

Controlled crystallization and granulation of nano-scale β -Ni(OH)₂ cathode materials for high power Ni-MH batteries

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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 μ m 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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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

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conductor, which has been hindering it from practical use to directly prepare cathode.

Therefore, nano-scale $\text{Ni}(\text{OH})_2$ can only be applied as adjuvant to improve the performance of micro-sized spherical $\text{Ni}(\text{OH})_2$, 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 $\text{Ni}(\text{OH})_2$.

In this study, nano-scale $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ which is obtained by mixing as-prepared nano-scale $\text{Ni}(\text{OH})_2$ with nano-scale $\text{Co}(\text{OH})_2$ and spray drying granulation, and electrochemically tested. The obtained granulated micro-sized spherical grains of nano-scale $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ refer to β - $\text{Ni}(\text{OH})_2$ phase.

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

2. Experimental

Hydrous nano-scale $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ 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

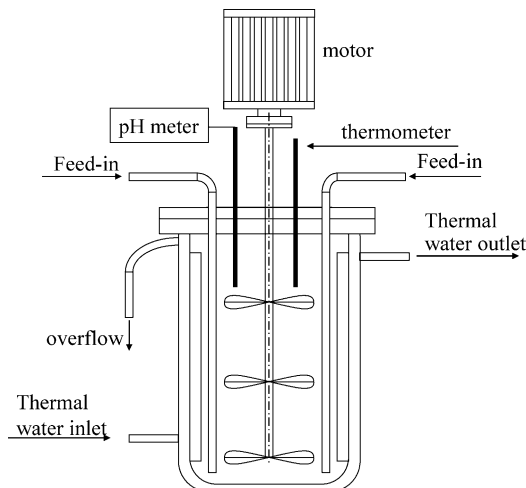


Fig. 1. Schematic diagram of reactor for controlled crystallization process.

of nano-scale $\text{Ni}(\text{OH})_2$. The colloid of nano-scale $\text{Co}(\text{OH})_2$ was also prepared as above procedures, and used as conductor.

The as-prepared colloid of nano-scale $\text{Co}(\text{OH})_2$ and deionized water were added into colloid of pre-distilled nano-scale $\text{Ni}(\text{OH})_2$ 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 $\text{Cu K}\alpha$ ($\lambda = 1.541 \text{ \AA}$), $40 \text{ kV} \times 120 \text{ mA}$ 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 $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ and as-prepared nano-scale $\text{Ni}(\text{OH})_2$, where all the prominent reflections can be indexed as the hexagonal phase of typical β - $\text{Ni}(\text{OH})_2$ 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 $\text{Ni}(\text{OH})_2$ [1]. The (001) diffraction line is the most intense

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