

The effect of Co addition on the positive active material in Ni–Cd pocket-plate batteries

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Abstract

The nickel electrodes in Ni–Cd pocket-plate batteries have been cobalt-doped (0.8–5.0 wt.%) either by coprecipitation during Ni(OH)₂ fabrication or by addition of cobalt oxide. It was observed that both methods of doping significantly improved the initial performance and performance after accelerated testing. In general, the higher the cobalt content, the higher the degree of material utilisation. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Ni–Cd batteries of the pocket-plate type have been produced in Oskarshamn, Sweden, for a long period of time. In this concept, the electrode material is pressed into briquettes, which are packed between perforated nickel-plated steel strips. Nickel hydroxide and cadmium hydroxide are used as the active components in the positive and negative electrodes, respectively. To establish a good electrical contact between the strip and the hydroxide, graphite flakes are mixed into the positive and an iron compound into the negative hydroxide before compacting. The strips are connected to the post via a nickel-plated steel lug. The Ni–Cd batteries employ potassium hydroxide as electrolyte, often with addition of lithium hydroxide.

As stated earlier, graphite is used for conducting purposes, and in the positive electrode, it can account for 20% by weight of the electrode material. It has been demonstrated that graphite can form carbon dioxide during overcharging at elevated temperatures [1]. This carbon dioxide easily transforms into carbonate in the electrolyte, which may affect battery performance. Due to the pocket-plate construction itself and to the physical and chemical properties of the active material, the addition of a cobalt com-

pound is sometimes a good choice for improving the properties of the positive electrode material. This was previously suggested by Edison in 1914 [2]. Cobalt raises the oxygen overpotential [3–5], increases the conductivity of the active material [4,6–11] and reduces the electrode swelling during charge/discharge cycling [12]. By adding cobalt, it is expected that during service, nickel hydroxide utilisation will be enhanced and battery deterioration reduced, especially under severe operating conditions. The factors against the use of cobalt are purely economical, although a slight decrease of the discharge voltage has been reported [5,13].

This work investigates the effect of cobalt addition on nickel hydroxide electrodes in pocket-plate batteries. Cobalt was added either by coprecipitation during nickel hydroxide fabrication, or by addition of solid cobalt oxide directly into the nickel hydroxide powder. Both short- and long-term effects are reported, and for comparison, a cobalt-free active material has been included in the test. As well as the determination of initial electrical performance, accelerated test methods were also employed to deteriorate the material within a reasonable period of time.

2. Experimental

The compositions of active materials (denoted A to H) referred to in this work are displayed in Table 1.

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Table 1
Nickel and cobalt content (wt.%)

Sample	A	B	C	D	E	F	G	H
Ni	44.5	44.0	42.4	44.1	43.9	43.4	42.8	41.7
Co	0.0	1.1 ^a	2.6 ^a	0.8 ^b	1.0 ^b	2.0 ^b	3.0 ^b	5.0 ^b

^aCoprecipitated during nickel hydroxide fabrication.

^bCoO added to the compacted Ni(OH)₂/graphite blend.

The nickel hydroxide is essentially the same in all samples with respect to crystallinity, particle size and surface area. It is fabricated from a nickel sulphate solution (containing cobalt when coprecipitated) by adding sodium hydroxide until nickel hydroxide is precipitated. A more detailed discussion of nickel hydroxide fabrication has been made by Falk and Salkind [14]. The nickel hydroxide powder and graphite flakes are mixed in a 4:1 ratio. After the blend has been compacted, sieving is performed to obtain the proper fraction of particles. This fraction is pressed into briquettes, which are encapsulated between the conducting strips. When cobalt oxide (CoO) was used as a conducting additive, it was added directly into the nickel hydroxide/graphite blend after the sieving step.

Electrical tests were conducted with mono-pockets fabricated as pocket electrodes and containing pressed briquettes of active material weighing 4.0 g each. Approximately 400 ml of potassium hydroxide (5.2 M) was used as the electrolyte for each test. The counter and reference electrodes consisted of a nickel plate and zinc rod, respectively. Formation was carried out at room temperature (RT) by two charge/discharge cycles at C/5 rate. Capacities were determined after discharge to 1.5 V vs. Zn/ZnO. The value of 1.5 V was, in most cases, used as the end voltage in order to avoid the reduction of trivalent cobalt [4,10,15]. At shallow discharge, cobalt is not assumed to contribute to the electrical capacity. When not stated otherwise, all charging was done at C/5 for 8 h.

Two tests were performed. Test I involved the determination of initial capacity at C/5 and C/1 rate discharge and RT. An extreme charging condition (C/1 for 8 h) at 60°C was then applied followed by discharge at the same rate and temperature. After recharging, a deep discharge to 0.3 V vs. Zn/ZnO was performed. A new capacity determination was then carried out. All capacity data in this test are represented as nickel hydroxide utilisation, where 100%

Table 2
Ni(OH)₂ utilisation (%) initially and after Test I

Sample	A	B	C	D	F	H
C/5 ^a	86	90	89	91	95	99
C/1 ^a	70	73	74	76	79	84
C/5 ^b	76	86	92	89	92	94

^aInitial test.

^bTest after C/1 rate charge/discharge at 60°C and C/5 rate charge/discharge at RT (to 0.3 V vs. Zn/ZnO).

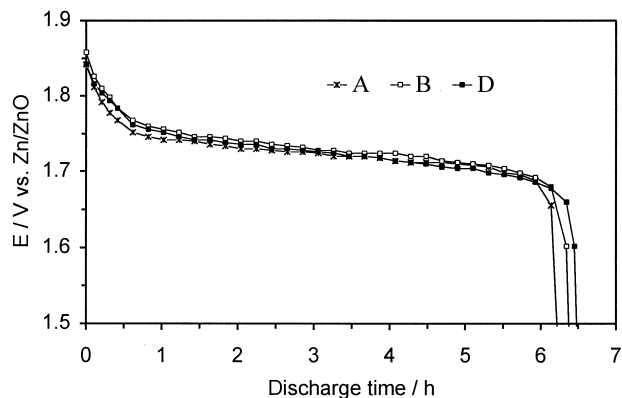


Fig. 1. Initial capacity at C/5 rate discharge and RT.

utilisation corresponds to a theoretical capacity of 289 mA h/g Ni(OH)₂. In Test II, the purpose was to accelerate the deterioration of the active material by constant charging at C/5 rate for 25 days at 60°C. This test also included a number of charge/discharge cycles in the beginning and at the end of the test (reconditioning). Capacity was finally determined at RT after C/5 rate discharge. The capacity values for Test II are given in mA h, since the intention

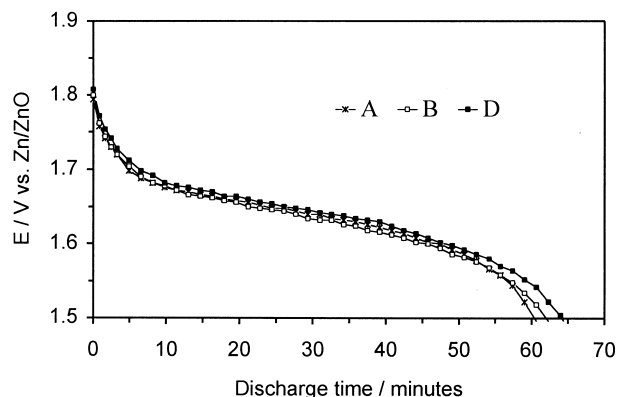


Fig. 2. Initial capacity at C/1 rate discharge and RT.

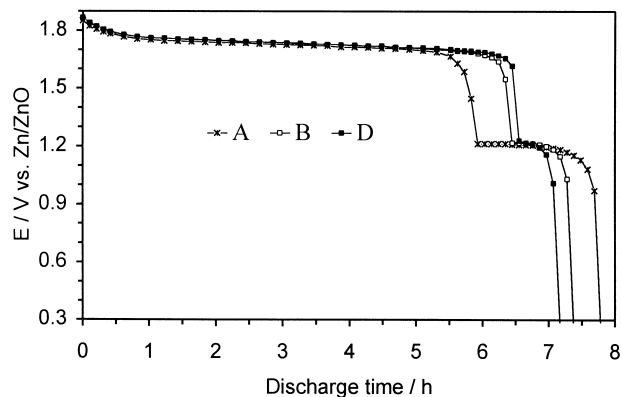


Fig. 3. Discharge at C/5 rate after prolonged charge/discharge at C/1 and 60°C followed by charge/discharge (to 0.3 V vs. Zn/ZnO) at C/5 rate and RT.

Table 3
Capacity (mA h) at C/5 rate discharge before and after Test II

Sample	A	B	C	E	G
Before	66	75	74	72	77
After	53	60	68	60	68

was to simulate real operating conditions. This means that weight loss was not accounted for during the test.

The electrical measurements were performed by means of a computer-controlled charge/discharge unit connected to a computerised data acquisition system.

The chemical analysis of the nickel and cobalt was carried out by means of atomic absorption spectroscopy.

3. Results

The initial RT capacities, or levels of nickel hydroxide utilisation, are displayed in Table 2. Both the C/5 and C/1 rate discharges demonstrate that all samples containing cobalt have higher utilisation than sample A (cobalt-free). The results for cobalt precipitated samples B and C are equivalent, while samples D, F and H, with CoO added, exhibit increased utilisation at higher cobalt contents. The typical discharge curves are displayed in Figs. 1 and 2. Note, however, that variation in nickel hydroxide content has not been taken into account in the figures. The small differences between A, B and C at both rates of discharge, as seen in Table 2, indicate that the effect of coprecipitated cobalt (up to 2.6 wt.%) is limited initially.

After prolonged C/1 rate charge/discharge at 60°C and after C/5 rate charge/discharge (to 0.3 V vs. Zn/ZnO) at RT, it is obvious that the cobalt-free material, A, has been affected the most (Table 2). This is clearly displayed in Fig. 3 where the duration of the second voltage plateau at 1.20 V is much longer for sample A, and consequently, the material utilisation is less efficient for this sample. There is also a trend of decreasing utilisation among the cobalt samples after this test, with the unexplained exception of sample C.

Results from the accelerated, constant current charging test at 60°C are displayed in Table 3. As was also observed in Test I, the initial capacity is higher for cobalt samples B, C, E and G. Moreover, it is evident that electrode material without cobalt, A, does not endure the accelerated testing to the same extent as do the cobalt-doped materials. All materials significantly lose capacity after 25 days at 60°C, but the capacity drop decreases with increasing cobalt content, irrespective of doping method.

In general terms, it can be stated that in nickel hydroxide with coprecipitated cobalt, the cobalt increases the

electrochemical efficiency of the hydroxide lattice resulting in improved chargeability [9,11,13]. On the other hand, when cobalt oxide is added to nickel hydroxide, a conducting network of cobalt oxyhydroxide, CoOOH, is created after charging of the material [3,6–8,10]. The CoOOH probably precipitates onto the nickel hydroxide particles, and due to its conducting properties, improves the contact between the hydroxide and the graphite flakes.

4. Conclusions

Both initial performance and performance after accelerated testing have shown that cobalt, either coprecipitated or added as CoO, significantly improves the electrode material utilisation in the pocket-plate electrode. In general, the higher the cobalt content, the higher the degree of material utilisation.

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