Spray deposited CeO₂–TiO₂ counter electrode for electrochromic devices

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Abstract. Optically passive thin films of CeO₂–TiO₂ mixed oxides with molar ratio of Ce/Ti of 0.05 were deposited by the spray pyrolysis technique (SPT) on a glass and fluorine-doped tin oxide (FTO)-coated glass substrates. Precursor solution containing cerium nitrate hexahydrate (Ce(NO₃)₂·6H₂O) and titanium tetraisopropoxide (Ti(OⁱPr)₄) having different volumetric proportions (0–5 vol% of Ti) in methanol were used. These films were characterized for structural, morphological, molecular, optical, electrochromic and colourimetric analysis. CeO₂–TiO₂ films deposited at 400°C were found to be polycrystalline with cubic fluorite crystal structure. Transformation from polycrystalline to amorphous phase was observed with increasing TiO₂ content. The band centred at 539 cm^{–1} is assigned to Ce–O stretching vibration and the two medium intensity bands assigned to (Ti–O) and (Ti–O–Ti) stretching modes at 798 and 451 cm^{–1}, which confirms the mixed CeO₂ and TiO₂ phases. The band gap energy decreases (E_g) from 3.45 eV for pristine CeO₂ to 2.98–3.09 eV for CeO₂–TiO₂ films. The ion storage capacity (ISC) of CeO₂–TiO₂ thin film with 3 vol% Ti (Ce–Ti₃ sample) was found to be 26 mC cm^{–2} and electrochemical stability up to 30,000 cycles in 0.5 M LiClO₄–PC electrolyte. The optically passive behaviour of CeO₂–TiO₂ thin film is confirmed by its negligible transmission modulation ($\Delta T \sim 2.5\%$) upon Li⁺ ion insertion/extraction, irrespective of the extent of Li⁺ ion intercalation. The optical modulation of sputter deposited electrochromic WO₃ thin film was found to be enhanced from 56 to 61% with rapid increase in colouration efficiency (CE) from 42 to 231 cm² C^{–1} when CeO₂–TiO₂ is coupled as a counter electrode with WO₃ in an electrochromic device (ECD). On reduction of WO₃ thin film with CeO₂–TiO₂ as counter electrode, the CIELAB 1931 2° colour space coordinates show the transition from colourless to the deep blue state ($L^* = 88.07$, $a^* = -2.37$, $b^* = 24.59$ and $L^* = 40.32$, $a^* = -1.16$, $b^* = -5.65$) with steady decrease in relative lightness. Y_{xy} and $L^*a^*b^*$ coordinates signify CeO₂–TiO₂ films and it also exhibits the application as counter electrode in electrochromic smart windows in which they are able to retain their transparency under charge insertion/extraction.

Keywords. CeO₂–TiO₂ thin films; WO₃ thin film; counter electrode; colour analysis; electrochromism.

1. Introduction

Electrochromic windows (ECW) have emerged in the last decade from laboratory studies to become a promising energy-conserving technology for buildings applications. WO₃ thin films have been investigated extensively for their application in smart window technology. The technological requirement of smart windows includes the electrochromic working electrode and ion storage layer that should be optically passive after intercalation/deintercalation process. There are only few materials which are used as an optically passive counter electrode with large ion storage capacity (ISC) such as CeO₂,¹ CeO₂–ZrO₂, CeO₂–TiO₂, CeO₂–SiO₂,² CeO₂–SnO₂³ and CeO₂–TiO₂–ZrO₂.⁴ However, for complimentary electrochromic system such as WO₃–NiO,⁵ WO₃–PANI,⁶ WO₃–PPy,⁷ WO₃–PB⁸ in which WO₃ serves as a working electrode and NiO, PANI, PPy and PB act

as counter electrode with another coloured state. So due to dual colour state of the electrochromic system, darkness and lightness of the system cannot be tailored easily. Optically passive counter electrode has an ability to overcome this drawback because, it can offer high transmission in the visible range, small transmission changes during the Li⁺ or H⁺ insertion and should optically passive, i.e., its transmittance should remain unchanged during insertion/extraction process. For an industrial application, transparent electrochromic devices (ECDs) must have (i) an electrochromic electrode producing variable optical absorption, and (ii) a counter electrode that is transparent when the electrochromic material is in its non-absorbing state. Ceria-based CeO₂–TiO₂ fulfill the above two requirements for an ideal counter electrode. Thin films of mixed oxides of CeO₂–TiO₂ remain colourless in insertion/extraction process contrary to WO₃ which becomes deep blue under similar electrochemical conditions.⁹ Thus, these films can be used in electrochromic smart windows due to their electro-optical performance.¹⁰ CeO₂–TiO₂ has good oxygen transport capacity and it

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can easily shift between reduced and oxidized states ($\text{Ce}^{3+} \leftrightarrow \text{Ce}^{4+}$).^{11–14} The structure and the conductivity of CeO_2 films were modified by the substitution of Ti for Ce atoms. It has been used as counter electrode in ECD^{15–17} and solid oxide fuel cell electrolytes.^{18,19} The first results concerning cerium–titanium sols have been reported.²⁰ Thin films of CeO_2 – TiO_2 have also been prepared^{21,22} and using the preparative method proposed by Makishima *et al.*²³ Research on the active or encapsulating materials, or both, and studies that address the influence of materials degradation on device performance are of critical importance. This is especially true if we understood the degradation of the materials used in ECWs. The use of CeO_2 as an optically passive counter electrode in smart window is an immense problem due to the slow reaction rate and electrochemical instability when it is coupled with the WO_3 electrode. In order to increase the electrochemical stability and ability to store and release oxygen during operations, other transition and non-transition metal ions could be introduced into the ceria cubic structure. Due to introduction of metal ions into it, redox properties of CeO_2 thin film could be greatly enhanced.

In this contribution, an effort has been taken on the study of structural, morphological, optical and electrochromic properties of titanium mixed cerium oxide (CeO_2 – TiO_2) thin films prepared by the spray pyrolysis technique (SPT) onto fluorine-doped tin oxide (FTO)-coated conducting glass substrate, which are helpful to enhance stability of ceria without diminishing its special features such as its unique redox properties.

2. Experimental

Stock solutions of concentration of 0.05 M of CeO_2 and TiO_2 were prepared by using cerium nitrate hexahydrate ($\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$) (99.5%, Acros Organics), and titanium tetra isopropoxide ($\text{Ti}(\text{O}^i\text{Pr})_4$) (99% Loba Chem) precursors in methanol. The solution was clear and colourless without any precipitation. Prior to film deposition, FTO substrates were cleaned with ultrasonic vibrations in acetone and de-ionized water, respectively. A precursor solution (50 ml) was sprayed with different volumetric proportions of above two stock solutions. Pristine CeO_2 and CeO_2 – TiO_2 thin films were prepared by varying the quantity of TiO_2 solution as 0, 2, 3, 4 and 5 vol% and the resulting films hereafter are referred to as Ce– Ti_0 , Ce– Ti_2 , Ce– Ti_3 , Ce– Ti_4 and Ce– Ti_5 , respectively. The preparative parameters such as nozzle to substrate distance (20 cm), quantity of spraying solution (50 ml), solution spray rate ($5 \text{ cm}^3 \text{ min}^{-1}$), solution concentration (0.05 M) and substrate temperature (400°C) were kept constant. The Chromel–Alumel thermocouple was used to measure the temperature of the hot plate using electronic temperature controller (Model 9601, Aplab make) with an accuracy of $\pm 5^\circ\text{C}$. The structural characterization of the films was carried out using a X-ray diffractometer (Philips, PW 1710, Almelo, Holland), operated at 25 kV, 20 mA with $\text{CuK}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). The Fourier transform

infrared (FT-IR) spectra of powder collected from all CeO_2 – TiO_2 samples were recorded using Perkin-Elmer IR spectrophotometer (model-100) in the spectral range of $400\text{--}4000 \text{ cm}^{-1}$ with a resolution of 1 cm^{-1} . The surface morphological features of the films were analysed from scanning electron microscopy (SEM) images, which were recorded using a scanning electron microscope (Model JEOL-JSM-6360, Japan), operated at 20 kV. The optical absorption–transmission study was carried out using UV–vis spectrophotometer (Shimadzu, model: UV-1800, Japan) in the wavelength range of 350–1100 nm. For the electrochromic characterization of the films, all the measurements were performed in an electrolyte of 0.5 M LiClO_4 in propylene carbonate (PC) in a conventional three-electrode arrangement of following configurations:

- (i) Glass/FTO/ CeO_2 – TiO_2 / LiClO_4 -PC/SCE/Graphite.
- (ii) Glass/FTO/ WO_3 / LiClO_4 -PC/SCE/Graphite.
- (iii) Glass/FTO/ WO_3 / LiClO_4 -PC/SCE/ CeO_2 – TiO_2 .

In first two configurations of electrochemical cell, CeO_2 – TiO_2 and WO_3 thin film coated on FTO acts as a working electrode (active area $\sim 2.5 \text{ cm}^2 \times 1 \text{ cm}^2$), saturated calomel electrode (SCE) serving as a reference electrode to which all measured voltages were referred. G is graphite plate, which acts as a counter electrode. The third configuration consists of WO_3 film as a working electrode and CeO_2 – TiO_2 film as a counter electrode. The cyclic voltammetry (CV) and chronocoulometry (CC) experiments were conducted at a scan rate of 20 mV s^{-1} using an electrochemical quartz crystal microbalance (EQCM) measurements (model-CHI-400A) made by CH Instruments, USA and the potential was swept between anodic ($+0.9 \text{ V}$) to cathodic (-0.9 V) cycle with respect to SCE. The transmission profiles of the CeO_2 – TiO_2 films were recorded in the visible spectral region upon intercalation and deintercalation of Li^+ ions vs. graphite as counter electrode in 0.5 M LiClO_4 –PC electrolyte upon application of $\pm 0.9 \text{ V}$ for 60 s. In later experiment, *ex-situ* transmittance curves were recorded for coloured and bleached WO_3 in same electrolyte with graphite and CeO_2 – TiO_2 as counter electrode separately in order to check the performance of CeO_2 – TiO_2 as an ion storage material. The WO_3 thin film (as a working electrode) was obtained by RF reactive sputtering. Depositions were taken on unheated glass plates, $2.5 \times 1 \text{ cm}^2$ in size, which were precoated with In_2O_3 : SnO_2 (ITO). The films were made in argon/oxygen atmosphere with different O_2/Ar flow ratios to achieve optimal transparency.

Colourimetric analyses were done with the help of Shimadzu made colour analysis software equipped with UV–vis spectrophotometer by analysing transmittance spectra of colour/bleach state to evaluate $L^*a^*b^*$ and Y_{xy} coordinate values. The obtained $L^*a^*b^*$ and Y_{xy} values were used as reference data in order to get the observed colour in reduced and oxidized state for all samples from online easy colour analysis software with 1931 2° observer and D-65 illuminant proposed by CIE Y_{xy} and $L^*a^*b^*$ coordinate.

3. Results and discussion

3.1 X-ray diffraction (XRD)

The resultant spray deposited CeO₂-TiO₂ films were adherent to the substrates. Figure 1 illustrates the XRD patterns of films with different Ce/Ti mole ratios and pristine CeO₂ (Ce-Ti₀) films. Cubic fluorite structured CeO₂ phase formation has been confirmed from standard JCPDS data (81-0792). The crystallite size evaluated along the plane (111) using Debey-Scherrer's equation (1) is 8 nm

$$D = \frac{K\lambda}{\beta \cos \theta}, \quad (1)$$

where 'k' is the dimensionless constant (0.95), 'β' the corrected broadening of diffraction line measured at half of its

Figure 1. XRD spectrum for pure CeO₂ (T₀), and CeO₂-TiO₂ (T₂-T₅) thin film samples deposited at 400°C.

Figure 2. FT-IR transmittance spectra of pristine CeO₂ (T₀) and CeO₂-TiO₂ (T₂-T₅).

maximum intensity (FWHM) and 'D' the crystallite size, λ and θ the wavelength of X-ray (1.5406 Å) and diffraction angle, respectively. Four different reflections along (111), (200), (331) and (422) are prominently seen in patterns of Ce-Ti₂ to Ce-Ti₄ samples. The crystallite size along the most intense peak (111) for Ce-Ti₃ sample is 7 nm. The decrease in crystallinity and intensity of reflection along the (111) plane was found to be diminished with further increase in TiO₂ content from 0 to 4 vol%. With the increase in TiO₂ content 5 vol%, (Ce-Ti₅ sample), the reflection (200), (422) diminished completely. No reflections of TiO₂ are detected in XRD patterns of CeO₂-TiO₂ films. The amorphicity of CeO₂ film increases while crystallite size decreases linearly with the increase in TiO₂ content.

3.2 Infrared spectroscopy (IR)

The FT-IR study gives the information about phase composition and the oxygen bounding to the metal ions. Figure 2 shows the FT-IR transmittance spectra of all the samples in the range of 400–4000 cm⁻¹. The broad absorption peak at 3390–3434 cm⁻¹ can be attributed to various O–H stretching modes of water molecules adsorbed or incorporated into the film structure.²⁴ The peak at (2923–2923 cm⁻¹) may be due to the residual NO₂ group originating from the precursor salt, cerium nitrate. Phoka *et al*²⁵ shown that the band at 2921 cm⁻¹ attributed to the C–H bonds of the organic compounds. The band at 1639–1456 cm⁻¹ corresponds to Ce=O terminal stretching. The band at 539 cm⁻¹ is assigned to Ce–O stretching vibration.¹⁷ The two medium intensity bands assigned to ν(Ti–O) and ν(Ti–O–Ti) stretching modes at 798 and 451 cm⁻¹, respectively.²⁶ The intense peak at 1102–1106 cm⁻¹ is due to water adsorption (O–H–H).²⁷ Hence, CeO₂ and TiO₂ phases for all the samples (CeK-Ti₂-Ce-Ti₅) are confirmed from IR study, and thereby samples acquire CeO₂/TiO₂ mixed composition.

3.3 Scanning electron microscopy (SEM)

Morphological features of thin films are helpful to explore their novel properties suitable for intended application. Figure 3 shows SEM images of the pristine CeO₂ (CeTi₀) and CeO₂-TiO₂ (Ce-Ti₂-Ce-Ti₅) thin films showing different surface morphologies. All samples consist of golf-ball-like bulky porous structure of 6–12 μm size having microvoids within the structure. Such morphology allows the easy passage for Li⁺ ion intercalation and deintercalation. Similar morphology was also observed for sol-gel and spray pyrolysis derived CeO₂ films.²⁸

3.4 UV-vis spectroscopy

The optical absorption spectra for the pristine CeO₂ and CeO₂-TiO₂ films were recorded in the wavelength range of 350–1100 nm. All the films have high optical transmittance in the visible region (at λ = 630 nm). To determine the fundamental gap accurately and to identify its nature, Tauc formulation²⁹ is used. The band gap energy (E_g) is

Figure 3. Scanning electron microscopy images of the pristine CeO_2 and $\text{CeO}_2\text{-TiO}_2$ thin film samples at $\times 2000$ magnification.

determined using optical absorption coefficient (α) from the experimental absorbance,³⁰ assuming both direct allowed transition. Figure 4 shows the Tauc plots, i.e., variation of $(\alpha h\nu)^2$ vs. photon energy ($h\nu$) for all the samples. E_g values are obtained by extrapolation of the linear region of higher photon energy to zero absorption coefficient ($\alpha = 0$), i.e., using linear fits close to the absorption edge. The E_g value was found to be 3.45 eV for pristine CeO_2 and it decreases from 3.09 to 2.98 eV for $\text{CeO}_2\text{-TiO}_2$ films. The E_g values for $\text{CeO}_2\text{-TiO}_2$ show red shift from the theoretical band gap of the CeO_2 (3.2 eV).³¹

3.5 Electrochromic study

Cyclic voltammetry (CV) is employed to investigate the cathodic/anodic behaviour of $\text{CeO}_2\text{-TiO}_2$ thin films in

$\text{LiClO}_4\text{-PC}$ electrolyte. Figure 5 shows CV of pristine CeO_2 (Ce-Ti_0) and $\text{CeO}_2\text{-TiO}_2$ (Ce-Ti_2 to Ce-Ti_5) thin films, within a potential window of ± 0.9 V vs. SCE recorded at the scan rate of 20 mV s^{-1} . A cathodic current flows, when the $\text{CeO}_2\text{-TiO}_2$ electrode is swept into the negative potential at -0.9 V vs. SCE, which signify the $\text{Ce}^{4+} \rightarrow \text{Ce}^{3+}$ reduction process and the Li^+ intercalation.¹¹ The anodic wave is however different for different samples, indicating almost similar intercalation process but dissimilar deintercalation process. The $\text{Ce}^{4+}/\text{Ce}^{3+}$ intervalancy charge transfer mechanism has been confirmed from the XPS results in our previous studies of pristine CeO_2 films.¹⁶ The area under CV curve increases and becomes optimum for Ce-Ti_3 sample and again decreases for Ce-Ti_4 and Ce-Ti_5 samples. The cathodic peak current density of Ce-Ti_3 sample was found to be $480 \mu\text{A cm}^{-2}$, which is less than the previous reports.³³ The low value of cathodic current density can be attributed

Figure 4. Tauc plot to estimate the band gap of pure CeO₂ (T₀) and CeO₂-TiO₂ (T₂-T₅).

to cathodic dissolution. Ce-Ti₃ sample has large ion storage capacity (ISC) than that of other samples (Ce-Ti₂, Ce-Ti₄, Ce-Ti₅).

Chronocoulometry (CC) gives quantitative information about the number of protons/ions intercalated or deintercalated on the application of a potential double step for a known time. Figure 6 shows CC plots of CeO₂-TiO₂ (Ce-Ti₂ to Ce-Ti₅) thin films recorded at a potential step of ± 0.9 V in their coloured and bleached states for 60 s in 0.5 M LiClO₄-PC electrolyte. The electrochromic reversibility of CeO₂-TiO₂ films is determined from CC curves by determining the amount of charge intercalated (Q_i), amount of charge de-intercalated (Q_{di}) and the residual charge ($Q_i - Q_{di}$) using relation (2)

$$\text{Reversibility} = \frac{Q_{di}}{Q_i} \quad (2)$$

A relatively maximum reversibility of 30% is observed for Ce-Ti₃ sample among the other samples as shown in table 1. Inset of figure 7 shows the ISC determined from CC curves of all the samples vs. TiO₂ content exhibiting maximum ISC value of 26 mC cm⁻² for the Ce-Ti₃ sample.

Electrochemical stability of the material is the cause of concern for commercialization of a counter electrode. Therefore, the electrochemical stability of all the samples is tested by repeating colouration (intercalation)-bleaching (deintercalation) processes up to 30,000 cycles in 0.5 M LiClO₄-PC electrolyte. Figure 7 shows the amount of intercalated charge density (Q_i) and its variation with electrochemical cycles. All the samples are cathodically polarized for 60 s. The maximum ISC value of 26 mC cm⁻² is observed for Ce-Ti₃ sample. Inset of figure 8 shows that initially, the rate of loss of Q_i is fast, then becomes slow and wanes down to 16 mC cm⁻² after 5000 cycles and reach to 13 mC cm⁻²

at the end of 30,000 cycles. The charge density for Ce-Ti₃ sample is larger than those reported by others.^{3,20,32} As established experimentally,^{34,35} ISC of the films depends profoundly on the number of active insertion sites, porous morphology, film thickness and crystallite size. The smaller crystallite size and higher film thickness are conducive for greater ion insertion capability. Verma *et al.*³² have shown that the ISC dependence in such case is predominately controlled by the porous morphology surpassing the influence of crystallite size or the film thickness. Similar explanation is valid for our samples as well and is consensus with the morphological studies. These results clearly demonstrate that the sample Ce-Ti₃ has larger ISC and high electrochemical stability.

To establish the suitability of films as passive counter electrode in electrochromic device, in first step the transmission modulation of all the CeO₂-TiO₂ films is studied. Figure 8 shows the transmission profiles of CeO₂-TiO₂ (sample Ce-Ti₃), and WO₃ thin film with and without CeO₂-TiO₂ as a counter electrode in its bleached and lithiated states recorded in 0.5 M LiClO₄-PC electrolyte upon application of ± 0.9 V vs. SCE for 60 s. Intercalation of Li⁺ ion is found to induce a minor change in transmission modulation measured at $\lambda = 630$ nm, while the deintercalation process retains the original transmission characteristics of the films. The transmission modulation (ΔT) is determined by difference between the transmittances of bleached (T_b) and coloured (T_c) states of the films measured at $\lambda = 630$ nm. The negligible $\Delta T \sim 2.5\%$ of CeO₂-TiO₂ with graphite as a counter electrode supports the film's candidature as a passive counter electrode material. However, an improvement in transmittance modulation of electrochromic WO₃ from 56 to 61% due to spray deposited CeO₂-TiO₂ as counter electrode is evident. The optical absorption by thin layer is described by the dimensionless quantity (αt) known as optical density (ΔOD). The CE (η) at a particular wavelength correlates with the optical contrast, i.e., the change in ΔOD with charge intercalated per unit electrode area (Q_i) and can be expressed as

$$\eta = \frac{\Delta OD_{\lambda=630 \text{ nm}}}{Q_i} = \frac{\ln(T_b/T_c)}{q/A} \quad (3)$$

The term ' η ' describes the efficiency of the charge to induce absorption in an electrochromic device. High value of η of electrochromic film means that electrochromic device should have adequate optical regulation upon less intercalation of charges and causing a better stability and reproducibility of coloured/bleached (c/b) cycles. The sample Ce-Ti₃ is used as counter electrode in electrochromic device to check the electrochromic performance of WO₃ film. The improvement in η of WO₃ film is observed from 41 to 231 cm² C⁻¹, when it is configured with CeO₂-TiO₂ (Ce-Ti₃) as counter electrode. This improvement in η of WO₃ is better than that (53 cm² C⁻¹) in case of pristine CeO₂ as counter electrode and CeO₂-ZrO₂ (107 cm² C⁻¹).^{16,17} The electrochemical stability of CeO₂-TiO₂ as a counter electrode is increased considerably as compared to pristine

Figure 5. Cyclic voltammograms of pristine CeO_2 and $\text{CeO}_2\text{-TiO}_2$ thin films within a potential window of ± 0.9 V vs. SCE.

CeO_2 ; this improvement is due to increased TiO_2 content in the films. The various parameters derived from the electrochromic characterizations of $\text{CeO}_2\text{-TiO}_2$ thin films are given in table 1.

3.6 Colourimetric analysis

The colours of $\text{CeO}_2\text{-TiO}_2$ (Ce-Ti₃ sample) and WO_3 thin films with and without $\text{CeO}_2\text{-TiO}_2$ as a counter electrode

were determined by performing colourimetry measurements, CIE 1931 $2^\circ Y_{xy}$ and $L^*a^*b^*$ coordinates recommended by the commission internationale de l'Eclairage (CIE) (CIE Publication No. 15, Paris 1971)³⁷ and were used as the quantitative scale to define the colours. The attributes of colour, hue- a (its position between red and green, where negative value tends toward green and positive value tends toward red), saturation- b (its position in between blue and yellow, where negative value tends toward blue and positive value tends toward yellow) and lightness- L (where 0 is black and 100 is white),³⁸ were measured using colour analysis software equipped with UV-vis spectrophotometer by analysing transmittance spectra of coloured and bleached states after electrochemical polarization at ± 0.9 V. Figure 9a shows the lightness (% L) of $\text{CeO}_2\text{-TiO}_2$ and sputtered WO_3 thin films with graphite as a counter electrode and WO_3 thin film with $\text{CeO}_2\text{-TiO}_2$ as a counter electrode in their coloured (reduced) and bleach (oxidized) state upon application of potential step of ± 0.9 V. The lightness difference (ΔL) of $\text{CeO}_2\text{-TiO}_2$ thin film with graphite as a counter electrode in their colour/bleach state was found to be $\sim 2.5\%$ which is negligible and it elucidates the film's candidature as a passive counter electrode material, whereas the ΔL of WO_3 thin film with graphite as a counter electrode was found to be

Figure 6. Chronocoulometry curves of CeO_2 and $\text{CeO}_2\text{-SnO}_2$ thin film samples recorded in 0.5 M $\text{LiClO}_4\text{+PC}$ electrolyte upon application of ± 0.9 vs. SCE for 60 s. Inset shows ion storage capacity (ISC) of all the samples.

Figure 7. Variation of amount of intercalated charge density (Q_i) with number of electrochemical cycles for $\text{CeO}_2\text{-TiO}_2$ ($T_2\text{-}T_5$).

Figure 8. (a, b) Transmission profiles of $\text{CeO}_2\text{-TiO}_2$ with graphite as a counter electrode for bleached and lithiated states recorded in 0.5 M $\text{LiClO}_4\text{+PC}$ electrolyte upon application of ± 0.9 V vs. SCE for 60 s, showing negligible optical modulation. The optical transmittance spectra of (c) bleached WO_3 , (d) coloured WO_3 without $\text{CeO}_2\text{-TiO}_2$ counter electrode and (e, f) bleached and coloured WO_3 with $\text{CeO}_2\text{-TiO}_2$ counter electrode. All the curves are recorded in the wavelength range of 350–1100 nm.

Table 1. Parameters derived from the electrochromic characterizations of $\text{CeO}_2\text{-TiO}_2$ thin film.

Sr. no.	Sample	Q_i (mC cm^{-2})	Q_{di} (mC cm^{-2})	Reversibility (%)	Optical density (ΔOD)	Colouration efficiency, CE ($\text{cm}^2 \text{C}^{-1}$)
1	Ce-Ti ₀	20.60	14.27	29.32	—	—
	Ce-Ti ₂	19.49	5.13	26.32	—	—
	Ce-Ti ₃	25.40	7.72	30.39	—	—
	Ce-Ti ₄	12.30	2.45	19.91	—	—
	Ce-Ti ₅	9.55	2.617	27.40	—	—
2	WO_3	95	50	52.63	1.60	41
3	WO_3/T_3	19.68	11.05	57.01	1.82	231

Figure 9. Relative lightness vs. applied potential, for $\text{CeO}_2\text{-TiO}_2$ with graphite, WO_3 with graphite, WO_3 with $\text{CeO}_2\text{-TiO}_2$, as a counter electrode in their colour/bleach state, the potential of -0.9 V was applied for colouring and $+0.9\text{ V}$ for bleaching (dashed horizontal lines indicate difference of relative luminance for WO_3 $\text{CeO}_2\text{-TiO}_2$, as a counter electrode in their coloured and bleached state); TGC, TGB and WGC, WGB denoted the $\text{CeO}_2\text{-TiO}_2$ and WO_3 thin film in their coloured and bleached state with graphite as a counter electrode, WTC, WTB denotes WO_3 thin film in their coloured and bleached state with $\text{CeO}_2\text{-TiO}_2$ as a counter electrode.

$\sim 38\%$, but with that of $\text{CeO}_2\text{-TiO}_2$ as a counter electrode was found to be $\sim 48\%$. This signifies that $\text{CeO}_2\text{-TiO}_2$ has a large ISC than that of graphite, manifest $\text{CeO}_2\text{-TiO}_2$ is a candidature material for passive counter electrode in smart window application. Figure 10 shows the hue- a and saturation- b of spray deposited $\text{CeO}_2\text{-TiO}_2$ and sputtered WO_3 , thin films with graphite as a counter electrode and WO_3 thin film with $\text{CeO}_2\text{-TiO}_2$ as a counter electrode, which indicates the colour of the films.

4. Conclusions

In the present investigation, $\text{CeO}_2\text{-TiO}_2$ thin films were prepared by spray pyrolysis using methanolic solutions of cerium nitrate hexahydrate and titanium tetraisopropoxide and turned out to be very promising material and can be used as passive counter electrode in smart window. From XRD, it is found that the films were cubic fluorite structure with prominent peak along the (111) direction. FT-IR spectra reveals that the band at 539 cm^{-1} is assigned to Ce-O stretching vibration and the two medium intensity bands assigned to $\nu(\text{Ti-O})$ and $\nu(\text{Ti-O-Ti})$ stretching modes at 798 and 451 cm^{-1} , which confirm the mixed CeO_2 and TiO_2 phases. The higher ISC for Ce-Ti_3 sample was found to be 26 mC cm^{-2} . The operational cycling life of $\text{CeO}_2\text{-TiO}_2$ thin films exhibit the highest electrochemical stability upto

Figure 10. a^*b^* showing the hue and saturation for $\text{CeO}_2\text{-TiO}_2$ with graphite, WO_3 with graphite, WO_3 with $\text{CeO}_2\text{-TiO}_2$, as a counter electrode in their coloured and bleached state upon application of potential step of -0.9 and $+0.9\text{ V}$ (TGC, TGB and WGC, WGB denoted the $\text{CeO}_2\text{-TiO}_2$ and WO_3 thin film in their coloured and bleached state with graphite as a counter electrode, WTC, WTB denotes WO_3 thin film in their coloured and bleached state with $\text{CeO}_2\text{-TiO}_2$ as a counter electrode and $L^* = 0$ – dark, 100 – white, $a^* = \text{red}(+)/\text{green}(-)$ and $b^* = \text{yellow}(+)/\text{blue}(-)$).

30,000 cycles. The enhancement in colouration efficiency from 41 to $231\text{ cm}^2\text{ C}^{-1}$ was observed when $\text{CeO}_2\text{-TiO}_2$ is coupled as a counter electrode with WO_3 is an electrochromic device (ECD). The *in situ*-colourimetric analysis method discussed in this paper is a significant step in the direction of precise measurement of the hue, saturation and luminance of colour states and allows the changes in these properties to be carefully monitored on redox (colour/bleach) switching between electrochromic colour states of WO_3 thin film with and without $\text{CeO}_2\text{-TiO}_2$ as a counter electrode. CIE 1931 2° Y_{xy} and $L^*a^*b^*$ colour space coordinates for $\text{CeO}_2\text{-TiO}_2$, and WO_3 thin film with $\text{CeO}_2\text{-TiO}_2$ as a counter electrode shows highest ion storage capacity than that of WO_3 thin film with graphite as a counter electrode.

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