Studies on electrochemical capacitance and hydrogen adsorption behavior of activated carbon derived from Cattail fiber

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August 22, 2023

Abstract

In this paper, we have reported the synthesis of activated carbon (AC) from biomass cattail fiber through hydrothermal carbonization followed by chemical activation and its electrochemical capacitance and hydrogen storage applications. The AC exhibits a specific BET surface area \((S_{\text{BET}})\) of 1597.5 m\(^2\)g\(^{-1}\), determined from low pressure N\(_2\) adsorption isotherm at 77 K using BET-multipoint plot. The activated carbon sample shows a reversible hydrogen adsorption capacity of 0.25 wt.% H\(_2\) (1.25 mmol H\(_2\) g\(^{-1}\)) at 293 K and 74 atm. The capacitance performance of AC was investigated with various conductive additives such as carbon nanotubes (CNTs), carbon black (CB) and reduced graphene oxide (rGO). From galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) measurements, the as-derived activated carbon with polymer binder exhibits the specific capacitance of 245.2 F g\(^{-1}\) at 0.2 A g\(^{-1}\) and 158.1 F g\(^{-1}\) at 5 mV s\(^{-1}\). Among the investigated conductive additives, CNTs mixed activated carbon in KOH electrolyte exhibit highest specific capacitance of 326 F g\(^{-1}\) at 0.2 A g\(^{-1}\) and 173 F g\(^{-1}\) at 5 mV s\(^{-1}\). Furthermore, the symmetrical two-electrode device fabricated using activated carbon with CNTs (as a conductive additive) in 1M aq. Na\(_2\)SO\(_4\) electrolyte shows the specific capacitance of 97.2 F g\(^{-1}\) at 0.1 A g\(^{-1}\). The energy and power densities of the two-electrode device was observed to be 26.4 Wh kg\(^{-1}\) and 28 kW kg\(^{-1}\), respectively.

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Abstract

In this paper, we have reported the synthesis of activated carbon (AC) from biomass cattail fiber through hydrothermal carbonization followed by chemical activation and its electrochemical capacitance and hydrogen storage applications. The AC exhibits a specific BET surface area \((S_{\text{BET}})\) of 1597.5 m\(^2\)g\(^{-1}\), determined from low pressure N\(_2\) adsorption isotherm at 77 K using BET-multipoint plot. The activated carbon sample shows a reversible hydrogen adsorption capacity of 0.25 wt.% H\(_2\) (1.25 mmol H\(_2\) g\(^{-1}\)) at 293 K and 74 atm. The capacitance performance of AC was investigated with various conductive additives such as carbon nanotubes (CNTs), carbon black (CB) and reduced graphene oxide (rGO). From galvanostatic charge-discharge (GCD) and cyclic voltammetry (CV) measurements, the as-derived activated carbon with polymer binder exhibits
the specific capacitance of 245.2 \text{ F g}^{-1} \text{ at } 0.2 \text{ A g}^{-1} \text{ and } 158.1 \text{ F g}^{-1} \text{ at } 5 \text{ mV s}^{-1}. \text{ Among the investigated conductive additives, CNTs mixed activated carbon in KOH electrolyte exhibit highest specific capacitance of 326 \text{ F g}^{-1} \text{ at } 0.2 \text{ A g}^{-1} \text{ and } 173 \text{ F g}^{-1} \text{ at } 5 \text{ mV s}^{-1}. \text{ Furthermore, the symmetrical two-electrode device fabricated using activated carbon with CNTs (as a conductive additive) in 1M aq. Na}_2\text{SO}_4 \text{ electrolyte shows the specific capacitance of } 97.2 \text{ F g}^{-1} \text{ at } 0.1 \text{ A g}^{-1}. \text{ The energy and power densities of the two-electrode device was observed to be } 26.4 \text{ Wh kg}^{-1} \text{ and } 28 \text{ kW kg}^{-1}, \text{ respectively.}

\textbf{Keyword}

Biomass, Electrical double layer capacitor, conductive additives, hydrogen storage, BET surface area.

\textbf{1. Introduction}

Due to the rapid growth of global population, \^1.36 lakh TWh equivalent of energy derived from fossil fuels, including oil, gas and coal are now being used particularly for automobile transportation.\textsuperscript{1} \text{ This excessive usage of fossil fuels has caused a sharp rise in global greenhouse gas emissions, beyond the predicted limit. Therefore, clean and environmentally friendly alternatives like electric and hydrogen fuel cell vehicles are promising options. The use of such clean energy alternatives not only reduce the dependency on fossil fuels, but also helps to minimize the greenhouse gas emissions. However, developing on-board energy storage system having high power and energy density is a crucial necessity for clean energy vehicles. The hydrogen-powered fuel-cell driven electric and supercapacitor-coupled battery vehicles with fast-charging capabilities are the prime focus. At present, the cost of electrically powered vehicles are relatively higher than fossil fuel powered IC engine vehicles, however, the overall cost of electric vehicles can be reduced with the use of cost-effective energy storage devices. Therefore, the ongoing research is on developing cost-effective and efficient energy storage devices for next-generation clean energy vehicles. Recent studies suggest that cost-effective and high durability energy storage devices can be developed with the use of carbon materials. Interestingly, porous carbon materials are prominent fit for electrochemical energy storage applications.\textsuperscript{2} Owing to the exceptional chemical stability of carbon materials, it is possible to deploy suitable additives for enhancing its capacitance performance. Furthermore, large-scale production of carbon materials using biomass precursor is one of the key methodologies for utilizing bio-wastes into cost-effective energy harvesting materials, which will help to protect the ecosystem from bio-waste accumulation. These biomass-derived carbon materials can be engineered to exhibit high surface area and ordered porosity, having micro-, meso-, and macro-pores.\textsuperscript{3} Materials with high specific surface area with accessible pores have gained considerable attention for gas storage,\textsuperscript{4} decolorization,\textsuperscript{5} desalination,\textsuperscript{6} and electrochemical applications.\textsuperscript{7} Particularly, for the electrochemical energy storage applications, electrode materials having high surface area with mixed micro- and meso-porosity exhibit higher ionic adsorption as well as high ionic permeation pathways. However, the electrical conductivity of these material decreases with increase in porosity due to lack of orderliness in its structure. The same is true for porous carbon materials. Hence, a highly porous material exhibit lack of electrical double layer formation (EDLC) and poor electrical/ionic conductivity.\textsuperscript{8,9} Therefore, in order to have higher electrochemical sorption and improved electrical-double layer formation, porous material must have an improved electrical/ionic conductivity to access the overall surface area, over the applied potential window. Generally, to improve the surface accessibilities and for increasing the electrochemical performance of electrode materials, conductive additives are employed. These additives will help the electrode materials to overcome its poor electrical conductivity, as a result, the electrochemical performance of the electrode materials can be extended for long-run applications.\textsuperscript{10} Therefore, considerable efforts have been carried out to enhance the electrical conductivity of porous carbon-based electrode materials through doping,\textsuperscript{11–13} and employing conductive additives. Additives such as reduced graphene oxide (rGO),\textsuperscript{14,15} carbon nanotubes (CNTs),\textsuperscript{16–18} and the other conductive composites has been reported to enhance the electrical/ionic conductivity of activated carbon (AC) based electrode materials.\textsuperscript{21} N. Jäckel and his co-workers\textsuperscript{19,20} described the use of carbon black (CB), carbon onions and expanded graphite with different mass ratio to improve the electrical conductivity and electrochemical performance of AC. Guoshen Yang et al.\textsuperscript{21} employed carbon nanohorns mixed with CNTs, graphene, and super P as a conductive additive for improving the electrical conductivity and redox reaction of cobalt aluminium layered double hydroxides. It has been reported that
the use of carbon nanofibers (CNFs) mixed with CB and CNTs as additives improves the packing density and capacitance of AC electrodes.\textsuperscript{22} Recently, conductive polymer was compared with composite of PVDF and CB as additive, conductive polymer additive was reported to improve the capacitive retention of AC from 93 to 95\%.\textsuperscript{23} Without additives, AC materials exhibit significant drop in specific capacitance during long term charge-discharge cycling.\textsuperscript{4,10} Therefore, conductive additive play a crucial role in improving the electrochemical energy storage properties of the AC.

Herein, we have prepared mixed micro- and meso-porous AC from a biomass derived cattail fiber as a carbon precursor. The electrochemical performance of the as-derived porous AC was investigated by employing different conductive additives such as CB, multi-walled CNTs (MWCNTs) and rGO (mentioned as graphene). The electrochemical analysis was done using CV, GCD and Nyquist plot. Among the investigated additive, the best one was chosen as conductive additive for determining the performance of a two-electrode cell with AC electrode. Additionally, near room temperature hydrogen adsorption characteristics of the cattail fiber derived AC has been investigated.

2. Experimental section

We have used narrowleaf cattail (Typha Angustifolia) fiber as a carbon precursor for synthesizing porous AC. The chemicals used, namely, KOH, H\textsubscript{2}SO\textsubscript{4} and HCl were procured from Merck, India. The conductive additives, CB and MWCNTs were procured from Alfa Aesar and SRL Chemical, respectively. rGO was prepared in our lab.\textsuperscript{24}

2.1. Sample Preparation

Figure 1. The schematic diagram showing the carbonization and activation process of cattail fiber adopted in the present study.

The schematic representation for AC preparation method adopted by us for the present investigation is shown in Fig. 1. The biomass carbon precursor of narrowleaf cattail fiber was collected from the local wetland area. First, the raw cattail fiber (CF) was separated from the stem, and cleaned by using 10 M of HCl, followed by distilled water and ethanol. The cleaned fiber was then heated at 60 °C for 24 hours using a hot air oven. After drying, the hydrothermal carbonization of cattail fiber was carried out using 1M
H\textsubscript{2}SO\textsubscript{4}. About 1 g of dried cattail fiber was mixed with 30 ml of 1M H\textsubscript{2}SO\textsubscript{4}, and the sample was loaded in a Teflon-lined stainless-steel autoclave and heated at 200 °C for 24 hours in a box furnace. The carbonized cattail fiber (CCF) thus obtained was collected and washed several times using DI water and dried at 60 °C. The pore activation of CCF was done through chemical activation using KOH. Initially, 1 g of CCF was mixed with a KOH solution of 1:2 mass ratio of KOH and water. After chemical activation, the sample was dried at 80 °C for overnight. The resultant sample was heated at 800 °C in argon atmosphere for 3 hours using a high temperature tubular furnace. The chemically activated material was cleaned thoroughly using 10 % of HCl and DI water. The activated porous carbon material thus obtained is described as activated and carbonized cattail fiber (ACCF) throughout the manuscript.

2.2. Material characterization:

Structural characterization of the sample was done through X-ray diffraction (XRD) analysis using a Malvern Panalytical Empyrean X-ray diffractometer employing Cu K\textsubscript{α} radiation (\(\lambda = 1.5406 \AA\)) operated at a potential of 45 kV and 40 mA. Surface morphology of the sample was characterized using JEOL scanning electron microscope (SEM) and microstructural characterization was done using FEI Tecnai G2 20 TWIN transmission electron microscope. The elemental composition and functionalities in sample was characterized using PHI 5000 VersaProbe III X-ray photoelectron spectroscopy (XPS) instrument and PerkinElmer Spectrum Two FTIR spectrometer. BET specific surface area and micropore analysis of sample was done using Quantachrome ASiQwin micropore and BET surface area analyzer through nitrogen isotherm at 77 K. Prior to nitrogen adsorption measurement, the sample was outgassed at 150 °C overnight to remove the surface-adsorbed moisture and other gas molecules. The Raman analysis of sample was done using a Horiba LabRam HR800 Raman spectrometer illuminated using an argon laser source of wavelength 514 nm. The electrochemical measurements such as CV, GCD, and impedance was done using a BioLogic VSP-300 electrochemical workstation.

2.3. Electrochemical measurements:

The working electrode was fabricated using ACCF with conductive additives. The conductive additives used in the present study was CB, MWCNTs and rGO. The working electrode fabricated using ACCF with additives such as CB, MWCNTs and rGO are termed as ACCF-CB, ACCF-CNT and ACCF-Graphene, respectively. The active material, conductive additive and binder (Polyvinylidene fluoride) were mixed thoroughly using NMP as a solvent. Subsequently, the mixture was coated over Ni foam (current collector) and dried at 80 °C for 12 hours. The active material, additive and binder in different mass ratio, x:y:z (where, x = 8/9, y = 0/1 and z = 1; y = 0 correspond to additive-free ACCF) has been investigated. The total mass loading of ~4 to 5 mg active material was coated on 1×1 cm\textsuperscript{2} Ni foam. For comparative analysis, electrodes with only conductive additive (mass loading of ~ 6.5 to 7.5 mg) has been prepared and its specific capacitance was measured and tabulated. The corresponding table and CV curves are given in the supplementary information as Table: T1 and Fig. S1. For every analysis, the mass ratio of active sample (ACCF), conductive additive and binder mixture was maintained at 9:1. The investigated electrode mass loading ratio are; ACCF-additive-PVDF = 9:0:1, ACCF-CB-PVDF = 8:1:1; ACCF-CNTs-PVDF = 8:1:1 and ACCF-Graphene-PVDF = 8:1:1.

After mass loading, the formation of air gap in the electrode was prevented by applying a uniform pressure of 8 MPa on the electrodes using a hydraulic press. The CV, GCD and Impedance analysis of the sample was carried out in 6M KOH aqueous solution. The electrochemical three-electrode setup consist of reference electrode, saturated calomel and platinum electrode (counter electrode). The impedance measurement was done in the frequency range of 200 kHz to 100 mHz. The specific capacitance (\(C_{S}\)) of materials was calculated using the following equations.

For three-electrode cell, the \(C_{S,three}\) from CV and GCD curves were determined using Eqn. (1) and Eqn. (2),
respectively.

\[
\text{Cs}_{\text{three (CV)}} = \frac{\int i \, dV}{2smV} \, \text{F} \, g^{-1} \tag{1}
\]

\[
\text{Cs}_{\text{three (GCD)}} = \frac{I}{m} \times \frac{t}{V} \, \text{F} \, g^{-1} \tag{2}
\]

where, \(s\) is the scan rate of CV, \(m\) is the active mass of the electrode, \(\Delta t\) and \(\Delta V\) are GCD discharge time and potential window, respectively.

For coin cell fabrication, Ni foam of mass \(\sim 6\) mg coated with electrode material and 1 M Na\(_2\)SO\(_4\) (electrolyte) was used. The process adopted for fabrication of coin cell has been described in our earlier paper.\(^{25}\) The CV and GCD measurement of coin cells were performed for the potential window 0 - 1.4V and the electrochemical impedance spectrum was measured from 20 kHz to 100 mHz.

The coin cell’s specific capacitance (\(Cs_{\text{two}}\)), energy density (\(E\)) and power density (\(P\)) were calculated from the GCD curve by using Eqn. (3), Eqn. (4) and Eqn. (5), respectively.

\[
\text{Cs}_{\text{two (GCD)}} = 4 \times \frac{I}{m} \times \frac{t}{V} \, \text{F} \, g^{-1} \tag{3}
\]

\[
\text{Energy density (E)} = \frac{1}{2} \times \frac{\text{Cs}_{\text{two (GCD)}} \times (V^2)}{3.6} \, \text{Wh kg}^{-1} \tag{4}
\]

\[
\text{Power density (P)} = \frac{E \times 3600}{t} \, \text{W kg}^{-1} \tag{5}
\]

where, \(m\) is the active mass of the electrode, \(\Delta t\) and \(\Delta V\) are GCD discharge time and potential window, respectively.

2. 4. Hydrogen Adsorption Measurement

The sample was outgassed prior to hydrogen isotherm measurement, by dynamically heating the sample at 1 °C min\(^{-1}\) from 25 °C to 200 °C and then at 200 °C the sample was evacuated continuously for 12 hours up to the level of 10\(^{-7}\) mbar. Outgassing of sample was done in a vacuum sealed quartz tube kept inside a tube furnace (Lindberg Blue M 1100 °C) using Edwards nEXPT turbo pumping station. Using Micromeritics AccuPyc II 1340 helium pycnometer, the sample’s skeletal density was determined.

Hydrogen isotherm was recorded at 293 K (20 °C) and 283 K (10 °C) between 0.1 to 75 atm H\(_2\) pressure using an automated four-channel Sievert’s apparatus supplied by Advanced Materials Corp., USA. The temperature stability, settling condition and determination of density of adsorptive has been discussed in our earlier paper.\(^{4}\)

3. Results and discussion:

The FTIR spectral curves of raw cattail fiber, carbonized cattail fiber (CCF) and KOH-activated CCF (ACCF) are shown in Fig. 2(a). The majority of the functional groups in un-carbonized cattail fiber get removed after carbonization. The broad IR absorption peak observed in un-carbonized sample between 3000 to 3600 cm\(^{-1}\) signifies the presence of O-H (hydroxyl) functionalities, due to moisture content in sample. And the IR absorption observed around wavenumber 2923 and 2853 cm\(^{-1}\), correspond to C–H stretching (Alkane) vibration, which is closely associated with the lignin polysaccharides in the cattail cellulose fiber.\(^{26}\)

After carbonization and post-activation of cattail fibers, the spectral peaks correspond to hydroxyl and alkane functionalities were not observed in FTIR spectra. The lignin polysaccharides were found to change from cellulose to amorphous carbon during carbonization. Hence, after carbonization, the absorbance peaks observed at 1703, 1607 and 1513 cm\(^{-1}\) correspond to carbonyl/carboxylic acids and aromatic functional
groups. The asymmetric bridge stretching (C-O) vibrations was observed at 1169, 1113 and 1047 cm\(^{-1}\) in both cellulose and carbon samples.\textsuperscript{27,28} The FTIR spectral analysis suggest the successful carbonization of cattail fiber.

Figure. 2 (a) FT-IR spectra of CF, CCF and ACCF, (b) X-ray diffraction, (c) Raman spectrum and (d) SEM morphology of ACCF sample.

X-ray diffractogram of AC presented in Fig. 2(b), displays the amorphous nature of AC, attributed to the short-range order of turbostratic carbon particles. Fig. 2(c) is the Raman spectra of ACCF sample. The intensity ratio of D-band and G-band peaks (I\(_D\)/I\(_G\)) observed at 1595 and 1353 cm\(^{-1}\), respectively in the Raman spectra is observed to be 1.04, which suggest the formation of turbostratic structured carbon. The SEM image of ACCF shown in Fig. 2(d) illustrates the presence of irregular rough surface morphology, due to KOH induced porosity in the sample.

Figure. 3 (a) Low pressure N\(_2\) adsorption/desorption isotherm at 77 K (inset shows the multi-point BET plot), (b) Cumulative and differential pore volume of ACCF sample derived from N\(_2\) isotherms.
Low-pressure N\textsubscript{2} adsorption and desorption isotherm of ACCF was determined at 77 K. Fig.3(a) shows the corresponding N\textsubscript{2} adsorption and desorption isotherms of ACCF at 77 K. The N\textsubscript{2} adsorption and desorption isotherms resembles with IUPAC IV-type isotherm with H4 hysteresis. The adsorbed amount gets saturated at very low relative pressures together with the formation H4 type hysteresis at higher relative pressures between adsorption and desorption isotherm, suggesting the sample containing mixed (micro and meso) porosity. The origin of steep hysteresis between the relative pressure range of 0.4 to 0.45 may attributed due to the occurrence of slit-type pores. The BET surface area of ACCF calculated from the low-pressure N\textsubscript{2} isotherm through multi-point BET plot between the relative pressure range of 0.04 to 0.16 is observed to be 1597.5 m\textsuperscript{2} g\textsuperscript{-1}. The corresponding Multi-point BET plot is shown in the inset of Fig.3(a). The cumulative and differential pore volume of ACCF determined from the N\textsubscript{2} isotherm is given in Fig.3(b). The total pore volume and pore size were derived using the NLDFT equilibrium model (N\textsubscript{2} at 77 K on carbon slit/cylindrical pore). The result illustrates the presence of micro- and meso-porosity in the sample. The total pore volume is determined to be 1.06 cm\textsuperscript{3} g\textsuperscript{-1} and the pore sizes are in the range of 1.3 to 5.3 nm. The presence of these mixed micro- and meso-porosity in the sample may help to increase the ionic accessibility during the electrochemical measurements.

The X-ray photoelectron spectrum of ACCF sample illustrates the presence of functionalities in ACCF. The C1s spectra exhibits three peaks at 284.6, 286.3 and 289.6 eV corresponding to C=C/C-C, C-O and O=C-O, respectively. Additionally, O1s core level spectra show three peaks at 531.2, 532.9 and 535.9 eV, corresponding to C=O, C-O and C-OH, respectively.

Figure 4 X-ray photoelectron spectrograph of ACCF sample, (a) survey spectrum of ACCF, (b) core spectra of C1s and (c) core spectra of O1s.

Figure 5 (a-b) Transmission electron micrograph of ACCF material and the inset is its SEAD pattern.
Fig. 5(a-b) shows the porous nature of carbonized cattail fiber derived after chemical activation. The inset of Fig.5(b), shows the SAED patterns of AC, suggesting its amorphous nature leading to high disorderliness in the sample after chemical activation. The poor electrical conductivity of activated porous is due to chemically activated porosity and lack of orderliness in the sample.

Fig. 6 shows the schematic diagram representing different conductive additives employed in the present study with porous carbon (ACCF) and its role in improving the electrical conductivity and ionic accessibilities of porous electrode materials. For ACCF-CB, the additive CB may establish a bridging path between the surface of ACCF particles and the current collector. Whereas, rGO (graphene) was anticipated to provide an interconnection between ACCF and current collector for electronic and ionic conduction. But, the active surfaces of the ACCF may get covered by crumpled graphene layers, thus preventing smooth ionic accessibility on the electrode surface during the EDLC formation. However, the use of 1D CNTs with ACCF provide an easy tunneling path for ionic accessibilities between ACCF particles and current collector electrode.

Figure. 6 Schematic diagrams representing the role of different conductive additives such as carbon black, graphene and carbon nanotubes for ACCF-based electrode materials.

3.1 Three-electrode cell

The cyclic voltammetry was carried out by varying scan rates from 5 to 200 mV s\(^{-1}\). The equation (1) was used to calculate the \(C_{\text{three(CV)}}\) of the three-electrode cell. With conductive additive, the AC-based electrodes exhibit the quasi-rectangular shaped CV curves, at different potential scan rates as shown in Fig. 7(a-d). The ACCF with CNTs as additive maintained the quasi-rectangular shaped CV curves at wide range of voltage sweep window. This may be attributed due to higher charge transportation in the active electrode materials through CNTs. It becomes evident from the CV curves, that the additive CNTs increased the electrical conductivity of active electrode material (ACCF) higher than that of CB and rGO additives.

The galvanostatic charge-discharge was performed by applying various current densities from 0.2 A g\(^{-1}\) to 20 A g\(^{-1}\) to the working electrodes fabricated using ACCF, ACCF-CB, ACCF-CNT, and ACCF-Graphene. The GCD curves are shown in Fig. 8(a-d). The GCD curves of ACCF with CNTs exhibit higher charge and discharge capability than that observed for additive-free ACCF and ACCF with other conductive additives. This may be due to CNTs mediated higher electrical contact between ACCF particles and electrode thereby, establishing effective ionic accessibility and EDLC formation.
**Figure. 7** The CV curves at various scan rates (a) additive-free ACCF, (b) ACCF with CB, (c) ACCF with CNTs, and (d) ACCF with rGO (graphene) electrodes.

**Figure. 8** Galvanostatic charge-discharge curve of (a) additive-free ACCF, (b) ACCF with CB, (c) ACCF with CNTs and (d) ACCF with rGO (graphene) at various current densities.
The $C_{3\text{three(CV)}}$ of ACCF was determined at different scan rates with various conductive additives and the corresponding curves are shown in Fig. 9(a). The $C_{3\text{three(CV)}}$ determined at 5 mV s$^{-1}$ for additive-free ACCF, ACCF-CB, ACCF-CNTs, ACCF-Graphene is 158, 156, 173, and 172.5 F g$^{-1}$, respectively. The $C_{3\text{three(CV)}}$ measured at different scan rates are given in Table 1. The $C_{3\text{three(CV)}}$ value determined for ACCF-CNTs at 200 mV s$^{-1}$ is 137.8 F g$^{-1}$, this is higher than that determined for additive-free ACCF and ACCF with other conductive additives. This improvement in the capacitance of ACCF could be due to the addition of CNTs, which can act as a bridge network between the active material and the electrode. Hence, the quasi-rectangular shape of EDLC was maintained even at the higher scan rates of 200 mV s$^{-1}$. However, graphene (rGO) hindered the ionic diffusion pathways due to its crumpled layers, which might have blocked the active surfaces of active material, thereby decreasing the ionic conductivity of active material. While in the case of CB, the carbon particles of the additive might have blocked the pores of the active material, thereby, reducing the ionic diffusion pathways and lowering its conductivity. Generally, CB are not suitable for active materials having poor conductivity. For comparative analysis, the capacitance of conductive additives with binder under identical experimental condition was also measured between 0.2 A g$^{-1}$ to 10 A g$^{-1}$ and the data is given in the supporting information (Table T1). The measured capacitance values of CB, CNTs and rGO (graphene) at 0.2 A g$^{-1}$ are 2.56, 51.74 and 114.16 F g$^{-1}$, respectively. Since, the conductive additives added with ACCF was 10 wt.%, the contribution of conductive additive’s capacitance with ACCF can be considered negligible. Table 1 and Table 2 gives the $C_{3}$ of ACCF with and without additives determined at different scan rates and different current densities, respectively.

Table 1 Specific capacitance of additive-free ACCF and ACCF with conductive additives

<p>| Specific-capacitance determined from CV (F g$^{-1}$) | Specific-capacitance determined from CV (F g$^{-1}$) | Specific-capacitance determined from CV (F g$^{-1}$) |</p>
<table>
<thead>
<tr>
<th>Scan rate (mV s$^{-1}$)</th>
<th>ACCF</th>
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Table 2 Specific capacitance at different current densities of additive-free ACCF and ACCF with conductive additives

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<tr>
<th>Current density (A g⁻¹)</th>
<th>ACCF</th>
<th>ACCF-CB</th>
<th>ACCF-CNT</th>
<th>ACCF-Graphene</th>
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<tr>
<td>0.2</td>
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<td>136.67</td>
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As inferred from Table 1 and Table 2, the additive CNTs improved the capacitance of ACCF when compared to other additives.

The impedance of electrode, fabricated using ACCF with various conductive additives, was measured in the frequency range of 200 kHz to 100mHz. The semicircle fit of Nyquist curves was used to calculate the resistance values. The impedance curves are divided into higher and lower frequency regions. The semi-circle region with the straight line parallel to the imaginary part of Nyquist indicates the redox and double-layered capacitive properties of the electrode material. The size of the semi-circle gives the charge transfer resistance of the electrode. The resistance value of the electrodes is tabulated in Table 3.

Table 3 The series and charge transfer resistances determined from Nyquist impedance curve of two-electrode cell fabricated using ACCF with various conductive additives.

<table>
<thead>
<tr>
<th>Electrode</th>
<th>Series resistance R1 (Ω)</th>
<th>Charge transfer resistance R2 (Ω)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACCF</td>
<td>0.54</td>
<td>0.018</td>
</tr>
<tr>
<td>ACCF-CB</td>
<td>0.43</td>
<td>0.016</td>
</tr>
<tr>
<td>ACCF-CNT</td>
<td>0.24</td>
<td>0.014</td>
</tr>
<tr>
<td>ACCF-Graphene</td>
<td>0.65</td>
<td>0.054</td>
</tr>
</tbody>
</table>

With additive CNTs, the series resistance of ACCF has decreased from 0.54 to 0.24 and the charge transfer resistance has decreased from 0.018 to 0.014. These values are comparatively lower than that of ACCF with other conductive additives such as CB and rGO (graphene). Hence, it becomes evident that CNTs act as...
an effective additive for enhancing the electrical conductivity of activated porous carbon.

### 3.2 Two-electrode Cell

The two-electrode cell setup was prepared with the ACCF-CNT as active electrode material. The cell potential window was selected from the CV measurements carried out at a fixed scan rate of 20 mV s\(^{-1}\) by varying the potential window from 0V, up to a maximum potential of 1, 1.2, 1.4, 1.6, and 1.8 V. The as-obtained CV curves are depicted in **Fig. 10 (a)**. It has been observed that the CV correspond to the potential window 0 - 1.4 V exhibit nearly rectangular shaped curve. Hence, this potential window (0 to 1.4 V) was used for the two electrode cell measurements.

**Figure. 10** The electrochemical measurement curves of two electrode cell (a) CV at 20 mVs\(^{-1}\) determined at different potential window (b) CV at different scan rates, (c) GCD at various current densities, (d) capacitance of two electrode cell at various current densities, (e) GCD cyclic retention curve up to 1000 cycles at 2 A g\(^{-1}\) (inset shows Nyquist impedance curve at 20 kHz to 0.1 Hz, before and after GCD cycles), (f) Ragone plot for energy and power density of two electrode cell.

As mentioned above, the CV measurements were carried out using the scan rates from 5 to 100 mVs\(^{-1}\) and the potential window chosen was 0-1.4 V. The as-obtained CV curves are shown in **Fig. 10(b)**. The rectangular shape CV curves even at 100 mVs\(^{-1}\), suggesting higher ionic diffusion in the electrode material. The \(C_{\text{st,200(GCD)}}\) calculated from the GCD curves for different current densities (0.1 to 10 A g\(^{-1}\)) is shown in **Fig.10 (c)&(d)**. The \(C_{\text{st,200(GCD)}}\) value determined at 0.1, 0.2, 0.3, 0.5, 0.8, 1, 2, 3, 5, 8, and 10 A g\(^{-1}\) are 97.2, 90.2, 94.2, 78.5,74.2, 72.2, 60.2, 50.9, 37.1, 19.4, and 9.7 F g\(^{-1}\), respectively. Furthermore, the Nyquist impedance was examined before and after 1000 GCD cycles and the corresponding Nyquist plot is shown as inset in **Fig.10 (e)**. The Nyquist plots are measured between the frequency ranges from 20 KHz to 100 mHz. Higher frequency region intersects of the Nyquist curve, and semicircle along with the straight line adjacent to the imaginary axis gives the charge transfer and capacitive characteristics of cell. The semicircle indicates the presence of functional groups C=O, C-O and C-OH, as inferred from the XPS and FTIR analysis. Moreover, the calculated total series resistance of the cell has decreased from 3.88 to 2.8 after 1000 GCD cycles, and the charge transfer resistance has decreased from 1.5 to 1.3. This might be attributed to the decrease in cell resistance due to high ionic diffusion rate. The cyclic retention values calculated from the GCD cycle curves show almost 100 % retention of the initial capacitance retention after 1000 cycles. The Ragone Plot shown in **Fig.10 (f)** correspond to the two electrode cell determined using equation (4) & (5), show energy density of 26.4 Wh kg\(^{-1}\) for the power density of 280 W kg\(^{-1}\) and 2.64 Wh kg\(^{-1}\) energy density for the power density 28,000 W kg\(^{-1}\), respectively. The tabulated energy and power density values are given in
supplementary information (Table. T2).

3.3 Hydrogen adsorption

The high-pressure hydrogen adsorption and desorption isotherm of ACCF was determined in the pressure range from 0.1 to 74 atm. The corresponding hydrogen adsorption and desorption isotherm is shown in Fig. 11. The sample exhibit reversible hydrogen uptake of 0.28 wt.% H\(_2\) (1.4 mmol H\(_2\) g\(^{-1}\)) at 10 °C and 74 atm. However, at 20 °C and 74 atm, the hydrogen uptake of ACCF was observed to be 0.25 wt.% H\(_2\) (1.25 mmol H\(_2\) g\(^{-1}\)). Fig. 11 (a), (b) and (c) shows the hydrogen uptake of ACCF in terms of volume, excess gravimetric capacity and millimole H\(_2\) g\(^{-1}\), respectively at 10 and 20 °C. The amount of hydrogen adsorbed by the sample is significantly less than the required gravimetric capacity for on board hydrogen storage in fuel cell vehicles. This may be attributed due to the low adsorption energy and weak binding force between hydrogen molecule and carbon. Therefore, it can be concluded that not the porosity of the sample accounts for higher hydrogen uptake capacity, but a strong binding force is required to increase the hydrogen adsorption capacity. Therefore, suitable metal nanoparticle decoration or infiltration of metal nanoparticles could increase the binding force for hydrogen adsorption and thereby improving the hydrogen adsorption capacity of porous carbon.

![Figure 11](image_url)

**Figure. 11.** Hydrogen adsorption and desorption isotherm of ACCF (a) adsorbed volume in cm\(^3\) H\(_2\) g\(^{-1}\) @STP (b) excess gravimetric uptake capacity in wt.% (c) uptake capacity in milli-moles/gram. The closed and open symbol correspond to adsorption and desorption data, respectively.

4. Conclusion:

Narrowleaf cattail (Typha Angustifolia) fiber biowaste was chemically carbonized and activated using KOH. The activated ACCF shows a specific BET surface area of **1597.47 m\(^2\) g\(^{-1}\)**. The AC sample shows a reversible hydrogen uptake of 0.28 wt.% H\(_2\) (1.4 mmol H\(_2\) g\(^{-1}\)) at 10 °C/74 atm and 0.25 wt.% H\(_2\) (1.25 mmol H\(_2\) g\(^{-1}\)) at 20 °C/74 atm. The Cs of the AC has been examined with different conductive additives such as multi-walled carbon nanotubes (CNTs), carbon black (CB) and reduced graphene oxide (graphene). The Cs derived from GCD for AC with 10 wt.% CB, CNTs and graphene determined at 0.2 A g\(^{-1}\) was observed to be 238.7, 326 and 291.4 F g\(^{-1}\), respectively. It has been observed that CNTs with AC acts as a superior electrode material for electrochemical supercapacitor application. This could be attributed to its low charge transfer resistance (0.014 ) and series resistance (0.24 ). The two-electrode cell was fabricated using AC with CNTs as conductive additive and its Cs value was determined to be 97.2 F g\(^{-1}\). The assembled two-electrode cell shows the energy and power density of 26.4 Wh kg\(^{-1}\) and 28 kW kg\(^{-1}\), respectively.

Acknowledgment
The authors are thankful to the Padma Shri. late Prof. O. N. Srivastava and Prof. P. Ravindran for their continuous support and encouragement. Financial support from DST, New Delhi through INSPIRE Faculty Award grant and IoE seed grant from Banaras Hindu University is also acknowledged.

**Conflict of interest**

The authors declare no conflict of interest.

**Reference:**


**Graphical abstract**

*Activated porous carbon derived from biomass of cattail fiber with different conductive additives of carbon black, graphene and CNT for electrochemical supercapacitor application*