Binder-Free Locally Developed Activated Carbon Powder Based Electrode for Supercapacitor

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Abstract: Nowadays, new technologies try to generate more energy to satisfy the demand of electricity. Therefore, storage of generated energy is becoming a highly important task. It is well known that the supercapacitors and batteries play a major role in the field of energy storage. When considering those options for storage electricity, supercapacitors were able to replace most of the capabilities encompassed in batteries and conventional capacitors with high energy density and the power density. In this research article, fabricating a novel supercapacitor using local coconut shell charcoal was discussed. It was focused on improving its performances without using a binder compound while keeping the fabrication process simple and inexpensive. Activated carbon powder used to fabricate the supercapacitor in this research was made from local coconut shell charcoal which was activated using steam activation method. The electrodes were fabricated as an electrode slurry made of activated carbon powder mixed with potassium hydroxide (KOH). It is found that the highest specific capacitance could obtain from the supercapacitor was 137 F/g. Charge-discharge curve indicated a power density of 42.6 Wkg^{-1} and energy density of 14.58 $Whkg^{-1}$ which was a remarkable improvement for a supercapacitor fabricated without a binder compound.

Keywords: Activated carbon powder, Aqueous electrolyte, Cyclic Voltammetry, Electrochemical impedance, Supercapacitors.

I. Introduction

Supercapacitors, also known as ultra-capacitors are the modern-day static electricity storage devices which have been developed based on the formation of the electric double layer (EDL) at electrode / electrolyte interface. They are different form conventional capacitors due to their ability of holding a much greater charge. The concept that charges can be separated and stored at the interface between a conductor and liquid electrolyte was discovered by Non-Helmholtz [1], Gouy [2], Chapman [3] and Stern. Unlike conventional capacitor in strong and concentrated electrolyte solutions, the distance between the charges of the opposite sign across the electrode / electrolyte interface can be in the range of angstroms therefore, high specific capacitance can be generated by choosing a suitable high surface area electrode material. So, Electrodes play a key role in defining the capacitance of the supercapacitor. As a result, research to improve its performance has been dramatically increased. Electrode material for double layer supercapacitors are generally carbonaceous materials such as activated carbon, mesoporous carbon, carbon nanotubes and graphene. In pseudo-supercapacitors electrode materials are transition metal oxide and conducting polymers.

In this experiment, electrodes were fabricated by using activated carbon powder and the main reason to use active carbon is to increase its surface area. Very fine pores on the activated carbon surface greatly increase the surface area of the electrode. As the electrode surface area is directly proportional to the amount of this concept leads the supercapacitor to achieve very high capacitance than the usual [4]. Apart from the ability to store more charge, low manufacturing cost, abundance, controllable morphology, and high electrical conductivity are ideal characteristic in active carbon that makes it one of most suitable material which is to be used to fabricate supercapacitors.

In supercapacitor capacitance is describing term a specific capacitance. Farad per gram (F/g) is used to measure specific capacitance. Unlike conventional capacitors, in supercapacitors the capacitance is determined by the thickness of the separator. Electrical double layer capacitor’s capacitance is determined by the thickness of the double layer is much smaller than that of the separator, indicating that EDLC must have a much higher capacitance than that of conventional capacitor [5]. In supercapacitor electrolytes directly affects the cell’s operational voltage window and its resistance. In aqueous electrolyte voltage window is 1 V, Organic electrolyte 2.5 - 4 V [6]. Energy density is proportional to the square of the voltage window, while the ionic resistivity is inversely proportional to the cell’s power capability [7].

Supercapacitor electrodes were fabricated by using activated carbon. Therefore, activated carbon is prepared by steam activation method. Also, a newly modified design was used to assemble a supercapacitor. After the manufactured supercapacitor, characteristics were done by cyclic voltammetry, chronopotentiometry and electrochemical impedance analysis. All electrochemical tests were carried out on a PGSTAT-128N Autolab potentiostat (Metrohm) with a two-electrode configuration.

II. Experimental

A. Preparation of Activated Carbon (AC)

Coconut shells were selected in a way that average size of a pieces of shells were nearly 2×2 cm. They were well cleaned by washing with de-ionized water several times. Afterwards, they were slowly burnt in air to obtain charcoal. Thereafter, freshly prepared charcoal was places in a sealed container to avoid absorption of water vapor until its temperature turned down to room temperature. Flow of steam was applied to the cooled charcoal afterwards and let it activate with steam for about 2 hours. It was vacuumed to get rid of the water vapors with the charcoal in the container. Once more, it was kept in the same chamber until it's cooled down to room temperature. Finally, Activate Carbon was grinded to its powder form by using Planetary PULVERISETTE 7 Fritsch. The particle size of the Activated Carbon was measured by particle size analyzer (Fritsch NanoTech PLUS ANALYSETTE22).

B. Preparation of Electrolyte

Potassium hydroxide (Sigma-Aldrich) 5.11 g was measured by electronic balance (OHAUS-PA413) then added 20 ml deionized water. 1 M potassium hydroxide solution was prepared as an electrolyte.

C. Fabrication of Supercapacitor

Stainless steel was used as the electrode substrate after subsequently washed with acetone, alcohol and deionized water for 5 minutes in an ultrasonic bath. Locally developed Activated Carbon Powder (AC) was used as active material for electrode. Fabrication process of electrode is as follows: a carbon slurry was prepared by mixing a certain mass of Activated Carbon Powder and potassium hydroxide (Sigma-Aldrich) were ultrasonically mixed and then the homogeneous slurry was pasted several times which led to obtain a certain areal mass was obtained. Then the electrode was dried in vacuum tube at 50 °C for 1 hour. In both electrodes kept same mass of electrode. Finally, positive negative electrodes were sandwiched by a paper separator. It contains with 1 M KOH as electrolyte. The electrode assembly holds tightly in designed test cell as shown in Fig. 1.

D. Electrochemical Measurements

Cyclic Voltammetry (CV) and Chronopotentiometry were performed to investigate capacitive performances of the supercapacitors. A two-electrode measurement technique was carried out for the electrochemical measurements. For both samples, Cyclic Voltammetry scans were carried out with a voltage window 1 V in the range -0.5 V to 0.5 V at different scan rates in the range 2 mVs^{-1} to 250 mVs^{-1}. The charge-discharge measurements were conducted under different currents densities. Electrochemical Impedance Spectroscopy measurements were performed between 0.1 Hz and 500 Hz for different the stability test was obtained at scan rate value 100 mV/s^{-1}.

III. Results and Discussion

A newly modified design was used for assemble the supercapacitor. This design was based on conventional test cell. It can be easily handle to fabricate supercapacitors and re use for experimental purpose. There is an easy technique to tight of two electrodes each other. Technique is tightening by two side nut. The distance between two electrodes reduced due to that reason. So, specific capacitance can be increase because of the capacitance inversely proportional to the distance between two electrodes. There is a certain place to keep the separator in this design. The main advantage of this design is, ability to maintain same distance between two electrodes for each experiment very easy way.

Fig. 1: Completed Newly Designed Test Cell with its Parts

In this research, Particle size was measured for getting information size of activated material. The following Fig. 2 shows the particle size distribution of the activated material. According to distribution, the mostly available particle size was 1.78 μm. Both samples are fabricated by using same Activated Carbon Powder with same particle size.

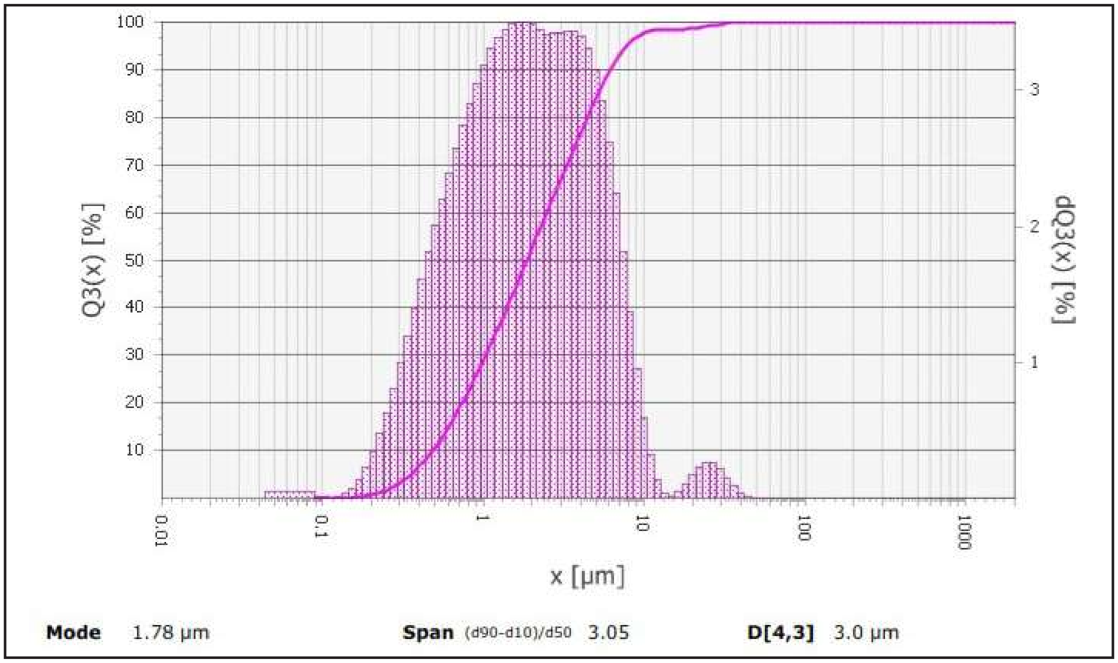

Fig. 2: Particle Size Distribution of the Activated Carbon

Cyclic Voltammetry (CV) is an electrochemical technique which measures the current that develops in an electrochemical cell under conditions where voltage is in excess of that predicted by the Nernst equation. CV is performed by cycling the potential of a working electrode, and measuring the resulting current.

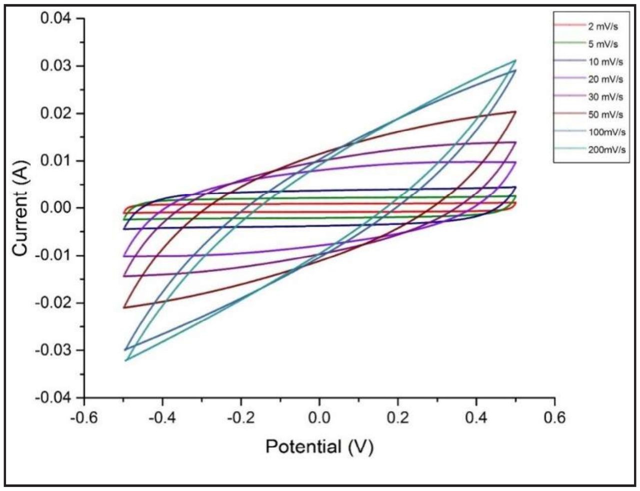

Fig. 3: Cyclic Voltammetry Measurements at Different Scan Rates

The Cyclic Voltammetry curves of binder free activate carbon supercapacitor at different scan rates are shown in Fig. 3. Scan rates were changed from 2 mV/s to 200 mV/s. At scan rate of 5 mV/s, the CV curve of the fabricated supercapacitor was close to rectangular shape, without obvious redox peaks. However, when the scan rate was increased to 100 mV/s, the rectangular shape became severely distorted and it changed into a diamond shape. When the scan was increased 200 mv/s indicative of poor rate performance. Inside the super capacitor, if there is reaction between electrolyte and electrode, then CV curve show peak point. Otherwise CV curve not indicate peak. In present study not obtained any peak from the CV. So, there is not redox reaction between electrode and electrolyte. That means supercapacitor act according to the double layer mechanism.

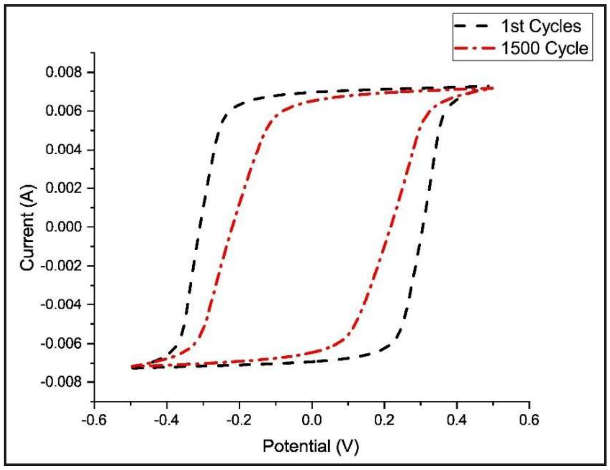

Fig. 4: Life Cycle Test for Fabricated Supercapacitor

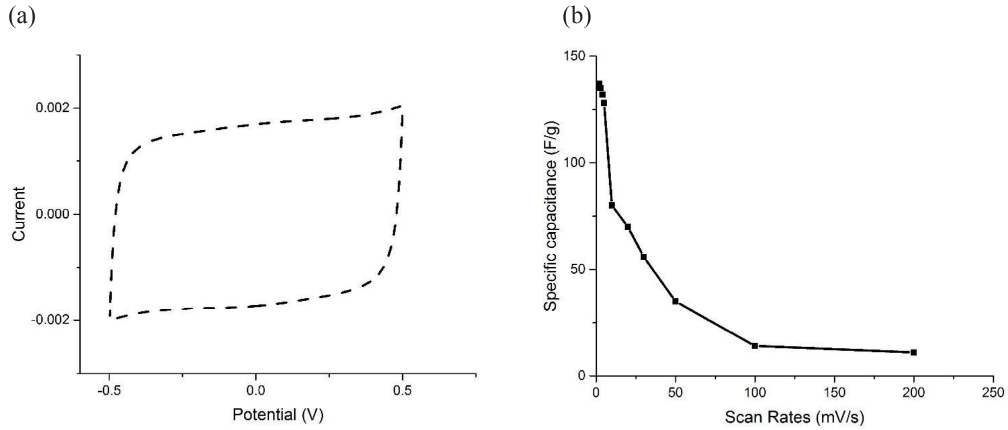

Fig. 5: (a) Cyclic Voltammetry Measurements at 5 mV/s, (b) The Graph of Specific Capacitance Vs Scan Rates

According to Fig. 5: (a), its show constant current throughout most of the potential range from -0.5 V to 0.5 V. That's means this capacitor show capacitive behavior more closely to ideal capacitor's behavior. Fig. 5: (b) explain how specific capacitance varying in with respective scan rates. Obliviously capacitance gradually decrease when increase the scan rate. Fabricated supercapacitors also obey that phenomena.

The specific capacitance of an electrode was calculated from the CV curves by using following equation.

$$Cs = \frac{2\int IdV}{m \times \Delta V \times S} \quad (1)$$

Where;

C_s represents the specific capacitance (Fg^{-1}),

I is the current (A),

V is the potential (V),

S is the potential scan rate (Vs^{-1}),

ΔV is the potential window (V), and

m is the mass of the electroactive materials in the electrodes (g).

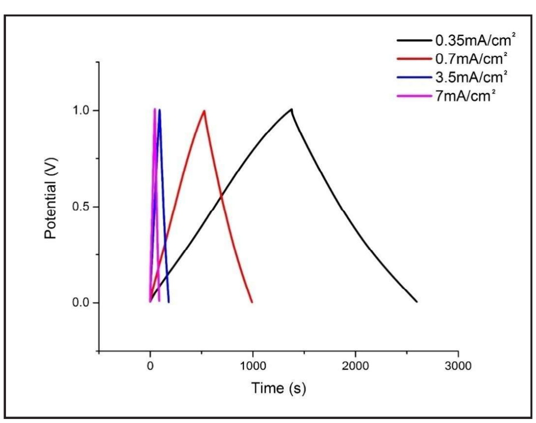

Fig. 6: Charge-Discharge Measurements for Different Current Densities

In the equation 1, IdV is the integral area under the CV curve [8]. Specific capacitances (F/g) were calculated by substituting all other variable value of equation 1. Since, highest specific capacitance was obtained at the scan rate 5 mV/s. It was 134 F/g for binder free Activated Carbon Powder electrode based supercapacitor.

Fig. 6 shows the charge discharge curves at the different current densities within the potential range between 0 V to 1 V. The specific capacitances at different current densities were calculated through following equation.

$$Cs = \frac{2i}{m \times \left(\frac{dV}{dt}\right)} \quad (2)$$

Where;

C_s represents the specific capacitance (Fg^{-1}),

I is the discharge current (A),

(dV/dt) is the slope of the discharge curve and

m is the mass of the electroactive materials in the electrodes (g) [8].

The slope of the discharge curve was obtained by linear fitting technique. Since, specific capacitance was calculated for 0.35 mA/cm^2, 0.7 mA/cm^2, 3.5 mA/cm^2 and 7 mA/cm^2 current densities. The highest specific capacitance of 105 F/g is obtained at the current density 0.35 mA/cm^2. As reported ACs achieved highest specific capacitance rage 100-165 F/g in aqueous electrolyte [9, 10]. So, locally developed binder free Activated Carbon Powder electrode based supercapacitor shows the good capacitive performance of with help of new design in aqueous electrolyte. Power density and Energy density were calculated based on the charge-discharge (chronopotentiometry) measurement results of fabricated supercapacitors by the following equation

$$E = \frac{1}{2} C_s(\Delta V)^2 \quad (3)$$

$$P = \frac{E}{t} \quad (4)$$

Where:

E represent of the Energy Density,

P is the Power density,

C_s represents the specific capacitance (Fg^{-1}) calculated from discharge curve,

ΔV is the potential window (V). Generally, which is 1 V for the aqueous electrolyte, and

t is the total discharge time of discharge [11].

For the fabricated supercapacitor shows highest power density 42.6 Wkg^{-1} at the Energy density 14.58 $Whkg^{-1}$. This is good performance because electrode fabricated by using only locally developed activated carbon. Another conductive regent can be used to increase power density. In the reported, highest power density is for Activated Carbon Powder based supercapacitor.

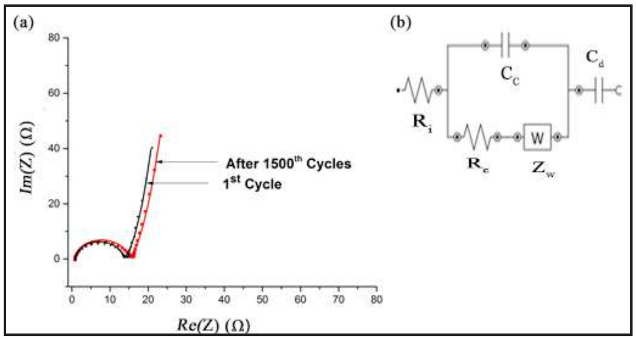

Fig. 7: (a) EIS Measurements of Fabricated Supercapacitor for After 1st Cycle and After 1500th Cycles (b) The Fitted Equivalent Circuit

Electrochemical impedance spectroscopy (EIS) is one of the best principle technique investigative the fundamental behavior of electrode materials of supercapacitor. In present study, EIS measurements were performed after 1st cycle, 1500th cycles to evaluate performance during the Cyclic Voltammetry test. Fig. 7: (a) shows Nyquist plot. Which was obtained from EIS test and equivalent circuit was determined by Fit and simulation of Nova 1.1. There are two axes such as real and imaginary of impedance. The Nyquist plot obtained with semi-circle and spike. In general, capacitor shows more capacitive behavior at low frequencies. So, Nyquist plot denotes spike at the low frequencies [12]. In the ideal super capacitor, this spike parallel to the imaginary axis. EIS curve has almost parallel spike, since fabricated supercapacitor show considerable performance at low frequencies and high frequencies. The following table show the results obtained from the fit and simulation curve fitting and Fig. 7: (b) illustrations an equivalent circuit model to simulate the capacitive and resistive elements of the sample under analysis. These elements indicate internal resistance (R_i), the capacitance and resistance due to the contact interface (C_c and R_c), a Warburg diffusion element attributable to the ion migration through the carbon electrode (Z_w), and the capacitance inside the pores (C_d) [13, 14].

Table I: Fitting Parameter Values of EIS Measurement

Sample	R_i (Ω)	R_c (Ω)	C_c (F/g)	W (Ω)	C_d (F/g)
After 1st Cycle	0.86364	13.8	0.131	0.33579	37
After 1500th Cycle	0.87298	12.5	0.104	0.44382	41

According to the R_i increased. That's about internal resistance increase with use of fabricated supercapacitor. The contact resistance with aqueous electrolyte was high. The C_d increased, which is in promise with the capacitance data.

IV. Conclusion

In this study, a new supercapacitor was fabricated by using Activated Carbon Powder electrodes. Activated Carbon used in this setup was activated from the steam activation technique. The particle size analyzer was used to measure the size of used material particles. The simple design, as shown in Fig. 1 was designed for fabricating supercapacitor by modified exist test cell. Supercapacitor electrode was fabricated from Activated Carbon Powder without any conductive regent or composite. It was succeeded to show considerable performance. The highest specific capacitance was 134 F/g. CV curves shape were showed almost close shape to the ideal behavior within the range of 2 mV/s to 30 mV/s. The energy density and power density were 14.58 $Whkg^{-1}$ and 42.6 kg^{-1}. During life test the specific capacitance reduce by 20 % which can be due to the less power density. So, present study can be concluded fabricated supercapacitor shows good electrical performance for that conclusion, reported performance and obtained performance from this study were considered.

Acknowledgment

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