Journal of Systemics, Cybernetics and Informatics (2023) 21(1), 26-30
https://doi.org/10.54808/JSCI.21.01.26

Flexible Electrochromic Organic Nanofilms (FEON) Applied in Civil Construction

Andre GUEDES
Research Group in Engineering and Advanced Technologies, University ESTACIO RS
Porto Alegre, Rio Grande do Sul, 91140-000 Brazil

Simone TARTARI
Nanotechnology Laboratory, INTELLECTOS
Torres, Rio Grande do Sul, 95560-000, Brazil

ABSTRACT [1]

Flexible Electrochromic Organic Nanofilms (FEON) have drawn intense attention due to their advantages over competing technologies. The method utilized to deposit as well as to integrate solutions and processed materials, manufacturing electrochromic organic nanofilms by the Electrodeposition System, has been presented in this research. The FEON device constructed in this work is electrochromic device are the base Poly (3,4-ethylenedioxythiophene), PEDOT:PSS, Poly(3-hexyl thiophene, P3HT, Phenyl-C61-butyric acid methyl ester, PCBM, Vanadium Pentoxide, V_2O_5, Lithium Perchlorate, $LiClO_4$ in Propylene Carbonate, PC and Polyaniline-X1, PANI-X1, that were deposited in Indium Tin Oxide, ITO, and characterized by Electrical Measurements and Scanning Electron Microscopy (SEM). In addition, the thin film obtained by the deposition of PANI, prepared in perchloric acid solution, was identified through PANI-X1. The maximum process temperature was 50°C, which corresponds to the baking of the active polymeric layer. The result obtained by electrical Measurements has demonstrated that the PET/ ITO/PEDOT:PSS/P3HT:PCBM-Blend/V_2O_5/$LiClO_4$/ PANI-X1/ITO/PET layer presents the characteristic curve of standard electrochromic organic device after spin-coating and electrodeposition. The Thin film obtained by electrodeposition of PANI-X1 on ITO/PET Blend was prepared in perchloric acid solution. The spectrum absorption in the spectral region of 200-1100 nm of the flexible electrochromic organic nanofilm device 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 450-850 nm. The thermal effects from ultraviolet irradiation under the device's surface, in the irradiation simulator chamber, demonstrated a 5% reduction in the device's lifetime. The inclusion of the PANI-X1 layer reduced the effects of degradation these electrochromic organic nanofilms induced for solar irradiation, a fact that also observed in the irradiation in the simulation chamber. In Scanning Electron Microscopy (SEM) these studies reveal that the surface of PANI-X1 layers is strongly conditioned by the surface morphology of the dielectric.

Keywords: PET, ITO, PANI-X1, P3HT/PCBM Blend, PEDOT:PSS, V_2O_5, $LiClO_4$

1. 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 [1][2][3]. 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 [4][5][6][7]. This new class of organic semiconductor materials are present in various electronic equipment that we use and today are part of our lifestyle. In addition, these materials have presented a wide variety of electrical and optical properties, which may be previously observed only in inorganic systems [8][9][10]. 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 radiation ultraviolet, visible and infrared [11][12][13]. The staining of an electrochromic material varies in a reversible manner when applying it an electric field and this versatility provides a series of applications in the interior and exterior architecture of buildings and residences [14][15][16]. 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. Liquid electrolytes, such as LiClO4, are

---

[1] Peer editing and final proofreading for this article by Vilmar Pedroso Guedes of postgraduate the Intellectos Group..

used in the manufacture of electrochromic devices; however, its application requires an excellent seal to prevent leakage and evaporation [17][18]. 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-X1 case, which provides stability in optical and electrical parameters, was utilized with the means of developing prototypes of organic electrochromic devices [19][20]. These materials were characterized by: Ultraviolet-Visible Spectroscopy Absorption (UV-Vis), Scanning Electron Microscopy (SEM) and Electrical Measurements (EM).

2. EXPERIMENTAL DETAILS

The electrochromic device developed in this study was constructed by utilizing, as an organic nanofilms 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 [21]. The organic flexible substrate, based on poly(ethylene terephthalate) (PET), and used for the electro-deposition of PANI-X1 was covered by a layer of ITO with a thickness of 400 nm. The PANI-X1 layer was deposited through the Electrodeposition system in solution prepared with perchloric acid (HClO4), and applying voltage of 10,0 Volts for 5 minutes, resulted in an active layer of PANI-X1, with thickness between 180 nm and 220 nm. Another organic flexible substrate, based on PET 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 μL 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 PET/ ITO / PEDOT: PSS / P3HT: PCBM Blend /V_2O_5/ $LiClO_4$/ PANI-X1/ ITO/ PET, as represented schematically in figure 1.

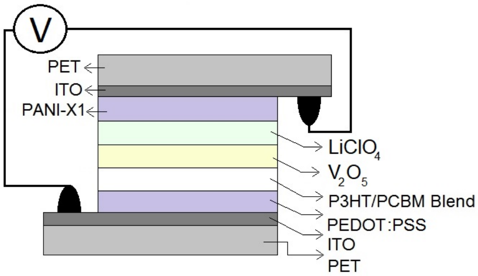

Figure 1. Configuration of flexible electrochromic device.

3. PISCUSSION

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 [22]. The spectrum absorption in the spectral region of 200-1100 nm of the flexible electrochromic device has been shown in figure 2.

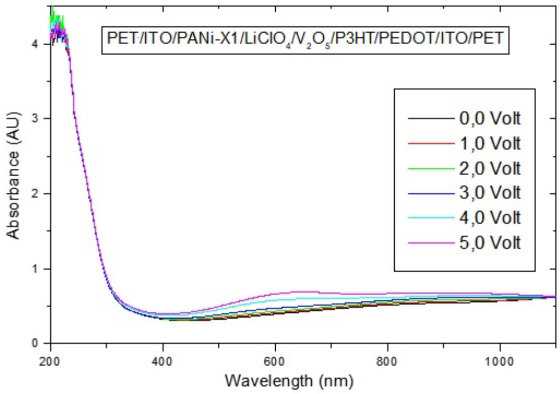

Figure 2. UV-Vis spectroscopy of flexible electrochromic device.

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, residences, and automobiles.

The electrical characterization of flexible electrochromic device was made at room temperature using an Electrometer Keithley 6517A semiconductor parameter analyzer. All measurements were made without vacuum and no precautions were taken to prevent the degradation of the multilayer polymeric nanofilms.

The analyses of electrical measurements were performed with the system with four 6517A Keithley probes. The results obtained in the electrical measurements for electrodes PET/ITO/PANI-X1 and PET/ITO/PEDOT: PSS/P3HT:PCBM Blend 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 [5][6][7]. See equations 1.

$$R_S = \frac{\rho}{\Delta x} = \left(\frac{\pi}{\ell n2}\right).\frac{V}{I} \qquad (1)$$

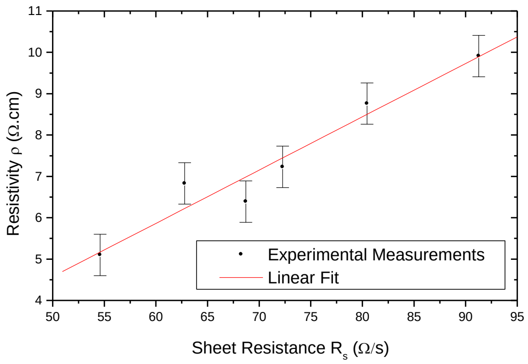

Figure 3. Electrical resistivity of the PET/ITO/PANI-X1 in function of sheet resistance.

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.

$$\rho = \alpha.R_s + B_{res} \qquad (2)$$

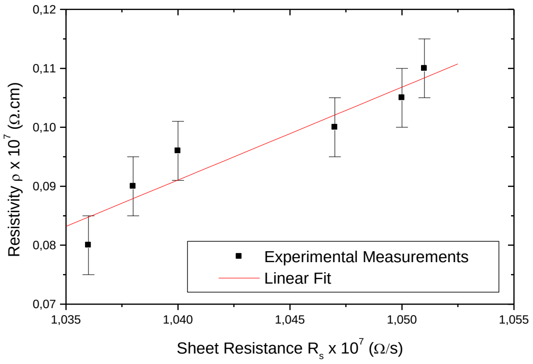

Figure 4. Electrical resistivity of the PET/ITO/ PEDOT:PSS/P3HT:PCBM Blend in function of sheet resistance.

In order to check the stability of flexible electrochromic device, 3000 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.

The microscopic analysis performed in the flexible electrochromic device by Scanning Electron Microscopy, has allowed us to observe the induction on the surface of the samples before and after the voltage of 5V. Figure 5 has shown the flexible electrochromic device before applying voltage. It may be observed that the surface of the sample has some homogeneous aspect, plane and without changes.

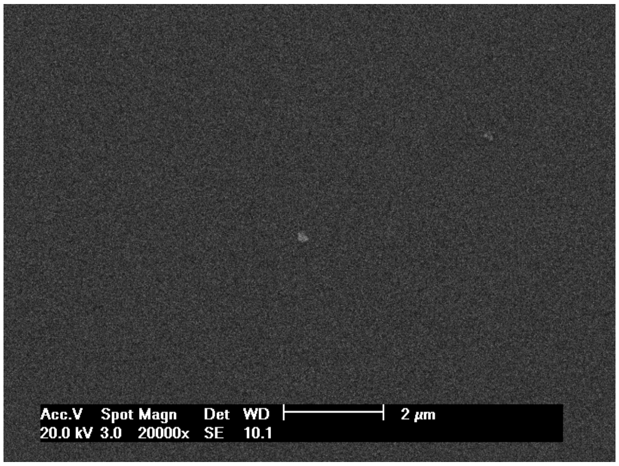

Figure 5. SEM of flexible electrochromic device before applying voltage.

Figure 6 has shown the micrograph of the flexible electrochromic device after voltage application of 5V during two minutes for a period totaling 30,000 minutes of device testing. In this micrograph, it may be observed the surface of the sample in some irregular aspect and with cracks. Therefore, these cracks can contribute to reducing the lifetime of the flexible electrochromic device, since the accumulation of organic semiconductor material may cause short circuit in the device.

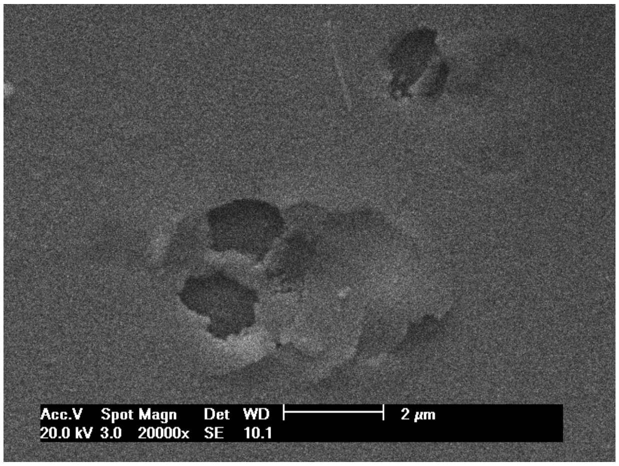

Figure 6. SEM of flexible electrochromic device after applying voltage.

4. CONCLUSIONS

The production of flexible electrochromic devices, using electrodes PET/ITO/PEDOT:PSS/P3HT:PCBM Blend 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 PET/ITO/PEDOT:PSS/P3HT: PCBM Blend and PET/ ITO/PANI-X1.

5. ACKNOWLEDGMENTS

GPETA/ University ESTACIO of RS and LabNANO/ INTELLECTOS.

6. REFERENCES

[1] MacDiarmid, A. G., "Synthetic metals: a novel role for organic polymers," Current applied physics 1, 269-279 (2001).

[2] Shirakawa, H. et alii, "Synthesis of electrically conducting organic polymers: halogen derivatives of polyacetylene, (CH)x," Chem. Soc. 99, 578 (1977).

[3] Varela, H. et alii, "MATERIAIS PARA CÁTODOS DE BATERIAS SECUNDÁRIAS DE LÍTIO," Química Nova 25(2), 287-299 (2002).

[4] Guedes, A. F. S., Costa, E. M., Guedes, V. P., "Formation of Nanoparticles in Organic Materials used in Semiconductors Optoelectronic Devices," ECS Trans. 31, 231-236 (2010).

[5] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., Souza, M. L., "New Electronic Technology Applied in Flexible Organic Optical System," Journal of Systemics Cybernetics and Informatics. 12, 1-4 (2014).

[6] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., Souza, M. L., "NEW OPTOELECTRONIC TECHNOLOGY SIMPLIFIED FOR ORGANIC LIGHT EMITTING DIODE (OLED)," Journal of Systemics Cybernetics and Informatics. 12, 72-74 (2014).

[7] Jaeger, R.C., "Introduction to microelectronic fabrication," Addison-Wesley Publishing Co. Massachusetts 5, 230 (1989).

[8] Yun, S. 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] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., Souza, M. L.,"NEW ORGANIC SEMICONDUCTOR MATERIALS APPLIED IN ORGANIC PHOTOVOLTAIC AND OPTICAL DEVICES," Journal of Systemics Cybernetics and Informatics 13, 38-40 (2015).

[10] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., Souza, M. L., "The Electrodeposition of Multilayers on a Polymeric Substrate in Flexible Organic Photovoltaic Solar Cells," Proc. SPIE 9561, 1-6 (2015).

[11] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., Souza, M. L., "The Electrodeposition of Multilayers on a Polymeric Substrate in Flexible Organic Light Emitting Diode," Proc. SPIE 9941, 1-6 (2016).

[12] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., Souza, M. L., "Thin Film of the PVK and PPV Applied in Optoelectronic Organic Sensor," Proc. SPIE 9929, 1-6 (2016).

[13] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., " Flexible Optoelectronic Technology Applied in Organic Light Emitting Diode (OLED)," Journal of Systemics Cybernetics and Informatics 15, 90-92 (2017).

[14] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J., "Flexible Synthetic Semiconductor Applied in Optoelectronic Organic Sensor," Journal of Systemics Cybernetics and Informatics 15, 76-79 (2017).

[15] Guedes, A .F. S., Tartari, S., Guedes, V. P., Cunha, I. J.,"Flexible Organic Battery Technology Applied in OLED," Journal of Systemics Cybernetics and Informatics 16, 31-34 (2018).

[16] Guedes, A .F. S., Tartari, S., Cunha, I. J., “The New Flexible Optoelectronic Organic Sensor (FOOS),” Proc. SPIE 110891, 61-66 (2019).

[17] Guedes, A .F. S., Tartari, S., Cardoso, E., Silva, F., “ Flexible organic photovoltaic solar cells applied in the educational platform Arduino,” Proc. SPIE 11089, 60-65 (2019).

[18] Guedes, A .F. S., Tartari, S., Cunha, I. J., “New Flexible OLED of Longer Lifetime,” Proc. 23rd WMSCI VII, 101-104 (2019).

[19] Guedes, A .F. S., Tartari, S., “New Transparent Flexible Organic Photovoltaic Solar Cell,” Proc. 24th WMSCI VI, 17-19 (2020).

[20] Guedes, A .F. S., Tartari, S., “New organic semiconductor materials applied in transparent flexible organic photovoltaic solar cells,” Proc. SPIE 11722, 1-5 (2021).

[21] Guedes, A .F. S., Tartari, S., “Flexible optoelectronic organic sensor for infrared detection,” Proc. SPIE 11741, 1-7 (2021).

[22] Guedes, A .F. S., Krischke, R.M., Machado, M.G.M, Tartari, S., “Thermal Effects in Hybrid Optical Photonic Organic Devices,” Proc. SPIE 11802, 1-5 (2021).

[23] Guedes, A .F. S., Krischke, R.M., Machado, M.G.M, Tartari, S., “Thermal Effects on the Surface of Flexible Organic Photovoltaic Solar Cells (FOPSC),” Proc. SPIE 12090, 1-6 (2022).