

## A MICROSCOPIC ANALYZE OF THE CONDUCTION MECHANISM OF IRON DOPED POLYANILINE UNDER THE UV EXPOSURE

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*Abstract:* The major target of conductive polymer technology development has been to combine the electrical and optical properties of conducting materials with the mechanical and processability properties of commodity bulk polymers. Polyaniline was synthesized at  $-15^{\circ}\text{C}$  using a polyethylenglycole / ice bath and doped with  $\text{Fe}^{3+}$  ions. Polyaniline films (tenths of  $\mu\text{m}$ ) were prepared by the gravity method. The dried films were exposed to UV ( $300\text{nm} < \lambda < 500\text{nm}$ ,  $10\text{mW}/\text{cm}^2$ ), up to 25 min. The conduction mechanism vs. the exposure time was analyzed by resistively measurements and Mössbauer spectroscopy. Mössbauer measurements show that by applying the UV exposure, electrons from the polymer chains are trapped by the Fe ions, changing their valence from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ . Corroborating this effect with the decreasing trend of the resistance in the UV exposed Fe doped polyaniline, it results directly that the polarons are the charge carries in the analyzed films and the final effect of the UV light is to increase their concentration.

*Keywords:* conducting polymers, polarons, and UV exposure

## 1.INTRODUCTION

Conducting polymers are important from a basic scientific point of view and for various technological applications. Many conjugated polymers have been produced to obtain conducting polymers with higher conductivity. Conducting polymer doped with a variety of chemical species has been synthesized extensively to obtain system having semi-conducting or metallic properties [6].

The electrochemical or chemical doping technique using electron acceptors or donors obtains these materials. A few popular examples of conducting polymers are polyacetylene, polyaniline, polypyrrole and polythiophene. The conductivity of doped conducting polymers can be assigned to the delocalization of  $\Pi$ -conjugated systems [7].

In this paper we present the conduction mechanism of polyaniline doped with Fe ions.

## 2.EXPERIMENTAL

Polyaniline was synthesized at  $-15^{\circ}\text{C}$ , using a polyethylenglycole / ice bath. 10g aniline were dissolved in 150 ml of HCl 1M and aqueous LiCl 5M solution. The obtained solution was transferred in polyethylenglycole / ice bath; when it reached a temperature of  $-15^{\circ}\text{C}$  an ammonium persulphate solution (13.1g ammonium persulphate dissolved in 120 ml HCl 1M and lise 5M) was added in small partions.

The solution was mechanically stirred throughout the course of the reaction. Twenty-four hours later, the solution was bluish green in color, indicating the formation of doped polyaniline in its emeraldine hydrochloride form. The polyaniline

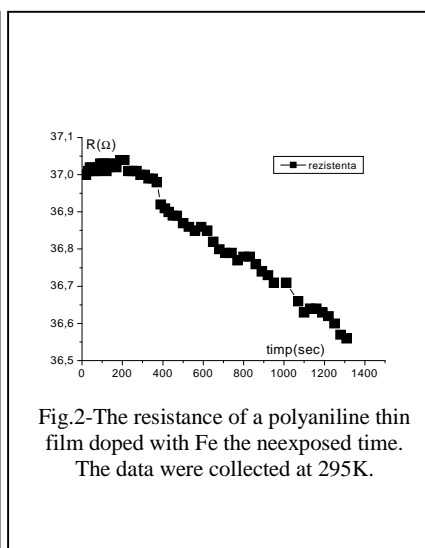
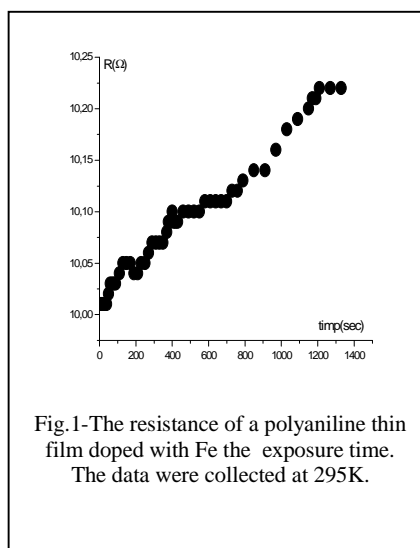
powder was collected by vacuum filtration and subsequently was washed with HCl 1M and water until the filtrate become colorless. The powder was transferred in a solution containing 250ml of NH<sub>4</sub>OH 0.1 M, stirred for 1 hour and vacuum filtered to collect polyaniline in its emeraldine base (EB) form. The EB powder was dried under dynamic vacuum 10<sup>-2</sup> torr for 2h to remove residual water. Emeraldine base, 1g was mixed with 1.277g CSA (+-) 10<sup>-2</sup> camphor-sulfonic acid using on agate mortar and pestle. A quantity (1.275) of resulting mixture was placed in to 61g m-cresol, treated for ten minutes in an ultrasonic bath and subsequently left for 24h at room temperature.

The obtained solution was filtered on a cotton wool. Part of the solution was casted a glass slide. After evaporation of the solvent at 70°C a film was obtained. In an other experiment, 1ml solution of triethyl iron (acetylacetonate) iron, Fe (CH<sub>3</sub>COCHCOCH<sub>3</sub>)<sub>3</sub> in chloroform was added at 5ml EB/CSA/m-cresol solution. After evaporation of solvents at 70°C the film obtained on a glass slide, contains 4.7% Fe.

### 3. RESULTS AND DISCUSSION

Thick polyaniline films (tenths of μm) were prepared by the gravity deposition method.

The films were exposed by a UV lamp (300 nm < λ < 500 nm ) with an intensity of about 10 mW/cm at the film surface, for exposure time up to maximum 25 <sup>57</sup>Fe Mössbauer spectra were collected with a constant acceleration spectrometer, using a <sup>57</sup>Co(Rh) radioactive source (25 mCi). For low temperature measurements down to 12 K, the samples were inserted in a close cycle cryostat. The isomer shifts were reported relative to α-Fe. The resistance at different exposure time was measured by a dc method using a two points configuration.



Conducting polymers presents overlapping sets of molecular orbital, which provide carriers mobility along the polymer chains. However appropriate carriers in organic polymers are mainly due to various doping elements (Fe in the present case). Possible models for the electrical conduction via different mechanisms have been reported [1], [2], [3], [4], [5]. For example, in Polyaniline per-chlorate a polaron hopping conduction was found [6]. The dependence of the resistance vs.

the exposure time in sample S1 is presented in Fig.1. It is observed that for exposure time up to 1200 s the resistance increases almost linearly with the exposure time/exposure energy. That is, the number of carriers overpassing the activation energy is increased under the UV excitation. Contrary, the resistance of sample S2 (doped additionally with  $\text{Fe}^{3+}$  ions) show a decreasing tren vs. the exposure energy suggesting a loss of charge carriers under the exposure. In order to enter the details of the conduction mechanism under the UV exposure it was proceeded to the acquisition of the Mössbauer spectra of sample S2, before and after an exposure of 1200 s.

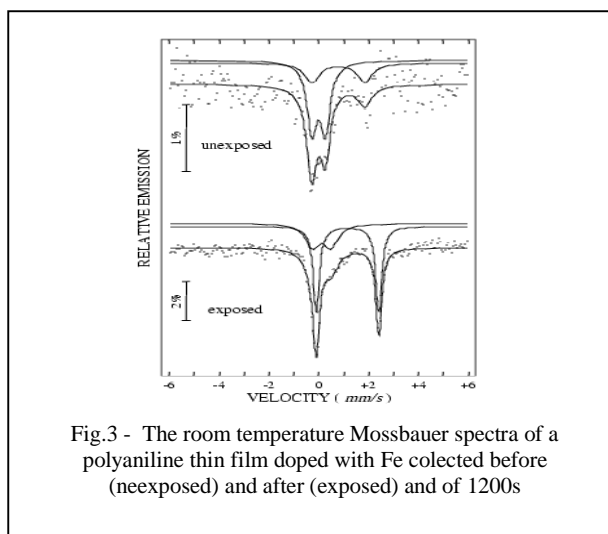


Fig.3 - The room temperature Mossbauer spectra of a polyaniline thin film doped with Fe collected before (neexposed) and after (exposed) and of 1200s

The spectra, shown in Fig.3, present two paramagnetic components. A first doublet with a high quadrupole splitting (QS of about 2.5 mm/s) and isomer shift (IS of about 1.1 mm/s) is assigned to  $\text{Fe}^{2+}$  ions in high spin state. A second doublet, with relatively small quadrupole splitting (QS of about 0.6 mm/s) and isomer shift (IS of about 0.2 mm/s) is assigned to  $\text{Fe}^{3+}$  ions in high spin configuration. The main difference between the two Mössbauer spectra consists in the relative contribution of the two patterns. In the unexposed sample, more than 70% of iron is in the high ( $\text{Fe}^{3+}$ ) oxidation state. The relative fraction of  $\text{Fe}^{3+}$  decreases at one half after exposure, on the account of the  $\text{Fe}^{2+}$  phase, which increases from about 30% in the unexposed samples up to about 65% in the exposed sample. So, by the UV exposure, electrons from the polymer chains are trapped by the Fe ions, which change their valence from +3 to +2. Corroborating this result with the decreased resistance (increased conductivity) in the UV exposed Fe doped polyaniline, it results directly that the polarons are the charge carriers in the analyzed films and the effect of the UV light is to increase the concentration of polarons.

#### 4.CONCLUSIONS

The conduction mechanism vs. the exposure time was analyzed by resistivity measurements and Mössbauer spectroscopy. The Mössbauer spectra present two paramagnetic components: a first doublet is assigned to  $\text{Fe}^{2+}$  ions in high spin state and a second doublet is assigned to  $\text{Fe}^{3+}$  ions in high spin configuration. By the UV exposure, electrons from the polymer chains are trapped by the Fe ions, changing their valence state from +3 to +2.

Corroborating this result with the decreasing of the resistance in the UV exposed Fe doped polyaniline, we can definitely say that the polarons are the charge carriers in the analyzed films due to the effect of the UV light which is to increase their concentration.

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