



Flower-like nickel–cobalt binary hydroxides with high specific capacitance: Tuning the composition and asymmetric capacitor application



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ABSTRACT

Nickel and cobalt binary hydroxides with hydrotalcite-like structure were successfully synthesized by a one-step hydrothermal method without any surfactants. The contents of Ni and Co in the binary hydroxides could be easily tuned by altering the molar ratio of metal salts in the reaction solution. Five typical hydroxides were prepared with different Ni–Co molar ratios of 1:0, 7:3, 5:5, 3:7 and 0:1. Structure analysis confirmed that the hydroxides formed as 3D microflowers in shape with a good hydrotalcite-like structure. The Ni–Co binary hydroxides showed significant improvement in specific capacitance compared to unary hydroxides due to their higher interlayer spacings and improved electrical conductivity. As the content of nickel increased, the hydroxides tended to have a higher specific capacitance with a gradually deteriorative rate capability. Electrochemical data demonstrated that the binary hydroxide with Ni–Co molar ratio of 7:3 could deliver the maximum specific capacitance of 1803.6 F g^{-1} , while the binary hydroxide with Ni–Co molar ratio of 3:7 exhibited a high rate capability. An asymmetric capacitor using a typical binary hydroxide as positive material and activated carbon as negative material exhibited an excellent comprehensive performance. Our experimental results also gave a clue that the charge storage stability and rate capability of these hydroxides highly depend on their interlayer spacing.

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1. Introduction

Electrochemical capacitors (ECs), or supercapacitors, have raised extensive concerns as novel energy storage devices, due to the high power density, long cycle life and a bridging function for power energy gap between traditional dielectric capacitors and batteries [1–9]. Transition metal oxides/hydroxides and conducting polymers as the electrode materials of ECs that exhibit multiple oxidation states are capable of rich redox reactions [9–12]. Conducting polymers face the problem of mechanical degradation during cycling. Metal oxides/hydroxides have higher specific capacitance and faster redox kinetics, though they usually suffer from low specific surface area and poor electrical conductivity [9,10]. Among various transition metal oxides/hydroxides, RuO_2 has shown a promising capacitance and energy density, while it is limited by its scarcity, high cost, and toxic feature [11–13]. Consequently, considerable efforts have been devoted to developing inexpensive metal oxides and hydroxides, such as NiO [14],

Co_3O_4 [15,16], MnO_2 [17], $\text{Ni}(\text{OH})_2$ [18,19], and $\text{Co}(\text{OH})_2$ [20,21] et al. with high specific capacitance for the sustainable development of ECs.

Nickel hydroxide has gradually received increasing interest as an electrode material of ECs, due to its high theoretical specific capacitance (*ca.* 3750 F g^{-1}), low cost and environmental benignity [22,23]. It has a hexagonal layered structure with two polymorphs, *i.e.* $\alpha\text{-Ni}(\text{OH})_2$ and $\beta\text{-Ni}(\text{OH})_2$. $\alpha\text{-Ni}(\text{OH})_2$ is hydroxyl-deficient with a hydrotalcite-like structure, containing intercalated anions and water molecules in the interlayer space to restore charge neutrality [22–24]. Due to its unique structure, $\alpha\text{-Ni}(\text{OH})_2$ usually exhibits a much higher specific capacitance than β -form. However, $\text{Ni}(\text{OH})_2$ material is a p-type semiconductor with a rather low electrical conductivity ($\sim 10^{-5}$ to $10^{-9} \text{ S cm}^{-1}$) [25,26], which usually limits its performance at high charge–discharge rates and cycling stability. Thus, doping it with guest-metal atoms [27,28] or coupling it with carbon-based materials (*e.g.* carbon nanotubes and graphene) [18,29] has been widely studied.

Previous reports demonstrated that binary or ternary nickel-based hydroxide composites could exhibit enhanced performance and distinct advantages over single metal system [9,11,13]. For

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instance, binary Ni–Co hydroxides can yield much higher specific capacitance than monometallic hydroxides. $\text{Co}(\text{OH})_2$ has a high electrochemical activity and similar structure to $\text{Ni}(\text{OH})_2$. Substitution of cobalt into nickel hydroxide may increase the conductivity of binary Ni–Co hydroxides, because the highly conductive CoOOH can serve as a good conductor during the charge–discharge process [9,23]. The addition of Co atom can also raise the oxygen overpotential and reduce the mechanical stress during charge–discharge process, thus preventing electrode degradation as well as increasing the charge density [18,30]. Though some other binary metal hydroxides such as Ni–Mg [31], Mn–Sn [32], and Ni–Mn [33] systems have been reported to show effective capability to improve electrochemical performance, Ni–Co hydroxides have attracted general interest, because of their facile synthesis, low-cost, and excellent performance.

There are several methods reported to synthesize α -phase Ni–Co binary hydroxides, such as chemical bath deposition [10], hydrothermal method [24], co-precipitation [25], electrodeposition [34], and high-temperature vapor-phase approaches [35]. Electrodeposition suffers from small area of deposition, extreme cleaning after deposition, and high cost, while vapor-phase approaches are expensive and energy-consuming. Thus, chemical solution methods are considered to be more suitable for scalable application and industrialization. For those solution methods concerning surfactants or organic solvent, removal of the surfactant from the resultant hydroxide is difficult and time-consuming, and needs extra process. Surfactant-free hydrothermal synthetic strategy in a pure water system is considered as a simpler and more robust choice then. In addition, it may have a fast reaction speed, low reaction temperature, and fairly high yield and efficiency.

In this work, we successfully synthesized three dimensional (3D) flowerlike Ni–Co binary hydroxides by a facile surfactant-free hydrothermal method in a 2-h reaction. The as-prepared hydroxides had a fairly large interlayer spacing of 9.22 Å with a hydrotalcite-like structure. By simply tuning the Ni–Co molar ratio in the precursor solution, their composition and electrochemical performance were changed accordingly. The specific capacitance and cycling stability of binary hydroxides were apparently enhanced as compared to those of unary systems. The specific capacitance and rate capability were closely related to the composition of the binary hydroxides. We also used a typical binary hydroxide as a positive electrode with activated carbon as a negative electrode to fabricate an asymmetry hybrid capacitor. The hybrid capacitor could work in a wide voltage range (1.75 V) and have a high energy density as well as excellent cycling stability.

2. Experimental

2.1. Materials and preparation

All chemicals including $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and hexamethylenetetramine (HMT) used in our experiments were of analytical grade and used as received without further purification.

0.01 mol metal nitrates, such as $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ or their mixture, and 0.015 mol HMT were dissolved into 32 mL deionized water by stirring at room temperature. The solution was transferred into a 100 mL Teflon-lined autoclave, which was sealed and placed into an oven. After maintaining at 120 °C for 2 h reaction, it was cooled down to room temperature. Subsequently, the green solid was filtered, washed thoroughly with distilled water and ethanol to remove the residual ions, and finally dried in vacuum at 80 °C for 5 h.

The total amount of metal salts and HMT were fixed in each batch. We only adjusted the molar ratio of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and

$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in the mixed solution. The molar ratios of nickel and cobalt were changed to be 1:0 (α - $\text{Ni}(\text{OH})_2$), 7:3 (Co_3Ni_7), 5:5 (Co_5Ni_5), 3:7 (Co_7Ni_3) and 0:1 (α - $\text{Co}(\text{OH})_2$).

2.2. Characterization

The crystal structures and phase composition of the synthesized hydroxides were characterized using X-ray diffractometer (Shimadzu, XRD-6000) with Cu $K\alpha$ irradiation (40 kV, 40 mA, $\lambda = 1.5406 \text{ \AA}$). The morphology and microstructure of the hydroxide samples were characterized by a scanning electron microscope (SEM, Hitachi, S-4800) and a transmission electron microscope (TEM, Phillips CM200) operated at 160 kV. The chemical compositions of the samples were also analyzed by energy dispersive spectroscopy (EDS). Fourier transform infrared (FTIR) spectra were measured for a KBr diluted sample by a Bruker spectrometer (TENSOR 27). Thermogravimetric (TG) analysis was carried out using a TA Q600 instrument with 100 mL min^{-1} of air flow in a temperature range from 25 to 600 °C with a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$.

2.3. Electrochemical measurements

The working electrode was prepared by mixing active material, acetylene black and polyvinylidene fluoride (PVDF) with a weight ratio of 80:10:10 in N-methyl-2-pyrrolidone and then coating the homogeneous mixture onto a Ni foam substrate (1.5 cm \times 1.5 cm). The Ni foam supported electrode was completely dried at 80 °C for 5 h in vacuum and then pressed at 10 MPa before each test so as to assure a good electronic contact between Ni foam and the active material. Each working electrode contained about 6 mg of electroactive material. The electrochemical measurements were conducted under a conventional three-electrode system in a 2 mol L^{-1} KOH aqueous solution as electrolyte. The platinum foil and Ag/AgCl electrode served as the counter electrode and reference electrode, respectively. Cyclic voltammograms (CV), galvanostatic charge–discharge and electrochemical impedance spectroscopy (EIS) were measured on a CHI660D electrochemical workstation. The cycling stability was characterized by a LAND CT2001A test system by galvanostatic charge–discharge techniques.

The specific capacitance of the electrode can be evaluated on the basis of their galvanostatic discharge curves by the following equation [1,25]:

$$C = I \cdot \Delta t / (m \cdot \Delta V), \quad (1)$$

where C (F g^{-1}) is the specific capacitance of the electrode based on the mass of active material, I (A) is the discharge current, Δt (s) is the discharge time, ΔV (V) is the potential window, and m (g) is the mass of active material within the working electrode.

An asymmetric capacitor was fabricated using a hydroxide (sample Co_7Ni_3) electrode as a positive electrode and activated carbon (AC) as a negative electrode. The mass of these two electrodes was balanced to ensure efficient charge storage by the equation of $Q_+ = Q_-$, where Q_+ and Q_- are the storage charges of the positive and negative electrodes, respectively. The charge can be calculated by [36]:

$$Q = C \cdot m \cdot \Delta V, \quad (2)$$

where C , m , ΔV represent the same as the above mentioned. In consequence, the mass ratio between AC and sample Co_7Ni_3 should be $m_{\text{AC}}/m_{\text{Co}_7\text{Ni}_3} = 3.9$. Asymmetric capacitor was tested using CV and galvanostatic charge–discharge techniques at different current densities. The energy density (E) and power density (P) of the hybrid capacitor could be then calculated according to the following equations [36,37]:

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