

Electrochromism of mixed phosphotungstic acid - titanium oxide xerogel thin solid films

Elektrokromizem tankih filmov fosfovolframove kisline v kserogelu titanovega oksida

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Thin solid films composed of phosphotungstic acid (PWA) incorporated in titanium oxide xerogel have been made via sol - gel route by dip coating technique. Electrochromism of as - deposited films has been studied with the help of cyclic voltammetric (CV) measurements in HClO_4 electrolyte. In situ UV - VIS spectroelectrochemical measurements have been applied for quantification of optical changes of the films during colouring / bleaching process. With the help of ex situ Near Grazing Incidence Angle (NGIA) reflection spectroscopy it has been demonstrated that electrochromism is related to the intensity change of the W-O-W vibrations indicating redistribution of charges in Keggin's ions.

Key words: electrochromism, electrochromic and ion conductive material, in situ spectroelectrochemistry, infrared spectra

Po sol-gel metodi in z dip coating tehniko nanašanja tankih plasti smo pripravili stabilne in optično kvalitetne mešane PWA/Ti tanke filme kserogelov na različnih substratih. Tako pripravljeni filmi so homogeni in amorfni.

Elektrokromizem PWA/Ti smo preučevali s pomočjo cikličnovoltametričnih in kronokulometričnih meritev. Stabilnost filmov v HClO_4 elektrolitu je dobra (>200 ciklov), interkaliran naboj doseže vrednosti do 35 mC/cm^2 . In situ UV-VIS spektroeletrokemijske meritve smo uporabili za ovrednotenje optičnih sprememb med obarvanim in razbarvanim (prepustnim) stanjem. Prepustnost se spremeni za $\sim 40\%$ pri filmu z debelino 400 nm , kar pomeni, da je vsebnost vgrajene PWA v mreži Ti-kserogela dovolj velika, da opazimo elektrokromni efekt mešanega sistema.

Ex situ NGIA FT-IR spektroskopske meritve na obarvanih in razbarvanih vzorcih so pokazale, da se interkalacija H^+ ionov iz elektrolita (proces obarvanja) odraža na intenzitetnih spremembah W-O-W valenčnih nihanj Kegginovega aniona zaradi prerazporeditve naboja.

Ključne besede: elektrokromizem, elektrokromni in ionsko prevodni material, in situ spektroeletrokemija, infrardeči spektri

1 Introduction

Electrochromism is described as reversible change of colour of the material under the application of electric current or voltage. Schematically, phenomenon could be visualised as double injection of electrons and ions into the structure of the material. For practical utilisation of the electrochromic effect five layers of materials each of them performing specific function in device are required; trans-

parent electronic conductors^{1,5}, electrochromic material², fast ionic conductor³ and ionic storage material⁴. For attaining transmissive electrochromic device all of the layers have to be optically transparent giving rise to undistorted view through the device. From practical and technological reasons it is wise to reduce number of layers by using material exhibiting combined properties required for functioning of the device, e.g. electronic conductor - ion storage material or electrochromic material - ion conductor.

Phosphotungstic acid ($H_3PW_{12}O_{40} \cdot xH_2O$ - noted PWA) consisting of PO_4 tetrahedra which are surrounded by four W_3O_{13} sets has been proposed as a candidate which could perform simultaneously as electrochromic material and ion conductor¹. Tell² and Mohapatra³ exploited electrochromism of PWA by making diffusely reflecting electrochromic device where PWA was used in a powder form. Electrochromic properties of PWA diluted in aqueous solution have been demonstrated by Maheswari and Habib⁴. The corresponding colouring efficiency was found to be $16.8 \text{ cm}^2/\text{C}$ which is still lower compared to the colouring efficiency of WO_3 ($51 \text{ cm}^2/\text{C}$).

The main drawback which prevents that PWA could be used in transmissive electrochromic devices stems from the fact that beside having strong acidity, it is extremely soluble in water and some organic solvents. Thin films of PWA are unstable in a humid environment and tarnish quickly by absorbing water molecules. Recently, Tatsumisago and Minami⁵ succeeded to prepare thin solid films from phosphomolybdic acid (PMoA) inbedded into the SiO_2 xerogel. Films containing 42 wt. % PMoA exhibit conductivity $3 \times 10^{-3} \text{ S/cm}$ at 90 % of relative humidity, but their electrochromic properties have not been investigated yet.

We followed the same approach (5) but PWA was included in TiO_2 xerogel. The main objective of our work was to prepare stable films of mixed PWA/Ti and to demonstrate their electrochromic properties. Beside this, structural features of films and the corresponding gels and xerogels have been elucidated. Finally, near grazing incidence angle FT-IR spectroscopy has been used in order to show in which way the FT-IR spectra of films change upon the inserted charge.

2 Experimental

Preparation of Sols, Gels and Coatings

PWA/Ti sols were prepared by diluting 1 g of phosphotungstic acid PWA (Fluka) in 20 ml of 2-methoxy-ethanol (Fluka). Titanium isopropoxide (Aldrich), which served as a precursor leading to a host material for PWA, was added to this solution. At the first stage the precipitation of titanium was observed which turned over to a clear solution when the molar ratio $PWA/Ti(OPr)_4 = 0.03$ was achieved. In order to obtain maximum concentration of electrochromic active species (PWA) in the TiO_2 gel matrix the smallest amount of $Ti(OPr)_4$ (~4ml) assuring a clear and relatively stable solution was used. As prepared sol should be kept dry since it tends to hydrolyse rather easily in a humid environment. The reason of using 2-methoxy-ethanol as a solvent is in slowing down this reaction due to steric effect of a bigger - $OCH_2CH_2OCH_3$ group, whereas in some more common solvents, e.g. ethanol, propanol, isopropanol, precipitation cannot be overcome.

Viscous yellow gels were prepared by removing volatiles on a rotary evaporator at an ambient temperature. For obtaining pure TiO_2 sols, gels and films an analogous procedure was applied to compare properties of both systems.

Coatings were made on the dip coating unit with pulling

speeds up to 5 cm/min. The supporting conductive ITO glass plates ($\rho_s \approx 100 \Omega/\square$) were previously ultrasonically cleaned. Substrates were repeatedly dipped up to 3 times in order to increase the film thickness. Since larger number of dips is not efficient, more viscous sols have to be used to achieve thicker films.

Instrumental

Thickness measurements were performed on a Surface Profiler Alfa Step 200 having maximal resolution of 5 nm /100 nm.

Cyclic voltammetric and chronocoulometric experiments were done with an EG&G PAR model 273 computer controlled potentiostat - galvanostat, driven by a model 270 Electrochemical Analysis software. A Metrohm type voltammetric cell (50 ml) and a three - electrode system were employed. A working (test) electrode consisted of a roughly 2 cm^2 ITO / (PWA/Ti) covered glass positioned so that exactly 1 cm^2 (one side) of it was in a physical contact with an electrolyte solution. A Pt rod served as a counter electrode and $Ag/AgCl/0.2 \text{ M KCl}$ as a reference electrode. Single scan or multi scan cycling and chronocoulometric measurements were performed within and at potentials +0.4 V and -1.2 V, respectively.

In situ UV-VIS spectroelectrochemical measurements were performed on HP 8451 A diode array spectrophotometer with EG&G PAR model 264 A polarographic analyser. Samples with dimensions $\sim 1 \times 1 \text{ cm}^2$ were accommodated into spectroelectrochemical cell equipped with Pt counter and $Ag/AgCl$ reference electrode and $HClO_4$ electrolyte. *In situ* chronocoulometric measurements were done at cathodic potential, i.e. -1.2 V vs. $Ag/AgCl$ within the spectral range 350 - 800 nm as a function of time.

FT-IR spectra were recorded on a FTS-80 Digilab Spectrometer at resolution 8 cm^{-1} (256 scans) equipped with NGIA (Barnes) cell using p-polariser for obtaining LO spectra of thin films deposited on aluminised glass substrate. The incidence angle was 80° .

3 Results and discussion

Electrochemical Investigations

Cyclic voltammetric recordings were performed in order to obtain electrochemical fingerprints of the studied xerogel films as a function of different conditions and parameters. The potential in each measurement was swept from anodic to cathodic region and then reversed to the initial value. A multi-sweep mode was applied to check voltammetric stability of a film (fig. 1). (PWA/Ti) / $HClO_4$ system revealed a relative increase in peak current density during the initial stabilisation process, whereas only a small change was observed between voltammograms after further 50. and 200. cycles (fig. 1). At cathodic reduction blue coloration is observed (-1.0 - -1.2 V) and bleaching occurs at anodic oxidation (-0.2 - -0.1 V). In spite of the absence of the cathodic peak all the CV measurements were performed in cathodic potentials up to -1.2 V because

further voltage increase produced irreversible film changes.

Electrochemical stability of pure Ti xerogel coating prepared under the same conditions as mixed PWA/Ti films was poor since destroying of the film was achieved already after 10 cycles in HClO_4 water solution electrolyte. This is surprising because it is known that Ti xerogel film derived from $\text{Ti}(\text{O}i\text{Bu})_4$ gave stable response and exhibited electrochromic properties⁶.

The dependence of the CV response on the film thickness is depicted in **fig. 2**. Thicker PWA/Ti films exhibited larger peak current densities but a relative decrease in reversibility. It means that a greater anodic potential has to be applied to achieve a complete bleaching (from -0.45 V for 80 nm to -0.15 V for 430 nm thick film).

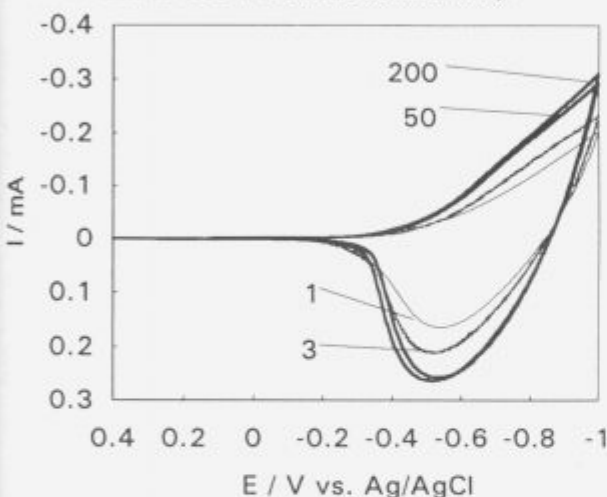


Figure 1. Multi-cyclic voltammograms of a PWA/Ti film (thickness = 135 nm) in 0.001 M HClO_4 ; number of cycles are indicated, potential scan rate: 20 mV/s.

Slika 1. Ciklični voltamogrami PWA/Ti filma debeline 135 nm v 0.001 M HClO_4 (1., 3., 50. in 200. cikel); hitrost preleta potenciala: 20 mV/s.

Chronocoulometric measurements were performed at constant potentials, determined from the sweep voltammetric measurements (-1.1 V and 0.4 V). The total charge (Q) loaded or unloaded into or out of a film is recorded as a function of time (t) (**fig. 3a**). The coulombic efficiency (ratio of anodic to cathodic charge) is smaller with a thicker film and when more concentrated electrolyte is used while the total charge density is larger. In this case, total charge density exceeds 30 mC/cm² in cathodic direction taking into account limiting time (30 s) and 20 mC/cm² in anodic direction (corresponding cyclic voltammogram is shown in **fig. 3b**).

In situ UV-VIS spectroelectrochemical measurements were done to prove the electrochromism of PWA/Ti films since they don't exhibit a long time open circuit memory and therefore the *ex situ* measurements may be difficult to perform. The process of cathodic coloration and anodic bleaching expressed with absorbance changes of the film as a function of applied potential (spectral range 350 - 800 nm) was recorded (not shown here). The potential was swept from 0.4 to -1.2 V and then reversed to the initial

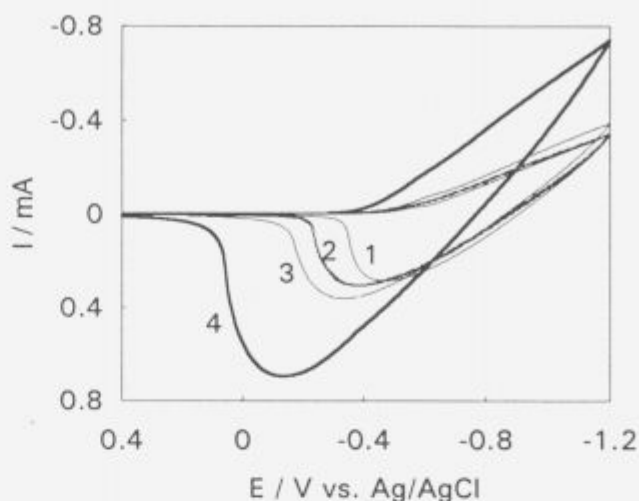


Figure 2. Cyclic voltammograms of PWA/Ti films at different thickness: (1) 80 nm, (2) 135 nm, (3) 255 nm, (4) 430 nm; electrolyte and scan rate: as in **fig. 1**.

Slika 2. Ciklični voltamogrami PWA/Ti filmov različnih debelin: (1) 80 nm, (2) 135 nm, (3) 255 nm, (4) 430 nm; elektrolit in hitrost preleta potenciala: kot pri sl. 1.

value at the scan rate 20 mV/s. From the absorbance changes in cathodic and anodic scan a relative change in transmittance was calculated yielded about 0.3 for the visible range. A bigger change was expected with *in situ* chronocoulometric measurements since the potential was kept constant at -1.2 V for 60 s (**fig. 4**). A relative transmittance change (decrease) in the spectral range 350 - 800 nm was determined. Transmission was reduced for about 40% after the application of cathodic voltage to the 400 nm thick PWA/Ti film.

Spectroscopic Investigations

In order to detect spectral changes of intercalated samples the cyclic voltammogram was interrupted at the voltage giving peak current, i.e. at $U = -1.9$ V for the films deposited on aluminised glass plates and cycled in 0.01 M HClO_4 . After first removing of the coloured coatings from the electrolytic cell (~1 min) the NGIA spectrum has been recorded (**fig. 5-2**). The basic features of the NGIA FT-IR spectrum of uncharged sample (**fig. 5-1**) have been retained except pronounced intensity decrease of the LO modes in the spectral range 800 - 900 cm⁻¹ was noticed. These modes⁷ are assigned to inter and intra W-O-W vibrations involving corner-sharing and edge-sharing oxygen atoms in W_3O_{13} units, respectively. Moreover, LO mode at 839 cm⁻¹ attributed to the intra γ W-O-W TO mode at 816 cm⁻¹ was shifted to 859 cm⁻¹ while the inter γ W-O-W band at 901 cm⁻¹, W-O mode at 968 cm⁻¹ and γ P-O at 1066 cm⁻¹ remained nearly undisplaced. Additional band at 1144 cm⁻¹ also appeared which assignment remains unclear.

We could conclude that due to the intercalation of H^+ ions charges which are contained in Keggin's ions become redistributed in such a way that corner-sharing and edge-sharing vibrations become more polar in respect to the vibrations having pure stretching character (γ W-O).

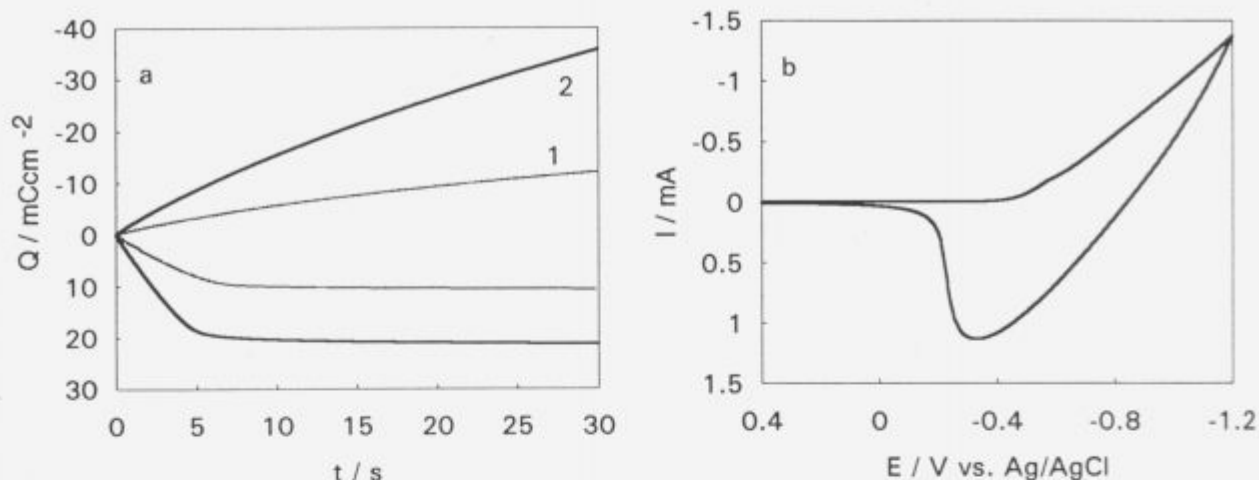


Figure 3. a - Cathodic and anodic total charge density (Q) at different PWA/Ti film thickness and electrolyte concentration as a function of time: (1) 255 nm, 0.001 M HClO₄, (2) 430 nm, 0.01 M HClO₄; b - cyclic voltammogram corresponding to chronocoulometric curve a-2, potential scan rate: 20 mV/s.

Slika 3. a - Katodna in anodna celotna gostota naboja (Q) za PWA/Ti film kserogela pri dveh debelinah in koncentracijah elektrolita v odvisnosti od časa: (1) 255 nm, 0.001 M HClO₄, (2) 430 nm, 0.01 M HClO₄; b - ciklovoltamogram, ki ustreza kronokoulometrični meritvi a-2, hitrost preleta potenciala: 20 mV/s.

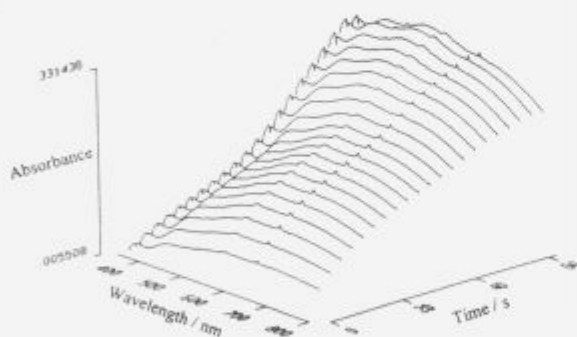


Figure 4. *In situ* chronocoulometric measurement of PWA/Ti film (thickness = ~400 nm).

Slika 4. *In situ* kronokoulometrična meritev PWA/Ti filma - debeline ~400 nm.

Reversibility of the colouring / bleaching process was verified by leaving the coloured sample in the NGIA cell and measured again after 10 min. Discoloration was accompanied by regaining initial intensity of the LO bands characteristic for the uncoloured PWA/Ti film.

4 Conclusions

Stable mixed PWA/Ti xerogel films have been made via sol - gel route by dip coating technique. Films exhibit excellent optical quality and are characterised with homogenous and amorphous structure.

Optical density changes which were observed during colouring and bleaching cycles were about 40% (in transmission) indicating that the concentration of the incorporat-

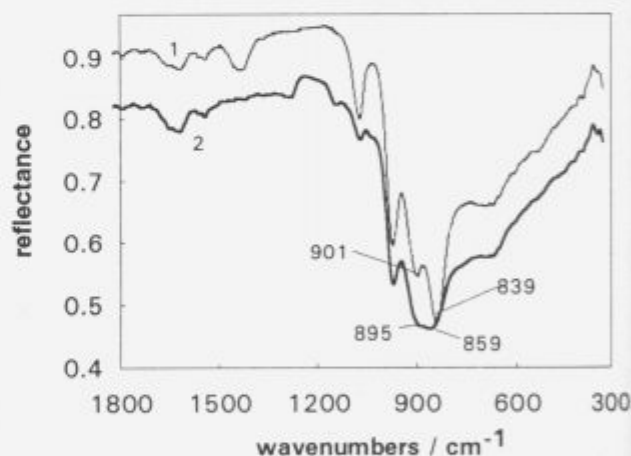


Figure 5. FT-IR NGIA spectra of bleached (1) and coloured (2) PWA/Ti film in the spectral range 1800 - 300 cm⁻¹.

Slika 5. FT-IR NGIA spektra razbarvanega (1) in obarvanega (2) PWA/Ti filma v spektralnem območju 1800 - 300 cm⁻¹.

ed PWA in Ti xerogel matrix was sufficient for obtaining electrochromic effect of the mixed films. Electrochemical stability of the (PWA/Ti) / HClO₄ is very good (> 200 cycles) with intercalated charge up to 35 mC/cm².

NGIA FT-IR spectroscopic studies performed *ex situ* on coloured and bleached films revealed that intercalation of H⁺ ions is related to the changes of intensity of the W-O-W stretching vibrations of Keggin's ions, indicating redistribution of charges.

5 References

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