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Spherical Al-substituted α-nickel hydroxide with high tapping density applied in Ni-MH battery

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HIGHLIGHTS

- High tapping density of 1.37 g cm^{-3} α-$Ni(OH)_2$ is successfully synthesized.
- The optimal reaction conditions are calculated out based on theoretical analysis.
- Electrochemical capacity have a 35% enhancement at 5C.
- The formula derived can be reference for the production of spherical powders.

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ABSTRACT

Spherical Al-substituted α-$Ni(OH)_2$ with high tapping density are prepared with controlled crystallization method, where the synthesis parameters are previously calculated out according to theoretical analysis. The formation mechanism of $Ni(OH)_2$ particles is analyzed based on theoretical calculation, the optimal conditions for the formation of spherical Al-substituted α-$Ni(OH)_2$ with high tapping density are figured out and a formula indicates the restrictions among main synthesis parameters is derived, which is reference meaningful for the synthesis of commercialized electrode powders. Synthesized by using the calculated parameters, the obtained α-$Ni(OH)_2$ shows uniform spherical morphology, high crystal phase purity and reasonable high tapping density of 1.37 g cm^{-3}, which demonstrates the feasibility of the derived formula. Since the electrical conductivity of the pure $Ni(OH)_2$ is quite low, 5 wt% of CoOOH are coated on the α-$Ni(OH)_2$ surface to improve their electrochemical performances. The synthesized CoOOH coated α-$Ni(OH)_2$ shows relative high specific capacity of 327 mAh g^{-1} at 0.1 C and acceptable high-rate dischargeability. The simultaneously achieving of high tapping density and high specific capacity in α-$Ni(OH)_2$ makes it own the great potential to be applied in new generation of Ni-MH batteries.

1. Introduction

Energy sources are hot topics in this information age, and the need of high performance secondary battery is urgent with the development of new electronic equipment. As a universal secondary battery, Ni-MH batteries have been widely used for their advantages including high-capacity, pollution-free, safety and cheapness [1]. The positive electrode material used in Ni-MH batteries is $Ni(OH)_2$. As is known, there are two polymorphs for $Ni(OH)_2$: one is α-$Ni(OH)_2$ and the other is β-$Ni(OH)_2$ [2]. Due to the high tapping density and good electrochemical performances, spherical β-$Ni(OH)_2$ is widely applied in commercial Ni-MH batteries. Comparing to non-spherical β-$Ni(OH)_2$, spherical one shows higher volume capacity for its high tapping density and the spherical morphology will bring the better mobility which is helpful in easily filling the electrode paste into nickel foam. As $Ni(OH)_2$ is a p-type semiconductor, its electrical conductivity is quite low, which limits the fully utilizing of its specific capacity. Lots of works have been focused on improving the electrical conductivity of the $Ni(OH)_2$ [3–10]. Among them, the most effective method is coating a conductive network such as CoOOH on the surface [3]. After CoOOH coating, the conductivity of $Ni(OH)_2$ is greatly enhanced and their electrochemical capacity can be well released. This method is also widely applied in commercial Ni-MH

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batteries. After years of research, The capacity of β-$Ni(OH)_2$ has approached to its theoretical value, however, the relative low value of 289 mAh g^{-1} is still far from satisfaction. Furthermore, as shown in Fig. 1, γ-NiOOH is easily formed when β-$Ni(OH)_2$ is overcharged, which will result in an undesired volume expansion in the positive electrodes [11]. These shortages become the bottlenecks of the further development of β-$Ni(OH)_2$.

α-$Ni(OH)_2$ has draw lots of attentions in recent years because of its higher theoretical specific capacity (482 mAh g^{-1}) and there are no risks of overcharge during using [12–20]. As reported [14], the theoretical specific capacity of α-$Ni(OH)_2$ is much higher than that of β-$Ni(OH)_2$ [13], and its advantages on high rate charge-discharge capacity and cycle stability of α-$Ni(OH)_2$ are also remarkable [16]. The structure of α-$Ni(OH)_2$ is hydrotalcite type double hydroxide, and the interlayer water makes the interlayer spacing of α-$Ni(OH)_2$ maintain at about 0.8 nm. However, α-$Ni(OH)_2$ is not stable in alkaline liquor because the interlayer water may run off in alkaline liquor then the phase type will turn into β-$Ni(OH)_2$, which has a stable lattice structure in alkaline liquor. The settlement is using certain proportion metallic ions such as Al^{3+} [13–23], Co^{2+} [24,25], Fe^{2+} [26], Mn^{2+} [22,27] or Zn^{2+} [12,28] to partly replace Ni^{2+} in the crystal lattice during the preparation to improve the stability of α-$Ni(OH)_2$ lattice structure. Among these metallic ions, Al^{3+} is considered the most effective one in achieving both high structural stability and good electrochemical performance. As Al^{3+} has charge of plus three, it can adsorb negative ions and hydrones to keep electric neutrality and structural stability. Because Al-element is inactive in electrochemical reactions, more substitution amount of Al-element will lead the decrease of capacity. Thus, the amount of Al-element substitution should be suitable and the optimal value is proved to be around 20% in molar content by previous researches [14,16,18], tapping density is another important factor for electrode materials because it determines the volume capacity of the batteries. Due to the large layer-spacing of α-$Ni(OH)_2$, its tapping density is lower than that of β-$Ni(OH)_2$, especially for the irregularly shaped powders. This limits the commercial application of α-$Ni(OH)_2$. Therefore, it's quite meaningful subject to improve the tapping density of α-$Ni(OH)_2$.

In this work, we focus on fabricating of spherical α-$Ni(OH)_2$ with high tapping density by optimizing the synthesis parameters. As results, spherical Al-substituted α-$Ni(OH)_2$ with a tapping density of 1.37 g cm^{-3} was prepared by controlled crystallization method. As contract, there are hardly works reported a higher tapping density than 1.30 g cm^{-3} with this method [14,16]. Then $Co(OH)_2$ was coated on the surface of spherical Al-substituted α-$Ni(OH)_2$, which was then oxidized into CoOOH with H_2O_2 in alkaline liquor. It turned out that the electrochemical performances are greatly promoted after coating and the CoOOH coated α-$Ni(OH)_2$ shows reasonable high specific capacity. Consequently, We believe that this α-$Ni(OH)_2$ with reasonable good over-all performances may have great potential in applying for commercial Ni-MH battery applications.

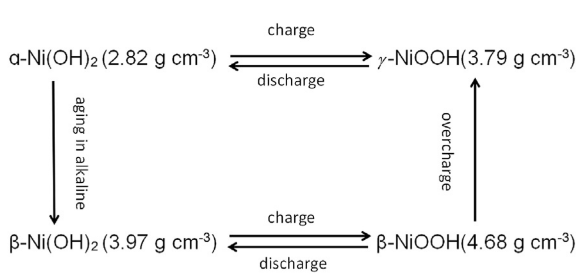

Fig. 1. State-transition diagram of $Ni(OH)_2$ during charge and discharge.

2. Experimental

2.1. Preparation of Al-substituted α-$Ni(OH)_2$

All reagents used in this experiment are of analytical grade and are used as received. A aqueous solution of $NiSO_4$ (1 M), and a mixed aqueous solution of NaOH (2 M), $Al_2(SO_4)_3$ (in a fixed molar ratio of [Ni^{2+}/Al^{3+}] equals to 4:1) and ammonia (1 M) were simultaneously dropped to a well-sealed reaction flask containing base solution of 0.5 M ammonia with vigorous stirring at 800 rpm. Control the dropping speed of $NiSO_4$ at 40 ml h^{-1}, and the pH value of reaction solution was controlled at 10.75 ± 0.05 by adjusting the dropping speed of NaOH. Reaction temperature was controlled at 60 ± 1 °C. After reacting for 24 h, the product was aged in mother solution for another 17 h at the same temperature. The product was then centrifuged, washed several times with deionized water until neutral, and dried at 60 °C in drying oven for 12 h.

2.2. CoOOH coating on the surface of Al-substituted α-$Ni(OH)_2$

The α-$Ni(OH)_2$ coated with 5 wt% CoOOH was prepared by liquid phase precipitation method. 10 g α-$Ni(OH)_2$, 1.51 g $CoSO_4 \cdot 7H_2O$ and 50 ml ammonia were added in 100 ml water to form dispersion liquid. Then added 1 M NaOH solution dropwise into the dispersion liquid at 50 °C till the red color faded. Kept the mother solution aging for 3 h in the flask. Followed, the product was centrifuged, washed several times with deionized water until neutral and re-dispersed in alkaline solution. 4 ml of 30% H_2O_2 was then added to the solution and left for 2 h. At last, the product was centrifuged, washed several times with deionized water until neutral, then dried at 60 °C in drying oven for 3 h.

2.3. Preparation of positive electrode of Ni-MH battery

The pasted nickel electrodes were prepared as followed: mix α-$Ni(OH)_2$, graphite and CoO at fixed weight ratio of 100:10:5. Then a certain amount of water and 3.5 wt% Carboxymethyl Cellulose (CMC) solution were added to obtain a slurry under vacuum stirring. Coat the slurry on porous foam nickel sheet and completely dried. The electrode was cut into 10 cm × 3.5 cm in size and pressed under 15 MPa for 3 min to obtain a shin sheet about 0.4 mm in thickness.

2.4. Characterizations

The morphology observation and the energy spectrum analysis were conducted on a scanning electron microscope (SEM, Hitachi S-4300, Japan). The phase structure was characterized by X-ray diffraction (XRD, D8 focus, Germany) on an X-ray diffractometer with Cu Ka radiation (λ= 0.154 nm) between $2\theta = 4°$ and $2\theta = 90°$). Fourier transform infrared spectroscopy (FTIR) spectra was obtained by using a Bruker Tensor 27 spectrometer (Excalibur 3100, US). The α-$Ni(OH)_2$ powders were deposited on a KBr tablet and 60 scans were collected and the averaged data was taken. Electrochemical performances were obtained by using cell test station (LANHE CT2001A, China), the cyclic voltammetry curves were obtained by using an electrochemical workstation (Xinwei, CHI760E, China).

3. Results and discussion

3.1. Analysis of optimal synthesis conditions

Based on the theory of Klaus Borho [29], the mechanism assumed in precipitation reaction involves six steps: micro mixing