



Cathodic electrocrystallization and electrochromic properties of doped rechargeable oxotungstates

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ABSTRACT

We extend the technique of preparing oxotungstate thin films by cathodic electrocrystallization from metastable acidic solutions to fabricate vanadium- and molybdenum-doped films on platinum and fluorine-doped tin oxide (FTO). By means of cyclic voltammetry, we demonstrate a wider potential interval of highly reversible redox activity for these doped films, as compared to purely tungstate films. Electrochromic behavior in this region is dependent on the nature of the doping element. We characterize the microstructure of these films using scanning tunneling and atomic force microscopy. We also apply Raman and UV–vis spectroscopy to characterize the acidic deposition solutions. In tungstate–vanadate bath, we observe evidence of mixed isopolyanions. We also found some features of less stable mixed anions in the tungstate–molybdate bath, characterized phase composition of these films by means of XRD, and explain the results in the terms of parallel deposition from coexisting molecular precursors.

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1. Introduction

Recently [1], we proposed a new electrodeposition technique to fabricate crystalline oxotungstate films on conducting supports. In contrast to previously described techniques based on peroxide-containing deposition baths (peroxotungstate solutions prepared by dissolution of tungsten metal); our procedure utilizes a long-lived metastable acidic solution of isopolytungstates. This procedure results in the formation of highly rechargeable films. These films undergo electrochromic transition at potentials 0.4–0.5 V more positive than conventional sputtered films of tungsten oxide [2]. These electrocrystallized films are composed mainly of tungsten oxohydroxo compounds, which are able to stabilize the W(V) oxidation state, even under open circuit [3,4].

Our electrocrystallization procedure [1] is tunable, in that it can be modified in order to obtain more complex materials of desired functionality. In particular, our technique can be combined with Pt deposition [5] to provide hydrogen spill over, a phenomenon of interest for catalysis. Another possible modification of this technique is described below. This modification consists of doping oxotungstate with vanadium or molybdenum in order to extend the potential region of rechargeability to even more positive potentials. Such a modification can affect the electrochromic characteristics

as well, as was already demonstrated for doped sol–gel and sputtered films (see, for example [6–9]). In these previous works, the authors attempted to improve the reversibility of the film redox response and the width of the potential region corresponding to electrochromic transition. They found that the potential boundary shifted to more positive values, but they were not completely successful with reversibility. This lack of success was likely due insufficient mixing of the components at an atomic level.

We rely on isopolyanions as the molecular precursors of electrodeposited films. Mixed W–V and W–Mo anions are widely known [10]. Our goal is to understand how tungstates and doping oxoanions interact in the deposition solution, and what their respective initial locations are in a solid electrodeposited film. The latter aspect is rather challenging, as the available spatial resolution of microanalysis is insufficient to study the heterogeneous distribution of elements in a nanocrystalline material. As for the former aspect, we found no data in literature on the formation of mixed polyanions in highly acidic solutions (in particular for pH close to zero, which is crucial for oxide electrodeposition). With this study, we will attempt to fill in this gap.

2. Experimental

Deposition solutions were prepared from Na₂WO₄·2H₂O and NaVO₃·2H₂O (Solution I) or Na₂WO₄·2H₂O and Na₂MoO₄·2H₂O (Solution II) using Milli-Q water (18 MΩ). All of these reagents were of pro-analysis quality. Deposition of electrochromic films

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was performed from solution with a 9:1 molar ratio of tungstate to doping oxometalate, and a total concentration of 12 mM (based on the oxometalate monomeric unit). To avoid precipitation of tungstic, molybdic, and vanadic acids, the supporting electrolyte (sulphuric acid, Merck) was added carefully to hot aqueous solutions of oxometalates only after complete dissolution of salts. The final acid concentration (0.5 M, pH ~ 0.4) was always the same. Argon was used for deaeration of solutions (usual deaeration time was 30–60 min).

Solution I appeared to be stable if two separate acidic solutions of tungstate and vanadate were mixed. However immediate precipitation took place if the same procedure was performed with solution II. We were able to obtain solution II in a stable form only by mixing tungstate and molybdate aqueous solutions, with subsequent acidification of this mixture.

For preliminary characterization of deposition solutions, DC polarography, UV–vis spectroscopy, and Raman spectroscopy were applied.

Raman spectra were measured with a RamanRXN1 fiber-optic spectrometer (Kaiser Optical Systems) utilizing a 532 nm laser. To avoid overlap of the most intensive SO_4^{2-} band (980 cm^{-1}) with the oxometalate bands, 0.5 M HCl was used in the Raman series (this HCl concentration is much lower than the concentration required for oxochloride formation [11]). Spectra were normalized to the intensity of the water band ($\sim 1600\text{ cm}^{-1}$) to avoid the effects of variable solution transparency, and to exclude the dependence of data on the rate of solution aging. To create the W–V solutions, the overall concentration was kept the same as in solution I, and the ratio of the components was varied. For the W–Mo series, the tungstate concentration was kept the same as in solution II (10.8 mM), and various amounts of molybdate were added. Spectra were collected 15 min after solution preparation (it takes 8–10 min to collect one spectrum). For longer aging times of ca. 30 min, no significant changes in the spectra were observed.

For electrochemistry, a PAR273 potentiostat and a cell with three separated compartments were used. The potentials are reported versus Ag/AgCl reference electrode. Potentiodynamic deposition mode was used, with a -0.17 V lower potential boundary, and an upper potential boundary of 1.05 or 0.9 V. The scan rate was set to 50 or 100 mV s^{-1} . Supports were 0.1–0.2 mm thick Pt foils, or glass coated with fluorine-doped tin oxide (FTO, Solaronix SA, typically $20\text{ mm} \times 10\text{ mm} \times 1\text{ mm}$). Other details of the electrochemical experiments can be found in Refs. [1–3].

For polarography details, see Ref. [12]. Current was registered at the end of the drop lifetime, because the polarograms were affected by adsorption/self-inhibition phenomena typical at least for tungstates, and molybdates. Solutions were similar to I and II, but more diluted (total concentration 1.2 mM, with a varied ratio of components). Direct polarographic study of 12 mM solutions presented the risk of excessively high currents and ‘inheritance’ effects induced by subsequent chemical steps. Aging time was ca. 60 min because of the need to deaerate the solutions.

XRD experiments were performed as described in Ref. [4].

Transmission spectra (250–700 nm) were collected with the use of a Unicam SP 1800 UV–vis spectrophotometer in a 1 cm quartz cuvette. The total concentration of the solutions was 1.2 mM, as in polarographic experiments, to avoid an unmeasurably large light absorption. Aging time was 15–60 min, and no noticeable dependence of the spectral properties on aging time was observed. To monitor electrochromic transitions (350–700 nm), a FTO sample with a predeposited film was placed in a 1 cm glass cuvette, which was filled with 0.5 M H_2SO_4 and equipped with a small platinum counter electrode and a miniature salt-bridge (connected to a small Ag/AgCl reference electrode). Potential was controlled using a Zahner IM6ex potentiostat. In contrast to all purely electrochemical

experiments, the solutions remained aerated in the course of these measurements.

All STM measurements were performed using a commercial *ex situ* scanning tunneling microscope, ‘‘UMKA’’, with extended spectroscopic facilities (Concern ‘‘Nanoindustry’’, Moscow). A Pt–Ir tip (10% Ir) of 0.5 mm diameter was mechanically sharpened. For topographic measurements, $\pm 0.3\text{ V}$ tunneling voltage was applied (positive voltage corresponds to positive tip polarization), in combination with a 0.3–1.0 nA tunneling current (the exact value was specially chosen for each particular sample). The samples were either heat treated or washed with ethanol (to remove excess moisture and salts from the surface) and dried in air at temperatures up to 50°C . AFM measurements were performed in tapping mode using a Multimode SPM System equipped with a Nanoscope V controller (Veeco Instruments).

Quantitative elemental analysis was performed with a JEOL JSM6490LV scanning electron microscope (SEM) equipped with an Oxford Instruments attachment for energy dispersive X-ray analysis (EDX). This tool was operated under INCA software. The presence of doping elements in the films was confirmed unambiguously.

3. Results and discussion

3.1. Solution composition

UV–vis spectra of both W–V and W–Mo solutions exhibit non-zero absorption below 400–500 nm. Wavelength-independent absorption in the visible region (typical of colloidal particles) is absent. Solution I starts to absorb at a higher wavelength than does

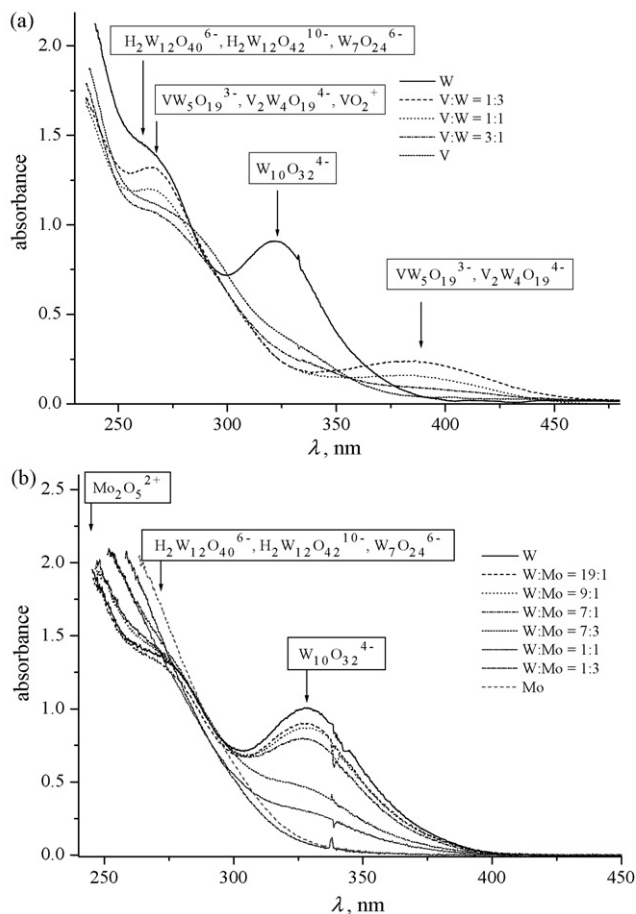


Fig. 1. Absorption spectra measured in 1.2 mM ($\text{Na}_2\text{WO}_4 + \text{NH}_4\text{VO}_3$) (a) and ($\text{Na}_2\text{WO}_4 + \text{Na}_2\text{MoO}_4$) (b) solutions in 0.5 M H_2SO_4 .

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