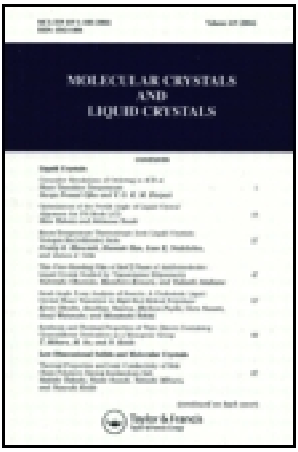

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SOL-GEL Synthesis and Characterization of TiO 2 and TiO 2 -V 2 O 5 Films for Electrode in Asymmetric Liquid Crystal Cells

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SOL-GEL Synthesis and Characterization of TiO_2 and TiO_2-V_2O_5 Films for Electrode in Asymmetric Liquid Crystal Cells

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Abstract Titania and titania/vanadia thin films were prepared via sol-gel process, starting from alcoholic solution of Ti $(OBu)_4$ for pure titania films and from Ti $(OBu)_4/VO(OPr^i)_3$ for mixed oxide films. The main requirements of these materials for applications in electrochromic devices were investigated, i.e. high charge capacity and electrochemical stability. Microstructural and electrochemical characterizations were carried out both on gels and films leading to the following results: titania films showed a high electro-chemical stability associated with a good charge capacity, whereas mixed oxide systems displayed a high stability again but a lower intercalation/deintercalation charges. The first electro-optic measurements were also performed for two films with different Ti:V atomic ratio, to check the interaction with liquid crystals in modified nematic liquid crystal cells: the cell containing films poorer in vanadia give some rectification effect, but they have a very complex dependence on the applied potential and very slow relaxation times; on the contrary films richer in vanadia exhibits very good response in the liquid crystal cells, compared with another mixed conductivity oxides.

Keywords: titania-vanadia films; sol-gel synthesis; electrochemical stability; charge intercalation; nematic liquid crystals

1. INTRODUCTION

The improvement of the counterelectrodes is among the major problem facing the developing technology of electrochromic devices [1,2]. The candidates materials for this purpose have to match the charge capacity of the electrochromic active electrode, but at the same time some others requirements are needed: fast charge transfer between the electrode and the electrolyte, easy processing, high reversibility and a good optical neutrality with respect to the intercalation-deintercalation process. Furthermore, other factors like costs and environmental impact must be considered to make the resulting devices suitable for large-scale technological applications.

Vanadium pentoxide was among the most studied materials for this purpose [3-6] but several problems of reversibility remain to be solved, and the optical gap changes of this material with respect to the intercalation–deintercalation process do not insure the best level of optical neutrality wanted for the use as counterelectrode.

On the other side films of titanium dioxide, mostly used for its photocatalytic properties [7,8], exhibits very good structural and electrochemical stability with respect to intercalation-deintercalation cycles, high transparency for the visible radiation, scarcely affected by the ionic charge insertion, and a good level of electronic conductivity, also important for the counterelectrodes. However, the charge capacity of this compound is not high enough [9] to match the one of the active electrode WO_3, still the most used.

The optimization of mixed film electrodes, containing both TiO2 and V_2O_5 could represent a promising approach to obtain a reasonable compromise between all the requirements needed for an electrochromic device [9-11].

In addition, another possible application has been discovered for these transparent materials having ionic and electronic conductivity, i.e. rectifying layers in liquid crystal based electrooptic devices. In fact, the deposition of a submicron layer of WO3 on one of the two transparent electrodes interfaced with a nematic liquid crystal (NLC) layer, strongly modifies the electrooptical response of such device, when analyzed between two crossed polarizers [12-14]. While the usual NLC cells (i.e. having purely electron conducting electrodes) exhibits an impulsive response, of doubled frequency with respect to the square wave electric stimulus [15,16], the modified cells (containing a layer of mixed conductivity material deposited on one electrode) show a rectified square-wave-like response, with the same frequency of the applied electric potential. An exhaustive explanation of such phenomenon is not yet completed, but it is reasonable to assume that charge redistribution occurs at the interfaces between the various layers, modifying the effective field acting on the NLC molecules [17]. It is worth to remark that such electro-optic rectification can be induced by small amounts of ionic charges, comparable to those naturally given by the protons always present in metal oxide thin films, like WO_3 [18-21] or V_2O_5 [22,23] when no special care is adopted to reduce their number [24]. For this new particular application no charge capacity matching is necessary; the most wanted requirements are the high transparency and long term stability of the films. For such reasons titanium oxide and TiO_2-V_2O_5 mixed systems are quite promising.

The sol-gel method was used to obtain films of various compositions [25,26]; in the present work a slightly different route has been tested and the synthesis parameters were modified to have the best wanted performances from the samples.

2. EXPERIMENTALS

2.1 Sol-gel synthesis

Titania sols were produced starting from titanium butoxide, $Ti(OBu)_4$ (Sigma Aldrich) allowed to react with acetic acid, CH_3COOH, in an equimolar ratio; after the weak exothermic reaction took place, a mixture of butanol and 2-propanol (1/2 molar ratio) was added. Hydrolysis reaction was carried out after a day by means of water acidified with HCl at pH = 0. Dip-coated films, both monolayer and multilayers, were deposited on ITO-glass (20 Ω/□, provided by Balzers) after a couple of hours and exsiccated at 120 °C up to one day. For titanium and vanadium mixed oxide the alkoxide route of preparation of thin film was used again, employing vanadium oxide iso-propoxide, $VO(OPr^i)_3$ (provided by ABCR), as a vanadium source. Samples with an atomic V/Ti ratio of 1/10 and 1/2 were prepared and underwent the previously described treatments.

2.2 Sample characterizations

DTA-TG were performed on a Netzsch STA 409 instrument, gel samples were heated up to 900 °C with a heating rate of 10°C/min.

XRD spectra were collected by using a Rigaku Dmax powder diffractometer, working in Bragg-Brentano configuration, employing as X-ray radiation the Cu K_α line, filtered by a graphite monochromator.

N_2 physisorption analysis were made in isothermal conditions with a

Micromeritics ASAP 2010 instrument, working on the sample at 77 K. The BET (Brunauer, Emmet and Teller) equation [27, 28] was applied for the evaluation of the specific surface area, whereas the BJH (Barret, Joyner, Halenda) method [27,29] was used for calculating the pore size distribution.

Cyclic voltammetry was performed by using the film sample as working electrode in an electrochemical cell where Li was the counterelectrode and reference electrode. 1M solution of $LiClO_4$ in propylene carbonate was used as electrolyte. Scan rates of 10mV/s, 20 mV/s and 50 mV/s were adopted for the voltammogramm.

2.3 NLC cells preparation

The ITO-coated glasses used as counter electrode in NLC cells, after careful cleaning in chromic mixtures and repeated cleansing with acetone, were covered with polyimmide and underwent a rubbing process, to insure a better planar alignment of the NLC molecules.

For the electrodes covered by titania or titania-vanadia, on the contrary, no surface treatment has been performed. The two plates were closed in the standard sandwich configuration [12] by using metallic clamps. The thickness of the cells was ensured by stripes of Mylar (8-36 μm), and the final value were deduced by analyzing the interference patterns in the transmittance spectrum of the empty cell, measured by a spectrophotometer.

The two cells here investigated had a measured thickness of 21 μm for the first one, containing a film with Ti:V = 10:1 atomic ratio, and 14 μm for the second, containing a more vanadia rich film (Ti:V ratio 2:1).

The introduction of the liquid crystal in the space enclosed between the asymmetric glass plates was made slowly to prevent any orientational alignment induced by the flow. The cell was filled with a *NLC* called *BL001* by Merck (former E7) with initial planar alignment. The range of temperature of existence of the nematic mesophase is from 20°C up to 61°C and the dielectric anisotropy $\Delta\varepsilon=\varepsilon_{//}-\varepsilon_{\perp}=+13.8$ (at 20°C).

Observations of the electro-optical response of the cells, between crossed polarizers, were made by a polarizing microscope Axioskop Pol (Zeiss). The cell was oriented in such a way to have maximum transmitted light. Videomicroscopy was performed by a 3CCD color camera TCM 112 (GDS Elettronica) connected to a PC equipped to visualize and to capture the images of the samples. The investigation of the transmitted light intensities was carried out by a large area silicon photodiode (Hamamatsu) mounted on the polarizing microscope. The electrical signal proportional to the light intensity was collected by a digital oscilloscope (Tektronics, Mod. TDS 784).

3. RESULTS

3.1 Structural and electrochemical characterizations

TiO_2 amorphous gels displayed, as measured by the physisorption of nitrogen at 77 K, a high specific surface area (about 300 m2/g) and an average pore size of 3 n (this value is in agreement with another titania gels [27]). Thermal analysis in air, as shown in the Fig. 1, revealed the crystallization of the gel at 400 °C leading to the anatase polymorph; a weak effect was also observed at around 700 °C, associable with the anatase–rutile transformation. XRD spectra confirmed this microstructural evolution, as shown in Fig. 2.

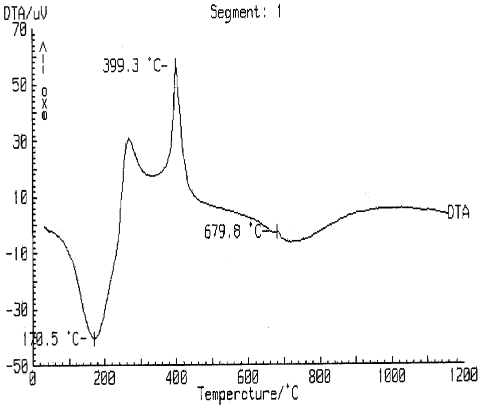

FIGURE 1 DTA curve for the gels of pure TiO$_2$ obtained via the route described in the text. Heating rate of 10 °C/min

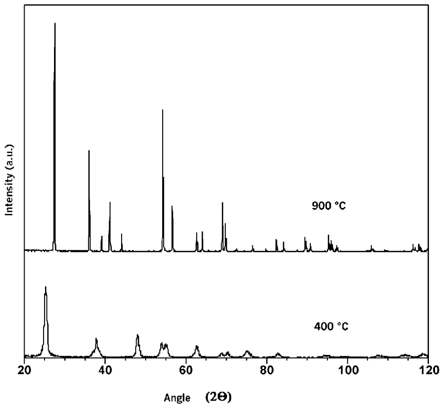

FIGURE 2 XRD of the pure titania gels at 400 °C and 900 °C, showing the structural evolution at increasing temperatures.

Mixed titania-vanadia compositions, labeled in the following after the metals atomic ratio, have been also synthesized and deposited onto the ITO-coated glasses.

Thermal analyses revealed a less intense exothermic effect due to the crystallization, also shifted at higher temperatures, as reported in Table 1:

Sample	T peak (°C)
TiO_2	400
Ti:V (10:1)	470
Ti:V (2:1)	565

TABLE 1 Crystallization temperatures of the gels.

Moreover, XRD spectra of 10:1 sample, fired at 400 °C, showed a weak crystallization of anatase-TiO2, whereas the 2:1 sample displayed a diffraction spectrum assignable to a metastable monoclinic- TiO_2 phase (see Fig.3); in both the cases no signal associated to a separate crystallization of vanadia was detected.

Only at higher temperatures, the presence of the two oxides, rutile-TiO_2 and V_2O_5, was detected. On the other hand, nitrogen physisorption analysis for the 2:1 sample, not annealed but only dried at 120 °C, reveals an isothermal curve close to that typical of non-porous solid. In fact the specific surface area is lower (about 50 m2/g), while the average pore size is slightly smaller (about 2 nm). A different charge capacity is found for the sample with higher vanadia content, but the change goes in the opposite way to that expected on the basis of the pure compounds properties: while the pure titania film showed a 13.1 mC/cm2, the mixed films having 2:1 ratio had a decreased capacity, down to 3.5 mC/ cm2.

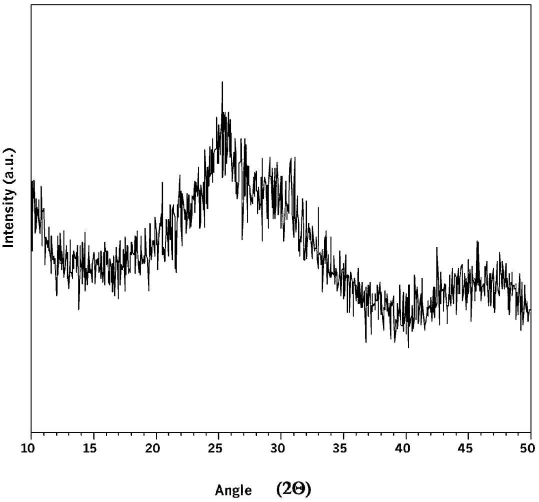

FIGURE 3 XRD of the 2:1 gel sample, after annealing at 400°C for 1 hour.

This unexpected findings can be understood by considering the microstructural modifications occurring for higher vanadium content: the preferred orientation of the void channels typical of anatase phase, found for pure titania gels, is destroyed in the mixed gels with higher vanadia content, in such a way to decrease the amount of foreign charges possible to accommodate in the structure. This highly disordered mixed phase is modified only at higher temperature, when separate crystallization start; indeed the exothermic crystallization peaks shift at higher temperatures as the vanadia fraction increase.

3.2 Electrooptical response

The schematic picture of the asymmetric NLC cells discussed in the present work are quite similar to those containing tungsten trioxide, described previously [12-14]. The investigation has been performed on two different compositions, the first having a Ti:V ratio of 10:1, the second one, more rich in vanadia, with a ratio of 2:1; in both cases the mixed oxide films were not annealed, but only dried up to 120 °C .

In the first sample several frequencies of the applied square wave potential were investigated, starting from 0.01 Hz up to 300 Hz, and for any frequency the dependence on the field amplitude was explored, for voltage values ranging from 0.5 V up to 7 V (modulus values of the square wave applied potential). The response times to the sign change of the square wave applied potential were at least of the order of the seconds, thus the lowest frequency investigations at 0.01 Hz were more significant, and are shown in Fig. 4.

For the lowest applied potentials the long time electrooptical response of the cell is practically not affected by the presence of the titania/vanadia film; in fact it is independent from the sign of the field, as usually observed in symmetric cells with purely electronic conductors inside [15,16]. The short time behavior is due to field gradient effects, but for low voltages it is also nearly symmetric. When the potential difference between the two electrodes increases, a more complex behavior can be observed.

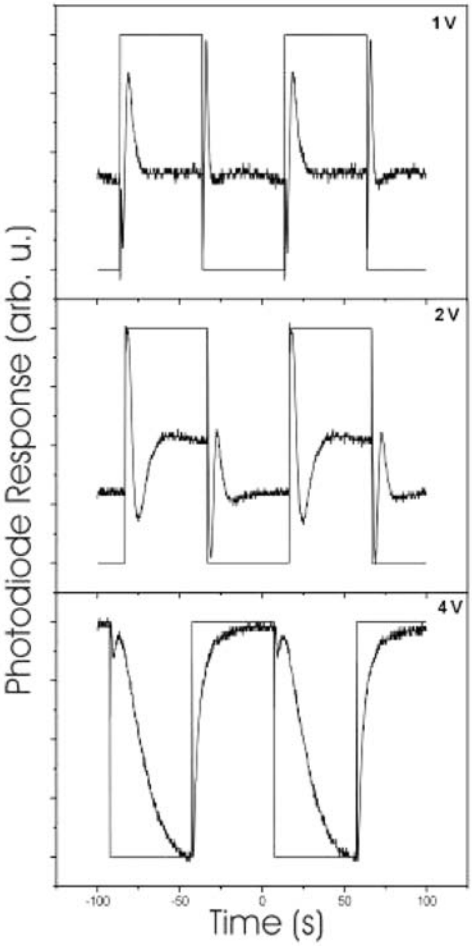

FIGURE 4 Transmitted light through a nematic liquid crystal cell between two crossed polarizers, having one electrode coated with a sol-gel deposited film with Ti:V ratio of 10:1. A 0.01 Hz square wave is applied and the increased values of voltage amplitude are indicated near the various patterns. The units of photodiode response are arbitrary, but the scale is the same for all the represented patterns.

The time dependent oscillations of the electrooptical response are due to time dependent variations of refractive index in the NLC layer, inducing typical thin slab interference patterns, not perfectly averaged because of the finite wavelength range of the light source. The long time response changes depending on the amplitude of the applied potential: for the highest value of 5V (10 volts peak-to-peak) a remarkable asymmetry of the photodiode response is obtained, but the very long relaxation times make this kind of material not promising for the most investigated display applications.

It should be noted that the viscoelastic response of the liquid crystal generates characteristic relaxation times much shorter than those observed in Fig. 4. Thus, the longer times we observe for the electrooptical response have to be ascribed to the inner charge redistribution dynamics in the metal oxide film and at the interfaces, determining the effective field experienced by the NLC molecules.

For the sample with higher vanadia content, atomic ratio Ti:V=2: 1, a quite different and more simple behavior has been observed: the relaxation times appear much faster, and a very good rectifying effect is obtained, not strongly dependent on the applied potential. The electrooptic response to a 1 Hz square wave potential, for increasing voltages, can be seen in Fig. 5.

A satisfactory pattern is obtained or 1 V applied potential, and it does not change very much for higher fields. The rectifying behavior can be easily observed even for higher frequencies (about 10 Hz), more interesting for the applications. At frequencies above 100 Hz the electrooptic response becomes always triangular, for all the cell samples, as well as for the previously investigated WO_3-containing cells [13] and reduces its amplitude.

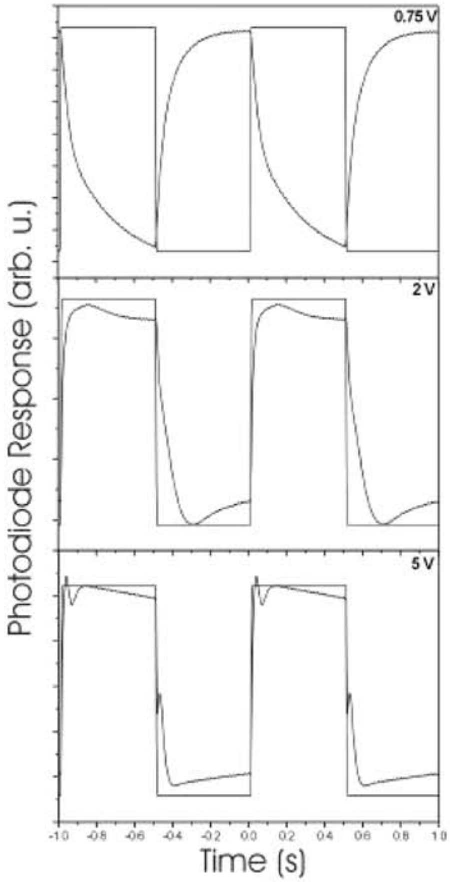

FIGURE 5 Same experimental setting as in Fig. 4, but for a NLC cell containing a mixed titania-vanadia film of atomic ratio 2:1. Three patterns corresponding to different voltage amplitude are shown, for the same square wave frequency of 1 Hz. The scale of the detector is the same.

4. CONCLUSIONS

The change of composition in mixed system titania-vanadia provide good electrochemical stability, but poor charge capacity, when the vanadia content is increased up to an atomic ratio Ti:V =2:1, depending from microstructural modifications. In fact the holes allowing a good intercalation of foreign cations in pure titania and low vanadia concentration systems, lose their long-range direction characters due to synthesis methods. Perspectives of improvements have been tested, however, even for higher vanadia concentration systems, by applying modified synthesis conditions, i.e. increasing the pH of the water used for the hydrolysis process. The charge capacity however, do not constitute a problem for the application concerning NLC; in fact the rectifying electrooptical response, for low vanadia compositions, is found only after long relaxation times, and its value appears modulated in a very complex way by the applied potential value. Further studies, combining other electrooptical and electrochemical measurements, are in program. In any case these low vanadia systems are not interesting for potential display applications.

On the contrary, the higher vanadia composition (ratio 2:1) shows a good and faster electrooptical response, even at low applied voltages and for frequencies high enough to be interesting for the applications.

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References

1) C.G. Granqvist, "Handbook of Inorganic Electrochromic Materials", Elsevier, Amsterdam (1995), 1.
2) C.M. Lampert, Solar Energy Materials, **11** (1984), 1.
3) M. Nabavi, S. Doeuff, C. Sanchez, J. Livage, Mater. Sci. Eng. **3** (1989), 203.
4) M. Nabavi, C. Sanchez and J. Livage, Philos. Mag. B **63** (1991), 941
5) J. Livage, G. Guzman, F. Beteille and E. Davidson, J. Sol-Gel Sci. and Technol. **8** (1997), 857
6) A. Talledo, C. G. Granqvist, J. Appl. Phys. **77** (1995), 4655
7) R. Campostrini, G. Carturan, L. Palmisano, M. Schiavello and A. Sclafani, Mater. Chem. & Phys. **38** (1994), 277
8) M.P. Cantão, J.I. Cisneros and R.M. Torresi, Thin Solid Films **259** (1995), 70
9) A. Surca, S. Bencic, B. Orel, B. Pihlar, Electrochim. Acta, **44** (1999), 3075.
10) A. Davies, R.J. Hobson, M. J. Hudson, W.J. Macklin, R.J. Neat, J. Mater. Chem., **6** (1996), 49.
11) M.S. Burdis, Thin Solid Films **311** (1997), 286
12) G. Strangi, D. E. Lucchetta, E. Cazzanelli, N. Scaramuzza, C. Versace and R. Bartolino, Appl. Phys. Lett. **4** (1999), 534
13) E. Cazzanelli, N. Scaramuzza, G. Strangi, C. Versace, A. Pennisi and F. Simone, Electrochimica Acta **44** (1999), 3101
14) G. Strangi, N. Scaramuzza, C. Versace, E. Cazzanelli, F. Simone, A. Pennisi and R. Bartolino, Ionics, **3 & 4** (1999), 275.
15) P. G. de Gennes, J. Prost: "The Physics of Liquid Crystals", Oxford University Press 1993.
16) L. M. Blinov, V. G. Chigrinov, Electrooptic effects in Liquid Crystal Materials, Springer – Verlag. New York, 1994.
17) G. Strangi, E. Cazzanelli, N. Scaramuzza, C.Versace and R.Bartolino, Phys. Rev. E **62** (2000), 2263
18) C. Bohnke, O. Bohnke, Solid State Ionics **39** (1990), 195

19) F. Rauch, W. Wagner, K. Bange, Nucl. Instr. and Meth. **B 42** (1989), 264

20) O. Bohnke, G. Frand, M. Fromm, J. Weber, O. Greim, Appl. Surf. Science **93** (1996), 45

21) J. Vondrak, J. Bludska, Solid State Ionics **68** (1994), 317

22) A.Gorenstein, A. Laurenco, F.D. Origo, S. Passerini, W.H. Smyrl, M.C.A. Fantini and M. Tabacknics; Proc. ECS Symposium "Electrochromic Materials and Their Application III, 1996, S. Antonio,TX, USA, n. 664, p. 206

23) I.C. Faria, M. Kleinke, A. Gorenstein, M.C.A. Fantini, M.Tabacnicks, C. Salvadori; Proc. ECS Symposium "Electrochromic Materials and Their Application III, 1996, S. Antonio,TX, USA, n. 654, p. 79

24) M. Green, A. Travlos, Philos. Mag**. B 51** (1985), 501

25) M.A. Aegerter, C.O. Avellaneda, A. Pawlicka, M. Atik, J. Sol-Gel Sci. Technol., **8** (1997), 689.

26) O. Lev, Z. Wu, S. Bharathi, V. Glezer, A. Modestov, J. Gun, L. Rabinovich, S. Sampath, Chem. Mater. **9** (1997), 2354.

27) F. Rouquerol, J. Rouquerol, K. Sing, “Adsorption by Powders & Porous Solids”, Academic Press, San Diego, 1999

28) S. Brunauer, P.H. Emmett, E. Teller, J.Am. Chem. Soc. **60** (1938), 309

29) E.P. Barrett, L.G. Joyner, P.H. Halenda, J.Am. Chem. Soc. **73** (1951), 373