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Toxic Gas and Vapour Detection by Polyaniline Gas Sensors

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ABSTRACT

The response mechanism of polyaniline to a selection of gases and vapours was investigated by measuring its conductance and mass changes by using a four-probe method, elemental analysis, and X-Ray fluorescence (XRF) technique. The prepared films were exposed to hydrogen halides, hydrogen cyanide, hydrogen sulphide, halogens, acetic acid, mono-, di-, and trichloroacetic acid, formaldehyde, hexachloroacetone, 1,3,5-trichloromethyl benzene, methylbenzyl bromide, bromoacetone and cyanogen bromide. It is observed that the polyaniline conductance changes are partly due to two-stage sorption perhaps involving the swelling of the polymer and gas diffusion. All the films were exposed to dilute ammonia solution or vapours of organic solvents and swelled before doping, which could modify the mass and electrical measurements. It was demonstrated that slightly additional amounts of HCl gas in tested gases will significantly influence the conductivity. It is concluded that the response mechanism of polyaniline sensing of different gases and vapours is due to a mixed response involving electronic and physical effects.

Key Words:
gas sensor;
polyaniline sensor;
conducting polymer;
X-ray fluorescence (XRF);
mass changes;
conductivity changes.

INTRODUCTION

About 60 years have passed since the invention of chemical sensors. The devices, which in the beginning were called by a variety of names, gradually are known by the single term, sensor , and their classification into physical and chemical types has been established. Over the past 60 years, the chemical sensors have made great advances and have taken root in human life and industry as a feature of modern technology. In recent years, polymers have found an increasing role in sensorics due to

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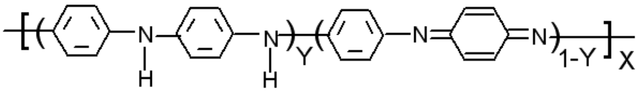
their unique characteristics, and a number of new sensors have been developed [1]. Their application is relatively new in this field, but they seem to be very promising for building up cheap and reliable sensors. The great variety of their properties gives a lot of application possibilities. As materials and technologies are mostly in the state of development. The active sensing polymers are used as sheets or films form built into inorganic solid-state devices as an integral part [2]. The various sensors have been grouped according to parameters such as temperature [3], mechanical [4,5], acoustic [6], radiation [7], gas [8], and humidity [9] to be measured.

Conducting Polymer Gas Sensors

Early work on conducting polymers as gas sensors was undertaken by numbers of groups. Bartlett s group compared the response of four different polymers; polypyrrole (PPy), polyaniline (PANi), poly-N-methylpyrrole, and poly-5-carboxyindole to vapours of alcohols, acetone and ethers [10]. Among them, poly-5-carboxyindole was found to give the most consistent response to all tested vapours.

The first disclosure of the gas-sensing properties of conducting polymers was made at a conference in 1983 [11]. This involved the use of filter paper impregnated with PPy, functioning as an ammonia sensor. The sensor also displayed responses to other amines. Like many other conducting polymers, polyaniline was known long before the current interest. This was in the form of "aniline blacks", an undesirable black deposits formed on the anode in electrolyses involving aniline [12]. In most conditions the polymeric films are passivating but electrolysis in acidic aqueous solutions gives conducting films [13]. According to Ohsaka et al. [14] only in acidic aqueous the polymer solution is formed by head-to-tail coupling; in other media head-to-head coupling gives non-conjugated polymers.

Recent studies of PANi have been reviewed by McDiarmid et al. [15]. They suggest that the polymer can exist in a wide range of structures, which can be regarded as copolymers of reduced (amine) and oxidized (imine) unites of the form:



When 0<Y<1 these structures are the poly(*p*-phenyleneamineimines), in which the oxidation state of the polymer increases with increasing content of the imine form. The fully reduced form (Y=1) is leucoemeraldine , the fully oxidized form (Y=0) is perenigraniline , and the 50% oxidized structure (Y=0.5) is emeraldine . Each structure can exist as base or as its salt, formed by protonation. Thus, we can envisage four repeat units in the polymer chain, in amounts which depend on the extent of both oxidation and protonation of the structure (Figure 1).

Wnek [16] proposed that the structure of the oxidized insulating form of conventionally formed PANi is approximately a 50% copolymer of diamine and diimine units. Corresponding to the emeraldine structure, Hjertberg et al. [17] obtained CPMAS NMR evidence for this conclusion. Some confirmation of the structure has also been obtained by chemical synthesis of the polymer [18].

However, Pekmez et al. [19] have suggested that the normal electrochemical synthesis leads to partially cross-linked polymers. The PANi is electroactive and switches on-off in aqueous solutions in the potential range of 0.1 - 0.8 V anodic to the hydrogen electrode [20], producing broad oxidation / reduction waves in the voltammogram. The reaction is accompanied by a change in the conductivity of the material by a factor of 10^6. It was quickly recognized that this material could be useful in technological applications such as carbon electrode [21], redox membranes with permselective properties [20], pH sensor [22], charge storges [23], and other sensors [8,24-28].

Here, we report the enhanced response of PANi towards toxic gases and vapours. In addition, gases which are oxidizing or reducing agents naturally affect the electrical conductivity of the polymer films. The expected behaviour is an increase in conductivity by gases such as hydrogen halides, halogens and halomethyl compounds and a decrease in the case of ammonia and HCA.

In this paper, we have investigated mass and conductivity changes for sensing polymer exposed to toxic gases and vapours. The gas absorption into polymer is caused doping or undoping of polymer and these process is approximately stable. Therefore, we can use the gases and vapours for sensing this behaviour. In addition, gas absorption by polymer can cause mass increasing and

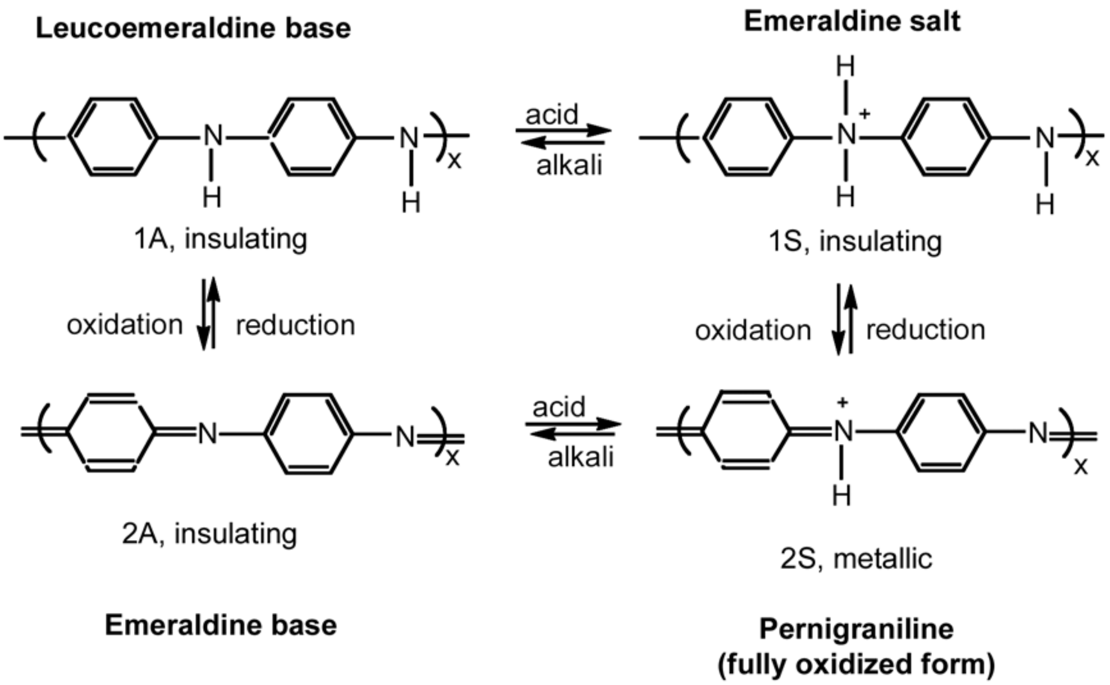


Figure 1. The possible structures of polyaniline chain.

XRF was used as a method to determine the mass.

EXPERIMENTAL

Instruments and Materials

Mass changes were measured by X-Ray fluorescence technique (XRF), mode 1; EDXRF 300 link. Conductivity changes were measured by a four probe device (home-made). Aniline was purified, after refluxing with 10% acetone for 10 h, aniline was acidified with HCl and extracted with Et_2O until colourless, then dried with solid KOH, and distillated under reduced pressure. All the other materials and gases used in this work were purchased from Merck chemicals and purified, or were prepared by methods in literature.

Films Preparation

Electropolymerization of PANi was done at 200 mC/cm^2 in an aqueous solution containing aniline 1.5 M in the HCl 3M. The polymer films with the thickness of 50-100 nm are formed on the working electrode in the 0.66 V versus saturated calomel electrode.

Chemical polymerization of PANi was done in an aqueous protonic acid solution. 45.6 g of ammonium persulphate was dissolved in 250 mL of HCl 1.7 M solution. Then, this was added to 20 mL of aniline dissolved in 250 mL of HCl 1.7 M. Various temperatures in the range of -10 to 25^{o}C have been employed to prepare PANi powder. One gram of the powder was then slowly added (over 1 h) to 40 mL of NMP (*N*-methylpyrrolidinone) solution, and magnetically stirred at room temperature for 7 h. It was found that if the polymer powder was added too rapidly to the NMP, it tended to aggregate. The resulting viscous solution was pre-filtered twice through a Buchner funnel using Whatman paper No. 541 to remove large particles. Finally it was filtered with Whatman paper No. 542. The produced viscous solution of PANi was spread over a piece of glass to obtain an even layer of emeraldine. Then it was dried under vacuum.

In general, slower drying gave films more uniform thickness. The dry film was removed from the glass by immersion in water. The films were prepared by casting 3 mL of solution over a piece of glass (8×8 cm) which gave a film of ≈15 μm thickness.

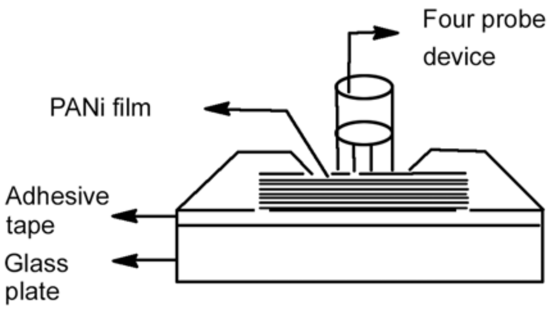


Figure 2. Schematic illustration of polyaniline gas sensor.

Sensor Fabrication

The device as is shown in Figure 2 was fabricated for testing the gases sensitivity by using the polymer films prepared in this manner. For this purpose by using adhesive tapes, prepared films were fixed onto glass plates.

Toxic Gas-vapour Generation Apparatus

The test gases and vapours were introduced into the sensors with the argon carrier gas in a double impinger exposure cell as described previously [29]. However, the method of gas and vapour generation was different. A system (as shown in Figure 3) was designed consisting of a series of needle valves, controlling the gas flow rates, which could be monitored via a bank of flow meters. The argon flow constitutes the main flow in the cell and is adjustable in the range of 1- 1000 cm^{3}min^{-1}.

A test gas or vapour flow, adjustable from 1 to 20 cm^{3}min^{-1}, is mixed with the vector argon flow, so by controlling both gas and vapour flows, different dilutions can be made. Target samples were produced in two ways. Organic vapours were generated by bubbling a stream of argon carrier gas (via gas wash bottles) through the volatile liquids (HBr, HI, Br$_2$, I$_2$, acetic acid (AA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), trichloroacetic acid (TCAA), hexachloroacetone (HCA), bromoacetone (BA), 1,3,5-trichloromethyl benzene (TCMB), and methylbenzyl bromide (MBB)). Thus producing a continuous flow of saturated vapour, which its concentration depends on the vapour pressure of the liquid. Analyte samples that are normally in a gaseous state at room temperature were prepared by dilution of HF, HCl, F$_2$, Cl$_2$, formaldehyde (FA), and cyanogen bromide (CB) of 99.8% purity.

Experimental Procedure

Before each experiment, the films were pre-swelled by suitable reagents such as diluted basic and acidic solutions and then heated at 70ºC in a 5 mmHg vacuum to desorb the residual solvents and humidity out of the polymer film, which could modify the mass and electrical measurements. Then the samples temperature was

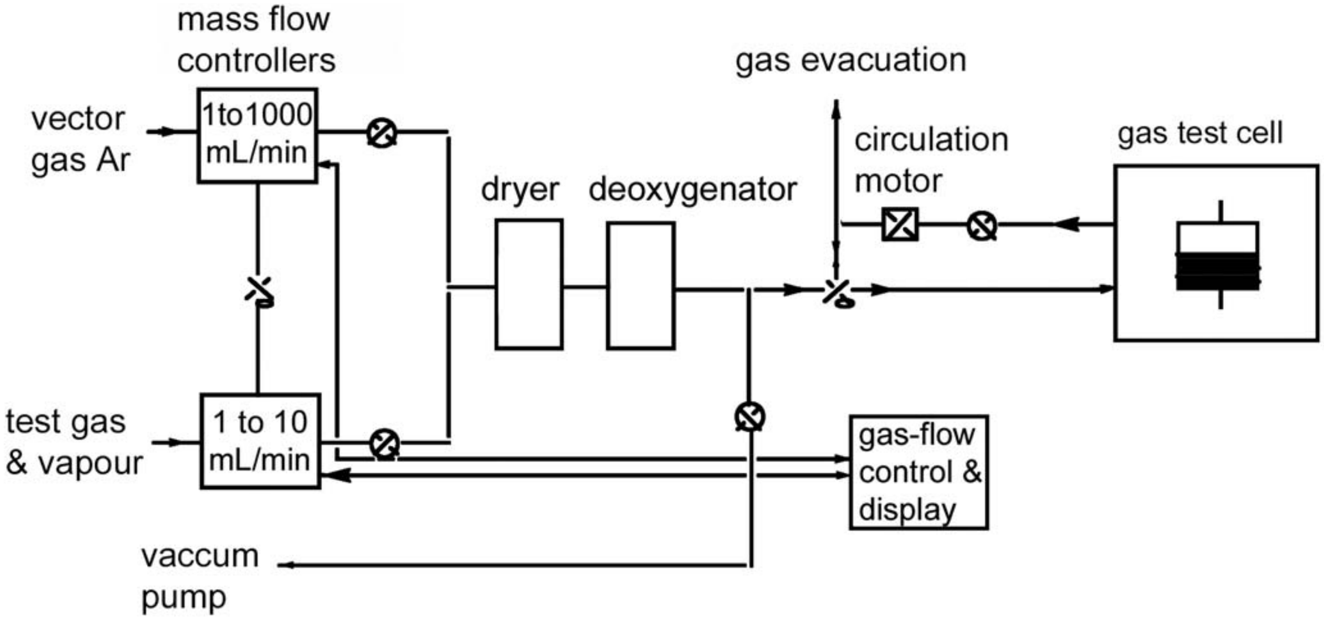


Figure 3. Controlled gas-flow system: dilution of the polluting gas in a vector gas and regulation of the gas flow introduced into the cell.

Table 1. Elemental analysis, XRF, and conductivity of PANi ($\delta_0 = 1.2\times10^{-5}$ Scm^{-1}) in different concentrations of CB.

Rel. Concentration BrCN (ppm)	C (%)	H (%)	N (%)	Relative percent Br (XRF)	Conductance (Scm^{-1})
500	76.1	5.6	15.7	0.5	1.8×10^{-5}
800	75.2	5.3	15.3	2.3	8.3×10^{-5}
1100	75.9	5.5	16.1	3.8	2.9×10^{-4}
1400	76.8	5.6	17.2	4.2	8.2×10^{-4}

regulated at 20ºC and a constant gas flow of pure argon is established (100 mL min^{-1}) through the cell. A polluting gas or vapour is diluted in the argon flow at different ratios: 500 to 2000 ppm for test samples after the 10-20 min exposure. Vapours and gases are sufficiently dry (moisture$\leq$0.6 ppm) to differentiate dry experiments on samples. In this work, electrochemical measurement have not been accomplished but all the conductivities produced on the film and solid state were measured by using four probe method.

RESULTS AND DISCUSSION

The results of elemental analysis, XRF and conductance measurements of PANi films exposed to cyanogen bromide (CB) were reported in Table 1. Chlorine arises from a dopants anion and bromine existence and mass increasing of C and N is related to presence of BrCN in polymers chain. The results of XRF and elemental analysis of PANi after exposing to CB show that absorption is increased with increasing the

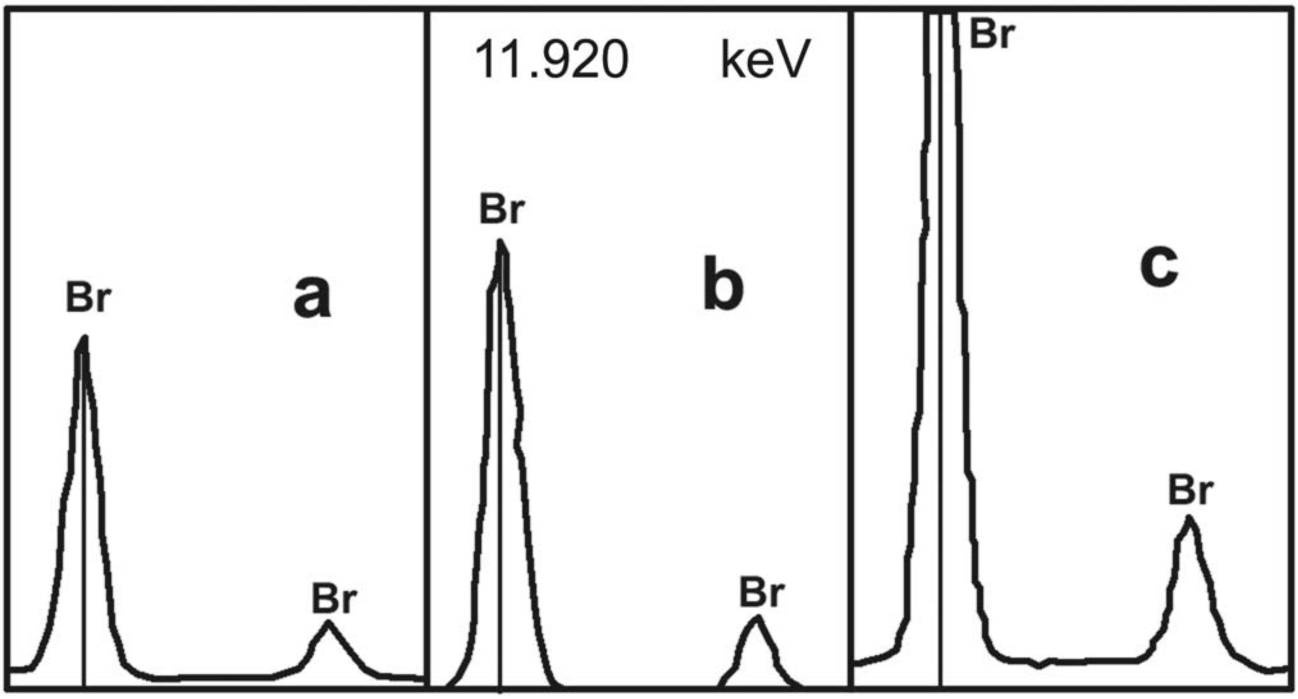


Figure 4. XRF PA film at different concentrations of BrCN (a) 500 ppm; Intensity: 2028 cts, (b) 1000 ppm; Intensity: 2673 cts, (c) 1500 ppm; Intensity: 5217 cts; X-RAY: 0-20 keV; 100s, Preset: 100s; Real: 129s, 22% Dead.

concentration of samples (Figure 4). Tables 2 and 3 show the results of conductivity measurements of PANi films which are affected by different concentration of hydrogen halides, hydrogen cyanide, hydrogen sulphide, and halogens, respectively. The results of conductivity measurements of PANi is affected by various concentrations of toxic gases and vapours as acetic acid (AA), monochloroacetic acid (MCAA), dichloroacetic acid (DCAA), and trichloroacetic acid (TCAA) are reported in Table 4. Hexachloroacetone (HCA), bromoacetone (BA), 1,3,5-trichloromethyl benzene (TCMB), methylbenzyl bromide (MBB), and formaldehyde (FA) are presented in Table 5, as well. Table 6 shows the results of XRF measurement of

Table 2. Conductance changes of PANi ($\delta_0 = 1.7\times10^{-6}$ Scm^{-1}) in different concentrations of hydrogen halides, hydrogen cyanide and hydrogen sulphide.

Relative concentration (ppm)	HF	HCl	HBr	HI	HCN	H_2S
500	1.2×10^{-5}	8.9×10^{-5}	2.1×10^{-4}	3.2×10^{-4}	5.6×10^{-5}	8.3×10^{-6}
800	9.8×10^{-5}	7.4×10^{-4}	5.9×10^{-3}	5.7×10^{-2}	2.3×10^{-4}	5.7×10^{-5}
1100	3.1×10^{-3}	9.3×10^{-3}	7.6×10^{-2}	0.21	6.7×10^{-3}	1.3×10^{-3}
1400	9.3×10^{-3}	0.11	0.69	3.7	9.8×10^{-2}	2.1×10^{-2}

Table 3. Conductance changes of PANi ($\delta_0 = 1.3\times10^{-5}$ Scm^{-1}) in different concentrations of halogens.

Relative concentration (ppm)	F_2	Cl_2	Br_2	I_2
500	2.4×10^{-6}	9.4×10^{-6}	2.3×10^{-3}	3.4×10^{-5}
800	6.7×10^{-6}	1.2×10^{-5}	7.8×10^{-5}	1.2×10^{-3}
1100	1.4×10^{-5}	8.9×10^{-5}	4.3×10^{-3}	3.3×10^{-3}
1400	7.6×10^{-5}	3.4×10^{-4}	1.2×10^{-3}	2.6×10^{-2}

Table 4. Conductance changes of PANi ($\delta_0 = 1.3\times10^{-5}$ Scm^{-1}) in different concentrations of acetic acid and their chloro derivatives.

Relative concentration (ppm)	AA	MCAA	DCAA	TCAA
500	4.3×10^{-6}	8.5×10^{-6}	9.1×10^{-6}	9.8×10^{-6}
800	8.7×10^{-6}	4.6×10^{-5}	5.3×10^{-5}	4.6×10^{-5}
1100	3.8×10^{-5}	1.1×10^{-4}	2.1×10^{-5}	8.6×10^{-5}
1400	8.1×10^{-5}	8.4×10^{-4}	9.1×10^{-4}	3.2×10^{-4}

Table 5. Conductance changes of PANi ($\delta_0 = 1.5\times10^{-5}$ Scm^{-1}) in different concentrations of HCA,BA,TCMB, MBB, and FA.

Relative concentration (ppm)	HCA	BA	TCMB	MBB	FA
500	6.4×10^{-6}	7.4×10^{-6}	3.4×10^{-5}	6.4×10^{-6}	7.3×10^{-6}
800	5.8×10^{-6}	3.9×10^{-5}	2.3×10^{-4}	7.3×10^{-5}	1.5×10^{-5}
1100	4.9×10^{-6}	1.2×10^{-4}	8.9×10^{-3}	6.3×10^{-4}	6.3×10^{-5}
1400	4.1×10^{-6}	6.6×10^{-4}	2.3×10^{-2}	1.2×10^{-3}	1.3×10^{-4}

Table 6. Mass changes determinated by XRF technique (relative percentage halogens) PANi for different concentrations of toxic gases and vapours ; X-Ray: 0-20 keV ; Intensity: 2000-6000 cts.

Relative concentration (ppm)	500	800	1100	1400
HCl	1.1	2.2	2.9	4.1
HBr	1.9	3.1	4.8	6.3
HI	2.8	5.8	9.2	11.7
Cl_2	0.52	1.2	2.1	3.0
Br_2	1.3	2.8	3.7	5.9
I_2	3.0	6.4	11.2	16.3
MCAA	0.21	0.41	0.63	0.84
DCAA	0.31	0.73	1.6	2.8
TCAA	0.52	1.6	3.4	6.1
HCA	4.3	6.4	9.4	13
TCMB	0.31	0.84	2.1	4.6
MBB	0.42	0.81	1.4	2.2
BA	0.8	2.1	5.7	8.0

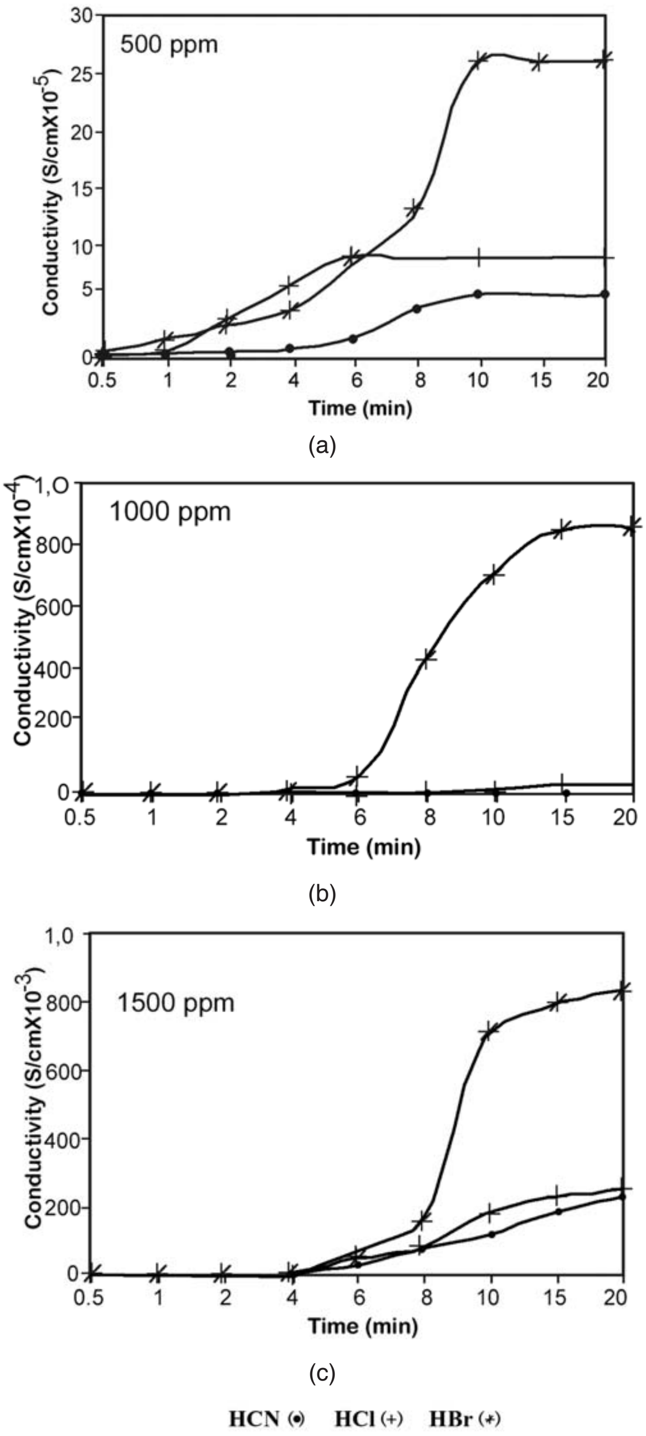


Figure 5. Conductivity of PANi ($\delta_0 = 1.7\times10^{-6}$ Scm^{-1}) vs. time for (a) 500 ppm, (b) 1000 ppm, and (c) 1500 ppm of HCN, HCl, and HBr at room temperature.

PANi films that have been affected by different concentrations of toxic gases and vapours containing halogen groups. All the results that have been shown in Tables 1,2 and 4-7 are produced after a 10 min and 60 min exposure to toxic gases and vapours, respectively.

Response Times

Reducing response times of conducting polymers to toxic gases is very important. If concentration of the test samples have been increased, the conductivities, also has been increasing as are shown in Tables 1-5. In the constant concentration, if doping time has been changed, the conductivity will increase. In this case, we have plotted conductivity changes of PANi versus doping time at constant concentrations of gases and vapours tested, which are represented in Figures 5-8.

Of the various possible structures of PANi, the neutral aromatic amine and the neutral quinonediimine that are both insulators, only repeated units which are both oxidized and protonated give rise to conducting segments. One consequence is that PANi exhibits an unusual form of doping behaviour, i.e. it can be switched from conducting to insulating forms by variation in pH, without any change in the electronic oxidation state [30]. The gas absorption of polymer causes doping or undoping of polymer and this processes is approximately stable. Therefore, we can use the gases

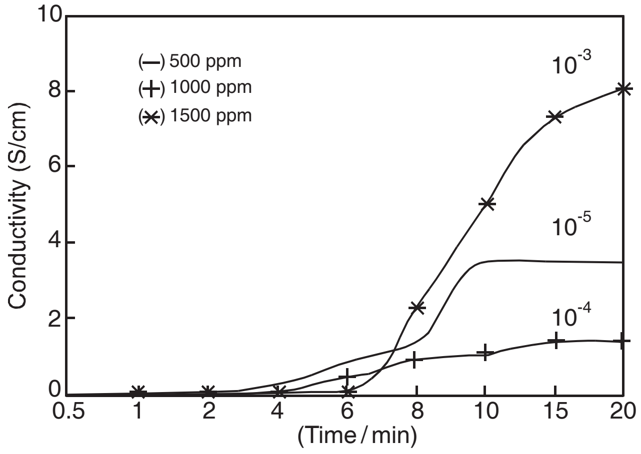


Figure 6. Conductivity of PANi ($\delta_0 = 1.7\times10^{-6}$ Scm^{-1}) vs. time for 500 ppm, 1000 ppm, and 1500 ppm of HI at room temperature.

and vapours for sensing this behaviour. conductivity changes between 5-7 order of magnitudes are completely reliable (Tables 1-5).

The results in Tables 2-5 showed that gases and vapours concentration affect conductivity of polymer in defined doping times. Therefore, it can be concluded that some of gases and vapours have influenced sensing properties rather than the others. For example, HI and HBr in Table 2, I_2 and Br_2 in Table 3, TCAA in Table 4, and MBB and TCMB in Table 5 have produced the best sensing results. The reason is that the conductivity changes versus concentration, are acceptable in defineded times. In Table 5, HCA have showed the reversed results and it was explained here.

In addition, the gas absorption by polymer can cause its mass increasing and XRF technique was used to determine the mass. The measurement of mass changes showed that increasing in halogens concentrations increase the mass of polymer (Table 6). These results showed that change in mass is sufficiently enough for sensing the halogen containing gases and vapours.

The combination of the XRF technique and four probe method enable us for a quantitative evaluation of the interactions between conducting polymer and organic gases and vapours.

Mechanism of Absorption

The good reproducibility of the XRF due to vapour sorption/desorption proved the reversibility of the doping/unedoping process. The direct observation of chemical interactions taking place within the band gap

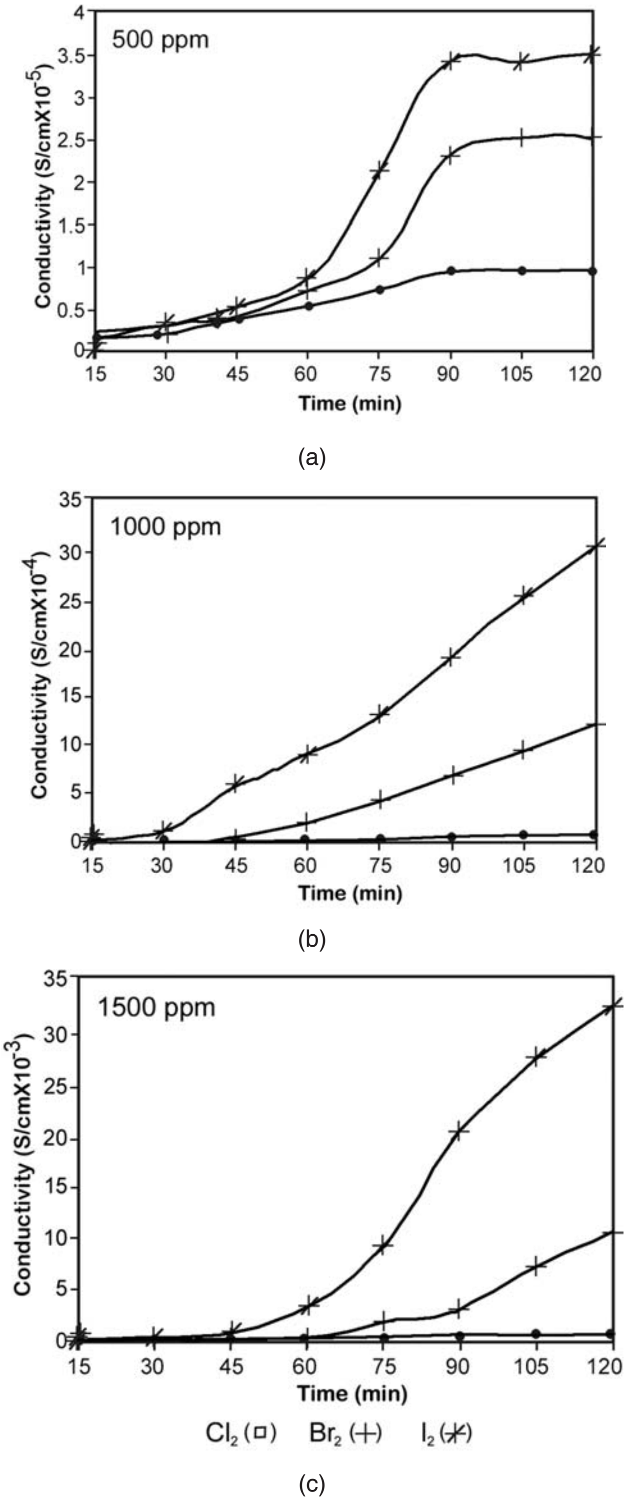
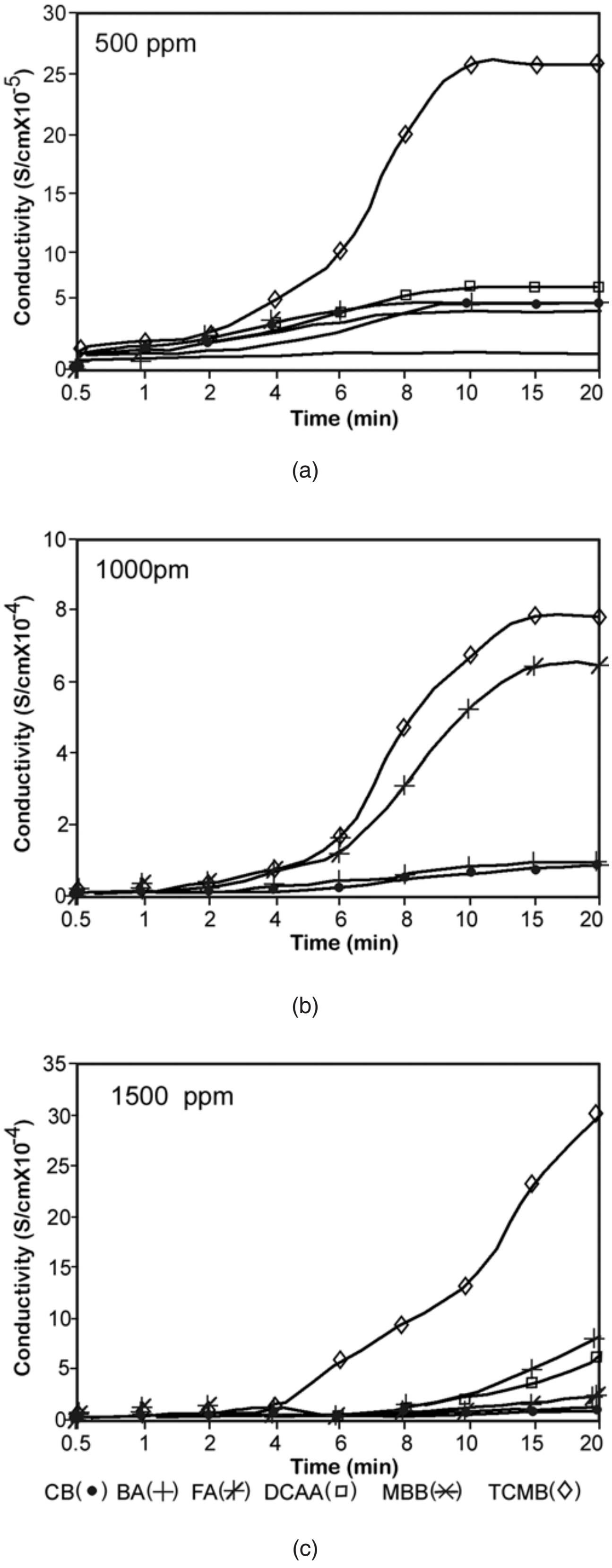


Figure 7. Conductivity of PANi ($\delta_0 = 1.3\times10^{-6}$ Scm^{-1}) vs. time for (a) 500 ppm, (b) 1000 ppm, and (c) 1500 ppm of Cl_2, Br_2 and I_2 at room temperature.



(a)

(b)

(c)

Figure 8. Conductivity of PANi ($\delta_0 = 1.5\times10^{-6}$ Scm^{-1}) vs. time for (a) 500 ppm, (b) 1000 ppm, and (c) 1500 ppm of CB, BA, FA, DCAA, MBB, and TCMB at room temperature.

of the organic semiconductor clearly indicates that electrical charges, i.e. electrons, have been transferred from polymer to the dopant molecules. The removal of the electrons by the gas and vapour dopants in the PANi is due to the formation of a weak charge-transfer complex between the matrix which is acting as a donor and the gases and vapours which are acting as acceptors.

The absorption of gases and vapours into PANi appears to be a two stage process involving firstly, the penetration of vapours into the polymer accompanied by swelling and secondly, the diffusion of vapours into the swelled rubbery material with an increased rate. Full recovery is not attained after the first exposure leading to a second exposure with a modified polymer containing initial concentrations of gas and vapour. As swelling is the rate determining step of the sorption.

In this work, all the films were exposed to diluted ammonia solution or vapours of organic solvents and swelled before doping. It is resulted in faster gas absorption and diffusion into polymer. However, the polymer response time to toxic gases and vapours was decreased and the rheology of polymer was slightly degraded.

Conductivity, Stability, and Recovery Times

The investigation of conductivity and stability of doped PANi shows significant changes in conductivity when the polymer is exposed to hydrogen halides, hydrogen cyanide, hydrogen sulphide, halogens and halomethyl compounds. It shows that the diffusion of halogens into polymer chains is a slow process probably, because they are molecular species. The stability of doped films with hydrogen halides, hydrogen cyanide, hydrogen sulphide, halogens and halomethyl compounds were from one week to several months.

The results of XRF and conductivity of exposed polymers to the toxic vapours show that conductivity and absorption are increased with increasing the concentration of the samples.

The chloroacetic acid derivatives show a better conductivity than the acetic acid. However, increasing the number of chlorine atoms have small effect on conductivity. In fact, with size increasing, molecular diffusion into films is decreased as shown in Table 4.

The halomethyl compounds show better conductivity than similar compounds, because the rate of molecular diffusion and doping process are increased by release of $Cl^{\bullet}$ and $Br^{\bullet}$ radicals (Table 5). Sensors stability and recovery times are different. The sensitivities of

Table 7. Variation of the conductivity of PANi ($\delta_0 = 1.5\times10^{-5}$ Scm^{-1}) with catalytical co-insertion HCl gas less than 100 ppm in 1400 ppm concentration (samples) at room temperature.

Sample	I_2	AA	CB	FA	BA	HCA
Conductivity (S/cm)	1.0	2.4×10^{-4}	2.1×10^{-4}	2.0×10^{-4}	1.2×10^{-5}	9.2×10^{-6}

films, that have not been swelled by solutions or organic solvents, before the test, were approximately reversible. The recovery times of the films that were exposed to halogens, hydrogen halides, hydrogen cyanide, hydrogen sulphide, AA, MCAA, DCAA, TCAA, HCA and FA were between 2-7 days. The recovery times of the films that were exposed to CB, MBB and TCMB were between 6-10 days and their sensitivities were completely irreversible. On the other hand, if all the films have been swelled before doping, they have showed irreversibility for all samples but halomethyl compounds showed conductance stability for a few months. In this research, the curves related to the conductivity changes via time of some toxic gases and vapours are not showing, briefly.

Mechanism of Conductivity

Beniere [31] using results on p-doped conducting polymers, have expressed the conductivity as a function of the dopants concentration. They have been able to demonstrate that the conductivities of the doped polymers depend on the dopants concentration and not on the types of dopants. But the theoretical calculations on the electronic structure of the conducting polymers by Ignatious and François, [32] suggest that the geometry of the counter ions will significantly influence the electronic conductivity. This recent discovery has incited great enthusiasm to ascertain the factors, limiting the measured macroscopic conductivities in the conjugated systems, so as to further improve and to predict them correctly. Hence it became important to distinguish between the interchain and intrachain transport processes and assign the predominance of one over the other. The large increase of electronic conductivity brought about by treating the emeraldine base form of polyaniline with toxic oxidant samples involves a new type of doping of conducting polymers. It occurs by toxic oxidants and hydrogen halides addition to the polymer rather than by partial oxidation of the polymer system, as is the case in the p-doping of other conducting polymers [33]. The formation of a nitrogen base salt rather than a potentially highly reactive carbonium ion is believed to be responsible for the high chemical stability of the material in the environment. Unlike all other conducting polymers, the conductivity of polyaniline depends on two variables instead of one, viz, the degrees of oxidation and protonation of polyaniline. The proton and oxidant addition results in partial depopulation of the system. It is proposed that the emeraldine salt form of polyaniline shows high conductivity because of extensive conjugation in the polymer chain. The resulting highly conjugated system, in addition to contribution to the high conductivity, would also be expected to impart extra stability to this form of polyaniline. It would also be expected to increase the strength of the emeraldine base to a value greater than that was found in amines containing phenyl-nitrogen bonds. Such amines are known to be very weak bases (pK_a $(C_6H_5)_2NH^{2+}$= 1.0) [34].

Doping by toxic samples produces notable swellings in the films. Although no quantitative study of this kind has been made, the increase in the dimensions of the films that are doped by the larger samples such as HI, I_2, TCAA, TCMB, and HCA compared to the ones that are doped with the smaller ones can be estimated around 10%. For the calculation of the conductivities, the initial dimensions of the films (after the primary swelling) have been used which introduced a systematic deviation. This effect can be neglected in comparison to the variation of the studied conductivities.

The doping kinetics for halogens, FA, CB, HCA, AA, MCAA, DCAA, and TCAA are extremely slow and after a few days the maximum doping levels were attained, resulting in low conductivity values, but by hydrogen halides, hydrogen cyanide, hydrogen sulphide and halomethyl compounds, conductivities reach a maximum value within 1 h, depending on the film thickness and density. The maximum conductivity value of the doped films depends strongly on the quality of the films and their history prior to doping.

Effect of Co-inserted HCl Gas on the Conductivity

The experimental results demonstrate that slight additional amounts of co-insertion of HCl gas in tested gases will significantly influence the conductivity. The co-inserted HCl gas less than 100 ppm is found to influence drastically the transport and magnetic properties of the doped films, depending on the doping level and the nature of the dopants. Table 7 shows the results of some tested gases and vapours after 10 min exposure.

This investigation justify that to what extent interchain transport may become the limiting process between two competing but complementary mechanisms that contribute to the macroscopic conductivities. The decrease in conductivity by two orders of magnitude by increasing the size of the HCA species in vapour and a further increase by amount of co-inserted HCl gas, whose efficiency depends on the nature of the tested toxic gases and vapours, furnish ample evidence for this mechanism.

CONCLUSION

The presented results in this work show that HCl, HBr, HI, Br_2, I_2, and halomethyl compounds are good candidates for sensitive device in gas and vapour sensors. Investigation of the conductivity of doped PANi showed significant changes in conductivity when the polymer was affected by these samples. The diffusion of halogens into the polymer chains is a slow process for larger molecular such as HCA. They decrease the conductivity by decreasing intrachain electron transfers. Finally, the results of mass and conductivity measurements of these polymers exposed to the toxic gases and vapours show that conductivity and the absorption increase with increasing the samples concentration. Swelled PANi film tends to decrease the response times of polymer to toxic gases and vapours.

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