GRANULATION OF NANO-SCALE $Ni(OH)_2$ CATHODE MATERIALS FOR HIGH POWER Ni-MH BATTERIES

Xiangming He; Weihua Pu; Hongwei Cheng; Changyin Jiang; Chunrong Wan

Materials Chemistry Lab, INET, Tsinghua University, P.O.Box 1021, Beijing 102201 PR China

Abstract

Nano-scale β-$Ni(OH)_2$ and $Co(OH)_2$ were prepared by controlled crystallization, mixed by ball milling, and granulated to form about 5μm spherical grains by spray drying granulation. The granulation significantly enhanced electrochemical performance of nano-scale $Ni(OH)_2$, probably because of good size matching between active material and electric conductor. The granulated grains of nano-scale $Ni(OH)_2$ presented the high performance at high discharge C-rate, and its specific capacity at 10C exceeded that of conventional spherical micro-scale $Ni(OH)_2$ at 3C. The granulated nano-scale β-$Ni(OH)_2$ is a promising cathode active material for high power Ni-MH batteries.

Keywords: nano-scale nickel hydroxide; granulation; high power; Ni-MH Batteries

Introduction

The increasing concerns over air pollution and depletion of natural petroleum reserves have spurred renewed interest in electric vehicles (EV), where high power batteries are playing important role. Being of high power and low cost, Ni-MH batteries are considered to be one of the most promising choices for EV application. Active electrode materials for high power batteries need to be of high proton diffusion coefficient and high electronic conductivity.
Nickel hydroxide with a smaller crystalline size shows a high proton diffusion coefficient, giving excellent electrochemical performance [1, 2]. Nano-scale hexagonal β-$Ni(OH)_2$ was synthesized and was anticipated to significantly boost performance of Ni-MH batteries [3]. It was reported that the specific capacity can be increased over 10% from 214 mAh g^{-1} to 235 mAh g^{-1} at 0.2C when the active material was prepared by mixing nano-scale $Ni(OH)_2$ with conventional spherical $Ni(OH)_2$ [4, 5]. When electrode formulation of pasting slurry was consisted of only 60 wt.% active nano-scale $Ni(OH)_2$ and large amount of conductor, the capacity reached 400 mAh g^{-1}-Ni (253 mAh g^{-1}-$Ni(OH)_2$) at 1C [6].

Corresponding author: Xiangming He
E-mail: hexm@tsinghua.edu.cn
Tel: +86 10 89796073, Fax: +86 10 89796031

Whilst, it was experimentally found that the electrode prepared by nano-scale $Ni(OH)_2$ with normal conductor showed even worse performance, probably because of poor conductivities both between conductor and nano-scale $Ni(OH)_2$ particles, and among nano-scale $Ni(OH)_2$ particles. Nano-scale $Ni(OH)_2$ is of small inner crystal resistance, but big inter-crystal resistance and contacting resistance with conventional conductor, which has been hindering it from practical use to directly prepare cathode.
Therefore, nano-scale $Ni(OH)_2$ can only be applied as adjuvant to improve the performance of micro-sized spherical $Ni(OH)_2$, which can also be electrochemically enhanced by surface modification. But the surface modification is not effective to reduce inner resistance of particles. So it is needed to reduce both inner and inter-crystal resistances for performance improvement of $Ni(OH)_2$.
In this study, nano-scale $Ni(OH)_2$ was prepared, mixed with nano-scale $Co(OH)_2$, then granulated by spray drying granulation. The obtained granulated micro-sized spherical grains of nano-scale $Ni(OH)_2$ showed high performance at high C-rate. All references to $Ni(OH)_2$ refer to β-$Ni(OH)_2$ phase.

Experimental

Hydrous colloid of nano-scale $Ni(OH)_2$ was prepared from $NiSO_4$ and NaOH by controlled crystallization. The details of preparation were described in reference [7]. Then, n-butanol was added into the colloid with agitation, and distilled at the azeotropic temperature of n-butanol till all n-butanol was completely evaporated. The product was dispersive powder of nano-scale $Ni(OH)_2$. Nano-scale $Co(OH)_2$ was also prepared as above procedures, and used as conductor.
The as-prepared colloid of nano-scale $Co(OH)_2$ and deioned water were added into colloid of pre-distilled nano-scale $Ni(OH)_2$ and ball-milled to form slurry, from which the spherical grains were prepared by spray drying granulation technique as described in reference [8].
Positive electrodes were made by pasting a slurry mixture of active $Ni(OH)_2$ grains, carbon black, graphite, carboxymethylcellulose (CMC) and Teflon in water on nickel foam, and dried at 80°C for 4 hours. The electrode formulation of pasting slurry consisted of 85 wt.% active grains, 10 wt.% graphite, 3 wt.% carbon black, and 2 wt.% others. The electrolyte was 30 w% KOH solution. The discharge performance with cut-off voltage of 1.0V was carried at room temperature.

Results and discussions

By the qualitatively large widths of X-ray diffraction lines of as-prepared nano-scale $Ni(OH)_2$, its crystalline size is evaluated to be 2.77 nm and 10.5 nm from the width of the diffraction lines of (001) and (100), respectively, according to Scherrer's equation [9]. An average length is evaluated to be 6.75 nm by formula proposed in reference [10].

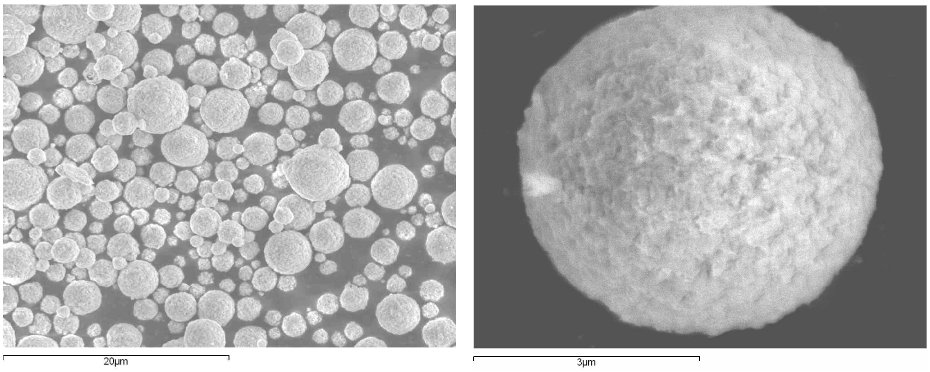

Fig. 1 *SEM images of granular grains of nano-scale $Ni(OH)_2$*

Figure 1 shows the SEM images of granulated grains of nano-scale $Ni(OH)_2$. Its particle size is about 2~5 µm. No crystalline grains can be observed on the surface of particle at magnifying level of micron because it is still nano-sized. Four processes were adopted to prepare electrode, whose electrochemical performance was tested at a discharge rate of 1C. First, nano-scale $Ni(OH)_2$ was directly used to prepared positive electrodes by weight percentage of 85%, as described in experimental section, resulting in its specific capacity reaching only 183 mAh g^{-1} as shown in Table 1. Secondly, it was granulated to form micro-sized grains before used to prepare electrode, its capacity increased to 215 mAh g^{-1}. Thirdly, it was mixed by ball milling with nano-scale $Co(OH)_2$ at Co/Ni mole ratio of 1/20 before used to prepare electrode, its capacity further increased to 258 mAh g^{-1}. Fourthly, it was mixed by ball milling with nano-scale $Co(OH)_2$ at Co/Ni mole ratio of 1/20 and then granulated to form micro-sized grains before used to prepare electrode, its capacity increased up to 289 mAh g^{-1}.

Table 1 *Specific capacity of nano-scale $Ni(OH)_2$ at a rate of 1C.*

Preparation process	mAhg^{-1}
1.Nano-scale $Ni(OH)_2$ without granulation	183
2.Granulation of $Ni(OH)_2$ without $Co(OH)_2$	215
3.Mixing with nano-scale $Co(OH)_2$ at Co/Ni=1/20	258
4.Granulation after mixing with of nano-scale $Co(OH)_2$ at Co/Ni=1/20	289

Above experimental results demonstrate that the addition of $Co(OH)_2$ plays a crucial role in improving the performance of nano-scale $Ni(OH)_2$ because it enhances the conductivity of the active material when it transforms into CoO(OH), of which the conductivity is high, during charging [11, 12]. By comparison of process 1 and 3 in Table 1, it is found that the addition of $Co(OH)_2$ leads to a specific capacity increase as high as 75 mAh g^{-1} for the un-granulated samples. After granulation, the addition of $Co(OH)_2$ makes an increase of 74 mAh g^{-1} from 215 to 289 mAh g^{-1} by comparison of process 2 and 4. The proper Co/Ni mole ratio is experimentally optimized to be 0.05.

However, what is more notable is that granulation can further enhance the specific capacity of nano-scale $Ni(OH)_2$. By comparison of process 1 and 2, it is found that the granulation leads to a specific capacity increase of 32 mAh g^{-1} for the samples without addition of $Co(OH)_2$. After addition of $Co(OH)_2$, the granulation makes an increase of 31 mAh g^{-1} from 258 to 289 mAh g^{-1} by comparison of process 3 and 4.

Therefore, the above results have shown that the granulation can significantly enhance the capacity of nano-scale $Ni(OH)_2$. Whilst nano-scale $Co(OH)_2$ also plays crucial role for capacity of nano-scale $Ni(OH)_2$ as an electronic conductor, leading to a capacity increase as high as 75mAh/g when nano-scale $Co(OH)_2$ mixed by Co/Ni mole ratio of 1/20, and even an increase of 106mAh/g after further granulation by spray drying granulation.

The specific capacities of granulated grains of nano-scale $Ni(OH)_2$ with Co/Ni=1/20 and conventional micro-scale spherical $Ni(OH)_2$ at high C-rate are shown in Figure 2. The granulated grains of nano-scale $Ni(OH)_2$ mixed with $Co(OH)_2$ at Co/Ni=1/20 reaches the capacity of 289 mAh g^{-1} at 1C, at which conventional micro-sized spherical $Ni(OH)_2$ reaches only 272 mAh g^{-1}. The former presents the capacity in excess of 258 mAh g^{-1} at 10C and the latter go down to 218 mAh g^{-1} even at 3C. Being compared with conventional spherical $Ni(OH)_2$, granulated grains of nano-scale $Ni(OH)_2$ mixed with nano-scale $Co(OH)_2$ reveals excellent performance at high C-rate up to 10C.

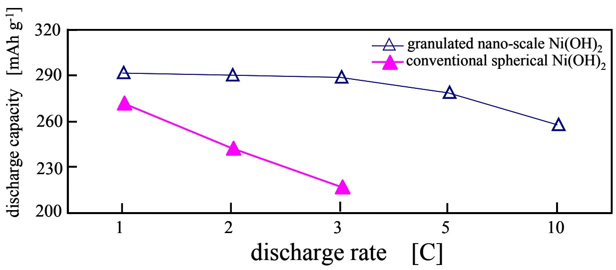

***Fig. 2** Comparison of capacities of the granulated grains of nano-scale $Ni(OH)_2$ mixed with nano-scale $Co(OH)_2$ and conventional spherical micro-sized $Ni(OH)_2$ at high C-rate.*

The effect of granulation of nano-scale $Ni(OH)_2$ on its electrochemical performance is probably as follows. Sizes of active material and electronic conductor need to be match properly. Generally, electronic conductor is made up of 1~3 μm particles. When nano-scale $Ni(OH)_2$ is granulated to be about 5 μm grains, the electronic conductor is smaller. When they are mixed to prepare electrode, electronic conductor, smaller particles, surrounds the grains of $Ni(OH)_2$, bigger particles, and forms a conductive network in the electrode, leading to good electrochemical performance, as illustrated in Figure 3 (a). Whereas, nano-scale $Ni(OH)_2$ is directly mixed with conventional conductor, nano-scale particles of $Ni(OH)_2$ surround micro-scale particles of conductor, that is isolated by nano-scale $Ni(OH)_2$, leading to poor electronic conductivity, as shown in Figure 3 (b). This is the reason why nano-scale $Ni(OH)_2$ always presents poor electrochemical performance when its electrode preparation is according to conventional method. Only when nano-scale $Ni(OH)_2$ is mixed with a large amount of conductor, it shows good performance. But this is not practical for preparation of electrode. Therefore, size of electronic conductor does not match with that of nano-scale $Ni(OH)_2$, this hindered nano-scale $Ni(OH)_2$ from being used to directly prepare electrode. Granulation makes nano-scale $Ni(OH)_2$ particles to form micro-scale grains, which match well with conventional electronic conductor particles.

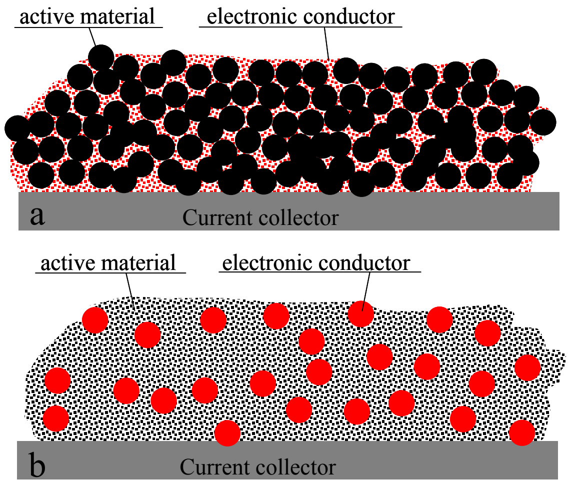

Fig. 3 *Illustrations of nano-scale $Ni(OH)_2$ and electronic conductor in electrode. (a) Granulation. (b) Without granulation*

Conclusion

Addition of nano-scale $Co(OH)_2$ can significantly improve electrochemical performance of nano-scale $Ni(OH)_2$. Further granulation of nano-scale $Ni(OH)_2$ by spray drying granulation, by which nano-scale $Ni(OH)_2$ is granulated to form micro-scale spherical grains, takes effect for improvement of its performance during preparation of cathode materials. The granulated nano-scale $Ni(OH)_2$ shows excellent performance at high discharge capacity rates. It achieves high utilizations of $Ni(OH)_2$ in excess of 89% at 10C. It is a promising material for high power Ni-MH batteries.

Reference

1. K. Watanabe, T. Kikuoka and N. Kumagai, Physical and electrochemical characteristics of nickel hydroxide as a positive material for rechargeable alkaline batteries, J Appl Electrochem **25**(1995), pp.219-226.
2. Z. Zhou, J. Yan and J. Lin et al. Studies on proton diffusion behavior of nanometer-size $Ni(OH)_2$, Chinese J Power Sources **23**(1999), pp.319-321.
3. D.E. Reisner, A.J. Salkind and P.R. Strutt et al. Nickel hydroxide and other nanophase cathode materials for rechargeable batteries, J Power Sources **65** (1997), pp.231-233.
4. X.J. Han, X.M. Xie and C.Q. Xu et al. Morphology and electrochemical performance of nano-scale nickel hydroxide prepared by supersonic coordination-precipitation method, Optical Materials **23** (2003), pp.465-470.

5. X.H. Liu and L.Yu, Influence of nanosized $Ni(OH)_2$ addition on the electrochemical performance of nickel hydroxide electrode, J Power Sources **128** (2004), pp.326-330.
6. R.S. Jayashree, P. Vishnu Kamath and G.N. Subbanna, Effect of crystallinity on the reversible discharge capacity of nickel hydroxide, J Electrochem Soc **147** (2000), pp.2029-2032.
7. X.M. He, J.J. Li and H.W. Cheng et al. Controlled Crystallization of nano-scale nickel hydroxide, J Inorg Mat, 2005, in press.
8. H. Minoshima, K. Matsushima and H. Liang et al. Basic model of spray drying granulation, J Chem Eng Jpn **34** (2001), pp.72-478.
9. H.P. Klug and E.A. Leroy, X-ray Diffraction Procedure, Wiley, New York, 1974, p.656.
10. M.C. Bernard, R. Cortes and M. Keddam et al. Structural defects and electrochemical reactivity of β-$Ni(OH)_2$, J Power Sources **63** (1996), pp.247-254.
11. Q.S. Song, Z.Y. Tang and H.T. Guo et al. Structural characteristics of nickel hydroxide synthesized by a chemical precipitation route under different pH values, J Power Sources **112** (2002), pp.428-434.
12. M. Butel, L. Gautier and C. Delmas, Cobalt oxyhydroxides obtained by 'chimie douce' reactions: structure and electronic conductivity properties, Solid State Ionics **122**(1999), pp.271-284.