

SYNTHESIS AND CHARACTERIZATION OF ROUGH ELECTROCHROMIC PHOSPHOTUNGSTIC ACID FILMS OBTAINED BY SPRAY-GEL PROCESS

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ABSTRACT

Rough electrochromic phosphotungstic acid (PWA) films were fabricated by spraying a gel of phosphotungstate anions with a molar ratio of P:W = 1:12 onto glass substrates precoated with transparent and electrically conducting SnO₂:F at 300 °C. The analysis by X-ray photoelectron spectroscopy (XPS) determined that the P:W molar ratio in the films was approximately 1:14. Infrared spectroscopy (IR) and X-ray diffraction (XRD) showed that the film is a polycrystalline phosphotungstic acid. SEM micrographs showed that the films present a rough morphology based on fiber-shape bridges. Optoelectrochemical measurements demonstrated pronounced electrochromism in the PWA films upon H⁺ intercalation/deintercalation with a high diffuse reflectance (R_d) and transmittance (T_d). We found for as-deposited films that R_d /total reflectance (R_t) and T_d /total transmittance (T_t) at 550 nm was around 0.83 and 0.68, respectively. This ratio decreases at bleached state to 0.74 and 0.41 for R_d/R_t and T_d/T_t , respectively.

1. INTRODUCTION

Electrochromic materials are characterized by their ability to attain different optical properties under the action of an electric field [1,2]. They have several interesting applications in emerging technologies: transmittance modulation in energy efficient "smart windows", contrast modulation in nonemissive information displays, reflectance modulation in "antidazzling" mirrors, etc. Electrochromism is associated with a reversible insertion/extraction of small cations, generally lithium and protons, under a voltage application.

Electrochromism was discovered in W oxide [3], and this material remains the most viable one for applications; however there are still interesting possibilities with other materials based on tungsten-oxide compounds which are yet scarcely explored such as the heteropoly compounds. Several heteropoly tungsten are

known to exhibit deep coloration upon reduction in aqueous solution [4,5,6]; the heteropoly anions undergo reduction to mixed-valence species without change of structure. Those materials also give the possibility to simplify an electrochromic system because it can function as both ion conducting and electrochromic material [6]. The heteropoly compound we fabricated in this work using the spray-gel technique was phosphotungstic acid (PWA). This material is known to be a good proton conductor in the solid state and besides its electrochromic behaviour it has also been proposed recently as a high temperature membrane for fuel cells [7].

Most electrochromic materials for architectural applications are thought to be specular surfaces at the visible range, however electrochromic rough surfaces can also be interesting for some kind of applications in which, without losing light transmittance, it behaves as a highly diffusing surface for which the intensity of reflected radiation is almost independent of direction (Lambert surface). Very few works have been reported about electrochromism related to the diffuse reflectance and transmittance in the visible range [8,9,10].

Sol-gel technique and spray pyrolysis are interesting techniques for thin films fabrication (simple and low cost) and when they are combined properly can be very useful for large area applications and the films morphology can be easily monitored controlling the precursors and deposition conditions.

In this work, we report the electrochromism of highly diffuse PWA coating produced by the spray-gel technique as a continuation of our previous works [11, 12].

2. EXPERIMENTAL

Combined spray pyrolysis and sol-gel techniques were used to obtain the phosphotungstic acid (PWA) films onto either glass slide or glass slide precoated with

transparent and electrically conducting $\text{SnO}_2:\text{F}$ having a resistance/square of around 15Ω . The process basically consists in producing an aerosol from a gel, which is sprayed over a hot substrate, where the film is going to grow. The outline of the spray system used in this work is described elsewhere [12]. Precursor of the spraying solution for preparing the phosphotungstic acid films was an aqueous solution of 0.1 M sodium tungstate ($\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$, 99% MERCK) mixed with orthophosphoric acid (H_3PO_4 , 85% Riedel-de Haën) with a molar ratio P:W of 1:12 (at % P:W = 8.3). The gel was obtained via acidification of the aqueous solution through a proton exchange resin (Dowex 50WX8, 60-170 mesh, MERCK). In order to study the influence of the addition of orthophosphoric acid to the polytungstic acid in the polymerization process a home-made light scattering equipment was used. Light scattering results are shown in Figure 1. Molecular weight as a function of polymerization time for different phosphorous to tungsten atomic ratios (%P:W) were plotted; results showed that the addition of phosphorous to the polytungstic acid retards the polymerization process.

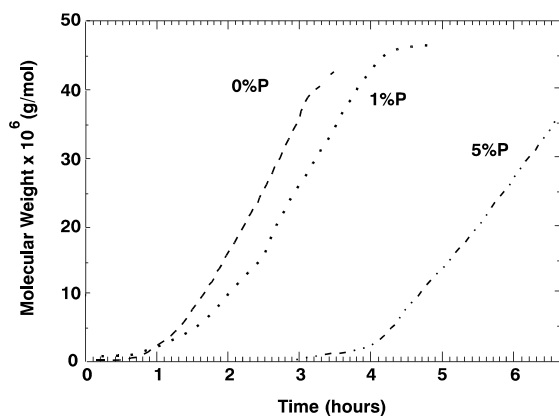


Figure 1. Polymerization curves in function of time for solutions with different at. % ratios of P:W, showing the beginning of the polymerization.

The films were obtained spraying the gel (at % P:W = 8.3) onto substrates at $300 \text{ }^\circ\text{C}$ for 60 min. The experimental processes for obtaining the phosphotungstic acid film is shown in Figure 2. The gas carrier flux and air pressure were kept at 11 l/min and $8.8 \times 10^5 \text{ Pa}$, respectively.

The crystalline structure of the as-deposited phosphotungstic acid films were characterized by x-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) using a Phillips X Pert diffractometer (Cu K_α radiation) and a Shimadzu 8300 spectrophotometer ($450 - 4000 \text{ cm}^{-1}$ wave number range), respectively. FTIR

data were obtained using unpolarized infrared light and an aluminum mirror as a reference. X-ray photoelectron spectroscopy (XPS) studies were done using a Leybold-Heraeus LHS-10 spectrometer, under a vacuum $\leq 1 \times 10^{-8}$ torr, and Al K_α radiation. The morphology characterization of the films were carried out using a Scanning Electron Microscope Philips 500.

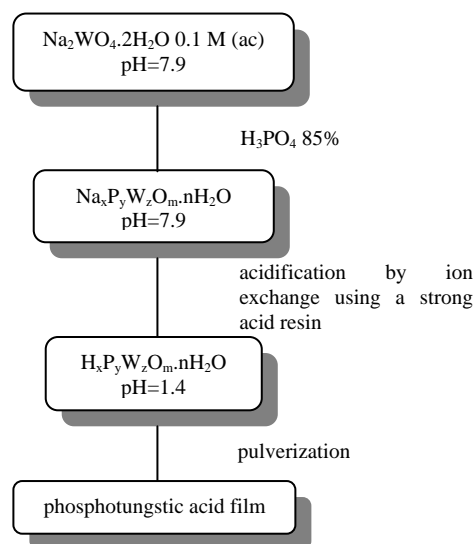


Figure 2. Schematic representation of the procedure followed in the fabrication of phosphotungstic acid films.

An EG&G PAR 273 potencioscan/galvanostat instrument was used for cyclic voltammetry for charge insertion/extraction. A three electrode-cell with an electrolyte of 1 M H_2SO_4 aqueous solution was set; the electrochromic film was placed as the working electrode (WE), a platinum layer as the counter electrode (CE) and a Saturated Calomel (SCE) as the reference electrode (RE). The voltage span was between -0.8 and 0.6 V vs SCE at a scan rate of 10 mV/s .

Total and diffuse spectral normal transmittance/reflectance were recorded in the $400 < \lambda < 850 \text{ nm}$ wavelength range using a double beam Perkin-Elmer Lambda 9 spectrophotometer equipped with an integrating sphere. Those measurements were performed ex situ, i.e., with the sample extracted from the electrolyte, rinsed, dried, and mounted in the sample compartment of the spectrophotometer.

3. SUMMARY AND REMARKS

Figure 3 shows the XRD diffractograms obtained for the films deposited at $300 \text{ }^\circ\text{C}$ onto glass (bottom) and glass precoated with

transparent and electrically conducting SnO₂:F (top). The relevant atomic planes are ascribed to phosphotungstic acid (H₃PW₁₂O₄₀·21 H₂O) [13]; the asterisks marked peaks in the figure correspond to the SnO₂:F precoated glass substrate.

The infrared reflectance spectrum of the as-deposited film is shown in Figure 4. The presence of phosphotungstic acid can be recognized by the presence of the finger-print bands below 1100 cm⁻¹ which are characteristic of the PW₁₂O₄₀³⁻ ion [14]. The observed bands are indicated in the Fig. 4 according to the common assignments as reported in the literature [14, 15]. The peak attributed to the P-O band is around 1077 cm⁻¹, while the peaks assigned for the symmetric stretching band of corner-shared octahedra, W-O_c-W, and the symmetric stretching band of edge-shared octahedra, W-O_e-W, are at around 900 – 850 cm⁻¹ and 772 cm⁻¹, respectively. The W=O_t stretching band where O_t is the terminal oxygen is around 1000 – 980 cm⁻¹.

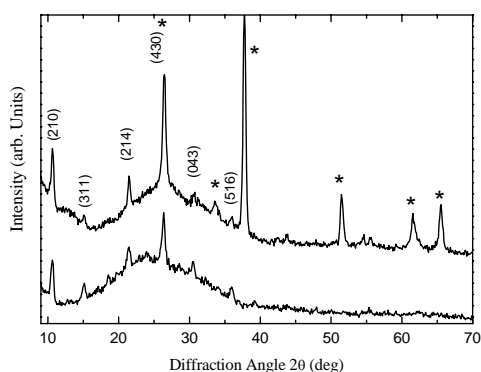


Figure 3. X-ray diffractograms for a phosphotungstic acid films on a glass substrate (bottom) and glass substrate precoated with transparent and electrically conducting SnO₂:F obtained at 300 °C (top). The relevant atomic planes are indicated. Asterisks show peaks due to SnO₂:F.

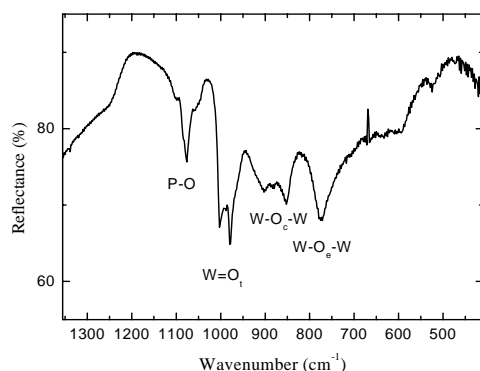


Figure 4. Infrared reflectance spectra for a phosphotungstic acid film.

The films were analyzed by XPS, and the peaks corresponding to oxygen, tungsten and phosphorous are shown in Figures 5(a), 5(b) and 5(c), respectively. Figure 5(a) shows the tungsten peak W⁺⁶ 4f with a binding energy of 36.5 eV, indicating that the films contain W-O bonding [16]. Figure 5(b) shows the contribution of the O²⁻ 1s at 530 eV, which is related to a O-H bonding. This would indicate that the compound is hydrated. The phosphorous signal P⁵⁺ 2p at 134.4 eV could be associated with a compound that contains P-O bonding. The ratio P:W has been obtained from the relations between the integrated intensity of the singlet 2p phosphorous signal to the doublet 4f tungsten peak multiplied by the corresponding sensitivities. It was determined that the molar rate P:W is around 1:14

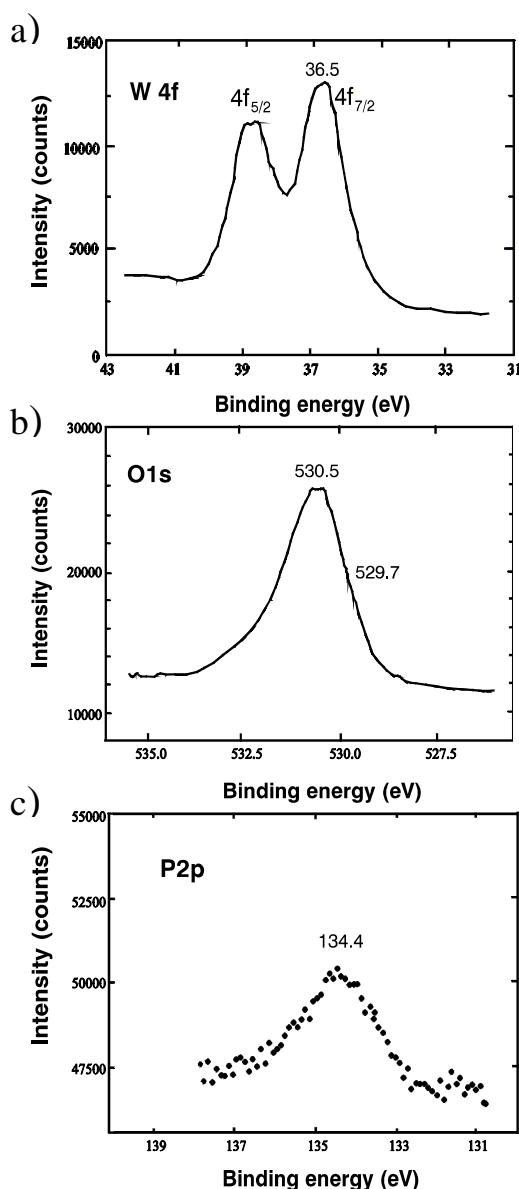


Figure 5. XPS spectrum for a phosphotungstic acid film; amplification of (a) the 4f tungsten peak, (b) the O 1s oxygen peak and (c) the 2p phosphorous peak.

A typical SEM micrograph of a phosphotungstic acid film is shown in Figure 6. The film showed a morphology based on fiber-shape bridges. This type of configuration was distributed uniformly through out the film surface, and behaves as highly diffusing surface in the visible range.

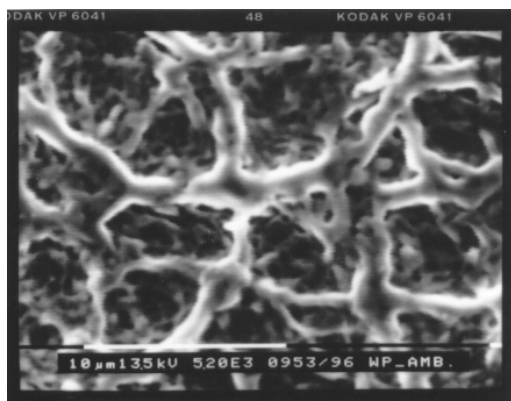


Figure 6. SEM micrograph for a phosphotungstic acid film.

Figure 7 displays a typical cyclic voltammogram for a phosphotungstic acid film with an effective area of 1.5 cm^2 ; the voltage sweep rate was 10 mV s^{-1} and this was stopped for optical ex-situ measurements at voltages indicated by arrows in the figure for the colored and bleached states. The inserted charge densities during cyclic voltammetry were calculated by numerical integration of the current density with respect to time. The inserted/extracted charge density was 55.6 mC cm^{-2} for the data in Fig. 7.

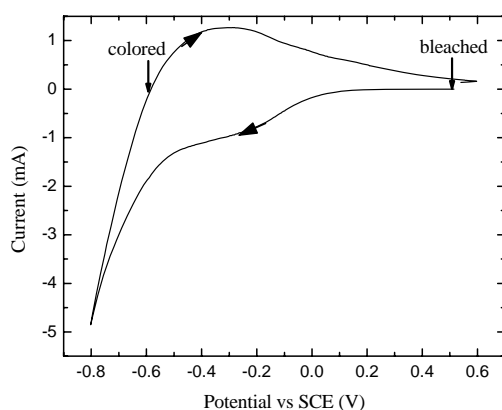


Figure 7. Cyclic voltammogram for H^+ intercalation/deintercalation in a phosphotungstic acid film. The voltage sweep rate was 10 mV s^{-1} . Arrows denote voltage sweep directions.

The total (a) and diffuse (b) optical transmittance and reflectance spectra for a phosphotungstic acid film are shown in Fig. 8. Measurements have been performed for as-

deposited, colored and bleached states, as indicated in the figure. For ex-situ optical measurements in the colored and bleached states the samples were taken out from the electrochemical cell at voltages in the voltammogram as indicated in Fig. 7.

Optical measurements showed that PWA films present a pronounced electrochromism at all visible range. At 550 nm there is a total optical transmittance contrast of around 23 % (see Fig. 8a) between the bleached and colored state. The diffusing optical transmittance and reflectance are showed in Fig. 8b. The as-deposited film presents a highly diffusing transmittance and reflectance; at 550 nm the ratio between diffuse transmittance (T_d) and total transmittance (T_t) is around 0.68, and between diffuse reflectance (R_d) and total reflectance (R_t) around 0.83. This proportion decreases for bleached and colored state. For instance for bleached state at 550 nm T_d/T_t is around 0.41 and R_d/R_t is around 0.74; this means that when the samples are electrochemically treated the surface became smoother like, i.e. it is less dispersive. For instance at 550 nm the diffuse transmittance for the bleached state decreases in 23 % respect to as-deposited one.

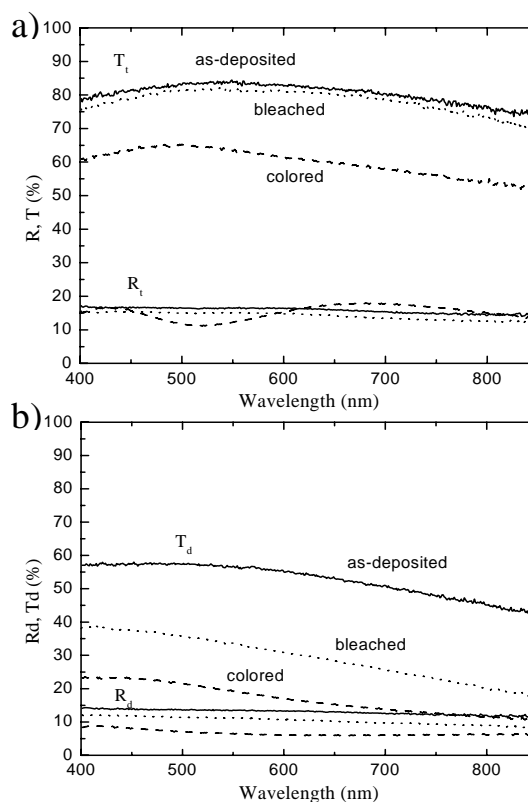


Figure 8. The total (a) and diffuse (b) spectral transmittance and reflectance for a phosphotungstic acid film in as-deposited (solid line) state and after coloration (dotted line) and bleaching (dashed line) by H^+ intercalation/deintercalation.

Those results indicate that at appropriate conditions an electrochromic film with uniform "irregularities" can be grown using the spray-gel technique. Those films present a highly diffusing component in the transmittance and reflectance spectra.

4. CONCLUSIONS

The pneumatic spraying of a gel brings new possibilities for fabricating highly optical diffusing films of PWA. The phosphotungstic acid fabricated in this work showed high insertion charge capacity with good electrochromic behaviour.

ACKNOWLEDGEMENTS

This work has been financially supported by the International Program for Physical Science of Uppsala University (IPPS), the Instituto de Investigación of Universidad Nacional de Ingeniería. The authors are also grateful to Prof. Annette Gorenstein and Dr. Antonio Costa for their help with the optical and electrochemical measurements, and Lic. Angelica Damian for helping in preparing the films.

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