Conductivity modeling of gas sensors based on copper phthalocyanine thin films

Modélisation de la conductivité de capteurs de gaz à base de couches minces de phtalocyanine de cuivre

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الملخص:

يهدف هذا البحث أساسًا إلى دراسة الناقلية الكهربائية لأغشية رقيقة من فثالوسيانين النحاس (CuPc) في وجود بعض الغازات الـمؤكسدة القوية التي تساهم في تلويث الهواء، خاصة منها NO_2، وذلك لإستخدامها في أجهزةٍ لإستشعار الغاز. و لتحقيق هذه الغاية، يعرض الجزء الأول للبحث دراسة تطور التوصيل الكهربائي لهذه المِجسّات، من أجل التوصل إلى أفضل درجة حرارة للتشغيل، وكذا لتحسين حركية امتصاص جزيئات الغاز على سطح الطبقة الرقيقة. في مرحلة ثانية، حاولنا تطوير نموذج رياضي يصف بأكبر قدر ممكن من الدقة السلوك الكهربائي لهذه المِجسّات لمحاكاة تشغيلها ولتحسين أدائها. وقد تم تطبيق نماذج "Elovich" على حد سواء في مرحلتي امتصاص الغاز و مجّه على سطح الطبقة الحسّاسة ، وأدت المقارنة إلى وجود تشابه كبير بين منحنيات الإستجابة النظرية و التطبيقية.

الكلمات المفتاحية : *مِجسّات الغاز - طبقة رقيقة - فثالوسيانين - الناقلية - النمذجة* .

Résumé

L'objectif principal de ce travail est l'étude de la conductivité électrique de couches minces de phtalocyanine de cuivre (CuPc), en présence de certains gaz oxydants forts impliqués dans la pollution de l'air, particulièrement le NO_2, pour une utilisation en tant que dispositifs de détection de gaz. Pour atteindre cet objectif, la première partie présente l'étude de l'évolution de la conductivité de ces capteurs de gaz afin de trouver la température optimale de fonctionnement et d'améliorer la cinétique d'adsorption des molécules de gaz sur la surface de la couche mince. Dans une deuxième étape, nous avons essayé de développer un modèle mathématique qui décrit le plus fidèlement possible le comportement électrique de ces capteurs afin de simuler leur fonctionnement et d'optimiser leurs performances. Les modèles d'Elovich ont été appliqués à la fois à la phase d'adsorption et à la phase de désorption de gaz par la couche sensible et ont conduit à de bonnes similitudes entre les courbes de réponse théoriques et mesurées.

Mots clés : *Capteurs de gaz - couche mince - phtalocyanine - conductivité - modélisation.*

Abstract

The main objective of this work is to study the electronic conductivity of copper phthalocyanine (CuPc) thin films in presence of certain strong oxidizing gases involved in air pollution, particularly NO_2, for use as gas sensor devices. To achieve this objective, the first part presents a study of the conductivity evolution of these sensors, in order to find the optimal operating temperature and to improve the kinetics of adsorption of gas molecules on the surface of the thin layer. In a second step, we tried to develop a mathematical model that describes as closely as possible the electrical behavior of these sensors in order to simulate their operation and optimize their performances. Elovich models have been applied to both gas adsorption and desorption phases and have led to good similarities between theoretical and measured response curves.

Keywords : *Gas sensors - thin layer - phthalocyanine - conductivity - modeling.*

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1. INTRODUCTION

Nowadays, there is an increasing interest in developing conductometric sensors for gas detection. A way of detecting gas with conductance techniques could be using a material whose electrical properties vary in the presence of that gas [1]. To perform the continuous monitoring of pollutants in troposphere, national agencies of air quality control networks use expensive commercial analyzers based on spectroscopic techniques. Despite their satisfying performances for such application (high selectivity, low threshold, good resolution and weak response times), gas analyzers are not appropriate to realize pollutant cartography with high spatial resolution because of their price, their dimensions, their difficult implementation and their poor mobility. To compensate these disadvantages for such application, the use of chemical gas sensors constitutes a very attractive alternative [2].

Amongst all pollutants present into the troposphere, some of them are dangerous in high concentrations and must be monitored [3] such as NO_2 [4], NO [5], SO_2 [6, 7] and some volatile organic compounds (VOC) [8, 9]. Nitrogen oxides (NO_X: NO and NO_2) are released from cars exhausts and combustion processes. They cause lung irritations, decrease the fixation of oxygen molecules on red blood corpuscles and contribute to acid rains. Nitrogen dioxide, NO_2, remains a pollutant which requires a special monitoring in view of its dangerousness for health and environment. Its health hazards are well-established: above 80 ppb, respiratory troubles begin to be acute [10]. In urban atmosphere, NO_2 is the reaction product of nitrogen monoxide (NO) oxidation process with oxygen according to the reaction (1), the kinetics of reaction being fast because of the chemical instability of NO in air.

$$NO + \frac{1}{2}O_2 \rightarrow NO_2 \qquad (1)$$

Phthalocyanines (Pcs) have been studied for many years and they are still the subject of intense investigations. Pc and its transition metal complexes have been used in various technological applications, such as gas sensors [11 - 13], catalysts [14], solar cells [15], liquid crystals [16, 17], nonlinear optics [18], electrochromic displays [19] and photodynamic therapy (PDT) [20 - 22].

2. MATERIAL AND METHODS

The sensor system developed in this work takes advantage of the partial selectivity of phthalocyanine-based chemoresistors to strong oxidizing analytes (NO_2 and O_3) [23 - 25]. Thus, the sensitive element of our gas sensor device consists in a copper phthalocyanine (CuPc) thin films of 300 nm prepared by physical vapor deposition (PVD) (evaporation rate was 0.2 nm/s) under vacuum (approximately 2.10^{-6} mbar) onto interdigitated electrodes screen-printed on the upper side of an alumina substrate (3mm × 5mm × 0.3mm). On the lower side of the substrate, a screen-printed platinum resistor is devoted to sensor temperature control (Fig. 1). Interdigitated Pt electrodes (IDEs), polarized under 1 volt dc, are used to measure conductivity variations of the CuPc thin film which depend, in time, of gas concentration in sensor environment [26].

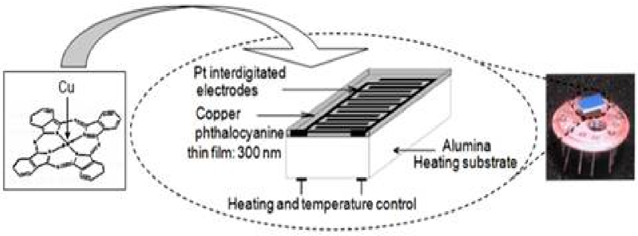

Figure 1: Copper phthalocyanine thin film evaporated on alumina substrate and placed on integrated circuit socket (TO8 type).

A methodology of measurements which exploits the kinetics of sensor response is applied. It overcomes the problem of the long response time these sensors suffer and improves the reproducibility of measurements by reducing drifts in sensor responses.

The dimensions of the interdigitated electrodes being perfectly determined (*L*: length = 25 mm; l_S: inter-electrode space = 0.125 mm), the electronic conductivity σ of CuPc thin film with thickness *e* can be determined from electrical current *I* passing through the sensor polarized under bias voltage *U* according to the following equation:

$$\sigma = \frac{l \cdot l_s}{U \cdot L \cdot e} \qquad (2)$$

The current delivered by the structure and linked to conductivity variations is measured at regular time intervals by means of a Keithley digital multimeter. Data are then transferred by RS232 serial link to a computer to be recorded and easily treated.

3. EXPERIMENTAL

The presence of oxidizing gases such as NO_2 in the environment of the sensor causes a change in its conductivity (increase). This results from a combination of physico-chemical reactions between the sensitive layer of the sensor and the gas molecules adsorbed on its surface (Fig. 2).

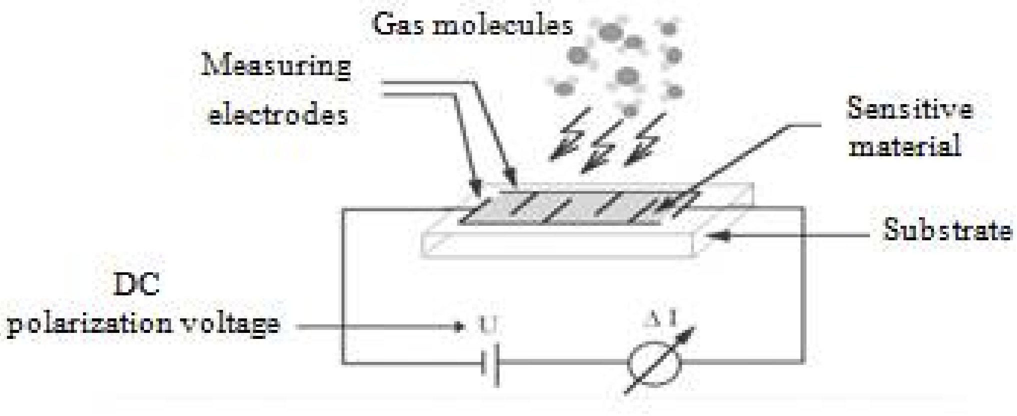

Figure 2: CuPc-based sensor conductivity measuring method.

The levels of nitrogen dioxide in the atmosphere may change from a few ppb to about 100 ppb, depending on weather conditions, human activities and seasons. Therefore, the behavior of our structures has been tested for NO_2 concentrations ranging between 20 to 100 ppb and for temperatures ranging between 50 to 150 °C.

Figures 3 and 4 show the behavior of a CuPc thin layer exposed alternately to NO_2 doping cycles during one hour, followed by desorption phase in pure nitrogen during three hours at various operating temperatures (50, 80, 120 and 150 °C). The exposure time is chosen in line with the evolution dynamic of NO_2 in the atmosphere. At relatively low temperatures, i.e. 50 °C and 80 °C, the reaction kinetics do not allow obtaining a stable conductivity value, and despite a ratio of 1/3 between exposure time / rest time, the reversibility of the physico-chemical processes is not complete (Fig. 3). The average conductivity increases due to the gradual occupation of the adsorption sites in the bulk of the layer. However, the response of our structure depends on the concentration of nitrogen dioxide, and the amplitude of the conductivity variations found for various increasing concentrations during the same time interval increases. Similar behavior is observed for higher temperatures (120 °C and 150 °C) as illustrated in Fig. 4. However, the reversibility of the sensor response is significantly improved in this case.

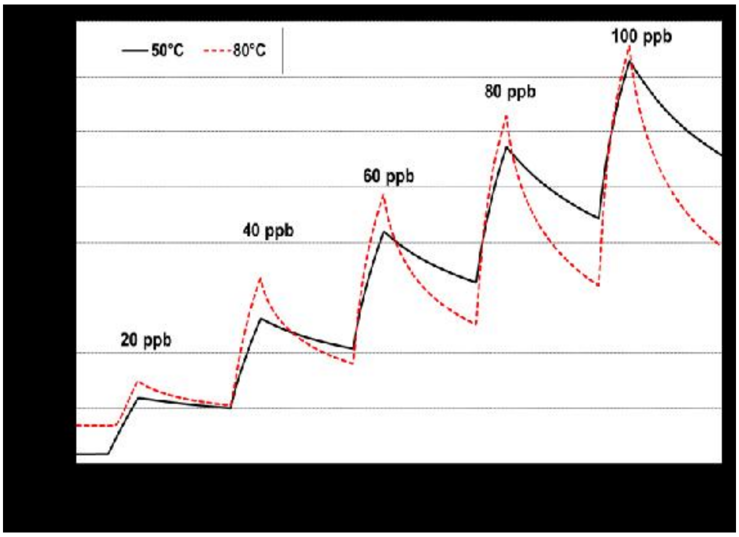

Figure 3: Conductivity variations versus time of CuPc thin layer (300 nm) at various temperatures (5O °C and 80 °C), exposed alternatively to NO_2 concentration increments followed by return under clean air after each exposure.

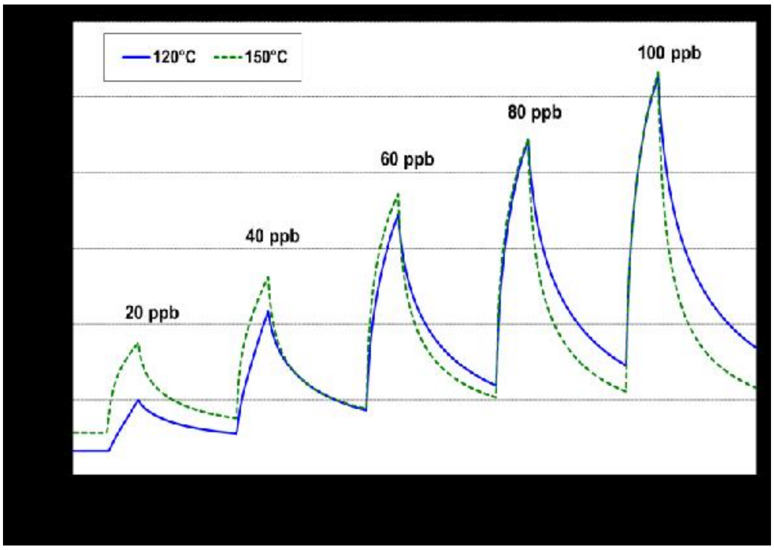

Figure 4: Conductivity variations versus time of CuPc thin layer (300 nm) at various temperatures (12O °C and 150 °C), exposed alternatively to NO_2 concentration increments followed by return under clean air after each exposure.

4. MODELING AND SIMULATION

4.1 Modeling of the conductivity evolution according to the concentration of doping gas at various temperatures

In constant temperature, the conductivity increases according to the concentration of NO_2 in the range 20 to 100 ppb. If the temperature is enough brought up, a good reversibility of the adsorption process is observed for increasing then decreasing of the doping gas concentration [26 - 30].

We use the following relation:

$$\sigma = K \cdot C^{\alpha} \qquad (3)$$

Where *C* is the concentration of the doping gas.
K and *α* are constants.

A passage by the natural logarithm makes it possible to linearize the equation (3), and to deduce the coefficient α by means of the method of least squares. The values obtained for various temperatures are presented in Table 1:

Table 1 : Coefficient α for different T°

T (°C)	50	80	120	150
A	1.135	0.999	1.052	0.695

The conductivity is proportional to C^{α}, where C is the concentration of NO_2. When the temperature increases, the coefficient α decreases as well as the sensibility of the material as shown in Table 1. The experimental results show that the optimal temperature for the adsorption phase is located around 50 °C (Fig. 5).

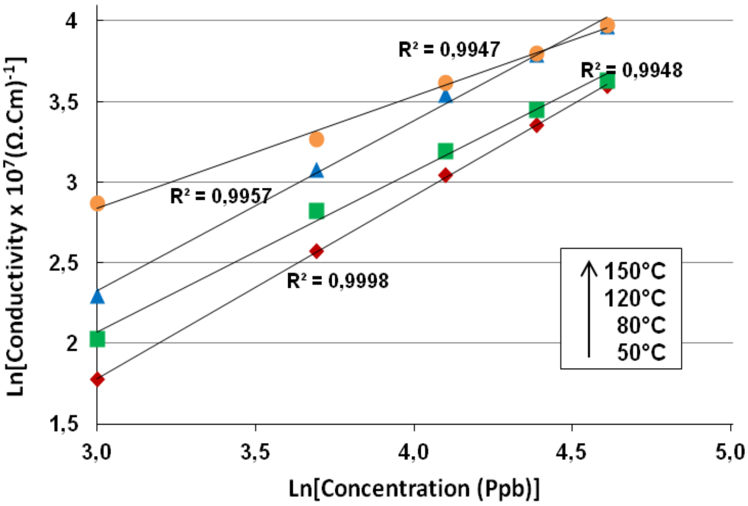

Figure 5: Log – Log plot of the conductivity evolution vs. NO_2 concentration.

4.2 Modeling of the adsorption and desorption phases

The modeling of the adsorption / desorption kinetics of NO_2 by metallo-phthalocyanines (MPc) thin films has always attracted researchers interest [32, 33]. Some of them have suggested that information about NO_2 concentration may be derived from the initial conductivity changes of an MPc film, rather than from data obtained under saturation conditions [34].

There are several isotherms for modeling the adsorption processes of gaseous species on solid [36, 37]. Elovich equation has been widely used to describe the adsorption of gas onto solid systems and adopted to examine the mechanism of the adsorption process [38]. Thus, it was suggested that the initial response of CuPc thin films to NO_2 exposure follows the Elovich equation [1]:

$$\frac{d\theta}{dt} = a \cdot e^{(-b.\theta)} \qquad (4)$$

Where $d\theta/dt$ represents the rate of change of the surface coverage θ, and a, b are constants: a is the initial sorption rate and b is the desorption constant during any one experiment [1, 34].

4.2.1 Adsorption phase

Integrating equation (4) and applying the initial condition: at $t = 0$, $\theta = \theta_0$: initial coverage rate, give:

$$e^{(b\cdot\theta)} = a\cdot b\cdot t + e^{(b\cdot\theta_0)} \qquad (5)$$

Assuming that the change in electrical conductivity is proportional to the change of surface coverage ($\sigma \sim \theta$), it follows that:

$$e^{(b'\cdot\sigma)} = a'\cdot b'\cdot t + e^{(b'\cdot\sigma_0)} \qquad (6)$$

and:

$$\sigma = \frac{1}{b'}\cdot\ln(a'\cdot b') + \frac{1}{b'}\cdot\ln(t + t_0) \qquad (7)$$

$$t_0 = \frac{1}{a'\cdot b'}\cdot e^{(b'\cdot\sigma_0)}$$

Where *b'* is a constant, σ_0 initial conductivity before exposure to the gas and *a'* is a coefficient depending on the dopant gas concentration.

This relationship is particularly correlated with the results of the NO_2 action on copper phthalocyanine obtained by Zhou and Gould (1998) [37, 39].

Figure 6 shows the comparison of experimental measurements and data calculated from equation (7) with the coefficients shown in Table 2, for one hour doping with various NO_2 concentrations of a CuPc thin layer maintained at 50 °C, and of which complete response is given in Figure 3.

Table 2 : Coefficients associated to Elovich model and determination coefficient values (R^2) for various NO_2 concentrations, describing the sensor response at 50 °C in adsorption phase.

NO_2 Concentration (ppb)	***a'***	***b'***	***t_0***	***R^2***
20	$1.12\ 10^{-8}$	$7.69\ 10^{-5}$	122.3	0.99865
40	$2.75\ 10^{-8}$	$7.69\ 10^{-5}$	69.0	0.99972
60	$6.04\ 10^{-8}$	$7.69\ 10^{-5}$	47.6	0.99978
80	$1.19\ 10^{-7}$	$7.69\ 10^{-5}$	38.1	0.99985
100	$2.37\ 10^{-7}$	$7.69\ 10^{-5}$	29.8	0.99991

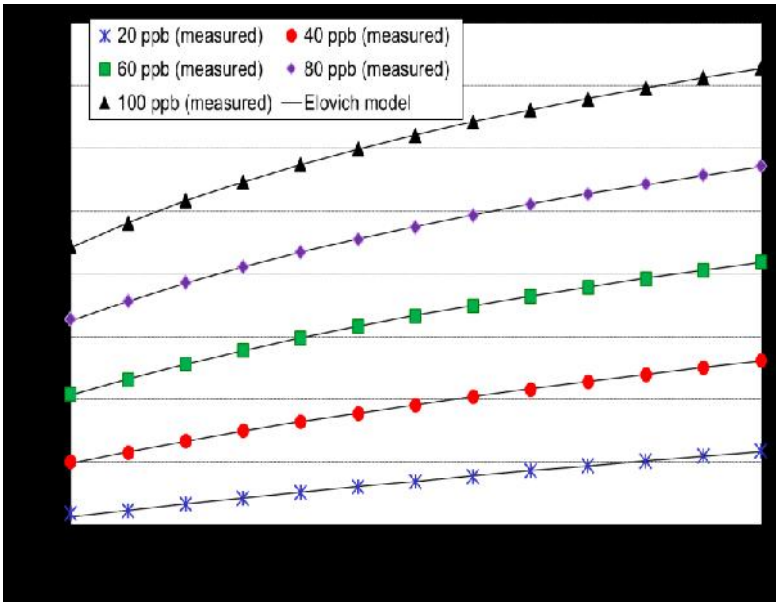

Figure 6: Confrontation between the experimental data and Elovich model for a CuPC thin film exposed to various NO_2 concentrations at T = 50 °C in adsorption phase.

4.2.2. Desorption phase

In terms of modeling of the gas sensors response kinetics, most of the researchers are solely interested in the gas adsorption phase onto the sensitive layer [35, 40]. However, a satisfactory behavior of these structures as gas sensors requires a good reversibility of the phenomenon, resulting in a rapid return to the rest state as soon as the action of the target gas stops. This property follows directly from the reversibility of physisorption and chemisorption reactions between target gas and sensitive material, and affects the reproducibility of measurements.

Applying the Elovich model, and using the equation (5) for the NO_2 desorption phase yield a best fitting to the experimental data as shown in Figure 7. This good matching is performed for the values of the parameters shown in Table 3.

Figure 7 shows the comparison of experimental measurements and data calculated from equation (7) with the coefficients shown in Table 3, for one hour dedoping under clean air after exposure to various NO_2 concentrations of a CuPc thin layer maintained at 50 °C, and of which complete response is given in Figure 3.

Table 3: Coefficients associated to Elovich model and Determination coefficient values (R^2) for various NO_2 concentrations, describing the sensor response at 50 °C in desorption phase.

NO_2 Concentration (ppb)	***a'***	***b'***	***t_0***	***R^2***
20	$-1.74\ 10^{-11}$	$-6.2\ 10^{-6}$	231	0.99907
40	$-1.57\ 10^{-11}$	$-3.92\ 10^{-6}$	92.5	0.99987
60	$-4.13\ 10^{-11}$	$-2.23\ 10^{-6}$	99.3	0.99995
80	$-7.91\ 10^{-11}$	$-1.52\ 10^{-6}$	106.3	0.99996
100	$-9.25\ 10^{-11}$	$-1.24\ 10^{-6}$	93.3	0.99987

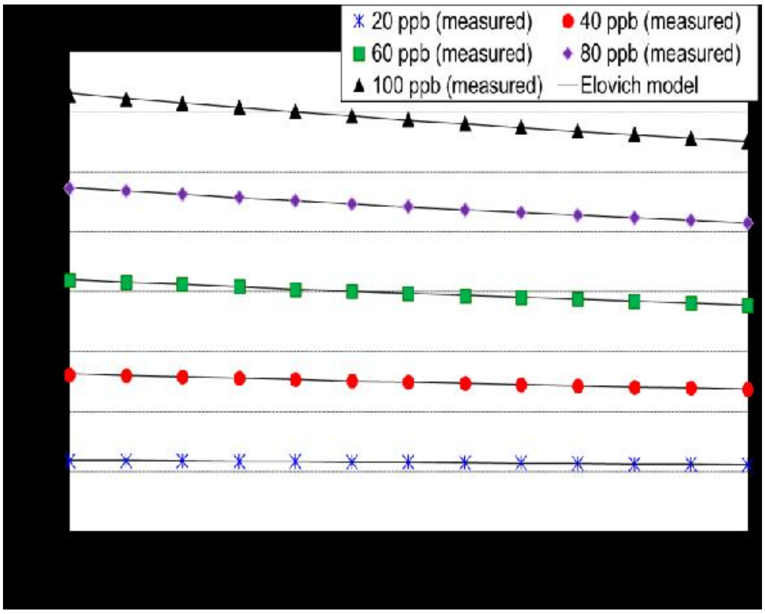

Figure 7: Confrontation between the experimental data and Elovich model for a CuPC thin film exposed to various NO_2 concentrations at T = 50 °C in desorption phase.

4.2.3. Discussion

Figure 6 and Figure 7 highlight a very good correlation between the experimental data and those calculated from the Elovich model, thus allowing to affirm that this model describes with a good accuracy the response of our gas sensor to the dopant gas both in adsorption and desorption phases.

5. CONCLUSION

The present study deals with a sensor-system achieving the monitoring of nitrogen dioxide in an environmental context. The sensing element consists of a copper phthalocyanine thin film chemoresistor which exhibits a partial selectivity to strong oxidizing species in air, i.e. ozone and nitrogen dioxide. Because of its high sensitivity and its partial selectivity towards oxidizing pollutants (nitrogen dioxide and ozone), copper phthalocyanine-based chemoresistors are relevant.

We have demonstrated their high sensitivity to the nitrogen dioxide at very low concentrations (ppb) and relatively low temperature (50 °C). Their small dimensions, compatible with microelectronics techniques, and their low cost make them an attractive alternative to conventional gas analyzers. Then, in order to find the optimal operating temperature, and to improve the adsorption kinetics of gas molecules on the surface of the thin layer, modeling the law of conductivity evolution versus the concentration of the doping gas at different temperatures suggests an optimal operating temperature, favoring the adsorption process of the gas molecules by the thin layer, around 50 °C. On the other hand, we tried to model the electrical conductivity of these devices toward the target gas concentration. We found that the response curves derived from experimental data coincide perfectly with the proposed Elovich model, both in adsorption and desorption phases with determination coefficient (R^2) values close to 1. The analysis of experimental data and those provided by the proposed model has revealed the existence of a relationship between the dopant gas concentration and the parameter *a'* of the Elovich model thus allowing to estimate the concentration of the target gas from this parameter value.

REFERENCES

[1] Altındal A., Kurt Ö., Şengül A. & Bekaroğlu Ö. 2014. Kinetics of CO_2 adsorption on ball-type dicopper phthalocyanine thin film, *Sensors and Actuators B: Chemical*, Vol. 202, 373 - 381

[2] Brunet J., Pauly A., Dubois M., Rodriguez-Mendez M. L., Ndiaye A. L., Varenne C. & Guérin K. 2014. Improved selectivity towards NO_2 of phthalocyanine-based chemosensors by means of original indigo / nanocarbons hybrid material, *Talanta1*, Vol. 27, 100 - 107.

[3] Mane A.T., Navale S.T. & Patil, V.B. 2015. Room temperature NO_2 gas sensing properties of DBSA doped PPy–WO 3 hybrid nano-composite sensor. *Organic Electronics*, Vol. 19, 15 – 25.

[4] Newton M.I., Starke T.K.H., Willis M.R. & McHale G. 2000. NO_2 detection at room temperature with copper phthalocyanine thin film devices. *Sensors and Actuators B: Chemical*, Vol. 67 (3), 307 – 311.

[5] Liu C.J., Shih J.J. & Ju Y.H. 2004. Surface morphology and gas sensing characteristics of nickel phthalocyanine thin films. *Sensors and Actuators B: Chemical*, Vol. 99 (2), 344 - 349.

[6] Do J.S. & Chen P.J. 2007. Amperometric sensor array for NO_x, CO, O_2 and SO_2 detection. *Sensors and Actuators B: Chemical*, Vol. 122 (1), 165 – 173.

[7] Özer M., Altındal A., Özkaya, A.R. & Bekaroğlu Ö. 2009. Ball-type supramolecular metallophthalocyanines with eight perfluorodecyl units: chemosensors for SO_2 and electrocatalysts for oxygen reduction. *Dalton Transactions*, (17), 3175 – 3181.

[8] Rodríguez-Méndez M.L., Souto J., de Saja R., Martínez J. & de Saja J.A. 1999. Lutetium bisphthalocyanine thin films as sensors for volatile organic components (VOCs) of aromas. *Sensors and Actuators B: Chemical*, Vol. 58 (1), 544 – 551.

[9] Odabaş Z., Altındal A., Özkaya A.R., Salih B. & Bekaroğlu Ö. 2010. Novel ball-type homo-and hetero-dinuclear phthalocyanines with four 1, 1′-methylenedinaphthalen-2-ol bridges: synthesis and characterization, electrical and gas sensing properties and electro-catalytic performance towards oxygen reduction. *Sensors and Actuators B: Chemical*, Vol. 145 (1), 355 – 366.

[10] International Center for Technology Assessment, In-Car Air Pollution: the Hidden Threat to Automobile Drivers: Report No. 4, *An Assessment of the Air Quality inside Automobile Passenger Compartments*, July 2000.

[11] Bouvet M. 2006. Phthalocyanine-based field-effect transistors as gas sensors, *Analytical and Bioanalytical Chemistry*, Vol. 384, 366 – 373.

[12] Altun S., Altındal A., Özkaya A.R., Bulut M. & Bekaroğlu, Ö. 2008. Synthesis, characterization, electrochemical and CO_2 sensing properties of novel mono and ball-type phthalocyanines with four phenolphthalein units, *Tetrahedron Letters*, Vol. 49, 4483 – 4486.

[13] Özer M., Altındal A., Özkaya A.R. & Bekaroğlu Ö. 2009. Ball-type supra molecular metallo-phthalocyanines with eight perfluorodecyl units: chemosensors for SO_2 and electrocatalysts for oxygen reduction, *Dalton Transactions*. (17), 3175 – 3181.

[14] Yılmaz F., Özer M., Kani İ. & Bekaroğlu Ö. 2009. Catalytic activity of a thermo regulated, phase-separable Pd(II)-perfluoroalkyl-phthalocyanine complex in anorganic / fluorous biphasic system: hydrogenation of olefins, *Catalysis Letters*, Vol. 130 (3 – 4), 42 – 647.

[15] Yang F. & Forrest S.R. 2008. Photocurrent generation in nanostructured organic solar cells, *ACS Nano*, Vol. 2 (5), 1022 - 1032.

[16] Eichhorn H., Wohrle D. & Pressner D. 1997. Glasses of new 2, 3, 9, 10, 16, 17, 23, 24-octasubstituted phthalocyanines forming thermotropic and lyotropic discotic mesophases. *Liquid crystals*, Vol. 22 (5), 643 – 653.

[17] Leznoff C.C., A.B.P. 1993. Lewer, Phthalocyanines, Properties and Applications, Vol. 2, *VCH Publisher*, New York.

[18] De La Torre G., Vazquez P., Agullo-Lopez F. & Torres T. 1998. Phthalocyanines and related compounds: organic targets for nonlinear optical applications, *Journal of Materials Chemistry*, Vol. 8 (8). 1671 – 1683.

[19] Abdurrahmanoğlu Ş., Özkaya A.R., Bulut M. & Bekaroğlu Ö. 2004. Synthesis, characterization, and electrochemical and electrochromic properties of sandwich dilutetium tetraphthalocyanine. *Dalton Transactions*, (23), 4022 – 4029.

[20] Rodriguez M.E., Zhang P., Azizuddin K., Delos Santos G.B., Chiu S.M., Xue L.Y. & Nieminen A.L. 2009. Structural factors and mechanisms underlying the improved photodynamic cell killing with silicon phthalocyanine photosensitizers directed to lysosomes versus mitochondria. *Photochemistry and Photobiology*, Vol.85 (5), 1189 – 1200.

[21] Camerin M., Magaraggia M., Soncin M., Jori G., Moreno M., Chambrier I. & Russell D.A. 2010. The in vivo efficacy of phthalocyanine nanoparticle conjugates for the photodynamic therapy of amelanotic melanoma, *European Journal of Cancer*, Vol. 46 (10). 1910 – 1918.

[22] Kakı E., Özkaya A.R., Altındal A., Salih B. & Bekaroğlu Ö. 2013. Synthesis, characterization, electrochemistry and VOC sensing properties of novel metallophthalocyanines with four cyclohexyl-phenoxyphthalonitrile groups. *Sensors and Actuators B: Chemical*, Vol. 188, 1033 – 1042.

[23] Larbi A., 1987. Evaluation des propriétés capteur de gaz d'un polymère électroactif et automatisation du banc de mesures, Thèse de Doctorat. Clermont-Ferrand II, France.

[24] Heilmann A., Lantto V., Müller M. & Hamann C., 1992. NO_2 monitoring as an air pollutant using lead phthalocyanine thin film sensors. *Sensors and Actuators B: Chemical*, Vol. 7 (1), 522 – 525.

[25] Zhou R., Josse F., Göpel W., Öztürk Z.Z. & Bekaroğlu Ö. 1996. Phthalocyanines as sensitive materials for chemical sensors. *Applied Organometallic Chemistry*, Vol. 10 (8), 557 – 577.

[26] Brunet J., Pauly A., Varenne C. & Lauron B., 2008. On-board phthalocyanine gas sensor microsystem dedicated to the monitoring of oxidizing gases level in passenger compartments. *Sensors and Actuators B: Chemical*, Vol. 130 (2), 908 – 916.

[27] Padma N., Joshi A., Singh A., Deshpande S.K., Aswal D.K., Gupta S.K. & Yakhmi J.V. 2009. NO_2 sensors with room temperature operation and long-term stability using copper phthalocyanine thin films. *Sensors and Actuators B: Chemical*, Vol. 143 (1), 246 – 252.

[28] Lee Y.L., Hsiao C.Y., Chang C.H. & Yang Y.M., 2003. Effects of sensing temperature on the gas sensing properties of copper phthalocyanine and copper tetra-tert-butyl phthalocyanine films. *Sensors and Actuators B: Chemical*, Vol. 94 (2), 169 – 175.

[29] Zuo X., Wang B. & Wu Y.Q., 2007. Effects of sensing temperature on the NO_2-sensing properties of octa-iso-pentyloxymetallonaphthalocyanine spin-coated films. *Sensors and Actuators B: Chemical*, Vol. 123 (1), 94 – 100.

[30] Lee Y.L., Tsai W.C. & Maa J.R., 2001. Effects of substrate temperature on the film characteristics and gas-sensing properties of copper phthalocyanine films. *Applied surface science*, Vol. 173 (3), 352 – 361.

[31] Berthet G., Blanc J.P., Germain J.P., Larbi A., Maleysson C. & Robert H. 1987. Electroactive polymers in thin layers: a potential application as a gas sensor. *Synthetic Metals*, Vol. 18 (1), 715 – 720.

[32] Iskandarani M.Z. 2010. Mathematical Modeling and Characterization of Thin Film, Narrow Gap Sensor Array Units (SAU). *American Journal of Applied Sciences*, Vol. 7 (9), 1277.

[33] Low M.J.D., 1960. Kinetics of Chemisorption of Gases on Solids. *Chemical Reviews*, Vol. 60 (3), 267 – 312.

[34] Ritchie A.G., 1977. Alternative to the Elovich equation for the kinetics of adsorption of gases on solids. *Journal of the Chemical Society, Faraday Transactions 1: Physical Chemistry in Condensed Phases*, Vol. 73, 1650 – 1653.

[35] López-Sancho J. & De Segovia J. 1972. Adsorption kinetics and electron desorption of O_2 on polycrystalline tungsten. *Surface Science*, Vol. 30 (2), 419 – 439.

[36] Morishige K., Tomoyasu S. & Iwano G., 1997. Adsorption of CO, O_2, NO_2, and NH_3 by metallophthalocyanine monolayers supported on graphite. *Langmuir*, Vol. 13 (19), 5184 – 5188.

[37] Wright J.D., 1989. Gas adsorption on phthalocyanines and its effects on electrical properties. *Progress in Surface Science*, Vol. 31 (1 - 2), 1 – 60.

[38] Tongpool R. & Yoriya S., 2005. Kinetics of nitrogen dioxide exposure in lead phthalocyanine sensors. *Thin Solid Films*, Vol. 477 (1), 148 – 152.

[39] Zhou Q. & Gould R.D., 1998. A study of the response rate to nitrogen dioxide exposure in metal phthalocyanine thin film sensors. *Thin Solid Films*, Vol. 317 (1), 436 – 439.

[40] Aharoni C, Tompkins F.C., 1970. Kinetics of adsorption and desorption and the Elovich equation. *Advances in catalysis*, Vol. 21, 1 – 49.