OPTIMISATION OF ACTIVE MATERIAL FOR POSITIVE ELECTRODES OF Ni–Cd ACCUMULATORS*

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Summary

The conditions for the preparation of the active material for positive plastic-bonded electrodes of Ni–Cd alkaline accumulators were investigated in order to obtain the maximum discharge capacity. It was shown that nickel hydroxide precipitated from a neutral medium is superior to that precipitated from a strongly alkaline medium. This, together with the choice of a conducting component and other conditions of preparation served as a basis for obtaining an active material which does not require an additional doping, *e.g.*, with cobalt, its discharge capacity being comparable with the "classical" active materials doped with cobalt.

Introduction

The known methods of preparation of active material for positive electrodes of alkaline Ni–Cd accumulators have one feature in common [1 - 3]: a solution of nickel salt (sulphate) is gradually added to a sodium hydroxide solution at a temperature between 40 °C and the boiling point. The precipitate of $Ni(OH)_2$ is gradually washed to remove soluble impurities, then dried, ground, mixed with powdered graphite, and homogenised. Graphite is sometimes added to the solution of NaOH, so that the precipitate is formed in its presence and partly on the particles of graphite [4].

The discharge capacity of the active material thus prepared is relatively poor and with the use of coarse graphite (flakes) its electrical conductivity is not good, having a negative effect on the capacity obtained on discharge at high current densities. It is therefore necessary to treat the active material in some way to improve its performance. This was referred to by some authors as "activation" [3, 5], although the term "doping" is, in our opinion, more

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suitable. This consists in adding certain materials, usually cobalt compounds. Cobaltous sulphate is already added sometimes to the starting $NiSO_4$ solution, but wetting of the dried active material with a solution of $CoSO_4$ and subsequent alkalization is a more efficient procedure [5]. Thus, both the capacity and the cycle life of nickel oxide electrodes are increased [1].

Doping with cobalt salts is economically unattractive since cobalt is much more expensive than nickel. Therefore, it has been proposed that lithium and barium [3], which, however, are not as efficient, should replace cobalt. The Czechoslovak active material KBL (Lachema, Bohumín) [2, 3], which is doped with hydroxides of lithium and barium, should theoretically give a charge of 214 A h/kg during conversion of Ni(III) to Ni(II). However, in practice, the attained values are substantially lower, although the oxidation state of nickel in a charged electrode is somewhat higher than 3, corresponding to a nonstoichiometric oxide NiO_y, where y lies between 1.5 and 1.8 [6, 7]. Hence, it seemed worthwhile to study the possibilities of the development of an improved nickel oxide mix with a higher specific capacity.

Basic considerations

The electrochemical and crystallographic properties of nickel hydroxides have been studied in detail [6 - 10]. The electrochemical behaviour of solids ("depolarizers") such as nickel oxides, depends, however, not only on their crystallographic structure, but still more on the concentration of defects in their crystal lattice, admixtures of foreign ions, and water; these favour the rate of diffusion of protons, which, in turn, is essential for an easy electrochemical reduction [11]. Preparations with a highly developed surface area usually have the highest concentration of defects (the case of extremely small and imperfect crystals).

It may be assumed that the most suitable method of nickel hydroxide preparation for accumulators consists of the slow precipitation of a nickel salt with alkali hydroxide to favour the formation of the more active alpha modification [8]. Even if the latter changes more or less by a topochemical reaction in the course of further operations to the beta modification, its crystal structure will be disordered (the reaction proceeding at conditions far from optimum) and thus it will favour the diffusion of protons.

In the preparation of electrodes, it is further necessary to shorten as far as possible the charge carrier paths in the nickel hydroxide particles. Hence, the total contacting area between the nickel hydroxide and the conducting component must be as large as possible, i.e., both these components must be highly dispersed. From the theoretical point of view, the distribution of electric current in the electrode is to some extent analogous to the distribution of current in an electrical network, where there is a condition of minimum voltage loss with minimum consumption of material for the leads: the main line is a thicker wire, and the branch lines to the electrical appliances are

relatively thin. Accordingly, it may be assumed that the conducting component should contain particles of medium size, ensuring good electrical conductivity of the electrode as a whole, together with very fine particles which ensure the conduction of electrons even to the finest nickel hydroxide particles. These considerations led us to add acetylene black to powdered graphite and to precipitate the nickel hydroxide in the presence of a suspension of the conducting component.

Experimental

The electrochemical activity of active material samples was expressed in percent. of the theoretical capacity, C_t, and was measured by discharging test electrodes prepared as follows. A homogenised mixture of 2.40 g of the active material and 0.27 g of powdered Teflon (Fluon CD-1, ICI, Great Britain) was pressed at 100 MPa in the form of a disc of 31 mm dia. and 1.8 - 2.0 mm thickness together with a nickel net on each side (1.08 mm mesh). This disc was wrapped in a fine Ni gauze (0.10 mm mesh), serving as current lead, and in a polyamide separator and placed in a test cell with a Ni foil counter electrode. The electrodes were pressed in the cell at about 50 kPa by means of a steel spring and a spacer. The cell was filled with a solution of 1.2 g/cm^3 density KOH and the electrode charged at 50 mA for about 16 h, then discharged at 70 mA and the electrode potential against Hg/HgO in the same solution recorded. The time at which the potential reached zero volts was denoted as the discharge time.

The nickel content (as Ni(OH)$_2$) of the active material samples was determined by dissolving in diluted HCl (1:3), converting to a triethylamine complex and titrating with ethylenediaminetetraacetic acid with murexide as indicator (giving a violet coloration).

The specific surface area was measured by adsorption of nitrogen according to the simplified BET method of Haul and Dümbgen [12].

The starting material was technical grade NiSO$_4 \cdot$7H$_2$O (Lachema, ČSSR) containing 20.21% Ni, 0.008% Ca, 0.024% Mg, and 0.29% Co; the iron and copper content was below 0.01%. Acetylene black, P 1042, was from Stickstoffwerke Piesteritz (GDR). Graphite CR-12 of mean particle diameter about 12 μm was a product of Rudné doly, Týn nad Vltavou, ČSSR. The method of preparation of the active material forms the subject of our patent [15].

Results

Comparative experiments revealed, in turn, the following facts (the values of the activity were always obtained from 3 - 5 charge–discharge cycles).

Influence of precipitation temperature

An elevated temperature (up to the boiling point) favours the formation of a more easily filterable precipitate of $Ni(OH)_2$. The activity of the material precipitated at, or near to the boiling point was practically the same as that of the material precipitated at room temperature. In the former case, comparative tests showed values several percent. higher (98 - 89 - 88% C_t in the first 3 cycles) than in the latter case (90 - 84 - 84% C_t), which can be attributed to the fact that the product precipitated at boiling point can be more easily washed with water (see below).

Influence of ions

Products obtained by precipitating from a solution of $Ni(NO_3)_2$ with alkali hydroxide showed a substantially lower activity than those precipitated from an $NiSO_4$ solution, hence we preferred $NiSO_4$ in further experiments. The divalent SO_4^{2-} anions obviously facilitate precipitation by their adsorption, thereby lowering the quantity of adsorbed impurities on the nickel hydroxide, analogous to the case of $Fe(OH)_3$ [13]. On the other hand, replacement of KOH by NaOH had no effect on the quality of the precipitate.

Influence of pH

Comparative experiments in which the $Ni(OH)_2$ precipitate was obtained either from an alkaline medium (by adding a solution of $NiSO_4$ to KOH) or from a neutral medium (by adding a solution of KOH to $NiSO_4$) substantiated our expectations (*cf.* "Basic considerations"): The activity of electrodes in the latter case was appreciably higher (84 - 90% C_t) than in the former case (52 - 60% C_t), other conditions being equal (about 30% of conducting component composed of 4 parts graphite CR-12 and 1 part acetylene black).

Influence of washing

The precipitate of $Ni(OH)_2$ must be washed with hot distilled (or deionized) water to remove adhering or adsorbed electrolytes (mainly K_2SO_4). To obtain a filterable precipitate, the solution of KOH is added to the solution of $NiSO_4$ until the supernatant liquid is alkaline (*e.g.*, pH 12). After filtering, drying, and grinding, the product is washed on a suction filter until the filtrate shows no reaction with a $BaCl_2$ solution. Imperfect washing results in a decreased specific surface area (under 50 m^2/g) and in a lowered activity (*e.g.*, only 15 - 30% C_t).

Influence of conducting component

The conducting component was mostly CR-12 powdered graphite mixed with 20% acetylene black; this mixture gave the best results. With a higher content of the black, the material with added Teflon cannot be pressed to form a tablet (*e.g.*, 3 parts graphite and 2 parts black); at a lower content (9:1), the activity of the electrode material is lower (Table 1). The

TABLE 1

Influence of conducting component on electrode activity

Conducting component	Electrode activity ($\% C_t$)	Ni(OH)$_2$ content (%)
Graphite CR-12	59 - 64	71.8
CR-12 + black 9:1	79 - 84	59.8
CR-12 + black 4:1	84 - 90	59.8
Graphite + flakes	81 - 84	68.0

TABLE 2

Relation between content of Ni(OH)$_2$, electrode activity, and specific capacity

Ni(OH)$_2$ cont. (%)	Activity ($\% C_t$)	Sp. capacity (A h/kg), mean
59.8	84 - 90	149
66.3	88 - 89	170
71.6	77 - 86	173
76.5	80 - 83	180

last line in Table 1 refers to powdered graphite with graphite flakes, which is similar to the conducting component recommended by some manufacturers. Since the active material was homogenized in a mill in the final stage, the graphite flakes were crushed (original size 300 - 400 μm) and the resulting graphite particles were found by sedimentation analysis to be in the range 5 - 100 μm. Also, this example shows that the presence of finer particles in addition to the larger ones is favourable for the activity of the material. The graphite flakes contribute little to the conductivity of the pressed disc electrode as compared with powdered graphite; this was revealed by direct measurements on dry, pressed tablets.

The content of the conducting component can be decreased to 20 - 25% without affecting the electrode capacity; however lowering below 20% is not desirable. For example, some results obtained with a 4:1 mixture of CR-12 graphite and carbon black are given in Table 2. The specific capacity in A h/kg increases with the content of Ni(OH)$_2$ up to a certain limit given by the minimum necessary content of the conducting component, so that active materials containing 80% or more of Ni(OH)$_2$ have a significantly lower specific capacity.

Influence of doping

The active material can be doped with cobalt according to Winkler [5], i.e., by wetting with a $CoSO_4$ solution and subsequent alkalization. It was found during our experiments that materials with a relatively low activity are considerably improved by this procedure, whereas materials with a high

TABLE 3

Influence of doping with cobalt on activity and specific capacity of electrodes

Active material	Activity ($\% \, C_t$)	A h/kg (mean)	Conducting component (% approx.)
Prior to doping	88 - 89	170	30
After doping	100 - 105	188	30
Prior to doping	80 - 83	180	20
After doping	89 - 92	200	20

TABLE 4

Influence of drying temperature on activity of electrode material

Temp. (°C)	20	50	70	90	110	130
Activity ($\% \, C_t$)	78 - 81	80 - 83	72 - 74	63 - 75	67 - 77	72 - 81

activity (near to 90% C_t) show a less pronounced improvement. It seems that cobalt hydroxide behaves as an electrocatalyst, making the electron transfer more reversible [16]. Thus, it is possible to obtain a capacity as high as 100 - 105% C_t from electrodes containing 3% Co as $Co(OH)_2$. (*Cf.* Table 3.)

Influence of drying temperature
The washed, active material is best dried at a temperature near to 50 °C; drying at lower temperatures is too time-consuming and higher temperatures favour structural changes of the product. Activities of non-doped materials dried at different temperatures are given in Table 4.

Influence of specific surface area
A weak correlation was observed between the specific surface area of $Ni(OH)_2$ and its electrochemical activity. With a specific surface area smaller than about 40 m^2/g, the activity of the prepared electrodes was also low (below 70% C_t). With a specific surface area higher than 40 m^2/g, the activity of the electrodes was mostly above 70% C_t. However, other effects also obviously play a role. The best non-doped materials had specific surface areas in the range 60 - 110 m^2/g. The thickness of the disc pressed from the active material with 10% Teflon (see "Experimental") was roughly correlated with the specific surface area: when the latter was higher, the electrodes were usually thicker, showing an increasing content of micropores in the nickel hydroxide. For example, the thinnest electrode was 1.58 mm thick and its specific surface was 4 m^2/g (activity 18% C_t), whereas the thickest was 2.07 mm thick and its specific surface was 110 m^2/g (activity 88% C_t).

TABLE 5

Water content of different samples of $Ni(OH)_2$

Sample	Drying temp. (°C)	H_2O cont. (%)
A, from neutral medium	50	16.8
B, from neutral medium	130	12.2
C, from alkaline medium	50	12.2
D, from alkaline medium	130	8.8

TABLE 6

Relative intensity of X-ray diffraction lines of samples from Table 5

Sample	Miller index							
	001	100	101	102	110	111	200	201
A	6	15	11.5	3	7	2.5	—	—
B	7	18	14	3	7	3	—	—
C	10	14	12	3	8	3.5	—	—
D	15	16	14	3	10	5	2	2

Other characteristics of Ni(OH)₂ preparations

Samples of $Ni(OH)_2$ obtained by precipitation from a neutral medium (without the conducting component) had a markedly lighter colour and an increased water content (Table 5). Sample A had the highest water content, in accord with the finding that more active preparations of $Ni(OH)_2$ contain more water [7, 8]. The water content of the samples precipitated in the presence of a suspension of the conducting component was, however, significantly lower, since these lost their water in the drying oven more easily. During washing samples A and B by centrifugation, a certain colloidal fraction separated toward the end of the washing procedure and did not form a sediment (the field of gravity used was up to 200 G), evidence for the presence of a nearly amorphous form of $Ni(OH)_2$. Also, the X-ray analysis showed that these preparations had a less perfect crystal structure, since they gave weaker, diffuse reflexes or lower maxima. We did not find reflexes corresponding to α-$Ni(OH)_2$ owing, apparently, to the fact that this modification has a highly disordered structure making the X-ray analysis difficult; this circumstance was also pointed out by Barnard and coworkers [14]. The X-ray diagrams showed only diffraction lines of β-$Ni(OH)_2$ as given in Table 6 (heights of maxima in arbitrary units). It will be seen that samples A and B have some lines less intense as compared with C and D (from the alkaline medium), and that higher drying temperature together with the alkaline medium favours the formation of the β-$Ni(OH)_2$ structure (sample D).

Cycle life tests

Two electrodes prepared from two samples of the optimized, non-doped active material containing 30% of conducting component (*cf.* 3rd line of Table 1) were subjected to accelerated cycling (90 min charging at 300 mA, 90 min discharging at 160 mA) in the cell arrangement described (see "Experimental"), except that the electrolyte was doped with 10 g of LiOH per liter. Their capacities, measured from time to time by charging at 50 mA for 16 h and discharging at 100 mA (6.6 mA/cm^2), were in the range 0.41 - 0.46 A h, corresponding to 87 - 99% C_t at the beginning of the test and after the 30th cycle. The values after the 140th cycle were 70 - 80% C_t.

Conclusions

A method for the preparation of the active material for plastic-bonded positive electrodes of alkaline accumulators is proposed, based on slow precipitation, by the addition of a solution of KOH at elevated temperature to a solution of $NiSO_4$ containing a suspension of a conducting component. The product has a discharge capacity, without doping with cobalt, that has been attained hitherto only with materials doped with cobalt, *i.e.*, 80 - 90% C_t or 170 - 180 A h/kg.

Acknowledgements

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