



Superior capacitive performances of binary nickel–cobalt hydroxide nanonetwork prepared by cathodic deposition



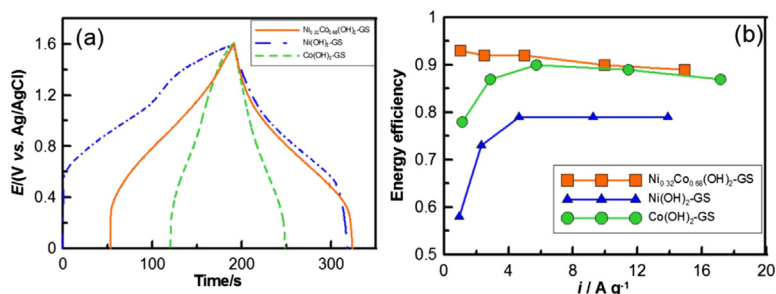
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HIGHLIGHTS

- $\text{Ni}_{0.32}\text{Co}_{0.68}(\text{OH})_2$ shows C_S of 1000 F g^{-1} , 100% C_S cycle-retention, and 69% C_S rate-retention at 500 mV s^{-1} .
- $\text{Ni}_{0.32}\text{Co}_{0.68}(\text{OH})_2$ is desired for the asymmetric design with 90% energy efficiency at 10 A g^{-1} .
- Small current densities facilitate the formation of porous nanonetwork microstructures.
- pH and deposition temperature affect the Co/Ni ratio and capacitive performances of $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$.

GRAPHICAL ABSTRACT



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ABSTRACT

Binary nickel–cobalt hydroxides (denoted as $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$) with advanced capacitive performances, such as the superior rate capability, energy efficiency, and capacitance rate-/cycle-retention, are synthesized by cathodic deposition. The effects of deposition variables are systematically investigated and discussed. The deposition current density has been found to determine the morphology of hydroxides whereby a small current density facilitates the formation of porous nanonetwork microstructures. Both pH and temperature of the precursor solution affect the Co/Ni ratio of hydroxides, which in turn influence the capacitive performances. Eventually, $\text{Ni}_{0.32}\text{Co}_{0.68}(\text{OH})_2$ synthesized under our proposed deposition condition exhibits a specific capacitance value of ca. 1000 F g^{-1} at 5 mV s^{-1} , 100% capacitance cycle-retention over 1000 cycles, and 69% capacitance rate-retention (varying from 5 to 500 mV s^{-1}). These superior capacitive performances make $\text{Ni}_{0.32}\text{Co}_{0.68}(\text{OH})_2$ a promising material of the positive electrode for an asymmetric supercapacitor with an energy efficiency of 90% at 10 A g^{-1} .

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1. Introduction

Energy storage has been a critical concern as the demands of energy supply become challenging in recent years. For instance, high-tech products such as mobile phones and hybrid electric

vehicles/electric vehicles require the power supply system with both high energy density and high power supply at the same time. However, even though newly-developed batteries, like lithium batteries [1] and fuel cells [2], retain very high specific energy, the high power supply is still an issue. Accordingly, electrochemical capacitors (ECs), also known as supercapacitors, have attracted plenty of attention because they show the promising potential to meet such energy-storing demands, not to mention their extremely long cycle life [3].

ECs can be sorted into two types by the mechanism of energy storage. The electrical double-layer capacitors (EDLCs) store energy

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by the electrical double-layer formed at the interface between electrode and electrolyte with their specific capacitance mainly determined by the electrolyte-accessible surface area [3]. The pseudocapacitors, on the other hand, utilizing surface redox reactions of electrochemically active materials generally show higher specific capacitance than porous carbons [3,4]. Furthermore, designed porous microstructures of such active materials have been proposed to simultaneously enhance the utilization of double-layer and redox capacitances [5], leading to extensive research attention in the materials sciences/engineering. Recently, in order to enhance the specific energy of devices, asymmetric supercapacitors consisting of two different electrode materials with complementary working potential windows are designed to broaden their cell voltage [6].

Undoubtedly, specific energy is an important property in developing ECs [6], but seems to be overemphasized in the research field. The cell voltage plays a crucial role in specific energy of ECs [6], while ECs with high specific energy but poor energy efficiency could generate huge heat during discharge because of the significant energy loss [7]. Also, drastic temperature increase might happen at high discharge rates, which not only damages the capacitive performances but also leaves the whole cell under a dangerous state. The energy efficiency of a device generally depends on the electrochemical reversibility of electroactive materials on both electrodes [3], although the influence of iR drop on the energy efficiency becomes more significant at higher rates. Accordingly, the original asymmetric supercapacitor consisting of a battery-type material and one double-layer-type material [8] has to be redesigned since the enhanced specific energy of such systems generally comes with the trade-off in specific power [6] because of the worse electrochemical reversibility of the battery-type materials in one of the electrodes. Moreover, the charge capacity of the battery-type electrode must be much larger than that of the double-layer one because 80% (or more) loss in the charge capacity at very high rates is commonly found for a battery-type material [7,9]. This effect also reduces the specific energy (i.e., specific energy is not optimized). Therefore, how to improve the electrochemical reversibility of a battery-type material (e.g., $\text{Ni}(\text{OH})_2$ in this work) with a complementary working potential window to its double-layer-type counterpart is the new challenge in developing ECs of the asymmetric design.

For pseudocapacitive materials, RuO_2 is well known to be an ideal compound with superior reversibility and high specific capacitance [3,10]. However, due to its high cost and environmental issues, RuO_2 cannot be widely commercialized. Therefore, many researchers paid much attention on utilizing nickel and cobalt oxides/hydroxides because of being cost-effective and environmentally friendly [7,11]. Recently, binary Ni–Co oxides/hydroxides have been of interests because of their enhanced characteristics over the individual materials [12]. The doping of Co^{2+} into the nickel oxide was found to improve the utilization of electroactive materials, depress the capacity loss during long charge–discharge cycles, decrease the redox peak potential difference (ΔE_p), and increase the electronic conductivity [13–19]. As a result, many studies focused on synthesis and characterization of $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$ and NiCo_2O_4 for the asymmetric supercapacitors. For example, $\text{Co}_x\text{Ni}_{1-x}$ layered double hydroxides (LDHs) by both chemical co-precipitation and potentiostatic deposition showed specific capacitance of 1809 and 2104 F g^{-1} , respectively [20,21]. Meanwhile, mesoporous $\text{Co}_3\text{O}_4/\text{Ni}(\text{OH})_2$ nanosheet networks were reported to exhibit specific capacitance of 1144 F g^{-1} [22]. Nonetheless, several challenges, such as energy efficiency and joule-heating effect at high discharge rates as well as the long-term cycle life, need to be addressed for utilizing binary Ni–Co oxy-hydroxides.

In this work, $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$ was prepared by electrochemical deposition because of many advantages: (1) one-step process and low-cost equipment, (2) low operation temperature and energy-saving, (3) direct deposition onto porous/curved surfaces without binders, and (4) easy control on thickness, composition, and microstructure by varying deposition parameters, although several methods have been proposed to enhance the performances, such as chemical precipitation, sol–gel [23–25], sputtering [26], thermal decomposition [27,28] and electrochemical deposition [29–31]. Moreover, cathodic deposition was employed to synthesize $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$ in the attempt to synergistically attain the high specific capacitance from $\text{Ni}(\text{OH})_2$ (battery material) and the high reversibility from $\text{Co}(\text{OH})_2$ (capacitor material). This method was applied because the capacitive characteristics of deposits could be effectively controlled by varying the deposition variables. The effects of deposition factors on the capacitive performances were systematically discussed to give a fundamental understanding in order to approach superior capacitive performances. Eventually, $\text{Ni}_{0.32}\text{Co}_{0.68}(\text{OH})_2$ synthesized under our proposed deposition condition exhibits excellent performances in energy efficiency and cycle life retention, credited to the synergistic effect of $\text{Ni}(\text{OH})_2$ and $\text{Co}(\text{OH})_2$.

2. Experimental

$\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$ was cathodically deposited onto $10 \times 10 \times 3$ mm graphite substrates from the deposition baths containing 60 mM NaNO_3 , $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, and $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ in variable concentrations. The substrate preparation and pre-treatment procedures followed our previous work [32]. The substrates were carefully coated with a thick film of PTFE with an exposed surface area of 1 cm^2 . The deposition variables studied in this work include the Ni/Co ratio, temperature, pH of the deposition bath, and the deposition current density. Typically, $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$ was deposited at 1 mA cm^{-2} for 750 s (see Fig. S1 and Table S1) from a bath with the $\text{Co}^{2+}/\text{Ni}^{2+}$ ratio = 2 at 70°C [7,22,29,33]. The passed charge density of deposition is constant (0.75 C cm^{-2}) meanwhile the total concentration of Co^{2+} and Ni^{2+} was fixed at 30 mM. After deposition, the PTFE film was removed and the deposits were rinsed with deionized water several times and dried at room temperature under a reduced pressure. The mass of all hydroxide deposits was measured by an analytical balance (XS105DU, Mettler Toledo, Switzerland) with its minimum digit at 0.01 mg. The mass of all deposits has been confirmed to be $0.5 \pm 0.05 \text{ mg cm}^{-2}$ with the exception of the deposit prepared at 14 mA cm^{-2} .

The electrochemical characteristics of $\text{Ni}_x\text{Co}_{1-x}(\text{OH})_2$ were examined by an electrochemical analyzer (CHI633c, CH Instruments) in 1 M NaOH. The reference and counter electrodes in the three-electrode system were Ag/AgCl (Argenthal, 3 M KCl, 0.207 V vs. SHE at 25°C) and a platinum wire (99.95%, 0.5 mm in diameter and 8 cm in length), respectively. A Luggin capillary was used to minimize errors due to iR drop in the electrolytes. The specific capacitance value of all binary hydroxide deposits was estimated from CV curves using the following equation:

$$C_S = \frac{1}{m(V_{\text{SU}} - V_{\text{SL}})} \int_{V_{\text{SL}}}^{V_{\text{SU}}} I dt = \frac{1}{m(V_{\text{SU}} - V_{\text{SL}})} \int_{V_{\text{SL}}}^{V_{\text{SU}}} I \left(\frac{dV}{v} \right)$$

where C_S is the specific capacitance (F g^{-1}); m is the mass of the pseudocapacitive material (g); v is the potential scan rate (V s^{-1}); V_{SU} and V_{SL} are the integration limits of the voltammetric curve (in V); and I denotes the response current (A). Note that in order to avoid any possible contribution from the oxygen evolution reaction,

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