

Electrochemical and optical properties of CeO₂ and mixed CeO₂/SnO₂ coatings

Elektrokemijske in optične lastnosti CeO₂ in mešanih CeO₂/SnO₂ tankih filmov

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Ion storage CeO₂ and CeO₂/SnO₂ coatings were prepared by sol-gel dip-coating method using aqueous-based process. The influence of added SnO₂ in the CeO₂ oxide coatings on the inserted/extracted charge was determined by chronocoulometric measurements. It was found that for 60 nm thick film the inserted/extracted charge was two times larger ($Q=10\text{mC/cm}^2$) for films containing 17 mol% SnO₂, if compared to pure CeO₂. The addition of SnO₂ to the mixed oxides coatings on their optical properties and structural characteristics were studied.

Key words: sol-gel, counter electrode, charge density

ionske hranilnike CeO₂ in CeO₂/SnO₂ v tankih filmih smo pripravili iz anorganskih prekurzorjev po sol gel postopku. Vpliv dodanega SnO₂ v CeO₂ filmih na interkalirani/deinterkalirani naboj smo določali s kronokulometrijskimi meritvami. Ugotovili smo, da je za 60 nm debele filme interkalirani/deinterkalirani naboj najmanj dvakrat večji po dodatku 17 mol % SnO₂ ($Q=10\text{mC/cm}^2$). Vpliv dodanega SnO₂ na optične in strukturne lastnosti smo študirali s spektrofotometričnimi metodami.

Ključne besede: sol-gel, ionski hranilnik, gostota naboja

1 Introduction

Cerium dioxide (CeO₂) has been considered as a useful material with high-refractive index film in single- and multilayered optical coating. Beside that, films are highly efficient for absorbing ultraviolet radiation and glass with 2-4% CeO₂ is valuable in protecting light-sensitive materials¹. Cation doped ceria is potential electrolyte for solid oxide fuel cell due to its high oxygen ionic conductivity².

Sol-gel deposited CeO₂ based films were studied^{3,4} as counter electrode in electrochromic devices. To improve slow kinetics of pure CeO₂ prepared by the evaporation technique they substitute cerium atoms by another element of a smaller radius as titanium. Cathodic and anodic peaks for so prepared mixed CeO₂/SnO₂ films showed reversible insertion for lithium ions and the charge inserted and extracted at sweep rate 10 mV was approximately 10 mC/cm² for three dippings³.

According to Baudry et al.³ in our study tin was used (atomic radius 0.71Å) instead of titanium (atomic radius 0.68 Å) and mixed SnO₂-CeO₂ films were prepared by dip-coating method via sol-gel route. In the present work we investigated in which extent ion storage capability in CeO₂ coatings could be improved by the addition of SnO₂ previously investigated^{5,6,7} in the mixed oxide coatings and its influence on optical and structural properties.

2 Experimental

Preparation of an aqueous dispersion of CeO₂ and mixed CeO₂/SnO₂ started from solution of metallic salts Ce(NH₄)₃(NO₃)₆ and SnCl₄. Precipitates were obtained by addition of NH₄OH until pH = 9 was reached. After washing the precipitate in order to remove residual NH₄⁺, Cl⁻, NO₃⁻ with distilled water the peptization was performed by addition of equimolar quantity of HNO₃ (pH ≈ 1). The colloidal sols were aged at temperature up to 90°C for 20 min, giving yellowish semitransparent sol.

Films were prepared with dip coating methods with pulling speed 10 cm/min on ITO glass plates with repeated dipping of 8 times. EG & PAR - Mod 273 potentiostat galvanostat with electrochemical analysis software was used for cyclic voltammetric and chronocoulometric experiments. A Ramp acquisition mode was employed in all cyclic voltammetric measurements. A Pt rod and Ag/AgCl/0.2 M KCl served as counter and reference electrode, respectively. The working electrode area was 1 cm² in electrolyte solution (30 ml 0.1 M LiOH). Scanning rate was 20 mV/sec. Cycling and chronocoulometric measurements were performed at potentials of +0.4 V and -1.3 V.

X-ray diffraction analyses of oxide powders and dip coated films were performed on Philips PW 1710 x-ray diffractometer.

Transmittance spectra, in the spectral range 0.3-2.5 μm were measured with Perkin-Elmer Lambda 9 spectrometer at resolution 2nm. Obtained T(λ) values were used for the calculation of normal solar transmittance according to the equation

$$T_s = \frac{\int_{0.3\mu m}^{2.5\mu m} T(\lambda) P_s(\lambda) d\lambda}{\int_{0.3\mu m}^{2.5\mu m} P_s(\lambda) d\lambda}$$

where P_s(λ) is solar spectrum at air mass of 2.

Surface Profiler Alfa Step 200 was used for thickness measurements.

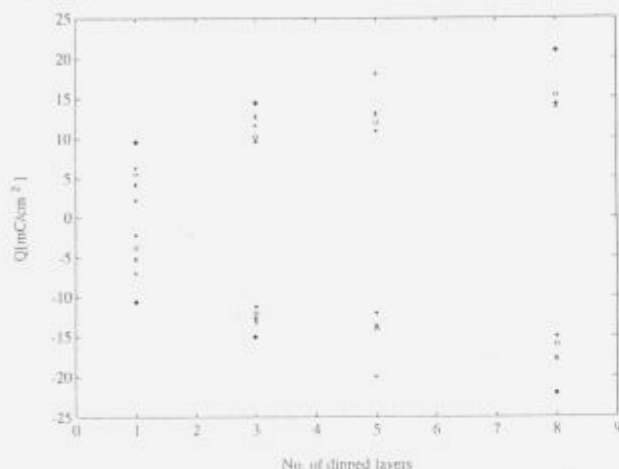


Figure 1: Cathodic and anodic total charge density Q (mC/cm²) as a function of added SnO₂ and a number of dipped layers: ○ - pure SnO₂, * - 3.2 mol% SnO₂, × - 6.25 mol% SnO₂, + - 9.1 mol% SnO₂, ● - 17 mol% SnO₂.

Slika 1: Katodna in anodna gostota naboja Q (mC/cm²) kot funkcija dodanega SnO₂ in števila plasti; ○ - čisti SnO₂, * - 3.2 mol% SnO₂, × - 6.25 mol% SnO₂, + - 9.1 mol% SnO₂, ● - 17 mol% SnO₂.

3 Results and discussion

Cyclic voltammetry was employed to investigate the usefulness of CeO₂ and CeO₂/SnO₂ dip-coated films as a counter electrode for electrochromic device for "smart window". This technique measures the capability of the films to reversibly intercalate and deintercalate mobile ions. In our work all measurements were performed for Li⁺ ions. The dependence of cyclic voltammogram (CV) for CeO₂ dip coated films prepared from different sols concentrations was studied. The obtained CV revealed that the electrochemical response depended on the concentration used. The peak current density of the films, prepared from the 7.2 10⁻³ mol and 9.6 10⁻³ mol in 20 ml (H₂O) starting sols, was very similar and much higher than for the film prepared from 4.8 10⁻³ mol in 20 ml H₂O. Chronocoulometric measurements were also performed for CeO₂ films prepared from the same concentration of sols with different number of dipped layers. Charge capacity (mC/cm²) refers to the amount of charge stored or extracted per cycle for an electrode and were recorded as a function of time (to 60 s) for each film. For three different concentrations it was found that charge density was in close connection with the concentration

used and with the number of dipping. The charge density was high if the starting concentration of used sol was high and the number of dipping was large.

According to results obtained the concentration of 7.2 10⁻³ mol was chosen for the preparation of pure CeO₂ and mixed CeO₂/SnO₂ dip coated films. It was found that for one layer charge density was about 4 Q (mC/cm²). The concentration of SnO₂ added was maximally 50 mol percents. For all of them, cathodic and anodic total charge density Q (mC) after 60 s, were determined. In **figure 1** the influence of added SnO₂ up to 17 mol% is presented. For that concentration the amount of charge density (Q) was about 10 mC/cm² for one layer and about 22 mC/cm² for 8 layers. The number of dipped layers is closely connected with charge density. If the concentration of added SnO₂ is higher than 17 mol % the charge density of mixed CeO₂/SnO₂ starts to decrease.

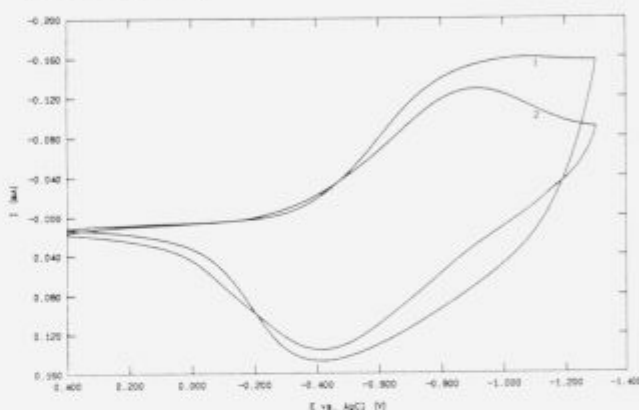


Figure 2: Cyclic voltammograms of CeO₂ thin film (one layer) at 17mol% added SnO₂. 1(fifth cycle), 2(400th cycle).

Slika 2: Ciklični voltamogram tankega filma (ena plast) CeO₂ s 17mol% dodanega SnO₂. 1(peti cikel), 2(400. cikel).

The best sample with only one layer, prepared by addition of 17 mol% of SnO₂ was tested for voltammetric stability. Four hundred sweep mode was applied and CV for initial and last cycle (400th cycle) are presented on **figure 2**. The film after cycling looks the same, without any visible changes.

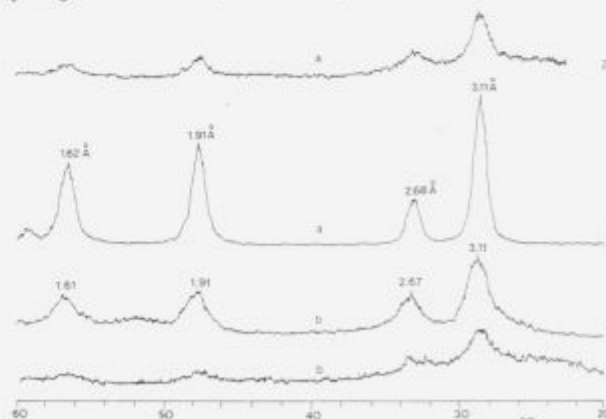


Figure 3: X-ray diffraction patterns of CeO₂ powder and thin dip-coatings films heated at 500°C: a) pure CeO₂, b) CeO₂/SnO₂ = 1, 1-powder, 2-films.

Slika 3: Rentgenski difraktogrami vzorcev, gretih na 500°C: a) čisti CeO₂, b) CeO₂/SnO₂ = 1, 1-prašek, 2-film.

X-ray diffraction measurement of powders and thin films, heated at 500°C, showed formations of crystalline cerianite. According to X-ray measurements (Figure 3), the addition of SnO₂ did not influence the position of peaks at 2θ = 28.6, 33.34, 47.5, and 56.5, only increased the broadening of diffraction lines with increased amount of SnO₂, is observed.

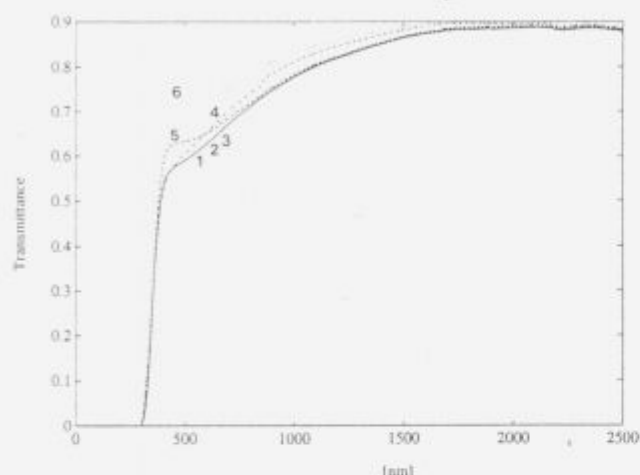


Figure 4: Transmittance (UV-VIS-NIR) spectra of CeO₂ with different concentrations of added SnO₂: 1-3.2 mol% SnO₂, 2-6.25 mol% SnO₂, 3-9.1 mol% SnO₂, 4-25 mol% SnO₂, 5-33 mol% SnO₂, 6-50 mol% SnO₂.

Slika 4: Transmisijski (UV-VIS-NIR) spektri tankih filmov CeO₂ pri različnih koncentracijah dodanega SnO₂: 1-3.2 mol% SnO₂, 2-6.25 mol% SnO₂, 3-9.1 mol% SnO₂, 4-25 mol% SnO₂, 5-33 mol% SnO₂, 6-50 mol% SnO₂.

Transmission spectra of CeO₂ and CeO₂/SnO₂ > 1 for one layer on ITO cover glass previously treated at 500°C are presented in figure 4. The transmission cut-off in the spectral range at 300-400 nm is observed. Spectra obtained for pure CeO₂ thin films and by addition 17 mol% of SnO₂ are very similar. Calculated solar transmittance T_S for all samples in the spectral range 0.3-2μm are high (T_S > 63%). In table 1, T_S for approximately the same thicknesses of applied pure CeO₂ and CeO₂ with 17 mol% of SnO₂ are 20% lower than calculated T_S of pure ITO on the glass.

Table 1: Solar transmittance T_S of CeO₂ (EC1-3) and CeO₂ with 17 mol% of SnO₂ (EC551-3) on ITO covered glass

Sample	thickness [nm]	T _S 0.3-2.0μm
EC1	120	0.645
EC2	180	0.655
EC3	560	0.656
EC551	120	0.648
EC552	200	0.665
EC553	560	0.639
ITO	30	0.80

4 Conclusions

Aqueous-based process was successfully used for the preparation of CeO₂ and CeO₂/SnO₂ dip-coating films for counter electrode. The best sample obtained at 17 mol% SnO₂ has a very good possibility for the intercalation/deintercalation of Li⁺ ions. Cathodic and anodic charge density of 10mC and 22mC was obtained for one- and eight layers, respectively.

5 Acknowledgement

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6 References

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