



Nano-vanadium pentoxide films for electrochromic displays



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ABSTRACT

We demonstrate the benefit of homemade nanopowder precursors on the electrochromism of V₂O₅ films deposited by the “Doctor Blade” method. Using the polyol process, nanostructured V₂O₅ powder were synthesized. Orthorhombic V₂O₅ thin films deposited from as-synthesized powder exhibit good cycling stability associated with significant reflectance modulation in both lithium- and sodium-based electrolytes. The orange to green reversible color change appears well suitable for display application. To conclude, the electrochromic performances of complete devices using WO₃ as complementary electrode and 0.3 M Lithium Bis(Trifluoromethanesulfonyl)imide LiTFSI in BMITFSI plastified with polymethylmetacrylate (PMMA) membrane electrolyte are reported.

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1. Introduction

Electrochromism is a phenomenon in which materials and devices are able to change their optical properties in a reversible and persistent way under an applied voltage [1–4]. The applications of electrochromic devices, ECDs, are multifold from smart windows in cars and buildings to spacecraft thermal control, as transmittive or reflective properties and visible or infrared domain are concerned. Among varieties of electrochromic materials, transition metal oxides have received special interest [5] partially due to their higher stability as compared to organic EC. The modification of the optical properties often results from an insertion of small ions (i.e; H⁺ or Li⁺) associated with reversible redox reactions between the different valence states of the metal. Tungsten trioxide, WO₃, remains by far the typical electrochromic inorganic material, switching to a blue color upon reduction and cation insertion. For practical use and device construction, WO₃ needs to be associated with complementary oxides. If anodically colored IrO_x [6–8] and NiO [9–13] based thin films have been largely studied, V₂O₅ appears to be an interesting alternative candidate. Indeed, orthorhombic V₂O₅ has been investigated for a number of applications, such as lithium batteries, in respect of its layered structure with good cation intercalation ability and low voltage required [14,15]. Due to their layered structures, intercalation of sodium into the structure of V₂O₅ has been investigated for novel applications in sodium ion batteries [16]. To our knowledge, the

electrochromic properties in V₂O₅ associated with Na insertion has not yet been reported.

V₂O₅ exhibits both anodic and cathodic electrochromism properties and multicolor display [17]. However, the lithiation processes in V₂O₅ bulk are relatively slow because the low electric conductivity (10⁻³–10⁻² S.m⁻¹) and the low Li⁺ diffusion coefficients (10⁻¹³–10⁻¹² cm².s⁻¹) [18–20]. In comparison with V₂O₅ bulk, the nanostructured of V₂O₅ is characterized by a large electrochemical surface area and good interconnectivity for electronic conductivity [21]. The electrochromic performance of vanadium pentoxide depends on several parameters including the pore size of intercalation sites, the film thickness and the deposition method. Several methods, including pulsed laser deposition [22], vacuum evaporation [23,24], thermal evaporation [25], sputtering [26], ultrasonic spraying [27] and sol-gel [28], have been used for the deposition of V₂O₅ thin films. Nearly all of them deal with transparent thin films whereas the properties of non-transparent “thick” films remains poorly investigated. In addition, the performance of the electrochromic materials is directly related to the penetration depth of the cations and the accessibility of the electroactive sites, thus explaining the growing interest for nanomaterials.

Herein, nano-sized vanadium pentoxide powders were synthesized by the polyol method. Focusing on EC displays as application, mainly correlated to a modulation of the reflectance, micrometer-thick films were prepared from the as-synthesized V₂O₅ nanopowders using a simple and cost-effective method, namely, Doctor Blade, at low temperatures (150 °C), suitable even for plastic or paper substrates.

Finally, the electrochromic activity of V₂O₅ films is reported both in lithium- and sodium-based electrolytes, while their integration in a complete device shows good optical reflectance modulation, nice

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cyclability, and stability. The current results encourage future research in the area of multicolored (flexible) displays based on inorganic EC.

2. Experimental details

2.1. Polyol synthesis of V_2O_5 powder and characterization

All of the chemical reagents were purchased from Acros Organics and utilized without further purification. Ammonium metavanadate (NH_4VO_3) was used as vanadium source and ethylene glycol ($H_6C_2O_2$) as template. In a typical synthesis, NH_4VO_3 (1.669 g) was added to 100 mL $H_6C_2O_2$. The resulting mixture was heated to 70 °C under continuous stirring to obtain a yellow sol which was then transferred into a 100 mL glass flask and refluxed at 170 °C for 3 h. At the end of the reaction, a vanadylglycolate (VEG) precipitate was obtained. The precipitate was centrifuged and washed several times with ethanol to remove the organic product and dried in an oven at 80 °C. To prepare the final V_2O_5 powder, the VEG precursors were calcined for 2 h at 500 °C. This method in which the polyol serves as both the solvent and the reducing agent offers several advantages as compared to other chemical methods. Indeed, the polyol process is commonly considered as an energy efficient and environmentally benign process, also allowing the preparation of large quantity of powders. The powder structure was characterized by X-ray diffraction analysis (Philips PW 1820, PANalyticalX'Pert instrument, 2θ range from 8 to 80° and $\lambda_{CuK\alpha 1} = 1.54056$ Å). Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images were recorded with a SEI instrument (operating at 5 kV) microscope and JEOL JSM-6700F (operating at 5 kV) microscope, respectively.

3. Film preparation and characterization

V_2O_5 films were deposited by the “Doctor Blade” method from homemade powder, synthesized by the polyol method. Firstly, 0.725 g of powder was dispersed into 2.5 ml distilled water and acetyl acetone (AcAc). The resulting dilute was stirred for 12 h at room temperature and after aliquots of the as-prepared colloidal V_2O_5 solution were deposited on the ITO ($In_2O_3:Sn$) coated glass. After deposition, V_2O_5 thin films were dried at 150 °C for 3 h to eliminate organic products and ensure adhesion to the substrates. The thickness of the V_2O_5 films, measured using a Dektak mechanical profilometer, was of about 3.9 ± 0.2 μm. The films' structure was characterized by X-ray diffraction (XRD) analysis (Philips PW 1820, PANalyticalX'Pert instrument, 2θ range from 8 to 80° and $\lambda_{CuK\alpha 1} = 1.54056$ Å). The morphology of the layers was investigated using a JEOL JSM-840 (operating at 15 kV) microscope.

4. Electrochromic measurements

Electrochemical measurements of V_2O_5 films on ITO/glass were carried out in a three electrodes cell configuration using a BioLogic SP50 potentiostat/galvanostat apparatus. The counter-electrode and reference electrode consisted of a platinum foil and Saturated Calomel Electrode, SCE ($E_{SCE} = 0.234$ V/ENH), respectively. The operating voltage was controlled between -0.4 and 1.8 V at different scan rates, from 2 to 50 mV/s, in both lithium- and sodium-based electrolytes, namely, 0.3 M lithium bis-trifluoromethanesulfonimide (LiTFSI, Solvionic, purity > 99.99%) in 1-butyl-3-methylimidazoliumbis-(trifluoromethanesulfonyl)-imide (BMITFSI) and sodium bis-(trifluoromethanesulfonate)-imide (NaTFSI, Solvionic, purity > 99.99%) in 1-butyl-3-methylimidazoliumbis-(trifluoromethanesulfonyl)-imide (BMITFSI). All the electrochemical measurements were performed at room temperature. The optical reflectance of V_2O_5 thin films was measured in situ using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. The film reflectance was also analyzed using a Konica Minolta CM-700D spectrophotometer allowing the direct determination of colorimetric

parameters in the CIE $L^*a^*b^*$ colorimetric space. The optical contrast (ΔE^*) between two color states was calculated following the equation:

$$\Delta E^* = [(L^*_1 - L^*_2)^2 + (a^*_1 - a^*_2)^2 + (b^*_1 - b^*_2)^2]^{1/2} \quad (1)$$

5. Results and discussion

5.1. V_2O_5 powders

The crystallinity of the orange powder synthesized by the polyol process before and after calcination was studied by XRD. Before calcination, the XRD pattern (Fig. 1a) indicates that the d-spacing values of all diffraction peaks are identical to those of the VEG (JCPDS No 49-2497) with space group C2/c. After calcination (Fig. 1b), the XRD pattern reveals the presence of narrow peaks, suggesting a material with high crystallinity. The d-spacing values of all diffraction peaks are identical to those of the orthorhombic crystalline phase V_2O_5 (Space Group: Pmmn) with lattice constants $a = 3.564$ Å, $b = 11.510$ Å, and $c = 4.373$ Å (JCPDS # 85-0601). No peak of any other phase or impurity was detected from the XRD pattern showing that V_2O_5 with high purity can be synthesized via polyol synthesis at 170 °C for 3 h. The average crystallite size was calculated using the Scherrer's formula [29]:

$$L = 0.89\lambda/\beta \cos\theta \quad (2)$$

where L is the average crystallite size in nm, $\lambda = 0.154056$ nm, β is the full width at the half maximum, and θ is the diffraction angle. The average crystallite size value, calculated from three of the main peaks of the XRD pattern, is about 86 nm.

The SEM and TEM micrographs (Fig. 2) show that the morphology of the as-synthesized V_2O_5 powder is homogenous. At low magnification (Fig. 2a), packs of quasi-spherical agglomerates with individual size of about 2–3 μm diameter are visible. At intermediate magnification, hierarchical structuration is observed: the agglomerates are constituted from the assembly of over-micrometric crystallite strands or acicular platelets (Fig. 2b). The TEM images (Fig. 2c, d) captured on the few non-agglomerated crystallites show various crystallite sizes ranging

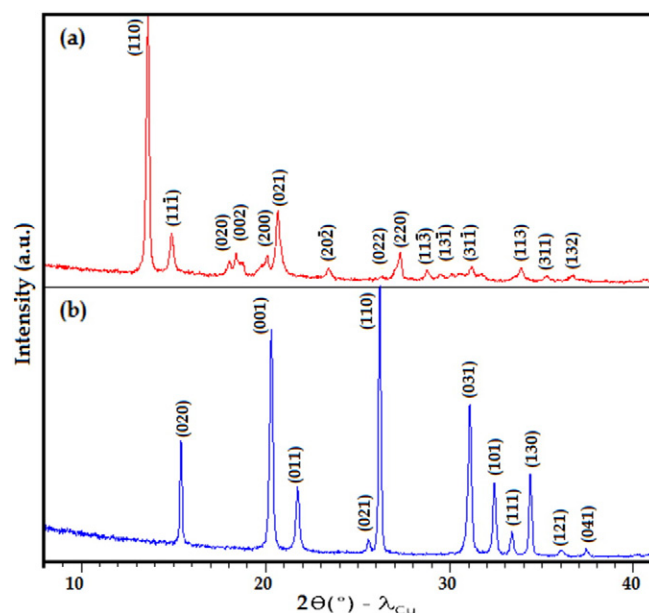


Fig. 1. Powder X-ray diffraction patterns of the as-synthesized V_2O_5 powders before (a) and after (b) calcination.

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