

# Electrodeposition of V<sub>2</sub>O<sub>5</sub> using ammonium metavanadate at room room temperature

Dimitra Vernardou<sup>1\*</sup>, Emmanouil Spanakis<sup>2</sup>, Nikolaos Katsarakis<sup>1,3</sup>, Emmanouil Koudoumas<sup>1,4</sup>

<sup>1</sup>Center of Materials Technology and Photonics, School of Applied Technology, Technological Educational Institute of Crete, 710 04 Heraklion, Crete, Greece

<sup>2</sup>Department of Materials Science and Technology, University of Crete, 710 03 Heraklion, Crete, Greece

<sup>3</sup>Institute of Electronic Structure and Laser, Foundation for Research & Technology-Hellas, P.O. Box 1527, Vassilika Vouton, 711 10 Heraklion, Crete, Greece

<sup>4</sup>Electrical Engineering Department, Technological Educational Institute of Crete, 710 04 Heraklion, Crete, Greece

\*Corresponding author. Tel: (+30) 2810379774; Fax: (+30) 2810379157; E-mail: [dimitra@iesl.forth.gr](mailto:dimitra@iesl.forth.gr)

Received: 21 January 2014, Revised: 28 March 2014 and Accepted: 10 April 2014

## ABSTRACT

Vanadium oxides were electrodeposited on fluorine doped tin dioxide glass substrates using an aqueous solution of ammonium metavanadate at room temperature for various growth periods keeping the current density constant. The deposition period was found to affect the structure and the morphology of the oxides indicating low crystalline quality and smooth surfaces respectively for periods < 2000 s. It has been found that crystalline vanadium pentoxide grown for 2000 s presented the highest amount of charge, being 0.43 C interchanged between the oxide and the electrolyte with a respective specific capacitance of 286 F g<sup>-1</sup> having a satisfactory stability after 500 continuous scans. The significance of achieving crystalline low-cost vanadium pentoxide at room temperature with enhanced electrochemical properties for applications as electroactive material is highlighted. Copyright © 2014 VBRI press.

**Keywords:** Electrodeposition; vanadium oxides; deposition period; electrochemical response.

## Introduction

Vanadium pentoxide (V<sub>2</sub>O<sub>5</sub>) has attracted much attention due to its application as cathode material in batteries [1] and electrochromics [2]. However, the electrochemical performance is limited by the low diffusion coefficient of Li ions in the V<sub>2</sub>O<sub>5</sub> matrix [3]. Hence, attention has been turned to porous materials because of the high surface area, which can result in a very short diffusion path for lithium ions allowing rapid charging-discharging response [4].

Various chemical methods have been used for the fabrication of V<sub>2</sub>O<sub>5</sub> including chemical vapour deposition [5], sol-gel [6], spray pyrolysis [7], hydrothermal growth [7,8] and electrodeposition [9-11]. Among those, electrodeposition has advantages such as low-cost and simplicity at as low as room temperature without the requirement of toxic chemicals. With proper attention to electrolyte's properties and coating growth parameters such as current density, potential and deposition time, the morphology and structure of the oxides can be efficiently controlled [11,12]. The vanadium precursor in electrodeposition mainly involves VOSO<sub>4</sub> at ≤ 65 °C [13,14], while in some cases, higher temperatures (200 [10] and 350 °C [4]) are utilized. In addition, V<sub>2</sub>O<sub>5</sub> in powder form [11] and vanadyl (IV) acetylacetonate [12] dissolved in methanol and water at room temperature is employed.

In this work, the electrodeposition of crystalline V<sub>2</sub>O<sub>5</sub> was performed using ammonium metavanadate as the vanadium precursor dissolved in water at room temperature. This is one of the simplest routes, which has not been studied before in the literature, to the best of our knowledge. The correlation of structure and morphology with the electrochemical activity comprising charge storage, specific capacitance and repeatability of the charge transfer through the vanadium pentoxide is studied.

## Experimental

The electrolyte for the deposition of vanadium pentoxide coatings was an aqueous yellow solution of 0.06 M, ammonium metavanadate (NH<sub>4</sub>VO<sub>3</sub>). Prior to electrodeposition, fluorine doped tin dioxide (FTO) glass substrates were ultrasonically cleaned with 2-propanol, acetone, water and dried with N<sub>2</sub>. The current density for all depositions was kept constant at 40 mA cm<sup>-2</sup> for growth periods of 600, 1200 and 2000 s. Platinum, Ag/AgCl and FTO substrate were used as the counter, reference and working electrodes respectively. After the end of each deposition period, the samples were dried in air at room temperature for 10 min.

Structural analysis was performed using a Siemens D5000 Diffractometer for 2-theta = 10.0-60.0 degrees and a

Nicolet Almega micro-Raman system for a range of 100–1100  $\text{cm}^{-1}$  at 473 nm laser line. Morphological evaluation was employed using a JEOL JSM-6390LV electron microscope. For these measurements, it was necessary a thin film of gold on the samples to improve their conductivity. Finally, electrochemical measurements were done using a three-electrode cell in 1 M  $\text{LiClO}_4$ /polypropylene carbonate solution using a scan rate of 10  $\text{mV s}^{-1}$  through the voltage range of -500 mV to +250 mV as reported previously [15]. The area of the working electrode exposed to the electrolyte was 1  $\text{cm}^2$ .

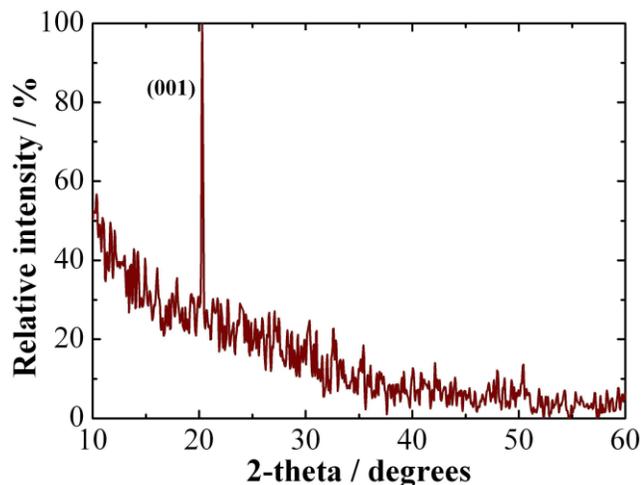


Fig. 1. XRD pattern of the as-prepared coating for 2000s at room temperature.

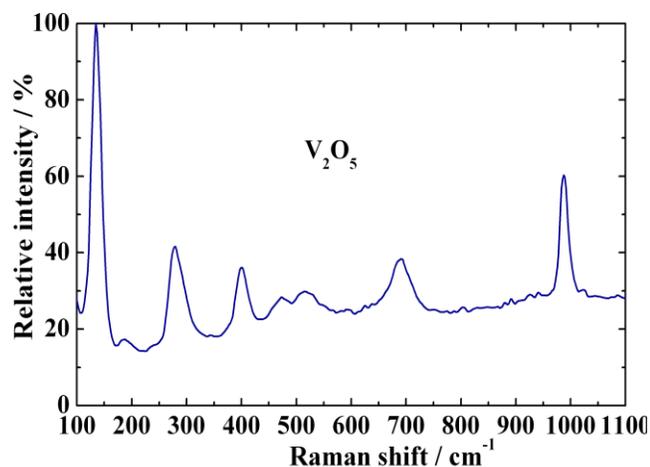


Fig. 2. Raman spectrum of the  $\text{V}_2\text{O}_5$  coating grown for 2000 s at room temperature.

## Results and discussion

Fig. 1 shows the XRD pattern of the sample grown for 2000 s. As can be seen, one characteristic peak at 20.3 degrees with Miller index (001) is obtained, which is assigned to  $\text{V}_2\text{O}_5$  [11]. It did not give sufficient number of reflections to allow the calculation of the cell parameters; hence Miller index was assigned by comparison with the literature. Furthermore, for deposition periods < 2000 s, there were no peaks observed related with vanadium oxide possibly due to the low oxide coverage of the FTO glass substrate. Fig. 2 presents the Raman spectrum of  $\text{V}_2\text{O}_5$ ,

which is in excellent agreement with what reported previously [15]. Regarding the coatings grown for deposition periods < 2000 s, the peaks were lower in intensity and broader suggesting that the results from the XRD and micro-Raman spectroscopy are in full agreement.

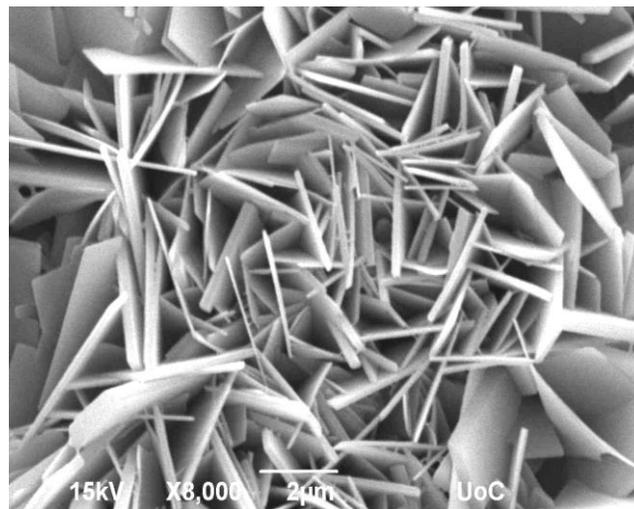


Fig. 3. SEM image of the  $\text{V}_2\text{O}_5$  coating grown for 2000 s.

SEM images of the grown samples for 600 and 1200 s present smooth surfaces with sparsely distributed structures, while for the 2000 s, a porous structure is observed that is consisted of microplates (Fig. 3).

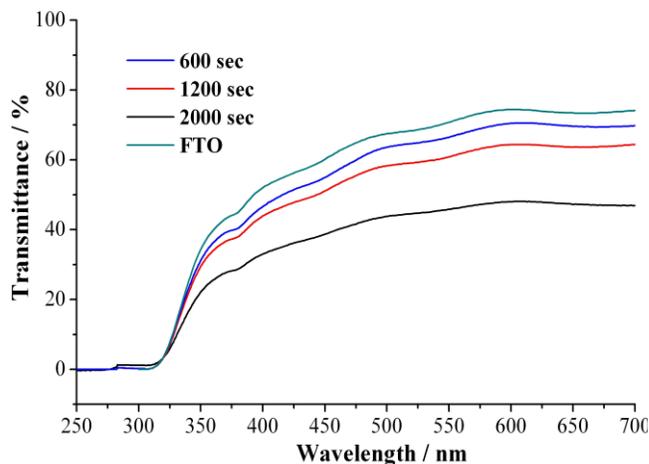


Fig. 4. Transmission spectra of the FTO glass substrate and the as-prepared coatings for 600, 1200 and 2000 s.

Transmission spectra of the vanadium oxide samples grown for 600, 1200 and 2000 s, and the reference FTO glass substrate are also shown in Fig. 4. The transmission of the oxide sample grown for 2000 s has the lowest absolute value reaching 48 % at 600 nm compared with the rest. Increase of the growth period has the expected effect on the deposited mass as observed by comparing the morphology and the transmission values of the two lowest periods. It is thus expected that the electrochemical properties of the 2000 s sample will be the best in the series. Since one would assume the wider is the exposed surface of the sample, the higher value of the interchanged charge is expected.

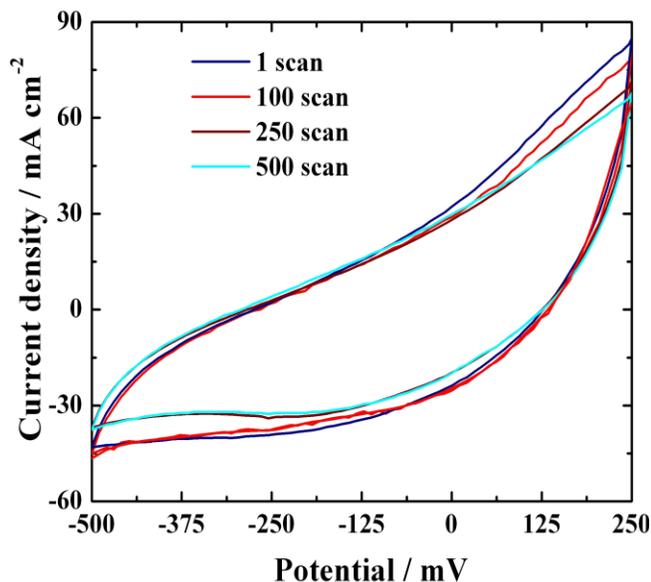


Fig. 5. Cyclic voltammograms for the as-prepared  $V_2O_5$  for 2000 s at a scan rate of  $10 \text{ mV s}^{-1}$  and 1, 100, 250 and 500 scans. Electrode area was  $1 \text{ cm}^2$ .

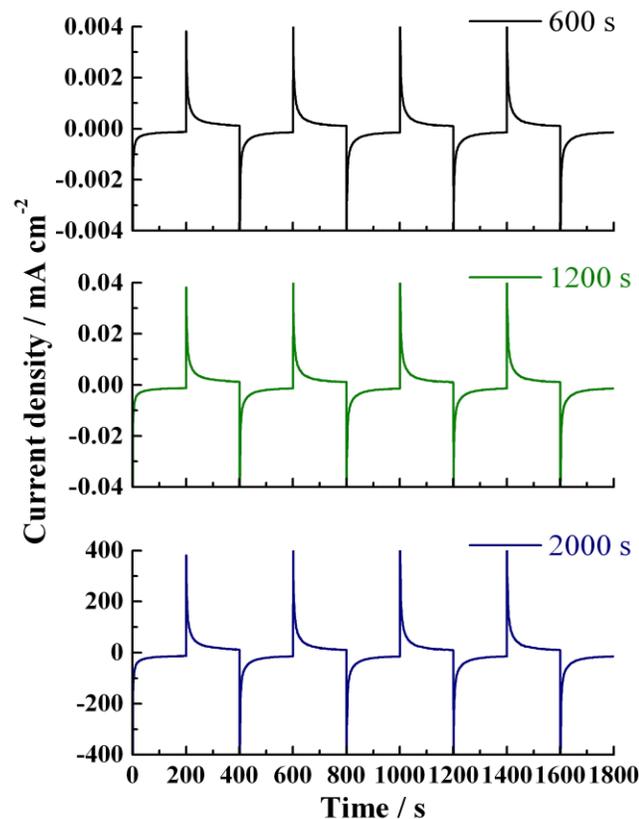


Fig. 6. The chronoamperometric response recorded at  $-500 \text{ mV}$  and  $+250 \text{ mV}$  at an interval of  $200 \text{ s}$  for the vanadium oxides grown on FTO glass substrate for 2000 s.

To evaluate the stability of the  $V_2O_5$  coating grown for 2000 s as a function of the scan numbers, cyclic voltammetry experiments were conducted switching the potential from  $-500 \text{ mV}$  to  $+250 \text{ mV}$  at a scan rate of  $10 \text{ mV s}^{-1}$  (Fig. 5). No long-term degradation can be observed for the sample grown for 2000 s especially after 250 scans as evident from the similarity between the 250<sup>th</sup> and the

500<sup>th</sup> scan. In terms of the other samples, a decrease of current density by two degrees of magnitude is observed after the first five runs because the amorphous materials dissolve more easily than crystalline ones during lithium ion intercalation/deintercalation as already reported by others [16, 17].

Finally, the switching response for all samples was studied using chronoamperometry in the same range of potential as previously (Fig. 6). The amount of lithium charge interchanged between the oxide and the electrolyte was calculated by integration of current density [15]. We found that the intercalated and deintercalated charges are similar to each other within 10 % per cycle. However, the amount of charge for the 2000 s sample is  $0.43 \pm 0.02 \text{ C cm}^{-2}$  i.e. three degrees of magnitude higher than the one grown for 1200 s. Based on the charge value, the specific capacitance of the sample was calculated to be  $286 \text{ F g}^{-1}$  as derived from the equation in [11] if one considers  $m = 0.002 \text{ g}$  and  $\Delta V = 750 \text{ mV}$ .

## Conclusion

Vanadium pentoxide has been simply electrodeposited using an aqueous solution of  $NH_4VO_3$  at room temperature for various deposition periods. The  $V_2O_5$  coating grown for 2000 s presented a porous structure that is consisted of microplates with a crystalline signature albeit being prepared at room temperature. Electrochemical studies of the same sample revealed a high and reversible amount of charge being  $0.43 \text{ C}$ , interchanged between the oxide and the electrolyte with a respective specific capacitance of  $286 \text{ F g}^{-1}$ . This notable response was attributed to the high surface area that favors charge transfer between the oxide and the electrolyte. We may then propose that electrodeposition is a suitable technique for the environmental-friendly growth of low-cost  $V_2O_5$  electrodes that could lead in significant advances for energy-related applications in plastic industry.

## Reference

- Liu, Y.; Clark, Q.; Zhang, D.; Yu, D.; Liu, D.; Liu, J.; Cao, G.; *Adv. Energy Mater.* **2011**, *1*, 194.  
DOI: [10.1002/aenm.201000037](https://doi.org/10.1002/aenm.201000037)
- Granqvist, C.G.; *Sol. Energ. Mat. Sol. C* **2000**, *60*, 201.  
DOI: [10.1016/S0927-0248\(99\)00088-4](https://doi.org/10.1016/S0927-0248(99)00088-4)
- Lantelme, F.; Mantoux, A.; Groult, H.; Lincot, D.; *J. Electrochem. Soc.* **2003**, *150*, A1202  
DOI: [10.1149/1.1595658](https://doi.org/10.1149/1.1595658)
- Lee, J.K.; Kim, G.P.; Kyu Song, I.; Baeck, S.H.; *Electrochem. Commun.* **2009**, *11*, 1571.  
DOI: [10.1016/j.elecom.2009.05.053](https://doi.org/10.1016/j.elecom.2009.05.053)
- Vernardou, D.; Pemble, M.E.; Sheel, D.W.; *Chem. Vapor Depos.* **2006**, *12*, 263.  
DOI: [10.1002/cvde.200506419](https://doi.org/10.1002/cvde.200506419)
- Livage, J.; *Chem. Mater.* **1991**, *3*, 578.  
DOI: [10.1021/cm00016a006](https://doi.org/10.1021/cm00016a006)
- Bouzir, A.; Benramdane, N.; Nakrela, A.; Mathieu, C.; Khelifa, B.; Desfeux, R.; Da Costa, A.; *Mater. Sci. Eng.* **2002**, *95*, 141.  
DOI: [10.1016/S0921-5107\(02\)00224-6](https://doi.org/10.1016/S0921-5107(02)00224-6)
- Vernardou, D.; Spanakis, E.; Kenanakis, G.; Koudoumas, E.; Katsarakis, N.; *Mater. Chem. Phys.* **2010**, *124*, 319.  
DOI: [10.1016/j.matchemphys.2010.06.040](https://doi.org/10.1016/j.matchemphys.2010.06.040)
- Vernardou, D.; Drosos, H.; Fasoulas, J.; Koudoumas, E.; Katsarakis, N.; *Thin Solid Films*, **2014**, 555, 169.  
DOI: [10.1016/j.tsf.2013.05.144](https://doi.org/10.1016/j.tsf.2013.05.144)
- Ghosh, A.; Ra, E.J.; Jin, M.; Jeong, H.-K.; Kim, T.H.; Biswas, C.; Lee, Y.H.; *Adv. Funct. Mater.* **2011**, *21*, 2541.  
DOI: [10.1002/adfm.201002603](https://doi.org/10.1002/adfm.201002603)

11. Vernardou, D.; Sapountzis, A.; Spanakis, E.; Kenanakis, G.; Koudoumas, E.; Katsarakis, N.; *J. Electrochem. Soc.* **2013**, *160*, D6.  
DOI: [10.1149/2.054301jes](https://doi.org/10.1149/2.054301jes)
12. Drosos, H.; Sapountzis, A.; Koudoumas, E.; Katsarakis, N.; Vernardou, D.; *J. Electrochem. Soc.* **2012**, *159*, E145.  
DOI: [10.1149/2.017208jes](https://doi.org/10.1149/2.017208jes)
13. Lee, J.W.; Pyun, S.I.; *J. Power Sources* **2003**, *119-121*, 760.  
DOI: [10.1016/S0378-7753\(03\)00217-9](https://doi.org/10.1016/S0378-7753(03)00217-9)
14. Hu, C.C.; Huang, C.M.; Chang, K.H.; *J. Power Sources* **2008**, *185*, 1594.  
DOI: [10.1016/j.jpowsour.2008.08.017](https://doi.org/10.1016/j.jpowsour.2008.08.017)
15. Vernardou, D.; Paterakis, P.; Drosos, H.; Spanakis, E.; Povey, I.M.; Pemble, M.E.; Koudoumas, E.; Katsarakis, N.; *Sol. Energ. Mat. Sol. C.* **2011**, *95*, 2842.  
DOI: [10.1016/j.solmat.2011.05.046](https://doi.org/10.1016/j.solmat.2011.05.046)
16. Arnoldussen, T.C.; *J. Electrochem. Soc.* **1981**, *128*, 117.  
DOI: [10.1149/1.2127350](https://doi.org/10.1149/1.2127350)
17. Ng, S.H.; Chew, S.Y.; Wang, J.; Wexler, D.; Tournayre, Y.; Konstantinov, K.; Liu, H.K.; *J. Power Sources* **2007**, *174*, 1032.  
DOI: [10.1016/j.jpowsour.2007.06.166](https://doi.org/10.1016/j.jpowsour.2007.06.166)

## Advanced Materials Letters

### Publish your article in this journal

[ADVANCED MATERIALS Letters](#) is an international journal published quarterly. The journal is intended to provide top-quality peer-reviewed research papers in the fascinating field of materials science particularly in the area of structure, synthesis and processing, characterization, advanced-state properties, and applications of materials. All articles are indexed on various databases including [DOAJ](#) and are available for download for free. The manuscript management system is completely electronic and has fast and fair peer-review process. The journal includes review articles, research articles, notes, letter to editor and short communications.

