PTh/PVAc composites-based sensor for CO_2 monitoring

S. A. WAGHULEY, R. S. BOBADE[a], A. V. KOHLE[b], G. G. MULEY, S. S. YAWALE[c], F. C. RAGHUVANSHI[d],
B. H. PAWAR, S. P. YAWALE[c]
Department of Physics, Sant Gadge Baba Amravati University, Amravati, 444 602, India
[a]Department of Physics, Prof. Ram Meghe Institute of Technology and Research, Badnera, 444 701, India
[b]Department of Physics, P. R. Patil College of Engineering and Technology, Amravati, 444 602, India
[c]Department of Physics, Government Vidarbha Institute of Science and Humanities, Amravati, 444 604, India
[d]Department of Physics, Vidhyabharati Mahavidhyaya, Amravati, 444 603, India

Polythiophe (PTh) has attracted special interest because of its high electrical conductivity, good environmental stability, ease and high flexibility in preparation, stability and good mechanical properties. The films of composite polythiophene (PTh)-poly (vinyl acetate) (PVAc) were prepared by chemical oxidative polymerization method with the solution of ferric chloride ($FeCl_3$) oxidant in methanol. Two sensor films of oxidant to monomer ratio 140 (PTh-I) and 150 (PTh-II) were used for CO_2 gas sensing investigation at room temperature (303 K). Sensitivity of sensors at different concentrations of CO_2 gas was measured. At certain higher concentration of CO_2 gas, a saturation effect was observed with both sensors. The response and recovery time of higher sensitivity sensor PTh-I were found ~2.86 and ~10.5 min respectively. The films were characterized through FTIR, XRD and TG-DTA techniques which may help to understand sensing mechanism. The increase in $FeCl_3$ increases the loading of PTh in the composite, which leads to coordination of more $FeCl_2^+$ ions with sulfur of PTh chains. Therefore effect of $FeCl_3$ is to increase the $FeCl_4^-$ ions in the composites. The CO_2 molecules affect the mobility of $FeCl_4^-$ ions of the PTh-PVAc surface, which results in a decrease of conductivity or an increase in film resistance.

1. Introduction

Polythiophene (PTh) compounds have very high application prospects due to their high ionization potential and storage stability. Recent developments in chemical gas sensor have provided simple, yet efficient strategic suited to environmental applications. Indeed, chemical sensors are often cheap, reliable, real time and field portable alternatives that do not compromise detection sensitivity.

Gas sensors are devices, which allow for the determination of information about the ambient gas atmosphere, consisting of a sensitive layer and signal transfer component the so-called transducer. The sensitive layer is optimized by a proper choice of materials while signal transfer component i.e. transducer by a suitable technology. The idea of using semiconductor as gas sensitive devices leads back to 1952, when Brattain and Bardeen [1] first reported gas sensitive effects on germanium. Later, Seiyama et al [2] and Taguchi [3] applied this discovery to gas detection by producing the first chemo-resistive semiconductor gas sensor. The type of metal-oxide sensor sold by Figaro [4] is known as 'Taguchi sensor'', named after the developer of SnO_2 sensor.

A sensor device that can keep to the actual limits depends on the overall performance of the chemical active layer. On the other hand, sensitive layers based on organic polymers inhibit many positive features and, consequently, are of wide interest and widely used in

chemical gas sensors. The first disclosure of the gas sensitive properties of conducting polymers was made at a conference in 1983 [5]. This involved the use of filter paper impregnated with polypyrrole (PPy), functioning as an ammonia gas sensor. The gas detention is based on fact that changes in the gaseous atmosphere after the properties of sensing layer in a characteristic way. In case of conductance sensors e.g. Metal Oxide (MOX) sensors, Conductive Polymer (CP) sensors, Ionic conductors etc. that are respond with changes in resistance/conductance, which is normally determined by 2-or 4-point resistance/conductance measurement.

In recent years, a great attention has been paid to the development and application of environmental gas sensors. CO_2 is very difficult to detect by conventional gas sensor due to high stability at ambient temperature. Many efforts have been made to develop chemical sensors base on solid-state technology, exploiting either the surface characteristic or the bulk conduction properties of ceramics. Based on the surface characteristic, there are two kinds of sensor, capacitive and resistive type (chemoresister). Maier et al [6] in 1986, first time demonstrated the CO_2 gas detection, since then many researchers [7-9] reported CO_2 gas detection by using MOXs, zeolites and CPs.

In comparison with most of gas sensors, based usually on metal oxides and operated to high temperatures (>200°C), and less sensitive and selective for low gas concentration, many researchers [10-12] have developed conductive polymers for gas sensor

applications, such as polypyrrole (PPy), polyaniline (PANI), polyacetylene (PAc), polythiophene (PTh) and their derivatives. The advantages of conducting polymer gas sensors are low cost, suitable for fabrication on various substrates, high sensitivity, short response time, good mechanical properties and room temperature operation [13, 14]. Conducting polymers are easy to be synthesized through chemical or electrochemical processes, and their molecular chain structure can be modified conveniently by copolymerization or structural derivatives.

Resistive type conducting polymer gas sensors are the most common type of sensors [15-17], called chemoresistor, whose electric resistance is sensitive to chemical environment. They can be fabricated through cheap and convenient process.

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 [18]. Among the known conducting polymers, PTh has been mostly highlighted due to its high conductivity [19]. It has very high application prospects due to high ionization potential and storage stability [20]. Many researchers [21-23] have extensively investigated structure, properties, function, and applications of PTh and its derivatives.

In the present work, sensor films of composite PTh-PVAc prepared by chemical oxidative polymerization method with oxidant to monomer ratio 140 (PTh-I) and 150 (PTh-II). The sensing application of films for CO_2 gas is studied. They are characterized through FTIR, XRD and TG-DTA techniques.

2. Experimental

2.1 Preparation of PTh-PVAc composite films

Thiophene monomer, anhydrous iron (III) chloride ($FeCl_3$), polyvinyl acetate (PVAc) and methanol from SD Fine Chemicals (AR grade) were used in the present study. The thiophene monomer was used as-received.

For the preparation of PTh-I film, PTh was synthesized at room temperature (303K) by mixing 0.4ml thiophene monomer with solution of oxidant $FeCl_3$ (0.70M) 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 $FeCl_3$/PVAc, a light brown homogeneous solution was obtained, this was then poured on chemically cleaned and leveled 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 film PTh-II was prepared with 0.75M concentration of $FeCl_3$.

The thickness of films was measured by Digimatic Outside Micrometer (Series-293, JAPAN) having a resolution of ±0.0001mm. The thickness of the films PTh-I and PTh-II were 22 and 24 μm respectively. The electrodes of silver (Ag) were deposited on the surface of the film to measure the surface resistance.

The resistance (in air) of films was measured on Ultra high resistance meter (Zentech, Model-702A) and found to be 1.19 x10^9 Ω for PTh-I and 1.15 x10^9 Ω for PTh-II respectively.

2.2 Sensing response measurement

Sensing response of the films was measured for different concentration (ppm) of CO_2 gas at room temperature (303K). 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. Results and discussion

3.1 FTIR analysis

FTIR spectra of film PTh-I and PTh-II displayed in fig. 1. The spectra recorded in the range of 4000-650 cm^{-1} to confirm polymerization. Broadening of peaks obtained at and around 668, 874, 1013 and 1394 cm^{-1} for both films 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 [24]. The conjugation band around 1583 cm^{-1} may imply polymerization and conductivity.
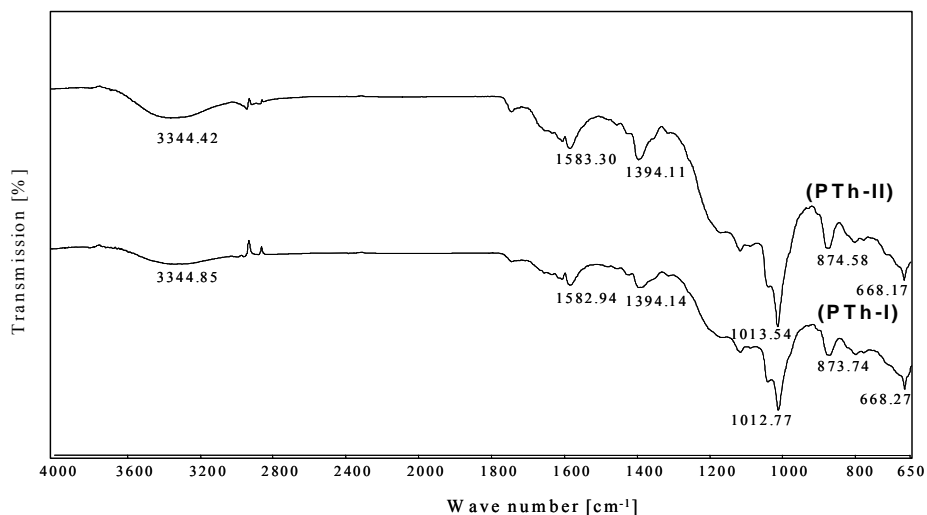
Fig. 1. FTIR spectra of PTh-PVAc composite films.

3.2 XRD analysis

The X-ray diffraction pattern of PTh-I and PTh-II shows amorphous nature (Fig. 2). In each case, a broad peak was observed at about $2\theta = 26.83$ (PTh-I) and 27.31 (PTh-II). 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 both samples. It may be interesting to note that the peak position of these amorphous halos depends on the strength of oxidant (FeCl₃). The average chain separation can be calculated from the maxima using relation reported in reference [25]. The average chain separation was found to be 4.15 and 4.07 Å for PTh-I and PTh-II respectively.
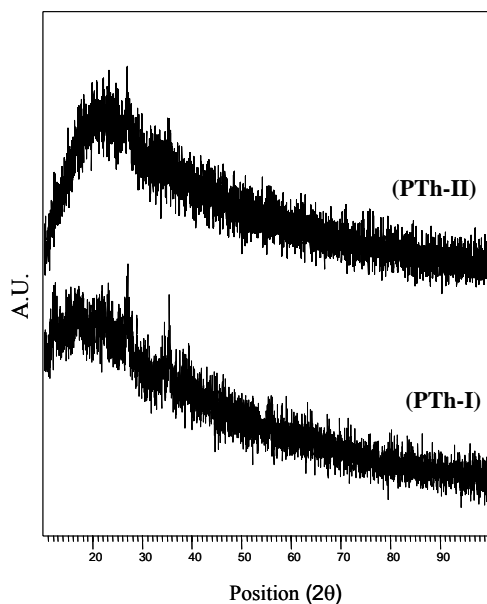

Fig. 2. XRD spectra of PTh-PVAc composite films.

3.3 TG-DTA analysis

The TG and DTA of PTh-PVAc composite films PTh-I and PTh-II are plotted as a function of temperature in Fig. 3.
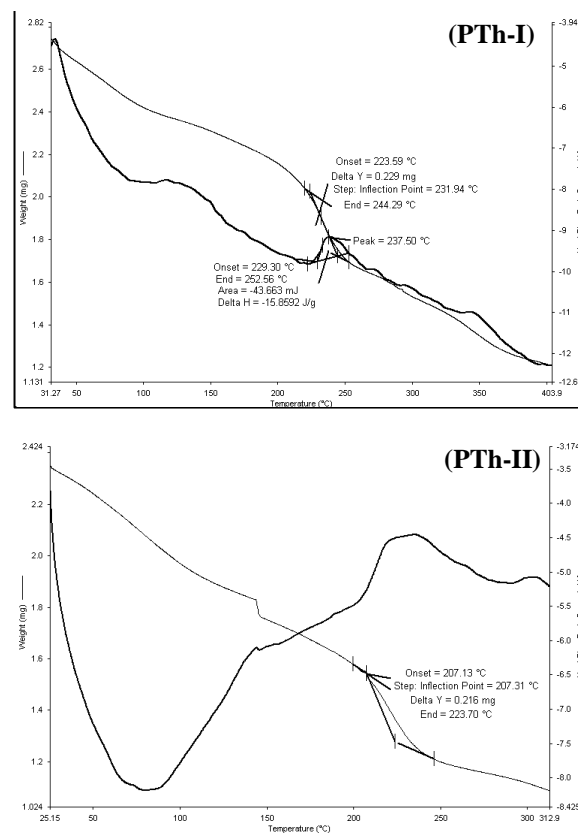

Fig. 3. TG-DTA plots of PTh-PVAc composite films.

Continuous weight loss is observed for both samples. The weight loss at 50 °C is 4% for PTh-I and 5% for PTh-II. The PTh-I shows minimum weight loss and hence it is stable as compared to PTh-II. The ΔCp for PTh-I and PTh-II is found to be 0.229 and 0.216 J/g °C respectively. The maximum value of ΔCp is observed for sample PTh-I. An endothermic peak appears for PTh-I and PTh-II at 75 and 78 °C respectively on the DTA curve. The change in enthalpy (ΔH) for PTh-I is -15.859 J/g. The total weight loss is also observed minimum i.e. 56% for PTh-I. The thermal properties of PTh-I, 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 CO_2 gas

The sensor response is defined as in reference [25]. The resistance of films 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. 4) at room temperature (313 K) up to certain value. A saturation reach after certain ppm value for films PTh-I and PTh-II respectively.

The film PTh-I shows high response to CO_2 as compared PTh-II. The average sensor resistance change per ppm of CO_2 or sensitivity is found to be 2.1×10^6 Ω/ppm for PTh-I and 1.03×10^6 Ω/ppm for PTh-II.
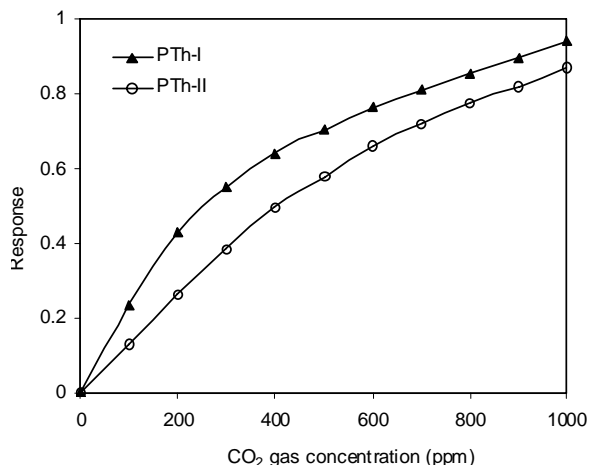

Fig. 4. Response of PTh-PVAc composite films as a function of CO_2 gas concentration at room temperature.

The dynamic response of film PTh-I to 100 and 400 ppm CO_2 at room temperature is as shown in Fig. 5. 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 PTh-I was exposed to air and time-dependant changes were recorded till the original value of resistance was reached. The recovery time is found to be ~10.5 min.
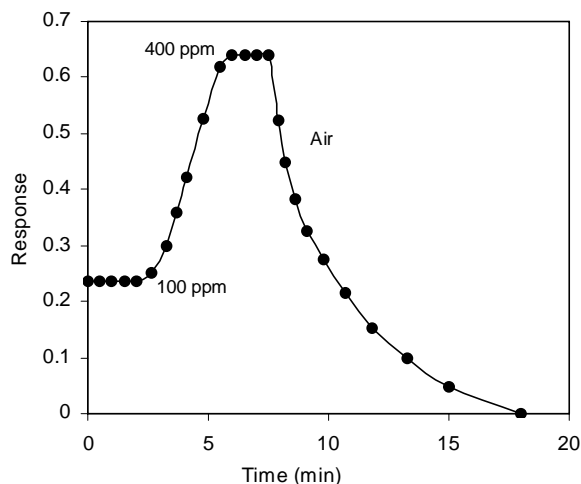

Fig. 5. Dynamic response of PTh-I to 100 and 400 ppm CO_2 at room temperature.

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 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 [26]. At the polymer molecule level, parameters like polymer backbone planarity, side chain length, conjugation length, and reorganization energies [27] 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 [23].

In PTh-PVAc composite, $FeCl_2^+$ ions may get coordinated with sulfur of the PTh. Such interaction may result in the formation of $FeCl_4^-$ ions. The increase in $FeCl_3$ increases the loading of PTh in the composite, which leads to coordination of more $FeCl_2^+$ ions with sulfur of PTh chains. Therefore effect of $FeCl_3$ is to increase the $FeCl_4^-$ ions in the composites. The lower value of resistance (in air) of PTh-II may be attributed to the well-dispersed positively charged PTh chains in the PVAc phase. Because well dispersed network of PTh chains in the PVAc phase leads to enhance the mobility of $FeCl_4^-$ ions and hence lower the resistance. CO_2 has two lone pair of electrons with π-type C=O bindings [28].

It may be possible that CO_2 molecules affect the mobility of $FeCl_4^-$ ions of the PTh-PVAc surface, which results in a decrease of conductivity or an increase in film resistance. The process of adsorption of CO_2 gas is reversible.

The highest response to CO_2 is observed for PTh-I. This perhaps may be due to large average chain separation (4.15 Å) and mobility of $FeCl_4^-$ ions.

4. Conclusions

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 PTh-I showed highest response to CO_2 gas. XRD study reveals that average chain separation for PTh-I was found to be 4.15Å. The average resistance change per ppm of CO_2 or sensitivity for PTh-I was found to be 2.1×10^6 Ω/ppm TG-DTA analysis showed that PTh-I has total weight loss 56% and highest ΔCp. FTIR study confirms the polymerization of thiophene monomer. The CO_2 molecules affect the mobility of $FeCl_4^-$ ions of the PTh-PVAc surface. This causes an increase in resistance of the material in the presence of CO_2 gas.

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[*]Corresponding author: sawaghuley@yahoo.co.in