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Performance of Biocarbon Based Electrodes for Electrochemical Capacitor

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Abstract

We examined bio-carbon electrodes-based electrochemical capacitor. The electrodes were produced from gelam wood activated carbon. Six types of carbon electrodes in separator – electrodes assemblies were tested using galvanostatic charging – discharging (GCD) and electrochemical impedance spectroscopy (EIS) instrumentation. Eight types of aqueous solution from acid, base and salt were used as electrolytes. Three of six electrodes were prepared from carbon pelletsand others were prepared from powdered carbons. Carbon pellets were shaped and sized into electrode monoliths, and therefore those pellets were becoming binder-less. The powdered carbon were compacted along with binder and surfactant into 20 mm in diameter electrodes. The GCD and EIS measurements clearly indicated that both binderless and binderized carbon electrodes (CE) in electrochemical capacitor (EC) have 0.01 – 28 Fg-1 and 0.001 – 2.8 Fg-1 of specific capacitance, respectively. Performance tests of EC measured with EIS and GCD methods respectively have 0.001 – 0.15 F and 0.001 – 0.203 F of capacitance.

*Keywords:*gelam wood; electrochemical capacitors;carbon electrodes; galvanostatic charging-discharging; electrochemical impedance spectroscopy

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1. Introduction

Activated carbon is a porous material which has high surface area and exhibits good adsorptive capacities [1]. It can classified into sustainable material because it reuses the byproduct of pyrolysis process of biomass, including forest residues such as bark, sawdust, shavings [2, 3]. It is nontoxic [4] and will not harm soil when it is disposed. Organic-based carbonaceous materials or biochar are amongst the most widely used as starting or precursor materials for electrodes [5, 6] because they are relatively inexpensive

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[7] and easy to fabricate. The biochar electrodes can be used in a wide array of energy-needing things, like hybrid car batteries or home solar panels. The demand for clean, sustainable energy sources is very high. The facts are biocarbon is cheap and its availability, make the perfect substitute for polymer-based carbon electrodes in supercapacitors.

2. Experimental

Carbon electrodes (CE) were placed in the separator – electrodes assembly that consists of two pieces of 20 mm diameter carbon electrode, a thin plate of metal titanium as current collectors, separator material i.e. Polytetrafluoroethylene (PTFE) - glass fabric with a thickness of 0.8 mm, the applicator was made of stainless steel rods. The houses were made of PTFE cylinder. The EC was made by covering a separator material with carbon electrodes on both sides and flanked by current collector plates as illustrated in Figure 1.

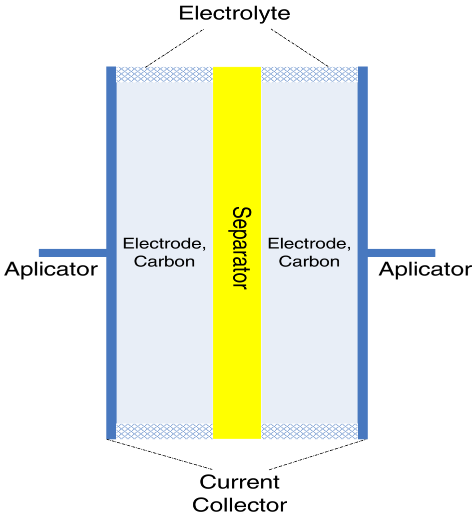


Fig.1 The structure of electrochemical capacitor

ECs were tested on two different systems, i.e. galvanostatic charging-discharging and electrochemical impedance spectroscopy. The two measurement systems will yield information relevant to the performance of CE, the specific capacitance, potential window, charging-discharging stability, life time, and electrical resistance.

3. Results

3.1. Electrochemical Impedance Spectroscopy Profiles

Electrochemical impedance spectroscopy (EIS) was used not just to study CE's performance but also to determine the resistance and electrode capacitance of all components that built EC, in response to frequency. One of many factors that affects the stability of voltage in EC is electrolyte[8]. This factor makes performance and life cycles limitation in ECs.

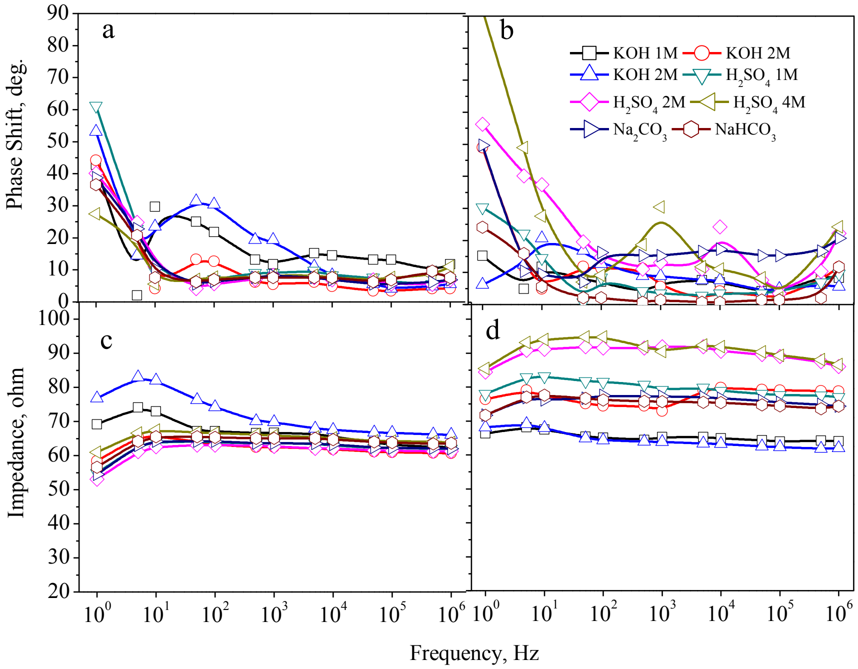


Fig. 2 Bode plot (phase shift and impedance) of EC using binderless electrode (a and c), binderized electrode (b and d) and electrolyte H_2SO_4, KOH, Na_2CO_3 and $NaHCO_3$

Phase shifts of two ECs in various frequencies are given in Fig. 2 a – b. The results show capacitance values ECs drastically reduced when operated at high frequencies. At low frequencies most ECs show the phase shift relatively close to 90. It can be said that the EC works relatively ideal as supercapacitor at low frequencies [9]. The results are shown in Fig. 2c – d. Both types of ECs have relatively the same impedance ranging from 50 – 100 ohm. EC with binderized CE shows reduction in impedance value lower than 10Hz and inversely no changing in higher than 10 Hz. The differences of impedance response on each of ECs came up from the differences in conductivity, mobility of cations and anions, as well as the size of hydrated ion electrolyte [10].

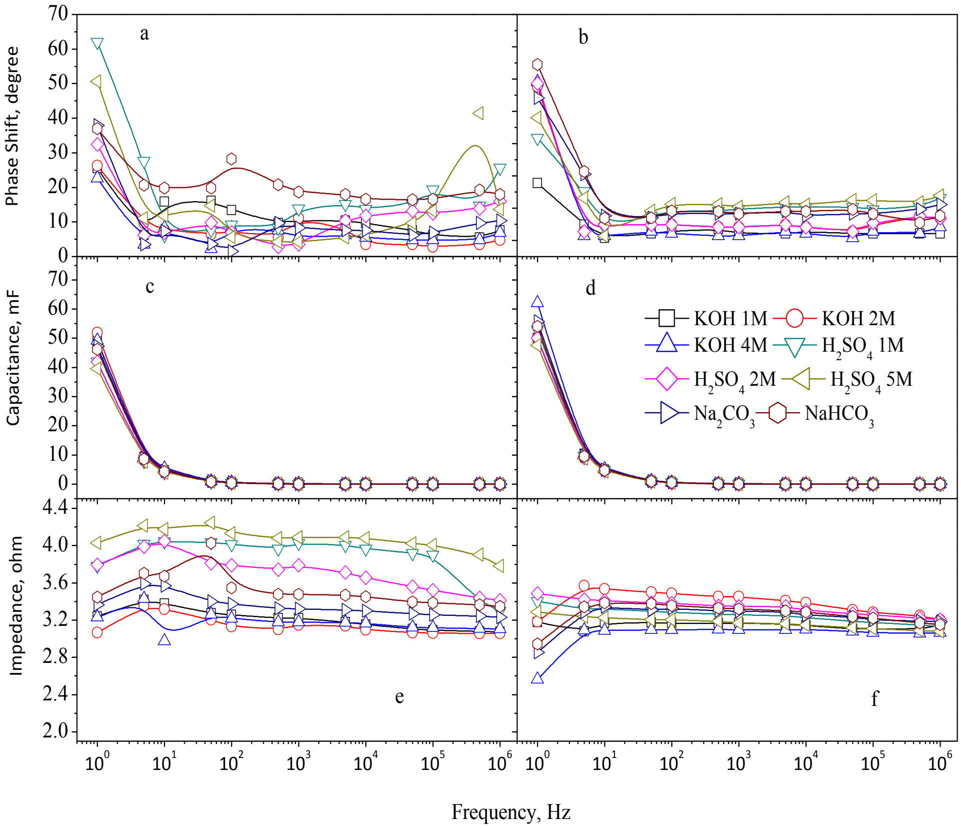


Fig. 3 Bode plot (phase shift, capacitance and impedance) of ECs using PTFE (a, c and e), epoxy resin (b, d and f) as CE binder and electrolyte H_2SO_4, KOH, Na_2CO_3 and $NaHCO_3$

The presence of binder that affects the mobility of ion in the electrode matrices has been reported by several researchers [11, 12]. Fig. 3 (a – f) give the ideas of the mobility that affects the performance of ECs. It can be shown in Fig. 3 that the use of epoxy resin as binder in carbon electrode relatively more stable in impedance compared with the electrode with PTFE. Furthermore, capacitance values can be calculated using impedance – frequency relationship in equation (1).

$$C = \frac{1}{\log(Z)\, 2\pi f} \qquad (1)$$

The application of higher frequencies to ECs only slightly affects the capacitance in Fig. 3 (c and d), i.e. 0.01mF – 10 mF. At low frequencies, the capacitance of ECs with epoxy resin binding electrodes (60mF) is relatively higher than CEs with PTFE (50mF) binding electrodes, but it is lower than the binderless CEs, i.e. 150mF (not shown).

3.2. Galvanostatic Charging Discharging Profiles

Galvanostatic charging – discharging (GCD) is one of the methods that widely used for examining the result of capacitance measurement which can easily connected with the load applied to the CE for an application[13]. GCD profiles in Figure 4 shows some of the characteristics associated with the application of the EC. EC with binderless electrodes in the $NaHCO_3$ (CCP/NaHCO3) electrolyte has a relatively the same height with 0.22 F curve but with area approximately ¾ times of the area of 0.22 F.

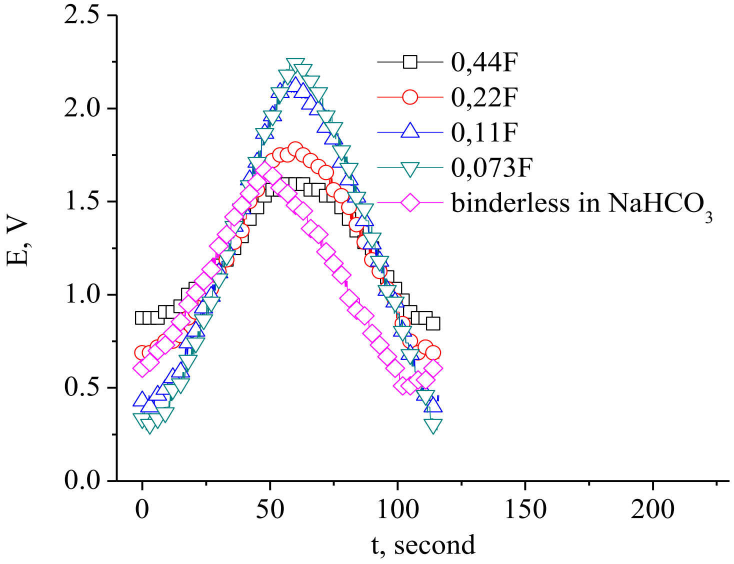


Fig. 5 Some GCD profiles of commercial CE (0.073 – 0.44F) and binderless electrode in $NaHCO_3$

More details for GCD profiles which was made in this study are shown in Fig. 6. Two benchmark profiles (Fig.6(h) and (i)) showed the relationship between capacitance with voltage measured as a function of time. Some binderless and binderized CEs (Fig.6 (d) and (e)) showed a curve that is relatively equals to the references. Some of them showed the smaller curve indicating that CEs have higher capacitance values. It can be seen that despite having the same capacitance or even larger, but CE product has relatively low working voltage (1.2V). Reference CEs have working voltages of 1.6V.

Graphical analyses were applied to quantify the capacitance of EC methods such those used by other researchers [13]. Calculating the slope of both curve in charging – discharging of ECs with binderless and binderized electrodes (Fig. 6 (d) and (e)) and reference (Fig 6 (i)) had approximately the same values. The reference EC has 0.22F of capacitance. By using the equation (2), the capacitance of CE with binderless electrode can be calculated, i.e.

$$C = \frac{i}{dV/dt} = 0.0052382/0.02604 = 0.203\ F \tag{2}$$

Two of ECs in Fig. 6 (b and c) showed relatively smaller curves indicating greater capacitance values. The others (Fig. 6(a), (f) and (g)) showed inversely.

The evolution cycles of capacitance in charging – discharging term of ECs were studied using the same approximation. The results of the capacitance binderized electrodes are shown in the Fig. 8. It can be interpreted from the slope value (Fig. 7, panel) that capacitance only decreased in the first 50 cycles, followed by increasing value of the slope approaching the initial value indicating the existence of non-linearity in both of the charging and discharging direction.The same tendencies are shown in ECs with binder-less electrodes.

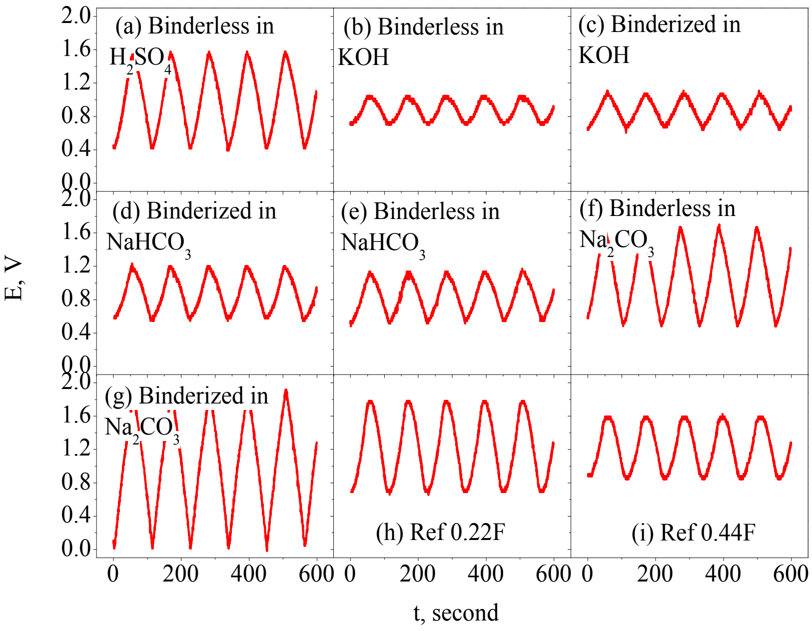
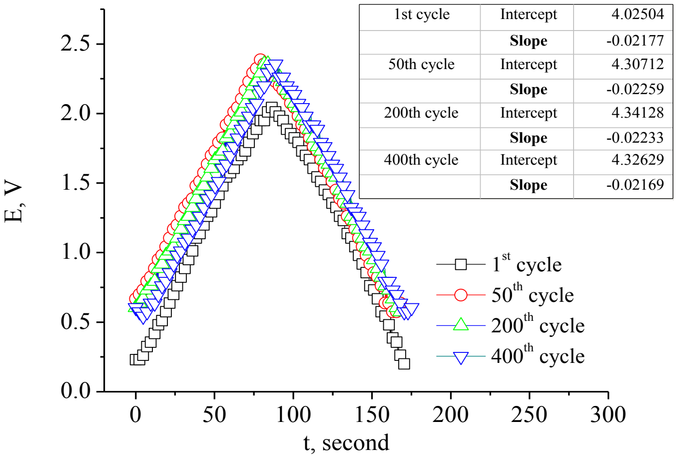


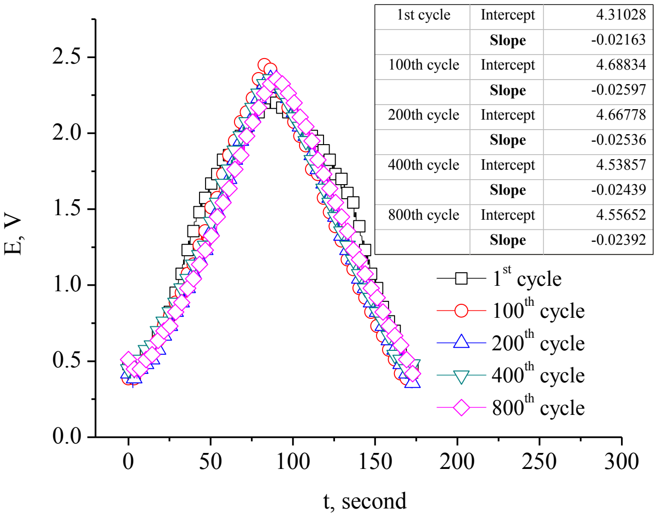
Fig. 6 GCD profiles of ECs vary with electrodes and electrolyte. Also benchmark profiles (Ref0.22F and Ref0.44F). Data was taken after fiftieth cycle of ECs charging – discharging



1st cycle	Intercept	4.02504
	Slope	-0.02177
50th cycle	Intercept	4.30712
	Slope	-0.02259
200th cycle	Intercept	4.34128
	Slope	-0.02233
400th cycle	Intercept	4.32629
	Slope	-0.02169

Fig. 7 GCD Profiles of EC with binderized electrodes in the first cycles and thereafter. In panes are intercepts and slope values from linear regression calculations

The transition at the beginning of the charging – discharging cycle occurred at the first used is shown in Figure 7 and 8. The difference between the earlier cycle and subsequent cycle is related to the distribution and arrangement of dislocations at the molecular scale [14]. An arrangement phenomenon can be detected by dilatometer as expanding and contracting of electrode matrices[15]. Electrode would inflate when electrical load was filled and shrunk when charge was drawn. Steady state will be reached after 11 or 12 cycles, and CEs will be fully worked there after.



1st cycle	Intercept	4.31028
	Slope	-0.02163
100th cycle	Intercept	4.68834
	Slope	-0.02597
200th cycle	Intercept	4.66778
	Slope	-0.02536
400th cycle	Intercept	4.53857
	Slope	-0.02439
800th cycle	Intercept	4.55652
	Slope	-0.02392

Fig. 8 GCD Profiles of EC with binderless electrodes in the first cycles and thereafter. In panes are intercepts and slope values from linear regression calculations.

Furthermore, wetting process for electrode body by water which combined with the cycle of charging – discharging will cause a reduction of internal resistance [16]. Reduced resistance causes displacement of electrons in microcrystalline much better and have impact on the increasing of the value of the capacitance.

4. Conclusion

Performance tests conducted using the EIS method gave the capacitance range from 0.01 to 0.150 F, with the highest value was obtained from ECs with binderless electrodes.The application of higher frequencies to ECs only slightly affects the capacitance, i.e. 0.001mF – 10 mF. At low frequencies, the capacitance of ECs with epoxy resin binder (60mF) is relatively higher than ECs with PTFE (50mF), but it is lower than the binderless ECs, i.e. 150mF. Performance tests conducted using the GCD method gave the capacitance range from 0.01 to 0.203 F. The highest value was obtained from ECs with binderless electrodes.

Acknowledgements

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