ABSTRACT
A prototype electrode was constructed to study the optimization of composition of materials used for the supercapacitors. Electrodes were prepared from a selected active carbon, a conductive carbon, binder and aluminum foil with various compositions and thicknesses with a technique developed. An electrochemical test cell was used for measuring impedance characteristics of electrodes. The electrode was tested for capacitance & ESR to get the optimum conductive carbon content. Results showed that capacitance increases to a maximum level of capacitance value at 7% by weight of conductive carbon and the capacitance starts to decrease as conductive carbon content increases further. The ESR didn’t change significantly with carbon content. Effect of carbon layer thickness was evaluated with 7% conductive carbon composition for thicknesses varying from 50 microns to 250 microns. Results show capacitance increases monotonically while ESR is almost independent of thickness in this range.

1) INTRODUCTION:
Supercapacitors have gained interest over the years as they are good storage devices and can supply high power in very short pulses. This leads to their increased use in applications such as hybrid vehicles, Uninterrupted Power Supplies etc. (1),(2). Storing electricity in compact size and in large amounts is presumed to be a challenge and lot of focus has been shifted in this area of research. Earlier batteries were evolved for storage of electric energy but its low power density and shorter life lead to the formation of capacitor which works on electrostatic phenomenon for storage of energy. But for high energy applications capacitors of enormous sizes are required as capacitance is directly proportional to the area of electrode plates. Thus, eventually it led to development of supercapacitors due to its compactness and high energy density (2),(13). In 1879, Helmholtz had discovered the storage process, based on separation of charges in an electrolytic double layer (12). In the 1950’s and later companies like GE, Sohio, Matsushita have made significant contribution to this field of study(3),(13). Supercapacitor materials and their construction is an important aspect on which research is going on for years in the last century and even today (13). Optimization of the electrode with increase in power and energy density along with lowering the cost is major need for current applications. The electrode being the integral and most important part of the supercapacitor, the electrode materials are the most important factors to determine their properties (5). Activated carbons are widely used as the electrode material for the supercapacitors due to their favorable properties like low cost, high effective surface area, availability, and established production technologies (3)-(7),(10), (11). The active carbon is the basis of energy storage in the supercapacitor while the conductive carbons are the important additives for increasing conductivity across the electrode surface(5)(9). In this paper, we will look into the optimization of electrode material composition and its thickness based on performance in terms of capacitance of the electrode. The study is focused on effect of conductive carbon content on the performance of supercapacitor electrode and the effect of thickness of carbon layer of the electrode. The thickness of the electrode is important to be optimized as excessive thickness affects the mechanical integrity of the electrode while reduction in thickness reduces its capacitance.

2) MATERIAL SELECTION AND ELECTRODE PREPARATION
2.1 Material Selection for Electrode
The electrodes considered in this study were primarily prepared from active carbons and conductive additives along with the binders. Conductive additives in right amount are important in increasing connectivity between active carbons. (9),(14). The active carbon for the study was selected from the 4 active carbons provided by IOXUS Inc. on the basis of results obtained from their characterization. Characterization was based on SEM Images, particle size analysis and surface area analysis.

2.1a. Surface Area Analysis of Active Carbons
Surface area analysis was performed using SA 3100 surface area analyzer from Beckman and Coulter on the 4 active carbons namely MSP 20 (High activated surface area carbon), carbon B, carbon C and carbon D. The results showed that MSP 20 had highest BET surface area of 2150.28 m²/g. Active carbon B had 1759.70 m²/g. Active carbon C had BET surface area of 1549.55 m²/g while
active carbon D had 1296.85 m²/g. This characterization showed that the active carbon MSP 20 has a very large surface area, which is important in terms of capacitance of the super capacitor. (8)

2.1.b SEM Images and Particle Size Analysis : SEM Images were taken from Supra55 FEG-SEM and particle analysis was performed on LS 13320 particle size analyzer.

Fig.2.a SEM Image MSP 20
Fig.2.b SEM Image Active Carbon B
Fig.2.c SEM Image Active Carbon C
Fig.2.d SEM Image Active Carbon D

Fig. 2.e: Overlay of particle size distribution of the 4 active carbons considered (vol %vs particle diameter)

From table 1 it can be said that the active carbons have large particles ranging from 5to 15 microns and also fine particles ranging from 2-5 microns. SEM Images and particle size distribution analysis shows results in consensus with each other. The large particles have pores which are the factor in capacitance of the super capacitor. (5)

2.2 Electrode Preparation:
Overall characterization of active carbons concluded MSP20 to be appropriate selection for electrode preparation alongwith conductive carbon Super P, Aluminum foil as provided by Ioxus Inc. The binder constituents were CMC, PTFE and fluorosurfactant. Fluorosurfactant is an additive added to the binder as it plays an important role in electrode slurry preparation in overcoming the defect of conductive carbons of hydrophobicity and also reduces electrical resistance without affecting physical properties of the electrode (12). The materials required were provided by Ioxus Inc. Samples of specimen electrodes were prepared to test for capacitance and ESR. The preparation procedure was referenced from IOXUS Inc(12). The total weight considering carbons and binder solution neglecting the amount of water was considered 20gm. The active and conductive carbons of required amount were dry mixed in a planetary mixer. The dry mixing time was 50 min.

<table>
<thead>
<tr>
<th>Act. Carb.</th>
<th>Particlesize analysis(particle size range)vol %</th>
<th>SEM Image (particle size distribution range)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MSP20</td>
<td>Vol. occupied by particles of 5-15 microns.</td>
<td>8-14 micron particles surrounded by small particles.</td>
</tr>
<tr>
<td>B</td>
<td>3-8 micron particles along with 06 to 1.5 micron particles</td>
<td>8-10 microns along with small particles in 2-4 micron range.</td>
</tr>
<tr>
<td>C</td>
<td>Vol. occupied by 5-10 micron particles.</td>
<td>8-10 micron particles.</td>
</tr>
<tr>
<td>D</td>
<td>6-14 microns particles along with particles of size 2-5 microns</td>
<td>Particles having sizes 6-15 microns with few having3-6 microns size.</td>
</tr>
</tbody>
</table>

Table 1: tabulated format of particle size characterization

Binder solution was prepared by mixing 2.5 % by wt. of CMC, 0.6% by weight of PTFE and 0.2 % by wt. of fluorosurfactant with di-ionised water weighing about 65 gms. Magnetic stirrer was used to prepare the binder solution with mixing time of 50 mins. Slurry was prepared by mixing dry mixture of carbons and binder solution for 50 min in the planetary mixture. The aluminum foil was coated on the single side by using automatic film applicator. The drying process of coated electrode was carried out in an oven for 60 min the temperature being kept 75°C. TGA was performed to determine the temperature and time required for complete drying of electrode. The thickness of electrode was kept as desired by using variable doctor blade. Electrode coupons were prepared of size 2cm X 2cm for the purpose of measuring impedance characteristics with an electrochemical test cell setup.

3) EXPERIMENTAL PROCEDURE

3.1) Electrode Coupons:
For the first step of testing, coupons of electrode with various conductive carbon percentages as additives were prepared to find out optimum composition of active and conductive carbon for efficient performance. The electrode coupons of 2cm X 2cm size with thickness of 100 microns (excluding thickness of aluminum foil) were prepared with compositions of 5%, 7%, 10% & 15% by weight of conductive carbons. For each composition binder % remains 8% by weight. The remaining percent by wt. was active carbons. The optimum composition was determined and the electrodes were prepared for the next step i.e. effect of carbon layer thickness with this composition. For this analysis, electrodes of 7 different thicknesses namely 50 microns, 75 microns, 100 microns 125 microns 150, 200
and 250 microns were prepared (excluding collector thickness). They were electrochemically tested under same conditions as for the previous analysis of compositions of electrode materials.

3.2) Electrode Test Cell Setup:

3.2.a Electrode Testing Equipment

An electrochemical test cell, having prepared electrode as working electrode and a reference electrode submerged in electrolyte in a sealed container was constructed. It was tested at Ioxus Inc. with the help of instrument Potentiostat HCP-803 (Biologic, USA) available at the site. Tests were performed to analyze impedance characteristics of the electrode specifically capacitance and the ESR.

3.2b Testing Procedure & Calculations

The electrochemical test cell was charged to a voltage of 1.4 Volts by using a 0.02A current and was held for 10mins and then discharged. The charge-discharge characteristics were analyzed to calculate the Capacitance and the ESR of the electrode specimen. The Calculations were carried out by following formulae (15)

\[
\text{Capacitance} = \frac{I*(t_f-t_i)}{(V_1-V_f)} \quad [1]
\]

where \( I = \text{Current} \), \( V_1 = \text{Initial voltage} \), \( V_f = \text{final voltage} \), \( V_2 = \text{voltage after sudden down surge of voltage.} \), \( t_f = \text{final time} \) and \( t_i = \text{initial time} \)

\[
\text{ESR} = \frac{(V_1-V_2)}{I} \quad [2]
\]

4) RESULTS AND DISCUSSION

In our study, we will mainly focus on the effect conductive carbon has on the performance of a supercapacitor. For finding optimum composition each composition had 6 electrodes tested. The charge and discharge characteristics of each electrode were analyzed to calculate Capacitance in Farads/g of carbon and ESR in Ohms/g of carbon. The values are measured per gram to minimize the effect due to inaccuracy in the area of electrode coupons. The Fig. 4.1 shows that as the conductive carbon percentage increases from 5 to 7 % the capacitance increases from around 100F/g to 120 F/g. This indicates that the conductive carbons have a positive effect on the electrode when we increase the the conductive carbon content till 7 %. But as we increase further till 15 % it starts decreasing and reaches 97 F/g for 15 % conductive carbon by weight. This suggests that the electrode starts having a negative effect of the conductive carbon as it affects the effective surface area available for energy storage by blocking the pores in the activated carbons and hindering ion transfer(5). In terms of ESR, trend in Fig. 4.2 shows that there is large variations in the readings for each electrode of the same composition, the range over the entire electrode set remains almost same for each composition (12). Hao Zhang et.al(5) suggested that as conductive additive percentage increases its ESR slightly decreases and beyond a certain percentage it levels off. The errors are contributed due to imperfect test setup, thus the resistance included along with electrode the factors of electrolyte & connections in the setup. According to Ioxus Inc. research data, their pressed R&D samples were showing 25% error in ESR measurement with the potentiostat setup. The electrodes prepared in this study did not undergo pressing so there is an addition of error since connectivity between the carbon particles is not uniform.

Figure 4.1 Capacitance behavior with change in electrode composition

Figure 4.2 ESR behavior with change in electrode composition

Errors in the values are also contributed due to inaccurate area of coupons from prepared samples. From the overall behavior, 7 % by weight of conductive carbon was deduced to be optimum amount to be added to the active carbon to enhance the performance of supercapacitor electrode. This composition of active and conductive carbons is used to prepare 5 electrodes of each of the thicknesses ranging from 50 to 250 microns. The coupons are tested for measuring capacitance and ESR. The results are obtained for capacitance in Farads and ESR in Ohms for coupon area of 4 cm². The capacitance trend depicted in the fig 4.3 shows that capacitance increases monotonically as we increase the thickness of the electrode. This suggests that electrolyte is permeable through the entire thickness of electrode. Beyond 250 microns the electrodes start to flake off as the withholding force of the coat onto the foil reduces below minimum. This limits preparation of more thicker electrodes as it affects its mechanical integrity. The fig 4.4 shows that the ESR remains almost the same for all the thicknesses as large variations are seen in reading of ESR but they lie in the same range for each of the thicknesses. The trend expected is capacitance should increase and the ESR should remain constant as we increase the thickness.
until a certain limiting thickness is achieved beyond which capacitance is not affected while the ESR increases drastically. This happens because the energy stored in the porous electrode becomes more than the energy paths available through the carbon and the substrate. This condition could not be achieved in our study due to production limitation discussed earlier.

The error bar suggests that ESR results have inconsistencies similar to that of the composition results with added factors such as non-uniformity in overall thickness of the electrode and manufacturing hindrances for thicker electrodes.

5) CONCLUSION

The active carbons for electrode were characterized to obtain the most suitable active carbon for electrode preparation. Electrode prototype was prepared with the selected materials. It was tested to measure impedance characteristics of the electrode. In the first step, the behavior of electrode was predicted for various compositions. The capacitance value increased with increase in conductive carbon wt. percentage from 5 to 7% and then capacitance decreased as it increased further. This showed that the composition of 7% conductive carbon was efficient composition amongst the 4 tested. The ESR behavior was also observed but the data didn’t serve good due numerous factors affecting the consistency of the ESR values. The optimum composition was used to prepare electrodes with increasing thicknesses. The capacitance results suggested that capacitance increases almost monotonically with increase in thickness of the electrode. ESR remains almost constant for the entire range of thicknesses. ESR inconsistencies can be defined due to manufacturing factors as well imperfectness in the test cell setup.

REFERENCES