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2013

Lu, Y., Liu, L., Mandler, D., & Lee, P. S. (2013). High switching speed and coloration efficiency of titanium-doped vanadium oxide thin film electrochromic devices. *Journal of materials chemistry C*, 1(44), 7380-7386.

<https://hdl.handle.net/10356/105895>

<https://doi.org/10.1039/c3tc31508h>

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[<http://dx.doi.org/10.1039/c3tc31508h>].

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High switching speed and coloration efficiency of titanium-doped vanadium oxide thin film electrochromic devices

Cite this: *J. Mater. Chem. C*, 2013, **1**, 7380

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Titanium (Ti)-doped vanadium oxide thin films were fabricated by electrochemical deposition on linear polyethylenimine (LPEI)-modified indium tin oxide-coated glass from mixed vanadium oxide and titanium oxide solutions with different Ti concentrations. The as-prepared films were investigated by X-ray diffraction (XRD), atomic force microscopy (AFM), and X-ray photoelectron spectroscopy (XPS). The electrochemical behaviour of the films was studied using cyclic voltammetry (CV) in 1.0 M LiClO₄/propylene carbonate solution. Electrochromism of the oxide films upon Li-ion intercalation/deintercalation was investigated by transmittance measurements during the CV process. The charge transfer resistance of the Ti-doped vanadium oxide film was systematically analyzed with electrochemical impedance spectroscopy (EIS). The amorphous Ti-doped vanadium oxide film containing 4 mol% Ti exhibited the highest transmittance contrast ($\Delta T = T_{\max} - T_{\min}$) of ca. 51.1%*T*, and coloration efficiency of 95.7 cm² C⁻¹ at 415 nm. By increasing the Ti content to 10 mol%, the Ti-doped vanadium oxide film exhibited high switching speed and good cycling reversibility reaching 80% of colouring and bleaching time of 5 and 6 s, respectively. Furthermore, the transmittance contrast drops by only 10% after 600 cycles in a two-electrode system.

Received 2nd August 2013

Accepted 17th September 2013

DOI: 10.1039/c3tc31508h

www.rsc.org/MaterialsC

1. Introduction

Electrochromic materials are envisioned to be applied in energy-efficient glazing, automobile sunroofs and mirrors, and smart windows.^{1–4} Transition metal oxides such as tungsten, vanadium, titanium, molybdenum and nickel oxides are some of the well-known electrochromic materials.^{5–8} Among these, vanadium oxide shows significant anodic and cathodic coloration, which is attributed to chemically reversible reduction/oxidation processes accompanying the intercalation/deintercalation of cations. The typical electrochromic reaction of vanadium pentoxide in lithium perchlorate electrolyte can be written as follows:

Vanadium oxide has been studied extensively as a counter electrode in electrochromic devices,^{4,9–11} in which it provides electrochemical oxidation and reduction reactions that balance charge transfer at the electrochromic working electrode during optical switching. However, reports on its intrinsic

electrochromic properties are very limited as compared with other metal oxides due to several disadvantages originating from its low conductivity, narrow optical modulation, and poor cycling reversibility and stability. Therefore great efforts have been made in order to improve or modify its electrochromic property. It has been shown that by doping with high-valence cations, such as Mo⁶⁺ and W⁶⁺, the optical and electrical conductivity of vanadium oxide films can be improved. This is attributed to generating donor-like defects due to the supply of quasi-free electrons and the formation of substitution solid solution.^{12–14} Recently Xiong *et al.* reported that silver-doped V₂O₅ nanowires exhibited better electrical conductivity and higher diffusion coefficient of Li-ions as compared with pure V₂O₅ nanowires. As a result, an enhanced electrochromic device with a high colour-switching speed of 0.2 s and a high transmittance contrast of 60% was fabricated. Nevertheless, this kind of silver-doped V₂O₅ nanowire was not very stable in its reduced state as Ag nanoparticles could promote undesired catalytic oxidation.^{15,16} Furthermore, it is generally accepted that the cycling stability of vanadium oxide films can be improved by incorporating other electrochemically active species such as titanium oxide (TiO₂).^{17–19} Özer *et al.* found that 5 mol% TiO₂ added to V₂O₅ films greatly improved the lithium intercalation capacity.¹⁸ Sahana *et al.* attributed the difference in the lithium intercalation capacity of the 5% Ti-doped V₂O₅ films prepared from different precursors to the variation in the non-stoichiometry and the particle size.¹⁹ However, all these V₂O₅ films

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were annealed at high temperature (over 300 °C) to complete hydrolysis, condensation and densification. This seriously limits the application of electrochromic materials particularly on plastic substrates.

The preparation of the mixed-oxide $\text{TiO}_2\text{-V}_2\text{O}_5$ films by hydrothermal synthesis,¹⁵ sol-gel based dip coating,¹⁸ spin coating,¹⁹ and electrochemical deposition⁶ has been previously reported. Among these methods, the electrochemical deposition can be carried out at room temperature and under ambient pressure. The vanadium oxide film can be directly fabricated on the working electrode surface, which is formed by a redox process. Furthermore, fabrication of the film can be controlled by varying the electrodeposition conditions, such as deposition potential, time and precursor concentration.

In this work, Ti-doped vanadium oxide thin films were electrochemically deposited on the linear polyethylenimine (LPEI)-modified indium tin oxide-coated glass (ITO) from a stable mixture of vanadium oxide and titanium oxide solutions. Our previous study showed that modification of the LPEI polymer layer on the ITO substrates resulted in the formation of stable amorphous Ti-doped vanadium oxide films without any thermal treatment.²⁰ The effect of Ti concentration on the structural, electrochemical and electrochromic properties of the vanadium oxide films was systematically investigated. It is shown that the Ti-doped vanadium oxide film with a suitable concentration of the Ti component exhibits higher current density, better cycling reversibility and enhanced electrochromic properties as compared with pure vanadium oxide films.

2. Experimental

2.1. Preparation of precursor solutions and film fabrication

The vanadium precursor solution was prepared using a method reported by Fontenot *et al.*²¹ V_2O_5 powder (99.9% metal basis, Alfa Aesar) was dissolved in H_2O_2 (30 wt%, Merck KGaA) aqueous solution with a vanadium concentration of 0.11 M. The resultant gel was then redispersed in deionized (DI) water before use.

The procedure for preparation of peroxo-polytitanic acid (PPT acid) is detailed elsewhere.²² Titanium powder (<20 μm , 93%, Alfa Aesar) was added into a 30 wt% H_2O_2 solution and the solution was stirred for 3 days at room temperature. Non-reacted Ti powder was removed by a filter paper. As a result, a yellowish PPT acid was obtained. The above two precursor solutions were mixed in different ratios to obtain a series of deposition solutions with different titanium to vanadium atomic percentages (noted as x mol%). These solutions were kept still for at least one week and a suitable amount of ethanol was added to the above mixture solutions before electrodeposition.

The Ti-doped vanadium oxide thin films were prepared by cathodic electrochemical deposition from the vanadium and titanium precursor solutions. LPEI (M_w 25 000, PolySciences, Inc.)-modified ITO glass²⁰ (sheet resistance of 8–12 ohms, Delta Technologies) was used as the working electrode, Ag/AgCl (sat. KCl) as the reference electrode and platinum foil (Pt, $10 \times 20 \times 0.2 \text{ mm}^3$) as the counter electrode. The deposition potential was -0.5 V , and the deposition time was 10 min. Following

deposition, the electrodeposited oxide films were dried in air at room temperature ($\sim 25^\circ\text{C}$) without any further thermal treatment. The electrodeposited oxide films had a thickness of 220–290 nm, as measured using an Alpha-Step IQ surface profilometer (KLA-Tencor).

2.2. Measurements

The chemical states and compositions of the Ti-doped vanadium oxide films were analyzed by X-ray photoelectron spectroscopy (XPS) using a Thermo Fisher Scientific Theta Probe system. XPS spectra were recorded using $\text{Al-K}\alpha$ radiation (1486.68 eV) as the excitation source. The take-off angle of the emitted photoelectrons was adjusted to 50° with respect to the surface normal. The data were obtained at room temperature and typically the operating pressure in the analysis chamber was below $5 \times 10^{-9} \text{ Pa}$. All the regional XPS spectra were calibrated with the binding energy of the adventitious C1s peak (285 eV), and a Shirley-type background was subtracted. X-ray diffraction was carried out on a Shimadzu XRD-6000 with $\text{Cu-K}\alpha$ radiation (2.7 kW) operated at 40 kV and 30 mA. Atomic force microscopy (AFM) was carried out with a DI 3100 (Veeco, Digital Instruments) under ambient conditions. AFM was operated in the tapping mode with an optical readout using Al-coated silicon cantilevers (Tap300Al-G, Budget Sensors). The surface roughness (root-mean-square roughness) was calculated by the Nanoscope Control software.

Optical transmittance spectra were measured using a Shimadzu UV-3600 spectrophotometer. A three-electrode cell was used to investigate the electrochemical properties of the Ti-doped vanadium oxide films with different Ti concentrations. A Pt foil was used as the counter electrode and Ag/AgNO_3 serves as the reference electrode (0.01 M AgNO_3 dissolved with acetonitrile). This Ag/Ag^+ reference electrode was previously used by others.^{18,23} The electrolyte was 1.0 M lithium perchlorate (LiClO_4 , 99.99%, Sigma-Aldrich) in propylene carbonate (PC, 99.7%, Sigma-Aldrich). The potentiostatic and chronoamperometric measurements were accomplished on a Solartron 1470E electrochemical interface analyzer. Cyclic voltammetry was performed between the potential region of -1.0 V and $+1.0 \text{ V}$ vs. Ag/Ag^+ at a scan rate of 20 mV s^{-1} . Electrochemical impedance spectroscopy was performed by applying DC potentials of $+0.6 \text{ V}$ and -0.6 V , with 5 mV of AC amplitude in the frequency range of 100 mHz to 10 kHz.

3. Results and discussion

3.1. Physical properties of Ti-doped vanadium oxide films

In general, the as-prepared Ti-doped vanadium oxide films show smooth and featureless surface morphology; no detectable cracks or pinholes are observed as shown in Fig. 1. In order to clearly present the structure of the vanadium oxide, enlarged phase images with a scan area of $1 \times 1 \mu\text{m}^2$ were also inserted. From AFM images, the vanadium oxide presents a ribbon-like structure, similar to that reported in the literature.⁶ The root-mean-square (RMS) roughness and thickness of the as-prepared pure vanadium oxide film are 6.6 nm and 231 nm, respectively.

Fig. 1 AFM height images of surface morphologies of Ti-doped vanadium oxide films with different Ti concentrations: (a) 0, (b) 4, (c) 10 and (d) 20 mol%. The scan size is $5 \times 5 \mu\text{m}^2$. The inset in (b) and (c) shows the phase image corresponding to the red marked area with $1 \times 1 \mu\text{m}^2$.

Both values increase up to 10.5 nm and 297 nm, respectively, upon increasing the Ti concentration to 20 mol%.

X-ray diffraction (XRD) studies were carried out on the Ti-doped vanadium oxide films before and after thermal treatment. As reference, bare ITO was also tested. In Fig. 2a, XRD patterns are indicative of an amorphous nature of the structure for the as-prepared vanadium oxide film and similar to those of $\text{V}_2\text{O}_5 \cdot n\text{H}_2\text{O}$ reported in the literature.^{5,7} The most intense peak corresponds to (001) diffraction, which is characteristic of the V_2O_5 xerogel structure described as a double layer of V_2O_5 stacked along the c -axis of a monoclinic unit cell.⁵ Furthermore, the increase of crystallinity is indicated by the decrease of the line width and increase of the peak intensity upon increasing the Ti content. In addition, peaks related to titanium oxide are not observed in Ti-doped vanadium oxide films as well as in the

pure titanium oxide film, which is possible, related to the fact that the Ti precursor in thin films forms some amorphous oxide in our current work. In order to further examine the composition of the as-prepared Ti-doped vanadium oxide films, XRD patterns were investigated after heating the films to 450°C for 1 h (Fig. 2). Pure TiO_2 films prepared using the PPT acid precursor remain amorphous, and no peaks corresponding to TiO_2 or complex vanadium/titanium oxide compounds are detected.

Ti-doped vanadium oxide films with Ti concentrations from 0 to 20 mol% demonstrate a strong preferential orientation along (001) diffraction, which is ascribed to orthorhombic V_2O_5 . No peaks corresponding to any other phases are observed, suggesting that there are no secondary vanadium oxide phases within the XRD detection limits. To analyse the shift in XRD peak positions of V_2O_5 , due to Ti addition, the peaks corresponding to ITO are taken as the internal standard. There is no observable shift in peak positions, suggesting that there is no noticeable influence on the lattice constant of V_2O_5 upon Ti incorporation. It is known that poor crystallinity is observed due to increased diffusion lengths for crystallization in a mixed oxide system.

Fig. 2 XRD patterns of Ti-doped vanadium oxide films with different Ti concentrations from 0 to 20 mol%: (a) as-prepared films without thermal treatment and (b) films heated at 450°C for 1 h.

3.2. XPS analysis of Ti-doped vanadium oxide films

Although the titanium component in the film was not detected by XRD, its presence was further examined by XPS. A typical survey spectrum (Fig. 3a) for the electrodeposited Ti-doped vanadium oxide film with a Ti concentration of 20 mol% (without any further thermal treatment) shows two intense peaks of C1s and N1s. Nitrogen may originate from the synthesis procedure or surface contamination. The main C1s peak at 285.0 eV is assigned to hydrocarbons and $-\text{CH}_2\text{CH}_2-$,²⁴ which could originate from the ethanol used as a solvent in the deposition solution. The binding energy and full-width at half-maximum (FWHM) of the O1s, $\text{V}2\text{p}_{3/2}$, $\text{Ti}2\text{p}_{3/2}$ peaks for the Ti-doped vanadium oxide films with different concentrations of Ti are summarized in Table 1.

Fig. 3b shows the highly resolved O1s and $\text{V}2\text{p}$ core-level spectra of the Ti-doped vanadium oxide film with a Ti concentration of 20 mol%. The $\text{V}2\text{p}_{3/2}$ peak can be described as the sum of two components centred at 517.7 eV (A) and 516.4 eV (B), which are related to the two oxidation states, $\text{V}(\text{v})$ and $\text{V}(\text{iv})$, respectively. This is in agreement with the reported values.^{25,26} Depending on samples, the proportion of $\text{V}(\text{v})$ varies from 62.8% to 83.0% of the total vanadium signal upon increasing the concentration of Ti from 0 to 20 mol%. The existence of $\text{V}(\text{iv})$ in the films is a consequence of the cathodic electrodeposition.

Fig. 3 XPS spectra of Ti-doped vanadium oxide films with a Ti concentration of 20 mol%: (a) a wide range scan spectrum and (b) O1s and V2p energy regions; (c) the variation of the Ti2p energy region with different Ti concentrations in Ti-doped vanadium oxide films. The experimental and fitting curves are also shown.

On the LPEI-modified ITO surface, the vanadium oxide is reduced to V(IV) at -0.5 V to form a dark greenish film. Upon drying under ambient conditions, the vanadium oxide on the outer surface gradually oxidizes, and the colour of the film changes to brown-red. The increase in the proportion of V(V) might be due to the replacement of vanadium atoms by titanium during the course of electrodeposition.

The two peaks in the Ti2p XPS spectra (Fig. 3c) at about 458.8 and 464.4 eV are assigned to $\text{Ti}2\text{p}_{3/2}$ and $\text{Ti}2\text{p}_{1/2}$, respectively, which is in agreement with the literature.²⁷ The shapes of the peaks are symmetrical, indicating that Ti(IV) exists essentially in this oxidation state. The intensity of the peaks increases with the increase of the Ti content. The oxygen signal at 530.4 eV (A) corresponds to the metal oxygen ions of the oxide layer; and the additional oxygen component at 531.8 eV (B) can be ascribed to C–O bonds originating from ethanol solvent or other surface contamination (Fig. 3c).²⁴ However, it is too complicated to further discern in the O1s photoemission spectrum, since the reported O1s binding energies of TiO_2 range from 429.8 to 530.2 eV,^{27,28} within the same range found for V_2O_3 (530.1 eV), VO_2 (529.9 eV), V_2O_5 (530.5 eV)²⁵ and VO_2/TiO_2 (530.4 eV).²⁷ The XPS results above indicate that electrochemically deposited Ti-doped vanadium oxide films mainly contain mixed oxides of V(IV), V(V) and Ti(IV).

3.3. Electrochemical behaviour of Ti-doped vanadium oxide films

The electrochemical behaviour of Ti-doped vanadium oxide films was studied using cyclic voltammetry in 1.0 M LiClO_4/PC

solution (Fig. 4). The CV curve of pure vanadium oxide is similar to that reported previously^{13,29} and significantly depends on the method of preparation, *i.e.* sputtering, CVD, electrodeposition and sol-gel method and the crystallinity of the vanadium oxide film. V_2O_5 usually exhibits three sets of quasi-reversible redox waves that are associated with the intercalation and deintercalation of Li-ions to and from its framework structure, respectively. Specifically, the cathodic current is associated with the $\text{V}^{5+} \rightarrow \text{V}^{4+}$ reduction process which corresponds to Li-ion intercalation. This process leads to film coloration (from orange to blue). By reversing the scan direction, the anodic peaks are observed corresponding to the Li-ion deintercalation, and the film colour changes from blue to orange. Fig. 4 shows the CV curves of Ti-doped vanadium oxide films with different Ti contents. The CV curves of the vanadium oxide films containing Ti consist of multiple steps and are not significantly different from the pure vanadium oxide, although the peak potentials are slightly different. This suggests that incorporation of Ti does not significantly affect the coloration mechanism of the films. For the anodic peaks, not only the peak position but also the shape is changed as compared with the curve of the pure vanadium oxide film, which suggests a more facile kinetics of electrochromism (see Table 3). On the other hand, the Ti incorporation remarkably increases the current density. These indicate that the vanadium oxide film after adding the Ti component has a better reaction reversibility and higher electrochemical activity associated with better electrochromic properties. This is in contrast to the report by Özer *et al.*,¹⁸ who found that the current density decreases upon increasing the Ti content to 20% (Ti/V mol%). Yet, the methods of film

Table 1 Binding energy and full-width at half-maximum (FWHM) of the O1s, $\text{V}2\text{p}_{3/2}$, $\text{Ti}2\text{p}_{3/2}$ peaks for the Ti-doped vanadium oxide films with different concentrations of Ti components^a

X (Ti : V, mol%)	Binding energy (eV)										
	O1s				$\text{V}2\text{p}_{3/2}$				$\text{Ti}2\text{p}_{3/2}$		
	A	FWHM	B	FWHM	A	FWHM	B	FWHM	δ	Ti(IV)	FWHM
0	530.3	1.2	531.5	2.6	517.5	1.3	516.4	1.4	62.8%	—	—
4	530.2	1.2	531.3	2.3	517.5	1.2	516.2	1.3	76.3%	458.7	1.1
10	530.4	1.2	531.8	2.8	517.6	1.2	516.3	1.4	81.3%	458.8	1.1
20	530.4	1.2	531.8	2.7	517.7	1.2	516.4	1.3	83.0%	458.9	1.0

^a δ represents the proportion percentage of V(V)/(V(IV) + V(V)) on the surface of Ti-doped vanadium oxide films, and is calculated using the corresponding spectrum area. V(V) is A and V(IV) is B for the $\text{V}2\text{p}_{3/2}$.

Fig. 4 Cyclic voltammetry (CV) of Ti-doped vanadium oxide films electro-deposited on ITO with different Ti contents. The CV is recorded in 1.0 M LiClO₄/PC at a scan rate of 20 mV s⁻¹.

preparation are different as is also manifested by the CV of the pure V₂O₅.

3.4. Electrochemical impedance spectroscopy

In order to better understand the effect of Ti incorporation on the electrochemical behaviour of the Ti-doped vanadium oxide films, electrochemical impedance spectroscopy (EIS) of the oxide films was measured using the same electrolyte. Fig. 5 displays the Nyquist diagrams acquired at +0.6 and -0.6 V. At +0.6 V (Fig. 5a), the films are under an oxidation state, which are mainly composed of V⁵⁺ centres. The oxide films show a capacitive arc in the high-frequency region and diffusion in the low-frequency domain. The charge-transfer resistance (R_{ct}) fitted decreases as the Ti component increases up to 10% (Table 2). This corroborates the increasing current response as observed in CV, and may be interpreted by the increase in the active component quantity. However, the film with 20% Ti has abnormally high R_{ct} . This might suggest that the film has poor conductivity due to the inert characteristic of excess Ti component. At -0.6 V (Fig. 5b), the films are under a reduction state intercalated with Li-ions. The curves are similar to those in Fig. 5a, but with high-frequency arcs they are more depressed. The R_{ct} values of the oxide films are much lower than those measured at +0.6 V, suggesting that the films are more reactive towards redox reactions at this potential. As the Ti component in the film increases, the R_{ct} gradually decreases indicating an increase in the reaction rate, which is consistent with the trend of CV.

3.5. Electrochromic properties of Ti-doped vanadium oxide films

Optical and electrochromic properties of the various Ti-doped vanadium oxide films with different Ti contents deposited on the LPEI-modified ITO glasses were investigated, and the detailed electrochromic performance is summarized in Table 3. Fig. 6a shows the typical optical transmittance spectra of the Ti-doped vanadium oxide film containing 10 mol% Ti in different coloration states. The films were measured by UV-vis-NIR spectroscopy, in which the vanadium oxide film was polarized at +2.1 V and -2.0 V in 1.0 M LiClO₄/PC solution using a two-electrode system. As can be seen, the film switches from a

Fig. 5 Nyquist diagrams of Ti-doped vanadium oxide films with different Ti concentrations in 1.0 M LiClO₄/PC at different polarized potentials: (a) +0.6 V and (b) -0.6 V. AC amplitude is 5 mV, and frequency range is 100 mHz to 10 kHz.

transparent orange colour when oxidized (+2.1 V) to a dark blue colour when reduced (-2.0 V), which is in agreement with the corresponding absorbance peaks (720 and 430 nm, respectively) in the transmittance spectra. The highest contrast ($\Delta T = T_{\max} - T_{\min}$) value for each different Ti-doped vanadium oxide film is shown in Table 3. The highest contrast is 51.1%T at 415 nm for the Ti-doped vanadium oxide film with 4 mol% Ti. On the other hand, the transmittance contrast at 720 nm increases upon increasing the Ti content from 0 mol% to 20 mol%.

Fig. 6b shows the typical transmittance variations of the Ti-doped vanadium oxide film with 10 mol% Ti on the LPEI-modified ITO at 415 nm during continuous double potential step measurements between -2.0 V and +2.1 V vs. Pt wire. After 600 running cycles, the transmittance contrast decreases from 39.7%T to 35.7%T, with a contrast drop of only 10%. This cycling reversibility is comparable with other vanadium oxide materials.^{1,18,30} It has been proved that Ti-doping in electrochromic materials improved the electrochromic performance especially in terms of durability. For example, Ti-doped vanadium pent-oxide films after thermally treated at 300 °C for 1 h showed cyclic

Table 2 The R_{ct} obtained by fitting the Nyquist diagrams using the ZView software

X (Ti : V, mol%)	0	4	10	20
$R_{ct}/\Omega \text{ cm}^{-2}$ (+0.6 V)	14258	4159	1119	14216
$R_{ct}/\Omega \text{ cm}^{-2}$ (-0.6 V)	—	1439	578	556

Table 3 Electrochromic performances and the film characteristics of the Ti-doped vanadium oxide thin films with different concentrations of Ti components

X (Ti : V, mol%)	Film thickness (nm)	RMS (nm)	$\Delta\%T$ @ 415 nm	η @ 415 nm ($\text{cm}^2 \text{C}^{-1}$)	Colouring/bleaching time for 80% modulation (s)	Running cycles/contrast drop	$\Delta\%T$ @ 720 nm	η @ 720 nm ($\text{cm}^2 \text{C}^{-1}$)
0	231	6.61	36.0	53.1	6/6	40 cycles/96%	24.7	31.3
4	242	9.96	51.1	95.7	6/8	600 cycles/35%	37.1	37.7
10	291	10.18	39.7	63.0	5/6	600 cycles/10%	42.7	28.2
20	297	10.48	11.2	54.7	9/15	600 cycles/10%	44.2	23.7

stability up to 1100 cycles in the three-electrode cell.¹⁸ Hashimoto *et al.* reasoned that the number of defect bonds as a trapping site of lithium reduced due to the presence of titanium, and therefore lithium could not accumulate in the structure of the $\text{WO}_3\text{-TiO}_2$ film. This increased the lifetime of the $\text{WO}_3\text{-TiO}_2$ film by five times as compared with pure WO_3 films.³¹ We believe that a similar explanation can account for our prepared Ti-doped vanadium oxide films. Upon increasing the Ti concentration from 0 mol% to 4 mol%, the contrast drop was reduced dramatically from 96% to 35% after 600 cycles (Table 3). By further increasing the Ti concentration to 10 mol%, the contrast drop systematically minimizes to 10%. But the contrast drop does not continually improve when the Ti concentration reaches 20 mol%. Hence, it is evident that the addition of Ti into the vanadium oxide film can dramatically improve the cyclic stability and an improved electrochromic performance can be obtained with the Ti concentration of 10 mol%.

Another important criterion for the electrochromic materials is the coloration efficiency (η), which is defined as the change in optical density (ΔOD) divided by the inserted (extracted) charge per unit area (q), as expressed in the following equation:¹

$$\eta = \Delta\text{OD}/q = \log(T_{\text{bleached}}/T_{\text{coloured}})/q$$

where, T_{bleached} and T_{coloured} are the transmittances of the film in the bleached state and in the coloured state, respectively. The high coloration efficiency can provide a large optical modulation with low charge insertion or extraction and is a crucial parameter for practical electrochromic devices. Fig. 6c shows a plot of OD *versus* the extracted charge density at +2.1 V of bleaching potential at 415 nm. The value of η was extracted as the slope of the line fitted to the linear region of the curve. The finally calculated η at 415 nm is as high as $95.7 \text{ cm}^2 \text{C}^{-1}$ and

$63.0 \text{ cm}^2 \text{C}^{-1}$ for the Ti-doped vanadium oxide film with Ti concentrations of 4 mol% and 10 mol%, respectively. This value is much higher as compared with those of the best known vanadium electrochromic materials.^{1,10,18,32} Electrodeposited molybdenum doped vanadium pentoxide films switched between -1 and $+1$ V showed η of $64 \text{ cm}^2 \text{C}^{-1}$ at 640 nm.¹⁰ Sputtered V_2O_{5-x} thin films on flexible PET/ITO offered a high η of $102.5 \text{ cm}^2 \text{C}^{-1}$ at a wavelength of 400 nm.¹ In our current work, the Ti-doped vanadium oxide thin film with a Ti concentration of 4 mol% delivers the highest coloration efficiency, both at 415 nm and 720 nm. Yet, further increase of the Ti concentration deteriorates the coloration efficiency.

It is noteworthy that the OD value changes almost linearly as the charge density continuously increases under the biasing, due to a short biasing duration of 20 s. Relating back to Fig. 6b, for the Ti-doped vanadium oxide film with a Ti concentration of 10 mol%, the colouring time for 80% optical modulation is only 5 s from a fully bleached state and the charge density at this moment corresponds to 6.89 mC cm^{-2} , while the bleaching time for 80% modulation is 6 s from a fully coloured state. It implies that the major optical modulation was completed in a short duration during the voltage switching, whereas further biasing only leads to small optical modulation. The switching speed of the Ti-doped vanadium oxide thin film prepared on the LPEI-modified ITO is much higher in comparison with other vanadium electrochromic materials.³⁰ It is mainly attributed to the almost amorphous structure of the Ti-doped vanadium oxide film. In addition, we believe that the layer of LPEI polymer on the ITO substrate stabilizes the electrodeposited Ti-doped vanadium oxide film by electrostatic and hydrogen-bonding interactions between the V=O groups in the vanadium oxide framework and the secondary amine groups in the LPEI

Fig. 6 (a) Optical transmittance spectra and (b) transmittance variations at 415 nm of Ti-doped vanadium oxide films with a Ti concentration of 10 mol% in 1.0 M LiClO_4/PC solution during continuous double potential step measurements between $+2.1$ and -2.0 V vs. Pt wire in a two-electrode system. (—) 1st to 5th cycles and (...) 596th to 600th cycles. (c) Optical density (OD) variation with respect to the charge density (measured at 415 nm) for Ti-doped vanadium oxide films with Ti concentrations of 4 mol% ($\square$) and 10 mol% ($\circ$), respectively.

polymer. The presence of self-assembled LPEI eliminates the need for the thermal treatment of the as-prepared film, which in turn preserves the amorphous nature of the oxide film.²⁰

4. Conclusions

The Ti-doped vanadium oxide thin films with different Ti concentrations were successfully electrodeposited on the LPEI-modified ITO glasses by electrochemical deposition. The presence of self-assembled LPEI polymer layers eliminates the need for the further thermal treatment for the as-prepared films, which in turn preserves the amorphous nature of the oxide film. Therefore, this kind of Ti-doped vanadium oxide film exhibits high electrochromic performance. With a Ti concentration of 4 mol%, the oxide film exhibited its highest transmittance contrast of 51.1%T, and highest η of 95.7 cm² C⁻¹ at 415 nm. By increasing the Ti concentration to 10 mol%, the oxide film exhibited rapid switching speed and better reversibility. It took only 5 s and 6 s to reach 80% of colouring and bleaching, respectively. Furthermore, the transmittance contrast drops by only 10% after 600 cycles in a two-electrode system.

Acknowledgements

This work is supported by the NRF-Create programme: Nano-materials for Energy and Water Management, and A*Star-MND Green Building Joint Grant 1321760013.

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