

SUPPORTING INFORMATION

Three-Colors Electrochromic Lithiated Vanadium Oxides: The Role of Surface Superoxide in the Electro-generation of Red State

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Synthesis of PS and EFS samples and Deposition on FTO glass.

Amorphous vanadium oxide (α -V₂O₅) was synthesized by direct precipitation from a 0.2 M water solution of ammonium metavanadate (NH₄VO₃ ACS reagent \geq 99.0% from Sigma-Aldrich) and nitric acid (69% hyperpure from Panreac). Precipitation was carried out pouring a diluted nitric acid solution into the hot ammonium metavanadate solution (80 °C), using an optimized H⁺/V ratio of 2. Crystalline orthorhombic vanadium oxide (α -V₂O₅) was obtained by calcination of amorphous vanadium oxide at 375 °C for 2h, in closed muffle furnace in air atmosphere. As prepared starting material α -V₂O₅ was carefully mixed with Li₂CO₃ (puriss. p.a. from Sigma-Aldrich) in the stoichiometric ratio 2:1. Such mixture was treated for 6 hours at 400 °C in a tubular furnace (Carbolite MTF 12/38/400) under nitrogen flushing. Then, the obtained powder (hereafter indicated as PS, Precursor Sample) was manually ground in an agate mortar. Afterwards, the water soluble fraction of PS sample was extracted according to the following procedure: 40 mg of PS powder were dispersed in 5 mL of ultrapure water and left to settle for 12 h, then the yellow solution was removed from sediment. The precipitate was dried in oven at 50 °C for 3 h yielding ca. 12 mg of product indicated as EFS (Electrochromic Fraction Sample). 3.5 mg of EFS sample were dispersed in 200 μ L of distilled water and sonicated for 5 minutes. 20 μ L of the suspension was drop casted in a masked circular area (diameter 8 mm) of glass FTO (From Solaronix, 30 Ω /sq) and dried in oven at 50 °C for 1 h.

Structural and Morphological Characterization

X-ray diffraction profiles of the sample PS was obtained using a Philips Xpert PW3040/00 MPD, equipped with Co K α radiation ($V = 40$ kV, $i = 40$ mA) and a curved graphite monochromator. The diffraction profile, collected in the 2θ range between 5° and 100° with an acquisition step of 0.05° and a time per step of 5 s, is reported in Fig. S1. Samples morphologies were analysed by means of field-emission scanning electron microscopy (FESEM, JEOL-JSM-6700F).

XPS analysis.

The XPS measurements were carried out with a PHI Model 5000 electron spectrometer equipped with an Aluminum anode (1486 eV) monochromatic source with a power of 25.6 W and the high resolution scan with a 11.75 eV pass energy. The instrument typically operates at pressures below 5×10^{-8} mbar. Electrochromic materials were analysed in the form of thin film on glass/FTO support; samples were preliminary degassed overnight at r.t. A PHI patented dual beam charge neutralization method, combining low energy ions and electrons, was employed to reduce the possible charging effect of the X-rays on the samples. The binding energies obtained in the XPS analysis were corrected for specimen charging by referencing the C 1s line to 284.6 eV. XPS spectra were measured for the V2p 3/2 and O1s peaks before and after the application of +2 and -2 V of potential and were decomposed (where necessary) by means of an automatic least squares fit procedure.

Electrochemical and Spectro-Electrochemical Measurements.

CH Instrument 600D Station (galvanostat/potentiostat, CHI instruments, Austin, USA) was used for electrochemical and spectro-electrochemical measurements by registering current vs. potential and current vs. time curves. Cyclic voltammeteries of FTO/EFS samples were registered in 0.5 M LiTFSi(Lithium

Bis(Trifluoromethanesulfonyl)Imide) in Propylene Carbonate (PC) with a customized three electrodes optical glass cell (see Fig. S5 for Setup) with glass FTO/EFS as working electrode, a Platinum plate as counter electrode and a commercial aqueous Ag/AgCl electrode (from CH Instruments Austin Texas) as reference electrode. Spectro-electrochemical measurements were carried out by placing the customized optical glass cell in the sample compartment of a Varian Cary 5000 UV-VIS spectrophotometer. Two different types of measurement were performed by coupling the spectrophotometer with the CH 600D potentiostat. The first type of experiment was the registration of the ECD complete UV-VIS absorption spectrum as function of applied potential; the second type of experiment consisted in the acquisition of the ECD absorption at a specific wavelength as function of time during potential modulation i. e. repeated bleaching and coloring cycles. The wavelength selected was that showing maximum variation of Percent Transmittance ($\Delta T\%$) in the corresponding full spectrum measurement. The second type of experiment was necessary to measure the switching time of bleaching (ST_B) and the switching time of coloring (ST_C) for the FTO/EFS samples. The switching time for Bleaching (ST_B) and the switching time for coloring (ST_C) can be easily calculated from the T% vs. time curves by the time necessary after bias inversion to reach the 80% of the maximum (bleaching, oxidation) or minimum (coloring, reduction) T% starting from previous potential step minimum or maximum T% respectively.

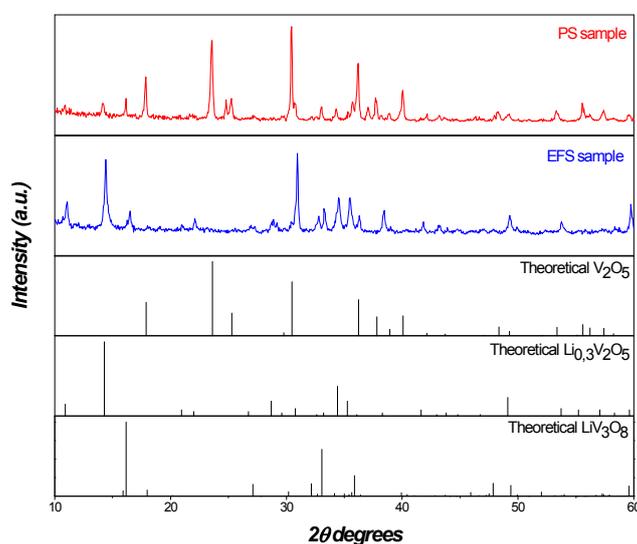


Figure S1. X-ray powder diffraction pattern of PS and EFS, along with the reference patterns of identified phases V₂O₅ (JCPDS No. 01-072-0433), Li_{0.3}V₂O₅ (JCPDS No. 00-018-0755) and LiV₃O₈ (JCPDS No. 01-072-1193).

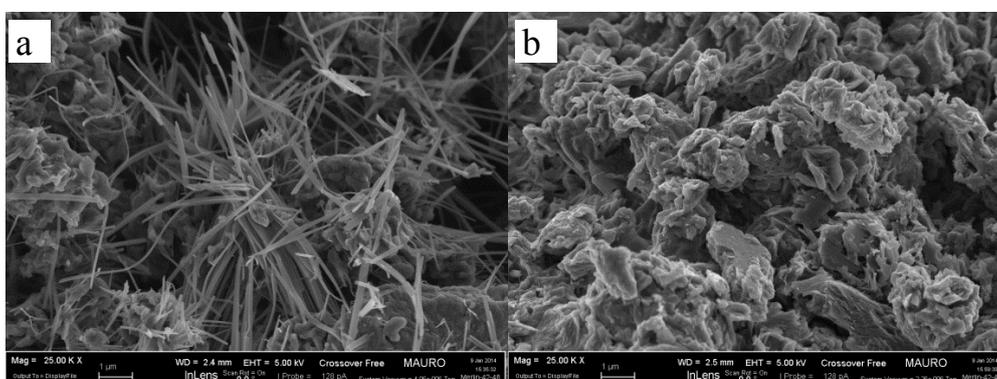


Figure S2. FESEM micrographs (field-emission scanning electron microscopy FESEM, JEOL-JSM-6700F) of (a) PS and (b) EFS .

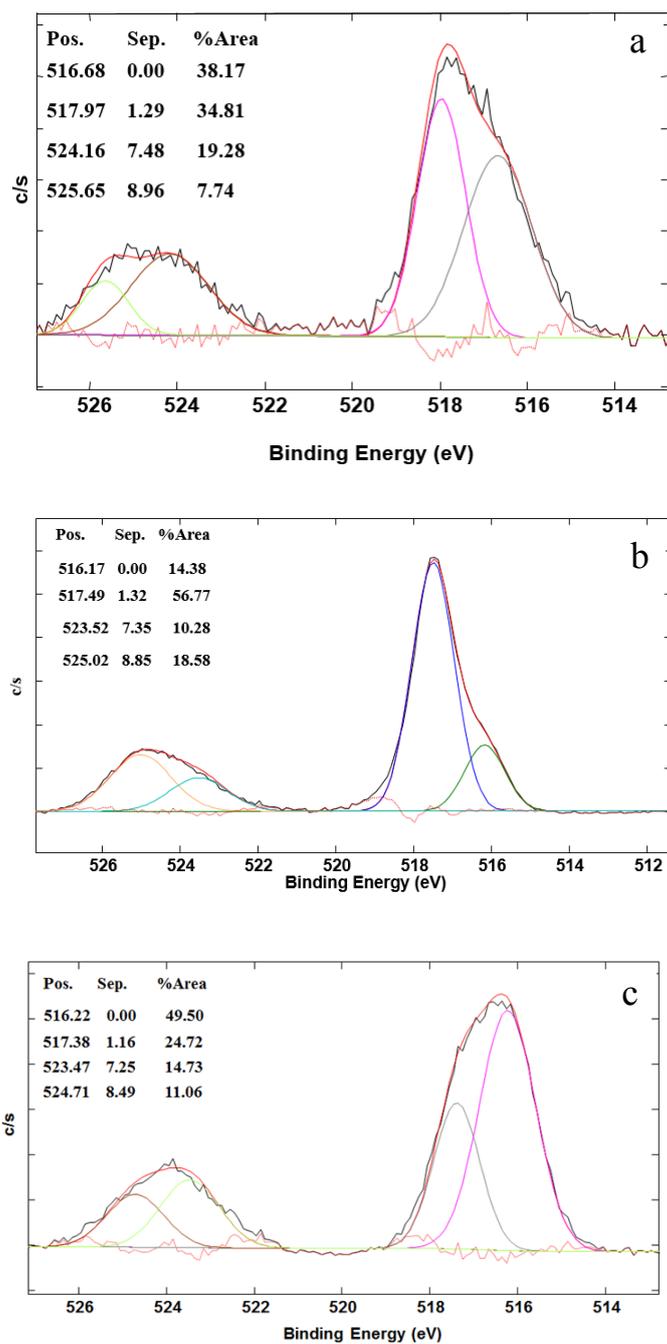


Figure S3. V2p3 XPS spectrum collected from EFS (a) before the application of any potential; (b) after the application of +2V vs. Ag/AgCl for 60 s; (c) after the application of -2V vs. Ag/AgCl for 60 s .

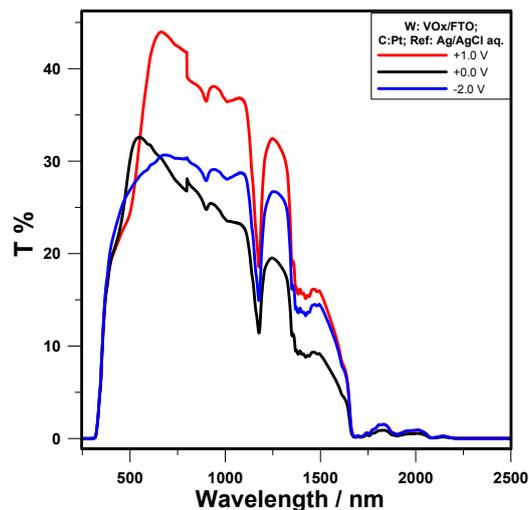


Figure S4. Full range UV-VIS absorption spectrum of EFS deposited on glass FTO after biasing at different potentials for 60s.



Figure S5. Setup of customized optical glass cell for Spectro-Electrochemical measurements. W: FTO glass/EFS Working Electrode; C: Platinum Plate Counter Electrode; R: aqueous Ag/AgCl Reference Electrode.

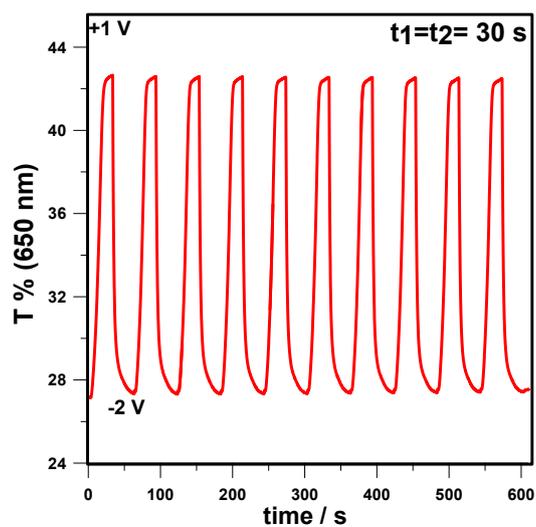


Figure S6. Typical T%(650 nm) vs. time curve of FTO/EFS electrode during repeated potential switching cycles.