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Similarity between optical response kinetics of conducting polymer thin film based gas sensors and electrochromic devices

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Chemically deposited polyaniline (PANI) thin films were used as optically active materials in optochemical gas sensors (OGS) as well as in electrochromic devices (ECDs). An electrochemically deposited poly(3-methylthiophene) (P3MT) thin film based ECD was also prepared to be compared to PANI based ECDs. In all these optical devices, the optical response kinetic curves of PANI and P3MT films can be fitted quite well with two terms of the same exponential expression: one faster and one slower. The faster one could be attributed to a rapid specific surface or interface reaction process, and the slower one to a volumetric or bulk diffusion-reaction process. The physical meanings of the fitting parameters come from the Langmuir adsorption theory and Freundlich isotherm in the case of OGS and the Butler-Volmer equation for polymer based ECDs.

Keywords: Polyaniline; poly(3-methylthiophene); optical response kinetics; diffusion-reaction; gas sensors; electrochromic devices.

Películas delgadas de polianilina (PANI) depositadas por métodos químicos fueron empleadas como elementos ópticamente activos tanto en sensores ópticos de gases (OGS) como en dispositivos electrocrómicos (ECDs). Otro dispositivo electrocrómico en base de películas de poli-3-metiltiofeno preparadas por métodos electroquímicos fue construido para comparar con el de PANI. En todos estos dispositivos ópticos, la cinética de las respuestas ópticas se puede ajustar muy bien con dos términos de la misma expresión exponencial: uno más rápido y otro más lento. El más rápido se puede atribuir a un proceso de reacción interfacial o superficial específico, y el más lento a un proceso de reacción – difusión volumétrica. Los significados físicos de los parámetros de ajuste provienen de la teoría de adsorción de Langmuir y del isoterma de Freundlich en el caso de OGS, y de la ecuación de Butler-Volmer en el caso de los ECDs.

Descriptores: Polianilina; poli(3-metiltiofeno); cinética de la respuesta óptica; difusión-reacción; sensores de gases; dispositivos electrocrómicos.

PACS: 71.20.Rv; 73.61.Ph; 78.40.Me; 78.66.Qn; 82.35.Cd; 82.47.Tp

1. Introduction

Conducting polymers are those conjugated macromolecules that their electronic structures and consequently their electrical and optical properties change as they are reduced or oxidized. The redox reaction in these polymers can be initiated by a chemical agent or an electric stimulation. A conducting and electroactive polymer based electrochromic device (ECD) provides optical transmittance or reflectance switch with an applied electric potential step. And a redox reaction between electron donor or acceptor gas molecules and conjugated macromolecules results in an electrical or optical signal change in them.

Since the discovery of the conducting polymers in 1977, the prominent applications of these materials in different industries keep on motivating worldwide scientists in research and development of synthetic metal based devices with a better performance and stability. Polyaniline (PANI) is a well known conducting polymer that has been studied for gas sensors [1-4] and electrochromic device [5] applications. In our laboratory we have been working on the applications of PANI and polythiophene thin films in optochemical gas sensors (OGS) [6,7] and electrochromic devices [8]. Several theoretical models have been proposed to elucidate the redox mechanisms in these macromolecules [9,10]. This paper tries to understand the kinetic responses of different conducting polymer based optical devices. A morphological model is proposed to explain the apparent disagreement between the experimental data and theoretical predictions.

2. Experimental

PANI thin film of thickness of about 100-120 nm was deposited at 0-5°C by a solution method [11]. Using the same method a composite PANI thin film doped with a macromolecular acid such as poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) can also be deposited on different substrates. The incorporation of this electroinactive macromolecular acid lowers the ECD switch potential and gives a better performance than the single PANI based device [8]. The film thickness was estimated by peeling off a strip of the film and measuring the height profile difference between the film surface and the substrate surface in an Atomic Force Microscopy (AFM) (Autoprobe CP, Park Scientific). AFM topographic images of the polymer samples were also taken in the same instrument.

Composite PANI-polymethyl methacrylate (PMMA) films were formed on glass substrates by oxidation of aniline embedded in the PMMA matrix [12]. 5 wt% of aniline was mixed with a PMMA solution to obtain the coatings. The thickness of these was about 21 μm, measured with a vernier. Surface morphology of PANI-PMMA samples was analyzed by a Scanning Electron Microscopy (SEM, Cambridge LEICA, Stereoscan 440).

Electrochemically deposited poly(3-methylthiophene) (P3MT) film was obtained on an Indium-Tin Oxide (ITO) glass (Delta Technologies, Ltd, sheet resistance of 8-12$\Omega/\Box$) in a three electrode BAS CV50 system with a platinum mesh as auxiliary electrode. The deposition was carried out by cyclic voltammetry in 0-2 V (vs. Ag/AgCl) in acetonitrile with 0.1 M $LiClO_4$ as electrolyte and a 0.1M of monomer concentration.

The ECDs consisted of a working electrode ITO glass coated with a thin film of PANI or P3MT. The counter-electrode of ECDs was another ITO glass. And the solid electrolyte in between was made from: (a) an organic solution of PMMA containing salt of lithium ($LiClO_4$), or (b) a mixture of an aqueous solution of polyethylenimine (PEI) and concentrated sulfuric acid (H_2SO_4) [8]. Shimadzu UV-VIS spectrophotometer UV3101PC coupled with a homemade electric potential control unit was used to measure the optical kinetics of ECDs. For kinetic measurements, the wavelength of incident beam can be any value between 290 and 3100 nm. As shown in previous works [6,8,11] the optical transmittance spectra of PANI thin films are a function of wavelength. However, the kinetic mechanism of the optical responses observed in conducting polymer based ECDs and OGS does not depend on the wavelength value of incident light. For a PANI based ECD, we chose 632 nm as the incident wavelength because the light source used in the PANI based sensor was a He-Ne laser [6,7]. And in the case of P3MT based ECD, the device showed a maximum transmittance at a 500-550 nm wavelength range. Therefore, a 550 nm value has been chosen to test the device's optical response.

The optochemical gas detection system is based on an optical transmittance bridge [13]. PANI films had been placed inside a room temperature and atmospheric pressure chamber, in which a NH_3 flux was passing through to be detected by PANI samples [6,7]. In order to obtain a low and variable NH_3 gas concentration (from 3 to 1000 ppm), the ammonia had to be diluted in a dried N_2 gas. The reversible optical transmittance changes at 632 nm were observed in these polymer films due to the redox process between PANI and NH_3. As showed in Ref. 7, the maximum or equilibrium value of the optical response of PANI films increases with the NH_3 gas concentration. However, this response shows the same behavior as a function of time for different ammonia concentrations, leading to the conclusion that any value of NH_3 gas concentration in the mentioned gas concentration range can be chosen for the kinetic study. In this work we show the optical response of two PANI based gas sensors for a 400 ppm NH_3 gas concentration.

3. Results and discussion

3.1. Two optical devices and one fitting equation

Figure 1a shows an optical transmittance kinetic curve at 550 nm of a P3MT based ECD with PMMA-$LiClO_4$ as the solid electrolyte, polarized at –1.5 and +1.5 V. It is observed that in visible range this electrochromic device is turned to be less transparent as it is reduced (-1.5V) and more transparent as it is oxidized (+1.5). On the other hand, PANI thin film coated electrode shows a complementary electrochromic behavior compared with P3MT one in the same range of wavelength, namely it obscures at oxidation and bleaches at reduction. Fig. 1b exhibits an optical transmittance kinetic curve at 632 nm of a PANI-PAMPS/PMMA-$LiClO_4$ based ECD.

On the other hand, the detection of NH_3 gas by the PANI based optochemical sensor comes from the fact that interaction between the protonated polyaniline (Emeraldine salt, ES) and the NH_3 molecules results in the formation of NH_4^+ ions on PANI surface [14]. Consequently the original PANI(ES) loses protons to convert to emeraldine base (EB), an insulated semi-oxidized form of PANI, leading the PANI film color change from green (ES) to blue (EB) during this deprotonation process. Fig. 1c shows optical transmittance

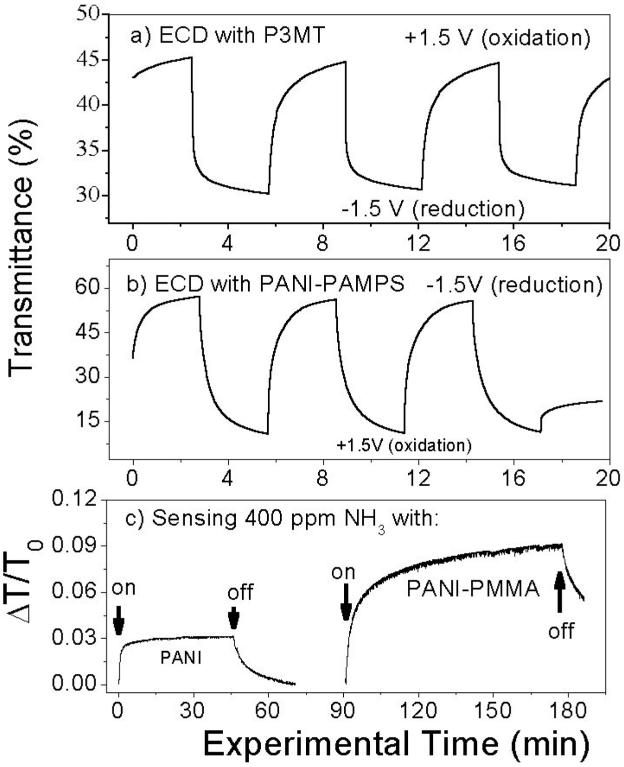

FIGURE 1. Kinetic optical transmittance curves (a) at 550 nm of P3MT based ECD with PMMA-$LiClO_4$as solid electrolyte, and (b) at 632 nm of PANI-PAMPS based ECD with PMMA-$LiClO_4$ as solid electrolyte. (c) Optical transmittance change ($\Delta T/T_0$) at 632 nm of PANI and PANI-PMMA films as they are exposed to 400 ppm NH_3 gas.

changes (ΔT/T$_0$) at 632 nm of PANI and PANI-PMMA films exposed to 400 ppm ammonia gas. It is noticed that the high value of ΔT/T$_0$ of the PANI-PMMA gas sensor compared to that of the single PANI one is due to a much thicker composite film than the single PANI thin films.

From Fig. 1 it is concluded that optical properties of conducting polymers can be switched under different external stimulation and used for different applications. In the case of gas sensors, the mechanism of adsorption obeys to Langmuir absorption theory and Freundlich isotherm [7,15], whereas the mechanism of charge transfer in ECDs is described by Butler-Volmer theory of electron transfer [8,10,16]. Assuming that the NH_3 molecules to be adsorbed behave like an ideal gas in the gas sensors and, on the other side, that charge carrier diffusion rate be much lower than the charge extraction rate at metal/polymer interface in ECDs, then the two theories derive to the same type of kinetic equation:

$$Y = A(1 - \exp(-t/\tau)) \qquad (1)$$

Table I shows the physical meanings of the parameters A and τ for the two devices. It is observed that A is related with the external stimulation like gas pressure (or concentration) P or applied electrical voltage E, as well as the system characteristics such as heat of adsorption Q of the adsorbed molecule or the formal potential of the redox couple $E^0_{A/B}$. The second parameter, τ, is also a function of the same symbols. Although Langmuir theory does not predict the gas pressure dependence of τ, experimental evidence shows a clearly decrease of τ as a function of P, described by Freundlich isotherm [7]. And in the case of ECDs the electron transfer theory does predict the influence of the step potential E on the parameter τ.

In literature, the problem of gas sensing by conducting polymers has been treated by P.N.Bartlett and J.W.Gardner in an unified model of coupled diffusion and reversible binding of species to immobile sites within a uniform homogeneous film [9]. The time-dependent concentration profile of the gas and the concomitant time-dependent fraction of occupied binding sites within the polymer film are modeled in order to understand the dynamic response of gas sensors. It is concluded that the response of a thin polymeric gas-sensitive film corresponds to cases of a linear diffusion-reaction (low adsorbate concentrations where the film is never saturated) with a faster diffusion coefficient than the rate of reaction of the species with the sites. In this case the equation to describe the fraction of occupied sites by diffused species inside the polymeric film is exactly the type of Eq. (1), the Langmuir isotherm.

When we try to fit the optical response kinetic curves of the conducting polymer based gas sensors and electrochromic devices, it is found that they can be well fitted only by using two terms of Eq. (1) in visible range:

a) Adsorption of NH_3 on PANI, reduction of PANI or oxidation of P3MT,

$$Y = A_1(1 - \exp(- t/\tau_1)) + A_2(1 - \exp(-t/\tau_2)) \qquad (2)$$

b) Desorption of NH_3 on PANI, oxidation of PANI or reduction of P3MT,

$$Y = A_3 \exp(-t/\tau_3) + A_4 \exp(-t/\tau_4) \qquad (3)$$

From numerical point of view, Eq. (3) can be easily converted to Eq. (2) by adding some constant, so only Eq. (2) will be discussed in the following sections. Before answering the question of why should be two terms of Eq. (1) to describe kinetic behavior of conducting polymer based optical devices, it is necessary to analyze the general characteristics of kinetic fitting parameters in Eq. (2).

3.2. Effect of experimental conditions on kinetic fitting parameters

We will call the smaller value of τ_1 and τ_2 as τ_1, so the term with τ_1 in Eq. (2) will be the faster part of the kinetic behavior. And if A$_1$ is bigger than A$_2$, the faster term will prevail in the kinetic process, as showed in Fig. 2a. In this case, thin film of PANI was exposed to ammonia gas of 400 ppm, and more than 70% of total response at final experimental time comes from the faster term of Eq. (2). It is shown in Fig. 2b that for a NH_3 gas concentration interval from 10 to 1000 ppm, the value of A$_1$ increases much more rapidly than that of A$_2$ in this PANI gas sensor.

However, the slower term can also be prominent in a kinetic process, as in the case of PANI-PMMA composite films exposed to the same gas (Fig. 3a). The term A$_2$ gives a value of about 45% of the total optical response at final experimental time. From the increasing Fig. 3b it is observed that A$_1$ and A$_2$ show the same increasing speed as a function of the gas concentration. The difference of kinetic behavior in these two PANI films comes from the different film microscopic morphology. In PANI-PMMA composite coatings PANI grains are formed inside the transparent and insulated PMMA, and from SEM micrographs [12] it was observed that they are embedded inside the insulated matrix, showing a phase separation between the two polymers.

Similar kinetic behaviors are also observed in conducting polymer based ECDs. Fig. 4a shows fitting curves of reduction kinetics of a PANI-PAMPS based ECD with PEI-H_2SO_4 as the solid electrolyte. The device shows an optical switch with a predominant faster term, where the effect of increasing applied voltage is very similar to the case of gas sensor with an increasing gas concentration (Table II): A$_1$ increases much more rapidly than A$_2$ does as the applied potential changes from 1.0 to 1.2 V. However, the same conducting polymer, PANI-PAMPS gives balanced optical responses of the two terms when the solid electrolyte it ionic (Fig. 4b). The optical responses of the P3MT based ECD (Fig. 4c) looks like that of the PANI-PAMPS/PMMA-$LiClO_4$ based ECD (Fig. 4b), probably because of the same type of electrolyte in both devices.

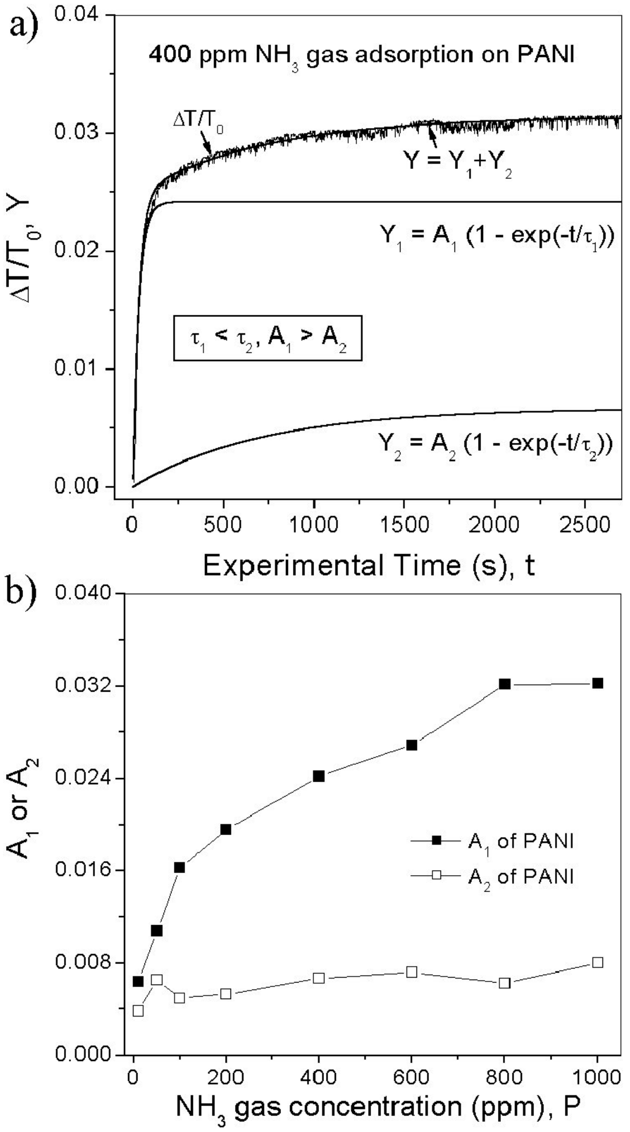

FIGURE 2. a) Fitting of the kinetic adsorption curve of PANI film exposed to 400 ppm NH_3 gas in Fig. 1c. b) Fitting parameters A_1 and A_2 of the PANI single film based optochemical gas sensor as a function of NH_3 gas concentration.

As described in Ref. 7, the values of τ_1 and τ_2 were inversely proportional to the NH_3 gas concentration in our optochemical sensor system. Since the adsorption energy E_A and heat of adsorption Q of ammonia molecule on PANI or PANI-PMMA surface are related to the parameter τ [7,15], the effect of the external stimulation (the gas concentration in this case) on τ is quite evident.

For ECDs, the case of the PANI based ECD with protonic polyelectrolyte (PEI-H_2SO_4) envisages the effect of external stimulation (the applied electrical potential E) on the parameter τ. Table 2 shows that τ_1 and τ_2 decrease with E. It means that κ_E and/or α could increase with E. We believe that the charge extraction rate at ITO/conducting polymer interface (κ_E) should not be notably affected by applied voltage since it is not associated with a slow diffusion process. The coefficient of charge transfer across the conducting/nonconducting boundary (α), by definition, is related with the transition process between the conducting (oxidized chains) and nonconducting phases (reduced chains) inside the polymer. So it could be related with the hopping process, which generally is a function of external stimulation like temperature or external electric potential.

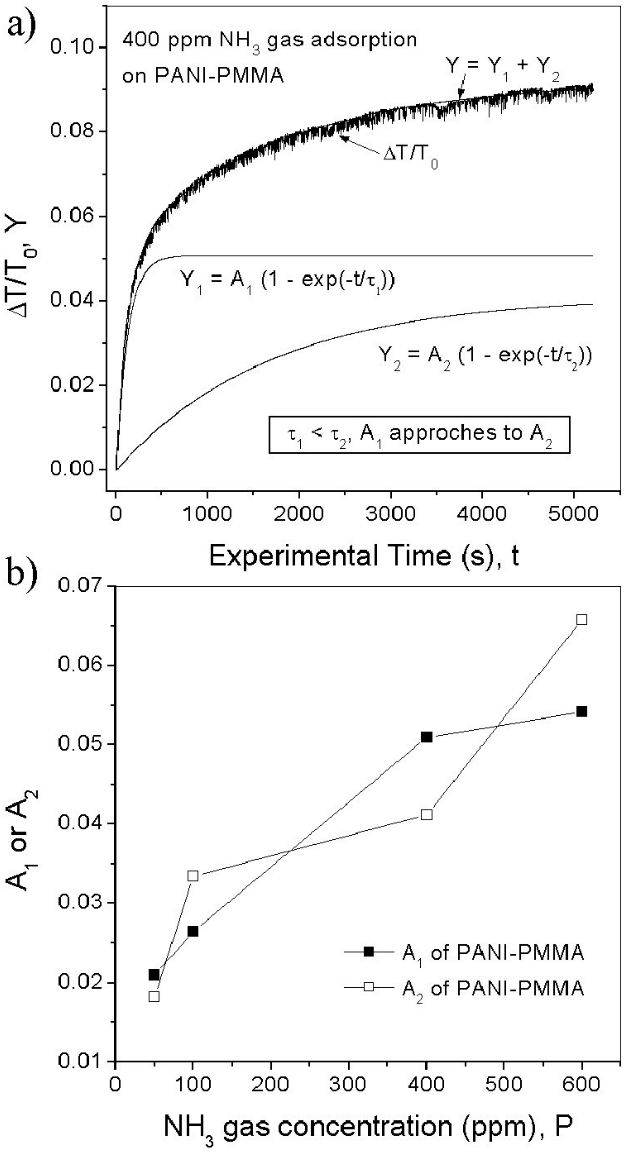

FIGURE 3. a) Fitting of the kinetic adsorption curve of PANI-PMMA film exposed to 400 ppm NH_3 gas in Fig. 1c. b) Fitting parameters A_1 and A_2 of the PANI-PMMA composite film based optochemical gas sensor as a function of NH_3 gas concentration.

3.3. A proposed phenomenological redox kinetic model in conducting polymer thin films.

From our experimental, results it is observed that two kinetic reactions are always involved in conducting polymer thin film based optical switch devices, no matter the molecular structure of the polymer neither the external stimulation. So there

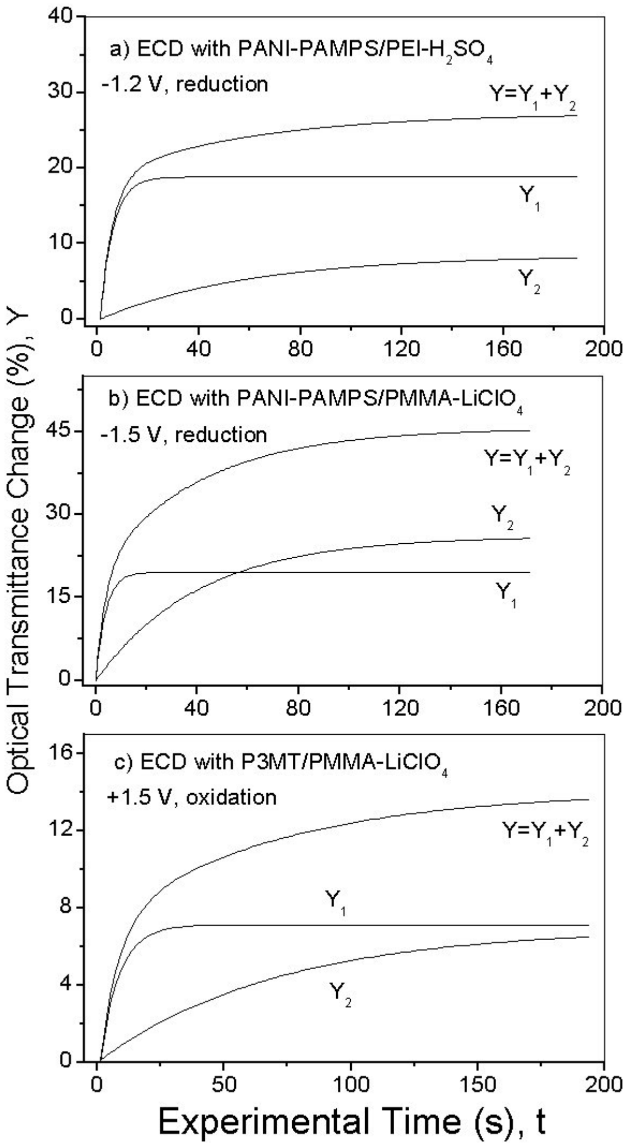

FIGURE 4. Fitting of the optical transmittance changes of ECDs as a function of experimental time: a) at 632 nm of PANI-PAMPS based device with PEI-H_2SO_4 as solid electrolyte; b) 632 nm of PANI-PAMPS based device with PMMA-$LiClO_4$ as solid electrolyte; c) at 550 nm of P3MT based device with PMMA-$LiClO_4$ as solid electrolyte.

must be some common characteristics in these devices. We believe that the faster term (smaller τ) could be attributed to a specific surface or interface reaction process and the slower one (bigger τ) should correspond to a volumetric or bulk diffusion-reaction process. Because of the isotropic interaction of conducting polymer thin films with external stimulation and the three dimensional device configuration, just two terms are needed for fitting all the kinetic curves. The faster term (surface interaction term) could be perceived as (1) an interaction of gas molecules with conducting polymeric chains on specific surface area of polymer films, or (2) extraction or injection of electrons from or to interconnected conducting polymer network. The slower term (volumetric diffusion-interaction term) could be perceived as (1) a diffusion-reaction process of gas molecules into the particles or grains formed by conjugated polymer chains, or (2) a hopping process of electrons into or out of the isolated conjugated polymer clusters and the consequent redox process of the polymeric chains inside these clusters.

Taking into account that polymeric materials are permeable and porous materials [17], their specific surface area can be quite extensive. A clearly porous and granular surface morphology is observed on them. Therefore an increasing NH_3 gas concentration, (in a relatively low concentration range so that there are always available sites to be occupied by NH_3 molecules in PANI) in the sensor chamber will proportionate more NH_3 molecules to interact with original PANI(ES) molecules. A notable increase of A_1 value and a relatively invariant A_2 as a function of the NH_3 gas concentration (Fig. 2b) leads to the assumption that chemically deposited PANI thin films are formed by a large specific surface area (open porous structure), and a small portion of densely packed conjugated chain clusters or grains. AFM micrograph of the surface of a PANI thin film sample, deposited at 0-5°C, confirms this assumption (Fig. 5a). A similar surface morphology was also observed in a P3MT sample (Fig. 5b), except that this forms a chain structure instead of spherical one. In the case of PANI-PMMA gas sensor device, the NH_3 gas concentration increases evenly the values of A_1 and A_2 (Fig. 3b), which means that the percentage of closely packed conjugated polymeric chains in form of grains or compact clusters is as the same order of magnitude as that of the open porous structure. SEM micrograph of the surface of a PANI-PMMA sample shows a high percentage of PANI grains or clusters embedded in the PMMA matrix (Fig. 6). The high value of percolation point in electrical conduction of these composite coatings confirms their granular morphology [18].

For conducting polymer based ECDs, it is clear that Eq. (2) also fits quite well to the kinetic curves within the experimental time. Since the electrons should be withdrawn from or injected into conjugated polymeric chains, it is supposed that the faster term corresponds to redox process of a network formed by interconnected conjugated polymeric chains on which charge transport is relatively fast. On the other hand, it is shown in Ref. [8] that most of the capacitive current is given in the first two or three seconds during the kinetic experiments, where the contribution of the slower term Eq. (2) does not relate with any measurable current in the electrochemical systems. Therefore it is supposed that there should be isolated conducting polymer grains embedded in the electrically interconnected network of the same polymer, and they should be in contact with ions from the electrolyte. The last ones can diffuse into the isolated clusters and reduce or oxidize the conjugated chains inside the grains during application of the potential step. This diffusion-reaction causes the appearance of a second term in the kinetic fitting equation for conducting polymer based ECDs.

Finally, the similar electrochromic kinetic behavior observed in the two different conducting polymers, PANI (and its composite PANI-PAMPS) and P3MT, obeys the electrochemical kinetic equation, Butler-Volmer relation. It means that optical response of ECDs is governed by the polymer redox reaction. The experimental conditions, such as the conducting polymer (PANI or P3MT), the films (single or composite), the applied voltage, the type of the polymer electrolyte (ionic or protonic), etc., affect the fitting parameter values, but not on the general kinetic behavior of the devices. Furthermore, the similarity of the optical response kinetics between PANI based ECDs and OGS is also based on the same reduction-oxidation reaction involved in both kinds of devices, with the difference on external stimulation. Although Butler-Volmer equation originates from the charge transfer across the conducting/nonconducting boundary, and the Langmuir Isotherm comes from the dynamics of gas evaporation- condensation, both are solutions of first order linear differential equations. And a geometric simplification in the case of ECDs [8] leads to the same kinetic expression as that of OGS.

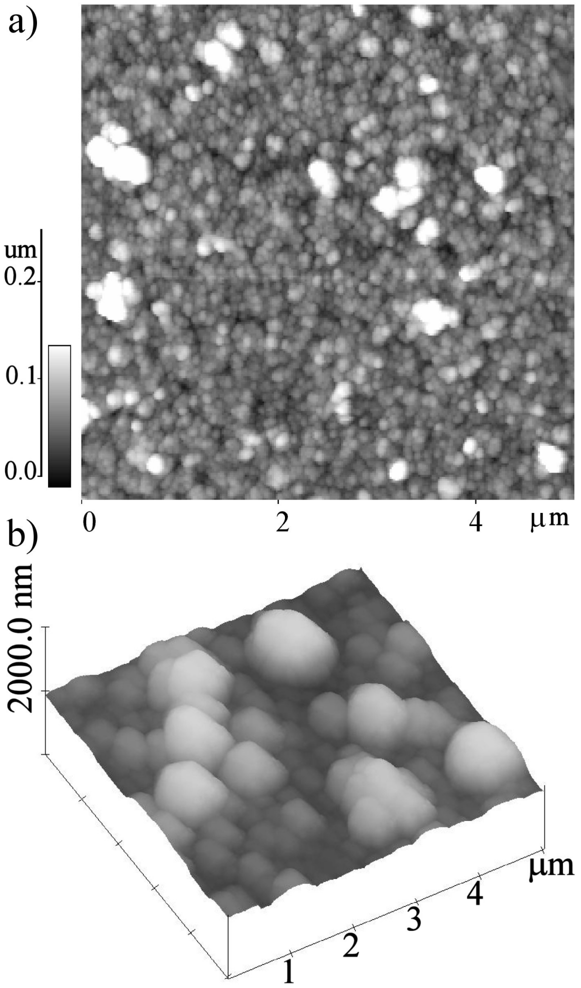

FIGURE 5. AFM micrograph of: a) a polyaniline thin film sample, deposited at 5°C, showing a porous and granular surface morphology. b) a P3MT thin film sample, prepared by the electrochemical method.

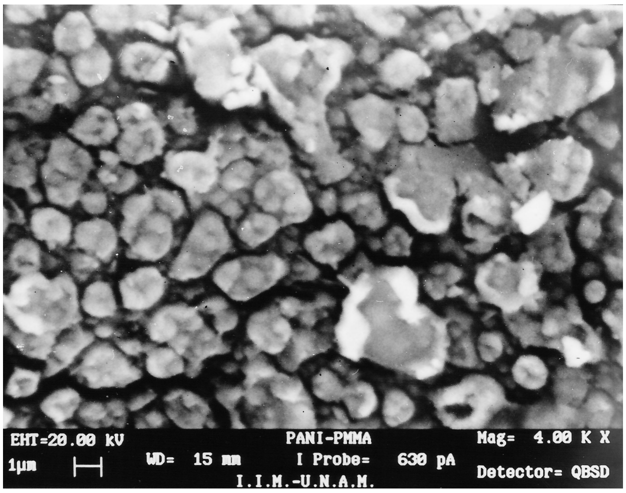

FIGURE 6. SEM micrograph of a PANI-PMMA sample, with 5 wt% aniline in the composite film.

4. Conclusions

Thin films of polyaniline have been used as electroactive coatings in electrochromic devices as well as in optochemical gas sensors. Both Butler-Volmer and Langmuir-Freundlich theories predict a similar exponential expression for the kinetic responses of these two optical devices. However, experimental results can only be well fitted by two terms of the predicted equation, a faster one and a slower one. The same situation is also observed with a poly(3-methylthiophene) based electrochromic device. Taking into account the high permeability and porosity of polymeric materials, the microstructure of conducting polymer films is proposed to be divided into two zones: (1) an electrically interconnected network inside the polymeric films or an extensive specific surface area, on which a rapid charge transfer can be taken place and, (2) the rest of isolated clusters or particles formed by closely packed conjugated chains. The interface or surface interaction of the system with the external stimulation gives the faster term of the optical kinetic responses, and the volumetric or bulk diffusion-reaction of the charge carriers into the particulate ensemble originates the slower term of the same signals.

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1. P.N. Bartlett and S.K. Ling-Chung, *Sens. Actuators* **20** (1989) 287.
2. M. Hirata and L. Sun, *Sens. Actuators* **40** (1994) 159.
3. S. Unde, J. Ganu, S. Radhakrishnan, *Adv. Mater. Opt. Electron.* **6** (1996) 151.
4. K. Ogura, T. Saino, N. Nakayama, and Shiigi, *J. Mater. Chem.* **7** (1997) 2363.
5. D.C. Trevedi, in: *Conductive Polymers: Synthesis and Electrical Properties*, (Handbook of Organic Conductive Molecules and Polymers, Vol.2, H.S.Nalwa Ed., Wiley, New York, 1997) pp.505-572.
6. M.E. Nicho *et al.*, *Sensors and Actuators B: Chemical* **76** (2001) 18.
7. H. Hu, M. Trejo, M.E. Nicho, J.M. Saniger and A. García-Valenzuela, *Sensors and Actuators B: Chemical* **82** (2002) 14.
8. H. Hu, L. Hechavarría and J. Campos, *Solid State Ionics* 161 (2003) 165.
9. P.N. Bartlett and J.W. Gardner, Phil. Trans. R. Soc. Lond. A **354** (1996) 35.
10. K. Aoki and Y. Tezuka, *J. Electroanal. Chem.* **267** (1989) 55.
11. L. Hechavarría, H. Hu, and M.E. Rincón, *Thin Solid Films* **441** (2003) 56.
12. J.L. Cadenas and H. Hu, *Solar Energy Materials and Solar Cells* **55** (1998) 105.
13. V. Argueta Díaz, M. Trejo Valdez, and A.García Valenzuela, *Rev. Sci. Instrum.* **71** (2000) 2995.
14. S. Wu, F. Zeng, F. Li, and Y. Zhu, *Eur. Polym.J.* **36** (2000) 679.
15. L. Yu Kupriyanov, *Handbook of Sensors and Actuators*, Semiconductor Sensors in Physico-Chemical Studies, (Vol.4, Elsevier, Amsterdam, 1996) pp.13-23.
16. M.E.G. Lyons, in *Electroactive Polymer Chemistry. Part 1: Fundamentals*, M.E.G. Lyons (Ed., Plenum Press, New York and London, 1994), pp.66-72.
17. Wolfgang Göpel and Klaus-Dieter Schierbaum, *Molecular recognition for chemical sensing: General Survey and the Specific Role of π-conjugated systems*, in Handbook of Organic Conductive Molecules and Polymers: Vol-4. Conductive polymers: Transport, Photophysics and Applications. H.S. Nalwa (Ed., John Wiley & Sons Ltd., Chischester, 1997) pp.621-659.
18. M.E. Nicho, L. Rivera, and H. Hu, *Adv. Mater. Opt. Electron.* **9** (1999) 47.