Nanostructured PLD-grown gadolinia doped ceria: Chemical and structural characterization by transmission electron microscopy techniques


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Abstract

The morphology as well as the spatially resolved elemental and chemical characterization of 10 mol% gadolinia doped ceria (CGO10) structures prepared by pulsed laser deposition (PLD) technique are investigated by scanning transmission electron microscopy accompanied with electron energy loss spectroscopy and energy dispersive X-ray spectroscopy. A dense, columnar and structurally inhomogeneous CGO10 film, i.e. exhibiting grain size refinement across the film thickness, is obtained in the deposition process. The cerium M4,5 edges, used to monitor the local electronic structure of the grains, indicate apparent variation of the ceria valence state across and along the film. No element segregation to the grain boundaries is detected. These results are discussed in the context of solid oxide fuel cell applications.

1. Introduction

Thin nano-structured layers of solid oxide fuel cell (SOFC) materials obtained by pulsed laser deposition (PLD) are of technological importance due to their prospective applications in portable electronics [1,2]. This study focuses on thin films of gadolinia doped ceria, i.e. 10 mol% Gd2O3 doped CeO2 (CGO10) – an SOFC electrolyte material, which is characterized by higher ionic conductivity than the conventionally used yttria stabilized zirconia (YSZ) [3–5]. However, compared to YSZ, ceria-based materials are susceptible to reduction, i.e. tetravalent ceria (Ce4+) adapts the trivalent state (Ce3+) in an oxygen lean atmosphere, e.g. at the anode side of the SOFC under operating conditions [6]. This ceria reduction results in an increase of the partial n-type electronic conductivity that degrades the SOFC performance due to the internal cell short-circuiting [6,7]. Despite this detrimental ceria behavior, CGO10 is successfully applied by commercial enterprises as an electrolyte material, which is characterized by high ionic conductivity compared to YSZ [3–5]. However, it has been reported, in the context of electrical properties of pure [9,10] and doped ceria [10], that ceria reducibility is enhanced in the nano-grained form of the material. This ceria property, being in fact fundamental for catalytic ceria applications [11], has been studied extensively on monodisperse nano-powders [12–15], and on crystallographically well-defined surfaces of substrate supported ceria films [11,16]. These investigations have led to concepts of ceria grain size dependent reducibility [9–16]. The present work extends the above-mentioned investigations to PLD-prepared CGO10 films investigated across their thickness. In the case of the PLD-grown films, the aspect of the morphology related ceria susceptibility for reduction is particularly interesting. This is due to the large variability of the nanocrystalline film morphologies which can be obtained in the PLD process [17,18] and their possible implications to the extent of the electrolytic domain, i.e. the oxygen pressure range where ionic conduction dominates [19–22].

This work reports on the chemical and structural characterization of the as-deposited CGO10 thin films, prepared on a polycrystalline silver (Ag) support, and the effects of the substrate support on the film properties. The films are studied by transmission electron microscopy (TEM) imaging and analytical TEM techniques like energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). The use of the metal substrate is attractive from a technological perspective, since metal supported SOFCs are emerging as a new generation of fuel cells competing with the state-of-the-art SOFCs due to the promise of high power generation at reduced temperatures, both in the micro [23] and the macro [24,25] designs.

2. Experimental

The CGO10 films were prepared on Ag/MgO(1 0 0) substrates by PLD in a deposition system described in detail elsewhere [26].
films were deposited by KrF laser (248 nm) for 120 min at a laser fluence of 1.1 J/cm² with a laser beam spot of 0.036 cm², laser repetition rate of 10 Hz, substrate–target distance of approximately 68 mm, and substrate temperature 400 °C. After the deposition process, the Ag coating was sputter deposited on top of the CGO10/Ag/MgO(1 0 0) structure. The Ag/CGO/Ag/MgO(1 0 0) layered structure was subsequently coated with a thin layer of gold (Au), in order to ensure good electrical contact between the sample and the sample holder used for the TEM foil preparation. 

The TEM thin foil (about 100 nm thick) was prepared by the focused-ion beam (FIB) milling utilizing a Zeiss 1540XB Crossbeam system. Prior to the milling procedure, a platinum layer was locally deposited on top of the Au/Ag/CGO/Ag/MgO(1 0 0) structure. 

The TEM analysis was performed on a JEOL 3000F, a field-emission analytical 300 kV TEM equipped with a Gatan imaging filter (GIF) and a scanning TEM (STEM) unit. The imaging was performed in bright field (BF) and high angle annular dark field (HAADF) STEM modes. The elemental analysis was performed along and across the CGO10 layer with a 1 nm probe size STEM-
EDS. The electronic structure of the film was characterized along and across the film at both interfaces of the CGO10 coating. This was done by EELS utilizing the Ce-M_{4,5} edges. In order to eliminate effects of varying foil thickness in the spectrum, the same background-subtracted window was applied to all spectra acquired from STEM-EELS, followed by plural scattering removal. A 1 nm spot size, 6 cm camera length were used for the STEM-EELS acquisition. 5 s integration time was utilized in all STEM-EELS experiments, in order to avoid electron-beam damage of the films [15]. The M_{4}/M_{5} signal ratio, utilized to estimate the cerium valence state, was determined by the second derivative method [13] performed on the raw data.

3. Results and discussion

In Fig. 1 a detailed view of the investigated layered structure is shown. The layers notable in the BF-STEM micrograph (see Fig. 1a) are identified by the EDS signals presented in Fig. 1b. The visible microstructural difference of the Ag layers (see Fig. 1a) results from the fact that the bottom Ag layer has undergone a heat treatment up to 400 °C during the process of CGO10 deposition, whereas the top Ag layer has not been thermally treated. The BF-STEM overview of the CGO10 layer, shown in Fig. 2, illustrates clearly the anisotropy of the grains' morphology concerning both the grain shapes and sizes. The presence of distinct columnar grains in the CGO10 film indicates the polycrystalline character of the material that was also confirmed by X-ray diffraction (data not shown here). The polydisperse character of the grain sizes throughout the film thickness is clearly visible. A high density of small grains, i.e. 10–20 nm width, is encountered close to the CGO10 film–substrate interface, whereas structures larger than 50 nm width are present in the upper part of the film. This indicates that competitive growth of crystallites occurs during the film deposition process – a mechanism that is often observed during PLD and sputtering deposition [27,28].
apparent film depth dependent morphology signifies the variable contribution of grain boundaries throughout the film. In the context of electrical performance of ceramic materials, the grain boundary density is often invoked, in order to explain the overall material conductivity [29]. In the case of thin polycrystalline films, the thickness-related anisotropy of grain boundary distribution indicates that depth dependent film conductivity might be anticipated. For example, the large grain boundary density in the vicinity of the film–substrate interface together with the often low conductivity of grain boundaries has been suggested to be responsible for the deteriorated electrical conduction in thin films [26,30]. In the micro-grained bulk materials, the resistive properties of grain boundaries are often associated with a preferential solute segregation to grain boundaries that occurs at high temperature sintering of ceramic materials [31]. However, this effect is expected to be undetectable in nano-structured materials [32] and materials prepared at relatively low temperatures [33]. Indeed, the STEM-EDS analysis performed across and along the films do not evidence obvious element segregation. A Gd:Ce cation ratio close to 0.1 is found in the grain interiors and across the grain boundaries.

The spatially resolved EELS analysis (approximate areas of the analysis are indicated as dotted lines in Fig. 2) based on the high energy near edge EELS (ELNES) of the cerium edges, originating from various electronic transitions, has been used for the identification of cerium valence states, i.e. Ce4+ or Ce3+. The cerium electronic configuration \([\text{Xe}]4f^26s^2\), yields \([\text{Xe}]4f^06s^0\) for Ce4+ and \([\text{Xe}]4f^16s^0\) for Ce3+. The ceria M-edge region resulting from the 3d104fn to the 3d\(^{n-1}\)4f\(^{n+1}\) quasi-atonic electronic transitions \((n = 0 \text{ or } 1\) for Ce4+ and Ce3+ respectively) is utilized in the analysis. As shown in Fig. 3, two distinct electronic transitions can be observed in this region due to the spin–orbit coupling, i.e. M4 and M5 lines originating from the 3d\(^{3/2}\) to 4f\(^{5/2}\) and respectively from the 3d\(^{5/2}\) to 4f\(^{7/2}\) transition. The position, the relative intensity and the structure of the sharp M4,5 lines give an insight into the valence state of cerium in cerium oxides, as shown in Fig. 3 and in agreement with previously published data [34,35]. The pure Ce4+ and Ce3+ states, clearly distinguishable in Fig. 3a, are often observed in a mixed form (see Fig. 3b), indicating the presence of both states in the examined sample volume. Qualitative analysis based on the ELNES spectra shape, performed along the main axis of the columnar grains span-
reduction, i.e. increasing Ce\textsuperscript{3+} grain volume fraction with decreasing grain size [12], can be observed. However, in the case of the PLD-prepared CGO10 films, the spatial origin of the Ce\textsuperscript{3+} signal is ambiguous. This is probably due to the structural anisotropy of the films and the overall sample volume analyzed in the experiments. The structural factors influencing the ELNES signal can be divided into the following: (i) the width of the grains along the electron beam direction (ii) the alignment of the grains along this direction, and (iii) the alignment of the beam with respect to the grain surfaces in the direction of the passing beam. The volume probed by the electron beam depends on the foil thickness and yields approximately 1400 nm\textsuperscript{2} in the case of 100 nm thick CGO10 foil. This estimation is based on the lateral electron beam spread [37] of about 7 nm. The abovementioned facts suggest that multiple grains stacked together along the direction of the passing electron beam can be examined in the experiments. In the case of a single grain analysis performed in the vicinity of the main grain axis, situation corresponding to data presented in Fig. 4a, a pure Ce\textsuperscript{4+} state can be observed. When the beam crosses multiple grains, a situation corresponding to data presented in Figs. 4b and 5, the reduced ceria volume fraction is expected to increase due to the increase of the analyzed grain surface. This brings about the mixed Ce\textsuperscript{4+} to Ce\textsuperscript{3+} signal. It is notable that among all examined areas, the pure Ce\textsuperscript{3+} state is found only in the size refined column part, along the film–substrate interface, where only grain surfaces are encountered (see Fig. 4b). The above discussion indicates that, in this case, the exact relationship between the film grain structure and the material chemistry is not clear, however a qualitative agreement with the observations for pure ceria nano-particles can be inferred.

The presented results indicate, in the context of the solid oxide fuel cell applications, that dense, nano-structured PLD-prepared films of CGO10 are suited for applications on the anode side of the fuel cells. This is due to the fact, that the preferential surface defect formation, together with an abundance of the grain surface area, facilitates the presence of quasi free electrons i.e. \((\text{CeCe}\cdot\cdot\cdot\cdot\cdot)^{'},)\) and, as a consequence, the presence of surface oxygen [36,38,39] – a factor believed to be responsible for the redox activity increase in the nano-material [40]. The use of nano-grained CGO10 as fuel cell electrolyte seems to be unfavorable, unless micrometer range grains [9] can be obtained in the deposition process. In addition, the appropriate material thickness has to be taken into consideration [7,25]. Our data give also an insight into the reported variability of thin film CGO electrolytic domain [19–21,26]. The extent of the electrolytic domain could be correlated with the density of the reduction susceptible grain surfaces defined by the film structure and the thickness. However, this aspect of the nano-structured CGO10 films requires further investigation.

### 4. Conclusions

Dense, columnar and polycrystalline CGO10 thin films prepared by PLD are characterized by depth varying morphology. The STEM study reveals that the width of the columnar grains increases from 10 to 20 nm to at least 50 nm at the top of the 420 nm thick films. The TEM-EDS analysis indicates a constant Gd:Ce cation ratio of 0.1 throughout the film thickness. No indication of a segregation of the dopant to the grain boundaries is observed. The ELNES investigation performed on the Ce-M\textsubscript{4,5} edges shows the presence of Ce\textsuperscript{4+} and Ce\textsuperscript{3+} in the films. The exact spatial origin of the Ce\textsuperscript{3+} signal is unclear. However, preferential grain surface reduction can be inferred from the data. This fact indicates that the nano-structured CGO10 films are more suitable for anodic rather than electrolytic SOFC applications.

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References