Low-cost Supercapacitor Using Graphite-based Graphene and Activated Carbon Derived from Scrap Rubber Tyre

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***Abstract*: Supercapacitors has been researched extensively to meet increasing demand for energy storage devices possessing high power, high energy, and long cycle life. Activated carbon materials used in the supercapacitor electrodes have limited specific capacitance, and energy density in-spite of possessing the advantage of long cycle life and high-power density. To mitigate these shortfalls in the activated carbon materials, the graphene, a monolayer of carbon atoms which is extremely thin, chemically stable, and lightweight material, is an attractive option for the SC electrodes. The thermally and chemically synthesized activated carbon nano materials (AC_{SRT}) is derived from the scrap rubber tyre (SRT) and synthesized graphene (G_{SO}) is derived from the graphite oxide (G_O) as a cost-effective alternative to obtain higher capacitance and conductivity of the developed prototype supercapacitors. The SCs using two separate electrodes of G_{SO} and AC_{SRT} are also used to develop hybrid supercapacitor for exploring its performance in terms of enhanced capacitance, internal resistance and voltage window for higher power and energy density. The performance of the developed prototype supercapacitors is investigated and presented in this research paper.**

***Index Terms: Supercapacitor, graphene, oxidation, microwave*, grinding, sieving.**

I. INTRODUCTION

The electrochemical double layer capacitor (EDLC), often known as a supercapacitor, has the unique capability to supply fluctuating, transient, as well as instantaneous power demands [1]. Supercapacitor have gained an importance in the field of peak power supplies, medical equipment, pulsed lasers, space crafts, regenerative braking energy recovery in elevators [2], military equipment and hybrid energy storages comprising of batteries and supercapacitors (SCs) for electric vehicles. Supercapacitor electrode materials mainly comprise of carbon nano materials in different forms such as graphene (G), nano tubes, nano wires which give superior characteristics in an organic electrolyte but their overall commercial costs are much higher. Most commercial supercapacitor use activated carbon obtained from the carbon precursors for electrodes with active surface area ranging from 1000-1500 $m^2.g^{-1}$, that result in up to 500 $F.g^{-1}$ [3, 4]. The developed surface area of such activated carbon materials is essentially consisting of micropores (<2nm), mesopores (2-50nm) and macropores (>50nm), which gives a specific area as high as 3500 m^2g [5]. It is reported that the rice husk as a precursor material to derive activated carbon material resulted in 2523.4 m^2g^{-1} area with average pore size of 2.2 nm [6]. Biomass such as tea bark, Aloe vera, oil palm shell, banana peel, tea waste, kenaf etc as a precursor carbon material has been researched by the researchers to obtain AC. One of the reported studies is associated to activated carbon derived from kenaf as carbon precursor material which give capacitance up to 242 Fg^{-1} on pyrolysis [7]. Novel green approach research has also been reported wherein biomass of bougainvillea flowers is used to derive mesoporous perforated graphene which resulted into surface area of 850 m^2g^{-1} with specific capacitance of 458 Fg^{-1} [8]. An appropriately selected materials followed by their activation process yields cost-effective carbon material for supercapacitor electrodes with desired characteristics. The scrap rubber tyre as precursor carbon material have not been researched extensively and its use with synthesized graphene (G_{SO}) obtained from the graphite oxide to form hybrid electrode of the SCs, which is new research explored through laboratory testing of prototypes. Activated Carbon (AC) obtained from the SRT and graphite oxide along with synthesization methodology and fabrication of prototype SCs is discussed in this research paper.

This paper is organized as follows; section II focuses on the literature research, section III deals with information about experimental setup and methodologies used in the research work and section IV presents results obtained with various experimental trials followed by concluding remarks in section V.

II. MATERIAL TECHNOLOGY

A. Activated Carbon from SRT

The solid residue after pyrolysis of scrap rubber tyre (SRT) contains carbon black and the mineral matters. Only few studies are researched based on pyrolysis of SRT in a nitrogen atmosphere using a fixed-bed batch reactor at 300-720^{O}C [9]. Elemental analysis of the carbon obtained from SRT gives 71-80 % of carbon, 7 % of H, 5.4 % of Fe, 0.4 % of N, 2.8 % of S, 2.3 % of Zn, 1.3 % of Ca, ZnO-2%, 8 % of ash [10]. Such carbon material from SRT need to be synthesized to obtain activated carbon nano particles.

B. Carbon Synthesisation and Activation

The synthesisation of carbon material is done through appropriate ball milling to obtain nano particle size and this method refers to creation of functional materials by mechanochemical synthesis. Under certain processing conditions, the carbon particles can be ground to as small as 100 nm. This process has been employed to transform carbon nano tubes into smaller nano particles. It is reported that the unique carbon nanostructures including carbon nanotubes and carbon onions are synthesized by high-speed ball milling of steel balls under high temperatures induced by collision-friction energy resulted in phase separated unique carbon nano material [11]. It is reported that the supercapacitor capacitance is increased on grinding the metal oxide and carbon materials up to twelve hours. It is also reported that the iron oxide takes the form of 6-7 nm particle size on 14 to 28 hours of ball milling [12].

Porosity properties, especially surface area is one of the key factors in producing supercapacitors with the higher energy with electrical conductivity and porosity properties influenced by the particle size in electrodes made from carbon precursor materials. The variations in particle size are obtained by different treatments along with grinding and sieving process on the AC. In the case of rubber wood carbon, the KOH activation with carbonization of electrodes at 600^{0}C in N_2 gas environment and then activation by CO_2 at 900^{0}C for 2 hours resulted in 38-53 μm particle size [13].

The nitrogenated carbon material exhibits pseudocapacitive behaviour with an increase in capacitance twice to that of plain porous carbon. Further, nitrogenated carbon resulted in improved cyclic stability due high capacitance retention even after widespread cycling. Most importantly, the nitrogenated carbon show battery-like characteristics [14]. The adsorption of nitrogen molecules affects the available surface area for the double-layer formation in the micropore region. This structural and chemical modification of the nitrogenated carbon serves as a control mechanism to access the active molecules in the micropores, thus, increasing its capacitance while cycling. The nitrogen adsorption isotherms lead to development of the porosity by the activation process.

C. Graphene Oxide and Graphene

Graphene oxide (G_O) is useful and promising material for graphene-based applications in electronic, optics, energy storage, and biology. The G_O was only a simple and multilayer graphene films and bulk structures by reduction. Graphene prepared from the G_O is considered as new electrode material as it has high conductivity, large surface area, flexibility, and chemical stability. In contrast to the conventional materials, the effective surface area of graphene material does not depend on the distribution of pores at solid state, therefore, this leads to the better performance of the supercapacitor. Recent studies demonstrated a great amount of unique chemical, optical and electronic properties of G_O that allow it as independent nanomaterial possessing a large area of applications. It represents the ultra-large organic molecule containing 2D carbon mesh. G_O particles are highly hydrophilic and form stable aqueous dispersions in wide range of concentrations in organic solvents [15]. It is single atom carbon layer with both surfaces modified by oxygen containing functional groups, like 2D carbon G_O with single or multilayer structure. Basically, graphene is a single layer of carbon atoms in a hexagonal arrangement with sp2 hybridization.

Graphite is a stack of a large number of layers of graphene on each carbon atom, having the z-axis perpendicular to the layers of graphene. The conventional graphene-based SCs use G_{RO} in a powder form wherein, the particle size can be one of the important factors affecting the SC performance. The study associated to effect of particle size of G_O powders for the electrochemical performance of graphene-based supercapacitors has been reported, wherein the G_O powders with three different particle size distributions were used for the electrochemical tests using simple microwave irradiation. The chemical characteristics and specific surface areas of such G_{RO} powders synthesized by microwave irradiation were nearly the same for all cases. However, the SC using these powders with a medium particle size showed a higher specific capacitance of 109.1 F g^{-1} [16] with a lower internal resistance and efficient charge transfer and thus, provides an effective method to enhance the performance of the G_{RO}.

D. Synthesis of Graphene Oxide

The recent methods of making graphite oxide (G_O) based on the ability of layered graphite for intercalation. It allows atoms of active metals and some types of oxidation agents to penetrate between flat carbon layers of crystalline graphite increasing interlayer distance and modifying the surfaces of layers by chemically bonded functional groups. The action of suitable oxidation agents causes complete disassembling of graphitic crystal into separate carbon monolayers with chemically modified surface. The known methods for preparation of G_O include application of strong acids (nitric and/or sulfuric) and potassium chlorate. The most popular method uses a mixture of concentrated H_2SO_4, $NaNO_3$ and $KMnO_4$. The reaction catalysed by potassium hydroxide (KOH) gives partially reduced G_{RO} for dispersibility in wide range of solvents [17]. A general two step method reported for growing hydroxide and oxide nanocrystals of the iron family elements (Ni, Co, Fe) on graphene with two degrees of oxidation, which leads to different nanocrystal growth behaviours on low-oxidation graphene sheets (G_S) and highly oxidised G_O in hydrothermal reactions. Adjusting the reaction temperature can further control the material grown on graphene. For materials with weak interactions with graphene, increasing the reaction temperature can lead to diffusion and recrystallization of surface species into larger crystals, even on highly oxidized and defective G_O [18]. The results suggest an interesting new approach for controlling the morphology of nanomaterials grown on graphene by tuning the surface chemistry of graphene substrates.

E. Aqueous and Semi-aqueous Electrolytes

The desired characteristics of the SC is coupled with the selection of electrolyte materials with trade-off between high power density and high energy density. Power density is strongly reliant on the electrolyte conductivity and hence internal resistance and high energy density on the voltage window. Organic or non-aqueous electrolytes, such as acetonitrile is the most commonly used in commercial devices, due to their higher dissociation voltage. However, the resistivity of organic electrolytes is higher and therefore, limits the cell power. An aqueous electrolyte, such as sulphuric acid and potassium hydroxide [19] have higher conductivity than organic electrolytes and lower internal resistance and thus higher pulse power delivery. It is reported that the hydrogel possesses the conductivity of 0.0154 Sm^{-1} and introduction of Aloe vera gel (AVG) to polyvinyl alcohol (PVA) increases the conductivity of hydrogel [20].

III. METHODOLOGY

The experimental work done is associated to develop AC_{SRT} material from the scrap rubber tyre and G_{SO} material from the G_O by chemical and thermal synthesization for the fabrication of SC electrodes. The electrolyte choice for the fabrication of prototype SCs is restricted to the aqueous H_2SO_4, KOH and semi-aqueous AVG for the experimental analysis. A laboratory set up for the preparation of electrode materials and testing of SC prototypes comprises of auto control muffle furnace, nitrogen gas cylinder with regulator control, ball milling machine with steel balls, magnetic stirrer with hot plate, hot press machine, least count digital weighing machine, small range LCR meter, cylindrical SS-310 reactor, DC regulated power supply, separators and substrate materials, chemicals. Typical instrumentation used in the laboratory and customised design of SS-310 cylindrical reactor for the pyrolysis and thermal synthesization is shown in the Figure 1.

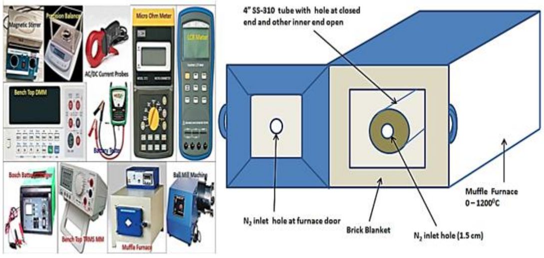

Figure 1. Instrumentation and Furnace Reactor

A. Carbon and Graphite Material Synthesis

Sample 50-gm SRT of lorry is selected for the nitrogenated pyrolysis in furnace reactor having inlet pipe connected to the nitrogen gas cylinder through gas pressure regulator to remove oxygen. The outlet pipe of the reactor is connected to the exhaust system. Furnace timer is set for $800^{O}C$. It took 50 minutes to reach to $550^{O}C$ and 70 minutes to reach $800^{O}C$. The selected sample SRT material is pyrolyzed for two hours at $800^{O}C$ and allowed to cool for several hours. Final char residue of 50 gm SRT found to be 16 gm. This residue is ball milled for 12-14 hours to reduce material particle size. The ball milled material is then heated in the reactor for an hour at $800^{O}C$ in a nitrogenated atmosphere. The balance residue after second stage heating was found to be 13 gm. To mitigate impurities in final residue, filtration and several steps of chemical synthesisation is done on 5 gm of derived carbon in a 100 ml hydrofluoric acid (40%) and 5 ml nitric acid and stirred it for 8 hours. Then it was filtered by using Watman filter paper No.42 and thereafter water wash was done three times followed by filtering every time and then finally ethanol wash was done with 50 ml ethanol. After this process, the remaining new carbon powder was allowed to heat in the furnace at $200^{O}C$ for 1 hour. The powder residue after complete process of activation was 4.2 gms, which is named as AC_{SRT}. Characterization of the AC_{SRT} is done in the C-MET Pune laboratory on cyclic voltammetry to confirm its capacitive behaviour. In the second stage, the graphite oxide (G_O) is derived from the raw graphite in the powder form by mechanochemical synthesis and then thermal synthesis carried out in the furnace reactor at $500^{0}C$ for 2 hrs. The final G_O thus obtained is chemically synthesised in the same manner as that of AC_{SRT} synthesis to obtain graphene from synthesized graphite oxide G_{SO}.

B. Fabrication of Supercapacitor

SC electrodes of using $3cm^2$ current collector are fabricated by pasting the slurry of AC_{SRT}, G_{SO} and AC_{SRT}-G_{SO} material on the current collector. The slurry is made by using propanol as a binder. The current collector used are of SS-310 wire mesh of 100 holes / inch. The fabricated electrodes were given mild heat treatment to make it completely dry. A different SC cells are then made by using fabricated electrodes with porous polyethylene battery type separator in between the two electrodes. The H_2SO_4 and KOH are used as aqueous electrolyte as choice to obtain higher conductivity. Similarly, SC cells are fabricated by using AVG as semi-aqueous gel electrolyte to exhibit the characteristics in between aqueous and organic electrolyte with higher voltage window. The commercially available AVG with 97 % moisture / water and 3 % of alcohol-based matters selected as semi-aqueous electrolyte for the developed SC prototype cells. Figure 2 show the fabricated prototype electrode design and laboratory characterization of the fabricated SC cell.

Figure 2. Prototype electrode and SC cell testing

IV. RESULTS AND CONCLUSION

A. Electrical Characteristic Results

The results as tabulated in Table 1 are obtained from the 3 cm^2 electrode used in the prototype SCs fabricated from the AC_{SRT} and G_{SO} electrodes with H_2SO_4 and KOH as aqueous electrolyte. The similar results are also tabulated in Table 2 with AVG as semi-aqueous electrolyte. These results are corelated and compared in terms of the maximum discharge current (I_{max}), internal resistance (R_{in}), voltage window (V) and Capacitance (C) for the selected electrolyte used in the developed SC prototypes.

Table 1. SC results with aqueous electrolyte

Electrode Material	I_{max} (mA)	R_{in} (Ω)	C (F)	V (V)	Electrolyte Aqueous (2 mole)
AC_{SRT}	43	24	0.8	0.9	H_2SO_4
G_{SO}	67	9	1.0	1.0	
AC_{SRT}-G_{SO}	56	14	0.9	0.9	
AC_{SRT}	49	13	0.9	0.9	KOH
G_{SO}	69	7.5	1.1	1.1	
AC_{SRT}-G_{SO}	62	12	0.9	1.0	

Table 2. SC results with semi-aqueous electrolyte

Electrode Material	I_{max} (mA)	R_{in} (Ω)	C (F)	V (V)	Electrolyte Semi-aqueous
AC_{SRT}	36	22.8	0.9	1.9	AVG
G_{SO}	41	18	1.2	2.1	
AC_{SRT}-G_{SO}	37	19	1	2.0	

B. Conclusion

Obtained results of the SCs developed from the AC_{SRT} seems somewhat inferior as compared to results obtained from the G_{SO} and AC_{SRT}-G_{SO}

electrodes. It is observed that the SC using AVG as semi-aqueous electrolyte exhibit higher voltage window, which is desirable for the higher energy density. On the contrary the dissociation voltage for the aqueous electrolytes is low as expected. It is also observed that the capacitance value in the case of G_{SO} electrodes with semi-aqueous electrolyte is superior as compared to the aqueous electrolytes, however, the conductivity in the case of aqueous electrolytes is observed to be superior. Thus, it is concluded that the SCs fabricated from the G_{SO} and AC_{SRT}-G_{SO} exhibit somewhat higher values of capacitance and dissociation voltage for the semi-aqueous electrolyte.

V. REFERENCES

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