

Synthesis and Characterization of Ni.Co(OH)₂ Material for Supercapacitor Application

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Abstract: Nanosized β -Ni(OH)₂ is being widely used as an electrode material for supercapacitor because of its high power density, high specific energy and low toxicity. But with addition of dope material like Co, Al specific capacitance of Ni(OH)₂ significantly increased. Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂ was successfully synthesized by conventional precipitation method. Developed materials were characterized by using X-ray Diffraction (XRD), Scanning electron microscope (SEM), Atomic Force Microscopy (AFM), Fourier Transform Infrared Spectroscopy (FTIR). XRD result confirmed the substitution of cobalt in nickel hydroxide. Electrochemical studies were carried out by using cyclic voltammetric (CV). Specific capacitance obtained from Ni.Co(OH)₂ significantly higher than Ni(OH)₂ and Co(OH)₂ and was found to be 708 F/g at scan rate 1 mV/s.

Keywords: Supercapacitor; Electrochemical; pseudocapacitor; nanocomposites.

1. INTRODUCTION

Supercapacitor, also called electrochemical capacitor or ultracapacitor, is a class of energy storage device similar to a battery. Supercapacitors became a promising candidate for energy storage because of their high power performance, long cycle life and low maintenance cost.^{1,2} It is used as a major power source in hybrid electric vehicle, backup memory power, emergency door of airplane, portable electronics, micro devices etc. Based on the charge storage mechanism, supercapacitor can be classified into electrical double layer capacitor and pseudocapacitor.^{3,4} In electrical double layer capacitor, capacitance arises from charge separation at electrode/electrolyte interface while in case of pseudocapacitor, capacitance arises from fast, reversible faradaic reactions occurring at or near the solid electrode surface. Carbon based materials (activated carbon⁹, carbon nanotubes⁷, carbon aerogels) comes under EDLC while transition metal oxides, hydroxide (RuO₂⁵, MnO₂⁸, Ni(OH)₂⁷, Co(OH)₂⁹ etc.) and conducting polymers (polyaniline) comes under pseudocapacitance.

From material point of view, transition metal oxides and hydroxides plays a vital role in supercapacitor. In transition metal oxides RuO₂ is best because of its good electrical conductivity and specific capacitance.¹⁰ However, it is not widely used owing to its high cost and toxic nature. Therefore other environmentally friendly and cheap material like Ni(OH)₂ substitute RuO₂. Ni(OH)₂ is less expensive and has high theoretical capacitance. This theoretical capacitance can be achieved using some doped element like Al, Co etc. Substitution of cobalt compounds into nickel system increases electronic conductivity while nickel compound in the cobalt system improves electrochemical performance. J. H. Zhong et al. synthesized Co₃O₄/Ni(OH)₂ composite mesoporous nanosheet network grown on conductive substrate.¹¹ J. Li et al. reported hydrothermal and chemical deposition

combined method for preparation of Ni(OH)₂/Co(OH)₂ composite. Specific capacitance obtained from this composite is 1144 F/g at scan rate 5 mV/s.¹² Novel three dimensional porous nano Ni/Co(OH)₂ nanoflake composite film also used as an electrode for supercapacitor application. Impressively energy density as high as 80Wh/kg and power density 11 kW/kg were obtained from this Co(OH)₂ nanoflakes in the composite film.¹³ A. Audemer et al. did electrochemical and Raman study for beta nickel hydroxide Ni_{1-x}Co_x(OH)₂ as an electrode material.¹⁴ Nickel and cobalt hydroxide synthesized by sonochemical method, deposited on ITO electrodes were used as electrodes for supercapacitor application.¹⁵ L. Su et al. Studied electrochemical performance of the Co(OH)₂/Ni(OH)₂ composite in lithium hydroxide solution.¹⁶

In this paper we synthesized Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂ by conventional precipitation method. The specific capacitance of Ni(OH)₂ used as a single material is very less than Co(OH)₂ and Ni.Co(OH)₂. The significantly improvement of specific capacitance and cyclic stability in case of in case of Ni.Co(OH)₂.

II. EXPERIMENTAL

A. Materials and methods

Synthesis of Ni(OH)₂: Ni(OH)₂ was synthesized by the chemical precipitation method. In typical synthesis 2g Ni(NO₃)₂ · 6H₂O were dissolved in 100 ml of DI water under magnetic stirring. After 15 minutes 1M NaOH solution (14ml) were added drop-wise in the above solution to maintain pH up to 10. Because of NaOH addition solution colour changed greenish to faint greenish. This solution was stirred for 2 hours and precipitated particles separated using a centrifuge. These particles were washed three-four times with distilled water

and then kept in oven at 70⁰ C for drying purposes for 8 hours. Dry powder is used for making active electrode.

Synthesis of Co(OH)₂ : In the case of Co(OH)₂ , 2g of Co(NO₃)₂ were dissolved in 100 ml DI water under continuous stirring about 15 minute. After that 1 M NaOH was added dropwise in the above solution up to Ph 11 and because of this solution colour changed from reddish to reddish black. Above solution stirred for 2 hours and then particles were separated by using centrifuge also washed three four time by DI water and once ethanol. This precipitate particles dried in oven at 70⁰C about a 8 hours and in this way blakish coloured powder of Co(OH)₂ was synthesized.

Synthesis of Ni.Co(OH)₂ hybrid: Same procedure was followed in this case, 1 g Ni(NO₃)₂ . 6H₂O, 1 g Co(NO₃)₂ . 6 H₂O was dissolved in DI water. Solution stirred 15 min far the sake of proper dissolution purpose. 1 M NaOH solution was added after that up to pH became 10 and because of this solution clour became some what greenish blue. After 2 hour stirring precipitated particles were separated using centrifuse. Wahsed this particles with DI water and Ethanol three four time. And this particle were transferred to oven at 65⁰C about 8 hour for drying purpose. In this way we got Ni.Co(OH)₂ powder.

B. Characterization:

The structure and lattice constant information of prepared sample was obtained by using Powder X-Ray Diffraction (PXRD) pattern using a Philips powder diffractometer PW3050/60. The measurement was performed by using 40 kV, 30 mA graphite filtered Cu-Ka radiation ($\lambda=1.54060$ Å). To testify topography of obtained materials, SEM and AFM of samples were observed using 3400N SEM and Asylum Research MPF3D respectively. The electrochemical experiments were carried out using an Eco-Chemie (The Netherlands) make electrochemical system Autolab PGSTAT 100 running with GPES (General Purpose Electrochemical System) version 4.9, software. Cyclic voltammetric and impedance experiments were carried at room temperature (25⁰ C) in a three-electrode cell set up. The working electrode was carbon paste electrode with 2 mm diameter. Carbon paste made from spectroscopic grade carbon powder and silicon oil was mixed thoroughly using mortar and pestle with the supercapacitor materials (oxides and hydroxides of cobalt and nickel) material at 1:1 ratio forming homogeneous mixture with carbon paste. Saturated calomel (SCE) was used as a reference electrode and platinum wire was used as the counter electrode. All general chemicals used in the present study are of analytical-reagent grade. Nano pure water was used in all the experiments and also for the washing of the electrochemical cell set up.

III. RESULT AND DISCUSSION

Figure 1(a) shows the XRD patterns of the as-synthesized Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂ materials. The diffractions at the 2 θ values of 19.77⁰, 33.36⁰, 38.83⁰, 52.59⁰, and 62.97⁰ in Fig. 1A are typical for the hexagonal phase of Ni(OH)₂ (JCPDS: 14-0117) and indexed to the

(001), (100), (101), (102), (110) and (111) planes, respectively,⁴ confirming the formation of β -Ni(OH)₂. Reflection peaks at the 2 θ values 19.27⁰, 31.65⁰, 37.12⁰,45.09⁰, 59.64⁰ and 65.6⁰ shown in Figure 1 (b) are attributed to the Co(OH)₂ material.

From fig 1 (c) it is clearly shown than reflection peaks at angle 11.14⁰, 19.35⁰, 38.49⁰, and 51.92⁰ corresponding to plane (003), (001), (101) and (102) and shifting the peaks confirms that substitution of Co in nickel hydroxide. The low intensity and broad diffraction peaks that material is nanocrystalline and which good for supercapacitor application because proton can easily permeate through the bulk of Ni(OH)₂ material.

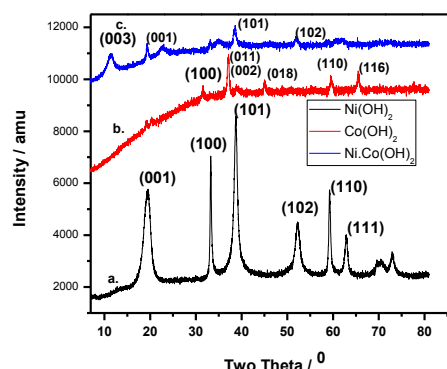


Figure I. The XRD pattern of the as synthesized β -Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂

AFM characterization it is justified that morphology and height measurement of the Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂ materials. As shown in figure 2 (a), (b) and (c) distribution of particles is very good in case of Ni.Co(OH)₂ Fig. 2 (d), (e) and (f) shows 3D view of the AFM image of Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂.

Morphology and microstructure of samples was observed using Field Emission Scanning electron micrographs (FESEM). FESEM at a high magnification for hexagonal and nanosheet Ni(OH)₂ shown in Figure 6.3(a). Particles formed is a hexagonal shape for β -Ni(OH)₂ while in case of modified Co(OH)₂ spherical shape like nanosheets. Ni.Co(OH)₂ forming flower leaf like structure interconnected each other.

(Figure 6.3 (c)) forming porous structure. FTIR (Fourier transform infrared spectroscopy) results show various peaks in figure 6.4(a) and (b) for β -Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂, peaks between 500 and 750 cm⁻¹ confirms the presence of metal hydroxide stretching.

In all cases the sharp peak at 3636 cm⁻¹ is assigned to the stretching vibration mode (ν OH) of non hydrogen bonded hydroxyl group in hydroxide.

The symmetric and antisymmetric stretching of carbonate anions present in the interlayer space of Ni(OH)₂ is exhibited at 1630 and 1381 cm⁻¹ respectively. S-O stretching peak shown at 1051 cm⁻¹ in case of Ni.Co(OH)₂, which is absent in β -Ni(OH)₂ and Co(OH)₂.

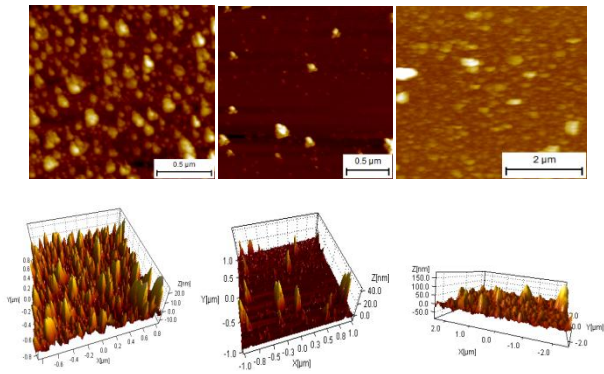


Figure II. The AFM image for a) β -Ni(OH)₂ b) Co(OH)₂ c) Ni.Co(OH)₂

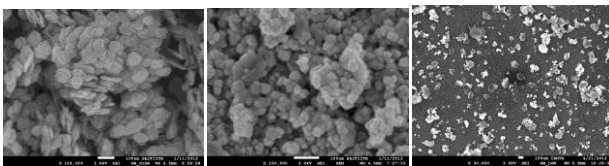


Figure III. The FESEM image of a) β -Ni(OH)₂ b) Co(OH)₂ c) Ni.Co(OH)₂.

TG and DTA curve shown in figure 6.5 describe properties of material as change with temperature. There are two stages of mass loss for both samples. The first thermogravimetric step represents the loss of adsorbed water or intercalated water.

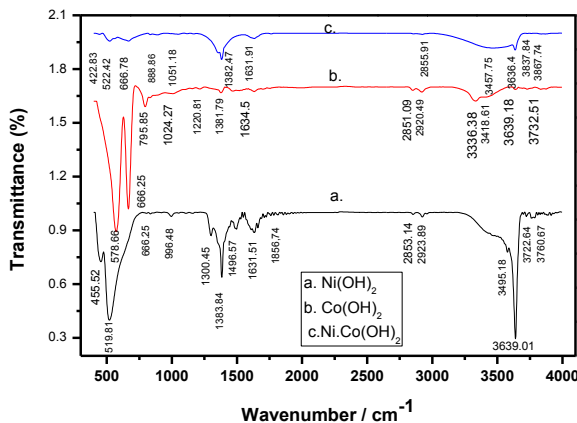


Figure IV. FTIR curves for a) β -Ni(OH)₂ b) Co(OH)₂ c) Ni.Co(OH)₂.

The mass loss at first stage is 18.33%, 4.52% and 23.265% for sample Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂. Second stage corresponding to the decomposition of hydroxide to oxide emerged at 350°C, 350°C and 400°C and mass loss is 4.128 %, 1.352% and 6.944%.

In DTA analysis Ni(OH)₂ showed only one peak at 284.54°C giving 236.1 J energy while in case of Co(OH)₂ showed two exothermic peaks at 219. 72°C and 304.45°C took energy 77.44J and 21.42J. Ni.Co(OH)₂ exhibited three peaks one endothermic at 272.27°C gave energy 618.7 J and two exothermic at 545.27°C and 767.71°C took 3538J and 26.24 J energy.

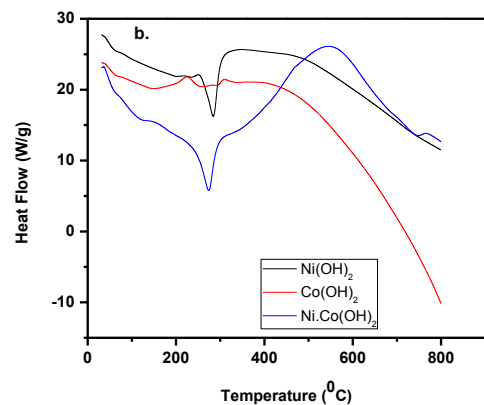
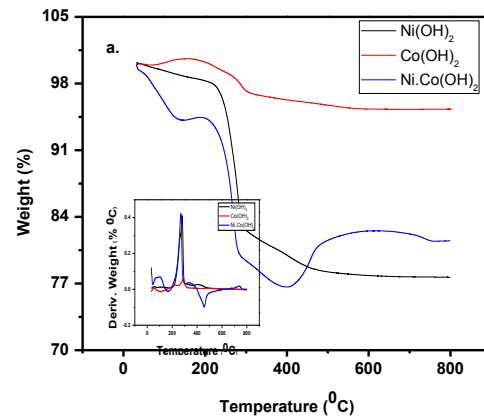


Fig. V a. TG b. DTA analysis of Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂.

In electrochemical characterization figure 6 (a) and (c) shows the CV curves of Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂ in 1M KOH solution at the scan rate 1, 5, 10, 50, 100, 200, 300, 400 and 500 mV/s. The specific capacitance calculated at scan rate 1 mV/s is 20o F/g, 512 F/g and 708 F/g for Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂ respectively.

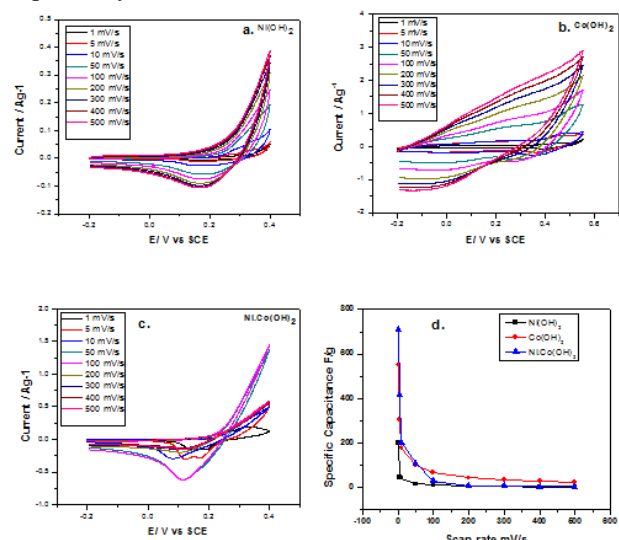


Figure VI. CV curve for a. Ni(OH)₂, b. Co(OH)₂ and c. Ni.Co(OH)₂ at Scan rate 1, 5, 10, 50, 100, 200, 300, 400 and 500 mV/s d. Variation of specific capacitance vs scan rate.

From the above result it is clear that because of addition of cobalt in nickel hydroxide specific capacitance increases significantly. As shown in figure 6 b) and d) β -Ni(OH)₂ and Ni.Co(OH)₂ electrode exhibits decreasing specific capacitance as scan rate goes in increasing. The electrochemical impedance spectra (EIS) clear electrodes charge transfer process. Semicircle in the high frequency region is related to the charge transfer process, and its diameter is charge –transfer resistance. In the middle frequency region, it displays a spike characteristic of capacitive behavior. Figure 7 shows Nyquist plots for Ni(OH)₂, Co(OH)₂ and hybrid Ni.Co(OH)₂ of this material. It can be seen that low frequency tail for the three samples is different. Hybrid sample showing nearly vertical line, indicating a higher electron mobility, owing to broader interlayer space. Minor induction loop at the low frequency region are also indicative of the porous nature of the material.

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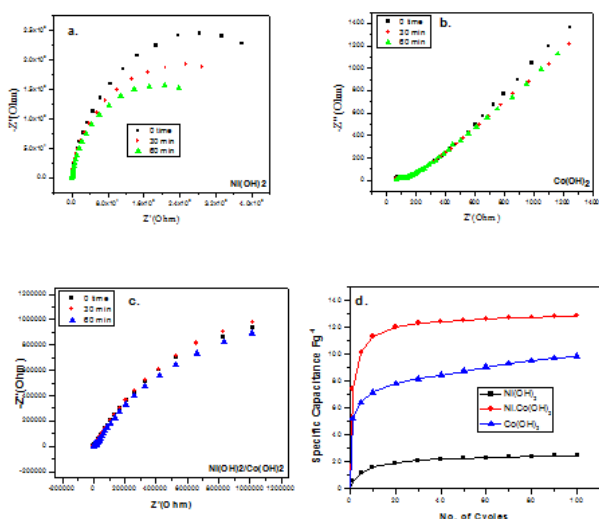


Figure VII. Nyquist plot for a. Ni(OH)₂, b. Co(OH)₂ and c. Ni.Co(OH)₂ d. Cyclic stability of . Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂

IV. CONCLUSION

Ni(OH)₂ plays an important role in supercapacitor application because of its theoretical high capacitance and low cost. And this theoretical capacitance can be achieved by doping other transition metals like cobalt. XRD result and FTIR (3636 cm⁻¹ peak) confirm substitution of cobalt in nickel hydroxide. SEM reveals that hexagonal shape of nanoparticles for β -Ni(OH)₂, Co(OH)₂ and Ni.Co(OH)₂. From cyclic voltammetric result specific capacitance of Ni.Co(OH)₂ gives a better capacitive performance than simple Ni(OH)₂ and Co(OH)₂ and which was 708 F/g. Also cyclic stability of Ni.Co(OH)₂ is significantly improved.

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