A COMPREHENSIVE STUDY ON SYNTHESIS, CHARACTERIZATION, AND ELECTROCHEMICAL PERFORMANCE OF PVA AND PAN-DERIVED CARBON FIBERS FOR ENERGY STORAGE*

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Abstract

This research investigates the synthesis, characterization, and electrochemical performance of electrospun carbon fibers derived from Polyvinyl Alcohol (PVA) and Polyacrylonitrile (PAN) precursors under a nitrogen atmosphere. The electrospinning process produces nanofiber mats, which are subsequently carbonized in a nitrogen environment to form carbon fibers. Comprehensive characterization using Raman spectroscopy, Energy Dispersive X-ray Fluorescence (EDXRF), X-ray Diffraction analysis (XRD), and Scanning Electron Microscopy (SEM) elucidates their structural and elemental properties. The synthesized carbon fibers are then prepared for electrodes, and their electrochemical properties, including specific capacitances and energy densities are evaluated. This research seeks to determine the suitability of PVA and PAN-based carbon fibers for advanced energy storage applications, potentially advancing the development of high-performance super capacitors and batteries for sustainable energy solutions

Keywords: Carbon fibers, electro spinning, cyclic voltammetry, energy storage.

Introduction

In an era marked by the ever-increasing demand for sustainable energy solutions, the exploration and development of advanced materials for energy storage applications have become paramount. Carbon fibers, owing to their exceptional properties, have emerged as promising candidates in this pursuit. This research proposal embarks on a comprehensive investigation into the synthesis, characterization, and electrochemical evaluation of electro spun carbon fibers derived from two distinct precursors: Polyvinyl Alcohol (PVA) and Polyacrylonitrile (PAN). These carbon fibers, synthesized under a nitrogen-rich environment, hold the potential to revolutionize the landscape of energy storage devices, such as super capacitors and batteries.

The process begins with the electro spinning of PVA and PAN solutions, yielding nanofiber mats that serve as the foundational materials for subsequent carbonization. Carbonization is executed in a nitrogen atmosphere, a critical step that imparts unique properties to the resulting carbon fibers. The structural and elemental properties of these fibers are meticulously investigated through advanced techniques, including Raman spectroscopy, X-ray Diffraction (XRD) analysis, and Scanning Electron Microscopy (SEM).

Furthermore, this research endeavors to bridge the gap between material synthesis and practical application by integrating these carbon fibers into electrodes. Through a thorough electrochemical evaluation, encompassing specific capacitance and impedance measurements, we aim to gain a deep understanding of their performance in real-world energy storage scenarios.

Ultimately, this research aspires to elucidate the potential of PVA-derived and PAN-derived carbon fibers as high-performance materials in the realm of energy storage. The insights garnered from this study hold the promise of propelling the development of sustainable and efficient energy storage solutions, contributing significantly to our collective journey towards a greener and more energy-conscious future.

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Materials and Methods

Materials

The chemical reagents used were polyvinyl alcohol (PVA) (Mw 80,000), polyacrylonitrile (PAN), dimethylformamide, iodine and distilled water in pure condition for preparing nanofibers. Potassium Chloride (KCL) (1 M) solution was used as electrolyte solution.

Characterization

The characterization of PVA-derived and PAN-derived carbon fibers were analyzed by X-ray diffractometer (Rigaku-RINT 2000). Raman spectra of PVA and PAN carbon fibers were also recorded with Horiba Lab RAM HR Evolution. The surface morphology of the PVA and PAN carbon fibers were examined with Scanning Electron Microscope (JEOL-JSM 5610LV). The cyclic voltammetry (CV) were measured using a three electrodes system to analyze the characteristics of the capacitance, impedance, electrical adsorption, and desorption of the fabricated PVA and PAN carbon fibers electrodes.

Experimental

Preparation of Electrospun Fibers

Polyvinyl Alcohol (PVA) 13 wt% solutions were prepared by dissolving PVA powder 13 g in 100 ml of distilled water. PVA powder was stirred into the distilled water at room temperature for 30 min. Then the temperature was gradually raised to 80°C while the mixture was constantly stirred for 5 hrs to obtain homogenize the solution. The transparent PVA solutions obtained were refrigerated overnight. Polyacrylonitrile (PAN) 6 wt% was dissolved in DMF solution. This mixture was continuously stirred at 60°C for 3 hrs until a homogeneous solution was obtained and then cooled down to room temperature.

Electrospinning method was used for the preparation of nanofibers. PVA and PAN solutions were loaded into the syringe which is connected to a needle via a flexible tube. The needle was connected to a high-voltage DC power supply. The syringe was loaded to the syringe pump to control the flow rate of the solution. After switching on the power supply and syringe pump, PVA and PAN fibers were collected to the rotating collector which was covered by aluminum foils. The processing parameters were given in table 1. The fiber collection time was set to 3 hrs. Finally, PVA and PAN fibers were found on the aluminum foils.

Carbonization

Before carbonization process, firstly PVA fibers were heated ionization treatment. Electrospun PVA fibers were iodized by adding iodine crystals into a closed glass vessel for 24 hrs at 80°C. During the heating, the iodine was vaporized in that vessel. The color of the samples became dark brown due to complex formation of the sample with iodine. After that, OTF-1200X-S high temperature vacuum tube furnace was used for the carbonization process. Carbon fiber synthesis was performed into two-step calcination process. The softening point of PVA fibers were accepted at 215–224°C. Thus, to obtain a stable process, pre-heat treatment should be employed before the carbonization due to the fusion of the nanofibers at high temperatures. Firstly iodinated PVA fibers were calcinated for 1 hr at 180 °C under atmospheric conditions. Then, the second calcination step was carried out at 500°C for 6 hrs with 5°C min^{-1} heating rate under nitrogen environment.

Table 1 Processing parameters for electrospinning

voltage	15 kV
flow rate	0.2 mL/hr
needle-to-collector distance	15 cm
collector geometry and velocity	Cylinder, 8 m/s
Needle diameter	0.2 mm
Temperature	31 ºC
Humidity	42 %

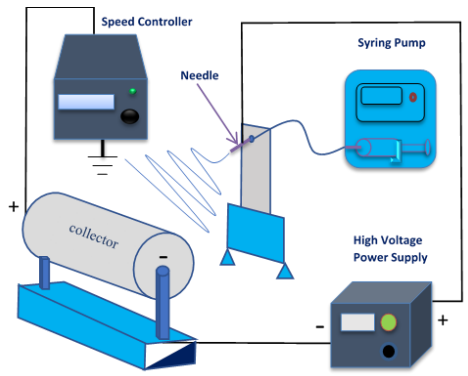


Figure 1. Electrospinning system setup

The carbonization process plays a crucial role in the manufacture of carbon fibers derived from Polyacrylonitrile (PAN). Prior to carbonization, PAN precursor fibers undergo a critical stabilization phase. This involves subjecting the fibers to heat in an oxidizing environment, typically air, at a temperature of 280°C for a duration of 1 hour, using a heating rate of 5°C per minute. During stabilization, the PAN molecules undergo cross-linking and cyclization reactions, reinforcing the fibers and reducing their susceptibility to shrinking during the subsequent carbonization stage. Following stabilization, the PAN fibers are advanced to the carbonization step, conducted at even higher temperatures within an inert atmosphere. Specifically, carbonization is carried out at a temperature of 950°C for a duration of 1 hour, with a heating rate of 5°C per minute in a nitrogen environment. This process entails the pyrolysis of the PAN fibers, leading to the elimination of most non-carbon elements such as hydrogen, oxygen, and nitrogen in the form of volatile gases. Consequently, this transformation results in the PAN fibers evolving into a state of nearly pure carbon, characterized by a hexagonal graphite-like crystal structure.

Praperation of Electrodes

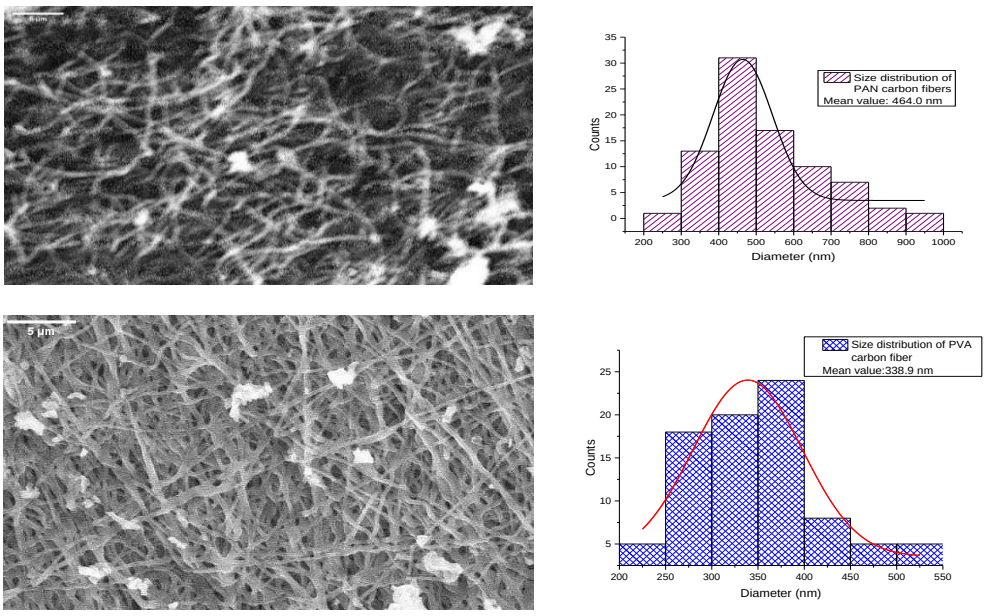
To prepare electrode materials, Copper tape was chosen to be used as a substrate because of its high electrical conductivity and low cost. The copper tape was cut into a 5 mm squares and then attached to acrylic sheets to make a flat and insulated surface on another side of electrode. The PVA-derived carbon fibers and PAN-derived carbon fibers were coated on the copper using spin coating method. The coated electrodes were dried at 70 ˚C in a drying oven for 30 mins to remove all organic solvents remaining in the micro pores of the electrode.

Results and Discussion

Morphology Analysis by Scanning Electron Microscope

The scanning electron microscope (SEM) images of carbon fibers reveal several important characteristics that are vital for understanding the material's structure and quality.

The average diameter of PVA-derived and PAN-derived carbon fibers are 339±11 nm and 464±13 nm respectively as shown in Fig 2. The size distribution of carbon fibers in the SEM images can be determined from σ values which are 138.9±40.1 for PVA and 186.9±33.7 PAN based carbon fibers respectively. Although PVA fibers have lass diameter than PAN fibers they have wider range of size distribution. In the preparation of polymer solutions, PAN was dissolved in the DMF solution which has faster rate of evaporation than water that used in PVA solution. So, the fiber size of PAN is larger than that of PVA. This range indicates that the fibers in the sample are relatively uniform in size, with a slight variation around the mean. The narrow size distribution suggests a consistent manufacturing process or controlled growth conditions for the fibers.



(a) (b)

Figure 2. SEM images and fiber size distributions of (a) PVA-derived and (b) PAN-derived carbon fibers

The SEM images also reveal that the formation of the carbon fibers is irregular. This irregularity can manifest as variations in fiber diameter, branching, or twists and turns in the fiber structure. Irregular fiber formation can occur due to factors such as variations in growth conditions. Another noteworthy observation from the SEM analysis is the absence of significant residual materials or contaminants on the surface of the carbon fibers. This finding suggests that the manufacturing or preparation process effectively removes impurities or residues, ensuring the purity and quality of the carbon fibers. the SEM analysis of the carbon fiber sample provides valuable insights into its size distribution, irregular fiber formation, and the absence of significant residuals. These findings are essential for both quality control and optimizing the material for current research.

XRD Analysis

The XRD pattern of PVA-derived and PAN-derived carbon fibers shown in figure 3 were obtained from X-ray diffraction analysis. The sharp peaks of PVA-derived carbon fibers at 2θ values of ≈26.6° corresponded to the reflection from the (002) plane was observed in XRD spectrum of carbon. The pattern revealed that the phase precipitated out in the sample was hexagonal structure. The observed characteristic diffraction peaks at 2θ ≈ 25.6° was corresponded to (002) crystalline plane of the PAN-derived carbon fibers. The (002) diffraction peak between individual carbon layers was an indicator of the degree of carbonization. (Eluyemi *et al.*, 2016).

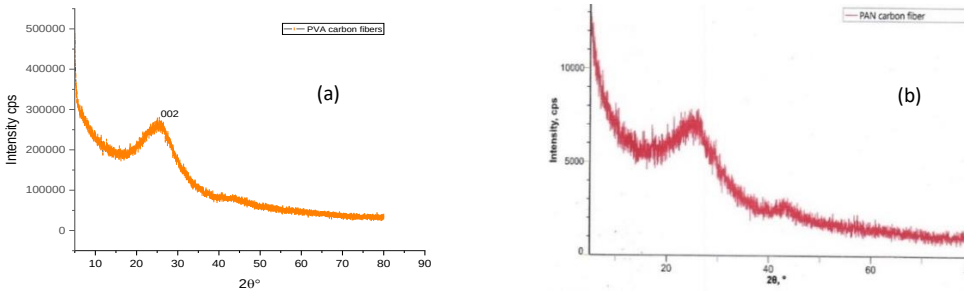


Figure 3. XRD patterns of (a) PVA-derived and (b) PAN-based carbon fibers

Raman Spectroscopy Analysis

Raman spectroscopy serves as an effective technique for assessing the proportions of structured and disordered regions within carbon-based structures (Choi, 2010). Fig. 3 displays Raman spectra for carbon fibers synthesized from PVA and PAN, highlighting distinctive characteristics. The carbon lattice for PVA-derived fibers appears at 1580.43 cm^{-1}, while PAN-based fibers exhibit it at 1559.21 cm^{-1}; both correspond to C=C stretching vibrations inherent to sp2-bonded carbon atoms. Conversely, the D band at 1344.26 cm^{-1} (PVA-derived) and 1327.32 cm^{-1} (PAN-derived) arises from phonon modes originating from sp2-bonded carbon atoms situated near localized lattice distortions (defects) in the graphitic network. The ratio of D to G bands (I_D/I_G) serves as an indicator of graphene material defects, with PVA-based and PAN-based carbon fibers displaying intensity ratios of 0.84 and 0.85, respectively. Furthermore, the presence of a peak at 2796.09 cm^{-1} in the PAN-based carbon fiber's 2D band spectrum indicates C-H stretching within PAN.

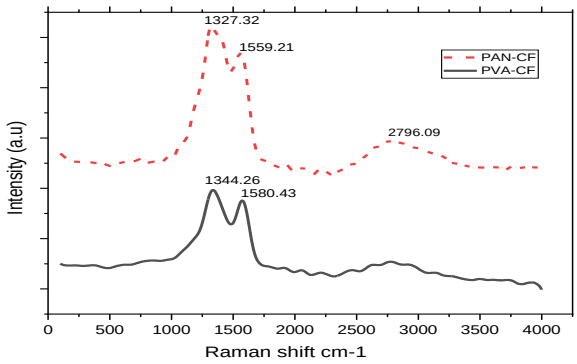
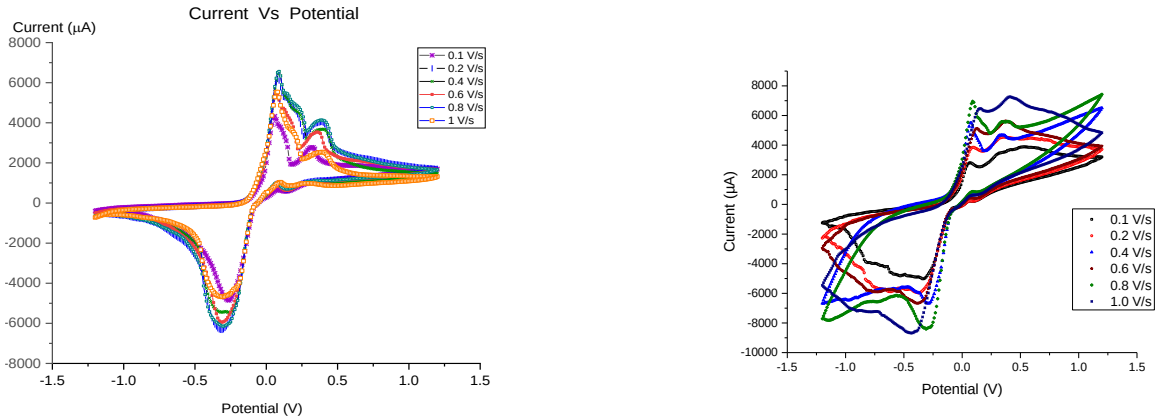


Figure 4. Raman spectra of PVA-based and PAN-based carbon fibers

Electrochemical Characterizations

The microstructural analysis and ion transport behavior of the electrospun carbon fibers materials were analyzed by cyclic voltammetry. The cyclic voltammetry (CV) prepared electrodes were carried out in KCl (1 M) electrolyte solution with three-electrode cell setup. The curves obtained in cyclic voltammetry for different scan rates: 0.1, 0.2, 0.4, 0.6, 0.8 and 1.0 Vs^{-1} are described in Fig.5(a) and (b), and the graphs show the battery nature rather than the pseudocapacitive behavior of the electrodes. By increasing scan rate, the cathodic peaks move towards lower potential whereas the anodic peaks shift towards higher voltage proposing an electrochemical reversibility. In the cyclic voltammograms of PVA-derived carbon electrode, there are double reduction and oxidation peaks. The main reason is electrochemical reactions of the iodine residuals in carbon fiber. PVA fibers were made by iodine treatment to enhance the stability during the carbonization process. The EDXRF analysis of PVA-derived carbon fibers gives the information of iodine and nitrogen residual in the sample. Iodine is known to undergo reversible redox reactions in the presence of various electrolytes. The presence of residual in the carbon fiber can lead to redox processes that appear as distinct peaks in the CV curve. Nitrogen doping can also introduce new redox-active sites on the carbon material. These nitrogen-containing functional groups can undergo redox reactions at specific potentials, resulting in additional peaks in the CV curve. There are extra reduction peaks in PAN-derived carbon fiber's voltammogram. Nitrogen doping can modify the electronic structure of carbon materials. Depending on the type and concentration of nitrogen dopants, it can change the conductivity and electron transfer kinetics of the electrode, leading to variations in the CV response.



(a) (b)

Figure 5. Cyclic voltammograms of (a) PVA-derived and (b) PAN-derived carbon fibers

The specific capacitance values of PVA-derived carbon fiber and PAN-derived carbon fiber electrodes were determined from the area enclosed by the CV curve of different scan rates using the following equation.

$$C_p = \frac{A}{2kmΔV}$$

A is area enclosed by the CV curve, k is a scan rate, m is the mass of the active material and ΔV is the potential window. The results obtained are given in table 2 and Fig 6. At all scan rates, except 0.1V/s the PAN-derived carbon fiber electrodes consistently exhibit a higher specific capacitance (Cp) compared to the PVA-derived electrodes. This suggests that the PAN-

derived carbon fibers have a greater ability to store electrical charge per unit mass than PVA-derived fibers.

The differences in specific capacitance can be attributed to variations in the microstructure, surface area, and chemical properties of the two types of carbon fibers. It's evident that as the scan rate increases, both types of carbon fibers experience a decrease in specific capacitance. This behavior is typical for supercapacitor electrodes, where higher scan rates may limit the kinetics of charge storage, resulting in reduced capacitance. The PVA-derived fibers exhibit a more significant drop in specific capacitance with increasing scan rate compared to the PAN-derived fibers. This suggests that the PAN-derived fibers may have better charge kinetics or ion diffusion characteristics.

Energy density (Eg) is a crucial parameter as it quantifies the amount of energy a supercapacitor can store per unit mass. In terms of energy density, the PAN-derived carbon fibers consistently outperform the PVA-derived fibers across higher scan rates. This implies that for energy storage applications, the PAN-derived carbon fibers are more favorable due to their higher energy density. The data highlights that PVA-derived carbon fibers offer superior specific capacitance and energy density compared to PAN-derived fibers at lower scan rate. On the other hand, PAN based fibers have better performance than PVA ones. However, the choice of carbon fiber should consider other practical factors as well as specific application requirements.

Table 2. Specific capacitances and energy densities of the carbon fibers electrodes

Scan rate (V/s)	PVA-derived carbon fiber		PAN-derived carbon fiber	
	Cp (F/g)	E_g (J/g)	Cp (F/g)	E_g (J/g)
0.1	19.09	54.99	12.80	36.85
0.2	4.40	12.67	8.52	24.53
0.4	2.92	8.42	5.94	17.11
0.6	2.25	6.49	3.41	9.82
0.8	1.72	4.96	2.70	7.77
1.0	1.21	3.49	2.55	7.35
1.2	0.80	2.31	2.85	8.21

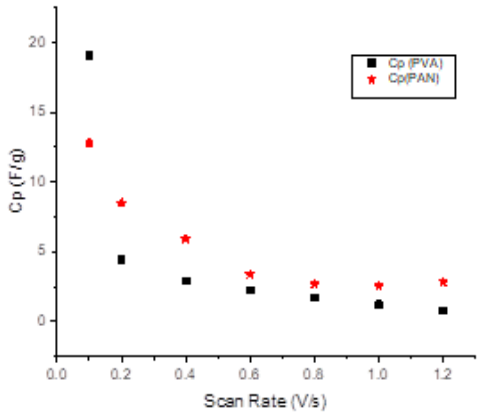


Figure 6. Dependence of specific capacitances of carbon fibers on scan rates

Conclusion

In this study, a comprehensive analysis of carbon fibers was conducted using various techniques, including scanning electron microscopy (SEM), X-ray diffraction (XRD), Raman spectroscopy, and electrochemical characterizations, providing valuable insights into their structural and performance characteristics. SEM images revealed that the carbon fibers exhibited a relatively uniform size distribution, indicating consistent manufacturing processes and high purity, as the absence of contaminants on their surfaces was observed. XRD analysis confirmed their crystalline nature and provided information on the degree of carbonization.

Raman spectroscopy indicated the presence of ordered and disordered regions within the carbon fibers, with both PVA-derived and PAN-derived fibers showing similar levels of disorder. Additionally, nitrogen doping was identified in PAN-derived fibers, influencing their electronic structure and electrochemical behavior. Electrochemical characterizations through cyclic voltammetry revealed battery-like behavior with redox reactions involving iodine residuals in PVA-derived fibers and nitrogen-containing functional groups in PAN-derived fibers. Specific capacitance and energy density varied with scan rates, with PVA-derived fibers excelling at lower rates and PAN-derived fibers outperforming at higher rates.

In summary, this research underscores the importance of tailoring carbon fiber selection to specific application requirements. PVA-derived fibers offer advantages in specific capacitance and energy density at lower scan rates, while PAN-derived fibers excel under high-rate conditions. These findings contribute to a better understanding of carbon fiber properties, guiding their utilization in diverse applications, such as energy storage and composites, with potential for further optimization.

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