

RF Sputtered SnO₂, Sn-Doped In₂O₃ and Ce-Doped TiO₂ Films as Transparent Counter Electrodes for Electrochromic Window

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The SnO₂, Sn-doped In₂O₃ and Ce-doped TiO₂ films have been prepared by RF sputtering method, and their opto-electrochemical properties were investigated in view of the applicability as counter electrodes in the electrochromic window system. These oxide films could reversibly intercalate Li⁺ ions owing to the nanocrystalline texture, but remained colorless and transparent. The high transmittance of the lithiated films could be attributed to the prevalence of the Sn⁴⁺/Sn²⁺ and Ce⁴⁺/Ce³⁺ redox couples having 5s and 6s character conduction bands, respectively. For the Ce-doped TiO₂ film, (TiO₂)_{1-x}(CeO₂)_x, an optimized electrochemical reversibility was found in the film with the composition of $x = 0.1$.

Introduction

Since the first discovery of electrochromism in WO₃ by Deb,¹ there have been extensive studies on the electrochromic materials and their application to the light-modulating devices such as smart window, glare-free mirror, information display, and *etc.* Most electrochromic devices include an ion storage layer that operates in a complementary redox mode to the active electrochromic film. The ion storage electrode is often referred to the counter electrode of the devices. The requirements for such counter electrodes depend on the main purpose of the device; *i.e.* whether it is designed for reflectance modulation or transmittance one. In the former, the role of counter electrode is mainly as the ion-storage layer and only its electrochemical properties are of interest, where various materials such as carbon²⁻⁶ and metallic Al, Ti, Pt, Au, *etc.*^{4,7,8} have been used. On the other hand, in the latter transmittance modulation device, both the electrochemical and optical properties are of importance, since the device should be operated between the colored and fully transparent states.

Because the electro-optical properties should be taken into account as well as electrochemical ones, the choice of counter electrode material is more complex for the transmittance-type electrochromic device than the reflection-type one. As the counter electrode for transmittance-type device, it is possible to use one of the following three types of films: (i) electrochromic films those which exhibit reversible coloring/bleaching behavior in a manner that is complementary to the function of the primary electrochromic film, (ii) electrochromic films with low coloration efficiency and (iii) transparent films with optical properties that remain unchanged upon ion insertion/deinsertion. Films corresponding to option (i) are composed of either the anodic or cathodic coloring materials depending on the nature of the primary electrochromic film. With regard to (ii), it is possible to use

the V₂O₅^{9,10} film or the crystalline WO₃ one¹¹ as the counter electrode for cathodic electrochromic film. Thin films of (SnO₂)_x(In₂O₃)_{1-x}¹²⁻¹⁶ or (TiO₂)_{1-x}(CeO₂)_x¹⁷⁻²⁰ can be placed under the category (iii).

Recently, we have investigated the influence of crystalline size on the electrochemical insertion process of Li⁺ ion into polycrystalline SnO₂, and found that Li⁺ ion could be inserted into (deinserted from) the nano-crystalline SnO₂, although the rutile structure of SnO₂ inhibits the intercalation of Li⁺ ion, because the nano-crystalline surface could provide a reversible grafting site for Li⁺ ion.²¹ Therefore, it could be expected that the thin film with nano-crystalline structure may be a good candidate as counter electrode for transparent electrochromic device. In this paper, we report the optical and electrochemical properties of the nano-crystalline SnO₂, Sn-doped In₂O₃ and Ce-doped TiO₂ films which are promising as the transparent counter electrodes in the variable transmittance electrochromic device.

Experimental

The SnO₂ and Sn-doped In₂O₃ (ITO) films were prepared on glass substrate by RF sputtering of home made targets, SnO₂, and (SnO₂)_{0.1}(In₂O₃)_{0.9}, respectively. The Ce-doped TiO₂ films were deposited on the commercial ITO substrate by RF sputtering with (TiO₂)_{1-x}(CeO₂)_x targets. The RF sputtering conditions are listed in Table 1.

Electrochemical experiments were performed with a computer-controlled potentiostat/galvanostat (TACUSSEL, PGS 201T). Each oxide film and the Li foil were used as working electrode and counter-reference electrode, respectively. Both electrodes were immersed in 1.0 M LiClO₄-propylene carbonate (PC) electrolyte. The electrode potential of Li metal was stable under the present experimental condition, and therefore could serve as the reference electrode.

Optical data were collected using a UV-Vis-NIR spectrophotometer (Varian Cary 2415), equipped with DS15 Data Station.

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Table 1. Sputtering condition for the SnO₂, Sn-doped In₂O₃ (ITO), and Ce-doped TiO₂ films

Films	Target ($\phi=5$ cm)	Atmosphere	Power	T _s
SnO ₂	SnO ₂	Ar, 5×10^{-3} mbar	50 W	50 °C
(SnO ₂) _x (In ₂ O ₃) _{1-x}	(SnO ₂) _{0.1} (In ₂ O ₃) _{0.9}	Ar, 5×10^{-3} mbar	50 W	150 °C
	TiO ₂		60 W	
	(TiO ₂) _{0.9} (CeO ₂) _{0.1}	O ₂ , O ₂ /Ar=1	50 W	
(TiO ₂) _x (CeO ₂) _{1-x}	(TiO ₂) _{0.5} (CeO ₂) _{0.5}	5×10^{-2} mbar	47.5 W	50 °C
	(TiO ₂) _{0.2} (CeO ₂) _{0.8}		42.5 W	
	CeO ₂		40 W	

For all cases, the target to substrate distances are 10 cm.

Results and Discussion

From the opto-electrochemical investigation during the Li⁺-insertion into SnO₂ film, it was found that SnO₂ is able to sustain a reversible Li⁺ insertion due to its porous nanocrystalline nature. For the Li⁺-discharge/charge of the SnO₂ electrode, the main electrochemical process is considered to be a reversible grafting of the Li⁺ ions on the granular surface defects. The Li⁺-capacity of the nanocrystalline oxide specimen, having a large electrochemical surface, is about three times larger than that of the well crystallized one with a smaller electrochemical surface.²² Consequently, the well textured SnO₂, having a porous nanocrystalline structure, can act as an efficient counter electrode. It can remain transparent in both the Li⁺-inserted and deinserted states owing to its broad conduction band of 5s character. The 5s character band can accommodate a large density of conduction electrons which nearly do not absorb the visible light.

Also for the Li⁺-insertion into ITO, a similar optical behavior is observed as in SnO₂. For the redox chemistry of ITO, it can be expected that the Sn⁴⁺/Sn²⁺ or In³⁺/In⁺ couples are involved. However, considering the band structure of n-type semiconductor ITO, the reduction of Sn⁴⁺ is more probable than that of In³⁺, because the dopant Sn-levels, slightly below the conduction band, can provide electron accepting center. Therefore, the remaining transparency of the Li⁺ inserted ITO could be also explained by the presence of a broad conduction band with s character. The optical spectra of nanocrystalline Li_xSnO₂ and Li_xITO films, shown in Figure 1, indicates that both the electrodes maintain high transmittance, at the Li⁺-inserted state, and therefore can be useful as transparent counter electrodes.

We have also established that Ce-doped Ti oxide, (TiO₂)_{1-x}(CeO₂)_x, is another efficient transparent counter electrode. Similarly as WO₃, TiO₂ has a conduction band of d character. Consequently, the pure TiO₂ films absorb the visible light when they undergo the reversible Li⁺ insertion as follows.

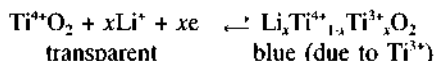


Figure 2 shows that, in fact, the absorption coefficient ($\Delta\alpha$) for the TiO₂ film gradually increases with the Li⁺-insertion. Therefore, in order to achieve a constant tran-

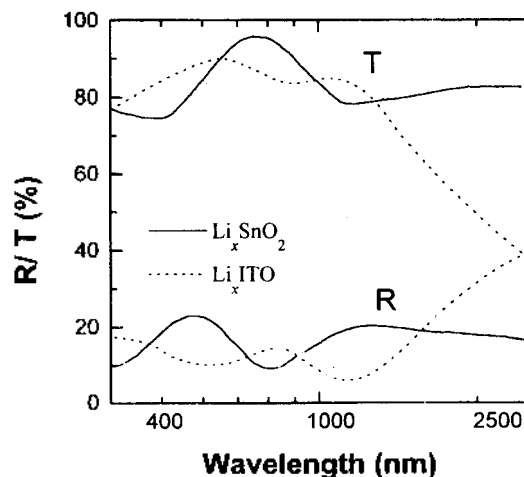


Figure 1. Transmittance (T) and reflectance (R) spectra for the lithiated SnO₂ (—) and ITO (---) films.

sparency in both the Li⁺-inserted and deinserted states, it was necessary to consider the doping of TiO₂ with other cations. For this purpose, Ce⁴⁺ could be a good candidate, since it can act as a deep accepting center for the electrons. Namely, in the Ce-doped TiO₂, the Ce⁴⁺/Ce³⁺ redox reaction will take place during the Li⁺ insertion/deinsertion and can avoid the Ti⁴⁺ reduction, thereby maintaining the film transparency.

The Ce-doped TiO₂, (TiO₂)_{1-x}(CeO₂)_x films were prepared for x=0, 0.1, 0.5, 0.8, and 1. Among them, only the two composites of x=0.1 and 0.5 were revealed to be amorphous according to the electron diffraction analysis, implying the nanocrystalline nature of the films. Their electrochemical and optical properties were also investigated, where (TiO₂)_{0.9}(CeO₂)_{0.1} was found to be most appropriate for the transparent counter electrode. Figure 3 shows the cyclic voltammetric behaviors of the TiO₂, (TiO₂)_{0.9}(CeO₂)_{0.1} and (TiO₂)_{0.5}(CeO₂)_{0.5} films involving Ti⁴⁺/Ti³⁺ and Ce⁴⁺/Ce³⁺ redox peaks. The distinct cathodic (around 2.5 V vs. Li/Li⁺) and anodic (around 3.1 V) peaks corresponding to Ce⁴⁺/Ce³⁺ redox process occur reversibly during the Li⁺ insertion/deins-

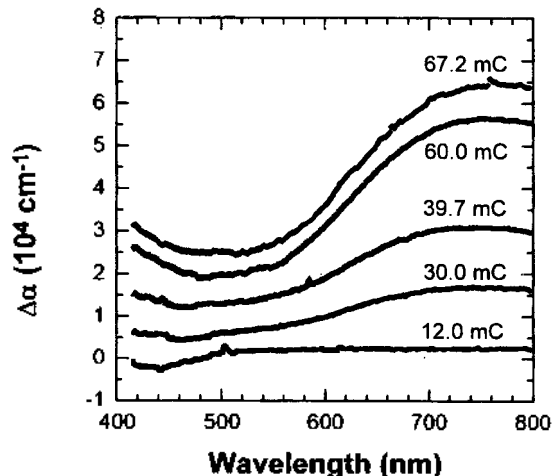


Figure 2. Variation of the absorption coefficients ($\Delta\alpha$) as a function of the inserted charge for TiO₂ film deposited on ITO-coated glass.

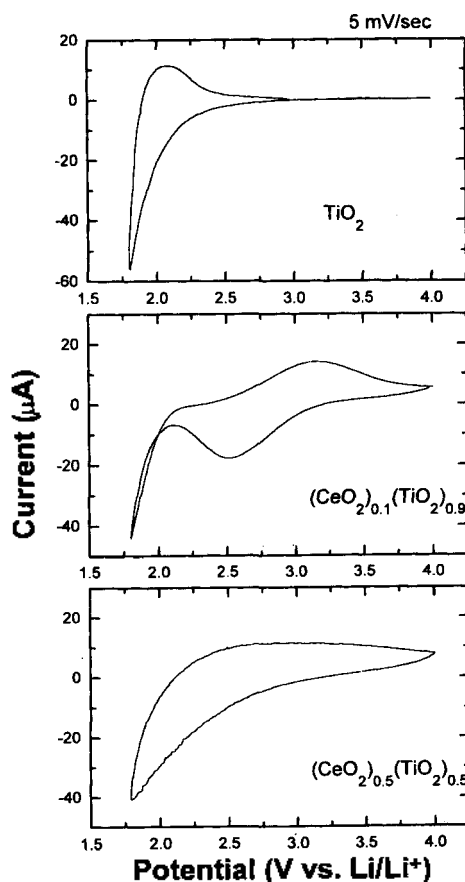


Figure 3. Cyclic voltammograms for the TiO₂, (CeO₂)_{0.1}(TiO₂)_{0.9}, and (CeO₂)_{0.5}(TiO₂)_{0.5} films.

ertion for the composition (TiO₂)_{0.9}(CeO₂)_{0.1}, while no cathodic peak occurs for the 50% Ce-doped TiO₂ film. As shown in the cyclic voltammogram for 10% Ce-doped film, the electrode potential should remain higher than ~2 V vs. Li/Li⁺, in order to avoid the Ti⁴⁺ reduction.

For the composition (TiO₂)_{0.9}(CeO₂)_{0.1}, the achievement of a high transparency in both Li⁺-inserted and deinserted states is illustrated in Figure 4, where the absorption coef-

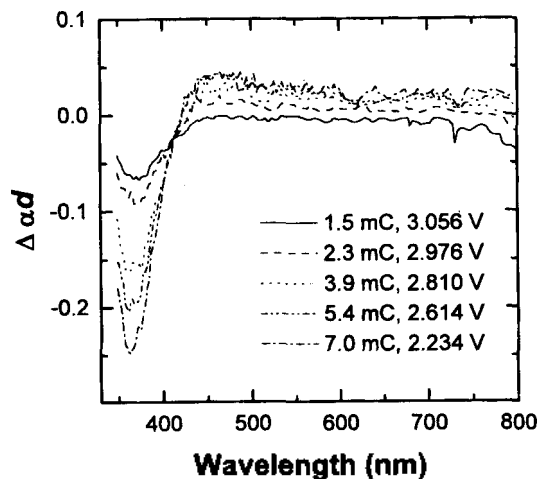


Figure 4. Variation of the absorption coefficients ($\Delta\alpha$) as a function of the electrode potential (vs. Li/Li⁺) and inserted charge, for (CeO₂)_{0.1}(TiO₂)_{0.9} film deposited on ITO-coated glass.

ficient does not change in the whole visible range upon Li⁺ insertion.

Summary

Optical and electrochemical properties of the RF sputtered SnO₂, Sn-doped In₂O₃ and Ce-doped TiO₂ films were studied. The transparency after insertion of Li⁺ ion could be observed and explained by the 5s character of Sn⁴⁺ and the deep electron accepting center provided by Ce⁴⁺ dopant for the Sn-containing oxide films and Ce-containing one, respectively. Consequently, these films can be used as the counter electrode in variable transmittance electrochromic device.

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