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Structural and electrochemical investigations of Ce/Cu mixed oxide thin films

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ABSTRACT

Thin films of Ce/Cu mixed oxide with molar ratios of 1 and 2 were prepared from inorganic precursors using the sol–gel route. Various electrochemical and spectroscopic techniques were used for characterization of the films and investigation of their optical and electrochemical properties. It was found that the redox behaviour significantly depends on the Ce/Cu ratio and on the concentration of Li^+ ions. Slow kinetics of the charge transfer reactions was evident from cyclic voltammetry measurements of both types of films only at low scan rates ($< 20 \text{ mV/s}$). Measurement of X-ray absorption fine structure (XAFS) indicated that the local structure of Ce and Cu ions is not affected by the Ce/Cu molar ratio.

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1. Introduction

In the last two decades various materials with electrochromic (EC) properties have been studied, in the first place WO_3 , which is very often used in EC devices [1–6]. Less research has been dedicated to the development of ion storage films. Two main types of suitable counter electrode are known:

- Counter electrodes with EC properties complementary to the EC film (a cathodic EC film requires an anodic EC ion storage film and vice versa).
- Passive counter electrodes transparent in the visible range both in the reduced and oxidized state.

The most thoroughly investigated optically passive material is CeO_2 . Various techniques have been used to deposit CeO_2 thin films on glass substrates: thermal decomposition of $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ [7], magnetron sputtering [8], electron beam evaporation [9], spray pyrolysis [10] and the sol–gel method [11]. A liquid solution, prepared by sol–gel technique, can be deposited on glass by dip-coating [11], spinning [12] or spraying [13]. Intercalation and deintercalation of Li^+ ions into cerium oxide films is a reversible process and when the film is thick enough, its ion capacity can be used as a counter electrode in EC devices. However, the intercalation of Li^+ ions into a CeO_2 thin film is very slow and therefore the response of the EC device is limited. To overcome the slow reaction

kinetics of Li^+ intercalation in CeO_2 films, several cerium mixed oxides, with W [14], Ti [14,15], V [16], Si [17], Sn [18] and Zr [19] have been synthesized.

The aim of our work was the preparation of new ion storage films based on CeO_2 . We report the structural, electrochemical and optical characterization of an ion storage layer of Ce/Cu mixed oxide prepared by the sol–gel process.

2. Experimental

2.1. Preparation of the films

A sol of CeO_2 was prepared by dissolving $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ in a mixture of citric acid and ethanol [20]. Sols of the Ce/Cu precursor at the metal molar ratios of 1 and 2 were obtained by adding $\text{Cu}(\text{CH}_3\text{COO})_2 \cdot \text{H}_2\text{O}$. The prepared sols were dark green and they were stable for several days at room temperature or two to three months at temperatures not exceeding 5°C . In the following discussion, thin films with a molar ratio of 2 will be denoted by (a), and those with a molar ratio of 1 by (b).

For electrochemical measurements, all the films were deposited by the dip-coating technique on transparent glass with a conductive coating of fluorine-doped SnO_2 (SnO_2/F , Pilkington, K-glass, $R_\square = 13 \Omega^{-1}$, OTE—optically transparent electrode), left to dry at room temperature in air and then heat-treated for 20 min at the optimal temperature of 400°C determined by thermogravimetric (TG) measurements. For XAFS measurements, an Al foil was used as the substrate. The thickness of both films was between 20 and 30 nm.

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2.2. Instrumental

X-ray Absorption Fine Structure (XAFS) spectra of the films at the Ce L₃ edge (5723 eV) and Cu K edge (8979 eV) were measured in the transmission mode at the E4 experimental station of Hasylab at DESY, Hamburg. A double crystal Si (1,1,1) monochromator with spectral resolution of ~ 1 eV was slightly detuned to reduce higher harmonics. Three consecutive ionization chambers were filled, respectively, with 800 mbar N₂, 200 mbar Ar and 300 mbar Ar for the Ce edge measurements, and with 100 mbar Ar, 600 mbar Ar and 1000 mbar Ar for the Cu edge. Stacks of 8 and 16 films on Al supports for the respective edges were measured between the first pair of ionization detectors, giving absorption jumps of ~ 0.1 and ~ 0.05 , respectively. Energy calibration was established by simultaneously measured Cr and Cu metal foils between the second and the third ionization chambers. CeO₂, CeVO₄, CuO and Cu₂O powders on several layers of adhesive tape were measured as standards with the same set-up. The spectra were analysed by the IFEFFIT program package [21,22].

Electrochemical measurements were performed using an EG&G PAR273 computer-controlled potentiostat-galvanostat consisting of a three-electrode cell, filled with 1 M LiClO₄ in propylene carbonate (PC). The working electrode was a Ce/Cu mixed oxide film deposited on the OTE while approximately 1.0 cm² of film was exposed to the solution. An Ag/AgCl reference electrode was filled with a mixture of 1 M LiCl in methanol and 1 M LiClO₄ in PC with a

molar ratio of 1:9 and a platinum electrode was used as counter electrode. Cyclic voltammetry (CV) was performed from +1.6 to -1.6 V with scanning rates between 1 and 20 mV s⁻¹. Chronocoulometric (CPC) measurements were performed at -1.6 (inserted charge, Q_i) and $+1.6$ V (extracted charge, Q_e) for 100 s during the 1st, 10th, 50th and 100th cycles. The environment for all measurements was an air atmosphere at an air-conditioned room temperature of 22 ± 2 °C.

The electrochromic properties of the thin films in the wavelength range $350 < \lambda < 1100$ nm were measured during electrochemical cycling using a Perkin Elmer Lambda 2 spectrometer and an optically transparent cell containing the working Ce/Cu OTE, reference and Pt counter electrodes connected to the potentiostat-galvanostat mentioned earlier.

A field emission scanning microscope (Zeiss Supra 35 VP) equipped with an Inca 400 energy dispersive spectroscope (Oxford Instruments) was used to study the surface of the thin films deposited on SnO₂/F covered glass and to determine their thickness.

3. Results and discussion

The exact position and shape of the X-ray absorption edges depend on the oxidation number of the target element Ce or Cu. Comparison with X-ray Absorption Near Edge Structure (XANES) spectra of the standard compounds CeO₂, CeVO₄, CuO and Cu₂O

Fig. 1. XANES spectra of thin films (a) and (b) in comparison with standard compounds (A—Ce edge, B—Cu edge).

Fig. 2. Fourier transforms of the EXAFS signal of films (a) and (b) with standard oxides, k^1 weighting: A—Ce edge, $k=3\text{--}10$ Å⁻¹; B—Cu edge, $k=3\text{--}12$ Å⁻¹.

Table 1

Parameters of the EXAFS models at Ce edge ($k=3\text{--}10\text{ Å}^{-1}$, $r=1.5\text{--}4.0\text{ Å}$, weighing k^1). Uncertainties of the last digit are given in parentheses unless the parameter is fixed.

	(a)	(b)	CeO ₂
N_1 (O)	8	8	8
r_1 [Å]	2.34(1)	2.33(1)	2.34(1)
σ_1^2 [Å ²]	0.008(1)	0.008(3)	0.001(3)
N_2 (Ce)	6.4(13)	6.5(29)	12
r_2 [Å]	3.86(2)	3.85(2)	3.86(2)
σ_2^2 [Å ²]	0.008	0.008(5)	0.003(2)
rfit	0.011	0.008	0.023

Table 2

Parameters of the EXAFS models at Cu edge ($k=3\text{--}12\text{ Å}^{-1}$, $r=1.3\text{--}2.0\text{ Å}$, multiple k^1 , k^2 and k^3 weighing). Uncertainties of the last digit are given in parentheses unless the parameter is fixed.

	(a)	(b)	CuO
N (O)	4	4	4
r [Å]	1.95(3)	1.96(7)	1.94(2)
σ^2 [Å ²]	0.002(2)	0.002(5)	0.005(3)
rfit	0.003	0.011	0.001

Fig. 3. EXAFS models, k^1 weighing: A—Ce edge, $k=3\text{--}10\text{ Å}^{-1}$, sample (b); B—Cu edge, $k=3\text{--}12\text{ Å}^{-1}$, sample (a).

showed that only Ce^{4+} and Cu^{2+} species were present in both samples (Fig. 1) with no admixture of Ce^{3+} and Cu^{1+} . This is in agreement with X-ray Photoemission Spectroscopy (XPS) measurements of the surface of the Ce/Cu thin films [23].

Although Al foil was used instead of glass to reduce X-ray absorption in the support material, the substrate absorption was still very high, preventing the use of a thicker stack of films. Even with the maximum feasible number of films, the recorded edge jumps – especially at the Cu edge – were at the lower limit of the Extended X-ray Absorption Fine Structure (EXAFS) sensitivity, with a rather high noise-to-signal ratio. Additional unfavourable factors were the short energy range of Ce data due to the proximity of the Ce L_2 edge, and a strong nonstructural signal of Ce $2p_{3/2}4d \rightarrow 5d^2$ multielectron photoexcitation in the middle of the EXAFS region (at $k \approx 6\text{ Å}^{-1}$). The latter was almost completely removed by subtracting a Ce^{4+} atomic absorption model [24,25].

In Fig. 2 Fourier transforms (FT) of the EXAFS signals are shown together with those of the standards CeO_2 and CuO . Films (a) and (b) exhibited very similar structural signals, indicating that the local structure of Ce and Cu ions was not affected by the Ce/Cu molar ratio. The first peak in the FT represents the contribution of the first shell of neighbours to the central metal atom (Ce or Cu). Its position and shape are the same as in the oxide standards, confirming the information from XANES, which is sensitive to the immediate vicinity of the target element. The peaks in the FT at distances beyond 3 Å in Ce and 2 Å in Cu were much lower than in the standard oxides, pointing to a lower degree of order. No additional structural peaks were observed, which would provide evidence of CeO_2/CuO solid solution.

Fig. 4. SEM images of the surface of the thin films (a) and (b).

Using quantitative EXAFS modelling of the data, some relevant structural information could still be extracted in spite of the short range of the signal and the high noise level, provided that the analysis was restricted to the few most salient parameters. This meant focusing the model on the dominant model constituents *i.e.* the first direct scattering paths. Only the first shell of neighbours was modelled at the Cu edge and the first two shells at the Ce edge, using CuO (tenorite, monoclinic, C 2/C [26]) and CeO₂ (cerianite, cubic, Fm3m [27]) crystal structures as starting models.

The multiple-scattering (MS) paths were neglected: in the CeO₂ model there is a single path within the *r*-range of the fit and a further two rather close beyond its endpoint. Although the integrated probability of each MS path was between 10% and 15% of the dominant path, their distribution was spread out more

widely, so that their contribution to the signal amplitude at any point was small. Since the least-squares fitting was performed in the complex domain, sensitive to the phase of the signal, the presence (or absence) of one component had a limited effect on the parameters of another component. We estimated that the relative error of the coordination number of the dominant shell introduced by a neglected MS path was of the order of the relative MS amplitude, *i.e.* below 15%. The effect on the σ^2 parameter was of the same order, and the effect on the length of the scattering path was negligible.

The results of the modelling are presented in Tables 1 and 2 and in Fig. 3. As expected from a visual inspection of the spectra, the parameters of the first (oxygen) shell agreed with those of the standards, while the average number of second Ce neighbours – cerium atoms – was reduced to ~ 6.5 from 12 in bulk CeO₂. Cu spectra showed no significant residue due to the omission of the higher shells in the model.

Even the rough estimates of the number of second Ce and Cu neighbours provided useful clues to the local structure of the films: the number of metallic neighbours of a target Cu atom was below the sensitivity of the experiment ($\sim$ below 10–20% of the CuO bulk value) indicating the predominantly amorphous state of the CuO component with no fixed medium or long-range order. It also precluded the presence of an ordered CeO₂–CuO solid solution. Hence a plausible conclusion from the EXAFS analysis that the metallic neighbours of the target Ce atoms were Ce, *i.e.* CeO₂ crystallites are segregated; this also in accordance with the literature data [28]. The low signal of Ce–Ce neighbours in the films relative to the bulk suggested that CeO₂ phase is nanocrystalline; the number of the neighbours could provide some information on the average size of the nanocrystals.

These findings were in agreement with an X-ray diffraction (XRD) study of the corresponding xerogels [23] suggesting very small CeO₂ crystallites, while the CuO signal was not detected. Marban's study of CuO/CeO₂ powder catalysts [29] suggested that CuO acts as a bridging agent between the neighbouring CeO₂ crystallites and reduces their growth, as is also evident from the SEM pictures (Fig. 4)

Fig. 5. The average number of first Ce neighbours vs. cluster diameter for spherical clusters as counted from the list of atom sites (dots) and calculated by Calvin's formula [30] (solid line). The EXAFS best fit value and uncertainty region for the thin film samples are marked with solid and dotted horizontal lines, respectively.

Fig. 6. Cyclic voltammetry (A) and chronocoulometric (B) measurements of mixed oxide thin films (a) and (b) after 100 cycles at different LiClO₄ concentrations. CV scan rate: 50 mV/s, CPC measurements at potentials of -1.6 and $+1.6$ V for 100 s.

From the average number of Ce neighbours the size of the CeO_2 clusters could be estimated. For this purpose we used a list of atom positions generated in EXAFS calculation by the ATOMS routine of the IFEFFIT package. For clusters within consecutive filled shells of Ce atoms around the central site, the number of Ce neighbours to each individual atom was counted. The averaged number rose from 5.5, for the smallest cluster with 13 atoms and 0.76 nm diameter, to 12 for the bulk (Fig. 5), i.e. from 46% to 100% in relative measure. This result was consistent with the approximate formula for spherical clusters given by Calvin et al. [30]. The value 6.5 ± 2 neighbours found in EXAFS modelling for both thin films suggested very small clusters (diameter 1–2 nm, less than 100 Ce atoms).

It should be noted that EXAFS gave the average over *all* Ce atoms in the sample, while – in the case of a wide distribution of cluster sizes – techniques like XRD and Transmission electron microscopy (TEM) favour larger clusters and neglect the smaller ones, which are invisible to these methods. As a result, EXAFS size estimates are consistently smaller than those from XRD and TEM [29]. In this sense the real sizes of Marban's clusters in powder catalysts (6–11 nm, [29]) may not be far from ours. In any case, the grains seen in atomic force microscopy (AFM) images of the thin films (50–70 nm, [23]) are almost certainly polycrystalline. The reduction in the average diameter to 20–50 nm after cycling could be the result of crumbling of the grains into smaller aggregates of CeO_2 clusters.

The properties of the film changed markedly with Ce/Cu molar ratio and concentration of Li^+ ions. In films (a) (Fig. 6Aa), reduction of Ce(IV) to Ce(III) and intercalation of Li^+ ions proceed between –1.0 and –1.5 V and the reaction rate depended mainly on the concentration and transport of Li^+ ions through the film. The reverse processes (Ce(III) oxidation and Li^+ deintercalation) also depended on the LiClO_4 concentration and only became noticeable at higher concentrations of the electrolyte (> 0.5 M). The mixed oxide films (a) and pure CeO_2 films [11] exhibited a similar shape and change in cyclovoltammograms on cycling around ± 1.6 V. CeO_2 and copper did not form a solid solution. This is probably the reason for the similarity in the shapes of the cyclovoltammograms between films (a) and CeO_2 . The shape of voltammograms of films (b) (Fig. 6Ab) differed and both processes (reduction/oxidation) proceeded at significantly lower overpotentials. It seems that two consecutive reduction/oxidation reactions proceeded where a copper couple was followed by a cerium one, and both of them depended on the lithium concentration. Cathodic and anodic processes were controlled by diffusion and that there was only a weak influence of electrolyte concentration on the charge capacity after more than 10 cycles.

The form of the CPCs of films (a) (Fig. 6Ba) exhibited a similar Q - t profile as pure CeO_2 films, but the total charge was 50% higher [11]. CPC measurements show that in films (b) the amount of exchanged charge depended more significantly on the electrolyte concentration and number of cycles than in films (a). Also the kinetics of the reduction/intercalation process deviated markedly from the characteristic for diffusion control. As evident from the Q - t relationship shown in Fig. 6Bb, the initial slow process was followed by a second one. At 0.1 M LiClO_4 the slow process prevailed during the first 70 s of the potential step and at 1.5 M Li^+ ions this period decreased to about 30 s. This indicates that the cathodic process in these films consisted of a charge transfer reaction conditioned by diffusion and/or slow structural changes. This is also evident from changes in the electrochemical properties on cycling. The reduction in the exchange charge depended on the Li^+ concentration, being about 20% for 1.0 M electrolyte and less than 10% for 1.5 M, between 50 and 100 cycles. The reason for the decrease in the ion storage capacity could be irreversible deintercalation of Li^+ ions from the structure. During cycling the Li^+ ions were found to be incorporated into mixed Ce/Cu oxide thin film

[23]. Structural changes were also evident optically since during cycling the colour of the film (b) changed from brownish to yellow.

The colour change 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. 7). The film (a) was transparent in the visible range ($T > 80\%$). Comparison between CeO_2 films and films (a) showed that the absorption edge at approximately 400 nm, characteristic of CeO_2 , was less sharp and that the transmittance decreased less rapidly towards shorter wavelengths. Film (a) exhibited weak cathodic colouring over the whole visible region. The transparency of film (b) was above 70% over the whole visible range and exhibited strong cathodic colouring over the whole visible region (Fig. 7b).

Transmittance changes during the electrochemical cycling process of films (a) and (b) were recorded at 570 nm, where the change in the optical transmittance during charging/discharging cycle was maximal. The transmittance of the conditioned films did not change significantly during cycling between the charged and discharged state, since the total change in transparency for both films was less than 2%.

From the in situ transmittance–time response curves shown in Fig. 8 it can be seen that the monochromatic transmittance at 570 nm decreased during the intercalation process at –1.6 V and increased during the deintercalation step at 1.6 V. The change

Fig. 7. Transmittance (UV–vis) of thin films (a) and (b) as deposited, charged (at –1.6 V for 100 s) and discharged (at +1.6 V for 100 s) after 100 cycles; concentration of electrolyte: 1.0 M LiClO_4/PC .

Fig. 8. In situ monochromatic changes at 570 nm for films (a) and (b) during intercalation and deintercalation of Li^+ ions at potentials of -1.6 and $+1.6$ V, concentration of electrolyte: $1.0 \text{ M LiClO}_4/\text{PC}$.

between the coloured and bleached state increased with the number of cycles for both films and the shape of the T – t curves were very similar to the Q – t response. The colour change was more intensive for film (b) where the transparency at 570 nm changed by approximately 25%. During deintercalation of Li^+ ions the bleaching persisted until the transmittance reached the initial value.

4. Conclusions

Mixed oxide Ce/Cu thin films with molar ratios of 1 and 2 were prepared by the sol–gel process and deposited by the dip-coating technique. The thickness of both thin films was between 20 and 30 nm. The local structure of Ce and Cu ions was not affected by the Ce:Cu molar ratio and both the thin films consisted of small clusters (from 1 to 2 nm). The redox processes of oxidation and reduction of both thin films depended on the concentration of Li^+ ions. Films with a Ce/Cu molar ratio of 2 exhibited a similar shape and change of cyclic voltammograms as pure CeO_2 thin films, but their total charge was higher by approximately 50%. Films with a molar ratio of 1 showed less stability during cycling than films with a molar ratio of 2 due to the occurrence of some structural changes. Both films were transparent ($T > 70\%$) over the whole visible region, but exhibited considerable cathodic colouring.

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