UNIVERSITI TEKNIKAL MALAYSIA MELAKA

ACTIVATED CARBON AND GRAPHENE BASED ELECTROCHEMICAL CAPASITOR IN AQUEOUS ELECTROLYTE

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

by

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2014

DECLARATION

I hereby, declared this report entitled "Activated carbon and graphene based electrochemical capacitor in aqueous electrolyte " is the results of my own research except as cited in references.

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APPROVAL

This report is submitted to the Faculty of Manufacturing Engineering of UTeM as a partial fulfillment of the requirements for the degree of Bachelor of Manufacturing Engineering (Engineering Material). The member of the supervisory is as follow:

……………………………

(Dr Mohd Asyadi Azam bin Mohd Abid)

ABSTRAK

Laporan ini membincangkan tentang kapasitan satu kapasitor elektrokimia (SPR) dengan menggunakan jenis yang sama bahan elektrod elektrolit tetapi berbeza. Penggunaan elektrod dalam eksperimen ini diaktifkan karbon dicampur dengan graphene. Terdapat dua elektrolit yang telah digunakan yang kalium hidroksida (KOH) dan asid sulfurik (H_2SO_4). Fabrikasi satu EC meningkatkan permintaan dalam penggunaan bateri dan kapasitor. Walau bagaimanapun, ketumpatan tenaga yang rendah EC mengehadkan permohonannya. Oleh itu, penyelidik cuba untuk membangunkan EC yang lebih baik dengan meningkatkan kawasan permukaan mereka dengan menggunakan bahan berliang. Selain itu, kajian terdahulu mendapati bahawa elektrolit yang berbeza memberi kesan yang kecil dalam kapasitan daripada SPR. Kaedah yang digunakan dalam laporan ini adalah teknik keadaan pepejal. Graphene itu melintang berorientasikan dan dengan itu menurunkan turun kemuatan tertentu (C_{sp}) nilai. Nilai kapasitan tertentu yang diperolehi daripada eksperimen adalah 13 F g^{-1} dan 14 masing-masing F g^{-1} dalam KOH dan H_2SO_4 elektrolit.

ABSTRACT

This report discuss about the capacitance of an electrochemical capacitor (EC) by using same type of electrode material but different electrolyte. The electrode use in this experiment is activated carbon mixed with graphene. There are two electrolytes that are being use which are potassium hydroxide (KOH) and sulphuric acid (H_2SO_4). The fabrication of an EC improves the demands in the usage of batteries and capacitor. However, low energy density of EC limiting its application. Hence, researchers try to develop a better EC by increasing their surface area by using a porous material. Apart from that, previous researches found out that different electrolytes give out small effect in the capacitance of an EC. The method used in this report is solid state technique. The graphene was horizontally oriented and hence lowering down the specific capacitance (C*sp*) value. The specific capacitance value gained from the experiment was 13 F g^{-1} and 14 F g^{-1} in KOH and H_2SO_4 electrolytes respectively.

DEDICATION

This report is dedicated to my parents (Mr Dorah bin Tajallah and Mdm Minah binti Amit) and my siblings (Mohd Asri, Hajmin, Mohd Romi, Lijawati, Norhasmi, Mohd Hamdan, Mohd Nazri, and Mohd Arif).

I love you all.

ACKNOWLEDGEMENT

I would like to offer my unreserved gratitude and praises to Almighty Allah for His generous blessing and the undying strength bestowed upon me during the course of this research.

Special thanks to my supervisor, Dr. Mohd Asyadi Azam bin Mohd Abid who guide, assist and advise me all the way through this project.

Next, I want to thank my lovely parents whom with their prayers and moral support, I have gained strength to endure in this study.

Thank you very much also to my mentors and friends especially to Elyas bin Talib, Nor Syafira binti Abdul Manaf and Raja Noor Amalina binti Raja Seman.

Not forgotten, thank you to Tunku Ishak Tunku Kudin and Ainnur Sherene Kamisan from iMADE Lab, UiTM Shah Alam for their technical support and guidance throughout the experiment.

Last but not least, to the person who always there when needed, Malik Younis Omar Kreishan, thank you so much.

TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

AC	-	Activated carbon
$C_4H_60_3$	-	Propylene carbonate
C_2H_3N	-	Acetonitrile
CV	-	Cyclic voltammetry
CNT	-	Carbon nanotube
C*sp*	-	Specific capacitance value
EC	-	Electrochemical capacitor
EDLC	-	Electrochemical double layer capacitor
EDX	-	Energy dispersive x-ray
G	-	Graphene
H_2SO_4	-	Sulphuric acid
KOH	-	Potassium hydroxide
NMP	-	N-methylpyrrolidinone
OLC	-	Onion-like carbon
PF	-	Phenol-furfural
PVDF	-	Polyvinileidene difluoride
RF	-	Resorcinol-formaldehyde
SEM	-	Scanning electron microscop

CHAPTER 1

INTRODUCTION

This chapter discusses about the background and the different types of electrochemical capacitor (ECs) that exist. The types of each energy storage device are compared as long as its working mechanism which will be discussed in Chapter 2. The limitations of the batteries and conventional capacitors are brought upon and the advantages of EC are being explained.

1.1 Background

Currently, energy has become a major focus in the scientific and industrial societies due to climate change and fast development of the global economy. With the increasing in environmental pollution and consumption of fossil fuel, there is high demand to seek renewable and clean energy sources to ensure the sustainable development of economies and societies (Azam, 2012). Alternatively, energy storage devices such as batteries, fuel cells, and electrochemical capacitors (ECs) are being used to store energy for various applications including mobile phones, laptops, airplanes, buses, hybrid electric vehicles and etc. (Cary L. Pint, 2011). Recently, ECs are considered as one of the most promising energy storage devices due to its high rate performance, such as long life cycle and outstanding power density (Byungwoo

Kim, 2012). As for today, the three major commercialized energy storage devices are capacitors, batteries and fuel cells. To illustrate the advantage of ECs, the structure, mechanism and performance comparison of those devices are discussed in the following sections of this chapter.

1.1.2 Energy storage devices

Basically, energy storage devices can be classified into three parts which are Pconventional capacitors, ECs, and batteries. Conventional capacitors are defined as fundamental electric circuit elements that store electrical energy in microfarads and assist in filtering. It varies in terms of shape and size but possesses similar basic configuration. Capacitor consists of two conductors carrying equal but opposite charges. There are many important applications for capacitor in electronics field including storing electric potential energy, delaying voltage changes when coupled with resistors, filtering out unwanted frequency signals, forming resonant circuits and making frequency dependent and independent voltage dividers when combined with resistors.

Electrochemical capacitors (ECs) or supercapacitors work as energy storage devices due to its high power densities and excellent cycling stability (Yuan, 2005). It competes with another three energy storage devices which are conventional capacitors, batteries and fuel cells. It also differs from conventional capacitors due to its porous conductor of electrodes that comes from the same material for both electrodes. These electrodes have huge surface area, and collect a large number of charges in its thin layer of electrodes/electrolytes interface through electrostatic force (EDLC) or non-faradic effect (pseudocapacitor), in order to possess a huge capacitance (Yuan, 2005). Another type of EC is hybrid capacitor. Hybrid capacitor combines the mechanism of a faradic and non-faradic electrode (Katsuhiko Naoi, 2013).

The working principle of batteries is based on the chemical separation. Due to this principle, it possesses chemical reaction that limits its life cycles. Generally battery consists of two unlike metals or conducting substances (electrodes) that are placed in a liquid which causes a greater chemical change in one of the electrode than in the other. Hence, an electrical pressure or electromotive force is caused to exist between the two electrodes. The greater the difference in the chemical action on the electrodes, the greater will be the electrical pressure. By connecting wires or any electrical conductor to the terminals of the battery, an electric current will flow through the path or circuit. As the current flows though the system, one or both electrodes will undergo chemical changes and it will continue to flow until one or both electrodes change entirely.

Figure 1.1 shows the ragone plot for power and energy densities of conventional capacitors, electrochemical capacitors (ECs) and batteries. From the figure below, conventional capacitors have higher power density compared to ECs and batteries. Meanwhile, batteries have higher energy density compared conventional capacitors and ECs. However, ECs possess medium power density and energy density, and hence filling the gap between conventional capacitors and batteries.

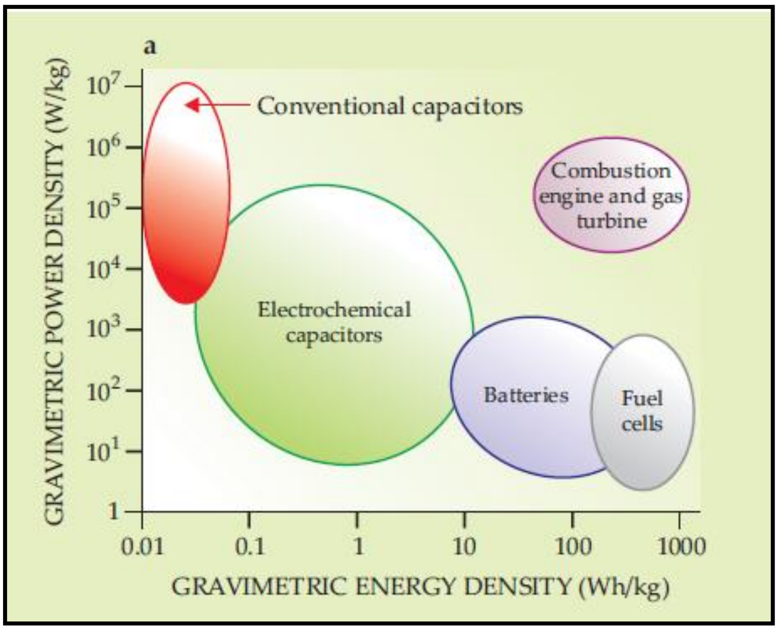

Figure 1.1: Ragone plot of power density versus energy density (Abruña, 2008).

Table 1.1 shows the differences between battery and EC. Battery and EC are different in power limitation, storage mechanism, energy limitation, charge rate, output voltage, life limitation and even in their cycle life limitation. Battery is used in conventional applications due to its high energy. Unlike battery, EC has a higher power density with longer cycle life time. Recent efforts have been focused on the development of EC that has high power density in order to have a better performance and to be used in a high demand application.

Table 1.1: The differences between capacitor, electrochemical capacitor, and battery (Steve Knoth, 2010).

Property	**Capacitor**	**Electrochemical capacitor (EC)**	**Battery**
Storage mechanism	Physical separation	Physical separation	Chemical separation
Energy storage	W-s of energy	W-s of energy	W-Hr of energy
Charge method	Voltage across terminal i.e. battery	Voltage across terminal i.e. battery	Current and voltage
Power delivered	Rapid discharge, linear or exponential voltage decay	Rapid discharge, linear or exponential voltage decay	Constant voltage over long time period
Charge/ discharge time	ps to ms	ms to s	1 to 10 hours
Form factor	Small to large	Small	Large
Weight	1g to 10kg	1-2g	1 to >10kg
Energy density	0.01 to 0.05Wh/kg	1 to 5Wh/kg	8 to 600Wh/kg
Power density	High, >5000W/kg	High, >4000W/kg	Low, 100-3000W/kg
Operating voltage	6V – 800V	2.3V – 2.75V/cell	1.2V – 4.2V/cell
Lifetime	>100k cycles	>100 cycles	150 to 1500 cycles

1.2 Problem statement

The study of conventional capacitors to replace batteries has been widely focused into supercapacitosr which also known as ultracapacitors or in this study as electrochemical capacitors (ECs). ECs possess remarkable property as it fills the gap between conventional capacitors and batteries. Batteries have been used in conventional application and conventional capacitors are applied on electronic devices replacing batteries. However, the applications of conventional capacitors are restricted by its low energy density. ECs have more power density than batteries but low energy density. Hence, researchers are trying to overcome this problem by varying the materials used as electrode to achieve a better performance. This study will cover the effect of mixing activated carbon (AC) with graphene (G) as electrode in two different aqueous electrolytes which are potassium hydroxide (KOH) and sulphuric acid (H_2SO_4) on specific capacitance. In order to do so, basic understanding of cyclic voltammetry (CV) is crucial. There are two parameters that may affect the result obtained, which are the scan rate and voltage window. Apart from that, CV will help to determine the type of EC whether it is electrochemical double layer capacitor (EDLC) or pseudocapacitor.

1.3 Objective

The objectives of this research project are:

1. To fabricate the electrochemical capacitor by using activated carbon mixed with graphene as electrode material in aqueous electrolytes.
2. To analyze the fabricated electrochemical capacitor by using cyclic voltammetry (CV) analysis in aqueous electrolytes.

1.4 Scope

This experiment had used activated carbon and graphene as electrode and KOH and H_2SO_4 as electrolyte. Note that 6M of KOH and 1M H_2SO_4 were used in this experiment. Basically, this experiment will be focusing on the performance of EC with two different electrolytes. This report will discuss about the activated carbon and graphene, their applications and the importance of both in the electric device field. The experiment was mostly done in the Material Laboratory, Faculty of Manufacturing, University Teknikal Malaysia Melaka (UTeM). Fabrication of the EC was done at UiTM Shah Alam before it was characterize in the material laboratory UTeM. The electrochemical performance of working electrode, stainless steel mesh coated with AC/G was evaluated using cyclic voltammetry to obtain a desired gravimetric specific capacitance.

CHAPTER 2

LITERATURE REVIEW

This chapter discusses the three types of ECs that exist. The working principles of each EC are also explained. Nonetheless, this topic is focusing more on EDLC and the types of electrolyte that are being used in the experiment. Apart from that, the material characterization and electrochemical performance that were used to test the fabricated EC are also discussed in this chapter.

2.1 Classification of electrochemical capacitor (EC)

EC is divided into three; according to their energy storage modes to achieve capacitance. Electrochemical double layer capacitor (EDLC) is known for its ions polarization in which when a voltage is applied, current is generated due to the rearrangement of charges. Pseudocapacitor in contrast, is popular with its faradic processes and fast redox reaction that takes place at the electrode/electrolyte interface due to change in oxidation state (Dar *et al*, 2013). EC has magnificient power density ability compared to batteries. According to that fact, ECs can be put as having good acceleration but poor range. From a viewpoint, ECs are a device with excellent cycle life that can be used in a longer time but small in size compared to the batteries (Scherson, 2006). The unit cell of an EC is based on its electrode/electrolyte interface of high surface area (activated carbon). ECs stores electrical energy like conventional capacitor which is based on the separation of the positive and negative phase inside its interface.

The working principle of EDLC is based on the interface between electrode and electrolyte. Inside EDLC, there are two terminals that are separated by a dielectric or separator. This dielectric can be any kind of material that does not conduct electricity. The dielectric works as a separator between the two terminals to prevent any short circuit. Once these two materials come in contact with each other, the negative and positive poles are distributed over an extremely short distance. This phenomenon is called electrochemical double layer. Figure 2.1 below shows the schematic diagram of an EDLC.

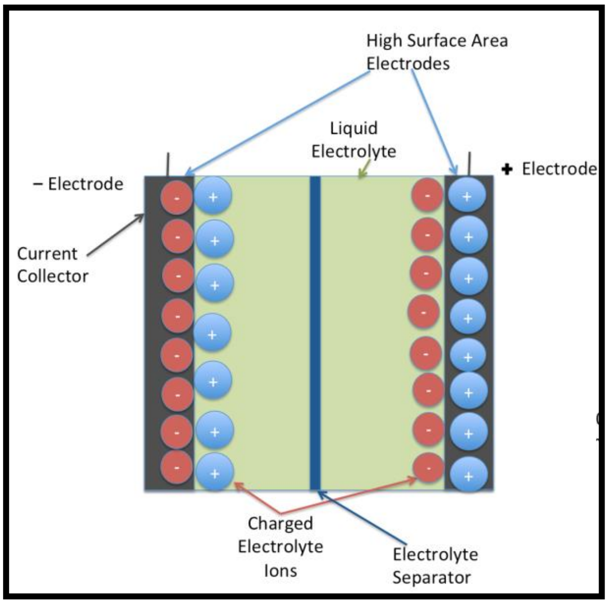

Figure 2.1: Schematic diagram of EDLC (Aslani, 2012)

EDLCs also consist of other devices that did not exhibit Faradic reaction. The accumulated charges will build up a double layer between electrode/electrolyte interfaces. Some insignificant Faradic reactions might occur in the potential voltage window, such as redox reaction impurities. Redox reaction impurities can be considered as self-discharge reaction of EC. The effect of this insignificant reaction is the accumulated charges cross the interface will be consumed in those reactions, and the total amount of the charges in the double layer will decrease. Therefore, the side reaction of Faradic that are mostly the redox impurities in the solution should be avoided.

Stern in 1924 has discovered that charges can form a double layer when it is separated, cross a conductor and a liquid electrolyte. Interface models had been establish to further explain about the phenomenon of the double layer. Qu in1998 indicates from the models, when DC voltage is introduced to the interface of an electrode, electric double-layer is then begun to store electric energy. Figure 2.2 shows a schematic diagram of an EDLC in charging and discharging states.

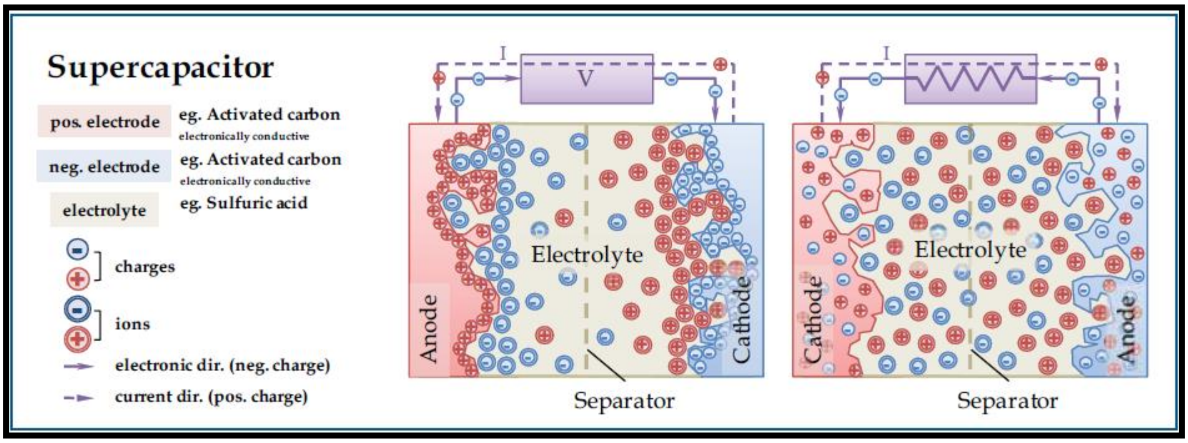

Figure 2.2: Schematic diagram of an electrochemical double layer capacitor showing charging (left) and discharging (right) (Source: <http://www.netl.doe.gov>09/12/13)

Some application of EC is to modify the rate of response of other components to improve the transfer of actual power to a load and to stabilize the frequency response of circuits. EC's ability to store charge makes them a critical component in a circuit that used to regulate the voltage from alternating energy sources, such as wind powered generators and solar arrays. Since these powers are generated by nature, hence the output of these energy sources is not usually in sync with the demands of the energy consumer. Therefore, the help of EC to store energy produced at off-peak hours and to supply or replace the alternative energy source is necessarily useful.

The relationship between the amounts of energy stored (Q) in an EC, the voltage applied (V) to drive the charge onto the plates of the EC, and the capacitance (C) is given below;

$$Q=CV \qquad \text{(Eq. 2.1)}$$

Helmholtz explains that the capacitance per unit area of an EC is determined by the distance between the parallel plates and the dielectric constant of a material between the plates. These parameters can be translated into;

$$C = \frac{\varepsilon_r \varepsilon_o A}{d} \qquad \text{Eq. (2.2)}$$

Where ε_r is the relative dielectric constant of the material between the plates, ε_o is the vacuum permeability, *A* is the cross-sectional area of the plates, and *d* is the distance between plates.

In contrast to EDLC where the charge is stored electrostatically at the interfaces of the electrodes, pseudocapacitor stored charge through redox process at the electrodes surface. This process originally comes from faradic process since it involves electron transfer across the double layer at the electrode/electrolyte interfaces (John, 2009). Pseudocapacitance is produced by the faradic charge transfer from species adsorbed ineffective contact with the electrode surface or forming the electrode surface. The charge storage possess by this mechanism is approximately one order of magnitude higher than EDLC mechanism (Conway, 1999). However, when the electrostatic stresses are produced by charge transfer and built up of charge on the surface, it will lead to the mechanical strain within the electrode that will decrease the charge storage capacity. Pseudocapacitors lose capacity much more rapidly than EDLC. High charge and discharge rate also can produce extra stress that will shorter the device lifetimes. In principle, pseudocapacitance is controlled by thermodynamics, where the amount of charge accumulation (ΔQ) from faradic charge transfer processes which depends on the change in applied potential (ΔV). Therefore, pseudocapacitance corresponds to the derivative of $\Delta Q/\Delta V \cdot dQ/dV$ (John, 2009). Figure 2.3 shows the working mechanism of EDLC and pseudocapacitor.