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Storage characteristics of mercury-free alkaline manganese batteries

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The amount and distribution of additive species in zinc alloy particles containing 0.025 wt % bismuth modified with 0.10 wt % indium for mercury-free alkaline manganese batteries were examined after storage at various discharging levels at 60 °C. The amount of hydrogen gas evolution due to the self-discharging reactions of zinc and the internal cell impedance were also evaluated. The amount of additive species in the zinc alloy particles was found to increase with increasing depth of discharge. Indium was homogeneously distributed on the surface even after partial discharge and also after storage for 1200 h at 60 °C. This behaviour is considered to contribute to the suppression of hydrogen gas evolution and increase in the internal cell impedance to the same level as when mercury is employed. As a result, mercury-free alkaline manganese batteries showed the same storage characteristics as conventional batteries containing mercury.

Keywords: *alkaline manganese battery*, *zinc*, *mercury-free*, *additives*, *hydrogen gas*

1. Introduction

Zinc is widely used as a negative active material for batteries (e.g., Leclanché batteries and alkaline manganese batteries) because it has a large energy capacity and economic advantages. Zinc has been added with mercury to suppress the evolution of hydrogen gas brought on by the self-discharge reactions of zinc and by the increase in internal cell impedance [1–14]. The use of mercury has become an environmental issue and attention has been focused on developing mercury-free batteries.

Miura *et al.* [9–11] and Yamakawa *et al.* [12] reported that the addition of indium, lead, bismuth, calcium or tin to a zinc particle has the effect of suppressing hydrogen gas evolution. Sato *et al.* [15] reported that the addition of indium oxide to zinc alloy powder is also effective. However, zinc alloy powder containing such additives has also been reported to increase the internal cell impedance, resulting in a decrease in the discharge capacity, especially at high rate discharge [11].

We have shown that zinc alloy powder containing 0.025 wt % bismuth modified with 0.10 wt % indium by a dry coating process, where the zinc alloy powder is mixed with indium metal in a nitrogen gas atmosphere, improves the electrochemical characteristics, including the internal cell impedance and the self-discharge to the same level as in the case of using mercury [6–8]. Consequently, we have succeeded in developing high-performance mercury-free alkaline manganese batteries by using zinc alloy powder.

In practical use, however, batteries are often stored in a state of partial discharge and at high temperature. Therefore, suppressing the deterioration of the storage characteristics under such conditions is very important. In this work, the amount of hydrogen gas evolution at partial discharge and the internal cell impedance under high-temperature storage were investigated.

2. Experimental details

2.1. *Sample preparation*

Preparation of the zinc alloy powder followed our past approach. A dry coating process [6] was used to modify the zinc alloy particle with indium.

In addition, zinc powder modified with mercury was prepared, as previously described [9].

2.2. *Qualitative and quantitative analysis*

Zinc alloy powder was dissolved in aqueous 30 wt % nitric acid and its composition was determined by atomic absorption analysis. Content changes of the additive species versus the depth of discharge were also determined by atomic absorption analysis.

Test cells were fabricated to be of the LR6 type with a diameter of 14 mm and a height of 50 mm, by using 10 g of manganese dioxide and 3.7 g of zinc alloy powder for the positive and negative electrodes, respectively. As a result, the capacity of the positive electrode was 1.2 times that of the negative electrode. These cells were discharged with a constant load of 3.9 Ω at 20 °C to various depths of discharge and the zinc alloy powder was removed. The zinc oxide in the zinc alloy powder was dissolved in aqueous 5 wt % ammonia and the additive species were analysed quantitatively by the same procedure.

The distribution of indium in the zinc alloy particles was observed with an electron probe X-ray microanalyser (EPMA) (model X-650, Hitachi Co., Ltd). The cross section of the particle was observed with a transmission electron microscope (TEM) (model H-9000UHR, Hitachi Co., Ltd). The indium composition was determined by energy dispersive X-ray spectroscopy (EDX) method which included a process of ion etching in argon gas.

2.3. *Measurement of hydrogen gas evolution*

The amount of hydrogen gas evolution under the various depths of discharge was measured by a previously described procedure [8]. Discharges of 25%, 50%, 75% and 100% the cell capacity was achieved using a constant load of 3.9 Ω at 20 °C. Storage for 480 h at a constant temperature of 60 ± 1 °C was made possible using a water bath.

2.4. *Measurement of the electrochemical characteristics*

The test cells were stored in an oven at 60 ± 1 °C. After 240, 480, 720, 960 and 1200 h storage, the internal cell impedance was measured using an LCR meter (Yokokawa Electric. Co., Ltd). In addition, discharge was carried out a constant load of 3.9 Ω at 20 °C to 0.9 V.

3. Results and discussion

3.1. *Influence of state of partial discharge on hydrogen gas evolution*

Figure 1 shows the amount of hydrogen gas evolution in test cells with zinc alloy powder containing 0.025 wt % bismuth modified with 0.10 wt % indium (Zn–In–Bi) and in cells with zinc powder modified with 0.15 wt % mercury (Zn–Hg) under various depths of discharge (DOD).

The amount of hydrogen evolution increased with increasing DOD. The Zn–In–Bi alloy powder exhibited almost the same behaviour as the Zn–Hg alloy powder.

Figure 2 shows the change in the amount of indium, bismuth and mercury in the zinc alloy particles under various DOD values. The amount increased with increasing DOD. This is because zinc with more negative redox potential than indium, bismuth and mercury [16] dissolves into the electrolyte as Zn(OH)$_4^{2-}$ during discharge [1]. Therefore, the concentrations of the indium, bismuth and mercury increase in the zinc alloy particles. Figure 3 shows a typical indium distribution on Zn–In–Bi alloy particles after 100% discharge. Even after discharge, the indium showed a homogeneous distribution on the surface.

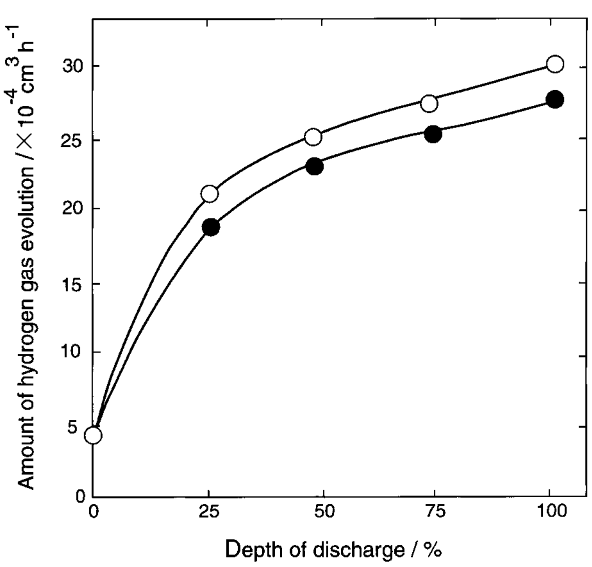

Fig. 1. Relation between the depth of discharge and the amount of hydrogen gas evolution in testing cells with Zn–In–Bi (○) and Zn–Hg (●).

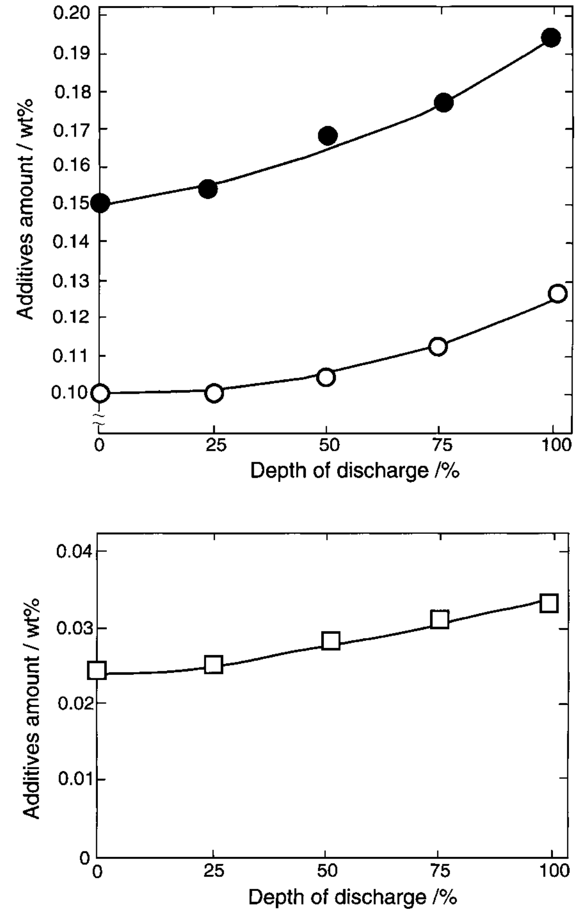

Fig. 2. Relation between the depth of discharge and the amount of In (○), Bi (□) and Hg (●) in Zn–In (0.10 wt %)–Bi (0.025 wt %) and Zn–Hg (0.15 wt %).

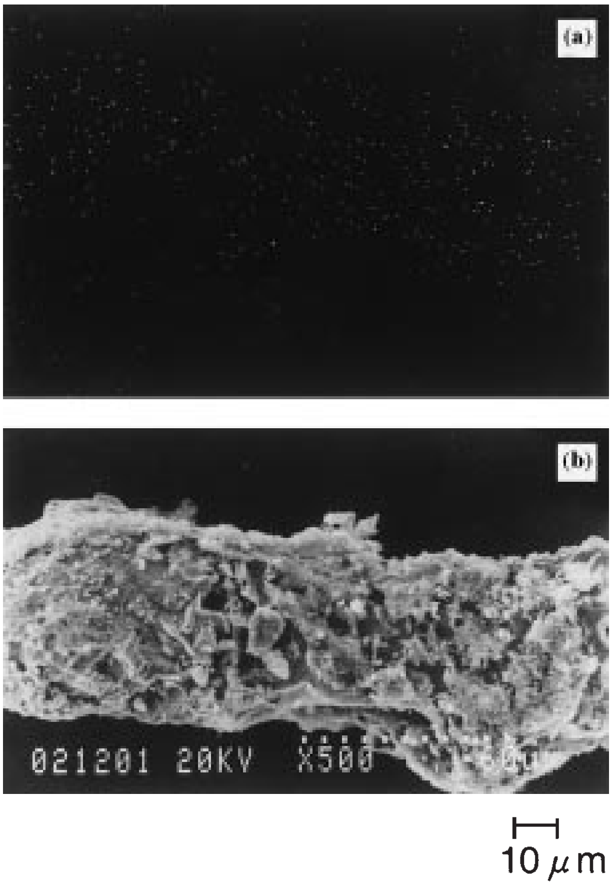

Fig. 3. X-ray image of In (a) and SEM micrograph (b) for a Zn–In (0.10 wt %)–Bi (0.025 wt %) alloy particle after discharge at 20 °C.

Yamasoto *et al.* [14] reported that the evolution of hydrogen at partial discharge can be suppressed by increasing the content of the additive species in a zinc alloy particle with increasing DOD. This hydrogen gas evolution suppression can be maintained despite the content change of the additive species; this applies even if the mercury content in a zinc alloy particle is reduced from 3.0 to 1.5 wt %. Sato *et al.* [15] reported that the addition of indium oxide to zinc alloy powder is effective in suppressing the evolution of hydrogen gas at partial discharge. This is because the surface is modified with indium metal due to reduction of indium oxide during discharge. The indium increases the hydrogen overvoltage on the surface.

The results obtained are in good agreement with those reported above. Consequently, the effect of Zn–In–Bi on suppression of the evolution of hydrogen under partial discharge was considered to be due to the increase additive species content with increasing DOD and to the homogeneous surface distribution of indium, even on 100% discharge.

3.2. *Influence of temperature on cell impedance*

The internal cell impedance is likely to increase strongly during high-temperature storage so that the cell cannot discharge at all. This is because zinc oxide forms on the zinc alloy particles causing increased contact resistance. The internal cell impedance increased with increasing storage time as shown in Fig. 4; both Zn–In–Bi alloy powder and Zn–Hg alloy powder exhibited almost the same result.

Figure 5 shows the discharge characteristics of testing cells in the initial state and after 1200 h storage at 60 °C. The results with the Zn–In–Bi alloy powder were almost the same as those with the Zn–Hg alloy powder even after high-temperature storage.

Figure 6 shows the distribution of indium after storage for 1200 h at 60 °C. The indium exhibited homogeneous surface distribution.

Figure 7 shows a TEM micrograph of the cross section of a Zn–In–Bi alloy particle after storage for 1200 h at 60 °C. Table 1 shows the content of the

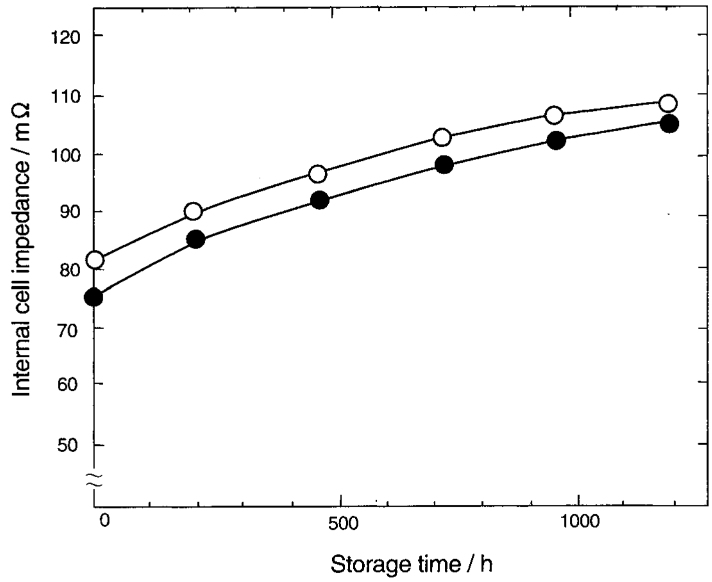

Fig. 4. Relation between the storage time at 60 °C and the internal cell impedance for Zn–In (0.10 wt %)–Bi (0.025 wt %) (○) and Zn–Hg (0.15 wt %) (●).

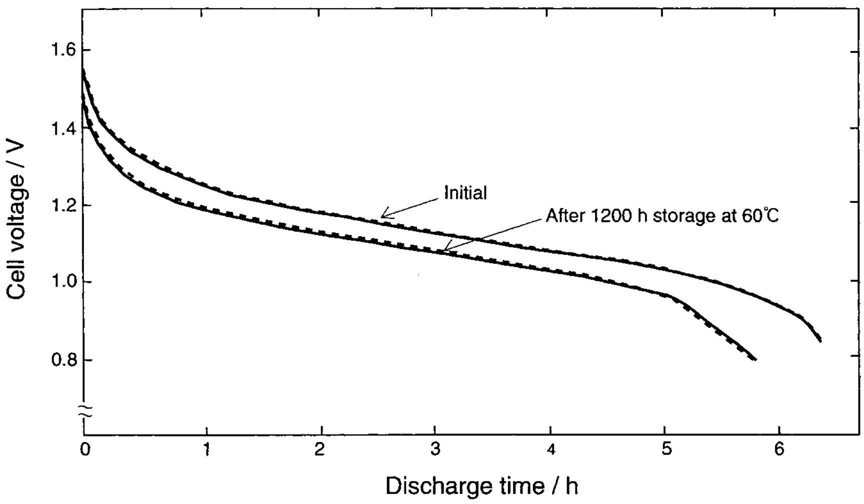

Fig. 5. Continuous discharge curves of Zn–In (0.10 wt %)–Bi (0.025 wt %) (—) and Zn–Hg (0.15 wt %) (- - -) under a constant load of 3.9 Ω at 20 °C.

additive species on the surface and in the bulk. The surface exhibited the same double-layer structure as that existing before storage [8]. The composition of the surface layer determined by the EDX method, did not change and no indium content was detected in the bulk.

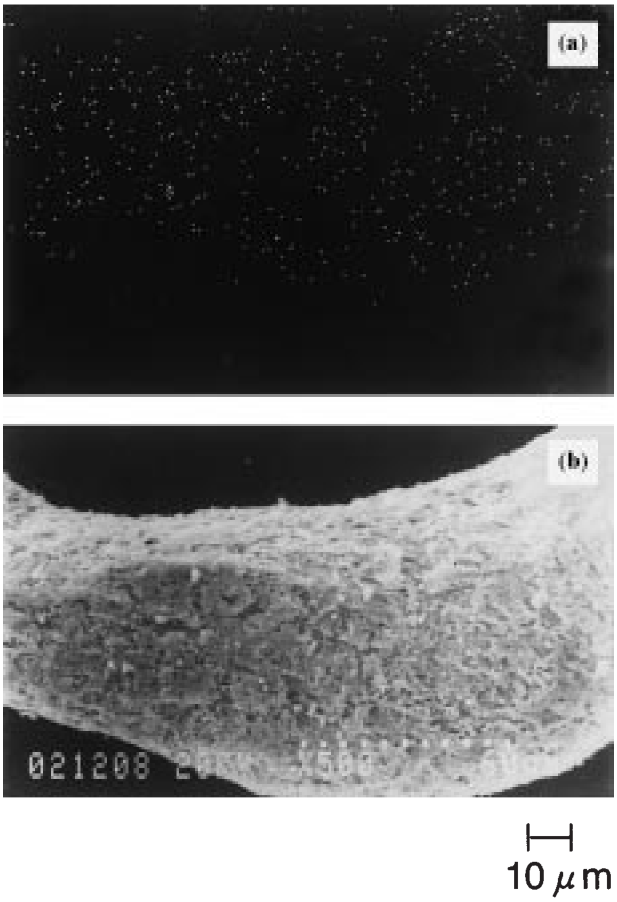

Fig. 6. X-ray image of In (a) and SEM micrograph (b) for a Zn–In (0.10 wt %)–Bi (0.025 wt %) alloy particle after storage for 1200 h at 60 °C.

It is known that mercury on zinc alloy powder diffuses into the bulk during storage, as reported by Koda *et al.* [17] and Miura *et al.* [10]. The increase in internal cell impedance with Zn–Hg alloy powder is considered to be due to mercury diffusion into the bulk and the self-discharge reactions of zinc.

By contrast, the effect of Zn–In–Bi alloy powder in suppressing the increase in internal cell impedance during high-temperature storage is considered to be due to homogeneous surface distribution of indium. This is because the conductive matrix between particles is maintained by the indium [6]. Hence, Zn–In–Bi alloy powder exhibits the same storage characteristics as Zn–Hg alloy powder.

4. Conclusions

The content change and the distribution of additive species in Zn–In–Bi alloy powder were examined to investigate their influence on the storage characteristics of mercury-free alkaline manganese batteries.

The results suggest:

(i) The amount of bismuth in the Zn–In–Bi alloy particles increases as DOD increases and indium distribution on the surface remains homogeneous. This helps maintain the hydrogen overvoltage at its initial level during the entire discharge.

(ii) After storage at 60 °C, indium distribution on the surface of the Zn–In–Bi alloy particles also remains homogeneous. This contributes to maintaining conductivity between the alloy particles.

(iii) The self-discharge characteristics after partial discharge and the discharge characteristics after high-temperature storage can be maintained at the same level as when employing zinc powder containing 0.15 wt % mercury as a negative electrode.

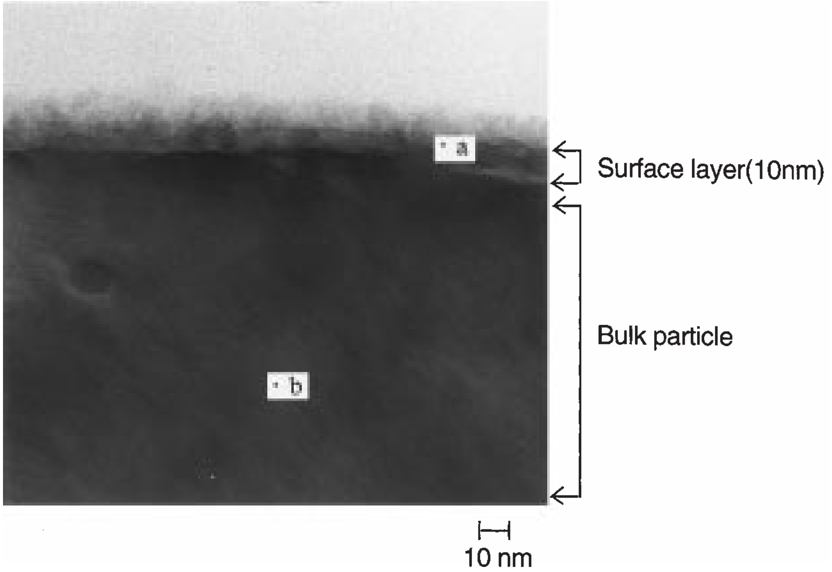

Fig. 7. TEM micrograph of the cross section of a Zn–In (0.10 wt %)–Bi (0.025 wt %) alloy particle after storage for 1200 h at 60 °C. (a) and (b) are analysed points by EDX.

Table 1. Content of In and Bi on the surface layer and in the bulk of a Zn–In (0.10 wt %)–Bi (0.025 wt %) alloy particle

Additives	*Content of In and Bi*/wt %			
	Surface layer		*Bulk*	
	Initial	*After 1200 h storage at 60 °C*	*Initial*	*After 1200 h storage at 60 °C*
In	86	87	–	–
Bi	14	13	0.01	0.01

References

[1] K. V. Kordesch, 'Batteries', Vol. 1 (Marcel Dekker, New York, 1974), p. 324.

[2] T. D. Dirkse and R. Timmer, *J. Electrochem. Soc.* **116** (1969) 162.

[3] M. Meeus, Y. Strauven and L. Groothhaert, Extended Abstracts 15th International Power Sources Symposium (1986), p. 1.

[4] L. Z. Vorkapic, D. M. Drazic and A. R. Despic, *J. Electrochem. Soc.* **121** (1974) 1385.

[5] M. Takahashi, Research report for zinc electrode in alkaline solution (1985), The Electrochemical Society of Japan (1986), pp. 1–12.

[6] M. Yano, M. Nogami, I. Yonezu, K. Nishio, Y. Akai and M. Kurimura, *Denki Kagaku* **65** (1997) 154.

[7] M. Yano, Y. Akai, M. Kurimura, S. Fujitani and K. Nishio, *ibid.* **65** (1997) 650.

[8] M. Yano, Y. Akai, M. Kurimura, S. Fujitani and K. Nishio, *J. Power Sources*, **74** (1998) 129.

[9] A. Miura, K. Takada, R. Okazaki, H. Ogawa, T. Uemura, Y. Nakamura and N. Kasahara, *Denki Kagaku* **57** (1989) 459.

[10] A. Miura, K. Takada, R. Okazaki and H. Ogawa, T. Uemura, Y. Nakamura and N. Kasahara, Extended Abstracts 55th Electrochemical Society of Japan (1988), p.16.

[11] A. Miura, Extended Abstracts Third colloidal and surface chemistry symposium in Japan (1996), p. 66.

[12] K. Yamakawa, H. Tsubakino and K. Kawanishi, *Denki Kagaku* **59** (1991) 325.

[13] N. Kasahara, T. Uemura and A. Okada, Extended Abstracts 27th Battery Symposium in Japan (1986), p. 7.

[14] T. Yamasoto, T. Uemura, M. Nakamura, N. Kasahara, A. Miura, K. Takada, R. Okazaki and H. Ogawa, Extended Abstracts 28th Battery Symposium in Japan (1987), p. 37.

[15] Y. Sato, M. Takahashi, H. Akakura, K. Kobayakawa, N. Chiba and K. Yoshida, *J. Power Sources* **38** (1992) 317.

[16] M, Pourbaix, 'Atlas of Electrochemical Equilibrium', National Association of corrosion Engineers, Houston, TX (1962).

[17] S. Koda and H. Yoshinaga, *J. Inst. of Metals* **97** (1969) 125.