Electrodeposition of Tungsten and Titanium Oxides from Peroxo Precursors

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A large variety of metal oxides (TiO_2, WO_3, IrO_2, CoO, MoO_3…) can be deposited cathodically from a precursor based on a dissolved metal complexed by hydrogen peroxide. We will describe the preparation of two such oxides--titania and tungsten trioxide in this paper. Both these oxides have been intensely studied in recent years from both fundamental and practical application perspectives.

Classically, WO_3 thin films are prepared by evaporation or by sputtering. These methods are expensive and need huge energy consumption. Cathodic electrodeposition is a promising alternative route for electrochromic WO_3 thin film deposition. It is a low cost process, which allows the deposition onto substrates of very large area. Hydrogen peroxide is known for forming peroxo complexes with tungsten. These precursors can undergo a reduction and give rise to WO_3 film formation. Unfortunately, the preparation method of the precursor described in the literature [1,2] are long and complicated. Moreover the solutions obtained are very unstable.

We present a new, simple and fast method for preparing the deposition solution [3]. Typically it consists in mixing Na_2WO_4 and H_2O_2. The solution is subsequently acidified at pH 1.2 by perchloric acid addition. Films are deposited between 0.06 and 0.34 V versus NHE at room temperature. The films observed by SEM are smooth and well covering. They are amorphous by X-ray diffraction study. Voltammograms in H_2SO_4 and $LiClO_4$-PC have been recorded. The curves are typical of electrochromic WO_3 and are the signature of the compound. By comparing the tungsten content of the films and their thickness measured by profilometry the film porosity has been measured. It is shown that the porosity is a function of layer thickness: if films up to 100 nm thick are dense, the thicker ones are porous.

The optical and electrochromic properties have been studied by absorption measurements. The variation of the optical density has been studied as a function of injected charge. The coloration efficiencies measured at a wavelength of 633 nm for H^+ and Li^+ intercalation range between 62 and 66 $cm^2.C^{-1}$ and are similar to the results obtained with evaporated films.

The deposition process has been studied by the electrochemical quartz crystal microbalance technique. We have found that the deposition efficiency is unchanged after more that two days of storage of the deposition solution at room temperature. The deposition current along with the growth rate decrease slightly with the storage time. The deposition solution is thus remarkably stable for a peroxy-tungstate solution. An important parameter is the concentration ratio between hydrogen peroxide and sodium tungstate, α. Particular behaviours are observed when α is less than 0.8. Above 0.8 the deposition efficiency is found constant and the deposition efficiency decreases markedly with this parameter. It means that the precursor concentration has reached a maximum value then. An important point is the description of the precursor formed as a function of α. From the results of the present study and the literature data we suggest that the precursor species varies with α. For instance, the EQCM data show that the precursor formed at low α contains less than one peroxide per tungsten atom.

We will also describe data on the cathodic electrodeposition of titania thin films using peroxo precursors.

References:
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