PARTICLE SIZE EFFECT ON SUPERCAPACITOR PERFORMANCE MADE BY COCONUT SHELL ACTIVATED CARBON

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DEDICATION

This thesis is deicated to my father, mother, sibling and Akhwat for giving me tremendous support. May this knowledge be benefit for mandkind and islam

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ABSTRACT

Over the years, biomass-based activated carbon (AC) supercapacitor electrodes have gained interest among researchers because there are wide ranges of abundant biomass such as coconut shell that can easily convert into AC. Fabrication of the electrode using AC fine particle and small portion of coarse particle has been recommended in the past. It is found that the particle size could potentially affect the electrode's physical and electrochemical properties. Nevertheless, information on the relationship between particle size and supercapacitor performance is very limited. The main objective of the research was to characterize a coconut shell-based AC as supercapacitor's electrode in term of its physical and electrochemical properties at different particle size distributions. Particle size distributions of sieved AC powders that came from 75, 150, 180 and 300 μm mesh size were measured using laser diffraction method. Each AC electrode was fabricated with 88%wt AC powder, 6%wt carbon black and 6%wt polyvinyl difluoride. The electrodes were denoted as 75AC/+0AC, 75AC/+150AC, 75AC/+180AC and 75AC/+300AC. The 75AC/ was fabricated based on 90% AC powder with 75 μm particle size while the '+' sign indicates the mixture of 10% coarse AC particle powder which comprise of either 150, 180 or 300 μm. Both AC powder and fabricated electrodes were characterized their physical properties in terms of surface area, pore size, micropore volume and morphology. Surface area and micropore volume were calculated using the Brunauer-Emmett-Teller (BET) and Barret-Joyner-Helenda (BJH) models' respectively. The electrochemical properties of AC electrodes were analysed using cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy. It was found that some of the AC pore structures were blocked by carbon black after the fabricating process which eventually led to major reduction in surface area. The addition of coarse particles causes microcrack on the electrode surface in all samples. However, it increases the surface area and specific capacitance of the electrode where both increments increase the energy density of the supercapacitor. As a comparison between 75AC/+0AC and 75AC/+150AC, the electrode BET surface area, BJH micropore volume and specific capacitance increased up to 20.00%, 20.12% and 22.74%, respectively. On the other hand, the addition of higher coarse particle size than +150AC has demonstrated a major drawback on the electrolyte decomposition. It can be concluded that the performance of supercapacitor can be improved further with the mixture of fine and coarse particles as opposed to single composition of fine powder alone. However, the coarse particle size should not be too big as it will affect on the electrolyte decomposition properties.

ABSTRAK

Sekian tahun, elektrod superkapasitor yang berdasarkan karbon teraktif (AC) biojisim telah mendapat perhatian dari para pengkaji kerana terdapat banyak biojisim seperti tempurung kelapa yang mudah digunakan untuk dijadikan sebagai AC. Fabrikasi elektrod menggunakan campuran zarah AC yang halus dan sebahagian zarah kasar telah dicadangkan pada masa lalu. Didapati bahawa saiz zarah berupaya memberi kesan kepada sifat fizikal dan elektrokimia elektrod. Namun, maklumat tentang hubungan antara saiz zarah dan prestasi superkapasitor adalah sangat terhad. Objektif utama kajian ini adalah mencirikan AC berasaskan tempurung kelapa sebagai elektrod superkapasitor dari segi sifat fizikal dan elektrokimia pada taburan saiz zarah yang berbeza. Taburan saiz zarah serbuk AC yang telah diayak menggunakan saiz mesh 75, 150, 180 dan 300 μm serta diukur menggunakan teknik pembelauan cahaya laser. Setiap elektrod AC dihasilkan menggunakan 88%wt serbuk AC, 6%wt karbon hitam dan 6%wt polyvinyl difluorida. Elektrod tersebut dilabelkan sebagai 75AC/+0AC, 75AC/+150AC, 75AC/+180AC dan 75AC/+300AC. Elektrod 75AC/ difabrikasi menggunakan serbuk AC berdasarkan kepada 90% serbuk AC dengan saiz zarah 75 μm, manakala simbol '+' menunjukkan campuran sebanyak 10% serbuk zarah kasar yang terdiri daripada saiz 150, 180 atau 300 μm. Kedua-dua serbuk AC dan elektrod telah dicirikan dari segi luas permukaan, saiz pori, isipadu mikropori dan morfologi. Luas permukaan dan isipadu mikropori dikira dengan menggunakan model Brunauer-Emmett-Teller (BET) dan Barret-Joyner-Helenda (BJH). Sifat elektrokimia elektrod AC telah dianalisa menggunakan kitaran voltametri, caj nyahcaj galvanostatik dan spektroskopi rintangan elektrokimia. Didapati bahawa sebahagian struktur pori AC telah tertutup oleh karbon hitam selepas melalui proses fabrikasi yang mana ia mengurangkan luas permukaan dengan banyak. Tambahan campuran zarah kasar telah menyebabkan keretakan mikro ke atas permukaan elektrod dalam semua sampel. Walau bagaimanapun, ia meningkatkan luas permukaan dan kemuatan tentu elektrod yang mana kedua-dua kenaikan meningkatkan ketumpatan tenaga superkapasitor. Sebagai satu perbandingan antara 75AC/+0AC dan 75/+150AC, luas permukaan BET elektrod, isipadu mikropori BJH dan kemuatan tentu telah meningkat sebanyak 20.00%, 20.12% dan 22.74%, masing-masing. Sebaliknya, penambahan saiz zarah kasar yang besar daripada +150AC telah mempamerkan kelemahan utama ke atas penguraian elektrolit. Dapat disimpulkan bahawa prestasi superkapasitor dapat diperbaiki dengan lebih lanjut dengan percampuran zarah halus dan kasar berbanding dengan komposisi tunggal serbuk halus semata-mata. Walau bagaimanapun, saiz zarah kasar tidak sepatutnya terlalu besar kerana ia boleh memberi kesan ke atas sifat penguraian elektrolit.

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LIST OF ABBREVIATIONS

H_2SO_4	-	Sulphuric acid
CNT	-	Carbon nanotube
AC	-	Activated carbon
CV	-	Cyclic Voltammetry
GCD	-	Galvanostatic charge-discharge
EIS	-	Electrochemical impedance spectroscopy
PVdF	-	polyvinylidene fluoride
NMP	-	N-Methyl-2-pyrrolidone
CB	-	Carbon black
XRD	-	X-ray diffraction
BET	-	Brunauer–Emmett–Teller
IUPAC	-	Union of Pure and Applied Chemistry
PSD	-	Pore size distribution
BJH	-	Barret, Joyner and Halenda
t-plot	-	Lippens and de Boer
DR	-	Dubinin and Raduskevich
HK	-	Horvath and Kawazoe
SEM	-	Scanning electron microscopy
EDLC	-	Electric double layer capacitor
ZnCI	-	Zinc chloride
H_3PO_4	-	Phosphoric acid
KOH	-	Potassium hydroxide
K_2CO_3	-	Potassium carbonate
CO_2	-	Carbon dioxide
PTFE	-	Polytetrafluoroethylene
N_2	-	Nitrogen gas
H^+	-	Hydrogen ion
Li^+	-	Lithium ion
Na^+	-	Sodium ion
K^+	-	Potassium ion

NH_4^+	-	Ammonium ion
Mg_2^+	-	Magnesium ion
Ca_2^+	-	Calcium ion
Ba_2^+	-	Barium ion
CI^-	-	Chloride ion
NO_3^-	-	Nitrate ion
SO_4^{2-}	-	Sulphate ion
OH^-	-	Hydroxide ion
CIO_4^-	-	Perchlorate ion
PO_4^{3-}	-	Phosphate ion
CO_3^{2-}	-	Carbonate ion
LiCI	-	Lithium chloride
Na_2SO_4	-	Sodium sulphate
KNO_3	-	Potassium nitrate
K_2SO_4	-	Potassium sulphate
PVC	-	Polyvinyl chloride
a.c	-	Alternating current
R_{ct}	-	Charge transfer resistance
R_{ESR}	-	Electrical series resistance
R_w	-	Warburg resistance
DDDC-rGO	-	Ligand reduced graphene oxide
MS	-	Mesh size
V_{loss}	-	Voltage drop
V_{micro}	-	Micropore volume
V_{meso}	-	Mesopore volume
S_{BET}	-	BET surface area
D	-	Interlayer spacing
a.c	-	Alternating current
EDX	-	Energy dispersive X-ray

LIST OF SYMBOLS

A	-	Current or area
Hz	-	Hertz
V	-	Voltage
°C	-	Degree celcius
°	-	Degree
Ω	-	Ohm
s	-	Second
F	-	Farad
C	-	Capacitance
Z'_{real}	-	Real resistance
$Z"_{img}$	-	Imaginary resistance
∅	-	Phase difference
R	-	Resistance
ω	-	Angular frequency
V_m	-	Maximum Voltage
I_m	-	Maximum current
j	-	Imaginary
Exp	-	Exponential
V	-	Voltage
I	-	Current
C_{sp}	-	Specific capacitance
I_d	-	Discharge current
Δt	-	Time differences
M	-	Concentration
ΔV	-	Voltage difference
F	-	Farad
S	-	Siemen
Mol	-	Molar
Å	-	Angstorm
β	-	Full width at half maximum radian

N	-	Order
λ	-	Wavelength
D	-	Interlayer spacing
θ	-	Angle
D	-	Portion of particle size
E	-	Energy
cc	-	Cubic centimetre

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CHAPTER 1

INTRODUCTION

1.1 Problem background

Back in 1957, supercapacitor had filed its patent and starting gained interest in 1990 due to the innovation of electrical hybrid technology system. Supercapacitor had both high power and energy densities which makes it considered to be combination of capacitor and battery. Its potential to charge and discharge faster had even made it to be coupled with a battery inside the power plant to provide power back up supply during a power disruption. However, the problem with the supercapacitor was its low energy compared to conventional battery. Increasing the energy would challenge the commercially available battery to be exchanged with the supercapacitor (Wang et al., 2012).

Based on Figure 1.1, there were two types of supercapacitor which were double layer capacitor (EDLC) (Figure 1.1 (a)) and pseudocapacitor (Figure 1.1 (b)). EDLC stored their energy by accumulating the ion on the electrode surface while pseudocapacitor used reversible redox reaction to store charge. The mechanism was different when compared with Li-ion battery (Figure 1.1 (c)). Battery used reversible redox reaction through the intercalation process of Li-ion into the graphite (Jost et al., 2014). However, both pseudocapacitor and Li-ion battery had low conductivity which makes it had slower charging time compared to EDLC type of supercapacitor. Despite of EDLC low energy, this can be overcome by using high surface area (1000 $m^2 g^{-1}$) carbon material such as activated carbon (AC) (Wang et al., 2012).

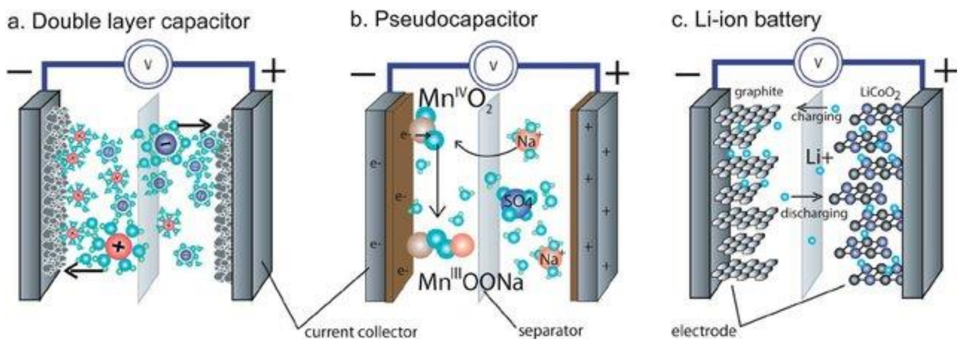

Figure 1.1 Schematic drawing of (a) EDLC (b) pseudocapacitance type of supercapacitors and (d) Li-ion battery (Jost et al., 2014).

Supercapacitor energy can be increased by increasing the capacitance and operating voltage. Capacitance was depended on the electrode material properties while operating voltage depend on the type of electrolyte. The commercially available supercapacitor normally used organic electrolyte due to high operating voltage that can reach between 2.5 – 2.8 V. However, it had been reported that organic electrolytes needed a special compartment to avoid flammability (Zhong et al., 2015). Therefore, previous researchers used aqueous electrolyte since it was cheap, high conductivity and easy to handle. Neutral, alkali or acidic type of aqueous solution can be possibly used as the supercapacitor electrolyte but among those solutions, sulphuric acid (H_2SO_4) electrolyte was normally chosen since it had the highest conductivity (Zhong et al., 2015). Despite of aqueous electrolyte operating voltage was limited to 1.0 V, the supercapacitor energy still can be increased through the increased of capacitance.

Supercapacitor capacitance was depended on the electrode type of material. The material can be from a metal oxide, conducting polymer or carbon material. Among those material, metal oxide and conducting polymer managed to produce 10-100 times greater specific capacitance than carbon material. However, it suffered from low conductivity, required the electrode to have nanometer thickness and complex production procedure. Thus, commercially available supercapacitors used carbon-type material due to its long lifetime, high conductivity and easy production compared to other types of material. Carbon type material can be in the form of graphite, carbon onion, carbon nanotube (CNT) or activated carbon (AC). Since the capacitance was inversely proportional to the electrode surface area, to this day AC was normally applied as commercial supercapacitor electrode since it had a surface area of more than 1000 $m^2\ g^{-1}$ (Wang et al., 2012; Ghosh and Lee, 2012).

AC can be easily made from biomass such as crops, solid waste and animal residue. Production of AC just needed the biomass to undergo thermal decomposition by carbonizing and activating it at a temperature between 400 – 1000 °C in the absence of oxygen. From those thermal decomposition process, biomass developed a porous structure which led AC to have surface area for more than 1000 $m^2\ g^{-1}$ (Abioye and Ani, 2015). Previous researches had successfully made AC using plastic (Kumar et al., 2018), wood fiber (Jin et al., 2014), oil palm kernel shell (Misnon et al., 2015), corncob (Qu et al., 2015; Wang et al., 2015), fabric (Su et al., 2014), sugarcane (Rufford et al., 2010), ginkgo shell (Jiang et al., 2013), coffee endocarp (Nabais et al., 2011), paulownia flower (Chang et al., 2015), lotus root shell (Wang et al., 2016b), rice husk (He et al., 2013), firwood (Wu et al., 2004), sawdust (Taer et al., 2011), soybean (Sun et al., 2020), cattail (Yu et al., 2017), willow (Jiang et al., 2020) and coconut shell (Barzegar et al., 2016; Fahmi et al., 2020; Jain and Tripathi, 2014). But, among of those types of material, majority of commercial supercapacitor electrode was based on coconut shell AC since it had hierarchical porous structure, high conductivity and well-ordered microstructure (Jain and Tripathi, 2014).

AC electrode was produced by binding all AC and conducting agent together with binder. Its fabrication process involved mixing all electrode material (AC, conducting agent and binder) in solvent, casting on the current collector, drying and cutting into a desired electrode shape. However, before fabricating the electrode, AC must firstly be milled and sieve to produce fine powder for better electrode mechanical stability (Azaıs, 2013). Particle size distribution in the AC powder needed to be determined as there had been report that particle size can potentially affecting electrode physical and electrochemical properties (Rennie et al., 2016; Fahmi et al., 2020). The term physical properties included electrode surface area, pore size, carbon crystal dimension and morphology. Finding suitable particle size distribution was needed since AC physical properties correlate with supercapacitor electrochemical properties.

Electrochemical properties of a supercapacitor can be analysed using cyclic voltammetry (CV), galvanostatic charge-discharge (GCD) and electrochemical impedance spectroscopy (EIS). The main function of CV was to know charge mechanism at increased voltage rate while GCD was used to test the supercapacitor performance by charge discharge until reaching the required voltage (Abioye and Ani, 2015). In case of EIS, Bode and Nyquist plots were used to measure the supercapacitor resistance and capacitance at increased frequency with the application of alternating current (a.c) (Ghosh and Lee, 2012). The plots were used to understand ion kinetic behaviour inside supercapacitor electrode. According to (Cooper et al., 2017) and (Cericola and Spahr, 2016), Nyquist plot pattern can showed the influence of pore structure and particle size to supercapacitor resistance. Nevertheless, understanding the particle size distribution effect using Nyquist plot was still recent.

1.2 Problem statement

Before fabricating the electrode, AC must be in the form of fine powder. Fine powder was usually produced by sieving the AC. After that, the sieve mesh size was used as AC particle size indicator as stated by Taer et al. (2019), Wu et al. (2004), Wu et al. (2005), Abioye et al. (2017) and Farma et al. (2013). Nevertheless, Pratsinis (2010) stated that using mesh size as particle size indicator was not accurate as not all particles within the sample had same size with the mesh size. Therefore, stating AC particle size in the form of particle size distribution was proper and this can be possibly measured using laser diffraction (Rennie et al., 2016). Since this technique had been performed by Rennie et al. (2016) and Pandolfo et al. (2010), it can be used at the tool to validate whether using sieve mesh size as particle size indicator was suitable or not.

Based on Azaıs (2013), it was recommended that the electrode was fabricated with fine particle that was range between 4 – 8 μm. However, According to Taer et al. (2019) and Eguchi et al. (2020), adding small amount of coarse particles can improve the ion transportion in electrode. Both researches had managed to fabricate electrode with coarse particle at size 53 and 135 μm. Some cases such as Dyatkin et al. (2016) had even prove that it was possible to fabricate electrode solely based on coarse particle at 250 μm and as a result it managed to produce high capacitance that was comparable to fine particle electrode. This showed that coarse particle can increased the supercapacitor capacitance. However, fabricating electrode solely based on coarse particle was hard since the electrode can easily brake (Rennie et al., 2016). Further, including small portion of coarse particle in electrode that was beyond 135 μm was not done yet. By knowing suitable coarse particle size, the cost of electrode production can be cut (Dyatkin et al., 2016).

Studying in term of understanding the effect of particle size to supercapacitor performance was considered to be new since this topic was opened starting at year 1996 by Yoshida et al. (1996) and later revisited by Portet et al. (2008), Jäckel et al. (2016), Dyatkin et al. (2016) and Rennie et al. (2016). Knowing the particle size distribution in biomass AC accurately was vital as it determined the electrode physical properties which eventually affecting supercapacitor performance (Rennie et al., 2016; Eguchi et al., 2020). For instance, changing sizes of the original AC by milling can shifting the carbon crystal dimension. This eventually affecting the conductivity of AC (Li et al., 2007). Cases like Rennie et al. (2016), had found that there was sudden high specific capacitance, surface area and pore volume at certain point of particle size distribution. Studying on the relationship between particle size to supercapacitor performance was still considered to be new. Therefore, widening this topic may open up a new concept of understanding supercapacitor performance which was the effect of particle size.

1.3 Research objectives

The objectives of the research are:

(a) To evaluate the particle size distribution in sieved coconut shell activated carbon powder using laser diffraction particle size analysis.

(b) To fabricate coconut shell activated carbon supercapacitor electrode at different particle size distribution.

(c) To characterize the coconut shell activated carbon and supercapacitor electrode in term of physical and electrochemical properties at different particle size distribution.

1.4 Scope of Studies

Scope of study is consisting of:

(a) Commercial activated carbon was based on coconut shell.

(b) The milled activated carbon powder undergone sieving process using 75, 150, 180 and 300 μm mesh size.

(c) The sieved activated carbon powder particle size was measured using laser diffraction particle size analysis.

(d) 75, 150, 180 and 300 μm activated carbon powder undergo physical characterization which consist of surface area, pore size, x-ray diffraction and captured scanning electron microscopy images

(e) Electrode was fabricated from activated carbon as active material, carbon black as conducting agent and polyvinylidene fluoride as binder with N-Methyl-2-pyrrolidone solution as the solvent.

(f) The active material was either be in pure fine particle (75 μm) or having small portion of coarse AC particle. Active material that included small portion of coarse particle contained 90% fine particle and 10% coarse particle (150, 180 or 300 μm).

(g) The electrodes undergo physical characterization which consist of surface area, pore size and captured scanning electron microscopy images

(h) The supercapacitor cell was set up using activated carbon as electrode, nickel foam as current collector and 1 M H_2SO_4 as electrolyte.

(i) Supercapacitor electrochemical analysis consist of cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy

1.5 Significance of the study

This study was targeted to understand the effect of particle size on supercapacitor performance. This will help in identifying suitable particle size to manufacture AC electrode. Before this, it was known that AC electrode needed to built from fine particle only. If knowing that it was possible to mixed coarse particle with fine particle for AC electrode fabrication, this can cut the cost of production in reducing the AC coarse particle into fine powder.

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LIST OF PUBLICATIONS

Proceeding

1. **Zulkefli, S. A**., Ani, F. N., & Noorden, Z. A. (2017). Redox Deposition of Manganese Oxide-Carbon Materials for Supercapacitor Applications: Brief Review. *The Colloquium*, (1), 1 – 4.