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Synthesis, Characterization and CO2 Gas Sensing Response Of Conducting PTh/PVAc Composite Films

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Abstract: The gas sensing response of Conducting composite films of polythiophene (PTh) and poly (vinyl acetate) (PVAc) produced by chemical oxidative polymerization using a ferric chloride (FeCl3) oxidant solution in methanol was studied. The sensing response of composite film was investigated for different concentration of FeCl3 and CO2 gas at room temperature. It was observed that the resistance of films increases with concentration of CO2 gas. The response of film prepared with 0.70M concentration of FeCl3 to CO2 gas was found to be highest, and ~2.86 min response time and ~10.5 min recovery time. The films were then characterized using XRD, FTIR and TG-DTA techniques.

Keywords: Polythiophene; Polymer Composite Materials; Oxidant (FeCl3); CO2 gas.

1. INTRODUCTION

One of the most difficult challenges today is to find materials for gas sensors that have good sensing response, stability, selectivity, short response time and low temperature operation. A conducting polymer presents the property of changing the resistance of the sensing material when exposed to ambient gas atmosphere. Most of the commercially available sensors, based on metal oxides and operated at high temperatures, the sensors made of conducting polymers such as polypyrrole (PPy), polyaniline (PANI), polythiophene (PTh) and their derivatives, have many improved characteristics. They have high sensitivities and short response time; especially feathers are ensured at room temperature [1]. PTh is a conjugated polymer like polyacetylene (PA), poly (p-phenylene) (PPP), and PANI. It has a heterocyclic structure like PPy. Hence, it is obtained from the polymerization of thiophene through chain propagation by radical cations [2]. Among the known conducting polymers, PTh has been mostly highlighted due to its high conductivity [3]. It has very high application prospects due to high ionization potential and storage stability [4]. Many researchers [5-9] have extensively investigated structure, properties, function, and applications of PTh and its derivatives. The CO_2 gas, which is known as a greenh ouse gas, responsible for global warming, hence there is need of detection of it with sensing materials of high sensitivity.

In Present study presents CO_2 gas sensing application of PTh-PVAc composite films prepared by chemical oxidative polymerization method with the solution of ferric chloride ($FeCl_3$) oxidant in methanol with different concentrations of $FeCl_3$ viz. 0.55, 0.65, 0.70 and 0.75M. The films are characterized using FTIR, XRD and TG-DTA techniques.

2. EXPERIMENTAL

2.1 Preparation of PTh-PVAc Composite Films

Thiophene monomer, anhydrous iron (III) chloride (FeCl3), polyvinyl acetate (PVAc) and methanol from SD Fine Chemicals (AR grade) were used in the present study. The thiophene monomer was used as-received. PTh was synthesized at room temperature (303K) by mixing 0.4ml thiophene monomer with solution of oxidant FeCl3 (0.55M) and 0.5g PVAc in 10ml methanol. The mixture was then stirred for 2h by adding drop-by-drop 0.4ml thiophene monomer. When monomer added to solution of FeCl3/PVAc, a light brown homogeneous solution was obtained, this was then poured on chemically cleaned and levelled glass plate to prepare the films of composite. The thiophene polymerization progresses because the evaporation of solvent increases the oxidation potential of cast solution.

In similar way, the films were prepared with different concentrations of FeCl3 i.e. 0.65, 0.70 and 0.75M respectively.

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The thickness of films was measured by Digimatic Outside Micro meter (Series-293, JAPAN) having a resolution of ±0.0001mm. The thickness of the films was in the range of 15-24 µm. The electrodes of silver (Ag) were deposited on the surface of the film to measure the surface resistance. The cross sectional view of sensor film with Ag electrodes is as shown in fig.1. The optimal preparation parameters are large surface area, ohmic electrical contacts, rough surface area etc. The resistance of films was measured on Ultra high resistance meter (Zentech, Model-702A). Table 1 displayed the resistance of each film in air prepared with different concentrations of FeCl3 and their coding.

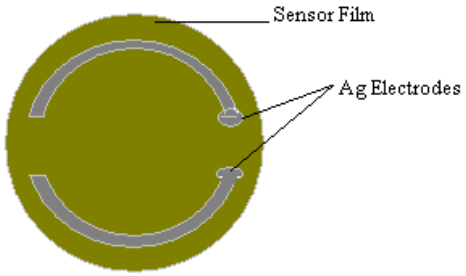

Fig.1. Cross sectional view of sensor film

Table 1. Resistance in air and thickness of films for different strength of FeCl3 with their coding.

Film Code	Concentration of $FeCl_3$ (M)	Thickness (µm)	Resistance in air (10^9 Ω)
S1	0.55	15	1.42
S2	0.65	20	1.67
S3	0.70	18	1.19
S4	0.75	24	1.15

2.2 Sensing Response Measurement

Sensing response of the films was measured for different concentration (ppm) of CO_2 gas at room temperature. The measurements were carried out in the laboratory of Department of Physics. The gas chamber having volume 5 L with an attached CO_2 gas flow meter (Flowtron, India) was used for keeping the sensors for testing. The gas flow was adjusted to 1 ml/min. The experiment was carried out 4-5 times for reproducibility of sensor response. Also the stability of sensors was checked at a fixed concentration of CO_2 gas for 4-5h. No change in sensor resistance was observed at that concentration.

2.3 FTIR, XRD and TG-DTA Characterizations:

The films were characterized by using infrared (FTIR), X-ray (XRD) and thermogravimetric- differential thermal analysis (TG-DTA). The IR spectra were recorded on Perkin-Elmer (Spectrum-1) FTIR spectrophotometer in KBr medium at room temperature in the range of 4000-650 cm^{-1}. The X- ray diffraction pattern of the films was recorded on a Philips-1730 (PANalytical) X-ray diffractometer using CuKα radiation (λ=1.54Å). The diffractogram was recorded in 2θ range of 10-100°. The thermal studies were carried out under argon atmosphere at a flow rate of 200 ml/min with a heating rate of 10°C/min on Perkin-Elmer 7 thermal analyzer.

3. RESULT AND DISCUSSION

3.1 FTIR analysis

FTIR spectra of samples S1 to S4 displayed in fig. 2. The spectra recorded in the range of 4000-650 cm^{-1} to confirm polymerization. Broadening of peaks obtained at and around 779, 856, 1016 and 1363 cm^{-1} for all samples indicates formation of polythiophene in counter polymer (PVAc) matrix. The slight shifting of peaks may be due to different concentration of $FeCl_3$. The peak around 3344 cm^{-1} is assigned for C-H stretching. The variation in intensity of bands due to C-H stretching is attributed to α-hydrogen of the terminal thiophene rings of the chains and can also be indicative of α-α coupling [10]. The conjugation band around 1632 cm^{-1} may imply polymerization and conductivity.

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3.2 XRD analysis:

The X-ray diffraction pattern of all samples shows amorphous nature (fig. 3). In each case, a broad peak was observed at about 2θ = 27.12 (S1), 28.79 (S2), 26.83 (S3) and 27.31 (S4). These peaks are due to the scattering from PTh chains at the interplanar spacing. However, the position of maximum intensity of the amorphous halos was different from each other for the all samples. It may be interesting to note that the peak position of these amorphous halos depends on the strength of oxidant ($FeCl_3$). The average chain separation can be calculated from the maxima using relation reported in reference [11]. The average chain separation was found to be 4.11, 3.87, 4.15 and 4.07 Å for S1, S2, S3 and S4 samples respectively.

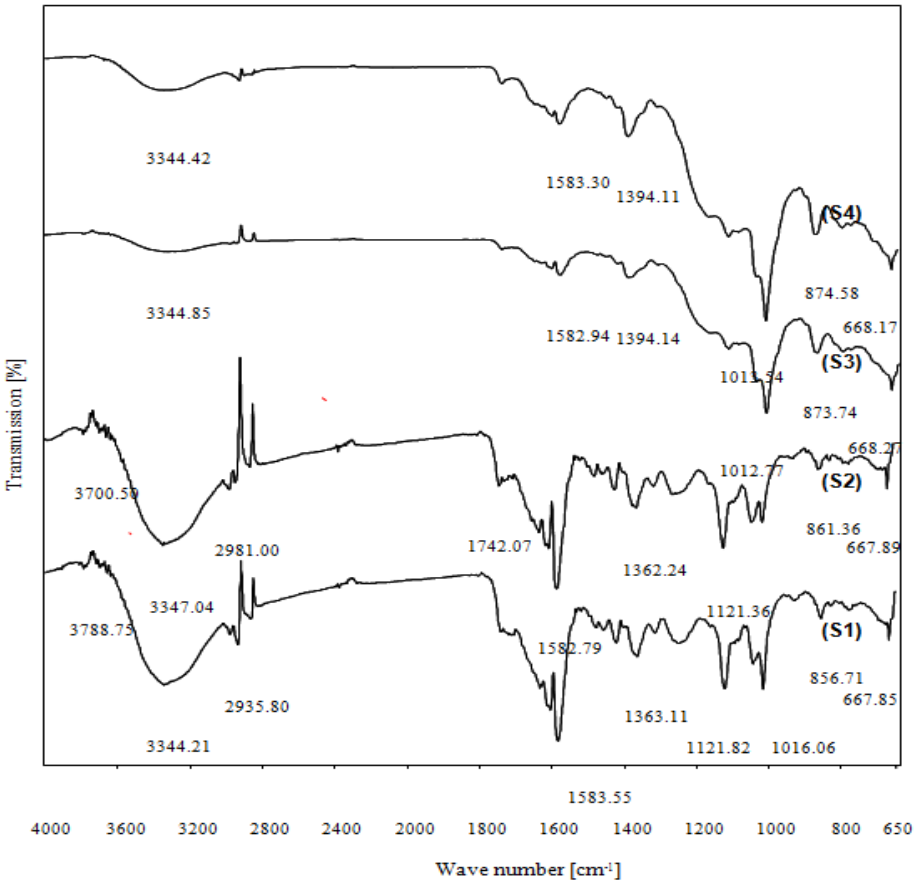

Fig. 2. FTIR spectra of PTh-PVAc composite films.

3.3 TG-DTA analysis

The TG and DTA of PTh-PVAc composite films S1 to S4 are plotted as a function of temperature in fig. 4. Continuous weight loss is observed for all samples. The weight loss at 50 °C is 7% for S1, 6% for S2, 4% for S3 and 5% for S4. The samples S3 show minimum weight loss and hence it is stable as compared to others. The ΔCp for S1, S2, S3 and S4 is found to be 0.113, 0.092, 0.229 and 0.216 J/g °C respectively. The maximum value of ΔCp is observed for sample S3. An endothermic peak appears for S1, S2, S3 and S4 at 70, 50, 75 and 78 °C respectively on the DTA curve. The change in enthalpy (ΔH) for S3 is –15.859 J/g. the total weight loss is also observed minimum i.e. 56% for S3. The thermal properties of S3, revealed by the TG-DTA analysis, are well reflected in the sensing application. In addition, the response to CO_2 is found to be better for this material.

3.4 Response to CO2 gas

The sensor response is defined as in reference [11]. The resistance of samples is found to increase with increase the CO_2 gas concentration. The response values increases linearly with CO_2 gas concentration for an exposition time of 5 min (Fig. 5) at room temperature (313 K) for the sample S2, however for others it is nonlinear. A saturation reach after certain ppm value for samples S1, S3 and S4 respectively.

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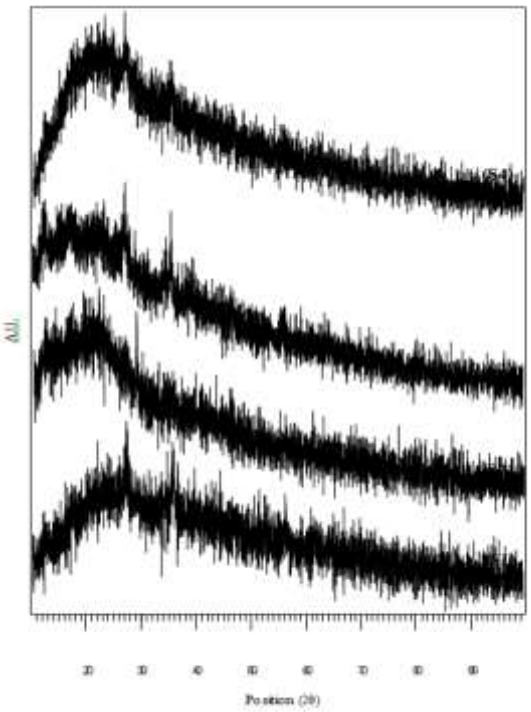

Fig. 3. XRD spectra of PTh-PVAc composite films.

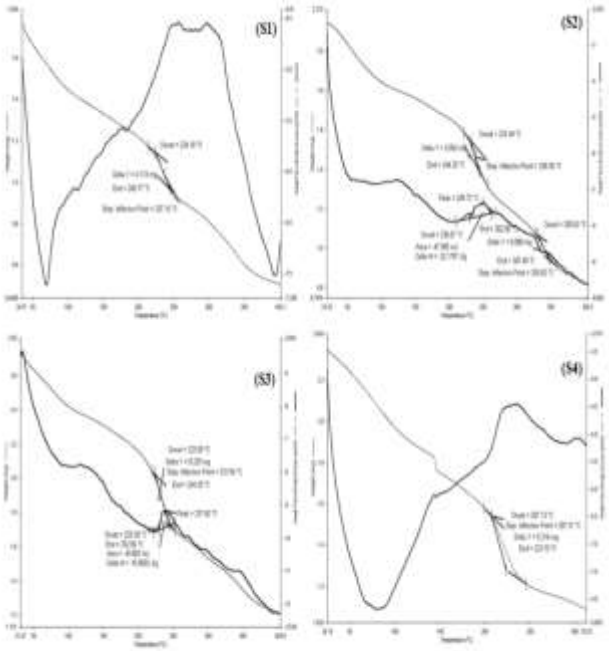

Fig. 4. TG-DTA plots of PTh-PVAc composite films.

The film S1 shows a saturation effect at 200 ppm CO_2 while other films show continuous response more or less upto 1000 ppm CO_2. The film S3 shows high response to CO_2 as compared all other films. The average sensor resistance change per ppm of CO_2 or sensitivity is found to be 0.83×10^6 Ω/ppm for S1, 1.03×10^6 Ω/ppm for S2, 2.1×10^6 Ω/ppm for S3 and 1.03×10^6 Ω/ppm for S4.

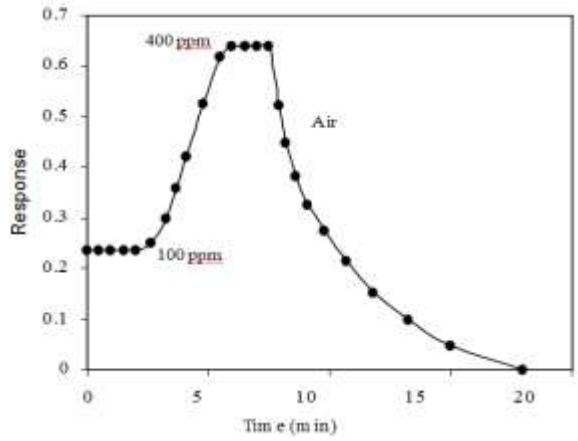

Fig. 5. Response of PTh-PVAc composite films as a function of CO_2 gas concentration at room temperature

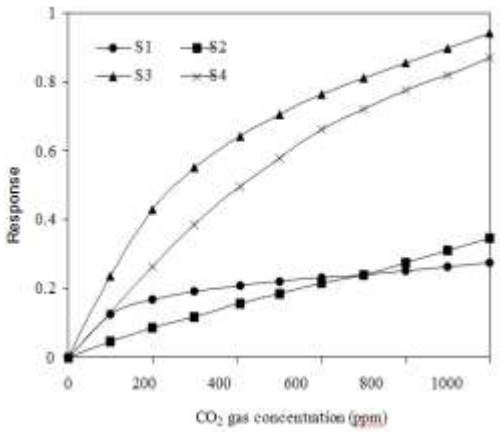

Fig. 6. Dynamic response of film S3 to 100 and 400 ppm CO_2 at room temperature

The dynamic response of film S3 to 100 and 400 ppm CO_2 at room temperature is as shown in fig. 6. The response time is found to be ~2.86 min to the change by 300 ppm of CO_2 gas. After about 7.5 min, the film S3 was exposed to air and time-dependant changes were recorded till the original value of resistance was reached (as shown in table 1). The recovery time is found to be ~10.5 min. Thus the film S3 has shorter response and recovery time at room temperature as compared to both the sensors reported in reference [11].

In general, the sensing behaviors of polymers are related to molecular interactions such as bonding, chemical reactions, dipole interaction and the van der Waals force between the analytes and polymer molecules. For polycrystalline films the behaviors are also related to the microstructure of the material. These interactions possibly modify the charge

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transportation inside the polymer molecules, or inside the grains, or at the grain boundaries of the nanostructures. At room temperature, phonon- assisted polaron hopping has been proposed to be the conduction mechanism for both inter- and intra- grain charge transportation inside conductive polymers [12]. At the polymer molecule level, parameters like polymer backbone planarity, side chain length, conjugation length, and reorganization energies [13] may influence the conductivity. The interactions between analytes and polymers most likely modulate one or more of these parameters, thus modulating the current density through the thin film polymers. This implies the possibility of multiple sensing mechanisms acting at the same time. Upon exposure of a specific polymer to a particular analyte, one mechanism possibly dominates the others, resulting in either a conductivity increase or decrease. As the microstructure is changed, by choice of polymer chemical construction or even by film processing conditions, the potential dominant sensing mechanism may change [9].

4. CONCLUSION

Composite films of PTh-PVAc prepared by chemical oxidative polymerization method with $FeCl_{3\ as}$ oxidant in methanol were used to investigate for sensing the $CO_{2\ gas}$ at room temperature. The film (S3) with 0.70M $FeCl_3$ showed highest response to CO_2 gas. XRD study reveals that average chain separation for S3 was found to be 4.15Å. The average resistance change per ppm of $CO_{2\ or}$ sensitivity for S3 was found to be 2.1×10^6 Ω/ppm TG-DTA analysis showed that S3 has total weight loss 56% and highest ΔCp. FTIR study confirms the polymerization of thiophene monomer.

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