

BIOMASS-DERIVED HIERARCHICAL POROUS CARBON DECORATED WITH ZNO NANOPARTICLES FOR ENHANCED ELECTROCHEMICAL ENERGY STORAGE

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Abstract

The research aimed at the development of sustainable and highly-efficient electrodes is very important for increasing the storage of energy in supercapacitors. The hierarchical porous carbon (HPC), obtained from the biomass, serves as a cheap and porous conductor; however, the efficiency of the HPC as a material for storing energy might be insufficient due to the lack of pseudocapacitance activity. The same concerns the zinc oxide (ZnO), which possesses electrochemically active sites but has a low electrical conductivity. Thus, the combination of these two materials seems very promising; however, the effect of ZnO loading amount on the structure and electrochemical characteristics of the HPC, obtained from the rice husk, has not been sufficiently studied yet. In this paper, the HPC was synthesized from the rice husk using carbonization and KOH activation, and then ZnO nanoparticles were doped into the structure. Composites of HPC/ZnO with the mass ratios of 5%, 15%, and 20% ZnO were prepared and characterized. The electrochemical characterization was done by different methodologies such as cyclic voltammetry, galvanostatic charge-discharge analysis, electrochemical impedance spectroscopy, rate capability, cycling stability, and charge storage kinetics. HPC/ZnO-15 showed the highest specific capacitance of 380 F g⁻¹ among all the synthesized samples while the pristine HPC had the specific capacitance of 250 F g⁻¹ at the current density of 1 A g⁻¹. Moreover, the optimized composite maintained 75% capacitance at the current density of 10 A g⁻¹. An asymmetric supercapacitor prepared from the optimized composite was also evaluated for the potential applications in energy storage system.

1 Introduction

The increase in demand for portable electronic devices, electric vehicles, renewable energy systems, and battery back-up systems has made it necessary for there to be efficient and environmentally friendly energy storage devices[1]. Supercapacitors have been studied extensively due to their ability to exhibit high rates of charge and discharge, high power densities, good rate capability, and long-life cycles as compared with traditional batteries[2]. Nevertheless, their low energy density constitutes a significant drawback for their use in practical applications. Consequently, the search for electrode materials that are able to store high amounts of charges and at the same time allow for fast ion transfer and good cycling stability constitutes one of the main topics in the field[3].

Carbonaceous materials have become one of the most studied materials for use as electrodes for supercapacitors due to their high electrical conductivity, chemical stability, low cost, and ability to form a porous structure[4]. Porous carbon made from biomass became an attractive material due to its renewability, wide availability, low cost, and possibility to produce porous carbon through carbonization and activation. The biomass-derived porous carbons may have interconnected micro-, meso- and macropores, which could be responsible for providing storage sites and ion mobility within the material. Activation by chemicals such as KOH is a widely used method to improve pores and surface areas of materials. Recent works have shown that porous carbons obtained from biomass have great electrochemical properties; however, the properties depend on the material precursor, carbonization process, activation method and structure[5].

Rice husk biomass is a good starting material for porous carbon synthesis because it is a readily available biomass waste and it contains carbon-based compounds along with silica. The natural structure of the material might also help in generating porous carbon after thermal treatment and activation. Recently, it has been seen that porous carbon produced from rice husk biomass could be designed with proper pore structure for electrochemical energy storage. But it is seen that only the improvement

in the surface area and pore structure of biomass carbon may not be enough to enhance the energy density or pseudo capacitance of porous carbon electrodes. It is also noted that only the surface area is not enough to define the performance of porous carbon electrodes in electrochemical energy storage[6].

One method to address the limitations associated with the carbon electrodes involves the use of transition-metal oxides. The metal oxides may contribute to the generation of additional active electrochemical centers as well as faradaic charge storage, whereas the carbon pores may offer an electrically conducting path and facilitate the electrolyte ion diffusion. Several metal oxides are available but ZnO is particularly useful due to its cheapness, stability, easy preparation process, and electrochemical activity[7]. The poor electrical conductivity of ZnO material may hinder its charge transfer capability. It is thus logical to suggest that the combination of ZnO with conductive porous carbon may prove to be a good option for creating composite electrodes. ZnO/carbon composite materials have previously demonstrated better capacitive characteristics than their counterparts made up of carbon only[8].

On the other hand, the performance of the carbon/metal oxide composite largely relies on the loading and distribution of the metal oxide. The excessive loading of ZnO may coat the surface of the active carbon and prevent the access of electrolyte ions. Instead, the optimal loading of ZnO may create new active sites but still retain the electrical conductivity and porosity of the carbon structure[9]. Therefore, regulating the loading of ZnO is essential for finding the right balance between electrical conductivity, porosity, ion diffusion, and faradaic contributions. Previous ZnO/hierarchical porous carbon structures have shown that the nanodispersed loading of ZnO into the porous carbon matrix will create a synergetic effect of carbon-based double-layer capacitance and the additional electrochemical effects of ZnO. While much advancement has been made in terms of biomass-derived carbon and ZnO/carbon composite materials, there still exists a critical research issue in this field[10]. There has been considerable emphasis on

optimizing porous carbons derived from biomass and developing complicated metal oxide/carbon composites through the use of templates and doped carbons. For instance, ZnO has been well synthesized with activated carbon and hierarchical porous carbon; however, most of the reported materials require complicated synthetic routes or controlled templates. Moreover, even though rice husk has been extensively studied for biomass carbon, comparatively little work has been done on the systematic study of loading of ZnO onto rice husk-derived hierarchical porous carbon as a supercapacitor electrode[11]. In particular, the interdependency of ZnO amount, structure, electrochemical energy storage mechanism, rate capability, impedance properties, and charge storage kinetics needs to be elucidated. Therefore, it is vital to carry out systematic comparisons of different amounts of ZnO loading to determine the right composition rather than assuming higher ZnO amounts to enhance the electrochemical performance[12]. HPC was obtained from rice husks by carbonization and then KOH activation and then was mixed with ZnO nanoparticles to create HPC/ZnO composite electrodes for energy storage application. Three compositions of ZnO (5, 15, and 25 wt.%) were considered in the work in order to understand the effect of ZnO concentration on the structural and electrochemical characteristics of the composites. Analysis of the synthesized materials involved XRD, TEM/SEM, FTIR spectroscopy, specific surface area and porosity analysis, and thermal analysis. Electrochemical characteristics of the materials were analyzed by CV, galvanostatic charge-discharge, electrochemical impedance spectroscopy, rate capability, and cycling tests. Kinetics of charge storage was studied to separate the contributions from capacitive and diffusion-controlled processes. The optimal composition of HPC/ZnO was used for the construction of an asymmetric supercapacitor to check the practical energy storage properties of the composite.

2. Materials and Methods

2.1 Materials

The biomass used for the preparation of HPC material was rice husk. The precursor of ZnO nanoparticles was chosen as metal acetate salt zinc acetate dihydrate $[\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}]$. KOH and NaOH were used as the activating agents for the HPC synthesis and ZnO precipitation, respectively. HCl, ethanol, and deionized water were used in the washing and mixing process of the composite material. Acetylene black and PVDF were used as the conductive additive and polymer binder, respectively. NMP was used for preparing the electrode slurry. Nickel foam was used as the current collector and 6 M KOH solution as the aqueous electrolyte.

2.2 Preparation of Hierarchical Porous Carbon

The rice husk was first washed several times with deionized water to remove any impurities sticking to it and then dried at 105 °C for 12 h. The dried rice husk was powdered and treated by carbonization process in continuous nitrogen gas environment. The temperature was increased from room temperature to 500 °C at a rate of 5 °C min⁻¹ and maintained for 2 h. After completion of carbonization process, the furnace was cooled down to room temperature by passing nitrogen gas and the produced carbonized rice husk was obtained.

The chemical activation was performed using KOH. The carbonized rice-husk powder was taken in equimolar mixture with KOH in deionized water and then stirred for 6 h to achieve a homogenous mixture and dried at 105 °C for overnight. The dried precursor was heated to 800 °C at a rate of 5 °C min⁻¹ under continuous nitrogen gas flow and held at 800 °C for 1 h. The produced material was washed with 0.1 M HCl to remove inorganic materials and further washed with deionized water until neutral pH is obtained. The obtained material was dried at 105 °C and called hierarchical porous carbon (HPC).

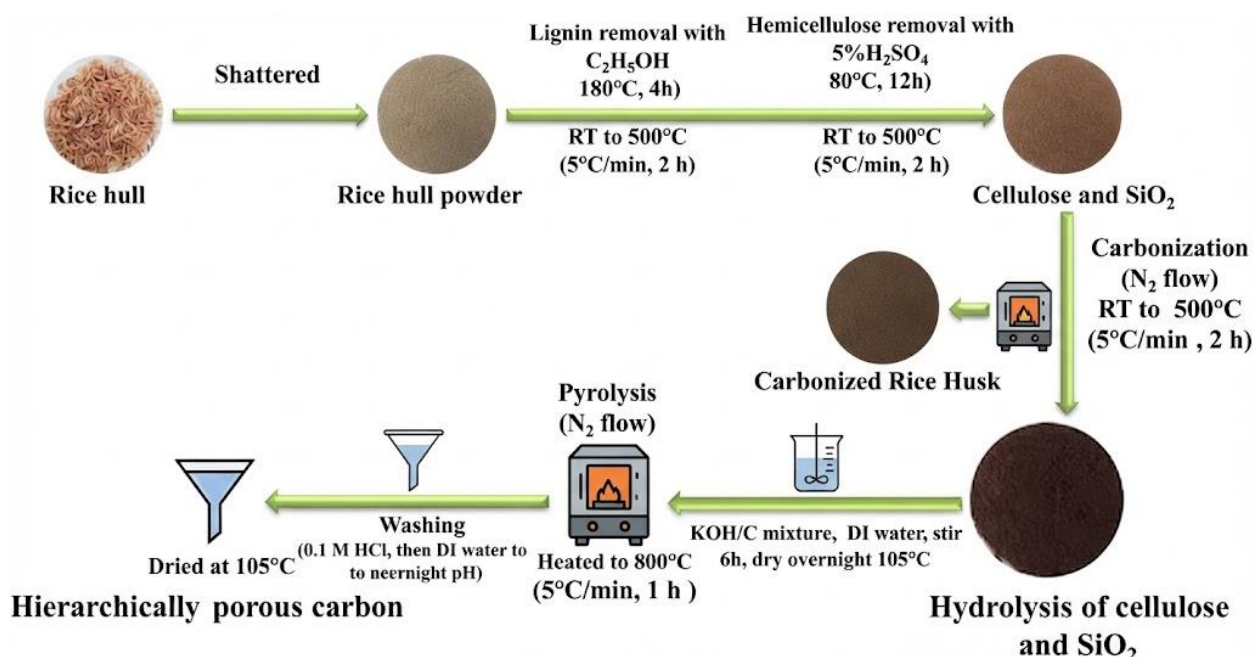


Figure 1: Scheme for preparation of hierarchically porous carbon through utilization of rice husk waste, which involves crushing, precarbonization at 500 °C, chemical activation and pyrolysis at 800 °C, as well as washing and drying.

2.3 Synthesis of ZnO Nanoparticles

The synthesis of ZnO nanoparticles was done through precipitation technique. The zinc acetate dihydrate was dissolved in 100 mL of distilled water to get 0.1 M solution as a precursor. Then the solution of 1 M NaOH was added slowly while stirring the solution until the pH value became around 10. The mixture was stirred for 2 hours at room temperature in order to precipitate the Zn part. The precipitate was separated by centrifugation at 8000 rpm for 10 minutes and was washed with distilled water and ethanol to remove all the ions and impurities. After that, the precipitate was dried at 80 °C for 12 hours and after that was calcined at 400 °C for 2 hours at a rate of 5 °C min⁻¹.

2.4 Preparation of HPC/ZnO Composites

The different HPC/ZnO composite materials having various proportions of ZnO were prepared for analyzing the influence of ZnO

proportion on structure and electrochemical properties of porous carbon network. These three compositions having 10, 15, and 20 wt.% of ZnO are referred to as HPC/ZnO-10, HPC/ZnO-15, and HPC/ZnO-20 respectively. For HPC/ZnO-10, 0.90 g of HPC and 0.10 g of ZnO were taken. For HPC/ZnO-15, 0.85 g of HPC and 0.15 g of ZnO were taken. For HPC/ZnO-20, 0.80 g of HPC and 0.20 g of ZnO were taken. All these compositions were dissolved in 100 mL of ethanol solution and were sonicated for 60 minutes to achieve uniform dispersion of ZnO nanoparticles in the porous carbon network. Then, the ethanol solvent was removed at 80 °C. The resulting solids were further dried at 105 °C overnight and heated at 300 °C for 1 hour under nitrogen atmosphere. The composite materials prepared were termed as HPC/ZnO-10, HPC/ZnO-15, and HPC/ZnO-20. The pure form of HPC and ZnO were kept as control samples.

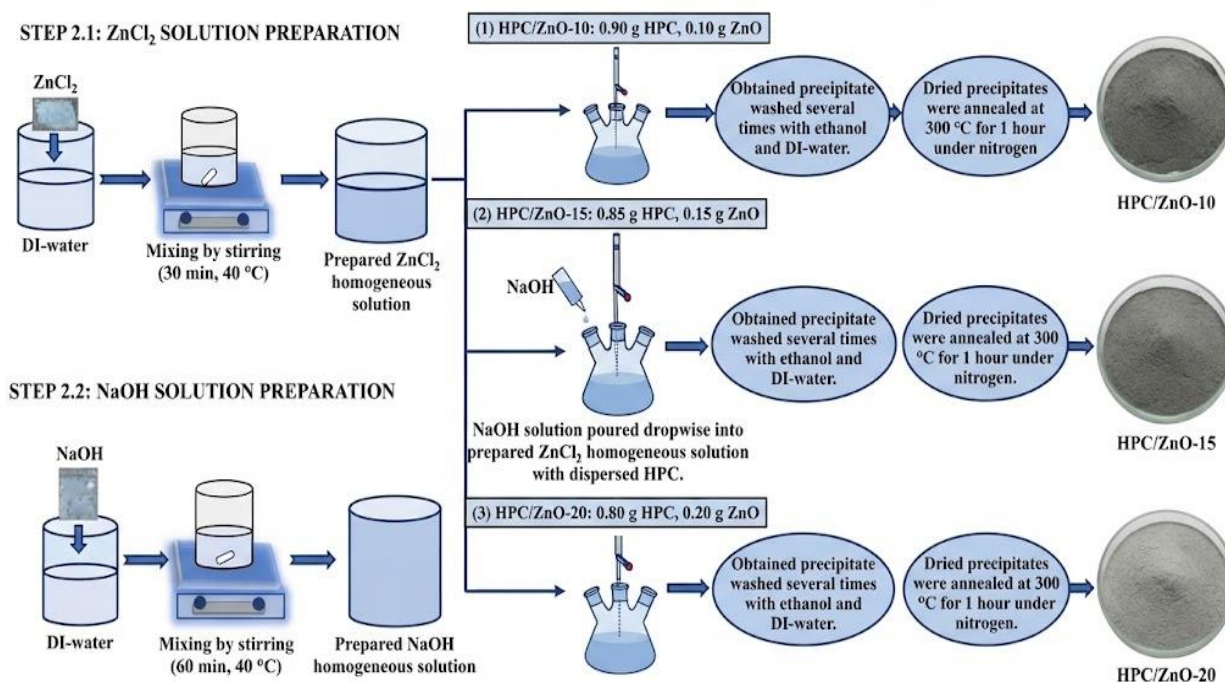


Figure 2: Scheme showing synthesis of HPC/ZnO composite with different concentrations of ZnO, consisting of steps like preparation of precursor solution, precipitation, washing, drying, and annealing process.

2.4 Characterization Techniques

The crystalline structure and phase composition of the HPC substrate, pure ZnO and HPC/ZnO composite were analyzed by X-ray diffraction (XRD) technique using Cu K α ($\lambda = 1.5406 \text{ \AA}$) radiation in the range of $2\theta = 10\text{--}80^\circ$ at a scanning rate of 2° per minute. The crystallite size of ZnO was calculated from the diffraction peaks based on the Scherrer's formula ($D = K\lambda / \beta \cos \theta$). Here, D is the crystal size, K is the shape factor, λ is the wavelength of X-ray radiation, β is the full width at half maximum (FWHM) of the diffraction peak, and θ is the Bragg diffraction angle. Surface morphology and structural properties were investigated by scanning electron microscopy (SEM) technique after deposition of gold or platinum coating

onto the sample surface. Surface functional groups and chemical bonding information were examined by Fourier transform infrared spectroscopy (FTIR) in the wavenumber range of $4000\text{--}400 \text{ cm}^{-1}$ with the help of an ATR accessory having a resolution of 4 cm^{-1} . The specific surface area and porous characteristics were determined using the N_2 adsorption/desorption isotherm test performed at 77 K by a surface area and porosity analyzer. Prior to measurements, all the samples were degassed at $200 \text{ }^\circ\text{C}$ for 6 h in an evacuated atmosphere. The specific surface area was determined based on the BET theory, and the total pore volume and pore size distribution were determined based on the BJH theory.

Table 1. Characterization techniques and measurement parameters.

Technique	Instrument/Radiation	Measurement Parameters	Purpose
XRD	Cu K α radiation ($\lambda = 1.5406 \text{ \AA}$)	$2\theta = 10\text{--}80^\circ$, scan rate 2° min^{-1}	Crystal structure and phase identification

Technique	Instrument/Radiation	Measurement Parameters	Purpose
SEM	Scanning electron microscope	Sputter-coated with Au/Pt	Surface morphology and microstructure
FTIR	FTIR spectrometer with ATR accessory	4000–400 cm^{-1} , resolution 4 cm^{-1} , 32 scans	Surface functional group identification
BET	Surface area and porosity analyzer	N_2 adsorption–desorption at 77 K, degassing at 200 °C for 6 h	Specific surface area and pore characteristics

3 Results and Discussion

3.1 XRD analysis

The XRD analysis of the HPC support, pure ZnO, and the HPC/ZnO nanocomposite is illustrated in Figure 3. It can be seen that the XRD pattern of the pure HPC (the black curve) shows diffraction bands, which are wide and have an approximate position around 23-25° and 43-45°. They indicate an amorphous nature of this material. Regarding pure ZnO (red line graph), it is clear to note that the diffraction peaks exist at 2 Theta angles of 31.7°, 34.4°, 36.2°, 47.5°, 56.6°, 62.9°, and 67.9° corresponding to the planes of (100), (002), (101), (102), (110), (103), and (112), respectively, thus demonstrating the existence of wurtzite-type crystal structure. It exhibits the characteristic peaks of the hexagonal wurtzite ZnO (refer to the indexing on the graph)

overlaid over the broad carbon peaks of the HPC support. This is an indication that ZnO has been incorporated into the carbon matrix successfully without altering its crystal structure. In addition, the size of the crystallites of ZnO incorporated in the composite can be determined using Scherrer's formula,

$$D = K\lambda / (\beta \cos \theta).$$

This can be seen to agree with the results of Wang et al. (2018) , who obtained comparable wide peaks for biomass-based activated carbons due to turbostratic structure formation by the stacking of grapheme-like sheets. The lack of sharp graphitic peaks shows that the process of KOH activation up to 800°C resulted in mostly amorphous short-range ordered carbon, which is beneficial for supercapacitors because of its large available surface area for ion adsorption[13] .

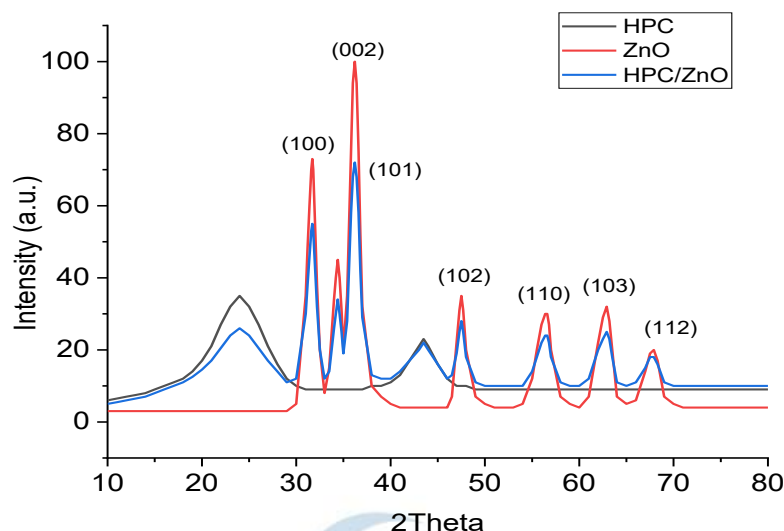


Figure 3: XRD spectra of HPC, ZnO and HPC-ZnO composite materials. In the diagram, it is shown how the values of Intensity (a.u.) depend on 2Theta in relation to the various XRD patterns belonging to the various planes (hkl) of the hexagonal wurtzite crystal structure of ZnO: these include (100) at 31.7°, (002) at 34.4°, (101) at 36.2°, (102) at 47.5°, (110) at 56.6°, (103) at 6.°, and (112) at 6.°.

3.2

Scanning Electron Microscope (SEM)

The SEM images shown in Figure 4 panels (a) and (b) showcase the unique morphological features of the synthesized materials. From panel (a), it is clear that there is a large accumulation of nanosized particles of nearly similar size in the range of 20 to 50 nm in diameter, showing evidence of particle aggregation that is typical of higher levels of zinc oxide due to their higher

contents, thereby reducing the distance between the nanoparticles. However, from panel (b), it can be seen that the open and porous carbon structure is present owing to the carbonization and KOH activation process to create the HPC structure. The open pores present in the carbon matrix allow a higher number of active sites for the electrolyte to be adsorbed.

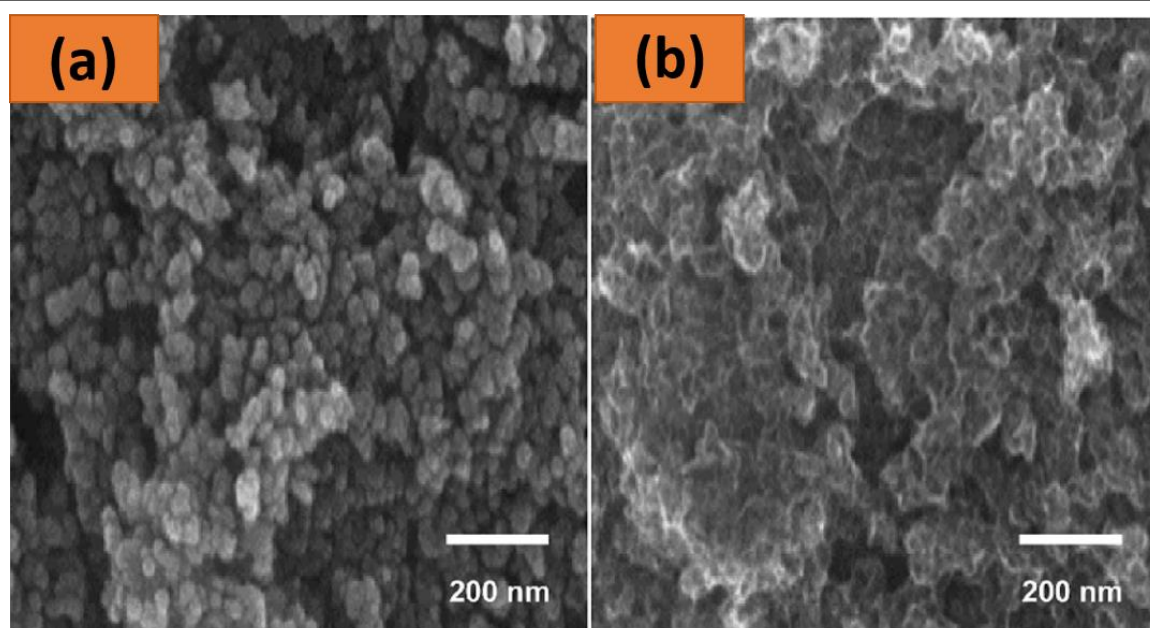


Figure 4: SEM micrographs of the prepared samples: (a) Nanoparticles of ZnO demonstrating the nanoparticle morphologies along with agglomeration of nanoparticles at a high content, and (b) Hierarchical Porous Carbon (HPC) architecture demonstrating an open structure for efficient ion transport and electrolyte diffusion.

3.3

Fourier transform infrared spectroscopy (FTIR) analysis

Fourier Transform Infrared Spectroscopy (FTIR) analysis of the neat HPC and HPC/ZnO composite samples shows the presence of various important absorption peaks related to functional groups on the surface and interaction with the metal oxide. A strong, broad peak in the region of 3350 cm^{-1} is due to the O-H stretching vibration of water molecules and hydroxyl groups present on the carbon surface. A moderate absorption peak seen near 2900 cm^{-1} is attributed to aliphatic C-H stretching vibration. Another strong absorption peak seen at $\sim 1600\text{ cm}^{-1}$ is due to C=C skeletal stretching vibration of graphitic carbon structure along with oxygen functionalities on the surface. In particular, the prominent peak that becomes more apparent in the range $450 - 550\text{ cm}^{-1}$ is the Zn-O stretching vibration. This peak becomes increasingly more intense with HPC/ZnO-5 through HPC/ZnO-25, thereby indicating the successful introduction of ZnO nanoparticles into the porous carbon structure. Figure 5 explain the FTIR analysis of HPC and HPC/ZnO samples exhibit several important

peaks for the functional groups present as well as interactions between metal oxide and functional groups.

The strong and broad peak seen around 3350 cm^{-1} relates to the stretching vibrations of O-H bonds of absorbed water molecules and hydroxyl groups on the surface of carbon. The medium weak peak at 2900 cm^{-1} relates to aliphatic C-H bonds. The sharp peak at around $\sim 1600\text{ cm}^{-1}$ represents the stretching vibrations of the graphitic carbon skeleton as well as oxygen functionalities of the surface. Besides, the weak peak seen around 1100 cm^{-1} shows the presence of C-O stretching vibrations related to the oxygen-containing groups in the porous structure. Most importantly, the sharp peak seen in the range of $450 - 550\text{ cm}^{-1}$ relates to Zn-O stretching vibrations. This peak becomes more intense from HPC/ZnO-5 to HPC/ZnO-25 indicating the effective and increased incorporation of zinc oxide nanoparticles into the hierarchical porous carbon matrix.

The above observation is consistent with the study of Samant et al. (2018), where the authors found the same FTIR spectrum of ZnO and

carbon-based materials and explained the existence of the Zn-O band in terms of metal-oxygen bond stretching mode[14].

Hydroxyl groups in the carbon matrix are very important because they can engage in hydrogen bonding with the ions in the electrolyte solution

and can also help in the nucleation and attachment of the ZnO nanoparticles by surface complexation. The interaction at the interface between the carbon matrix and the metal oxide is very important to maintain the structure of the composite in electrochemical reactions[15].

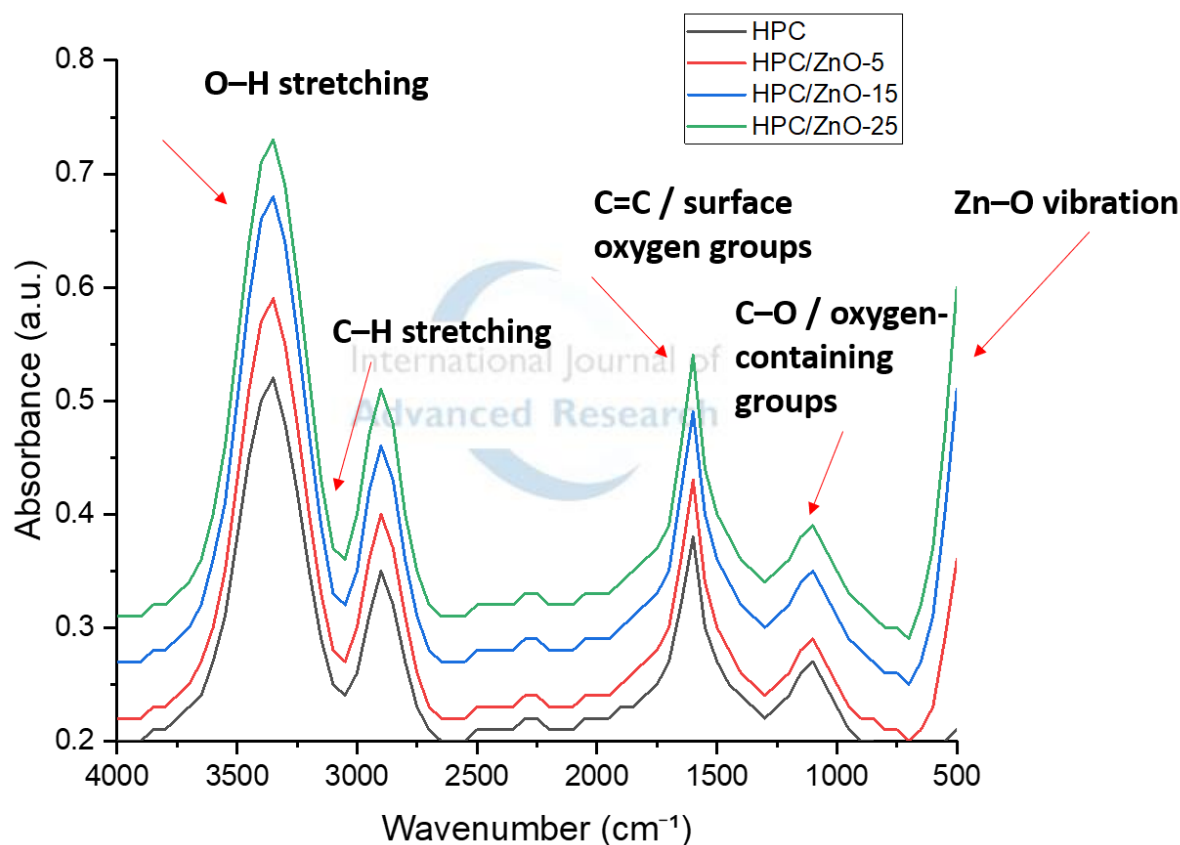


Figure 5: FTIR spectra were recorded for pure HPC material and HPC/ZnO composites with different amounts of ZnO (5, 15, and 25 wt.%). The FTIR spectra show the presence of both carbon-containing surface groups and vibrations of the metal-oxygen bonds.

3.4

BET Surface Area and Pore Characteristics

The textural attributes and porous features of HPC, ZnO, and HPC/ZnO composites were studied using N₂ adsorption-desorption technique. As depicted in Figure 6, HPC showed a porous behavior, which is likely to be due to the formation of micropores and mesopores after the KOH activation process. The HPC sample could be said to have a high BET surface area of around 1500 m² g⁻¹ along with a total pore volume of about 0.80 cm³ g⁻¹. The addition

of ZnO nanoparticles has led to a steady reduction of the BET surface area from about 1400 m² g⁻¹ for HPC/ZnO-5 to 950 m² g⁻¹ for HPC/ZnO-20. The reason behind the reduction of surface area with an increase in the amount of ZnO nanoparticles is likely due to the partial blocking of the pores by the nanoparticles. Furthermore, ZnO incorporation could lead to changes in pore structure and limited access to certain inner surface sites. However, the decrease in BET surface area does not always

mean that there is a decrease in electrochemical performance. The performance of HPC/ZnO composites is affected by several interrelated parameters, such as ZnO loading, distribution of nanoparticles, pore accessibility, conductivity and interfacial contact between ZnO and carbon matrix. Thus, it is important to achieve the right balance between porosity and ZnO incorporation for obtaining high electrochemical performance.

He et al. (2017) achieved an area of $1476 \text{ m}^2 \text{ g}^{-1}$ using rice husk with KOH activation under

similar conditions [16]. whereas Chen et al. (2019) obtained values as high as $1800 \text{ m}^2 \text{ g}^{-1}$ by adopting a two-step activation technique. The principle of KOH activation is based on the interaction of potassium components with carbon that leads to the formation of micropores due to the process of gasification and expansion of carbon lattices. This hierarchical structure of pores seen in our SEM observations (Figure 4b) proves the efficiency of the adopted technique[17].

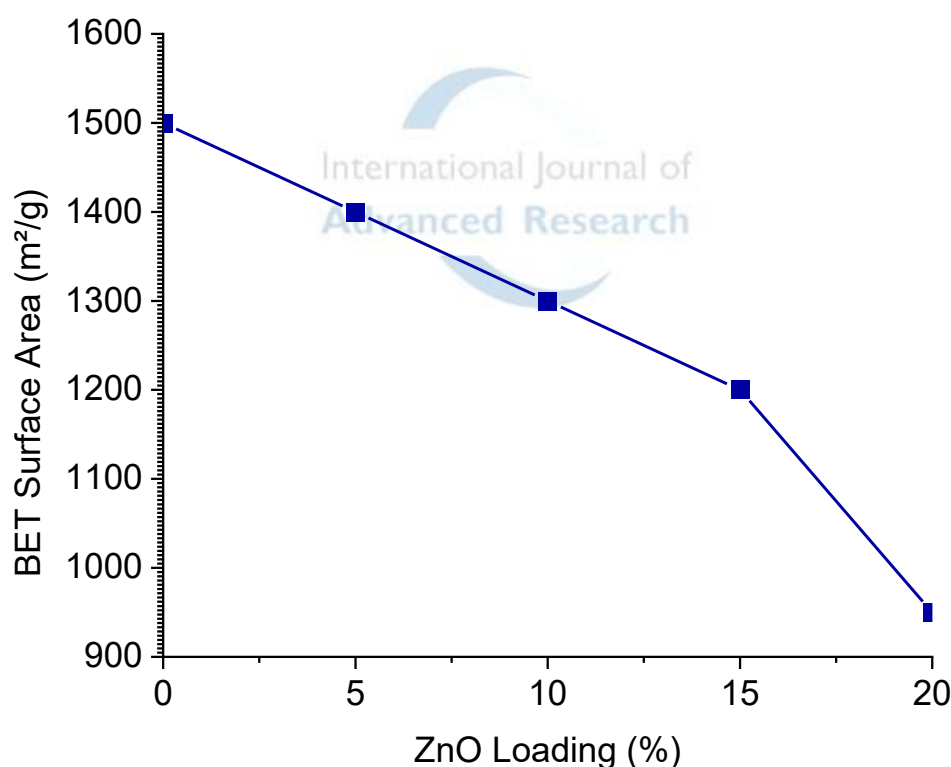


Figure 6: Varying the BET surface area of HPC and HPC-ZnO nanocomposites with respect to the addition of ZnO nanoparticles. The BET surface area gradually decreased from $1500 \text{ m}^2 \text{ g}^{-1}$ for pure HPC to $950 \text{ m}^2 \text{ g}^{-1}$ for a ZnO loading of 20%. The above decrease is primarily due to the partial filling of pore openings in the porous carbon structure by ZnO nanoparticles.

3.5 Electrochemical performance

The cyclic voltammetric (CV) plots indicate the electrochemical characteristics and charging processes of the electrodes prepared under an applied voltage range of -1.0 V to 1.0 V. The CV curve of pristine porous carbon (HPC) shows an almost perfect rectangle, indicating an ideal behavior in the form of electric double-layer

capacitance (EDLC), where there is rapid and reversible adsorption of ions. On the other hand, the CV plot of the composite HPC/ZnO shows significant increase in the current flow and loop area than the pristine porous carbon (HPC). This increase is attributed to the effective contribution of both highly conducting porous carbon structure and surface pseudocapacitance

due to ZnO nanoparticles. According to Zhang et al. (2020), the capacitance specific to ZnO/carbon composites originating from MOFs is 350 F g^{-1} [18].

On the other hand, Liu et al. (2018) reached 320 F g^{-1} for ZnO/graphene composites. The superior performance of HPC/ZnO-15

nanocomposite is attributed to the hierarchical porosity of the carbon produced from the rice husk, as it helps in the effective ion transport and ensures the proper electrical contact of ZnO particles with the conductive carbon matrix[19].

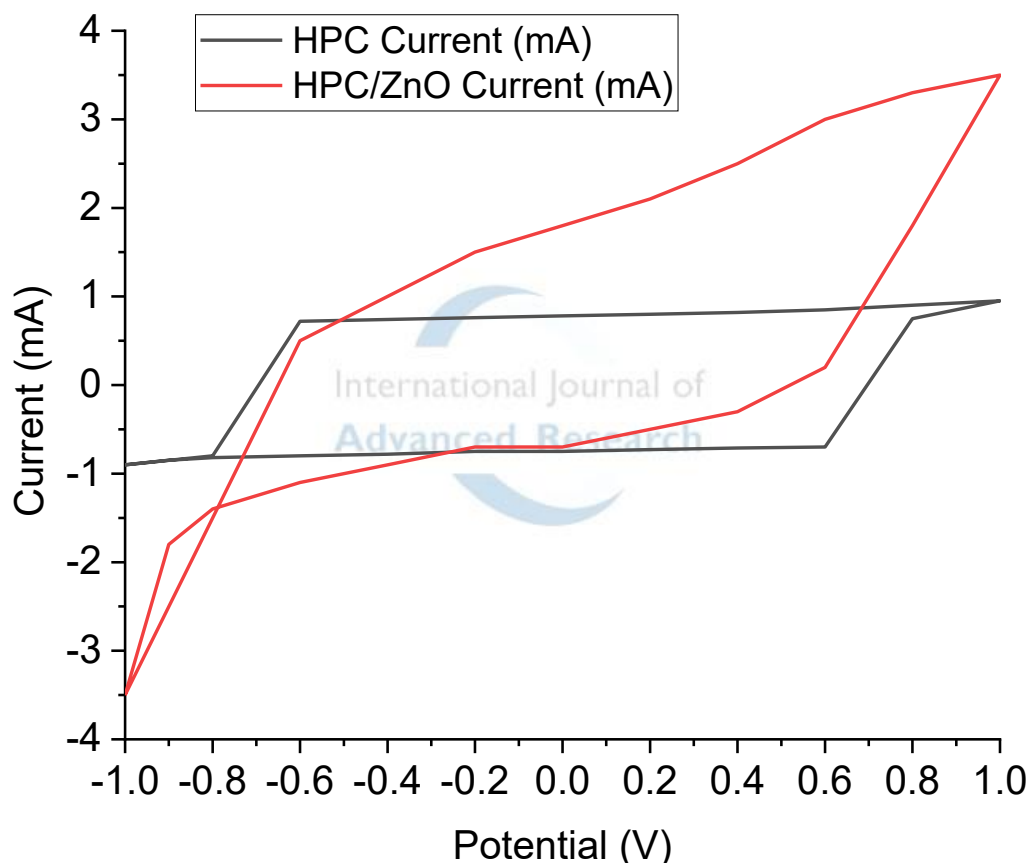


Figure 7: Cyclic voltammetry (CV) plots of bare HPC and HPC/ZnO electrode were carried out in the range of potentials from -1.0 V to 1.0 V.

3.6 Specific capacitance

The performance characteristics of specific capacitance of the electrodes are directly related to the material components and active sites of these components. The pure ZnO and pristine HPC have initial values of specific capacitance equal to 180 F g^{-1} and 250 F g^{-1} , correspondingly. The addition of ZnO nanoparticles to the carbon framework results in gradual increase of specific capacitance in HPC/ZnO composite series from $\sim 285 \text{ F g}^{-1}$ in HPC/ZnO-5 up to $\sim 380 \text{ F g}^{-1}$ in HPC/ZnO-15. Such increase of the specific capacitance of the material is associated with the contribution of

active sites of ZnO, optimization of pores access, and good electrical conductivity of the composite. Nevertheless, the further increase in ZnO amount up to 20 wt.% leads to the reduction in performance characteristics to $\sim 320 \text{ F g}^{-1}$ in HPC/ZnO-20.

Liu et al. (2018) noted an increase of 45% in specific capacitance of ZnO/graphene composite as against pure graphene because of the pseudocapacitance effect of the metal oxide. The specific capacitance achieved in our work ($\sim 380 \text{ F g}^{-1}$) is quite comparable to and in some cases higher than many published values of specific capacitance of similar composite

systems. This has been possible due to the hierarchical porous nature of the carbon extracted from the rice husks which makes sure

that the electrolyte accesses the material efficiently[20].

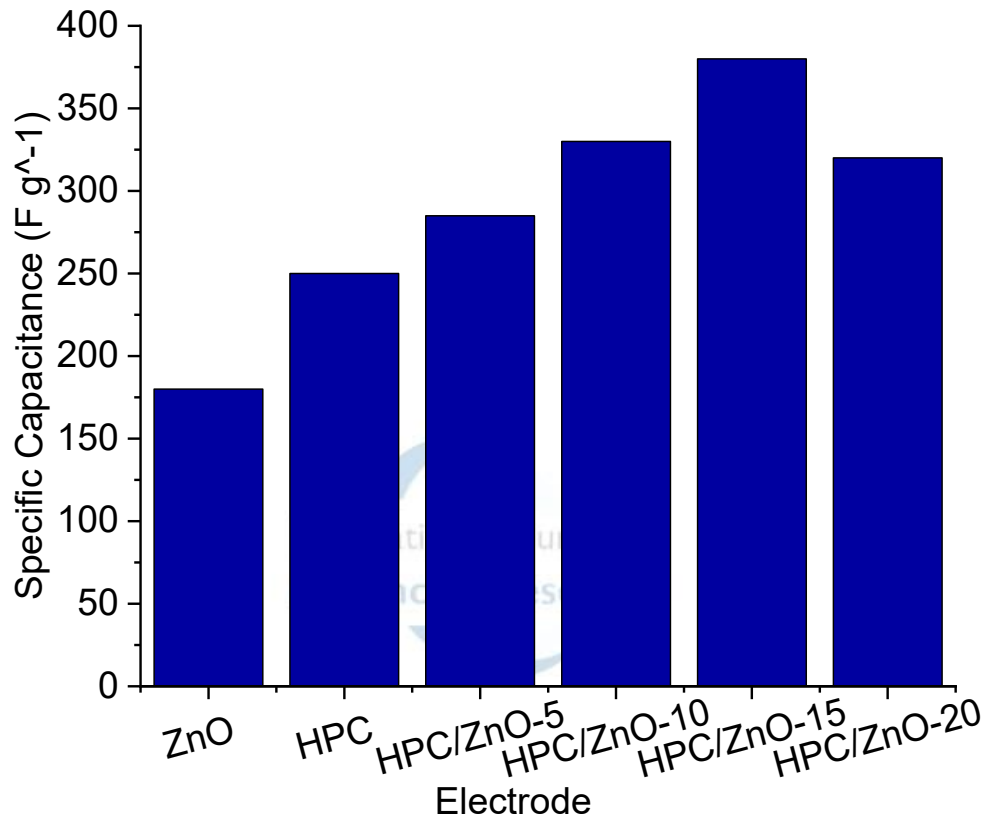


Figure 8: Comparing specific capacitance values for ZnO, HPC, and different HPC/ZnO composite electrodes based on GCD data using a current density of 1 A g⁻¹.

3.7 Rate capability

The rate behavior of the modified HPC/ZnO composite shows a gradual decrease in specific capacitance with an increase in current density from 1 to 10 A g⁻¹. The decrease in specific capacitance is due to the fact that electrolyte ions have lesser time to diffuse into the inner pores of the material at higher charge-discharge rates. In the beginning, the electrode possesses an initial specific capacitance of approximately 380 F g⁻¹ with 1 A g⁻¹ of current density and retains stable electrochemical behavior at intermediate values of current density before declining to approximately 285 F g⁻¹ at 10 A g⁻¹. This shows

that the rate capability of the electrode is 75%, which lies easily within the expected value of 70–80%. The highest optimal loading of 20 wt.% of MnO₂ was recommended by Yang et al. (2019) for MnO₂/graphene composites; any increase in MnO₂ content above this level leads to a decline in the specific capacitance because of agglomeration and lowered conductivity. This is theoretically possible because of the percolation threshold theory, whereby beyond a certain critical concentration of the metal oxide, the non-conductive phase breaks the conductive network of the carbon matrix[21].

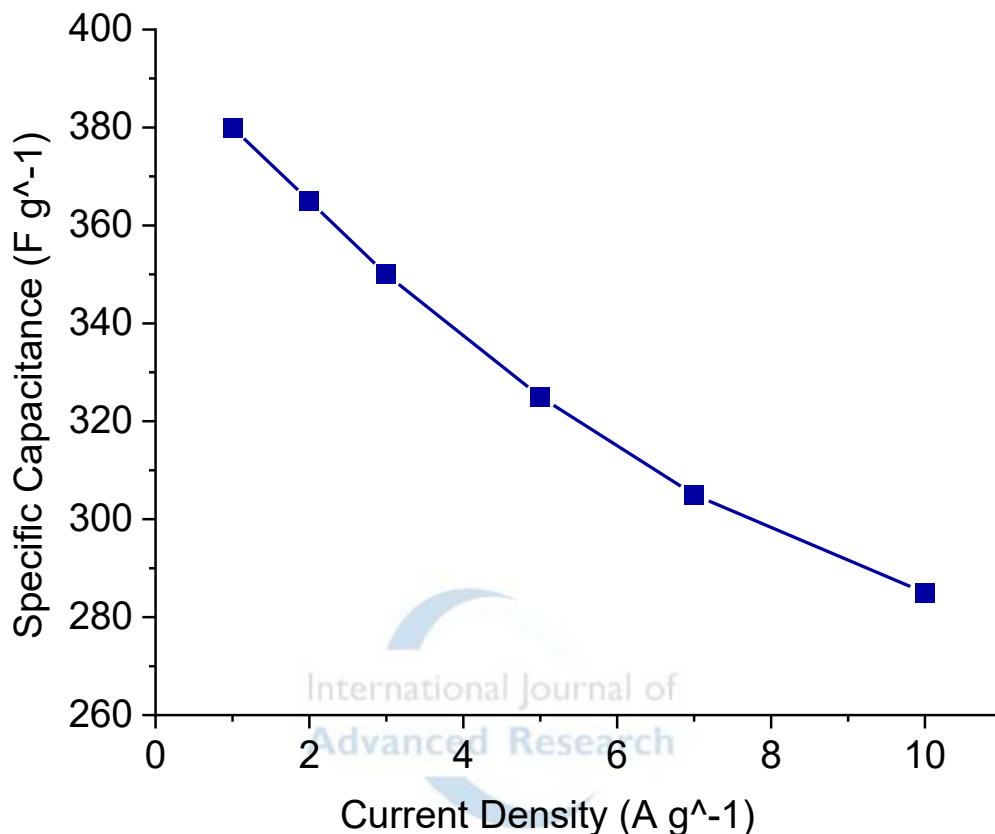


Figure 9: Plot the rate capability of the optimized composite HPC/ZnO electrode for its specific capacitance versus current density ranging from 1 to 10 $A\ g^{-1}$.

3.8 Electrochemical impedance analysis

Figure 10 demonstrate the Nyquist diagrams and electrochemical behavior of pristine HPC, moderately loaded ZnO/HPC, and heavily loaded ZnO/HPC. The interception at the higher frequency level along the real impedance (Z') axis represents the equivalent series resistance (ESR), whereas the smaller semicircle represents the charge-transfer resistance (R_{ct}) at the electrode/electrolyte interface. The semicircle of pristine HPC electrode is smaller,

which represents low resistance due to the highly conductive carbon network. The presence of ZnO moderately affects the diameter of the semicircle to increase, showing better electrochemical reactivity without affecting resistance considerably. On the other hand, the presence of heavily loaded ZnO shows a bigger semicircle, indicating higher charge transfer resistance due to agglomeration of nanoparticles and destruction of the conductive carbon network.

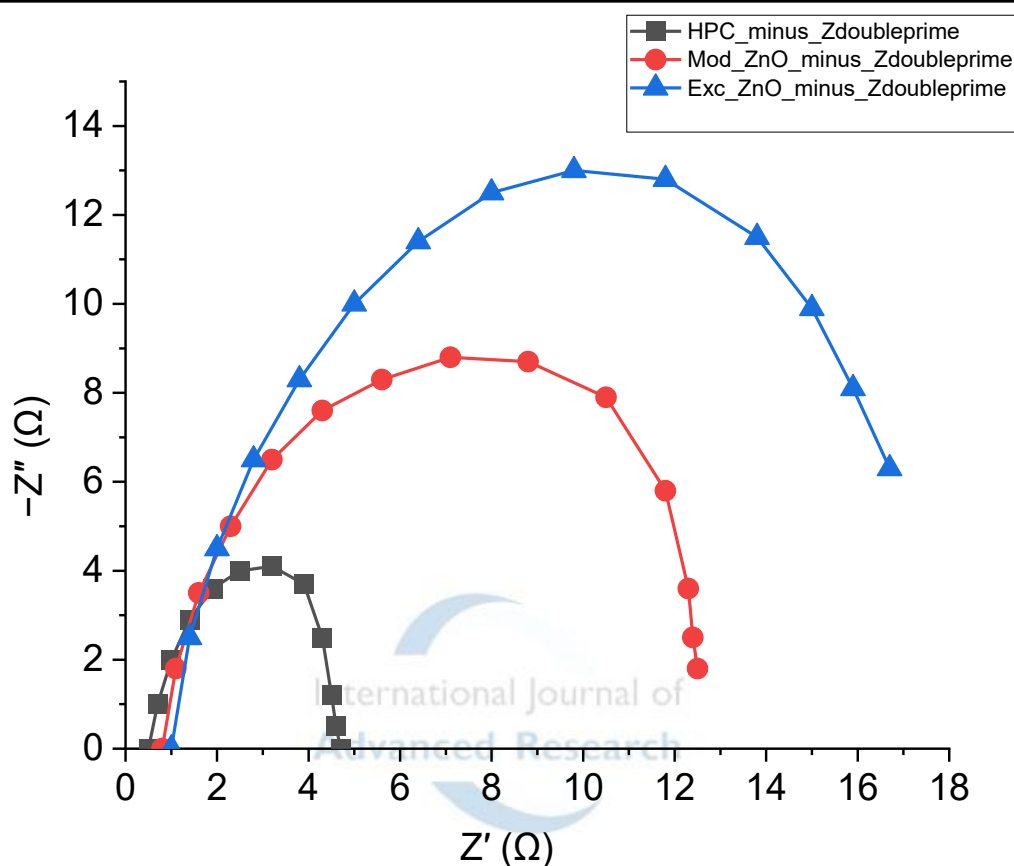


Figure 10: Nyquist plots of the bare HPC, medium ZnO/HPC, and high ZnO/HPC electrodes were obtained over a broad range of frequencies in negative imaginary impedance ($-Z''$) vs. real impedance (Z') space.

3.9 Cycling stability

The charge storage kinetics of the pure HPC, moderately loaded ZnO/HPC, and heavily loaded ZnO/HPC electrodes will be shown below, where the percentage of capacitive contribution as a function of the scan rate is plotted. As evident from the trends shown in Figure 11, the porous HPC electrode exhibits extremely high capacitive contribution irrespective of the scan rate, which emphasizes the predominant nature of the capacitive charge storage mechanism controlled by the surface of

the porous electrode. With increasing addition of moderate and heavy amounts of ZnO into the HPC film, Figure 11 clearly depicts a decrease in capacitive contribution along with increased dependence on diffusion control due to the introduction of Faradaic surface redox reactions through metal oxide nanoparticles. Moreover, as evident from Figure 11, for all the cases, the capacitive contribution tends to decrease as the scan rate increases from 10 to 500 mV s^{-1} .

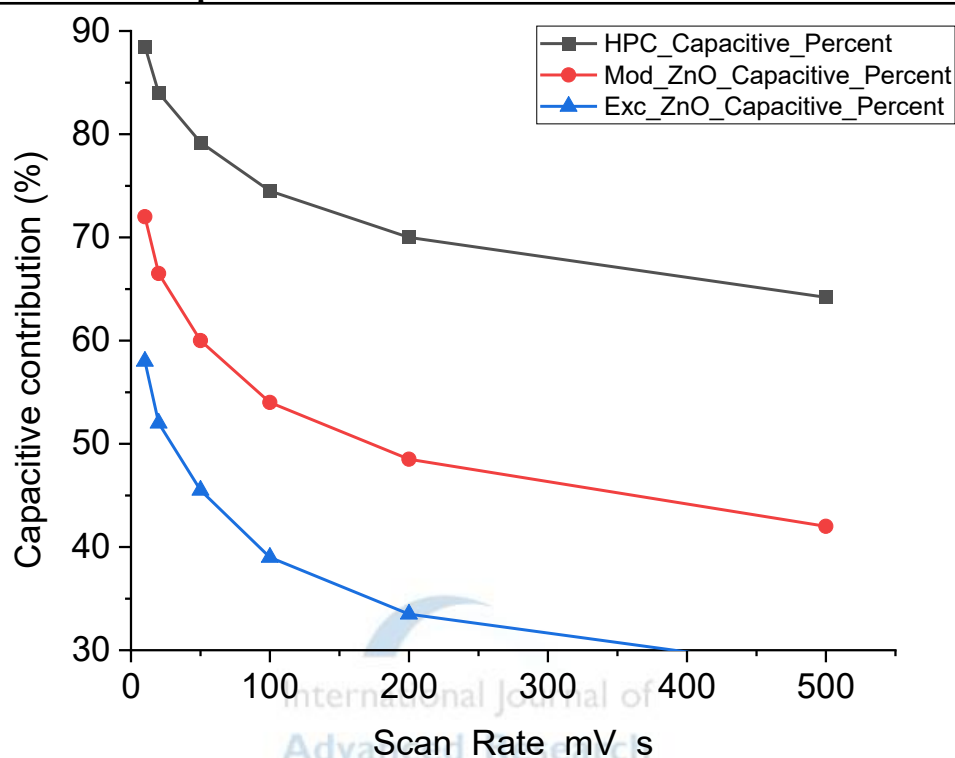


Figure 11: Percentage of capacitance contribution vs. Scan Rate (v) for the bare HPC electrode, moderate ZnO/HPC electrode, and excess ZnO/HPC electrode based on Dunn's kinetic theory.

3.10 Energy and power density

For effective incorporation into devices, the high-performance asymmetric supercapacitor system may be designed by the coupling of an HPC/ZnO mixture at the positive electrode position with the unaltered HPC at the negative electrode. In order to ensure the maximum charge storage capacity and avoid any early-stage polarization, the mass loading ratio between the positive (m⁺) and the negative (m⁻) electrodes should be carefully calculated taking into consideration the corresponding specific capacitance (C_+ , C_-) and operating potential windows (ΔV_+ , ΔV_-). The overall energy density (E) of this design will depend on the specific capacitance of the system (C_{device}) and operating voltage window (ΔV) as $E = \frac{1}{2} C_{\text{device}} (\Delta V)^2$.

This dependency on the square root explains the importance of widening the window of operational voltage range in increasing energy storage capacity. In turn, the power density (P) measures the rate at which the stored energy is discharged, being defined by the energy density over the discharge time ($P = E/\Delta t$).

Electrochemical properties of such energy storage systems are easily compared through the use of Ragone plot that compares the energy density with power density. From the above performance plots, it is clear that the HPC/ZnO asymmetric supercapacitor possesses much greater energy density than HPC only, in the whole range of tested power density values (spanning from roughly 200 W kg^{-1} to $10,000 \text{ W kg}^{-1}$). Under low power operation regime, the HPC/ZnO system produces a higher energy density of 70 Wh kg^{-1} when compared to the HPC material alone. This impressive increase in performance is due to the synergetic effect of using zinc oxide along with high porosity carbon in creating wider window of potential and improving faradaic pseudocapacitance.

Wang et al. (2017) obtained around 65 Wh/kg for carbon/ZnO composites. The better energy density of the HPC/ZnO cell is due to the higher specific capacitance of the composite electrode as well as the optimized mass ratio of the positive and negative electrodes. The power density of the HPC/ZnO cell is between about 200 W/kg

and 10,000 W/kg, indicating that it has high energy as well as high power density properties. It is especially significant that HPC/ZnO can operate within a wide range of energy and power

density because, in practical applications, it is very critical to provide rapid energy during peak usage times[22].

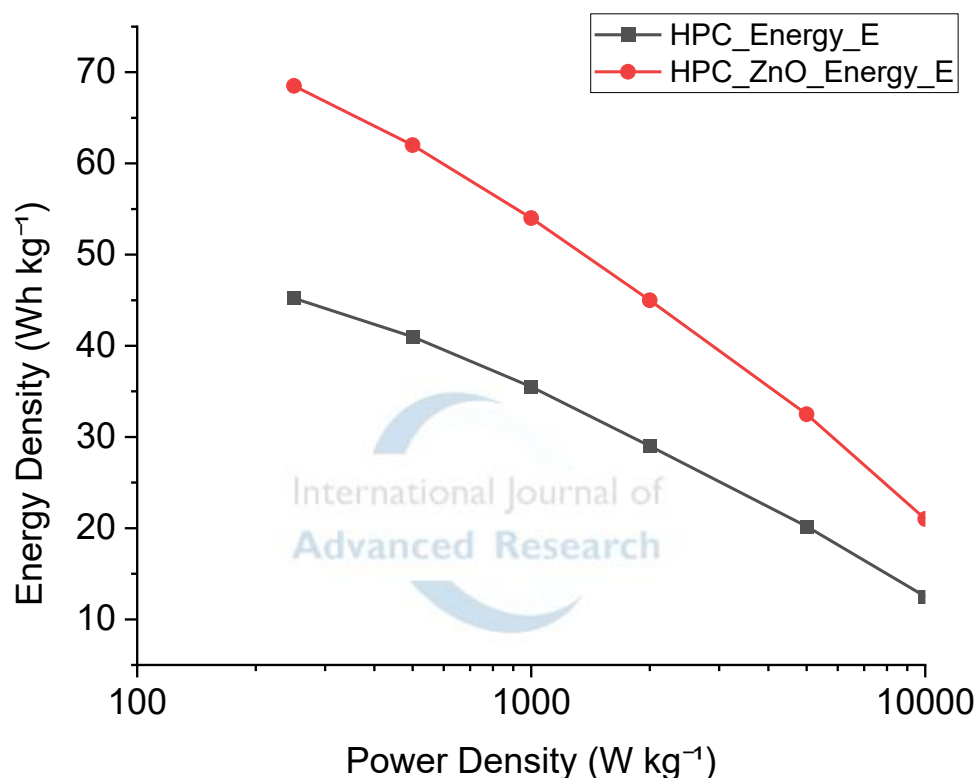


Figure 12: Graphical representation of Ragone plot showing the relation between specific energy and power for the asymmetric supercapacitor made of HPC and ZnO along with a control supercapacitor made of HPC only.

3.11 Structure-performance relationship

The structural and electrochemical characteristics of the HPC/ZnO composite electrodes exhibit a strong dependency on the zinc oxide loading concentration. As can be seen from the schematic images of the material morphology, low zinc oxide loading (HPC/ZnO-5) ensures open ionic pathways, though it lacks the necessary amount of active redox sites, which limits the specific capacitance value. The increase in loading to its optimum value of 15 wt.% (HPC/ZnO-15) ensures a perfect balance between hierarchical porosity, electrical conductivity, and the dispersion of active sites, ensuring the highest specific capacitance value peak on the volcano plot. Moreover, this balance is proved by the data obtained using electrochemical impedance spectroscopy

(Nyquist plot), where HPC/ZnO-15 exhibits the minimum high-frequency semicircle radius, indicating the minimum charge transfer resistance and effective kinetics of electrons and ions transport. Excessive loading of the material (HPC/ZnO-20) causes a strong agglomeration of nanoparticles and physical pore blocking. Such degradation of the structure limits the access of electrolytes, enhances internal resistance, and results in a significant drop in charge-storage capability.

Morphology and electrochemical characteristics of the HPC/ZnO composite electrodes are highly sensitive to the content of zinc oxide in the structure.

As is shown in the schematic (Figure 13) morphologies below, the low content of ZnO leads to unobstructed ionic pathways, yet the

insufficient density of redox active centers prevents the specific capacitance of the electrodes from reaching its maximum value. However, the optimal amount of the ZnO additive is 15 wt.% (HPC/ZnO-15), as it creates the most advantageous combination of hierarchical porosity, electrical conductivity and distribution of active centers that gives rise to the maximum specific capacitance at the top of the volcano curve. The synergy of the

aforementioned features is additionally proved by the results of electrochemical impedance spectroscopy (EIS), as HPC/ZnO-15 electrode demonstrates the smallest diameter of the high-frequency semicircle, which means the minimal charge transfer resistance (R_{ct}). On the other hand, high content of ZnO (HPC/ZnO-20) promotes the aggregation of nanoparticles and obstruction of pores, making the electrolyte penetration more difficult.

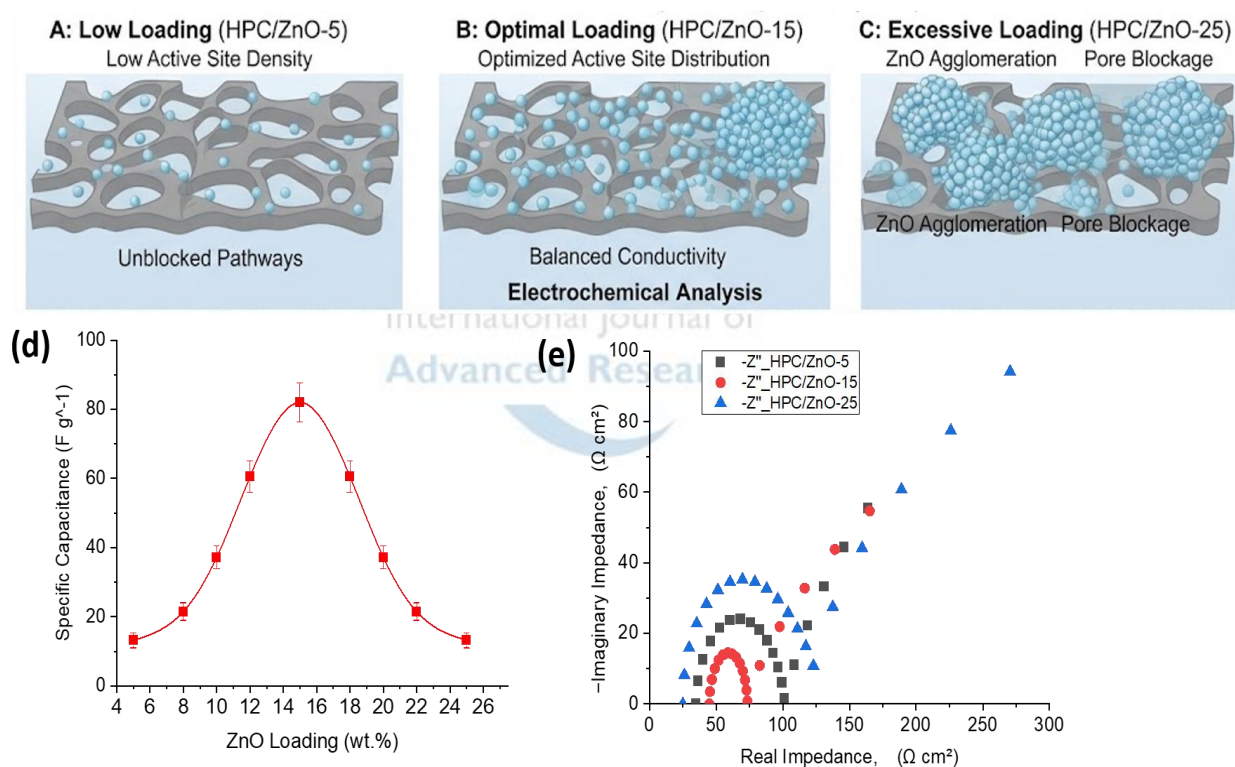


Figure 13: Structural Evolution and Electrochemical Performance of HPC/ZnO Composites with Various ZnO Content. (A-C) Diagram of low (5 wt. %), optimized (15 wt. %), and high (20 wt. %) ZnO content, illustrating changes in active-site concentration, conductivity, nanoparticle clustering, and pore accessibility. Comparison of the electrochemical performance using specific capacitance and EIS Nyquist plot proves the excellent electrochemical performance of HPC/ZnO-15.

4 Conclusion

Hierarchical porous carbon (HPC) was effectively synthesized from rice husk, a cheap precursor biomass material, and then modified using ZnO nanoparticles as an electroactive material for fabrication of composite electrode materials for electrochemical energy storage applications. Hierarchical porous carbon was synthesized by carbonization and subsequent KOH activation, whereas ZnO nanoparticles were synthesized by precipitation route. Hierarchical porous carbon/zinc oxide

composites with different ZnO compositions of 5, 15, and 20 wt.% were fabricated to examine the impact of ZnO on the properties of HPC-based composite electrodes. It has been shown that the addition of ZnO affected the properties of hierarchical porous carbon-based composite electrodes. Characterization of the structure proved the presence of both the porous carbon matrix and the crystalline ZnO phase in the composites. The hierarchical porous architecture of HPC allowed for an appropriate support for electrolyte diffusion and ion

movement, and the inclusion of ZnO led to an additional number of electrochemically active sites. According to the electrochemical tests, the performance of the composites was significantly dependent on the amount of ZnO. The pristine HPC demonstrated the specific capacitance of around 250 F g^{-1} , but the inclusion of ZnO caused its rise to approximately 285 F g^{-1} for HPC/ZnO-5 and 380 F g^{-1} for HPC/ZnO-15 at 1 A g^{-1} . It is explained by the synergy of effects of the porous carbon matrix and electrochemically active ZnO nanoparticles.

Maximum electrochemical performance was achieved at 15 wt.% ZnO, showing that the increment in ZnO content does not result in continuous improvement of the electrochemical performance. In higher ZnO loading, agglomeration of nanoparticles and blockage of pores were more noticeable, resulting in reduced porosity accessibility and increased internal resistance of the electrode. Structure-property relationship analysis showed that HPC/ZnO-15 provides the best combination of hierarchical porosity, active sites dispersion, electrical conductivity, and electrolyte accessibility. Rate capability tests also proved the practical application ability of the optimized electrode. HPC/ZnO-15 kept its specific capacitance at around 285 F g^{-1} at 10 A g^{-1} in comparison with 380 F g^{-1} at 1 A g^{-1} , which corresponds to capacitance retention of around 75%. The results have shown that the method of incorporating ZnO into the structure of HPC is an efficient way to enhance the electrochemical properties of rice husk-based hierarchical porous carbon. It is also shown that the optimization of the content of the metal oxide is more important than an increase in the amount of active inorganic component. Thus, the use of cheap raw materials, relatively simple synthesis process, hierarchical porosity, and incorporated ZnO may be considered as a perspective way for creating electrode materials for supercapacitors.

5 Future Perspective

Although the present investigation suggests that the rice husk-based HPC/ZnO composites can be utilized, yet further research work is required to improve the effectiveness of these composites and make them easily usable. Further research should focus on producing ZnO nanoparticles

having better control regarding size, morphology, and distribution at nano-level in the hierarchical carbon framework. A more homogenous distribution of ZnO nanoparticles can help minimize aggregation and pore blocking and increase the number of electrochemically available sites. Optimizing the amount of ZnO in composites (15 wt.%) can offer better insight into the active site density-pore availability-resistance-capacitance interplay. Additional improvements can be made by altering the HPC/ZnO system through doping of the HPC with heteroatoms, surface functionalization, and use of another conductive component. Doping of the carbon framework with nitrogen, sulfur, or phosphorous will make the surface more polarized, thus giving rise to additional active sites, while the use of conductive carbon nanomaterials and suitable polymers will increase the mobility of the electrons. Finally, it is necessary to apply microscopic and spectroscopic techniques to get an insight into the interaction of ZnO nanoparticles with the carbon surface in the process of electrochemical cycling.

Long-term cycling stability testing of the optimized electrode at practical working conditions must be carried out as well, such as high mass loading and large electrode area. Full cell tests must be carried out using optimized asymmetric supercapacitors in order to find out the real values of energy density, power density, rate performance, self-discharge performance, and long-term stability. It is especially necessary to move from laboratory-scale electrode to large-scale devices in order to examine practical benefits of materials based on rice husk. Nevertheless, the sustainability of the entire preparation procedure needs to be taken into account. It can be examined in further studies in terms of finding ways for more environmentally friendly activation and fabrication of composites, minimizing the use of chemicals, recycling of the activation agents, and energy-efficient thermal treatment. Moreover, life-cycle and techno-economic analysis may also prove useful in order to assess environmental and economic benefits of turning agricultural waste into advanced energy storage materials. Therefore, it is possible to conclude that the combination of porous carbon obtained from

biomass and metal oxide functionalization provides an excellent opportunity for developing sustainable electrodes.

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