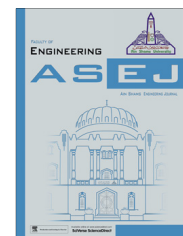




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ELECTRICAL ENGINEERING

Synthesis, characterization and performance of $\text{Co}_x\text{Ni}_{1-x}\text{S}$ compounds for application in lithium batteries



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Abstract This study reports a process to prepare $\text{Co}_x\text{Ni}_{1-x}\text{S}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) samples by hydrothermal process at $250\text{ }^\circ\text{C}$ using stoichiometric weight ratios of raw materials. The prepared powder samples were annealed in Ar atmosphere at $450\text{ }^\circ\text{C}$ for 3 h. The crystal structure of prepared annealed $\text{Co}_x\text{Ni}_{1-x}\text{S}$ samples was characterized by XRD. SEM investigations were carried out explaining the morphology of these samples. Electrochemical impedance spectra (EIS) measurements, Cyclic voltammetric (CV) and galvanostatic measurements were carried out. The life cycle performance was carried out for the cells and $\text{Li}/\text{Co}_{0.25}\text{Ni}_{0.75}\text{S}$ cell gave specific discharge capacities of about 330 mA h g^{-1} .

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1. Introduction

The electrochemical storage of energy and its conversion are of great interest for many practical applications. Electrical energy can be stored through primary and secondary (rechargeable) batteries. The rechargeable lithium ion batteries for portable electronic devices (e.g. PC and laptop computers, wireless and mobile phones, camcorders) have lately a strong tendency to expansion [1–11].

Wang et al. succeeded to synthesize nano-sized cobalt sulfides through a one step chemical reaction method at room temperature [12]. The cobalt sulfide nanopowders were characterized by X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy and electrochemical testing. The results revealed that the cobalt sulfide is a semiconductor; the reversible capacity was increased with increasing content of electronic conductors in the active material of electrodes. The prepared cells showed good electrochemical properties.

Hydrothermal/solvothermal route is most widely used for synthesis of various cobalt sulfide nanostructures due to its low cost and high efficiency [11]. A facile and efficient solvothermal process was developed to produce cobalt sulfide (CoS) nanoflakes and cobalt disulfide (CoS_2) nanoparticles using thiourea and sulfur powder as precursors, respectively. The structural properties of CoS nanoflakes and CoS_2

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nanoparticles were investigated and the possible formation mechanisms of these nanostructures were proposed.

The nanocomposite of the NiS active material and the 80Li₂S·20P₂S₅ (mol%) electrolyte was synthesized via a mechanochemical reaction and applied as an electrode to all-solid-state lithium secondary cells [13]. The capacity of the cell with the nanocomposite electrode was greater than that with an electrode prepared by hand-mixing of the active material and the electrolyte powder.

To reduce the reaction time, electrical energy consumption, and cost, binary α -NiS and β -NiS were synthesized by a rapid, one-pot, hydrothermal autoclave microwave method within 15 min at temperatures of 160–180 °C [14]. At 140 °C, pure hexagonal type α -NiS phase was identified from the XRD patterns. With increasing reaction temperature (160–180 °C), the XRD evidence indicates that an increasing fraction of rhombohedral millerite-like β -NiS is formed as a secondary phase. The α -NiS- β -NiS sample synthesized at 160 °C yielded good electrochemical performance in terms of high reversible capacity. The likely contributing factor to the superior electrochemical performance of the α -NiS- β -NiS sample could be related to the improved morphology.

To the best of our knowledge, few works were done on NiS and CoS as anode materials. Co_xNi_{1-x}S material ($x = 0, 0.25, 0.5, 0.75$ and 1) samples have not been studied as a lithium battery anode material. In this work, different ratios of Co and Ni in the sulfide compound were used to improve the capacity performance of NiS and CoS through the hydrothermal process using triethanolamine.

2. Experimental

Co_xNi_{1-x}S ($x = 0, 0.25, 0.5, 0.75$ and 1) samples were prepared by hydrothermal process using stoichiometric ratio weights of Co(CH₃COO)₂·4H₂O (99.5% Sigma Aldrich), Ni(CH₃COO)₂·4H₂O (99.5%, Sigma Aldrich) and thiourea (99% Sigma Aldrich). Each compound was dissolved in 25 ml bi-distilled water separately. 25 ml of tri ethanolamine (TEA) (99%, s.d. fine, Mumbai) was added for each sample. The mixture was stirred and heated at 150 °C in 100 cm³ beaker until its volume became 60 ml. After that, it was transferred into an autoclave 150 cm³ Teflon vessel and was put inside stainless steel holder and heated in an oven at 250 °C for 24 h. The obtained black sulfide compound was filtered and several times washed with distilled water and acetone until the filtrate solution was clear. After that, the powder was dried in a vacuum oven at 100 °C for 10 h. The prepared powder samples were annealed in Ar atmosphere at 450 °C for 3 h in order to improve the crystallinity and the crystal structure of these samples. The crystalline phases were identified by X-ray diffraction (XRD) on a Bruker axis D8 diffractometer with crystallographic data software Topas 2 using Cu-K α ($\lambda = 1.5406$ Å) radiation operating at 40 kV and 30 mA at a rate of 2°/min. The particle morphology was observed using the scanning electron microscope (JEOL, SEM and JSM-5040). Elemental compositions of the various Co_xNi_{1-x}S samples were analyzed by inductively coupled plasma (ICP, Perkin-Elmer Optima 2000 DV).

The working electrode (WE) was prepared from slurry of the 85% active material, 10% C-black and 5% binder PVDF (polyvinylidene difluoride). The slurry was pasted with some

drops of N-methyl pyrrolidone (NMP). Copper disk substrate (1 cm² area) was coated with this active material to form the WE. The WE was dried in vacuum oven at 120 °C. A Teflon cell was used to house the lithium foil metal that acted as counter and reference electrode. The separator was Celgrad (micro-porous poly propylene). The electrolyte was 1 M LiAsF₆ dissolved in mixture of 1:1 PC (propylene carbonate) and EC (ethylene carbonate). CV measurements were carried out for Co_xNi_{1-x}S samples between 0.1 and 3 V vs. Li⁺ with scan rate 0.1 mV s⁻¹. Furthermore, impedance measurements were applied using frequency range between 10⁶ and 10⁻² Hz using amplitude of 10 mV using Solartron 1287 with FRA 1255B. Also, galvanostatic charging and discharging cycling of the cells were achieved with almost the same potentials windows 0.1–3 V and 3.0–1.6 V for Li/Co_{0.25}Ni_{0.75}S cell only using charging and discharging current intensity of 0.1 mA using Bitrode MCV8.

3. Results and discussion

3.1. Sample characterization

The crystal structure of the annealed samples Co_xNi_{1-x}S was studied using XRD investigations as shown in Fig. 1. The diffraction peaks of samples containing the following: $x = 1.0, 0.75, 0.5$ can be indexed well on the basis of standard hexagonal wurtzite CoS (ICDD-PDF No.: 65-3418 and No. 02-9305) [7–10]. The unit cell parameters are given in Table 1. The crystal structure composition is hexagonal phase [space group: *P6/mmm*]. The reported unit cell parameters are as follows: $a = 3.366$ Å and $c = 5.14$ Å [9]. Our calculated data are similar to the reported ones. Co_{0.5}Ni_{0.5}S and Co_{0.75}Ni_{0.25}S patterns have peaks for hexagonal phase similar to the patterns of CoS and α -NiS but with little differences in the position of the peaks.

On the other hand, the phase composition of samples containing $x = 0.0$ is rhombohedral millerite β -NiS phase (*R*3m), which are in good consistent with the literature data (JCPDS file Card, No. 12-0041) [14]. The reported unit cell parameters are $a = 9.6191$ Å and $c = 3.1557$ Å for β -NiS. With respect to $x = 0.25$, the crystal structure is trigonal *H*-3m1. It is observed that increasing the Ni atom ratio in the sample structure increases the unit cell parameter “a” but decreases the “c” one. This is due to the ionic radii of Co²⁺ and Ni²⁺: 74 and 69 pm, respectively [16]. On the other hand, Co_{0.25}Ni_{0.75}S pattern has peaks for hexagonal phase, which differs from both CoS and NiS samples. Also, its crystalline planes have different Miller indices in comparison with pure samples. The average crystallite diameter “L” of the obtained samples was estimated from the Debye-Scherrer equation [3]:

$$L = k\lambda/b \cos \theta \quad (1)$$

where b is the breadth of the observed diffraction line at its half intensity maximum, k is the so-called shape factor (0.94), and λ is the wavelength of the X-ray source used in the XRD. By using the peak of highest intensity for each sample, the crystallite diameter of the prepared samples was calculated. The lowest one (22.96 nm) was achieved with Co_{0.25}Ni_{0.75}S sample. The strain values are also calculated showing the highest value with this sample.

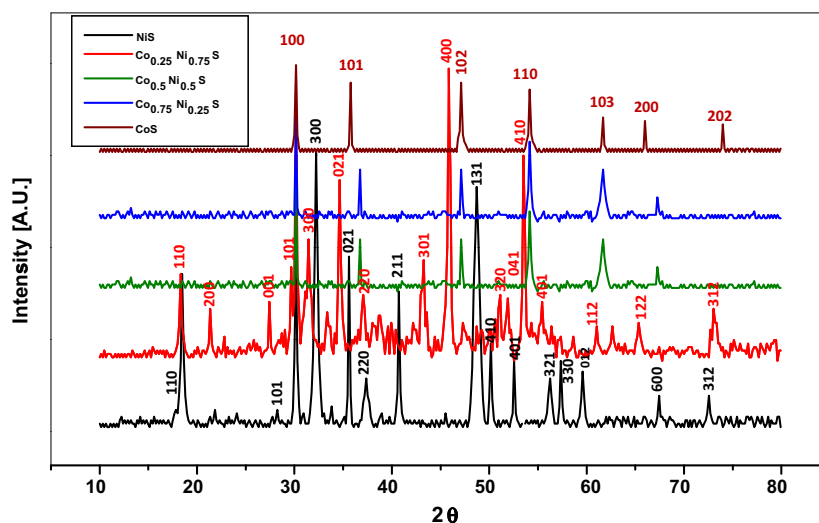


Figure 1 XRD patterns of $\text{Co}_x\text{Ni}_{1-x}\text{S}$ ($x = 0, 0.25, 0.5, 0.75$ and 1.0) samples powder prepared by hydrothermal process at $250\text{ }^\circ\text{C}$ for 24 h and annealed at $450\text{ }^\circ\text{C}$ for 3 h in Ar atmosphere.

Table 1 Unit cell parameters of $\text{Co}_x\text{Ni}_{1-x}\text{S}$ powders ($x = 0, 0.25, 0.5, 0.75$ and 1).

Cell type	a (Å)	c (Å)	V (Å ³)	L (nm)	$\varepsilon \times 10^{-4}$
NiS	9.618	3.158	253	38.3	9.63
$\text{Co}_{0.25}\text{Ni}_{0.75}\text{S}$	7.22	3.66	165.23	22.96	15.77
$\text{Co}_{0.5}\text{Ni}_{0.5}\text{S}$	3.40	5.05	51.56	24.7	14.66
$\text{Co}_{0.75}\text{Ni}_{0.25}\text{S}$	3.38	5.09	50.36	27.1	13.36
CoS	3.368	5.148	50.57	30.7	11.79

SEM morphologies of the samples were inspected as shown in Fig. 2. The morphological structure of $\text{Co}_{0.25}\text{Ni}_{0.75}\text{S}$, $\text{Co}_{0.5}\text{Ni}_{0.5}\text{S}$ is spherical, while CoS has sticks shape like potatoes frites. The particle size of the sample powders is 1–3 μm . The average particle size of sample $\text{Co}_{0.25}\text{Ni}_{0.75}\text{S}$ is 1 μm . We expect that the lower crystallite and particle size may give more active surface area. This more active surface area may enhance the conductivity of this sample as will be explained in the next Section 3.2.

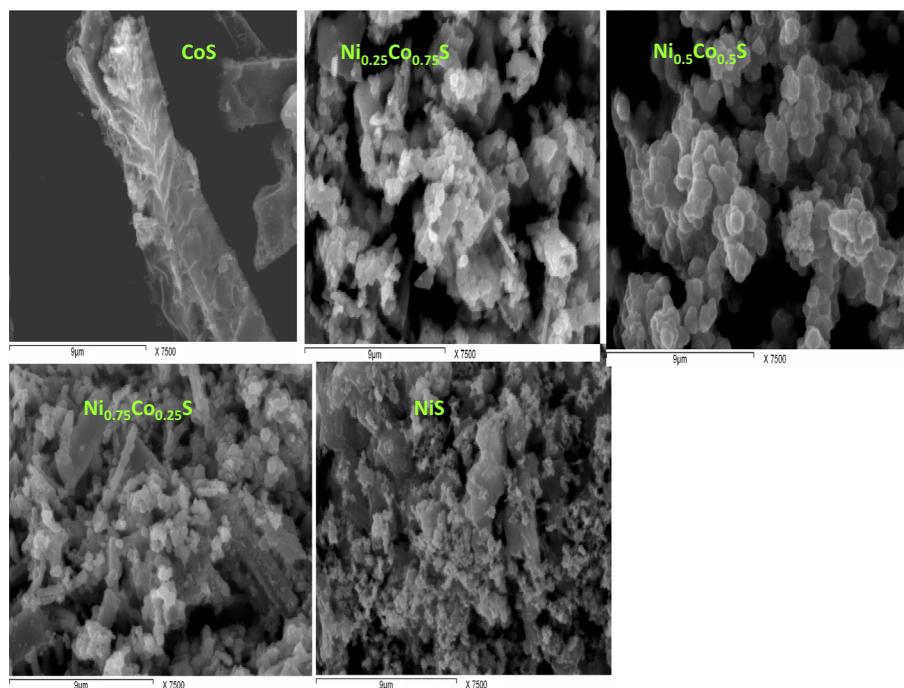


Figure 2 SEM of $\text{Co}_x\text{Ni}_{1-x}\text{S}$ ($x = 0, 0.25, 0.5, 0.75$ and 1) samples powder prepared by hydrothermal process at $250\text{ }^\circ\text{C}$ for 24 h and annealed at $450\text{ }^\circ\text{C}$ for 3 h in Ar atmosphere.

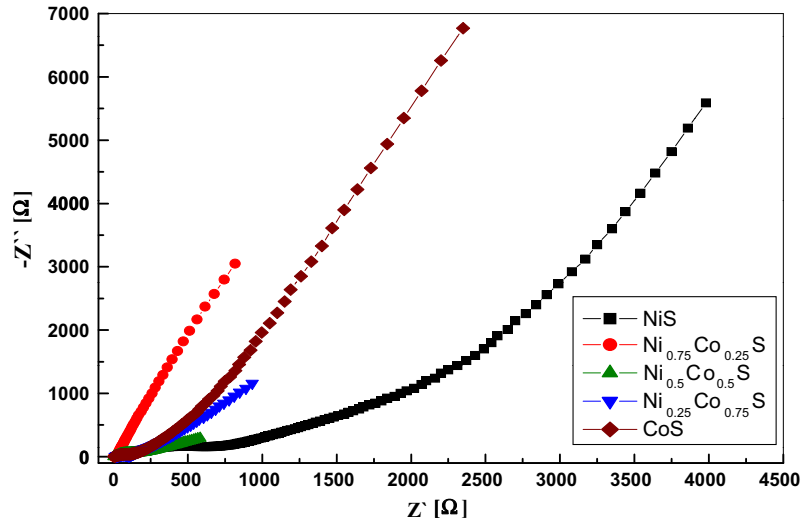


Figure 3 EIS of Li/Co_xNi_{1-x}S cells ($x = 0, 0.25, 0.5, 0.75$ and 1) for samples powder prepared by hydrothermal process at $250\text{ }^{\circ}\text{C}$ for 24 h and annealed at $450\text{ }^{\circ}\text{C}$ for 3 h in Ar atmosphere.

3.2. Electrochemical performance

The electrochemical impedance spectra (EIS) of the cells as illustrated in Fig. 3 show an intercept at high frequency for the resistance of the electrolyte, R_e on the real axis Z' , followed by a semicircle in the high-middle frequency region, and a straight line in the low frequency region. The numerical value of the diameter of the semicircle on the Z_{re} axis is approximately equal to the charge transfer resistance, R_{ct} ; therefore, it can be seen that there is a marked decrease in R_{ct} after adding Ni to Co in comparison with CoS or NiS only. The low frequency region of the straight line is attributed to the diffusion of the lithium ions into the bulk of the electrode material, the so-called Warburg diffusion. In fact, electrochemical impedance spectroscopy (EIS) may be considered as one of the most sensitive tools for the study of differences in the electrode behavior due to surface modification. It is observed that the cell prepared from Co_{0.25}Ni_{0.75}S has the lowest real Z_{re} in comparison with the other cells. The lower resistance of sample cell Co_{0.25}Ni_{0.75}S may be due to nanoparticle size.

The plot of the Z_{re} versus the reciprocal square root of the lower angular frequencies is illustrated in Fig. 4. The straight lines are attributed to the diffusion of the lithium ions into the bulk of the electrode materials [15]. This relation is governed by Eq. (2). It is observed that the Warburg impedance coefficient (σ_w) is $114.44\text{ }\Omega\text{ s}^{0.5}$ for cell of sample composition Co_{0.25}Ni_{0.75}S, and this is the lowest value in comparison with those of the other samples. Also, the diffusion coefficient values of the lithium ions in the bulk electrode materials are calculated using Eq. (3).

$$Z_{re} = R_e + R_{ct} + \sigma_w \cdot \omega^{-0.5} \quad (2)$$

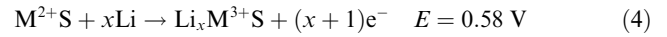
$$D = 0.5(RT/An^2F^2\sigma_w C)^2 \quad (3)$$

where ω : angular frequency in the low frequency region, D : diffusion coefficient, R : the gas constant, T : the absolute temperature, F : Faraday's constant, A : the area of the electrode surface, and C : molar concentration of Li^+ ions. Furthermore,

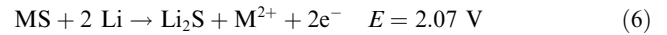
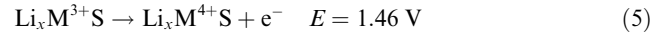
the exchange current density ($i^{\circ} = RT/nFR_{ct}$). The impedance parameters of the samples are recorded in Table 2.

The cyclic voltammogram of Co_{0.25}Ni_{0.75}S of about 5 cycles starting from the open circuit potential, 2.02 V is shown in Fig. 5. It is observed that three anodic peaks take place at 0.58, 1.46 and 2.07 V, respectively. We label Co_{0.25}Ni_{0.75}S as MS. The interpretation of these peaks as follows:

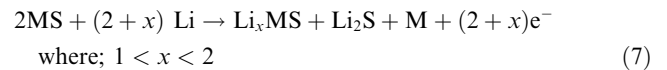
Insertion of x Li into MS



The oxidation of M^{3+} to M^{4+} is given by the following:



So the total reaction will be the following:



For the previous reaction represented by Eq. (6), the maximum theoretical capacity is 733 mA h g^{-1} as calculated by using $x = 2\text{e}^-$.

On the other hand, there are two cathodic reduction peaks take place at 1.14 and 0.48 V for the first cycle and for the other cycles at 1.7 and 1.25 V. These reduction reactions are mainly for the reverse reactions of the anodic oxidation reactions as mentioned previously. The obtained results are in agreement with the reported similar ones for [14,16–18].

The life cycle performance was carried out for the Co_xNi_{1-x}S for cells prepared from annealed as shown in Fig. 6. It is observed that Li/Co_{0.25}Ni_{0.75}S cell delivered specific discharge capacities in the range of 320 mA h g^{-1} . The initial capacity loss is attributed to the surface film formation, which is known as solid electrolyte interface (SEI) film [14,18,19]. The loss in the initial capacity suggests that the reaction in this potential region is a reversible topotactic reaction. Yan et al. reported a mechanism of CoS₂ with lithium [19]. Lithium was proposed as $x\text{Li}^+ + x\text{e}^- + \text{CoS}_2 \rightarrow \text{Li}_x\text{CoS}_2$. They explained that the reaction was an intercalation reaction when

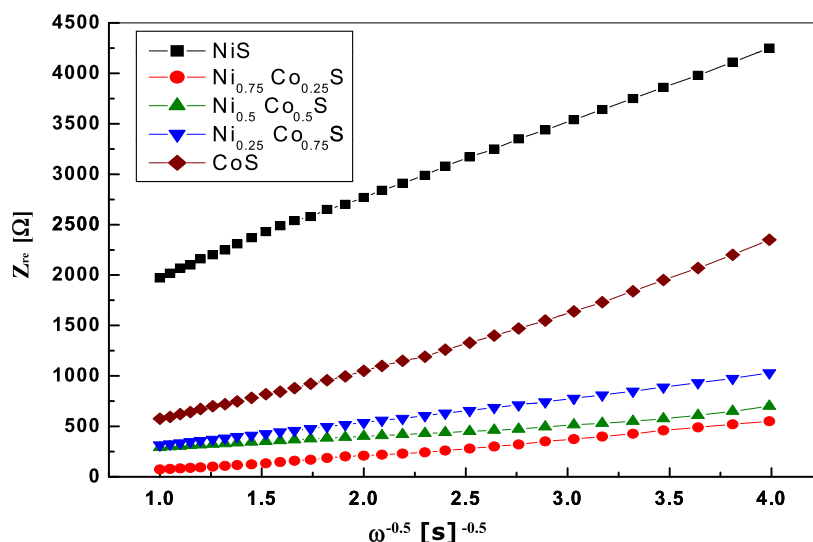


Figure 4 Relationship between real impedance with the angular frequency for Li/Co_xNi_{1-x}S cells ($x = 0, 0.25, 0.5, 0.75$ and 1) for samples powder prepared by hydrothermal process at $250\text{ }^{\circ}\text{C}$ for 24 h and annealed at $450\text{ }^{\circ}\text{C}$ for 3 h in Ar atmosphere.

Table 2 Electrochemical Impedance parameters of Li/Co_xNi_{1-x}S cells ($x = 0, 0.25, 0.5, 0.75$ and 1).

Cell type	R_s (Ω)	R_{ct} (Ω)	σ_w ($\Omega\text{ s}^{0.5}$)	D (cm^2/s)	i (mA cm^{-2})
NiS	63.8	669	789.474	$6.09\text{E}-14$	$3.84\text{E}-05$
Co _{0.25} Ni _{0.75} S	1.59	15.9	114.447	$1.48\text{E}-12$	0.00162
Co _{0.5} Ni _{0.5} S	6.22	172	117.263	$1.39\text{E}-12$	$1.50\text{E}-04$
Co _{0.75} Ni _{0.25} S	13.9	97.1	225.658	$6.19\text{E}-13$	$2.65\text{E}-04$
CoS	6.67	124	495.395	$1.01\text{E}-13$	$2.0\text{E}-04$

the discharge voltage was limited at 1.6 V , the frame structure of material almost was not destroyed, and however, the reaction was a probable redox reaction when the discharge voltage went to lower potential (i.e. $1.6\text{--}0.02\text{ V}$); then, the structure of

the materials was entirely destroyed at very low potential and cannot be recovered. They suggested that the reaction could be proposed as $\text{CoS}_2 + 4\text{Li}^+ + 4\text{e}^- \rightarrow \text{Co} + 2\text{Li}_2\text{S}$. They expected that the charge/discharge voltage is the key factor to affect the cyclic performance.

Thus, Li/Co_{0.25}Ni_{0.75}S cells were assembled and galvanostatically charged and discharged in the different voltage ranges of $3.0\text{--}1.6$ and $3.0\text{--}0.1\text{ V}$, respectively, in order to test their cyclic stability. Fig. 7 shows the curves of the discharge capacity vs. the cycle number of the samples in the different discharge voltage ranging $3.0\text{--}0.1$ and $3.0\text{--}1.6\text{ V}$. The capacity can be retained to about 50% of the first discharge capacity after 60 cycles, respectively. Although the first cycle capacity of the material decreased, however, the cycling stability has been greatly improved when the voltage range changed from $3.0\text{--}0.1$ to $3.0\text{--}1.6\text{ V}$. This result is consistent with the above reaction mechanism analysis proposed by Yan et al. [19].

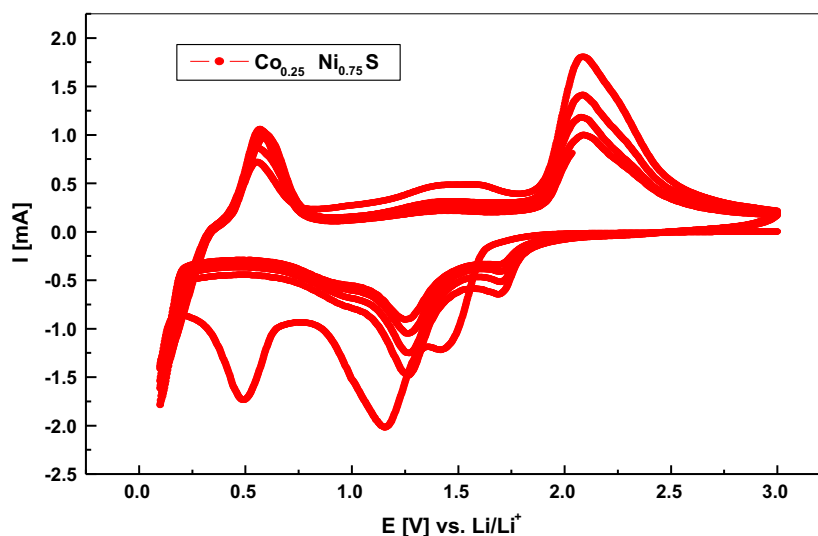


Figure 5 CV of Li/Co_{0.25}Ni_{0.75}S cell from sample powder prepared by hydrothermal process at $250\text{ }^{\circ}\text{C}$ for 24 h and annealed at $450\text{ }^{\circ}\text{C}$ for 3 h in Ar atmosphere.

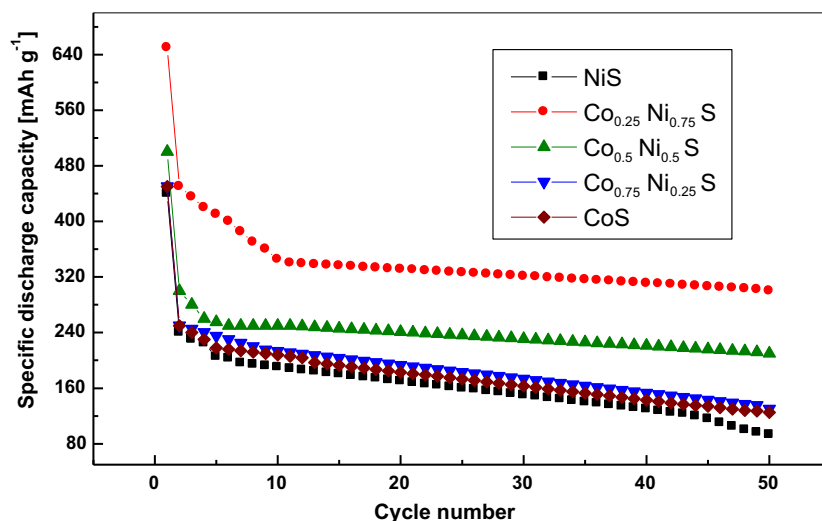


Figure 6 Life cycle performance of Li/Co_xNi_{1-x}S cells; ($x = 0, 0.25, 0.5, 0.75$ and 1) for samples powder prepared by hydrothermal process at $250\text{ }^{\circ}\text{C}$ for 24 h and annealed at $450\text{ }^{\circ}\text{C}$ for 3 h in Ar atmosphere.

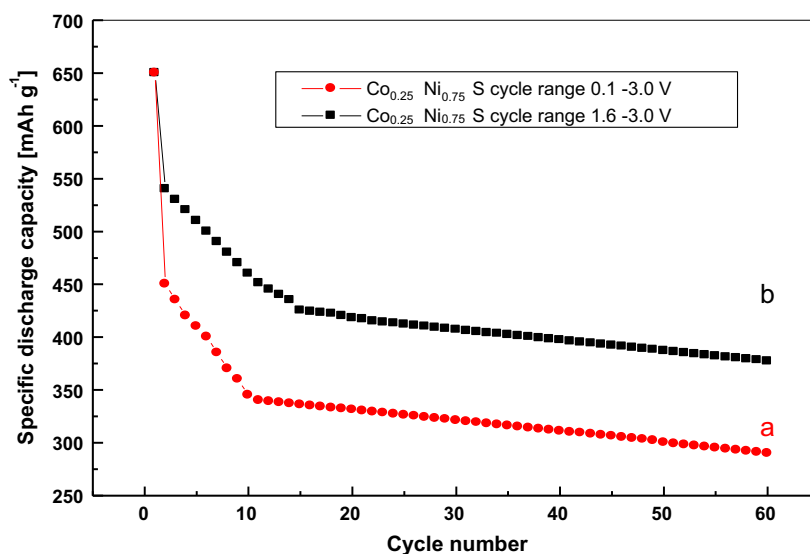


Figure 7 Life cycle performance of Li/Co_{0.25}Ni_{0.75}S cells in the different voltage ranges of: (a) 3.0–0.1 and (b) 3.0–1.6 V.

4. Conclusions

The structure of prepared samples of Co_xNi_{1-x}S is characterized by XRD. The crystal structure of samples having: $x = 0.5, 0.75$ and 1.0 is indexed to hexagonal phase. The NiS sample is rhombohedral millerite β -NiS. The sample Co_{0.25}Ni_{0.75}S is trigonal of $H-3m1$ class. The lowest Warburg impedance coefficient (σ_w), $114.44\ \Omega\text{ s}^{0.5}$ is achieved with cell prepared from sample composition Co_{0.25}Ni_{0.75}S. Li/Co_{0.25}Ni_{0.75}S cell gives specific discharge capacities within 330 mA h g^{-1} .

References

- [1] Shenouda AY. *Electrochim Acta* 2006;51:5973.
- [2] Shenouda AY, Murali KR. *J Power Sources* 2008;176:332.
- [3] Shenouda AY, Liu Hua Kun. *J Power Sources* 2008;185:1386.
- [4] Shenouda AY, Liu Hua Kun. *J Alloys Compd* 2009;477:498.
- [5] Shenouda AY, Liu Hua Kun. *J Electrochem Soc* 2010;157(A):1183.
- [6] Shenouda AY, El Sayed El Sayed M, Liu Hua Kun. *J New Mater Electrochem Syst* 2011;14:19–26.
- [7] Wu SH, Hsiao KM, Liu WR. *J Power Sources* 2005;146:550.
- [8] Hu QR, Wang SL, Zhang Y, Tang WH. *J Alloys Compd* 2010;491:707–11.
- [9] Mane ST, Kamble SS, Deshmukh LP. *Mater Lett* 2011;65:2639–41.
- [10] Lei M, Fu XL, Zhang YB, Yang HJ, Huang YT, Zhang L, Wang YG. *Mater Lett* 2012;71:11.
- [11] Yang MR, Ke WH, Wu SH. *J Power Sources* 2005;146:539.
- [12] Wang J, Ng SH, Wang GX, Chen J, Zhao L, Chen Y, Liu HK. *J Power Sources* 2006;159:287.
- [13] Nishio Y, Kitaura H, Hayashi A, Tatsumisago M. *J Power Sources* 2009;189:629.
- [14] Idris NH, Rahman MM, Chou SL, Wang JZ, Wexler D, Liu HK. *Electrochim Acta* 2011;58:456.
- [15] Bard AJ, Faulkner LR. *Electrochemical methods*. 2nd ed. New York: John Wiley & Sons; 2001. p. 231.

- [16] Barbalace Kenneth. Periodic table of elements – cobalt and nickel. Environmental Chemistry.com. 1995–2013.
- [17] Ruan H, Li Y, Qiu H, Wei M. *J Alloys Compd* 2014;588:357–60.
- [18] Ni SB, Yang XL, Li T. *J Mater Chem* 2012;22:2395–7.
- [19] Yan JM, Huang HZ, Zhang J, Liu ZJ, Yang Y. *J Power Sources* 2005;146:264–9.



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