



Organic Conjugated Polymers (Polypyrrol) based sensors for detection of hazardous gases

KEYWORDS

Organic Conjugated Polymer, Polypyrrol (Ppy), Chemical Sensors, Gas Sensors.

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ABSTRACT

Organic conjugated polymers (conducting polymers) have emerged as potential candidates for electrochemical sensors. Due to their straightforward preparation methods, unique properties, and stability in air, conducting polymers have been applied to chemical sensors.

Polypyrrole (Ppy) was synthesized using Ferric Chloride (FeCl₃) as an oxidants. The ratio of monomer to oxidants was 1: 2.4 and polymerization was carried out at room temperature. Attempts were made to increase the electrical conductivity by using Para-toluene Sulfonate (p-TS) as a dopants. The electrical conductivity was measured by two probe method was found to be in the range of 10⁻³ to 10⁻² S/cm. Thin films of these preparations were casted on the interdigitated electrodes to study the detection of ammonia gas. It was found that for the virgin Ppy, when ammonia gas was allowed to flow in there was a sudden increase in the current, which decreased rapidly when gas was stopped. However when doped Ppy was used, the trend was reversed.

Introduction:

Since the discovery of conducting polymers, the research has been focused on two classes of polymers. First, those based on polyacetylene (PA) and its derivatives [1,2] and secondly, those built around polyheterocyclic materials [3,4]. The study of PA has shown that this polymer gets a high electrical conductivity upon chemical or electrochemical doping ($\sigma = 10^3 \text{ S/cm}$) [5, 6]. However, doped PA has also been shown to exhibit poor stability towards aerial oxidation and so its practical uses may be limited [7]. The study of polyheterocyclic has revealed that one of the important polymer viz: polypyrrole (Ppy), when suitably doped, becomes highly conducting and shows reasonable stability under ambient conditions [8]. Polypyrrole (Ppy) is one of the most studied conducting polymers because of its rather straightforward preparation methods. Ppy materials are reasonably stable in air, have high conductivity, good electrochemical properties, good thermal stability and are easily generated both chemically and electrochemically [9]. Polypyrrole exhibits a wide range of surface conductivities depending on the functionality and substitution pattern of the monomer and the nature of the counter ion or dopant [10].

Organic conjugated polymer (conducting polymers) [11-13] are mainly organic compounds that have an extended π -orbital system, through which electrons can move from one end of the polymer to the other. The conducting polymers are known to have considerable flexibility in chemical structures that can be modified. By chemical modeling and synthesis, it is possible to modulate the required electronic and mechanical properties of conducting polymers. Common classes [13] of organic conductive polymers include poly(acetylene)s, poly(pyrrole)s, poly(thiophene)s, poly(terthiophene)s, poly(aniline)s, poly(fluorine)s, poly(3-alkylthiophene)s, polytetrafulvalenes, polynaphthalenes, poly(p-phenylene sulfide), poly(para-phenylenevinylene)s etc.. Diverse applications of these conducting polymers have been studied [13]. Of many desirable properties for the application of these conducting polymers in various practical devices, polymer stability is one of the most important criteria. The growths and stabilities of poly(aniline)s

[14, 15], poly(pyrrole)s, and poly(azulene)s have been studied. Poly(thiophene)s possess excellent thermal and environmental stability, solubility, processibility, and high conductivity when doped, which makes it an important class of conducting polymers.

The electrical conductivity of conducting polymers changes over several orders of magnitude in response to change in pH, applied potentials, or their environments. Grafting of organometallics to the backbone of the conducting polymer can also tune their physical properties.

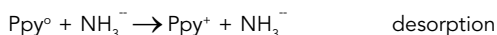
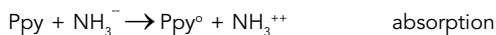
Many types of analytical applications of the conducting polymers have been reported since their discovery. These compounds have useful applications in the development of chemical sensors. During the last two decades, conducting polymers have emerged as one of the most interesting materials for the fabrication of electrochemical sensors [12].

Reliable sensing of Ammonia (NH₃) gas is required in many applications like detection of leaks, explosives, fertilizer industries, compressors of air conditioners, breath analysis for medical diagnosis etc. Further, its high toxicity also warrants a rapid detection at very low concentrations.[11]

The physical properties of conducting polymers strongly depend on their doping levels. The doping levels can be easily changed by chemical reactions with many analytes at room temperatures and this provides a simple technique to detect the several gases.

Most of the conducting polymers are doped / undoped by redox reactions, their doping level can be altered by transferring electrons from or to the analytes. Electron transferring can cause the change in resistance and work function of the sensing material. When Ppy is exposed to some gases, Redox reaction can take place. Gases such as NO₂ and I₂ which are electron acceptors can remove electrons from the aromatic ring of polypyrrole. When this occurs, for a p-type conductive polymer, the doping level as well as electric conductance of the conductive polymers is enhanced. On the other hand an electron donating gas such as ammonia reacts with the Ppy and the electrical conduct-

ance falls down sharply. However when desorption of the gas occurs the process can be reversed. In spite of such advances, the mechanism while determining the electron donating gas has not been understood clearly. The following reaction is involved in the process.[12]



Experimental methods and preparations :

Pyrrrole (Sisco Research lab / Sepctrochem lab 99%) was distilled before use. All other reagents and solvents obtained from commercial sources were reagent grade purity and were used as received. All solutions were prepared using de-ionized water. All reactions were conducted at a temperature of 5°C [9]. Both the oxidizing agents FeCl₃ and APS were used in the ratio of 1: 2.4 (monomer: oxidants) prepared using de-ionized water.

The Polypyrrole was prepared by chemical polymerization method. 1 M Pyrrole solution was prepared using de-ionized water and then mixed with oxidizing agents mentioned above, slowly under constant stirring for 30 minutes. Then the polymerization was conducted for 4 hours under constant stirring. Polypyrrole is kept unagitated for 24 hours so that Ppy powder settled down. The Polypyrrole powder is filter out under vacuum and washed with distilled water several times to remove any impurities present. The Polypyrrole is dried for 2 days at room temperature.

The Polypyrrole was tested for conductivity by preparing its pellets of area of cross section of 1 sq.cm. and 1mm. thickness. The conductivity was tested by two probe method at room temperature and various temperatures up to 70° C in the voltage range from 0 to 12 V.

Morphology of Polypyrrole was examined using Scanning Electron Microscope (SEM) JEOL make JSM – 5400 model.

Chemical structure was examined by FTIR measurements on Perkin – Elmer Ltd. make FTIR spectrometer model system 2000 using KBr pellets.

The Polypyrrole was characterized by XRD using PANalytical (Philips), Netherland model XpertPro. The XRD pattern was recorded between 2θ = 10° to 40°. The X – ray diffractometer uses CuKα radiation of λ = 1.5418 Å generated at 40Kv/ 20 ma.

In order to measure the gas response, interdigitated electrodes separated by 1mm. from all sides were prepared on a printed circuit board (PCB) and the slurry of Polypyrrole powder prepared with distilled water was spread over it uniformly and dried for 24 hours under vacuum at room temperature. A specially prepared gas chamber was used in which the PCB was fitted firmly. Ammonia gas was passed through the chamber at room temperature with Nitrogen gas as a carrier. The variation in the current was recorded at a constant voltage for intervals of 15 seconds each up to 3 minutes. By stopping the gas flow, the desorption is also recorded for every 10 seconds till current is recovered up to 90 % of its original value. The gas response was recorded continuously for 3 cycles.

Result and Discussions:

Characterization of Ppy:

The Ppy prepared in different ways were analyzed by FTIR,

XRD and SEM. FTIR spectra showed the main characteristic peaks at 1558.45 cm⁻¹ to 1540.66 cm⁻¹ and 1467.20 cm⁻¹ corresponding to the fundamental vibrations of polypyrrole ring. The peaks at 1685 m⁻¹ and 1315.4 cm⁻¹ represents C = N and C- N bonds. These peaks observed in a present work for oxidants like, FeCl₃ and APS alone and with their dopants like p-TS and NSA agree well with the ones available the literature, confirming the formation of Polypyrrole.

The XRD Pattern reveals that the resulting polypyrroles were amorphous in nature, showing a broad peaks in the region 15° < 2θ < 30° indicating that short range chain arrangement dominates.

A typical SEM image of Polypyrrole is shown in Fig.1. The photograph shows a globular structure. The average size of globules is 0.6 μm. The granular morphology is considered to be good for gas sensing applications.

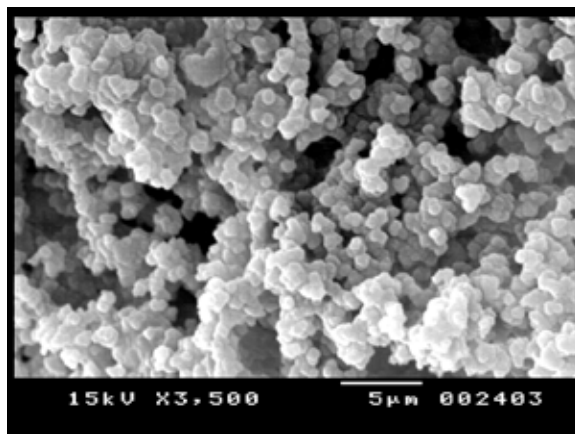


Fig. 1: SEM of Polypyrrole using FeCl₃ as an oxidant

FTIR spectroscopy:

The FTIR spectrum of Ppy prepared is represented in Fig.2. It shows strong absorption bands at around 3436 cm⁻¹ corresponding to N-H stretching. Other medium intensity peaks are observed at around 2922 cm⁻¹ - 2854 cm⁻¹ which can be attributed to aromatic C-H stretching

vibrations. The absorption band at 1534 cm⁻¹ is related to C=C / C-C stretching vibrations of the

Pyrrrole ring. The band at 1448 cm⁻¹ reflects the C-N stretching vibrations of the ring. The region

at 1261 cm⁻¹ - 1164 cm⁻¹ corresponds to breathing vibrations of the Pyrrole ring. The peak at 1291cm⁻¹ attributable to C-N in plane deformation vibration mode. The bond of C-H in plane

deformation vibration is situated at 1035 cm⁻¹ and of the C-C out of plane ring deformation vibrations or C-H rocking is at 677 cm⁻¹. The C-H out of plane deformation vibration band of the ring has a peak at 901 cm⁻¹.

In order to determine the mode of bonding, we used the bands at 730cm⁻¹ and 820 cm⁻¹. When α – α' bonding i.e. 2, 5 coupling exists a strong absorption band occurs at 788 cm⁻¹. On the other hand when α – β' bonding i.e. 2,4 coupling occurs, we get absorption band at 730 cm⁻¹ and 820 cm⁻¹. It was indeed observed that when FeCl₃ was used as oxidants in chemical polymerization method we

observed only 799 cm⁻¹ band. This shows that predominantly $\alpha - \alpha'$ bonding exist.

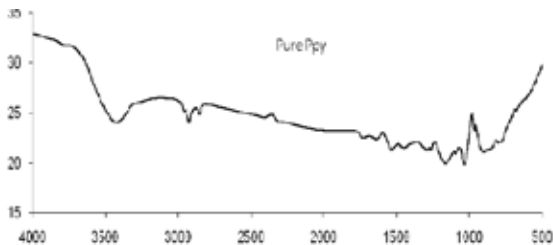


Fig.2 FTIR spectrum of Ppy

X-ray diffraction analysis:

A typical X ray diffraction pattern for polypyrrole prepared using FeCl₃ as oxidant is shown in Fig.3. The XRD patterns for sample show broad peak in the region $15^\circ < 2\theta < 30^\circ$ revealing that the resulting polypyrrole powder is amorphous in nature. Such broad peak usually indicates short range arrangement of chains. The half width is measured from the diffraction curve from the angle higher than the peak position and assuming Gaussian distribution for the low angle part of the diffraction curve. It was noted that the diffraction profile is highly asymmetrical and there is considerable broadening towards lower angles from the peak positions.

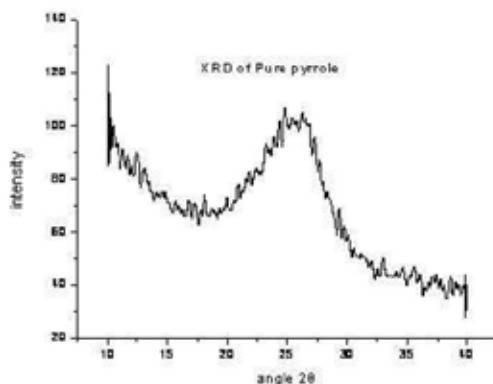


Fig.3. SEM of Ppy using FeCl₃ as an oxidant

I-V characteristics:

The Polypyrrole was tested for conductivity by preparing its pellets of area of cross section of

1 sq.cm. and 1 mm. thickness. The conductivity was tested by two probe method at room temperature and various temperatures up to 70°C in the voltage range from 0 to 12 V. The temperature dependence of the electrical conductivity of the polypyrrole, prepared with FeCl₃, was studied at various temperatures from 30°C up to 70°C. It was observed that the electrical conductivity decreased gradually for all the samples as the temperature increased from 30°C to 70°C. This behavior resembles the metallic conductors. It may be mentioned that pure pyrrole is more like insulator but behaves like semiconductor in the doped form. Here the doping is due to Cl⁻ ions held near the Ppy chains, which compensates the + charge on polypyrrole chains. The mechanism of conduction is supposed to be by polarons and bipolarons formation due to the dopant molecules [20]. In case of polypyrrole the absence of electron in the chain leads to formation of holes i.e. p-type conduction.

Thus it is expected that increasing temperature will lead to increase of energy for an electron in the valance band which jumps to conduction band and hence the conductivity should increase with the temperature. However the present studies revealed that the materials do not behave

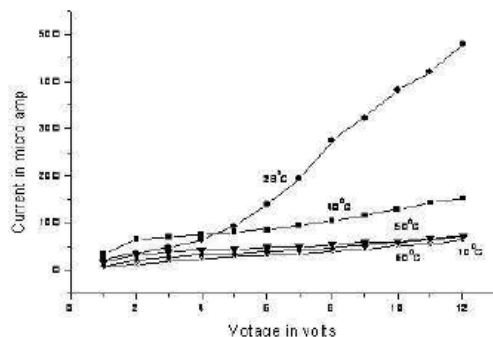


Fig.4 I vs V temperature dependence graph of Ppy prepared with FeCl₃

Gas sensor:

The behavior of all polypyrrole samples were studied for detection of ammonia gas. A typical plot of current vs. time for polypyrrole prepared using FeCl₃ as oxidant and exposed to ammonia gas is given in Fig.3. Sensitivity factor is calculated using the equation where resistances with gas and without are gas (in air) respectively. All samples were studied for 3 cycles to check their reproducibility and absorption and desorption process. It may be seen from the Fig. 5 that the I vs t plot for 2nd and 3rd cycles somewhat drift towards higher current. This may be because desorption may be not completed within the given time.

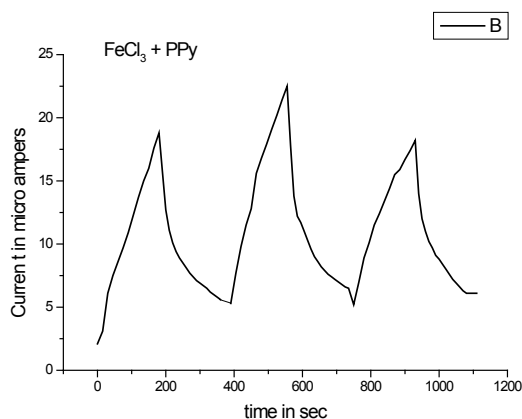


Fig . 5: Gas sensing response of Polypyrrole prepared using FeCl₃,

The gas response was recorded continuously for 3 cycles. It may be seen from the 6 that the i - t plot for 2nd and 3rd cycles somewhat differ from the first cycle. This may be because desorption may be not completed within the given time. This may be the reason for the drift in the graph toward lower value of current in later cycles. The Sensitivity factor was calculated during the present investigation for Pure Polypyrrole sensors is 0.99.

Sensing mechanism:

It is difficult to explain the sensing mechanism in terms of a single physical process. A number of different mecha-

nisms might lead to a change in the conductivity of the Ppy. For example, the presence of the organic vapour could:

- (i) Oxidize or reduce the polymer, changing the number of charge carriers on the polymer chains;
- (ii) Interact with the mobile charge carriers on the polymer chain and affect their mobility;
- (iii) Modify the potential barrier for the hopping process of charge carriers between the polymer chains;
- (iv) Interact with the dopant molecules or
- (v) Provide a morphological change, for example, by swelling and producing self-assemblies of conductive polymers clusters [22].

It is considered that mechanism (i) is an unlikely process in this investigation as alcohols are not strong oxidation or reducing agents. The increase in the steady state conductivity (i.e. that observed following the initial current transient) may be attributed to the dielectric properties of the vapor molecules [23,24]. Polar solvents with high dielectric constants can induce a screening effect between the counter ions and the charge carriers on a polymer backbone. This reduces the Coulomb interaction between the polypyrrole and the dopant molecules, thereby enhancing the hopping rate and dc conductivity i.e. process (iii) mentioned above. The higher sensitivity and faster response time for ethanol may be related to the small size of the ethanol molecules, allowing these to interact and diffuse efficiently in the polymer layer. Furthermore, the large dielectric constant of ethanol (~23) probably results in better interaction between its molecules and the polymer film, e.g. with the nitrogen atoms of the polypyrrole [25], perhaps also affecting the film morphology.

Conclusion:

It is found that Pyrrole can be polymerized by chemical oxidative method and the conductivity of the product is good. The sensors prepared by this polypyrrole can detect hazardous gases at room temperature. These sensors can be reused for number of times and time taken for desorption is reasonably less as compared to the sensors available in the market for the same purpose.

REFERENCE

- [1]. H. Shirakawa, E.J. Louis, A.G. Mac Diarmid, C.K. Chiang and A.J. Heeger, *J. Chem. Soc. Chem. Commu.* 578 (1977) [2]. A. G. Mac Diarmid and A. J. Heeger, *Synth. Met.* 1, 101, (1979/1980) [3]. A. F. Diaz, *Chem. Ser.* 17, 145 (1981) [4]. G. Tourillon and F. Garnier, *J. Electroanal. Chem.* 135, 173 (1982) [5]. C.K. Chang, C. R. Fincher S. C. Garnier Y.W. Park, A. J. Heeger, H. Shirakawa, E.J. Louis and A.G. Mac Diarmid *Phys. Rev. Lett.* 39, 1098 (1977) [6]. P. J. Nigrey, A. G. Mac Diarmid and A. J. Heeger, *J. Chem. Soc. Chem. Commu.* 594(1979) [7]. W. Deits, P. Cukor, M. J. Jonson, *Synth Met.* 4, 189 (1982) [8]. A. F. Diaz, K. K. Kanazawa and G. P. Gardian, *J. Chem. Soc. Commu.* 635 (1979) [9]. Wang Lin-Xia, Lia Xin-Gui, and Yang Yu-Liang. 2001. *Reactive and Functional Polymers* 47:125. [10]. da Cruz, A.G.B., J.L. Wardell, and A.M. Rocco. 2006. *Synth. Met.* [11] S.C. Hernandez, D. Chaudhari, W. Chen, N. Myung, A. Mulchandani, *Interscience* 2007, 19, 2125-2130 [12] H. Bai, G. Shi, *Sensors*, 2007, 7, 267-307 [13] D.B. Dupare, M.D. Shirsat, A.S. Aswar, *The Pacific Journal of Science and Technology*, May 2009, 10, 417-422 [14] M.F. Marbrook, C. Pearson, M.C. Petty, *Sensor and actuators B*, May 2006, 115, 547-557 [15] A. Joshi, S.A. Gangal, N. Padma, D.K. Aswal, S.K. Gupta, *BARC newsletter*, issue no 297, Oct. 2008 236-239 [16]. Zhang et al., *J Am Chem Soc* 2004, 126, 6572. [17]. Hsueh, C.; Brajter-Toth, A. *Anal. Chem.* 1994, 66, 2458-2464. [18]. Garcia, J.; Quintela, P. A.; Kaifer, A. E. *Anal. Chem.* 1989, 61, 979-981. [19]. Chastel, O.; Kauffmann, J. M.; Patriarche, G. *J. Anal. Chem.* 1989, 61, 170-173. [19a]. T. K. Vishnuvardhan, V. R. Kulkarni, C. Basavaraja, S. C. Raghavendra, " Synthesis, characterization and a.c. conductivity of polypyrrole / Y2O3 composites", *Material Science*, Vol. 29, No.1, 2006, pp.77-83. [20]. Tanaka, K.; Tamamushi, R. *J. Electroanal. Chem.* 1987, 236, 305-307. [21]. Nofle, R. E.; Pletcher, D. J. *Electrochem. Chem.* 1990, 293, 273-2n. [22] N.V. Bhat., A.P. Gadre, V. A. Bambole, " Structural, Mechanical and Electrical Properties of Electro polymerized Polypyrrole Composite Films" *J. Appl. Poly. Sc.*, Vol. 80, 2001, pp. 2511-2517, [23]. S.A. Waghule, S. M. Yenorkar, S. S. Yawale, S. P. Yawale, "SnO2/PPy Screen – printed Multilayer CO2 gas sensor." *Sensors and Transducers Vol. 79*, 2007, pp. 1180-1185 [24]. E. Segal, R. Tchoudakov, M. Narkis, A. Siegmann, Y. Wei, *Polystyrene/polyaniline nanoblends for sensing of aliphatic alcohols*, *Sens. Actuators B* 104 (2005) 140–150. [25]. M.F. Mabrook, C. Pearson, M.C. Petty, *An inkjet-printed chemical fuse*, *Appl. Phys. Lett.* 86(2005), art. No. 013507 (1–3).