

10/105

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 10-097856

(43)Date of publication of application : 14.04.1998

(51)Int.Cl. H01M 4/52
C01G 53/04

(21)Application number : 08-250474

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(22)Date of filing : 20.09.1996

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(54) NICKEL HYDROXIDE FOR ALKALINE STORAGE BATTERY AND MANUFACTURE THEREOF

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a dense nickel hydroxide used as a positive electrode in an alkaline storage battery, which has a higher utilization factor and a cycle with suppressed degradation under higher temperature.

SOLUTION: A dense nickel hydroxide used as a positive active material in an alkaline storage battery comprises a solid solution including 3 to 8% by weight of zinc, 0.5 to 5% by weight of cobalt, and 0.1 to 3% by weight of at least either of yttrium and calcium. The nickel hydroxide has, in its (101) plane by the X-ray diffraction, peak widths at half height of 0.85 to 1.2°/2θ, tapping densities of 2.0 g/cc or more, specific surface areas of eight to 30m²/g, and mean particle sizes of five to 15μm.

LEGAL STATUS

[Date of request for examination]

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of

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CLAIMS

[Claim(s)]

[Claim 1] In the nickel hydroxide used as a positive active material of an alkaline battery Zn dissolves [at least one or more sorts of 0.5 - 5 % of the weight and an yttrium, or calcium] three to 8% of the weight, and cobalt dissolves 0.1 - 3 % of the weight. High-density nickel hydroxide to which the field full width at half maximum in an X diffraction (101) is characterized by 2.0g [cc] /or more and specific surface area being [8-30m²/g and a mean particle diameter] 5-20 micrometers for 0.85-1.2degree/2theta, and tapping density.

[Claim 2] The manufacture method of the high-density nickel hydroxide of the claim 1 which carries out continuation supply of the nickel salt solution which contains zinc, cobalt and calcium, and/or an yttrium in a reaction vessel, an ammonium-ion supply object, and the alkali-metal hydroxide, is made to carry out a continuation crystal growth and is characterized by taking out to continuation.

[Claim 3] The manufacture method of the high-density nickel hydroxide of the claim 2 characterized by taking out nickel hydroxide to continuation while control the salt concentration in a reaction vessel in the range of 50 - 200 mS/cm in **5 mS/cm, ammonium-ion concentration is controlled in the range of 1 - 10 g/l in **0.5 g/l, Reaction pH is held in **0.05 in 11.0-13.0 and reaction temperature is held in **0.5 ** in 25-80 degrees C.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] this invention relates to the positive-active-material slack high-density nickel hydroxide for the alkaline batteries which use zinc, a hydrogen storing metal alloy, etc. as a negative electrode, and its manufacturing method.

[0002]

[The technical field to which invention belongs] In recent years, as a cell of cordless electronic equipment, such as a cellular phone and a notebook sized personal computer, although the alkaline battery is used, improvement of high-capacity-izing and an elevated-temperature property is called for. The alkaline battery which makes especially a nickel oxide a positive electrode and, on the other hand, uses a hydrogen storing metal alloy as a negative electrode also in an alkaline battery as a cell for electric vehicles, i.e., a nickel hydride battery, attracts attention. Although the nickel hydride battery is seen as a hopeful from other cells by high capacity and the cycle life, high-capacity-izing and the long cycle life under the elevated temperature of 45 degrees C or more are searched for. Irrespective of the object for portable, and the object for electric vehicles, it also sets to a positive active material and development of the material which contributes to high-capacity-izing and the long cycle life under an elevated temperature similarly is called for. Then, various proposals are made in order to satisfy these properties.

[0003] 1) In JP, 8-162111, A, an yttrium and zinc were made to dissolve to nickel hydroxide, and suppression of high capacity and electrode swelling is attained.

2) In JP, 7-201326, A, calcium and zinc were made to dissolve to nickel hydroxide, and the decline in the utilization factor accompanying a charge-and-discharge cycle and suppression of electrode swelling are attained.

3) In JP, 5-314983, A, nickel hydroxide and a calcium hydroxide are mixed, initial charge is devised, and the utilization factor at the time of an elevated temperature is raised.

[0004]

[Problem(s) to be Solved by the Invention] However, it is unknown how [that there is no description in the charging efficiency and service capacity at the time of an elevated-temperature property, i.e., an elevated temperature, and is suitable for elevated-temperature correspondence by the method of 1] it is. By the method of 2), like 1, there is only comparison at 25 degrees C and the property in an elevated temperature is unknown. By the method of 3), if initial-activity-ization is not devised, a property does not come out.

[0005] Therefore, in the manufacturing method of the above nickel hydroxide, as an object for the positive electrodes of an alkaline battery, it is still inadequate, and under the elevated temperature, it has the stable high utilization factor and development of high-density nickel hydroxide with little cycle degradation has been an important technical problem.

[0006]

[Means for Solving the Problem] In the optimal nickel hydroxide for which this invention is used as an object for the positive electrodes of an alkaline battery Zn dissolves [at least one or more sorts of an yttrium or calcium] 0.5 to 5% of the weight three to 8% of the weight, and cobalt dissolves 0.1 - 3 %

of the weight. $0.85-1.2^{\circ}/2\theta$, and tapping density aim [the field full width at half maximum in an X diffraction (101) / $2.0\text{g} / \text{cc} / \text{or more}$ and specific surface area] to let $8-20\text{m}^2/\text{g}$ and a mean particle diameter offer the high-density nickel hydroxide which is $5-20$ micrometers.

[0007] this invention manufactures high-density nickel hydroxide by carrying out continuation supply, carrying out the continuation crystal growth of the nickel salt solution containing cobalt and calcium, and/or an yttrium, an ammonium-ion supply object, and the alkali-metal hydroxide to a reaction vessel, and taking out the obtained precipitate to continuation.

[0008] At this time, the nickel hydroxide by which fine-particles physical properties, such as crystallinity, tapping density, specific surface area, and a particle diameter, were controlled well can be obtained by maintaining the salt concentration in a reaction vessel, ammonium-ion concentration, pH, and temperature within fixed limits.

[0009] That is, Zn dissolves [at least one or more sorts of $0.5 - 5\%$ of the weight and an yttrium, or calcium] three to 8% of the weight, cobalt dissolves $0.1 - 3\%$ of the weight, and the high-density nickel hydroxide $8-30\text{m}^2/\text{g}$ and whose mean particle diameter $2.0\text{g} [\text{cc}] / \text{or more}$ and specific surface area are [the field full width at half maximum in an X diffraction (101)] $5-20$ micrometers for $0.85-1.2^{\circ}/2\theta$, and tapping density is obtained.

[0010] The aforementioned nickel hydroxide is obtained by holding the salt concentration in a tub in 5 mS/cm in the range of $50 - 200\text{ mS/cm}$, and holding ammonium-ion concentration in 0.5 g/l in the range of $1 - 10\text{ g/l}$.

[0011] Moreover, the aforementioned nickel hydroxide is obtained by holding Reaction pH in 0.05 in $11.0-13.0$, and holding reaction temperature in 0.5 in $25-80$ degrees C.

[0012] As a modifier of salt concentration, a sodium chloride, potassium chloride, a sodium sulfate, potassium sulfate, hydrochloric-acid ammonium, an ammonium sulfate, etc. are mentioned.

[0013] As a calcium salt, nitrates, acetate, oxalates, etc. other than a sulfate are used. Since a calcium sulfate is poorly soluble, it is not used for water.

[0014]

[Embodiments of the Invention] If the concentration gradient is large in case a solid-state crystal is generally deposited from the inside of solution, the deposit of a particle will increase. That is, as for the mechanism which deposits a solid-state crystal from the inside of solution, solution serves as a semi-saturation state \rightarrow saturation state \rightarrow supersaturation state \rightarrow crystal deposit. For that, it is necessary to perform the above-mentioned mechanism smoothly as slowly as possible to grow up a particle, and to take the small concentration gradient near a saturation state.

[0015] However, the solubility curve of nickel hydroxide changes very a lot to pH. That is, the concentration gradient of nickel to pH is very large in solution. Therefore, only generation of a particle can be desired by the usual method. In this invention, by making nickel into ammonium complex salt, the concentration gradient of nickel to pH in the inside of solution was made small, and the particle was grown up.

[0016] Only by making three components into a constant rate and controlling pH, the ammonium-ion concentration in liquid changes with decomposition and evaporation of ammonia, and generating of the crystalline nucleus produced from ammonium complex salt becomes unstable. By controlling the ammonium-ion concentration in liquid, generating of a crystalline nucleus becomes fixed for the first time, and it becomes that to which the degree of growth of a particle was equal.

[0017] Since the ammonium-ion supply object and alkali-metal hydroxide corresponding to the amount of nickel to need are always needed in order to hold the state of the above-mentioned mechanism, a reaction process is considered as continuation. Here, the spherical high-density nickel hydroxide by which a fluidity is accompanied is obtained, scouring of particles being put together and repeating polish and growth by carrying out an agitating speed early.

[0018] In addition, the ammonium-ion supply object used at the reaction in this invention is used as a reaction intermediate so that it may be expressed with a reaction formula (1) and (2). The case of a nickel sulfate, ammonia, and a sodium hydroxide is shown for nickel salt, an ammonium-ion supply object, and an alkali-metal hydroxide, respectively (in order to simplify a formula, although cobalt, calcium, and the yttrium were excluded, they go via ammonium complex salt similarly). the Ming kana from a formula -- like, ammonia 4Eq or more is unnecessary, and can be managed with about at most

0.5Eq small quantity

[0019]

$\text{NiSO}_4 + 4\text{NH}_3 + 2\text{NaOH} \rightarrow \text{nickel}(\text{NH}_3)_4(\text{OH})_2 + \text{Na}_2\text{SO}_4$ (1)

$\text{nickel}(\text{NH}_3)_4(\text{OH})_2 \rightarrow \text{nickel}(\text{OH})_2 + 4\text{NH}_3$ (2)

The reason which limited the reaction condition by the claim 3 is as follows.

[0020] - Salt concentration <50 in a tub (mS/cm) A crystal growth is suppressed and only the thing of low density is obtained.

> 200 (mS/cm) It becomes easy to crystallize nickel salt solution, and it becomes impossible to supply adequately.

> **5 (mS/cm) If dispersion becomes large five or more, the non-set of crystallinity will increase.

[0021] - Ammonium-ion concentration <1 in a tub (g/l) Formation of complex salt decreases and a minute particle increases. Stabilization becomes difficult.

> 10 (g/l) The ammonia residue in nickel hydroxide increases.

> **0.5 (g/l) If dispersion becomes large 0.5 or more, the non-set of crystallinity will increase.

[0022] - Reaction pH<11.0 in a tub A crystal growth becomes quick and a crystal becomes large too much.

> 13.0 A crystal growth is suppressed and only the thing of low density is obtained.

> **0.05 Dispersion of a crystal and the distribution width of face of a particle diameter become small.

[0023] - Reaction temperature <25 degree C in a tub The crystal of mineral salt becomes easy to deposit and high concentration cannot be maintained.

> 85 degrees C Adjustment by the pH meter becomes difficult.

> **0.5 degrees C Dispersion of a crystal and the distribution width of face of a particle diameter become small.

[0024] In a claim 1, an operation of the dissolution element in nickel hydroxide and the reason of range limitation are as follows.

[0025] - In order that Zn addition may distort the crystal lattice of nickel hydroxide and may make movement of a proton smooth, it has the effect which is a charge by-product and suppresses generation of low gamma-NiOOH of a utilization factor.

[0026] The reason for numerical limitation: <3 (%) There are few effects of gamma-NiOOH generation suppression. That is, an electrode swells and cycle degradation is caused.

> 8 (%) A nickel content decreases and capacity falls. Moreover, particle growth becomes slow and high-density nickel hydroxide is hard to be obtained.

[0027] - Co addition makes smooth conversion to beta-NiOOH of the beta-nickel 2 at the time of charge (OH), and has the effect which suppresses the oxygen-evolution competitive reaction at the time of an elevated temperature by compound addition with Zn.

[0028] The reason for numerical limitation: <0.5 (%) The effect of elevated-temperature property improvement does not show up.

> 5 (%) A discharge potential is lowered. A nickel content decreases and capacity falls. In compound dissolution with Zn, high-density nickel hydroxide is hard to be obtained.

[0029] - Y addition has the effect which is a charge by-product at the time of an elevated temperature, suppresses generation of low gamma-NiOOH of a utilization factor, and suppresses electrode swelling by compound addition with Zn.

[0030] The reason for numerical limitation: <0.1 (%) The effect of elevated-temperature property improvement does not show up. A cycle improvement effect does not show up.

> 3 (%) A nickel content decreases and capacity falls. In compound dissolution with Zn and Co, high-density nickel hydroxide is hard to be obtained.

[0031] - calcium addition is effective in raising the utilization factor at the time of an elevated temperature.

[0032] The reason for numerical limitation: <0.1 (%) The effect of elevated-temperature property improvement does not show up. A cycle improvement effect does not show up.

> 3 (%) A nickel content decreases and capacity falls. In compound dissolution with Zn and Co, high-density nickel hydroxide is hard to be obtained.

[0033] The reason which limited the physical properties of nickel hydroxide by the claim 1 is as

follows.

[0034] - Field full-width-at-half-maximum < 0.85 in an X diffraction (101) (degree) Movement of the proton in the inside of liquid is not smooth.

> 1.2 (degree) A crystal collapses.

[0035] - Tapping density < 2.0 (g/cc) Restoration nature becomes bad.

[0036] - Specific-surface-area < 8 (m²/g) A giant particle increases and restoration nature becomes bad.

> 30 (m²/g) Hole capacity increases.

[0037] - Mean-particle-diameter < 5 (μ) A particle increases and restoration nature becomes bad.

> 20 (μ) A giant particle increases and restoration nature becomes bad.

[0038]

[Example]

(Example 1) Carrying out the continuation injection of the nickel nitrate solution of 2 mol/L, the zinc nitrate solution of 0.13 mol/L, the cobalt-nitrate solution of 0.035 mol/L, the calcium-nitrate solution of 0.058 mol/L, and the ammonium-nitrate solution of 5 mol/L, the sodium-hydroxide solution of 10 mol/L was supplied to the reaction vessel with an agitator so that pH in a reaction vessel might be maintained automatically 12.0. Moreover, the sodium nitrate was added, salt concentration was adjusted to 100 mS/cm, and the temperature in a reaction vessel was maintained at 40 degrees C, and was always stirred from the agitator. Dryness processing of the generated hydroxide was taken [make it overflow from an overflow pipe and] out and carried out [rinsed, dehydrated and]. Thus, high-density nickel hydroxide was obtained.

[0039] (Examples 2-5 and examples 1-4 of comparison) Although the manufacture procedure was the same as that of an example 1, an alloying element, its compounding ratio, and the reaction condition were changed. They are shown in Table 1.

[0040]

[Table 1]

| | Zn (mol/ L) | Co (mol/ L) | Ca (mol/ L) | Y (mol/ L) | 塩濃度 (mS/cm) | アモニウム イオン濃度 (g/L) | pH | 温度 (℃) |
|-------|-------------------|-------------------|-------------------|------------------|----------------|-------------------------|------|-----------|
| 実施例 1 | 0.13 | 0.035 | 0.058 | 0 | 100 | 2 | 12.0 | 40 |
| 実施例 2 | 0.15 | 0.035 | 0 | 0.0088 | 120 | 8 | 12.5 | 45 |
| 実施例 3 | 0.26 | 0.045 | 0.028 | 0 | 60 | 3 | 11.5 | 40 |
| 実施例 4 | 0.10 | 0.12 | 0.032 | 0.011 | 180 | 5 | 11.0 | 50 |
| 実施例 5 | 0.11 | 0.19 | 0.071 | 0.024 | 150 | 10 | 12.5 | 60 |
| 比較例 1 | 0.067 | 0 | 0.028 | 0.013 | 40 | 3 | 12.0 | 40 |
| 比較例 2 | 0.13 | 0.035 | 0 | 0 | 100 | 0.5 | 12.0 | 20 |
| 比較例 3 | 0.18 | 0.035 | 0.17 | 0 | 150 | 4 | 11.8 | 50 |
| 比較例 4 | 0.17 | 0.035 | 0 | 0.07 | 250 | 4 | 12.0 | 50 |

[0041] (Measuring method of physical properties)

[Table 2]

| 項目 | 測定方法 |
|---------------|---|
| Zn, Co, Ca, Y | ICP (セイコー電子製 SPS7000S) を使用。 |
| タップング密度 | SEISINN TAPDENSER KYT3000を用いる。20ccセルの重量を測定する。(A) 480meshフルイで本品を自然落下して充填する。200回のタップング後セルの重量(B)と充填容積(C)を測定し、算出する。(B-A)/C。 |
| 半値幅 | (101)面…X線回折装置(理学製RINT2000)を用い、38.4deg.で測定。 |
| 比表面積 | 窒素を吸着質とし、「オートソープ1」(クアンタークロム社製)を用い脱離等温線を求め、算出する。 |
| 平均粒径 | 粒度分布計(堀場製作所製、LA910)を用いた。レーザー法により測定し、累積50%に相当する値を求める。 |

[0042]
[Table 3]

表1の実施例及び比較例を、表2の測定方法で、粉体物性を測定した。

| | Zn (%) | Co (%) | Ca (%) | Y (%) | タップング密度 (cc/g) | 半値幅 [101] (°) | 比表面積 (m ² /g) | 平均粒径 (μ) |
|------|--------|--------|--------|-------|----------------|---------------|--------------------------|----------|
| 実施例1 | 4.0 | 0.9 | 1.1 | 0 | 2.18 | 1.002 | 18.2 | 10.6 |
| 実施例2 | 4.8 | 1.0 | 0 | 0.4 | 2.10 | 0.974 | 17.1 | 11.9 |
| 実施例3 | 7.7 | 1.2 | 0.5 | 0 | 2.01 | 0.903 | 12.7 | 7.3 |
| 実施例4 | 3.2 | 3.3 | 0.6 | 0.5 | 2.08 | 0.992 | 13.6 | 8.8 |
| 実施例5 | 3.1 | 5.0 | 1.3 | 0.9 | 2.06 | 0.875 | 10.4 | 8.5 |
| 比較例1 | 2.2 | 0 | 0.5 | 0.6 | 2.16 | 0.923 | 18.1 | 8.3 |
| 比較例2 | 4.1 | 1.1 | 0 | 0 | 2.14 | 0.884 | 16.8 | 10.5 |
| 比較例3 | 5.2 | 1.0 | 3.1 | 0 | 1.78 | 0.833 | 12.2 | 4.2 |
| 比較例4 | 5.0 | 0.9 | 0 | 2.9 | 1.82 | 0.819 | 9.6 | 3.6 |

[0043] (The evaluation method as a cell) The positive electrode was produced using each nickel hydroxide obtained in examples 1-5 and the examples 1-4 of comparison, respectively. That is, little 1 cobalt-oxide powder was mixed, CMC (carboxymethyl cellulose) solution was added and this mixture was made into the shape of a paste, and the foaming nickel base which is a base material was filled up, and dryness pressurization was carried out, and it was made into the positive electrode at nickel hydroxide. The charge and discharge of this positive electrode were carried out in potassium-hydroxide solution by having made the cadmium negative electrode into the partner pole, and the active material utilization factor and the charge-and-discharge cycle life were measured. At this time, temperature was held at 50 degrees C.

[0044] It asked for the active material utilization factor as follows. That is, it charged to 150% of geometric capacity by the charging current of 0.1C to the geometric capacity of a positive electrode, and discharged to 1.0V by the discharge current of 1/5C after that, and the survey service capacity to geometric capacity was expressed with percentage.

Active material utilization factor (%) = (1.0 by V service-capacity / nickel hydroxide geometric capacity) x 100. [0045] It charged by the charging current of 1C for 1 hour, and continuous discharge of the cycle life was carried out to 1.0V by the discharge current of 1C after the 30-minute pause, and it repeated this charge and discharge and considered it as the time of a charging time value falling to 60% to early continuous discharge time. The obtained active material utilization factor is shown in Table 4.

[0046]

[Table 4]

| | 活物質利用率 (%) | 充放電サイクル寿命 (サイクル) |
|-------|---------------|---------------------|
| 実施例 1 | 96 | 560 |
| 実施例 2 | 94 | 543 |
| 実施例 3 | 97 | 579 |
| 実施例 4 | 95 | 551 |
| 実施例 5 | 93 | 524 |
| 比較例 1 | 90 | 435 |
| 比較例 2 | 88 | 468 |
| 比較例 3 | 89 | 452 |
| 比較例 4 | 86 | 472 |

[0047] In comparison with the example of Table 4, and the example of comparison cobalt three to 8% of the weight 0.5 - 5 % of the weight, [Zn] At least one or more sorts of an yttrium or calcium dissolve 0.1 - 3 % of the weight. 0.85-1.2degree/2theta, and tapping density use [the field full width at half maximum in an X diffraction (101) / 2.0g / cc / /or more and specific surface area / 8-30m2/g and a mean particle diameter] the nickel hydroxide which is 5-15 micrometers. The rate for high interest and long cycle life at the time of an elevated temperature are attained.

[0048]

[Effect of the Invention] the above explanation -- the Ming kana -- like, the utilization factor of this invention in an elevated temperature is high as an object for the paste formula nickel positive electrodes of an alkaline battery, high-density nickel hydroxide with a long cycle life is offered, and industrial value is size very much

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