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Towards electrochromic stability in sol–gel-derived tungsten oxide films: cyclic voltammetric and spectrophotometric investigations

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Abstract

Hitherto unexplored irreversible changes during initial coloration/bleaching cycles for sol–gel-derived tungsten oxide (WO_3) films have been investigated using cyclic voltammetric and spectrophotometric techniques. Non-ideal features appearing in the initial five anodic (deintercalation) cycles in the voltammogram with simultaneous decreased optical transmission of the bleached films have been explained in terms of possible stoichiometric variations affecting the coloration efficiency (CE) of the films and the associated mechanisms. Electrochromic stability attained thereafter manifests in retraceable voltammograms and almost invariant value of the CE.

Keywords: Sol–gel; Tungsten oxide; Cyclic voltammetry; Electrochromic; Coloration efficiency; Stoichiometry

1. Introduction

Electrochromic (EC) tungsten oxide (WO_3) films show considerable promise as solar energy control coatings for automotive antidazzling rearview mirrors, high

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contrast displays and smart windows [1,2]. In smart windows, thin films of active EC materials, in response to the variation in the brightness of the environment dynamically modulate optical transmittance by the application of electric potential or current. It opens possibilities in energy efficient architecture wherein the air conditioning and heating requirements can be brought down considerably by EC "smart windows" [1,3]. Such windows use WO_3 as the primary EC electrode as it happens to be the most extensively studied chromogenic material till date [4–9]. It also offers high coloration efficiency (CE), possesses good chemical stability and requisite ionic and electronic conductivity imperative for switching between the colored and bleached states [1].

Different techniques have been adopted for depositing WO_3 films, however, sol–gel processing is most popular because of its cost effectiveness, ease of depositing uniform large area films for window application and more importantly, it allows tailormaking of the microstructure of the films by the introduction of chemical dopants to the reactant sols or by control over annealing conditions improving the properties of the films. Films spin deposited using ethanolic solution of acetylated peroxotungstic acid (APTA) with oxalic acid (OAD) in appropriate amount have been shown by us to be highly transparent, having good adherence to substrates and of cosmetic quality. Incorporation of OAD modifies the microstructure of the films so as to have faster bleaching characteristics and gives reproducible stoichiometry, crystallinity, porosity and thickness [7,10].

Cyclic voltammetric (CV) and spectrophotometric techniques have been applied to WO_3 films prepared by various techniques to investigate Li^+ inter/deintercalation processes responsible for optical modulation these films can offer and to quantitatively determine their cyclic life and CE. In order to avoid effects due to the irreversibility of Li^+ insertion/extraction it is customary that the data presented is taken after a few coloration/bleaching cycles, when the films show clearly reversible behaviour. The voltammogram of a highly disordered WO_3 film is characterized by no cathodic peak and ill-defined anodic peak, but the cathodic and anodic currents represent the efficiency of the electrochemical reaction responsible for coloration and bleaching.

Non-ideal intercalation effects have been encountered frequently in EC WO_3 films [11,12]. For amorphous sputter deposited WO_3 films it was found [13] that large amounts of lithium could be inserted irreversibly without any coloration. This was attributed to Li trapping in "overstoichiometric" WO_3 films, forming Li_2O in the film. Lithium trapping manifested in the CV studies in precyclic voltammograms in the form of a pronounced peak during the "first" lithium insertion (cathodic cycle) [13]. During the second and subsequent cycles this peak was no longer observed. This characteristic feature was resolved properly only at sufficiently low scan rates ($100\,\mu V/s$).

Alternate to normal accomplishment of oxide network by post-deposition furnace heating, Taylor et al. [2] laser fired their sol–gel-derived WO_3 films, following a $100\,^{\circ}C$ prebake, using absorbed laser radiation. The deposition solution was ethanolic solution of peroxotungstic ester derivative modified by oxalic acid dihydrate. An inflection in the voltammogram during "coloring" of these films has