UNIVERSITI TEKNIKAL MALAYSIA MELAKA (UTeM)

EFFECT OF VOLTAGE'S PAUSE WIDTH ON MICROSTRUCTURE, CRYSTALLINITY AND ELECTROCHEMICAL PERFORMANCE OF ELECTROPHORETIC DEPOSITED ACTIVATED CARBON / CARBON NANOTUBE FILMS

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

by

NUR AMIRAH BINTI YAACOB @ RAZAK

B051110329

881012-06-5796

FACULTY OF MANUFACTURING ENGINEERING

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ABSTRAK

Permintaan yang semakin meningkat untuk keperluan tenaga telah menarik perhatian di kalangan penyelidik untuk membangunkan peranti penyimpanan tenaga yang cekap. Antara, kapasitor elektrokimia (EC) mempunyai potensi besar sebagai peranti penyimpanan tenaga untuk menyampaikan lebih banyak kuasa daripada bateri dan menyimpan lebih banyak tenaga daripada kapasitor konvensional. Elektrod atau bahan aktif adalah faktor yang paling penting dalam menentukan ciri-ciri peranti. Baru-baru ini, bahan-bahan karbon berdasarkan memainkan peranan penting sebagai bahan elektrod dan mempunyai pencapaian yang amat penting ke arah pembangunan aplikasi penyimpanan tenaga yang mampan. Teknik pembuatan elektrod adalah satu lagi faktor penting yang perlu dipertimbangkan. Oleh itu, projek ini adalah bertujuan untuk menghasilkan bahan elektrod dengan menggunakan teknik. Pemendapan elektroforetik berdasarkan Karbon Diaktifkan / Carbon Nanotube., Persembahan EC mereka diukur dengan teknik seperti kitaran voltammetry dan ciri-ciri Galvanostatic. Manakala, morfologi permukaan akan diperhatikan dengan menggunakan Mikroskop Imbasan Elektron (SEM) dan Raman Spektroskopi.

ABSTRACT

Increasing demand for energy requirement has attracted considerable attention among researchers to develop an efficient energy storage device. Among, electrochemical capacitor (EC) has great potential as energy storage device for delivering more power than batteries and store more energy than conventional capacitors. The electrode or active material is the most crucial factor in determining the device properties. Recently, carbon based materials played significant roles as electrode materials and possesses remarkably significant achievements toward the development of sustainable energy storage applications. The electrode fabrication technique is another important factor to be considered. Hence, this final year project Pulsed Electrophoretic Deposition fabrication techniques for EC based on Activated Carbon/Carbon Nanotubes., their EC performances measured by techniques such as cyclic voltammetry and Galvanostatic charge discharge characteristics and the surface morphology will be observed by using Scanning Electron Microscope (SEM) and Raman Spectroscopy.

DEDICATION

To my beloved parents

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TABLE OF CONTENT

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND

Energy storage device is an important component for equipments like vehicle, electrical device etc (Whittingham, 2012).Examples of energy storage device are batteries, conventional capacitor and electrochemical capacitor (EC). Presently, renewable energy has been utilized in many applications due to the decreasing availability of fossil fuels. Renewable energy sources, such as wind and solar, need energy storage facility to store converted electrical energy before been utilized. The energy storage facility is consisted of energy storage device which is to smooth the electrical output into the grid.

Each of the storage deviceshave their own advantages and disadvantages (Nor et al., 2013). Batteries able to store energy for a long time (i.e. more than 100 s), whereas conventional capacitor only stores energy for less than 0.01 s. However, battery has a lower power density (i.e. less than 100 W.kg-1) and life cycle than the conventional capacitor (i.e. power density more than 103 kW.kg-1 and life cycle is 10 times longer than the battery). Since conventional capacitor has low energy density (i.e. 70 mWh kg-1) and could not cater the need for high energy storage, electrochemical capacitor (EC) has been developed since its discovery in 1978 (Miller, 2010).

Besides that, EC has high energy density, large power density and long life cycle (i.e. higher than 100,000 times) (Nor et al., 2013). It has very high specific and volumetric capacitances and does not require dielectric materials (that is used in a conventional capacitor) that can cause dielectric breakdown. The widespread use of EC in applications such as electric vehicles, satellite propulsion and pulse power application has intensify studies on factors that can enhance the performance of EC. EC is divided into electrical double layer capacitor (EDLC), pseudocapacitor and hybrid capacitors.

EDLC involves electrostatic or physical separation of charge at the interface between electrode and electrolyte during operation (Nur et al., 2013). Whereas, pseudocapacitor stores energy using highly reversible surface redox (Faradaic) through transfer of charge between electrode and electrolyte interface. Hybrid capacitor is a combination of batteries and EDLC, thus has advantages of both power density and energy energy .

1.2 Problem Statement

The development of energy storage devices based on activated carbon (AC) and carbon nanotube (CNT) are under investigation due to their unique properties, such as electrical, mechanical, thermal properties and very large specific surface area (Elyas et al., 2015). Composite films based on these carbon materials has been used for electrical double layer capacitor (EDLC) to resolve aggregation and restacking problem of the carbon materials.EDLC-typedcapacitors have been intensively studied to improve their capacitance performanceto fulfill the need of new emerging market such as portable electronic appliances. Main contributing factors to improve the energy density of the EDLC are electrode materials, deposition techniques and electrolyte that have been used. For the current study, activated carbon (AC) and carbon nanotubes (CNTs) were deposited by pulsed electrophoretic deposition (EPD) onto iron alloy (YEF50-grade) substrate. Pulsed EPD mode had been used instead of continuous mode in order to improve microstructure and density of carbon films for electrode materials of EDLC capacitor(Chávez-Valdez and Boccaccini, 2012). Pulsed EPD allows the formation of composite and multilayer materials with high density electrode by low voltage mode and various types of suspension (i.e. aqueous or organic suspensions) (Ammam 2012). In addition, pulsed EPD is chosen because of the simplicity of synthesis set-up and their control flexibility.

1.3 Objectives

The objectives of this study are:

a) To characterize yield of activated carbon (AC), carbon nanotubes (CNT), and AC/CNT deposited by different pulsed electrophoretic deposition (EPD) parameters (i.e. voltage, deposition time, AC or/and CNTs suspension concentrations).

b) To characterize crystallinity and surface microstructuresof the deposited films.

c) To characterize electrochemical capacitorsassembled with the deposited films, in terms of their specific capacitances and galvanostatic charge discharge characteristics.

1.4 Scope

AC, CNT and AC/CNT composites films are deposited onto YEF50-grade iron alloy by EPD using different EPD parameters: applied voltage, deposition time and suspension concentrations. All the films were characterized in terms of their depositedyield using weight gain method. Films samples with high yields are then further characterized in terms oftheir crystallinity using Raman spectroscopy. Considering higher crystallinity in CNT film samples as compared to AC and AC/CNT films,only CNT-based samples were characterized in terms of their specific capacitances and galvanostatic charge discharge efficiencyusing cyclic voltammetry (CV) method.These results were also supported by their surface microstructure images, obtained using scanning electrode microscope (SEM).

CHAPTER 2

LITERATURE REVIEW

In this chapter a literature review on previous research works in various areas which is relevant to this research is presented.

2.1 Introduction of carbon Material for Carbon Based ECs

The foremost component of ECs are electrode materials; types of electrode material used influences the capacitance and charge storing capacity(Nor et al., 2013).Carbon material with high surface area material such as activated carbon, CNTs, graphene and carbon black are typically used as electrode material for EDLCs (Jost et al., 2011).

Carbon is an element that exists in various polymorphic forms, as well as in the amorphous state (Callister and Rethwisch,2011).This material is unique because it is ability to bond to many elements in many different way, it is the sixth most abundant element in this world. The most known type of carbon material are carbon black, activated carbon, graphene and carbon nanotubes (Ashby et al., 2009).

2.1.1 Activated Carbon (AC)

AC is a high surface area carbon material, it is usually used as electrode material for ECs because it contribute to high capacitanceperformance (Nor et al., 2013). There are two forms of activated carbon, which are particles/powder and AC fibre cloth.The low cost AC is commerciallyavailable in market and issynthesized from natural sources such as fruit shell,pitch,wood,coke or from synthetic precursors.

2.1.2 Graphene

Graphene consists of one atom thick 2D single layer of sp^2 bonded carbon.It is also synthesized in form of doped graphene to enhance its electrochemical properties (Nor et al., 2013). It has unique properties including high electrical conductivity (108 Sm^{-1}), high thermal(~5,000 $W.m^{-1}.K^{-1}$), high transparency (absorbance of 2.3%), great mechanical strength (breaking strength of 42 $N.m^{-1}$ and Young's modulus of 1.0 TPa), high aspect ratio, inherent flexibility, and large specific surface area (2.63×10^6 m^2 kg^{-1}).

2.1.3 Carbon Black

According to Nor et al. (2013), for ECs application carbon black generally utilized as conductive fillers because of their electrical conductive properties. In polymer design and electrochemical industry, carbon blacks are added to improve conductivity of materials. Carbon black appears in form of circular particles (essential particles) with size of 10–75 nm with aggregate size of 50–400 nm in width. Carbon black forms a compact one-, two-or three dimensional systems when itis homogeneously scattered and blended with the matrix.

2.1.4 Carbon Nanotubes (CNT)

CNT is a conducting or semiconductingtube-shaped material, made of carbon and having a diameter of nanometer scale. CNTs have various structures: difference in length, thickness, type of helicity and number of layers.There are two types of CNTs namely single walled carbon nanotubes (SWCNTs) and multi walled carbon nanotubes (MWCNTs) (Boccaccini et at., 2006).

SWCNTs exhibit better electric conductivity than MWCNTs variants. Figure 2.1 showsnanostructure of SWCNTs. SWNTshave a diameter of 1 nanometer, with a tube length of millions of times longer. Single-walled carbon nanotubes exist in a variety of structures corresponding to different ways of a sheet of graphene wrapped/rolled (i.e. different wrapping angle) into a seamless tube.

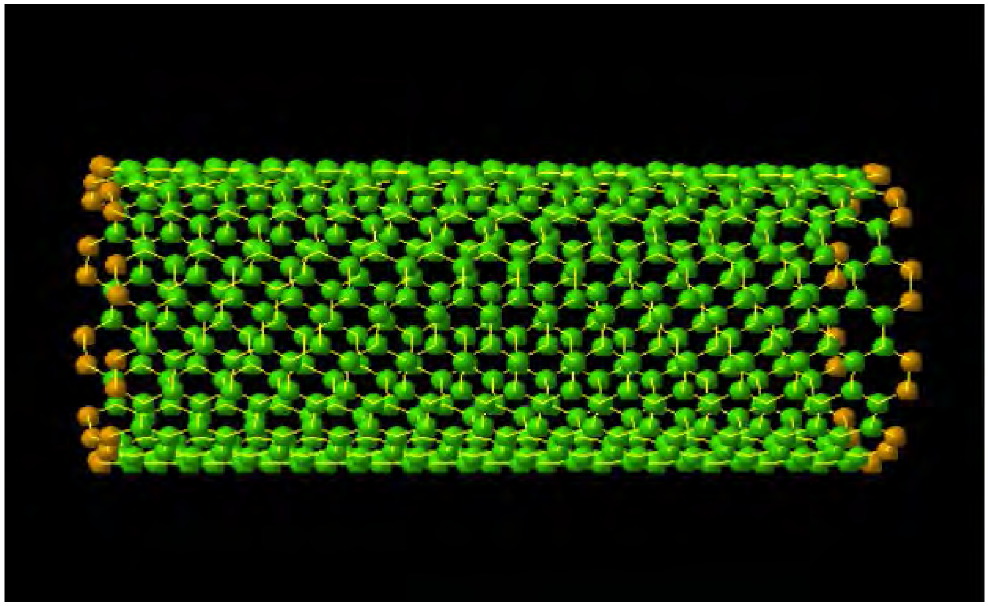

Figure 2.1: Structure of single-walled carbon nanotubes (SWCNTs) (Ashby et al., 2009).

Multi-walled nanotubes (MWNT) consist of multiple rolled layers (concentric tubes) of graphene (Figure 2.2). There are two models that can be used to describe the structures of multi-walled nanotubes, which are Russian Doll model and Parchment model.In the Russian Doll model, sheets of graphene are arranged in concentric cylinders while in Parchment model, a single sheet of graphene is rolled in around itself, like a scroll of parchment or a rolled newspaper.

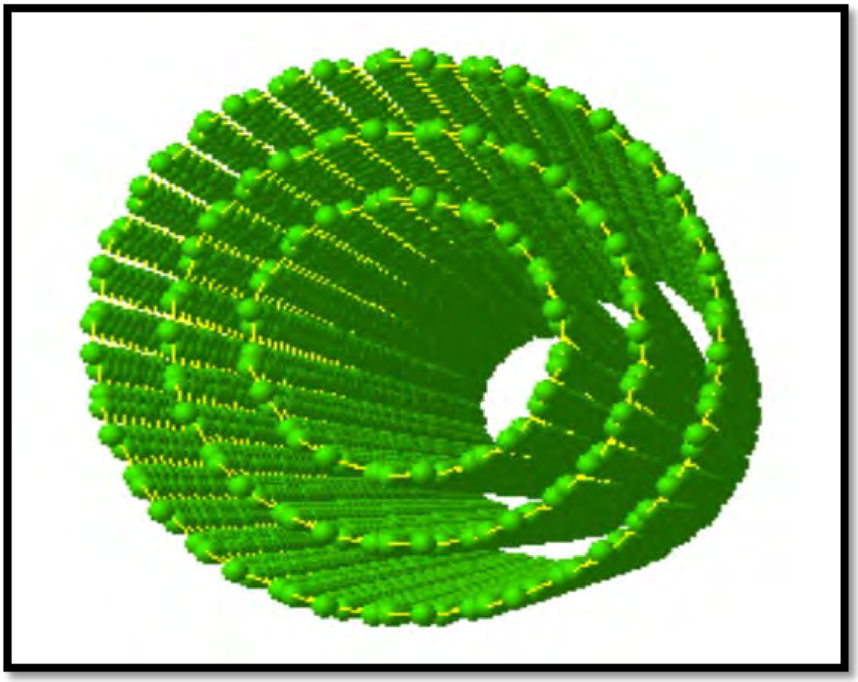

Figure 2.2: structure of multi-walled carbon nanotubes (Ashby et al., 2009).

Additionally, CNTs have amazing properties, quality, and thermal conductivity which surpass all other known manufactured materials because of their consistent structure, little breadth and versatility of individual carbon bonds.CNTs have been perceived as exceptionally potential electrode carbon materials for EC compared to other carbon materials due to their outstanding electrical charge storage capability,high accessible surface area, low mass density, excellent electrical conductivity, great chemical stability and interconnected network structure.

2.2 Carbon Based Electrode for EC

A carbon based electrode is an active material in EC. EC unit cell consists of a pair of symmetric electrodes deposited on current collector and immersed in an electrolyte, separated by a porous separator (refer Figure 2.3).

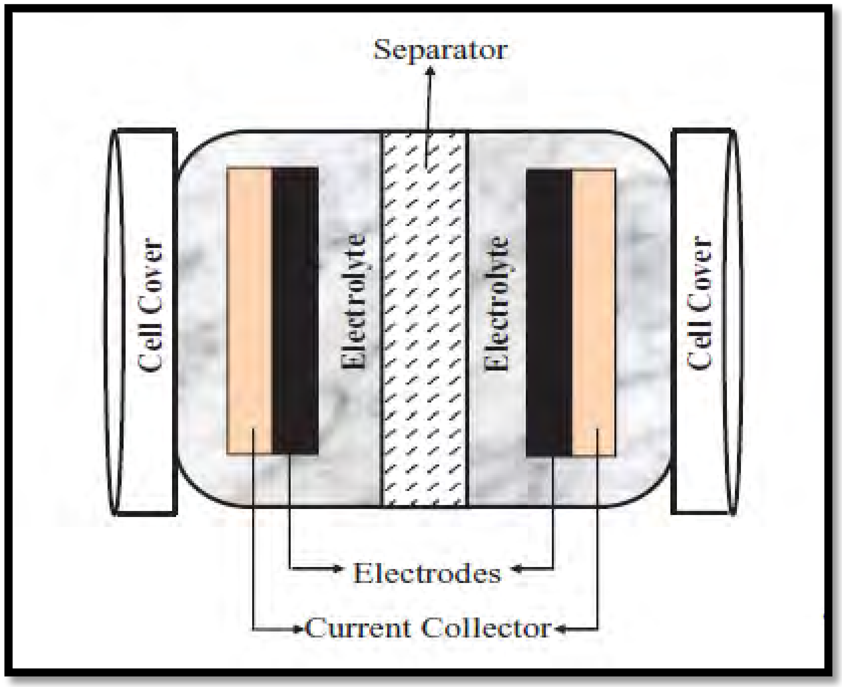

Figure 2.3: Common symmetric electrode cell component for EC (Nor et al., 2013).

Supply the electrical current is the function of current collector and preventing electric current from discharging in the cell while ionic current are flow is the function of the separator when the electrode are impregnated in the electrolyte. Interface between electrode and electrolytes, active material used as electrode and nature of electrolyte are the part of parameters that can affect the performance of ECs

2.2.1 Techniques for Fabrication Carbon Based Film

According to Ashby et al. (2009) there are several techniques can be used to fabricate carbon based film. Among them are electrodeposition (EPD), physical vapor deposition (PVD) and chemical vapor deposition (CVD). EPD is long established way to deposit metal layers on a conductingsubstrate. The EPD fabrication technique is illustrate in Figure 2.4where it is composed of substrate, counter electrode and solution. Ions in solution, replenished from anode (counter electrode) and deposited ontonegatively charged cathode. This technique are relatively low and cost and have a lot of advantage such as nuniformity of film, film thickness and deposition rate of rigid control and the possibility of film formation on large surface substrate.

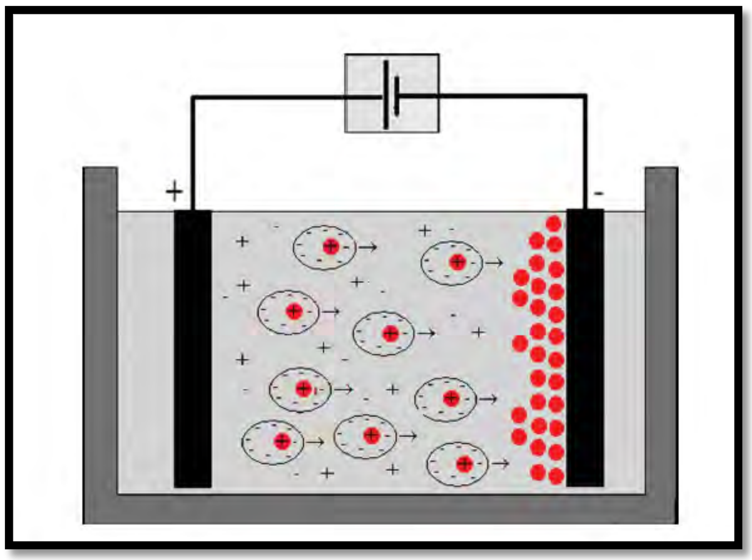

Figure 2.4: Schematic diagram of electrophoretic deposition of charged particles on the anode of an EPD cell with planar electrodes (Ammam, 2012).

The second technique or method used is physical vapor deposition (PVD). In this technique a thin layer of a material (usually metal) is deposited form a vapor onto the object to be coated.Vapor condenses onto the coldsubstrate (like steam from a hotbath condensing on a bathroommirror). In PVD plating, no potential difference between bath andwork pieceFigure 2.5 is illustration of PVD technique it show the material are evaporated by heating, by ion bombardment, or by laser ablation, is deposited on a substrate target. The deposited layer can be of nano thickness. The work piece is the cathode while the metalizing source material is the anode.

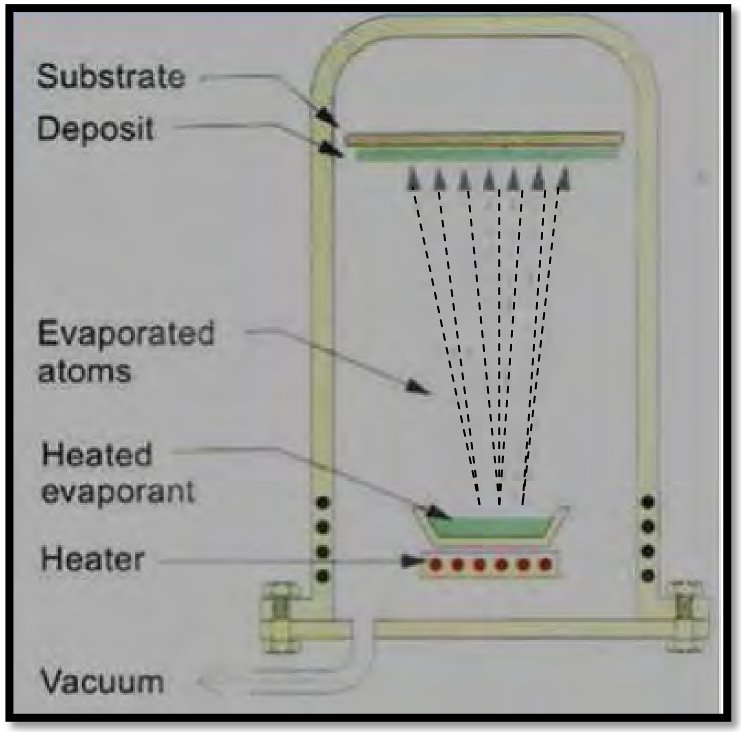

Figure 2.5: Physical vapor deposition (Ashby et al., 2009)

The third technique is CVD; in this technique film was deposited through chemical reaction and surface absorption. Figure 2.6 show the mechanism of CVD method. CVD is more conformal and allows for batch processing. Besides that, this technique has higher risks and costs due to gaseous materials, it is typically used to deposit dielectric materials, but can be used for metals. This process steps are very complicated because of the combination of chemical reactions and gas kinetics

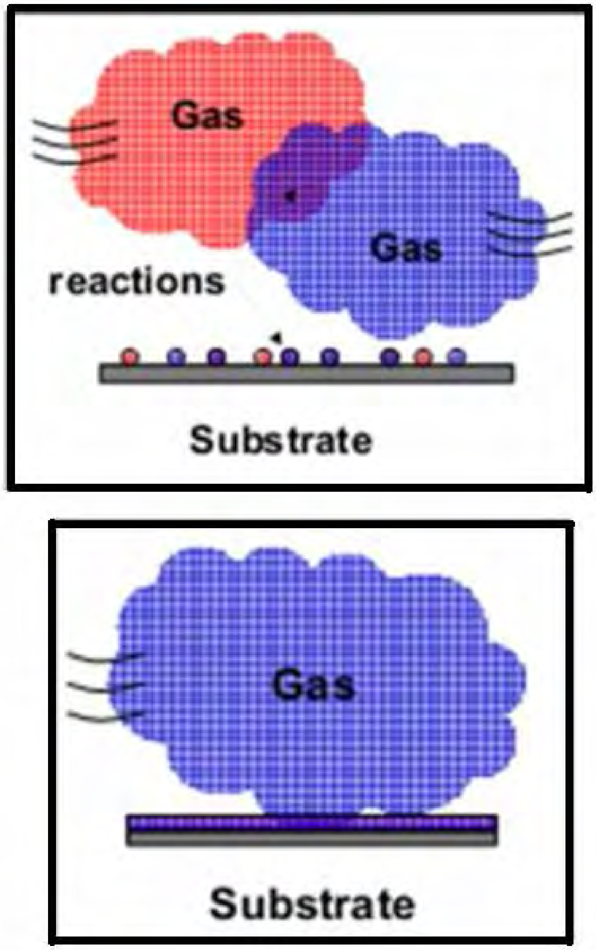

Figure 2.6: The mechanism of CVD technique (Ashby et al., 2009)

2.3 Pulsed EPD

Pulsed EPD process is one of the ways to used EPD technique. By using pulsed direct current or voltage during EPD the amount of bubble formation at the electrode was decrease, so that the homogenous deposits from water suspension will be produced (Chavez-Valdez and Boccaccini, 2012).The electrical signal for pulsed EPD is represented schematically in Figure 2.7, the voltage is constant while the time system was in an active state.