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# Cation-exchange induced high power electrochemical properties of core–shell $Ni(OH)_2$@CoOOH

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ABSTRACT

New applications such as hybrid electric vehicles and power backup require rechargeable batteries to combine high energy density with high charge and discharge rate capability. In this study, the core–shell $Ni(OH)_2$@CoOOH composite is constructed via a simple cation-exchange route at moderate conditions. X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM) with energy dispersive X-ray (EDX), and inductively coupled plasma (ICP) are used to characterize the resulting $Ni(OH)_2$@CoOOH composites. The $Ni(OH)_2$@CoOOH electrode exhibits high power, higher capacity and longer life cycle when it is chosen as an positive electrode material for rechargeable alkaline MH-Ni battery. The enhanced electrochemical performance is attributed to the seamless combination of the CoOOH shell and the $Ni(OH)_2$ core, avoiding the contact resistance between them at a large current density. It is believed that our methodology provides a simple and environment friendly route to a variety of core–shell materials with different composition and novel function.



## 1. Introduction

Nickel hydroxide particles with controlled structures have long been of great interest due to its significant applications in advanced nickel-based batteries [1–3], catalysts [4–6], magnetics [7,8] and ionic exchangers [9–11]. Recently, great efforts have been focused on enhancing the high power performance of it for suitable use in hybrid electric vehicles (HEVs) and electric vehicles (EVs) to overcome the shortage of energy sources and the pollution of our environment that have become more and more important [12,13]. It follows that increasing the power capabilities of this material is essential and important for raising the power performance of such batteries. However, the poor electric conductivity of $Ni(OH)_2$ (a p-type semiconductor) is the main factor that blocks the performance of it at high-rate charge and discharge [14].

Core–shell macro/nano-structures exhibit unusual catalytic, electronic, magnetic and electrochemical properties owing to its special structure [15–18]. This structure has been successfully introduced into electrochemistry system to tuning the electrochemical properties. However, only examples of surface-modified nickel hydroxide currently exist to improve the conductivity characteristics of this electrode [19–22] although significant advances have been made in developing synthetic methods to prepare nickel hydroxide particles. In addition, the regularly used coating methods including precipitation [23] and plating [19] are either difficult to be controlled or complicated and environment unfriendly. More importantly, the coating layer cannot adhere to the surface of spherical $Ni(OH)_2$ closely enough that the conductivity and cycle life of the electrode cannot be guaranteed. Therefore, it is imperative to develop alternative effective routes for the purpose of overcoming the drawbacks of the above mentioned surface-modified spherical $Ni(OH)_2$ itself and the preparation method.

Cation-exchange provides a facile method to make a chemical transformation from one solid to another via insertion and exchange of central metal atoms [24]. This method attracts intense interest recently. A range of nanocrystals of varying composition, size and shape have been achieved successfully by this effective and powerful method [24–29]. Herein, we explore to modify the surface of spherical $Ni(OH)_2$ via the exchange of nickel ions by cobalt ones to give rise to a core–shell $Ni(OH)_2$@CoOOH to improve its electrochemical properties. To the best of our knowledge, no work on cation-exchange route for modifying commercial spherical $Ni(OH)_2$ resulting core–shell structured $Ni(OH)_2$@CoOOH has been reported.

## 2. Experiment

### 2.1. Materials

All chemicals except commercial β-type spherical $Ni(OH)_2$ powder (named as $A_0$) used in our experiments were all of analytical

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**Table 1**
EDX and ICP results of starting commercial spherical $Ni(OH)_2$($A_0$) and cation-exchange induced core–shell $Ni(OH)_2$@CoOOH product ($A_1$), respectively.

| Sample | EDS (at.) | ICP (wt.%) | | ICP (at.) |
|---|---|---|---|---|
| | Ni/Co | Ni | Co | Ni/Co |
| $A_0$ | 38.2 | 58.72 | 1.41 | 41.8 |
| $A_1$ | 13.22 | 56.50 | 3.32 | 17.1 |

grade, purchased from Shanghai Chemicals Co. Ltd. (China), and used without further purification. The water used for solution preparation is deionized water (resistivity ≥18 MΩ, water purification system). The commercial β-type spherical nickel hydroxide powder was purchased from Kelong Co. Ltd. (China) used as precursor.

### 2.2. Sample preparation

The core–shell $Ni(OH)_2$@CoOOH ($A_1$) was prepared as follows: firstly, 2.25 mmol $Co(NO_3)_2{\cdot}6H_2O$ was dissolved in 50 mL deionized water, and then, the commercial β-type spherical $Ni(OH)_2$ powder (10 mmol) was launched into the solution followed by dropwise adding a 30% $H_2O_2$ solution (8 mL) at 90 °C. After the mixed solution was continuously stirred for 2 h, it was cooled naturally to room temperature and was centrifugated. The solid product was subsequently washed for several times with deionized water and ethanol, and then dried in air at 65 °C for 12 h. By operating the whole process, ca. 1 g solid powder of sample $A_1$ was obtained at a time. The metal compositions of as-synthesized $A_1$ and the starting material $A_0$ were listed in Table 1.

When the reaction conditions of the aforementioned procedure, such as nickel source, reaction temperature or ratio of reactants, were changed, a series of products could be obtained. The specific conditions were listed in Table 2. The corresponding samples were named and also listed in Table 2.

### 2.3. Physical characterization

The lattice structures of the reactant and resulted spherical core–shell $Ni(OH)_2$@CoOOH particles were examined by taking powder X-ray diffraction (XRD) patterns for the dried samples with a XRD-6000 (Cu Kα radiation, Shimadzu, Japan). Scanning electron micrographs (SEM) of the spherical particles were acquired using a JSM-6390/LV (JEOL, Japan) scanning electron microscope. The elemental composition of as-synthesized $Ni(OH)_2$@CoOOH was obtained from energy dispersive X-ray analysis (EDX) and inductively coupled plasma (ICP) measurements (Thermo., USA), respectively. The oxidation states of Ni and Co cations in the product phase were determined from X-ray photoelectron spectroscopy (XPS) (XSAM800, Kratos Ltd., UK).

### 2.4. Electrochemical characterization

Galvanostatic charge–discharge of sample $A_1$ was measured as follows: powder of sample $A_1$ was mixed with graphite powder and PTFE suspension (60% suspension) in weight ratios of 87:10:3 with a mixed solvent of water and organic one. The thoroughly mixed paste was sandwiched into two nickel foams. They were pressed at pressure of 120 kg $cm^{-2}$ at room temperature and dried at 70 °C for several hours. Galvanostatic charge–discharge tests were conducted with a battery performance-testing instrument (Land Test Equipment, CT2001A), with two pieces of negative electrodes made from commercial $AB_5$ hydrogen storage alloys as counter electrodes on either side of the working electrode, and a 6 M KOH solution as the electrolyte. All capacities are normalized to the nickel content of the active materials (estimated by ICP). All the tests were conducted at 25 ± 2 °C.

In addition, a 6 Ah prismatic power battery was assembled employed the positive electrode which consists of powder of sample $A_1$ and PTFE suspension (60% suspension) in weight ratios of 98:2. The negative electrode made from commercial $AB_5$ hydrogen storage alloys. The electrolyte is 6 M KOH solution. Galvanostatic charge–discharge tests were conducted with a battery performance-testing instrument (Arbin BT-2000). The cell resistance was measured by the dc-pulse method. All the tests were conducted at 25 ± 2 °C.

## 3. Results and discussions

Cation-exchange treatment of commercial spherical $Ni(OH)_2$ ($A_0$) by cobalt ions in the presence of $H_2O_2$ was used to modify the surface of nickel hydroxide particles (Scheme 1). After the cation-exchange treatment, the beige-colored product ($A_1$) indicating the formation of CoOOH could be obtained as shown in their photos in the inserts of Fig. 1a and d, different from the light green color of $A_0$. Here, the $H_2O_2$ behaves as the oxidant to form CoOOH. The exchange of $Ni^{2+}$ by $Co^{2+}$ proceeds difficultly in the surface layer of nickel hydroxide particles because of the nature of these two kinds of cations that ion radii of $Co^{2+}$ (74 pm) is much similar with that of $Ni^{2+}$ (72 pm) as well as their similar Ksp values [29]. Fortunately, the obtained $Co(OH)_2$ is prone to be oxidized to CoOOH in aqueous solution at the presence of oxidants which benefits the cation-exchange process.

The central metal compositions of $A_0$ and $A_1$ were analyzed by ICP-OES and EDX shown in Table 1. The molar ratio of Ni/Co (i.e. 38.2) of $A_1$ coming from EDX result (the inset of Fig. 1c) is quite close to ICP result (41.8) because of the well-proportioned distribution of cobalt ions in it. Whereas the EDX result (Ni/Co = 13.22) of cation-exchange induced $A_1$ (the inset of Fig. 1f) is obviously smaller than ICP result (Ni/Co = 17.1) of it. This means that the content of cobalt in the surface layer of the spherical particles, which is in the depth extension of EDX, is much higher than the average content of the whole particle bodies in accordance with the color

**Table 2**
Preparation conditions and relative element content for different samples.

| Sample | Cobalt source | Molar ratio of reaction solution (Ni/Co) | 30% $H_2O_2$ (mL) | Temperature (°C) | Reaction time (h) | ICP (wt.%) (Co) |
|---|---|---|---|---|---|---|
| $A_0$ | – | – | – | – | – | 1.41 |
| B | Sulphates | 9:2 | 8 | 90 | 2 | 3.56 |
| C | Chlorides | 9:2 | 8 | 90 | 2 | 3.27 |
| D | Ethanoates | 9:2 | 8 | 90 | 2 | 1.99 |
| $A_1$ | Nitrates | 9:2 | 8 | 90 | 2 | 3.32 |
| $A_2$ | Nitrates | 9:2 | 8 | 70 | 2 | 2.76 |
| $A_3$ | Nitrates | 9:2 | 8 | 50 | 2 | 2.14 |
| $A_4$ | Nitrates | 9: 0.5 | 2 | 90 | 2 | 1.99 |
| $A_5$ | Nitrates | 9:1 | 4 | 90 | 2 | 2.61 |
| $A_6$ | Nitrates | 9:3 | 12 | 90 | 2 | 4.16 |