

Counter electrodes for WO₃-based electrochromic coatings

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Thin polycrystalline electrochromic tungsten trioxide as well as nickel, vanadium and titanium oxide films with and without lithium additive were prepared by spray pyrolysis on glass coated with SnO₂:F, using acetylacetonates as precursor materials. The substrate temperature was held at 600 °C for WO₃ and 680 °C for the other metal oxide films. Electrochromic colouration and bleaching characteristics were examined in the transmissive electrochromic cell arrangement, using LiClO₄ – poly(ethylene oxide) polymer electrolyte and significant changes of optical transmission in visible and solar range, up to 70%, were observed. The obtained films were electrochemically stable and colouration and bleaching cycles were reversible at a voltage of $\pm(1-2.5)$ V. Start of the electrochemical reactions for most of the films obtained was observed in the range of $\pm(3.5-4)$ V.

1. Introduction

In recent years intensive research efforts have been made in the area of electrochromic materials, especially transition metal oxide thin films, because of their potential for use in windows and mirrors with dynamically variable transmission and/or reflection, displays and variable-emittance electrochromic devices [1]–[3].

Tungsten trioxide films are known to have the most promising characteristics for electrochromic device applications [4]–[6]. The cathodic mechanism of the electrochromic colouration in tungsten trioxide involves simultaneous injection of electrons and monovalent cations or protons, forming deep blue intercalated compounds M_xWO₃ (M \equiv H⁺, alkali metal ions, Ag⁺), where $0 < x \leq 1$ [6]–[8].

Electrochromic devices operating in transmissive window mode typically consist of two sheets of glass coated with thin transparent conductor film (indium tin oxide or SnO₂) and with WO₃ film for active electrochromic electrode, whereas the other glass sheet is coated with a complementary, charge storage electrochromic material. The set of two electrodes of the electrochromic cell is separated by an electrolyte layer, usually lithium salt-doped polymer electrolyte. Thin films of anodically coloured transition metal oxides, especially of nickel and vanadium oxides, or metal oxides exhibiting poor cathodic colouration, such as titanium oxide films, have been extensively studied as potential materials for charge storage counter electrodes [6]–[9]. On the other hand, the majority of materials used for counter electrodes have been found to have smaller charge storage capacity than tungsten oxide. Much work is therefore concentrated on the properties of counter electrodes [8], [9].

The structural order degree and electrochromic properties, such as characteristics of the response to voltage applied and lifetime of the electrochromic films and electrochromic cells, are known to be strongly influenced by method and conditions of the film preparation process [10]–[13]. Spray pyrolysis is one of the chemical deposition methods which offer opportunity to modify the properties of coatings by changing the composition of precursor solutions and/or heat treatment conditions [14].

In this work, all thin electrochromic metal oxide films (thickness range 110–160 nm), *i.e.*, tungsten oxide for active electrode and nickel, vanadium and titanium oxides with and without lithium doping for counter electrodes, have been obtained by spray pyrolysis on glass coated with transparent conductor. Some structural, optical and electrochromic properties of the films prepared for counter electrodes were examined with the aim of estimating their ability to be used in WO_3 -based transmissive electrochromic cells.

2. Experimental procedure

Thin films of tungsten, nickel, vanadium and titanium oxides were prepared by spray pyrolysis on substrates held at a temperature of 600 °C for WO_3 and 680 °C for the other metal oxide films. The substrates were sheets of glass (50 × 50 mm, 4 mm thick), coated with fluorine doped SnO_2 ($\text{SnO}_2:\text{F}$, 19 Ω/\square sheet resistance), carefully cleaned before coating. After washing in ammonium hydroxide (15%) and detergent solution they were rinsed with water, etched for ten minutes in hydrofluoric acid (6%), washed again in detergent solution, rinsed with distilled water and ethanol and dried in hot air.

Tungsten(VI) oxide, nickel, vanadyl, tytanil and lithium acetylacetonates (98% purity) with mixed acetylacetone, dichloromethane and *N,N*-dimethyl formamide solvents were used as coating precursors with and without lithium doping, respectively. The fraction of lithium in films of $\text{Li}_x\text{M}_n\text{O}_m$ formula was calculated for $x = 0.3$. Compressed air at a pressure of 0.35 MPa was used as carrier gas.

Thickness of the films obtained was measured with "Talystep" microprofilometer. The morphology and elemental chemical composition were observed by SEM/EDX, using scanning electron microscope (JEOL JSM 5400) equipped with energy dispersive X-ray spectrometer (LINK ISIS). The crystalline character of the films prepared was checked by XRD diffraction – grazing incidence X-ray technique (XRD 7, Seifert diffractometer), using Cu K_α radiation (40 kV, 30 mA). Spectral measurements were made in wavelength range of 350–2250 nm with Jasco V-570 spectrometer, and IR spectra were taken in the wave number range of 300–3900 cm^{-1} , using Specord M80 (C. Zeiss) spectrometer. The X-ray photoelectron spectroscopy (XPS) measurements were performed with the VG ESCA-3 spectrometer, using Al K_α radiation (1486.6 kV). Electrochromic behaviour and current-voltage characteristics were observed in transmissive window arrangement cells built up of the prepared thin film electrodes. The active area of the cells under investigation was about 7 cm^2 . Colouration and bleaching cycles were observed

by applying d.c. voltage of $\pm(1-2.5)$ V and $\pm(2.5-4)$ V, using lithium perchlorate/propylene carbonate-poly(ethylene oxide) ($LiClO_4/PC-PEO$, M.W. 600.000) polymer electrolyte.

3. Results and discussion

At visual observation all the metal oxide films coated by spray pyrolysis onto transparent conductor are bright and homogeneous. Figure 1 shows the SEM micrographs of typical surface of the films: nickel oxide (a), vanadium oxide (b), lithium-titanium oxide (c) and tungsten oxide (d).

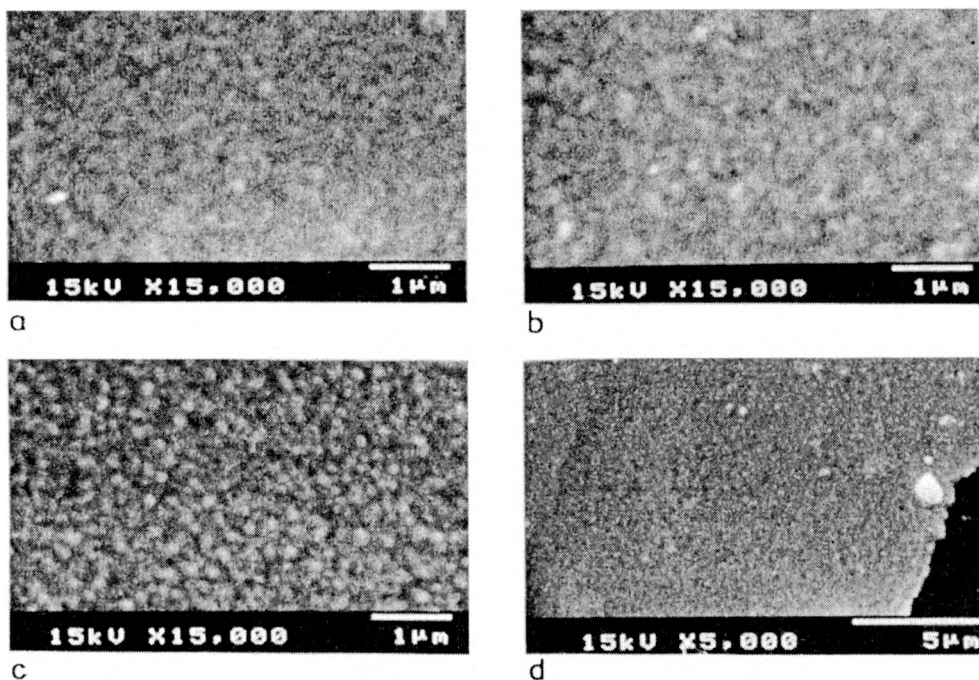


Fig. 1. SEM micrographs of the typical surface of the films obtained: nickel oxide (a), vanadium oxide (b), lithium-titanium oxide (c) and tungsten oxide (d).

All the films obtained have proved to be polycrystalline with uniformly distributed nanocrystalline grains and pores. Significantly more porous surface morphology has been revealed for lithium containing films, and such an open microstructure can be generally more available for alkali ions diffusion. The results of planar view and cross-sectional EDX analysis have revealed only film and glass components (apart from lithium, undeterminable by that method).

The polycrystalline structure of the films obtained is confirmed by results of XRD investigations. The XRD patterns of the films containing lithium have revealed formation of $Li_xM_nO_m$ compounds with x value close to assumed 0.3. The completely oxidized and/or partly reduced phases of film oxides, together with relatively strong

cassiterite signals from much thicker SnO_2 layer have also been found. Typical diffraction patterns of lithium-vanadium oxide and pure vanadium oxide are given in Fig. 2.

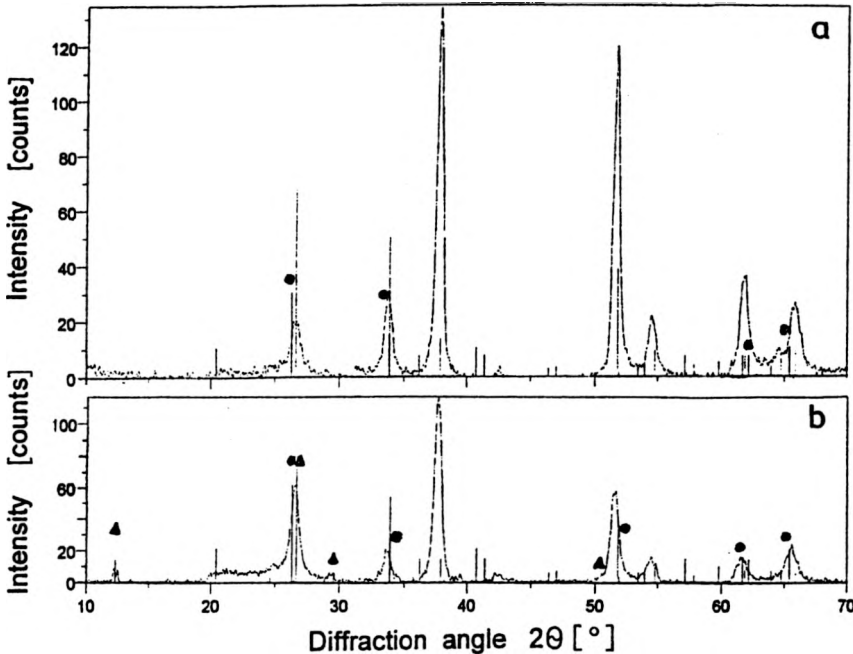


Fig. 2. The XRD patterns of vanadium oxide (a) and lithium vanadium oxide (b) taken at electrochromic electrode configuration, angle of incidence $\omega = 2^\circ$; (---- cassiterite (SnO_2), ● — paramontroseite (VO_2), ▲ — lithium vanadium oxide $\text{Li}_{0.30}\text{V}_2\text{O}_5$).

The XRD results for WO_3 electrode have shown tungsten trioxide phase reduced to $\text{WO}_{2.92}$ and also lower oxidized vanadium phase indicating contribution of lower oxidized states (probably W^{5+} and V^{-4}), respectively, in the films under investigation. These data are in good agreement with results of an earlier investigation of WO_3 films prepared from the same precursor but at substrate temperature of 680°C [15].

In this work, the nickel and titanium oxide films were examined by XPS in the same configuration as for XRD and SEM/EDX investigations. Binding energy (BE) values, measured after surface etching with Ar^+ -ion beam for a short time (2 min), have revealed the presence of the lower oxidized phases both in titanium oxide (Ti $2p_{3/2}$ band with BE of 458.5 eV in relation to BE value of 459.0 eV, expected for TiO_2) and in the nickel oxide films. The BE values found for Ni $2p_{3/2}$ doublets situated at BE of 854.1 eV and 855.8 eV can be assigned to NiO and Ni_2O_3 or $\text{Ni}(\text{OH})_2$, respectively [16]. The XPS spectra of the Ti $2p$ and Ni $2p$ bands are shown in Fig. 3 (a and b, respectively).

The IR spectra for nickel oxide films with (curve a) and without lithium additive (curve b) are shown in Fig. 4. The new absorption band at 760 cm^{-1} can be assigned

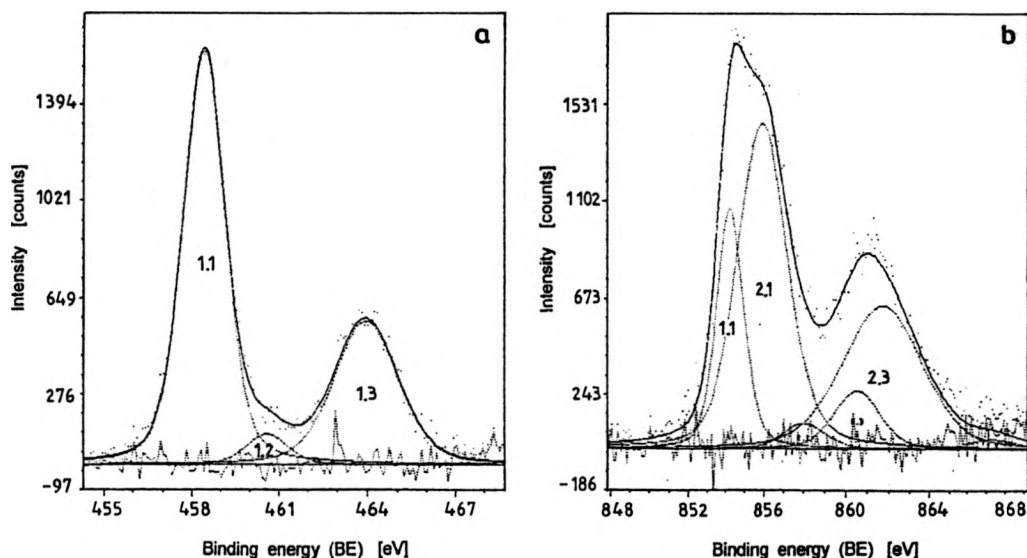
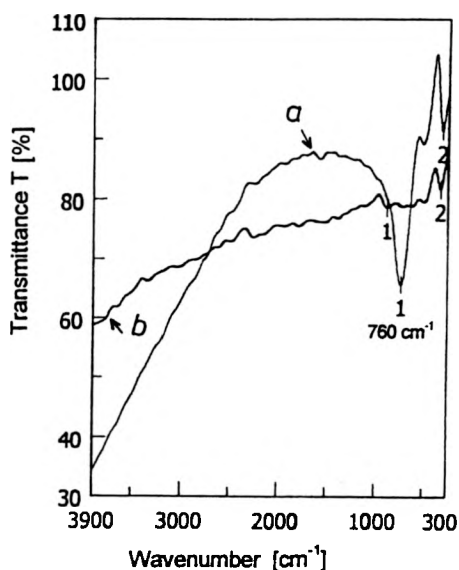


Fig. 3. Ti 2p (a) and Ni 2p (b) X-ray photoelectron spectra for thin titanium oxide and nickel oxide films.



a - NiO/Li: 1: 760.00, 65.5789 2: 352.00, 91.2958
 b - NiO: 1: 916.00, 78.5967 2: 368.00, 81.5992;

Fig. 4. IR spectra of thin nickel oxide films with (a) and without lithium (b).

to strong stretching lattice vibration mode of Ni-O – bonds strongly affected by lithium atoms.

Changes of transmittance and optical density ($OD/\Delta OD$) under charging with voltage applied ($\pm 2.5\text{ V}$) were observed for electrochromic cells containing the

electrodes and LiClO_4 -PEO polymer electrolyte. All the metal oxide films obtained have revealed electrochromic properties. The average differences of total transmission values ΔT between bleached and coloured states of the counter electrode films ranged from 28.5% for lithium-nickel oxide film to over 50% for lithium vanadium oxide, depending on film thickness, and ΔT values were generally higher for films containing lithium. Optical density differences as a function of wavelength, for metal oxide counter electrodes in coloured state are shown in Fig. 5.

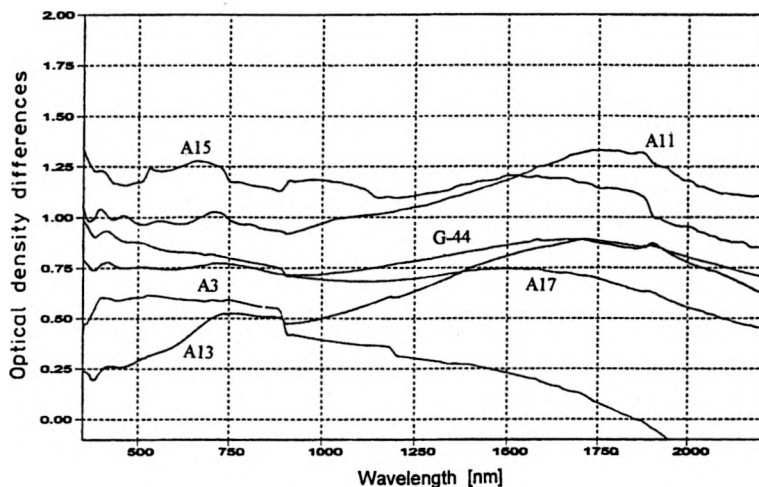


Fig. 5. Optical density differences (ΔOD) as a function of wavelength for thin metal oxide counter electrodes in coloured state: titanium oxide (A3), nickel oxide (G-44), vanadium oxide (A15), and lithiated oxides: lithium-titanium (A13), lithium-nickel (A11) and lithium vanadium (A17), respectively.

Transmission spectra for electrochromic cell containing tungsten oxide and nickel oxide thin film electrodes: in a coloured state (G-W Ni) and for these electrodes in a bleached state (G-W and G-Ni, respectively) are shown in Fig. 6. This window is able to be switched between over 70% to 7.5% of total transmittance. Absorption of cathodically coloured thin films, especially titanium oxide in coloured state seems to be strongly affected by contribution of the excess of free electrons resulting in step-like shape of the spectra and shift of spectral absorption towards higher wavelength values, characteristic of polycrystalline films [10], [17].

Electrochemical behaviour and lifetime of the films obtained were examined by cyclic voltammetry performed at the voltage of $\pm(1-4)$ V, with the scan rate 10–50 mV/s. The cycled area of the electrochromic cells was about 7 cm². Typical results for electrochromic cells containing WO_3 electrode and metal oxide counter electrodes are shown in Fig. 7. Electrochromic cell response to voltage applied was stable and reversible up to the voltage of about ± 3.5 V, depending on the thickness of electrochromic films. In most cases the cells under investigation, electrochemical reactions seem to start at voltage values higher than ± 3.5 V. It was observed that too high a voltage applied during the first cycles had resulted in difficulties with

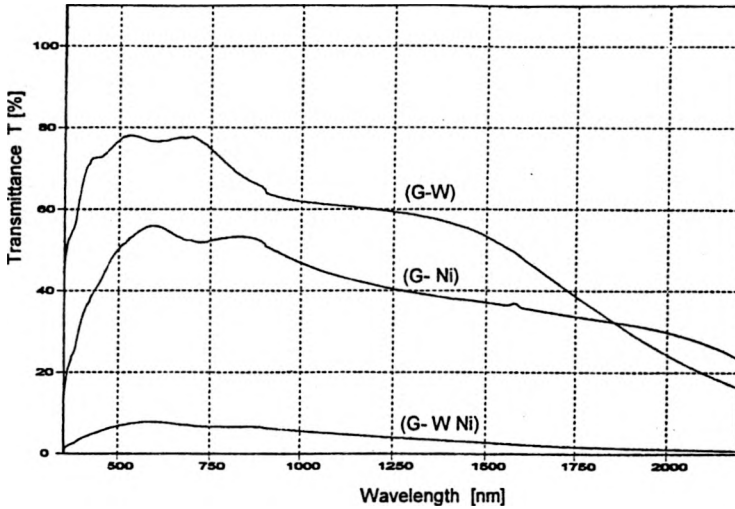


Fig. 6. Transmission spectra of the prepared metal oxide electrodes: tungsten oxide (G-W); nickel oxide (G-Ni) in bleached state; and set of these electrodes in coloured state (G-W Ni).

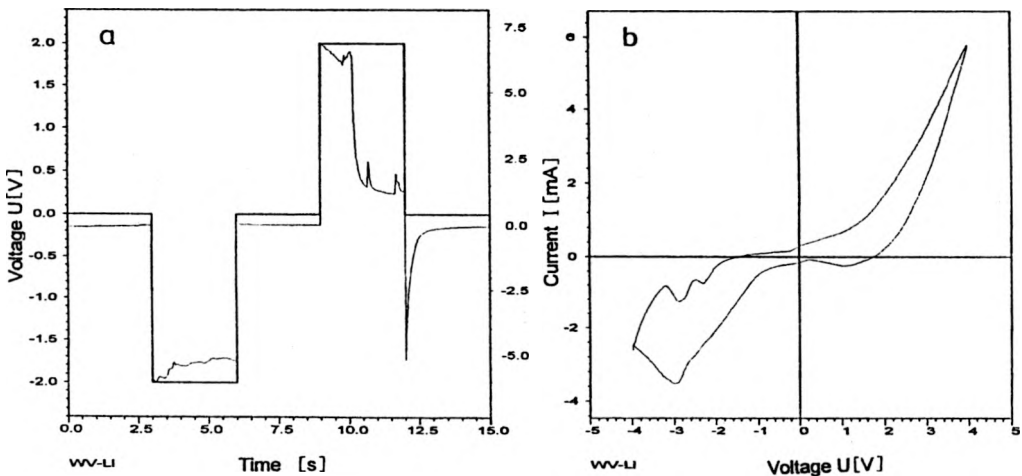


Fig. 7. Current response (a) and cyclic voltammogram (b) for tungsten oxide-($LiClO_4$ -PEO)-lithium vanadium oxide electrochromic cell after cycling with voltage of ± 4 V (cycled area 7 cm^2 , scan rate 50 mV/s).

reversibility of the coloured films. The start of electrochemical reactions was observed as characteristic broadening of the voltammograms. The current-voltage characteristics and electrochemical behaviour of the thin metal oxide counter electrodes seem to be good enough for using them in WO_3 based electrochromic coatings with dynamically controlled optical properties in visible as well as solar range of spectrum.

4. Conclusions

Thin metal oxide films of tungsten for active electrode as well as nickel, vanadium and titanium oxide films with and without lithium additive for counter electrodes of the electrochromic WO_3 -based cells were obtained by spray pyrolysis method over the temperature range of 600–680 °C, using metal acetylacetonates as precursor materials. All the films obtained have proved to be polycrystalline when examined by SEM and XRD. Doping with lithium has resulted in the more open surface morphology of the films of $\text{Li}_x\text{Mn}_n\text{O}_m$ ($x = 0.3$) formula. All the transition metal oxide films obtained within this work and examined as electrodes in WO_3 -based transmissive electrochromic cells were electrochromic with good optical and current-voltage response as well as electrochemical durability sufficient for their being used in WO_3 -based electrochromic coatings for dynamically controlled absorption in visible as well as solar ranges of spectrum.

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