

High Rate Performance of Surface Metalized Spherical Nickel Hydroxide via in situ Chemical Reduction



Gaoliang Fu^a, Kun Chang^{b,*}, Bao Li^a, EnBo Shangguan^a, Hongwei Tang^a, Caixia Zhang^a, Zhaorong Chang^{a,**}, Xiao-Zi Yuan^c

^a Collaborative Innovation Center of Henan Province for Green Manufacturing of Fine Chemicals, Key Laboratory of Green Chemical Media and Reactions, Ministry of Education, School of Chemistry and Chemical Engineering, Henan Normal University, Xixiang, Henan 453007, PR China

^b National Institute for Materials Science (NIMS), 1-1 Namiki, Tsukuba, Ibaraki, 305-0044, Japan

^c National Research Council of Canada, Vancouver, BC V6 T 1W5, Canada

ARTICLE INFO

Article history:

Received 27 December 2015

Received in revised form 10 April 2016

Accepted 27 April 2016

Available online 28 April 2016

Keywords:

Nickel hydroxide
cathode materials
in-situ reduction
surface modification
high rate capability

ABSTRACT

The surface modified Ni(OH)₂ samples with Ni and Ni–cobalt (Ni–Co) layer, respectively, are prepared by an in-situ chemical reduction method using hydrazine hydrate as reductant and silver ion as activating agent. The samples are characterized by X-ray diffraction, energy dispersive spectroscopy, and scanning electron microscopy. As the Ni electrode cathode, the material is analyzed, and the electrochemical properties such as rate capability, cyclic voltammetry, and AC impedance are investigated. The results indicate that the metallization of the Ni(OH)₂ surface does not change the original morphologies and crystal structure of the sample. The in-situ reduced Ni–Co layer bonds tightly with the matrix, which increases the conductivity of Ni(OH)₂ particles, reduces the electrode polarization, lowers the charging voltage of the battery, and improves the reversibility of the electrode reaction of Ni(OH)₂. Moreover, it effectively increases the rate capability, energy density, and utilization rate of the active material of the Ni electrode.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Nickel (Ni) based alkaline secondary batteries (MH/Ni, Zn/Ni, Fe/Ni) have extensively been used in electric tools, electric vehicles, military industries, aerospace industries, and other fields due to their outstanding safety performance [1–8]. The main active material of the cathode material for the Ni based alkaline secondary battery is nickel hydroxide (Ni(OH)₂), a p-type semiconductor with relatively poor conductivity [9–11]. Thus, during the preparation of electrodes, additives such as acetylene black, graphite powder, or Ni powder, are usually added to improve the conductivity of the Ni(OH)₂ electrodes [12–18]. To some extent, the addition of these inactive substances improves the conductivity of the Ni electrodes, however, it also decreases the specific volumetric capacity of the electrodes, as well as the active material ratio in the electrodes.

It is well known that high specific energy, high safety performance, and high rate capability are the main indicators for the performance of the electric vehicle power battery. Apparently, the high rate capability of the Ni electrode is related to the conductivity of the active material Ni(OH)₂ [19–24]. Therefore, improvement in the conductivity of the Ni(OH)₂ is highly desirable in order to increase the electrode rate capability, without lowering the electrode specific volumetric capacity. Previous researchers coated Ni(OH)₂ particles with cobalt (Co), Ni-conducting layer, and metallic oxides of Co to improve the electrochemical properties of Ni electrodes [25–30]. Chemical precipitation method has been considered the main technique to coat metallic oxides of Co. In the presence of complexing agents including ammonia, Co ions in solution could be deposited on the spherical Ni(OH)₂ surface. The main components of the coating layers were Co(OH)₂ and CoOOH [31–33]. According to the literature, electroless plating method has also been used to coat Co and Ni layers. In this method, the sulfates or chlorides of Co or Ni were used as Co or Ni metal sources and sodium hypophosphite was used as reductant. Following the sensitization of noble metal ions such as platinum and silver (Ag), the metal ions in the bath

* Corresponding author.

** Corresponding author.

E-mail addresses: changkun1984@sina.com (K. Chang), czr_56@163.com (Z. Chang).

were reductively deposited onto the surfaces of $\text{Ni}(\text{OH})_2$ particles [34–38]. There are a few disadvantages of this method. First, this technical process involves complicated operations, and therefore, it is costly. Second, the generated wastes contain a large amount of hazardous substances such as phosphates and phosphites, causing severe environmental issues. Furthermore, the precipitated Co or Ni layer does not bond tightly with the surface of the $\text{Ni}(\text{OH})_2$ particle; therefore, it peels off easily, which adversely influences the electrochemical properties of the $\text{Ni}(\text{OH})_2$ particles.

In this study, we propose a novel approach involving the in-situ reduction of the metal ions on the $\text{Ni}(\text{OH})_2$ particle surface using a small amount of hydrazine hydrate as reductant and Ag ions as activating agent. This method is simple, economical, and environmentally friendly, and it offers strong and tight bonding of the reduced metal layer with the $\text{Ni}(\text{OH})_2$ particle matrix. This significantly improves the conductivity of the $\text{Ni}(\text{OH})_2$ particles, decreasing the electrode polarization, as well as promoting the high rate capability of the material. To our knowledge, in-situ reduction of the metal ions on the spherical $\text{Ni}(\text{OH})_2$ surface has never been reported.

2. Experimental

Spherical $\text{Ni}(\text{OH})_2$ particles were supplied by China Henan Kelong Co., Ltd. Hydrazine hydrate (80%) and sodium hydroxide (NaOH) were analytically pure and used as received without further purification.

2.1. In-situ reduction of the nickel ions on the spherical nickel hydroxide surface

Spherical $\text{Ni}(\text{OH})_2$ particles (labeled as sample A) was used as the raw material for the preparation of different $\text{Ni}(\text{OH})_2$ samples with surfaces having different reduction degrees by adjusting the hydrazine hydrate amount. The detailed procedure was as follows:

$\text{Ni}(\text{OH})_2$ powder with spherical particles (15 g) was weighed and wetted with silver nitrate (AgNO_3 , 0.5 g L^{-1}). Next, the wetted powder was added to NaOH solution (250 mL) at pH 12. Subsequently, the flask was placed in the water bath and the temperature was increased with stirring. When the temperature was 70°C , hydrazine hydrate (0.5 mL) was added. When the temperature reached 80°C , another 2, 3, 4, 5, 5.5, 6, and 7 mL hydrazine hydrate was added, respectively. The solution was heated until the $\text{Ni}(\text{OH})_2$ particles turned black from apple green and the bubbles in the solution disappeared. Then the solution was filtered, washed, and the products were vacuum dried sequentially

to obtain different samples. Among them, the samples prepared by adding 4, 5, 6, and 7 mL of hydrazine hydrate were labeled as samples B, C, D, and E, respectively.

2.2. In-situ reduction of the nickel–cobalt ions on the spherical nickel hydroxide surface

The cobalt hydroxide ($\text{Co}(\text{OH})_2$) coated spherical $\text{Ni}(\text{OH})_2$ (labeled as sample F; the body phase was doped with 1.5 wt.% Co and the outer layer was coated with 2.4 wt.% $\text{Co}(\text{OH})_2$) was used as raw material. According to the in-situ reduction method described above, hydrazine hydrate (2.5 mL) was added to prepare the reduced sample, which was labeled as sample G.

2.3. Material Characterization

The X-Ray polycrystal diffractometer (D-8 type, German Bruker Corporation) was used to analyze the crystal structures of samples. The instrument was equipped with Cu target. The samples were scanned at a rate of $0.02^\circ \text{ s}^{-1}$ over the range of $5\text{--}80^\circ$ with the working voltage of 40 KV and working current of 40 mA. Morphology characterization of the samples was accomplished by field emission scanning electron microscopy (FE-SEM, S4800, Hitachi).

2.4. Measurement of the Electrochemical Properties

To investigate the impact of the reduction degree on the electrochemical properties, the samples prepared by adding 4, 5, 6, and 7 mL of hydrazine hydrate (labeled as samples B, C, D, and E; Table S1), respectively, were selected and their electrochemical properties were compared to that of the baseline sample (Sample A).

The samples A, B, C, D, and E were, respectively, blended with CoO and polytetrafluoroethylene (PTFE) in a weight ratio 90:5:5, and a paste with adequate rheological properties was produced. The slurries were scraped to foam nickel sheet with a dimension of $1.0 \times 1.0 \text{ cm}^2$. The coated foam Ni sheet were vacuum dried at 80°C for 1 h, and then pressed into Ni electrode plates under 20 MPa pressure, followed by vacuum drying again at 100°C for 5 h.

As samples F and G already contained Co element, CoO was not added when the impact of Co layer on the electrochemical properties of the samples was investigated. As such, samples F and G were blended with PTFE only in a weight ratio of 95:5. The slurries were scraped into foamed Ni with a size of $1.0 \times 1.0 \text{ cm}^2$. The coated foamed Ni sheets were vacuum dried at 80°C for 1 h,

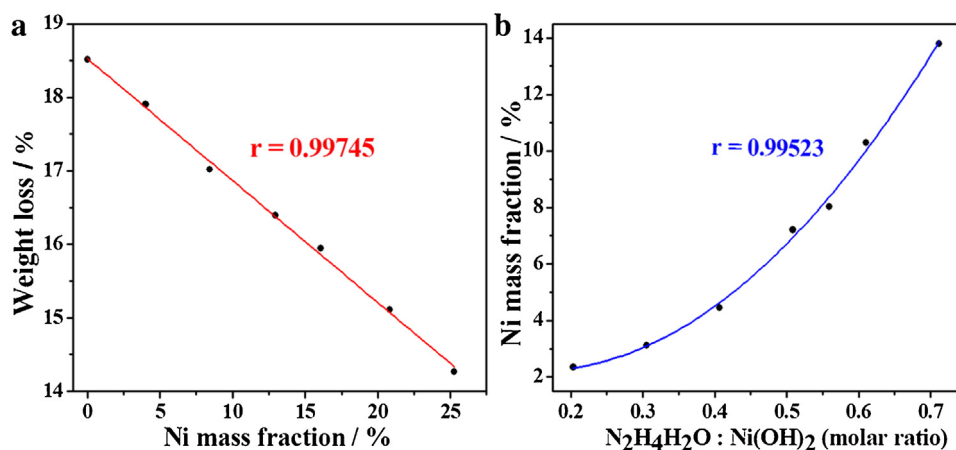


Fig. 1. (a) The standard curve of the Ni content. (b) The relationship curve of the amount of hydrazine hydrate versus Ni content on $\text{Ni}(\text{OH})_2$ surface.

Download English Version:

<https://daneshyari.com/en/article/183013>

Download Persian Version:

<https://daneshyari.com/article/183013>

[Daneshyari.com](https://daneshyari.com)