

SYNTHESIS OF HYBRID ELECTROCHROMIC MATERIAL BASED ON TUNGSTEN OXIDE

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This paper reports first on general considerations on electrochromic materials in order to present, afterwards, electrochromic films having a hybrid PAA (polyacrylic acid)-WO₃ structure. The films are prepared by successive coatings of polyacrylic acid-ethanol solution and tungsten oxide NH₄OH-water one.

Keywords: Electrochromism; hybrid PAA-WO₃ films

I. INTRODUCTION

Electrochromic materials exhibit new optical absorption bands in accompaniment with electron-transfer or 'redox' reaction, and show new colors as the consequence. Such coloration was first termed 'electrochromism' in 1961 by Platt [1] to represent electric field-dependent changes in optical absorption spectra of organic dye molecules dissolved in organic solvents. This property makes them of considerable interest for optical devices of several types, such as elements for information displays [2], light shutters [3–6], smart windows [7, 8], variable reflectance mirrors [9], *etc.*

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There is a large number of electrochromic materials which are either inorganic or/and organic [10–16]. Among them, metal oxide-based materials can be fabricated in the form of thin films. Consequently, a considerable interest has been directed toward the thin film technologies. Table I lists the main ones.

A typical electrochromic device is illustrated on Figure 1. Both 'EC' and 'EC or IS' (Fig. 1) have mixed electronic and ionic conduction, and if ions are introduced from IS to EC as it occurs in Figure 1, there is a corresponding charge-balancing counterflow of electrons from the transparent electrode, and thereby a change of the optical properties of the system from the transparent to the colored state. The process is obviously reversible. If the ionic conductor has negligible electron conductivity, the device will exhibit open circuit memory, so that the optical properties remain stable for long periods of time.

In our research during these last years, we have concentrated mainly on (i) sol-gel or derived sol-gel chemical technologies [17] for fabricating electrochromic films (EC), counter electrodes (IS or EC) and transparent electrode (TE) [18]. The sol-gel technology is indeed economical and particularly suited for the production of large area electrochromic devices such as smart windows [19,20]. In the conventional sol-gel technique, the gelatinous material is applied onto 'TE' prior to thermal

TABLE I Major techniques for making thin films of electrochromic oxides

<i>Category</i>	<i>Method</i>	<i>Variety</i>
Physical	Evaporation	Vacuum Reactive (O ₂ , N ₂ , H ₂ O) Ion assisted
	Sputtering	Non-reactive (Ar) Reactive (Ar + O ₂) Chemical (O ₂ + CF ₄)
Electrochemical	Electrodeposition Anodization	
Chemical	Vapor deposition	Atmospheric pressure Low pressure Plasma enhanced
	Sol-gel	Dipping Spin-coating Spraying
	Spray pyrolysis	
	Decomposition reaction Thermal oxidation	

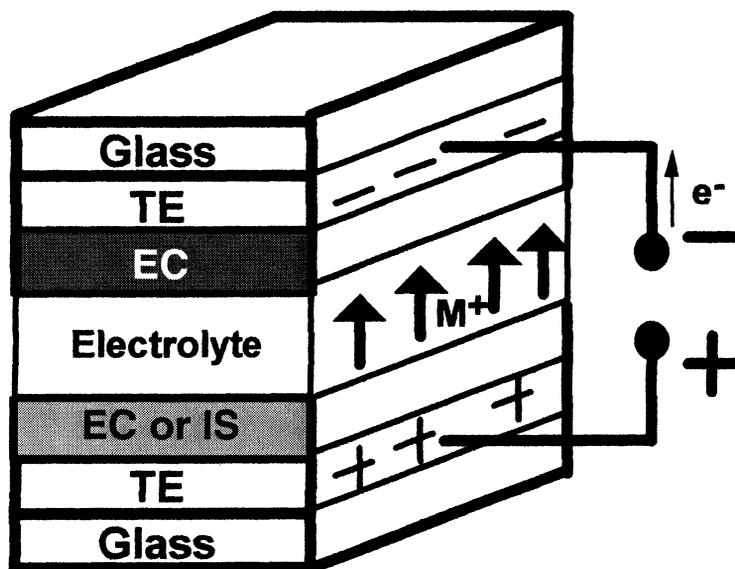


FIGURE 1 Basic design of electrochromic device, indicating transport of the positive ions M^+ under the action of an electric field. TE stands for 'Transparent Electrode', EC for 'Electrochromic Material', IS for 'Ion (M^+) Storage' material which can also be an electrochromic material.

curing. The dip, spin coating or spray pyrolysis procedures are the most convenient manufacturing technologies for thin films.

Figures 2 and 3 show the stages of the dip coating processes. The batch dip coating process (Fig. 2) can be divided into five steps: immersion, start-up, deposition, drainage and evaporation [21]. The first three are necessarily sequential; the third and fourth, concomitant; the fifth, evaporation of solvents from the liquid, proceeds throughout the process unless precautions are taken.

A competition between as many as six forces in the film deposition region governs the film thickness and position of the streamline: (1) viscous drag upward on the liquid by the moving substrate, (2) gravity force, (3) resultant force of substrate tension in the concave meniscus, (4) inertial force of the boundary layer liquid arriving at the deposition region, (5) surface tension gradient and (6) the disjoining or conjoining pressure which is important for films less than $1\ \mu\text{m}$ thick.

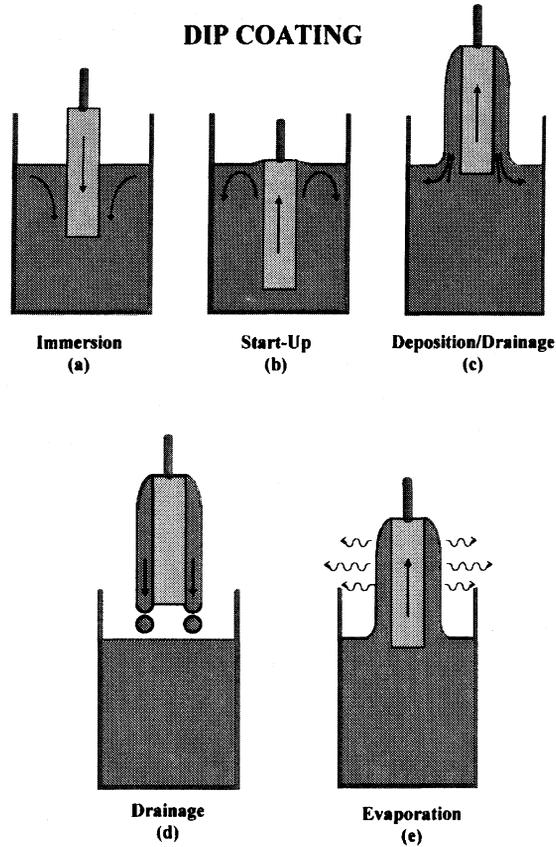


FIGURE 2 Stages of batch dip coating process.

When the liquid viscosity (η) and withdrawal speed (U) are high enough to lower the curvature of the meniscus, the deposited film thickness (h) is the one that balances the viscous drag ($\propto \eta U/h$) and gravitational force (ρgh) [21, 22].

$$h \approx (\eta U / \rho g)^{1/2} \quad (1)$$

When the substrate speed and liquid viscosity are not high enough, as is often the case in sol-gel processing, the balance is modulated by

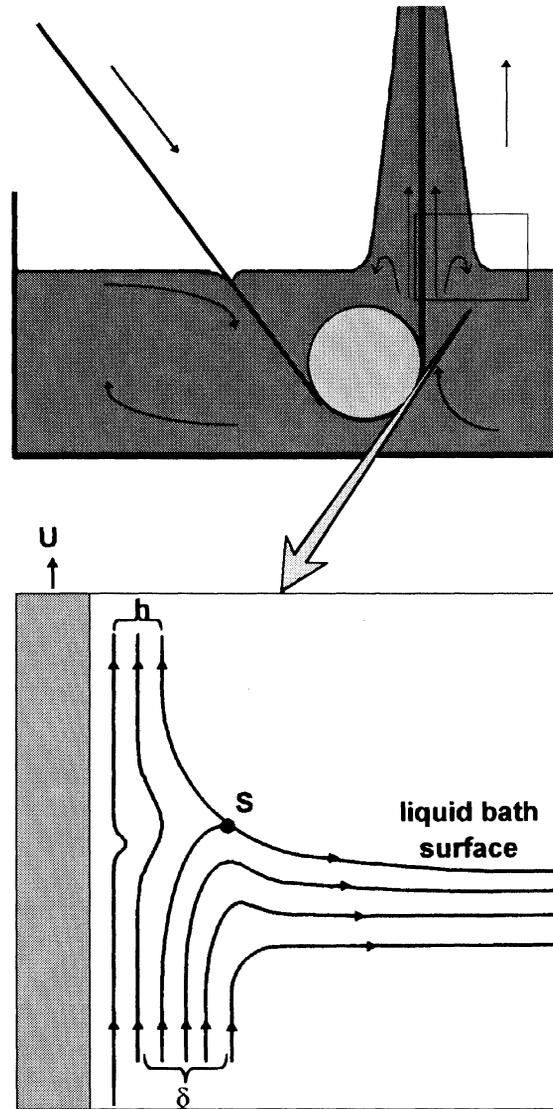


FIGURE 3 The continuous dip coating process: detail of the liquid flow patterns in area of special region, U is the withdrawal speed, S is the stagnation point, δ is the boundary layer, and h is the thickness of the fluid film.

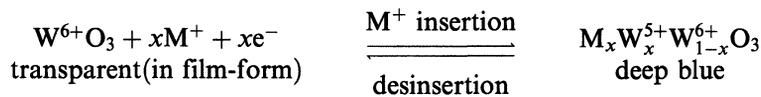
the ratio of viscous drag to liquid-vapor surface tension (γ_{LV}) according to the following relationship [23].

$$h \approx (\eta U)^{2/3} / \gamma_{LV}^{1/6} (\rho g)^{1/2} \quad (2)$$

These relations show that the viscosity and the withdrawal speed are good parameters for the control of the film thickness.

II. THE ELECTROCHROMIC (EC) WO₃ FILM BASED ON A HYBRID STRUCTURE

Tungsten oxide has been by far the most extensively studied as an electrochromic material because of its deep blue color change through reversible 'redox' reaction by intercalation/deintercalation [24] of H⁺, Li⁺, Na⁺ and K⁺:



The insertion proceeds under synchronous uptake of ions and electrons into the solid. Among the possible cations, H⁺ and Li⁺ intercalated tungsten oxide has been the most widely studied because of its proper value of diffusion constant, strong optical contrasts and good memory effect [25–29]. Highly disordered or amorphous tungsten oxide films are usually employed in works related to electrochromism. We have recently reported a convenient way to easily produce uniform WO₃-based films showing good electrochemi-chromic properties [17, 30]. In fact Refs. [17, 30] deal with hybrid structural tungsten oxide films: they are indeed based on nanocrystallites embedded within a porous matrix. The tungsten oxide films were coated onto ITO coated glass which is one of the most widely used and commercially available transparent electrodes ('TE' in Fig. 1). The originality of our procedure lays in the fact that we developed a method to coat basic tungsten oxide solution which cannot be well coated directly onto the transparent electrode because of the basic character its surface. In fact, we have developed two methods (1) and (2) to coat the

basic tungsten oxide solution: (1) polyacrylic acid-ethanol solution is first coated onto ITO glass which is, afterward, dipped into the tungsten- NH_4OH water solution [17, 30], (2) a mixed water solution of polyacrylic acid and tungsten oxide can also be coated [30]. Following a pre-bake at 100°C , the films were finally electrochemically treated in 1 N HCl solution to induce polycondensation.

However method (1) lead to the best results in term of electrochemichromic performances [17, 30].

III. THE TUNGSTEN OXIDE FILMS PREPARED BY SUCCESSIVE COATING

The electrochromic composite films were deposited *via* successive coatings of polyacrylic acid-ethanol solution and tungsten oxide NH_4OH -water one, which were prepared as depicted in Figure 4. The

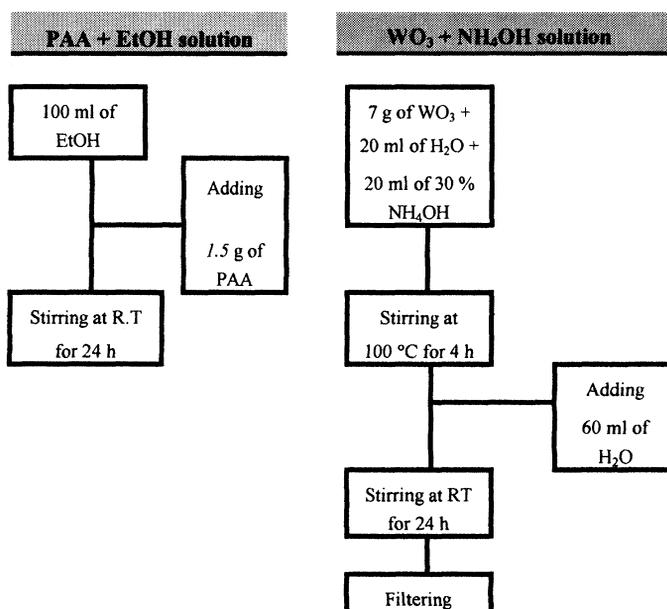


FIGURE 4 Diagrams for preparing the two coating solutions: the polyacrylic acid and tungsten oxide ones.

procedure for preparing the electrochromic composite films is shown on Figure 5.

The tungsten oxide basic solution was prepared *via* somewhat complicated method because the solubility of tungsten oxide is strongly dependent upon pH. According to the solubility diagram of WO_4^{2-} , shown in Figure 6, the pH domain of stable WO_4^{2-} species is $\text{pH} > 7$.

The pH value for the 15% NH_4OH solution is 12.7, and after adding 1.5 times with water, it is still higher than 12, so the pH of the final solution is high enough to sustain the WO_4^{2-} species in solution. But great care should be considered when adding extra water since its too abrupt addition can result in white precipitates which cannot be dissolved again even under vigorous stirring for a long time.

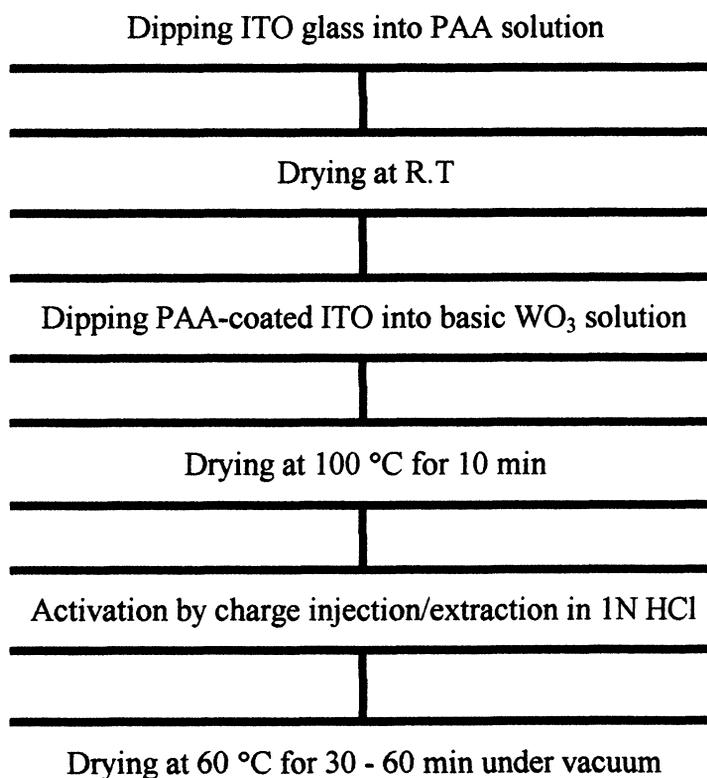


FIGURE 5 Diagram for preparing electrochromic composite film.

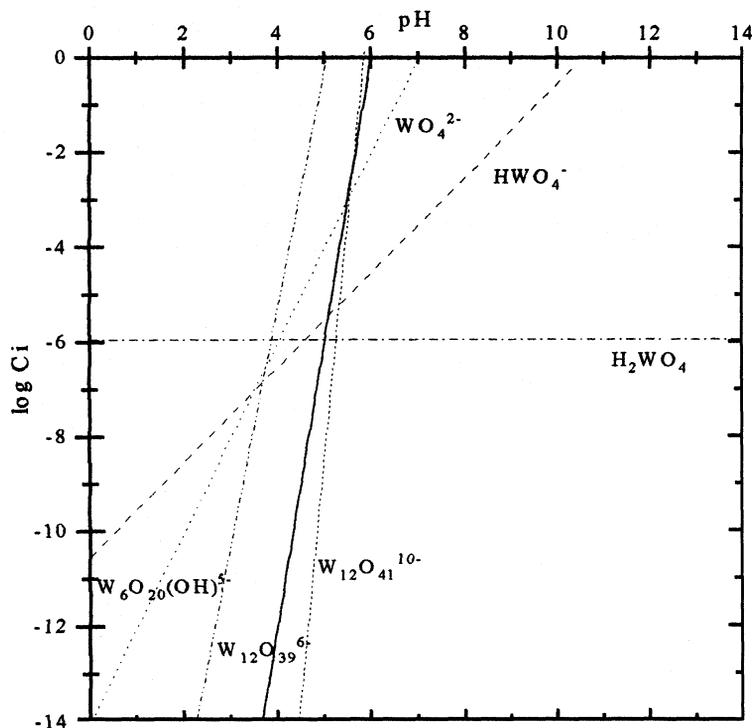


FIGURE 6 Solubility diagram for $\text{W}^{\text{VI}}\text{-O}_x\text{H}_y$ species.

As quoted above, the dip coating technique was used to manufacture the composite films. The previously coated polyacrylic acid layer enables the tungsten oxide one to be firmly adhered onto the ITO glass ($15\ \Omega/\square$, 0.7 mm thick) due to the porosity of the polyacrylic acid layer.

Figure 7 represents the electrochromic device consisting of the PAA- WO_3 composite film, the above Li^+ ionic conductor embedded within a polymeric membrane (100 μm thick), a nanocrystalline SnO_2 film as counter electrode [31]. Its electrochemi-chromic performances will be presented elsewhere [32].

X-ray diffraction spectra were collected for an as-prepared 1.5% PAA- WO_3 film and an electrochemically treated one with 1 N HCl using Cu $K\alpha$ radiation.

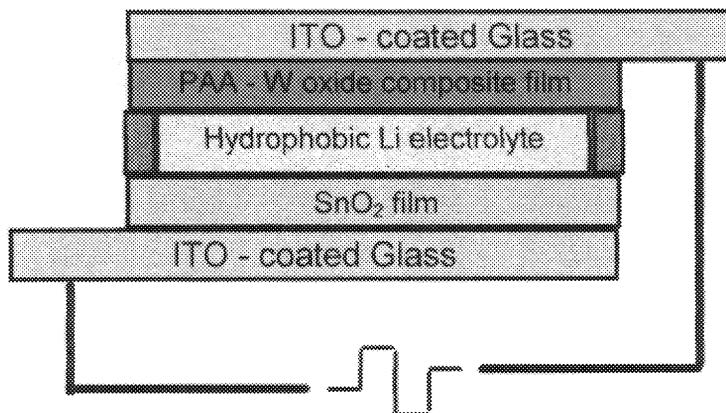


FIGURE 7 Electrochromic device attached with a potentiostat/galvanostat.

Figure 8 represents the XRD patterns for ITO film (a), the PAA-coated ITO film (b), the as-prepared PAA-tungsten oxide-coated ITO film (c), and the colored PAA-tungsten oxide-coated ITO film after injection of $Q = 10 \text{ mC/cm}^2$ in 1 N HCl (d).

As can be seen in Figure 8(c), the as-prepared PAA-tungsten oxide composite film is XRD amorphous. The heat treatment at 100°C , for 10 min. gives rise to some changes in this amorphous structure. The as-prepared film was found to be unstable even in the air, indicating that polycondensation is not completed. Moreover, the peak around 10° which is attributed to the presence of ammonium tungstate confirms the incomplete polycondensation. Polycondensation may be completed after electrochemical treatment in 1 N HCl solution; that would account for the broad peak below 10° shown in Figure 8(d). The appearance of this peak would indicate a structural transformation in the film. But from only these XRD patterns, it is not clear that the electrochemical treatment induces significant structural changes in the film. This point will be discussed elsewhere [32] for the sake of clarity. Temperature dependent XRD measurements are shown in Figure 9. As the temperature increases, the XRD peak around 10° is depressed while the peak at 26° , which is characteristic of WO_3 , is enhanced due to the increase of the size of the nanocrystallites [32]. The depression of the peak at 10° suggests that ammonia in ammonium tungstate is removed by heat treatment. The electrochromic properties of the films

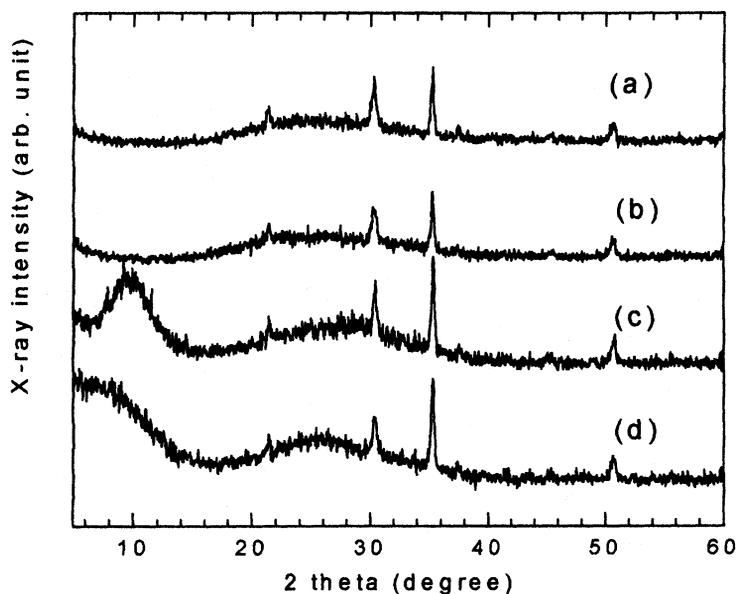


FIGURE 8 X-ray diffraction profiles for the ITO film (a), the PAA-coated ITO film (b), the as-prepared PAA-W oxide-coated ITO film (c) and the colored PAA-W oxide-coated ITO film after injection of $Q = 10 \text{ mC/cm}^2$ in 1 N HCl (d).

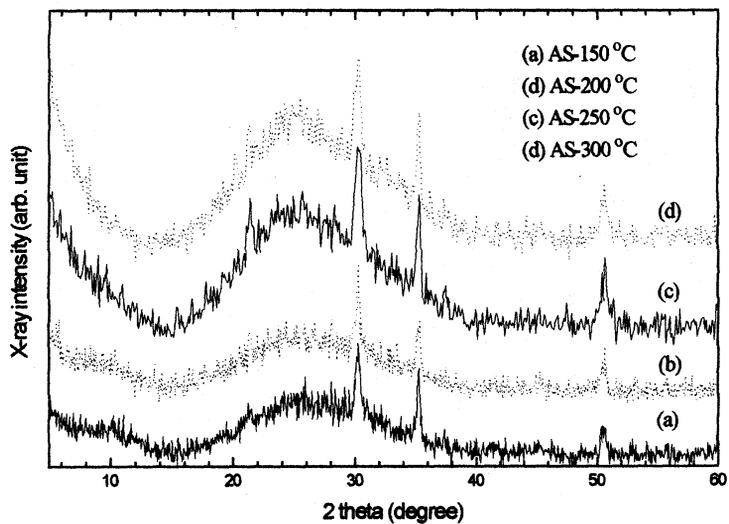


FIGURE 9 XRD profiles for the heat treated as-prepared PAA-W oxide film at 150°C (a), 200°C (b), 250°C (c) and 300°C (d) for 30 min., respectively.

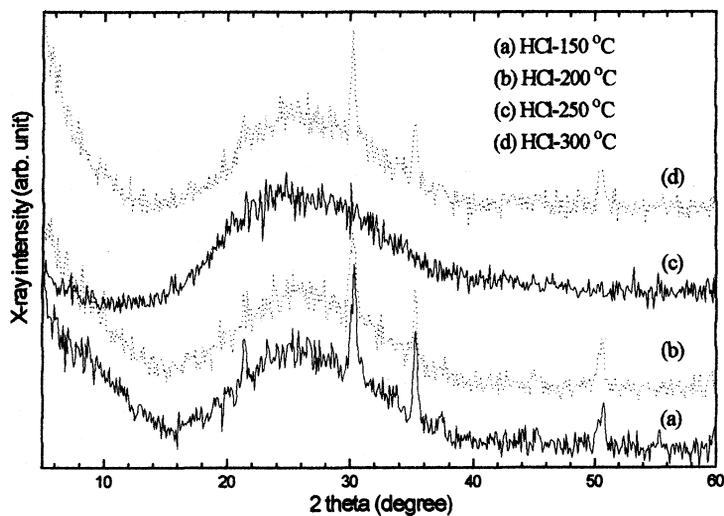


FIGURE 10 XRD profiles for the electrochemically treated PAA-W oxide film, heated at 150°C (a), 200°C (b), 250°C (c) and 300°C (d) for 30 min.

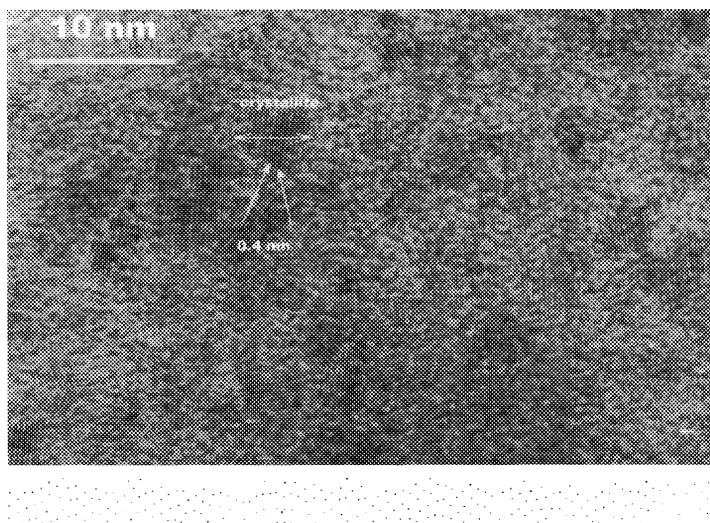


FIGURE 11 The TEM image of the 1.5% PAA-WO₃ composite material after H⁺ intercalation (*i.e.*, corresponding to Fig. 8d).

are nearly the same whatever the heat-treatment temperature (from 150°C to 300°C) [32]; it would imply that the basic structure of tungsten oxide is not significantly modified by heating at 300°C. The temperature dependent X-ray diffraction patterns for the 1 N HCl electrochemically treated sample are illustrated on Figure 10. The overall features including the peak around 26° are found to be nearly the same for all the present XRD patterns, indicating that the structural transformation accompanying polycondensation can be achieved not only by the heat treatment but also by the electrochemical one.

Finally, the X-ray amorphous nanocrystalline structure of the film, which corresponds to the XRD diagram reported on Figure 8d, is illustrated on Figure 11. This structure is highly suitable for an efficient electrochemical grafting process of the M⁺ cations (M = H⁺, Li⁺ etc.) leading to efficient electrochemi-chromic properties [32] in agreement with our previously reported 'electrochemical model' [33–35].

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