ISSN: 0128-7680
Pertanika J. Sci. & Technol. **18 (2)**: 351– 363 (2010)

Symmetrical Supercapacitor Using Coconut Shell-Based Activated Carbon

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ABSTRACT

Two different supercapacitor configurations were fabricated using coconut shell-based activated carbon. Results for cyclic voltammetry (CV), electrochemical impedance *spectroscopy (*EIS), and charge-discharge measurements are presented and discussed for both configurations. The results show that coconut shell-based activated carbon is viable economical alternative electrode material to expensive activated carbon (AC) and carbon nano tubes (CNT). Meanwhile, the calculations from the charge-discharge characteristics show that the disk-shape supercapacitor, with 10% polyvinylidene fluoride binder (PVdF), has the highest specific capacitance (70F/g). Thus, the testing shows that the flat-laminated super-capacitor with 10% binder (PVdF) has the lowest (10.1ohms). Sources of high equivalent series resistance (ESR) are proposed and methods of reducing it are also discussed in this paper.

Keywords: Symmetrical supercapacitor, coconut shell-based activated carbon

INTRODUCTION

Supercapacitors (EDLCs), as a kind of energy storage devices, have high energy density, great power density and long cycle life (Conway, 1999). Electrochemical double-layer capacitors (EDLCs) are power sources that store energy within the electrochemical double layer which is formed at the solid (active material) and the solution (electrolyte) interface (Nishino, 1996).

Many different types of electrode materials have been intensely studied in the past years for fabricating EDLCs electrodes. Some of the mostly used materials include activated carbon (Kierzek *et al.*, 2004; Frackowaik and Beguin, 2001; Qu, 2002), carbon nano tubes (CNT) (Arabale *et al.,* 2003; Qun *et al.*, 2004; Frackowaik and Beguin, 2002; Emmenegger *et al.*, 2003), carbon aerogels (Probstle, Schmitt and Fricke, 2002), and conducting polymer-based nano composites (Xiao and Zhou, 2003; Chen, Wen and Teng, 2003).

Activated carbons are recognized as an essential component for the electrode of an electric double layer capacitor (EDLC) (Bonnefoi *et al.*, 1999; Qu and Shi, 1998; Oh, Korai and Mochida, 1999; Hal-Bon Gu, Jong-Uk Kim and Hee-Woong Song, 2000). Activated carbon (AC) is the electrode material used most frequently for EDLCs due to the low cost, high surface area, availability, and established production technologies (Nishino, 1996). The activated carbon grains are mixed with binder, cured (stabilized) and carbonized into an activated carbon artifact so as to be connected to the collector. The form should have a large surface area, the correct pore size distribution, as well sufficient electric conductivity and mechanical strength. Such properties appear to be governed by

Received: 27 March 2009
Accepted: 9 February 2010
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the activated carbon even when the binder and forming procedure are carefully selected (Wenming, 2002).

At present, because of its stable electrochemical behaviour, good cycling performance, and low cost, activated carbon has become a mainstream electrode material for commercial supercapacitors (Zhou Shao-yun, 2007). The reasons for the use of coconut shell-based activated carbon in this work were because it has a significantly lower price, and it is excellent in term of electrochemical performances.

Carbon materials are available with specific surface areas of up to 500–3000 m^2 /g (Shi, 1996). Early electrochemical capacitors were rated at a few volts and had capacitance values measured from fractions of farads up to several farads. The trend today is for cells ranging in size, i.e. from small millifarad-size devices with exceptional pulse power performance up to devices rated at several kilofarads. Some specialized electrochemical capacitors (EC) cells in production at present for traction applications have ratings of more than 100 kilo Farads (kF) (Varakin, 1997).

The purpose of this work was to fabricate a symmetrical (1V, 1F) supercapacitor using coconut shell-based activated carbon with aqueous electrolyte.

EXPERIMENTAL DESIGN

Two supercapacitor configurations were fabricated using coconut shell-based activated carbon (AC), with different packaging and different concentrations of binder.

A: Supercapacitor Cap#1 Disk-shape
B: Supercapacitor Cap#2 Flat-Laminated shape

Two prototypes of supercapacitors of the disk-shape and three prototype of the flat-laminated-shape were fabricated to test the effects of different binder concentrations on the specific capacitance and equivalent series resistance (ESR) in each configuration.

Materials

The materials used in this study are listed in Table 1.

TABLE 1
Materials used for fabrication

No.	Material	Specifications	Company	Role
1	Coconut shell-based activated carbon	LAJU PAC	Laju group	Active material
2	Poly vinylidene fluoride PVdf	182702	*Sigma Aldrich*	*Binder*
3	Isoprobanol	99.5% S42647	*Sigma Aldrich*	*Solvent*

All the materials were used without any further purification

Preparation of Electrode Materials

The coconut activated carbon used in this research is (LAJU PAC) of Laju group, while poly vinylidene fluoride (PVdF) was used as a binder and isoprobanol as solvent for all the supercapacitors with different concentrations.

Supercapacitor Cap#1

This disk-shaped supercapacitor was fabricated using coconut shell-based activated carbon, with 1M potassium chloride (KCl) electrolyte. *Fig. 1* shows the two prototypes of disk-shape supercapacitors labelled as Cap#1.1 and Cap#1.2.

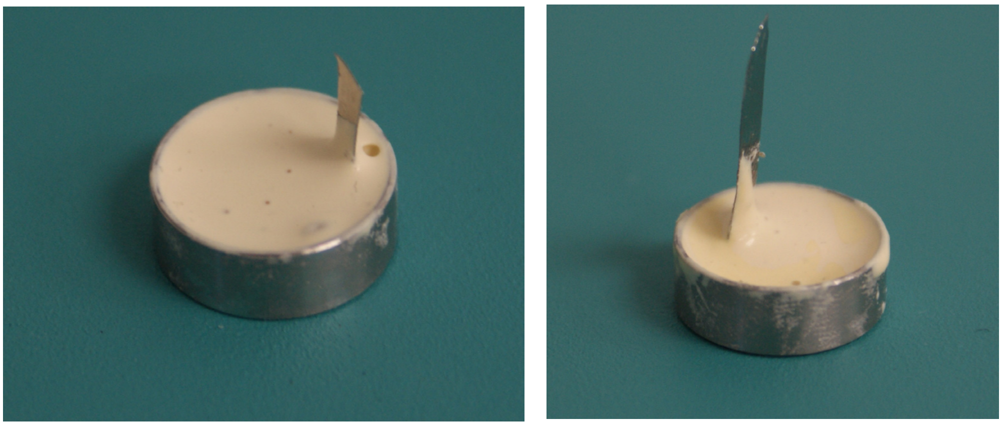


Fig. 1: Picture of supercapacitors (Cap#1.1 and Cap#1.2)

For Cap#1.1, the active material was prepared using coconut shell-based activated carbon (90%) with poly vinylidene fluoride (PVdF) polymer powder (10%). In the case of Cap#1.2, 15% of binder was used. Isopropanol was added to the mixed powders as mixing and solvent solutions. The slurry was then mixed using a mechanical stirrer for 1 hr, and this was followed by an ultrasonic mixing for 30 minutes.

For both samples, the slurry was dried in a vacuum oven at 100^{o}C to remove all the isopropanol. The dried powder was then used to fabricate the supercapacitor electrode active material. The active material (AC) was pressed using hydraulic press with a die set (13 mm) at 3 tones to form coin-shape electrodes. After that, the two coin-shaped electrodes were sandwiched between the stainless steel mesh current collectors and were separated by porous membrane to allow the transfer of ions through the electrolytes and prevent these electrodes from short circuiting. Later, the electrodes were placed in a can-shaped casing and the whole set was dried again in the vacuum oven for 1hr. One mole KCL solution was impregnated into the pores of the electrodes as electrolyte, and then the set was pressed. An epoxy was used to seal the supercapacitor to prevent the electrolyte from evaporating. The casing and the current collectors mesh were made from stainless steel. *Fig. 2* shows the dimensions of both prototypes. The dimensions of the electrode are as shown.

Current collector mesh thickness = 0.1mm
Electrode diameter = 13mm

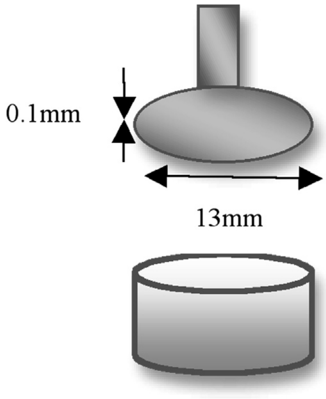


Fig. 2: Dimension of Cap#1

Supercapacitor Cap#2

Three prototypes of flat-shaped supercapacitor were fabricated using coconut shell-based activated carbon. The electrolyte used in this supercapacitor was aqueous (KCl, 1M). *Fig. 3* depicts the three prototypes of Cap#2.

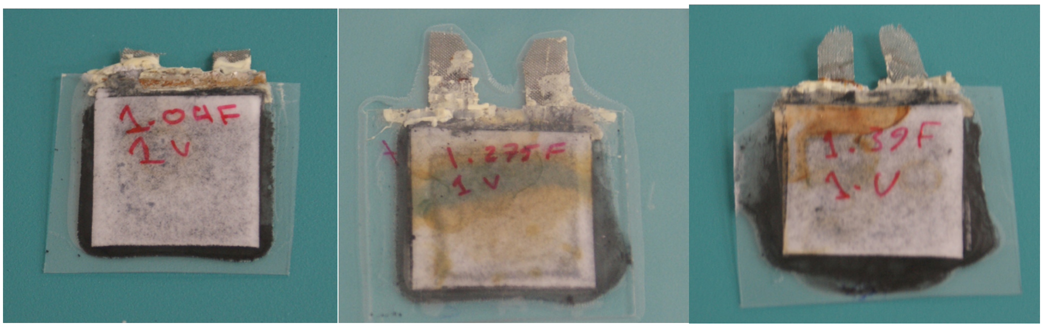


Fig. 3: Supercapacitors (Cap#2.1, Cap#2.2, and Cap#2.3)

As for the previous supercapacitors, the active material used was the coconut shell-based activated carbon mixed with poly vinylidene fluoride (PVdF) polymer powder in the percentages of 10, 15, and 20%. Isopropanol was added to all the samples as solvent and mixing agent. Then, the slurry was mechanically mixed using the mechanical stirrer for 1 hr, followed by an ultrasonic mixing for 30 minutes.

After mixing, the slurry was heated to remove some of the isopropanol solutions and to make thicker slurry. Then, the slurry was spread on the stainless steel mesh current collector to make sure a uniform layer of the AC was achieved. The set of electrodes was then dried in a vacuum oven for 2 hr. Every set of two electrodes is sandwiched together and separated by a porous membrane which allows the transfer of ions and prevents the electrodes from short circuiting. The electrodes were laminated and the whole set was dried again in a vacuum oven for 1 hr and 1M of KCL was used as electrolyte for this capacitor. Later, the supercapacitors were laminated and sealed to prevent the electrolytes from evaporating. The dimensions of the electrodes are shown in *Fig. 4* below.

Current collector mesh thickness = 0.1 mm
Electrode dimensions = 2x2 cm

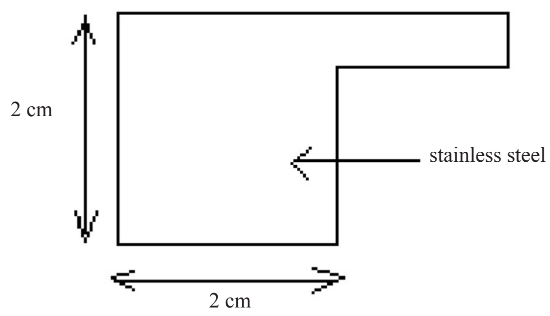


Fig. 4: Dimensions of the supercapacitor (Cap#2)

RESULTS AND DISCUSSION

Cyclic Voltammetry

Cyclic voltammetry (CV) of the unit cells was measured at the scan rate of 10mV/s. *Fig. 5* shows the CV of the (Cap#1.1 and Cap#1.2) supercapacitors.

As it can be seen from the CV in *Fig. 5*, both the cells show capacitor behaviour. According to the principal, specific capacitance keeps a direct ratio with specific current at the same scan rate [22], while Cap#1.1 shows a bigger specific capacitance which that can be attributed to the less percentage of binder (10%) used in this supercapacitor than in Cap#1.2. The more binder is used, the more blockages of the porous of the activated carbon, indicating less usable porous surface area accessible by the electrolyte that leads to less specific capacitance.

Cap#1.2, on the other hand, shows a more ideal rectangular capacitor behaviour which is more close to ideal capacitor CV (rectangular). Table 2 illustrates the specific capacitance and the ESR for both the prototypes. The capacitance measurements were confirmed by CV, charge-discharge curve and EIS measurements, and all the results are closely matched. The equivalent series resistance (ESR) was measured from the drop in the charge-discharge curve.

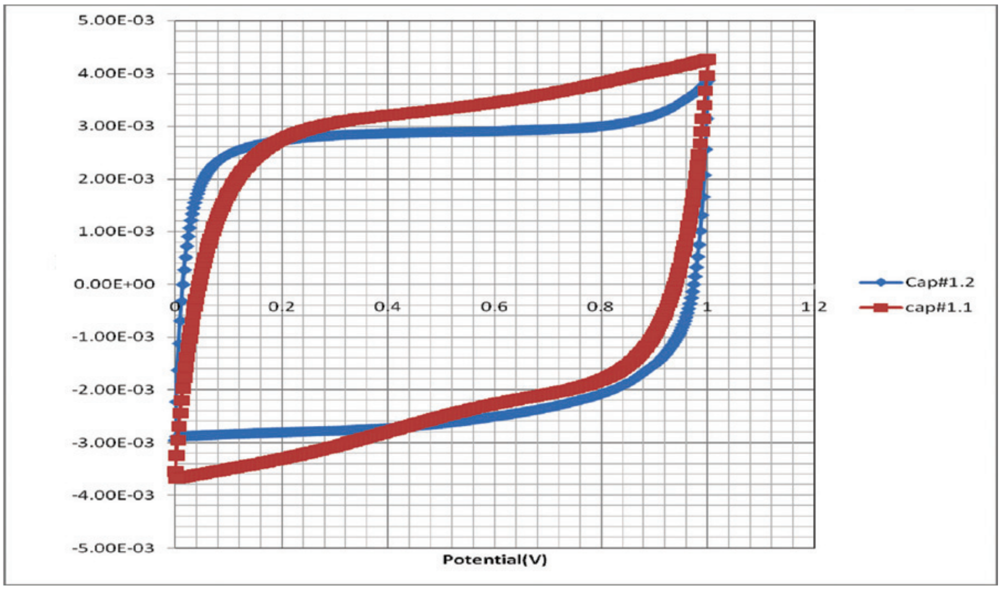


Fig. 5: CV measurement for the supercapacitors (Caps#1.1 and #1.2)

TABLE 2
Specific capacitance and ESR results for Supercapacitor, Cap#1

	Cap#1.1	Cap#1.2
Specific capacitance (F/g)	70F/g	56F/g
ESR (Ohms)	16.5	14.3

In the case of supercapacitor Cap#2 and its variations, namely Cap#2.1 (10%PVdF), Cap#2.2 (15%PVdF) and Cap#2.3 (20%PVdF), *Fig. 6* shows the CV characteristic (Autolab AUT83475) which was used to perform the measurements in this study. The CV was measured at (5mV/s) and it was confirmed that all the cells showed the characteristics of a capacitor. Cap#2.1 shows the most ideal capacitor behaviour, but the Cap#2.3 reveals the highest specific capacitance.

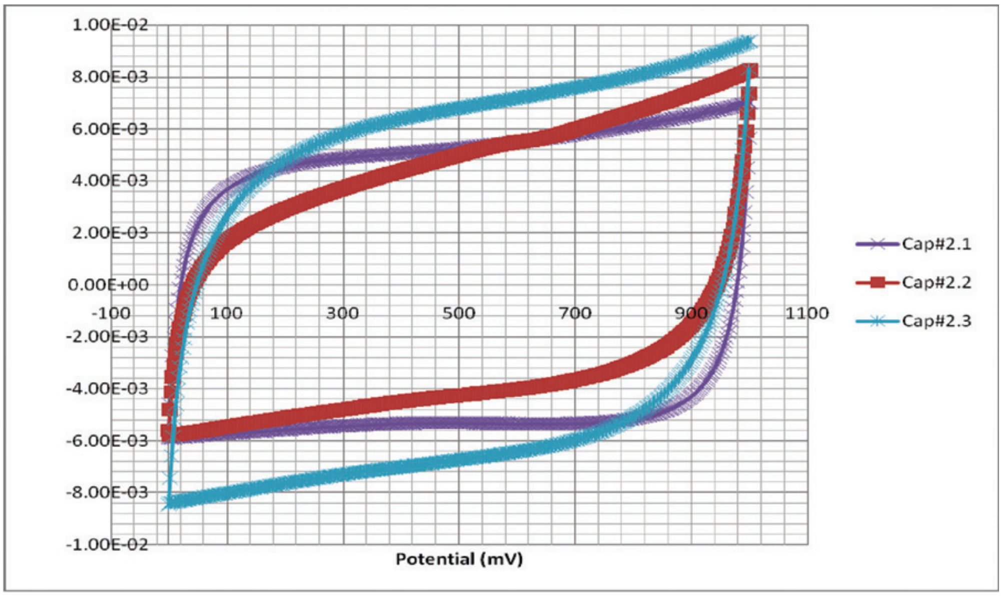


Fig. 6: CV measurements for the flat-laminated supercapacitors (Cap#2.1, Cap#2.2, and Cap#2.3)

TABLE 3
ESR and the specific capacitance of supercapacitors: cap#2.1-2.3

Supercapacitor	Equivalent Series Resistances ESR (Ω)	Specific Capacitance (F/g)
Cap#2.1 %10 PVdF	10.1	40
Cap#2.2 %15 PVdF	11	32.7
Cap#2.3 %20 PVdF	22	44

Table 3 shows the specific capacitance and the ESR measurement for Cap#2.1, Cap#2.2, and Cap#2.3. The capacitance was measured using Autolab AUT83475; by measuring the charge on the capacitor (Q area under the curve) and knowing the voltage applied, the capacitance was calculated using the following equation (Eq1) (Marin, Halper and Ellenbogen, 2006):

$$C = \frac{Q}{V} \qquad \text{(Eq. 1)}$$

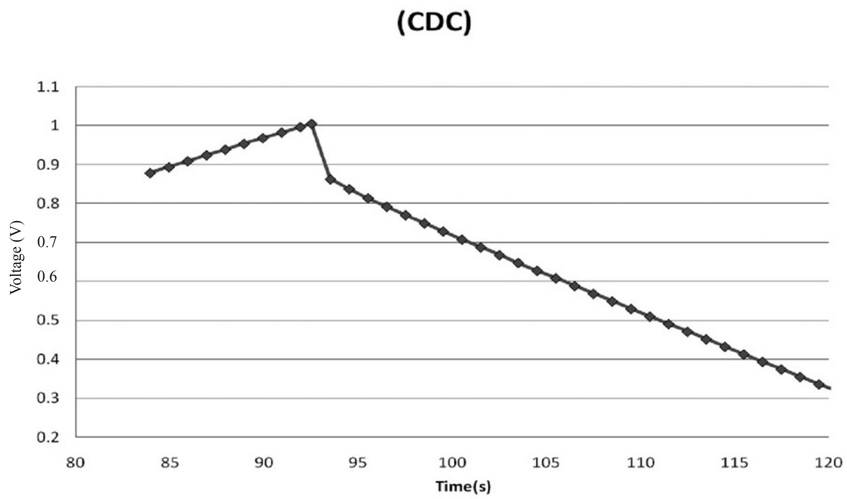
The ESR was measured from the drop in the discharge curve at the beginning of discharge, using Eq2. [24]

$$V = ixR \qquad \text{(Eq. 2)}$$

where;

V = voltage drop (V)
i = current = 15mA
R = ESR

The trend for the specific capacitance depicted in Table 3 might be due to two reasons: the variance in the pressure used to register the two capacitor electrodes together and the inconsistency of the activated carbon particle size used in the three samples. *Fig. 7* shows the voltage drop in the charge-discharge curve used to measure the ESR for all the supercapacitors. Eq. 2 was used to calculate the ESR and the values are listed in Table 3.



V)

Fig.7: Measuring ESR from the voltage drop in charge-discharge curve Cap#2.1

The measured ESR (Table 3) was found to be bigger than the ones reported (in the range of few ohms) (Kyong-Min Kima, Jin-Woo Hura, Se-Il Junga and An-Soo Kanga, 2004). The authors attributed that to the low conductivity of the coconut shell-based activated carbon, and the lack of any conducting additives (carbon black) to lower the resistance of the active material (AC).

EIS Testing

EIS (Electrochemical Impedance Spectroscopy) testing is an effective method to measure and analyze the parameters of supercapacitors. In this study, a sinusoidal voltage was applied to the supercapacitor at a well-defined frequency range. The amplitude and phase of the voltage were recorded when the signal swept though the range repeatedly and the Nyquist curve was plotted to get the equivalent impedance of the supercapacitor (Namisnyk, 2003; Mullet, 1999).

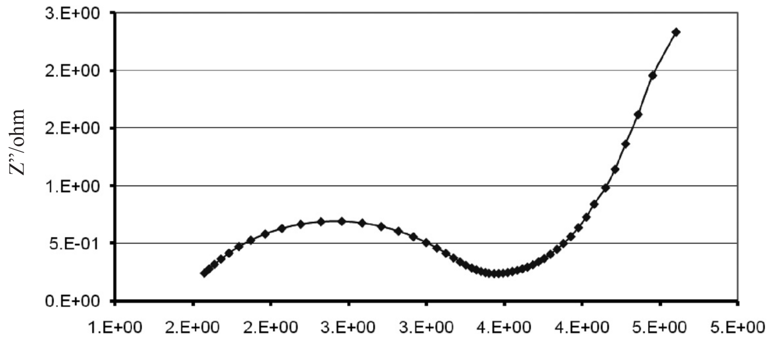


Fig. 8: EIS measurement for Cap#2.1

Fig. 8 shows the Nyquist curve for Cap#2.1. At high frequencies, the imaginary part of the impedance tends to become zero and the resistance measured is related to the ionic resistance of the electrolyte. In the range of medium frequencies, a semi-circle is associated with the resistance of porous structure of the electrodes (Mullet, 1999) with the current collector (Nian and Teng, 2003).

Typical complex plane plots for Cap#1.1 and Cap#1.2 are presented in *Fig. 9*. The double-layer charging, charge-transfer resistance and diffusion-controlled kinetics are all well-separated in the plots. The charge-transfer process, at the electrodes-electrolyte interface, is determined by the semi-circle at high frequencies and the 45^o angled straight line represents the diffusion-controlled electrode kinetics at lower frequencies.

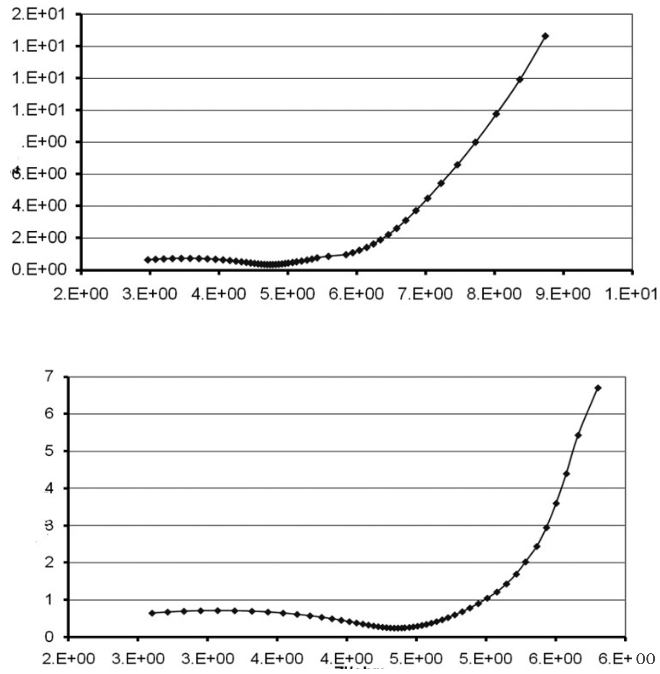


Fig. 9: EIS measurements for the supercapacitors (Cap#1.1 and Cap#1.2)

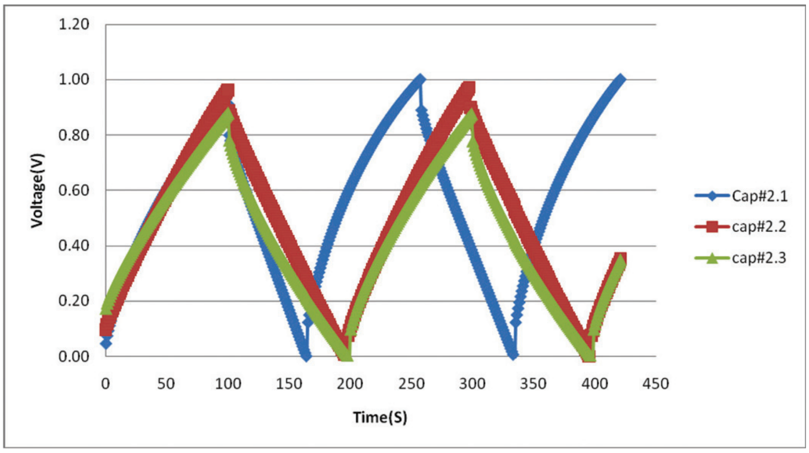


Fig. 10: Charge-discharge curves for the supercapacitors (20mA); Cap#2.1, Cap#2.2, and Cap#2.3

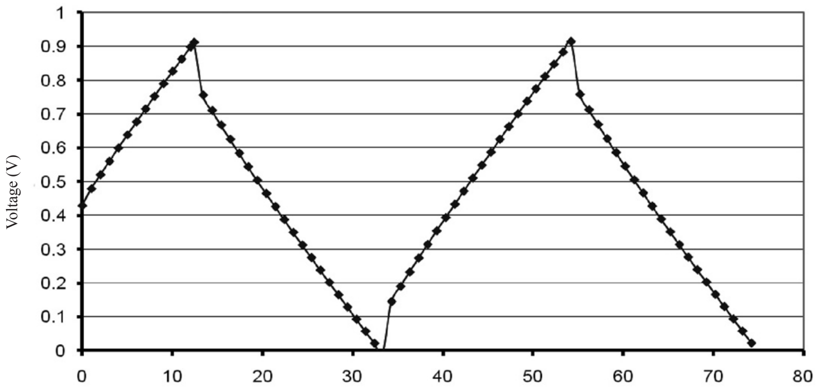


Fig. 11: Constant current (10mA) charge-discharge for Cap#1.2

Fig. 9 shows the EIS measurement for Cap#1.1 and Cap# 1.2 using the (Autolab). The capacitance measurements from EIS (0.2399F) and CV (0.24F) were found to be very close in value.

Charge-Discharge Measurements

The capacity of the supercapacitors was also obtained from the charge-discharge measurement curve to confirm the measurement by CV. The constant current charge-discharge measurements in this research were mainly used to measure the ESR for the supercapacitor. The values of the ESR for all the manufactured supercapacitor were reported earlier in Tables 1 and 2. *Fig. 10* shows the comparison between the charge-discharge characteristics of Cap#2.1, Cap#2.2, and Cap#2.3 at the same constant current (20mA).

From the charge-discharge curve, it is clear that Cap#2.1 (i.e. with the lowest ESR value) is charging and discharging the fastest in the group, and this can be attributed to the lower resistance of the activated carbon because of low binder percentage used in this supercapacitor.

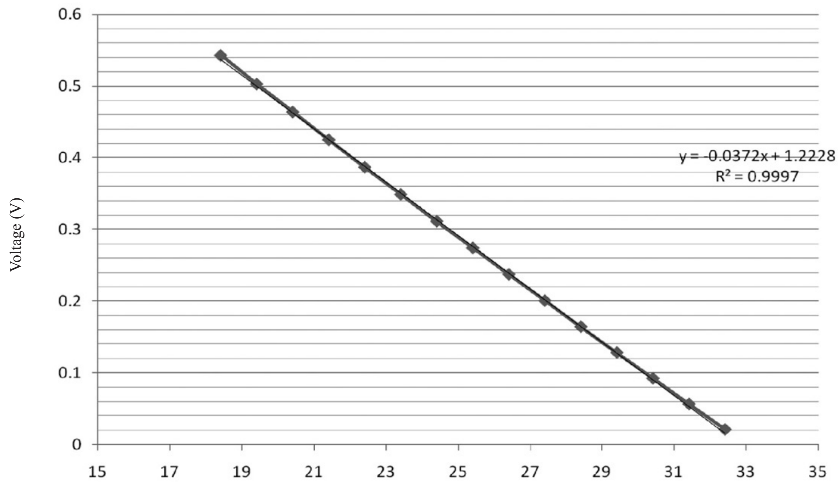


Fig. 12: Measuring the capacitance from the charge-discharge curve Cap#1.2

The constant current charge-discharge characteristics for the Supercapacitor Cap#1.2 are shown in *Fig. 11*. The curve shows the behaviour of supercapacitor charge-discharge characteristics. The constant charging current is 10mA. The voltage drop in the curve, at the beginning of the discharge curve, was used to calculate the ESR, according to Eq 2, while the slope of the straight line was used to confirm the capacitance measurement of the supercapacitor.

Fig. 12 shows a part of the discharge curve that was used to calculate the capacitance for the Cap#1.2. The capacitance was calculated using the following equation:

$$C = i/Slope \qquad \text{(Eq. 3)}$$

where,

C is the capacitance of the supercapacitor;
i is the constant charging or discharging current;
Slope is the slope of the discharge line.

In this case, the discharging current was 10mA while the slope (*Fig. 12*) is 0.0372. Using Eq. 3, the capacitance was found to be 0.268F, and the capacitance calculated from the CV was found to be 0.25F.

CONCLUSIONS

Coconut shell-based activated carbon is a good choice for supercapacitor electrode active material compared to the more expensive AC and CNT. In this study, Autolab (AUT83475) was used for all the measurements and all the materials were used without any further purification. The best composition for the electrodes material was found to be 90% coconut shell-based activated carbon and 10% binder, which KCL was employed as electrolyte to give the highest specific capacitance 70F/g at 5mV/s (Cap#1.1). The capacitance measurements were confirmed by CV, EIS, and charge-discharge characteristics and all the results were in close proximity. Meanwhile, the aqueous electrolyte limited the maximum supercapacitor voltage to 1V.

The ESR was calculated from the voltage drop at the beginning of the discharge cycle, and the smallest value was 10.1 Ohms, which was found in the supercapacitor with the lowest binder percentage of 10% (Cap#2.1). The ESR value was somewhat high, and this could be attributed to the low electrical conductivity of the coconut activated carbon. This could be reduced by adding some conductive additives (carbon black).

ACKNOWLEDGEMENTS

The work described in this paper was supported by the Malaysian Minister of Science, Technology and Innovation (MOSTI TechnoFund). The authors wish to acknowledge the assistance of Sahz Holdings Sdn Bhd.

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