

## 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  $\text{NH}_4\text{VO}_3$  with methanol or distilled water as a solvent and dip-coated on  $\text{SnO}_2/\text{F}$ -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  $13 \text{ mC cm}^{-2}$  and those prepared with distilled water, 40 nm thick, more than  $20 \text{ mC cm}^{-2}$ . The ion-storage capacity of the films annealed at 400 °C was approximately  $1 \text{ mC cm}^{-2}$ . X-ray absorption fine structure analysis showed that crystallization process of  $\text{CeVO}_4$  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  $\text{V}_2\text{O}_5$  were studied [1–8].

Among the most studied mixed oxide is Ce/V mixed oxide.  $\text{CeO}_2$  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  $\text{V}_2\text{O}_5$  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  $\text{V}_2\text{O}_5$  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  $\text{NH}_4\text{VO}_3$ . In this case the synthesis of sols was limited by the solubility of the  $\text{NH}_4\text{VO}_3$  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  $\text{NH}_4\text{VO}_3$  in a mixture of citric acid and ethanol [4]. The reduction of the Ce/V molar ratio is limited with the solubility of  $\text{NH}_4\text{VO}_3$  in ethanol. A gel forms before the reaction mixture is dissolved. To avoid this process the Ce/V sols was mixed from inorganic precursors  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$  and  $\text{NH}_4\text{VO}_3$  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  $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ ,  $\text{NH}_4\text{VO}_3$  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  $\text{H}_2\text{O}$  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<sup>e</sup> 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  $\text{LiClO}_4$  in propylene carbonate (PC). The working electrode was a Ce/V=1 mixed oxide thin film deposited on  $\text{SnO}_2/\text{F}$ -coated glass with a surface area of 1 cm<sup>2</sup>. The reference electrode was Ag/AgCl filled with a mixture of 1 M LiCl in methanol and 1 M  $\text{LiClO}_4$  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 <  $\lambda$  < 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  $\text{LiClO}_4$  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  $\text{SnO}_2/\text{F}$ -covered glass and to determine their thickness.

Standard cerium  $L_3$  edge XAFS (X-ray absorption fine structure) spectra ( $E_{L_3}=5723 \text{ eV}$ ) of films prepared with  $\text{H}_2\text{O}$  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  $\mu\text{m}$  aluminium foil instead of glass. A stack of 8 foils provided  $L_3$  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  $\text{CeO}_2$  and  $\text{CeVO}_4$  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 lfeffit 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<sup>-2</sup>.

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

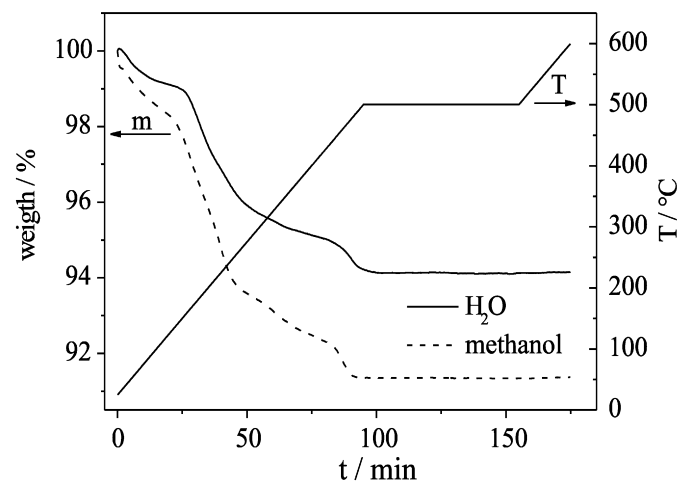


Fig. 1. Isothermal TG curves of the mixed oxide thin films at 500 °C. The heating rate was 5 K min<sup>-1</sup>.

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