FABRICATION AND CHARACTERIZATION OF ACTIVATED CARBON / GRAPHENE SUPERCAPACITOR AS AN ENERGY STORAGE DEVICE AND ITS EQUIVALENT CIRCUIT MODEL

BY

ABDUL HAKIM BIN AB. RAHIM

A thesis submitted in fulfillment of the requirement for the degree of Doctor of Philosophy (Engineering)

Kulliyyah of Engineering
International Islamic University Malaysia

JUNE 2022

ABSTRACT

This thesis presents the investigations of graphene materials' contribution when used in combination with the traditional supercapacitor electrode material, the Activated Carbon (AC). The analyses were conducted via material characterization and electrochemical characterization methods. The study also proposed a new Equivalent Circuit Model (ECM) that can be used as another characterization approach besides producing a better supercapacitor model in a virtual electronic system environment. Literature works show that a small amount of graphene addition on the AC electrode enhanced the performance of the electrode in an improved specific capacitance and lowered the internal resistance. However, some researchers reported that further graphene addition would offset the improvement as graphene typically has a lower specific surface area compared to the AC. This work explores the performance of supercapacitor electrodes with pure AC, pure graphene, and several AC-graphene composites ratios. Two types of graphene were used, two-dimensional graphene using Graphene Nanoplatelets (GNP) and three-dimensional graphene using Graphene Aerogel (GA). It was found that increasing GNP wt% in the electrode would increase the prototype's specific capacitance in a linear relationship, with an insignificant effect on the internal resistance. On the other hand, 20 wt% GA on the electrode performs the best capacitance among the GA-based prototypes, while further GA wt% increase decreases the capacitance. Higher internal resistances were also recorded with higher GA wt%. Besides the capacitance and internal resistance, the role of graphene addition was also observed in the prototypes' self-discharge behavior, especially on the charge-redistribution effect under the Open Cell Voltage (OCV) procedure. 20 wt% addition of GNP retained the most charges among the prototypes after being left for 60 minutes in OCV. The self-discharge result was used for the ECM profile fitting. The proposed ECM produces the best circuit fitting on self-discharge among works of literature, especially on the short-term response. This was achieved by introducing an intermediate layer of *RC* circuit branch that represents the transitional charge location domain between the Helmholtz layer and the Diffuse layer. The ECM was successfully tested on commercial supercapacitors and the prototypes from this study with an average Root Mean Squared Error of 0.2 %. Applications with a short-term open circuit such as the stop/start features in micro-hybrid vehicles can benefit from this ECM by getting a more accurate State of Charge of the energy storage system used. New insights can be extracted from the ECM as the simulation shows that the graphene addition facilitated the ions' movement into the Helmholtz layer, whereas for the prototype without graphene, most of the ions were restricted at the intermediate layer. The new ECM has the potential to be used as a new characterization method for understanding the supercapacitor's electrode-electrolyte interface.

خلاصة البحث

تقدم هذه الرسالة بحوث حول مساهمات مواد الجرافين عند دمجها مع قطب المكثف الفائق التقليدي وهو الفحم أجريت التحليلات عن طريق تعريف خصائص المواد وطرق التعريف الكهروكيميائية .اقترحت .(AC) النشط يمكن استخدامه كنهج آخر لتعريف الخصائص بالإضافة إلى (ECM) الدراسة نموذجًا جديدًا للدائرة المكافئة إنتاج أفضل نموذج للمكثف الفائق في بيئة نظام إلكتروني افتراضية .أظهرت الدراسات السابقة أن إضافة كمية صغيرة من الجرافين إلى قطب الفحم النشط عززت من أداء القطب في سعة كهربية مخصصة وقللت من المقاومة الداخلية .ومع ذلك ، أفاد بعض الباحثين أن إضافة كمية أكبر من الجرافين ستكون له نتيجة عكسية لأن الجرافين عادةً ما تكون مساحة سطحه المخصصة أقل مقارنةً بالفحم النشط .يستكشف هذا البحث أداء .أقطاب المكثف الفائق مع الفحم النشط النقي والجرافين النقي ونسب مختلفة من مركبات الجرافين والفحم النشط ،(GNP) تم استخدام نوعين من الجرافين :الجرافين ثنائي الأبعاد باستخدام الصفائح الدموية النانوية للجرافين أشارت النتائج إلى أن الصفائح .(GA) والجرافين ثلاثي الأبعاد باستخدام الهلام الهوائي للجرافين أو الإيروجيل الدموية النانوية للجرافين في القطب مرتبطة بالسعة الكهربية المخصوص بعلاقة خطية أي أن زيادة النسبة المئوية لهذه الصفائح سوف تزيد من السعة الكهربية المخصصة للنموذج الأولي، ولكن تأثيرها ضئيل على المقاومة الداخلية .من ناحية أخرى ، فإن إضافة نسبة 20٪ من الهلام الهوائي للجرافين أو الإيروجيل إلى القطب تؤدي إلى حصولها على أفضل سعة كهربية ضمن النماذج الأولية المعتمدة على الهلام الهوائي أو الإيروجيل ، و تؤدي زيادة هذه النسبة المئوية إلى تقليل السعة الكهربية .تم أيضًا تسجيل مقاومات داخلية أعلى عند استخدام نسبة مئوية أعلى من هذا الهلام .تم ملاحظة تأثير زيادة الجرافين أيضًا على سلوك التفريغ الذاتي للنماذج الأولية– بالإضافة إلى خاصية السعة الكهربية والمقاومة الداخلية– خاصةً تلك المتعلقة بتأثير إعادة توزيع الشحنة تحت حصلت نسبة إضافة 20٪ من الصفائح الدموية النانوية للجرافين على .(OCV) إجراء جهد الدائرة المفتوحة معظم الشحنات مقارنة بالنماذج الأولية بعد تركها لمدة 60 دقيقة في جهد الدائرة المفتوحة .تم استخدام نتيجة بالنظر إلى الدراسات السابقة، فإن هذا النموذج .ECM التفريغ الذاتي لمطابقة شكل نموذج الدائرة المكافئة .يعد أكثرهم مطابقة لشكل نموذج الدائرة المكافئة عند التفريغ الذاتي، خاصة في حالة الاستجابة قصيرة المدى والتي تمثل مجال موقع الشحنة RC تم تحقيق ذلك من خلال إدخال طبقة وسيطة لفرع دائرة المقاومة والمكثف تم اختبار نموذج الدائرة المكافئة بنجاح على .diffuse الانتقالية بين طبقة هلمهولتز وطبقة الانتشار الثنائية المكثفات الفائقة التجارية والنماذج الأولية لهذه الدراسة وحصل على متوسط جذر متوسط للخطأ التربيعي يبلغ يمكن للتطبيقات ذات الدائرة المفتوحة قصيرة المدى –كخصائص التوقف /البدء في المركبات الهجينة .٪0.2 الصغيرة– الاستفادة من نموذج الدائرة المكافئة من خلال الحصول على حالة شحن أكثر دقة للنظام المستخدم لتخزين الطاقة .يمكن استخلاص رؤى جديدة من نموذج الدائرة المكافئة حيث توضح المحاكاة أن إضافة الجرافين سهلت حركة الأيونات في طبقة هلمهولتز، أما بالنسبة للنموذج الأولي الخالي من الجرافين ، فكانت معظم الأيونات فيه مقيدة في الطبقة الوسطى .يتمتع نموذج الدائرة المكافئة الجديدة بإمكانية استخدامه كطريقة تعريف .جديدة لفهم طريقة تفاعل قطب وإلكتروليت المكثف الفائق.

APPROVAL PAGE

The thesis of Abdul Hakim Ab. Rahim has been approved by the following:

Nabilah Ramli
Supervisor

Anis Nurashikin Nordin
Co-Supervisor

Mohd Hanafi Ani
Internal Examiner

Muhd Zuazhan Yahya
External Examiner

Akram Zeki Kheder
Chairman

DECLARATION

I hereby declare that this thesis is the result of my own investigations, except where otherwise stated. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at IIUM or other institutions.

Abdul Hakim Ab. Rahim

Signature ..... Date .....

INTERNATIONAL ISLAMIC UNIVERSITY MALAYSIA

DECLARATION OF COPYRIGHT AND AFFIRMATION OF FAIR USE OF UNPUBLISHED RESEARCH

FABRICATION AND CHARACTERIZATION OF ACTIVATED CARBON / GRAPHENE SUPERCAPACITOR AS AN ENERGY STORAGE DEVICE AND ITS EQUIVALENT CIRCUIT MODEL

I declare that the copyright holder of this thesis is International Islamic University Malaysia

No part of this unpublished research may be reproduced, stored in a retrieval system, or transmitted, in any form or by any means, electronic, mechanical, photocopying, recording or otherwise without prior written permission of the copyright holder except as provided below

1. Any material contained in or derived from this unpublished research may only be used by others in their writing with due acknowledgement.

2. IIUM or its library will have the right to make and transmit copies (print or electronic) for institutional and academic purpose.

3. The IIUM library will have the right to make, store in a retrieval system and supply copies of this unpublished research if requested by other universities and research libraries.

By signing this form, I acknowledged that I have read and understand the IIUM Intellectual Property Right and Commercialization policy.

Affirmed by Abdul Hakim Ab. Rahim

……. ……..
Signature Date

ACKNOWLEDGEMENTS

Firstly, my gratitude to Allah s.w.t who granted me strength and knowledge to finally be able to reach this stage of completion of my thesis.

It is my utmost pleasure to dedicate this work to my dear wife, the queen of my life, Husna Madiha, I can never repay your love, kindness and charity to our family. May Allah reward you with the best place in Jannah for your patience in being by my side through this journey.

To my children, Hanif and Fahad, I wanted to show you the importance of hardships and perseverance in being a part of people who think, people of understanding. I hope I can be a good role model to you in the exploration of knowledge and intelligence. Allahumma faqqihna fiddeen, wa'allimna ta'weel.

To my father, Ab. Rahim and my mother, Rosmawati, my in laws, Chu, my family who granted me the gift of their unwavering belief in my ability to accomplish this goal: thank you for your support and patience.

A special thanks to Dr. Nabilah Ramli who professionally guided me and gave complete support and insightful suggestions in my research direction. Her guidance and enthusiasm are excellent examples and inspiring towards my learning curve in IIUM. My heartfelt appreciation is extended to my co-supervisors, Prof. Dr. Anis Nurashikin Nordin, for the continuous support and encouragement in my Ph.D. journey, and for that, I will be forever grateful

I wish to express my appreciation and thanks to those who provided their ideas, efforts and support for this project. To the members of the VLSI and SDG lab, thank you for being there for me.

May this accomplishment benefit the ummah, and the barakah and reward be the companion for us to Jannah.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

wt%	Weight percentage
AC	Activated Carbon
BET	Brauner-Emmett-Teller
BJH	Barret-Joyner-Halenda
BTS	Battery Testing System
CB	Carbon Black
CV	Cyclic Voltammetry
ECM	Equivalent Circuit Model
EDLC	Electrical Double Layer Capacitance
EIS	Electrochemical Impedance Spectroscopy
ESR	Equivalent Series Resistance
FESEM	Field Emission Scanning Electron Microscope
GA	Graphene Aerogel
GNP	Graphene Nanoplatelets
KOH	Potassium Hydroxide
OCV	Open Circuit Voltage
RC	Resistance-Capacitance
RMSE	Root Mean Squared Error
SEM	Scanning Electron Microscope
SSA	Specific surface area

LIST OF SYMBOLS

A	Surface area (m^2/g)
C	Capacitance (Farad)
c	Concentration of ion
d	Distance (m)
D	Diffusion coefficient
E	Energy Density (Wh/kg)
F	Faraday Constant
f	Frequency
I	Current (A)
k_B	Boltzmann constant
m	Mass (kg)
N	Molar flux
P	Power Density (W/kg)
Q	Charge
R	Resistance (Ω)
R	Gas Constant
T	Temperature (°C)
u	Fluid Velocity
V	Voltage (V)
v	Scan rate (V/s)
z	Electron valance
Z	Impedance (Ω)
ε	Permittivity
λ	Deby length
Φ	Electric Potential (V)
Γ	Tortuosity

CHAPTER ONE

INTRODUCTION

1.1 BACKGROUND

Supercapacitors, batteries, and fuel cells are the three categories of electrochemical energy storage. Batteries are the most common device that is used in many applications, from automotive to personal electronics. In this age of fast technologies, supercapacitors have started to get increasing attention as an alternative energy storage device because of their well-known ability of rapid charge and discharge. In addition to much higher power density performance than the battery, the supercapacitor's high life cycle is attractive to minimize maintenance costs.

The current commercial supercapacitor can store a very high amount of charge up to several thousands of Farads. Activated Carbon (AC) is commonly used as the primary material of the device's electrodes. This porous carbon comprises of an extensive surface area that provides more space for the charge to occupy. However, as can be seen from Figure 1.1, the energy density of a supercapacitor is still $1/10^{th}$ of battery energy density (Xie et al., 2018). Many approaches are being explored to increase energy density, including introducing new active materials such as Carbon Nanotube (CNT) and Graphene.

Graphene is a new carbon material that has the potential to boost supercapacitor to a new level of the energy storage device. Graphene is said to have much better electronic properties compared to AC but is more expensive to produce in bulk. The

limited technology to attain low-cost graphene is the barrier for graphene to take over as the leading material for the supercapacitor's electrode (Lemine et al., 2018).

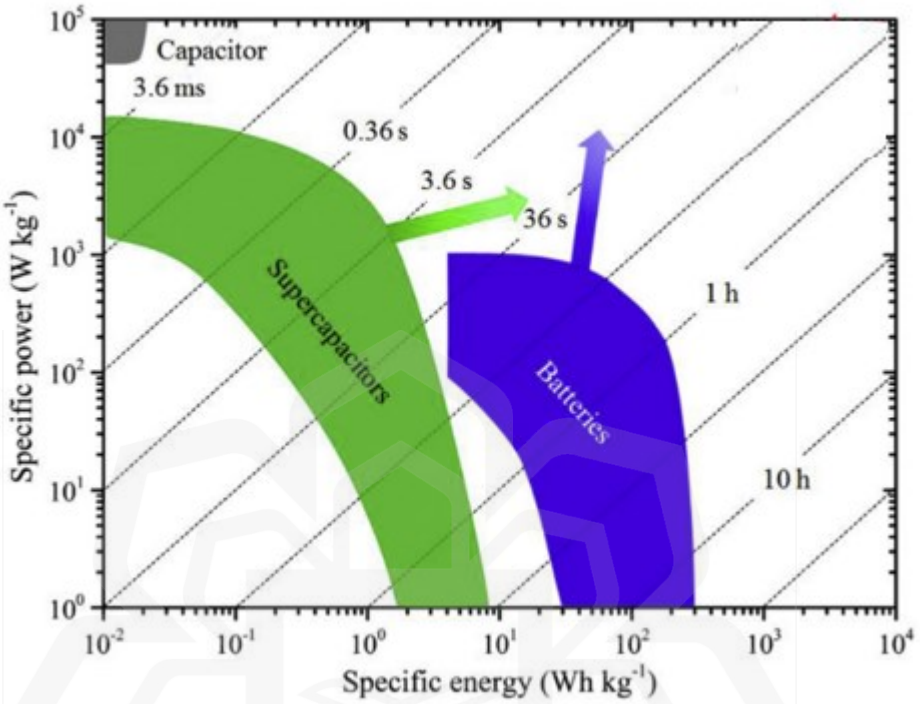

Figure 1.1: Specific power and specific energy for supercapacitors compared to batteries (Xie et al., 2018)

Many works of literature have shown that graphene-based electrode has better capacitance than the AC electrode even though graphene's theoretical specific surface area is 2675 m^2/g (Ke et al., 2016), much lower compared to AC which is as high as 4000 m^2/g (H. Chen et al., 2012). Since the capacitance of a supercapacitor is a function of the specific surface area (SSA) of the active material on the electrode (Simon et al., 2013), this raises the question of whether the surface area estimation method used is a correct tool to estimate the capacitance potential, or what are the advantages of graphene's surface area that are more suitable for ion adsorption?

Many types of graphene are available in the research market ranging from 0-Dimensional (0-D) to 3-Dimensional (3-D) graphene (Ke et al., 2016). A 0-D or

graphene dots and particles are in the form of powder; 1D graphene is produced in the structure of the fibrous yarn, 2D graphene in the shape of carbon film, and 3D graphene is produced in the form of aerogels or foam-template. The different graphene synthesis methods result in various grades of graphene purity and affect its desired properties.

Graphene also faces another physical challenge as graphene sheets tend to agglomerate and restack because of the van der Walls forces (Atif et al., 2016). This phenomenon causes the layers of graphene material to rejoin, and the pores are blocked, preventing maximum ion adsorption on all the available surfaces. Graphene powders and films have a higher tendency to aggregate compared to the 3D Graphene Aerogels (GA) due to GA's hexagonally bonded carbon atom structure (Mao et al., 2018). The opening of layers in GA can better facilitate ion movements compared to dense and packed layers of graphene in powders or films.

There are a few works that reported a combination of the AC and graphene as the electrode materials in order to improve the device capacitance and internal resistance. The graphene was used either to act as the conductive agent to enhance the performance of the supercapacitor (Zhang et al., 2017) or as the primary material together with the AC (Azam et al., 2015). While the addition is expected to improve the device's performance, that is not always the case since there are trade-offs between the combined material's advantages and drawbacks.

Besides capacitance and internal resistance, self-discharge is another characteristic that is less focused and reported for a supercapacitor. When a fully charged supercapacitor is left in an open circuit, the device will gradually lose its charge between 10 – 20 % within a few days (Gualous et al., 2013). The decline in supercapacitor voltage in an open circuit creates an unreliable factor that affects the energy-storing task performance (Conway, 1999). Even though the self-discharge