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Sol–gel derived nanocrystalline CeO_2–TiO_2 coatings for electrochromic windows

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Abstract

Mixed CeO_2–TiO_2 coatings synthesized by sol–gel spin coating process using mixed organic–inorganic $Ti(OC_3H_7)_4$ and $CeCl_3 \cdot 7H_2O$ precursors with different Ce/Ti mole ratios were investigated by a wide range of characterization techniques. The attempts were directed towards achieving coatings with high transparency in the visible region and good electrochemical properties. Elucidation of the structural and optical features of the films yielded information on the aspects relevant to their usage in transmissive electrochromic devices. The films have been found to exhibit properties for counter electrode in electrochromic smart windows in which they are able to retain their transparency under charge insertion, high enough for practical uses. The high optical modulation and fastest switching for WO_3 film in the device configuration with the Ce/Ti (1:1) film is interpreted in terms of conducive microstructural changes induced by addition of TiO_2 in an amount equivalent to CeO_2.

Keywords: Sol–gel; Passive counter electrode; CeO_2–TiO_2; Nanocrystalline; Electrochromic devices

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1. Introduction

Two forms of counter electrodes in transmissive electrochromic devices (ECDs) are well-known. One possibility involves an active counter electrode, which is an electrochromic (EC) layer, complementary with the selected electrochromic electrode for e.g. tungsten trioxide (WO_3). The second alternative is an optically passive counter electrode, which remains colorless in both charged and discharged states. Whether active or passive the counter electrode has to balance the charge shuttled from the active EC film through the electrolyte based primarily on the Li ion. Thus the ion storage capacity of the counter electrode should equal the ion storage capacity of EC WO_3. Good cycling stability within the operational voltage and temperature range of the ECDs is another requirement of the counter electrode.

Among extensively investigated optically passive counter electrode materials, vanadium pentoxide (V_2O_5) is known for its high Li^+ storage capability and reversible intercalation kinetics for lithium, but low transmission in bleached state puts a limitation on its application. Tin oxide doped with different dopants like Mo and Sb has also been studied as a candidate for a passive counter electrode, but instability of SnO_2 towards Li^+ intercalation and the likely reaction leading to the formation of SnO, Sn and Li_2O prompted exploratory work on other suitable passive counter electrode materials for ECDs. In comparison with the above-mentioned materials, CeO_2 appears to be more promising optically passive counter electrode material. The reversibility of the lithium ion intercalation reaction in CeO_2 is reasonably good but the reaction kinetics is very slow [1]. Several attempts have been made in order to improve the reaction kinetics by way of mixing the oxide with other materials such as Ti, Zr, V, Sn, Mo and Si individually or with their mixtures [2–6]. Films of pure and doped CeO_2 have been made by different techniques. Sputtering technique has been adopted by Granqvist et. al. [7] and the films thus obtained have been extensively studied. The potential of such films as passive counter electrodes has been reported.

In the developmental process of WO_3 based transmissive ECDs, we are concentrating our efforts for developing ion storage counter electrode films with a high transmittance for visible light both in the charged and discharged state and an ion storage capacity exceeding $20\,mC\,cm^{-2}$ or comparable to WO_3 to provide sufficient number of ions for deep coloration. In this direction, some work was undertaken for the synthesis of CeO_2 precursors mixed with TiO_2 via a wet chemistry route.

Synthesis of mixed CeO_2–TiO_2 films by sol–gel technique has been attempted following route based on salt of cerium i.e. $CeCl_3 \cdot 7H_2O$ in combination with Ti propoxide [8]. This study gives in detail the preparation of the precursor sols, deposition of films and study of their properties.

2. Experimental

2.1. Preparation of deposition solutions

To 2.5 g of $CeCl_3 \cdot 7H_2O$ (Merck) dissolved in 30 ml of C_2H_5OH, 1.907 g of titanium propoxide (Aldrich) was added to obtain a deposition solution containing