



## Sol-Gel Synthesis of Vanadate-Based Thin Films as Counter Electrodes in Electrochromic Devices

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**Abstract.**  $V_2O_5$ -based thin films were prepared via the sol-gel method in order to obtain semiconductive films suitable as counter electrodes in electrochemical devices (e.g. electrochromic windows). Different metal precursors (nickel 2,4-pentanedionate,  $NiCl_2$ ,  $BiCl_3$ ,  $SbCl_3$ ) were added, after dissolution, into the starting vanadium oxo-triisopropoxide solution in the presence of acetic acid as a chelating agent. Preventing different synthesis conditions due to the ambient moisture, the hydrolysis reaction was carried out in controlled acidic conditions. Stable sols were obtained and thin films were dipped on transparent substrates coated with a conductive layer (ITO,  $SnO_2:F$ ). Different techniques were employed on as-prepared and heat treated (673 K) films, and the corresponding gels in order to characterize the microstructural, surface and electrochemical features of the samples. Better results were obtained for Ni/V oxides thin films: unless their charge capacity was not very high ( $\sim 10$  mC/cm<sup>2</sup>), their electrochemical stability was unchanged after 1000 cycles and their transmittance spectra showed high transparency ( $>80\%$ ) in all the visible region during both the intercalation and deintercalation steps. On the other hand, preliminary analysis on Sb/V mixed oxides showed a higher charge capacity but irreversible electrochemical reactions took place during the first working cycles.

**Keywords:**  $V_2O_5$ -based thin films, nickel(II) 2,4-pentanedionate, dip-coating, transmittance spectra, cyclic voltammetry

### Introduction

Vanadium(V) oxide ( $V_2O_5$ ) films have been extensively studied for their electrochemical applications, as rechargeable microbatteries and electrochromic devices, due to their layered structure that allows the intercalation of monovalent cations, as  $Li^+$ , and the simultaneous occurrence of the redox process  $V(V) \rightarrow V(IV)$  [1]. Thus, the high obtained values of charge capacity have made  $V_2O_5$  as a suitable material for the preparation of thin film electrodes, among the

inorganic oxides. There are different methods for film deposition, ranging from RF-sputtering [2], to physical vapour deposition [3] and sol-gel process [4], the latter being usually advantageous because of the less expensive apparatus and its versatility. As an electrochromic material, however, vanadium pentoxide shows a complicated colouration behaviour [1], mainly depending on the intercalation degree [5] and on the film thickness [6]; as an alternative way, the use of  $V_2O_5$  as an optically passive counterelectrode has been studied [7]. For improving this material, the addition of a second transparent oxide has been proposed [8], (as  $TiO_2$ ,  $ZrO_2$ ,  $CeO_2$ ) in order to decrease the residual colouration

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due to the vanadium oxide and increasing at the same time the charge capacity and the electrochemical stability of the counter-electrode. These requirements are needed to support the electrochromic process regarding  $\text{WO}_3$  film, the material with better performances in such devices.

In this work, vanadate-based thin films have been produced, with  $\text{NiO}$ ,  $\text{Sb}_2\text{O}_3$  or  $\text{Bi}_2\text{O}_3$  oxides as a second phase:  $\text{NiO}$  has been used for its electrochromic behaviour, showing anodic colouration complementary to the cathodic  $\text{WO}_3$  one [9]; antimony(III) and bismuth(III) oxides are known to be transparent in the visible region and to support oxidative processes to  $\text{Sb(V)}$  and  $\text{Bi(V)}$ . Thin films have been deposited by a dip-coating system on transparent glass sheets coated by a conductive layer; the sols have been produced by the hydrolytic route starting from vanadium oxo-triisopropoxide, while the second oxide has been added or as an alkoxide (nickel derivative) or as a chloride. Usually, the hydrolysis reaction was provided by the ambient moisture: this could represent a drawback, because it could modify the final features of the films; here, we carried out the hydrolysis in acidic and controlled conditions in order to obtain films with reproducible features. In this case, the high reactivity of vanadium alkoxide against hydrolysis have been controlled using acetic acid which acts as a bidentate ligand, as determined for titanium alkoxides [10]. Amorphous monolayered thin films have been obtained: structural, optical and electrochemical analyses have been performed on the as-deposited and the heat-treated films, to understand the influence of the synthesis procedure on the film features, like transparency and electrochemical stability.

## Experimental

Vanadium oxo-triisopropoxide (ABCR) was allowed to react with acetic acid (Baker Analyzers) in a 1/1 molar amount for few minutes under stirring and flowing nitrogen; then 2-propanol (Baker Analyzers) was added to obtain a  $\text{V/alkohol} = 1/20$  molar ratio. Solutions with the nominal  $\text{Ni/V} = 1/10$  and  $2/10$  molar ratios were prepared by quickly adding calculated amounts of nickel(II) 2,4-pentanedionate (ABCR) dissolved in toluene (Carlo Erba) ( $\text{Ni}$  concentration = 10 g/l) to the transparent pale green alcoholic solution: a sudden red-brown colouration was observed. The solution was kept for two hours under stirring in nitrogen atmosphere.

Then, water at different pH values (usually  $\text{pH} = 0, 1$ ), obtained by  $\text{HCl}$  addition, was added dropwise under vigorous stirring; the  $\text{V/H}_2\text{O}$  molar ratio = 1/1 was kept fixed for all compositions. As regards the preparation of metal chlorides/vanadium alkoxide solutions, the above parameters were kept unchanged unless the solvent used for the dissolution of the salt: absolute ethanol (Baker Analyzers) was used for  $\text{NiCl}_2$  and  $\text{BiCl}_3$  and 2-propanol for  $\text{SbCl}_3$  (all chlorides were provided by Sigma Aldrich); nominal metal/V molar ratio of 1/10 was kept for all systems;  $\text{Sb/V} = 1/1$  composition was also prepared.

Obtained sols remained stable for some hours, except  $\text{Sb/V}$  solutions whose stability remained unchanged for almost one month. The deposition of the thin films was performed one hour after the hydrolysis by means a home-made dip-coating apparatus. Pulling rate was kept fixed at 6 cm/sec. The substrates used were: optical grade silica glass (Arbore Cataldo), silica with an ITO layer (Unaxis) and K-glass (SIV). All films were kept in the deposition chamber for one day; final heat treatment was carried out under static air in a quartz furnace (Heraeus) up to 673 K with a heating rate of 2 K/min, followed by an isothermal step of one hour at the same temperature. X-ray Diffraction (XRD) spectra were collected on a Rigaku DMax III diffractometer using  $\text{CuK}\alpha$  radiation and a graphite monochromator in the diffracted beam; asymmetric scattering configuration was adopted for these measurements with an incidence grazing angle in the range  $0.1^\circ \div 0.5^\circ$ .

Infra-Red (FT-IR) film analysis was performed with a Nicolet 5DXC spectrophotometer equipped with a Spectra-Tech FT-85 Grazing Angle External Reflectance fitting, provided with a fixed  $85^\circ$  incidence angle; all scans were registered with a resolution of  $4 \text{ cm}^{-1}$ .

Electrochemical analyses and in-situ transmittance spectra on the films were performed using a three-electrode cell, operating in nitrogen atmosphere, having lithium foils as reference and counter-electrode; a 1 M solution of  $\text{LiClO}_4$  in propylene carbonate (PC) was used as an electrolyte. Cyclic voltammetry measurements were performed with an EG&G PAR 273 potentiostat/galvanostat within the potential limits of 1.0 and 4.5 V vs. Li and with different scan rates, usually  $5 \div 20 \text{ mV/sec}$ . In-situ transmittance spectra were measured by spectrophotometry in the 290–2000 nm wavelength range using a Perkin-Elmer  $\lambda$ -9 spectrophotometer.

## Results and Discussion

Thin films were obtained without macroscopic defects, as revealed by SEM analysis. All films were yellow, with slight changes in colour intensity due to the different oxides and thermal treatment. Their thickness, determined by the profilograph, were into the range  $60 \div 80$  nm for the heat treated samples and  $100 \div 130$  nm for the as-deposited ones; as an exception, Sb/V films showed higher thickness; 130 nm for the cured and 190 nm for the untreated samples were determined for the Sb/V 1/1 composition.

Differential thermal analysis performed on the corresponding gels revealed exothermal peaks attributable to crystallization processes in the interval  $593 \div 663$  K. Only Sb/V 1/1 gel did not present any exo effect up to 1073 K.

XRD spectra collected on the films confirmed the occurrence of the crystallization process; the as-deposited films were amorphous and the isothermal treatment at 673 K in air led to the appearance of crystalline phases. In Fig. 1 the spectrum of Ni/V 1/10 film (pH of hydrolysis = 1, Ni-pentanedionate precursor) is reported: a single peak corresponding to the (010) reflection of orthorhombic  $V_2O_5$  was present; as already reported for sputtered films [2], a crystallographic orientation parallel to the substrate could be proposed for the annealed sample. No other peaks were detectable in the spectrum, except the small bump at  $22^\circ$  ( $2\theta$ ) that could

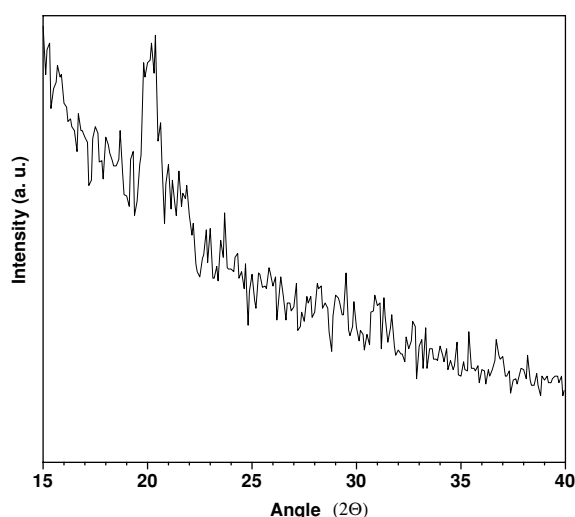


Figure 1. XRD spectrum of Ni/V 1/10 film treated at 673 K. Incidence angle:  $0.3^\circ$ . Substrate: silica glass.

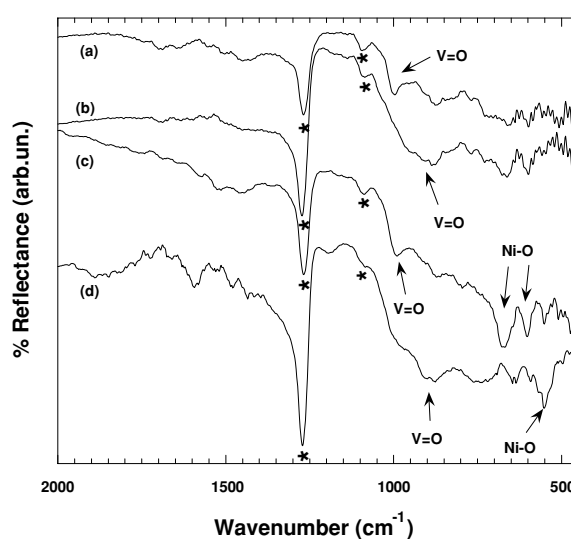


Figure 2. NGIA-IR spectra of: (a) as-deposited and (b) 673 K treated Ni/V 1/10 films; (c) as-deposited and (d) 673 K treated Ni/V 2/10 films. \* is related to the ITO layer of the substrate.

be attributed to a nickel vanadate phase,  $NiV_3O_8$  (PDF card n° 22-455).

On the other hand, the thermal treatment led to the modification of the film structure, as revealed by the near-grazing incidence angle IR spectra (Fig. 2, curves (a) and (b)): the as-deposited film was characterized by a peak at above  $1000\text{ cm}^{-1}$ , typical of the vibrational mode of isolated  $V=O$  bonds in vanadium pentoxide [11]. The spectrum of the heat treated film showed the disappearance of this peak and the increase of the broad band at lower wavenumbers (below  $1000\text{ cm}^{-1}$ ). Similar results were observed in vitreous vanadate systems, where some divalent cations could occupy some positions in the vanadium pentoxide network, affecting the  $V=O$  bond length [12], and changing the coordination number of vanadium. It seemed reasonable to invoke this effect also in our films. This behaviour was enhanced in Ni/V 2/10 films (Fig. 2, curves (c) and (d)), as revealed by the spectroscopic analysis; again, the thermal treatment led to the shift of the  $V=O$  vibrational mode to lower wavenumbers, associated with the modification of  $Ni-O$  bonds (peaks in  $650 \div 550\text{ cm}^{-1}$  range).

Other systems showed different microstructures: the XRD pattern of Bi/V 1/10 heated films presented only a peak attributable to  $Bi_4V_6O_{21}$  (PDF card n° 33-222), while no crystalline  $V_2O_5$  signal was observed.

Cyclic voltammogram of the as-deposited Ni/V 1/10 film revealed a featureless current vs. voltage diagram,

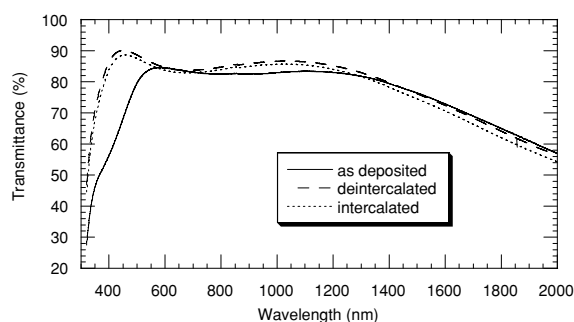


Figure 3. Transmittance spectra of as-deposited Ni/V 1/10 film during Li-insertion/extraction processes.

as reported for amorphous sol-gel derived thin films [4]; it is noteworthy that no changes during insertion/extraction processes were visible. The transmittance spectrum of this film (Fig. 3) highlighted a high transparency (>80%) throughout the whole visible region and a reversible behaviour during intercalation/deintercalation steps.

The voltammogram of the heat treated film is shown in Fig. 4: both oxidation and reduction peaks were visible. Again, high electrochemical stability was revealed, as the curves did not show important changes up to 1000 cycles, while the charge capacity remained low (about 10 mC/cm<sup>2</sup> for a 70 nm thick film). This feature can probably be due to the presence of non equivalent vanadate sites. Moreover, N<sub>2</sub>-sorption measurements performed on the corresponding xerogels revealed microporosity; work is in progress on other vanadate-based systems to establish if the film porosity can influence the electrochemical behaviour.

NiCl<sub>2</sub>-derived films showed similar structural features, but their electrochemical stability were lower than the alkoxide-derived films, as determined by the CV analyses.

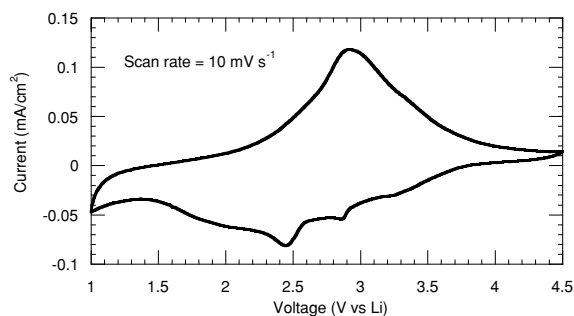


Figure 4. Cyclic Voltammogram of Ni/V 1/10 film, treated at 673 K.

Preliminary electrochemical results on films with different compositions gave for the cured Sb/V 1/1 film a high charge capacity (>30 mC/cm<sup>2</sup>) but also irreversibility effects: till now, the cause of this behaviour is not clear, even though the porosity of the surface seems to play a key role.

## Conclusions

Vanadium pentoxide-based thin films were prepared by controlled hydrolysis of vanadium alkoxide solutions where a second inorganic oxide precursor was dissolved. The synthesis procedure influenced the electrochemical behaviour of the as-deposited and heat treated films; for the Ni/V 1/10 system, high electrochemical stability was found, associated to a low charge capacity. Transmittance spectra, recorded during intercalation and deintercalation steps, revealed high transparency for these films in the whole visible region and complete reversibility against the electrochemical process, making them suitable as counter-electrode in electrochromic devices.

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