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Synthesis, characterization and properties of a melanin-like/vanadium pentoxide hybrid compound

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An intercalated material has been prepared consisting of a regular alternation of organic/inorganic layers. The products were obtained by reacting 3,4-dihydroxyphenylalanine (DL-DOPA) with $V_2O_5 \cdot nH_2O$ gel, which underwent an oxidative polymerization/intercalation process, forming a dark blue metallic colored film. The films were characterized using thermogravimetric analysis, UV–VIS transmission spectroscopy, FTIR, EPR, X-ray diffraction, dc conductivity, and cyclic voltammetry. The X-ray diffractograms indicate that the lamellar structure of the V_2O_5 is preserved but that the interplanar spacing increases from 1.18 to 1.38 nm. The FTIR and EPR spectra confirm that the V_2O_5 structure is preserved; however the presence of melanin-like structures induces the reduction of V^V ions to V^{IV}. The increase in the interplanar spacing is observed to increase the stability and reproducibility of the electrochemical insertion/deinsertion of Li^+. This increase in stability is also observed in the electrochromic properties of the film, which are fully reproducible even after >60 oxidation–reduction cycles. The incorporation of melanin-like structures also affects the activation energy of the dc conductivity, which is reduced from 0.35 to 0.20 eV.

Introduction

The possibility of combining the properties of organic and inorganic compounds in a unique material is a well established challenge. Such new materials which are considered as innovative advanced materials, promise new applications in many fields such as optics, electronics, ionics, mechanics and biology.[1,2] The design and synthesis of hybrid organic–inorganic materials can be attained by intercalation reactions of layered solids, based on self-assembly approaches,[2,3] with the formation of stable covalent units linked together by weaker and less directional interactions such as hydrogen and van der Waals bonds. V_2O_5 xerogels have interesting conducting as well as electrochemical properties in addition to lamellar (or 2D) structure suitable for intercalation reactions.[4] Melanin is a biopolymer which shows a high photo-absorption over a wide range of photon energies resulting in good photoconductivity.[5] Here, we report the synthesis and characterization of a melanin-like/V_2O_5 intercalate, as well the study of its conductivity and electrochemical properties.

Experimental

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^+ form, Dowex-50X). A pale yellow solution of polyvanadic acid was obtained and, after several days, a red polymerized $V_2O_5 \cdot nH_2O$ gel was formed by spontaneous polycondensation at room temperature.[6] The intercalated compound was prepared by the direct reaction of 4.0 ml of a 5.0 mM aqueous solution of DL-DOPA ($C_9H_{11}NO_4$) with 20.0 ml of the $V_2O_5 \cdot nH_2O$ gel. The reaction was carried out at room temperature (24 °C) under stirring for 4 h in air, resulting in a dark green suspension. This suspension was cast into a film on a glass plate by slow evaporation of the water at room temperature and in air, leading to a metallic dark blue film. After the film was rinsed with nanopure water and dried, the samples, in film form, were carefully removed from the glass plate and stored in vacuum.

Measurements

X-Ray diffraction data were recorded on a Siemens D5005 diffractometer using a graphite monochromator and Cu-Kα emission lines (1.541 Å, 40 kV, 40 mA). The samples, in film form, were deposited onto a glass plate and data were collected at room temperature over the range $2 \leqslant 2\theta \leqslant 50°$ with a step size of 0.020°. UV–VIS spectra were recorded on a Varian Cary 50 spectrophotometer with the intercalation compound as a film on a quartz plate (also used as the reference) or on an indium tin oxide (ITO) electrode. Electron paramagnetic resonance (EPR) spectra were obtained at room temperature (24 °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-β-picrylhydrazyl (DPPH) signal. IR spectra were recorded from 4000 to 400 cm^{-1} on a Nicolet 5ZDX FT-IR spectrometer, with the samples dispersed in KBr and pressed into pellets. Thermogravimetric data were registered on a Thermal Analyst equipment model 2100-TA in air atmosphere and at a heating rate of 1.0 °C min^{-1}. Raman spectra were taken using a double-monochromator and the 514.5 nm line of an argon laser. The samples were in the form of films deposited on glass. To minimize heating, the maximum power used was 50 mW, corresponding to a power density on the sample of *ca.* 20 kW cm^{-2}. In order to measure the electrochemical influence of melanin in the matrix, cyclic voltammetry experiments were carried out with a Princeton Applied Research model 273 potentiostat/galvanostat interface. 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 [Ag/$AgNO_3$ (0.010 mol l^{-1}) in 0.1 mol l^{-1} $LiClO_4$ in acetonitrile adapted to a Luggin capillary in order to reduce the ohmic drop]. The intercalation compound and the matrix were deposited on ITO surfaces by evaporating 5 µl suspensions at room temperature. The experiments were carried out at room temperature and in an inert atmosphere by bubbling N_2 through the solution. All potentials were referred to SHE by adding 0.50 V. For the spectroelectrochemical experiments, the potentiostat was coupled with a spectrophotometer, and the three-electrode system was assembled in a quartz cell of 1.00 cm optical path length. The dc conductivity was measured as a function of temperature in the range 150–350 K. Reproducibility 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.

Results and discussion

The composition of the material was determined by thermal and elemental analysis. The molecular structure of melanin is still only partially known owing to its heteropolymeric nature, being comprised of heteroaromatic molecules containing planar five- and six-membered rings resulting in condensed ring systems with random organization.[7] Thus, in order to evaluate the composition by elemental analysis, we have taken into account that the polymeric repetitive unit is similar to the indole-5,6-quinone structure ($C_8H_9NO_2$). Results (C, $2.1 \pm 0.2\%$; N, $0.32 \pm 0.06\%$) and the relation $C/N = 7.6 \pm 0.7$ are in accord with the theoretical calculation ($C/N = 8.0$). The thermogravimetric curve of the V_2O_5 matrix is shown in Fig. 1(a) which shows two main weight losses. The first weight loss extends to *ca.* 130 °C, and is attributed to the loss of interlamellar water. The second weight loss extends up to *ca.* 270 °C, and is attributed to the release of the intramolecular water and the water molecules bounded to vanadium. Above 330 °C formation of crystalline vanadium pentoxide occurs. For the intercalation product, Fig. 1(b), the thermogravimetric curve shows a loss of 12 mass% up to 100 °C that can be attributed to weakly bonded water molecules. In the temperature range 120–230 °C the mass loss (1%) can be related to a small amount of strongly bound water to vanadium. Above 230 °C and primarily at 280–350 °C, the mass loss was *ca.* 2.5% and was attributed to the organic phase. Moreover, with a further increase of temperature there was a gain in mass that could be related to the oxidation of V^{IV} centers by oxygen concomitant with the conversion to crystalline vanadium pentoxide. Note also that the release of weakly bound water molecules in the composite occurred up to 100 °C while for the V_2O_5 matrix this was extended to 120 °C. The weight loss is also more pronounced up to 120 °C in the composite compared to the V_2O_5 matrix. These results suggest that the presence of the polymer facilitates the release of water molecules, presumably owing to an increase in the interlamellar distance, as observed in X-ray diffraction spectra (Fig. 2). As we do not have further evidence for the melanin structure, we use the expression "melanin-like" for the organic phase between V_2O_5 sheets. Thus, combining elemental analysis and TGA data, the obtained material has the following approximate formula: $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$.

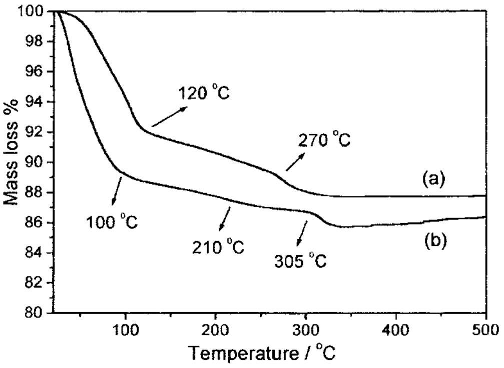

Fig. 1 Thermogravimetric curves of (a) the hydrated vanadium pentoxide matrix ($V_2O_5 \cdot 1.8H_2O$) and (b) $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$.

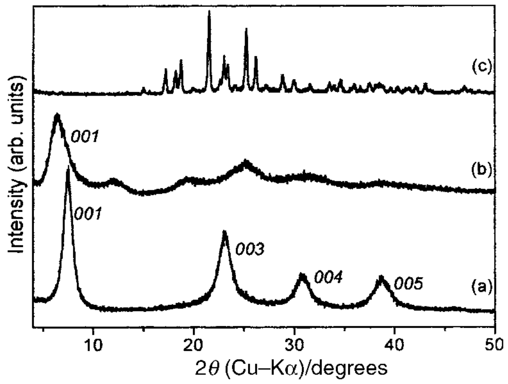

Fig. 2 Cu-Kα X-ray diffraction patterns of (a) the hydrated vanadium pentoxide matrix, (b) $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$ and (c) DL-DOPA.

Fig. 2 shows typical powder X-ray diffraction patterns for the vanadium pentoxide matrix, the intercalation compound with melanin and DL-DOPA.[8] Fig. 2 clearly shows that the precursor reacts during intercalation since the typical reflections of DL-DOPA were not observed. The diffraction pattern of the intercalation product in comparison with the matrix exhibits a lamellar structure but with a lower degree of crystallinity, suggesting maintenance of the layered framework of the V_2O_5 xerogel.

An increase in the interlayer spacing with the insertion of the polymeric species is observed with the *d*-spacing changing from 1.18 to 1.38 nm. 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 with the sheets interacting through van der Waals forces. The overall dimension is *ca.* 2 nm in lateral extent and 0.8 nm in height, while the distance between sheets is *ca.* 0.34 nm. Taking into account the interlayer expansion ($\Delta d = 0.2$ nm) and considering the amount of water molecules, the possibility of the melanin-like structure being incorporated as stacked sheets can be ruled out. If two stacked sheets were intercalated, the interlayer spacing should increase by *ca.* 0.35 nm rather than 0.2 nm. Thus, interaction with the matrix appears to suppress the formation of stacked sheets (as commonly observed in pure melanin), otherwise a higher interlayer spacing would be expected. Probably, the melanin-like structure formed is constituted by one planar polymer sheet assembled in parallel fashion between the V_2O_5 layers. Presumably, the water molecules take part in 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 oxidation state of vanadium. As will be discussed below, intercalation is responsible for the partial reduction of V^V to V^{IV}. Thus, in order to investigate this possibility, the matrix, in film form, was reduced by reacting it with a solution of potassium iodide. The XRD result showed a decrease in the interlamellar spacing from 1.18 to 1.12 nm. Thus, the increase of the basal spacing cannot be attributed to the reduction of V^V to V^{IV}.

Fig. 3 shows the FTIR spectra of synthetic melanin,[8] DL-DOPA and the intercalation compound. The characteristic bands of the V_2O_5 framework can be observed at 1007 [ν(V=O)], 765 [ν(VOV)] and 527 cm^{-1} [δ(VOV)]. The spectrum of the hybrid material shows a composite band in the 1600 cm^{-1} region ascribed to C=O, COOH stretching with an OH bending (H_2O) contribution. The band near 1400 cm^{-1}

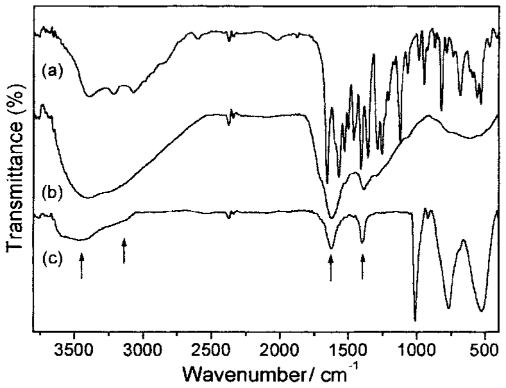

Fig. 3 FTIR spectra of (a) DL-DOPA; (b) synthetic melanin and (c) $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$.

is related to C–O stretching of a carboxylic group. The large band at 3400 cm^{-1} arises from OH–H stretching and the band at *ca.* 3160 cm^{-1} is ascribed to N–H stretching.[10] These data suggest that the melanin essentially does not affect the framework, indicating only a weak interaction with the lattice and consistent with a topotactic phenomenon.

The EPR spectra for $V_2O_5 \cdot 1.8H_2O$ and $(C_8H_9NO_2)_{0.02}$-$V_2O_5 \cdot 1.5H_2O$ obtained in film form are quite different, as shown in Fig. 4. In the latter, the EPR signal has a lorentzian lineshape to a first approximation. The signal is dominated by the host with a broad line ($\Delta H_{pp} \approx 100$ G), centered at $g \approx 1.97$, typical for a $V_2O_5 \cdot 1.8H_2O$ film where $V^{IV}/(V^{IV}+V^{V}) \geqslant 16\%$.[9] In other words, the presence of DL-DOPA during the intercalation process reduces V^{V} ions to V^{IV}. Also, in order to evaluate any anisotropic character, the EPR spectra were recorded at different angles between the magnetic field and the film surface. The data suggest that the new compound shows anisotropic behavior with g varying from $g_{\parallel} = 1.957$ to $g_{\perp} = 1.969$, which further indicates that the lamellar structure is preserved. Note that melanin is an intrinsic free radical giving an EPR signal at $g \approx 2.0037$ and $\Delta H_{pp} \approx 5$ G. As is clearly seen in Fig. 4, in the intercalated samples no signal arising from melanin could be observed. Among other reasons, most probably the fact that melanin is incorporated in small amounts contributes to the absence of a melanin signal. Another important effect is that oxidized DOPA melanin is known to show a strongly decreased EPR signal.[11] The semiquinone units, which are mainly responsible for the free radical content in melanins, are partially destroyed during oxidation, with simultaneous formation of –COOH groups. Even if the oxidation of melanin is not considered, the free radical signal from melanin in the presence of paramagnetic ions is known to decrease or even disappear owing to the strong magnetic interaction of the spins owing to their close proximity.[12]

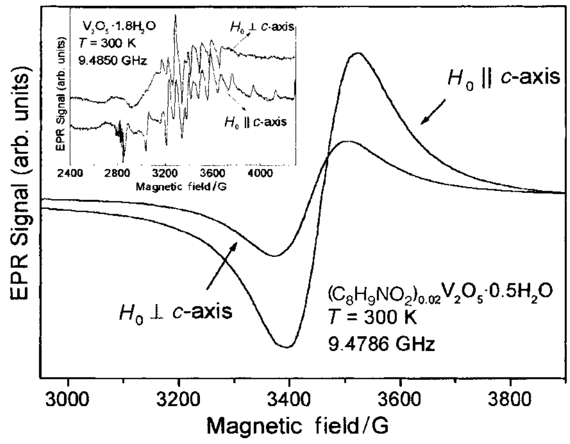

Fig. 4 EPR spectra of $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$ (insert: EPR signal of the hydrated vanadium pentoxide matrix), measured at different angles between the magnetic field and the product in film form at room temperature (24 °C).

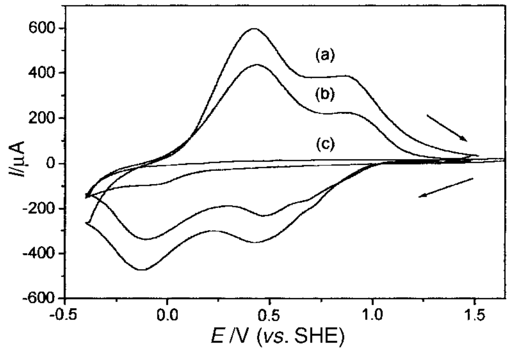

Fig. 5 Cyclic voltammograms of (a) the hydrated vanadium pentoxide matrix, (b) $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$ and (c) pure melanin: acetonitrile, 0.1 mol l^{-1} $LiClO_4$, potential range −0.50 to +0.50 V (*vs.* SHE), $v = 20$ mV s^{-1}.

Cyclic voltammograms of $V_2O_5 \cdot 1.8H_2O$ and $(C_8H_9NO_2)_{0.02}$-$V_2O_5 \cdot 1.5H_2O$ were similar (Fig. 5), exhibiting two characteristic reversible waves in the potential range −0.5 to +1.5 V (*vs.* SHE), in acetonitrile solutions containing 0.1 M $LiClO_4$. These waves are ascribed to the $V^{V/IV}$ redox pair, presumably due to Li^+ insertion in two non-equivalent sites in the vanadium oxide matrix. The width and asymmetric pattern of waves can be related to the heterogeneity of the film surface and the low rate of electronic transfer.

Although melanin is electrochemically active,[13] cyclic voltammetry of pure synthetic melanin deposited onto the electrode surface showed that the melanin has an irreversible low intensity cathodic peak at −0.1 V (*vs.* SHE) and apparently does not contribute to the overall redox process in the potential range employed [Fig. 5(c)].

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 (60), as shown in Fig. 6(a) and (b). This is attributed to enhanced Li^+ diffusion through the film owing to a decrease in steric and electrostatic effects[14] promoted by the greater interlamellar distance. The overall effect induced by the formation of melanin into the hydrated matrix is summarized in Fig. 7, in which maintenance of the total voltammetric charge during several scans for the hybrid material is observed.

During the Li^+ insertion process, changes in volume, lattice parameters and mechanical stress occur in the films, contributing to electrochemical instability under consecutive cycles, and consequently to a decrease in the total voltammetric charge.[15,16] A possible mechanism that could give rise to the stabilization effect observed in our samples is that the structure of the compound becomes more rigid, with the presence of polymeric units, and is thus less susceptible to environmental effects and structural changes. This effect can also be responsible for the creation of channels between the layers, which facilitate Li^+ diffusion through the films. Note also, in addition, in these samples the polymer has little effect on the redox process [Fig. 5(c)]. This is in contrast to the electrochemical response of a polyaniline/V_2O_5 nanocomposite studied by Leroux *et al.*,[14] which indicated an increase of faradaic and capacitive responses owing to a higher occupancy of the Li^+ in reduction sites, especially in the potential range in which the redox response of the polymer occurs, suggesting that the organic and inorganic components are simultaneously reduced/oxidized.

Another possibility, as suggested by previous work, is that the more dehydrated the V_2O_5 xerogel the better is the stability

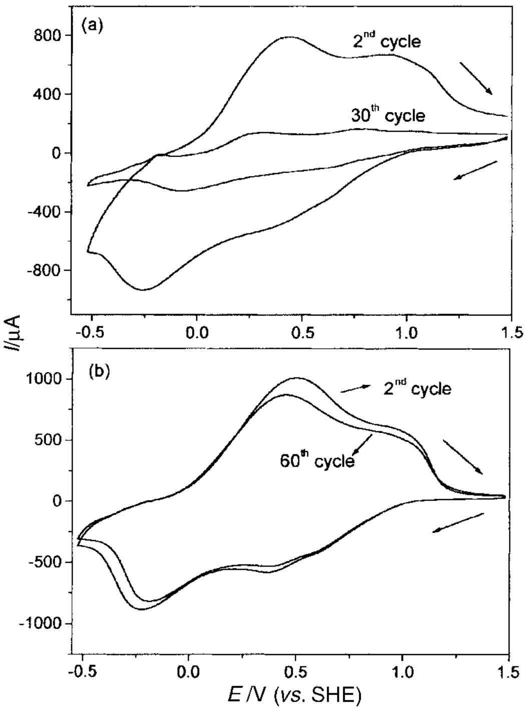

Fig. 6 Stability measurements of (a) the hydrated vanadium pentoxide matrix and (b) $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$: acetonitrile, 0.1 mol l^{-1} $LiClO_4$, potential range −0.50 to +1.50 V (*vs.* SHE), $v = 20$ mV s^{-1}.

of this compound to Li^+ insertion/deinsertion. West *et al.*[16] showed that lithium insertion into V_2O_5 xerogels is reversible provided all the weakly bounded water molecules are removed by thermal treatment. For samples treated at 100 °C in vacuum $(V_2O_5 \cdot 0.5H_2O)$, it is possible to insert reversibly *ca.* 1.5 mol Li per mol of V_2O_5. For the more crystalline compound $(V_2O_5 \cdot 0.1H_2O)$, after heat treatment above 250 °C, it is possible to insert nearly 2.0 mol of Li per mol of V_2O_5. However, crystalline V_2O_5 has a lower capacity for reversible insertion of Li (1 mol Li per mol V_2O_5), owing to irreversible phase changes.[17,18] Our results showed that the stabilization is not simply attributed to a decrease of the number of water molecules $[(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O]$. Another possibility that must be considered is the steric hindrance arising from the presence of polymeric species, restricting access of lithium ions to the electroactive centres. However, as the amount of the melanin is low, this hypothesis can be disregarded. Thus, it is possible that the contribution of the polymer is essentially structural, *i.e.*, the melanin-like units act 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 may also contribute to the enhanced reversibility. More work is underway to clarify the stabilization of the electrochemical response in this compound.

An electrochromic effect in the hybrid material was observed during the potential scans. In the reduced form (−0.4 V *vs.* SHE), the band at 397 nm, attributed to vanadium(V)–oxide CT transition, decreases in intensity and a broad band appears at *ca.* 800 nm, corresponding to weak transitions that should correspond to ligand field transitions within the V(IV)–oxide chromophore.[19] When the intercalation compound was submitted to a potential of +1.5 V (*vs.* SHE), *i.e.* to give the oxidized form, a reversible chromatic response was observed, even after several (60) successive scans.

The intercalation of melanin has a pronounced effect on the conductivity of $V_2O_5 \cdot 1.8H_2O$ (Fig. 8). The room temperature conductivity changed from 1.1×10^{-4} $(\Omega\ cm)^{-1}$ to 5.2×10^{-3} $(\Omega\ cm)^{-1}$ with introduction of melanin into the V_2O_5 structure. The activation energy also changed from 0.35 eV in $V_2O_5 \cdot 1.8H_2O$ to 0.20 eV in $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$. This change in the transport properties may arise from different factors. From the small polaron model[20] the activation energy (*W*) of the dark conductivity at higher temperatures reflects the polaron binding energy, the structural disorder, as well as a transfer integral (the coupling potential between two hopping sites). In the case of V_2O_5, it is especially difficult to separate these contributions to the activation energy, which can vary from 0.17 to 0.65 eV.[21] Higher activation energy is normally attributed to the disorder term. In our system, however, the disorder has not decreased with the incorporation of melanin, and thus the change in activation energy might be due to a change in the phonon spectra. To investigate this, Raman studies have been carried out. The Raman spectrum of the hydrated V_2O_5 matrix shows bands typical of $V_2O_5 \cdot nH_2O$ at 255, 325, 350, 510, 667, 707, and 895 cm^{-1} and is evidence of the good quality of our samples. For $(C_8H_9NO_2)_{0.02}$-$V_2O_5 \cdot 1.5H_2O$ the same lines were observed, but with somewhat lower intensity, which may be an indication of an increase in disorder, in good agreement with the X-ray diffraction results. In addition, there was also a clear enhancement in stray light, owing to the rougher surface of $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$ in comparison with $V_2O_5 \cdot 1.8H_2O$ films. The Raman results suggest no fundamental change in the phonon energy spectra upon incorporation of melanin. Thus, assuming that the small polaron hopping model is valid (which may not be the case since our samples are clearly inhomogeneous) a possible explanation for the decrease in activation energy arises from a change in the potential barrier sensed by the electron due to the presence of charged melanin near the vanadium sites. This model has been proposed by Chung and Mackenzie[22] to explain the different activation energies found in oxide glasses containing 55 mol% V_2O_5 and 45 mol% GeO_2, TeO_2, PbO, BaO or As_2O_3. According to this model, the activation energy decreases as a function of the increase in the charge present

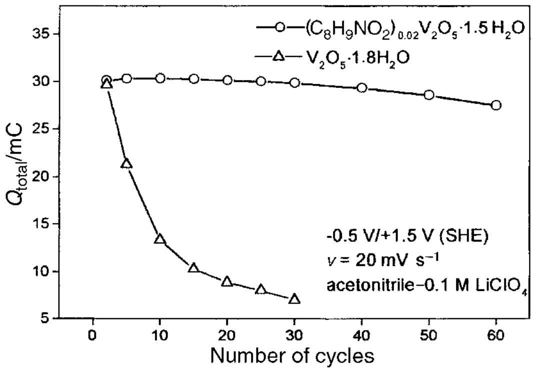

Fig. 7 Total voltammetric charge in the redox process as a function of the number of cycles: acetonitrile, 0.1 mol l^{-1} $LiClO_4$, potential range −0.50 to +1.50 V (*vs.* SHE), $v = 20$ mV s^{-1}.

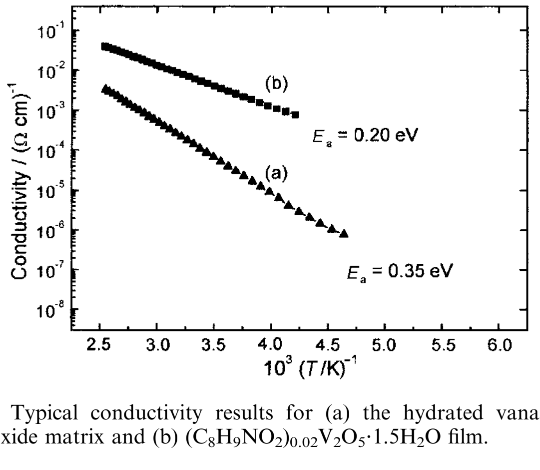

Fig. 8 Typical conductivity results for (a) the hydrated vanadium pentoxide matrix and (b) $(C_8H_9NO_2)_{0.02}V_2O_5 \cdot 1.5H_2O$ film.

near the vanadium atoms. Another plausible possibility is that part of the charge is being carried by melanin acting as a parallel resistor. However, melanin seems to have a very low conductivity,[23] even though, up to now, all conductivity measurements have been made for melanin in powder form, which may be dominated by grain boundaries. More work should be carried out to clarify the conductivity behavior. Nevertheless intercalating melanin-like species in V_2O_5 appears to be an efficient way to increase its conductivity. We have also carried out some experiments intercalating polyaniline into V_2O_5, which is known to increase the V_2O_5 conductivity,[4] and found very similar behavior in the conductivity changes to melanin intercalated to the V_2O_5 xerogel.

Conclusions

The structural and electronic properties as well as potential applications (electrochromism) of a new layered hybrid organic–inorganic material $(C_8H_9NO_2)_{0.02}V_2O_5\cdot1.5H_2O$ are described. IR, XRD as well as EPR studies showed that melanin is intercalated in the V_2O_5 matrix without strongly affecting the lamellar structure. The major effect is an increase in the interlayer spacing from 1.18 to 1.38 nm. 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 in the electrochromic response. The total charge involved in the redox process was practically unaffected in melanin intercalated V_2O_5 even after 60 cycles. By contrast, for $V_2O_5\cdot1.8H_2O$, the total charge decreased by a factor of 7 after 30 cycles. The conductivity is also affected by intercalation with an increase in dc conductivity at room temperature, from $1.1\times10^{-4}\ (\Omega\ \text{cm})^{-1}$ to $5.2\times10^{-3}\ (\Omega\ \text{cm})^{-1}$ and a decrease in the activation energy. Our results have indicated the formation of a new composite hybrid material, rather than a simple physical mixture of the starting reagents.

Acknowledgements

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