Electrical Characterization of V$_2$O$_5$/POMA Deposited by the Casting Technique

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Abstract: Conductive polymer derivatives, such as poly-*o*-methoxyaniline (POMA), have been broadly used in different applications because they present characteristics similar to those of polyaniline. POMA can intercalate into a V$_2$O$_5$ matrix to improve its structural and electrical properties, and thin films of V$_2$O$_5$/POMA can be deposited by different techniques to extend their technological applications after intercalation reactions. Then, V$_2$O$_5$/POMA hybrid material was deposited by casting technique and characterizated for, further, to be ued as component in amperometric ammonia gas sensor. Our results show the influence of the deposition technique on electrical properties. Indeed, the values of parameters such as resistance, interface effects and conductivity slightly change according to the deposition technique being used.

Keywords: V$_2$O$_5$/POMA, Thin film, Deposition technique, Casting.

1. INTRODUCTION

Conducting polymers are materials that have become a target for different studies because they present low cost, easy synthesis and high electrical conductivity as the most important characteristics [1]. Due to these features, conductive polymers are being studied and used in different applications, such as biosensors [2], field effect transistors (FET) [3], organic light emitting diodes (OLEDs) [4], batteries [5], solar cells [6] and electrochromic devices [7]. The electrical conductivity of these polymers comes from polarons and bipolarons produced by oxidation. This formation contributes to the increase in conductivity once an electron obtains sufficient energy to be promoted to the conduction band. Conducting polymers present a conjugated structure with a spatially delocalized band-like electronic structure [8]. One of the most important structural characteristics of conjugated polymers is a π system that extends over the polymeric chain. Some examples of conjugated polymers are polyacetylene, polythiophene, polyethylenedioxythiophene, polyaniline and poly-*o*-methoxyaniline. On the other hand, several inorganic materials are semiconductors, capable of intercalating organic molecules into their layers [3, 9-11]. Vanadium pentoxide (V$_2$O$_5$) is a transition metal oxide that has a lamellar structure when obtained from sol-gel synthesis [12]. The lamellar structure has negative residual charges along its chain keeping oxygen from the V-O bond. This charge can promote electrostatic interactions between inorganic material

and organic species, resulting in an intercalation reaction. After intercalation, the organic species, such as polymers, are inserted into the layers of the inorganic matrix, resulting in a synergic effect and improving the original properties [5]. As a consequence of this intercalation reaction, it is possible to obtain thin films of hybrid materials with mixed ionic–electronic conductivity. Thin films of hybrid materials can be used in different applications [13, 14] and for each application these materials can be laid in several deposition techniques. Thin films can be deposited by chemical or physical routes and it is possible to investigate how these routes can affect the final properties of materials or devices. Moreover, the choice of deposition process depends on the specific application [15]. Santos *et al*. [9] used V$_2$O$_5$/PANI hybrid material deposited by layer by layer (LbL) as component in amperometric ammonia gas sensor and verified a linearity and stability in the 0-54 pm range of concentration. Diniz *et al*. [11] verified a improving performance of V2O5/POMA hybrid material deposited by LbL as used in ammonia gas sensor. Therefore, this work has investigated the influence of the deposition technique by casting on the structural and electrical properties of V$_2$O$_5$/POMA thin films for a potential application in the ammonia gas sensor.

2. EXPERIMENTS

2.1. Poli-*o*-Methoxyaniline (POMA)

The distillation of *o*-methoxyaniline (Sigma Aldrich®) was performed under vacuum, in an oil bath at a temperature of 130 °C to obtain the POMA. Polymerization by chemical oxidation was performed as described by Mattoso and Bulhões [16]. The oxidant

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solution was obtained by solubilizing 0.28 g of ammonium persulfate (Proquimios®) in 5.0 mL of 1 mol·L^{-1} HCl, with a controlled temperature between 0 and 4 °C. The monomer solution was obtained by solubilizing 0.66 mL of distilled o-methoxyaniline in 7.5 mL of 1 mol·L^{-1} HCl at a controlled temperature between 0 and 4 °C. The oxidant solution was slowly dripped (~ 0.05 mL·min^{-1}) into the stirring monomer solution, in an ice bath to maintain the temperature between 0 and 4 °C. The solution changed from transparent to lilac and after 2 h of stirring exhibited a dark green color. The solution was filtered and washed with distilled water until the filtrate was practically colorless. The retained material was then washed with 25 mL of acetone (Synth®) to remove oligomers and other organic residues. The green solid retained in the filter consisted of the doped polymer in its conductive state that is insoluble in almost all solvents (Regaço, 2006). To make the polymer soluble and increase its applicability, 25 mL of ammonium hydroxide NH$_4$OH (Synth®) 1 mol·L^{-1} was doped with H$_2$SO$_4$ 1 mol·L^{-1} and stirring for 15 h. Next, the solution was filtered and placed in an oven at 40 °C. The obtained powder had the characteristic bluish coloration of the polymer in the disassembled state.

2.2. V$_2$O$_5$ Via Sol-Gel

Vanadium pentoxide xerogel was obtained by the sol-gel technique as described by Guerra [5]. A cation exchange column consisting of a burette with cotton was used to retain the solid resin. The cationic resin (Dowex® 50x8, AcrosOrganics) was inserted into the burette using 6 mol·L^{-1} HCl as the wash solution. When the resin was clean, a pH 2.0 HCl solution was used to adjust the pH. After the removal of all pH 2.0 acid, the 0.1 mol·L^{-1} ammonium vanadate (NH$_4$VO$_3$ - Vetec®) solution was added to the burette. After ion exchange, the transparent solution of ammonium vanadate became yellowish due to the increase in the vanadium coordination number from 4 to 6 by nucleophilic addition of 2 water molecules [12]. The HVO$_3$ vanadic acid solution obtained was collected and allowed to rest for one week at room temperature. This procedure was performed for the autocatalytic reaction to take place, and to form the vanadium pentoxide dark red gel of increased viscosity, which after simple evaporation becomes xerogel V$_2$O$_5$.nH$_2$O (n ~ 1.8) [17, 18].

2.3. V$_2$O$_5$/POMA Hybrid Material

The intercalation reaction was made based on the procedure described by Guerra *et al.* [5]. A 0.01 mol·L^{-1} solution of o-methoxyaniline in H$_2$SO$_4$ was prepared by

adding 0.1 mL of distilled monomer in 100 mL of 0.02 mol·L^{-1} H$_2$SO$_4$. Then, 1 mL of the o-methoxyaniline solution was added by dripping and under intense stirring in 7.5 ml of vanadium pentoxide. The obtained solution was stirred for 24 hours and after that, a bright dark green solution was obtained.

2.4. Deposition of V$_2$O$_5$/POMA by Casting

Films containing the V$_2$O$_5$/POMA hybrid material synthesized by intercalation reaction were deposited by the casting technique, which consists of dripping the solution onto a substrate supported on a flat surface and drying the solvent. The hybrid material solution was dripped onto the substrate and the solvent evaporated at room temperature.

2.5. Deposition of a Silver Electrode

Silk screen electrode deposition was performed by depositing a small amount of silver ink (CI-1001 ECM) across the mask, forming a continuous line, and distributing the ink through the substrate with the aid of a squeegee. The screens used for the silk screen, designed with the aid of Corel Draw X4, contain 20 masks of 10 mm length and 600 μm of electrode spacing.

2.6. Techniques

Films were characterized by FTIR in the spectrometer Cary 630 FTIR from Agilent Technologies in the wave number range of 650-4000 cm^{-1} and were then deposited on glass substrates, dried and removed for analysis. The absorption measurements in the UV-vis region were performed on a Shimadzu® spectrophotometer, model UV-1650 PC, which allows the performance of absorption measurements in the range between 190 to 1100 nm. Complex impedance measurements, $Z*(f) = Z'(f) – iZ''(f)$, of the fabricated V2O5/POMA were conducted using a 1260 Solartron frequency response analyzer in the 1 Hz to 1 MHz range. The voltage applied was 1.5 V. DC impedance measurements were conducted using a 6517A electrometer high resistance meter (Keithley).

3. RESULTS AND DISCUSSION

The POMA, V$_2$O$_5$/POMA and V$_2$O$_5$ samples were submitted to Fourier transform infrared spectrometry (FTIR) analysis and the spectra obtained are presented in Figure **1**. The spectrum obtained for the POMA sample has characteristic bands of an aromatic organic material. According to Pereira [19], the band that appears at 1227 cm^{-1} may be associated with the

stretching of C-N bonds. The bands at 1540 and 1689 cm^{-1} are related to the quinoid ring and the C-N stretch of the quinoid ring. The band at 1455 cm^{-1} refers to the deformation mode of the CH_3 group. The two bands at 1361 and 1302 cm^{-1} are absorption characteristics attributed to the stretching of the aromatic amine - CNH_2 group. The band at 780 cm^{-1} refers to the out-of-plane angular deformation of the benzene ring, and the 869 cm^{-1} bands refer to the asymmetric axial deformation of the ring. The bands at 1038 and 1144 cm^{-1} refer to the axial C-O deformation of the methoxy group ether. The spectrum obtained for V_2O_5 presents three bands below 1050 cm^{-1}, at 1035, 936 and 836 cm^{-1}, which are characteristic of the vibrational stretching of vanadila groups [5]. The band at 1041 cm^{-1} refers to the vanadila elongation V=O [20], the band at 936 cm^{-1} refers to the binding of an oxygen atom with an elongation of V-O-V bonds, and the band at 836 cm^{-1} refers to asymmetrical V-O-V stretching [21]. The spectrum obtained for the sample consisting of the V_2O_5/POMA presents a combination of the bands of the source materials. The bands for vanadila groups have changed due to the interaction between the polymer and inorganic material, with the shift of the band position from 1035 to 1026 cm^{-1} due to NH-O-V interaction [22]. The combination of bands referring to the two materials may indicate that the intercalation occurred, corroborating the results obtained by the analysis of diffractograms of the materials. This indicates that a third material may have formed from both organic and inorganic materials.
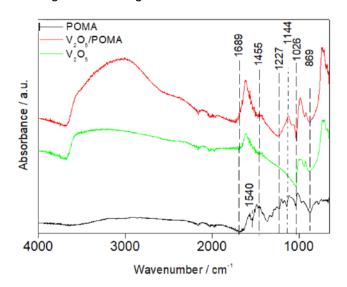

Figure 1: FTIR spectrum of POMA (black line), V_2O_5/POMA (red line) and V_2O_5 (green line).

The films that were characterized by UV-Vis spectroscopy (Figure **2**). The V_2O_5/POMA thin film has a band around 300 nm, characteristic of the π → π*

transition of the benzoic conjugate ring. It also presents a less intense band at 437 nm, representing the polaron-π* transition, and another one around 800 nm shows characteristics of the π-polaron transition. This spectrum indicates that the POMA is in its conductive doped state. The V_2O_5/POMA thin film features bands at 305 and 391 nm. These bands indicate the superposition of the π → π* transition of the benzenoid conjugated ring with the electronic transition from O2p to V3d [23]. This may indicate the formation of new material as presented in the previous characterizations.
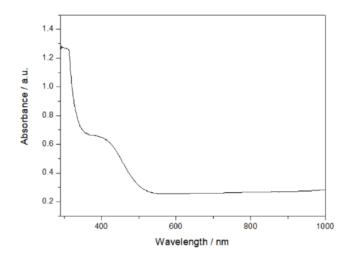

Figure 2: UV/Vis spectra of the V_2O_5/POMA.

Electrical measurements of impedance spectroscopy were performed with the films deposited by casting on silver electrodes. The films used in the electrical analysis are presented in Figure **3**. Complex impedance analysis of the films was performed to evaluate the alteration of the electrical responses. The results of the electrical impedance analysis for the V_2O_5/POMA are shown in Figure **4**.

Figure 3: V_2O_5/POMA thin film deposited by casting on a silver electrode. The length (L) and distance (W) between the Ag electrodes on the V2O5/POMA surface were 10mm and 600 μm, respectively.
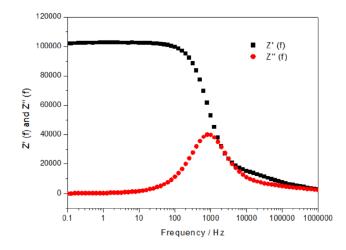
Figure 4: Real Z'(f) and imaginary Z''(f) components of impedance spectroscopy of V2O5/POMA by casting deposition.

Figure 5: Argand diagram of V_2O_5/POMA.

For the V_2O_5/POMA film (Figure **4**), at low frequencies the real component (Z') remains constant near $Z_0 = 4.3 \times 10^4$ Ω until reaching the relaxation frequency value around $f_c = 3.4 \times 10^3$ Hz, when it decreases smoothly with f. Volume processes are responsible for the impedance behavior of this film, and it is not possible to notice the interface effects. Therefore, it is possible to note the capacitive, resistive and interface contributions of the film. The real low frequency impedance (Z^0) value found for the V_2O_5/POMA by casting deposition was 4.3×10^4 Ω. This value indicates that the film has a lower resistance when compared to results from the literature [9, 11], that is, that the combination of polymer and inorganic material decreased the resistance of the film. The V_2O_5/POMA showed only one level and only one relaxation frequency, which may indicate that there are not two separate materials, but the formation of a composite, corroborating the findings based on the X-ray diffraction (XRD) and FTIR [11] characterizations. Indeed, there was an intercalation between the two compounds and the formation of the hydrogen bond of NH from POMA, with O-V from the V_2O_5 [22].

The Argand diagram obtained for the V_2O_5/POMA film is presented in Figure **5**. From this figure, it is possible to observe a semicircle with a coincident with the Z_0 (4.3×10^4 Ω), and no interface effects. The semicircle is attributed to the bulk properties of V_2O_5/POMA.

In order to characterize the disorder of the films, phenomenological models were applied and compared to the experimental values of impedance spectroscopy. The best theoretical model used to fit the experimental results was the Cole-Cole model approach [24]. In particular, to α ≠ 0 and β = 1, the model is call Cole-

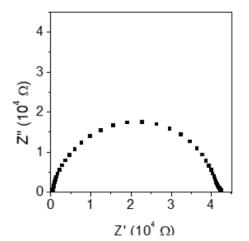Cole. The parameters α and β come from Havrilliak-Negami equation [25] based on a non-uniform distribution in relaxation times.It indicates a symmetrical distribution of relaxation frequency for the impedance of V_2O_5/POMA. Figure **6** shows the experimental curves and those adjusted by theoretical models. The values of resistance (R), capacitance (C), α, R_{int}, C_{int} and $α_{int}$ obtained through the theoretical model are listed in Table **2**.
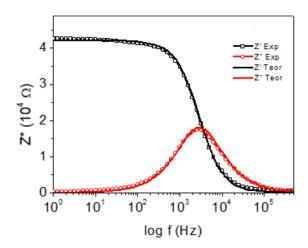

Figure 6: Phenomenological model and experimental curves of impedance spectroscopy of V_2O_5/POMA.

Table 1:   Z 'and Z'' component adjustment parameters

Parameter	V_2O_5/POMA by Casting
R (Ω)	4.20×10^4
C (F)	1.2×10^{-9}
α	0.89

The values presented in Table **1** indicate that the resistance values found in the model coincide with the

values of the semicircle diameters found in the Argand Diagram, Figure **5**.

The resistance value and the disorder parameter found for the V_2O_5/POMA were close to the values found by Santos [24] for the V_2O_5/PANI, which are 4.9 × 10^4 Ω and 0.86, respectively. The capacitance value has a difference of more than 3 orders of magnitude, and the value found for the film with the unsubstituted polymer is 9.5 × 10^{-12} F [24]. This indicates that the insertion of the O-CH_3 substituent into the casting film caused a slight decrease in film strength and clutter but increased the dielectric effect (bonded charges) of the material, probably due to the hydrogen bonds present in the structure. The impedance spectra obtained for the POMA films showed significant interface effects between materials, which were not verified in PANI films [24]. This may indicate that the bond between the material chains is stronger with the substituted polymer.

The real conductivity curve presents two levels. The value of the σ' constant at low frequencies corresponds to the value of direct current conductivity. The intersections between real and imaginary conductivity define the minimum (first stage) and maximum (second stage) critical frequencies. The value of γ'_{min} becomes smaller when the materials become more resistive. The second level is hardly measured experimentally because it exceeds the maximum operating limit of the measuring equipment and the value of γ'_{max} is much higher than that of γ'_{min} observed in Eq. 1.

$$\sigma_D^*(\omega) = \frac{\frac{\omega}{\gamma'_{min}}\sigma_0 i}{ln\left(1+\frac{\omega i}{\gamma'_{min}}\right)}$$

Eq.(1)

The theoretical model used to calculate the conductivity for the film V_2O_5/POMA is presented in Equation 1. The parameters obtained through the theoretical adjustment of the conductivity are shown in Table **2** and the values obtained through the experimental values and through the theoretical models are shown in Figure **7**.

Table 2: Parameters of Interest for the Conductivity Model for V₂O₅/POMA Deposited by Casting

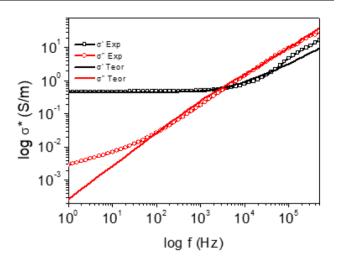| Parameter	POMA/V₂O₅ by Casting
σ_0 (S/m)	4.5 × 10^{-1}
γ_{min} (Hz)	5.32 × 10^3

Figure 7: Complex conductivity obtained through the theoretical equation (continuous line) and the experimental values of complex impedance (open symbols) for the film V_2O_5/POMA.

When comparing the curves obtained through the experimental impedance spectrum (open symbols) with the curves obtained through the theoretical model (continuous lines), shown in Figure **7**, it is possible to note that there is a deviation for the film. However, the combination of the RFEB model proposed by Dyre [26] with the Cole-Cole phenomenological model for the interface effects resulted in a good fit for the complex conductivity values of the analyzed films. When comparing the values of σ₀ for the films V_2O_5/POMA by casting deposition (4.5 × 10^{-1} S/m) and V_2O_5/POMA using layer by layer (LbL) as the deposition technique (7.3 × 10^{-1} S/m), as observed by Diniz [27], the former is lower than the latter. This result indicates that the different deposition method could be contributing to the decreased conductivity of the polymeric film. The dielectric contribution did not influence the complex conductivity of the V_2O_5/POMA by casting, meaning that the contribution of the dipoles in the current conduction is negligible for this film.

4. CONCLUSION

POMA was intercalated into the V_2O_5 matrix and the electrical characterization was evaluated. The structural characterization showed that the structure of the hybrid materials was maintained During the electrical studies, V_2O_5/POMA exhibited low resistance, similar to that of PANI, of which POMA is a derivate. In this case, the deposition technique, such as casting and LbL, practically does not interfere in the electrical properties of V_2O_5/POMA. Furthermore, V_2O_5/POMA by casting deposition is a potential candidate to be used in disposable ammonia amperometric gas sensors for animal confinement buildings.

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