



## Capacitor Behaviour of Activated Carbon from Used Tea Dust Powder

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Based on the energy form waste concepts we present the results of our study of utilizing used tea dust for preparing carbon, called the biomass carbon. Tea dust after decocting has been selected as a low cost source of producing the carbon. Virgin carbon is produced by heating the tea refuse around 280 °C for 2 h and activated carbon is produced using zinc chloride. After physical characterization, the biomass derived carbons have been tested in 3 M KOH electrolyte for the possible application as electrodes in electrochemical double layer capacitors. Cyclic voltammetric studies on the activated tea carbon show significant improvement in the capacitance values over the virgin sample. The study suggests the production of low-cost carbons from house-hold wastes for an important scientific and engineering application.

**Keywords:** Activated carbon, Electrochemical properties, Tea waste, Biomass carbon.

### INTRODUCTION

Biomass, the fourth largest energy source in the world, provides about 13 % of world's energy demand<sup>1</sup>. Globally, biomass has an annual production of 220 billion over-dry tons and India produces 350 million tons of biowaste per year<sup>2</sup>. A variety of biomass is being utilized as the low-cost source of producing activated carbon powders. The biomass precursor, such as agricultural residue including oil-palm stone<sup>3</sup>, pistachio-nut shells<sup>4</sup>, candle nut shell<sup>5</sup>, teak sawdust<sup>6</sup>, fir wood<sup>7</sup>, rice bran<sup>8</sup> and coffee endocarp<sup>9</sup> and rubber wood sawdust<sup>10,11</sup> are the most potential candidates for carbon with interesting physical, chemical as well as electrochemical features. Needless to mention that carbon and its varieties find multifarious applications in domestic, industrial, pharmaceutical, electronics and energy sectors.

Speaking of energy, electrochemical double-layer capacitors (EDLCs) are promising high power gadgets with the ability to meet high power demands, say for instance, in the fuel cell powered electric vehicles. Other applications include diesel engine starting systems, cordless power tools and emergency and safety systems. Capacitors predominantly store energy by the accumulation of charges at electrodes by electrostatic forces<sup>12</sup>, without relying on charge-transfer reactions like in the operation of conventional batteries (batteries use chemical reactions). Compared to a battery, an electrochemical capacitor has the advantages like higher charge and discharge rates (high

power density), longer cycle-life (> 100,000 cycles), low toxicity materials, operation over a wide temperature range, low cost per cycle. However, these are offset by certain limitations like higher self-discharge rate, lower energy density, lower cell voltage, poor voltage regulation, high initial cost. Hence addressing these issues has formed research topics since recent past.

Carbon is an engineering material and in electrochemical double-layer capacitor devices the carbon electrodes contribute to a larger extent towards the total material cost<sup>13</sup> and hence the development of low-cost carbons with high specific energy and specific power is a key to the widespread application and commercialization of electrochemical double-layer capacitor systems. A recent trend in carbon supercapacitor or electrochemical double-layer capacitors electrodes has been the use of biomass waste materials to produce activated carbons. Electrochemical double-layer capacitors with carbon electrodes derived from biomass such as seaweed biopolymers<sup>14</sup>, waste coffee beans<sup>15,16</sup>, fir wood<sup>17</sup>, corn grains<sup>18</sup>, banana fibers<sup>19</sup> and sugar cane bagasse<sup>20</sup> have been reported. The choice of carbon precursor and activation conditions determine the electrochemical performance, with carbon surface area, pore-size distribution, electrical conductivity and the presence of electrochemically active surface functional groups all affecting double-layer capacitance. In a way of sourcing out a low-cost precursor for quality carbon the authors have decided to convert a material *hitherto* thought as a waste or refuse, into a valuable

product, especially from a house-hold trash for an important application. Thus the aim of the study is to use decocted tea dust refuse/waste which is being collected daily at cafeterias or homes. More importantly, the tea dust waste has no nutrition or food value and hence it is considered a waste normally. So we have attempted to extract the potential of this day-to-day collected tea refuse by way of producing (activated) carbon samples. The tea waste derived activated carbon powders have been assessed for the possible application as electrode materials in electrochemical double-layer capacitor.

It is to be mentioned that commonly used activating agents like KOH, ZnCl<sub>2</sub>, K<sub>2</sub>CO<sub>3</sub> *etc.* accompany enormous heat evolution during the activation process and that subsequent heat liberation during the activation process has been attributed to the evolution of interesting physical features in final carbon material. Nevertheless, research activities with from other varieties of tea or activating with other chemicals may be indispensable but forms the objectives of future work. Hence, our preliminary work is to obtain carbon from used tea powder refuse by simple heating and further to produce activated carbon powder by activating with zinc chloride. Physical as well as electrochemical characterization studies were conducted to understand the capacitive behaviour of the virgin tea carbon (VTC) and zinc chloride activated tea carbon (ZATC) samples in KOH electrolyte for an important application as electrodes in electrochemical double layer capacitors.

## EXPERIMENTAL

**Preparation of virgin tea carbon (VTC) and zinc chloride activated tea carbon (ZATC):** The tea refuse was collected from our home and washed several times with hot distilled water. The raw material, now called the carbon precursor was dried overnight in an air oven and then heat treated in a furnace at 280 °C for 2 h and finally ground to produce VTC. To prepare ZATC, the washed and dried tea powder refuse was treated with concentrated solution of zinc chloride in the weight ratio of 1:1 tea:zinc chloride. The content was stirred well in a magnetic stirrer at 60 °C for 48 h and dried in an air oven and then heat treated in the furnace at 280 °C for 2 h. The heat treated sample was washed several times with de-ionized water until the filtrate is neutral to pH and its conductivity is minimal. This sample was dried, ground and sieved to 250 mesh in size.

**Physical characterization and electrochemical studies:** Thermal degradation characteristics of the tea dust refuse were studied using thermogravimetry. Experiments were performed on a TGA-50 Analyzer. 2 mg of the sample was heated up to 450 °C at a heating rate of 20 °C min<sup>-1</sup> in air. The elemental analysis (ultimate analysis) of the ZATC was carried out using Vario ELIII CHNS/O Analyzer. Powder X-ray diffraction patterns were recorded between 10 and 80 ° on an X'Pert Pro X-ray diffractometer with CuK<sub>α</sub> radiation source. The surface morphology of the VTC and ZATC was studied using S-3000H model microscope. Surface area of the synthesized powders was determined by BET (Brunauer, Emmet and Teller) method using low temperature nitrogen adsorption (Quanta Chrome Nova 1000, US). Cyclic voltammetric (CV) studies were carried out with an electrochemical workstation (from CH Instruments Inc., Model # CHI660a).

The specific capacitance of the electrodes was evaluated from the area of the charge and discharge curves of the cyclovoltammetric plot between the voltage window of +0.1 and +0.8 V. Cyclovoltammetric studies were conducted in a three-electrode cell setup using the prepared carbon slurry coated on stainless steel as the working electrode with a platinum wire and a saturated calomel electrode as the counter and the reference, respectively. 3 M KOH solution served as the electrolyte. Galvanostatic charge discharge experiments were also performed in the same setup as described above with a specific current of 10 mA g<sup>-1</sup>.

The electrodes for assessing the electrochemical features were fabricated by mixing 85 wt % of the biocarbon, 10 wt % Black Pearl 2000 carbon black and 5 wt % polyvinylidene-fluoride dissolved in N-methyl 2-pyrrolidone (NMP) to form slurry. The slurry was painted to one circular end of area 1 cm<sup>2</sup> of a stainless steel rod of 8 cm length with 2 mg biocarbon loading on each of the electrodes. Rest of the electrode portion was masked with Teflon sleeves. The electrodes were kept in a vacuum oven at 80 °C for 1 h to remove the solvent NMP.

## RESULTS AND DISCUSSION

**Thermogravimetric studies:** The thermo gravimetric study on the tea dust revealed that major decomposition occurred between 250-290 °C as shown in the Fig. 1.

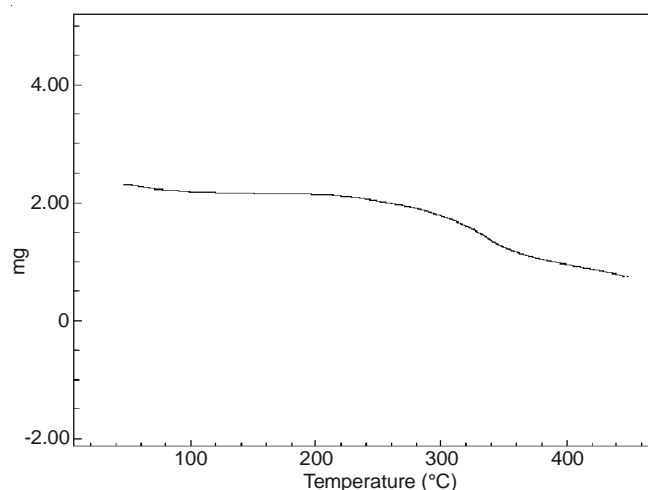


Fig. 1. Thermogram of tea powder waste

The weight loss around 68 % may be due to the escape of decomposition products like moisture, CO<sub>2</sub>, oxides of nitrogen and volatile organic compounds. It may be interesting to note that the escaping gases may impart porosity in the carbon samples. Porosity is one of the likely factors to modify the electrochemical feature of the carbon samples prepared.

**Ultimate elemental (CHNS) analysis:** The VTC as well as ZATC samples were subjected to ultimate analysis and observed to contain approximately C: 68 %, N: 7 %, S: 0.3 %, H: 3 % and rest probably oxygen. The results show that chemical activation does not lead to remarkable differences in the elemental composition. Significant % of N, S and H in VTC and ZATC shows the presence of various organic functional moieties. The presence of organic groups is also corroborated through vibrational spectroscopic studies and is expected to influence the electrochemical performance.

**Phase analysis:** X-ray diffraction (XRD) patterns of the VTC and ZATC are shown in the Fig. 2 and as an inset in Fig. 2, respectively. The appearance of a broad peak between 22 and 24° in the XRD patterns of both the samples indicates the presence of carbon and amorphous is nature and may present good capacitive features.

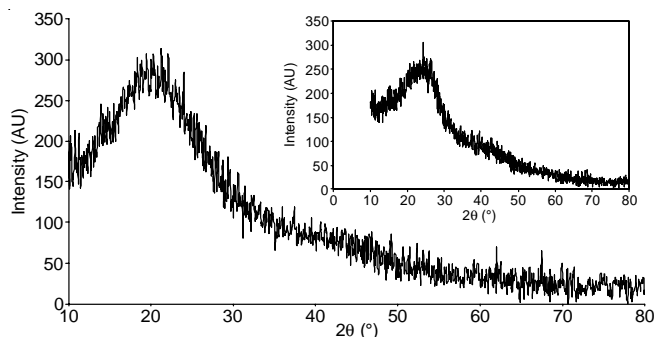


Fig. 2. XRD pattern of VTC (inset: XRD of ZATC)

#### Fourier transform infrared (FTIR) vibrational studies:

It is observed by several authors that the electrochemical properties of activated carbon depend upon the chemical reactivity of the functional groups at the carbon surface. Knowledge on surface functional groups would thus give insight to the electrochemical properties of the activated carbon. FTIR data were collected for such qualitative characterization of the surface functional groups in both the samples and presented in Fig. 3 is the FTIR spectrum of ZATC shown as a representative sample.

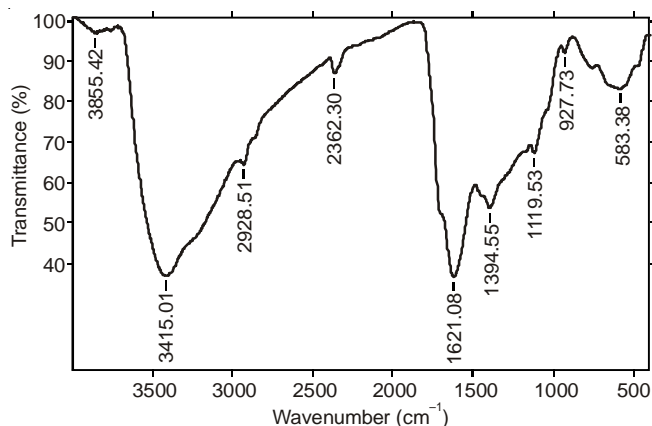


Fig. 3. FTIR spectrum of ZATC sample

The carbon matrix of ZATC contains heteroatoms like, oxygen, nitrogen, sulfur etc besides carbon and hydrogen atoms. These heteroatoms bonded to the edges of the carbon layers govern the surface chemistry of the carbon. The surface of the carbon material is basically determined by the acidity and basicity of their surface. The existence of surface functional groups such as carboxyl, lactone, phenol, carboxylic anhydride, etc., may constitute the source of surface acidity, while the basic properties of the carbon may likely be associated with two types of structures: (i) the presence of oxygen containing groups, i.e., carbonyl structures at the edge of carbon crystallite and (ii) oxygen free Lewis basic site on the graphene layers. The FTIR signature at 3402  $\text{cm}^{-1}$  indicates the presence

of the -NH group. It may also indicate the presence of moisture. The -CH stretching in methylene group is detected at 2924  $\text{cm}^{-1}$ . The band at 1625  $\text{cm}^{-1}$  indicates -N-H stretching in amine compounds. The presence of methyl group was identified from the peak around 1383  $\text{cm}^{-1}$ . The band in the region 1159-1025  $\text{cm}^{-1}$  indicates the presence of -O-H groups. Further, as reported by Subramanian *et al.*<sup>19</sup> that the organic groups with oxygen, typically, phenols, carbonyls, lactones, nitrogen containing pyrrolic, pyridinic, quinone and quinone-like structures are expected to form on the surface during the heating process of the tea derived samples also and may appear at the edge carbon atoms. These oxygen containing functionalities may help in imparting hydrophilicity to the carbon electrode, gives strong interaction of the aqueous electrolyte ions with the polar groups in the carbon material and thus plays an important role for the performance of electrochemical double-layer capacitor. Centeno *et al.*<sup>21</sup> has reported that oxygen containing functionalities impart good features to the performance of the carbons and hence acceptable electrochemical behaviour may be expected from ZATC. The influence of organic groups H, N, O on the electrochemical performance may be important but it is difficult to explain the electrochemical behaviour because we do not know the exact location of these elements in the carbon structures where these groups undergo electrochemical transformation under the influence of electrical signal during electrochemical studies or chemical reactions with the electrolyte species.

**Scanning electron microscopic (SEM) imaging and surface area measurements:** The surface morphology of the VTC and ZATC has been shown in Figs. 4a,b, respectively. It is observed from the SEM image that the particles are compacted and also uniformly distributed in ZATC unlike VTC where there is no definite shape or morphology is found. Further, there is no evidence of porosity in this sample. But a good network of interconnectivity in particles coupled with good porous nature is observed in ZATC, a nature requisite for good electrochemical performance in energy devices. This feature may be reflected in the improved electrochemical behaviour.

Surface area of VTC and ZATC powders has been estimated (by BET method) to be 937 and 1012  $\text{m}^2/\text{g}$ , respectively which lies within the range of many biomass derived activated carbons reported. Ismanto *et al.*<sup>22</sup> observed that improved surface area in addition to the presence of various organic surface functional groups in the carbon influence the specific capacitance. Further high surface area may be indicative of the presence of enormous electrochemically accessible sites or area thereby resulting in increased electrochemical performance. It is to be mentioned that surface functionalities would not be altered as a result of activating the sample and hence for these reasons the authors expect that the capacitance value observed for the ZATC sample may specifically be due to the improved surface area.

**Galvanostatic charge/discharge cycling studies:** Constant current charge/discharge studies with obtained carbon powders were performed between cell voltages of 0 and 1.0V at specific current 10  $\text{mA g}^{-1}$  and the trend observed has been illustrated for VTC and ZATC in Figs. 5 and 6, respectively. The charge-discharge curves followed a similar pattern and shape, which

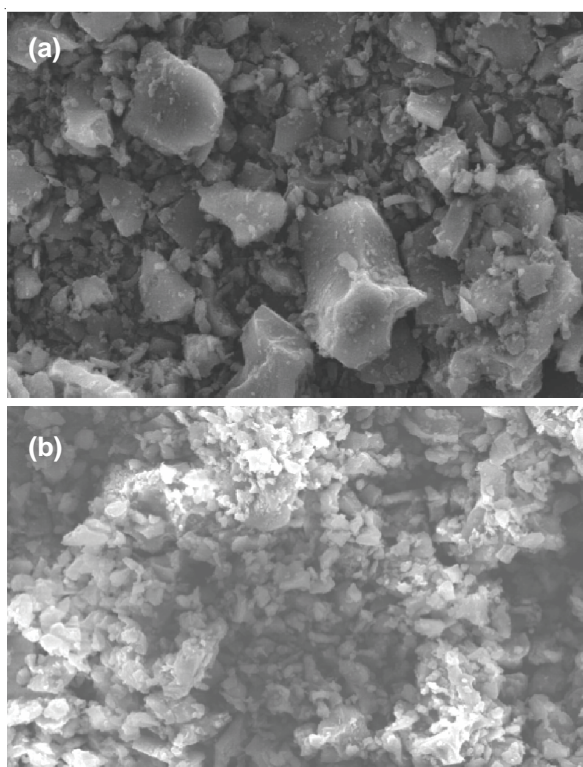
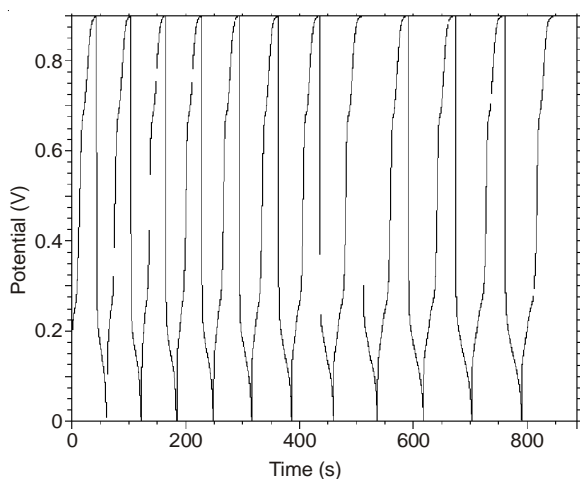
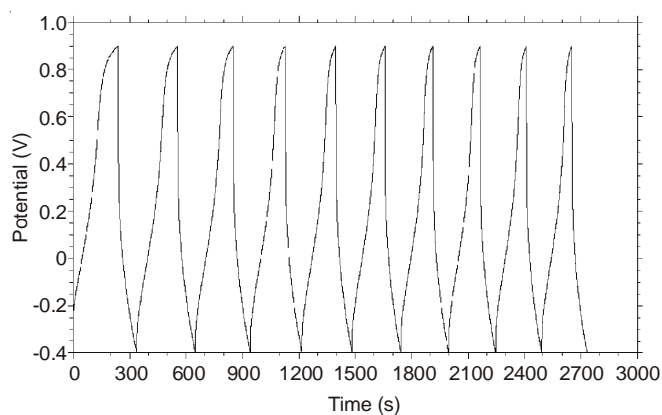


Fig. 4. SEM of (a) VTC and (b) ZATC

Fig. 5. Charge/discharge cycling performance of VTC sample in 3 M KOH electrolyte in the first 10 cycles (specific current = 10 mA g<sup>-1</sup>)Fig. 6. Charge/discharge cycling of ZATC sample in 3 M KOH electrolyte in the first 10 cycles (specific current = 10 mA g<sup>-1</sup>)

is typical for carbon electrode-based cells with capacitive nature<sup>23</sup>. The test cell with VTC electrode exhibited shorter discharge times than the ZATC electrode.

Unlike in VTC, all curves in ZATC extended isosceles triangular shape with discharge time close of that of charge, indicating high charge-discharge efficiency<sup>24</sup> of ZATC. This means that the ZATC electrodes have good hydrophilicity and have acquired good contact with the electrolyte. Interestingly, the charge and discharge time of the ZATC were longer than the VTC, indicative of the fact that the former electrode could be charged with more electrolyte ions or electrons than the latter<sup>22</sup>.

**Cyclic voltammetric studies:** Cyclic voltammetric curves were recorded in the potential window of -0.1 to -0.8 V at various scan rates *viz.*, 100, 200, 300, 400 and 500 mV/s for the VTC and ZATC samples in order to calculate the capacitance values and hence to evaluate the better performing carbon sample. Cyclic voltammetry of the VTC and ZATC samples has been presented, respectively in Figs. 7 and 8.

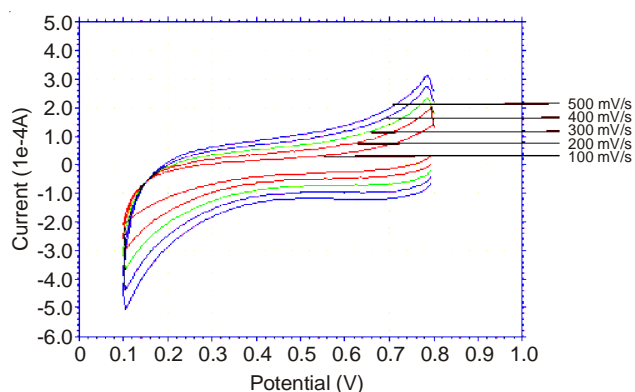


Fig. 7. Cyclic voltammetric curves of VTC at various scan rates

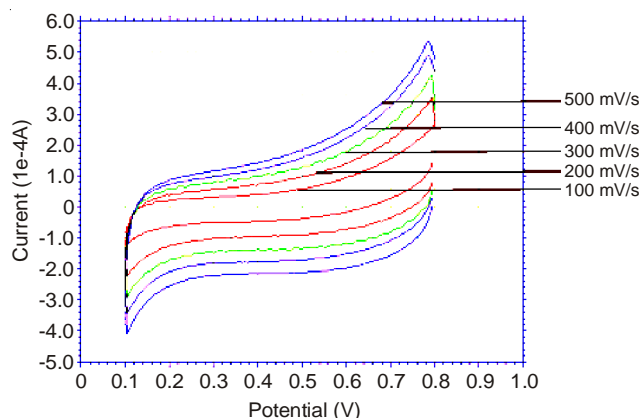


Fig. 8. Cyclic voltammetric curves of ZATC sample at various scan rates

The specific capacitance of the electrode was calculated using the following equation<sup>25</sup>.

$$C = \frac{i}{s} \times m \text{ (F g}^{-1}\text{)}$$

where C, i, s and m is the specific capacitance of electrode, discharge current, the scan rate and the weight of the electrode active material, respectively.

It is well proved that cyclic voltammetry of an ideal capacitor features a rectangular shape whereas the biomass

carbon samples prepared for the present investigation exhibited symmetric and near rectangular shaped cyclic voltammetry patterns without any observable redox behaviour in both the positive and negative sweeps in the potential window and at the scan rates followed in the present investigation. This result is to indicate the capacitive behaviour in these samples. The voltammetric charges accumulated on the positive and negative sweeps were approximately the same at all the scan rates, which demonstrates that the charge-discharge behaviour 3 M KOH is essentially reversible, indicating that the electrodes have good stability as well as capacitive behaviour.

It has already been told that VTC and ZATC contain organic functional moieties with nitrogen and oxygen. The nitrogen functional groups, especially the pyrrolic and pyridinic nitrogen have been reported by Frackowiak<sup>12,26</sup> to be electrochemically active taking part in the pseudo-faradaic reaction. Hence the capacitance calculated would have contribution both from Faradaic as well as pseudo-Faradaic reactions.

It was suggested by Hsieh and Teng<sup>27</sup> that increasing the population of carbonyl or quinone-type surface groups through oxygen treatment is advantageous in enhancing the specific capacitance, but the advantage can be counteracted due to inner resistance and leakage current. Surprisingly, there are no clear quantifying methods or theory to relate the capacity and the surface species reports available and thus remains a theme for research.

The specific capacitance of the ZATC sample was calculated to be around 98 F g<sup>-1</sup>, which was higher than the VTC having 69 F g<sup>-1</sup>. The enhancement in the capacitor value of the activated sample may be attributed to the improvement in the surface area of the sample powders activated with zinc chloride. It can thus be regarded that the ZATC powders may be useful as an electrode material in capacitor applications.

It is well known that for carbons that higher the capacitance longer is the time required to acquire or release charges. From the Figs. 7 and 8 it is seen that the capacitance is reduced when the scan rate is increased from 100-500 mV s<sup>-1</sup>. The high specific capacitance that is observed at the lowest scan rate may be attributed to the fact that the ions can diffuse into pores more easily (faster kinetic process) when the first cycle is completed<sup>28</sup>. The electrochemical storage in activated carbon electrodes has been explained by the electrical double layer theory and it is suggested that ions occupy the pores with the carbon electrode material to participate in the formation of the electrochemical double layer. So at higher scan rates when each cycle finishes quickly the ions cannot diffuse in to the pores as fast as the cycles are completed. Thus the poor performance at higher scan rates has been reasoned out<sup>29</sup>.

Carbon electrodes prepared from various biomass precursors for electrochemical double-layer capacitor applications is plenty and hence a comparison of the capacitance values reported for those samples with ours would gauge our samples. A partial list of specific capacitance values (with their BET specific surface areas) reported for various biomass derived carbons<sup>30</sup> including our samples has been provided in Table-1.

Nevertheless, a complete review on the similar subject has been carried out by the present authors and would be

TABLE-1  
FEATURES OF SUPERCAPACITORS ELECTRODES  
FROM VARIOUS BIOMASS<sup>30</sup>

Biomass precursor	Specific capacitance (F g <sup>-1</sup> )	BET surface area (m <sup>2</sup> g <sup>-1</sup> )	Reference
Coffee beans waste	368	1029	15, 16
Fir wood	197	2821	17
Banana fiber	74	1079	19
Sugar cane bagasse	300	1452	20
Cassava peel	153	1352	21
Rubber wood saw dust	138	912	22
Coffee shells	150	842	29
Cherry stones	232	1292	32
Bamboo	60	1025	33, 34
VTC	69	937	Present work
ZATC	98	1012	Present work

published elsewhere<sup>31</sup>. A comparison would show that our results lie within the typical range reported by other researchers, indicating that ZATC investigated proposed in the present study is suitable for the selected application though the exact role of zinc chloride in improving the surface area is not well understood as of now. Thus ZATC appears to be an attractive and environmentally generous substitute for commercial activated carbon as a capacitor electrode and could reduce costs of capacitors.

## Conclusion

Our preliminary studies may conclude that zinc chloride activated tea carbon powders might be exploited as an electrode material in capacitors. It is also evident that refuse can be a useful secondary source of energy-refuse derived energy. The present investigation highlights the potential to utilize waste biomass such as used tea dust refuse to produce low cost electrode materials for electrochemical double-layer capacitor. Zinc chloride activated tea carbon exhibited appreciable electrochemical performance due to a well developed connectivity and porosity in the particles and concomitant pseudo-Faradaic reactions involving oxygen and nitrogen functionalities. It is to be stressed that the observed performance may also be due to high surface area which activation with zinc chloride has introduced. This study may be a greener path in the search for new carbon materials for electrochemical double-layer capacitor applications because of the low cost associated with the precursor and the simplicity in the methodology involved. Thus the work establishes one of the aspects of the 3R principles. Lastly, the authors feel that framing methodologies for corroborating the observed electrochemical properties with the sources of the tea waste and other properties (like presence of metals) of tea powder waste may be an interesting area of research and hence the work has been reserved for the future.

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