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Chemically Treated Activated Carbon for Supercapacitor Electrode Derived from Starch of Solanum Tuberosum

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ABSTRACT

Because of the increasing demands in energy, growth in alternate energy sources is inevitable. By activation followed by carbonization of starch of solanum tuberosum makes a porous carbon network as electrode material for supercapacitor. To achieve an improvement in specific capacitance, activating the starch of solanum tuberosum using chemicals such as hydrochloric acid, phosphoric acid and sulphuric acid were done. The structural and electrochemical performance of activated carbon derived from the starch of solanum tuberosum is evaluated using FTIR, XRD, CV, GCD and EIS. The improved performance of chemically treated starch of solanum tuberosum in energy storage mechanism is ascribed to fast ionic diffusion of the electrolyte into and out of the pores. From the CV analysis, the higher specific capacitance (94 $F.g^{-1}$) is obtained for sulphuric acid treated activated carbon derived from the starch of solanum tuberosum with good capacity retention ratio. From GCD analysis, 78.3, 56.7, 82.7 and 74.9 Fg^{-1} of specific capacitance is obtained for POC, POCH, POCP and POCS, respectively. When compared to all the prepared samples, POC exhibited small equivalent series resistance and POCS exhibited small charge transfer resistance.

Keywords: *Electrode, Energy density, Solanum tuberosum, Supercapacitor, Power density*

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1. INTRODUCTION

Supercapacitor is the most excellent capacitor concept with high capacitance, minimum discharge rate and small size as the replacement of battery, which can provide 1-100 mA current and used to protect microcomputers from power shutdowns, also keep the CMOS contents for a prolonged period. Materials for the supercapacitor electrode should possess an excellent porous structure [1]. Carbonization and activation are the key factors for the porous nature of the material [2] and also it facilitates the fastest penetration of electrolyte ions. Usage of activated carbon as electrode in supercapacitor, increases the energy storage capacity, provides long shelf life because of no degradation, maintains short time recharge, and provides large power burst for short duration [3-4].

Biomaterial derived activated carbon is environmentally significant [5-7]. Mesoporous nature of activated carbon prepared from rice husk exhibited high specific surface area and specific capacitance [3]. Some of the biomaterials such as banana peels [8-17], cotton seed husk [18], rotten potatos [19], orange peel [20-21], etc. Addition of silica with corn starch electrolyte improves the specific capacitance [22]. Because of renewable, inexpensive and eco-friendly nature with low equivalent series resistance (<2 Ω) suggested that the potato based biomass carbon delivered an important role in batteries and supercapacitors when compared to carbon derived from other types of biomass [23]. Similarly, electrolyte obtained from potato starch also suggested low equivalent series resistance [24]. Both the good and rotten potato derived carbon can be served as electrode material for supercapacitor. Similarly, compared to most of the biomaterials, mass of the potato is almost higher. Also, the preprocessing and processing methods are very much simpler and harmless to the environment. It means that potato based biomass carbon is very simpler to prepare even in home itself without exhibiting toxicity. Because of the mass quantity and environmentally safe synthesis methods leads to make potato as the preferred candidate for renewable energy storage. Potato starch can even used as a substrate for the growth of carbon nanofibers [25]. By means of heating a potato starch, the obtained microporous disordered carbon can acted as an anode for battery [26] and used as an electrode for supercapacitor [27]. Currently, biomass resources are attracted for the development of energy storage materials. Herein, potato biomass porous carbon was prepared through a facile two-step carbonization approach.

2. EXPERIMENTAL SECTION

2.1 Materials Used

Solanum tuberosum were purchased from a local shop located at Erode, Tamilnadu.

Laboratory grade (approximately 40 to 45%) Sulphuric acid, phosphoric acid and hydrochloric acid were bought from Nice chemicals private limited and used.

2.2 Preparation of Biomass Carbon from Potato Starch

Initially 1.7 kg of *solanum tuberosum* was taken and washed and peeled of using razors. Then the potato was kept in 3.75 liters of water and boiled for 6 hours in medium flame using household gas stove. After that the boiled potato was kept in an open air environment and cooled off and then smashed it using hand and kept it overnight. Finally, it was kept in an oven for an hour. The weight of the *solanum tuberosum* after oven drying was 1.1 kg. Then once again, it was kept in an oven for about

48 hours. The further process was accomplished by consigning the starch to Sigma high temperature furnace. Initially high temperature (600 to 900° C) was tried and observed that high temperature led to more ash content. Similarly, low temperature is not sufficient to make carbonaceous materials. Finally, the optimized temperature was chosen. The temperature was maintained at 600°C for 2 hours. They were then allowed to cool down for about 20 hours and crushed into powder with the help of plunger. As a result, the biocarbon is extracted and named it as POC, which is the source material for the electrodes in supercapacitor.

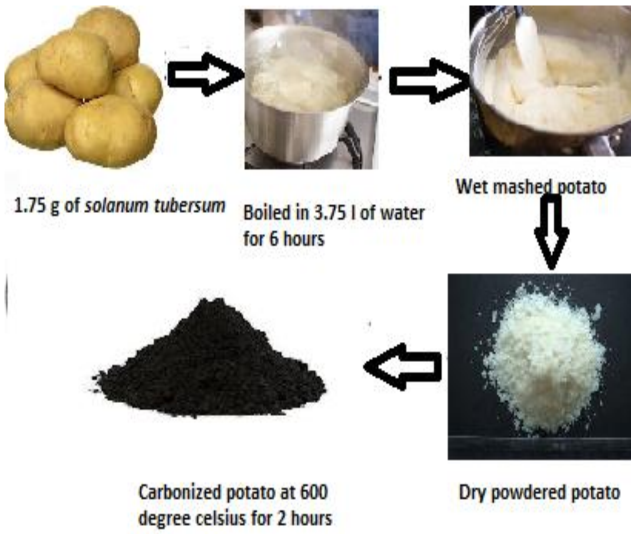


Figure 1. Carbonization process of solanum tuberosum

2.3 Chemical Activation of Biomass Carbon

Followed by the preparation of POC, it was activated using sulphuric acid, phosphoric acid and hydrochloric acid. Initially, 10 mg of POC was taken and dissolved in hydrochloric acid using magnetic stirrer. Afterthat, it was kept overnight for complete activation. The same process was done for sulphuric acid and phosphoric acid. Finally, the samples were taken and oven dried for about 8 hours and washed it with ethanol and water for removing the excessive amount of sulphuric acid, phosphoric acid and hydrochloric acid. The obtained samples were labeled as POCS, POCP and POCH, respectively.

2.4 Material Characterization Methods

The structural characterizations of all the samples were measured using FTIR and XRD measurements. FTIR spectroscopy measurements of POC, POCS, POCP and POCH were measured by the KBr method recorded on Shimadzu spectrometer over a range from 400 to 4000 cm^{-1}. The electrochemical analysis of oven dried, activated carbon was performed using Origalys electrochemical workstation. Three types of electrochemical tests namely Cyclic Voltammetry, Galvanostatic Charge Discharge and Electrochemical Impedance Spectroscopy were taken. To perform an analysis on electrochemistry, the electrode was congregated in 3 electrode system. The given steps were carefully considered for the devlopment of working electrode. To analyse the electrochemical performance in 0.5 M aqueous H_2SO_4, made the electrode using potato starch and chemically activated potato starch, mixed with high viscous rubber solution in the weight ratio of 60:40. Becuase of the viscous nature of rubber solution the obtained mixture is looked like as a slurry and it was coated over low-cost graphite lead with the thickness of 2 mm using normal paint brush. The biomass derived activated carbon coated graphite lead was dried at 24°C for 30 min. The measured loading quantity of biomass derived activated carbon is approximately 0.3 g. The electrochemical nature of the samples were tested in a high potential window of 0 to 2 V. Ag / AgCl /3 M KCl with electrode potential of 0.210 V, and a platinum wire were used as reference and counter electrode, respectively.

3 RESULTS AND DISCUSSION

Infrared spectrum of the prepared samples from 400 to 4000 cm^{-1} was obtained from Fourier transform infrared spectroscopy and shown in Figure 1. FTIR spectrum of all the samples showed a strong peak at 3526 cm^{-1} ascribed to hydroxyl stretching vibrations of C-OH groups. The value of the peak at 1733, 1721, cm^{-1} is assigned to the O-H deformation, and a weak band at 1468, 1497 cm^{-1} is assigned to C=O stretching. Finally, peak at 1000 cm^{-1} are assigned to C-O stretching.

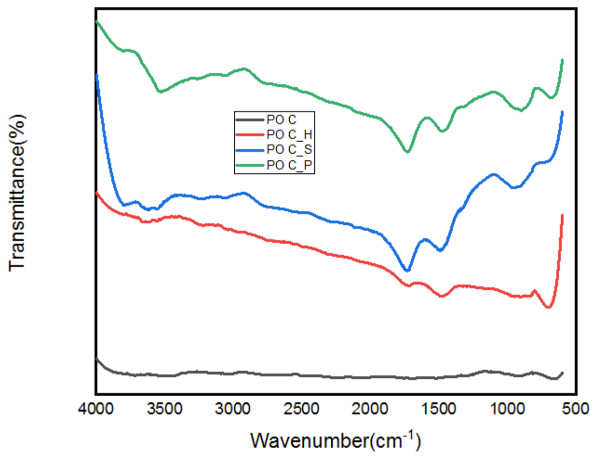


Figure 1. FTIR spectra of POC, POCH, POCP and POCS

Due to the chemical activation, the defects may be presented on the surface of carbon. To identify the defects of POC, POCH, POCS and POCP samples, patterns of XRD were recorded between 10° and 80° using CuKα radiation are shown in Figure 1. From the diffraction pattern of the POCS, at 22°, a broad peak is observed. Similarly, a peak is observed at 25° for POC. Finally, a broad peak is observed at 29° for both POCH and POCP, The weak band is observed at 43° for POCS and POCH respectively. From the presence of broad peak, an amorphous structure of the carbon is identified.

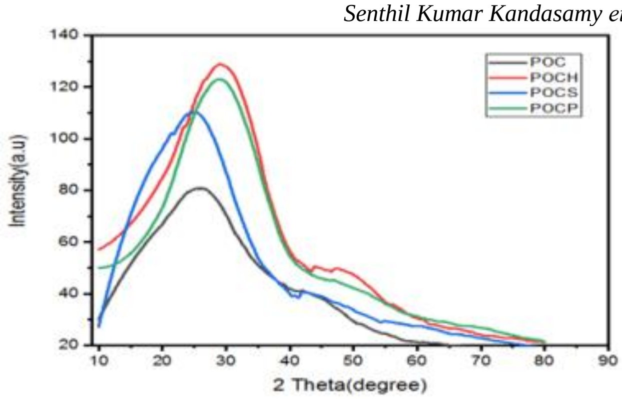


Figure 3. XRD spectra of POC, POCH, POCP and POCS

There are 3 electrodes in the workstation namely counter electrode (Platinum), reference electrode (Ag/AgCl/3 M KCl with electrode potential of 0.210 V) and working electrode. The prepared material was mixed with polyvinyl acetate, surface activated rubber, water and dispersion agent and then coated on the graphite rod, which is used as working electrode [28-30]. 0.5 M H_2SO_4 is used as an electrolyte for the entire measurement. CV is used as a suitable tool to characterize the capacitive behavior of the samples. Figure 3 shows the CV curves of POC, POCH, POCP and POCS at a scan rate of 30 mV s^{-1} within a potential window of 0 to 2 V in 0.5 M H_2SO_4 electrolyte solution. Because of the high potential window, the samples may produce high energy density as well as power density. Also, it is ascribed that the CV curve exhibited nearly ideal rectangular shape in the mid region, indicating that the specific capacitance primarily originates from the double layer capacitance based on ions adsorption/desorption.

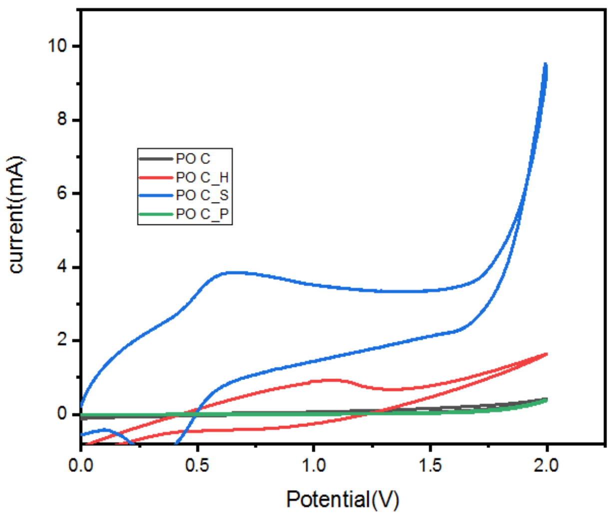


Figure 3. CV curves of POC, POCH, POCP and POCS

Since the oxygen-functional groups were mostly removed during the high temperature thermal treatment, the contribution of pseudo capacitance is negligible. But potato starch based activated carbon contributed both EDLC and Pseudocapacitance. From the Figure 3, the pesudocapacitance is clearly observed for the POCS and POCH samples. The specific capacitance for all the forms of carbon material was calculated. The mass of the carbon

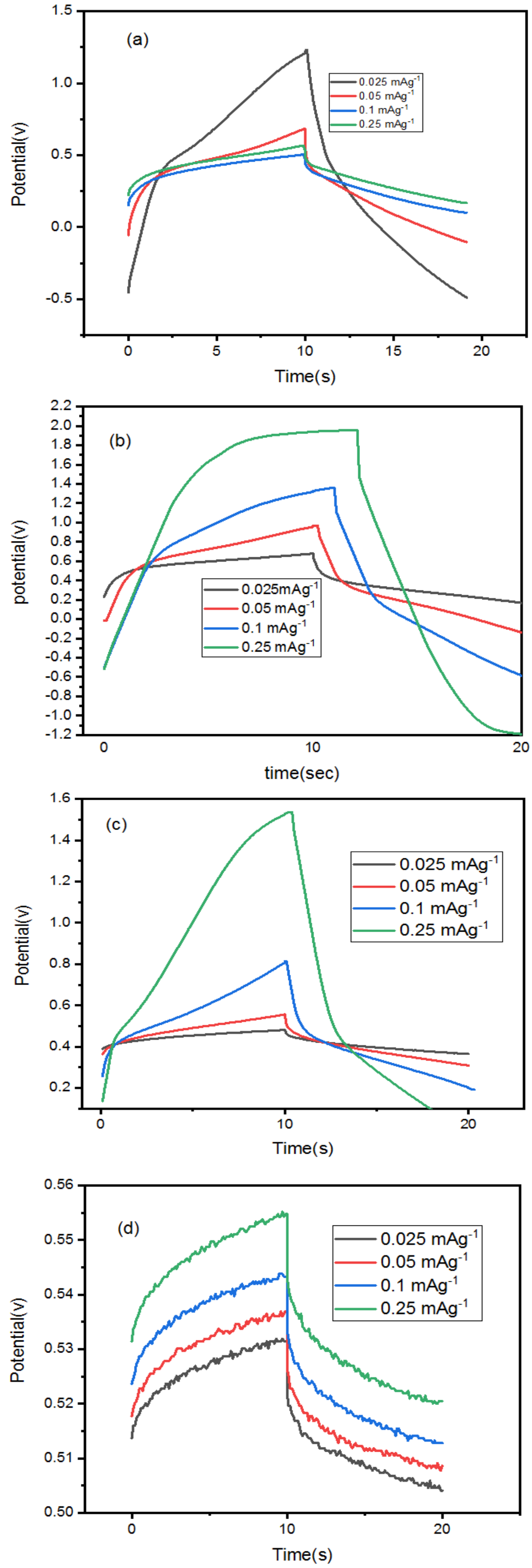
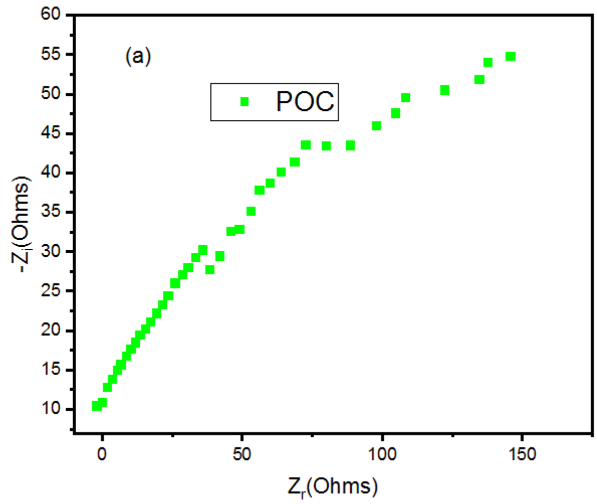


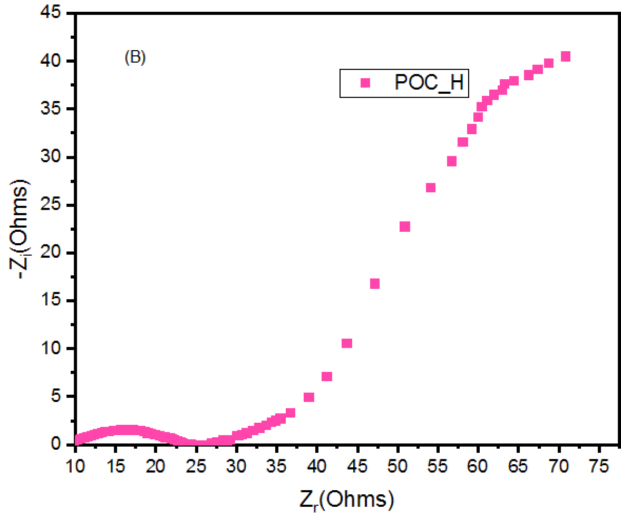
Figure 4. GCD curves of (a) POC, (b) POCH (c) POCP (d) POCS

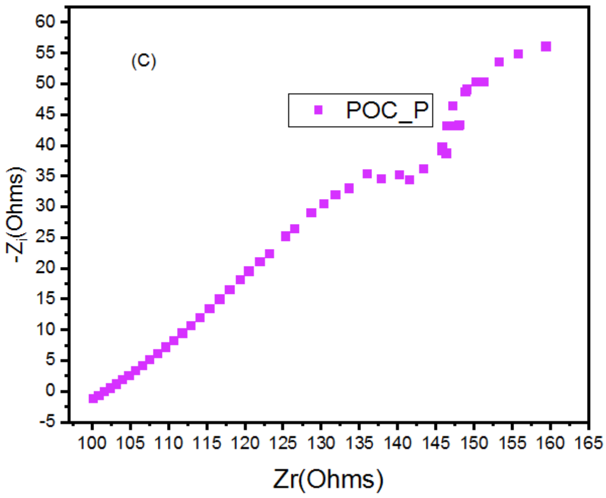
material was 0.3 grams and the applied potential was 2 volts. From, the specific capacitance of all the four carbon samples (19, 94, 19 and 59 $F.g^{-1}$ for POC, POCS, POCP and POCH, respectively), the hydrochloric acid activated sample showed the highest specific capacitance.

The charge discharge curve at current densities of 25 $mA.g^{-1}$, 50 $mA.g^{-1}$, 100 $mA.g^{-1}$, 250 $mA.g^{-1}$ for POC, POCH, POCP and POCS is shown in Figure 4. At higher discharge density, the voltage drops will increase due to the internal resistance of supercapacitor. Highest IR drop is observed for the samples in the following order: POCS, POCP, POC and POCH. From the GCD analysis, 32.89, 57.95, 78.3 and 67.35 $F.g^{-1}$, is for POC, 56.74, 40, 29.68 and 21.6 $F.g^{-1}$, is obtained for POCH, 82.66, 70.48, 47.46 and 24.73 $F.g^{-1}$, is for POCP, 74.94, 74.25, 73.25 and 71.64 $F.g^{-1}$, is for POCS.

With the help of EIS obtained from OrigaLys workstation, further able to understand and analyze the fundamental behavior of electrode materials for supercapacitor. All the samples such as POC, POCH, POCP and POCS exhibited linear response from high frequency region to low frequency region, corresponding to excellent capacitive performance. Figure 5. shows the nyquist spectrum is recorded within the range of 100 kHz to 0.1 Hz using electrochemical workstation. From the measured ESR and charge transfer resistance, the ion transport of the samples can be understood. Equivalent series resistance obtained for the samples POC, POCH, POCP and POCS, are 4.68 Ω, 11.85 Ω, 57.47 Ω and 6.52 Ω, respectively. When compared to ordinary samples, chemically activated samples exhibited very small charge transfer resistance, suggested the high electrolyte diffusion and conductivity of the samples especially for hydrochloric acid activated potato biomass. When compared to all the prepared samples, POC exhibited lowest ESR and POCS exhibited lowest R_{ct}, which further confirms with the GCD. Similarly, compared to the samples, POCH exhibited approximated vertical curve corresponds to the swift ion diffusion and adsorption. Warburg resistance of 45° is observed due to the diffusion of ions in the electrolyte in the low frequency region, for both POCP and POCS samples.







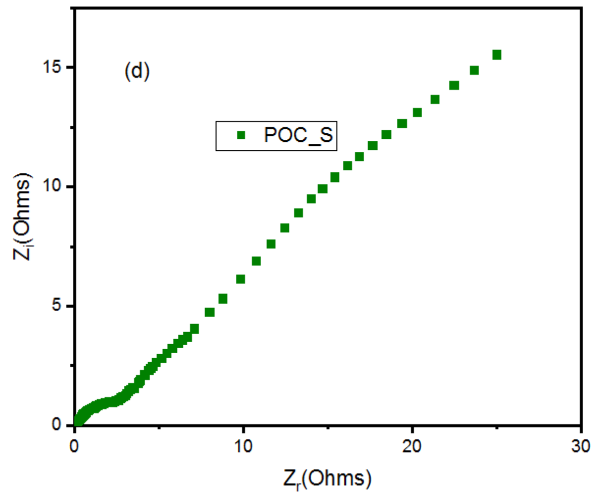


Figure 5. EIS analysis of (a) unactivated carbon (b) hydrochloric acid based activated carbon (c) sulphuric acid based activated carbon (d) phosphoric acid based activated carbon

4 CONCLUSION

Potato derived biomass carbons have been successfully prepared by carbonization and hence the POC activated using hydrochloric acid exhibited better performance had been implemented for the supercapacitor. The excellent electrochemical performance that POC displayed is mainly attributed to the unique hierarchical porous structure. The specific capacitance of POC activated using suplphuric acid is up to 94 Fg^{-1} at 30 mVs^{-1}, which is higher than that of the commercial activated carbon. The well-developed structure of sulphuric acid activated POC, is promising choice for the low-cost design of high- performance supercapacitor. More inspired studies should be focused on the recycling of the low-cost, sustainable and green carbon source for future energy storage applications. As the prepared organic carbon from potato showed a good performance as an electrode material, usage of these carbons as alternative will result in great advantage. Further, it is possible to infuse any inorganic chemicals with this potato derived carbon to enhance its electrochemical conductivity.

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NOMENCLATURE

mV s^{-1}	millivolt/sec
FTIR	fourier transform infrared spectroscopy
XRD	x-ray diffraction
CV	cyclic voltammetry
GCD	galvanostatic charge and discharge
EIS	electrochemical impedance spectroscopy
ESR	equivalent series resistance
m^2g^{-1}	meter square per gram
Ag^{-1}	ampere per gram