

CHEMICAL DEPOSITION OF NANO-SIZED ELECTROCHROMIC THIN FILMS
OF $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ XEROGELSS. Stojkovikj¹, V. Koleva², M. Najdoski¹¹Institute of Chemistry, Faculty of Natural Sciences and Mathematics, Ss. Cyril and Methodius University,
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Abstract: Electrochromic sodium intercalated vanadium(V) oxide xerogel thin films with composition $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ have been deposited on electroconductive FTO glass substrates by a simple chemical bath method. The deposition of the homogenous thin films is performed from an aqueous solution, containing sodium metavanadate and diethyl sulfate at 85 °C. The xerogel formation is based on the acidification of the metavanadate solution as a result of the hydrolysis of $(\text{C}_2\text{H}_5)_2\text{SO}_4$. Thin films with thickness of about 50 and 110 nm have been prepared for deposition times of 5 and 10 min, respectively. The composition, structure and morphology of the films are studied by XRD, TG and SEM. The film morphology is characterized by nano-particles with sizes between 80 and 100 nm that tightly stick to each other forming elongated ribbon-like units. The electrochemical and electrochromic properties have been studied in two non-aqueous electrolytes: $\text{LiClO}_4/\text{propylene carbonate}$ and $\text{LiCl}/\text{methanol}$. The cyclic voltammograms in $\text{LiClO}_4/\text{propylene carbonate}$ display two stable redox pairs related to the transitions between V(V) and V(IV), sites which give rise to colour changes: yellow/green/blue. The $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ thin films exhibit high electrochromic activity with transmittance variance of 42 % at 900 nm and this is a promising result for potential application in electrochromic devices.

Keywords: vanadium(V) oxide, nanomaterials, thin films, electrochromism, xerogels

1. Introduction

Electrochromic materials, which are the basis of the electrochromic devices, maintain reversible and persistent change in the optical properties when variable polarity voltage is applied to them, due to combined insertion and extraction of ions and electrons in the material in contact with an appropriate electrolyte [1,2]. Among the inorganic electrochromics vanadium(V) oxide-based materials, and especially vanadium(V) oxide xerogels have attracted a lot of interest since they exhibit a multi-coloured electrochromism [3,4]. Vanadium(V) oxide xerogels expressed by $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ adopt a layer structure made of double V_2O_5 sheets, stacked along the *c*-axis of a monoclinic unit cell, which are separated by water molecules [5]. Due to the layered structure $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ xerogels are able to intercalate wide variety of inorganic and organic guest species without change in the one-dimensional stacking of the layers [6,7]. Depending on the preparation conditions the xerogels can be designed in different forms and morphologies like nanoribbons, nanotubes, nanowires, nanorods, nanobelts, nanofibers, etc. which opens wide prospects for applications in electrochromic devices [8-10], batteries [11,12], sensors [13] and etc.

Our research is focused on the examination of the electrochromic activity of sodium intercalated vanadium(V) oxide thin films, prepared by a new chemical bath deposition method.

2. Experimental section

The thin films are prepared on transparent FTO (fluoride doped tin(IV) oxide) glass substrates. The chemical bath deposition is performed in an aqueous solution containing sodium metavanadate – NaVO_3 (0.016 mol/dm³) and diethyl sulphate – $(\text{C}_2\text{H}_5)_2\text{SO}_4$, (0.04 mol/dm³) at 85 °C. The beaker, containing precursor solutions, is covered with Petri dish during the deposition in order to avoid the water evaporation. The deposition time is measured from the moment when the solution becomes turbid. Yellow coloured thin films with thickness of about 50 and 110 nm are obtained for 5 and 10 min deposition time at 85 °C, respectively (as-deposited films) and they are further studied.

The thin film structure is examined by X-ray powder diffraction (Rigaku Ultima IV X-ray diffractometer using $\text{CuK}\alpha$ radiation). The sodium and water amounts are determined by atomic absorption spectrometry and thermogravimetric analysis, respectively. The film thickness is measured by Alpha Step D-100 profilometer. The morphology of the thin films is observed by scanning electron microscopy (JEOL JSM-5510). The optical properties of thin films are studied by Varian Cary 50 Scan spectrophotometer in non-aqueous electrolytes (1 mol/dm³): LiClO_4 in propylene carbonate (PC) and LiCl in methanol (MeOH). The electrochemical behavior is analyzed by cyclic voltammetry using micro AUTOLAB II (Eco-Chemie) in the same non-aqueous electrolytes. The reference electrode is Ag/AgCl (saturated KCl) and the auxiliary electrode is a platinum electrode.

3. Results and discussion

The chemistry of the deposition process is based on the acidification of the NaVO_3 solution that occurs as a result of the hydrolysis of the diethyl sulfate at temperatures above 65 °C (in our case 85 °C). The XRD pattern of the film (Figure 1) exhibits small number of broad diffraction peaks with a prominent first peak, centered at 7.89 ° ($d = 11.20 \text{ \AA}$) in agreement with previous reports on pristine $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ and intercalated $\text{M}_x\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ xerogels [5-7]. This XRD feature is consistent with the limited structural coherence, suggesting that the V_2O_5 sheets are not stacked in perfect order [5]. The first (001)

diffraction peak reflects the basal distance between the double V_2O_5 sheets stacked perpendicularly to the substrate [5-7]. The basal distance depends on the amount of the water molecules between the layers and it varies between 11.55 Å for $n \approx 1.5$ -1.6 (usual case) and 8.75 Å for $n \approx 0.5$ [6]. Therefore, from the XRD data it can be concluded that the water content of the as-prepared films is smaller than 1.5 moles.

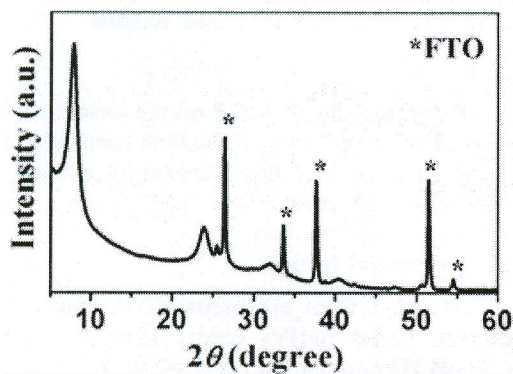


Figure 1. XRD pattern of an as-deposited film.

Considering the obtained data for the sodium and water amounts measured for the precipitate from the chemical bath (it has the same XRD pattern and IR spectrum as these for the films) the composition of the xerogel is expressed by the formula $Na_{0.33}V_2O_5 \cdot H_2O$.

The morphology of the thin films is shown in Figure 2. The surface is well covered with the deposited material in spite of the small film thickness. The film morphology is characterized by nano-particles with dimensions about 80-100 nm and randomly distributed elongated ribbon-like units, which are about 200 nm wide and between 1 and 3 μm long. Possibly, the ribbons are composed of nano-particles that are tightly stuck to each other.

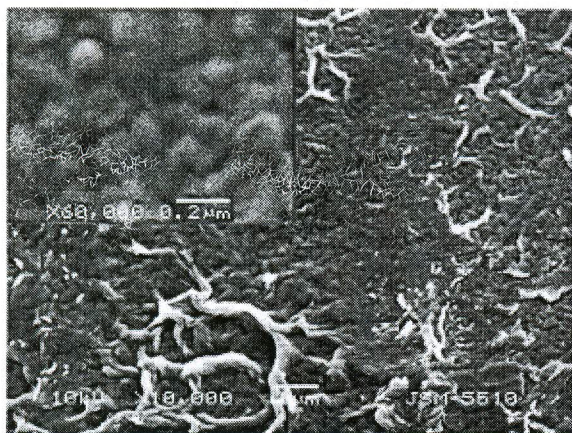


Figure 2. SEM images of $Na_{0.33}V_2O_5 \cdot H_2O$ thin film having 110 nm thickness.

The electrochemical behavior of the thin films is examined by cyclic voltammetry (CV) at scan rate of 10 mV/s in a range from -1.5 V to +1.5 V. No electrochemical activity was observed in $LiCl(MeOH)$ as an electro-

lyte, most probably due to reaction between the methanol and the xerogel material. However, the films exhibit considerable electrochemical activity, when the electrolyte is $LiClO_4(PC)$ (Figure 3). The CV curves (Figure 3) clearly show two redox pairs (A1/C2 and A2/C1). The anodic (oxidation) peaks, A1 and A2, appear at -0.05 and 0.15 V, the latter being slightly shifted to higher potentials after each next scan (e.g. 0.19 V for the 5th scan). The two cathodic (reduction) peaks, C1 and C2, have negative potentials: -0.16 and -0.53 V, respectively (Figure 3).

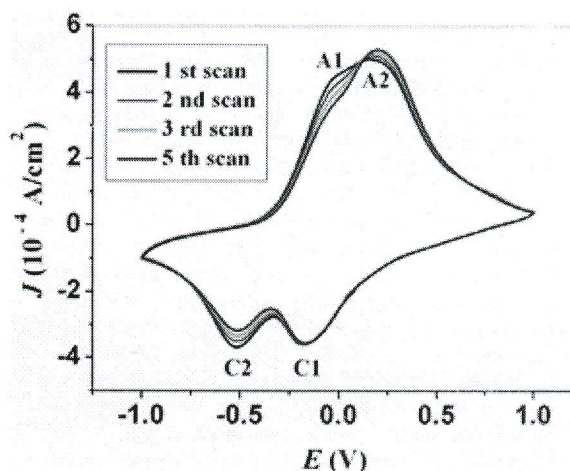


Figure 3. Five cyclic voltammograms of $Na_{0.33}V_2O_5 \cdot H_2O$ xerogel thin film with 110 nm thickness in $LiClO_4(PC)$.

The observation of two redox pairs in the cyclic voltammograms of $Na_{0.33}V_2O_5 \cdot H_2O$ thin films is consistent with previous reports on vanadium(V) oxide xerogels [14,15]. The redox peaks can be related to two-step reduction of V(V) to V(IV) [14,16] concomitant with formation of different crystalline states $Li_xV_2O_5$, and accordingly, reversible V(IV) oxidation and Li-deintercalation [17].

When the $Na_{0.33}V_2O_5 \cdot H_2O$ films are placed in the electrochromic cell and a reducing voltage of -2.5 V is applied, a noticeable change from yellow to green and then from green to blue colour is observed. By changing the voltage polarity from -2.5 V to +2.5 V the colour reversibly changes from blue to yellow. The observed colour changes are typical of electrochromic vanadium(V) oxide-based materials [4,16] and they are related to the transition between two oxidation states, V(V) (yellow) and V(IV) (blue). The green colour arises by mixing yellow and blue due to the presence of both types of vanadium ions.

The optical transmittance spectra of the $Na_{0.33}V_2O_5 \cdot H_2O$ thin films recorded in $LiClO_4(PC)$ and $LiCl(MeOH)$ are shown in Figure 4. Transmittance variance (ΔT) defined as a difference in the transmittance between the reduced (bleached) and oxidized (coloured) state at given wavelength is an important characteristic used to quantify the electrochromic effect: the higher the ΔT value, the better the electrochromic effect. Concerning vanadium(V) oxide xerogels, the reported ΔT values vary within broad limits of 10 - 50 % and the best achievements are 40 % [4,18] and 50 % [19].

As it is seen from Figure 4 (c) in $LiCl(MeOH)$ for

the 1st cycle the $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ film exhibits a remarkable high ΔT value of 51 % at 900 nm. Unfortunately, due to the film dissolution in this electrolyte ΔT drops down after several cycles to the value of 5 % (Figure 4 d). In $\text{LiClO}_4(\text{PC})$ however, the two films demonstrate a stable behaviour for ten cycles and high electrochromic activity at 900 nm with ΔT of 33 % and 42 % for the films with 50 nm and 110 nm thickness, respectively (Figure 4 a and b). The good result for ΔT can be related, at least partially, to the nano-sized morphology of the prepared thin films.

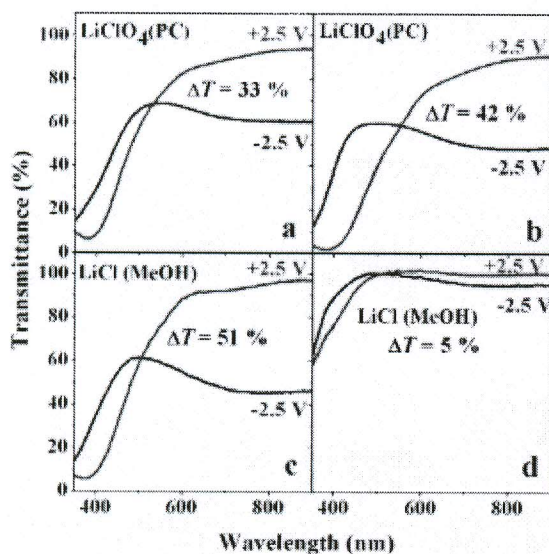


Figure 4. Optical transmittance spectra of $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ thin films: a) film with 50 nm thickness in $\text{LiClO}_4(\text{PC})$; b) film with 110 nm thickness in $\text{LiClO}_4(\text{PC})$; c) film with 50 nm thickness in $\text{LiCl}(\text{MeOH})$, 1st cycle; d) film with 50 nm thickness in $\text{LiCl}(\text{MeOH})$, 5th cycle.

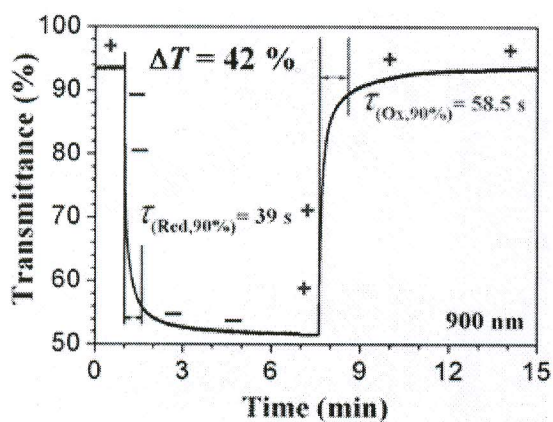


Figure 5. Optical response time of $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ xerogel thin film with 110 nm thickness in $\text{LiClO}_4(\text{PC})$.

The optical response time, defined as a time required for the film to obtain 90 % of the needed coloration, is determined for the better film with 110 nm thickness in $\text{LiClO}_4(\text{PC})$ (Figure 5). The kinetic curves evidence that the response time for the reduction process accompanied by colour change from yellow to blue is 39 s, while that for the oxidation process (from blue to yellow

state) is 58.5 s, i.e. the reduction process is faster than the oxidation one.

4. Conclusions

Sodium intercalated vanadium(V) oxide xerogel films with the composition $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ have been prepared by a simple low temperature chemical bath deposition method. The thin films demonstrate a high electrochromic activity in $\text{LiClO}_4(\text{PC})$ with transmittance variance of 42 % at 900 nm. The good achievement can be related to the nano-sized morphology of the prepared films. $\text{Na}_{0.33}\text{V}_2\text{O}_5 \cdot \text{H}_2\text{O}$ thin films are established to be slowly responding electrochromic materials and they would be appropriate as materials for electrochromic windows.

Acknowledgments

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References:

- [1] A. Hjelm, C.G. Granqvist, J.M. Wills, *Phys. Rev. B* **54** (1996) 2436-2445.
- [2] R. Chatten, A.V. Chadwick, A. Rougier, P.J.D. Lindan, *J. Phys. Chem. B* **109** (2005) 3146-3156.
- [3] N.M. Rowley, R.J. Mortimer, *Sci. Prog.* **85** (3) (2002) 243-262.
- [4] C. Costa, C. Pinheiro, I. Henriques, C.A.T. Laia, *Appl. Mater. Interfaces* **4** (5267) (2012) 5266-5275.
- [5] V. Petkov, P.N. Trikalitis, E.S. Bozin, S.J.L. Billinge, T. Vogt, M.G. Kanatzidis, *J. Am. Chem. Soc.* **124** (2002) 10157-10162.
- [6] J. Livage, *Chem. Mater.* **3** (1991) 578-593.
- [7] O. Durupthy, N. Steunou, T. Coradin, J. Maquet, C. Bonhomme, J. Livage, *J. Mater. Chem.* **15** (2005) 1090-1098.
- [8] R. Ceccato, G. Carturan, *J. Sol-Gel Sci. Technol.* **26** (2003) 1071-1074.
- [9] D. Gillaspie, A. Norman, C.E. Tracy, J.R. Pitts, S.H. Lee, A. Dillon, *J. Electrochem. Soc.* **157** (2010) 328-331.
- [10] R. Baetens, B.P. Jelle, A. Gustavsen, *Sol. Energy Mater. Sol. Cells* **94** (2010) 87-105.
- [11] Y. Wang, G. Cao, *Adv. Mater.* **20** (2008) 2251-2269.
- [12] F.C. Bazito, R.M. Torresi *J. Braz. Chem. Soc.* **17** (2006) 627-642.
- [13] H. Yin, K. Yu, H. Peng, Z. Zhang, R. Huang, J. Travas-Sejdic, Z. Zhua, *J. Mater. Chem.* **22** (2012) 5013-5019.
- [14] M. Benmoussa, A. Outzourhit, R. Jourdani, A. Bennouna and E.L. Ameziene, *Active and Passive Elec. Comp.* **26** (2003) 245-256.
- [15] N. T. Bay, P.M. Tien, S. Badilescu, Y. Djaoued, G. Bader, F.E. Girouard, V.V. Truong and L. Q. Nguyen, *J. Appl. Phys.* **80** (1996) 7041-7045.
- [16] M. Najdoski, V. Koleva, S. Demiri, *Mater. Res. Bull.* **47** (2012) 737-743.
- [17] S.F. Cogan, N.M. Nguyen, S.J. Perrotti, R.D. Rauh, *J. Appl. Phys.* **66** (1989) 1333-1337.
- [18] W. Zhongchun, C. Jiefeng, H. Xingfang, *Thin Solid Films* **375** (2000) 238-241.
- [19] M.R.J. Scherer, L. Li, P.M.S. Cunha, O.A. Scherman, U. Steiner, *Adv. Mater.* **24** (2012) 1217-1221.