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Influence of thermal treatment on the ion-storage capacity of Ce oxide and Ce–V mixed oxide films

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Abstract

Thin films and the corresponding xerogels of CeO_2 and Ce–V mixed oxides with a molar ratio equal to 2 (Ce/V = 2) were prepared from $CeCl_3 \cdot 7H_2O$ and NH_4VO_3 precursors using the sol–gel route and the dip-coating technique. The thermal decomposition of both forms of samples (thin films and xerogels) were studied by dynamic TG and DSC in two different atmospheres (air and argon). For the thermal studies the thin films were deposited on aluminium foil to reduce the unfavourable substrate to film mass ratio S/F, which is a consequence of using a glass substrate. The mode of heat treatment in a tube furnace of films deposited on conductive glass was defined from the TG curves of the films. The influence of annealing conditions (temperature, atmosphere and time) on the charge capacity of the films during application of the cycling process is reported.

Keywords: TG/DSC; CeO_2; Ce/V mixed oxide; Thin films; Ion-storage capacity

1. Introduction

In the last two decades much research work has been dedicated to development of electrochromic devices (ECDs). The basic layout of an ECD consists of five layers [1]. On a transparent conducting electrode (1st layer) an active electochromic material is deposited in the form of a thin film (2nd layer). A solid or gel electrolyte (3rd layer) connects the optically active material with an ion-storage material (4th layer), which is deposited on a second transparent conductive electrode (5th layer). When a voltage is applied through an external circuit, intercalation or extraction of ions causes the colouration or bleaching of the optically active material. The use of an ECD seems promising as a smart window application where the degree of colouration is controlled by the voltage.

The desired properties of ion-storage thin film materials are high charge capacity and transparency in the visible region in both reduced and oxidized states [2]. CeO_2 [3–7] and CeO_2 mixed with other oxides (TiO_2, ZrO_2) [8–12] have been extensively studied as candidates for these purposes in recent years. Recently, Ce–V mixed oxides films have been investigated 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 the undesired residual colouration of V_2O_5 films in the bleached state [13–17]. Every step in the preparation of a thin film affects its structure and consequently its electrochemical and optical properties. The influence of the precursor and the degree of thermal treatment on the properties of such thin films prepared by the sol–gel method has already been reported [18].

TG analysis of thin films is a demanding procedure and direct measurements of thin films are still not very common [19–21]. Because of the enormous dilution effect caused by the massive substrate, the observed mass changes are in the range of buoyancy and aerodynamic effects. In DSC measurements the heat evolved or absorbed is consumed by the substrate and therefore the measured effect is very small.

Differences in the microstructure between thin films and xerogels cause distinct thermal stabilities [22]. CeO_2 and Ce/V = 2 thin films also adhere very strongly to the substrate and it is impossible to remove them from it. Therefore we performed TG and DSC analyses of thin films deposited on aluminium foil, and for the corresponding xerogels. The

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lighter substrate diminishes the unfavourable substrate to film mass ratio [18] and consequently the mass and enthalpy changes could be more easily detected than in the case of a massive substrate. In the present work we compared TG and DSC curves of CeO_2 and $Ce/V = 2$ thin films and xerogels to define the annealing conditions for the corresponding films deposited on conductive glass for ion storage application.

2. Experimental

2.1. Preparation of sols

A sol of the CeO_2 precursor was prepared by dissolving $CeCl_3{\cdot}7H_2O$ in a mixture of citric acid and ethanol according to a literature method [15]. Then NH_4VO_3 was added and sols of Ce–V mixed oxides were obtained at the molar ratio $Ce/V = 2$, 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 CeO_2 sol was colourless while the $Ce/V = 2$ sols were bluish. All sols were stable for several days at room temperature, or one month at temperatures below 5 °C.

2.2. Preparation of thin films and xerogels

For TG measurements thin films were deposited on Al foil (thickness 0.01 mm) using the dip-coating technique, with a pulling velocity of 10 cm min^{-1}. To determine the electrochemical properties of these films, the film was deposited on transparent glass coated with a conductive layer of fluorine-doped tin oxide (SnO_2/F glass, Pilkington), left to dry at room temperature in air and then heat-treated for 15 min at 275, 400 or 450 °C in air or argon (see Table 1). After the annealing process they were taken out from the furnace still hot.

For the preparation of xerogels, sols were poured into petri-dishes and left in air for a few weeks to dry. The sticky xerogels were then finally dried in a drier at 50 °C.

Table 1
Chronocoulometric measurements of CeO_2 and Ce–V mixed oxide thin films annealed in air or argon with the corresponding intercalated (Q_i) and extracted (Q_e) charges

Sample			Q_i (mC cm^{-2})/Q_e (mC cm^{-2})		
			10th cycle	20th cycle	100th cycle
CeO_2	Air	275 °C	−10.4/7.9	−10.1/8.0	−10.5/9.1
	Air	400 °C	−3.1/2.2	−3.0/2.0	−3.5/2.0
	Argon	400 °C	−12.5/12.3	−13.8/13.5	−15.9/15.7
$Ce/V = 2$	Air	400 °C	−15.1/14.3	−15.7/14.6	−17.3/15.0
	Air	450 °C	−13.2/11.5	−18.0/16.8	−12.3/11.5
	Argon	400 °C	−1.3/1.1	−2.1/1.8	−3.9/3.5
	Argon	450 °C	−25.7/23.9	−23.9/23.3	−23.5/23.0

The thickness of the films was approximately 80 nm.

2.3. Instrumental

Thermogravimetric (TG) measurements of thin films and xerogels were performed in a dynamic air or argon atmosphere with a flow rate of 100 ml min^{-1} using a Mettler Toledo TA/SDTA 851^e thermoanalyser in the temperature range from 25 up to 600 °C. The heating rate was 5 K min^{-1}. Platinum crucibles (diameter 8 mm) were used. Before measurement in an argon atmosphere began, the furnace with the sample was purged with argon for 60 min. The baseline was subtracted in all cases. The sample masses were from 10.5 to 12.6 mg for thin film samples and from 10.6 to 12.0 mg for xerogels.

The effect of the atmospheric switch from argon to air on TG/SDTA (SDTA = single DTA) curves was measured at 400° in the case of a CeO_2 thin film sample and at 450 °C in the case of a $Ce/V = 2$ film. For these measurements the furnace with the loaded sample was purged with argon as mentioned above. After that the temperature was increased up to 400 °C (450 °C) at a heating rate of 5 K min^{-1} and held at the final temperature for 15 min. The purge gas was then switched to an air atmosphere. The flow rate of both gases was 100 ml min^{-1} and the baseline was substracted in all cases.

Differential scanning calorimetry (DSC) of the samples was performed under the same conditions (heating rate, atmosphere, gas flow) as TG measurements, using 40 μl aluminium crucibles. The thin film sample mass (Al foil with deposited film) was always 3.3 mg. The reference crucible was filled with the same mass of Al foil. In the case of xerogel samples the mass of the sample ranged from 4.3 to 5.6 mg. An empty crucible served as a reference. The baseline was subtracted in all cases.

Electrochemical measurements were performed using an EG&G PAR273 computer-controlled potentiostat-galvanostat consisting of a three-electrode cell, filled with 1 M $LiClO_4$ in propylene carbonate (PC). The working electrode was a CeO_2 or 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 1 M LiCl in methanol and 1 M $LiClO_4$ in PC with a molar ratio of 1:9. Cyclic voltammetry (CV) was performed at potentials between +1.6 and −1.6 V with a scanning rate of 50 mV s^{-1} and chronocoulometric (CPC) measurements at +1.6 and −1.6 V for 100 s. The working electrode area was 1 cm^2.

Thicknesses of the thin films deposited on conducting glass were measured using an Alfa Step 200 Profiler.

3. Results and discussion

3.1. Thermal analysis of xerogels and thin films

In Fig. 1 dynamic TG and DSC curves of CeO_2 (a and b) and $Ce/V = 2$ (c and d) xerogels are presented in both

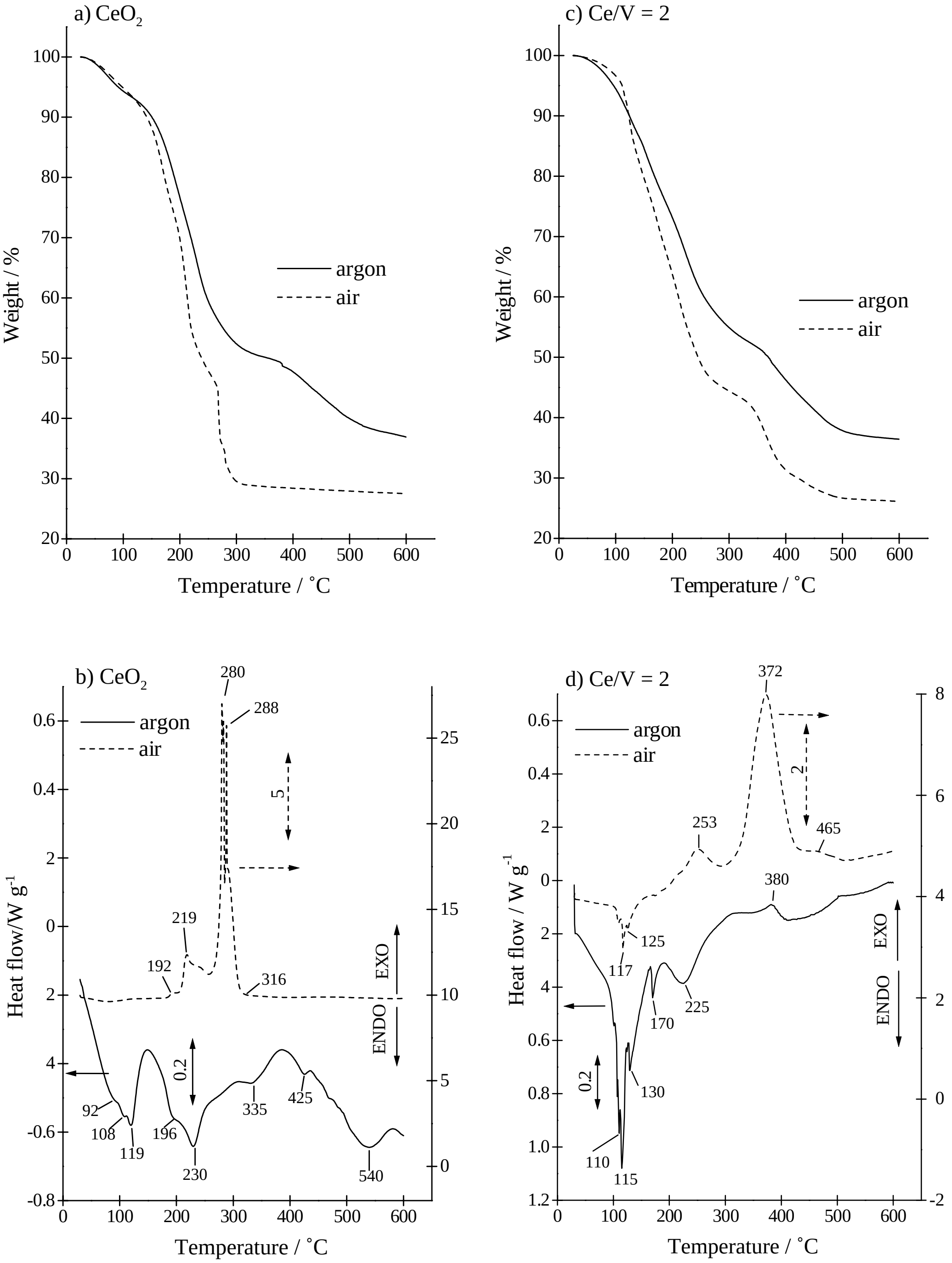

Fig. 1. Dynamic TG and DSC curves of CeO$_2$ (a and b) and Ce/V = 2 (c and d) xerogels annealed in argon and air atmospheres.

atmospheres. The TG curves of CeO$_2$ xerogel shows three distinct steps. We ascribe the first mass loss in the temperature range from 25 up to 150 °C (approximately 5%) to evaporation of ethanol and water. The second and the third weight losses are associated with thermal decomposition of citric acid. The weight loss is approximately 50% (in air) and 45% (in argon) for the second step and 17% (in air) and 14% (in argon) for the third step. The thermal decomposition is finished by 300 °C in air, whereas the total weight loss up to 600 °C is approximately 8% lower in argon, which means that decomposition is not complete.

On the DSC curve recorded in argon successive endothermic peaks are observed within all three steps, whereas two sharp exothermic peaks are positioned at 280 and 288 °C on the DSC curve recorded in air due to combustion of citric acid. No signal associated with solvent evaporation is observed because the ordinate scale is 25 times larger and the corresponding peaks are for that reason hidden.

On the TG curves of Ce/V = 2 xerogels recorded in both atmospheres (Fig. 1c and d) the process of solvent evaporation and the beginning of thermal decomposition are not clearly separated. The weight loss in the first step is 49% in argon and 56% in an air atmosphere.

The weight continues to decrease up to 600 °C in the case of the sample recorded in argon, whereas thermal decomposition of the sample recorded in air finished by 530 °C, with a final weight loss of 73% which is also approximately 10% higher than in the case of the argon atmosphere (63% by 600 °C). On the DSC curves of samples recorded in argon or air several endothermic peaks positioned in the temperature range from 110 to 225 °C are followed by upward turns of the signal, with a small exothermic peak at 380 °C on the DSC curve recorded in argon and two exothermic peaks (253 and 372 °C) on the DSC curve recorded in air.

A comparison of TG and DSC curves of thin films and xerogels is also required, because buoyancy and aerodynamic effects in TG measurements and the extremely small signals on DSC curves usually occur in thin film samples

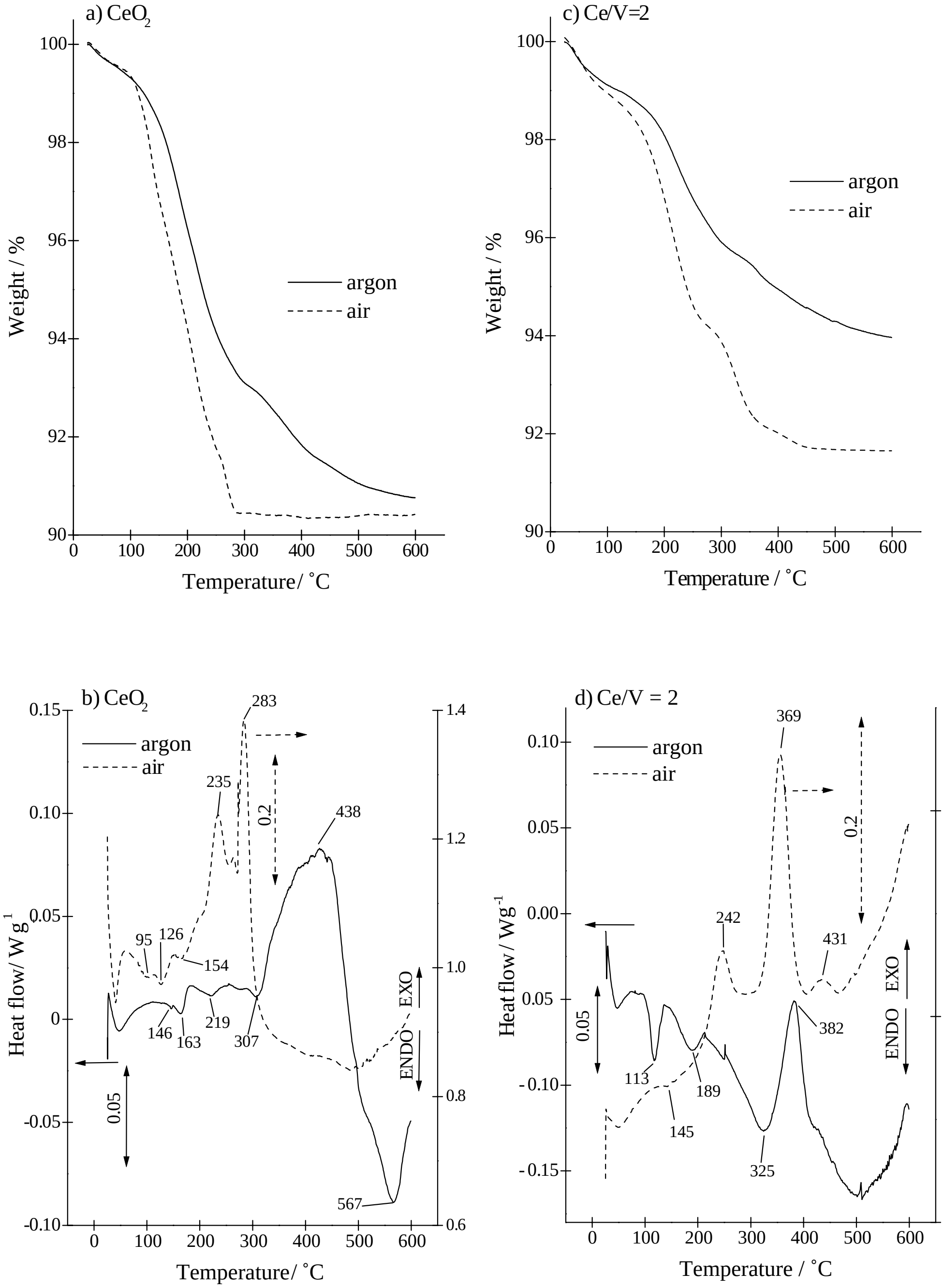

Fig. 2. Dynamic TG and DSC curves of CeO_2 (a and b) and Ce/V = 2 (c and d) thin films deposited on an aluminium foil and annealed in argon and air atmospheres.

deposited on a substrate [18]. In our study, low substrate to film mass ratios (S/F) were obtained using aluminium foil as a substrate. S/F ratios for CeO_2 and $Ce/V = 2$ thin films calculated from TG curves of xerogels were 6 and 8.5, respectively. As a consequence a weight loss of approximately 10% in thin film samples is observed, and buoyancy and aerodynamic effects are very small as compared to a weight loss of 10% and therefore negligible.

TG curves of CeO_2 and $Ce/V = 2$ thin films deposited on aluminium foil are shown in Fig. 2a and b. The decomposition reaction in thin film samples take place simultaneously, due to suppressed diffusion of gases by the substrate on one side and therefore the plateaus seen are not so clear as in the xerogel samples. For the same reason the DSC curves of thin films are different from the DSC curves of xerogel samples. However, we could not find a satisfactory explanation for the relatively strong exothermal peaks at 438 (CeO_2) and 382 °C ($Ce/V = 2$) for thin films recorded in an argon atmosphere where only endothermic effects were expected with respect to xerogel samples.

3.2. Chronocoulometric measurements of films prepared under various thermal conditions

We found in our previous studies [14,17,23] that the charge capacity of the films increased not only with increasing content of vanadium species, but that its enlargement also depends on the thermal treatment of the films as follows: (i) too high an annealing temperature is harmful to the ion-storage capacity and reversibility of the ion storage process of the films; (ii) in all cases the heating process should be very short (15 min); (iii) films annealed in argon have a higher charge capacity (34–51%) than films heat-treated in air.

The amount of charge inserted/extracted during chronocoulometric measurements is shown in Table 1. Low values were obtained in the case of CeO_2 thin films heat-treated at 400 °C in an air atmosphere. Knowing the shape of the dynamic TG curve of a thin film (Fig. 2a), we prepared another film of CeO_2, heat-treated at 275 °C, i.e. thermal decomposition was just completed on the TG curve (Fig. 2a). In this case, values of exchanged charge more than three times larger were observed. The amount of cycled charge remains practically the same during successive cycling. Although the ratio between inserted/extracted charges improves from 0.75 (in the 10th cycle) to 0.86 (in the 100th cycle), the reversibility of the ion storage process remains poor. Because there is no change in the weight loss curve from 300 to 400 °C, we can conclude that an excessive processing temperature affects the structure so that the process of insertion/extraction process of guest ions is suppressed during the cycling process. On the TG curve of a CeO_2 film annealed in argon (Fig. 2a) decomposition was not finished up to 600 °C and films annealed in the tube furnace at temperatures equal or higher than 450 °C were cracked and useless. The TG curve, which represents the real annealing process of a CeO_2 thin film in the tube furnace in an argon atmosphere at 400 °C, is presented in Fig. 3a. In both cases (in a tube furnace or in the furnace of the TG module) the temperature was increased from 25 up to 400 °C and held at 400 °C for 15 min. The film annealed in the tube furnace was then taken out of the furnace. When the atmosphere was changed to an oxidizing one, oxidation took place and a red glow occurred on the surface

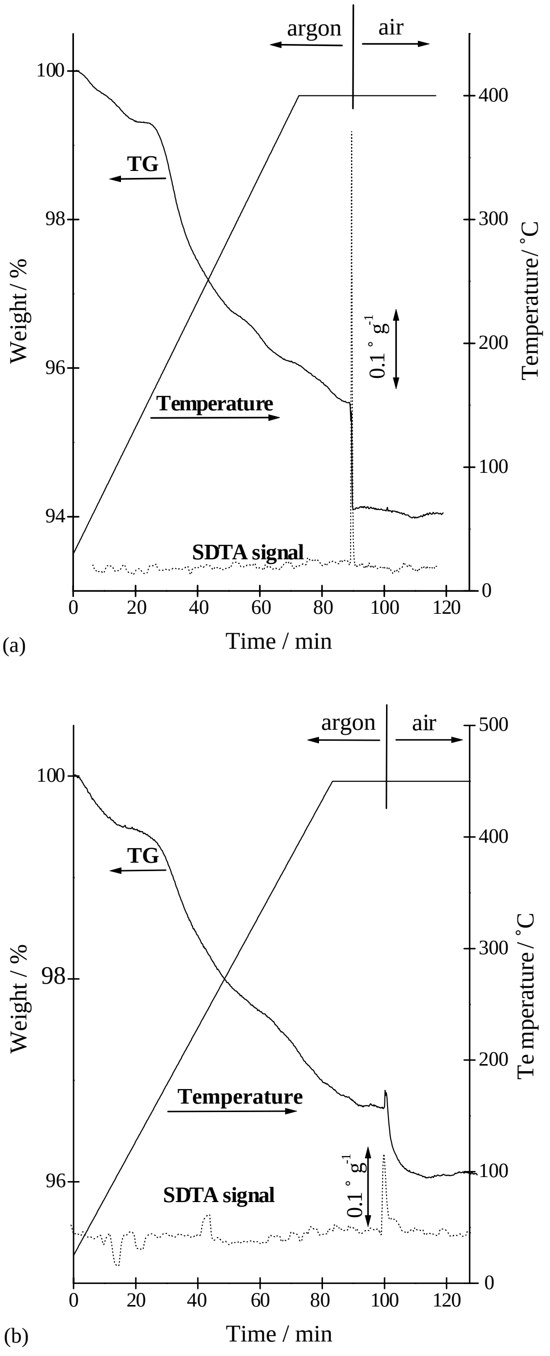

Fig. 3. TG/SDTA curves of CeO_2 (a) and $Ce/V = 2$ (b) thin films heat-treated in an argon atmosphere between 25 and 400 °C (CeO_2 sample) or 25 and 450 °C ($Ce/V = 2$ sample) and isothermally treated at the final temperature for 15 min. The purge gas was then switched to an air atmosphere.

of the conducting glass where the thin film was deposited. On the TG curve of such a film thermal decomposition of citric acid was just completed during isothermal treatment at 400 °C (Fig. 3a). After the change of atmosphere an additional weight loss was observed on the TG curve, together with a strong and sharp exothermic signal on the SDTA curve, due to burning of residual carbon, which remained in the film after thermal decomposition in argon. At the same time, the final oxidation and crystallisation of the film took place. The charge capacity of these films increases during the cycling process and achieves a value of 15.9 mC cm^{-2} after the 100th cycle. The ratio of charge inserted to that extracted remains constant: $Q_i/Q_e = 0.98$–0.99, which confirms the notable reversibility of the ion-storage process.

The structure of a CeO_2 film heat treated in air and argon was recently evaluated by high-resolution transmission electron microscopy (HRTEM) [23]. We found the microstructural order was higher in films annealed in argon than in films annealed in air. In both cases crystallised domains up to 10 nm were observed. Thin films heat-treated in air showed amorphous areas interchanging with crystallised domains, whereas films annealed in argon were completely crystallised. From the dynamic TG curve of the thin film (Fig. 2a) we can see that thermal decomposition is not so rapid in an argon atmosphere as in air. During the decomposition process crystalline nuclei are probably formed more slowly and the final microstructure possesses better order as compared to that formed in an air atmosphere.

Knowing the shapes of the dynamic TG curves of $Ce/V = 2$ thin films recorded in air or argon, we prepared these films at 450 and 400 °C, heat-treated for 15 min (in air or argon). The film heat-treated in air at 450 °C has lower charge capacities than film annealed in air at 400 °C. Although the amount of charge inserted increased up to 20th cycles (∼36%,) it dropped after the 100th cycle (∼46%), which means unfavourable ion-storage properties of the film. It is also evident from the Table 1 that the charge capacity and reversibility of the ion-storage process of a Ce/V film annealed in an air atmosphere at 400 °C are comparable with the values of pure CeO_2 thin films heat-treated in argon at 400 °C. Such thin films ($Ce/V = 2$) heat-treated in argon at 400 °C have very low charge values in comparison with films annealed at 450 °C. Several decreases in charge capacity of the film heat-treated at 450 °C were detected between the 10th and 20th cycle (∼7%), and the capacity reached an approximately constant value after the 20th cycle, and also indicated excellent reversibility even after the 100th cycle: $Q_i/Q_e = 0.98$ (Table 1). In Fig. 3b TG and SDTA curves of the heat-treatment process are shown. The course of the thermal reaction resembles the reaction of CeO_2 film (Fig. 3a), i.e. after isothermal annealing at 450 °C thermal decomposition of citric acid is completed and additional weight loss occurred when the atmosphere was switched to an oxidative one.

4. Conclusions

From the results of the current study it is clear that the ion-storage properties of CeO_2 and $Ce/V = 2$ thin films prepared by the sol–gel route also depend on annealing atmosphere and the degree of thermal decomposition.

Aluminium was used as a substrate for the films to obtain a low S/F ratio (<10).

The processing temperatures of the films heat-treated in a tube furnace in an air atmosphere were chosen on the basis of their dynamic TG curves. The decomposition and oxidation processes have to be just complete, whereas a further increase in temperature is harmful for the ion storage properties of these films. In the corresponding xerogels the final oxide material is formed at higher temperatures (approximately 20° in case of CeO_2 and 50° in case of $Ce/V = 2$ films). For this reason, TG curves of xerogels can not be used to determine the annealing temperatures of films.

TG/SDTA measurements simulating the real annealing process of films annealed in argon in the tube furnace show in all cases that the decomposition of citric acid had to be just complete to obtain films with appropriate ion-storage properties. The films annealed in argon had better ion-storage properties, due to the quick final oxidation process occurring when the films were exposed to air at the end of the heating process, which resulted in better crystallinity of the films as observed by HRTEM [23]. The reasons for the better ion-storage capacity of films annealed in argon are still not clear. The range of order observed in HRTEM is a few nm (crystallized domains and amorphous areas of the films) whereas the degree of order in the range of a few Å (neighbourhood of atoms) and also the molar ratios of Ce^{3+}/Ce^{4+} and V^{4+}/V^{5+} species in the films are not known. Further research is planned to elucidate these questions.

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References

[1] C.G. Granqvist, Handbook of Inorganic Electrochromic Materials, Elsevier Science, Amsterdam, 1995.
[2] C.G. Granqvist, A. Azens, A. Hjelm, L. Kullman, G.A. Niklasson, D. Rönnow, M. Strømme Mattsson, M. Veszelei, G. Vaivars, Solar Energy 63 (1998) 199.
[3] N. Özer, Solar Energy Mater. Solar Cells 68 (2001) 391.
[4] B. Elidrissi, M. Addou, M. Regragui, C. Monty, A. Bougrine, A. Kachouane, Thin Solid Films 379 (2000) 23.
[5] P. Baudry, A.C.M. Rodrigues, M.A. Aegerter, L.O. Bulhões, J. Non-Cryst. Solids 121 (1990) 319.
[6] M. Veszelei, M. Strømme Mattsson, L. Kullman, A. Azens, C.G. Granqvist, Solar Energy Mater. Solar Cells 56 (1999) 223.
[7] F. Varsano, F. Decker, E. Masetti, F. Cardellini, A. Licciulli, Electrochim. Acta 44 (1999) 3149.

[8] D. Kéomany, J.-P. Petit, D. Deroo, Solar Energy Mater. Solar Cells 36 (1995) 397.
[9] U. Lavrenčič Štangar, B. Orel, I. Grabec, B. Ogorevc, K. Kalcher, Solar Energy Mater. Solar Cells 31 (1993) 171.
[10] J. Purans, A. Azens, C.G. Granqvist, Electrochim. Acta 46 (2001) 2055.
[11] F.E. Ghodsi, F.Z. Tepehan, G.G. Tepehan, Electrochim. Acta 44 (1999) 3127.
[12] A. Azens, L. Kullman, D.D. Ragan, C.G. Granqvist, Solar Energy Mater. Solar Cells 54 (1998) 85.
[13] E. Masetti, F. Varsano, F. Decker, A. Krasilnikova, Electrochim. Acta 46 (2001) 2085.
[14] U. Opara Krašovec, B. Orel, A. Šurca, N. Bukovec, R. Reisfeld, Solid State Ionics 118 (1999) 195.
[15] G. Picardi, F. Varsano, F. Decker, U. Opara-Krašovec, A. Šurca, B. Orel, Electrochim. Acta 44 (1999) 3157.
[16] F. Varsano, F. Decker, E. Masetti, F. Croce, Electrochim. Acta 46 (2001) 2069.
[17] I. Kozjek Škofic, N. Bukovec, Acta Chim. Slov. 49 (2002) 267.
[18] R. Cerc Korošec, P. Bukovec, B. Pihlar, J. Padežnik Gomilšek, Thermochim. Acta 402 (2003) 57.
[19] P.K. Gallagher, J. Thermal. Anal. 38 (1992) 17.
[20] M. Leskelä, T. Leskelä, L. Niinistö, J. Therm. Anal. 40 (1993) 1077.
[21] L. Niinistö, J. Therm. Anal. Cal. 56 (1999) 7.
[22] M. Kawarada, Y, Nishina, Jpn. J. Appl. Phys. 16 (1977) 1531.
[23] I. Kozjek Škofic, S. Šturm, M. Ceh, N. Bukovec, Thin Solid Films 422 (2002) 170.