

A Study On Carbon Electrode Supercapacitors

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Abstract

Six carbon electrode supercapacitors were fabricated to see the effect of various supercapacitor materials on its capacitance. The effects of activated carbon surface area, type of electrolyte used and electrolyte concentration were observed. Results have shown that the surface area of the activated carbon is no longer the most important factor of getting large capacitance value. Meanwhile activated carbon with a lesser surface area with larger pore size could do better than that with a larger surface area and small pore size. It was also discovered that interposing a micro grid in between each current collector and its electrode could boost conductivity there by enhancing capacitance.

Keywords: Activated carbon, BET surface area measurements, cyclic voltammetry, capacitance.

1 Introduction

Super capacitors that have higher energy density than a normal capacitor have been developed. Though the energy density of a supercapacitor is less than that of a battery, its power density is higher which makes it suitable for applications that require a sudden initial amount of current due to its ability to discharge immediately. Supercapacitors are used in conjunction with batteries to boost its power supply capability. In some cases, batteries have now been replaced by supercapacitors.

A super capacitor differs from a normal capacitor because it is made up of two electrodes, a separator and an ion carrier (electrolyte). Another distinct feature that differentiates super capacitor from a normal capacitor is high values in capacitances which could be up to hundreds or even some few thousands of farads while it is very hard to find a normal capacitor with a value up to one farad [1], [2].

Researches have shown that such capacitance values could be achieved by using porous carbon as the electrode material which provides a larger surface area and thus boost the capacitance value. Carbon is one of the cheapest available resources on earth which can be from different sources, implying that the porosity differs from one source to another [1], [2] and [3]. To improve the performance of supercapacitor, research has been carried out by investigating different materials that could be applied in this aspect. Besides, the electrolyte, the separator as well as the packaging have effects on the overall performance of the supercapacitor [4], [5]. Similar to battery performance measurements, there are different types of measurements applicable to supercapacitors as well. Such measurements include charge/discharge tests, cyclic Voltammetry and impedance spectroscopy. The study will be focused on cyclic voltammetry analysis.

Cyclic voltammetry involves applying a preset increasing voltage to the working electrode until it reaches a set value. Upon reaching the set value, the voltage is being decreased down to its initial value. During the process, the current at the working electrodes is recorded and plotted against the applied voltage. The resulting plot obtained is called a voltammogram. The applied voltage waveform is triangular since it is ramped linearly and then decreased as shown in figure 1. The rate at which it is ramped is called the scan rate. Figure 2 is an example of a voltammogram for a reversible reaction. The measurement taken is for a single cycle. In some instances, measurements are taken for a multiple number of cycles [6] [7].

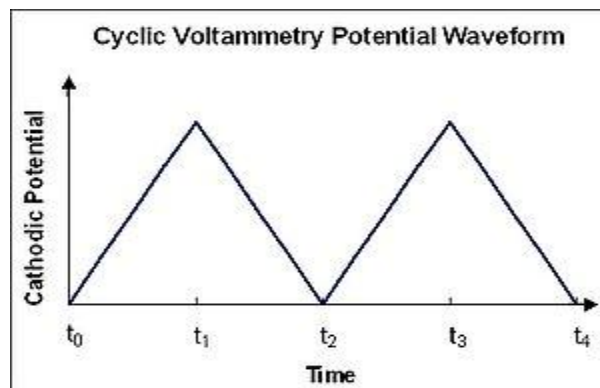


Fig1: Input voltage waveform used in cyclic Voltammetry [7].

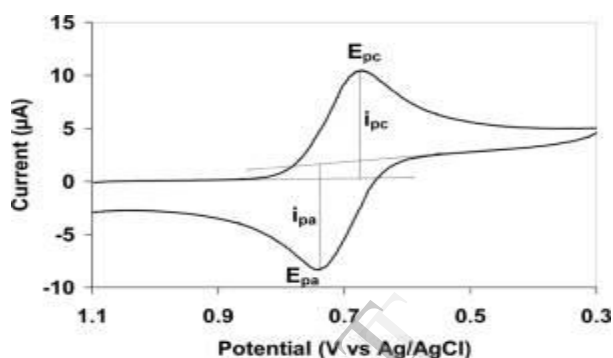


Fig 2: An example of a voltammogram [7].

Cyclic Voltammetry is used in studying the quantification of concentrations, diffusion effects, irreversibility, reaction intermediates and in identification of electron transfer steps. It is sometimes used in determining voltage levels for stable operations, which is carried out because instability can lead to gas evolution and metal electroplating [8], [9].

Figure 2 above showed four parameters E_{pc} , I_{pc} , E_{pa} and I_{pa} which represent the cathodic peak potential, cathodic peak current, anodic peak potential and anodic peak current respectively. Sometimes the terms cathodic and anodic are replaced by the terms reduction and oxidation when describing cyclic Voltammetry parameters. If the rate of electron transfer is very high, the value of the peak potentials becomes independent of scan rate. This phenomenon is an indicator for a reversible electrode reaction and following relationship then holds [10], [11]:

$$|E_{pc} - E_{pa}| = \frac{57mV}{n} \quad (1)$$

Where n is the number of electrons involved in the process. Since E_{pc} and E_{pa} are determined experimentally, n could be determined from equation below:

$$n = \frac{57mv}{|E_{pc} - E_{pa}|} \quad (2)$$

Another important parameter that could also be observed from the voltammogram is the thermodynamic reversible potential denoted E° . It is a parameter that is independent of scan rate which takes a value 85% that of the peak potential [11]. Cyclic Voltammetry is also used in capacitance computation by dividing the anodic current at a particular point by the scan rate [12].

2 Methodology

Carbon electrode supercapacitors were prepared using two different samples of activated carbon labeled sample1 and sample2. BET surface area measurements taken resulted in an area of $1064.3623m^2/g$ and $3659.9832m^2/g$ for sample1 and sample2 respectively, with pore sizes of 18.3647\AA and 11.2262\AA respectively from a micromeritics ASAP 2020 surface area and porosity analyzer. Each of the fabricated

supercapacitors was labeled with an alphabet that ranged from A to F for reference. Supercapacitor A was fabricated as a starter. Supercapacitors B and C were fabricated to test the effect of using different electrolytes. Super capacitor D was fabricated to test the effect of concentration of electrolyte in comparison with the one used in C while supercapacitor E was fabricated to test the effect of the surface area of activated carbon on the capacitance of a supercapacitor by comparing it with supercapacitor D. Activated carbon sample2 was used in the fabrication of supercapacitor D while sample1 was used in the preparation of E.

2.1 Fabrication of supercapacitors A to D

The process of fabricating each supercapacitor is described below:

2.1.1 Supercapacitor A

The electrodes for supercapacitor A were developed by mixing 0.16g sample1 (palm shell) activated carbon, 0.02g carbon black (XC72R) and 0.02g Teflon. The purpose of adding XC72R is to increase the conductivity of the activated carbon sample1. Teflon will then act as a binder for both activated carbon and XC72R. The resulting mixture was pounded in a mortar until a paste was formed. Two electrodes of diameter 12.7mm were cut out of the paste. The formed electrodes were placed in a beaker containing a solution of prepared 2MKOH. It was then inserted into a vacuum and degassed for 20 minutes in order to evacuate any gas present in the pores of the carbon electrode thereby enhancing the penetration of the electrolyte into the pores. A separator with a diameter slightly greater than that of the electrodes was cut out of what man filter paper in order to avoid electrode contact. The separator was soaked into the KOH electrolyte. The two electrodes and separator were then taken out one by one from the electrolyte solution and assembled into a supercapacitor test cell.

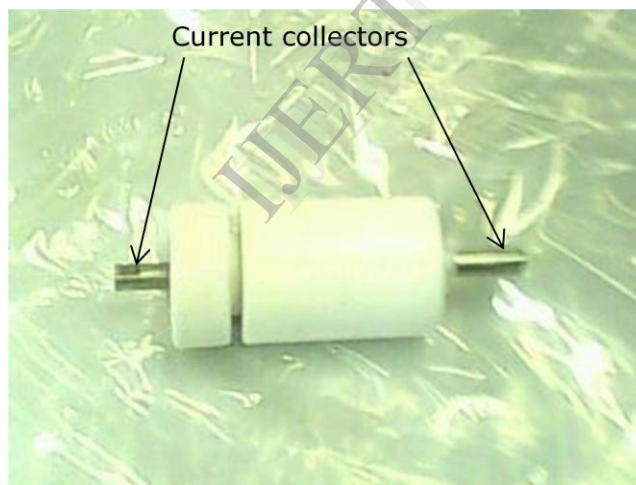


Fig 3: An assembled supercapacitor test cell.

2.1.2 Supercapacitor B

0.8g of activated carbon sample2, 0.12g XL6 (conductive carbon/carbon black) and 0.133 PTFE emulsion were mixed thoroughly and rolled to form a paste. Two 12.7mm electrodes were cut out of it. A 4 AL 12-125 micro grid with was attached to each electrode on one side to improve conductivity. A supercapacitor was assembled using the two electrodes, 2M KOH prepared as electrolyte and filter paper as the separator in a supercapacitor test cell, in which the electrodes were positioned such that the side with the micro grid made direct contact with the current collectors.

2.1.3 Supercapacitor C

Supercapacitor C differs from supercapacitor B only in the type of electrolyte used. In this case, a prepared 1M aqueous Potassium chloride was used. The electrodes were cut out of the mixture of

activated carbon sample 2, XL6 and PTFE emulsion that remained while preparing supercapacitor B. A micro grid was also attached to each electrode as in the case of supercapacitor B.

2.1.4 Supercapacitor D

Super capacitor D was fabricated with electrodes prepared in the same way the electrodes in C were prepared. But in this case 2M KCl was used as electrolyte.

2.1.5 Supercapacitor E

Supercapacitor E was fabricated in the same manner supercapacitor D was fabricated. The only difference is that the electrode consists of activated carbon sample1 instead of sample2.

2.1.6 Supercapacitor F

Supercapacitor F has the same electrode, separator and electrolyte as in the case of supercapacitor E. The only difference is that no micro grid was placed in between the electrodes and current collector. In essence, the effect of the micro grids on the performance of the supercapacitor E is to be observed when compared with F.

Cyclic Voltammetry test was conducted for each of the fabricated supercapacitors using VersaSTAT 3. Though experiments were not conducted under the same settings, information regarding how well their capacitance is was deduced from their voltammograms.

3 Results

The voltammogram obtained from the cyclic voltammetry of each supercapacitor is shown below:

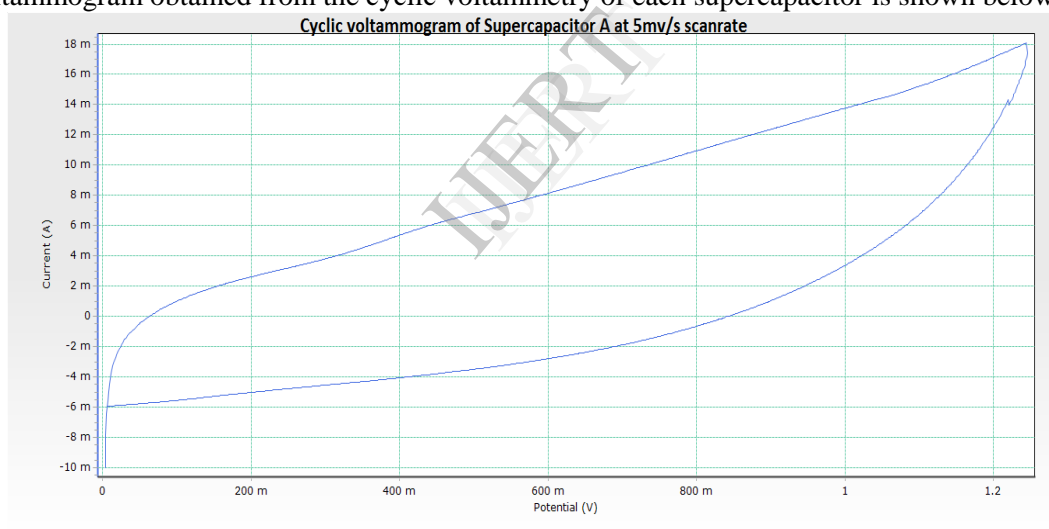


Fig 4: Cyclic Voltammogram of supercapacitor A at 5mV/s scan rate.

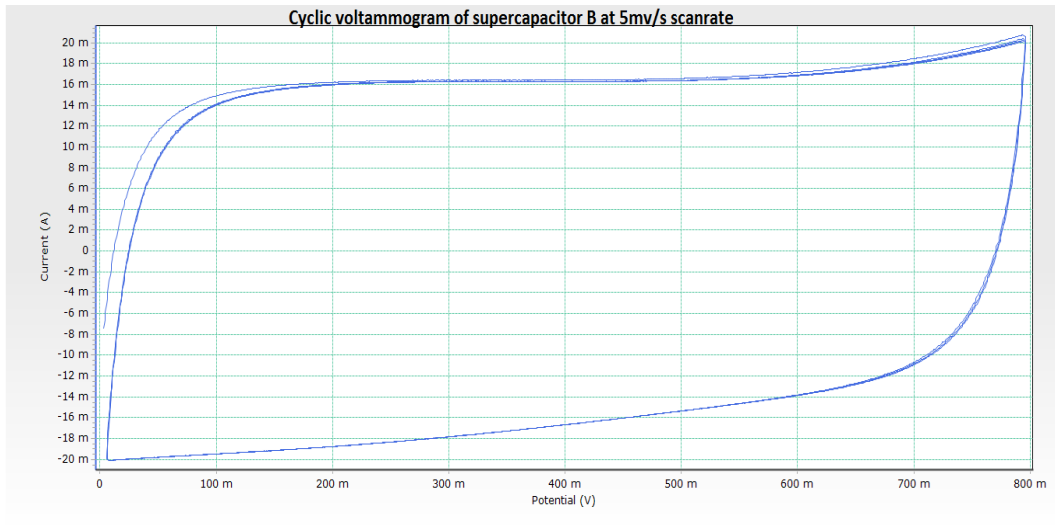


Fig 5: Cyclic Voltammogram of supercapacitor B at 5mV/s scan rate.

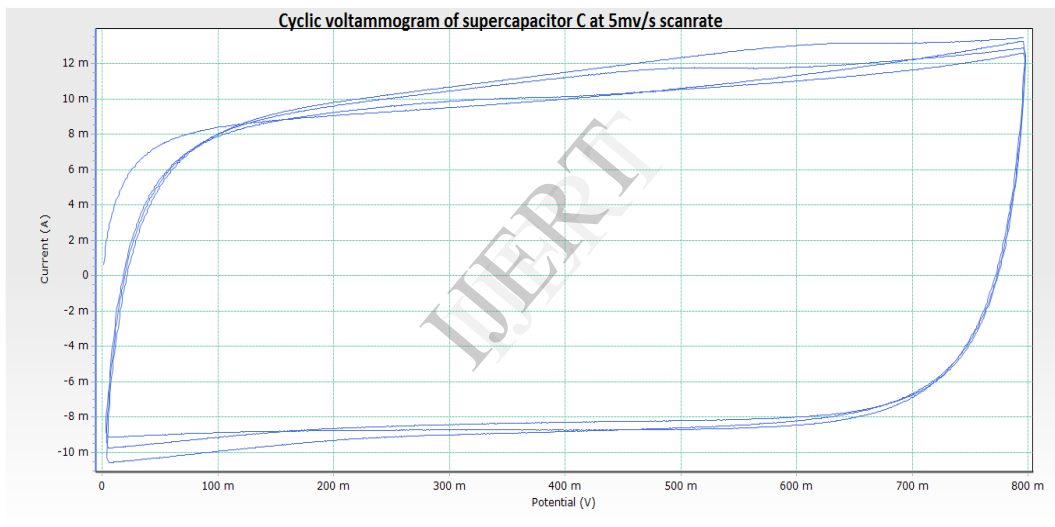


Fig 6: Cyclic Voltammogram of supercapacitor C at 5mV/s scan rate.

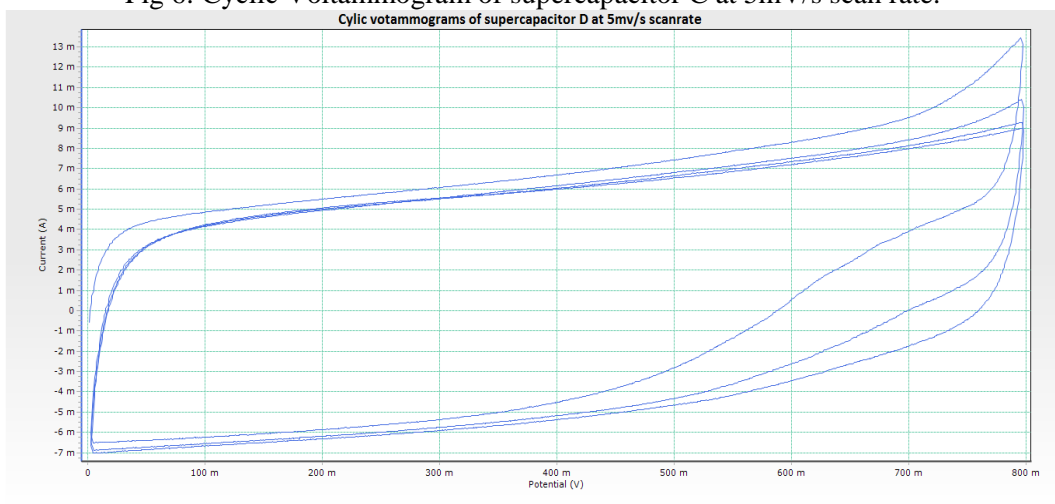


Fig 7: Cyclic Voltammogram of supercapacitor D at 5mV/s scan rate.

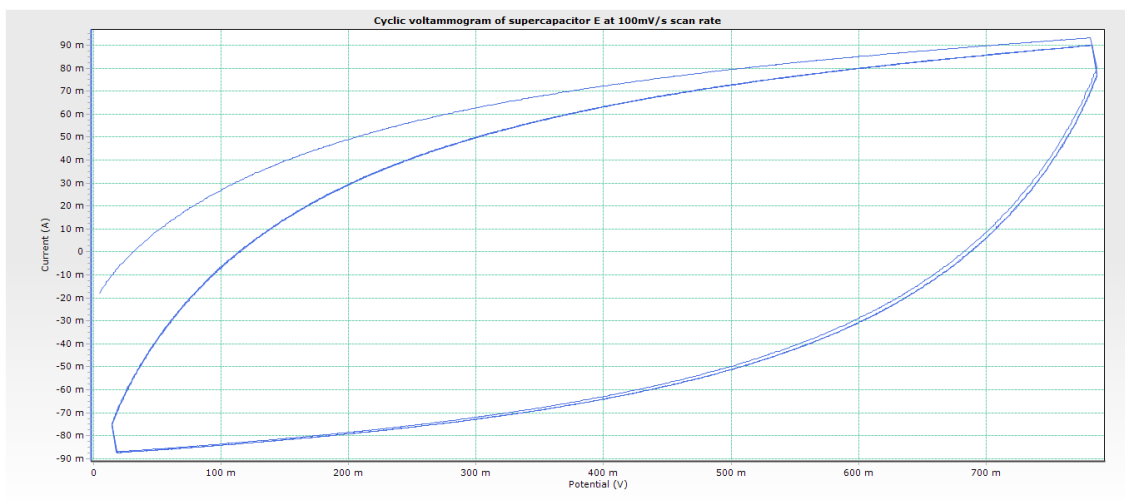


Fig 8: Cyclic Voltammogram of supercapacitor E at 100mV/s scan rate.

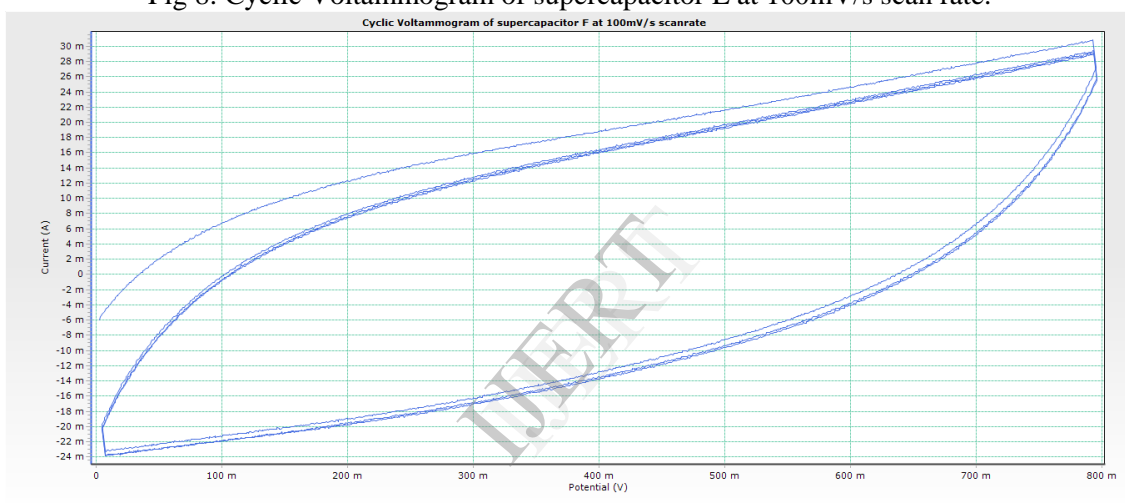


Fig 9: Cyclic Voltammogram of supercapacitor F at 100mV/s scan rate.

4 Discussion of Results

Amongst the fabricated supercapacitors, E and F had very high values of current as indicated in their voltammograms. This yielded capacitance values of 9F and 2.9F respectively. A summary of the capacitances calculated for each supercapacitor are shown in table below:

Table 1 Capacitance Values of supercapacitors.

Supercapacitor	Capacitance (F)
A	2.2
B	4.0
C	2.5
D	2.6
E	9.0
F	2.9

The capacitances were obtained by dividing the current at 0.8V by the scan rate used while performing the experiment. The electrolytes used in all the supercapacitors are aqueous electrolytes. This means that their voltage should not exceed 1.4V. In most cases, the decomposition voltage is taken to be 1V. Their cyclic voltammetry test was thus conducted at a scan rate of 5mV/s and a voltage range of 0V to 0.8V

with the exception of supercapacitor A in which the voltage range extended to 1V and supercapacitors E and F in which the scan rate was set as 100mV/s. It could then be clearly seen from figure 5 that supercapacitor B had the largest capacitance value among the remaining four supercapacitors since its current is the highest at 0.8V, followed by D, then C and then A had the least. Though the surface area of activated carbon sample 1 is less than that of carbon sample 2, the capacitance of supercapacitor D was supposed to be higher than that of E. Unfortunately this did not happen. But when the surface area of the samples was measured, the pore width was indicated by the report generated by the "micromeritics ASAP 2020 surface area and porosity analyzer instrument" as 18.3647Å and 11.2262Å for sample 1 and sample 2 respectively. Thus the issue of electrolyte ion radius comes into consideration. That is the electrolyte ions penetrate more into the pores of activated carbon sample 1 than in sample 2 and as a result the capacitance of supercapacitor E became greater than that of D.

The performance of supercapacitors B and D showed that using 2MKOH will be preferred in obtaining large capacitances than in the case of 2M KCl. So also 2M KCl performed better than 1M KCl in enhancing capacitance as observed in the cases of supercapacitors C and D. Thus the higher the concentration of the electrolyte, the higher is the capacitance.

Supercapacitor F had a capacitance value higher than that of supercapacitor E. This shows how the micro grid used in between the electrodes and the current collectors in supercapacitor E enhanced conductivity there by increasing capacitance. The same effect should be expected in any other supercapacitor that has such arrangement.

But not only the materials used, expertise developed along the process must have contributed to the increased values in capacitance of supercapacitors E and F. Therefore low value of capacitance of supercapacitor A must have been caused by poor materials selection coupled with low level of expertise at the initial stage.

5 Conclusions

Based on results obtained, the following points were deduced:

- The type of electrolyte used in a supercapacitor affects the performance of the supercapacitor. For example potassium hydroxide performed better than potassium chloride. This observation was made from the performance of supercapacitors B and D.
- An electrolyte with a higher concentration yields a higher capacitance value since the number of ions in it is large. This was observed in the case of supercapacitors C and D.
- High Surface area of an activated carbon alone does not yield high capacitance value but a high surface area coupled with a larger pore size yields a high capacitance value because the electrolyte ions can penetrate deep into the pores, thereby leading to a highly conductive cell with a high capacitance value. This observation was made by comparing supercapacitors D and E.
- Interposing a micro grid in between the electrodes and the current collectors boosts capacitance as observed from results of supercapacitors E and F.

6 References

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