ES Materials and Manufacturing
DOI: https://dx.doi.org/10.30919/esmm5f938

Chemically Deposited $NiCo_2O_4$ Thin Films for Electrochemical Study

Ramesh J. Deokate*

Abstract

Nickel cobalt oxide ($NiCo_2O_4$) thin films were grown by using chemical spray pyrolysis on conducting substrate (FTO) for energy storage application. The physical and electrochemical properties of prepared $NiCo_2O_4$ thin films were reported via various analytical techniques such as X-ray diffraction (XRD), scanning electron microscopy (SEM) and electrochemical measurements. The higher specific capacitance of the $NiCo_2O_4$ thin films demonstrated their suitability as outstanding candidates in electrochemical applications. The maximum evaluated specific capacitance of 777 F/g obtained at scan rate 5 mV/s.

Keywords: Thin film; XRD; $NiCo_2O_4$; Supercapacitor.
Received: 18 May 2020; Accepted date: 19 November 2020.
Article type: Communication.

1. Introduction

Supercapacitor is one of the excellent energy storage devices because of best power density, ultrafast charging discharging rate, stability and economically cheap.[1-2] The extraordinary power density and good stabilities are tremendously attracted to make the supercapacitor promising material for wide range of applications.[3] However, scientific have been focused on increasing electrochemical properties of electrode elements like oxides, carbonous materials and conducting polymers. [4] Now presently, oxides like RuO_2, NiO, MnO_2, Co_3O_4 have been extensive functional elements as electrodes in future-generation supercapacitors application due to the extraordinary ability to storing charge and exhibiting high capacitance values resulted from fast redox reactions.[5-10]

The cubic spinel structure such as ternary metal oxides is important material owing their multifunctional property towards the energy storage device uses. The $NiCo_2O_4$ is a cheap and more oxidation states with better electrochemical property and electronic conductivity with at least two orders greater than single NiO or Co_3O_4.[11-12] Moreover, $NiCo_2O_4$ have been gained attention as pseudo-capacitors as well as theoretical capacitance values, environmentally friendliness and naturally abundance. Additionally, the nickel cobalt oxide is effectively utilized as an electrode material in different applications, alkaline batteries, Li-air batteries, and lithium ion.[13- 19] Hence, researchers are working on the pure phase synthesis of this functional compound at lower temperatures by using different preparation methods. To date numerous chemical methods are utilized such as co-precipitation, nanocasting, sol–gel, hydrothermal, combustion, chemical spray, hydroxyl-carbonates, and metal hydroxides. [11, 17,18, 20-23] This paper reports the facile synthesis of $NiCo_2O_4$ thin films by a chemical spray technique. These films were characterized by X-ray diffraction (XRD), field emission scanning electron microscope (FESEM) and electrochemical properties reported in details. Further electrochemical performance of $NiCo_2O_4$ thin film is examined by cyclic voltammetry and charge discharge measurement.

2. Experimental and characterizations

The $NiCo_2O_4$ thin films were prepared using a spray pyrolysis method on conducting glass (FTO) substrate. Two different aqueous solutions of 0.1 M $NiCl_2{\cdot}6H_2O$ and 0.1 M $CoCl_2{\cdot}6H_2O$ were prepared with a volume ratio of 1:2 and were deposited on FTO substrate.[24] Structural analysis of $NiCo_2O_4$ thin films was performed on (XRD Bruker AXS D8 Advance Model) with the radiation source Cu-Kα (λ=1.5406 Å) at 2θ in the range 20 to 80°. Field emission scanning electron microscope (FE-SEM, SU8000, Hitachi) was used to study the surface morphology. The electrochemical measurements of the $NiCo_2O_4$ thin film electrodes were reported using cyclic voltammetry and galvanostatic charge discharge analysis. Computer controlled potentiostat (CHI

Department of Physics, Vidya Pratishthans, Arts Science and Commerce College, Baramati- 413 133, (MS), India.
* *Email:* deokate2000@yahoo.co.in

6005E Made in USA), and (CHI 6002E Made in USA) were used with three electrode electrochemical cell.

3. Results and discussion

In the chemical spray pyrolysis aqueous solutions of nickel and cobalt precursor were sprayed over the FTO coated glass substrates kept at 548 K spray pyrolysis unit. The chemical reaction involved for the formation of $NiCo_2O_4$ film can be presented as:

$$NiCl_2 6H_2O + 2CoCl_2.6H_2O \Rightarrow NiCo_2O_4 + 6HCl + H_2 + 14\,H_2O \quad (1)$$

The $NiCo_2O_4$ films synthesized at 548 K were highly adhered to the FTO glass substrate. Further, the structural properties of films were analyzed with the help of X-ray diffractometer as given in Fig. 1. The peaks corresponding to the planes (111) (220) (311) (400) (422) (511) and (440) indicated that $NiCo_2O_4$ has polycrystalline face-centered cubic spinel nature (JCPDS No. 20-0781)[25], the absence of NiO and Co_3O_4 characteristic peaks affirming phase-purity of $NiCo_2O_4$ crystal. The diffraction peaks of $NiCo_2O_4$ were broad and weak, indicating the small particle size, provide favorable path ways for intercalation/deintercalation of protons or alkali metal cations. The surface morphology of $NiCo_2O_4$ films were studied by FE-SEM, as shown in Fig 2. The morphology obtained for $NiCo_2O_4$ thin film represents smooth surface with smaller grains having uniform particle distribution size between 100–200 nm.

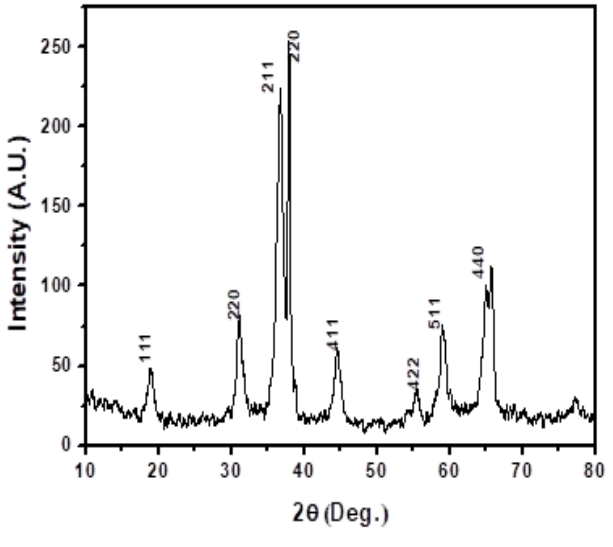

Fig. 1 The X-ray diffraction pattern of $NiCo_2O_4$ thin film on FTO substrate.

Cyclic voltammetry (CV) is a best technique to analyze the electrochemical performance of any active component. A voltammogram with rectangular shape, displaying large current values, and identical in anodic and cathodic directions, is an indicative of perfect capacitor material.[7] The cyclic voltammograms of $NiCo_2O_4$ thin film deposited at different temperatures is shown in Fig. 3 (a). The CV was measured in aqueous 2M KOH electrolyte in potential window 0 to 0.5 V at scan rates of 5 to 200 mV s^{-1}. The shapes of the CV profile deviated from ideal rectangle; clearly signify the pseudocapacitive nature of $NiCo_2O_4$ thin films produced by electrochemical reactions at the electrode surface. It is noticed that the profile of the CV plot does not appear to alter significantly even at large scan rates and the total charge accumulation increases with increasing scan rates. The CV results reveal a good rate performance and excellent capacitive behavior for $NiCo_2O_4$ electrode. Further, it is obvious that current densities obtained in CV plots are directly proportional to the scan rate of CV, signifying ideal capacitive behavior. [26, 27] Moreover, it is noticed that the separation between the reduction and oxidation peaks becomes larger with the increase in current density as a function of scan rate. This separation in the redox peaks can be attributed to the polarization of the cell under the relatively high scan rate.

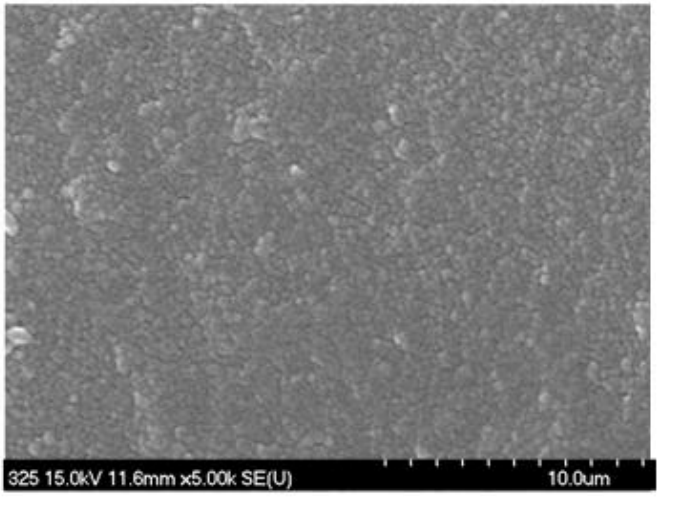

Fig. 2 FE-SEM micrographs of $NiCo_2O_4$ thin film.

The faradic reactions occurring on the $NiCo_2O_4$ electrodes surface during the charge stowage process are responsible for the observation of redox peaks. Furthermore, the two different reversible reactions associated with transitions of Ni^{2+}/Ni^{3+} and Co^{3+}/Co^{4+} occurring in the alkaline electrolyte contribute to the redox peaks. The faradic reactions corresponding to the reversible charge stowage mechanism is as follows. [28-29]

$$NiCo_2O_4 + H_2O \Leftrightarrow NiOOH + 2CoOOH + 2e^- \quad (2)$$

$$MOOH + OH^- \Leftrightarrow MO_2 + H_2O + e^- \quad (3)$$

where M is Co or Ni. It is worthwhile to note that the changes in the valence states from Co^{3+} to Co^{4+} and from Ni^{2+} to Ni^{3+} in the due course of charge/discharge process are occurring on the material surface, where fast and reversible redox reactions occur. However, the changes in the oxidation states of the material cannot be observed, because the redox potentials of Ni^{2+}/Ni^{3+} and Co^{3+}/Co^{4+} transitions during electrochemical reaction are so close that the redox peaks may get overlapped. The specific capacitance (C_s) was calculated using following relations:

$$C = \frac{I_{max}}{dv/dt},\ C_i = \frac{C}{A} \text{ and } \quad C_s = \frac{C_i}{m} \quad (4)$$

where C is the differential capacitance, I is the average current in ampere and dV/dt is voltage scanning rate, C_i is the interfacial capacitance, A is the area of active material dipped in the electrolyte, and m is the weight of $NiCo_2O_4$ film dipped in electrolyte. The specific capacitance value found to be 777 F/g at the scan rate 5mV/s for the $NiCo_2O_4$ thin film electrode. Fig. 3 (b) shows the variation of specific capacitance and interfacial capacitance with different scan rates. The obtained values of specific and interfacial capacitance are decreased from 777 to 145 F/g and 0.31 to 0.02 F/cm, respectively. The maximum specific capacitance 777 F/g was obtained at the scan rate 5 mV/s. The decrease in capacitance has been attributed to the presence of inner active sites that cannot sustain the redox transitions completely at higher scan rates. This is probably due to the diffusion effect of protons within the electrode. The decreasing trend of the capacitance suggests that parts of the surface of the electrode are inaccessible at high charging–discharging rates.[23]

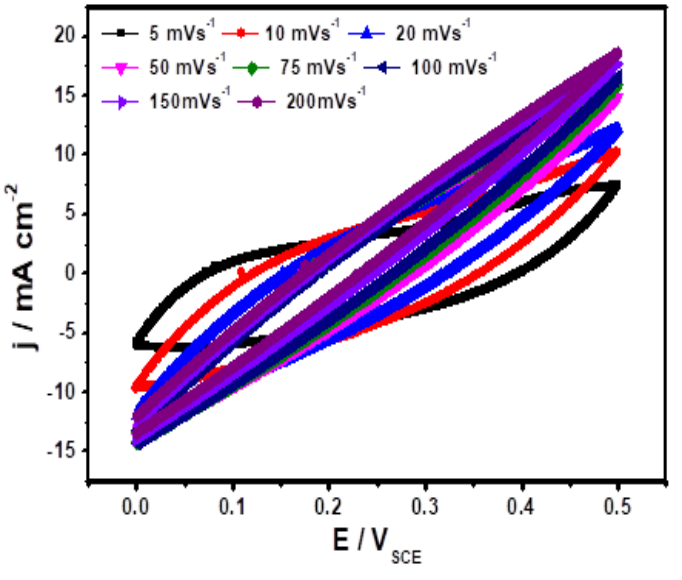

Fig.3 (a) Cyclic voltammogram of $NiCo_2O_4$ thin film at different scan rates in 2 M KOH electrolyte.

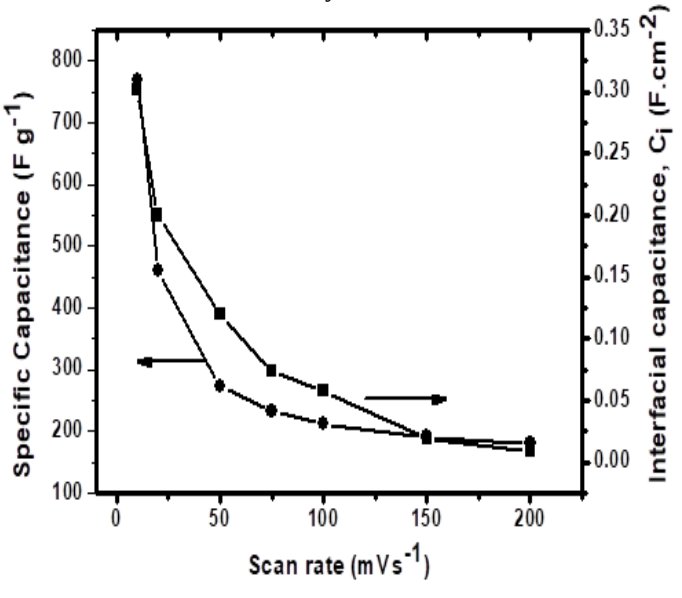

Fig. 3 (b) Variation of specific and interfacial capacitances.

Fig. 4 (a) shows the galvanostatic charge–discharge curves of $NiCo_2O_4$ electrode in 2 M KOH electrolyte at 1 mA/cm^2 current density. The obtained curve showed particular straight discharge slope and the excellent discharge capabilities. The specific capacitance values are calculated by the following relationship, *i.e.*

$$C_s = \frac{I \times t_d}{m \times v} \quad (5)$$

where I (mA), the discharge current density, v (V), the working potential window, and td (s), the discharge time. A specific capacitance value of 217 F/g was obtained for $NiCo_2O_4$ electrode material. Fig. 4 (b) shows electrochemical impedance spectra in the form of Nyquist plot the NiCo2O4 electrode exhibits a small real axis intercept and negligible semicircle, suggesting a low interfacial resistance between current collector and active material, active material resistance, electrolyte resistance as well as low charge transfer resistance, which is in agreement with the CV analysis.

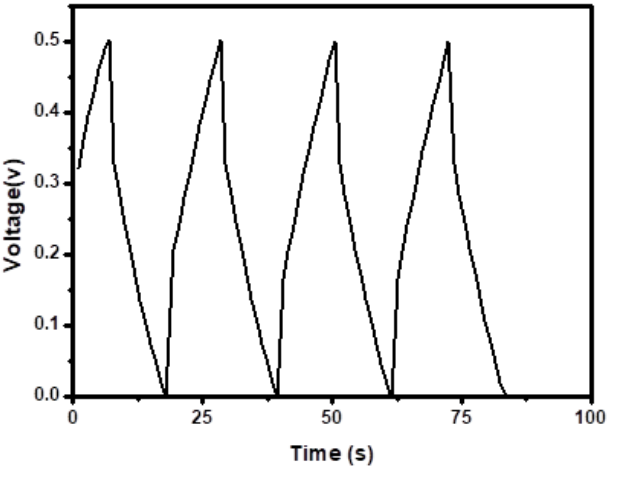

Fig. 4 (a) Galvanostatic charge–discharge curves of $NiCo_2O_4$ thin film.

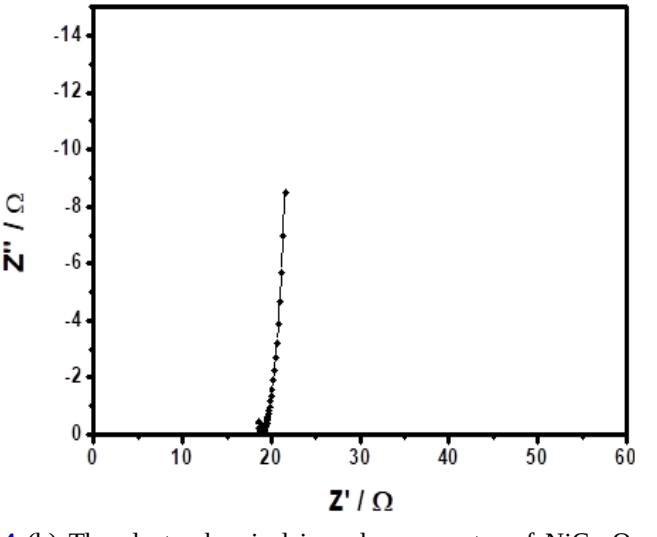

Fig. 4 (b) The electrochemical impedance spectra of $NiCo_2O_4$ thin film.

4. Conclusion

The nanocrystalline $NiCo_2O_4$ thin films were prepared by spray pyrolysis method. The structural study revealed that the $NiCo_2O_4$ thin film exhibits spinal structure. The nanocrystalline grain surface morphology was observed from field emission scanning electron micrograph images. The $NiCo_2O_4$ electrode exhibited the specific capacitance of 777 F/g and interfacial capacitance of 0.31 F/cm^2 at a scan rate 5 mV/s. Therefore, $NiCo_2O_4$ electrode can be used for the supercapacitor applications.

Conflict of Interest

There is no conflict of interest.

Supporting Information

Not Applicable

References

[1] S. Xu, D. Yang, Fan Zhang, J. Liu, A. Guo, F. Hou, *RSC Adv.*, 2015, **5**, 74032-74039, doi: 10.1039/C5RA12855B.

[2] B. L. Ellis, P. Knauth, T. Djenizian, *Adv. Mater.*, 2014, **26**, 3368-3397, doi: 10.1002/adma.201306126.

[3] C. H. Ng, H. N. Lim, S. Hayase, I. Harrison, A. Pandikumar, N. M. Huang, *J. Power Sources*, 2015, **296**, 169-185, doi: 10.1016/j.jpowsour.2015.07.006.

[4] G. Wang, L. Zhang, J. Zhang, *J. Chem. Soc. Rev.*, 2012, **41**, 797-828, doi: 10.1039/C1CS15060J.

[5] C. C. Hu, W. C. Chen, *Electrochmica. Acta*, 2004, **49**, 3469-3478, doi: 10.1016/j.electacta.2004.03.017.

[6] Y. J. Yang, E. Liu, L. Li, Z. Z. Huang, H. J. Shen, X. X. Xiang, *J. Alloys Comp.*, 2010, **505**, 555-559, doi: 10.1016/j.jallcom.2010.06.072.

[7] X. Wang, Y. Li, *J. Am. Chem. Soc.*, 2002, **124**, 2880-2881, doi: 10.1021/ja0177105.

[87] M. Wu, J. Gao, S. A. Zhang, *Chen, J. Power Sour.*, 2006, **159**, 365-369, doi: 10.1016/j.jpowsour.2006.04.013.

[9] S. K. Meher, G. R. Rao, *J. Phys. Chem. C*, 2011, **115**, 15646-654, doi: 10.1021/jp201200e.

[10] V. Srinivasan, J. W. Weidner, *J. Power Sources*, 2002, **108**, 15-20, doi: 10.1016/S0378-7753(01)01012-6.

[11] T. Y. Wei, C. H. Chen, S. Y. Lu, C. C. Hu, *Adv. Mater*, 2010, **22**, 347-357, doi: 10.1002/adma.200902175.

[12] S. Verma, H. M. Joshi, T. Jagadale, A. Chawla, R. Chandra, S. Ogale, *J. Phys. Chem. C*, 2008, **112**, 15106-15112, doi: 10.1021/jp804923t.

[13] I. Serebrennikova, V. I. Birss, *J. Electrochem. Soc.*, 1997, **144**, 566, doi: 10.1149/1.1837449.

[14] A. C. Tavares, M. A. M. Cartaxo, M. I. D. Pereira, *J. Solid State Electrochem.*, 2001, **5**, 57-67, doi: 10.1007/s100089900091.

[15] L. Zhang, S. Zhang, K. Zhang, G. Xu, X. He, S. Dong, Z. Liu, C. Huang, L. Guc, G. Cui, *Chem. Commun.*, 2013, **49**, 3540-3542, doi: 10.1039/C3CC40393A.

[16] H. S. Jadhav, R. S. Kalubarme, J. W. Roh, K. N. Jung, K. H. Shin, C. N. Park, C. J. Park, *J. Electrochem. Soc.*, 2014, **161**, A2188, doi: 10.1149/2.0771414jes.

[17] Z. Sun, M. H. Sedghkerdar, J. Saayman, N. Mahinpey,, N. Ellis, D. Zhaod, S. Kaliaguine, *J. Mater. Chem. A*, 2014, **2**, 16577-16588, doi: 10.1039/C4TA03854A.

[18] H. S. Jadhav, R. S. Kalubarme, C. N. Park, J. Kim, C. Park, *J. Nanoscale*, 2014, **6**, 10071-10076, doi: 10.1039/C4NR02183E.

[19] P. Peshev, A. Joshev, G. Gyurov, *Mater. Res. Bull.*, 1989, **24**, 33-40, doi: 10.1016/0025-5408(89)90005-6.

[20] J. E. Marco, J. R. Gancedo, M. Gracia, J. L. Gautier, E. Ri, F. J. Berry, *Solid State Chem.*, 2000, **153**, 74-81, doi: 10.1006/jssc.2000.8749.

[21] M. E Baydi., S. K. Tiwari, R. N. Singh, J. L. Rehspring, P. Chartier J. F. Koening Poillerat G., *J. Solid State Chem.*, 1995, **116**, 157-169, doi: 10.1006/jssc.1995.1197.

[22] A. V. Chadwick, S. L. P. Savin, S. Fiddy, R. Alcántara, D. P. Lisbona, P. Lavela, G. F. Ortiz, J. L. Tirado, *J. Phys. Chem. C*, 2007, **111**, 4636-4642, doi: 10.1021/jp066417u.

[23] B. Chi, J. Li, Y. Han, Y. Chen, *Int. J. Hydrogen Energy*, 2004, **29**, 605-610, doi: 10.1016/S0360-3199(03)00219-2.

[24] R. Deokate, A. Adsool, N. Shinde, S. Pawar, C. Lokhande, *Energy Procedia*, 2014, **54**, 627-633, doi: 10.1016/j.egypro.2014.07.304.

[25] JCPDS No. 20-0781.

[26] A. J. Jaworek, *J. Mater. Sci.*, 2006, **42**, 266-270, 10.1007/s10853-006-0842-9.

[27] D. P. Dubal, V. J. Fulari, C. D. Lokand, *Nano Energy*, 2015, **11**, 377-399, doi: 10.1016/j.nanoen.2014.11.013.

[28] D. P. Dubal, R. Holze, P. Gomez-Romero, *Microporous Mesoporous Mater.*, 2012, **151**, 511-516, doi: 10.1016/j.micromeso.2011.08.034.

[29] X. X. Wang, D. Han, M. F. Lim, N. D. Singh, C. L. Gan, M. Jan, P. S. Lee, *J. Phys. Chem. C*, 2012, **116**, 12448-12454, doi: 10.1021/jp3028353.

Author information

Ramesh Deokate *received his Ph.D. (2010) in Physics from Shivaji University, Kolhapur (India). Since 2010 he is regular Assistant Professor in Vidya Pratishthan's Arts Science and Commerce College, Baramati (MS), India. He also worked as a postdoctoral fellow at Missouri University Science and Technology, USA. Currently, he focused his research on the in synthesis of 2D and 3D metal oxides/chalcogenides for solar cells, electrochemical supercapacitors, water splitting and chemical sensor applications. His major interests include synthesis of novel nanostructures for energy conversion and storage device technologies.*