Low-cost supercapacitor based on multi-walled carbon nanotubes and activated carbon derived from *Moringa Oleifera* fruit shells

Shirley Palisoca,b, Joshua Marco Dungoa, Michelle Natividada,b,*

*Condensed Matter Physics Laboratory, De La Salle University, Manila, 922, Philippines*

**Condensed Matter Research Unit, CENSER, De La Salle University, 2401 Taft Avenue, Manila, 922, Philippines**

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**ABSTRACT**

An electric double-layer capacitor (EDLC) was fabricated using multi-walled carbon nanotubes (MWCNT) and activated carbon (AC) derived from *Moringa Oleifera* fruit shells as electrode material. The carbonization temperature and the weight ratio of the fruit shells to the activating agent were varied to determine the best condition in the fabrication of the electrodes. Activation of the carbonized fruit shells by ZnCl₂ resulted in the formation of pores as verified by the scanning electron micrographs. Energy dispersive X-ray analyses show that the washing of the carbonized sample resulted in the removal of zinc and chlorine residues. The supercapacitor electrodes were fabricated by adding polyvinylidene fluoride and N-methylpyrrolidone to the MWCNT-AC mixture to form a slurry and was cast onto a nickel foam. The capacitance of the fabricated electrodes was determined using a potentiostat. The activated carbon with a carbonization temperature of 800 °C and a 1:2 weight ratio between the fruit shells and ZnCl₂ was observed to have the highest capacitance of 130 F g⁻¹ and was duplicated to fabricate the supercapacitor electrodes. A glass microfiber filter was soaked in 3 M KOH and placed in between the two electrodes. The specific capacitance of the EDLC was found to be 122 F g⁻¹ at a current density of 0.5 A g⁻¹, average energy density of 17 W h kg⁻¹, average power density of 1.5 kW kg⁻¹ and an equivalent series resistance of 1.6 Ω. After 100 scans with a scan rate of 0.1 V s⁻¹, the percent decrease in capacitance was calculated to be 2.65 % of its original capacitance.

1. Introduction

Electricity is the most sought-out form of energy, the need for which is very ubiquitous in almost everything that people use. Powering devices, motors, and other equipment in today’s standards mostly require electricity. Currently, fossil fuels are the world’s major source of electricity. However, burning fossil fuels emits harmful products which are hazardous to human health and the environment. In order to reduce the world’s dependence on fossil fuels and to deal with the imminent depletion of these nonrenewable resources, other energy sources and storage technologies are being developed [1, 2, 3].

Stored energy has always been an inherent necessity for the advancement of technology. Gaining and delivering energy instantaneously is widely sought after, particularly in the automotive industry. Interestingly, the existing technology to address the aforementioned need is the supercapacitor. Supercapacitors are capacitors with high capacitance and have high energy density. What sets supercapacitors apart from batteries is that while batteries have the ability to store energy for longer usage, supercapacitors can be charged and discharged quickly, hence, they have a very high power density [4]. Given their differences in function, making one totally distinct from the other can be an unnecessary endeavor. For application purposes, sometimes both are even used together [5].

The two types of supercapacitors are the pseudocapacitors and the electrostatic double-layer capacitors (EDLC). Pseudocapacitors have a chemical reaction at the electrode and store charge electrochemically while EDLCs use carbon electrodes with a high double layer capacitance and store charge electrostatically [6, 7, 8]. This type of capacitor contains no conventional dielectrics. Alternatively, an electrolyte is placed between the two electrodes [9, 10, 11, 12]. The charge and discharge of an EDLC are mechanically contributed by the absorption and desorption to the electrical double layer. Given that both types of capacitors are very costly to make, thus making the need for the less expensive ones indeed an urgency. At present, activated carbon (AC) derived from biomass materials such as corncobs [13], enteromorpha [14], hemp [15], infested ash trees [16], loofah sponges [17], melons [18], olive pits [19],

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* Corresponding author.

E-mail address: michelle.natividad@dlsu.edu.ph (M. Natividad).

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pinecones [20], peanut shell [21], rice husk [22], starch [23], shiitake mushrooms [24], tobacco waste [25], and willow catkins [26], have been employed as carbon precursors for fabricating electrode materials for supercapacitors due to their abundance, renewability, low-cost and environment friendly properties. In previous studies [27, 28], addition of multi-walled carbon nanotubes (MWCNT) to commercially available activated carbon increased the energy density and specific capacitance of supercapacitor cells. The increase is attributed to the large surface area of the AC and the good conducting property of the MWCNT network.

*Moringa Oleifera*, also known as the drumstick tree, is a fast-growing deciduous tree. It is native to India but has been planted in other countries such as the Philippines, Africa, and South America [29]. It belongs to the family of *Moringaceae* which is abundant in nature and produces highly nutritious fruits [30]. The shells or pods of the *Moringa Oleifera* fruits contain cellulose, hemicellulose, and lignin which are the essential components of precursors for the production of porous activated carbon that are well suited for electrochemical and energy storage applications [8].

This paper reports a facile method of preparing AC/MWCNT based electrodes for EDLC supercapacitors. The activated carbon was derived from *Moringa Oleifera* fruit shells (MOFS) which makes the supercapacitor not only cost-effective but environment-friendly as well. Characterization of the precursors and components of the supercapacitors was performed using scanning electron microscopy, energy dispersive X-ray spectroscopy, cyclic voltammetry, chronopotentiometry, and electrochemical impedance spectroscopy.

**Table 1. Identification of AC samples based on their variations.**

| Sample | A | B | C | D | E | F | G |
|--------|---|---|---|---|---|---|---|
| Carbonization Temperature | 600 °C | 600 °C | 700 °C | 700 °C | 800 °C | 800 °C | 900 °C |
| MOFS to ZnCl₂ ratio | 1:3 | 1:2 | 1:3 | 1:2 | 1:3 | 1:2 | 1:2 |
2. Methodology

2.1. Reagents and solutions

The *Moringa Oleifera* fruit shells were sourced from a farm in Laguna, Philippines. Zinc chloride (ZnCl₂), potassium hydroxide (KOH), multi-walled carbon nanotubes (MWCNT), N-methylpyrrolidone (NMP), hydrochloric acid (HCl), and polyvinylidene fluoride (PVDF) were purchased from Sigma Aldrich (Singapore). The reagents were analytical grade and were used without further purification.

2.2. Preparation of activated carbon

The MOFS were sun-dried for a day. The dried fruit shells were cut into small pieces and weighed initially using a BOSCH SAE200 electronic balance. The weighed fruit shells were placed in a ceramic crucible and were dried in a furnace at 150 °C for 4 h. The oven-dried fruit shells were ground and a chemical activation agent, ZnCl₂, was added to the ground fruit shells. The MOFS to ZnCl₂ weight ratio was varied at 1:2 and 1:3. The mixtures were divided into four and were subjected to different carbonization temperatures (600 °C, 700 °C, 800 °C, and 900 °C) for 5 h at a rate of 10 °C/min in a nitrogen atmosphere and then cooled to room temperature. The typical carbonization temperature range, 600 °C – 900 °C, is where moisture, volatiles, and most of the non-carbon hetero-elements in biomass (oxygen, hydrogen, nitrogen, and sulfur) are removed resulting to a much higher carbon content [31]. The carbonized MOFS were then washed five times with 1.0 M HCl through a filter membrane to remove the ZnCl₂ impurities. It was then further washed with deionized water through a filter membrane five times to remove the HCl residue as shown in the schematic diagram in Figure 1.

2.3. Fabrication of electrodes

The electrodes were fabricated by mixing the generated AC (85 wt%) and MWCNT (15 wt%) with 0.4 mL of NMP and PVDF to form a homogenous slurry. The slurry was cast onto a nickel foam with a dimension of 1 cm × 1 cm and dried in a vacuum oven overnight at 80 °C. Figure 2 shows a schematic diagram of the fabrication process.

2.4. Fabrication of the EDLC

A glass microfiber separator was soaked in a 3 M KOH electrolyte for 1 h. The fabricated electrodes were carefully placed on each side of the separator. Electrical tape was used to hold the electrodes and separator in place.

2.5. Electrochemical characterization

The electrochemical properties of the AC/MWCNT electrodes were assessed using cyclic voltammetry (CV), chronopotentiometry, and electrochemical impedance spectroscopy (EIS) on a PalmSens4 potentiostat. For the three-electrode system, the fabricated AC/MWCNT electrode served as the working electrode, an Ag/AgCl electrode as the reference electrode and a platinum wire as the counter electrode. For the two-electrode system, the fabricated EDLC was used. The electrolyte solution was composed of 1.0 M KOH. The CV scans for the three-electrode system were done in the potential range of -0.7 V to 0.3 V, current density of 1 A g⁻¹ and scan rate of 0.05 V/s for 3 cycles. For the two-electrode system, the CV curves were obtained at scan rates of 0.07, 0.1, 0.2, 0.3, and 0.5 V/s over the potential window of -0.8 to 0.4 V. The galvanostatic charge-discharge (GCD) curve was obtained over a potential range of -0.1 V to 0.2 V and current density of 0.5 A g⁻¹. The EIS

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Figure 3. SEM images of (a) dried MOFS, (b) activated MOFS with ZnCl₂ residues (encircled in red), (c) activated MOFS with pore formation, and (d) AC/MWCNT.
measurements were carried out between the frequency range of 1 MHz and 100 Hz.

2.6. Physical characterization

A JSM-5310 JEOL scanning electron microscope coupled with energy dispersive X-ray spectroscopy was used to investigate the morphology and the elemental composition of the synthesized activated carbon. A BTX-285 x-ray powder diffractometer was used for the crystal structure analysis. The diffractometer consists of an X-ray tube, a sample holder, and an X-ray detector. The X-ray beam was collimated at an angle $\theta$ and the X-ray detector collect the diffracted X-rays at an angle of $2\theta$. A Fourier transform-infrared spectrometer was utilized for the identification of the chemical components of the samples.

3. Results and discussion

3.1. Determination of the best electrode

Seven different variations of activated carbon were produced to achieve the objective of determining the ideal amounts of MOFS and activating agent for optimum supercapacitor performance. The parameters that were varied are the carbonization temperature ($600^\circ\text{C}$, $700^\circ\text{C}$, $800^\circ\text{C}$, and $900^\circ\text{C}$) and the weight ratio between MOFS and ZnCl$_2$ (1:3 and 1:2). Table 1 shows the identification of the AC samples based on their variations.

3.2. Physical characterization

The surface morphology of the MOFS prior to and after the activation process was studied using scanning electron microscopy. Figure 3a shows the SEM image of the dried MOFS. The surface is relatively rough with minimal signs of pore formations. The SEM image of the activated MOFS is shown in Figure 3b. It can be observed from the micrograph that residues of ZnCl$_2$ (encircled in red) are present on the surface of the activated MOFS. The disappearance of these ZnCl$_2$ residues which led to the formation of pores [32] is shown in Figure 3c. A more porous surface compared with the activated carbon without MWCNT is shown in Figure 3d. The MWCNT structures are visible, as evidenced by the string-like structures on the surface.

The elemental composition of the AC/MWCNT sample was analyzed using EDX. Figure 4a shows the elements that are present in the carbonized sample before it was washed with HCl and deionized water. The high percentage of carbon implies that most of the volatiles and non-carbon content of the MOFS were removed during the activation process which led to a much higher carbon content [31]. The high
percentages of zinc and chlorine came from the activation agent, the
low level of nitrogen came from the uniformly flowing nitrogen gas
during the carbonization process and oxygen came from the organic
material itself [33]. Figure 4b shows the elements present after the
sample has been washed with 1.0M HCl and deionized water. It can be
observed from the figure that the amounts of zinc and chlorine were
greatly reduced which implies that the washing eliminated most of the
zinc and chlorine residues resulting to the formation of pores in the
sample.

**Figure 6. FT-IR spectra of AC/MWCNT.**

\[
C = \frac{1}{vm\Delta V} \int I dv
\]

where the integrated area under the CV curve \( I \) is the oxidation or
reduction current (A), \( v \) is the scan rate (V/s), \( m \) is the mass of the
electrode material (g), and \( \Delta V \) is the voltage range (V).

### 3.3. Cyclic voltammetry

Cyclic voltammetry was performed to study the performance of the
AC/MWCNT electrodes. The specific capacitance \( C \) was calculated from
the resulting cyclic voltammograms using [34].

#### 3.3.1. Three-electrode system

The CV curves of the electrodes are shown in Figure 7. It can be
observed from the figure that the CV curve of the electrode fabricated
using sample A shows a large peak at the bottom suggesting that oxida-
tion took place. The electrodes fabricated using samples B, G and H also
show oxidation peaks but much smaller than that of sample A. The
electrode fabricated using sample C shows two peaks at either side of the
curve which suggests that both reduction and oxidation took place.

Figures 7d-7f show that reduction and oxidation did not take place in
samples D, E, and F. According to Eq. (1), capacitance is directly pro-
portional to the area of the curves generated by the cyclic voltammetry
scan. It can be seen from the CV curves that the samples with a MOFS to
ZnCl₂ weight ratio of 1:3 have smaller areas enclosed by the CV curves as
compared to their 1:2 counterparts. Hence, their capacitance, energy
density, and power density are lower than those of their 1:2 counterparts
(Table 2). The redox reaction that took place in the CV scans and the
lower capacitance output of the 1:3 samples are due to the greater
amounts of ZnCl₂ residues that were not washed away by HCl and hence
less pores were formed [35]. It can be seen in Table 2 that the electrode
with a MOFS to ZnCl₂ weight ratio of 1:2 at 800 °C carbonization tem-
perature was observed to have the highest specific capacitance, average
energy density, and average power density, hence, it was used for the
remaining tests. It can also be observed from the table that the addition of
MWCNT to AC enhanced the capacity of the electrode.

#### 3.3.2. Two-electrode system

The CV curves of the EDLC are shown in Figure 8. It can be seen in the
figure that the CV curves maintained their shape at different scan rates
Figure 7. CV curves of the electrodes fabricated using activated carbon (a) sample A, (b) sample B, (c) sample C, (d) sample D, (e) sample E, (f) sample F, (g) sample G, and (h) sample H.
and multiple scans indicating that the EDLC has excellent capacitive characteristics and reversibility [34]. The two electrode system yields values approximately half of the capacitance of the three-electrode system while the mass of the electrode doubles [36]. In this case, calculating for the specific capacitance of the two electrode system requires a multiplier of 4 in Eq. (1) to adjust the capacitance of the cell and the combined mass of the two electrodes to the capacitance and mass of a single electrode. A two-electrode system generates almost half the capacitance value compared to a three-electrode system hence the resulting capacitance should be doubled and since a two-electrode system uses two symmetrical working electrodes, another multiplier of 2 is needed to adjust the value to its specific capacitance. The specific capacitance of the fabricated EDLC was found to be 122 F g⁻¹ at a current density of 0.5 A g⁻¹ and the average energy density and average power density are 17 W h kg⁻¹ and 1.5 kW kg⁻¹, respectively (Table 2).

### 3.4. Chronopotentiometry

The two-electrode system was used for chronopotentiometry over a potential range of -0.1 V–0.2 V and current density of 0.5 A g⁻¹. The

Table 2. Values obtained in terms of capacitance, average energy density, and average power density of each sample.

| Sample | A  | B  | C  | D  | E  | F  | G  | (F w/o MWCNT) | EDLC |
|--------|----|----|----|----|----|----|----|----------------|------|
| Capacitance (F g⁻¹) | 47 | 122 | 78 | 116 | 124 | 130 | 94 | 126            | 122  |
| Avg. energy density (W h kg⁻¹) | 7  | 17 | 11 | 16 | 17 | 18 | 13 | 18            | 17   |
| Avg. power density (kW kg⁻¹) | 0.6 | 1.5 | 1.0 | 1.4 | 1.5 | 1.6 | 1.1 | 1.6            | 1.5   |

Figure 8. CV curves of the EDLC (a) at different scan rates and (b) for three scans.

Figure 9. Galvanostatic charge-discharge curve of the EDLC.

Figure 10. (a) Nyquist plot of the fabricated EDLC, and (b) the equivalent circuit used for fitting of EIS measurements.
triangular-shaped GCD profile (Figure 9) shows good symmetry and nearly linear discharge slope, implying that the EDLC has excellent reversibility and capacitive characteristics \cite{37, 38} confirming the CV result. A small potential drop (\(-0.013\) V) was observed suggesting that the fabricated EDLC has a low internal resistance \cite{39}.

### 3.5. Electrochemical impedance spectroscopy

Using the two-electrode system, an EIS scan was run over the frequency range of 1 MHz–100 Hz. The resulting Nyquist plot (Figure 10a) is comparable to the usual shape of Nyquist plots of most EDLCs, wherein a semi-circle occurs at higher frequencies, followed by a nonvertical line at intermediate frequencies and a nearly vertical line at lower frequencies \cite{40}. The nonvertical line is related to the ion transport limitation in the electrolyte and the nearly vertical line is related to the dominant capacitive behavior of the electric double layer formed at the electrode/electrolyte interface \cite{40, 41}. The low equivalent series resistance or internal resistance of the EDLC (1.6 \(\Omega\)) which was obtained from the x-intercept of the semi-circle in the plot confirms the GCD result. The nearly vertical line in the low frequency region suggests that the EDLC has an excellent capacitive behavior \cite{31} confirming the CV and GCD results. An equivalent circuit (Figure 10b) was generated by fitting the EIS data. The Randles circuit shows an electrolyte resistance (R1) value of 3.7 \(\Omega\), a charge transfer resistance (R2) value of 1.0 \(\mu\Omega\), a double layer capacitance (C1) value of 3.0 \(\mu\)F, and the Warburg open (W0) elements with values of 0.077 for K0, 0.66 for \(\sqrt{\mu}\), and 0.19 for \(\phi\).

### 3.6. Comparison with other works

Table 3 shows the performance comparison of the fabricated EDLC with previous works. It can be seen from the table that the performance of the fabricated EDLC in terms of specific capacitance is at par with those in the literature. Further improvements in the fabrication of the MOFS/MWCNT electrodes is recommended to further increase the specific capacitance of the EDLC.

| Electrode Material | Electrolyte | Current Density (A g\(^{-1}\)) | Potential range (V) | Specific capacitance (F g\(^{-1}\)) | Ref. |
|--------------------|-------------|--------------------------------|---------------------|--------------------------------------|-----|
| CNT/Microporous carbon | 3 M H\(_2\)SO\(_4\) | 0.1–50 | 0.9 | 125–237 | [42] |
| Graphene-coated CNT aerogel | EMF/TEOS | 0.01–10 | 3.0 | 60–130 | [43] |
| Graphene/CNT composite fibers | 0.5 M H\(_2\)SO\(_4\) | 0.2–2 | 0.8 | 6–35 | [44] |
| Carbonized PPy** nanotubes | 1 M KCl | 1.5 | 40–140 | [45] |
| Carbonized halogen-containing plastic waste | 6 M KOH | 0.5–40 | 1.0 | 110–313 | [46] |
| Activated carbon/CNT | - | 5 | 0.8 | 96–213 | [28] |
| Activated MOFS carbon/MWCNT | 3M KOH | 0.5 | 1.2 | 122 | This work |

\*1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide. \**Polypyrrole.

The specific capacitance of the EDLC was found to be 122 F g\(^{-1}\) at a current density of 0.5 A g\(^{-1}\), average energy density of 17 W h kg\(^{-1}\), average power density of 1.5 kW kg\(^{-1}\) and an equivalent resistance of 1.6 \(\Omega\). After 100 scans with a scan rate of 0.1 V s\(^{-1}\), the percent decrease in capacitance was calculated to be 2.65% of its original capacitance.

### Declarations

**Author contribution statement**

Shirley Palisoc & Michelle Natividad: Conceived and designed the experiments; Performed the experiments; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Joshua Marco Dungo: Performed the experiments; Analyzed and interpreted the data; Wrote the paper.

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**Competing interest statement**

The authors declare no conflict of interest.

**Additional information**

No additional information is available for this paper.

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