

## Gas evolution behavior of Zn alloy powder in KOH solution

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### Abstract

To reduce the mercury content in an alkaline manganese battery, a Zn alloy is used. In the absence or presence of small amounts of mercury, hydrogen gas evolution from the Zn alloy in KOH solution was found to be accelerated by the addition of ZnO or Zn(OH)<sub>2</sub> which is the discharge product of Zn. Partly discharged Zn alloy also evolved hydrogen more vigorously compared to undischarged Zn alloy. An optimum quantity of In<sub>2</sub>O<sub>3</sub> added to the Zn reduced hydrogen evolution. Indium metal deposited on Zn by the reduction of In<sub>2</sub>O<sub>3</sub> by Zn will suppress hydrogen evolution because of its large overpotential for the hydrogen evolution reaction. Indium metal was detected by X-ray diffraction analysis of the Zn alloy containing In<sub>2</sub>O<sub>3</sub>.

### Introduction

The alkaline manganese battery is widely used because of its superior performance at higher current drains and at lower temperatures compared to either Leclanché or zinc chloride batteries. In order to increase its activity, the zinc anode is a high surface area, amalgamated zinc powder, suspended in a gelling agent such as carboxymethylcellulose. Several years ago, the zinc powder contained 9% or higher concentrations of mercury by weight to prevent Zn corrosion, but in Japan no mercury is added now. A great deal of effort has been put into the project to reduce the mercury content because of environmental pollution [1]. In place of mercury, many sorts of additives to Zn have been tested [2-4] to reduce the gas evolution from Zn in concentrated KOH solution. A zinc alloy containing Pb, In and Al is used as the anode active material in the alkaline manganese battery [4].

Although the Zn alloy containing Pb, In and Al showed good anti-corrosive properties nearly equal to the amalgamated Zn in the undischarged or initially discharged

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state, it was found that the partly discharged Zn alloy vigorously evolved hydrogen gas in the absence of mercury. So, the gas evolution rate of the Zn alloy in various discharged states was measured in the absence and the presence of mercury. The effect of  $\text{In}_2\text{O}_3$  addition to Zn to reduce the gas evolution rate was also studied.

## Experimental

The gas evolution speed was measured using an apparatus consisting of a sealed glass tube of about  $18 \text{ cm}^3$  to which a calibrated pipette was attached as shown in Fig. 1. Two ml of 40% KOH solution and 0.2 g of Zn gel were put in the tube and then it was filled with liquid paraffin. The entire assembly except for the pipette was immersed in a liquid constant temperature bath at  $60 \pm 0.1 \text{ }^\circ\text{C}$ . As hydrogen was evolved, liquid paraffin was forced into the pipette. Consequently, the rise in the paraffin level in the pipette was a measure of the rate at which hydrogen was evolved. Three types of Zn alloy supplied by Toho Zinc Co. were tested. The compositions of these zincs are given in Table 1. Zinc gel was prepared by mixing 10 g Zn powder, 0.1 g gelling agent and 4.9 ml 40% KOH solution saturated with ZnO and ZnO powder, if necessary. In some cases, this Zn gel was discharged at a constant current to various depths of discharge and then placed in the gas measuring tube to measure the gas evolution rate from the discharged state of Zn. To prevent gas evolution,  $\text{In}_2\text{O}_3$  was added to the Zn gel and gas evolution rate was then tested.

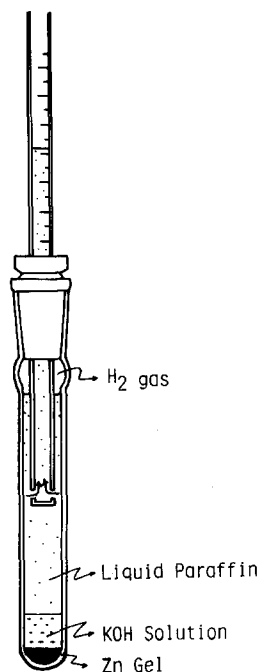


Fig. 1. Schematic illustration of the experimental cell.

TABLE 1

Composition of Zn alloy powder (wt.%)<sup>a</sup>

	1	2	3
Hg	0	1.000	2.000
Ga	0.011	0.010	0.009
In	0.025	0.041	0.043
Pb	0.055	0.050	0.049
Al	0.020	0.020	0.021

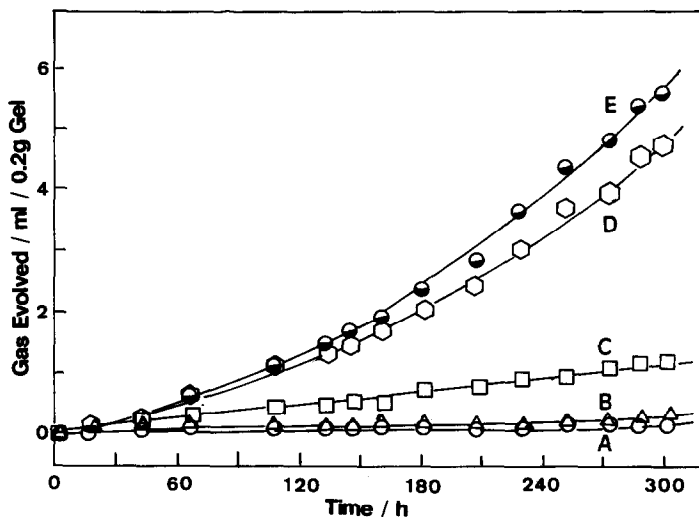
<sup>a</sup>The balance is Zn.

Fig. 2. Gas evolution behavior from alloy (No. 1) gel at 60 °C at various discharge depths after discharge at 30 mA of 0.2 g gel.

### Results and discussion

Figure 2 shows the gas evolution behavior from Zn alloy (No. 1) gel after various depths of discharge. Discharge was carried out for 0.2 g of Zn gel at 30 mA. If the Zn alloy is virgin and not discharged, it exhibits very good anticorrosive effects and evolves almost no hydrogen for over twelve days (curve A). However, if it was discharged, hydrogen began to evolve. The deeper the depth of discharge, the larger the volume of gas evolved.

If the Zn alloy was amalgamated, gas evolution was remarkably suppressed (Fig. 3). Even in that case, however, the gas evolution rate increased as the depth of discharge progressed. Amalgamated Zn with 2% Hg (No. 3) evolved 12  $\mu$ l per day per 0.2 g Zn gel of gas, if it was discharged to about 70% depth of discharge. These results suggest the reaction products accelerate gas evolution from the Zn gel. In Fig. 4, gas evolution rates from 50% discharged Zn gel, which was obtained by discharging at various discharge currents, are shown. This Figure indicates that the gas evolution rate increases with increasing current density even at the same depth

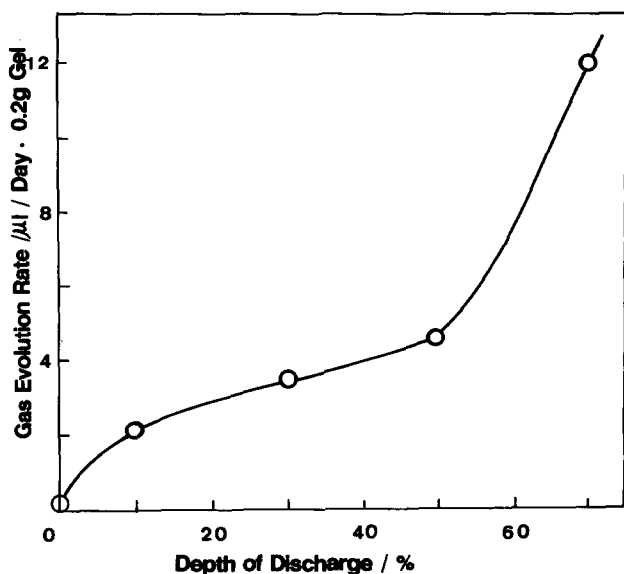


Fig. 3. Gas evolution rate from Zn alloy with 2% Hg (No. 3) at 60 °C at various discharge depths after discharge at 30 mA for 0.2 g gel.

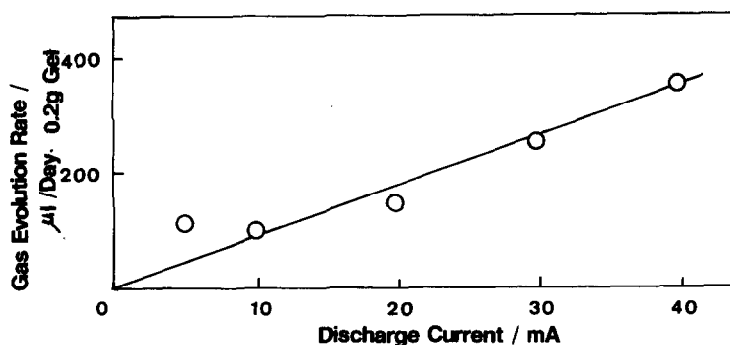


Fig. 4. Gas evolution rate from 50% discharged Zn alloy (No. 1) at various currents for 0.2 g gel at 60 °C.

of discharge, i.e. the residual amount of Zn metal may be equal. With increasing discharge current density, the concentration of the oxidation product,  $[\text{Zn}(\text{OH})_4]^{2-}$ , will increase in the solution close to the electrode surface (Zn powder surface) for a constant time, which causes the amount of final products such as ZnO and/or  $\text{Zn}(\text{OH})_2$  on the electrode surface to increase. If the electrolytic oxidation product, ZnO or  $\text{Zn}(\text{OH})_2$ , accelerates the gas evolution rate from Zn powder, these results can be understood, i.e. the larger the discharge current at a constant discharge depth, the larger the amount of gas evolved. If so, the addition of a chemical reagent, ZnO, to Zn powder will accelerate the gas evolution rate. This was confirmed for the Zn alloy with (Nos. 2 and 3) and without (No. 1, Fig. 5) Hg by adding ZnO powder. For amalgamated Zn, ZnO formed by discharge or added ZnO powder may hinder

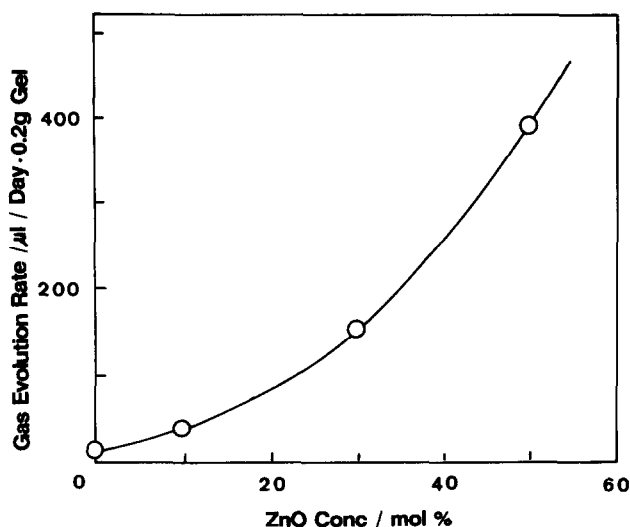
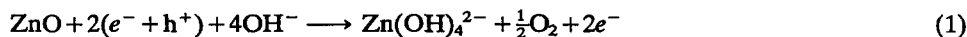


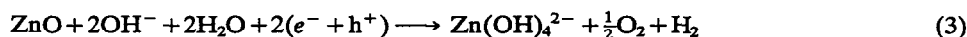
Fig. 5. Gas evolution rate from Zn alloy (No. 1) containing various concentrations of ZnO at 60 °C.

the mercury diffusion into the inside of the Zn metal phase, which decreases the Hg effect on Zn corrosion and causes an increasing gas evolution rate. This was disproved by the fact that the gas evolution rate for the Zn alloy without amalgamation also increased with increasing concentration of ZnO (Fig. 5). The addition of  $\text{Zn(OH)}_2$  to Zn gel also accelerated the gas evolution rate. In place of ZnO, MgO or CaO powder addition into Zn alloy with or without Hg showed no accelerating effect on the gas evolution rate, i.e. gas evolution was almost not detected for 480 h.

ZnO is a well known photo-semiconductor and is decomposed by the irradiation of light to evolve hydrogen and oxygen [5]:

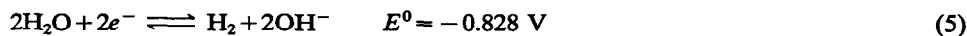


where  $h^+$  is a positive hole produced by photo-irradiation. The total reaction is:

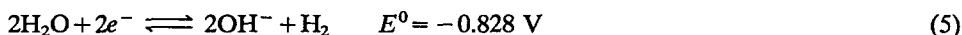


Since the gas evolution experiment was carried out in a well-lit room, it was feared that reaction (3) may occur and accelerate gas evolution in the presence of ZnO in the Zn gel. To confirm this light effect, the gas evolution test was carried out in the dark. However, the gas evolution rate in the dark and under daylight conditions was almost the same and the light effect was not detectable in our case.

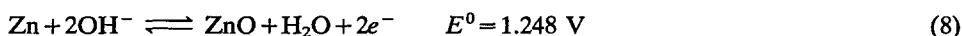
The presence of zincate ions,  $\text{Zn(OH)}_4^{2-}$ , in the KOH solution reduces the rate of hydrogen evolution from Zn [6], therefore, ZnO is added to the alkaline manganese battery. When ZnO is dissolved in KOH solution, reaction (4) proceeds, the activity of the water is lowered and this should decrease the rate of reaction (5) [7]



Our experiments showed that excess of ZnO or Zn(OH)<sub>2</sub> present as a solid in Zn accelerates gas evolution. This acceleration effect was postulated as follows. Hydrogen evolution due to Zn dissolution will proceed according to the reactions:



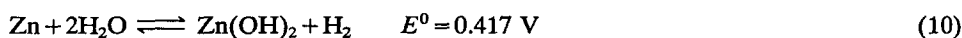
The standard potential,  $E^0$ , for reaction (8) obtained by combining reactions (6) and (7) is +1.248 V [7].



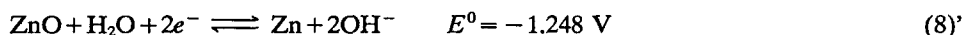
Combining reactions (5) and (8) gives:



If the corrosion product is Zn(OH)<sub>2</sub>, the reaction (10) holds [7]:



For both overall reactions (9) and (10),  $E^0$  is positive and the driving force, energetically, is favorable. If Zn contacts with the ZnO reaction product, some electrons liberated from Zn by reaction (6), might reduce ZnO, in place of the reduction of water (reaction (5)) because the over-potential for reaction (5) may be larger than reaction (8)'. Zinc formed by reaction (8)' will be very active because it is the same as that obtained by electrolysis and will react with H<sub>2</sub>O to immediately produce hydrogen:

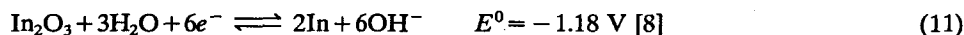


or

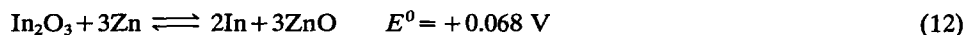


The larger the quantity of ZnO or Zn(OH)<sub>2</sub> contacting with Zn, the larger the volume of hydrogen evolved, since reaction (8)' and the following reaction (9) or (10) is likely to occur. The postulated reaction (8)' is expected to occur only in the solid state of ZnO. For all these schemes, reaction (5) is postulated as the rate determining step.

In the place of Hg, some additives that suppress hydrogen evolution were surveyed, and indium oxide (In<sub>2</sub>O<sub>3</sub>) added to the Zn gel was found to have a beneficial effect (Fig. 6). Immediately after the gel preparation containing In<sub>2</sub>O<sub>3</sub>, evolved gas volume is larger compared to the gel without In<sub>2</sub>O<sub>3</sub>. By varying the In<sub>2</sub>O<sub>3</sub> concentration, an optimum point was found. From this point the gas evolution rate increased with increasing In<sub>2</sub>O<sub>3</sub> concentration (Fig. 7). The mechanism for these phenomena was considered as:



By combining reactions (8)' and (11), reaction (12) was obtained:



Since the standard potential for reaction (12) is positive, the reaction will proceed from left to right to deposit In metal on Zn. This In metal deposited on Zn will act

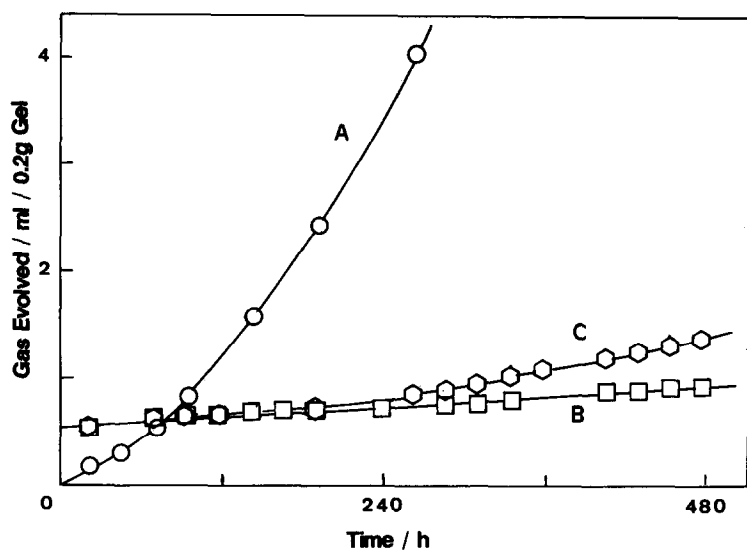


Fig. 6. Gas evolution behavior from Zn alloy (No. 1) mixed with equal mol of ZnO at 60 °C containing (A) no  $\text{In}_2\text{O}_3$ , (B) 0.7 wt.%  $\text{In}_2\text{O}_3$ , (C) 1.0 wt.%  $\text{In}_2\text{O}_3$ .

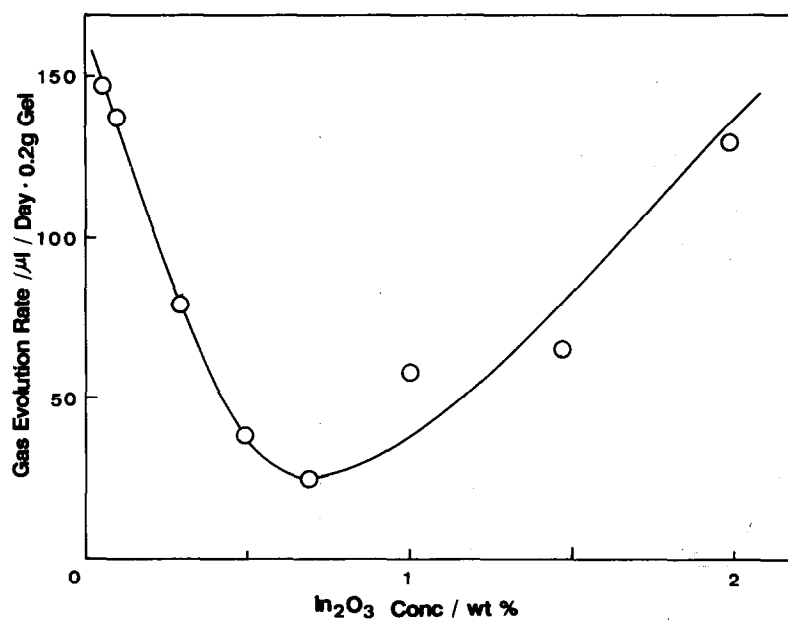
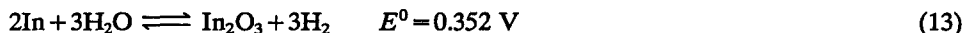


Fig. 7. Gas evolution rate from Zn alloy (No. 1) mixed with equal mol of ZnO containing various concentrations of  $\text{In}_2\text{O}_3$  at 60 °C.

as a hydrogen evolution suppressor like In in the Zn alloy [4], when the  $\text{In}_2\text{O}_3$  concentration is low. In the case of the Zn-In alloy, the optimum concentration of In for hydrogen evolution suppression also exists [4]. The reason why In in the alloy or deposited by reaction (12) suppresses hydrogen evolution at its low concentration range is not clear. However, an  $\text{In}_2\text{O}_3$  concentration higher than the optimum concentration will produce hydrogen according to reaction (13), as seen in Fig. 7:



where In is produced by reaction (12) and the larger the amount of  $\text{In}_2\text{O}_3$  in the Zn gel, the larger is the quantity of In deposited. Reaction (13) is obtained by combining reactions (5) and (11). In order to confirm that reaction (12) takes place, an X-ray diffraction analysis was carried out for the Zn gel containing  $\text{In}_2\text{O}_3$  after washing the Zn gel with water and drying (Fig. 8). For comparison, the X-ray diffraction patterns of In and  $\text{In}_2\text{O}_3$  are also shown. As seen in Fig. 8, the X-ray diffraction peak due to In metal was clearly detected for the Zn gel mixed with  $\text{In}_2\text{O}_3$ . The diffraction peak that appeared at about  $33^\circ$  is considered to be due to In metal (101), which is not

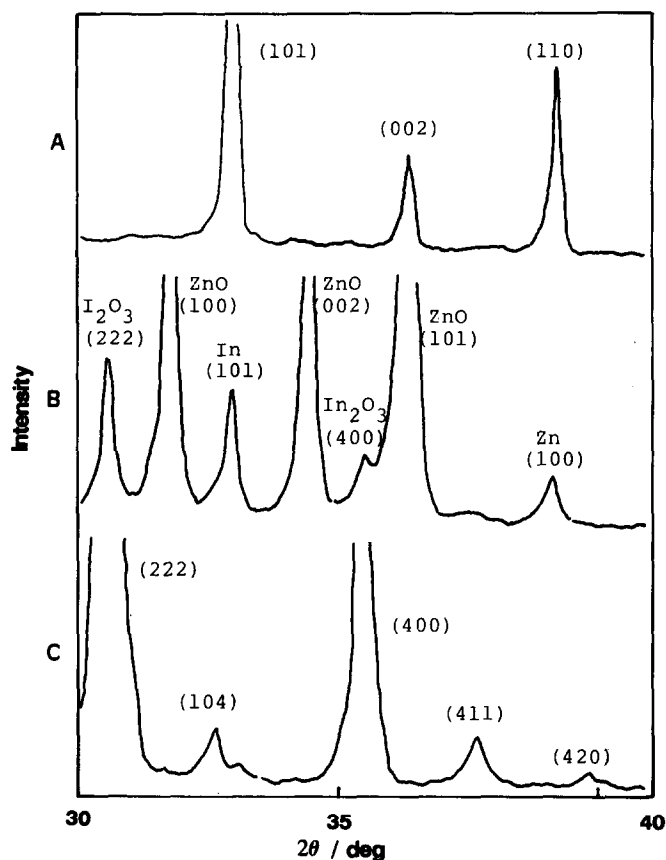


Fig. 8. X-ray diffraction patterns of: (A) In metal, (B) mixture of Zn (No. 1): $\text{In}_2\text{O}_3$ =20:1 (mol ratio), (C)  $\text{In}_2\text{O}_3$ .



due to In in the Zn alloy, because the Zn alloy itself did not give a diffraction peak in this region. After preparation of Zn gel mixed with  $\text{In}_2\text{O}_3$  passed, the peak height at  $33^\circ$  of diffraction angle increased with time. This suggests that reaction (12) proceeds.

## Conclusions

The rate of gas evolution from Zn alloy powder containing Pb, In and Al was measured. The partly discharged Zn alloy or Zn alloy mixed with ZnO or  $\text{Zn}(\text{OH})_2$  was found to accelerate gas evolution. The optimum quantity of  $\text{In}_2\text{O}_3$  added to the Zn gel reduced the hydrogen evolution rate. The mechanism of these phenomena was discussed by considering oxidation reduction potentials.

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