Journal of Engineering and Applied Sciences 1 (2) : 195-198, 2006

A Potential Application as Gas Sensor of Electroactive Polymers in Thin Layers

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Abstract: Thin layers of poly (fluoro aluminium phthalocyanine), (AlPcF)n, are doped by NO_2 diluted at various concentrations in N_2 and their conductivity variations are studied as a function of time, temperature and doping gas concentration. The doping is reversible. The experimental results are interpreted in terms of adsorption and diffusion of the gas in the polymer, charge transfer and transport of the injected carriers in the polymer. An application of (AlPcF)n thin layers as sensitive part of gas sensor could be considered.

Key words: Electroactive polymer, thin layers, conductivity, doping, dedoping, adsorption, diffusion, gas sensor

INTRODUCTION

An increasing interest for electroactive polymers has developed since it has been demonstrated that these materials, which are generally insulator or semi-conductor in their pristine state, may have their electrical conductivity enhanced by several orders of magnitude when they are exposed to oxidizing or reducing agents (dopants). This comes from the charge transfer between the polymer and the dopant and the mobility along the conjugated polymer chains of the so-injected charge carriers.

Since the doping of some polymers may be achieved by electrons acceptor or donor gases, the subsequent increase in the polymer conductivity could be related to the gas concentration so the use of these polymers as sensitive element of gas sensors could be possible.

With this aim in mind, we have performed various dopings with oxidizing gases (particularly NO_2) on the poly(fluoro aluminium phthalocyanine), (AlPcF)n and interpreted the results with the help of theories on gas adsorption and diffusion in solid and on conduction processes in electroactive polymers.

(AlPcF)n has been chosen because of its high air and thermal stability, its sensitivity to oxidants and its capacity to be sublimated and therefore deposited as thin layers on convenient substrates.

MATERIALS AND METHODS

The poly(fluoro aluminium phthalocyanine) powder is synthesized according to the method of Kenney and *et al.*[1]. The (AlPcF)n molecule consists of a linear Al-F- backbone surrounded by a sheath of Pc macrocycles separated from each other by 3.6 Å (Fig. 1).

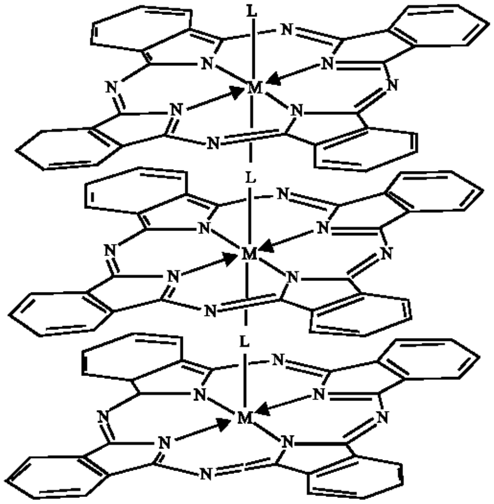

Fig. 1: (AlPcF)n molecule

Thin layers of (AlPcF)n (300 or 2500 Å thick) are elaborated by vacuum evaporation of (AlPcF)n with control of the deposition rate (2 or 20 Å/sec).

These layers are characterized by IR and UV spectroscopy (which give the same spectra as those published for the (AlPcF)n powder[2]) and by X-ray diffraction[3].

For doping experiments, the (AlPcF)n is deposited on alumina substrates provided with interdigitated electrodes on one side for conductivity measurements and a heating resistor on the other side (Fig. 2).

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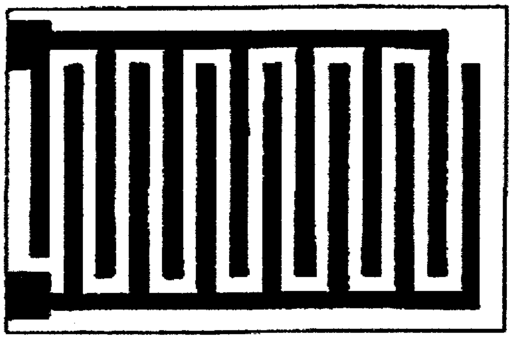
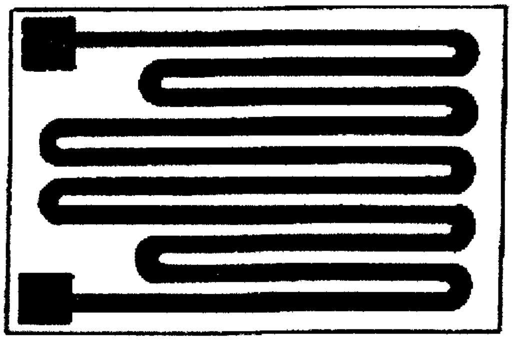


Side (a)



Side (b)

Fig. 2: Alumina substrate
Side (a): interdigitated electrodes
Side (b): heating resistor

RESULTS

Undoped (AlPcF)n: In a pure nitrogen flow, the room temperature conductivity of a thin layer is:

$$\sigma_{RT} \approx 5.10^{-5}\ (\Omega.\ \mathrm{cm})^{-1}$$

Between 190 and 390°K, the conductivity varies as:

$\sigma = \sigma_0.\ \exp\ (-Ea\ /\ kT)$, with the activation energy $Ea = 0.24$ eV.

The relatively high value of σ_{RT} and low value of Ea compared to the theoretical intrinsic gap are probably due to the presence of impurities (i.e. O_2, because the layers were kept in ambient air before use).

Heating the layer at about 240°C makes the conductivity decrease to $\sigma < 10^{-8}$ $(\Omega.\ \mathrm{cm})^{-1}$ without destruction of the polymer[4,5].

NO_2 doped (AlPcF)n: Dopings by a flow of NO_2 diluted in N_2 at increasing then decreasing concentrations C (0, 20, 50, 100 and 200 ppm) have been performed at different temperatures (at T = 100°C on Fig. 3a and T = 180°C on Fig. 3b).

Table 1: Variations of the coefficient a with the temperature

T(°C)	100	120	140	160	180	200
a	0.33	0.33	0.26	0.20	0.18	0.13

For each temperature T, the conductivity of the (AlPcF)n layers appears to be proportional to C° where a varies with T as shown in Table 1 below:

The increase of T shortens the response time at a variation of NO_2 concentration and increases the reversibility of the doping (Fig. 3a and b) but decreases the sensibility to the gas (represented by the coefficient a) and enhances the destruction of the polymer. The choice of T = 160°C for the doping experiments takes into account these opposite effects[6].

During dopings at high NO_2 concentrations and high temperatures (200°C or more), a slow decrease in the conductivity is observed (faster at higher T) and attributed to the thermal instability of the strongly oxidized form of (AlPcF)n[7,8].

DISCUSSION

The action of an oxidizing gas such as NO_2 can be described by a gas adsorption followed, if the electroaffinity of the gas and the ionization potential of the polymer are convenient, by a charge transfer between the gas and the polymer which produces an increase in the polymer conductivity.

In order to study these phenomena, thin layers of (AlPcF)n of various thicknesses and deposition rates have been doped at 100 ppm then 50 ppm NO_2 during 2 hours at a constant temperature of 160°C. The results are similar on all samples (Fig. 4).

Whatever the layer thickness is and although the electrodes lie under the polymer layer, we note that the conductivity increases as soon as NO_2 is introduced into the cell, thus demonstrating that the layer is spongious and that all the grains are rapidly in contact with the gas.

With the hypothesis that each NO_2 adsorbed molecule participates to the charge transfer and thus to the macroscopic conductivity of the layer, we can apply the chemisorption and diffusion theories to our experimental curve of Fig. 4.

This has been plotted, both for 100 ppm (doping) and 50 ppm (dedoping) phases, in the forms: σ vs $\log\ (t + t_0)$ (Elovich plot), $\log |\sigma - \sigma_{lim}|$ vs t and $\log (\sigma)$ vs (diffusion laws). Linearity is obtained for: σ vs $\log\ (t + t_0)$ at short times (Fig. 5) and for: $\log |\sigma - \sigma_{lim}|$ vs t at long time (Fig. 6).

This means that during doping, the gas is primarily adsorbed at the surface of the grains, according to an Elovich equation, then diffuses in their bulk, with an exponential time law. When the NO_2 concentration is decreased from 100 to 50 ppm, desorption of the gaseous

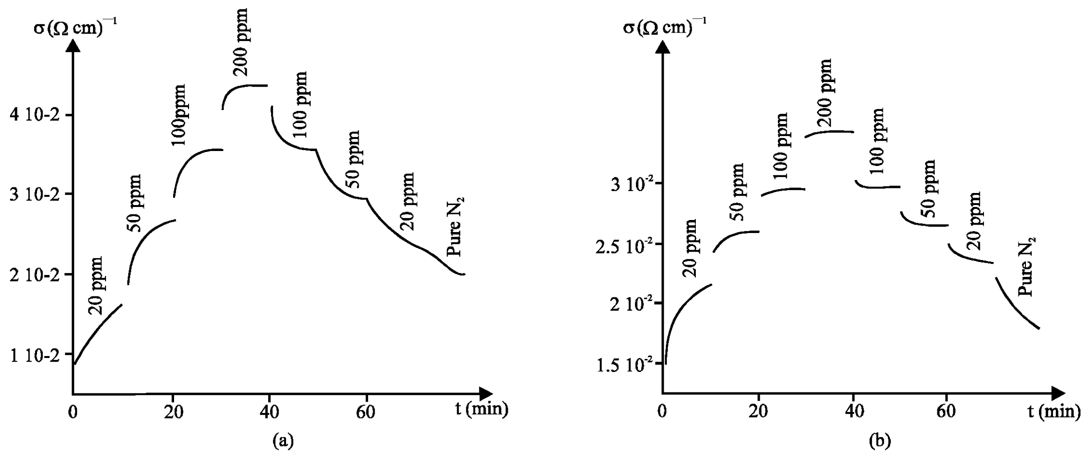


Fig. 3: (AlPcF)n conductivity versus time for dopings by increasing and decreasing concentrations of NO_2 in N_2 a: at T = 100°C, b: at T = 180°C

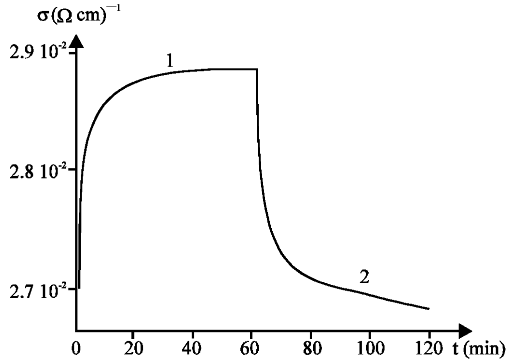


Fig. 4: (AlPcF)n conductivity versus time for doping by 100 ppm NO_2 (1) and 50 ppm NO_2 (2) at T = 160°C.

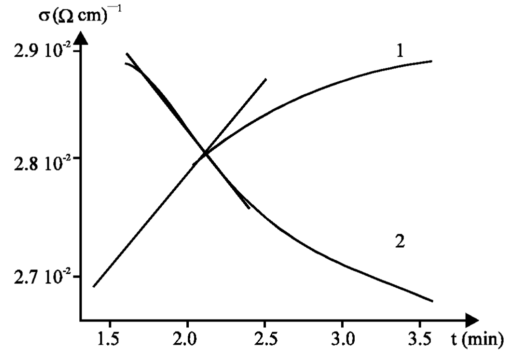


Fig. 5: Same as figure 4 but plotted as conductivity versus log(t + t_0) t_0 is adjusted for best fits: t_0 = 20 s for 1 and t_0 = 40 s for 2

molecules previously adsorbed on the surface proceeds first, followed by the gas diffusion out of the bulk of the grains[9].

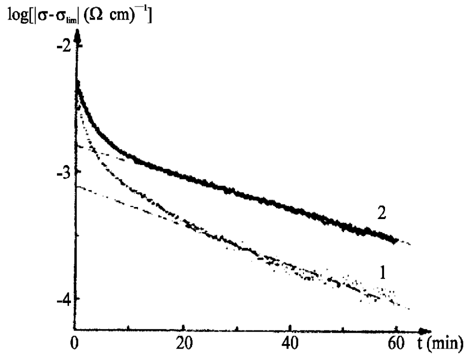


Fig. 6: Same as Fig. 4 but plotted as log |σ – σ_{lim}| versus time

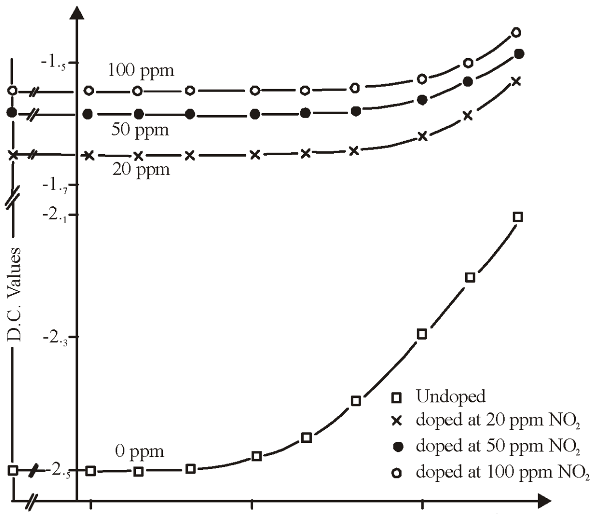


Fig. 7: log (conductivity) versus log (frequency) of (AlPcF)n at T = 160°C

After the penetration of NO_2 into (AlPcF)n, the charge transfer occurs and charge carriers (holes) are injected into the polymer. The mechanism of their transport can be studied by measurements of the a.c. and d.c. conductivities (Fig. 7).

The conductivity can be expressed as: $\sigma(f,T) = \sigma_{DC}(T) + \sigma_H(f,T)$. $\sigma_H = \sigma - \sigma_{DC}$ is found to be proportional to f^S, with $0.7 < S < 1.3$ depending on NO_2 concentration.

The frequency independent part of the conductivity is generally attributed to thermally activated band conduction along the polymer chains, whereas the frequency dependent term could arise from charge carriers hopping between localized states (interchain and intergrain hopping)[10,11]. At constant temperature, σ_H does not noticeably vary with the NO_2 concentration (number of carriers), while σ_{DC} increases with it. Consequently, the conduction in NO_2 doped (AlPcF)n appears to be dominated by band effects[12].

CONCLUSION

(AlPcF)n thin layers have proved to be a suitable material for the study of doping processes by oxidizing gases. The NO_2 doping kinetics has been successfully interpreted in agreement with the theories of gas adsorption on the surface of the polymer grains and diffusion in their bulk.

The conductivity which results from the charge transfer between polymer chains and sorbed gaseous molecules involves both band conduction and hopping processes.

The reversibility of charge transfer and gas sorption makes the dedoping of (AlPcF)n possible.

The response of (AlPcF)n thin layers to NO_2 presents some interesting characteristics (reversibility, short response times, sensitivity to the gas concentration, ...) for use of this material as sensitive element of gas sensors.

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