Self-Supporting Hybrid Supercapacitor Electrodes Based on Carbon Nanotube and Activated Carbons

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Article info

Abstract

Self-supporting AC (activated carbon)-FWCNT (few-wall carbon nanotubes) hybrid electrodes were fabricated by mixing of ACs with high specific surface area (SSA) and sub-millimeter-long FWCNTs. In order to fabricate the hybrid electrodes, AC and FWCNT were mixed in a weight ratio of 9:1, dispersed by bath-sonication and vacuum-filtrated on a membrane filter. The addition of FWCNTs gives conductivity and mechanical strength, and replace metallic current collectors in thick (0.1 mm) electrodes. For making an electrode, three different ACs that derived from walnut shell (WS), that from apricot stones (AS), and that commercially used for capacitors (YP-80F, Kuraray Chemical Co., Osaka Japan), were used with FWCNT in weight ratio of AC:FWCNT = 9:1. An electrode based only on FWCNT was also prepared as a reference for comparison. Electrochemical properties of the obtained electrodes were investigated by the cyclic voltammetry method (CV). Electrochemical characteristics were measured using the three-electrode cell contained of YP80F-FWCNT, AS-FWCNT, WS-FWCNT as a working electrode, a YP-80F-FWCNT counter electrode and a Ag/AgCl reference electrode with an electrolyte of 1 M Na_2SO_4 aqueous solution. Also, the morphological properties of obtained electrodes were studied using scanning electron microscope (SEM), the SSA was investigated by the Brunauer-Emmett-Teller analysis. SSA, conductivity, and resistivity of AS-FWCNT and WS-FWCNT electrodes were summarized. Both the AS-FWCNT and WS-FWCNT hybrid electrodes showed specific capacitances of about 140 F/g at 1 mV/s and about 100 F/g at 100 mV/s, which are similar or even better than the AC-CNT hybrid electrode made of commercialized AC (YP-80F).

1. Introduction

The storage of electrical energy has become one of the fundamental enablers for sustainable society in the 21st century. Electrochemical capacitors (ECs), including electric double-layer (EDL) capacitors, supercapacitors, and ultracapacitors, are energy storage devices that can be charged or discharged in a few seconds, via ion adsorption or fast surface redox reactions [1]. Supercapacitors can store large charge because of the larger available surface area (1.000–2.000 m²/g) accessible for charge storage in EDL. However, the energy density of supercapacitors is lower than batteries, this fact leads to the limitation of optimal time of discharge to seconds, while for practical applications need enhanced energy density and discharge time [2].

The activated carbons are used in powdered form to create a porous structure with high SSA which is available for electrochemical reactions. Activated carbons can be obtained using carbon-containing organic materials by carbonization (heat treatment) in inert atmosphere with following activation processes as oxidation in CO_2 or water vapor and chemical treatment with KOH. Biomass-derived raw materials such as coconut shells, wood, apricot stones, walnut shell [3] and

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rice husk can be used as precursors in addition to the fossil-derived materials such as pitch, coal, and synthetic polymers [4].

Polymer materials are usually added as binder to active material to form usable electrode. Related to the insulating nature of the polymer materials, different forms of conductive carbon materials are added in order to increase the conductivity of electrode. The typical weight percentage of polymer binder is 10–20 wt%, and that of conductive additive is 5–15 wt% of the electrode. However, even with the addition of conductive agents, the electrode conductivity is still comparatively low (usually around 1 S/cm or less). The low conductivity of the electrode enforces the use of highly conductive metals, referred to current collector [5, 6]. The main objective of metal collector application is to reduce the electrical resistance of electrochemical capacitor; therefore, to minimize contact resistance between active material and metal collector, its contact surface area is improved by adding the conductive fillers. ECs investigation reports the specific capacitance due to weight of active material, if replace metal current collectors with lighter materials, the total performance of the capacitor can be improved. Following this approach, combining the lightweight current collector and active materials could contribute to obtain the flexible, lightweight electrodes.

One of the carbonaceous materials which are widely used for electrochemical energy storage devices is carbon nanotubes (CNTs) [7, 8]. CNTs represent graphite allotrope with a cylindrical structure and usually have diameter less than 30 nm, but can have length more than a millimeter. They are excellent electric and thermal conductors and can grow on various metal and nonmetallic surfaces. The most important, the CNTs grown in the forest form by supported catalyst can be made extremely clean and do not need polymeric binders to achieve mechanical stability. Because CNTs can play all the roles of binder, conductive filler, and current collector, we can increase the content of active material in the device and thus the energy density of supercapacitors. Single-wall CNTs (SWCNTs) have a higher SSA of about 1320 m^2/g. Pure SWCNT electrodes show a high rate performance, but according to their cost up to 1000 USD per g, their application is limited. Also, due to the strong van der Waals interactions between SWCNTs, they easily form bundles and disordered networks, and as a consequence there is difficulties on pull out their excellent mechanical and electronic prop-

erties [9, 10]. Another type of CNTs is multi-wall CNTs (MWCNTs) that are available at low cost of about 100 USD per kg, but they have some disadvantages such as smaller conductivity and smaller surface area of 300 m^2/g. MWCNTs can be synthesized by CVD method using different types of hydrocarbons, for example, propane-butane gas mixture and Ni particle catalyst at 650–800 °C [11].

In the previous work [12], the sub-millimeter-long few-wall CNTs (FWCNTs) were synthesized using a single fluidized bed reactor. Fluidized CVD method can quickly convert C_2H_2 into sub-millimeter-long CNTs with a yield of about 70% and a residence time less than 0.3 s. This method promotes to decrease the time and energy which is needed for controlling of a temperature, because processes for catalyst preparation, growth and separation of CNTs can be done multiple times just by switching the gas flow.

In the work of Smithyman [7], CNT networks were used as the host matrix for activated carbon particles with size about several micrometers. This research showed the ability of CNTs to form freestanding flexible electrodes with AC without using of polymeric binders. The weight ratio of SWCNTs and AC was equal to 1:1. Self-supporting hybrid electrodes based on AC and CNTs have been studied [8, 9] and light weight electrodes with high specific capacity have been realized without using metal collectors, which lead to light-weight devices.

In order to obtain the light weight, flexible, self-supporting electrodes and replace conventional conductive additives as acetylene black it is necessary to combine the FWCNTs with AC in hybrid electrodes.

2. Experimental

AC-FWCNT composite electrodes were prepared by mixing the AC particles with FWCNTs in a weight ratio of 9:1. Carbon nanomaterials were dispersed in ethanol at 0.1 mg/mL concentration. Three different ACs were examined as capacitive particles: AC obtained from apricot stones (AS), that from walnut shell (WS), and YP-80F (particle diameter of 5–20 μm, SSA of about 2042 m^2/g, Kuraray Chemical Co., Tokyo, Japan). Also FWCNT films were prepared as reference and compared with AC-FWCNT electrodes. The mixture of AC with FWCNT was dispersed in ethanol using a bath-type 600-W sonicator for 20 min with a cooling unit set at 20 °C. To obtain the electrode films,

vacuum filtration of AC-FWCNT dispersions were carried out through polytetrafluoroethylene membrane filters (PTFE) with a pore size of 5 μm. Residual ethanol was removed by drying at 90 °C for 2 h. As a result, mechanically-strong films of interwoven FWCNTs that held the AC particles were obtained.

Microstructures of the AC-FWCNT films were analysed by scanning electron microscopy (SEM; Hitachi S-4800, Tokyo, Japan). SSAs were investigated by Brunauer-Emmett-Teller (BET) analysis of nitrogen absorption isotherms measured at 77 K (BEL Japan Belsorp-28SA, Osaka, Japan).

In order to evaluate the electrochemical performance of the AC-FWCNT electrodes, Ti-mesh (200 L *200 S) connected to the fabricated electrodes was prepared. Obtained electrodes were used to run cyclic voltammetry (CV).

The three-electrode cell with AC-FWCNT as a working electrode, a YP-80F-FWCNT as counter electrode and a Ag/AgCl electrode as reference electrode were used for capacitance measurements; the electrolyte was 1M Na_2SO_4 aqueous solution.

3. Results and discussion

From the point of view of practical application, it is important to take into account the dispersability and cost of CNTs. In the manufacturing of AC-CNT electrodes, the type of CNTs will affect characteristics of final electrode, mainly in terms of electrical conductivity due to the different ease of manipulation between them. Figure 1 shown SEM images of FWCNT paper. As can be seen from Fig. 1, CNTs are intertwined together, forming a flexible film. The pore sizes are less than 50 nm, and the carbon nanotubes have a length of several micrometers or more. As can be seen from SEM images, the CNTs are evenly distributed without forming thick bundles, which suggests good dispersability in ethanol.

The CV plots in Fig. 2a,b provide information on the rate capability of FWCNT electrodes. The gravimetric capacitance of the pure FWCNT electrodes was 16 F/g at 10 mV/s and the shapes of the CVs (Fig. 2b) were narrowed which did not indicate high capacitive behavior of the obtained film.
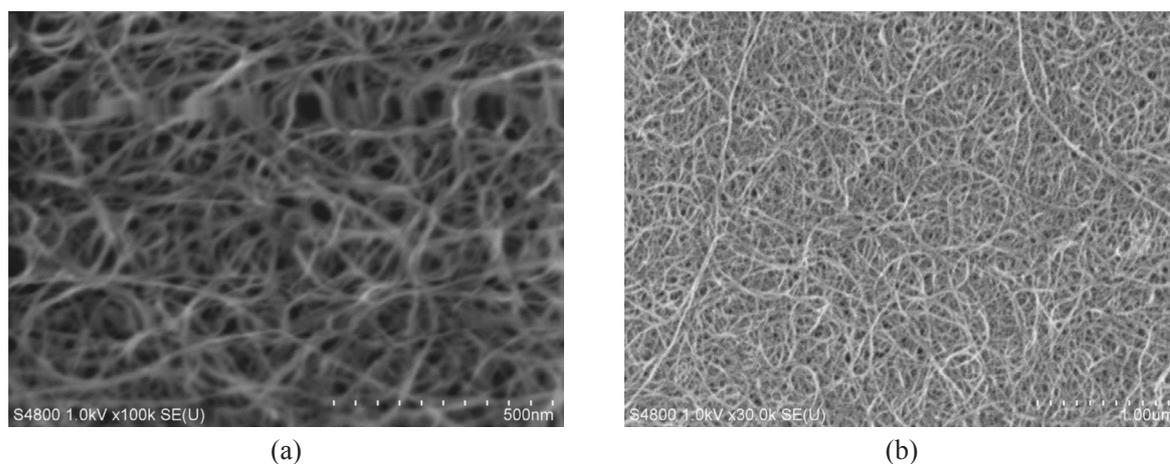

(a)   (b)

Fig. 1. SEM images of FWCNT papers: (a) – magnification of 30 000 times; (b) – magnification of 100 000 times.

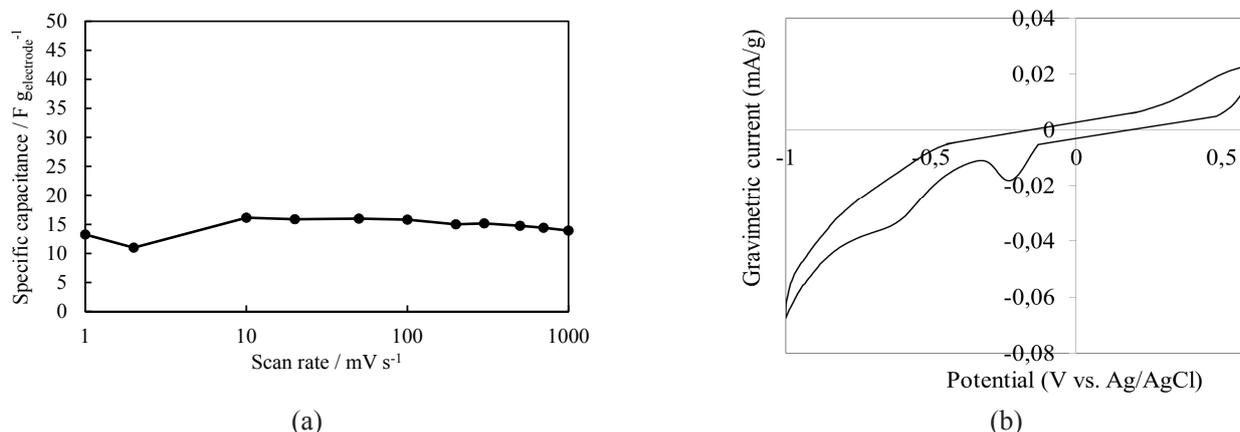(a)   (b)

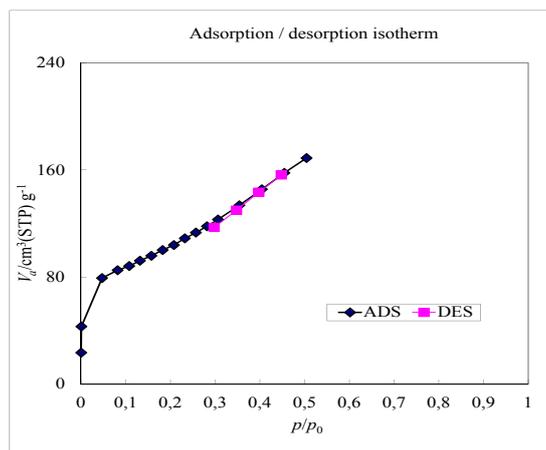Fig. 2. (a) Specific capacitance and (b) CVs of FWCNT electrodes.

Fig. 3. The results of BET of CNT paper.

Figure 3 shows N_2 adsorption and desorption isotherms at 77 K of the FWCNT electrodes. The isotherms of FWCNT showed the hysteresis phenomena typical to porous materials [14]. The low pressure segment of the electrode has a longer vertical segment that suggests a higher proportion of micropores. SSA of FWCNT paper is about 361 m^2/g. This SSA value is relatively low for obtaining electrodes with high specific capacitances. Considering the specific EDL capacitance of car-

bon materials of 10 F/m^2, the capacitance values correlate well with the surface areas of 360 m^2/g in the case of FWCNTs. The dispersion of FWCNT is hard to achieve and the strong agglomeration makes a large part of their surface not available for charge storage. This is the reason why the measured value of ~16 F/g is below of the theoretical maximum of ~130 F/g. Due to the lack of surface for the transfer of ions of electrolytes, the resulting film shows a specific capacitance below 20 F/g.

The preparation of electrodes by mixing capacitive AC particles with conductive CNTs is an effective method to fabricate electrodes with high electrochemical performance. One of the important characteristics that determine the energy characteristics of supercapacitors is the SSA of ACs.

Table 1 shows the methods and conditions of activation and the SSA values. The standard processing of the nitrogen adsorption isoterms was carried out by the BET method using a conventional cylindrical pore model (BDC) with the calculation of the total SSA.

The synthesized AC have SSAs of 1615 m^2/g for AS and 2552 m^2/g for WS. The sample of WS shows the highest value.

Table 1
Synthesis condition of ACs and their SSA

Name of raw materials	Walnut shell	Apricot stone	YP-80F
Activating agent	H_3PO_4 (70%)	H_3PO_4 (70%)	steam
Weight ratio of raw material/agent	1/3	1/3	N/A
Duration time/temperature of activation, °C/min	12/115	12/115	N/A
Temperature and time of carbonization, °C/min	850/90	850/90	N/A
Atmosphere	argon	argon	N/A
Washing with H_2O	up to pH = 7	up to pH = 7	N/A
Output of the obtained AC, %	30	30	N/A
SSA, m^2/g	2552	1615	2042
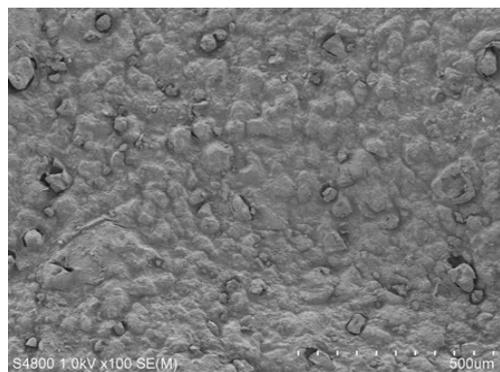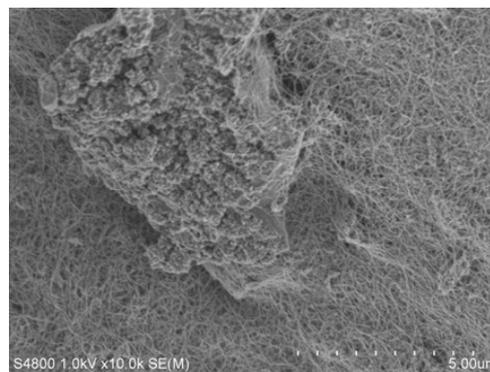
(a)   (b)

Fig. 4. SEM images of AS-FWCNT electrode: (a) – 100 times magnification; (b) –10000 times magnification.
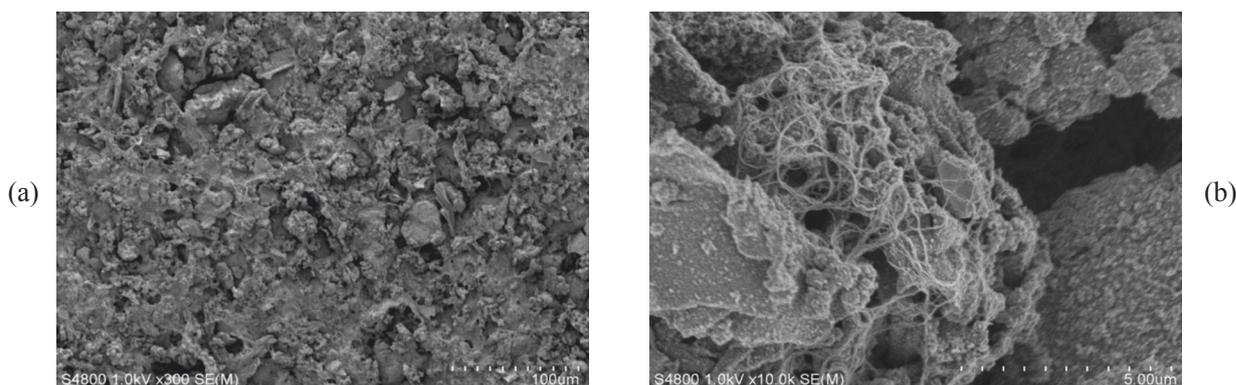
Fig. 5. SEM images of WS-FWCNT electrodes: (a) – 300 times magnification; (b) – 10000 times magnification.

Morphological structure of the obtained AC-FWCNT electrodes was observed by SEM. Figure 4a shows that AS is uniformly distributed and covered with FWCNTs. The long flexible FWCNTs wrap around AC particles, which is not possible with other conventional conductive materials such as acetylene black. Due to the CNTs that cover AC particles, the AC-CNT hybrid has self-supporting flexible nature. Figure 4b shows a high magnification SEM image of AS-FWCNT electrodes. Some of the AC particles are not covered with the CNTs possibly due to their imperfect dispersion with the sonication conditions.

Figure 5 shows the SEM images of the WS-FWCNT sample taken at (a) 300 times and (b) 10000 times. The obtained electrode has a developed porous structure with a plurality of cells and voids. CNTs cover the surface of AC particles thereby facilitating the creation of self-supporting films of the WS-FWCNT.

Different morphologies of AC-CNT interactions can be observed at the surface of the electrodes. Some AC particles have CNTs extending from their surface and appear to be included into the CNT network. However, most particles apparently have limited interfacial interaction with the CNTs and are sandwiched between compact CNT networks which have smooth surfaces. From the SEM results, it can be concluded that all obtained electrodes have a characteristic surface morphology for an electrode based on AC with CNTs and have a rough, self-supporting nature. The main purpose of CNT dispersion is the formation of three-dimensional networks capable of covering as large surface area as possible in order to effectively reinforce other materials [15] and transport electric charges. The use of CNT matrices as 3D current collectors is shown effective to obtain lightweight, high performance electrodes without binding additives.

The SSA and conductivity values of hybrid electrodes are summarized in Table 2. The SSAs of the obtained electrodes comprised the individual contributions of both AC and CNTs. A higher conductivity (σ) of 4.28 S/cm was achieved for YP-80F-FWCNT. The conductivity of the AS-FWCNT and WS-FWCNT electrodes are about 2 S/cm. The higher electrical conductivity of the YP-80F-FWCNT electrode is possibly due to the smaller disturbance of the electro-conductive pathway by the smaller YP-80F particles than by the bigger AS and WS particles. The electrical conductivity was different because the morphology of hybrid electrodes is not the same. The smaller particles in the YP-80F Kuraray activated carbons electrode is mostly covered with FWCNTs in contrast with the other ACs.

Table 2
Specific surface area, conductivity, resistivity
of AC-CNT electrodes

Physical properties	AS-FWCNT	WS-FWCNT	YP-80F-FWCNT
Conductivity (S/cm)	2.06	1.88	4.28
Specific surface area (m²/g)	1344	1145	-
Resistivity (Ω cm)	0.485	0.531	0.234

The results of electrochemical measurements were obtained from CV tests in a three-electrode cell in the range of -1–0.6 V vs. Ag/AgCl, using a full-contact Ti-mesh configuration.

The specific capacitance of electrodes was calculated from the CV curves by the equation:

$$C = \frac{Q}{V} = \frac{1}{v}\frac{\int_{E_1}^{E_2} i(E)dE}{E_2 - E_1}$$

where C is a specific capacitance, Q is an electric charge, V is a voltage, E is a potential and i is a current. In capacitance calculation the weight of AC-FWCNT paper [7, 8] is considered.

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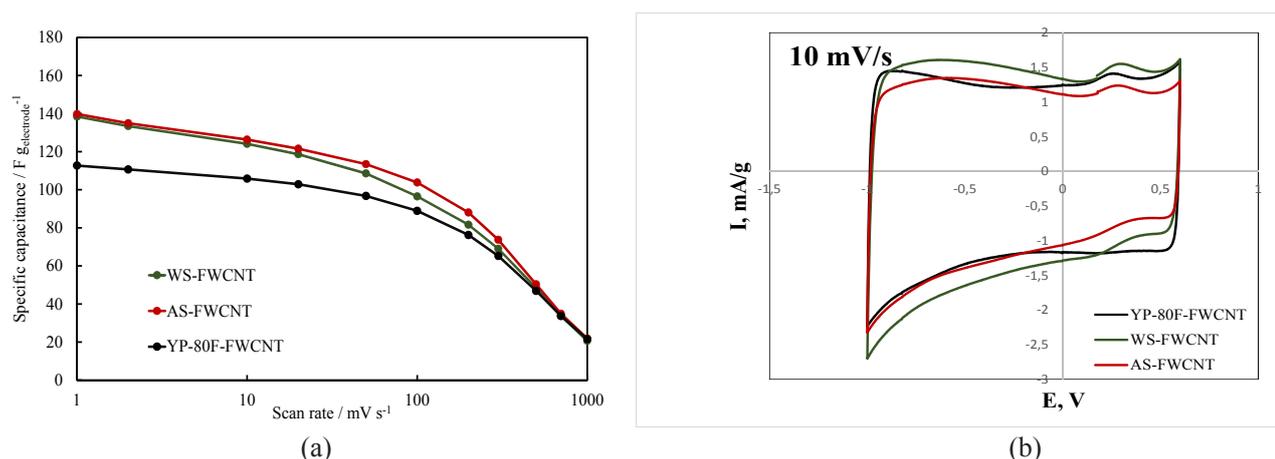<tr><td>(a)</td><td>(b)</td></tr>
</table>

Fig. 6. Electrochemical characterization of AC-FWCNT hybrid electrodes: (a) – specific capacitance, (b) – CVs at 10 mV/s.

Specific capacitance of the hybrid electrodes made of WS (Fig. 6a) and AS (Fig. 6b) particles is presented in Fig. 6. The electrochemical performances of the AS-FWCNT and WS-FWCNT hybrid electrodes are similar. AS-FWCNT and WS-FWCNT hybrid electrodes shows about 140 F/g at 1 mV/s and about 100 F/g at 100 mV/s.

The shapes of the CVs were similar for the electrode prepared from different activated carbons (YP-80F, AS, WS) and FWCNT. The CVs at a scan rate of 10 mV/s have the regular quasirectangular shapes without any large peaks. This behavior is similar to the CV curve of an ideal capacitor:

$$q = CV \qquad (2)$$

where electric charge (q) is proportional to applied voltage (V), and the value of proportionality is capacitance (C). High electrical conductivity and absence of parasitic reactions led to the formation of rectangular CV curves, which indicates on uniform diffusion of ions and high specific capacitance [14].

From the CV measurement results, it is clear that the hybrid electrodes obtained from the ACs synthesized from biomass (AS and WS) show the higher capacitances than YP-80F-FWCNT electrodes. Due to porous structure of ACs (AS and WS) which led to the formation of an electrically conductive network with higher electrolyte-accessible surface area, the hybrid electrodes show better rate performance than the YP-80F-FWCNT electrode.

4. Conclusions

It was obtained self-supporting, flexible hybrid supercapacitor electrodes by combination of high capacitive ACs with an electrically con-ductive matrix of FWCNTs. Pure CNT electrode was also prepared as a reference for comparison of electrochemical characteristics. To enhance the capacitance, hybrid electrodes were prepared from biomass derived ACs, such as apricot stones and walnut shells. The use of long FWCNTs enabled self-supporting electrodes without addition of polymeric binders, which shows low resistance and sufficient mechanical strength.

Presented method of obtaining of hybrid electrodes contributes to rapid and easy fabrication of lightweight electrodes with fairly low thicknesses for different applications.

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