Preliminary Study of Utilizing Polyaniline as Electrode Material for Supercapacitor Application: Juxtaposition of Electrochemical Performances

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Abstract Polyaniline (PANI) were prepared via a one-step electrochemical polymerization method in 0.2 M aniline and 0.2 M dopants for supercapacitors (SCs) application. To determine the appropriate conditions and materials for SCs application, the type of substrate, scan rate, dopants, and electrolyte on PANI were varied. The PANI composite's potential to store energy was conducted and evaluated using cyclic voltammetry in a three-electrode setup. The PANI-carbon felt demonstrated the best electrochemical performance compared to other substrate namely carbon and stainless steel. It is found that utilising H\textsubscript{2}SO\textsubscript{4} as both dopant and electrolyte results in high specific capacitance.

Keywords: Substrate, dopants, electrolyte, specific capacitance.

Introduction

The implementation of innovative clean energy and energy storage are crucial issues that must be resolved due to the worsening of environmental degradation and resource scarcity. Due to its rapid charge and discharge rates, high power density, long cycle life, and environmentally friendly design, supercapacitors (SCs) are a revolutionary type of energy storage that has generated a lot of attention \cite{1}. Nevertheless, SCs have a lower energy density than conventional energy storage systems, which results in various restrictions on its application. With that, the development of novel high-performance electrode materials became a hot topic in the SCs industry since electrode material is a significant component of the devices. Power, energy density, and stability performance factors are influenced by the electrode material. \cite{2}. The three primary types of electrode materials utilized in energy storage devices are carbon species, metal compounds, and conducting polymers. A conducting polymer with fascinating features and prospective uses, notably in the area of energy storage, is polyaniline (PANI). The variable pseudocapacitive performance of PANI, which results from its multiple oxidation states, has made it a popular choice, both as a conductor and a substance that is directly electroactive. This is because PANI stores energy through redox transitions among the several oxidations states it displays during protonation. Furthermore, it is a common conductive polymer material with low cost, easy manufacture, high theoretical specific capacitance, and high conductivity \cite{3}. Despite PANI SCs have been around for more than three decades, the possibility for practical use has only recently attracted attention. Several research initiatives were made to improve the processability, conductivity, and stability of PANI for technological application. The simplest approach is the oxidation state, dopant, and polymerization conditions are altered. Researchers are interested in enhancing PANI's features, such as its electrical conductivity, by selecting the suitable dopants since it creates charge carriers which is in charge of the conducting polymer's conductivity \cite{4}. In addition, the scan rates and electrolyte utilised also may affect the PANI's features. Therefore, in this work, study on the different type of substrate along...
with effects of scan rate, dopants and electrolyte on polyaniline is conducted to determine the appropriate conditions and materials for technological applications. The electrochemical performance was collected and analyses using cyclic voltammetry (CV).

Materials and Methods

Chemical, Reagents, and Materials
Aniline (C₆H₅NH₂), sulphuric acid (H₂SO₄), hydrochloric acid (HCl, 37%), potassium chloride (KCl), ferrocyanide (C₆FeN₆⁻) x (Na₂SO₄), all of which were purchased from Sigma Aldrich were used. The chemicals were of analytical purity thus it was used without further processing. All of the solutions were made with deionized water. Platinum wire (0.5 mm 37 mm, China) and Ag/AgCl electrode (4 mm, China) were used as counter and reference electrodes accordingly. Carbon, stainless steel, and carbon felt were utilized as working electrodes (WE)/substrate to electroplate conductive polymers over an area of 1.9 cm².

PANI-WE Synthesis
The PANI was synthesized through the electrodeposition method employed a three-electrode configuration a three-electrode setup. 0.1 M Na₂SO₄ was prepared and utilized as pretreatment solution. The electropolymerization of aniline was carried out in 0.2 M aniline and either 0.2 M H₂SO₄ or 0.2 M HCl. PANI was deposited using the cyclic voltammetry (CV) process with a potential range of -0.5 to 1 V and variable scan rates. A continuous voltage of 0.002 V was given to the electrode materials in order to improve PANI adherence to WE. PANI was deposited onto the working electrode after 15 cycles of CV [5]. As illustrated in Figure 1, PANI exists in three diverse forms depending on its oxidation or protonation state: leucoemaraldine (completely reduced form), pernigraniline (totally oxidized form) and emeraldine (partially reduced or partially oxidized form) [6]. Leucoemaraldine, emeraldine, and pernigraniline vary from each other by two electrons for each aniline monomer.

![Figure 1. Schematic diagram describing PANI transitions](image-url)
Electrochemical measurements
In this work, study on the different type of substrate (carbon, stainless steel, and carbon felt) along with effects of scan rate (8, 10, 20, 50, 00 mV.s⁻¹), dopants (H₂SO₄, HCl) and electrolyte (H₂SO₄, C₆FeK₄N₆) on polyaniline is conducted to determine the appropriate conditions and materials for technological applications. The performance of the electrode was evaluated using the CV approach. 1 M H₂SO₄ was produced and utilized as an electrolyte in conjunction with C₆FeK₄N₆. The specifics cover reactivity, reversibility of electron transfer mechanisms, and the complexed transition metal oxidation state's stability. A preliminary determination concerning the property of PANI can be established by analyzing the CV curve.

Results and Discussion
Specific capacitance of different electrodes was conducted and calculated at each scan rate as tabulated in Table 1. The scan rate of the introduced nano composite was measured at 8, 10, 20, 50, and 100 mV.s⁻¹. The integral equation below was used to compute the specific capacitance, \( C_{sp} \) (F.g⁻¹) from the CV curves.

\[
C_{sp} = \frac{\int_0^{\Delta V} iv dv}{\mu m \Delta V} \quad (1)
\]

\[
C_{sp} = \frac{I t}{m \Delta V} \quad (2)
\]

where I and V represent the current and potential used in the CV, \( \mu \) is the scan rate (V.s⁻¹), m represents active materials mass (g), \( \Delta V \) is the potential discharge window, I represents the constant discharge, and t is the time of discharge (s).

PANI’s \( C_{sp} \) is averagely high at a low scan rate of 8 mV.s⁻¹, as tabulated in table 1. At low scan rates, electrosorption capacitance is frequently large because scattered ions from the solution would more easily contact the electrode surface, resulting in enhanced ion surface adsorption/desorption [7]. With high scan rates, nevertheless, the effective inner-surface adsorption of ions reduced. Thus, the greater the scan rate, the lower and more stable the specific capacitance achieved, suggesting that the electrodes had fewer ions deposited in them [8]. This demonstrates that the ions don’t have sufficient time to reach the electrode material’s overall electrochemical surface.

<table>
<thead>
<tr>
<th>Scanrate (mV.s⁻¹)</th>
<th>Specific capacitance, ( C_{sp} ) (F.g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Carbon</td>
</tr>
<tr>
<td>8.0000</td>
<td>251.60</td>
</tr>
<tr>
<td>10.0000</td>
<td>239.82</td>
</tr>
<tr>
<td>20.0000</td>
<td>170.80</td>
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<tr>
<td>50.0000</td>
<td>63.15</td>
</tr>
<tr>
<td>100.0000</td>
<td>22.62</td>
</tr>
</tbody>
</table>

Based on Table 1, it is apparent that the highest specific capacitance was achieved using carbon felt, followed by carbon and stainless steel electrode. This is mainly attributable to its the high surface area owing to its porous morphology and dense fiber network in carbon felt materials which enable PANI to polymerize on top of the electrode compared to others [9]. Additionally, carbon felt has noticeable dissimilar textures from carbon since it is made of unwoven, randomly aligned carbon fibers. In contrast, stainless steel delivers the low specific capacitance compared to carbon felt and carbon. It's possible that stainless steel had already attained electrochemical stability since no redox peaks were seen during CV measurements [10]. PANI is a very thin coating that does not spall off and inhibits further oxidation of the stainless steel, resulting in no redox reaction on the stainless steel electrode. Carbon felt was used to further study different parameters that could affect and improve the specific capacitance for SCs application.
Figure 2 (a) demonstrates the CV measurements of the prepared electrodes with and without pre-treatment. The aerial-specific concentration on the treated carbon felt electrode was greater than it was on the untreated electrode. The carbon felt with treatment is higher than without treatment due to the pore size which allows access to hydrated ions, which is significant because pore size is essential for ion movement inside carbon materials [11]. Furthermore, carbon felt has a high surface area and porosity, allowing it to provide a large number of redox reaction sites as well as excellent electrolytic efficiency [12]. As a result, it primes the electrode surfaces for a more effective inclusion of PANI [5]. Meanwhile, figure 2 (b) shows that the specific capacitance in different type of dopants-electrolyte for treated and untreated electrode. Overall, the treated electrode is relatively higher compared to untreated electrode. The electrode which was treated with H$_2$SO$_4$ as the dopants and electrolyte showed the highest specific capacitance, recorded at 300.73 F.g$^{-1}$. Ultimately, having a good surface area and adequate access to the electrolyte allow for the transmission of charge and ideal storage.
One of PANI fascinating features are its controllable electric behaviour whereby its determined by the amount of polymerization and oxidation states. The degree of polymerization is determined by the pH of the solution used to produce it, and an acidic pH is preferable for generating PANI with long chains [13]. Furthermore, depending on the dopants, the amount of electrons on the polymer backbone can be lowered or raised [14]. Thus, as depicted in figure 3 (a) inorganic acids like HCl and H₂SO₄ were employed as the dopants and compared. Meanwhile, figure 3 (b) compares the specific capacitance of the PANI- carbon felt electrode prepared by using different acidic medium.

Based on the figure below, generally in both electrolytes used (H₂SO₄ and ferrocyanide), electrode doped using H₂SO₄ yields higher specific capacitance. With H₂SO₄ as the dopants and electrolyte, the maximum specific capacitance was achieved. In terms of CV measurements and specific capacitance, H₂SO₄ is determined to be more efficient than HCl. Nunoo, Joseph Asare Awuah [15] found that PANI- H₂SO₄ have higher conductivity than PANI-HCl which might be related to polaron charge carriers responsible for the increased conductivity in H₂SO₄ doped PANI. This is also in line with Nde, Tamfuh [16] which discover that H₂SO₄ is better compared to HCl as the acid activation. The conductivity is substantially dependent on the anion present and follows the pattern HSO₄⁻ >Cl⁻ >NO₃⁻ >PO₄³⁻ > ClO₄⁻ > COO⁻, where this reliance may be due to electrolyte species adsorption.

![Figure 3](image.png)

**Figure 3.** (a) CV measurements of carbon felt electrodes prepared with different dopants, recorded in three electrode setups at 8 mV.s⁻¹ (b) Corresponding anodic current determined
The findings demonstrate in figure 4 (a) that the electrode exhibit greater electrochemical response and sensitivity toward H₂SO₄ compared to ferrocyanide as electrolyte. The examined redox system of H₂SO₄ shows a modest pair of reversible redox peaks with cathodic and anodic peak potential, as shown in the CV. In comparison to ferrocyanide solution, H₂SO₄ aqueous solution has a higher ion conductivity/concentration. PANI is often doped under acidic circumstances, its electrical conductivity significantly reduces as the pH of the aqueous electrolytes rises. Consequently, almost all PANI-based SCs have used acidic aqueous electrolytes, notably the 1 molL⁻¹ H₂SO₄ electrolyte [17]. The specific capacitance at lower scan rate shows that carbon felt using both H₂SO₄ as dopants and electrolytes produce the higher capacitive behavior compared to others. As seen in figure 4 (b), the specific capacitance falls as the scan rate increases. Carbon felt electrodes using H₂SO₄ as both dopants and electrolytes demonstrated the greatest specific capacitance.

Figure 4. (a) CV measurements of carbon felt electrodes with different electrolyte, recorded in three electrode setups at 8 mV.s⁻¹
(b) Specific capacitance of carbon felt electrodes in different electrolyte
Conclusions

In summary, PANI-carbon felt demonstrated enhanced electrochemical performance compared to other electrode material. The effects of scan rate, dopants, and electrolyte on polyaniline was studied. 300.73 F.g⁻¹ is the highest specific capacitance, with H₂SO₄ as an electrolyte and dopant at a low scan rate. These findings highlight the potential of carbon felt materials, particularly as electrodes for SCs devices. Further improvement on the carbon felt surface can be improved and optimize that would lead to a better utilization of carbon felt as electrode.

Conflicts of Interest

The author(s) declare(s) that there is no conflict of interest regarding the publication of this paper.

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References


