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Guillaume Salek, Brice Bellanger, Issam Mjejri, Manuel Gaudon, Aline Rougier. Polyol synthesis of Ti-V₂O₅ nanoparticles and their use as electrochromic films. *Inorganic Chemistry*, 2016, 55 (19), pp.9838 - 9847. 10.1021/acs.inorgchem.6b01662 . hal-01391268

HAL Id: hal-01391268

<https://hal.science/hal-01391268>

Submitted on 8 Feb 2021

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Polyol synthesis of Ti-doped V_2O_5 nanoparticles and their use as electrochromic films.

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KEYWORDS. Pseudobrookite, Phase Diagram, X-Ray Diffraction, Pigment.

ABSTRACT: In this publication is shown the synthesis of Ti-doped di-vanadium pentoxide from polyol process. Very high Ti concentration (near 10 mol% of the total metallic content) can be inserted in vanadium oxide thanks to the used synthesis route thank to the obtaining of nanometric crystallites. X-ray diffraction patterns were refined and the insertion of the titanium ions inside the free pentacoordinated sites in opposition to the vanadium square pyramidal sites. This crystal organization was shown in good agreement to the *ab-initio* positioning performed from valence calculation. The NPs of Ti-doped V_2O_5 compounds were tested as electrochromic materials. Films elaborated from dip-coating process from oxide particles suspensions were shown to exhibit three distinct colorations during the redox cycling (with lithium-based electrolyte). These colors are associated with three distinct oxidation numbers for the vanadium ions: +III (blue), +IV (green) and +V (orange). The morphology of the films was shown to drastically impact the capacity and the stability of the electrochromic performances.

Introduction. Electrochromism is a term used for a material exhibiting a reversible color change with an applied voltage; the first description of the phenomenon can be attributed to Platt, in 1969 [1]. Soon after, the idea to use electrochromic materials in devices working as electrochemical batteries was proposed [2]. Complete electrochromic devices built from stacking of different layers (active cathode but also electrolyte, counter electrode and Transparent Conductive Oxides (TCOs) used as carrier collectors) were developed [3]. Smart windows represent one key application. As illustration, Saint Gobain research has developed tunable transmission windows for buildings via the SageGlass® sub-company [4]. Electrochromic glasses can also be used for opening roofs of rear-view mirrors in some luxurious cars [5-6], as well as smart displays [7]. The inorganic electrochromic oxides can be divided in three classes: cathode materials which are colored in the reductive state and bleached in the oxidative state, in opposition the anodic materials are colored in oxidative state, and finally, the permanent color materials which exhibit a different color between the oxidized and the reduced states [8]. Among this latter category, vanadium oxides are of growing interest. Indeed, per analogy with the colors of the free ion in aqueous solution (forming with *aqua* ligands octahedral complexes) vanadium could exhibit three different oxidation numbers: +V, +IV and +III leading to three colorations for vanadium oxide thin films: respectively orange, green and blue for +V, +IV and +III oxidation numbers. The shift in the oxidation number can be well controlled starting from the vanadium pentoxide thin films thanks to the intercalation-

deintercalation of the alkaline cations within the electrolyte (Li^+ as well as Na^+ , typically). In the **Figure 1**, is reported the crystalline organization of the V_2O_5 oxide, with *Pmmn* orthorhombic space group, which can be described as an alternation of planes built by edge-sharing square pyramidal sites. These penta-coordinated sites can be described as issued from the drastic distortion along the *c*-axis of the parent octahedral site cages, the distortion being also associated with the metal cation decentering. One of the consequences of this distortion is the disappearance of the sixth oxygen anions from the first coordination sphere.

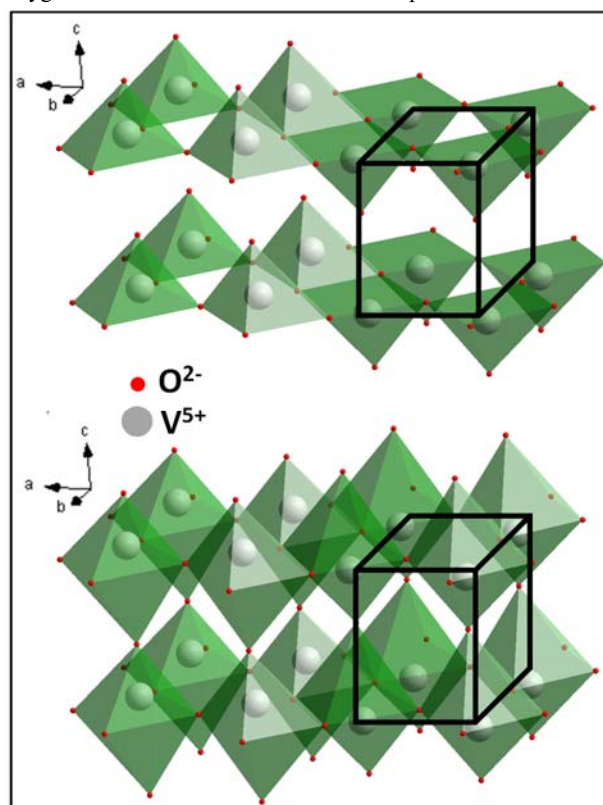


Figure 1: Representation of the vanadium pentoxide. Standard representation considering square pyramidal sites for the vanadium metal site (top side); representation built from the parent octahedral sites (bottom side).

Herein, we propose to study the electrochromic behavior of Ti-doped V_2O_5 films. The films are dip-coated using a suspension of Nano-Particles (NPs) of Ti-doped V_2O_5 elaborated by polyol synthesis route [refs]. The first part describes the synthesis and the

physico-chemical characterizations of the Ti-doped vanadium pentoxide NPs. Especially, the accurate characterization of the titanium insertion inside the matrix crystallographic network is performed combining TEM, chemical titration and X-ray diffraction pattern refinement. In a second part, films of various morphologies (obtained without or with an additional thermal post-treatment) are compared to underline the impact of the elaboration process on the electrochromic performances.

Experimental. In a first step, titanium-doped vanadylglycolate salt (Ti:VEG) was obtained by a coprecipitation process. Ti:VEG coprecipitation was based on previous works reported in literature on VEG precipitation [refs]; the polyol process is commonly considered as an energy efficient and environmentally benign process, also allowing the preparation of large quantity of powders. Titanium oxy-chloride (TiOCl_2 -Aldrich) and ammonium-metavanadate (NH_4VO_3 -Aldrich) were added in a round flask equipped with a reflux column and dissolved in various proportions (with Ti/(Ti+V) ratio varying between 0 and 30 mol%) in ethylene glycol ($\text{H}_6\text{C}_2\text{O}_2$). The total cation metal concentration in DEG was 0.1 M. The temperature of the reactive medium was increased slowly up to 160°C under continuous stirring. After the complete dissolution of the precursor salt occurring at about 120°C , the reflux was let operated at 160°C during 1 hr to induce the complete coprecipitation. The precipitate was then separated by centrifugation and washed several times with ethanol. The titanium-doped vanadium oxides were obtained after annealing at 500°C , 10 hrs under air atmosphere.

The X-ray powder diffraction experiments were carried out on a Bragg Nentano diffractometer with copper source ($\text{Cu-K}\alpha$ radiation with $\lambda = 1.5432 \text{ \AA}$ wavelength). All profiles and structure refinements were carried out using the Fullprof suite package [refs].

For Scanning Electron Microscopy (SEM) analysis, we used a Field Emissive Gun microscope (FEG-SEM) in order to characterize the crystallite sizes on which the spatial resolution can be estimated about 1 nm. Transmission Electron Microscopy (TEM) was performed on a TECNAI F20 equipment with a Field Emissive Gun (FEG), operating at 200 kV and with a point resolution of 0.24 nm. Film thickness was determined using an interferential profiler XXXXXXXX.

ICP measurements were made to determine V/(V+Ti) molar ratio of the $\text{Ti}:\text{V}_2\text{O}_5$ powder samples. Measurements were carried out on aqueous solutions obtained after complete dissolution of the powder thanks to HCl with high purity using the Varian ICP-OES 720ES apparatus.

Voltamperometric studies are made with three electrodes cell using thin films as working electrode (Pt as counter electrode) using 0.3 M LiTFSI – BMITFSI (lithium-based solution) electrolyte to characterize the following electrochemical reaction: $x\text{Li}^+ + \text{V}_2\text{O}_5 \rightarrow \text{Li}_x\text{V}_2\text{O}_5$. The studies were conducted with the voltage ranging from 1 V to -0.5 V with 10 mV/s velocity.

Thin films transmission on glass substrates were recorded from 200 to 800 nm on a Cary 17 spectrophotometer using an integration sphere (spectral resolution: 1 nm and band length: 2 nm). The thin films were placed in our apparatus in order to cut the light source just before the integration sphere. Diffuse and specular transmissions are hence both collected.

Results and discussion.

Ti :V₂O₅ powder: synthesis and characterization

The first study has dealt with the structural characterization (using X-ray powder diffraction technique) of the Ti:VEG obtained by

coprecipitation (**Figure 2**). Up to 15 mol% of titanium introduced in the ethylene glycol bath, patterns with all the peaks which can be indexed in the VEG phase were obtained whereas the product obtained with 30 mol% of titanium is clearly amorphous. The increase of the titanium concentration induces a clear decrease of the average crystallite size of the precipitated glycolate which can be followed by the significant enlarging of the diffraction peak widths. The evolution of the crystallite size morphology seems indicating the efficient introduction of the titanium dopant inside the vanadium ethyleneglycolate structure. On the contrary, the peak position is not significantly impacted versus the Ti concentration.

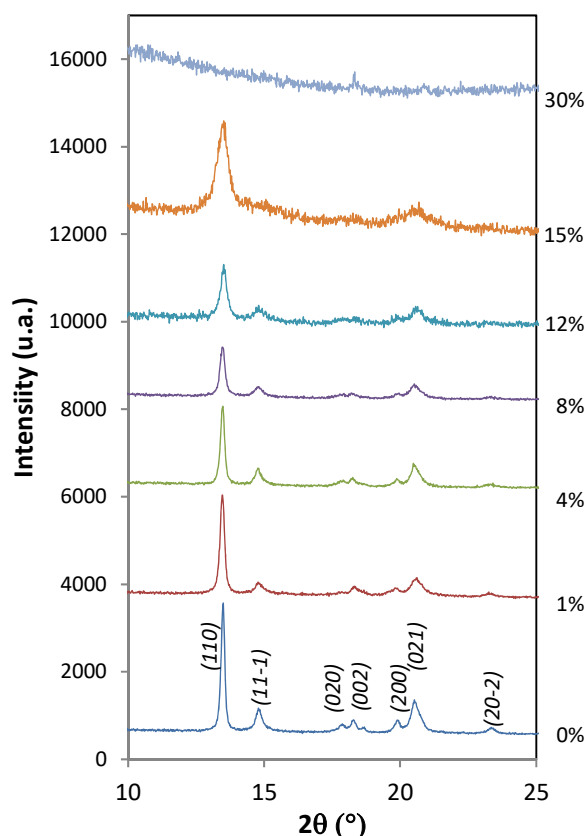


Figure 2: X-ray diffraction patterns of the precipitate (Ti/VEG) obtained from polyol synthesis for various Ti/(V+Ti) mol%.

The products obtained for the annealing at 500°C under air of the Ti:VEG were then analyzed using X-ray diffraction (**Figure 3**). Up to 15 mol% of titanium introduced in the ethylene glycol bath, patterns with all peaks which can be indexed in the V_2O_5 phase (complete indexation for the un-doped compound was reported in the **Figure 3**) were obtained whereas the product obtained with 30 mol% of titanium is clearly different. The latter was not indexed, none JCPDS data corresponding to the so unidentified oxide or oxide mixtures. The introduction of titanium ions induces a slight decrease of the average crystallite size of the $\text{Ti}:\text{V}_2\text{O}_5$ oxide in comparison with the un-doped compound.

At this stage, ICP measurements were performed on the various $\text{Ti}:\text{V}_2\text{O}_5$ compounds to confirm the Ti incorporation in V_2O_5 structure. In the **Figure 4** the correlation curve describing the evolution of the efficiently introduced Ti molar ratio inside the vanadium oxide versus the Ti molar ratio inside the ethylene glycol bath is reported. The evolution can be fitted with a 2nd

order polynomial function what can be ascribed as the signature of two different regimes for the efficiency of the precipitation of V and Ti ions versus their own concentration into the synthesis bath: the efficiency of V precipitation is less positively correlated to its concentration than for Ti.

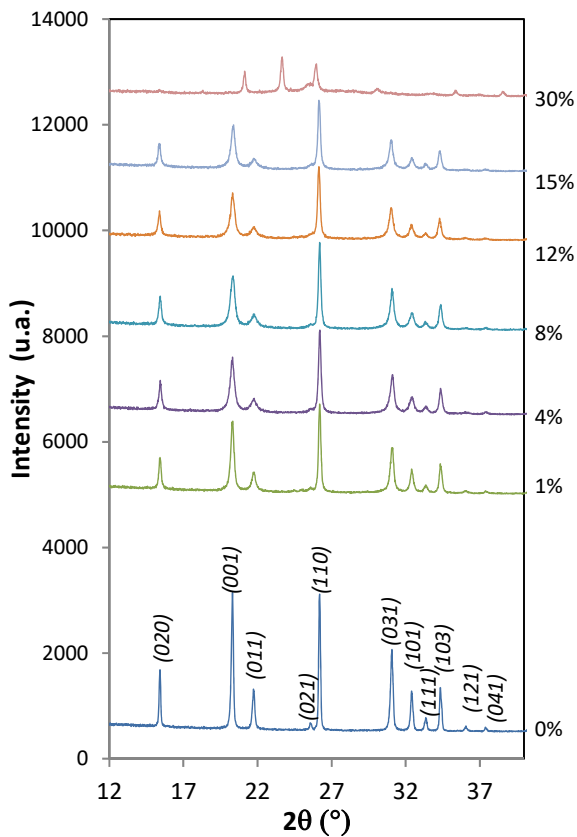


Figure 3: X-ray diffraction patterns of the Ti/V₂O₅ oxides obtained after a thermal treatment at 500°C under air.

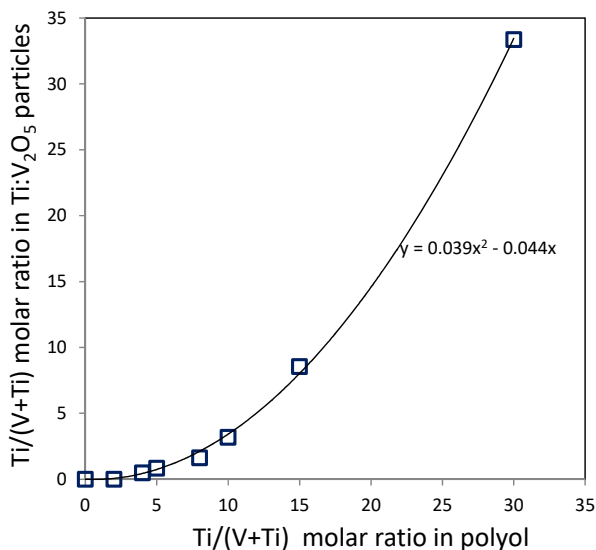


Figure 4: Ti/(V+Ti) molar ratio analyzed in Ti:V₂O₅ oxides versus the Ti/(V+Ti) molar ratio introduced in the ethylene-glycol bath.

Next, the undoped compound and the 8.5 mol% Ti-doped compound (efficient molar ratio introduced in the oxide) are compared. TEM images on the un-doped and the doped V₂O₅ compound are reported in the **Figure 5**. The photographs show the oxides are with submicronic crystallite aggregated in packs. In good agreement with the X-ray diffraction width, an average crystallite size bigger for the un-doped compound than for the Ti-doped one is observed.

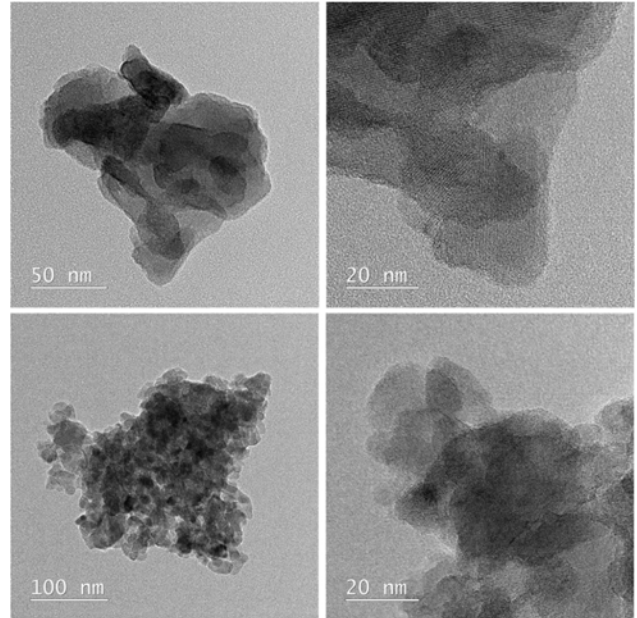


Figure 5: TEM images on un-doped V₂O₅ compound (left side) and the 5 mol% Ti: V₂O₅ compound (right side).

Full pattern matching was performed in order to extract the cell parameters of all the compounds. The various cell parameters of the Ti:V₂O₅ compounds are plotted versus Ti efficient molar ratio. The evolution of the cell parameters versus the titanium concentration in substitution for vanadium is complex as shown in the **Figure 6**; it does not follow a trivial Vegard law. Indeed, the evolution is different for the three orthorhombic unit-cell parameters. For the *a* unit-cell parameter, an asymptotic increase is observed, a linear increase is found for the *b* unit-cell parameter while a more complex evolution: bell shape curve is shown for the *c* unit-cell parameter. The complex steric impact of the substitution of vanadium for titanium can be explained by the aliovalent character of the substitution. The lack of one electron consequent to the replacement of vanadium (V) for the titanium (IV) ion makes the cell evolution complex and one should not reduce the analysis to a comparison of the respective ionic radii: the Ti(IV) ions are bigger than the V(V) ions with respectively in 5-coordinated sites Shannon radii equal to 0.51 and 0.46 Å [ref]. Indeed, this substitution is accompanied by the creation of oxygen vacancies (for electroneutrality conservation) as well as V-O bond length variations near the Ti doping ions due to the local mismatch between the dopant and matrix cation charges. Whatever the monotonic variations of the three cell parameters versus the Ti molar concentration, well show its introduction into the crystal bulk.

To complete the structural studies, Rietveld refinements were performed on the 8.5 mol% Ti:V₂O₅ compound. In the **Figure 7** refinements obtained using four models are compared: a) Full pattern matching using an isotropic peak profile function (Caglioti function); b) Full pattern matching using an anisotropic peak

profile function (function 7) with a crystallographic direction corresponding to (110) axis; c) Rietveld refinement with fixed composition respecting ICP analyses and a single refined position for both Ti and V cations; d) Rietveld refinement with fixed composition in respect to the ICP analyses but with two distinct refined positions for respectively Ti and V cations. It can be noted

that the isotropic displacement factors were not refined and just fixed to standard values equal 0.5 \AA^2 for all the cations et 1 \AA^2 for all the anions. By comparison of the results obtained with the two full-pattern matching, the crystallite shapes are clearly anisotropic with an elongation along the (110) crystallographic axis. The use of anisotropic model allows the significant decrease of the

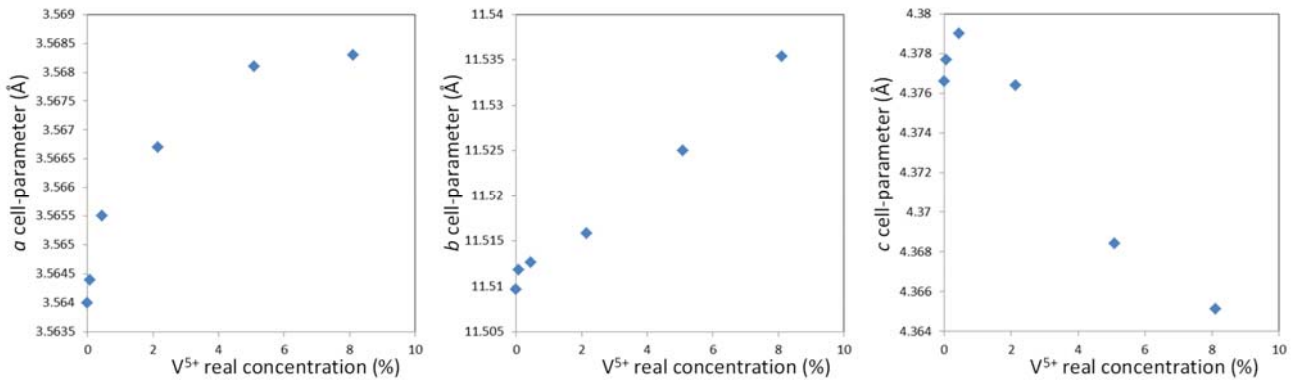


Figure 6: Evolution of the orthorhombic unit-cell parameters of Ti-doped vanadium pentoxide versus the titanium concentration.

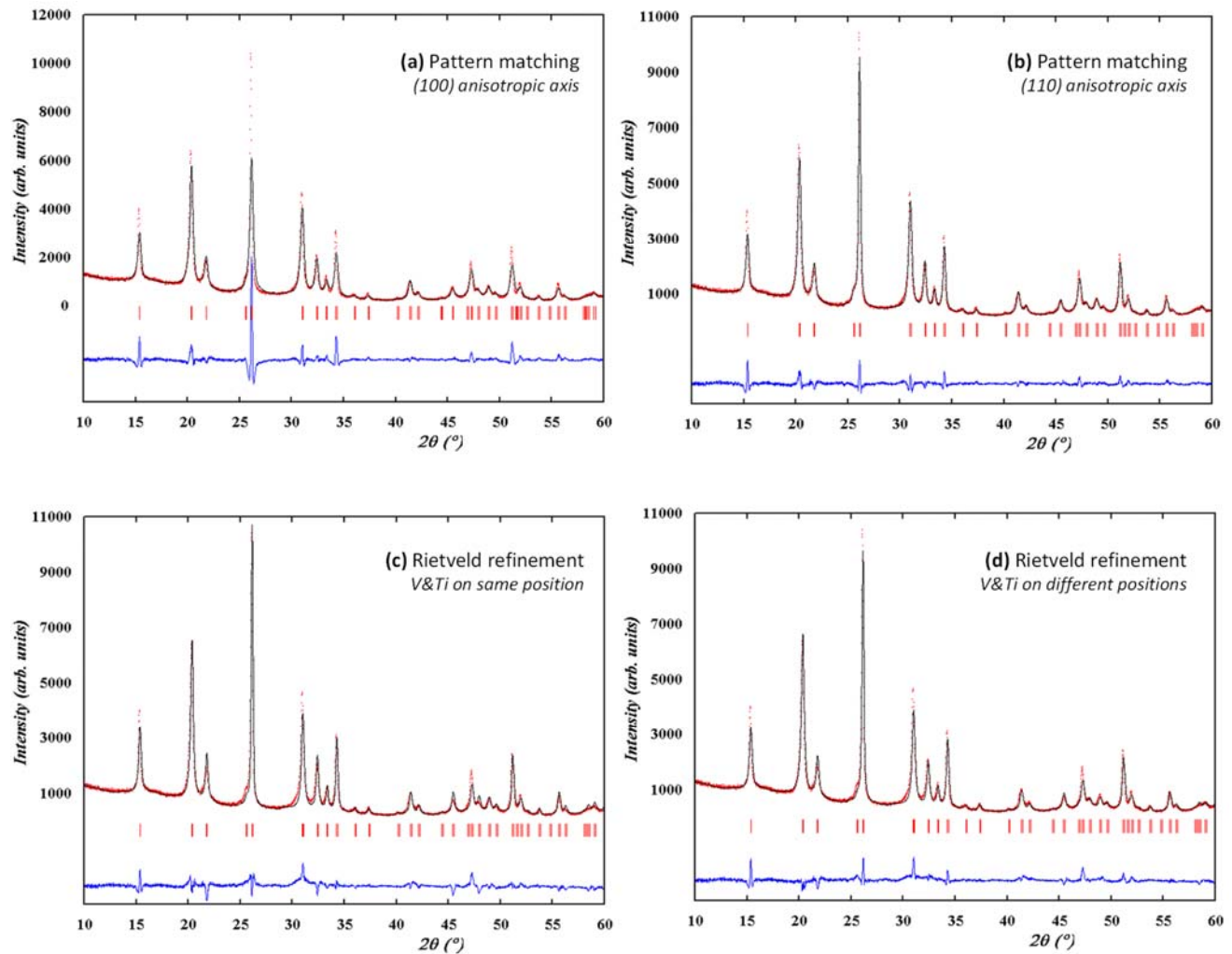


Figure 7: (a) Full pattern matching using isotropic peak profile function; (b) Full pattern matching using an anisotropic peak profile function along (110) axis; (c) Rietveld refinement with one single refined position for both Ti and V cations; (d) Rietveld refinement with two distinct refined positions for respectively Ti and V cations.

R_p , R_{wp} and R_{exp} correlation factors for isotropic models are found equal to 9.4, 13.5 and 3.9 whereas for the (110) anisotropic model these three factors are respectively found equal to 5.7, 7.2 and 3.8. The Rietveld refinements with (110) anisotropic peak profile function and with Ti and V ions both fixed on a same crystallographic position or let free to be placed on two different positions are then compared. The possibility to let differentiate vanadium and titanium site positioning improves the fitting between experimental and calculated spectra. It was assumed for the second refinement that Ti(IV) ions remain on $4f$ Wyckoff position: *i.e.* with $(x, \frac{1}{4}, z)$ coordinates. The R_{Bragg} factor decreases from 15 to 11.1 when only the additional x and z parameters for Ti(IV) ion positioning were added to the fit. The titanium position is located near the center of the penta-coordinated square pyramids sharing a same square plane but on the opposite c axis direction of the vanadium pyramids. The Ti and V positions are drawn in the **Figure 8**, as all the positions are occupied. These positions are diverging especially according to the z coordinate: the x , y and z calculated values for V^{5+} ions and Ti^{4+} ions are respectively 0.1010(2); $\frac{1}{4}$; 0.8862(4) and 0.1070(2); $\frac{1}{4}$; 0.0730(33). Obviously only 8 % of the titanium positions and 92 % of the vanadium ones are efficiently occupied and, from the very short distances between these two transition metal positions, it can be reasonably assumed that in a single octahedral cage (constituted of the two square base sharing pyramids), either the titanium occupies its position either the vanadium occupies its own position.

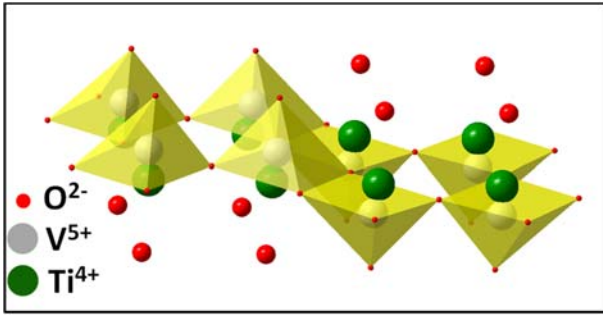


Figure 8: Representation of the vanadium pentoxide showing the Ti^{4+} doping ion positions.

The position of the Ti doping ions which is calculated from X-ray pattern refinements can be explained by the larger volume of the Ti square base pyramids, in agreement with the larger ionic radius of Ti^{4+} ion in comparison with the V^{5+} radius. It can also be noted that the relatively high solubility limit reached for the Ti^{4+} doping ions, despite its aliovalent character and the mismatch of its ionic radius with the V^{5+} host matrix cation, could be explained by the occurrence of these empty interstitial square pyramids in the divanadium pentoxide crystallographic network. To confirm this hypothesis, the valences of the vanadium and titanium ions are *ab-initio* calculated depending on their positioning from Brown and Altermatt, formulae:

$$V_i = \sum_j s_{ij} = \sum_j \exp\left(\frac{r'_o - r_{ij}}{B}\right),$$

with V_i the valence of i cation, B a constant, with length dimension, and fixed to 0.37 Å, r'_o a tabulated constant depending on the j anion - i cation pairs, r_{ij} the j anion - i cation bond length.

The results of the *ab-initio* positioning from valence calculations is presented in the **Figure 9**. The calculation was performed from all the oxygen anion refined positions and considering $(0.1, \frac{1}{4}, z)$ as set of coordinates for V^{5+} or Ti^{4+} ions. In our representation the

$z = 0$ coordinate corresponds to the square plane height of the pyramid, z positive values correspond to a positioning inside the small volume pyramids (the ones occupied by V^{5+} ions in V_2O_5) and negative z values correspond to a positioning in the opposite side penta-coordinated sites (large volume pyramids). Assuming that the valence mismatch between experimental values extracted from atomic positions and the theoretical value (IV or V oxidation number for Ti and V ions, respectively) can be considered as relative to the position potential, it is shown that double-well potential curve can be plotted for V ions, and single-well potential curve for Ti ions. For vanadium ions, the expected position deduced from the *ab-initio* calculation is about +0.07 considering the settlement of the small square pyramidal site (the other equilibrium position in the large pyramidal site leads to very distributed V-O bonds in term of length, what does not correspond to a realistic positioning). For titanium ions, the single-well potential never is null, what is the signature of the occurrence of a valence mismatch and so the creation of associated constrains whatever the titanium ion positioning. This phenomenon is also the signature of the too big Ti^{4+} ionic radius. The optimal value so corresponds to the single-well curve minimum, *i.e.* for a z coordinate value about -0.11. Hence, the expected positions for both transition metals are in perfect agreement with the experimental values validating *de facto* our consideration of a position potential which is proportional to the valence mismatch.

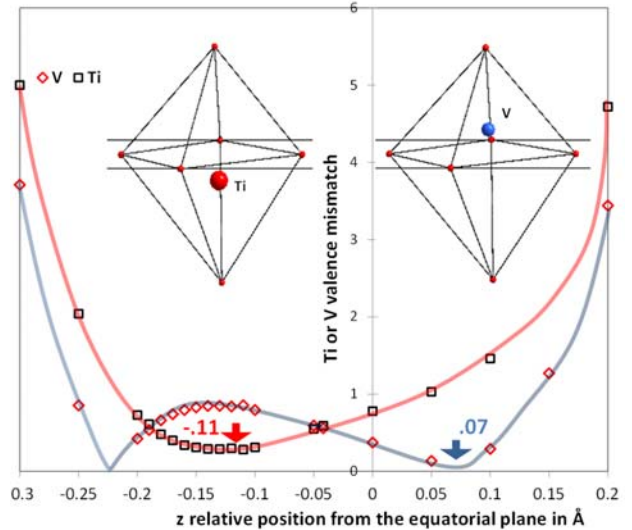


Figure 9: Ti and V valence mismatch between their calculated valence (from atomic positions) and their theoretical oxidation number versus the z positioning of the cations inside the V_2O_5 crystal network.

From Ti:V₂O₅ powder to electrochromic films

The Ti:V₂O₅ powder can be applied as the working electrode in electrochromic devices, as thick film for displays or thin films for smart windows applications, *i.e.* for reflective or transmission systems. Our general scheme is not to propose an exhaustive study on the optimization of the chromic contrast versus cyclic voltammetry of various electrochromic layers, but to demonstrate as “proof of concept” the possibility to use the sub-micronic Ti-doped V₂O₅ powder prepared by polyol mediated synthesis as active electrochromic base in translucent inorganic films. Numerous studies in literature have clearly shown that the device performance is related to the structural properties and morphological features of the film, which in turn dependant on the deposition technique as well as the preparative parameters [refs].

Herein, the work is focused on the elaboration of purely inorganic thin film (with high transmission) from the as-prepared powder by dip-coating what represents a real difficulty in comparison with the obtaining of thick opaque films (by doctor blade process, screen printing, painting or another technique). The first difficulty is the obtaining of stable suspensions of as-prepared Ti:V₂O₅ submicronic particles. Isopropanol was chosen as suspension medium, since it exhibits a low boiling point as well as a low surface tension and so a high wettability. Various powder weight fractions (wt. %) were tested, between 5 and 20 wt.%. The dip-coating speed was fixed to 0.7 cm.s⁻¹, 3 cm² (1 cm × 3 cm) tin oxide (ITO) coated alumino-silica glasses were used as substrates. Despite, the obtaining of stable suspension, the oxide layers are of high roughness coefficient, revealing the occurrence of some agglomerates into the suspensions; furthermore, after drying the adhesion with the substrate is very poor. The idea was then to dissolve the raw Ti:VEG salts previously obtained in isopropanol to get a mineral binder with same main transition metal than the Ti:V₂O₅ powder in order to not mask the electrochromic properties. To achieve the dissolution of Ti-doped VEG salt into propanol, few mL of hydrogen peroxide (H₂O₂) was added to the suspension. As illustration, solution of propanol with 20 g.L⁻¹ of Ti:VEG salt and about 1 g.L⁻¹ of hydrogen peroxide can be used as suspension medium (SM solution) for the dispersion of the Ti:V₂O₅ powder. “Green films” obtained directly after drying in an oven (about 100°C) from the pure SM solution (“binder films”) and from a suspension prepared with 5 wt% of Ti:V₂O₅ powder dispersed in the SM solution (“composite films”) are of high transmission in the visible range, perfectly homogeneous at the millimeter scale, and with a quite good adhesion on the substrate. SEM top-surface images of both these two films are reported in the **Figure 10 (a & c)**.

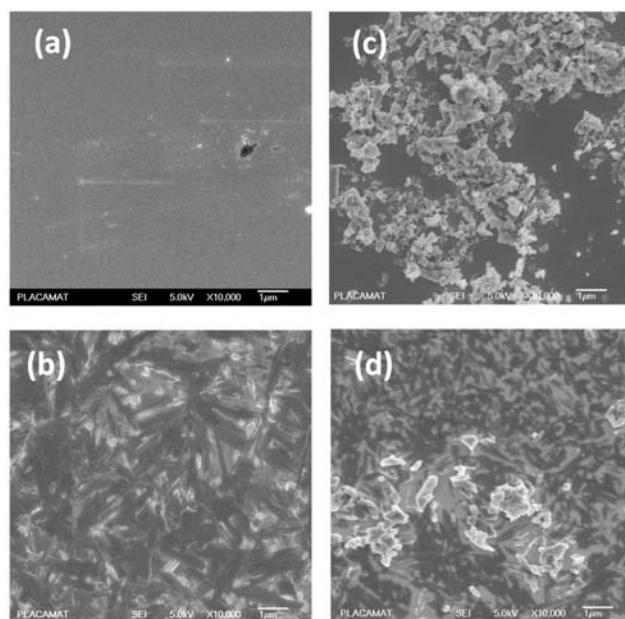


Figure 10: Top-surface photographs of green/350°C-annealed binder films obtained from a pure SM solution (a)/(b), and composite films issued from suspension of Ti:V₂O₅ powder dispersed in SM solution (c)/(d).

Thin films prepared from pure SM solution are very thin and transparent with an olive hue whereas films prepared from Ti:V₂O₅ suspensions (composite films) are translucent and with

an orange coloration. Thickness measurements with the optical profiler leads to 50 nm about for the binder films and 90 nm about for the composite films issued from Ti:V₂O₅ suspensions. For the latter, the thickness deviation is very large. Indeed, the photograph of the **Figure 10c** shows that the dispersion of the powder is not yet optimized since the top surfaces SEM photographs show di-vanadium oxide particles agglomeration. Nevertheless, the satisfying adhesion allows cyclic voltammetry measurements vs lithium. In a first step, the voltamperograms obtained on the two green films: binder films and composite films, are compared (**Figure 11**).

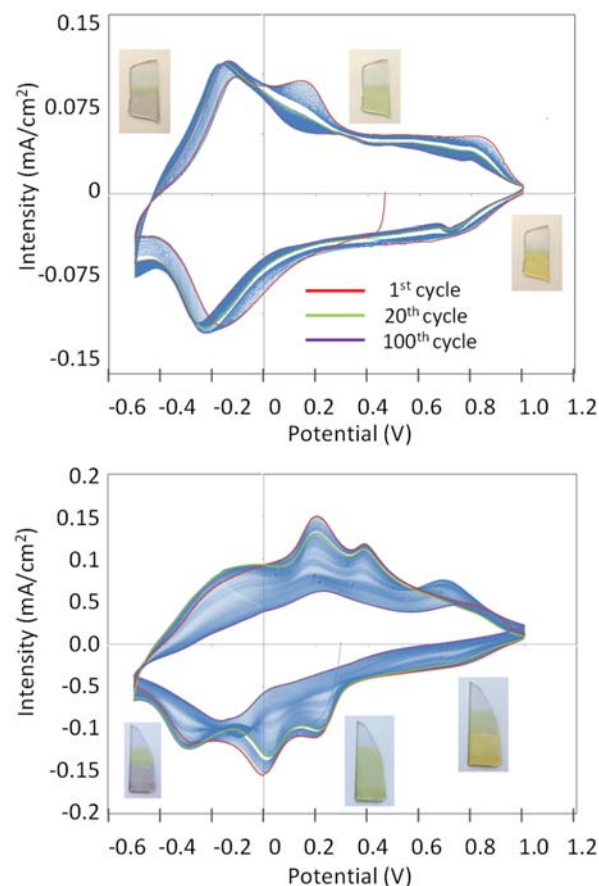


Figure 11: Voltamperogram of a green films obtained from a pure SM solution (top side), a suspension of Ti:V₂O₅ powder dispersed in SM solution (bottom side)

In the first case, the film is initially olive green-colored and amorphous; it exhibits a blue coloration at -0.5 V and an orange coloration at +1 V. Per analogy with the colours of the V³⁺, V⁴⁺ and V⁵⁺ in aqueous solutions *i.e.* in an octahedral ligand field with *aqua* ligands with a very near effect of the oxygen ligand field around the vanadium ions into VO_x oxide networks, and also per analogy to the orange coloration of V₂O₅ oxide, it seems clear that the voltamperometric cycling induces redox reaction via lithium insertion/desinsertion. Without presuming of the vanadium/oxygen ratio in the raw binder film, the electrochromic behavior can be described following the electrochemical chain: $xLi^+ + xe^- + VO_y \rightarrow Li_xVO_y$. The voltamperometric diagrams show two peaks which can be correlated to the two changes of vanadium oxidation number. This two steps electrochromism: yellow to green and green to blue during the reduction was previously ob-

served by several authors [benmoussa]. On crystallized V_2O_5 thin films, these two steps are often indexed as corresponding to the two $Li_xV_2O_5$ orthorhombic phases identified by Dickens and Reynolds [ref]. Our experiments show that from VO_y amorphous film with an olive-green coloration which can be presumed relevant of an oxidation number near 4 for vanadium ions, the same two-steps electrochromic behavior is observed. It can be concluded that the two peaks are not associated with well identified phase transition but, in a more general way, associated to the two successive redox reactions between the three accessible oxidation numbers. Moreover, it can be seen an attenuation of the peaks versus the cycle number.

In the second case, the coloration of the raw films is orange, this coloration corresponding to the main constituent of the film: the $Ti:V_2O_5$ powder. The cycling of these composite films leads also to the two changes of coloration from orange to green then green to blue decreasing the applied voltage. The shape of the voltamperograms is quite the same than for the films issued from pure SM solution. The capacity reached is for the first cycle significantly higher (nearly two times) that for the film issued from pure SM solution showing the large impact of the incorporated oxide particles.

The drastic decrease of the capacity (between 40 and 45 %) of the green films versus the cycle number shows a deterioration of the composite film morphology with the cycling. Hence, annealing treatments at $350^\circ C$ were applied to the as-prepared films to consolidate via a partial sintering the adherence and chemical resistance of these films. The voltamperograms obtained on the two $350^\circ C$ annealed films: binder and composite films, are reported in the **Figure 12**.

For both films: for the films issued from the pure SM solution as well as for the composite films the annealing treatment lead to a significant improvement of capacity stability versus cycling. The two steps redox still present but some secondary phenomena can also be noted, especially for the binder films. Combination of bulk and surfaces processes could be at the origin of the increase of peaks appearing on cyclic voltametry. The film colors still varying between blue and orange with an intermediate green coloration. The voltamperometric cycling, as previously, can be without any doubt attributed to the redox mechanism: $xLi^+ + xe^- + V_2O_5 \rightarrow Li_xV_2O_5$. Nevertheless, for both cases the intensity reached during the electrochemical cycle is drastically decreased (about 50%) in comparison with the green films. This decrease of the electrochemical capacity can be attributed to a diminution of the contact areas between the electrochromic films and the electrolyte due to the V_2O_5 sintering. Our experiments clearly demonstrate the drastic impact of the films morphology on the electrochemical performance.

Briefly, from the deposit by a dip coating process on ITO coated glass substrate of a polyol ionic solution (within V^{5+} ions) or composite films issued from the same V^{5+} polyol solution in which has been dispersed Ti-doped V_2O_5 powder, a drying step leads to electrochromic thin films able to exhibit three distinctive colorations versus applied voltage. Actually, the effect of the incorporation of the Ti-doped V_2O_5 powder is not so primordial, since the voltamperograms exhibit in both cases two distinctive peaks which can be associated to $V^{5+} \rightarrow V^{4+}$ and $V^{4+} \rightarrow V^{3+}$ redox reactions. Our original idea to use V^{5+} ions as mineral binder has allowed the getting of a sufficient film adherence to record the electrochromic performances but a large deterioration of the capacity versus cycle number still occur. The annealing of these films stabilizes the cyclability, but the capacity is deteriorated due

to the partial sintering of the films associated to a decrease of the electrolyte-film surface exchange.

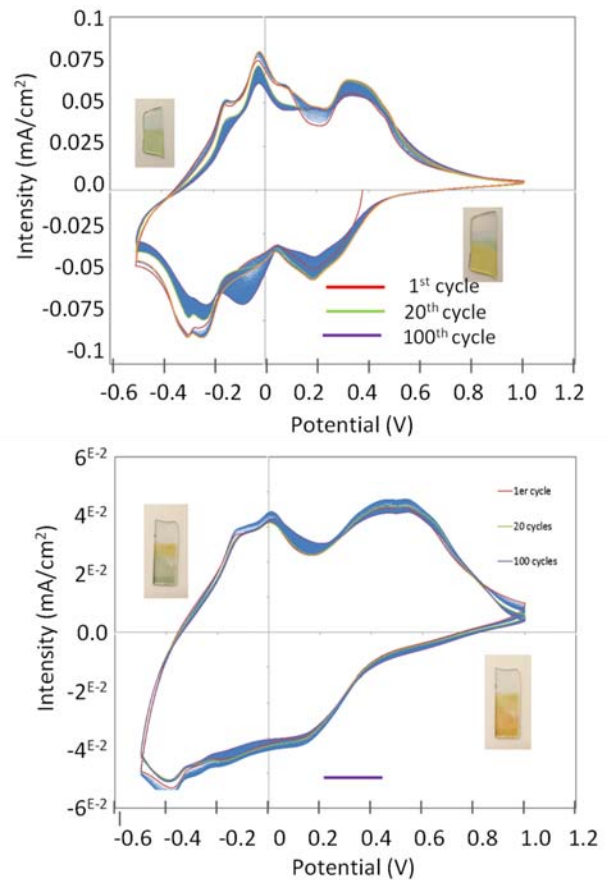


Figure 12: Voltamperogramm of annealed films obtained from a pure SM solution (top side), a suspension of $Ti:V_2O_5$ powder dispersed in SM solution (bottom side)

In the last part, the optical transmission through the two as-prepared annealed films (both the binder film and the composite film) is studied. Optical spectra are recorded for different cycle number (1st cycle, 20th cycle and 100th cycle) and at different points of the redox cycle (at -0.5 V and $+1$ V, *i.e.* potentials corresponding to the extreme reductive and oxidative conditions). The transmission spectra are reported in the **Figure 13**.

All the ITO-coated glasses exhibit the ITO frank gap at 280 nm. This gap is always visible on the ITO-coated glasses on which are deposited the electrochromic films. Results shows that the binder films, even if they exhibit interesting behavior on cyclic voltametry, present a weak optical contrast between the two extreme applied voltages: at the maximum, for a wavelength of 450 nm the $\Delta T\%$ (difference between optical transmission in oxidation and reduction states) is about 10%. The composite films, thicker and with an adequate haze coefficient exhibit a largely more important optical contrast between oxidation and reduction states about 30% at 450 nm. Hence, the composite films obtained from Ti-doped V_2O_5 suspensions show a particularly interesting electrochromic behavior. The curve of the oxidized film (orange hue) is characteristic of the V_2O_5 oxide with a gap associated to oxygen \rightarrow vanadium (from a valence band within $2p$ oxygen electrons to a conduction band within $3d$ vanadium levels) charge transfers located at about 480 nm [refs].

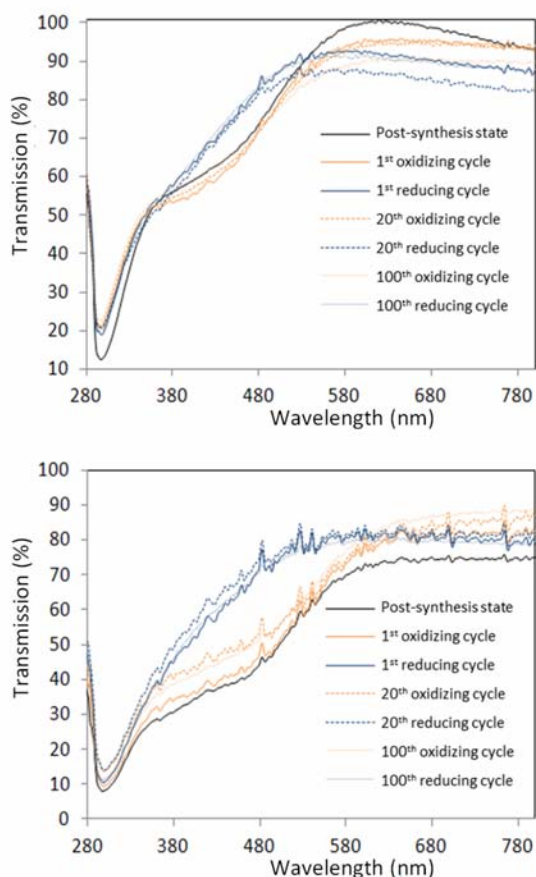


Figure 13: Optical transmission through annealed films obtained from a pure SM solution (top side), a suspension of Ti:V₂O₅ powder dispersed in SM solution (bottom side). The films were analyzed *ex-situ* after different applied voltage and for different electrochemical cycle numbers.

The curve of the reduced film (blue hue) exhibits only a single gap at about 350 nm also associated to oxygen→vanadium charge transfer. The V₂O₅ electrochromic behavior was already reported [ref] as associated to a blue shift of the inter-atomic charge transfer due to the increase of the bond ionicity with the V ion reduction. It has to be noted that the drastic change of coloration versus the vanadium reduction results from one key point: the exotic orange coloration of V⁵⁺ ion in oxides. The absorption spectrum of V₂O₅ is not so well interpreted and controversies appear while the literature data are apprehended. The visible gap is very dispersed in energy and at very low energy, explaining the orange hue. The gap positioning can be attributed to the high V⁵⁺ electronegativity (covalent bonds) but elsewhere the long absorption tail of the gap is reported as a consequence of scattering phenomena [refcolor1] and finally surface defects of V₂O₅ oxides were also been pointed out as at the origin of the shape/position of this visible absorption band [[58c1] and [59c1]. Per analogy with hematite for which a quite energy-dispersed and low energy gap was interpreted as the splitting of the Fe(III) *t*_{2g} levels consecutive to the strong octahedral distortion [refnus], reasonably, the gap in V₂O₅ leading to its characteristic orange coloration can be interpreted as the consequence (in part) of *t*_{2g} level splitting due to the non-centro-symmetry of the V(V) pentacoordinated site. This hypothesis can explain why the

composite films with the crystallized Ti-doped V₂O₅ particles exhibit a so more important optical contrast in comparison with the VO_x binder films.

Conclusion. The synthesis of Ti-doped V₂O₅ from polyol process leads to pure phase with crystallite size of few nm and so with a high Ti solubility limit. The Ti doping ions were accurately positioned combining X-ray pattern refinement and from valence calculation: the Ti ions exit of the V square pyramid sites to be located on the other side of the planar square base of the pyramids. Films elaborated from dip-coating process from particle suspensions were shown to exhibit drastic coloration changes during redox reactions induced by cyclic voltametry. We have shown the three accessible colors are associated with three distinct oxidation numbers for the vanadium ions: +III (blue), +IV (green) and +V (orange) in correlation with the two step voltamperometric diagrams. The morphology of the films was shown to drastically impact the capacity and the stability of the electrochromic performances. Green films, *i.e.* films only dried at 100°C with Ti-doped V₂O₅ nanoparticles thanks to high surface exchange with the electrolyte exhibits great capacity and good optical contrast during the first cycles. Unfortunately, the capacity collapses due to the weak film adherence to the substrate and an annealing treatment should be applied. Hence, capacity/optical contrast are maintained at least upon 100 cycles but the partial sintering of the film particles leads to a decrease of the electrochromic capacity.

Due to its limited optical modulation, VO_x films are ordinary reported to may be useful as a passive counter electrode in conjunction with an active working electrode in complementary electrochromic devices. This study opens a new path for the use of optimized Ti-doped V₂O₅ base films as working electrode in future devices. Future would aim to combine nanometric particles dimension as with as-prepared green films and the cycling stability reached with the as-prepared annealed films. The use after optimization of V⁵⁺ ions acting as mineral binders in the coated suspensions was shown to be a promising window for such a target.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

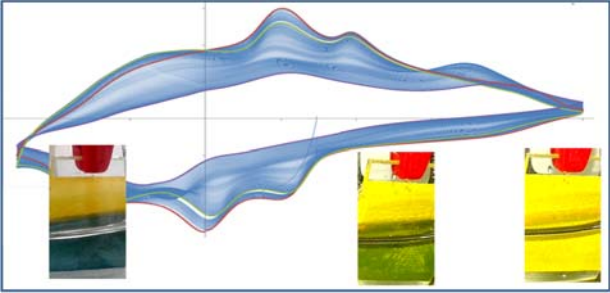
Notes

The authors declare no competing financial interests.

REFERENCES

- (1) Taylor, R.W. *Am. Mineral.* **1964**, *49*, 1016–1030.
- (2) Ishikawa, Y. *J. Phys. Soc. Jpn.* **1957**, *12*, 1083–1098.
- (3) Hamelin, M. *Bull. Soc. Chim. France* **1958**, *67*, 1559-1566.

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