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CONTRIBUTION TO THE KNOWLEDGE OF NICKEL HYDROXIDE ELECTRODES  
V. ANALYSIS AND ELECTROCHEMICAL BEHAVIOR  
OF CADMIUM-NICKEL HYDROXIDES

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# CONTRIBUTION TO THE KNOWLEDGE OF NICKEL HYDROXIDE ELECTRODES. V. ANALYSIS AND ELECTROCHEMICAL BEHAVIOR OF CADMIUM-NICKEL HYDROXIDE\*

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**SUMMARY.** Cadmium hydroxide dissolves homogeneously in  $\alpha$ -nickel hydroxide up to 28 mol.%; in  $\beta$ -nickel hydroxide to a maximum of 10 mol.%. By treatment with potassium hydroxide, the  $\alpha$ -cadmium hydroxide is transformed into  $\beta$ -cadmium hydroxide, as is the case with pure  $\alpha$ -nickel hydroxide. If an  $\alpha$ -hydroxide contains more cadmium than is soluble homogeneously in the  $\beta$ -hydroxide, then during the transformation with potassium hydroxide the excess will appear as  $\beta$ -cadmium hydroxide, next to the  $\beta$ -nickel hydroxide.

Electrochemical experiments performed at sintered and bulk electrodes show that  $\beta$ -nickel hydroxide can contain an electrochemically inactive proportion of cadmium hydroxide of up to 10%. The electrochemically ineffective cadmium hydroxide is homogeneously dissolved in  $\beta$ -nickel hydroxide.

## 1 INTRODUCTION

After the previous four papers [1 - 4] on the characteristics and reactions of pure nickel hydroxide, in the present paper we submit experimental results on mixtures and solid solutions of cadmium hydroxide and nickel hydroxide. The motivation for

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\* Manuscript received March 16, 1971

these experiments is the use of cadmium hydroxide as antipolar mass in nickel hydroxide electrodes; to date there is no precise idea available on its manner of action. In addition, when sintered nickel electrodes are impregnated with acidic cadmium salt solutions, a certain corrosion can not be avoided; in the process cadmium-nickel hydroxides are formed, which may react with the former.

The literature contains only sparse information on the cadmium hydroxide/nickel hydroxide system. Natta [5] did not obtain a solid solution upon complete precipitation of the hydroxides, but only mixed crystals of both components. The fact that no solution is formed is explained in terms of the large ionic radii difference in the metal hydroxides.

In this investigation we prepared cadmium-nickel hydroxides through incomplete precipitation, both by cathodic and by chemical precipitation. It was possible to identify the hydroxide phase obtained. The electrochemical effectiveness of cadmium as an antipolar mass was investigated both as a function of the participating quantity and the state of dissolution.

## 2 EXPERIMENTAL METHODS

The electrochemical precipitation of the hydroxide was obtained from 120 ml of a solution of cadmium and nickel nitrates with a 0.1 m overall concentration. The mole ratio  $\text{Cd}^{2+}/\text{Ni}^{2+}$  was varied between 0 and 1 (See Table 2, page 4). The cathode was a 24 cm<sup>2</sup> nickel plate roughened in HCl, flanked by two nickel plates of the same size as counter-electrodes, at a distance of 1 cm each. Cathodic precipitation was performed at room temperature, at 48 mA (= 1 ma/cm<sup>2</sup> of the two-sided surface), in 20 min. The electrodes were rinsed with distilled water and dried at 80°C to constant weight. It was subsequently possible to scrape the precipitate off the electrode. The yield was approximately 30 mg,

TABLE 1. Defined compounds for comparison in Cd-Ni-hydroxide phase analyses

Compound	Space group	Lattice const.(A)			Angle $\beta$		Reference
		a	b	c			
$\alpha$ -Ni(OH) <sub>2</sub> ·2H <sub>2</sub> O	P31m	3,34		2,50			Bode u.s. <sup>1</sup>
$\beta$ -Ni(OH) <sub>2</sub>	P31m	3,114		4,617			ASTM 3-0177
$\beta$ -Cd(OH) <sub>2</sub>	P31m	3,496		4,702			ASTM 13-226
$\gamma$ -Cd(OH) <sub>2</sub>	Im	3,67	10,25	3,41	91,4		de Wolff <sup>2</sup>
Cd-Metall	Fm $\bar{3}$ mm	2,9793		3,6181			ASTM 5-0674
CdO	Fm $\bar{3}$ m	4,6953					ASTM 5-0640
CdCO <sub>3</sub>	R3c	4,930		16,27			ASTM 8-456

TABLE 2. Electrochemical precipitation of Cd-Ni-hydroxides

Solution composition: mol. Cd <sup>++</sup>	Precipitate composition (mole fract)	Water & foreign ions wt. %	X-ray identified phases :			
			$\alpha$ -nickel hydroxide	$\beta$ -nickel hydroxide	$\beta$ -cadmium hydroxide	
mol. (Cu <sup>++</sup> + Ni <sup>++</sup> )	Cd(OH) <sub>2</sub> Ni(OH) <sub>2</sub>					
0	0	1	25,6	H	—	—
0,05	0,080	0,920	26,9	H	—	—
0,1	0,107	0,893	26,3	H	—	—
0,2	0,132	0,868	26,2	H	—	—
0,3	0,174	0,826	24,7	H	—	—
0,4	0,193	0,807	24,0	H	—	—
0,5	0,222	0,778	26,7	H	—	—
0,6	0,266	0,734	20,9	H	—	—
0,65	0,295	0,705	14,8	H	N	N
0,7	0,365	0,635	16,3	S	—	H
0,75	0,456	0,544	15,6	S	S	H
0,75	0,443	0,557	16,0	—	—	H
0,8	0,630	0,370	13,9	—	—	H
0,85	0,811	0,189	14,0	S	—	H
0,875	0,860	0,140	12,8	S	—	H
0,9	0,856	0,144	12,5	—	—	H
0,95	0,945	0,055	11,5	—	—	H
1,0	0,988	0,012*	11,3	—	—	H

\* Due to corrosion of the Ni-carrier H: Main constituent N: secondary constituent S: Trace

i.e., 2 to 3 percent of the available mass.

The chemical precipitation of the hydroxides occurred in 1 liter

TABLE 3. Chemical precipitation of Cd-Ni-hydroxides

Solution composition Mol. Cd <sup>++</sup>	Precipitate composition (Mol. fractn)	Water and foreign ions	Phases identified by X-rays			
			α-nickel hydroxide	Basic Ni Nitrate	β-nickel hydroxide	β-cadmium hydroxide
Mol. (Cd <sup>++</sup> + Ni <sup>++</sup> )	Cd(OH) <sub>2</sub> : Ni(OH) <sub>2</sub>	wt. %				
0.2	0.022	11.3	—	H	—	—
0.4	0.065	9.6	—	H	—	—
0.6	0.083	15.0	N	—	H	—
0.7	0.247	13.9	N	—	H	—
0.75	0.364	14.3	H	—	N	N-S
0.8	0.596	11.2	H	—	N	H
0.9	0.973	9.5	—	—	S	H
0.95	0.967	6.1	—	—	—	H
1.0	1	5.7	—	—	—	H

H: Main constituent N: Secondary constituent S: Trace

of a cadmium-nickel nitrate solution that was 0.1 M with respect to  $(\text{Cd}^{2+} + \text{Ni}^{2+})$ . The  $\text{Cd}^{2+}$  to  $\text{Ni}^{2+}$  ratio was varied as shown in Table 3 (page 5). Then, 10 ml of 1 N NaOH was added at room temperature and with vigorous stirring. The addition was completed within 10 minutes, stirring was 15 minutes, overall. This leads to incomplete precipitation. The precipitate was allowed to settle overnight, was filtered through a pleated filter, and washed. Because of its slimy consistence, it could be washed free of alkali but not free of anions. The precipitate in the filter was then dried at 45°C for 65 hours, then 15 hours at 60°C and finally over  $\text{P}_2\text{O}_5$  to constant weight. The yield varied between 0.2 and 0.6 g, i.e., between 1.4 and 4%.

The chemical analysis of the hydroxides included nickel precipitation with dimethylglyoxime and complexometric titration of cadmium.

The X-Ray analyses were based on pictures taken by the Debye-Scherrer method with Cu-K $\alpha$  radiation and cameras of 57.3 and 114.6 mm diameter. Evaluation of the diagrams was by comparison to the known diagrams of the compounds listed in Table 1 (page 4).

The conversion of cadmium-containing  $\alpha$ -hydroxides to  $\beta$ -hydroxides was performed by an hour-long interaction with 1 or 9-14 N KOH at 90°C. The concentrated hydroxide is used in those cases in which dissolution of the cadmium is intended. The conversion of the electrochemically generated compounds is performed in the electrodes, to the extent that they are contained in the sintered electrodes.

The electrochemical experiments are performed both of sintered and bulk electrodes; a description of the experimental details is provided together with the experimental results.

### 3 EXPERIMENTAL RESULTS AND DISCUSSION

### 3.1 Chemical composition of the hydroxides

The composition of the solution and the hydroxides obtained are described in Table 2 (page 4) for the electrochemically precipitated compounds and in Table 3 (page 5) for those chemically precipitated. Figures in the first column indicate the cadmium content of the cadmium-nickel nitrate solution; those in the second column, the mole ratio  $\text{Cd}(\text{OH})_2:\text{Ni}(\text{OH})_2$  in the precipitate. Hence these figures are a measure of the doping of nickel hydroxide with cadmium hydroxide. The third column lists the analytical remainder, in weight %. It is known, from parallel experiments, that after chemical precipitation of nickel hydroxides it consists of water. Nitrate content is approximately 1% by weight. Samples with higher cadmium content also contained some carbonate.

The relationship between the molar ratio Cd/Ni in the nitrate solution and in the hydroxide precipitate is shown in Figure 1 (page 8) for electrochemically precipitated compounds and in Figure 2 (page 8) for those chemically precipitated. The curves show the ratio between molar composition of the solution and that of the precipitate. In order of magnitude it corresponds to the ratio of the solubility products of the respective hydroxides [7]. The agreement is good for the case of the chemical precipitation, occurring by pH displacement in the entire solution volume and thus making it possible to reach solution equilibrium. In contrast the electrochemical precipitation occurs only in the vicinity of the electrode, where the composition of the precipitate will depend substantially on diffusion of the ions in the solution. Thus, the lack of an equilibrium condition at the electrode explains the difference between curves 1 and 2.

### 3.2 X-ray results for the hydroxides

By comparison with the pictures of anticipated known compounds it is generally possible to assign the Debye lines and thus identify the phases present. The proportions are established after visual intensity estimates for the main constituent (H), the secondary

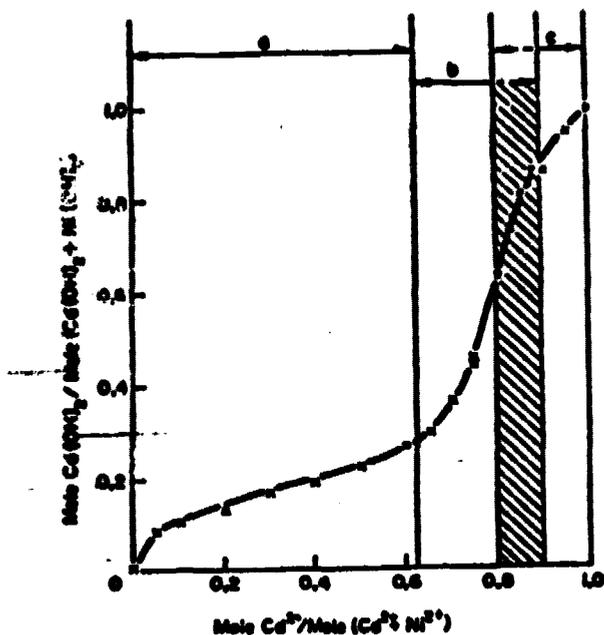


Figure 1. Molar composition of the electrochemically generated precipitates as a function of solution composition. Sections: a:  $\alpha$ -nickel hydroxide with  $\text{Cd}(\text{OH})_2$  b:  $\alpha$ -nickel hydroxide and  $\beta$ -cadmium hydroxide c:  $\beta$ -cadmium hydroxide doped with  $\text{Ni}(\text{OH})_2$

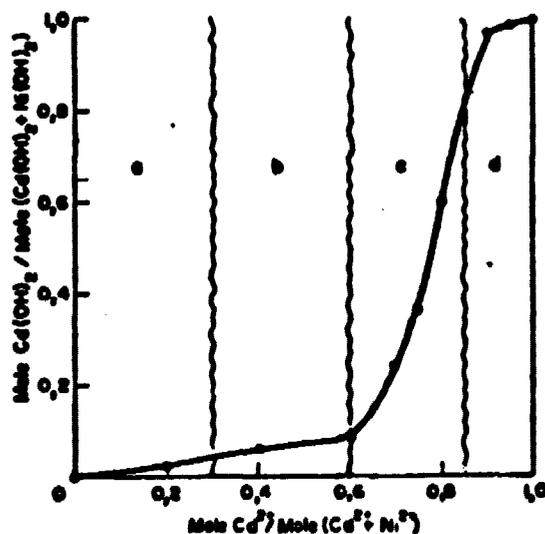


Figure 2. Molar compositions of chemically precipitated hydroxides as a function of solution composition. Sections: a: basic nickel salt b:  $\alpha$  and  $\beta$ -nickel hydroxides doped with  $\text{Cd}(\text{OH})_2$  c:  $\alpha, \beta$ -nickel hydroxide and  $\beta$ -cadmium hydroxide d:  $\beta$ -cadmium hydroxide

constituent (N) and trace(s) (S). This evaluation of the Debye graph is reported, next to the analytical results, in Table 2 for the electrochemically precipitated hydroxides and in Table 3 for those chemically precipitated.

Besides the hydroxides, cadmium oxide is also found, since it is easily formed reversibly from the hydroxide. Many of the electrochemically generated samples contained cadmium reduced to the metal. Cadmium carbonate was found as an impurity in several of the hydroxides rich in cadmium.

According to X-ray results, electrochemically generated hydroxides present the following phases: up to a cadmium content of 26-28 mole %, cadmium-nickel hydroxide precipitates as a homogeneous  $\alpha$ -nickel hydroxide doped with cadmium (see Figure 1, a on page 8). From a content of 26 mole % cadmium on,  $\alpha$ -nickel hydroxide is formed (doped) and, in addition,  $\beta$ -cadmium hydroxide (Figure 1, b). If the hydroxide has a cadmium content of over 85 mole %, then the X-rays report only homogeneous  $\beta$ -cadmium hydroxide doped with nickel ions (Figure 1, c). The precise limit of the two-phase region in the upper range was not determined.

Chemically precipitated hydroxides show the following phase composition, as a function of cadmium concentration: to a content of approximately 5 mole % cadmium hydroxide, a basic nickel salt is formed reproducibly under these experimental conditions (Figure 2, a on page 8). The X-ray diagram shows a similarity with the diagrams for basic nickel nitrate shown by Feitknecht and Collet [8].

In the range 6-8 mole % cadmium hydroxide in the hydroxide precipitate (Figure 2, b), a heterogeneous precipitate of  $\alpha$ - and  $\beta$ -nickel hydroxides is formed, both doped with cadmium hydroxide. On the solubility of cadmium hydroxide in  $\beta$ -nickel hydroxide see section 3.4.

Hydroxides with a cadmium hydroxide content of 10 to 60 mole % form a mixture of  $\alpha$  and  $\beta$ -nickel hydroxides and  $\beta$ -cadmium hydroxide (Figure 2, c).

In the range above 95 mole % of cadmium hydroxide, only the phase of  $\beta$ -cadmium hydroxide occurs (Figure 2, d). The limit of the homogeneity range - between 2c and 2d - was not more precisely established.

### 3.3 Special X-ray findings

The X-ray diagram of the basic nickel nitrate contains the lines contained in Table 4, below.

TABLE 4. X-Ray diagram of the chemically produced basic nickel nitrate  
(Cu K $\alpha$ )

Angle °	J	d Å	$\frac{10^3}{d^2}$	$\beta$ -Ni(OH) <sub>2</sub> hkl	$\alpha$ -3Ni(OH) <sub>2</sub> · 2H <sub>2</sub> O hkl
3	84	15	4,5		
5,50	24	8,04	15,5		(001)
7,8	104	5,7	31		
10,5	54	4,23	55,9		
16,5	10	2,71	136,2	(100)	(110)
19,25	84	2,34	183	(101)(002)	(200)
26,0	34	1,75	327	(102)	
29,5	10	1,564	406	(110)(003)	(300)
31,0	44	1,500	448	(111)	
34,50	24	1,360	541	(200)	(220)
36,0	24	1,310	583	(201)(112)	
41,0	14	1,174	725	(202)	

TABLE 5. X-Ray diagram of the chemically precipitated Cd hydroxide  
(Cu K $\alpha$ )

Angle °	J	$\frac{10^3}{d^2}$	$\beta$ -Cd(OH) <sub>2</sub> hkl
3,55	2	6,45	
4,58	4	26,75	
5,48	3	13,4	
6,55	24	21,9	
7,45	44	28,3	
8,63	41	38,0	
9,48	4	45,8	(001)
14,50	1	111	(100)

The diagram is characterized by the absence of the base line (001) of  $\beta$ -nickel hydroxide. In contrast, lines with higher indices agree with the known nickel hydroxide lines.

The X-Ray diagram of the chemically precipitated pure cadmium hydroxide and that doped with 1.3 mole % of nickel hydroxide, show a series of new lines in the low-angle range that are not contained in the diagrams of known compounds, and that points to a super-structure (see Table 5, page 10).

### 3.4 The conversion

As we have shown, during the electrochemical precipitation are formed cadmium-nickel hydroxides with the structure of  $\alpha$ -nickel hydroxide and an isomorphically included portion of cadmium hydroxide not to exceed 26-28 mole %. In order to obtain information on the solubility of cadmium hydroxide in  $\beta$ -nickel hydroxide, cadmium-doped  $\alpha$ -nickel hydroxide is converted to  $\beta$ -nickel hydroxide in lye.

In this experiment electrochemically precipitated cadmium-nickel hydroxide of  $\alpha$ -structure and a content of 23 mole % Cd hydroxide, is treated for 1 hour with 1 n KOH, at 90°C. During this treatment the conversion from  $\alpha$ - to  $\beta$ -nickel hydroxide takes place, with simultaneous liberation of  $\beta$ -cadmium hydroxide. Chemical analysis shows no change in precipitate composition.

If cadmium-nickel hydroxide of the same composition, following the treatment in 1 n KOH, is treated for an additional hour with 9 n KOH at 90°C, then X-ray analyses show that it contains only  $\beta$ -Ni(OH)<sub>2</sub>. Chemical analysis, however, indicates 10 mole % cadmium hydroxide and 90 mole % nickel hydroxide. The missing portion of cadmium has gone into solution as cadmate.

Even after longer treatment in 9 n KOH at 90°C, the samples continue with a proportion of 8-12 mole % cadmium hydroxide that is

1. Without pretreatment

Compound before oxidation	$\alpha\text{-Ni(OH)}_2 \cdot 2\text{H}_2\text{O}$	$\alpha\text{-Ni(OH)}_2 \cdot 2\text{H}_2\text{O}$ and $\beta\text{-Cd(OH)}_2$
Oxidation in KOH	$\gamma\text{-Ni hydroxide}$	$\gamma\text{-Nickelhydroxid}$ and $\beta\text{-Cd(OH)}_2$
Conversion in Q1 n KOH	$\alpha\text{-Ni(OH)}_2 \cdot 2\text{H}_2\text{O}$	$\alpha\text{-Ni(OH)}_2 \cdot 2\text{H}_2\text{O}$ and Cd
	Q1	Q2
		Q3 Mole $\text{Cd(OH)}_2$ Mole $[\text{Cd(OH)}_2 \cdot \text{Ni(OH)}_2]$

2. Treatment in KOH: 1 h at 90°C or long-term at room temperature

Compound before oxidation	$\beta\text{-Ni(OH)}_2$	$\beta\text{-Ni(OH)}_2$ and $\beta\text{-Cd(OH)}_2$
Oxidation in 1n KOH	$\beta\text{-NiOOH}$	$\beta\text{-NiOOH}$ and $\beta\text{-Cd(OH)}_2$
Conversion in 1n KOH	$\beta\text{-Ni(OH)}_2$	$\beta\text{-Ni(OH)}_2$ and Cd
	Q1	Q2
		Q3 Mole $\text{Cd(OH)}_2$ Mole $[\text{Cd(OH)}_2 \cdot \text{Ni(OH)}_2]$

3. Treatment in 9 n KOH: 1 h at 90°C

Compound before oxidation	$\beta\text{-Ni(OH)}_2$	Dissolution of the $\text{Cd(OH)}_2$ in lye
Oxidation in 1n KOH	$\beta\text{-NiOOH}$	
Conversion in 1n KOH	$\beta\text{-Ni(OH)}_2$	
	Q1	Q2
		Q3 Mole $\text{Cd(OH)}_2$ Mole $[\text{Cd(OH)}_2 \cdot \text{Ni(OH)}_2]$

Figure 3. Phase formation of Cadmium-nickel hydroxides during electrochemical oxidation and reduction

not recorded by X-ray analyses.

During treatment in 1 n or 9 n KOH at 90°C,  $\alpha$ -cadmium-nickel hydroxide with a cadmium hydroxide content of 12-15 mole %, suffers a conversion to a uniform  $\beta$ -hydroxide.

According to these experiments, approximately 10 mole % of cadmium hydroxide can be homogeneously incorporated into  $\beta$ -nickel hydroxide. The respective first lines in Figure 3, above, summarize the

experimental results.

### 3.5 Effectiveness of Cd-hydroxide as an antipolar mass

In this section of our efforts we shall clarify the behavior of the homogeneously incorporated portion of cadmium hydroxide during loading and unloading of the nickel hydroxides. For this investigation we used primarily the nickel-rich cadmium-nickel hydroxides. The electrochemical experiments were performed with both sintered and bulk electrodes.

3.5.1 Sintered electrodes. Sintered discs of 19.5 mm diameter and 0.8 mm thickness are impregnated in a solution 0.05 M each in nickel and cadmium nitrate, for 17 hours at a current density of 1 mA/cm<sup>2</sup> of electrode surface.

One portion of the electrodes thus prepared is readied for cycle experiments without further pretreatment; a second portion is treated for 1 hour in 1 N KOH at 90°C, and a third portion is treated for 1 hour in 14 N KOH at 90°C. During these treatments the conversion described above to  $\beta$ -nickel hydroxide and  $\beta$ -cadmium hydroxide takes place, as described above, and that can be observed by X-ray measurements. In the third portion,  $\beta$ -cadmium hydroxide is dissolved and can no longer be detected by X-rays after the treatment.

The reactivity of the nickel and cadmium hydroxides is determined in a cycle experiment. In it, the electrodes are cycled in 1 N KOH at 5 mA, corresponding to 3 hours of current; voltage is measured against Cd<sup>0</sup>/Cd<sup>2+</sup> reference electrodes. The capacity of the nickel hydroxides results directly from the discharge stage for the oxidized nickel hydroxide electrode. To measure the capacity of the cadmium electrode, the electrode is deep-discharged (reduced) for 9 hours at the potential of the Cd<sup>0</sup>/Cd<sup>2+</sup> or, respectively, the H<sub>2</sub>/H<sup>+</sup> electrode, and then recharged (oxidized). The recharge takes place initially at the Cd<sup>0</sup>/Cd<sup>2+</sup> potential, later at the potential of the nickel hydroxide electrode. The capacity

**TABLE 6. Effectiveness of cadmium hydroxide as antipolar mass in sintered electrodes**

Pre-treatment	Pore filling %	Composition of impregnating solution		Electrochemically active portion	
		Ni(OH) <sub>2</sub> mol.%	Cd(OH) <sub>2</sub> mol.%	Ni(OH) <sub>2</sub> mol.%	Cd(OH) <sub>2</sub> mol.%
None	17.1	87.3	12.7	63.9	3.3
1 n KOH	10.5	83.6	16.4	71.5	5.9
14 n KOH	12.0	91.8	8.2	37.1	0.04

**TABLE 7. Effectiveness of cadmium hydroxide as antipolar mass in bulk electrodes**

Manufacture of the mass	Electrochemically active portion	
	Ni(OH) <sub>2</sub> mol.%	Cd(OH) <sub>2</sub> mol.%
Mass simultaneously precipitated	24.7 (Nickel hydroxide step)	0.5
	35.6 (Nickel hydroxide step + additional graphite step)	
Cadmium oxide added later	17.9 (Nickel hydroxide step)	8.1
	24.1 (Nickel hydroxide step + additional graphite step)	

of the cadmium hydroxide - i.e., of the antipolar mass - is calculated from the magnitude of the first charging step.

The analytically found quantities of nickel and of cadmium hydroxide and the electrochemically effective portions are summarized in Table 6, above (Figure 3, page 12). It can be seen from the results that 10 mole % of homogeneously incorporated cadmium hydroxide are not reduced, and hence do not act as an antipolar mass.

3.5.2 Bulk electrodes. In the case of bulk electrodes, the electrochemical effectiveness depends on whether the cadmium hydroxide is precipitated homogeneously or heterogeneously. To investigate the relationship, two cadmium-nickel hydroxide masses were prepared as follows.

The first mass is obtained by complete precipitation with 9 n KOH. The precipitate is washed with hot 9 n KOH to dissolve any not homogeneously incorporated cadmium hydroxide. According to the X-ray data, the mass consists of pure  $\beta$ -nickel hydroxide; analytically it contains 84.3 mole % nickel hydroxide and 15.7 mole % cadmium hydroxide. The second mass is precipitated from a 1 m nickel nitrate solution and washed, in the same manner as the first mass. After drying, the required quantity of cadmium oxide is mixed in, in order to obtain the same molar composition in the second mass - with respect to nickel and cadmium content - as was obtained in the first one.

Both masses receive, in addition, a 25% addition, by weight, of graphite. After thorough grinding in a mortar, the mass is compressed into 1.2 g tablets and wrapped in nickel wire meshing. The cycle test is performed in an electrolyte 4.5 n in KOH with an addition of 4.5 g LiOH/l, in a current of 20 mA, corresponding to a three-hour current using  $\text{Cd}^0/\text{Cd}^{2+}$  reference electrodes. The experimental results are summarized in Table 7 (page 14). In bulk electrodes, too, only the cadmium hydroxide admixed and not homogeneously incorporated, is effective as antipolar mass.

Remark: We would like to acknowledge gratefully the assistance of Mr. K. Dehmelt and Dr. W. Löser in the experimental part.

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