Controlled crystallization and granulation of nano-scale β-Ni(OH)$_2$ cathode materials for high power Ni-MH batteries

Xiangming He [*], Jianjun Li, Hongwei Cheng, Changyin Jiang, Chunrong Wan

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

Abstract

A novel synthesis of controlled crystallization and granulation was attempted to prepare nano-scale β-Ni(OH)$_2$ cathode materials for high power Ni-MH batteries. Nano-scale β-Ni(OH)$_2$ and Co(OH)$_2$ with a diameter of 20 nm were prepared by controlled crystallization, mixed by ball milling, and granulated to form about 5 μm spherical grains by spray drying granulation. Both the addition of nano-scale Co(OH)$_2$ and granulation significantly enhanced electrochemical performance of nano-scale Ni(OH)$_2$. The XRD and TEM analysis shown that there were a large amount of defects among the crystal lattice of as-prepared nano-scale Ni(OH)$_2$, and the DTA–TG analysis shown that it had both lower decomposition temperature and higher decomposition reaction rate, indicating less thermal stability, as compared with conventional micro-scale Ni(OH)$_2$, and indicating that it had higher electrochemical performance. The granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ at Co/Ni = 1/20 presented the highest specific capacity reaching its theoretical value of 289 mAh g^{-1} at 1 C, and also exhibited much improved electrochemical performance at high discharge capacity rate up to 10 C. The granulated grains of nano-scale β-Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ is a promising cathode active material for high power Ni-MH batteries.
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Keywords: Nano-scale; Nickel hydroxide; Cobalt hydroxide; Granulation; High power; Ni-MH batteries

1. 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. Ni-MH batteries have been widely utilized in the many sectors. Presently, the further spreading of Ni-MH batteries runs under the strong competition by the rechargeable Li-ion batteries, which have a considerable advantage in terms of specific energy. Nonetheless, they have been mainly used for those applications where Li-ion batteries exhibit weak behavior, for example, high power and low cost. Therefore, 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 to 235 mAh g^{-1} at 0.2 C 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 1 C [6].

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

* Corresponding author. Tel.: +86 10 89796073; fax: +86 10 69771464.
E-mail address: hexm@tsinguha.edu.cn (X. He).

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 by controlled crystallization, which is a wet synthesis process that is scaleable to large volume manufacturing and anticipated to be low in cost, and characterized by X-ray diffraction (XRD), BET surface analyzer and transmission electron microscopy (TEM). The obtained nano-scale $Ni(OH)_2$ was then dehydrated by azeotropic distillation with *n*-butanol, and analyzed by TEM and XRD. The cathode was prepared using granulated micro-sized spherical grains of nano-scale $Ni(OH)_2$ which is obtained by mixing as-prepared nano-scale $Ni(OH)_2$ with nano-scale $Co(OH)_2$ and spray drying granulation, and electrochemically tested. The obtained granulated micro-sized spherical grains of nano-scale $Ni(OH)_2$ were analyzed by SEM and DTA and TG technique. Additionally, granulation with different amount of conductor was carried out to optimize its electrochemical performance. All references to $Ni(OH)_2$ refer to β-$Ni(OH)_2$ phase.

The granulation of nano-scale $Ni(OH)_2$ is a new approach to organize the electrode in nano-scale $Ni(OH)_2$ particles embedded in micro-scale granulated grains, whose size is conventionally adopted to prepare the electrode of $Ni(OH)_2$, in order to enhance interconnectivity of nano-scale particles to improve the electrochemical performance of nano-scale $Ni(OH)_2$ at high C-rate.

2. Experimental

Hydrous nano-scale $Ni(OH)_2$ was firstly synthesized as follows. The solutions of $NiSO_4$, NaOH, dispersant and chelating reagent were fed continuously by peristaltic pumps into a crystallization reactor with agitation, as shown in Fig. 1, and colloid solution containing nano-scale $Ni(OH)_2$ precipitate overflowed out of the reactor. NH_3 was used as the chelating reagent of Ni^{2+} ions to control their activity for expected crystallization process. The concentration of the solutions, flow rates, agitating intensity, temperature, and pH of the solution in the reactor were optimized, and the runs were operated carefully to effectively control the precipitation and growth of $Ni(OH)_2$ crystal particles in the reactor to obtain the expected products. The details of preparation were described in reference [7]. The colloid was washed and filtrated repeatedly, and ceased until SO_4^{2-} could not be detected by precipitation with Ba^{2+}. Successively, *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
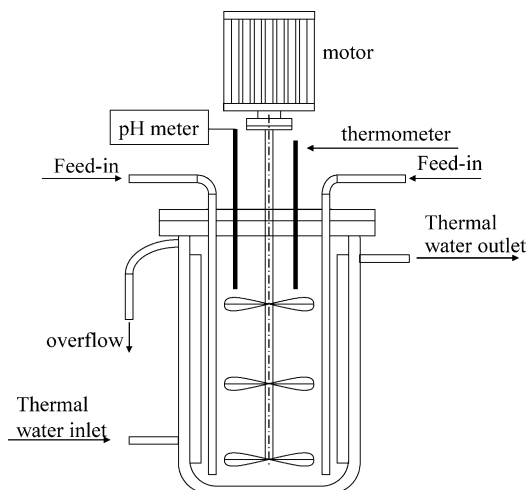

Fig. 1. Schematic diagram of reactor for controlled crystallization process.

of nano-scale $Ni(OH)_2$. The colloid of 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].

Crystal phase of samples were characterized by X-ray diffraction (XRD, D/max-rB) using Cu Kα (λ = 1.541 Å), $40 \, kV \times 120 \, mA$ radiation with step of $0.02°$ at $6° \, min^{-1}$. The particle morphology of the powders was observed using a scanning electron microscopy (SEM, JSM6301F) and transmission electron microscopy (TEM, JEM-200 CX).

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 h. 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 wt.% KOH solution. The discharge performance with cut-off voltage of 1.0 V was carried at room temperature.

3. Results and discussions

In Fig. 2 are shown the XRD patterns of the conventional spherical $Ni(OH)_2$ and as-prepared nano-scale $Ni(OH)_2$, where all the prominent reflections can be indexed as the hexagonal phase of typical β-$Ni(OH)_2$ by comparison with those reported earlier [9]. Obviously, a few distinguishing features of these XRD patterns can be found out. The prominent diffraction lines in pattern (b) are considerably broadened as compared with those in the pattern (a), indicating the poor crystallinity or smaller crystalline size of nano-scale $Ni(OH)_2$ [1]. The (0 0 1) diffraction line is the most intense

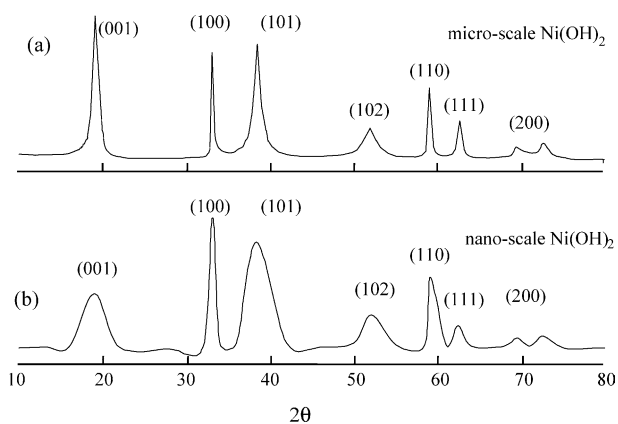Fig. 2. XRD patterns of micro-scale and nano-scale Ni(OH)$_2$.

Fig. 4. Thermal analysis (DTA and TG) of conventional spherical micro-sized Ni(OH)$_2$ (a) and granular grains of nano-scale Ni(OH)$_2$ (b).

in pattern (a), while the (1 0 0) diffraction line is the most intense in pattern (b), indicating that crystal of nano-scale Ni(OH)$_2$ grows mainly in the direction perpendicular to the (1 0 0) plane to form sheet structure.

The reasons for broadening of the (0 0 1) reflection is due to small particle size, increased disorderliness on account of the existence of stack faults, and the presence of other polymorphic modifications as interstratified phases [6], those are identified to be crystal defects. Therefore, the abnormal width of (0 0 1) and (1 0 1) reflections are caused by the existence of defects in the material. A large amount of structural defects are distributed among the volume of the crystal lattice of as-prepared nano-scale Ni(OH)$_2$; the more defects, the more efficient the nickel hydroxide, indicating the as-prepared Ni(OH)$_2$ has good electrochemical performance.

Fig. 3 shows TEM image of the as-prepared nano-scale Ni(OH)$_2$, that is dispersive particles. Its average size is measured to be about 20 nm by observation. By the qualitatively large widths of diffraction lines in Fig. 2(b), the crystalline size is evaluated to be 2.77 and 10.5 nm from the width of the diffraction lines of (0 0 1) and (1 0 0), respectively, according to Scherrer's equation [10]. An average length is evaluated to be 6.75 nm by formula proposed in reference [11]. A poor
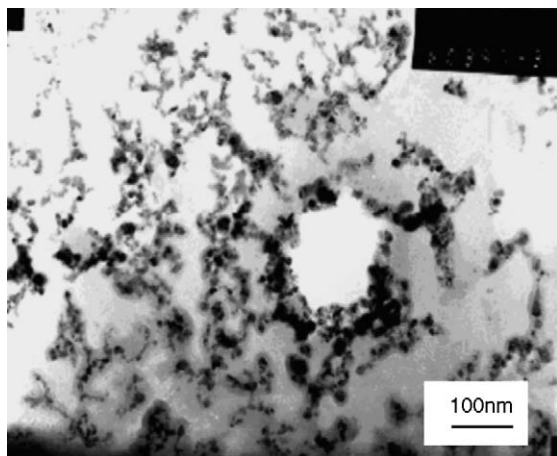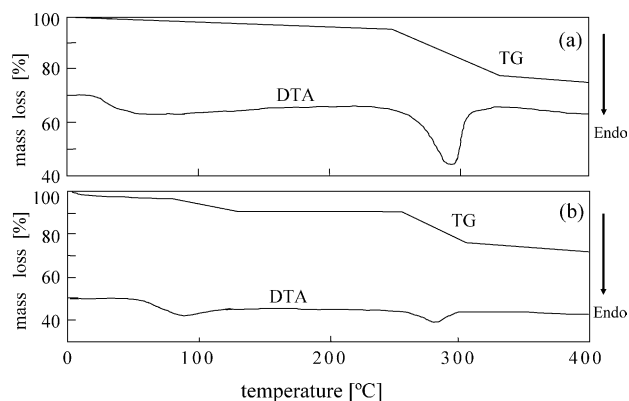
agreement between the observed and the evaluated values of crystalline size is caused by the large amount of structural defects in the particles. Its BET specific surface area is measured to be as large as 207 m^2 g^{-1}. The dispersant is experimentally found to be crucial to obtain dispersive powder of nano-scale Ni(OH)$_2$.

Fig. 4 presents DTA and TG results on Ni(OH)$_2$. The DTA peaks located at 87 and 282 °C correspond closely to the mass changes observed in the TG curve of granular grains of nano-scale Ni(OH)$_2$, as shown in Fig. 4(b). The first mass loss starts at about 60 °C, achieves a constant level of 11% at about 125 °C, due to the evaporation of adsorption water. The second mass loss starts at about 240 °C, and reaches a constant level of 28.4% at about 340 °C, namely 19.4% for second mass loss, due to dehydration of Ni(OH)$_2$ to form NiO. Therefore, 282 °C is the thermal decomposition temperature of granular grains of nano-scale Ni(OH)$_2$, which is below that of conventional spherical micro-sized Ni(OH)$_2$ at the DTA peak of 293 °C as shown in Fig. 4(a). Higher thermal decomposition temperature indicates more compact structure of crystalline grain, stronger interaction force of molecules and more stable chemistry, leading to more difficult electro-chemical reaction, bigger charge/discharge inner resistance and lower specific capacity of Ni(OH)$_2$. So lower thermal decomposition temperature of granular grains of nano-scale Ni(OH)$_2$ should present better specific capacity.

Additionally, the slope of weight loss step corresponding to decomposition of Ni(OH)$_2$ in TG curve (b) increases, as compared with that of curve (a), indicating higher reaction rate of decomposition. Both lower decomposition temperature and higher decomposition rate indicate less thermal stability, leading to higher electrochemical performance of Ni(OH)$_2$. Such a relationship between decomposition temperature and performance was also investigated in conventional micro-sized Ni(OH)$_2$ system in Refs. [1,12].

It is also observed that the decomposition exothermic peak of granular grains of nano-scale Ni(OH)$_2$ is much lower than that of conventional spherical micro-sized Ni(OH)$_2$. The height of the exothermic peak is related to the quantity of heat evolved from the decomposition reaction of Ni(OH)$_2$,
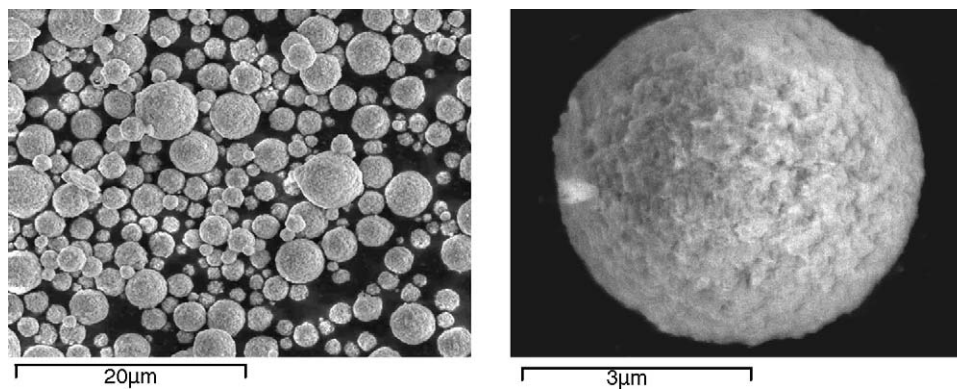

Fig. 3. TEM image of nano-scale Ni(OH)$_2$.
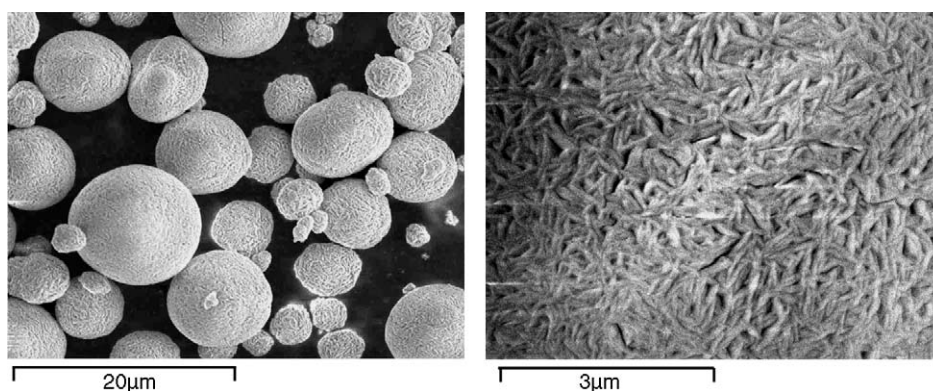
Fig. 5. SEM images of granular grains of nano-scale $Ni(OH)_2$.

Fig. 6. SEM images of conventional spherical micro-sized $Ni(OH)_2$.

namely, change of its chemical bonds. β-Nickel hydroxide consists of a hexagonal packing of hydroxyl ions with Ni^{2+} occupying alternate rows of octahedral sites. This results in an orderly stacking of charge-neutral slabs of composition $Ni(OH)_2$. Being ionic bond compound, $Ni(OH)_2$ presents its mole bond energy by continuous alternant interaction chains of Ni^{2+} ions and OH^- ions, where the ions at the ends of the interaction chains have no contribution to the bond energy. In the other word, the ions at the surface of crystal give much less bond decomposition energy. Therefore, having more proportion of surface ions, nano-scale $Ni(OH)_2$ presents much less quantity of decomposition heat as compared with micro-sized one.

Both XRD and DTA–TG analysis indicate that the nano-scale $Ni(OH)_2$ prepared in this study shall present good electrochemical performance.

Fig. 5 shows the SEM images of granulated grains of nano-scale $Ni(OH)_2$. It is of excellent dispersivity and fluidity, and 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. Contrarily, conventional spherical micro-sized $Ni(OH)_2$ particles are made up of hundreds of nanometer crystals, which can be clearly observed on the surface at the same magnifying level, as shown in Fig. 6.

Five processes were adopted to prepare electrode, whose electrochemical performance was tested at a discharge rate of 1 C. First, nano-scale $Ni(OH)_2$ was directly used to prepared positive electrodes by weight percentage of 85%, as described in Section 2, 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

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

Preparation process	mAh g^{-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
5. Granulation using co-precipitated nano-scale $Ni_{20/21}Co_{1/21}(OH)_2$	236

up to 289 mAh g^{-1}. Finally, nano-scale Ni$_{20/21}$Co$_{1/21}$(OH)$_2$ was prepared by co-precipitation during controlled crystallization process, and was directly used to prepared positive electrodes after granulation, resulting in its specific capacity reaching only 236 mAh g^{-1}.

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 [13,14]. By comparison of processes 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 processes 2 and 4.

However, what is more notable is that granulation can further enhance the specific capacity of nano-scale Ni(OH)$_2$. By comparison of processes 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 processes 3 and 4.

Probably, the granulation makes the contact of nano-scale particles better, leading to a resistance decrease, and finally resulting in an electrochemical performance improvement.

It is also noticed that the granulation of co-precipitated nickel and cobalt hydroxide, Ni$_{20/21}$Co$_{1/21}$(OH)$_2$, at the same Co/Ni ratio of 1/20 as addition level of Co(OH)$_2$ can make sample reach a specific capacity of only 236 mAh g^{-1}, which is much lower that that of samples by addition of nano-scale Co(OH)$_2$ at Co/Ni = 1/20. The reason is probably that the cobalt located at the lattice site of hydroxide does not play a role of conductor as well as the nano-scale Co(OH)$_2$ particle does when it is dispersed among nano-scale Ni(OH)$_2$ particles.

The good effect of nano-scale Co(OH)$_2$ addition is also demonstrated by the high C-rate discharge capacities of samples, which are prepared by processes 2, 4 and 5 described in Table 1. Their discharge capacities at 1, 3, 5 and 10 C-rate are shown in Fig. 7. At all of C-rate, the discharge capacities of granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ at Co/Ni = 1/20 get the biggest values; the discharge capacities of granulated grains of nano-scale Ni$_{20/21}$Co$_{1/21}$(OH)$_2$ prepared by co-precipitation are much lower than that of granulated mixture of nano-scale Ni(OH)$_2$ and nano-scale Co(OH)$_2$ at the same Co/Ni mole ratio, and only a little bit higher than that of granulated grains of nano-scale Ni(OH)$_2$ without addition of Co(OH)$_2$.

The experimental results described in Table 1 have shown that the combination of granulation and addition of nano-scale Co(OH)$_2$ takes effect to improve the electrochemical performance of nano-scale Ni(OH)$_2$.

The granulations with different Co/Ni mole ratio were carried out to find proper amount for addition of nano-scale
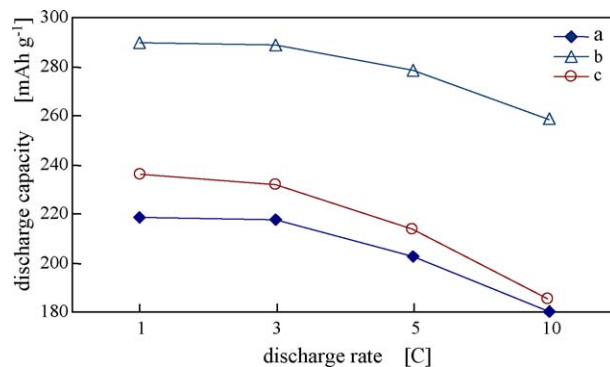

Fig. 7. Comparison of the capacities of different samples at high C-rate: (a) granulated grains of nano-scale Ni(OH)$_2$ without addition of Co(OH)$_2$; (b) granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ at Co/Ni = 1/20; (c) granulated grains of nano-scale Ni$_{20/21}$Co$_{1/21}$(OH)$_2$ prepared by co-precipitation.

Co(OH)$_2$. The specific capacities of the granulated grains at different discharge capacity rate are shown in Fig. 8. When the content of nano-scale Co(OH)$_2$ increases, specific capacity of granulated grains of nano-scale Ni(OH)$_2$ increases to the maximum value at the Co/Ni mole ratio of 1/20, over which the capacity increases no more at discharge capacity rate of 1 C and decreases instead at higher rate. Therefore, proper Co/Ni mole ratio is experimentally determined to be 0.05.

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 Fig. 9. 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 1 C, 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 10 C and the latter go down to 218 mAh g^{-1} even at 3 C. 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 10 C.
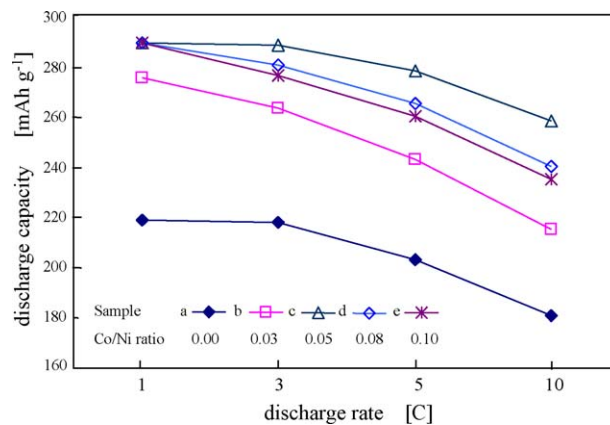

Fig. 8. Discharge capacities of granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ at high C-rate. Co/Ni mole ratios are (a) 0, (b) 0.03, (c) 0.05, (d) 0.08, and (e) 0.10.
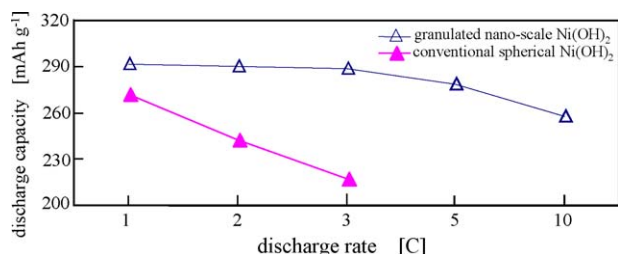
Fig. 9. Comparison of capacities of the granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ and conventional spherical micro-sized Ni(OH)$_2$ at high C-rate.

Above experimental results demonstrate that the enhancement of conductivity in electrode is a key factor to improve the performance of nano-scale Ni(OH)$_2$. When nano-scale Co(OH)$_2$ is mixed with nano-scale Ni(OH)$_2$, its particles are uniformly dispersed in the interspaces of nano-scale Ni(OH)$_2$ particles, and forms conducting network of CoO(OH) during charging, resulting in improving conductivity among nano-scale particles. Ordering the nano-scale particles to micro-scale grains by granulation reduces the resistance between nano-scale particles as a higher number of contacts are formed between the nano-scale particles during spray drying. Therefore, the combination of granulation and the addition of nano-scale Co(OH)$_2$ can lead to a significantly improved performance of nano-scale Ni(OH)$_2$.

The granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ at Co/Ni = 1/20 is a promising alternative material for high power Ni-MH batteries, which owes to improvement of electrical conductivity by both granulation and addition of nano-scale Co(OH)$_2$ and high proton diffusion coefficient in the crystalline grains of nano-scale Ni(OH)$_2$. As shown in Fig. 9, its discharge capacity at 5 C exceeds that of conventional Ni(OH)$_2$ at 1 C. Even at 10 C rate, it surpasses that of conventional Ni(OH)$_2$ at 2 C rate.

4. Conclusion

The dispersive active nano-scale Ni(OH)$_2$ was synthesized by controlled crystallization. The XRD and TEM analysis results show that there are a large amount of defects among the volume of the crystal lattice of as-prepared nano-scale Ni(OH)$_2$, and the DTA–TG analysis result show that it has both lower decomposition temperature and higher decomposition rate, indicating less thermal stability, as compared with conventional micro-scale Ni(OH)$_2$. 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 on improvement of its performance. The granulated grains of nano-scale Ni(OH)$_2$ mixed with nano-scale Co(OH)$_2$ shows excellent performance at high discharge capacity rates. It achieves high capacity in excess of 289, 289, 288, 277, 258 mAh g^{-1} at 1, 2, 3, 5, 10 C, respectively. Therefore, it is a promising material for high power Ni-MH batteries.

Acknowledgement

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