All Sciences Proceedings
http://as-proceeding.com/

1st International Conference on Pioneer and Innovative Studies

June 5-7, 2023 : Konya, Turkey

ICPIS
https://as-proceeding.com/index.php/icpis

Binder-Free NiS@PPy Nanocomposite Cathode for High-Performance Supercapacitors

Hamza DUNYA[1], Recep TAS[1], Mahir GULEN[2] and Ebru KOROGLU[1*]

[1]*Department of Biotechnology, Faculty of Science, Bartin University, Turkey*
[2]*Department of Mechanical Engineering, Faculty of Engineering, Architecture and Design, Bartin University, Turkey*

[*]*(ebrukoroglu14@gmail.com) Email of the corresponding author*

Abstract – Industrialization and the increase in the world population increase the need for energy. Supercapacitors are preferred because of their features such as high specific power, long life, environmental friendliness, fast charge, and discharge rates. Supercapacitors are divided into two categories as EDLC and pseudo capacitors. Pseudo capacitors use materials that exhibit pseudo capacitance, such as transition metal oxides/sulphides and conductive polymers. Electrochemical studies and synthesis methods of polymer-based metal oxide composites, polyaniline and polypyrrole are examined in detail. Evaluating the various methods used in the preparation of supercapacitor electrodes, an idea is presented on the selection of suitable materials for electrochemical applications. Conductive polymers have good capacitance behavior but low cyclic stability. Transition metal sulfides exhibit electrochemical performance with high capacitance values and excellent redox reversibility. This study investigates NiS/PPy polymer as supercapacitor electrode material. The NiS structure was synthesized using Na_2S and nickel foam. NiS-PPy coating was carried out by electrochemical coating method. Structures were characterized by XRD and SEM, electrochemical studies such as cyclic voltammetry (CV), galvanostatic discharge (GCD) were carried out. By incorporating NiS into the PPy matrix, the C value was increased from 22.22 to 1404 F g^{-1}.

Keywords – NiS, PPy, NiS@PPy, Binder-Free, Supercapacitors

I. Introduction

As a result of the rapid increase in the world population and industrialization, the need for energy is increasing rapidly. With the depletion and widespread use of fossil fuels increasing environmental problems, the interest in sustainable, clean and safe energy sources is also increasing. In line with these developments, renewable energy systems, which are an important alternative to fossil fuels, are being developed (1). Clean and sustainable energy studies are examined under two main headings: using renewable resources for energy production and high-performance energy storage systems. Today's energy systems make it possible to produce high amounts of electrical energy from renewable energy sources. However, the desired results cannot be achieved in the storage process of the produced energy, and the targeted levels of capacity and cost/performance ratios cannot be reached. Therefore, there is an urgent need for high-performance and environmentally friendly energy storage devices (2,3).

Supercapacitors are preferred in energy storage systems due to their features such as high specific power, long life, environmental friendliness, fast charge, and discharge rates (4,5). Supercapacitors offer advantages such as memory backup capabilities and minimal maintenance requirements. Supercapacitors are basically evaluated in two categories: (i) electrical double layer capacitors (EDLC) AND (II) pseudo capacitors. Charge-discharge rates in EDLCs are very high as energy storage occurs by the formation of an electrical double layer on the surface of the electrode/electrolyte junction. No charge transfer occurs in this process, but the electrical potential difference applied on the electrodes attracts opposite charges in the electrolyte to the electrode surface, causing an electrical double layer formation along the electrodes. Therefore, EDLCs show high performance in terms of cyclic stability as they operate with a non-faradaic reaction. EDLCs have high power density while their energy density is lower. Materials such as carbon foam, graphene and activated carbon are used in the manufacture of such capacitors (6,7). Charge storage in pseudo capacitors occurs by faradaic surface redox reactions, and charge is transmitted across the interface. Because these redox reactions occur more slowly than bilayer formation, pseudo capacitors provide higher energy density and higher specific capacitance values compared to EDLCs. However, pseudo capacitors have lower energy density and cyclic stability than EDLCs. Materials exhibiting pseudo capacitance such as transition metal oxides/sulphides and conductive polymers are used in pseudo capacitors (8-13).

The most used polymers include polypyrrole, polyaniline and polythiophene. The use of these polymer-based composites has been increasing recently due to their high capacitive properties (14). Polypyrrole (PPy) is neutral in its natural state and is an insulator with a wide band gap of 3.16 eV. PPy is oxidized by doping and converts a π-electron from the neutral PPy chain from benzene (aromatic) to the quinoid structure. In this process a polaron is formed and further oxidation removes a second electron from the PPy chain, creating a doubly charged bipolaron. Chemical or electrochemical doping can be used to increase the conductivity of PPy. However, many efforts have been made to improve its capacitive properties due to its weaknesses such as low cyclicity, low speed, and short life (15-17). Recently, transition metal sulphides have attracted great interest as electrode materials for supercapacitors. Transition metal sulfides (eg NiSx, CuSx, CoSx and VSx) exhibit excellent electrochemical performance due to their high capacitance values and excellent redox reversibility (18-21). In particular, nickel sulfides offer advantages such as good electronic conductivity, high redox activity, low cost and easy fabrication (22). Compounds such as nickel sulfide family, NiS, NiS_2 and Ni_3S_2, which have different phases, have been widely investigated as promising electrode materials for supercapacitors and are still being investigated (21,23-25).

This work reveals the potential of NiS and PPy coated NiS in supercapacitor applications. NiS is a promising material for supercapacitors due to its high energy density and good electrical conductivity. The PPy coating process, on the other hand, improves the cyclic stability by increasing the mechanical strength of NiS, affecting the supercapacitor performance. In this study, the synthesis and characterization of NiS and NiS@PPy were investigated. The PPy coating process was carried out using the electrochemical polymerization method. The characterization results showed that as a result of a successful PPy coating process, the NiS surface was homogeneously coated and the composite material formed had the desired properties.

II. Materials and Method

A. *Materials and Equipment*

Ni foam, pyrrole, Na2S, and ((NH4)2S2O8) were employed in their analytical purity, without any additional pretreatment. All the reagents utilized in the experiments were procured from Sigma-Aldrich Co. LLC. The reactions were conducted using the ZIVE SP1 potentiostat-galvanostat electrochemical method.

B. *Synthesis of NiS*

NiS was formed at 130 °C by adding 2M Na_2S dropwise onto the Ni foam prepared in a 1x2 cm ratio. The NiS particles on the resulting Ni foam were washed 2 times with deionized water. It was then dried in a vacuum oven at 60°C for 12 hours.

C. *Synthesis of PPy and Preparation of NiS@PPy films*

Firstly, the NiS structures was synthesized by sulfurization of nickel foam with Na_2S precursor. 2 M Na_2S was prepared in de-ionized water and heated up to 80 ^{0}C. Next, the cleaned nickel foam immersed into Na_2S solution for 1 min. and dried at 60 ^{0}C for 5 min. This process was repeated 5 times. Finally, the samples were dried at 60 ^{0}C for 24 h. On the other hand, the PPy was electropolymerized on NiS samples using cycling voltammetry method in range of -1.2V/1.2 V 10 cycles. The electro polymerization method was conducted in three-electrode system includes Pt foil as counter electrode, Ag/AgCl as reference electrode and the prepared nanocomposite cathode as working electrode.

D. *Electrochemical Measurements*

The cyclic voltammograms (CV) of the films were recorded using a ZIVE SP1 potentiostat-galvanostat system with a three-electrode setup. The counter electrode was a platinum (Pt) foil, the working electrode was the fabricated films, and the reference electrode was Ag/AgCl. The liquid medium was used of 2M KOH redox electrolyte. For electrochemical impedance spectroscopy (EIS), Galvanostatic constant current (GCD) and cyclic voltammetry (CV) measurements.

III. RESULTS

A. *X-ray diffraction analysis*

Figure 1 displays the XRD spectrum of NiS obtained at temperatures ranging from 20 to 80 degrees. According to the XRD patterns (Fig. 1), the corresponding XRD peaks at 2θ=33.16, 38.49, 41.12 and 50.68° correspond to the (300), (220), (221) and (131) planes for NiS, respectively. Also, the diffraction points Ni found at 45.10, 52.35 and 76.88° are Ni peaks caused by foam.

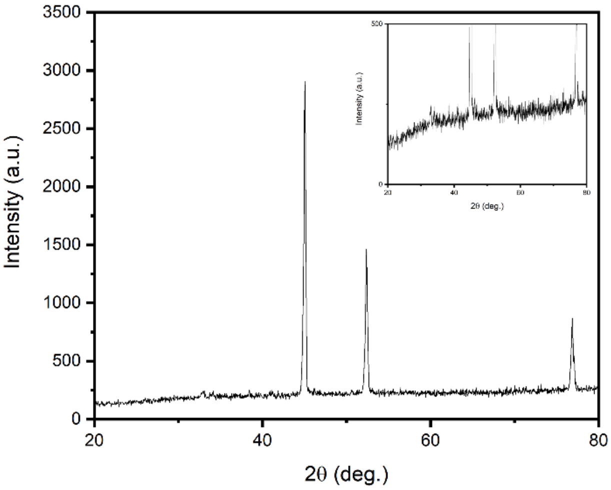

Figure 1. XRD pattern of nanoparticle of NiS

B. *Microstructure SEM and EDX analysis*

Figure 2 shows SEM images and EDX spectra of pure polypyrrole polymer, NiS and PANI/NiS composites. Figure 2 shows the SEM images of the surface morphology of pure NiS (Figure 2a), polypyrrole (Figure 2b) and NiS@PPy (Figure 2c) binder free. Homogeneous morphology is observed in SEM images of PPy given in Figure 2b. In addition, it is seen that the NiS given in Figure 2a grows in the form of a sheet. In the NiS@PPy structure shown in Figure 2c, since PPy is grown on NiS, it is seen that the morphology is layered, mimicking the sheet-shaped growth with NiS morphology.

When the EDX spectrum of NiS is examined (Figure 2d), it is seen that there are only Ni and S in the structure. The elemental composition analysis determined by looking at the EDX spectrum of PPy (Figure 2e) reveals C, Ni and N signals. In addition, when the EDX spectrum of NiS@PPy is examined, C, Ni and S signals are seen in the structure. When all EDX spectra are examined together, it shows that the distribution of the ratios among each other is balanced.

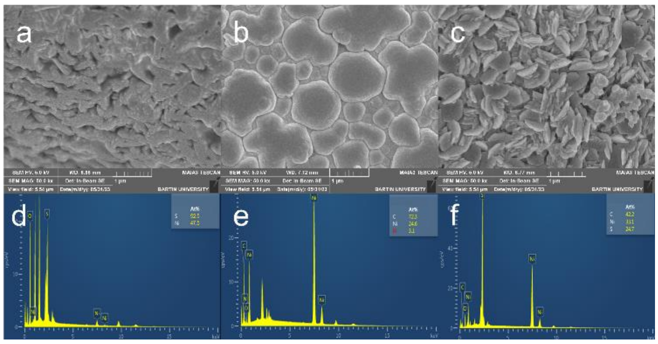

Figure 2. a) NiS, b) PPy, c) NiS@PPy SEM images and d) NiS, e) PPy, f) NiS@PPy EDX spectra

C. *Electrochemical Analysis*

Figure 3 (a-c) displays the cyclic voltammetry (CV) curves of pristine PPy, NiS and the nanocomposite NiS/PPy, respectively, while Fig 3. (d-f) shows the galvanostatic charge-discharge times for these materials. The discharge curves shown in Figure 3 (d-f) exhibits demonstrate a consistent linear and flat pattern, indicating that the capacitance primarily arises from Faradaic redox reactions, which is consistent with the observations in the CV curves (Figure 3 (a-c)). The CV of NiS@PPy shows different scan rates ranging from 10 to 100 mV s^{-1} with an increase in current response as the scan rate rises. This increase in the scan rate indicates good electrochemical property of NiS@PPy nanocomposite material. Comparing the curves in Figure 3 (d-f), the NiS@PPy electrode material exhibited a remarkable increase in discharge from 10s and 73.5s to 631.8s at a current density of 1 A g^{-1} within a voltage range of 0-0.45V. The capacitances of PPy, NiS, and

NiS@PPy are 22.22, 163.5 and 1404 F g^{-1}, respectively which were calculated from the following formula:

$$C = (I_m \Delta t)/\Delta V$$

where i_m is the current density, V is the voltage range, and t is the discharge time is second. By incorporation of NiS into PPy matrix increased the C value about 64 times.

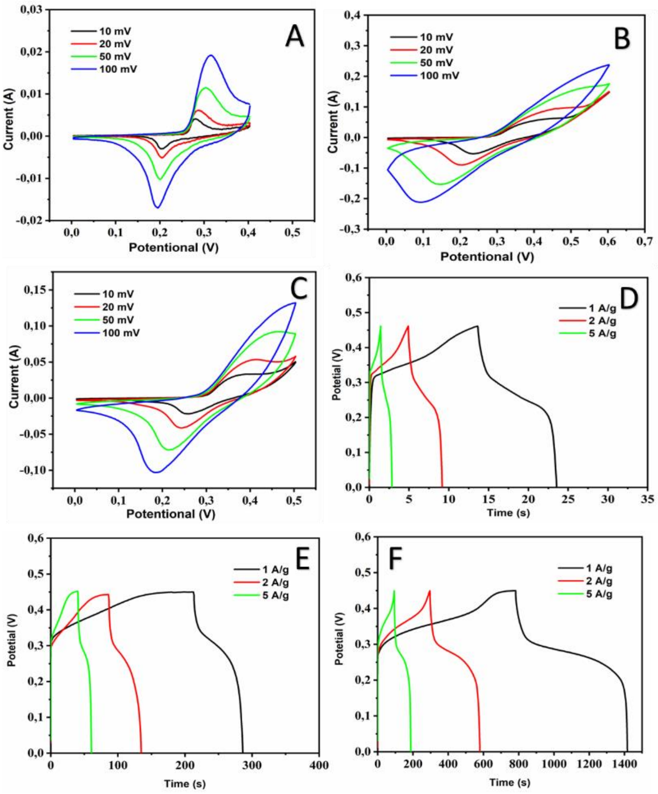

Figure 3. CV curves of a) PPy, b) NiS, c) NiS@PPy, GCD plot of d) PPy, e) NiS and f) NiS@PPy.

IV. DISCUSSION

In this study, the usability of nickel sulfide (NiS) and polypyrrole (PPy) coated NiS used in supercapacitor applications was investigated. NiS is a potential material for supercapacitors due to its properties such as high energy density and good electrical conductivity. However, the low mechanical strength and volume changes of pure NiS can create problems in terms of cyclic stability. Therefore, the mechanical strength of NiS is increased and the cyclic stability is improved by using the PPy coating method. In this study, synthesis and characterization of NiS and NiS@PPy were carried out in detail. The PPy coating process was carried out using the electrochemical polymerization method. The characterization results showed that because of a successful PPy coating process, the surface of NiS was coated homogeneously and the composite material formed had the desired properties.

Electrochemical performance evaluation was carried out using methods such as loop voltammetry and continuous charge-discharge tests. The results showed that PPy coated NiS showed high capacitance, good energy storage properties and cyclic stability in supercapacitor devices. The PPy coating layer increased the mechanical strength of NiS, limiting volume changes and improving cyclic stability. These results show that NiS and PPy coated NiS is a promising material combination for supercapacitors.

V. CONCLUSION

This study reveals the potential of NiS and PPy coated NiS in supercapacitor applications. The PPy coating process increases the mechanical strength of NiS, improving cyclic stability and optimizing supercapacitor performance. The results of this study are an important step in the development of supercapacitor technology. NiS and PPy coated NiS can provide efficiency and reliability in energy storage systems by offering advantages such as high energy storage capacity, good electrical conductivity, cyclic stability and mechanical durability. Future studies should focus on optimizing the PPy coating layer, examining different PPy coating methods, and synthesizing different ratios of NiS-PPy composites. In addition, it is important to evaluate the performances of NiS and PPy coated NiS in different application areas. In this way, the use potential of NiS and PPy coated NiS in supercapacitors can be further optimized and more efficient solutions can be obtained in the field of energy storage.

REFERENCES

[1] Ren, J., Cao, J. P., Zhao, X. Y., Yang, F. L., & Wei, X. Y., Recent advances in syngas production from biomass catalytic gasification: A critical review on reactors, catalysts, catalytic mechanisms and mathematical models. Renewable and Sustainable Energy Reviews, 116, 109426, 2019.

[2] Shao, Y., El-Kady, M. F., Sun, J., Li, Y., Zhang, Q., Zhu, M., ... & Kaner, R. B., Design and mechanisms of

asymmetric supercapacitors. Chemical reviews, 118(18), 9233-9280, 2018

[3] Dubal, D. P., Chodankar, N. R., Kim, D. H., & Gomez-Romero, P. , Towards flexible solid-state supercapacitors for smart and wearable electronics. Chemical Society Reviews, 47(6), 2065-2129, 2018

[4] Mu, X., Du, J., Zhang, Y., Liang, Z., Wang, H., Huang, B., ... & Xie, E. , Construction of hierarchical CNT/rGO-supported MnMoO4 nanosheets on Ni foam for high-performance aqueous hybrid supercapacitors. ACS applied materials & interfaces, 9(41), 35775-35784, 2017

[5] Zhang, J., & Zhao, X. S. , On the configuration of supercapacitors for maximizing electrochemical performance. ChemSusChem, 5(5), 818-841, 2012

[6] Theerthagiri, J., Senthil, R. A., Nithyadharseni, P., Lee, S. J., Durai, G., Kuppusami, P., ... & Choi, M. Y. , Recent progress and emerging challenges of transition metal sulfides based composite electrodes for electrochemical supercapacitive energy storage. Ceramics international, 46(10), 14317-14345, 2020

[7] Theerthagiri, J., Murthy, A. P., Lee, S. J., Karuppasamy, K., Arumugam, S. R., Yu, Y., ... & Choi, M. Y. , Recent progress on synthetic strategies and applications of transition metal phosphides in energy storage and conversion. Ceramics International, 47(4), 4404-4425, 2021

[8] Tomy, M., Ambika Rajappan, A., VM, V., & Thankappan Suryabai, X. , Emergence of novel 2D materials for high-performance supercapacitor electrode applications: a brief review. Energy & Fuels, 35(24), 19881-19900, 2021

[9] Abdel Maksoud, M. I. A., Fahim, R. A., Shalan, A. E., Abd Elkodous, M., Olojede, S. O., Osman, A. I., ... & Rooney, D. W. , Advanced materials and technologies for supercapacitors used in energy conversion and storage: a review. Environmental Chemistry Letters, 19, 375-439, 2021

[10] Balaji, T. E., Tanaya Das, H., & Maiyalagan, T. , Recent trends in bimetallic oxides and their composites as electrode materials for supercapacitor applications. ChemElectroChem, 8(10), 1723-1746, 2021

[11] Kumar, R., Joanni, E., Sahoo, S., Shim, J. J., Tan, W. K., Matsuda, A., & Singh, R. K. , An overview of recent progress in nanostructured carbon-based supercapacitor electrodes: from zero to bi-dimensional materials. Carbon, 193, 298-338, 2022

[12] Wang, Y., Zhang, L., Hou, H., Xu, W., Duan, G., He, S., ... & Jiang, S. , Recent progress in carbon-based materials for supercapacitor electrodes: a review. Journal of Materials Science, 56, 173-200, 2021

[13] Peng, S., Fan, L., Rao, W., Bai, Z., Xu, W., & Xu, J. , Bacterial cellulose membranes coated by polypyrrole/copper oxide as flexible supercapacitor electrodes. Journal of Materials Science, 52, 1930-1942, 2017

[14] Salleh, N. A., Kheawhom, S., Hamid, N. A. A., Rahiman, W., & Mohamad, A. A. , Electrode polymer binders for supercapacitor applications: a review. Journal of Materials Research and Technology, 2023

[15] BoopathiRaja, R., Vadivel, S., Rathinavel, S., Parthibavarman, M., & Ezhilarasan, M. , Shape-controlled synthesis of polypyrrole incorporated urchin-flower like Ni2P2O7 cathode material for asymmetric supercapacitor applications. Inorganic Chemistry Communications, 151, 110634, 2023

[16] Pineda, E. G., Azpeitia, L. A., Presa, M. R., Bolzán, A. E., & Gervasi, C. A. Benchmarking electrodes modified with bi-doped polypyrrole for sensing applications. Electrochimica Acta, 444, 142011, 2023

[17] Habib, S. A., Saafan, S. A., Meaz, T. M., Darwish, M. A., Zhou, D., Khandaker, M. U., ... & Omar, M. K. , Structural, magnetic, and AC measurements of nanoferrites/graphene composites. Nanomaterials, 12(6), 931, 2022

[18] Feng, J., Sun, X., Wu, C., Peng, L., Lin, C., Hu, S., ... & Xie, Y. , Metallic few-layered VS2 ultrathin nanosheets: high two-dimensional conductivity for in-plane supercapacitors. Journal of the American Chemical Society, 133(44), 17832-17838, 2011

[19] Wan, H., Ji, X., Jiang, J., Yu, J., Miao, L., Zhang, L., ... & Ruan, Y. , Hydrothermal synthesis of cobalt sulfide nanotubes: the size control and its application in supercapacitors. Journal of Power Sources, 243, 396-402, 2013

[20] Xia, X., Zhu, C., Luo, J., Zeng, Z., Guan, C., Ng, C. F., ... & Fan, H. J. , Synthesis of free-standing metal sulfide nanoarrays via anion exchange reaction and their electrochemical energy storage application. small, 10(4), 766-773, 2014

[21] Peng, L., Ji, X., Wan, H., Ruan, Y., Xu, K., Chen, C., ... & Jiang, J. , Nickel sulfide nanoparticles synthesized by microwave-assisted method as promising supercapacitor electrodes: an experimental and computational study. Electrochimica Acta, 182, 361-367, 2015

[22] Li, Y., Ye, K., Cheng, K., Yin, J., Cao, D., & Wang, G., Electrodeposition of nickel sulfide on graphene-covered make-up cotton as a flexible electrode material for high-performance supercapacitors. Journal of Power Sources, 274, 943-950, 2015

[23] Zhu, T., Wu, H. B., Wang, Y., Xu, R., & Lou, X. W. , Formation of 1D hierarchical structures composed of Ni3S2 nanosheets on CNTs backbone for supercapacitors and photocatalytic H2 production. Advanced Energy Materials, 2(12), 1497-1502, 2012

[24] Yang, J., Duan, X., Qin, Q., & Zheng, W. , Solvothermal synthesis of hierarchical flower-like β-NiS with excellent electrochemical performance for supercapacitors. Journal of Materials Chemistry A, 1(27), 7880-7884, 2013

[25] Pang, H., Wei, C., Li, X., Li, G., Ma, Y., Li, S., ... & Zhang, J. Microwave-assisted synthesis of NiS2 nanostructures for supercapacitors and cocatalytic enhancing photocatalytic H2 production. Scientific reports, 4(1), 3577, 2014