Optimization of Biomass-Based

By Nirwan Syarif

Optimization of Biomass-Based Electrochemical Capacitor Performance

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Abstract. The electrochemical capacitor (EC) from various carbon materials, i.e., carbon nanosheet from gelam wood, carbon nanotube from sesame oil, carbon honeycomb-like from sengon wood used as electrodes were studied, as well as the solvent used, i.e., dimethylsulphoxide, ethyleneglycol, propilene carbonate and the electrolytes, i.e., disodiumtetraboratdecahidrate (DSTB) and sodiumdietyldithiocarbaminate (SDEDTC). Their performance were optimized for three factors by using full factorial design of experiment technique. The three factors chosen for experiments were the controllable variables that have key role to play in the EC performance, i.e., carbon types applied in electrodes, organic solvent that dispersed electrolytes, and electrolytes. Types of carbon has highest effect on capacitance value and carbon from gelam wood bark has the best capacitance value. There exist strong interaction effect between type of carbon and solvent as well as between type of carbon and electrolyte contribute capacitance of ECs. Operating voltage of EC from the beginning cycle until cycle-2000 is about 1.2 to 1.4 volts, i.e., using CNS electrode with 20% SDEDTC electrolyte and DMSO as solvent.

Keywords: supercapacitor, voltammetry, galvanostatic, electrodes, full-factorial, capacitance, ESR

INTRODUCTION

Human activities and machinary are always need supply energy to proceed. Research about energy conversion and storage run simultaneously to achieve energy security. Energy storage device, such as electrochemical capacitor (EC), also known as supercapacitor must have characters, i.e., long cycle life, high efficiency, high power density an environmental friendly[1] .

Biomass based carbon materials have gained considerable attention in the last few years due to their high chemical and thermal stability, tunable pore size distribution, and high specific surface areas, which lead to become a choice in support EC manufacture [2]. The facts are biomass based carbon is cheap and its availability, make the perfect substitute for polymer-based carbon electrodes in EC [3]. However, the usage the carbons in EC are very limited because of their distinct crystallographies and morphologies or allotropes [4].

It should be noted, however, that the information comes up from the "one variable at time" (OVAT) observations do not have satisfactory. Such observations do not analyzed simultaneously and reduce a part obsevations that normally must do. This method does not count the possibility of intervariable action that affect the outcome or parameter [5]. The whole pictures of a system can be unify, by deconvulated the effects of each variable from possible variable interactions that contribute to the same observed effects [6]. Some additional observations must be provided in order to achieve good understanding of the contribution of the each variables [7].

Factorial design is the method for such situation and has been used as Design of Experiment (DOE). The three factors observation is chosen for the experiment. The controllable variables that have key role to play in the

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EC character, i.e., carbon types applied in electrodes, organic solvent that dispersed electrolytes, and electrolytes. Main effects and interaction between main effects are affecting the performance parameters, i.e. capacitance and equivalent series resistance (ESR). The novelty of this research is that biomass can be applied to electrochemical capacitor, so forth this research found a low cost material with high capacitance at low resistance (ESR).

METHODOLOGY

Preparation

Carbon nanosheet was prepared from gelam wood bark as mentioned in elsewhere [8]. Carbon nanotube was prepared by using plasma pyrolysis technique [9]. Honeycomb carbon was prepared by using hydrotermal-assisted microwave pyrolysis from sengon wood. The electrodes were made by mixing each carbons and graphite mixture (1:2), xylene based marking ink is coated on one side of aluminium sheet and is spread smoothly using coating machine. The EC is assembled using 2 electrodes and 3 sheets of dacrone as separator. Two sheets of separator are places below and above of one of film / layer electrodes. A small quantity of organic solvent (dimethyl sulphoxide (DMSO), ethylenenglicol (EG), propilene carbonate (PC)) based electrolyte was dropped between the cathode and separator and between the anode and separator. Electrolytes used are disodiumtetraborat-decahidrate (DSTB) and sodiumdietyldithio-carbaminate (SDEDTC). The anode, separators, and cathode are arranged to be compact are packaged by using winding machine, tightened and taped. EC roll is incorporated into its case and seal canned. The performance of ECs were measured by using voltammetry and galvanostatic techniques.

Performance Tests

Electrochemical properties were studied using cyclic voltammetry (CV). Electrochemical test for the electrodes were conducted in potentiostat (Cheapstat University of California Santa Barbara, CA, USA) [10]. The ESC values were derived from CV measurements. The device was then discharged potentiostatically, holding the device at 0 V for 60 s. The device was held at 0 mA for 10 seconds before galvanostatically test were proceed.

Optimization

The first task before conducting the experiments is selection of potential parameters to be varied and the factors to be addressed. Factorial experiment design to three design factors namely: 1) carbon types applied in electrodes (A), 2) organic solvent that dispersed electrolytes (B), 3) electrolytes (C). The three factors chosen for experiment are the controllable variables that have a key role to play in the performance test. ECs are evaluated based on parameters such as capacitance, ESR, operating voltage, weight, volume, shape and self discharge and so forth. However capacitance and ESR value are most significant parameters.

The levels of each factors are given in the Table 1. Since we have three factors to be considered, the experiment design is called a 18 full factorial design, each with combinations of the three factors across three or two levels of each. According to the general statistical approach for experimental design four replicates were obtained to get a reliable and precise estimate of the effects. Some observations were taken in all to employ full factorial design as shown in Table 2. The experiment was assumed that the factor is fixed. The design was completely randomized and the usual normality assumptions of the data were satisfied.

Interaction and main effects plot are obtained to examine effects of factors on parameter. Minitab provides two or more levels in full of fractional factorial designs, Plackett-Burman designs, and full factorials for designs with more than two levels. For n factors and p levels p n trials are required to be carried out. For linear parameter variation p can be taken as 2 and to reduce the complexity, n is taken as 3. The usage of three level DOE can be considered if there is a non-linierity in the system [11].

RESULTS AND DISCUSSION

Effects Of Carbon Types, Organic Solvent And Electrolytes On Capacitance

Capacitive performances of the EC have been found to depend not only on performance of electrode but also on other factors such as electrolyte. Specific surface area of the carbon material in electrode and accessible surface area of the electrode are related [12]. Both factors have important role in deciding value of the charge stored and hence the capacitance. It can be shown in Fig. 1 (a) that types of carbon has highest effect on capacitance value and carbon from gelam wood bark (CNS) has capacitance value. Previous research suggests that CNS has highest surface area compare to the two others. The electrolyte and solvent also plays role in contributing capacitance of the EC. It affects the ionic conduction capability of electrolyte and hence it also affects the capacitance value. Carbons with large micropores as in CNS are found to be more suitable for this application since their size fit with ionic size of electrolytes.

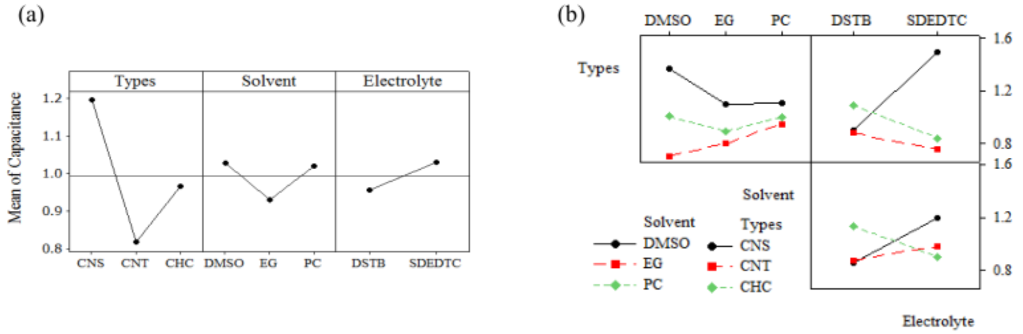

FIGURE 1. Main effect (a) and interfactor effects (b) the analyses on capacitance

The ion can be entered more deeper and readily interact with the surface of carbon. Pore size of CNSs are found dominating with micropore [8]. The pores non-accessible to the electrolyte do not contribute to the capacitance [13].

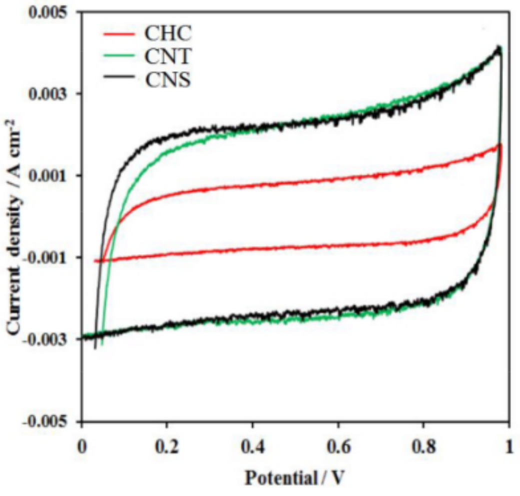

FIGURE 2. Voltammogram of three type of carbons using electrolyte SDEDTC in DMSO

The optimum pore size will be dependent on the size of the electrolyte used [14]. Therefore, electrolyte is one of the major parameter which affects the value of capacitance as it changes the charge storing capacity of the electrode.

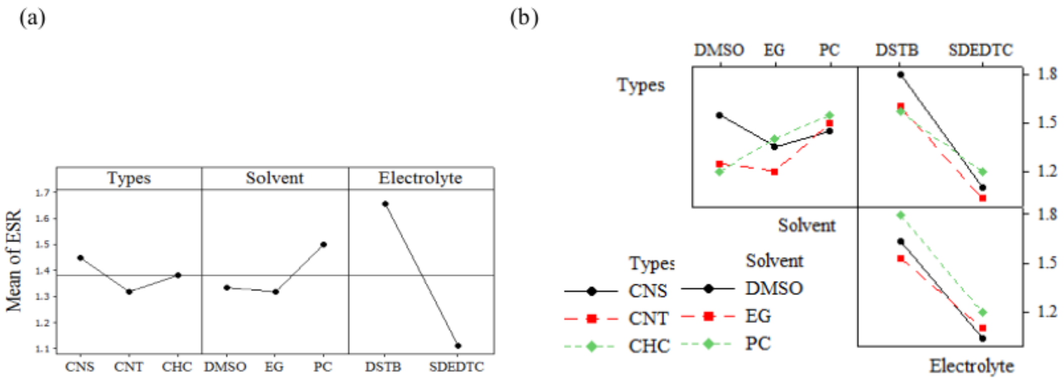

FIGURE 3. Main effect (a) and (b) interfactor effects analyses on ESR

Voltammogram in Fig. 2 confirm this feature. SDEDTC act as electrolyte has more effect on capacitance. DMSO slightly has more effect on capacitance compare to the others. Interaction effects in Fig. 1 (b) show that the factors have more less the same magnitude to main effect contributing capacitance of EC. These plots show that there exist a strong interaction effect between type of carbon and solvent as well as between type of carbon and electrolyte contribute capacitance of ECs. It is clearly reflected in the main and interaction plots that the strength of the electrolyte has less role in this scheme.

It can be shown in Fig. 3 (a) that electrolyte has highest effect on ESR value followed by solvent and types of carbon. Interaction effects in Fig. 3 (b) show that the factors have more less the same magnitude to main effect contributing ESR value of EC. These plots show that there exist a strong interaction effect between type of carbon and electrolyte as well as between solvent and electrolyte.

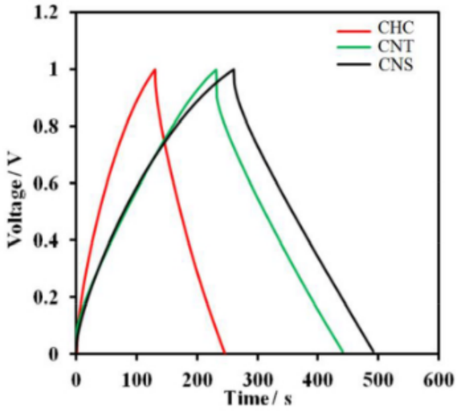

FIGURE 4. Galvanostatic charging discharging profiles of three types of carbons

Effects of Carbon Types, Organic Solvent and Electrolytes on Equivalent Series Resistance

The selection of electrode and electrolyte materials strongly reflects the electrode conductivity and hence the value of equivalent series resistance (ESR) of the ECs is low. Since the power density of the ECs depends on the ESR, the choice of electrolyte should be optimised to suit the electrode materials. In other words, the best selection for electrode pore size will subject to the size of the ion in the electrolyte materials.

The calculation of ESR usually involves the process of charging and discharging a capacitor to its rated voltage over a substantial period of time. Since this empirical study involves only a short time of charging and discharging up to only few minutes, the ESR can be disregarded due to its large time constant of capacitance. Thus, the equivalent circuit in this paper is assumed to comprise of only the capacitance and its ESR, which can be calculated based on the change in voltage, ΔV with respect to its current, ΔI d

The value of ESR varies according to the operating temperature of an EC [15]. As the operating temperature affects the breakdown voltage of the terminals and the porosity of carbon materials on the electrodes, the choice of electrolyte and solvent are also essential for the EC.The response of the capacitor voltage to the consecutive charge and discharge cycles for the three types of carbon are measured and plotted against time, as shown in Fig. 4. It can be shown that there is slightly change in ESR regarding the type of carbons. These profiles confirm full factorial analysis of DOE in Fig. 3 (A).

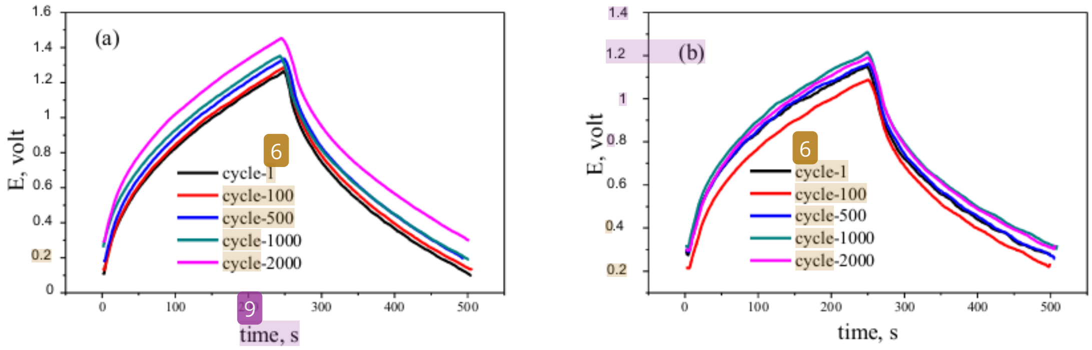

FIGURE 5. GCD Profile of EC in some cycles using SDEDTC (a) and DSTB (b) in DMSO

In order to study the influence of ESR and hence electrode porosity on the charge rate of the EC, the measured voltage for the charge and discharge cycles is re-plotted with charge against time, as shown in Fig. 5 (a) and Fig. 5 (b). There is a slightly change in ESR for thereafter cycles both by using SDEDTC and DSTB. In overall, operating voltage of EC from the beginning cycle until cycle-2000 is about 1.2 to 1.4 volts, i.e., using CNS electrode with 20% SDEDTC electrolyte and DMSO as solvent. Based on mathematical relationships C = Q/V, where the value of capacitance (C) inversely related to voltage (V). Therefore, if EC has higher voltage read then the value of capacitance should be lower. It is assumed that the number of charge stored (Q) in electrode remained the same.

The GCD profile shows that the process of electrical storage in EC could take place after initial use (cycle-1) and the charging discharging stabilization has been faster. It is characterized by the respective tight cycle curves. Transition at the beginning of the cycle always occurs on the first cycle EC was used. The difference between the initial cycle and cycles thereafter due to the regulation of distribution and dislocation at the molecular scale [16]. The reduced resistance caused the displacement of electrons to be better and have an impact on the increase in the capacitance value. Other studies have reported that the presence of micropores on the electrode greatly affect the electrolyte resistivity than the pore meso [18]. The use of electrolyte SDEDTC practically better than the use of electrolyte DSTB in terms of improving and stabilizing the charge. It is characterized by the shape and size of the same curve in the profile GCD of ECs which use electrolyte SDEDTC (Fig. 5 (a)), but there was an increase in voltage compared with GCD for DSTB profile (Fig. 5 (b)).

CONCLUSIONS

The types of carbon has highest effect on capacitance value while carbon from gelam wood bark (CNS) has capacitance value as well as equivalent series resistance (ESR). Types of carbon has highest effect on capacitance value and carbon from gelam wood bark (CNS) has the best capacitance value. There exist a strong interaction effect between type of carbon and solvent as well as between type of carbon and electrolyte contribute capacitance of ECs. Electrolyte factor has highest effect on ESR value, followed by solvent and types of carbon. operating voltage of EC from the beginning cycle until cycle-2000 is about 1.2 to 1.4 volts, i.e., using CNS electrode with 20% SDEDTC electrolyte and DMSO as solvent. The GCD profile shows that the process of electrical storage in EC could take place after initial use and the charging discharging stabilization has been faster.

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