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Ni-Co Double Hydroxides Electrode Materials for Supercapacitor

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ABSTRACT

Ni-Co hydroxides with different Ni:Co ratio were synthesized using 2-electrode electrodeposition method. The effects of Ni:Co with different ratio on the hydroxides' structural and optical properties were investigated using Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD) method and scanning electron microscopy (SEM). The shifting, changing in shapes and intensity of the corresponding $Ni(OH)_2$ and $Co(OH)_2$ characteristic bands in Ni-Co hydroxides FTIR spectra confirmed that the Ni-Co hydroxides were successfully deposited onto the substrate's surface. SEM micrographs of Ni-Co hydroxides also showed that all corresponding particles were uniformly distributed and meet the ratio of Ni:Co accordingly. Moreover, XRD patterns confirmed the amorphous nature of nano-sized Ni-Co hydroxides as they were thinly coated. The effects of cobalt on the physical and electrochemical properties of $Ni(OH)_2$ were also investigated. SEM images of Ni-Co hydroxides portrayed that cobalt creates flower-like pores on $Ni(OH)_2$ surface where such pores are important for facile ions diffusion for better electrochemical performance. The Ni-Co hydroxides' electrochemical properties were also characterized by means of cyclic voltammetry and electrochemical impedance spectroscopy. It was further confirmed in the cyclic voltammetric and impedance spectroscopic studies that Ni:Co=1:3 ratio has the best electrochemical performance.

Keywords: Supercapacitor; nickel nitrates; cobalt nitrates; hydroxides; electrodeposition

INTRODUCTION

Electrochemical capacitors (ECs) have been regarded as efficient energy storage devices and become the research focus in the field of energy storage due its high power density, fast charge discharge rate, and long life cycles [1,2,3]. The urgent need of ECs with high energy density highlights the importance to develop electrode materials with excellent electrochemical performances. Recently, transition metal hydroxide (TMH) has attracted great attentions due to its high theoretical specific capacity. The multiple oxidation states of TMH result in a rich variety of redox reactions [4,5,6]. Up to now, the most studied binary TMHs are Ni/Co double hydroxides due to their simple synthesis, low cost, great capacity, high redox activity (providing multiple oxidation states for Faradaic reactions), and higher cycle stability than pure $Ni(OH)_2$ [7,8].

While Ni-Co double hydroxides show promise as advanced electrode materials for supercapacitors, their performance is highly dependent on the specific Ni:Co ratio. Variations in this ratio significantly influence the material's structural, optical, and electrochemical properties. However, there is a lack of comprehensive understanding of how cobalt incorporation affects nickel hydroxide and the interplay between these elements in optimizing electrochemical behavior. Furthermore, the optimal Ni:Co ratio that maximizes energy storage capacity and cycle stability has yet to be systematically identified. This knowledge gap presents a challenge for designing high-performance and cost-effective electrode materials for next-generation energy storage applications. The appeal of TMHs in supercapacitor applications lies in their potential to bridge the gap between traditional capacitors and batteries by combining high power capabilities with considerable energy densities. Ni-Co double hydroxides, in particular, leverage the complementary advantages of nickel and cobalt. Nickel provides exceptional charge storage capacity, while cobalt enhances structural integrity and conductivity, ensuring efficient electron transfer. By modulating the Ni:Co ratio, researchers can tailor these materials to optimize their physical and electrochemical characteristics for energy storage applications.

This study systematically investigates the influence of varying Ni:Co ratios on the performance of Ni-Co double hydroxides synthesized via electrodeposition. Advanced characterization techniques, including Fourier transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and scanning electron microscopy (SEM), provide insights into the structural and optical modifications induced by cobalt incorporation. Electrochemical assessments, such as cyclic voltammetry and impedance spectroscopy, further evaluate the functional performance of these materials. The findings aim to address the identified knowledge gap, provide a deeper understanding of the role of cobalt in enhancing the properties of nickel hydroxide, and identify the composition that delivers optimal performance for supercapacitor applications.

MATERIALS AND METHODS

Preparation of Ni-Co Double Hydroxides

Nickel (II) nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$), cobalt (II) nitrate hexahydrate ($Co(NO_3)_2.6H_2O$), and nickel foil (thickness = 0.125 mm) were obtained from Sigma Aldrich (Germany). All chemicals were analytical grade and used without further purification. Ni-Co-DH were prepared by chronoamperometric electrophoretic deposition technique. Electrolyte for Ni-Co-DH deposition were prepared by

dissolving $Ni(NO_3)_2 \cdot 6H_2O$ and $Co(NO_3)_2 \cdot 6H_2O$ in deionized water with varied nickel to cobalt molar ratio (1:0, 3:2, 1:1, 2:3, 0:1; fixed to 0.01M metal ion). Prior to electrodeposition, nickel foil, with a size of 20×20 mm^2 was first ultrasonically cleaned with ethanol and distilled water before dried in oven for 24 h. The electrodeposition was carried out with a constant current density of -1.00 mA cm^{-2} for 5 min. The samples were then dried in vacuum oven for 24 h. The mass of the deposited active materials was obtained by the weight difference of nickel foil before and after deposition. The average mass of the deposited active materials is 0.14 ± 10^{-5} mg cm^{-2}.

Ni-Co Double Hydroxide Characterization

The phase determination of the samples was performed using a PAN Analytical X-ray diffractometer with CuK_α radiation of wavelength λ = 1.540598 Å. The 2θ angular regions between 5° and 90° were explored at scan rate of 5°/min and voltage of 45 kV with current 20 mA. The Fourier transform infrared spectroscopy (FTIR) spectra of samples were recorded by Thermo Nicolet NEXUS spectrometer and operated under transmittance mode. The optical properties of the samples were analyzed using Phenom XL desktop SEM operated under low vacuum mode. The electrochemical properties of the materials were characterized by three-electrode method in 1 M KOH aqueous solution at room temperature. Ni-Co-OH-rGO was used as working electrode. A platinum foil (1×1 cm^2) was used as the counter electrode and silver/silver chloride (Ag/AgCl) as the reference electrode. The cyclic voltammetry (CV) was measured on WonATech WBCS3000 (Seoul, South Korea) at potential window 0.1 to 0.5 V and scan rate ranging from 1 to 50 mV s^{-1}. The electrochemical impedance spectra (EIS) applied an AC voltage with 5 mV amplitude in a frequency range from 0.01 to 200 kHz were measured on WonATech WEIS510 (Seoul, South Korea).

RESULTS AND DISCUSSION

Optical and Structural Characteristics of Ni-Co Double Hydroxides

Figure 1 represents the FTIR spectra of Ni-Co-OH ranging from 450 to 4000 cm^{-1}. For $Co(OH)_2$ (Figure 1), the broad band at ~3500 cm^{-1} is corresponding to stretching vibration of hydroxyl groups, ν(O-H) [9,11]. The band at 1625 cm^{-1} is due to the bending mode of water molecules. The bands observed at 1000 cm^{-1} is ascribed to δ(Co-OH) bending modes and the band at 539 cm^{-1} is ascribed to ρ(Co-OH) vibration [12]. Distinctive bands at 670 cm^{-1} is attributed to the characteristics Co-O stretching vibrations in [13] and the band located at 1331 cm^{-1} is due to the presence of nitrate anions [14]. In addition, the weak adsorptions at 3404 and 1583 cm^{-1} correspond to the bending and stretching vibration modes of absorbed water molecules on the surface. ν(Co-O) band of $Co(OH)_2$ located at 670 cm^{-1} can be seen shifted to 660 cm^{-1}, narrowed and increased in intensity for Ni:Co=1:3. This band got even narrower, sharper, and shifted more to 634 cm^{-1} in Ni:Co=3:1 spectrum due to $Ni(OH)_2$ characteristic band at 747 cm^{-1} attributed to Ni-O. This suggested that Ni-Co hydroxides were successfully formed.

As all samples were deposited on nickel foil, the XRD patterns in Figure 2 show three prominent diffraction peaks associated to nickel at 2θ = ~44°, ~52° and ~76°. The small peak at 2θ = ~11° is associated with a-$Co(OH)_2$. The peak is weak due to the nano-sized of a-$Co(OH)_2$ as all samples were thinly deposited which results in loss of intensity and is in agreement with Kong et al. [15]. It can be clearly seen that this peak becomes more evident as the amount of Co escalates. A small decrease in the intensity can be noticed for nickel peaks at 2θ = ~44°, ~52° and ~76° as ratio of cobalt to nickel

was higher in $Ni(OH)_2$. Apart from the discussed peaks, there is no other peak appeared in regard to $Ni(OH)_2$ and $Co(OH)_2$, further confirming the amorphous nature of the as-prepared Ni-Co hydroxides.

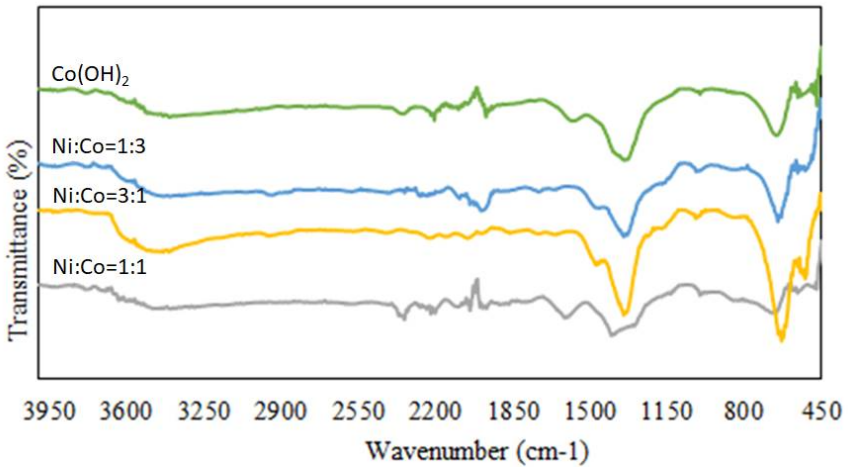

Figure 1. Vibration spectra of $Co(OH)_2$, Ni:Co=1:3, Ni:Co=3:1, and Ni:Co=1:1

Figure 3 depicts the 3D SEM micrographs of (a) $Ni(OH)_2$ and (b) $Co(OH)_2$, (c) Ni:Co=1:1, (d) Ni:Co=1:3, and (e) Ni:Co=2:3 at higher magnification. $Ni(OH)_2$ shows nanoparticles agglomerates with cauliflower-like structure while $Co(OH)_2$ exhibits flower-petal structure crumpled nanosheets. This is consistent with Yuan et al. [16] and Nguyen et al. [17] who reported Co_3O_4 and NiO surface morphologies produced by electrodeposition. It can be seen that $Ni(OH)_2$ has a smaller particle size compared with $Co(OH)_2$ and both hydroxides grow roughly perpendicular to the stainless-steel substrates. Although Ni-Co hydroxides were synthesized by co-electrodeposition and not by layer-by-layer deposition, it can be clearly seen in Figure 3(c) that $Co(OH)_2$ actually grow on $Ni(OH)_2$. Co addition creates flower-like pores on $Ni(OH)_2$ surface which can be seen when cobalt ratio is more than nickel. Such pores are important in facilitating electrolyte ions diffusion for better electrochemical performance.

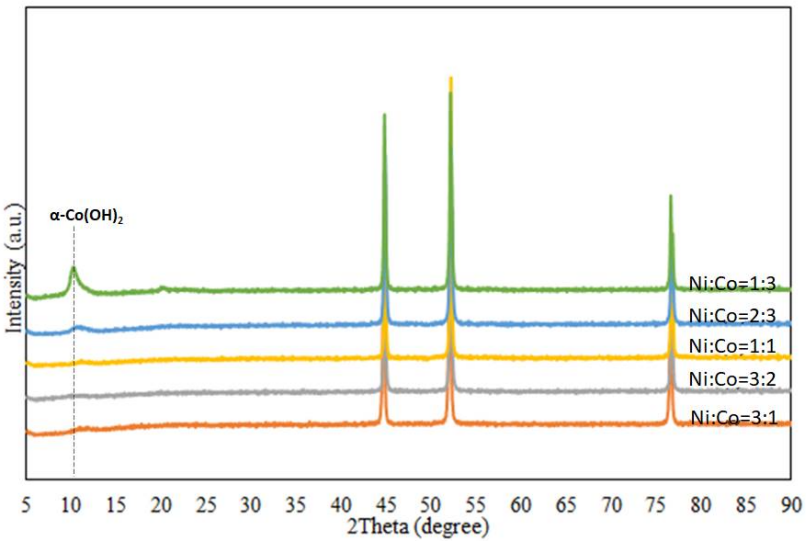

Figure 2. XRD patterns of Ni-Co hydroxides with (i) Ni:Co=3:1, (ii) Ni:Co=3:2, (iii) Ni:Co=1:1, (iv) Ni:Co=2:3, and (v) Ni:Co=1:3

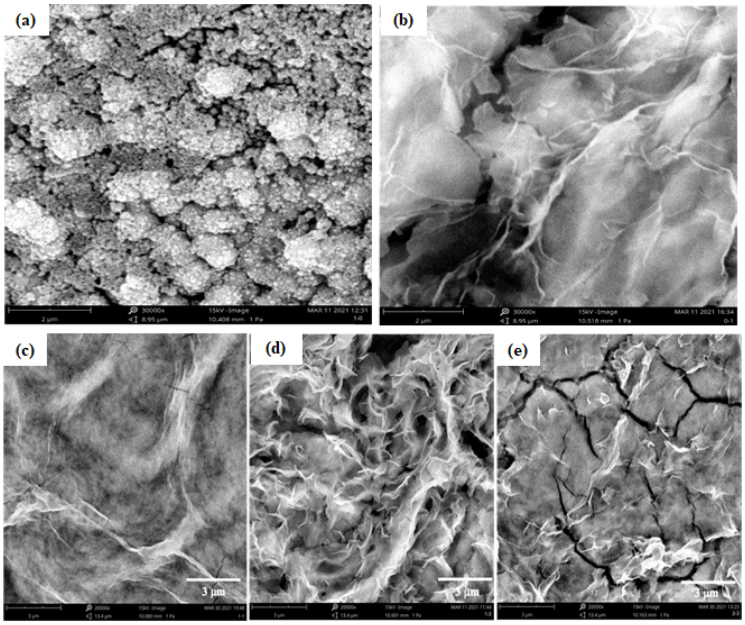

Figure 3. SEM images of (a) Ni(OH)2, (b) Co(OH)2, (c) Ni:Co=1:1, (d) Ni:Co=1:3, and (e) Ni:Co=2:3 at higher magnification

Electrochemical Characteristics of Ni-Co Double Hydroxide

Ni-Co hydroxides voltammograms with various Ni to Co mole ratio composition are illustrated in Figure 4. It can clearly be seen that all deposited samples possessed pseudocapacitive behavior due to a pair of well-defined redox peaks that are present in the CV curves within potential range of 0-0.5 at scan rate of 1 mV s^{-1}. These anodic and cathodic redox peaks can be attributed to the faradaic reactions given below:

$$Ni(OH)_2 + OH^- \leftrightarrow NiOOH + H_2O + e^- \quad (1)$$

$$Co(OH)_2 + OH^- \leftrightarrow CoOOH + H_2O + e^- \quad (2)$$

$$CoOOH + OH^- \leftrightarrow CoO_2 + H_2O + e^- \quad (3)$$

$Ni(OH)_2$ has redox peak potential near 0.5 and redox peak potential of $Co(OH)_2$ is at 0.15. CV curve of sample with 1:3 nickel to cobalt ratio shows broad anodic peak at approximately 0.29 V which is in the middle of $Ni(OH)_2$ and $Co(OH)_2$ redox peak potential. The single broad redox peaks in Ni:Co=1:3 CV curve may be caused by the uniform doping of cobalt into nickel hydroxide. Furthermore, it has higher current response compared to its corresponding single oxides; $Ni(OH)_2$ and $Co(OH)_2$ and largest under curve integrated area among all Ni-Co hydroxides samples indicates the presence of synergistic redox reactions leading to good electrochemical properties[18,19].

Figure 5 shows geometric capacitance, C_A for all Ni-Co hydroxides films recorded at 1, 5, 10, 20, 30, 40, and 50 mV s^{-1}. Value of capacitance was calculated from equation below:

$$C_A = \frac{\int i \times dV}{2 \times \mathcal{V} \times \Delta V \times A} \quad (4)$$

where i is the current response (A), dV is potential difference (V), n is the scan rate (V s^{-1}), and ΔV is the investigated potential window (V) and A is the active area of Ni-Co hydroxide electrodes. Correspondingly, $\int i \times dV$ is area under the CV curve. At 1

mV s^{-1}, it can be seen that pure Ni hydroxide has poorer capacitance compared to $Co(OH)_2$ which is in agreement with (ref.) where they report band gap value for Co slightly lower than Ni. Even though pure Co hydroxide can only retain ~30% of its initial capacitance at 5 mV s^{-1}, it becomes very stable after that. By adding Co ions into $Ni(OH)_2$, its capacitance slightly increase (Ni-Co=3:2) and capacitance value continue increasing until the highest capacitance reached (0.338 F cm^{-2}) where nickel to cobalt ratio is 1:3 followed by Ni-Co=2:3 and Ni-Co=1:1 with capacitance 0.269 F cm^{-2} and 0.239 F cm^{-2}, respectively.

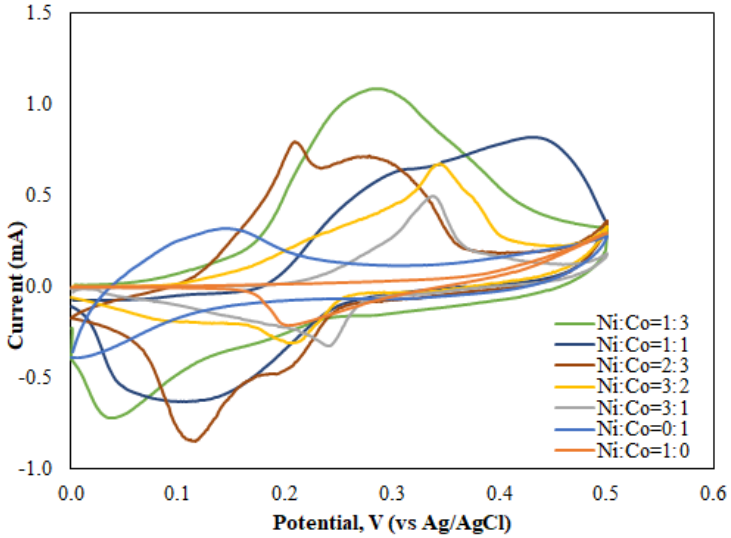

Figure 4. Voltammograms of Ni-Co hydroxide at scan rate of 1 mV s^{-1}

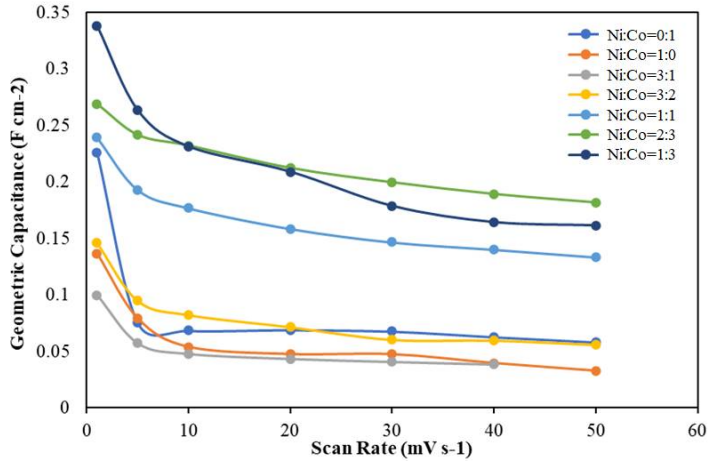

Figure 5. Geometric capacitance value of Ni-Co hydroxides at various scan rates

Figure 6 shows Nyquist plots of Ni-Co hydroxides electrodes with different ratios of Ni:Co. All curves exhibit a semicircle at high frequency and a straight line in the low frequency region. The semicircles in the high frequency region can be ascribed to the charge transfer resistance and the straight lines at low frequency are due to the diffusive resistance of the ions in the electrolyte within the pores of the electrodes [20,21].

It clearly shows that Ni:Co=1:3 has smaller semicircle plus steeper slope and shorter straight line compared to its corresponding single hydroxides and other Ni-Co hydroxides which indicates smaller interfacial charge transfer resistance and lower

diffusion resistance. Co addition to $Ni(OH)_2$ shortened the corresponding lines of Ni-Co hydroxides which lowered the ionic diffusion resistance by creating more flower-like pores to facilitate more ions resulting to higher specific capacitance as proven earlier in morphological and electrochemical studies.

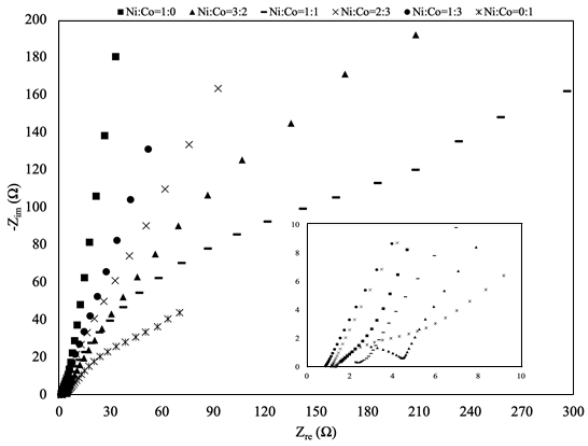

Figure 6. Nyquist plot of Ni-Co hydroxides

CONCLUSIONS

Ni-Co hydroxides with different Ni:Co ratio were synthesized using 2-electrode electrodeposition. The shifting, changing in shapes and intensity of corresponding $Ni(OH)_2$ and $Co(OH)_2$ characteristic bands in Ni-Co hydroxides FTIR spectra confirmed that the Ni-Co hydroxides were successfully deposited onto substrate's surface. SEM micrographs of Ni-Co hydroxides also showed that all corresponding particles were uniformly distributed and meet the ratio of Ni:Co accordingly. Moreover, XRD patterns confirmed the amorphous nature of nano-sized Ni-Co hydroxides as they were thinly coated.

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