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Enhanced electrochemical performance of hierarchical porous carbon/polyaniline composite for supercapacitor applications

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Abstract

In this work, activated carbon/polyaniline (AC/PANi) composites were synthesized by low temperature in situ polymerization and their electrochemical performance was investigated. Microstructure and morphology examination of the samples confirmed a uniform coating of polyaniline on AC surfaces without any change in the structure. The electrochemical studies of the samples confirmed the improvement in the electrochemical performance of AC/PANi composites. Despite a decrease in the specific surface area a substantial increase in electrochemical performance is recorded for the AC/PANi composites due to the synergistic effect between the pseudocapacitance and double layer capacitance. The highest specific capacitance of 1021 F g⁻¹ was calculated for the APA-29.4 composite in neutral aqueous electrolyte (1 M Na₂SO₄) which is many times greater than the specific capacitance values for AC (253 F g⁻¹) and PANi (389 F g⁻¹). The enhancement in the electrochemical performance of AC after polymerization with PANi in composites favours its use as a favourable electrode material for the energy storage devices.

1. Introduction

With a fast and continuously growing techno-savvy young population, flexible, lightweight and portable electronic devices have led to the urgent demand for the bio-friendly energy storage devices. In this expedition, electrochemical capacitors or supercapacitors represents a smart alternative for already existing energy storage devices [1–3]. These supercapacitors can serve a good substitute for the rising power supply demand in various sectors such as for hybrid electric vehicles and other power sectors as they provide high power density at low-cost fabrication using ecofriendly bioresources [4]. Supercapacitors store charge by the electric double layer formation and by redox reactions or pseudocapacitance. Charge storage by double-layer formation is a non-faradic mechanism and charge is stored electrostatically by the reversible ion adsorption at the electrode/electrolyte interface [5–7]. While, in pseudocapacitors, charge transfer occurs by oxidation and reduction reactions at the electrode material. Different forms of carbon like activated carbon, CNT’s, carbon nanofibres, carbon aerogel and graphene with tunable pore size and large surface area shows the good electrochemical performance when used for electric double-layer capacitors (EDLCs) [8]. Whereas, transition metal oxides, for instance, MnO₂, NiO, Mn₃O₄ and RuO₂ and certain conducting polymers like polyaniline, polythiophene and polypyrrole are well-thought-out suitable materials for pseudocapacitors [9–16]. Metal oxides give remarkably great capacitance and high energy and power density values along with excellent reversibility but their toxicity and high cost of fabrication is a great hindrance for their application in the energy sector.

Ubiquitous presence and versatility of carbonaceous materials make them a subject of study in diverse applications including the energy sector. Porous activated carbon derived from the bioresources is environment friendly and can be synthesized by inexpensive activation method. This makes it a good study material for
supercapacitor applications and gives very long cycle life however low energy density and low capacitance values limits their applications in this area. The low energy density of EDLCs can be enhanced by two ways first either by increasing capacitance values or by increasing the voltage window of the SCs as energy density depends on both capacitance value and voltage \((E = \frac{C V^2}{2})\). Capacitance values can be enhanced by using the hybrid electrode of the composite material by a right stoichiometric mixture of carbonaceous materials with conducting polymers or by heteroatom doping of pure carbon material \([17–22]\). Heteroatom doping in the base carbonaceous materials provides more reaction sites and anisotropic charge distribution in the material which causes the enhancement in the supercapacitive performance of the devices. So, the ongoing interest in the energy sector is to enhance the performance of supercapacitors instigated from the appropriate combination of good conducting and pseudocapacitive properties of carbonaceous materials and conducting polymers \([23–25]\).

Conductive polymers and its composites have been extensively researched for high energy-consuming applications, for instance, energy storage devices and hybrid electric vehicles as Pseudocapacitors. The pseudocapacitors store charge by faradic mechanism just like batteries. Conducting polymers shows environment stability, good electronic conductivity and flexibility. Also, the electronic stability of the conducting polymers can be controlled by varying the oxidation state or protonation number. All these properties make them a good candidate for the pseudocapacitors and flexible electrodes can be fabricated from conducting polymers.

Among all these conducting polymers, polyaniline (PANI) is most explored for supercapacitor applications as it can be synthesized by a very inexpensive method from aniline and possess very high energy density \([26]\). Polyaniline owing to its high conductivity provides fast electron transmission during the oxidation reduction process. However, its swelling or shrinkage property and slow ionic transport kinetics decrease the power density and cycle lifetime which limits its practical application. The hybridisation of polyaniline with various electrode materials (such as carbon based materials) with improved morphologies and microstructures can be considered for the fabrication of supercapacitor electrodes with enhanced electrochemical properties. The hybridization of polyaniline should be such that it decreases the diffusion distance and provides strong adhesion with a conductive substrate. Therefore, to minimize the disadvantage of activated carbon, the micro and mesopores of activated carbon with suitable pore size and high specific surface area, are decorated with PANi by chemical and electrochemical polymerizations. Jun Yan et al reported a very high specific capacitance value \((1046 \text{ F g}^{-1})\) for graphene nanosheet/polyaniline composite as compared to \(115 \text{ F g}^{-1}\) for PANi \([27]\). It was found that the aspect ratio of the nanostructures and the morphology are the important factors affecting the electrochemical performance of pseudocapacitors as the oxidation level increases with aspect ratio. Park et al \([28]\) observed that for different kind of nanostructures, nanofibres showed the highest specific capacitance values as these nanostructures show faster kinetics.

Here, in this paper, we presented the synthesis of highly porous carbon and polyaniline composites by low temperature \textit{in situ} polymerisation and the electrochemical performance in \(1 \text{ M Na}_2\text{SO}_4\). Activated carbon used in the composite is synthesized from a novel bioresource \textit{Saccharum bengalense} plant. Activated carbon having good pore size distribution (PSD) and the high specific surface area provides the diffusion path for electrons during redox reaction and leads to enhancement in the volumetric capacitance values. In addition, during the charging process, the walls or boundary of the activated carbon pores absorb the expansion of polyaniline and hence increases the cycle life of the composite material. Also, the composites show advantages because of their synergistic performance resulting from each constituent. The composite material shows an enhancement in the specific capacitance values. The correlation between the amount of PANi and its effect on the structure, porosity and electrochemical properties of the composite material, were studied in detail.

2. Experimental details

2.1. Chemicals

For the synthesis of materials, aniline monomer (stored at low temperature in the refrigerator), Amoniumperoxydisulphate or APS \((\text{NH}_4)_2\text{S}_2\text{O}_8\), sodium hypochlorite (NaOCl), Polyvinylidene fluoride-co-hexafluoropropylene (PVdF–HFP) \([\text{Sigma Aldrich}]\), Ethanol, Acetone, Hydrochloric acid (HCl) and Sodium Sulphate \((\text{Na}_2\text{SO}_4)\) \([\text{Merck}]\) of analytical grade are used without additional purification. Distilled water was used during the synthesis process.

2.2. Synthesis of activated carbon (AC)

Activated carbon was obtained from a bioresource (leaves of \textit{Saccharum bengalense} plant). Activated carbon is synthesized by the chemical activation method in the presence of an activating agent \((\text{ZnCl}_2)\). A thick paste was obtained which was then heated at a high temperature \((800 \, ^\circ\text{C})\) in an inert atmosphere for half an hour. The
synthesized material was washed several times by dilute HCl and de-ionized water and then dried in a vacuum oven to get the final product.

2.3. Synthesis of activated carbon/polyaniline composite

The composite material was synthesized by low temperature in situ polymerisation method as described in our previous work [29]. Synthesis of the composite material was carried out in acidic medium and HCl was chosen for the same. The complete schematic demonstration of the synthesis process is shown in figure 1. 0.25 g AC was sonicated before use to disperse it completely and was maintained at 0 to 5 °C for half an hour and then APS solution (dissolved in 1 M HCl) was added to the AC solution and left for 30 min with continuous stirring at low temperature. Aniline monomer was added dropwise followed by NaOCl. After adding the monomer the colour of the product changed to dark green indicating the initiation of the polymerization process. NaOCl was added to make the reaction fast. The reaction was carried out at low temperature for 6 h for the completion of the reaction and after this stirrer is stopped and the solution is left at low temperature for 1 h without stirring. Finally, the product was washed with HCl, acetone, ethanol and DI water thoroughly and then vacuum dried overnight in a vacuum oven at 60 °C. The composites synthesized by the varying amounts of aniline (0.5 ml, 1 ml, 2 ml) correspond to mass loading of 17.2%, 29.4% and 41.1% of PANi in the composites and the composite samples were denoted as APA-17.2, APA-29.4 and APA-41.1 respectively. Different compositions of composites were synthesized by varying the amount of AC and aniline monomer. Pure PANi was also prepared via a similar method without AC for the comparative study.

2.4. Preparation of electrode and supercapacitor cell

The fabrication of the electrodes using the composite and PANi for the supercapacitor cell was accomplished with the same method as discussed in our previous work [29]. For making the electrodes, the synthesized material (AC, PANi and composite), Polyvinylidene fluoride-co-hexafluoropropylene (PVdF-HFP) and carbon...
black were mixed in the 85:5:10 ratio respectively and intersperse in acetone to make a slurry or thick paste. The paste was coated on to the graphite sheets of 1 × 1 cm² dimension followed by drying overnight at 100 °C temperature in a vacuum oven. The electrochemical study was carried out in 1 M Na₂SO₄ aqueous electrolyte.

2.5. Characterization methods
X-ray diffraction (XRD) technique was used for the crystallographic analysis of the material. Bruker AXS diffractometer was used for the XRD measurements. The diffractometer was operated at 40 mA and 20 kV, Cu Kα radiations of wavelength 1.5418 Å was used and 2θ range was taken from 10° to 80°. Raman spectra were recorded with Renishaw Invia Raman Microscope which consists of Ar⁺ ion laser source (50 mW). Surface

![Figure 2. SEM images of (a) AC; (b) APA-17.2; (c) APA-29.4 and (d) APA-41.1 composites, respectively. EDX spectra of as synthesized (e) AC and (f) APA-29.4 composite.](image-url)
morphology of the samples was carried out using Carl Zeiss model Ultra Plus Field Emission Scanning Electron Microscope (Carl Zeiss model, Ultra Plus). Transmission Electron Microscope or TEM (FEI TECNAIG²) was used for the microstructural analysis and surface elemental composition was carried out with XPS (Perkin Elmer model 1257). The surface area and pore size distribution of the samples were determined with Micromet-rics ASAP 2010 analyzer by the Brunauer–Emmett–Teller (BET) method.

CV measurements were performed by the electrochemical analyzer (model number 608C) and CH Instruments. Charge–discharge behaviours of the designed cells was studied by BT-2000 model; Arbin Instruments. Impedance/Gain-Phase Analyzer (Solartron 1260) was used for studying the Electrochemical Impedance Spectroscopy (EIS) characteristics of the cells (10 mHz to 100 kHz).

3. Results and discussion

3.1. Microstructure, morphological and elemental composition analysis

3.1.1. SEM and TEM analysis
To investigate the surface morphology of AC and composite, FESEM study was carried out. As revealed in figure 2(a), the SEM image of pure AC shows a highly porous structure wherein small bulk carbon material are stacked together to form microns of large size. AC possess randomly oriented flakes with a large number of micro, meso/macro pores with gives rise to high specific surface area (table 1) and favours the formation of the electric double layer at the electrode surface. These pores in the carbon structure favours the diffusion of electrolyte ions i.e. sodium and sulphate ions in the structure. The composites images (figures 2(b)–(d)) reveals no change in the structure and continuous distribution of PANi chains on AC surfaces. PANi is present not only on the surface of the AC but also inside the pores. But this distribution of PANi chains and their interconnection through the pores decreases the specific surface area which is evident from the BET analysis (figure 5) as well and is discussed in later sections. Large macropores between the particles can be seen for small mass loading of PANi which increases the shielding of electrolyte ions. Furthermore, the large weight percentage of PANi may lead to more intercalation and adsorption of PANi in the AC porous structure. The pores of the activated carbon are now covered with PANi chains which acts as a conductive path for the electrolyte ions and provides more sites for the redox reaction in the composite which subsequently enhances the specific capacitance value of the composites.

The elemental analysis of AC and APA-29.4 composite is presented in figures 2(e)–(f). As projected, the EDX data for AC shows the distribution of only oxygen, chlorine and mainly carbon elements (87.51 wt%). Though, composite displays nitrogen (15.20 wt%) along with carbon (78.28 wt%), oxygen and chlorine can be confirmed from the EDX. The presence of nitrogen element in composite again confirms the coating of PANi on AC surfaces.

The TEM image of AC (figure 3(a)) displays interconnected spherical beads of an average diameter of 50 nm. This kind of spherical shape of activated carbon particles has been reported earlier also.

Figure 3(b) illustrates the uniform distribution of PANi on AC in APA-29.4 composite. It can be seen that there is a uniform coating on AC surfaces without any agglomeration (inset figure 3(b)). The TEM image of the
composites its fibrous structure which is in good agreement with the SEM images. This homogeneous distribution of PANi shortens the electronic path length and enhances the supercapacitive properties.

3.1.2. XRD analysis
For the structural analysis, XRD study of all the samples was carried out from the range of 10° to 80° as shown in figure 4(a). It is observed that the AC sample shows two broad characteristic XRD peaks at 24.9° and 43.6° corresponding to the (002) and (101) planes of the carbon. The broad nature of the peaks illustrates the amorphous nature of the carbon structure in AC [27, 30, 31]. XRD patterns of pure PANi displays the crystalline peaks at 15.2°, 20.7° and 25.3° corresponding to (011), (020) and (200) planes in its emeraldine salt form which are in agreement of previously reported results [30–34]. The sharp peaks at 25.2° might be attributed to the periodicity of the polyaniline polymer chains. These peaks direct the semicrystalline nature of PANi. X-ray diffraction data of composites display characteristic peaks of its components but the peaks are found to be sharper and matching to those obtained in PANi. Moreover, for APA-29.4 and APA-41.1 composites, the peak at 43.6° becomes very small indicating that AC has wholly interacted with PANi molecules [27, 32]. Therefore, it can be concluded that the desired composite have a more ordered crystalline structure of PANi and which in turn is due to more grafting of PANi with AC and better electrochemical properties can be obtained from the composites.

3.1.3. FTIR analysis
To further explicate the carboxylation of activated carbon and its interaction with polyaniline the infrared analysis of samples were carried out for a range from 4000 to 500 cm⁻¹ (figure 4(b)). FTIR spectra of AC shows the presence of five characteristic peaks. The strong peak at 3557 cm⁻¹ is contributed by the O-H stretching by the alcohols, phenols and carboxylic groups present in the AC. The characteristic peak at 1618 cm⁻¹ may be allocated to C=C stretching of the quinoid ring, C=O C=N stretching corresponding to the inherent structure of AC [32, 33, 35]. The peak at 1076 cm⁻¹ with lesser intensity is attributed to the CO single bonds of acids, esters, ethers and phenols. Two more peaks observed at 825 and 705 cm⁻¹ respectively which may be attributed to the presence of C–H bends.

Table 1. Specific surface area, total pore volume and average pore size (nm) of AC, AC/PANI composites and PANi.

| Sample Name | BET surface area (m² g⁻¹) | Total pore volume (cm³ g⁻¹) | Average pore size (nm) |
|-------------|---------------------------|-----------------------------|-----------------------|
| AC          | 1990                      | 0.262                       | 2.04                  |
| APA-29.4    | 880                       | 0.105                       | 4.92                  |
| APA-41.1    | 412                       | 0.127                       | 5.23                  |
| PANi        | 340                       | 0.051                       | 4.2                   |

Figure 4. (a) XRD spectra AC, PANi and AC/PANI composites; (b) FTIR spectra AC, PANi and AC/PANI composites; (c) Raman spectra of AC, PANi and APA-29.4 composite.
Further information regarding the structure and surface chemistry was investigated by the nitrogen adsorption desorption test. Nitrogen sorption isotherms of pure AC and composites are shown in Figure 5(a). As depicted from the figure the isotherm is a type IV adsorption characteristics for the composites and type-I isotherm for the AC according to IUAC classification [7, 40].

A large amount of N\textsubscript{2} adsorption at low pressure value is an indication of the presence of a large number of micropores in activated carbon. Further, a gradual rise in the adsorption curve near the \( P/P_0 \) of 1.0 value in the adsorption spectra implies the existence of many micropores. AC sample displays significantly large BET surface area value of 1990 m\textsuperscript{2} g\textsuperscript{-1} and a total pore volume of 0.262 m\textsuperscript{3} g\textsuperscript{-1} which is very high as compared to the BET

![Figure 5. (a) Adsorption/Desorption isotherms of AC, PANi and AC/PANI composites and (b) pore size distribution curves of AC (inset), PANi and AC/PANI composites.](image-url)

After the polymerization, the main peaks at 1478 cm\textsuperscript{-1} and 1574 cm\textsuperscript{-1} correspond to the benzenoid amine (–NH–) and quinoid amine (–N=) structure of PANi. Furthermore, the peaks at 3450 and 2930 cm\textsuperscript{-1} are consigned to N–H and C–H stretching modes. The strong and characteristic band at 1115 cm\textsuperscript{-1} in all the composites can be ascribed to vibration or electronic band of nitrogen quinoid (N=Q=) [30, 34]. Absorption bands of all composites displayed the characteristic peak of PANi and AC which confirms the successful coating of PANi on the surface of the AC. For pure PANi, the spectrum comprises of the distinct peaks at 1560, 1480, 1308 and 1130 cm\textsuperscript{-1} which are assigned to quinoid amine (–N=) and benzenoid amine (–NH–). The shifting of these characteristic peaks in composites implies the interactions between PANi and AC in the composites and leads to a decrease in band vibration energy [36]. Therefore, enhanced electrochemical performance can be expected in the composites due to easy transitions of electrons after the polymerization.

3.1.4. RAMAN analysis
Raman scattering was performed to analyse the chemical bonding between AC and PANi. Raman spectra of the AC, pure PANi and composites for different compositions is presented in Figure 4(c) and a clear structural change can be interpreted from the spectra. As expected, the Raman spectra of activated carbon show two bands 1335 and 1592 cm\textsuperscript{-1} given by the vibrational modes of carbon. The band at 1335 cm\textsuperscript{-1}, labelled as D band, is due to the defected and disordered graphite lattice structure of AC which may be related to the dangling bonds. Another band at 1592 cm\textsuperscript{-1} is the well-defined G band and occurs due to the vibrations of the perfectly ordered graphite lattice structure. The intensity ratio of D and G band (\( I_D/I_G \)) is found to be more than one indicating a more disordered structure of AC as reported earlier also [27, 37].

The disordered structure of AC provides more defect sites for the incorporation of aniline monomer and further \textit{in situ} polymerization of PANi on AC surfaces. The composites exhibited Raman bands for both AC and PANi. The composites show peaks that there must be electron transfer between PANi and AC during their interaction. Two small bands at 810 and 770 cm\textsuperscript{-1} may be present due to the deformations of the benzene ring and amine deformation in the bipolaronic form of the emeraldine salt. The band at 1556 cm\textsuperscript{-1} is contributed to C=C stretching of the quinoid ring [37, 38]. The more intense peak at 1480 cm\textsuperscript{-1} is contributed by the C=N vibration stretching of quinoid rings. The C=N+ vibration of the delocalized structures gives rise to the band at 1373 cm\textsuperscript{-1}. The band at 1230 cm\textsuperscript{-1} may correspond to C–N stretching of benzenoid, benzene and quinoid ring deformations. The band at 1165 cm\textsuperscript{-1} is contributed to C–H bending of the quinoid or semi-quinoid rings, confirming the presence of PANi on the AC surfaces [27, 35, 39, 40]. The D and G bands of the composites coincide with these peaks verifying that the chemical composition of the synthesized composites is AC and PANi.

3.1.5. BET analysis
Further information regarding the structure and surface chemistry was investigated by the nitrogen adsorption desorption test. Nitrogen sorption isotherms of pure AC and composites are shown in Figure 5(a). As depicted from the figure the isotherm is a type IV adsorption characteristics for the composites and type-I isotherm for the AC according to IUAC classification [7, 40].
It is found that the introduction of PANi in the AC material causes a reduction in the BET specific surface area and pore volume for the composites. AC contains oxygen complexes on its surface and near to pores entrance which reacts with the aniline and blocks the porosity in the composites after the polymerization [41]. PANi loading leads to filling of the micropores and decreases the number of micropores and an increase in the average pore size for the composites [42]. This leads to an increase in the pore size and total pore volume due to the creation of more macropores (figure 5(b)).

3.1.6. XPS analysis
To understand the chemical characteristics and surface functionalities of the composites, XPS analysis was done. Figure 6(a) demonstrates survey spectra of APA-29.4 composite. The spectra confirmed the existence of carbon, nitrogen and oxygen positioned at 283.8 eV, 398.2 eV and 530.6 eV respectively. The sharp C1s peak of AC/PANi composite can be further deconvoluted into 3 peaks (figure 6(b)) at 283.66 eV, 284.36 eV and 287 eV confirming the presence of C–C, C–OH and HO–C=O respectively. The predominant O1s resolution spectra of AC/PANi is deconvoluted into 2 peaks (figure 6(c)) at 530.8 eV and 529.7 eV corresponding to C=O and O=C–OH bonds respectively, indicating the existence of oxygen-containing functional groups at the surface of AC/PANi composite [34]. The N1s spectra of AC/PANi are fitted into 2 peaks 397.7 eV and 398.8 eV. The low binding energy peak at 397.7 eV can be attributed to imine nitrogen (N=) and the major peak at 398.8 eV is ascribed to a neutral amine group (N–H). These peaks correspond to the presence of different nitrogen forms N=C–O and HN–C–O which further confirms the presence of amide groups in the composite and indicate the successful coating of PANi on the AC [39–44].

3.2. Electrochemical properties of electrodes
The electrochemical characterization of the electrodes was carried out using two electrode system. The symmetric supercapacitors were assembled by using two working electrodes with a separator (Whatman) and 1M Na2SO4 aqueous electrolyte.
The symmetric supercapacitor cell configurations which were studied further is mentioned below:

GCC|active material|1M Na₂SO₄|separator|1M Na₂SO₄|active material|GCC
(GCC: graphite current collector)

3.2.1. Cyclic voltammetry analysis

Figure 7(a) displays the CV curves of AC, PANi and AC/PANI composites (with different PANi contents) in the potential range of 0 to 1 V at the sweep rate of 2 mV s⁻¹. The CV curves shape of AC electrodes demonstrates the double layer capacitive behaviour but CV curves for composites exhibit a little deviation from this shape due to the pseudocapacitive effect. The specific capacitance values of the electrode materials were calculated from the CV curves by the following equation.

\[ C_s = \frac{I}{\nu m v} \]  

where \( I \) is the average current (A), \( m \) is the mass of the active material and \( \nu \) is scan rate (V s⁻¹).
As the specific capacitance is proportional to the area under the CV curve (figure 7(a)), it is found that APA-29.4 composite exhibits the larger area at the same scan rate among all the synthesized materials [7, 45, 46]. AC gives 235 F g\(^{-1}\) value of specific capacitance and it is found that this value increases for the composites due to the addition of pseudocapacitive contribution in the total capacitance value by polyaniline. 17.2 wt% addition of polyaniline increases the value to 448 F g\(^{-1}\) for APA-17.2 and APA-29.4 gives 947 F g\(^{-1}\) specific capacitance value which is approximately four times greater than that for AC (235 F g\(^{-1}\)) and more than twice for pure PANi (371 F g\(^{-1}\)). Specific capacitance value starts decreasing with more loading of PANi on AC and it reduces to 755 F g\(^{-1}\) for APA-41.1. These studies prove that APA-29.4 gives the best electrochemical performance.

Cyclic voltammograms at various scan rates also explored for AC, PANi and APA-29.4 and the specific capacitance values are plotted in figure 7(e). All CV curves displayed in figures 7(b)–(d) are found to exhibit symmetrical behaviour even at 100 mV s\(^{-1}\) which specifies good reversibility behaviour. The specific capacitance of AC at the lowest scan rate (2 mV s\(^{-1}\)) is found to be 236 F g\(^{-1}\) while this value increases to 943 F g\(^{-1}\) for the APA-29.4 composite. It is also observed experimentally that the pure PANi gives the specific capacitance value of 371 F g\(^{-1}\).

Hence, APA-29.4 composite shows PANi contribution of 707 F g\(^{-1}\) which is 2 times greater than the pure PANi (371 F g\(^{-1}\)). It suggests that PANi is very well dispersed on AC surfaces and there is a better possibility of ionic accessibility to the electroactive sites on the composite electrode surface. At highest sweep rate (100 mV s\(^{-1}\)) the contribution of PANi capacitance reduces to 75 F g\(^{-1}\) and pure PANi gives 50 F g\(^{-1}\) signifying less contribution of PANi at higher scan rates. Furthermore, this observation is attributed to the fact that the higher scan rates limit the diffusion of the electrolyte ions [26, 47–50]. Hence, it can be concluded that the electrochemical capacitance values of the material can be enhanced by the controlled combination of AC and PANi and these properties are greatly influenced by the amount of PANi loading [36, 51].

3.2.2. Charge/discharge analysis

Capacitive behaviour of AC, PANi and AC/PANI electrodes were obtained by the galvanostatic charge-discharge measurements at varying current densities potential window of 0 to 1.0 V. The specific capacitance
values $C_s \left( \text{F g}^{-1} \right)$ are evaluated by the following equation (2).

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

Where $i$ is the discharge current in ampere (A), $m$ is the mass of the mass loaded on the electrode (mg), $\Delta t$ corresponds to the discharge time (s) and the $\Delta V$ represents the voltage change (exclusive of the IR drop for the duration of the discharge process) in volt (V). The GCD curves of the synthesized materials are displayed in figures 8(a)–(c) and the specific capacitance values obtained from these curves by using equation (2) are displayed in figure 8(d). The specific capacitance value of AC/PANI composite (APA-29.4) at 1 $\text{A g}^{-1}$ (1021 $\text{F g}^{-1}$) is found to be much higher than that of the AC (253 $\text{F g}^{-1}$) and PANi (389 $\text{F g}^{-1}$). This increase in the capacitance value for the composite is due to the interaction between AC and PANi which gives a double layer capacitance and pseudocapacitance together after loading PANi on the surface of AC.

This can be confirmed from the non-symmetrical charge-discharge curve of APA-29.4 which shows the contribution of redox reaction from 0 to 0.4 V [20, 36, 51]. Therefore, it can be concluded that AC/PANI composite is more appropriate electrode material compared to pure AC and pure PANi. The specific capacitance for AC/PANI composite is greater than that of the composite of PANi and different forms of carbon [7, 17, 18, 21, 23, 26, 35].

3.2.3. EIS analysis

The EIS study of the synthesized materials is performed in 1 M Na$_2$SO$_4$ electrolyte. Nyquist plots of AC, PANi and APA-29.4 composite exhibiting the frequency response of symmetrical supercapacitor cells at the electrode/electrolyte interface are presented in figure 9(a). The collective spectra of all the samples show a steep rise feature in low frequency region whereas a semi-circular feature corresponds to the high frequency region. The point of contact of the spectra on the Z" or real axis is attributed to the contact or internal resistance ($R_s$) of the electrodes. Semi-circle in the middle frequency region occurs due to the faradic processes. APA-29.4 displays the bigger semicircle than the AC that is an indication of more faradic reactions in the composite (figure 9(b)) [34]. Polyaniline being an electron donor forms a weak charge transfer complex and provides less charge transfer barrier to the carriers [33, 42, 51]. The intersection of the loop in the low frequency region at the real axis (x-axis) gives the bulk electrolyte resistance ($R_s$). The combination of $R_s$ and $R_i$ gives the total resistance ($R_t = R_s + R_i$) (figure 9(b) and table 2). The equivalent circuit for the impedance data is also displayed in inset of figure 9(b). $Z_w$ represents the Warburg resistance and is determined by the slope of the curve in the high frequency region. Warburg resistance occurs due to the diffusion of the ions from the electrolyte to the electrode. $C_{dl}$ and $C_{ef}$ represent the electric double layer capacitance and pseudocapacitance respectively. AC shows a vertical line representing the 90° slope which is a characteristic of electric double layer phenomena of the charge storage. The decrease in the slope of the vertical line for the composite in the high frequency region is attributed to the pseudocapacitive effect and electrolyte ion diffusion.

Various parameters related to electrolytes properties and electrode-electrolyte interfaces such as potential-dependent faradaic impedances or resistances, charge-transfer resistance and capacitance values for low frequency can be evaluated by the EIS technique. APA-29.4 provides smaller resistance than PANi. [35–37, 51–53] and this small value of ESR for the composite is preferred for better device performance as power is inversely proportional to the ESR value for a capacitor.

Energy density $E$ (Wh g$^{-1}$) and power density $P$ (W kg$^{-1}$) of APA-29.4 is also evaluated for different current densities by equations (3) and (4) respectively:

$$E = \frac{1}{2} C V^2$$

$$P = \frac{E}{t}$$
Where \(C_s\) represents the specific capacitance and \(D_V\) is the potential window.

Here \(E\) represents the energy density and \(\Delta t\) corresponds to the discharge time and the corresponding Ragone plot for the composite is displayed in figure 10(b).

Power densities increase with the decrease in current densities. A maximum power density of 5.9 kW kg\(^{-1}\) is obtained for an energy density of 16.3 Wh kg\(^{-1}\) and decreases to 1.4 kW kg\(^{-1}\) for 90.7 Wh kg\(^{-1}\) energy density. The comparison of the present work with previously reported work in terms of specific capacitance, capacitance retention, electrolyte, energy density and power density is presented in table 3.

The cycle ability of the composite material (APA-29.4) is recorded up to 2000 cycles at 2 A g\(^{-1}\) current density (figure 10(a)). The composite material exhibits 78% capacitance retention of its initial value. The good cyclic ability of the composite can be attributed to the better correlation between the PANi and activated carbon [31, 35, 51, 53].

Figure 10. (a) Cyclic stability of the APA-29.4 composite. (b) Ragone plot of APA-29.4 composite.

### Table 2. \(R_c, R_s\) and \(R_t\) value of AC, PANi and AC/PANI composite (APA-29.4).

| Sample Name | \(R_c\) (\(\Omega\)) | \(R_s\) (\(\Omega\)) | \(R_t\) (\(\Omega\)) |
|-------------|---------------------|---------------------|---------------------|
| AC          | 0.4                 | 1.87                | 2.27                |
| APA-29.4    | 1.16                | 2.92                | 4.08                |
| PANi        | 3.11                | 4.11                | 7.26                |

### Table 3. Performance comparison of the present work (APA-29.4 composite) in the aqueous electrolyte with other composites from the literature in terms of specific capacitance, capacitance retention, type of electrolyte, energy density and power density.

| Sample Name    | Electrolyte     | Specific capacitance \((\text{F g}^{-1})\) | Capacitance retention \((\%)/\text{number of cycles}\) | Energy density \((\text{Wh kg}^{-1})\) | Power density \((\text{W kg}^{-1})\) | References |
|----------------|-----------------|-----------------------------------|------------------------------------------------|-----------------------------------|-----------------------------------|------------|
| PC/PANi        | 1M H\(_2\)SO\(_4\) | 478                               | 58/200                                         | 23.9                              |                                   | [7]        |
| PANi/PC        | 1M H\(_2\)SO\(_4\) | 180                               | 98/1000                                        |                                   |                                   | [18]       |
| AC/PANI        | 0.5 M H\(_2\)SO\(_4\) | 587                               | 93/50                                          |                                   |                                   | [23]       |
| GNS/PANI       | 6 MKOH          | 1046                              | —                                              | 39                                | 70 000                            | [27]       |
| PANi/CNF       | 1M H\(_2\)SO\(_4\) | 557                               | 86/2000                                        |                                   |                                   | [34]       |
| AC/PANI        | 1M H\(_2\)SO\(_4\) | 534                               | 86/2000                                        | 78.49                             |                                   | [35]       |
| PANi/AC/Ni     | 1M Na\(_2\)SO\(_4\) | 1661                              | 93/2000                                        |                                   |                                   | [44]       |
| (This work)    | 1M Na\(_2\)SO\(_4\) | 1021                              | 78/2000                                        | 16.3                              | 5900                              |            |

AC: activated carbon; PC: porous carbon; CNF: carbon nanofibres; GNS: Graphene nanosheets

\[
E = \frac{C_s \times \Delta V^2}{2 \times 3.6}
\]  

(3)

Where \(C_s\) represents the specific capacitance and \(\Delta V\) is the potential window.

\[
P = \frac{3600 \times E}{\Delta t}
\]  

(4)

Here \(E\) represents the energy density and \(\Delta t\) corresponds to the discharge time and the corresponding Ragone plot for the composite is displayed in figure 10(b).
These results suggest that polyaniline coating on AC surfaces improves the electrochemical performance of the AC due to a synergistic effect of electric double layer capacitance from AC and pseudocapacitance from PANi.

4. Conclusion

Through facile modification of AC with in situ polymerization of polyaniline, we have developed multifunctional composite for electrochemical activity. Analytical results obtained from different techniques confirmed a thin layer self-coating of polyaniline with no other secondary phase structure of AC/PANI composites and displayed enhanced electrochemical behaviour. Electrochemical performance tested by EIS, CV and Galvanostatic charge-discharge demonstrates an enhancement in the performance of composite material. The highest specific capacitance of 1021 F g$^{-1}$ is found for AC/PANI (APA-29.4) composite. The highest power density of 5.9 kW kg$^{-1}$ is obtained for an energy density of 16.3 Wh kg$^{-1}$, which may be attributed to the additional significant pseudocapacitive behaviour of PANi in addition to double layer capacitance of AC. In anticipation, the finding demonstrates the new insight into the supercapacitor realm to develop a stable proficient composite and bears extensive potential applications in the field of electrochemistry.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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