INVESTIGATION OF THE HEAT TREATMENT PROCESS TO THE ADHESION OF GRAPHENE ON COPPER FOIL FOR PRISMATIC GRAPHENE SUPERCAPACITOR

This report is submitted in accordance with requirement of the University Teknikal Malaysia Melaka (UTeM) for Bachelor Degree of Manufacturing Engineering (Hons.)

by

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DECLARATION

I hereby, declared this report entitled “Investigation of Heat Treatment Process to the Adhesion of Graphene for Prismatic Graphene Supercapacitor” is the result of my own research except as cited in references.

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Date : 3 June 2019

APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment of the requirement for Degree of Manufacturing Engineering (Hons). The member of the supervisory committee is as follow:

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(Assoc. Prof. Ir Dr Mohd Asyadi Azam Bin Mohd Abid)

ABSTRAK

Kapasitor sedia ada memiliki ketumpatan tenaga yang rendah yang mengehadkan penggunaannya dalam pelbagai aplikasi yang memerlukan kitaran masa yang panjang. Sehubungan dengan itu, kapasitor telah digantikan dengan superkapasitor. Superkapasitor adalah satu alat yang menyimpan tenaga dan digunakan secara meluas dalam alatan elektronik, kereta elektrik dan peralatan dalam rumah. Terdapat tiga jenis superkapasitor iaitu Kapasitor dengan Dua Lapisan Elektrik (EDLC), Pseudokapasitor dan Hibrid superkapasitor. Projek ini memilih EDLC superkapasitor untuk kajian. Bahan elektrod superkapasitor menentukan bilangan cas penyimpanan dan kapasiti sesuatu kapasitor. Superkapasitor yang menggunakan Karbon Aktif (AC) sebagai bahan elektrod memiliki ketumpatan tenaga yang rendah dibandingkan dengan elektrod yang menggunakan graphene. Projek ini memfokuskan cara untuk meningkatkan ketumpatan tenaga superkapasitor dengan cara menyadurkan graphene di atas kepingan kuprum (cu) yang bertindak sebagai elektrod kepada superkapasitor. Elektrod tersebut kemudian diuji menggunakan tiga ujian yang berbeza iaitu ujian rendaman dan analisis menggunakan mikroskop elektron pengimbas pancaran medan (SEM) dan Raman. Ujikaji elektrokimia dijalankan dengan merendam elektrod dalam elektrolit 6M potassium hydrosid (KOH) selama 15 minit. Proses perincian elektrokimia telah dijalankan menggunakan voltammetri berkitaran (CV) menggunakan mesin Wonatech 3000 WBS dengan sistem 2 elektrod. Nilai suhu dan juga tempoh masa untuk graphene disadur di atas kepingan kuprum (Cu) telah direkodkan untuk aliran elektrik yang lebih baik. Daripada ujian rendaman, terdapat hanya 4 daripada 16 elektrod yang sesuai untuk dianalisa menggunakan SEM dan Raman. Kesimpulan dari hasil kajian ini ialah untuk proses penyaduran graphene di atas kepingan kuprum, suhu yang paling optimum ialah 100°C dalam masa 8 jam.

ABSTRACT

Conventional supercapacitors have low energy density which limits them from various applications that need devices with longer cycle time, hence, capacitor has been replaced with supercapacitor. Supercapacitor is one of energy storage device that has been used widely especially in portal electronics, electric vehicles and commercial household equipment. There are three types of supercapacitor which are Electric Double-Layer Capacitor (EDLC), Pseudocapacitor and Hybrid supercapacitor. In this study, the electrodes of EDLC supercapacitor has been extensively studied. Electrode materials of a supercapacitor determine the storage charge and capacity of a supercapacitor. Supercapacitors that utilized Activated Carbon (AC) as electrode materials have low electrochemical performances compare to graphene. This study reported a method for improving energy density of a supercapacitor by coating graphene slurry onto copper foil that act as supercapacitors electrode and. The electrodes were then tested with 3 different tests which are immersion test, Scanning Electron Microscopy (SEM) and Raman spectroscopy. For immersion test, the electrodes were immersed in 15ml of 6M potassium hydroxide (KOH) electrolyte for 15 minutes. The electrochemical characterization of the electrodes was further analyzed using cyclic voltammetry (CV) and by using the Wonatech 3000 WBS Potentiostat machine with 2 electrode system. The optimum value for temperature and annealing time in order to paste graphene onto copper foil was determined to ensure a better transfer of electricity. From immersion test, 4 out of 16 electrodes were compatible to be further tested in SEM and Raman spectroscopy. From this study, it can be concluded that the optimum temperature and duration in order to coat graphene onto copper foil is 100°C and 8hours respectively.

DEDICATION

To my beloved parents, Mohd Hizul Azri Bin Md Noor and Syakirah Bt Mohd Nadzir, family, lecturers and friends; thank you for everything.

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LIST OF ABBREVIATIONS

AC	–	Activated Carbon
ASCs	–	Asymmetric Supercapacitors
CD	–	Charge-discharge
CNT	–	Carbon Nanotube
CV	–	Cyclic Voltammetry
CVD	–	Chemical Vapor Deposition
EDLCs	–	Electric Double Layer Capacitors
EES	–	Electrical Energy Storage
ESDs	–	Energy Storage Devices
ESR	–	Equivalent Series Resistance
G	–	Graphene
GO	–	Graphene Oxide
ILs	–	Ionic Liquids
KOH	–	Potassium Hydroxide
NMP	–	N-methyl-2-pyrrolidone
PCs	–	Personal Computers
PS	–	Pseudocapacitance
SEM	–	Scanning Electron Microscopy
UPS	–	Uninterruptible Power Supply

LIST OF SYMBOLS

a.u.	–	arbitrary unit
g	–	graphene
mVs^{-1}	–	mili volt per second
wt (%)	–	weight percent
° C	–	Degree Celsius

CHAPTER 1
INTRODUCTION

This chapter explains the main idea of the project whereas it introduces the title, the synopsis of study, objectives, problem statement, scope of study, significant of the project and structure of the thesis. The detail of the study highlighted in this chapter as guidance and information about this project.

1.1 Background of Project

In few years back, due to the rising in the application of electrical device which demand a huge amount of power or voltage for a short period of time, energy storage device have had a huge impact upon the electrical grid. Supercapacitor has emerged as one of energy storage device that has been used widely especially in portal electronics, electric vehicles and commercial household equipment. One of the biggest concern in electrochemical energy storage device which increase the demand of electronic equipment including supercapacitor is global energy consumption. Supercapacitor exhibits higher power and energy density such as electrical/hybrid electrical vehicles, energy back-up systems, consumer portable devices and also greater cyclic stability which makes it most likely to replace the use of energy storage applications.

Supercapacitor can be categorized into three group depend on the energy storage mechanisms, which are Electric Double-Layer Capacitor (EDLC) in regard to its ion adsorption, pseudocapacitor in reference to its electrochemical redox reaction and hybrid which is the combination of both EDLC and Pseudocapacitor. EDLCs are developed from electrodes that are made of carbon, an electrolyte and a separator which isolates the two electrodes electrically. EDLCs store charge electrostatically in contrast to pseudocapacitors which are Faradaically-charged via transfer of charge between both electrode and electrolyte. This study focused on discussing the application of prismatic cell of EDLC supercapacitor. However, current EDLCs capacitor has several disadvantages such as individual cell has low voltage, have high self-discharge rate and highly cost. For the purpose to improve and enhance the supercapacitor performance, some component need to be modified and upgraded. In this thesis, copper foil is used as the electrodes with Graphene slurry pasted onto it.

The most common material used in producing the electrode of EDLC's capacitor are activated carbon, carbon nanotubes and graphene. Graphene, known for its outstanding properties of chemical stability, wide surface area and high electrical conductivity is gaining much attention as one of promising carbon materials with potentials for electrochemical energy storage device application. Graphene is a two-dimensional carbon sheet that have unique chemistry, mechanics and physics properties which make research in laboratories and industries have been done extensively on graphene. In this paper, graphene slurry undergoes heat treatment process under certain temperature and period of time to paste it onto current collector which are the copper electrodes.

1.2 Problem Statement

Supercapacitors are known as important type of devices for energy storage in conjunction to their high power densities and outstanding cycling stability. Nowadays, most application of electrical devices require high power usage and also longer process cycle. This bring to more research being conducted to upgrade the supercapacitor's performance such as increasing the supercapacitor capacitance and also the energy density. Kwon (2018) states that the storage for charge and capacity of a SCs is heavily depending on the materials used for the electrode. Thus, the main objective of this research is to utilize the usage of the materials which have been newly designed to possess a high capacity and improved performance in comparison with existing materials.

In practice, there are several type of supercapacitor that usually being used, however, prismatic type of graphene supercapacitor has been the state-of the art of any energy storage device including battery and supercapacitor. Despite their promising features, there are several distinct challenges in the current applications of supercapacitors that needed to be overcome before supercapacitors are built as advanced energy storage. In previous study, there is a problem concerning on pasting the graphene slurry onto current collector which is copper foil. The interaction between both graphene and copper are very crucial in order to ensure better transfer of electricity and also increase contact quality between both materials. The challenges in this study is to quantify the optimum temperature and duration of time in order for graphene to be pasted onto copper since most copper foils are polycrystalline. CMC/SBR binder will be used as binder material in this work. Temperature and time will be the variables to this project. Prior to the success of heat treatment process, the electrochemical testing of the prismatic electrode will be performed also using CV and charge discharge analyses.

1.3 Objectives

The objectives of this study are:

i. To prepare graphene slurry before it is being coated onto copper foil that act as electrodes in prismatic cells supercapacitor.
ii. To study the effect of time and temperature in heat treatment process in conjunction to paste graphene slurry onto copper foil.
iii. To assess the electrochemical performance of prismatic supercapacitor using cyclic voltammetry (CV) analysis.

1.4 Scope of Project

In this project, Copper foil is used as supercapacitor electrode. Graphene slurry will be pasted onto copper foil by using heat treatment process to enhance supercapacitor performance. The tools used in this study to further evaluate the electrochemical performance of the supercapacitor are cyclic voltammetry (CV) analysis. The following are three scopes to support the objectives of the study;

- Scopes to support Objective 1

Preparation of graphene slurry will use graphene slurry method. All these process are conducted in Synthetic Laboratory, Faculty of Manufacturing Engineering at Universiti Teknikal Malaysia Melaka.

- Scopes to support Objective 2

Provide the optimum temperature and period of time in heat treatment process for graphene slurry to be pasted onto copper foil that acts as electrode in prismatic supercapacitor. The materials will undergo material characterization process such as Scanning Electron Microscope (SEM) to

investigate the morphology of the materials and also Raman spectroscopy to investigate the microstructural change of the materials, if any. All these process will be done at Material Laboratory, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka.

- Scopes to support Objective 3

For CV analysis, the electrochemical performance analysis is evaluated by using prismatic-type cells. The samples of electrochemical review analysis are conducted by using 6M of potassium hydroxide (KOH) that is an aqueous solution as electrolyte where the analysis is done with two electrode system cell. This process is done at the polymer synthesis lab in the Material Laboratory, Faculty of Manufacturing Engineering at Universiti Teknikal Malaysia Melaka

1.5 Rational of Research

The rational of research are as follows:

a) The performance of electronic devices will be upgraded. Electrode materials of a supercapacitor have a vital role in determining performance of a supercapacitor. By improving the electrode materials of a supercapacitor, the electrochemical performance of a supercapacitor will increased.

b) Generate specific information about annealing time and temperature in order to paste graphene onto copper foil. Some of previous research reviewed that both parameter give significant effect to surface roughness and microstructural change of the materials.

1.6 Organization of Report

This report begins with Chapter 1 which includes the background of the study, problem statement, objectives and scope of study which will be the overall basics and fundamental to the whole study. An overview problem statement is presented as to set the objectives of this study.

Chapter 2 covered the literature review conducted before which is defined and explored by several researches to enhance the understanding of relevant topics for this study. It includes a thorough research of all types published works and helps to measure how much work has been done or currently being done.

Chapter 3 described the basic study method and elaborated compatible and relevant method chosen in order to conduct this study. It contained the fundamental approach taken to achieve the goals.

Chapter 4 presented and discussed all the results gained from four test method which are immersion test, Raman spectroscopy, scanning electron microscopy and cyclic voltammetry.

Chapter 5 conclude all the findings in this study in accordance to the objective. Recommendation for future project was also included in this chapter along with the importance of sustainability

CHAPTER 2
LITERATURE REVIEW

Chapter 2 elaborates more on supercapacitor including the types, principles, components and characteristics of supercapacitor. Besides, this section discussed more on fabrication of supercapacitor, characterization of supercapacitor's electrode and also the analysis of electrochemical characterization of supercapacitor using CV and GCD analysis. Literature review elaborates the findings from previous researches and analysis and also trough brief summary, classification and comparison of previous research studies, a segment of published body of knowledge is critically analyzed.

2.1 Introduction to Supercapacitor

Supercapacitor or previously called electrochemical capacitor has emerged as an electrical component that have the ability not limited to only store but also release large number of energy in a said period of time. Libich *et al.* (2018) claimed that supercapacitors were first found in the 50s of the 20^{th} century and started to gain tremendous attention ever since their advantage of having high power density, long life cycle and bridging function for the power and energy gap between dielectric capacitors, which consist of high power output and batteries which consists of high storage of energy are being discovered. Libich *et al.*, (2018) also claimed that hybrid vehicles such

as Electric Vehicles (EV), Hybrid Electric Vehicles (HEV) and Fuel Cell Vehicles (FEV) like cars, trains, trolley buses are some of applications that utilize the application of supercapacitor. Among all types of vehicles, Hybrid Electric Vehicles (HEV) seem to gain the most benefit from supercapacitor since HEV's engine are usually turn off totally when the car halts. So, by utilizing the energy stored in supercapacitors, HEV can be start again efficiently. Supercapacitors also play a significant role in Uninterruptible Power Supply (UPS) which is an electronic device used in computer that allows computer running in a short period of time even after power is being cut. Besides, memory backup in PCs also utilize the use of supercapacitors. Supercapacitors also started replacing conventional batteries in the application of solar arrays, wind turbines and also energy harvesting systems (Libich *et al*., 2018).

2.1.1 Types of Supercapacitor

Liu *et al*., (2018) state that supercapacitors can be categorized to three basic types based on energy storage principle. Electric Double-Layer Capacitors (EDLC) supercapacitor where energy is stored non-faraidacally via reversible adsorption of ions are has the most application among other three. This statement is also supported by Mohanpriya & Jha (2018). EDLC is preferable among other types of supercapacitors because it has good durability and also known as its ability to operate for very long durations, often millions of cycles, without losing the capacity of energy storage. For the fabrication of EDLC supercapacitor, activated carbon (AC) is one of the materials usually being used to build the electrode of EDLC because of its large specific surface area.

Another type of supercapacitors is pseudocapacitor or also known as faradaic supercapacitors. According to Čech (2018), the mechanism of pseudocapacitors is similar to conventional batteries which made it much less frequent used compare to EDLC supercapacitors. Pseudocapacitance is a condition where pseudocapacitors undergo redox reaction and electrode