

NEW ELECTRONIC TECHNOLOGY APPLIED IN FLEXIBLE ORGANIC OPTICAL SYSTEM

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ABSTRACT

The synthesis and application of new organic materials, nanostructured, for developing technology based on organic devices, have been the main focus of the scientific community. In recent years, the first polymeric electronics products have entered the market (organic semiconductor materials) and there are some electrochromic devices among them that have been called smart windows, once they control the passage of light or heat through a closed environment as an ordinary window. The main functional aspect of electrochromic devices, when being used in architectural and automotive industry, is to control the passage of light and temperature with thermal and visual comfort. These devices can be flexible and very thin, not containing heavy metals, and formed by layers of organic material deposited in several architectures. In this study, the electro-deposition of organic materials in the Polyaniline, PANI case, which provide stability in optical and electrical parameters, was utilized with the means of developing prototypes of organic electrochromic devices. These materials were characterized by: ultraviolet-visible spectroscopy absorption (UV-Vis), measurement of thickness (MT) and electrical measurements (EM). This study aims to establish the relationship between the thickness of the active layer and the value of the electrical resistivity of the layer deposited through an electro-deposition technique. The experimental results enabled the equating of the electrical resistivity related to the thickness of the deposited layer. The linear fit of these results has expressed the thickness of the conducting layer, α , and the lowest value of the electrical resistivity, β , associated with the gap between the valence band and the conduction band. Thus, the results have demonstrated that, when the layer of organic material is completely conductive, we may obtain the thickness of the organic material deposited on the substrate.

Keywords: organic materials, optical system, flexible electrochromic devices, electronic technology.

INTRODUCTION

When studying the properties of several classes of materials, the consensus has been to assume that metals and inorganic semiconductors are more suitable to applications requiring materials with high electrical conductivity. Moreover, the polymers are further explored in applications requiring excellent properties from an insulator. However, this narrow view regarding the application of polymers in the electronic industry has rapidly changed with the appearance of new organic semiconductor materials [1]. In addition, these materials have presented a wide variety of electrical and optical properties, which may be previously observed only in inorganic systems. Although these materials have been still in the early stages of development, it has been highly considered utilizing them in organic semiconductor devices, requiring special electro-optical responses, such as smart windows for commercial buildings, which change their transmittance, reducing the passage of ultraviolet radiation, visible and infrared. The staining of an electrochromic material varies in a reversible manner when applying it an electric field [2-5]. Essentially, an electrochromic device is an electrochemical cell transmission in which the electrode surface, generally present in transparent glasses coated with electrochromic material, is separated from the counter electrode surface by a liquid electrolyte, solid or gel [6]. Liquid electrolytes, such as LiClO_4 , are used in the manufacture of electrochromic devices; however, its application requires an excellent seal to prevent leakage and evaporation. This factor prevents greater durability of the device although recent studies have been using electrolytes in solid solution and gel [7]. The techniques utilized for

characterizing electrochromic materials are carried out by optical and electrical analysis. In this research, the electro-deposition of organic materials in PANI case, which provides stability in optical and electrical parameters, was utilized with the means of developing prototypes of organic electrochromic devices. These materials were characterized by: UV-Vis, MT and EM.

EXPERIMENTAL DETAILS

The electrochromic device developed in this study was constructed by utilizing, as an organic material, flexible substrate covered on the surface with Indium Tin Oxide (ITO), deposited by sputtering. The ITO presents a high conductivity and transmittance in the visible region of the electromagnetic spectrum, which enables their utilization, for instance, as organic solar cells, gas sensors, antiglare coatings and electrochromic devices [8]. The organic flexible substrate, based on Polyvinylidene Fluoride (PVDF), and used for the electro-deposition of PANI, with thickness 200 nm, was covered by a layer of ITO with a thickness of 400 nm [9]. Another organic flexible substrate, based on PVDF and ITO, was deposited on the first layer of the Poly (3,4-ethylenedioxythiophene), PEDOT, with thickness of 200 nm, and then, on one layer of Vanadium Pentoxide, V_2O_5 , with thickness of 200 nm. Both layers were deposited through the spin-coating technique, adding from 100 to 100 μ L at 750 rpm for ten seconds to each deposition. The electrolyte used in the devices was Lithium Perchlorate, $LiClO_4$ in Propylene Carbonate, PC, with 0.5 mol/L and thickness of 1000 nm. The developed flexible electrochromic device has presented a configuration layered of PVDF/ITO/PANI/ $LiClO_4$ / V_2O_5 /PEDOT/ITO/PVDF, as represented schematically in figure 1.

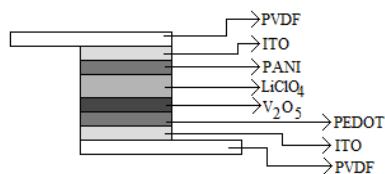


Figure 1. Configuration of flexible electrochromic device.

DISCUSSION

The analysis of a sample through the ultraviolet-visible spectroscopy is the result in a spectrum of light, obtained by a graph of wavelength or frequency versus the intensity of

absorption (absorbance or transmittance) [10]. When utilizing experimental results found in the literature as reference, completely saturated compounds may be verified, which have not demonstrated selective absorption in visible and ultraviolet regions. However, compounds with benzene and aromatic hydrocarbons have been associated with effects of vibrational transitions $\pi \rightarrow \pi^*$. When benzene is replaced by a simple functional group, the serial of bands of fine structure reduces the complexity; the intensity of this absorption is increased and there is generally a shift with greater wavelengths. The substitution for groups containing electrons, not binding such as sulfur, produces a very pronounced displacement and an increased absorption due to transitions $n \rightarrow \pi^*$. Yet, if the number of aromatic nuclei is sufficiently large, the intense absorption extends into the visible. This would be the cause, for instance, of high intrinsic absorption of PANI, for wavelengths equal and/or with 400 nm. The addition of one or more covalent unsaturated groups, in conjugation, shifts the position of absorption of the system for greater wavelengths. The molar absorption coefficient increases gradually, depending on the number of groups present in the conjugates. The system of electrons π extended results in a greater delocalization of electrons π , which makes the energy required for the transition $\pi \rightarrow \pi^*$ smaller, and the likelihood of occurrence of these transitions greater. By considering data above, it may be inferred that the displacement has originated the absorption in the red direction due to the formation of conjugated C = C bonds, i.e., the formation of extended orbital π [11]. The spectrum absorption in the spectral region of 200-1100 nm of the flexible electrochromic device has been shown in figure 2.

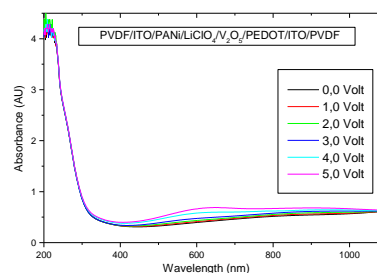


Figure 2. UV-Vis spectroscopy of flexible electrochromic device.

This result has indicated that the gradual increase of ddp of 0.0 Volt to 5.0 Volt generates a greater deviation in the optical spectral region

between 400-700 nm. This result has characterized the device as a good attenuator to the radiation from the visible region. In the spectrum of the flexible electrochromic device, it can be also observed that there is an increase in the optical absorption in the infrared region, which prescribes this device to be utilized as a film attenuating the infrared radiation in buildings and automobiles.

The analyses of electrical measurements were performed with the system with four 6517A Keithley probes. The results obtained in the electrical measurements for electrodes PVDF/ITO/PANI and PVDF/ITO/ PEDOT/V₂O₅ have been shown in figure 3 and figure 4. Note that there is an increasing in the electrical resistance, R_s, and electrical resistivity, ρ, after the deposition of thin film layers. The electrical resistivity was calculated from the equation 1, where V is the voltage in volts, I is the electric current, ρ is the electrical resistivity and Δx is the thickness of the deposited material [12]. See equations 1.

$$R_s = \frac{\rho}{\Delta x} = \left(\frac{\pi}{\ln 2} \right) \cdot \frac{V}{I} \quad (1)$$

These graphs have indicated that the electrical resistivity is related to the sheet resistance and thickness, Δx, of the deposited thin film. With the linear fit of the experimental results from the equation 2, one obtains the conductive layer of thin film deposited, α, and the lowest resistivity, B_{res}, associated with the gap between the valence band and conduction band. See equations 2.

$$\rho = \alpha \cdot R_s + B_{res} \quad (2)$$

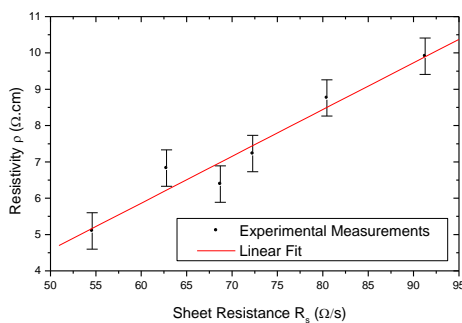


Figure 3. Electrical resistivity of the PVDF/ITO/PANI in function of sheet resistance.

Table I has shown the values obtained as Δx thickness, utilizing the equipment with the mark HANATEK FT3, resolution of 0.1 μm, the values obtained for the conductive layer of organic material deposited, α, and the minimum value found for the electrical resistivity in linear fit, B_{res}.

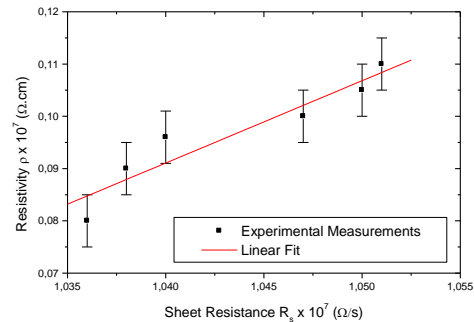


Figure 4. Electrical resistivity of the PVDF/ITO/PEDOT/V₂O₅ in function of sheet resistance.

Table I. Thickness Δx and electrical parameters α and B_{res}.

Electrodes	Δx (nm)	α (nm)	B _{res} (Ω.cm)
PVDF/ITO	(411.4 ± 1.9)	(401.5 ± 1.9)	(1,09 ± 0,06)
PVDF/ITO/ PANI	(594.3 ± 1.2)	(605.3 ± 1.7)	(4,61 ± 0,09)
PVDF/ITO/ PANI/LiClO ₄	(1,587.3 ± 1.1)	(1,605.3 ± 1.7)	(4,91 ± 0,09)
PVDF/ITO/ PEDOT	(615.1 ± 4.3)	(610.6 ± 3.5)	(0,82 ± 0,04)
PVDF/ITO/ PEDOT/ V ₂ O ₅	(802.8 ± 5.6)	(794.8 ± 4.6)	(0,81 ± 0,04)

In the analysis of the results for α, by comparing the value obtained with Δx of thickness in Table I, it can be verified that the samples have presented thickness consistent with the values found in the α electrical parameter. The results have demonstrated that, when the layer of organic material is completely conductive, we may obtain the thickness of the organic material deposited on the substrate. In order to check the stability of flexible electrochromic device, 2500 replicates were performed, simulating its activation with the voltage of 5.0 V. The test was consisted of applying some voltage for two minutes at intervals of ten minutes. The electrical parameters obtained after the simulation remained unchanged for this period of analysis, emphasizing its proper operation, even after 30,000 minutes of operation.

CONCLUSIONS

The production of flexible electrochromic devices, using electrodes PVDF/ITO/PEDOT provides a change in the observed UV-Vis spectral behavior. Whereas PEDOT do not have benzene rings, which may present absorption in the region of 300-500 nm, and the PC have not caused the displacement of bands, we can infer the optical absorption in the infrared region due to the proposed innovative architecture. The results of electrical measurements have demonstrated that, when the layer of organic material is completely conductive, we can obtain the thickness of the organic material deposited on the substrate. Therefore, the flexible electrochromic device developed with the proposed architecture has presented the best optical and electric result, demonstrating the feasibility for manufacturing flexible electrochromic devices, which have electrodes with PVDF/ITO/PEDOT and PVDF/ITO/PANI.

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REFERENCES

- [1] P. R. Somani, S. Radhakrishnan Electrochromic materials and device: present and future. *Mater. Chem. and Phys.* **77**, 117-133 (2002).
- [2] D. R. Rosseinsky, R. J. Mortimer, Electrochromic Systems and the Prospects for Devices. *Adv. Mater.* **13**, 783-793 (2001).
- [3] S. Taunier, et alli. Design and characterization of a three-electrode electrochromic device, based on the system WO_3/IrO_2 . *Electrochemical Acta*, **44**, 3219-3225 (1999).
- [4] R. J. Mortimer, Organic electrochromic materials. *Electrochemical Acta*, **44**, 2971-2981 (1999).
- [5] M. A. Paoli, W. A. Gazotti, Electrochemistry, Polymers and Opto-Electronic Devices: A Combination with a Future. *Journal Brazilian Chemical Society* **13**, 1-15 (2002).
- [6] J. Livage, D. Ganguli, Sol-gel electrochromic coatings and devices: A review. *Solar Energy Materials Solar Cells* **68**, 365-381 (2001).
- [7] D. F. Vieira, C. O. Avellaneda, A. Pawlicka, Conductivity study of a gelatin-based polymer electrolyte. *Electrochemical Acta* **53**, 1404-1408 (2007).
- [8] S. Yun et alli. Noncontact characterization of sheet resistance of indium-tin-oxide thin films by using a near-field microwave microprobe. *Thin Solid Films* **515**, 1354-1357 (2006).
- [9] A. F. S. Guedes, E. M. Costa, V. P. Guedes, Formation of Nanoparticles in Organic Materials used in Semiconductors Optoelectronic Devices. *ECS Trans.* **31**, 231-236 (2010).
- [10] D. Voet, J. G. Voet, *Biochemistry*, 2nd ed., John Wiley & Sons, Inc., New York (1995).
- [11] J. R. Dyer, *Aplicações da Espectroscopia de Absorção dos Compostos Orgânicos*. Edgard Blucher Ltda, São Paulo (1969).
- [12] R. C. Jaeger, Introduction to microelectronic fabrication. Addison-Wesley Publishing Co., Massachusetts, **5**, (1989) 230p.