ELECTROCHEMICAL PERFORMANCE OF GRAPHENE/MOLYBDENUM DISULFIDE ELECTRODES BASED SUPERCAPACITOR

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

by

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BORANG PENGESAHAN STATUS LAPORAN PROJEK SARJANA MUDA

Tajuk: **ELECTROCHEMICAL PERFORMANCE OF GRAPHENE/MOLYBDENUM DISULFIDE ELECTRODE BASED SUPERCAPACITOR**

Sesi Pengajian: **2016/2017 Semester 2**

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Sekian dimaklumkan. Terima kasih.

Yang benar,

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I hereby, declared this report entitled "Electrochemical Performance of Graphene/Molybdenum Disulfide Electrodes Based Supercapacitor" is the result of my own research except as cited in references.

Signature : ....

Author's Name : TUNKU AIDIL ILHAM BIN TUNKU ADAHAM

Date : 19 June 2017

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 (Engineering Materials) (Hons). The member of the supervisory committee are as follow:

....

(Assc. Prof. Dr. Mohd Asyadi 'Azam Bin Mohd Abid)

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ABSTRAK

Tujuan kajian bagi projek tahun akhir ini adalah untuk mengakses prestasi elektrokimia elektrod berdasarkan graphene/molibdenum disulfida komposit dalam supercapacitors. Penggunaan N-methylpyrrolidone sebagai pelarut semasa fasa pengelupasan cecair adalah sesuai untuk kedua-dua graphene dan MoS_2. Ini disokong dengan data yang diperoleh daripada Raman spektroskopi dan XRD menunjukkan bahawa serbuk pukal sedang terkelupas kepada beberapa lapisan serpih. Eksperimen ternyata bahawa komposit 75G-25 MoS_2 dipamerkan elektrod berprestasi saksama yang kemuatan tertentu adalah 24.71 F/g bawah 1 mA/mg ketumpatan semasa bagi 10,000 kitaran. Ia juga memberikan nilai saksama dalam kemuatan tertentu pada tahap paling rendah imbasan kadar pada 1 mVs^{-1} iaitu 38.64 F/g dalam elektrolit pH neutral 0.5M natrium sulfat (Na_2SO_4). Pengekalan kapasitan elektrod komposit juga ternyata lebih baik daripada graphene tulen sebanyak 24% selepas dibekalkan mampatan arus pada 1 mA/mg sebanyak 10,000 kitaran.

ABSTRACT

The aim of the study for this final year project is to access the electrochemical performance of graphene/molybdenum disulfide composite based electrode in supercapacitors. The use of N-methylpyrrolidone as solvent during the liquid phase exfoliation is suitable for both graphene and MoS_2. This is supported with the data collected from Raman spectroscopy and XRD shows that the bulk powders are exfoliated to few layers of flakes. The experiment turned out to be that the composite of 75G-25MoS_2 exhibited a fair performing electrode which the specific capacitance is 24.71 F/g under 1 mA/mg of current density for 10,000 cycles. It also gives a fair value in specific capacitance at lowest scan rate at 1 mVs^{-1} which is 38.64 F/g in a neutral pH electrolyte of 0.5M of sodium sulfate (Na_2SO_4). The capacitance retention of the composite electrode also turned out to be better than pure graphene by 24% after 10,000 cycles.

DEDICATION

To my beloved parents, Tunku Adaham and Nor Hayati

To my supporting brother and sister, Tunku Amrul Ilham and Tunku Nur Aina Athira

for all the moral supports, the financial, and the cooperation given.

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LIST OF ABBREVIATIONS

G	-	Graphene
MoS_2	-	Molybdenum Disulfide
CV	-	Cyclic Voltammetry
GCD	-	Galvanostatic Charge Discharge
SEM	-	Scanning Electron Microscopy
EDLC	-	Electrical Double Layer Capacitance
PVDF	-	Polyvinylidine fluoride
PTFE	-	Polytetraflouroethylene
XRD	-	X-Ray Diffractometer
H_2SO_4	-	Sulphuric Acid
Na_2SO_4	-	Sodium Sulphate
KOH	-	Potassium Hydroxide

LIST OF SYMBOLS

mVs^{-1}	-	millivolt per second
V	-	Volt
mA	-	milliAmpere
F/g	-	Farad per gram
mg	-	milligram
cm^{-1}	-	Raman shift

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Take a moment and try to look at the surrounding people. Most of them use a device that requires an energy storage system. These energy storage systems are needed to be as efficient as possible in terms of electrically and environmentally. In ever growing electronic industry, the urge of finding a better energy storage system is in motion. This motion ripples to the search of electrochemical energy storage system to be embedded in hand-held electronic devices, transportation and storage of renewable energy for the power grid of which leads to the development of electrochemical capacitors known as supercapacitors.

Supercapacitor has attracted a lot of attention because of the charge-discharge rate, dynamic energy and power density, long cycle ability and simple working principle. They can be fabricated from films to coin cells to disks to a much bigger scales like modules of supercapacitors arrange in series or parallel to build a hybrid car battery or energy storage in the power grid. The electrochemical performance of the supercapacitor will affect the energy storage in a certain system. This can be further improved when the materials of the electrodes in the supercapacitor exhibits a good electronic conductivity and capacitance.

Synthesizing a good performing electrode in the supercapacitor had been a challenging route for the energy researchers. The use of high-capacitance materials such as high surface area or pseudo-active species is a main element to ensure high energy density. In contrast, a high electrical conductivity of the electrode materials as well as the electrolyte solution is necessary for a high rate capability.

A proper development of study had been done to find the best performing supercapacitor in market. The issues related to the electrochemical performace will be discussed in the next subtopics.

1.2 Problem Statement

Late years have yielded real advance in the hypothetical and commonsense innovative work of supercapacitor, as revealed by countless articles and specialized reports. A statement that can be directly quote into this section is the statement from Wang et. al (2014) stating, “The electrode, the heart of the cell, determines the supercapacitor performance in terms of self-discharge, life expectancy, capacity, resistance, and so on. Therefore, the electrode fabrication including an active material coating process is the most important step. As a result, strictly controlling the preparation process is necessary for achieving both high performance and durability”. The drawbacks that would happen if the materials of the electrode are not controlled are the supercapacitor exhibits lower energy density and higher production cost.

The specific issue that is being exhibited by graphene is that it has high surface areas for charge storage. But in spite of these large specific surface areas, the charges physically stored on the carbon particles in porous electrode layers are unfortunately limited. This shows that graphene has a great conductivity but lacks in capacitive behaviour and the restacking of other carbon atom to form graphitic structures. As for the molybdenum disulfide, the problem that it faced is the resistivity of it in conducting electrons and the very low specific surface area that it exhibits but showing a good capacitive behaviour.

In accordance to the statement above it can be interpreted that in order to achieve a higher performing supercapacitor, a proper synthesizing of the material preparation used in the electrode is crucial to control the criteria of a working supercapacitor. Many developed researches had been done to improve the electrochemical performance of a supercapacitor. Given the situation, it is high time for the study of electrochemical performance of supercapacitor to be done since that energy storage technology is ever increasing up until today.

The solution proposed in increasing the electrochemical performance is combining the benefits of these 2D materials to produce highly efficient composite electrochemical supercapacitor devices.

1.3 Objective of the Study

Given that the problem that would face in the study on the electrochemical performance of supercapacitor had been discussed previously, the emergence of the research objective is possible. These objectives are done in such a manner to tackle any research gap related to the electrochemical performance of graphene/molybdenum disulfide based electrode supercapacitor. The objectives are:

1. To synthesize graphene and molybdenum disulfide (G/MoS_2) as electrode material for supercapacitor.
2. To characterize the morphology and structural properties of graphene and molybdenum disulfide.
3. To evaluate the electrochemical performance of G/MoS_2 by using cyclic voltammetry and charge/discharge.

1.4 Scope of Study

The composition mixture was adapted from the study done by Bisset et. al (2015). In the study, there were no conductive agent and binders were used to fabricate the electrode materials. However, in this study the mixture will be introduced with conductive agent called SuperP and PTFE binder. Percent ratio of G: MoS_2 are adapted from the journal are (75:25%, 50:50%, 25:75%, 100%G and 100%MoS2). These composite mixes except the intrinsic ones are to be mixed with small number of conductive agent (10-15%) and binder (3-5%). As the fabricated electrode or the prepared samples are done, material characterization techniques is to be done in getting the morphological and analytical data through the use of Raman spectroscopes, Scanning Electron Microscope (SEM) and X-Ray Diffractometer. Finally, in obtaining the electrochemistry of the electrode fabricated a series of cyclic voltammetry of scan rates of 1, 10, 100 and 500 $\mathrm{mVs^{-1}}$ is to be done. The galvanostatic charge/discharge of current density of 1 $\mathrm{mA\,cm^{-2}}$ for 10,000 cycles to acquire the stability of the device fabricated. A proper calculation from the CV plot data and GCD data are able to obtain the electrochemical performance of the working electrode.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction to Supercapacitor

In the ever increasing advances in technology, the pursuit of finding a better performing energy storage system is needed. The emergence of a supercapacitor was caused by the founding of conventional capacitors and Lithium-based batteries. Supercapacitor is a very important categories in the electrochemical energy storage devices because the combination of the two different types of storage devices such as the high energy density of conventional batteries and the high power density of a conventional capacitor. As adapted from Dale (2014), the performance of a supercapacitor is mainly measured on the fundamentals of conformance in following these criteria. The criteria of the supercapacitor is the power density substantially more than batteries with acceptably high energy densities, tremendous amount of cycles, quick charge-discharge processes, low self charging, safe operations and low cost. Supercapacitor is known to be having two different types of energy storage mechanism in the system. The energy storage mechanisms that are related to this device are the electrical double layer capacitance (EDLC) and the pseudocapacitance. The details of the mechanism will be discussed in the next subtopic. Figure 2.1 shows the graphical image of a supercapacitor.

Figure 2.1: Image of a supercapacitor. Photo copyright of Maxwell Technologies

2.1.1 Working principles of supercapacitor

The working principles of the storage mechanism in a supercapacitor are electrochemical double layer capacitance (EDLC) and pseudocapacitance or the combination of both. Adapted from Bisset et. al. (2015), EDLC is the storage principle that is exhibited at the interface of electrode with electrolyte through the accumulated of ions at that interface, which makes it dependent to the surface area of the electrode, pore size, and electrical conductivity. Figure 2.2 the elliptical outline shows the accumulation of ions on the surface of the electrode. When the device is being charge the ions are accumulated on top of each other on the surface of the electrode. As soon at the device is being discharge the accumulated ions are freely move in the electrode-electrolyte solution to be transferred in Faradaic reaction.

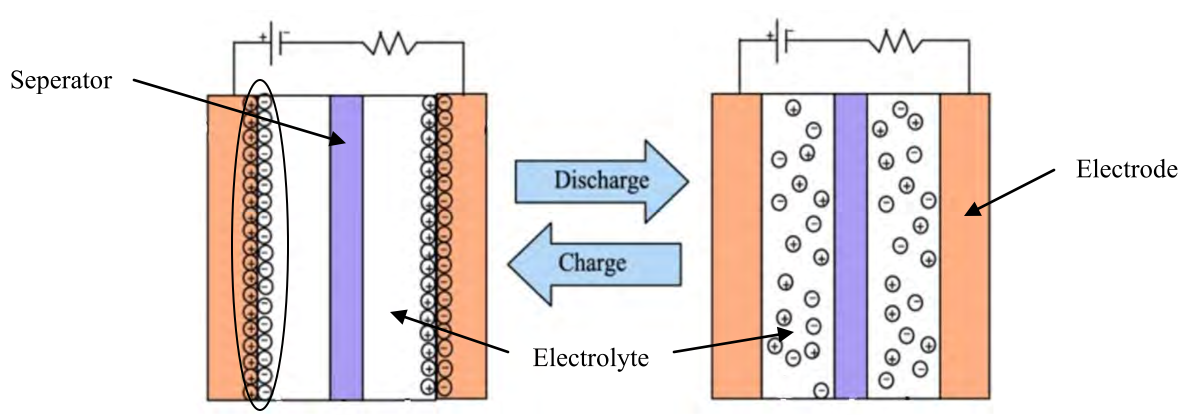

Figure 2.2: Schematic diagram of EDLC (Ike and Sunny,2015)