International e-Conference on Recent Trends in Nano-Materials and Its Applications-2021
In Association with International Journal of Scientific Research in Science and Technology
Volume 9 | Issue 2 | Print ISSN: 2395-6011 | Online ISSN: 2395-602X (www.ijsrst.com)

Sol-gel spin coated Nickel oxide (NiO) thin film Electrode for Electrochemical Pseudocapacitor Applications

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ABSTRACT

The nickel oxide (NiO) thin films were prepared from nickel chloride precursor by sol–gel dip coating method. The films were characterized in support of their structural, compositional, morphological, and optical and electrochromical measurement using X-ray photoelectron spectroscopy, Field effect scanning electron microscopy, and cyclic voltammetry. XPS measurements discovered that the films exhibited existence of NiO phase. FESEM images showed porous micro granules nature of NiO thin film. The pseudocapacitive properties are tested using cyclic voltammetry, charge–discharge and electrochemical impedance Spectroscopy. The maximum value of specific capacitance obtained is 152Fg^{-1}.

Keywords : Nickel Oxide, X-Ray Photoelectron Spectroscopy, Field Effect Scanning Electron Microscopy, Cyclic Voltammetry

I. INTRODUCTION

Corresponding to the double-layer capacitor of electrochemical capacitor technology is that based on redox pseudo-capacitance concerning oxidation state changes in metal oxides[1], such as amorphous phase of hydrated ruthenium oxide (RuO) [2], MnO2[3], NiO [4], Co_3O_4 [5], are regularly reported with their relatively different microstructures. Conducting polymers such as polypyrrole [6], polyaniline [7], and polythiophene [8] are reported as the electrode materials in pseudocapacitor. The RuO2 is outstanding electrode material, exhibits exceptional electrochemical properties such as high conductivity, a variety of oxidation states and superior electrochemical stability. Since the toxicity and price of RuO2 hold back its potential application in pseudocapacitors. The metal oxides like MnO_2, MoO, CuO, NiO and Co_3O_4 have good electrochemical properties with low cost and abundance in nature. Amongst these metal oxides; NiO is reported with greater values of electrochemical parameters. In fact, the values of specific capacitance of NiO are mainly recognized to the morphology and Corresponding surface area of the material. The fine nanoparticles of NiO have been reported by Yeager et al. [10] as a pseudocapacitive electrode with the value of specific capacitance 243 Fg^{-1}. The single- crystalline NiO nanoplatelet arrays as supercapacitor electrodes have reported by Li et al. [11]. The loose-packed nanoflakes of NiO for supercapacitors have been reported by Lang et al. [13].Nickel oxide has been

expansively prepared by thermal treatment of electrodeposited [12] and sol–gel derived [13] NiO thin films for pseudo-capacitor applications. There are number applications of NiO thin films collectively with LCD, LED, and memory devices and in energy conversion systems like solar cells, Li-ion batteries and supercapacitors [14, 15]. There are various methods to synthesize NiO thin films, in general physical vapor deposition(PVD), electron beam evaporation, electrodeposition, spray pyrolysis, chemical bath deposition, Successive ionic layer adsorption and reaction (SILAR), and Sol-Gel dip coating are used [16].Sol-Gel method is preferred because of its advantages such as low cost, possibility for large area deposition[17]. It offers a low-temperature method for deposition of materials on large area that both inorganic and organic in nature. Sol–gel deposition of NiO.

In the present work, NiO thin films were synthesized using sol–gel dip coating method from nickel chloride precursor and structural morphological properties and electro chemical properties were studied and are reported in this paper.

II. Experimental details

2.1 Synthesis of NiO thin film electrode

The Nickel Oxide (NiO) thin films were synthesized by sol gel method using Nickel Chloride ($NiCl_2.6H_2O$) as a precursor of Nickel oxide and isopropyl alcohol as a starting material and reagent respectively.

A 0.1 M precursor solution was prepared by mixing nickel chloride and 50ml double distilled water and it was stirred well using magnetic stirrer until it became transparent solution, then isopropyl alcohol was added slowly [18]. The prepared solution was stirred again for 6 hours at temperature 50^0 C and then aged for 24 hours to the gel in the viscous form and the gel is deposited on SS substrate by spin coating unit. Before deposition the steel substrate was mirror polished by zero grade polish paper and then kept in ultrasonic bath for 10 mins. The deposited sample was the rotated at 2000rpm for 2min and the film were annealed at 500^0C for 30mins.

2.2 Material characterizations

The XRD pattern was carried out using X-ray diffractometer A D2 PHASER diffractometer with source CuKα1 with λ =1.54184, the 2θ angle is varied from 30^0 to 80^0. The surface morphology has been carried out from FESEM image using FESEM: FEI NoavaSEM 450 Instrument. The XPS measurements were carried out by a Thermo K alpha+ spectrometer using micro focused and monochromated Al Kα radiation with energy 1486.6 eV. The electrochemical supercapacitive performance of the NiO electrode was studied with the help of cyclic voltammetry (C-V) plots.

III. Result and Discussion

Fig-1 shows the XRD patterns of NiO thin film. The deposited films were uniform and well adherent to the substrate. The main peaks present at (2θ) 37.25 (111), 43.23 (200), 62.83 (220), reflections which are matched with the standard diffraction pattern of NiO cubic structure (JCPDS 47–1049) [19].

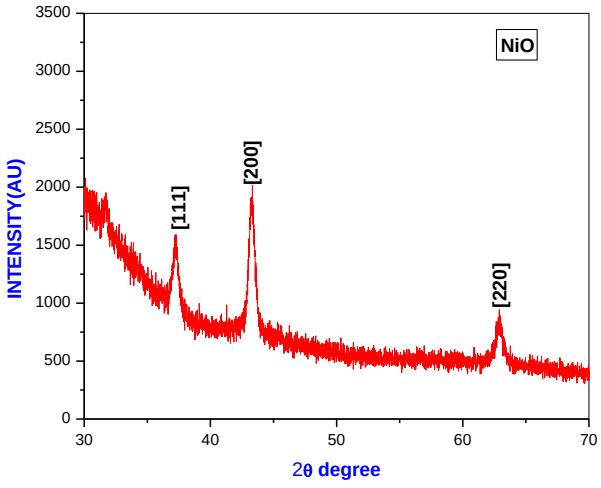
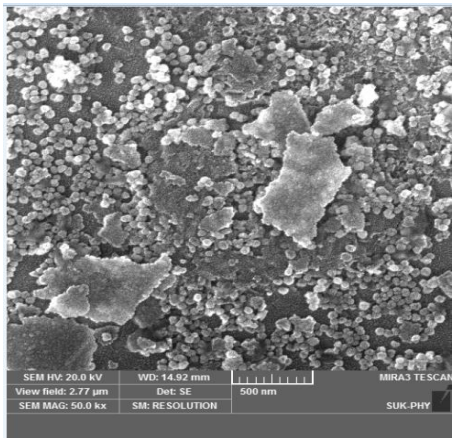
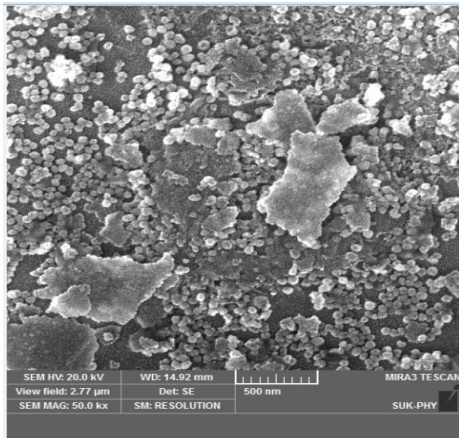


Figure 1 XRD pattern of NiO Thin Film electrode.

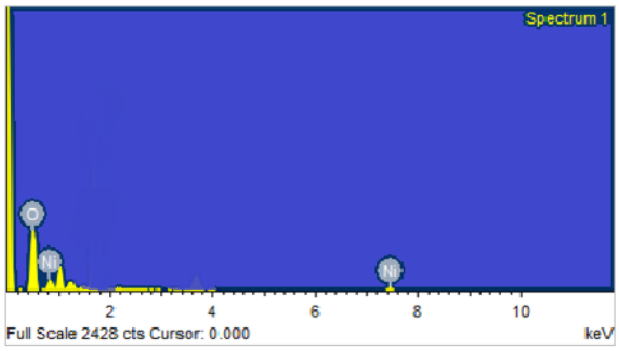
IV. Surface morphological studies

Surface morphology of NiO thin films deposited on stainless steel substrate (SS) substrates by sol-gel spin coating method. The resultant morphology observed under microscopy is shown in Fig 2. It is observed that the SS substrate is well covered with NiO material with smooth and porous micro granules which are advantageous for electrolyte penetration into the film structure which increase the electro chromic performance. In supercapacitors, increased amount of charge can be stored on the highly extended surface area created by large number of pores. Nanocrystalline and porous materials as electrode material exhibit good electrochemical performance because these materials possess both a high surface area and pores [20,21]. EDS demonstrates that Ni, O elements were contained, indicating the formation of NiO, which is reliable with the XPS data. The average weight percentages of O (83.36%) and Ni (16.64%) elements.





(a)



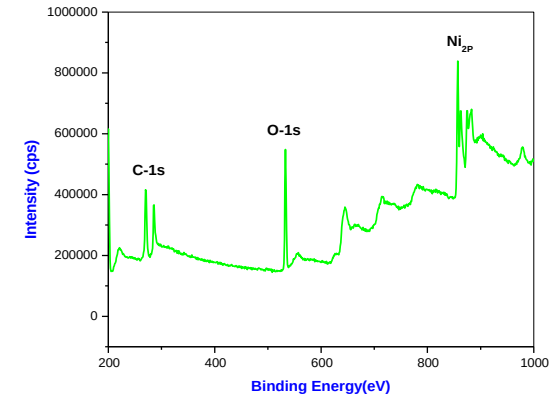
(b)

Fig 2: (a) FESEM image, (b) EDS of NiO Film

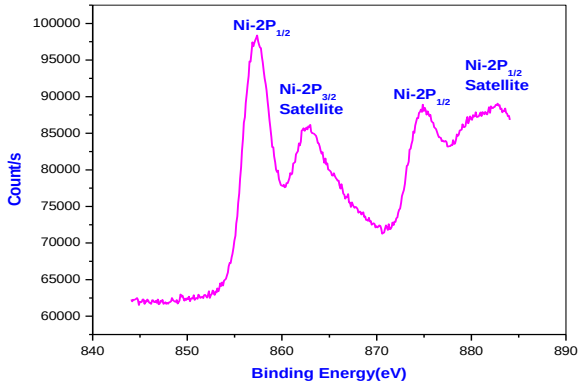
V. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) technique is used to investigate the chemical state of elements present in NiO nanoplatelets as shown in Fig. 3a The Ni 2p spectral peaks in XPS were deconvoluted by way of Gaussian curves.

The Ni2p signal could be deconvoluted into four peaks in the range of 850 to889 eV. Figure 4b shows, the peaks centered at 857.34 and 862.94 eV are featured to Ni2p3/2, and the peaks located at 874.89 and 882.75 eV are featured to Ni2p1/2. This shows highly determined Ni 2p core level spectrum of NiO. The peak of Ni (2p3/2) at a binding energy of 862.94 eV with their associate shake-up satellite peaks at 882.75 eV showed the presence of Ni^{2+} cations. This observation confirmed the NiO pores compiled of pure NiO phase [18]. The Ni (2p3/2) and Ni (2p1/2) peaks are separated by 17.55 eV, which furthermore confirms the formation of only NiO relatively than any additional phase of nickel oxide [22].



(a)



(b)

Fig. 3 (a) Survey XPS spectrum of NiO nanoplatelets grown on SS substrate,(b) Ni 2p core- level spectrum.

VI. Surface wetabillity

Surface wettabilities were evaluated by water contact angle measurements, Surface wettability test which involves the interaction between a liquid and a solid in contact, (sagar bhise). Wettability measurement was carried out for investigating electrolyte/nickel oxide electrode interaction. In general, if the wettability is high, contact angle (θ) will be small and Fig shows the digital photograph of water contact measurement on NiO electrode surface is considered as hydrophilic. As water contact angle is75 ° (less than 90° means more wettability), the Nickel oxide films are hydrophilic in nature. This was because of the strong cohesive force between the oxide present in the nickel oxide compound and water droplet. Generally, low contact angle increases the electrochemical performance [23].

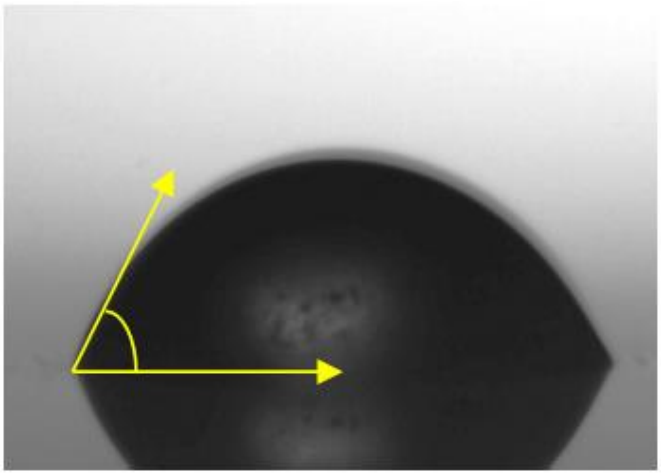


Fig.4 Contact angle image of NiO film electrode

VII. Electrochemical measurements

The elctrochemical performance of sol-gel deposited NiO thin film electrode was tested using cyclic voltameterry measurement. The capacitance (C) was calculated using following relation

$$C = I / (dV/dt) \quad \text{.....(1)}$$

Where I is the average current in ampere and dV/dt is the voltage scanning rate.

The SC of NiO electrode was calculated using following relation;

$$SC = C/ W \quad \text{.....(2)}$$

Where W is the mass of NiO film dipped in electrolyte.

VIII. Effect of scan rate

The CV curves of NiO electrode in 0.1M KOH electrolyte at different scan rates within voltage range of -0.8 to 0.8 are shown in Fig 5. The measurements were performed with NiO thin films as working

electrode and platinum wire as counter electrode and Saturates Calomel Electrode (SCE) as a reference electrode in 0.1M KOH electrolyte. From the cyclic voltametery (CV) curves, the area under curve increased gradually with the scan rate. This indicates that the current is directly proportional to the scan rate, representing an ideal capacitive behavior [24]. The maximum specific capacitance of 152 Fg^{-1} obtained at minimum scan rate of $10mVs^{-1}$.

Obtained results are better than the value previously reported by Wu et al (138 F g^{-1} in 0.5M KOH by electrochemical deposition) [25], Zheng et al (131.6 F g^{-1} in 2M KOH by Hydrothermal method and followed by thermal decomposition) [26].

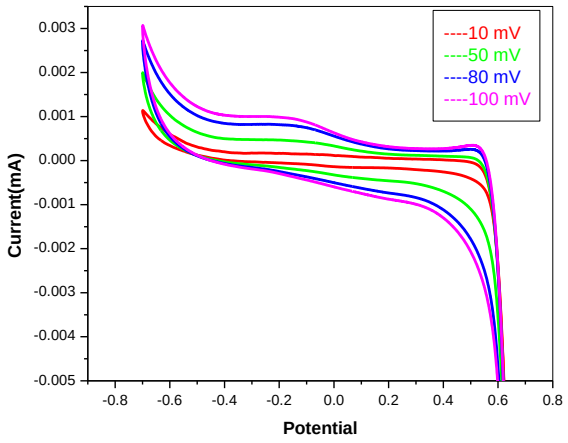


Figure 5: Cyclic voltameterry of NiO electrode in 0.1M KOH electrolyte

IX. Galvanometric charge–discharge studies

In addition, the electrochemical performances of the annealed NiO thin films were studied by galvanostatic charge–discharge cycles (GCD), as shown in Fig. 6. The GCD study was performed at 1 $mAcm^{-2}$ current density between -1.2 to +0.6 V potential windows in 0.1 M aq. KOH. The quick drop in the potential at the starting of the discharge cycles is due to the small equivalent series resistance (ESR) of NiO. The electrochemical parameters such as specific capacitance, energy, and power density of the materials are calculated from the curve by using the equations below [26].

$$C_{sp} = \frac{I_d \times T_d}{m \times dV} \quad (3)$$

$$E.D = \frac{0.5 \times Csp \times dV^2}{3.6} \quad (4)$$

$$P.D = \frac{E.D \times 3600}{T_d} \quad (5)$$

C_{sp} is the specific capacitance of the material, I_d is the discharged current density, T_d is the time required for discharging the device, m is the mass of deposited active material, and dV is the potential window.

The specific capacitance is calculated of energy density, and power density from GCD is 165 Fg^{-1}, 50 $Whkg^{-1}$, 0.72 $kWkg^{-1}$ at $1mAcm^{-1}$.

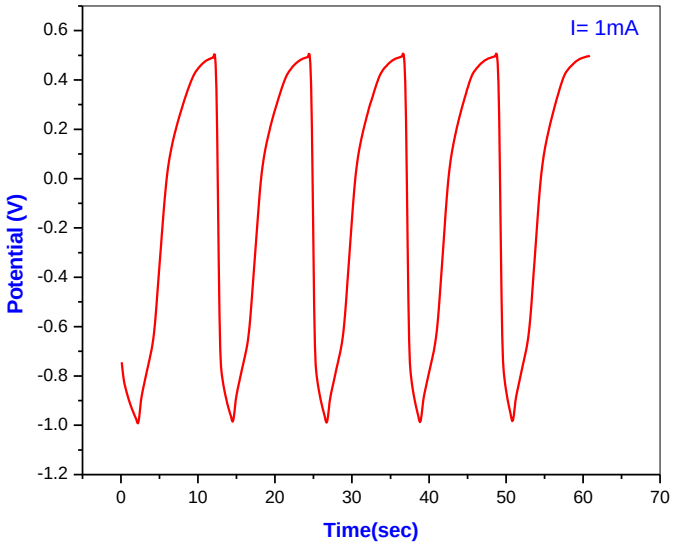


Figure 6: the charge–discharge measurements of NiO electrode in 0.1M KOH electrolyte

X. Conclusion

In this work, we have successfully synthesized NiO thin film electrodes using Sol-Gel method and studied electrochemical supercapacitor application. The XRD pattern confirmed cubic nature of NiO. It was found from the FESEM image that NiO film surface was well-covered with spherical micro granules. The presence of characteristics bonds of NiO were confirmed by XPS analysis. Contact angle measurement revealed the hydrophilic nature of NiO

surface as surface water 75° contact angle was smaller than 90°. The NiO electrode exhibited specific capacitance of 152 F g^{-1}. Energy density and power density from GCD 50 $Whkg^{-1}$, 0.72 $kWkg^{-1}$ at 1$mAcm^{-1}$.

These results reveal that sol gel deposited NiO thin film can be a good candidate as electrode material for electrochemical supercapacitor.

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