



# Effect of additives in zinc alloy powder on suppressing hydrogen evolution

M. Yano <sup>a,\*</sup>, S. Fujitani <sup>a</sup>, K. Nishio <sup>a</sup>, Y. Akai <sup>b</sup>, M. Kurimura <sup>b</sup>

<sup>a</sup> *New Materials Research Center, Sanyo Electric Co. Ltd., 1-18-13, Hashiridani, Hirakata, Osaka 573, Japan*

<sup>b</sup> *Sanyo Excell Co. Ltd., 28, Oota, Iwami-cho, Iwami-gun, Tottori 680, Japan*

Received 1 December 1997; accepted 19 January 1998

## Abstract

The addition of 0.025 wt.% bismuth and 0.025 wt.% lead to zinc particles modified with 0.10 wt.% indium by a dry-coating process, or a conventional wet-coating process is examined to clarify the effect on suppressing hydrogen gas evolution due to the self-discharging reactions of zinc in alkaline manganese batteries. The dry-coating process of indium metal modifies the zinc alloy powder, such that oxidation of the powder is less, and hydrogen-gas evolution is suppressed more effectively than in the case of the conventional wet-coating process. In the dry-coating process, the bismuth diffuses into the surface to be alloyed with the indium. As a result, zinc alloy powder containing 0.025 wt.% bismuth modified with 0.10 wt.% indium (Zn–In–Bi) by the dry-coating process suppresses hydrogen gas evolution on a competitive level with zinc powder containing 0.15 wt.% mercury (Zn–Hg). © 1998 Elsevier Science S.A. All rights reserved.

*Keywords:* Alkaline manganese battery; Zinc alloy; Mercury-free; Hydrogen evolution; Bismuth; Indium

## 1. Introduction

Alkaline manganese batteries are powerful primary batteries and are used widely to operate portable devices, such as cameras and portable cassette players, which require a lot of electric power. They have a twofold advantage in specific energy over classical Leclanche batteries. For a long time, mercury has been employed in alkaline manganese batteries, since it is the most useful additive to the zinc anode material for suppressing hydrogen gas evolution that is caused by self-discharge reactions [1–10]. Due to environmental concerns, however, a much recent research has been carried out to diminish the content of mercury in the zinc powder.

Zinc has a more negative redox potential than hydrogen and thus promotes hydrogen gas evolution. This condition makes it difficult for batteries to be sealed. Consequently, a considerable number of attempts has been made to substitute mercury with other additives [7–14]. Yamakawa et al. [8] reported that adding multiple components, viz., indium, lead, bismuth and tin, to zinc particles is effective in suppressing hydrogen gas evolution. Miura et al. [10]

reported that indium, bismuth and calcium with an organic inhibitor also suppresses hydrogen gas evolution.

It has been reported, however, that zinc alloy powder with additives increases the cell impedance. This causes a drop in the discharge potential, especially for high-rate discharges [10]. We have shown that modifying zinc particles with indium metal can decrease the cell impedance to the same level as that obtained with Zn–Hg [6]. We have also shown that adding bismuth can effectively suppresses hydrogen gas evolution [7]. Consequently, this has enabled us to develop a high-performance, mercury-free, alkaline manganese battery.

In this paper, the structure of zinc particles alloyed with bismuth and lead [12–15] and modified with indium are investigated to clarify their effect on suppressing hydrogen gas evolution. In addition, the influence of an indium modification process on the structure and the oxidation behaviour of zinc particles is investigated.

## 2. Experimental

### 2.1. Sample preparation

Zinc alloy powder samples containing bismuth and lead were prepared by a gas-atomization process with com-

\* Corresponding author.

pressed air. The samples were sieved between 20 and 200 mesh. A dry-coating process [5] or a wet-coating process [15] was used to modify the zinc alloy surface with indium. In the dry-coating process, the zinc alloy powder was mixed thoroughly with indium metal (99.99%) in a nitrogen gas atmosphere at 180°C. During the mixing, the indium (m.p. 156.4°C) becomes melted and covers the zinc alloy particles.

In the wet-coating process, the zinc alloy powder was mixed in 5 wt.% acetic acid aqueous solution. It dissolved the indium nitrate. The powder was washed with distilled water and dried under 90 Pa at 60°C. The indium nitrate contained mostly iron and lead as impurities (< 0.005 wt.%).

Additionally, zinc powder modified with mercury was prepared using the procedure of Miura et al. [9]. The zinc powder was mixed with mercury in 5 wt.% potassium hydroxide aqueous solution and was treated by the same procedure.

## 2.2. Qualitative and quantitative analysis

Zinc alloy powder was dissolved in 30 wt.% nitric acid aqueous solution and the composition was determined by atomic absorption spectrometry.

To determine the content of zinc oxide, the procedure of Kasahara et al. was employed [14]. The zinc oxide was dissolved into 5 wt.% ammonia aqueous solution and was analyzed by atomic absorption spectrometry.

The distribution of additive species in the zinc alloy particles was determined by secondary ion mass spectrometry (SIMS) with IMS-4F (CAMECA Co., Ltd.) using a first ion source of O<sub>2</sub> with an ion voltage of 8 kV and an ion current of 65 nA.

The cross-section of the zinc alloy particles was observed with a transmission electron microscope (TEM), H-9000UHR (Hitachi Co., Ltd.). The indium content was determined by energy dispersive X-ray spectroscopy (EDX method) with ion etching.

## 2.3. Measurement of hydrogen gas evolution

LR6 type testing cells with a diameter of 14 mm and a height of 50 mm were employed to measure the amount of hydrogen gas evolution. These cells used 10 g of manganese dioxide and 3.7 g of the zinc alloy as the positive and negative electrodes, respectively. The capacity of the positive electrode was 1.2 times as large as that of the negative electrode.

The amount of hydrogen gas evolution in the testing cells was evaluated by a volumetric method. After discharging them with a constant load of 3.9 Ω up to a capacity of about 20%, a part of the negative electrode side was opened. Then, the testing cells were placed on the bottom of a glass cell of 50 cm<sup>3</sup>, with a calibrated pipet as shown in Fig. 1. The glass cell was filled with liquid

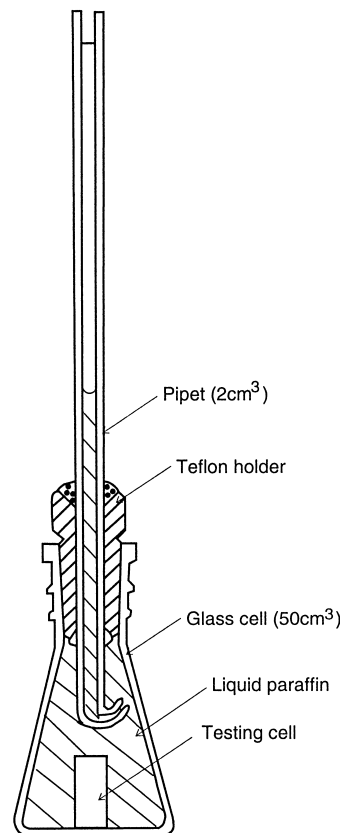


Fig. 1. Apparatus for measuring hydrogen gas evolution.

paraffin and sealed. The apparatus was kept at a constant temperature of  $60 \pm 1^\circ\text{C}$  in a water bath. After 480 h, the amount of hydrogen gas evolution was determined by the rise of the liquid paraffin level in the pipet.

## 2.4. Measurement of self-discharging characteristics

The testing cells were kept at  $60 \pm 1^\circ\text{C}$  in an oven. After 480 h, they were discharged with a constant load of 3.9 Ω at 20°C down to 0.9 V.

## 3. Results and discussion

Table 1 shows the amount of hydrogen gas evolution in the testing cells. The testing cells with the zinc alloy powder containing bismuth and those containing lead showed almost the same value. They had values that were approximately four times larger than cells with mercury addition.

The zinc alloy powder samples modified with indium exhibited a remarkable effect in suppressing the amount of hydrogen gas evolution. In particular, the combination of bismuth addition and indium modification by the dry-coating process reduced the amount of hydrogen gas evolution

Table 1  
Effects of additives and the In modifying process on hydrogen gas evolution

In modifying process	Amount of hydrogen gas evolution ( $\text{cm}^3 \text{h}^{-1}$ )		
	Zn–Pb(0.025 wt.%)	Zn–Bi(0.025 wt.%)	Zn–Hg(0.15 wt.%)
No modification	$9.4 \times 10^{-3}$	$8.3 \times 10^{-3}$	$2.0 \times 10^{-3}$
Wet-coating process	–	$3.3 \times 10^{-3}$	–
Dry-coating process	$5.2 \times 10^{-3}$	$2.1 \times 10^{-3}$	–

to the same level as the case when mercury was employed. On the other hand, the wet-coating process with indium increased the amount of hydrogen gas evolution up to 1.6 times as that produced with the dry-coating process. Thus, the Zn–In–Bi in the dry-coating process suppressed hydrogen gas evolution the most effectively when using mercury-free zinc alloy powder species.

Fig. 2 shows the distributions of indium and bismuth in a Zn–In–Bi particle for the dry-coating process. Fig. 3 shows distributions of indium and lead for the same particle containing 0.025 wt.% lead modified with 0.10 wt.% indium by the dry-coating process.

It has been reported [8] that bismuth is distributed homogeneously in the bulk when indium modification is not employed. In this work, however, it is observed that bismuth partially diffuses into the indium of the surface layer (see Fig. 2). By contrast, lead is found to be distributed heterogeneously in the bulk, as reported by Yamakawa et al. [8], and not diffused into the surface layer.

According to the binary alloy phase diagrams for Bi–In and Bi–Zn, bismuth forms intermetallic compounds with indium, viz.,  $\text{BiIn}_2$  and  $\text{Bi}_5\text{In}_3$ , but does not form any compounds with zinc [16]. Lead does not form any compounds with either indium or zinc [16]. Therefore, the

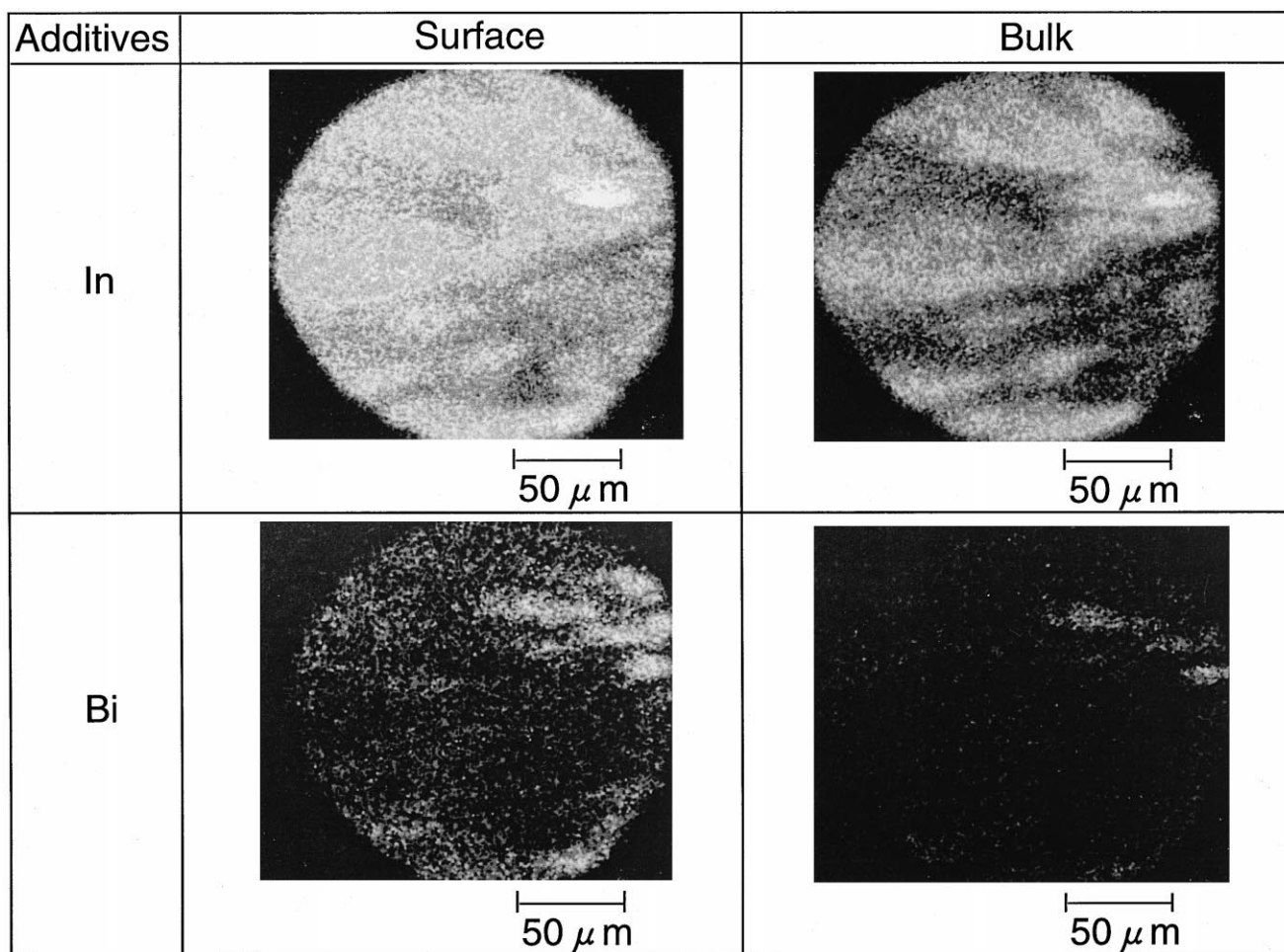


Fig. 2. SIMS images of In and Bi on the surface of a Zn–Bi (0.025 wt.%) alloy particle modified with 0.10 wt.% In by the dry-coating process.

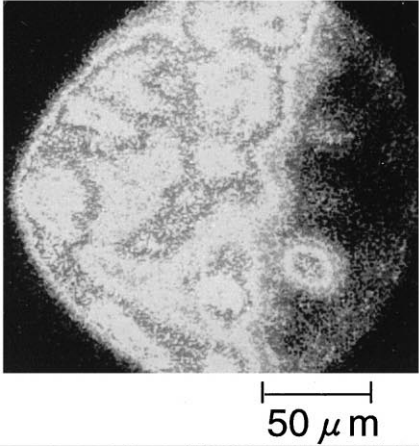
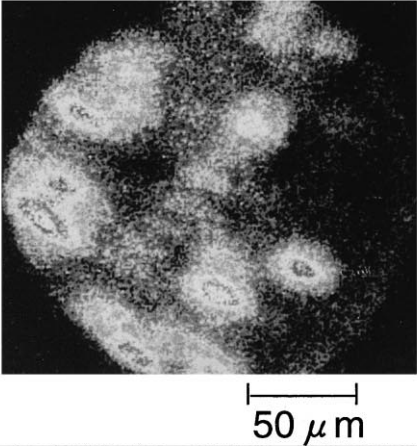
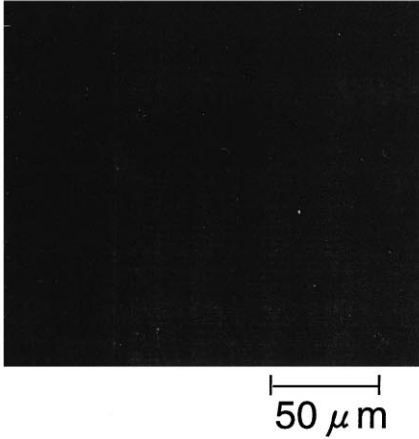
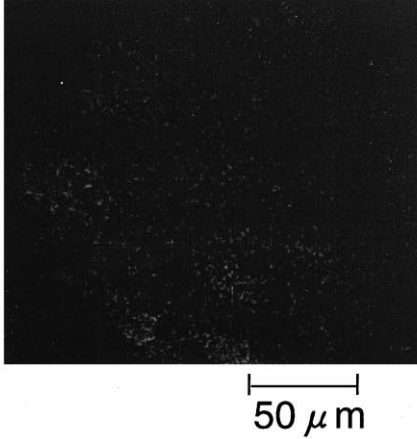
Additives	Surface	Bulk
In		
Pb		

Fig. 3. SIMS images of In and Pb on surface of a Zn–Pb (0.025 wt.%) alloy particle modified with 0.10 wt.% In by the dry-coating process.

diffusion of bismuth into the surface layer can be attributed to the strong binding energy between bismuth and indium [7]. Fig. 4 shows a TEM micrograph of the cross-section of a Zn–In–Bi particle produced by the dry-coating process. The surface of the particle has a double-layered structure with a thickness of 10 nm. The composition of the surface layer, as determined by the EDX method, is 86 wt.% indium and 14 wt.% bismuth.

Fig. 5 shows the distributions of indium and bismuth in a particle by the wet-coating process. The bismuth distributes homogeneously in the bulk. This behaviour is in good agreement with the results reported by Yamakawa et al. [8]. With this wet-coating process, however, the bismuth in the bulk did not diffuse into the surface layer. Therefore, the diffusion of bismuth occurs during the mixing process at a high temperature brought about by the dry-coating process.

It has been reported [6,17] that the amount of hydrogen gas evolution increases with the content of zinc oxide in zinc alloys. The content of zinc oxide in the Zn–In–Bi alloy in the dry-coating process is 0.10 wt.%, and that in the wet-coating process is 0.25 wt.%. This shows that the

dry-coating process is more effective in suppressing hydrogen gas evolution than the wet-coating process, as shown in Table 1.

Consequently, it is considered that for Zn–In–Bi alloy prepared by the dry-coating process, the suppression of

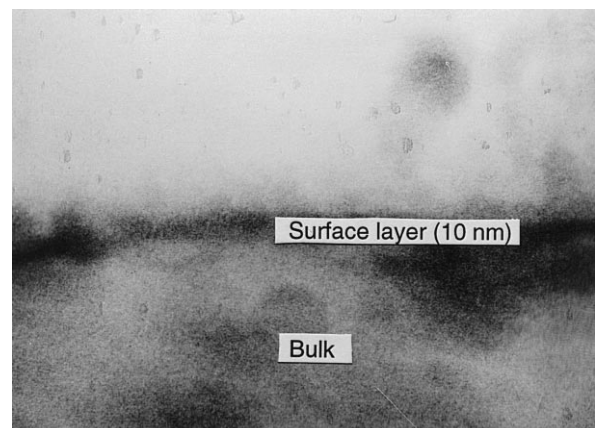


Fig. 4. TEM micrograph of cross-section of a Zn–Bi (0.025 wt.%) alloy particle modified with 0.10 wt.% In by the dry-coating process.

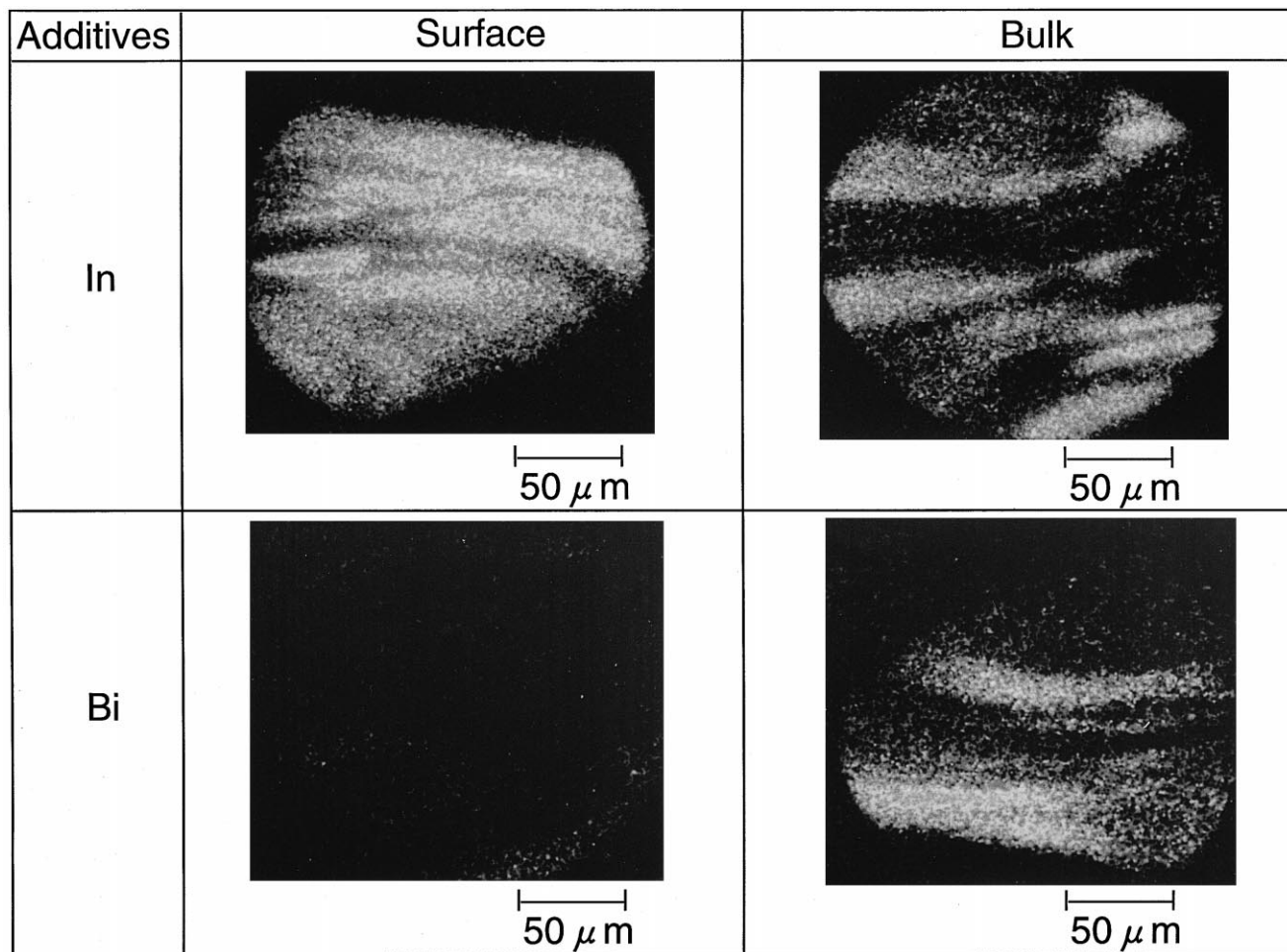


Fig. 5. SIMS images of In and Bi on the surface of a Zn–Bi (0.025 wt.%) alloy particle modified with 0.10 wt.% In by the wet-coating process.

hydrogen gas evolution is attributable to an increase in the hydrogen overvoltage on the zinc surface caused by indium–bismuth alloy formation and a low zinc oxide content.

The discharge characteristics of the test cells are shown in Fig. 6. The test cells using Zn–In–Bi alloy prepared by the dry-coating process yield a discharge capacity of 1700 mA h despite pre- and post-storage for 480 h at 60°C. This

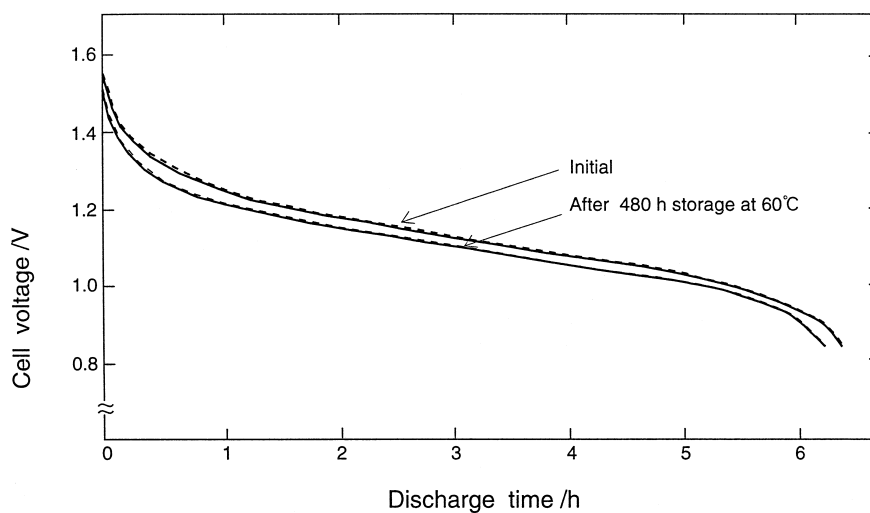


Fig. 6. Continuous discharge curves of (—) Zn–In(0.10 wt.%)–Bi(0.025 wt.%) and (---) Zn–Hg(0.15 wt.%) under a constant load of 3.9 Ω at 20°C.

performance is competitive with that of conventional cells with a zinc negative electrode that contains 0.15 wt.% mercury.

#### 4. Conclusions

The particle structure and the content of zinc oxide in zinc alloy powder containing bismuth and lead modified with indium by a dry- or wet-coating process are examined to clarify the effect of the powder on suppressing hydrogen gas evolution due to the self-discharging reactions of zinc in LR6 type alkaline manganese batteries. The following conclusions are reached.

(i) Hydrogen gas evolution is suppressed by the combination of bismuth addition and modification with indium by the dry-coating process. This suppression is attributable to a large hydrogen overvoltage due to the formation of an indium and bismuth phase and to a reduced formation of oxide.

(ii) Zn–In–Bi alloy powder prepared by the dry-coating process exhibits the same properties in suppressing hydrogen gas evolution as Zn–Hg alloy powder with 0.15 wt.% mercury.

(iii) After long-term storage (480 h) at 60°C, the discharge characteristics of the mercury-free zinc alloy powder are competitive with conventional zinc powder modified with 0.15 wt.% mercury.

#### References

- [1] K.V. Kordesch, Batteries, Vol. 1, Marcel Dekker, New York, 1974, p. 324.
- [2] T.D. Dirkse, R. Timmer, J. Electrochem. Soc. 116 (1969) 162.
- [3] M. Meeus, Y. Strauven, L. Groothaert, Extended Abstracts of the 15th International Power Sources Symposium, 1986, p. 1.
- [4] L.Z. Vorkapic, D.M. Dracic, A.R. Despic, J. Electrochem. Soc. 121 (1974) 1385.
- [5] M. Takahashi, Research report for zinc electrode in alkaline solution (1985), Electrochem. Soc. Jpn. (1986) 1–12.
- [6] M. Yano, M. Nogami, I. Yonezu, K. Nishio, Y. Akai, M. Kurimura, Denki Kagaku 65 (1997) 154.
- [7] M. Yano, Y. Akai, M. Kurimura, S. Fujitani, K. Nishio, Denki Kagaku 65 (1997) 650.
- [8] K. Yamakawa, H. Tsubakino, K. Kawanishi, Denki Kagaku 59 (1991) 325.
- [9] A. Miura, K. Takada, R. Okazaki, H. Ogawa, T. Uemura, Y. Nakamura, N. Kasahara, Denki Kagaku 57 (1989) 459.
- [10] A. Miura, Extended Abstracts of the Third Colloidal and Surface Chemistry Symposium in Japan, 1996, p. 66.
- [11] F. Mansfield, S. Gilman, J. Electrochem. Soc. 117 (1970) 1328.
- [12] T.S. Lee, J. Electrochem. Soc. 120 (1973) 707.
- [13] T.S. Lee, J. Electrochem. Soc. 122 (1975) 171.
- [14] N. Kasahara, T. Uemura, A. Okada, Extended Abstracts of the 27th Battery Symposium in Japan, 1986, p. 7.
- [15] H. Ikeda, S. Nakaido, M. Yano, Extended Abstr. Electrochem. Soc. 84 (1984) 231.
- [16] T.B. Massliski, Binary Alloy Phase Diagrams, American Society for Metals, 1986.
- [17] Y. Sato, M. Takahashi, H. Akakura, K. Kobayakawa, N. Chiba, K. Yoshida, J. Power Sources 38 (1992) 317.