper was made on the production line of a pasted paper factory using PA instead of mercuric chloride for preparing the electrolyte paste.

Figures 2 and 3 give, respectively, the continuous high-rate discharge (on 3.9 Ω load) curve and the intermittent medium-rate discharge (on 10 Ω load) curve for mercury-free test cells in comparison with the correponding curves for conventional mercury-containing cells assembled under the same conditions. Both the high-rate and medium-rate discharge characteristics for the mercury-free test cell appear to be satisfactory.

In order to obtain a thorough understanding of the quality and technical performance of the mercury-free cell, a number of sample cells were sent to one of the national authorized dry-cell quality supervision and inspection stations for a comprehensive inspection according to Chinese national standard GB 7112-86. The results are listed in Table 3. The data confirmed that the mercury-free cells meet the national standard
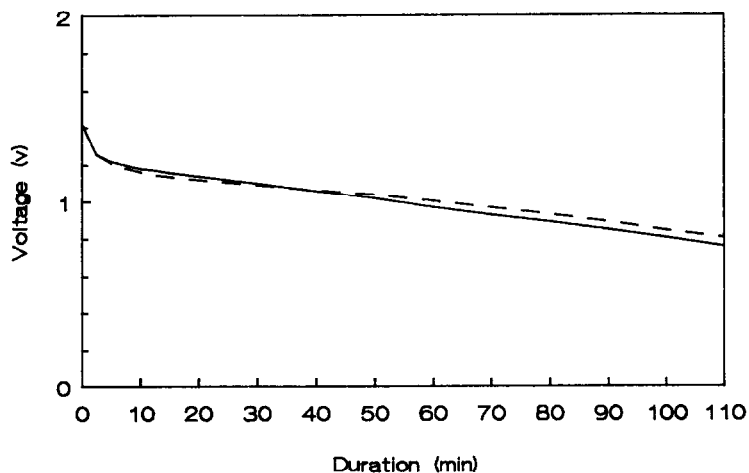
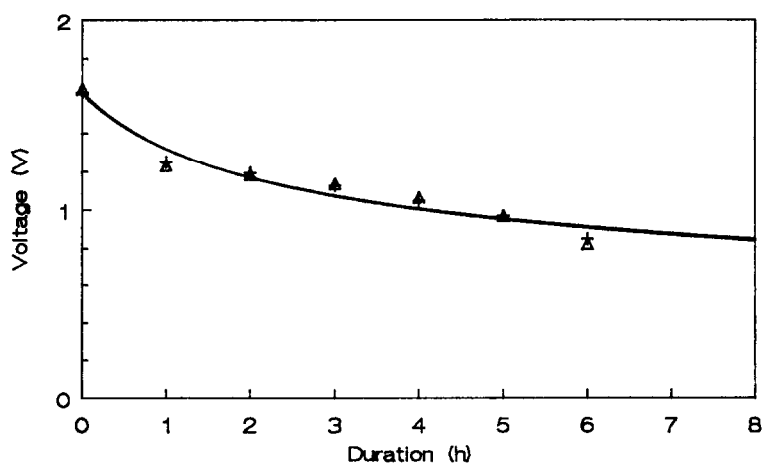Fig. 2. High-rate continuous discharge curves on 3.9 Ω load: (——) cell with mercury, and (– – –) cell with PA.



Fig. 3. Medium-rate, intermittent, discharge curve on 10 Ω load; 1 h/day: ( + ) cell with mercury, and (△) cell with PA. The cell voltage values are taken at the end of each 1 h discharge.

TABLE 3

Performance of R6P test cells

| Addition agent | Total discharge time (min) on 10 Ω load (60 min/day) | | | Total discharge time (h) on 75 Ω load (4 h/day) | | |
|---|---|---|---|---|---|---|
| | New | 6 month | 12 month | New | 6 month | 12 month |
| PA | 315 | 299 | 300 | 48 | 49 | 47 |
| HgCl$_2$ | 318 | 291 | 290 | 48 | 48 | 47 |

GB 7112-86 in all aspects with, in some cases, a performance better than that required by the standard. For example, the percentage maintenance of discharge capacity by the mercury-free cell is over 95% after storage for 12 months. Besides, no leakage or deformation was observed after a 3.9 $\Omega$ continuous discharge to 0.35 V.

*A.c. impedance spectra of test cells*

For an insight into the effect of polarization behaviour on the discharge capacity of the test cells, their a.c. impedance spectra, before and after discharge, were determined by M378 Software System V2.31 of EG&G PARC. The Nyquist plots of the results are given in Figs. 4 and 5.

The measured impedance spectra can be roughly considered as reflecting the behaviour of the zinc electrode. This is because the opposite $MnO_2$ electrode has a much higher surface area with a small charge-transfer resistance and a large double-layer capacitance and, therefore, has only a minor effect on the total impedance [4]. Referring to a rather simplified equivalent circuit of the zinc electrode given in Fig. 6, where $R_s$, $R_{ct}$, $Z_w$ and $C_{dl}$ represent electrolyte resistance, charge-transfer resistance, Warburg impedance and double-layer capacitance, respectively, a rough estimation of the $R_{ct}$ value of the zinc electrode can be made before and after discharge by curve fitting of the experimental impedance data.

It can be seen from Table 4 that in the presence of PA, the zinc electrode initially exhibits quite large value of $R_{ct}$, but after discharge it drops to a reasonable value compared with that observed in the presence of mercuric chloride. This probably
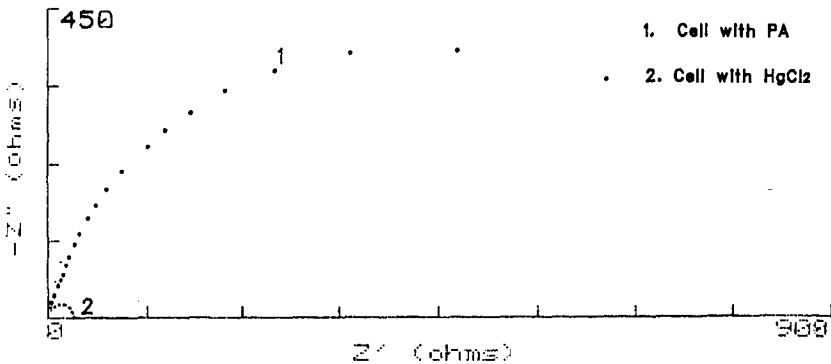


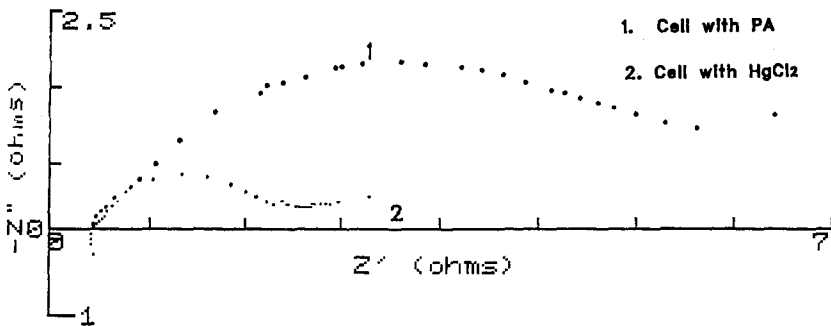Fig. 4. Nyquist impedance plots of test cells before discharge.



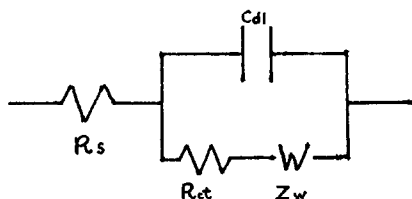Fig. 5. Nyquist impedance plots of test cells after discharge on 10 $\Omega$ for 4 h.

Fig. 6. Zinc electrode equivalent circuit.

TABLE 4

$R_{ct}$ value of zinc electrode estimated from impedance data

| Cell | $R_{ct}$ value | |
|---|---|---|
| | Before discharge | After discharge on 10 $\Omega$ for 4 h |
| With PA | 803 | 5.52 |
| With HgCl$_2$ | 27.2 | 1.69 |

implies that with PA in solution, there initially exists a passivation film on the surface of the zinc but that, upon discharge, it soon deteriorates and hence the latter process is not seriously affected.

## Summary

The nonpoisonous composite organic addition agent PA has been shown to be quite good as a corrosion inhibitor for zinc/manganese dry cells. Mercury-free sample cells assembled with this addition agent meet, or even surpass, all the requirements of the Chinese national standard GB 7112-86. This provides a solution to the serious mercury pollution problem. A patent has been applied for the PA addition agent. It is now ready for industrial application.

## Acknowledgements

## References

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