Synthesis and electrochemical study of phosphorus-doped porous carbon for supercapacitor applications

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Abstract

In the present investigation, we report the incorporation of phosphorous (P) atoms in the activated carbon and study its effect on the electrochemical performance. Porous carbon is synthesized by the chemical activation method from a bioresource and then pretreated with nitric acid. Phosphorus atoms were doped by the simple chemical method. The obtained phosphorous-doped nano-materials show an appreciable change of porosity and creation of a more wide range of meso- and macropores, and this affects their adsorption and electrochemical performance. The electrochemical study shows that doped carbon obtained at 850 °C (AC_tP-850) delivers the maximum specific capacitance (328 Fg⁻¹) in neutral aqueous electrolyte (1 M Na₂SO₄). The doped carbon material not only exhibits good cycling performance but also the highest specific energy of 29 Wh kg⁻¹ corresponding to a specific power of 646 W kg⁻¹. The improved capacitive performance of phosphorous-doped porous carbon material proposes its use in energy storage applications.

Keywords Activated carbon · Na₂SO₄ · Supercapacitor · Pretreatment · P doping

1 Introduction

Electrochemical capacitors (ECs) or supercapacitors are favorable for many applications demanding a large fast pulse of power and high energy with fast repetitive recharging due to their unique power density and excellent cycling ability comparative to other power storage devices [1–10]. The remarkable progress of high-power devices, such as hybrid electric vehicles, has encouraged great demand for high-performance supercapacitors. Supercapacitors are of two types, i.e. pseudo-capacitors and electric double-layer capacitors based on the electrode materials. Electrical double-layer capacitors (EDLCs) store energy by adsorbing cations and anions at the electrode/electrolyte interface of carbon-based electrodes and possess limited capacity and energy density. Pseudocapacitors electrode is made up of transition metal oxides

for example MnO₂, TiO₂, RuO₂, and electrically conducting polymers such as polypyrrole and polyaniline. Pseudocapacitors store charges by surface redox reactions and show specific area-based capacitances many times more than the electrical double-layer capacitors. Though pseudocapacitors show poor stabilities or high capacitance decay rates, but they offer large specific capacitance values [11–18].

The capacitance of EDLCs can be enhanced by utilizing carbon electrodes possessing surface areas and suitable pore-size distributions [19, 20]. Different forms of carbon comprising carbon nanotubes, activated carbon, templated porous carbons, carbon spheres, and graphene have high gravimetric surface areas [21–27]. And these kinds of electrodes can provide very high specific capacitance value as high as 250 F g⁻¹. But these carbon electrodes possess low packing density parameter

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(< 0.75 g cm⁻³), and it becomes a barrier for achieving high specific capacitance values. M. Ghaffari et al [28]. in their work reported a low value (200 F cm⁻³) of volumetric capacitance for the graphene-based supercapacitor electrodes. Hence, to improve their capacitive performance, Yang et al. [14] recently reported an increase in the packing density of graphene films (0.13–1.3 g cm⁻³) which yielded a C_{vol} of 255.5 F cm⁻³. Though the specific capacitance of such graphene films was found to be greater than other forms of carbon, still it is not successful for independent energy storage devices. Electrochemical performance of an EDLC can be enhanced by heteroatom doping or by making its composite with other materials. Mainly, heteroatom doping has been shown as an effective mode of improving the performance of carbon materials due to the difference in atomic size and electronegativity and by the addition of more functional groups. Certain surface functional groups comprising oxygen (O), fluorine (F), nitrogen (N), boron (B), or phosphorus (P) can significantly increase the capacitance value of carbon electrodes due to the induced pseudocapacitance effect. Nitrogen doping involves pseudo-capacitance by increasing the charge mobility of negatively charged particles on carbon-based surfaces and thus enhancing the capacitance value many times [29, 30]. Fluorine doping also improves the electrochemical performances of the carbon material by increasing the electrical conductivity [31, 32]. Oxygen and phosphorus doping in the carbon material improves the wettability due to which the electrolyte ions can quickly spread on the electrode surface [33]. It is observed that heteroatom doping leads to an increment in the number of reaction sites, introduces more defects at the material surface, and offers an anisotropic charge distribution which in turn changes the charge density of the material. Also, heteroatom doping broadens the operating voltage [34]. Also, due to the difference in charge and size of heteroatom and base material, doping leads to a change in the charge density of the material and introduces defects in the material.

Recently, biomass has been preferred as a good carbon precursor for EDLCs owing to their environmental friendliness, low cost, and abundant resources [35–38]. Additionally, biomasses are found to be rich in protein and carbohydrates and hence can be considered as an ideal phosphorous, oxygen, and nitrogen-rich precursor for the synthesis of heteroatom-doped carbon. Various biomass resources like coffee, human hair, corncob, kitchen scrub, bagasse bottom ash, waste tea leaves, almond shells, cow dung, and nutshell have been used as biomass resources for supercapacitor applications [3, 35]. Heteroatom-doped activated carbon can be prepared by mixing the heteroatom containing precursor with carbon precursors before the carbonization process. Such as, Lin et al. mixed the

phosphoric acid with biomass sawdust to get the phosphorus-doped carbon [39]. Wang et al. reported 317 F g⁻¹ in 6 M KOH for N and P co-doped microporous carbon synthesized by polar nonaqueous solvent-assisted microwave method [40].

It is found from the literature survey that phosphorus doping in activated carbon materials is not studied much and not many reports are available on this material to the best of our knowledge. Therefore, in this work, we have chosen phosphorus for heteroatom doping in activated carbon (derived from a novel bioresource). The phosphorus-doped activated carbon is synthesized by a simple and low-cost method. By performing the electrochemical performance measurements, it can be stated that the doped material shows great potential to be a promising additive for supercapacitor applications.

2 Experimental section

2.1 Synthesis of porous activated carbon (AC) and phosphorus-doped porous carbon (AC_P)

2.1.1 Synthesis of activated carbon

Activated carbon was obtained using a novel bioresource (leaves of *Saccharum bengalense* plant) by chemical activation method. To synthesize porous carbon, the bioresource was thoroughly cleaned, vacuum dried, and then crushed into powder form. The obtained powder was then mixed with the activating agent (ZnCl₂) in the weight ratio of 1:2 and placed in an oven at 100 °C for drying. Dry powder was obtained which was heated in a tube furnace at 850 °C in an inert atmosphere for half an hour for the chemical activation process. The resultant product was washed several times with hot de-ionized water and dilute HCl to remove zinc and chloride ions and then dried in a vacuum oven to get the final product and named AC.

2.1.2 Nitric acid treatment

For the nitric acid-treatment of carbon, measured amount of AC was pre-treated with 3 mol L⁻¹ nitric acid solution and heated at 80 °C for three to four hours. The resultant thick paste was dried overnight in a vacuum oven and named as nitric acid-treated carbon (AC_N).

2.1.3 Phosphorus doping

For the phosphorus doping AC_N was added to 2 mol L⁻¹ solution of phosphoric acid and stirred continuously at 90 °C overnight. This was further heated for a few hours until a thick slurry is obtained. The thick slurry

was further calcined in an inert atmosphere. The calcined powder was thoroughly washed with DI water several times, and then the resultant powder was dried overnight in an oven at 100 °C. The resultant powder was named AC_tP-700 and AC_tP-850 corresponding to the different calcination temperatures 700 and 850 °C respectively. Figure 1 presents the synthesis process of phosphorus-doped nitric acid-treated activated carbon.

2.2 Characterization

X-ray diffractometer Bruker AXS was used for the crystallographic analysis of the material. FTIR analysis was carried out by Nicolet NEXUS Agilent 1100 instrument; Raman spectra were recorded with Renishaw Invia Raman Microscope which consists of Ar⁺ ion laser source (50 mW). The surface morphology of the samples was carried out using field emission scanning electron microscope (Carl Zeiss model Ultra Plus Field). XPS (PerkinElmer model 1257 X-Ray Photoelectron Spectrometer) was used for the elemental composition of the surface. The specific surface area analysis and pore size distribution were determined with Micrometrics ASAP 2010 analyzer. Electrochemical analyzer with model number 608C (CH instruments, USA) was used for CV analysis. Impedance/Gain-Phase Analyzer (C-50 Alpha A) was used for carrying out the electrochemical impedance spectroscopic (EIS) features of the cells from low (10 mHz) to high (100 kHz) frequency regions.

Fig. 1 Schematic representation of phosphorus-doped nitric acid-treated activated carbon

2.3 Electrode preparation

To prepare the electrode for studying the electrochemical performances, the active material, polyvinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) as the binder and conducting carbon were mixed thoroughly in the weight ratio 85:5:10 ratio with the help of mortar and pestle by adding few drops of acetone. The paste was coated on the current collectors (graphite sheet) with a mass loading of 0.87 mg cm⁻² and then vacuum dried at 60 °C overnight. The specific capacitance of the electrode was evaluated from cyclic voltammetry (CV) curves and galvanostatic charge discharge (GCD) curves using Eqs. (1) and (2), respectively.

$$C_s = \frac{I}{ms} \quad (1)$$

where C_s is the specific capacitance (F g⁻¹), I represents the applied current (A), m corresponds to the mass of the active material (mg) and s is scan rate (Vs⁻¹).

$$C_s = \frac{I\Delta t}{m\Delta V} \quad (2)$$

where I is the discharge current in Ampere (A), m is the mass of one working electrode in gram (mg), Δt represents the discharge time (sec) and ΔV represents the potential window (V).

Energy density E (Wh g⁻¹) and power density P (W kg⁻¹) are also evaluated for different current densities by Eqs. (3) and (4) respectively:

$$E = \frac{C_s \times \Delta V^2}{2 \times 3.6} \quad (3)$$

where C_s represents the specific capacitance and ΔV is the potential window.

$$P = \frac{3600 \times E}{\Delta t} \quad (4)$$

where E represents the energy density and Δt corresponds to the discharge time.

3 Results and discussion

3.1 Structural and morphological and analysis

3.1.1 X-Ray diffraction (XRD)

Diffraction analysis of the materials was performed in the range of 10° to 80° to observe the relative changes in the crystal structure of porous carbon after nitric acid treatment

Fig. 2 XRD spectra of AC, AC_t , AC_tP-700 and AC_tP-850 materials

Table 1 Layer spacings (d_{002}) and crystalline sizes of AC, AC_t , AC_tP-700 and AC_tP-850 electrode materials

Sample	d_{002} (nm)	Crystallite size (nm)
AC	0.3524	8.846
AC_t	0.3563	6.727
AC_tP-700	0.3590	9.551
AC_tP-850	0.3628	9.524

and phosphorus doping. XRD patterns (Fig. 2) of all samples display two broad diffraction peaks at 2θ values of 24° and 44° which correspond to the (002) and (101) planes of the amorphous carbon [41, 42].

It is noticed that diffraction peaks for the phosphorus-doped nanomaterials are broader in comparison with pure carbon indicating a decrease in graphitization degree for phosphorus-doped nanomaterials [42, 43].

The layer spacing of the synthesized materials is calculated using the Bragg formula (Eq. 5) from the main diffraction peak (002).

$$d = \frac{\lambda}{2 \sin \theta_{002}} \quad (5)$$

where λ (0.1540 nm) represents the radiation wavelength and θ_{002} is the angle of reflection. Furthermore, the crystallite size is calculated by the Scherrer formula (Eq. 6) and is shown in Table 1.

$$L_c = \frac{0.9\lambda}{\beta_{002} \cos \theta_{002}} \quad (6)$$

where β_{002} denotes the full width at half-width of (002) diffraction peak. 8.846 nm crystallite size and 0.3524 nm layer spacing are obtained for pure carbon (AC). The layer spacing of AC is found to be greater than the layer spacing of graphite (0.335 nm) pointing to a low graphitization degree. After nitric acid treatment, crystallite size decreases to 6.727 nm while layer spacing (0.3563 nm) shows a small change. Therefore, a subsequent decrease in the crystallite size for AC_t may be due to the structure collapse after the oxidation reaction caused by the nitric acid treatment [2]. Again, the phosphorus doping increases the layer spacing and crystallite size and this is favorable for the transportation of the electrolyte ions which further leads to the enhancement in supercapacitive performance [5, 8, 44, 45].

3.1.2 FESEM analysis

The FESEM images of the AC, AC_t , AC_tP-700 , AC_tP-850 (Fig. 3) display a change in microstructures and surface morphologies. As evident from the FESEM images, porous grains of the activated carbon (Fig. 3a) get converted into smaller flake structure after the treatment with nitric acid. The SEM images exhibit that HNO_3 treatment has a destructive and corrosive effect on the activated carbon surface which results in pores coalescence or collapse and promotes the production of very large macropores (Fig. 3b,c). This results in an appreciable loss of porosity because of the removal and/or distortion in neighboring micropores after the nitric acid oxidation [45, 46]. These results are further verified by BET results presented in Table 2. The EDX data of AC_tP-850 (Fig. 3d) indicate a decrease in carbon content and an increase in oxygen content after modification. Pretreatment with nitric acid introduces additional carboxylic groups which are discussed later in the FTIR section.

Irregular protrusion, cracks, cavities, and widely dispersed pores are seen in the FESEM images of AC_t . This kind of structure forms a route for the heteroatoms to move in the micropores of the carbon structure [47]. This causes more adsorption of phosphorus atoms in the nitric acid-treated carbon (12 at% in the present work) which is higher than the adsorption in raw activated carbon [4, 8, 44, 48, 49]. There is exfoliation of the carbon structure by phosphoric acid and a change of morphology can be seen in Fig. 3c. As confirmed by the XRD and BET results phosphorus doping results in interlayer expansion and production of more mesopores (Table 2).

The EDX analysis of the AC_tP-850 nanomaterial (Fig. 3d) confirms the presence of phosphorous, oxygen, nitrogen, and carbon [45]. Hence, it can be concluded that phosphorus doping in the nitric acid-treated carbon gives a change of structure which is helpful for the easy transport of the

Fig. 3 FESEM images of (a) pure AC, (b) nitric acid (HNO_3) treated activated carbon (AC_t), (c) phosphorus-doped nitric acid (HNO_3) treated activated carbon ($\text{AC}_t\text{P-850}$), and (d) EDX spectra of phosphorus-doped (calcined temp 850 °) nitric acid treated activated carbon ($\text{AC}_t\text{P-850}$)

Table 2 Specific surface area, total pore volume, and average pore size (nm) of AC, AC_t , $\text{AC}_t\text{P-700}$, and $\text{AC}_t\text{P-850}$, respectively

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$) specific surface area	V_{micro} ($\text{cm}^3 \text{g}^{-1}$) micropore volume	V_{meso} ($\text{cm}^3 \text{g}^{-1}$) mesopore volume	V_t ($\text{cm}^3 \text{g}^{-1}$) total pore volume	Average pore size (nm)
AC	1890	0.361	0.0392	0.40	2.1
AC_t	612	0.09	0.02	0.11	3.2
$\text{AC}_t\text{P-700}$	1460	0.296	0.135	0.431	3.3
$\text{AC}_t\text{P-850}$	1920	0.324	0.243	0.567	4.07

electrolyte ions during the electrochemical phenomena [39].

3.1.3 Raman studies

Figure 4a represents the comparative Raman spectra of AC and phosphorous-doped nanomaterials ($\text{AC}_t\text{P-850}$). Both electrode materials show two typical bands located at 1332 (D band) and 1588 cm^{-1} (G band). The D band is ascribed to disordered or defective carbon and the G band is related to the graphitic carbon structure. I_D/I_G (the intensity ratio of D and G band) can be used to get the structural information or the quality of the graphitic materials.

From the spectra, I_D/I_G is found to be 1.1 for phosphorous-doped nanomaterials which are greater than the AC (0.9). This agrees with the XRD results indicating that after the heat treatment and phosphorous doping, more structural defects are introduced into the structure [4, 39, 42, 50, 51].

3.1.4 Fourier transform infra-red (FTIR) spectroscopic studies

FTIR measurements play a very important role in the structural analysis as they provide an insight into the functional groups present in the synthesized materials. The bands above 3500 cm^{-1} in AC and AC_t correspond to

Fig. 4 (a) Raman bands of AC and AC_tP-850 materials and (b) FTIR spectra of AC, AC_t, AC_tP-700 and AC_tP-850 samples

the stretching vibrations of the O–H due to the existence of hydroxyl groups in the carbon structure (Fig. 4b). The change in intensity and formation of new groups between 1440 and 700 cm⁻¹ in AC_t in comparison with pure AC may be due to the creation of new oxygen-containing surface groups and N–O bands [52]. The small intensity peak in the lower region at 675 cm⁻¹ for all the samples may be due to the presence of alkene sp² C–H bend and aromatic sp² stretch [53]. The broad peak at 3450 cm⁻¹ in the phosphorous-doped nanomaterials may be attributed to the hydroxyl group and N–H stretching vibrations [54, 55]. Another characteristic peak at 1650 cm⁻¹ and 1386 cm⁻¹ in the doped materials is assigned to the N–H, O–H, C–X (X=O, N, C) stretching vibrations [41, 56].

The presence of two bands between 1200 and 1000 cm⁻¹ in AC_tP-700 and AC_tP-850 may be ascribed to C–O stretching, hydrogen-bonded modes in lactones, phenolic structures, P=O stretching vibrations, and P=OOH stretching vibrations [41, 56]. Another peak at 1010 cm⁻¹ in the phosphorous-doped material is attributed to the presence of several C–O bonds of phenols, ethers, and hydroxyl groups. Hence, it can be concluded from the FTIR analysis that the oxidation treatment by HNO₃ and phosphorus doping causes the formation of many oxygens, nitrogen, and phosphorus groups in the phosphorous-doped nanomaterials. The presence of these groups increases the electrochemical performance by introducing pseudocapacitance in addition to electric double-layer capacitance.

3.1.5 X-Ray photoelectron (XPS) analysis

To further explore the bonding configurations of phosphorous-doped atoms, the XPS measurement was taken at AC_tP-850 electrode material and the results are shown in Fig. 5. The complete scan (Fig. 5a) exhibits

two predominant peaks of carbon at 283.7 eV, oxygen at 530.6 eV, and a small peak of phosphorus at 134.2 eV. The narrow C1s spectra (Fig. 5b) can be divided into four regions with peaks at binding energies of 283.6, 284.3, 285.5 and 286.5 eV. The main dominating peak at 283.6 and another peak at 284.3 eV corresponds to carbide carbon, graphite carbon, the carbon in alcohol, ether groups. These two peaks are associated with sp² and sp³-hybridized C–C or C–O bonds. The third peak at 285.5 eV is associated with C–P linkage and the carbonyl group, while the small peak at 286.5 eV corresponds to the ester and carboxyl and C–O groups [4]. The O1s spectrum (Fig. 5c) exhibits the main peaks at 530.3 eV correspond to the quinone and carbonyl group (C=O). The more concentration of these carbonyl and quinone groups in the AC_tP-850 material indicates the better electrochemical performance. The second peak at 531.6 eV represents the C=O and phosphate groups (P=O). Phosphate groups provide the electroactive sites for the redox reaction and enhance the capacitive performances [4, 5].

The sharp P2p peak (Fig. 5d) centered at 134.2 eV can be deconvoluted into 2 peaks at binding energies of 133.8 eV and 134.5 eV. These high energy peaks in P2p are associated with P–O and C–O–P groups, such as (CO)₂PO₂, (CO)₃PO, and (CO)PO₃. These groups are characteristics of P bonding with C atoms and O atoms.

The presence of more oxygen content in the phosphorous-doped nanomaterials (Fig. 4a) confirms the successful incorporation of phosphorous atoms in the porous carbon structure [5, 8, 41, 49, 57]. It indicates that the P atoms are incorporated into AC_tP-850 along with large amounts of oxygen-functional groups (carbonyls, C–O bonds, and carboxylates) which are beneficial for the improvement of capacitive performance.

Fig. 5 XPS survey spectra of (a) AC_tP-850 material. The high-resolution XPS spectrum of (b) C1s (c) O1s and (d) and P2p

3.1.6 Surface area and porosity measurements

Further, N₂ adsorption–desorption test method was performed to get more information about the structure and surface chemistry. The surface area is determined by the Brunauer–Emmett–Teller (BET) method and displayed in Fig. 6a. Total surface area (S_{BET}), total pore volume (V_t), micropore volume (V_{micro}), mesopore volume (V_{meso}), and average pore size of all the materials are presented in Table 2. Nitrogen sorption isotherms of AC display a type I isotherm indicating microporous characteristic and a hierarchal porous structure with high nitrogen uptake below 0.1 P/P₀ value. Chemical activation by ZnCl₂ gives a dehydrating effect which results in the production of more micropores and fewer mesopores [57, 58]. However, after the nitric acid treatment number of mesopores increases and isotherm demonstrates a slight shift from typical type I characteristic due to a contribution from type IV and results in a decrease in total surface area for AC_t.

In pure AC, there is an abrupt increase in adsorption while in AC_t there is a steady increase which implies AC has more micropores, whereas AC_t has more meso- and macropores. It is analyzed that there is a major decrease in specific surface area for AC_t (612 m² g⁻¹) in comparison to AC (1890 m² g⁻¹) as the porous structure has changed into a flake kind of structure after the treatment with nitric [43, 46, 52, 59]. The decrease in V_t and S_{BET} in the case of AC_t may be due to the gasification of the carbon structure. After phosphorus loading again an increase in total surface area and broad pore size distribution is obtained. Nitrogen sorption isotherms of the doped nanomaterials display a type IV isotherm which indicates more mesopores (Table 2). The pore size distribution is calculated by the Barrett–Joyner–Halenda (BJH) method. The treatment of nitric acid causes partial destruction of the porous structure and blockage of the pore opening which results in the creation of more mesopores and widening of average pore radii from 2.1 to 3.2 nm (Fig. 6b).

Fig. 6 (a) Adsorption/Desorption isotherms of AC, AC_t , $\text{AC}_t\text{P-700}$ and $\text{AC}_t\text{P-850}$ materials and (b) pore size distribution curves of AC, AC_t , $\text{AC}_t\text{P-700}$ and $\text{AC}_t\text{P-850}$ materials

The increase in the average pore size V_t and total surface area after phosphorus doping can be related to that thermal treatment during the doping process. As heating at such a high temperature has created more mesopores that were blocked during the oxidation by nitric acid and that is the reason that $\text{AC}_t\text{P-850}$ has the highest S_{BET} and V_t [4, 39, 48, 60]. More pore widening also occurs after the thermal treatment and $\text{AC}_t\text{P-850}$ displays 4.07 nm average pore size [8, 41, 44, 49]. The pore size of $\text{AC}_t\text{P-850}$ is relatively suitable for the movement of electrolyte ions (Na^+ and SO_4^-). The erosive action of nitric acid on the porosity and modification of the structure due to harsh modification conditions was also established by SEM results (Fig. 2). The decrease in total surface area can be related to the presence of oxygen functional groups at the carbon surface and the extent of these new oxygen-carbon groups in AC_t will affect the availability of the adsorbate to the active carbon site and hence decrease in the surface area [54].

3.2 Electrochemical performances

The supercapacitor cell is prepared by joining 2 electrodes and separated by the separator. The symmetric supercapacitor cell configurations which were studied further is mentioned below:

CC|Active Electrode Material||1 M Na_2SO_4 |separator||Active Electrode Material||CC
CC (current collector): Graphite sheet
Separator: Whatman filter paper

3.2.1 Cyclic voltammetry (CV) studies

Cyclic voltammograms of all the synthesized materials were recorded within the potential window 0–1.0 V in 2 electrode cell configuration. Comparative CV plots of AC, $\text{AC}_t\text{P-700}$, and $\text{AC}_t\text{P-850}$ are displayed in Fig. 7a. Although AC possesses a higher surface area, it shows a narrow current response than $\text{AC}_t\text{P-700}$ and $\text{AC}_t\text{P-850}$ samples. This may be due to the presence of more micropores and fewer mesopores in AC (Table 2) as micropores do not get easy access during the charging process (Fig. 7a). The wider current response of the doped materials ($\text{AC}_t\text{P-700}$ and $\text{AC}_t\text{P-850}$) is assigned to the wider pore size distribution response and more percentage of the mesopores (Table 2).

It is observed from Fig. 7a that doped materials calcined at a higher temperature ($\text{AC}_t\text{P-850}$) present better current response than the doped materials calcined at lower temperature ($\text{AC}_t\text{P-700}$) at the same scan rate (5 mV s^{-1}). It can be stated that at such higher calcined temperature more phosphate groups are introduced which accounts for additional pseudocapacitance. Again, the cyclic voltammogram of the $\text{AC}_t\text{P-850}$ displays a deviation from the typical rectangular shape that is ascribed to the presence of phosphorous atoms that contribute to the pseudocapacitance [41, 54, 60]. Further, the current response of $\text{AC}_t\text{P-850}$ is analyzed for different scan rates (5 – 100 mV s^{-1}). No distortion in CV response for $\text{AC}_t\text{P-850}$ even at a higher scan rate (Fig. 7a) proves the good capacitive response of the material. 347 F g^{-1} specific capacitance is obtained for $\text{AC}_t\text{P-850}$ material at 5 mV s^{-1} . Figure 8 depicts the variation of specific capacitance (calculated from the CV plots) with scan rates. At a higher scan rate, the movement of the electrolyte through the electrode surface decreases and

Fig. 7 (a) Comparative CV curves of AC, AC_t, AC_tP-700, and AC_tP-850 nanomaterials at the sweep rate of 5 mVs⁻¹. (b) CV curves of AC_tP-850 nanomaterials at varying scan rates (5–100 mV s⁻¹)

Fig. 8 Variation of specific capacitance AC_tP-850 nanomaterials with the scan rate

a reduction in charge storage occurs which is reflected in the decrease in the specific capacitance values at higher scan rates [5, 8, 60].

3.2.2 Galvanostatic charge–discharge (GCD) studies

Figure 9a depicts the comparative GCD curves of AC, AC_tP-700 and AC_tP-850 electrode material at different current densities. AC discharge curves display the symmetrical behavior confirming the pure double-layer charge storage mechanism. The deviation of the charge–discharge curves from linearity for AC_tP-700 and AC_tP-850 reveals the presence of redox reaction due to the phosphorous doping [5, 45]. Charge discharge curves for AC_tP-850 electrode

material at varying current densities (0.5–10 A g⁻¹) are plotted in Fig. 9b. Specific capacitance values obtained from the charge–discharge curves using Eq. 2 for AC_tP-850 at varying current densities are displayed in Fig. 10. Maximum specific capacitance (328 F g⁻¹) is obtained at a minimum current density of 0.5 A g⁻¹. Furthermore, the value of specific capacitance drops with an increase in the current density as at such high current the accessibility of the micropores decreases due to fast charge–discharge rates. Low capacitance retention at high current density is linked to the presence of more oxygen functional groups which adds to the pseudocapacitance but also deteriorates the capacitance performance [7].

3.2.3 Impedance spectroscopic studies

Nyquist plots (the plot of imaginary component (−Z'') alongside the real component (Z')) of all the synthesized materials are plotted to study the charge transfer resistance. The Nyquist plot (Fig. 11) displays the sharp increase of $\text{img } Z$ values as the frequency changes from high (100 kHz) to low values (10 MHz). The total resistance R_t of an electrode consists of three parts, i.e.

$$R_t = R_1 + R_2 + R_3$$

where R_1 characterizes the internal resistance or impedance of the electrode, R_2 represents the polarization resistance and R_3 is the diffusional resistance.

R_2 and R_3 together give the charge transfer resistance or

$$R_{ct} = R_2 + R_3$$

Internal resistance (R_1) can be obtained from the intersecting point with the x (real) axis in the high-frequency

Fig. 9 (a) Comparative GCD profiles of AC AC_tP-700 and AC_tP-850 nanomaterials (b) Variation of specific capacitance of AC_tP-850 nanomaterial with increasing current density (0.5–10 A g⁻¹)

region of the Nyquist plot. The polarization resistance (R_2) is given by the diameter of the semicircle in the middle-frequency region. Hence, the more the diameter of the semicircle, more the polarization resistance. And this represents the penetrating ability of the electrolyte ions in the electrode material. The diffusional resistance (R_3) is given by the straight-line length of the Nyquist plot in the middle-frequency region [5, 49, 55, 58, 61].

The Nyquist plot of AC shows a straight line in the high-frequency region and semi-circle in the low-frequency region (Fig. 11). It can be evaluated from the Nyquist spectra that pure AC has a bigger semi-circular arc which gives rise to more polarization resistance in the high-frequency region, and AC_tP-850 displays the lowest value of the polarization resistance. As evident from the plot, there is

a reduction in the semi-circular arc for AC_t, AC_tP-700, and AC_tP-850 in comparison with pure AC which may be due to the abundance of mesopores implying the low value of the charge transfer resistance for the doped nanomaterials.

However, there is not much difference in the internal resistance of all the electrode materials. Besides, AC shows better capacitive behavior as the straight-line shape in the low-frequency region represents the capacitive which is contributed by the double-layer effect. Deviation from the straight line or more slope for the AC_tP-850 electrode is due to the pseudocapacitance contribution to the total specific capacitance by the oxygen, nitrogen, and phosphorus functional groups. Hence, it can be concluded that AC_tP-850 offers less charge transfer resistance and shows pseudocapacitive behavior in addition to the electric double-layer behavior which enhances the electrochemical performance of the AC_tP-850 nanomaterial [42, 43].

Fig. 10 Variation of specific capacitance with current density of AC_tP-850 nanomaterial

The fabricated symmetric device designed from AC_tP-850 delivered maximum specific energy of 29 Wh kg⁻¹ at a specific power of 646 W kg⁻¹. The specific power attained the highest value of 3676 W kg⁻¹ at the specific energy of 6.5 Wh kg⁻¹. The achieved results recommend that the AC_tP-850-based symmetric device exhibits great potential for energy storage applications. The long-term cycling stability of the doped nanomaterials was investigated by charge/discharge measurement at 5 A g⁻¹. The result (Fig. 12) exhibits 99.4% capacitance retention in the specific capacitance even after 5000 cycles of charging/discharging, representing the excellent cycle stability of the carbon material after phosphorous doping [55]. The GCD curves at 5 A g⁻¹ current density of initial and final cycles are displayed in the inset of Fig. 12. Consequently, the phosphorus-doped hierarchical porous carbon AC_tP-85 has more mesoporous kind of structure, resulting in a low value of equivalent resistance. This

Fig. 11 (a) Nyquist plots of AC, AC_tP-700 and AC_tP-850 nanomaterials, (b) Expanded Nyquist plot of AC, AC_tP-700 and AC_tP-850 nanomaterials

Fig. 12 Variation of specific capacitance of AC_tP-850 nanomaterials with cycle numbers (inset shows the GCD cycles for initial and final cycles)

exhibits enhanced electrochemical performance and this can be attributed to pseudocapacitance contributed by various oxygen and phosphorus-containing functional groups in the material.

We have compared the present work with other P doped work in terms of specific capacitance, electrolyte, cyclic stability, and power performance (Table 3).

Phosphorus doping generates structural defects in the carbon structure as the atomic size of the phosphorus atom is bigger than that of carbon atom and these defects act as the electroactive sites during the electrochemical process. The low electronegativity of phosphorus changes the charge and spin densities of the carbon structure and improves the electrochemical performance.

Table 3 Performance comparison of the previously reported P-doped carbon with the present work (AC_tP-850)

Sample name	Electrolyte	Specific capacitance (F g ⁻¹)	Capacitance retention (%) / number of cycles	Ref
P-doped PC	6 M KOH	367	96.5/10,000	[4]
N, P Co-doped CNF	1 M H ₂ SO ₄	224.9	–	[5]
N, P-doped AC	6 M KOH	312.4	97/2000	[8]
P, N-doped AC	7 M KOH	227	93.8/3000	[56]
N, O and P-doped PC	Na ₂ SO ₄	93.5	81.4/2000	[54]
P-doped PC	1 M H ₂ SO ₄	228.7	–	[51]
P-doped AC	1 M H ₂ SO ₄	292	98.3/5000	[39]
P-doped AC (This work)	1 M Na ₂ SO ₄	328	99.4/5000	

AC activated carbon, PC porous carbon, CNF carbon nanofibers, GNS Graphene nanosheets

4 Conclusion

Phosphorous heteroatoms were successfully doped in nitric acid-treated biomass-derived porous carbon material by a simple carbonization process at different carbonization temperatures. By controlling the carbonization temperature, the sample AC_P-850 with the best supercapacitive performance was obtained. The specific capacitance of AC_P-850 reached the maximum value (328 F g⁻¹) for the current density of 0.5 A g⁻¹ in aqueous electrolyte. The product displayed no change in the specific capacitance value up to 5000 cycles and presented excellent cyclic performance. The excellent electrochemical performance of the phosphorus-doped activated carbon sample is ascribed to its better distribution of micro/macropores and efficient bonding states between P–C and P–O bonding. Importantly, micropores in the sample accumulate sufficient electrolyte ions and mesopores provide the passage for the ion diffusion and transport. Additionally, the incorporation of phosphorous atoms in the porous carbon structure contributes pseudocapacitance to both electric double-layer capacitance from carbon structure owing to its high surface area and pseudocapacitance due to the redox reactions by the heteroatoms. Hence, this study provides a simple and low-cost method for the synthesis of phosphorous-doped porous carbon with tunable surface and texture properties and enhanced supercapacitive properties.

Compliance with ethical standards

Conflict of interest On behalf of all authors, the corresponding author states that there is no conflict of interest.

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