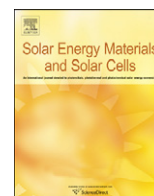




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The effect of precursor aging on the morphology and electrochromic performance of electrodeposited tungsten oxide films

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ABSTRACT

Tungsten oxide films that have larger effective surface area or extensive grain boundaries tend to be more suitable for use in electrochromic devices. We propose in this paper a simple methodology for increasing the roughness and thus the effective surface area of WO₃ films. This method is based on the tendency of the peroxytungstate precursor to form large aggregates within its solution with time. To this aim, a systematic study of the precursor aging effect on the resulting WO₃ film properties was conducted. It was established that with increasing aging time of the precursor solution, more and larger aggregates are formed, which are then deposited on the film surface. The deposition of the aggregates causes the formation of large cracks on the film surface, thereby increasing its effective area.

An optimum of the precursor aging time was found to be around 80 h. Films prepared with such an aged solution were found to have the highest Li⁺ diffusion coefficient and voltammetrically intercalated charge density per unit film thickness. It was also observed that the coloration efficiency of films prepared using the aforementioned method was higher than that of equivalent electron-gun deposited films throughout the visible spectrum and especially in the near infrared. The enhanced properties of these films indicate their improved electrochromic performance, which is mainly due to their increased surface area.

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1. Introduction

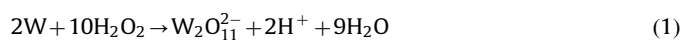
Tungsten oxide is a compound with interesting properties that include electrochromism, photochromism, gas sorption and catalysis [1,2]. During the last decades WO₃ has received significant attention and many applications have been envisaged for it, such as switchable windows, displays, mirrors and gas sensors, some of which have already been commercialised [3,4].

A number of methods for the production of WO₃ thin films have been developed, including physical vapour deposition (thermal, electron beam gun evaporation and sputtering [1,2]) and chemical methods such as sol–gel, spin coating, electrodeposition and spray pyrolysis [5–8].

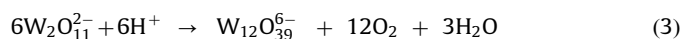
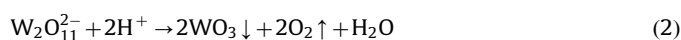
Of these, electrodeposition is a straightforward yet versatile method that yields a variety of film morphologies depending on the pre- and post-deposition conditions, starting materials, solution chemistry [8–11], applied voltage [9] and thermal treatment of the films [8,12]. It is also a low cost technique, well suited for coating of large areas [4].

The direct cathodic electrodeposition of WO₃ from a peroxytungstate precursor (also called peroxotungstic acid [7]) in solution

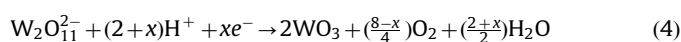
was first reported in [13]. The predominant peroxytungstate in such an acidic solution is reported to be the dimer W₂O₁₁²⁻ or ((O)W(O)₂(O)(O₂)₂W(O))²⁻, in which tungsten is in a (+VI) oxidation state and (O₂) denotes a peroxide ligand [14,15]. The anion is formed by the dissolution of tungsten metal in concentrated hydrogen peroxide, according to the following reaction [14]:



It has been shown [14,15] that peroxytungstates are thermodynamically unstable and decompose slowly generating solid tungsten trioxide as precipitate through the reduction of free H₂O₂ and polytungstate, according to the following reactions [14]:



The addition of ethanol or isopropanol in the solution has been found to improve its stability [14]. During electrodeposition, the dimeric peroxytungstate species undergoes a reduction and gives rise to tungsten trioxide and molecular oxygen according to the following reaction [14]:



In our earlier work [16] we demonstrated that aging of the precursor solution causes morphological modifications

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of electrodeposited WO₃ films. WO₃ films were electrodeposited 48 h after the precursor synthesis and were found to incorporate grape-like formations. However, the electrochromic devices fabricated with such films, exhibited a rather low coloration efficiency (24.7 cm²/C at 532 nm) which was attributed to excessive film thickness (about 1300 nm). The reduction of the film thickness could bring about an increase of the coloration efficiency, as less charge would be necessary for coloration.

In the present paper a systematic experimental study of the precursor aging phenomenon was conducted and films were prepared at different time intervals, ranging from 1 to 122 h after the precursor formation. The morphology of these films was investigated, as well as their optical and electrochemical properties. The film thickness was kept at approximately 600 nm in order to improve the performance of the resulting devices. Such electrochromic devices were fabricated and their properties and performance was investigated.

It was demonstrated that films prepared using aged solution exhibit improved ion mobility over films prepared using fresh solution. The highest values of the Li ion diffusion coefficient and the intercalated charge density per unit thickness were observed at 80 h of the precursor aging time. Moreover, films prepared using precursor solution that was aged for approximately that time yielded considerably higher values of the coloration efficiency than electron-gun deposited films, indicating their enhanced electrochromic properties.

2. Experimental

2.1. Preparation of the peroxytungstate solution

For the preparation of the peroxytungstate solution 6.5 g of W powder (99.9% pure) were dissolved in 40 ml H₂O₂ (30% dense) and 4 ml of distilled water, as described in [8]. The addition of W powder into H₂O₂ was conducted in a chilled water bath under continuous agitation. Then, the tungsten-peroxide solution was kept in a refrigerator at about 2 °C. At such low temperatures it takes about seven days for all of the W quantity to be dissolved. At that stage, a clear solution of a slightly yellowish colour is obtained. However, this solution still contains an excess quantity of H₂O₂ that is involved in parasitic reactions ((2) and (3)) and impedes an efficient electrodeposition [14]. To dispose of it, a further 5 days at low temperature (2 °C) are required. The gradual reduction of peroxide at low temperatures was preferred over other less time consuming methods (such as treatment with tungsten bronze at room temperature) as it prevents the precipitation of WO₃ sediment (yellow powder). Obviously, the low temperature decreases the speed of reaction (2). The peroxytungstate precursor [7], obtained by this procedure can be kept at 2 °C for a few weeks.

2.2. Deposition of WO₃

Part of the above solution was mixed with an equal volume of anhydrous ethanol at room temperature under continuous agitation and yielded a bright yellow liquid, which was heated to 60° for 15–20 min prior to deposition.

The electrodeposition of WO₃ from this solution was performed under a voltage of –450 mV for 7 min, with current densities of the order of 1–2 mA cm^{–2}. A typical three-electrode configuration was used with a SnO₂:F coated glass sheet (trade name: K-glass) with dimensions 2.5 × 3.5 cm² as the working electrode, an Ag/AgCl reference electrode and a Pt counter electrode. The films present a deep blue colour during the preparation process (signifying a reduced oxidation state for

tungsten [17]), which vanishes almost immediately after their removal from the solution. The films were then rinsed with de-ionised water and dried in air. This process yields WO₃ films of good quality with a typical thickness of about 600 nm, and with good adherence to the substrate.

In order to study the precursor aging, the aforementioned solution was used for several electrodepositions at different time intervals, ranging from 1 to 122 h after the precursor formation. Between electrodepositions the solution was kept at 2 °C.

Electron gun deposited WO₃ films were also prepared for comparison with electrodeposited films. They were grown in high vacuum (pressure less than 10^{–5} mbar), in a stainless steel chamber evacuated by turbo-molecular and mechanical pumps. WO₃ powder (99.99% pure) pressed in a pellet was used as the starting material and glass samples (of dimensions 2.5 × 4.0 cm²) were used as substrates. Some of these samples were Pilkington K-glass (SnO₂:F-coated glass) serving as the transparent conducting electrode in the EC devices, other being uncoated microscope slides used to verify the film thickness. The thickness of the films was measured in situ with ± 5 nm accuracy, by a quartz crystal monitor calibrated by independent thickness measurements.

2.3. Instrumentation and experimental techniques

The thickness of the films was measured using an Ambios XP-1 profilometer. Step height measurements between film-coated and uncoated areas were conducted to determine film thickness. This instrument was also used to assess the surface morphology and roughness of the films.

Transmission electron microscopy (TEM) pictures of the dried precursor were taken using a JEOL JEM 2100 microscope at 160 kV. A drop of the precursor solution was placed on a carbon coated copper substrate (grid) and was allowed to dry prior to the measurements.

Scanning electron microscopy (SEM) pictures of the films were taken using a JEOL 6300 microscope. This instrument has capabilities of composition analysis of the films with use of the Energy-Dispersive X-ray Spectroscopy (EDS) method.

In order to assess the electrochemical properties of the films, cyclic voltammetry (CV) and Galvanostatic Intermittent Titration (GITT) were performed using the following instruments: a potentiostat-galvanostat (AMEL, model 2053), a function generator (AMEL, model 586) and a noise reducer (AMEL NR 2000). The electrochemical cell used for these experiments has already been described elsewhere [17].

During the cyclic voltammetry tests, the potential between the working (WO₃/K-glass) and the reference (Pt) electrode was varied linearly in the range (–0.8 V, +1.3 V) at a rate of 50 mV/s.

During the GITT experiments, a series of 100 square current pulses with amplitude 0.2 mA and duration 5 s were fed into the electrochemical cell, each followed by an equilibration period of 30 s. The potential between working and reference electrodes (corresponding to the emf of the film) versus the inserted charge density was measured.

The chemical diffusion coefficient of Li⁺ was calculated using the formula

$$D = \frac{4L}{\pi\tau} \left(\frac{\Delta E_s}{\Delta E_t} \right)^2 \quad (5)$$

with ΔE_s is the change in the steady-state voltage as a result of the current pulse and ΔE_t the total change in overvoltage during the pulse, eliminating the IR drop τ the duration of each pulse (s) and L the film thickness. Eq. (5) can be applied to our

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