CYCLIC VOLTAMMETRY AND CHARGE/DISCHARGE ANALYSES OF ASYMMETRIC SUPERCAPACITOR BASED ON GRAPHENE/MoS_2 AND GRAPHENE ELECTRODES

Submitted in accordance with the requirement of the Universiti Teknikal Malaysia Melaka (UTeM) for the Bachelor Degree of Manufacturing Engineering (Hons.)

by

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Tajuk: **CYCLIC VOLTAMMETRY AND CHARGE/DISCHARGE ANALYSES OF ASYMMETRIC SUPERCAPACITOR BASED ON GRAPHENE/MoS_2 AND GRAPHENE ELECTRODES**

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I hereby declare this report entitled "Cyclic Voltammetry and Charge/Discharge Analyses of Asymmetric Supercapacitor Based on Graphene/MoS_2 and Graphene Electrodes" is the results of my own research except as cited in reference.

Signature : …….....

Author's Name : IMANINA MOHAMMAD HANIFF

Date : June 26th 2019

APPROVAL

This report is submitted in accordance to the Faculty of Manufacturing Engineering of Universiti Teknikal Malaysia Melaka as a partial fulfilment for the requirements for the degree of Bachelor Degree of Manufacturing Engineering (Hons.)

The members of the supervisory committee are as follows:

……..

(Associate Professor Ir. Dr. Mohd. Asyadi ‘Azam Abid CEng) – Signature & Stamp

ABSTRAK

Bahan elektrod yang menarik dari sifat elektrokimia yang cemerlang telah membawa kepada kemunculan graphene dalam fabrikasi elektrod untuk superkapacitors, yang pada masa kini telah menariknya untuk superkapasitor asimetrik (ASCs) berprestasi tinggi. Bertindak sebagai substrat yang sesuai untuk pertumbuhan dan penangkapan sulfida logam untuk meneroka komposit hibrid, dalam projek penyelidikan ini, graphene dalam salah satu elektrod akan dihibridisasikan dengan logam transisi dichalcogenides (TMDs), molibdenum disulfida (MoS_2) yang mempunyai sifat unik dan struktur dua dimensi seperti graphene. Komposisi bahan buburan elektrod, bahan aktif untuk pengikat kepada pelarut dipaparkan dengan ideal 80:10:10 di mana elektroda G/MoS_2 80 wt% dibahagikan separuh untuk serbuk G dan MoS_2. N-methyl-2-pyrrolidone (NMP) bertindak sebagai pelarut dan Polytetrafluoroethylene (PTFE) meningkatkan hubungan elektrik bahan aktif dan lekatan kepada substrat, yang dalam projek penyelidikan ini adalah busa Nikel (Ni). Elektrod dihasilkan dalam sel syiling yang kemudiannya menjalani analisis prestasi elektrokimia dalam elektrolit akueus 6M Potassium Hydroxide (KOH) di dalam jig bateri menggunakan Wonatech WBCS3000 untuk voltammetry kitaran (CV) dan caj/pelepasan (CD). Diekstrak daripada analisis CV dan CD, lengkung CV bagi setiap kadar imbasan menunjukkan bentuk segi empat tepat. Arus maksimum yang mengarkibkan melalui analisis CV adalah pada 1.5mV/s dan arus pada 1.5A, hampir hampir kepada ideal boleh dilihat dari cerun CD yang linear kerana lengkung simetri, yang kurva menggambarkan corak hampir tetap pada 0.6V.

ABSTRACT

Robust and attractive electrode material tailing from brilliant electrochemical properties has led to the emergence of graphene in the fabrication of electrodes for supercapacitors, which in the present day has attracted it for high performance of asymmetric supercapacitors (ASCs). Acting as a fitting substrate for growth and anchoring of metal sulphide to explore hybrid composite, in this research project, graphene in one of the electrodes was hybridised with a transition metal dichalcogenides (TMDs), molybdenum disulphide (MoS_2) which possesses unique properties and graphene-like two-dimensional structure. The composition of electrode materials slurry, active materials to binder to solvent is displayed by an ideal of 80:10:10 which the 80 wt% in G/MoS_2 electrode were segregated in half for G and MoS_2 powders. N-methyl-2-pyrrolidone (NMP) acts as a solvent and Polytetrafluoroethylene (PTFE) provides enhancement of electrical contact of active materials and adhesion to the substrate, which in this research project is Nickel (Ni) foam. Electrodes were fabricated in coin cells underwent electrochemical performance analyses in an aqueous electrolyte of 6M Potassium Hydroxide (KOH) in a battery jig using Wonatech WBCS3000 for cyclic voltammetry (CV) and charge/discharge (CD). Encapsulated from the CV and CD analyses, the CV curves for every scan rate show almost rectangular shape. Maximum current that was archiving through the CV analysis is at 1.5mV/s and current at 1.5A, almost nearing to ideal can be observed from the CD slopes that is linear due to its symmetry curves, which the curve depicts an almost constant pattern at 0.6V.

DEDICATION

Love, warmth, all the world's supplies of gratitude along with my genuine prayers to each and everyone who has helped – because you deserve nothing less.

Especially, my walking heavens;

Mohammad Haniff Idris

Nani Afeda Mohamed Ismail

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Inclusive of my family, friends, colleagues and other individuals who have succoured me and relentlessly shower me with encouragements in times of need, grateful would be an understatement and I would want to thank them fervently. Be it directly or on the contrary, their involvement in throwing in constructive feedbacks has more or less contributed to my career development and my improvements.

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LIST OF ABBREVIATIONS AND NOCLEMENTURES

2D	Two-dimensional
3D	Three-dimensional
AC	Activated Carbon
ASCs	Asymmetric Supercapacitors
CD	Charge-discharge
CNT	Carbon Nanotubes
CV	Cyclic Voltammetry
CVD	Chemical Vapour Deposition
ECs	Electrochemical Capacitors
EDLCs	Electric Double Layer Capacitors
EES	Electrical Energy Storage
ESDs	Energy Storage Devices
ESR	Equivalent Series Resistance
EV	Electric Vehicle
G	Graphene
GF	Graphene Foam

H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
HEV	Hybrid Electric Vehicle
KOH	Potassium Hydroxide
MnO_2	Manganese Oxide
MoS_2	Molybdenum Disulphide
$MoSe_2$	Molybdenum Diselenide
Na_2SO_4	Sodium Sulphate
NMP	N-methyl-2-pyrrolidone
Li_2So_4	Lithium Sulphate
PP	Polypropylene
PTFE	Polytetrafluoroethane
PVA	Poly(vinyl) Alcohol
rGO	Reduced Graphene Oxide
SCs	Supercapacitors
SEM	Scanning Electron Microscopy
SME	Superconducting Magnetic Energy
SSA	Specific Surface Area
TEABF4	Tetraethylammonium Tetrafluoroborate
TMDs	Transition Metal Dichalcogenides

UPS	Uninterruptible Power Supplies
vdWs	Van Der Waals
VS_2	Vanadium Disulfide
VSe_2	Vanadium Diselenide
XRD	X-Ray Diffraction

CHAPTER 1

INTRODUCTION

This particular chapter establishes the basis of the investigation encompassing the existence of regular and future energy fixating on the drive towards a higher power and reliable energy storage device. Prior to that, the practices of the energy storage devices are studied along with the different types of them that have been fabricated and applied. The interest in the certain type of energy storage devices and their drawbacks are evoked in the discourse with corroborations from several formal studies and investigations that have been performed.

1.1 Research Background

Pivotal urge on the supplies of sustainable, cost-effective and non-polluting energy are not foreign to the environment when the immense globalisation is prospering fast, contributing to the near exhaustion of fossil fuels, elevation of pollution and critical environmental issues which then calls for the introduction of technologies that contributes to the development on the energy conversion and storage. This is corroborated by Fan et. al., (2015) stating that the development of environmental-friendly and novel system emphasising on energy conversion and storage basing on innovative and unconventional materials are vital due to constraint of fossil fuels reservation. It has also been supported by

Barzegar et. al., (2017) that the phenomena that are naturally happening around the world play a huge role in affecting the availability resources that are renewable. For maximum utilisation of the aforementioned resources; solid, dependable and rigid systems are required to enable accessible energy storage whenever and wherever usage is due.

This further has led to the emergence of supercapacitors (SCs) which have been deemed as excellent for applications that demand power in a high supply. The abilities for SCs possessing specific energy that is relatively higher than the usual capacitors and power density as well as stability in terms of its cyclability rivalling batteries have enabled it to fill the void that exist between usual capacitors and batteries. Implementation of SCs in a multitude of application has been extensively acknowledged including in the vehicles that are electrically generated as well as hybrid, smart grids, aircrafts and in electronics. SCs too have gained attention for its capability to give quick and uninterruptible power as a backup as a result from sudden shutdown of power or surge of energy. Batteries have been deemed as putting a higher cost and able to evoke temperature increment that is uncontrollable for the mentioned application.

Vastly opted for the fabrication of electrodes, carbon materials are brilliant candidates and are used in prolific forms such as activated carbon (AC), carbon aerogels, carbon nanotubes (CNTs) and graphene. Graphene is in a honeycomb shape of two-dimensional of the carbon sheets, which it also happens to be the building block of other materials that are carbon. Attracting the interest of many for the application of SCs, this is due to its stability in terms of chemical, huge SSA, strong mechanical strength, favourable electrical as well as thermal conductivity and graphene also differentiates itself from other carbon materials that are competitive. Transition metal dichalcogenides (TMDs) are also attractive for the application in SCs barring for their huge specific surface area (SSA) and structures of their crystal that are unique as well as their good electrochemical properties. Molybdenum Disulphide (MoS_2) to be exact is favoured due to its excellent pseudocapacitance and Electric Double Layer Capacitance (EDLC) with Mo states of

oxidation that is plenty (+2 to +6) (Choudhary et al., 2017). In this research, graphene will be employed as a single electrode and another electrode will be the product of hybridising graphene and MoS_2. The following sub-chapter will specifically discuss the types of energy storage and its benefits and/or disadvantages.

Figure 1.1 below depicts the segregation of percentages for fossil fuels, renewable energy and nuclear power that have been used.

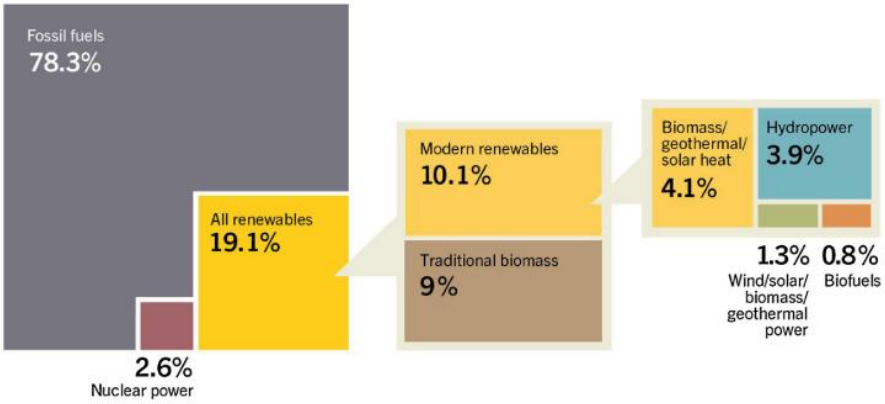

Figure 1.1 Percentage segregation of fossil fuels, renewable energy as well as nuclear power used (Barzegar et al., 2017).

1.2 Problem Statement

Supercapacitors (SCs) have harboured attraction in vast researches of outstanding effort, regardless of purposes pertaining academic or industrial use, due to its excellent charge/discharge rate, power density that is admirable, lengthy cycle of life (>100 000 cycles). However, the mere capability of its energy density when compared to batteries is ineptitude and in present day, a robust and rigid energy storage system is in huge demand with the elevation of use in applications of vary. Electrical vehicles (EV), application in military appliances, smart phones as well as plug-in hybrids have fuelled many researchers

to probe on ways to expand SCs energy density without compromising its power density. This has then tracked down to the option of producing electrodes to cater exceptional electrochemical performance as well as designing controllable assembled SCs (asymmetric).

This is due to the fact that even when SCs operating in aqueous solution is low cost, it produces a scarce energy density due to operating voltage-window that is rather small. The aforementioned trait has then led researches to resort to organic electrolytes that allow cell voltage reaching up until 2.5-2.85V, however, with ASCs, cell voltage surpassing 2.0V can still be attained even when aqueous electrolyte is used, according to (Raza et al., 2018). For this research project, an aqueous solution of 6M Potassium Hydroxide (KOH) will be opted and the designing of an asymmetric SCs will be propelled which will then be tested using cyclic voltammetry (CV) and charge/discharge (CD) analyses.

Furthermore, the individual performance of both graphene and MoS_2 govern this research project of which a single electrode consisting graphene and another electrode consisting graphene and MoS_2. The hybridisation between carbon material and transition metal dichalcogenides come from enhancing the performance of both materials together. Even though graphene is known for being an excellent electrode material, they are embedded with an inclination to agglomerate from graphite through van Der Waals (vWD) interaction that can contribute to reduction of surface area that is significant and will then restrict diffusion of ions into small pores, leading to lower specific capacitance. MoS_2 also is equipped with stacking issue between adjacent sheets that result in functional properties reduction, inflicting low efficiency. Properties of the both aforementioned nanomaterials pertaining to their restacking when applied individually too cause activity decrement as well as impeding their ability for a multitude of applications.

1.3 Project Objectives

The objectives of this particular study are as follows:

1) To fabricate asymmetric novel electrodes consisting of graphene for supercapacitor including a hybrid using graphene/MoS_2 in a battery jig.
2) To characterise the microstructure, composition, quality and morphology of graphene (G) and molybdenum disulphide (MoS_2) hybrid.
3) To measure performance of fabricated electrodes by integrating the application of cyclic voltammetry (CV) and charge-discharge (CD) analyses.

1.4 Scopes of Project

The essence of this very research project fixates on the CV and CD analyses testing on the fabricated asymmetric electrodes of the SC in order to generate and come up with a CV curve as well as for CD. The fabrication of the aforementioned asymmetric electrodes employs Graphene (G) as well as hybridising graphene and Molybdenum Disulphide (MoS_2). As per mentioned, the three objectives will be supported by the following three scopes:

1) Objective 1 supporting scope

The two distinct electrodes in the assembly of SC with asymmetric electrodes involve graphene with the hybridisation of Graphene together and Molybdenum Disulphides (MoS_2) are fabricated by mixing them respectively with PTFE as a binder and later NMP as a solvent. The slurry will then be brushed on the cleaned Nickel foam that will then be arranged together with the PP separator in a battery jig.

2) Objective 2 supporting scope

Three techniques of material characterisation are opted in this project to determine the morphology, composition microstructure and mechanical characteristics as well their agility in reaction of chemical. Characterisation will be performed at Materials Laboratory, Faculty of Manufacturing Engineering at Universiti Teknikal Malaysia.

3) Objective 3 supporting scope

The electrochemical performance analyses of the coin cell sized electrodes are tested using CV and CD analysis. The electrolyte utilised for the electrochemical testing is 6M potassium hydroxide (KOH), which is an aqueous solution. Testing will be performed at polymer synthesis lab in Materials Laboratory, Faculty of Manufacturing Engineering at Universiti Teknikal Malaysia.

1.5 Organisation of Report

Chapter 1: Introduction

This chapter consists of general information of SCs and the study of this thesis. This chapter is divided into five subtopics which are the background, problem statement, objectives, scopes and organisation of the report. The background provides clear information of this study which will give the reader the necessary information of what the study is about. The problems that arise will be stated also the reason this study should be done and the objectives need to be achieved.

Chapter 2: Literature review

This chapter discussed on the theories, ideologies and the purposes of the topics. This chapter need ample search of journals, books, articles, research papers and etc in

order to get plentiful knowledge and study materials to ensure the studies done is relevant. This chapter is provided to the introduction, body and conclusions. The introductions will give a quick review on the topic of the literature review, the body parts contains the discussion of the study sources and the conclusion is discuss on what has been achieves from doing this literature review.

Chapter 3: Methodology

Methodology is the method on how the study is conducted. It presents the sequential, methodical and the organised procedure on the study. In this chapter compose of the independent, dependent and controlled variables of the experiment design. It provides detail information on how the experiment is conducted and also the checklist before conducting the experiment.

Chapter 4: Results and discussion

This chapter presents the results that are obtained from the experiment. It also comments on the results obtained and interpret the data obtained. The discussion part of the report is where the discussion on the results and the issues occur are discussed. It aims to distinguish the main project findings with the results obtained.

Chapter 5: Conclusion and Recommendations

In this chapter, the topic of this study is concluded. The hypothesis is synthesised and the importance of the contents is discussed. In the recommendation, it will propose the improvement of the project that may solve or overcome the limitation of the projects.