

PLASTIC-BONDED ELECTRODES FOR NICKEL-CADMIUM ACCUMULATORS.

V. INFLUENCE OF THE CURRENT COLLECTOR AND MECHANICAL COMPRESSION ON THE CURRENT CARRYING CAPABILITY OF THE NICKEL OXIDE ELECTRODE

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Summary

Plastic-bonded nickel oxide electrodes, prepared by rolling a mixture of active material, conductive component and poly(tetrafluoroethylene), were subjected to high rate discharge cycling at 100 mA/cm^2 and to an accelerated cycling regime at 20 mA/cm^2 . The number of cycles, the position of the discharge curve on high rate discharge, and the electrode impedance were found to depend on the quality and size of the collector surface and on the compression acting upon the electrode group in the cell.

Introduction

Alkaline accumulators with plastic-bonded electrodes have, by comparison with classical accumulators with pocket electrodes, a higher energy per unit mass and their production requires less labour. Their properties and method of manufacture have been described earlier [1 - 5]. The plastic-bonded electrode is not screened by a perforated sheet, hence it has a lower polarisation resistance than the pocket electrode and thus fills the gap between electrodes of the pocket and sintered types.

Since there is a tendency to use the accumulators with plastic-bonded electrodes in high-rate discharges also, the research and development on plastic-bonded nickel oxide electrodes (PB-Ni electrodes) has also been concerned with their behaviour during high-rate and deep discharges. Some

properties of the PB-Ni electrode observed during high-rate discharges, mainly the dependence of the course of the discharge on the type of current collector and quality of its surface, have been reported already [1, 4]. The present communication deals with the dependence of the discharge curve of the PB-Ni electrode at 100 mA/cm^2 , on the current collector and the compression under which the electrode operates, with the dependence of the cycle life during high-rate and deep discharge on the quality of the collector and the compression of the electrode group, and finally with the dependence of the number of cycles during accelerated cycling on the compression of the electrode group and the depth of the discharge.

Experimental

The method of manufacture of the electrodes and the method of basic measurements have been described earlier [1 - 5], hence, we indicate here only additional important data or differences in procedure.

The electrodes tested were prepared by rolling and subsequent pressing at 100 MPa of a mixture of the commercial Czechoslovak active material KBL (Lachema, Bohumín) and carbon black impregnated with poly(tetrafluoroethylene), or a mixture of KBL active material, graphite and PTFE, onto a current collector in the form of a nickel-plated steel mesh or a nickel-plated, perforated steel sheet. The theoretical capacity, C_t , of the KBL active material was 0.214 A h/g . The electrodes, of dimensions $4 \times 7.5 \text{ cm}$, contained 9 - 10 g of the active material, hence their theoretical capacity was 1.9 - 2.1 A h. They were assembled in a cell with two negative pocket or PB-Cd electrodes of the same dimensions. The separator was a polyethylene screen and a polyamide fabric. The electrolyte was aqueous KOH of 1.2 g/cm^3 density containing 20 g of $\text{LiOH} \cdot \text{H}_2\text{O}$ per litre. The electrodes were placed in the test cell either free or tightened by means of fillers inserted between the electrode group and the wall of the polyethylene casing. In some cells, the electrode group operated under a chosen compression. This was achieved by using a steel sheet, 0.6 - 0.8 mm in thickness, in which numerous tongues were cut and bent so as to form springs, or by using coiled springs. The compression was controlled by the width of the slot into which the compression element was inserted on the basis of the known dependence of the deformation with applied pressure.

Prior to testing, the electrodes were subjected to three formation cycles (5 h discharge, 10 - 15 h charge) [6]. They were then rapidly discharged at 100 mA/cm^2 (6 A per electrode) to a potential of -0.5 V against an Hg/HgO electrode in the same solution, separated from electrode with a Haber-Luggin capillary. The electrode potential was recorded on a pen recorder. The impedance of the cell, or of the electrode, was measured at 2.2 kHz at a current density of 6.6 mA/cm^2 , the voltage response being measured either on the cell or between the test and reference electrodes.

Subsequently, the electrodes were cycled by discharging at 100 mA/cm^2 to a cell voltage of 0.0 V and charging at about 3 mA/cm^2 for 15 h (150% C_t). During every 15th cycle, the discharge curve was recorded together with the course of the impedance. The number of cycles up to the drop of the electrode potential after 5 min discharge to below -0.3 V (Hg/HgO) was determined by interpolation between two test discharges.

On one electrode the dependence of the discharge curve on the compression under which it operated was measured. The PB-Ni electrode, together with the counter electrodes, was inserted into a polyethylene bag which served as the cell casing, the electrolyte was added, and the electrode system was compressed in a special device by means of four screws. The compression was measured with an electric tensometer. The electrodes were compressed at 82 kPa, subjected to formation cycles, and the discharge curve at 100 mA/cm^2 was recorded. At the same time, the time dependence of the cell impedance, Z , at 2.2 kHz was measured. The compression was kept constant during the discharge; in the subsequent cycle it was lowered, one curing cycle followed (5 h discharge, 15 h charge), and after charging to 150% C_t the discharge curve was recorded and so on. Decreasing the compression had a favourable effect on the reproducibility of the results and also caused more pronounced changes in the electrode behaviour during cycling (see below).

In addition, we measured the dependence of the cycle life of PB-Ni electrodes during accelerated cycling; charging at 17 mA/cm^2 and discharging at 20 mA/cm^2 to a final voltage of 1.1 or 0.9 V per cell, on the compression. The cell voltage was measured automatically during discharge, which was stopped by an electronic switch after reaching the end voltage. After about 50 cycles, a test discharge was carried out (also at 20 mA/cm^2 to 0.9 V per cell). The electrolyte was renewed after about 200 cycles. The cycle life of the electrode was defined by a decrease in its capacity to 32% C_t .

Results and discussion

The dependence of the discharge curve of the PB-Ni electrode at 100 mA/cm^2 during the first rapid discharge cycle on the type of collector is shown in Fig. 1. Galvanically-nickel-plated steel screens served as current collectors; their characteristics are given in Table 1. A discharge curve of a classical pocket NKS-type electrode (for Ni/Cd starter batteries) is shown for comparison. It is apparent that the shape of the discharge curve depends greatly on the type of collector and also there is an obvious correlation with the electrode impedance.

The discharge curves and impedances for the first rapid discharge cycle for PB-Ni electrodes with the same collectors, but whose surfaces had been suitably modified, are shown in Fig. 2. A smooth surface was obtained by electroplating the nickel; a fine, rough surface by metallizing with nickel in one layer; and a rough surface by metallizing in two layers. The surface roughening caused an increase in the collector-active material contact area,

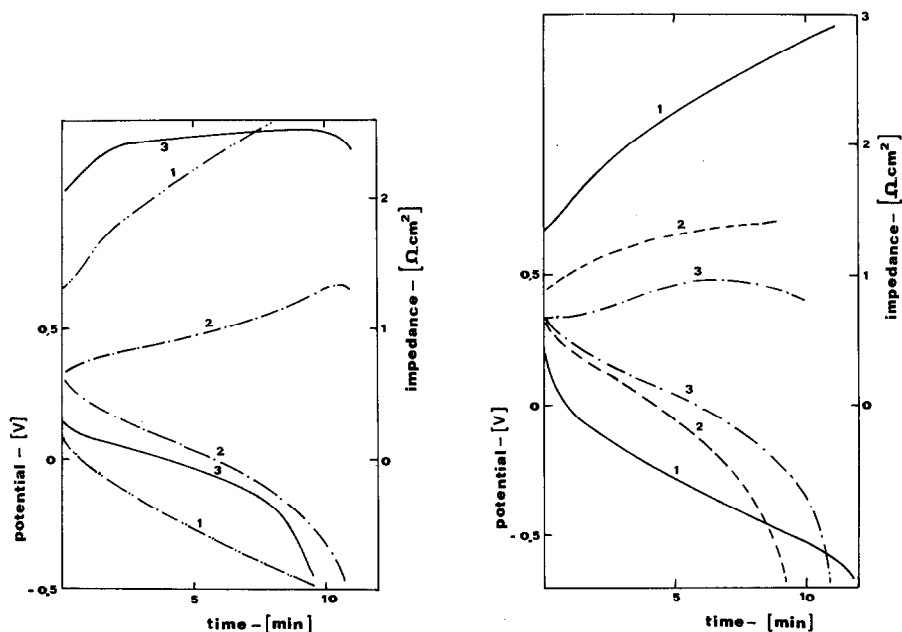


Fig. 1. Discharge (lower curves) and impedance (upper curves) characteristics at 100 mA/cm^2 during the first discharge cycle of PB-Ni electrodes with different current collectors and an NKS pocket electrode: 1. Collector type M (nickel plated); 2. Collector type F 0.8 (nickel plated); 3. pocket electrode.

Fig. 2. Discharge (lower curves) and impedance (upper curves) characteristics at 100 mA/cm^2 during the first discharge cycle of PB-Ni electrode with a type M collector: 1. nickel plated; 2. metallized once with nickel; 3. metallized twice with nickel.

TABLE 1

Collector				No. of cycles to the limit	
Type	Surface treatment	Wire dia. (mm)	Mesh size (mm)	Electrode packing	
				Loose	Close
M	Nickel plated	1.12	4.5	2 - 10	10 - 35
M	Nickel metallized	1.12	4.5	55 - 63	60 - 75
F 0.7	Nickel plated	0.71	2.8	25 - 45	40 - 55
F 0.8	Nickel plated	0.8	3.15	20 - 40	35 - 45
Pocket electrode				145 - 190	105 - 150

a decrease in the electrode impedance, and a shift of the discharge curve toward more positive potentials. Although this effect cannot be evaluated quantitatively, it seems that the changes in the electrode impedance and position of the discharge curve are due mainly to a change in the contact resistance between the collector and the active layer.

Discharge curves for a PB-Ni electrode with a type M collector, metallized with nickel, after various cycles of deep, rapid discharge at 100 mA/cm^2 are shown in Fig. 3. The electrode impedance increases with the number of cycles and the position of the discharge curve changes accordingly.

The number of cycles which could be obtained with the PB-Ni electrodes to the predetermined limit was dependent also on the method of cell assembly. In Table 1 the numbers of cycles attained, for electrodes with different collectors assembled in cells with either a loose or a close packing are given. In this case the compression was not determined; nevertheless, there is a significant difference in the number of cycles attained. We therefore made further experiments with controlled compression of the electrode group.

The dependence of the cycle life during deep, high-rate discharge on the compression of the electrode group is given in Table 2. With increasing com-

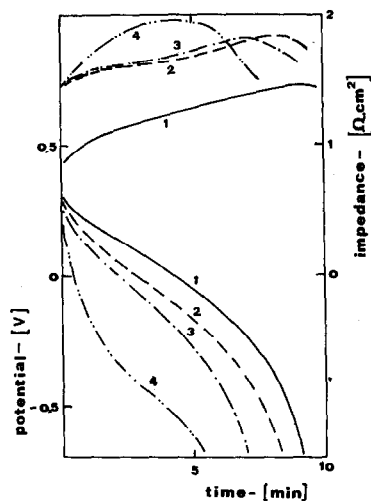


Fig. 3. Discharge (lower curves) and impedance (upper curves) characteristics at 100 mA/cm^2 for PB-Ni electrodes with a type M collector metallized with nickel after: 1. 1st cycle; 2. 22nd cycle; 3. 46th cycle; 4. 64th cycle.

TABLE 2

Collector		No. of cycles to the limit				
Type	Surface treatment	Compression (kPa)				
		1.6	6.5	15	65	88
M	Nickel plated	2	—	36	—	109
M	Nickel metallized	60	—	70	—	150
F 0.7	Nickel metallized	38	—	31	—	81
F 0.8	Nickel metallized	44	—	88	—	95
F 0.8	Nickel plated	—	51	—	56	—
Perf. steel sheet, Ni plated		—	40	—	—	80

pression, the cycle life approaches that of pocket electrodes (Table 1), for which no such dependence has been reported. Figure 4 illustrates this dependence for electrodes with a type M collector, either galvanically nickel-plated or metallized, and for an electrode with a type M collector and additionally pressed-in fine nickel gauzes as second, outer, collectors. This electrode is characterized by a pronounced maximum of the cycle life at a certain value of compression. We assume that this phenomenon occurs also with other types of collector, the optimum compression being dependent on the type and surface area of the collector.

Hence, it is obvious that the quality and magnitude of the contact between the collector and the active layer, or the contact resistance between the two, controls both the short-time behaviour and the cycle life of the PB-Ni electrode. The life can be influenced also, for example, by the quality of the contact between the active layer particles (hydrated nickel oxide and conducting component), which can be worsened by oxidation of the graphite or carbon black [7, 8]. A certain compression of the PB-Ni electrode is necessary to preserve a lasting, good contact between the collector and the active layer (low resistance of the path from the collector to the conducting component and electroactive particles), as can be deduced from the observations we have mentioned. The PB-Ni electrode described has an elastic binding skeleton which responds to the volume changes of the active layer apparently causing a gradual loss of contact; the compression acts so as to suppress these volume changes [8]. This interpretation is supported by the observed gradual increase of the electrode impedance during the tests and by the related shift of the discharge curve during rapid discharge (Fig. 3). The rate of these changes and the cycle life depend on the compression, but the correlation between the impedance and the position of the discharge curve is only qualitative.

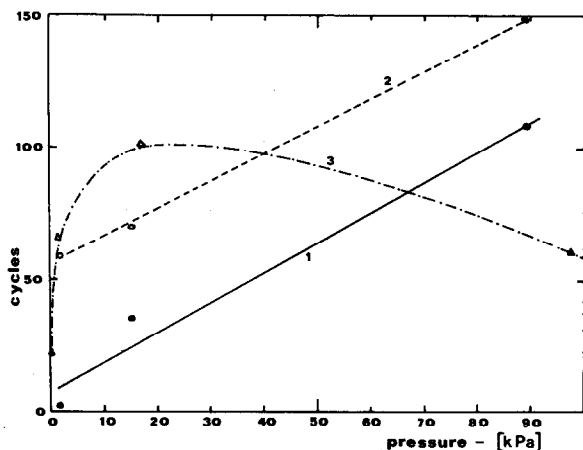


Fig. 4. Cycle life as a function of compression at 100 mA/cm^2 discharge rate for PB-Ni electrodes with a type M collector. The collector was: 1. nickel plated; 2. metallized with nickel; 3. nickel plated with additional nickel gauze.

Discharge curves for a PB-Ni electrode, with a galvanically-nickel-plated type F 0.8 collector, at various compressions are shown in Fig. 5. The favourable influence of the compression on the level of the discharge curve is still more apparent from Fig. 6, where the dependences of the electrode potential and cell impedance in the first and fifth minute of discharge at 100 mA/cm^2 are shown. Both these characteristics have a flat maximum at 50 - 100 kPa. The interpretation is analogous with the dependence of the cycle life on the compression.

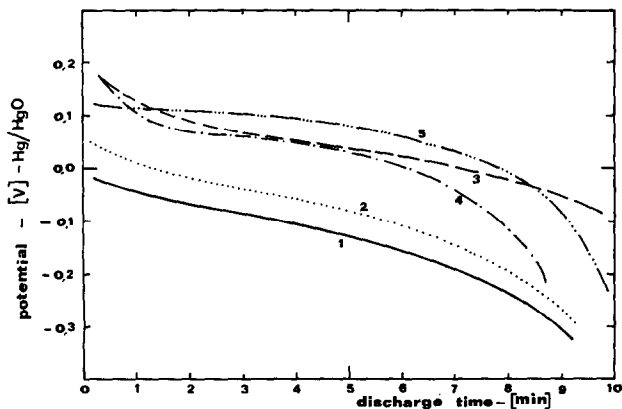


Fig. 5. Discharge characteristics at 100 mA/cm^2 for PB-Ni electrodes with type F 0.8 (nickel plated) collectors at different compressions: 1. 16 kPa; 2. 33 kPa; 3. 49 kPa; 4. 65 kPa; 5. 82 kPa.

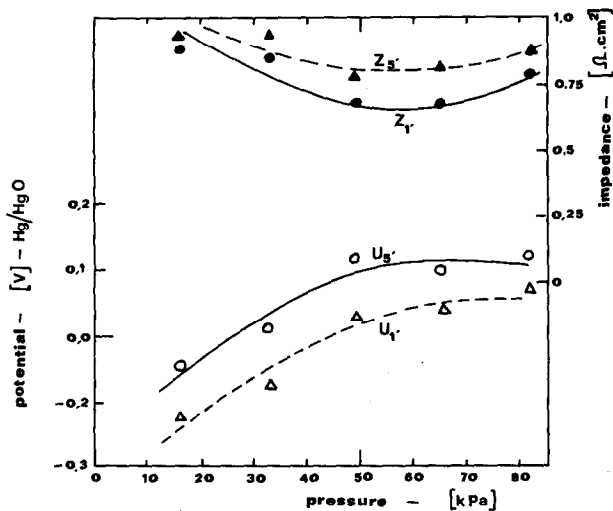


Fig. 6. Potential, U , and impedance, Z , of a PB-Ni electrode with a type F 0.8 (nickel plated) collector at 100 mA/cm^2 discharge rate as a function of compression at different discharge times: Z_1 , impedance after 1 min; Z_5 , impedance after 5 min; U_1 , potential after 1 min; U_5 , potential after 5 min.

The definite dependence of the PB-Ni electrode characteristics on the compression during deep, high-rate discharge was supplemented by similar observations during accelerated cycling with discharges at 20 mA/cm^2 , which were stopped either at 1.1 V or at 0.9 V per cell. The results are summarized in Table 3; the favourable influence of the compression on the cycle life is again obvious. A comparison with the earlier mentioned test is difficult since, in that case, the charge delivered by the electrode in every cycle was kept constant. The depth of discharge has no marked effect in the case of electrodes under compression, but with electrodes in a loose arrangement the deep discharge seems to be rather favourable. With pocket electrodes, no influence of compression on cycle life was observed, but the latter decreased with increasing depth of discharge, in accord with the literature [9]. This different behaviour is obviously due to the fact that the perforated metal envelope ensures good contact with the active mass, independent of the compression of the electrode group, whereas the PB-Ni electrode with its elastic skeleton is rather sensitive to compression.

It follows that satisfactory operation of the PB-Ni electrode is conditioned by a well-developed collector surface to optimize its contact with the active layer and, at the same time, by compression of the electrode group. These findings constitute the subject of our patent applications [10, 11].

TABLE 3

Compression (kPa)	Cut-off voltage (V)	No. of cycles to the limit		
		Plastic bonded electrodes		Pocket electrodes
		Collector F 0.8 type	Collector M type	
0	1.1	280 ± 2	240 ± 40	600
49	1.1	560 ± 5	540 ± 30	650 ± 150
0	0.9	212 ± 2	190 ± 5	600 ± 200
49	0.9	590 ± 40	555 ± 5	450 ± 40

Conclusions

The impedance of PB-Ni electrodes depends on the size and quality of the contact between the collector and the active layer as well as on the compression under which the electrode group operates. A correlation exists between the electrode impedance and the position of the discharge curve during high-rate discharge. The character and size of the collector surface and the compression of the electrode group also determine the cycle life of the PB-Ni electrode during cycling with deep, high-rate discharges (100 mA/cm^2), as well as during accelerated cycling at 20 mA/cm^2 . No dependence of the cycle life on the depth of discharge was found during accelerated cycling of the PB-Ni electrode.

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