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Evaluation of Electrochemical Performance of Cobalt Sulphide on Various Current Collectors

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Abstract

In the present study, cobalt sulphide was successfully synthesised via a simple, one-step hydrothermal route. The material has been characterised via infrared (FTIR) spectroscopy, electron microscopy (FESEM), and X-ray diffraction (XRD). The FTIR spectrum reveals a peak at 1126 cm^{-1}, which corresponds to the S-O bending mode, and a peak at 663 cm^{-1}, which represents sulphide stretching. According to XRD analysis, cobalt sulphide formed with the CoS1.097 configuration. FESEM study reveals that cobalt sulphide hexagonal sheets with a thickness of less than 100 nm have been prepared that are further arranged in a floral pattern. Cobalt and sulphide concentrations were found to be proportional in EDX analyses. Further, Electrochemical testing was performed with a two-electrode setup, 6M KOH as the electrolyte, and various current collectors (including nickel foam and aluminium foil). The galvanostatic charge-discharge characteristics and capacitance values have been compared using impedance spectroscopy and other techniques. Details of the analysis are presented.

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Introduction

As the world's population has been rising, demand for the world's finite energy resources is increasing. As a result, researchers are becoming increasingly interested in the use of renewable energy sources. Extensive research has been conducted in energy storage devices in addition to energy conversion. There are two types of electrochemical storage: batteries and supercapacitors. Dual-ion battery systems have been the most innovative type of battery to date.[1] Similarly in supercapacitors, pristine or composite materials with higher power density and energy density have been reported. Transition metal sulphide has received the most attention in the field of supercapacitors. Cobalt sulphide is a sulphide of a transition metal. It has many stichometry configurations due to its multiple oxidation states, such as Co_xS_y, where x=1,2,3

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and y=1,2,4,9. CoS,[2-4] Co_3S_4,[5] and Co_9S_8[6] have all been investigated. Researchers used composite formation to improve the electrochemistry of cobalt sulphide.[7] The electrolyte and current collector, in addition to the electrode material, have an impact on supercapacitor performance. A current collector must have low resistance, high porosity, and stability. The electrolyte and current collector, in addition to the electrode material, play an important role in improving electrochemical performance in supercapacitors. When choosing a current collector, many factors should be considered, including low resistance, high porosity, and stability.

In this article, we will look at how current collectors affect the electrochemical performance of a material. In this case, cobalt sulphide is used as an electrode material, which is prepared using a hydrothermal technique. Furthermore, a variety of synthesis techniques are used to support their synthesis. Two electrode configurations were used to investigate electrochemical performance. Furthermore, Ni foam and Al foil current collectors are used to investigate the electrochemical performance. Details are presented.

Experimental Section

Required Material

Cobalt chloride hexahydrate (ACS reagent, 98%), thioacetamide (ACS reagent,> 99%), and potassium hydroxide (KOH)were purchased from Lobaa Chemie. N-Methylpyrrolidone (NMP), Carbon Black and PVDF (polyvinylidene fluoride) were purchase from Sigma Aldrich. Nickel Foam was purchased form Vritra Technology, India.

Synthesis Procedure

A single-step hydrothermal route is used to synthesise cobalt sulphide.[8] 237.9 mg of cobalt chloride hexahydrate and 300.5 mg of thioacetamide were added to 40 mL of ethanol. After 30 minutes of stirring, the mixture turned blue. This mixture was placed in a Teflon autoclave and heated for 24 hours in a furnace at 160 °C. When the reaction was finished, a black-coloured solution with precipitate was obtained. The precipitates were collected via centrifugation process and rinsed three to four times with pure water. The sample was dried at 60°C and stored in the vial. The schematic of synthesis process is shown in Figure 1.

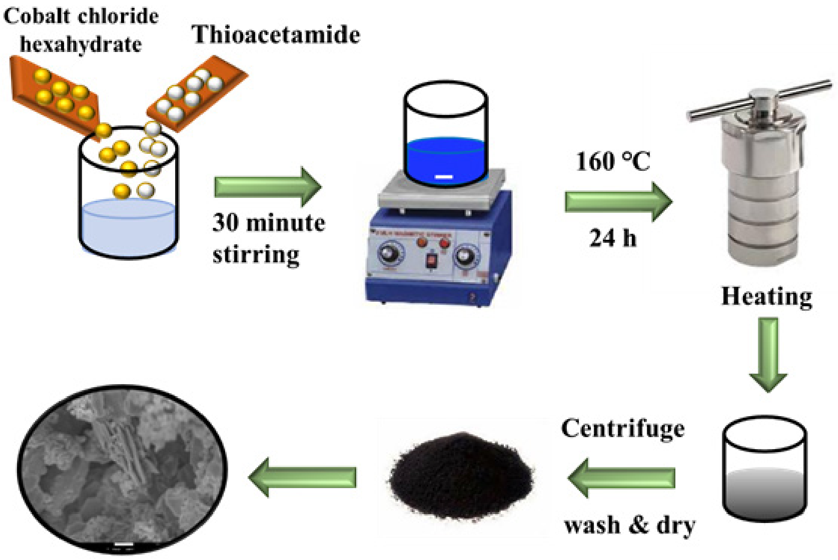

Fig. 1: Synthesis methodology for cobalt sulphide.

Characterization

Fourier transform infrared spectroscopic (FTIR; manufacturer: Bruker; model: Tensor 27) technique are used to examine the functional groups present in the prepared sample over the wavenumber range of 600- 4000 cm^{-1} The powdered x-ray diffraction technique (XRD, make: PANalytical, model: Empyrean) with Cu Kα 1.54 excitation wavelength was used to analyse the crystal structure and phase of the material. Energy dispersive x-ray analysis (EDS) and field emission scanning electron microscopy (FESEM, make: Carl Zeiss, model: Merlin Compact) were used with a working distance of 7.8 mm to examine the surface morphologies of the synthesised sample. Additionally, the electrochemical performance was evaluated using the CHI-760 Electrochemical workstation.

Electrode Preparation for Supercapacitor Studies

To evaluate electrochemical performance, commercial nickel foam was used as a current collector. The active component, carbon black, and PVDF were weighed and measured in the following ratio: 70:20:10. After grinding the mixture with a mortar and pestle, a few drops of NMP solution are added to form a homogenous slurry paste. This homogeneous slurry coated a nickel foam with a surface area of ~1 cm^2. Then dry overnight at 60 °C. The loaded mass over nickel foam is 3mg. Whatman paper was used as a separator, and 6M KOH was used as an electrolyte solution. The electrochemical performance was evaluated using a configuration system with two electrodes. Further, the electrochemical performance of the synthesized material was examined using aluminium foil as a current collector.

Result and Discussion

The FTIR spectrum of prepared cobalt sulphideis shown in Figure 2. The peak appeared at ~ 663 cm^{-1} assigned to sulphide stretching group band.[9] The peak emerged 868 cm^{-1} corresponds to the C-S stretching bond.[10] Moreover, peak at 1126 cm^{-1} is attributed to S-O functional groups.[11] The absorption peaks lie in the range of 1300-1470 cm-1 shows the stretching C-H and deform C-O-H bands.[10,12] The peak near 2926 cm^{-1} is correspond to C-H vibration bond.[13] Peaks at 1640 and 3450 cm^{-1} attributed to bending and stretching vibration of -OH group.[14] The absorption peak below 500 to 1200 cm^{-1} confirm the formation of cobalt sulphides.

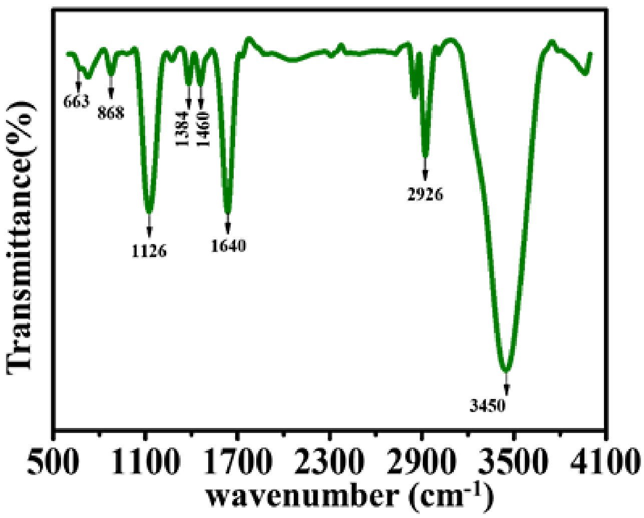

Fig. 2: Recorded FTIR spectrum.

Figure 3 depicts the recorded XRD spectrum. The XRD pattern have peaks at 2Θ of 31, 35, 59, 47, 22, 50, 23, 52, 5, 5, 60, 73, 62.5, 67.1, 69.5, 73, 45, and 75.12. All peaks are closely related to the X'pert high score pdf number 00-019-0366. They are related to the planes (204), (220), (306), (412), (500), (330), (1110), (2110), and so on. It signifies that all xrd peaks are consistent with CoS1.097, which has a hexagonal crystal structure with a=b=10.1 and c=15.48 lattice parameters. The surface morphology has been investigated using FESEM technology.

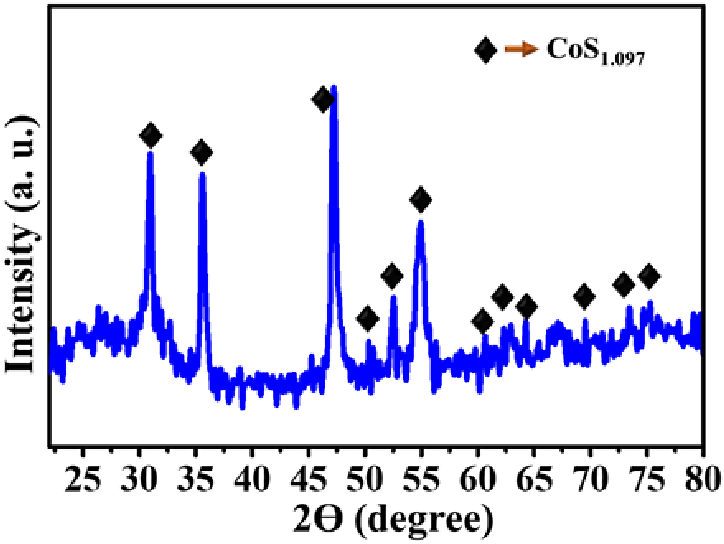

Fig. 3: XRD spectrum of cobalt sulphide.

Figure 4 (a–c) depicts FESEM images at various magnifications. It has been found that a micro-flower of cobalt sulphide has been formed. A side view of the micro-flower has been shown in Figure 4(b) where it has been observed that the sheet is combined in such a manner of nanoflower shape. Further, a closer view of the micro flower has been displayed in Figure 4(c).

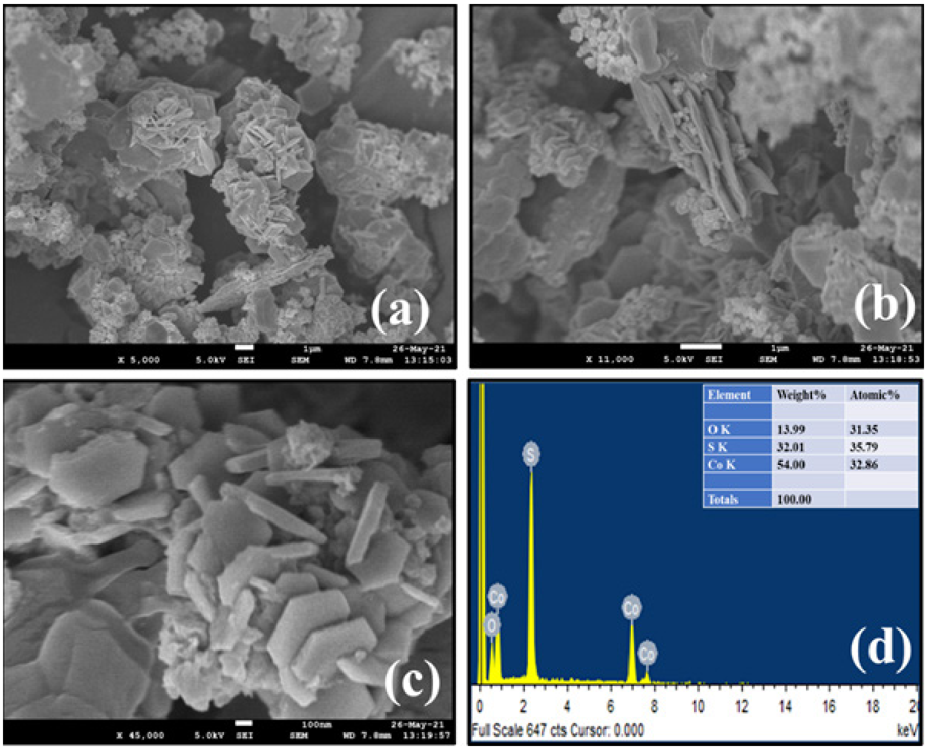

Fig. 4 (a-c): FESEM image of synthesized cobalt sulphide at different magnifications, (d) EDS spectrum.

Figure 4(c) revealed that a hexagonal sheet array is formed which in the collection formed a flower shape. A hexagonal sheet has a thickness smaller than 100 nm. Along with this, an EDX study has been done for the analysis of elemental composition. In Figure 4 (d), the EDX spectrum has both Co and S elemental peaks and both elements are present in the 32:35 (atomic %) ratio. The EDX data is commensurate with the XRD study.

Additionally, the electrochemical properties of synthesised cobalt sulphide were studied using Nyquist, CV, and GCD plots. Nickel foam and aluminium foil were used as current collectors in the electrochemical measurement. Figure 5 shows a comparison of how cobalt sulphide behaves over a number of different current collectors. Cobalt sulphide's CV behaviour at a scan rate of 100 mV with an Al foil and Ni foam current collector is shown in Figure 5(a). Cobalt sulphide has a low anodic and cathodic current when an Al-foil current collector is used. Therefore, the area under the CV curve of cobalt sulphide is greater with a Ni foam current collector than with an Al foil current collector. More area under the curve indicates a higher specific charge storage capacity. The specific capacitance from CV is determined by using the following equation.[15]

C_{sp}=(area under the curve)/(mass*scan rate*potential window)

At 100 mV/sec, with Ni-foam the specific capacitance value is 12.3 F/g or 36.8 mF/cm^2 and for Al foil the determined specific capacitance is 3.36 F/g or 10.1 mF/cm^2. This shows that the specific capacitance of Ni-foam as a current collector is roughly four times that of Al foil. Furthermore, a GCD comparison plot is shown in Figure 5(b). The GCD displays a shape

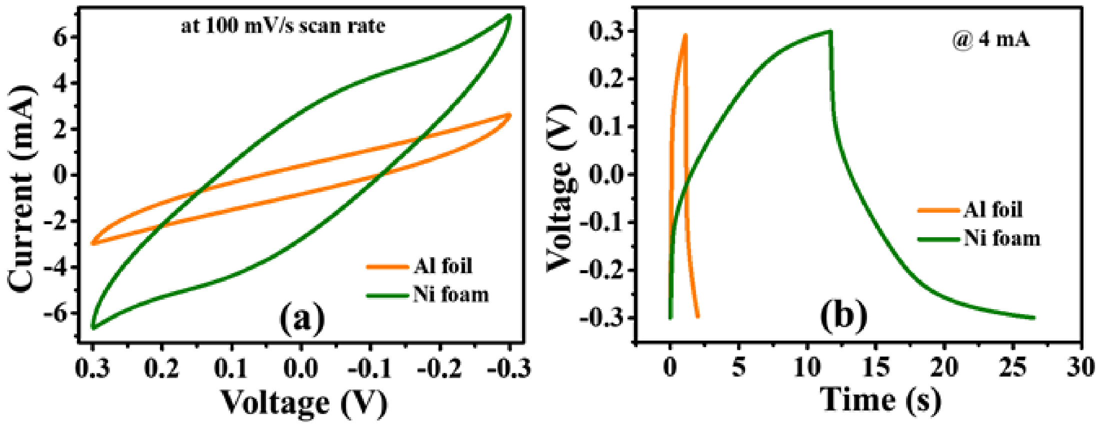

Fig. 5: Comparative plots (a) CV graph, (b) GCD graph.

similar to a distorted triangle,which is indicative of the quasi-type storage behaviour exhibited by cobalt sulphide (i.e., both faradic and non-faradic behaviour). It has been observed that when using Ni foam as a current collector, cobalt sulphide has a longer discharge time than when using Al-foil. Electrochemical performance is further quantified using the IR voltage drop parameter. At 4mA current, the IR drop value with nickel foam is 0.12 V and with Al- foil the value becomes 0.37V. IR drop determines self-discharge. The more the IR drop value, the more the self-discharging and vice-versa. The specific capacitance from GCD curves find out as.[15]

C_{sp}= (I×Δt)/(m×ΔV)

where *I* is current, Δt is the discharging time; m is the mass of electroactive material and ΔV is a potential window.At 4mA or 1.34 A/g current density, the calculated specific capacitance values for Ni foam and Al foil are 33 F/g and 2.23 F/g, respectively. This concludes that Nickel foam is a better current collector for electrochemical studies. Further using Ni foam as a current collector, CV @ different scan rate and GCD @ different current density has been shown in Figure 6. As shown in Figure 6(a), the area under the curve grows as the scan rate increases. Figure 6 (b) shows that as current densities increased, charging-discharging times decreased. This demonstrates the good reversibility of cobalt sulphide.

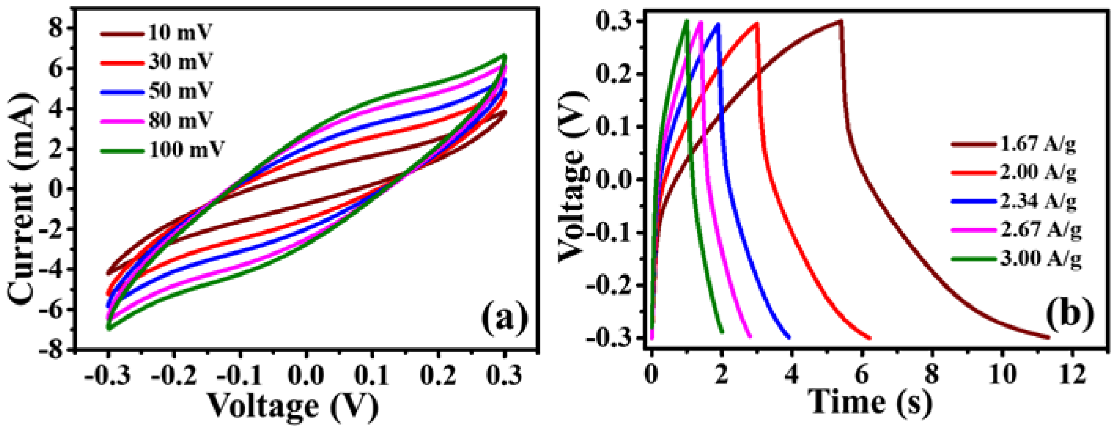

Fig. 6: (a) CV curves, (b) GCD curve using Ni foam as a current collector.

Generally, charge storage occurs in any material in two ways. First is EDLC /surface-controlled capacitance and the second is diffusion-controlled capacitance. The type of storage action can be determined using Equation 16: $I = a. v^b$, where I is the current density, v is the scan rate, and a and b are the variable quantity. Here a and b are determined by linear fitting of log i and log v plots. Figure 7 displays the corresponding plot of logi versus logv. From the literature, if the value of b approaches 0.5, then diffusion-controlled action of storage is observed.

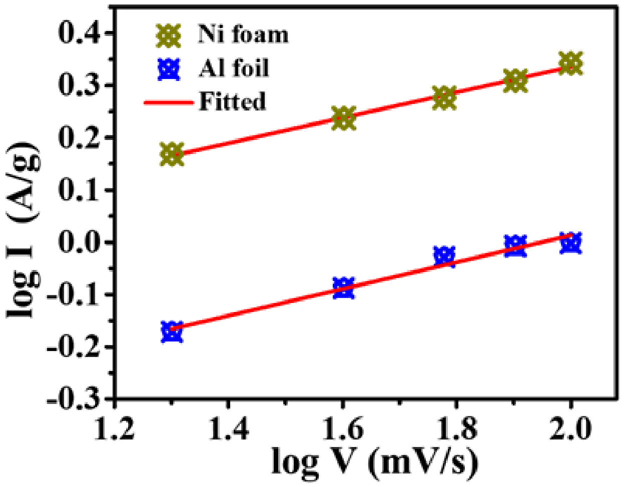

Fig. 7: log I vs log v plot.

On another side, if b is nearly equal to 1, a capacitive action has been dominating. In the current study, cobalt sulphide has b 2.5. It revealed that in cobalt sulphide diffusion-controlled capacitance dominates surface-controlled capacitance.

Furthermore, impedance measurements were taken at 5mV amplitudes in the frequency range of 100 kHz-5mHz. The Nyquist plot of cobalt sulphide with both current collectors is shown in Figure 8(a). The impedance spectrum was fitted using the

ZSimpWin 3.20 d demo software. The fitted circuit is depicted in inset of Figure 8(a). A non-zero intercept on the x-axis indicates the material's series resistance (Rs).[17] Ni foam has a lower Rs (3.75 value) as a current collector than Al foil (27.03). A semi-circle feature has been observed in the Nyquist plot near the high-frequency region.

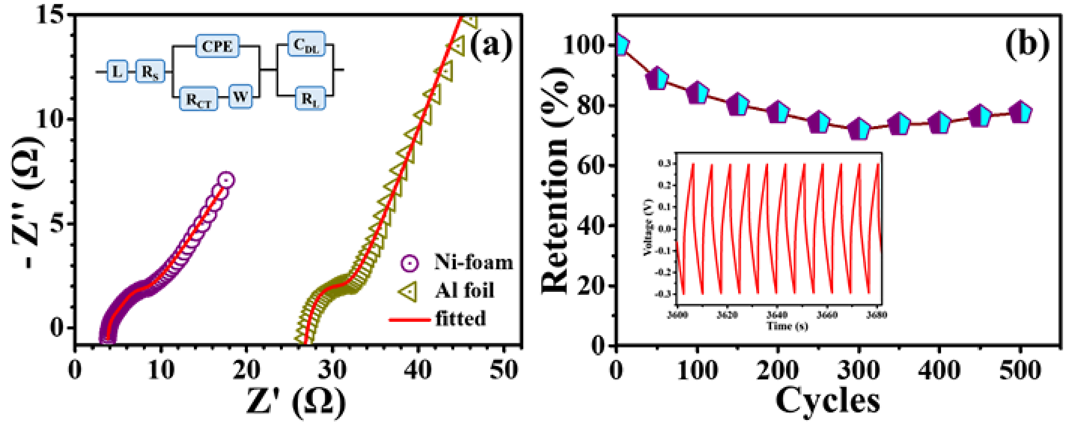

Fig. 8: (a) Nyquist plot, (b) cyclic stability at 5mA.

The diameter of the semicircle determines the charge transfer resistance (Rct). The estimated Rct values for Ni foam and Al foil are 5.3 Ω and 6.8 Ω, respectively. The sloped curve line reveals Warburg impedance in mid-frequency regions (W). The constant phase element displays the resistance observed during the diffusion process, and RL describes the leakage current. Further, cyclic stability has been measured using GCD characteristics. A few cycles at 5mA are shown in inset of Figure 8(b). After 500 cycles, the capacitance retention was found approximately 78% as shown in Figure 8(b). The results of cyclic stability are consistent with previous reports.[18] In the future, we will improve the electrochemical performance of cobalt sulphide by combining it with another material.

Overall Electrochemical measurements show that the bulk resistance and charge transfer resistance of cobalt sulphide are both lower when using Ni-foam as the current collector rather than Al-foil. This may be because the surface of Ni foam has high porosity but the surface of Al foil has a compact layer. The porous surface has a higher contact area with the coated material than a compact layer. As a result, the porous material facilitates the transport of charge. Due to their low resistance, Ni-foams provide excellent electrochemical performance.

Conclusion

XRD analysis shows that the as-prepared cobaltsulphide has a hexagonal crystal structure with the formula CoS1.07. A current collector made of Al-foil was found to have a lower anodic and cathodic current than a Ni-foam current collector. With a Ni-foam current collector, cobaltsulphide was found to have a higher specific capacitance than Al foil. Impedance studies show that a lower IR drop of cobalt sulphideis observed with Ni-foam than with aluminium foil as a current collector. With nickel foam, an improvement in electrochemical performance is found. Furthermore, Ni foam has lower series and charge transfer resistance than Al foil.

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N/a

Conflict of interest

The authors declare that there is no conflict of interest.

Reference

1. Ji, B., Zhang, F., Song, X., & Tang, Y. (2017). A novel potassium-ion-based dual-ion battery. Advanced materials, 29(19), 1700519.
2. S.J. Bao, C.M. Li, C.X. Guo, Y. Qiao: J. Power Sources 180 (2008) 676. DOI: 10.1016/j.jpowsour.2008.01.085
3. Li, J., Chen, D., & Wu, Q. (2019). Facile synthesis of CoS porous nanoflake for high performance supercapacitor electrode materials. Journal of Energy Storage, 23, 511-514.
4. Chen, Y., Xu, S., Zhu, S., Jacob, R. J., Pastel, G., Wang, Y., ... & Hu, L. (2019). Millisecond synthesis of CoS nanoparticles for highly efficient overall water splitting. *Nano Research,* 12(9), 2259-2267.
5. Li, Z., Ren, J., Yang, C., He, Y., Liang, Y., Liu, J., ... & Qian, D. (2021). Sodium 5-sulfosalicylate-assisted hydrothermal synthesis of a self-supported Co3S4−Ni3S2@ nickel foam electrode for all-solid-state asymmetric supercapacitors. *Journal of Alloys and Compounds,* 889, 161661.
6. Cheng, H., Li, T., Li, X., Feng, J., Tang, T., & Qin, D. (2021). Facile synthesis of Co9S8 nanocages as an electrochemical sensor for luteolin detection. *Journal of The Electrochemical Society,* 168(8), 087504.
7. T. Wu, X. Ma, T. Zhu: Mater. Lett. 183 (2016) 290. DOI: 10.1016/j.matlet.2016.07.106
8. Q. Wang, L. Jiao, H. Du, W. Peng, Y. Han, D. Song, Y. Si, Y. Wang, H. Yuan: J. Mater. Chem. 21 (2011) 327. DOI: 10.1039/C0JM03121F
9. Kristl, M., Dojer, B., Gyergyek, S., &Kristl, J. (2017). Synthesis of nickel and cobalt sulfide nanoparticles using a low cost sonochemical method. Heliyon, 3(3), e00273.
10. Bagabas, A. A., Alsawalha, M., Sohail, M., Alhoshan, S., &Arasheed, R. (2019). Synthesis, crystal structure, and characterization of cyclohexy lammoniu mtetraisothio cyanatoco baltate (II): A single-source precursor for cobalt sulfide and oxide nanostructures. *Heliyon,* 5(1), e01139.
11. Vijayakumar, E., Subramania, A., Fei, Z., & Dyson, P. J. (2015). High-performance dye-sensitized solar cell based on an electrospun poly (vinylidene fluoride-co-hexafluoropropylene)/ cobalt sulfide nanocomposite membrane electrolyte. Rsc Advances, 5(64), 52026-52032.
12. Abza, T., Dadi, D. G., Hone, F. G., Meharu, T. C., Tekle, G., Abebe, E. B., & Ahmed, K. S. (2020). Characterization of cobalt sulfide thin films synthesized from acidic chemical baths. *Advances in Materials Science and Engineering*, 2020.
13. Swathi, S., Rani, B. J., Yuvakkumar, R., Ravi, G., Babu, E. S., Pannipara, M., ... &Velauthapillai, D. (2021). Cobalt-based derivatives oxygen evolution reaction. *Applied Nanoscience*, 11(4), 1367-1378.
14. Zhang, F., Yuan, C., Lu, X., Zhang, L., Che, Q., & Zhang, X. (2012). Facile growth of mesoporous Co3O4 nanowire arrays on Ni foam for high performance electrochemical capacitors. *Journal of Power Sources*, 203, 250-256.
15. Sun, P., Li, N., Wang, C., Yin, J., Zhao, G., Hou, P., & Xu, X. (2019). Nickel-cobalt based aqueous flexible solid-state supercapacitors with high energy density by controllable surface modification. *Journal of Power Sources,* 427, 56-61.
16. Iqbal, M. Z., Haider, S. S., Siddique, S., Karim, M. R. A., Zakar, S., Tayyab, M., ... & Hussain, T. (2020). Capacitive and diffusion-controlled mechanism of strontium oxide based symmetric and asymmetric devices. *Journal of Energy Storage,* 27, 101056.
17. Mei, B. A., Munteshari, O., Lau, J., Dunn, B., & Pilon, L. (2018). Physical interpretations of Nyquist plots for EDLC electrodes and devices. *The Journal of Physical Chemistry* C, 122(1), 194-206.
18. Wang, R., Luo, Y., Chen, Z., Zhang, M., & Wang, T. (2016). The effect of loading density of nickel-cobalt sulfide arrays on their cyclic stability and rate performance for supercapacitors. *Science China Materials*, 59(8), 629-638.