PLASTIC BONDED ELECTRODES FOR NICKEL–CADMIUM ACCUMULATORS
I. CADMIUM ELECTRODE

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Summary

Plastic bonded cadmium electrodes of outstanding electrochemical properties, capable of replacing the commercial pocket-type electrodes of vented Ni–Cd batteries, were produced by rolling the active mass, blended with powdered plastic polymer, onto a metallic current collector at normal temperature.

Introduction

Increasing the volume production of electrochemical current sources forces the manufacturer to increase both the efficiency of the manufacturing process (to lower the production costs and to save material) and the specific electrochemical parameters of the batteries. This is exemplified by the production of Ni–Cd accumulators. Two types of electrodes are mainly manufactured: the pocket-type and the sintered type. Both types help to solve some of the problems associated with the accumulators, but other problems become even more accentuated. For example, sintered electrodes result in high electrochemical parameters (energy per unit weight and volume, performance, etc.) at the expense of high production and material costs. The pocket-type electrodes are, by contrast, cheaper and less difficult to produce, but their electrochemical parameters are generally lower.

Nickel–cadmium accumulators, both of the vented and sealed type, occupy a firm position among the electrochemical current sources owing to their long life. Their high production and material costs, however, represent a distinct drawback in comparison with lead–acid batteries. Therefore, research and development laboratories aim to overcome these important disadvantages. The question is whether innovation of existing types of battery is at all possible and practical, and in what respect is it to be expected. An

economical advantage can be achieved mainly by increasing the life expectancy of the system together with saving of material and labour, for example, by introducing the manufacture of plastic bonded electrodes. This would result in a saving of both material and labour. An analysis at the beginning of our work showed the advantages of plastic bonded electrodes in some directions (see Table 1).

The concept of plastic bonded electrodes for secondary cells is not new. The preparation of such electrodes is the subject of a number of patents and publications [1], and is essentially based on the following techniques: (1) pressing, (2) pressing and sintering, and (3) rolling a mixture of the active material with the plastic binder. All these methods were used with various plastic binders [1].

Plastic bonded, porous electrodes are two-phase electrodes whose solid phase consists of two components, the active material and an organic polymer. The former exists in two forms, the reduced and the oxidised form (e.g., Cd and CdO). The organic polymer must be resistant to the electrolyte and its porous skeleton must ensure sufficient electrode mechanical strength during its cycling. These demands are met mainly by fluoroplasts (PTFE) and polyethylene. With respect to the conductivity of the porous electrode, it is necessary to use fibrous particles of the plastic binder [2]: isolated fibres present practically no hindrance to current conduction, and their presence, even at a low concentration, makes a significant contribution to the electrode strength. The fibres are equivalent to chains of plastic particles of maximum strength and minimum volume.

Theoretical considerations led us to the following conditions for plastic bonded cadmium electrodes:

(1) Fine particles of the active material and plastic binder, whose dimensions are negligible compared with the thickness of the electrode;

(2) uniform distribution of the binder;

(3) uniform thickness and porosity (condition of macrohomogeneity);

(4) sufficient conductivity of the solid phase;

(5) chemical and mechanical stability of the solid phase.

Although it is difficult to fulfil all these conditions, they were fulfilled to a considerable extent with our plastic bonded cadmium electrodes.

Experimental

Materials

The commercial active material of the type KANS (Lachema Brno, Č.S.S.R.), used in manufacturing Czechoslovak pocket-type electrodes, served as active material in the present work. It is essentially a mixture of cadmium oxide and iron oxide. Its theoretical capacity is $C_t = 0.30$ A h/g as given by the cadmium content.

The plastic binder was either poly(tetrafluoroethylene) (PTFE), type Fluon CD-1 (ICI, Great Britain) or powdered polyethylene (PE), type Hostalene Gur (Hoechst, F.R.G.), m.p. 170 °C.

TABLE 1

Comparison of parameters of classical and new types of Ni–Cd accumulators

Accumulator	Electrode type	Coefficient of labour consumption	Price index	W h/kg	W h/dm^3	W/kg	Life (number of cycles)
Starter	pocket	16	3.7 - 4	18	34	80	750
Traction	pocket	7	3.7 - 4	14	38	50	750
	sintered	unknown	7	25	47	200	750
Starter	plastic bonded	still undetermined	still undetermined	18*	34*	100*	800*

*Preliminary results (this Institute and Pražská akumulátorka) obtained during spring 1979; details will be published later.

Current collectors were: (a) expanded steel sheet of 0.2 mm thickness, (b) steel net (diameter of wire 0.7 - 0.8 mm, mesh 3 mm), (c) perforated steel sheet (deep-drawn, 0.2 mm in thickness, height of perforation 2.3 mm).

Preparation of electrodes

A mixture of 90 - 95 weight percent. KANS material and 10 - 5 weight percent. plastic, suitably wetted with a plasticizer (*e.g.*, ethyl alcohol), is spread onto the current collector by one step rolling at normal temperature [2]. The flow of the mixture during rolling is positively influenced by a suitable particle shape and size of the plastic binder which is wetted with the plasticizer. The thickness of the electrodes depends on the chosen collector and on the distance between the rolls of the rolling machine; it is only slightly reduced during the last phase of the preparation — pressing — since the pressure is only up to 10 MPa (100 kg/cm^2). The electrodes thus prepared have a uniform porosity and thickness and are mechanically resistant. The whole method of electrode preparation is given schematically in Fig. 1.

Electrochemical measurements

These have been described earlier [2]. They include life tests of laboratory electrodes of dimensions 4 × 7.5 cm on an accelerated cycling regime (114 min charging, 66 min discharging, both at a current density of 15 mA/ cm^2) (the minimum utilization of the active material was $\beta \approx 28\%$ C_t), measurement of current–voltage characteristics and current carrying capacity, discharge tests at 1 - 2 and 5 h rate, tests of electrodes and cells according to
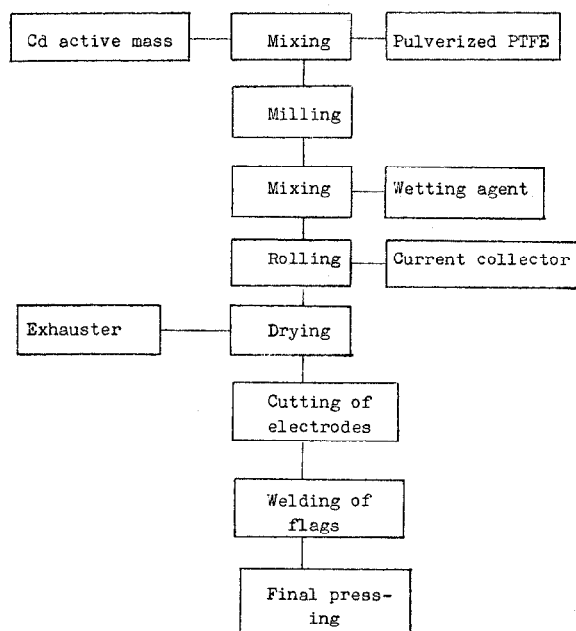

Fig. 1. Flow chart for manufacturing plastic bonded cadmium electrodes.

ČSN 364350 (corresponding to DIN 40764), rapid discharge at 100 mA/cm^2, starter shock (electrical), and measurement of electrode impedance as voltage response to a sine-wave signal of 6.6 mA/cm^2 intensity and 2 200 Hz frequency between the electrode terminal and the tip of a Luggin capillary with an Hg/HgO reference electrode. The electrolyte was a solution of KOH of 1.2 g/cm^3 density. All electrode potentials are referred to an Hg/HgO reference electrode in the same electrolyte.

Results and discussion

The results of life tests [3] of three types of plastic bonded, laboratory made, cadmium electrodes are summarized in Table 2. It is seen that the capacity of all the electrodes decreased up to about the 700th accelerated cycle. During further cycling, this decrease becomes much less marked. The marked decrease of the capacity can be attributed to a gradual loosening of a certain number of the bonds formed by the plastic binder resulting in a lower cohesion of the electrode; in this way some particles of the active material lose contact with each other and cease to function. The slow decrease of the capacity can be attributed to recrystallization of the active material.

The life of the electrodes was determined according to ČSN 364350 and also in a real Ni–Cd cell of 42 A h capacity assembled from plastic bonded negative and commercial pocket-type positive electrodes [4]. The cells were subjected to a number of cycles consisting of 4 h charging at 10.5 A and 2 h discharging at 12.6 A with a periodical capacity test. For comparison, cells assembled with commercial positive and negative pocket-type electrodes approached the limit of the life test, 125 mA h/g, after 740 cycles, whereas the cells with plastic bonded Cd electrodes were still well above this limit after 1 000 cycles (Fig. 2).

TABLE 2

Mean capacities of plastic bonded laboratory cadmium electrodes

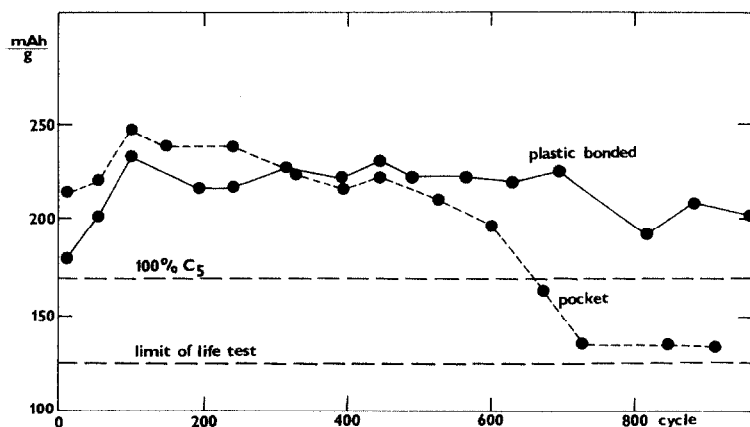| Cycle no.	Percent. theoretical capacity in discharge test					
	10% PTFE		5% PTFE		2.5% PTFE + 10% PE	
	1 - 2 h	5 h	1 - 2 h	5 h	1 - 2 h	5 h
50	—	—	—	—	70	78
150	72	83	70	83	—	—
600	—	—	62	70	59	70
700	56	67	—	—	—	—
1 000	57	66	61	70	—	—
1 650	53	62	57	58	53	58
2 009	52	62	53	—	53	—
2 058	—	—	50	—	50	—
2 500	54	60	—	—	—	—
2 889	51	—	—	—	—	—

Fig. 2. Cycle life of NKS 42 cells. Grams are related to KANS.

Current–voltage characteristics of the electrodes measured during the life tests showed a slope of about 1 - 2 ohm cm^2, which is less than with commercial pocket-type electrodes where we have obviously to deal with the screening effect of the perforated sheet, which hinders the transport of ions and current. With plastic bonded electrodes, the active mass is not screened and its current carrying capability is better [3] (Fig. 3).

The specific capacity of the electrodes being investigated was measured in the previously mentioned 42 A h Ni–Cd battery and referred to 1 g of the KANS material at 25 °C and $i = 1.8$ mA/cm^2 (see Fig. 4). We obtained 235 mA h/g for plastic bonded electrodes and 247 mA h/g for pocket-type electrodes. At a current density of 75 mA/cm^2, however, there is a difference in favour of the plastic bonded electrodes (157 and 134 mA h/g). The situation is similar for $i = 75$ mA/cm^2 at −20 °C (103 and 90 mA h/g). The open surface of the plastic bonded electrodes results in a better utilization of the
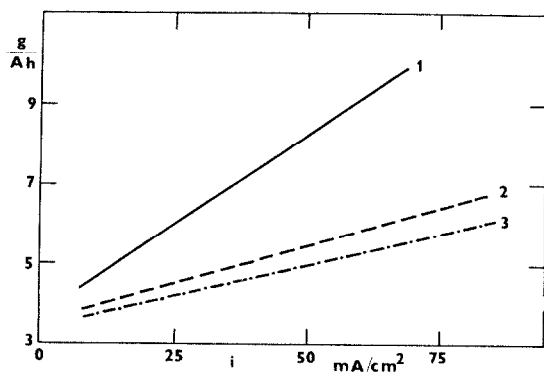

Fig. 3. Comparison of current carrying capability of plastic bonded with pocket-type cadmium electrodes. 1, Pocket electrode; 2, plastic bonded (10% PTFE) electrode; 3, same but 5% PTFE. Grams are related to KANS.
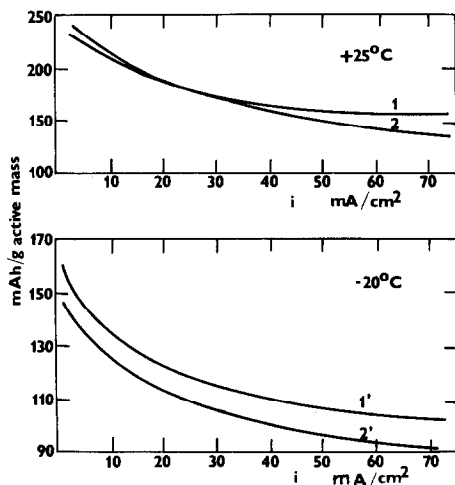
Fig. 4. Comparison of specific capacity of cadmium electrodes in NKS 42 cells with plastic bonded and pocket electrodes. 1, 1', plastic bonded; 2, 2', pocket electrodes.

active material as compared with the pocket-type electrodes at higher current densities both at normal and low temperatures. Hence, with plastic bonded electrodes it would be possible to save about 5.5% cadmium in high rate applications.

In the practical use of the electrodes, their volumetric capacity (A h/cm^3) is important. For electrodes of the commercial 15 × 18 cm size, the volumetric capacity of plastic bonded Cd electrodes is about 20 - 25% higher than pocket-type electrodes.

We also studied the influence of the PTFE content and the depth of discharge of the electrodes on their life [5]. For this purpose, small labora-tory electrodes (4 × 7.5 cm) with an expanded metal collector were cycled on an accelerated regime. The depth of discharge was 38 - 44% C_t. The results are shown in Fig. 5. In the range 5 - 10% PTFE within the indicated conditions, no essential differences in the attainable capacities of the elec-trodes were observed. The current–voltage characteristics measured during these tests showed slopes in the range 0.8 - 1.2 ohm cm^2, which hardly changed during the whole life test. Hence, it follows that the stability and life time of the studied electrodes are ensured by the addition of only 5% PTFE to the active material.

The capacities of electrodes with different types of collectors (i = 15 mA/cm^2) are compared in Table 3. The data in parentheses refer to capacities during discharge at 7 mA/cm^2. It is seen that after 800 cycles the capacities reached a steady value of 50 - 53% C_t, which is comparable with electrodes containing an expanded metal collector. After 700 cycles the electrodes with a perforated sheet collector showed lower values of the slope of the current–voltage characteristic (0.65 - 0.80 ohm cm^2). It is noteworthy that even deep discharge during accelerated cycling (53 and 57% C_t) has practically no influence on the capacity attained by the electrodes.
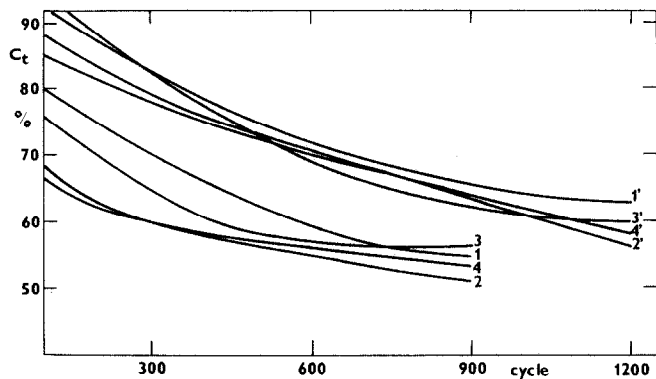
Fig. 5. Life of plastic bonded cadmium electrodes with different contents of binder, discharged to different depths of discharge (β) during accelerated cycling. 1, 2, 5% PTFE; 3, 4, 10% PTFE; 1, 3, β = 38% C_t; 2, 4, β = 44% C_t; 1 - 4 test discharge at 11 - 13 mA/cm^2; 1' = 4' test discharge at 6 mA/cm^2.

TABLE 3

Life tests of plastic bonded cadmium electrodes with different current collectors

Separator type	Collector	Depth of discharge (%)	Percent. theoretical capacity attained in cycle no.					
			67	200	354	400	600	800
	perforated Fe sheet	42	—	60 (68)	—	54 (66)	51 (67)	53 (67)
	perforated Fe sheet	53	—	56 (70)	—	51 (65)	49 (64)	50 (65)
UMU	iron net	57	60	51	48	—	—	—
MU	iron net	57	84	63	58	—	—	—

The advantages of the perforated sheet collector are apparent also from the data in Table 4 showing the results of capacity tests during rapid discharge (130 mA/cm^2) and tests at low temperatures. The life time of the electrodes is practically independent of the type of the collector, but from the technological point of view the use of a steel net is preferable.

An important property of the electrodes is their resistance to deep (to zero V against Hg/HgO) and rapid (i = 100 mA/cm^2) discharge, which was the main problem with the plastic bonded nickel oxide electrode. The life time of the electrode in this regime can be characterized by the number of cycles after which the electrode potential drops, at the end of the 5th minute, below —0.5 V. With plastic bonded laboratory cadmium electrodes with a net collector, 80 ± 1 rapid discharge cycles were attained, and in the case of a perforated sheet collector this figure was 96 ± 16, which is satisfactory. In the latter case, the resistance of the electrodes to rapid deep discharge depends on the pressure exerted upon the electrode during discharge. Electrodes pressed at 15 kPa attained 104 deep discharge cycles to a given limit, while those pressed at 90 kPa attained 120 cycles.

TABLE 4

Capacities attained by laboratory cadmium electrodes during accelerated cycling

Collector	Separator	Percentage theoretical capacity attained in cycle no.			
		800, 25 °C 130 mA/cm^2	32, −25 °C 18 mA/cm^2	650, −29 °C 18 mA/cm^2	981, −26 °C 18 mA/cm^2
Expanded Fe sheet	UPUP	22	42	29	31
Perfor. Fe sheet	UPUP	39	46	30	37
Expanded Fe sheet	UD	38	43	32	31
Perfor. Fe sheet	UD	41	44	30	34
Fe pocket	T	10	34	–	20

While testing the resistance of the electrodes to rapid and deep discharge, neither a gradual shifting of the discharge curves toward positive potentials nor an increase of the electrode impedance was observed up to the 118th cycle (as long as the electrode was capable of functioning) (see Fig. 6). The ageing of the electrode during this regime is accompanied by a gradual decrease of the electrode capacity on rapid discharge, which accelerates the undesirable recrystallization of cadmium.

Laboratory-type, plastic bonded cadmium electrodes with a perforated sheet collector were subjected to so-called starter shocks, *i.e.*, they were periodically loaded with 100 mA/cm^2 pulses of 10 s duration at 30 s intervals. Even after 100 such shocks the potential of the loaded electrode did not drop below —0.78 V (Hg/HgO).

It is, hence, apparent that plastic bonded cadmium electrodes are suitable for Ni–Cd starter batteries. However, other types of alkaline batteries containing thicker electrodes (for traction, lighting, etc.) are also of interest. Electrochemical tests of plastic bonded cadmium electrodes of different thickness with net collectors, discharged at the current shown to zero V (Hg/HgO), are summarized in Table 5. The capacities attained with thicker electrodes are also very high during slow discharge (about 90% C_t during initial cycles), evidence of the good utilization of the active material and good current conduction through the net collectors.

Conclusions

Plastic bonded cadmium electrodes prepared by rolling a mixture of the active material with a plastic binder onto a current collector meet the require-
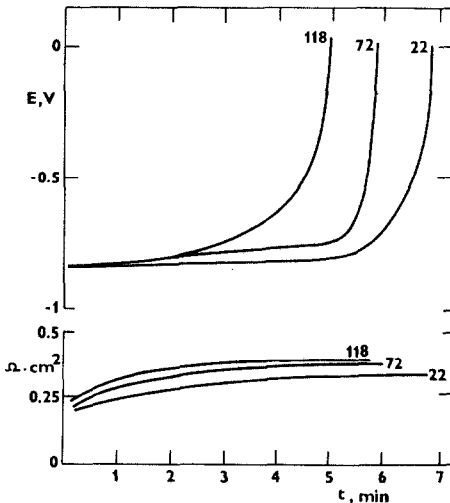

Fig. 6. Potential dependence of a plastic bonded cadmium electrode and its impedance as a function of discharge time after different numbers of cycles during deep and rapid discharge. Numbers of cycles are given in the Figure.

TABLE 5

Capacities attained by plastic bonded laboratory cadmium electrodes of different thicknesses

Diam. of wire in net (mm)	0.50	0.63	0.80	1.12	1.12
Electrode thickness (mm)	1.06	1.40	1.68	2.15	2.80

Discharge current (mA/cm^2)	Percent. theoretical capacity				
7.4	87	90	—	—	—
10	—	—	91	90	—
18.5	—	—	—	—	85
37	69	75	83	81	65
100	59	68	60	65	54

ments for electrodes for secondary batteries: high life time (over 1 000 charge–discharge cycles), high current carrying capability (higher than with commercial, pocket-type electrodes), and outstanding resistance against deep and rapid discharge. A content of 5% PTFE in the rolled mixture is sufficient. A wire net as current collector is most advantageous from the technological point of view. In the large scale production of these electrodes, savings of labour and cadmium and steel can be expected. Since a moderately wetted mixture of the active material and plastic is used in the manufacture, the dustiness and, hence, the content of toxic cadmium in the air is substantially decreased.

References

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