Stellingen

1 De door Yokokawa et al. berekende standaard formatie-enthalpie ($\Delta_f H_{298}^0$) van de fictieve perovskiet La(Cr$_{0.5}$Mg$_{0.5}$)O$_3$, die gebruikt wordt voor het schatten van de thermodynamische parameters van magnesium-gedoteerd lanthaanchromiet, is onjuist.

2 Om aan te tonen dat de experimenteel gevonden aangroei van EVD-films van YSZ parabolisch is, had men het kwadraat van de filmdikte tegen de depositietijd moeten uitzetten in plaats van de filmdikte tegen de wortel van de depositietijd.

3 Voor zowel magnesium- als strontium-gedoteerd lanthaanchromiet wordt de interactie tussen de vaste stof en zuurstof beschreven door hetzelfde evenwicht en zijn de vergelijkingen voor de evenwichtsconstanten identiek. De bewering dat de vergelijkingen voor de evenwichtsconstanten in termen van molsfracties van de betrokken deeltjes ook identiek zijn, is onjuist.

4 Het ware beter geweest als de juistheid van het $<\text{Mg}^{2+}_\text{Cr}^3-,\text{V}^{5+}_\text{O}_3^{-},\text{Mg}^{2+}_\text{Cr}^3>^x$-clustermodel in magnesium-gedoteerd lanthaanchromiet gecreëerd was aan de hand van de experimentele TGA-data voor LaCr$_{0.9}$Mg$_{0.1}$O$_3$ in plaats van de data voor LaCr$_{0.8}$Mg$_{0.2}$O$_3$.

5 Het is onmogelijk om met het EVD proces films van magnesium-gedoteerd lanthaanchromiet te maken met een even hoog magnesiumgehalte als mogelijk is via poedersynthese-technieken.
   Dit proefschrift.

6 Bij het gebruik van een H$_2$/H$_2$O mengsel als zuurstofbron in het EVD proces, is aluminiumoxide geen geschikt substraat om gedoteerde lanthaanchromiet films op af te zetten.
   Dit proefschrift.
7 De bewering van Haanappel et. al. dat bij de chloor-geïnduceerde corrosie van roestvast staal onder oxiderende/sulfiderende condities de niet-stoechiometrie in het ijzersubrooster als gevolg van de chloorinbouw in het pyrrhotien (FeS), in het geval dat de chloor-partiaaldruk vele ordes groter is dan de zwavel-partiaaldruk, alleen een functie is van de chloor-partiaaldruk en niet van de zwavel-partiaaldruk, is onjuist.

8 De in de wolfram-CVD veelvuldig gebruikte termen "waterstofreductie" en "silaanreductie" zijn onjuist en dienen vermeden te worden.

9 Hoewel in de wolfram-CVD experimenten van Rosler et al. de depositsnelheid een eerste orde afhankelijkheid in silaan laat zien, concluderen zij ten onrechte dat de kinetiek van het silaanproces eerste orde in silaan is.

10 Het boek 'High Temperature Corrosion' van Per Kofstad is het beste bewijs dat hoge concentraties (zet)fouten aanleiding geven tot clustervorming.

11 Het (net) voldoende beoordelen van practica tijdens de opleiding tot scheikundig ingenieur gebeurt te vaak op gronden anders dan de kwaliteit van het afgeleverde werk.

Stellingen behorende bij het proefschrift

**ELECTROCHEMICAL VAPOUR DEPOSITION OF SOFC INTERCONNECTION MATERIALS**

Vincent van Diemen
ELECTROCHEMICAL VAPOUR DEPOSITION
OF
SOFC INTERCONNECTION MATERIALS
ELECTROCHEMICAL VAPOUR DEPOSITION
OF
SOFC INTERCONNECTION MATERIALS

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Aan mijn ouders
Aan Silvia
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Chapter 1

INTRODUCTION

1.1 GENERAL

Since the invention of the fuel cell in 1839 by William Grove [1,2], a period of development of over 150 years has elapsed, without commercialization of any large-scale applications. This has to be considered an exceptional case for an invention that has always been looked upon as very important, because of its powerful potentials. Especially if one considers the fact that during the first 100 years of development many great scientists as Mond [3,4], Nernst [5,6], Haber [7-10], and Baur [11-15] have done a lot of research on various types of fuel cells, which were all predecessors of the present types. Although in this period most of the problems, as well as the measures taken nowadays to overcome these problems, were recognized, experimental work was restricted to small size cells in small stacks (max. 20), delivering small currents for only a short period of time. There was, however, one exception in the work of W.W. Jacques, an American engineer. In 1896 he built by far the largest fuel cell stack of the first 100 years of fuel cell development. The single cells consisted of an iron vessel, serving as cathode, with molten potassium hydroxide (KOH) at 400-500°C as electrolyte, and a carbon rod as anode, with air being blown in at the bottom of the vessel near the wall [16]. His 1.5 kW (1) unit consisted of 100 cells in series, delivering a current density of 100mA/cm² at 1V.

Modern days enthusiasm, stimulation, and necessity to persevere in the development of fuel cells evolved in the space era in the 1960s, and was reinforced by the oil crisis in 1973, the increased environmental awareness in the 1980s, and the Gulf crisis in 1990. Because of rapidly changing environmental legislation, and increased awareness that the world’s limited fossil fuel reserves should be used as efficiently as possible, industries are developing technologies making it possible to use cleaner fuels, including the ultimate fuel hydrogen (H₂), at higher efficiencies. Furthermore, there seems to be a world-wide irreversible trend from centralized very-large-scale power production towards decentralized small-scale power production, prompted by the fact that the largest growth in energy demand will be in the densely populated and least developed part of the world.
For the governments in that area, the only realistic options to counter the growing energy demand are low investment costs, short-term planning, and phased installation, leading automatically to decentralized power generation units. This also makes more sense because of infrastructural requirements and, in many of these countries, political instability. Fuel cell technology will play an increasingly important role in the field of decentralized power generation, because it enables small-scale units to be highly efficient and much more clean [17].

1.2 FUEL CELLS

Fuel cells are electrochemical devices for the continuous production of direct-current electric power by electrochemical reaction of a fuel with an oxidant. They belong to the family of the primary batteries. A schematic representation of a fuel cell is given in Figure 1.1.

![Fuel Cell Schematic](image)

**Figure 1.1:** Schematic drawing of a fuel cell with an ion conducting electrolyte. a) AFC (OH⁻), b) MCFC (CO₃⁻), and c) SOFC (O²⁻). In the PAFC and SPFC hydrogen ions are transported through the electrolyte, and H₂O is formed at the cathode instead of the anode.
The basic fuel cell unit consists of a porous anode or fuel electrode (negative electrode), an electrolyte phase, and a porous cathode or oxygen electrode (positive electrode). The electrolyte has to be gastight in order to prevent cross-leakage of fuel and oxidant gases. The electrodes have to be porous in order to allow easy gas transport to the electrode/electrolyte interfaces. The charge transfer reactions take place in the region of the three-phase boundaries established at the gas/electrode/electrolyte interfaces in the porous electrode structures. Typically, the fuel gases fed to the anode are reforming gas, methane, methanol, or hydrogen. Air or pure oxygen is used as oxidant, and is fed to the cathode. When an external load is applied to the fuel cell, oxygen reacts at the cathode with the incoming electrons and the electrolyte to form mobile ions. These ions are transported through the electrolyte, owing to the large electrochemical potential gradient present. At the anode, fuel reacts with the mobile ions forming oxidation products and electrons, which are released into the external circuit, and transported back to the cathode. In principle, a fuel cell can produce electricity as long as fuel and oxidant gases are fed to the system. In reality, degradation or malfunctioning of cell components limits the practical operating life time of a fuel cell.

In order to build a power generation unit, individual fuel cells have to be electrically connected in series and parallel. The interconnect forms the electrical connection between the individual cells. This interconnect has to function as current collector, and as gas separation barrier, preventing cross-leakage of fuel and oxidant from one cell to the next. Therefore, the interconnect must be electronically conducting and gastight [18,19].

An advantage which fuel cell technology has over conventional forms of power generation is that it is not Carnot limited. While many modes of power generation involve the thermodynamic inefficient conversion of heat into mechanical energy, fuel cells directly convert the free energy of a reaction into electrical energy. This does not necessarily mean that fuel cells have higher efficiencies than heat engines. Like heat engines, fuel cells are subject to thermodynamic limitations. However, in general, fuel cells have higher efficiencies than heat engines, because, normally, irreversible heat losses in thermal engines are greater than in fuel cells [18].

Nowadays it is customary to classify fuel cells by the type of electrolyte used. The five types of fuel cells are:

- alkaline fuel cell (AFC), normally with KOH as electrolyte,
- phosphoric acid fuel cell (PAFC), with H₃PO₄ as electrolyte,
- molten carbonate fuel cell (MCFC), with e.g. Li₂CO₃/K₂CO₃ (62/38) mixture as electrolyte,
- solid oxide fuel cell (SOFC), with yttria-stabilized zirconia (YSZ) as state-of-the-art electrolyte,
- solid polymer fuel cell (SPFC), with a proton conducting membrane, e.g. Nafion®, from DuPont, as electrolyte.
The AFC, PAFC, and SPFC are low-temperature fuel cells, with operating temperatures ranging from 60-80°C for the AFC, to 80-100°C for the SPFC, and 150-200°C for the PAFC. The MCFC and SOFC are high-temperature fuel cells. Nowadays, the MCFC operates at a temperature of about 650°C, and the SOFC at about 1000°C. Because of these differences in operating temperature, and the resulting advantages or disadvantages, each type of fuel cell has strong potentials for different fields of application. An overview of the technological market applications for each type of fuel cell is shown in Table 1.1.

Table 1.1: Technological market applications for different types of fuel cells, from ref. [20].

<table>
<thead>
<tr>
<th>Market</th>
<th>AFC</th>
<th>SPFC</th>
<th>PAFC</th>
<th>MCFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electric utility</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Remote</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Dispersed (stationary)</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>On-site cogeneration</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
</tr>
<tr>
<td>Portable/mobile</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Commercial, portable</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Military, portable</td>
<td></td>
<td>✓</td>
<td></td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Underground mining</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vehicular</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Automotive</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Buses, trucks</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td>✓</td>
</tr>
<tr>
<td>Railway</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Space</td>
<td>✓</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Submersibles</td>
<td>✓</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

The low-temperature fuel cells, especially the AFC and SPFC, are best applicable in the vehicular and portable or mobile market segments, where small systems with a generally small thermal footprint are required. The high-temperature fuel cells do not meet this market requirement. This type of fuel cells is suited best for the generation and
industrial market segments, where much larger systems are required. The PAFC is potentially applicable in the intermediate scale markets, e.g. light industrial [20].

After over 150 years of R&D, the introduction of fuel cell systems on a commercial scale has only just started. One of the major problems in the commercialization of these systems is that potential customers consider fuel cells as non-attractive, because they still have not been commercialized on a wide scale, despite the long period of R&D and all the money spent. The main reason for this is the limited reliability and availability of the systems so far. Indeed, many problems still have to be solved, but it is expected that, under pressure of the exhausting fossil fuel reserves and the environmental situation, R&D in this field will continue, and that the fuel cells will get an acceptable performance, and get commercialized in the near future. After all, in the energy scenarios that guarantee supply of energy meeting the world's increasing demand until beyond the second half of the next century, and with an acceptable environmental impact, fuel cells are still considered to play an important role.

1.3 SOLID OXIDE FUEL CELLS

1.3.1 General description

Solid oxide fuel cells are all-solid-state devices for the direct conversion of the free energy of a chemical reaction into electrical energy (viz. Fig. 1.1). At the cathode, the incoming electrons react with oxygen to form oxygen ions. The oxygen ions diffuse through the oxygen ion conducting electrolyte to the anode, where they react with the fuel to form oxidation product and electrons. If hydrogen is used as a fuel, the reactions taking place in the cell are given by

\[
\text{cathode:} \quad \frac{1}{2} \text{O}_2(g) + V^{-} \rightarrow O^{x}_O + 2e^{-} \tag{1.1a}
\]

\[
\text{anode:} \quad \text{H}_2(g) + O^{x}_O \rightarrow \text{H}_2\text{O}(g) + V^{-} + 2e^{-} \tag{1.1b}
\]

\[
\text{cell:} \quad \text{H}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{H}_2\text{O}(g) \tag{1.1c}
\]

The reversible standard potential \((E_0)\) of this reaction is 1.18 V at room temperature.

Solid oxide fuel cells operate at a temperature of about 1000°C. This high operating temperature is necessary to ensure adequate ionic conductivity of the state-of-the-art
electrolyte yttria-stabilized zirconia (YSZ). The high operating temperature induces some disadvantages. The enthalpy change ($\Delta H$) for fuel cell reactions is negative, and almost independent of temperature, as long as no phase transformations occur. The free energy change ($\Delta G$) becomes less negative with increasing temperature, because the entropy change ($\Delta S$) for most fuel cell reactions is negative. Hence, the thermodynamic efficiency of fuel cells ($\Delta G/\Delta H$) decreases with increasing temperature, and is, therefore, smallest for SOFCs. Furthermore, because the SOFC is an all-solid-state device, the high operating temperature imposes stringent requirements upon the materials to be used as cell component.

The disadvantage of the reduced thermodynamic efficiency is easily compensated by the advantages resulting from the high operating temperature. Activation overpotentials, *i.e.* electrode polarization, are low, expensive noble metal catalysts are superfluous, because electrode kinetics are fast, the system provides for internal reforming of methane or other hydrocarbons to generate carbon monoxide and hydrogen, and SOFCs provide high-quality waste heat for cogeneration applications, or bottoming cycles using conventional steam engines for additional power generation. Therefore, fuel cell efficiencies over 70% are possible. Solid oxide fuel cells also have the advantage that their concept can be more simple than that of other fuel cells, *i.e.* AFC, PAFC, and MCFC, because these types of fuel cells require a liquid electrolyte. With no liquid electrolyte present in the SOFC, corrosion problems are reduced, and electrolyte management problems are absent [17-23].

Three major concepts for SOFCs are currently being developed, *i.e.* tubular, monolithic, and planar. The tubular concept developed by Westinghouse is by far the most developed design, and is on the verge of commercialization [24].

![Figure 1.2: Schematic representation of a cross-section of the Westinghouse tubular concept SOFC.](image-url)
A schematic representation of a cross-section of this cell is shown in Figure 1.2. The components are sequentially deposited on the close-ended porous support tube, using thin film deposition techniques like slurry coating for the cathode, electrochemical vapour deposition (EVD) for the electrolyte and interconnect, and a combination of slurry coating and EVD for the anode, i.e. nickel powder is applied over the electrolyte by slurry coating, and, subsequently, YSZ is grown around the nickel particles by the EVD process. Great advantage of this tubular design is that high-temperature gas seals are superfluous. Disadvantage of this design is the long current-collection pathway, imposing limitations on the tube diameter, because of the large ohmic loss in the cathode.

The bipolar structure, which is the conventional structure for the MCFC and PAFC, is the most common planar configuration, and is shown schematically in Figure 1.3. The individual cells comprise thin flat layers of the components, separated by a gastight bipolar separator plate that is corrugated to allow easy gas transport to the electrodes. Advantage of this configuration is that ohmic resistance is minimized because of the short current-conduction pathway through the cell. Therefore, higher power densities can be obtained than with tubular cells. Major disadvantage is that high-temperature gas seals are necessary to prevent leakage. Solving the sealing problems is a major challenge in the development of the planar SOFC [18,23].

A schematic representation of the coflow monolithic concept, designed by Argonne National Laboratory, is given in Figure 1.4. They have also designed a crossflow concept. Because of the corrugated structure, the components support themselves. Therefore, very high power densities can be obtained. Thin films of the components are tape casted, and subsequently laminated, corrugated, stacked, and sintered. The monolithic SOFCs are still only in the early development stage [23,25].

![Figure 1.3: Schematic representation of a cross-section of a crossflow bipolar concept planar SOFC.](image)
Figure 1.4: Schematic representation of a cross-section of a coflow monolithic concept SOFC.

Because of the high operating temperature, the materials used for the cell components are limited by the following stringent requirements [18,22,23]:
- good mechanical and chemical stability in oxidizing and/or reducing conditions up to fabrication temperatures,
- good chemical compatibility (or stability) with contacting materials up to fabrication temperatures,
- high ionic and/or electronic conductivity, i.e. for the electrodes mixed conducting materials are preferred, because then charge transfer reactions can take place on the whole electrode surface; for the electrolyte good ionic conductivity with the ionic transference number equal to unity is required, and for the interconnect good electronic conductivity with the electronic transference number equal to unity,
- thermal expansion coefficients (TEC) matching with other components,
- phase stability in the temperature range from room temperature to operating temperature,
- minimal volatilization losses,
- minimal sintering behaviour of the porous electrode materials.

Additional properties for the cell components, from practical view points, are high toughness and strength, ease of fabrication, and low costs [22]. When the components are built up one by one, the sintering temperature of each successive component should be lower than that of the preceding one, in order to avoid microstructural changes. The state-of-the-art materials currently used for the cell components are summarized in Table 1.2.

Development of intermediate temperature SOFCs, with operating temperatures between 600 and 800°C, has received much interest recently. Major effort is put in the development of new electrolyte materials with sufficient ionic conductivity at these
Table 1.2: State-of-the-art materials used for SOFC cell components [19,21,22].

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
<th>Porosity (%)</th>
<th>Layer thickness (µm)</th>
<th>Resistivity @1000°C (Ω·cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>Ni-YSZ cermet, 8 mol% Y₂O₃, &gt;35 vol% Ni</td>
<td>20-40</td>
<td>~100</td>
<td>0.001 electronic</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>YSZ, 8 mol% Y₂O₃</td>
<td>&lt;6% gas tight</td>
<td>~10-40</td>
<td>10 ionic</td>
</tr>
<tr>
<td>Cathode</td>
<td>La₀.₉₋ₓSrₓCrO₃₃, xₛₓ=0.1-0.15</td>
<td>30-40</td>
<td>~700</td>
<td>0.013 electronic</td>
</tr>
<tr>
<td>Interconnect</td>
<td>LaCr₁₋ₓMgₓO₃, xₘₐₕ=0.02-0.15</td>
<td>&lt;6% gas tight</td>
<td>~20-50</td>
<td>0.5 electronic</td>
</tr>
</tbody>
</table>

intermediate temperatures. Replacement of the YSZ electrolyte by an intermediate temperature electrolyte would largely reduce the materials and fabrication problems, and would improve the long term reliability of the cells. Alternative electrolyte materials are doped ceria (CeO₂), with a very thin layer of YSZ on the fuel side to prevent electronic current [26], and doped perovskite oxides (ABO₃) like BaCe₀.₉Gd₀.₁O₃, CaAl₀.₇Te₀.₃O₃, and SrZr₀.₉Sc₀.₁O₃ [22]. To date, research on these perovskite oxide electrolytes has only been preliminary.

1.3.2 History of R&D

The electrolyte of an SOFC is formed by a solid ionically conducting oxide material, usually YSZ. The potential application of this material as electrolyte in a fuel cell was first suggested by W. Nernst [5,6]. In 1897 he invented the so-called Nernst glower. The incandescent body of this lamp consisted of a solid solution of 85 mol% zirconia and 15 mol% yttria, the so-called Nernst mass. In 1899 Nernst reported on the remarkable electrolyte properties, or ionic conductivity, of these incandescent bodies at very high temperatures. In 1935 W. Schottky, one of Nernst’s pupils, published a theoretical paper on the possibility to produce electric current in a concentration cell comprising solid electrolytes [27]. Based on this paper, the first working SOFC was constructed by Baur and Preis in 1937 [13]. This cell comprised a thin-walled tube of Nernst mass as solid electrolyte, filled with coke or iron powder serving as anode, and placed in a bed of iron oxide (magnetite, Fe₃O₄) powder serving as cathode. The cell was operated at about 1050°C using hydrogen and air as reactants. A battery comprising eight cells in parallel
gave an open circuit voltage (OCV) of 0.83 V, which is 0.2 V below the theoretical value. At a current density of 0.35 mA/cm², the voltage had dropped to 0.65 V. The internal resistance of one single cell was 12 to 15 Ω; hence, the internal resistance of the battery was about 2 Ω. Baur and Preis also tested other electrolytes, but none performed better than the Nernst mass. The most promising alternative electrolyte was made of three parts of tungsten trioxide (WO₃), two parts of clay, and one part of CeO₂ (from monazite ore, hence, with lanthanum and yttrium impurity). A battery comprising six units of three single cells in parallel, with one unit damaged, gave an OCV of 3.5 V, or 0.7 V/cell. The power output of the battery was 0.176 W at 90% of the OCV [14].

In the late 1950s modern day's R&D on SOFCs commenced in the United States, initiated by the new energy demands in space, submarine, and military uses. In the early 1960s Weisbart and Ruka at Westinghouse constructed an SOFC with a calcia-stabilized zirconia (CSZ) electrolyte, using hydrogen as well as hydrocarbons as fuel [28]. Cell performance was limited by the resistance of the thick electrolyte. From then on it became apparent that for the development of the SOFC it was of crucial importance to develop thin film technologies, to minimize the thickness of the components. Westinghouse adopted the tubular design concept, which, owing to their extensive research efforts, is currently the most developed technology. First generation fuel cells comprised a 2 mm thick, 13 mm diameter CSZ porous support tube of 30 cm length, onto which the components were deposited. Power output was increased by increasing the length of the cells to 50 cm, and recently to 100 cm. The second generation fuel cells does not have a CSZ support tube, but uses the air electrode as support tube. The combined effect of the increased cell length, and the use of the air electrode tube resulted in a six-fold increase in the power output per cell from 20 to 120 W. In 1992 a 25 kW DC power generator, and a 25 kW cogeneration unit to produce AC power and intermediate pressure steam were built, and installed in Japan [24]. It is planned to start testing a 100 kW AC power generator in 1994 [29]. In 1983 the monolithic SOFC was invented at the Argonne National Laboratory, and is currently being developed in collaboration with Allied Signal [25]. With a 100 W stack recently tested, this technology is still in the bench-scale phase of development. The U.S. Department of Energy (DOE) is currently funding Allied Signal and Westinghouse to develop fuel cell stacks with the goal of selling on-site, industrial, and electric utility units, using the monolithic and tubular SOFC concept, respectively [29].

Solid oxide fuel cell research in Europe started in the early 1960s at ABB Company in Germany. Like at Westinghouse, a tubular concept was adopted. Research was stopped in 1977 at the 100 W level, because at that time the market potential for SOFCs seemed to be rather low, and cost estimates showed that building large-scale batteries from tube-shaped cells was far too expensive with the available technology, making a change to thin film technology necessary [30,31]. Only in 1987 R&D of SOFCs restarted again in Europe under impulse from the Commission of the European Communities.
(CEC) -nowadays the Commission of the European Union-. The objective of this program was to restart the R&D activities on SOFCs by reactivating the knowledge already available in the community. Research in the CEC is, since 1989, concentrated on the development of flat plate concept SOFCs with different design concepts. Currently, there are six ongoing CEC projects with Dornier, KFA Jülich, and Siemens (Germany), Risø (Denmark), ECN and TNO (The Netherlands), and GEC, Imperial College, and British Gas (UK) as main contractors [32].

In Japan R&D on SOFCs started in 1981 with the Moonlight Project. This research was, and is, carried out by the National Laboratories. In parallel, the New Energy and Industrial Technology Development Organization (NEDO) started a three year program in 1989, followed by a new program in 1992. Apart from these projects, many public and private organizations carry out R&D on SOFCs on their own, or organized in consortiums with SOFC developers like Westinghouse [33].

Modern day's SOFC research includes cell and system development, performance testing and modelling, and optimization and fabrication of cell components. A comprehensive overview of the progress in these fields in the past six years is provided by a series of conference proceedings [34-37].

1.3.3 Interconnection material

The interconnection material forms the electrical connection between the anode and cathode of two adjacent cells. The main requirements for the interconnection material are:

- high electronic conductivity with negligible ionic conductivity,
- chemical stability in oxidizing and reducing atmospheres,
- TEC compatible with that of other cell components,
- mechanical stability,
- chemical compatibility with other cell components,
- gastight.

The choice of materials is limited to noble metals, certain nickel-containing alloys, and perovskite oxides. Noble metals are prohibited, because of the excessive costs, while metallic interconnects have too large TECs to be applicable at an operating temperature of 1000°C. Therefore, the perovskite oxides, especially the LaCrO$_3$-based solid solutions, are the most appropriate materials for the SOFC interconnect. Pure LaCrO$_2$ is not a suitable candidate, because (1) its electronic conductivity in reducing atmospheres is too low, (2) it exhibits an orthorhombic to rhombohedral phase transformation at about 240°C, and (3) its TEC is lower than that of YSZ, which is considered to be the reference material. However, part -or all- of the lanthanum (La) and chromium (Cr) ions
can be substituted by isovalent or aliovalent ions, thereby altering the properties of the material. Electronic conductivity, phase transformation behaviour, thermal expansion, and sinterability can be influenced by doping LaCrO$_3$. Calcium (Ca) and strontium (Sr) substitute on the La-site, whereas magnesium (Mg), aluminium (Al), cobalt (Co), copper (Cu), iron (Fe), zinc (Zn), and titanium (Ti) substitute on the Cr-site.

LaCrO$_3$ is known to be a \textit{p-type} electronic conductor, owing to the presence of electron holes in the 3\textit{d}-band of the Cr ions (Cr\textsuperscript{3+}). Conduction occurs by the thermally activated hopping of localized charge carriers, \textit{i.e.} Cr\textsuperscript{3+} [38]. The electronic conductivity of LaCrO$_3$ is strongly enhanced by doping with a relatively small amount of lower-valence ions, usually Mg, Sr, or Ca. Under oxidizing conditions, charge compensation takes place by a Cr\textsuperscript{3+} to Cr\textsuperscript{4+} transition of an equal fraction of chromium ions, thereby increasing the concentration of electronic charge carriers. Under reducing conditions, charge compensation will take place by the formation of oxygen ion vacancies, and no increased electronic conductivity is expected. For low doping levels, the electronic conductivity is found to be proportional to the dopant concentration, but it levels off at higher doping levels [38-40]. Because in an SOFC the interconnect is subjected to both an oxidizing and a reducing atmosphere, a charge carrier concentration gradient, and, hence, a conductivity gradient will exist across the interconnect. However, under fuel cell conditions the overall conductivity of doped LaCrO$_3$ exceeds the interconnect's conductivity requirement [22,41].

The temperature of the orthorhombic to rhombohedral phase transformation can be controlled by addition of certain dopants. Because phase transformations are unwanted, the transformation temperature should be shifted to below room temperature. Strontium substitution not only increases the electronic conductivity, but also lowers the phase transformation temperature. Addition of 10 at\% Sr stabilizes the rhombohedral phase at room temperature [42]. The transformation temperature is raised by doping with Ni or Ca, while Mg substitution has no influence on the transformation temperature [43,44].

The TEC of LaCrO$_3$ can also be controlled by substitution of aliovalent or isovalent ions into the structure. Substitution of Mg has no influence on the TEC, and, therefore, the TEC of Mg-doped LaCrO$_3$ is lower than that of YSZ. Substitution of Ca or Sr leads to an increase in TEC, and, hence, to a better match [44,45]. The substitution of Al or Co causes a significant increase in TEC [22].

Thin films of the interconnect can be produced by tape casting or slurry coating, and subsequent sintering. However, most doped lanthanum chromites cannot be sintered to full density at conditions that can be sustained by the other cell components. Under these conditions the porosity of the interconnect remains high, leading to cross-leakage of fuel and oxidant gases.

Lanthanum chromite, like many chromium containing oxidic compounds, cannot be sintered to full density in air, because of the volatility of "higher-valence" chromium oxides, especially chromium trioxide (CrO$_3$), which causes the formation of chromium
sesquioxide (Cr$_2$O$_3$) at the inter-particle neck during the initial state of sintering [46]. Dense LaCrO$_3$ films can be obtained by sintering at high temperatures (>1600°C) in highly reducing atmospheres, with the oxygen partial pressure near the Cr/Cr$_2$O$_3$ phase boundary [47]. These conditions are not suited for co-sintering an entire SOFC, because the cathode material Sr-doped LaMnO$_3$ is not stable under these circumstances.

Several methods to improve the sinterability of LaCrO$_3$ in air at temperatures far below 1600°C have been tried. Addition of several percents of a sintering aid, e.g. CSZ [48], LaF$_3$, or MgF$_2$ [49,50], resulted in densification of LaCrO$_3$ in air at temperatures below 1400°C. The main problem with the addition of liquid-phase sintering aids is that, in co-firing the interconnect with other SOFC components, these liquid phases tend to migrate into other cell components, causing elemental migration and morphological changes, leading to poor densification of the interconnect and reduced performance and life-time of the other components.

Chromium deficiency remarkably enhances the sinterability [45,51,52]. For Sr-doped LaCrO$_3$ higher densities have been obtained in case of chromium-deficient samples. La$_{0.7}$Ca$_{0.3}$CrO$_3$ could not be densified in air at 1300°C, whereas La$_{0.7}$Ca$_{0.3}$Cr$_{1-y}$O$_3$ (0<y<0.02) could be sintered to 94% of the theoretical density. The mechanism of this enhanced sinterability in chromium-deficient LaCrO$_3$ based solid solutions is not yet fully understood.

The addition of certain dopants also remarkably improves the air sinterability of LaCrO$_3$. Substitution of Al for Cr decreases the volatility of chromium from the surface, leading to improved sinterability [53]. Another effect dopants can have is the formation of liquid phases during the sintering process, which act as sintering aid. Enhanced sinterability of Sr-doped LaCrO$_3$ may be caused by the formation of a SrCrO$_4$ melt, while the improved sinterability of Ca-doped LaCrO$_3$ is caused by the formation of liquid calcium oxychromates (Ca$_m$(CrO$_4$)$_n$, m>n) [54,55]. Calcium and nickel, and calcium and cobalt co-doped LaCrO$_3$ show even further enhanced sinterability compared with Ca-doped LaCrO$_3$. However, these materials appear to be unstable in reducing atmospheres [56-58].

Sinterability can also be improved by using non-agglomerated, uniform, high-surface-area powders. Such ultrafine (25-100 nm) La$_{0.82}$Sr$_{0.15}$Cr$_{0.85}$Al$_{0.15}$O$_3$ powders have been synthesized by the so-called glycine/nitrate process, and sintered to near-full density in air at 1550°C [59].

Slightly chromium-deficient Ca-doped LaCrO$_3$, with x$_{Ca}$≥0.3, is the best air-sinterable material so far, with a sintering temperature of about 1300°C [52]. The composition La$_{0.82}$Sr$_{0.15}$Cr$_{0.85}$Al$_{0.15}$O$_3$ is also considered to be a promising candidate for the interconnection material, because it has been found that this material has a high electronic conductivity, and a TEC matching that of the electrolyte very closely, while it can be sintered to near-full density, with only closed porosity, in air at 1550°C [59]. Only the long-term stability of this material needs to be verified. Although some candidates
with promising properties have been proposed, the development of an interconnection material that can be sintered under conditions which do not affect the other SOFC materials has not yet been completed.

Because fabrication techniques as tape casting and screen printing cannot be used on curved surfaces, a new synthesis technique for the deposition of the gastight components of the tubular concept SOFC was developed at Westinghouse in the mid-seventies. This so-called electrochemical vapour deposition (EVD) process is a modification of the conventional chemical vapour deposition (CVD) process [57]. Using this technique it is possible to grow very thin (<10 μm) gastight films of ionically or mixed conducting oxides onto porous substrates without the necessity of a sintering step. The principle of the process will be discussed in Chapter 2. Nowadays, the process has become a key technology for the fabrication of the anode, electrolyte and interconnect of the Westinghouse tubular concept SOFC [24,60,61]. An important drawback of the EVD technique is that the range of LaCrO₃ compositions that can be synthesized is limited. Only Sr and Mg-doped LaCrO₃ have been synthesized by means of EVD. Moreover, the maximum amount of dopant that can be incorporated appears to be limited to a few percent, whereas with conventional powder processing techniques much higher doping levels can be obtained [62]. As mentioned above, the electronic conductivity of LaCrO₃ increases with increasing doping level. Hence, with a reported maximum Mg doping level of 2 at% to be obtained in the EVD process, this process poses limitations on the maximum obtainable electronic conductivity. Furthermore, the thermal expansion properties cannot be fully matched with that of YSZ. Still, the EVD films fulfill the SOFC interconnect's requirements, because, in comparison with tape casting, much thinner gastight films can be prepared, which compensates for the limited electronic conductivity and TEC mismatch. It should be noted that, for the tubular SOFC concept with the state-of-the-art materials for the SOFC components, the contribution of the interconnect to the total cell resistance is only 1% [63]. According to the long-term stability tests on the SOFC units, the TEC mismatch does not seem to be a problem either.

Recently, Kajimura et al. [64] have tested tubular concept SOFCs with the Sr-doped LaCrO₃ interconnects made by means of laser ablation, using a high power KrF excimer laser. The interconnects are gastight and about 20 μm thick. No data are given on the composition of the films. The laser ablation technique may be a very suitable and powerful synthesis technique, because, as there appears to be no limitation in the target composition, and as the composition of the deposited films nearly equals that of the source material, it offers the opportunity of careful control of the film composition by using the appropriate target. Therefore, using this technique it may be possible to optimize the composition of the interconnect with respect to electronic conductivity, TEC, phase transformation temperature, and chemical compatibility.
1.4 SCOPE OF THIS THESIS

The aim of this thesis is to investigate the synthesis of the SOFC interconnection material Mg-doped LaCrO$_3$ by means of EVD. Although the EVD process is the key technology for the fabrication of the interconnect of the Westinghouse tubular concept SOFC, very little has been published on this subject. Nearly all publications on EVD are dealing with the synthesis of the electrolyte material YSZ.

In Chapter 2 the principle of the EVD process is described, as well as the experimental setups used for the synthesis experiments. As mentioned earlier, the EVD process appears to pose limitations on the amount of magnesium that can be incorporated in LaCrO$_3$. In Chapter 3 a thermodynamic analysis of the La-Cr-Mg-O-H-Cl-Ar system is made in order to determine how the EVD process conditions may affect the incorporation of magnesium in LaCrO$_3$, and to predict the range of experimental conditions for the synthesis of Mg-doped LaCrO$_3$ by means of CVD/EVD. This analysis is also used to calculate the equilibrium gas phase compositions during the EVD stage of the growth process. This information is essential for modelling of the process, because during the EVD stage, film growth depends on the oxygen partial pressure gradient across the growing film [60,61]. In Chapter 4 the EVD stage of the growth process is modelled. This chapter comprises three parts. In the first part the EVD growth of the electrolyte material YSZ is modelled, and the results are compared with literature data. In the second part the EVD growth of Mg-doped LaCrO$_3$ on porous substrates is modelled, whereas in part three the EVD growth of Mg-doped LaCrO$_3$ on gastight YSZ is described. This last part is intended to illustrate the complex growth behaviour that will occur when a material is grown on a gastight substrate with different conduction properties, e.g. to form a composite electrolyte [26]. The experimental results of the synthesis of Mg-doped LaCrO$_3$ on porous and gastight substrates are described in Chapter 5.

In Chapter 6 the first results on the synthesis of the perovskite oxide YCrO$_3$, a material resembling LaCrO$_3$, by means of particle-precipitation-aided CVD (PP-CVD) are described, as well as the principles of the process. PP-CVD might be an attractive alternative for the EVD process for the synthesis of SOFC components, because it has been proven that highly porous to fully dense structures can be obtained using this technique [65].

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Chapter 2

PRINCIPLE OF THE EVD PROCESS AND EXPERIMENTAL SETUPS USED

2.1 INTRODUCTION

A variety of configurations is currently being considered for the solid oxide fuel cell (SOFC) stack. Among these are tubular, planar, and monolithic types, and for each type different fabrication methods can be chosen to manufacture the individual cell components. Major progress to date has been achieved with the tubular SOFC design, developed by Westinghouse Electric Corporation. In the Westinghouse tubular SOFC design, the active cell components are deposited as thin films on a porous calcia-stabilized zirconia support tube (PST). For the early tubular SOFCs, 2 mm thick support tubes with an active length of 30 cm were used. At Westinghouse emphasis was put on increasing the active cell length, and on decreasing the thickness of the PST. In 1992 two 25 kW power generation field test units have been fabricated, which are currently in operation. These units represent a major milestone in the commercialization of zirconia-based SOFCs for power generation. The individual units comprise 1,152 single cells with an active length of 50 cm, which makes them capable of producing 40 kW at peak operation [1]. Recently, single cells with an active length of 100 cm have been produced. Gradually, the thickness of the PST has been reduced, and lately the PST has even been eliminated completely from the single cells. In order to maintain the mechanical integrity of the cells, the thickness of the air electrode has been increased. Hence, in the new technology SOFC the air electrode serves as support tube, onto which the other cell components are deposited. The combined effect of increasing the active cell length and eliminating the PST caused the single cell power output to increase from 20 W to 120 W [1].

One of the major advantages of the tubular SOFC design is that high-temperature gas seals, preventing direct contact between the oxidant and the fuel, are superfluous. A disadvantage of this design is that fabrication methods which are easily amenable to mass
production on planar designs, e.g. tape casting and screen printing, cannot be used on curved surfaces. Therefore, it was of prime importance in the successful development of the tubular SOFC design to develop a method for the deposition of thin gastight layers of the electrolyte and interconnection material onto curved porous structures. Several fabrication methods have been attempted including, among others, sintering, RF sputtering, flame- and plasma-spraying, and chemical vapour deposition (CVD) [2].

In the mid-seventies Isenberg, at Westinghouse, developed the electrochemical vapour deposition (EVD) process, which is a modification of the conventional CVD process [2]. Using this technique, it was possible to deposit thin gastight metal oxide layers of uniform thickness onto the PST. The main difference with the conventional CVD process is that the gaseous reactants are separated by the deposited reaction product, while film growth can only proceed if the reaction product exhibits some electronic as well as ionic conductivity. The principle of the process will be discussed in detail in the next paragraph.

To date, the EVD process has become a state-of-the-art fabrication method for the SOFC electrolyte material yttria-stabilized zirconia (YSZ) [3-17], which is an almost pure ionic conductor, and for the interconnection material magnesium- (Mg) or strontium (Sr)-doped lanthanum chromite (LaCrO$_3$) [18-20], which is an almost pure $p$-type electronic conductor. Recently, the EVD process has been applied for the synthesis of thin films of terbia- and yttria-co-doped zirconia (Tb$_x$Y$_{1-x}$)-ZrO$_2$ [21], and ceria (CeO$_2$) [22,23]. Other materials which have been synthesized by means of EVD are tin-oxide-doped indium oxide (In$_2$O$_3$) [24], alumina (Al$_2$O$_3$), and chromium sesquioxide (Cr$_2$O$_3$) [18].

Some years ago, questions were raised whether the Westinghouse tubular SOFC design could be scaled up to an active length of 100 cm, and whether the EVD process, which is a vital step in the production of these cells, could be scaled up for mass production [25]. In a collaborative effort between Westinghouse and Abar Ipsen Industries, a vacuum-furnace-based large scale reactor was designed, with Kinney Vacuum Co. playing an important role in the design of the pumping systems. In 1988 the first EVD reactor system was installed by Abar Ipsen at Westinghouse's SOFC facility at Monroeville, Pennsylvania [26,27]. This $1$ million-plus unit was the first of three to be delivered at Westinghouse. These reactor systems are able to automatically process batches of as many as 60 fuel cells. Using these reactor systems, the single cells for the 25 kW power generation units, mentioned earlier, have been fabricated.

With the field tests on these first SOFC power generation units of commercially meaningful size currently under progress, it appears that the technical questions raised earlier have been answered satisfactorily, to a major extent. Therefore, commercialization of the Westinghouse tubular SOFC design, using the EVD technique as prime fabrication method for the cell components, appears to be only a matter of time.
2.2 PRINCIPLE OF THE EVD PROCESS

The EVD process is a modified form of the conventional CVD process. It utilizes a chemical potential gradient to grow thin gastight films of ioniically conducting metal oxides with a small contribution of electronic conductivity, or mixed ioniically and electronically conducting metal oxides onto porous substrates. The process resembles the operation of an internally shorted galvanic concentration cell, where the deposited material acts as solid electrolyte. The main characteristic of the process is that the reactor is divided into two separated compartments by a porous substrate. One compartment contains the metal source reactants, and the other the oxygen source reactants. The film growth process itself can be divided into two steps. These steps are shown schematically in Figure 2.1.

\[
\text{MeCl}_x(g) + \frac{3}{2} \text{H}_2\text{O}(g) \rightarrow \text{MeO}_{x/2}(s) + x \text{HCl}(g) \\
\text{MeCl}_x(g) + \frac{3}{2} \text{O}_2(g) \rightarrow \text{MeO}_{x/2}(s) + x \cdot e^{-} + \frac{3}{2} \text{V}_0^{-} + \frac{3}{2} \text{Cl}_x(g)
\]

**Figure 2.1:** Principle of the two stages of the EVD process. The possible diffusion processes during the second (EVD) stage of the growth process are also shown.

2.2.1 CVD stage

At the start of the process, the reactants, which are fed to opposite sides of the porous substrate, diffuse into the pores of the substrate, and react to form a solid reaction product, which is deposited onto the walls of the pores. If this process is continued long enough, the pores will eventually get blocked by the solid deposit. Therefore, the first step in the film formation involves pore closure by a conventional CVD-type reaction between the metal source reactants, usually metal chlorides, and the oxygen source reactants, e.g., a mixture of oxygen and steam. The formation of LaCrO$_3$ can be described as
LaCl₃(g) + CrCl₃(g) + 3 H₂O(g) → LaCrO₃(s) + 6 HCl(g)  

(2.1)

In principle, it is possible to control the deposition profile in the pores, and the location of pore closure by changing the reaction conditions. In order to do so, knowledge of the mass transport of the reactants in the pores, which have continuously changing dimensions, and of the kinetics of the CVD reaction is vital. This CVD stage of the EVD process has a number of aspects in common with the conventional chemical vapour infiltration (CVI) process. The main difference between these two processes is that in the CVI process the reactants are introduced on the same side of the porous preform, whereas in the CVD stage of the EVD process the reactants are introduced on opposite sides of the substrate. Theoretical analysis of the CVI process started with the work of van den Brekel et al. [28], who presented an analytical solution for a mass balance in which both diffusion in the axial direction of a cylindrical tube, and deposition by a first order heterogeneous reaction on the inner tube wall were taken into account. This work was followed by other reports on the theoretical analysis of the isobaric and isothermal CVI process, including the work of Rossignol et al. [29], Tai and Chou [30,31], Lin [13], Moene et al. [32], and Dekker et al. [33].

There are few reports on the theoretical analysis of the CVD stage of the EVD process. Carolan and Michaels [34] developed a phenomenological model to predict the penetration depth of the deposits into the porous substrates for the CVD stage of the EVD process for the synthesis of YSZ. The CVD reaction was modelled as Knudsen diffusion and heterogeneous reaction in a one dimensional pore, where the reactants, steam and metal chlorides, interdiffuse. Because the reaction kinetics of the oxidation of ZrCl₄ with steam were unknown, different rate expressions were incorporated into the model. The effect of the decrease of the pore radius on the effective diffusivity of the reactants was neglected in this study, and viscous flow was not taken into account, making the model only applicable for isobaric conditions. Lin [13] has made a theoretical analysis of the CVI process, and the CVD stage of the EVD process using one model to describe both these processes. This model takes into account chemical reaction, deposition, diffusion, viscous flow, change of pore radius, and its effect on transport properties.

The pore closure step is very important in determining the ultimate properties of the deposited (EVD) film. Ideally, the pore-plugging (CVD) layer should be formed on the substrate surface on the metal chloride side without penetrating the substrate pores, be thin, and as close to the composition of the EVD layer as possible. In the production of YSZ films by means of EVD, the maximum penetration depth of the electrolyte in the substrate appears to be limited to 2 to 3 times the pore diameter [2,3,34]. Understanding and control of the CVD stage of the EVD process is also of vital importance for the production of ceramic membranes by pore structure modification [12,13,35-37].
2.2.2 EVD stage

Once pore closure is complete, the reactants are no longer in direct contact. Film growth then proceeds by solid state diffusion of oxygen ions, owing to the presence of a large oxygen chemical potential gradient across the deposited film. On the oxygen-rich side, oxygen ions are incorporated into the lattice of the deposited film by reduction of the oxygen source reactant at the gas/film interface. For the deposition of Mg-doped LaCrO$_3$, using a mixture of steam and oxygen as oxygen source reactants, the reduction reactions can be written as,

$$\text{H}_2\text{O}(g) + V^-_O \rightarrow \text{H}_2(g) + O^x_O + 2\text{h}^+ \tag{2.2}$$

where the hydrogen formed reacts with the oxygen present to form steam, and

$$\frac{1}{2}\text{O}_2(g) + V^-_O \rightarrow O^x_O + 2\text{h}^+ \tag{2.3}$$

The oxygen ion vacancies in these reactions are formed at the gas/film interface on the metal chloride side, and diffuse through the deposited film to the oxygen-rich side to react with the oxygen source reactant. This oxygen ion vacancy diffusion results in a net flux of oxygen ions towards the metal chloride side. There, at the gas/film interface on the metal chloride side, the metal chlorides are electrochemically oxidized to form the desired metal oxide product, leading to continued film growth. The reaction to form LaCrO$_3$ can be written as follows:

$$\text{LaCl}_3(g) + \text{CrCl}_3(g) + 3\text{O}_x^x + 6\text{h}^+ \rightarrow \text{LaCrO}_3(s) + 3V^-_O + 3\text{Cl}_2(g) \tag{2.4}$$

The diffusion processes which take place during the second stage of the EVD process are also shown schematically in Figure 2.1. Oxygen ion diffusion - or rather oxygen ion vacancy diffusion - can only take place, if, at the same time, a counterdiffusion of a species with the same charge, or a parallel diffusion of a species with opposite charge takes place to preserve electroneutrality. Metal ion diffusion can be neglected in doped LaCrO$_3$ and YSZ. Therefore, because in steady state no net current flows, the sum over the anionic, electron, and electron hole currents in the deposited film is zero.

Film growth during the second stage of the EVD process can be limited by a) gas diffusion in the substrate pores, b) surface kinetics on either side of the film, c) solid state diffusion in the growing film, or d) a combination of either of these processes. If gas diffusion in the substrate pores or surface kinetics are the rate-determining steps in
the process, growth behaviour is expected to be linear [11,13]. When the growth process is determined by solid state diffusion, the kinetics are similar to the Wagner oxidation of metals, leading to parabolic growth behaviour [38,39]. In case of a combination of rate limiting processes, growth behaviour can become much more complex. The second stage of the EVD process, for the case that solid state diffusion is the rate-determining step, is modelled in Chapter 4.

Because the EVD process is usually conducted at low pressures, i.e. less than 1 kPa (10⁻² atm), and high temperatures, i.e. from 1273 K onwards, gas diffusion rates and surface reaction rates are expected to be high. Under these conditions, solid state diffusion is expected to be the rate-determining step. It should be borne in mind that during the deposition a change in rate-determining process may occur. Initially, gas diffusion or surface kinetics may be rate-limiting, but with increasing film thickness solid state diffusion will become the rate-limiting step eventually, because the ionic flux through the growing film is inversely proportional to the film thickness [39]. Therefore, when solid state diffusion is rate limiting, the process is 'self-levelling', i.e. for thinner films the growth rate is faster, leading to the formation of films of uniform thickness, which is one of the advantages of the EVD process.

Another advantage of the EVD process is that, in comparison with other fabrication techniques as tape casting or plasma spraying, very thin, i.e. less than 10 μm, gastight films can be produced. Furthermore, the technique is not restricted to flat substrates.

The EVD process also has a number of drawbacks. Because solid state transport is the rate-determining process, relatively high reaction temperatures are necessary in order to obtain acceptable growth rates. Furthermore, because normally the metal chlorides are used as precursors, corrosive gases are present in the reactor, and the rather complicated experimental setup and long process times make the EVD process quite expensive.

Recently, Virkar et al. [22,23] developed the idea to deposit two-layer composite electrolytes by means of EVD. In order to lower the operating temperature of SOFCs, electrolytes with much higher ionic conductivity than YSZ should be used. Ceria-based electrolytes are promising candidates to be used in low-temperature SOFCs, because their ionic conductivity at 700°C is about 20 times higher than that of YSZ. However, ceria exhibits considerable electronic conductivity in reducing ambients. Therefore, a thin layer of YSZ should be deposited on the fuel side of the ceria-based electrolyte in order to prevent electronic current.

The ceria-based layer is deposited by the conventional EVD process, as described above. The YSZ layer is deposited on top of the ceria-based layer using the same deposition technique, but with different reactants, and different reaction conditions. In fact, the second step of the EVD process is continued, with just another material being deposited. The rate of film growth of this second layer depends on the conduction properties of the first (ceria) as well as the second (YSZ) layer. The growth behaviour of this second film is more complex than that of the first one, which is deposited onto
a porous support. Modelling of the growth behaviour of ceria on dense yttria-doped ceria, which are both ionic conductors, is described by Virkar et al. [22,23], whereas in Chapter 4 the EVD growth of Mg-doped LaCrO$_3$, which is an electronic conductor, on dense YSZ is described.

2.3 EXPERIMENTAL SETUPS FOR EVD OF DOPED LaCrO$_3$

2.3.1 Large EVD reactor

2.3.1.1 Description of the equipment

The large EVD reactor has been designed and built in our laboratory. A schematic representation of the reactor is given in Figure 2.2. The system can be divided into three sections: the reactor, the gas and reactant delivery system, and the vacuum system. The main part of the reactor is a gastight alumina tube of 1200 mm length with an inner diameter (ID) of 80 mm, suited to accommodate square substrates of 56×56 mm$^2$.

![Figure 2.2: Schematic representation of the large EVD reactor, with (1) metal chloride evaporators, (2) porous substrate, (3) three zone furnace, and (4) water evaporator. See also the list of symbols at the end of this chapter.](image)

25
Stainless steel flanges are attached to both ends of this tube by home-made rubber O-ring-based fittings to secure vacuum integrity. These fittings are water-cooled to prevent burning of the rubber O-rings. A 14-mm-ID gastight alumina tube is screwed onto the right flange. On top of this tube the porous substrates are mounted, using an alumina-based ceramic cement (Ceramabond 569), thus dividing the reactor into two separate compartments, i.e. a metal chloride compartment and an oxygen compartment. The oxygen source reactants are fed to the inside of the small tube (oxygen compartment), through a 4-mm-ID alumina inlet tube, which has its outlet at approximately 10 mm from the substrate. The metal chloride evaporators -or sublimation beds- are placed inside the large alumina reactor tube (metal chloride compartment). The evaporators for chromium trichloride (CrCl₃) and magnesium chloride (MgCl₂) are made of quartz, and consist of a long gas inlet tube, a compartment for the metal chloride powder, comprising two separate 16-mm-ID chambers in series, and a cap with a gas outlet tube. Quartz filters in front and on top of the powder compartment prevent the powder from being blown away during evacuation of the system, and allow free gas flow through the powder bed. The lanthanum chloride (LaCl₃) evaporator is slightly different. Because LaCl₃ has to be evaporated at temperatures above its melting point in order to obtain reasonable vapour pressures, the powder is put into an alumina container with a diameter of 28 mm, which is placed in the powder compartment in order to protect the quartz from being attacked by the LaCl₃ melt. In this evaporator, the carrier gas flows over the LaCl₃ melt. The evaporators are attached to the left flange using Cajon Ultra-Torr® fittings. Therefore, the position of the evaporators can be changed during the process without disturbing the vacuum.

The reactor has been placed inside a three zone furnace (Carbolite). This furnace has a total length of 1000 mm. The two zones on the left are of 200 mm length each, separated by a space of 25 mm. The heating elements comprise canthal resistance wire wound around a ceramic tube. The temperature in each zone is controlled by a Eurotherm 91e digital PID controller to establish the desired temperature profile for the evaporation of the metal chlorides. The third zone (on the right) provides the high temperatures necessary for the EVD process to a maximum of 1773 K. This zone is of 250 mm length, and is separated by a space of 75 mm from the middle zone. Heat is provided by six silicon carbide (SiC) heating elements mounted parallel to the reactor tube. The temperature is controlled by a Eurotherm 808P programmable controller, which provides the possibility to control the heating and cooling rate in this zone. The substrates are positioned in the middle of this high-temperature zone, i.e. in the region with uniform temperature. Because of the large temperature differences between the three zones, insulation rings have been placed on the outside of the reactor tube in the free space between the zones, in order to prevent heat transfer between the zones.

During each experiment, the metal chloride evaporators have to be positioned at the desired evaporation temperature. The correct position for the evaporators is determined
using thermocouples. The thermocouples are placed in quartz sheaths to protect them against the corrosive ambient. The sheaths are connected to the flange using Cajon Ultra-Torr® fittings, so their position can easily be changed without disturbing the vacuum. All temperatures are measured with commercial chromel-alumel thermocouples, except the evaporation temperature of LaCl$_3$ and the substrate temperature, which are determined using a Pt/Pt-10%Rh thermocouple because of the high temperatures, protected by an alumina sheath.

Low pressure is maintained by a 40 m$^3$/h dual-stage rotary-vane mechanical pump (Leybold D40B). The pressure in both compartments of the reactor is monitored and controlled separately. In each compartment, the pressure is monitored by a diaphragm gauge (MKS Baratron type 122A), and controlled by an automatic pressure controller (MKS type 152), which regulates the pumping capacity by adjusting a butterfly valve (MKS type 253 AG-20-40-1). Two multi-gas controllers (MKS type 147) monitor the gas flows, and regulate the mass flow controllers.

The metal chloride compartment has been provided with four gas inlets. One gas inlet is for the diluent gas stream, while carrier gas is provided to the metal chloride evaporators through the other three gas inlets. The gas flows are adjusted by mass flow controllers (MFC, MKS type 259 CY), with a range of 0 to 1440 sccm (standard cubic centimetre per minute; 1 sccm corresponds to 7.44×10$^{-7}$ mol/s @ 273.15 K and 1.013×10$^5$ Pa) for the diluent gas, and 0 to 144 sccm for the carrier gas flows. Argon (Air Products, 99.98% to 99.9999% purity) is used as carrier and diluent gas. Before entering the reactor, the gas is led through a standard gas cleaning unit (Chrompack) comprising a moisture filter (No. 7971), and a charcoal oxygen filter (No. 7970).

In most experiments, a mixture of steam and oxygen is used as oxygen source reactant. The mixture of oxygen and steam is generated by bubbling oxygen (Hoekloos, 99.5% minimum purity) through a heated water evaporator, filled with distilled water. The water-containing oxygen stream is then passed through a reflux column. The temperature of the reflux column is chosen such that the desired ratio of oxygen and steam in the gas stream is obtained. The water bath is heated to a temperature which is at least 10°C higher than the temperature of the reflux column, to ensure sufficient saturation of the oxygen stream. The temperature of the reflux column is controlled by a thermostat bath (Tamson TS00). The flow of oxygen is controlled by an MFC with a range of 0 to 100 sccm. The total pressure in the water evaporator is controlled by an automatic pressure control unit (MKS type 250), which regulates an electromagnetic control valve (MKS type 248A). The oxygen stream can also be fed directly to the reactor, bypassing the water evaporator. The gas lines connecting the water evaporator to the reactor are heated to approximately 100°C to prevent recondensation of water from the oxygen/steam mixture. The argon flow to the oxygen compartment is controlled by an MFC with a range of 0 to 720 sccm. The exhaust gases pass through a liquid nitrogen trap in order to protect the pump from unreacted precursors and corrosive byproducts.
2.3.1.2 Vacuum integrity

The EVD process is carried out at low pressures. Therefore, leaks in the equipment will cause air to enter the reactor during the process. Especially in the metal chloride compartment leaks should be avoided, because they may have a two-fold influence on the process: in the first place, the metal chlorides may become (partially) oxidized, to form metal oxides or oxychlorides. These compounds are, in general, much less volatile than the metal chlorides, and, hence, depletion of metal source reactant will then occur. The second effect may be that the oxygen partial pressure in the metal chloride compartment is increased, leading to a decrease of the oxygen chemical potential gradient, and, hence, to a decrease in film growth rate. Air leakage in the oxygen compartment will hardly influence the process.

The vacuum integrity of the various parts of the reactor has been checked regularly using a helium leak detector. Before and after each experiment the vacuum integrity of the system was checked by monitoring the rate of pressure increase, when the system was at low pressure, i.e. $p_{\text{system}} < 130$ Pa, with no input of feed gases, and with the pumping unit isolated from the system. The pressure increase in the entire reactor volume was measured. The average pressure increase was determined to be 0.19 Pa/s. The reactor volume was determined to be approximately $15 \times 10^{-3}$ m$^3$, with an average temperature of 560 K. It was assumed that one third of the reactor volume was at an estimated average temperature of 1073 K, while the other two thirds of the volume were at a temperature of approximately 303 K. Using the ideal gas law, the average pressure increase can be converted to an additional oxygen flow caused by the leakage. The calculations reveal an additional oxygen flow of 0.17 sccm or 0.11% of the total gas flow during most of the experiments. Although this is a rather large leak, it was not possible to detect one single 'large leak' using the helium leak detector.

Depending on the location of the leakage, this additional oxygen stream can have a large influence on the deposition process, as discussed above. Therefore, in order to prevent oxidation of the metal chlorides, graphite powder or titanium grains were placed inside the metal chloride evaporators, to act as oxygen getter. Because, in most cases, the metal chlorides evaporated readily, and because the CrCl$_3$ was still purple at the end of the depositions (oxidized CrCl$_3$ turns grey or green), it was concluded that the leakage was not located in the gas supply lines of the metal chloride evaporators. As discussed above, leakages in the oxygen compartment, as well as leakages near or beyond the reactor outlet will have little influence on the process. Therefore, although the exact oxygen partial pressure on the metal chloride side has not been measured, it was assumed that the leakage had no major influence on the growth process.
2.3.1.3 Temperature profile in the reactor

All EVD experiments have been carried out using the metal chlorides as metal source reactants. The concentrations of the metal chlorides in the gas phase are determined by their vapour pressures, which depend on temperature, reactor pressure, gas flow through the evaporators, and bulk gas flow. The vapour pressures of the metal chlorides have been calculated using the following equations:

for CrCl$_3$, in the temperature ($T_{\text{CrCl}_3}$) range of 298 to 1220 K [40],

$$\log \left( \frac{P}{\text{Torr}} \right) = 17.49 - \frac{13950K}{T_{\text{CrCl}_3}} - 0.73\log \left( \frac{T_{\text{CrCl}_3}}{K} \right) - \frac{0.00077T_{\text{CrCl}_3}}{K} \tag{2.5}$$

for MgCl$_2$(s), for $T_{\text{MgCl}_2} < 987$ K [41],

$$\log \left( \frac{P}{\text{Torr}} \right) = 8.97 - \frac{9699K}{T_{\text{MgCl}_2}} \tag{2.6}$$

for MgCl$_2$(l), for $T_{\text{MgCl}_2} > 987$ K [41],

$$\log \left( \frac{P}{\text{Torr}} \right) = 6.87 - \frac{7335K}{T_{\text{MgCl}_2}} \tag{2.7}$$

and for LaCl$_3$(l), in the temperature ($T_{\text{LaCl}_3}$) range of 1273 to 1673 K [42]

$$\log \left( \frac{P}{\text{Torr}} \right) = 10.19 - \frac{13930K}{T_{\text{LaCl}_3}} \tag{2.8}$$

It should be noted that the actual evaporation temperatures of LaCl$_3$ ranged from 1123 to 1250 K. Because these evaporation temperatures come closest to the temperature range in which Equation (2.8) is valid, this equation has been used to calculate the concentration of LaCl$_3$ in the gas phase. CrCl$_3$ and MgCl$_2$ were sublimed/evaporated at temperatures between 893 and 993 K, with the evaporation temperature of MgCl$_2$ being about 50 to 80 K higher than that of CrCl$_3$. The actual concentration of the metal chlorides in the reaction chamber is calculated assuming saturation of each carrier gas stream with its corresponding reactant.

Because only a three zone furnace was available, it was not possible to position each metal chloride evaporator in a region of homogeneous temperature. Therefore, the temperature settings of each zone had to be chosen such that the temperature gradients
across the metal chloride containers were as small as possible. Figure 2.3 shows three temperature profiles along the length of the reactor for some typical experimental conditions. It can be seen that only in the high-temperature zone (zone 3) there is a region of uniform temperature. The substrates were positioned in the middle of this region. Furthermore, it can be seen that neither in zone 2, nor in zone 1 there is a region of uniform temperature.

During the experiments, the LaCl$_3$-evaporator was positioned in zone 2, while the CrCl$_3$ and MgCl$_2$-evaporators were positioned in zone 1. Because of their dimensions, the temperature gradient across the metal chloride evaporators amounted to 20 to 25 K. Therefore, in order to calculate the concentrations of the metal chlorides in the gas stream, the temperatures in the middle of the metal chloride compartments were considered to be the evaporation temperatures, giving rise to an unknown, and probably considerable, uncertainty in the calculated concentrations. It is obvious that for more accurate control of the reactant concentrations an elongated furnace with at least six heating zones should be used.

![Temperature Profile](image)

**Figure 2.3**: Temperature profile inside the large EVD reactor under deposition conditions, for different temperature settings for the high-temperature zone, with $T_{\text{zone 1}} = 978$ K, $T_{\text{zone 2}} = 1223$ K, $\phi_{\text{Ar}} = 161$ sccm, and $P_{\text{reactor}} = 800$ Pa. Line A: $T_{\text{zone 3}} = 1473$ K, line B: $T_{\text{zone 3}} = 1523$ K, and line C: $T_{\text{zone 3}} = 1573$ K.
Figure 2.4: Schematic representation of the small EVD/PP-CVD reactor, with (1) metal chloride evaporation unit, (2) substrate, (3) two zone furnace, (4) water evaporator, (5) scrubber, and (6) pressurized air for cooling the cold finger. See also list of symbols at the end of this chapter.

2.3.2 Small EVD/PP-CVD reactor

2.3.2.1 Reactor for EVD experiments

The small EVD reactor, shown schematically in Figure 2.4, has been used for the EVD experiments on gastight YSZ substrates. The set up has been designed in such a way that it was also suited for PP-CVD experiments. The principle of the PP-CVD process will be discussed in Chapter 7.

The principle of this small reactor is the same as that of the large EVD reactor. The reactor comprises a 42-mm-ID quartz tube of 820 mm length in a horizontal resistance-heated two-zone furnace, with zones of 300 mm length each. The 12.5 mm-diameter
gastight YSZ substrates are mounted on the quartz substrate holder using Ceramabond 569 cement, and positioned in the middle of the left heating zone. Like in the large EVD reactor, a mixture of oxygen and steam is fed to the inside of the substrate holder, using a water evaporation system as described in section 2.3.1.1. Valve A is opened, while valve B remains closed. The metal chloride evaporation unit comprises a sledge with several containers in series, to contain the metal chlorides. This sledge is placed inside a 23-mm-ID quartz tube with a 4-mm-ID flow exit. Both, the tube and the sledge are connected to the right flange using Cajon Ultra-Torr® fittings, so their position in the reactor tube can easily be changed without disturbing the vacuum. Which containers are to be filled with metal chlorides depends on the temperature gradient in the right-hand side of the reactor. Chromel-alumel thermocouples are used to monitor the temperature at the position of the metal chloride containing containers. The Ar carrier gas flows over the metal chloride containers. The concentration of the reactants in the carrier gas stream is calculated using Equations (2.4) to (2.7).

The starting qualities of the gases, and the gas purification system are identical with those of the large EVD reactor. The flow rates of the gases are controlled by flow meters, with a range of 20 to 240 sccm for the O₂ flow, and ranges varying from 10 to 120 sccm, to 200 to 2500 sccm for the Ar flows. Low pressure is maintained by a 40 m³/hr dual-stage rotary-vane mechanical pump (Leybold D40B). The pressure in each reactor chamber is monitored by a diaphragm gauge (Leybold Membranovac). In order to protect the pump from unreacted precursors and corrosive byproducts, the exhaust gas is passed through a liquid nitrogen trap. At the end of a deposition, the reactor is brought to atmospheric pressure. During the cooling down period, the reactor is flushed with a small Ar stream, which is passed through a water-filled scrubber. Regularly, deposits are removed from the reactor wall, the substrate holder, and the metal chloride evaporation unit using diluted hydrofluoric acid.

Another way to generate the metal chloride vapours is by chlorination of the metals using chlorine or hydrogen chloride. In that case, the vessels of the metal chloride evaporator are filled with powder or chips of the pure metals. A stream of Cl₂ or HCl, diluted in Ar, is passed over these metals to generate the metal chlorides.

2.3.2.2 Reactor for PP-CVD experiments

The same experimental set up has also been used for PP-CVD experiments. For these experiments, the open-ended substrate holder has been replaced by a close-ended tube (cold finger). This tube is internally cooled by a stream of pressurized air in order to establish a temperature gradient between the tube and the gas phase, necessary for the thermophoresis-induced collection of the powder particles formed by homogeneous reaction in the gas phase, as will be discussed in Chapter 6. A mixture of argon and
steam, or oxygen and steam is fed to the right-hand side of the reactor, by opening valve B, while keeping valve A closed. This gas mixture enters the reactor on the outside of the metal chloride evaporator tube in order to prevent oxidation of the reactants. After each experiment, the powder is collected from the cold finger, and analyzed. The cold finger is cleaned after each experiment using diluted hydrofluoric acid.

**LIST OF SYMBOLS**

- Pneumatic valve
- Manual valve
- Needle valve
- Throttle valve
- Butterfly valve
- Electromagnetic valve
- Thermocouple
- Pressure gauge
- Rotary-vane pump
- Liquid nitrogen trap
- Rotameter
- Mass flow controller
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Chapter 3

CHEMICAL THERMODYNAMIC ANALYSIS OF
THE La-Cr-Mg-O-H-Cl-Ar SYSTEM FOR
THE CVD AND EVD OF Mg-DOPED LaCrO$_3$

ABSTRACT

A thermodynamic analysis of the La-Cr-Mg-O-Cl-H-Ar system has been carried out in order to obtain information about the solubility of MgO in LaCrO$_3$, to predict experimental conditions for the CVD/EVD process for deposition of Mg-doped LaCrO$_3$, and to calculate the composition of EVD films of Mg-doped LaCrO$_3$ as a function of temperature and input amount of MgCl$_2$. The thermodynamic parameters of the LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ phase had to be estimated, because experimental data were not available. Chemical potential diagrams for the La-Cr-O system have been calculated as a function of temperature. The decomposition oxygen partial pressure of LaCrO$_3$ increases with increasing temperature. At 1273 K, LaCrO$_3$ only decomposes in highly reducing atmospheres, i.e. $p_{O_2} < 10^{-22}$ atm. At 1873 K, LaCrO$_3$ starts to decompose at $p_{O_2} = 10^{-12}$ atm. The calculated ternary phase diagrams reveal that the solubility of MgO in LaCrO$_3$ decreases with decreasing equilibrium oxygen partial pressure. Hence, as EVD films grow in highly reducing atmospheres, the magnesium content of such Mg-doped LaCrO$_3$ films is limited to a few atom percent. The calculated CVD diagrams reveal that with increasing input partial pressure of oxygen the region in which LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ is the only stable solid compound shifts to lower temperatures and higher Mg/(Mg+(La+Cr)) values, i.e. higher input concentrations of MgCl$_2$. The conversion of LaCl$_3$ to LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ is virtually 100% for all reaction conditions considered. Excess CrCl$_3$ and MgCl$_2$ leads to the formation of second phases. Because the CVD step is the first stage of the CVD/EVD process, lasting only until pore closure, deposition of a small amount of other phases, besides Mg-doped LaCrO$_3$, may neither influence the film growth during the EVD stage, nor the final performance of the interconnection material.
3.1 INTRODUCTION

LaCrO$_3$-based perovskites are nowadays most commonly used as interconnection material in solid oxide fuel cells (SOFCs), because their intrinsic physical properties match closely the stringent requirements, which materials, used as SOFC component, have to fulfil. Most importantly, they exhibit good electronic conductivity -even in reducing atmospheres- when doped with alkaline earth oxides. Furthermore, they are quite stable in both oxidizing and reducing ambients, most of them are chemically compatible with other cell components, and they have thermal expansion coefficients which sufficiently match those of the other cell components [1-3].

Part -or all- of the lanthanum (La) and chromium (Cr) ions can be substituted by other ions -of equal or lower valence-, thereby altering the properties of the material in many respects, including phase transformations, oxygen non-stoichiometry, thermal expansion, and electronic conductivity. Karim and Aldred [4] found that the electronic conductivity of undoped and strontium (Sr)-doped LaCrO$_3$ occurs by the thermally activated hopping of localized charge carriers, because, amongst others, the plots of ln($\sigma$T) versus 1/T yield straight lines. The localization of the charge carriers is caused by the formation of small polarons in the chromium sublattice. The plots of ln($\sigma$T) versus 1/T for LaCrO$_3$ doped with other ions, e.g. magnesium (Mg), calcium (Ca), or copper (Cu), show linearity too, indicating that thermally activated hopping of small polarons is the conduction mechanism [5-7]. If under oxidizing conditions part of the lanthanum or chromium ions is replaced by cations of lower valence, then a charge compensating Cr$^{3+}$ to Cr$^{4+}$ transition will take place, thereby increasing the concentration of electronic charge carriers, i.e. [Cr$^\cdot$], giving rise to enhanced $p$-type electronic conductivity. Under reducing conditions, charge compensation will take place by creation of oxygen ion vacancies ($V_O^\cdot$), and no increase of the electronic conductivity is expected. The corresponding defect equilibrium is given by

$$O_O^{\cdot\cdot\cdot\cdot} + 2Cr_{Cr}^{\cdot\cdot\cdot\cdot} = 2Cr_{Cr}^{\cdot\cdot\cdot\cdot} + V_O^{\cdot\cdot\cdot\cdot} + \frac{1}{2}O_2(g)$$  \hspace{1cm} (3.1)

For the substitution of chromium ions by magnesium ions the electroneutrality condition then reads

$$[Mg_{Cr}^{\cdot\cdot\cdot\cdot}] = [Cr_{Cr}^{\cdot\cdot\cdot\cdot}] + 2[V_O^{\cdot\cdot\cdot\cdot}]$$  \hspace{1cm} (3.2)

Under oxidizing conditions, the oxygen ion vacancy concentration can be neglected and the electronic conductivity should increase proportionally with increasing doping level. For low doping levels, the electronic conductivity is found to be proportional to the dopant concentration, but it levels off at higher doping levels, probably due to defect
interactions [4,8,9].

In a SOFC the LaCrO$_3$ interconnect is subjected to both an oxidizing and a reducing atmosphere. Therefore, a conductivity gradient across the interconnect shall exist, because the concentration of electronic charge carriers is a function of the oxygen chemical potential. However, under fuel cell conditions, the overall conductivity of the material exceeds the interconnect's conductivity requirement [1,10]. The exact relation between the electronic charge carrier concentration and the equilibrium oxygen partial pressure can be found from the material's defect chemistry. The defect chemistry of Mg-doped LaCrO$_3$ will be discussed in detail in Chapter 4. Here, it is sufficient to know that under oxidizing conditions the electronic conductivity is maximal. The electronic conductivity starts to decrease significantly when the oxygen partial pressure drops below a critical value, owing to the formation of oxygen ion vacancies. This critical oxygen partial pressure depends on both temperature and doping level, and is lower at lower temperatures and lower doping levels [1,5].

Thin films of the interconnection material are commonly produced by tape casting and subsequent sintering, or electrochemical vapour deposition (EVD). Other processing techniques are plasma spraying, radio frequency sputtering, and laser ablation. The choice of SOFC design, i.e. tubular, monolithic, or planar, largely determines which processing techniques are feasible, e.g. tubular components can not be produced by tape casting. The main problem in the fabrication of the interconnect by tape casting is the poor sinterability of LaCrO$_3$. This poor sinterability is ascribed to the volatility of "higher-valence" chromium oxides, especially chromium trioxide (CrO$_3$), which causes the formation of chromium sesquioxide (Cr$_2$O$_3$) at the inter-particle neck during the initial stage of air sintering [11]. Dense LaCrO$_3$ films can be obtained by sintering in highly reducing atmospheres [12], by adding several percents of a sintering aid, e.g. calcium stabilized zirconia (CSZ) [13], or by partially substituting the chromium ions by aluminium (Al), zinc (Zn), or copper (Cu) [14,15]. Slightly chromium-deficient Ca-doped LaCrO$_3$ with $x_{\text{Ca}} > 0.3$ is the best air-sinterable material so far, owing to the formation of liquid calcium oxychromates ($\text{Ca}_m(\text{CrO}_4)^n_{\text{aq}}$, $m > n$), which act as sintering aid [16,17].

CVD/EVD has become a key technology for the synthesis of thin gas-impervious films of Mg- or Sr-doped LaCrO$_3$ on porous supports [18-20]. Gastight layers of homogeneous thickness are formed using this technique. Drawbacks of the technique are the high reaction temperatures necessary to obtain reasonable growth rates, and the presence of corrosive gaseous species like chlorine (Cl$_2$) or hydrogen chloride (HCl). For the synthesis of thin films of the interconnection material, the EVD technique may suffer from another drawback. As discussed above, the electronic conductivity of doped LaCrO$_3$ increases with increasing dopant concentration. Hence, in order to obtain the highest electronic conductivity the dopant concentration should be as high as possible, with the restriction that the other requirements remain fulfilled. From the work of Pal and Singhal [18], and Feduska and Isenberg [21] it became apparent that EVD films of Mg-
doped LaCrO$_3$ contained only a small amount of magnesium. With a La:Mg:Cr reactant input ratio of approximately 1:2:3, the ratio of these elements in the deposited films was 1:0.02:0.98. Feduska and Isenberg believed that the alkaline earth chlorides, which were used as reactants, are thermodynamically more stable than the alkaline earth oxides, and that, therefore, a large excess of the alkaline earth chlorides in the gas phase is necessary in order to incorporate these elements into LaCrO$_3$.

With a maximum magnesium doping level of 2 at%, the electronic conductivity will be lower than that for Mg-doped LaCrO$_3$ samples made by tape casting, or other powder processing techniques, where magnesium doping levels of 15 to 20 at% can be achieved [5]. Still, the EVD films fulfil the SOFC interconnect's requirements, because, in comparison with tape casting, much thinner fully gastight films can be prepared, which compensates for the limited electronic conductivity. Furthermore, it should be noted that for the tubular SOFC concept, with the state-of-the-art materials for the SOFC components, the contribution of the interconnect to the total cell resistance is only about 1% [22].

In this study, a chemical thermodynamic analysis of the La-Cr-Mg-O-H-Cl-Ar system has been carried out in order to determine how the EVD process conditions may affect the incorporation of magnesium in LaCrO$_3$, and to predict the range of experimental conditions for the synthesis of Mg-doped LaCrO$_3$ by means of CVD/EVD. This thermodynamic analysis can also be used to calculate equilibrium gas phase compositions during the EVD stage of the growth process. This information is necessary for modelling the EVD process, because film growth during the EVD stage depends on the oxygen partial pressure gradient across the growing film [18,20]. The modelling of the EVD growth will be discussed in detail in Chapter 4.

Thermodynamic equilibrium calculations have been performed using the Chemsage computer program developed by Eriksson and Hack [23]. The thermodynamic data of the species considered were primarily taken from the JANAF Tables [24] and Barin [25]. The thermodynamic parameters of the Mg-doped LaCrO$_3$ phase (LaCr$_{1-x}$Mg$_x$O$_{3.5}$), taking into account oxygen non-stoichiometry, were not available. Therefore, it was necessary to obtain a thermochemical description of the LaCr$_{1-x}$Mg$_x$O$_{3.5}$ phase and to estimate the accompanying thermodynamic parameters. The method for estimation of these parameters is discussed below.

### 3.2 THERMODYNAMICS

The thermodynamic data of the species of interest for the analysis of the La-Cr-Mg-O-H-Cl-Ar system are presented in Appendix A. Because reliable thermodynamic data were lacking for Mg-doped LaCrO$_3$, the thermodynamic parameters of this phase had to be estimated. These parameters were estimated according to the method of Yokokawa et
using an empirical relation between the stabilization energy \( d \) and the tolerance factor \( t_p \) for rare-earth transition-metal perovskite oxides [11, 26-31]. For ABO\(_3\) type perovskites, the tolerance factor is defined as,

\[
t_p = \frac{(r_A + r_B)}{\sqrt{2}(r_B + r_O)}
\]  

(3.3)

where \( r_A \), \( r_B \), and \( r_O \) are the ionic radii of A, B, and O, respectively.

In LaCrO\(_3\), part of the chromium ions can be replaced by magnesium ions, with charge compensation by Cr\(^{3+}\) to Cr\(^{4+}\) transition, or by oxygen ion vacancy formation. In order to determine the magnesium oxide solubility and the oxygen non-stoichiometry thermodynamically, the LaCr\(_{1-x}\)Mg\(_x\)O\(_{3.5}\) phase was treated as an ideal solid solution of LaCrO\(_3\), La(Cr\(_{0.5}\)Mg\(_{0.5}\))O\(_3\), and La(Cr\(_{0.5}\)Mg\(_{0.5}\))O\(_{2.75}\), similar to the work of Yokokawa et al. [11,28]. However, they did not take into account the oxygen non-stoichiometry in their description of the Mg-doped LaCrO\(_3\) phase, as they actually did in their thermodynamic description of the SOFC cathode material LaMnO\(_3\).

In the imaginary species La(Cr\(_{0.5}\)Mg\(_{0.5}\))O\(_3\), half of the chromium ions is substituted by magnesium ions and the charge is fully compensated by the Cr\(^{3+}\) to Cr\(^{4+}\) transition, whereas in the, also imaginary, species La(Cr\(_{0.5}\)Mg\(_{0.5}\))O\(_{2.75}\), the charge is fully compensated by oxygen ion vacancies. The molar Gibbs free energy of the solid solution is given by,

\[
G_m = \sum_i x_i \Delta_f G_i^0 + RT \sum_i x_i \ln x_i
\]  

(3.4)

where \( x_i \) is the mole fraction of species \( i \) in the solid solution, \( \Delta_f G_i^0 \) the standard Gibbs free energy of formation of species \( i \), and \( R \) the gas constant. The thermodynamic parameters of the imaginary species of the solid solution were estimated in the same way as those of other lanthanum transition-metal perovskite oxides [11,26-31].

According to Yokokawa et al. [26], the standard enthalpy of formation \( \Delta_f H_{298}^0 \) of rare-earth transition-metal perovskite oxides ABO\(_3\) can be estimated using an empirical relation between the stabilization energy \( d \) of the perovskite oxide and its tolerance factor \( t_p \). The stabilization energy, \( d \), or standard reaction enthalpy for formation of the perovskite oxides from their constituent binary oxides \( \Delta_f H_{298}^0 \) is defined as,

\[
d = \Delta_f H_{298}^0 (\text{perovskite}) - \sum_j n_j \Delta_f H_{298}^0 (\text{binary oxide})_j
\]  

(3.5)

where \( n_j \) is the mole fraction of the binary oxide \( j \) in the perovskite oxide. For \( A^{3+}B^{3+}O_3\)-type perovskites Yokokawa et al. found the following empirical relation

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between \( d \) and \( t_p \):

\[
d \text{(kJ/mol)} = -90 + 720(1 - t_p)
\]  

(3.6)

Combination of Equations (3.5) and (3.6) yields the expression for \( \Delta_f H_{298}^0 \) of \( A^3+ B^3+ O_3 \) type perovskites

\[
\Delta_f H_{298}^0 (ABO_3) = -90 + 720(1 - t_p) + \frac{1}{2} \left( \Delta_f H_{298}^0 (A_2O_3) + \Delta_f H_{298}^0 (B_2O_3) \right)
\]  

(3.7)

For the Mg-substituted components the average B-site ionic radius is taken. Shannon's values for the effective ionic radii of 12-coordinated lanthanum ions, and 6-coordinated chromium and magnesium ions were adopted to calculate the tolerance factors [32].

The standard entropy of the perovskite oxides can be estimated from the standard entropy of the constituent binary oxides, assuming that

\[
\Delta_f S_{298}^0 = S_{298}^0 \text{(perovskite)} - \sum_j n_j S_{298}^0 \text{(binary oxide)}_j
\]  

(3.8)

where, according to Yokokawa et al. [11,26], the entropy change for formation of the perovskite oxides from their constituent binary oxides \( \Delta_f S_{298}^0 \) is estimated to be +10 J/(K mol). Finally, the coefficients of the heat capacity polynomial equation were estimated. The simplest method to obtain reasonable estimates for the heat capacity of double oxides is to sum up the heat capacities of the constituent binary oxides [33,34]. Hence,

\[
\alpha \text{(perovskite)} = \sum_j n_j \alpha \text{(binary oxide)}_j
\]  

(3.9)

where \( \alpha \) is each of the coefficients of the heat capacity equation.

The estimated values of the thermodynamic parameters of the species of the \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_{3-\delta} \) phase are presented in Table 3.1. The parameter values of pure \( \text{LaCrO}_3 \) were already calculated by Yokokawa et al. [11]. From these values, the standard Gibbs free energy of formation \( \Delta_f G^0 \) at 1273 K is calculated to be -1170.8 kJ/mol, using the \( C_p \) data of all reaction components [35]. The standard Gibbs free energy of formation was determined experimentally at 1273 K as \( \Delta_f G^0 = -1184 \) kJ/mol by Chen et al. [36] using a solid-electrolyte galvanic cell. Therefore, the estimated values of Yokokawa et al. appear to be reliable, since the difference between the estimated and experimentally determined values for \( \Delta_f G^0 \) is only 1.1%. 

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Table 3.1: Estimated thermodynamic parameters for the compounds of the LaCr\textsubscript{1-x}Mg\textsubscript{x}O\textsubscript{3-δ} phase: standard enthalpy of formation \(\Delta H_{298}^0\), standard absolute entropy \(S_{298}^0\), and heat capacity coefficients a-d. The heat capacity is given by the following equation: \(C_p = a + b \times 10^{-3}(T/K) + c \times 10^5(T/K)^2 + d \times 10^8(T/K)^3\)

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\Delta H_{298}^0) (kJ/mol)</th>
<th>(S_{298}^0) (J/mol K)</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>d</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LaCrO\textsubscript{3}</td>
<td>-1534.4</td>
<td>114.0</td>
<td>119.30</td>
<td>12.05</td>
<td>-14.64</td>
<td></td>
<td>[5]</td>
</tr>
<tr>
<td>LaCr\textsubscript{0.5}Mg\textsubscript{0.5}O\textsubscript{3}</td>
<td>-1557.1</td>
<td>112.7</td>
<td>115.78</td>
<td>17.71</td>
<td>-19.21</td>
<td>0.76</td>
<td>Est.</td>
</tr>
<tr>
<td>LaCr\textsubscript{0.5}Mg\textsubscript{0.5}O\textsubscript{2.75}</td>
<td>-1532.3</td>
<td>107.4</td>
<td>114.3</td>
<td>11.31</td>
<td>-19.21</td>
<td></td>
<td>Est.</td>
</tr>
<tr>
<td>LaCr\textsubscript{0.5}Mg\textsubscript{0.5}O\textsubscript{2.75} adjusted parameters</td>
<td>-1502.3</td>
<td>95.0</td>
<td>114.3</td>
<td>11.31</td>
<td>-19.21</td>
<td></td>
<td>Adj. Est.</td>
</tr>
</tbody>
</table>

Vyshnyakov and Suponitskii [37,38] estimated a standard entropy at 298.15 K using an empirical correlation yielding \(S_{298}^0 = 111.3\) J/(K mol). Azad et al. [39] measured the standard Gibbs free energy of formation of LaCrO\textsubscript{3} in the temperature range of 850 < T < 1073 K by a CaF\textsubscript{2}-based EMF method. They performed a third-law analysis [40] based on their EMF results in order to obtain a value for \(\Delta H_{298}^0\) or \(\Delta S_{298}\). By iteration they obtained a best value of 79.5 J/(K mol) for \(S_{298}^0\) with a value of -61.5 kJ/mol for \(\Delta H_{298}^0\), which is in reasonable agreement with the value of -67.7 kJ/mol obtained by the method of Yokokawa et al. However, the value of \(S_{298}^0\) is far too low. When Azad et al. used \(S_{298}^0 = 111\) J/(K mol) in their third-law analysis, \(\Delta H_{298}^0\) was in the range of -22.5 to -12.9 kJ/mol, which is not in agreement with the estimated value.

The thermodynamic parameters of the La(Cr\textsubscript{0.5}Mg\textsubscript{0.5})O\textsubscript{3} species were also calculated by Yokokawa et al. [11]. However, they estimated a value of -1547.0 kJ/mol for \(\Delta H_{298}^0\) and 108.4 J/(K mol) for \(S_{298}^0\). The difference between the present and Yokokawa's estimated \(S_{298}^0\) values may be caused by a difference in the thermodynamic parameters used for CrO\textsubscript{2}(s), which is the constituent chromium-containing oxide. In our calculations the thermodynamic parameters were taken from Barin [25], whereas it is not clear what parameter values were used by Yokokawa et al. The value of -1547.0 kJ/mol for \(\Delta H_{298}^0\) as calculated by Yokokawa et al. is not correct. They mistakenly used the Cr\textsuperscript{3+} ionic
radius to calculate the tolerance factor instead of the $\text{Cr}^{4+}$ ionic radius. Therefore, the tolerance factor and stabilization energy they calculated for the $\text{La(Cr}_{0.5}\text{Mg}_{0.5})\text{O}_3$ species were, in fact, the $t_p$ and $d$ values for the $\text{La(Cr}_{0.3}\text{Mg}_{0.7})\text{O}_{2.75}$ species.

In order to check the validity of the estimated thermodynamic parameters, the results of thermodynamic equilibrium calculations were compared with thermogravimetric analysis (TGA) data of Flandermeyer [5]. Flandermeyer measured the oxygen non-stoichiometry in Mg-doped LaCrO$_3$ as a function of equilibrium oxygen partial pressure ($p_{O_2}$) for various Mg doping levels and temperatures. He let the powdered samples equilibrate with an atmosphere of known $p_{O_2}$ and measured the weight loss or gain caused by the loss or uptake of oxygen. The oxygen non-stoichiometry has also been determined with thermodynamic equilibrium calculations using the above-mentioned thermochemical description and estimated thermodynamic parameters for the $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ phase.

In Figure 3.1 the experimentally determined and the calculated oxygen non-stoichiometries are shown for $\text{LaCr}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta}$ at a temperature of 1532 K. It is clear that the calculated oxygen non-stoichiometry did not match the experimentally determined values. Therefore, the estimated thermodynamic parameters needed to be

![Figure 3.1: Oxygen non-stoichiometry in $\text{LaCr}_{0.95}\text{Mg}_{0.05}\text{O}_{3-\delta}$ as a function of equilibrium oxygen partial pressure for $T=1532$ K; (▲): TGA data from Flandermeyer [5], (■): data obtained from thermodynamic equilibrium calculations using original estimates, (×): data obtained from thermodynamic equilibrium calculations using adjusted estimates.](image-url)
adjusted, in order to obtain a better agreement with the experimental results. Because
the calculated oxygen non-stoichiometry was far too large, it was concluded that the
estimates for the thermodynamic parameters of the La(Cr_{0.5}Mg_{0.5})O_{2.75} species were
such that the species had become "too stable". Therefore, only the thermodynamic
parameters of this species were adjusted. Increasing of the standard enthalpy of
formation with 30 kJ/mol and decreasing of the absolute entropy with 12.4 J/(K mol)
resulted in a calculated oxygen non-stoichiometry which is in far better agreement with
the experimental results, as is shown in Figure 3.1. The resulting adjusted thermodynamic
parameters for the La(Cr_{0.5}Mg_{0.5})O_{2.75} species are listed at the bottom of Table 3.1, and
these values have been used in all other calculations. It should be borne in mind that
these adjusted thermodynamic parameters are not the result of a multi-parameter
optimization procedure. However, using these adjusted parameters the experimentally
determined oxygen non-stoichiometry can be described reasonably well, also for other
Mg-doping levels and temperatures, as is shown in Figure 3.2. The same method of
adjusting the estimated parameters was applied by Yokokawa et al. in order to obtain
the thermodynamic parameters for A-site substituted LaMO_{3}-type perovskites [11,30,31].

Using the estimated thermodynamic parameters listed in Table 3.1 for the
LaCr_{1-x}Mg_{x}O_{3-δ} phase, chemical potential diagrams have been calculated for the
La-Cr-O and La-Cr-Mg-O systems as a function of temperature and equilibrium oxygen
partial pressure. Also the condensed-phase relations in the La_{2}O_{3}-Cr_{2}O_{3}-MgO system
have been calculated as a function of temperature and equilibrium oxygen partial
pressure. In order to determine the range of experimental conditions in which the
synthesis of Mg-doped LaCrO_{3} by means of CVD is possible, some CVD-diagrams for
the reactant system LaCl_{3}-CrCl_{3}-MgCl_{2}-H_{2}O-O_{2}-Ar have been calculated. Finally, the
relation between the composition of the EVD films and the input amount of MgCl_{2} in
the gas phase has been calculated for the reactant system LaCl_{3}-CrCl_{3}-MgCl_{2}-Ar.

3.3 RESULTS AND DISCUSSION

3.3.1 Chemical potential diagrams

3.3.1.1 La-Cr-O system

Figure 3.3 shows the chemical potential diagram for the La-Cr-O system as a function
of temperature. This kind of diagrams is commonly used to visualize complicated
thermodynamic equilibria in A-X-Y systems (X, Y are non-metals). Yokokawa et al.
[11,28,31,41] have constructed chemical potential diagrams for A-B-O systems, where A
and B are metallic elements, to visualize the thermodynamic stability of double oxides.
Figure 3.2a: Oxygen non-stoichiometry in LaCr$_{0.98}$Mg$_{0.02}$O$_{3-\delta}$ as a function of equilibrium oxygen partial pressure for T=1469 K; (▲): TGA data from Flandermeier [5], (×): data obtained from thermodynamic equilibrium calculations using adjusted estimates.

Figure 3.2b: Oxygen non-stoichiometry in LaCr$_{0.9}$Mg$_{0.1}$O$_{3-\delta}$ as a function of equilibrium oxygen partial pressure for T=1641 K; (▲) and (×): same as in Figure 3.2a.
Figure 3.3: Calculated chemical potential diagrams for the La-Cr-O system as a function of temperature.
The major advantage of the chemical potential diagrams over the conventional stability diagrams, i.e. mole fraction versus oxygen potential plots, is that the stability areas of single compounds, i.e. metallic elements, binary oxides, and double oxides, are represented as convex polygons and that two-phase coexistence is shown as border lines between two polygons. On the other hand, in stability diagrams stoichiometric compounds are presented as lines, which makes it rather difficult to distinguish them from equilibrium tie lines [41].

In Figure 3.3 it can be seen that LaCrO$_3$ is stable in a very broad oxygen partial pressure range, as was shown also by Yokokawa et al. [11,28,31]. LaCrO$_3$ decomposes in highly reducing atmospheres according to the reaction

$$2\text{LaCrO}_3(\text{s}) = \text{La}_2\text{O}_3(\text{s}) + 2\text{Cr}(\text{s}) + \frac{3}{2}\text{O}_2(\text{g})$$

(3.10)

This decomposition is represented by the three-phase point A in Figure 3.3. The decomposition oxygen partial pressure changes with temperature. At a given temperature the decomposition oxygen partial pressure is given by the following polynomial equation

$$\log(\text{pO}_2\text{eq/atm}) = -115.6 + 0.1303T - 6.018\times10^{-5}T^2 + 1.028\times10^{-8}T^3$$

(3.11)

This empirical relation was obtained from a linear least-squares fit of the calculated three-phase points and is valid in the temperature range of 1073 to 1873 K. With increasing temperature the decomposition oxygen partial pressure increases. In the temperature range of 1273 to 1873 K the decomposition oxygen partial pressure increases from $4.3\times10^{-27}$ to $4.7\times10^{-16}$ atm. Therefore, reductive decomposition of LaCrO$_3$ is not expected under SOFC operating conditions.

3.3.1.2 La-Cr-Mg-O system

Pure LaCrO$_3$ is quite stable under highly reducing conditions. However, undoped LaCrO$_3$ is not used as SOFC interconnection material. Doping of the material will cause a change in the stability. In order to study the effect of the presence of magnesium as a dopant, chemical potential diagrams have been constructed for the La-Cr-Mg-O system. A convenient way to construct these diagrams is to plot $\log(a(\text{La})/a(\text{Cr}))$ versus $\log(a(\text{Mg})/a(\text{Cr}))$. In Figure 3.4 chemical potential diagrams for the system La-Cr-Mg-O at temperatures of 1273 and 1573 K are constructed for $p_{\text{O}_2\text{eq}} = 10^{-16}$ and 0.213 atm, respectively.

All four diagrams are essentially the same. Magnesium-doped LaCrO$_3$ is stable in highly reducing atmospheres, even at temperatures exceeding the SOFC operating
Figure 3.4a: Calculated chemical potential diagram for the La-Cr-Mg-O system for $T=1573$ K and $p_{O_2\,eq}=10^{-16}$ atm. (\textasteriskcentered): Stability area of MgCr$_2$O$_4$.

Figure 3.4b: Calculated chemical potential diagram for the La-Cr-Mg-O system for $T=1573$ K and $p_{O_2\,eq}=0.213$ atm. (\textasteriskcentered): Stability area of MgCr$_2$O$_4$. 
Figure 3.4c: Calculated chemical potential diagram for the La-Cr-Mg-O system for $T=1273$ K and $p_{O_2 \text{ eq}} = 10^{-16}$ atm. (*): Stability area of MgCr$_2$O$_4$.

Figure 3.4d: Calculated chemical potential diagram for the La-Cr-Mg-O system for $T=1273$ K and $p_{O_2 \text{ eq}} = 0.213$ atm. (*): Stability area of MgCr$_2$O$_4$. 
temperature. However, there is a significant difference between the chemical potential diagrams for reducing and for oxidizing atmospheres. The stability field of the \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) phase stretches to much higher \( \log\{a(\text{Mg})/a(\text{Cr})\} \) values in oxidizing atmospheres. Furthermore, the border lines between the stability areas of \( \text{La}_2\text{O}_3 \) and \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \), and between \( \text{MgO} \) and \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) are slightly curved. This curvature is caused by the increased Mg-substitution in \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_3 \). Owing to this Mg-substitution the \( \text{Cr}_2\text{O}_3 \)-activity along the \( \text{La}_2\text{O}_3/\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) border line is not constant. An increase in the magnesium content of \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) leads to a decrease in \( \text{Cr}_2\text{O}_3 \)-activity, and hence in Cr-activity. Therefore, \( \log\{a(\text{La})/a(\text{Cr})\} \) will increase, because the La-activity remains unaffected, leading to the curved border line.

The amount of magnesium that can be incorporated in \( \text{LaCrO}_3 \) under oxidizing conditions is significantly higher than under reducing conditions. Therefore, the stability field of \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) is stretched to much higher \( \log\{a(\text{Mg})/a(\text{Cr})\} \) values under oxidizing conditions. The temperature and oxygen partial pressure dependence of the Mg-substitution in \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) will be discussed in the next section.

### 3.3.2 Condensed-phase relations in the \( \text{La}_2\text{O}_3-\text{Cr}_2\text{O}_3-\text{MgO} \) system

Condensed-phase relations have been calculated for the La-Cr-Mg-O system as a function of equilibrium oxygen partial pressure and temperature. The calculations have been performed in the oxygen partial pressure range of \( 10^{-16} \) to 0.213 atm, which is above the reductive decomposition oxygen partial pressure as calculated earlier. Therefore, the condensed-phase relations can be represented in triangular pseudo-ternary phase diagrams with the binary oxides \( \text{La}_2\text{O}_3 \), \( \text{Cr}_2\text{O}_3 \), and \( \text{MgO} \) at the corners. Figure 3.5 shows the calculated pseudo-ternary phase diagram for \( P_{\text{O}_2} \) \( \text{eq} = 0.213 \) atm at a temperature of 1573 K. Figure 3.6 shows the calculated pseudo-ternary phase diagrams as a function of equilibrium oxygen partial pressure at a temperature of 1573 K. Figure 3.7 shows the maximum magnesium content in \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) as a function of temperature for \( P_{\text{O}_2} \) \( \text{eq} = 0.213 \) and \( 10^{-8} \) atm, respectively.

The phase diagram in Figure 3.5 is typical for the whole range of conditions calculated, i.e., there are no phases appearing or disappearing in this range of conditions. The Mg-substitution in \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) is represented by the line originating in the point representing pure \( \text{LaCrO}_3 \). The length of this line is proportional to the maximum magnesium content in \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \). The dashed regions in the phase diagram in Figure 3.5 are two-phase regions, in which \( \text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta} \) is in equilibrium with the oxide indicated at the edge of the phase diagram. The white areas are three-phase regions, in which the phases indicated at the corners are in equilibrium.
Figure 3.5: Calculated pseudo ternary phase diagram for the $\text{La}_2\text{O}_3$-$\text{Cr}_2\text{O}_3$-$\text{MgO}$ system for $T=1573 \text{ K}$ and $p_{\text{O}_2 \text{ eq}}=0.213 \text{ atm}$.

In the $\text{Cr}_2\text{O}_3$-rich part of the phase diagram, the region in which $\text{Cr}_2\text{O}_3$ can coexist with $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ is very narrow. With increasing Mg-substitution, the phases coexisting with $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ change from $\text{Cr}_2\text{O}_3$ through $\text{MgCr}_2\text{O}_4$ to $\text{MgO}$. In the $\text{La}_2\text{O}_3$-rich part of the phase diagram, $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ is always in equilibrium with $\text{La}_2\text{O}_3$.

Figure 3.6 shows that the maximum amount of magnesium that can be substituted for chromium in $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ decreases with decreasing equilibrium oxygen partial pressure. As a result, the two-phase regions become much narrower. At 1573 K, the calculated maximum amount of magnesium in $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ is 46 at% for $p_{\text{O}_2 \text{ eq}}=0.213 \text{ atm}$, and decreases to 7.5 at% for $p_{\text{O}_2 \text{ eq}}=10^{-16} \text{ atm}$. The maximum magnesium content of 46 at% in $\text{LaCr}_{1-x}\text{Mg}_x\text{O}_{3-\delta}$ in air ambient, according to the thermodynamic equilibrium calculations, seems to be far too high in comparison with the reported experimental results of Flandermeyer [5] and Tadashi et al. [42]. The results of Flandermeyer indicate a maximum magnesium content between 10 and 20 at%, because in the production of $\text{LaCr}_{0.8}\text{Mg}_{0.2}\text{O}_3$ powders by a liquid mix process second phases were formed. Tadashi et al. reported a maximum magnesium content of about 35 at%.
They observed formation of second phases (La$_2$O$_3$ and La(OH)$_3$) only when they tried to incorporate larger amounts of magnesium. Therefore, it might be concluded that the MgO solubility limit in LaCrO$_3$, as determined by Flandermeyer, is too low.

Obviously, the estimates of the thermodynamic parameters of the La(Cr$_{0.5}$Mg$_{0.5}$)O$_3$ and La(Cr$_{0.5}$Mg$_{0.5}$)O$_{2.75}$ compounds of the LaCr$_{1-x}$Mg$_x$O$_{3+δ}$ phase are such that these compounds have become too stable with respect to the LaCrO$_3$ compound, leading to too high values for the maximum magnesium content. If oxygen non-stoichiometry is not taken into account, the maximum magnesium content in LaCr$_{1-x}$Mg$_x$O$_3$ is about 28 at%, which is in better agreement with the experimentally found values.
Figure 3.7: Maximum magnesium content in LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ as a function of temperature for equilibrium oxygen partial pressures of 0.213 and $10^{-8}$ atm, respectively.

With decreasing equilibrium oxygen partial pressure, the maximum magnesium content in LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ decreases. The same trend is also observed when oxygen non-stoichiometry is not taken into account. Therefore, although the absolute values of the calculated maximum magnesium content in LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ may be too high, it is expected that in reducing ambients Mg-doped LaCrO$_3$ cannot contain as much magnesium as in oxidizing ambients. A maximum magnesium content of 7.5 at% was calculated for P$_{O_2\ eq}$ = $10^{-16}$ atm. Because it appears that the calculated maximum magnesium contents are far too high, it is expected that the thermodynamically-maximum magnesium content in highly reducing atmospheres is less than 7.5 at%.

In the EVD process, film growth proceeds on the side of the substrate exposed to the metal-chloride-rich atmosphere. Hence, film growth takes place in a highly reducing atmosphere. According to the results of the thermodynamic equilibrium calculations, the maximum magnesium content in Mg-doped LaCrO$_3$ is limited to a few atom percent under reducing conditions, which explains why films of Mg-doped LaCrO$_3$ synthesized by means of EVD only contained up to 2 at% magnesium, although a large excess of
MgCl₂ was used in the gas phase [18,21]. This limit in doping level is one of the drawbacks of the synthesis of Mg-doped LaCrO₃ by means of EVD. However, as discussed earlier, the effect of this limited doping level on the total cell performance may be marginal, especially in the tubular SOFC, where the contribution of the interconnect to the total cell resistance is only 1% [22].

Another consequence of the calculated limited maximum magnesium content in Mg-doped LaCrO₃ in reducing ambients is that, in an operating SOFC, the side of an interconnect containing 7.5 at% magnesium that is exposed to the fuel should be thermodynamically unstable. However, there is no evidence that under SOFC operating conditions exclusion of magnesium or magnesium-rich phases from the Mg-doped LaCrO₃ interconnect on the fuel-containing side takes place. Mori et al. [43] have investigated the stability -or reactivity- of doped LaCrO₃ against other cell components. They have studied the reactivity of alkaline earth metal-doped LaCrO₃ (Mg, Sr, and Ca) with 7.5 mol% YSZ at temperatures between 1273 K and 1773 K in air. No reaction products were observed between YSZ and LaCr₁₋ₓMgₓO₃ (x=0, 0.1, 0.2) after heating for 1000 hours at 1273 K. LaCrO₃ and LaCr₀.5Mg₀.5O₃ showed no reactivity with YSZ after 168 hours of heating at 1773 K, whereas the formation of La₂Zr₂O₇ was observed for LaCr₀.8Mg₀.2O₃ after heating for 96 hours at the same temperature. These observations indicate that under SOFC operating conditions, Mg-doped LaCrO₃ is stable against YSZ in oxygen-rich (air) ambients. However, no information is given for the stability of the interconnection material in fuel-containing, highly reducing, atmospheres.

Although LaCr₁₋ₓMgₓO₃ (x>0.075) appears to be thermodynamically unstable in reducing ambients, it has been reported that optimal sintering of Mg-doped LaCrO₃ without the use of sintering aids occurs in highly reducing atmospheres, at oxygen partial pressures in the vicinity of the Cr/Cr₂O₃ phase boundary in order to prevent volatilization of chromium oxides, at a temperature of 1973 K [1,12].

These observations indicate that the kinetics of decomposition of Mg-doped LaCrO₃ are very slow and that, therefore, the Mg-doped LaCrO₃ phase does not decompose upon decreasing the equilibrium oxygen partial pressure.

### 3.3.3 CVD diagrams for the reactant system LaCl₃-CrCl₃-MgCl₂-H₂O-O₂-Ar

The first step of the EVD film growth involves pore closure by a conventional CVD reaction of the reactant metal chloride vapours with oxygen and/or steam. The reaction conditions should be chosen such that the composition of the CVD deposit is (nearly) equal to the desired composition of the EVD film. Formation of second phases should be avoided, because they may have a negative influence on the EVD film growth behaviour and on the performance of the interconnect in an operating SOFC.

In order to determine the range of process conditions for the CVD growth of Mg-
doped LaCrO₂, CVD diagrams have been constructed for the reactant system LaCl₃-CrCl₃-MgCl₂-H₂O-O₂-Ar in the temperature range of 1273-1773 K. In these diagrams, the thermodynamic stable solid phases are shown as a function of input amount of MgCl₂ and temperature. All CVD diagrams have been calculated for a reactor pressure of 0.01 atm. In Table 3.2 the input partial pressures of the precursors are given for the three cases that have been investigated. In cases 1 and 2 equal, and constant, input amounts of LaCl₃ and CrCl₃ were used, as well as an excess of oxygen. In case 1 water was not considered as input species, whereas in cases 2 and 3 it was. In cases 1 and 2 the effect of addition of MgCl₂ to the input stream is investigated, while in case 3 the effect of substitution of CrCl₃ by MgCl₂ in the input stream is investigated. Because the thermodynamic properties of gaseous MgO were not available, this species has not been taken into account in these calculations.

Table 3.2: Input partial pressures (pₓₓ) of the precursors for the calculation of the CVD diagrams for the reactant system LaCl₃-CrCl₃-MgCl₂-H₂O-O₂-Ar, with P_total = 0.01 atm.

<table>
<thead>
<tr>
<th></th>
<th>CASE 1</th>
<th>CASE 2A</th>
<th>CASE 2B</th>
<th>CASE 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>pₓₓ (atm)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LaCl₃</td>
<td>5x10⁻⁵</td>
<td>5x10⁻⁵</td>
<td>1x10⁻⁵</td>
<td>5x10⁻⁵</td>
</tr>
<tr>
<td>CrCl₃</td>
<td>5x10⁻⁵</td>
<td>5x10⁻⁵</td>
<td>1x10⁻⁵</td>
<td>5x10⁻⁵ - 4x10⁻⁵</td>
</tr>
<tr>
<td>MgCl₂</td>
<td>0 - 3.33x10⁻⁵</td>
<td>0 - 3.33x10⁻⁵</td>
<td>0 - 6.67x10⁻⁶</td>
<td>0 - 1x10⁻⁵</td>
</tr>
<tr>
<td>H₂O</td>
<td>0</td>
<td>1.5x10⁻⁴ - 1.83x10⁻⁴</td>
<td>3x10⁻⁵ - 3.667x10⁻⁵</td>
<td>1.5x10⁻⁴ - 1.45x10⁻⁴</td>
</tr>
<tr>
<td>O₂</td>
<td>1x10⁻³</td>
<td>1x10⁻³</td>
<td>9.95x10⁻³ - 9.9433x10⁻³</td>
<td>1x10⁻³</td>
</tr>
<tr>
<td>Ar</td>
<td>8.9x10⁻³ - 8.867x10⁻³</td>
<td>8.75x10⁻³ - 8.683x10⁻³</td>
<td>0</td>
<td>8.75x10⁻³ - 8.755x10⁻³</td>
</tr>
</tbody>
</table>

Figure 3.8 shows the CVD diagram for case 1, where water is not used as input species. The input amount of oxygen is about a tenfold excess with respect to the metal chlorides. Figures 3.9(a) and (b) show the corresponding equilibrium partial pressures of the main species as a function of temperature for Mg/(Mg+La+Cr)=0.1. Figure 3.10 shows the equilibrium partial pressures of the metal-containing species as a function of
the input amount of magnesium at a temperature of 1473 K. The other species are not shown, because they hardly change with increasing input amount of magnesium. In Figures 3.11, the CVD diagram shown is calculated using a mixture of steam and oxygen as oxygen source reactants (case 2A). The input amount of steam is such that the feed gas contains equal amounts of hydrogen (H) and chlorine (Cl) atoms, i.e. $H/(H+Cl)=0.5$. Figure 3.12 shows the corresponding equilibrium partial pressures of the main species as a function of temperature for $Mg/(Mg+La+Cr)=0.1$. Figure 3.13 shows the CVD diagram for the same input as for Figure 3.11 except that oxygen is used as bulk gas instead of argon (case 2B).

Figure 3.8: Thermodynamically stable solid phases as a function of temperature and input amount of MgCl₂ for the reactant system LaCl₃-CrCl₃-MgCl₂-O₂-Ar at a total pressure of 0.01 atm, where the input partial pressures of LaCl₃ and CrCl₃ are $5\times10^{-5}$ atm, and the input partial pressure of oxygen is $10^{-3}$ atm. (\textasteriskcentered): Stability region of LaCr$_{1-x}$Mg$_x$O$_3$ + Cr$_2$O$_3$ + MgCrO$_4$. 

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Figure 3.9a: Equilibrium partial pressures of all magnesium- and chromium-free species as a function of temperature for \( \text{Mg}/(\text{Mg}+\text{La}+\text{Cr})=0.1 \) at a total pressure of 0.01 atm, where the input partial pressures of \( \text{LaCl}_3 \) and \( \text{CrCl}_3 \) are \( 5 \times 10^{-5} \) atm, and the input partial pressure of oxygen is \( 10^{-3} \) atm.

Figure 3.9b: Equilibrium partial pressures of all magnesium- and chromium-containing species as a function of temperature for the same conditions as in Figure 3.9(a).
Figure 3.10: Equilibrium partial pressures of all metal-containing species as a function of the input amount of MgCl₂ at a temperature of 1473 K and a total pressure of 0.01 atm, where the input partial pressures of LaCl₃ and CrCl₃ are $5\times10^{-5}$ atm, and the input partial pressure of oxygen is $10^{-3}$ atm.

From all calculations it became apparent that, irrespective of process conditions, LaCrₙ₋ₓMgₓO₃ is the most stable solid phase, because in the temperature range investigated LaCrₙ₋ₓMgₓO₃ is formed at all, arbitrarily chosen, LaCl₃/CrCl₃ ratios. The conversion of the limiting (in amount) reactant to LaCr₁₋ₓMgₓO₃ is always virtually 100%. Therefore, in the whole range of process conditions covered by cases 1 and 2, the conversion of LaCl₃ to LaCr₁₋ₓMgₓO₃ is virtually complete.

3.3.3.1 LaCl₃/CrCl₃=1

By increasing the input amount of MgCl₂, an increasing part of the chromium ions in LaCrO₃ is substituted by magnesium ions. Therefore, upon increasing the input amount of MgCl₂, an increasing excess of CrCl₃, with respect to LaCl₃, will be present in the input stream, because the input amounts of LaCl₃ and CrCl₃ were kept equal throughout all calculations. Whether or not this will lead to the formation of other solid phases depends on the process conditions. Especially the presence of water - or, in fact, hydrogen- plays an important role, as can be concluded from a comparison between Figures 3.8 and 3.11.
Figure 3.11: Thermodynamically stable solid phases as a function of temperature and input amount of MgCl₂ for the reactant system LaCl₃-CrCl₃-MgCl₂-H₂O-O₂-Ar at a total pressure of 0.01 atm, where the input partial pressures of LaCl₃ and CrCl₃ are 5×10⁻⁵ atm, the input partial pressure of oxygen is 10⁻³ atm, and H/(H+Cl)=0.5. (*): Stability region of LaCr₁₋ₓMgₓO₃.

Figure 3.12: Equilibrium partial pressures of the main species as a function of temperature for Mg/(Mg+La+Cr)=0.1, and the same conditions as in Figure 3.11.
Owing to the stability of MgCl₂(g) and CrO₂Cl₂(g) in the absence of hydrogen, formation of single-phase LaCr₁₋ₓMgₓO₃ is predicted in a wide range of process conditions. Figure 3.9(b) shows that in the absence of hydrogen the conversion of MgCl₂(g) is very low, only about 6%, and that the chromium, which has been displaced by magnesium, is converted to CrO₂Cl₂(g), which indicates that MgCl₂(g) and CrO₂Cl₂(g) are more stable at these conditions than the solid oxides. As a consequence of the low conversion of MgCl₂(g), the magnesium content in LaCr₁₋ₓMgₓO₃ will be small, and therefore, the amount of CrO₂Cl₂(g) formed will be small too. The region of formation of single-phase LaCr₁₋ₓMgₓO₃ has curved borders. The major part of this region lies within the range of 0≤Mg/(Mg+La+Cr)<0.183 and 1273≤T≤1523 K. The magnesium content in the LaCr₁₋ₓMgₓO₃ phase varies between 0 and 2.7 at% in that region, and increases with increasing input amount of MgCl₂ and decreases with increasing temperature. For Mg/(Mg+La+Cr)>0.183, codeposition of LaCr₁₋ₓMgₓO₃ and MgCr₂O₄ is expected in the whole temperature range covered. If the input amount of MgCl₂ is increased high enough, MgO will eventually be codeposited too. For T>1523 K and 0.022<Mg/(Mg+La+Cr)<0.15, Cr₂O₃ will be formed as second solid phase, owing to the increasing conversion of CrO₂Cl₂(g), as indicated by its decreasing equilibrium partial pressure in Figure 3.9(b).

For 0.1≤Mg/(Mg+La+Cr)≤0.183 and low temperatures, LaCr₁₋ₓMgₓO₃ and MgCr₂O₄ are the stable solid phases. With increasing temperature, the amount of MgCr₂O₄ formed decreases until LaCr₁₋ₓMgₓO₃ is the only stable solid phase. With a further increase in temperature, the (LaCr₁₋ₓMgₓO₃+MgCr₂O₄) region is re-entered. In the temperature range 1273≤T≤T_B, with T_B the temperature where the boundary between the LaCr₁₋ₓMgₓO₃ region and the (LaCr₁₋ₓMgₓO₃+MgCr₂O₄) region is located, the equilibrium partial pressures of MgCl₂ and CrO₂Cl₂ increase with increasing temperature, indicating that less MgCr₂O₄ will be formed. Furthermore, less chromium is available to form chromium-containing solid phases, because the magnesium content of the LaCr₁₋ₓMgₓO₃ decreases with increasing temperature. Therefore, above the temperature T_B, only LaCr₁₋ₓMgₓO₃ will be formed. With further increasing temperature, decomposition of CrO₂Cl₂(g) becomes increasingly important, leading, again, to the formation of MgCr₂O₄ above a certain temperature. However, at the same time the equilibrium partial pressures of CrO₂ and Cr₂O₃ increase significantly with increasing temperature, as is shown in Figure 3.9(b). Therefore, owing to the increasing volatility of these chromium oxide species, the amount of MgCr₂O₄ will decrease with increasing temperature, until above a certain temperature it will no longer be formed. This high-temperature boundary between the (LaCr₁₋ₓMgₓO₃+MgCr₂O₄) region and the LaCr₁₋ₓMgₓO₃ region is located at T>1773 K, and is, therefore, not shown in Figure 3.8. The appearance of this high-temperature boundary is clearly shown in Figure 3.13.

Similarly, at higher temperatures and smaller Mg/(Mg+La+Cr) values the stability regions of single-phase LaCr₁₋ₓMgₓO₃, LaCr₁₋ₓMgₓO₃+Cr₂O₃, and again single-phase
LaCr\(_{1-x}\)Mg\(_x\)O\(_3\) are successively encountered upon increasing the temperature.

The main effect of the addition of water-or hydrogen- to the input stream (case 2A) is that the LaCr\(_{1-x}\)Mg\(_x\)O\(_3\) region is restricted to very small Mg/(Mg + La + Cr) values or very high temperatures (Figure 3.11). The formation of HCl is favoured to such extent that the metal chloride precursors are completely converted to metal oxide products for H/(H + Cl) ≥ 0.5. This can be seen in Figure 3.12, where it is shown that HCl has become the most abundant gas phase species, while the equilibrium partial pressures of the metal chloride species are several orders of magnitude lower than in Figures 3.9(a) and (b). It should be noted that the equilibrium partial pressures of argon and oxygen are not considered here, because they are present in excess. Hence, their equilibrium partial pressures are hardly affected by the reaction conditions. The conversion of LaCl\(_3\) to LaCr\(_{1-x}\)Mg\(_x\)O\(_3\) is 100% for all reaction conditions considered. The excess amounts of CrCl\(_3\) and MgCl\(_2\) are converted to Cr\(_2\)O\(_3\), MgCr\(_2\)O\(_4\), and MgO depending on the MgCl\(_2\) input amount and temperature. If all argon in the input stream is replaced by oxygen (case 2B), the LaCr\(_{1-x}\)Mg\(_x\)O\(_3\) region shifts to lower temperatures (Figure 3.13), owing to the increased volatility of the chromium oxide species Cr\(_2\)O\(_3\) and CrO\(_2\), as discussed earlier.

![Figure 3.13: Thermodynamically stable solid phases as a function of temperature and input amount of MgCl\(_2\) for the reactant system LaCl\(_3\)-CrCl\(_3\)-MgCl\(_2\)-H\(_2\)O-O\(_2\)-Ar at a total pressure of 0.01 atm, where oxygen is the bulk gas, the input partial pressures of LaCl\(_3\) and CrCl\(_3\) are 5×10\(^{-5}\) atm, and H/(H + Cl) = 0.5.](image)
3.3.3.2 \( \text{LaCl}_3/\text{CrCl}_3 > 1 \)

Since in the presence of hydrogen all excess metal chlorides are converted to metal oxides, a possible way to increase the range of reaction conditions for formation of single-phase \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) is to substitute \( \text{CrCl}_3 \) in the input stream by \( \text{MgCl}_2 \) instead of adding \( \text{MgCl}_2 \), i.e. the ratio \( \text{La}/(\text{La} + \text{Mg} + \text{Cr}) \) remains constant. The calculations reveal that in the whole range of reaction conditions covered, i.e. \( 0 \leq \text{Mg}/(\text{Mg} + \text{Cr}) \leq 0.2 \), \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) and \( \text{La}_2 \text{O}_3 \) are the stable solid phases. Since the conversion of metal chlorides to \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) is virtually 100%, the magnesium content in the \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) phase is proportional to the \( \text{MgCl}_2 \) input amount. Although \( \text{La}_2 \text{O}_3 \) is stable under all conditions, its concentration in the deposits is negligible and ranges from <0.2 ppb at 1273 K to 6 ppm at 1773 K. The formation of \( \text{La}_2 \text{O}_3 \) is caused by the volatility of the chromium oxide species \( \text{CrO}_2 \) and \( \text{CrO}_3 \). Therefore, the \( \text{La}_2 \text{O}_3 \) concentration increases with increasing temperature and decreases with increasing \( \text{Mg}/(\text{Mg} + \text{Cr}) \) ratio.

In conclusion, the widest range of process conditions in which \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) is the only stable phase is obtained by substituting part of the \( \text{CrCl}_3 \) in the input stream by \( \text{MgCl}_2 \) while maintaining \( \text{La}/(\text{La} + \text{Mg} + \text{Cr}) = 1 \), and by using a mixture of steam and oxygen as oxygen source reactants, in order to enhance the conversion of \( \text{MgCl}_2 \) and \( \text{CrO}_2 \text{Cl}_2 \).

3.3.4 EVD film composition for the reactant system \( \text{LaCl}_3-\text{CrCl}_3-\text{MgCl}_2-\text{Ar} \)

Feduska and Isenberg [21] deposited EVD films of Mg-doped \( \text{LaCrO}_3 \) at 1623 K using a \( \text{H}_2/\text{H}_2\text{O} \) mixture, with an oxygen partial pressure of \( \approx 10^{-13} \) atm, as oxygen source. Upon increasing the \( \text{Mg}/(\text{La} + \text{Mg}) \) ratio in the gas phase, they observed an increasing film growth rate along with an increasing room temperature conductivity, indicating an increasing incorporation of magnesium into the \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) film. All EVD films consisted of Mg-doped \( \text{LaCrO}_3 \), but no indication was given about the composition of the pore-plugging CVD deposit. According to the thermodynamic calculations, the CVD deposits should consist of \( \text{LaCr}_{1-x} \text{Mg}_x \text{O}_3 \) and \( \text{MgCr}_2\text{O}_4 \).

The CVD step is just the first stage of the CVD/EVD process, which only lasts until pore closure. Therefore, if only small amounts of other phases besides Mg-doped \( \text{LaCrO}_3 \) are formed, this will have a negligible influence on the film growth during the EVD stage. Furthermore, the final performance of the interconnection material will not be affected by these small amounts of second phases.

It should be noted that the magnesium content in the EVD films may be considerably lower than in the pore-plugging CVD deposits, because in the EVD stage of film growth the low oxygen partial pressure on the metal chloride side or the stability of \( \text{MgCl}_2 \) may
be the limiting factor for the incorporation of magnesium into LaCr$_{1-x}$Mg$_x$O$_3$. In order to obtain some information on the influence of the process conditions on the composition of the EVD film, the magnesium content in the EVD films of Mg-doped LaCrO$_3$ has been calculated as a function of the input amount of MgCl$_2$ in the input stream and temperature, and the results are shown in Figure 3.14.

The composition of the EVD films has been calculated by an iterative procedure from the thermodynamic equilibrium between the input gas stream, containing LaCl$_3$, CrCl$_3$, MgCl$_2$, and Ar, and an excess of Mg-doped LaCrO$_3$ with a certain composition representing the EVD film, starting with the composition of the CVD deposit. In the calculations it has been assumed that during the CVD stage of the process LaCr$_{0.9}$Mg$_{0.1}$O$_3$ is formed. The calculated equilibrium composition of the Mg-doped LaCrO$_3$ phase is used as input in the next calculation, and, subsequently, the equilibrium composition of the Mg-doped LaCrO$_3$ phase is calculated. This procedure is repeated until the composition of the Mg-doped LaCrO$_3$ phase remains constant.

It is shown in Figure 3.14 that the amount of magnesium which will be incorporated in the EVD film increases with increasing Mg/(La+Cr+Mg) input ratio, and with increasing temperature. If, at a constant Mg/(La+Cr+Mg) input ratio, the total concentration of metal chlorides is decreased, then the magnesium content in the EVD film will also decrease.

**Figure 3.14:** Calculated magnesium content in EVD films of LaCr$_{1-x}$Mg$_x$O$_3$ as a function of input concentration of MgCl$_2$ for temperatures of 1473, 1573, and 1673 K, respectively, where the input concentrations of LaCl$_3$ and CrCl$_3$ are 1%.

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film will slightly increase. The amount of magnesium incorporated in the EVD film is far less than the amount of MgCl$_2$ present in the input stream, owing to the stability of MgCl$_2$, which was also found experimentally by Feduska and Isenberg [21], as discussed earlier. Hence, in order to obtain a reasonable doping level, a large excess of MgCl$_2$ should be present in the reactant stream.

3.4 CONCLUSIONS

A thermochemical description has been given for Mg-doped LaCrO$_3$, taking into account oxygen non-stoichiometry, and the accompanying thermodynamic parameters have been estimated. The oxygen non-stoichiometry calculations show reasonable agreement with the experimental TGA results, whereas the calculated maximum magnesium content in Mg-doped LaCrO$_3$ appears to be too high. Therefore, in the future emphasis should be focused on obtaining more accurate estimates for the thermodynamic parameters of the compounds of the Mg-doped LaCrO$_3$ phase, e.g. by assuming that the three compounds of the phase do not form an ideal solution.

Stability calculations revealed that Mg-doped LaCrO$_3$ is stable under SOFC operating conditions. The amount of magnesium that can be incorporated into LaCrO$_3$ decreases significantly with decreasing equilibrium oxygen partial pressure and with increasing temperature. Hence, the magnesium content of Mg-doped LaCrO$_3$ films synthesized by means of EVD is limited to a maximum of a few atom percent.

In order to obtain the widest range of process conditions for deposition of single-phase Mg-doped LaCrO$_3$ in the CVD stage of the CVD/EVD process, the ratio of La/(La+Mg+Cr) in the input reactant stream should be equal to 1, and the ratio Mg/(Mg+Cr) should lie between 0 and 0.2, while a mixture of steam and oxygen should be used as oxygen source reactants.

The magnesium content of EVD films of Mg-doped LaCrO$_3$ increases with increasing input concentration of MgCl$_2$ and increasing temperature. Owing to the stability of MgCl$_2$, the magnesium content of EVD films of Mg-doped LaCrO$_3$ is far less than the input concentration of MgCl$_2$. Therefore, it is necessary to use a large excess of MgCl$_2$ in the input stream in order to obtain a reasonable doping level.
REFERENCES


APPENDIX A

Thermodynamic parameters of the species of the La-Cr-Mg-O-H-Cl-Ar system

The input data for the thermodynamic equilibrium calculations consist of the standard enthalpy of formation $\Delta_f H_{298}^0$, the standard absolute entropy $S_{298}^0$, and the heat capacity $c_p$ of the species. The reference states for the elements are the solid state of lanthanum (La), chromium (Cr), and magnesium (Mg), and the gaseous state of argon (Ar), chlorine (Cl$_2$), hydrogen (H$_2$), and oxygen (O$_2$), respectively; all at a temperature of 298.15 K and a pressure of 1 atm. The heat capacity of the species is described by the polynomial function

$$c_p = A + BT + \frac{C}{T^2} + DT^2 + \frac{E}{T^3} \quad (3A.1)$$

The gaseous species with their thermodynamic parameters are listed in Table 3A.1 and the solid species in Table 3A.2. The estimated thermodynamic parameters of the compounds of the LaCr$_{1-x}$Mg$_x$O$_{3-\delta}$ phase are listed in Table 3.1. The thermodynamic data of the species are primarily taken from the JANAF Tables [24] and Barin [25]. The thermodynamic data of the gaseous lanthanum oxides La$_2$O$_2$, LaO, and La$_2$O are taken from Cordfunke and Konings [44].

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Table 3A.2: Thermodynamic parameters of the solid species. Temperatures and enthalpies of phase transitions are indicated in italics. Temperatures of transition to the liquid phase are denoted by $T_m$, vaporization temperatures by $T_v$, and decomposition temperatures by $T_d$.

<table>
<thead>
<tr>
<th>species</th>
<th>$\Delta H^0_{298}$ (kJ mol$^{-1}$)</th>
<th>$S^0_{298}$ (J K$^{-1}$ mol$^{-1}$)</th>
<th>A (J K$^{-1}$ mol$^{-1}$)</th>
<th>B$\times 10^4$ (J K$^{-2}$ mol$^{-1}$)</th>
<th>C$\times 10^4$ (J K mol$^{-1}$)</th>
<th>D$\times 10^8$ (J K$^3$ mol$^{-1}$)</th>
<th>E$\times 10^6$ (J K$^2$ mol$^{-1}$)</th>
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<td>Cr</td>
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<td>24.51</td>
<td>20.50</td>
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<td>129.96</td>
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<td>109.65</td>
<td>154.56</td>
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Chapter 4

MODELLING OF THE EVD PROCESS FOR
YSZ AND Mg-DOPED LaCrO₃

ABSTRACT

Electrochemical vapour deposition (EVD) has become a key technology for the
deposition of gastight films of the solid oxide fuel cell (SOFC) electrolyte material yttria-
stabilized zirconia (YSZ), and the interconnection material Mg-doped lanthanum
chromium oxide (LaCrO₃) on porous substrates. In order to obtain a better
understanding of the kinetics of the EVD process, the EVD growth of YSZ and Mg-
doped LaCrO₃ has been modelled, assuming solid state diffusion to be rate-determining.
For YSZ, the experimentally observed growth rates are compared with the modelling
results. The apparent activation energy for the EVD growth is not equal to the apparent
activation energy for electronic conduction in YSZ. This inconsistency can be understood
considering the thermodynamic equilibrium at the gas/film interface on the metal
chloride side. Thermodynamic equilibrium calculations are used to predict the EVD
growth rates for the experimental conditions used in literature. The results show that the
EVD growth of YSZ is probably governed by a combination of defect transport through
the EVD film, and some mass transfer limitation at the surface of the growing film.
Because literature data for the EVD growth of Mg-doped LaCrO₃ are lacking, the results
of the model calculations for the EVD growth can not be verified.

Composite electrolytes comprising ceria (CeO₂) and a thin top layer of YSZ on the
fuel side are promising candidates for use in low-temperature SOFCs. These composite
electrolytes can be fabricated by the EVD process. The kinetics of the growth of the top
layer differ from that of the bottom layer, as they are influenced by the transport
properties of both the bottom and the top layer. EVD growth of Mg-doped LaCrO₃, an
almost pure electronic conductor, on YSZ, which is an almost pure ionic conductor, has
been modelled assuming interface reactions to be rapid. Initially, growth behaviour is
linear, and then gradually changes to parabolic. The oxygen partial pressure at the
substrate/film interface is an important parameter in the growth process. The effect of
various process parameters on the film growth behaviour has been determined.
4.1 INTRODUCTION

The synthesis of thin gas impervious films of YSZ and Sr- or Mg-doped LaCrO$_3$ on porous supports is of great interest for the development of SOFCs. Various processing techniques have been explored for the synthesis of the gastight components of a SOFC. Among the synthesis routes for the solid electrolyte and interconnection material are both wet-type and gas phase techniques. Tape casting, extrusion, and calendering are wet-type processes, which have been developed for green sheet manufacturing. These processes start with powder of the desired component, which is manufactured by conventional powder processing techniques as co-precipitation, sol-gel, and spray drying [1]. The final stage of these wet-type processes is always a high-temperature sintering step. Examples of gas phase techniques are, laser ablation, RF sputtering, electron beam evaporation, chemical vapour deposition (CVD), and electrochemical vapour deposition (EVD) [1]. One of the advantages of gas phase techniques is the fact that products can be formed in one process step.

The choice of SOFC design, i.e. tubular, planar or monolithic, is of great influence on the fabrication method to be used, e.g. tubular components can not be fabricated by tape casting. Furthermore, Sr- and Mg-doped LaCrO$_3$ are difficult to sinter to full density, because of the volatility of chromium oxide species under oxidizing conditions [2,3]. Traditionally, sintering temperatures of over 1600 K in a chromium-rich atmosphere have been used. These temperatures are unacceptably high for the other SOFC components.

Nowadays EVD has become a key technology for the synthesis of uniform gastight layers of YSZ and Mg-doped LaCrO$_3$ for tubular SOFCs. The EVD process is a modified form of the conventional CVD process, and was developed by Isenberg at Westinghouse [4]. The process utilizes an electrochemical potential gradient to form thin gastight layers of either ionically or electronically conducting metal oxides on porous supports. The principle of the process has been discussed in detail in Chapter 2. During the process an oxygen source reactant is continuously reduced at the gas/film interface on the oxygen-rich side of the growing film. The oxygen ions formed diffuse through this film owing to the presence of a large oxygen chemical potential gradient across the film. On the metal chloride side oxygen ions react with the metal chlorides to form the metal oxide product. Oxygen ion vacancies and electrons formed on the metal chloride side diffuse to the oxygen-rich side to preserve electroneutrality.

In order to obtain a better understanding of the growth kinetics of the EVD process, and to be able to control the process, a theoretical analysis of the growth kinetics is very important. In this chapter the growth kinetics of the EVD process will be modelled, assuming that solid state transport is the rate-determining process. A distinction is made between two different systems.

The first system involves the growth of EVD layers on porous supports. This section is divided into two parts: in the first part the kinetics of the growth of the SOFC
electrolyte material YSZ, which is almost a pure oxygen ion conductor, is modelled, whereas in the second part the growth of the interconnection material Mg-doped LaCrO$_3$, which is almost a pure electronic conductor, is analyzed. The influence of the oxygen partial pressure, on either side of the film, and the temperature on the growth rate is investigated.

Literature on the kinetics of the EVD growth of YSZ and Mg-doped LaCrO$_3$ on porous supports is scarce. Only Isenberg [4], Pal and Singhal [5], Carolan and Michaels [6], Schoonman et al. [7-9], Lin et al. [10-12], and Sasaki et al. [13] have reported on the kinetics of the growth of YSZ by EVD. The reported data on the growth of YSZ have been collected, and a comparison with the modelling results is made in order to explain the observed growth rates. Only Pal and Singhal [14,15] have reported on the kinetics of the EVD growth of Mg-doped LaCrO$_3$. Their experiments were restricted to one temperature (1600 K) only. Therefore, a comparison between literature data and modelling results can not be made.

The second system involves the growth of EVD layers on gastight oxygen ion conducting substrates. In this section, the EVD growth of Mg-doped LaCrO$_3$ on gastight YSZ is modelled. The idea to deposit two-layer composite films by means of EVD has been developed by Virkar et al. [16-18]. They suggested that in order to lower the operating temperature of SOFCs, electrolytes with considerably higher ionic conductivity than zirconia should be used. Ceria (CeO$_2$)-based electrolytes are among the most promising candidates to replace YSZ for use in low-temperature SOFCs, because it has an ionic conductivity in excess of 0.01 S/cm at 700°C, which is about 10-20 times higher than that of zirconia, and it is not reduced in fuel-containing atmospheres. However, ceria exhibits considerable electronic conductivity in reducing environments. Therefore, a thin layer of YSZ should be deposited on the fuel side of the electrolyte in order to block off electronic current. The specific resistance of a composite electrolyte of 20 µm CeO$_2$ and 2 µm YSZ at 800 °C is 0.06 Ω/cm$^2$, whereas an YSZ electrolyte of the same thickness has a specific resistance is 0.22 Ω/cm$^2$ [17].

Both layers of the composite electrolyte can be deposited by means of EVD. It can easily be understood that the growth kinetics of the second layer depend on the transport properties of both the first and the second layer, the thickness of the first layer, and the reaction conditions. In case of a ceria/YSZ composite electrolyte, an oxygen ion conductor (YSZ) is deposited on another, better, oxygen ion conductor (CeO$_2$). In our case we have studied the growth of an electronic conductor (doped LaCrO$_3$), with only very small oxygen ion conductivity, on an oxygen ion conductor (YSZ). This system was chosen in order to investigate the EVD growth of composite layers with different conductivity behaviour. Besides the influence of the oxygen partial pressure and the temperature, the influence of the ratio of the substrate thickness and the film thickness on the growth kinetics of the LaCrO$_3$ film has been investigated.
4.2 SOLID STATE TRANSPORT IN EVD FILMS DEPOSITED ON POROUS SUBSTRATES.

During the EVD growth on a porous substrate, the overall film growth can be limited by a) gas diffusion in the substrate pores, b) surface kinetics on either side of the film, or c) solid state diffusion in the growing film, or partly by either. When the rate of film growth is controlled by solid state diffusion, the kinetics are similar to the Wagner oxidation of metals. In Wagner oxidation, the rate of film growth is inversely proportional to the oxide thickness [19,20],

\[
\frac{dL}{dt} = \frac{K_0}{L}
\]  \hspace{1cm} (4.1)

where \( L \) is the film thickness and \( K_0 \) the parabolic growth rate constant. The integrated form of Equation (4.1) yields the parabolic rate law,

\[
L^2 = 2K_0t + C_0
\]  \hspace{1cm} (4.2)

where \( t \) is the total time of the EVD growth stage, and \( C_0 \) a constant of integration.

The diffusion processes which can take place during EVD growth are shown schematically in Figure 4.1. The large oxygen partial pressure gradient across the growing film results in a flux of oxygen ions. Oxygen ion diffusion is only possible if at the same time a counter diffusion of a species with the same charge or a parallel diffusion of a species with opposite charge occurs to preserve electroneutrality. At steady state there is no net flow of current. Hence, the sum of the cationic, anionic, electron, and electron hole currents is zero. In the SOFC electrolyte material YSZ and the SOFC interconnection material Mg-doped LaCrO\(_3\), the metal ion diffusion can be neglected.

\[\text{O}_2/\text{H}_2\text{O} \quad p_{O_2} \quad p_{O_2}^{\prime} \]

\[\begin{array}{c}
\text{O}_0^x \\
\text{Me}^x \\
\text{Me}^y \\
\text{VO} \\
\text{Me} \\
\text{h} \\
\text{e} \\
\end{array}
\]

\[\text{MeCl}_y \]

\[\text{metal oxide}\]

**Figure 4.1:** Diffusing species during EVD growth on a porous substrate
When solid state diffusion in the growing film is rate-limiting, the reactions at the gas/solid interfaces are considered to be so fast that thermodynamic equilibria at these interfaces are established. The partial pressure of oxygen on the oxygen-rich side \( (P_{O_2}^*) \) is determined by the equilibrium between the gaseous species present, e.g. \( O_2/H_2O \) or \( H_2/H_2O \). The oxygen partial pressure on the metal chloride side \( (P_{O_2}^*) \) is determined by the equilibrium between the metal chlorides, impurity oxygen, and the growing film. In terms of ionic flux \( (j_i) \), the growth rate can be expressed as \([20]\):

\[
\frac{dL}{dt} = \frac{2}{C} j_i V_m
\]  

where \( C \) is the total charge of the cations in one "molecular" oxide unit, and \( V_m \) the molar volume of the growing oxide. If it is assumed that local equilibrium exists within the oxide, the general expression for the ionic flux (in \( \text{mol/cm}^2\text{s} \)) is given by,

\[
j_i = -\left( \frac{RT}{8F^2} \int_{P_{O_2}}^{P_{O_2}^*} \sigma_{\text{ion}} \sigma_{\text{el}} \frac{d \ln P_{O_2}}{\Delta L} \right) \frac{1}{\Delta L} \]  

where \( R \) is the gas constant, \( F \) the Faraday constant, \( T \) the absolute temperature, \( \sigma \) the total electrical conductivity, \( \sigma_{\text{ion}} + \sigma_{\text{el}} \) \( \tau_{\text{ion}} \) the ionic transference number, and \( \tau_{\text{el}} \) the electronic transference number. By combining Equations (4.1), (4.3), and (4.4), an expression for the parabolic growth rate constant can be derived, depending on the type of conductivity which is predominant in the growing oxide.

### 4.2.1 Parabolic growth rate constant for YSZ.

YSZ is an almost pure oxygen ion conductor \( (\tau_{\text{ion}} \approx 1) \), with a small contribution of electronic conductivity. Therefore, Equation (4.4) can be written as,

\[
j_i = -\left( \frac{RT}{8F^2} \int_{P_{O_2}}^{P_{O_2}^*} \sigma_{\text{el}} \frac{d \ln P_{O_2}}{\Delta L} \right) \frac{1}{\Delta L} \]  

where \( \sigma_{\text{el}} \) is the total electronic conductivity. The oxygen partial pressure dependence of \( \sigma_{\text{el}} \) can be understood considering the oxygen partial pressure dependence of the electron and electron hole concentrations in YSZ, which can be derived from the defect equilibria responsible for their formation.
Expressions for the electron and electron hole conductivities of YSZ as a function of its surrounding atmosphere can be derived. Using Kröger-Vink notation [21], and assuming that all defects are fully ionized, the defect reaction for YSZ can be written as

\[ Y_2O_3 \rightarrow 2 \ Y'_Zr + 3 \ O^X_O + V'^\cdot \]  

(4.6)

At low oxygen partial pressures, the non-stoichiometric defect reaction for YSZ can be written as [22],

\[ O^X_O = 2 \ e'^\cdot + V'^\cdot + \frac{1}{2}O_2(g) \]  

(4.7)

and at high oxygen partial pressures as

\[ O^X_O + 2 \ h^\cdot = V'^\cdot + \frac{1}{2}O_2(g) \]  

(4.8)

The equilibrium constant \( K_7 \) for reaction (4.7) is given by,

\[ K_7 = [V'^\cdot] \ [e'^\cdot]^2 \ P_{O_2}^{1/2} \]  

(4.9)

where \( [V'^\cdot] \) is the concentration of fully ionized oxygen ion vacancies in the oxygen sub-lattice, and \( [e'^\cdot] \) the electron concentration in the conduction band. The equilibrium constant \( K_8 \) for reaction (4.8) is given by,

\[ K_8 = \frac{[V'^\cdot]}{[h^\cdot]^2} \ P_{O_2}^{1/2} \]  

(4.10)

where \( [h^\cdot] \) is the electron hole concentration in the valence band. In the growing YSZ film, the electroneutrality condition

\[ 2[V'^\cdot] + [h^\cdot] = [Y'_Zr] + [e'^\cdot] \]  

(4.11)

must always be fulfilled. Under EVD conditions, YSZ is in its electrolytic domain. Therefore, the oxygen ion vacancy concentration is determined only by the dopant concentration of yttria, and the electron and electron hole concentrations in Equation (4.11) can be neglected. Thus, at a given dopant concentration and
temperature, the concentrations of electrons and electron holes are determined by the partial pressure of oxygen.

The conductivity of electrons, $\sigma_n$, and electron holes, $\sigma_p$, is given by [20],

$$\sigma_n = [e^+] |q| \mu_n$$  \hspace{1cm} (4.12)

and,

$$\sigma_p = [h^+] |q| \mu_p$$  \hspace{1cm} (4.13)

where $q$ is the electronic charge, $\mu_n$ the electron mobility, and $\mu_p$ the electron hole mobility. If the mobility is independent of the carrier concentration, then the conductivity is proportional to the carrier concentration. Assuming that the equilibria in reactions (4.7) and (4.8) are present, expressions for the electron and electron hole conductivities can be obtained by combining Equations (4.9) and (4.12), and Equations (4.10) and (4.13), respectively, yielding,

$$\sigma_n = \frac{|q| \mu_n}{[V_O]^{1/2}} K_7^{1/2} P_{O_2}^{-1/4}$$  \hspace{1cm} (4.14)

and

$$\sigma_p = \frac{[V_O]^{1/2} |q| \mu_p}{K_8^{1/2}} P_{O_2}^{1/4}$$  \hspace{1cm} (4.15)

From Equations (4.1), (4.3), (4.5), (4.14), and (4.15) the parabolic growth rate constant can be derived to yield [5-13],

$$K_0 = \frac{RT V_m}{C F^2} \left( \sigma_p^0 (P_{O_2}^{1/4} - P_{O_2}^{-1/4}) + \sigma_n^0 (P_{O_2}^{-1/4} - P_{O_2}^{-1/4}) \right)$$  \hspace{1cm} (4.16)

where $C$ is the total cation charge in one "molecular" unit of YSZ, $\sigma_p^0$ the electron hole conductivity at an oxygen partial pressure of 1 atm, and $\sigma_n^0$ the electron conductivity at an oxygen partial pressure of 1 atm. The value of the constant $C$ depends on the yttria content in the deposited YSZ film, and it is given by,

$$C = \frac{4 + 0.02x}{1 + 0.01x}$$  \hspace{1cm} (4.17)

where $x$ is the yttria content in YSZ in mol%.
Equation (4.16) can be used to calculate the parabolic growth rate constant, provided the oxygen partial pressure on the metal chloride side, as well as the electron and electron hole conductivities as a function of temperature and oxygen partial pressure are known. Substituting values expected to be typical for EVD experiments, i.e. low oxygen partial pressures, in Equation (4.16) reveals that this equation can be simplified to

\[
K_0 = \frac{RTV_m}{C_F^2} \sigma_n^0 \sigma_m^{-1/4} P_{O_2}^{-\frac{1}{2}}
\]  

(4.18)

It should be noted that Equation (4.18) is valid only if the oxygen partial pressure is low enough to maintain an electron-controlled electronic conductivity.

\( P_{O_2} \) is assumed to be determined by the thermodynamic equilibrium between the species present on the metal chloride side, and can be calculated using the SOLGASMIX and ChemSage computer programs [23,24]. The thermochemical data of the species necessary for these calculations can be obtained from the JANAF Tables [25]. In this way \( P_{O_2} \) can be calculated as a function of reaction conditions, and thence, values of the parabolic growth rate constant.

Thermodynamic equilibria are calculated as a function of temperature and input concentration of reactants. Using the results of these calculations, values of the parabolic growth rate constant are determined. Finally, these calculated parabolic growth rate constants are compared with the fitted growth rate constants from the experiments reported in the literature [4-13], and the results are discussed.

4.2.2 Parabolic growth rate constant for Mg-doped LaCrO₃

Mg-doped LaCrO₃ is known to be a p-type electronic conductor with a small contribution of oxygen ion conductivity [26,27]. As stated earlier, the contribution of the cationic conductivity to the total ionic conductivity can be neglected. For an electronic conductor, with \( t_{el}=1 \), the general expression for the ionic flux, i.e. Equation (4.4), can be written as,

\[
j_\text{i} = \frac{RT}{8F^2} \int_{P_{O_2}}^1 \sigma_{\text{ion}} d \ln P_{O_2} \left( \frac{1}{\Delta L} \right)
\]  

(4.19)

where \( \sigma_{\text{ion}} \) is the ionic conductivity of the electronic conductor. For Mg-doped LaCrO₃,
using the Nernst-Einstein relation, Equation (4.19) can be written as,

\[ j_i = - \left( \frac{1}{2} \int_{p_{O_2}}^{p_{O_2}^*} c_O D_O \, d \ln p_{O_2} \right) \frac{1}{A_L} \] (4.20)

where \( c_O \) is the concentration of oxygen ions in mol/cm\(^3\), and \( D_O \) the oxygen ion self-diffusion coefficient. The relation between the oxygen ion self diffusion coefficient and the oxygen ion vacancy diffusion coefficient is given by [20],

\[ c_O D_O = D_{V_O^-} [V_O^-] \] (4.21)

where \( D_{V_O^-} \) is the oxygen ion vacancy diffusion coefficient, and \([V_O^-]\) the concentration of vacant oxygen lattice sites. The concentration of oxygen ions in Mg-doped LaCrO\(_3\) is approximately equal to \(3/V_m\), and the concentration of oxygen ion vacancies is equal to \(\delta/V_m\), where \(\delta\) is the mole fraction of oxygen ion vacancies. By combining Equations (4.1), (4.3), (4.20), and (4.21) the parabolic growth rate constant for the EVD growth of Mg-doped LaCrO\(_3\) is derived, yielding

\[ K_0 = - \frac{D_{V_O^-} p_{O_2}^*}{C} \int_{p_{O_2}}^{p_{O_2}^*} \delta \, d \ln p_{O_2} \] (4.22)

The value of the constant \(C\) depends on the magnesium content in the LaCrO\(_3\) film and is equal to \(6-x\), where \(x\) is the fraction of chromium ions substituted by magnesium ions. Because the magnesium content in EVD layers will only be a few percent, as was discussed in Chapter 3, \(x\) can be neglected, and Equation (4.22) can be written as

\[ K_0 = - \frac{D_{V_O^-} p_{O_2}^*}{\delta} \int_{p_{O_2}}^{p_{O_2}^*} \delta \, d \ln p_{O_2} \] (4.23)

The oxygen partial pressure dependence of \(\delta\) can be derived, considering the defect chemistry of Mg-doped LaCrO\(_3\). For simplicity it is assumed that all defects are fully ionized. Doping of LaCrO\(_3\) with Mg\(^{2+}\) will result in the substitution of Cr\(^{3+}\) on normal lattice sites. The effective negative charge of the acceptor dopant (Mg\(_{Cr}^+\)) can be compensated by either a Cr\(^{3+}\) to Cr\(^{4+}\) transition [26,27], or the formation of oxygen ion
vacancies. The electroneutrality condition is given by

$$[\text{Mg}^\cdot_{\text{Cr}}] = [\text{Cr}^\cdot_{\text{Cr}}] + 2[V_{\text{O}}^\cdot]$$

(4.24)

At low oxygen partial pressures, the formation of oxygen ion vacancies is favoured, whereas at high oxygen partial pressures, charge compensation will occur by Cr$^{3+}$ to Cr$^{4+}$ transition. If it is assumed that all defects are randomly distributed over the lattice, the corresponding defect equilibrium can be written as

$$O_{\text{O}}^x + 2\text{Cr}^\cdot_{\text{Cr}} = 2\text{Cr}^x_{\text{Cr}} + V_{\text{O}}^\cdot + \frac{1}{2}O_2(\text{g})$$

(4.25)

Another way of representing this equilibrium is

$$\left(\text{La}_{1-x}^x\text{Cr}_{1-x}^\cdot_{\text{Cr}} \right) \left(\text{Cr}_{1-x+2\delta}^\cdot_{\text{Cr}} \right) \left(\text{Mg}^\cdot_{\text{Cr}} \right) \left(\text{O}_{3-\delta}^\cdot_{\text{O}} \right) =$$

$$\left(\text{La}_{1-x}^x\text{Cr}_{1-x+2\delta}^\cdot_{\text{Cr}} \right) \left(\text{Cr}_{1-x+2\delta}^\cdot_{\text{Cr}} \right) \left(\text{Mg}^\cdot_{\text{Cr}} \right) \left(\text{O}_{3-\delta}^\cdot_{\text{O}} \right) + \frac{1}{2}O_2(\text{g})$$

(4.26)

The equilibrium constant $K_{25}$ for reaction (4.25) is given by,

$$K_{25} = \frac{[\text{Cr}^x_{\text{Cr}}]^2 [V_{\text{O}}^\cdot]}{[O_{\text{O}}^x] [\text{Cr}^\cdot_{\text{Cr}}]^2} p_{O_2}^{1/2}$$

(4.27)

or in terms of mole fractions

$$K_{25} = \frac{(1-2x+2\delta)^2 \delta}{(x-2\delta)^2 (3-\delta)} p_{O_2}^{1/2}$$

(4.28)

This equation can be solved analytically for $\delta$, assuming $1-2x+2\delta = 1$ and $3-\delta = 3$, yielding the physically relevant solution [9]

$$\delta = \frac{1}{2} \left[ x - \frac{p_{O_2}^{1/2}}{12 K_{25}} \left( 24 x K_{25} p_{O_2}^{-1/2} + 1 \right)^{1/2} - 1 \right]$$

(4.29)
The assumption that $1-2x+2\delta = 1$ is valid for low magnesium doping levels, which is the case for EVD layers of Mg-doped LaCrO$_3$, as was discussed in Chapter 3.

Also other defect models have been proposed for Mg-doped LaCrO$_3$ [28-34]. Flandermeyer et al. [28-31] used a defect model based on the Schottky equilibrium, which is expressed by

$$n\text{il} = V_{\text{La}}^{m''} + V_{\text{Cr}}^{m''} + 3V_O^{\cdot}$$

(4.30)

To determine the influence of the oxygen partial pressure on the oxygen ion vacancy concentration, the following defect equilibrium was assumed

$$V_{\text{La}}^{m''} + V_{\text{Cr}}^{m''} + 6\text{Cr}^{\cdot} + 3O_O^x = 6\text{Cr}^{x} + \frac{3}{2}O_2(g)$$

(4.31)

However, it is unlikely that this defect equilibrium determines the oxygen ion vacancy concentration in Mg-doped LaCrO$_3$, because the presence of trivalent cation vacancies in ternary metal oxides is not favoured thermodynamically [35].

In the proposed defect model, it is assumed that all defects are randomly distributed over the lattice. Singhal et al. [32], and Van Roosmalen and Cordfunke [34] have proposed defect models in which the formation of defect clusters is assumed. They suggest that the Cr$^{3+}$ ions next to an oxygen ion vacancy are different from the other Cr$^{3+}$ ions in the lattice. This assumption that Cr$^{3+}$ ions and V$_O^{\cdot}$ form clusters is rather questionable, because oxygen ion vacancies move as isolated defects through the lattice, and, therefore, they are after every jump surrounded by other Cr$^{3+}$ ions. Furthermore, no explanation could be given why regular lattice Cr$^{3+}$ ions should trap oxygen ion vacancies. Van Roosmalen and Cordfunke [34] have also proposed a defect model in which the preferential formation of (Mg$^{\cdot}$Cr$^{\cdot}$-$V_O^{\cdot}$-Mg$^{\cdot}$Cr$^{\cdot}$)$^x$ clusters is assumed. The corresponding defect equilibrium can be represented by

$$(La_{La}^x)[Cr_{Cr}^{\cdot}]_x[Cr_{Cr}^{x}]_{1-2x}[Mg_{Cr}^{'\cdot}]_x[O_O^x]_3 =$$

(4.32)

$$(La_{La}^x)[Cr_{Cr}^{\cdot}]_{x-2\delta}[Cr_{Cr}^{x}]_{1-2x+2\delta}[Mg_{Cr}^{'\cdot}]_{x-2\delta}[(Mg_{Cr}^{'\cdot}-V_O^{\cdot}-Mg_{Cr}^{'\cdot})]^x[O_O^x]_{3-\delta} + \frac{\delta}{2}O_2(g)$$

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The equilibrium constant $K_{32}$ for this equilibrium is given by

$$K_{32} = \frac{(1 - 2x + 2\delta)^2 \delta}{(x - 2\delta)^4 (3 - \delta)} p_{O_2}^{1/2} \quad (4.33)$$

Although this model seems to describe the experimentally determined oxygen ion vacancy concentrations as a function of $p_{O_2}$ by Flandermeyer et al. [28-31] best, it is not used for the modelling of the EVD process, because it is impossible to derive an intelligible analytical expression for $\delta$ as a function of $p_{O_2}$ from Equation (4.33). Furthermore, no corroborating evidence is given that $(\text{Mg}_{Cr}^\text{O};\text{O}_{Cr})^x$ clusters are indeed present in Mg-doped LaCrO$_3$ at the high temperatures at which the EVD process is performed, and why these should be the only type of defect clusters present. If this type of cluster were to be present, then isolated defects and $(\text{Mg}_{Cr}^\text{O};\text{O}_{Cr})$ associates are to be expected as well.

By combining Equations (4.23) and (4.29), the expression for the parabolic growth rate constant becomes

$$K_0 = -\frac{D_L}{6} p_{O_2}^\circ \int_0^{p_{O_2}} \left\{ 1 - \frac{1}{12} \left[ \frac{24xK_{25}p_{O_2}^{1/2} + 1}{(A^{1/2} + 1)^{1/2}} \right] \right\} \ d \ln p_{O_2} \quad (4.34)$$

Integration of Equation (4.34) yields,

$$K_0 = \frac{D_L}{6} \left[ x \ln \left( \frac{A^{1/2} + 1}{2} \right) - \frac{2x}{A^{1/2} + 1} \right] \quad (4.35)$$

with

$$A = 24xK_{25}p_{O_2}^{-1/2} + 1 \quad (4.36)$$

The derivation of Equation (4.35) is given in Appendix A.

Numerical values of the equilibrium constant $K_{25}$ can be obtained from experimental TGA-data from Flandermeyer et al. [28-31]. Quantitative values of the parabolic growth
rate constant can be calculated, provided the oxygen ion vacancy diffusion coefficient and the oxygen partial pressure on the metal chloride side are known. The oxygen ion vacancy diffusion coefficient is determined from literature data. Using this diffusion coefficient the parabolic growth rate constant is calculated as a function of various process parameters, and the results are discussed.

4.3 SOLID STATE TRANSPORT IN EVD LAYERS DEPOSITED ON GASTIGHT SUBSTRATES.

When a film is grown on a gastight oxide ion conducting substrate by means of EVD, film growth can be limited either by surface kinetics or by solid state diffusion through the substrate and/or the growing film. A schematic representation of the diffusion processes, which take place during the growth process, is given in Figure 4.2. Again, solid state diffusion is considered to determine the growth process, and it is assumed that thermodynamic equilibrium is established at the gas/solid interfaces, and at the substrate/film interface. Therefore, there will be no discontinuity in the oxygen chemical potential at the substrate/film interface. The oxygen chemical potential at this interface will be expressed in terms of an interface oxygen partial pressure $p_{O_2}^I$.

During the EVD process, the substrate thickness $L_s$ remains constant. At the start of the process, when the film thickness $L_f=0$, the interface oxygen partial pressure $p_{O_2}^I$ is equal to the oxygen partial pressure on the metal chloride side ($p_{O_2}^*$). With increasing film thickness, the interface oxygen partial pressure has to increase also, because the oxygen chemical potentials (or partial pressures) at the gas/solid interfaces are fixed, and the oxygen chemical potential at the substrate/film interface has to lie between these limits. Hence, the interface oxygen partial pressure is a function of the film thickness, and, as a consequence, a function of time.

![Figure 4.2: Diffusing species during EVD growth on a gastight substrate.](image)

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The interface oxygen partial pressure is an important parameter in the growth process, because it determines the ionic transport in the substrate as well as in the growing film. Therefore, it is essential to obtain an accurate description or accurate estimates of this parameter as a function of film thickness or process time in order to be able to predict the film growth behaviour.

During the growth process, the system is in a quasi steady state, and the ionic and electronic fluxes in both the substrate and the growing film must be uniform [18, 20]. Inevitably, the oxygen ion flux through the substrate must be equal to the oxygen ion flux through the growing film. In our case, the deposition of an electronic conductor on an almost pure oxygen ion conductor, i.e. the deposition of Mg-doped LaCrO₃ on YSZ, is considered. Therefore, the ionic flux through the substrate (YSZ) is given by Equation (4.3), substituting $p_{O_2}^i$ for $p_{O_2}^{*}$. Similarly, the ionic flux through the growing film (Mg-doped LaCrO₃) is given by Equation (4.19), substituting $p_{O_2}^i$ for $p_{O_2}^{*}$. The oxygen ion flux through the composite is now given by,

$$
J_i = -\left(\frac{RT}{8F^2} \int \sigma_{cl}^s d\ln p_{O_2}^s \right) \frac{1}{L_s} = -\left(\frac{RT}{8F^2} \int \sigma_{ion}^f d\ln p_{O_2}^f \right) \frac{1}{L_f}
$$

(4.37)

where s stands for substrate, and f for film.

The growth rate of the film is determined by the ionic flux according to Equation (4.3). Therefore, by combining Equations (4.3), (4.20), and (4.21) with the right-hand side of Equation (4.37), the growth rate of the LaCrO₃ film is given by,

$$
\frac{dL_f}{dt} = -\left(\frac{D^f}{6 \int \sigma_{O_2}^f d\ln p_{O_2}^f} \right) \frac{1}{L_f} = K_1
$$

(4.38)

where $K_1$ is a growth rate parameter, which is a function of $p_{O_2}^i$ and which equals $K_0$ when $p_{O_2}^i = p_{O_2}^{*}$. This equation can not readily be solved, because the integral itself is, through $p_{O_2}^i$, a function of $L_f$ [18]. Hence, after substitution of Equation (4.29) for $\delta^f$, the time dependence of the film thickness is given by

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\[
\frac{L_f}{L_s} = \frac{\int_{0}^{\rho_{O_2}} \frac{L_f dL_f}{\int_{p_{O_2}}^{1/2} x \left[ \frac{p_{O_2}^{f/2}}{12K_{25}[(24xK_{25}p_{O_2}^{f-1/2} + 1)^{1/2} - 1]} \right] d \ln p_{O_2}}}{\frac{D_{v_o}^{f}}{6}} = -\frac{4F^2D_{V_o}^{f} p_{O_2}^s}{RTV_m^f L_f p_{O_2}} \frac{\int_0^1 (\sigma_p^0 p_{O_2}^{1/4} + \sigma_n^0 p_{O_2}^{-1/4})^s d \ln p_{O_2}}{\int_0^1 \delta^f d \ln p_{O_2}}
\]

This equation can be solved when an analytical description for \(p_{O_2}^f\) as a function of \(L_f\) is known. An expression for \(p_{O_2}^f\) as a function of \(L_f\) might be obtained from Equation (4.37). Combining this equation with Equations (4.14), (4.15), (4.20), and (4.21) yields

\[
\frac{1}{L_s} \int_{p_{O_2}}^{1/4} \frac{(\sigma_p^0 p_{O_2}^{1/4} + \sigma_n^0 p_{O_2}^{-1/4})^s d \ln p_{O_2}}{\int_0^1 (\sigma_p^0 p_{O_2}^{1/4} + \sigma_n^0 p_{O_2}^{-1/4})^s d \ln p_{O_2}} = 4F^2D_{V_o}^{f} p_{O_2}^s = \frac{\int_0^1 \delta^f d \ln p_{O_2}}{\int_0^1 \delta^f d \ln p_{O_2}}
\]

By integration of Equation (4.40), after substituting Equation (4.29) for \(\delta^f\), the following expression is obtained,

\[
\frac{L_f}{L_s} = \frac{A(p_{O_2}^f)}{\left(\sigma_p^0 p_{O_2}^{1/4} + \sigma_n^0 p_{O_2}^{-1/4}\right)^s}
\]

where \(A\) is given by Equation (4.36). From Equation (4.41) it is clear that, at fixed reaction conditions, \(p_{O_2}^i\) is constant for a given \(L_f/L_s\) ratio. Because it is not possible to obtain an intelligible analytical description for \(p_{O_2}^i\) as a function of \(L_f/L_s\), Equation (4.41) has to be solved numerically for discrete values of \(L_f/L_s\). The solutions of these calculations are used to calculate the time to grow films of thickness \(L_f\) on a substrate of thickness \(L_s\), using Equation (4.38). In this way, the time dependence of the film thickness can be calculated for different values of \(L_s\). In order to determine the influence of \(p_{O_2}\) and the temperature on the process, these calculations have to be repeated for various values of \(p_{O_2}^i\) and \(T\).
At the start of the EVD process \((L_f=0)\), the film growth rate is determined by the oxygen ion flux through the YSZ substrate. Therefore, the film growth rate at \(t=0\) is found by combining Equations (4.3), (4.5), (4.14), and (4.15), yielding,

\[
\left( \frac{dL_f}{dt} \right)_{t=0} = k_0 = \frac{RT V_m^f}{6F^2 L_s} \left( \sigma^0_p (p_{O_2}^{1/4} - p_{O_2}^{1/4}) + \sigma^0_n (p_{O_2}^{1/4} - p_{O_2}^{1/4}) \right) \tag{4.42}
\]

For \(t>0\), the film growth rate is given by Equation (4.39), as discussed earlier. Numerical values of \(p_{O_2}^\ddagger\) are determined as a function of various process parameters. Using these values, the time dependence of the film thickness is determined and the results are evaluated.

### 4.4 Modelling of EVD Growth on Porous Supports

#### 4.4.1 Modelling of EVD growth of YSZ

##### 4.4.1.1 Thermodynamic calculations

In order to calculate the parabolic growth rate constant using Equation (4.18), the oxygen partial pressure on the metal chloride side of the YSZ film has been calculated as a function of reaction conditions. Although yttrium chloride \((YCl_3)\) is a reactant in the EVD process, only the presence of zirconium-containing species has been considered in the calculations for simplicity. It is assumed that the equilibrium oxygen partial pressure near the surface of the EVD film is determined by the equilibrium between the growing film and the gaseous input species. For low oxygen partial pressures, the actual equilibrium between zirconium tetrachloride \((ZrCl_4)\) and zirconia \((ZrO_2)\), i.e. the EVD film of YSZ, can be written as,

\[
ZrCl_4(g) + 2O^X_O = ZrO_2(s) + 4e^- + 2V^\ddagger_O + 2Cl_2(g) \tag{4.43}
\]

and for high oxygen partial pressures as

\[
ZrCl_4(g) + 4h^- + 2O^X_O = ZrO_2(s) + 2V^\ddagger_O + 2Cl_2(g) \tag{4.44}
\]

These equilibria, describing non-stoichiometry, can be expressed as a function of oxygen
partial pressure by incorporating the equilibrium between ZrCl₄ and oxygen

\[
\text{ZrCl}_4(g) + \text{O}_2(g) = \text{ZrO}_2(s) + 2\text{Cl}_2(g)
\]  \hspace{1cm} (4.45)

The actual partial pressure of oxygen on the metal chloride side can be governed by experimental conditions which affect the partial pressures of the species in reaction (4.45).

As long as the conversion of reactant in the EVD process is relatively low, \(p_{\text{O}_2}^*\) can be determined, provided the partial pressure of chlorine is known. Chlorine is not an input species in the EVD process, but it is a product formed by chemical reaction. So, the partial pressure of chlorine will be determined in one of the following ways:

(a) by the conversion of metal chloride reactant at the metal oxide surface. However, this partial pressure of chlorine is determined by the growth rate of the film itself and is dependent on several mass transport processes such as adsorption, desorption, and gas phase diffusion. This complex set of mass transport processes makes it very difficult to obtain realistic values of the chlorine partial pressure.

(b) by the dissociation of ZrCl₄.

\[
3 \text{ZrCl}_4(g) = \sum_{n=1}^{3} \left( \text{ZrCl}_n(g) + (4-n)\left[\frac{(1-a)}{2}\text{Cl}_2(g) + a\text{Cl}(g)\right] \right) \hspace{1cm} a \in [0,1] \]  \hspace{1cm} (4.46)

Because the equilibrium in reaction (4.45) still holds, \(p_{\text{O}_2}^*\) can be calculated from this equilibrium.

(c) by the presence of oxygen in the carrier gas stream. This will have a major influence on the partial pressures of the species present in reaction (4.45).

Cases (b) and (c) can be studied by calculation of the thermodynamic equilibrium present in the gas phase on the metal chloride side.

The thermodynamic equilibria have been computed as a function of temperature and partial pressures of the input species. It was assumed that the species listed in Appendix B can be present in the reactor. Throughout all calculations, the total pressure was kept constant at 0.01 atm.

The presence of yttrium-containing species is neglected for simplicity. In general, the presence of yttrium-containing species in the gas phase will result in lower equilibrium partial pressures of oxygen-containing species, due to the formation of solid YOCl, as was shown by calculations in which yttrium-containing species were taken into account. Consequently, for the thermodynamic calculations, the EVD film is considered to consist of pure ZrO₂.

The thermodynamic calculations were split into two sections. The first section comprised thermodynamic calculations with only ZrCl₄, Ar, and ZrO₂(s) as input species, while a large excess of ZrO₂(s) with respect to ZrCl₄, i.e. \(\left[ZrO_2\right]_{\text{input}} \geq 100\times\left[ZrCl_4\right]_{\text{input}}\)
was chosen in order to simulate the presence of the EVD film. This set of calculations is used to study the effect of the dissociation of ZrCl₄, *i.e.* case (b). In Figure 4.3, the equilibrium partial pressures of the main species, with the exception of the input species, because of their large excess, are presented as a function of temperature. The equilibrium partial pressures of all species, with exception of ZrCl₄, increase with increasing temperature, indicating that the decomposition of ZrCl₄ and ZrO₂(s) becomes more important. The thermodynamic calculations as a function of the input amount of ZrCl₄ reveal that the equilibrium partial pressures of all species are proportional or inversely proportional to a n-th power of the input amount of ZrCl₄, because of its large excess, where n can be 0, 0.5, and 1, respectively [36]. From these results all existing equilibria can be calculated.

The second set of calculations comprised calculations with ZrO₂(s), ZrCl₄, and O₂ as input species. This set of calculations is used to study the effect of the presence of oxygen in the input carrier gas, *i.e.* case (c). These calculations may be of more practical use, because the carrier gas always contains a small amount (<1 ppm) of oxygen and water impurities, even if a conventional gas cleaning system is used.

**Figure 4.3:** The equilibrium partial pressure $p_{xx}$ of the main species as a function of temperature, where the input partial pressure of ZrCl₄ is $10^{-3}$ atm, and the input partial pressure of oxygen is kept zero. ZrO₂(s) is present in large excess.
Only the influence of oxygen impurity has been considered in the calculations, because at these low impurity levels the effect of a certain amount of water on the equilibrium oxygen partial pressure is nearly equal to the effect which half of the same amount of oxygen has. The variation of the input partial pressure of oxygen may have a large influence on the equilibrium partial pressures of the other species. The thermodynamic calculations as a function of temperature reveal that the equilibrium partial pressure of oxygen is high with respect to the equilibrium partial pressure of oxygen for case (b), where no oxygen was taken into account as input species.

The equilibrium partial pressures of the main species as a function of the input partial pressure of oxygen are presented in Figure 4.4. The equilibrium partial pressures of the species are determined by the input amount of ZrCl₄ as long as the input partial pressure of oxygen is less than 10⁻⁸ atm. However, if the input partial pressure of oxygen exceeds 10⁻⁸ atm, then the equilibrium partial pressure of oxygen increases steeply. From these observations it can be concluded that the presence of oxygen in the carrier gas stream has no influence on the equilibrium partial pressures of the gas phase species provided the oxygen impurity in the carrier gas stream is less than 1 ppm, i.e. 10⁻⁸ atm in the reactor as calculated.

**Figure 4.4:** The equilibrium partial pressure $p_{xx}$ of the main species as a function of the input partial pressure of oxygen at a temperature of 1373 K, where the input partial pressure of ZrCl₄ is 10⁻³ atm. ZrO₂(s) is present in large excess.
4.4.1.2 Review of EVD experiments

All the reported data of film thickness as a function of deposition time have been fitted according to Equation (4.2). This equation was chosen to verify as to whether solid state diffusion is the general rate-limiting step in the EVD growth of YSZ in the reported studies [4-13]. In all EVD growth experiments approximately 8 to 10 mol% yttria was formed. All reported EVD growth data could be fitted well by the parabolic growth rate equation (4.2), except the data of Isenberg [4], who obtained linear growth behaviour, indicating that either gas phase diffusion or surface reaction kinetics was the rate-limiting step.

There are two factors which cause uncertainties in the determination of $K_0$ from experimental data. First, there is the uncertainty in the EVD growth time. Often the growth rate is represented as a function of the total process time [4,6,10-13], which also includes the pore closure time. This pore closure time is not always exactly known. Secondly, the film thickness is determined from SEM micrographs. This means that the film thickness is measured from the substrate surface, and that it is assumed that pore closure has taken place on the substrate surface. However, it is very well possible that pore closure has occurred somewhere in the pores of the substrate. Lin et al. [12] have discussed the influence of the CVD reaction mechanism, the reaction conditions, and the pore geometry on the pore closure. In case the pore closure has taken place in the pores of the substrate, the real thickness of the EVD film is larger than the measured one, leading to too small values of $K_0$. Another source of error can be the presence of a porous CVD layer on the substrate surface. The formation of porous CVD layers has been described by Isenberg [4], for the EVD growth of gadolinia-doped ceria, and by Schoonman et al. [7-9], for the EVD growth of YSZ under certain experimental conditions. When such a layer is present, the EVD film thickness is smaller than the total film thickness in the SEM micrograph. If the porous films are difficult to distinguish on the SEM micrographs, this may lead to errors in the values of $K_0$.

The reported growth rate data have been evaluated, taking the uncertainties described above into account. Therefore, where possible, the minimum and maximum value of $K_0$ has been determined from the experimental data. The fitted parabolic growth rate constants derived from the experimental data are given in Table 4.1, and presented as an Arrhenius plot in Figure 4.5. The strong temperature dependence justifies the assumption that the process is indeed controlled by solid state diffusion. The slope of the fitted line is proportional to the apparent activation energy of the process. This apparent activation energy is a function of the activation energy for electron conduction in YSZ, and the change in enthalpy of the equilibrium on the metal chloride side, if solid state diffusion is assumed to be rate-limiting, and all other reaction rates are assumed to be infinite. The apparent activation energy is determined to be $3.6\pm0.6$ eV, which is nearly
equal to the activation energy for electron conduction in YSZ, i.e. 3.88 eV [22], or 3.72 eV [37], indicating that the change of \( p_{O_2} \) with temperature is very small.

**Table 4.1:** Minimum and maximum values of \( K_0 \) for EVD growth of YSZ, determined from growth rate data (10^{-10}cm^2/s).

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<td>-</td>
<td>-</td>
<td>0.12-0.25</td>
</tr>
<tr>
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<td>0.11-0.35</td>
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<td>38</td>
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**Figure 4.5:** Arrhenius plot of the experimental parabolic growth rate constants. (*) minimum \( K_0 \) values; (■): maximum \( K_0 \) values. The solid line represents the least squares fit through the data points.
4.4.1.3 Modelling results

Theoretical parabolic growth rate constants have been calculated from Equation (4.18), using the data of Park and Blumenthal [22], and of Kleitz et al. [37] for the electron conductivity of YSZ, respectively. The parameters necessary for the calculation are given in Table 4.2.

First, the parabolic growth rate constants were calculated for the case that dissociation of ZrCl₄ determines the equilibrium oxygen partial pressure on the metal chloride side, i.e. case (b). The equilibrium oxygen partial pressures were obtained from the calculations where only ZrCl₄, ZrO₂(s), and Ar were used as input species. The results of these calculations for different input concentrations of ZrCl₄ are presented in Figures 4.6(a) and (b). The parabolic growth rate constant in Figures 4.6(a) and (b) decreases with increasing ZrCl₄ input concentration owing to the increasing equilibrium partial pressure of oxygen, thereby reducing the chemical potential gradient across the film.

Table 4.2: Parameters used to calculate the theoretical values of K₀ for EVD growth of YSZ.

<table>
<thead>
<tr>
<th>Parameter</th>
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<tr>
<td>Vₘ(cm³/mol)</td>
<td>20.7</td>
<td>molar volume of ZrO₂</td>
</tr>
<tr>
<td>C</td>
<td>3.82</td>
<td>for 8 m/o YSZ</td>
</tr>
<tr>
<td>σₙ₀ (10⁷ S/cm)</td>
<td>1.31</td>
<td>pre-exponential factor for electron conduction for 8 m/o YSZ for pO₂ = 1 atm, from ref. [22]</td>
</tr>
<tr>
<td>Eₐ (eV)</td>
<td>3.88</td>
<td>activation energy for electron conduction for 8 m/o YSZ, from ref. [22]</td>
</tr>
<tr>
<td>σₙ₀ (10⁵ S/cm)</td>
<td>5.5</td>
<td>pre-exponential factor for electron conduction for 8 m/o YSZ for pO₂ = 1 atm, from ref. [37]</td>
</tr>
<tr>
<td>Eₐ (eV)</td>
<td>3.72</td>
<td>activation energy for electron conduction for 8 m/o YSZ, from ref. [37]</td>
</tr>
</tbody>
</table>
Figure 4.6a: The calculated parabolic growth rate constant as a function of temperature, when oxygen is not considered to be an input species; electron conductivity data taken from Park and Blumenthal [22].

Line A: $P_{ZrCl_4}^{(input)} = 10^{-6}$ atm, line B: $P_{ZrCl_4}^{(input)} = 10^{-5}$ atm,
line C: $P_{ZrCl_4}^{(input)} = 10^{-4}$ atm, and line D: $P_{ZrCl_4}^{(input)} = 10^{-3}$ atm.

Figure 4.6b: Same as Figure 4.6a; electron conductivity data taken from Kleitz et al. [37]
As can be seen in Figure 4.4, the equilibrium oxygen partial pressures used for the
calculation of the parabolic growth rate constants are so low that YSZ is not in its
electrolytic domain, which means that the oxygen ion vacancy concentration can not be
considered constant. The oxygen ion vacancy concentration and electron concentration
are then proportional to the oxygen partial pressure to the power -1/6 [20]. Thus, the
electron conductivity data used are not valid anymore. In this oxygen partial pressure
region it is even possible that the mass transport in YSZ is determined by the oxygen ion
conductivity instead of the electron conductivity.

However, these calculations remain indicative and can still be used to evaluate the
experimental data of EVD growth. The predicted parabolic growth rate constants are far
too high with respect to the observed parabolic growth rate constants. This discrepancy
can not be explained by the fact that YSZ is not in its electrolytic domain, because the
calculated parabolic growth rate constant is still far too high when the low oxygen partial
pressure limit of the electrolytic domain of YSZ, i.e. $p_{O_2} = 10^{-23}$ atm, is used.

Yttrium-containing species have not been considered within the thermodynamic
calculations. However, this can not be the explanation for the calculated parabolic
growth rate constant being too high, because the calculated equilibrium partial pressure
of oxygen is even lower if yttrium-containing species are taken into account. This would
result in still higher theoretical parabolic growth rate constants.

Only ZrCl$_4$, Ar, and ZrO$_2$(s) were considered as input species in the thermodynamic
calculations discussed above. However, it is not likely that the carrier gases used in the
experiments, i.e. argon and helium, are completely free of oxygen. Hence, the influence
of small amounts of oxygen in the carrier gas stream on the growth rate has to be
investigated.

In order to study the influence of oxygen as an impurity in the carrier gas stream,
thermodynamic calculations have been performed using O$_2$, ZrCl$_4$, ZrO$_2$(s), and Ar as
input species. Again, the parabolic growth rate constants were calculated using Equation
(4.18). The results of these calculations are presented in Figures 4.7(a) and (b). If the
input partial pressure of oxygen drops below $10^{-12}$ atm, the calculated parabolic growth
rate constant remains unaffected. The equilibrium partial pressure of oxygen in this case
is determined by the input amounts of ZrCl$_4$ and ZrO$_2$(s). Hence, the parabolic growth
rate constant is the same as in the situation where oxygen is not an input species. Thus,
lines D in Figures 4.6(a) and (b) are equal to lines A and B in Figure 4.7(a), and to line
A in Figure 4.7(b), respectively.

If the conductivity data of Park and Blumenthal [22] are considered to be correct, the
temperature dependence of the calculated theoretical parabolic growth rate constant,
represented by solid line E in Figure 4.7(a), seems to describe the experimental parabolic
growth rate constant reasonably well. This calculated parabolic growth rate constant is
obtained using an input oxygen partial pressure of $10^{-4}$ atm.

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Figure 4.7a: The calculated parabolic growth rate constant as a function of temperature at a ZrCl₄ input partial pressure of 10⁻³ atm for different input partial pressures of oxygen; electron conductivity data taken from Park and Blumenthal [22].

(■): experimental parabolic growth rate constants.
Line A: p₀₂ (input) = 10⁻¹⁶ atm, line B: p₀₂ (input) = 10⁻¹² atm,
line C: p₀₂ (input) = 10⁻⁸ atm, line D: p₀₂ (input) = 10⁻⁶ atm,
line E: p₀₂ (input) = 10⁻⁵ atm, and line F: p₀₂ (input) = 10⁻⁴ atm.

Figure 4.7b: Same as Figure 4.7a; electron conductivity data taken from Kleitz et al. [37].
For that input amount of oxygen, the equilibrium oxygen partial pressure ranges from $9 \times 10^{-12}$ atm at 1273 K to $3 \times 10^{-11}$ atm at 1473 K. The apparent activation energy of this parabolic growth rate constant, calculated from the slope of the line, is 3.5 eV. This activation energy is slightly smaller than the activation energy for electron conduction in YSZ, because $P_{O_2}^*$ decreases with increasing temperature, which has a retarding effect on the growth rate. Hence, the experimental results can be understood assuming an oxygen impurity concentration in the carrier gas of $10^4$ ppm.

If the conductivity data of Kleitz et al. [37] are considered to be correct, the experimental parabolic growth rate constant is described best if an oxygen impurity concentration of $10^{-5}$ atm, i.e. $10^3$ ppm, is assumed. Then, the equilibrium oxygen partial pressure is approximately $3 \times 10^{-14}$ atm in the temperature range from 1273 to 1473 K. The apparent activation energy of this parabolic growth rate constant is 3.7 eV. This activation energy is close to the activation energy for electron conduction, because $P_{O_2}^*$ remains almost constant in this temperature region. Therefore, it has no influence on the apparent activation energy of the process. The apparent activation energies determined from the model calculations are almost equal to the apparent activation energy determined from the experimental data.

However, it is unlikely that the amounts of oxygen, giving rise to good agreement between model calculations and experiments, are present in the carrier gas. In the EVD experiments reviewed, the oxygen impurity level in the carrier gases ranged from 1 to 600 ppm [5,12]. Yet, if parabolic growth is assumed and the oxygen concentration in the carrier gas is assumed to be of the order of 1 to 10 ppm, the predicted growth rate is too high, as discussed earlier. A possible explanation is that the expressions used to describe the electron conduction in YSZ are not valid for EVD films.

As can be seen in Table 4.2 the activation energies for electron conduction found by Park and Blumenthal [22], and Kleitz et al. [37] are in reasonable agreement. Also other investigators have found activation energies for electron conduction in the range of 3.7 to 3.8 eV [37]. However, there is a considerable difference in the pre-exponential factors. These differences may be caused by the different experimental conditions used for measuring the electronic conductivity, or by questionable interpretation of the experimental data, as was discussed by Kleitz et al. [37]. Furthermore, it should be noted that the electronic conductivity data used for these calculations were obtained from sintered YSZ samples. Therefore, it might be possible that the actual electronic conductivity in the EVD layers differs from the electronic conductivity data used in the calculations, e.g. owing to the incorporation of chlorine or hydrogen during the EVD process, or grain boundary polarization phenomena, owing to differences in microstructure, resulting in a lower electronic conductivity of the YSZ.

There are no data available on the electronic conductivity of EVD layers of YSZ. However, it is possible to determine the expression for the electron conduction from the EVD experiments, if solid state transport is the rate-determining step. If an oxygen
impurity level of 10 ppm is assumed, then the equilibrium oxygen partial pressure is on the order of $5 \times 10^{-21}$ atm in the temperature range from 1273 to 1473 K. If it is also assumed that the activation energy for electron conduction equals 3.8 eV, then the pre-exponential factor of the electron conduction in EVD layers of YSZ at an oxygen partial pressure of 1 atm ($\sigma^0_n$, $\sigma^0_p$) can be determined from Figure 4.5 and Equation (4.18), yielding a value of $2.6 \times 10^4$ atm$^{1/4}$S/cm, which is a factor 20 smaller than the value obtained by Kleitz et al. [37]. Because of this large difference, it is impossible that uncertainties or variations in the yttrium doping concentration of the various EVD films can account for this discrepancy. After all, the pre-exponential factor is only inversely proportional to the square root of the yttrium dopant concentration. To find out whether the electronic conductivity in EVD films of YSZ is indeed smaller than in sintered samples e.g. oxygen semipermeability measurements need to be performed.

Another explanation for the fact that the predicted growth rate constant is too high is that solid state diffusion is not the only rate-limiting step. If the EVD layer grows thick enough, solid state diffusion will eventually become the only rate-limiting step, but in the early stages of the process, one of the other three transport steps in the EVD process, or a combination of steps, may be rate-limiting. If one of the other transport steps, i.e. charge transfer across the interfaces or pore diffusion, is rate-limiting, linear growth behaviour is expected. Since all experimental data could be fitted well by the parabolic growth equation, it is not expected that one of these transport steps is the only rate-limiting step in the EVD experiments reviewed.

In case of a combination of rate-limiting steps, the situation becomes more complex, and growth behaviour between linear and parabolic might be possible. From the observation that the predicted growth rate is too high, it might be concluded that the EVD layer acts as an oxygen pump, and that only a small portion of the total oxygen flux through the EVD layer contributes to the actual growth. This might result in an increase of the oxygen chemical potential (or partial pressure) on the metal chloride side.

The ratio between the observed and the predicted growth rate is then proportional to the conversion of transported oxygen to metal oxide. For low input oxygen partial pressures, i.e. $\leq 10^{-12}$ atm, this ratio (conversion) increases with increasing temperature, and varies from a few tenths of a percent to a few percent typically, as can be seen in Figure 4.8. This information can only be used in a qualitative way, because the low conversion of oxygen will affect the actual oxygen partial pressure on the metal chloride side, and, consequently, the oxygen flux through the film. Besides, the assumption that solid state diffusion is rate-limiting, and that all other reaction rates are infinite can not be valid anymore. These observations suggest an EVD process which is determined by a combination of solid state diffusion and surface kinetics.
Figure 4.8: The conversion of oxygen to metal oxide at the surface of the EVD layer on the metal chloride side as a function of temperature, for low input partial pressures of oxygen, calculated using electron conductivity data of Park and Blumenthal [22].

The increase in conversion with increasing temperature might be explained in terms of some limitations in the surface kinetics. However, at this stage this suggestion for the mechanism of EVD growth can not readily be verified, because to our knowledge there are no reliable data available concerning the surface kinetics between $O_2$ and $ZrCl_4$. Furthermore, a reaction model comprising the elementary steps of the major reaction pathways for the formation of the EVD film has to be developed. In principle, an EVD growth rate constant can be calculated by a numerical solution of the mass transport through the film and the kinetics at the surface, provided that the required data are known. Consequently, this calculated growth rate constant has to be compared with experimental data of EVD growth to verify as to whether the EVD growth is indeed controlled by a combination of solid state diffusion and surface kinetics.

Recently, Sasaki et al. [13] have proposed a reaction mechanism for EVD growth of YSZ, assuming a combination of rate-limiting steps. They suggest that their experimental results can be explained best if a combination of electron transport through the YSZ film and the reaction between surface oxygen and the metal chlorides is assumed to be rate-limiting. They conclude that a combination of electron transport and surface kinetics is rate-limiting because they measure a homogeneous yttrium distribution across the YSZ film. According to them, it is impossible to obtain a homogeneous yttrium distribution
across the YSZ film if electron transport is the only rate-limiting step, because the ratio of yttria over zirconia in the EVD film is a function of the ratio \( p_{Cl_2}^2 / p_{O_2}^2 \), and \( p_{Cl_2} \) is not constant during the EVD process. However, this conclusion is not correct, because if it is assumed that electron transport through the YSZ film is the only rate-limiting step, then it is also assumed that the chemical reactions are rapid such that thermodynamic equilibrium exists at the film/gas interface. According to the thermodynamic equilibrium calculations the ratio \( p_{Cl_2}^2 / p_{O_2} \) is constant during the process, and thus the ratio of yttria over zirconia in the YSZ film should also be constant.

4.4.2 Modelling of EVD growth of Mg-doped LaCrO₃

4.4.2.1 Determination of the temperature dependence of \( K_{25} \) and \( D_{V_O} \)

Before the EVD growth of Mg-doped LaCrO₃ can be modelled, the temperature dependence of the defect equilibrium constant \( K_{25} \) and the oxygen ion vacancy diffusion coefficient \( D_{V_O} \) have to be known. An expression for \( K_{25} \) as a function of temperature has been determined from oxygen loss measurement data of Flandermeyer et al. [28-31]. Because the magnesium doping level in EVD layers of Mg-doped LaCrO₃ is a few percent at the most, the temperature dependence of \( K_{25} \) has been determined from the results of TGA measurements on LaCr₉₈%Mg₀₂O₃₋δ samples. Flandermeyer et al. have measured the oxygen loss of this material as a function of oxygen partial pressure at various temperatures. These data were fitted to Equation (4.29) using a non-linear least-squares fit routine, yielding values of \( K_{25} \) at various temperatures. From an Arrhenius plot of these equilibrium constants, the temperature dependence of \( K_{25} \) was calculated to be

\[
K_{25} = 4.0 \times 10^5 \exp \left( \frac{-3.2 \text{eV}}{kT} \right) \tag{4.47}
\]

Now, the oxygen ion vacancy concentration in Mg-doped LaCrO₃ is known as a function of oxygen partial pressure and temperature. Figure 4.9 shows the oxygen ion vacancy concentration as a function of oxygen partial pressure for various temperatures, calculated with Equations (4.29) and (4.47). \([V^-_O]\) approaches the limiting value of 0.5×[MgCr] at low oxygen partial pressures, and zero at high oxygen partial pressures. In the figure, the data points of Flandermeyer et al. at 1473 K are also shown. In general, there is a reasonable agreement between the proposed model and the data points, except at high oxygen partial pressures, where the weight loss of the samples is dominated by impurities, leading to too high measured values of \([V^-_O]\) [28].

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Figure 4.9: The oxygen ion vacancy concentration in LaCr\textsubscript{0.98}Mg\textsubscript{0.02}O\textsubscript{3-δ} as a function of equilibrium oxygen partial pressure for different temperatures. Line A: T=1673 K, line B: T=1573 K, line C: T=1473 K, line D: T=1373 K, and line E: T=1273 K. (■): experimental data at 1473 K from Flandermeyer [28].

An expression for the oxygen ion vacancy diffusion coefficient had to be determined as well, because no expressions for $D_{Vo}$ were available. Singhal et al. [32] have measured the oxygen permeability of a 30 μm thick, leak-free, EVD layer of Mg-doped LaCrO$_3$ at 1273 K. From their measurements, $D_{Vo}$ was calculated to be 2.1×10^{-9} cm$^2$/s. The calculation of this value is given in Appendix C. A value of $D_{Vo}$ at another temperature, was obtained from the time dependence of the film thickness of EVD grown LaCr\textsubscript{0.98}Mg\textsubscript{0.02}O\textsubscript{3}, deposited at 1603 K, by Pal and Singhal [14,15]. They calculated a value of $0.18\times10^{-8}$ cm$^2$/s for the parabolic growth rate constant. Substituting this value in Equation (4.35), with $p_{O_2}=10^{-4}$ atm and $p_{O_2}^* = 10^{-15}$ atm, $D_{Vo}$ was calculated to be $9.8\times10^{-8}$ cm$^2$/s. From the two calculated values of $D_{Vo}$ its temperature dependence was determined to yield

$$D_{Vo} = 0.287 \exp \left( \frac{-2.1 \text{eV}}{kT} \right) \text{ (cm}^2/\text{s})$$  \hspace{1cm} (4.48)

In comparison with other perovskite oxides, $D_{Vo}$-values obtained from Equation (4.48) are rather small. The activation energy falls within the range of activation energies for
oxygen ion vacancy diffusion in perovskite oxides, although it is near the upper limit [39]. By incorporating Equations (4.47) and (4.48) in Equations (4.35) and (4.36), the EVD growth of Mg-doped LaCrO$_3$ can be modelled. The model calculations will be discussed in the next paragraph.

4.4.2.2 Modelling results

In this paragraph, the effect of various process parameters on the EVD growth of Mg-doped LaCrO$_3$ will be modelled. The model calculations were performed using Equations (4.35), (4.36), (4.47), and (4.48). The conditions and parameter values used are listed in Table 4.3. In the model calculations it is assumed that the magnesium content in the EVD layers is 0.02, and that it is independent of process conditions.

First, the effect of the oxygen partial pressure on either side of the growing film on the parabolic growth rate constant is investigated. Figure 4.10 shows the effect of the oxygen partial pressure on the oxygen-rich side ($p_{O_2}^*$) on $K_0$ for different values of $p_{O_2}$. The growth rate remains virtually unaffected in a large range of $p_{O_2}^*$ for the case of $p_{O_2}$ being at least three orders of magnitude larger than $p_{O_2}$. If the difference between $p_{O_2}$ and $p_{O_2}^*$ is less than three orders of magnitude, $K_0$ decreases with decreasing $p_{O_2}$. For example, $K_0$ decreases from $1.0\times10^{-9}$ cm$^2$/s to $7.4\times10^{-10}$ cm$^2$/s with $p_{O_2}$ decreasing from $10^{-4}$ atm to $10^{-11}$ atm, for the case of $p_{O_2}^* = 10^{-14}$ atm. A further decrease of $p_{O_2}$ with two orders of magnitude to $10^{-13}$ atm leads to a decrease of $K_0$ to $2.7\times10^{-10}$ cm$^2$/s.

Table 4.3: Conditions and parameters used to calculate the theoretical values of $K_0$ for EVD growth of Mg-doped LaCrO$_3$.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Remark</th>
</tr>
</thead>
<tbody>
<tr>
<td>T (K)</td>
<td>1273-1673 K</td>
<td></td>
</tr>
<tr>
<td>$p_{O_2}$ (atm)</td>
<td>$10^{-16}$-$10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>$p_{O_2}^*$ (atm)</td>
<td>$10^{-16}$-$10^{-4}$</td>
<td></td>
</tr>
<tr>
<td>x</td>
<td>0.02</td>
<td>Mg doping level</td>
</tr>
<tr>
<td>$V_m$ (cm$^3$/mol)</td>
<td>35.44</td>
<td>molar volume of LaCrO$_3$, from ref. [38]</td>
</tr>
<tr>
<td>$P_{reactor}$ (atm)</td>
<td>0.01</td>
<td></td>
</tr>
</tbody>
</table>
Figure 4.10: The calculated parabolic growth rate constant for Mg-doped LaCrO$_3$ ($x_{Mg}=0.02$) at 1573 K as a function of $p_{O_2}$ for different values of $p_{O_2}^*$. 

Line A: $p_{O_2}^* = 10^{-16}$ atm, line B: $p_{O_2}^* = 10^{-14}$ atm, line C: $p_{O_2}^* = 10^{-12}$ atm, 
line D: $p_{O_2}^* = 10^{-10}$ atm, and line E: $p_{O_2}^* = 10^{-8}$ atm.

Furthermore, it can be seen in Figure 4.10 that the growth rate increases with decreasing $p_{O_2}^*$. So, as long as a low oxygen partial pressure is established on the metal chloride side, $p_{O_2}$ has little influence on the growth rate. Hence, careful control of $p_{O_2}$ during the growth process, in order to obtain a constant film growth, is not necessary.

Figure 4.11 shows the effect of $p_{O_2}$ on $K_0$ for different values of $p_{O_2}$. For $p_{O_2}^* > 10^{-14}$ atm, $K_0$ decreases sharply with increasing $p_{O_2}^*$. For $p_{O_2} = 10^{-6}$ atm, $K_0$ decreases from $4.7 \times 10^{-10}$ cm$^2$/s to $3.3 \times 10^{-12}$ cm$^2$/s with $p_{O_2}^*$ increasing from $10^{-12}$ atm to $10^{-7}$ atm. For $p_{O_2}^* < 10^{-14}$ atm, $K_0$ increases only slightly with decreasing $p_{O_2}^*$, and it seems to approach a limiting value. This can be explained by the fact that film growth is limited by the oxygen ion conductivity of the film, which depends on the concentration of oxygen ion vacancies. Therefore, it is obvious that $K_0$ shows a similar dependence of the oxygen partial pressure as $[V_{O}^-]$. As discussed earlier, $[V_{O}^-]$ approaches the limiting value of $0.5x[\text{MgCr}_3]$ at low oxygen partial pressures, so $K_0$ is also expected to reach a limit. Thus, the highest film growth rate is obtained when $p_{O_2}^* \leq 10^{-16}$ atm. Like Figure 4.10, Figure 4.11 shows that $K_0$ is independent of $p_{O_2}$ for large differences between $p_{O_2}$ and $p_{O_2}^*$.
Figure 4.11: The calculated parabolic growth rate constant for Mg-doped LaCrO$_3$ ($x_{Mg}=0.02$) as a function of p$_{O_2}^*$ at 1573 K, for different values of p$_{O_2}$.
Line A: p$_{O_2}$ = $10^{-10}$ atm, line B: p$_{O_2}$ = $10^{-8}$ atm, line C: p$_{O_2}$ = $10^{-6}$ atm, and line D: p$_{O_2}$ = $10^{-4}$ atm.

K$_0$ is strongly dependent on p$_{O_2}^*$ especially for p$_{O_2}^*>10^{-14}$ atm. Because p$_{O_2}^*$ is assumed to be determined by the thermodynamic equilibrium between the metal chlorides and the growing film, it may have a strong temperature dependence, and, therefore, may exert a strong influence on the relation between the parabolic growth rate constant and temperature.

Thermodynamic equilibrium calculations in the La-Cr-O-Cl-Ar system, using the data file given in Appendix A of Chapter 3, and neglecting the presence of magnesium-containing species, were performed in order to obtain estimates for p$_{O_2}^*$ as a function of temperature. These calculations are similar to case (c) in paragraph 4.4.1.1, i.e. the equilibrium oxygen partial pressure is assumed to be determined by the following equilibrium between the metal chlorides, the EVD film, and the oxygen present as impurity in the carrier gas:

$$\text{LaCl}_3(g) + \text{CrCl}_3(g) + \frac{3}{2} \text{O}_2(g) = \text{LaCrO}_3(s) + 3\text{Cl}_2(g)$$  (4.49)
The input concentrations of LaCl$_3$ and CrCl$_3$ were taken to be 1%, and the input partial pressure of oxygen was increased from $10^{-16}$ atm to $10^{-4}$ atm. The total reactor pressure was kept at 0.01 atm.

Figure 4.12 shows the equilibrium oxygen partial pressure as a function of temperature, for different input (impurity) oxygen partial pressures. An increase of the input oxygen partial pressure from zero to $10^{-8}$ atm, i.e. an impurity level of 1 ppm, has no effect on the equilibrium oxygen partial pressure (line A). A further increase of the input oxygen partial pressure with two orders of magnitude to $10^{-6}$ atm leads to a small increase in the equilibrium oxygen partial pressure (line B). For temperatures up to 1473 K, the equilibrium oxygen partial pressure increases with increasing temperature. In this temperature region, both Cr$_2$O$_3$ and LaCrO$_3$ are stable solid species. Therefore, in order to obtain pure LaCrO$_3$, the temperature should be higher than 1473 K, because beyond this temperature LaCrO$_3$ is the only stable solid species, as was discussed in Chapter 3. Beyond 1473 K the equilibrium oxygen partial pressure increases only marginally with increasing temperature, i.e. from $3.8\times10^{-10}$ atm at 1473 K to $5.6\times10^{-10}$ atm at 1673 K. Hence, the temperature dependence of $K_\Omega$ for $T>1473$ K, only contains the temperature dependencies of the defect equilibrium constant and the oxygen ion vacancy diffusion coefficient.

![Figure 4.12: The equilibrium oxygen partial pressure in the metal chloride chamber as a function of temperature, for different input oxygen partial pressures. Line A: $P_{O_2}(\text{input})\leq10^{-8}$ atm, and line B: $P_{O_2}(\text{input})=10^{-6}$ atm.](image_url)
Figure 4.13: The calculated parabolic growth rate constant for $\text{LaCr}_{0.08}\text{Mg}_{0.02}\text{O}_3$ as a function of temperature, in the temperature range of 1473-1673 K, with $P_{O_2}^* = 4.5 \times 10^{-10}$ atm.

Figure 4.13 shows the temperature dependence of the EVD process. From Equations (4.35) and (4.36) it can be understood that the parabolic growth rate will not obey the Arrhenius law. However, if the calculated parabolic growth rate constant is represented in an Arrhenius plot, the resulting line shows only a very slight curvature. Therefore, it is possible to determine an apparent activation energy for the EVD growth of Mg-doped LaCrO$_3$, by fitting the curved line to the Arrhenius equation. In the temperature range of 1473 to 1673 K, with $P_{O_2}^* = 4.5 \times 10^{-10}$ atm, $K_0$ can be estimated from the equation

\[ K_0 = 1.94 \times 10^5 \exp \left( -\frac{4.8 \text{ eV}}{kT} \right) \]  

(4.50)

Hence, in this temperature region the apparent activation energy for the EVD growth of Mg-doped LaCrO$_3$ is 4.8 eV.

Figure 4.14 shows the parabolic growth rate constant as a function of the magnesium content in the EVD film, at 1573 K, assuming all other reaction conditions to be constant. The plot has been calculated for magnesium contents less then 4 at%, because under EVD conditions the maximum magnesium solubility in LaCrO$_3$ is only a few percent, as was discussed in Chapter 3. The parabolic growth rate constant increases with
increasing magnesium content in the EVD film. This can be explained by the fact that, at the low equilibrium oxygen partial pressure on the metal chloride side, part of the incorporated magnesium ions is compensated by oxygen ion vacancies, as can be seen in Figure 4.9. According to Equation (4.29), the oxygen ion vacancy concentration will increase with increasing magnesium content, and, therefore, the parabolic growth rate constant will increase too. An increase in the magnesium content in the EVD film, and, hence, a higher growth rate, can be achieved by increasing the input amount of MgCl₂ in the reactor, as was discussed in Chapter 3.

The information in Figure 4.14 can be used to determine whether or not, for certain reaction conditions, the EVD film contains the maximum amount of magnesium. This knowledge is important, because, with the low maximum magnesium solubility in LaCrO₃ under EVD conditions, it is desired that the magnesium doping level is as high as possible, because then the EVD film is expected to have the highest electronic conductivity. By increasing the input amount of MgCl₂ in the reactant stream, with respect to LaCl₃ and CrCl₃, while keeping the other reaction conditions constant, the growth rate will increase, until from a certain input amount of MgCl₂ it will remain constant. This is an indication that, for the reaction conditions used, the maximum possible magnesium doping level is reached.

![Graph](image)

**Figure 4.14:** The calculated parabolic growth rate constant for Mg-doped LaCrO₃ as a function of the mole fraction of magnesium, for T=1573 K and pO₂ = 4.5×10⁻¹⁰ atm.
4.5 MODELLING OF EVD GROWTH OF DOPED LaCrO₃ ON GASTIGHT YSZ

4.5.1 Determination of \( p_{O_2}^0 \)

\( P_{O_2}^0 \) is an important parameter in the EVD film growth on gastight substrates. Knowledge of \( p_{O_2}^0 \) is necessary in order to be able to determine the film growth behaviour. As discussed in paragraph 4.3, it is not possible to obtain an analytical solution for \( p_{O_2}^0 \) as a function of the film thickness. Therefore, \( p_{O_2}^0 \) has been calculated numerically for a large number of \( L_f/L_s \) ratios, in the range of \( 10^{-6} \leq L_f/L_s \leq 2 \), for \( 1273 \leq T \leq 1673 \), and \(-16 \leq \log(p_{O_2}^0) \leq -10\), using Equation (4.41). The calculations have been performed using the data of Park and Blumenthal [22] for the electronic conductivity of YSZ. Furthermore, it is assumed that the magnesium content in the deposited Mg-doped LaCrO₃ films is 0.02, and that it is independent of process conditions.

Figure 4.15 shows \( p_{O_2}^0 \) as a function of the ratio \( L_f/L_s \) for different values of \( p_{O_2}^* \) at temperatures of 1273 K, 1473 K, and 1673 K, respectively, with \( p_{O_2} = 10^{-4} \) atm. The curves are obtained by linear interpolation between the calculated points. For very small \( L_f/L_s \) ratios, \( p_{O_2}^0 \) approaches \( p_{O_2}^* \), because at the start of the process \( L_f = 0 \), and thus \( p_{O_2}^0 = p_{O_2}^* \). In the early stages of the growth process, \( i.e. \) at small \( L_f/L_s \) ratios, the difference between \( p_{O_2}^0 \) and \( p_{O_2}^* \) is still very small, and the oxygen chemical potential gradient is almost completely located in the substrate. In that case, the growth process is (mainly) determined by the oxygen ion diffusion through the YSZ substrate. Assuming all other reaction steps to be rapid such that they are in thermodynamic equilibrium, the oxygen ion flux through the YSZ substrate is inversely proportional to the substrate thickness, and, because the thickness of the YSZ substrate is constant during the growth process, linear growth behaviour is expected in the early stages of the growth process. From a certain \( L_f/L_s \) ratio on, \( p_{O_2}^0 \) starts to increase considerably with increasing \( L_f/L_s \) ratio. At low temperature (1273 K), this increase is very steep. Because \( p_{O_2}^0 \) increases, the oxygen chemical potential gradient gradually shifts from the substrate to the growing film. With increasing \( p_{O_2}^* \), the oxygen chemical potential gradient shifts to the growing film at smaller \( L_f/L_s \) ratios. With increasing temperature, the increase in \( p_{O_2}^0 \) becomes more gradual, and starts at larger \( L_f/L_s \) ratios for \( p_{O_2} = 10^{-10} \) atm, whereas for \( p_{O_2} \geq 10^{-13} \) atm this increase in \( p_{O_2}^0 \) starts at smaller \( L_f/L_s \) ratios. Eventually, for large \( L_f/L_s \) ratios \( p_{O_2}^0 \) approaches \( p_{O_2}^* \). The chemical potential gradient is then completely located in the growing film, and growth behaviour should be identical to the EVD growth on porous supports. Using the numerically calculated values of \( p_{O_2}^0 \), the influence of the process parameters on the film growth behaviour has been determined, and the results will be discussed.
Figure 4.15a: The calculated interface oxygen partial pressure ($p_{O_2}^i$) as a function of the ratio of film thickness and substrate thickness, for $T=1273$ K.

Line A: $p_{O_2}^i = 10^{-10}$ atm, line B: $p_{O_2}^i = 10^{-13}$ atm, and line C: $p_{O_2}^i = 10^{-16}$ atm.

Figure 4.15b: The same as Figure 4.15a, for $T=1473$ K.
Figure 4.15c: The same as Figure 4.15a, for $T=1673$ K.

4.5.2 Time dependence of $L_t$

The EVD film growth rate is given by Equation (4.38), which is equal to the growth rate equation for parabolic growth if $p_{O_2}^i$ is replaced by $p_{O_2}^*$. Because $p_{O_2}^i$ is a function of $L_t$, the growth rate parameter $K_1$ will be a function of $L_t$ and, as a consequence, growth will not be parabolic. Growth behaviour will be parabolic when $K_1$ has become independent of $p_{O_2}^*$.

Information on the effect of a change in $p_{O_2}^i$ on $K_1$ can be obtained from Figure 4.10. It is clear from Figure 4.10 that only for relatively small differences between $p_{O_2}^i$ and $p_{O_2}^*$, i.e., $<4$ orders of magnitude, $K_1$ is affected by a change in $p_{O_2}^i$. Hence, in the early stages of the growth process, when the ratio $L_{t}/L_s$ is small, $K_1$ will be a function of film thickness (or time), because the difference between $p_{O_2}^i$ and $p_{O_2}^*$ is small, and growth behaviour will not be parabolic. If the difference between $p_{O_2}^i$ and $p_{O_2}^*$ is more than 4 orders of magnitude, which will happen if the $L_{t}/L_s$ ratio becomes large enough, $K_1$ will be virtually unaffected by a change in $p_{O_2}^i$, and film growth will obey parabolic law.

The interface oxygen partial pressure has been calculated for a large number of $L_{t}/L_s$ ratios. Hence, for a given value of $L_s$, $p_{O_2}^i$ is known for a large number of values of $L_t$. Using Equation (4.38) the film growth rate has been calculated at these values of $L_t$. Figure 4.16 shows some typical graphs of the film growth rate as a function of the reciprocal film thickness, for different process conditions.
Figure 4.16a: The calculated EVD film growth rate as a function of the reciprocal film thickness, for $T=1473$ K and $p_{O_2} = 10^{-10}$ atm.
Line A: $L_s=0.004$ cm, line B: $L_s=0.02$ cm, and line C: $L_s=0.1$ cm.

Figure 4.16b: The same as Figure 4.16a, for $T=1473$ K and $p_{O_2} = 10^{-13}$ atm.
In these plots, the growth rate is shown for four values of $L_s$, i.e. $L_s = 0 \text{ cm}, 0.004 \text{ cm}, 0.02 \text{ cm}, \text{ and } 0.1 \text{ cm}$, respectively. The growth rate of films deposited on porous supports is also shown. From these plots (lines B and C) it is clear that initially the growth rate is almost constant, and that, for large film thicknesses, the growth rate becomes proportional to the reciprocal film thickness, and equal to the growth rate of EVD films deposited on porous substrates. Therefore, it can be concluded that, during the deposition of Mg-doped LaCrO$_3$ films on gastight YSZ, initially growth behaviour is linear and that it gradually changes to parabolic with increasing film thickness. This growth behaviour can be explained as follows: in the early stages of the growth process, oxygen ion diffusion through the substrate is the limiting factor. At given reaction conditions, this flux is inversely proportional to $L_s$. Because $L_s$ remains constant, the oxygen ion flux through the substrate remains constant and, as a consequence, the growth rate also remains constant. As $L_f$ increases, the oxygen ion transport through the growing film becomes more important, and the growth rate starts to decrease. Because YSZ is a much better oxygen ion conductor than Mg-doped LaCrO$_3$, this decrease already starts at very small $L_f/L_s$ ratios, depending on process conditions. If $L_f$ increases further, the growth rate is increasingly limited by the oxygen ion transport through the growing film, until finally it is the only rate-limiting step in the growth process. In that case, growth behaviour has become parabolic.

It is obvious that, as soon as film growth has started, the growth rate starts to decrease. However, initially the decrease in growth rate is negligible and growth can be regarded to be linear. Therefore, for given reaction conditions, the film thickness, above which growth can no longer be regarded linear ($L_{f_{\text{max}}}$), only depends on arbitrarily chosen criteria. The same holds for the film thickness above which growth behaviour can be regarded parabolic ($L_{f_{\text{min}}}$). In this study, growth is considered to be linear as long as the difference between $L_f(t)$, according to the model, and $L_f(t)$, i.e. the film thickness that would be obtained if the initial growth rate is maintained, is less than 5%. Growth is considered to be parabolic as soon as the difference between the growth rate according to the model, i.e. Equation (4.38), and the growth rate in case of permanent parabolic growth behaviour, i.e. Equation (4.23), is less than 5%.

The growth rate data have been used to calculate the time dependence of $L_f$. The time to grow a film of thickness $L_f$ on a substrate of thickness $L_s$ has been calculated assuming that, as long as film growth is not parabolic, the growth rate is constant in a small interval $\Delta L_f$. The film growth rate has been calculated for $n$ values of $L_f$, i.e. $L_{f_1}$, ..., $L_{f_n}$. In the interval $\Delta L_{f_k} = L_{f_k} - L_{f_{k-1}}$ the growth rate is assumed to be equal to the mean growth rate $\frac{1}{\Delta L_f}(K_{L,f}/L_{f_k} + K_{L,k-1}/L_{f_{k-1}})$. If the film thickness exceeds a certain minimum value $L_{f_{\text{min}}}$, growth behaviour becomes parabolic, and $K$ will be independent of $L_f$. 111
Therefore, the time to grow a film of thickness $L_{f,k} < L_{f,m}$ is given by,

$$
t_k = \sum_{i=1}^{k(sm)} \frac{(L_{f,i} - L_{f,i-1})}{1 \left[ \frac{K_{l,i}}{L_{f,i}} + \frac{K_{l,i-1}}{L_{f,i-1}} \right] + \frac{K_{l,i}}{2}} \left( \frac{L_{f,i} - L_{f,i-1}}{L_{f,i} + L_{f,i-1}} \right)
$$

(4.51)

whereas the time to grow a film of thickness $L_{f,k} > L_{f,m}$ is given by

$$
t_k = \sum_{i=1}^{m} \frac{(L_{f,i} - L_{f,i-1})}{1 \left[ \frac{K_{l,i}}{L_{f,i}} + \frac{K_{l,i-1}}{L_{f,i-1}} \right]} + \sum_{i=m}^{k} \frac{(L_{f,i} - L_{f,i-1})}{2K_{l,i}}
$$

(4.52)

The value of $m$ depends on the criteria for growth to be considered parabolic. Figure 4.17 shows some typical graphs of the time dependence of $L_f$ for different process conditions, and for the same values of $L_s$ as in Figure 4.16. As discussed above, growth behaviour should gradually change from linear to parabolic, irrespective of the substrate thickness. However, the time scale for this transition to take place depends on the substrate thickness and process conditions. Figure 4.17 shows that, for reasonable process times, film growth behaviour can still be linear for thick substrates, whereas for much thinner substrates the growth behaviour is already parabolic.

Figure 4.17a: The calculated EVD film thickness as a function of deposition time for $T=1273\ K$ and $p_{O_2} = 10^{-16}\ atm$.
Line A: $L_s=0.004\ cm$, line B: $L_s=0.02\ cm$, and line C: $L_s=0.1\ cm$. 

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Figure 4.17b: Same as Figure 4.17a, for $T=1473$ K and $p_{O_2}^* = 10^{-16}$ atm.

Figure 4.17c: Same as Figure 4.17a, for $T=1473$ K and $p_{O_2}^* = 10^{-10}$ atm.
It is clear that the initial linear growth rate \((k_0)\), \(L_{f,max}\) and \(L_{f,min}\) all depend on the substrate thickness and process conditions. The parameters \(L_{f,max}\) and \(L_{f,min}\), as well as the time to deposit films of these thicknesses, \(t_{max}\) and \(t_{min}\), have been determined from the calculated growth rate data, for different values of \(L_s\). The initial linear growth rate and the parabolic growth rate constant have been calculated using Equations (4.42) and (4.23), respectively. The results of these calculations are summarized in Table 4.4.

From Table 4.4 it is clear that, at given reaction conditions, \(L_{f,max}\) and \(L_{f,min}\) are proportional to \(L_s\), indicating that the film growth behaviour depends on the \(L_f/L_s\) ratio. This is not surprising, because the right hand side of Equation (4.41) only contains parameters which are independent of \(L_f\) and \(L_s\). Thus, once \(L_{f,max}\) and \(L_{f,min}\) are known for one value of \(L_s\), they are known for all values of \(L_s\).

The initial linear growth rate, \(k_0\), is proportional to the oxygen ion flux through the substrate, and, therefore, inversely proportional to \(L_s\). The marked points in Figure 4.17 are calculated assuming linear growth with a growth rate \(k_0\). Hence, the conclusion is justified that, according to the model, in the early stages of the EVD process, growth is controlled by oxygen ion diffusion through the YSZ substrate.

With increasing substrate thickness, the period of linear growth is extended. The film thickness \(L_{f,max}\) is proportional to \(L_s\), and \(k_0\) is inversely proportional to \(L_s\), which implies that the period of linear growth, \(t_{max}\), is proportional to \(L_s^2\). For example, at 1273 K, with \(p_{O_2} = 10^{-4}\) atm and \(p_{O_2} = 10^{-16}\) atm, and \(L_s = 0.1\) cm, growth behaviour is linear for \(t < 6.3 \times 10^4\) s, with \(k_0 = 4.22 \times 10^5\) \(\mu m/s\). Under the same conditions, using a substrate with \(L_s = 0.02\) cm, growth is linear for \(t < 2.5 \times 10^3\) s, with \(k_0 = 2.11 \times 10^4\) \(\mu m/s\).

After the period of linear growth, the growth behaviour gradually changes to parabolic. As discussed above, the \(L_f/L_s\) ratio at which film growth becomes purely parabolic is fixed for given process conditions. Therefore, \(L_{f,min}\) is proportional to \(L_s\), and \(t_{min}\) is, like \(t_{max}\), proportional to \(L_s^2\).

The temperature and \(p_{O_2}\) dependence of \(L_{f,max}\), \(L_{f,min}\), \(t_{max}\) and \(t_{min}\) are more complicated. The temperature dependence of these parameters depends on \(p_{O_2}\) and vice versa, because the oxygen ion flux through YSZ and the oxygen ion flux through Mg-doped LaCrO\(_3\) have different temperature and oxygen partial pressure dependencies. With increasing temperature, \(t_{max}\) and \(t_{min}\) decrease, as illustrated by Figure 4.18. With increasing temperature and with decreasing \(p_{O_2}\), \(L_{f,min}\) decreases. For \(L_{f,max}\), however, the temperature and \(p_{O_2}\) dependence show no general tendency.

Irrespective of the temperature and \(p_{O_2}\) dependence of \(L_{f,max}\), \(L_{f,min}\), \(t_{max}\) and \(t_{min}\), the characteristics of the film growth behaviour remain the same for all process conditions. Film growth will start linearly, and will end up parabolically. However, in practice this behaviour may not always be observed because, at high temperatures (\(T > 1473\) K), the period of linear growth is too short to be noticed. If, at these high temperatures, thin substrates are used (\(L_s < 200\) \(\mu m\)), it might not even be possible to discriminate between the transitional growth behaviour, according to the model, and pure parabolic growth.
Table 4.4: Results of the modelling of EVD growth of Mg-doped LaCrO$_3$ on gastight YSZ, with $p_{O_2} = 10^{-4}$ atm.

<table>
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<th>$p_{O_2}$(atm)</th>
<th>T (K)</th>
<th>$L_2$ (cm)</th>
<th>$k_0$ (µm/s)</th>
<th>$L_{i,max}$(µm)</th>
<th>$t_{max}$(s)</th>
<th>$L_{i,min}$(µm)</th>
<th>$t_{min}$(s)</th>
<th>$K_0$(µm$^2$/s)</th>
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Figure 4.18: The calculated transition times $t_{\text{max}}$ (solid lines) and $t_{\text{min}}$ (dashed lines) as a function of temperature, for $L_s=0.02$ cm. Lines A and A': $p_{O_2}^{\alpha} = 10^{-10}$ atm, lines B and B': $p_{O_2}^{\alpha} = 10^{-13}$ atm, and lines C and C': $p_{O_2}^{\alpha} = 10^{-16}$ atm.

In the foregoing discussion, the oxygen partial pressure dependencies of the ionic and electronic conductivities were taken into account. Therefore, it was neither possible to derive an analytical expression for either $p_{O_2}^i$ as a function of $L_p$ nor for $L_f$ as a function of time. Virkar et al. [16-18] have also performed a theoretical analysis of the kinetics of EVD growth on gastight substrates. They have modelled the deposition of a thin film of CeO$_2$ on gastight Y$_2$O$_3$-doped CeO$_2$ for the fabrication of two-layer composite electrolytes for a low-temperature SOFC. They assumed that the ionic and electronic conductivities of the film and the substrate could be considered to be independent of the oxygen partial pressure, thereby simplifying the model.

By applying this simplification, an analytical expression for $p_{O_2}^i$ can be derived from Equation (4.37), yielding,

$$\ln(p_{O_2}^i) = \frac{L_s \sigma_{\text{ion}}^f \ln(p_{O_2}^{\alpha}) + L_f \sigma_{\text{el}}^s \ln(p_{O_2})}{L_f \sigma_{\text{el}}^s + L_s \sigma_{\text{ion}}^f}$$  \hspace{1cm} (4.53)
where $\overline{\sigma}_{\text{ion}}^f$ is the average $p_{O_2}$-independent ionic conductivity of the Mg-doped LaCrO$_3$ film, and $\overline{\sigma}_{\text{el}}^s$ is the average $p_{O_2}$-independent electronic conductivity of the YSZ substrate. Combining this expression for $\overline{p}_{O_2}$ with the right-hand side of Equation (4.37) and Equation (4.3) yields the following expression for the time dependence of $L_f$:

$$L_f^2 + 2 \frac{K_f}{K_s} L_s L_f = 2K_f t$$  \hspace{1cm} (4.54)

with,

$$K_f = -\frac{RT V_{m}^{f} \overline{\sigma}_{\text{ion}}^f}{24F^2} \ln \left( \frac{p_{O_2}}{\overline{p}_{O_2}} \right)$$  \hspace{1cm} (4.55)

and

$$K_s = -\frac{RT V_{m}^{f} \overline{\sigma}_{\text{el}}^s}{24F^2} \ln \left( \frac{p_{O_2}}{\overline{p}_{O_2}} \right)$$  \hspace{1cm} (4.56)

For $L_s=0$, Equation (4.54) reduces to the parabolic growth equation. Because, in fact, the conductivities are dependent on the oxygen partial pressure, it should be checked whether this simplification is justified or not, by presenting the previously calculated film growth data in a plot of $L_f^2$ versus $L_s L_f$. If the simplification is justified, then, for a fixed process time, this plot should yield a straight line. From the slope of this line and its intercept the average $p_{O_2}$-independent conductivities could be determined. Tanner et al. [18] showed that, for the deposition of CeO$_2$ on gastight Y$_2$O$_3$-doped CeO$_2$, the simplification was justified. Figure 4.19 shows a plot of $L_f^2$ versus $L_s L_f$ for $t=1800$ s, 5400 s, and 10800 s, respectively, with $T=1473$ K, $p_{O_2}=10^{-4}$ atm, and $p_{O_2}=10^{-16}$ atm. It is obvious that, for the EVD growth of Mg-doped LaCrO$_3$ on YSZ, at the conditions given, the simplification suggested by Virkar et al. [16-18] is not justified. Hence, the process cannot be modelled by simply determining the average $p_{O_2}$ independent conductivities.

It should be noted that in the previous discussion it was assumed that film growth is determined by solid state transport. However, it might also be possible that in the early stages of the process, especially when very thin substrates are used, film growth is determined by surface kinetics. In that case, film growth behaviour will also be linear initially, and it will indeed change to parabolic if the process is continued long enough.
When surface kinetics are rate-limiting, the observed initial linear growth rate will be smaller than the growth rate calculated from Equation (4.42). The observed initial linear growth rate will remain unaffected if the substrate thickness is halved, whereas it will be doubled if oxygen ion diffusion is the rate-limiting step. Furthermore, if the metal chloride concentrations are changed, without changing the equilibrium oxygen partial pressure, the initial linear growth rate might change if surface kinetics are rate-limiting, otherwise it will remain unaffected.

![Figure 4.19: Numerically calculated plot of $L_i^2$ versus $L_s L_D$ for different process times at $T=1473$ K, with $p_{O_2}^{\infty} = 10^{-16}$ atm and $p_{O_2} = 10^{-4}$ atm. Line A: $t=1800$ s, line B: $t=5400$ s, and line C: $t=10800$ s.](image)

4.6 CONCLUSIONS

The temperature dependence of the experimental parabolic growth rate constant of YSZ is used to verify whether the EVD growth is limited by solid state diffusion. The high observed apparent activation energy of $3.6 \pm 0.6$ eV of the EVD growth justifies the assumption that solid state diffusion is the rate-limiting step. However, the calculated
parabolic growth rate constant is higher than the experimentally determined parabolic growth rate constant.

Traces of oxygen in the metal-chloride-containing compartment of the reactor have a large influence on the calculated parabolic growth rate constant. The experimentally determined parabolic growth rate constant of YSZ can be understood if the presence of $10^4$ or $10^3$ ppm of oxygen in the carrier gas is assumed, depending on the electronic conductivity data for YSZ used. However, it is unlikely that these amounts of oxygen were present in the carrier gases. Hence, the conductivity data used for the calculations are not valid for EVD layers of YSZ, or the growth rate mechanism is more complex than originally assumed, and it might be concluded that only a small portion of the total oxygen flux reacts with the metal chloride to form the metal oxide product. In principle this process can be modelled provided that more data become available on the electronic conductivity of EVD layers, and on the kinetics of EVD and CVD of YSZ using ZrCl$_4$ and O$_2$.

The effect of various process parameters on the EVD growth of Mg-doped LaCrO$_3$ on porous substrates has been investigated, using an expression for the oxygen ion vacancy diffusion coefficient which has been determined from literature data. As long as a low oxygen partial pressure is established on the metal chloride side of the growing film, careful control of the oxygen partial pressure on the oxygen-rich side of the film, in order to obtain constant film growth, is not necessary. The parabolic growth rate constant does not increase continuously with decreasing oxygen partial pressure on the metal chloride side, but approaches a certain limit, because the oxygen ion vacancy concentration, which determines the oxygen ion conductivity, approaches the limiting value of $0.5x[MgCr^+].$

Thermodynamic equilibrium calculations reveal that, for temperatures above 1473 K, the equilibrium oxygen partial pressure on the metal chloride side is almost constant. Hence, at these temperatures the temperature dependence of the parabolic growth rate constant only contains the temperature dependencies of the defect equilibrium constant and the oxygen ion diffusion coefficient. If the parabolic growth rate constant is presented in an Arrhenius plot, the curve shows only a very slight curvature, although the parabolic growth rate constant is not expected to obey Arrhenius law. Therefore, the apparent activation energy of the parabolic growth rate constant could be determined in the temperature range of 1473 to 1673 K, to yield a value of 4.8 eV.

When Mg-doped LaCrO$_3$ is grown on a gastight YSZ substrate, film growth behaviour will initially be linear, and gradually change to parabolic. The oxygen partial pressure at the interface substrate/film is an important parameter in the growth process. This interface oxygen partial pressure is a function of the ratio of the film thickness and the substrate thickness. Growth behaviour will be parabolic, when the difference between the
interface oxygen partial pressure and the oxygen partial pressure on the metal chloride side is more than 4 orders of magnitude. If the oxygen partial pressure dependence of the ionic and electronic conductivities is taken into account, it is not possible to derive an analytical expression for the interface oxygen partial pressure as a function of the film thickness. Therefore, it is also not possible to derive an analytical expression for the time dependence of the film thickness.

The film thickness up to which growth can be considered linear is proportional to the substrate thickness, just as the film thickness from which growth can be considered parabolic. The corresponding process times are proportional to the square of the substrate thickness. The temperature and oxygen partial pressure dependence of these parameters show no regular trend, because of the completely different temperature and oxygen partial pressure dependence of the oxygen ion flux in YSZ, and Mg-doped LaCrO$_3$.

An analytical expression for the time dependence of the film thickness can be derived, when average oxygen partial pressure independent transport properties are used. However, according to the model calculations this simplification is not allowed.

REFERENCES

APPENDIX A

Derivation of the equation for the parabolic growth rate constant for Mg-doped LaCrO$_3$

The parabolic growth rate constant is given by

$$K_0 = -\frac{D_{V^*}^{pO_2}}{6} \int \frac{1}{pO_2} \left[ x - \frac{pO_2^{1/2}}{12 K_{25^1}} [ (24 x K_{25 pO_2^{-1/2}} + 1)^{1/2} - 1 ] \right] d \ln pO_2 \tag{4A.1}$$

This equation can be integrated in three parts:

$$K_A = -\frac{D_{V^*}^{pO_2}}{12} \int \frac{x}{pO_2} d \ln pO_2 \tag{4A.2}$$

$$K_B = -\frac{D_{V^*}^{pO_2}}{144 K_{25^1}} \int pO_2^{1/2} d \ln pO_2 \tag{4A.3}$$

$$K_C = -\frac{D_{V^*}^{pO_2}}{144 K_{25^1}} \int pO_2^{1/2} (24 x K_{25 pO_2^{-1/2}} + 1)^{1/2} d \ln pO_2 \tag{4A.4}$$

Integration of these equations yields

$$K_A = -\frac{D_{V^*}^{pO_2}}{6} x \ln pO_2^{1/2} \left| \begin{array}{c} pO_2 \\ pO_2 \end{array} \right. \tag{4A.5}$$

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\[ K_B = -\frac{D_{V_0}^0}{6} \left( \frac{2x}{(A-1)} \right) \left| \frac{A(\rho_{O_2})}{A(p_{O_2})} \right| \]  

(4A.6)

\[ K_C = \frac{D_{V_0}^0}{6} x \ln p_{O_2}^{1/2} \left. \frac{p_{O_2}^{''}}{p_{O_2}} \right| + \frac{D_{V_0}^0}{6} \left[ x \ln \left( \frac{(A^{1/2}+1)^2}{2} \right) - \frac{2xA^{1/2}}{A-1} \right] \left| \frac{A(\rho_{O_2})}{A(p_{O_2})} \right| \]  

(4A.7)

with

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

(4A.8)

The solution of the integral in Equation (4A.4) has been determined using the software package Mathematica® developed by Wolfram [40]. The overall parabolic growth rate constant is obtained by summation of Equations (4A.5), (4A.6), and (4A.7), i.e. \( K_0 = K_A + K_B + K_C \). The first term on the right-hand side (RHS) of Equation (4A.7) is eliminated by Equation (4A.5), while summation of the second term of the RHS of Equation (4A.7) and Equation (4A.6) is yielding the expression for the parabolic growth rate constant given in Equation (4.35):

\[ K_0 = \frac{D_{V_0}^0}{6} \left[ x \ln \left( \frac{(A^{1/2}+1)^2}{2} \right) - \frac{2xA^{1/2}}{(A^{1/2}+1)} \right] \left| \frac{A(\rho_{O_2})}{A(p_{O_2})} \right| \]  

(4A.9)

This equation is similar to the equation for the parabolic growth rate constant obtained by Schoonman et al. [9].
APPENDIX B

Thermodynamic parameters of the species of the Zr-O-Cl-Ar system.

The input data for the thermodynamic equilibrium calculations consist of the standard enthalpy of formation $\Delta_f^0 H_{298}$, the standard absolute entropy $S^0_{298}$, and the heat capacity $c_p$ of the species. The reference states for the elements are the solid state of zirconium (Zr), and the gaseous state of argon (Ar), chlorine (Cl₂), and oxygen (O₂); all at a temperature of 298.15 K and a pressure of 1×10⁵ Pa. The heat capacity data obtained from the JANAF tables [41] are fitted by the following polynomial function

$$c_p = A + BT + \frac{C}{T^2} + DT^2 + \frac{E}{T^3}$$

(4B.1)

The gaseous species, with their thermodynamic parameters, are listed in Table 4B.1 and the solid species in Table 4B.2. Several species have been omitted, because their influence on the calculations is negligible.

Table 4B.1: Thermodynamic parameters of the gaseous species.

<table>
<thead>
<tr>
<th>species</th>
<th>$\Delta_f^0 H_{298}$</th>
<th>S²⁹⁸</th>
<th>A</th>
<th>B×10⁴</th>
<th>C×10⁻⁴</th>
<th>D×10⁸</th>
<th>E×10⁻⁶</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cl</td>
<td>121.30</td>
<td>165.19</td>
<td>26.54</td>
<td>-52.89</td>
<td>-51.60</td>
<td>144.50</td>
<td>67.50</td>
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<tr>
<td>Cl₂</td>
<td>0.00</td>
<td>233.08</td>
<td>37.62</td>
<td>1.53</td>
<td>-54.23</td>
<td>14.68</td>
<td>62.92</td>
</tr>
<tr>
<td>ClO</td>
<td>101.22</td>
<td>226.65</td>
<td>37.03</td>
<td>9.56</td>
<td>-112.20</td>
<td>-16.59</td>
<td>182.20</td>
</tr>
<tr>
<td>ClO₂</td>
<td>104.60</td>
<td>257.23</td>
<td>56.26</td>
<td>26.80</td>
<td>-315.50</td>
<td>-54.36</td>
<td>543.60</td>
</tr>
<tr>
<td>Cl₂O</td>
<td>87.86</td>
<td>267.96</td>
<td>58.43</td>
<td>-1.62</td>
<td>-164.30</td>
<td>3.48</td>
<td>209.60</td>
</tr>
<tr>
<td>O</td>
<td>249.17</td>
<td>161.06</td>
<td>20.78</td>
<td>0.08</td>
<td>14.70</td>
<td>-0.19</td>
<td>-13.77</td>
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<td>O₂</td>
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<td>205.15</td>
<td>30.34</td>
<td>71.71</td>
<td>-105.30</td>
<td>-184.30</td>
<td>236.80</td>
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<td>ZrCl</td>
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<td>29.06</td>
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<td>878.40</td>
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<td>ZrCl₂</td>
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<td>292.56</td>
<td>65.14</td>
<td>-48.73</td>
<td>-92.91</td>
<td>248.60</td>
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<td>ZrCl₃</td>
<td>-524.26</td>
<td>339.34</td>
<td>83.41</td>
<td>70.94</td>
<td>-170.00</td>
<td>-261.60</td>
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<td>ZrCl₄</td>
<td>-869.98</td>
<td>367.72</td>
<td>108.40</td>
<td>-2.81</td>
<td>-119.80</td>
<td>8.05</td>
<td>90.33</td>
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<tr>
<td>Zr</td>
<td>610.03</td>
<td>183.03</td>
<td>109.40</td>
<td>1347.00</td>
<td>-111.60</td>
<td>-1500.00</td>
<td>0.00</td>
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<tr>
<td>ZrO</td>
<td>58.58</td>
<td>227.63</td>
<td>-107.20</td>
<td>964.90</td>
<td>-258.50</td>
<td>-2140.00</td>
<td>0.00</td>
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<td>ZrO₂</td>
<td>-286.19</td>
<td>273.75</td>
<td>57.56</td>
<td>8.54</td>
<td>-224.60</td>
<td>-29.08</td>
<td>359.00</td>
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<td>Ar</td>
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<td>154.73</td>
<td>20.79</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
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Table 4B.2: Thermodynamic parameters of the solid species. Temperatures and enthalpies of phase transitions, and temperatures of changes in heat capacity functions are indicated in italics.

<table>
<thead>
<tr>
<th>species</th>
<th>$\Delta H^0_{298}$</th>
<th>$S^0_{298}$</th>
<th>A</th>
<th>B$\times10^4$</th>
<th>C$\times10^{-4}$</th>
<th>D$\times10^8$</th>
<th>E$\times10^{-6}$</th>
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</thead>
<tbody>
<tr>
<td>ZrCl$_2$</td>
<td>-430.95</td>
<td>110.04</td>
<td>73.08</td>
<td>139.50</td>
<td>-41.31</td>
<td>-70.60</td>
<td>2.63</td>
</tr>
<tr>
<td>ZrCl$_3$</td>
<td>-714.21</td>
<td>145.81</td>
<td>95.75</td>
<td>207.90</td>
<td>-29.97</td>
<td>-427.60</td>
<td>-52.87</td>
</tr>
<tr>
<td>ZrCl$_4$</td>
<td>-980.52</td>
<td>181.42</td>
<td>124.60</td>
<td>148.00</td>
<td>-78.91</td>
<td>-37.34</td>
<td>-9.18</td>
</tr>
<tr>
<td>Zr</td>
<td>0.00</td>
<td>38.87</td>
<td>22.99</td>
<td>38.78</td>
<td>29.63</td>
<td>400.90</td>
<td>-69.96</td>
</tr>
<tr>
<td>$T=1135 \text{ K}$</td>
<td>4.02</td>
<td>31.84</td>
<td>-92.13</td>
<td>50.67</td>
<td>523.10</td>
<td>-270.60</td>
<td></td>
</tr>
<tr>
<td>ZrO$_2$</td>
<td>-1097.46</td>
<td>50.36</td>
<td>69.62</td>
<td>75.34</td>
<td>-140.50</td>
<td>-0.05</td>
<td>-0.18</td>
</tr>
<tr>
<td>$T=1478 \text{ K}$</td>
<td>5.95</td>
<td>74.48</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td></td>
</tr>
</tbody>
</table>
APPENDIX C.

Calculation of $D_{V_O}$ from permeability measurement data of Singhal et al. [32].

Singhal et al. [32] have measured the oxygen permeability of a 30 μm thick, leak-free, EVD layer of Mg-doped LaCrO$_3$ at 1273 K. The oxygen partial pressure ($p_{O_2}$) on the oxygen rich side of the film was 0.2 atm. On the other side of the film the oxygen partial pressure was determined by the thermodynamic equilibrium of the H$_2$/H$_2$O mixture. At the start of the measurement, the H$_2$/H$_2$O ratio was 2, and the hydrogen partial pressure was 6.5×10$^{-4}$ atm. The equilibrium oxygen partial pressure is calculated to be 1.1×10$^{-14}$ atm. The oxygen flux through the EVD film was determined by monitoring the increase of the water concentration in the H$_2$/H$_2$O mixture, and yielded:

$$j_{V_O} = 3.8 \times 10^{-11} \text{ mole/cm}^2\text{s} \quad (4C.1)$$

Combining Equations (4.1) and (4.3), with for C=6-x=6, yields,

$$j_{V_O} = \frac{3K_0}{V_mL} \quad (4C.2)$$

which is equal to

$$j_{V_O} = \frac{3(K_0/D_{V_O})}{V_mL} \frac{D_{V_O}}{L} \quad (4C.3)$$

$K_0/D_{V_O}$ can be calculated from Equations (4.35) and (4.36), using the above mentioned experimental conditions. From Equation (4C.3), using the value 35.44 cm$^3$/mol for the molar volume of Mg-doped LaCrO$_3$ from ref. [38], $D_{V_O}$ was calculated to be 2.1×10$^{-9}$ cm$^2$/s at 1273 K.
Chapter 5

ELECTROCHEMICAL VAPOUR DEPOSITION
OF UNDOPED AND DOPED LaCrO₃

ABSTRACT

Electrochemical vapour deposition (EVD) is a key technology for the synthesis of the solid oxide fuel cell (SOFC) interconnection material Mg-doped LaCrO₃. CVD/EVD of undoped and Mg-doped LaCrO₃ on porous alumina and calcia-stabilized zirconia (CSZ) has been investigated in the temperature range of 1323 to 1573 K, using the metal chlorides as reactants. When a H₂/H₂O mixture is used as oxygen source, Cr-doped LaAlO₃ films are formed on porous alumina instead of LaCrO₃. When O₂/H₂O mixtures are used, the pore-plugging CVD deposits consist of LaCrO₃ and Cr₂O₃, whereas the EVD films primarily consist of LaCrO₃. Aluminium can easily be incorporated into LaCrO₃ during EVD growth. The electronic conductivities of the undoped LaCrO₃ films in air range from 0.03 to 1.25 S/cm at 1273 K, with activation energies ranging from 0.18 to 0.23 eV, depending on the Cr₂O₃ content. When MgCl₂ is added to the reactant stream, Cr₂O₃, MgCr₂O₄, and LaCrO₃ are formed in the CVD pore-plugging deposits. 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 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.

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5.1 INTRODUCTION

In recent years there has been an enormous increase in the application of thin film technologies in the fabrication of solid state electrochemical devices. Thin film technologies offer the possibility to miniaturize these devices, and to decrease their internal resistance by minimizing the thickness of the individual components. Devices in which thin films are utilized are, e.g. thin-film rechargeable batteries, chemical gas sensors, and solid oxide fuel cells (SOFCs).

In an SOFC, the electrolyte and interconnection material have to be gastight in order to prevent cross-leakage of fuel and oxidant gases. Because the fabrication techniques which are easily amenable for mass production, e.g. tape casting and screen printing, cannot be used on curved surfaces, other methods for the fabrication of the electrolyte and interconnect for the tubular concept SOFC had to be developed. Among the fabrication techniques that have been explored are RF-sputtering, conventional chemical vapour deposition (CVD), and electrochemical vapour deposition (EVD) [1,2]. However, the RF-sputtering process was considered to be too complex, while with conventional CVD it is very difficult to deposit pinhole-free layers on porous substrates.

Electrochemical vapour deposition has become a key technology for the synthesis of the gastight components of the SOFC. The EVD process, which is a modification of the conventional CVD process, was developed in the mid-seventies by Westinghouse [1]. The principle of the EVD process is discussed in detail in Chapter 2. A schematic representation of the two stages of the process is shown in Figure 5.1. In the EVD process, metal halides are volatilized, and passed over one side of a porous substrate. An oxidant gas, e.g. oxygen mixed with steam, is passed over the other side of the substrate. The reactant gases diffuse into the pores of the substrate, where they react. The reaction conditions have to be chosen such that the desired metal oxide product is formed during this CVD stage. After pore closure, film growth proceeds by solid state

\[
\begin{align*}
\text{MeCl}_x(g) + \frac{x}{2} \text{H}_2\text{O}(g) & \rightarrow \text{MeO}_x\text{Cl}_x(s) + x \text{HCl}(g) \\
\text{MeCl}_x(g) + \frac{x}{2} \text{O}_2 & \rightarrow \text{MeO}_x\text{Cl}_x(s) + x e^- + \frac{x}{2} \text{V}_2\text{O}_5 + x \text{Cl}_2(g)
\end{align*}
\]

**Figure 5.1:** Principle of the EVD process.
electrochemical transport through the deposited oxide, owing to the large oxygen chemical potential gradient across the pore-plugging deposit. During this stage of the growth process, the growth rate is limited by a) gas phase diffusion of the reactants, b) solid state diffusion through the deposited material, or c) surface reaction kinetics. If solid state diffusion is the rate-limiting step, the growth process resembles Wagner's oxidation of metals, and growth behaviour is found to be parabolic [3-7]. If gas phase diffusion in the substrate pores or surface reaction kinetics are rate-limiting, growth behaviour is found to be linear [1,2,8,9]. If it is assumed that solid state diffusion and surface reaction kinetics are both rate-determining, the growth behaviour is expected to be intermediate between linear and parabolic [10]. In order to avoid gas phase diffusion control of the EVD reaction, the process is generally carried out at low pressures.

Using the EVD technique, ionically as well as mixed and electronically conducting metal oxides can be synthesized. 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 LaCrO$_3$. Other materials that have been successfully deposited by means of EVD are terbia (Tb$_2$O$_3$) and yttria-co-doped zirconia [11], ceria (CeO$_2$) [12,13], tin (Sn)-doped indium oxide (In$_2$O$_3$) [14], alumina (Al$_2$O$_3$), and chromia (Cr$_2$O$_3$) [2]. A detailed theoretical analysis of the EVD growth of YSZ and Mg-doped LaCrO$_3$ on porous substrates, and of the EVD growth of Mg-doped LaCrO$_3$ on gastight YSZ, assuming solid state electrochemical transport to be rate-determining, has been given in Chapter 4.

To date, very little has been published on the EVD growth of the SOFC interconnection material Mg-doped LaCrO$_3$, and little is known about the kinetics of the process. Only Pal and Singhal [4,5] have reported on the kinetics of the EVD growth of Mg-doped LaCrO$_3$. At a temperature of 1603 K and a pressure less then 30 Pa (3x10$^{-4}$ atm), Mg-doped LaCrO$_3$ was deposited on porous substrates. The oxygen partial pressure on the oxygen-rich side (p$_{O_2}$) was estimated to be 10$^{-9}$ Pa, and on the metal chloride side (p$_{O_2}$) 10$^{-20}$ Pa. No information was given on the concentrations of the metal chlorides in the gas phase, or their ratio. Probably, the La:Mg:Cr ratio in the gas phase was 1:2:3, as reported earlier by Feduska and Isenberg [2], because the composition of the EVD films deposited by Pal and Singhal was the same as those of Isenberg, i.e. LaCr$_{0.98}$Mg$_{0.02}$O$_3$. In Chapter 3, a thermodynamic analysis of the reaction system has been given, which shows 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$_2$. Therefore, a large excess of MgCl$_2$ in the gas phase is necessary to obtain a reasonable doping level [2,15]. At the above-mentioned conditions, the growth of the EVD films appeared to be parabolic. The parabolic growth rate constant was determined to be 0.18x10$^{-8}$ cm$^2$/s.

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

Strontium-doped LaCrO$_3$ has been grown on gastight YSZ substrates. 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. As discussed in Chapter 4, growth behaviour of doped LaCrO$_3$ on gastight YSZ can vary from linear to parabolic, depending on substrate thickness and reaction conditions.

The results of these investigations are presented in this chapter. The observations will be discussed, and compared with the results from the thermodynamic analysis and model calculations presented in Chapters 3 and 4, respectively.

### 5.2 EXPERIMENTAL ASPECTS

#### 5.2.1 Depositions on porous substrates

The majority of the depictions on porous substrates was carried out in the large EVD reactor which has been described in detail in Chapter 2. Two types of substrates were used in these experiments, plasma-sprayed alumina (Groneman) and calcia-stabilized zirconia (CSZ) with approximately 5 wt% CaO (ZR 25, Groneman). The open porosity and pore size distribution of these substrate materials have been determined by mercury porosimetry. Substrate data are summarized in Table 5.1. For each experiment, a substrate was mounted on the alumina support tube, using an alumina-based cement (Ceramabond 569), and left to dry at room temperature for at least one hour. Then, the support tube was placed in the reactor, and the cement was dried overnight at a temperature of 423 K. Between the experiments, the reactor was always kept at this temperature, in order to prevent adsorption of water on the reactor tube.

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Thickness (mm)</th>
<th>Mean pore size (µm)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Plasma-sprayed Al$_2$O$_3$</td>
<td>2.1</td>
<td>1.0</td>
<td>13</td>
</tr>
<tr>
<td>CSZ (ZR25)</td>
<td>1.2 - 2.0</td>
<td>4.7</td>
<td>13</td>
</tr>
</tbody>
</table>

Table 5.1: General data of the two types of porous substrates used.
Anhydrous metal chloride powders, \textit{i.e.} LaCl$_3$ (99.9\%, Aldrich 29,818-2), CrCl$_3$ (99\%, Aldrich 20,005-0), and MgCl$_2$ (98\%, Aldrich 24,413-9) were used as metal source reactants. After filling the metal chloride evaporators, the reactor was closed, and evacuated and refilled with argon three times to remove oxygen and moisture. In most experiments, some titanium grains were put in the gas inlet tubes of the metal chloride evaporators as extra oxygen getters. During heating and stabilization, the metal chloride evaporators were withdrawn from the furnace. No special heating procedure was used to bring the system to the deposition temperature. After the set points had been reached according to the temperature controllers of the furnace, the system was left to stabilize for at least one hour. The system was then checked for (large) leakages, by closing the throttle valve in the pumping line, and, with all flows shut off, monitoring the pressure increase in the reactor. Finally, the in-situ argon permeability of the substrate was measured by applying a pressure difference across it. The pressure in the oxygen compartment was kept at 12 kPa by the pressure control unit, while the pressure in the metal chloride compartment was kept as low as possible by pumping at full capacity. At time $t=0$, the oxygen compartment was isolated from the pump, and the argon flow was stopped. The pressure in the oxygen compartment decreases because argon permeates through the substrate. The pressure decrease was monitored using a recorder that was connected to the pressure transducer.

After these tests the deposition was started. First, the argon bulk flow on the metal chloride side was set at the desired value. Then, the position of the metal chloride evaporators was determined using the corresponding thermocouples on the metal chloride side, and the evaporators were put into position, which led to an immediate temperature drop as was registered by the thermocouples. The evaporators were left to heat up to the desired temperatures, which took about fifteen minutes. Meanwhile, the oxygen (or hydrogen) flow was started, and the desired mixture of oxygen (or hydrogen) and steam was generated by controlling the temperature and pressure of the reflux cooler on the water evaporator. When the metal chloride evaporators were at their desired temperatures, the argon flows through the evaporators were switched on. This was marked as the beginning of the deposition.

At the end of the deposition, the argon flows through the evaporators and the oxygen flows were switched off, and the reactor was evacuated and flushed with argon. After flushing the reactor, the in-situ argon permeability of the substrate was measured again. Finally, the system was cooled down with an average cooling rate of 4 K/min.

The experimental details of the depositions of undoped and Mg-doped LaCrO$_3$ are summarized in Tables 5.2 and 5.3, respectively.
<table>
<thead>
<tr>
<th></th>
<th>Temperatures:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$T_{\text{substrate}}$</td>
</tr>
<tr>
<td></td>
<td>1323 - 1523 K</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{LaCl}_3}$</td>
</tr>
<tr>
<td></td>
<td>1173 - 1240 K</td>
</tr>
<tr>
<td></td>
<td>$T_{\text{CrCl}_3}$</td>
</tr>
<tr>
<td></td>
<td>897 - 927 K</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Reactant flows:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>metal chloride compartment</strong></td>
<td></td>
</tr>
<tr>
<td>$\text{Ar flow}$</td>
<td>0.300 - 0.325 mmol/s</td>
</tr>
<tr>
<td>$\text{LaCl}_3$ flow</td>
<td>0.22 - 1.04 $\mu$mol/s</td>
</tr>
<tr>
<td>$\text{CrCl}_3$ flow</td>
<td>1.78 - 4.01 $\mu$mol/s</td>
</tr>
</tbody>
</table>

|                  | oxygen compartment experiments with $H_2$ experiments with $O_2$ |
|------------------|---------------------------------------------------|---------------------------------------------------|
| $H_2$ flow       | 17.8 $\mu$mol/s                                  | 0 $\mu$mol/s                                      |
| $O_2$ flow       | 0 $\mu$mol/s                                     | 17.8 $\mu$mol/s                                  |
| $H_2O$ flow      | 11.9 $\mu$mol/s                                  | 11.9 $\mu$mol/s                                  |

<table>
<thead>
<tr>
<th></th>
<th>Pressures:</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>metal chloride compartment</strong></td>
<td></td>
</tr>
<tr>
<td>1333 Pa</td>
<td>267 Pa</td>
</tr>
<tr>
<td><strong>oxygen compartment</strong></td>
<td>1333 - 5332 Pa</td>
</tr>
<tr>
<td>1333 Pa</td>
<td>1333 - 2667 Pa</td>
</tr>
<tr>
<td><strong>water evaporator</strong></td>
<td>57.6 kPa</td>
</tr>
<tr>
<td>57.6 kPa</td>
<td>57.6 kPa</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>Reaction time:</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1800 - 9000 s</td>
</tr>
</tbody>
</table>
Table 5.3: Process conditions for the synthesis of Mg-doped LaCrO$_3$ on porous substrates.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperatures:</td>
<td></td>
</tr>
<tr>
<td>$T_{\text{substrate}}$</td>
<td>1413 - 1570 K</td>
</tr>
<tr>
<td>$T_{\text{LaCl}_3}$</td>
<td>1158 - 1249 K</td>
</tr>
<tr>
<td>$T_{\text{CrCl}_3}$</td>
<td>885 - 942 K</td>
</tr>
<tr>
<td>$T_{\text{MgCl}_2}$</td>
<td>951 - 997 K</td>
</tr>
<tr>
<td>Reactant flows:</td>
<td></td>
</tr>
<tr>
<td>Metal chloride compartment</td>
<td></td>
</tr>
<tr>
<td>Ar flow</td>
<td>0.120 mmol/s</td>
</tr>
<tr>
<td>LaCl$_3$ flow</td>
<td>0.43 - 0.54 $\mu$mol/s</td>
</tr>
<tr>
<td>CrCl$_3$ flow</td>
<td>1.17 - 2.26 $\mu$mol/s</td>
</tr>
<tr>
<td>MgCl$_2$ flow</td>
<td>0.22 - 0.81 $\mu$mol/s</td>
</tr>
<tr>
<td>Oxygen compartment</td>
<td></td>
</tr>
<tr>
<td>O$_2$ flow</td>
<td>3.72 $\mu$mol/s</td>
</tr>
<tr>
<td>H$_2$O flow</td>
<td>2.48 $\mu$mol/s</td>
</tr>
<tr>
<td>Pressures:</td>
<td></td>
</tr>
<tr>
<td>Metal chloride compartment</td>
<td>133 - 800 Pa</td>
</tr>
<tr>
<td>Oxygen compartment</td>
<td>100 - 1467 Pa</td>
</tr>
<tr>
<td>Water evaporator</td>
<td>57.6 kPa</td>
</tr>
<tr>
<td>Reaction time:</td>
<td>1800 - 18000 s</td>
</tr>
</tbody>
</table>
The crystalline phases present in the deposits were identified from X-ray diffraction (XRD) patterns which have been recorded using a Philips PW 1840 automated diffractometer with a copper (Cu) X-ray tube. Scanning electron microscopy (SEM) (JEOL JSM-35) was used to obtain film thickness values, and to study the morphology of the deposited layers. Film thickness values were also obtained by optical microscopy, using a Zeiss-Jena Neophot 30 microscope with polarized light. The chemical composition of the deposited films was determined by semi-quantitative energy dispersive X-ray micro analysis (EDX) (Link ISIS, Oxford Instruments Ltd., connected to the JEOL JSM-35), at an acceleration voltage of 20 kV.

The (ex-situ) argon permeability of the films at room temperature was measured by a forced-flow method. The permeability $P$ can be defined as

$$P = \frac{J}{A(P_h - P_f)}$$  \hspace{1cm} (5.1)

where $J$ is the molar flux of the feed gas (mol/s), $A$ the surface area (m$^2$), $P_h$ is the pressure on the feed side (Pa), and $P_f$ is the pressure on the permeate side (Pa). The permeability is proportional to the average pressure across the samples

$$P = C_K + C_P \frac{(P_h + P_f)}{2}$$  \hspace{1cm} (5.2)

where $C_K$ and $C_P$ are constants related to the Knudsen flow and Poiseuille or viscous flow, respectively. The Ar permeability is measured as a function of the average pressure, and the constants $C_K$ and $C_P$ are determined. The EVD films are characterized by the relative permeability,

$$P_{rel} = \frac{P_{tot}}{P_s}$$  \hspace{1cm} (5.3)

where $P_{tot}$ is the permeability of the sample after deposition and $P_s$ the permeability of the bare substrate. The relative permeability is calculated at an arbitrarily chosen fixed average pressure. For a layered structure, e.g. an EVD film on a porous support, the total permeability is given by,

$$\frac{1}{P_{tot}} = \frac{1}{P_{f}} + \frac{1}{P_{s}}$$  \hspace{1cm} (5.4)

where $P_f$ is the permeability of the film. The film permeability can be calculated from the total permeability, assuming that the permeability of the substrate has not changed during the process.
The electronic conductivity of the films deposited on alumina was measured by a conventional two-probe dc measurement technique. Rectangular shaped specimens were cut from the samples, and the electrodes were applied on the film surface. The electrodes were made of platinum lead wires, mounted on the surface with platinum paste to minimize the contact resistance. A constant current was induced in the films, and the potential difference between the two electrodes was measured. The conductivity was measured as a function of temperature in an air ambient. After each temperature change, the specimens were left to equilibrate until the conductivity reached a stationary value.

5.2.2 Depositions on gastight YSZ

Doped LaCrO$_3$ was deposited on gastight YSZ in the small EVD reactor which has been described in detail in Chapter 2. Substrates varying in thickness from 0.250 to 0.500 mm were cut from a fully dense YSZ rod (Gimex, electronic grade, 99.9%, 8 mol% Y$_2$O$_3$) with a diameter of 12 mm.

The substrates were ultrasonically cleaned in concentrated nitric acid or hydrochloric acid, and hexane or acetone. Then they were mounted on the quartz substrate holder with the alumina-based ceramic cement Ceramabond 569, and dried at room temperature for at least six hours. The reactor was heated slowly, with a heating rate of 0.7 to 1.5 K/min. During the warm-up period, the metal chloride evaporation unit was withdrawn from the reactor. When the system reached the deposition temperature, a pressure difference of 2000 Pa was applied across the substrate to check whether the substrate was cracked, by monitoring the pressure increase on the low pressure side. Next, the metal chloride evaporation unit was positioned in the reactor, leading to a large temperature drop. The metal chloride evaporation unit was heated up for fifteen minutes. After this period, the oxygen flow through the water evaporator was switched on, as well as the argon flow through the metal chloride evaporation unit. This was considered to be the start of the deposition. At the end of the deposition, the oxygen flow and the argon flow through the metal chloride evaporation unit were switched off, and it was checked whether the substrate was cracked during the experiment. The evaporation unit was withdrawn from the reactor, and the reactor was flushed several times with argon. After the final flushing, the reactor was brought to atmospheric pressure for cooling down. The cooling rate was the same as the heating rate.

Sr-doped LaCrO$_3$ has been grown on gastight YSZ substrates. For the deposition of Sr-doped LaCrO$_3$, the metal chlorides were generated in-situ by chlorination of the metals, i.e. lanthanum (99.9%, Aldrich 26,311-7), chromium (99.5%, Aldrich 26,626-4), and strontium (99%, Aldrich 34,373-0), with HCl gas (Air Products, 99.9990%). In these experiments, the metal chloride evaporation unit was filled with the metals, and the
argon flow through the evaporation unit was mixed with a small HCl flow. The experimental details of the depositions are summarized in Table 5.4. The deposited films were analyzed by XRD, SEM, and EDX.

**Table 5.4: Process conditions for the deposition of Sr-doped LaCrO$_3$ on gastight YSZ.**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Temperatures:</strong></td>
<td></td>
</tr>
<tr>
<td>$T_{\text{substrate}}$</td>
<td>1348 - 1438 K</td>
</tr>
<tr>
<td>$T_{\text{La}}$</td>
<td>1288 - 1351 K</td>
</tr>
<tr>
<td>$T_{\text{Cr}}$</td>
<td>1251 - 1321 K</td>
</tr>
<tr>
<td>$T_{\text{Sr}}$</td>
<td>930 - 1029 K</td>
</tr>
<tr>
<td><strong>Reactant flows:</strong></td>
<td></td>
</tr>
<tr>
<td>metal chloride compartment</td>
<td></td>
</tr>
<tr>
<td>Ar flow</td>
<td>87 $\mu$mol/s</td>
</tr>
<tr>
<td>HCl flow</td>
<td>2.5 - 3.7 $\mu$mol/s</td>
</tr>
<tr>
<td>oxygen compartment</td>
<td></td>
</tr>
<tr>
<td>$O_2$ flow</td>
<td>17 - 32 $\mu$mol/s</td>
</tr>
<tr>
<td>$H_2O$ flow</td>
<td>1.7 - 3.2 $\mu$mol/s</td>
</tr>
<tr>
<td><strong>Pressures:</strong></td>
<td></td>
</tr>
<tr>
<td>metal chloride compartment</td>
<td>2800 Pa</td>
</tr>
<tr>
<td>oxygen compartment</td>
<td>2000 Pa</td>
</tr>
<tr>
<td>water evaporator</td>
<td>101 kPa</td>
</tr>
<tr>
<td><strong>Reaction time:</strong></td>
<td>1800 - 14400 s</td>
</tr>
</tbody>
</table>
5.3 RESULTS

5.3.1 Depositions on porous substrates

5.3.1.1 Deposition of undoped LaCrO$_3$

5.3.1.1.1 Film morphology

The deposits obtained in the experiments using the H$_2$/H$_2$O mixture as oxygen source reactant (reducing conditions) appear to be very thin, which is illustrated by the facts that the surface structure of the bare alumina substrate can still be recognized, and that on cross-sectional views no film can be observed. Therefore, no values for the film thickness of these samples can be given. The surface of the deposits is faceted. The crystallite size is about 0.5 to 1 $\mu$m. Figure 5.2 shows a typical example of the surface of such a deposit. The deposit is smooth and homogeneously covering the substrate surface. On the surface also several large smooth crystallites of 3 to 6 $\mu$m are observed. These crystallites are also observed on the surface of the bare substrate, and, therefore, most probably part of the substrate material.

The films deposited using a O$_2$/H$_2$O mixture as oxygen source reactant (oxidizing conditions) show different morphologies. Only in the case of short deposition times, the structure of the bare substrate can still be recognized. Two kinds of morphologies are observed, depending on the CrCl$_3$/LaCl$_3$ input ratio. Figure 5.3 shows a surface and a cross-sectional view of a film deposited at 1523 K, with a CrCl$_3$/LaCl$_3$ input ratio of 3.4.

![5.2: SEM micrograph of the surface of a deposit obtained at 1523 K using H$_2$/H$_2$O mixture as oxygen source reactant.](image)

Figure 5.2: SEM micrograph of the surface of a deposit obtained at 1523 K using H$_2$/H$_2$O mixture as oxygen source reactant.
Figure 5.3(a): SEM micrograph of the surface of a LaCrO$_3$ film deposited at 1523 K with a CrCl$_3$/LaCl$_3$ input ratio of 3.4, using a O$_2$/H$_2$O mixture as oxygen source reactant.

Figure 5.3(b): Cross-sectional view of the film shown in Figure 5.3(a).

The surface of this film is faceted, and has a cauliflower-type morphology. Also some trenches can be observed in the deposit. These trenches suggest that the deposits are not fully dense. However, SEM micrographs of cross-sections of these films reveal that the films are fully dense and homogeneous in thickness, indicating growth by the EVD mechanism. The appearance of these trenches is most probably the result of the surface roughness of the bare substrate. The same film morphology was observed for films deposited at 1473 K.

Figure 5.4 shows the surface and a cross-sectional view of a film deposited at 1373 K with a CrCl$_3$/LaCl$_3$ input ratio of 5.5. The surface of the films deposited at these conditions are rough, and the shape of the crystallites has changed considerably. Cross-sectional views show that these films have a porous columnar structure. Therefore, it is expected that these films are grown by a conventional CVD mechanism. Furthermore, it is expected that the gas permeability of these films is higher than that of the fully dense films shown in Figure 5.3.

Film thickness has been determined from SEM micrographs of cross-sections of the samples, when possible. The results are gathered in Table 5.5. The number of experiments is too small to obtain quantitative information about the kinetics of the EVD growth of undoped LaCrO$_3$. 

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Table 5.5: Summary of results of depositions of undoped LaCrO$_3$ on porous alumina. Included in the table are deposition temperature ($T_{\text{dep}}$), deposition time ($t_{\text{dep}}$), CrCl$_3$/LaCl$_3$ input ratio, carrier gas for H$_2$O (H$_2$/O$_2$), film thickness (d), crystalline phases with the relative intensity of the strongest reflections$^1$, La/Cr ratio in deposits$^2$, relative permeability ($P_{\text{rel}}$), activation energy for electronic conduction in air ($E_a$), and electronic conductivity in air at 1273 K ($\sigma_{1273}$).

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_{\text{dep}}$ (K)</th>
<th>$t_{\text{dep}}$ (min)</th>
<th>CrCl$_3$/LaCl$_3$</th>
<th>H$_2$/O$_2$</th>
<th>d (μm)</th>
<th>cryst. phases + rel. int.</th>
<th>La/Cr</th>
<th>$P_{\text{rel}}$</th>
<th>$E_a$ (eV)</th>
<th>$\sigma_{1273}$ (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S1</td>
<td>1473</td>
<td>105</td>
<td>0.29</td>
<td>H$_2$</td>
<td>-</td>
<td>LaCr$_{1-x}$Al$_x$O$_3$ 100</td>
<td>6</td>
<td>2×10^{-3} *</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S2</td>
<td>1523</td>
<td>120</td>
<td>0.22</td>
<td>H$_2$</td>
<td>-</td>
<td>LaCr$_{1-x}$Al$_x$O$_3$ 83</td>
<td>5</td>
<td>&lt;10^{-6} *</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S3</td>
<td>1523</td>
<td>120</td>
<td>0.29</td>
<td>H$_2$</td>
<td>-</td>
<td>LaCr$_{1-x}$Al$_x$O$_3$ 24</td>
<td>3</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S4</td>
<td>1523</td>
<td>120</td>
<td>0.29</td>
<td>O$_2$</td>
<td>12 - 15</td>
<td>LaCrO$_3$ 100</td>
<td>0.9</td>
<td>8×10^{-4} *</td>
<td>0.18</td>
<td>0.47</td>
</tr>
<tr>
<td>S5</td>
<td>1523</td>
<td>30</td>
<td>0.53</td>
<td>O$_2$</td>
<td>-</td>
<td>LaCrO$_3$ 29 Al$_2$O$_3$ 5</td>
<td>0.5</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S6</td>
<td>1473</td>
<td>90</td>
<td>0.38</td>
<td>O$_2$</td>
<td>10 - 22</td>
<td>LaCrO$_3$ 100</td>
<td>0.9</td>
<td>5×10^{-2}</td>
<td>0.19</td>
<td>0.74</td>
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<td>S7</td>
<td>1323</td>
<td>150</td>
<td>0.08</td>
<td>O$_2$</td>
<td>-</td>
<td>LaCrO$_3$ 4 Cr$_2$O$_3$ 6</td>
<td>0.08</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>S8</td>
<td>1373</td>
<td>120</td>
<td>0.18</td>
<td>O$_2$</td>
<td>7 - 10</td>
<td>LaCrO$_3$ 100</td>
<td>0.7</td>
<td>-</td>
<td>0.22</td>
<td>0.18</td>
</tr>
<tr>
<td>S9</td>
<td>1373</td>
<td>95</td>
<td>0.18</td>
<td>O$_2$</td>
<td>3</td>
<td>LaCrO$_3$ 42 Cr$_2$O$_3$ 50</td>
<td>0.05</td>
<td>1</td>
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<td>0.013</td>
</tr>
<tr>
<td>S10</td>
<td>1373</td>
<td>60</td>
<td>0.18</td>
<td>O$_2$</td>
<td>2</td>
<td>LaCrO$_3$ 7 Cr$_2$O$_3$ 16</td>
<td>0.02</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

$^1$ The presence of Al$_2$O$_3$ reflections has not been taken into account. $^2$ From EDX surface analysis.
Figure 5.4(a): SEM micrograph of the surface of a LaCrO$_3$ film deposited at 1373 K with a CrCl$_3$/LaCl$_3$ input ratio of 5.5, using a O$_2$/H$_2$O mixture as oxygen source reactant.

Figure 5.4(b): Cross-sectional view of the film shown in Figure 5.4(a).

5.3.1.1.2 Film structure and composition.

The results of the XRD and EDX analyses are summarized in Table 5.5. Some typical examples of XRD patterns of depositions of undoped LaCrO$_3$ on alumina are shown in Figure 5.5. The diffraction patterns reveal the formation of LaCrO$_3$ [16]. In some films deposited using the O$_2$/H$_2$O mixture (patterns B and C), formation of Cr$_2$O$_3$ is also observed [17]. In the films deposited using the H$_2$/H$_2$O mixture (pattern A), the presence of Cr$_2$O$_3$ was not confirmed. Compared to the ICDD$^1$ data, all diffraction peaks have been shifted to higher 2θ-values. This peak shift is primarily caused by displacement of the specimen from the diffractometer axis. In order to determine the peak positions more accurately, the diffraction pattern was corrected for this misalignment by using the alumina diffraction pattern as reference [18]. If it is assumed that the peak positions of the alumina substrate material match the ICDD data, then a correction curve can be constructed for each diffraction pattern. The correction curve is plotted as the difference between the observed and calculated values of sin$^2$θ for the

---

$^1$International Centre for Diffraction Data
Figure 5.5: XRD patterns of films obtained when depositing undoped LaCrO₃ films on alumina. A: film deposited at 1523 K with CrCl₃/LaCl₃ = 3.4, using H₂/H₂O (S1); B: film deposited at 1523 K with CrCl₃/LaCl₃ = 3.4, using O₂/H₂O (S4); C: film deposited at 1373 K with CrCl₃/LaCl₃ = 5.5, using O₂/H₂O (S8).

(x): LaCrO₃ reflection; (o): Cr₂O₃ reflection; (+): Al₂O₃ reflection.

diffraction peaks of alumina (Δsin²θ) as a function of the observed values of sin²θ [19]. By subtracting the errors, represented by the ordinates of this curve, from the observed values of sin²θ for the diffraction peaks of the deposited material, a corrected and more accurate diffraction pattern is obtained. In Table 5.6, the corrected values for 2θ and the plane spacing (d) for some depositions are given. The ICDD values of 2θ and d for LaCrO₃ and Cr₂O₃ are given for comparison.

A peculiar feature of the LaCrO₃ diffraction peaks in pattern A is that even after correction the peak shift is still considerable, and increasing with increasing diffraction angle. The peak shift of the diffraction peaks of LaCrO₃ and Cr₂O₃ in patterns B and C is considerably less, and is independent of the diffraction angle. Therefore, it appears that in the experiments using the H₂/H₂O mixture another phase than LaCrO₃ has been deposited. Because the diffraction pattern of this phase strongly resembles the diffraction pattern of LaCrO₃, also with regard to the peak intensities, the crystal structure of this unknown phase has to resemble the crystal structure of LaCrO₃.
Table 5.6: Plane spacings (d) of the reflecting planes in the deposits after correction for misalignment of the specimens. The literature values of the spacings of the reflecting planes of LaCrO$_3$, Cr$_2$O$_3$, and LaAlO$_3$ are given for comparison [16,17,20].

<table>
<thead>
<tr>
<th>specimen</th>
<th>S1</th>
<th>S2</th>
<th>S4</th>
<th>S6</th>
<th>S8</th>
<th>LaCrO$_3$</th>
<th>Cr$_2$O$_3$</th>
<th>LaAlO$_3$</th>
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<tbody>
<tr>
<td>d (Å)</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>3.789</td>
<td>3.879</td>
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<td>phase 1</td>
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<td></td>
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<td>3.633</td>
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<td>phase 2</td>
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<td>Cr-content in LaAl$_{1-x}$Cr$_x$O$_3$</td>
<td>0.05</td>
<td>0.12</td>
<td>0.93</td>
<td>0.97</td>
<td>0.94</td>
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<tr>
<td>La/Cr in LaAl$_{1-x}$Cr$_x$O$_3$</td>
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<td>8.3</td>
<td>1.1</td>
<td>1.0</td>
<td>1.1</td>
<td></td>
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<td></td>
</tr>
</tbody>
</table>

144
The series of corrected $d$-values of this unknown phase matches closely the diffraction data of the perovskite oxide LaAlO$_3$ [20]. Hence, under reducing conditions during the CVD stage of the growth process, the intended deposition of LaCrO$_3$ on alumina will result in the formation of LaAlO$_3$ or Cr-doped LaAlO$_3$, i.e. LaAl$_{1-x}$Cr$_x$O$_3$. In principle, every composition with $x \in [0,1]$ is possible, as LaCrO$_3$ and LaAlO$_3$ form mutual stable solid solutions in every ratio [21]. Under oxidizing conditions during the CVD stage of the growth process the main constituent of the deposits is (Al-doped) LaCrO$_3$.

Some spectra obtained from EDX analysis of the surface of the as-deposited films are shown in Figure 5.6. The films deposited using the H$_2$/H$_2$O mixture contain much more lanthanum than chromium, whereas the films deposited using the O$_2$/H$_2$O mixture contain almost the same amount of lanthanum and chromium, or somewhat more chromium than lanthanum. These results are in agreement with the XRD results, and, therefore, it can be concluded that under reducing CVD conditions deposition of LaCrO$_3$ on alumina will lead to the formation of Cr-doped LaAlO$_3$, while under oxidizing conditions (Al-doped) LaCrO$_3$, and, depending on process conditions, some Cr$_2$O$_3$ are formed.

**Figure 5.6:** EDX spectra obtained from surface analysis of undoped LaCrO$_3$ deposits. A: film deposited at 1523 K with CrCl$_3$/LaCl$_3$=3.4, using H$_2$/H$_2$O (S1); B: film deposited at 1523 K with CrCl$_3$/LaCl$_3$= 3.4, using O$_2$/H$_2$O (S4); C: film deposited at 1373 K with CrCl$_3$/LaCl$_3$ = 5.5, using O$_2$/H$_2$O (S8).

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The La/Cr ratio obtained from the EDX surface analysis provides an indication of the chromium content of the Cr-doped LaAlO$_3$ deposits. This chromium content can also be calculated from the lattice parameters obtained from the X-ray diffraction data. Using these lattice parameters, the volume of one unit cell of the deposited material can be determined, and compared with the cell volumes of undoped LaAlO$_3$ and LaCrO$_3$. Assuming that Vegard's law [19] applies, the chromium content of the Cr-doped LaAlO$_3$ deposits are determined. The results are summarized in Table 5.6. The chromium contents obtained from the EDX and XRD data show the same trend, i.e. sample S1 has the highest chromium content and sample S3 the lowest. However, the chromium contents obtained from the XRD results are much smaller than those obtained from the EDX measurements.

The aluminium contents of the Al-doped LaCrO$_3$ films deposited under oxidizing CVD conditions are determined from the XRD patterns in the same way as the chromium content in the Cr-doped LaAlO$_3$ deposits, and can be found also in Table 5.6. Comparison of the relative intensities of the strongest X-ray reflections of LaCrO$_3$ and Cr$_2$O$_3$, and the La/Cr ratio obtained from the EDX surface analysis results reveal that the analysis results are in qualitative agreement, as the La/Cr ratio in the deposit determined by EDX is decreasing with increasing Cr$_2$O$_3$ content as determined by XRD.

EDX analysis of cross-sections of the deposited films shows that the dense (EVD) films are homogeneous in composition, with a La/Cr ratio of approximately one. The small amount of aluminium present in the films is homogeneously distributed through the films. In the CVD films containing both LaCrO$_3$ and Cr$_2$O$_3$, a decrease of the La/Cr ratio towards the surface of the film is observed, which explains why the La/Cr ratio in the films obtained from EDX surface analysis is much smaller than expected from the intensities of the LaCrO$_3$ and Cr$_2$O$_3$ reflections in the XRD patterns.

5.3.1.1.3 Film permeability

The total Ar permeabilities measured by the forced-flow method could all be fitted well to Equation (5.2). The results of these measurements are summarized in Table 5.5. The relative permeability values are calculated for an average pressure of 5×10$^4$ Pa. The film permeability values are calculated using Equation (5.4). The relative permeability values marked with an asterisk are measured by a different method, using nitrogen instead of argon [22]. From Table 5.5 it is clear that the permeability of the porous films (viz. Fig. 5.4 (b)) is much higher than that of the fully dense films. The permeability of the porous film is so high, that the total permeability of the system substrate+film is completely determined by the permeability of the substrate, as the total permeability remained unchanged.
5.3.1.4 Film conductivity measurements

The electronic conductivity of the films deposited, using the O₂/H₂O mixture, has been measured by a two-probe dc measurement technique. The conductivity has been measured as a function of temperature in an air ambient. The reproducibility of the measurements remained within 10%. Figure 5.7 shows an Arrhenius plot of the measured film conductivity of three different samples. The activation energy for electronic conduction is determined from the slope of the lines. The results are gathered in Table 5.5. For the single-phase LaCrO₃ films or LaCrO₃ films with a small amount of Cr₂O₃, the activation energy and electronic conductivity at 1273 K are in good agreement with the values reported in literature, i.e. \(E_a = 0.18 - 0.23\) eV, and \(\sigma_{1273} = 0.03 - 1.25\) S/cm [22-26]. The activation energy increases with increasing Cr₂O₃ content, as can be seen in Table 5.5.

![Arrhenius plot](image)

**Figure 5.7**: Film conductivity as a function of temperature, measured in air. A: sample S6; B: sample S4; C: sample S8
5.3.1.2 Deposition of Mg-doped LaCrO₃

5.3.1.2.1 Film structure and morphology

A summary of the deposition results of Mg-doped LaCrO₃ on Ca-doped zirconia is given in Table 5.7. The XRD patterns of the films reveal the presence of either single-phase LaCrO₃, or mixtures of LaCrO₃ and Cr₂O₃. In one diffraction pattern (S30), only Cr₂O₃ reflections were present, while in one other experiment (S41), magnesium chromite (MgCr₂O₄) was detected. Diffraction peaks of the cubic Ca-doped zirconia substrate were not observed. Instead, in some diffraction patterns very small peaks were present which could be ascribed to the two strongest reflections of monoclinic zirconia ((-111) and (111)), indicating that (part of) the substrate had undergone a phase transformation from cubic to monoclinic calcia-doped zirconia. The XRD patterns of the rear side of the substrates showed the presence of both monoclinic and cubic zirconia. This partial phase transformation is concordant with the CaO-ZrO₂ phase diagram, as for calcia doping levels less than 15 mol%, monoclinic and cubic calcia-doped zirconia are both stable at temperatures below 900 K [27]. However, in most XRD patterns, diffraction peaks of the substrate material are absent.

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. I(121)LaCrO₃ and I(104)Cr₂O₃. These figures are shown in Table 5.7.

The chemical composition of the deposits is analyzed by EDX spectroscopy. Two examples of EDX spectra of the surface of as-deposited films are shown in Figure 5.8. These results show that in the single-phase LaCrO₃ films -according to XRD analysis- the La/Cr ratio is larger than 1, while a considerable amount of aluminium, i.e. 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 a large amount of aluminium, i.e. 10-35 at%, appears to be present.

The XRD patterns could not be used to obtain estimates for the aluminium contents of the LaCrO₃ phases, according to the method described earlier, because there are no peaks present in the XRD patterns that can be used as reference peaks to construct the corrected diffraction patterns. However, a qualitative statement about the diffraction patterns can be made. If the LaCrO₃ phase contains a large amount of aluminium, the peak shift of the diffraction peaks, with respect to the literature data, will increase with increasing diffraction angle. This is the case for the LaCrO₃ phases marked with an asterisk in Table 5.7. If the aluminium content in the LaCrO₃ phase is small, the peak shift owing to the changed lattice parameters is much smaller, and negligible compared to the peak shift owing to specimen misalignment, as is the case for the other LaCrO₃ diffraction patterns.
Table 5.7: Summary of results of depositions of Mg-doped LaCrO$_3$ on porous CSZ. Included in the table are deposition temperature ($T_{\text{dep}}$), deposition time ($t_{\text{dep}}$), input ratio of the reactants (La:Mg:Cr), colour, film thickness ($d$), crystalline phases present, and their relative amounts based on the intensity of the strongest X-ray reflections, and the La:Cr:Mg:Al ratio in the deposits as obtained from EDX surface analysis.

<table>
<thead>
<tr>
<th>sample</th>
<th>$T_{\text{dep}}$ (K)</th>
<th>$t_{\text{dep}}$ (min)</th>
<th>La:Mg:Cr$_{\text{input}}$</th>
<th>colour</th>
<th>d ($\mu$m)</th>
<th>cryst. phases + relative amounts (%)</th>
<th>La:Cr:Mg:Al$_{\text{film}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>S23</td>
<td>1468</td>
<td>180</td>
<td>1 : 2 : 2</td>
<td>brown</td>
<td>9</td>
<td>LaCrO$_3^*$ (100)</td>
<td>4 : 2 : 0.1 : 1</td>
</tr>
<tr>
<td>S24</td>
<td>1468</td>
<td>180</td>
<td>2 : 1 : 8</td>
<td>dark brown</td>
<td>12</td>
<td>LaCrO$_3^*$ (100)</td>
<td>6 : 3 : 0 : 1</td>
</tr>
<tr>
<td>S26</td>
<td>1468</td>
<td>120</td>
<td>1 : 1 : 5</td>
<td>dark green</td>
<td>8</td>
<td>LaCrO$_3$ (100)</td>
<td>4 : 3 : 0 : 1</td>
</tr>
<tr>
<td>S28</td>
<td>1468</td>
<td>180</td>
<td>1 : 0.8 : 4</td>
<td>dark green</td>
<td>8</td>
<td>LaCrO$_3$ (100)</td>
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</tr>
<tr>
<td>S29</td>
<td>1474</td>
<td>60</td>
<td>1 : 1 : 4</td>
<td>dark green</td>
<td>7.5</td>
<td>LaCrO$_3$ (100)</td>
<td></td>
</tr>
<tr>
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<td>1477</td>
<td>180</td>
<td>1 : 1 : 5</td>
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<td>Cr$_2$O$_3$ (100)</td>
<td>0 : 7 : 0 : 2</td>
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<tr>
<td>S31</td>
<td>1480</td>
<td>120</td>
<td>2 : 1 : 6</td>
<td>dark green</td>
<td>9</td>
<td>LaCrO$_3$ (55) + Cr$_2$O$_3$ (45)</td>
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</tr>
<tr>
<td>S32</td>
<td>1478</td>
<td>300</td>
<td>1 : 1 : 4</td>
<td>green</td>
<td>17</td>
<td>LaCrO$_3$ (68) + Cr$_2$O$_3$ (32)</td>
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<tr>
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<td>1475</td>
<td>30</td>
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<td>LaCrO$_3$ (100)</td>
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<tr>
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<td>1526</td>
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<td>1 : 1 : 4</td>
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<td>8</td>
<td>LaCrO$_3$ (73) + Cr$_2$O$_3$ (27)</td>
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<tr>
<td>S35</td>
<td>1524</td>
<td>180</td>
<td>1 : 1 : 4</td>
<td>dark green</td>
<td>15</td>
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<td>S36</td>
<td>1526</td>
<td>300</td>
<td>1 : 1 : 3</td>
<td>green</td>
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<td>LaCrO$_3$ (100)</td>
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<tr>
<td>S37</td>
<td>1523</td>
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<td>1.5 : 1 : 6</td>
<td>olive green</td>
<td>4</td>
<td>LaCrO$_3$ (90) + Cr$_2$O$_3$ (10)</td>
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<td>1527</td>
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<td>1 : 1 : 3</td>
<td>dark green</td>
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<td>LaCrO$_3$ (60) + Cr$_2$O$_3$ (40)</td>
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<td>1572</td>
<td>60</td>
<td>1 : 1 : 2</td>
<td>dark green</td>
<td>14</td>
<td>LaCrO$_3$ (41) + Cr$_2$O$_3$ (59)</td>
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<td>1 : 1 : 3</td>
<td>olive green</td>
<td>17</td>
<td>LaCrO$_3$ (100)</td>
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<tr>
<td>S41</td>
<td>1569</td>
<td>30</td>
<td>1 : 1 : 2</td>
<td>dark green</td>
<td>8</td>
<td>LaCrO$_3$ (87) + MgCr$_2$O$_4$ (13)</td>
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<td>1 : 1 : 3</td>
<td>olive green</td>
<td>25</td>
<td>LaCrO$_3$ (59) + Cr$_2$O$_3$ (41)</td>
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<tr>
<td>S43</td>
<td>1568</td>
<td>120</td>
<td>1 : 1 : 3</td>
<td>dark green</td>
<td>17</td>
<td>LaCrO$_3$ (17) + Cr$_2$O$_3$ (83)</td>
<td>0.1 : 4 : 0 : 1</td>
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</table>
In Table 5.7 the colour of the deposits is given. Except for the outer edge of the samples, the surface of the deposits is homogeneous in colour. The deposits containing single-phase LaCrO₃, or LaCrO₃ with a small amount of Cr₂O₃ are brown or light to olive green in colour. The deposits containing a large amount of Cr₂O₃, or single-phase Cr₂O₃ are very dark green (almost black) in colour. Brown-coloured deposits indicate the formation of doped LaCrO₃, as the colour of LaCrO₃ powders changes from light green to brown when a dopant (Mg or Sr) is added.

Optical and SEM micrographs of cross-sections of deposited films show that most films follow the irregularities of the substrate surface, and that they are reasonably homogeneous in thickness. 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 5.9 shows the difference in surface morphology between deposits with LaCrO₃ and Cr₂O₃ as major constituents, respectively. The crystal facets of the Cr₂O₃ deposits are much more pronounced than those of the LaCrO₃ deposits. Some preliminary depositions of Cr₂O₃ also showed the faceted surface morphology.

SEM micrographs of some cross-sections of deposited films are shown in Figure 5.10.
Figure 5.9(a): SEM micrograph of the surface of a single-phase LaCrO$_3$ film on CSZ (S28).

Figure 5.9(b): SEM micrograph of the surface of a single-phase Cr$_2$O$_3$ film on CSZ (S30).

Figure 5.10(a): SEM micrograph of a cross-section of the dense EVD film obtained in experiment S24.

Figure 5.10(b): SEM micrograph of a cross-section of the dense EVD film obtained in experiment S40.
From these micrographs it is clear that the structure changes during the growth process. In Figure 5.10(a) and (b) dense films are shown, which appear to comprise two parts. EDX analysis of the cross-sections reveal that the change in film structure is caused by a change in composition, as illustrated in Figure 5.11. 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) LaCrO$_3$ is the main constituent, and that in some films Cr$_2$O$_3$ 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 (viz. Fig 5.11, B2). 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. In the bottom parts of the films, magnesium is detected (viz. Fig 5.11, A2 and B2). The highest magnesium contents are observed in parts of the deposits in which lanthanum is not or hardly present, indicating the formation of MgCr$_2$O$_4$. This phase has also been identified once by XRD, as discussed above. Aluminium is found through the entire film. In general, the aluminium content is high in regions where the lanthanum content is low.

Although the CSZ substrates were flat upon entering the reactor, a number of them came out buckled after deposition. Some samples showed extreme buckling, with the centre of the specimen being displaced 3 to 4 mm from its original position. Seen from the metal chloride side, the samples have become buckled convexly.

**Figure 5.11:** EDX spectra obtained from cross-section analysis of films shown in Figure 5.10. A1: Fig. 5.10(a), top; A2: Fig. 5.10(a), bottom; B1: Fig. 5.10(b), top; B2: Fig.5.10(b), bottom.
5.3.1.2.2 Film permeability

The in-situ Ar permeability of the bare substrate and of the specimen after deposition have been calculated from the rate of pressure decrease in the oxygen compartment, using Equation (5.1) and the ideal gas law. The total volume of the oxygen compartment is calculated to be $2.5\times10^{-3}$ m$^3$. Because approximately 95% of this volume is located outside the furnace at a temperature of 308 K, this temperature is used in the calculations. The relative permeability values were calculated for an average pressure of $6\times10^3$ Pa, and the film permeability values were calculated using Equation (5.4).

The total permeabilities, measured by the forced-flow method, did show linear behaviour with increasing average pressure, according to Equation (5.2), although for some samples deviation of linear behaviour was observed at higher average pressures. Again, the relative permeability values were calculated for an average pressure of $6\times10^3$ Pa. The results of the in-situ and ex-situ Ar permeability measurements are summarized in Table 5.8. In Figure 5.12 the in-situ Ar permeability is given as a function of total deposition time for a deposition temperature of 1473 K, and is found to decrease with increasing deposition time, and, hence, with increasing film thickness. The average in-situ Ar permeability of the bare CSZ samples is $36\times10^{-6}$ mol/m$^2$sPa.

![Graph](image_url)

**Figure 5.12:** 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.
Table 5.8: Summary of the results of the Ar permeability measurements on Mg-doped LaCrO₃ films on CSZ.

<table>
<thead>
<tr>
<th>Sample</th>
<th>t_{dep} (min)</th>
<th>P_{tot}×10^6 (mol/m²sPa)</th>
<th>P_{rel} (-)</th>
<th>P_{r}×10^6 (mol/m²sPa)</th>
<th>P_{tot}×10^6 (mol/m²sPa)</th>
<th>P_{rel} (-)</th>
<th>P_{r}×10^6 (mol/m²sPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>S33</td>
<td>30</td>
<td>4.4</td>
<td>0.13</td>
<td>5.1</td>
<td>24.4</td>
<td>0.040</td>
<td>25.4</td>
</tr>
<tr>
<td>S29</td>
<td>60</td>
<td>4.4</td>
<td>0.10</td>
<td>4.9</td>
<td>47.8</td>
<td>0.078</td>
<td>51.8</td>
</tr>
<tr>
<td>S31</td>
<td>120</td>
<td>1.2</td>
<td>0.026</td>
<td>1.3</td>
<td>12.2</td>
<td>0.020</td>
<td>12.4</td>
</tr>
<tr>
<td>S30</td>
<td>180</td>
<td>0.46</td>
<td>0.014</td>
<td>0.46</td>
<td>3.0</td>
<td>0.0049</td>
<td>3.1</td>
</tr>
<tr>
<td>S32</td>
<td>300</td>
<td>0.091</td>
<td>0.0025</td>
<td>0.091</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S37</td>
<td>30</td>
<td>4.8</td>
<td>0.12</td>
<td>5.4</td>
<td>4.3</td>
<td>0.0070</td>
<td>4.4</td>
</tr>
<tr>
<td>S34</td>
<td>60</td>
<td>2.4</td>
<td>0.066</td>
<td>2.6</td>
<td>8.8</td>
<td>0.014</td>
<td>8.9</td>
</tr>
<tr>
<td>S38</td>
<td>120</td>
<td>5.6</td>
<td>0.17</td>
<td>6.7</td>
<td>78.4</td>
<td>0.13</td>
<td>89.9</td>
</tr>
<tr>
<td>S35</td>
<td>180</td>
<td>1.6</td>
<td>0.041</td>
<td>1.7</td>
<td>64.3</td>
<td>0.10</td>
<td>71.8</td>
</tr>
<tr>
<td>S36</td>
<td>300</td>
<td>0.60</td>
<td>0.019</td>
<td>0.61</td>
<td>10.3</td>
<td>0.017</td>
<td>10.5</td>
</tr>
<tr>
<td>S41</td>
<td>30</td>
<td>1.7</td>
<td>0.063</td>
<td>1.8</td>
<td>69.5</td>
<td>0.10</td>
<td>69.5</td>
</tr>
<tr>
<td>S39</td>
<td>60</td>
<td>2.1</td>
<td>0.064</td>
<td>2.2</td>
<td>5.0</td>
<td>0.0082</td>
<td>5.0</td>
</tr>
<tr>
<td>S43</td>
<td>120</td>
<td>1.0</td>
<td>0.031</td>
<td>1.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S40</td>
<td>180</td>
<td>1.7</td>
<td>0.048</td>
<td>1.8</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>S42</td>
<td>300</td>
<td>0.25</td>
<td>0.0065</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

5.3.1.2.3 Film thickness

Film thickness values were determined primarily from polished cross-sections by optical microscopy. The measurements were performed at a magnification of 1000× with an accuracy of 0.5 μm. If possible, the film thickness was determined on at least 10 different locations on the cross-section. Figure 5.13 shows the measured film thickness as a function of total deposition time for different deposition temperatures. Film composition and structure were not considered in this plot. The vertical lines indicate the uncertainty in the measured thicknesses. The uncertainty in the film thickness is largest for the films deposited at 1573 K. At this temperature, the films deposited in 3600, 7200, and 10800 seconds are not fully dense. These films are dense at the bottom, and porous
at the top, and not homogeneous in thickness. The dense part of the film is rich in magnesium and chromium, indicating the presence of \(\text{MgCr}_2\text{O}_4\) and \(\text{Cr}_2\text{O}_3\), whereas the porous part consists of a mixture of \(\text{Cr}_2\text{O}_3\) and \(\text{LaCrO}_3\).

If growth behaviour is parabolic, then the square of the film thickness as a function of deposition time yields straight lines, with the slope being equal to twice the parabolic growth rate constant \(K_0\) (viz. Eq. (4.2)). These plots are shown in Figure 5.14. The lines in this figure represent the linear least squares fit through the data points, yielding \(K_0 = 8.2 \times 10^{-11}\) cm\(^2\)/s at 1473 K, \(K_0 = 1.1 \times 10^{-10}\) cm\(^2\)/s at 1523 K, and \(K_0 = 1.6 \times 10^{-10}\) cm\(^2\)/s at 1573 K, respectively. Compared to the parabolic growth rate constant \(K_0 = 1.8 \times 10^{-9}\) cm\(^2\)/s at 1603 K determined by Pal and Singhal [2,15], 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 an estimate can be obtained from Figure 5.14 by extrapolation of the lines to \(L_1^2 = 0\). In this way the CVD times are estimated to be 720 seconds at 1473 K, and 600 seconds at 1523 K. For \(T = 1573\) K, the CVD time could not be estimated, because this line intersects the x-axis at a negative value. As mentioned above, the films deposited at this temperature were partially porous and not homogeneous in thickness, indicating that these films were not grown by the EVD process. Therefore, non-parabolic growth behaviour is expected for these films. In the discussion on the kinetics of the EVD process the depositions at 1573 K will not be considered.

![Graph](image)

**Figure 5.13:** Total film thickness as a function of total deposition time. A: \(T = 1473\) K; B: \(T = 1523\) K; C: \(T = 1573\) K.
Figure 5.14: The square of the film thickness as a function of deposition time. A: T = 1473 K; B: T = 1523 K; C: T = 1573 K.

5.3.2 Deposition of Sr-doped LaCrO$_3$ on gastight YSZ

5.3.2.1 Film structure and morphology

All diffraction patterns of the films, deposited in the range of process conditions specified in Table 5.4, showed the characteristic diffraction peaks of LaCrO$_3$. No evidence was found for the formation of the binary oxides (La$_2$O$_3$, Cr$_2$O$_3$, and SrO). In only one experiment LaOCl was detected. The formation of LaOCl has occurred in an experiment performed at the relative high pressure of 4.3×10$^3$ Pa, and may be ascribed to the low chlorination rate of chromium, which decreases with increasing pressure for pressures above 2.0×10$^3$ Pa [28].

The diffraction peaks of YSZ are present in all diffraction patterns, whereas alumina peaks are observed only occasionally. The alumina reflections are caused by the ceramic cement used to mount the substrates onto the substrate holder. On the outer edge of the samples, always a small fringe of the bare substrate was visible, contributing to the intensity of the YSZ reflections. Therefore, the intensity ratio of the LaCrO$_3$ and YSZ reflections cannot be used as a measure for the film thickness.
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 LaCrO$_3$ film on gastight YSZ is shown in Figure 5.15.

5.3.2.2. Film composition

Film compositions have been determined by EDX spectroscopy. 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. There appears to be a relation between the aluminium and silicon impurity content, as silicon is not detected in films with low aluminium content, while in films with high aluminium content, the silicon content increases with increasing aluminium content. 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. Analysis of cross-sections of the EVD films shows that some of the films are not homogeneous in composition, as parts of the film do not contain chlorine, while other parts contain up to 35 at% chlorine. In the regions of high chlorine content, the chromium content is low, while the lanthanum content remains constant, indicating the presence of both LaCrO$_3$ and LaOCl.

![SEM micrograph of an EVD film of LaCrO$_3$ on gastight YSZ, deposited at 1401 K, in 240 minutes.](image)

**Figure 5.15:** SEM micrograph of an EVD film of LaCrO$_3$ on gastight YSZ, deposited at 1401 K, in 240 minutes.
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. In the EDX spectrum of La$_{0.97}$Sr$_{0.03}$CrO$_3$ powder only a very small Sr peak appears, whereas in the spectrum of La$_{0.99}$Sr$_{0.01}$CrO$_3$ powder the Sr-signal does not rise above the noise level. The total strontium consumption, and hence the strontium chloride production, in each experiment was such that the assumption is justified that reasonable concentrations of SrCl$_2$ were present in the reactor.

5.3.2.3 Growth rate

Figure 5.16 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. 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 $K_0$ is calculated to be $6.5 \times 10^{-11}$ cm$^2$/s.

![Graph showing the 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.]

Figure 5.16: 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.
5.4 DISCUSSION

5.4.1 Depositions on porous substrates

5.4.1.1 Film composition

Deposition of LaCrO₃ on porous alumina, using a H₂/H₂O mixture in the ratio 3:2, with an equilibrium oxygen partial pressure of about 10⁻¹⁷ Pa, results in the formation of single-phase Cr-doped LaAlO₃. Despite the excess of CrCl₃ in the reactant stream, Cr₂O₃ formation is not observed. The permeability of these samples has decreased by over 4 orders of magnitude, indicating complete pore closure. Therefore, part of the film growth takes place by the EVD mechanism. Because the pore closure time has not been determined in these experiments, the period of EVD growth is unknown. Compared to the films deposited using the O₂/H₂O mixture, the Cr-doped LaAlO₃ films are very thin. Several reasons can be given for the low growth rate. In the first place, pore closure may take place farther from the substrate surface, hence it will take longer before the EVD film reaches the substrate surface, and a film is formed on top of the substrate. Secondly, the equilibrium oxygen partial pressure on the metal chloride side for the H₂/H₂O mixture is about 10 orders of magnitude smaller than for the O₂/H₂O mixture, leading to a reduced growth rate during the EVD stage, in case the difference between the oxygen partial pressure on either side of the growing film has become less than 4 orders of magnitude, as shown previously [29]. Furthermore, the possibility that the oxygen ion conductivity of Cr-doped LaAlO₃ is smaller than that of undoped or Al-doped LaCrO₃ can be ignored, as Dᵥ₂ for Ca-doped LaAlO₃ ranges from 10⁻⁸ to 10⁻⁶ cm²/s in the temperature range of 1273 to 1423 K [30,31].

Because the aluminium content in the films deposited under oxidizing CVD conditions is much smaller than in the films deposited under reducing CVD conditions, it is expected that the alumina substrates are involved in the CVD reaction under reducing conditions. To check whether the aluminium in the Cr-doped LaAlO₃ films originates from the substrate, much thicker films need to be grown under the same conditions. If the alumina substrate is the aluminium source in the CVD reaction, it is expected that in the EVD stage, when film growth proceeds on the metal chloride side, aluminium-free LaCrO₃ will be formed, because then the substrate is separated from the surface of the growing film, while the aluminium conductivity in LaAlO₃ is negligible. Based on these observations, it can be concluded that for the investigation of the kinetics of EVD growth of (doped) LaCrO₃, using a H₂/H₂O mixture, alumina is not a suitable substrate. In that case, it may be better to use substrates of the SOFC cathode material Sr-doped LaMnO₃, which appear to be stable under these reducing conditions [2].

The depositions of undoped and Mg-doped LaCrO₃, using a O₂/H₂O mixture as oxygen source reactant, have been carried out with LaCl₃/CrCl₃ input ratios in the range
of 0.18-0.53, hence, with an excess of CrCl$_3$ with respect to LaCl$_3$. The use of an excess of CrCl$_3$ was based on results published by Feduska and Isenberg [2]. Feduska and Isenberg deposited EVD films of Mg-doped LaCrO$_3$ at 1623 K, using a H$_2$/H$_2$O mixture as oxygen source reactant, with an oxygen partial pressure of about 10$^{-8}$ Pa. The ratio of LaCl$_3$/CrCl$_3$ used in deposition of undoped LaCrO$_3$ is not given, but in optimizing the deposition conditions for Mg-doped LaCrO$_3$, with respect to film growth rate and electrical conductivity, they gradually decreased the LaCl$_3$ concentration, while simultaneously the MgCl$_2$ concentration was increased. Optimal results were obtained for the La:Mg:Cr input ratio of 1:2:3. In all experiments, dense (Mg-doped) LaCrO$_3$ films are formed, although no details are given on the homogeneity of the composition of the EVD films, and neither on the composition of the pore-plugging CVD deposits. Differences in composition between the pore-plugging CVD deposit and the EVD film can be expected, as various kinetic and thermodynamic aspects determine which material will be formed. According to thermodynamic equilibrium calculations, the CVD pore-plugging deposit in the experiments of Feduska and Isenberg should consist of LaCr$_{1-x}$Mg$_x$O$_3$ and MgCr$_2$O$_4$ [15].

In our experiments with LaCl$_3$/CrCl$_3$<1 and no MgCl$_2$, the CVD deposits should consist of LaCrO$_3$ and Cr$_2$O$_3$ [15]. This is confirmed experimentally, as the porous films obtained in depositions with LaCl$_3$/CrCl$_3$=0.2, which are believed to be grown by a conventional CVD reaction, consist of a mixture of LaCrO$_3$ and Cr$_2$O$_3$. Altogether, the CVD deposit is expected to comprise a mixture of phases. Although the composition of the CVD deposits will differ from the desired composition of the EVD film, it does not necessarily mean that film growth during the EVD stage is affected, because Cr$_2$O$_3$ also exhibits oxygen ion conductivity [32].

If the EVD conditions are selected such that solid state diffusion is rate-determining, then the composition of the EVD film is determined by the solid state transport properties in both the CVD deposit and the EVD film. If the CVD deposit only exhibits oxygen ion conductivity, the oxide with the highest oxygen ion conductivity will be formed during the EVD stage of the film growth, provided that it is thermodynamically stable. This is illustrated by the fact that attempts to grow YCrO$_3$ by means of EVD resulted in the formation of Cr$_2$O$_3$-doped Y$_2$O$_3$ instead of YCrO$_3$ [2]. The oxygen ion conductivity of Cr$_2$O$_3$-doped Y$_2$O$_3$ is higher than that of YCrO$_3$.

Because Cr$_2$O$_3$, like LaCrO$_3$, exhibits oxygen ion conductivity with negligible cation conductivity, it can be expected that on top of CVD deposits of the composition $(1-x)$ LaCrO$_3$ + $x$ Cr$_2$O$_3$ with $x$ ∈ [0,1], EVD films of (doped) LaCrO$_3$ will grow. The experimental results seem to support this, as the dense films of undoped -or Al-doped- LaCrO$_3$, which are believed to be grown by the EVD process, hardly contain Cr$_2$O$_3$ according to X-ray analysis, and are homogeneous in composition, with La/Cr=1. The aluminium present in the LaCrO$_3$ films may originate from the reactor wall, the substrate, or the ceramic cement. Because the latter two are isolated from the metal-
chloride-containing atmosphere during the EVD stage of the growth process, and because the aluminium appears to be present throughout the EVD films, it seems likely that the aluminium originates from the reactor wall. To avoid contamination of the EVD films with aluminium from the reactor wall, a graphite lining should be placed into the reactor.

The presence of aluminium in all LaCrO$_3$ films indicates that doping of the interconnection material with aluminium can easily be done in the EVD process, as was also suggested by Feduska and Isenberg [2]. Incorporation of aluminium in the interconnection material may be advantageous, because the TEC of the material will be increased, and, therefore, it matches more closely to the TEC's of the other components, and because the orthorhombic to rhombohedral phase transformation temperature will be shifted below room temperature [21]. A disadvantage of doping the interconnection material with aluminium is that the electronic conductivity decreases with increasing aluminium content [21]. Because the contribution of the interconnect to the total resistivity of the fuel cell is small, the reduced electronic conductivity will not have a large influence on the total cell performance.

In the experiments with MgCl$_2$ as reactant, formation of LaCr$_{1-x}$Mg$_x$O$_3$, MgCr$_2$O$_4$, and Cr$_2$O$_3$ during the CVD stage is predicted by the thermodynamic equilibrium calculations. Formation of the latter phase depends on the excess of CrCl$_3$ used [15]. According to XRD analysis, the deposits contain single-phase (doped) LaCrO$_3$, or mixtures of (doped) LaCrO$_3$ and Cr$_2$O$_3$. Only in two experiments MgCr$_2$O$_4$ was identified. In one experiment single-phase Cr$_2$O$_3$ appeared to be formed. EDX analysis of cross-sections of the films reveals that chromium is present throughout the whole film. The lanthanum content is low in the bottom parts of the films, and in one case lanthanum is even completely absent (viz. Figs. 5.10 (b) and 5.11, B2). In the dense upper parts of the films the lanthanum content is highest. These parts of the films consist of (Al-doped) LaCrO$_3$, i.e. La/Cr=1, or of a mixture of LaCrO$_3$ and some Cr$_2$O$_3$, i.e. La/Cr<1, as is shown in Figure 5.11. Magnesium is detected in the bottom parts of the films, where the lanthanum content is low, indicating the formation of MgCr$_2$O$_4$, besides Cr$_2$O$_3$ and LaCrO$_3$. In the upper parts of the films, i.e. the parts of the film grown by the EVD mechanism, magnesium is not detected, which proves that magnesium can hardly be incorporated in LaCrO$_3$ during the EVD process, as was also observed by Feduska and Isenberg [2], and Pal and Singhal [4]. Like in the depositions of undoped LaCrO$_3$, aluminium appears to be present in almost all deposited films. The aluminium content appears to be related to the lanthanum content, and is (relatively) high in regions with low lanthanum content. This trend is also observed in the EDX analysis of the surface of the as-deposited films.

Because crystalline alumina or other aluminium-containing phases were not identified by XRD, the aluminium has to be present as dopant in the LaCrO$_3$ and Cr$_2$O$_3$ phases,
or in the form of amorphous alumina. In the XRD patterns no increasing peak shift with increasing diffraction angle is observed for the LaCrO$_3$ diffraction peaks. Therefore, it is expected that the aluminium doping level of the LaCrO$_3$ phase is small, which means that aluminium also has to be present as dopant in the Cr$_2$O$_3$ phase or in an amorphous phase. This is also illustrated by the fact that a large amount of aluminium is detected in the single-phase Cr$_2$O$_3$ film, according to XRD analysis.

The aluminium present in the deposits may originate either from the alumina-based cement, the reactor wall, or from the alumina evaporation source, in which the LaCl$_3$ is kept during these experiments. The latter possibility is the most probable, because in the undoped LaCrO$_3$ films little aluminium is present, as can be seen in Figure 5.6 (spectra B and C). During these experiments, the LaCl$_3$ powder was not stored in an alumina evaporation source, but stored directly in the quartz evaporator. The alumina evaporation source was introduced, because the quartz evaporators were severely attacked by the LaCl$_3$ melt. The presence of aluminium in the deposits indicates that the alumina evaporation source is also attacked by the LaCl$_3$ melt, leading to the formation of a volatile aluminium-containing compound, e.g. AlCl$_3$, and a less volatile lanthanum-containing compound, e.g. LaOCl, which leads to a decrease of the gas phase concentration of LaCl$_3$. Apparently, the gas-phase concentration of the lanthanum precursor 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 LaCrO$_3$ and Cr$_2$O$_3$ during the EVD stage in some experiments. Simultaneous formation of LaCrO$_3$ and Cr$_2$O$_3$ during the EVD stage is possible, because Cr$_2$O$_3$ also exhibits oxygen ion conductivity. In the first EVD experiments for fabrication of the interconnect, Cr$_2$O$_3$ was synthesized [1]. However, Cr$_2$O$_3$ is not very well suited as interconnect, because its TEC does not match the TEC's of other cell components. If during the EVD growth of LaCrO$_3$ the LaCl$_3$ supply is sufficient, LaCrO$_3$ will grow, because this material has the highest oxygen ion conductivity. If the LaCl$_3$ supply will be cut off completely, a Cr$_2$O$_3$ film will continue to grow. If, however, the LaCl$_3$ supply drops below a critical level, that it cannot keep up with the CrCl$_3$ oxidation rate, then the ratio of La/Cr in the film becomes smaller than unity, and Cr$_2$O$_3$ will be formed next to LaCrO$_3$.

These results show that during the CVD stage of the growth process, the phases which are expected according to the thermodynamic equilibrium calculations are formed indeed. Secondly, it is shown that, although the composition of the CVD deposits varies considerably, the main constituent of the EVD films is LaCrO$_3$, and that Cr$_2$O$_3$ can be formed simultaneously during the EVD growth. Furthermore, it is shown that doping of LaCrO$_3$ with magnesium is very difficult, whereas doping with aluminium can easily be done in the EVD process. In order to avoid contamination of the EVD films, it is probably best to keep the metal chlorides, especially the LaCl$_3$, in graphite containers.
5.4.1.2 Film permeability

It is clear from Figure 5.12 that the Ar permeability of the samples deposited at 1473 K strongly decreases during the first 1800 seconds of the deposition. After 1800 seconds, the permeability has decreased to \(4 \times 10^{-5} \text{ mol/m}^2\text{sPa}\). The experiments at higher deposition temperatures showed a similar behaviour. For deposition times beyond 1800 s, the permeability of the samples decreases even further to about \(10^{-7} \text{ mol/m}^2\text{sPa}\). The permeability values after 1800 s are of the same order of magnitude as the permeability values at which Carolan and Michaels considered their substrates to be plugged [33], but they are 200 times larger than the boundary value used by Lin [34].

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 criterium is arbitrarily chosen, pore closure time is less then 1800 seconds. Extrapolation of the plots of the square of the film thickness versus deposition time supports this conclusion.

The relative high permeability values may be ascribed to the presence of cracks in the ceramic cement that is used to mount the substrates onto the substrate holder, because after removal from the reactor, these cracks are always observed. Although these cracks will eventually get filled by the CVD deposit, this will take a relatively long time, and the effect on the permeability will be different in every experiment.

5.4.1.3 Film growth

The linear relation between the square of the LaCrO\(_3\) film thickness and the total deposition time (viz. Fig. 5.14) suggests that the EVD growth is governed by solid state diffusion. As mentioned earlier, most of the films deposited at 1573 K do not have the typical dense structure and uniform film thickness that is common for EVD films, and, therefore, it is likely that another growth mechanism is involved in their formation. Hence, although the relation between film thickness and time suggests parabolic growth behaviour, these data are not considered further.

In Chapter 4 of this thesis, model calculations are described, to determine the effect of various process parameters on the parabolic growth rate constant. In these calculations, it is assumed that, under all process conditions, EVD films with the composition LaCr\(_{0.98}\)Mg\(_{0.02}\)O\(_3\) are formed. The magnesium content of the EVD films from our experiments is certainly not exceeding that amount. Still, the experimentally determined values for the parabolic growth rate constant will be compared with those calculated for 2 at% Mg, which may give rise to differences, as the parabolic growth rate constant decreases with decreasing magnesium content.

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 chloride side \( (p_{O_2}^*) \) is not known, because it cannot be determined. In principle it is possible to measure \( p_{O_2} \) with a solid electrolyte oxygen sensor, but as any metallic electrode will be consumed rapidly in the reactive metal chloride atmosphere, it is impractical to use such oxygen sensing devices [6,34]. Therefore, an estimation for \( p_{O_2}^* \) has to be made. In the discussions on the kinetics of EVD growth for YSZ and Mg-doped LaCrO\(_3\), it is assumed that the oxygen partial pressure on the metal chloride side is determined by the thermodynamic equilibrium between oxygen, the metal chlorides, the EVD film, and chlorine [3-8,29,34]. 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. Oxygen and water impurity contents up to 1 ppm in the carrier gas have no influence on the calculated equilibrium oxygen partial pressure, as has been shown earlier in similar calculations [29].

The theoretical value for \( K_0 \) can now be calculated from the expression derived in Chapter 4

\[
K_0 = \frac{D_{V_{O}}} {6} \left[ x \ln \left( \frac{(A^{1/2}+1)^2} {2} \right) - \frac{2x} {A^{1/2}+1} \right] \frac{A(p_{O_2}^*)} {A(p_{O_2})} \tag{5.5}
\]

with,

\[
A = 24xK_{25}p_{O_2}^{1/2} + 1 \tag{5.6}
\]

\[
D_{V_{O}} = 0.287 \exp \left( \frac{-2.1 \text{eV}} {kT} \right) \tag{5.7}
\]

and

\[
K_{25} = 4.0 \times 10^5 \exp \left( \frac{-3.2 \text{eV}} {kT} \right) \tag{5.8}
\]

For EVD films of the composition \( \text{LaCr}_{0.98}\text{Mg}_{0.02}\text{O}_3 \), calculation of the parabolic growth rate constant, using Equation (5.5), yields \( K_0 = 1.0 \times 10^{-11} \) cm\(^2\)/s at 1473 K, \( K_0 = 3.8 \times 10^{-11} \) cm\(^2\)/s at 1523 K, and \( K_0 = 1.2 \times 10^{-10} \) cm\(^2\)/s at 1573 K. Figure 5.17 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 H$_2$/H$_2$O mixture with $p_{O_2} = 10^{-18}$ Pa was used as oxygen source reactant to grow films of Mg-doped LaCrO$_3$. As EVD film growth takes place, the oxygen partial pressure on the metal chloride side has to be smaller than $10^{-18}$ Pa. Therefore, it is very well possible that the actual oxygen partial pressure on the metal chloride side is less than the calculated $10^{-15}$ Pa, and that the calculated value for $K_0$ is larger.

In the calculations, it is also assumed that $p_{O_2}$ does not change with temperature. If in the experiments $p_{O_2}$ is not constant but increasing with increasing temperature, then a less strong temperature dependence of the calculated $K_0$ will result.

![Graph](image)

**Figure 5.17**: Comparison of the calculated and experimentally obtained values for the parabolic growth rate constant for EVD growth of Mg-doped LaCrO$_3$ on CSZ.

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Then, there is the fact that to date no reliable numerical values are available for the oxygen ion vacancy diffusion coefficient for Mg-doped LaCrO$_3$ as a function of temperature. The activation energy of 2.1 eV for $D_{V_O}$ as determined in Chapter 4, is near the upper limit of the range of activation energies for oxygen ion vacancy diffusion coefficients in perovskite oxides, and is in reality probably smaller. Preliminary impedance spectroscopy measurements to determine $D_{V_O}$ in dynamically compacted LaCr$_{0.85}$Mg$_{0.15}$O$_3$ indicate an activation energy of 1.2-1.3 eV [35]. A smaller activation energy for $D_{V_O}$ will result in a smaller temperature dependence of $K_0$.

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) LaCrO$_3$ and Cr$_2$O$_3$ instead of single-phase, doped LaCrO$_3$. The influence of this inhomogeneity in the film composition is difficult to predict. In contrast with doped LaCrO$_3$, definite conclusions as to the defect structure and defect dependent properties of Cr$_2$O$_3$ cannot be drawn [32].

Chromium- and oxygen-self-diffusion studies in polycrystalline and single-crystalline samples showed that in polycrystalline samples diffusion of both chromium and oxygen predominantly involves rapid grain boundary diffusion, as the diffusion coefficients in single-crystalline samples are several orders of magnitude smaller than in polycrystalline samples. The chromium and oxygen self-diffusion coefficients for lattice diffusion as well as for grain boundary diffusion are of the same order of magnitude [32]. Comparison of the parabolic growth rate constants for the formation of chromia scales on chromium-containing alloys shows discrepancies of over 3 to 4 orders of magnitude. These differences are related to grain size, microstructure, and pretreatment of the alloy, and to the experimental procedure. The parabolic growth rate constants for chromia formation on binary chromium-containing alloys are of the order of $10^{-13}$ to $10^{-11}$ cm$^2$/s at 1373 K and $10^{-12}$ to $10^{-10}$ cm$^2$/s at 1473 K [32]. The fact that scale growth is strongly influenced by grain size, microstructure, and morphology of the scale suggests that the high-temperature corrosion rates, and, hence, the EVD growth rates, are determined by grain boundary diffusion. Therefore, the influence of the presence of Cr$_2$O$_3$ in the EVD films on the overall growth rate cannot be described quantitatively.

As chromia formation involves counter-diffusional transport of chromium and oxygen ions along grain boundaries, new oxide crystallites will be formed on the grain boundaries. Therefore, chromia scales not only grow in thickness, but they also grow laterally, inducing high compressive stresses in the scales. Owing to this lateral expansion, chromia oxide scales are convolutely buckled [32]. This might explain why most of the samples containing both doped LaCrO$_3$ and Cr$_2$O$_3$ were buckled after deposition, although it should be noted that one sample (S40) that was identified by XRD as single-phase LaCrO$_3$ was buckled too.

All in all, in order to be able to model the EVD growth of Mg-doped LaCrO$_3$, care should be taken that single-phase Mg-doped LaCrO$_3$ films are deposited with an
accurately known oxygen partial pressure on the metal chloride side. The oxygen ion conductivity of Mg-doped LaCrO$_3$ EVD films, or sintered dense samples, has to be determined as a function of temperature using electrochemical measurement techniques, but as discussed earlier, preparation of fully dense sintered Mg-doped LaCrO$_3$ is very difficult.

In principle, if the EVD growth is governed by solid state diffusion, the EVD experiments themselves can be used to determine the oxygen ion vacancy diffusion coefficient, as was illustrated in Chapter 4, and by Pal and Singhal [4,5]. However, uncertainty about the oxygen partial pressure on the metal chloride side can cause severe errors in the calculated $D_{\text{VO}}$. It is also possible, if $D_{\text{VO}}$ has been determined, to use the EVD experiments to determine the actual oxygen partial pressure on the metal chloride side, as discussed in Chapter 4. If the calculated oxygen partial pressure on the metal chloride side appears to be unrealistic, then also other processes might play a role in the rate-determining step, apart from solid state diffusion, as was discussed earlier for the EVD growth of YSZ [29].

5.4.2 Deposition of Sr-doped LaCrO$_3$ on gastight YSZ

As the YSZ substrates used in these experiments were fully dense, film growth could only take place by solid state transport of anionic and/or cationic species. In the early stages of the deposition process, there is also a CVD pore-plugging reaction taking place, to fill the pores of the ceramic cement used to mount the substrates. Pore closure time was typically on the order of 3600 to 5400 seconds, for the reaction conditions chosen. Pore closure time was measured by monitoring the pressure decrease in the substrate holder, which was done at regular intervals during the depositions. The variation in pore closure time may be caused by the presence of cracks in the cement. As the dimensions of the cracks vary, so do the pore closure times.

The initial porosity of the cement may have an effect on the EVD growth on the gastight substrate in the early stages of the deposition. Initially, oxygen transport will preferably take place through the pores of the cement, and a pore-plugging CVD deposit will be formed in the pores or on the surface of the cement. The question is whether the conversion of oxygen (and water) transported through the pores of the cement is so small, that during the period of pore closure the oxygen partial pressure gradient across the substrate, and, hence the driving force for oxygen diffusion through the substrate, is smaller then after pore closure. If that is the case, then the EVD growth rate on the YSZ substrate will be smaller than expected, or in the extreme case, be zero. Because the EVD experiments are performed in a flowing reactor at low pressure with relatively large gas flow rates, the oxygen will be rapidly removed from the metal chloride compartment. Furthermore, the oxygen transported through the pores enter the metal chloride
compartment downstream from the substrate surface. All in all, it is expected that the EVD growth on the YSZ substrate during the pore closure period is not seriously affected, and, therefore, it is assumed that the EVD conditions are constant throughout the whole experiment.

The plot of the square of the measured film thickness as a function of the total deposition time is linear, as shown in Figure 5.16, indicating that the growth process is controlled by solid state diffusion through the growing film, as was discussed in Chapter 4. It should be noted that in the construction of this plot, 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 the parabolic growth rate constant obtained in experiments on porous supports. The parabolic growth rate constant for the EVD growth of (Sr, Al)-doped LaCrO$_3$ is calculated to be $6.5 \times 10^{-11}$ cm$^2$/s at 1410 K, which is high in comparison with the parabolic growth rate constant obtained for the EVD growth of Mg-doped LaCrO$_3$ on porous CSZ, i.e. $1.0 \times 10^{-11}$ cm$^2$/s at 1473 K.

This high value for the parabolic growth rate constant 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 $p_{O_2}$ 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.

Although in the model calculations, described in Chapter 4, the same uncertainties as discussed above (film composition, $D_{V+O_2}$, $p_{O_2}$) contribute to deviations between the experimental results and the model calculations, a comparison can still be made. From the experiments it is clear that at a deposition temperature of 1410 K EVD film growth behaviour of doped LaCrO$_3$ on 200 to 600 μm thick gastight YSZ substrates is already parabolic at a film thickness of 2 μm. This indicates that for these reaction conditions the period of linear and transitional growth behaviour is very short, and that the time beyond which growth can be considered parabolic ($t_{min}$) is less than 1800 seconds. The results of the model calculations indicate that the period of linear growth for these reaction conditions is of the order of 300 seconds, while $t_{min}$ is calculated to be 2 to 3 hours. The experiments and model calculations are in reasonable agreement, although it appears that the period of parabolic growth is much longer than expected from the model calculations. To illustrate the agreement, Figure 5.18 shows a plot of the square of the calculated film thickness as a function of deposition time for $T_{dep} = 1423$ K, and
\( p_{O_2} = 10^{-18} \) Pa \((10^{-13} \) atm). For these reaction conditions, \( t_{\text{min}} \) was calculated to be of the order of 5 hours. However, from Figure 5.19 it is clear that for deposition times in the range of \(3 \times 10^3\) to \(2 \times 10^4\) s growth behaviour is indistinguishable from parabolic. It should be noted that \( t_{\text{min}} \) was arbitrarily chosen as the time at which the difference between the growth rate in case of permanent parabolic growth behaviour, and the growth rate according to the model for composite systems is reduced to 5\%. If a larger difference would have been chosen, \( t_{\text{min}} \) would have been shorter, which, for the system considered, appears to be reasonable. An indication that the deposition of doped LaCrO\(_3\) on YSZ is not parabolic in the early stages of the deposition is the fact that extrapolation of the straight line in Figure 5.16 gives a positive intersection of the time axis, which is in accordance with the model (viz. Fig. 5.18).

Because of the large difference in conduction properties between YSZ and doped LaCrO\(_3\), 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

![Figure 5.18: The square of the calculated film thickness as a function of the deposition time for the EVD growth of Mg-doped LaCrO\(_3\) on gastight YSZ for T=1423 K and \( p_{O_2} = 10^{-18} \) Pa.](image-url)
Tanner et al. [13], who deposited undoped CeO₂ onto yttria-doped CeO₂. 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 LaCrO₃ on YSZ, the period of linear and transitional growth can be extended by using much thicker substrates.

5.5 CONCLUSIONS

Deposition of undoped LaCrO₃ on porous alumina by the EVD process produces Cr-doped LaAlO₃ films when using H₂/H₂O mixtures as oxygen source reactant. When O₂/H₂O mixtures are used instead, LaCrO₃ films are formed during the EVD stage, whereas the subsequent CVD deposits consist of a mixture of LaCrO₃ and Cr₂O₃, which is in accordance with thermodynamic equilibrium calculations. Aluminium, presumably originating from the reactor wall, can easily be incorporated in the LaCrO₃ films during the growth process. The electronic conductivity of the LaCrO₃ films in air at 1273 K ranges from 0.03 to 1.25 S/cm, with an activation energy of 0.18 to 0.23 eV, which is comparable with literature data measured on sintered undoped LaCrO₃ samples. The activation energy increases with increasing Cr₂O₃ content.

Addition of MgCl₂ to the reactant stream leads to the additional formation of MgCr₂O₄ during the CVD stage. The amount of magnesium incorporated in the LaCrO₃ films is very small (<2%), even though an excess of MgCl₂ is present in the reactant stream. Regardless of the composition of the CVD deposit, LaCrO₃ continues to grow during the EVD stage, as long as the LaCl₃ supply suffices. Depletion of LaCl₃ during the EVD stage results in the simultaneous formation of Cr₂O₃.

Alumina is not suited as container for the LaCl₃ melt during the process, as the aluminium content in the deposits increases with decreasing lanthanum content, indicating the formation of a volatile aluminium compound (AlCl₃) and a non- or less volatile lanthanum compound (LaOCl). Therefore, it is better to use graphite containers for the LaCl₃ melt. Furthermore, a graphite reactor lining should be used to avoid contamination of the LaCrO₃ films with aluminium. An additional advantage is that graphite acts as oxygen getter.

The EVD growth of doped LaCrO₃ on porous CSZ is parabolic for the reaction conditions investigated, with parabolic growth rate constants of 8.2×10⁻¹¹ cm²/s at 1473 K, and 1.1×10⁻¹⁰ cm²/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 LaCrO$_3$ 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 $6.5 \times 10^{-11}$ 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.

These experiments are very well suited for determining the kinetics of the EVD growth of doped LaCrO$_3$ under solid state diffusion limited conditions, because problems concerning the CVD stage are avoided.

REFERENCES

15. V.E.J. van Dieten, Chapter 3 of this thesis.
29. V.E.J. van Dieten, Chapter 4 of this thesis.
PARTICLE-PRECIPITATION-AIDED CHEMICAL VAPOUR DEPOSITION OF THE PEROVSKITE OXIDE YCrO$_3$

ABSTRACT

In the particle-precipitation-aided chemical vapour deposition (PP-CVD) process, an aerosol is formed in the gas phase at elevated temperatures. The particles are deposited on a cooled substrate. Coherent layers with a controlled porosity are obtained by a simultaneous heterogeneous reaction, which interconnects the deposited particles. The synthesis of submicron powder of the perovskite oxide yttrium chromite (YCrO$_3$) by gas to particle conversion, which is the first step of the PP-CVD process, has been investigated. The powders have been synthesised using yttrium trichloride vapour (YCl$_3$), chromium trichloride vapour (CrCl$_3$), and steam and oxygen as reactants. The influence of the input molar ratio of the elements on the composition and characteristics of the powders has been investigated. Phase composition has been determined by X-ray diffraction (XRD). The powders have been characterized by transmission electron microscopy (TEM), and sedimentation field flow fractionation (SF$^3$). At a reaction temperature of 1283 K the powders consist of chromium sesquioxide (Cr$_2$O$_3$), or a mixture of Cr$_2$O$_3$ and YCrO$_3$. At stoichiometric input amounts of metal chlorides and steam the formation of YCrO$_3$ seems to be favoured. Two typical particle size distributions have been observed. The primary particle size ranges from 5 to 30 nm for small particles, and from 40 to 250 nm for large particles, depending on the process conditions. The particles tend to be agglomerated. The weight of the agglomerates is independent of the primary particle diameter.
6.1 INTRODUCTION

A solid oxide fuel cell (SOFC) is an all-solid-state device for the generation of direct-current electric power by electrochemical oxidation of a fuel gas. The operating principles of the SOFC are discussed in detail in Chapter 1. Because of the high operating temperature, the materials used in a SOFC have to fulfil stringent requirements, among which:

- good chemical and mechanical stability at operating conditions,
- high electrical conductivity of the individual components, i.e. good mixed (electronic and ionic) conducting materials are preferred for the electrodes, good electronic conductivity, with negligible ionic conductivity is required for the interconnection material, and good oxygen ion conductivity, with negligible electronic conductivity is required for the solid electrolyte,
- thermal expansion coefficients of the individual components should match.

Perovskite oxides ABO$_3$, containing a rare earth metal ion (3$^+$) on the A-site, and a transition metal ion (3$^+$) on the B-site, are the most promising materials for application as SOFC component [1,2], because their intrinsic physical properties match closely the above-mentioned requirements. Furthermore, these properties can easily be changed by (partially) substituting the A or B ions by other metal ions. The state-of-the-art materials used for the cathode and the interconnect are perovskite oxides, as can be seen in Table 1.2 in Chapter 1.

The performance of a SOFC can be improved by using materials with superior electrical properties or by minimizing the thickness of the cell components. Both methods will lead to a reduction of the ohmic polarization losses. In recent years there has been an increased interest in the use of thin film components in SOFCs. Thin films of the interconnection material are produced by tape casting and subsequent sintering, or electrochemical vapour deposition (EVD). These processes require very high temperatures, because they both are limited by solid state mass transport. However, the other cell components may not be chemically stable at these high temperatures.

Another synthesis method for thin films is conventional chemical vapour deposition (CVD). This technique allows one to synthesize thin films of metal oxides at moderate temperatures. However, it is difficult to form pinhole-free layers on a porous substrate. Therefore, this technique as such is not well suited for the production of the interconnection material.

A modified form of conventional CVD is particle-precipitation-aided CVD (PP-CVD). In the formation of homogeneous layers by the conventional CVD process, reaction conditions are generally chosen such that powder formation in the gas phase is avoided, because this may lead to depletion of reactants necessary for the heterogeneous reaction, or, if the particles are deposited onto the substrate, to undesired microstructures.
However, in the process of film formation by means of PP-CVD, powder formation is an essential step, as it appeared that under certain experimental conditions it is possible to control the microstructure of the deposited layers by a controlled deposition of powder particles on the substrate [3].

The PP-CVD process consists of three steps which are shown schematically in Figure 6.1. In the first step of the PP-CVD process, an aerosol is formed by a homogeneous reaction at elevated temperatures. In the second step, deposition of powder particles onto the substrate is induced by imposing an external force, e.g. thermophoresis, electrophoresis, or forced flow, on the powder particles. Finally, in order to obtain a layer with good mechanical stability, the deposited particles are interconnected by sintering, or by a simultaneous heterogeneous reaction.

The PP-CVD process was developed by the group of Komiyama [4-8]. Using this technique, they have synthesized titania (TiO₂) [5,6], zirconia (ZrO₂) [6], and aluminium nitride (AlN) [7,8]. By altering the process conditions they were able to deposit dense to highly porous layers. The microstructure of the layers appeared to depend on particle deposition, sintering, and heterogeneous reaction.

Dekker et al. [3,9] have investigated the synthesis of titanium nitride by the PP-CVD method, using thermophoresis as the driving force for particle deposition. Because TiN has a poor sinterability, a heterogeneous reaction is necessary to interconnect the
deposited particles. Hence, the reactant mixture used in the PP-CVD process has to serve as a source for the homogeneous reaction (powder formation), as well as for the heterogeneous reaction. In this case, the desired material has to be formed by two separate reaction mechanisms, i.e. one for the powder formation, and one for the heterogeneous reaction, which can occur at the same temperature and reactor pressure. By changing the process conditions, Dekker et al. were able to deposit fully dense to highly porous TiN layers. In particular, the driving force for particle deposition had a large influence on the microstructure of the deposited layers. Dense microstructures were obtained when the driving force for particle deposition, i.e. the temperature difference between the gas phase and the substrate, was small ($\Delta T<5$ K). By increasing the temperature difference, they obtained porous coherent layers. Under these conditions, the heterogeneous reaction which is responsible for the interconnection of the deposited particles can keep up with the rate of particle precipitation. A further increase in the temperature difference between the gas phase and the substrate ($\Delta T>20$ K) resulted only in the formation of loose powder deposits.

Because it has been shown that it is possible to control the porosity of the deposited layers, and that also dense layers can be formed, PP-CVD might be a suitable technique for the synthesis of SOFC components. In theory, this technique can be used to produce all components of a single SOFC. Hence, a complete SOFC can be formed using one production technique by only altering the reaction conditions. This production method has the following advantages over the conventional way of producing a complete SOFC:
- less temperature cycles during production; hence, less risk of mechanical failure of the components,
- if produced at operating temperature, the SOFC will be stress-free during operation,
- thin film components are produced, so ohmic polarization losses will be minimal,
- no contamination of the interfaces between the components.

Because there are few reports on powder synthesis of perovskite oxides in the gas phase, we have started to investigate the possibility to synthesize a perovskite oxide powder by a *homogeneous* gas phase reaction. In this paper the results of the powder synthesis of the perovskite oxide yttrium chromite ($\text{YCrO}_3$) are described. The experiments are performed at conditions which are expected to be suited also for the formation of the perovskite oxide by a *heterogeneous* reaction, which is necessary for the synthesis of the SOFC interconnect by means of PP-CVD.

Yttrium chromite can be formed using yttrium trichloride ($\text{YCl}_3$), chromium trichloride ($\text{CrCl}_3$), and steam ($\text{H}_2\text{O}$) and/or oxygen ($\text{O}_2$), as precursors according to the reactions [10]:

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\[ \text{YCl}_3(\text{g}) + \text{CrCl}_3(\text{g}) + 3 \text{H}_2\text{O}(\text{g}) \rightarrow \text{YCrO}_3(\text{s}) + 6 \text{HCl}(\text{g}) \]  \hspace{1cm} (6.1)

\[ 2 \text{YCl}_3(\text{g}) + 2 \text{CrCl}_3(\text{g}) + 3 \text{O}_2(\text{g}) \rightarrow 2 \text{YCrO}_3(\text{s}) + 6 \text{Cl}_2(\text{g}) \]  \hspace{1cm} (6.2)

The reason why this reactant system was chosen can be explained as follows: for the formation of binary oxides by CVD using the metal chlorides as reactants, oxidant vapours as H\textsubscript{2}O, O\textsubscript{2}, nitrogen oxides, or a CO\textsubscript{2}/H\textsubscript{2} mixture can be used [11,12]. For example, Funk \textit{et al.} [13] described the formation of alumina particles in the vapour phase in the reaction temperature region of 873 K to 1273 K, using AlCl\textsubscript{3} and H\textsubscript{2}O as reactants. In general, at elevated temperatures a mixture of metal chloride vapours and steam will react homogeneously, which results in powder formation. Hence, water is an appropriate reactant for the \textit{homogeneous} formation of the perovskite oxide.

In order to form films of metal oxides, often a CO\textsubscript{2}/H\textsubscript{2} mixture is used as oxygen source reactant [12-15]. This mixture produces H\textsubscript{2}O at a very slow rate, and, because metal halides react rapidly with H\textsubscript{2}O, this water formation reaction is often the rate-determining step in the process of film growth. Several metal oxide surfaces, such as alumina and zirconia, were found to catalyze the water formation reaction [14]. This formation takes place on the metal oxide surface, giving rise to adsorbed water molecules. Consequently, these molecules will react with the metal chlorides at the surface, and the formation of metal oxide powder by homogeneous reaction will not occur. Hence, in principle, a CO\textsubscript{2}/H\textsubscript{2} mixture may be used for the \textit{heterogeneous} formation of the perovskite oxide.

Metal oxide films, \textit{e.g.} SiO\textsubscript{2}, FeO, CoO, and Al\textsubscript{2}O\textsubscript{3}, are also synthesized by oxidation of the metal halides with oxygen [12]. Therefore, oxygen might also be an appropriate reactant for the \textit{heterogeneous} formation of the perovskite oxide, which is necessary in the PP-CVD process to interconnect the powder particles that were formed \textit{homogeneously} by reaction between the metal chlorides and steam.

An indication whether the formation of a solid will occur by a heterogeneous or a homogeneous reaction can be obtained by evaluating the thermodynamic equilibrium constant of the formation reaction. Kato \textit{et al.} [16] have studied the relation between the equilibrium constant of a reaction and the occurrence of powder formation for nitrides, carbides, and oxides. They observed the tendency that powder formation only occurs when the equilibrium constant is large. Comparison of the equilibrium constants for the formation of binary oxides, using either steam or oxygen as oxidant, reveals that the equilibrium constants of the reactions using steam as oxidant are always larger. Hence, it may be possible that, under certain experimental conditions, using a mixture of steam and oxygen, the YCrO\textsubscript{3} aerosol is formed by reaction (6.1), while simultaneously the formation of YCrO\textsubscript{3} by heterogeneous reaction (6.2) takes place.
YCrO₃ is chosen instead of LaCrO₃, which is commonly used as interconnection material in a SOFC, for practical reasons. It is easier to obtain the necessary high gas phase concentration of YCl₃ than of LaCl₃, because LaCl₃ is much less volatile than YCl₃. YCrO₃ is isostructural with LaCrO₃, and has almost the same electrical and thermal properties as LaCrO₃ [17]. Therefore, it has been considered to be a possible alternative for LaCrO₃ as interconnection material.

YCrO₃ powder has been precipitated on a cooled quartz tube. The influence of the input molar ratio of the elements on the composition of the powder has been investigated.

6.2 EXPERIMENTAL ASPECTS

A schematic representation of the PP-CVD reactor is given in Figure 6.2. A conventional gas distribution system, as described in Chapter 2, is used. The reactor consists of a 42-mm-ID quartz tube of 800 mm length in a two zone resistance-heated furnace comprising two zones of 300 mm length.

![Schematic representation of the PP-CVD reactor](image)

**Figure 6.2:** Schematic representation of the PP-CVD reactor for the synthesis of perovskite oxides.

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The powders formed are collected on a cooled susceptor. The susceptor consists of a
dead-end hollow quartz tube. The cooling of the susceptor is regulated by an externally
controlled flow of pressurized air. The tip of the susceptor is positioned in the centre of
the reactor tube, in the middle of the left heating zone. The metal chloride evaporator
consists of a 22-mm-ID quartz tube of 450 mm length. Inside this tube there is a row of
quartz containers for the solid metal trichlorides. The axial position of the evaporator
can be varied. Argon (Ar) is used as carrier gas to transport the metal chloride vapours
into the reactor. It is assumed that the gas phase concentration of the metal chlorides
is determined by their vapour pressures at the evaporation temperature. By altering the
place of the reactants in the reactor, their evaporation temperatures can be changed,
owing to the axial temperature gradient in the reactor. Hence, the ratio of the
concentration of metal chlorides in the gas phase can be controlled by varying the
respective evaporation temperatures. The nozzle has an inner diameter of 4 mm. High
linear gas velocities in the nozzle are used to prevent diffusion of steam and oxygen into
the evaporator, avoiding oxidation of the solid metal chlorides. A mixture of Ar/H₂O or
O₂/H₂O is fed into the reactor, on the outside of the metal chloride evaporator.
Temperatures are measured with chromel-alumel thermocouples. The reaction
temperature is measured at the outlet of the nozzle, where the reactants are in direct
contact. Also, the temperatures of the solid metal chlorides, the temperature of the gas
phase at the tip of the susceptor, at about 10 mm above the tip, as well as the
temperature at the tip within the susceptor, are monitored.

In all experiments the reactor pressure was 1x10⁴ Pa. Because of the low vapour
pressures of the CrCl₃ and YCl₃, a low reactor pressure was used in order to obtain high
concentrations of the metal chlorides. The reaction temperature was kept constant at
about 1283 K. The temperature in the reactor at the tip of the susceptor was about
1327 K. The temperature at the quartz tip within the susceptor varied between 1013 K
and 1161 K. The experimental conditions are summarized in Table 6.1.

The phase composition of the powders collected on the susceptor is determined by X-
ray diffraction (XRD) (Philips PW 1840, CuKα). Particle sizes are obtained using
transmission electron microscopy (TEM) (Philips EM 400) and sedimentation field flow
fractionation (SF³) (Du Pont). The principle of this SF³ apparatus is described by
Scarlett et al. [18].

For TEM analysis, part of the collected powder is suspended in methanol, and a TEM
grid is dipped into the suspension. For SF³ analysis part of the collected powder is
suspended in an aqueous solution of 0.1 vol% di-octyl sodium sulfosuccinate. The powder
concentration in the suspensions is about 1.5 weight%. 
Table 6.1: Process parameters for the synthesis of YCrO$_3$ by PP-CVD.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature of gas phase at the tip of the susceptor</td>
<td>1327 K ± 15 K</td>
</tr>
<tr>
<td>Temperature in the susceptor</td>
<td>1013 - 1161 K</td>
</tr>
<tr>
<td>Temperature of gas phase at the outlet of the nozzle</td>
<td>1283 K ± 13 K</td>
</tr>
<tr>
<td>Reactant flows (φ) outside metal chloride evaporator</td>
<td></td>
</tr>
<tr>
<td>H$_2$O flow</td>
<td>8 or 16</td>
</tr>
<tr>
<td>O$_2$ flow</td>
<td>0</td>
</tr>
<tr>
<td>Ar flow</td>
<td>0.031 - 1.8</td>
</tr>
<tr>
<td>Reactant flows (φ) inside metal chloride evaporator</td>
<td></td>
</tr>
<tr>
<td>CrCl$_3$ flow</td>
<td>0.18 - 2.01</td>
</tr>
<tr>
<td>YCl$_3$ flow</td>
<td>0.17 - 1.33</td>
</tr>
<tr>
<td>Ar flow</td>
<td>19 - 93</td>
</tr>
<tr>
<td>Cr/Y ratio</td>
<td>1 - 1.75</td>
</tr>
<tr>
<td>Reactor pressure</td>
<td>1×10$^4$ Pa</td>
</tr>
<tr>
<td>Reaction time</td>
<td>5400 - 10800 s</td>
</tr>
</tbody>
</table>

6.3 RESULTS AND DISCUSSION

During the syntheses without oxygen, a light green powder was collected on the cooled susceptor. During the experiments with a mixture of steam and oxygen, in most cases, light green powder was collected on the part of the susceptor within the furnace, whereas on the part of the susceptor outside the furnace the collected powder was dark green. In some experiments, however, only powder was collected on the part of the susceptor within the furnace, whereas on the part of the susceptor outside the furnace no powder was collected. There is no clear relation between process conditions and appearance of a powder deposit outside the furnace. In principle, the difference between the colour of the particles collected inside, and outside the furnace may be caused by a difference in composition or particle size.

In experiments where only oxygen was present as oxidant, no powder was formed, and only deposition on the reactor wall by a heterogeneous reaction could be observed. This indicates that the reactivity of the gas mixture without steam is not high enough to induce nucleation in the gas phase, and that oxygen may be a suitable reactant for heterogeneous CVD of YCrO$_3$. Hence, for powder formation the presence of steam is necessary.
Figure 6.3: XRD patterns of powders synthesised by PP-CVD. For comparison the XRD patterns of Cr$_2$O$_3$, Y$_2$O$_3$, and YCrO$_3$ are shown as well.

Synthesis conditions: powder 1:  
\[ \phi_{\text{H}_2\text{O}} = 2.43 \, \text{μmole/s}, \quad \phi_{\text{O}_2} = 48.4 \, \text{μmole/s}, \]
\[ \phi_{\text{CrCl}_3} = 0.69 \, \text{μmole/s}, \text{ and } \phi_{\text{YCl}_3} = 0.49 \, \text{μmole/s}; \]

powder 2:  
\[ \phi_{\text{H}_2\text{O}} = 2.48 \, \text{μmole/s}, \quad \phi_{\text{O}_2} = 48.4 \, \text{μmole/s}, \]
\[ \phi_{\text{CrCl}_3} = 0.65 \, \text{μmole/s}, \text{ and } \phi_{\text{YCl}_3} = 1.00 \, \text{μmole/s}. \]

Two XRD patterns, typical for the powders collected, are shown in Figure 6.3. For comparison, the XRD patterns of single-phase chromium sesquisioxide (Cr$_2$O$_3$), yttria (Y$_2$O$_3$), and YCrO$_3$ are shown as well. The YCrO$_3$ powder used as reference was made by a solid state reaction between equimolar amounts of Cr$_2$O$_3$ and Y$_2$O$_3$, at 1548 K during 63 hours, according to the method of Strakhov and Novikov [19]. In Figure 6.4 XRD patterns of two powders are shown, which have been synthesized in the same experiment, and were collected inside and outside the furnace, respectively. In all experiments where powder was collected inside, as well as outside the furnace, the powders were single-phase Cr$_2$O$_3$, as determined by XRD analysis. Due to the low conversion of reactants, the amount of powder formed is very small, resulting in the poor signal to background ratio in the XRD patterns. Therefore, line-broadening XRD analysis, to obtain quantitative values for the primary particle size is not possible.
Figure 6.4: XRD patterns of a light, and dark green powder from one experiment. For comparison the XRD pattern of Cr₂O₃ is shown as well.

Synthesis conditions: $\phi_{\text{H}_2\text{O}} = 2.84 \, \mu\text{mole/s}$, $\phi_{\text{O}_2} = 48.4 \, \mu\text{mole/s}$, $\phi_{\text{CrCl}_3} = 1.43 \, \mu\text{mole/s}$, and $\phi_{\text{YCl}_3} = 0.92 \, \mu\text{mole/s}$.

Comparison of the XRD patterns of the powders, collected inside and outside the furnace (Figure 6.4), reveals that there is no difference in phase composition. The diffraction peaks in the XRD pattern of the powder collected outside the furnace are broad in comparison with those of the powder collected inside the furnace. This might be caused by a difference in particle size, indicating that the particle size of the powder collected outside the furnace is smaller than that of the powder collected inside the furnace. Furthermore, small particles may appear to be dark, because of a more diffuse light scattering. From TEM analysis, it could be concluded that the powder collected outside the furnace has a smaller particle size than the powder collected inside the furnace. This is in agreement with the results of the XRD analysis. Hence, the dark colour of the particles collected outside the furnace is caused by a more diffuse light scattering, owing to the small particle size, and not by a different phase composition.

The possible difference in particle size could be explained by the difference in residence time in the hot reaction zone. The residence time in the hot reaction zone for the particles collected outside the furnace is on the order of $10^{-1}$ to 1 s, which is determined by the linear gas velocity in the reactor, whereas for the particles collected
inside the furnace this residence time is on the order of $10^3$ to $10^4$ s, which is determined by the total process time. Hence, the particle size of the particles inside the furnace could increase, due to sintering, or heterogeneous reaction, whereas outside the furnace the temperature is too low for these processes to occur.

From the XRD patterns it can be seen that always $\text{Cr}_2\text{O}_3$ (Figure 6.4) or a mixture of $\text{Cr}_2\text{O}_3$ and $\text{YCrO}_3$ is formed (Figure 6.3). Only in a few cases, $\text{Y}_2\text{O}_3$ has been identified.

Various amounts of $\text{YCrO}_3$, with respect to $\text{Cr}_2\text{O}_3$, have been observed for different experimental conditions. In principle, there are several parameters which may affect the total amount of $\text{YCrO}_3$ formed. Besides reaction temperature, the input molar ratios of the elements determine which solid product will be formed. In our experiments, the input molar ratios have been chosen such that a broad range of ratios were covered, e.g. $0.18 < \text{Cr}/(\text{Cr+Y}) < 0.60$.

In order to obtain semi-quantitative values for the ratio of the amount of $\text{YCrO}_3$ over $\text{Cr}_2\text{O}_3$ present in the collected powders, the ratio of the intensity of the $\text{YCrO}_3$ (202) reflection ($2\theta = 47.800^\circ$, relative intensity = 24%) over the $\text{Cr}_2\text{O}_3$ (012) reflection ($2\theta = 24.483^\circ$, relative intensity = 75%) is calculated from the XRD patterns (Figure 6.3). The strongest reflections of both $\text{Cr}_2\text{O}_3$ (104) and $\text{YCrO}_3$ (121) could not be used, because these reflections do overlap.

At this stage, no relationship has been observed between the formation of single-phase $\text{Cr}_2\text{O}_3$, or a mixture of $\text{Cr}_2\text{O}_3$ and $\text{YCrO}_3$, and the input molar ratios of the elements. The same holds for the ratio of $\text{Cr}_2\text{O}_3$ over $\text{YCrO}_3$ in the two-phase mixtures, although there is a tendency that near-stoichiometric input amounts of the elements, i.e. $\text{Cr}:\text{Y}:\text{O}_{\text{from H}_2\text{O}}:\text{H} = 1:1:3:6$, the formation of $\text{YCrO}_3$ is favoured mostly. To illustrate this, the ratio $I_{\text{YCrO}_3(202)}/(I_{\text{YCrO}_3(202)} + I_{\text{Cr}_2\text{O}_3(012)})$ is shown as a function of the ratio of the input concentrations of the metal chlorides in Figure 6.5. From this figure it can be seen that there is a maximum in the relative amount of $\text{YCrO}_3$ formed, with respect to $\text{Cr}_2\text{O}_3$, at a $\text{CrCl}_3/(\text{CrCl}_3+\text{YCl}_3)$ ratio of 0.4.

In general, at the reaction conditions chosen, the formation of the binary oxide $\text{Cr}_2\text{O}_3$ is favoured over the formation of $\text{YCrO}_3$ and $\text{Y}_2\text{O}_3$. This could be caused by either kinetic or thermodynamic limitations. Thermodynamic equilibrium calculations may elucidate this problem. These calculations can be performed using the SOLGASMIX program by Eriksson [20], or the Chemsage program by Eriksson and Hack [21]. These programs minimize the free Gibbs energy of a system, considering all species. In case of thermodynamic limitations, experimental conditions have to be chosen such that $\text{YCrO}_3$ is the only stable solid species. In case of kinetic limitations, it is possible that, although according to thermodynamic equilibrium calculations only one solid phase is stable, e.g. $\text{YCrO}_3$, other solid phases, e.g. $\text{Cr}_2\text{O}_3$, are formed. In that case, it is more difficult to obtain the optimal reaction conditions.
Figure 6.5: The ratio of the intensity of the YCrO₃ (202) and Cr₂O₃ (012) reflections as a function of the fraction of CrCl₃ in the total metal chloride flux.

The most obvious reaction parameter to be changed is the reaction temperature. Probably higher reaction temperatures are necessary to form single-phase YCrO₃, since thermodynamic calculations in the strongly related system La-Cr-O-Cl-H-Ar reveal that at reaction temperatures below 1573 K both LaCrO₃ and Cr₂O₃ are stable, whereas at reaction temperatures above 1573 K LaCrO₃ is the only stable solid phase [22].

Figure 6.6 shows TEM micrographs of some typical examples of collected powders. The TEM micrographs reveal that the particles are agglomerated. From these micrographs it is not clear whether agglomeration is caused by evaporation of the liquid phase (methanol) during TEM sample preparation, or is a result of synthesis conditions. In some experiments, two different primary particle sizes were found in one micrograph, as is illustrated by Figure 6.6(c). This bimodal particle size distribution is typical for the initial stage of the gas to particle conversion [23], assuming simultaneous chemical reaction and agglomeration of the particles in the gas phase.

There is no relation between the primary particle size, determined from the TEM micrographs ($d_{TEM}$), and the ratio of the concentration of metal chlorides, or the total metal chloride flux at constant reactor pressure, i.e. the total metal chloride concentration. The size of the small particles ranges from 5 to 30 nm, whereas the size of the larger particles ranges from 40 to 250 nm.
Figure 6.6: TEM micrographs of powders precipitated at different conditions.

a) $\phi_{\text{H}_2\text{O}} = 2.84$ μmole/s, $\phi_{\text{O}_2} = 48.4$ μmole/s, $\phi_{\text{CrCl}_3} = 0.25$ μmole/s, $\phi_{\text{YCl}_3} = 0.95$ μmole/s

b) $\phi_{\text{H}_2\text{O}} = 2.42$ μmole/s, $\phi_{\text{O}_2} = 48.4$ μmole/s, $\phi_{\text{CrCl}_3} = 0.32$ μmole/s, $\phi_{\text{YCl}_3} = 0.33$ μmole/s

c) $\phi_{\text{H}_2\text{O}} = 8.00$ μmole/s, $\phi_{\text{CrCl}_3} = 0.91$ μmole/s, $\phi_{\text{YCl}_3} = 0.62$ μmole/s
The mass mean diameter, as determined by SF³ measurements (d_{SF³}), is independent of the process conditions, and varies between 140 and 190 nm. This mass mean diameter differs significantly from the primary particle diameter, as determined from TEM micrographs (d_{TEM}). Hence, it can be concluded that the particles are agglomerated. Whether agglomeration is a result of the experimental conditions, has been determined by comparison of d_{SF³} with an equivalent mass diameter, determined from TEM micrographs. This equivalent mass diameter has been obtained by counting the number of primary particles in the agglomerates. By multiplying this number by the mass of the primary particles, the weight of the agglomerates is obtained, assuming that the primary particles are fully dense. The weight of the agglomerates, determined in this way, must fall within the mass distribution, obtained by SF³ analysis. The number of primary particles in the agglomerates is typical on the order of 100 to 500, for the small particles. The number of primary particles in the agglomerates decreases with increasing particle size. Hence, the weight of the agglomerates seems to be independent of the primary particle diameter, which was also found by SF³ analysis. The average weight of the agglomerates as determined from TEM micrographs results in an equivalent mass diameter of about 150 nm. This value is in agreement with the results of the SF³ analysis. So it can be concluded that agglomeration did occur during the synthesis process, and is not a result of TEM sample preparation.

6.4 CONCLUSIONS

It is possible to synthesise the perovskite oxide YCrO₃ from the gas phase, using metal chlorides, and steam and oxygen as precursors. At the reaction conditions chosen Cr₂O₃, or mixtures of Cr₂O₃ and YCrO₃ are formed. In the temperature range of 1270 to 1296 K, formation of single-phase YCrO₃ is inhibited by either thermodynamic or kinetic limitations. Thermodynamic equilibrium equations may elucidate this problem. In combination with these calculations, further experiments need to be performed in order to determine the range of reaction conditions in which single-phase YCrO₃ powder is formed.

If these conditions are known, it is useful to determine the conditions for the heterogeneous formation of YCrO₃ in separate experiments, using experimental conditions within the range necessary for the homogeneous reaction to take place.

Then, it may be possible to choose reaction conditions such that the homogeneous and heterogeneous reactions occur simultaneously, which is a necessity in the PP-CVD process for the formation of films of perovskite oxides with controlled morphology.
REFERENCES


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Summary

Electrochemical vapour deposition (EVD) is a modified form of the conventional CVD process, which utilizes a chemical potential gradient to grow thin, gas impervious layers of either ionically or electronically conducting metal oxides on porous substrates. The primary application to date has been in the fabrication of the solid electrolyte, yttria-stabilized zirconia (YSZ), and the interconnection material, magnesium-doped lanthanum chromite (LaCrO₃), of the solid oxide fuel cell (SOFC). Fuel cells are devices for the generation of direct-current electric power by electrochemical reaction between a fuel (H₂, CO) and an oxidant (air). The electrolyte has to be gastight in order to prevent cross-leakage of fuel and oxidant gases, and, hence, direct combustion of the fuel. In order to build a power generation unit, individual fuel cells have to be electrically connected in series and parallel. The individual cells are connected by the interconnect. This interconnect has to function as a current collector, providing electrical connection between the cells, and as gas separation barrier, preventing cross-leakage of fuel and oxidant gases from one cell to the next. Therefore, the interconnection material must be electronically conducting, and gastight. Because of the high operating temperature (900-1000°C), SOFCs are all-ceramic devices. LaCrO₃, doped with either magnesium, strontium, or calcium, is the most commonly used SOFC interconnection material. In intermediate temperature SOFCs, with operating temperatures below 850°C, metallic high-temperature alloys are being used. Because it is very difficult to sinter LaCrO₃ to full density, synthesis methods were developed in which a high-temperature sintering step is superfluous. The EVD process is such a method. The development of the EVD process has been of prime importance to the successful development (and commercialization) of the tubular concept SOFC, introduced by Westinghouse.

The research described in this thesis comprises three parts. The first part (chapters 3 and 4) is dedicated to theoretical aspects of the synthesis of Mg-doped LaCrO₃. In the second part (chapter 5), the experimental results of the synthesis of (doped) LaCrO₃ by means of EVD are described. In the last part (chapter 6), the first results of the synthesis of the perovskite oxide yttrium chromite (YCrO₃) by means of particle-precipitation-aided CVD (PP-CVD) are presented. In principle, PP-CVD may be an attractive alternative for the EVD process, as it has been proven that fully dense layers can be formed on porous substrates.

In chapter 3, thermodynamic calculations are carried out in order to obtain information about the solubility of MgO in LaCrO₃, to predict experimental conditions for the CVD/EVD process for deposition of Mg-doped LaCrO₃, and to calculate the composition of EVD films of Mg-doped LaCrO₃ as a function of temperature and input
amount of MgCl₂. A thermochemical description has been given for Mg-doped LaCrO₃, taking into account oxygen non-stoichiometry, and the accompanying thermodynamic parameters have been estimated. The oxygen non-stoichiometry calculations show reasonable agreement with the experimental TGA results, whereas the calculated maximum magnesium contents in Mg-doped LaCrO₃ appear to be too high. Therefore, in the future emphasis should be focused on obtaining more accurate estimates for the thermodynamic parameters of the compounds of the Mg-doped LaCrO₃ phase.

The amount of magnesium that can be incorporated into LaCrO₃ decreases significantly with decreasing equilibrium oxygen partial pressure and with increasing temperature. Hence, the magnesium content of Mg-doped LaCrO₃ films synthesized by means of EVD is limited to a maximum of a few atom percent.

In order to obtain the widest range of process conditions for deposition of single-phase Mg-doped LaCrO₃ in the CVD stage of the CVD/EVD process, the ratio of La/(La+Mg+Cr) in the input reactant stream should be equal to 1, and the ratio Mg/(Mg+Cr) should lie between 0 and 0.2. A mixture of steam and oxygen should be used as oxygen source reactants.

The magnesium content of EVD films of Mg-doped LaCrO₃ increases with increasing input concentration of MgCl₂ and increasing temperature. Owing to the stability of MgCl₂, the magnesium content of EVD films of Mg-doped LaCrO₃ is far less than the input concentration of MgCl₂. Therefore, it is necessary to use a large excess of MgCl₂ in the input stream in order to obtain a reasonable doping level.

In chapter 4, the EVD growth of YSZ and Mg-doped LaCrO₃ is modelled, assuming solid state diffusion to be rate determining. For YSZ, the experimentally observed growth rates gathered from literature are compared with the modelling results. This comparison reveals a discrepancy between the model calculations and the experimental data. This discrepancy indicates that either the electronic conductivity data used in the calculations are not valid for EVD layers of YSZ, or that the growth mechanism is more complex than originally assumed. The growth rate seems to be determined by a combination of rate limiting steps.

The EVD growth of Mg-doped LaCrO₃ is modelled in the same way as the EVD growth of YSZ. Because experimental data on the kinetics of EVD growth of Mg-doped LaCrO₃ are lacking, it is not possible to verify the model calculations. Because of the defect chemistry involved, the model calculations predict a complex temperature and oxygen partial pressure dependence for the parabolic growth rate constant.

Composite electrolytes comprising ceria (CeO₂) and a thin top layer of YSZ on the fuel side are promising candidates for use in low temperature SOFCs. These composite electrolytes can be fabricated by the EVD process. The kinetics of the growth of the top layer differ from that of the bottom layer, as they are influenced by the transport properties of both the bottom and the top layer. EVD growth of Mg-doped LaCrO₃, an
almost pure electronic conductor, on YSZ, which is a pure ionic conductor, has been modelled assuming interface reactions to be rapid. Initially, growth behaviour is linear, and then gradually changes to parabolic. The oxygen partial pressure at the substrate/film interface is an important parameter in the growth process. The effect of various process parameters on the film growth behaviour has been determined. If the oxygen partial pressure dependencies of the electronic and ionic conductivities of both layers are taken into account, it is not possible to derive an analytical expression for the time dependence of the film thickness of the top layer.

The synthesis of undoped and Mg-doped LaCrO$_3$ on porous alumina and calcia stabilized zirconia (CSZ) by means of CVD/EVD has been investigated in the temperature range of 1323 to 1573 K, using the metal chlorides as reactants. When a H$_2$/H$_2$O mixture is used as oxygen source, Cr-doped LaAlO$_3$ films instead of LaCrO$_3$ films are formed on porous alumina. When O$_2$/H$_2$O mixtures are used, the pore-plugging CVD deposits consist of LaCrO$_3$ and Cr$_2$O$_3$, whereas the EVD films primarily consist of LaCrO$_3$. Aluminium can easily be incorporated into LaCrO$_3$ during EVD growth. When MgCl$_2$ is added to the reactant stream, Cr$_2$O$_3$, MgCr$_2$O$_4$, and LaCrO$_3$ are formed in the CVD-pore-plugging deposits. During the EVD stage doped LaCrO$_3$ is formed, as long as the supply of LaCl$_3$ is sufficient, otherwise Cr$_2$O$_3$ will be formed simultaneously. The magnesium content of the LaCrO$_3$ films is low (<2%), despite the excess of MgCl$_2$ 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$^{-11}$ cm$^2$/s at 1473 K, and 1.1×10$^{-10}$ cm$^2$/s at 1523 K. Dense films of doped LaCrO$_3$ can be grown by the EVD process on gastight oxygen ion conducting substrates. Sr-doped LaCrO$_3$ has been deposited on gastight YSZ at a temperature of about 1413 K. Like magnesium, strontium is difficult to incorporate into EVD-grown LaCrO$_3$ films. 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$^{-11}$cm$^2$/s.

In the PP-CVD process, an aerosol is formed in the gas phase at elevated temperatures. The particles are deposited on a cooled substrate. Coherent layers with a controlled porosity are obtained by a simultaneous heterogeneous reaction, which interconnects the deposited particles. The synthesis of submicron powder of the perovskite oxide yttrium chromite (YCrO$_3$) by gas-to-particle conversion, which is the first step of the PP-CVD process, has been investigated. The powders have been synthesised using yttrium trichloride vapour (YCl$_3$), chromium trichloride vapour (CrCl$_3$), and steam/oxygen mixtures as reactants. The influence of the input molar ratio of the
elements on the composition and characteristics of the powders has been investigated. At a reaction temperature of 1283 K the powders consist of chromium sesquioxide (Cr$_2$O$_3$), or a mixture of Cr$_2$O$_3$ and YCrO$_3$. Formation of single-phase YCrO$_3$ is inhibited by either thermodynamic or kinetic limitations. Thermodynamic equilibrium calculations may elucidate this problem. In combination with these calculations, further experiments need to be performed in order to determine the range of experimental conditions in which single-phase YCrO$_3$ is formed. Furthermore, the conditions for the heterogeneous formation of YCrO$_3$ have to be determined in separate experiments. Then it will become clear whether there are reaction conditions at which the homogeneous and heterogeneous reactions can occur simultaneously, which is a necessity in the PP-CVD process.
ELECTROCHEMISCHE VORMING UIT DAMP VAN INTERCONNECTIEMATERIALEN VAN VASTE OXIDE BRANDSTOFCELLEN

Samenvatting

In dit proefschrift zijn de resultaten beschreven van de theoretische en experimentele onderzoekingen aan de synthese van ongedoteerd en magnesium gedoteerd lanthaanchromiet (LaCrO₃) door middel van electrochemische vorming uit damp (EVD). EVD is een gemodificeerde vorm van het conventionele CVD proces, die speciaal ontwikkeld is voor de synthese van gasdichte lagen op poreuze substraten. Het EVD proces is ontwikkeld bij Westinghouse voor de synthese van de gasdichte componenten van hun buisvormige vasteoxide brandstofcel (SOFC). In een brandstofcel wordt continu electriciteit geproduceerd door een electrochemische reactie tussen een brandstof (waterstof, koolmonoxide) en een oxidant (lucht). De brandstof en oxidant moeten van elkaar gescheiden zijn om rechtstreekse verbranding en dus de vorming van warmte in plaats van electriciteit te voorkomen. Daarom moet het electrolyt van een SOFC gasdicht zijn. Een praktische eenheid voor het opwekken van electriciteit bestaat uit een groot aantal in serie geschakelde brandstofcellen. Daarbij wordt de kathode van de ene cel elektrisch verbonden met de anode van de volgende cel. Daarvoor wordt een interconnectiemateriaal gebruikt, dat net als het electrolyt gasdicht moet zijn. Het interconnectiemateriaal moet een goede electronische geleider zijn bij de bedrijfstemperatuur van de brandstofcel en een minimale zuurstofionen-geleidbaarheid vertonen. Vanwege de hoge bedrijfstemperatuur (900-1000°C) worden voor de componenten van de SOFC keramische materialen gebruikt. De perovskiet LaCrO₃, gedoteerd met magnesium, strontium, of calcium is het meest gebruikte interconnectiemateriaal, hoewel in SOFCs die bij lagere temperatuur werken (<800°C) ook hoge temperatuur metaalallegeringen gebruikt worden. Vanwege het feit dat LaCrO₃ zeer moeilijk volledig gasdicht te sinteren is, zijn synthesemethoden gezocht waarbij een sinterstap bij hoge temperatuur overbodig is. Het EVD proces is zo'n synthesemethode. De ontwikkeling van dit proces is van cruciaal belang geweest voor de ontwikkeling (en commercialisering) van de buisvormige SOFC, zoals ontwikkeld door Westinghouse.

Het in dit proefschrift beschreven onderzoek is in drie delen op te splitsen. Het eerste deel (hoofdstukken 3 en 4) is gewijd aan de theoretische aspecten van de synthese van gedoteerd LaCrO₃ door middel van het EVD proces. In het tweede deel (hoofdstuk 5) worden de experimentele resultaten van de synthese van (gedoteerd) LaCrO₃ door middel van het CVD/EVD proces beschreven. In het laatste deel (hoofdstuk 6) worden
de eerste resultaten beschreven van de synthese van de perovskiet yttrimchromiet \((\text{YCrO}_3)\), een zeer sterk op \(\text{LaCrO}_3\) gelijkend materiaal, door middel van poeder precipitatie ondersteunde CVD (PP-CVD). Dit PP-CVD proces is mogelijk een aantrekkelijk alternatief voor het EVD proces, omdat met deze techniek ook volledig dichte lagen op poreuze structuren zijn aan te brengen.

In hoofdstuk 3 is met thermodynamische berekeningen bepaald hoe de oplosbaarheid van magnesiumoxide in \(\text{LaCrO}_3\) afhanger van de evenwichts-zuurstofpartiaalduik en de temperatuur. Tevens is bepaald in welk gebied van procescondities Mg-gedoteerd \(\text{LaCrO}_3\) kan worden gesynthetiseerd door middel van CVD/EVD. Tevens is bepaald hoe het magnesiumgehalte in de EVD films afhanger van de procescondities. Allereerst moest een schatting worden gemaakt van de thermodynamische parameters van Mg-gedoteerd \(\text{LaCrO}_2\). Daartoe is een thermochemische beschrijving van het Mg-gedoteerd \(\text{LaCrO}_3\) gegeven, waarin zowel ladingcompensatie door \(\text{Cr}^{4+}\) vorming als door zuurstofvacature vorming is meegenomen. De met de geschatte thermodynamische parameters berekende zuurstofvacature-concentraties komen goed overeen met in de literatuur gevonden experimenteel bepaalde waarden. De berekende maximale magnesiumgehaltes lijken echter te hoog.

De berekende ternaire fasendiagrammen laten zien dat het maximum magnesiumgehalte in \(\text{LaCrO}_3\) afneemt met afnemende zuurstofpartiaalduik. Omdat EVD films aangroeien in een sterk reducerende atmosfeer, zal het maximum magnesiumgehalte beperkt zijn tot een paar atoomprocent en niet zo hoog kunnen worden als met poedersynthese-technieken of PP-CVD mogelijk is. De berekende CVD diagrammen laten zien dat bij alle beschouwde procescondities Mg-gedoteerd \(\text{LaCrO}_3\) de meest stabiele vaste fase is en dat de conversie van de (in hoeveelheid) limiterende reactant naar Mg-gedoteerd \(\text{LaCrO}_2\) nagenoeg 100% is. Vorming van andere vaste fasen treedt alleen op als reactanten in overmaat aanwezig zijn. Volgens de berekeningen neemt het magnesiumgehalte in de EVD films toe met toenemende concentratie magnesiumchloride in de invoer. Om een kleine hoeveelheid magnesium in het \(\text{LaCrO}_3\) in te kunnen bouwen is, relatief gezien, een grote overmaat magnesiumchloride in de invoerstroom noodzakelijk. Dit komt overeen met de in de literatuur beschreven experimentele waarnemingen.

In hoofdstuk 4 wordt de EVD stap van het groeiproces gemodelleerd. Dit hoofdstuk bestaat uit drie gedeelten. In het eerste deel wordt de EVD groei van yttria- gestabiliseerd zirconia (YSZ) gemodelleerd onder de aannames dat vastestof-transport de snelheidsbepalende stap in het groeiproces is. Tevens worden de resultaten van de berekeningen vergeleken met de experimenteel gevonden kinetiekgegevens uit de literatuur. Deze vergelijking laat zien dat er een discreпantie is tussen de modelberekeningen en de experimentele gegevens. Mogelijke verklaringen voor de
verschillen zijn, dat de electronische geleiding in EVD films van YSZ verschilt van die van gesinterde YSZ pillen, of dat vastestof-transport niet de enige snelheidsbepalende stap in het groeiproces is en dat er sprake is van een combinatie van snelheidsbepalende stappen.

In het tweede gedeelte wordt de EVD groei van Mg-gedoteerd LaCrO₃ op poreuze substraten gemodelleerd, analoog aan het modelleren van de EVD groei van YSZ. Omdat er nauwelijks experimenten beschreven zijn in de literatuur, kunnen de modelberekeningen niet geverifieerd worden. Uit de modelberekeningen volgt dat, rekening houdend met de defectchemie, de parabolische groeisnelheidsconstante een zeer complexe temperatuur- en zuurstofpartiaaldruk-afhankelijkheid heeft.

In het derde gedeelte wordt de EVD groei van Mg-gedoteerd LaCrO₃, een electronische geleider, op gashoudend YSZ, een ionengeleider, beschreven. Ook in deze berekeningen is aangenomen dat de aangroei bepaald wordt door vastestof-transport. Deze modelberekeningen laten zien hoe bij de synthese van twee-laags composiet-electrolyten de kinetiek van de aangroei van de toplaag afwijkt van die van de onderste laag. De aangroei van de toplaag is in eerste instantie lineair. Met toenemende laagdikte vindt een geleidelijke overgang plaats naar parabolische groei. Het verloop van deze overgang wordt bepaald door de geleidingseigenschappen van de beide lagen, door de dikte van de onderste laag en door de chemische potentiagradieënt over de beide lagen. Als de zuurstofpartiaaldruk-afhankelijkheid van de electronische en ionengeleiding in de beide lagen wordt meegenomen, dan is het niet mogelijk om een analytische uitdrukking te vinden voor de dikte van de toplaag als functie van de depositietijd.

De synthese van ongedoteerd en Mg-gedoteerd LaCrO₃ op poreus aluminiumoxide en calcia-gestabiliseerd zirconia (CSZ) door middel van CVD/EVD is onderzocht in het temperatuurgebied van 1323 tot 1573 K. Hierbij zijn de metaalchlorides gebruikt als reactanten. Indien een H₂/H₂O mengsel wordt gebruikt als bron voor zuurstof, wordt op poreus alumina Cr-gedoteerd LaAlO₃ gevormd in plaats van LaCrO₃. Bij gebruik van O₂/H₂O mengsels bestaan de porievullende CVD deposities uit een mengsel van Cr₂O₃ en LaCrO₃, terwijl de EVD lagen voornamelijk uit LaCrO₃ bestaan. Het is gebleken dat in de EVD fase aluminium gemakkelijk in het LaCrO₃ is in te bouwen. Als aan de reactantenstroom ook MgCl₂ wordt toegevoegd, wordt in de porievullende deposities naast LaCrO₃ en Cr₂O₃ ook MgCr₂O₄ gevormd. In de EVD fase wordt LaCrO₃ gevormd zolang er voldoende La₃O₃ wordt aangevoerd, anders wordt er simultaan Cr₂O₃ gevormd. Ondanks een grote overmaat MgCl₂ in de gasfase is het magnesiumgehalte in de EVD films zeer laag (<2%), hetgeen verwacht wordt op basis van de thermodynamische berekeningen en de gegevens uit de literatuur. De aangroei van de EVD films lijkt parabolisch, met parabolische groeisnelheidsconstanten van 8.2×10⁻¹¹ cm²/s bij 1473 K en 1.1×10⁻¹⁰ cm²/s bij 1523 K.

Films van Sr-gedoteerd LaCrO₃ zijn gegroeid op gashoudend YSZ door middel van EVD,
bij een temperatuur van ongeveer 1410 K. Strontium is net als magnesium moeilijk in te bouwen in LaCrO₃ tijdens de EVD groei. Op substraten met diktes varierend van 200 tot 600 μm blijkt dat de filmgroei al parabolisch is voor filmdiktes vanaf 2 μm. De parabolische groeisnelheidsconstante bij deze temperatuur bedraagt 6.5×10⁻¹¹ cm²/s.

In het PP-CVD proces wordt bij hoge temperaturen door een homogene reactie in de gasfase een aerosol gevormd. De poederdeeltjes worden op een gekoeld substraat gedeponeerd. Mechanisch stabiele lagen met een gecontroleerde porositeit worden verkregen door de poederdeeltjes met elkaar te verbinden door middel van een simultane heterogene reactie. De eerste resultaten van de synthese van submicron poederdeeltjes van de perovskiet YCrO₃ door middel van een homogene reactie -de eerste stap in het PP-CVD proces- zijn beschreven in hoofdstuk 6. Hierbij zijn de metaalchloriden YCl₃ en CrCl₃, H₂O en O₂ gebruikt als reactanten. Het is mogelijk gebleken om YCrO₃ via een homogene reactie te maken, hoewel bij de gebruikte reactiecondities Cr₂O₃ of mengsels van Cr₂O₃ en YCrO₃ gevormd werden. Nader onderzoek moet uitwijzen of de vorming van éénfasig YCrO₃ gereemd wordt door thermodynamische of kinetische factoren. Daarnaast zal in aparte experimenten uitgezocht moeten worden bij welke condities YCrO₃ heterogeen gevormd wordt. Dan zal moeten blijken of reactiecondities gevonden kunnen worden waarbij de homogene en heterogene reacties simultaan optreden, hetgeen essentieel is voor het PP-CVD proces.
Nawoord

Op de rug en de kaft van dit proefschrift prijkt slechts één naam. Dit is alleen terecht voor wat betreft het typen van de tekst en het maken van de tekeningen (op één na) en grafieken van dit proefschrift. Aan de totstandkoming van dit proefschrift hebben natuurlijk veel meer personen dan alleen de promovendus een bijdrage geleverd. Hiervoor ben ik een groot aantal mensen mijn dank verschuldigd, waarvan ik er een aantal met name wil noemen.

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*Ceterum censeo Carthaginem esse delendam.*

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Curriculum Vitae

List of Publications


