UNIVERSITI TEKNIKAL MALAYSIA MELAKA

GRAPHENE AND CARBON NANOTUBE BASED ELECTROCHEMICAL CAPACITOR 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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DECLARATION

I hereby, declared this report entitled "Graphene and Carbon Nanotube Based Electrochemical Capacitor in Aqueous Electrolyte" is the result 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 Materials) (Hons.). The members of the supervisory committee are as follow :

………………………………

(DR MOHD ASYADI AZAM BIN MOHD ABID)

ABSTRAK

Kapasitor elektrokimia (EC) adalah alat penyimpanan elektrokimia yang mempunyai kepadatan tenaga dan ketumpatan kuasa yang melengkapi peranan sebagai bateri (tenaga yang tinggi) dan kapasitor konvensional (kuasa yang tinggi) untuk menyimpan tenaga dan mengalirkan kuasa. Menariknya terdapat daya tarikan yang besar daripada penyelidik mengenai penggunaan bahan-bahan berasaskan karbon bagi menghasilkan elektrod untuk EC . Ini adalah kerana, karbon mempunyai banyak kebaikan antaranya ialah ianya mudah dihasilkan, mesra alam, konduksi elektrik yang bagus, luas permukaan yang tinggi dan kos yang agak rendah. Dalam kajian ini, EC telah dihasilkan dengan menggunakan graphene dan nanotiub karbon menjajar pelbagai dinding (MWCNTs) sebagai bahan elektrod dan juga campuran bahan pengikat dengan nisbah 47.5:47.5:5. 6M KOH dan 1M H2SO4 juga telah digunakan sebagai elektrolit. Ukuran voltammetri berkitar (CV) telah dijalankan untuk menentukan nilai kapasiti, kitaran hayat dan penentuan jenis EC. Prestasi cemerlang oleh EC, boleh dikaitkan dengan struktur fizikal dan kekonduksian intrinsik yang terdapat pada graphene dan MWCNT sebagai bahan elektrod. Nilai kapasitan tertentu yang diperolehi daripada eksperimen adalah 12.07 F/g (6M KOH elekrolit) dan 4.34 F/g (1M H_2SO_4).

ABSTRACT

Electrochemical capacitors (ECs) are electrochemical storage devices which possess the energy densities and power densities which complement the role of batteries (high energy) and conventional capacitors (high power) for storing energy and delivering power. Interestingly there are of great interest from researchers about using carbon materials based electrode for ECs due to their accessibility, an easy processability, environmental friendly, good electrical conductivity, high surface area, and relatively low cost. In this study, ECs were fabricated by using graphene and multiwalled carbon nanotubes (MWCNTs) as EC electrode material as well as binder with ratio 47.5:47.5:5. Also, 6M KOH and 1M H_2SO_4 were used as electrolyte. Electrochemical measurements such as cyclic voltammetry (CV) were performed to determine the capacitance value, lifecycle and determination of fabricated EC. The excellent performance can be attributed to the physical structures and the intrinsic conductivity owing by the EDLC graphene and MWCNT electrode. The specific capacitance value gained from the experiment was 12.07 F/g (6M KOH electrolyte) and 4.34 F/g (1M H_2SO_4).

DEDICATION

I dedicated this entire work to my beloved family especially to my husband, my father and mother and also to my fellow friends, supervisor and lecturers for their support and encouragement throughout this project

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LIST OF ABBREVIATIONS, SYMBOLS, AND NOMENCLATURE

AC	-	Activated Carbon
°C	-	Degree Celsius
CNT	-	Carbon Nanotube
Csp	-	Cpecific Cpacitance
CV	-	Cyclic Voltammetry
EC	-	Elecrochemical Capacitor
EDLC	-	Electrochemical Double Layer Capacitor
EDX	-	Energy Dispersive X-ray
FGS	-	Functionalized Graphene Sheets
H_2SO_4	-	Sulfuric Acid
KOH	-	Potasium Hydroxide
$LiPF_4$	-	Lithium
MWCNT	-	Multiwall Carbon Nanotube
SEM	-	Scanning Electron Microscopy
SSA	-	Specific Surface Area
SWCNT	-	Singlewall Carbon Nanotube

CHAPTER 1

INTRODUCTION

1.1 Background

Nowadays, the need of energy has become increasing because both of households and industries require large amounts of power. Due to a lot of problems in environmental pollution, there is a need for green and clean renewable energy to assure the sustainable growth of communities As a result, the electrochemical capacitors (ECs) have become as an alternative to conventional electric energy storage device.

ECs, also known as supercapacitors or ultracapacitors are energy storage devices that combine the high energy storage capability of batteries with the high power delivery capability of capacitors (Burke, 2000). Basically, ECs can be classified into three types which are electrochemical double layer capacitors (EDLCs), pseudocapacitors, and hybrid capacitors. Among them, the EDLCs are the most common type for ECs because of the least cost to manufacture.

In addition, it have to tend great attention not only for the established applications as backup power for mobile devices and electronic equipments, but also for high power applications in pulsed lasers and electric vehicles.

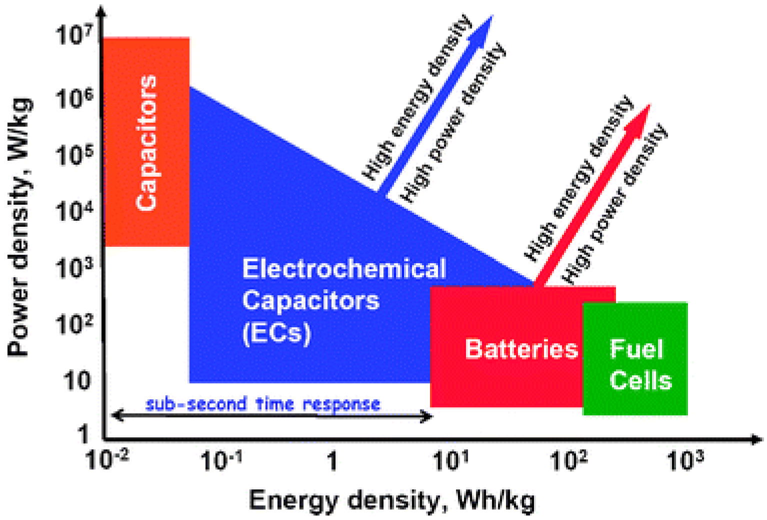

Figure 1.1 : Plot of power density (Wkg^{-1}) versus energy density ($Whkg^{-1}$) of different storage devices (Rolison *et al.*, 2009)

From Figure 1.1, the ECs resides in between batteries and conventional capacitors, these clearly shows that the ECs have both high energy density and power density than any other storage device.

Table 1.1 : Comparison of Batteries, ECs and Capacitors (Rolison *et al.*, 2009)

Available Performance	**Batteries**	**Electrochemical Capacitors (ECs)**	**Conventional Capacitors**
Charge Time	1 to 5 hrs	0.3 to 30 s	10^{-3} to 10^{-6} s
Discharge Time	0.3 to 3 hrs	0.3 to 30 s	10^{-3} to 10^{-6} s
Energy ($Whkg^{-1}$)	20 to 100	1 to 10	< 0.1
Lifecycle	1000	>500,000	>500,000
Power Density (Wkg^{-1})	50 ~ 200	1,000 ~ 2,000	>10,000
Charge / discharge efficiency	0.7 to 0.85	0.85 to 0.98	>0.95
Operating Temperature	-20 to 100 °C	-40 to 65 °C	-20 to 65 °C

Table 1.1 shows the comparison between the batteries, ECs can store large amount of amount of energy and power compared to conventional capacitors and battery compared to conventional capacitors. Furthermore, it also can be recharged in seconds rather than hours, it can withstand with cold temperature, shocks, and vibrations and it can be charged and discharged hundreds of thousands of times before they wear out. The EC is much easier on the environment than batteries, because the ECs contain earth abundant and nontoxic materials.

Although all the above devices have different mechanism, but there are also electrochemical similarities of these three systems. The common features are the energy providing processes that take place at the phase boundary of the electrode interface and the separation of electron and ion during the transportation processes.

In this study, graphene and carbon nanotube (CNT) were used as electrode materials because graphene has been known as one of the most promising active material for ECs which posses outstanding electrical conductivity and large surface area. Since the CNT is known as a porous material, it becomes a potential candidates to fabricate EC. All of the carbon atoms are surface atoms is consequently and extremely large surface areas may be obtainable if the CNTs can be assembled in a manner that maximizes the surface area by minimizing CNT bundling and optimizing the porosity of the CNT electrode.

1.2 Problem Statement

The production of energy by using the conventional method will leads to the global warming problems such as environmental pollution, petroleum exhaustion, climate change and the greenhouse effect. In response to reduce the output of carbon dioxide, the several countries have been decided to shut down the old nuclear power plants and not to build it with new ones. Apart from that, the energy demand has risen and the price of conventional energy sources has increased dramatically. This situation makes the reliance of national economies on a continuous and undistorted supply of such sources has become critical.

Thus, the old energy production method need to be replaced with new ones which include the concepts that enriching the life style, diminishing wasteful energy and environment friendly. These new method including solar power, wind power, and hydroelectricity in its many forms, but these new methods have the disadvantages compared to the older methods. The output of the older methods is easy to adjust based on the power requirements. The new energy production method is more directly by using the power of the nature and as their peak power outputs may not match with the power requirement. These may result to large volatilities the power output in monthly or even annual cycles and also the demand can vary monthly or annually.

Therefore, the energy storage is a very important factor to make these new sources to become completely reliable as the main sources of energy. Essentially, when the production level is less than the required need, the energy from these sources must be stored when extra is produced and then released. These energy storage technologies show the largeness of an important part of efficient and effective renewable and distributed generation unit. It is important to develop low cost, high performance and environmental friendly energy conversion and storage systems in order to make the effective use of renewable energy. Fuel cells, batteries, ECs and conventional capacitors are the system required for promising electrochemical energy conversion and storage. Nowadays, researchers focus on the EC to improve their energy density since its power density and lifecycle had been already higher than batteries.

In order to increase energy storage, EC must use the porous materials as electrode in order to store ions in the pores at an atomic level. Usually the activated carbon is used to fabricate the EC's electrodes. The fact that activated carbon is not suitable as electrode material due to the charge carriers are larger size to the pores in the material and some of them cannot fit into smaller pores. As a result, it will reduce the storage capacity in the EC performance.

There are many factors that need to take as consideration in order to improve the energy density of the ECs such as type of electrode and electrolyte material. In this report, carbon material (graphene and carbon nanotube) will be used as electrode material because of its contributed to a high value capacitance. This is due to their special characteristic which is a porous material. The cyclic voltammetry (CV) will be used to measure the value of capacitance and to determine whether the fabricated EC is EDLC or pseudocapacitor, and lifecycle. If EC can increase its energy density in the future, then the use of the battery can be replaced.

1.3 Objectives

In this study, there are two parameters were made constant throughout the experiment which are the substrate (stainless steel mesh) and electrode material (graphene and CNT). The main objectives of this research are :

(i) To fabricate the EC by using graphene and CNT as the electrode material.

(ii) To analyze the fabricated electrochemical capacitor by using cyclic voltammetry.

1.4 Scope of Research

In this study, the major scope will be focused on the fabrication of EC and analyze the fabricated EC by using CV. The experiment was conducted at the Ionic Materials & Devices Research Laboratory (iMade) Faculty of Applied Science, University Teknologi Mara (UiTM) Shah alam and Material Laboratory Faculty of Manufacturing, Universiti Teknikal Malaysia Melaka (UTeM). Fabrication and analyze of EC was carried out in UiTM Shah Alam before it is testing by using model development in the Material Laboratory in UTeM. In this experiment, carbon materials use as an electrode are graphene and CNT. 1M H_2SO_4 and 6M KOH was used as an electrolyte material. Then, the electrode are characterized by using SEM to obtain the morphology of electrode material. The CV was used to measure to obtain the capacitance value, lifecycle, and determination of the fabricated EC. The result obtained was compared to the previous research to see the difference.

CHAPTER 2

LITERATURE REVIEW

2.1 Electrochemical Capacitors (ECs)

Basically ECs can be categorized into two parts which are electrochemical double layer capacitors (EDLCs) and pseudocapacitors. The difference between these capacitors are their storage principle, which is for EDLC, the electrostatic storage of the electrical energy can be achieved by separation of charge in a Helmholtz double layer at the interface between the electrode and electrolyte surface. The distance of the static separation of charge in a double-layer is of the order of a few Å (0.3–0.8 nm) which is extremely small. Meanwhile for pseudocapacitor, the electrochemical storage of the electrical energy with electron transfer was achieved by a redox reaction with specifically adsorbed ions from the electrolyte, The intercalation of atoms in the layer lattice or electrosorption, under potential deposition of hydrogen or metal adatoms in surface lattice sites which result in a reversible faradaic charge-transfer (Namisny, 2013).

2.1.1 Electrochemical Double Layer Capacitor (EDLC)

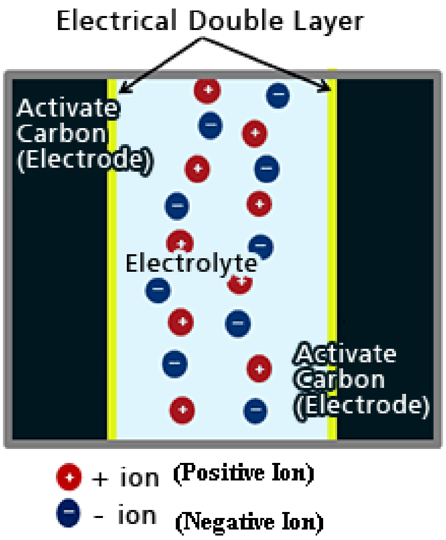

Figure 2.1 : The Schematic EDLC (Retrieved from http://www.murata.com)

Figure 2.1 shows how an EDLC is made up from a separator, electrolyte, activated carbon and current collector. Usually the activated carbon is used as the electrode, because it gives the extremely high specific surface area, relatively low cost, ultra high capacitances are possible within a small package size. EDLC can achieve high life cycle seems it has no chemical reaction

The operating principle of EDLC is based on the electrical double layer that can be formed between the electrode and electrolyte interface. Figure 2.2 shows the basic principle behind the capacitor. Electrolytic fluid is used in its solid form, and the electrode is solid form. When the electrode and electrolyte material come in contact with each other, the positive and negative poles are distributed relative to each other over and extremely short distance. This phenomena was known as an electrical double layer. When an external electric field is applied, the electrical double-layer that is formed in the vicinity of the electrode's surface within the electrolytic fluid is used as the fundamental capacitor structure. (Elna, 2011)

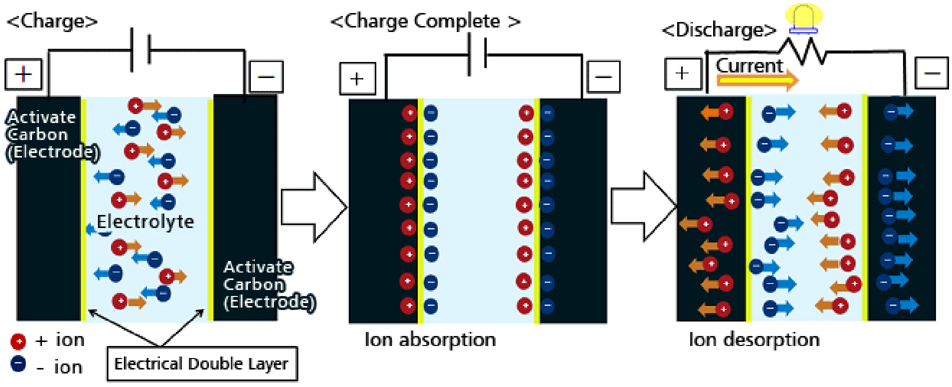

Figure 2.2 : The Operating Principle in Electrical Double-layer Capacitors (Retrieved from http://www.murata.com)

2.1.2 Pseudocapacitor

The pseudocapacitor is the combination of battery and capacitor. For EDLC the storage principle is electrostatically, whereas pseudocapacitors also store energy through a chemical reaction whereby a faradic charge transfer occurs between the electrolyte and the electrode. Pseudocapacitor is asymmetric in that sense that one of the two electrode layers is a carbon based capacitor electrode while the second electrode is similar with secondary batteries that use a transition metal oxide. The storage mechanisms are both reversible and can be charged and discharged 10000 of time. The Figure 2.3 shows how the pseudocapacitor is made up from faradaic reaction similar to the battery at the positive electrode. While in negative electrode, they use the double layer phenomena by using activated carbon with high surface area to give the great performance of pseudocapacitor. (Josie, 2011)

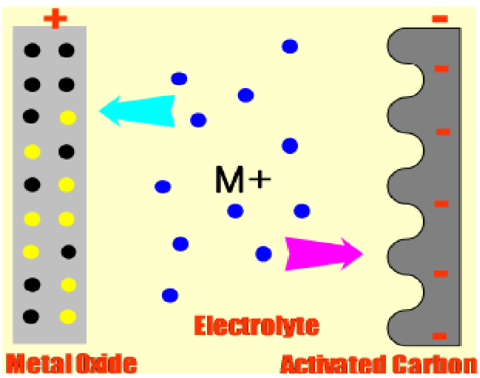

Figure 2.3 : Schematic of Pseudocapacitor (Josie, 2011)

2.2 Electrode Material

The electrode material is a very important part for the ECs to determine the properties of ECs. Nowadays more work has been done by using microporous carbons compared with the other materials and most of the commercially available devices commonly use are carbon electrodes. Below, will discuss about why the carbon materials always be used as an electrode. In this experiment, the electrode material that will use is graphene and CNT.

2.2.1 Carbon as Electrode Material

Carbon due to different allotropes (diamond, graphite, fullerenes/nanotube), various microtextures (more or less ordered) owning to the degree of graphitization, a rich variety of dimensionality from 0 to 3D and ability for existence under different forms (from powders to fibres, foams, fabrics and composite) represents a very attractive material for electrochemical application, especially for the storage of energy (Frackowiak *et al.*, 2001).

EC can deliver and store energy at relatively high rates because the mechanism of energy storage is simple charge operation. The EC vasts increase in capacitance in achieved due to the combination of an extremely small distance that separates the opposite charges, as defined by the electric double layer; and highly porous electrodes that embody very high surface areas.

Carbon has becoming more atterctive as an electrode material due to its combination of chemical and physical properties such as high conductivity, good corrosion resistance, high surface–area (~1 to >2000 m^2/g^2), high temperature stability, controlled pore structure, and good processabillity and compatibility

A variety of porous forms of carbon are currently preferred as the electrode materials because they have relatively high electronic conductivity and exceptionally high surface areas. The physical and chemical characteristic of the carbon electrodes