

## SELF-DISCHARGE OF LOW-MERCURY ZINC/SILVER-OXIDE BUTTON CELLS

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### Summary

The self-discharge of zinc/silver-oxide cells has been evaluated by measuring the quantity of hydrogen evolved in a KOH electrolyte. The efficiencies of various corrosion inhibitors have been estimated by measuring the polarization curves and cell discharge capacities. It has been found that a hydrogen evolution rate near to that of a zinc powder electrode containing 14 wt.% Hg may be obtained at the 1 wt.% Hg level by using a special electrolyte consisting of KOH solution with ZnO and trimethyl-dodecyl ammonium chloride ( $C_{12}H_{25}N(CH_3)_3Cl$ ), expressed as DT for simplicity, as a cation active agent. Button cells with such materials exhibit initial capacities that are greater than those of cells with 14 wt.% Hg. After high-temperature/high-humidity storage, and one-year and two-year room-temperature storage, discharge tests have shown that the electrical properties of the new cells are close to those of similar cells containing 14 wt.% Hg. After two-and-a-half-years of storage, the new cells yield lower capacities than those with a high mercury content. However, extensive studies have indicated that with the technical formulation mentioned above, the mercury content of Zn/Ag<sub>2</sub>O and alkaline Zn/MnO<sub>2</sub> button cells may be lowered to less than 1.2 wt.%.

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### Introduction

In various primary cells employing zinc negative electrodes (*e.g.*, Zn/Ag<sub>2</sub>O Zn/MnO<sub>2</sub>) mercury is generally used as a corrosion inhibitor to retard the rate of self-discharge. Mercury is toxic, however, and thus there are environmental problems associated with its use. In addition, Dirkse [1] has shown that amalgamated zinc is not effective as a self-discharge inhibitor in tropical climates. For these reasons, increasing attention is being paid towards finding a substitute for mercury. Lead and cadmium have been considered, but these metals are not as effective as mercury in increasing the corrosion resistance of zinc.

A Japanese patent [2] has suggested that an improvement in zinc stability can be obtained by the incorporation of certain additives; these include

indium oxide or hydroxide, and aminonaphthalenesulfonic acid and its derivatives [3]. Alternative approaches are to add  $V_2O_5$  to the electrolyte [4], or to use zinc powder covered with Th, In, Ga, Sn, Pb, Cd in conjunction with Hg [5,6]. In 1981, Keily and Sinclair [7] proposed that the most effective corrosion inhibitor for zinc electrodes is ZnO in combination with a certain quaternary ammonium salt.

The work reported here was initiated at a time when there was a strong local desire to lower the mercury content of Zn/Ag<sub>2</sub>O button cells. The ultimate aim of the studies is to remove the need for mercury entirely, with low-mercury cells being developed for use in the interim period.

## Results

### *Efficiency of self-discharge inhibition*

In alkaline sealed primary cells, the zinc self-discharge reaction is coupled with that of hydrogen evolution, *i.e.*,



Whereas the overpotential for hydrogen evolution is relatively large, that for zinc dissolution is small. The rate of cell self-dicharge is therefore controlled by the rate of hydrogen evolution, *i.e.*, there is a direct relationship between the quantity of dissolved zinc and the amount of hydrogen evolved. Thus, it is possible to determine the extent of self-discharge by placing a known quantity of zinc powder in KOH solution and measuring the amount of hydrogen evolved. The method used in this work to collect hydrogen is commonplace: a sealed glass container was filled with zinc powder and the electrolyte was connected to a volumetric tube also filled with electrolyte. The quantity of hydrogen emanating from the container was determined by measurement of the water volume displaced by the gas. The solution was kept at 25 °C. The efficiency (%) of zinc inhibition is given by:  $(A - B)/A \times 100$ , where  $A$  and  $B$  are the amounts of hydrogen evolved daily per gram of zinc without and with inhibitor, respectively.

### *Polarization curves*

Polarization experiments were carried out galvanostatically, and the overpotential for hydrogen evolution was determined from the polarization curves at a steady state. The zinc powder was pressed into a solid pellet under high pressure. The area of the actual active surface was estimated by measuring the differential capacitance of the electrode. The constants  $a$  and  $b$  in the Tafel equation were calculated by curve fitting, using the least-squares minimization technique.

### Cell discharge capacity

Two series of cells, labelled SR41 and SR43, were tested. The SR41 cells were discharged continuously at 20 °C across a 17.5 k $\Omega$  resistance. Tests were conducted on SR43 cells with five different formulations: cells 1 - 4 contained 1.14 - 2.26 wt.% Hg with Pb, ZnO and DT in different ratios, whereas cell 5 served as a reference sample and contained 11.89 wt.% Hg. Cell discharge was carried out at a constant current of 1 mA for 20 days in an environment having a temperature of 60 °C and a relative humidity of 90%. The cut-off voltage was 1.2 V.

### Differential capacitance curves

In order to examine the action of DT, the differential capacitance curves of zinc electrodes (both with and without DT) in KOH solution were determined by employing a linear potential sweep superimposed with a small sinusoidal wave.

### Discussion

The results given in Table 1 show that the most effective means to inhibit zinc corrosion is to use an electrode with 2 wt.% Hg + 1 wt.% Pb, and with ZnO and DT in the KOH electrolyte. This combination results in a hydrogen evolution rate equal to, or less than, that of 14 wt.% Hg. The mechanism by which this complex combination proves beneficial has still to be determined.

TABLE 1

Evolution of hydrogen during storage

Sample	Electrolyte	Hydrogen evolution (ml/g Zn/day)	Inhibition efficiency (%)
Zn powder	KOH	1.326	—
Zn + 2 wt.% Pb	KOH	0.3995	69.80
Zn powder + 1 wt.% Pb	KOH	0.8492	36.00
Zn powder	KOH + ZnO	0.8492	88.80
Zn powder	KOH + DT	0.8107	38.90
Zn powder + 2 wt.% Hg	KOH + ZnO	0.1320	90.00
Zn powder + 2 wt.% Hg + 1 wt.% Pb	KOH + ZnO	0.1257	90.50
Zn powder + 2 wt.% Hg	KOH + ZnO + DT	0.1192	91.00
Zn powder + 2 wt.% Hg + 1 wt.% Pb	KOH + ZnO + DT	0.0152	98.80
Zn powder + 14 wt.% Hg	KOH + ZnO	0.0334	97.50

Results of Tafel plots obtained from steady-state polarization studies (Table 2) indicate that the addition of ZnO, Pb or DT does not individually affect the value,  $b$ , of the slope. In all cases, the latter is greater than 118 mV. This means that the hydrogen evolution reaction is controlled by a

TABLE 2

Values of Tafel constants

Sample	Tafel constants (V)	
	<i>a</i>	<i>b</i>
Zn + KOH	1.150	0.125
Zn + KOH + DT	1.251	0.132
Zn + Pb + KOH	1.500	0.125
Zn + KOH + ZnO	1.500	0.125

delayed discharge and that each material, when added alone, does not influence the mechanism or kinetics of the process. Data in the second column of Table 2, however, show that the *a* values increase with addition of the inhibitors; this implies an increase in the overpotential for hydrogen evolution.

Results given in Table 3 reveal that all the cells with the new inhibitors yield better performance under high-temperature and high-humidity conditions than those cells containing a higher content of mercury. That is, the former cells exhibit higher capacities in the fresh state.

From data given in Table 4 and the amount of zinc contained in each cell, it is possible to calculate the utilization of the zinc. This utilization was 98.6, 97.8, 82.3, 93.7 and 87.4% for cells 1 - 5, respectively. Such data show that the utilization increases by 5 - 10% on addition of the inhibitors. Cell 3 proved to be the exception.

As can be seen from the discharge curves in Fig. 1, the inhibitors recommended have practical value, for they may replace most of the mercury. In particular, the data for the two-and-a-half-year storage show the extent to which such inhibitors prove beneficial.

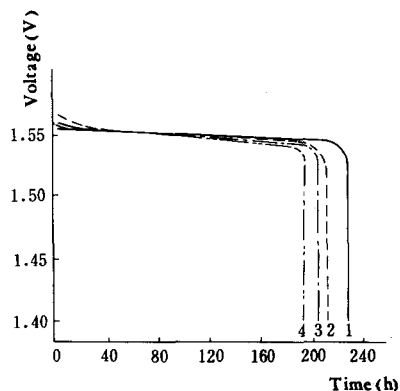


Fig. 1. Discharge curves of Zn/Ag<sub>2</sub>O button cells through a resistance of 7.5 kΩ. 1, 2 wt.% Hg + 1 wt.% Pb + DT, new cell; 2, 14 wt.% Hg, new cell; 3, 2 wt.% Hg + 1 wt.% Pb + DT, after storage for one year; 4, 14 wt.% Hg, after storage for one year.

TABLE 3

Discharge of Zn/Ag<sub>2</sub>O button cells

	14 wt.% Hg			2 wt.% Hg + 1 wt.% Pb + DT		
	Initial	0.5 year	1 year	Initial	0.5 year	1 year
	60 °C, high humidity, 20 days			60 °C, high humidity, 20 days		
Discharge time (h)	209	—	192	222	215	200
Self discharge rate (%)	—	—	8.1	3.1	9.1	4.5
			195			212
			5.2			

TABLE 4

Discharge capacities and capacity losses after different storage periods at 60 °C

Cell no.	Capacity (mA h)		Capacity loss (%)				
	Initial	Storage					
			20 days	1 year	2.5 year	1 year	2.5 year
1	119.60	101.00	107.30	103.84	18.56	11.16	14.31
2	118.40	89.54	100.10	105.48	24.54	14.83	11.08
3	100.40	76.80	93.70	95.62	23.69	6.56	5.77
4	112.40	88.20	98.10	101.69	20.60	13.02	10.36
5	106.00	98.18	103.20	78.22	7.44	2.52	24.33

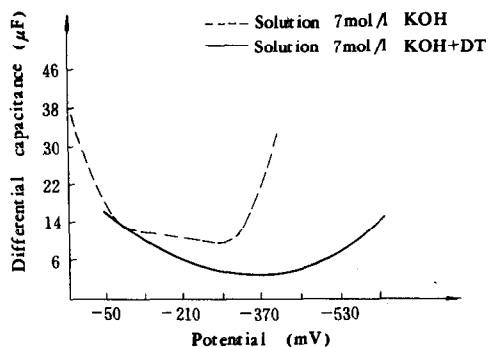


Fig. 2. Differential capacitance curves (potential measured *vs.* Zn).

Within the potential range where the differential capacitance is measured (Fig. 2), a large quantity of negative charge is expected on the electrode surface. Since DT is a surface-active material of cation type, the powerful electrostatic force should enhance the adsorption of DT on the zinc electrode surface. Thus, adsorption of DT results in a decrease in the differential capacitance of the zinc electrode. In turn, the structure of the diffuse double layer changes so that protons have now to overcome a higher energy barrier to penetrate the layer and, consequently, an increase in the overpotential of hydrogen evolution is observed.

## Conclusion

(i) Amalgamated, distilled zinc powder containing 1 - 2 wt.% Hg and 1 wt.% Pb, in conjunction with ZnO and DT additives to the electrolyte, provides an effective corrosion inhibitor for zinc electrodes in alkaline electrolyte. The effect is equivalent to that experienced with 14 wt.% Hg, thus such a material combination may be used for many types of zinc electrode operating in alkaline electrolyte.

(ii) All four additives, *i.e.*, ZnO, Pb, DT, and mercury, should be used simultaneously for maximum inhibition.

(iii) The advantages of the inhibitor formulation are low cost and simple implementation.

(iv) As occurs with mercury alone, the inhibitive effect of the formulation deteriorates after storage at high temperature.

## References

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