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BINDER-FREE FLEXIBLE SUPERCAPACITOR ELECTRODES BASED ON 1-DECANOL-ASSISTED POLYANILINENANOFIBERS

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ABSTRACT: A flexible electrode with high electrochemical performance is crucial for powering next-generation flexible electronic devices. In this study, a 1-decanol-assisted polyaniline Nano fibers coated flexible electrode was developed for super capacitor applications. The Polyaniline-Decanol-Sulfate Salt (PANI-DSS) electrode demonstrated a high specific capacitance of 264 F g^{-1} at a current of 1 mA, along with a maximum energy density of 36.6 Wh kg^{-1}. Furthermore, a flexible supercapacitor device with an active area of 100cm² was assembled to evaluate the practical performance of the electrode. The device exhibited an initial specific capacitance of 107 F g^{-1} at a current of 2 mA. A cycling stability test over 1000 charge–discharge cycles revealed capacitance retention of 52%, indicating good electrochemical durability.

Keywords: *Polyaniline, 1-Decanol, Flexible electrode, Super capacior, device*

1. INTRODUCTION

Supercapacitor attains great attention due to having advantages such as greater power density, durable cycle life, smart charge-discharge rate, and comprehensive operating temperature range. They are highly suitable as energy storage devices for various applications including electrical vehicles, regenerative braking systems, and airbags. Flexible super capacitors have garnered significant interest due to the increasing demand for flexible electronics. Polyaniline have attracted attention because of possessing high conductivity, unique redox behavior, chemical stability and low cost, and owning fast electron carrying through redox-reactions. The small size and highly conductive polyaniline nano structured materials are well applied for batteries and supercapacitors.

Dandanet studied small alcohol like methanol and ethanol influenced in morphology as well as enhancing the electrochemical performance of the polyaniline salt due to hydrogen bonding between polyaniline chains and alcohol. Among the studied alcohols, ethanol, and methanol as small alcohols from that greater performance were observed with polyanilines salt prepared with ethanol. In previous studies conducted by our research group, β-naphthol was employed as a dopant for polyaniline, resulting in enhanced crystallinity compared to undopedpolyaniline. Alcohols play a pivotal role in tailoring the structural and morphological characteristics of polyaniline, which are critical for enhancing its performance in supercapacitor applications. When employed as dopants or structure-directing agents during the polymerization process, these alcohols can substantially influence molecular ordering, increase crystallinity, and facilitate the formation of well-defined nanostructures.

These structural modifications contribute to improved charge transport, greater surface area, and enhanced electrochemical activity, ultimately leading to superiorcapacitance and overall device performance. In previous studies, extensive research has been devoted to the use of low molecular weight alcohols such as methanol, ethanol, isopropanol, and ethylene glycol as well as polyhydroxy compounds like poly(vinyl alcohol) (PVA), in the development of polyaniline (PANI) and its composite systems. These alcohols have

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been utilized not only as solvents and processing aids but also as dopants and stabilizing agents. Their incorporation has been shown to markedly affect the morphology, electrical conductivity, and electrochemical performance of the resulting PANI-based materials, underscoring their critical role in enhancing the functional properties required for high-performance energy storage and sensing applications.

In this study, polyaniline salt was synthesized using 1-decanol, which served both as a dopant and a surfactant. The resulting polyaniline exhibited enhanced electrical conductivity and excellent film-forming properties. Notably, the synthesis was conducted without the use of corrosive protic acids, offering a more environmentally benign approach. The synthesized polyaniline salt displayed a nanofibrous morphology with strong adhesion to the electrode surface, which proved advantageous during electrochemical performance testing. Furthermore, no additional binder was required for electrode fabrication, and the material demonstrated compatibility with various types of current collectors. The electrochemical behavior of the electrodes was evaluated using cyclic voltammetry (CV) and galvanostatic charge–discharge (CD) techniques. To assess practical applicability, a device with an active area of 100 cm² was assembled, and its electrochemical performance was systematically investigated.

2. EXPERIMENTAL MATERIALS

Aniline (ACS reagent, ≥99.5%) was vacuum distilled prior to use, Ammonium per sulfate (ACS reagent, ≥99.5%),1-Decanol (Analytical grade, ≥98%), Ethyl acetate (Reagent grade), all chemicals were procured from Sigma Aldrich, India. All the reactions were carried out with doubled distilled water purified by the Milli-Q-SQ-200 instrument.

Materials Characterization

The electrical resistance of the PANI-DSS sample was measured using a standard four-probe technique. Pellets were prepared by compressing the powder sample under a pressure of approximately 120 kg cm^{-2} at ambient temperature. A constant current source (Keithley 6220) and a nanovoltmeter (Keithley 2182A, Cleveland, OH, USA) were employed to determine the resistivity. FTIR spectra of the PANI-DSS sample in powder form were recorded using a Nicolet Nexus 670 FTIR spectrometer (Thermo Scientific, MN, USA) equipped with a gas chromatography interface. The spectra were obtained using the KBr pellet technique.XRD analysis was performed using a Bruker AXS D8 Advance diffractometer (Karlsruhe, Germany) with Cu-Kα radiation ($\lambda = 1.5406$ Å). The diffraction patterns were recorded in continuous mode at a scan speed of 0.045° min^{-1} to examine the crystalline structure of the PANI-DSS powder. The surface morphology of the PANI-DSS sample was studied using a Hitachi S-3400 scanning electron microscope (Tokyo, Japan). Prior to imaging, the sample was mounted on a double-sided adhesive carbon tape and sputter-coated with a ~500 Å gold layer to prevent charging during analysis.

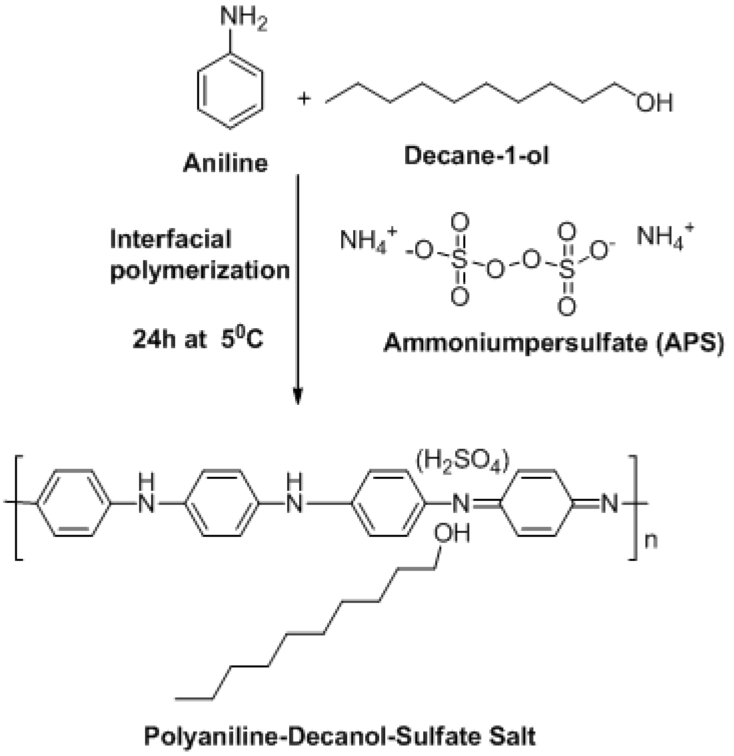
Electrochemical characterization

Stainless steel foil substrates were first cleaned using a soap solution to remove surface contaminants, followed by rinsing with distilled water. The substrates were then mechanically polished with sandpaper to eliminate surface oxides and ensure uniform roughness. Subsequently, a second cleaning cycle was performed using the same soap and distilled water sequence. The cleaned foils were then dried in a hot air oven at 120 °C for 1 hour. Following the cleaning process, the substrates were coated with a polyaniline–decanol sulfate salt (PANI–DSS) composite using the doctor blade technique, achieving a uniform film thickness of approximately 200 µm. The coated electrodes were air-dried at room temperature for 2 hours and further dried in a hot air oven at 120 °C for an additional 4 hours. The final electrode mass loading was approximately 1 mg/cm². An Absorbent Glass Mat (AGM) was employed as the separator, and 1 M H_2SO_4

was used as the electrolyte. Prior to assembly, the electrodes were immersed in the electrolyte for 30 minutes to ensure complete wetting. The fully prepared electrodes were then assembled and used directly for electrochemical characterization.

Synthesis PANI-Decanol-sulfate salt (PANI-DSS)

The PANI-DSS was synthesized using four different amounts of 1-decanol such as 1 ml, 1.5 mL, 2 mL and 3 ml.The synthesis procedure involved uniformly dispersing 1-Decanol in 25 mL of ethyl acetate, followed by sonication for 1 hour with respective 5 min rest after every 15 min sonication. Next, 1 mL of aniline was added to the 1-decanol solution in ethyl acetate. An aqueous solution of 2.8 g of ammonium persulfate (APS) was added to a mixture of aniline and 1-decanol. The resulting mixtures were placed in a refrigerator set to an internal temperature of 5 °C and left reaction for 24 hours. The overall synthesis pathway of PANI-DSS is depicted in Scheme 1. During oxidative polymerization, sulfuric acid (H_2SO_4) is generated in situ from the decomposition of ammonium persulfate, which serves as the oxidant.



Scheme 1. Schematic Representation of Polyaniline- Decanol Sulfate salt (PANI-DSS) Formation.

After the reaction, the green solution of polyaniline was transferred to a separating funnel and leaves it for settle to separate the two layers of ethyl acetate and water. The polyaniline salt in ethyl acetate was separated from the unwanted water layer, and washed this solution with deionized water until clear water observed. The resulting solution denoted as ANI-DSS and stored in refrigerator for future use.

3. RESULTS AND DISCUSSION

Polyaniline-Decanol-Sulfate Salt (PANI-DSS) salt was synthesized via interfacial polymerization employing 1-Decanol as both a surfactant and dopant. The polymerization was conducted at 5 °C for 24 hours, using varying volumes of 1-Decanol (1.0, 1.5, 2.0, and 3.0 mL) with fixed quantities of aniline (1 mL) and ammonium persulfate (APS) as the oxidant. The reaction proceeded through a biphasic system, wherein the PANI-DSS salt formed in the organic ethyl acetate layer and was effectively separated from the aqueous

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phase using a separating funnel. In the absence of 1-Decanol, clear separation of the PANI-DSS salt in the ethyl acetate phase was not achieved, indicating the critical role of 1-Decanol as a surfactant.

Table 1.Conductive Properties of PANI-DSS

1-Decanol mL	Yield	Conductivity (S cm^{-1})
1	0.60	0.39
1.5	0.65	0.69
2	0.70	1.29
3	0.75	0.23
0	0.55	0.1

Its presence facilitated the stabilization of the interface and enhanced phase separation, underscoring its dual function in the synthesis process.

The PANI-DSS achieved a maximum electrical conductivity of 1.29 S·cm^{-1} upon the addition of 2 mL of 1-decanol. Accordingly, this optimized formulation was employed for electrode fabrication. The selection of high-conductivity materials for electrode development is consistent with prior reports, which emphasize their critical role in enhancing electrochemical performance.

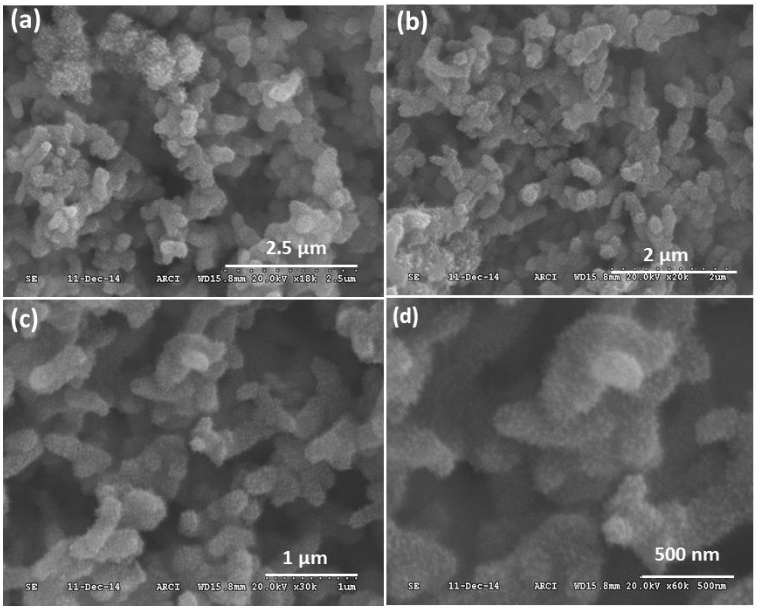

Figure 1. FE-SEM images of PANI-DSS at different magnification

The conductivity of the PANI-DSS salt was found to increase with the incremental addition of 1-decanol, reaching an optimal value of 2 mL. Beyond this concentration, a decline in conductivity was observed, which may be attributed to de-doping effects or alterations in the polymer morphology that disrupt charge transport pathways.

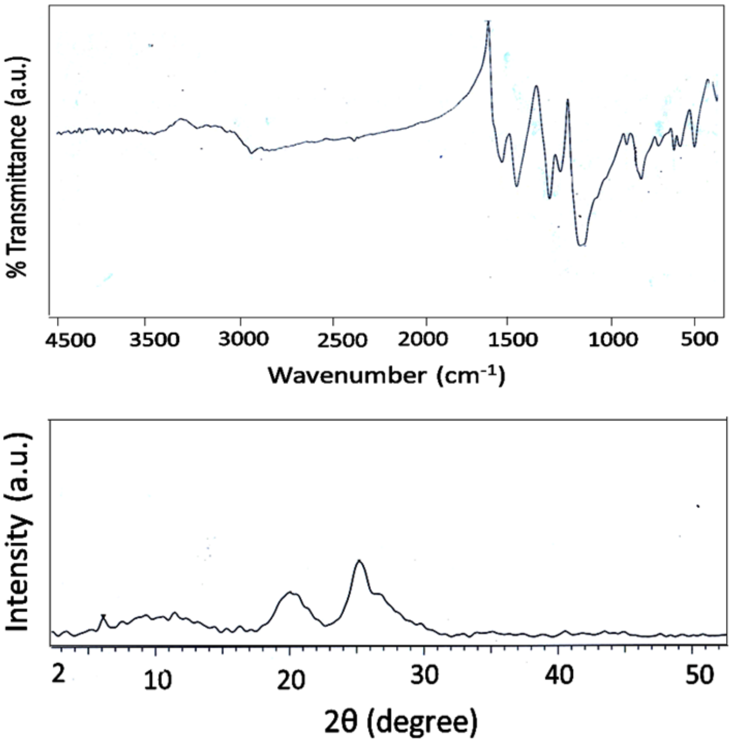

Figure 2. (a) FT-IR and (b) XRD of PANI-DSS sample.

The conductivity of without doped PANI exhibited value of 0.1 S cm^{-1}. The yield of PANI-DSS salt gradually increasing the addition of 1-Decanol (Table 1).

Field Emission Scanning Electron Microscopy (FE-SEM) images at various magnifications of PANI-DSS salt is presented in Figure 1. As illustrated in Figure 1a–d, the images reveal a uniform nanofiber morphology, which may be attributed to the consistent growth of PANI nanofibers through interfacial polymerization. The PANI-DSS nanofibers exhibited lengths of at least 1 µm and widths of approximately 150 nm. Moreover, the uniform morphology of Nanofibers offers a significant advantage for enhancing specific capacitance by reducing the electron transport path length.

The FT-IR spectrum of PANI-DSS (Figure 2a) displays characteristic absorption bands consistent with those reported for polyaniline (PANI) salts. The broad band observed at 3445 cm^{-1} is attributed to N–H stretching vibrations, while the peak at 2920 cm^{-1} corresponds to aliphatic C–H stretching. The absorption bands at 1560 cm^{-1} and 1480 cm^{-1} are assigned to the C=C stretching vibrations of the quinonoid and benzenoid rings, respectively, indicating the presence of both structural units. The bands at 1302 cm^{-1} and 1242 cm^{-1} are associated with C–N stretching vibrations of the quinonoid and benzenoid structures, respectively. A prominent peak at 1137 cm^{-1} is ascribed to the N=Q=N vibrational mode, where ‘Q’ denotes the quinonoid ring, signifying the doped state of PANI. Additionally, the band at 799 cm^{-1} corresponds to out-of-plane bending vibrations of the 1, 4-disubstituted benzene ring.

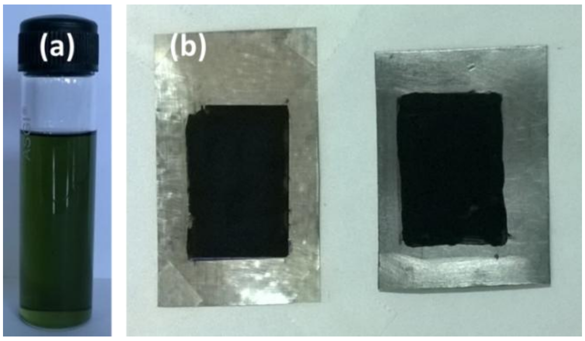

Figure 3.(a) The solution form of PANI-DSS electrode, (b) PANI-DSS coated images of electrodes.

The X-ray diffraction (XRD) pattern of PANI–DSS nanofibers, as shown in Figure 2b, reveals a distinct peak at $2\theta \approx 6.2°$, which is attributed to the interaction between the dopant (DSS) and the aniline monomer. Additional peaks observed at approximately $2\theta \approx 20°$ and 25° correspond to the characteristic reflections of the emeraldine salt form of polyaniline. These peaks are indexed to the (020) and (200) crystallographic planes, respectively, indicating the semi-crystalline nature of the PANI backbone and its ordered chain alignment.

Figure 3a presents the organic solution of the PANI-DSS salt, exhibiting a characteristic green coloration, which is indicative of the emeraldine salt form of polyaniline. Figure 3b illustrates the PANI-DSS-coated stainless steel electrode, where a uniform and continuous coating is distinctly visible. Importantly, the electrode was fabricated without the incorporation of any binder, which offers a significant advantage by enhancing both the energy density and the gravimetric specific capacitance. The strong and uniform adhesion of the active material onto the current collector plays a vital role in ensuring efficient charge transfer and contributes to the superior electrochemical performance of the electrode.

The electrochemical behavior of the PANI-DSS electrode was evaluated using cyclic voltammetry (CV) and galvanostatic charge-discharge (CD) measurements, as presented in Figure 4a. CV measurements were performed at various scan rates ranging from 1 to 5 mV s^{-1}. As the scan rate increased, the current response of the CV curves also increased correspondingly, indicating a typical capacitive behavior. The consistently uniform shape of the cyclic voltammetry (CV) curves across various scan rates indicates excellent electrochemical reversibility and efficient charge transport, underscoring the electrode's strong potential for high-performance energy storage applications. The specific capacitance of the PANI-DSS electrode was calculated to be 268 F g^{-1} at a scan rate of 1 mV s^{-1} in 1M H_2SO_4 electrolyte. However, with increasing scan rates (2, 3, 4, and 5 mV s^{-1}), a gradual decrease in specific capacitance was observed. This reduction can be attributed to the limited time available for electrolyte ions to diffuse and penetrate into the deeper active sites of the electrode material at higher scan rates. Such behavior is consistent with the typical performance of pseudo-capacitive materials.

The charge-discharge study of the PANI-DSS electrode was measured at different current densities (Figure 4b). The voltage of the electrode can be extended up to 1V. The specific capacitance is calculated from GCD curves using following equations $Cs= I\times\Delta t/ (m\times \Delta V)$, where Cs is specific capacitance (F g^{-1}), I is the discharge current (A), Δt is the discharge time (s), m is the mass of the active materials in grams, ΔV is the potential window (V). The energy density calculated using as per equation of $E_d= 0.5\times CV^2$, and power density calculated by using $Pd=E_d/ \Delta t$.

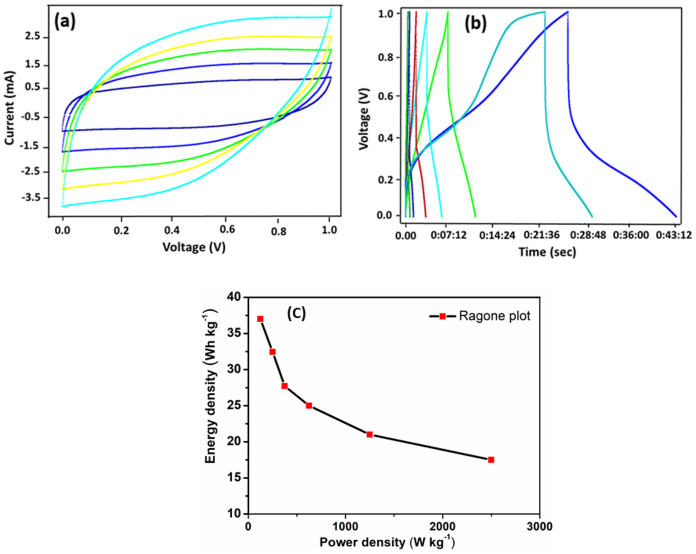

Figure 4. (a) Cyclic voltammetry (CV) curves of PAN-DSS electrode at scan rates of 1, 2, 3, 4, and 5 mV s^{-1} in 1 M H_2SO_4 electrolyte. (b) Charge discharge curves (CD) curves of PANI-DSS at current densities of 1, 2, 3, 5, 10, and 20 mA. (c) Ragone plot illustrating the energy and power density of the PANI-DSS electrode.

The PANI-DSS electrode exhibited a maximum specific capacitance of 264 F g^{-1} at a current density of 1 mA cm^{-2} in 1M H_2SO_4 electrolyte. The specific capacitance decreased with increasing current densities, showing values of 232, 200, 178, 150, and 125 F g^{-1} at 2, 3, 5, 10, and 20 mA cm^{-2}, respectively. The galvanostatic charge-discharge (GCD) curves displayed slight redox plateaus, indicative of the pseudo-capacitive behavior of the polyaniline salt, which involves faradaic redox reactions.

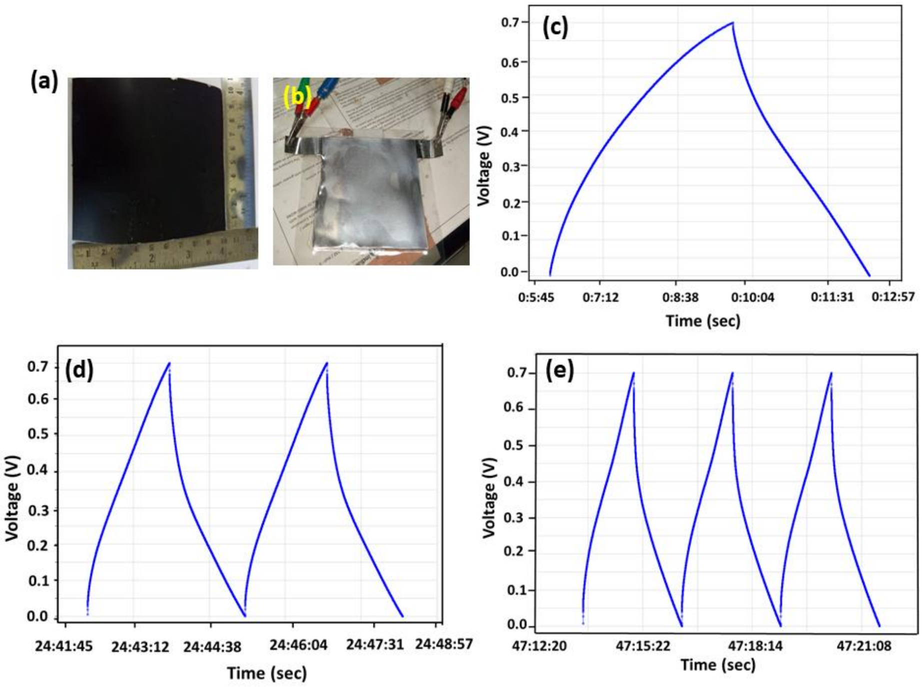

Figure 5. (a) PANI-DSS coated electrode (b) Second cycle (c) 498-500 cycle (d) 997-1000 cycles of 1000 cycles.

A maximum energy density of 36.6 Wh kg^{-1} was achieved at a power density of 125 W kg^{-1}, demonstrating the excellent energy storage capability of the electrode material. The Ragone plot, shown in Figure 4C, illustrates the variation of energy density with respect to power density. Notably, the electrode maintained a high power density of 2500 W kg^{-1} at an energy density of 17.5 Wh kg^{-1}, confirming its suitability for high-performance supercapacitor applications

The electrode coated over a 10 cm × 10 cm area and the corresponding assembled device is presented in Figure 5a and 5b, respectively. The electrochemical performance of the device was evaluated via galvanostatic charge–discharge (CD) cycling over 1000 continuous cycles. The device retained 52% of its initial specific capacitance at the end of the test, demonstrating notable long-term cycling behavior. The initial specific capacitance was measured to be 107 F g^{-1}, delivering an energy density of 11 Wh kg^{-1} and a corresponding power density of 106 W kg^{-1}. Representative GCD curves corresponding to the 2nd cycle, cycles 498–500, and cycles 997–1000 are illustrated in Figures 5(c–e), respectively. The device exhibited stable and consistent cycling performance over 1000 cycles, underscoring the mechanical integrity and electrochemical robustness of the PANI-DSS electrode coating. Furthermore, the absence of significant voltage drop between the initial and final cycles confirms the structural and electrochemical stability of the electrode in the acidic aqueous electrolyte environment.

4. CONCLUSION

The PANI-DSS were prepared by interfacial polymerization using 1-Decanol as dopant as well as surfactant, and uniform electrode coating was achieved by doctor blade coting technique respectively. The conductivity of polyamine salt showed 1.29 S cm^{-1}. The specific capacitance of the PANI-DSS electrode achieved as 268 F/g from CV at 1 mV s^{-1} and 264 F g^{-1} from CD at 1 Ma current. Moreover in this work assembled the device to know the realistic performance of the electrode is of 10 cm× 10 cm. The PANI-DSS symmetric device showed specific capacitance 107 F g^{-1} at 2 mA current and performed cycle life maintain retention 52% after 1000 cycles.

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