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by

H. Bode, K. Dehmelt and J. Witte

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ON THE NICKEL HYDROXIDE ELECTRODE

I. ON NICKEL (II) HYDROXIDE HYDRATE*

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Abstract—In a series of papers, experimental results leading to a new understanding of reactions and reaction products on the nickel oxide electrode of the alkaline storage battery are reported. The first communication deals with a hitherto unknown compound of bivalent nickel, which is genetically similar to the oxidation products found on a charged nickel oxide electrode.

Although the nickel hydroxide electrode has been the subject of chemical and electrochemical investigations for more than 50 years [1] there is still no picture of the reaction mechanism that is free of contradictions, or of the states of the compounds on the electrode in the charged (oxidized) and uncharged (reduced) state. Some studies [2-6] show clearly that there is doubt about possible content of potassium in the reaction products, and also about the participation of water in the reaction. There are also uncertainties about the thermodynamic data for the reaction. The values for reaction enthalpy, free enthalpy, entropy and temperature coefficients for the reaction show significant difference among the various observers [5, 7-9].

We have reported in a series of lectures and publications [10-12] on portions of our work in this field. A work by Tuomi [6] stimulated us to present a summarizing review with experimental data, although our work is not yet complete in all points. By publishing our results, we hope to provide the broadest possible base for further discussion of these problems.

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The results of our work can be summarized in three statements:

1. The charge-discharge process at the nickel hydroxide electrode cannot be represented in a single reaction equation, as there are several starting materials and end products.
2. X-ray and electrochemical findings show that the reactions which have been studied are heterogeneous.
3. Even at the lowest current densities, the reaction proceeds at a higher potential than the discharge process.

The difference in the potentials amounts to some 60 mV in one case, and 100 mV in another case. Thermodynamically, this means that the reactions cannot be described with a reversible potential, as is possible with a $Cd/Cd(OH)_2$ or $PbO_2/PbSO_4$ electrode.

Systematics of the Phases and Nomenclature

The reaction equation given by Glemser and Einerhand [13]

$$Ni(OH)_2 + OH^- = \beta\text{-}NiOOH + H_2O + e^-$$

appears to be a general conclusion of the older investigations. The starting material on the left side of the equation is the hydroxide of bivalent nickel, a compound crystallizing in the manner of brucite, $Mg(OH)_2$, also called the C 6 type [14, 15]. This well-characterized hydroxide will be called β-$Ni(OH)_2$ in this work to distinguish it from another hydroxide of bivalent nickel which we shall describe below. This can be oxidized chemically or electrochemically to a nickel (III) oxide-hydroxide, which Glemser called β-NiOOH.

The newly prepared hydroxide of bivalent nickel proves to be a hydrate of nickel (II) hydroxide with the formula $3\ Ni(OH)_2 \cdot 2H_2O$. It can be obtained chemically or electrochemically and is distinguished by a characteristic X-ray diagram. Feitknecht [16] has already described analogous compounds with similar X-ray patterns, although not compounds of nickel. To distinguish them from the well-known hydroxides of the C 6 type he called them α-hydroxides. We shall also use the α-hydroxide designation for the nickel hydroxide hydrate, $3\ Ni(OH)_2 \cdot 2\ H_2O$ which we have prepared.

This α-nickel hydroxide can be converted by oxidation into a higher-valent nickel hydroxide. In this manner, one obtains two analytically different substances. The X-ray patterns are practically identical, and are distinguished only by the sharpness of the lines, as always dependent on the type of the preparation, and by the presence or absence of weak reflections. The Debyograms correspond to those of the γ-NiOOH of Glemser and Einerhand [17]. One compound, (A), which Glemser and Einerhand produced by hydrolysis of $NaNiO_2$ is a nickel (III) oxide hydroxide hydrate

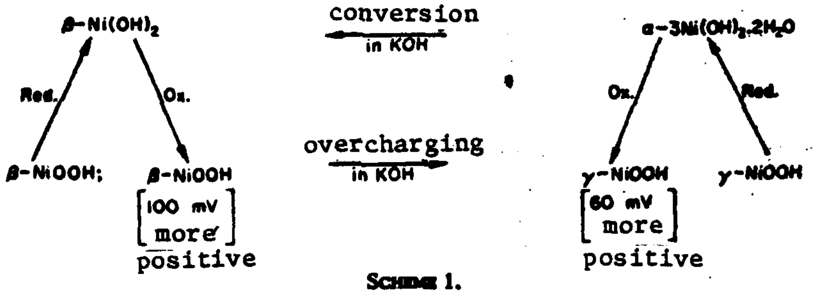
(A) $$4NiOOH \cdot 3H_2O$$

with the oxidation value of $NiO_{1.5}$. It contains water of hydration. The second substance (B) is obtained by oxidation with potassium hypobromite, or electrochemically using potassium hydroxide electrolyte. It contains potassium and has a higher oxidation number than $NiO_{1.5}$. It can be called a potassium - nickel (III, IV) oxide hydroxide. The compound with the highest oxidation number has the analytical composition $4\ NiO_{1.81} \cdot 2.25\ H_2O \cdot 0.5\ K_2O$. As discussed later, we derive from that the following structural formula:

(B) $$[Ni_4O_4(OH)_4]O_{1,5}(OH)_{0,5}K.$$

The potassium ion can be replaced by Ba^{2+} as well as by Na^+ and probably also by H_3O^+, but not by Rb^+ or Cs^+ ions. Li^+ could be incorporated in another manner. It is not known whether substance (A) occurs at all in a working accumulator. On the other hand, the potassium-containing highly oxidized phase (B) can be demonstrated on long overcharging (Feitknecht [2]; Salkind and Bruins [5]). The designation γ-form should be reserved for compound (B). Tuomi [6] has called the material that occurs on overcharging the α phase. This nomenclature should be avoided, though, as Glemser and Einerhand [17] have suggested the designation α-NiO(OH) for another oxidized nickel hydroxide.

The genetic relations of these nickel hydroxides are shown in the following scheme:



SCHEME 1.

The importance of these reaction sequences for the behavior of the nickel hydroxide electrode in an alkaline cell is the subject of this and subsequent work.

Experimental Portion

Preparation of 3 $Ni(OH)_2 \cdot 2\ H_2O$

For electrochemical preparation of the α hydroxide, a nickel sheet (60 x 40 x 0.1 mm) is connected as the cathode at a distance of 3 - 4 cm between two equally large anode plates. The electrolyte is a 0.1 N nickel nitrate solution

(Merck, highest purity), the pH of which is maintained at 4.8 by addition of nitric acid. The electrolysis is done at room temperature without stirring the electrolyte, at a current density of 0.1 mA/cm^2. After about ½ hour, about 1 mg/cm^2 of the α hydroxide has deposited on the cathode. The electrode with the deposit is washed free of nitrate and dried over P_2O_5 an a vacuum desiccator. Then the preparation can be scraped off the support.

For the chemical preparation of the α hydroxide, 100 ml of 0.01 N nickel nitrate solution is added dropwise to 1 liter of 0.001 N KOH, with stirring and continuous gassing with CO_2-free nitrigen. As the alkali is always in excess, formation of basic nickel nitrates is prevented. After precipitation, the deposit is filtered off, washed free of nitrate and alkali, and then dried in vacuum over P_2O_5. Use of such dilute alkali makes it difficult to produce larger amounts of the pure α hydroxide.

Larger amounts of the material can be obtained more easily by another procedure. For the preparation, $Ni(OH)_2$ is dissolved in approximately 8 N ammonia solution until it is saturated. The blue solution is filtered into a polyethylene beaker of appropriate size, and the beaker is kept in a desiccator over concentrated sulfuric acid. After about 1 - 2 weeks the solution has completely evaporated, and the α hydroxide appears as a generally well-crystallized powder.

Nickel and total water content are determined to analyze the preparations. The nickel content is calculated as $Ni(OH)_2$, and the remainder of the total water as water of hydration. The pycnometric density is determined with anhydrous petroleum (b. p. 150-200°) as the sealing liquid. The pycnometric density of a well crystallized anhydrous β-$Ni(OH)_2$, prepared by heating a normal precipitated product in the autoclave for 3 days at 270° is 3.85 g/cm^2. The X-ray density is 3.97 g/cm^2. Table 1 shows

Table 1.

$Ni(OH)_2$	H_2O	$Ni(OH)_2$	H_2O	Density
%	%	Mol	Mol	g/cm^3
89,90	10,43	1	0,60	2,52 (pycn.)
89,00	10,94	1	0,63	
89,00	11,97	1	0,69	
89,90	10,12	1	0,58	2,48 (pycn)
Calculated for 3 $Ni(OH)_2 \cdot 2\ H_2O$				
88,50	11,45	1	0,67	2,62 (X ray)

some of the data. α nickel hydroxide cannot be differentiated by color from the normal green β-$Ni(OH)_2$. It is stable in the dry state. In alkali hydroxide solutions, though, it converts into β-$Ni(OH)_2$ with loss of water of hydration. The reaction goes faster the higher the temperature and the more concentrated the hydroxide solution is. In strong alkali (about 6 to 9 N) the conversion is complete within a few hours at 90°, while the material remains unchanged for several days in 0.1 to 1 N alkali at room temperature. The process is not reversible.

Some stabilization of the α hydroxide can be achieved if certain additived are added to the precipitation solutions in preparation. Certain substances, particularly those containing OH groups, such as glucose, boric acid, and mannitol, etc., are stabilizing. Under these conditions, of course, a nonstoichiometric amount of the additive is co-precipitated and incorporated into the α hydroxide. These products can be characterized as α forms by their X-ray diagrams (appearance of a line with d = 8.1 Å).

In thermogravimetric study, the α hydroxide gives off the water of hydration at about 150°, but does not transform into the β-$Ni(OH)_2$.

Other α Hydroxides

The mixed nickel-zinc hydroxide hydrates of the form 3 $(Ni,Zn)(OH)_2 \cdot 2\ H_2O$ are especially resistant. They can be obtained by the same methods as α nickel hydroxide. The nickel-zinc hydroxides are considerably more stable, so that pure α hydroxides are obtained on precipitation in 0.5 N alkali. Here, then, one has the capability of producing larger amounts of an α hydroxide. The zinc content is variable within wide limits without structural change. The mixed hydroxides, as well as the pure α-$Zn(OH)_2$ have already been prepared by Feitknecht [16]. One obtains well-crystallized substances with moderate zinc contents. Some analytical data for them are reported in Table 2. Preparation of pure α cobalt hydroxide is considerably more difficult, as it converts much more easily into the β form, and is also very easily oxidized by oxygen. On the other hand, this example is especially interesting because the forms differ in color: α-$3Co(OH)_2 \cdot 2H_2O$ is intensely blue, and β-$Co(OH)_2$ is pink.

Table 2.

$Ni(OH)_2$	$Zn(OH)_2$	H_2O	$Ni,Zn(OH)_2$	H_2O	Pycnometric density
%	%	%	Mol	Mol	g/cm^3
58,10	29,30	12,54	1	0,75	—
61,50	27,40	11,10	1	0,66	2,69
62,00	29,30	8,97	1	0,52	2,78

On electrochemical deposition from 0.1 N cobalt nitrate solution, the pure blue α form is obtained at the cathode. This is immediately converted into the pink $Co(OH)_2$ by immersing the electrode into dilute alkali. Therefore, one must work very rapidly through the washing and drying processes after the deposition, and air must be excluded. Then one obtains blue preparations initially; they take on a greenish tone on slight action of oxygen. The total water content of these substances is always somewhat less than corresponds to the formula above. Chemical precipitation gives blue preparations in the presence of stabilizing additives (see Feitknecht [16]). These additives are incorporated into the precipitates and affect the analytical composition of the α hydroxide. Still, the identity of the blue cobalt hydroxide with the α nickel hydroxide can be recognized from the densities and especially from the X-ray diagrams: density of a cathodically deposited blue cobalt hydroxide, $D_{pycn.} = 2.89$ g/cm^3; $D_{X\text{-}ray} = 2.57$ g/cm^3; density of a product stabilized with glucose, $D_{pycn.} = 2.27$ g/cm^3. The differences of the X-ray densities from the pycnometric densities are due to the fact that in the cathodically deposited product a small portion has converted into pink β-Co(OH)$_2$ (D = 3.79 g/cm^3) while the chemically precipitated blue cobalt hydroxide contains a certain percentage of glucose.

We have other results on compounds of the types $3(Ni, Cd)(OH)_2 \cdot 2H_2O$ and $3(Ni, Fe)(OH)_2 \cdot 2H_2O$. Because of the special importance of these compounds in cell technology we shall report on them elsewhere.

Discussion

The nickel hydroxide formed by cathodic deposition shows a Debyogram which differs from that of normal $Ni(OH)_2$ (see also Briggs and Wynne-Jones [18]). On the assumption that the pH at the cathode rises on electrolysis, this form of nickel hydroxide should also be precipitable from alkaline solutions at relatively low pH values. Precipitations from millinormal potassium hydroxide give products which never have the same X-ray diagram as from cathodic deposition.

These compounds, which we call α forms, also arise from ammonia-containing hexammine-enveloped salt solutions.

The Debye patterns of the α hydroxides described in the experimental portion are shown in Figures 1 - 4, along with two other powder diagrams of β-type nickel hydroxides. The discovery of this group of materials goes back to Feitknecht [16]. He explained the structure of the α hydroxides as a double-layer lattice consisting of ordered hydroxide layers of the corresponding C 6 type (as in β-$Ni(OH)_2$) in which 'unordered material' , which in this case means "amorphous $Ni(OH)_2$", is intercalated with extension of the c axis. But this concept would lead to a considerably higher density, near or equal to that of the β-$Ni(OH)_2$.

According to our investigations, the water of hydration must be considered as an essential structural component of the α hydroxides, so that we suggest the following structure. The α hydroxides form a layered lattice consisting of hydroxide layers of the brucite type, in which the layer separation is enlarged by incorporation of an intermediate water layer. A considerably lower density, corresponding to that observed (Table 1) is calculated from this suggested model. The suggestion can be demonstrated unambiguously only through complete structural analysis using monocrystals, but their preparation encounters great difficulties, as this class of materials deals with unidimensionally disordered compounds [16].

The following viewpoints apply for the derivation of the suggested structure. The X-ray diagram of α nickel hydroxide has considerably fewer lines than that of the β-$Ni(OH)_2$ (as Figures 1 and 2 show). Like it, though, it appears to be hexagonal, from which it appears that only the cross lattice reflections (hk0) and the basic reflections (001) are present.

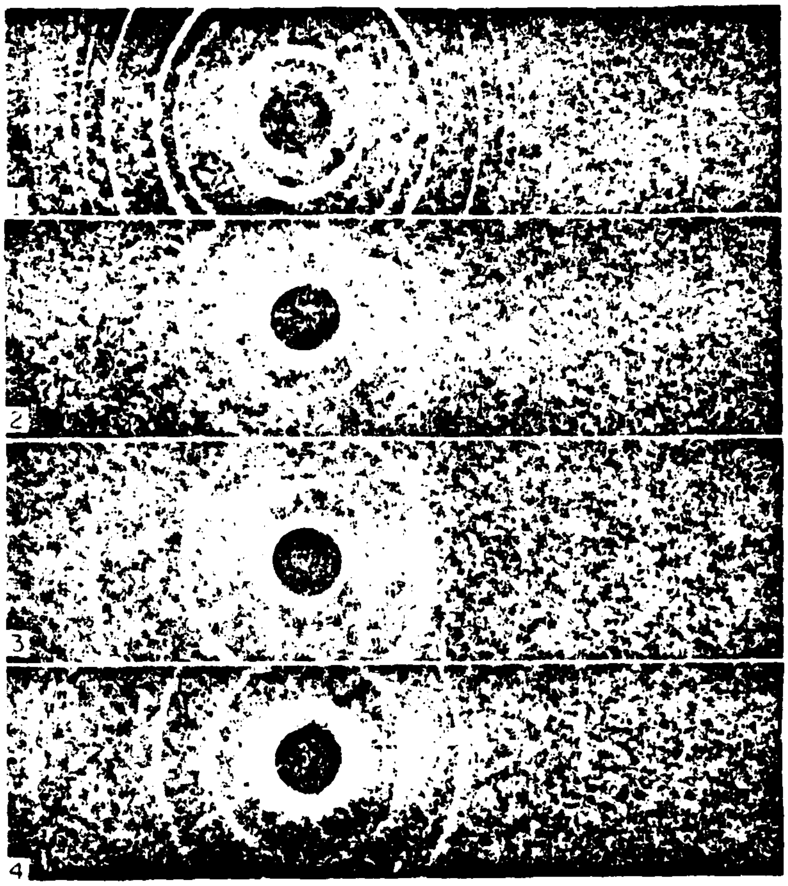


Figure 1. β-$Ni(OH)_2$, recrystallized (CuK_α)

Figure 2. α-$3Ni(OH)_2 \cdot 2H_2O$ (CuK_α)

Figure 3. α-$3(Ni,Zn)(OH)_2 \cdot 2H_2O$ (CuK_α)

Figure 4. α-$3Co(OH)_2 \cdot 2H_2O$ (blue) (FeK_α) (with traces of β-$Co(OH)_2$ (pink).

Table 3.

α-3Ni(OH)$_2\cdot$2H$_2$O			β-Ni(OH)$_2$		
d_{hkl}	hkl	J_0	d_{hkl}	hkl	J_0
8,07	001	s-st	4,60	001	st
4,05	002	st	2,70	100	st
2,65	100	st	2,30	002	s
2,02	004	s	1,56	110	st
1,54	110	m-st	1,349	200	m
1,333	200	m	1,148	004	s
1,010	210	m	1,022	210	s-m
0,893	300	m	0,900	300	m

The latter indicate an enlargement of the c axis corresponding to incorporation of water. Pyramidal reflections are not seen. Table 3 presents, along with all the reflections observed for α nickel hydroxide, the prismatic and basal reflections of β-Ni(OH)$_2$. With similar indexing, the lattice constants are found to be

$a = 3.08$ and $c = 8.09$ Å for α-3Ni(OH)$_2\cdot$2H$_2$O and
$a = 3.12$ and $c = 4.60$ Å for β-Ni(OH)$_2$.

While the a axis is only slightly contracted, the c axis is considerably extended.

The lattice constants above would give a density of 7.85 g/cm^3 for the α hydroxide with one formula unit in the elementary cell. From the pycnometrically measured density of 2.52 g/cm^3, a threefold larger cell must be required. This can be achieved in the hexagonal system either through selection of a structure rotated by 90° ($P\bar{3}m1 \rightarrow P\bar{3}m1$) or by selection of a rhombohedral space group. As the prism reflections allow exact sequencing of the hexagonal indexing (small deviations must occur with the rhombohedral condition), a new a axis is selected with the value of $a = 5.34 = 3.08\sqrt{(3)}$ Å. With this value and c = 8.09 Å an X-ray density of 2.62 g/cm^3 is calculated.

An intensity calculation was carried out to test the suggested structure derived here. It was based on the space group D_{3d}^{1} – $P\bar{3}m1$.

Point positions (see Figure 5):
3Ni (a): 000; (c): 1/3 2/3 0
6OH (k): x0z with x = 1/3 and z ~ 1/6
$2H_2O$ (d): 1/3 2/3 1/2

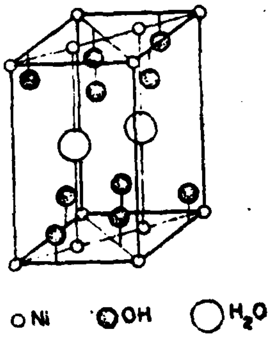


Table 4

$3Ni(OH)_2 \cdot 2H_2O$		$a = 5{,}34$ Å $c = 8{,}09$ Å	
hkl	$\sin^2\theta \cdot 10^{-4}$	J_o	J_c
001	9,1	60	62
002	36,1	7	8,3
110	84,5	10	8,9
004	145,8	0,5	1,3
300	250,8	6	4,2
220	334,7	1	0,9
410	580,8	1	0,8
330	746,3	1,5	0,9

Figure 5. Lattice of $3Ni(OH)_2 \cdot 2H_2O$.

The result of the intensity calculation is presented in Table 4. The indexing is, of course, changed to correspond with the larger cell.

We believe that the good agreement of the observed and calculated intensities proves the basic correctness of the structure of the α nickel hydroxide.

Because of the choice of a larger cell – and also the limitation to prism reflections – fewer lines are to be expected, such as (100), (200), (210), etc. The structural amplitudes of these reflections are always very low, as neither the Ni nor the OH atoms contribute to their intensity. Thus, it is understandable that they are not observed. For example, one would calculate for the (100) reflection an intensity (on the above scale) of 0.2, and for the (200) reflection an intensity of only 0.02.

The water molecules are arranged in flat six-rings in the intermediate layer according to the concept derived above. It is still necessary to clarify whether this occurs or whether a statistical distribution to (1 + 2) layers (b) and (d) is realized. In the latter case, the Feitknecht concept of an "unordered intermediate layer" (which he assumed to consist of $Ni(OH)_2$ while we postulate water molecules) could have a certain justification. In any case, this intermediate layer, which is only loosely bound – IR spectra indicate weak hydrogen bonds – can be considered responsible for the instability of this compound. The absence of pyramid reflections indicates unidimensional disorder of the layer packets and may be explained by lattice disorders such as, for instance, weak mutual displacement of the hydroxide layers.

The structure has analogs in some water-containing clay minerals. Those, too, are layer structures, although more complex because double or multiple layers occur, as in $Al_2Si_2O_5(OH)_4$ with hexagonally arranged oxygen atoms having other atoms lying in their octahedral or tetrahedral vacancies. The anhydrous material built up of these layers is kaolin, with d_{001} = 7.15 A (analogous to β-$Ni(OH)_2$ with d_{001} = 4.60 A), and the hydrous form is halloysite, $Al_2Si_2O_5(OH)_4 \cdot 2H_2O$ with d_{001} = 10.25 A (analogous to α-$3Ni(OH)_2 \cdot 2H_2O$ with d_{001} = 8.07 A). On heating of halloysite, the entire intermediate layer water is lost at about 150° C, as for α nickel hydroxide, without the hydroxide layer separation significantly reducing to metahalloysite.

The conversion of the α form under the influence of alkali goes only in one direction. This monotropic course of the reaction suggests that this is a transformation from a thermodynamically unstable material to a stable one.

For these hydroxides, there are some data on the solubility products of "active" and "inactive" forms [19]:

$Ni(OH)_2$ (active) Log K_0 = -14.7
$Ni(OH)_2$ (inactive) Log K_0 = -17.2
$Co(OH)_2$ (blue) Log K_0 = -14.2
$Co(OH)_2$ (pink, inactive) Log K_0 = -15.7

If one assumes that the "active" hydroxides correspond to the α form, and the colors of the cobalt hydroxides give some basis for that, then one can calculate the free reaction enthalpy of the conversion

$$\alpha[Ni(OH)_2 \cdot \tfrac{2}{3}H_2O] \rightarrow \beta\text{-}Ni(OH)_2 + \tfrac{2}{3}H_2O$$

It is $\Delta G = - 3.4$ Kcal/mol and, for the corresponding Co compounds, $\Delta G = - 2.0$ Kcal/mol. Even though the numerical values for the solubility products include a certain uncertainty, the sign of ΔG shows that the reaction can go only from α to β.

The other α hydroxides also have the structure of the α nickel hydroxide. The lattice constants for the blue cobalt hydroxide (Figure 4) were calculated as a = 5.40 Å and c = 8.07 Å, giving an X-ray density of $D_{X\text{-ray}} = 2.57$ g/cm^3. To be sure, the pycnometric densities differ from that, for reasons given above.

The following values were found for a mixed nickel-zinc hydroxide hydrate, $3(Ni, Zn)(OH)_2 \cdot 2H_2O$ (Figure 3) with 61.5% $Ni(OH)_2$ and 27.4% $Zn(OH)_2$:

$a = 5.32$ Å $c = 8.04$ Å

$D_{X\text{-ray}} = 2.67\ g/cm^3$ $D_{pycn.} = 2.69\ g/cm^3$

Feinknecht [16] reports $a = 5.39$ Å and $c = 7.8$ Å for pure α-$Zn(OH)_2$.

We thank Mrs. M. Herrman for performing the work. We also thank the management of Varta AG, especially for allowing the publication.

Literature titles:

1 ... (contains a general literature survey up to 1962)

19 Solubility constants

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