Amorphous Ni–Co binary hydroxide with super-long cycle life and ultrahigh rate capability as asymmetric supercapacitors

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Abstract

Ni–Co binary hydroxide (Ni_{x}Co_{1-x}(OH)_2) with nanostructure is prepared by one-step electrochemical deposition process with de-ionized water as electrolyte. The molar ratio of Ni/Co for Ni_{x}Co_{1-x}(OH)_2 can be accurately controlled via changing the composition of the alloy target. A series of typical hydroxides are synthesized with Ni/Co molar ratios of 1:2, 1:3, 1:4, 1:6, 6:1, 4:1, 3:1, 2:1 and 1:1. The electrochemical performances of Ni_{x}Co_{1-x}(OH)_2 exhibit remarkable improvement in rate capability and cycling stability compared to monometallic hydroxide. Electrochemical test results reveal that Ni_{4/5}Co_{1/5}(OH)_2 delivers the maximum specific capacitance of 2425 F g^{-1}, while Ni_{0.5}Co_{0.5}(OH)_2 exhibits ultrahigh rate capability (a 14% capacity decrease after a 100-fold increase in scan rate and 7% capacity decrease after a 40-fold increase in current density) and super-long cycle life (no capacitance loss after 50 000 cycles). Especially, the Ni_{0.5}Co_{0.5}(OH)_2/AC supercapacitor exhibits a super-long cycle life with a 2% capacitance loss after 100 000 cycles, which is quite better than that of crystalline devices.

Supplementary material for this article is available online

Keywords: amorphous, Co–Ni hydroxide, super-long cycle life, ultra-high rate capability

(Some figures may appear in colour only in the online journal)

1. Introduction

With notable advantages of rapid energy storage/release, high power density and long cycle life, supercapacitors (SCs) exhibit great potential in energy consumption fields such as hybrid electric vehicle, consumer electronic, portable device, etc. Electrical double-layer capacitors (EDLCs) and pseudo-capacitors as two typical types of SCs are currently being extensively studied [1, 2]. The conventional EDLCs such as carbon-based EDLCs, are dominated by reversible charge adsorption/desorption on the electrode surface. However, pseudo-capacitors governed by reversible Faradaic reactions, can provide remarkably better charge storage and release capacity than EDLCs [3, 4]. The SCs have drawn a large number of researchers to develop and design new active pseudo-capacitors materials with high specific capacitance. Conductive polymer [5], metal oxide [6], hydroxide [7] and sulfide [8] are currently being widely studied as pseudo-capacitive electrode materials for SCs, especially transitional metal oxide/hydroxide for their low-cost, abundance in Earth, facile fabrication, flexible nanostructures and environmental benignity [9].

Among them, nickel and cobalt hydroxide/oxide based active materials have been gradually considered as promising...
candidates of pseudo-capacitive materials for SCs [9–13]. But, with high specific capacitance, the single transitional metal based materials would usually be afflicted with poor rate capability and cycle life because of their bad conductivity, which limits their widely used in practice. For the sake of outstanding electrochemical behavior materials, binary or ternary metal hydroxide/oxide hybrids are introduced as novel type active materials for SCs. Based on better electrical conductivity and richer efficient redox reactions resulting from synergistic effect of Faradaic reactions with Co and Ni, Co-Ni based composites are extensively investigated for their enhanced electrochemical capacitance behavior over the single metal compounds [14–18]. Recently, a major expenditure of time and energy are put into the synthesis and modification of various bimetallic Ni–Co hydroxide hybrids as potential electrode materials because of high theoretical specific capacitances of nickel hydroxide (3750 F g⁻¹ [14]) and cobalt hydroxide (3560 F g⁻¹ [15]) as well as the similar structures. What’s more, highly conductive CoOOH formed from Co(OH)₂ during charging–discharging process not only make the rate capability of bimetallic Ni–Co hydroxide enhancement by furnishing a faster access to charge for intercalating and deintercalating, but also enhance the stability and charge density by reducing the mechanical stress and raising the oxygen overpotential during cycling process [14]. For example, the study of Chen and co-workers showed that Ni–Co LHD performed significantly enhanced specific capacitance with 2682 F g⁻¹ and rate behavior with 63.6% capacity retention at 20 A g⁻¹ [17]. Yan and co-workers successfully fabricated Ni-Co LHD hollow microspheres which displayed excellent electrochemical performances for SCs with specific capacitance of 2158.7 F g⁻¹, rate behavior of 75.8% retained after the current density increased by 40 times and long cycle life of 97.5% retention after 1500 cycles [18].

It is mentionable that almost all of the Ni–Co hydroxides prepared by previous reports are crystalline phase and rare attention is focus on amorphous phase [14–22]. Nevertheless, the amorphous materials offer a quite special electrochemical nature for their high structural disorder and abundant structural defects. Previous studies reveal that the comprehensive electrochemical performances of amorphous Ni(OH)₂ and Co(OH)₂ are equivalent to that of crystalline ones in SCs [12, 13]. The disorder nature can relax the electrostatic force generated by the charge of charge and release it, which is beneficial to long-term electrochemical stability. Thus, in view of the advantages of amorphous state in SCs, we put a good deal of concentration in synthesis and electrochemical characteristics of amorphous Ni–Co hydroxides. Here, a series of amorphous NiₓCo₁₋ₓ(OH)₂ with various Ni, Co content are prepared by electrochemical cathode deposition technique. Influence of Ni/Co content on the electrochemical capacitive performances is studied. The novel of this work is the synthesis of amorphous electrode materials with super-long cycle life and ultrahigh rate capability by a simple method. The as-synthesized NiₓCo₀.₅(OH)₂ exhibits a superior performance as positive SC electrode than the other candidates (Co/Ni = 1:2, 1:3, 1:4, 1:6, 6:1, 4:1, 3:1, 2:1), especially displaying a high rate capability (a 14% capacity decrease after a 100-fold increase in scan rate and 93% retained after the current density increased by 40 times) and a super long-term cycling stability (98% retention after 100,000 cycles). The experimental results through the research of NiₓCo₀.₅(OH)₂ electrode demonstrates the broad applicability of amorphous material in the development of new electrode supercapacitor materials with long life and fast charging.

2. Experiments

2.1. Synthesis of materials

An idiographic electrochemical cathode deposition technique reported in our previous work is used to synthesize various amorphous NiₓCo₁₋ₓ(OH)₂ with different Ni/Co molar ratios on the graphite substrate in one step [13]. Briefly, the electrochemical deposition reaction performed in constant potential mode is carried out in a quartz chamber filled with high-purity de-ionized water, a Co–Ni alloy target and two parallel graphite electrodes. The products with amorphous nature prepared in this work are grown on the cathodic graphite substrate directly under an operating potential of 90 V for 10 h. Co–Ni alloy target and molar ratios of 1:2, 1:3, 1:4, 1:6, 1:1, 6:1, 4:1, 3:1, 2:1 is used to prepare diverse Co, Ni content of amorphous NiₓCo₁₋ₓ(OH)₂.

2.2. Characterizations

The morphology and structural characteristics of amorphous Ni–Co hydroxides are characterized by field-emission scanning electron microscopy (SEM) (JSM-7600F SEM), transmission electron microscopy (TEM) (FEI Tecnai G2 F30, 300 KV). The surface chemical state and chemical composition are studied by Raman spectroscopy (Renishaw inVia), X-ray photoelectron spectroscopy (XPS) (ESCALab250) and inductively coupled plasma-atomic emission spectrometry (ICP) (OPTIMAL4300DV).

2.3. Electrochemical measurements

The electrochemical performances of amorphous Ni–Co hydroxides electrodes are investigated by cyclic voltammetry (CV) and chronopotentiometry (CP) techniques using a CHI-760E electrochemical workstation. The electrochemical tests are accomplished via a typical three-electrode cell: working electrode of amorphous Co–Ni hydroxide/graphite, reference electrode of Hg/HgO, counter electrode of Pt, electrolyte of 2 M KOH solution. The electrochemical performances of the amorphous NiₓCo₁₋ₓ(OH)₂/active carbon (AC) asymmetric capacitor (ASC) are investigated via a two-electrode electrochemical cell: NiₓCo₁₋ₓ(OH)₂/graphite for working electrode and AC/graphite for counter electrode. The procedures of preparing the AC/graphite are described by following: Firstly, mix together AC (80 wt%), carbon black (10 wt%) and PVDF (10 wt%) to make a blend. Secondly, disperse the above mixture in N-methyl pyrrolidone to make a turbid liquid, and uniformly load it on the graphite substrate. Finally, the AC/graphite electrode is dried for 24 h.
3. Results and discussion

3.1. Synthesis and characterization

A series of amorphous Ni$_{x}$Co$_{1-x}$(OH)$_{2}$ with various proportion of Ni/Co on graphite substrate are synthesized successfully by electrochemical cathode deposition process. The detail formation process of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ is shown in supporting information S1. To illustrate the morphology of as-prepared Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$, SEM images of products are measured (supporting information S2–(3)). It can be seen clearly that the morphology of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ changes along with the Ni/Co molar ratio changing. The x values of Ni$_{0.5}$Co$_{1-x}$(OH)$_{2}$ are measured by ICP analysis. The metal contents of all the contents are listed in table S1 in the supplementary information. It can be found that by using Co–Ni alloy targets with molar ratio of 1:2, 1:3, 1:4, 1:6, 6:1, 4:1, 3:1, 2:1 and 1:1 as metal sources, the Ni$_{0.5}$Co$_{1-x}$(OH)$_{2}$ with Co/Ni molar ratios of about 1:2, 1:3, 1:4, 1:6, 6:1, 4:1, 3:1, 2:1 and 1:1 are synthesized respectively. This result suggest that the composition of Ni$_{0.5}$Co$_{1-x}$(OH)$_{2}$ can be regulated by changing the proportion of cobalt to nickel in the alloy target. Based on electrochemical test result, Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ is further characterized and discussed by following.

Figures 1(a)–(b) list the SEM images of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ electrode with flower-like nanostructure, whose diameter is mainly about 200 nm. The flower-like surface is conducive to the increase of electroactive site and reaction area, thus improving the electrochemical property. The detailed morphology and structure are further characterized by TEM images in figures 1(c)–(d). As shown in figure 1(d), we could not found obvious lattice fringe, but a wide and diffuse halo can be found in the selected area electron diffraction pattern (inset in figure 1(d)), suggesting an amorphous nature of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$. The element distribution of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ is characterized by the element mapping images (figures 1(f)–(h)), which exhibits an extraordinarily uniform distribution of O, Co and Ni. These results reveal that an amorphous phase of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ with well-homogeneous nanostructure is synthesized in this work. Furthermore, XRD pattern is detected as shown in figure S4(a). No other peaks appear except the diffraction peaks from graphite, confirming an amorphous feature of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$. At the same time, XRD patterns of all samples are shown in figure S4(b). We find that the XRD patterns of all samples are similar to that of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$. The result confirms that all samples of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ electrodes are amorphous.

XPS spectra of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$, a reliable technique for analyzing the elemental composition and chemical valence, are illustrated in figures 2(a)–(c). Figure 2(a) performs a typical spectrum of O 1s with a major peak at 531.1 eV, which can be attributed to OH$^-$ groups. Using Gaussian fitting to fit the high-resolution Ni 2p spectrum, figure 2(b) performs two strong spin–orbit doublets peaks at 856.3 and 873.9 eV with corresponding shake-up satellite peaks at 862.2 and 880.1 eV, respectively, which are generally associated with Ni$^{2+}$. Furthermore, the spectrum shape and spin-energy separation of 17.6 eV are completely consistent with the characteristics of Ni(OH)$_{2}$ reported in the literature [23]. The XPS spectrum of Co 2p (figure 2(c)), analyzed by the same analysis method, exhibits the peak of Co 2p$_{3/2}$ at 797.1 eV and Co 2p$_{1/2}$ at 781.5 eV, suggesting the Co$^{2+}$ in the prepared product [23].

The surface chemical composition information of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ has been further analyzed by Raman spectroscopy (figure 2(d)). Five peaks at 188, 252, 467, 516 and 657 cm$^{-1}$ appear in the spectrum. Concretely, the peaks of 467, and 516 cm$^{-1}$ represent the Ni(OH)$_{2}$ formation, while the peaks of 188, 252, 467, 516 and 657 cm$^{-1}$ represent Co(OH)$_{2}$ formation [24, 25]. The peaks with broadened and shifted at 467 and 516 cm$^{-1}$, may be generated by the symmetric stretching modes of M–OH (M=Ni, Co) and O–M–O (M=Ni, Co), respectively. The peaks at 188, 252, and 657 cm$^{-1}$ can be generated by $E_g$ and $A_{1g}$ modes of Co(OH)$_{2}$. In a word, the amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ with flower-like nanostructure is fabricated in this work.

3.2. Electrochemical behavior of amorphous Ni$_{x}$Co$_{1-x}$(OH)$_{2}$

To investigate the electrochemical behavior of Ni$_{0.5}$Co$_{1-x}$(OH)$_{2}$ electrode, we first carry out a series of electrochemical measurements by using CV and CP techniques. CV curves of Ni$_{0.5}$Co$_{1-x}$(OH)$_{2}$ in various values of x have obtained (supporting information S5). The characterization results reveal that optimum atomic ratio of cobalt to nickel for binary hydroxide as pseudocapacitive electrode materials is 1:1.

Figure 3(a) illustrates a series typical CV curves of amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ electrode at various scan rates in a potential range of 0.05–0.55 V. The Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ electrode displays typical pseudocapacitive behavior rather than an EDLC one for the appearance of redox peaks in CV curves, which stand for pseudocapacitive characteristic. For Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ electrode, the strong Faradaic redox peaks is caused by the following Faradaic reactions on the surface of active electrode:

\[
\begin{align*}
\text{Ni(OH)}_2 + \text{OH}^- & \leftrightarrow \text{NiOOH} + \text{H}_2\text{O} + e^- \quad (1) \\
\text{Co(OH)}_2 + \text{OH}^- & \leftrightarrow \text{CoOOH} + \text{H}_2\text{O} + e^- \quad (2) \\
\text{CoOOH} + \text{OH}^- & \leftrightarrow \text{Co}_2\text{O}_2 + \text{H}_2\text{O} + e^- \quad (3)
\end{align*}
\]

It can be easily found that when the scanning rate is increased from 1 to 100 mV s$^{-1}$, the redox peaks shift slightly and the shape are almost unchanged, revealing outstanding conductivity and reaction reversibility on the surface of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$.

As the specific capacitance C (F g$^{-1}$) is a critical factor to characterize the electrochemical behavior of capacitor, we first evaluate the specific capacitance of Ni$_{0.5}$Co$_{0.5}$(OH)$_{2}$ according to CV curves applying the formula of

\[
C = \frac{1}{m \cdot \Delta V} \int_{V_1}^{V_2} I(V) \text{d}V
\]

Here, m represents mass of electroactive material (g), $\Delta V$ represents scan rate (V s$^{-1}$), I(V) represents current density (A), dV represents potential differential (V), V$_1$ and V$_2$ represent starting and ending potential (V), respectively. The calculations of the specific capacitances
of Ni$_{0.5}$Co$_{0.5}$\,(OH)$_2$ under different scan rates in three-electrode system are presented in figure 3(d). Clearly, the $C$ values display a gradual decrease with the scan rate increase. This phenomenon is mainly caused by the diffusion effect, which makes electrolytic ions cannot transfer rapidly at high scanning rate. In detail, the Ni$_{0.5}$Co$_{0.5}$\,(OH)$_2$ delivers high specific capacitances of 1136, 1123, 1097, 1078, 1054, 1040, 1028, 1019, 1011, 1003, 996, 989 and 985 F g$^{-1}$ at scan rates of 1, 2, 5, 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 mV s$^{-1}$, respectively. Interestingly, when the scan rates increase from 1 to 100 mV s$^{-1}$, the values of $C$ decrease from 1136 to 985 F g$^{-1}$. Only 13% loss implies excellent capacitive property and outstanding high rate-capability of Ni$_{0.5}$Co$_{0.5}$\,(OH)$_2$ electrode. Furthermore, to study the electrochemical behavior of graphite substrate, CV curves of pure graphite substrate without deposition of Ni$_{0.5}$Co$_{0.5}$\,(OH)$_2$ active materials are tested under homologous conditions as shown in figure S6. These curves exhibit a typical rectangular shape and the integrated CV area...
are far less than that of Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub>, implying that contribution of blank graphite electrode to the total capacity can be neglected.

Study on electrochemical charging and discharging behavior of Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> is carried out by CP technique. Charging–discharging curves described in figure 3(c) perform nearly symmetrical and nonlinear, that further implies its pseudo-capacitive behavior. According to equation of \[ C = \frac{\Delta t \cdot m}{I \cdot \Delta V} \] the specific capacitance \( C \) can be calculated on the basis of discharge time. Where, \( I \), \( \Delta t \), \( m \) and \( \Delta V \) represent the current (A), time (s), mass (g) and potential range (V) during discharging process, respectively. Figure 3(d) shows the \( C \) value of Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> electrode as a function of current density. Clearly, the specific capacitance decreases by degrees with current density increase. With an increasing current density in the range of 1 to 40 A g<sup>−1</sup>, the specific capacitance decreases from 1014.8 to 944 F g<sup>−1</sup>. Only 7% loss after the current density increase by 40 times confirms outstanding high-rate capability of the sample. The Ni-rich provide high specific capacitance and the Co-rich ensure high rate performance because of high electronic conductivity of Co(OH)<sub>2</sub>. The highly conductive CoOOH formed from Co(OH)<sub>2</sub> during charging–discharging process can make the rate capability of bimetallic Ni–Co hydroxide enhancement by furnishing a faster access to charge for intercalating and deintercalating. The synergistic effect of nickel and cobalt make Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> electrode has a remarkable high-rate capability, which leads to a small capacitance loss at high current density. Table 1 contrasts the rate capability of Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> with that of reported in the literature, which testifies to the high-rate capability of Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub>. Electrochemical impedance spectroscopy (EIS) of Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> is measured in a frequency range of 0.1 to 10<sup>6</sup> Hz to detect the interface resistance of the electrode as shown in figure 3(e). The plot is composed of two parts: one part is a small semi-circle in high frequency region, which is attributed to the charge transfer resistance in Faraday reaction; the other part is a diagonal line in the low frequency region, which is related to the ion diffusion resistance. The charge transfer resistance is estimated to be 1.4 Ω through the diameter of the semi-circle, indicating that the small resistance of charge transfer for Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub>.

Cycling stability, a critical factor for high-performance SCs in practical applications, is measured using the CP technique. Figure 3(f) displays the cycling measurement of amorphous Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> electrode at a current density of 25 A g<sup>−1</sup> for 50 000 cycles. The Ni<sub>0.5</sub>Co<sub>0.5</sub>(OH)<sub>2</sub> performed an unexpected long-term cycle life with 110% capacity
retention after 50,000 cycles. Comparisons between amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ and the other reported Ni-Co based electrode on the cycling stability, rate capability and specific capacitance are listed in table 1. Notably, the capacitive behavior of the amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ prepared in this work is better than most Ni-Co based electrode materials. Especially, the ultrahigh rate capability and super-long cycle life of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ nanospheres are the best among of reported Ni-Co based electrode materials in the literature, which provides a very bright future for industrial use.

Further investigation on the electrochemical behavior of Ni$_x$Co$_{1-x}$(OH)$_2$ electrode is illustrated in figure 4. The electrochemical properties of Ni$_x$Co$_{1-x}$(OH)$_2$ electrodes with different Co/Ni ratios are compared in table 2. CV curves of Ni$_x$Co$_{1-x}$(OH)$_2$ with various Ni/Co atomic ratios at a scan rate of 10 mV s$^{-1}$ in 2 M KOH are displayed in figure 4(a) for the purpose of comparison. Each Ni$_x$Co$_{1-x}$(OH)$_2$ electrode exhibits a typical pseudocapacitive behavior rather than an electrical EDLC one for redox peaks clearly appear in each curve with a pseudocapacitive characteristic. These redox peaks are due to the reversible redox reaction illustrated by equations (1), (2) and (3). Figure S5 in the supporting information illustrates a series typical CV curves of Ni$_x$Co$_{1-x}$(OH)$_2$ electrode under different scan rates. Clearly,
Table 1. Comparison of the electrochemical performance of amorphous Co–Ni hydroxide with other reported Ni–Co based hydroxides.

| Electrode                                      | Specific capacitance (F g\(^{-1}\)) | Rate capability                      | Cycling stability (capacitance retention) | References |
|------------------------------------------------|--------------------------------------|--------------------------------------|-------------------------------------------|------------|
| Flower-like Co\(_7\)Ni\(_3\) binary hydroxides | 1403.6 at current density of 1 A g\(^{-1}\) | 61.9% after a 10-fold increase       | 73.8% after 3 000 cycles                  | 14         |
| 3D concentration gradient Ni–Co hydroxide nanostructures | 1760 at current density of 1 A g\(^{-1}\) | 62.5% after a 100-fold increase      | 87.3% after 20 000 cycles                 | 15         |
| Ni–Co hydroxide nanoflakes                      | 1151 at current density of 1 A g\(^{-1}\) | 61% after a 70-fold increase         | 77% after 10 000 cycles                   | 17         |
| Ni–Co layered double hydroxide linked by carbon nanotubes | 1628 at current density of 1 A g\(^{-1}\) | 45% after a 10-fold increase         | 75.1% after 5 000 cycles                  | 19         |
| Hierarchical Ni/Co-Layered Double Hydroxide Microspheres | 1652 at current density of 1 A g\(^{-1}\) | 78.7% after a 10-fold increase       | 99.4% after 2 000 cycles                  | 20         |
| Nickel cobalt bimetallic metal-organic frameworks | 1333 at current density of 2 A g\(^{-1}\) | 78.7% after a 10-fold increase       | 79% after 2 000 cycles                    | 21         |
| Amorphous Ni\(_{0.5}\)Co\(_{0.5}\)(OH)\(_2\) nanospheres | 1136 at scan rate of 1 mV s\(^{-1}\)  | 87% after a 100-fold increase        | 110% after 50 000 cycles                  | this work  |
|                                                | 1014.8 at current density of 1 A g\(^{-1}\) |                                  |                                            | this work  |
| Amorphous Ni\(_{4/5}\)Co\(_{1/5}\)(OH)\(_2\) nanospheres | 2425 at scan rate of 1 mV s\(^{-1}\)  | 55.6% after a 100-fold increase      | 70% after 50 000 cycles                   | this work  |
|                                                | 1820 at current density of 10 A g\(^{-1}\) |                                  |                                            | this work  |
all the CV curves are almost unchanged in shape as scan rate increases from 1 to 100 mV s⁻¹. Ni₀.₅Co₀.₅(OH)₂ performed a minimal anodic/cathodic peaks shift of +0.070 V/-0.058 V compared with that of other NiₓCo₁₋ₓ(OH)₂ electrode. These results reveal that the Ni₀.₅Co₀.₅(OH)₂ electrode performs the superior electron conductivity, fastest conversion rate of Co²⁺/Co³⁺/Co⁴⁺ and Ni²⁺/Ni³⁺, best redox reaction reversibility among these NiₓCo₁₋ₓ(OH)₂ materials. Additionally, the specific capacitance of all electrodes with different Ni/Co ratios and the capacity retention as a function of scan rate are further summarized in figures 4(b) and (c), respectively. In detail, the Ni₁.₅Co₁.₅(OH)₂ electrode exhibits a maximum specific capacitance of 2425 F g⁻¹ at scan rate of 1 mV s⁻¹. However, the specific capacitance drops sharply to 1348 F g⁻¹ as the scan rate increasing to 100 mV s⁻¹, the capacitance retention is only 55.6% compared with the initial capacitance. This value is much lower than that of Ni₀.₅Co₀.₅(OH)₂ (87%). This phenomenon may be owing to Ni enrichment which can make Ni₁.₅Co₁.₅(OH)₂ electrode suffer from inferior electronic conductivity, resulting in the

Figure 4. Electrochemical behaviors of NiₓCo₁₋ₓ(OH)₂ in 2 M KOH. (a) CV curves of NiₓCo₁₋ₓ(OH)₂ with different Co/Ni ratios at a scan rate of 10 mV s⁻¹. (b), (c) Corresponding specific capacitance and retention as a function of scan rates for NiₓCo₁₋ₓ(OH)₂. (d) Cycle performances of all products.

| Ratio of Co/Ni | Specific capacitance (F g⁻¹) | Capacitance retention after a 100-fold increase in scan rates | Cycling stability (capacitance retention after 20 000 cycles) |
|---------------|------------------------------|------------------------------------------------------------|-------------------------------------------------------------|
|               | 1 mV s⁻¹ | 100 mV s⁻¹ |                                      |                               |                       |
| 1:6           | 1187    | 687       | 57.8%                                  | 72.7%                       |
| 1:4           | 2425    | 1348      | 55.6%                                  | 68.0%                       |
| 1:3           | 1240    | 603       | 48.7%                                  | 75.5%                       |
| 1:2           | 1509    | 692       | 45.8%                                  | 86.4%                       |
| 1:1           | 1059    | 914       | 86.4%                                  | 116.3%                      |
| 2:1           | 936     | 356       | 38.0%                                  | 79.9                        |
| 3:1           | 490     | 296       | 60.5%                                  | 84.6                        |
| 4:1           | 276     | 58        | 21.0%                                  | 80.0                        |
| 6:1           | 67      | 34        | 50.4                                   | 96.5                        |
charge cannot be transferred timely and fully at high scan rate. Additionally, the Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ electrode exhibits a best rate capability as shown in figure 4(c). Above calculation results suggest that the amorphous nanostructured Ni$_x$Co$_{1-x}$(OH)$_2$ electrode with Ni/Co ratio of 1:1 can more effectively support fast and reversible Faradaic reaction under high scan rate conditions compared with that of other Ni/Co ratios. Thus can result in drastically improved rate capability of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ electrode. Furthermore, all Ni$_x$Co$_{1-x}$(OH)$_2$ electrodes exhibit unexpected cycling capabilities as shown in figure 4(d), the specific capacitance remnants of all samples are almost more than 70% after 20 000 cycles of charge/discharge. Table 1 contrasts the rate capability of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ with other Ni/Co-based electrodes reported in the literature. Obviously, the cycling stability performances of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ are superior to most Ni/Co-based electrode materials reported in the literature. Based on above analysis, the amorphous multi-metal composites are beneficial to improvement of cycling stability. Especially, Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ shows remarkable long-term stability with a 110% capacitance retention after 50 000 cycles.

In summary, optimum atomic ratio of cobalt to nickel of binary hydroxide Ni$_x$Co$_{1-x}$(OH)$_2$ as pseudocapacitive electrode materials is 1:1, owing to best comprehensive electrochemical behavior of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ with a good...
combination between the high specific capacitance, splendid high-rate capability and super-long cycling stability.

3.3. Electrochemical behavior of ASC

To thoroughly examine the actual performance of the amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ based ASC with other reported Ni–Co hydroxide based ASCs.

Table 3. Comparison of the electrochemical performance of amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ based ASC with other reported Ni–Co hydroxide based ASCs.

| Electrode | Specific capacitance ($F \cdot g^{-1}$) | Cycling stability (capacitance retention) | References |
|-----------|---------------------------------------|------------------------------------------|------------|
| 3D concentration gradient Ni–Co hydroxide nanostructures | 332 | 97.3% after 20 000 cycles | 15 |
| Ni–Co layered double hydroxide linked by carbon nanotubes | 167 | 99.4% after 10 000 cycles | 19 |
| Hierarchical Ni/Co-Layered Double Hydroxide Microspheres | 106.2 | 83.5% after 10 000 cycles | 20 |
| Nickel cobalt bimetallic metal-organic frameworks | 97 | 83% after 2000 cycles | 21 |
| Hexagonal plate-like Ni–Co–Mn hydroxide | 136 | 78.8% after 5000 cycles | 22 |
| Amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ nanospheres | 198 | 103% after 90 000 cycles | this work |

When the power density is 2.59 kW kg$^{-1}$, the E value of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC achieves as high as 39.3 W h kg$^{-1}$. The cycle stability, another significant factor in the actual applications for the ASCs, is measured by CP method. Figure 5(f) performs the cycling performance of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC tested at a current density of 12 A g$^{-1}$ for 100 000 cycles. Notably, after the capacitor device undergoes 100 000 cycles, the total capacitance is lost only by 2%, suggesting a super-long-term cycling lifespan of ASC. Table 3 lists the comparisons of the electrochemical performances among amorphous Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC and the other reported Ni–Co-based electrode ASCs on the capacitance and cycling stability. Clearly, the capacitive performance of the Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC prepared in this work is better than that of most Ni–Co-based ASCs. Especially, cycling stability of the Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC ASCs in this work is the best among all of nickel/cobalt-based ASCs. The super-long cycle life of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC ASC is mainly attributed to the outstanding cycle stability of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ electrode, which can retain a 110% capacitance after 50 000 cycles in a three-electrode system.

4. Conclusions

In summarize, a series of bimetallic Co–Ni hydroxides with various Ni/Co atomic ratios are one step synthesized by an electrochemical deposition route. Influence of Ni/Co atomic ratios on the electrochemical capacitive performances is systematically studied. Due to the synergetic effect of Co and Ni as well as the advantages of the amorphous phase structure and morphology, the Ni$_{0.4}$Co$_{0.6}$(OH)$_2$ exhibit significant improvement in rate capability and cycling stability. The characterization results suggest that the optimum atomic ratio of cobalt to nickel for binary hydroxide as pseudocapacitive electrode materials is 1:1. The Ni$_{0.5}$Co$_{0.5}$(OH)$_2$ exhibits ultrahigh rate capability (a 14% capacity decrease after a 100-fold increase in scan rate and 7% capacity decrease after a 40-fold increase in current density) and super-long cycle life (no capacitance loss after 50 000 cycles). Especially, the fabricated Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC ASC performs an excellent electrochemical capacitive behavior, which is quite better than
that of other mixed-metal hydroxide-based devices reported by previous works. Particularly, a super-long cycle life of Ni$_{0.5}$Co$_{0.5}$(OH)$_2$/AC ASC with a 2% capacitance loss after 100 000 cycles, far surpasses that of crystalline devices. This study demonstrates the potential of amorphous bimetallic Ni$_i$Co$_{1-x}$(OH)$_2$ in energy storage applications.

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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