SHORT COMMUNICATION

Improved cycle life performance of Zn/NiOOH cells using a stabilized zinc electrode

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1. Introduction

Zinc secondary batteries are potential candidates for application in electric vehicles and electric utility load levelling. The advantages are high energy density, low energy cost and high discharge voltage. However, the commercial application of zinc alkaline cells is hindered by a limited cycle life resulting from dendritic growth and shape change in the zinc electrode. Numerous attempts have been made to delineate the factors responsible for these events and to find methods of retarding them. The efficacy of various metal oxides has been examined for this purpose [1–10]. Several reports point out that addition of CdO improves the cycle life of the zinc electrode [11–14]. Cadmium metal and cadmium compounds have also been used along with CdO [15, 16]. Some reports also discuss the combined effect of CdO, indium hydroxide, tin oxide or tin hydroxide [17–20]. A program has been initiated in our laboratory to perfect the zinc electrode for battery applications seeking various solutions to the zinc electrode problem [21, 22]. As a part of this work, a stabilised zinc electrode containing CdO has been tested for its discharge performance in a Zn/NiOOH secondary battery and the results are discussed here.

2. Experimental details

The zinc electrode was prepared from powder zinc oxide (4.5 A h capacity) mixed with cadmium oxide (1.25 A h capacity), and a Teflon binder and the mixture was pressed on to a nickel coated iron grid (7.5 cm × 6 cm). The nickel electrode was prepared by sintering carbonyl nickel powder (type 255) in an inert atmosphere on a punched nickel plated mild steel grid of dimension 7.5 cm × 6 cm. The thickness of the plate was 0.8 ± 0.05 mm and the porosity of the sintered plaque prior to forming range between 70 and 75%. The impregnating solution was prepared from AR nickel nitrate. A vacuum impregnation method generally adopted for preparing the plates was adopted.

The plaques were immersed in nickel nitrate solution containing about 5% cobalt nitrate and impregnated in vacuum. They were then electrolytically formed in a solution of 20% NaOH. After forming, the plates were washed free of nitrate and dried. This cycle of impregnation and forming was repeated until the plaques were impregnated with the desired weight of the active material (1.5 A h).

In the cell, a single nickel positive was positioned between two zinc anodes and made into a U fold configuration using 3 layers of cellophane separator. The cell was then left soaked in a minimum quantity of 30% KOH for about 17 h and subjected to 3 conditioning cycles. A conditioning cycle constitutes overcharging (~ 200%) and deep discharging.

The electrodes were charged at C/3 rate for 4 h and then discharged at the C/3 rate, the cut-off voltage being 1.1 V. For measuring the internal resistance of the cell, discharge curves were obtained at different constant current drains.

3. Results and discussion

The discharge curves of the test battery at various stages of cycle life are shown in Fig. 1. Curve a is the discharge pattern obtained after the initial conditioning cycles. The curve shows two steps, the first step corresponds to zinc oxidation and the second step is due to that of cadmium. The discharge curve of the control cell without cadmium oxide (Fig. 1, curve A) shows a single step which matches step I of the CdO containing cell. The absence of step II in this discharge curve proves that step II is only due to cadmium. This is further supported by the fact that plateau II lies in the potential region of the Ni–Cd cell (1.1 V). As the number of cycles increases, the plateau corresponding to cadmium contracts with a concomitant increase in zinc efficiency. Above 10 cycles (curves b to e in Fig. 1), Cd oxidation is not seen.

The increase in the capacity of the zinc electrode with increased number of cycles may be explained as follows. At a stage during cycling, cadmium may remain as cadmium metal resisting further oxidation/reduction processes. This cadmium may form a highly porous and a preferably conducting matrix facilitating greater material efficiency of zinc. A similar expla-

Table 1. The potentials of zinc electrode, nickel electrode and cell during discharge.

Time (min)	E_{Zn} (V)	E_{Ni} (V)	E_{cell} (V)
0.0	1.380	0.520	1.900
15.0	1.325	0.475	1.800
68.0	1.300	0.350	1.650
165.0	1.300	0.275	1.575
225.0	1.300	0.150	1.450

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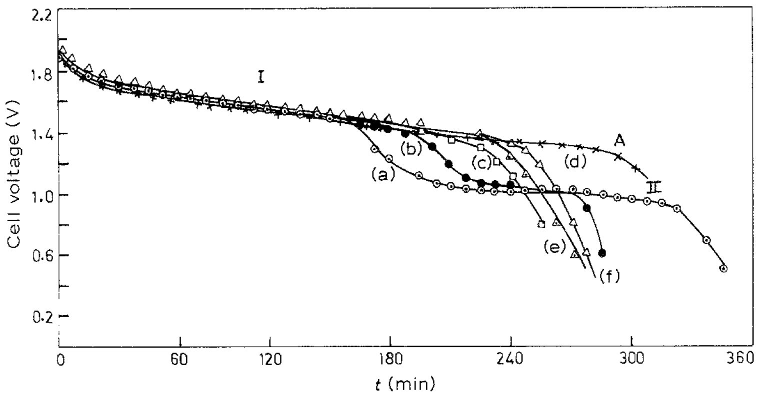

Fig. 1. Discharge curves at (a) 1, (b) 4, (c) 12, (d) 37.52, (e) 120 and (f) 5 cycles. Current drain: 500 mA.

nation has been given by McBreen and Gannon for the beneficial effect of bismuth oxide additive on zinc electrodes [23].

In general practice, nickel is chosen as the positive plate in zinc alkaline secondary batteries and the same applies to the present study. This was achieved by taking zinc oxide in large excess (3 times the capacity of the nickel electrode). The measurement of single electrode potentials during discharge shows that the cell capacity is limited by the nickel electrode (Table 1).

The internal resistance of the cell was determined by adopting the procedure of Shepherd [24]. Two discharge curves at constant current drains of 500 mA and 100 mA, respectively were chosen for this purpose. Figure 2 shows the variation of cell potential with available active material. The following parameters were evaluated by curve fitting:

- Closed circuit potential at $t = 0$: 1.52 V.
- Mean available active material: 0.69 A min cm^{-2}.
- Coefficient of polarisation: 0.073 ohm per cell.
- Internal resistance of the cell: 0.431 ohm per cell.

No shape change was observed up to the 100th cycle (Fig. 3). On the other hand, the control electrode was found to exhibit shape change and dendritic growth resulting in failure at the 35th cycle.

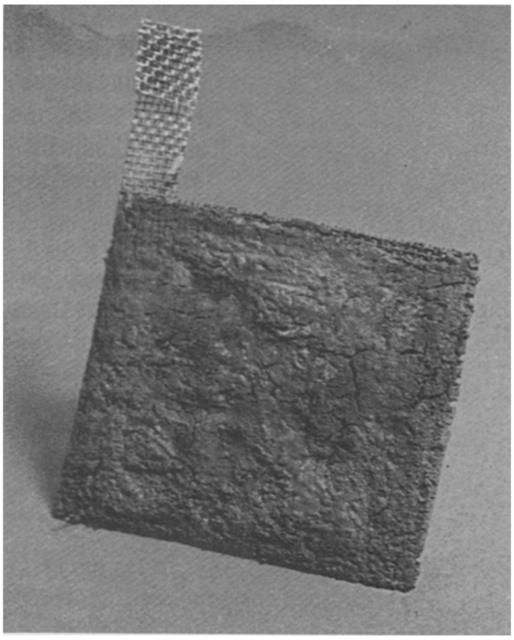

Fig. 3. Appearance of the CdO containing electrode at the 100th cycle.

In the presence of CdO, the capacity of the zinc electrode initially increased with cycling, between 30 and 90 cycles it remained constant and then decreased

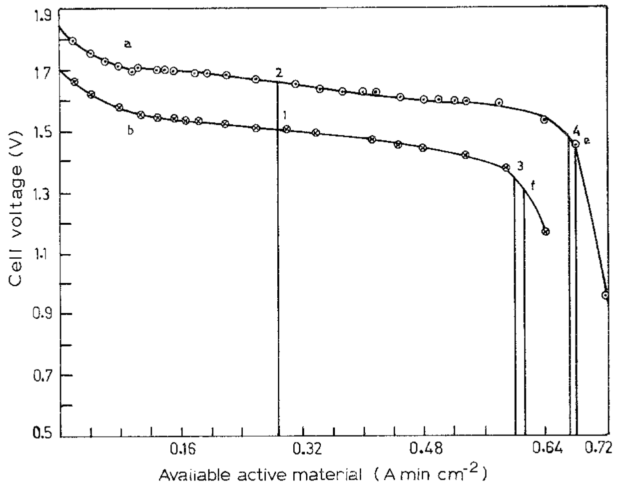

Fig. 2. Discharge curves used in the calculation of internal resistance by Shepherd's method. Current drain: (O) 100 mA and (x) 500 mA.

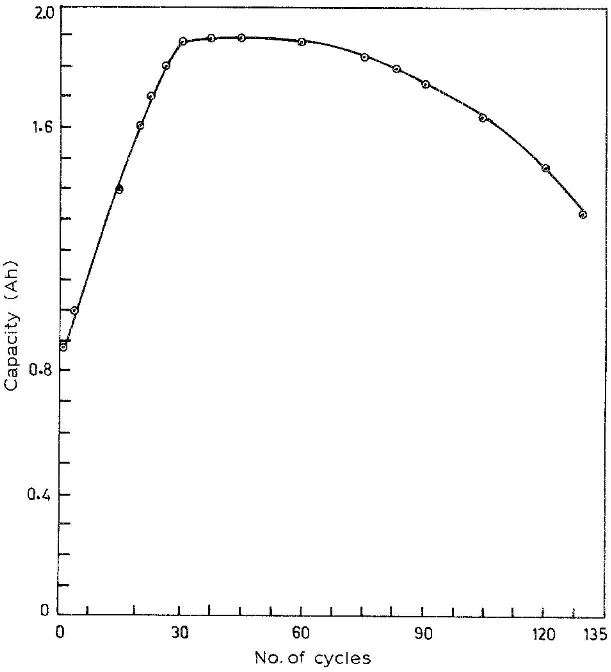

Fig. 4. Change in battery capacity with number of cycles.

slightly with increasing cycles (Fig. 4). The loss at the end of 130 cycles was 30%. The cycle life of the battery was limited by the degradation of the cellophane separator and the use of CELLGUARD separators would greatly enhance the cycle life efficiency [25].

4. Summary

A stabilized zinc electrode containing cadmium oxide was tested for its cycle life in Zn/NiOOH cells. 130 cycles were reached using a cellophane separator against 35 cycles for a control cell without CdO. Cellophane degradation further limits cycle life. Greatly reduced dendritic growth was observed and densification on the zinc electrode was absent. Further work on the measurement of electrical conductivity and porosity of the zinc electrode is underway.

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