



Comparison of Porous Carbon Electrodes Derived from *Madhuca longifolia* Leaves by Hydrothermal Technique and Direct Pyrolysis Techniques

M. SHANMUGA PRIYA*^{ORCID} and R. RAJALAKSHMI^{ORCID}

Department of Chemistry, Avinashilingam Institute for Home Science and Higher Education for Women, Coimbatore-641043, India

*Corresponding author: E-mail: shanmugapriyathechemist@gmail.com

Received: 6 February 2023;

Accepted: 24 March 2023;

Published online: 30 March 2023;

AJC-21207

In present study, porous conducting functional carbon material was prepared from *Madhuca longifolia* leaves by hydrothermal and direct pyrolysis techniques. Further, the prepared carbon materials from different techniques were activated to enhance their physico-chemical, morphological and electrochemical properties. The synthesized conductive carbon materials were characterized by X-ray diffraction studies, energy-dispersive X-ray spectroscopy (EDS), Raman spectroscopy, Fourier-transform infrared spectroscopy (FTIR), Brunauer-Emmett-Teller (BET), field emission scanning electron microscopy (FESEM) and transmission electron microscope (TEM) techniques. To evaluate the electrochemical performance of the prepared carbon material, cyclic voltammetry and galvanostatic charge-discharge studies were carried out in 1 M H₂SO₄ aqueous electrolyte in a three-electrode system. Compared to carbon material synthesized via the hydrothermal process (82.85 F/g), the capacitance of 173.75 F/g found in the *Madhuca longifolia* biowaste precursor obtained via direct pyrolysis is quite satisfactory. Thus, *Madhuca longifolia* derived functional carbon can be used as green, low-cost electrode materials for supercapacitors.

Keywords: Direct pyrolysis, Hydrothermal carbonization, *Madhuca longifolia* leaves, Electrochemical techniques, Supercapacitors.

INTRODUCTION

Biomass materials were commonly used to refer to plant materials, but it also relates to products and waste from animal husbandry, food processing and preparation and residential organic wastes [1]. The energy crisis, pollution and global warming were all critical issues causing widespread worry worldwide. The development of carbon materials that will be applicable in vast electrochemical sectors has growing research among researchers [2]. The development of electrical devices as energy and power storage device from renewable biomass sources has been sparked by growing global concerns about depletion in the energy supply. Electrochemical capacitors, among several possibilities have the more significant potential to recover biomass to energy-supplying storage devices [3,4]. Further advances in material properties and electrolyte modifications were required to meet the increased demands of future energy storage systems. Reduction in the cost of these bio-derived materials will also be a critical factor in their widespread commercialization [5]. Energy storage supercapacitors with distinctive

energy and power will become increasingly popular in constructing low-emission vehicles. Many efforts are made to reduce environmental contamination [6].

The supercapacitors also called ultracapacitors were divided into three categories based on energy storage methods for example, electric double-layer capacitors (EDLC), pseudocapacitors and hybrid supercapacitors. Among these types, EDLC has a long life, high energy and power density. They were non-toxic and environmentally friendly. The EDLC holds a prime position in the commercial world, while the pseudocapacitors use composites like RuO₂, Fe₃O₄, MnO₂ and stored charge by a Faradaic redox reaction at the interface of electrolyte and electrode [7].

Various researchers investigated the energy storage properties of biomass-derived carbon material without and with chemical activation. European deciduous tree [8], poplar catkins [9], celery [10], carbonized wood cell chamber [11], *Ficus religiosa* [12], starch [13], honeyvine milkweed [14], carrot [15], pine saw dust [16], chicken feather biopolymer [17], *Laminaria japonica* [18], natural bamboo [19], pine cone [20], corncobs

[21], kapok fibers [22], tree bark [23] and tremella (white fungus) [24] exhibits the specific capacitance of 24, 251, 245, 288, 3.4, 250, 215, 161, 175.6, 181, 192, 293, 137, 319, 144, 114 and 53.5 F/g, respectively. *Madhuca longifolia* (L.) J.F. Macbr, also known as the Mahua or the Indian butter tree is a member of the Sapotaceae family with a socio-economic value that grows throughout the Indian subcontinent's tropical and subtropical geographic areas [25]. To the best of our knowledge, no reports of biocarbon materials derived from *M. longifolia* leaves being used in the supercapacitor electrode applications have been found. In this study, the biomass source *Madhuca longifolia* leaves were chosen as the biomass precursor for fabricating sustainable, efficient and eco-friendly carbon-based electrode materials for supercapacitor applications.

EXPERIMENTAL

The blown-down, dried leaves of *Madhuca longifolia* (Mahua tree) were collected, powdered and pre heated in hot air oven at 60 °C for 24 h. The analytical-grade urea, potassium hydroxide, hydrochloric acid and sulphuric acid were procured from Sigma-Aldrich, USA and used as such.

Synthesis of carbon material: Dried *Madhuca longifolia* leaves (5 g) were mixed with KOH in a 3:1 ratio, transferred into a 10 mL Teflon-lined autoclave and subjected to a temperature of 180 °C for 4 h in muffle furnace. The obtained carbon was then acidified, dried at 90 °C for 12 h and kept in a dry place [26]. The obtained sample has been named as HTC-MLAC. Dried powdered leaves (10 g) were heated at different temperatures (600, 800 and 1000 °C) in an argon atmosphere using an alumina crucible in tubular furnace for 5 h. The resulting black powder was then washed with 5 M HCl and left to dry at 60 °C overnight. These carbonized materials were later identified as MLC-600, MLC-800 and MLC-1000. The carbonized sample at 800 °C was chemically activated using KOH as an activator in 1:3 ratio [27]. The carbon material and the activator were subjected to pyrolysis under an inert argon atmosphere for 5 h at 800 °C. The resulting activated carbon was rinsed using 5 M HCl and washed with deionized water till the supernatant became neutral pH. The resulting substance was then dried in an oven for 12 h at 60 °C [28]. The sample obtained was named as MLAC.

Characterization: The synthesized biocarbon material and activated carbon material were analyzed using various scientific instruments. The Perkin-Elmer FT-IR spectrophotometer with the software OPUS version 6.5 was used for physico-chemical characterization, along with the ULTIMA IV Model X-ray diffractometer with CuK α radiation ($\alpha = 1.5406 \text{ \AA}$) in the range of 10-90° with count time (0.2 s) at 0.02 steps and Confocal Raman Microscope with AFM imaging (WiTec alpha 300, Germany). TESCAN MIRA3 XMU Field emission scanning electron microscope and Transmission electron microscopy (TEM, 120 kV, FEI Tecnai G2) were also analyzed for the surface characterization.

Electrochemical characterization: The electrochemical properties of the newly prepared conductive carbon electrodes were studied using active materials, Super-P as a carbon conductive additive and polytetrafluoroethylene (PTFE) as a binder.

These materials were dissolved in N-methyl-2-pyrrolidone (NMP) in a weight ratio of 80:15:5 and the resulting slurry was coated onto a graphite sheet with a surface area of 1 cm². The slurry was dried in a vacuum oven at 100 °C for 24 h to allow the solvent to evaporate after it was thoroughly mixed. To test the functional carbon materials, a three-electrode system was used with 1 M H₂SO₄ as electrolyte. The synthesized carbon electrode active material of ML-derived carbon, a saturated calomel electrode (SCE) and a platinum rod were used as the working electrode, reference electrode and counter electrode, respectively. The functional carbon materials were tested using cyclic voltammetry (CV) and galvanostatic charge/discharge (GCD) analysis with CH Instrument, Model CHI608E, USA.

RESULTS AND DISCUSSION

XRD studies: To explore the surface properties of the carbon materials, the XRD analysis was performed. The MLC-600, MLC-800 and MLC-1000 unveiled peaks around 28.5° and 40.7° correspond to the stacks of graphitic amorphous carbon of the material and all the prepared material exhibits specific peak around 28.5° reveals the presence of SiO₂ inorganic compound (Fig. 1), which is present in the selected biomass precursor [29]. The MLAC and HTC-MLAC displays peak around 24° and 28° represents the amorphous nature [30].

FT-IR studies: FT-IR spectroscopy of the ML-derived carbon materials are shown in Fig. 2a-b. The surface of all three carbon materials exhibited the oxygen containing functional groups, as indicated by their spectra. Specifically, the absorption peaks at around 3363 and 3364 cm⁻¹ for MLC-600, MLC-800, MLC-1000 and MLAC were attributed to the stretching vibrations of surface hydroxyl groups (-OH) [31]. Additionally, the presence of various oxygen-containing functional groups, including C=O carbonyl stretching vibration, was indicated by the peaks observed around 1380 and 1065 cm⁻¹ [32]. Similar peaks were observed for HTC-MLAC, suggesting the presence of OH, C=O and C-O groups on the surface of the synthesized material. Table-1 infers the key peak assignment and functional groups present in the MLC derived carbon materials.

TABLE-1
FT-IR SPECTRAL ASSIGNMENT OF THE
CARBON MATERIALS DERIVED FROM
Madhuca longifolia LEAVES PRECURSOR

Precursor	Peak assignment (cm ⁻¹)	Functional groups
MLC-600	3363, 1380, 1055	OH, C=O, C-O stretching
MLC-800	3364, 1380, 1051	OH, C=O, C-O stretching
MLC-1000	3363, 1385, 1058	OH, C=O, C-O stretching
MLAC	3364, 1376, 1068	OH, C=O, C-O stretching
HTC-MLAC	3364, 1376, 1068	OH, C=O, C-O stretching

Raman studies: To evaluate the level of functionalization in carbon materials derived from biomass, Raman spectroscopy can be utilized. The ratio of the intensities of the D and G band signals on the carbon surface provides insight into the degree of graphitization and the prevalence of imperfections. Specifically, the presence of defects and graphitization in the MLC-800 can be detected through the appearance of peaks at 1358 cm⁻¹ (D band) and 1597 cm⁻¹ (G band) [14] and the corres-

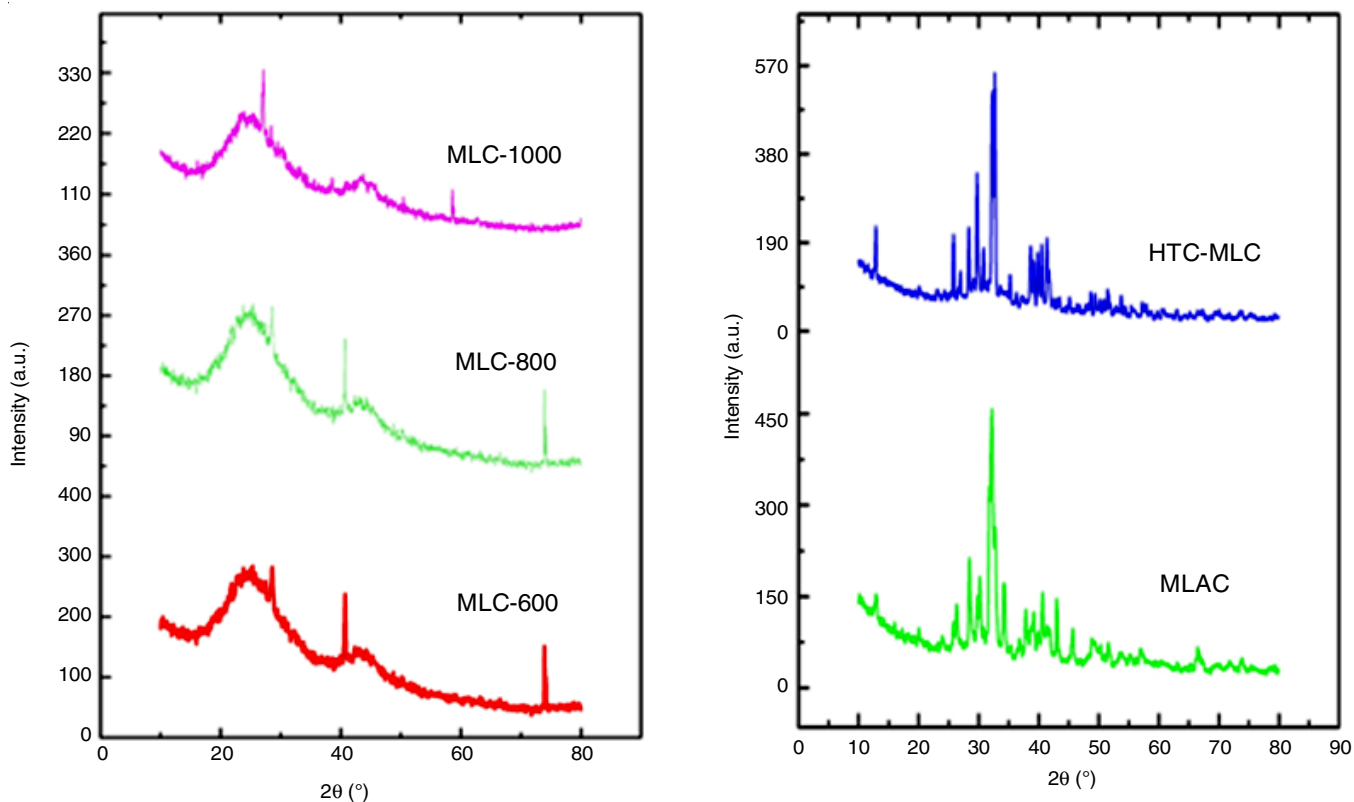


Fig. 1. XRD pattern of ML derived carbon from HTC and direct pyrolysis technique

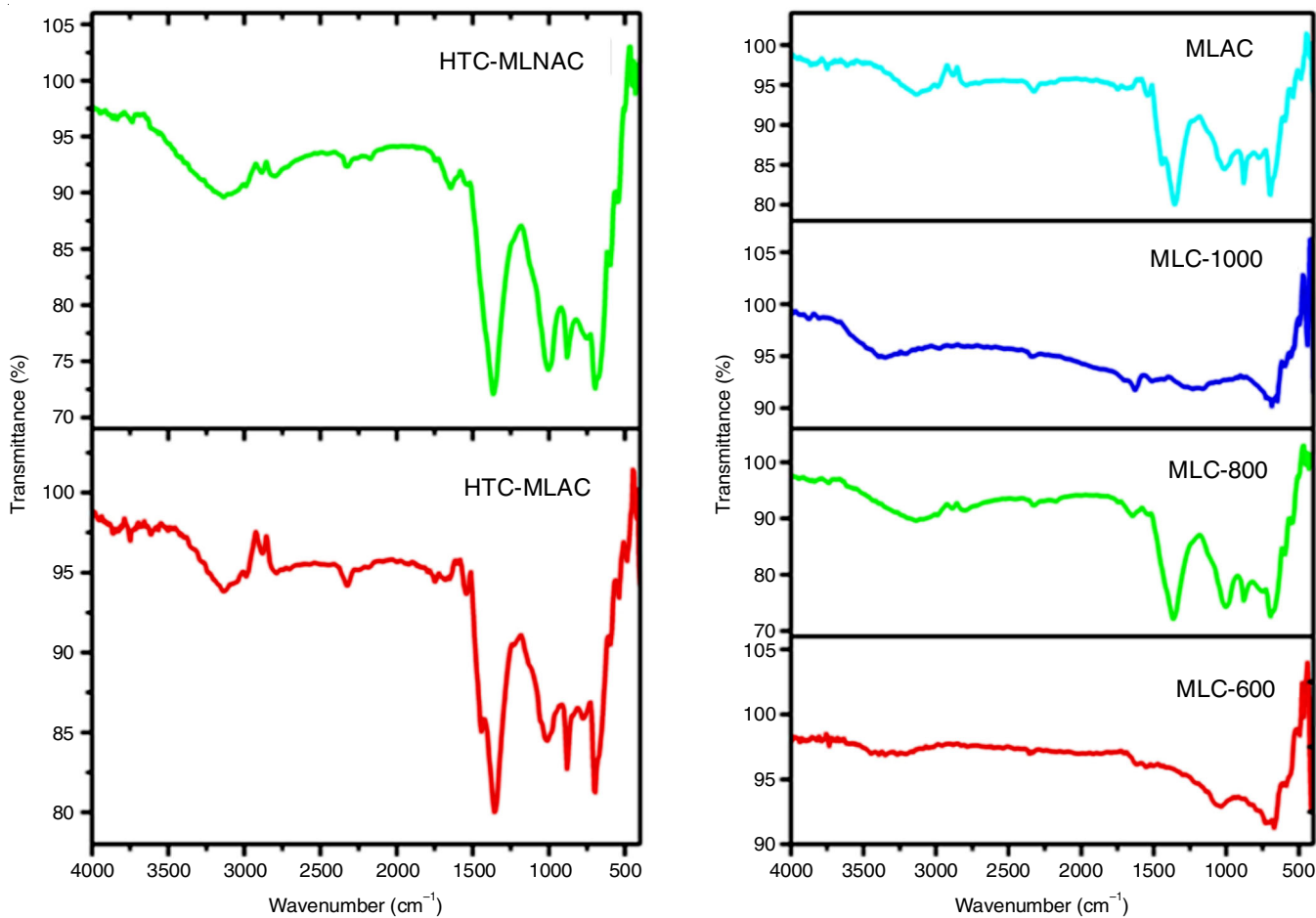


Fig. 2. FTIR spectrum of ML derived carbon from HTC and direct pyrolysis technique

ponding I_D/I_G value was 1.18 and on activation, the D band occurred around 1354 cm^{-1} and the G band was increased to 1617 cm^{-1} , which infers the higher degree of graphitization in the MLAC [33]. Raman spectra of MLC-800 and MLAC are depicted in Fig. 3.

Morphological studies: The porous nature and surface morphology of the prepared MLC-800 and MLAC furnishes the porous morphology that confirms the effective carbonization of the biomass materials in the inert atmosphere. A well-

developed interconnected porous networks with relatively thick rod like porous structures are formed in MLAC [34] and the TEM image confirms this porous morphology which are in good agreement with X-ray diffraction studies and FESEM results. Intertwined spherical morphology in the carbon matrix is confirmed in both MLC-800 and MLAC [35]. The FESEM and TEM images of MLC-800 and MLAC are shown in Fig. 4. EDS analysis (Table-2) indicated the presence of major amount of carbon and oxygen in MLC-800 and MLAC samples.

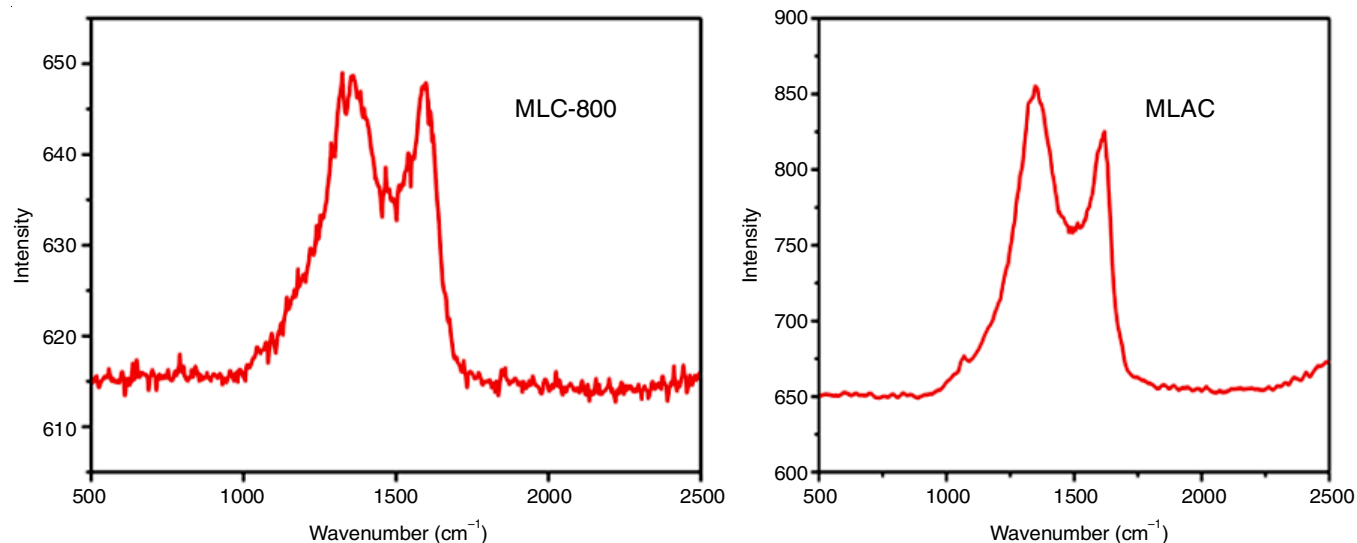


Fig. 3. Raman spectra of MLC-800 and MLAC

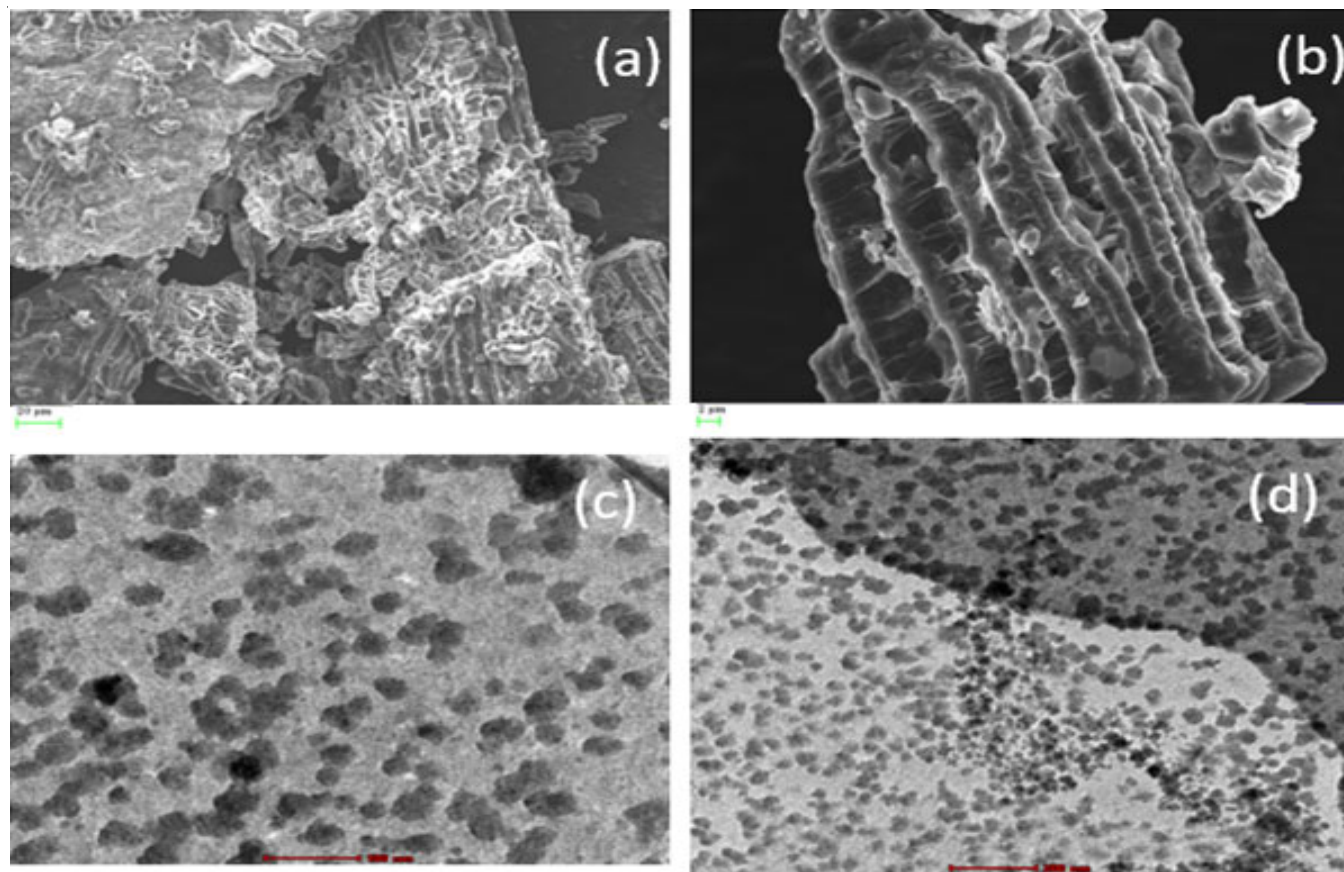


Fig. 4. FESEM and HRTEM image of (a) and (c) MLC-800 and (b) and (d) MLAC

Samples	C (%)	O (%)	N (%)	Mg (%)	Fe (%)
MLC-800	66.97	17.66	13.48	0.85	0.11
MLAC	68.48	15.08	14.96	0.87	0.08

Electrochemical studies: The electrochemical studies were carried out for performance evaluation of synthesized carbon materials as electrodes for the energy storage supercapacitors. The cyclic voltammetry studies were conducted in a three-electrode system consisting of a prepared carbon material as the working electrode, a saturated calomel electrode as the reference electrode and a platinum wire as the counter electrode. The studies aimed to investigate the electrochemical capacitive properties of the system in a 1 M H₂SO₄ electrolyte, using various scan rates ranging from 10 to 50 mV/s within a potential range of 0.8 to -0.2 V. Fig. 5 illustrates the CV profiles of MLC-600, MLC-800, MLC-1000 and MLAC. All the carbonized samples implied the quasi-rectangles between the positive and negative scan rates with deformations in the lower sweep rates indicating the existence of EDLC type behaviour.

Various galvanostatic charge discharge experiments were conducted using current densities ranging from 1.5 to 4 A/g to evaluate the CD profiles of MLC carbon materials, which were depicted in Fig. 6. The specific capacitance for single-step activation of *Madhuca longifolia* was determined to be 82.85, 76.52, 68.59, 63.87, 57.52 and 53.92 F/g at current densities of 0.5, 2, 2.5, 3, 3.5 and 4 A/g, respectively. The specific capacitance of MLC-600 was calculated to be 154.85 F/g at 1.5 A/g and decreased gradually with increasing current density to 2, 2.5, 3, 3.5 and 4 A/g were 130.85, 123.53, 114.11, 110.83 and

105.16 F/g, respectively. The MLC-800 sample exhibited a higher specific capacitance than carbon obtained through direct pyrolysis at 600 °C, with a greater capacitance of 173.75 F/g at 1.5 A/g and decreasing to 157.41, 144.13, 128.82, 115.86 and 90.13 F/g at 2, 2.5, 3, 3.5 and 4 A/g, respectively. Whereas the MLC-1000 sample showed a relatively lower capacitance than MLC-600 and MLC-800, with capacitance values of 148.96, 137.26, 128.29, 120.72, 101.89 and 93.47 F/g at current densities of 1.5, 2, 2.5, 3, 3.5 and 4 A/g, respectively. Finally, MLAC exhibited the highest capacitance of 216.6 F/g at 1.5 A/g, which reduced to 194.24, 176.27, 142.01, 127.35 and 103.28 F/g at current densities of 2, 2.5, 3, 3.5 and 4 A/g, respectively.

Table-3 specifies the specific capacitance of MLC derived carbon materials and Fig. 7 depicts the current density vs. specific capacitance curve. From the GCD results, it was revealed that MLAC obtained from direct pyrolysis technique imparts comparably higher capacitance than the HTC-MLAC obtained from hydrothermal technique.

Table-4 summarizes the specific capacitance achieved by various researchers with and without activation. From the table, the carbon material derived from *Madhuca longifolia* biowaste precursor affords the capacitance of about 216.6 F/g by direct pyrolysis technique with chemical activation, which were on par with the other waste materials derived from carbon materials like rice husk, pistachio shell [36], fir wood [36], banana fibers [37], waste newspaper [38] and seaweed biopolymer [39]. The MLC carbon materials from dry leaves of *Madhuca longifolia* acts as suitable low-cost electrodes for the supercapacitor devices.

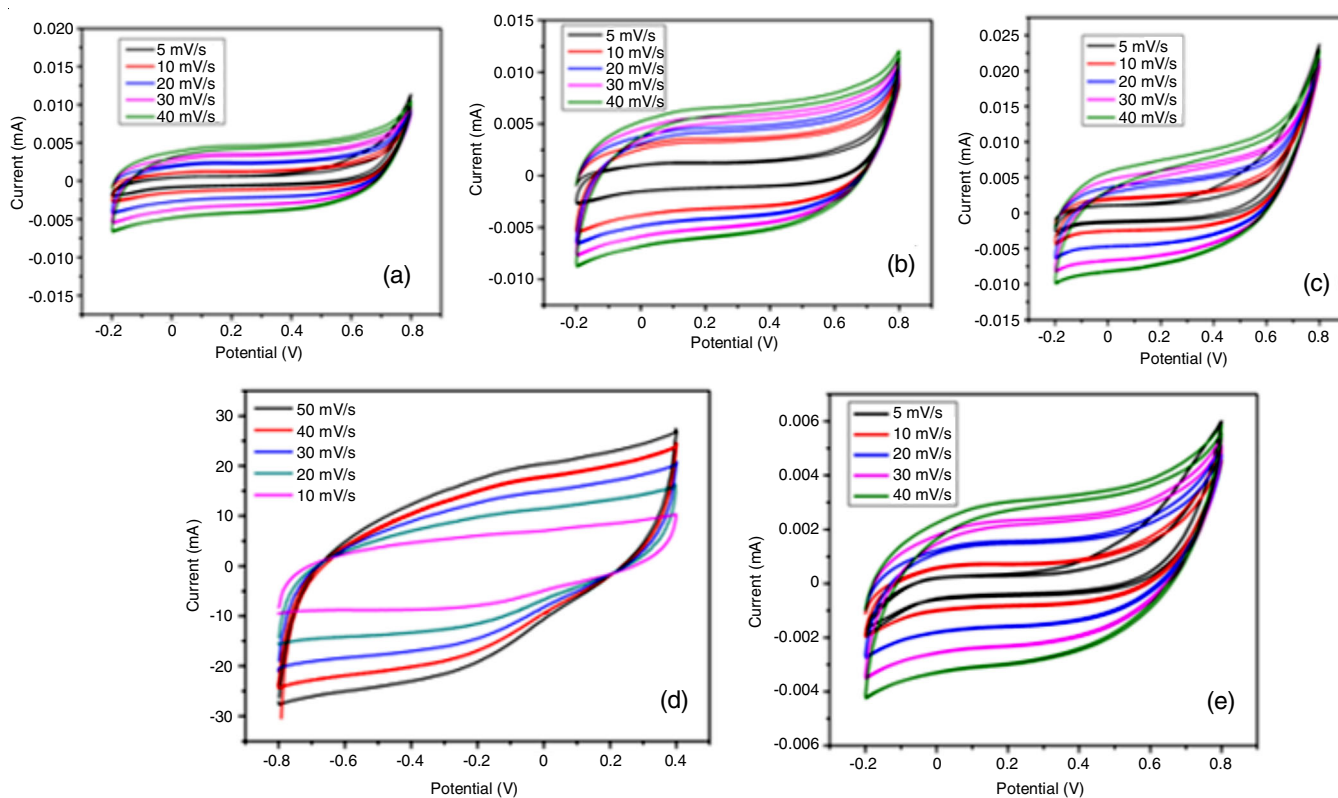


Fig. 5. Cyclic voltammograms of MLC-600 (a), MLC-800 (b), MLC-1000 (c), MLAC (d) and HTC-MLAC (e)

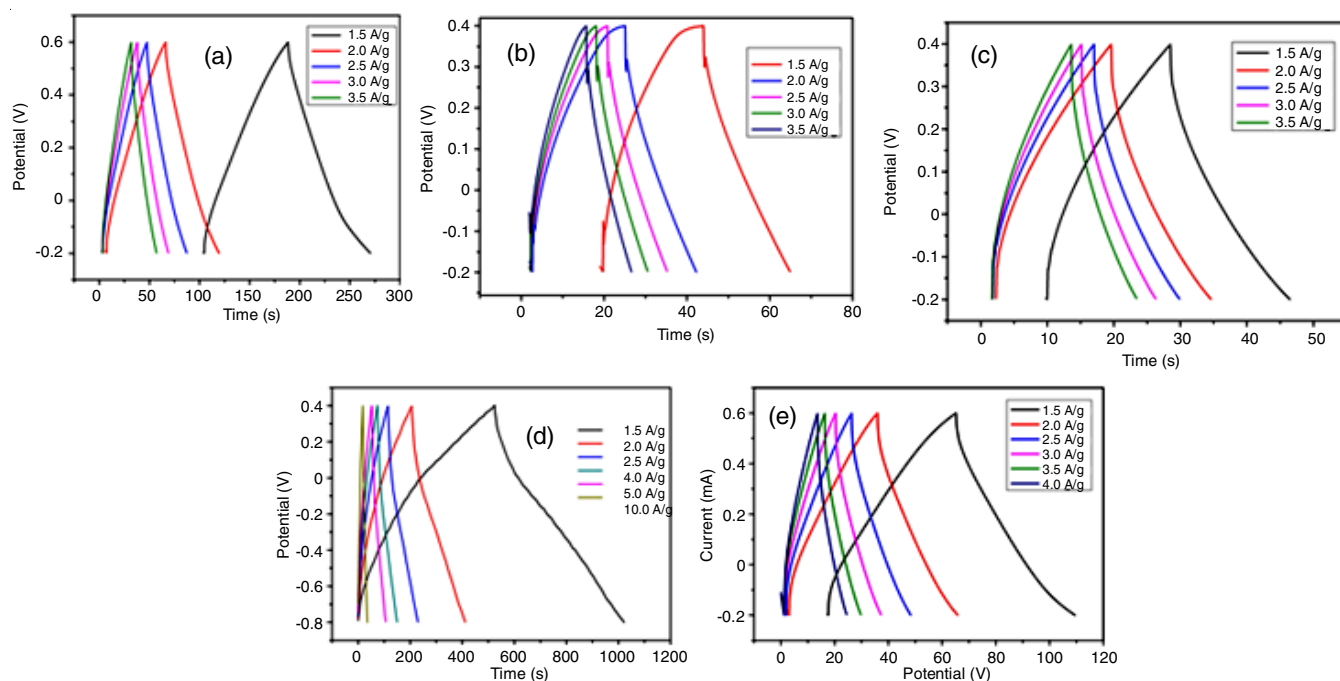


Fig. 6. GCD profiles of (a) MLC-600 (b) MLC-800 (c) MLC-1000 (d) MLAC and (e) HTC-MLAC

TABLE-3
SPECIFIC CAPACITANCE FOR HTC-MLAC, MLC AT VARIOUS PYROLYSIS TEMPERATURE AND ACTIVATED MLC

Carbon materials	Specific capacitance (F/g) at					
	1.5	2.0	2.5	3.0	3.5	4.0
HTC-MLAC	82.85	76.52	68.59	63.87	57.52	53.92
MLC-600	154.85	130.85	123.53	114.11	110.83	105.16
MLC-800	173.75	157.41	144.13	128.82	115.86	90.13
MLC-1000	148.96	137.26	128.29	120.72	101.89	93.47
MLAC	216.60	194.24	176.27	142.01	127.35	103.28

TABLE-4
ELECTROCHEMICAL PERFORMANCE COMPARISON OF VARIOUS BIOMASS
BASED ACTIVATED CARBON REPORTED IN LITERATURE vs. MLC AND MEC

Precursor	With/without activation	Activation agent	Specific capacitance	Ref
Pistachio shell	With activation	KOH	120	[36]
Firwood	With activation	KOH	180	[36]
Banana fibers	With activation	ZnCl ₂	74	[37]
Waste news paper	With activation	KOH	180	[38]
Seaweed bio polymer	Without activation	-	198	[39]
Rice husk	With activation	NaOH	210	[40]
Sugarcane bagasse	With activation	NaOH	109	[41]
Sugarcane bagasse	Without activation	-	20	[41]
Sugarcane bagasse	With activation	ZnCl ₂	230	[41]
Coffee shells	With activation	ZnCl ₂	150	[41]
HTC-MLAC	With activation	KOH	82.85	This work
MLC-600	Without activation	-	154.85	This work
MLC-800	Without activation	-	173.75	This work
MLC-1000	Without activation	-	148.96	This work
MLAC	With activation	KOH	216.6	This work

Conclusion

Madhuca longifolia derived carbon material prepared by single step hydrothermal carbonization and direct pyrolysis techniques revealed the amorphous nature from XRD studies. The FT-IR studies confirmed the presence of oxygen and carbon

rich functional groups on the surface of the synthesized materials and also corroborated by the EDS analysis. The amorphous nature was further confirmed with high degree of graphitization inferred from Raman studies. FESEM and TEM analysis of an MLAC sample confirms its porous shape. All the prepared materials shows electrical double layer behaviour in cyclic

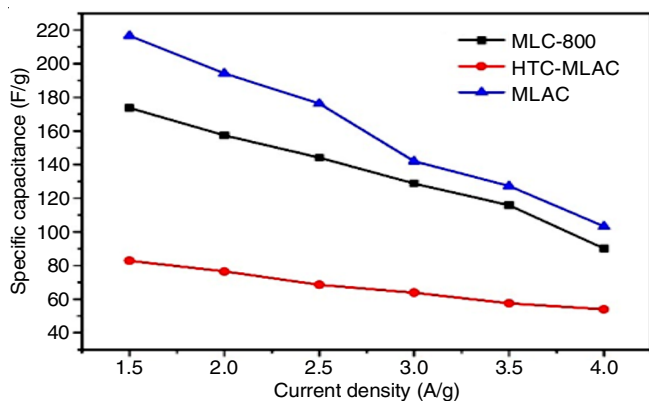


Fig. 7. Dependence of current density on specific capacitance

voltammetry and MLAC exhibits greater capacitance of 216.6 F/g obtained through direct pyrolysis procedure. Based on the results, the studied plant precursor affords the greater capacitance in direct pyrolysis technique. Therefore, these waste leaves could be used as electrodes in charge-storage supercapacitors.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

REFERENCES

- C. Zhou and Y. Wang, *Sci. Technol. Adv. Mater.*, **21**, 787 (2020); <https://doi.org/10.1080/14686996.2020.1848213>
- D.S. Priya, L.J. Kennedy and G.T. Anand, *Mater. Today Sustain.*, **21**, 100320 (2023); <https://doi.org/10.1016/j.mtsust.2023.100320>
- A.G. Olabi, Q. Abbas, A. Al-Makky and M.A. Abdelkareem, *Energy*, **248**, 123617 (2022); <https://doi.org/10.1016/j.energy.2022.123617>
- B. Hu, K. Wang, L. Wu, S. H. Yu, M. Antonietti, and M.M. Titirici, *Adv. Mater.*, **22**, 813 (2010); <https://doi.org/10.1002/adma.200902812>
- P. Purohit and V. Chaturvedi, *Environ. Sci. Pollut. Res.*, **25**, 29614 (2018); <https://doi.org/10.1007/s11356-018-2960-8>
- M.S. Priya, P. Divya and R. Rajalakshmi, *Sustain. Chem. Pharm.*, **16**, 100243 (2020); <https://doi.org/10.1016/j.scp.2020.100243>
- P. Divya, A. Prithiba, and R. Rajalakshmi, *IOP Conf. Ser. Mater. Sci. Eng.*, **561**, 012078 (2019); <https://doi.org/10.1088/1757-899X/561/1/012078>
- A. Jain, M. Ghosh, M. Krajewski, S. Kurungot and M. Michalska, *J. Energy Storage*, **34**, 102178 (2021); <https://doi.org/10.1016/j.est.2020.102178>
- X. Luo, S. Li, H. Xu, X. Zou, Y. Wang, J. Cheng, X. Li, Z. Shen, Y. Wang and L. Cui, *J. Colloid Interface Sci.*, **582**, 940 (2021); <https://doi.org/10.1016/j.jcis.2020.08.088>
- Y. Ma, J. Tian, L. Li, L. Kong, S. Liu, K. Guo and X. Chen, *Int. J. Energy Res.*, **45**, 9058 (2021); <https://doi.org/10.1002/er.6437>
- C. Xiong, B. Li, C. Duan, L. Dai, S. Nie, C. Qin, Y. Xu and Y. Ni, *Chem. Eng. J.*, **418**, 129518 (2021); <https://doi.org/10.1016/j.cej.2021.129518>
- S.T. Senthilkumar and R.K. Selvan, *ChemElectroChem*, **2**, 1111 (2015); <https://doi.org/10.1002/celec.201500090>
- S. Ghosh, R. Santhosh, S. Jennifer, V. Raghavan, G. Jacob, K. Nanaji, P. Kollu, S.K. Jeong and A.N. Grace, *Sci. Rep.*, **9**, 16315 (2019); <https://doi.org/10.1038/s41598-019-52006-x>
- A. Ariharan, K. Ramesh, R. Vinayagamoorthi, B. Viswanathan, M.S. Rani, S. Ramaprabhu and V. Nandhakumar, *J. Energy Storage*, **35**, 102185 (2021); <https://doi.org/10.1016/j.est.2020.102185>
- J. Liu, S. Min, F. Wang and Z. Zhang, *J. Power Sources*, **466**, 228347 (2020); <https://doi.org/10.1016/j.jpowsour.2020.228347>
- C. Quan, R. Su and N. Gao, *Int. J. Energy Res.*, **44**, 4335 (2020); <https://doi.org/10.1002/er.5206>
- Q. Wang, Q. Cao, X. Wang, B. Jing, H. Kuang and L. Zhou, *J. Power Sources*, **225**, 101 (2013); <https://doi.org/10.1016/j.jpowsour.2012.10.022>
- Y. Cheng, L. Wu, C. Fang, T. Li, J. Chen, M. Yang and Q. Zhang, *J. Mater. Res. Technol.*, **9**, 3261 (2020); <https://doi.org/10.1016/j.jmrt.2020.01.022>
- G. Zhang, Y. Chen, Y. Chen, and H. Guo, *Mater. Res. Bull.*, **102**, 391 (2018); <https://doi.org/10.1016/j.materresbull.2018.03.006>
- A. Bello, N. Manyala, F. Barzegar, A. A. Khaleed, D. Y. Momodu and J. K. Dangbegnon, *RSC Adv.*, **6**, 1800 (2016); <https://doi.org/10.1039/c5ra21708c>
- D. Xu, Y. Su, S. Zhang and Y. Xiong, *Energy Sources Part A*, **42**, 1797 (2020); <https://doi.org/10.1080/15567036.2019.1604890>
- J. Zhang, H. Chen, J. Bai, M. Xu, C. Luo, L. Yang, L. Bai, D. Wei, W. Wang and H. Yang, *J. Alloys Compd.*, **854**, 157207 (2021); <https://doi.org/10.1016/j.jallcom.2020.157207>
- D. Momodu, M. Madito, F. Barzegar, A. Bello, A. Khaleed, O. Olaniyan, J. Dangbegnon and N. Manyala, *J. Solid State Electrochem.*, **21**, 859 (2017); <https://doi.org/10.1007/s10008-016-3432-z>
- N. Guo, M. Li, X. Sun, F. Wang and R. Yang, *Mater. Chem. Phys.*, **201**, 399 (2017); <https://doi.org/10.1016/j.matchemphys.2017.08.054>
- V. Bisht, Neeraj, V. K. Solanki and N. Dalal, *J. Pharmacogn. Phytochem.*, **7**, 3414 (2018).
- M. Sevilla and A.B. Fuertes, *Carbon*, **47**, 2281 (2009); <https://doi.org/10.1016/j.carbon.2009.04.026>
- P. Divya and R. Rajalakshmi, *J. Energy Storage*, **27**, 1010149 (2020); <https://doi.org/10.1016/j.est.2019.101149>
- M. Karnan, K. Subramani, N. Sudhan, N. Hayaraja and M. Sathish, *ACS Appl. Mater. Interfaces*, **8**, 35191 (2016); <https://doi.org/10.1021/acsami.6b10704>
- Z. Husain, A.R. Shakeelur Raheman, K.B. Ansari, A.B. Pandit, M.S. Khan, M.A. Qyum and S.S. Lam, *Mater. Sci. Energy Technol.*, **5**, 99 (2022); <https://doi.org/10.1016/j.mset.2021.12.003>
- Y. Zhao, M. Liu, X. Deng, L. Miao, P.K. Tripathi, X. Ma, D. Zhu, Z. Xu, Z. Hao and L. Gan, *Electrochim. Acta*, **153**, 448 (2015); <https://doi.org/10.1016/j.electacta.2014.11.173>
- X. Ma, H. Wang, Q. Wu, J. Zhang, D. Liang, S. Lu and Y. Xiang, *J. Electrochem. Soc.*, **166**, A236 (2019); <https://doi.org/10.1149/2.0831902jes>
- N. Sudhan, K. Subramani, M. Karnan, N. Hayaraja and M. Sathish, *Energy Fuels*, **31**, 977 (2017); <https://doi.org/10.1021/acs.energyfuels.6b01829>
- N. Shimodaira and A. Masui, *J. Appl. Phys.*, **92**, 902 (2002); <https://doi.org/10.1063/1.1487434>
- S. Yang, S. Wang, X. Liu, and L. Li, *Carbon*, **147**, 549 (2019); <https://doi.org/10.1016/j.carbon.2019.03.023>
- M. Yang, D.S. Kim, S.B. Hong, J.-W. Sim, J. Kim, S.-S. Kim and B.G. Choi, *Langmuir*, **33**, 5140 (2017); <https://doi.org/10.1021/acs.langmuir.7b00589>
- F. Wu, R. Tseng, C. Hu, and C. Wang, *J. Power Sources*, **144**, 302 (2005); <https://doi.org/10.1016/j.jpowsour.2004.12.020>
- V. Subramanian, C. Luo, A. M. Stephan, K. S. Nahm, S. Thomas and B. Wei, *J. Phys. Chem. C*, **111**, 7527 (2007); <https://doi.org/10.1021/jp067009t>
- D. Kalpana, S.H. Cho, S.B. Lee, Y.S. Lee, R. Misra and N.G. Renganathan, *J. Power Sources*, **190**, 587 (2009); <https://doi.org/10.1016/j.jpowsour.2009.01.058>
- E. Raymundo-Piñero, F. Leroux and F. Béguin, *Adv. Mater.*, **18**, 1877 (2006); <https://doi.org/10.1002/adma.200501905>
- Y. Guo, J. Qi, Y. Jiang, S. Yang, Z. Wang and H. Xu, *Mater. Chem. Phys.*, **80**, 704 (2003); [https://doi.org/10.1016/S0254-0584\(03\)00105-6](https://doi.org/10.1016/S0254-0584(03)00105-6)
- T.E. Rufford, D. Hulicova-Jurcakova, K. Khosla, Z. Zhu and G.Q. Lu, *J. Power Sources*, **195**, 912 (2010); <https://doi.org/10.1016/j.jpowsour.2009.08.048>