LIMITATIONS IN THE USE OF PLASTIC-BONDED ELECTRODES IN SEALED NICKEL–CADMIUM CELLS AND THEIR REASONS II. BUTTON CELLS

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Summary

The behaviour of commercial, sealed 225 mA h button cells with lamellar-type electrodes had been compared with similar cells containing plastic-bonded electrodes prepared from the same active material. Cycle life tests, current–voltage characteristics, internal resistances, and electrochemical impedance diagrams have been carried out and it was shown that the basic difference between the commercial and the test cells lay in their internal resistances, which is higher for the cells with plastic-bonded electrodes. Their use, therefore, is restricted to low and medium rate applications although they are more economical.

Introduction

The reasons for the limited use of plastic-bonded (PB) electrodes in sealed prismatic and cylindrical cells have already been discussed elsewhere [1]. It was concluded that the ability of the PB Cd electrode to reduce oxygen was the controlling factor in prismatic cells. The greater this ability, the greater and the more stable is the capacity of the sealed cells during accelerated cycling. In cylindrical cells with a sintered positive and PB Cd electrode ("hybrid cells") the reduction of oxygen is enhanced by their favourable geometry. In addition the PB Cd electrodes are both cheaper and mechanically better than the older types. Difficulties were, however, met with in using PB Ni electrodes, which are difficult to prepare with a thickness matching that of the PB Cd electrodes. Limitations to the use of such PB electrodes in sealed button cells form the subject of the present work.

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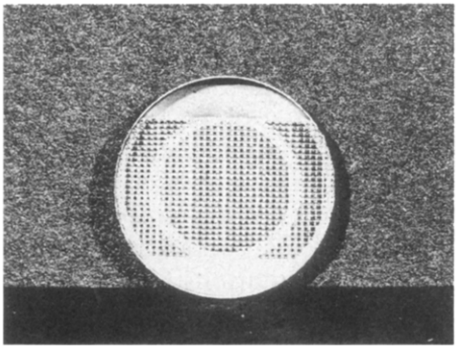
Experimental

All measurements were made using the construction elements and separator of 25 X 8.6 mm, 225 mA h nominal capacity, commercial sealed button cells with one positive and one negative electrode, which were immersed in the electrolyte for 24 h before use. PB electrodes were prepared by pressing the electrode mix (active material with PTFE as binder) into specially designed current collectors [2, 3] (Figs. 1 and 2). Lamellar type electrodes were prepared by pressing the same electrode mix into an envelope from a metal gauze or perforated foil. One side of the PB Cd electrode was in contact with the separator which also constituted the electrolyte support, and the other side contacted the current collector, a perforated metal dish, Fig. 1. The latter was in contact with the cell lid through a metal spring. The collector increased the mechanical strength of the electrode by its special form, and its fine perforations ensured a high rate of oxygen reduction. The collector for the PB Ni electrodes was similar except that it was provided with special contacts penetrating the whole electrode layer (Fig. 2) to improve current conduction [3]. This electrode arrangement was the optimum with regard to the reduction of oxygen.

The electrochemical impedance of the button cells was measured in the range 0.001 Hz - 10 kHz, as described in the literature [4, 5]. The cells were loaded galvanostatically with an alternating current of 9 mA causing voltage changes of about 3 - 5 mV. The impedance spectra were plotted at 25 °C and evaluated graphically. The cells were initially fully charged, then discharged at 22.5 mA for 1 h, and left open circuited for 24 h.

The cycling performance was also measured at 25 °C. The cells were charged at 34 mA and discharged at 54 mA except for the evaluative cycles when the discharge current was either 22.5 or 45 mA.

The current carrying capacity was measured by discharging with 180 mA at 20 °C and with 45 mA at −20 °C.



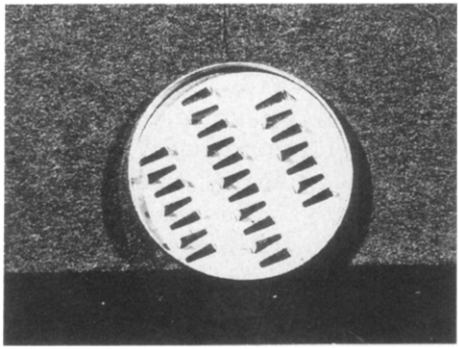


Fig. 1. View of a current collector of a PB Cd electrode.

Fig. 2. View of a current collector of a PB Ni electrode.

The internal resistance of the cells was measured by applying a step change of current.

The current/voltage characteristics of the cells were measured after 24 h under open circuit conditions by the current step method, the cells being loaded for 10 s at a constant current and increasing stepwise at 30 s intervals from 0 to 2 A.

Results and discussion

A comparison between sealed cells with PB and lamellar type electrodes during accelerated cycling is shown in Fig. 3. Their characteristics are also given in Table 1 together with the internal resistance R_i, both in the charged and the discharged state, and the time after which the cell voltage had decreased to 0.8 V with a constant 1.5 Ω load. It can be seen that there is no great difference in the cycling behaviour of the cells with lamellar type electrodes (curve 1) and with PB electrodes (curve 2). Dry separator was used in assembling the cells with commercial lamellar electrodes. The other cells, however, required a separator soaked with the electrolyte, its decrease (from 0.418 to 0.344 g) causing a drop in the discharge capacity (curve 3) and an increase in the internal resistance (Table 1).

When the Cd sponge was replaced by CdO as the active material, the rate of decrease of the discharge capacity during accelerated cycling diminished (Fig. 3, curve 4).

Table 1 also shows that the internal resistance of the cells with PB electrodes is higher than with lamellar electrodes, apparently owing to the content of the plastic binder (PTFE). It was therefore considered interesting to compare the current-carrying capability of the sealed cells with both types of electrodes and with the same active materials, namely, NICKO for

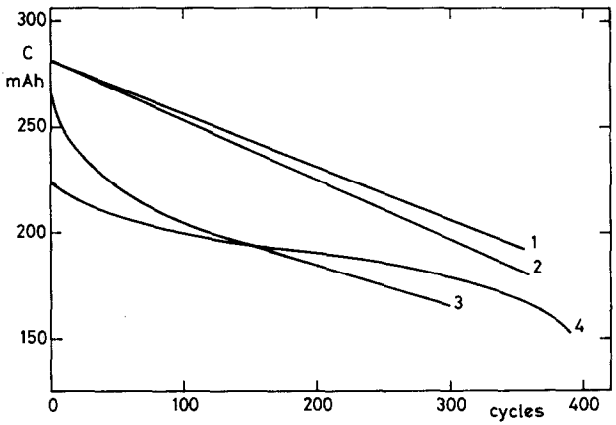


Fig. 3. Cycle life test of sealed button 225 mA h Ni–Cd cells with different Cd electrodes (details given in Table 1). 1, lamellar, Cd sponge; 2, 3, PB, Cd sponge; 4, PB, CdO.

TABLE 1

Cell characteristics

Cd electrode		Ni electrode	Amount of electrolyte (g)		Fig. 3	Internal resistance R_i (mΩ)		Discharge time (s)
Type	Active substance	Type	in electrodes	in separator		charged	discharged	
lamellar	Cd sponge	lamellar	1.416	0	curve 1	175 - 200	380 - 400	530 - 605
PB	Cd sponge	PB	0.929	0.418	curve 2	385 - 405	560 - 790	435 - 550
PB	Cd sponge	PB	0.927	0.344	curve 3	410 - 500	480 - 1020	300 - 475
PB	CdO	PB	—	—	curve 4	—	—	—

the positive electrodes [6] and CdO for the negative ones. The corresponding discharge curves are shown in Fig. 4 (at 180 mA and 20 °C) and Fig. 5 (at 45 mA and −20 °C).

The discharge curves in Figs. 4 and 5 are parallel, suggesting that the shift of the curves for the PB electrodes toward lower voltage values is ohmic in character. This is further supported by comparing the slopes of the current/voltage characteristics which are equal to 0.54 Ω and 0.87 Ω for cells with lamellar and PB electrodes, respectively. Both cell types have the

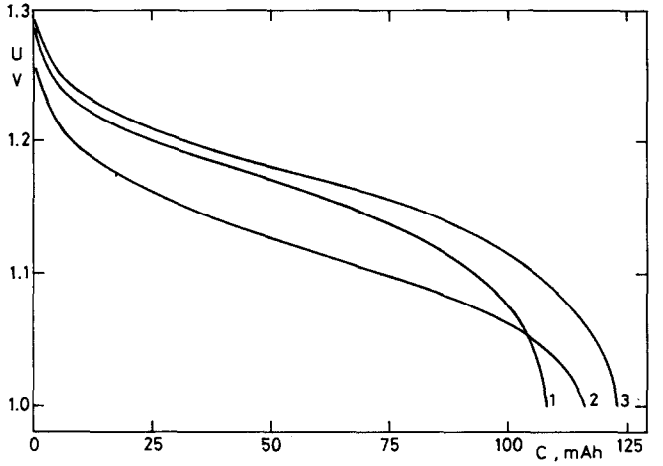


Fig. 4. Discharge characteristics for sealed button 225 mA h cells with different Cd electrodes (discharge current 180 mA, temperature 20 °C). 1, lamellar electrodes; 2, PB electrodes; 3, hybrid electrodes.

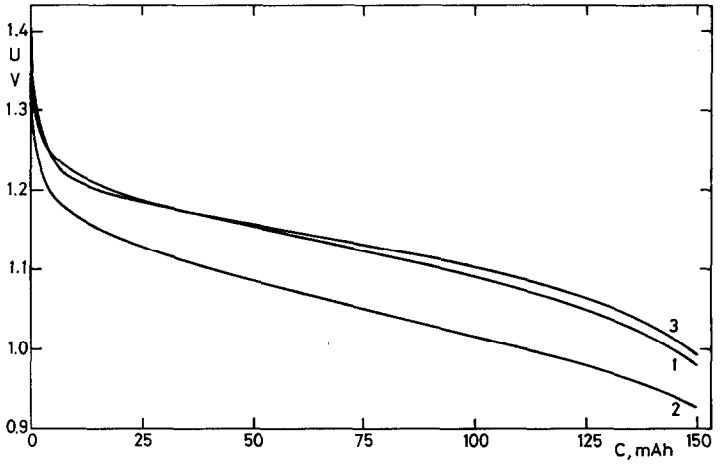


Fig. 5. Discharge characteristics for sealed button 225 mA h cells with different Cd electrodes (discharge current 45 mA, temperature −20 °C). 1, lamellar electrodes; 2, PB electrodes; 3, hybrid electrodes.

same capacity to cut-off voltages of 0.9 V at 180 mA and 20 °C and of 1.0 V at 45 mA and −20 °C. The discharge curves for cells with "hybrid" Cd electrodes prepared from the mix for PB electrodes and a metal gauze for lamellar electrodes are also shown in Figs. 4 and 5.

The measured impedance diagrams for sealed button cells with PB and lamellar type electrodes are shown in Figs. 6 and 7. The real component of the impedance at the highest frequency corresponds to the sum of the ohmic resistances in the cell. The main component is the resistance of the electrolyte in the pores of the electrodes and the separator (which functions also as the electrolyte support) but the electrode matrix also makes a contribution. The latter is influenced by the presence of the organic polymer binder in PB electrodes and by the design of the current collector. We compared the impedance diagrams of the two kinds of button cell having the same case design, separator, electrode contacts and electrolyte content (at the time of assembly). Therefore, the difference in the ohmic component, R, of the impedance (0.34 Ω for cells with PB electrodes against 0.14 Ω for cells with lamellar electrodes, Figs. 6 and 7) can be attributed both to the different collector design and to the presence of PTFE in PB electrodes.

The measured values of R can be related to the values of R_i (Table 1) and to the discharge curves in Figs. 4 and 5, from which the voltage after a

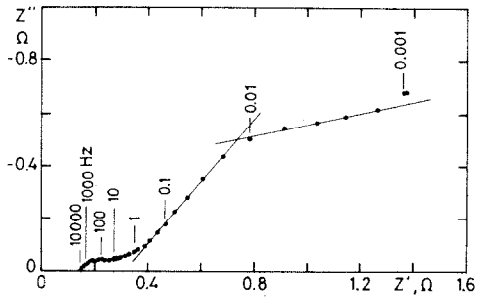


Fig. 6. Complex-plane impedance diagram for sealed button 225 mA h Ni–Cd cells with lamellar electrodes. Frequency range 10 kHz - 0.001 Hz.

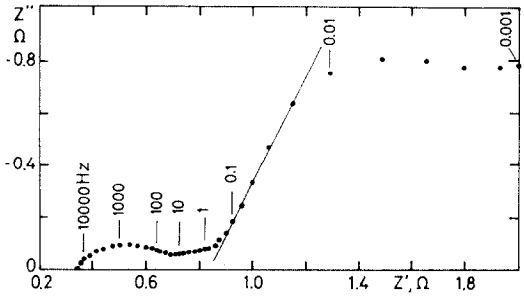


Fig. 7. Complex-plane impedance diagram for sealed button 225 mA h Ni–Cd cells with PB Cd electrodes. Frequency range 10 kHz - 0.001 Hz.

TABLE 2

Electric parameters of sealed button 225 mA h cells

Parameter	Lamellar electrodes	PB electrodes
Internal resistance, R_i (mΩ)	175 - 200 (charged) 380 - 400 (discharged)	385 - 405 (charged) 560 - 790 (discharged)
Cell voltage, $U_{50\,mA\,h}$ (mV)	1143 (Fig. 4) 1172 (Fig. 5)	1080 (Fig. 4) 1128 (Fig. 5)
Ohmic impedance, R (mΩ)	140 (Figs. 6, 7)	340 (Figs. 6, 7)

50 mA h discharge ($U_{50\ mA\ h}$) can be obtained. All these parameters substantiate the ohmic character of the difference between the electrode types (Table 2).

The high-frequency form of the curves in Figs. 6 and 7 ("semi-circle") is characteristic of the charge-transfer processes in the cell [7]; for the cell with PB electrodes it is displaced toward higher ohmic resistance values as expected, its "peak" being at about 600 Hz as compared with 100 Hz for the cells with lamellar electrodes. It is notable that the magnitude of this "semi-circle" for the former cells is about twice as large as that for the latter. This means that the cells with PB electrodes also have a higher charge-transfer resistance (different current collector design and amount of the electrolyte — see Table 1).

The deformations of the "semi-circles" may be due to a combination of several electrode reactions [7, 8]; a more exact discussion would require a study of the impedance of individual electrodes. As shown by Barton *et al.*, the high frequency flattened "semi-circle" should be raised mainly by the Ni positive electrode [9] because there is no evidence of charge-transfer control ("semi-circle") by the Cd electrode [10].

The linear Warburg region begins at about 0.1 Hz with both cell types (Figs. 6 and 7) and extends to almost 0.01 Hz. Its slope is 63° for the cells with PB electrodes and 49° for those with lamellar electrodes. Higher slope values are sometimes attributed to hindered diffusion in the electrode pores [11], which seems plausible in the case of PB electrodes containing a significant number of hydrophobic pores.

In the region of very low frequencies, 0.01 - 0.001 Hz, the slope of the impedance diagram is greatly reduced, approaching zero for the cells with PB electrodes (Fig. 7). This may be because the a.c. period becomes comparable with the time necessary for the electroactive species to diffuse between the electrodes [7, 12]. In our case, the most probable explanation is that the PB electrodes are (when compared with lamellar electrodes) working under diffusion control in the electrolyte phase (compare the electrolyte contents in Table 1).

Since our aim was to minimize the limitations of the use of PB electrodes, additional measurements were made on sealed button cells with "hybrid" Cd electrodes. Their discharge curves are shown in Figs. 4 and 5 (curves 3). The values of $U_{50\ mA\ h}$ for both mentioned discharge regimes were 1190 mV (20 °C, 80% of nominal capacity) and 1181 mV (−20 °C, 20% of nominal capacity). The slope of the E–i characteristic was 0.60 Ω at 20 °C. These results support the use of "hybrid" Cd electrodes, provided that an economic design of the current collector, which would permit the same uniform current as in modern commercial electrodes, is found. No deleterious effect from the PTFE binder in the electrode mix was noted.

It can be seen from the impedance diagram for the sealed cell with a hybrid Cd electrode (Fig. 8) that the ohmic component of the impedance is 0.22 Ω, a value intermediate between those in Table 2; the PTFE apparently causes no marked increase in the ohmic resistance. A comparison of the three impedance diagrams (Figs. 6 - 8) shows that the high-frequency "semi-circle" is influenced both by the different composition of the Cd electrode mix and by the different current collector design. The behaviour of the cells with Cd hybrid electrodes is similar to those with lamellar electrodes, *i.e.*, the design of the current collector in this case plays a greater role than the composition (presence or absence of PTFE) of the negative electrode mix. The high-frequency "semi-circle" for the cell with PB electrodes (Fig. 7) apparently has a larger diameter than that for the other cells. Generally, this diameter is considered to be a measure of the charge-transfer resistance [7]. This implies that the charge transfer process in the Cd electrode is controlled by the design of the current collector. At low frequencies the Warburg linear portion, with a slope of 61° - 63°, is identical for hybrid and PB Cd electrodes. This high value is caused only by the diffusion control in the liquid phase of the electrode, and the different current collector design has no marked influence. It seems that the design of the current collector is very important for satisfactory operation of the sealed button cells, indicating the need for future experiments in the field.

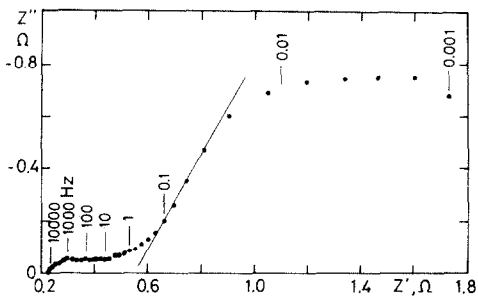


Fig. 8. Complex-plane impedance diagram for sealed button 225 mA h Ni–Cd cells with hybrid Cd electrodes. Frequency range 10 kHz - 0.001 Hz.

It should be stressed that our interpretation of the impedance diagrams was focused only on the *differences* between two types of sealed cell electrodes.

Conclusions

If PB electrodes are used in sealed button Ni–Cd cells containing only single positive and negative electrodes, there are no limitations during low-rate discharge, and the cells are economically attractive. During medium- and high-rate operation, however, the cell performance is limited by a high internal resistance, which is probably caused by the present design of the current collector of the PB Cd electrode rather than by the presence of PTFE in the electrode mix. The impedance measurements confirmed that the difference between PB and lamellar Cd electrodes is mainly ohmic in character. At low frequencies, however, a diffusion limitation has been found in cells with PB Cd electrodes.

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