Jurnal
Teknologi

Full Paper

IONIC CONDUCTIVITY OF POLYVINYL ALCOHOL-BASED GEL ELECTROLYTE CONTAINING DIETHYL CARBONATE PLASTICIZER FOR SUPERCAPACITOR APPLICATION

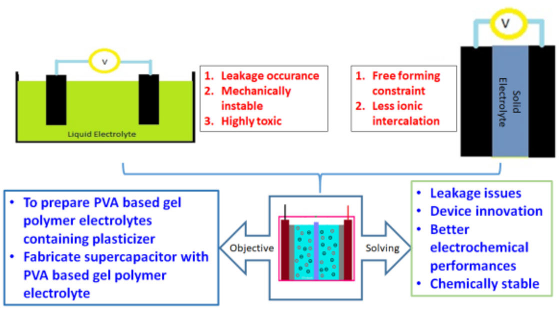
Mohd Asyadi Azam[a*], Tan Jun Yu[a], T. A. T. Adaham[a], M. F. Aziz[a,b], Akito Takasaki[c]

[a]Fakulti Kejuruteraan Pembuatan, Universiti Teknikal Malaysia Melaka, Hang Tuah Jaya, 76100 Durian Tunggal, Melaka, Malaysia
[b]School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
[c]Department of Engineering Science and Mechanics, Shibaura Institute of Technology, 3-7-5 Toyosu, Koto-ku, Tokyo, 135-8548, Japan

Article history
Received
16 November 2021
Received in revised form
15 June 2022
Accepted
25 July 2022
Published Online
31 October 2022

*Corresponding author
asyadi@utem.edu.my

Graphical abstract



Abstract

In this study, diethyl carbonate (DEC) as a plasticizer have been added to the gel electrolytes (GEs) system to influence the conductivity and storage performance of supercapacitor. The GE was prepared through a stirring method consisting of ethylene carbonate (EC), propylene carbonate (PC), potassium iodide (KI), polyvinyl alcohol (PVA) and dimethyl sulfoxide (DMSO). Consecutively, 5 wt. % DEC as a plasticizer was added for all samples. The GE preparation started with stirring all materials and heated until a homogenous gel was formed. The prepared GEs have been characterized with electrochemical impedance spectroscopy (EIS), which utilized to study the ionic conductivity of them. Sample with 15 wt. % of DEC in GE has the ionic conductivity of ~6 x 10^{-3} Scm^{-1}. This study shows that by adding DEC will cause the ionic conductivity improved which is suggested that this DEC enhanced the ion's mobility in the GEs' structures. In cyclic voltammetry, the gel electrolyte with 15 wt.% DEC attain the highest specific capacitance of 55.56 Fg^{-1} (scan rate of 10 mV s^{-1}). The charge-discharge curve of gel electrolyte acquires a shark fin-like shape which is alike with an ideal supercapacitor symmetric triangle shape. To summarize, the development of high conductivity GE may provide the path for high-performance supercapacitor.

Keywords: Poly(vinyl) alcohol, diethyl carbonate plasticizer, gel electrolyte, electrochemical impedance spectroscopy, cyclic voltammetry

Abstrak

Dalam kajian ini, dietil karbonat (DEC) bertindak sebagai pemplastik telah ditambah ke dalam sistem elektrolit gel (GEs) untuk mempengaruhi kekonduksian dan prestasi supercapacitor. GE disediakan melalui kaedah kacau yang terdiri daripada etilena karbonat (EC), propilena karbonat (PC), kalium iodida (KI), polivinil alkohol (PVA) dan dimetil sulfoksida (DMSO). Berturut-turut 5 wt. % DEC sebagai pemplastik telah ditambah untuk sampel. Penyediaan GE dimulakan dengan mengacau semua bahan dan dipanaskan sehingga gel homogen terbentuk. GE yang disediakan telah dicirikan dengan spektroskopi impedans elektrokimia (EIS), yang digunakan untuk mengkaji kekonduksian ionik elektrolit gel. Sampel dengan 15 wt. % DEC dalam GE mempunyai kekonduksian ionik ~6 x 10^{-3} Scm^{-1}. Kajian ini menunjukkan bahawa dengan menambah DEC akan menyebabkan kekonduksian ionik bertambah baik yang dicadangkan bahawa DEC ini meningkatkan mobiliti ion dalam struktur GE. Dalam voltammetri kitaran, elektrolit gel dengan 15 wt.% DEC mencapai kapasitans tentu tertinggi iaitu 55.56 Fg-1 (kadar imbasan 10 mV s-1). Keluk cas-nyahcas elektrolit gel memperoleh bentuk seperti sirip yu yang serupa dengan bentuk segi tiga simetri superkapasitor yang ideal. Untuk meringkaskan, pembangunan GE kekonduksian tinggi mungkin menyediakan laluan untuk superkapasitor berprestasi tinggi.

Kata kunci: poli(vinil) alcohol, pemplastik dietil karbonat, elektrolit gel, spektroskopi impedans elektrokimia, voltammetri kitaran

1.0 INTRODUCTION

The gel polymer electrolytes (GPEs) or gel electrolytes are important components in electrochemical device research. Gel electrolytes benefit both liquid and solid electrolytes, which involves the detrimental act of tackling leakage, chemical instability, and poor mechanical properties. In addition, a suitable gel electrolyte also should be showing a high ionic conductivity which influences the best performance in supercapacitor [1-3]. In achieving a high conductivity of GE, an additive should add to the system, such as a plasticizer. The study of plasticizer function is crucial to electrochemical performance [4].

A plasticizer in an electrolyte will improve the ionic conductivity. The amorphous phase of electrolytes will improve with the cooperation of the low viscosity of the plasticizer by decreasing glass transition temperature and melting temperature [2]. Addition, ionic conductivity can be enhanced with the existence of plasticizer. The plasticizer will decrease the ion pair effects in improving free charge carriers resulting in conduction activity [6]. The existence of DEC in the gel electrolyte also will soften the polymer backbone, which helps the better segmental motion of polymer chains [6]. Thus, the physical structure of the polymer has been modified where the ions are freely mobile through the polymer resulting in high ionic conductivity and total performance of the supercapacitor [6-8].

Thus, with high conductance electrolyte will provide the cell devices performance [9]. In this research, a diethyl carbonate (DEC) plasticizer (refer Figure 1) has been added to the gel electrolytes (GEs) system to enhance the ionic conductivity and supercapacitor performance [10]. The GEs are containing of PVA as polymer host, EC/PC and DMSO as solvent, KI as salt, and DEC as plasticizer.

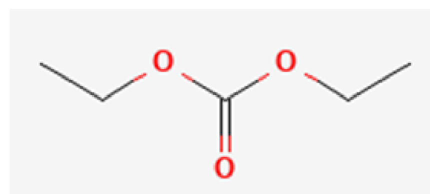


Figure 1 Chemical structure for diethyl carbonate (DEC) [10]

2.0 METHODOLOGY

The GE was prepared through a stirring method consisting of 8.52 wt. % ethylene carbonate (EC), 11.36 wt. % propylene carbonate (PC), 11.93 wt. % potassium iodide (KI), 5.68 wt. % of polyvinyl alcohol (PVA) and 62.50 wt. % dimethyl sulfoxide (DMSO). Consecutively 5 wt. % DEC plasticizer was added for the samples. The GPEs preparation started with mixing the EC, PC, DMSO, DEC, KI and PVA in a glass container and stirring until a homogenous mixture formed. This homogenous mixture was heated at 80 °C until a gel formed.

The GEs are fabricated into a supercapacitor with reduced graphene oxide activated carbon-based electrode. The rGO/AC electrode consists of 40 wt. % reduced graphene oxide (rGO), 50% wt. % activated carbon (AC), 4 wt. % carboxymethyl cellulose (CMC) and 6 wt. % styrene-butadiene rubber (SBR). The supercapacitor is fabricated in a battery jig.

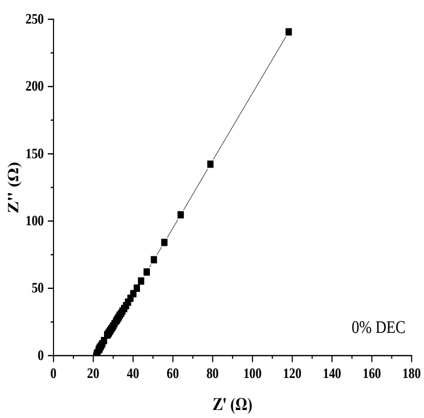
The prepared GEs will be characterized with electrochemical impedance spectroscopy (EIS) with a frequency range of 50 Hz to 1 MHz. From EIS results, the gel electrolyte's ionic conductivity will be obtained using the equation below; *t* is the thickness of the gel polymer electrolyte, R_b is the bulk resistance obtained from the intercept of the Nyquist plot with the x-axis and A is the interfacial area between electrode and electrolyte.

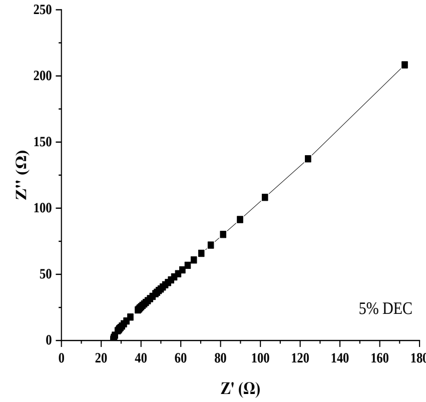
$$\sigma = t/(R_b \cdot A) \qquad (1)$$

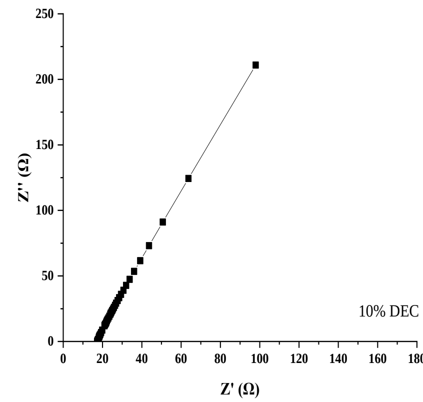
All GEs will be fabricated into a supercapacitor and tested with cyclic voltammetry (CV) measurement. The GEs were placed between two electrodes in a coin cell with thickness and area of 0.285 cm and 2.01 cm^2, respectively. Then the coin cell with the GEs will be located in the battery jig. The CV will be started with different scan rates (10, 25, 50, and 100 mVs^{-1}) and in the voltage range of 0 – 1.1 V. For the charge-discharge (CD) test, the voltage range will be started from 0 to 1.1 V at different current densities from 0.06 to 0.10 Ag^{-1}.

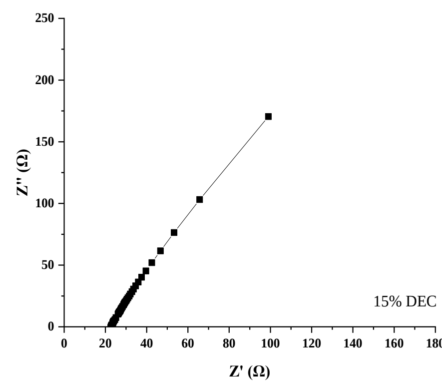
3.0 RESULTS AND DISCUSSION

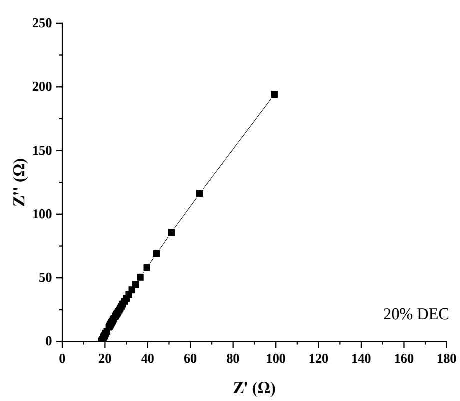
The GEs' ionic conductivity can be calculated by determining the bulk resistance (RB) from the intercept of the Nyquist plot and x-axis. As shown in Figure 2, the Nyquist plot of GEs for G1 is 21.80 Ω, G2 is 26.50 Ω, G3 is 18.50 Ω, G4 is 22.80 Ω, G5 is 18.50 Ω and G6 is 12.90 Ω. All Nyquist plots are shown in a steeply rising spike pattern. From Table 1, the highest conductivity of ~11 x 10^{-3} S cm^{-1} has shown by the G6 sample (25 wt. % DEC). The addition of plasticizer in GE increases ion dissociation, which will cause an increment of free charge carriers, which is vital in the conduction process [6]. The plasticizer's presence will also soften the polymer backbone to assist the high segmental motion of polymer chains, improving the ionic conductivity [11,12]. It proves that about 26% increment of conductivity has shown for the GE with the existence of DEC (G6) compared without DEC plasticizer (G1).











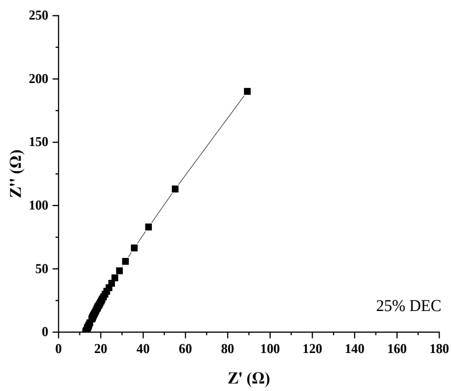


Figure 2 Nyquist Plots for 0, 5, 10, 15, 20 and 25 wt. % DEC gel electrolytes

Table 1 Bulk resistance and conductivity for all gel electrolyte samples

Sample	wt. % DEC	R_B (Ω)	Conductivity, σ ($x10^{-3}$ S cm^{-1})	Standard Deviation
G1	0	21.80	6.51	0.375
G2	5	26.50	5.35	0.220
G3	10	18.50	7.66	0.290
G4	15	22.80	6.24	0.690
G5	20	18.50	7.66	0.315
G6	25	12.90	10.99	0.085

From Figure 3, From CV curves (refer Figure 3), the specific capacitance, C_{sp} was obtained for all GEs. The specific capacitance at scan rate of 10 mV s^{-1} for G1, G2, G3, G4, G5, and G6 are shown as 30.30 Fg^{-1}, 26.09 Fg^{-1}, 30.30 Fg^{-1}, 55.56 Fg^{-1}, 24.41 Fg^{-1} and 37.88 Fg^{-1}, respectively. The G4 sample shows the highest C_{sp} of 55.56 Fg^{-1} which is it can observe that there is a significant increment of C_{sp} for G4 sample compared G1 sample (~30 Fg^{-1}) as expected. This scenario can prove that the adding of the DEC plasticizer can increase the ionic conductivity and charge stored in the supercapacitor [13].

From Table 2, it can be observed that the value of specific capacitance increases as the scan rate decreases. This phenomenon should be described since the reducing of scan rates will lessening ion diffusion coefficients in the gel electrolytes. At the lower scan rate, the gel electrolyte of the electrochemical devices has massive contact with the internal surface of the electrode by penetrating pores more thoroughly. This situation will cause the electrode surface has store more charge and resulting a large capacitance which is close to the intrinsic capacitance [14-16].

Figure 4 depicts the charge-discharge curves at different current densities ranging from 0.06 to 0.10 Ag^{-1}. From the CD curve, the specific capacitances (C_{sp}) for each scan rate were calculated, in which is the highest value of C_{sp} (0.16 Fg^{-1}) was at the current density of 0.10 Ag^{-1}. With regard to the voltage (IR) drop of the curves, the triangle shape of this composition is still considerable almost alike with an ideal supercapacitor. This scenario indicates this composition possesses a good supercapacitor behaviour [17-20].

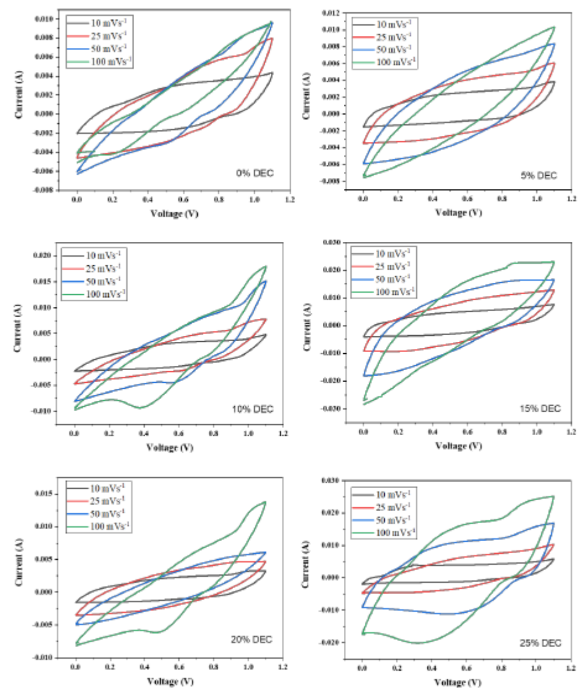


Figure 3 Cyclic voltammetry at different scan rates (10, 25, 50, and 100 mV s^{-1}) for 0, 5, 10, 15, 20 and 25 wt. % DEC gel electrolytes

Table 2 Specific capacitance for G4 (15 wt. % of DEC)

Scan rate, mVs^{-1}	Specific capacitance, C_{sp} (F g^{-1})
10	55.56
25	41.08
50	28.96
100	15.32

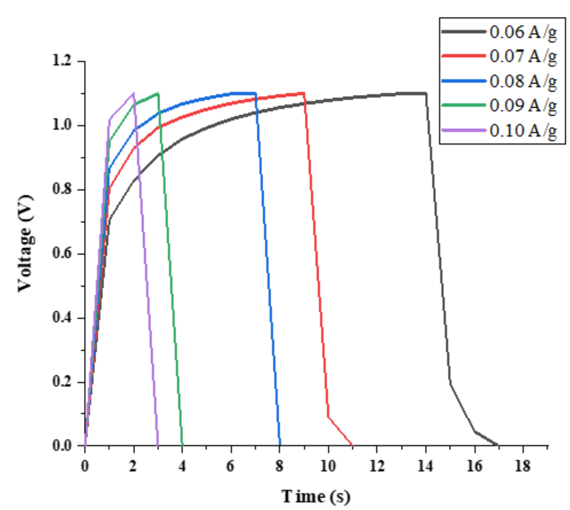


Figure 4 Charge-discharge at different scan rate (0.06, 0.07, 0.08, 0.09, and 0.10 Ag^{-1}) for G4 (15 wt. % of DEC)

4.0 CONCLUSIONS

Gel electrolytes with variation amount of DEC has been prepared. The G4 sample (15 wt. % DEC) shows the ionic conductivity of 6.24 x 10^{-3} Scm^{-1} and attain the highest specific capacitance of 55.56 Fg^{-1} (scan rates of 10 mVs^{-1}) in the cyclic voltammetry test. The charge-discharge curve of G4 sample acquires alike with an ideal supercapacitor symmetric triangle shape. It can be determined that the gel electrolyte with plasticizer modified the polymer structure and enhanced the ion mobility in the gel electrolyte, thus improving the ionic conductivity of the gel electrolyte resulting in a suitable electrolyte for high-performance supercapacitor fabrication.

Acknowledgement

Authors would like to acknowledge Universiti Teknikal Malaysia Melaka for the research grant numbered PJP/2020/FKP/PP/S01758 as well as the facilities support from Fakulti Kejuruteraan Pembuatan, UTeM.

References

[1] Niu, H., Wang, L., Guan, P., Zhang, N., Yan, C., Ding, M., Guo, X., Huang, T. and Hu, X. 2021. Recent Advances in Application of Ionic Liquids in Electrolyte of Lithium-Ion Batteries. *Journal of Energy Storage*. 40: 102659. DOI: https://doi.org/10.1016/j.est.2021.102659.

[2] Syali, M. S., Kumar, D., Mishra, K. and Kanchan, D. K. 2020. Recent Advances in Electrolytes for Room-Temperature Sodium-Sulfur Batteries: A Review. *Energy Storage Materials*. 31: 352-372. DOI: https://doi.org/10.1016/j.ensm.2020.06.023.

[3] Tan, S. J., Zeng, X. X., Ma, Q., Wu, X. W. and Guo, Y. G. 2018. Recent Advancements in Polymer-Based Composite Electrolytes for Rechargeable Lithium Batteries. *Electrochemical Energy Reviews*. 1(2): 113-138. DOI: https://doi.org/10.1007/s41918-018-0011-2.

[4] Pandey, K., Asthana, N., Dwivedi, M. M. and Chaturvedi, S. K. 2013. Effect of Plasticizers on Structural and Dielectric Behaviour of PEO. *Journal of Polymers*. DOI: https://doi.org/10.1155/2013/752596.

[5] Hirankumar, G. and Mehta, N. 2018. Effect of Incorporation of Different Plasticizers on Structural and Ion Transport Properties of PVA-LiClO4 Based Electrolytes. *Heliyon*. 4(12): 00992. DOI: https://doi.org/10.1016/j.heliyon.2018.e00992.

[6] Gohel, K., Kanchan, D. K., Machhi, H. K., Soni, S. S. and Maheshwaran, C. 2020. Gel Polymer Electrolyte Based on PVDF-HFP: PMMA Incorporated with Propylene Carbonate (PC) and Diethyl Carbonate (DEC) Plasticizers: Electrical, Morphology, Structural and Electrochemical Properties. *Materials Research Express*. 7(2): 025301. DOI: https://doi.org/10.1088/2053-1591/ab6c06.

[7] Das, S. and Ghosh, A. 2015. Effect of Plasticizers on Ionic Conductivity and Dielectric Relaxation of PEO-LiClO4 Polymer Electrolyte. *Electrochimica Acta*. 171: 59-65. DOI: https://doi.org/10.1016/j.electacta.2015.04.178.

[8] Pitawala, H. M. J. C., Dissanayake, M. A. K. L. and Seneviratne, V. A. 2007. Combined Effect of Al2O3 Nano-Fillers and EC Plasticizer on Ionic Conductivity Enhancement in the Solid Polymer Electrolyte (PEO) 9LiTf. *Solid State Ionics*. 178(13-14): 885-888. DOI: https://doi.org/10.1016/j.ssi.2007.04.008.

[9] Singh, P. K., Bhattacharya, B., Mehra, R. M. and Rhee, H. W. 2011. Plasticizer Doped Ionic Liquid Incorporated Solid Polymer Electrolytes for Photovoltaic Application. *Current Applied Physics*. 11(3): 616-619. DOI: https://doi.org/10.1016/j.cap.2010.10.012.

[10] Shukla, K. and Srivastava, V. C. 2016. Diethyl Carbonate: Critical Review of Synthesis Routes, Catalysts Used and Engineering Aspects. *RSC Advances*. 6(39): 32624-32645. DOI: https://doi.org/10.1039/C6RA02518H.

[11] Aziz, S. B., Woo, T. J., Kadir, M. F. Z. and Ahmed, H. M. 2018. A Conceptual Review on Polymer Electrolytes and Ion Transport Models. *Journal of Science: Advanced Materials and Devices*. 3(1): 1-17. DOI: https://doi.org/10.1016/j.jsamd.2018.01.002.

[12] Aziz, M. F., Azam, M. A., Noor, I. M., Buraidah, M. H. and Arof, A. K. 2021. Impact of Diethyl Carbonate in PVA Based Gel Polymer Electrolytes on Dye-Sensitized Solar Cells Performance. *Optical and Quantum Electronics*. 53(1): 1-16. DOI: https://doi.org/10.1007/s11082-020-02724-8.

[13] Aziz, S. B., M Hadi, J., Dannoun, E., Abdulwahid, R. T., R Saeed, S., Shahab Marf, A., Karim, W. O. and Kadir, M. F. 2020. The Study of Plasticized Amorphous Biopolymer Blend Electrolytes Based on Polyvinyl Alcohol (PVA): Chitosan with High Ion Conductivity for Energy Storage Electrical Double-Layer Capacitors (EDLC) Device Application. *Polymers*. 12(9): 1938. DOI: https://doi.org/10.3390/polym12091938.

[14] Yun, C. and Hwang, S. 2020. Analysis of the Charging Current in Cyclic Voltammetry and Supercapacitor's Galvanostatic Charging Profile Based on a Constant-Phase Element. *ACS Omega*. 6(1): 367-373. DOI: https://doi.org/10.1021/acsomega.0c04702.

[15] Chang, Q., Li, L., Qiao, H., Sai, L., Zhang, Y., Shi, W. and Huang, L. 2019. Enhanced Electrolyte Ion Penetration in Microdome-Like Graphene with High Mass Loading for High-Performance Flexible Supercapacitors. *ACS Applied Energy Materials*. 2(9): 6790-6799. DOI: https://doi.org/10.1021/acsaem.9b01240.

[16] Seman, R. N. A. R. and Azam, M. A. 2020. Hybrid Heterostructures of Graphene and Molybdenum Disulfide: the Structural Characterization and Its Supercapacitive Performance in 6M KOH Electrolyte. *Journal of Science: Advanced Materials and Devices*. 5(4): 554-559. DOI: https://doi.org/10.1016/j.jsamd.2020.09.010.

[17] Huang, M., Wang, L., Chen, S., Kang, L., Lei, Z., Shi, F., Xu, H. and Liu, Z.H. 2017. Highly Flexible All-Solid-State Cable-Type Supercapacitors Based on Cu/Reduced Graphene Oxide/Manganese Dioxide Fibers. *RSC Advances*. 7(17): 10092-10099. DOI: https://doi.org/10.1039/C6RA28117F.

[18] Liu, B., Yang, M., Chen, H., Liu, Y., Yang, D. and Li, H. 2018. Graphene-Like Porous Carbon Nanosheets Derived from Salvia Splendens for High-Rate Performance Supercapacitors. *Journal of Power Sources*. 397: 1-10. DOI: https://doi.org/10.1016/j.jpowsour.2018.06.100.

[19] Huang, A., El-Kady, M. F., Chang, X., Anderson, M., Lin, C. W., Turner, C. L. and Kaner, R. B. 2021. Facile Fabrication of Multivalent VOx/Graphene Nanocomposite Electrodes for High-Energy-Density Symmetric Supercapacitors. *Advanced Energy Materials*. 11(26): 2100768. DOI: https://doi.org/10.1002/aenm.202100768.

[20] Zhang, X., Wang, Y., Yu, X., Tu, J., Ruan, D. and Qiao, Z. 2021. High-Performance Discarded Separator-Based Activated Carbon for the Application of Supercapacitors. *Journal of Energy Storage*. 44: 103378. DOI: https://doi.org/10.1016/j.est.2021.103378.