

LIMITATIONS IN THE USE OF PLASTIC-BONDED ELECTRODES IN SEALED NICKEL-CADMIUM CELLS AND THEIR REASONS I. PRISMATIC AND CYLINDRICAL CELLS

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Summary

The use of plastic-bonded (PB) electrodes in prismatic, sealed Ni-Cd cells is limited by the need for a negative electrode layer (active material, plastic binder, activating agents) with the highest possible oxygen recombination rate. Otherwise, a non-uniform charge distribution occurs in the multi-electrode pack during accelerated cycling (the outer PB Cd electrodes differing from the central one). This leads to a decrease in the discharge capacity: evidence that the active material is not fully utilised in the current generating process. With cylindrical sealed cells, the demands imposed on the oxygen recombination rate of PB Cd electrodes are less severe, difficulties, in this case, being due more to the preparation of PB Ni electrodes with a thickness comparable with the negative electrodes (≤ 1 mm).

Introduction

During the seventies, plastic-bonded (PB) electrodes were developed to replace, for several reasons, the pocket-type and sintered electrodes in Ni-Cd accumulators. The new electrodes were initially intended for vented cells [1-11] and, later, for hermetically sealed cells [12]. The use of PB electrodes in hermetic systems, however, is subject to certain limitations which have to be clearly defined to eliminate the distrust of battery manufacturers and to enable the use of PB electrodes wherever possible.

Experimental

The Ni-Cd cells used were a standard type in that they contained the same construction elements as used in commercial prismatic and cylindrical

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cells. In many cases, the commercial pocket or sintered electrodes were replaced by PB electrodes prepared by the rolling technique [6 - 11]. With prismatic cells, the electrode mix (commercial active material + PTFE) was applied to the current collector — a metal gauze (Cd electrodes) or perforated nickel sheet (Ni electrodes). Special Ni electrodes for the R-6 type were prepared by the extrusion technique [19] using a metal spiral as the current collector.

Measurements were made with 6 A h prismatic, commercial type, sealed Ni-Cd cells containing three positive and four negative pocket electrodes which were immersed in the alkaline electrolyte for 16 - 24 h before sealing the cell. Their dimensions were 45×75 mm. We also used 40×75 mm PB electrodes prepared by rolling a mixture of commercial active material, PTFE, and graphite on both sides of a metal gauze.

Further measurements were made using R-6 (14 mm dia., 50 mm height) and R-20 (32 mm dia., 64 mm height) cylindrical cells. The former contained a central nickel oxide electrode (gauze segment type) surrounded by a PB Cd electrode, whereas the latter contained a coiled electrode system. In both cell types the Cd electrode contacted the wall of the cell container and the electrode system was subjected to formation in an excess of electrolyte before the cell was sealed. The electrodes in the R-20 cells were either commercial sintered or PB Cd prepared in the same way and with the same thickness as for the R-6 cells.

Cycle life tests of the prismatic cells (accelerated cycling) consisted of a 0.9 A, 5.5 h charge and a 1.44 A, 2.5 h discharge, *i.e.*, the depth of discharge (DOD) was 60% followed by a 137.5% recharge. The discharge capacity was measured at 0.6 - 1.2 A to a cut-off of 1.0 V after 14 - 16 h charging with a current of 0.6 A (evaluative cycle). Analogous tests of the cylindrical cells consisted of a 1.0 A, 3.17 h, charge and a 1.0 A, 2.5 h, discharge, *i.e.*, a 62.5% DOD and a 126.7% recharge. The evaluative cycle was a 16 h charge at 0.4 A and a 0.8 A discharge to a cut-off of 1.0 V.

Results and discussion

Our interest was concentrated mainly on the PB Cd electrodes which, in our previous communications, have been shown to have a widely variable ability to reduce oxygen during the final stage of charging and during overcharging, in model prismatic sealed cells [13 - 16]. The aim of the present work was to show how this ability is related to the time stability of the capacity of complete 6 A h cells during accelerated cycling.

Prismatic cells

The steady value of the overpressure in a sealed 6 A h cell is plotted as a function of the charging current in Fig. 1. The modifications were:

- (a) unmodified PB Cd electrodes were used;
- (b) the outer PB Cd electrodes in the electrode stack were contacted with a fine metal gauze;

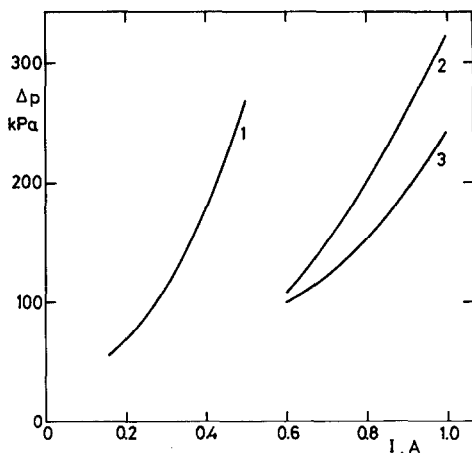


Fig. 1. Influence of charging current on the steady-state oxygen overpressure for 6 A h sealed, prismatic Ni-Cd cells with different Cd electrodes. 1, Cd electrode type a; 2, Cd electrode type b; 3, Cd electrode type c.

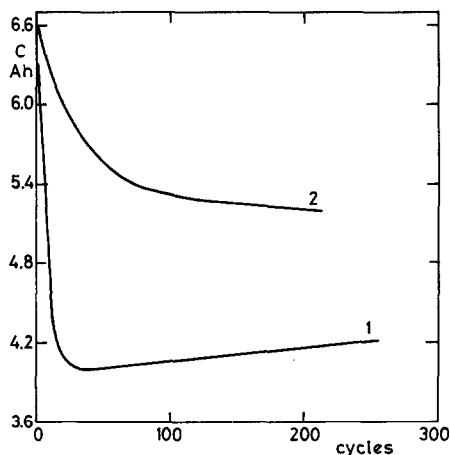


Fig. 2. Cycle life test of 6 A h sealed, prismatic Ni-Cd cells with two different Cd electrodes. 1, Cd electrode type b; 2, Cd electrode type c.

(c) commercial pocket Cd electrodes were used in place of PB Cd.

The electrodes were charged at 0.6 A, *i.e.*, a 10 h rate. It follows from Fig. 1 that in case 'a' the oxygen overpressure was too high, whereas in the other two cases the given charging rate could be used safely. This is in accord with our previous findings [13, 14] concerning reduction of oxygen on the metallic parts of the Cd electrode which are accessible to oxygen.

On accelerated cycling, the cells with electrodes 'b' and 'c' showed a marked difference (Fig. 2): the capacity of sealed cells with electrodes 'b' (with the metal gauze) decreased rapidly to 4 - 4.2 A h and were found to be negative-limited, whereas the capacity of sealed cells with electrodes 'c' (pocket type) reached 5.4 A h and decreased only slightly. In this case the capacity was found to be limited by both electrodes.

To elucidate this difference in the behaviour of the sealed cells, the PB Cd electrodes were precharged with 3 - 4 A h either directly in the cell, with the cell case serving as counter-electrode (Fig. 3, curves 1 and 2), or by using two symmetrical auxiliary electrodes before assembling the cell (Fig. 3, curve 3). It can be seen from Fig. 3, however, that precharging did not lead to stabilization of the cell capacity.

On dismantling some charged cells with precharged Cd electrodes after about 150 cycles, we found that the inner Cd electrodes were black on both sides, evidence for the presence of cadmium reduced to the metallic state, whereas the outer electrodes were dark only on the side facing the separator and light grey on the other side contacting the metal gauze, evidence for the presence of $\text{Cd}(\text{OH})_2$. Hence, the charge distribution during cycling was

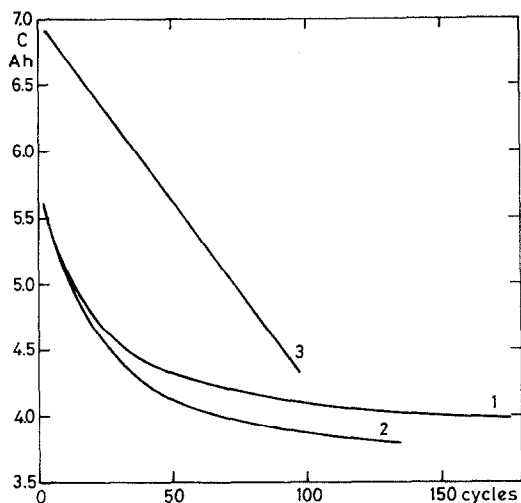


Fig. 3. Cycle life test of 6 A h sealed, prismatic Ni-Cd cells with Cd electrode type b under different precharging conditions. Curves 1 - 3 active material with 10 - 15% metallic Cd. 1, Precharge 3 A h against container walls; 2, precharge 4 A h against container walls; 3, precharge 3.6 A h against special counter-electrodes.

markedly non-uniform, caused, apparently, by preferential reduction of oxygen on the metal gauze. This non-uniformity is necessarily reflected on the positive electrodes adjacent to the negative ones, and it is doubtless the cause of the relatively rapid decrease in the cell capacity during initial cycles to 4 - 4.2 A h.

Thus it is apparent that the participation of the outer Cd electrodes of the multi-electrode stack in the current-generating process gradually decreased in the course of accelerated cycling, causing a decrease of the cell capacity, while the inner electrodes functioned normally, since they were not involved in the reduction of oxygen. We therefore thought it necessary to increase the rate of oxygen reduction on all negative electrodes without applying a metal gauze.

The starting active material for PB Cd electrodes was powdered cadmium with a surface oxide film formed in the course of drying (content of Cd metal 10 - 15%). The results of measurements of the rate of oxygen reduction on PB Cd electrodes prepared from this material are shown in Fig. 4 (curve 2), as obtained on prismatic sealed 2 A h Ni-Cd cells by a method described earlier [13 - 16]. Using an active material with a higher metal content (45% Cd metal), we found a higher rate of oxygen reduction, as indicated by curve 1. Still higher results were obtained with commercial pocket Cd electrodes (curve 3). The use of the latter material in 6 A h sealed cells led to a marked stabilization of the cell capacity during accelerated cycling. Thus, a better utilization of the active material in the whole elec-

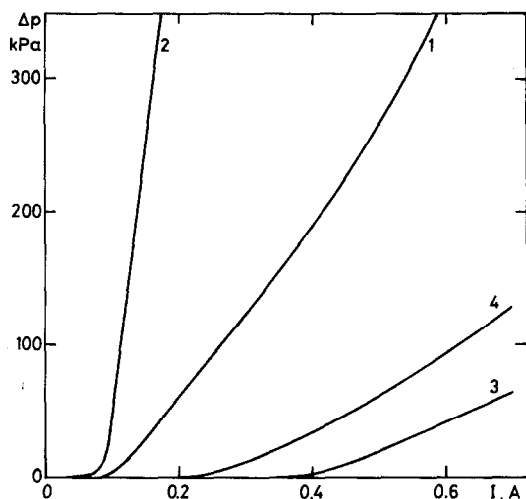


Fig. 4. Influence of charging current on the steady-state oxygen overpressure for 2 A h sealed, prismatic Ni-Cd cells with three different Cd electrodes. 1, PB Cd electrodes with active material containing 45% metallic Cd; 2, PB Cd electrodes with active material containing 10 - 15% metallic Cd; 3, pocket Cd electrodes with active material containing 10 - 15% metallic Cd; 4, PB Cd electrodes with "optimized" chemical composition of the active material.

trode stack was achieved. The results obtained with these cells were comparable with the commercial cells

The use of PB instead of pocket nickel oxide electrodes in accumulators had no appreciable effect on their capacity and long term stability. It can be concluded that the use of PB electrodes in prismatic sealed Ni-Cd cells with a multi-electrode stack is conditioned by the ability of the PB Cd electrodes to reduce oxygen. The higher this ability, the more uniform is the charge distribution in the stack and the more stable is the cell capacity during long-term cycling. In our case, the reduction ability of the electrode layer is controlled by the content of Cd metal in it.

Another way to increase the oxygen reduction ability of the active layer is to dope the active material with $\text{Ni}(\text{OH})_2$. This leads to a considerable improvement, as indicated by curve 4 in Fig. 4. More details are given in refs. 17 and 18.

Cylindrical cells

The use of PB Cd electrodes in cylindrical cells is favoured because of their elasticity, which permits them to be bent without cracking. Further advantages lie in their low price (cheap collector, simple technology) and good hygienic conditions during manufacture. PB Ni electrodes do, however, present some problems. For R-6 cells, PB Ni electrodes can be prepared by extrusion technology, yielding an endless rod which is cut into the form of electrodes. These are provided with a pressed-in, spiral, nickel-plated steel wire current collector [19]. Extensive tests of these electrodes have not

yet been made, but no severe limitations to their exploitation are expected.

PB Ni electrodes for R-20 cells, on the other hand, are difficult to prepare in the thickness corresponding to the PB Cd electrodes, although it appears possible that 1.3 mm-or-more-thick PB Ni electrodes of a smaller length can be made, *i.e.*, with a lower active area. In our measurements, we therefore used in addition to commercially made systems, hybrid-type cells containing PB Cd and commercial sintered nickel oxide electrodes.

A comparison of cycle life tests of commercial, 4 A h, and hybrid R-20 sealed Ni-Cd cells is shown in Fig. 5. It can be seen that the performance of the cells with PB Cd electrodes (curve 2) is similar to that of the cells with sintered electrodes (curve 1), the former having, in contrast to the prismatic cells, no major problems with non-uniform reduction of oxygen. This is because the fraction of the PB Cd electrode surface area not covered with separator is higher in the cylindrical cells, and, moreover, this surface is in contact with the wall of the cylindrical metal vessel, a circumstance which enhances the rate of oxygen reduction. The reduction apparently takes place uniformly over the entire outer surface of the cylindrical electrode system (*i.e.*, of the PB Cd electrode).

Cycle life tests of hybrid sealed Ni-Cd cells of the R-6 type are illustrated in Fig. 6. The cycling conditions were analogous to those for the R-20 type cells and their performance can be considered to be very good. Since the commercial Cd electrodes have a complicated form (three pressed segments per cell), there is an obvious advantage in using one PB Cd electrode prepared in a simple and hygienic way.

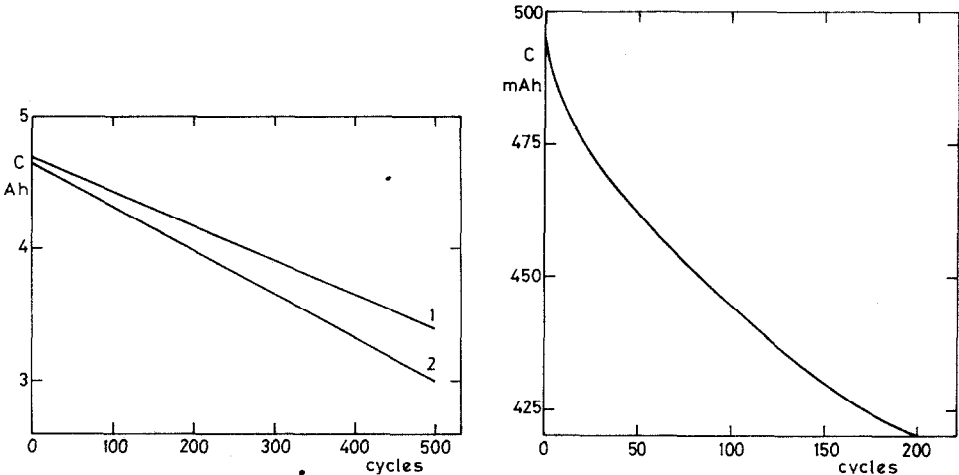


Fig. 5. Cycle life test of size R-20 sealed, cylindrical Ni-Cd cells with a sintered nickel oxide and with different Cd electrodes. 1, sintered Cd electrode; 2, PB Cd electrode ("hybrid").

Fig. 6. Cycle life test of size R-6 sealed, cylindrical Ni-Cd cells ("hybrid").

It follows that the manufacture of hybrid cylindrical cells does not appear to present any major problems as far as the PB Cd electrodes are concerned. The use of PB Ni electrodes brings technological difficulties (related to the electrode thickness) which can be overcome. Limitations in the use of PB Cd electrodes in cylindrical cells may be expected at high current loads, low temperatures, and high charging rates. In these cases the advantages of sintered electrodes, due to the character of the active material-collector contact, outweigh their higher cost.

Conclusions

(i) In multi-electrode, sealed Ni-Cd cells, especially of prismatic shape, the use of PB electrodes requires that the rate of oxygen reduction at the PB Cd electrode be as high as possible.

(ii) Additional metal parts (gauzes, grids) applied to the PB Cd electrodes complicate their manufacture or the assembly of the cells, thus eliminating the main advantage of PB electrodes — their low cost.

(iii) If a metal gauze is used to enhance the rate of oxygen reduction, the distribution of electrochemical reactions in the sealed cell becomes non-uniform, causing a rapid decrease in the cell capacity during accelerated cycling and thus a low utilization of both active materials.

(iv) In cylindrical, sealed cells, the use of PB electrodes is limited by difficulties in the preparation of 1 mm thick PB Ni electrodes. The rate of oxygen reduction at the PB Cd electrodes is enhanced by the favourable geometry of the cell system, hence the demands imposed on the oxygen reduction ability of the active layer are less severe than in prismatic cells.

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