STATISTICAL ANALYSIS OF ELECTRODE-ELECTROLYTE-SEPARATOR TO IMPROVE EFFECTIVENESS OF SUPERCAPACITOR

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ABSTRACT:

The supercapacitor is a booming technology whose popularity is increasing as the number of electric vehicles are increasing. The supercapacitor is a technology which will be a supporting pillar for electric vehicles and hydrogen vehicles to take the market. Supercapacitors will reduce stress on the main energy storage device thereby increasing their life and bettering performance. In the supercapacitor electrode, electrolyte and separators are the main parts. The effect of electrode, electrolytes, and separators have been extensively studiedseparately in the past, but their combined effect has not been studied. Each of the three parts has one important parameter which contributes the maximum in capacitance of supercapacitor. These parameters are taken into consideration and their individual and interaction effect on capacitance of supercapacitor is being studied in this paper. A statistical model has been used for analysis. The generated statistical model has been validated at a few points and error is within 5%. This statistical model can be utilized by researchers and manufacturers in due course.

KEYWORDS Capacitance, Electrode, Separator, Electrode, Separator

1. INTRODUCTION

A capacitor is an electrical storage device which has its electrical field separated by an insulator. The thing which makes supercapacitors "super" is their increased capacity for store large amount of energy which can be pushed in or flushed out very quickly. Today everyone wants to harness the electrical energy and for making that possible, it is crucial to have a good storage device [1]. Batteries have good storage capacity but their charging time is more as compared to supercapacitor and in today fast-moving world it is essential to have a storage device which can charge electrical energy just not fast but very fast [3]. Supercapacitors are used in hybrid vehicles, starter, uninterrupted power supplies, ships etc. They are also used in many sectors like space, defense, agriculture and communications [4][15]. There are various optimization and statistical techniques like artificial bee colony optimization, Ant colony optimization and genetic optimization which are incorporated for modeling of supercapacitor [5]. In this research full factorial sampling plan has been chosen with 3 factors and 2 level analysis. Capacitance is selected as an output parameter for optimization.

The popularity of supercapacitors is increasing day by day which improves in this device a very essential and important task. The electrode of a supercapacitor is where all the charges are stored. The various carbons used for electrode materials are biomass-derived Carbon, Vulcan Carbon, Pica Carbon, coconut-based activated carbon, carbon nanotubes, graphene, and various others. [6] [7] [8]. Metal oxides like Manganese Dioxide (MnO_2), Iridium Oxide (IrO_2), Niobium Oxide (Nb_2O_5), Ferrous Oxide (Fe_3O_4), and Vanadium Oxide (V_2O_5) are been extensively used for making supercapacitors. Several Types of Ternary Metal Oxide AB_2O_4, $ABO_{2/3/4}$, $A_3B_2O_8$are also finding its place as an electrode material [9] [10]. Out of this all electrode materials, manganese dioxide is extensively used for the manufacturing of supercapacitor electrodes. Electrodes are processed by various methods like conventional ball milling, forward reverse motion ball milling, jet milling and pulverization [11]. These methods do affect the capacitance values. The interface between or interaction between the current collector and electrode material also plays a role in deciding capacitance value.

Electrolytes play a role of charge-carrying in supercapacitors. Various Electrolyte materials are Potassium Hydroxide (KOH), Sulphuric Acid (H_2SO_4), Hydrochloric Acid (HCL), Lithium Hydroxide (LiOH), Sodium Hydroxide (NaOH), Sodium Sulphate (Na_2SO_4), Potassium Sulphate (K_2SO_4)and various others [12]. Non-acquis electrolytes like Molybdenum trioxide (MoO_3), Lithium Hexafluorophosphate ($LiPH_6$) and Lithium perchlorate (LiClO4)are also getting popular. Some solid or gel-type electrodes are also used like PVA/H_3PO_4 and PVA/LiOH [16] [17] [18]. The strength of these electrolytes affects the charge holding capacity of this device.

Another important component of the supercapacitor is separator but very less research has been done on it. Its interaction with electrode material and electrolyte materials need to be investigated. Separator does the work of separating the electrodes so that the positive and the negative charges do not short circuit. Polyamide and polypropylene polymer nonwoven fabrics, nylon, polyethylene, PVC and PVE are some materials that are used to make separators [13]. Organic materials are also used for making separators [14], but, very little attention has been given to separators for improving the performance of supercapacitors.

The main motive for this research paper is to improve the performance of supercapacitors by selecting the most significant factor from the electrode, electrolyte, and separators. Then use a statistical method to get the optimized results where the contribution of each factor and its interaction can be investigated to further work on it. This way best possible supercapacitor performance can be achieved.

In the second section of the paper is about various parameters of supercapacitors along with their significance. The selection of the most significant parameter along with its reasoning is done in the third section. It is followed by concluding remarks.

2. SIGNIFICANT PARAMETERS IN SUPERCAPACITORS

The main components of supercapacitors are electrode, electrolyte, and separators. There are many sub-parameters in these components which have been mentioned in Fig 1.

By referring various research articles by some of the co-authors and other researchers in same/similar areas, it was found that molar strength of electrolyte, Specific Surface Area (SSA) of electrode and absorption constant of separators have the most significant impact in the functioning of the supercapacitor in general and on capacitance value in particular. Absorption constant is the property of the separator and can be defined as the ratio of the wet weight of the separator upon the dry weight of the separator. In simple words, it can be desired as the capacity of the supercapacitor separator to store electrolytes. It also indicates the porosity of the separator material. A list of various parameters with decreasing order of their significance is given in Figure 1.

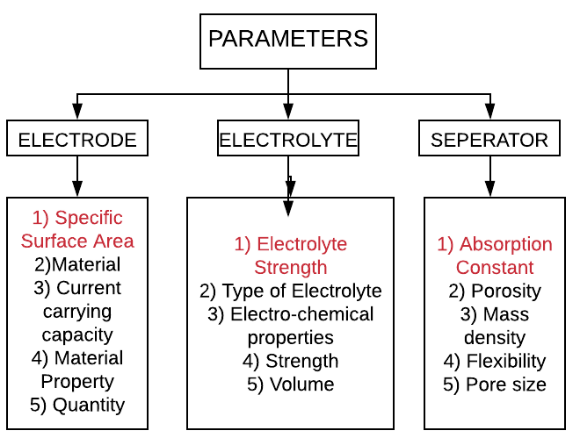

Figure 1. Various sub parameters of supercapacitors which affects the capacitance values

Parameters of supercapacitor for trials of full factorial design of experiments need a lot of investigations. Many factors may not have different levels of their values. There may be commercial or availability or technical or experimental constraints. Ideally, 3 or 4 levels 3-factor design of experiment trials for full factorial could have been taken. However, variation in separator materials parameters i.e. absorption constant is not possible for intermediate values between minimum and maximum. Similarly, SSA of carbon can be obtained in 3 to 4 levels as a limited number of carbons with various SSA are available in the market. Such restrictions are not there in electrolyte strength which is taken as the 3rd design of the experiment parameter. A full factorial sampling was created in which 5 levels of electrolytes were taken which are 0.1, 0.2, 0.3, 0.4 and 0.5. Molar of potassium sulphate. 2 levels of SSA were taken which are 250 and 900 grams per cubic centimetre and 2 levels of absorption constant were taken which are 3 and 13. The separator material polyethylene has absorption constant as 3 and AGM (All Glass Mat) separator has absorption constant as 13.

3. EXPERIMENTATION PROCEDURE

The supercapacitors are made according to the sampling table. The procedure for making supercapacitor module and testing is as follows:-

1) Wire mesh, separator and packing materials are cut according to the pre decided dimensions.
2) A paste of the electrode material made up of carbon materials and metal oxide is made, which is subsequently pasted on the wire mesh which is current collector.
3) Then the whole unit is packed as shown in Fig 2.
4) Then the packed unit is dipped in electrolyte to soak the electrolyte in it.
5) Then this unit is ready to use for electrical charging and discharging.
6) The supercapacitor is charged and discharged 12-15 times to make the electrons flow properly
7) Then the supercapacitor is charged with 2.2 Vsupply for about 5 minutes and then allowed to get discharged through short circuit wires.
8) From discharge curve capacitance and then by using concept of time constant, internal resistance is calculated as per requirement of their values.

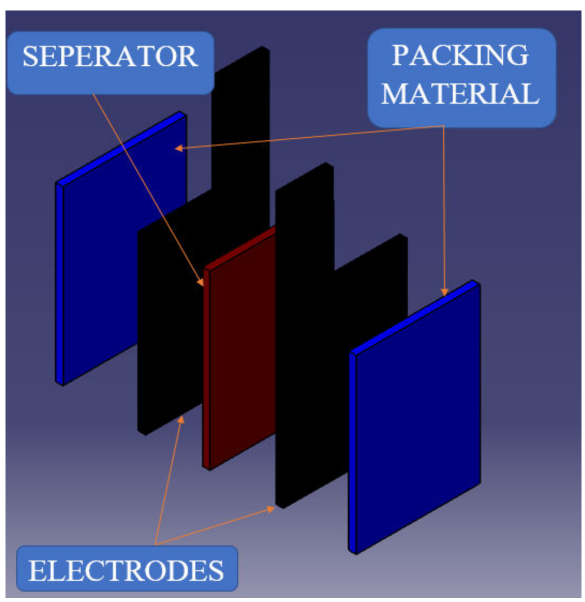

Figure 2. Assembly of supercapacitor module used for DoE trials

The output parameter selected for analysis is taken as the capacitance of the supercapacitor. There could be various output parameters for this experimentation such as equivalent series resistance, energy density, power density, total resistance and pulse current density. The true function of the supercapacitor is to store electrical energy and this can be calculated by capacitance, hence capacitance has been selected as the output parameter of this paper.

ANNOVA and Regression analysis are done which studies the effect of each parameter individually and combined which is an interaction effect on the capacitance of supercapacitor. The initial step is checking the multi-collinearity of the model. In statistics, multicollinearity (also collinearity) is a phenomenon in which one predictor variable in a multiple regression model can be linearly predicted from the others with a substantial degree of accuracy. The Variance Inflation Factor (VIF) is used for checking multicollinearity. In statistics, the variance inflation factor is the quotient of the variance in a model with multiple terms by the variance of a model with one term alone. It quantifies the severity of multicollinearity in an ordinary least squares regression analysis. It provides an index that measures how much the variance (the square of the estimate's standard deviation) of an estimated regression coefficient is increased because of collinearity.

Table 1. VIF values of various parameters

Term	VIF
Electrolyte Strength	1.01
SSA of electrode material	1.02
Absorption Constant of separator	1.01
Electrolyte Strength*SSAof electrode material	1.01
Electrolyte Strength * Absorption Constantof separator	1.01
SSA of electrode material* Absorption Constant of separator	1.01

From the table number 1 it can be inferred that the VIF is less. All the above selected parameters are free from multi collinearity.

FACTOR NAME
A – ELECTROLYTE STRENGTH
B – SSA OF ELECTRODE MATERIAL
C- ABSORPTION CONSTANT OF SEPERATOR

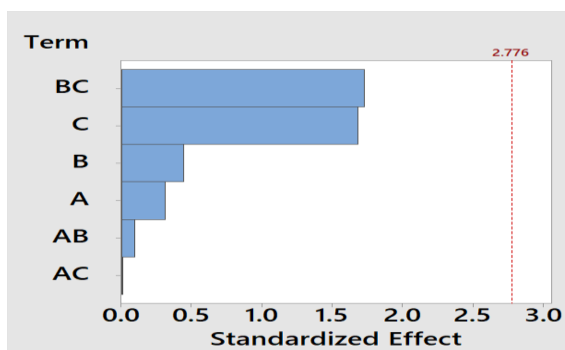

Figure 3. Pareto Chart of the standardized effect

Standard Pareto chart in figure 3 shows us how the three input parameters are affecting the capacitance of the supercapacitor. It has been inferred that specific surface area(SSA) of electrode material and absorption constant of separator has the good amount of significance on the capacitance of supercapacitor. In supercapacitor it is essential for the electrode material to be highly porous. But, the accessible surface area is more important than specific surface area. Since accessible surface area is not measurable, dependence on specific surface area increases. High SSA indicates that the pores on the electrode are highly scattered due to which the accessible surface area decreases. It is not possible to calculate accessible surface area by any measuring techniques or experimentation method. The reason why combined effect of SSA and absorption constant is high because the porosity of separator and electrode material play a very major role in determining the capacitance of the supercapacitor. Hence, it is been nicely shown in the experimentation that the combined effect of SSA and absorption constant has a good significance.

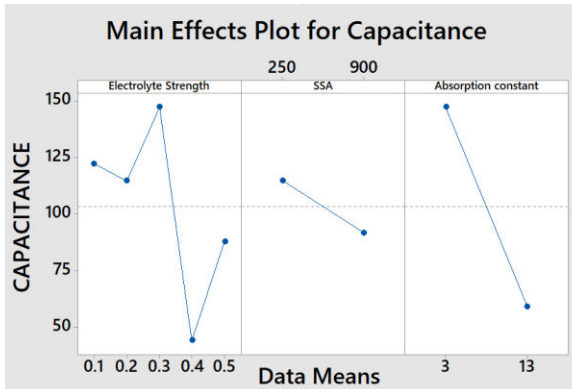

Figure 4. Main Effect plot for supercapacitor

Use a main effects plot as shown in figure 4 to examine differences between level means for one or more factors. There is a main effect when different levels of a factor affect the response differently. A main effects plot graphs the response mean for each factor level connected by a line. The capacitance of supercapacitor decreases significantly with increase of absorption constant. As the absorption constant increases, porosity increases of the separator along with pore density. This makes AGM separator structurally weak, making it prone to absorb carbon and metal oxide from the electrode. Thus due to absorption in separator the electrode material on current collector decreases and thus the Capacitance of the supercapacitor decreases. In PE separator which has absorption constant as 3 the carbon and the metal oxides from electrode are not absorbed by the separator and thus this makes PE structurally strong.

More electrolyte strength indicates that number of ions in the supercapacitor. But, number of ions have no role in the accumulation of the charge, hence what is observed that for any molarity the capacitance does not increase or decrease, but it has minimal effect. This is primarily because it does not play any role in holding the charge on the electrode surface. Electrolyte strength also does not have any effect on the redox reaction. From this output parameter a multi-variable and polynomial regression analysis is conducted and the equation achieved is as follows

Capacitance = -200.2 + 886.9*Electrolyte Strength + 0.7*SSA + 36.9*Absorption Constant 1.7*Electrolyte Strength*SSA - 0.08*SSA*Absorption Constant - 98.9*Electrolyte Strength*Absorption Constant + 0.17*Electrolyte Strength*SSA*Absorption Constant
-(1)

The R2 value of this equation is 88.87 % which is good as in models made by experimentation must have R2value more than 85%. The standard error of the estimate which is distance travelled by E-rickshaw shows the standard deviation of the residuals to be 20

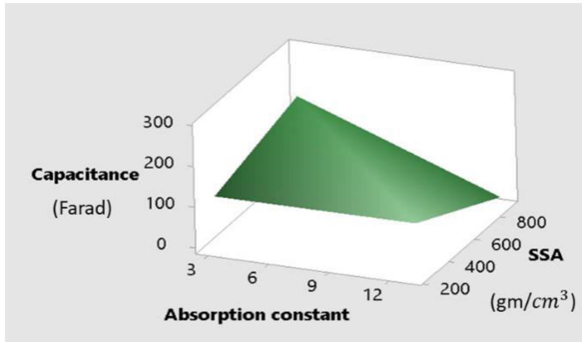

Figure 5.3D surface plot of specific surface area and absorption constant Vs capacitance of supercapacitor

In the surface plot which is in figure 5 electrolyte strength is kept constant as its significance on capacitance small. From the 3D surface plot it can be easily inferred that as absorption constant reduces the capacitance increases. The contour plot in figure 6 will give aneasier approach to determine the capacitance. In the figure 6. The electrolyte strength is kept constant, and the user can find the value of capacitance of the supercapacitor by plotting the points. It is observed in the figure 6. that highest capacitance of the supercapacitor is observed when the SSA is near 900 had absorption constant is near 4.

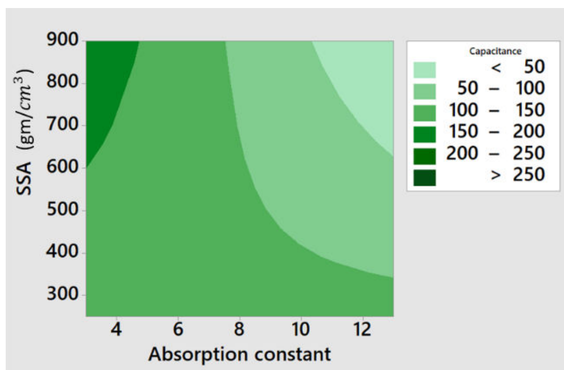

Fig 6. Contour plot of capacitance Vs specific surface area and absorption constant

4. CONCLUSIONS

It was expected that specific surface area would be more important than electrolyte strength and absorption constant. But, the role of absorption constant was unknown and in this research it ispredicted by using statistical method. There is need of looking at accessible surface area offered by each material by knowing its specific surface area. Interaction effects cannot be seen or predicted by any measuring technique. It is found that absorption constantis the most significant parameter. Supercapacitor manufacturers and researchers should take into consideration that the absorption constant of the material should be such that it maintains good structural stability for separator material which tends to become too spongy if absorption constant increases. Spongy separator ends up in absorbing some electrode materials which decreases the capacitance of the device. From this research, it is found that the separator material should be smooth with maximum amount of pores with compatible pore size to electrode materials. It is also found that further research can be carried out to study the exact behavior of the interaction between the absorption constant of separator and specific surface area of the electrode. It is also inferred that electrolyte strength does not play a major role in deciding the capacitance of supercapacitor. All the researchers working in the field of electrode materials and separators of electrical energy storage devices will be benefited by the presented results.

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