FURTHER WORK ON ADDITIVES IN THE ZINC PLATES OF NICKEL/ZINC TEST CELLS

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Introduction

Recently, considerable time, money and effort have been expended on the development of nickel/zinc batteries for electric vehicles [1]. Advances have been reported in nickel plate fabrication, separator technology and overall cell design [2]. Unfortunately, a problem that still remains is the limited cycle life of zinc plates in quiescent electrolytes [1 - 3].

From time to time it has been suggested that zinc plates could be improved by the incorporation of additives. Some that have been suggested are lead, cadmium, and tin salts [4 - 9], hydroxyalkyl celluloses [5], cadmium metal [6], carbon fibres [10], cobalt hydroxide [11], tin metal [12], inorganic titanates [13], calcium oxide [14], bismuth oxide [14] and PTFE [15]. However, their efficacies have been questioned [1] and it is also apparent that proper statistical controls were not used in much of the published research.

In our opinion, statistical controls are vital when testing additives; simply ranking them according to performance is not enough. The main reason for this is the existence of *outliers*. These are unusual data that are caused by discordant observations or contaminant observations, rather than genuine effects. (Discordant observations are those that occur because of statistically unusual combinations of circumstances, whereas contaminant observations are those that are not realizations from a target distribution [16]). Since both types of outliers are inevitable in battery research, it is obvious that some method is needed of lessening their influence. Statistical significance tests are one way of achieving this.

In the present work we apply a well-known statistical significance test (Student's t test) to the results of more than 200 cycling experiments on individual nickel/zinc test cells. Then we show that, using certain additives, significant improvements in ZnO utilization in zinc plates can be made.

Experimental

Zinc plates (25 cm^2) were prepared by spreading aqueous pastes of ZnO and additives onto silver-plated and bismuth-plated grids. Each of these was then compressed under a layer of polypropylene felt and dried *in vacuo*. The plate loadings were 0.13 ± 0.03 g cm^{-2}.

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Nickel electrodes were obtained commercially from Eagle-Picher Industries (USA), and the separator materials were similarly obtained from Celanese Plastics Corp. (USA). The Hg/HgO reference electrodes were made to our own design.

All test cells were charged and discharged at 500 mA constant current using Amel 545 galvanostats. The cells were maintained at 25 °C in thermostatically controlled water baths.

The cell design, and other experimental details, may be found elsewhere [17].

Results

Zinc oxide utilization was measured by calculating a "cumulative capacity", which was obtained as follows. Firstly, a nickel/zinc test cell, incorporating a reference electrode, was charged and discharged at 20 mA cm^{-2} between specified zinc electrode potentials rather than cell voltages. Then the cumulative capacity was calculated from the formula

$$\text{Cumulative capacity} = \frac{1}{m}\sum_{n=1}^{N} Q_n \qquad (1)$$

where Q_n was the discharge capacity recorded on cycle number n, N was the total number of cycles considered, and m was the mass of ZnO in the negative plate. (In our work, we always considered the case $N = 100$.)

As a measure of statistical significance we used Student's t test. This was applied to the 100-cycle cumulative capacity data obtained from more than 200 test cells. A small sample of the results is given in Table 1. It can be seen that the additives Bi_2O_3 and acetylene black yielded statistically significant improvements at the 0.05 confidence level.

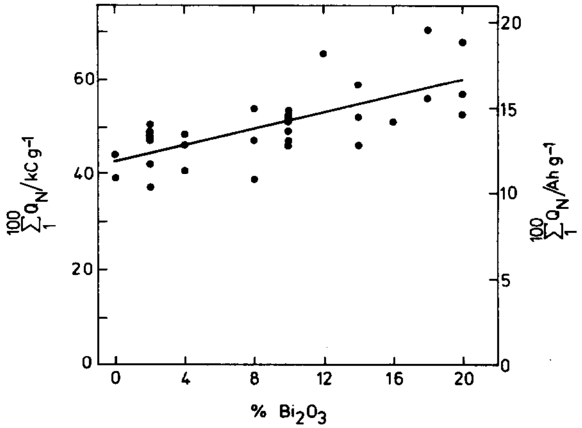

Fig. 1. Cumulative capacities of zinc plates in nickel/zinc test cells as a function of bismuth oxide percentage.

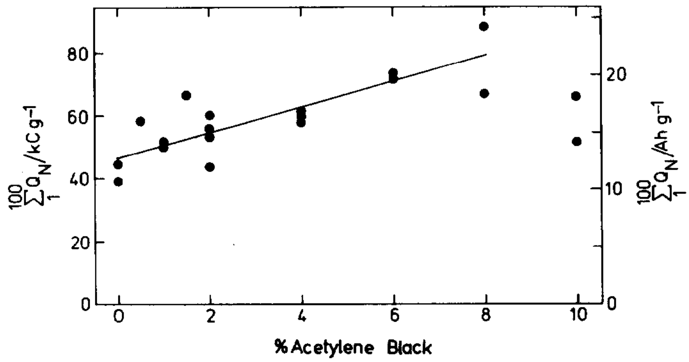

Fig. 2. Cumulative capacities of zinc plates in nickel/zinc test cells as a function of acetylene black percentage.

TABLE 1

t Tests of additive effects on 100-cycle cumulative capacities

Additive	$\sum_1^{100} Q_n$/A h g^{-1} Mean	Standard deviation	Number	t	Significant?[a]
Bi_2O_3 [b]	14.9	2.9	7	2.8	Yes
Acetylene black	16.7	1.9	3	3.0	Yes
PbO[b]	11.9	4.6	3	0.3	No
CdO + CMC[b]	13.1	0.1	3	1.1	No
Control[c]	11.2	3.0	17	—	—
TiO_2	11.9	2.5	3	0.4	No

[a]Test if mean of $\sum_1^{100} Q_N$ was significantly different from the mean of control group at 0.05 confidence level.
[b]Includes plates containing 2% HgO.
[c]Control group consisted of seventeen cells that exhibited no significant improvements.

The effects of different percentages of Bi_2O_3 and acetylene black on the cumulative capacities of zinc plates are shown in Figs. 1 and 2. In both cases there are correlations between increased amounts of additive and increased ZnO utilization. However, the data are somewhat scattered. The probable causes of this scatter are (a) uncontrolled variations between different batches of test materials, and (b) small differences in cell assembly procedures between different operatives. Despite the scatter there is evidence to suggest a definite improvement in ZnO utilization.

Conclusion

We have shown that the additives Bi_2O_3 and acetylene black yield statistically significant improvements in ZnO utilization in zinc plates of nickel/zinc test cells. Previously, the effects of these additives were unclear because of a lack of appropriate tests of statistical significance. However, the problem was remedied by using Student's t test.

Acknowledgements

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