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# Electrochemical supercapacitive studies of chemically deposited $Co_{1-x}Ni_xS$ thin films



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# ABSTRACT

In the present work, we demonstrate the synthesis of  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  ( $0 \le x \le 0.2$ ) metal chalcogenide thin films via a simple, inexpensive solution growth process and its subsequent studies aiming towards supercapacitive application. The as-prepared  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  thin films revealed microstructure similar to spirulina algae-like nanowires with uniform substrate coverage. The highest average, total roughness and particle height values were observed from atomic force microscopy measurement for x = 0.05 composition. The electrochemical measurements on thin-film electrodes have been done via cyclic voltammetry, galvanostatic charge-discharge studies, and electrochemical impedance spectroscopy. The as-grown  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  (x = 0.05) thin-film electrodes demonstrated a reversible electrochemical feature, offers a high specific capacitance of 880 F g<sup>-1</sup> at 6 mA cm<sup>-2</sup> current density and cycling stability of 79% after 5000 cycles. This performance of  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  electrodes at x = 0.05 was credited to its porous and large accessible area of entangled nanowire structure and effective intercalation of electrolyte ions through the electrode. This report opens new opportunities for the development of the metal chalcogenide thin films for high capacity electrochemical devices.

## 1. Introduction

The 21st century is the era of portable/wearable electronic gadgets viz. mobile phones, cameras, laptops, smartwatches, activity trackers, etc. The energy consumption of these smart electronic devices requires improved energy storage devices for better performance [1]. Therefore, the development of devices having high energy/power outputs and a long life with a short charging time is needed. Hence, the development of novel energy storage materials and devices is the need of the hour. This task must be handled with attention to the facts of fossil fuel

scarcity, human health hazards and environment/ecology/ecosystem impact [2,3]. The supercapacitor is one such proficient eco-friendly energy storage device with outstanding properties such as short charging time, safe operation and high power density with a longer life cycle achieved by the fine-tuning of the surface characteristics of the electrodes [2]. However, this redeemer (i.e. supercapacitor) is confronting issues of lower energy density in competition with lithium batteries [4], the problem of scarcity and the expensive nature of RuO<sub>2</sub> and platinum electrode materials have also hindered the progress of supercapacitor applications [5]. Therefore, ongoing research activities

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are focused on the development of efficient, abundant, inexpensive and eco-friendly alternatives. The transition metal oxides exhibit high pseudocapacitance among the different electrode materials and have a much higher specific capacitance owing to multiple oxidation states [6]. Therefore, numerous electrode materials have been explored such as metal oxides (MnO<sub>2</sub>, NiO, and MoO<sub>3</sub>) and hydroxides (Ni(OH)<sub>2</sub>) [7]. Recently various research groups are being involved in the engineering of microstructures of different metal chalcogenide/oxide/polymer/carbonaceous materials, since, the performance of supercapacitor strongly relies on the surface microstructure [8]. In the past few decades, transition metal sulfide and nanomaterials are gaining attention for being used as an electrode for electrochemical supercapacitors, lithium-ion batteries (LIBs), solar cells and photocatalytic applications [9,10]. The binary metal sulfides such as, CuS, CoS<sub>2</sub>, Co<sub>3</sub>S<sub>4</sub>, NiS, CoNiS, SnS, MnS, Bi<sub>2</sub>S<sub>3</sub>, CuS, La<sub>2</sub>S<sub>3</sub> and Sm<sub>2</sub>S<sub>3</sub> etc, utilized for supercapacitor applications [3,4,6] possess advantageous properties of high specific capacitance, long cycle stability, higher electrical conductivity, rich redox chemistry, high reversible capacity, mechanical and thermal stability [10,11]. The coupling of binary-to-ternary composite materials allows to improve the material properties and helps to improve the electrochemical performance [4]. The ternary transition sulfide materials such as Fe-Co-S, Ni-Co-S, Mn-Co-S are popular in this sense. Amongst ternary transition sulfides, Co-Ni-S is a significant material owing to its superior electrochemical characteristics and high capacitance than oxides [7]. Zardkhoshoui et al. reported the specific capacitance ( $C_s$ ) of 1379.16 F g<sup>-1</sup> with a significant rate performance of 67.2% for CoGa<sub>2</sub>O<sub>4</sub> (CGO)/nickel foam electrode [12]. Lately, ZnS/Ni- $Co_2S_4/Co_9S_8$  nanotube (ZNCN) revealed C<sub>s</sub> of 1618.1 F g<sup>-1</sup> at 1 A g<sup>-1</sup> current density in 2 M KOH electrolyte, Cs remains 77% of the original after 5000 cycles at  $15 \text{ Ag}^{-1}$ . This result proposes the 1.2-fold augmentation as compared to pure 1.44-fold improvement captured to pure NiCo<sub>2</sub>S<sub>4</sub> (1127 F g<sup>-1</sup>) [13]. The bimetallic sulfide NiCo<sub>2</sub>S<sub>4</sub> materials showed a vivid improvement in the cycle stability and voltammetric response with a little reduction in C<sub>s</sub> value of 516 F g<sup>-1</sup> of the NiS electrode  $C_s$  value of 897 F g<sup>-1</sup> [14]. Ni nanowires (NWs) surface was uniformly covered with optimized Ni-Co-S using electrodeposition technique revealed excellent rate capability and good 392.8 C cm<sup>-1</sup> volumetric capacity at  $0.5 \,\mathrm{A \, cm^{-3}}$  [15]. The hierarchical nanowire-like morphology, high surface area, and uniform pore distribution were obtained using ultrasonic treatment in NiCo<sub>2</sub>O<sub>4</sub> electrodes which showed 1460 F g<sup>-1</sup> specific capacitance with 84% electrochemical stability after 3000 cycles in 3 M KOH electrolyte at  $100 \text{ mV s}^{-1}$  [16]. A recent trial has made to explore the NiCo<sub>2</sub>S<sub>4</sub> with r-GO for improved electrochemical properties due to the outstanding chemical and physical characteristics of the graphene [17]. The electrochemical properties of  $CoS_x$ -NSA showed the highest specific capacitance of 448 F g<sup>-1</sup> at a current density of  $2 \text{ mA cm}^{-2}$  [18].

Herein, we report on the chemical synthesis of  $\text{Co}_{1-x}\text{Ni}_x\text{S}$ ( $0 \le x \le 0.2$ ) thin-film electrodes for the fabrication of high specific capacitive and excellent rate capability supercapacitor. Consequently, the current work also focuses on the study of microstructural, topographical and electrochemical characteristics change from a binary to ternary metal sulfides.

## 2. Methods and measurements

#### 2.1. Materials synthesis

The deposition of  $\text{Co}_{1-x}\text{Ni}_xS$  ( $0 \le x \le 0.2$ ) thin-film electrodes was done on an ultrasonically pre-cleaned mirror polished stainless steel (SS) substrates ( $1 \text{ cm} \times 7.5 \text{ cm}$ ) using a solution growth process. In the actual deposition, analytical reagent-grade cobalt sulfate ( $\text{Co}(\text{SO})_47\text{H}_2\text{O}$ ), thiourea ( $\text{CSN}_2\text{H}_4$ ), triethanolamine ( $\text{C}_6\text{H}_{15}\text{NO}_3$ ), ammonia ( $\text{NH}_3$ ) and nickel sulfate ( $\text{Ni}(\text{SO})_4\text{H}_2\text{O}$ ), were used. The typical deposition was carried out using 10 ml (1 M) cobalt sulfate, 6 ml (TEA), 15 ml (25%) ammonia and 10 ml (1 M) thiourea. The adequate amount of 1 M nickel

sulfate was added to define the value of dopant (x) between 0.05 and 0.2. The overall volume of the reactive solution was prepared up to 250 ml by adding double-distilled water. The stainless steel (SS) substrates were attached to a specially designed substrate holder which was then immersed vertically in a reacting solution. The reaction bath temperature was set at 80 °C using PID controlled unit within  $\pm 0.1$  °C accuracy. Finally, after 90 min deposition time, the substrates were detached from the holder, rinsed (5–6 times) with double distilled water and dried naturally at room temperature and preserved in the dark desiccator.

## 2.2. Materials characterization

The thickness of the Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) thin-film electrodes were measured using an AMBIOS Make XP-1 stylus profilometer. The surface wettability was measured by a contact angle meter (HO-IAD- CAM-01, Hallmark Opto-mechatronics, M.S. India). Raman spectroscopic measurement was done on a Jobin Yvon Raman system using an argon ion laser (514.5 nm) as the excitation source. The surface morphology and composition were acquired by scanning electron microscope (SEM) (TESCAN VEGA) equipped with energy dispersive spectroscopy (EDS) (Ultim Max: Oxford Instruments). The morphology was viewed using (JSM-7610F) ultra-high resolution Schottky field-emission scanning electron microscope (FE-SEM) of JEOL. Surface topographical features were observed using atomic force microscopy (DI3000 from Digital Instruments) in a Tapping Mode using Nanosensors Point probes (nominal tip radius  $r_{tip} = 10$  nm, resonance frequency range  $f_{res} = 306-353$  kHz, and spring constant  $k = 43-68 \text{ N m}^{-1}$ ). By using the same instrument, the electrostatic force microscopy (EFM) investigation was performed using Pt-Ir coated probes (resonance frequency = 75 kHz, tip curvature < 20 nm and k = 2.8 N m<sup>-1</sup>), the lift mode height was 40 nm and the bias voltage was 2 V. Also Kelvin Probe Force Microscopy (KPFM) measurements of the samples were performed (60 nm lift mode) using the abovementioned Pt-Ir probes. The acquired data were processed using SPIP software from Image Metrology company [19]. Electrochemical measurements such as cyclic voltammetry (CV), galvanostatic charge-discharge and electrochemical impedance spectroscopy (EIS) were carried out by an electrochemical workstation CHI 660 A (CH Instruments, USA) at room temperature. All the electrochemical measurements were carried out using a three-electrode electrochemical cell containing 2 M KOH aqueous solution as the electrolyte. Co<sub>1,r</sub>Ni<sub>r</sub>S  $(1 \text{ cm} \times 1 \text{ cm} \text{ working area})$  was directly used as the working electrode, a saturated calomel electrode (SCE) as a reference electrode, and a platinum coil as a counter electrode, respectively.

## 3. Results and discussion

## 3.1. Film growth and reaction mechanism

The principle of the solution growth technique is to control the rate of chemical reaction in such a way that, the deposition of a solid thin film from the reacting precursors can be realized [20,21]. This type of chemical deposition begins once the concentration of the cations and anions exceeds the solubility product ( $K_{sp}$  of  $CoS = 10^{-21}$ ) [21]. Here, the formation of  $Co_{1-x}Ni_xS$  film depends on the release rate of Co2+/Ni2+ and S2- ions and the responsible reactions can be written as follows [20,21];

$$CoSO_4 + n.(TEA) + O H \rightarrow [Co(TEA)_n]^{2+} + H_2SO_4 + H_2O$$
<sup>(1)</sup>

$$NiSO_4 + n.(TEA) + O H \rightarrow [Ni(TEA)_n]^{2+} + H_2SO_4 + H_2O$$
<sup>(2)</sup>

$$(NH_2)_2 CS + 2O H \leftrightarrow S^{2-} + 2H_2 O + CH_2 N_2$$
 (3)

$$x[Ni(TEA)_n]^{2+} + (1-x)[Co(TEA)_n]^{2+} + S^{2-} \to Co_{1-x}Ni_xS + n(TEA)$$
(4)

#### Table 1

Some physical and compositional parameters of  $Co_{1-x}Ni_xS$  ( $0 \le x \le 0.2$ ) thin film electrodes.

Composition (x)	Film thickness (nm)	Concentratio	on in the bath	(mol %)	Concentration in the film (atomic %)		
		Со	Ni	S	Со	Ni	s
0	4950	50	-	50	78.698	-	21.302
0.05	4290	47.5	2.5	50	76.014	3.538	20.448
0.1	3200	45	5	50	69.398	6.298	24.306
0.15	2520	42.5	7.5	50	68.046	8.854	23.1
0.2	2118	40	10	50	64.322	12.998	22.68



**Fig. 1.** Surface wettability studies on  $Co_{1-x}Ni_xS$  ( $0 \le x \le 0.2$ ) thin film electrodes.



Fig. 2. Raman spectra for the typical Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) thin film electrodes.

The color of the as-grown samples was found to be changed from greenish to greenish-blue with the addition of Ni into CoS host. The terminal thickness of as-grown layers was found to be decreased from 4950 nm to 2118 nm with the increased *x* from 0 to 0.2 (Table 1). This behavior can be accredited to the interstitial site occupancy of Ni-ions resulting in extensive scattering and thus hindering the film thickness [22]. Surface wettability of thin-film electrodes was examined to understand the nature of growth and surface modifications in the deposited films. From Fig. 1, it is observed that the pure CoS is super hydrophilic ( $\theta < 90^{\circ}$ ), whereas, with increasing Ni concentration the transformation of the surface from hydrophilic to hydrophobic takes place.

## 3.2. Compositional analysis

The energy-dispersive X-ray spectroscopy (EDS) measurement was carried on  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  thin films to detect the presence of Co, Ni and S elements. The as-deposited CoS electrode was found to be S-deficient, Co content was around  $\approx$ 79%, similar observations were shown in our earlier studies [23]. The atomic percentage of the Co, Ni and S elements obtained from the EDS measurement are documented in Table 1. Further, the replacement of Co ions by Ni ions was observed with the increased composition parameter (*x*). However, S-content was found to be almost constant throughout the composition range studied.

### 3.3. Raman study

Fig. 2 reveals the Raman spectra of  $Co_{1-x}Ni_xS$  ( $0 \le x \le 0.2$ ) electrodes in the range of  $100 \text{ cm}^{-1}$  to  $1000 \text{ cm}^{-1}$ . The peaks at  $664 \text{ cm}^{-1}$ ,  $600 \text{ cm}^{-1}$ ,  $509 \text{ cm}^{-1}$ ,  $467 \text{ cm}^{-1}$ , and  $188 \text{ cm}^{-1}$  are attributed to CoO or  $Co_3O_4$  [24]. However, these peak positions are shifted at x = 0.2 at  $656 \text{ cm}^{-1}$ ,  $612 \text{ cm}^{-1}$ ,  $501 \text{ cm}^{-1}$ ,  $458 \text{ cm}^{-1}$  and  $186 \text{ cm}^{-1}$  correspondingly. The shifts in Raman peaks detected for Co<sub>3</sub>O<sub>4</sub> due to the incorporation of Ni atom into CoS lattice. The oxide content present in as-deposited Co<sub>1-x</sub>Ni<sub>x</sub>S samples probably comes from the exposure of films to the air as cobalt eagerly gets oxidized in the air [24]. Generally, the formation of metal oxide affects the surface chemistry, topography and hence it improves the electrochemical properties of the material. Such materials then, in turn, provide higher rate capability and higher capacitance than double-layer capacitor [25,26]. The Cobalt oxide (CoO) shows high theoretical specific capacitance ( $\sim$ 3560 F g<sup>-1</sup>) and it is reported that the existence of CoO in the material may help to enhance the electronic and redox properties of metal composites [25,26]. The peaks at  $290 \text{ cm}^{-1}$ ,  $322 \text{ cm}^{-1}$ ,  $358 \text{ cm}^{-1}$  and  $820 \text{ cm}^{-1}$  show the presence of Ni<sub>3</sub>S<sub>2</sub> phase [16].



**Fig. 3.** Scanning electron micrographs of CoS and Co<sub>1-x</sub>Ni<sub>x</sub>S samples (a–b) x = 0, (c–d) x = 0.05, (e–f) x = 0.1, (g–h) x = 0.15 and (i–j) x = 0.2 at 5000 and 20 000× magnifications, respectively.



Fig. 4. AFM characterizations of  $Co_{1-x}Ni_xS$  ( $0 \le x \le 0.2$ ) thin films (a) 2D and 3D-AFM topography (b) Angular spectra, Sobel transformation and Height histograms.

## 3.4. Morphological observations

## 3.4.1. SEM observations

The morphologies of  $Co_{1-x}Ni_xS$  ( $0 \le x \le 0.2$ ) film electrodes were viewed via scanning electron microscopy. The micrographs (Fig. 3 a-b)

of pure CoS (x = 0) revealed complete substrate coverage of spirulina algae-like nanowires. Generally, this type of highly porous morphology is important for the electrode material to be developed as the super-capacitor device [23]. With increasing Ni concentration in CoS, the tendency of improved nucleation over the growth rate of nanowires was

Table 2

The surface roughness parameters obtained from AFM measurement.

Parameter	Particle height	Average roughness S <sub>a</sub>	RMS roughness	Total roughness	Skewness,	Kurtosis moment,	Surface area ratio,
(x)	(nm)	(nm)	S <sub>q</sub> (nm)	S <sub>t</sub> (nm)	S <sub>sk</sub>	S <sub>ku</sub>	S <sub>dr</sub> (%)
0	670	656.59	674.83	1189.8	1.077	1.212	102.33
0.05	810	719.69	634	1353.9	1.053	1.143	163.3
0.1	700	647.06	660.09	1117.5	1.053	1.142	136.5
0.15	380	369.23	385.68	1001.9	1.126	1.361	81.57
0.2	610	504.53	628.96	1212.3	1.115	1.328	146.65

observed. The development of a large number of nanowires occurs for x = 0.05 (Fig. 3 d). This surface modulation (a large number of pore formation) of Co<sub>1-x</sub>Ni<sub>x</sub>S electrodes with *x* increases the surface area which is can assist intercalation and de-intercalation of electrolyte ions to aid the charge storage mechanism [7]. Also, the nanowire morphology with a porous nature is advantageous as it offers more reaction active sites for energetic ions and electron transport. At, x > 0.05 concentration micrographs reveal nanowires anchored on an already grown microstructure and a sort of recrystallization owing to the addition of Ni was observed. Some crakes were also noticed at higher compositions. It is worth noting that such nanowire-based structures cause the surface to become hydrophobic by pinning the droplet or forming the air pockets, which leads to reduced solid-liquid interface area [27]. This morphological observation thus supports our wettability studies.

## 3.4.2. AFM observations

The surface topography of  $\text{Co}_{1-x}\text{Ni}_xS$  ( $0 \le x \le 0.2$ ) electrodes were viewed using an atomic force microscope. The 2D topography, at x = 0.05 shows spaghetti-like structures (Fig. 4 a) with porous topography. Such a porous topography is useful for effective intercalation of electrolyte into the electrode. The topography at x = 0.2 shows a network of multifaceted elongated nanowires/flakes. The 3D-topographs of Co<sub>1-x</sub>Ni<sub>x</sub>S electrodes (Fig. 4 a) consist of hillocks and valleys with complete substrate coverage signifies suitability of as-synthesized electrodes for energy storage application. The different AFM parameters such as average roughness  $(S_a)$ , RMS roughness  $(S_a)$  total roughness  $(S_t)$ , kurtosis  $(S_{ku})$ , skewness  $(S_{sk})$  and texture direction  $(S_{td})$  [19], were calculated by the standard relations and are documented in Table 2. One can notice that the topography shows enhanced crystalline nature by the integration of Ni into CoS and hence, the average and RMS roughness values were found to be increased up to x = 0.05. This increased RMS roughness can be accredited to improved grain growth and a more porous structure as shown by SEM. At a higher concentration of Ni into CoS host, roughness decreases except at x = 0.2. The positive skewness moment throughout the composition range ( $0 \le x \le 0.2$ ) indicates that the surface has more hillocks than valleys. The Kurtosis moment provides predictable insights about the imbalance of height distribution in topography [22], both the CoS (x = 0) and Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0.05 \le x \le 0.2$ ) film electrodes are platykurtic (S $_{ku}$  < 3). In addition Fig. 4 (b), shows the angular spectra of  $\text{Co}_{1-x}\text{Ni}_xS$  ( $0 \le x \le 0.2$ ) electrode. The beautiful structures and features can be assessed by utilization of a Sobel transformation, which is an edge detection process, allowing to section crystallites from the background areas. In our case, the Sobel transformation provided better readability of the topography (Fig. 4 b). Fig. 4 (b) also depicts the sharp height histogram for x = 0.05 sample suggesting a uniform distribution of crystallites with a maximum surface to area ratio ( $S_{dr} = 163.3$ ). Overall, the result of the topographical study point outs that the surface of the x = 0.05 electrode is favorable for maximum energy storage.

#### 3.4.3. KPFM observations

The contact potential difference between the sample surface and tip can be measured by Kelvin probe force microscopy (KPFM). To date, the KPFM has been effectively employed to study the surface potential and work function of semiconductor surfaces [28,29]. The topographic images for the Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) electrodes are typically flat with small wrinkles and protrusions (Fig. 5 (a)). The different variations of the surface potential can be observed. From Fig. 5 (b) the histogram profile indicates that the work function of pure CoS is 5.159 eV. Interestingly, the composition x = 0.05 shows higher work function 5.867 eV. However, the contact potential difference ( $\Delta$ VCPD) of the pure CoS thin film surface is 492 mV while it increased up to 1200 mV for x = 0.05 (Fig. 5 c). The space charge region formed at the electrode/electrolyte (Co<sub>1-x</sub>Ni<sub>x</sub>S/KOH) interface will contribute to superior capacitance value [30]. Therefore, the maximum values of work function and contact potential may offer augmented super-capacitive performance for x = 0.05 electrode.

## 3.4.4. EFM observations

The electrostatic force microscopy (EFM) allows the qualitative mapping of the electrostatic forces mostly caused by the electrical charges presence or locally biased structures. On the measurements, the Co1-rNirS electrodes showed a number of noticeable objects/hills on the surface. This existence of observable objects/hills demonstrates the presence of the electrical charges on the film surfaces [31]. Fig. 6 (a) shows the large EFM scan area of  $10 \,\mu\text{m} \times 10 \,\mu\text{m}$  with a uniform distribution of charged particles for x = 0.05 with some local irregularities. The color variations of EFM images can be ascribed to the existence of a number of electric domains in the arbitrary orientation. The changes in the internal resistance of the grains with increased (x) can be noticed by Z range parameter in EFM images, which is; 21.28 for x = 0; 3.040 for x = 0.05; 13.49 for x = 0.1; 71.84 for x = 0.15 and 3.12 for x = 0.2. Remarkably the internal resistance was found to be minimum for x = 0.05 electrode. Fig. 6 (b) shows the histogram of obtained values of surface potential/phase shift and it has the highest value of 0.7 for x = 0.05 composition. As the surface potential increases, the dielectric constant decreases and consequently capacitance increases [32]. Thus the results obtained from EFM measurements are also suggestive of the good performance of x = 0.05 sample. It has to be underlined, that the presence of the artifacts related to the morphological features must be taken into account [33]. Therefore, while the complex surfaces are investigated, one has to perform spatially selected data analysis. To avoid the influence of the artifact on the analysis process and verify the correctness of selected data, both: value at the peak's distribution height and the vale at the most elevated surfaces were acquired and compared. As there is a very good correlation between those values, one can assume the correctness of the approach and the analysis of the results. A similar procedure was performed in the case of KPFM data processing.

## 3.5. Electrochemical supercapacitor properties

The as-prepared electrodes were tested as a supercapacitor electrode in a three-electrode cell with Pt as a counter electrode and saturated calomel as a referring electrode. A 2 M KOH aqueous solution was used as an electrolyte.

## 3.5.1. Cyclic voltammetry (CV) study

The cyclic voltammetry (CV) graphs for the  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  ( $0 \le x \le 0.2$ ) thin-film electrodes at various scan rates within -0.2 to +0.5 V/SCE in aqueous 2 M KOH electrolyte are displayed in Fig. 7 (a). The obtained



**Fig. 5.** (a) KPFM map for the Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) thin film electrodes. (b) Work function histogram for the Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) thin film electrodes. (c) Contact potential histogram for the Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) thin film electrodes.









CV curve consists of a strong redox peak, suggesting the electrochemical capacitance is mostly owing to redox reactions and noticeable reversible charge transport which suggests a capacitive nature of the material. The redox peak in the CV plots is mostly originated because of the redox reactions associated with Co2+/Ni2+ redox couple which was perhaps arbitrated by the OH<sup>-</sup> ions in electrolyte [6]. The reversible redox reaction can be stated using the following equations [6,34];

$$CoS + OH^- \leftrightarrow CoSOH + e^-$$
 (5)

$$NiS + OH^- \leftrightarrow NiSOH + e^-$$
 (6)

Further, the CV curves for  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  at x = 0.05 electrode was studied at various scan rates (Fig. 7 b) and it was found that with an increase in scan rates the nature of CV curve changes, potentials of the cathodic and anodic peaks shift towards more negative and positive directions. This shifting of peaks takes place towards the higher

potential during the oxidation process and towards the lower potentials during the reduction process with an enhancement in the scan rate. This shifting of peaks can be accredited to the polarizability, the conductivity of the electrode, the existence of internal resistance, higher power character and excellent electrochemical reversibility [26,35,36].

The specific capacitance ( $C_s$ ) of  $Co_{1-x}Ni_xS$  electrodes was calculated using the following formula [37];

$$C_s = \frac{1}{mv(V_c - V_a)} \int_{V_a}^{V_c} I(V) dv$$
<sup>(7)</sup>

where  $C_s$  the specific capacitance (F g<sup>-1</sup>), v the potential scan rate (mV s<sup>-1</sup>), V<sub>c</sub> -V<sub>a</sub> the potential range (-0.2 to + 5 V/SCE), I the response current (mA) and m the active mass of the  $Co_{1-x}Ni_xS$  material (2.793 mg) on the electrode per the unit area (here 1 cm<sup>2</sup>) immersed in electrolyte. The specific capacitance (C<sub>s</sub>) of the optimized composition x = 0.05 electrode versus scan rate is displayed in Fig. 7 (c). The decrease in C<sub>s</sub>



**Fig. 6. (a)** EFM map for the  $\text{Co}_{1,x}\text{Ni}_xS$  ( $0 \le x \le 0.2$ ) thin film electrodes. **(b)** Surface potential histogram for the  $\text{Co}_{1,x}\text{Ni}_xS$  ( $0 \le x \le 0.2$ ) thin film electrodes.

with an increased scan rate can be credited to the existence of internal active sites that are unable to sustain the redox transition totally at high scan rates. In our case, the high surface area and small pore radius of spirulina algae-like microstructure lead to the maximum specific capacitance of  $856 \,\mathrm{F \,g^{-1}}$  at a  $5 \,\mathrm{mV \,s^{-1}}$  scan rate for  $\mathrm{Co}_{1-x}\mathrm{Ni}_x\mathrm{S}$  ( $0 \leq x \leq 0.2$ ) electrodes. In our case, the C<sub>s</sub> is greater than that of SILAR deposited cobalt oxide anchored multi-walled carbon nanotubes [37]. However, a low scan rate increases the utilization rate of electrode material throughout the electrochemical redox reaction and results in higher C<sub>s</sub> values at lower scan rates. If the scan rate increases, C<sub>s</sub> decreases, demonstrating that  $\mathrm{Co}_{1-x}\mathrm{Ni}_x\mathrm{S}$  ( $0 \leq x \leq 0.2$ ), electrode shows an excellent rate capability.

Fig. 7 (d) reveals the plot of  $C_{areal}$  versus scan rate. At the 5 mV s<sup>-1</sup> scan rate  $Co_{1.x}Ni_xS$  (x = 0.05) electrode presented areal capacitance value of 869 mF cm<sup>-2</sup>, which was found to be decreased with an increase in scan rate. The obtained  $C_{areal}$  value of the  $Co_{1.x}Ni_xS$  (x = 0.05) electrode is higher as compared to  $Co_3S_4$ -coated p-TiO<sub>2</sub> electrode ( $C_{areal} = 36.6 \text{ mF cm}^{-2}$ ), and NiCo<sub>2</sub>S<sub>4</sub>-coated p-TiO<sub>2</sub> composite electrode ( $C_{areal}$  of 47.2 mF cm<sup>-2</sup>) [38]. The advancement in the areal capacitance of  $Co_{1.x}Ni_xS$  electrodes can be accredited to the high conductivity of ternary metal sulfides [14].

# 3.5.2. Galvanostatic charge-discharge (GCD) study

To examine capacitive performance, charge-discharge measurements (Fig. 8 a) on  $Co_{1-x}Ni_xS$  (x = 0.05) electrode conducted in the potential window ranges from 0 to 0.42 V/SCE at current densities from  $6 \text{ mA cm}^{-2}$  to  $10 \text{ mA cm}^{-2}$  for optimized sample x = 0.05. In our case, a low current density was utilized to allow the complete reaction between electrode and electrolyte. Fig. 8 (a) revealed not so perfect straight-line nature of the discharging curves signifying the influence of faradaic reaction processes. Furthermore, the charging curves of Co<sub>1-x</sub>Ni<sub>x</sub>S are not symmetric to their corresponding discharging counterparts. The maximum specific capacitances were found to be  $880 \text{ Fg}^{-1}$  and  $685 \text{ Fg}^{-1}$  at a current density of  $6 \text{ mA cm}^{-2}$  and  $10 \text{ mA cm}^{-2}$  respectively. The C<sub>s</sub> decreases with enhancement in the current density. In our case, the areal capacitance was also calculated and it was found to be  $636 \,\mathrm{mF \, cm^{-2}}$  at  $6 \,\mathrm{mA \, cm^{-2}}$  current density, which is greater than the previously reported value, NiCo<sub>2</sub>O<sub>4</sub> electrode illustrates areal capacitance of  $0.46 \,\mathrm{F \, cm^{-2}}$  [38]. However, the observed value of areal capacitance is below the NiCo2O4@NiMoO4 electrode which shows  $C_{areal}$  of 3.74 F cm<sup>-2</sup> at 2 mA cm<sup>-2</sup> [38]. Xu et al. reported 7.2 F cm<sup>-2</sup> and 2.3 F cm<sup>-2</sup> areal capacitance at a current density of 10 mA cm<sup>-2</sup>, for HPNi@NiCo2O4 and LYNi@NiCo2O4 electrodes respectively [27]. Tang et al. reported areal specific capacitance of  $41.0 \,\mathrm{F \, cm^{-2}}$  for the Co1.5Ni1.5S4 electrode [39]. The Co-Ni sulfide nano-sheets displays  $2.28 \,\mathrm{F \, cm^{-2}}$  of the areal capacitance at a  $1 \,\mathrm{mA \, cm^{-2}}$  current density [40]. The hydrothermally deposited (CoNi)O<sub>x</sub>S<sub>y</sub> nano-aggregates demonstrated the areal capacitance as  $1628 \text{ mF cm}^{-2}$  at a current density of  $1.375 \text{ mA cm}^{-2}$  [41]. Furthermore, the Co<sub>1-x</sub>Ni<sub>x</sub>S electrode morphology has suitable pores that absorb water molecules enabling buffering reservoir to accommodate ions for the redox reaction [42]. This delivers conducting pathways and leads to enhancement in the kinetics of the reversible redox process for charge storage through diminishing internal resistance drop, as clearly confirmed in Fig. 8 (a). Therefore, the reason behind the good performance of Co<sub>1,r</sub>Ni<sub>r</sub>S electrodes is a fast charge transfer at the electrode/electrolyte interface owing to high surface area and maximum surface potential.

The Coulombic efficiency  $(\eta_t)$  and energy efficiency  $(\eta_E)$  is determined by using the following equations [43];

$$\eta_{t} = \frac{t_{D}}{t_{C}} \tag{8}$$

$$\eta_E = \frac{E_{\text{int/}D}}{E_{\text{int/}C}} \tag{9}$$

where t<sub>D</sub> and t<sub>C</sub> are the discharge and charge durations (s).

The Coulombic efficiency  $(\eta_t)$ , was found to be 91%, whereas, the energy efficiency  $(\eta_E)$ , was found to be 66.47% at a current density of 6 mA cm $^{-2}$ .

#### 3.5.3. Stability study

The stability performance of the  $\text{Co}_{1,x}\text{Ni}_x\text{S}$  (x = 0.05) electrode was examined in 2 M KOH electrolyte by repeated galvanostatic chargedischarge (GCD) studies at a current density of 6 mA cm<sup>-2</sup> as revealed in Fig. 8 (b). The electrode maintained 79% capacitance retention after 5000 cycles. The decrement in capacitance after 5000 cycles can be ascribed to the factors such as; i) degradation of the electrode material is



**Fig. 7.** Cyclic voltammograms of  $Co_{1.x}Ni_xS$  thin film electrodes. (a) Comparison of cyclic voltammograms at x = 0, 0.05, 0.15, (b) for x = 0.05 at different scan rates, respectively, (c) plots of specific capacitance versus potential scan rate for  $Co_{1.x}Ni_xS$  (x = 0.05) electrode and (d) plots of areal capacitance versus potential scan rate for  $Co_{1.x}Ni_xS$  (x = 0.05) electrode and (d) plots of areal capacitance versus potential scan rate for  $Co_{1.x}Ni_xS$  (x = 0.05) electrode.

quicker for porous structures than compact structures, ii) dissolution of active materials in the electrolytes, iii) mechanical faults in the electrode (e.g., agglomeration, expansion, and detachment of Co<sub>1-x</sub>Ni<sub>x</sub>S, corrosion of the current collector) and iv) capacity imbalances between the electrodes producing instabilities of the electrode potentials [44]. This retention capacity is remarkably better than the previous reports, the Co<sub>3</sub>O<sub>4</sub>/MWNTs electrodes showed a maximum 73% capacity retention over 5000 cycles [37]. The Ni(OH)<sub>2</sub> electrode material showed 78% capacity retention after 500 cycles [45]. The CoSx-NSA was deposited on a 3D nickel foam via a CBD technique showed 84% capacity retention after 3000 cycles [18]. The  $Co_{1-x}Ni_xS$  (x = 0.05) electrode shows no significant change in the microstructure of the material after 5000 GCD cycles as revealed from low and high magnification FESEM images (Fig. 8 (c) and (d)) respectively. It is found that the electrode material after cycling studies becomes more and more porous owing to electrolyte ions adsorption and desorption process. The improvement in the effective intercalation between electrode and electrolyte or charge-transfer process is credited to the activation of the electrode materials after initial charge-discharge cycles [46].

## 3.5.4. Electrochemical impedance spectroscopy (EIS) study

The electrochemical impedance spectrum of  $\text{Co}_{1-x}\text{Ni}_x\text{S}$  (x = 0.05) electrode was measured in the frequency ranges from 10 mHz to 1 MHz at OCV to realize Nyquist plots (Z' vs. Z'') as displayed in Fig. 9. Fig. 9 reveals the impedance spectrum exhibiting semicircle in a higher frequency region and almost straight line in a lower frequency region. A

resistance (R<sub>s</sub>) can be obtained by making the X-intercept of the plot, which consists of intrinsic resistance of the active material, the contact resistance between the electrode, ionic resistance of electrolyte and current collector interface [47]. The  $R_s$  is found to be  $0.5 \Omega \text{ cm}^2$  and  $0.21 \,\Omega \,\mathrm{cm}^2$  before and after 5000 cycles of the GCD measurement, respectively. A faradaic charge transfer resistance (Rct) was determined from the diameter of the semicircle in the higher frequency region and is related to the electrolyte accessible area of the electrode. And the low-frequency semicircular arc to the faradaic reactions at the interface. However, after stability, the EIS spectra consists of two semicircular arcs and a straight line. Therefore, the diameter of the high-frequency semicircle arc to the charge transfer resistance (R<sub>ct1</sub>), the low-frequency semicircular arc  $(R_{ct2})$  to the faradaic reactions at the interface [48]. The ( $R_{ct}$ ) for  $Co_{1-x}Ni_xS$  (x = 0.05) electrode was found to be  $1.83 \,\Omega \,\text{cm}^2$  before stability,  $R_{ct1}$ =6.41  $\Omega \,\text{cm}^2$  and  $R_{ct2}$  = 13.91  $\Omega \,\text{cm}^2$ after stability measurement respectively. The slight decrease in the capacitance after cyclic test accredited to increased R<sub>ct</sub> caused owing to the minor changes in the surface and transport properties of Co<sub>1-x</sub>Ni<sub>x</sub>S (x = 0.05) electrode during the cycling process [49]. Thus, the EIS results in signposts easy diffusion of the electrolyte into the electrode and availability of effective transport path for electrons and ions in the  $Co_{1-x}Ni_xS$  (x = 0.05) electrodes which is beneficial for increasing the storage capacity of the Co<sub>1-x</sub>Ni<sub>x</sub>S electrodes.



**Fig. 8.** (a) Galvanostatic charge discharge curves of  $Co_{1,x}Ni_xS$  (x = 0.05) at different current densities. (b) The capacity retention of  $Co_{1,x}Ni_xS$  (x = 0.05) electrode after 5000 galvanostatic charge discharge cycles and (**c**–**d**) Low and high magnification field emission scanning electron micrographs of  $Co_{1,x}Ni_xS$  (x = 0.05) electrode after 5000 galvanostatic charge discharge cycles.



**Fig. 9.** Nyquist plot for  $Co_{1-x}Ni_xS$  at x = 0.05 in 2 M KOH electrolyte before and after 5000 cycles.

## 4. Conclusions

We have demonstrated the solution growth of  $Co_{1-x}Ni_xS$  ( $0 \le x \le 0.2$ ) thin films. The as-prepared Co–Ni–S thin-film electrodes had a porous spirulina algae-like microstructure with a high surface area. The

electrochemical analysis demonstrated a noticeable influence of surface properties on supercapacitive performance of Co<sub>1-x</sub>Ni<sub>x</sub>S electrodes. The space charge region, formed at the Co<sub>1-x</sub>Ni<sub>x</sub>S/KOH interface is contributed to higher specific capacitance. The highest surface potential and lowest internal resistance resulted in the highest specific capacitance of 880 F g<sup>-1</sup> at a 6 mA cm<sup>-2</sup> current density with excellent rate capability for electrode composition x = 0.05. Besides the high specific capacitance the electrode of composition x = 0.05 maintained 79% capacitance retention after 5000 cycles. In the light of excellent electrochemical properties and cost-effective synthesis, the Co<sub>1-x</sub>Ni<sub>x</sub>S ( $0 \le x \le 0.2$ ) thinfilm electrodes provide great potential for efficient supercapacitor device fabrication.

## Declaration of competing interest

The authors declare that there is no conflict of interest.

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## Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.mssp.2019.104799.

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