

ANALYSIS OF ELECTROCHEMICAL PARAMETERS FOR ACTIVATED
CARBON SUPERCAPACITOR

MUHAMMAD AIMAN BIN AZIDZUL

A project report submitted in partial fulfilment of the
requirements for the award of the degree of
Master of Engineering (Electrical Power)

School of Electrical Engineering
Faculty of Engineering
Universiti Teknologi Malaysia

JULY 2020

DEDICATION

I dedicate this work to every soul who brought colours into my life.

ACKNOWLEDGEMENT

First and foremost, I thank God for making all these possible and saving me at those dark times.

I am grateful to my project supervisor, Dr. Zulkarnain Ahmad Noorden, for introducing me to the exciting world of supercapacitors and guiding me with the theoretical part. Without his support, this whole project will turn to dust due the Covid-19 pandemic.

I am indebted to my fellow postgraduate students, Nizam and Amalia, for helping me with the practical part of this project which could not be easily found through literature.

Last but not least, utmost appreciation to 'You', the one who are about to read the following pages of the report. Hope it would benefit you in some kind of ways.

ABSTRACT

This project investigates the correlation between the cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) tests, which are the most common tests done to evaluate the performance of supercapacitor. The main contribution of this work is to study the characteristic of those tests, as well as knowing the relevance of using activated carbon (AC) electrode for the supercapacitor, when abundance of electrode options is also available in the market. This is achieved by comparing the electrochemical performance of the fabricated supercapacitor with the other materials' performances found in literature. To validate the findings, AC supercapacitor is constructed, which starts with creating AC electrode from commercially available AC powder. Cellulose paper, which used as the separator is sandwiched between two electrodes, before sealed inside the two-electrode test cell together with 1M H₂SO₄ solution as the electrolyte. The fabricated AC supercapacitor is then tested with the three tests stated before using Gamry Interface 1000. It is found that the CV test gives out the highest specific capacitance value while the EIS test gives out the lowest equivalent series resistance value. When compared with other materials, the performance of AC supercapacitor trails behind other novel material like metal-oxide supercapacitor. It is envisaged that this findings can be useful when choosing supercapacitor types for any application.

ABSTRAK

Kajian ini menyiasat hubungkait diantara ujian ‘cyclic-voltammetry’ (CV), ‘galvanostatic charge-discharge’ (GCD), dan ‘electrochemical impedance spectroscopy’ (EIS), yang merupakan ujian-ujian lazim bagi menentukan prestasi superkapasitor. Sumbangan utama bagi kajian ini ialah untuk mengetahui ciri-ciri ujian tersebut, disamping mengkaji kesesuaian penggunaan elektrod karbon diaktifkan (AC) berbanding bahan-bahan elektrod lain yang terdapat dipasaran. Hal ini dicapai dengan membandingkan prestasi elektrokimia superkapasitor yang dibina, dengan superkapasitor lain yang didapati dari kertas-kertas kajian. Untuk mengesahkan dapatan, superkapasitor AC dibina, bermula dengan pembuatan elektrod AC dari serbuk AC yang didapati di pasaran. Kertas selulosa yang digunakan sebagai pemisah, diapit oleh dua keping elektrod, sebelum dimeteraikan didalam sel ujian bersama larutan cecair asid sulfurik. Superkapasitor AC yang siap dibina kemudiannya diuji dengan tiga ujian yang dinyatakan awal tadi dengan menggunakan ‘Gamry interface 1000’. Kajian mendapat bahawa ujian CV memberikan nilai tertinggi bagi kapasitansi tertentu, manakala ujian EIS memberikan nilai terendah bagi rintangan siri yang setara. Kajian turut mendapati, apabila dibandingkan dengan bahan-bahan lain, prestasi superkapasitor AC agak ketinggalan berbanding bahan baru seperti logam oksida. Diharapkan agar dapatan-dapatan ini bermanfaat dalam pemilihan jenis-jenis superkapasitor bagi apa-apa penggunaan.

TABLE OF CONTENTS

	TITLE	PAGE
	DECLARATION	iii
	DEDICATION	iv
	ACKNOWLEDGEMENT	v
	ABSTRACT	vi
	ABSTRAK	vii
	TABLE OF CONTENTS	viii
	LIST OF TABLES	x
	LIST OF FIGURES	xi
	LIST OF ABBREVIATIONS	xii
	LIST OF SYMBOLS	xiii
CHAPTER 1	INTRODUCTION	1
1.1	Background	1
1.1.1	Energy Storage Devices	1
1.1.2	Supercapacitor	2
1.1.3	Operation Principle of EDLC	3
1.2	Problem Statement	4
1.3	Research Goal	4
1.4	Research Scope	4
CHAPTER 2	LITERATURE REVIEW	5
2.1	Electrode Materials	5
2.1.1	Activation Process	6
2.2	Electrolyte	8
2.3	Research Gap	8
CHAPTER 3	RESEARCH METHODOLOGY	9
3.1	Introduction	9

3.2	Methodology	9
3.2.1	Preparation of Activated Carbon Electrode	9
3.2.2	Fabrication of Supercapacitor	11
3.3	Electrochemical Performances Analysis	12
3.3.1	Cyclic Voltammetry Test (CV)	15
3.3.2	Galvanostatic Charge/Discharge Test (GCD)	16
3.3.3	Electrochemical Impedance Spectroscopy Test (EIS)	17
3.4	Chapter Summary	18
CHAPTER 4	RESULTS AND DISCUSSION	19
4.1	Introduction	19
4.2	Results	20
4.2.1	Cyclic Voltammetry Test (CV)	20
4.2.2	Galvanostatic Charge/Discharge Test (GCD)	22
4.2.3	Electrochemical Impedance Spectroscopy Test (EIS)	28
4.3	Discussion	34
4.3.1	Cyclic Voltammetry Test (CV)	34
4.3.2	Galvanostatic Charge/Discharge Test (GCD)	35
4.3.3	Electrochemical Impedance Spectroscopy Test (EIS)	37
4.3.4	Tests Comparison	37
4.3.5	Electrode Materials Comparison	39
4.4	Chapter Summary	42
CHAPTER 5	CONCLUSION AND RECOMMENDATIONS	43
5.1	Research Outcomes	43
5.2	Future Works	43
REFERENCES		45

LIST OF TABLES

TABLE NO.	TITLE	PAGE
Table 3.1	Parameters for electrochemical tests	14
Table 4.1	Data obtained through CV test for AC electrode	21
Table 4.2	Data obtained through GCD test for AC electrode	27
Table 4.3	Resistances observed form the Nyquist plot	29
Table 4.4	Comparison of electrochemical parameters from all the tests	38
Table 4.5	Specific capacitance of electrodes from other materials	40

LIST OF FIGURES

FIGURE NO.	TITLE	PAGE
Figure 1.1	Commercial supercapacitor	2
Figure 1.2	EDLC operation	3
Figure 3.1	Procedures for the preparation of AC electrode	10
Figure 3.2	Procedures for the preparation of GO/AC electrode	11
Figure 3.3	Two-electrode test cell configuration	12
Figure 3.4	Gamry Interface 1000	12
Figure 3.5	Test cell and GAMRY Interface connection	13
Figure 3.6	Sample electrode	13
Figure 3.7	Cellulose paper	14
Figure 4.1	CV curves at different scan rate	20
Figure 4.2	GCD curves at different constant current	22
Figure 4.3	Zoomed-in graph in the instance of charge-discharge at different constant current; a) 5 mA b) 10 mA c) 20 mA d) 30 mA	26
Figure 4.4	Nyquist plot of imaginary impedance versus real impedance	28
Figure 4.5	Zoomed-in graph of Nyquist plot	29
Figure 4.6	$C_{S(EIS)}$ vs F curve from EIS test for AC electrode	30
Figure 4.7	Real part of capacitance versus frequency	31
Figure 4.8	Imaginary part of capacitance versus frequency	32
Figure 4.9	Imaginary part of capacitance versus frequency	33
Figure 4.10	Specific Capacitance versus scan rate	34
Figure 4.11	Specific capacitance versus constant current	35
Figure 4.12	Power density versus constant current	36
Figure 4.13	Energy density versus constant current	36
Figure 4.14	Scan rate and constant current versus specific capacitance	38
Figure 4.15	Ragone plot of power density versus energy density	41

LIST OF ABBREVIATIONS

AC	-	Activated Carbon
GCD	-	Galvanostatic charge/discharge
CV	-	Cyclic voltammetry
EIS	-	Electrochemical impedance spectroscopy
$C_{S(CV)}$	-	Specific capacitance obtained through CV test
$C_{S(GCD)}$	-	Specific capacitance obtained through GCD test
$C_{S(EIS)}$	-	Specific capacitance obtained through EIS test
E_D	-	Energy density
P_D	-	Power density

LIST OF SYMBOLS

Ω	-	Ohm
$^{\circ}\text{C}$	-	Degree Celsius
Hz	-	Hertz

CHAPTER 1

INTRODUCTION

1.1 Background

1.1.1 Energy Storage Devices

The World Health Organization (WHO), came out with a statistic of up to 160,000 of deaths per year are caused by both direct and indirect impact of climate change. The main cause identified of this environmental disaster is the production and usage of fossil fuels [1]. However. Given the deadly impact, it is unavoidable to use this resource before an affordable, realistic, and effective renewable energy source is implemented to meet the ever-increasing world energy demand.

Nowadays, there are a large number of energy storage devices with different energy conversion systems available, including mechanical, electrical and electrochemical systems. Flywheel power storage, supercapacitors and lithium-ion battery are some of the most commonly used devices [2]. Supercapacitors and lithium-ion battery have been the most interesting technologies to be studied for a long time, and they have garnered the attraction of investors from different fields of applications.

There are many factors that hinder the move towards the introduction of renewable sources of energy. There are many factors that hinder the move towards the introduction of renewable sources of energy. Some of them are scalability, specifications for inputs, and intermittency [3], which makes the said energy sources unstable and dangerous. However, with the increasing knowledge of environmental protection, several intensive works have been carried out in the quest for possible technologies to equip the power plants with renewable-green energy sources. The advancement of energy storage technology is intended to ensure the continuity of

energy supply, thereby reducing the dependence on fossil fuels to fulfill the World energy demand [4].

1.1.2 Supercapacitor

Thanks to their high-power density, incredibly long cycle life, low maintenance costs, and healthy operating features, electrochemical capacitors, also called supercapacitors, are considered highly complementary to batteries. Their excellent performance makes portable electronics, power back-up systems, hybrid electric vehicles, and other electronic products promising for supercapacitor. One of the drawback of supercapacitor when compared to batteries is the low energy density characteristic. The performance of a supercapacitor electrode material depends largely on its structural engineering, which can significantly affect the electrical conductivity, electrolyte penetration and electrode ion transfer [5]. Researchers in the industry have made various efforts to improve the specific capacitance value of the supercapacitors with different types of electrode material aiming to enhance their storage and power output.



Figure 1.1 Commercial supercapacitor

1.1.3 Operation Principle of EDLC

Supercapacitors can be categorized into electrochemical double layer capacitors (EDLC), pseudocapacitors, and hybrid capacitors according to the charging storage mechanism. An EDLC is typically composed of two activated carbon electrodes, separated by a porous membrane separator and soaked in an aqueous or non-aqueous electrolyte. Electrical charges are deposited on the electrode surface by reversible ion adsorption / desorption processes while the opposite charged ions are adsorbed on the electrolyte side to form electrical double layers. With a high specific surface area and plenty of nanopores of the activated carbon electrodes, EDLC generally have a high-power density of up to 105 W / kg and a long life cycle [5]

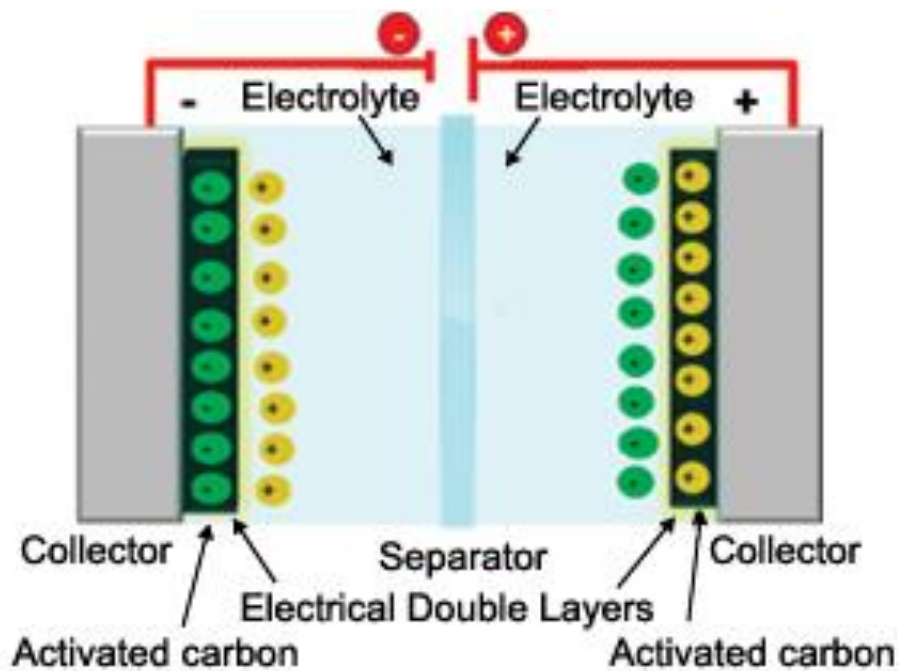


Figure 1.2 EDLC operation

1.2 Problem Statement

Through literature research conducted, it was found three types of tests; 1) cyclic voltammetry, 2) galvanostatic charge-discharge, and 3) electrochemical impedance spectroscopy, have been commonly chosen to assess the performance of the supercapacitor. However, limited studies have been carried out to explore the correlation between those three tests' results. This research investigates the correlation of these tests for an AC-based supercapacitor. The performance of the supercapacitor in comparison to other novel electrode materials-based supercapacitors is also carried out, thus, indicating the relevance of AC electrode.

1.3 Research Goal

There are three research objectives involved:

- (a) To fabricate supercapacitor with a pair of activated carbon sheets as the carbon electrodes.
- (b) To characterize the electrochemical performance of fabricated supercapacitor.
- (c) To carry out a performance comparison of the fabricated supercapacitor to other supercapacitors with various types of electrodes.

1.4 Research Scope

- (a) The research focuses on utilizing as precursor material for supercapacitor electrode
- (b) The electrochemical performance is evaluated based three electrochemical tests; cyclic voltammetry, galvanostatic charge-discharge and electrochemical impedance spectroscopy tests.
- (c) The supercapacitor performance is assessed in terms of specific capacitance.

REFERENCES

- [1] N. L. Panwar, S. C. Kaushik and S. Kothari, "Role of renewable energy sources in environmental protection: A review," *Renewable and Sustainable Energy Reviews*, pp. 1513-1524, 2011.
- [2] Y. Xu, Z. Lin, X. Zhong and et al, "Holey graphene frameworks for highly efficient capacitive energy storage," *Nat Commun*, 2014.
- [3] E. Miguel and L. David, "Current developments and future prospects of offshore wind and ocean energy," *Applied Energy*, pp. 128-136, 2012.
- [4] M. Aqib, M. B. Ahamed, K. Deshmukh and J. Thirumalai, "A review on recent advances in hybrid supercapacitors: Design, fabrication and applications," *Renewable and Sustainable Energy Review*, pp. 123-145, 2019.
- [5] Y.-E. Miao and T. Liu, Chapter 21 - Electrospun Nanofiber Electrodes: A Promising Platform for Supercapacitor Applications, William Andrew, 2019.
- [6] Poonam, K. Sharma, A. Arora and S. Trpathi, "Review of Supercapacitors: MAterials and Devices," *Journal of Energy Storage*, pp. 801-825, 2019.
- [7] A. Abioye and F. Ani, "Recent development in the production of activated carbon electrodes from agricultural waste biomass for supercapacitors: A review," *Suatainable Energy Reviews*, vol. 52, pp. 1282-1293, 2015.
- [8] X. Li, "Preparation of capacitor's electrode from sunflower seed shell," *Bioresource Technology*, vol. 102, pp. 1118-1123.
- [9] J. Nabais, P. Nunes, Carrott.P, A. Garcia and M. Diaz-Diez, "Production of activated carbons from coffee endocarp by CO₂ and steam activation," *Fuel Processing Technology*, vol. 89, pp. 262-268, 2008.
- [10] W. Li, L. Zhang, J. Peng, N. Li and N. Zhu, "Preparation of high surface area activated carbons from tobacco stems with K₂CO₃ activation using microwave radiation," *Industrial Crops and Products*, vol. 27, pp. 341-347, 2008.

- [11] Berruta, A., I. Ursua, I. Martin, A. Eftekhari and Sanchis, P., "Supercapacitors: Electrical Characteristics, Modeling, Applications, and Future Trends," *IEEE Access*, vol. 7, p. 50869, 2019.
- [12] A. Lewandowski, A. Olejniczak, M. Galinski and I. Stepniak, "Performance of carbon-carbon supercapacitors based on organic, aqueous and ionic liquid electrolytes," *Journal of Power Sources*, vol. 195, pp. 5814-5819, 2010.
- [13] Z. Noorden, S. Sugawara and S. Matsumoto, "Noncorrosive separator materials for electric double layer capacitor," *IEEJ Transactions on Electrical and Electronic Engineering*, vol. 9, pp. 235-240, 2014.
- [14] Z. A. Noorden, S. Sugawara and S. Matsumoto, "Electrical properties of hydrocarbon-derived electrolytes for supercapacitors," *IEEJ Transactions on Electrical and Electronic Engineering*, pp. 25-31, 2012.
- [15] M. f. M. Yaacob, Z. Ahmad Noorden, Jamian and J. Jamani, "Electrochemical Impedance behavior of Glass Wool-based supercapacitors with Different Concentration of Sulfuric Acid," in *IEEE 6th International Conference on Power and Energy*, Melaka, 2016.
- [16] European Committee for Electrotechnical Standardization, "Electric double-layer capacitors for use in hybrid electric vehicles-Test methods for electrical characteristics," BSI Standards Publication, Brussels, 2009.
- [17] Y. Kumar, S. Rawal, B. Joshi and S. Hashimi, "Background, fundamental understanding and progress in electrochemical capacitors," *Journal of Solid State Electrochemistry*, vol. 23, pp. 667-692, 2019.
- [18] K. Lota, V. Khomenko and E. Frackowiack, "Capacitance properties of poly(3,4-ethylenedioxythiophene)/carbon nanotubes composites," *Journal of Physics and Chemistry of Solids*, vol. 21, pp. 801-825, 2019.
- [19] N. A. Samsuddin, "Performance Analysis of Supercapacitor with Graphene Oxide-Doped Carbon Electrodes," Universiti Teknologi Malaysia, Johor, 2020.
- [20] H. Xiaojun, L. Pinghua, Q. Jieshan, Y. Moxin, Z. Xiaoyong, Y. Chang and Z. Mingdong, "Efficient preparation of biomass-based mesoporous carbons for supercapacitors with both high energy density and high power density," *Journal of Power Sources*, vol. 240, pp. 109-113, 2013.

- [21] Q. Wang, J. yan, Y. Wang, T. Wei, M. Zhang, X. Jing and Z. Fan, "Three-dimensional flower-like and hierarchical porous carbon materials as high-rate performance electrodes for supercapacitors," *Carbon*, vol. 67, pp. 119-127, 2014.
- [22] Q. Wang, J. Yan, Y. Wang, G. Ning, Z. Fan, T. Wei, J. Cheng, M. Zhang and X. Jiang, "Template synthesis of hollow carbon spheres anchored on carbon nanotubes for high rate performance supercapacitors," *Carbon*, vol. 52, pp. 209-218, 2013.