PLASTIC-BONDED ELECTRODES FOR NICKEL–CADMIUM ACCU-
MULATORS.
X. THE NATURE OF THE SECOND DISCHARGE STEP OF NICKEL
OXIDE ELECTRODES

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Summary

The second discharge step of nickel oxide accumulator electrodes is suppressed in the presence of a Teflon binder and/or cobalt, cerium, or manganese hydroxide, whereas the first discharge step increases. This behaviour is discussed in terms of ohmic resistance effects and semiconducting properties of the active material.

Introduction

The $E-t$ discharge curves of various types of nickel oxide electrodes are characterized by two steps. The first, main step is in the potential range 0.25 - 0.35 V *vs.* the Hg/HgO reference electrode in the same solution and is made use of in batteries. The second is at -0.1 to -0.6 V according to the type of electrode and the current load. According to our previous work [1], the stepped discharge curves of plastic bonded or pressed nickel oxide electrodes are mainly related, in general, to ohmic resistance effects among individual electroactive particles (on their periphery) and between the current collector and the electroactive layer.

Barnard and coworkers [2] also interpreted the second discharge step of sintered nickel electrodes on a conductivity basis, but discussed the conductivity in terms of the theory of semiconductors. Their results confirmed our concept of conductivity control as far as the second discharge step is concerned; according to them, the removal of n-type defects from the nickel(II)-rich phase during discharge is responsible for this step, which arises from the behaviour of the mixed $p-n$ semiconducting material under discharge conditions. A significant quantity of β- and γ-NiOOH (n-type semi-

conductors of higher conductivity) remains isolated in the α- and β-Ni(OH)$_2$ (p-type semiconductors of low conductivity) and can be reduced at sufficiently high negative potentials.

The present work was focused on the influence of cobalt, cerium, manganese, and the conducting component on the shape and position of the second discharge step of pressed nickel oxide electrodes.

Experimental

Test electrodes were prepared by pressing the electrode mix at 60 MPa into the form of a 10 mm dia. disc which was afterwards wrapped in a fine nickel gauze (0.05 mm wire, 0.08 mm mesh, 0.285 kg/m^2 mass) and finally pressed at 100 MPa to a thickness of 2.4 - 2.6 mm.

Three sorts of active material were used. The first was commercial powdered KBL active material containing 43 - 47% Ni in the form of hydroxide and 16 - 19% graphite VA, produced for pocket type electrodes by Lachema (Bohumin, CSSR). The second was NICKO powdered active material [3] containing about the same quantity of Ni as hydroxide and 22 - 25% graphite VA and activated with cobalt hydroxide. The third was similar to the latter except that the cobalt was replaced by cerium or manganese hydroxide. The starting compounds used for the activation were CoSO$_4\cdot$7H$_2$O (Lachema, Brno), CeCl$_3\cdot$7H$_2$O (Laborchemie Apolda, GDR), and MnSO$_4\cdot$5H$_2$O (Lachema, Brno, CSSR).

The NICKO active material was prepared as follows. A concentrated solution of KOH was mixed with powdered graphite of suitable granulometric composition and heated to boiling. A solution of nickel sulphate was added gradually with stirring, the precipitate, with excess alkali hydroxide, was filtered, dried, and homogenized to obtain an intermediate product (NICKO-a). This was activated by mixing with a solution of CoSO$_4$ to form a thick suspension, which, after a short interval was made alkaline with a solution of KOH and subjected to dilution, decantation, filtration, drying, and grinding to give the final product (NICKO-b - d). Activation with manganese and cerium was carried out analogously.

All test electrodes were prepared so as to give a theoretical capacity C_t = 64 mA h (corresponding to 1 F/mol Ni(OH)$_2$). Other components were acetylene carbon black P-1042 (Stickstoffwerk Piesteritz, GDR), graphite powder VA (Rudné doly, Týn/Vlt., CSSR) which contained particles in the range 10 - 200 μm without a significant maximum (the remainder on 0.16 mesh was at least 45%), type 255 carbonyl nickel powder (INCO, Great Britain) used for sintered nickel electrodes, and PTFE powder Fluon CD-1 (ICI, Great Britain).

The counter electrode was a nickel sheet on either side of the test electrode. The electrolyte was a solution of KOH of 1.2 g/cm^3 density. The potentials were measured against an Hg/HgO reference electrode in the same solution.

TABLE 1

Data for curves in Fig. 1

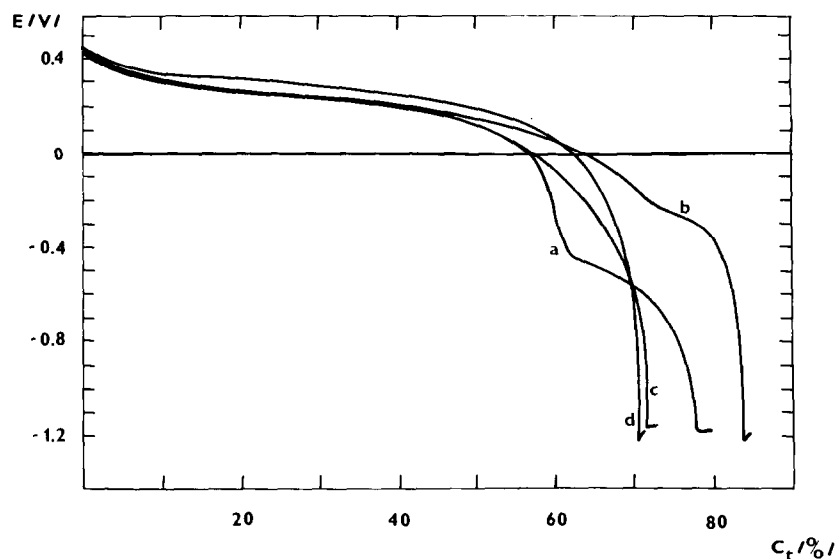| Active material	Cond. component	Capacity (% C_t)	
		to -0.2 V	to -1.1 V
KBL-a	None	61.3	77.5
KBL-b	Carbon black	72.3	83.6
KBL-c	Graphite VA	63.7	71.3
KBL-d	Carb. nickel	66.2	70.1

Fig. 1. Galvanostatic discharge curves for pressed electrodes of 10 mm dia. at a current of 50 mA. Active material: (a) pure KBL; (b) with addition of 9.6% PTFE and 7.9% carbon black; (c) graphite VA; (d) carbonyl nickel. See Table 1.

The test electrode was charged at the $C/10$ rate, discharged at the $C/1$ rate and the $E-t$ discharge curve was recorded up to the evolution of hydrogen (about -1.1 V). The discharge curves were usually satisfactorily reproducible after 3 - 4 cycles.

Results and discussion

Influence of conducting component

The discharge curves of electrodes with three different conductive components (Table 1) are shown in Fig. 1 (cf. Table 1 and Fig. 8 in ref. 1), where three distinct types of curves are noticeable. The first corresponds to the pressed active KBL material without additives, the second to relatively compact conducting materials (bulk density of powdered graphite 0.54 g/cm^3,

TABLE 2

Data for curves in Fig. 2

Active material	Co (%)	PTFE (%)	Capacity (% C_t)	
			to −0.2 V	to −1.1 V
NICKO-a		0	58.9	73.8
		10	71.0	77.7
NICKO-b	1.32	0	83.1	86.7
		10	84.6	88.7
NICKO-c	2.20	0	94.0	97.2
		10	93.4	96.7
NICKO-d	2.99	0	94.7	96.1
		10	95.6	98.0
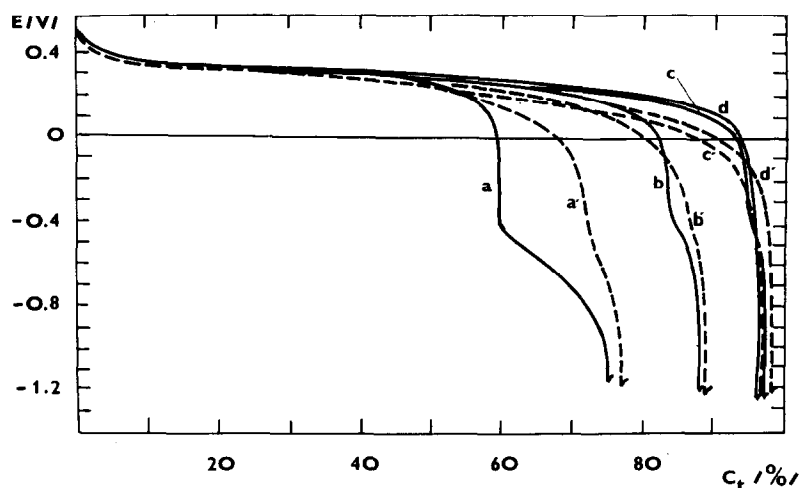
Fig. 2. As Fig. 1, but with NICKO active material doped with different concentrations of Co: (a) non-doped; (b) 1.3%; (c) 2.2%; (d) 3.0%. Dashed curves correspond to addition of 10% PTFE. See Table 2.

of carbonyl nickel 0.77 g/cm^3) and the third to voluminous carbon black (bulk density 0.04 g/cm^3). According to Barnard and coworkers [2], the effect of the conducting components can be attributed to an increase in the number of surface contact points between the conducting matrix and the electroactive particles, whereby the "residual capacity" (the second discharge step) is lowered. When a voluminous, highly dispersed conducting component (carbon black) is used, the "residual capacity" is minimized and the potential of the second discharge step is shifted towards more positive values. In the case of a less dispersed conducting component (graphite, carbonyl nickel), the number of peripheral contacts between it and the electroactive particles is only moderately increased and the first discharge step is consequently
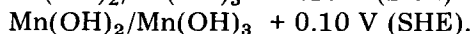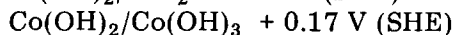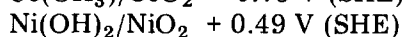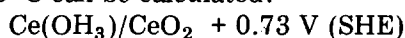
somewhat shorter than in the preceding case. The rest of the active material (with a nickel oxidation state higher than 2) is now more isolated owing to the relatively longer conduction paths between its grains, and cannot be reduced even at potentials close to the evolution of hydrogen.

Influence of cobalt and Teflon

The second discharge step of the pressed nickel oxide electrode can also be minimized by the addition of cobalt hydroxide to the active material. For this purpose, the active material NICKO-a was doped with various quantities of cobalt hydroxide and the electrodes were prepared either without, or with, PTFE binder (Table 2). The corresponding discharge curves are shown in Fig. 2. A distinct effect of the binder (dashed curves), when non-doped active material is used, is clearly visible. The presence of PTFE causes a suppression of the second discharge step, *i.e.*, the oxidized active material is reduced essentially in a single discharge step. The effect of the binder can be attributed to an improvement in the contact between the electroactive particles, which are reduced without losing their cohesion and thus without increase of contact resistance (the cause of the second discharge step of electrodes without plastic binder).

The presence of cobalt causes a significant increase in the electrode capacity, the "residual capacity" being nearly eliminated. The beneficial effect of cobalt can most probably be attributed, on the basis of the theory of Barnard and coworkers [2], to an increase in the hole conductivity of nickel hydroxide in its reduced state. This effect obviously counterbalances the relatively lower number of peripheral contact points between graphite and nickel oxide in the NICKO material. With the highest Co content, the capacity of the electrode is close to 100% C_t, *i.e.*, 1 F per mol $Ni(OH)_2$.

Redox couples similar to $Co(OH)_2/Co(OH)_3$ are also formed by certain other metals, and their effects on the discharge behaviour of the nickel oxide electrode could be expected to be similar. Some experimental results are shown in Fig. 3, for which the relevant data are given in Table 3. The couple $Mn(OH)_2/MnOOH$ has a negligible effect (curve b), which is enhanced by the addition of Teflon (curve b'). The couple $Ce(OH)_3/Ce(OH)_4$ has a pronounced effect (curve c), which on adding Teflon remains practically unchanged (curve c'), but still does not reach the effect of cobalt (curve d). According to Latimer [4], the following redox potentials in alkaline medium at 25 °C can be calculated:

$Ce(OH_3)/CeO_2$ + 0.73 V (SHE)
$Ni(OH)_2/NiO_2$ + 0.49 V (SHE)
$Co(OH)_2/Co(OH)_3$ + 0.17 V (SHE)
$Mn(OH)_2/Mn(OH)_3$ + 0.10 V (SHE).

From these data is is difficult to see why cobalt should be the best activator. Hence, the efficiency of the activating additive seems to bear no relation to its redox potential. An increase in the hole conductivity of the nickel hydroxide, as mentioned above, appears to be the only plausible explanation, although direct experimental evidence is missing.

TABLE 3

Data for curves in Fig. 3

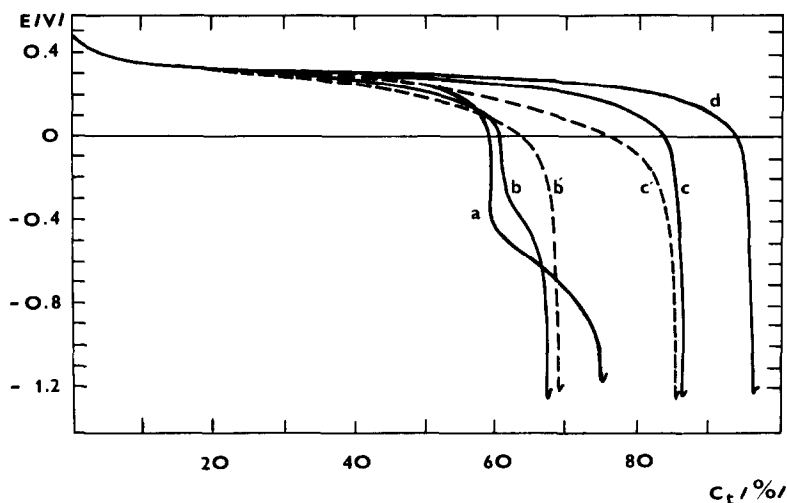| Active material	Dopant	PTFE (%)	Capacity (% C_t)	
			to −0.2 V	to −1.1 V
NICKO-a		0	58.9	73.8
NICMN-b	2.0% Mn	0	61.2	67.4
		10	64.9	68.9
NICCE-c	2.0% Ce	0	85.1	86.3
		10	82.5	85.3
NICKO-d	2.99% Co	0	94.7	96.1

Fig. 3. Galvanostatic discharge curves for pressed electrodes of 10 mm dia. at a current of 50 mA. NICKO active material: (a) nondoped; (b) doped with 2% Mn; (c) doped with 2% Ce; (d) doped with 3% Co. Dashed curves correspond to addition of 10% PTFE. See Table 3.

Theoretical aspects

The process of discharging a charged electrode involves acceptance of electrons from the current collector and H^+ ions from the electrolyte and a change of the relatively good n-type conductor, NiOOH, to a bad p-type conductor, $Ni(OH)_2$. This process can be influenced by five different interfaces:

(a) the Schottky junction between the current collector and NiOOH (n type), polarized in the backward direction;

(b) the p–n junction between both oxidation states, polarized in the forward direction;

(c) the junction NiOOH (n type)–electrolyte;

(d) the junction $Ni(OH)_2$ (p type)–electrolyte;

(e) the Schottky junction between the current collector and $Ni(OH)_2$ polarized in the forward direction.

The $E-t$ curves obtained can be interpreted as follows. At the beginning of the discharge, only junctions (a) and (c) are present. The former causes a certain increase in the electrode resistance. In the course of discharge, the reduced component is accumulated at the collector, whereby junction (e) appears, whose poor conductivity limits the current conduction to the oxidised form. Due to the constant current passing, the electrode potential is shifted to more negative values, at which the hole conductivity of the reduced form increases [2] and the second discharge step appears on the $E-t$ curve.

In respect of the secondary activation with cobalt, it can be assumed that cobalt hydroxide is adsorbed on the surface of the nickel hydroxide particles to form regions with a high concentration of additive, so-called surface states. These are known to decrease the ability of semiconductor junctions to block the passage of current in the backward direction; moreover they form a surface layer of high conductivity practically causing a short circuit of the potential barrier in the semiconductor. Thus, the particles become reducible in their whole volume without the need for a marked lowering of their potential to overcome the potential barrier.

References

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2 R. Barnard, C. F. Randell and F. L. Tye, *J. Appl. Electrochem., 10* (1980) 127 - 141.
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4 W. M. Latimer, *Oxidation Potentials*, Prentice-Hall, Englewood Cliffs, New York, 1961.