MJFAS
Malaysian Journal of Fundamental and Applied Sciences

Zaulkiflee *et al.* | Malaysian Journal of Fundamental and Applied Sciences, Vol. 19 (2023) 645-652

RESEARCH ARTICLE

Preliminary Study of Utilizing Polyaniline as Electrode Material for Supercapacitor Application: Juxtaposition of Electrochemical Performances

Nur Dina Zaulkiflee[a,b], Abdul Latif Ahmad[a]*, Nuur Fahanis Che Lah[c], Siew Chun Low[a], Norikazu Nishiyama[b]

[a]School of Chemical Engineering, Universiti Sains Malaysia, Engineering Campus, Seri Ampangan, 14300 Nibong Tebal S.P.S. Penang, Malaysia; [b]Graduate School of Engineering Science, Osaka University, Toyonaka, Osaka 560-8531, Japan; [c]Universiti Teknologi Petronas, Persiaran UTP, 32610 Seri Iskandar, Perak, Malaysia

Abstract Polyaniline (PANI) were prepared via a one-step electrochemical polymerization method in 0.2 M aniline and 0.2 M dopants for supercapacitors (SCs) application. To determine the appropriate conditions and materials for SCs application, the type of substrate, scan rate, dopants, and electrolyte on PANI were varied. The PANI composite's potential to store energy was conducted and evaluated using cyclic voltammetry in a three-electrode setup. The PANI-carbon felt demonstrated the best electrochemical performance compared to other substrate namely carbon and stainless steel. It is found that utilising H_2SO_4 as both dopant and electrolyte results in high specific capacitance.

Keywords: Substrate, dopants, electrolyte, specific capacitance.

Introduction

The implementation of innovative clean energy and energy storage are crucial issues that must be resolved due to the worsening of environmental degradation and resource scarcity. Due to its rapid charge and discharge rates, high power density, long cycle life, and environmentally friendly design, supercapacitors (SCs) are a revolutionary type of energy storage that has generated a lot of attention [1]. Nevertheless, SCs have a lower energy density than conventional energy storage systems, which results in various restrictions on its application. With that, the development of novel high-performance electrode materials became a hot topic in the SCs industry since electrode material is a significant component of the devices. Power, energy density, and stability performance factors are influenced by the electrode material. [2]. The three primary types of electrode materials utilized in energy storage devices are carbon species, metal compounds, and conducting polymers. A conducting polymer with fascinating features and prospective uses, notably in the area of energy storage, is polyaniline (PANI). The variable pseudocapacitive performance of PANI, which results from its multiple oxidation states, has made it a popular choice, both as a conductor and a substance that is directly electroactive. This is because PANI stores energy through redox transitions among the several oxidations states it displays during protonation. Furthermore, it is a common conductive polymer material with low cost, easy manufacture, high theoretical specific capacitance, and high conductivity [3]. Despite PANI SCs have been around for more than three decades, the possibility for practical use has only recently attracted attention. Several research initiatives were made to improve the processability, conductivity, and stability of PANI for technological application. The simplest approach is the oxidation state, dopant, and polymerization conditions are altered. Researchers are interested in enhancing PANI's features, such as its electrical conductivity, by selecting the suitable dopants since it creates charge carriers which is in charge of the conducting polymer's conductivity [4]. In addition, the scan rates and electrolyte utilised also may affect the PANI's features. Therefore, in this work, study on the different type of substrate along

***For correspondence:**
chlatif@usm.my

Received: 18 Oct. 2022
Accepted: 15 Feb. 2023

10.11113/mjfas.v19n4.2769

with effects of scan rate, dopants and electrolyte on polyaniline is conducted to determine the appropriate conditions and materials for technological applications. The electrochemical performance was collected and analyses using cyclic voltammetry (CV).

Materials and Methods

Chemical, Reagents, and Materials

Aniline ($C_6H_5NH_2$), sulphuric acid (H_2SO_4), hydrochloric acid (HCl, 37%), potassium chloride (KCl), ferrocyanide ($C_6FeN_6^{-4}$) x (Na_2SO_4), all of which were purchased from Sigma Aldrich were used. The chemicals were of analytical purity thus it was used without further processing. All of the solutions were made with deionized water. Platinum wire (0.5 mm 37 mm, China) and Ag/AgCl electrode (4 mm, China) were used as counter and reference electrodes accordingly. Carbon, stainless steel, and carbon felt were utilized as working electrodes (WE)/substrate to electroplate conductive polymers over an area of 1.9 cm^2.

PANI-WE Synthesis

The PANI was synthesized through the electrodeposition method employed a three-electrode configuration a three-electrode setup. 0.1 M Na_2SO_4 was prepared and utilized as pretreatment solution. The electropolymerization of aniline was carried out in 0.2 M aniline and either 0.2 M H_2SO_4 or 0.2 M HCl. PANI was deposited using the cyclic voltammetry (CV) process with a potential range of -0.5 to 1 V and variable scan rates. A continuous voltage of 0.002 V was given to the electrode materials in order to improve PANI adherence to WE. PANI was deposited onto the working electrode after 15 cycles of CV [5]. As illustrated in Figure 1, PANI exists in three diverse forms depending on its oxidation or protonation state: leucoemaraldine (completely reduced form), pernigraniline (totally oxidized form) and emeraldine (partially reduced or partially oxidized form) [6]. Leucoemaraldine, emearaldine, and pernigraniline vary from each other by two electrons for each aniline monomer.

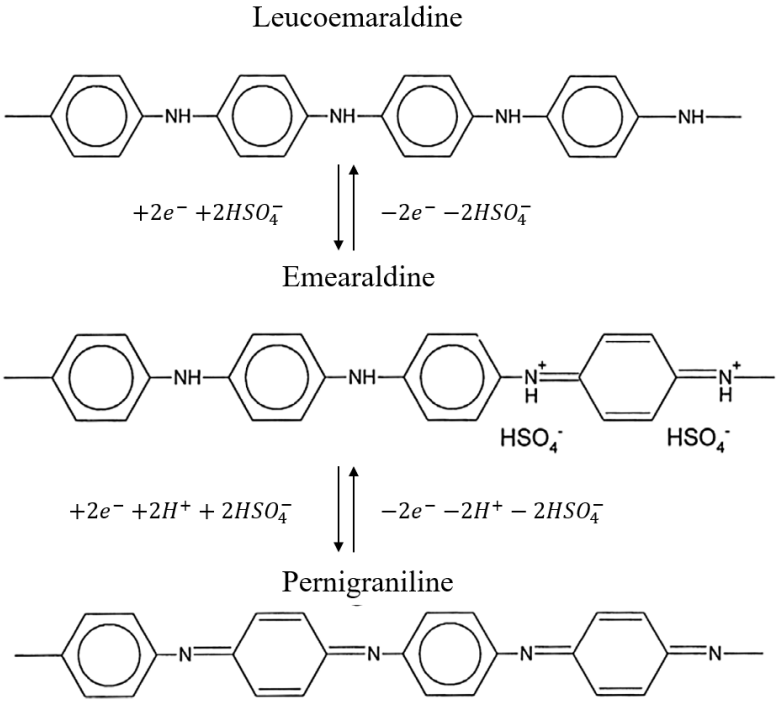

Figure 1. Schematic diagram describing PANI transitions

Electrochemical measurements

In this work, study on the different type of substrate (carbon, stainless steel, and carbon felt) along with effects of scan rate (8,10,20,50,00 mV.s^{-1}), dopants (H_2SO_4, HCl) and electrolyte (H_2SO_4, $C_6FeK_4N_6$.) on polyaniline is conducted to determine the appropriate conditions and materials for technological applications. The performance of the electrode was evaluated using the CV approach. 1 M H_2SO_4 was produced and utilized as an electrolyte in conjunction with $C_6FeK_4N_6$. The specifics cover reactivity, reversibility of electron transfer mechanisms, and the complexed transition metal oxidation state's stability. A preliminary determination concerning the property of PANI can be established by analyzing the CV curve.

Results and Discussion

Specific capacitance of different electrodes was conducted and calculated at each scan rate as tabulated in Table 1. The scan rate of the introduced nano composite was measured at 8, 10, 20, 50, and 100 mV.s^{-1}. The integral equation below was used to compute the specific capacitance, C_{sp} (F.g^{-1}) from the CV curves.

$$C_{sp} = \frac{\int iv\, dv}{\mu m \Delta V} \quad (1)$$

$$C_{sp} = \frac{It}{m\Delta V} \quad (2)$$

where I and V represent the current and potential used in the CV, μ is the scan rate (V.s-1), m represents active materials mass (g), ΔV is the potential discharge window, I represents the constant discharge, and t is the time of discharge (s).

PANI's C_{sp} is averagely high at a low scan rate of 8 mV.s^{-1}, as tabulated in table 1. At low scan rates, electrosorption capacitance is frequently large because scattered ions from the solution would more easily contact the electrode surface, resulting in enhanced ion surface adsorption/desorption [7]. With high scan rates, nevertheless, the effective inner-surface adsorption of ions reduced. Thus, the greater the scan rate, the lower and more stable the specific capacitance achieved, suggesting that the electrodes had fewer ions deposited in them [8]. This demonstrates that the ions don't have sufficient time to reach the electrode material's overall electrochemical surface.

Table 1. Csp of PANI at varies scan rate with different working electrodes

Scanrate (mV.s^{-1})	Specific capacitance, C_{sp} (F.g^{-1})		
	Carbon	Carbon Felt	Stainless steel
8.0000	251.60	300.73	186.62
10.0000	239.82	296.26	129.33
20.0000	170.80	248.38	54.87
50.0000	63.15	114.13	19.54
100.0000	22.62	48.34	10.80

Based on Table 1, it is apparent that the highest specific capacitance was achieved using carbon felt, followed by carbon and stainless steel electrode. This is mainly attributable to its the high surface area owing to its porous morphology and dense fiber network in carbon felt materials which enable PANI to polymerize on top of the electrode compared to others [9]. Additionally, carbon felt has noticeable dissimilar textures from carbon since it is made of unwoven, randomly aligned carbon fibers. In contrast, stainless steel delivers the low specific capacitance compared to carbon felt and carbon. It's possible that stainless steel had already attained electrochemical stability since no redox peaks were seen during CV measurements [10]. PANI is a very thin coating that does not spall off and inhibits further oxidation of the stainless steel, resulting in no redox reaction on the stainless steel electrode. Carbon felt was used to further study different parameters that could affect and improve the specific capacitance for SCs application.

Figure 2 (a) demonstrates the CV measurements of the prepared electrodes with and without pre-treatment. The arial-specific concentration on the treated carbon felt electrode was greater than it was on the untreated electrode. The carbon felt with treatment is higher than without treatment due to the pore size which allows access to hydrated ions, which is significant because pore size is essential for ion movement inside carbon materials [11]. Furthermore, carbon felt has a high surface area and porosity, allowing it to provide a large number of redox reaction sites as well as excellent electrolytic efficiency [12]. As a result, it primes the electrode surfaces for a more effective inclusion of PANI [5]. Meanwhile, figure 2 (b) shows that the specific capacitance in different type of dopants-electrolyte for treated and untreated electrode. Overall, the treated electrode is relatively higher compared to untreated electrode. The electrode which was treated with H_2SO_4 as the dopants and electrolyte showed the highest specific capacitance, recorded at 300.73 $F.g^{-1}$. Ultimately, having a good surface area and adequate access to the electrolyte allow for the transmission of charge and ideal storage.

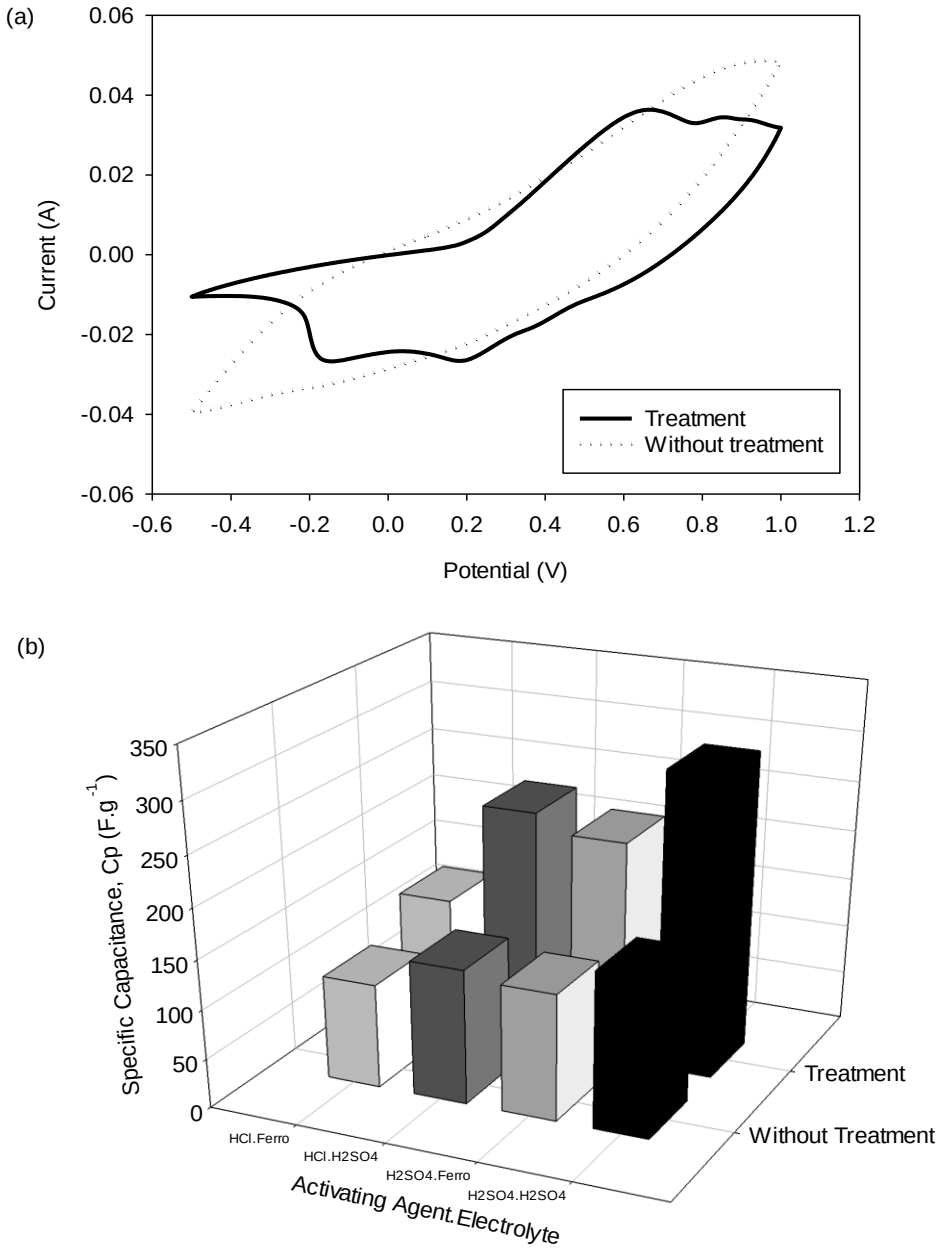

Figure 2. (a) CV measurements of carbon felt electrodes prepared with and without pre-treatment, recorded in three electrode setups. (b) Specific capacitance for carbon felt electrode in different type of dopants-electrolyte prepared with and without treatment

One of PANI fascinating features are its controllable electric behaviour whereby its determined by the amount of polymerization and oxidation states. The degree of polymerization is determined by the pH of the solution used to produce it, and an acidic pH is preferable for generating PANI with long chains [13]. Furthermore, depending on the dopants, the amount of electrons on the polymer backbone can be lowered or raised [14]. Thus, as depicted in figure 3 (a) inorganic acids like HCl and H_2SO_4 were employed as the dopants and compared. Meanwhile, figure 3 (b) compares the specific capacitance of the PANI- carbon felt electrode prepared by using different acidic medium.

Based on the figure below, generally in both electrolytes used (H_2SO_4 and ferrocyanide), electrode doped using H_2SO_4 yields higher specific capacitance. With H_2SO_4 as the dopants and electrolyte, the maximum specific capacitance was achieved. In terms of CV measurements and specific capacitance, H_2SO_4 is determined to be more efficient than HCl. Nunoo, Joseph Asare Awuah [15] found that PANI- H_2SO_4 have higher conductivity than PANI-HCl which might be related to polaron charge carriers responsible for the increased conductivity in H_2SO_4 doped PANI. This is also in line with Nde, Tamfuh [16] which discover that H_2SO_4 is better compared to HCl as the acid activation. The conductivity is substantially dependent on the anion present and follows the pattern HSO_4^- >Cl^- >NO_3^- >PO_4^- > ClO_4^- >COO^-, where this reliance may be due to electrolyte species adsorption.

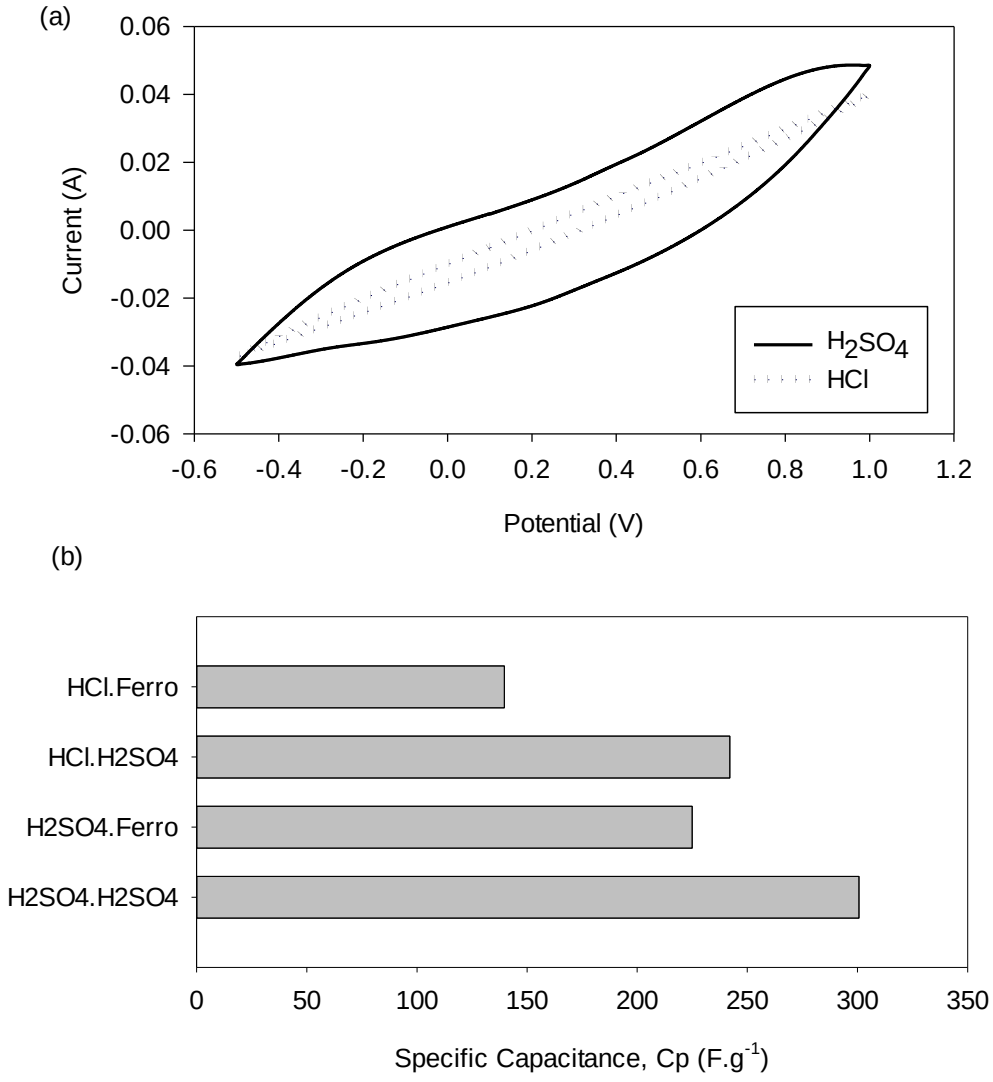

Figure 3. (a) CV measurements of carbon felt electrodes prepared with different dopants, recorded in three electrode setups at 8 $mV.s^{-1}$ (b) Corresponding anodic current determined

The findings demonstrate in figure 4 (a) that the electrode exhibit greater electrochemical response and sensitivity toward H_2SO_4 compared to ferrocyanide as electrolyte. The examined redox system of H_2SO_4 shows a modest pair of reversible redox peaks with cathodic and anodic peak potential, as shown in the CV. In comparison to ferrocyanide solution, H_2SO_4 aqueous solution has a higher ion conductivity/concentration. PANI is often doped under acidic circumstances, its electrical conductivity significantly reduces as the pH of the aqueous electrolytes rises. Consequently, almost all PANI-based SCs have used acidic aqueous electrolytes, notably the 1 $molL^{-1}$ H_2SO_4 electrolyte [17]. The specific capacitance at lower scan rate shows that carbon felt using both H_2SO_4 as dopants and electrolytes produce the higher capacitive behavior compared to others. As seen in figure 4 (b), the specific capacitance falls as the scan rate increases. Carbon felt electrodes using H_2SO_4 as both dopants and electrolytes demonstrated the greatest specific capacitance.

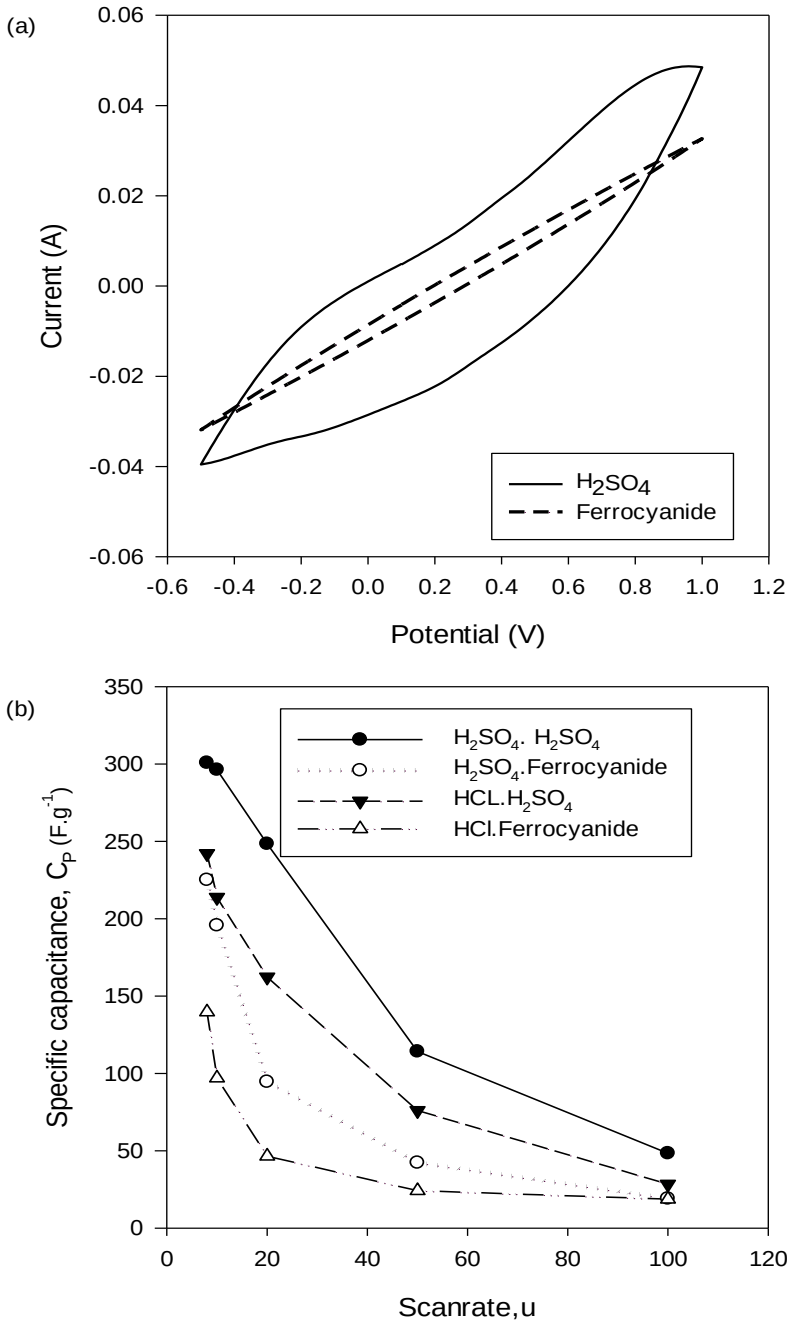

Figure 4. (a) CV measurements of carbon felt electrodes with different electrolyte, recorded in three electrode setups at 8 $mV.s^{-1}$ (b) Specific capacitance of carbon felt electrodes in different electrolyte

10.11113/mjfas.v19n4.2769

Conclusions

In summary, PANI- carbon felt demonstrated enhanced electrochemical performance compared to other electrode material. The effects of scan rate, dopants, and electrolyte on polyaniline was studied. 300.73 $F.g^{-1}$ is the highest specific capacitance, with H_2SO_4 as an electrolyte and dopant at a low scan rate. These findings highlight the potential of carbon felt materials, particularly as electrodes for SCs devices. Further improvement on the carbon felt surface can be improved and optimize that would lead to a better utilization of carbon felt as electrode.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

Acknowledgment

This work was financially supported by JASSO program and USM Fellowship program..

References

[1] K. Xie, M. Zhang, Y. Yang, L. Zhao, and W. Qi. (2018). Synthesis and supercapacitor performance of polyaniline/nitrogen-doped ordered mesoporous carbon composites. *Nanoscale Research Letters*, *13*, 163. 10.1186/s11671-018-2577-3.

[2] S. Rajagopal, R. Pulapparambil Vallikkattil, M. Mohamed Ibrahim, and D. G. Velev. (2022). Electrode materials for supercapacitors in hybrid electric vehicles: challenges and current progress. *Condensed Matter*, 7, 10.3390/condmat7010006.

[3] H. Wang, J. Lin, and Z.X. Shen. (2016). Polyaniline (PANi) based electrode materials for energy storage and conversion. *Journal of Science: Advanced Materials and Devices, 1*, 225-255. 10.1016/j.jsamd.2016.08.001.

[4] H. Fisal Alesary, H. Khalil Ismail, A. Fadhil Khudhair, and M. Qasim Mohammed. (2018). Effects of dopant ions on the properties of polyaniline conducting polymer. *Oriental Journal of Chemistry, 34*, 2525-2533. 10.13005/ojc/340539.

[5] J. Du, Y. Li, Q. Zhong, J. Yang, J. Xiao, Chen, F. Wang, Y. Luo, K. Chen, and W. Li. (2020). Boosting the utilization and electrochemical performances of polyaniline by forming a binder-free nanoscale coaxially coated polyaniline/carbon nanotube/carbon fiber paper hierarchical 3D microstructure composite as a supercapacitor electrode. *ACS Omega*, *5*, 22119-22130.

[6] A. Viswanathan and A. N. Shetty. (2022). Influence of different dopants and redox forms of PANI in its crystal structure, morphology, electrochemical energy storage to variable extent, unique properties and kinetics. *Bulletin of Materials Science*, *45*. 10.1007/s12034-021-02626-9.

[7] M. R. Islam, S. S. Gupta, S. K. Jana, and T. Pradeep. (2022). Industrial utilization of capacitive deionization technology for the removal of fluoride and toxic metal ions (As(3+/5+) and Pb(2+)). *Global Challenges, 6*, 2100129. 10.1002/gch2.202100129.

[8] Z. K. Ghouri, N. M. Barakat, and H. Y. Kim. (2015). Synthesis and Electrochemical Properties of MnO_2 and Co-Decorated Graphene as Novel Nanocomposite for Electrochemical Super Capacitors Application. *Energy and Environment Focus, 4*, 34-39, 10.1166/eef.2015.1136.

[9] A. A. Abaalkhail, B. A. Alshammari, G. N. Almutairi, F. S. Alenazey, M. F. Alotibi, A. M. Alenad, A. G. Alharbi, T. S. Almoneef, and B. M. AlOtaibi. (2022). enhancing the performance of a metal-free self-supported carbon felt-based supercapacitor with facile two-step electrochemical activation. *Nanomaterials (Basel), 12*, 10.3390/nano12030427.

[10] N. A. Salleh and A. A. Mohamad. (2020). Characterization of stainless steel mesh as a current collector in the supercapacitor application. *3rd International Postgraduate Conference on Materials, Minerals & Polymer (Mamip)*.

[11] H. Cao, X. Peng, M. Zhao, P. Liu, B. Xu, and J. Guo. (2018). Oxygen functional groups improve the energy storage performances of graphene electrochemical supercapacitors. *RSC Advances*, *8*, 2858-2865. 10.1039/c7ra12425b.

[12] Thi Xuan Huong Le, Mikhael Bechelany, and M. Cretin. (2017). Carbon felt based-electrodes for energy and environmental applications: A review. *Carbon*, *122*, 564-591.

[13] K. Bednarczyk, W. Matysiak, T. Tanski, H. Janeczek, E. Schab-Balcerzak, and M. Libera. (2021). Effect of polyaniline content and protonating dopants on electroconductive composites. Scientific Reports, 11, 7487. 10.1038/s41598-021-86950-4.

[14] Y. Lu, Z. D. Yu, Y. Liu, Y. F. Ding, C. Y. Yang, Z. F. Yao, Z. Y. Wang, H. Y. You, X. F. Cheng, B. Tang, J. Y. Wang, and J. Pei. (2020). The critical role of dopant cations in electrical conductivity and thermoelectric performance of n-Doped polymers. *Journal of American Chemical Society*, *142*, 15340-15348. 10.1021/jacs.0c05699.

[15] O. A. Nunoo, Joseph Asare Awuah, E. K. K. Abavare, and K. Singh. (2019). Effect of primary dopants on the

conductivity of polyaniline synthesized by electrochemical polymerization. *International Journal of Advanced Research in Engineering and Technology, 10*, 157-163.

[16] H. S. Nde, P. A. Tamfuh, G. Clet, J. Vieillard, M. T. Mbognou, and E. D. Woumfo (2019). Comparison of HCl and H_2SO_4 for the acid activation of a cameroonian smectite soil clay: palm oil discolouration and landfill leachate treatment. *Heliyon, 5*, e02926. 10.1016/j.heliyon.2019.e02926.

[17] A. Eftekhari, L. Li, and Y. Yang. (2017). Polyaniline supercapacitors. *Journal of Power Sources, 347*, 86-107. 10.1016/j.jpowsour.2017.02.054.