

Superior Supercapacitors based on Biowaste Materials

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Abstract

Carbon nano spheres derived from *Allium cepa* were synthesized at different temperatures in a one-step pyrolysis process for supercapacitor electrodes. Obtained carbon nano spheres were analyzed using SEM, FTIR, BET and XRD. The nano materials were fabricated into conducting electrodes for cyclic voltammetry, constant current charge-discharge and electrochemical impedance spectroscopy studies. All the studies were done in 3.0 M KOH electrolyte. Specific capacitance from charge discharge experiments were found to be 132.03 F/g and 149.49 F/g for nano materials synthesized at 500°C and 600°C respectively. Obtained values suggest a way forward in producing a green electrode for commercial applications.

Keywords: Carbon nano spheres, supercapacitor electrodes, bio material

I. INTRODUCTION

The ever increasing energy demand in today's globalized world is forcing the researchers to look for alternative energy sources as petroleum source is dwindling and the other fossil fuels are threatening the health of environment.[1] Lithium and Lithium ion-Batteries are one major alternative to conventional energy sources. There is however a flip side to batteries, as the electrochemical reactions responsible for the generation of current takes longer time to charge a battery. Then there is also problem of safe disposal of the used devices, which is posing new environmental problems [2]. Hence there is a need for energy sources which can have minimal impact on environment. One such is supercapacitors. Electrical double layer capacitors or simply, the supercapacitors store charge in the form of electrochemical reactions or absorptions of ions [3]. Supercapacitors though suffer from lower energy density when compared to batteries, have higher power density, which can help in bridging the gap between conventional capacitors and batteries [4].

The efforts are on to produce energy storage devices from waste bio materials which can solve impending energy crisis and also help in effectively using cheaply available raw materials for production thereby reducing the cost of devices [5, 6]. The present work is focused on converting such raw materials into useful nano materials for its application in making supercapacitors. We have used *Allium cepa* peel wastes as the raw material to produce carbon nano spheres (CNSs), possessing inherent porosity, high surface area, which are the required characteristics for energy storage devices [7]. The performance of such CNSs fabricated as electrodes were investigated in the present work.

II. MATERIALS AND METHODS

A. Synthesis of CNSs

Allium cepa waste peels were collected and washed with Millipore water to remove the dirt and contaminants. Washed peels were dried at 100 °C for 24 hours to remove the moisture. The dried peels were ground and sieved to get uniform particle size of 60 µm. Such particles were separately pyrolyzed in

nitrogen (N₂) atmosphere (at a flow rate of 150 mL cm⁻³) at 500 °C and 600 °C at heating rate of 10 °C min⁻¹ using quartz tube furnace (NoPo Nanotechnologies, India). The obtained carbonaceous materials here on words will be referred to as ON-5 and ON-6 respectively, was characterized to know the morphology and size of the particles.

B. Material characterization

The morphological nature of obtained CNSs (ON-5 and ON-6) was characterized by Field Emission Scanning Electron Microscopy (FESEM, JEOL JSM-7100F) at 15kV. The X-ray diffraction (XRD) natures were recorded by PANalytical-X-Ray. Fourier Transform Infrared Spectroscopy (FTIR) was done to understand the functional groups left behind after pyrolysis (FTIR, PerkinElmer, Spectrum 100). The pore size was determined by performing Brunauer-Emmett-Teller (BET) using N₂ adsorption-desorption mechanism (BELSORP-max, Microtrac, Japan).

C. Electrode fabrication and electrochemical studies

The working electrodes were prepared by homogeneous mixture of CNSs (ON-5 and ON-6), carbon black and PVDF in the ratio of 85%, 7.5% and 7.5% respectively in NMP onto stainless steel. All the electrochemical experiments were conducted using

1.0V (-1V to 0) at scan rate from 10 mV/s to 100 mV/s. Galvanostatic constant current charge discharge tests were performed at current densities varying from 0.1 A/g to 1.0 A/g. Impedance results were measured from 50 kHz to 0.01 Hz at 10 mV amplitude signal with AC current at open circuit potential (OCP).

III. RESULTS AND DISCUSSIONS

A. Structural characterization

The morphology and the mass percentages of elements present in the CNSs (ON-5 and ON-6) were examined using FESEM combined with EDX (Energy dispersive X-ray spectroscopy) (Fig. 1 (a,c)). The EDX confirms the high amount of carbon (74.2 % for ON-5 and 78.1 % for ON-6) along with other elements like, Na, Mg, K, Ca, with a small percentages, except O₂ which is present in fairly excess in both ON-5 and ON-6. (Fig.1 (b, d)).

FTIR was used to analyze the functional groups present in the sample. (Fig. 2 (a,d)). A peak at 1611 cm⁻¹ may be attributed to C=C stretching vibration, which is an indication of graphitic carbon. Bending vibrations appeared at 1443 cm⁻¹ and 875 cm⁻¹ for C-H and C=C respectively. A peak at 1120 cm⁻¹ hints at presence of C-O-C linkage along with a peak at 1380 cm⁻¹ which is for the stretching vibrations of S=O.

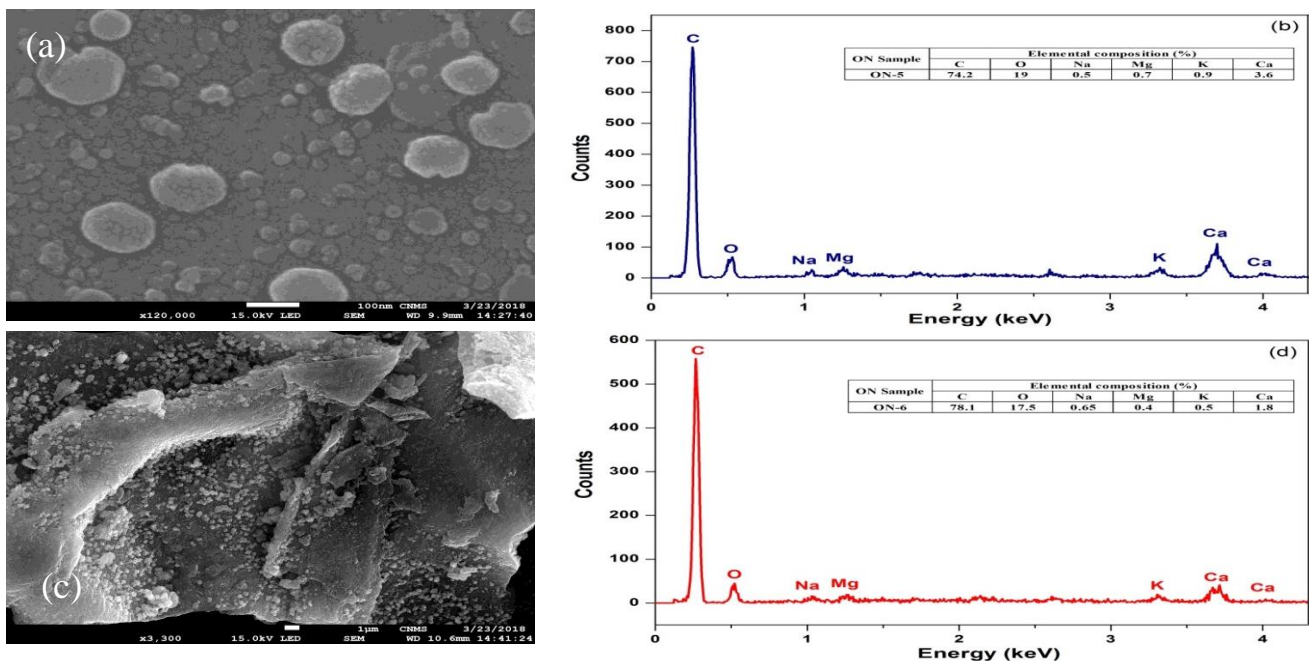


Figure 1. FESEM images of ON-5 (a), ON-6 (c) and EDS plots of ON-5 (b) and ON-6 (d). The inset is the percentage composition of elements present in ON-5 and ON-6 respectively.

MULTIAUTOLAB M2014 potentiostat/galvanostat. Platinum wire was used as counter electrode; saturated calomel electrode was used as reference electrode along with the working electrodes ON-5 and ON-6. The electrolyte used was 3.0 M KOH. Cyclic voltammetry tests were done with potential window of

Structural and particle arrangement were understood by XRD (Fig. 2 (b, e)). The Patterns show significant peaks at 26.6° and 44° which are inherent to nanocarbons.[8] The peaks suggest the graphitic nature of ON-5 and ON-6.[9] Porosity of the material

was determined by BET studies (Fig. 2 (c, f)). The mean pore diameter of CNSs ON-5 and ON-6 were found to be 1.40 nm and 3.1094 nm respectively.

B. Electrochemical measurements

Supercapacitor electrode performance

The electrochemical performance of the electrodes (ON-5 and ON-6) fabricated from carbon nanospheres synthesized from *Allium cepa* peels were studied in 3.0 M KOH after initial stabilization for 20 CV cycles at 5 mV/s in a potential window of -1V – 0V.

C. Effect of carbonization temperature

Effect of pyrolysis temperature on electrochemical behavior of CNSs derived from *Allium cepa* peels was studied using cyclic voltammetry, Galvanostatic

which stands at 132.03 F/g, as can be expected, with increase in synthesis temperature of CNSs, [8] which is calculated from equation (1).[11]

$$C = \frac{I\Delta t}{\Delta V m} \quad (1)$$

Where, I , t , V and m are discharge current (A), discharge time (s), potential window (V) and mass loaded onto the electrode (g). The charge-discharge curves are almost linear and there is negligible iR drop. As can be seen from Fig 4, the ion discharge time is larger than charging time for both ON-5 and ON-6. Discharge time is much larger for both ON-5 and ON-6 at lower current densities. Marked difference in discharge time is visible between ON-5

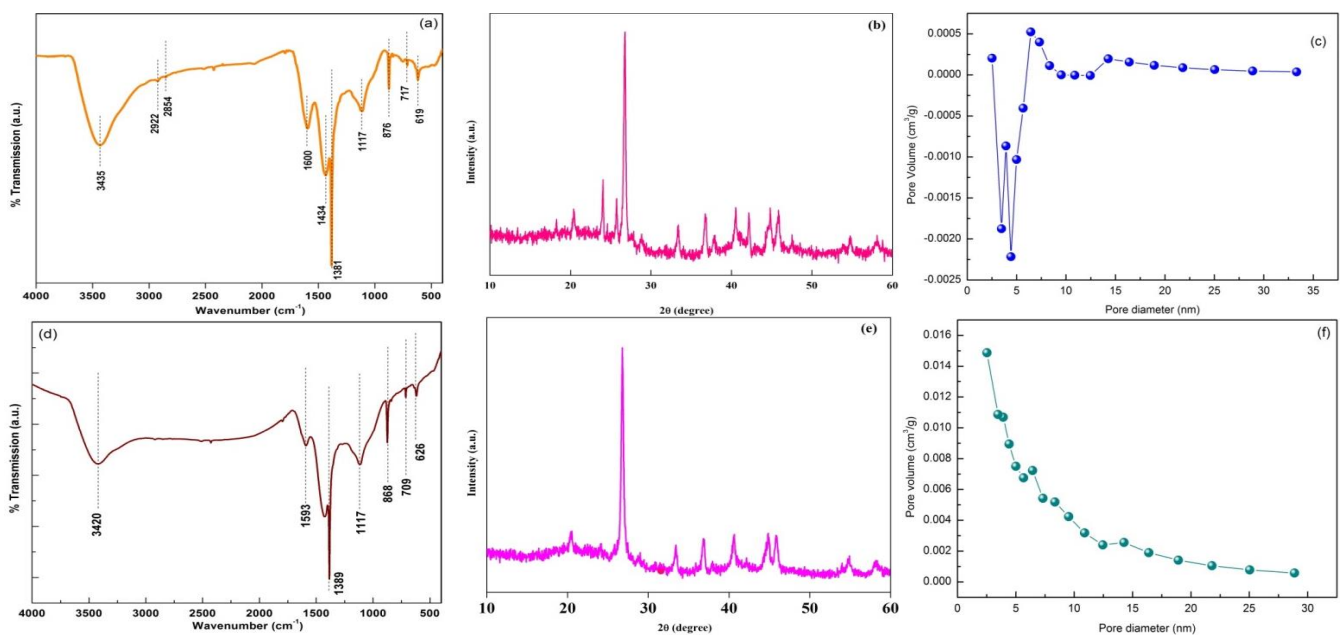


Figure 2. FTIR spectra of ON-5 (a) and ON-6 (d). XRD plots of ON-5 (b) and ON-6 (e). Pore size distribution of CNSs for ON-5 (c) and On-6 (f).

constant current charge discharge and impedance spectroscopy. Cyclic voltammetry curves of CNSs synthesized at 500 °C and 600 °C (ON-5 and ON-6) at different scan rates (10, 25, 50, 75 and 100 mV/s) are shown in Fig. 1 (a-c).

As can be seen from Fig. 3, there is noticeable increase in the area of the curve for ON-6, when compared with ON-5. The curves for ON-5 and ON-6 are also marked by absence of any redox peaks. The galvanostatic constant charge-discharge curves of carbon nano spheres (ON-5 and ON-6) at different current densities (Fig. 4 (a-c)) show a typical linear triangular pattern which is an intrinsic property of capacitors.[10] ON-6 has a slightly higher discharge capacitance of 149.49 F/g at 0.1 A/g, than ON-5,

and ON-6 at higher current density (1.0 A/g). The synthesized ON-6 gains importance as it shows good capacitance of 149.49 F/g without the need of activation, when compared to earlier reported works [3, 5, 12, 13].

D. Electrochemical impedance spectroscopy:

EIS of CNSs was studied to understand the frequency response and kinetics of electrochemical reactions of the fabricated electrodes. EIS was conducted in the frequency range of 0.01 Hz to 50 kHz. Nyquist plot of ON-5 and ON-6 are shown in Fig. 5 (a,b).

The plots show, a marked semi-circle at higher frequencies and at lower frequencies show a vertical linear tail, which can be attributed to existence of

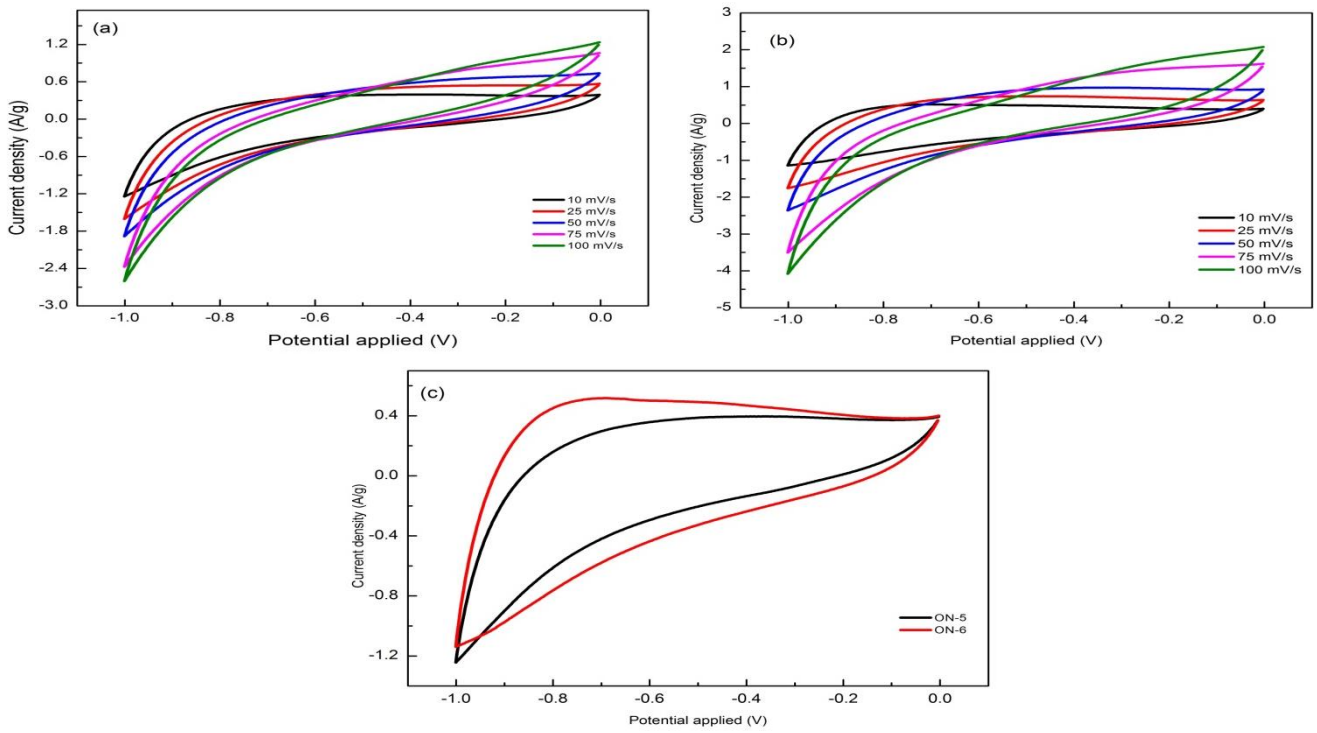


Figure 3. Cyclic voltammetry curves at different scan rates for ON-5 (a) and ON-6 (b). Comparative CV curves of both ON-5 and ON-6 (c) at 10 mV/s in 3.0 M KOH

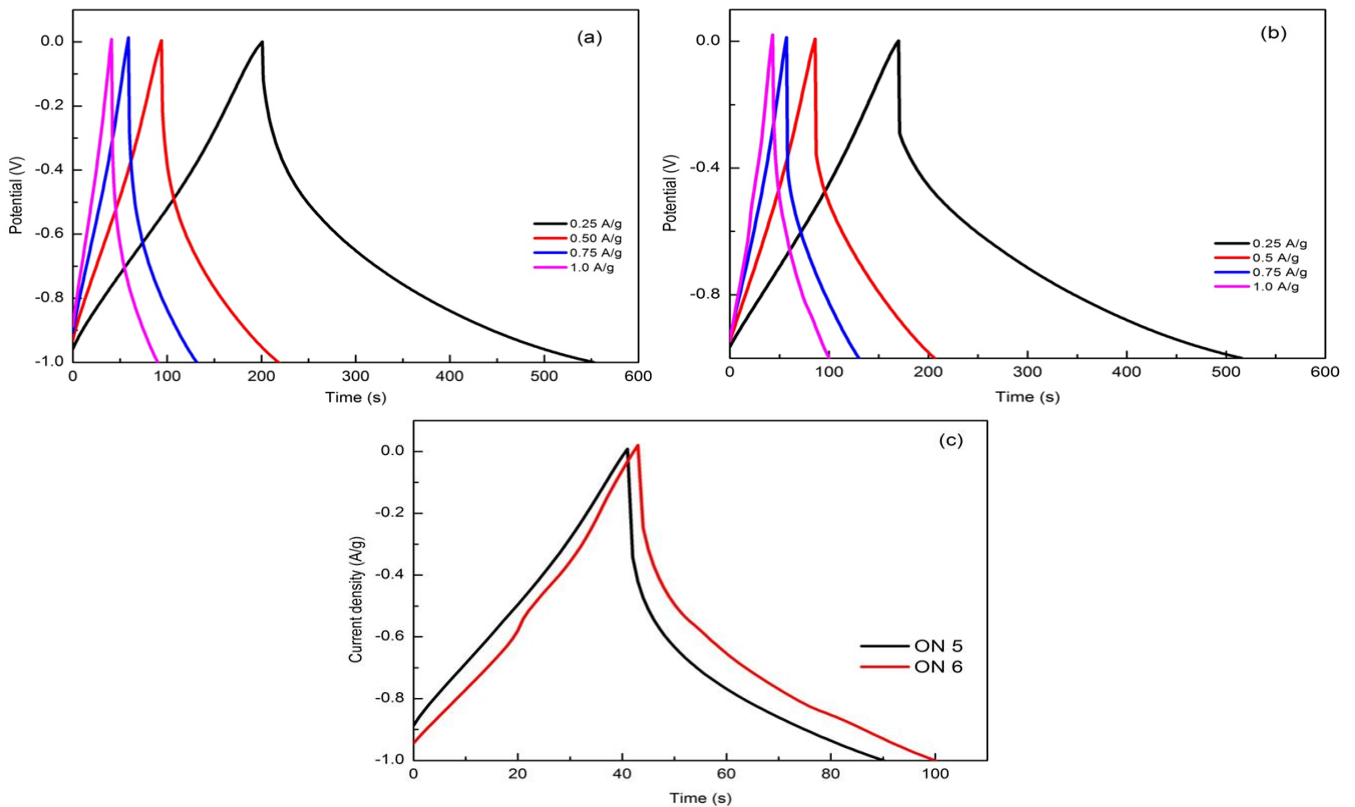


Figure 4. Galvanostatic constant current charge discharge curves at different current densities for ON-5 (a) and ON-6 (b). Comparative Charge-discharge curves of both ON-5 and ON-6 (c) at 1.0 A/g in 3.0 M KOH

impedance at the electrolyte/electrode interphase, solution resistance and Warburg impedance in the system.[14]

The equivalent circuit model was used to fit the experimental data to obtain impedance parameters, which are listed in Table (1).

Table 1. Fitting parameters of the experimental impedance data at OCP for CNSs ON-5 and ON-6 in 3.0 KOH electrolyte

Electrode	R_s (Ω)	R_p (Ω)	C (F)	CPE Y_0 10^{-5} ($S.s^n$)	W Y_0 ($S.s^{1/2}$)	τ (s)
ON-5	0.45	31.62	0.0079	4.89	0.022	2.5
ON-6	0.34	52.42	0.113	9.05	0.032	5.92

The vertical linear line in low frequency region indicates capacitive behavior [7]. CNSs exhibited small R_s values for both ON-5 and ON-6. The charge-transfer resistance (R_p) was however high which can be attributed to usage of steel plate substrate on which the CNSs were coated.

The correlation between phase angle and the frequency response of the materials are described by

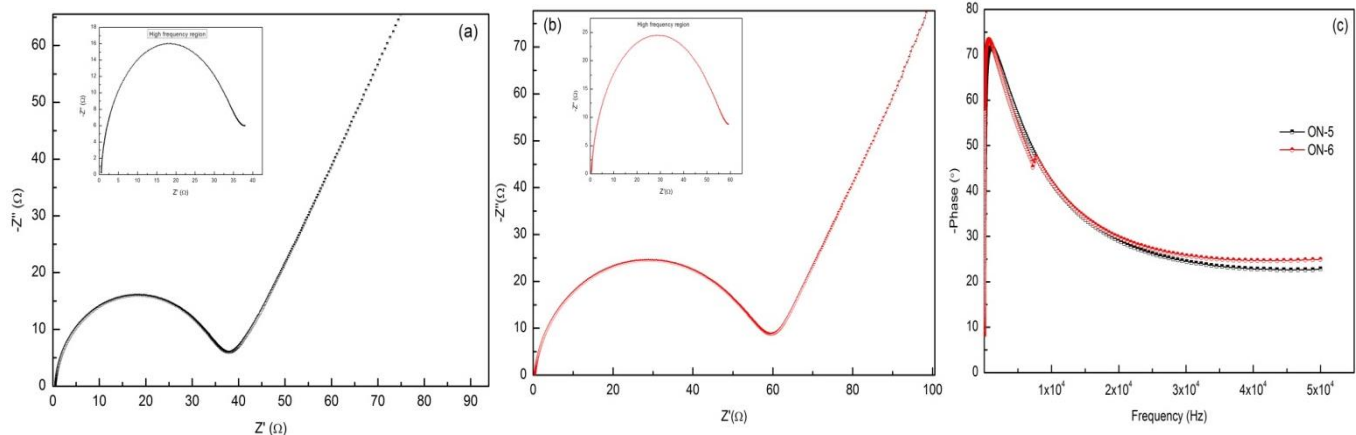


Figure 5. Nyquist plots (the insets are zoomed view of the plots at high frequency region) of ON-5 (a) and ON-6 (b). Bode phase angle plot (c) as a function of frequency for both ON-5 and ON-6

Bode plot (Fig. 3 (c)) [14]. The phase angle for ON-5 and ON-6 in 3.0 M KOH was found to be -71.6° and -73.34° respectively, which is comparable to ideal capacitor (-90°) [10, 15]. This indicates that, ON-6 is has a slightly better capacitive characteristics than ON-5. The transition between resistive and capacitive behavior is identified by the time constant (τ) which is significantly low for both ON-5 and ON-6. The frequencies above $1/\tau$ shows resistive behavior and below $1/\tau$ show capacitive behavior [10].

Specific capacitance of both ON-5 and ON-6 as a function of current density is plotted (Fig. 6). The specific capacitance though decreases with increase in current density [10, 14-16], as can be seen from Fig. 6, the decrease is not drastic and promises the use at versatile current densities.

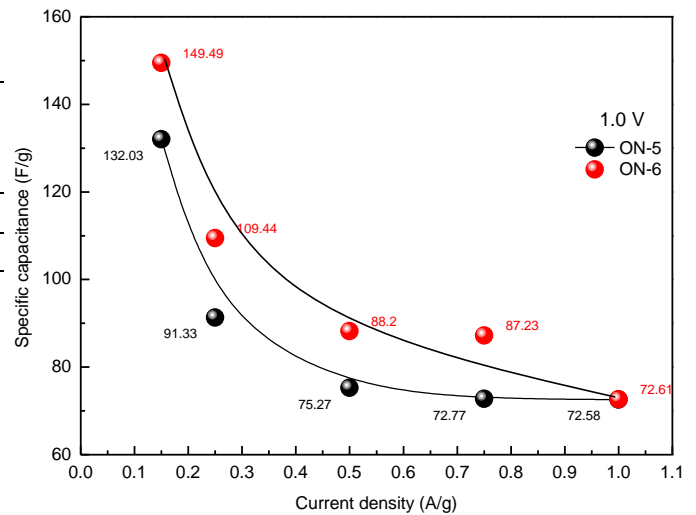


Figure 6. Plot of specific capacitance of ON-5 and ON-6 as a function of current density

The present study highlights the significance of spherical shaped nanoparticle derived from biological source, *Allium cepa* for electrochemical energy storage applications.

IV. CONCLUSIONS

The present paper signifies a more economical and green material for energy storage application synthesized from *Allium cepa* peels by a one-step pyrolysis process. ON-6 showed a specific capacitance of 149.49 F/g. A further increase in specific capacitance is possible if the materials are activated by suitable activating agents and those works are in progress.

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REFERENCES

- [1] M. Hoel, S. Kverndokk. (1996). Depletion of fossil fuels and the impacts of global warming. *Resour. Energ. Econ.* 18(2), pp. 115-136.
- [2] W. Zhang, C. Xu, W. He, G. Li, J. Huang. (2017). A review on management of spent lithium ion batteries and strategy for resource recycling of all components from them. *Waste Man. & Res.* 36(2), pp. 99-112.
- [3] A. Divyashree, G. Hegde. (2015). Activated carbon nanospheres derived from bio-waste materials for supercapacitor applications a review. *RSC Advances* 5(10), pp. 88339-88352.
- [4] B. E. Conway. (1991). Transition from Supercapacitor to Battery Behavior in Electrochemical Energy Storage. *J. The Electrochem. Soc.* 138(6), pp. 1539-1548.
- [5] A. Divyashree, S. A. B. A. Manaf, S. Yallappa, K. Chaitra, N. Kathyayini, G. Hegde, (2016). Low cost, high performance supercapacitor electrode using coconut wastes: eco-friendly approach. *J. Energ. Chem.* 25(5), pp. 880-887.
- [6] G. Hegde, S. A. Abdul Manaf, A. Kumar, G. A. M. Ali, K. F. Chong, Z. Ngaini, K. V. Sharma. (2015). Biowaste Sago Bark Based Catalyst Free Carbon Nanospheres: Waste to Wealth Approach. *ACS Sustain. Chem. & Eng.* 3(9), pp. 2247-2253.
- [7] G. A. M. Ali, S. A. B. A. Manaf, A. Kumar, K. F. Chong, G. Hegde. (2014). High performance supercapacitor using catalysis free porous carbon nanoparticles. *J. Phys. D: Appl. Phys.* 47(49), pp. 495307.
- [8] S. Supriya, G. Sriram, Z. Ngaini, C. Kavitha, M. Kurkuri, I. P. De Padova, G. Hegde. (2019). The Role of Temperature on Physical and Chemical Properties of Green Synthesized Porous Carbon Nanoparticles. *Waste and Biom. Valoriz.* pp. 1-11.
- [9] C. Ramirez-Castro, C. Schtter, S. Passerini, A. Balducci. (2016). Microporous carbonaceous materials prepared from biowaste for supercapacitor application. *Electrochim. Act.* 206, pp. 452-457.
- [10] G. A. M. Ali, A. Divyashree, S. Supriya, K. F. Chong, A. S. Ethiraj, M. V. Reddy, H. Algarni, G. Hegde. (2017). Carbon nanospheres derived from *Lablab purpureus* for high performance supercapacitor electrodes: a green approach. *Dalton Trans.* 46(40), pp. 14034-14044.
- [11] C. Zequine, C. K. Ranaweera, Z. Wang, S. Singh, P. Tripathi, O. N. Srivastava, B. K. Gupta, K. Ramasamy, P. K. Kahol, P. R. Dvornic, R.K. Gupta. (2016). High Performance and Flexible Supercapacitors based on Carbonized Bamboo Fibers for Wide Temperature Applications. *Scientific Rep.* 6, pp. 31704.
- [12] T. E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu, G. Q. Lu. (2010). Microstructure and electrochemical double-layer capacitance of carbon electrodes prepared by zinc chloride activation of sugar cane bagasse. *J. Power Sourc.* 195(3), pp. 912-918.
- [13] V. Subramanian, C. Luo, A. M. Stephan, K. S. Nahm, S. Thomas, B. Wei. (2007). Supercapacitors from Activated Carbon Derived from Banana Fibers. *The J. Phys. Chem. C.* 111(20), pp. 7527-7531.
- [14] W. H. Qu, Y. Y. Xu, A. H. Lu, X. Q. Zhang, W. C. Li. (2015). Converting biowaste corncob residue into high value added porous carbon for supercapacitor electrodes. *Biores. Technol.* 189, pp. 285-291.
- [15] W. Q. Tian, , Q. Gao, Y. Tan, K. Yang, L. Zhu, C. Yang, H. Zhang. (2015). Bio-inspired beehive-like hierarchical nanoporous carbon derived from bamboo-based industrial by-product as a high performance supercapacitor electrode material. *J. Mat. Chem. A.* 3(10), pp. 5656-5664.
- [16] H.Z. Wang, J. K. Li, K. Tak, C.M.B. Holt, X. Tan, Z. Xu, B.S. Amirkhiz, D. Harfield, A. Anyia, T. Stephenson, D. Mitlin. (2013). Supercapacitors based on carbons with tuned porosity derived from paper pulp mill sludge biowaste, *Carbon.* 57, pp. 317-328.