

ELECTROCHEMICAL CHARACTERIZATION OF SUPERCAPACITORS WITH  
GLASS WOOL SEPARATOR

MOHD FERDAUS BIN MOHAMMAD YAACOB

UNIVERSITI TEKNOLOGI MALAYSIA

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MOHD FERDAUS BIN MOHAMMAD YAACOB

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To my parents, my wife and daughter

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## ABSTRACT

Supercapacitor, also known as ultracapacitor exhibits higher power density, greater rapid charging and discharging rates, and superior life cycle than a rechargeable battery. The major drawback of supercapacitor is its relatively lower energy density. Previous researchers have proved that the specific capacitance of supercapacitor increases with the increment of electrolyte concentration, which contributes to the improvement of its energy density. Commercial separator, such as cellulose paper, is incapable of withstanding high concentration of electrolyte. A corrosive-resistant material, glass wool has been previously introduced as a potential material for the separator. Nonetheless, studies of the electrochemical performance of supercapacitors with glass wool separator under different types of electrolytes with different concentrations are very limited. This thesis aims to electrochemically evaluate glass wool-based supercapacitor under three types of electrolytes; 1 mol/dm<sup>3</sup> sulfuric acid (H<sub>2</sub>SO<sub>4</sub>), 6 mol/dm<sup>3</sup> potassium hydroxide (KOH) and 1 mol/dm<sup>3</sup> tetraethylammonium tetrafluoroborate (TEABF<sub>4</sub>) and compare the performance to an identical supercapacitor with cellulose separator. A systematic study on the effect of high concentrated electrolytes coupled with the glass wool separator was also carried out. The electrochemical performance of the constructed supercapacitors was evaluated through cyclic voltammetry, galvanostatic charge-discharge, electrochemical spectroscopy, and cyclability charge-discharge tests using a symmetrical two-electrode test cell. It is found that the glass wool separator has outperformed cellulose in terms of its internal resistance and power density under the acidic, basic, and organic electrolytes. Interestingly, the glass wool-based supercapacitor coupled with high concentrated H<sub>2</sub>SO<sub>4</sub> (18 mol/dm<sup>3</sup>) electrolyte exhibits 23% increment of specific capacitance and energy density with almost 100% retention throughout 3000 cycles of charge-discharge process as compared to the one with 1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub> electrolyte. The optimum concentration for basic electrolyte KOH suggested is 10 mol/dm<sup>3</sup> which gives 5.3% increment in energy density, 13% increments in power density and excellent cyclability compared to that of 6 mol/dm<sup>3</sup> KOH electrolytes. The application of 2.5 mol/dm<sup>3</sup> concentration of TEABF<sub>4</sub> improves the energy and power density by 153% and 3821%, respectively compared to 1 mol/dm<sup>3</sup> TEABF<sub>4</sub>.

## ABSTRAK

Superkapasitor, juga dikenali sebagai ultrakapasitor mempamerkan ketumpatan kuasa yang lebih tinggi, kadar pengecasan dan nyahcas yang lebih pantas, dan kitaran hayat yang lebih baik berbanding bateri yang boleh dicas semula. Kekurangan utama superkapasitor adalah ketumpatan tenaga yang agak rendah. Penyelidik sebelum ini telah membuktikan kekuatan spesifik superkapasitor meningkat dengan peningkatan kepekatan elektrolit, yang seterusnya menyumbang kepada peningkatan ketumpatan tenaga. Pemisah yang terdapat dipasaran seperti kertas selulosa tidak mampu bertahan dalam elektrolit berkepekatan tinggi. Bahan tahan hakisan iaitu wul kaca telah diperkenalkan sebelum ini sebagai bahan yang berpotensi sebagai pemisah. Walau bagaimanapun, kajian mengenai prestasi elektrokimia superkapasitor dengan pemisah wul kaca dengan pelbagai jenis elektrolit dengan kepekatan yang berlainan adalah amat terhad. Kajian ini bertujuan untuk menilai secara elektrokimia superkapasitor berasaskan wul kaca dengan tiga jenis elektrolit; 1 mol/dm<sup>3</sup> asid sulfurik (H<sub>2</sub>SO<sub>4</sub>), 6 mol/dm<sup>3</sup> kalium hidroksida (KOH) dan 1 mol/dm<sup>3</sup> tetraetilammonium tetrafluoroborat (TEABF<sub>4</sub>) dan kemudian membandingkan prestasinya dengan superkapasitor yang sama tetapi dengan pemisah kertas selulosa. Satu kajian yang sistematik mengenai kesan elektrolit berkepekatan tinggi beserta pemisah wul kaca juga dilakukan. Prestasi elektrokimia superkapasitor yang dibina dinilai melalui ujian kitaran voltametri, cas-nyahcas galvanostatik, spektroskopi elektrokimia, dan ujian cas-nyahcas menggunakan sel uji dua elektrod yang simetri. Didapati, pemisah wul kaca telah mengatasi pemisah kertas selulosa dari segi rintangan dalaman dan ketumpatan kuasa menggunakan elektrolit berasid, beralkali, dan jenis organik. Menariknya, superkapasitor yang dibina berasaskan wul kaca dan elektrolit berkepekatan tinggi, H<sub>2</sub>SO<sub>4</sub> (18 mol/dm<sup>3</sup>) menghasilkan 23% peningkatan kekuatan spesifik dan ketumpatan tenaga dengan hampir 100% pengekaluan kekuatan sepanjang 3000 kitaran cas-nyahcas berbanding dengan elektrolit 1 mol/dm<sup>3</sup> H<sub>2</sub>SO<sub>4</sub>. Kepekatan yang optimum didapati untuk elektrolit alkali KOH adalah 10 mol/dm<sup>3</sup> yang memberikan peningkatan sebanyak 5.3% kepada kepadatan tenaga, 13% ketumpatan kuasa dan kitaran cas-nyahcas yang sangat baik berbanding dengan 6 mol/dm<sup>3</sup> elektrolit. Penggunaan elektrolit 2.5 mol/dm<sup>3</sup> TEABF<sub>4</sub> meningkatkan kepadatan tenaga dan kuasa masing-masing sebanyak 153% dan 3821% berbanding 1 mol/dm<sup>3</sup> TEABF<sub>4</sub>.

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**LIST OF ABBREVIATIONS**

BET	-	Brunauer-Emmett-Teller
CV	-	Cyclic Voltammetry
CCD	-	Cyclic Charge Discharge
CNT	-	Carbon Nanotube
ESR	-	Equivalent Series Resistance
EDLC	-	Electrical Double Layer Capacitor
EIS	-	Electrochemical Impedance Spectroscopy
GCD	-	Galvanostatic Charge Discharge
H <sub>2</sub> SO <sub>4</sub>	-	Sulfuric Acid
KOH	-	Potassium Hydroxide
PC	-	Pseudocapacitor
SEM	-	Scanning Electron Microscopy
TEABF <sub>4</sub>	-	Tetraethylammonium Tetrafluoroborate

## LIST OF SYMBOLS

$A$	-	Area overlap of two plates, in square meters
$C$	-	Absolute capacitance
$C_{dl}$	-	Double layer capacitance
$C_H$	-	Helmholtz capacitance
$C_{diff}$	-	Diffusion region capacitance
$C_s$	-	Specific capacitance
$C_{s,cv}$	-	Static specific capacitance measured by cyclic voltammetry
$C_{s,gv}$	-	Static Specific capacitance measured by galvanostatic
$C_d$	-	Discharge capacitance
$C(\omega)$	-	Complex capacitance
$C'(\omega)$	-	Complex real capacitance
$C''(\omega)$	-	Complex imaginary capacitance
$d$	-	Separation between the plates, in meters
$dv$	-	Voltage response
$dt$	-	Discharge time
$E_d$	-	Energy density
$\epsilon_r$	-	Dielectric constant
$\epsilon_0$	-	Electric constant
$f_r$	-	Frequency
$m$	-	Mass of electrode, in gram
$m_t$	-	Total mass, in gram
$I$	-	Current
$\emptyset$	-	Phase angle
$P_d$	-	Power density
$Q$	-	Charge in coulombs
$R_{esr}$	-	Internal resistance
$\tau_r$	-	Relaxation time, in second

$\Delta V$	-	Potential window
$V$	-	Voltage
$V_{drop}$	-	Voltage drop
$\omega$	-	Angular frequency
$Z(\omega)$	-	Impedance
$Z'(\omega)$	-	Real impedance
$Z''(\omega)$	-	Imaginary Impedance
$ Z(\omega) $	-	Impedance vector
$\pi$	-	Pi

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## CHAPTER 1

### INTRODUCTION

#### 1.1 Research Background

Electrical energy storage devices have been playing an increasingly essential role in many rapidly growth application such as in electric vehicles and portable consumer electronics. Besides rechargeable battery, supercapacitor has been recognized as important and promising device for the energy storage purpose [1]. Compared to a conventional dielectric capacitor, supercapacitor possesses an extremely high capacitance and is capable of storing electrical charges up to  $10^6$  Farad [2]. Owing to its advantages of high power density, long life cycle, and economical, supercapacitor bridges the gap between conventional capacitor and rechargeable batteries.

Depending on the energy storage mechanism, supercapacitor can be categorized into three categories; non-faradic supercapacitor called electric double-layer capacitor (EDLC), faradaic supercapacitor known as pseudocapacitor, and hybrid supercapacitor. An EDLC stores electrical charges electrostatically at the interface layer of electrolyte-electrode and creates a double-layer capacitance effect within the capacitor. Meanwhile, for a pseudocapacitor, the charge-discharge process governs by a reversible Faradaic reduction-oxidation process between the electrode and electrolyte. Unlike rechargeable battery, the reduction-oxidation process in pseudocapacitor is much faster and makes the charging-discharging process relatively quicker than the battery. On the other hand, a hybrid supercapacitor combines both non-faradaic and faradaic charge-discharge mechanisms in a single capacitor [3].

In essence, supercapacitor consists of a pair of active electrodes, separated by a separator that filled with an electrolyte. The active electrode is typically made from activated carbon material. The activated carbon is pre-treated to possess tiny, low volume pores, which consequently increases its surface area for the charges accumulation process.

Besides activated carbon, electrolyte is critical component in supercapacitor construction that determines its operating voltage. The electrolytes can be generally grouped into three categories; aqueous, organic and ionic electrolytes. Both organic and ionic electrolytes possess high potential window of up to 3 V, however both electrolytes suffer from high internal resistance, which affects the power density. Even though the potential window of supercapacitor with an aqueous electrolyte is only limited to 1 V, the electrolyte possesses high ionic conductivity, which reduces the internal resistance of the supercapacitor. In addition, the electrolyte is known to be environment-friendly and inexpensive compared to organic and ionic electrolytes.

In the past decades, many researches have been carried out to improve supercapacitor performance in terms of its power and energy density as well as the cyclability. Beside the operating voltage, energy density is also influenced by the supercapacitor's capacitance, which is significantly depends on the active surface area of the activated electrodes, ions properties and electrolyte concentration. Previous researcher has proven that the increment of concentration of electrolyte significantly increases the specific capacitance of the supercapacitor, but only limited in water bath analysis [4]. Hence, one way to achieve superior power and energy density is by utilizing high concentrated electrolyte coupled with a corrosive-resistant separator. Considering conventional cellulose separator incapable of withstanding high concentrated electrolyte, a corrosive-resistant material, glass wool has been recently introduced as the separator material in supercapacitor application [5]. However, the study was only limited to 1 mol/dm<sup>3</sup> sulfuric acid (H<sub>2</sub>SO<sub>4</sub>) electrolyte and no further information available particular on high concentrated electrolyte.

Therefore, it is essential to further extend the characterization of supercapacitor containing glass wool as the separator to reveal its performance under different types of high concentrated electrolytes.

## 1.2 Problem Statement

A corrosive-resistant material, glass wool has been recently introduced as the separator material in supercapacitor application [5]. The glass wool-based supercapacitor outperformed supercapacitors with other separator materials such as cellulose, polypropylene and fiberglass. However, the study is only limited to an aqueous electrolyte of  $1 \text{ mol/dm}^3 \text{ H}_2\text{SO}_4$ . In addition, very limited reports are available on the performance of the supercapacitor with high concentrated electrolyte that claimed to own superior power and energy capacities. This research aims to systematically evaluate the electrochemical properties of glass wool material as the separator in supercapacitor construction under three types of electrolytes, which are acidic, basic and organic electrolytes. With the utilization of the glass wool material, study on the effect of high concentrated electrolytes in supercapacitor construction was also carried out.

## 1.3 Objectives

The objectives of this research are:

- i. To evaluate and compare the electrochemical properties of supercapacitor with glass wool separator to that of cellulose separator under acidic, basic and organic electrolytes.
- ii. To investigate the electrochemical performance of the glass wool-based supercapacitor under high concentration of acidic, basic and organic electrolytes.

## 1.4 Scope of the Research

The scopes of the research incorporated as follow:

- i. The utilization of acidic, basic and organic electrolytes of  $\text{H}_2\text{SO}_4$ , potassium hydroxide (KOH) and tetraethylammonium tetrafluoroborate ( $\text{TEABF}_4$ ), respectively as the electrolytes in supercapacitor construction.
- ii. The construction of supercapacitor with a symmetrical two-electrode system test cell for all electrochemical evaluation.
- iii. The evaluation of the electrochemical properties based on cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), cyclability, and electrochemical impedance spectroscopy (EIS) tests using an electrochemical measuring instrument of Gamry Interface 1000.
- iv. The cyclability charge-discharge test is up to 3000 cycles with the applied current that depends on the individual capacity based on GCD test.

## 1.5 Significance of the Research

Even though the glass wool material is known to be corrosive-resistant material, however its application in supercapacitor containing high concentrated electrolyte is yet to be reported in the past. This research provides beneficial information to researchers in developing superior supercapacitor in term of its power and energy density. The implementation of glass wool separator enables the utilization of high concentrated electrolytes, which consequently leads to higher-rating supercapacitor at relatively lower cost compared to organic solution-based capacitor.



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