A NEW TYPE OF AUXILIARY ELECTRODE FOR ALKALINE ZINC CELLS

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Summary

Auxiliary electrodes having a low hydrogen overpotential were prepared by electrodepositing active nickel onto chemically-metallized polypropylene fibre. They effectively overcame the problem of zinc anode shape change in alkaline electrolyte by dissolving residual zinc, which remained on the anode plates due to passivation and exhaustion of cathode capacity. Residual discharge with such an auxiliary electrode restores the balance of charge efficiencies. Polypropylene–nickel auxiliary electrodes with a very long lifespan can be made in various shapes and sizes. Their polarisation curves and the effect they have on the zinc anode discharge process are both illustrated.

Introduction

It is well known that zinc anodes prepared by the electro-reduction of zinc oxide, or by powder techniques, exhibit disadvantages such as relatively short cycle life, dendrite formation, and shape changes when cycled in alkaline electrolytes. Increased cycle life is reported to occur using a soluble type of anode [1]. This is protected against dendrite short-circuiting by setting up appropriate hydrodynamic conditions in the electrolyte [2]. A soluble zinc anode charged using a 3-component current pulse is a less complicated design [3]. The problem of shape change is overcome by completely discharging the anode using an auxiliary electrode [4]. During this periodic discharging, residual zinc dissolves into the electrolyte from the carrier whereas the anode surface is cleaned. Initially, a sintered nickel electrode with a low hydrogen overpotential was used [5] and, in a 3.5 A h Ni–Zn cell, we obtained a service life of over 1200 cycles. Unfortunately, the sintered nickel auxiliary electrode (SN) is heavy and susceptible to poisoning by the zincate electrolyte, thus requiring periodic reactivation. To overcome these drawbacks, we have developed the new type of auxiliary electrodes described below.

Experimental

The (patented [6]) new electrodes were prepared by coating polypropylene fibre (PP) with a thin layer of chemically deposited nickel and then forming an active nickel layer by one of the 2 following methods:

(a) by treatment of the metallized fibre in an appropriate H_2SO_4–HCl–HNO_3 mixture, followed by periodic cathodic–anodic processes in an acidic bath of nickel salts;

(b) by using a modified version of the second (electrochemical) step of method (a) without any previous chemical treatment.

Two kinds of PP were used: the first prepared by melt-blowing (MB-PP) and the second by needle-pinning (N-PP). Hydrogen liberated during the cathodic process facilitated the formation of porous, active nickel. The auxiliary nickel electrodes were provided with a nickel foil holder which also served as the current collector and terminal.

Results and discussion

Scanning electron microscope (SEM) photographs, Figs. 1 - 3, clearly show morphological differences between the inactive and active nickel layers. Thus, in contrast to the smooth surface of inactive nickel seen in Fig. 1, that of the active nickel (Figs. 2 and 3) contains many deep cracks, small cavities, and sharp edges.

Despite these defects the whole nickel layer is firmly bonded to the polypropylene substrate. Nickel layers of different thickness and activity can
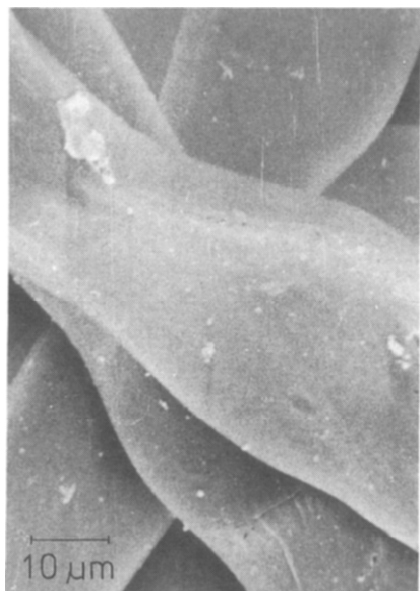

Fig. 1. SEM micrograph of polypropylene fibre chemically covered with inactive nickel.

Fig. 2. SEM micrograph of polypropylene–nickel auxiliary electrode (No. 5) prepared by electrochemical method.

Fig. 3. SEM micrograph of polypropylene–nickel auxiliary electrode (No. 5) prepared by electrochemical method.

be prepared, depending on the relative durations of the cathodic and anodic processes. Table 1 shows that all auxiliary electrodes prepared using a polypropylene base are lighter than the sintered nickel electrode (SN). Under appropriate current conditions a 2-step deposition of active nickel (electrode 3) gives almost the same electrode mass as that from a 1-step process (electrode 2). The 2-step process, however, produces a much more porous structure having decreased polarisation, particularly at high current densities, as shown in Fig. 4.

The hydrogen overpotential–current density curves in 30% KOH + 0.6 M ZnO (Fig. 4) were used to estimate the electrochemical activities of the polypropylene–nickel electrodes. The curves were plotted over a wide current density range up to 40 mA cm^{-2}. Above 20 mA cm^{-2}, electrodes 2 and 3, prepared by the 2-step process (chemical activation followed by electrochemical deposition of active nickel), gave a lower hydrogen overpotential than the sintered nickel electrode, the potential of the doubly-activated electrode 3 being about 120 mV lower than that of the SN electrode. In the practical current density range below 20 mA cm^{-2}, all the PPA electrodes appeared to perform better than the SN electrode and, in particular, the most active were electrodes 4 and 5 prepared with needle-pinned polypropylene fibre and electrochemically deposited nickel. The reason why the preparation method of the polypropylene fibres influences the electro-

TABLE 1

Characteristics of the auxiliary electrodes

Electrode no.	Electrode symbol	Method of preparation	Specific mass ($g\,dm^{-2}$)
1	SN*	Sintered nickel	16.3
2	MB-PPA-1	Active nickel deposited on polypropylene fibre by chemical–electrochemical method (single-plating process)	12.7
3	MB-PPA-4/2	Active nickel deposited on polypropylene fibre by chemical–electrochemical method (double-plating process)	12.0
4	N-PPA-16	Active nickel deposited on polypropylene fibre by electrochemical method only	9.0
5	N-PPA-17	Active nickel deposited on polypropylene fibre by electrochemical method only	7.8

*This electrode was kindly donated by the Central Laboratory of Batteries and Cells, Poznań, Poland.
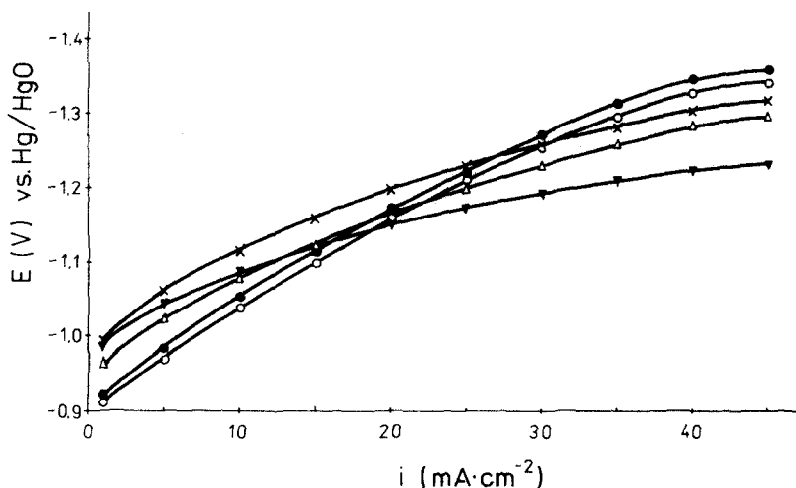

Fig. 4. Polarisation curves of auxiliary electrodes in 30% KOH + 0.6 M ZnO. ×, electrode No. 1 (SN); ▽, electrode No. 2 (MB-PPA-1); ▲, electrode No. 3 (MB-PPA-4/2); ○, electrode No. 4 (M-PPA-16); ●, electrode No. 5 (M-PPA-17).

chemical activity of the resulting auxiliary electrodes is not presently understood, but investigations are being carried out to elucidate this.

Figure 5 illustrates the course of the dissolution of the zinc anode in the above-mentioned electrolyte using different auxiliary electrodes. 0.6 A h
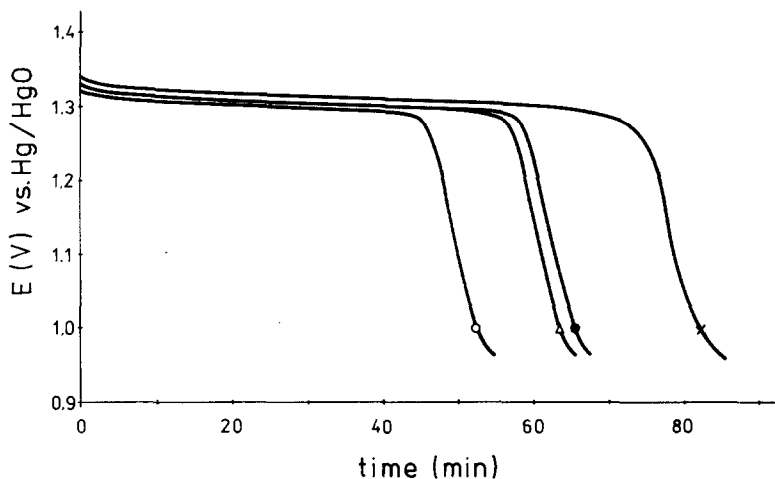
Fig. 5. Discharge curves of zinc anode using auxiliary electrodes via 0.4 ohm resistor. ×, electrode No. 1; ▽, electrode No. 2; ○, electrode No. 4; ●, electrode No. 5.

zinc anodes were short-circuited with the auxiliary electrodes through a 0.4 ohm resistor, and the changes in zinc potential with time were recorded. It is seen that the better electrochemical activity of the PPA electrodes (compared with the SN electrode in Fig. 4) improves their practical performance; the time required to dissolve the residual zinc from the anode was distinctly shorter using them than using the SN electrode. The polypropylene–nickel electrodes have other important features:

(i) having a higher activity they can be as little as half the weight of SN electrodes;

(ii) 200 cycles in a Ni–Zn cell have been completed without any observed change in their activity;

(iii) the simple preparation method allows electrodes of different shapes to be obtained, which is of great significance for the construction of alkaline batteries;

(iv) hydrogen evolved at the electrodes decreases the concentration gradient in the electrolyte which, in turn, lessens the shape change of the zinc anode. Table 1 gives details of the electrodes.

Taking into account such parameters as cost, activity, weight, and life-span, it may be concluded that the novel auxiliary electrodes described above are likely to find application in commercial batteries.

References

1 J. McBreen and E. J. Cairns, *Adv. Electrochem. Electrochem. Eng.,* Vol. 11, New York, 1978, p. 273.
2 C. von Krusenstierna, in D. H. Collins (ed.), *Power Sources 6,* Academic Press, London, 1977, p. 303.
3 K. Appelt and K. Jurewicz, *Electrochim. Acta, 27* (1982) 1701.

4 G. Benczur-Urmössy, K. von Benda and F. Haschka, in D. H. Collins (ed.), *Power Sources 5*, Academic Press, London, 1975, p. 303.
5 K. Appelt and K. Jurewicz, *J. Power Sources, 5* (1980) 235.
6 J. M. Skowroński, Wł. Rekść and K. Jurewicz, *Polish Pat. No. 140759.*