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ZnCl₂ activated Tomato waste derived porous carbon material for high power density for flexible supercapacitor applications

Abstract: - Developing economic and efficient energy storage devices is crucial in the shift towards sustainable energy solutions. Our present work explores the potential of utilizing decayed tomato as a sustainable precursor to produce activated porous carbon electrodes in the construction of supercapacitors. By utilizing the carbonization-activation process and carefully adjusting the preparation parameters, we have achieved an excellent specific surface area (SSA) of 880.33 $m^2 g^{-1}$. This tomato waste char (TWC) predominantly consists of nanopores with a total pore volume of 0.5713 $cm^3 g^{-1}$ and an average pore diameter of about 2.5958 nm. These parameters play a vital role in determining the supercapacitor behavior of the sample. A specific capacitance of 110 F g^{-1} at 1 mA has been recorded. Furthermore, an energy density of 14.97 Wh kg^{-1} at 1 mA is observed. This work has reported a high-value power density of about 4163.4 W kg^{-1} using a symmetric type supercapacitor.

Keywords: Tomato waste, sustainable precursor, activated porous carbon, supercapacitor electrodes.

I. INTRODUCTION

Indian population heavily relies on agriculture as the primary source of employment. India's horticulture production, surrounding vegetable and fruit crops, is estimated to reach around 309 million metric tons in the financial year 2023. Out of that, about forty percent of the whole food products are going to be wasted annually across India. It is crucial to note that perishable produce, such as vegetables, has limited shelf lives and contributes to more than two-thirds of food waste. This food wastage often occurs due to inadequate storage and transportation facilities, which can lead to deterioration when vegetables are transported over long distances and exposed to varying climates and environmental conditions [1]. India has consistently been a top producer of tomatoes since 2017, with an average annual production of over 20 million metric tons until 2023 [2]. Tomatoes are one of the most commonly cultivated horticultural products in India, making up about 10 percent of the agricultural production of the nation. Andhra Pradesh is a major contributor to tomato production, accounting for around 20% of the total output. Unfortunately, a significant portion of the harvested tomatoes end up being wasted due to inadequate packaging and mishandling during transportation. Environmental factors like humidity and fluctuations in temperature can cause biological degradation [3].

Using activated carbon made from sustainable sources, such as tomato waste, may produce beneficial outcomes for the environment and the production expenses of electrodes. Various waste biomass materials from industrial crops, such as rice husks [4], banana bract [5], corn husks [6], corncob [7], flowers [8], etc., are valuable resources for energy storage applications. These biomasses have been widely utilized as electrode material for supercapacitor applications by materials scientists. Using materials such as fungus bran [9], mangosteen peel waste [10], potato

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peel waste [11], sword bean shell waste [12], corn stover waste [13], poultry waste [14], soybean curd residue waste [15], soybean pod waste [16], bean dregs [17] based activated carbon is commonly utilized as electrode material in supercapacitor applications. Based on previous studies, porous carbon must own specific qualities to effectively function in supercapacitors. The material needs to have a significant surface area to hold a sufficient number of charges and achieve a high capacitance. Additionally, it is important to have efficient pathways for the rapid movement of electrons to enable fast charging and discharging.

Supercapacitors have gained significant recognition as highly promising energy storage devices that can bridge the divide between conventional capacitors and batteries. In recent years, porous carbon materials have shown remarkable performance in double-layer supercapacitors. These supercapacitors have attracted a lot of interest because of their impressive power density, eco-friendly nature, and extended life cycle [18]. Supercapacitors are known for their ability to store energy through two main mechanisms: Electrical Double Layer (EDL) and pseudocapacitors [19]. Classification of supercapacitor is shown in Fig. 1. For the EDL mechanism, the movement of voltage potential generates ions, which are transmitted as electrical charges and stored in the pores of the electrode by a physical process called adsorption. As a result, the porous properties of the electrode materials have a significant impact on EDL supercapacitor performance [20]. The strong correlation between the porous structure of carbon materials and the electrical double layer should be highlighted. The amount of energy stored by this process is determined by the number of ions in the electrode/electrolyte interphase. As a result, increasing the retention of ions on a carbon surface increases energy storage capacity. On the other hand, increased surface area improves the overall performance behavior of carbon materials in supercapacitor applications [21].

Typically, the process of producing porous carbon from biowaste involves two main steps: carbonization and activation. carbonization and activation. Biochar is produced by exposing the precursors to the carbonization process, which involves calcining them in an atmosphere of argon. Afterward, porous carbon is made through the formation of pores using $ZnCl_2$. When biomass is directly calcinated, the final product is typically limited to biochar [22]. In this study, a carbon-$ZnCl_2$ composite called tomato waste char (TWC) was produced through thermal decomposition. Our research focused on studying the physicochemical properties of TWC. A lab-scale symmetric supercapacitor was developed using TWC as the electrode material. Hydrothermally reduced carbon cloth (CCHy) was used as the current collectors, with an aqueous electrolyte sandwiched between two identical electrodes. The efficacy of TWC as a carbon-based electrode material for supercapacitors (SCs) was determined by using electrochemical studies such as cyclic voltammetry (CV), galvanostatic charge-discharge (GCD), and electrochemical impedance spectroscopy (EIS) in the full-cell configuration. We aim to determine the practicality of TWC as a potential carbon-based electrode material for SCs, derived from biological waste [23].

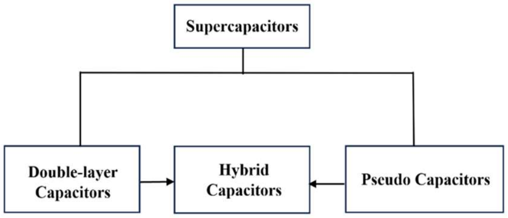


Fig. 1. Classification of supercapacitor

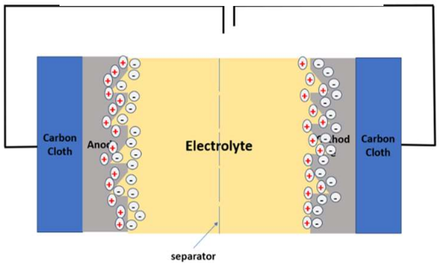


Fig. 2. Structure of supercapacitor

II. EXPERIMENTAL SECTION

Materials:

Tomato waste/rotten tomatoes were collected from the kitchen of the KL University hostel in India and used directly for the preparation of TWC. We have collected the carbon cloth from AvCarb, USA. The following chemicals and materials have been used in this process:

Table 1: List of chemicals and materials used

S.No.	**Chemicals used**	**Manufacturer & Product Code**
1	Isopropyl Alcohol (IPA)	Sisco Research Laboratory Pvt Ltd, 62986, extra pure AR, 99.5%
2	Sodium Hydroxide pellets (NaOH)	Pure, ST Fine Chem Ltd. 40167K05
3	absolute ethanol	Changshu Hongheng Fine Chemical Co. Ltd.
4	Hydrogen Peroxide (H_2O_2) 30 % w/v	Fisher Scientific 30w/w
5	polyvinylidene difluoride (PVDF) M.W.~ 320,000	SD Fine Chem Ltd
6	N-methyl-2-pyrrolidone (NMP)	Ranchem, M2333
7	Sulphuric Acid (H_2SO_4)	Merck Life Science Pvt Ltd, DH1D710939
8	Nitric Acid (HNO_3)	Merck Life Science Pvt Ltd
9	Polyvinyl Alcohol (PVA)	SD Fine Chem Ltd
10	Hydrochloric Acid (HCl)	Qualigens, 7647010
11	Potassium Permanganate ($KMnO_4$)	Loba Chemie Pvt. Ltd., 5410
12	Sodium Nitrate ($NaNO_3$)	Merck Specialities Pvt. Ltd
13	Zinc Chloride ($ZnCl_2$)	Loba Chemie Pvt. Ltd.
S.No.	**Materials used**	
1	Carbon Cloth	AvCarb, USA
2	Whatman® filter paper grade 1 with a diameter of 125 mm	GE Health Care Life Sciences

Whatman® filter paper of grade 1 with a diameter of 125 mm was utilized as a separator to develop a laboratory-scale supercapacitor device. Deionized water is used throughout the whole activity.

Synthesis Process:

Carbon cloth obtained from commercial sources was modified to obtain CCHy using a synthesis procedure described in another work [24]. Untreated carbon cloth was immersed in a mixture of H_2SO_4 and HNO_3 (2:1). 3g of Potassium Permanganate ($KMnO_4$) was added to the mixture and stirred. Afterward, 100 mL of deionized water is been added and stirred continuously for 3 h. DD Water was added to the mixture until the reaction became clear, ensuing in carbon cloths that were chemically oxidized. After collecting the oxidized carbon cloths, they were thoroughly rinsed multiple times. Then, they were placed in a PTFE-lined autoclave filled with DI water and further, heated at 180 °C for 14 h. Then the CCHy was picked and dried out in a vacuum environment. By using the prepared CCHy we utilized it as a current collector, and we conducted full-cell studies to test the TWC as an electrode material.

Supercapacitor Device Fabrication:

The mass of the electrode was calculated which is about 2.4 mg/cm^2. For the fabrication of a symmetric supercapacitor electrode, the mass of each electrode is approximately 2.4 and 2.9 mg. The obtained porous carbon (PC) was well mixed with carbon black and PVDF in an agate mortar with a mixing weight ratio of 8:1:1. The same mixture was stirred for 30 mins. A small amount of NMP drops is added to the mixture until the slurry is prepared. The mixture is then applied for coating, with approximately 2.4 mg of coating on each electrode, using a brush to ensure they are symmetric. The porous carbon-coated electrodes made from tomato waste were then dried in a vacuum oven at 50 °C overnight for ~12 h to eliminate water content. The dried electrodes are subsequently removed from the vacuum oven. Electrodes for supercapacitors are prepared using tomato vegetable waste. Next, the PVA/H_2SO_4 electrolyte was prepared using the procedure outlined in [25]. 1 g of PVA was mixed with 10 milliliters of DI water and stirred for 12 h on a magnetic stirrer. Next, 1.18 ml of H_2SO_4 was carefully added to the PVA gel and stirred for 1 h to create the PVA/H_2SO_4 gel electrolyte. The dried electrode and the polymer electrolyte film are cut into 1 cm×1 cm dimensions. Finally, they are sandwiched with two freshly prepared porous carbon electrodes to fabricate our supercapacitor device. The complete steps of synthesis process and making of supercapacitor device is shown in Fig. 3.

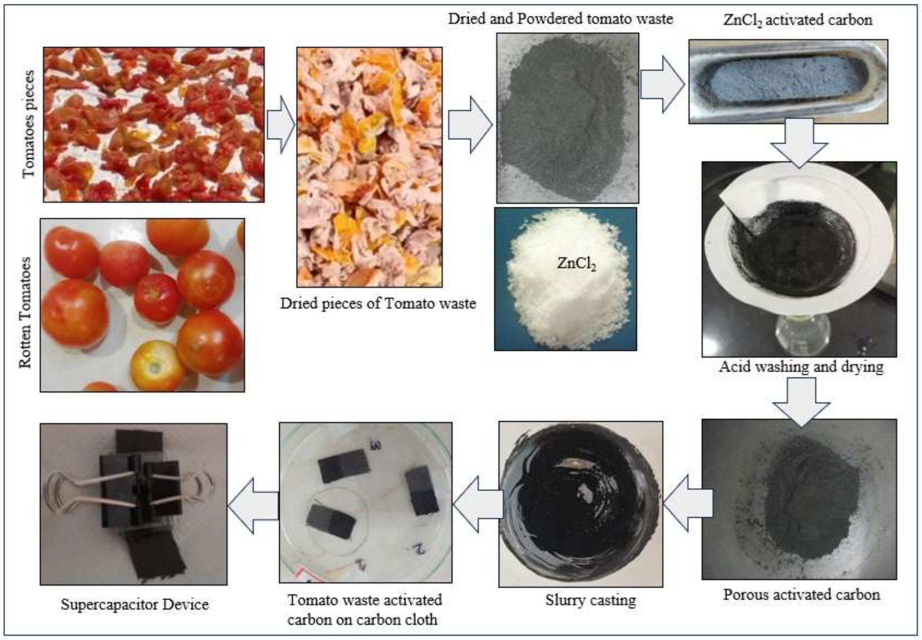


Fig.3. Process of making supercapacitor device

Material Characterization:

The phase structural properties and crystallinity were examined using X-ray diffraction (XRD) with the Xpert Pro instrument from PANalytical. The surface morphology was analyzed using FESEM (Zeiss Gemini 1Sigma 300) to determine its characteristics. The Raman Spectroscopy investigations were conducted using Renishaw’s In Via microscope. The surface area of the samples was determined and analyzed using the Brunauer−Emmett−Teller (BET) method with a BET surface area analyzer make and model of BEL SORP mini II, Microtrac Bel. The pore size distributions were calculated using the Barrett-Joyner-Halenda (BJH) method, based on the available BET data. The electrochemical behavior was investigated in a full-cell configuration using an electrochemical workstation (PARSTAT PMC 2000A) through performing CV, GCD, and EIS studies.

III. RESULTS AND DISCUSSION

Fig. 4 presents the data for the XRD pattern. It is evident that our prepared TWC-derived activated carbon exhibits broad diffraction peaks with low intensities at approximately 24.7° and 43.66°, which correspond to the (002) and

(100) planes of graphite, respectively. The carbon materials obtained from TWC exhibit characteristics commonly found in disordered carbons. The XRD result provides evidence of the graphitic phase of the carbon. The graphitic phase is a highly conductive form of carbon that can help decrease resistance in electrochemical processes. The two peaks displayed wide profiles, suggesting the existence of an amorphous structure in porous carbon. According to previous reports, the amorphous structure has been found to provide wider channels to ionically transport electrolyte ions, resulting in an enhanced rate capability for supercapacitors when compared to the graphitic structure.

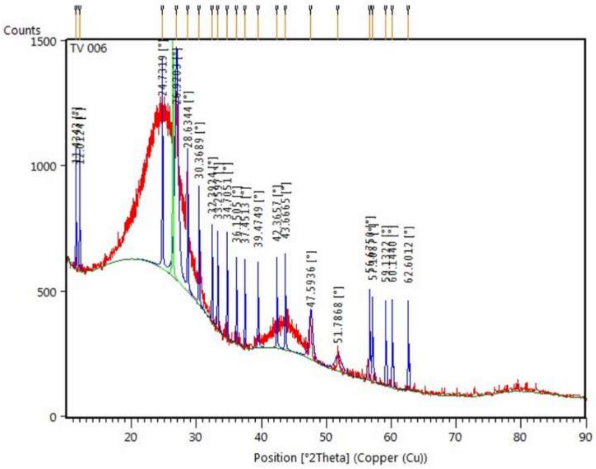


Fig.4. X-ray Diffraction Spectra

The defects degree of the porous carbon sample was evaluated using Raman spectroscopy, due to its high sensitivity. Here are the results, as shown in Fig. 5. Two characteristic peaks were observed, corresponding to the D-band at 1339 cm^{-1} and the G-band at 1595 cm^{-1}. It is worth mentioning that the presence of defects has a positive effect on absorbing more ions, which in turn increases the capacity that was provided by the faradaic reactions. Additionally, it also enhances the double-layer capacitance by altering the surface structure

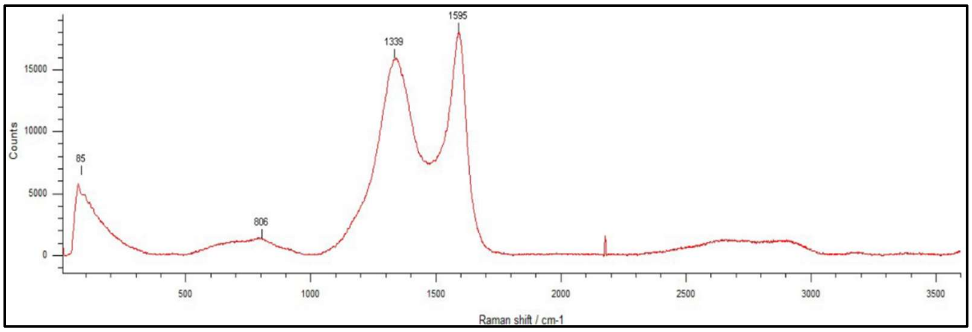


Fig.5. Raman Spectra

The measured surface area of tomato waste char is about 880.3 m^2 g^{-1}, based on the calculations. According to the BET analysis, it is found that TWC predominantly consists of nanopores, with a total pore volume of 0.5713 cm^3/g and an average pore diameter of around 2.5958 nm as shown in Fig. 6. The FESEM images with low magnification and high magnification of TWC are displayed in Fig. 7. It is seen from the image that the sample showed a 3D porous carbon network.

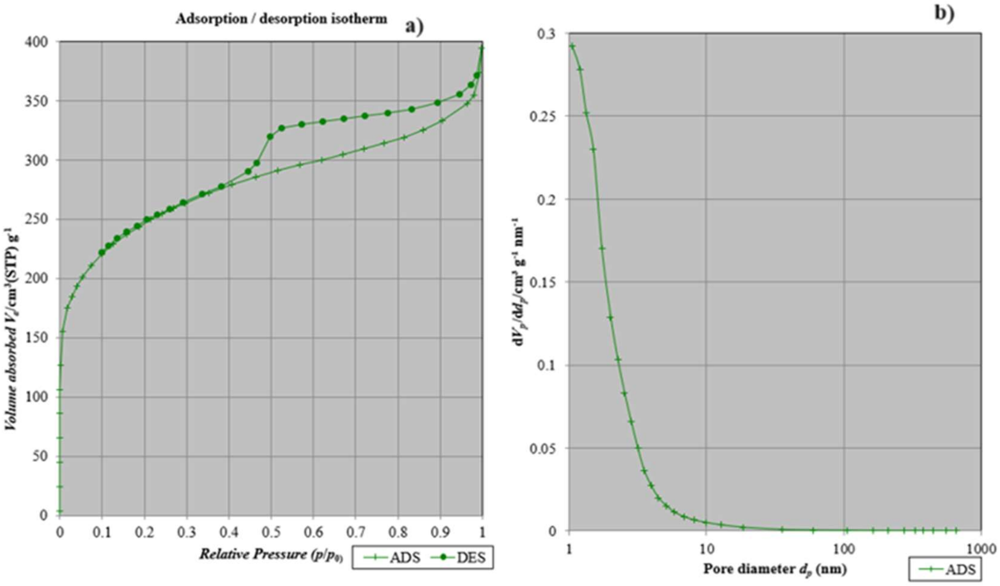


Fig. 6 (a) N_2-adsorption-desorption curves, (b) Pore size distribution of tomato waste char (TWC) powders

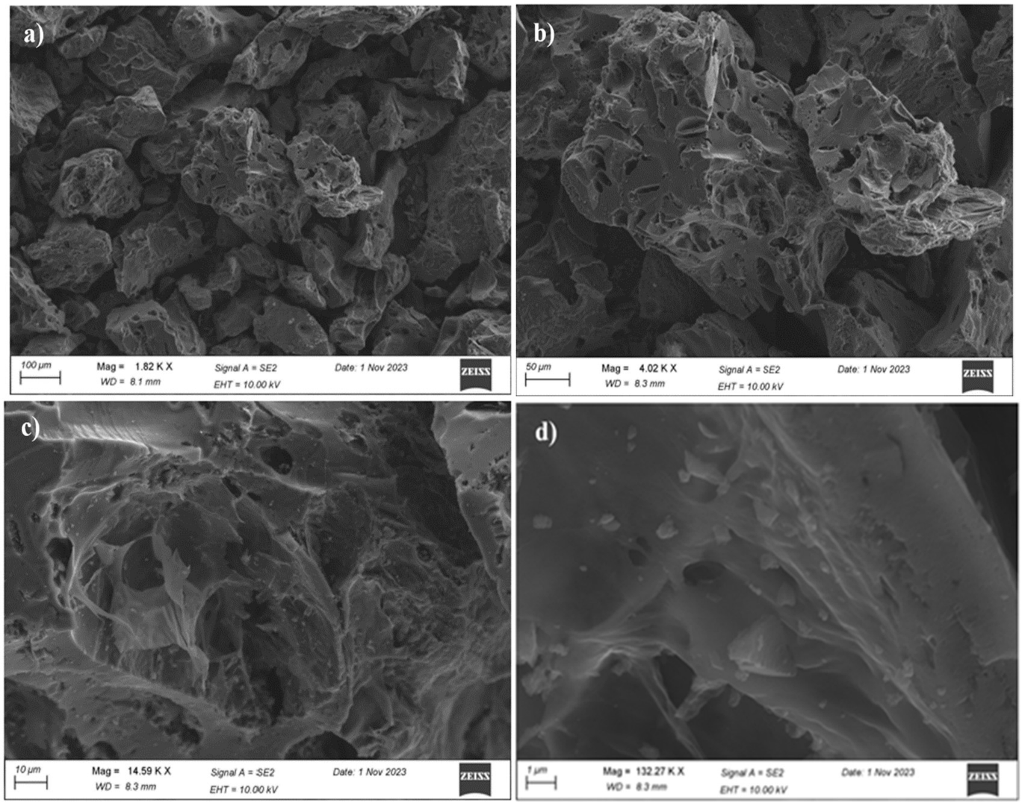


Fig.7 FESEM Images: Low (a-b) and high-magnification (c-d) images of TWC, showing the 3D porous framework of the carbon materials

An electrochemical investigation was conducted using a two-electrode setup of a symmetric supercapacitor device. The fabricated device consisted of two electrodes that were separated by an ion transport layer and were tested in a 1 M H_2SO_4 gel electrolyte. The CV profile of the electrode in the device configuration is displayed in Fig 8a, showcasing a rectangular shape that remains consistent even at high scan rates. This suggests that the device has excellent high-rate performance and demonstrates flawless double-layer charge storage at the electrode/electrolyte interface. The GCD profile with various current densities ranging from 1 mA to 20 mA is depicted in Fig. 8b. The charge-discharge curves exhibit remarkable symmetry and no voltage drop is evident even at high current density. This indicates that the material has excellent electrochemical properties even under elevated charge-discharge current circumstances, and the energy storage mechanism on the electrode primarily involves physical adsorption that forms double charge layers. GCD result is well matched with the obtained results of the CV profile. The specific capacitance reaches its highest value of 110.01 F g^{-1} when the current density is set at 1 mA g^{-1}.

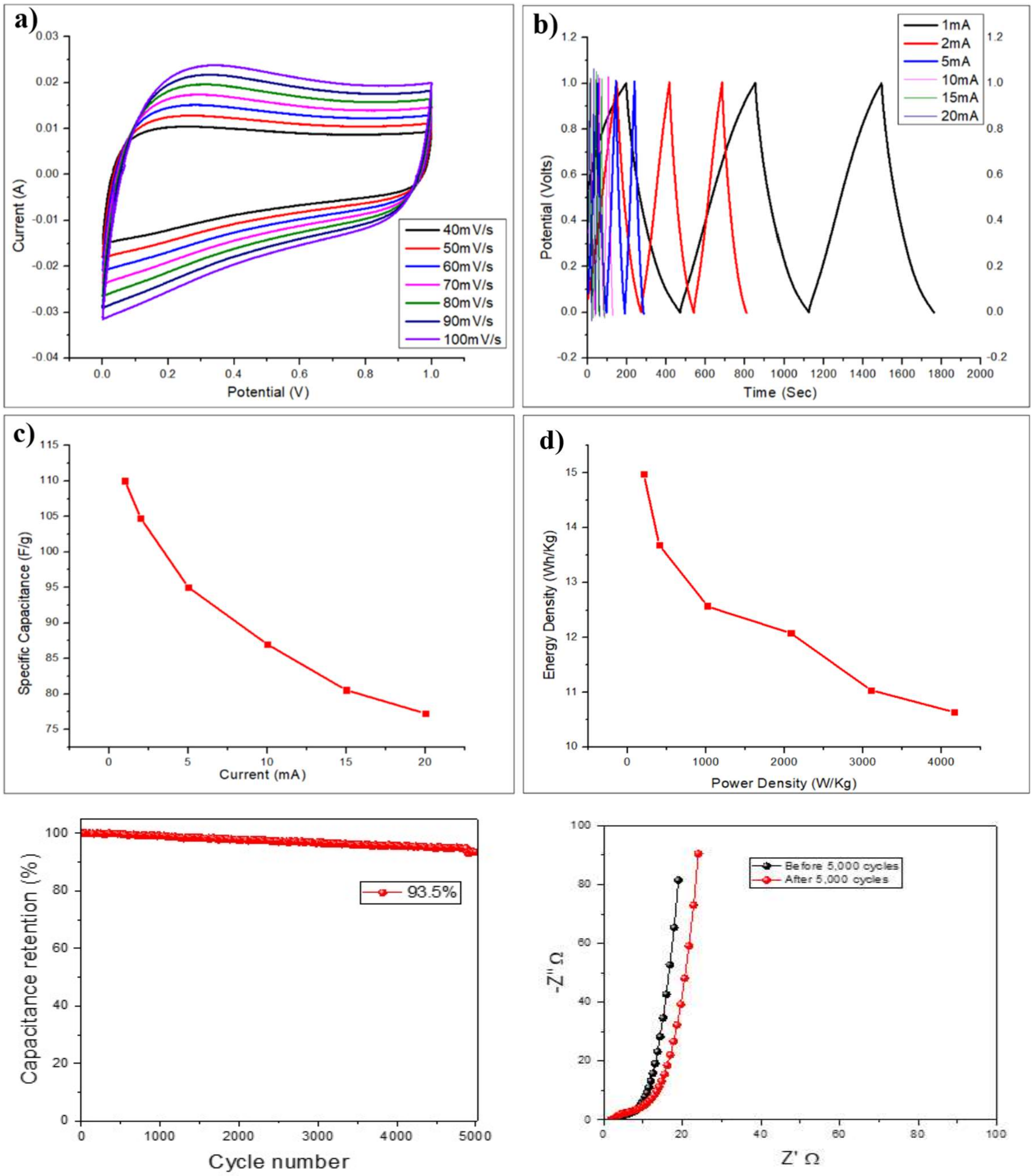
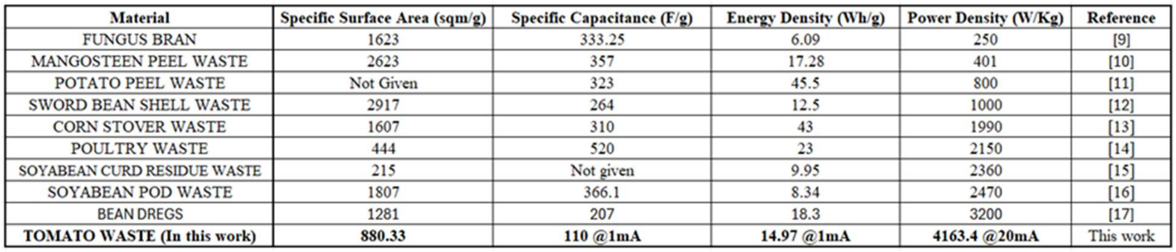


Fig. 8 (a) CV curves of the sample at multiple scan rates, (b) GCD curves of the sample at various current densities (c) Ragone plot of sample (d) power density vs energy density curve (e) retention graph (f) EIS graph

As we increase the current density from 1 mA g^{-1} to 20 mA g^{-1}, there is a progressive decrease in specific capacitance from 110.01 F g^{-1} to 77.27 F g^{-1}. This could be due to the limited time for the electrolyte ions to penetrate the electrode pores. It is worth noting that the discharge time decreases as the current density increases from 1 mA g^{-1} to 20 mA g^{-1}. An experiment was conducted to measure the voltage drop at various current densities. The results showed a voltage drop of 0.9V at 1 mA g^{-1} and 1 V at 20 mA g^{-1}.

Upon discovering the specific capacitance, we proceeded to compute the energy density and power density, as illustrated in the table below. Maximizing the specific capacitance and increasing the usable operating voltage can greatly enhance the energy density. This sample achieves a retention time of 93.5%. The comparison table in Table 2 displays the specific surface area details and electrochemical performance of supercapacitor devices made from different agricultural and vegetable waste



Material	Specific Surface Area (sqm/g)	Specific Capacitance (F/g)	Energy Density (Wh/g)	Power Density (W/Kg)	Reference
FUNGUS BRAN	1623	333.25	6.09	250	[9]
MANGOSTEEN PEEL WASTE	2623	357	17.28	401	[10]
POTATO PEEL WASTE	Not Given	323	45.5	800	[11]
SWORD BEAN SHELL WASTE	2917	264	12.5	1000	[12]
CORN STOVER WASTE	1607	310	43	1990	[13]
POULTRY WASTE	444	520	23	2150	[14]
SOYABEAN CURD RESIDUE WASTE	215	Not given	9.95	2360	[15]
SOYABEAN POD WASTE	1807	366.1	8.34	2470	[16]
BEAN DREGS	1281	207	18.3	3200	[17]
TOMATO WASTE (In this work)	**880.33**	**110 @1mA**	**14.97 @1mA**	**4163.4 @20mA**	This work

Table 2. Performance comparison of various agriculture and vegetable

IV. CONCLUSION

Tomato is the largely produced crop in Andhra Pradesh, India and much of them are rotten due to improper maintenance at municipal markets leading to various health diseases. A laboratory-scale symmetric supercapacitor was prepared in this work. Tomato waste-derived activated carbon material which is biodegradable is used as electrodes in this process. The mass of the electrode is about 2.4 mg/cm^2. The parameters such as specific surface area, energy density, and power density play an important role in understanding the behavior of supercapacitor devices. A specific surface area of 880.33 m^2 g^{-1} and a pore volume and diameter are about 0.5713 and 2.5958 nm respectively have been obtained with this tomato waste char. An excellent power density of about 4163.4 W kg^{-1} has been achieved which is relatively high compared with any potato peel and soybean waste materials. Hence, tomato waste-derived porous carbon-based electrode materials are the best materials that can be used as electrodes in supercapacitor devices.

CONFLICTS OF INTEREST

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the manuscript's contents and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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