IMPROVED ION-STORAGE CAPACITY OF Ce-V MIXED OXIDE FILMS[†]

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Abstract

Thin films of Ce-V mixed oxides with Ce/V molar ratios equal to 4 or 2 were prepared on SnO_2/F covered glass by the sol-gel dip-coating process using $CeCl_3 \cdot 7H_2O$ and NH_4VO_3 as precursors. The films were heat-treated in an air or argon atmosphere. The electrochemical and optical properties depend on the mode of preparation. The influence of the composition and preparation of the sols as well as annealing conditions (atmosphere, temperature and time) on the optical and electrochemical characteristics of the films were studied. Ce-V mixed oxide films annealed in an argon atmosphere have better electrochemical behaviour than films annealed in an air atmosphere. As expected, the ion-storage capacity increased with increasing content of vanadium species in the films and reached the value of 23.9 mC cm^{-2} at a Ce/V molar ratio of 2 (after the 20th cycle), with notable cycling stability ($Q_i/Q_e = 0.98$ after the 100th cycle) when heat-treated in an argon atmosphere. All the films are optically passive under charge insertion and have a high transmittance (> 90%) in the visible range.

Introduction

Various materials have been studied in the last two decades for their use as counter-electrodes in electrochromical devices. V_2O_5 has been among the most studied materials for such purposes.[1-6] Its charge capacity is appropriate (~ 30 mC cm^{-2}) for service as a counter-electrode in electrochromic devices that use WO_3 as an electrochromic layer.[7] The technical feasibility of various design options of smart windows using V_2O_5 as counter electrode has been mentioned.[8] The major deficiency of this material is its unfavourable brownish-grey coloration connected with its lithium intercalation.[7]

CeO_2 and CeO_2 mixed with other oxides (TiO_2, ZrO_2) were the next generation of materials to be thoroughly studied in recent years as optically passive counter-electrodes, because they are transparent in the visible region in the reduced and oxidized states.[9,10] Moreover, they can be used as a UV shield due to their strong absorption of wavelengths below 380 nm.[9] CeO_2 exhibits a good reversibility of lithium intercalation,

but its charge capacity is lower than that of V_2O_5[10-13] as well as of CeO_2 mixed with the other oxides mentioned above. Recently Ce-V mixed oxides films have been studied with a view to improving the unfavourable properties of CeO_2 and V_2O_5 when they are used as counter-electrodes i.e. the low charge capacity of CeO_2 films and/or the undesired residual coloration of V_2O_5 films in the bleached state. Ce-V mixed oxides films at various Ce/V molar ratios (9, 3, 2, 1, 0.5) were prepared by the sol-gel dip-coating method.[14] Films obtained at a Ce/V molar ratio = 1 consist of crystalline $CeVO_4$ having the tetragonal structure of natural Wakefieldite. They have a relatively high ion-storage capacity (27 mC cm^{-2} after 10th cycle). However their ion-storage capacity decreases during cycling and after the 300th cycle falls to 18 mC cm^{-2}. The films are colourless and transparent with an optical transmittance over 88 % in the wavelength range between 450-740 nm (thickness of the film ~ 70 nm). The lithium diffusion coefficient of these films determined by the galvanostatic intermittent titration technique (GITT) drops from 10^{-10} cm^2 s^{-1}, when the insertion reaction begins, to 10^{-13} cm^2 s^{-1} at the end of the insertion reaction (inserted charge 25 mC cm^{-2}).[15] Ce-V mixed oxide films deposited by reactive radio frequency sputtering of a target composed of a mixture of CeO_2 and V_2O_5 oxides at a CeO_2/V_2O_5 molar ratio = 1 have a charge capacity up to 60 mC cm^{-2}.[16] Moreover no significant degradation was observed during reversible cycling. The films change coloration from yellowish to transparent upon lithium ion insertion of ~ 30 mC cm^{-2}; further insertion of lithium ions decreases their transmittance over the visible range and the colour of the films turns to grey. The lithium diffusion coefficients in these films were determined by three independent electroanalytical techniques i.e. the potentionstatic intermittent titration technique, galvanostatic intermittent titration techniques and electrochemical impendance spectroscopy.[17] A non-monotonic dependence on the intercalation level x was observed with diffusion coefficients between $8 \cdot 10^{-12}$ and $5 \cdot 10^{-13}$ cm^2 s^{-1} ($0 \leq x \leq 1$).

It is clear the electrochemical properties of thin films also depend on their preparation mode. Different techniques may be used to prepare thin films. Among the various methods[16,18-22] the sol-gel method[22] has some advantages. It allows the preparation of films with a high degree of homogeneity even in a multicomponent

system, as well as large area coatings at low cost.[23] Thin films prepared by the sol-gel route usually have different electrochemical and optical behaviour from films deposited by physical vapour deposition techniques.[24] The influence of precursors on the properties of thin films prepared by the sol-gel method has also been reported. Ce-V mixed oxide films, having appropriate properties at Ce/V molar ratios ≤ 1, could be prepared using V-alkoxides.[14] We believe that every step in synthesis of the film affects its structure, as well as its electrochemical and optical properties. In the present work we studied Ce-V mixed oxide films prepared at Ce/V molar ratios > 1. Alcohol-based sols were obtained using $CeCl_3 \cdot 7H_2O$ and NH_4VO_3. The influence of annealing time and atmosphere was also studied.

Experimental

Sols of Ce-V mixed oxide films were prepared by dissolving $CeCl_3 \cdot 7H_2O$ in a mixture of citric acid and ethanol according to the literature.[14] Then NH_4VO_3 was added and sols of Ce-V mixed oxides were obtained at Ce/V molar ratios = 4 (**A**) or Ce/V = 2 (**B**), while the synthesis of sols at Ce/V molar ratios < 1 was limited by the solubility of NH_4VO_3 in the mixture of ethanol and citric acid. The bluish-transparent sols obtained were stable a few days at room temperature, or one month at temperatures below 5 °C. Films were deposited by the dip-coating technique on transparent glass with a conductive coating of fluorine-doped tin dioxide (SnO_2/F, Pilkington, K-glass). The glass plates were previously cleaned with de-ionised water using an ultrasonic cleaner, washed with ethanol and dried at room temperature. The film thickness was controlled by the lifting speed (10 cm/min). After pulling, the films were dried in air and then heat treated at 400 or 450 °C in air or argon (15-60 min).

Thermogravimetric (TG) measurements of the films dried in air were performed in a dynamic air or argon atmosphere using a Perkin Elmer TGA 7 in the temperature range from 25 to 600 °C. The heating rate was 5 K min^{-1}. Platinum crucibles (diameter 8 mm) were used. The samples for TG measurements were prepared as described elsewhere.[25]

The thicknesses of thin films were measured using an Alfa Step 200 Profiler.

X-ray diffraction (XRD) was measured using a Philips PW 1710 diffractometer with CuK_α radiation from 20 to 70° 2Θ with a step of 0.025° 2Θ per second.

Electrochemical measurements were performed using an EG&G PAR273 computer-controlled potentiostat-galvanostat consisting of a three-electrode cell, filled with 1M $LiClO_4$ in propylene carbonate (PC). The working electrode was a Ce-V mixed oxide film deposited on SnO_2/F coated glass. A platinum electrode served as the counter electrode and the reference electrode was Ag/AgCl filled with a mixture of 1M LiCl in methanol and 1M $LiClO_4$ in PC with a molar ratio of 1:9. Cyclic voltammetry (CV) was performed at potentials between +1.6 V and −1.6 V with a scanning rate of 50 mV/s and chronocoulometric (CPC) measurements at +1.6 V and −1.6 V for 100 s. The working electrode area was 1 cm^2.

The optical transmittance characteristics of the thin films in the $350 < \lambda < 800$ nm wavelength range were measured during electrochemical reaction using a Perkin Elmer Lambda2 spectrometer connected to the potentiostat-galvanostat mentioned above.

Results and discussion

Although sols for Ce-V mixed oxide films were stable for approximately one month at temperatures below 5 °C, the films prepared with aged sols showed worse electrochemical properties than films obtained using freshly prepared ones. Only one layer was deposited on the glass substrate, because adhesion between two layers was too weak. The second one tended to peel from the first one irrespective of the drying temperature. Thus the thicknesses of the films were between 70 and 80 nm. It is also evident that the films annealed in argon are approximately 10 nm thicker than films annealed in an air atmosphere.

We performed TG measurements to estimate appropriate annealing temperatures of the films. The TG curves of films **A** and **B** performed in an argon or an air atmosphere, respectively, are presented in Figure 1. The decomposition of films **A** was similar over the whole temperature range, irrespective of the atmosphere used (argon or air), and mass loss ended at 400 °C. The decomposition of films **B** performed in argon was somewhat different from that performed in air, which could be ascribed to the

different decomposition route of vanadium species. The decomposition of the films **B** ended at 450 °C in both cases.
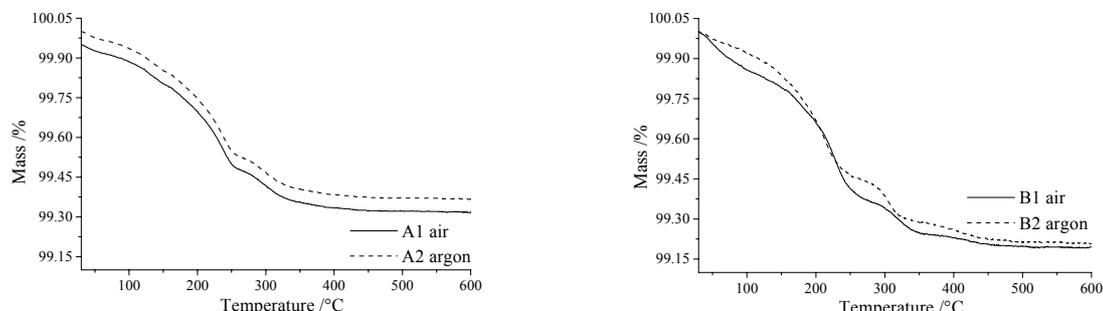
Figure 1. Comparison of thermogravimetric curves of thin films **A** and **B** deposited on micro-cover glasses in a dynamic air or argon atmosphere. The sample mass (thin film + micro-cover glass) was between 80 and 85 mg, the temperature range from 25 to 600 °C and the heating rate 5K/min.

Chronocoulometric measurements of films **A** and **B** heat-treated in air or argon atmospheres at 400 and 450 °C for different times are shown in Table 1. The amount of inserted charge decreased with increasing annealing time of the films. Films **B** generally have higher charge capacities than films **A**, according to the higher content of vanadium species. The influence of annealing time on the charge capacities of films **A** heat-treated in argon at 400 °C (**A2**) is the same as for the films **A** heat-treated in air (**A1**). In both cases the heating process had to be very short (15 min).

Cyclic voltammograms (CVs) of the films **A1** and **A2** are shown in Figure 2. Film **A1** exhibited great cycling stability. The changes of the shape of CVs of the films **A1** were very small. A very broad cathodic peak appeared during successive cycling, centred at ∼ −0.2 V vs. Ag/AgCl after the 50th cycle and it only slightly shifted to a lower value between the 50th and 100th cycle. The ratio between inserted/extracted charge was constant (Q_i/Q_e = 0.96-0.97). The shapes of CVs of the films **A2** changed during successive cycling because amount of the charge inserted increased while a broad minima, centred at ∼ −0.5 V vs. Ag/AgCl in the cathodic sweep direction, arose, which may be due to some structural modification of the film. The amount of charge inserted was approximately 34% higher in films **A2** than in films **A1**, but the reversibility of the

ion storage process was worse because the ratio between inserted/extracted charge dropped from 1.0 in the 10th cycle to 0.95 in the 100th cycle.
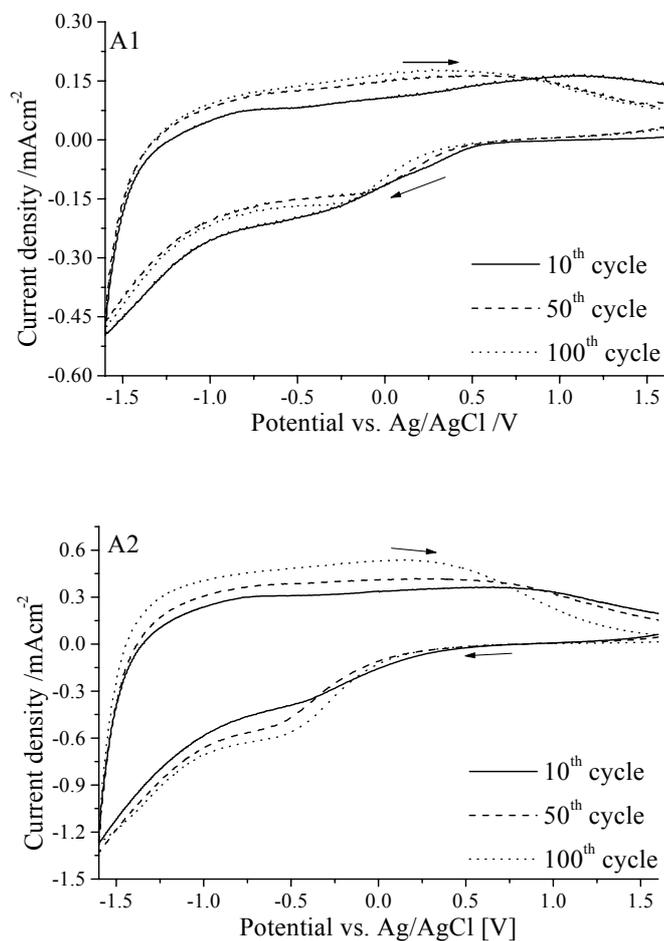
Figure 2. Cyclovoltammograms of thin films **A** annealed in air (**A1**) or argon (**A2**) for 15 min at 400 °C. Cyclic voltammetry was performed at potentials between +1.6 V and −1.6 V with a scanning rate of 50 mV/s. The thickness of thin film **A1** was ∼ 70 nm and the thickness of thin film **A2** ∼ 80 nm.

In accordance with the TG measurements we prepared films **B** at 450 °C in air and argon. Films **B** heat–treated in air for 15 minutes at 450 °C (Table 1) had lower charge capacities than films which were heat-treated in air at 400° C for the same time. Although the amount of inserted charge increased between the 10th and 20th cycles by ∼36%, it dropped after the 100th cycle by ∼46% compared with the 20th cycle and the reversibility of the ion-storage process was poor (Q_i/Q_e = 0.87-0.93).

Films **B** heat-treated in an argon atmosphere at 400 °C had very low charge capacities irrespective of the annealing time (Table 1).

Table 1
Chronocoulometric measurements of films **A** and **B** annealed at 400 and 450 °C in air or argon with the corresponding intercalated (Q_i) and extracted (Q_e) charges. Thicknesses of thin films annealed in air were $\sim$ 70 nm and those annealed in argon $\sim$ 80 nm.

Sample	Annealing time (min)	Q_i (mC cm^{-2}) / Q_e (mC cm^{-2})		
		10th cycle	20th cycle	100th cycle
A at 400 °C in air				
A1	15 min	–12.0/11.7	–12.9/12.4	–13.2/12.8
	60 min	–8.4/7.9	–8.6/7.9	–8.5/7.7
B at 400 °C in air				
B1	15 min	–15.1/14.3	–15.7/14.6	–17.3/15.0
	30 min	–9.5/8.5	–12.0/11.4	–
	45 min	–5.1/4.8	–6.5/6.4	–
	60 min	–6.4/6.2	–6.5/6.4	–6.6/6.4
B at 450 °C in air				
	15 min	–13.2/11.5	–18.0/16.8	–12.3/11.5
A at 400 °C in argon				
A2	15 min	–16.1/16.9	–17.0/16.5	–18.3/17.4
	30 min	–9.5/8.9	–10.0/9.5	–11.5/11.1
	45 min	–7.7/6.8	–8.0/7.5	–8.4/8.1
	60 min	–2.9/2.3	–3.5/3.0	–5.6/5.4
B at 400 °C in argon				
	15 min	–1.3/1.1	–2.1/1.8	–3.9/3.5
	30 min	–1.7/1.4	–2.7/2.2	–4.7/4.3
	45 min	–3.6/2.9	–4.3/3.8	–6.4/6.0
	60 min	–2.7/2.1	–3.3/2.6	–4.9/4.0
B at 450 °C in argon				
B2	15 min	–25.7/23.9	–23.9/23.3	–23.5/23.0

CVs of films **B** heat-treated at 400 °C in air (**B1**) and at 450 °C in argon (**B2**) for 15 min are shown in Figure 3. On the CVs of films **B1** broad cathodic ($\sim$ –0.1 V vs. Ag/AgCl) and anodic (+1.2 V vs. Ag/AgCl) peaks were observed from the start of the cycling (i.e. after the 10th cycle) and the amount of inserted charge tended to increase,

but the cathodic peak shifted to higher values (~ 0.0 V), while the anodic peak disappeared. The ratio of charge inserted to that extracted decreased from 0.95 in the 10th cycle to 0.87 in the 100th cycle. The amount of inserted charge appreciably increased when the films **B** were heat-treated in an argon atmosphere at 450 °C for 15 minutes (**B2**). The charge capacities of these films decreased between the 10th and 20th cycle by ~7 % and reached an approximately constant value after the 20th cycle. The CVs of films **B2** changed during successive cycling. Broad cathodic and anodic peaks appeared and became conspicuous after the 100th cycle (cathodic peak: 0.51 V; anodic peak: 0.75 V; vs. Ag/AgCl). At the same time the ratio of charge inserted to that extracted improved from 0.93 (10th cycle) to 0.98 (100th cycle), which confirms the increasing reversibility of the ion-storage process.

The structure of the films is not known because films obtained by the dipping process were too thin to perform XRD analysis. Only peaks of the SnO_2 layer on the coated glass corresponding to the dominant orientation (200) of the crystallites were detected in accordance with to the literature data.[26] It was reported recently[14] that in films **B** obtained with V-oxoisopropoxide as precursor (five layer deposited) and heat-treated in air for 30 or 90 min, CeO_2 and tetragonal $CeVO_4$ phases co-existed and exhibited high nanocrystallinity, as detected by XRD analysis.

We assumed the crystallinity of the film should be more pronounced in the films heat-treated in air than in the films annealed in argon. The structure of CeO_2 films heat-treated in air and argon atmospheres was recently evaluated by high-resolution transmission electron microscopy (HRTEM).[27] We found the order of the structure was higher in films annealed in argon than in films annealed in air. In both cases crystallised domains up to 10 nm were observed. But surprisingly the films heat-treated in air showed amorphous areas interchanging with crystallised domains, whereas the film annealed in argon was completely crystallised. So, we assume the different properties of films **A** and **B** heat-treated in air or argon atmospheres could be ascribed to a significant change in structural properties between the two differently processed films, with consequences for the electrochemical and optical behaviour of the films.
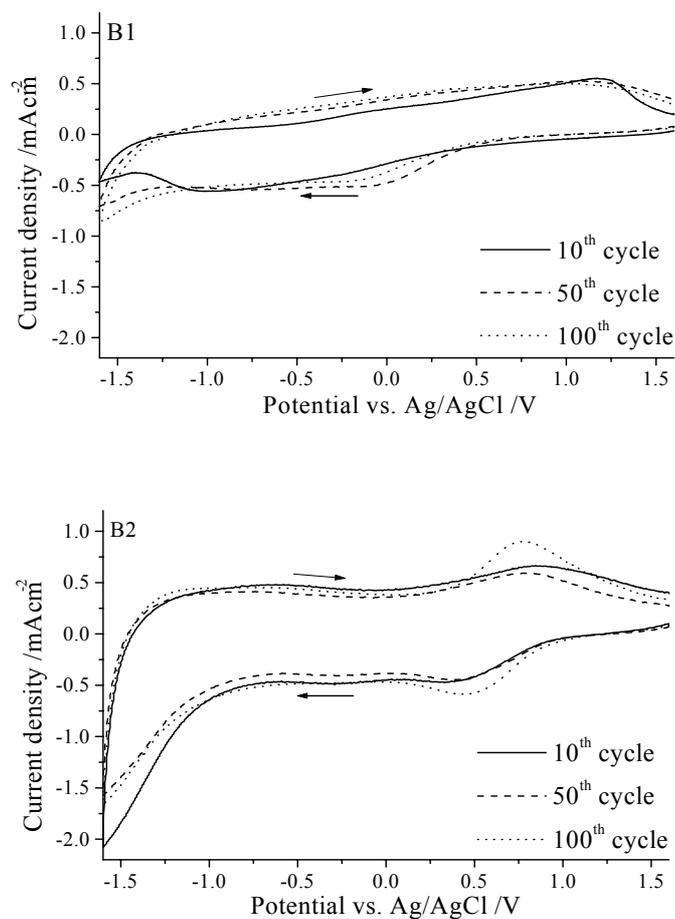
Figure 3. Cyclovoltammograms of thin films **B** heat-treated in an air atmosphere (**B1**) for 15 min at 400 °C or an argon atmosphere (**B2**) for 15 min at 450 °C. Cyclic voltammetry was performed at potentials between +1.6 V and −1.6 V with a scanning rate of 50 mV/s. The thickness of thin film **B1** was ∼ 70 nm and of **B2** ∼ 80 nm.

The optical transmittance spectra of films **A** and **B** were recorded in-situ during electrochemical charge/discharge cycles (Figure 4). All films were highly transparent in the visible range, irrespective on their ionic content. There was no sharp absorption edge as observed (at λ< 395 nm) in a pure CeO_2 film and/or in the mixed oxide films of Ti-Ce, W-Ce and Zr-Ce.[9] The absorption edges in the transmittance spectra of films **A** and **B** were broad and shifted towards higher wavelengths (up to 500 nm), which is typical of V-containing films.[14,16,28] It is interesting to note that the films annealed in air (**A1** and **B1**) exhibited cathodic bleaching at shorter wavelengths (film **A1** at λ < 500 nm, ΔT up to 17%; film **B1** at λ < 470 nm, ΔT up to 8%) with slightly improved

transmittance in discharged film **B1**, while high optical passiveness of these films was observed at longer wavelengths ($\lambda > 500$ nm) during the lithium intercalation/deintercalation process. All films annealed in argon exhibited high optical passiveness over the whole UV-visible range ($350 < \lambda < 800$ nm). In the transmittance spectra of film **A2** only slight cathodic bleaching ($\Delta T \sim 2\%$) was observed on intercalation of Li$^+$ ions over the whole recorded wavelengths range, while the charged film **B2** exhibited slightly lower transmittance in the same wavelength range ($\Delta T \sim 1\%$).
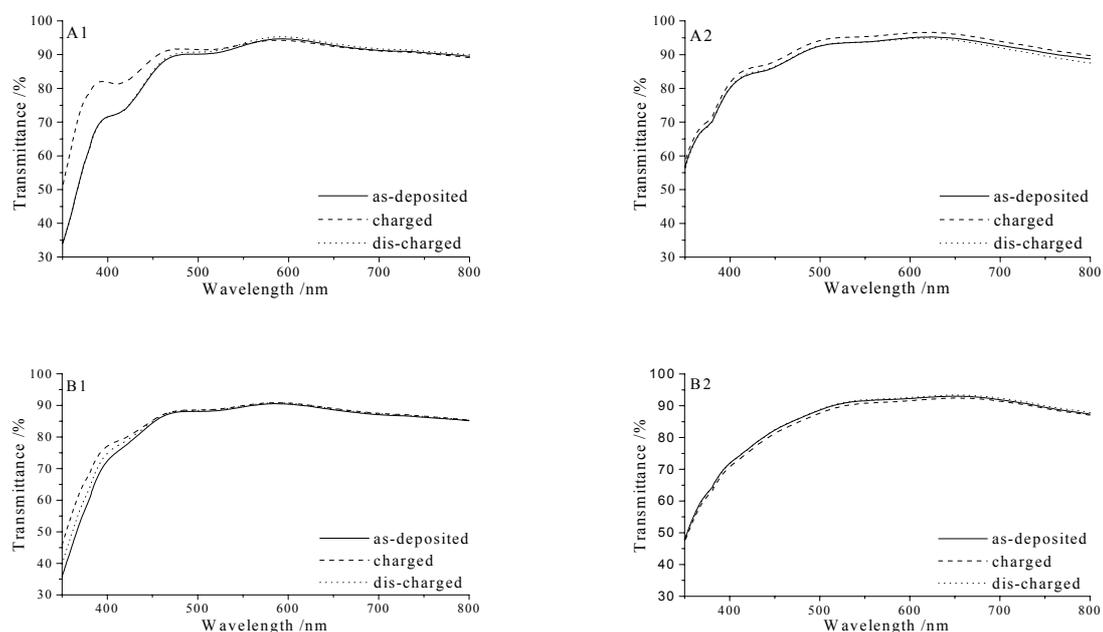
Figure 4. In-situ UV-vis spectroelectrochemical measurements of thin films **A** (heat-treated for 15 min at 400 °C in an air (**A1**) or argon (**A2**) atmosphere) and thin films **B** (heat-treated 15 min at 400 °C in air (**B1**) or 15 min at 450 °C in argon (**B2**)) obtained after charging and discharging the thin films at potentials of −1.6 V and +1.6 V for 100 s. The spectra of the initial and 10th cycle are shown.

Conclusions

Ce-V mixed oxide films of Ce/V molar ratios = 4 (films **A**) or 2 (films **B**) were prepared by the sol-gel process using CeCl$_3$ · 7H$_2$O and NH$_4$VO$_3$ as precursors. The thicknesses of the films were between 70 and 80 nm. The electrochemical and optical characteristics of these films depended on the chemical composition of the sols, as well as on annealing temperature, time and atmosphere. Films annealed in argon had a higher ion-storage capacity than films annealed in air and it increased with increasing content

of vanadium species in the films. Films **B2** had better electrochemical behaviour than all others, both in terms of total inserted charge and in terms of the reversibility of the ion-storage process. All films were highly transparent ($> 90\%$) in the visible range irrespective of their ionic content. The influence of annealing atmosphere on the structure of the films and /or on the molar ratios of Ce^{3+}/Ce^{4+} and V^{4+}/V^{5+} species in them is not known. Further research is planned to elucidate these questions.

Acknowledgements

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Povzetek

Tanke filme mešanih oksidov Ce-V z množinskim razmerjem 4 oziroma 2 smo z metodo potapljanja nanesli na SnO_2/F prevodno steklo. Sole smo pripravili iz $CeCl_3 \cdot 7H_2O$ in NH_4VO_3 po sol-gel postopku. Preučevali smo vpliv sestave in priprave solov, kot tudi pogojev gretja (atmosfera, temperatura in čas) na optične in elektrokemijske značlnosti tankih filmov. Mešani oksidni tanki filmi, žgani v atmosferi argona, imajo boljše elektrokemijske lastnosti kot tanki filmi žgani v atmosferi zraka. Kapaciteta interkaliranega naboja narašča z naraščajočo vsebnostjo vanadija in doseže vrednost 23.9 mC cm^{-2} pri množinskem razmerju Ce/V = 2 (po 20. ciklu). Reverzibilnost redoks procesov je pri filmih, žganih v atmosferi argona, po 100-tih ciklih, Q_i/Q_e = 0.98. Vsi filmi so med interkalacijo naboja optično pasivni in imajo visoko prepustnost (> 90%) v vidnem delu spektra.