



ELSEVIER

International Journal of Inorganic Materials 3 (2001) 727–731

International Journal of  
**Inorganic  
Materials**

# Melanin-like units concentration effects in melanin-like/vanadium pentoxide hybrid compounds<sup>☆</sup>

E. Arashiro<sup>a</sup>, E.C. Zampronio<sup>b</sup>, C.A. Brunello<sup>a</sup>, T.A.F. Lassali<sup>a</sup>, H.P. Oliveira<sup>b</sup>,  
C.F.O. Graeff<sup>a,\*</sup>

<sup>a</sup>Departamento de Física e Matemática – FFCLRP-USP, Ribeirão Preto, Brazil

<sup>b</sup>Departamento de Química – FFCLRP-USP, Ribeirão Preto, Brazil

Received 3 October 2000; accepted 11 August 2001

## Abstract

An intercalated material has been prepared consisting of a regular alternation of organic/inorganic layers. The films were obtained by reacting 3,4-dihydroxy-phenylalanine (DL-DOPA) with varying concentrations in a solution with freshly prepared HVO<sub>3</sub>, which suffered a oxidative polymerization/intercalation 'in situ' process, forming a green suspension, in which after de-hydration at room temperature produces a nanocomposite with a dark blue metallic color. Films (C<sub>8</sub>H<sub>9</sub>NO<sub>2</sub>)<sub>x</sub>V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O were characterized using FT-IR, ESR, powder X-ray diffraction, conductivity, and cyclic voltammetry. The X-ray diffractograms indicate that the lamellar structure of the V<sub>2</sub>O<sub>5</sub> is preserved for low concentrations of melanin-like units (x<0.02), but the inter-planar space increases from 1.2 nm to ca. 1.5 nm. The FT-IR and ESR spectra confirm that the V<sub>2</sub>O<sub>5</sub> structure is preserved, however the presence of melanin-like units induces the reduction of V(V) ions to V(IV) ions. The melanin insertion is observed to increase the stability and reproducibility of the electrochemical insertion/de-insertion of Li<sup>+</sup>. The incorporation of melanin-like structures increases the conductivity, followed by a decrease in its temperature activation energy. © 2001 Elsevier Science Ltd. All rights reserved.

**Keywords:** Vanadium pentoxide xerogel; Intercalation compounds; Melanin and nanocomposite

## 1. Introduction

Among its various properties, V<sub>2</sub>O<sub>5</sub> exhibits a lamellar structure, the [V<sub>2</sub>O<sub>5</sub>] layers being built up from VO<sub>5</sub> square pyramids sharing edges and corners [1,2]. The sheets are held together via weak interactions between the vanadium atoms and the oxygen atoms at the apex of the VO<sub>5</sub> square pyramids of neighboring layers. The lamellar structure of V<sub>2</sub>O<sub>5</sub> is adequate for intercalation, and thus inspired a lot of activity in the field of hybrid organic/inorganic materials. These new materials hybrid compounds are considered as innovative advanced materials, promise new applications in many fields such as optics, electronics, ionics, mechanics and biology [3,4]. We have recently undertaken the study of organic–inorganic hybrid

materials based on melanin-like/V<sub>2</sub>O<sub>5</sub> [5]. In that study it was shown that among other effects, melanin-like/V<sub>2</sub>O<sub>5</sub> is clearly more stable than V<sub>2</sub>O<sub>5</sub> xerogels with respect to the electrochemical response. Here we report a more systematic work varying the concentration of the bio-polymer intercalated in V<sub>2</sub>O<sub>5</sub>.

## 2. Experimental

### 2.1. Synthesis

The preparation of vanadium pentoxide via sol–gel processing has been extensively reported [6]. Sodium metavanadate (8.50 g, Alfa Ventron) was dissolved in deionized water (500 ml) and the resulting solution was passed through an ion-exchange column (H<sup>+</sup> form, Dowex-50X). A pale yellow solution of polyvanadic acid was obtained and, after several days, a red polymerized V<sub>2</sub>O<sub>5</sub>·nH<sub>2</sub>O gel was formed by the spontaneous polycondensation at room temperature [6]. The intercalated

<sup>☆</sup>This paper was presented at the Second International Conference on Inorganic Materials, UCSB, 2000.

\*Corresponding author. Tel.: +55-16-602-3763; fax: +55-16-633-9949.

E-mail address: cgraeff@dfm.ffclrp.usp.br (C.F.O. Graeff).

compound was prepared by the direct reaction of  $5.0 \times 10^{-3} \text{ mol l}^{-1}$  aqueous solution of DL-DOPA ( $\text{C}_9\text{H}_{11}\text{NO}_4$ ) with different volumes from 0.5 ml to 6.0 ml, dissolved into water purified by a Millipore Milli-Q System, with 20.0 ml of the  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  gel. The reaction was carried out at room temperature ( $24^\circ\text{C}$ ), stirred during 4 h in air, resulting in a dark green suspension. This suspension was cast into a film by the slow evaporation of water on a substrate (glass plate) at room temperature and in air, leading to a metallic dark blue film, and then, rinsed with nanopure water and dried again. Finally, the samples in film form were carefully removed, when necessary, from the glass plate and then stored in vacuum.

## 2.2. Measurements

X-ray diffraction data were recorded on a SIEMENS D5005 diffractometer using a graphite monochromator and  $\text{CuK}\alpha$  emission lines ( $1.541 \text{ \AA}$ , 40 kV, 40 mA). The samples, in film form, were deposited onto a glass plate and the data were collected at room temperature over the range of  $2 \leq 2\theta \leq 50^\circ$  with a step size of  $0.020^\circ$ . Electron spin resonance (ESR) spectra were obtained at room temperature ( $24^\circ\text{C}$ ) using a computer interfaced Varian E-4 spectrometer operating at 9.5 GHz (X band).  $g$  values were obtained by reference to the standard diphenyl- $\beta$ -picrylhydrazyl (DPPH) signal. IR spectra were recorded from 4000 to  $400 \text{ cm}^{-1}$  on a Nicolet 5ZDX FT-IR spectrometer, with the samples dispersed in KBr and pressed into pellets. In order to measure the electrochemical influence of melanin in the matrix, cyclic voltammetry experiments were carried out with an AUTOLAB (EcoChemie) model PGSTAT30 (GPES/FRA) potentiostat/galvanostat interfaced to a computer. A conventional three-electrode arrangement was used, consisting of a working electrode [sample in film form supported on ITO (indium tin oxide)], a platinum wire auxiliary electrode and a reference electrode [ $\text{Ag}/\text{AgNO}_3$  ( $0.010 \text{ mol l}^{-1}$ ) in  $0.1 \text{ mol l}^{-1}$   $\text{LiClO}_4$  in acetonitrile adapted to a Lugging Capillary in order to reduce the ohmic drop]. The intercalation compound and the matrix were deposited on the working electrode surface by dip-coating process. The experiments were carried out at room temperature and in an inert atmosphere by bubbling  $\text{N}_2$  through the solution. DC conductivity was measured as a function of temperature in the 150–350 K range. Reproducibility of the experiments was tested by two identical experiments for each sample. The measurements were performed in an evacuated chamber using a dc bias of 1 V between silver electrodes.

## 3. Results and discussion

The composition of the hybrid material was determined only for the sample synthesized with 4.0 ml of  $5.0 \times 10^{-3}$

$\text{mol l}^{-1}$  aqueous solution of DL-DOPA ( $\text{C}_9\text{H}_{11}\text{NO}_4$ ), dissolved into water purified by a Millipore Milli-Q System, with 20.0 ml of the  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  gel. As described elsewhere [5], for this composition, the obtained material has the following approximated formula:  $(\text{C}_8\text{H}_9\text{NO}_2)_{0.02}\text{V}_2\text{O}_5 \cdot 1.5\text{H}_2\text{O}$ . We are assuming that by varying the amount of DL-DOPA on the initial solution, there is a proportional change in the amount of the melanin-like part on the composition of the final material. Indirect evidences of such assumptions will be discussed in the following.

Fig. 1 shows typical powder X-ray diffraction patterns for the vanadium pentoxide matrix, and two differently composed films intercalated with melanin-like molecules. The powder diffraction patterns are clearly different from the precursor for all compositions [5], which shows that DL-DOPA reacts during intercalation. The diffraction pattern of the intercalation product in comparison with the matrix exhibit a lamellar structure but with a lower degree of crystallinity, suggesting maintenance of the layered framework of  $\text{V}_2\text{O}_5$  xerogel. An increase in the interlayer spacing with the insertion of the polymeric species is observed with  $d$ -spacing changing from 1.20 nm to 1.54 nm, as can be seen in Fig. 2. In Fig. 2 the concentration has been normalized by the sample synthesized with 4.0 ml of  $5.0 \times 10^{-3} \text{ mol l}^{-1}$  aqueous solution of DL-DOPA ( $\text{C}_9\text{H}_{11}\text{NO}_4$ ), dissolved into water purified by a Millipore Milli-Q System, with 20.0 ml of the  $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  gel, which is the only sample with known composition. Notice that the change in interlayer spacing is weakly dependent on the concentration of the organic part. This expansion is expected within the stacked ‘islands’ model of the melanin structure [7]. In this model, melanin is formed by three stacked sheets with polymers of 5,6-indolequinone units randomly linked, the sheets interacting through van der

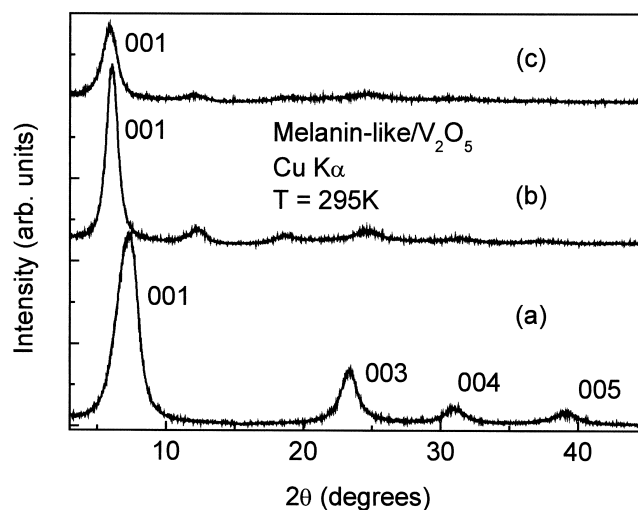


Fig. 1.  $\text{Cu-K}\alpha$  X-ray diffraction patterns of (a) the hydrated vanadium pentoxide matrix, (b)  $(\text{C}_8\text{H}_9\text{NO}_2)_{0.005}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$  (c)  $(\text{C}_8\text{H}_9\text{NO}_2)_{0.03}\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ .

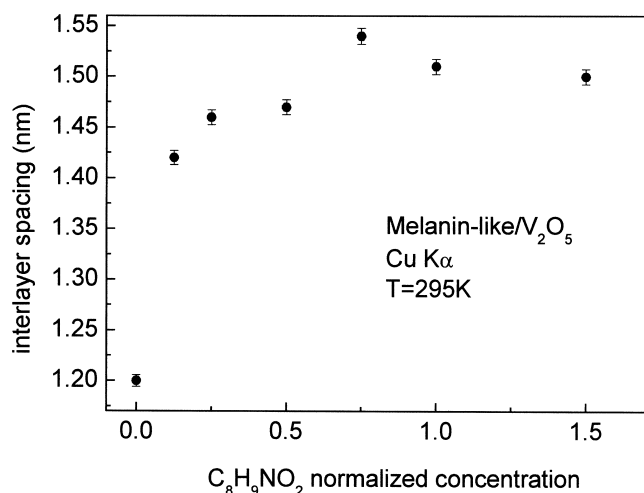


Fig. 2. Interlayer spacing as a function of the normalized concentration of  $C_8H_9NO_2$  in the film. The normalization procedure is described in the text.

Waals forces. The overall dimension is ca. 2 nm in lateral extent and 0.8 nm in height, being the distance between the sheets about 0.34 nm. If two stacked sheets were intercalated, the interlayer spacing should increase by ca. 0.35 nm in good agreement with what is found. Probably, the melanin-like structure formed is constituted by one or two planar polymer sheets assembled in parallel fashion between the  $V_2O_5$  layers. Presumably, the water molecules take part in the hydrogen bonding interactions between the melanin-like structure and  $V_2O_5$  layers, contributing to the stabilization of this arrangement between the macromolecules and the matrix. The increase in the basal spacing could be also attributed to the change in the reduction state of vanadium, however our previous work discards this possibility [5].

The FT-IR spectrum of the intercalation compound shows the presence of both organic and inorganic parts, independent on the relative concentration of melanin-like structures intercalated. The characteristic bands of  $V_2O_5$  framework can be observed, as well as bands related to the organic part, as described elsewhere [5]. With increasing DL-DOPA concentration in the starting material, it was observed that the C and N related bands increase proportionally without affecting the characteristic bands of  $V_2O_5$ , except for the water related bands that decrease slightly as expected [5]. These data suggest that the reaction product of DL-DOPA practically does not affect the matrix framework, indicating a weak interaction with the lattice and consistent with a topotactic phenomena.

The ESR spectra for the  $V_2O_5 \cdot 1.8H_2O$  and the  $(C_8H_9NO_2)_x V_2O_5 \cdot nH_2O$  obtained in film form are quite different. The signal is dominated in all cases by the host. However, the ESR signal changes with the increased amount of melanin-like structures intercalated in  $V_2O_5$ . The signal changes from a spectrum with well-resolved hyperfine lines to a broad line ( $\Delta H_{pp} \approx 100$  G), with a

$g \approx 1.97$  typical for a  $V_2O_5 \cdot 1.8H_2O$  film where  $V^{IV}/(V^{IV} + V^V) \geq 16\%$  [8]. In other words, the presence of DL-DOPA during the intercalation process reduces the  $V^V$  ions to  $V^{IV}$ . This result is indirect evidence that the polymerization process did start, since synthetic dopa-melanins is prepared by oxidation of DL-DOPA. In the conventional method of preparing dopa-melanin the oxidation is provided by air which is bubbled through stirred solution [9]. In the case presented here the oxidation of DL-DOPA is provided by the reduction of  $V^V$  ions. However, the polymerization process induced by oxidation from DL-DOPA to dopa-melanin passes through many intermediate states, which are not controlled under the preparation procedure we are using at the moment. Thus, it is expected that not just dopa-melanin is prepared but also many intermediate products. The anisotropic character of the ESR spectra with respect to the magnetic field orientation with respect to the film surface is preserved in all cases, further corroborating that the lamellar structure is preserved. Note that dopa-melanin has an intrinsic free radical giving an ESR signal around 2.0037 and  $\Delta H_{pp} \approx 5G$ , which however was not observed. Among other reasons, most probably the fact that dopa-melanin is synthesized in small amounts contributes to the insensitivity of the EPR system to dopa melanin.

The intercalation-polymerization of DL-DOPA has a pronounced effect on the conductivity of  $V_2O_5 \cdot 1.8H_2O$ , as shown in Fig. 3. The room temperature conductivity changed from  $1.1 \times 10^{-4} (\Omega \text{ cm})^{-1}$  to  $5.2 \times 10^{-3} (\Omega \text{ cm})^{-1}$  with increasing concentration of DL-DOPA in the starting solution. The activation energy did also change as can be seen in Fig. 4 from 0.35 eV in  $V_2O_5 \cdot 1.8H_2O$  to 0.20 eV. In Fig. 4 the concentration has been normalized by the sample synthesized with 4.0 ml of  $5.0 \times 10^{-3} \text{ mol l}^{-1}$  aqueous solution of DL-DOPA ( $C_9H_{11}NO_4$ ), dissolved into water purified by a Millipore Milli-Q System, with 20.0 ml of the

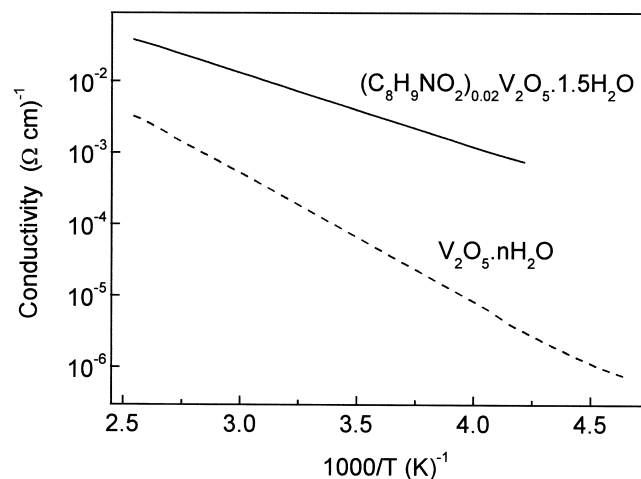


Fig. 3. Typical conductivity as a function of temperature results for the hydrated pentoxide vanadium matrix and  $(C_8H_9NO_2)_{0.02} V_2O_5 \cdot 1.5H_2O$  film.

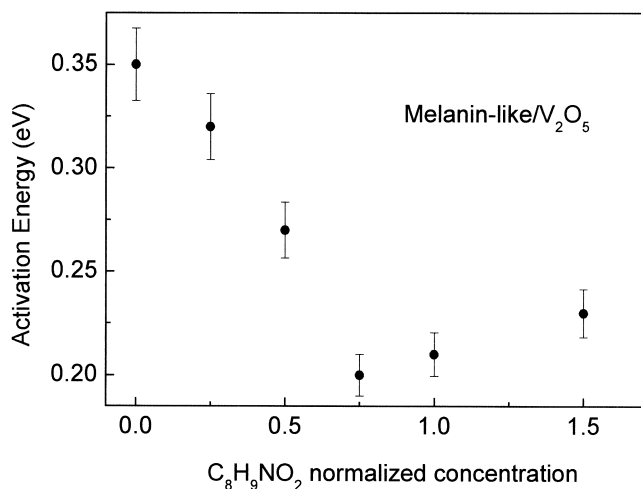


Fig. 4. Temperature activation energy of the DC conductivity as a function of the normalized concentration of  $C_8H_9NO_2$  in the film. The normalization procedure is described in the text.

$V_2O_5 \cdot nH_2O$  gel, which is the only sample with known composition. It is assumed that the organic content of the samples are proportional to the value in the starting solution. As can be seen, initially by increasing the concentration of the melanin-like part the activation energy tends to decrease, achieving a minimum and then it starts to grow slowly. For even higher concentrations the activation energy reaches the initial values, not shown in Fig. 4. The conduction properties of vanadium pentoxide xerogels ( $V_2O_5 \cdot 1.8H_2O$ ) are dominated by the thermally activated hopping of unpaired electrons between metal ions, which are best described by small polaron hopping process. Moreover, the conduction carriers in  $V_2O_5$  are predominantly  $V^{IV}$  ions, thus the conductivity in this materials increases with the  $V^{IV}$  concentrations [10,11]. From what has been discussed concerning the ESR data, there is an increase in  $V^{IV}$  species induced by the intercalation/polymerization of DL-DOPA, which could explain partially the increase in conductivity. Another plausible possibility is that part of the charge is being carried by the melanin-like structures acting as a parallel resistor. However, melanin seems to have a very low conductivity [12], even though up to now all conductivity measurements have been made for melanin in the powder form, which may be dominated by grain boundaries effects. More work should be done to clarify this point. Nevertheless intercalating melanin in  $V_2O_5$  appears to be an efficient way to increase its conductivity. In fact, we have done some experiments intercalating polyaniline, which is known to increase the  $V_2O_5$  conductivity, and found very little difference in the conductivity changes compared to melanin intercalated to  $V_2O_5$  xerogel [13].

Cyclic voltammograms of the  $V_2O_5 \cdot 1.8H_2O$  and melanin-like/ $V_2O_5 \cdot nH_2O$  were similar. A typical result is shown in Fig. 5, exhibiting two characteristic reversible waves in the potential range  $-0.5$  V to  $+1.5$  V (versus

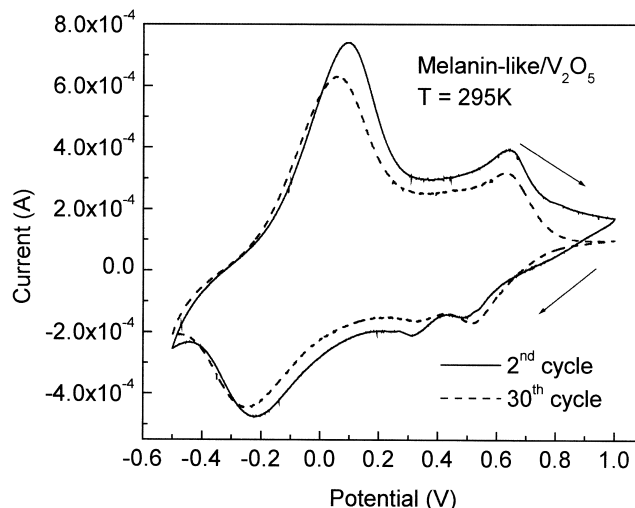


Fig. 5. Cyclic voltammograms as a function of cycling for  $(C_8H_9NO_2)_{0.01}V_2O_5 \cdot nH_2O$  film. The scan rate used was  $5 \text{ mV s}^{-1}$ .

SHE), in acetonitrile solutions containing  $0.1 \text{ mol l}^{-1}$   $LiClO_4$ . These waves are ascribed to the  $V^{V/IV}$  redox pair, presumably due to the  $Li^+$  insertion in two non-equivalent sites in the vanadium oxide matrix. The width and asymmetric pattern of waves can be related to heterogeneity of the film surface and to the low rate of electronic transfer. Although melanin is known to be electrochemically active, [14] in melanin-like/ $V_2O_5$  the organic part apparently does not contribute to the overall redox process in the potential range used. In spite of the similarity of the cyclic voltammograms, the insertion of the polymer into the matrix resulting in an assembled inorganic/organic hybrid structure led to a surprising stabilization of the electrochemical response over several cycles, as shown in Fig. 5. Typically after 30 cycles  $V_2O_5 \cdot 1.8H_2O$  total voltammetric charge drops by a factor of 3, while for melanin-like/ $V_2O_5$  the drop is of ca. 20%. This is attributed to enhanced  $Li^+$  diffusion through the film due to a decrease in steric and electrostatic effects promoted by the higher interlamellar distance. A detailed mechanism is still unknown, however, as discussed elsewhere [5] we are assuming that the contribution of the polymer is basically structural, i.e., the melanin-like units acts as pillars between the  $V_2O_5$  sheets, with resulting increased interlamellar separation, so decreasing the structural changes in the films caused by solvated  $Li^+$  insertion/deinsertion. However the lower amount of water molecules in the compound can contribute to the enhanced reversibility.

Not just the reversibility of the cyclic voltammograms is affected by the insertion of melanin-like units inside the  $V_2O_5$  sheets. As can be seen in Fig. 6 the total voltammetric charge can be largely enhanced in the hybrid compound. In Fig. 6 the concentration has been normalized by the sample synthesized with  $4.0 \text{ ml}$  of  $5.0 \times 10^{-3} \text{ mol l}^{-1}$  aqueous solution of DL-DOPA ( $C_9H_{11}NO_4$ ), dissolved into water purified by a Millipore Milli-Q System, with

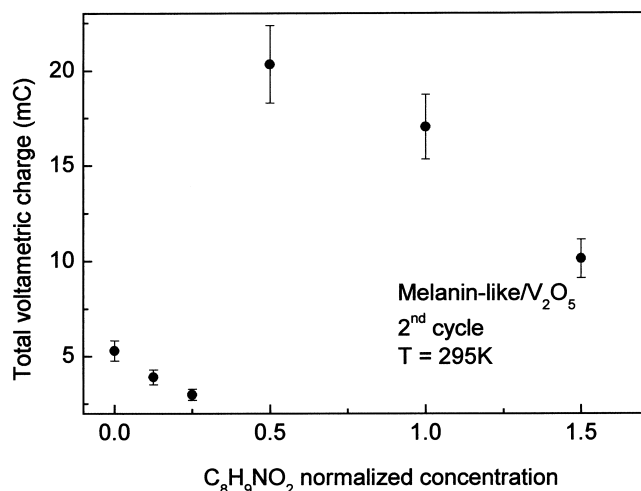


Fig. 6. Total voltammetric charge in redox process as a function of the normalized concentration of  $C_8H_9NO_2$  in the film. The normalization procedure is described in the text.

20.0 ml of the  $V_2O_5 \cdot nH_2O$  gel, which is the only sample with known composition. It is interesting to notice that the charge was increased by a factor 4, with a sharp transition for the sample with, in principle, half the content of the  $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$  sample. The sharp increase in total voltammetric charge is followed by a decrease for higher  $C_8H_9NO_2$  concentrations in the material. This result is somehow in contradiction with the assumption that melanin-like structures are only acting as pillar between the  $V_2O_5$  sheets, since as can be seen in Fig. 2, even for the lowest  $C_8H_9NO_2$  concentrations in the film, there is already a strong increase in the interlamellar distance. In fact Fig. 6 correlates better with Fig. 4, which shows us that one important contribution to the improvement in electrochemical response is due to an increase in conductivity of the film. For higher concentrations of melanin-like units the structural disorder increases, see Fig. 1, which compromises the conductivity as well as the electrochemical response. In fact, as can be seen in Figs. 2, 4 and 6, there is a clear optimum in  $C_8H_9NO_2$  concentration, around  $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$ . We have also tried higher concentrations of DL-DOPA in the starting solution, which resulted in very inhomogeneous gels, where segregation clearly took place.

#### 4. Conclusions

The structural and electronic properties of a layered hybrid organic–inorganic material are described;  $(C_8H_9NO_2)_xV_2O_5 \cdot nH_2O$ . IR, XRD as well as EPR studies showed that melanin-like units for  $x < 0.02$  is intercalated

in the  $V_2O_5$  matrix without strongly affecting the lamellar structure. For  $x > 0.02$ , disorder is induced. The major effect is an increase in the interlayer spacing from 1.2 nm to 1.5 nm for all compositions studied here. This change in interlayer spacing results in interesting effects in the electronic properties of the material. There is a clear improvement in the stabilization of the electrochemical response in relation to the free matrix, as well as an increase in total voltammetric charge, for  $x > 0.01$ . The total charge in the redox process was practically unaffected in the melanin-like intercalated  $V_2O_5$  even after 30 cycles. For the  $V_2O_5 \cdot 1.8H_2O$  in contrast, the total charge decreased by a factor of 4 after 30 cycles. The conductivity is also affected by the intercalation process with an increase in dc conductivity at room temperature, from  $1.1 \times 10^{-4} (\Omega \text{ cm})^{-1}$  to  $5.2 \times 10^{-3} (\Omega \text{ cm})^{-1}$  and a decrease in the temperature activation energy, both dependent on melanin-like units concentration. Our results indicate a formation of a new composite hybrid material, rather than a simple physical mixture of the starting reagents.

#### Acknowledgements

This research was supported by PADCT (n<sup>o</sup> 62.0238/97-6), FAPESP and CNPq. The authors are pleased to acknowledge J.M. Rosolen for the IR measurements.

#### References

- [1] Enjalbert R, Galy J. Acta Crystallogr Sect C: Cryst Struct Commun 1986;42:1467.
- [2] Zavalij PY, Whittingham MS. Acta Crystallogr Sect B: Struct Science 1999;55:627.
- [3] Cheetham AK. Science 1994;264:794.
- [4] Judeinstein P, Sanchez C. J Mater Chem 1996;6:511.
- [5] Oliveira HP, Graeff CFO, Zanta CLPS, Galina AC, Gonçalves PJ. J Mater Chem 2000;10:371.
- [6] Livage J. Solid States Ionics 1996;86–88:935.
- [7] Zajac GW, Gallas JM, Cheng J, Eisner M, Moss SC, Alvarado-Swaigoog AE. Biochem Biophys Acta 1994;1199:271.
- [8] Babonneau F, Barboux P, Josien FA, Livage J. J Chem Phys 1985;82:761.
- [9] Sealy RC. Methods in Enzymology 1984;105:479.
- [10] Gharbi N, Sanchez C, Livage J, Lemerle J, Nejem L, Lefebvre J. J Inorg Chem 1982;21:2758.
- [11] Livage J. In: Wright AF, Dupuy J, editors, NATO ASI — series E: applied sciences, Vol. 92, Martinus Nijhoff Publishers, 1985, p. 419.
- [12] Osak W, Tkacz K, Czternastek H, Slawinski J. Biopolymers 1989;28:1985.
- [13] Oliveira HP, Graeff CFO, Brunello CA, Guerra EM. J Non-Cryst Solids 2000;273:193.
- [14] Stanislaw S, Reszka K, Matuszak Z. Bioelectrochem Bioenerg 1980;7:153.