



Short communication

Influence of preparation conditions of spherical nickel hydroxide on its electrochemical properties

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Abstract

The influence of various conditions in spherical nickel hydroxide preparation on its electrochemical properties is studied. Experimental results show that several factors, such as pH and temperature, exert a great influence on the properties of the final product. Optimum conditions and reference data for preparing spherical nickel hydroxide with excellent properties are provided. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Spherical nickel hydroxide; Preparation; Electrochemical properties; Nickel/cadmium battery

1. Introduction

Nickel hydroxide is the active material for cathodes of alkaline nickel/cadmium and nickel/metal hydride batteries. In the traditional manufacturing process [1,2], the precipitate of nickel hydroxide easily forms a colloidal structure and turns into hard lumps after washing and drying. It is therefore necessary to grind the hard lumps into powder before the material can be used as active material. As a result of grinding, the nickel-hydroxide particles are converted into square form, with many voids present between the particles. Therefore, the resulting density is low and it is impossible to increase further the packing density on to a three-dimensional porous body. Thus, the specific energy of the nickel electrode reaches a limit.

To improve the specific energy and electrochemical performance of nickel electrodes, a method for the preparation of high density, spherical, nickel hydroxide is proposed. The influence of preparation conditions on the properties of this material is discussed.

2. Experimental*2.1. Preparation of spherical nickel hydroxide [3,4]*

Spherical nickel hydroxide was prepared by feeding an aqueous solution of a nickel salt and an aqueous solution of sodium hydroxide into a reactor under stirring. The concentration, feed rate, temperature and pH of the mixture in the reactor were all controlled. The nickel hydroxide was removed continuously from the reactor, then washed and dried without grinding. The nickel hydroxide takes the form of a powdered spherical particles, which have high tap density and an average size of 2 to 30 μm .

2.2. Electrochemical measurements

The test electrode was made by first mixing the prepared sample, powdered graphite and acetylene black (at a given weight ratio) and adding a binder of PTFE and CMC. The resulting paste was packed into a sponge-like nickel porous body support that had a porosity of 95% and a surface density of 300 g m^{-2} . The assembly was dried and pressed into a porous body. The test electrode had dimensions of $3.5 \times 2.0 \times 0.07$ cm. The electrodes were soaked in 6 M KOH for 24 h before coupling them with

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Table 1
Influence of reaction pH on the properties of Ni(OH)₂^a

Reaction pH	Tap density (g cm ⁻³)	Theoretical capacity (mA h)	Real capacity (mA h)	Utilization factor (%)	Specific capacity (mA h cm ⁻³)
9.0 ± 0.2	1.74	283	201	71	410
9.5 ± 0.2	1.80	292	216	74	441
10.0 ± 0.2	1.87	300	246	82	502
10.5 ± 0.2	1.92	306	260	85	531
11.0 ± 0.2	2.15	329	286	87	583
11.5 ± 0.2	2.10	322	280	87	571
12.0 ± 0.2	1.89	307	270	88	551

^aNiSO₄ used as reactant; reaction temperature = 50°C.

cadmium electrodes on either side to form nickel/cadmium secondary cells.

The electrodes were charged at a rate of 0.2 C to 150% of their theoretical capacity and discharged at 0.2 C to 1.0 V vs. Cd/CdO electrode for three repeated operations. The discharge capacity on the fourth cycle was determined at the 0.2 C rate after a charge process at 0.2 C for 7.5 h. The cycling tests were carried out at ambient temperature.

The nickel content (as Ni(OH)₂) of the test nickel electrode was determined by dissolving in dilute HCL (1:3), converting to a triethylamine complex, and titrating with ethylenediamine tetraacetic acid with murexide as indicator. The theoretical capacity of the electrodes was calculated from the Ni(OH)₂ content.

3. Result and discussion

3.1. Influence of reaction pH

The properties of the nickel hydroxide prepared at various pH values under given conditions are shown in

Table 1. With increase of pH, the tap density and specific volume capacity of the nickel hydroxide gradually increased and reached a maximum at a pH of 11.0 ± 0.2, and then began to decrease. The utilization factor of the active material gradually increased with pH. This is because the strong base medium not only favours the full utilization of nickel salt, but also favours the formation of a β-Ni(OH)₂ structure which has a higher electrochemical activity [5].

3.2. Influence of reaction temperature

The data given in Table 2, suggest that the tap density, utilization, and specific capacity of spherical hydroxide are poor when the reaction temperature is below 40°C. By contrast, these properties are excellent and stable when the reaction temperature is above 50°C. In order to save energy, the optimum reaction temperature should be in the range 50 to 60°C.

3.3. Influence of various nickel salts

The activity of nickel hydroxide prepared from NiSO₄ is higher than that prepared from Ni(NO₃)₂ or NiCl₂ (see Table 3). The reason for this behaviour is that the adsorp-

Table 2
Influence of reaction temperature on properties of Ni(OH)₂^a

Reaction temperature (°C)	Tap density (g cm ⁻³)	Theoretical capacity (mA h)	Real capacity (mA h)	Utilization factor (%)	Specific capacity (mA h cm ⁻³)
30	1.78	288	196	68	400
40	1.92	308	246	80	502
50	2.15	329	286	87	583
60	2.15	331	288	87	588
70	2.16	330	287	87	586

^aReaction pH = 11.0 ± 0.2.

Table 3
Influence of nickel salts on properties Ni(OH)₂^a

Nickel salts	Tap density (g cm ⁻³)	Theoretical capacity (mA h)	Real capacity (mA h)	Utilization factor (%)	Specific capacity (mA h cm ⁻³)
NiSO ₄	2.15	329	286	87	583
Ni(NO ₃) ₂	2.24	335	281	84	573
NiCl ₂	2.03	310	242	78	494

^aTemperature = 50°C; pH = 11.0 ± 0.2.

Table 4
Influence of drying temperature on properties of Ni(OH)₂

Drying temperature (°C)	Tap density (g cm ⁻³)	Theoretical capacity (mA h)	Real capacity (mA h)	Utilization factor (%)	Specific capacity (mA h cm ⁻³)
50	2.20	334	284	85	579
70	2.18	332	260	78	531
90	2.18	330	264	80	539
110	2.16	331	281	85	573
120	2.15	329	286	87	583
130	2.15	330	284	86	580

tion of SO₄²⁻ ions obviously facilitates precipitation and, thereby, lowers the quantity of adsorbed impurities on the nickel hydroxide; analogous behaviour is exhibited by Fe(OH)₃ [6]. Moreover, recent studies show [7] that the incorporation of some SO₄²⁻ ions in the crystal structure of nickel hydroxide favours electrochemical activity.

3.4. Influence of drying temperature

Because colloid formation is effectively prevented in the preparation process of spherical nickel hydroxide, the resulting particles are easily filtered and washed. Thus, powder composed of spherical particles 2 to 30 μm in size are directly produced without any grinding. The properties of the Ni(OH)₂ at different drying temperatures are given in Table 4. The electrochemical properties are excellent at drying temperatures of 50°C and 120°C. The Ni(OH)₂ dried at 50°C, which contains more crystal water, has high electrochemical activity because crystal water favours the rate of diffusion of protons. Drying at such a low temperature is, however, too time consuming. Therefore, a suitable drying temperature is between 110°C and 130°C. Though the content of crystal water is lower, the higher drying temperature favours the formation of β-Ni(OH)₂ which has a higher electroactivity [8]. X-ray diffraction shows that the sample of spherical nickel hydroxide prepared from an alkaline medium and dried at a temperature of 120°C has a typical β-Ni(OH)₂ structure (Fig 1).

3.5. Influence of doping

Many investigations have shown that cobalt is a beneficial additive [9,10]. Spherical nickel hydroxide powder

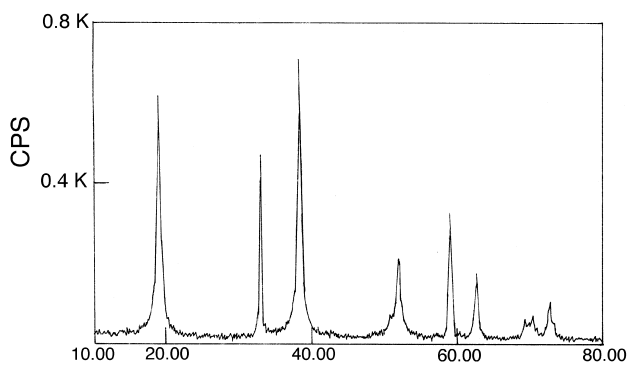


Fig. 1. X-ray diffraction pattern of nickel hydroxide.

Table 5
Influence of cobalt on properties of Ni(OH)₂

Cobalt content (wt.%)	0.5	1.0	2.0	3.0	4.0	5.0
Average discharge voltage (V)	1.215	1.217	1.218	1.218	1.211	1.203
Utilization factor (%)	90	95	97	98	99	99

doped with cobalt is prepared by adding CoSO₄ to the starting NiSO₄ solution. The electrochemical properties of Ni(OH)₂ are presented in Table 5. Although the addition of cobalt increases the utilization of active material, relatively larger amounts of cobalt tend to decrease the discharge voltage [11]. Hence, according to the data in Table 5, the amount of cobalt used should be 3 wt.% or less.

4. Conclusions

A method for preparing spherical nickel hydroxide is proposed, and the influence of the preparation conditions on its electrochemical properties are examined. The optimum conditions for preparing spherical nickel with high density and excellent electrochemical properties require the use of NiSO₄ solution and NaOH solution as the starting reactants, a reaction pH of 11.0 ± 0.2, a reaction temperature of between 50 and 60°C, a drying temperature of about 120°C, and the use of 3 wt.% or less of cobalt as dopant.

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