Effect of preparation conditions on the electrochemical properties of spherical Ni(OH)$_2$

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Abstract: Spherical nickel hydroxide is used as the active material of the positive electrode in alkaline recharged batteries,it determines the most important properties of the battery. Spherical nickel hydroxide made in China meets less than half of total demand of the Chinese batteries industry. Most of the spherical nickel hydroxide used for high performance MH/Ni batteries is imported because the Chinese one cannot reach the requirements of "fine crystal grain, high density and high-activity". In this thesis, the spherical nickel hydroxide with fine crystal grain high-density and high-activity was prepared with complexation-precipitation method. The effects of the preparation conditions on the electrochemical activity of the products were investigated by means of orthogonal test, comprehensive range analysis on all the used factors. And theirs levels showed that the optimum process parameters of preparation the fine crystal grain high-density and high-activity spherical nickel hydroxide is specified as reaction temperature 60℃, pH value 11.0, stronger stirring intensity, the mole ratio of ammonia and nickel 0.3,desiccation temperature 100℃. Furthermore, the relative influence degree of those technology factors is stirring intensity＞pH value＞reaction temperature＞desiccation temperature＞mole ratio of ammonia and nickel. The spherical nickel hydroxide made at those optimum process parameters is characterized as with high bulk density(1.78 g/cm^3), larger specific surface(11.9 m^2/g), higher discharged specific capacity (281 mAh/g), and fine crystal grain (15.8 nm). The full width of half maximum intensity(FWHM) of XRD patterns of samples in (101) lines can reach as high as 0.983°. All of these merits make it completely meet the requirements of spherical nickel hydroxide used for high performance MH/Ni batteries.

Key words: spherical nickel hydroxide; orthogonal test; preparation conditions; discharged specific capacity

CLC number: TF123.7　　　**Document code:** A

1　Introduction

Spherical nickel hydroxide (Ni(OH)$_2$) is widely used as the active material of the positive electrode in alkaline recharged batteries such as Cd-Ni, Fe-Ni, Zn-Ni and MH-Ni batteries. It determines the main properties of this kind of batteries. Used as a kind of new developed impetus for electromotive tools, electromotive aid bicycles and electromotive automobiles, the high performance MH-Ni battery has gained attention from all over the world. Recently, compared with Japan, the US and some other developed coun-

tries,.the quality of China's spherical Ni(OH)₂ is not so good, which prevent the application of China's MH-Ni battery in high power industry. Therefore, under Chinese government's encouragement, many institutes and manufacturers in China began their study on how to improve the performance of spherical Ni (OH)₂[1,2]. And there are now many papers on this topic. However, in this thesis, orthogonal test is for the first time applied to give a thorough study on the effects of the five preparation conditions on the electrochemical properties of the spherical Ni(OH)₂. These five factors[3] are the reaction temperature, the pH value of the solution, the stirring intensity, the mole ratio of ammonia and nickel and the desiccation temperature. Hope this thesis will give to the researchers some inspiration on the ways and methods of the study on this material.

2 Experiment and testing methods

2.1 Preparation of spherical Ni(OH)₂

Steps of the preparation are as follows: first infuse continuously through a precise measuring pump the nickel sulphate solution which including cobalt、zinc ion, sodium hydroxide solution and ammonia into a stainless steel reaction tank with stirs and water jacket. The pH value and the ammonia in the system are controlled by adjusting the rate of flow. The differences of the stirring intensity are achieved by using transducer and different oars to adjust the stirring speed. The crystal growing time is controlled by the flowing switch. After 48 hours get some sample and filtrate it. Use pure water to wash it until the pH value is of alkalescence. Desiccate the filtrated sample under a certain temperature to get the final sample[4]. Make a list about the five factors as shown in Table 1 and finish the 16 experiments at a random order. Every experiment need to be repeated for three times.

<div align="center">Table 1   Factors and levels of orthogonal test</div>

Factor level	Mole ratio of ammonia and nickel(A)	pH value (B)	Stirring intensity (C)	Reaction temperature (D)/℃	Desiccation temperature (E)/℃
1	0.1	9	weaker	40	80
2	0.2	10	weak	60	90
3	0.3	11	strong	80	100
4	0.5	12	stronger	90	110

2.2 Testing equipment

DC-5electro-properties testing apparatus for batteries (keep steady current), SSA-3500 BET specific surface area apparatus ,RISE-2006 laser particle sizer apparatus, TAS-986 Atomic Absorption spectrophotometers, GSM-5610LV(Japan) Scanning electron microscopy (SEM), DX-1000 X-ray diffraction (CuKα, CSC 40 kV/25mA Slit: 1deg & 1deg & 0.2 mm).

2.3 Testing method of the electrochemical properties

Weigh the final sample, and then well mix it with some electric conduction material. Infuse this together with PTFE and CMC into water to make it into a proper paste. Then cover the paste evenly on to a 60 mm×90 mm anode made in foam nickel. Dry the anode at 80 ℃ for 30 minutes. Wrap it with the hydrogen-storing alloy cathode to make them into the battery core. Immerge the core into electrolyte for 12 hours. Then begin the testing of the electrochemical properties. Under the temperature of (20±5)℃, charge the battery at 0.1C for 16 hours and then discharge it at 0.2C untill 1.0 V. The interval between

charge and discharge is 30 minutes. Recycle this process until the electric capacity is stabilized so that we can get the total discharge capacity. Dividing this total discharge capacity with the weight of the sample we can get the discharged specific capacity of the sample.

3 Results and analyses of the orthogonal test

Table 2 is an $L_{16}(4^5)$ orthogonal table designed according to Table 1. In order to maintain the rationality of this testing, every experiment must be repeated for three times. The each sample is made into batteries for testing. The figures of the average discharged specific capacity and the bulk density are filled in the table. The discharged specific capacity is the main figure to assess the orthogonal testing. The orthogonal testing results are analyzed according to the experiments data. The analyzing results are also shown in Table 2.

Table 2 Arrangement and analysis of orthogonal test results

No.	Mole ratio of ammonia and nickel (A)	pH (B)	Stirring intensity (C)	Reaction temperature (D)	Desiccation temperature (E)	Discharged specific capacity /$(mAh \cdot g^{-1})$	Bulk density /$(g \cdot cm^{-1})$
1	1	1	1	1	1	258.5	1.46
2	1	2	2	2	2	277.5	1.65
3	1	3	3	3	3	278.3	1.63
4	1	4	4	4	4	269.0	1.64
5	2	2	3	1	4	280.0	1.67
6	2	1	4	2	3	278.5	1.70
7	2	4	1	3	2	258.4	1.62
8	2	3	2	4	1	276.4	1.70
9	3	3	4	1	2	288.6	1.65
10	3	4	3	2	1	276.3	1.70
11	3	1	2	3	4	260.5	1.72
12	3	2	1	4	3	269.1	1.67
13	4	4	2	1	3	273.1	1.71
14	4	3	1	2	4	271.6	1.70
15	4	2	4	3	1	281.8	1.73
16	4	1	3	4	2	266.4	1.70
T_1	1083.3	1063.9	1057.6	1100.2	1093		
T_2	1093.3	1108.4	1087.6	1103.9	1090.9	$\sum T = 4364$	
T_3	1094.5	1114.9	1101	1079	1099	$\sum T^2 = 1191407$	
T_4	1092.9	1076.8	1117.9	1080.9	1081.1	$\overline{T} = 272.8$	
$T_1/4$	270.8	266	264.4	275.1	273.3	$N = 16$	
$T_2/4$	273.3	277.1	271.9	276	272.7	$S = 8.6650$	
$T_3/4$	273.6	278.7	275.3	269.8	274.8	$\delta = 8.3899$	
$T_4/4$	273.2	269.2	279.5	270.2	270.3		
Best grade	A3	B3	C4	D2	E3		
R	2.8	12.7	15.1	6.2	4.5		
Degree of the influence for each factor			C>B>D>E>A				

Note: The discharged specific capacity is used as the assessment of the orthogonal testing while the bulk density is mainly used for further discussion and comparison in the following text.

Put the testing results of the average discharged specific capacity of every factor under different levels into a chart as shown in Fig. 1. From this figure we can see the degree of effects of both different factors and the same factor under different levels. The comprehensive analyses of all the factors and level by comprehensive range analysis method show that optimum process conditions for producing spherical Ni(OH)₂ is $A_3 B_3 C_4 D_2 E_3$. That is to say, control the mole ratio of ammonia and nickel at 0.3 and the pH value at 11.0, strongly stir the solution at 60 ℃ for 48 hours and then desiccate the crystal at 100 ℃. Since the effects of all the factors are interactive, it is presumed that when discussing the influence of one factor, the other factors are regarded as constant temporarily.
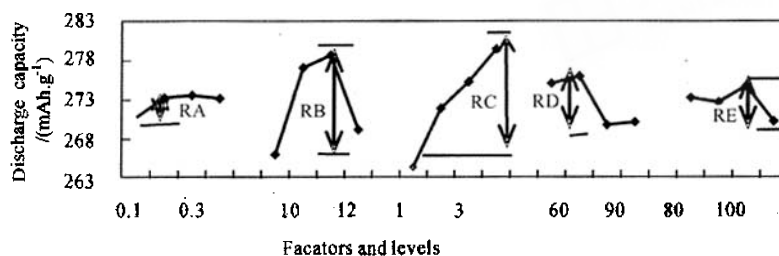

Fig. 1 Factors and levels on electrochemical properties of spherical Ni(OH)₂

A—the mole ratio of ammonia and nickel; B—pH value; C—stirring intensity; D—reaction temperature;

E—desiccation temperature

3.1 The effects of reaction temperature

The reaction temperature directly affects the rate of chemical reaction. When the reaction temperature is below 40 ℃ the reaction is slow and the time for Ni(OH)₂ crystal growing is increased. It is highly crystallized and there are fewer defects within the crystal structure, but the discharged specific capacity is lowered. When the reaction temperature is higher than 60 ℃, the crystal core forming rate is higher than its growth rate, so there will be more little crystal cores in the crystal. As crystallization is a heat releasing process, the much-released heat will prevent those cores from growing bigger. It even makes the newly grown crystal break off from the surface of the original crystal, which causes the decrease of the bulk density and the discharged specific capacity of the product. Furthermore, a much higher temperature process will increase the power consumption and the evaporation of ammonia, which will not only deteriorate the environment by also decrease the concentration of ammonia in the system, thus influences the thickness of the free nickel ion and eventually damages balance of reaction.

3.2 Effects of pH value

When the pH value is lower than 10, there will be $Ni_2(OH)_2SO_4$ within the Ni(OH)₂. The content of SO_4^{2-} will be high, making the internal resistance of the batteries increase. In addition, at this pH value, the core-forming rate is lower than the growth rate, which will form highly crystallized big grain. For this kind of spherical Ni(OH)₂, the particle size is big and the bulk density is high. However, because of its high crystallization, the branches will be thick, which will bring down the discharged specific capacity of the product.

When the pH value is beyond 12, the supersaturation of the system is high. The core-forming rate is extremely higher than the growth rate. It is easy to form small grains. The crystallization is poor. It will even form α-Ni(OH)₂. Meanwhile, as there are too much OH⁻ ions, the static exclusive force will increase,

which will prevent the growth of the grains. The small grains have larger specific surface, which increases the areas of interface between the solid and the liquid and promotes the transferring of protons. This kind of product has a favorable electrochemical activity. However, the lower bulk density will decrease the charge filling quantity of the nickel anode for the batteries. It also finds during testing that the over-fined $Ni(OH)_2$ grains will easily fall of the anode framework during the charge and discharge process. The loss of active material from the anode will also influence electrochemical activity of the batteries, causing the decrease of the discharged specific capacity of $Ni(OH)_2$.

Therefore, the pH value of the reaction solution is the main factor that affects the crystal growth, growing process, grain distribution, specific surface area, the density as well as the discharged specific capacity of spherical $Ni(OH)_2$.

3.3 The effects of the stirring intensity

The testing results gained by comprehensive range analysis method show that the stirring intensity has the biggest influence on the electrochemical properties of spherical $Ni(OH)_2$. By using different oars, controlling the stirring speed and adding different numbers of baffles into the reaction tank, there appears four different degrees of the stirring intensity. The stirring intensity is from weaker to stronger and the electrochemical properties of spherical $Ni(OH)_2$ will increase in turn. Analysis shows that when the stirring intensity is weak the PH value within the tank is not well distributed and the liquid is not well mixed and reacted, thus affects the balance of chemical reaction. In addition, in some part of the product there will be some small grains assembling, which affects the grain-distribution and the sphericity of the product will be poor. Production practices show that the particle size and distribution of $Ni(OH)_2$ will to some extent influence the capacity of the nickel anode. The finer the particle size is, the larger the specific surface and it will be more active. Therefore, the particle size of the spherical $Ni(OH)_2$ is in the tendency to growing much finer. For instance, in the past, the average particle size of the spherical $Ni(OH)_2$ used in nickel batteries was $25-50\mu m$. Now it has developed to $5-10\mu m$. Nevertheless, with the small particle size the bulk density will be lowered. In order to get high-density small-size spherical $Ni(OH)_2$ the stirring intensity must be increased so that the density of the small-sized spherical $Ni(OH)_2$ can reach above 1.70 g/cm^3. Moreover, when the sphericity of the grains in poor, the distribution of the charge currency will be not uniform. At some points it will react first while at others it will lag, thus at the points where reaction occurs first it will be over changed and there will appear some highly oxidized γ-NiOOH. After repeated charging cycles of this γ-NiOOH, the form of the anode will inflate and change, which will influence the capacity and the recycle life of the batteries. Since γ-NiOOH cannot change back into β-NiOOH the effective amount of active material within the anode will reduce, causing the discharged specific capacity of the spherical Ni $(OH)_2$ drop dramatically. On the contrary, a higher stirring intensity will not only guarantee a favorable sphericity of the $Ni(OH)_2$ grains, but also improve the minicrystal structure and increase the full width of half maximum intensity, showing a higher discharged specific capacity.

3.4 Effects of the mole ratio of ammonia and nickel

In the reaction, ammonia plays a role of complexation. When the mole ratio of ammonia and nickel is below 0.2, Ni^{2+} will combine directly with OH^-. When the supersaturation is higher, the grain surface congruence speed in the growth direction is greatly increased. While there will be not enough time for the combining water and absorbing water on the surface to break off. It even forms amorphous α-$Ni(OH)_2$. So the sphericity of the grains will be poor. The density and activity of $Ni(OH)_2$ will be decreased greatly. This is not suitable for its use in high performance batteries. However, when the mole ratio of ammonia

and nickel is above 0.5, since the ions are completely get into complexation, the speed of Ni^{2+} decomposing from the complexation is low, the reaction time for growing precipitation is prolonged. The branch grains are getting closer and the crystal structure is good but there will be less interspace. During charging and discharging, the passing speed of H^+ is getting slow. And the discharged specific capacity of spherical Ni $(OH)_2$ is decreased. Therefore, the crystal structure and the crystallization can be controlled by adjusting the mole ratio of ammonia and nickel.

3.5 Effects of the desiccation temperature

The moisture with in $Ni(OH)_2$ includes the absorbing water on the surface and the crystallized water within the crystal. The crystallized water exists within the crystal layers by hydrogen bonds. When desiccated under 100℃, the ambience is mild and there will be little damage for the hydrogen bonds within the $Ni(OH)_2$ crystal. The electrochemical activity will be higher. When desiccated above 100℃, most of the hydrogen bonds will be damaged as a result of the lower potential energy for the hydrogen bonds. The crystallized water and the surface water will be removed all together. The bulk density of the spherical Ni $(OH)_2$ will increase while the specific capacity will be lowered a little. When the temperature is beyond a certain degree, the spherical $Ni(OH)_2$ will irrevocably change into NiO and lost completely its electrochemical properties.

3.6 Verifying test

We can verify the resting results of the optimum process of $A_3B_3C_4D_2E_3$ during the orthogonal tests by comparing the sample with the first-class samples form all over the world as shown in Table 3.

Table 3   Compared properties of samples

Description	Ni /%	Bulk density /(g · cm⁻³)	Specific surface /(m² · g⁻¹)	D_{50} /μm	Specific capacity /(mAh · g⁻¹)	XRD			
						FWHM₁₀₁ / (°)	I₁₀₁/I₀₀₁	Crystallite size/nm	Phase
Testing sample	57.6	1.75	11.9	8.881	281	0.983	0.574	15.8	β
Japanese company A	57.1	1.74	14.2	7.536	279	0.956	0.563	16.7	β
A USA company	57.5	1.78	13.2	8.422	284	0.984	0.582	15.2	β
Japanese company B	57.4	1.75	11.6	9.82	281	1.002	0.612	14.8	β
A Chinese company	57.8	1.73	10.2	11.53	282	1.045	0.603	13.6	β

The testing sample is an emerald-colored powder and its average particle size is 8.881 μm. Under the ×400 microscope, it is spherical shaped, while under the ×10000 scanning electric microscope, it can be seen that the grain surface is not compact and smooth (Fig. 2). Instead there are numerous branches conglutinated. The branches are fine and in a radioactive shape. Therefore, every grain is composed of numerous conglutinated branches. These fine and radioactive shaped branches will develop high quality small openings on the surface and within the crystal. This kind of structure leads to a high specific surface (11.9 m²/g) and a higher discharged specific capacity (281 mAh/g). It has also illustrated the analysis results in the electrochemistry theory. That is to say, the fine grains of the minicrystal, the high pore-space rate and the branches directional growth will be in favor of the proton transferring. It will play an important role in improving the activation rate and the discharged specific capacity during charging and discharging. Form the XRD pattern (Fig. 3) it can be seen that the sample has a clear β-Ni(OH)₂ character. The proper intensity(0.574) and the higher full width of half maximum intensity(0.983°)in the 101 lines indicate that the particle size of the branch crystal is small and the sample has a higher bulk intensity (1.75 g/cm³). All of these characters full meet the requirement of fine-grained, high-density and high-activity spherical Ni(OH)₂
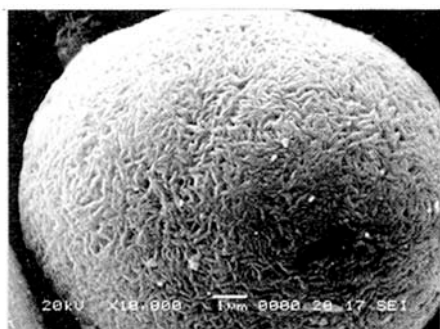
used in high performance MH/Ni batteries.
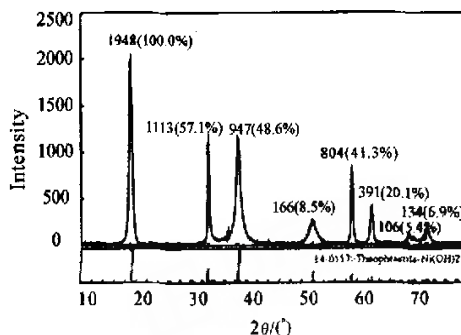

Fig. 2   SEM photograph of sample (×10000)

Fig. 3   XRD pattern of sample

4   Concluion

By applying orthogonal testing, the many key factors that affect the preparation of spherical Ni(OH)$_2$ were studied easily and thoroughly. From studying the effects of different reparation conditions on the performance of the spherical Ni(OH)$_2$, we can conclude that high quality spherical Ni(OH)$_2$ can be produced when controlling the mole ratio of ammonia and nickel at 0.3, and the pH value at 11.0, strongly stirring at 60℃, keeping the product growing for 48 hours and desiccating it at 100℃. Further testing and verifying show that this technical process will greatly improve the overall performance of the spherical Ni(OH)$_2$.

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