Flexible Type Symmetric Supercapacitor Electrode Fabrication Using Phosphoric Acid-Activated Carbon Nanomaterials Derived from Cow Dung for Renewable Energy Applications

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ABSTRACT: Porous-activated carbon (PAC) materials have been playing a vital role in meeting the challenges of the ever-increasing demand for alternative clean and sustainable energy technologies. In the present scenario, a facile approach is suggested to produce hierarchical PAC at different activation temperatures in the range of 600 to 900 °C by using cow dung (CD) waste as a precursor, and H₃PO₄ is adopted as the nonconventional activating agent to obtain large surface area values. The as-prepared cow dung-based PAC (CDPAC) is graphitic in nature with mixed micro- and mesoporous textures. High-resolution scanning electron microscopy depicts the morphology of CDPAC as nanoporous structures with a uniform arrangement. High-resolution transmission electron microscopy reveals spherical carbon dense nanoparticles with dense tiny spherical carbon particles. N₂ adsorption–desorption isotherms show a very high specific surface area of 2457 m²/g for the CDPAC 9 (CD 9) sample with a large pore volume of 1.965 cm³/g. Electrochemical measurements of the CD 9 sample show a good specific capacitance (Cₛ) of 347 F/g at a lower scan rate (5 mV/s) with improved cyclic stability, which is run up to 5000 cycles at a low current density (0.5 A/g). Hence, we choose an activated carbon prepared at 900 °C to fabricate the modified electrode material. In this regard, a flexible type symmetric supercapacitor device was fabricated, and the electrochemical test results show a supercapacitance value (Cₛ) of 208 F/g.

1. INTRODUCTION

Population growth creates a scarcity in various fields, such as water, land, and energy.¹ In the past few decades, a lot of technological developments and industrial revolutions have occurred. However, we are unable to solve the problem of scarcity of water, achieve an ecofriendly atmosphere, and improve the utilization of renewable energy resources.² In the present time, researchers are developing different kinds of energy storage systems such as batteries, solar cells, and fuel cells.³–⁵ Batteries have a high energy density with a low power density and a very short cyclic life. Solar cells are requiring intense sunlight energy and panels to reproduce the renewable energy for sustainable technology. Similarly, fuels cells need an external fuel source to produce energy and also raise issues in the transportation of fuel cell devices from one place to another.⁶–⁸

Supercapacitors are a potential power storage device for a sustainable energy storage medium toward next generation hybrid electric vehicle development.⁹ Supercapacitors comprise electrochemical double layer capacitors (EDLCs) that can deliver a high power density and a long cyclic duration than batteries. It is due to their charge storage mechanism, which is based on the surface reactions between the electrolyte and electrode materials.¹⁰ Consequently, EDLCs could be an alternative energy storage device to rechargeable batteries, when a high power density is required. However, rechargeable batteries have a comparatively high energy density than supercapacitors, and many researchers are trying to enhance their energy density in supercapacitors.¹¹ Generally, we know that the energy density of EDLCs depends upon the specific capacitance of an electrode material and the cell voltage present in an electrochemical cell setup.¹² Accordingly, the higher energy density increases the demand for porous and nanosized electrode material development to improve the specific capacitance of the whole device. In recent years, many researchers have made an effort to advance some nano-
structured porous electrode materials to reduce the ionic diffusion path length in order to increase the surface area for improving the performance of EDLCs.\textsuperscript{13}

Several nanostructured electrode materials are developed, such as nanometal oxides, nanocomposites, nanocarbonaceous materials like porous activated carbon (PAC), carbon nanotubes, and carbon aerogels.\textsuperscript{14–16} Among the upcoming electrode materials, cow dung (CD)-based PAC materials (CDPACs) have a huge surface area, which delivers high electrochemical double layer formation with less preparation cost to synthesize carbon nanomaterials with pores. One of the main objectives of the present research work is to control the huge solid pollution obtained from the natural organic solid wastes such as jackfruit peel,\textsuperscript{17} Borassus flabellifer flower,\textsuperscript{18} rice straw,\textsuperscript{19} corn stalk,\textsuperscript{20} and CD.\textsuperscript{21} In order to use the natural organic solid wastes, we have chosen the CD waste to prepare carbon nanomaterials because it is of low cost and could provide improved surface area values and porosity. CD has been used as a cooking fuel, for water proofing for floors and walls of houses in rural areas, and as a sanitizing cleaner in villages. Interestingly, CDPAC materials are not much explored in literature. Bhattachariya et al. reported the synthesis of PAC from CD using KOH activation and studied its electrochemical double layer capacitance activity in an organic electrolyte.\textsuperscript{22} Similarly, Das et al. reported the activated carbon prepared from CD, which was used for catalytic metal adsorption in water and waste water treatment.\textsuperscript{23} To the best of our knowledge, the use of phosphoric acid as an activating agent for preparing CDPAC with improved surface area values has not been reported for electrochemical supercapacitor applications. Generally, PAC is prepared from two activation methods, which are physical and chemical activation methods.\textsuperscript{24} However, chemical activation is preferably used to prepare hierarchical PAC because it delivers a good surface area and we can use simple chemical activating agents, such as ZnCl\textsubscript{2}, KOH, and H\textsubscript{3}PO\textsubscript{4} (orthophosphoric acid) under vacuum conditions.\textsuperscript{25} Physical activation needs a pyrolysis reactor using an inert gas for vacuum conditions to produce PAC at high temperatures.\textsuperscript{26,27}

Two types of supercapacitor device fabrication was carried out in the past decades such as symmetric and asymmetric type flexible supercapacitor electrode devices.\textsuperscript{28} In symmetric supercapacitors, there will be a positive (anode) and a negative (cathode) electrode made up of similar active materials. However, in the case of asymmetric supercapacitors, they have different active materials in positive and negative electrodes.\textsuperscript{29} Mostly, the active material is either PAC or nanometal oxide composites. The active materials of nanometal oxides and metal composites are expensive, and a long time duration is needed for their synthesis.\textsuperscript{30} Hence, the present study focuses on fabricating a flexible type symmetric supercapacitor (FT-SS) using an electrode material prepared from an easily available CD source (CDPAC). The CDPAC is prepared by a chemical activation method using H\textsubscript{3}PO\textsubscript{4} as an activating agent at four different temperatures. The physico-chemical and electrochemical analyses of CDPAC samples have been performed.

2. RESULTS AND DISCUSSION

2.1. X-ray Diffraction Studies. X-ray diffraction (XRD) patterns of CDPAC samples (CD 6–9) heated at different temperatures are shown in Figure 1. The broad peak at a 2θ value of 23° and a very little broad peak at 43° represent the amorphous nature of all the activated porous carbon samples. The corresponding Bragg’s reflection plane is (100) and (101), respectively.\textsuperscript{28} The sharp peak at 26° present in all the activated porous carbon samples depicts the graphitic carbon and the corresponding plane value at 002.\textsuperscript{29} In Figure 1, it clearly shows that the intensity of the sharp peak increases from CD 6 to CD 9 and it indicates that the graphitic carbon crystalline structure gets enhanced when the activation temperature increases.\textsuperscript{29} Hence, more graphitic nature enhances the electrical conductivity of the porous carbon materials and it replicates the higher capacitance values of CD 9. The XRD patterns at 2θ = 23, 43, and 26° matched well with the reported JCPDS card number 75-2078.\textsuperscript{30}

2.2. Morphological Studies. High-resolution scanning electron microscopy (HR-SEM) micrographs of CDPAC samples are shown in Figure 2A(a–e). Figure 2A(a) shows that the as-prepared precarbonized carbon (PCC) from CDPAC had a rough surface and the absence of pores. The pore size and the number of pores on the surface of CD 9 are much more fine and attractive than those on the surface of other samples such as CD 6 and CD 8, which are shown in Figure 2A(b,c). The number of pores seems to increase with the increase of the activation temperature in the activation processes. The creation of new pores is also caused by the activating agent (H\textsubscript{3}PO\textsubscript{4}), and it burns the carbon followed by the formation of an aggregated network of carbon channels and then micro-, meso- and nanopores. In Figure 2A(b), CD 6 depicts hierarchical pores in a nonarranged manner than CD 9 (Figure 2A(d,e)), and it clearly indicates that CD 9 has both micro- and mesoporous nature for the as-prepared activated carbon nanomaterials. However, CD 8 (Figure 2A(c)) and CD 9 in Figure 2A(d,e) show a comparative enlargement in pores, and both micro- and mesoporous structures are arranged more uniformly to create a more ideal and stable Helmholtz double layer arrangement.\textsuperscript{31} Similarly, CD 6 exhibited a smoother surface and a less degree of porosity, when compared to CD 9, which shows the presence of a hierarchical porous structure and irregular pores (Figure 2b). The differences may be attributed to the contribution of H\textsubscript{3}PO\textsubscript{4} which reacts with both the interior and exterior surfaces of CD 9, thus creating more pores on the surface. Cylinder-like pores are exhibited for CD 9, as shown in Figure 2A(e). More porous creation enhances the BET surface area, and it is evident from the results of N\textsubscript{2} adsorption–desorption isotherm analysis (Table
The CD 9 sample exhibits the arrangement of pore channels that are interconnected with each pore. The interconnected channels are very important for the fast charge transfer in the electrolyte solution to the electrode materials, and it is a promising one for EDLCs. The interconnected spherical particle morphology provides a unique open pore system with a high active surface area and it develops a short diffusion path for the electrolyte ions. The similarity between the SEM and TEM images of Figure 2B matched in terms of interconnected porous morphology with a carbon chain network with tiny spherical carbon particles with more dark particle aggregation. The fluffy glassy morphology together with a tiny carbon particle obtained were below 10−20 nm in size (Figure 2B).

### 2.3. N₂ Adsorption–Desorption Isotherms

N₂ adsorption–desorption isotherms are routinely used to analyze the porous nature of the activated carbon samples. These isotherms are helpful to find whether it contains micropores (below 2 nm), mesopores (2−50 nm), or macropores (above 50 nm). The isotherms of N₂ adsorption–desorption deliver the BET (Brunauer−Emmett−Teller) surface area values, and it explains the values of micro-, meso-, and macropores using the Barrett−Joyner−Halenda) method. Figure 3A shows the N₂ adsorption–desorption isotherms of the as-prepared CDPAC samples prepared under different temperature

![Figure 2](image-url)

**Figure 2.** (A) HR-SEM images of (a) pre-carbonized carbon, (b) CD 6, and (c) CD 8 at 200 nm. (d,e) High-resolution images of CD 9 at 500 nm. (B) HR-TEM images of CD 9 at different magnifications on 100 and 200 nm scales.

![Table 1](table-url)

| Sample (CD waste) | \( S_{\text{BET}}^a \) (m²/g) | \( S_{\text{micro}}^b \) (m²/g) | \( S_{\text{meso}}^c \) (m²/g) | \( V_{\text{micro}}^d \) (cm³/g) | \( V_{\text{meso}}^e \) (cm³/g) | \( V_{\text{Total}}^f \) (cm³/g) |
|-------------------|------------------|------------------|------------------|------------------|------------------|------------------|
| CD 6              | 489              | 249              | 240              | 0.393            | 0.202            | 0.595            |
| CD 7              | 984              | 498              | 486              | 0.585            | 0.379            | 0.964            |
| CD 8              | 1860             | 984              | 876              | 0.682            | 0.487            | 1.169            |
| CD 9              | 2457             | 1293             | 1164             | 0.985            | 0.980            | 1.965            |

\( a \) BET surface area. \( b \) Micropore surface area. \( c \) Mesopore surface area. \( d \) Micropore volume. \( e \) Mesopore volume. \( f \) Total pore volume.

![Figure 3](image-url)

**Figure 3.** (A) N₂ adsorption–desorption analysis of CDPAC samples (left side) and pore size distribution (right side) of the sample prepared at different temperatures [(a) CD-PCC, (b) CD 6, (c) CD 7, (d) CD 8, and (e) CD 9 samples]. (B) Pore size distribution of CD 6−9 samples.
The isotherms of Figure 3A reveal type I isotherms with small hysteresis loops of H4 type, and the resulting characteristics explain that all the CDPAC samples (CD 6, CD 7, CD 8, and CD 9) must have a microporous nature with respect to curves with a narrow knee at $p/p_0 < 0.05$ below 2 nm pore size together with mesoporous nature. The combination of narrow micro- and mesoporous structures could facilitate the diffusion at higher current densities.33 The textural parameters of CDPAC samples are summarized in Table 1. In Table 1, we did not mention the surface area for precarbonized carbon because it shows a very low BET surface area and poor porosity. It indicates that without an activation process at a suitable temperature, there is no possibility of micro- or mesopore formation in the network of carbon matrix. In Table 1, it can be observed that BET surface area values increase from CD 6 to CD 9, and it can be seen that the porosity of the CD sample is significantly influenced by the reaction conditions and the activation calcination temperature. When the calcination temperature increases from 600 to 900 °C, the values of BET surface area values have also increased. The CD 9 sample shows a high BET surface area (2457 m$^2$/g) with a hierarchical porous structure than the other precursor route-prepared PAC samples.34

During the heat treatment process, many bonds in the aromatic structures are incomplete and dangling, leading to the creation of molecular level internal and external pores on the carbon matrix present in the solid precarbonaceous material. The effect of the chemical activating agent ($\text{H}_3\text{PO}_4$) on the carbon mass ratio was studied in detail in recently reported literature.34a,b The mass ratios of 1:1, 1:2, and 1:4 (carbon/acid) are different in their surface area value and pore volume measurements. A higher amount of phosphoric acid addition causes pore blockage by the deposition of phosphate species and other phosphor species and thereby a decrease in the surface area value.34b Hence, in the present study, the optimized acid/mass ratio of 1:4 is adopted for achieving a better surface area and pore texture. Heat treatment employs random ordered imperfect aromatic sheets in the porous carbon matrix and it brings out the incompletely saturated unpaired electrons.34 The porous carbon chain structure formation is further connected with the gassy flaky morphology of the CD 9 sample obtained. In addition to the chemical activation process, the subsequent calcination (heat treatment) process expels out the bound volatiles from the carbon matrix, which easily depart over the surface and form cracks in the stable structure. The hierarchical porous structure increases the total pore volume (1.965 cm$^3$/g) with a huge pore diameter in the average pore size distribution graph, and is evidently shown in Figure 3B. The results indicate that the more hierarchical nanopores and mesopore formation in the carbon matrix could develop the huge Helmholtz double layer formation, which enhances the specific capacitance in EDLC devices.
3. ELECTROCHEMICAL ANALYSIS

3.1. Cyclic Voltammetry. Cyclic voltammetry (CV) studies were used to test the specific capacitances of CD 6—9. Figure 4 shows the cyclic voltammograms of CDPAC samples at different scan rates (5, 10, 20, 25, 50, 75, and 100 mV/s) in 6 M KOH with a 0–0.98 V potential window. Cyclic voltammograms show a leaf-like shape for the CD 6 sample, and the CD 7 sample depicts a quasirectangular shape. CD 8 and CD 9 samples reveal a more or less perfect rectangular shape. The area of the CV curve increased from CD 6 to CD 9 samples, which depicts that the CD 9 sample has obtained the ideal behavior properties of electric double layer capacitors. The specific capacitance ($C_s$) is calculated from eq 1.

$$C_s = \int \frac{\Delta I}{2Vm(V_2 - V_1)}$$

$$\therefore \Delta I = I_a - I_c$$  (1)

where $\Delta I$ is the half of the integration of the CV curve, $I_a$ is the anodic current, $I_c$ is the cathodic current, $V$ is the scan rate, $m$ is the mass of the active material, and $V_2 - V_1$ is the potential difference between the CV curves. Using the CV curve, we calculated the specific capacitance and the values are listed in Table 2. From Table 2, we can see that the specific capacitance of CD 6—9 is 148, 215, 294, and 347 F/g, respectively, at 5 mV/s. It is observed that the specific capacitance increased from CD 6 to CD 9. The CD 9 sample shows a high BET surface area and a high specific capacitance than CD 6, CD 7, and CD 8 samples. Because, in the preparation process, the activation temperature increases the creation and development of new pores, which later become gradually higher. The hierarchical porous structure helps to develop the highly static Helmholtz double layer and it enhances the specific capacitance. The hierarchical porous structure of CD 9 is responsible for the high specific capacitance, which simplifies the electrolyte ions retrieving the interior surfaces of the electrode and leads to an enlarged charge storage system. 34a,35

![Figure 4. Cyclic voltammograms of CDPAC samples at different scan rates (5, 10, 20, 25, 50, 75, and 100 mV/s) in 6 M KOH with a 0–0.98 V potential window.](image)

Table 2. Experimentally Calculated Specific Capacitance Values of CV and GCD for CD 6—9 Samples

| samples | specific capacitance calculated from CV (F/g) | specific capacitance calculated from GCD (F/g) |
|---------|----------------------------------|------------------------------------------|
|         | 5 mV/s | 10 mV/s | 20 mV/s | 25 mV/s | 50 mV/s | 75 mV/s | 100 mV/s | 0.5 A/g | 1 A/g | 3 A/g | 5 A/g | 10 A/g |
| CD 6    | 148    | 123     | 111     | 98      | 67      | 45      | 24       | 146     | 108   | 77    | 43    | 22     |
| CD 7    | 215    | 202     | 187     | 151     | 118     | 93      | 75       | 213     | 189   | 142   | 115   | 78     |
| CD 8    | 294    | 252     | 216     | 195     | 164     | 133     | 108      | 291     | 248   | 202   | 156   | 105    |
| CD 9    | 347    | 305     | 288     | 247     | 186     | 156     | 124      | 347     | 279   | 215   | 174   | 122    |

![Figure 5. GCD profiles of (a) CD 6, (b) CD 7, (c) CD 8, and (d) CD 9 samples at different current densities of 0.5, 1, 3, 5, and 10 A/g.](image)
the other heat-treated PAC nanomaterials. From the above discussion, it is clearly evident that the specific capacitance results coincide very well with the BET surface area values in terms of the pore size and surface properties, as listed in Table 1.

3.2. Galvanostatic Charge—Discharge Studies. Galvanostatic charge—discharge (GCD) studies are carried out to confirm the specific capacitance values. It is one of the techniques to calculate the specific capacitance from the charge—discharge rate. Figure 5 shows the GCD profiles of CD 6—9 samples at different current densities (0.5, 1, 3, 5, and 10 A/g), which were tested using a three-electrode system in 6 M KOH aqueous electrolyte. Hence, the GCD profile is plotted as time in seconds (s) versus the fixed potential (V). All the CDPAC samples (CD 6—9) derived from CD are triangular in shape (Figure S), and the GCD profiles are symmetric and linear, which further confirm the reversible charging and discharging properties. Hence, they depict the ideal capacitive behavior of the electric double layer capacitor.38 Using the GCD profiles, the specific capacitance is calculated from eq 2.

\[
C_s = \frac{\Delta t}{m \times \Delta V} \tag{2}
\]

where \(I\) is the current density (A/g), \(\Delta t\) is the time of charge—discharge in GCD profile (s), \(m\) is the mass of the active material in the working electrode (g), and \(\Delta V\) is the working potential window in GCD profiles (V). The calculated GCD values are tabulated in Table 2. From Table 2, the GCD values of CD 6—9 samples show 146, 213, 291, and 347 F/g at a low current density (0.5 A/g) and a high current density (10 A/g), and the GCD values show very low specific capacitance values of 22, 78, 104, and 122 F/g, respectively. At high current densities, the smaller \(C_s\) value can be attributed to the slower diffusion and migration of ions through the electrodes and electrolyte interface. At lower current densities, the \(C_s\) value is higher, which depicts a faster diffusion and migration of ions in the electrode and electrolyte interface.37 Table 2 clearly confirms that the tabulated GCD and CV capacitance values are in good agreement.

3.3. Electrochemical impedance Spectroscopy. Electrochemical impedance spectroscopy (EIS) is a powerful technique to examine the capacitive performance of the electrochemical cells. We compared the specific capacitance values obtained from EIS with respect to the results obtained from CV and GCD. In this EIS technique, it is preferable to determine the resistance and double layer capacitance of the as-prepared CDPAC-modified electrodes. The Nyquist plot is plotted between the real \(Z_r\) and imaginary \(Z_i\) impedance parts in ohms, as shown in Figure 6a. The Nyquist plot is employed using 6 M KOH electrolyte in the frequency range of 1 mHz to 100 kHz with 5 mV ac voltage. Figure 6a shows the EIS tests and depicts the Nyquist plots of CD 6—9 PAC electrodes. In general, the Nyquist plot produces a semicircle with a straight line at 90°. The semicircle indicates the charge transfer resistance \(R_{ct}\) between the electrode and electrolyte interface, and the straight line at 90° gives the double layer capacitance \(C_{dl}\). \(R_s\) is the solution or internal resistance present in aqueous 6 M KOH electrolyte. \(W\) is the Warburg resistance obtained in-between the \(C_{dl}\) and \(R_{ct}\). The electric resistance of \(R_{ct}\) and \(R_s\) includes the equivalent series resistances (ESRs).38 Finally, the ohmic resistance and the double layer capacitance are perfectly displayed in the Nyquist plot, as shown in the inset graph of Figure 6b, which is fitted with an open circuit of Nyquist plot, as depicted in the inset diagram of Figure 6c. Using the low-frequency data of Nyquist plot, the ohmic resistance double layer capacitance can be evaluated, and is calculated using eq 3 and 4.

\[
ESR = R_{ct} - R_s \tag{3}
\]

\[
C_{dl} = \frac{-1}{2\pi fZ_{im}} \tag{4}
\]

where \(C_{dl}\) is the double layer capacitance, \(f\) is the low-frequency data, and \(Z_{im}\) is the imaginary part of impedance. During the EIS tests, the open circuit is fixed as a standard value, which is used to compare the results obtained from the as-prepared PAC electrodes and the results are tabulated in Table 3. In

![Figure 6](image)

**Figure 6.** (a) Nyquist plot for CD 6—9, (b) inset diagram showing an enlarged Nyquist plot, and (c) insert circuit model showing the Warburg circuit.

### Table 3. EIS Analysis-Derived Parameters for CDPAC Samples

| Sample | \(R_s\) (Ω) | \(R_{ct}\) (Ω) | ESR (Ω) | \(W\) (Ω) | \(C_{dl}\) (F/g) |
|--------|-------------|---------------|---------|-----------|-----------------|
| CD 6   | 1.11        | 7.65          | 6.44    | 1.070     | 108             |
| CD 7   | 1.36        | 4.78          | 3.30    | 0.767     | 175             |
| CD 8   | 0.57        | 3.17          | 2.19    | 0.305     | 294             |
| CD 9   | 0.35        | 1.13          | 1.37    | 0.033     | 342             |

Figure 6a, the CD 9-modified electrode shows a small semicircle and a straight line at 90° compared to the other CDPAC sample electrodes, which characterize the property of low resistance with a high double layer capacitance. The results of the CD 9 electrode depict the fast diffusion of ions between the electrode and the electrolyte interface, which could produce a highly static Helmholz double layer and enhances the high capacitance.39 Evidently, the double layer capacitance of EIS as listed in Table 3 well matched with the specific capacitance of CV and GCD (Table 2).

3.4. Current Density and Scan Rate Capability. In supercapacitors, CV and GCD tests play a vital role and are used to calculate the \(C_s\) value. In both tests, the most important function is the rate performance. Figure 7a shows the scan rate capability (mV/s) versus specific capacitance (F/g) of CD 6—9 electrodes at different scan rates of 5, 10, 20, 25, 50, 75, and 100 mV/s. From Figure 7a, when the scan rate increases, the specific capacitance decreases gradually. During the gradual increase of low to high scan rate, the electrolyte ions do not
enter faster into the pores of the active material in the electrode. The result depicts the unstable form of the static Helmholtz double layer, and then the remaining restricted ions formed the solvated electrolyte ions in the electrolyte solution present in the electrochemical cell which gives a low $C_s$ value at a high scan rate and a high $C_s$ value at a low scan rate.\textsuperscript{40,41} CD 9 shows a high $C_s$ value due to the fast transport of electrolyte ions into the electrode interface.

Figure 7b shows the current density (A/g) versus specific capacitance (F/g) of CD 6−9 electrodes at different current densities, such as 0.5, 1, 3, S, and 10 A/g. In GCD tests, the charge−discharge process is important to develop a better electrode performance in device fabrication. The GCD profiles of different current densities help us to understand that the mass of electrode material is precious to choose better electrodes for a supercapacitor.\textsuperscript{41} From Figure 7b, it can be observed that the current densities decrease when the specific capacitance is increased due to the pore size effect and they varied at different amperes (0.5, 1, 3, S, and 10 A/g) at the same mass (4 mg) of the active material. At low current densities, the charge−discharge profile time duration of the CD 9 electrode depicts a high $C_s$ value. However, at high current densities, the charge−discharge profile time duration of the CD 9 electrode depicts a low $C_s$ value.

3.5. Cyclic Stability of the As-Prepared CDPAC. In EDLCs, the main advantage is the long-term cycle duration, and the test for long-term cyclic stability is one of the most important aspects for the as-prepared CDPAC-modified electrodes. Figure 8 shows the cyclic stability of CD 6−9 samples tested at a low current density of 0.5 A/g for 5000 cycles within a potential window from 0 to 0.98 V in 6 M KOH aqueous electrolyte using three-electrode systems. From Figure 8, the CD 9 sample indicates that there is no specific capacitance loss after 5000 cycles, and the samples CD 6−8 show a small loss in specific capacitance at the time of reaching 3500 cycles. The capacitance retention of CD 9 is up to 95%, which strongly exhibits excellent electrochemical stability. The excellent performance is closely correlated to the hierarchical nature of the CD 9 electrode as well as its high surface area and reasonable porous structure with pore size distribution.\textsuperscript{42}

4. FABRICATION OF THE FT-SS DEVICE

Overall, the as-prepared CDPAC-modified electrodes are tested to identify the better electrochemical performance with a high specific capacitance and long-term cyclic stability. From the above results, it is observed that the CD 9 electrode showed a higher specific capacitance of 347 F/g than CD 6 (148 F/g), CD 7 (215 F/g), and CD 8 (294 F/g), hence we have chosen the CD 9 electrode material for the flexible supercapacitor device fabrication. A new model device was fabricated by a novel systematic procedure, and we named the device flexible type symmetric supercapacitor (FT-SS). A schematic design of FT-SS is shown in Scheme 2, and a more detailed description of FT-SS has been published in our related patent work.\textsuperscript{43} Finally, the FT-SS was made as a symmetric supercapacitor device and it is tested for the electrochemical stability and efficiency. Tests such as CV, GCD, and cyclic stability were performed using a two-electrode system and the results are shown in Figure 9a−c. From Figure 9a, the CV curve of the FT-SS device shows a quasirectangular shape, which delivers an ideal behavior performance for the supercapacitor.\textsuperscript{44,45} The calculated $C_s$ value is 208 F/g at 5 mV/s. Furthermore, from Figure 9b, it is observed that the GCD profiles of charge−discharge segments show a perfect triangle, but the calculated GCD $C_s$ values (207 F/g at 0.5 A/g) are similar to the CV $C_s$ values. Figure 9c shows the cyclic stability; the test was carried out for the CD 9 sample for up to 5000 cycles and it gave up to 91% capacitance retention. The FT-SS device displayed a less specific capacitance than the individually checked CD 9-modified electrode in the three-electrode system. The energy density values for the two-
The electrode cell reaction like the FT-SS device have also been calculated using the following formula: \( \frac{1}{8} \times C_s \times V^2 \times \frac{1000}{3600} \). It gives the energy density value of 43.54 Wh/kg for the as-fabricated FT-SS device. The less \( C_s \) value is due to the solid type model in the two-electrode system, and we run the CD 9 electrode in a liquid form using 6 M KOH electrolyte in the electrochemical setup, whereas the FT-SS device used the gel form of 6 M KOH electrolyte with a PTFE separator. In comparison, the FT-SS device ion diffusion is slower than the individually checked CD 9 electrode which delivers a less \( C_s \) value.\(^{44-46}\) Hence, in the present research study, we adopted the low-cost precursor material to fabricate the CDPAC-based modified electrodes for supercapacitor applications. Hence, in the present study, a low-cost aqueous electrolyte solution is adopted in device fabrication instead of the organic electrolyte.

In conclusion, the fabricated FT-SS shows an improved specific capacitance for the CD 9 porous carbon nanomaterial with a high-rate performance as well as good stability in 6 M KOH aqueous electrolyte. In future, the as-prepared carbon nanomaterials’ performance in various inorganic and organic electrolyte media has potential for exploiting in electrochemical applications.

### 5. EXPERIMENTAL SECTION

#### 5.1. Preparation of PAC

The cattle feed CD waste was collected from nearby villages of Villupuram district, Tamil Nadu and used as a precursor material to prepare CDPAC. The CDPAC material was prepared by a two-step process and the same is shown in Scheme 1. The first step was the precarbonization process and the second step was the chemical.

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**Figure 9.** Electrochemical tests of the FT-SS device using CD 9: (a) cyclic voltammograms at different scan rates (5–100 mV/s), (b) GCD profiles at current densities of 0.5, 1, and 5 A/g, and (C) cyclic stability tests of FT-SS at 0.5 A/g.

**Scheme 1.** Schematic Diagram for the Preparation of CD 6–9

1. **STEP 1**
   - Cow dung waste (CDW)
   - (a) Washed/dried for 80 °C at 24 h
   - (b) 400 °C / 4 h under vacuum condition

2. **STEP 2**
   - Pre-carbonized carbon (PCC)
   - 50 g of PCC + 85 % of H₃PO₄ (4:1)
   - (a) Impregnated slurry kept aside for 12 h
   - (b) Filter/dried for 80 °C at 24 h/ground in mortar

   Grounded powder is split into four parts

   Four parts placed in muffle furnace at 600, 700, 800 & 900 °C/24 h under vacuum conditions
activation process. In the first step, the precursor CD was washed several times and dried at 80 °C for 24 h to remove the impurities. The dried sample was weighed approximately and placed in a muffle furnace at 400 °C for 4 h using a clay-sealed graphite crucible to create vacuum environmental conditions. The above-prepared material was labeled PCC. In the second step, 50 g of PCC was agitated with 85% H₃PO₄ with the mass ratio of 4:1. In the present study, we follow the optimized concentration like 85 wt % of phosphoric acid to study the temperature effect on the as-prepared PAC for the electrochemical performance. The impregnated slurry was kept aside for 12 h, filtered, and dried at 80 °C for 24 h. The dried slurry was ground in a mortar, which was split into four parts and placed in a muffle furnace at four different temperatures, 600, 700, 800, and 900 °C for 2 h using a clay-sealed graphite crucible, and it was used to create vacuum environmental conditions. Finally, the four different PAC samples were washed several times with cold water to remove the activating agent to maintain a neutral pH value, which were labeled CD 6, CD 7, CD 8, and CD 9.

5.2. Physico-Chemical Characterization. XRD patterns of CDPAC samples were recorded on a Shimadzu XD-3A (Japan) goniometer, using Cu Kα radiation operated at 40 kV and 35 mA. Surface morphology analysis of CDPAC was performed using a Quanta 200 FEG high-resolution scanning electron microscope and an FEI Tecnai G20 high-resolution transmission electron microscope instrument. The adsorption–desorption isotherms were obtained using a Quantachrome Autosorb-1 volumetric analyzer, and the specific surface area was determined by the BET method.

5.3. Electrode Preparation and Electrochemical Characterization. CDPAC electrodes were made using the as-prepared CD 6–9 samples as active materials. First, 4 mg of an active material was added to 2 mg of poly(vinylidene)-difluoride as a binder; 2 mg of acetylene black was added to avoid the resistance present in the binder and the organic solvent; and n-methyl pyrrolidinone was used to make a paste. The paste was coated on a nickel foil (1 × 1 cm) and it served as a current collector. Finally, the coated nickel foil was dried for a few minutes to stick the active material to the current collector. The weight of the coated material on the nickel foil was measured before and after the coating process for calculating the finally coated mass value, and the thickness was also measured manually using a Vernier caliper. The electrochemical measurements, CV, GCD, EIS, and cyclic stability (5000 cycles), were performed. Electrochemical tests of the as-prepared CDPAC-modified electrode were conducted on an Ametek PARSTAT 4000 instrument using a three-electrode system with 6 M KOH aqueous electrolyte. A platinum electrode was used to maintain the electroneutrality in the electrochemical cell and Ag/AgCl was used as the reference electrode (Ag/AgCl).

5.4. FT-SS Device Fabrication. In Scheme 2, the FT-SS shows seven layers, the first three layers on the anode side and the second three layers from the bottom of the cathode side. In-between the three layers of the anode and the cathode, there is a seventh layer, and it is called a separator. The first layer of the anode electrode is the nickel foil (3 × 3 cm) and it was used as a current collector; the thickness of the coated electrode is 1 mm. In the nickel foil, one side was coated with silver paste at the center point and it was used as a connectivity for the supply voltage, while the other side was a CD 9-modified electrode sample coated over the nickel foil (5 mg) using a binder [poly(vinylidene)difluoride] with the organic solvent n-methyl pyrrolidinone (5 mg) for sticking to the current collector, and this is the second layer. The third layer is the 6 M KOH electrolytic gel which acts as an electrolyte. In-between the anode and cathode electrodes, we introduce a polymer (polytetrafluoroethylene membrane) layer as a separator and the 6 M KOH electrolytic gel was made when the separator was soaked for 12 h in 6 M KOH electrolyte. Similarly, the cathode electrode was also made like the three layers of the anode electrode and finally, it was connected to the electrochemical analyzer with computerized software, as shown in Scheme 2.

![Scheme 2. Schematic Representation of FT-SS Device Arrangement](https://pubs.acs.org/doi/10.1021/acsomega.0c00848)
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