

Short Communication

On the Suppression of Self Discharge of the Zinc Electrodes of Zinc-Air Cells and Other Related Battery Systems

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Zinc-air cells and other related battery systems use pure zinc in various forms as anodes because of the following advantages:

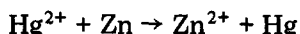
- (1) high electrode potential in neutral and alkaline media;
- (2) the metal is commonly available;
- (3) good stability in neutral and alkaline media without self discharge (hydrogen evolution).

In the anode fabrication process, however, metallic impurities such as iron are bound to contaminate the zinc, leading to self discharge which not only reduces the ampere hour output but also reduces the shelf life of the battery. In order to suppress the self discharge a small percentage of mercury is incorporated into the zinc as this increases the hydrogen overvoltage, minimising the self discharge, and also, as it provides an equipotential surface [1], corrosion will be uniform. Mercury may be incorporated by chemical displacement from a mercuric salt solution after anode fabrication or by alloying during anode fabrication.

This short communication describes a simple procedure to determine the mercury content, without resorting to any analytical procedure, in the chemically amalgamated zinc electrode. The effect of mercuric ion concentration and immersion time on the amalgamation of the zinc electrode is also shown. A simple alloying method is described as an alternative to the one reported by Bernard [2] who enclosed mercury in a thick-walled zinc capsule and submerged it in molten zinc. The ampere hour outputs of a few experimental 1.4 V, 50 A h zinc-air alkaline cells are given to show that the alloying procedure is more effective than the chemical method, especially when the amalgamated zinc is stored prior to use.

When zinc metal in the form of rod or sheet is chemically amalgamated using mercuric chloride solution, an acid must be present in the solution to remove surface oxide and for the subsequent chemical displacement leading to amalgamation. In addition to amalgamation there is also hydrogen evolution. If there is no hydrogen evolution the mercury uptake can be calculated from the increase in weight (say x g) of the zinc after amalgamation using

the formula: amount of mercury = $x \times 1.483$ g. The formula is arrived at from the displacement reaction, *viz.*,



It has been found by trials that A.R. hydrochloric acid, 1.5% by volume, is just sufficient to serve the purpose without hydrogen evolution. Less than 1.5% has been found to produce a brown film on the zinc and more than 1.5% has been found to give hydrogen evolution.

Zinc plates, each of known area and weight, were amalgamated in 10% by weight mercuric chloride solution containing 1.5% by volume of A.R. hydrochloric acid. Mercury contents were computed from the formula and also estimated by an analytical procedure [3]. The results were in good agreement, as shown in Table 1.

TABLE 1

Experiment no.	Mercury (%)	
	Calculated	Analysed
1	0.5	0.449
2	0.65	0.65
3	0.83	0.82
4	1.1	1.099

Amalgamation was carried out with mercuric chloride solutions of various concentrations. The mercury content in each experiment was computed at regular intervals. After a particular immersion time the calculated mercury content was found to decrease. At this stage fine mercury droplets were found to drain from the zinc surface. The time for the mercury draining was found to be concentration dependent as shown in Table 2.

TABLE 2

Mercuric chloride (%)	Time after which mercury drain occurs (s)
2.5	10
5	7
7.5	4
10 (saturated solution)	4

A known weight of A.R. zinc powder was placed in dilute acetic acid and the required quantity of mercury was added to form the amalgam. The amalgam or master alloy thus formed was washed well, dried, and stored in a

vacuum desiccator. This master alloy was added to molten zinc to obtain the required degree of amalgamation in the cast zinc anode. Quantitative analysis revealed that there was no mercury loss during casting. This is a simple procedure as compared with the direct mercury addition to molten zinc which is highly hazardous and leads to mercury loss by vapourisation.

Zinc anodes were cast and amalgamated chemically with 10% mercuric chloride solution. Identical anodes were fabricated by incorporating mercury while casting. Experimental 1.4 V 50 A h zinc-air cells were assembled using the amalgamated zinc anodes, tubular porous carbon air cathodes, and sodium hydroxide electrolyte. The cells were subjected to an intermittent discharge of 200 mA for 4 h daily over a period of 70 days to a cut off voltage of 0.9 for each cell. Amalgamated zinc anodes were stored under ambient conditions of $\sim 27^\circ\text{C}$ and $\sim 40\%$ relative humidity for 3 months and six months. The stored zinc anodes were also subjected to discharge studies. The results are given in Table 3.

TABLE 3

Cell no.	Mercury (%)	Method of amalgamation	Realised output against the rated output of 50 A h		
			Anodes used immediately (A h)	Anodes stored for 3 months (A h)	Anodes stored for 6 months (A h)
1	0	—	38	—	—
2	0.25	Chemical displacement	43	41	39
3	0.5	Chemical displacement	53	49	40
4	0.75	Chemical displacement	53.75	50	41
5	0.25	Alloying method	44	43	41
6	0.5	Alloying method	54	53	52
7	0.75	Alloying method	54	53	53

The results of the discharge studies reveal that a minimum of 0.5% of mercury is necessary in the case of the cast zinc anodes to minimise self discharge and to obtain the rated output from the anode. More than 0.5% does not have any beneficial effect. The zinc anodes amalgamated by the alloying method retain the amalgamation effect during storage, which is not the case with the chemically amalgamated zinc anodes.

In summary, it can be stated that in the case of chemical amalgamation of the zinc anodes the degree of amalgamation can be computed provided that the conditions given in this Short Communication are followed strictly. The alloying procedure described is a simple one. Amalgamation by alloying

is preferable to chemical amalgamation for the zinc anodes of electrochemical power sources since the amalgamation effect is better retained during storage.

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- 1 G. W. Heise and N. C. Cahoon, *The Primary Battery*, Vol. 1, Wiley, New York, 1971.
- 2 R. Bernard, *Brit. Pat. 1,182,466* (1970).
- 3 W. W. Scott and N. H. Furman, *Standard Methods of Chemical Analysis*, Vol. 1, N. H. Furman (ed.), Princeton, NJ, 1938.