UNIVERSITI TEKNIKAL MALAYSIA MELAKA

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FABRICATION AND CHARACTERIZATION OF REDOX-BASED ELECTROCHEMICAL CAPACITORS

This report is submitted 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 "Fabrication and characterization of redox-based electrochemical capacitor" is the results of my own research except as cited in the references

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Date	:	25th June 2015

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 member of the supervisory is as follow

…………………………………………..

(Dr Mohd Asyadi Azam bin Mohd Abid)

ABSTRAK

Laporan ini membincangkan tentang penyelidikan fabrikasi dan pencirian kapasitor elektrokimia (KE) berdasarkan redoks. Permintaan fabrikasi KE semakin meningkat kerana ia memenuhi jurang antara bateri dan kapasitor. Kapasitan KE yang menggunakan karbon diaktifkan dan ruthenium oksida berdasarkan nisbah komposisi yang berbeza sedang dikaji. Tujuan eksperimen ini adalah untuk mempelbagaikan bahan elektrod and proses fabrikasi yang digunakan untuk menghasilkan KE yang lebih baik. Selain itu, proses sol-gel digunakan untuk menyediakan RuO_2 hidrat untuk meningkatkan prestasi dengan dua kali lebih tinggi berbanding RuO_2 kristal dan bahan-bahan lain. Teknik sluri digunakan untuk menyediakn bahan elekrod dimana elektrolit yang digunakan adalah kalium hidroksida (KOH). Berdasarkan kajian sebelum ini, semakin tinggi penggunaan RuO_2, semakin tinggi prestasi kapasitan. Dari eksperimen, peningkatan komposisi RuO_2 telah menghasilkan kitaran kestabilan yang rendah untuk analisis caj dan nyahcas manakala kapasitan spesifik yang diperoleh semakin meningkat. Daripada pemerhatian, penyediaan RuO_2 hidrat memainkan peranan yang penting dalam mencapai prestasi kapasitan yang lebih baik. Maksimum kapasitan spesifik yang diperoleh daripada eksperimen ini ialah 5.1029 F/g pada komposisi tertinggi RuO_2 iaitu 50 wt%.

ABSTRACT

This report discuss about the research on fabrication and characterization of redox-based electrochemical capacitors (ECs). Fabrication of ECs are increasing in demand as it fills the gap between batteries and capacitor. The capacitance of ECs by using activated carbon mixed with ruthenium oxide (RuO_2) having different composition ratios are being study. The purpose of this experiment is to vary the electrode materials and fabrication process being used in order to develop a better ECs. Apart from that, sol-gel process is being used to prepare hydrous RuO_2 which increase the performance by at least two times greater as compared to crystalline RuO_2 and other materials. Slurry technique is used to prepare the electrode materials where the electrolyte being use is potassium hydroxide (KOH). Based on previous research, increase of RuO_2 improve the capacitance performance. From the experiment, the increment of RuO_2 compositions result in lower cycling stability for charge discharge analysis while the specific capacitance obtained increases. From observation, preparation of hydrous RuO_2 plays an important role in achieving better capacitance performance. The maximum specific capacitance obtained from this experiment was 5.1029 F/g at the highest compositions of RuO_2 of 50 wt%.

DEDICATION

To my beloved parents, Mohamed Effendi bin Hashim and Rozita binti Mohd Daim.

I love you both eternally.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURES

AC	-	Activated Carbon
Co_3O_4	-	Cobalt Oxide
CV	-	Cyclic voltammetry
CNT	-	Carbon nanotube
C_{sp}	-	Specific gravimetric capacitance (in this work)
ECs	-	Electrochemical capacitors
EDLCs	-	Electrochemical double layer capacitors
EDX	-	Energy dispersive x-ray
FESEM	-	Field emission scanning electron microscopy
H_2SO_4	-	Sulphuric acid
IR	-	Voltage
KOH	-	Potassium hydroxide
MnO_2	-	Manganese oxide
NMP	-	N-methylpyrrolidinone
PTFE	-	Polytetrafluoroethylene
RuO_2	-	Ruthenium (IV) oxide or ruthenium dioxide
$RuCl_3.xH_2O$	-	Hydrous ruthenium chloride
XRD	-	X-ray diffraction
XRF	-	X-ray fluorescence

CHAPTER 1

INTRODUCTION

This chapter deals with the background where conventional energy and future energy together with their application are discusses before deliberating into specific issue on the different types of energy storage device that exists. The types of energy storage devices are discusses based on the limitations of fuel cells and batteries as compared to electrochemical capacitors (ECs).

1.1 Background

The study of energy and energy conversion are very significant to us from the existence of a cell to implementing it in our living application. In this context, energy can be classified into two which are conventional energy and future energy. Conventional energy is an energy sources that are being used by human since ancient times. Due to its limited sources, it is challenging to discover more of this energy and exploit their new deposits. Lack of availability in fossil fuels and climate change require people to move towards sustainable resources (Simon and Gogotsi, 2008). In fossil fuels, the degradation of organic materials such as oil, coal and natural gas were gradually formed. Other than that, biomass energy that was formed by biological materials of plants and animal waste are one of the oldest source of conventional energy. It has been executed as the most inexpensive way of generating electricity. Hydroelectric energy is another form of conventional energy source generated by dam or flowing water driving a water turbine or generator.

Future energy includes solar and renewable energy that can be sustained for a limitless time. Solar energy (solar panels and solar cells) is the example of direct use of radiation coming from the sun (Nehrenheim, 2014). Applications for solar energy includes water pumps, photovoltaic domestic and street lights. Nuclear energy is a stored energy sources that can be transformed into different energy forms, but generates harmful waste that causes many acted against it. Luckily, nature has given generous supplies of renewable energy which is capable of being reaped to meet energy needs in a sustainable and non-polluting manner (Dell & Rand, 2001). Renewable energy has been derived for the application in heat and electricity production. Renewable energy technologies future development will help to drive the cost down (Chen et al., 2009). Conventional and future energy can be considered in this study on energy storage as we are still seeking for the energy and forces to be utilized. The process of converting electrical energy from a network of power into a stored form and able to be converted back to electrical energy whenever required is called Electrical Energy Storage (EES). The following sub-chapter specifically stated the types of energy storage devices, its advantages and/or limitations.

1.2 Energy storage devices

The development of reproducible energy has been force by energy crisis and increasing environmental pollution occurs nowadays. Electrical energy storage systems such as batteries and electrochemical capacitors (ECs) are at the forefront of these. Due to the emerging technology, we are required to achieve higher requirements of the future systems by improving their performance and capabilities through the development of storage systems using new materials at nanoscale. Burke (2000), indicated that the specifications for energy storage devices are set in terms of maximum power (W) and energy stored (W h) as well as the size, weight, initial cost and life. The classification of energy storage devices in this study which are fuel cells, batteries and ECs are discussed below. Figure 1.1 shows the specific energy and power capabilities, or so called energy density and power density of a capacitors, electrochemical capacitors, batteries and fuel cells. The importance of this figure are discussed in the next section.

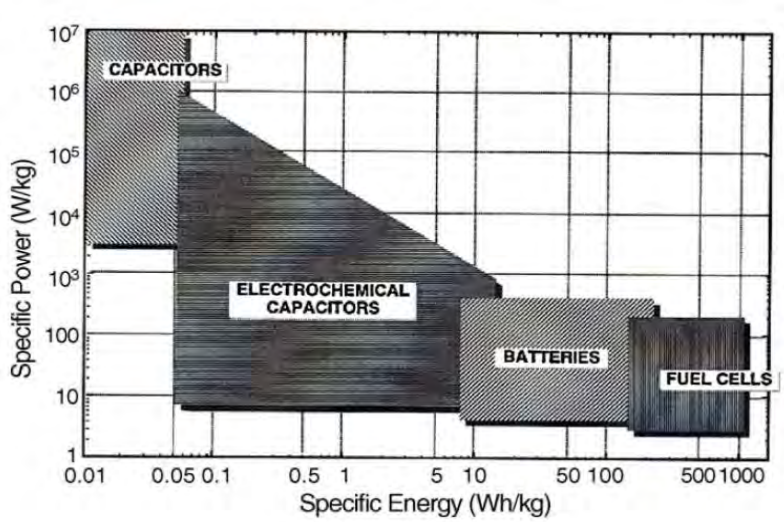

Figure 1.1: Ragone plot of power density versus energy density (Pandolfo et al., 2006)

1.2.1 Electrochemical capacitors

Progress have been made to improve the performance of batteries by using nanomaterials or organic redox couples but batteries suffered from low power density or uptake. Due to that, ECs have been given an important roles in energy storage systems. Main advantages of ECs include to provide high power capability (typically 60-120 s), excellent reversibility (≥90-95%), and long cycle life (>10^5) (Zhang et al., 2009).

By understanding Figure 1.1 showed above, ECs have higher power density compared to batteries and fuel cells but lower power density than capacitors. On the other hand, ECs have lower energy density than batteries and fuel cells while possess higher energy density than capacitors. This intermediate combination of high power capability and good specific energy helps electrochemical capacitors to fulfill a functional position as it complements to the deficiencies of other energy storage device.

1.2.2 Batteries

Batteries have been the most chosen technology for applications due to large amounts of energy that can be stored in a relatively low weight and volume. Batteries working principle are based on chemical separation when two electrodes are placed in a liquid that cause bigger chemical change in one electrode compare to the other. This will then causes electrical pressure to happen between the two electrodes. As electrical conductor connected to the terminals, electrical current will flow through circuit and undergoes chemical changes. Batteries are the best in terms of performance with energy densities that can reach up to 180 watt hours per kilogram (Wh/kg). Batteries main disadvantages in context of renewable energy storage are its poor performance at both low and high ambient temperature, limited charge–discharge cycle-life, and the need of periodic water maintenance.

1.2.3 Fuel cells

Like batteries, fuel cells are an energy storage devices for the direct production of low-voltage, dc electricity (Dell & Rand, 2001). Hydrogen fuel is provided to the negative electrode of the cell while oxygen or air to the positive electrode. Water and electricity will be generated by the resulting electrochemical reaction. Fuel cells are more similar to primary batteries where recharging could not store electricity. Fuel cells are not helpful in the contribution of sustainable energy unless the fuel is developed by renewable energy rather than from fossil fuels.

1.3 Problem statement

The development of electrochemical capacitors that are able to reproduce energy have caught more attention nowadays. Based on its charge storage mechanism, it is separated into EDLCs and pseudocapacitors, where alternatively, pseudocapacitors have significantly large energy density as compared to EDLCs. However, generally, ECs have lower energy density than batteries and fuel cells which contributes to fast fading of capacitance which will limit its commercial application. Besides that, metal oxides for pseudocapacitors have high cost of raw materials where 25 gram of hydrous RuO_2 at Sigma Aldrich exceeds RM10,000 compared to the hydrous $RuCl_3$ which cost about RM4,000 per 25 gram. It also possessed lack of stability during cycling due to redox reactions that occurs in each cycle.

Hence, researchers are trying to overcome this problem by varying the electrode materials and fabrication process in order to achieve better performance. Carbon-based materials complement with metal oxides helps to balance the cost while increasing the electrochemical performance. Efforts are being made to disperse the most promising metal oxides; ruthenium (IV) oxide (RuO_2) in carbon based materials in utilizing both faradaic capacitance of metal oxides and double layer capacitance of carbon. RuO_2 is utilized since it helps to increase the specific capacitance (C_{sp}) up to 720 F/g as compared to the current or commercial supercapacitor which possessed high power but are still lacking in terms of application. For carbon-based materials, activated carbon (AC) is used in order to increase the specific surface area (SSA) that contributes to good electrolyte accessibility and increase in C_{sp} besides having more stable cycles as the resistivity is lower.

This study covers the effect of mixing and determining the best composition ratio of AC with RuO_2 as electrode in aqueous electrolyte; potassium hydroxide (KOH) on specific capacitance. Due to that, general understanding on galvanostatic charge discharge (CD) and cyclic voltammetry (CV) of electrochemical characterization alongside Raman spectroscopy of materials characterization are crucial. The two parameters that may affect the results obtained includes scan rate and voltage window.

1.4 Objectives

The objectives of this research project are:

1. To study the AC/hydrous RuO_2 ECs prepared by slurry technique using electrochemical measurements.
2. To determine the factors that affect the specific gravimetric capacitance.

1.5 Scope of project

In this experiment, AC and RuO_2 was used as the electrode materials while 6 M of KOH as the electrolyte. In general, this experiment was focusing more on the ECs testing by using CV and CD in which the shape of CV and CD curves was interpreted. Besides that, the charge storage performance of the ECs was also analyzed by using C_{sp}. This report had also discussed on the electrode material itself, the factors of selecting the electrode material and their significance in the electric device field. The experiment were done in the Synthesis Laboratory located in Polymer Laboratory, Faculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka (UTeM). Fabrication of ECs was also conducted at Synthesis Laboratory, UTeM while characterization of the electrode material was conducted at Metrology Laboratory. The electrochemical performance of AC/RuO_2 ECs was analyzed using CD, CV, and Raman spectroscopy technique to achieve its objectives.

CHAPTER 2

LITERATURE REVIEW

This chapter discuss about the classification of ECs and its working principles. Even so, this chapter will emphasize on pseudocapacitors and the type of electrolyte to be used in the experiment. Besides that, the electrochemical characterization and material characterization used in analyzing the fabricated ECs are also discussed in this chapter.

2.1 Classification of electrochemical capacitors

Electrochemical capacitors (ECs) can be classified into three, based on the charge storage mechanism. Predominantly, the charge storage mechanism of these capacitors are due to the charging effect of double layer as it involves movement of ions to and from electrode surfaces. But then again, part of the observed capacitance may come from the pseudocapacitance contributions due to the presence of functional groups on the electrode surface. Charge is stored in the micropores at or near electrode/electrolyte interface. Capacitors that have high surface reactivity resultant in a double layer formation called electrical double layer capacitors (EDLCs) are the most commonly known ECs (Lokhande et al., 2011). Pseudocapacitors on the other hand, are known due to the oxidation-reduction reaction or fast redox reaction, causing induces of faradaic current that occurs on the electrode/electrolyte interface as the oxidation state changes. Another type of ECs is called hybrid capacitors that combines battery electrode with capacitive or pseudo-capacitive electrode and so exhibit both properties. The following section will discuss further on these two types of ECs followed by the working principle of these ECs.

2.1.1 Electrochemical double layer capacitors

As stated before, EDLCs stored energy by the formation of double layer of electrolyte ions on the conductive electrode surface. It differs from conventional capacitor because the electrode made up of porous material of carbon based such as activated carbon. It also has high surface area where it stores the charge on the electrode/electrolyte interface so that high capacitance is achieved. Apart from that, it has been used as a high power energy storage device due to their unique characteristics of high rate capability (<1 min charge-discharge) and long cycle life (>100,000 cycles) (Yoo et al., 2014).

Figure 2.1 below shows the charged supercapacitor mechanism. Electrical contact occurred between the metallic substrates or current collectors (1, 2) and porous material electrode (3, 4) are prevented by the use of separator (5). As parts containing pores (7) are immersed in the liquid electrolyte (6), bias voltage is applied between the two electrodes. Positive charge (8) at the exposed pore surface of one electrode attracts the negative ions (9) from the electrolyte and the negative charge (10) at the exposed pore surface of the other electrode attracts the positive ions (11) from the electrolyte existing in the pores (Obreja, 2008).

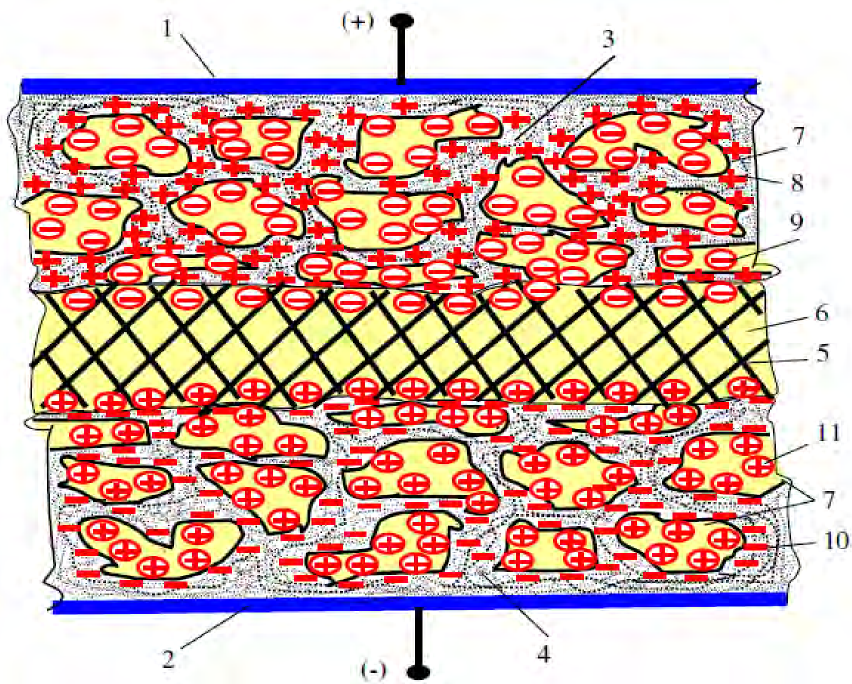

Figure 2.1: The schematic of charged supercapacitor mechanisms (Obreja, 2008)

In 1853, Hemholtz described the double layer capacitance as C,

$$C = \frac{\varepsilon_\tau \varepsilon_0 A}{d} \quad \text{(Eq. 2.1)}$$

where ε_τ is equal to electrolyte dielectric constant and ε_0 is vacuum dielectric constant, A is the surface area of electrode and d is the charge separation distance or the effective thickness of double layer, as charge separation (Angstroms) occurs on polarization at the electrode/electrolyte interface. Supercapacitors energy (E) and power (P_{max}) are calculated by the formula of

$$E = \frac{1}{2} CV^2 \quad \text{(Eq. 2.2)}$$

$$P_{max} = \frac{V^2}{4R} \quad \text{(Eq. 2.3)}$$

where C is dc capacitance in Farads, V is the operating voltage, and R in ohms of equivalent series resistance (ESR). Power density can be enhanced by utilizing the materials with high capacitance and low resistance (Azam et al., 2013). Energy density and power density SI unit can be defined as Wh kg^{-1} and W kg^{-1}, respectively.

2.1.2 Pseudocapacitors

In this study, the types of ECs that is being focused on is redox based ECs, or so called pseudocapacitors. Pandolfo and Hollenkamp (2006) stated that a reversible Faradaic-type charge transfer occurs in pseudocapacitors and the often large capacitance is not electrostatic in nature ('pseudo' prefix is to show the difference with electrostatic capacitance). In contrast to EDLCs, pseudocapacitors make charge storage between electrode/electrolyte interface by fast faradic redox reaction or electrosorption reaction of metal oxides or conducting polymers such as in Figure 2.2. The oxidation-reduction reactions, are resulted by an exchange of charge across the double-layer, rather than a static separation of charge across a finite distance.

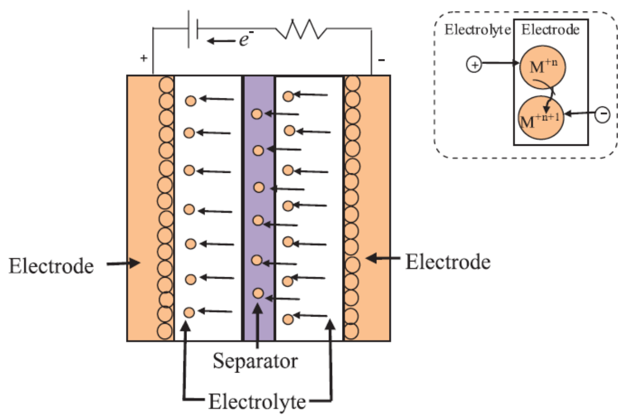

Figure 2.2: Energy storage mechanism for pseudocapacitors (Azam et al., 2013)

According to Conway and Pell (2003), redox systems are indicated by:

$$Ox + ze^{-} \rightleftharpoons Red \text{ and } O^{2-} + H^{+} \rightleftharpoons \text{in lattice} \qquad \text{(Eq. 2.4)}$$

Pseudocapacitors also displays a significantly large energy densities as compared to EDLCs. In addition, metal oxides electrical conductivity is far better than carbon and driven to higher inherent power densities (Ramani et al., 2001). Although this type of