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Study of Carbon Materials and Effect of Its Ball Milling, on Capacitance of Supercapacitor

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Abstract

The various forms of energy are available in nature, however the electrical energy is the most convenient form of energy for any application. Due to this reason, day by day the demand of electrical energy is rapidly growing in this decade. There is always mismatch in time zone between availability of energy especially from renewable energy sources and demand. Thus, the storage of electrical energy is now becoming important. However, amount of electrical energy which can be stored is again a critical issue in many renewable energy systems. Supercapacitor can be a new technology for the storage of electrical energy. Supercapacitors are currently a prominent area of research for energy storage devices as they have high power density, long cycling time, and short charging time. Due to a short charging time feature of supercapacitor, in future it can have application in hybrid cars. Supercapacitor is similar to a regular capacitor in operation, however it offers a very high capacitance in a small package for achieving the requirement of power supplies. Capacitance, internal resistance, self discharge, ageing, pulse current, size, shape are some of the parameters in selection of supercapacitor in various applications. Capacitance value of capacitor is very important in energy storage system as amount of energy stored by capacitor is directly proportional to its capacitance value. The capacitance value of supercapacitor depends on types of carbon material and method of construction of supercapacitor. Various kinds of activated carbon materials are available with different pore size, pore density and specific surface area, are found more suitable to get higher values of capacitor. In this research work, the properties of various carbons are studied to select appropriate carbon material to construct the supercapacitor. Supercapacitor along with fuel cell can address many issues related to effective electrical energy storage and it can have number of applications in future. This research work also presents the effect of ball milling of an electrode material on the value of capacitance of an aqueous metal oxide based supercapacitor.

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Keywords: Electrochemical double layer capacitor[ECDC];ultra capacitor; Supercapcitor; Ball milling.

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1. Introduction

The electrical energy can be stored in the form of chemical energy with help of primary and secondary cells. The chemical action in primary cells is not reversible and hence the entire cell is required to be replaced by new one if the cell is discharged. The various examples of primary cells are zinc-carbon dry cell, zinc-chloride, mercury cell etc. However, the chemical reaction of secondary cell is reversible. Thus, if cell is discharged, it can be charged to regain its original state by charging it and its examples are Lead-acid battery, Nickel-cadmium, alkaline cell etc. The supercapacitor will stand in secondary cell category.

The development of any new device involves many factors such as design, material selection, making of prototype and optimization of process. However, at the design stage, many times the manufacturing requirements are not taken into account, which may lead to failure in commercialization of that device. Hence, in this paper it has been decided to focus on some issues to improve the performance of supercapacitor and it is also seen that its manufacturing can be cost effective. The low cost Supercapacitor can be used for Electric hybrid vehicles to meet the pulse current requirement which is required during starting of vehicle. At present, supercapacitors are used along with batteries/ fuel cells for such applications and due to the joint operation of supercapacitor and battery/fuel cells, the life of a battery/ fuel cell can be increased in comparison to standalone unit of battery or fuel cell[1]. Thus development of a low cost supercapacitor can be a step forward in electrically operated vehicles. Various carbon materials, carbon nano tubes and carbon aerogel as electrode material can provide a solution for constructing supercapacitor [2].Supercapacitors as energy-storage device involve a charge accumulation on the electrodes due to double-layer charge effect and pseudo-capacitance. Its operation consists faradic as well as non- faradic processes where faradic process has simple chemical reactions and non-faradic process does not use a chemical mechanism [3],[4]. The surface structure, pore density and pore size of electrode material play an important role in the charge accumulation process [5]. Hence the particle size of the electrode material also plays an important role in the construction of supercapacitor. The construction of supercapacitor consist of two electrodes, an electrolyte and separator pieces. These all components are then packed together and used as a conventional high value capacitance, which is called as supercapacitor or electrochemical double layer capacitor.

Conventional capacitors use dielectric material between two electrodes, which can sustain high voltages therefore they have high voltage ratings. Supercapacitor has two electrodes of same materials. Electrolyte material present between the two electrodes has high conductivity [6]. Such high ionic liquids offer very low resistance due to large number of ions. The capacitance is mainly decided by the specific surface area of the electrode material. Activated carbon has high specific surface area as compared to carbon nano tubes [7],[8]. An internal resistance of supercapacitor plays an important role in the power density of the capacitor. Various techniques such as addition of transition metal oxides using various concentrations of aqueous electrolytes, etc. can reduce internal resistance. Power density can be increased by the use of two different electrodes which allow increase in voltage. For large scale production and applications, cost reduction is a very important issue in designing of supercapacitor [9].

There are various types of supercapacitors. On the basis of construction, they are stacked type or rolled type. However, the laboratory research can be done with stacked type of construction as it does not require any machinery, so stacked type is considered for present research work. Based on types of electrolyte used, it can be categorised as aqueous or non-aqueous. An aqueous type is taken for research as it is simple to construct, it has quick stabilisation and it's construction is also less costly. Metal oxide based aqueous supercapacitor is voltage compatible with conventional batteries as well as photovoltaic modules [10]-[12]. Careful selection of low cost activated carbon material and processing it as per requirement is going to play a key role in development of cost effective supercapacitor. Recently, new modelling techniques have been used to develop supercapacitor[13].

This paper is presenting as follows: Section II describes experimentation for selection of carbon materials. Section III contains study of effect of ball milling of effective carbon on capacitance of a supercapacitor. Section IV gives concluding remarks based on the experimentation on supercapacitor.

2. Selection Of Carbon Material For Supercapacitor

Supercapacitors are of various types. But, commercially available supercapacitors are of non-aqueous type. For higher capacitance value, rolled type of construction is more suitable. However, laboratory research is difficult on rolled type construction as it requires capacitor winding machine and other high end equipment used in conventional capacitor manufacturing. Generally, stacked type of supercapacitor, prototype is prepared in laboratory and then same materials are used in rolled type of supercapacitor fabrication at industry.[14] This paper presents the construction of stacked type of supercapacitor as shown in Figure1. This construction shows the two electrodes with alternate layers of separator material pieces. They are packed together by using adhesive which is pasted at the end of separator pieces.

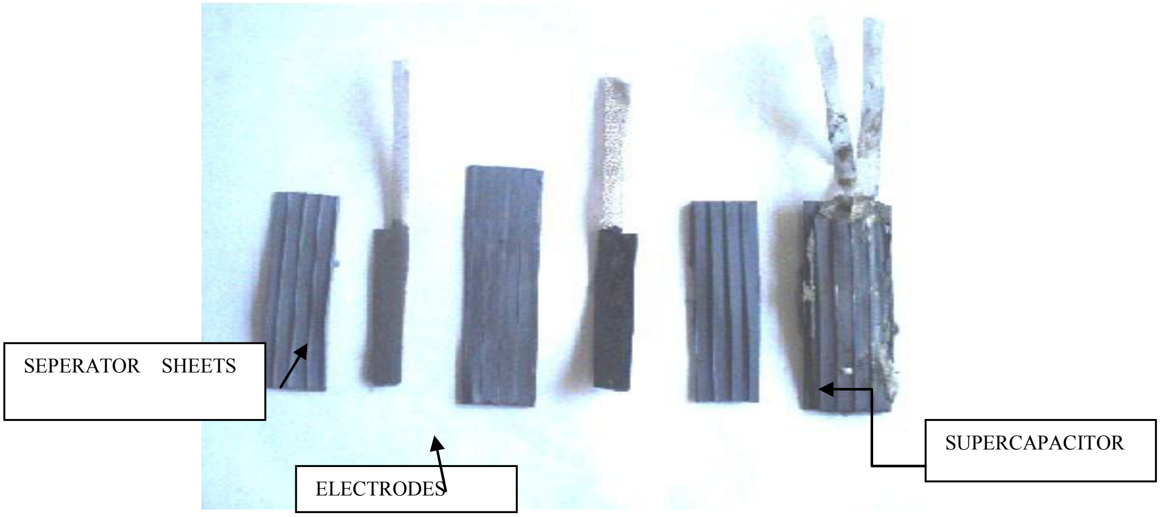

Fig.1. Construction of electrodes and capacitors

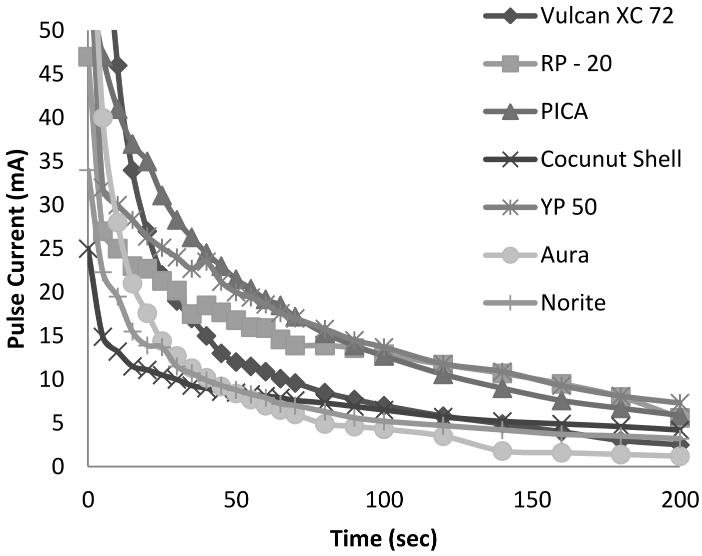

Fig. 2. Supercapacitor discharge currents with the use of various carbon materials

Almost all materials containing high fixed carbon content can potentially be activated. The most commonly used raw materials are coal, coconut shells, wood, walnut shells, peach pits, nutshell, peat and petroleum based residues, but invariably their commercial limitation lies in raw material supply. We selected 8 carbons having specific surface area more than 150 square metres per gram. Figure 2 shows the discharge characteristic of supercapacitor made up of various high specific surface area carbon materials such as Vulcan XC -72, RP-20, YP-50, PICA carbon (Phenolic Impregnated Carbon Ablator), Norite carbon, coconut shell and Aura carbon, which are commercially available.[15]

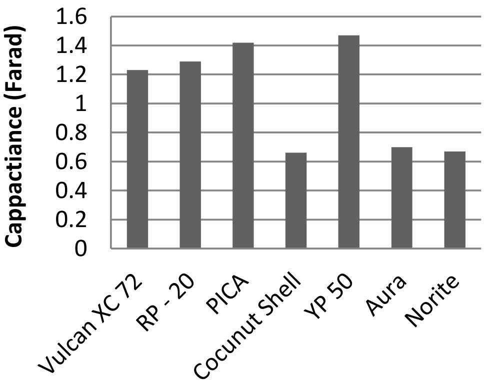

Fig. 3. Capacitance of supercapacitor with the use of various carbon materials

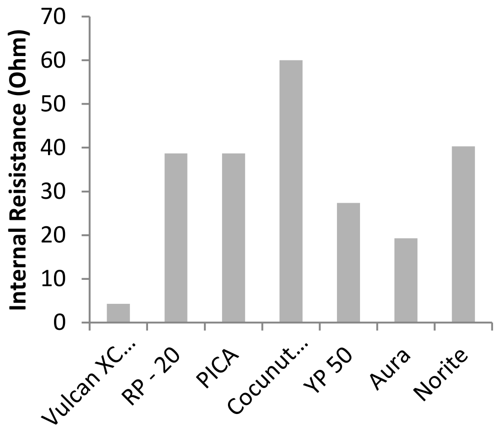

Fig. 4. Internal resistance of supercapacitor with the use of various carbon materials

Figure-3 and Figure-4 shows the capacitance and internal resistance of these supercapacitors which are made up of those carbon materials. Vulcan XC- 72 is more suitable for supercapacitor as it give low internal resistance and good capacitance. After selecting best carbon material for supercapacitor electrode, it was decided to see the effect of ball milling on the capacitance of supercapacitor.[16,17] The effect of loading of carbon material is also studied. The results are presented in following section.

3. Effect Of Ball Milling And Electrode Material Loading On Capacitance

All material having high contain of fixed carbon content can be activated. The most commonly used raw materials having high carbon contain are coal, coconut shells, wood, walnut shells, peach pits, nutshell and petroleum based residue. But, Vulcan XC -72 is used as a carbon material for making electrodes of electrochemical double layer capacitor as it gives better performance in comparison with other carbon material. Metal oxide i.e. manganese oxide is added in the carbon material to increase the capacitance. Many transition metal oxides are suitable in electrodes. The various metal oxides such as ruthenium oxide, stannic oxide, manganese oxide, vanadium pentoxide are generally used as they can sustain acidic environment. The particle size mismatch of carbon materials and these metal oxides is a main issue in charge storage on electrode surface. It was felt that mechanical processing i.e. crushing of electrode material can address this issue. Hence Vulcan XC- 72 and manganese oxide is mechanically crushed in ball mill. A ball mill, a type of grinder in which an electrode materials is crushed in presence of Zirconium oxide balls. Then it is used to make sandwich type of electrochemical double layer capacitor as shown in Figure 1. Thus, ball milling reduces the particle size of the metal oxide and the carbon material. Ball milling also helps in better mechanical mixing of metal oxide and Vulcan XC- 72, which is used as electrode material[18,19,20]. Ball milling up to 12 hours is considered as more ball milling results in increase in cost, thereby making the device very less cost effective. Figure-5 shows the effect of ball milling on capacitance with activated carbon/ manganese oxide based electrochemical double layer capacitor.

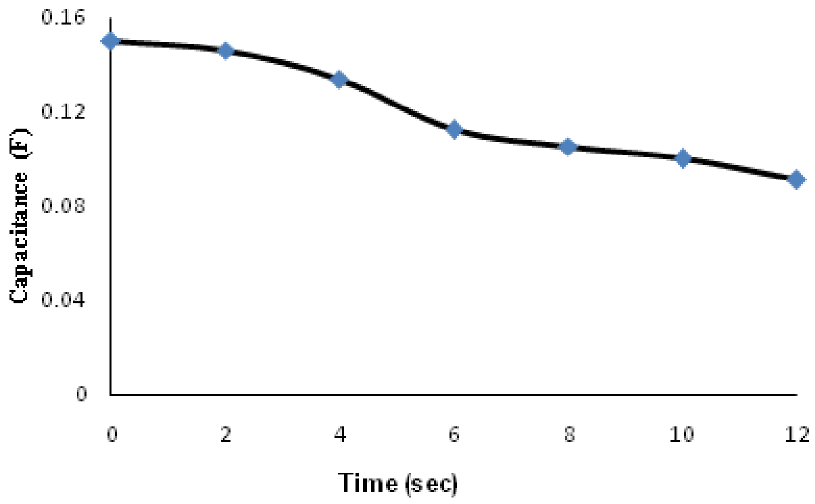

Fig. 5. Effect on capacitance value of supercapacitor for separately ball milled Manganese oxide and Vulcan XC-72

Figure-5 shows the variation in the capacitance value with ball milling time. It was observed that the capacitance is decreasing with increase in time of ball milling. The improvement in capacitance value was expected with increase in ball milling time, but capacitance was decreased. We felt that it could be due to mismatch of particle size[21,22].

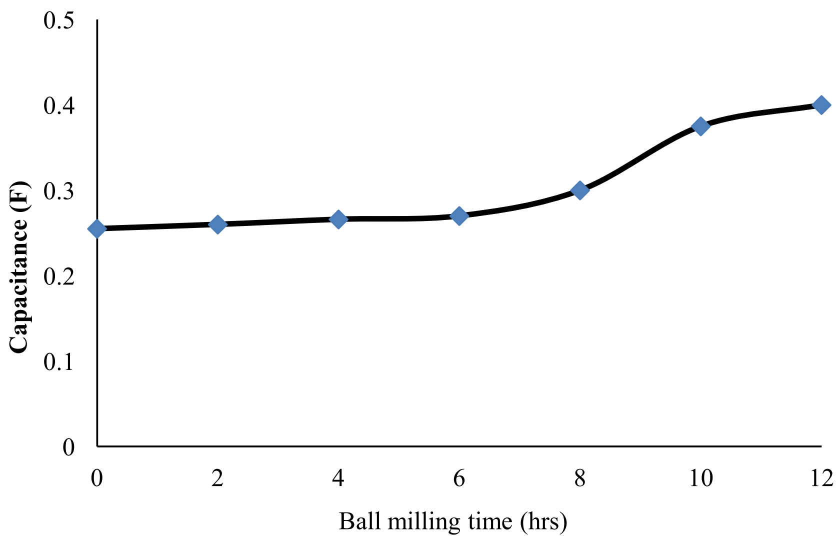

Fig. 6. Effect on capacitance value of supercapacitor for together ball milled Manganese oxide and Vulcan XC-72

So it was advisable to ball mill the manganese oxide separately and then mix it with Vulcan XC-72.When the capacitor was fabricated from separately ball milled manganese oxide, capacitance was increased with ball milling time, which is shown in Figure-6

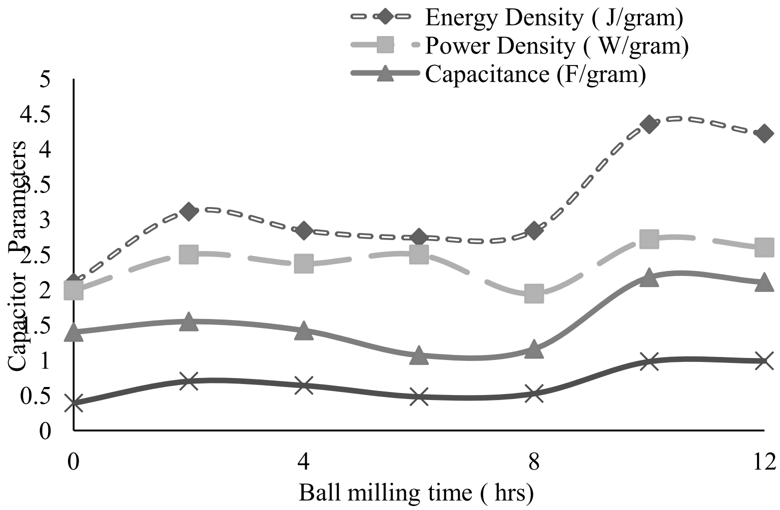

Fig. 7. Effect of ball milling on various parameters of a Manganese oxide and activated carbon based electrochemical double layer capacitor

Figure 7 shows the variation in the power density, energy density, capacitance density per gram and capacitance density per cm^2 for various ball milling time of electrode material consisting of manganese oxide and activated carbon in weight ratio of 1:1. It can be observed that these parameters are decreasing as the ball milling time is increased and again parameters are increasing with increase in ball milling time.

4. Conclusions

All Characterization of supercapacitors using various high specific surface area carbon materials has been studied. Manganese oxide is used as a metal oxide in electrodes of Supercapacitors. Size of metal oxide particles needs to be matched with size of carbon material particles to maximise the capacitance. Vulcan XC -72 is found to be better than many processed carbon grades especially made for supercapacitor electrodes. Effect of ball milling has been studied to decide its use in manufacturing processes. Ball milling improves the capacitance as the discharge characteristics gets shifted upwards. Loading of carbon material and metal oxide on current collector also affect the discharge characteristics. A loading of 20 to 30 mg / cm^2electrode material on current collector gives better discharge curves and hence the capacitance values. Various carbon materials may show better discharge characteristics. Weight density of the material plays important role in the value of material loading for electrode. Finally, we conclude that Vulcan XC- 72 and manganese oxide in the ratio of 1:1 with 10 hour ball milling and loading of about 25 mg /cm^2 is most suitable for development of low cost supercapacitor.

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