Influence of various Activated Carbon based Electrode Materials in the Performance of Super Capacitor

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Abstract: Various activated carbon based electrode materials with different surface areas was prepared on stainless steel based refillable super capacitor model using spin coating. Bio Synthesized Activated Carbon (BSAC), Activated Carbon (AC) and Graphite powder are chosen as electrode materials in this paper. Electrode materials prepared using binder solution which is 6% by wt. polyvinylidene difluoride, 94% by wt. dimethyl fluoride. 3M concentrated KOH solution is used as aqueous electrolyte with PVDF thin film as separator. It is tested for electrochemical characterizations and material characterizations. It is observed that the Specific capacitance of Graphite, Biosynthesized active carbon and Commercially available activated carbon are 16.1F g⁻¹, 53.4F g⁻¹ and 107.6F g⁻¹ respectively at 5mV s⁻¹ scan rate.

Keywords: Cyclic Voltammetry, Specific Capacitance, Scan rate.

1. Introduction

With the decreasing reserves of fossil fuels and severe impacts of their combustion on both human beings and environment have been significantly increasing the world’s attention towards the development of sustainable and clean energy. Large amount of clean and sustainable energy can be generated by transforming natural energy, such as wind, tide, and solar energies. Hence to store the harvested energy development of energy storage devices is extremely important for wide applications. The commonly used energy storage devices super capacitors, batteries, conventional capacitors and fuel cells. Among these energy storage devices, super capacitors which are also known as electrochemical capacitors or ultra-capacitors have attracted rapidly growing attention due to their unique features, such as long cycle life, high power density, and small size. There are however still some challenges in Super capacitors systems such as relatively low energy density and high manufacturing cost. Electrode materials with high conductivity, pore size, temperature stability & high surface area are considered as desirable characteristics for super capacitor application. However in order to satisfy the increasing energy demand there is a need for improved power density, energy density and cycle stability. Basically the performance of the super capacitors is determined by the electrode electrochemical and structural properties. Therefore it is important to develop new electrode material with increased power and Energy densities along with cycle stability. In the present days, super capacitors are exhibiting wide applications in pacemakers, consumer electronic devices, electric vehicles, and so on [1]. The power capabilities and specific energy of several energy storage and conversion systems (conventional capacitors, super capacitors, batteries, and fuel cells) are shown in Figure 1. It must be noted that no single energy source can match all energy and power region. The ideal electrochemical energy-storage systems are super capacitors and batteries, which fill up the gap between conventional capacitors and fuel cells. The important common features of both the systems are that the interface of electrode and electrolyte is where the energy release takes place, and that
electron and ion transports are separated. The characteristic performance of super capacitors sets
them apart from batteries owing to the inherent differences between batteries and super capacitors
with respect to energy storage mechanism and electrode materials.

![Graph](image.png)

**Figure 1** Ragone plot for energy storage and conversion devices [1].

Based on the type of capacitance exhibited the super capacitors are classified into Electric Double Layer
Capacitor (EDLC) (non-faradic process) and (Faradic Capacitors). In the EDLC type the super capacitors
are classified based on the type of Electrode materials used like Activated Carbon, Graphene based and
Carbon Nano Tubes. In the Pseudo capacitance type they are classified based on the type of the electrode
materials used like the metal oxides and conducting polymers. In present paper Various activated carbon
based electrode materials with different surface areas are used as electrode materials for super capacitor
application is listed below.

1.1 **Activated carbon** Activated carbon or activated charcoal in powder form, is one of the materials used
as electrode. The specifications of this material are as follows, specific surface area of 600m$^2$/g, melting
point of 3550°C, particle size 10 mesh (149 micron or 0.0058 inches). The important features of this
material are its specific surface area and the porosity.

1.2 **Bio synthesized activated carbon** Carbonization of Kapok fibers was performed in muffle furnace at
250 c for 3 hrs followed by steam activation for 2 hours. The color of kapok fiber was turned into black
color after carbonization and was almost powder form and it was sieved under 30 mesh size and was
subjected to heavy metal Chromium and Cadmium) adsorption. The adsorption process was performed in
batch mode and the analysis was done using atomic absorption spectrophotometer Steam activated kapok
fiber adsorbed more amount of heavy metal (Chromium and Cadmium) compared to natural kapok fibers.

1.3 **Graphite powder** Graphite has superior characteristics like chemical stability, large surface area and
high electrical conductivity. As per recent studies, it was observed that graphite can be used for super
capacitor applications due to its unique characteristics. The graphite powder used here has 150m$^2$/g
surface area is in the form of layers which makes it graphite that can be observed from its SEM images.
Because of this structure of the material, the specific surface area is not as high as expected for generally
available graphite powder.

2. Materials and Methods

2.1 **Current collectors and encasing Module** Two current collectors were designed with the help of
CATIA software. The basic shape of the module is circular and made of stainless steel. It is designed in
such a manner that the active portion of the collector where the electrode material is coated is elevated in
the center of the module. Nodes are provided for each of the current collectors to connect them to the circuit. The dimensions of the model are as follows: Diameter of the elevated part is 1.5cm and Height is 2.5mm as shown in Figure 2.1. A plastic ring was designed to keep the current collectors intact as shown in Figure 2.2. It also protects the electrode material from the various external factors in the atmosphere such as air, heat, moisture etc. The O-ring material is selected such that it is non-conductive and non-reactive with the electrode and electrolyte materials. The complete encasing module is as shown in Figure 2.3

![Figure 2.1 Current collectors with nodes.](image1)

![Figure 2.2 Plastic ‘O’ ring.](image2)

![Figure 2.3 Complete encasing module.](image3)

2.2 Preparation of electrode material DMF (Dimethylformamide) is an organic compound used as a common solvent used in chemical reactions. PVDF (Polyvinylidene difluoride) is used as a binder. Initially DMF solution + PVDF (in powder form) solution is prepared by mixing them in weight ratio of 94% : 6% respectively with the help of a magnetic stirrer for about 30 minutes at an rpm of 900. All Activated carbon electrode material is prepared by mixing it with a solution of DMF + PVDF in weight ratio of 80%:20% respectively using a magnetic stirrer for about 15-20 minutes at 800 rpm till a uniform slurry is formed. All the prepaid electrode materials were coated on the current collectors using spin coating technique. The material coated on the current collectors is to be dried, for this purpose a vacuum air dryer is used. The current collectors are kept inside the vacuum air dryer with an inside temperature of 45°C and 0.75 bar of pressure for 20 minutes and left unattended for 15 minutes. This procedure is repeated for two more times with a break of 15 minutes in between.

2.3 Preparation of electrolyte Using aqueous electrolyte for a super capacitor makes it more environment friendly compared to those where organic electrolytes are used. Some of the commonly used aqueous electrolytes are KCl, NaOH, KOH etc. The most commonly used aqueous electrolyte is 6M concentrated KOH because of its very high ionic conductivity.
The electrolyte used is 3M concentrated KOH solution, prepared by completely dissolving $56.1 \times 3 = 168.3$ g (where $56.1$ g is the weight of one mole of KOH, and multiplied by 3 as 3M solution is being prepared) of KOH pellets in 1 liter of distilled water.

2.4 Procedure of assembling the various components One of the current collectors is placed such that the electrode material is facing upwards, a few drops of the KOH electrolyte is put on the electrode with the help of a dripper. It is then allowed to soak for about 3-4 minutes as shown in Figure 2.4. Now the separator which is dipped in the electrolyte is placed on the current collector as shown in Figure 2.5 and the ‘O’ ring is fixed on the current collector firmly. Similarly, the second current collector whose electrode material is soaked in the electrolyte is placed on the separator through the ‘O’ ring fixing it firmly.

3. Results and Discussions

3.1 Physical & Structural Characterization The surface morphology of BSAC and graphite powder based electrode material was studied using scanning electron microscopy (SEM) with EDS. XRD peaks for BSAC are intense at 2theta values 43.70° and at 72.51° as shown in Figure 3.1 which represents multi-planar structure at the crystal lattice. But as the BSAC is mixed with binder solution there are other elements which resulted in the XRD peaks at 72.51°. From SEM images and the EDS peaks, as shown in Figure 3.2 and 3.3 it is evident that the percentage weight of carbon in the final material is greater than 80% leading to more carbon participated in the charge accumulation processes. Hence the obtained values match with the standard values of graphite. Also, the material is greater than 92% pure which can be confirmed from EDS results thus the impurities are less as shown in Figure 3.4 and Figure 3.5.
3.2 Electrochemical Characterization

The electrochemical properties of super capacitor electrodes were studied by means of electrochemical impedance spectroscopy, Cyclic Voltammetry and Galvano static charge and discharge using CH Instruments Electrochemical Analyser. The performance of super capacitor test cell was evaluated making use of two electrode configuration. The specific Capacitance was estimated from the CV according to the equation (1)

\[
\text{Specific Capacitance (Csp)} = \frac{\int i \, dV}{2 \cdot m \cdot v \cdot (V1 - V2)} \quad \text{F/g} \tag{1}
\]

Where \(i\) is instantaneous current in CV, \(dV\) is Differential Voltage, \(m\) is Mass of active material on both the electrodes, \(v\) is Scan Rate, \((V1 - V2)\) is voltage window, \(\int i \, dV\) is area bounded by CV curve. Specific Capacitance is calculated using the above equation and a multiplying factor of 4 for two electrodes and 2 for single electrode is multiplied. Using the specific capacitance calculated from the CV curves, energy density is calculated using the formula (2).

\[
\text{Energy density (E)} = \frac{\text{Csp} \cdot (\Delta V)^2}{2} \tag{2}
\]
Where $C_{sp}$ is specific capacitance and $\Delta V$ is voltage window.

Power density can be calculated using the GCD curves as shown in equation (3),

$$\text{Power density} = \frac{E}{\Delta t}$$

$E$ is energy density and $\Delta t$ is discharge time in GCD curve.

Various cyclic voltammetry curves for commercially available Activated Carbon for different scan rates is shown in Figure 3.6 the calculated specific capacitance was found to be 107.67 F/g at 5 mV/S which very high when compared to all set of experiments. From the Figure 3.7 it can be observed that the solution resistance is 57 ohms and charge transfer resistance is 3.33 ohms. Thus, AC is able to achieve more specific capacitance and near to ideal capacitance behaviour. Thus, ESR for AC is only 60.33 ohms.

![Figure 3.6](image1.png)  
**Figure 3.6** Activated carbon CV Curves at different Scan rates.

![Figure 3.7](image2.png)  
**Figure 3.7** Nyquist plot of Activated Carbon.

![Figure 3.8](image3.png)  
**Figure 3.8** CV curves of BSAC.

![Figure 3.9](image4.png)  
**Figure 3.9** Nyquist plots BSAC Electrode.

The Cyclic Voltammetry curves at different scan rates for BSAC are shown in Figure 3.8. The Specific capacitance is calculated for BSAC CV curve of 5mV/s scan rate. Area under the curve and voltage window is calculated using origin software. The mass of the active material is found out to be 11.2mg. From Nyquist plot shown in Figure 3.9 it is evident that the solution resistance is only 1 ohm and the charge transfer resistance is negligible as the semicircle portion in weaned out. Thus, ESR for BSAC is only 1 ohm.
Figure 3.10 CV of Graphite Powder.  

Figure 3.11 Nyquist plot of Graphite based Electrode.

Figure 3.10 shows the various Cyclic Voltammetry curves for graphite powder at different scan rates and calculated Specific Capacitance is 16.1 F/g at 5mVS\(^{-1}\). From Figure 3.11 it can be observed that only solution resistance exists and charge transfer resistance is negligible thus it’s neglected. The solution resistance is only 8.8ohms. Thus, ESR for graphite is only 8.8 ohms.

With GCD results given in Figure 3.12 it is found out that current density of the activated carbon is 1.12A/g and capacitance retention of 98% after 100 cycles. Energy density for this is 172.3wh/kg. Power density is 191.01w/kg. As the load for charge discharge test are set by the instrument the time required for discharge will vary according to the load. But the capacitance retention after 100cycles is 97% and current density being 1.61A/g as shown in Figure3.13 for graphite based electrode.

Figure 3.12 GCD curves for activated carbon.  

Figure 3.13 GCD curves for graphite based electrode.

4. Conclusions

In summary the specific capacitance of BSAC is found to be 53.49F/g with an energy density of 96.01wh/kg for a voltage window of 3.6volts. For Graphite Powder based electrode material specific capacitance 16.1F/g because of very low specific surface area of the material. Similarly, for AC it is found out to be 107.67F/g with energy density of 172.3wh/kg for a voltage window of 3.4 volts with a power density of 191.01w/kg and capacitance retention of 98% after 100 cycles. Among these three electrodes commercially available AC has achieved highest Specific capacitance due its high surface area of 600m\(^2\)/g.

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