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(54) Titre : HYDROXYDE DE NICKEL (II) RENFERMANT DU MANGANESE (III), UTILISE POUR LA FABRICATION  
D'ACCUMULATEURS  
(54) Title: MANGANESE(III)-CONTAINING NICKEL(II) HYDROXIDE FOR THE PRODUCTION OF SECONDARY  
BATTERIES

(57) **Abrégé/Abstract:**

Manganese(III)-containing nickel(II) hydroxide, a process for its production and its use as electrode material for secondary batteries.



2127496

Manganese(III)-containing Nickel(II) Hydroxide for the  
Production of Secondary Batteries

A b s t r a c t

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Manganese(III)-containing Nickel(II) Hydroxide for the  
Production of Secondary Batteries

BACKGROUND OF THE INVENTION

5 The present invention relates to manganese(III)-  
containing nickel(II) hydroxide, a process for its pro-  
duction and its use as electrode material for secondary  
batteries.

10 Nickel(II) hydroxide is used in the alkaline accumulator  
as positive electrode mass. Changes in certain electro-  
chemical properties are produced by incorporating various  
extraneous ions.

15 The incorporation of manganese ions in nickel(II)  
hydroxide is described in only a few publications. A  
reason for this is that the bivalent manganese in  $\beta$ -  
 $\text{Mn}(\text{OH})_2$  or in the mixed oxide with nickel is already very  
easily oxidized by atmospheric oxygen and the manganese in  
the end product does not exist in a defined oxidation  
state. The preparation of uniform products is thereby  
complicated.

20 Some references on the properties of manganese-doped nickel  
hydroxide electrodes are known from the literature:

25 J.P. Harivel, B. Morignat, J. Labat, J.F. Laurent, Power  
Sources 1966, Pergamon Press, ed. by D.H. Collins, p. 239,  
doped nickel(II) hydroxide with  $\text{Mn}^{2+}$  or  $\text{Mn}^{4+}$  by co-  
precipitation from aqueous sodium hydroxide solution. The  
doped hydroxides showed no improvements in the electro-  
chemical properties by comparison with pure nickel  
hydroxide.

30 Cordoba et al. investigated the effect of nickel hydroxides  
doped with manganese and/or iron on the application as

23189-7661

oxygen electrodes (S.I. Cordoba, M. Lopez Teijelo, V.A. Macagno, Electrochimica Acta 32 (1987), 1783, S.I. Cordoba, R.E. Carbonio, M. Lopez Teijelo, V.A. Macagno, Electrochimica Acta 31 (1986), 1321). The materials were  
5 here produced likewise by coprecipitation or else by deposition of the pure hydroxides above each other in layers.

D.A. Corrigan, R.M. Bendert, J. Electrochem. Soc. 136 (1989), 723 and D. Bélanger, G. Laperrière, J. Electrochem.  
10 Soc. 137 (1990), 2355 carried out cyclovoltammetric studies on cathodically deposited thin layers of  $Mn^{2+}$ -doped nickel hydroxide among other systems.

Practical conclusions with regard to the improvement of the properties and/or application of these materials in  
15 secondary batteries cannot, however, be derived from the literature mentioned.

The manganese-doped nickel hydroxide materials known from the prior art, as have been used up to now for the production of electrodes for secondary batteries, therefore  
20 have no important advantage over undoped material.

#### SUMMARY OF THE INVENTION

The invention improves the properties of manganese-doped  
25 nickel hydroxide powder for the production of battery electrodes so that the capacity of the nickel hydroxide electrodes is raised and the cyclic stability simultaneously improved.

It has now surprisingly been found that manganese as an additive to nickel hydroxide causes a particularly positive  
30 effect in the nickel hydroxide electrode when it exists in the nickel hydroxide electrode predominantly in the tri-valent oxidation state.



23189-7661

This invention consequently provides manganese-containing nickel (II) hydroxide powders in which more than 50 mol %, preferably at least 80 mol % and more preferably at least 90 mol % of the manganese exists in the trivalent  
5 oxidation state. Preferably, the molar ratio of Ni to Mn is in the range from 100:1 to 1:1 and more preferably in the range of from 5:1 to 3:1. Preferably, the nickel (II) hydroxide powder also contains one or more of Cd, Co, Zn, Ca and Mg in a total amount of no more than 8 mol %, based on the total amount of Ni  
10 and Mn. Preferably, the powder has a particle size of 1 to 100  $\mu\text{m}$ .

The invention also provides a process for the production of a nickel (II) hydroxide powder comprising Mn (III), comprising coprecipitating a nickel (II) and  
15 manganese (III) salt solution with an alkali solution, such that the manganese (III) is incorporated into the nickel (II) hydroxide powder lattice. The Mn (III) may be prepared by reacting a Mn (II) salt solution with an oxidizing agent, e.g., a permanganate solution, a peroxodisulphate or  $\text{H}_2\text{O}_2$ , and the  
20 reaction may produce peracetic acid. Preferably, the Mn (III) salt solution comprises a stabilizing anion. Preferably, the coprecipitation is carried out in the presence of a soluble salt of an element selected from the group consisting of Co, Zn, Cd, Ca and Mg. The invention also provides use of the  
25 Ni (II) hydroxide powder for making a secondary battery alkaline accumulator positive electrode. The invention also provides a secondary battery comprising an alkaline accumulator positive electrode comprising a nickel (II) hydroxide powder of the invention.

30 An important economic side-effect of the invention is to make possible the replacement of the relatively expensive nickel by an appropriate, less expensive, proportion of

23189-7661

manganese and thereby the achievement of an increased mass efficiency of the nickel hydroxide.

Nickel-manganese electrodes according to the invention, by comparison with undoped reference products, show  
5 a much increased efficiency of the one-electron step  $\text{Ni}^{2+} \rightarrow \text{Ni}^{3+}$  and in addition an improved cycle stability.

The doping occurs by the replacement of  $\text{Ni}^{2+}$  ions in the crystal lattice of the nickel hydroxide by  $\text{Mn}^{3+}$  ions. The  $\text{Mn}^{3+}$  ion proves to be very suitable for this by reason of the  
10 radius ratio  $\text{Ni}^{2+}/\text{Mn}^{3+} = 1.05$ .

The coprecipitation of the manganese (II) compound with the nickel hydroxide is carried out by dropping an acidified metal salt solution containing  $\text{Ni}^{2+}$  and  $\text{Mn}^{3+}$  ions into a feed of constant pH value. While the  $\text{Ni}^{2+}$  ion can be used in  
15 the form of its salts, the  $\text{Mn}^{3+}$  ion is prepared in the salt solution by reaction of  $\text{Mn}^{2+}$  ions with corresponding amounts of  $\text{MnO}_4^-$  ions. This is achieved by continuous combination of the corresponding solutions in a mixing chamber. Both solutions can at this time already contain nickel (II) salts.  
20 An  $\text{Mn}^{3+}$  solution can also be mixed with an  $\text{Ni}^{2+}$  solution later.

The  $\text{Mn}^{3+}$  ion is formed according to the equation:



The average degree of oxidation of the manganese ion in the nickel hydroxide matrix can be deliberately varied by an appropriate excess of  $\text{Mn}^{2+}$  or  $\text{MnO}_4^-$  ions.

5 Trivalent manganese is very unstable in solution. It  
disproportionates rapidly in aqueous solution with  
formation of hydrated oxides of manganese(II) and of  
manganese(IV). If this process goes to completion in its  
salt solution, the manganese can no longer be incorporated  
10 into the nickel hydroxide lattice and separate phases of  
hydrated manganese oxides in addition to nickel hydroxide  
precipitate in the precipitation step.

This disproportionation must be eliminated in order to  
bring about the incorporation of the manganese in the host  
matrix. It is sufficiently well known from the literature  
15 that the  $\text{Mn}^{3+}$  ion can be stabilized briefly in the presence  
of suitable anions (e.g. sulphate, phosphate, acetate  
etc.). It is therefore important for the production of the  
precipitation product that sufficient amounts of  
stabilizing anions or their mixtures are present in the  
20 combined salt solution to eliminate a premature decay  
reaction of the  $\text{Mn}^{3+}$  ions. In this process, the lifetime  
of the  $\text{Mn}^{3+}$  depends on the nature of the anions, their  
concentration in the solution and the solution's pH value.  
The length of the reaction zone must also be calculated  
25 according to this lifetime:

Too short a reaction zone can lead to an inadequate  
intermixing of the reacting solution or an incomplete  
reaction, and the products become non-uniform.

If the reaction zone is too long, the  $\text{Mn}^{3+}$  ions decompose  
30 too early, which prevents their incorporation in the  
 $\text{Ni}(\text{OH})_2$ .



In conclusion, the  $\text{Ni}^{2+}/\text{Mn}^{3+}$  mixed hydroxide is precipitated by dropwise addition of the acidic salt solution containing  $\text{Ni}^{2+}$  and stabilized  $\text{Mn}^{3+}$  to an alkaline feed of constant pH value. After the precipitation, the  $\text{Mn}^{3+}$  is fixed as such in the  $\text{Ni}(\text{OH})_2$  lattice, and disproportionation can no longer occur.

#### DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

In the following, the invention is illustrated by the following non-limiting examples.



Example 1:

Solution A: 10.04 g (0.04 moles)  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$   
 58.16 g (0.20 moles)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$   
 12.50 g  $\text{H}_2\text{SO}_4$  97 %  
 10.00 g HAc 99 %  
 10.00 g  $\text{H}_3\text{PO}_4$  85 %  
 $\text{H}_2\text{O}$  to 250 ml

Solution B: 1.58 g (0.01 moles)  $\text{KMnO}_4$   
 12.50 g  $\text{H}_2\text{SO}_4$  97 %  
 10.00 g HAc 99 %  
 10.00 g  $\text{H}_3\text{PO}_4$  85 %  
 $\text{H}_2\text{O}$  to 250 ml

Correction alkali: 250 ml KOH,  $c = 3.526 \text{ mole/l}$

Feed: 1000 ml KOH with pH  $12.50 \pm 0.02$   
 $T = 33 \pm 2^\circ\text{C}$

Example 2:

Solution A: 12.55 g (0.050 moles)  $\text{Mn}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$   
 54.53 g (0.188 moles)  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$   
 12.50 g  $\text{H}_2\text{SO}_4$  97 %  
 10.00 g HAc 99 %  
 10.00 g  $\text{H}_3\text{PO}_4$  85 %  
 $\text{H}_2\text{O}$  to 250 ml

Solution B: 1.98 g (0.0125 moles)  $\text{KMnO}_4$   
 12.50 g  $\text{H}_2\text{SO}_4$  97 %  
 10.00 g HAc 99 %  
 10.00 g  $\text{H}_3\text{PO}_4$  85 %  
 $\text{H}_2\text{O}$  to 250 ml

Correction alkali: 500 ml 3.5 m KOH

Feed: 1000 ml KOH with pH 12.50  $\pm$  0.02

Implementation of the process

5 The solutions A and B were brought together continuously  
with the aid of separate pumps at the same volumetric flow  
rate (100 ml/h) via a Y-shaped mixing chamber. During  
this, the spatially separated formation of  $\text{Mn}^{3+}$  could be  
followed in the subsequent reaction zone (glass tube). The  
colour change was from violet ( $\text{MnO}_4^-$ ) to red ( $\text{Mn}^{3+}$  in  
10 presence of  $\text{Ni}^{2+}$ ).

After a constant total reaction time of ca. 20 sec., the  
solution dropped into a feed of KOH, in which the pH value  
was checked with the aid of a glass electrode and held  
constant (pH 12.50  $\pm$  0.02) by addition of correction  
15 alkali. In this way both the reacting state of the  $\text{Mn}^{3+}$  to  
the precipitation point and the precipitation process  
itself were always standardized and controllable.

The brown-red product was centrifuged off after 15 hours  
ageing and washed 5 times, with 650 ml alkali of pH 12.50  
20 on each occasion, and then dried in vacuum at 51 °C for  
three days.

The product gave a characteristic X-ray spectrum. For more  
precise characterisation, the accurate analytical data were  
25 determined for Example 1:

2127496

# Chemical Analysis

(Example 1)	Element/ anion	Mean value [%]	Molar proportion N
	Ni	46.67	4.00
	Mn	10.87	1.00
	H	2.55	12.83
	MnO <sub>2</sub>	9.27	0.54
	SO <sub>4</sub> <sup>2-</sup>	<1	<
	PO <sub>4</sub> <sup>3-</sup>	1.54	0.08
C & N	outside the calibration range		

1. Degree of oxidation of the manganese:

$$5 \quad x \text{ in MnO}_x \quad x = \left[ 1 + \left( \frac{N_{\text{MnO}_2}}{N_{\text{Mn total}}} \right) \right]$$

$$X = 1.54$$

Mn<sup>3.08</sup> is present

Proportion of the nickel substituted:

- 10      A) Based on the molar ratios Ni/Mn, the nickel saving is 20 mole%.
- B) From the comparison of the analytical Ni content for pure nickel hydroxide (62 %) and for the doped product (46 %), a nickel saving of 26 % per unit mass is



found.

## 2. Investigation of the cycle behaviour

For the examination of the electrochemical properties of the active material, galvanostatic charges and discharges vs  $\text{Cd}/\text{Cd}(\text{OH})_2$  or  $\text{Hg}/\text{HgO}$  were carried out. The electrode was produced as a pellet from 1.00 g active mass, 0.25 g graphite and 0.03 g PTFE.

Electrolyte: 7 m KOH

Charge: 11 h at 50 mA

Discharge: 25 mA up to the cut-off voltage of V vs  $\text{Hg}/\text{HgO}$  or 1 V vs  $\text{Cd}/\text{Cd}(\text{OH})_2$

By comparison with a sample of pure nickel hydroxide, with the same preparation technique and under the same cyclisation conditions, the product shows a distinct improvement of the cycle stability:

The pure nickel hydroxide already reaches its maximum capacity after 10 cycles, followed by a continuous decline. This effect cannot be observed with the manganese-doped sample until between 150 and 200 cycles. (It was demonstrated by replacement of the electrolyte that at these high cycle numbers the carbonation of the alkali makes a definite contribution to the loss of capacity). For the manganese-doped mass the measured capacities were 205 mAh/g in the range from Cycle 100 to 150, followed by an insignificant decline of the capacity (198 mAh/g in Cycle 200).

In addition, the mass efficiency of the nickel is definitely raised in the manganese-doped product. More than 90 % of the theoretical one-electron step from  $\text{Ni}^{2+}$  to  $\text{Ni}^{3+}$  can be utilised over a wide cycle range. The undoped nickel hydroxide, on the other hand,

23189-7661

with only 60 % utilisation of the discharge capacity at the maximum, lies definitely lower under the same experimental conditions.

- 5 After an over-discharging (cycle 30), a manganese-doped sample lost ca. 10 % of its capacity based on the one-electron step, but the cycle behaviour showed no setback. The value for the discharge capacity remained almost constant over more than 200 cycles, with 75 % efficiency of the one-electron step.

23189-7661

CLAIMS:

1. A nickel (II) hydroxide powder comprising manganese (III) ions, wherein the manganese ions are incorporated into the nickel hydroxide powder lattice and more  
5 than 50 mol % of the manganese is present in the trivalent oxidation state.
2. A nickel (II) hydroxide powder according to claim 1, wherein at least 80 mol % of the manganese is present in the trivalent oxidation state.
- 10 3. A nickel (II) hydroxide powder according to claim 2, wherein at least 90 mol % of the manganese is present in the trivalent oxidation state.
4. A nickel (II) hydroxide powder according to claim 1, 2 or 3, wherein the molar ratio of Ni to Mn is in the range  
15 from 100:1 to 1:1.
5. A nickel (II) hydroxide powder according to claim 4, wherein the molar ratio of Ni to Mn is in the range from 5:1 to 3:1.
6. A nickel (II) hydroxide powder according to any one  
20 of claims 1 to 6, further comprising an element selected from the group consisting of Cd, Co, Zn, Ca, Mg and a mixture thereof in a total amount of no more than 8 mol %, based on the total amount of nickel and manganese.
7. A nickel (II) hydroxide powder according to any one  
25 of claims 1 to 6, having a particle size of 1 to 100  $\mu\text{m}$ .
8. A process for the production of a nickel (II) hydroxide powder comprising Mn (III), comprising coprecipitating a nickel (II) and manganese (III) salt solution



23189-7661

with an alkali solution, such that the manganese (III) is incorporated into the nickel (II) hydroxide powder lattice.

9. A process according to claim 8, wherein the manganese (III) is prepared by reacting a manganese (II) salt solution with an oxidizing agent.

10. A process according to claim 9, wherein the oxidizing agent is a permanganate solution, a peroxodisulphate or  $H_2O_2$ , and peracetic acid is produced by the reaction.

11. A process according to claim 8, 9 or 10, wherein the manganese (III) salt solution comprises a stabilizing anion.

12. A process according to any one of claims 8 to 11, wherein the coprecipitation is carried out in the presence of a soluble salt of an element selected from the group consisting of Co, Zn, Cd, Ca and Mg.

13. Use of a nickel (II) hydroxide powder according to any one of claims 1 to 7, for making a secondary battery alkaline accumulator positive electrode.

14. A secondary battery comprising an alkaline accumulator positive electrode comprising a nickel (II) hydroxide powder as recited in any one of claims 1 to 7.

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PATENT AGENTS