Efficient Energy Storage Performance of Polyaniline based Supercapacitor

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Abstract: The energy storage performance of fabricated solid state supercapacitor based upon the polyaniline (PANI) sample has been investigated in the present study. Fourier transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM) studies have been performed on simple chemistry based synthesized PANI to check the appropriate synthesis of sample with electrochemical analysis. The existence of required fundamental bands in the FTIR spectra of PANI confirms the facial growth of desired PANI sample in its highly conducting form. Scanning electron microscopy investigation designates the cotton-like morphology of prepared sample with particle size in the micro/nanometer range. The energy storage performance of the fabricated supercapacitor is noted using cyclic voltammetry analysis. The significantly high values of specific capacitance and energy density are 193.04 Fg\textsuperscript{-1} and 107.14 Whkg\textsuperscript{-1}, respectively, for prepared supercapacitor at the scan rate 40 mV/s. The high values of these parameters may be ascribed to high conductivity and low resistance of the supercapacitor. The PANI supercapacitor exhibits the efficient capacitance retention of more than 65% of initial capacitance after 10000 charging-discharging cycles.

INTRODUCTION

PANI is supreme favourable electrode material due to its extraordinary electrical conductivity, exceptional interconnectivity, and tremendous device efficiency [1]. Because of the above-mentioned properties, PANI is a highly used conjugated polymer in the various applications like EMI shielding [2], batteries [3], sensor [4], solar cell [5], solid-state supercapacitor [6], electrochemical display [7], antibacterial [8], etc. Out of these applications, the supercapacitor is the most fabricated device using conjugated polymers in the last few years due to high energy density related to the conventional capacitors. The capability of energy storage of the supercapacitor is governed by mechanisms, namely pseudo-capacitance and electric double-layer (EDL) capacitance [9,10]. The capacitance obtained in pseudo-capacitors is specified through reversible and fast faradic redox reaction in materials of electrodes, whereas, high specific capacitance is the function of charge accumulation at the interface of electrode and electrolyte [11]. The type of electrode material is the vigorous factor of solid-state supercapacitor performance therefore, lot of materials are investigated for energy storage devices. But, the easy synthesis route, low cost, high specific capacitance, and high energy density of conjugated polymers have been analyzed for electrode material application. Moreover, the smaller size of electroactive materials also enhances the device performance because of lesser diffusion length and large active surface area, which are basic requirements for the redox reaction [12]. Therefore, in the present study, we have synthesized the PANI sample and used to investigate the molecular and morphological properties. Finally, the prepared sample was used in fabrication of symmetric parallel electrode based solid state supercapacitor device with significant stability. The fabricated device is established for energy storage capability and cycle stability through cyclic voltammetry analysis.

SYNTHESIS OF PANI

The PANI sample has been synthesized through the \textit{in-situ} polymerization route. In the facial growth route, the three aqueous solutions of aniline-HCl (monomer-15 mM), ammonium persulphate (oxidant-25 mM), and methyl orange (surfactant-20 mM) were prepared separately after enthusiastic stirring for 1 hr, and all the solutions
cooled for 2 hrs in the refrigerator. After cooling of the solutions, the surfactant solution was placed in an ice bath maintained at temperature below 4 °C on a magnetic stirrer, and monomer and oxidant solutions were added drop-wise, respectively, under the continuous stirring. The polymerization process starts quickly with the addition of the oxidant solution. The resultant solution was left for proper mixing and then placed in the refrigerator for 24 hrs to complete the polymerization reaction. Next day, the precipitates of PANI were filtered out and washed with methanol and water alternatively. Finally, so obtained precipitates were dried and crushed to powder form.

RESULTS AND DISCUSSION

Molecular Spectroscopy and Morphological Analysis

Figure 1(a) represents the FTIR spectra of the PANI sample in the wavenumber range 4000-400 cm\(^{-1}\), which contains all the required fundamental bands which confirm the expected growth of PANI [13]. In the higher wavenumber side, the high absorption band present at 3450 cm\(^{-1}\) is associated with N-H stretching vibration in the polymeric chain [14]. The doublet perceived at ~2870 and 2920 cm\(^{-1}\) is associated with the symmetric and asymmetric stretching vibration of C-H groups. Another doublet was observed around the bands at ~1470 and 1565 cm\(^{-1}\) associated with the benzenoid and quinoid rings of the polymeric chains. These bands also belong to the electrical conductivity and conjugation length [15]. The quinoid rings reveal the concentration of bipolarons while benzenoid rings reveal the concentration of polarons which are charge carriers in PANI. The band situated at ~1140 cm\(^{-1}\) is associated with the –NH=+ stretching vibrations in polyaniline. The presence of this band in the prepared materials suggests the synthesis of good quality polyaniline with long conjugation length [16]. Figure 1(b) shows the morphological investigation of the prepared PANI sample through SEM, which indicates that the prepared PANI sample have cotton-like agglomerated morphology with the particle size approximately ~1 μm.

![Figure 1: (a) FTIR spectra and (b) FESEM image of the PANI sample.](image)

Electrochemical Analysis

The electrochemical properties have been investigated through cyclic voltammetry (CV) measurements using in house AUTOLAB PGSTAT302N characterization tool, in which a prepared PANI sample is used as electrode material for solid-state supercapacitor (Fig.2). In the facial fabrication of supercapacitor, asymmetric parallel electrode geometry is used, i.e. two parallel electrodes were used as anode and cathode, whereas, polyvinyl alcohol/sulphuric acid (PVA/H\(_2\)SO\(_4\)) gel was used as electrolyte/separat or material. For the preparation of electrolyte/separat or, the appropriate amount of PVA is disbanded in 60 ml of de-ionized water, and heated for 2 hrs at the 80 °C under magnetic stirring. Thereafter, homogeneous mixing of PVA and water, few amounts of H\(_2\)SO\(_4\) is added to the solution and mixed enthusiastically for 1 hr, and homogeneou s transparent electrolyte gel is achieved after the cooling. Thus obtained electrolyte was sandwiched between two equal mass electrodes of PANI, and left to
dry. The anode and cathode electrodes' size aluminum electrodes are used for testing the contrived solid state supercapacitor.

![Figure 2: Schematic representation of PANI based solid-state supercapacitor.](image)

To investigate the charge storage performance of PANI based solid-state supercapacitor, the CV curves at altered scan rates of values 10, 20, 30, 40 mV/s, in the applied potential frame of -0.1 to 0.9 V are obtained as shown in Fig. 3(a). The CV curves of the sample at every scan rate consist of the two different peaks associated with the oxidation and reduction characteristics which indicate the pseudo-capacitive performance of the prepared sample. The oxidation and reduction peaks become more articulate with the increase in scan rates. The existence of oxidation and reduction (redox) peaks in CV curves indicates the faradic redox mechanism and pseudo-faradic charge propagation mechanism in which the semi-conducting state transforms into a conducting state or conducting state transit into the insulating state of the PANI [17]. The conducting polymers generally liberate and accumulate the charges throughout the redox reaction over π-conjugated polymer chains. Moreover, the electrical current density and area inside the CV curves enhance with an enhancement in scan rate along with hysteresis of the anodic and cathodic peaks, which reveals the standard characteristics of pseudo-capacitors. The current density of CV curves is found to intensification with the rise in scan rates from 10 to 40 mV/s. This happened because of improvement in aspect ratio prominent to superior electrolytic characteristics and minor internal resistance [18]. The increase in current density and internal area of the CV curves reveals the enhancement in specific capacitance i.e. enhancement in energy storage capability. The ions from electrolyte gel are transferred on the conjugated polymer surface as p-type doping during the oxidation evolution, whereas, the transferred ions returned to the electrolyte solution during the reduction evolution as n-type doping.
The energy storage ability of fabricated supercapacitor is investigated in terms of specific capacitance ($C_s$) and energy density ($E_s$). The specific capacitance of symmetric parallel electrodes supercapacitor can be intended by expression [19]

$$C_s = \frac{I \Delta t}{m \Delta V}$$  

(1)

Where $I$ is charging-discharging current (A), $\Delta V$ is drop in potential in discharging time $\Delta t$ throughout the discharging progression, and $m$ is the mass of electrode (pellet). The calculated values of specific capacitance are tabulated in table 1, which indicates that specific capacitance for PANI sample enhances with the enhancement in scan rate. The sample attains the maximum specific capacitance at the scan rate 40 mV/s and minimum at 10 mV/s which are 193.04 and 56.15 F/g, respectively. The specific capacitance exhibit the three-fold degeneracy as the scan rate increases from 10 to 40 mV/s. The analyzed behavior of enhancement in specific capacitance with an increase in scan rate is well validated with the ostensible behavior from CV measurements.

The energy storage ($E$), another supercapacitor performance parameter can be calculated using relation [20]

$$E = \frac{1}{2 \times 3.6} x C_s x \Delta V^2$$  

(2)

Where $C_s$ indicates specific capacitance. The calculated values of energy density using equation (2) are tabulated in table 1. It is analyzed that energy density increases from 31.19 to 107.14 W/kg with rise in scan rate from 10 to 40 mV/s, which proves an increase in the energy storage capability.

**Table 1:** The specific capacitance and energy density of the PANI sample at different scan rates.

<table>
<thead>
<tr>
<th>Scan Rate (mV/s)</th>
<th>Specific Capacitance (F/g)</th>
<th>Energy Density (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>56.15</td>
<td>31.19</td>
</tr>
<tr>
<td>20</td>
<td>89.47</td>
<td>49.71</td>
</tr>
<tr>
<td>30</td>
<td>134.58</td>
<td>74.76</td>
</tr>
<tr>
<td>40</td>
<td>193.04</td>
<td>107.14</td>
</tr>
</tbody>
</table>

The cycle stability test was also performed on presently prepared PANI based supercapacitor and it is observed that this supercapacitor has good cyclic stability. The supercapacitor exhibits 67.39% of its initial value of specific capacitance after 10000 cycles (Fig.3(b)). However, supercapacitor attains 94.25, 87.53, 80.84, 73.24% specific capacitance of its initial value after 2000, 4000, 6000, 8000 charging-discharging cycles, respectively.
CONCLUSION

PANI sample has been synthesized using the chemical oxidative polymerization synthesis route and its electrochemical properties were analyzed. The presence of required fundamental bands in the FTIR spectra of PANI evident the growth of good quality PANI. SEM study of the prepared sample indicates that the prepared sample has an agglomerated cotton-like structure having particle size ~1μm. The solid-state supercapacitor has been fabricated using a prepared PANI sample and investigated using cyclic voltammetry for energy storage performance. The calculated high values of specific capacitance and energy density make this sample appropriate for industrial applications. At the 40 mV/s scan rate, this supercapacitor exhibit a specific capacitance of 193.04 F/g and an energy density of 107.14 Wh/kg, which indicates the high electrical conductivity and low internal resistance of the supercapacitor. The prepared supercapacitor exhibits 67.39% capacitance retention value of initial capacitance after 10000 charging-discharging cycles.

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REFERENCES