

# Electrode Fabrication, Material Characterization and Capacitance Measurement Studies of Polyacrylonitrile/Polypyrrole(PAN/PPY) Composite

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**Abstract:** For the fabrication of the electrode, the Polyvinyl alcohol/polyaniline composite was prepared by the sol-gel method. The electrical conductivity of the composite was determined on compressed pellets by using a 4-in-line-probe dc electrical conductivity-measuring instrument. The electrical conductivity measurement studies revealed that the composite possessed the electrical conductivity in the range of  $10^{-4}$  to  $10^{-2}$  S cm<sup>-1</sup>, i.e., in the semiconductor region and followed the Arrhenius equation. The thermal stability of the composite material (HCl treated) in terms of dc electrical conductivity retention was studied under isothermal conditions (at 50, 70, 90, 110, 130, and 150 °C) at 15 min intervals. The stability of the material (HCl treated) in terms of electrical conductivity retention was also monitored for five cycles at increasing temperatures with 1 h intervals. The composite material was found thermally and environmentally stable in terms of dc electrical conductivity retention.

**Keywords:** Electrode fabrication; characterization; thermal stability; organic/organic composite; polyvinyl alcohol/polyaniline.

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## 1. Introduction

Supercapacitors are known as electrochemical storage devices that can store the energy and power densities to complement the function of batteries and conventional capacitors for storing energy and delivering power [1]. For the development of electrochemical devices, various types of electrode materials have been extensively investigated because the property of the electrode materials directly influences the performance of supercapacitors. However, activated carbon is one of the most important conventional supercapacitor electrode materials [2,3]. It has been significantly used due to its low cost, large capacitance, and long cycling life [4]. However, the energy storage mechanism of activated carbon is through a double-layer process, resulting in lower energy density and specific capacitance comparing with the energy storage mechanism in redox reaction [5]. Therefore, some of the conducting polymers like polyaniline and polypyrrole have also been used because of their high conductivity, low cost, easy polymerization, and reversible doping/dedoping property [6-10]. However, these intrinsically conducting polymers have several disadvantages of low processability and mechanical stability. To solve these problems, conducting polymers of various conducting composites have been synthesized and studied by several researchers [11]. In the present work,

polyacrylonitrile/polypyrrole (PAN/Ppy) composite was synthesized, and the structure, composition and electrochemical performance were examined.

## 2. Materials and Methods

The reagents used for the synthesis of the material were obtained from CDH, Loba Chemie, E- Merck, and Qualigens (India Ltd.). All other reagents and chemicals were of analytical reagent grade. A four-in-line probe electrical conductivity-measuring instrument, Scientific Equipment (India), was used for measuring the dc electrical conductivity. A hydraulic pressure instrument was used for making pellets of sample materials. An electronic balance (digital), Sartorius (Japan), model 21 OS was used for weighing purposes.

### 2.1. Preparation of composite material.

Various samples of polyacrylonitrile/polypyrrole (PAN/Ppy) were prepared by mixing one volume of 5 weight% solution of polyacrylonitrile solution with different volumes of pyrrole (approximately 3.33 wt% solutions in toluene) as given in Table 1. FeCl<sub>3</sub> solution (0.1 M) was mixed thoroughly with the PAN/Pyrrole. Continuous stirring was done during the addition of FeCl<sub>3</sub> solution, slowly the white gel of precipitate gel PAN/Ppy turned first to green and then to black. The reaction mixture was kept for 24 h under ambient condition (25 ± 2 °C). The reaction mixture was then kept for 24 h under ambient conditions (25 ± 2 °C). Then the polypyrrole based composite gel was filtered off, washed with 0.75 M HCl and then washed thoroughly with DMW to remove excess acids and any adhering traces of ferric chloride. After filtration, the gel was dried at 50 °C in an air oven for 48 h. The dry product was then crushed into small granules when immersed in DMW. The material was again washed with acetone in a soxhlet, finally dried at 50 °C and kept in a desiccator. Hence a number of composite samples of PAN/Ppy were prepared.

### 2.2. Preparation of composite pellet.

The polyacrylonitrile/polypyrrole (PAN/Ppy) composite material and polystyrene were ground into fine powder separately using mortar pestle and sieved through 200 mesh (granule size <0.07 mm) sieve. The composite material (0.5 g) was mixed with 0.2 g of polystyrene with the help of mortar and pestle. The pellets of this material were made at room temperature with the help of a hydraulic pressure instrument at 25 KN pressure for 20 min. The pellet casting die was placed in an oven maintained at 200 °C for about 1 h to equilibrate the reaction mixture [12].

**Table 1.** Conditions of the preparation of PAN/Ppy composite.

Samples	Mixing volume ratio (v/v)			Appearance of beads after drying
	PAN 5% in DMF	FeCl <sub>3</sub> (1 M in 1 M HCl)	Pyrrole in toluene (33.33%)	
S-1	1	1	1	Black
S-2	1	1	2	Black
S-3	1	1	3	Black
S-4	1	1	4	Black
S-5	1	1	5	Black

### 2.3. X-ray diffraction (XRD) study.

X-ray diffraction pattern of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material was recorded by Miniflex-II, X-Ray diffractometer (Rigaku Corporation) with Cu K $\alpha$  radiation.

#### 2.4. Fourier transform infrared (FTIR) spectroscopic study.

The FTIR spectrum of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material was recorded by the Interspec-20 FTIR spectrometer, Spectrolab (U.K.). The sample compartment was 200 mm wide, 290 mm deep, and 255 mm high. The entrance and exit beam to the sample compartment were sealed with a coated KBr window, and there was a hinged cover to seal it from the environment.

#### 2.5. Thermogravimetric analysis (TGA)/differential thermal analysis (DTA)/ differential thermogravimetric analysis (DTG).

The degradation process and thermal stability of polyacrylonitrile/polypyrrole (PAN/Ppy) composite were investigated using thermogravimetric analysis (TGA) (Exstar TG/DTA-6300), under a nitrogen atmosphere using a heating rate of 20 °C per min from 28 to 800 °C.

#### 2.6 Scanning electron microscopic (SEM) studies.

Scanning electron microscopic images of polyacrylonitrile/polypyrrole (PAN/Ppy) composite was taken by JEOL, JSM, 6510-LV, (Japan) scanning electron microscope at an accelerating voltage of 20 kV. The sample was mounted on a copper stub and sputter-coated with gold to minimize the charging.

#### 2.7. Energy dispersive x-ray analysis (EDX) studies.

Energy-dispersive X-ray analysis studies were performed to get the elemental composition of polyacrylonitrile/polypyrrole (PAN/Ppy) composite while taking scanning electron microphotographs of chemically prepared polyacrylonitrile/polypyrrole (PAN/Ppy) composite by JEOL, JSM, 6510-LV, (Japan) scanning electron microscope.

#### 2.8. Measurement of capacitance.

The capacitance of polyacrylonitrile/polypyrrole (PAN/Ppy) composite was evaluated by cyclic voltammetry in 0.1 M NaClO<sub>4</sub> aqueous electrolyte within the potential range of -3.0V to 3.0 V at various scan rates. The capacitance characteristics of the polyacrylonitrile/polypyrrole (PAN/Ppy) composite was carried out in 0.1 M NaClO<sub>4</sub> aqueous solution in a three-electrode cell, as mentioned above. The specific capacitance can be obtained from the CV curves by the following equation:

$$C_{sp} = \frac{i}{sm} \quad (\text{F g}^{-1})$$

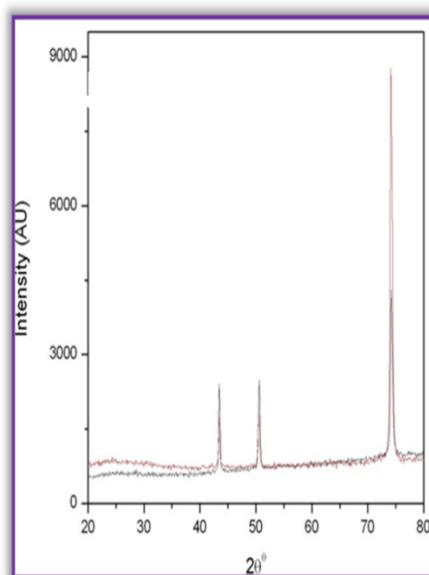
Here *i* present the average cathodic current; *s* and *m* present the scanning rate and the mass of the electrode, respectively [13].

### 3. Results and Discussion

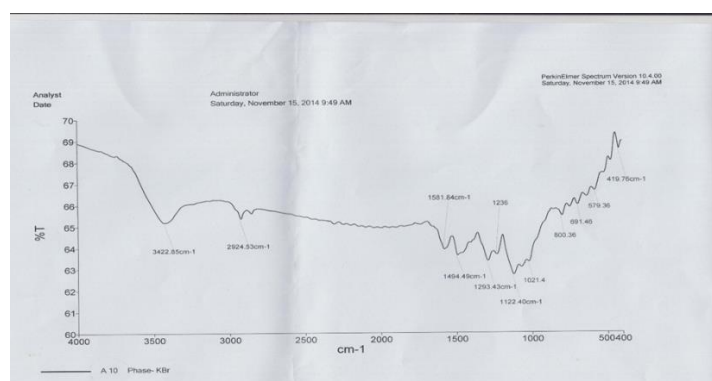
In this study, various samples of polyacrylonitrile/polypyrrole (PAN/Ppy) composite materials were prepared by the incorporation of polypyrrole into the matrices of PAN by mixing different concentrations (vol. %) of organic monomers pyrrole into the fixed volume of PAN solution. The variation of ambient temperature on electrical conductivity ( $\sigma$ ) of PAN/Ppy

composite samples was carried out, and sample (S-3) having high electrical conductivity was selected for further studies (Table 1). The X-ray diffraction analysis (Fig. 1) showed very strong peaks to confirm the crystalline nature of composite material and supporting the ordered arrangement of molecules.

FTIR spectra for the PAN/Ppy composite is shown in Fig. 2. A broadband dip around  $3500\text{ cm}^{-1}$  is expected for the N-H stretching vibrations [14, 15]. The band at  $1557.39\text{ cm}^{-1}$  is related to C=C/C-C stretching vibrations in the pyrrole rings. The band at approximately  $1452.43\text{ cm}^{-1}$  reflects C-N stretching vibrations in the rings. The peak at  $1316.38\text{ cm}^{-1}$  is attributed to C-N in-plane deformation modes, and a band related to C-H in-plane deformation vibrations is shown at  $1046.10\text{ cm}^{-1}$ . The bands at  $927.22$  and  $789.72\text{ cm}^{-1}$  are related to the C-H out-of-plane deformation vibrations of the polymer rings. The peak at  $685.05\text{ cm}^{-1}$  may be related to C-C out-of-plane ring deformation vibrations or C-H rocking. The positions of different peaks in the spectrum indicate the formation of composite by the combination of constituting components.



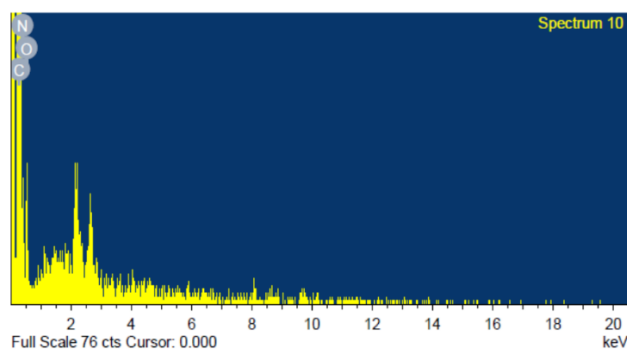
**Figure 1.** X-ray diffraction pattern of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material.



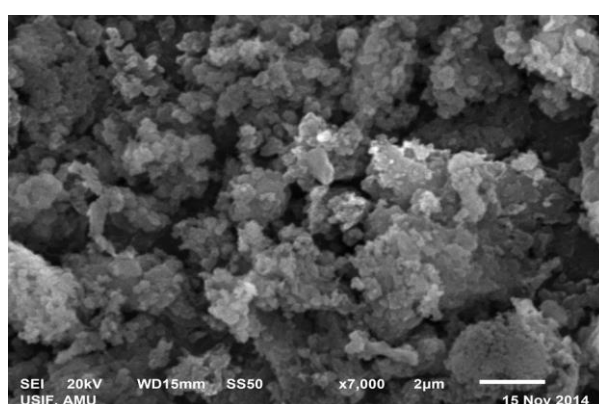
**Figure 2.** FTIR spectra of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material.

The energy dispersive X-ray analysis showed the presence of C, N, O confirming the formation of polyacrylonitrile/polypyrrole (PAN/Ppy) composite (Fig. 3). The weight percent elemental composition of the constituents of the composite is as C=61.63%, N=27.12, O=13.84.

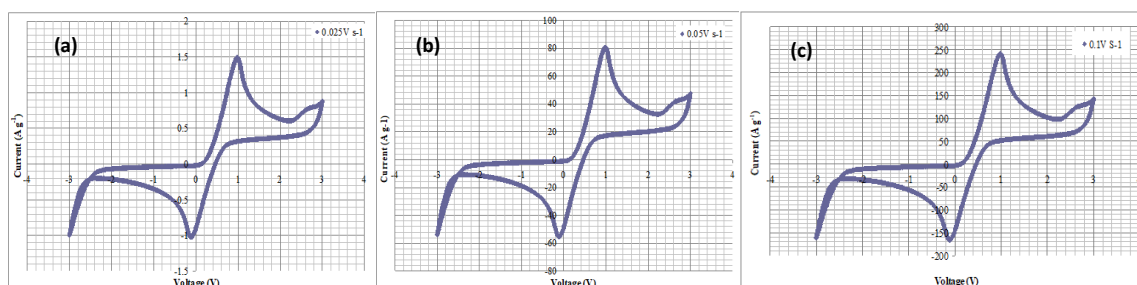
The SEM image of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material is shown in Fig. 4. The scanning electron micrograph of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material showed uniform granular surface morphology.



**Figure 3.** X-ray photoelectron spectra of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material.



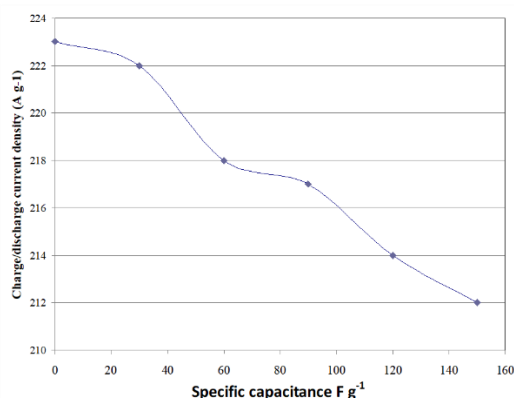
**Figure 4.** The SEM image of polyacrylonitrile/polypyrrole (PAN/Ppy) composite material.



**Figure 5.** Cyclic voltammety curves in 0.1M NaClO<sub>4</sub> with different scan rates (a) 0.025 V s<sup>-1</sup>, (b) 0.05 V s<sup>-1</sup> and 0.1 V s<sup>-1</sup> for polyacrylonitrile/polypyrrole (PAN/Ppy) composite material electrode.

It can be seen from cyclic voltammety curves that the composite showed redox cyclability at each scan rate (Fig. 5 a-c). It is also clear from the graphs that the composite showed the capacitive cyclic voltammety curve [13]. The current density is increasing with the increase in the scan rate, and a maximum of the anodic and cathodic current density of 248 and 149 A g<sup>-1</sup>, respectively, was achieved during cyclic voltammety. The specific capacitance was also calculated from the cyclic voltammety curve using the above-mentioned formula and was found to be 222 F g<sup>-1</sup>. Fig. 6 showed the galvanic charge/discharge curves of polypyrrole/PAN composite in a three-electrode system. It is clear from the figure that as the charge/discharge current density increases from 0 A g<sup>-1</sup> upto 222 A g<sup>-1</sup>, the specific capacitance of the electrode is retained for about 95%. This retention is the specific capacitance

of the electrode may be due to high redox cyclability of the electrode may be due to the presence of polypyrrole in polypyrrole/PAN composite.



**Figure 6.** Charge/discharge curve of polyacrylonitrile/polypyrrole (PAN/Ppy) composite electrode at different current density.

#### 4. Conclusions

In this study, a new polyacrylonitrile/polypyrrole (PAN/Ppy) composite was prepared and characterized by instrumental and electrochemical methods. The electrochemical characteristics of the composite showed good capacitive properties. The galvanic charge-discharge studies showed good capacitance retention at different current densities.

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#### Conflicts of Interest

The authors declare no conflict of interest.

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