ELECTROCHEMICAL VAPOUR DEPOSITION OF DOPED LaCrO₃

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ABSTRACT

CVD/EVD of Mg-doped LaCrO₃ on porous calcia-stabilized zirconia (CSZ) has been investigated in the temperature range of 1473 to 1523 K, using the metal chlorides as reactants. During the EVD stage, doped LaCrO₃ is formed as long as the supply of LaCl₃ is sufficient, otherwise Cr₂O₃ will be formed simultaneously. The magnesium content of the LaCrO₃ films is very low (<2%), despite the excess of MgCl₂ in the reactant stream, as expected from thermodynamic calculations. Film growth shows parabolic behaviour, indicating that the deposition is controlled by solid state diffusion. The parabolic growth rate constant is determined to be 8.2×10⁻¹¹ cm²/s at 1473 K, and 1.1×10⁻¹⁰ cm²/s at 1523 K. Dense films of doped LaCrO₃ can also be grown by the EVD process on gastight oxygen ion conducting substrates. Sr-doped LaCrO₃ has been deposited on gastight YSZ at a temperature of about 1413 K. The metal chlorides were generated by chlorination of the metals with HCl. Like magnesium, strontium is difficult to incorporate into EVD grown LaCrO₃ films, as the presence of strontium was not confirmed using EDX analysis. At a temperature of 1410 K, film growth on 200 to 600 µm thick YSZ substrates is parabolic beyond 2 µm film thickness, indicating that the reaction is solely determined by solid state diffusion through the growing film. The parabolic growth rate constant at that temperature is determined to be 6.5×10⁻¹¹ cm²/s.

INTRODUCTION

EVD has become a key technology for the synthesis of gastight components of the SOFC. The principle of the process has been described in detail in literature (1-9). The EVD process is used primarily for the synthesis of the ionically conducting SOFC electrolyte material yttria-stabilized zirconia (YSZ), and for the electronically conducting SOFC interconnection material Mg-doped LaCrO₃. To date, very little has been published on the EVD growth of the SOFC interconnection material Mg-doped LaCrO₃, and little is known about the kinetics of the process. Only Pal and Singhal (4) have reported on the kinetics of the EVD growth of Mg-doped LaCrO₃. At a temperature of 1603 K and a pressure less then 30 Pa, Mg-doped LaCrO₃ was deposited on Sr-doped LaMnO₃. Probably, the La:Mg:Cr ratio in the gas phase was
1:2:3, as reported earlier by Feduska and Isenberg (2), because EVD films of identical composition were obtained, i.e. LaCr$_{0.95}$Mg$_{0.05}$O$_3$. At the above-mentioned conditions, the growth of the EVD film appeared to be parabolic, with a parabolic growth rate constant of 0.18×10^6 cm$^2$/s (4). A thermodynamic analysis of the reaction system has revealed that the low magnesium content in the EVD films is a result of the reduced solubility of MgO in LaCrO$_3$ at low oxygen partial pressures and of the stability of gaseous MgCl$_2$ (10,11). Therefore, a large excess of MgCl$_2$ in the gas phase is necessary to obtain a reasonable doping level.

In the present work, the EVD growth of doped LaCrO$_3$ is investigated. Films of Mg-doped LaCrO$_3$ have been deposited on porous calcia-stabilized zirconia (CSZ) substrates, using the metal chlorides as precursors. The time dependence of the film thickness has been determined for different temperatures.

Strontium-doped LaCrO$_3$ has been grown on gastight YSZ substrates, similar to the experiments of Virkar et al. (12,13). The use of non-porous substrates eliminates contributions of the initial CVD stage to the EVD growth process. These experiments have been conducted on substrates of variable thicknesses in order to determine the influence of solid state electrochemical transport through the substrate on the film growth behaviour. Growth behaviour of doped LaCrO$_3$ on gastight YSZ can vary from linear to parabolic, depending on substrate thickness and reaction conditions (14).

EXPERIMENTAL ASPECTS

Mg-doped LaCrO$_3$ has been deposited on porous CSZ substrates. Anhydrous metal chloride powders, i.e. LaCl$_3$, CrCl$_3$, and MgCl$_2$, were used as metal source reactants. The experimental details of the depositions are summarized in Table 1. First, the in-situ Ar permeability of the specimen was measured by applying a pressure difference across it and then monitoring the pressure decrease as a function of time. After deposition, the in-situ Ar permeability was measured again. The crystalline phases present in the deposits were identified by X-ray diffraction (XRD). Scanning electron microscopy (SEM) was used to measure the film thickness, and to study the morphology of the deposited layers. Film thickness was also measured by optical microscopy. The chemical composition of the deposited films was determined by semi-quantitative energy dispersive X-ray micro analysis (EDX).

Sr-doped LaCrO$_3$ has been deposited on gastight YSZ substrates varying in thickness from 200 to 650 μm. The metal chlorides were generated in-situ by chlorination of the metals, i.e. lanthanum, chromium, and strontium, with HCl gas. The experimental details of the depositions are summarized in Table 2. The deposited films were analyzed by XRD, SEM, and EDX.
### Table 1: Process conditions for the synthesis of Mg-doped LaCrO$_3$ on porous substrates.

<table>
<thead>
<tr>
<th>Substrate temperature: $T_{\text{substrate}}$</th>
<th>1473 - 1523 K</th>
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Reactant flows metal chloride compartment:

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<tbody>
<tr>
<td>Ar flow</td>
<td>0.120 mmol/s</td>
</tr>
<tr>
<td>LaCl$_3$ flow</td>
<td>0.43 - 0.54 μmol/s</td>
</tr>
<tr>
<td>CrCl$_3$ flow</td>
<td>1.17 - 2.26 μmol/s</td>
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<tr>
<td>MgCl$_2$ flow</td>
<td>0.22 - 0.81 μmol/s</td>
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Reactant flows oxygen compartment:

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<tr>
<td>$O_2$ flow</td>
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<td>$H_2O$ flow</td>
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</tbody>
</table>

Pressures: metal chloride compartment 133 - 800 Pa

Pressures: oxygen compartment 100 - 1467 Pa

Reaction time: 1800 - 18000 s

### Table 2: Process conditions for the synthesis of Sr-doped LaCrO$_3$ on gastight YSZ.

<table>
<thead>
<tr>
<th>Substrate temperatures: $T_{\text{substrate}}$</th>
<th>1348 - 1438 K</th>
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Reactant flows metal chloride compartment:

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<tr>
<td>Ar flow</td>
<td>87 μmol/s</td>
</tr>
<tr>
<td>HCl flow</td>
<td>2.5 - 3.7 μmol/s</td>
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Reactant flows oxygen compartment:

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<tr>
<td>$O_2$ flow</td>
<td>17 - 32 μmol/s</td>
</tr>
<tr>
<td>$H_2O$ flow</td>
<td>1.7 - 3.2 μmol/s</td>
</tr>
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Pressures: metal chloride compartment 2800 Pa

Pressures: oxygen compartment 2000 Pa

Reaction time: 1800 - 14400 s
RESULTS AND DISCUSSION

Deposition of Mg-doped LaCrO₃

The XRD patterns of the films reveal the presence of either single-phase LaCrO₃ or mixtures of LaCrO₃ and Cr₂O₃. An estimate for the amounts of LaCrO₃ and Cr₂O₃ in the films is obtained from a comparison of the relative intensities of the strongest diffraction peaks of both phases, i.e., (211)LaCrO₃ and (104)Cr₂O₃. The EDX results show that in the single-phase LaCrO₃ films the La/Cr ratio is larger than 1, while aluminium (5-15 at%) is present as well, whereas magnesium is not detected. In the films comprising LaCrO₃ and Cr₂O₃, the La/Cr ratio is smaller than 1, and again aluminium (10-35 at%) appears to be present.

Optical and SEM micrographs of cross-sections of deposited films show that the films follow the irregularities of the substrate surface, and that they are homogeneous in thickness, which is typical for films grown by the EVD mechanism. Optical micrographs show that, in some cases, the colour of the deposit changes across the film, which may be caused by a change in composition, although a change in morphology may also be responsible for the colour change. Furthermore, the colour (composition) of the pore-plugging deposits differs from that of the films. Figure 1a shows a SEM micrograph of a cross-section of a LaCrO₃ film, while the surface morphology of a deposited film is shown in Figure 1b.

EDX analysis of the cross-sections reveals that the change in film structure is caused by a change in composition. In general, a large amount of chromium is present across the entire film. The lanthanum content is highest in the part of the films grown during the EVD stage. The La/Cr ratio in this part of the films is equal to or smaller than one, indicating that (doped) LaCrO₃ is the main constituent, and that in some films Cr₂O₃ is present as well. The lanthanum content in the bottom part of the films is much lower, and in some places lanthanum is not detected at all. Magnesium is not or only just detected in the top parts of the films, which implies that the magnesium content in the EVD films is very low, which proves that magnesium can hardly be incorporated in LaCrO₃ during the EVD process, as was observed earlier by Feduska and Isenberg (2) and Fal and Singhal (3), and as was proven by thermodynamic calculations (10,11).

In the bottom parts of the films, which are probably grown during the CVD stage of the growth process, magnesium is detected. The highest magnesium contents are observed in parts of the deposits in which lanthanum is not or hardly present, indicating the formation of MgCr₂O₄. This phase has also been identified occasionally by XRD. Aluminium is found through the entire film. In general, the aluminium content is high in regions where the lanthanum content is low.
aluminium present in the deposits is probably originating from the alumina evaporation source, in which the LaCl₃ was kept during the experiments. Apparently, the alumina is attacked by the LaCl₃ melt, leading to the formation of a volatile aluminium-containing species and a less volatile lanthanum-containing species, which results in a decrease in the gas phase concentration of LaCl₃. This explains why the aluminium content is higher in films comprising LaCrO₃ as well as Cr₂O₃ than in films of single-phase LaCrO₃. Apparently, in some experiments, the gas phase concentration of LaCl₃ drops below a critical value, leading to a shortage in the supply of lanthanum to the surface of the growing film, resulting in the formation of both LaCrO₃ and Cr₂O₃ during the EVD stage. Simultaneous formation of LaCrO₃ and Cr₂O₃ during the EVD stage is possible, because Cr₂O₃ also exhibits oxygen ion conductivity. If during the EVD growth of LaCrO₃ the LaCl₃ supply is sufficient, LaCrO₃ will grow, because this material has the highest oxygen ion conductivity. If, however, the LaCl₃ supply drops below a critical level, that it cannot keep up with the CrCl₃ oxidation rate, then the ratio of La/ Cr in the film becomes smaller then unity, and Cr₂O₃ will be formed next to LaCrO₃.

In Figure 2, the in-situ Ar permeability is given as a function of total deposition time for a deposition temperature of 1473 K, and it is found to decrease with increasing deposition time, especially in the first 1800 s of the process. The accuracy of the determination of the pore closure time depends on the time intervals at which the permeability is measured. From these experiments it can be concluded only that, although the criterion is arbitrarily chosen, pore closure time is less than 1800 seconds. Extrapolation of the plots of the square of the film thickness versus deposition time supports this conclusion.

Figure 3 shows the square of the measured film thickness as a function of total deposition time for deposition temperatures of 1473 and 1523 K, respectively. The vertical lines indicate the uncertainty in the data. The linear relation between the square of the LaCrO₃ film thickness and the total deposition time suggests that the EVD growth is governed by solid state diffusion, with the slope being equal to twice the parabolic growth rate constant Kp. The lines in Figure 3 represent the linear least squares fit through the data points, yielding Kp = 8.2 × 10⁻¹¹ cm²/s at 1473 K and Kp = 1.5 × 10⁻¹⁰ cm²/s at 1523 K, respectively. Compared to the parabolic growth rate constant Kp = 1.8 × 10⁻⁹ cm²/s at 1603 K determined by Pal and Singhal (4), there is a difference of one order of magnitude. The lines do not cross the origin, because the total deposition time is chosen as ordinate. The total time of the EVD stage is the total deposition time minus the time of the CVD stage. This CVD time has not been determined for every experiment, but a rough estimate can be obtained from Figure 3 by extrapolation of the lines to L² = 0. In this way the CVD times are estimated to be 720 seconds at 1473 K, and 600 seconds at 1523 K.

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The EVD experiments considered have been performed at 1473 K and 1523 K, respectively, with an oxygen partial pressure on the oxygen-rich side of the substrate \( (p_{O_2}) \) of 10^8 Pa. The oxygen partial pressure on the metal chlorde side \( (p_{O_2}) \) is not known, because it cannot readily be determined. Therefore, an estimation for \( p_{O_2} \) has to be made. For the experimental conditions used, \( p_{O_2} \) is calculated to be of the order of 10^15 Pa, and, in the temperature region considered, to be approximately constant. The theoretical value for \( K_0 \) can now be calculated from the expression derived elsewhere (14,15)

\[
K_0 = \frac{D_{V_O^*}}{6} \left[ x \ln \left( \frac{A^{1/2} + 1}{2} \right) \right] \times A(p_{O_2}) \tag{1}
\]

with,

\[
A = 24xK_{25}p_{O_2}^{1/2} + 1 \tag{2}
\]

\[
D_{V_O^*} = 0.287 \exp \left( \frac{-2.1 \text{ eV}}{kT} \right) \tag{3}
\]

and

\[
K_{25} = 4.0 \times 10^5 \exp \left( \frac{-3.2 \text{ eV}}{kT} \right) \tag{4}
\]

where \( x \) is the Mg-doping level, \( D_{V_O^*} \) the oxygen ion vacancy diffusion coefficient in Mg-doped LaCrO_3, and \( K_{25} \) the equilibrium constant of the defect equilibrium involved. For EVD films of the composition LaCr_{0.85}Mg_{0.15}O_3, calculation of the parabolic growth rate constant, using Equation (1), yields \( K_0 = 1.0 \times 10^{-11} \text{ cm}^2/\text{s} \) at 1473 K, and \( K_0 = 3.8 \times 10^{-11} \text{ cm}^2/\text{s} \) at 1523 K. Figure 4 shows the experimentally determined and calculated values for \( K_0 \).

The experimentally determined values for \( K_0 \) are larger than the values obtained from the model calculations. Furthermore, although it is rather premature to make a statement on the temperature dependence based on two data points only, the apparent activation energy of the experimental parabolic growth rate constant is
smaller than the calculated one. However, it should be borne in mind that there are several uncertainties contributing to the deviation between model calculations and experiments. First of all, there is the uncertainty about the actual oxygen partial pressure on the metal chloride side, which has already been discussed. In the EVD experiments of Feduska and Isenberg (2), a H₂/H₂O mixture with pO₂ = 10⁻²⁸ Pa was used as oxygen source reactant to grow films of Mg-doped LaCrO₃. As EVD film growth took place, the oxygen partial pressure on the metal chloride side had to be smaller than 10⁻¹⁸ Pa. Therefore, it is very well possible that the oxygen partial pressure on the metal chloride side in our experiments is less than the calculated 10⁻¹⁵ Pa, and that the calculated value for K₀ is larger. In the calculations, it is also assumed that pO₂ does not change with temperature. If in the experiments pO₂ is not constant but increasing with increasing temperature, then a less strong temperature dependence of the calculated K₀ will result.

Then, there is the fact that to date no reliable numerical values are available for the oxygen ion vacancy diffusion coefficient for Mg-doped LaCrO₃ as a function of temperature. The activation energy of 2.1 eV for DᵥO, which is near the upper limit of the range of activation energies for DᵥO in perovskite oxides, is estimated from experiments in literature (14), and is in reality probably smaller. A smaller activation energy for DᵥO will result in a smaller temperature dependence of K₀.

Another aspect which makes it difficult to compare the calculated and the experimentally determined parabolic growth rate constants is that the deposited EVD films consist of mixtures of (Mg and Al-doped) LaCrO₃ and Cr₂O₃ instead of single-phase, doped LaCrO₃. The influence of this inhomogeneity in the film composition is difficult to predict. In contrast with doped LaCrO₃, definite conclusions as to the defect structure and defect dependent properties of Cr₂O₃ cannot be drawn (16). Therefore, the influence of the presence of Cr₂O₃ in the EVD films on the overall growth rate cannot be described quantitatively.

Deposition of Sr-doped LaCrO₃ on gastight YSZ

All diffraction patterns of the films, deposited in the range of process conditions specified in Table 2, showed the characteristic diffraction peaks of LaCrO₃. No evidence was found for the formation of the binary oxides (La₂O₃, Cr₂O₃, and SrO). The deposited films are homogeneous in thickness, as is expected for this type of deposition process. A typical example of a cross-section of a LaCrO₃ film on gastight YSZ is shown in Figure 5.

Film compositions have been determined by EDX spectroscopy. Although in all experiments strontium was used as reactant, no evidence is found for the presence of strontium in the EVD films. Therefore, strontium is not present at all in the films,
or the strontium content is very small. The total strontium consumption, and, hence, the SrCl₂ production, in each experiment was such that the assumption is justified that reasonable concentrations of SrCl₂ were present in the reactor. The La/Cr ratio in the films is equal to or larger than unity. This La/Cr ratio is related to the impurity content in the films. The La/Cr ratio equals unity when impurity contents are negligible, and increases with increasing impurity content. Aluminium, silicon and chlorine are identified as impurity elements. Aluminium is detected in most films, in varying contents up to 12 at%. Silicon is detected in a few films only, and in much smaller contents. The aluminium and silicon may both originate from the ceramic cement used to mount the substrates onto the substrate holder, although the silicon may also originate from the quartz reactor parts. The most important impurity present in the films is chlorine. In the regions of high chlorine content, the chromium content is low, while the lanthanum content remains constant, indicating the presence of both LaCrO₃ and LaOCl.

Figure 6 shows the time dependence of the square of the EVD film thickness at a deposition temperature of 1410 K. This plot shows that the growth behaviour is parabolic and, hence, controlled by solid state diffusion through the growing film. The solid line represents the linear least-squares fit through the data points, neglecting the point at \( t_{dep} = 10800 \) s. From the slope of the line the parabolic growth rate constant \( K_p \) is calculated to be \( 6.5 \times 10^{-3} \) cm²/s. As the YSZ substrates used in these experiments were fully dense, film growth could only take place by solid state transport of ionic species. It should be noted that in the construction of Figure 6, the substrate thickness has not been considered. The substrate thickness in these experiments varied from 240 µm to 630 µm. The substrate thickness in the experiment with \( t_{dep} = 10800 \) s, i.e. the experiment with the largest deviation from the fitted curve, was 355 µm. This supports the suggestion that in these experiments the growth process is governed indeed by solid state diffusion through the growing film. Then, in principle, the parabolic growth rate constant obtained from these experiments should be the same as that obtained from experiments on porous supports.

The parabolic growth rate constant for the EVD growth of doped LaCrO₃ on gas-tight YSZ is high in comparison with the parabolic growth rate constant obtained for the EVD growth of doped LaCrO₃ on porous CSZ. This high value for \( K_p \) can be explained by the fact that in these experiments HCl is used for chlorination of the metals, so that hydrogen is present in the reactor on the metal chloride side. Therefore, it is likely that PO₂ is considerably lower in these experiments than in the experiments with the porous substrates in which hydrogen was not present on the metal chloride side, leading to larger oxygen ion fluxes through the substrates and films, and, hence, to higher growth rates.

Because of the large difference in conduction properties between YSZ and doped LaCrO₃, after all YSZ is an almost purely ionic conductor, whereas doped
LaCrO$_3$ is an almost purely electronic conductor, film growth behaviour becomes parabolic after short deposition times (or small film thicknesses). If the same experiments are performed with substrates and deposits having the same type of conduction (either ionic or electronic) and of the same order of magnitude, then the period of linear and transitional growth behaviour is much longer. This is illustrated by the experiments of Jue et al. (12) and Tanner et al. (13), who deposited undoped CeO$_2$ onto yttria-doped CeO$_2$. At a deposition temperature of 1473 K, using 425±25 µm thick substrates, film growth behaviour was clearly linear up to the longest deposition time of 4 hours, with a growth rate of 15 µm/hr. For the deposition of doped LaCrO$_3$ on YSZ, the period of linear and transitional growth can be extended by using much thicker substrates.

CONCLUSIONS

The amount of magnesium incorporated in the LaCrO$_3$ films is very small (<2%), even though an excess of MgCl$_2$ is present in the reactant stream. Regardless of the composition of the CVD deposit, LaCrO$_3$ continues to grow during the EVD stage, as long as the LaCl$_3$ supply suffices. Depletion of LaCl$_3$ during the EVD stage results in the simultaneous formation of Cr$_2$O$_3$.

Alumina is not suited as container for the LaCl$_3$ melt during the process, as the aluminium content in the deposits increases with decreasing lanthanum content, indicating the formation of a volatile aluminium compound and a non- or less volatile lanthanum compound.

The EVD growth of doped LaCrO$_3$ on porous CSZ is parabolic for the reaction conditions investigated, with parabolic growth rate constants of 8.2×10$^{-11}$ cm$^2$/s at 1473 K, and 1.1×10$^{-10}$ cm$^2$/s at 1523 K. These values only give an indication of the parabolic growth rate constant, as not all deposited films are homogeneous in composition.

Dense films of doped LaCrO$_3$ can be deposited on dense oxygen ion conducting substrates by the EVD process. Like magnesium, strontium is difficult to incorporate into LaCr$_2$O$_3$ during the EVD growth. At a temperature of 1410 K and an oxygen partial pressure on the metal chloride side on the order of 10$^{-18}$ Pa, film growth on 200 to 600 µm thick YSZ substrates appears to be parabolic from 2 µm film thickness on. The parabolic growth rate constant is determined to be 6.5×10$^{-11}$ cm$^2$/s. In order to observe linear or transitional growth behaviour, much thicker YSZ substrates, or substrates with similar conduction properties as doped LaCrO$_3$ should be used.
REFERENCES


Figure 1a: SEM micrograph of a cross-section of a LaCrO$_3$ film on CSZ.
Figure 1b: SEM micrograph of the surface of a LaCrO$_3$ film on CSZ.

Figure 2: The in-situ Ar permeability as a function of total deposition time for depositions at $T=1473$ K, measured at an average pressure of 6 kPa.

Figure 3: The square of the film thickness as a function of deposition time. A: $T=1473$ K; B: $T=1523$ K.
Figure 4: Comparison of the calculated and experimentally obtained values for the parabolic growth rate constant for EVD growth of Mg-doped LaCrO$_3$ on CSZ.

Figure 5: SEM micrograph of an EVD film of LaCrO$_3$ on gastight YSZ, deposited at 1401 K, in 240 minutes.

Figure 6: Square of the EVD film thickness as a function of deposition time for depositions of Sr-doped LaCrO$_3$ on gastight YSZ at $T=1410$ K.