PERFORMANCE ANALYSIS OF SUPERCAPACITOR WITH GRAPHENE OXIDE-DOPED CARBON ELECTRODES

NOR AMALIA SAMSUDDIN

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> School of Electrical Engineering Faculty of Engineering Universiti Teknologi Malaysia

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DEDICATION

This is solely dedicated to my parents, the strongest love and support I can ever have. Abah who taught me to have faith in everything I do, always reminds me that Allah is the best planner. Ummi who taught me to see the beauty in the most unexpected things, to be strong and never give up.

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ABSTRACT

Even though supercapacitor possesses superior power density, its main limitation is the relatively poor energy density as compared to other energy storage devices such as battery and fuel cell. One way to enhance the energy density is by increasing its capacitance, which is inevitably depend on its activated carbon electrode properties, precisely the surface area. The purpose of this study is to investigate the performance of graphene-doped electrodes in supercapacitor. A commercially available activated carbon powder was used to fabricate the activated carbon sheet. Two supercapacitors were fabricated by sandwiching a cellulose paper as the separator, which pre-immersed in an aqueous solution of sulfuric acid with a pair of untreated graphene-doped activated carbon sheets. The effect of different electrode materials configuration on the performance of the fabricated supercapacitors was analysed. The advantages and disadvantages of graphene oxide-doped on the carbon electrode are further discussed. The supercapacitors' behaviours and performances were inspected using an electrochemical measuring system, GAMRY Interface 1000. Electrochemical results for AC electrode and GO/AC electrode were compared. It is found that the implementation of graphene oxide-doped carbon as the electrode's material increases the energy storing capability of the fabricated supercapacitor.

ABSTRAK

Walaupun superkapasitor mempunyai ketumpatan kuasa yang unggul, namun kelemahan utama yang dihadapi ialah kepadatan tenaga yang secara relatifnya lebih rendah berbanding peranti storan tenaga yang lain seperti bateri dan sel bahan api. Salah satu cara untuk meningkatkan kepadatan tenaga adalah dengan meningkatkan kapasitansi, yang mana bergantung kepada ciri-ciri elektrod karbon diaktifkan, secara tepatnya lagi ialah kawasan permukaannya. Tujuan kajian ini dijalankan adalah untuk mengkaji prestasi elektrod graphene oxide-doped dalam superkapasitor. Serbuk karbon diaktifkan yang boleh didapati di pasaran telah digunakan untuk menghasilkan kepingan karbon diaktifkan. Dua superkapasitor telah direka bentuk dengan mengapit kertas selulosa sebagai pemisah, yang mana telah direndamkan didalam larutan cecair asid sulfuric terlebih dahulu, bersama dengan dua keping graphene oxide-doped karbon diaktifkan. Kesan konfigurasi bahan elektrod yang berbeza terhadap prestasi superkapasitor telah dianalisis. Kelebihan dan kelemahan graphene oxide-doped ke atas elektrod karbon telah dibincangkan dengan lebih lanjut. Sistem pengukur elektrokimia, GAMRY Interface 1000 telah diguna pakai untuk memeriksa tingkah laku dan juga prestasi superkapasitor. Keputusan elektrokimia untuk elektrod AC dan elektrod GO/AC telah dibandingkan. Telah didapati bahawa penggunaan graphene oxide-doped karbon sebagai bahan elektrod mampu meningkatkan kebolehan penyimpanan tenaga superkapasitor yang telah dibina.

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LIST OF ABBREVIATIONS

-	Graphene Oxide
-	Activated Carbon
-	Graphene oxide-doped activated carbon
-	Specific surface area
-	Galvanostatic charge/discharge
-	Cyclic voltammetry
-	Electrochemical impedance spectroscopy
-	Specific capacitance obtained through CV test
-	Specific capacitance obtained through GCD test
-	Specific capacitance obtained through EIS test
-	Energy density
-	Power density

LIST OF SYMBOLS

Ω	-	Ohm
°C	-	Degree Celsius
Hz	-	Hertz
wt%	-	Weight percentage ratio
π	-	Pi

CHAPTER 1

INTRODUCTION

1.1 Problem Background

Based on the statistics provided by World Health Organization (WHO), the number of deaths per year caused by climate changes (direct or indirect impacts) has added up to 160,000. This number is predicted to increase in twofold by 2020. The main cause of this environmental impact is the production and usage of fossil fuels (petroleum, coal, etc.) (Panwar, Kaushik, & Kothari, 2011). Despite the deadly effect, it is inevitable to use this resource to fulfil the ever increasing world energy demand until the deployment of an efficient, practical and reliable renewable energy source.

There are various factors that hinder the shifting towards the implementation of alternative energy sources. Some of them are scalability, input requirements and intermittency (Miguel & David, 2012), making the said energy sources to be unreliable and risky. However, with the growing awareness of environmental protection, many intensive researches have been conducted in the search of possible technology to equip the renewable-green energy source power plants. The advancement in energy storage technology is envisaged to ensure the continuity of the energy supply thus reducing the dependency on fossil fuels to generate the world energy (Aqib, Ahamed, Deshmukh, & Thirumalai, 2019).

Having said that, a vast number of energy storage devices with different energy conversion system, namely mechanical, electrical and electrochemical systems are available. Some of the most widely used devices are Flywheel Energy Storage, Supercapacitors and Lithium-ion battery (Xu, Lin, Zhong, & et al, 2014). For a long time prognosis, supercapacitors and lithium-ion battery have been the most interesting technologies to be studied and they have garnered the investors' attraction from

various field of applications. The present paper aims to study on supercapacitor as an efficient energy storing device for renewable energy power plant.

One of the main issue faces by supercapacitors is the fact that they have a relatively poor energy density (Zhu, Murali, & et al, 2011). The fact that they managed to be fully charged and discharged within short duration of time does not compensate the poor energy density. This is because renewable power plant needed a high-power energy storage devices with the capability to hold a huge amount of energy at a time and deliver the energy whenever is needed by the connected system. A plausible way to cater this issue is by optimizing the electrode material used in the fabrication of supercapacitors. Thus making the supercapacitors to be further divided into three categories, as the result of using different materials with different energy storing mechanism (Xu, Lin, Zhong, & et al, 2014).

This paper provides the method of electrode fabrication of supercapacitor by compositing graphene oxide with activated carbon. The proposed fabrication process involves an addition of single-step procedure in the fabrication process of activated carbon electrode. This fabricated electrode will then be tested by using GAMRY Interface 1000 in order to analyse the electrochemical properties exhibited. It is expected that the usage of graphene oxide-doped carbon composites as the electrodes material will increase the energy storing and delivering capability of supercapacitor. In order to validate the conviction, an activated carbon-based electrodes will also be fabricated and be used as the baseline. The electrochemical properties of the fabricated electrodes will be tested through three different tests, namely GCD, CV and EIS.

Numerous efforts have been made by researchers in the industry as regards of increasing specific capacitance value of the supercapacitors with various kind of electrode material hoping to boost their storing and delivering capabilities. It is expected that a lot more researches and studies to be conducted in the near future aiming to produce energy storage devices with high reliability and maximum efficiency. Thus, the implementation of renewable energy storage devices to supply energy, wind energy, etc.) with the aid of optimum energy storing devices to supply energy

will be highly possible and interesting making the sole dependency towards fossil fuels to be reduced.

1.2 Problem Statement

Through literature research conducted, it was found that supercapacitors with pure carbon electrodes are not able to meet the high energy storage requirements. This is mainly due to the fact that carbon possess low specific capacitance value thus resulting in a limited energy density (Xiaoying, et al., 2019). Low energy density restricts the applications to power delivery over only a short amount of time (few seconds). Numerous efforts have been done in order to overcome this limitation. One of them is by implementing graphene oxide as the electrode material for supercapacitor.

1.3 Research Goal

There are three research objectives involved:

- (a) To prepare activated carbon sheet for supercapacitor electrode.
- (b) To fabricate supercapacitors with activated carbon sheets and graphene-doped activated carbon sheets.
- (c) To perform electrochemical analysis of the fabricated supercapacitors.

REFERENCES

- A. Noorden, Z., Sugawara, S., & Matsumoto, S. (2012). Electrical properties of hydrocarbon-derived electrolytes for supercapacitors. *IEEJ Transactions on Electrical and Electronic Engineering*, 25-31.
- Aqib, M., Ahamed, M. B., Deshmukh, K., & Thirumalai, J. (2019). A review on recent advances in hybrid supercapacitors: Design, fabrication and applications. *Renewable and Sustainable Energy Review*, 123-145.
- Chavhan, M. P., & Ganguly, S. (2016). Electrospray of precursor sol on carbon paper and in situ carbonization for making supercapacitor electrodes. *Industrial & Engineering Chemistry Research*.
- Chen, S., Zhu, J., Wu, X., & et al. (2010). Graphene oxide-MnO2 nanocomposites for supercapacitors. *ACS Nano*.
- Chen, X., Paul, R., & Dai, L. (2017). Carbon-based supercapacitors for efficient energy storage. *National Science Review*, 453-489.
- Choi, J.-H., Lee, C., Cho, S., Moon, G.-D., Kim, B.-S., Chang, H., & Jang, H.-D. (2018). High capacitance and energy density supercapacitor based on biomass-derived activated carbons with reduced graphene oxide binder. *Carbon*, 16-24.
- Gao, H., Xiao, F., Ching, C., & et al. (2012). Flexible all-solid-state asymmetric supercapacitors based on free-standing carbon nanotube/graphene and Mn3O4 nanoparticle/graphene paper electrodes. ACS Appl Mater Interfaces.
- Jeong, H., Lee, J., & Shin, W. (2011). Nitrogen-doped graphene for high performance ultracapacitors and the Iimportance of nitrogen-doped sites at basal planes. *Nano Lett*.
- Miguel, E., & David, L. (2012). Current developments and future prospects of offshore wind and ocean energy. *Applied Energy*, 128-136.
- Panwar, N. L., Kaushik, S. C., & Kothari, S. (2011). Role of renewable energy sources in environmental protection: A review. *Renewable and Sustainable Energy Reviews*, 1513-1524.

- Seyedsalehi, M., Goodarzi, M., & Barzanouni, H. (2014). Use of carbon in Increasing the quality of drinking water- Case study: The wells of Savejbolagh villages. J Biodivers Environ Sci, 102-111.
- Wei, L. (2015). Composite polymer/graphite/oxide electrode systems for supercapacitors. Ohio: University of CinCinnati.
- Winter, M., & J. Brodd, R. (2004). What Are Batteries, Fuel Cells, and Supercapacitors? *Chemical Reviews*, 4247.
- Wu, Z., Wang, D., Ren, W., & et al. (2010). Anchoring hydrous RuO2 on graphene sheets for high performance electrochemical capacitors. *Adv Funct Mater*.
- Xiaoying, H., Haoshan, N., Miao, L., Shujie, L., Tao, A., & Hongwei, T. (2019). Battery-like MnCo2O4 electrode materials combined with active carbon for hybrid supercapacitors. *Electrochimica Acta*, 599-609.
- Xu, Y., Lin, Z., Zhong, X., & et al. (2014). Holey graphene frameworks for highly efficient capacitive energy storage. *Nat Commun*.
- Yan, J., Fan, Z., Wei, T., & et al. (2010). Fast and reversible surface redox reaction of graphene-MnO2 composites as supercapacitor electrode. *Carbon*.
- Yan, J., Wei, T., Shao, B., & et al. (2010). Electrochemical Properties of Graphene Nanosheet/Carbon Black Composites as Electrodes for Supercapacitors. *Carbon*.
- Zhao, Y., Hu, C., & Hu, Y. (2012). A versatile, ultralight, nitrogen-doped graphene framework. *Angew Chem Int Ed*.
- Zhu, Y., Murali, S., & et al. (2011). Carbon-based supercapacitors produced by activation of graphene. *Science*.