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Synthesis and Characterization of Chemically Deposited Nickel Sulphide Thin Film Electrodes for Electrochemical Supercapacitor Application

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ABSTRACT

Nickel sulphide (NiS) thin films were synthesized on glass and stainless steel (SS) substrates using a simple chemical bath deposition route. The structural, surface morphology were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM) respectively. The electrochemical capacitor performances were examined by using cyclic voltammetry, galvanostatic charge-discharge test and electrochemical impedance spectroscopy. In cyclic voltammetry (CV) studies, the NiS electrode exhibits the specific capacitance of 441 Fg^{-1} has been obtained in 2 M KOH solution at a scan rate 10 mVs^{-1} within the potential range 0 to 0.8 V vs. Ag/AgCl. In charge-discharge behaviors, the supercapacitive parameters such as specific energy (S.E.) and specific power (S.P.) are 10.1 $Whkg^{-1}$ and 4.5 $KWkg^{-1}$ respectively. Impedance spectroscopic analysis revealed that the ESR is 11 Ω in KOH electrolyte.

1. Introduction

Electrochemical supercapacitors are powerful energy storage systems, which have higher energy density than dielectric capacitors and have higher power density than batteries [1, 2]. Supercapacitors play an important role in various power and energy source applications [3]. Supercapacitors are classified into two types based on charge storage mechanisms, electrical double-layer capacitors dominated by electrostatic charge diffusion and accumulation at the interface of the electrode/ electrolyte and pseudocapacitors governed by Faradaic reactions at the electrode materials [4-6].

Supercapacitor electrode materials have three types such as carbon, metal oxides and polymers. Among the electroactive materials, RuO_2 possesses pseudocapacitance property and exhibits much higher specific capacitance, highly reversible redox reaction and excellent cycle life [7-9]. However, the high cost and toxic nature of RuO_2 has prompted the search for other transition metal oxides/hydroxides [4]. In the last few years, metal sulfides have recently emerged as a new type of electroactive materials due to their excellent redox reversibility and relatively high capacity/capacitance [10-13]. We have chosen NiS as an electrode for supercapacitor because of its higher stability, high abundance, low cost, better safety, and environmental friendliness in comparison with other metal sulphide. Many techniques have been currently used in order to produce NiS thin films electrode. Ting Zhu et al. synthesized hierarchical NiS hollow spheres by an efficient template-engaged conversion method. Researchers found that, NiS hollow spheres exhibit high specific capacitances of 583-927 Fg^{-1} at various current densities of 4.08-10.2 Ag^{-1} [14]. Jiaqin Yang et al. studied the novel hierarchical flower-like nickel sulfide assembled by nanoplates has been successfully synthesized via a template-free and one-step solvothermal method. Researchers investigated that the sample with more nanoplates shows a higher specific capacitance and promising cycling stability. After 3000 cycles, a high specific capacitance of 778.8 Fg^{-1} maintains at current density is 4 Ag^{-1} [15]. Apostolova et al. reported a thin-layer NiS electrode is capable of reversible electrochemical transformation during more than 200 cycles with an output capacitance of 143 Fg^{-1} [16]. Among these deposition techniques, chemical bath deposition presently attracts considerable attention, as it does not require sophisticated instrument. Any insoluble surface to which the solution has a free access will be a suitable substrate for deposition. The low temperature deposition avoids oxidation and corrosion of metallic substrates. Chemical deposition results in pinhole free and uniform deposits are easily obtained since the basic building blocks are ions instead of atoms [17]. The preparative parameters such as bath temperature, stirring rate, pH, solution concentration, etc. are easily controllable and better orientations and improved grain structure can be obtained [18].

In the present work, we report the synthesis of NiS thin films by chemical bath deposition method onto stainless steel substrate using chemical bath deposition method. The supercapacitive behavior of NiS film electrodes in KOH electrolyte was studied in terms of with respect to various parameters such as, scan rates, stability cycles, charging-discharging, EIS study and efficiency.

2. Experimental Methods

The stainless steel (SS) substrates were used for the prepared of NiS thin film electrode. This substrate was polished with polish paper to a rough finish, and ultrasonicated before use. In the present work, the chemical bath deposition method was used to deposit the NiS thin films on SS substrates which had been treated as described above.

Deposition of NiS thin films using analytical reagent grade (Loba, India) nickel sulphate and thioacetamide, are generally used as source of nickel and sulphide respectively. The films were prepared by taking solutions of 10 mL of 0.8 M nickel sulphate in 100 mL beaker to which 15 mL of 7.4 M triethanolamine (TEA) and 10 mL of 0.8 M thioacetamide added successively. The solution was stirred well so that homogeneous solution is formed. Then 35 mL of 14 M ammonia was added and total volume of beaker made up to 100 mL at room temperature. The pH after the mixture thoroughly stirred with glass stirring rod come to ~10. The SS substrates were vertically immersed into the solution and supported on the walls of the beaker. The substrates were taken out from the beaker after 10 hours. The deposited NiS thin film was adhesive, uniform, black color with polycrystalline nature [17,19].

The thickness of the NiS film was measured by weight difference method using sensitive microbalance. The pseudocapactive properties of NiS thin films electrodes were studied using cyclic voltammetry (CV), galvanostatic charge/discharge test and electrochemical impedance spectroscopy (EIS) in 2 M KOH aqueous solution. These experiments were carried out with potentiostat/galvanostat (Princeton Applied Research,

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PARSTAT 4000). A typical three electrode cell was employed; NiS as a working electrode platinum wire as the counter electrode, and Ag/AgCl used as the reference electrode. All electrochemical experiments were carried out at room temperature.

3. Results and Discussion

3.1 Structural and Morphological Analysis

The morphology and crystal structure of nanocrystalline NiS thin films were investigated by scanning electron microscopy and X-ray diffraction techniques respectively. Structural analysis of NiS thin films was carried out by X-ray diffraction technique. Fig. 1 shows typical XRD pattern of NiS thin film on glass substrate. Nanocrystalline nature of NiS films is confirmed from XRD pattern since observed diffraction peaks are weak and are of low intensity. Comparison of *d*-values with JCPDS 02-1280 and 86-2280 data for NiS shows that the material is NiS having hexagonal and rhombohedral structure. The NiS thin film having four diffraction peaks at angles 2θ ~37.42°, 46.57°, 60.68° and 81.62° are correspond to (220), (102), (103) and (161) plane respectively [19-21]. It is observed that, NiS film is prepared at room temperature having grain size is ~21 nm.

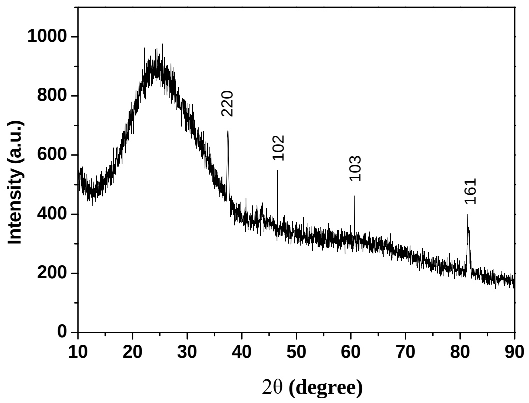

Fig. 1 XRD pattern of NiS thin films

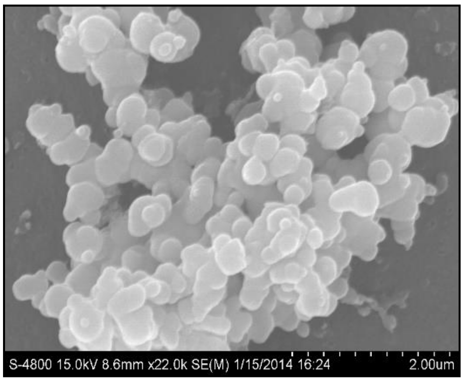

Fig. 2 The SEM image of as-deposited NiS film

Fig. 2 shows the SEM image of the MCBD deposited NiS thin film. It is observed from the micrographs that NiS film is homogeneous, fine grained and well covered to the substrate with overgrowth of some particles. The overall surface structure is seen to have grains of spherical shape. These films revealed that grains were very small in size with no well-defined grain boundaries. The average grain size of NiS film is found that 300 nm. Some micro porous space between the fine particles can also be seen. The porosity of films can enhance the redox [20].

3.2 Supercapacitive Properties of the NiS Thin Film Electrode

Chemically deposited NiS electrodes were used in the electrochemical capacitor and their performances were tested using CV. To perform cyclic voltammetry tests a series of changing voltages at a constant sweep rate (dV/dt) is applied and the response current is recorded. The supercapacitive studies carried out by means of effect of scan rate and stability studies. The capacitance can be estimated by the following equation [6,22],

$$C(V_f - V_i) = q = \frac{1}{v}\int_{V_i}^{V_f} I(V)dV \quad (1)$$

where, C is the total capacitance, I the current density (A/cm²), v the sweep rate (V/s), v_i the initial and v_f the final voltages (V). The integral on the right-hand side of Eq.(1) is the area under the CV. Thus, the total surface charge, (or total capacitance) of the deposit material can be estimated by evaluating the area under the capacitive current-voltage curve portion of a CV. The specific capacitance (Fg^{-1}) of the electrode was obtained by dividing the capacitance to weight dipped in the electrolyte. The interfacial capacitance (Fcm^{-2}) was obtained by dividing the capacitance to area dipped in the electrolyte.

Cyclic voltamogram of the NiS electrode of thickness 0.00016 g/cm², in aqueous electrolyte 2 M solution of KOH were studied in the voltage range of 0 to 0.8 V Vs Ag/AgCl. The KOH electrolyte gave the largest current, which was greater than the other electrolytes. The area of working electrode was 1 cm². The voltammetric responses of NiS electrode at different scan rates are shown in Fig. 3. It was found that the current under curve is slowly increased with scan rate. This showed that voltammetric currents are directly proportional to the scan rate of CV, indicating an ideally capacitive behavior [14-16,23-25].

Variation of specific capacitance and interfacial capacitance values with scan rate is shown in Fig. 4. The specific and interfacial capacitance values are decreased from 441 to 160 Fg^{-1} and 0.071 to 0.026 Fcm^{-2} respectively, as the scan rate was increased from 10 to 100 mVs^{-1}. As the scan rate is increased, there is a slight decrease in the specific capacitance that is comparable to previously reported data. At lowest scan rate 10 mVs^{-1}, maximum capacitance is found to be 441 Fg^{-1}.

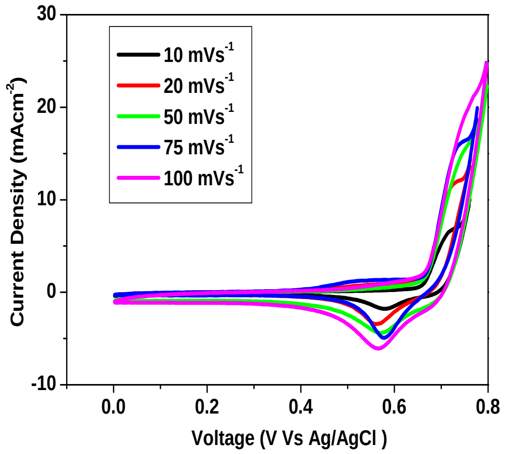

Fig. 3 The CV curves of NiS electrode at 10 to 100 mVs^{-1} scan rates in 2 M KOH electrolyte

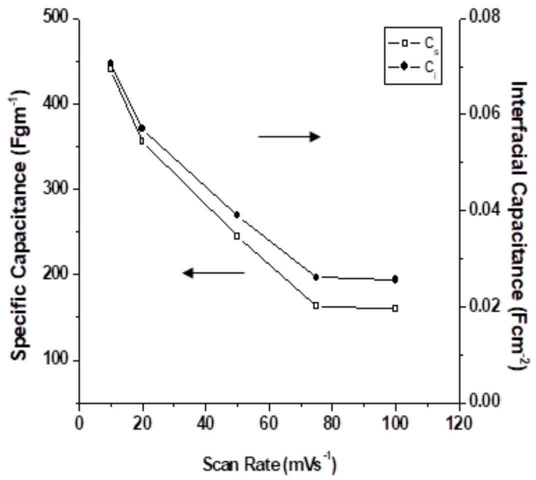

Fig. 4 The specific and interfacial capacitances of NiS electrode at 10 to 100 mVs^{-1} scan rates in 2 M KOH electrolyte

3.3 Galvanostatic Charge-Discharge Studies

The electrodes of NiS were subjected to galvanostatic charge-discharge cycling between 0 and 0.8 V in 2 M KOH solution at different current density of 0.5, 1 and 2 $mAcm^{-2}$. Typical curves of potential variation with time of cycling are shown in Fig. 5, it can be seen that, the nonsymmetric behavior of voltage-time curve was seen, that is IR drop was observed. The discharge profile showed two parts; a resistive component arising from the sudden voltage drop (linear portion parallel to y-axis) representing the voltage change due to the internal resistance and a capacitive component

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(curved portion) related to the voltage change due to the change in energy within the capacitor. The specific energy (E), and specific power (P) and coulomb efficiency (η%) are calculated using following equations [4,6,26],

$$E = \left(\frac{0.5}{3.6}\right) C_s (\Delta V)^2 \quad (2)$$

$$P = \left(\frac{E}{t_d}\right) \quad (3)$$

And, Columbic efficiency (%) $\eta = \left(\frac{t_d}{t_c}\right) \times 100$ (4)

where, C_s is the specific capacitance and ΔV (V) is the voltage window. t_d is discharging time (s), t_c is charging time (s).

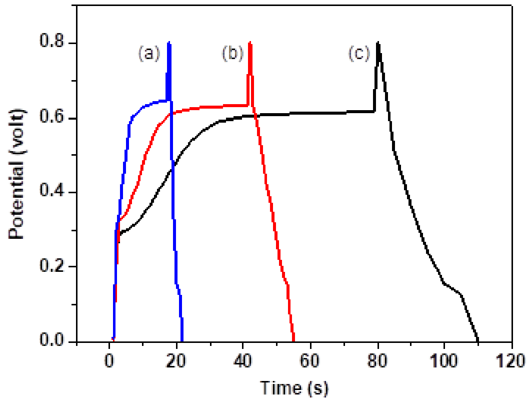

Fig. 5 Charging-discharging behavior of NiS electrode at a current density of (a) 2, (b) 1, (c) 0.5 mAcm^{-2} in 2 M KOH electrolyte

The capacitance, energy density and power density of the NiS electrode were calculated using Eqs.(2-4). The specific capacitance value is 113, 94 and 47 Fg^{-1} for NiS thin film electrode at current density 0.5, 1 and 2 mAcm^{-2}, respectively. The maximum energy density of 10.1 Whkg^{-1} and power density of 4.5 kWkg^{-1} were obtained at a current density 0.5 mA/cm^2. This increase in specific energy and power may be due to increased time for charging and discharging of capacitor. The energy efficiency, 36%, was obtained. Variation of energy density with power density values of NiS electrode at different current densities is shown in Fig. 6.

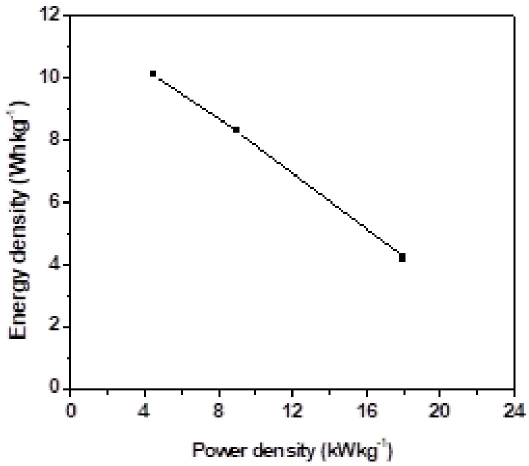

Fig. 6 Variation of energy density with power density values of NiS electrode at different current densities

3.4 Electrochemical Impedance Analysis (EIS Studies)

Electrochemical impedance spectroscopy, a powerful technique for the investigation of the capacitive behavior of electrochemical cells, has been also used to characterize our materials.

Nyquist plots obtained for as deposited NiS electrodes at 0.8 V Vs Ag/AgCl is shown in Fig. 7, where Z_{re}' and Z_{im}'' are the real and imaginary parts of the impedance, respectively. It displays a semicircle in the high frequency and a linear curve in the low-frequency region. The semicircle in the high-frequency region is related to the reaction kinetics at the electrode and electrolyte interfaces. The linear curve at the low-frequency region can be attributed to the diffusion-controlled process in the electrolyte [15, 24, 25]. The initial non-zero intercepts in high frequency regime at the beginning of the semicircle and is due to the electrical resistance of the electrolyte (R_{ele}). The value for ESR for as deposited NiS a thin film is 11 Ω in KOH electrolyte.

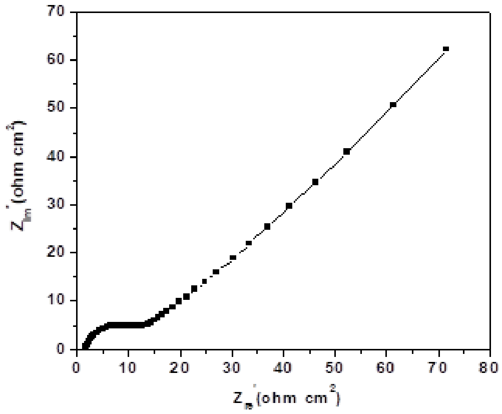

Fig. 7 Nyquist plots of nickel sulphide electrode in 2 M KOH

4. Conclusion

In conclusion, NiS thin film electrodes have been prepared successfully at room temperature by chemical bath deposition method and used in supercapacitors. The XRD analysis showed the NiS thin films are amorphous. The SEM image of NiS film showed porous structure and the film surface covered with agglomerates of different sizes. The as-prepared NiS thin film electrode has excellent electrochemical capacitive characteristic with potential range 0 to +0.8 V Vs Ag/AgCl at constant concentration 2 M KOH solution. The electrochemical study revealed that the NiS electrode showed high specific capacitance of 441 Fg^{-1}. Charge-discharge curves confirmed that the capacitance consisted from EDLC and pseudocapacitance. The specific energy (E), specific power (P) and coulomb efficiency (η%) was 10.1 Whkg^{-1} and 4.5 kWkg^{-1}, and 36%, respectively. Impedance spectroscopic analysis revealed that the ESR is 11 Ω in KOH electrolyte.

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