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Electrochemical, optical and X-ray absorption studies of Ce/V mixed oxides thin films

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ABSTRACT

Ce/V mixed oxide thin films with molar ratio 1 were prepared by sol–gel method from $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NH_4VO_3 with methanol or distilled water as a solvent and dip-coated on SnO_2/F -covered glass. The electrochemical, optical and structural properties of thin films depend on the solvent and heat treatment. The ion-storage capacities of the films annealed at 500 °C, prepared from methanol, 60 nm thick, was approximately 13 mC cm^{-2} and those prepared with distilled water, 40 nm thick, more than 20 mC cm^{-2} . The ion-storage capacity of the films annealed at 400 °C was approximately 1 mC cm^{-2} . X-ray absorption fine structure analysis showed that crystallization process of CeVO_4 occurs in temperature range between 400 and 500 °C.

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1. Introduction

Vanadium(V) oxide is one of the most investigated materials for its use as a counter-electrode in electrochromic devices. Its charge capacity is appropriate to serve as ion-storage film, but other electrochromic characteristics are suboptimal. To improve these deficiencies mixed oxides of several elements (W, Mo, Ti, Ce, Cu, Ni, Cr, Nb) with V_2O_5 were studied [1–8].

Among the most studied mixed oxide is Ce/V mixed oxide. CeO_2 alone exhibits good transparency in reduced and oxidized states in the visible region, it shows strong absorption of light below 380 nm and good reversibility of lithium intercalation. However, its charge capacity is too low for a counter-electrode in electrochromic devices. On the other hand the charge capacity of the V_2O_5 is appropriate for use as a counter-electrode, but during the lithium intercalation an unfavourable brownish-grey coloration occurs. The Ce/V mixed oxide might combine excellent properties of both oxides. Several methods were applied to prepare mixed Ce/V oxides: reactive r.f. sputtering, electrolysis, pulsed laser ablation and sol–gel [9–12].

Sol–gel processing has many advantages over other techniques. A high degree of homogeneity of the thin films can be attained on the molecular level, a variety of dopants can be added to the initial sol and different molar ratios of the oxides can be

achieved with the purpose of improvement of the structural, electrochemical and optical properties.

Two different sol–gel routes are used in general: metal salts in aqueous solutions or metal alkoxides in organic solvents. Crnjak Orel et al. [13] reported on the preparation of aqueous sols from V_2O_5 and $\text{Ce}(\text{NH}_4)_2(\text{NO}_3)_6$. Opara Krašovec et al. [12] prepared Ce/V sols from $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and citric acid in a proportion 1:2 then added V-oxoisopropoxide in various ratios and dissolved the mixture in ethanol. V-alkoxides are quite expensive and sensitive to the moisture, so they were replaced with NH_4VO_3 . In this case the synthesis of sols was limited by the solubility of the NH_4VO_3 in the mixture of ethanol and citric acid and only sols with Ce/V molar ratio > 1 could be prepared [4]. In previous papers [4,14,15] we reported the influence of the annealing process on the properties of the mixed oxide Ce/V thin film. With a careful selection of atmosphere, temperature and duration of the heat treatment the ion-storage capacities and the reversibility of the redox process were improved. The thin films annealed in argon were found superior to thin films annealed in air. The thickness of all prepared thin films was less than 60 nm, so the X-ray diffraction (XRD) analysis yielded only substrate peaks. X-ray absorption fine structure (XAFS) provided information on the oxidation number and the local structure around the constituent metal ions [16,17]. The aim of our subsequent investigation was to modify the basic synthesis in order to decrease the Ce/V molar ratio. In this paper, we report on the mixed oxides Ce/V=1 coatings prepared by sol–gel technique.

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2. Experimental

Ce/V sols with a molar ratio of about 2 can be prepared by dissolving $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NH_4VO_3 in a mixture of citric acid and ethanol [4]. The reduction of the Ce/V molar ratio is limited with the solubility of NH_4VO_3 in ethanol. A gel forms before the reaction mixture is dissolved. To avoid this process the Ce/V sols were mixed from inorganic precursors $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NH_4VO_3 dissolved in a mixture of citric acid and methanol or distilled water. When the sols with a molar ratio 1 were prepared in methanol, the reaction had to be carried in a thermostatic room under anhydrous conditions to prevent the hydrolysis to proceed too fast and the formation of gel to form before the reaction mixture of $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$, NH_4VO_3 and citric acid in methanol was dissolved. The sols were clear dark blue and were stable for a few days in a refrigerator. When distilled water was used as a solvent, the mixture was dissolved quite fast, but the formation of the sol was finished after two days, as state the colour of the sol showed. The sol was very stable, without changing colour; no gelation was observed even after two months at room temperature. The films were deposited by dip-coating technique on a transparent glass with a conductive coating of fluorine-doped tin dioxide (Pilkington, K-glass, $R_{\square}=13\ \Omega\ \square^{-1}$). The plates were previously cleaned with ethanol in an ultrasonic cleaner, washed with distilled water and dried in air at room temperature. For the thin films prepared from H_2O prior to dip-coating, the substrates were dipped into a wetting agent (1 wt% of Etolat TD-60 in ethanol) and left to dry in air. The films, all with Ce/V=1, were prepared by a single dip with pulling velocity of 10 cm/min. Higher speed resulted in a thicker film. After pulling, the films were dried in air and then annealed at 400 and 500 °C in air for 20 min. They exhibited good adhesion to the glass substrate. In the following discussion, the films prepared with methanol will be denoted by (a), and those prepared with distilled water, by (b).

Thermogravimetric (TG) measurements of the thin films, deposited on Al foil, were carried out using a Mettler Toledo TA/SDTA 851^e thermoanalyser in the temperature range between 25 and 600 °C. Air flow rate was 100 mL/min and the heating rate was 5 K/min. Platinum crucibles were used. The base line 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 80 mL of 1 M LiClO_4 in propylene carbonate (PC). The working electrode was a Ce/V=1 mixed oxide thin film deposited on SnO_2/F -coated glass with a surface area of 1 cm². 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 1:9. A platinum electrode served as a counter-electrode. Cyclic voltammetry (CV) was performed at potentials between +1.6 and –1.6 V at the scan rate 50 mV/s. Chronocoulometric (CPC) measurements were made at potentials –1.6 and +1.6 V for 100 s.

The optical transmittance characteristics of the Ce/V=1 mixed oxide thin films (b) in the 350 < λ < 1100 nm wavelength range were measured during the electrochemical reaction using a Perkin Elmer Lambda2 spectrometer connected to the potentiostat-galvanostat mentioned above. A homemade spectroelectrochemical transmission cell, filled with 40 mL of 1 M LiClO_4 in PC was used. A potential scan rate of 50 mV/s was used for CV measurements. For background measurements, a cell filled only with electrolyte was used.

Field emission scanning microscope (Zeiss Supra 35 VP) equipped with energy dispersive spectroscopy Inca 400 (Oxford Instruments) was used to study the surface of the thin films deposited on SnO_2/F -covered glass and to determine their thickness.

Standard cerium L₃ edge XAFS (X-ray absorption fine structure) spectra ($E_{L_3}=5723\text{ eV}$) of films prepared with H_2O and annealed to 400 and 500 °C were measured at the E4 experimental station of HASYLAB at DESY, Hamburg. To reduce absorption in the support material, films were prepared on 10 μm aluminium foil instead of glass. A stack of 8 foils provided L₃ edge jump of 0.1, while vanadium K-edge signal ($E_K=5465\text{ eV}$) was too low to record. A further increase in number of foils would not be reasonable because of the higher noise/signal ratio due to increase in the total absorption of the sample. Powder samples of CeO_2 and CeVO_4 on multiple layers of adhesive tapes were measured as standards. Energy calibration was established by simultaneous measurement of Cr foil ($E_K=5989\text{ eV}$) in the posterior position. The spectra were analysed with Iffeffit program package [18,19].

3. Results and discussion

TG measurements of thin films were used to determine the appropriate annealing temperatures. Fig. 1 shows that the decomposition of films prepared either with methanol (a) or distilled water (b) were similar over the entire temperature range. A minor difference between the TG curves appeared only in the initial stage, where the evaporation of the solvent occurred. The isothermal TG curve of thin film (a) showed that the final mass loss was achieved just before the temperature reached 500 °C. The final mass loss for thin film (b) occurred after a few minutes at 500 °C. According to these measurements, thin films with Ce/V=1 were annealed at 500 °C for 20 minutes. Some of the thin films were annealed at 400 °C to compare their structure and electrochemical properties to the films heat-treated at 500 °C and also to those annealed at 400 °C published in the literature [12]. Their current densities were lower by about 75% in comparison with the same films annealed at 500 °C. The ion-storage capacities do not exceed value of 1 mC cm^{–2}.

Cyclic voltammograms of the thin films (a) and (b) heat-treated at 500 °C are presented in Fig. 2. X-ray absorption studies showed that cerium is in the lower (3+) oxidation state so we assumed that the principal electrochemical activities arise from vanadium redox processes. During the first 50 cycles the charge exchanged increased because of the activation process. The same effect was also reported for some other vanadates [20]. Two distinct electrochemically active regions appeared: the first at potentials between 1.6 and –0.3 V and the second between –0.9 and –1.6 V. In the first region two cathodic peaks were positioned

Fig. 1. Isothermal TG curves of the mixed oxide thin films at 500 °C. The heating rate was 5 K min^{–1}.

Fig. 2. Cyclic voltammograms of mixed oxide thin films (a) and (b) at scan rate 50 mV/s.

in the first cycle at potentials of 1.25 and -0.1 V and two anodic peaks at potentials of 0.9 and 1.4 V. During cycling both cathodic peaks increased and shifted to 0.0 V. The anodic peak at 0.9 V shifted to 0.3 V and the second one shifted outside the cycling area. According to the literature, these peaks are correlated to V^{5+}/V^{4+} redox process [21]. Between -0.9 and -1.6 V two cathodic and one anodic peak were also observed. These peaks resulted from the redox process of the lower states of vanadium (V^{4+}/V^{3+}). The shape of the CVs of the thin film prepared with distilled water (b) is quite different from the CVs of thin film (a). Only one cathodic (0.0 V) and two anodic current peaks (~ -1.2 and 0.4 V) were observed. The cathodic peak was enlarged and shifted from -0.1 V in the first cycle to 0.0 V at the 10th. The increasing current density at potentials lower than -1.1 V was connected to reduction of V^{4+} . All anodic peaks were increased during cycling. The peak at -1.25 V stayed at the same position, whereas the peak at 0.5 V shifted to a less positive potential. The ion-storage capacity (Q_i and Q_e) for both thin films was determined from CPC measurements by charging the thin films at limiting potentials of -1.6 and $+1.6$ V vs. Ag/AgCl for 100 s (Fig. 3). The shape of the CPC curves also showed the difference between the two thin films. For thin film (a), the maximum value of inserted charge was attained after 25 s. The slope of the curve increased and the speed of the insertion of lithium ions improved with increasing number of cycles. The amount of inserted charge

Fig. 3. Chronocoulometric curves of mixed oxide thin films (a) and (b) at potentials -1.6 and $+1.6$ V. Measurement time: 100 s.

increased during the first 50 cycles, then remained stable. The maximum value of inserted Li^+ ions was about 8 mC cm^{-2} in the first cycle and increased up to 13 mC cm^{-2} in the 10th cycle, then remained stable. The amount of inserted charge in the thin film (b) was greater than for thin film (a) and increased from approximately 21 mC cm^{-2} in the first cycle to 22.7 in the 10th cycle and then decreased to 20.7 mC cm^{-2} until the 100th cycle, then remained stable for the next 200 cycles. The reversibility of the inserted and extracted charge was between 0.92 and 0.94 for 300 cycles.

There was no difference in stoichiometry between the two prepared thin films. To explain the differences found in electrochemical studies of the films, scanning electron spectroscopy (SEM) was applied. The thickness of the films (a) was between 50 and 60 nm and film (b) about 40 nm. SEM images of the surface showed that the surface of film (a) was more closed and smoother in comparison to film (b), where the structure of surface was more open and irregular (Fig. 4).

The electrochemical investigations showed that the ion-storage capacity of thin films (a) was too small for use as a counter-electrode, so no further structural, electrochemical and optical investigations were made on them.

We investigated the influence of the electrolyte concentration on the ion-storage capacity of the thin film prepared from H_2O (Fig. 5). The first cycle differed from the subsequent cycles by the rather small current peak at -1.3 V. With increasing electrolyte concentration the current peaks were shifted to more positive

Fig. 4. SEM images of the surface of the thin film (A) and (B) (on the left side) and cross-sectional micrographs of both thin films (on the right side). The bottom layer is a glass substrate, the middle one is a conducting SnO₂/F layer and the upper is the deposited thin film.

values of potential. A new current peak appeared at approximately -1.4 V in 1.0 or 1.5 M electrolyte. CPCs confirmed that an electrolyte concentration above 0.5 M of LiClO₄ in the PC was sufficient to assure enough Li⁺ ions for the electrochemical reaction in the thin films.

A change in colour of the thin films (b) was recorded by *in situ* UV–vis transmittance measurements in the wavelength range from 350 to 1100 nm during the electrochemical charge/discharge cycles (Fig. 6). The results showed that the film was transparent over the whole visible range ($T > 80\%$). The transmittance changed during charging by less than 2% with the exception of shorter wavelengths ($\lambda < 470$ nm), where the transmittance increased by about 40%.

The responses of the thin films were measured at 400 nm where the change of the optical transmittance as a function of the applied potential was considerable (Fig. 7). The major cathodic bleaching was observed between 1.6 and -0.25 V ($\sim 12\%$) where the current peaks could be attributed to change of the vanadium oxidation state (V^{5+}/V^{4+}). At more negative potentials the monochromatic spectral transmittance changed during reduction of V^{4+} by approximately 2% and when the potential was swept up, the bleaching persisted until the potential reached 0.0 V [21]. Then the transmittance decreased almost to the initial

Fig. 5. Cyclic voltammograms (A) and chronocoulometric curves (B) of the thin film (b) according to concentration of the electrolyte. Scan rate: 50 mV/s for (A), time of measurement: 100 s for (B).

Fig. 6. Transmittance (UV–vis) of thin film (b) as deposited, charged and discharged after 300 cycles.

value. It can be seen that the spectroelectrochemical response depends on the potential range.

In X-ray absorption spectra, the oxidation number of the target element is reflected in the position and the shape

Fig. 7. Observed spectral monochromatic changes at 400 nm and corresponding cyclovoltammetric response at scan rate 50 mV/s for thin film (b).

Fig. 8. Ce L_3 edge profiles of films (b) (400, 500 °C) and $CeVO_4$, CeO_2 standards.

of the absorption edge. Fig. 8 reveals a strong similarity between the Ce L_3 edge in the two thin films and the standard $CeVO_4$, pointing to cerium being in oxidation state +3 and excluding the admixture of Ce^{4+} , exemplified by the CeO_2 edge in the graph.

Since the Ce L_3 edge is sandwiched between the V K edge and the Ce L_2 edge, only limited information can be gained from Ce L_3 EXAFS (extended X-ray absorption fine structure) analysis: (i) the admixture of the signal from the close lying vanadium K edge cannot be eliminated ($E_{CeL_3} - E_{VK} = 258$ eV, i.e. $k = 8.2 \text{ \AA}^{-1}$); (ii) the range of the signal is very short due to the proximity of the Ce L_2 edge ($E_{CeL_2} - E_{CeL_3} = 438$ eV, i.e. $k = 10.7 \text{ \AA}^{-1}$); (iii) the $2p_{3/2}4d \rightarrow 5d^2$ double-electron transition contributes a strong non-structural admixture to the signal at $k \sim 6 \text{ \AA}^{-1}$. While there is no remedy for points (i) and (ii), the double-electron contribution can be eliminated by the procedure described in [16,17] since the double-electron excitation is an intra-atomic effect, dependent on the ion charge but largely independent of the chemical surroundings of the atom. An estimate of the contribution in E - or k -space may be extracted from the absorption spectra of suitable Ce^{3+} compounds with known structure. When the estimate is subtracted from the measured thin film absorption,

practically pure structural signals for EXAFS analysis are obtained.

The spectra are shown in Fig. 9. The EXAFS signal of the films basically followed the oscillations of the $CeVO_4$ standard but the effect of the annealing temperature was evident: the oscillations in the 400 °C sample annealed at lower temperature were more strongly damped than in the 500 °C sample or $CeVO_4$ (Fig. 9a).

Due to the short k -space range available for the analysis, only the parameters of the first-neighbour shell could be determined. The starting model for the relaxation of parameters was built from crystallographic data on $CeVO_4$ (tetragonal cell $I 4_1/a$ m d [22] with 4+4 oxygen atoms at 2.42 and 2.52 Å). Since no change in the oxidation state of the Ce ion was observed in XANES (Fig. 9), vacancies in the first shell of neighbours were not expected. The parameters defining the number of oxygen neighbours were therefore kept fixed at the model values while the two Ce–O distances and the width of their distribution were varied (Table 1). Relatively good agreement with the model was found for both films. The main difference between the samples was in the distribution widths σ^2 , i.e. in the degree of static disorder. The value $0.013(3) \text{ \AA}^2$ was obtained both for the $CeVO_4$ standard and the 500 °C film, and $0.017(3) \text{ \AA}^2$ for the 400 °C film. The effect is seen in Fig. 9b in the lower amplitude of the 400 °C peak in Fourier transform at 2 Å. It can be concluded that the intense

Fig. 9. EXAFS spectra of the films (b) (400, 500 °C) and standard $CeVO_4$, in k -space (a) and r -space (b). Weighing k^2 , $k = 2.5 - 7.0 \text{ \AA}^{-1}$.

Table 1

Parameters of the best fit first shell EXAFS model for the spectra of the thin films and CeVO_2 as a standard: $k=2.5\text{--}7.0\text{ \AA}^{-1}$, $r=1.5\text{--}2.5\text{ \AA}$, weighing k^2 , $N_1=N_2=4$, $S_0^2=1$, $E_0=5\text{ eV}$.

	400 °C	500 °C	CeVO_4
r_1 [Å]	2.46(2)	2.45(2)	2.43(1)
r_2 [Å]	2.56(2)	2.55(2)	2.53(1)
σ^2 [Å ²]	0.017(3)	0.013(3)	0.013(2)
r_{fit}	0.015	0.014	0.005

Uncertainties of the last digit are given in parentheses.

process of crystallization toward the CeVO_4 structure takes place between 400 and 500 °C, resulting in complete formation of the first shell of neighbours at 500 °C. Conceivably, the electrochemical properties of the material, the ion-storage capacity in our case, depend on the ordering of the atomic neighbourhoods.

4. Conclusions

Ce/V mixed oxide thin films with Ce/V molar ratio 1 were prepared by sol–gel process using $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ and NH_4VO_3 as precursors and methanol or distilled water as a solvent. The thin films prepared from distilled water (b) had higher ion-storage capacities than those prepared from methanol (a). Electrochemical characteristics were strongly dependent on the temperature and the duration of annealing. In thin films (b) heat-treated at 400 °C, the ion-storage capacity was less than 1 mC cm^{-2} and EXAFS showed strong disorder in their structure. Films (b) annealed at 500 °C (40 nm thick) had ion-storage capacities $> 20\text{ mC cm}^{-2}$, they were highly transparent except in near UV, where strong cathodic bleaching occurred. EXAFS analysis suggests that the ion-storage capacity correlates with the degree of crystallization: while the immediate neighbourhood of Ce ion exhibits the crystal structure of CeVO_4 in films (b) (annealed at 400 and 500 °C), the weaker heat-treatment leaves some static disorder even in the range of first neighbours. The incompletely formed oxygen shell of Ce atoms may hinder the storage of ions.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.solmat.2009.11.023.

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