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EVALUATION OF ELECTRICAL RESPONSE OF *POLY-ANILINES* IN THE EMERALDINE OXIDATION STATE AS ACTIVE LAYER TO DISPOSABLE SENSOR

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A disposable electronic nose was used to evaluate the difference in electrical response of the poly-aniles (conductive polymers (polyaniline) and oligomer (phenyl/-NH_2 end capped tetraniline (PhECT))) both doped with dodecylbenzenesulfonic acid (HDBSA) and hexafluoro – 2 – propanol (HFIP) as solvent to detected vapor of toluene using the line patterning of graphite to developed interdigitated electrodes atop overhead transparency (poly(ethylene terephthalate) (PET)). In the same concentration of toluene vapor (5000ppm$_v$) the sensibility (ΔR%) of the two sensors were quite different. The ΔR% of the conducting oligomer response $\approx$ 7.4 times than polymer (PANI) at the same concentration. The 1H NMR of the PhECT was used to check the synthesis.

Introduction

In the last ten years the interest for developing new sensors for industry, agriculture, the environmental, medicine and military applications has increased [1-2]. Special interest has been devoted in sensing air-borne volatile organic compounds, VOCs, especially for compounds that have no chemical reaction with conducting polymers, such as aromatic and aliphatic compounds, alcohols, ethers, esters and halocarbons (1).

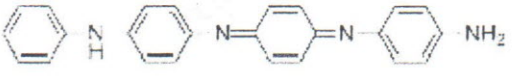
MacDiarmid and collaborators (1999) showed that oligoanilines has important interaction with VOC (2). The authors have concluded that the nature of the solvent may be play an important role to defining the positional isomeric composition in solution .

Hopkins and collaborators have found that hexafluoro – 2 – propanol (HFIP), a low boiling point (59^0 C) and mildly acidic (pKa=9.3) solvent, fully dissolves both the PANI-EB and PANI-ES forms (3). Feng and MacDiarmid have reported that when a more polar and hydrogen bonding solvent such as m-cresol or HFIP is introduced into the doped polymer, the solvation of the dopant anion and positive charges on the polymer chains, as well as increased interactions between solvent and polymer chains, result in an expansion of the polymer chain with concomitant delocalization of polarons along the chains (4).

The doping of polyanilines and oligoanilines is in principle an acid-base reaction. The doping acids react with the basic nitrogen atoms of the oligoanilines and polyanilines.

A proposal of structure to PhECT-EB and PANI-EB are showed in the figure below:

Polyanilie in the emeraldine oxidation state (PANI-EB)



Phenyl/-NH_2 end capped tetraaniline emeraldine oxidation state (PhECT-EB)

The main objective of this work was to investigate the electric response of the sensor, developed with line patterning technique (LPT) (5), and the behavior of active layer PhECT and PANI, both in emeraldine oxidation state, doped with dodecylbenzenesulfonic acid (HDBSA) and hexafluoro – 2 – propanol (HFIP) as solvent to detected toluene vapor (C=5000ppm$_v$). As well to check the synthesis of the oligomer, using 1H NMR The investigation could be useful to developed nanolayer of conductive polymers and oligomers to vapor sensors.

Experimental

In this experiment a synthesis (oxidative coupling) of PhECT was prepared following directions described in Feng's dissertation (4), and it was used to prepare a 2.9% Tetraaniline Emeraldine•DBSA and 2.9% Polyaniline Emeraldine•DBSA in both case using HFIP as solvent.

The sensor developed with LPT (5) was kept in the presence of the static lab air for 5 minutes, and in the sequence it was placed inside the jar for 35 minutes, after this time the toluene (5000ppm$_v$) and during 5 minutes the sensor was exposed to toluene vapor. Then

it was removed from the jar and kept in the static lab air for 5 minutes.

Results and Discussion

The results of the electrical response of the sensors developed with LPT and using PhECT doped with HDBSA and HFIP as solvent as well PANI doped with HDBSA and HFIP as solvent both in the emeraldine oxidation state (EB) are showing in the Figure 1 and . Figure 2 respectively.

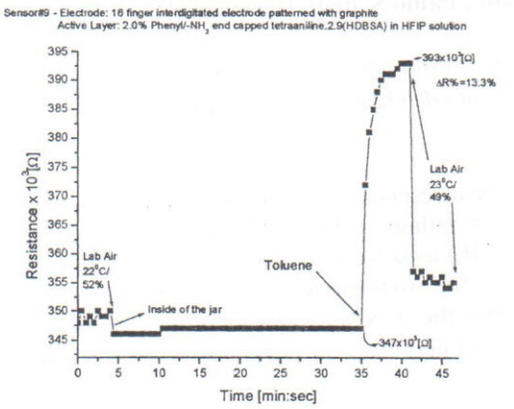


Figure 1 - Electrical response to toluene vapor (5000ppm$_v$) to sensor prepared with tetraaniline emeraldine and 16-finger interdigitated electrode patterned with graphite.

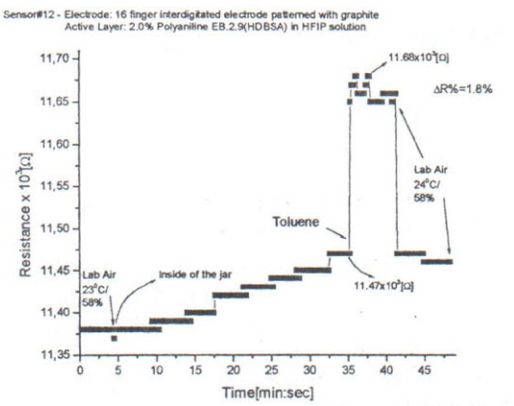


Figure 2 - Electrical response to toluene vapor (5000ppm$_v$) to two sensors prepared with polyaniline emeraldine base and 16-finger interdigitated electrode patterned with graphite.

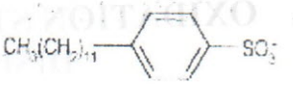
The sensitivity (ΔR%) was investigate to both sensors and the results are presented in the table 1. The electrical response (Ω) of PhECT-EB•DBSA/HFIP is 7.4 times higher than PANI-EB•DBSA/HFIP.

Table 1 – The sensitivity (ΔR%) to toluene vapor (5000ppm$_v$)

Active layer	Electrode	ΔR%
Tetraaniline EB.2.9 HDBSA	16-finger	13.3
Polyaniline EB 2.9 HDBSA	16-finger	1.8

The investigation suggest that isomerization is catalyzed by both acidic and basic solvents by a tautomeric.

It has been found that some dopant, for example camphor sulfonic acid (CSA) and p-dodecylbenzenesulfonic acid (DBSA), render polyaniline soluble in organic solvents with high conductivity (6). The longest aliphatic sulfonate counteranion (HDBSA) prevents the PANI-ES chains from packing and reduces any long-range order, actuating as "inert" spacers (2).



DBSA

To evaluated the quality of synthesis of the phenyl/–NH_2 end capped tetraaniline in the emeraldine oxidation state (PhECT-EB) was used chemical shift from NMR showed in the figure 3. In this figure the signal from 6.5 to 7.5ppm are attributed to the hydrogen's in the aromatic rings and above 7.5ppm is related to hydrogen's in amine group, as was expected .

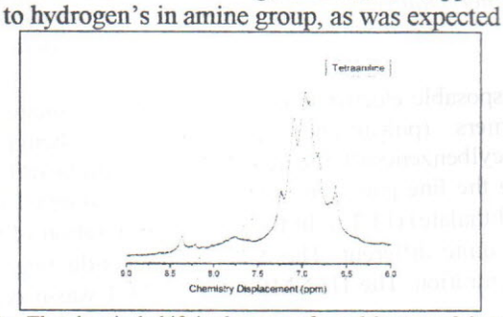


Figure 3 – The chemical shift in the range from 6.0ppm to 9.0ppm obtained with use of NMR spectroscopy of the PhECT-EB in the solution of DMSO-d_6 deuterium

One explanation of the difference in the electrical response behavior, could be due the different morphology of the PhECT and PANI atop plastic substrate with HFIP solvent, as was seen in the image, using Atomic Force Microscopy (AFM) (data not show).

Conclusions

The graphite interdigitated electrode on to plastic developed by using LPT and PhECT-EB•DBSA, as active layer and using HFIP as solvent has shown good sensitivity to organic vapor and it can be used as a sensor to toluene vapor.

Aknowledgements

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References

1 B.A. Snopok and I.V. Kruglenko, Multisensor Systems for Chemical Analysis: State-of-the-Art in Electronic Nose Technology and New Trends in Machine Olfaction, *Thin Solid Films*, 2002, *418*, 21-41;

2. MacDiarmid, A.G.; Zhou, Y.; Feng, J. Oligomers and isomers: new horizons in poly-anilines. *Synthetic Metals*, 1999, .*100*, 131-140;

3. Hopkins, A.R.; Rasmussen, P.G.; Basher, R.A. Characterization of solution and solid state properties of undoped and doped polyanilines processed from Hexafluoro – 2 – propanol. *Macromolecules*, 1996, *29*, 7838-7846;
4. Feng, J. Poly-anilines: Synthesis, characterization and applications. Tese de Doutorado em Química, UPENN, p.i-xxiv; 1-233, 1999;
5 Herrmann, P. S. P.; Venâncio, E. C. ; Mattoso, L H C.; MacDiamird, A G. Polyaniline-based sensor obtained by using line patterning technique on plastic. In: CONGRESSO BRASILEIRO DE ENGENHARIA E CIÊNCIA DOS MATERIAIS, 16, 2004, Porto Alegre. Trabalhos Completos. Porto Alegre, RS : CBECIMAT, v. CD ROM. p. n.pg.-13fl.. 2004;
6. Shen, Y.; Wan, M. *In-situ* doping polymerization of polypyrrole with sulfonic acid as a dopant, *Synthetic Metals*, 1998, *96*, 127-132.