

Electrochromic performance of the mixed V_2O_5 – WO_3 thin films synthesized by pulsed spray pyrolysis technique



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ABSTRACT

Vanadium pentoxide (V_2O_5) mixed tungsten trioxide (WO_3) thin films have been synthesized by a novel pulsed spray pyrolysis technique (PSPT) on glass and fluorine doped tin oxide (FTO) coated glass substrates at 400 °C. Aqueous solutions of equimolar vanadium chloride and ammonium tungstate were mixed in volume proportions (5%, 10% and 15%) for the deposition of V_2O_5 – WO_3 thin films. The structural, morphological, optical and electrochemical properties of V_2O_5 – WO_3 thin films were investigated by FT-IR, XRD, SEM, cyclic voltammetry, chronoamperometry and chronocoulometry techniques. The results showed that the electrochemical properties of V_2O_5 were altered by mixing WO_3 . All the films exhibited cathodic electrochromism in lithium containing electrolyte (0.5 M $LiClO_4$ + propylene carbonate (PC)). Maximum coloration efficiency (CE) of about $49 \text{ cm}^2 \text{ C}^{-1}$ was observed for the V_2O_5 film mixed with 15% WO_3 . The electrochemical stability of the sample was examined and it was found to be stable up to 1000 cycles.

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1. Introduction

Electrochromic materials with semiconducting nature are capable of changing their optical properties under the action of an applied electric field or an electric current [1,2]. These materials can be put into two categories: cathodically coloring ones, which darken under charge insertion and anodically coloring ones, which darken under charge extraction. They can be used for several industrial applications [3], energy efficient glazing, privacy glass, partitions, skylights, large area displays, sunroofs and mirrors. Potential advantages offered by electrochromic materials include a long circuit memory and low power requirement. The primary

energy benefits of electrochromic windows are reduced cooling, heating and ventilating loads and the ability to reduce electric lighting use by managing day light admittance. The mechanism responsible for electrochromism has been subject to considerable controversy over the years, but now it is generally accepted that the optical effects are explained by a combinational injection and extraction of electrons and ions. During an electrochromic process, at a given voltage, electrons are injected (reduction) or extracted (oxidation) and, at the same time, ions are moved into or out of the electrochromic materials to balance charge neutrality.

Transition metal oxides have been widely used as inorganic electrochromic materials and are based on a reversible change in the optical properties during electrochemical oxidation or reduction processes [4]. Among transition metal oxides, V_2O_5 has been widely studied as an electrochromic counter electrode [5,6]. It was first reported as a cathode material by Day and Sullivan [7] for intercalation. It can be used as a cathode material because (i) it offers high specific energy density [8], (ii) it undergoes reversible topotactic reaction with lithium [9] and (iii) it has a higher

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electrochemical activity with the highest stability. In addition, it shows both anodic and cathodic electrochromism. Nevertheless, it has low conductivity, narrow color variation and poor coloration efficiency.

Binary combinations of oxides have been investigated to improve or modify the electrochromic properties of different oxides. Possible beneficiary effects on the host electrochromic material are increased coloration efficiency, improved durability, color neutrality, a larger switching potential range or faster reaction kinetics. Both Monk and Granqvist reviewed mixed metal oxides and gave a useful summary [2,4]. Prior investigations on V_2O_5 + metal oxide (MO_x) systems have indicated the improvement over the basic electrochromic properties of V_2O_5 . W has the similar ionic radius and the structure with V_2O_5 in the highest oxidation, vanadium and tungsten oxides have drawn attention because of their current and considerable technological applications [10]. The properties of mixed vanadium–tungsten oxide thin films have been investigated due to their potential use in electrochromic devices by Rougier et al. [11]. The W doped V_2O_5 nanotubes were prepared via a rheological phase reaction followed by self-assembling process, as reported by Li et al. [12]. Also, Ozer et al. [13] reported that the mixed phase tungsten trioxide–vanadium pentoxide films with compositions ranging from 0 to 10 mol% vanadium pentoxide by the sol–gel method by reacting a peroxo-tungstic ester with vanadium triisopropoxide in ethanol. Yang et al. [14] reported the novel tungsten-doped vanadium oxide xerogel films with high electrochromic performances, which were prepared by the sol–gel and hydrothermal route for electrochromic electrodes.

However, these applications depend on the techniques used to grow the films and the performance linked with the crystallinity and morphology of the films [15]. Composite WO_3 + MO_x films have been prepared by techniques such as sol–gel deposition [13,14], vacuum evaporation [16], sputtering [17] and electron-beam evaporation [18], PSPT [19], etc. The PSPT, in which the spray rate can be easily controlled by adjusting spray ON/OFF time, will be a suitable processing technique for the EC device fabrication. The PSPT, designed and patented by us [20] is less capital-intensive and also offers good-quality thin films on large substrate area using low-price precursor. It also facilitates precise control over droplet residence time. It offers several advantages over conventional deposition techniques for the control of stoichiometry and film structure. The chemistry and structure of electrochromic compounds influences the kinetics, reversibility, coloration efficiency and charge capacity.

In our previous studies, we have reported the synthesis of V_2O_5 thin films by the novel PSPT at 300 °C [21] and studied the EC phenomenon using Li^+ ions as intercalating agents exhibiting coloration efficiency of $13 \text{ cm}^2 \text{ C}^{-1}$. The efforts were concentrated on the enhancement of the electrochromic parameters of V_2O_5 thin films by mixing MoO_3 [19]. The MoO_3 mixed V_2O_5 thin films exhibited an excellent electrochromic CE of $35.27 \text{ cm}^2 \text{ C}^{-1}$ as compared to pristine V_2O_5 thin films. However, in this paper we have demonstrated the results of enhancement in the CE and charge storage capacity of PSPT grown V_2O_5 thin films by mixing appropriate ratio of WO_3 . Also, the structural, morphological, optical and electrochromic properties of V_2O_5 – WO_3 thin films were investigated.

2. Experimental

V_2O_5 – WO_3 thin films were grown on glass and FTO coated glass substrates using PSPT. Films deposited on glass substrates were used for structural and morphological characterizations whereas those deposited onto the FTO-coated glass substrates

were used for electrochromic characterization. Preparative parameters of V_2O_5 thin films deposited using the PSPT have been reported by us [21]. In brief, the precursor solution was sprayed on to the pre-heated substrates maintained at 400 °C with compressed air as a carrier gas at the flow rate of 18 L min^{-1} . The nozzle-to-substrate distance was optimized at 22 cm and 20 ml of the precursor solution used for the deposition of the films, was sprayed onto the substrate. The equimolar (0.05 M) solutions of VCl_3 and ammonium tungstate were added in a proper proportion to achieve 5%, 10% and 15% content of WO_3 in V_2O_5 . The final solution (20 ml) was pneumatically pulverized onto the glass and conducting FTO coated glass substrates heated at 400 °C. The 5%, 10% and 15% WO_3 -mixed V_2O_5 samples were referred to as VW_1 , VW_2 and VW_3 , respectively. The sample of pure V_2O_5 was deposited under the same preparative conditions and was referred as VW_0 .

The thickness of the pure V_2O_5 (VW_0) and WO_3 mixed V_2O_5 thin films (VW_1 , VW_2 and VW_3) deposited at 400 °C were determined using fully computerized AMBIOS Make XP-1 surface profiler with 1 Å vertical resolution and were found to be $\sim 308 \text{ nm}$, 320 nm , 339 nm and 368 nm , respectively.

The structural and morphological characterizations were carried out using X-ray diffractometer (Philips Model PW 3710) with CuK_α radiation having wavelength 1.5405 \AA in the range of diffraction angle (2θ) between 20° and 80° and scanning electron microscopy (JEOL Model JSM-6360), respectively. The powder collected from the deposited film was characterized by infrared (IR) spectroscopy using the Perkin Elmer IR spectrometer model 783 in the spectral range 450 – 4000 cm^{-1} . To record IR patterns, the pellet was prepared by mixing KBr with V_2O_5 – WO_3 powder, collected from a thin film, in the ratio 300:1 and then pressing the pellet between two pieces of polished steel. The optical absorption and transmittance spectra were recorded using UV–Vis–NIR spectrophotometer (Systronics Model 119) over the wavelength range of 350 – 1000 nm . The electrochromic cell consists of a conventional three-electrode cell, in which the V_2O_5 thin film deposited onto FTO coated glass substrate (15 – $20 \text{ } \Omega \text{ cm}^{-1}$), a graphite plate and a saturated calomel electrode (SCE) served as working electrode, counter electrode and the reference electrode, respectively. A $0.5 \text{ M LiClO}_4 + \text{PC}$ was used as an electrolyte solution. The cyclic voltammetry (CV), chronoamperometry (CA) and chronocoulometry (CC) experiments were carried out using a Versa Stat-II (EG&G) potentiostat/galvanostat, controlled by M270 software. All the potentials were measured with respect to SCE.

3. Results and discussion

3.1. X-ray diffraction

The structural identification and changes in crystallinity of V_2O_5 thin films with the different concentration of WO_3 were studied with XRD technique. The XRD patterns of the all samples deposited at 400 °C, are shown in Fig. 1. It was found that with increase in percentage of WO_3 the peaks belonging to tetragonal phase of V_2O_5 eventually disappear and the (101) orthorhombic V_2O_5 phase is observed. From the patterns, it is observed that the sample VW_3 exhibits amorphous structure with a broad hump centered at 27° . For all the samples, no reflection belonging to WO_3 is observed. As mixing percentage of WO_3 with V_2O_5 increases the peak intensity of (101) peak decreases. For VW_3 sample amorphous phase formation was observed with no characteristic peak for V_2O_5 and WO_3 . The addition of WO_3 thus can rupture the crystalline character of V_2O_5 and lead to amorphous nature, favorable for electrochromic ion intercalation/deintercalation processes.

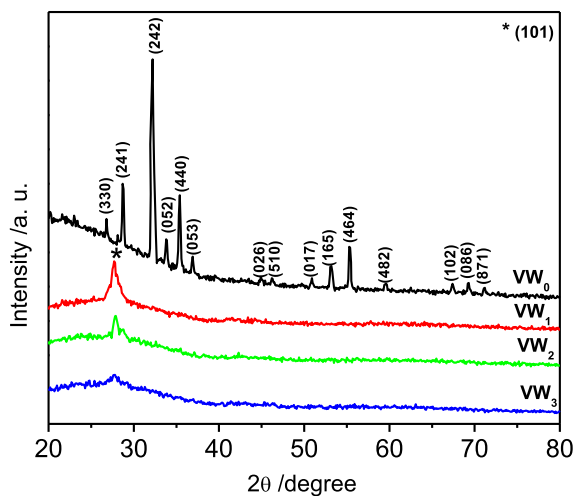


Fig. 1. XRD patterns of the V_2O_5 thin films with various WO_3 contents: 0% (VW_0), 5% (VW_1), 10% (VW_2) and 15% (VW_3).

3.2. Scanning electron microscopy

SEM images were used to determine the influence of the doping concentration of the WO_3 on the morphology of V_2O_5 thin films. Fig. 2(a)–(d) shows the SEM images of VW_0 , VW_1 , VW_2 and VW_3 samples. Changes in the film morphology with the doping percentage were observed. Micro thread-like reticulated morphology

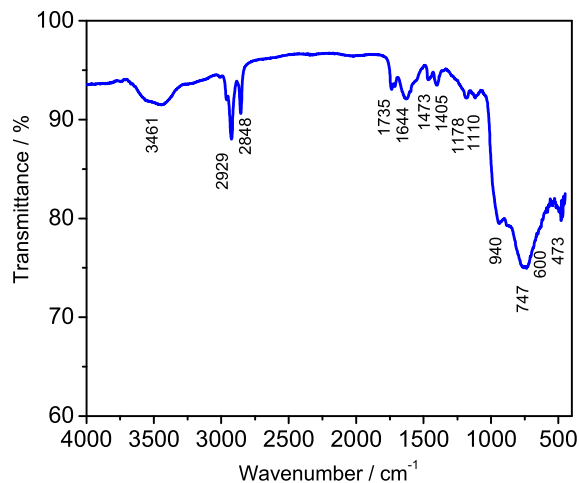


Fig. 3. FT-IR spectrum of the V_2O_5 thin film with 15% WO_3 content (VW_3 sample).

were observed with average thread width from $\sim 2 \mu\text{m}$ to $0.9 \mu\text{m}$. The VW_1 sample exhibits onset of characteristic growth of WO_3 in fibrous reticulated network. It also shows spherical grains varying from 2 to $3 \mu\text{m}$ on the surface as shown in inset, while sample VW_2 and VW_3 shows over growth. Sample VW_2 shows some little bit decrement in the width of fiber. The fibers width of $1\text{--}2 \mu\text{m}$ and length of several μm were observed for VW_3 sample. Such fibrous morphology facilitates the control over surface area and porosity/

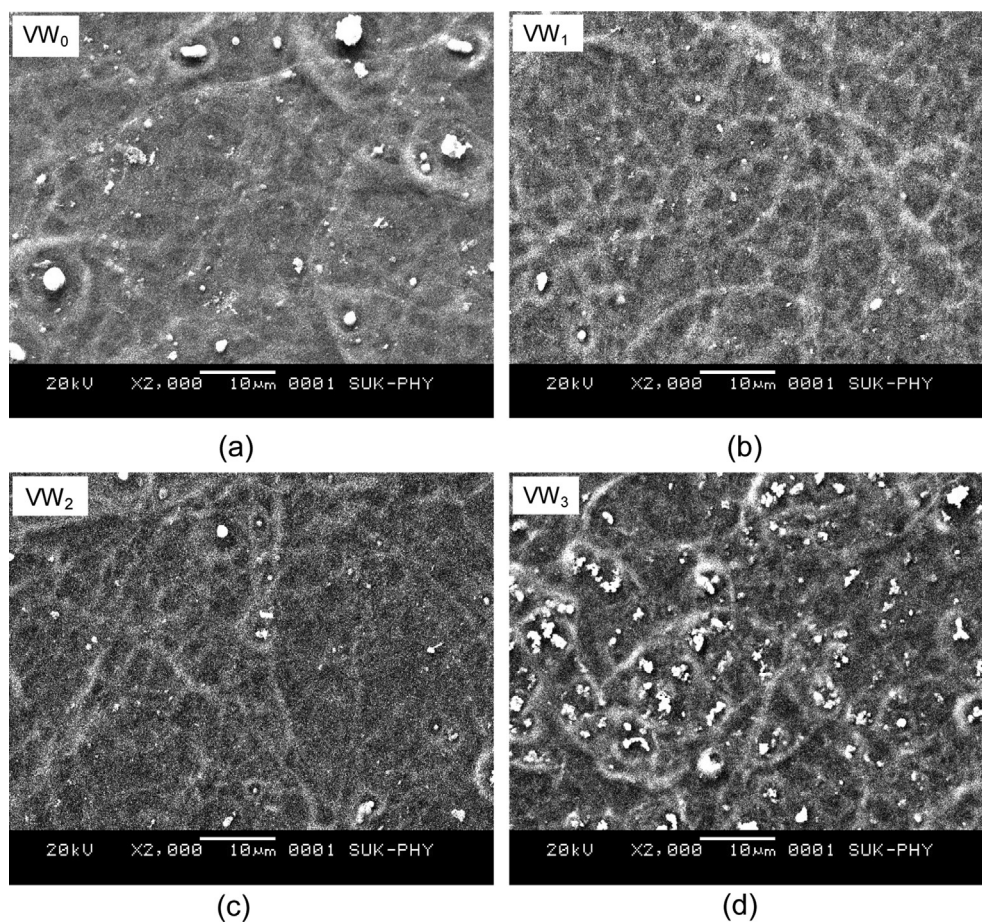


Fig. 2. SEM micrographs for V_2O_5 thin films with various WO_3 contents: (a) 0% (VW_0), (b) 5% (VW_1), (c) 10% (VW_2) and (d) 15% (VW_3).

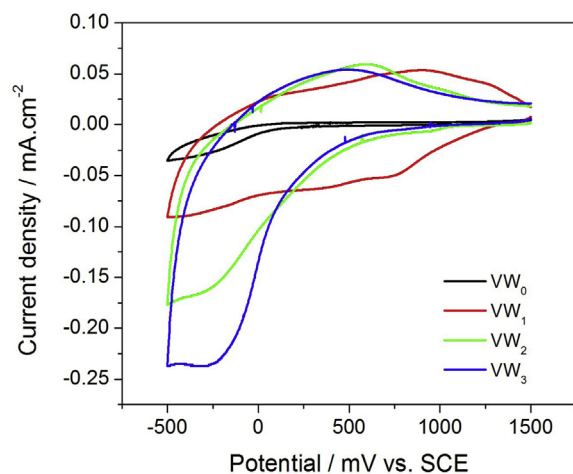


Fig. 4. Cyclic voltammograms recorded for V_2O_5 thin films with various WO_3 contents: 0% (VW₀), 5% (VW₁), 10% (VW₂) and 15% (VW₃) at 100 mV/s scan rate in Li^+ containing electrolyte, within the potential window +1.5 to -0.5 V versus SCE.

open structures, thus affecting the ion insertion kinetics (ion diffusion length and time, ionic mobility, etc.) that may lead to enhanced EC performance.

3.3. FT-IR

The FT-IR transmittance spectrum presents information about phase composition as well as the way oxygen is bound to the metal ions (M–O structure). The FT-IR transmittance spectrum of the powder collected from the VW₃ film in the range $450\text{--}4000\text{ cm}^{-1}$ is shown in Fig. 3. The spectrum comprises of 13 transmittance peaks. The characteristic features of oxides appear below 1200 cm^{-1} . Three broad bands at 940 , 600 and 473 cm^{-1} for amorphous V_2O_5 , which can be attributed to V–O stretching vibrations of the vanadyl group, asymmetric and symmetric stretching vibrations of V–O–V bands, respectively. Meanwhile, the band 747 cm^{-1} belongs to the W–O–W stretching vibration of WO_3 [22]. The peaks at 1405 to 1644 cm^{-1} are due to the bending vibrations of the water molecules. The band at 3641 cm^{-1} indicates the presence of OH bands in addition to the water molecules. The bands at 2929 and 2848 cm^{-1} illustrates the asymmetric and symmetric stretching vibration of H–C–H respectively, while peak at 1735 cm^{-1} band show C=O stretching vibration. This result confirms the formation of a mixed $V_2O_5\text{--}WO_3$ phase, rather than a solid solution of vanadium and tungsten oxide.

3.4. Electrochemical measurements

3.4.1. Cyclic voltammetry

The potential was cycled from $+1.5$ to -0.5 V (versus SCE) at potential sweep rate 20 mV/s in $0.5\text{ M LiClO}_4 + \text{PC}$. During the

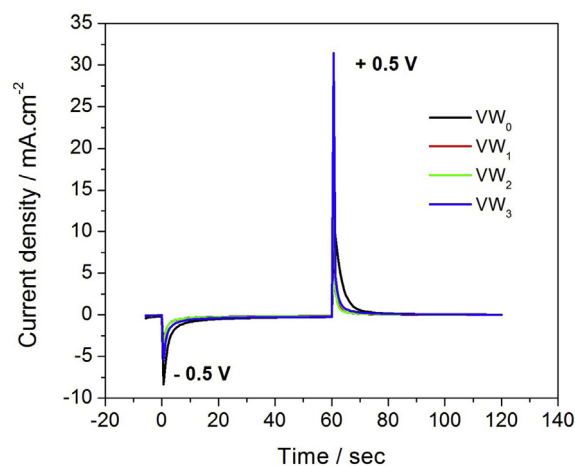


Fig. 5. Chronoamperometric (CA) curves recorded for V_2O_5 thin films with various WO_3 contents: 0% (VW₀), 5% (VW₁), 10% (VW₂) and 15% (VW₃) recorded in $0.5\text{ M LiClO}_4 + \text{PC}$ electrolyte upon application of ± 0.5 V versus SCE for 60 s .

potential sweep, the current resulting from ions intercalation and deintercalation was recorded and the variation is shown in Fig. 4. At the cathodic potential end (-0.5 V), the film is in the bleached state and at the anodic potential end ($+1.5$ V) it acquires colored state. The bleaching and coloration of $WO_3\text{--}V_2O_5$ thin films is associated with intercalation and deintercalation of Li^+ ions and electrons in the film. It is observed that with increase in WO_3 concentration the cathodic peak current density shifts from -90 to $-237\text{ }\mu\text{A cm}^{-2}$. An increase in the area of voltammograms with increasing the WO_3 content suggests that the structure offers an easy way to diffusion and charge transfer process of ions. The charge intercalation–deintercalation capability of VW₃ sample is larger than other samples. Hence, VW₃ sample offers excellent host matrix for intervalency charge transfer process. This is consistent with results reported by Ozer et al. [13]. A shift in anodic peak potential (E_{pa}) from 878 to 460 mV is observed as a function of increase in mixing of WO_3 content. This observed shift in E_{pa} could be related to the difference in the energy necessary to extract the intercalated Li^+ ions from the film and probably the extraction of Li^+ ions requires less energy for highly doped samples, suggesting that lithium insertion is more facile in the doped film [23].

Diffusion coefficients of Li^+ ions for all the samples are calculated using Randles–Sevcik Equation (1)

$$i_p = 2.69 \times 10^5 A n^{\frac{3}{2}} D^{\frac{1}{2}} C_0 \nu^{\frac{1}{2}}, \quad (1)$$

where, D is the diffusion coefficient, C_0 the concentration of active ions in the solution, A is the electrode area (cm^2). In our case it is 1 cm^2 , ν is the scan rate, n is the number of electrons assumed to be 1 and i_p is the peak current density.

With respect to increase in WO_3 content, the diffusion coefficient increases (order of $10^{-18}\text{ cm}^2\text{ s}^{-1}$) as compared to pure V_2O_5

Table 1

Various electrochemical parameters calculated from electrochemical and iono-optical studies of the V_2O_5 thin films with various WO_3 contents.

Sample code	Response time (s)		Charge density (mC cm^{-2})		ΔOD	Reversibility (%)	CE ($\text{cm}^2\text{ C}^{-1}$)	Diffusion coefficient ($\text{cm}^2\text{ s}^{-1}$)
	T_b	T_c	Q_{di}	Q_i				
VW ₀	20	23	22	24	0.14	95.59	14.96	1.12×10^{-18}
VW ₁	12	11	20.5	31.4	0.23	65.3	18.3	7.91×10^{-18}
VW ₂	12	10	12.7	21.2	0.24	71.7	28.3	9.75×10^{-18}
VW ₃	10	9	11.3	19.3	0.37	94.3	49	8.09×10^{-18}

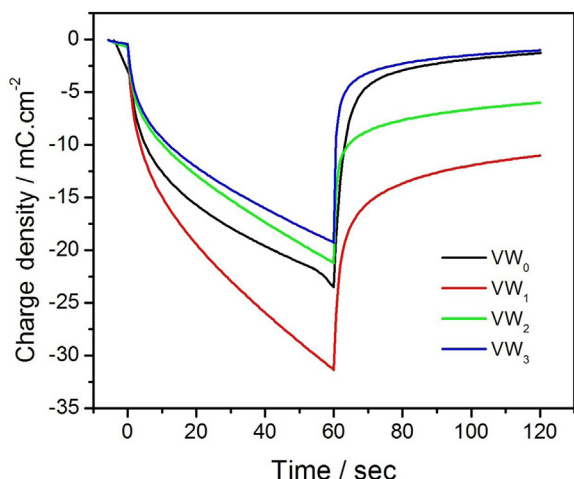


Fig. 6. Chronocoulometric (CC) curves recorded for V_2O_5 thin films with various WO_3 contents: 0% (VW_0), 5% (VW_1), 10% (VW_2) and 15% (VW_3) recorded in 0.5 M $LiClO_4 + PC$ electrolyte upon application of ± 0.5 V versus SCE for 60 s.

film. The diffusion coefficient depends on the conductivity (σ) of diffusing ionic species Li^+ , the nature of film (crystallinity, porosity, hydration, etc.) and the electrolyte. The calculated values of diffusion coefficient for VW_0 , VW_1 , VW_2 and VW_3 samples are given in Table 1.

3.4.2. Chronoamperometry

Potential step experiments were carried out to determine the kinetics of redox reaction. The speed with which EC devices

can be switched from one state to another state is of great importance for determining its application capability. In this case, CA cycling was performed on $V_2O_5-WO_3$ films between $+0.5$ V and -0.5 V versus SCE for 60 s and the resultant current–time responses for the VW_0 , VW_1 , VW_2 and VW_3 samples are shown in Fig. 5.

From the current versus time transients, it is clearly observed that both coloration current and bleaching current following the step was smooth and decreased continuously with time. This decrease in current with time has been used to measure the speed of EC response of $V_2O_5-WO_3$ thin films. The coloration and bleaching times were calculated from the current time transients. The coloration and bleaching times are defined as, ‘the time taken by the film for its coloration and bleaching states’, respectively. It is generally denoted as T_c and T_b , respectively. From figure, it is observed that with increase in mixing of WO_3 content, coloration and bleaching kinetics becomes easier and faster. The response time for all the samples is calculated from these CA plots and is reported in Table 1.

3.4.3. Chronocoulometry

Charges intercalated/de-intercalated versus time transients for all the films (VW_0 , VW_1 , VW_2 and VW_3) at ± 0.5 V (versus SCE) for the step of 60 s are shown in Fig. 6. In forward scan, the charges are intercalated into the film by diffusion process, resulting in coloration due to reduction of V^{5+} to V^{4+} and W^{6+} to W^{5+} states. In reverse scan, the intercalated charge is removed from the film, resulting in bleaching due to oxidation of V^{4+} to V^{5+} and W^{5+} to W^{6+} states. The reversibility of the films calculated as the ratio of de-intercalated charge (Q_{di}) to intercalated charge (Q_i) in the film. It is apparently seen that, WO_3 percentage helps increasing the reversibility of V_2O_5 in $LiClO_4 + PC$ electrolyte.

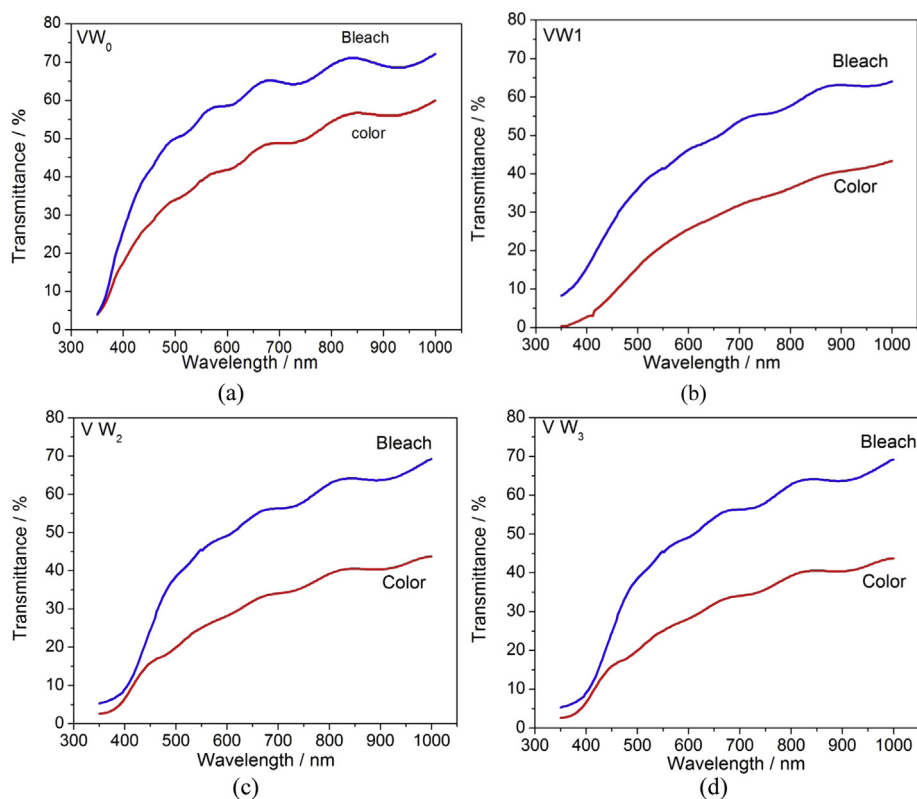


Fig. 7. Transmittance spectra for V_2O_5 thin films with various WO_3 contents: (a) 0% (VW_0), (b) 5% (VW_1), (c) 10% (VW_2) and (d) 15% (VW_3) in colored and bleached states.

3.5. In situ optical studies

The coloration of all the four samples changed progressively during the reduction–oxidation cycle. The transmittance spectra for these thin films in their colored and bleached states were recorded in the wavelength range of 350 nm–1000 nm, at the room temperature and shown in Fig. 7. The optical absorption by the thin layer is described by the dimensionless quantity (αt), which is called as optical density (ΔOD). The changes in ΔOD and coloration efficiency (CE) are calculated using relation (2) and (3), respectively.

$$\Delta OD = \ln\left(\frac{T_b}{T_c}\right), \quad (2)$$

where, T_b and T_c is the transmittance of the V_2O_5 films in its bleached and colored states, respectively. The CE is defined as the change in optical density per unit-inserted charge and it is calculated using relation (3).

$$CE = \frac{\Delta OD}{Q_i} = \frac{\ln[T_b/T_c]_{\lambda=630 \text{ nm}}}{q/A}, \quad (3)$$

where, Q_i is the amount of charge intercalated in the sample to cause change in optical density, which was calculated by integrating the area under the curve of current density versus time.

The optical density has been observed with increase in WO_3 percentage that transmittance modulation (ΔT) increases, which improves ΔOD . This indicates that the WO_3 mixed films have more efficient coloration compared with V_2O_5 film. According to the preferential model of mixed-metal oxides by Faughnan and Crandall [24], higher electrochromic properties may be a result of enhanced additional electron intervalence transfer between V^{4+} and W^{6+} sites. Reversibility and CE values are found to be 94.3% and $49 \text{ cm}^2 \text{ C}^{-1}$, respectively, for VW_3 sample. Various electrochromic parameters derived from electrochemical characterization of spray deposited V_2O_5 – WO_3 thin films are given in Table 1.

Hence, it is concluded that VW_3 sample exhibits better EC properties by virtue of having greater WO_3 content. Further experiment in increasing WO_3 content in V_2O_5 failed due to the formation of powdery (inferior) quality films. Therefore, 15% mixing of WO_3 in V_2O_5 is an optimum amount to yield better EC properties.

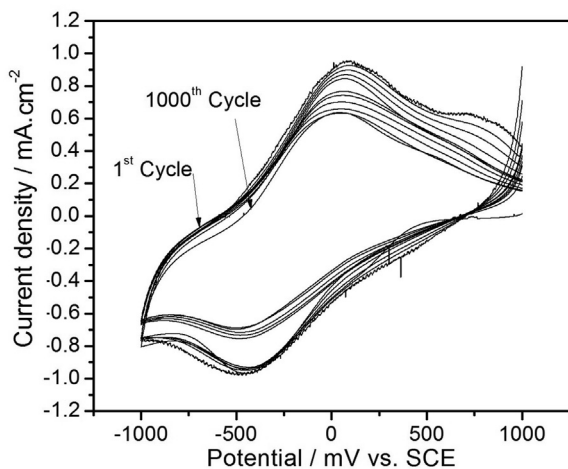


Fig. 8. Electrochemical stability of the V_2O_5 thin film with 15% WO_3 content (VW_3 sample) recorded up to 1000 cycles at sweep rate of 100 mV/s in 0.5 M $LiClO_4$ + PC electrolyte.

3.6. Electrochemical stability

The electrochemical stability of the film is one of the important parameters to be taken into account when one looks for its applications. Hence, the electrochemical stability of the sample is tested by repeating coloration (intercalation)–bleaching (deintercalation) processes up to 1000 cycles in 0.5 M $LiClO_4$ + PC electrolyte. The CV recorded for 1st cycle and the 1000th cycle at the sweep rate 100 mV/s are nearly same which indicates the VW_3 sample is highly stable up to 1000 cycles in the $LiClO_4$ + PC electrolyte, as shown in Fig. 8. The reduced performance after 1000 cycles may result from the electrochemical dissolution of active materials, as it is an intrinsic problem with oxide materials [25,26]. Hence, such highly stable thin films can be used for charge-balanced devices for display purposes in informatics, variable reflectance mirrors, smart windows and surfaces with tunable emittance for temperature control of space vehicles.

4. Conclusions

Thin films of V_2O_5 – WO_3 have been prepared at 400 °C by pulsed spray pyrolysis technique. With increasing WO_3 percentage the negative effect on the crystallization of V_2O_5 – WO_3 thin film has been observed. Preservation of amorphous structure improves the EC properties of V_2O_5 thin films. With increasing percentage of WO_3 , the structure of V_2O_5 undergoes a phase transformation from tetragonal to orthorhombic with clear formation of nano-sized grains. The 15% WO_3 – V_2O_5 sample exhibits best EC properties viz. $CE = 49 \text{ cm}^2 \text{ C}^{-1}$ and reversibility = 94.3%. This increase in CE is attributed to the defects and disorder produced in the V_2O_5 films due to WO_3 mixing.

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