



# Effect of Al substitution on the microstructure and lithium storage performance of nickel hydroxide



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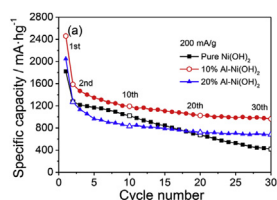
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## HIGHLIGHTS

- Hierarchical structured nickel hydroxides are prepared by coprecipitation method.
- The influence of Al substitution on the electrode performances has been studied.
- Phase structure and morphology of nickel hydroxide are tuned by Al substitution.
- Mixed phase nickel hydroxide with hierarchical nanosheets/nanoparticle morphology.
- The mixed phase nickel hydroxide show high capacity and good cycling stability.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Al-substituted Ni(OH)<sub>2</sub> samples with Al<sup>3+</sup>/Ni<sup>2+</sup> mole ratio of 0%, 10% and 20% have been prepared by a very facile chemical co-precipitation method. The microstructure of the prepared samples are analyzed by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), thermo-gravimetric analysis (TGA), and Field emission scanning electron microscopy (FESEM). The results reveal that the pure Ni(OH)<sub>2</sub> sample is β-Ni(OH)<sub>2</sub> with nanosheets hierarchical structure; the sample with 10% Al is mixed phase α/β-Ni(OH)<sub>2</sub> with hybrid nanosheets/nanoparticles hierarchical structure; the sample with 20% Al is α-Ni(OH)<sub>2</sub> with irregular nanoparticles hierarchical structure. The lithium storage performances of the prepared samples are characterized by cyclic voltammograms (CV), electrochemical impedance spectroscopy (EIS), and charge–discharge tests. The results demonstrate that Al substitution could improve the lithium storage performances of nickel hydroxide. In particular, the mixed phase α/β-Ni(OH)<sub>2</sub> with 10% Al exhibited the highest electrochemical activity, the best rate performance, and superior cycling stability. For example, after 30 charge/discharge cycles under a current density of 200 mA g<sup>-1</sup>, the mixed phase α/β-Ni(OH)<sub>2</sub> with 10% Al can still deliver a specific discharge capacity of 964 mAh g<sup>-1</sup>, much higher than of for the α-Ni(OH)<sub>2</sub> with 20% Al (681 mAh g<sup>-1</sup>) and the pure Ni(OH)<sub>2</sub> (419 mAh g<sup>-1</sup>).

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## 1. Introduction

High energy density, high rate capability, and long cycling life

are essential properties of lithium ion batteries (LIBs) for future electric vehicles and renewable energy storage [1,2]. The development of advanced electrode materials for lithium storage has been one of the important tasks for building high-performance LIBs [3,4]. To this end, the pursuit of anode materials with a reversible capacity well about that of graphite ( $372 \text{ mAh g}^{-1}$ ) has been a major research thrust in the field of LIBs [5]. Generally, transition-metal oxides have been proposed as carbon alternative materials due to their high lithium storage capacity [6]. In comparison, transition metal hydroxides as anode materials for LIBs have been less commonly reported.

$\text{Ni}(\text{OH})_2$  with the typical layered structure has drawn much attention as positive materials in alkaline secondary batteries, electrochemical super-capacitors, light catalysis, electro-catalytic oxidation, water treatment and other fields [7]. Cao et al. [8] firstly investigated the  $\beta\text{-Ni}(\text{OH})_2/\text{RGO}$  composite materials as anode material for lithium ion batteries. It reveals the composite materials have a specific capacity of  $930 \text{ mAh g}^{-1}$  at a current density of  $200 \text{ mA g}^{-1}$  and it still delivers  $507 \text{ mAh g}^{-1}$  after 30 cycles, indicating that the  $\beta\text{-Ni}(\text{OH})_2$  has a very high lithium storage activity. To improve the cycling performance of nickel nickel hydroxide, Ni [9] and Tian [10] fabricated ultrathin  $\beta\text{-Ni}(\text{OH})_2$  nano-film on nickel foam substrate by hydrothermal method; Zhu [11] and Tian [12] prepared the  $\beta\text{-Ni}(\text{OH})_2/\text{RGO}$  composite materials. For the above mentioned methods, the authors improved the electrochemical performance of  $\beta\text{-Ni}(\text{OH})_2$  materials by constructing nano-structured materials and/or fabricating nickel hydroxide/graphene hybrid materials. Cation substitution is a commonly used method to improve the electrochemical performance of electrode materials by modifying the microstructure and electronic structure of materials [13–15]. Other than  $\beta\text{-Ni}(\text{OH})_2$ , nickel hydroxide can also exist in  $\alpha\text{-Ni}(\text{OH})_2$ , which has a turbostratic-disordered structure and a much larger interlayer distance. However, the effects of cation substitution and phase structures on the lithium ion storage activity of nickel hydroxide have not been reported till now.

The current researches on nickel hydroxide used as anode materials for LIBs mainly focus on the  $\beta\text{-Ni}(\text{OH})_2$  materials. There is no reports on the  $\alpha\text{-Ni}(\text{OH})_2$  and mixed phase  $\alpha/\beta\text{-Ni}(\text{OH})_2$  materials used as anode materials for LIBs. It has been proved that the phase structure of nickel hydroxide has great effect on its electrochemical performance when used as electrode materials for Ni/MH batteries [16–19]. In this work, we studied the electrochemical behavior of Al-substituted  $\text{Ni}(\text{OH})_2$  as anode materials for LIBs. The Al-substituted  $\text{Ni}(\text{OH})_2$  samples were prepared by a very facile chemical co-precipitation method. The influence of Al substitution on the morphology, phase structure, and lithium storage performance of nickel hydroxide are discussed. It revealed that the mixed phase  $\alpha/\beta\text{-Ni}(\text{OH})_2$  with 10% Al exhibited the highest electrochemical activity, the best rate performance, and superior cycling stability.

## 2. Experimental

### 2.1. The synthesis of Al-substituted $\text{Ni}(\text{OH})_2$ samples

All of the reagents used in this work are analytical grade without further purification. The Al-substituted  $\text{Ni}(\text{OH})_2$  samples were prepared as follows:  $1 \text{ mol L}^{-1}$  NaOH was added dropwise into a mixture solution containing  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (with a  $[\text{Al}^{3+}/\text{Ni}^{2+}]$  molar ratio of 0%, 10%, and 20%, respectively) under stirring at  $50^\circ\text{C}$ . The final pH value of the mixture solution was controlled to be about 11. After continual stirring for 3 h, the suspension obtained was kept in the mother solution at  $60^\circ\text{C}$  for 20 h and allowed to settle, then washed with distilled water, filtered, and freeze dried to a constant weight. The prepared

samples with  $[\text{Al}^{3+}/\text{Ni}^{2+}]$  molar ratio of 0%, 10%, and 20% are denoted as pure  $\text{Ni}(\text{OH})_2$ , 10%Al– $\text{Ni}(\text{OH})_2$ , and 20%Al– $\text{Ni}(\text{OH})_2$  hereafter, respectively.

### 2.2. Physical characterizations

The crystal structure of the prepared samples were analyzed by multi-function X-ray diffractometer (Dutch PANalytica X'Pert<sup>3</sup> powder) at the scanning range of  $5\text{--}80^\circ$  with a scanning speed of  $4^\circ\text{min}^{-1}$ . The surface morphologies of the prepared samples were characterized by field emission scanning electron microscope (SEM, Japan Hitachi S-4800). EDS analysis was done using oxford system (X-Max) attached to the Hitachi S-4800 SEM system. Fourier transform infrared spectra (FT-IR) and thermal gravity analysis (TGA) of the prepared samples were obtained on a Fourier transform infrared spectrometer (Thermo Nicolet NEXUS 470) and thermal analyzer (American TA SDTQ 600), respectively. For TGA test, the samples were heated from 25 to  $500^\circ\text{C}$  in nitrogen atmosphere at a heating rate of  $10^\circ\text{C min}^{-1}$ .

### 2.3. Electrochemical measurements

The electrochemical performances of the prepared samples were tested in coin-type cells (CR2025), which were assembled in an argon-filled glove box. The electrode slurry was prepared by mixing the prepared nickel hydroxide sample, super P carbon black, and PVDF binder with a weight ratio of 60:30:10 in NMP solvent. The slurry was then spread onto copper foil current collector and dried in a vacuum oven at  $80^\circ\text{C}$  for 12 h. Lithium metal foil, 1 M  $\text{LiPF}_6$  in ethylene carbonate (EC)/dimethyl carbonate (DMC)/diethyl carbonate (DEC) (1:1:1 by volume), and Celgard 2400 membrane were used as the counter electrode, electrolyte, and separator, respectively.

Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were measured using an electrochemical workstation (CHI860D) at room temperature. The scan rate for CV measurement was  $0.08 \text{ mV s}^{-1}$  and the potential ranged from 0.02 V to 3.0 V (vs.  $\text{Li}/\text{Li}^+$ ). For EIS measurement, the frequency range was explored from 100 mHz to 100 kHz and the AC amplitude was 5 mV at the open circuit potential of working electrode in a fully charged condition. Charge/discharge measurements were performed using a Land battery testing system (China, LAND-CT2001C) in the voltage range of 0.02–3.0 V (vs.  $\text{Li}/\text{Li}^+$ ).

## 3. Results and discussion

### 3.1. Structure analysis of the prepared samples

Fig. 1 shows the XRD patterns of the pure  $\text{Ni}(\text{OH})_2$ , 10% Al– $\text{Ni}(\text{OH})_2$ , and 20%Al– $\text{Ni}(\text{OH})_2$  samples. For comparison, the positions of the standard diffraction peaks of  $\alpha\text{-Ni}(\text{OH})_2 \cdot 0.75\text{H}_2\text{O}$  (JCPDS 38–715) and  $\beta\text{-Ni}(\text{OH})_2$  (JCPDS 14–117) are also given at the bottom of Fig. 1. All the diffraction peaks of the pure  $\text{Ni}(\text{OH})_2$  sample are in good agreement with the standard spectrum (JCPDS 14–117) of  $\beta\text{-Ni}(\text{OH})_2$ , suggesting the sample is  $\beta\text{-Ni}(\text{OH})_2$ . The interlayer distance of this pure  $\text{Ni}(\text{OH})_2$  evaluated from Bragg formula is 4.70 Å. For 10%Al– $\text{Ni}(\text{OH})_2$  sample, diffraction peaks from both  $\beta\text{-Ni}(\text{OH})_2$  and  $\alpha\text{-Ni}(\text{OH})_2$  are observed, indicating that the sample is mixed phase  $\alpha/\beta\text{-Ni}(\text{OH})_2$ . The interlayer distance of the  $\alpha$ -motifs in the mixed phase  $\alpha/\beta\text{-Ni}(\text{OH})_2$  evaluated from Bragg formula is 7.78 Å, which is much larger than that (4.67 Å) of the  $\beta$  motifs. For 20%Al– $\text{Ni}(\text{OH})_2$  sample, all diffraction peaks can be indexed as  $\alpha\text{-Ni}(\text{OH})_2$ , showing that the sample is  $\alpha\text{-Ni}(\text{OH})_2$ . The interlayer distance of this  $\alpha\text{-Ni}(\text{OH})_2$  evaluated from Bragg formula is 7.81 Å. Based on the above results, one can conclude that with the increase

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