

Active material for rechargeable batteries

The present invention relates to an active material for rechargeable batteries, in particular a metal(III) ion-substituted nickel hydroxide with brucite-type structure, a process for the production thereof and use thereof as an electrode material for secondary batteries.

Nickel hydroxide is used as a cathode material for alkaline secondary batteries such as nickel/cadmium or nickel/metal hydride batteries. An electrochemical variable crucial for industrial use is capacity per unit mass. It is a function of the nickel content of the nickel hydroxide and of nickel utilisation. The interrelationship between capacity per unit mass Q in mAh/g, the nickel content in wt.% of the cathode material and nickel utilisation in % EES (one-electron step) is obtained as follows:

$$Q = \frac{\text{wt.\% Ni} \cdot \% \text{ EES} \cdot F}{58.69 \cdot 3600 \cdot 10} \quad [\text{mAh/g}]$$

wherein

$F =$ Faraday constant = $96487 \text{ A}\cdot\text{s/mol}$
 $58.69 =$ Molar mass of nickel, g/mol
 $3600 =$ factor for converting seconds into hours
 $10 =$ factor for converting % into ratio figures and mA into A.

This provides a theoretical capacity per unit mass at 100 % EES of 289 mAh/g. Nickel hydroxides suitable for industrial use, however, comprise modification metal contents of between 4 and 6 % and 1 to 2 % water relative to the total metal content, such that, in the case of 100 % nickel utilisation, these comprise a capacity per unit mass of only 252 to 266 mAh/g. The 100 % nickel utilisation of this nickel hydroxide is associated with the 1-electron step (and 1-proton step) per nickel atom which occurs on conversion of $\beta\text{-Ni}^{(\text{II})}(\text{OH})_2$ into $\beta\text{-Ni}^{(\text{III})}\text{OOH}$ during battery charging.

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Overcharging of the battery results in further deprotonation and oxidation of some of the nickel into $\text{Ni}^{(\text{VI})}$, i.e. in the formation of $\gamma\text{-NiOOH}$. For charge compensation, water molecules and alkali ions are incorporated in intermediate layers. Formation of $\gamma\text{-NiOOH}$ is consequently associated with an expansion of the nickel layer spacing in the lattice. Discharging of the $\gamma\text{-NiOOH}$ proceeds by release of alkali ions into the electrolyte, wherein $\alpha\text{-Ni(OH)}_2$ forms. The $\alpha\text{-}\gamma$ transition is theoretically provided with a 1.67-electron step, i.e. 167 % EES. However, this 1.67-electron step cannot be used industrially, since the $\alpha\text{-Ni(OH)}_2$ in the alkaline electrolyte is unstable and is converted by ageing into $\beta\text{-Ni(OH)}_2$, with reformation of the volume increase which occurred during the $\beta\text{-NiOOH}$ - $\gamma\text{-NiOOH}$ transition.

By introducing trivalent metals into nickel hydroxide it is possible to stabilise the α structure (pyroaurite). However, in the case of a pyroaurite structure, anions and water molecules are incorporated between the nickel hydroxide layers to ensure charge neutrality, such that the lattice is expanded. Although it is possible to achieve a stable 1.5-electron step per nickel atom in the case of such nickel hydroxides with pyroaurite structure modified by trivalent ions, the storage density is reduced on the one hand by the electrochemically inactive trivalent ions and on the other hand by the incorporated anions and water molecules.

It has now been found that it is possible, by suspending the pyroaurite nickel hydroxide, modified with trivalent ions, in alkali solution, performing separation from the alkali solution and drying with the alkali solution which still remains, to convert the pyroaurite structure into a brucite-type structure while retaining the 1.67-electron step. In the process, intermediate layer anions and water are removed from the lattice, such that the layer spacing is reduced, while the storage density is increased.

The present invention consequently provides a mixed metal hydroxide with brucite structure, which contains nickel hydroxide as its main component and at least one trivalent metal selected from the group consisting of Co, Fe, Al, Ga, In, Sc, Y and La

in an amount of from 12 to 30 atom % relative to the sum of the metal components including nickel.

5 The trivalent metal is preferably present in an amount of from 12 to 25 atom %, relative to the sum of all the metal components.

Preferred trivalent metals are Co, Fe and Al, Al being particularly preferred.

10 Particularly preferred mixed metal hydroxides with brucite structure according to the invention contain, in addition to the above-mentioned first group of trivalent metals, at least one of the elements Co, Fe, Mn, Cr, Ti, Zr and Cu, wherein the element from this second group is different from the trivalent metal of the first group and replaces the trivalent metal from the first group in an amount of up to 40 atom %.

15 Preferred mixed metal hydroxides according to the invention contain Al and Co, wherein the atomic ratio of Al to Co amounts to from 2 to 4, particularly preferably from 2.5 to 3.5.

20 The mixed metal hydroxides according to the invention are additionally determined by a layer spacing of 4.3 to 4.8 Å determined by X-ray diffraction. The reflection diverges to the smaller angle θ owing to a shoulder corresponding to a lattice spacing of from 5.2 to 5.7 Å.

25 The invention further provides a process for producing the mixed hydroxides according to the invention by co-precipitation of mixed hydroxides with pyroaurite structure from corresponding metal salt solutions, suspension of the precipitation product in alkali solution, separation from the alkali solution and drying in the presence of the entrained alkali solution.

30 An at least 0.5 molar alkali metal hydroxide solution is preferably used.

An at least 0.9 molar alkali metal hydroxide solution is preferably used for alkaline drying, particularly preferably an at least 1 molar alkali metal hydroxide solution. The preferred alkali metal hydroxide is sodium hydroxide.

5 Production of the mixed hydroxides with pyroaurite structure proceeds by production of an aqueous solution by dissolving appropriate water-soluble metal salts of the metal components in the desired ratio and performing precipitation from the solution by adjusting the pH value to 10 to 13 by adding alkali metal hydroxide solutions. The process may be performed discontinuously or continuously by simultaneously
10 supplying metal salt solution and alkali metal hydroxide solution to a reaction vessel with continuous withdrawal of the precipitation suspension. Suitable metal salts are halides (preferably fluorides or chlorides), carbonates, sulfates, nitrates, acetates, oxalates, borates and/or phosphates, provided that these exhibit sufficient solubility.

15 In order to oxidise divalent modification metal ions optionally present in the precipitation suspension into the trivalent stage, it may additionally be expedient to add oxidation agents to the precipitation suspension, such as for example oxygen, H_2O_2 , hypochlorite or peroxodisulfates.

20 Ammonium hydroxide, lithium hydroxide, potassium hydroxide or sodium hydroxide are suitable alkali solutions for performing precipitation. Sodium hydroxide is preferred.

It may additionally be expedient, after precipitation, initially to exchange the anions
25 of the pyroaurite structure incorporated into the mixed metal hydroxide for carbonate ions. This may be performed by treating the precipitation product with alkali carbonate or alkali hydrogencarbonate solution.

After separation from the mother liquor and washing to remove residual mother
30 liquor, the precipitation product is resuspended in an alkali metal hydroxide solution preferably without intermediate drying. After separation from the alkali metal hydroxide solution, drying is performed carefully at temperatures below 80 °C, in

particular below 60 °C, more preferably at reduced pressure. The lower is the pressure during drying, the higher should be the minimum concentration of the alkali metal hydroxide solution. For example, at a drying pressure of 10 mbar, an alkali metal hydroxide concentration of at least 1.3 molar is preferred.

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The mixed metal hydroxides with brucite structure obtainable according to the invention are at the same time excellent starting materials for producing lithium mixed metal oxides. Lithium mixed metal oxides are produced in that the mixed metal hydroxides are mixed with suitable lithium compounds such as lithium hydroxide or
10 lithium nitrate and the mixture is then fired at temperatures above 600 °C.

Fig. 1 explains in an idealised representation the electron transitions achievable with the various nickel hydroxides. The top four structures show the Bode diagram known
per se.

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Fig. 2 shows X-ray diffraction spectra of mixed hydroxides dried alkalinely in sodium hydroxide solution of various concentrations, according to the following Example.

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Fig. 3 shows the discharge capacity of the mixed hydroxide of the brucite type as a function of the cycle number according to the following Example.

Examples**a) Production**

5 Coprecipitation of the substituted nickel hydroxides is performed by introducing the mixed metal salt solution dropwise into an initial mixture of constant pH value. The composition of the metal salt solution, the equalising liquor and the initial mixture is described here in relation to the example of precipitation of 0.125 mol of a nickel hydroxide of the metal ion composition $\text{Ni}_4\text{Al}_{0.75}\text{Co}_{0.25}$ at a precipitation pH value of

10 12.5. The composition of the metal salt solution is modified appropriately for other metal ion compositions. With this batch size, approximately 10 g of dried hydroxide are obtained.

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| 15 | <p>1. Salt solution: Total metal ion concentration 0.5 M</p> <p>26.28 g $\text{NiSO}_4 \cdot 6 \text{H}_2\text{O}$ ($= 0.10 \text{ mol Ni}^{2+}$)</p> <p>12.48 g $\text{Al}_2(\text{SO}_4)_3 \cdot 18 \text{H}_2\text{O}$ ($= 1.88 \cdot 10^{-2} \text{ mol Al}^{3+}$)</p> <p>1.76 g $\text{CoSO}_4 \cdot 7 \text{H}_2\text{O}$ ($= 6.25 \cdot 10^{-3} \text{ mol Co}^{2+}$)</p> <p>demineralised water to make up to 250 ml</p> |
| 20 | <p>2. Equalising liquor: Hydroxide ion concentration 1.0 M</p> <p>10 g NaOH pellets (99.5 %)</p> <p>demineralised water to make up to 250 ml</p> |
| 25 | <p>3. Initial liquor: Carbonate ion concentration 0.5 M</p> <p>26.50 g Na_2CO_3</p> <p>demineralised water to make up to 500 ml</p> <p>prior to start of precipitation, dropwise addition of 8M NaOH to pH 12.5</p> |

30 The initial mixture is thermostatted to a temperature of 34 °C prior to precipitation. During precipitation, the pH value is measured and kept constant by variation of the

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equalising liquor addition rate. The stirring speed during precipitation amounts to 300 rev/min.

5 The salt solution is added to the initial mixture at a speed of 5 ml/minute using diaphragm pumps and the pH value is kept constant at 12.5 by the addition of the equalising liquor.

After completion of precipitation, the precipitate is allowed to age for 18 hours at room temperature without stirring.

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The precipitate is centrifuged off for 10 minutes at 6000 rev/min, the remaining liquor is discarded and the product is suspended using a stirring apparatus in a litre of washing liquor (NaOH) of precipitation pH at room temperature for approx. 3 minutes and then centrifuged off again. This process is repeated until the anion to be washed out can no longer be detected.

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After the last centrifugation, the washed gel is suspended in 200 ml of sodium hydroxide solution of a given concentration according to Table 1, stirred for an hour, centrifuged and dried with the attached liquor at 50 °C in a water-jet vacuum. This procedure is here designated alkaline drying. In the products, the degree of conversion increases with the hydroxide ion concentration of the suspension liquor used (Fig. 2). Thus, after drying, a pyroaurite type is obtained from 0.03 molar and 0.1 molar liquor, while a spectrum with low brucite content is obtained from 0.4 molar liquor. During drying from 0.7 molar liquor, conversion into the brucite type is virtually complete.

20 The ratio of metal ions to one another does not vary through this treatment. Thus, no aluminium is dissolved out of the substance by alkaline drying.

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The brucite type obtained differs from the conventional brucite type in that the 001 reflection is shifted somewhat to smaller d values of 4.56 Å instead of 4.63 Å. In addition, a small shoulder of the 001 reflection arises in the area of 5.20 Å, which indicates a partial expansion of the layer spacing relative to the normal brucite type. With a pure nickel hydroxide, these deviations from the known brucite structure are

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not found after alkaline drying, the 001 peak is at 4.63 Å and there is no shoulder at higher d values.

The nickel content of the $\text{Ni}_4\text{Al}_{0.75}\text{Co}_{0.25}$ hydroxides increases with an increasing brucite structure proportion (Table 1), as does the pycnometric density.

Table 1: Analysis values for $\text{Ni}_4\text{Al}_{0.75}\text{Co}_{0.25}$ hydroxides with pyroaurite structure (top) and brucite structure (bottom)

Drying liquor for $\text{Ni}_4\text{Al}_{0.75}\text{Co}_{0.25}$	Nickel content	Nickel : carbon ratio	Nickel : hydro-gen ratio	Pycnometric density
0.03M (pH 12.5)	45.03 %	1:0.138	1:3.85	2.65 g/cm ³
0.7M	46.66 %	1:0.076	1:3.71	3.05 g/cm ³
1.0M	49.16 %	1:0.071	1:3.58	3.21 g/cm ³

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In pyroaurite-type nickel hydroxides, the hydroxide layers have a positive charge owing to the partial substitution with trivalent cations (Al^{3+} , Co^{3+} or Fe^{3+}). Because of the necessary charge equalisation by carbonate ions or other anions, the spacing of the hydroxide layers from one another is widened to 7.8 Å. In addition, water molecules are located in the intermediate layer. In order to achieve conversion to the brucite structure, the positive charge of the hydroxide layers must be dissipated.

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Partial deprotonation of the hydroxide ions is adopted as the mechanism for dissipating the main layer charge. This process could proceed according to the following programme:

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1. One hydroxide group of the main layer is deprotonated per metal(III) ion.
2. The positive main layer charge is dissipated by the removal of H^+ ions.
3. The negative intermediate layer of water molecules and carbonate ions is then no longer necessary for the electron neutrality of the structure and may depart.

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4. The layer spacing reduces from 7.8 Å to 4.6 Å.

5 The completely converted product (drying from 1.0M NaOH) has a pycnometric density of 3.21 g/cm³. A pure nickel(II) hydroxide produced according to the same precipitation parameters has a pycnometric density of 3.57 g/cm³. If 17.65 % of the nickel ions in this pure nickel hydroxide are replaced, according to the formula Ni₄Al_{0.75}Co_{0.25}, by lighter aluminium ions, a density of 3.23 g/cm³ may be obtained by calculation, which corresponds well with the measured value of 3.21 g/cm³.

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b) Examination of cycle behaviour

To test electrochemical properties, galvanostatic charging and discharging was performed. 10 M KOH served as the electrolyte. 100 mg of the active material were
15 mixed with 50 mg of graphite and 3 mg of PTFE powder, ground to a dry paste and incorporated into nickel foam. Forming proceeds for 14 hours at 5 mA and further charging for 12 hours at the same current strength. Discharging was performed with a current of 2.5 mA to a cut-off voltage of 0.9 V against Cd/Cd(OH₂) or 0V against Hg/HgO. During cycling in 10 M KOH of the Ni₄Al_{0.75}Co_{0.25} brucite produced by
20 drying from 0.7 M NaOH, maximum nickel utilisation is over 147 %. This corresponds to a maximum capacity per unit mass of 313 m Ah/g (Fig. 2). The nickel content of this material amounts to 46.7 %.

At 147 %, maximum nickel utilisation of the Ni₄Al_{0.75}Co_{0.25} brucite type is of a value
25 similar to that of 144 % for an Ni₄Al_{0.75}Co_{0.25} pyroaurite. However, since the nickel content of the brucite type is, at 46.7 %, 6.1 % higher than that of the pyroaurite type, at 44.0 %, the capacity per unit mass thereof is higher, at 310 mAh/g, than that of the pyroaurite type, at 290 mAh/g.

Claims

1. A mixed metal hydroxide with brucite structure containing nickel hydroxide as its main component and at least one trivalent metal selected from the group consisting of Co, Fe, Al, Ga, In, Sc, Y and La in an amount of from 12 to 30 atom % relative to the sum of the metal components including Ni.
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2. A mixed metal hydroxide according to claim 1, additionally containing at least one of the elements Co, Fe, Mn, Cr, Ti, Zr or Cu which is different from the trivalent metal, in an amount of up to 15 atom % relative to the sum all the metal components.
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3. A mixed metal hydroxide according to claim 1 or claim 2, containing 12 to 25 atom % Al.
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4. A mixed metal hydroxide according to one of claims 1 to 3, containing 4 to 9 atom % Co.
5. A mixed metal hydroxide according to one of claims 1 to 4, exhibiting nickel layer spacing, determined by X-ray diffraction, of 4.3 to 4.8.
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6. A rechargeable battery containing a mixed metal hydroxide according to one of claims 1 to 5 as electrochemically active material.
- 25 7. A process for producing mixed hydroxides according to one of claims 1 to 6 by precipitation of mixed hydroxide with pyroaurite structure from corresponding metal salt solutions, suspension of the precipitation product in at least 0.5 molar alkali solution, separation from the alkali solution and drying in the presence of the attached alkali solution.
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8. A process according to claim 7, wherein at least 0.9 molar sodium hydroxide solution is used.

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9. A process according to claim 7 or claim 8, wherein precipitation is performed in the presence of oxidation agents.
- 5 10. A process according to one of claims 7 to 9, wherein the precipitated nickel hydroxide is suspended in carbonate solution prior to suspension in alkali solution, separated therefrom and washed.
- 10 11. A secondary battery containing a mixed metal hydroxide according to one of claims 1 to 6.