Doctoral Thesis

Cathode supported thin electrolytes i.e. electrolytes and nano sized ceria solid solutions for solid oxide fuel cells

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CATHODE SUPPORTED THIN ELECTOLYTES AND NANO SIZED CERIA SOLID SOLUTIONS FOR SOLID OXIDE FUEL CELLS

A thesis submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY ZURICH
for the degree of
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presented by
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1999
CONTENTS

Summary 1
Zusammenfassung 3

1 Introduction 5
  1.1 Background 5
  1.2 Solid oxide fuel cells 6
  1.3 State-of-the-art SOFC 8
  1.4 Trends in SOFC development 9
References 12

2 Aim of the Thesis 15

3 Intermediate Temperature SOFC with Cathode Supported
  Thin Film Electrolytes 17
  3.1 Introduction 17
    3.1.1 General 17
    3.1.2 Aim of the study 18
  3.2 Experimental Procedure 19
    3.2.1 Cell design 19
    3.2.2 Substrate preparation 19
    3.2.3 Electrolyte deposition 21
    3.2.4 Anode deposition 22
    3.2.5 Electrochemical measurements 24
  3.3 Results and Discussion 28
    3.3.1 Support structure 28
    3.3.2 Electrolyte characterization 31
    3.3.3 Anode characterization 35
    3.3.4 Fuel cell test 39
3.4 Conclusions
References

4 Activated Sintering of Cerium Oxide

4.1 Introduction
  4.1.1 General
  4.1.2 Aim of the study

4.2 Experimental Procedure
  4.2.1 Sample preparation
  4.2.2 Experimental methods

4.3 Results and Discussion
  4.3.1 Densification of cerium oxide nanopowders with transition metal oxides
  4.3.2 Densification of CGO nanopowders with cobalt oxide
  4.3.3 Microstructure

4.4 Model for the Densification of CGO Nanopowders with Transition Metal Doping
  4.4.1 Activated sintering in other systems
  4.4.2 Cobalt oxide activated sintering of CGO

4.5 Summary and Conclusions
References

4-A.1 Phase diagram of the cerium oxide / cobalt oxide system
4-A.1 Ionic radius and solubility of MeO\textsubscript{x} in CeO\textsubscript{2}

5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

5.1 Introduction
  5.1.1 General
  5.1.2 Aim of the study
5.2 Experimental Procedures 91
5.2.1 Sample preparation 91
5.2.2 Impedance spectroscopy and 4-point conductivity measurements 92
5.2.3 Microstructural modelling 92
5.2.4 Defect chemistry of gadolinium doped cerium oxide containing ions of variable charges 98

5.3 Results 102
5.3.1 Total conductivity 102
5.3.2 Impedance analysis of grain/grain-boundary contribution to total conductivity 108
5.3.3 Correlation of conductivity data with microstructure 115

5.4 Summary and Conclusions 116

References 117

Outlook 121

Abbreviations 123

Acknowledgments 125

Curriculum Vitae 127
Current solid oxide fuel cells (SOFC) employ stabilized zirconia as electrolyte with a typical thickness of 150 to 200 μm. Due to the high resistivity towards ionic current at intermediate temperatures (600-700°C), fuel cells using this electrolyte material have to be operated at temperatures of 900°C and higher. Decreasing the operation temperature to intermediate temperatures would reduce system cost and enhance reliability. In order to retain the same power output, the ionic resistance of the fuel cell has to be lowered. This can be achieved either by thinning the electrolyte thickness e.g. using thin-film zirconia based electrolytes or by an electrolyte material with a lower specific resistivity in this temperature range. Ceria based solid solutions are promising candidates for such alternative electrolytes. They exhibit an ionic conductivity which is 3 to 5 times higher compared to zirconia electrolytes.

The goal of the present study is to develop a new SOFC design for electrolytes prepared by thin-film deposition techniques and to improve the material properties of cerium solid solutions so that they can be used as alternative electrolyte material.

A cell design was developed based on cathode support structures with a 5 μm thin electrolyte bi-layer deposited by reactive magnetron sputtering. The electrolyte bi-layer consists of an yttria doped ceria interlayer (1 μm) and an yttria stabilized zirconia electrolyte layer (4 μm). The ceria buffer layer prevents undesirable reaction products with the perovskite cathode material. The thin zirconia electrolyte provides low ohmic losses. The cells were operated with humidified H₂/N₂ as fuel against air and exhibited open circuit voltages as high as 1.06 V at 700°C indicating a dense and crack-free electrolyte layer. High power densities of 340 and 325 mW/cm² at 600 and 700°C, respectively have been achieved using sputter deposited Ni-YSZ anodes. These power densities are comparable to state-of-the-art SOFC systems operated at much higher temperatures of 900 to 1000°C.
Summary

In order to improve alternative electrolyte materials such as ceria, a new procedure was found to obtain nanosized ceria ceramics. The effects of small amounts (<5 mol%) of transition metal oxides on the sintering characteristics of cerium oxide solid solutions were evaluated. Commercially available $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ powder with an average crystallite size of ~20 nm served as model substance for electrolytes with a high oxygen ionic conductivity and low electronic conductivity. Cobalt oxide doping of this powder lead to >99% dense material at sintering temperatures below 900°C compared to 1400°C for the undoped material. Due to this low sintering temperature the average grain size in the sintered body is reduced from the micrometer range down to less than 120 nm.

We found an amorphous cobalt rich grain boundary layer of about 2 nm thickness in the material sintered at 900°C for a short time (10 min). This layer disappears upon further annealing at 900°C or at higher sintering temperatures due to incorporation of the cobalt cations in the ceria lattice. The rapid densification at unusually low sintering temperatures is attributed to the formation of a metastable subeutectic liquid phase.

Furthermore, the doping of the CGO powder by cobalt oxide with concentrations below 2 mol% did not change the ionic conductivity nor the electronic domain boundary when annealed for 2 hrs at temperatures above 900°C. Then the cobalt oxide forms a solid solution with ceria. However, short sintering times or higher dopant concentrations lead to an electronic conducting grain boundary phase short circuiting the ionic conductivity of the CGO grains. Proper selection of the doping level, sintering time and temperature allows to taylor mixed conducting oxides based on CGO from pure electronic to pure ionic conducting.

The materials developed in this thesis have potential use as electrolytes and/or anodes in solid oxide fuel cells and in ion separation membranes.
Zusammenfassung


Das Ziel der vorliegenden Arbeit ist die Entwicklung eines neuen Brennstoffzellendesigns für die Abscheidung von Dünnschichtelektrolyten und die Verbesserung der Materialeigenschaften von Ceroxid Festkörpern als alternatives Elektrolytmaterial.

Zusammenfassung

tungsichten sind vergleichbar mit Standard Brennstoffzellensystemen die bei wesentlich höheren Temperaturen von 900 - 1000°C betrieben werden.


Im kurz (10 Min.) gesinterten Material (bei 900°C) fanden wir eine amorphe, ungefähr 2 nm dicke Kobalt reiche Korngrenzschicht. Diese Schicht verschwand nach weiterem Glühen bei 900°C oder bei höheren Sintertemperaturen aufgrund des Einbaus der Kobalt Kationen im Kristallgitter des Ceroxides.


Das im Rahmen dieser Arbeit entwickelte Material kann als Elektrolyt und in Anoden für Festelektrolytbrennstoffzellen und in Sauerstofftrennmembranen eingesetzt werden.
1 INTRODUCTION

Abstract

An introduction to the basic operation principle of a solid oxide fuel cell (SOFC) is given. The state-of-the-art SOFC system is outlined and the operational limitations of the system are discussed. Potential improvements of the SOFC system are presented. The most relevant literature in the field is reviewed.

1.1 Background

Present technologies for utilizing natural gas for electric energy production are based on combustion processes to produce hot gases driving turbines and mechanical generators. These processes are limited by the Carnot efficiency and are amenable to production of toxic exhaust gases. Fuel cells are not limited by the Carnot efficiency because they rely on electrochemical, rather than thermo-mechanical processes, in converting chemical energy into electricity.

One of the viable processes for electrochemical conversion of natural gas to produce electric energy is the solid oxide fuel cell (SOFC) employing ceramic cell components. The cell operates at 900 - 1000°C, which is low for the formation of toxic oxides, but sufficiently for high energy efficiency. The thermodynamic efficiency of the cell for methane conversion is nearly 100% at this temperature. Chemical-to-electrical efficiencies exceeding 45% can be obtained even in small (~kW) scale applications up to 60-70% in large (~ 100 kW to MW) scale applications [1,2].
1.2 Solid oxide fuel cells

Principle of operation

A schematic view of a single SOFC cell, frequently referred to as a PEN\(^1\) is shown in Fig. 1.1. A SOFC is a current producing device in which the electrodes are exposed to atmospheres of different oxygen partial pressures. At the cathode, oxygen is reduced by taking electrons from the external circuit and is incorporated into the electrolyte which is typically an oxygen ion conductor. Fuel e.g. hydrogen, methane or carbon monoxide is fed to the anode, where it is oxidized, and electrons are released into the external circuit. The overall conversion reactions are:

\[
2H_2 + O_2 \leftrightarrow 2H_2O \tag{1.1}
\]

\[
CO + \frac{1}{2}O_2 \leftrightarrow CO_2 \tag{1.2}
\]

The exhaust products are water and carbon dioxide. Unlike other types of fuel cells, SOFCs can be operated with a variety of fuels due to their high operating temperature such as methane, carbon monoxide, naphta, gas oil, kerosine, biogas, gases from biomass and landfill wastes \([4]\).

The electromotive force (emf) that develops across the cell under equilibrium conditions, i.e. if no current is flowing through the device, is given by the Nernst equation

\[
E_{emf} = \frac{RT}{4F} \ln \left( \frac{p_{O_2}^{\text{high}}}{p_{O_2}^{\text{low}}} \right) \tag{1.1}
\]

where \(p_{O_2}^{\text{high}}\) and \(p_{O_2}^{\text{low}}\) are the oxygen partial pressures at the cathode and at the anode, respectively. \(R, T\) and \(F\) have their usual meanings. The emf given by Eqn. (1.1) is the open circuit voltage (OCV), and is reached with an ideal gas tight

---

1. PEN: **positive electrode** - **electrolyte** - **negative electrode**
1.2 Solid oxide fuel cells

For reviews on SOFCs the reader is referred to [3-5].
1 Introduction

Fig. 1.2 Schematic diagram of the current-voltage characteristics as well as the different losses in a solid oxide fuel cell. For abbreviations see text.

1.3 State-of-the-art SOFC

Two SOFC systems are currently the most advanced. The Siemens/Westinghouse system which is based on one end closed tubes [10] and the Sulzer HEXIS\(^1\) system which is based on flat plates [6].

The currently most widely investigated concept is the planar or flat-plate design. This concept relies on a thick self-supporting yttria doped zirconium oxide electrolytes on which thin porous electrodes (anode and cathode) are applied. The single cells are stacked between metallic or ceramic interconnector plates to achieve the desired voltage and power output. Due to the ohmic resistance of the 100 to 200 µm thick zirconia electrolyte, these cells have to be operated at temperatures as high as 900-1000°C to limit the ohmic losses. SOFCs based on this concept allow reasonable power densities and use conventional ceramic fabrication methods. Other planar concepts were developed at Siemens [7], in Riso [8], and at Tokyo Gas [9].

---

1. HEXIS: heat exchanger integrated stack.
Due to the high operating temperature of a SOFC, the cell components have to fulfill several chemical, thermal and physical requirements in order to avoid the formation of interfacial secondary phases, delamination due to thermal stresses and material interdiffusion. It is therefore a challenge for material science to select and develop appropriate materials with respect to their chemical and physical compatibility but also in terms of cost effectiveness (Fig. 1.1). SOFC components, materials, their characteristics, and requirements are listed in Table 1.1.

![Fig. 1.3 Sketch of a solid oxide fuel cell (SOFC) stack repeat element consisting of cathode, electrolyte, anode, and interconnector (bi-polar plate). Material interfaces and possible reaction zones are indicated.](image)

### 1.4 Trends in SOFC development

Major efforts are underway to lower the operating temperature to 600-800°C. This would drastically lower the material costs for interconnector components and the insulation. In addition, increased lifetime due to highly reduced interface reactions, material stress, and interdiffusion is expected. However, one problem associated with lowering the operation temperature is the increasing ohmic loss occurring in the 100-200 μm thick zirconia based electrolyte. This can be overcome by lowering the electrolyte resistance either by decreasing the electrolyte thickness down to some μm or by using materials of higher specific ionic conductivity.
Tab. 1.1 Materials and characteristics of the different cell components used in state-of-the-art solid oxide fuel cells.

<table>
<thead>
<tr>
<th>component</th>
<th>material</th>
<th>characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>electrolyte</td>
<td>stabilized zirconia</td>
<td>• 100-250 µm thick&lt;br&gt;• high ionic conductivity&lt;br&gt;• gas tightness&lt;br&gt;• mechanical stability</td>
</tr>
<tr>
<td>cathode</td>
<td>doped LaMnO$_3$</td>
<td>• 5-50 µm thick&lt;br&gt;• electronic conductivity&lt;br&gt;• activity for O$_2$ reduction</td>
</tr>
<tr>
<td>anode</td>
<td>Ni-cermet</td>
<td>• 5-50 µm thick&lt;br&gt;• electronic conductivity&lt;br&gt;• activity for fuel oxidation</td>
</tr>
<tr>
<td>interconnector</td>
<td>doped LaCrO$_3$&lt;br&gt;Cr-based alloys or oxide dispersion strength alloys</td>
<td>• 2-6 mm thick&lt;br&gt;• electronic conductivity&lt;br&gt;• expensive</td>
</tr>
</tbody>
</table>

These potential electrolytes materials are scandia doped zirconia, ceria solid solutions, and doped bismuth oxide [11].

In case the electrolyte thickness is reduced to the µm range it cannot act as mechanical supporting element for the electrodes and the bipolar plate any more and a new design for the SOFC structure is needed. There are two basic designs which can then be applied: (i) the cathode supported, and (ii) the anode supported SOFC. The advantages and disadvantages of each design are summarized in Table 1.2.

Some SOFCs based on thin film electrolytes have already been tested and exhibited excellent electrochemical performance [12-20]. Up to now, the most critical step in fabricating electrode supported thin-film SOFC is the deposition of the thin, crack free, and well adherent electrolyte layer. Many methods have been applied for depositing thin and dense electrolyte films on dense or porous substrates. They are based on ceramic powder techniques or chemical, and physical processes. These techniques mainly differ in deposition rates, substrate temperature during deposition, precursor materials, necessary equipment, upscaleability,
1.4 Trends in SOFC development

<table>
<thead>
<tr>
<th>design</th>
<th>advantage</th>
<th>disadvantage</th>
</tr>
</thead>
</table>
| electrolyte supported | • supporting electrolyte, 150-200 µm thick  
• anode and cathode can be adapted       | • high ohmic electrolyte loss at intermediate temperature                  |
| cathode supported   | • deposition of µm thin electrolyte possible  
• anode can be adjusted  
• high fuel utilization expected  
• low ohmic losses in electrolyte       | • fabrication sequence starts at rather low sintering temperatures  
• mechanical stability                |
| anode supported     | • deposition of µm thin electrolyte possible  
• high mechanical stability  
• cathode can be adjusted  
• fabrication sequence starts at high sintering temperature       | • low fuel utilization expected  
• increased stresses during oxidizing - reducing cycles             |

* Tab. 1.2 Characteristics of the different fuel cell designs.

... cost, and quality of the resulting films [21]. We want to point out that although many thin-film deposition techniques for SOFC have been successfully demonstrated on lab-scale (∼30 mm in diam.) only two techniques have been upscaled and successfully applied on demonstration units: reactive magnetron sputtering (PVD) [13] and chemical vapor deposition (CVD) [10].

Development trends and their impact on SOFC are summarized in Table 1.3. It is evident from this table that a highly positive effect on performance, long-term stability and cost will be achieved when the operating temperature is lowered by using alternative electrolyte materials and applying thin-film electrolytes.
**Tab. 1.3** Influence of different development trends on performance, long-term stability and cost of a SOFC system ($T_{\text{operation}}$: operation temperature of SOFC system; $T_{\text{process}}$: processing and fabrication temperature; $\eta_{\text{C}}$, $\eta_{\text{A}}$: denotes cathodic and anodic overpotential losses).

<table>
<thead>
<tr>
<th>development trends</th>
<th>performance</th>
<th>long-term stab.</th>
<th>cost material</th>
<th>cost operation</th>
<th>cost fabrication</th>
</tr>
</thead>
<tbody>
<tr>
<td>deposition method</td>
<td>0(^a)</td>
<td>0</td>
<td>+</td>
<td>0</td>
<td>+</td>
</tr>
<tr>
<td>lowering of $T_{\text{operation}}$</td>
<td>--</td>
<td>++</td>
<td>++</td>
<td>++</td>
<td>0</td>
</tr>
<tr>
<td>thin-film electrolyte</td>
<td>++</td>
<td>-</td>
<td>+</td>
<td>++</td>
<td>0</td>
</tr>
<tr>
<td>alternative electrolyte material</td>
<td>++</td>
<td>0</td>
<td>0</td>
<td>++</td>
<td>0</td>
</tr>
<tr>
<td>lower $T_{\text{process}}$</td>
<td>+</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>++</td>
</tr>
<tr>
<td>reducing $\eta_{\text{C}}$, $\eta_{\text{A}}$</td>
<td>++</td>
<td>0</td>
<td>+</td>
<td>+</td>
<td>0</td>
</tr>
</tbody>
</table>

\(^a\): strong positive, +: positive, o: not defined, -: negative, --: strong negative effect.

**References**


1.4 Trends in SOFC development

2 Aim of the Thesis

Cost reduction is essential for market acceptance and competitiveness of a solid oxide fuel cell. Therefore, the main purpose of this work is to develop a SOFC for intermediate temperature operation. Two main topics are addressed:

(i) cathode substrate development for electrolyte thin-film deposition, and
(ii) improving the sintering characteristics and microstructure of cerium oxide based solid solutions.

Intermediate temperature SOFC with cathode supported thin film electrolytes

A novel design of a cathode supported thin-film electrolyte SOFC for intermediate temperature operation is developed. The cathode support is based on a ceramic foam structure with a microporous active cathode layer on top. The deposition of the thin electrolyte will be achieved by physical vapor deposition. The anode should be applied either by screen-printing or by sputtering. The different cell components as well as the whole cell will be characterized in terms of microstructure and electrochemical performance. (Chapter 3)

Activated sintering of cerium oxide

The sintering of ceria solid solutions, an alternative electrolyte, with transition metal oxide additives will be investigated. Sintering temperature to obtain dense cerium oxide material should be reduced in order to retain fine grained, dense material. Sintering characteristics and microstructural evolution as a function of dopant concentration and temperature will be analysed. (Chapter 4)

Mixed electronic-Ionic conductivity of cobalt doped cerium gadolinium oxide

The effect of small amounts of transition metal oxide dopants such as cobalt oxide on the electrical properties of cerium oxide solid solutions will be evaluated. (Chapter 5)
2 Aim of the Thesis
3 Intermediate Temperature
SOFC with Cathode Supported
Thin Film Electrolytes

Abstract

The performance of solid oxide fuel cells operating at intermediate temperatures (600-700°C) strongly depends on the ohmic loss of the electrolyte and on the overpotential losses of the electrodes. In this paper, we describe fuel cells based on cathode support structures with a 5 μm thin electrolyte bi-layer deposited by reactive magnetron sputtering. The electrolyte bi-layer consists of an yttria doped ceria interlayer (1 μm) to prevent chemical reaction with the cathode material and to decrease the interfacial resistance, and an yttria stabilized zirconia electrolyte layer (4 μm) to provide low ohmic loss. The cells were operated with humidified \( \text{H}_2/\text{N}_2 \) as fuel against air and exhibited open circuit voltages as high as 1.06 V at 700°C indicating a dense and crack-free electrolyte layer. High power densities, e.g. 340 and 325 mW/cm\(^2\) at 600 and 700°C, respectively were obtained using sputter deposited Ni-YSZ anodes.

Keywords: Intermediate temperature, solid oxide fuel cell, thin film electrolyte, physical vapor deposition.

3.1 Introduction

3.1.1 General

Solid oxide fuel cells (SOFCs) based on yttria-stabilized zirconia (YSZ) have to be operated at high temperatures (800-1000°C) to insure sufficient ionic conductivity. These high operating temperatures (\( T_{\text{op}} \)) result in high material costs for interconnector materials and insulation. In addition high operating temperatures cause system degradations due to interface reactions and high thermal cycling stress [1,2]. Lowering the operating temperature in the range of 600 to 700°C allows to use low cost interconnects and potentially causes less degradation. In
order to lower the ohmic losses, the YSZ layer should be as thin as possible, dense and uniform [3].

Studies have been made by several groups on thin-film (< 10 \( \mu \)m) SOFCs using conventional electrode materials such as Sr doped LaMnO\(_3\) (LSM), LSM/YSZ composite cathodes and Ni-YSZ anodes [4,5,6]. A detailed overview of thin-film deposition techniques on various substrates for SOFC applications is given in [7].

Whereas good performance at \( T_{op} \geq 800^\circ\)C has been demonstrated, decreasing \( T_{op} \) to 700\(^\circ\)C leads to a rapid increase of the electrode polarization and of the electrolyte resistance thus limiting the SOFC performance [8,9,10]. New materials have been proposed for cathodes in IT-SOFC such as \( \text{La}_{1-x}\text{Sr}_x\text{Co}_{1-y}\text{Fe}_y\text{O}_3 \) (LSCF). They exhibit higher electronic and ionic conductivity than LSM [11,12,13] and higher catalytic activity for oxygen reduction already at temperatures as low as 250\(^\circ\)C [14]. However, formation of zirconate phases at the LSCF-YSZ interface degrades these cathodes [2,15,16]. As there is no intermediate compound formed between CeO\(_2\) and La\(_2\)O\(_3\) neither between CeO\(_2\) and ZrO\(_2\) at temperatures below 1300\(^\circ\)C [17], it would be desirable to use a CeO\(_2\)ss interlayer. This CeO\(_2\)/YSZ bi-layer will then act as electrolyte [18] whereby YSZ blocks the electrons and CeO\(_2\) prevents the zirconate formation of YSZ with the lanthanum and cobalt oxide based cathode. In addition, we expect a promoting effect from the CeO\(_2\) interlayer on the electrochemical reactions at the cathode/electrolyte interface due to the about 10 times higher oxygen surface-exchange coefficient compared to yttria stabilized zirconia [19,5].

### 3.1.2 Aim of the study

The objective is to develop a planar SOFC with a mixed conducting cathode composite serving as substrate for a thin (1 \( \mu \)m) CeO\(_2\)ss interlayer and an electron-blocking thin (4 \( \mu \)m) YSZ electrolyte layer. As anode sputtered Ni-YSZ and screen-printed Ni-CeO\(_2\)ss cermets will be used. This cell is designed to operate at temperatures as low as 600-700\(^\circ\)C. Single cells (\( \phi 35 \) mm) should be tested in fuel cell mode using air and humidified H\(_2\)/N\(_2\) gases as fuel. Cell losses should be measured and the ohmic contributions and electrode overpotentials identified.
3.2 Experimental Procedure

3.2.1 Cell design

The design of the cathode support structure relies on a perovskite foam with a perovskite cathode layer as cover. The foam structure is used as mechanical support for the cathode layer, as current collector, and air distributor. Therefore, high mechanical stability, high electron conductivity, and high gas permeability are basic demands. The cathode layer bonded on top of this ceramic foam serves as active cathode and must have a high activity for oxygen reduction at intermediate temperatures. Since the active cathode layer acts as substrate for the deposition of the electrolyte thin-film optimized microstructure and surface quality in terms of surface roughness and pore size are required.

The cathode material was prepared from a mixture of perovskite \((\text{La}_{0.8}\text{Sr}_{0.2}\text{Co}_{0.2}\text{Fe}_{0.8}, \text{denoted LSCF})\) and ceria solid solutions \((\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}, \text{denoted CGO})\) powder. It is recognized that LSCF is a mixed ionic electronic conductor with high catalytic activity for oxygen reduction at temperatures below 800°C \([20,21]\). The properties (e.g. mechanical strength, thermal expansion coefficient, microstructure) of this composite material were adjusted to that of the electrolyte. On top of the cathode support structure a 4 µm thick YSZ electrolyte has been deposited by PVD. To prevent chemical reaction between the electrolyte and the perovskite substrate an about 1 µm thick CYO chemical compatibility layer was introduced. In a final step a Ni-YSZ or a Ni-CGO anode was deposited by PVD or screen-printing, respectively. Details about each process step will be given in the following subsections.

3.2.2 Substrate preparation

Active cathode layer

Tape casting was chosen as the most suitable method for preparing thin porous cathode structures for subsequent electrolyte thin-film deposition \([22,23]\). The composition of the tape casting slurry is given in Table 3.1. The ceramic powders were dispersed in a mixture of solvent and dispersant and ball milled in a polyethylene bottle for six hours with 10 mm zirconia milling balls. Afterwards the plasticizer, release agent, and binder were added and the suspension was
homogenized again by ball milling for another 30 min followed by a degassing step.

<table>
<thead>
<tr>
<th>material</th>
<th>amount [wt%]</th>
<th>function</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Co}<em>{0.8}\text{Fe}</em>{0.2}\text{O}_3 )</td>
<td>40</td>
<td>powder</td>
<td>Praxair Speciality Ceramics, USA, #03-P1916DM</td>
</tr>
<tr>
<td>( \text{Ce}<em>{0.8}\text{Gd}</em>{0.2}\text{O}_{2-x} )</td>
<td>28</td>
<td>powder</td>
<td>Rhodia, Frankfurt, GER, #595250A</td>
</tr>
<tr>
<td>Toluene</td>
<td>16</td>
<td>solvent</td>
<td>FEROSA, Barcelona, ES</td>
</tr>
<tr>
<td>KD 1</td>
<td>1.6</td>
<td>dispersant</td>
<td>Fluka Chemie, Buchs, CH</td>
</tr>
<tr>
<td>PEG 600</td>
<td>5</td>
<td>plasticizer</td>
<td>Fluka Chemie, Buchs, CH</td>
</tr>
<tr>
<td>Bis(2-ethylhexyl) phtalate</td>
<td>5.8</td>
<td>release agent</td>
<td>Fluka Chemie, Buchs, CH</td>
</tr>
<tr>
<td>Polyvinylbutyral (PVB)</td>
<td>3.6</td>
<td>binder</td>
<td>Hoechst, Frankfurt, FRG</td>
</tr>
</tbody>
</table>

*Tab. 3.1 Slurry composition for tape casting of the active cathode substrate.*

Subsequently, the slurry was poured onto a glass plate which has been covered with a PE-foil before. Tape casting was performed using a doctor blade with an opening of 250 \( \mu \)m at a speed of 30 cm/min. The tape was dried at room temperature for 12 hrs. Round shaped plates were cut out from the green tapes and sintered in a controllable furnace on alumina sheets. They were slowly heated with 0.5 K/min up to 400°C and one hour holding time to carefully burn out the organic additives. The tapes were then heated with 3 K/min up to the desired sintering temperature in order to increase their strength and to meet the requirements for electrolyte deposition. These requirements are fine microstructure with a maximum pore size below 1 \( \mu \)m, a surface roughness of less than 1 \( \mu \)m, and no back-cutting edges (Fig. 3.1). After sintering the tapes exhibited an open porosity of 30% and a thickness of 150 to 170 \( \mu \)m depending on sintering temperature.

*Ceramic foam support preparation and bonding of active cathode layer*

The foams are manufactured by infiltrating a polyurethane foam (60 ppi) with the same ceramic slurry as described above (c.f. Table 3.1) for reasons of
3.2 Experimental Procedure

compatibility and sinter adjustments. After drying, the polymer has been slowly burned out in order to minimize damage to the coating. Once the polymer has been removed, the ceramic was sintered to the desired density at 1350°C with 2 hrs annealing time. The resulting foam consists of three dimensionally connected ceramic struts forming an open cell structure with 90 to 93 vol% open porosity. A detailed description of this “polymer sponge method” is given in [24, 25].

The foam support and the active cathode layer are joined together with a ceramic interlayer which was applied by dipping the sintered ceramic foam into the ceramic suspension described in Table 3.1 and then pressed onto the sintered cathode tape. Special care was taken to coat the single struts of the foams with as little ceramic as possible in order to obtain good electronic and mechanical contact without decreasing the accessibility of air to the active cathode layer. Sintering has been carried out at a temperature 50 K below the sintering temperature of the active cathode layer in order to prevent further sintering of this layer. An overview of the complete cathode substrate preparation is given in Fig. 3.2.

3.2.3 Electrolyte deposition

A UDP Plasmatron (TEER Ltd, GB) with four symmetrical vertical magnetrons was used for DC reactive magnetron sputtering [26]. Thin ceria 10 mol% yttria solid solutions (CYO) and 8 mol% yttria stabilized zirconia (YSZ) bilayers were deposited on the cathode substrates in an O$_2$-Ar plasma using CeY-alloy and

1. ppi = number of pores per inch
ZrY-alloy targets. The substrates were sputter-cleaned for 60 min prior to film deposition by applying a RF bias to the substrate holder with a power of 500 Watt. The cleaning process raised the substrate temperature up to 170°C. Reactive magnetron sputtering was carried out at a chamber pressure of 1.5 to 3.5 mbar, operating the alloy target with a current of 5 A. Typically, deposition rates of 4 µm per hour for CYO and 5 µm for YSZ were obtained. The substrate temperature did not exceed 200°C during deposition. More details are reported in [6].

3.2.4 Anode deposition

As we will see later on, the temperature of the last step in the cathode preparation limits the temperature for anode preparation to 1050°C. Therefore, standard Ni-YSZ anodes which are usually sintered at 1300°C and above cannot be applied [27,28]. To overcome this problem we first used a screen-printed Ni-CGO cermet
3.2 Experimental Procedure

where the nano sized CGO particles of the starting powder were coated with cobalt nitrate as described in Chapter 4 to enhance the sintering performance. Secondly we deposited a Ni-YSZ anode by reactive magnetron sputtering (as described in Subsection 3.2.3) from a nickel-zirconia-yttria alloy target at temperatures as low as 250°C.

Table 3.2 shows the composition of the screen-printing paste used for the Ni-CGO anode. The weight ratio of NiO to CGO was 2:1 corresponding to a volume fraction of 54% Ni after reduction. The ceramic powders and organic ingredients were mixed in a planetary mill for 1 hr. The paste was stable and exhibited no tendency of sedimentation. Cermet anodes of 1x1 cm² were screen-printed on the YSZ thin-film electrolyte by the use of a screen with a wire thickness of 20 μm.

The materials selected, specific thickness and preparation methods used for the different cell components are summarized in Table 3.3.

<table>
<thead>
<tr>
<th>material</th>
<th>amount</th>
<th>function</th>
<th>supplier</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO(^a)</td>
<td>50 wt%</td>
<td>powder</td>
<td>J.T. Baker, 1313-99-1</td>
</tr>
<tr>
<td>Ce(<em>{0.8})Gd(</em>{0.2})O(_{2-x}) + 1 mol% CoO(^b)</td>
<td>25 wt%</td>
<td>powder</td>
<td>Rhodia, #595250A, GER; Fluka, Buchs, CH</td>
</tr>
<tr>
<td>Diethylene glycol monobutyl acetate</td>
<td>20 wt%</td>
<td>solvent</td>
<td>Fluka, Buchs, CH</td>
</tr>
<tr>
<td>Furan-2-carboxylic acid</td>
<td>0.7 wt%</td>
<td>dispersant</td>
<td>Fluka, Buchs, CH</td>
</tr>
<tr>
<td>Ethocel 90004-57-3</td>
<td>4.3 wt%</td>
<td>binder</td>
<td>Aldrich, Milwaukee, WI, USA</td>
</tr>
</tbody>
</table>

Tab. 3.2 Slurry composition for screen-printing of the Ni-CGO anode.

a. >99%, \(d_{50} = 0.1\) μm, BET ~8.2 m²/g.
b. For cobalt doping of Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{2-x}\) refer to Chapter 4.
3 Intermediate Temperature SOFC with Cathode Supported Thin Film Electrolytes

<table>
<thead>
<tr>
<th>component</th>
<th>material</th>
<th>thickness [μm]</th>
<th>preparation method</th>
</tr>
</thead>
<tbody>
<tr>
<td>anode</td>
<td>Ni-YSZ / Ni-CGO</td>
<td>1-20</td>
<td>screen-printing</td>
</tr>
<tr>
<td>electrolyte</td>
<td>YSZ</td>
<td>4</td>
<td>PVD</td>
</tr>
<tr>
<td>chemical compatibility layer</td>
<td>CYO</td>
<td>1</td>
<td>PVD</td>
</tr>
<tr>
<td>cathode layer</td>
<td>LSCF/CGO (60 wt% / 40 wt%) composite</td>
<td>~150</td>
<td>tape-casting</td>
</tr>
<tr>
<td>foam support</td>
<td>LSCF/CGO (60 wt% / 40 wt%) composite</td>
<td>3-4 mm</td>
<td>slurry infiltration</td>
</tr>
</tbody>
</table>

Tab. 3.3 Components of the cathode supported SOFC. Materials selection, thickness and preparation methods of the different cell components.

3.2.5 Electrochemical measurements

DC-conductivity

Different measurement setups have been used to determine the total conductivity, \( \sigma_{\text{tot}} \), of ceramic samples. Due to the special structure of the ceramic foams the Van-der-Pauw method [29,30] was used. Electrical contacts were achieved by pressing ball shaped ends (1 mm diam) of platinum wires on the samples.

4-pt conductivity measurements have been conducted on sintered cathode substrate tape strips of 0.5·3 cm\(^2\) with a thickness of 200 μm as well as on sample bars of 30·4·4 mm\(^3\) (length·width·height) of pressed bulk material. The potential and current leads were contacted by applying platinum paste and fixing platinum wires with a ceramic two-component binder\(^1\). The distance between the voltage probes was kept at 1 cm. Measurements were taken in air during heating up to 900°C as well as during annealing and cooling to room temperature to confirm the reproducibility.

---

1. Firag, type 1500, two component system.
3.2 Experimental Procedure

Cell measurements

A schematic picture of the cathode supported cell is shown in Fig. 3.3a. Pt meshes used as current collector were attached to the electrodes with Pt paste and fixed with ceramic binder. The cell was placed between quartz glass tubes for gas supply as shown in Fig. 3.3b. All tests were conducted at temperatures from 500 to 700°C using air as oxidant and a mixture of 70% N₂/30% H₂ containing 3% H₂O as fuel. The cell voltage between anode and cathode was measured with a
high impedance scanning digital multimeter (Keithley 197A). The current was controlled with a laboratory power supply which was used in its galvanostatic mode. The test cells were heated to the desired operating temperature and equilibrated at this temperature until they gave stable cell current and voltage. Besides the steady state measurements, we determined the total electrical conductivity, $\sigma_{\text{tot}}$, with four-probe A.C. impedance spectroscopy using a Zahner FRA (model IM6, Zahner GmbH, FRG) in the range 0.1 Hz - 2 MHz with an excitation voltage of 40 mV. The high frequency real axis intercepts on Nyquist impedance plots, which give the total cell ohmic resistance have been used to calculate $\sigma_{\text{tot}}$ of the cell.

To accurately determine the electrode polarizations in electrolyte supported SOFCs, three electrode arrangements are commonly used (Fig. 3.4a). In this setup

![Diagram](image)

**Fig. 3.4** Sketch of three electrode setup for electrode polarisation loss determination on self supporting electrolyte (a) and electrode supported thin-film electrolyte cell (b). WE denotes working electrode, CE counter electrode.
two electrodes act as current collecting electrodes (working and counter) whereas the reference electrode is held on a steady potential. From the measurement of the potential difference between reference and working electrode under different operation conditions the polarization associated with the working electrode can be derived. The ohmic contribution of the electrolyte is usually determined by either applying the current interruption method [31] or by impedance spectroscopy [32]. However, it is important to note that accurate results are only obtained if the geometry of the electrode arrangement ensures a homogeneous current distribution. It has been shown by several authors, that this boundary condition holds only for limited cases and many design suggestions for electrode arrangements have been evaluated earlier [33,34,35,36,37].

It is important to note, that for electrode supported, thin-film electrolyte SOFCs it is not possible to have a symmetrical electrode setup as sketched in Fig. 3.4a and polarization measurements will be completely misleading. Neither the overpotential of the ‘supporting’ electrode, in our case the cathode, nor that of the last deposited electrode (WE in Fig. 3.4b, i.e. in our case the anode) are directly accessible. The only possibility to get information about the electrode overpotential are measurements of the same electrode system on self-supporting electrolytes in a symmetrical setup. This can only be done for the sputtered or screen-printed anode in the case of our cathode supported cell. However, the sputtered electrolyte/cathode substrate interface is expected to be very different compared to an interface of a cathode deposited on a polycrystalline substrate.

Therefore, we performed separate measurements on self-supporting electrolytes using a three-electrode, four-lead configuration as shown in Fig. 3.4. The Ni-YSZ sputtered anodes and the Ni-CGO cermet and reference anodes were applied on 200 μm thick YSZ polycrystals1 following the same experimental methods as described above (Subsection 3.2.4). For the counter electrodes (arranged symmetrically to the working electrodes) a ~50 nm Pt-layer was sputtered on the YSZ surface and coated with a Pt paste (C3605P, Heraeus GmbH, Hanau, FRG). Electrochemical impedance spectra were recorded at different cell currents under fuel cell operating conditions. The polarisation resistance, $R_p$, was obtained from the real-axis intercepts in the complex plane plot after correction for ohmic contribution of

1. Kerafol, Keramische Folien GmbH, Eschenbach, GER
the electrolyte. The anodic overpotential, $\eta_A$, could then be calculated. The procedure of determination of the different cell losses is sketched in Fig. 3.5.

1. determine the I-V characteristic of the cathode supported SOFC
2. deposite the anode on thick-film electrolyte and determine $\eta_A$
3. subtract $\delta U_Q$ as well as $\eta_A$ from the I-V curve to obtain an estimation of $\eta_C$

Fig. 3.5 Three step procedure to determine the cathode overpotential in a cathode supported thin-film electrolyte cell.

3.3 Results and Discussion

3.3.1 Support structure

In Fig. 3.6 the microstructures of the cathode layers sintered at different temperatures are shown. The 1000°C sintered sample exhibits a very fine microstructure with an average grain size of about 0.2 μm and a mean pore size of about 0.05 μm. However, we found poor particle to particle connection in this low temperature sintered material and therefore mechanical properties insufficient for handling, bonding on foam support, and for electrolyte deposition. When sintering at 1100 and 1200°C (Fig. 3.6(a) and (b)) a higher mechanical stability was obtained with maximum pore sizes still below 1 μm. Further increase of the sintering temperature to 1350°C leads to almost dense microstructures with an open porosity <5% determined by Hg porosimetry. However, with pore sizes >1 μm which is not
suitable for electrolyte deposition by PVD. The dependence of open porosity and mean pore size on sintering temperature of these cathode tapes is plotted in Fig. 3.7. To meet the requirements for the cathode substrate for PVD electrolyte deposition in terms of mechanical stability, pore size, and surface roughness we selected the 1100°C sintered cathode layer. Fig. 3.8 shows a 1100°C sintered cathode on ceramic foam substrate (left) and a SEM picture of the foam-cathode interface (right).

Electrical properties of the support structure

The total conductivity, $\sigma_{\text{tot}}$, of the cathode substrate is shown in Fig. 3.9 as a function of porosity consisting of LSCF/CGO sintered at 1000, 1100, 1200, and 1300°C as well as that for the ceramic foam support. The highest conductivity was
Fig. 3.7 Open porosity and mean pore size of cathode substrate as a function of sintering temperature, $T_{\text{sinter}}$, determined by Hg-porosimetry.

Fig. 3.8 Microporous active cathode layer on top of macroporous ceramic foam support structure (left). Joint of cathode layer with ceramic foam using a ceramic interlayer (right).

obtained for the 1300°C sintered sample similar to that we found for bulk material. With decreasing sintering temperature (increasing porosity) the conductivity decreases but even those sintered at 1000°C show still 1000 S/m at 700°C. The
activation energy was about 0.064 eV up to 850°C indicating a metallic like conduction mechanism which is typical for this type of perovskite materials [12].

Table 3.4 summarizes the results on conductivity for the cathode layers sintered at different temperature. For the foam support we found a total conductivity of about 1600 S/m (700°C) corresponding to an area specific resistance, $R_F^A$, of about 0.02 $\Omega\text{cm}^2$. We will show later that the area specific resistance of the electrolyte layer, $R_E^A$, is about 6 times this value and therefore contributes most to the ohmic losses of the cell structure. However, at higher operating temperatures as well as for thinner electrolytes the ohmic contribution of the foam support structure becomes important and can no longer be neglected.

### 3.3.2 Electrolyte characterization

A cross section of a CYO/YSZ bi-layer electrolyte is shown in Fig. 3.10. It was deposited on top of the microporous LSCF/CGO cathode layer which was sin-
3 Intermediate Temperature SOFC with Cathode Supported Thin Film Electrolytes

<table>
<thead>
<tr>
<th>$T_{\text{sinter}}$ [$^\circ$C]</th>
<th>Porosity [%]</th>
<th>Mean Pore Size [$\mu$m]</th>
<th>Electrical Conductivity (700°C) [$S/m$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1000</td>
<td>50</td>
<td>0.075</td>
<td>1000</td>
</tr>
<tr>
<td>1100</td>
<td>30</td>
<td>0.1</td>
<td>2150</td>
</tr>
<tr>
<td>1200</td>
<td>20</td>
<td>0.15</td>
<td>4470</td>
</tr>
<tr>
<td>1300</td>
<td>5</td>
<td>0.25</td>
<td>5100</td>
</tr>
</tbody>
</table>

*Tab. 3.4 Electrical conductivity of cathode substrates as a function of sintering temperature at 700°C.*

Fig. 3.10 Cross sectional view of electrolyte bi-layer deposited by PVD. The SEM image (left) and the back-scattered image (right) show the ~1 $\mu$m thick CYO chemical compatibility layer and the ~4 $\mu$m thick YSZ electrolyte on top.

tered at 1100°C for 2 hrs. Dense, micro-columnar CYO and YSZ films were already obtained at substrate temperatures as low as 250°C during deposition. The films appeared totally transparent and were fully crystallized showing a cubic lattice. No separate interface between the two PVD layers can be seen in the scan-
ning micrographs of the cross section indicating a good adherence of these layers (Fig. 3.10). From back scattering images we determined a thickness of 4 μm for the YSZ layer and 1 μm for the CYO layer. The influence of the annealing temperature on surface morphology of sputtered YSZ layers is shown in Fig. 3.11. The as-deposited layer exhibits grains of about 2 μm size with a topography typical for sputtered YSZ layers. Heat treatment at 1200°C for 2 hrs does not significantly change the microstructure of this PVD layer. However, after annealing at 1300°C for 2 hrs we found grain-coarsening accompanied by pore formation leading to pin-holes in the electrolyte layer.

![SEM images of the surface of YSZ electrolyte layer deposited by PVD. As deposited (a), after annealing at 1200°C (b) and 1300°C (c).](image)

The influence of temperature during the post preparation annealing on the microstructure is shown in Fig. 3.12. As previously discussed (c.f. Fig. 3.6) increasing the sintering temperature of the active cathode substrate layer leads to large pores (>1 μm, sintered at 1200°C) and to a dense surface (sintered at 1350°C). When depositing electrolyte layers on top of these substrates we observed the formation of defects resulting in pin-holes, delamination, and/or microcracks. The best electrolyte quality in terms of homogeneity and adherence was achieved for sputtering on the 1100°C sintered cathode substrate. At lower sintering temperature the mechanical properties were poor and even handling of these substrates was difficult.
4-pt conductivity of deposited electrolyte film

The total conductivity, $\sigma_{\text{tot}}$, for the whole cell structure consisting of foam support, active cathode layer, electrolyte bi-layer, and platinum contacts is plotted in Fig. 3.13. At 700°C, the total conductivity, $\sigma_{\text{tot}}$, is 0.32 S/m which corresponds to an ohmic loss of 0.12 $\Omega\text{cm}^2$ for an electrolyte thickness of 4 $\mu$m. This is about 1/3 of the value for polycrystalline 8 mol% yttria doped zirconia (YSZ) bulk material at this temperature. At 650°C we determined an ohmic loss of 0.20 $\Omega\text{cm}^2$. The ohmic contribution of the 1 $\mu$m thin CYO layer has been neglected here since its conductivity is about a factor of 3-4 higher than that for YSZ. Tsai, et al. [5] reported an ohmic loss of 0.25 $\Omega\text{cm}^2$ (650°C) for an 8 $\mu$m thick YSZ layer deposited by PVD which compares well with our result. We found an activation energy, $E_A$, of about 0.92 eV which is in the range of CGO/YSZ bulk material (c.f. Chapter 5) [38].
3.3 Results and Discussion

Fig. 3.13 Total conductivity of the electrolyte bi-layer determined by impedance spectroscopy in air.

3.3.3 Anode characterization

Sputtered Ni-YSZ anode

A SEM picture of the Ni-YSZ layer on top of the thin-film electrolyte after operation is shown in Fig. 3.14. The film exhibits a thickness of 1 μm and a good adherence to the YSZ electrolyte. In order to determine the electrochemical performance of this anode, impedance spectra were recorded at different cell currents ranging from 0 to about 550 mA/cm² under fuel cell operating conditions. The anodic overpotential, \( \eta_A \), calculated from the polarisation resistance, \( R_p \), is shown in Fig. 3.15. At 800°C we found \( \eta_A \) being less than 20 mV up to a current density of 500 mA/cm². Even at an operating temperature as low as 600°C the anodic polarisation, \( \eta_A \) did not exceed 70 mV at 420 mA/cm². For all temperatures a decreasing slope of overpotential towards increasing current densities was found. This behavior strongly indicates that the anode performance is charge-transfer controlled [18,39]. In Table 3.5 results on anode performance are listed and compared with literature.
Fig. 3.14 2 μm thick sputtered Ni-YSZ anode on top of electrolyte bi-layer.

Fig. 3.15 Anodic overpotential of Ni-YSZ cermet anodes deposited by PVD on thick-film 8YSZ electrolytes. The measurement was recorded in 20% H₂ / 80% N₂ + 3% water.

The long-term stability of the sputtered Ni-YSZ anode has been determined at a constant current of 300 mA/cm² for 624 hrs at 700°C (Fig. 3.16). The anodic
3.3 Results and Discussion

<table>
<thead>
<tr>
<th>system</th>
<th>$T_{\text{sinter}}$ [°C]</th>
<th>$I$ [mA/cm$^2$]</th>
<th>$\eta_A$ [mV]</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-YSZ (PVD)</td>
<td>250$^a$</td>
<td>500</td>
<td>60</td>
<td>this study</td>
</tr>
<tr>
<td>Ni-CGO (screen-printed)</td>
<td>1050</td>
<td>500</td>
<td>400</td>
<td>this study</td>
</tr>
<tr>
<td>Ni-Ce$<em>{0.9}$Ca$</em>{0.1}$O$_{1.9}$</td>
<td>1350</td>
<td>500</td>
<td>90</td>
<td>[18]</td>
</tr>
<tr>
<td>Ni-YSZ</td>
<td>1350</td>
<td>100</td>
<td>80</td>
<td>[28]</td>
</tr>
</tbody>
</table>

*Tab. 3.5* Anodic overpotential, $\eta_A$, for different anodes at 700°C. For comparison literature data are given.

*a. maximum temperature during deposition*

Fig. 3.16 Change in anode overpotential of sputtered Ni-YSZ with time at $T_{\text{op}}=700°C$ and a constant cell load of 300 mA/cm$^2$.

Overpotential increases rapidly within the first 15 days (360 hrs) but then seems to approach a limiting value of below 140 mV. Comparing the microstructure of a long-term operated anode with a short term operated one we did not find a noticeable change in terms of grain coarsening, delamination, or interface formation. To further investigate a possible change in microstructure, we heat treated a PVD Ni-YSZ anode at 900°C for two hours in reducing atmosphere. The results are shown
in Fig. 3.17(a) and (b). A change in morphology from the as deposited layer (Fig. 3.17a) towards sintered YSZ grains with spherical nickel particles located at grain-boundaries can be clearly seen (Fig. 3.17b). From these findings we assume that two major effects are responsible for the increase in anodic overpotential: (a) coarsening of nickel particles which leads to a drastic decrease of the in-plane conductivity and hence increasing the ohmic losses of the anode; (b) sintering and microstructural coarsening which decreases the active surface area for fuel oxidation. These results indicate that sputtered anodes change in performance when operated at temperatures higher than 600°C.

**Screen-printed Ni-CGO anode**

Fig. 3.18 shows a screen-printed Ni-CGO anode on top of the sputtered YSZ/CYO electrolyte bi-layer after operation. The anode was sintered at a temperature as low as 1050°C. For good electrochemical performance it is necessary to have an intimate contact between the anode and the electrolyte, a good grain to grain connectivity, and high surface active area. It is seen that the microstructure of the anode is very fine and that the average grain size is in the 100 nm range. The
3.3 Results and Discussion

bonding to the electrolyte seems to be good. However, simple scratching experiments with a knife indicate a low bonding strength.

The electrochemical performance of the anode on a self supporting YSZ electrolyte determined by impedance spectroscopy is plotted in Fig. 3.19. We found an increasing anode overpotential, $\eta_A$, with increasing current and with decreasing temperature. At 800°C the anodic overpotential was below 30 mV up to a current densities of 550 mA/cm$^2$. However, at an operating temperature of 700°C, the anodic overpotential increases drastically up to 368 mV at 550 mA/cm$^2$.

3.3.4 Fuel cell test

In the following we will present performance data of test cells operated at different temperatures in air and humidified H$_2$/N$_2$ gases as fuel. Fig. 3.20 shows results of cell voltage, V, versus current density, J, at 500, 600 and 700°C. The power density, P, as a function of current density is shown in Fig. 3.21. At 700°C we found a maximum power density, $P_{Max}$, of 325 mW/cm$^2$ at a cell voltage of about 0.7 V. The mass flow of hydrogen was 20 ml/min corresponding to a fuel
Fig. 3.19 Current/overpotential characteristic of a screen printed Ni- CGO anode on a thick electrolyte sintered at 1050°C for 2 hrs.

utilization of about 17%. No attempt was made to raise the fuel utilization. Decreasing the operating temperature, T_op, to 600°C leads to an increase of P_{Max} to 340 mW/cm^2 at a cell voltage as high as 0.62 V. However, a further decrease to 500°C resulted in a lower P_{Max} of 170 mW/cm^2. The voltage at zero current, i.e. the open circuit voltage, OCV, lies between 0.96 V (700°C) and 1.02 V (500°C). The theoretical electromotive force, E_{th}, calculated from the Nernst equation at these conditions is 1.06 V (at 700°C). The OCV corresponds to E_{th} and can be regarded as a measure of the quality of the electrolyte at a given oxygen chemical potential. An OCV close to the theoretical value means that the electrolyte is gastight. However, this holds only for an experimental setup where also the cell is gas-tight sealed and no mixing of the air with the fuel gases occurs. For a ceramic foam supported SOFC only limited sealing of the ‘foam-electrode’ gas chamber is possible (c.f. Fig. 3.3). Therefore, mixing of air and fuel gas occurred due to gas leakage resulting in a somewhat lower E_{th}. Consequently, we assume that reaching an OCV of >90% of the theoretical value already indicates a sufficiently dense and crackfree electrolyte layer. Lower OCVs indicate the presence of pin-holes and cracks in the electrolyte layer leading to gas leakage across the electrolyte. Table
Fig. 3.20 Cell voltage at different temperatures of a thin-film cell with PVD deposited Ni-YSZ anode.

Fig. 3.21 Power output at different temperatures for cathode supported thin-film cell with PVD Ni-YSZ anode.
3.6 shows OCV values determined for thin-film electrolytes deposited on various substrates. Dense and crack free electrolytes could be deposited on low sintered cathode substrates (900-1000°C). For cathode substrates sintered at 1200 and 1350°C the OCVs measured are below 60% of $E_{\text{th}}$. This indicates that these substrates had larger holes which were not closed by the PVD layer (c.f. Fig. 3.12).

<table>
<thead>
<tr>
<th>active cathode substrate $T_{\text{sinter}}$ [°C]</th>
<th>average pore size of active cathode [μm]</th>
<th>OCV [V]</th>
<th>$P_{\text{Max}}$ [mW/cm²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>900-1100</td>
<td>&lt; 1</td>
<td>0.96-1.06</td>
<td>325</td>
</tr>
<tr>
<td>1200</td>
<td>1-2</td>
<td>0.65</td>
<td>220</td>
</tr>
<tr>
<td>1350</td>
<td>&gt;2</td>
<td>0.2-0.3</td>
<td>not measured</td>
</tr>
</tbody>
</table>

*Tab. 3.6 Technology assessment of thin-film electrolytes deposited on cathode substrates showing different pore sizes (OCV: open circuit voltage, $P_{\text{Max}}$: maximum power output achieved at 700°C).*

**Determination of the specific cell losses**

We have already described the difficulty in determining the specific cell losses in terms of cathodic, anodic overpotentials, and ohmic contributions due to the asymmetric cell set up (Subsection 3.2.5). However, using the results obtained above on total cell ohmic losses (c.f. Fig. 3.13) and on anode overpotentials determined on self supporting electrolytes (c.f. Fig. 3.15 and Fig. 3.17) we can now further analyze the current voltage curve and estimate the cathode overpotential contribution.

The I-V characteristic of the cell as well as the ohmic and anodic overpotential losses determined following the above described method are shown in Fig. 3.22. It is evident that the ohmic contribution to the overall cell losses, $R_Q$, are reasonably low as well as the anodic overpotential, $\eta_A$. However, the major part of voltage drop is due to the cathode overpotential which shows a linear behavior up to about 450 mA/cm² but becomes more pronounced at higher current densities. This points to a current-limiting behavior due to mass-transport limitations in the cathode layer.
A similar analysis of the current voltage curve has been undertaken for the sample cell with a screen-printed Ni-CGO anode. The result is plotted in Fig. 3.23. We found that the anodic overpotential losses are the major contribution to the overall losses whereas the cathodic contribution is similar to that previously shown (c.f. Fig. 3.22). The results are summarized in Table 3.7 in terms of ohmic and non-ohmic losses at different current densities.

<table>
<thead>
<tr>
<th>anode type</th>
<th>$I$ [mA/cm$^2$]</th>
<th>$\eta_c$ [mV]</th>
<th>$\eta_A$ [mV]</th>
<th>$\Delta U_{\Omega}$ [mV]</th>
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</thead>
<tbody>
<tr>
<td>Ni-YSZ (sputtered)</td>
<td>300</td>
<td>70</td>
<td>40</td>
<td>29</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>220</td>
<td>59</td>
<td>50</td>
</tr>
<tr>
<td>Ni-CGO (screen-printed)</td>
<td>300</td>
<td>77</td>
<td>263</td>
<td>30</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>218</td>
<td>353</td>
<td>53</td>
</tr>
</tbody>
</table>

*Fig. 3.22 Current-voltage characteristics of cathode supported cell with sputtered electrolyte bi-layer and Ni-YSZ anode (PVD).*

*Tab. 3.7 Ohmic and non-ohmic cell losses at 700°C for different current densities and different anodes.*
The mass-transport limitations in the cathode layer we found at higher current densities can arise from surface diffusion, gas diffusion, or dissociative adsorption steps [40]. It should be noted, however, that the limiting current has not been observed at lower operating temperatures (600, 500°C). The porosity of the active cathode layers was ~30% and the average pore size ~0.1 μm. For comparison, Tsai, et al. [4, 5] deposited a CYO/YSZ electrolyte bi-layer on La$_{0.85}$Sr$_{0.15}$MnO$_3$ (LSM) substrates. The substrate porosity was in the range from 40 to 50% with an average pore size 0.2 and 0.3 μm, respectively. They found an increase in limiting current with higher porosity and larger pore size. However, this limiting current was independent of temperature. They suggested that this limitation is due to gas diffusion through the LSM cathode.

Since the porosity and pore size of our substrates is ~30% we assume that the limiting current at 700°C is due to hindered gas diffusion in the active cathode layer. At temperatures <700°C this limitation vanishes due to lower viscosity of air and therefore improved accessibility to the cathode/electrolyte interface. Further measurements in pure O$_2$ as oxydant will clarify this assumption.
3.4 Conclusions

Intermediate temperature solid oxide fuel cells have been prepared based on a macroporous ceramic foam support structure with a microporous active cathode layer bonded on top. We successfully deposited dense thin electrolyte layers of yttria doped cerium oxide (1 μm) and yttria doped zirconium oxide (4 μm) by physical vapor deposition on the microporous cathode.

The cerium oxide based chemical compatibility layer in contact with the perovskite cathode showed no new phase formation and a good adherence. The high open circuit voltage of 1.05 V proves that the electronic conductivity of the mixed ionic electronic conducting CYO could be blocked by the YSZ layer and that the deposited electrolyte layer is crackfree and dense.

Cells with sputter deposited nickel zirconia anode exhibited a power output of 345 and 325 mW/cm² at 600 and 700°C, respectively. This demonstrates that the application of an electrolyte thin-film on a cathode substrate allows to extend the range of SOFC operation down to 700°C.

We have also shown that cell losses in terms of ohmic losses and electrode polarisation in asymmetric cells can be determined by using data obtained from similar electrode systems on self-supporting electrolytes. Reduction of the major cathode interfacial losses will lead to a further increase in power densities at lower temperatures.

References


3.4 Conclusions

3 Intermediate Temperature SOFC with Cathode Supported Thin Film Electrolytes
4 Activated Sintering of Cerium Oxide

Abstract

The effect of small amounts (<5 mol%) of transition metal oxides on the sintering characteristics of cerium oxide solid solutions have been evaluated. Commercially available Ce₀.₈Gd₀.₂O₂₋ₓ powder with an average crystallite size of ~20 nm served as model substance for electrolytes with a high oxygen ionic conductivity and low electronic conductivity. Transition metal oxide doping was used to facilitate densification of this powder at sintering temperatures below 900°C. The sintered material exhibited an average grain size of less than 120 nm. We found an amorphous about 2 nm thick cobalt rich grain boundary layer when interrupting sintering at 900°C after 10 min. This layer disappears upon further annealing at 900°C or at higher sintering temperatures due to solid solution formation of the cobalt cations in the ceria lattice.

Keywords: nanosized ceramic, transition metal oxides, cobalt oxide, ceria, ceria solid solutions, low temperature sintering, solid oxide fuel cells, gas separation membranes

4.1 Introduction

4.1.1 General

Ceria solid solutions have been shown to exhibit 4 to 5 times higher ionic conductivities at intermediate temperatures (600-700°C) compared to zirconia solid solutions [1]. Therefore, solid electrolytes based on ceria are of special interest for application in electrochemical devices such as solid oxide fuel cells (SOFCs), sensors, oxygen separation membranes and syngas production. Although ceria is slightly reduced at low oxygen partial pressures and develops

1. parts of this chapter have been published in [2,3].
increasingly electronic conductivity [4], it has been shown that CeO$_2$ss based SOFCs can be operated at temperatures as low as 700°C with high power output and high efficiency [5,6].

It has been recognized that mixed oxide-ion/electronic conductors such as CeO$_2$ss are promising candidates for electrodes for SOFCs designed for intermediate operation temperature [7,8,9]. CeO$_2$ss adopt mixed Ce$^{4+}$/Ce$^{3+}$ valency in the reducing atmosphere present at the anode of SOFCs. This leads to a high n-type electronic conductivity and catalytic activity thus increasing the electrode performance [4,10,11]. Recently, Murray et al. reported that CeO$_2$ containing anodes offer the possibility to operate SOFCs with dry methane as fuel without carbon deposition at a temperature as low as 650°C [12]. Therefore, CeO$_2$ss are attractive as electrolyte and electrode component in electrochemical devices such as SOFCs.

Dense ceramic bodies of CeO$_2$ are difficult to obtain since sintering of this material typically requires temperatures above 1500°C. However, these high temperatures lead to a decrease in density and microcracking. This is believed to be due to the reduction of Ce$^{4+}$ to Ce$^{3+}$ above 1200°C which causes the formation of an oxygen vacancy for each pair of Ce$^{4+}$ ions being reduced, i.e.:

$$2Ce_{Ce}^{x} + O_{O}^{x} \leftrightarrow 2Ce_{Ce}^{x'} + V_{O}^{1} + \frac{1}{2} O_{2} (g) \quad (4.1)$$

Since the diffusivity of oxygen in pure CeO$_2$ is very low, the expansion effect, microcracking and thus poor sinterability is mainly attributed to the liberation of oxygen [13,14]. Therefore, much research has been directed to decrease the sintering temperature. To our knowledge, fully dense sintered CeO$_2$ has not been obtained prior to the work of Chen in 1993 [15], who succeeded in sintering CeO$_2$ at temperatures <1300°C using nano powders exhibiting high sintering activity. However, due to the high sintering temperature large grains of about 1.5 μm were obtained.

It has been shown that additive cations in CeO$_2$ can produce significant changes in sintering behavior and grain boundary mobility. Chen, et al. [16] showed that grain boundary mobility in 0.1-1 mol% rare earth doped CeO$_2$ is controlled by cation diffusion and that at high dopant concentrations (1 mol%), a solute drag mechanism suppresses grain boundary mobility. Zhou, et al. [13] and
Rahaman, et al. [17] found that doping CeO$_2$ with divalent and trivalent cations strongly effects the sintering and grain growth. They obtained material of >98% density with an average grain size of 100 nm when sintering 3 mol% Y$_2$O$_3$ doped CeO$_2$ at 1150°C for two hrs. In the case of gadolinium doped cerium oxide (CGO), sintering temperatures of 1300-1700°C are typically required to obtain a sufficiently dense ceramic for use as electrolyte in SOFCs. These high sintering temperatures imply considerable grain coarsening and thus poor mechanical properties. Also they present difficulties when cofiring these components with other materials due to solid state reactions and interdiffusion.

Therefore, many attempts have been made to increase the sinterability of CGO by e.g. using fine powders with high sintering activity [18,19,20] and the addition of sintering aids [21].

Recently, Yoshida et al. [21] reported the influence of gallium on the sintering of Ce$_{0.8}$Sm$_{0.2-y}$Ga$_y$O$_{2-x}$ ($0 \leq y \leq 5$). The sintering temperature required to obtain dense ceramic bodies was lowered from 1600°C to 1450°C with grain sizes in the range from 2 to about 20 μm. The effect of lowering the sintering temperature was mainly attributed to an increased grain-boundary mobility, leading to an improved sintering behavior. However the grain sizes for the 1 at% Ga doped CeO$_2$ ss, sintered at 1450°C, were comparable to those of undoped samples sintered at 1600°C. The ionic conductivity of this material was not significantly affected by the Ga dopant as long as the gallium concentration was kept below 0.5 at%.

### 4.1.2 Aim of the study

The purpose of this work was to investigate the sintering of cerium oxide and cerium gadolinium oxide nanopowders with small amounts of transition metal oxide additives.

### 4.2 Experimental Procedure

The study was performed using commercially available nano sized Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ (CGO) powder where the MeO dopant was precipitated on the crystallite surface in form of a nitrate solution. Dilatometer measurements were...
used to record shrinkage during sintering. Thermogravimetric and differential thermal analysis were performed to analyse the decomposition of the nitrates and phase changes during thermal treatment. X-ray diffraction analysis (XRD) was applied for phase analysis. Electron microscopy (SEM) was used to monitor the grain size during sintering as a function of dopant concentration and sintering temperature. The distribution of the dopant was studied by transmission electron microscopy (TEM), as well as the elemental distribution in grains and grain-bounds.

4.2.1 Sample preparation

\( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x} \) (denoted CGO; #595250A, Rhodia GmbH, Frankfurt, FRG) with a crystallite size of 40 nm and a specific surface area of about 24 m\(^2\)/g was used as starting powder to which the transition metal oxide (MeO) dopant was added in the form of nitrates (e.g. Co(NO\(_3\))\(_2\)·6H\(_2\)O, Fluka AG, Buchs, CH). Samples with different MeO concentrations (0 - 30 mol%) were prepared by first dispersing the CGO powder in ethanol (Fluka, puriss.p.a.), using an agate mortar. The desired amount of nitrate was then added. After drying at 120°C for two hours the powders were first uniaxially dry pressed at 50 MPa to pellets with a diameter of 10 mm followed by isostatic pressing at 840 MPa for 3 min. The green density of the pellets after isostatic pressing was in the range of 55 to 62% of the theoretical density. CeO\(_2\) powders from different suppliers (denoted CeO\(_2\)-Ref1 and CeO\(_2\)-Ref2) were used. The impurities present in the powders as quoted by the manufacturer and as determined by own SIMS analyses are listed in Table 4.1. Powder characteristics as well as the fabrication routes are listed in Table 4.2.

4.2.2 Experimental methods

The densification rate was studied using samples of 6 mm length and a thickness of 3 mm. The samples were sintered in a dilatometer (Bähr, Type 801) up to the desired temperature using a constant heating rate of 5 K/min and they cooled with 10 K/min to room temperature. The shrinkage was recorded during heating and cooling. The temperature was measured close to the sample with a Pt-Pt10Rh thermocouple.
4.2 Experimental Procedure

<table>
<thead>
<tr>
<th>material</th>
<th>denoted</th>
<th>main impurities [ppm]</th>
<th>trace impurities [&lt;50 ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce_{0.8}Gd_{0.2}O_{2-x}</td>
<td>CGO</td>
<td>La (&lt;0.2%)</td>
<td>Pr, Eu, Yb, Si^a</td>
</tr>
<tr>
<td>CeO_2</td>
<td>CeO_2-Ref1</td>
<td>n.q.</td>
<td>Si, Pr, La, Al</td>
</tr>
<tr>
<td>CeO_2</td>
<td>CeO_2-Ref2</td>
<td>Mg (&lt;520) Fe (&lt;270) Ca (&lt;120)</td>
<td>La_2O_3, Cu, Na</td>
</tr>
</tbody>
</table>

*Tab. 4.1 Main and trace impurities present in the powders under investigation.\(^a\) determined by SIMS analysis.*

<table>
<thead>
<tr>
<th>material</th>
<th>crystallite size [nm]</th>
<th>BET [m^2/g]</th>
<th>fabrication route</th>
<th>supplier / reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>20</td>
<td>24</td>
<td>coprecipitation</td>
<td>Rhodia(^a)</td>
</tr>
<tr>
<td>CeO_2-Ref1</td>
<td>12</td>
<td>43</td>
<td>oxalate coprecipitation</td>
<td>[19](^b)</td>
</tr>
<tr>
<td>CeO_2-Ref2</td>
<td>11</td>
<td>63</td>
<td>physical vapor synthesis (PVS)</td>
<td>nanophase(^c)</td>
</tr>
</tbody>
</table>

*Tab. 4.2 Characteristics of CeO_2 powders from different suppliers and prepared with different fabrication routes. The characteristics of the powder used throughout this study is denoted CGO.*

\(^a\) Rhodia GmbH, Frankfurt, GER.
\(^b\) supplier: Swiss Federal Institut of Technology, Lausanne, EPFL-LPI.
\(^c\) Nanophase Technologies Corp., Illinois 60521, USA.

The lattice parameters, unit cell volume, and phases of sintered samples as well as of non sintered powder were determined by means of X-ray diffraction using CuK\(\alpha\) radiation (model D5000, Siemens, Karlsruhe, Germany).

The reactions and phase formation in the system CeO_2(ss)-CoO were monitored by simultaneous thermal analysis (TG-DTA model STA 501, Bähr, Germany) up to 1200\(^\circ\)C for CGO with 2 mol% CoO and up to 1700\(^\circ\)C for the 20 mol% CeO_2 - 80 mol% CoO system. For both measurements a heating rate of 10\(^\circ\)C/min was used.
For microstructural characterisation, some samples were sintered in a controllable furnace in air at a temperature, $T_s$, in the range of $900^\circ C \leq T_s \leq 1400^\circ C$. Dwell times were varied from 10 min to several hours. The heating rate was $1^\circ C/min$ up to $400^\circ C$, followed by $3^\circ C/min$ up to the final temperature $T_s$. After holding for the desired time at $T_s$ the samples were cooled down to room temperature with a rate of $5^\circ C/min$. The final density of each sintered pellet was determined according to the Archimedes method. The microstructure was then characterized by scanning electron microscopy (SEM, model Jeol 6400) after polishing and etching in concentrated $H_2SO_4$ at $140^\circ C$ for 1 min and sputtering with platinum. The sintering program is shown in Fig. 4.1.

![Fig. 4.1 Sintering program for CeO$_2$ solid solutions. A: slow heating during solvent evaporation and nitrate decomposition; B, C: sintering; D: cooling](image)

Samples for TEM analysis were prepared by cutting, polishing, and final thinning to electron transparency by argon-ion beam thinning. Micrographs were obtained using a TEM (model Phillips CM30 with LaB$_6$ cathode) operating at 300 kV. Elemental distribution profiles were obtained by parallel energy loss spectroscopy (PEELS). The spatial resolution of this method is ±2.5 nm. Phase analysis was performed using convergent-beam electron diffraction (CBED) and selected area diffraction (SAD).
4.3 Results and Discussion

4.3.1 Densification of cerium oxide nanopowders with transition metal oxides

Nanosized $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ (CGO) powders

The sintering of CGO with different transition metal oxides added in concentrations of 2 mol% is shown in Fig. 4.2. We plotted the relative density as a function of temperature at a constant heating rate of 5 K/min. From this figure we can deduce that all dopants are extremely effective in promoting the densification of CGO. CoO, CuO, and NiO as dopant lead to > 98% dense CGO bodies at $T_{\text{sinter}}$ below 1000°C. For NiO, MnO, FeO as dopant >98% dense samples are obtained at temperatures below 1100°C.

![Graph showing relative density versus temperature for the compacted $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ powder pure and doped with 2 mol% of different metal oxides (constant heating rate of 5 K/min to 1200°C)](image)

Fig. 4.2 Relative density versus temperature for the compacted $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ powder pure and doped with 2 mol% of different metal oxides (constant heating rate of 5 K/min to 1200°C)
We can also note from this figure that exceeding the temperature of 98% density leads to oversintering and expansion of the doped samples. In the case of CuO this effect is promoted by the phase transition \[221:

\[
CuO \rightarrow Cu_2O + \frac{1}{2}O_2 \rightarrow \text{liquid}
\] (4.1)

Table 4.3 summarizes the results of the sintering experiments for the different dopants including the temperature of maximum shrinkage rate \((d(\Delta L/L_0)/dT)_{\text{max}}\). We want to point out that \((d(\Delta L/L_0)/dT)_{\text{max}}\) increases drastically for doped samples compared to pure CGO. For e.g. the 2 cat% CuO sample has a 3.5 times faster shrinkage rate compared to undoped CGO. The densification process is terminated within a temperature range of about 50 K which suggests that a liquid phase sintering process to be predominant. The pure CGO shows a broad sintering range of about 400 K indicating solid state sintering.

<table>
<thead>
<tr>
<th>dopant concentration [2 mol%]</th>
<th>sintering Start [°C]</th>
<th>shrinkage rate ((d(\Delta L/L_0)/dT)_{\text{max}}) [°C]</th>
<th>sintering end (T_{98%}) [°C]</th>
<th>sintering interval ((d(\Delta L/L_0)/dT)<em>{\text{max}} - T</em>{98%})</th>
</tr>
</thead>
<tbody>
<tr>
<td>-</td>
<td>500</td>
<td>912</td>
<td>1300</td>
<td>370</td>
</tr>
<tr>
<td>Co</td>
<td>656</td>
<td>870</td>
<td>&lt;1000</td>
<td>&lt;130</td>
</tr>
<tr>
<td>Cu</td>
<td>600</td>
<td>870</td>
<td>&lt;1000</td>
<td>&lt;130</td>
</tr>
<tr>
<td>Ni</td>
<td>520</td>
<td>870</td>
<td>1050</td>
<td>180</td>
</tr>
<tr>
<td>Mn</td>
<td>750</td>
<td>1000</td>
<td>1100</td>
<td>100</td>
</tr>
<tr>
<td>Fe</td>
<td>750</td>
<td>1000</td>
<td>1100</td>
<td>100</td>
</tr>
</tbody>
</table>

Tab. 4.3 Sintering characteristics of \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}\) pellets containing different transition metal oxides (2 mol% each). \(T_{98\%}\): temperature at which >98% of theoretical density is reached; \(T_{95\%}\), \(T_{92\%}\), \(T_{89\%}\) resp. Sintering start is defined when 2% densification \((p/p_{th})\) is reached.

Effect on nanosized \(\text{CeO}_2\) powders

Metal oxide activated sintering is not restricted to the coprecipitated CGO nano powder used (see Table 4.2). Also nanosized \(\text{CeO}_2\) powders from other sources show the same behavior. Characteristics of these powders made via dif-
4.3 Results and Discussion

Different processes have already been listed (c.f. Table 4.2). The sintering behavior with and without CoO doping has been tested. We found that CoO doping has the same effect on these powders as on CGO in terms of enhanced shrinkage rate and reduced sintering temperature. Fully dense specimen are obtained although the characteristic temperatures are slightly different. For CeO$_2$-Ref1 doped with 1 mol% CoO a >98% dense material is obtained already at a temperature as low as 1150°C compared to 1350°C needed for the undoped powder (Fig. 4.3). For the second type of powder, CeO$_2$-Ref2, a strong influence of 1 mol% CoO doping on sintering characteristics has also been found (Fig. 4.4). The densification rate was strongly increased and we obtained a 98% dense body at sintering temperatures as low as 1100°C.

![Fig. 4.3 Sintering characteristics of pure and 1 mol% CoO doped nanocrystalline CeO$_2$ powder (CeO$_2$-Ref1) (heating rate 5°C/min).](image)

These experiments demonstrate, that nanoscaled CeO$_2$ and CGO powders from different synthesis procedures can be sintered to full density at rather low temperatures when doped with transition metal oxides via nitrate solutions.
4 Activated Sintering of Cerium Oxide

![Graph showing sintering characteristics of pure and 1 mol% CoO doped nanocrystalline CeO$_2$ powder (CeO$_2$-Ref2) (heating rate 5 °C/min).]

Fig. 4.4  Sintering characteristics of pure and 1 mol% CoO doped nanocrystalline CeO$_2$ powder (CeO$_2$-Ref2) (heating rate 5 °C/min).

4.3.2 Densification of CGO nanopowders with cobalt oxide

For all further investigations of the sintering mechanism and microstructure evolution we concentrated on cobalt oxide doped CGO as model system.

Dopant concentration dependence

The sintering of CGO doped with different concentrations of CoO (0, 0.01, 0.1, 0.5, 1, 2 and 5 mol%) is shown in Fig. 4.5. The relative density, $\rho$, is plotted as a function of temperature, $T$. The sintering curve for the powder doped with 0.01 mol% was nearly identical to the pure CGO and, to maintain clarity, was omitted from the figure.

It was found that cobalt oxide additions as low as 0.5 mol% are extremely effective in promoting the densification of CGO (Fig. 4.5 and Fig. 4.6). The sintering temperature where $>98\%$ of the theoretical density is reached ($T_{98\%}$) decreases from above $1300^\circ$C for pure CGO to below $1000^\circ$C with increasing dopant concentration. For 1 mol% cobalt doping we obtained $>99\%$ dense samples after sintering at a temperature as low as $900^\circ$C for two hours. Furthermore,
4.3 Results and Discussion

Fig. 4.5 Relative density versus temperature for the compacted $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x}$ powder pure and doped with different mol% of cobalt oxide (constant heating rate of 5 K/min to 1300°C).

we found that the onset of measurable sintering (2% densification) occurred at approximately the same temperature (~600-700°C) for all samples. A slight tendency to shift towards higher temperatures with increasing doping level can be noted. However, after sintering started, the rate of densification increased significantly with increasing dopant concentration. This behavior is shown in Fig. 4.6 where the shrinkage rate $(d(\Delta L/L_0)/dT)$ is plotted for all samples.

The results of Fig. 4.6 show the maximum shrinkage rate $(d(\Delta L/L_0)/dT)_{\text{max}}$ to increase drastically for samples with a CoO addition of >0.5 mol%. When doping CGO with e.g. 1 mol% CoO (curve (4) in Fig. 4.6) a 3 fold shrinkage rate is observed compared to pure CGO and the densification process is finished within a temperature range of about 50 K (region (A) in Fig. 4.6).

Further adding of cobalt oxide up to 30 mol% (Fig. 4.7 and Fig. 4.8) reduces the shrinkage rate and the final density, $\rho_{\text{final}}$, and lowers the maximum shrinkage rate, $(d(\Delta L/L_0)/dT)_{\text{max}}$. Data obtained for pure cobalt oxide after calcination at 400°C for 2 hrs are also plotted. Only poor densification has been observed for specimens with a green density of ~42% and a particle size of $d_{50}\sim 0.2 \mu m$. From
Fig. 4.6  Linear shrinkage rate \( \frac{d(\Delta L/L_0)}{dT} \) as a function of temperature and CoO concentration for the Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{2-x}\) - CoO system. (A) denotes the temperature range for the 1 mol% doped sample within which densification is completed after reaching the point of maximum densification rate.

Fig. 4.7 we also note that increasing the cobalt oxide concentration decreases the green density of the pressed body.

Fig. 4.9 illustrates the change in temperature of maximum shrinkage rate and the evolution of temperature where maximum density is reached as a function of cobalt oxide concentration. The results of the sintering experiments for different dopant concentrations are summarized in Table 4.4. We found that by varying the doping level as well as the sintering conditions in terms of temperature and heating rate the temperature of maximum density can be changed within a certain
4.3 Results and Discussion

Fig. 4.7 Relative density versus temperature for high CoO additions in \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x} \) powder and for pure cobalt oxide obtained after calcination of cobalt nitrate at 400°C for 2 hrs.

Fig. 4.8 Linear shrinkage rate \( (d(\Delta L)/L_0)/dT \) as a function of temperature for \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x} \) with high CoO dopant levels and for pure cobalt oxide.
Fig. 4.9  Temperature of maximum shrinkage rate, \( T(\frac{d(\Delta L/L_0)}{dT})_{\text{max}} \), and temperature where 95% of the theoretical density is reached, \( T(>95\% \rho_{th}) \), for compacted powders of CGO pure and doped with up to 30 mol% CoO. Sintered at a constant heating rate of 5 K/min.

range. The optimum dopant concentration for dense sintered bodies is about 1 cat% at a sintering temperature ranging from 900 to 1000°C.

<table>
<thead>
<tr>
<th>dopant concentration [mol%]</th>
<th>sintering start [°C]</th>
<th>shrinkage rate ((\frac{d(\Delta L/L_0)}{dT})_{\text{max}}) [°C]</th>
<th>sintering end (T_{98%}) [°C]</th>
<th>sintering interval ((\frac{d(\Delta L/L_0)}{dT})<em>{\text{max}}-T</em>{98%}) [°C]</th>
</tr>
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<tbody>
<tr>
<td>0</td>
<td>618</td>
<td>930</td>
<td>1300</td>
<td>370</td>
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<tr>
<td>0.01</td>
<td>630</td>
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<td>1200</td>
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</tr>
<tr>
<td>1</td>
<td>692</td>
<td>950</td>
<td>&lt;1000</td>
<td>&lt;50</td>
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Tab. 4.4 Sintering characteristics of Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{2-x}\) pellets containing different cobalt concentrations \(T_{98\%}\): temperature at which >98% of theoretical density is reached; \(T_{95\%}\), \(T_{92\%}\), \(T_{89\%}\) resp.). Sintering start is defined when 2% densification \(\rho/\rho_{th}\) is reached.
4.3 Results and Discussion

<table>
<thead>
<tr>
<th>dopant concentration [mol%]</th>
<th>sintering start [°C]</th>
<th>shrinkage rate $(d(\Delta L/L_0)/dT)_{\text{max}}$ [°C]</th>
<th>sintering end $T_{98%}$ [°C]</th>
<th>sintering interval $(d(\Delta L/L_0)/dT)<em>{\text{max}} - T</em>{98%}$ [°C]</th>
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<tr>
<td>2</td>
<td>656</td>
<td>870</td>
<td>&lt;1000</td>
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<tr>
<td>5</td>
<td>676</td>
<td>820</td>
<td>1150 (T_{95%})</td>
<td>&gt;330</td>
</tr>
<tr>
<td>15</td>
<td>647</td>
<td>790</td>
<td>1120 (T_{92%})</td>
<td>&gt;330</td>
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<td>800</td>
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<td>&gt;330</td>
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<tr>
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<td>625</td>
<td>850</td>
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<td>&lt;40</td>
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</table>

Tab. 4.4 Sintering characteristics of $Ce_{0.8}Gd_{0.2}O_{2-x}$ pellets containing different cobalt concentrations ($T_{98\%}$: temperature at which >98% of theoretical density is reached; $T_{95\%}$, $T_{92\%}$, $T_{89\%}$ resp.). Sintering start is defined when 2% densification ($p/p_0 > \text{th}$) is reached.

a. at a heating rate of 0.5°C/min
b. at a heating rate of 0.25°C/min

**DTA and TG measurements**

In order to elucidate reactions between the cobalt-nitrate dopant and the CGO powder, DTA-TG experiments were performed. The DTA and TG results for pure and 2 mol% CoO doped CGO, and for pure Co-nitrate are plotted in Fig. 4.10 and Fig. 4.11 respectively. The heating rate was 10 K/min up to a temperature of about 1200°C in air. Remaining solvent and water of hydration is liberated at about 100-200°C followed by Co-nitrate decomposition which is terminated at ~340°C. All these processes are accompanied by a strong weight loss as recorded in TG plots which are shown in Fig. 4.11. Further heating of pure CGO does not show any endo- or exothermic peak nor a significant weight change up to the final temperature 1200°C. For doped CGO and pure Co-nitrate however, an endothermic peak as well as a weight loss can be observed at 900°C.

XRD measurements on Co-nitrate calcined at 350°C for 2 hrs revealed that both CoO and Co$_2$O$_3$ phases are present (Fig. 4.12). This result suggests that the endothermic reaction observed at about 900°C is related to the reduction of
Fig. 4.10 Differential thermal analysis of pure and 2 mol% CoO doped \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x} \) and of pure cobalt nitrate.

\( \text{Co}_2\text{O}_3 \), which is formed between 200\(^\circ\)C and 400\(^\circ\)C after Co-nitrate decomposition, to CoO with liberation of oxygen, according to the reaction:

\[
\text{Co}_2\text{O}_3 \xrightarrow{900^\circ\text{C}} 2\text{CoO} + (1/2)\text{O}_2(g) \tag{4.1}
\]

It might be argued that the sintering effect relies on the reduction of \( \text{Co}_2\text{O}_3 \) which occurs at temperatures of about 900\(^\circ\)C. However, we obtained similar sintering results with e.g. copper oxide doped CGO (c.f. Fig. 4.2) even though no phase change is observed for the CuO/Cu\(_2\)O system in the temperature region of 400-1000\(^\circ\)C.
4.3 Results and Discussion

Fig. 4.11 Thermo gravimetric analysis of pure and 2 mol% CoO doped \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-x} \) and of pure cobalt nitrate.

Fig. 4.12 X-ray diffraction pattern of Co-nitrate decomposed at 350°C for 2 hrs.
Dependence on heating rate

Fig. 4.13 and Fig. 4.14 illustrate that lower heating rates of 0.5 and 0.25°C/min further decrease the temperature of maximum shrinkage rate from 950°C (5°C/min) to about 875°C and 850°C respectively. The temperature where 98% of the theoretical density is reached, T_{98\%}, is lowered from about 1000°C to below 900°C for a rate of 0.25°C/min, whereas T_{98\%} does not change significantly above a heating rate of 0.5°C/min (c.f. Table 4.4). This result implies that even at sintering temperatures as low as 900°C fully dense CGO material can be obtained.

Isothermal sintering

The influence of the sintering time, t, on the relative shrinkage, ΔL/L₀, of CGO doped with 1 mol% CoO is shown in Fig. 4.15 and Fig. 4.16 for different sintering temperatures. Although the heat capacity of the dilatometer device has to be considered, the experimental variation of ln(ΔL/L₀) versus ln(t) can be approximated by a succession of linear relationships for each temperature. There-
4.3 Results and Discussion

Fig. 4.14 Linear shrinkage rate \((\frac{d(L/L_0)}{dT})\) as a function of heating rate for the 1 mol% CoO doped \(Ce_{0.8}Gd_{0.2}O_{2-x}\).

Fig. 4.15 Isothermal sintering of \(Ce_{0.8}Gd_{0.2}O_{2-x}\) doped with 1 mol% CoO as a function of sintering temperature.
Therefore, the following relationship (Eqn. (4.1)) can be derived and several different $t$-$T_{\text{sinter}}$ domains, depending on $p$ values, identified [23]:

$$|\Delta(L/L_0)| = A t^p$$  \hspace{1cm} (4.1)

During the first sintering step ($1.02 < p < 1.45$), a fast shrinkage occurs; $p$ values are larger than 1 and increase with $T_{\text{sinter}}$ up to 1.5. Such a behavior is often considered as characteristic of grain rearrangement [24]. During the second sintering step $p$ values of up to ~7 are reached, which cannot be correlated with a common solid state sintering process and are indicative for liquid-phase sintering. In the third region two ranges of $p$ have been found: in the lower temperature region $p$ values are of the order of 0.2 to 0.3 indicating that a solution-precipitation process which is diffusion rate controlled is predominant. At high temperatures $p$ ranges from 0.06 to 0.15 and reaches a constant value which corresponds to the final solid state sintering regime.
4.3 Results and Discussion

**TEM analysis**

The TEM picture from a microstructure of a 1 mol% CoO doped CGO sample when sintering was interrupted at 900°C after 10 min is shown in Fig. 4.17. The dark field TEM (Fig. 4.17a) as well as the bright field image (Fig. 4.17b) shows an amorphous grain boundary film of 2-4 nm thickness at the grain contacts.

![TEM images](image)

Fig. 4.17 Dark field TEM (a) and bright field TEM (b) of Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ doped with 1 mol% CoO and sintered at 900°C for 10 min showing an amorphous grain boundary phase of about 2 nm thickness.

By using selected area electron diffraction (SAD) the different phases of the above described grain boundary region can be identified. Fig. 4.18a shows the grain boundary phase of the 5 mol% doped CGO sample and Fig. 4.18b the SAD pattern of the grain-boundary region. The wide and intense diffraction spots are caused by the CGO grains of the host lattice having fluorite structure and the large white halo is a clear indication for an amorphous grain boundary phase being present. The PEELS analysis of the composition of this grain boundary layer has been determined to consist of 60 cat% Co, 30 cat% Gd and 10 cat% Ce. The spatial resolution of the PEELS method is given by the TEM spot size, which is 5 nm. Therefore, care should be taken in interpreting this result since the dimension of
the grain boundary layer was similar to the spatial resolution of the PEELS signal leading to an increasing background signal from the adjoining crystals.

The cobalt distribution from the near grain-boundary region to the grain interior of CGO samples doped with different amounts of CoO and sintered at 900°C for 2 hrs is plotted in Fig. 4.19. Cobalt concentrations as high as 40 cat% in the CGO grain is present in the near grain boundary region. The concentration goes down exponentially to about 0.5 cat% towards the grain interior.

In order to obtain information about the cobalt oxide distribution on the surface of the CGO nano particles after calcination we conducted STEM analysis on 5 mol% doped CGO powder calcined at 900°C for 2 hrs. The STEM image and the elemental maps for Ce and Co for the same section of the sample are illustrated in Fig. 4.20a-c. It is seen that the cobalt is highly dispersed in the sample and we did not find evidence for Co-rich clusters. However, evidence of an amorphous cobalt rich grain-boundary film with an equilibrium thickness of about 1-2 nm was found (Fig. 4.20b). Recent studies on \( \text{Cu}_{0.15}\text{Ce}_{0.85}\text{O}_{2-x} \) nanocrystals synthesized by inert gas condensation have shown that Cu is ultrahighly dispersed on Ce\( \text{O}_{2-x} \) nanocrystals after low-temperature annealing (411°C) [25]. After further heat
4.3 Results and Discussion

Fig. 4.19 PEELS analysis of cobalt distribution in doped CGO starting from grain boundary to grain interior ($T_{\text{sinter}} = 900^\circ\text{C}, 2\ h$).

treatment at 650$^\circ\text{C}$ it was found that Cu remained highly dispersed, however, distinct CuO nanoclusters were observed.

Fig. 4.20 HRTEM image of 5 mol% cobalt oxide doped CGO powder calcined at 900$^\circ\text{C}$ (a). Cobalt mapping (b) and cerium mapping (c).
The conventional TEM and HRTEM micrograph of a 5 mol% CoO doped CGO sample equilibrated at 1400°C for 2 hrs is depicted in Fig. 4.21. The conventional TEM micrograph shows a triple grain junction exhibiting a grain boundary angle of about 120° which is typical for solid-state sintered materials. The thickness of the grain-boundary has been determined to be less than 5 Å and the cobalt concentration 3-4 cat% distributed homogeneously inside the grains. No amorphous grain-boundary phase could be detected. The HRTEM image indicates the grain boundary being of the type $\Sigma = 13$.

![Fig. 4.21 TEM (left) and HRTEM image (right) of 5 mol% CoO doped CGO equilibrated at $T_{\text{sinter}} = 1400^\circ\text{C}$ for 2 hrs. CB-SEAD revealed an equally distributed cobalt concentration of 3-4 cat%. The grain boundary thickness is less than 0.5 nm.](image)

The XRD phase and crystal analysis of pure (Fig. 4.22) and highly doped CGO samples (Fig. 4.23) sintered at 1400°C for 2 hrs, revealed that only cubic CeO$_2$ solid solution is present, up to 15 mol% dopant. However, in the 30 mol% doped sample, CoO was detected. The lattice parameter, $a$, was determined as 5.4209 Å for pure CGO. We found a decrease of the cubic lattice constant due to the smaller sizes of the cobalt cations from $a = 5.4206$ Å for the 15 mol% doped to $a = 5.4200$ Å for the 30 mol% doped sample. Based on Vegard’s rule we can derive a negative slope of $-0.03$ pm/mol%.
4.3 Results and Discussion

**Fig. 4.22** X-ray diffraction pattern of pure CGO powder.

**Fig. 4.23** X-ray diffraction pattern of CGO containing 15 and 30 mol% CoO. Sintering was performed at 1200°C with 2 hrs dwell time. The peak observed at 2θ = 36.5° for the 30 mol% doped sample can be correlated with the CoO (111) peak (c.f. Fig. 4.12).

### 4.3.3 Microstructure

In order to illustrate the effect of dopant concentration on the densification behavior and on the microstructure of CGO, scanning electron micrographs of sin-
tered CGO compacts have been made. Fig. 4.24 shows the polished surface of CGO samples doped with CoO in concentrations ranging from 0 to 1 mol%. The samples have been sintered at 1000°C for 2 hrs. For a doping level <0.5 mol% CoO (Fig. 4.24(a)-(c)) the sintered specimens exhibit low density and poor particle to particle interconnection despite some shrinkage having occurred. The average grain size is about 170 nm. With increasing dopant concentration (Fig. 4.24 (d),(e)) the microstructure becomes more homogeneous and the density as well as the mechanical stability increases. At a dopant concentration of 1 mol% CoO a more than 98% dense ceramic body with an average grain size of about 0.2 μm is obtained.

To further illustrate the effect of CoO doping on the sintering and microstructure evolution, 1 mol% doped samples were sintered at temperatures ranging from 900 to 1400°C. The microstructures are shown in Fig. 4.25(a-f). Already at a sintering temperature as low as 900°C a >99% dense body with an average grain size of about 120 nm was obtained (a). Further increase of the sintering temperature leads to coarsening of the microstructure in terms of grain growth (b-e). Sintering at 1400°C for 2 hrs results in an average grain sizes of about 1.5 μm. This is the same grain size as for the undoped reference specimen sintered at 1400°C for 2 hrs (f). No exaggerated grain growth was observed.
4.3 Results and Discussion

Fig. 4.24 Microstructure of undoped and CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ (CGO) sintered at 1000°C for 2 h: (a) pure, (b) +0.01 mol%, (c) +0.1 mol%, (d) +0.5 mol%, (e) +1 mol% CoO.
Fig. 4.25  Microstructure evolution of Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ doped with 1 mol% CoO at different sintering temperatures (2h dwell time each): (a) 900°C, (b) 1000°C, (c) 1200°C, (d) 1300°C, (e) 1400°C. Image (f) represents the microstructure of undoped CGO sintered at 1400°C for 2h.
4.4 Model for the Densification of CGO Nanopowders with Transition Metal Doping

In the following subsection we first want to give a literature survey of activated sintering in other systems, and secondly to summarize the results in order to establish a model for cobalt oxide promoted sintering of CGO nanopowders.

4.4.1 Activated sintering in other systems

Activated sintering generally refers to the phenomenon whereby sintering rates are improved because of solid-state additives and has been attributed to the presence of a subeutectic secondary or "activator" phase. The phenomenon has been reported to occur in various metallic and ceramic systems [26]. The "activator" phase usually consists of only a few monolayers and high resolution techniques, such as high resolution transmission electron microscopy (HRTEM) or scanning transmission electron microscopy (STEM) are necessary to image and analyse these layers. To date, there have been only a few reports about these subeutectic activator phases [27,28]. In the following we will give a survey of recent literature concerning activated sintering in systems such as SnO₂ and ZnO.

Bismuth-doped ZnO is a well known material for e.g. varistor applications [29,30]. It has been extensively studied as model system for liquid-phase sintering. However, it has also been shown that enhanced sintering occur already at temperatures below the eutectic temperature (740°C) [31,32,33]. Rahaman et al. [31] have observed that doping of ZnO with Bi₂O₃, MnO, and CoO leads to the formation of a "preeutectic liquid phase" at about 650°C which promotes sintering at this temperature. Similar results have been reported by other authors [32,33]. Recently, Wang and Chiang [28] have shown that intergranular amorphous films of ~1 nm thickness are formed below the eutectic temperature. These films possess a ZnO-rich composition that is distinct from the eutectic liquid or any intermediate compounds in this binary system. They found that this intergranular amorphous films is energetically favored compared to a crystal-crystal grain boundary and is likely to be responsible for activated sintering in Bi₂O₃-doped ZnO ceramics [26].
Several authors have reported that sintering of nanocrystalline SnO$_2$ is strongly promoted by small amounts of copper oxide (1 mol%) [34]. They found densification between 940 and 1000°C is controlled by a dissolution process. At higher temperatures the transfer of matter is limited by liquid-state diffusion [35]. However, it has been shown that the presence of CuO also promotes the densification of SnO$_2$ at temperatures 40 to 90°C lower than the liquid phase formation (940°C). Several mechanisms were proposed to explain this effect. Some authors [36] proposed that solid-state bulk diffusion is activated by the formation of lattice defects due to the dissolution of Cu(II) in the SnO$_2$ network. Others attributed the densification to a fast copper distribution on the SnO$_2$-based grain surface. Recently, the effect of CoO and MnO$_2$ additions on sintering of SnO$_2$ has been reported [37,38]. It was found that these dopants act as acceptors leading to the creation of additional oxygen vacancies in the SnO$_2$ lattice, resulting in an increase in the densification rate.

4.4.2 Cobalt oxide activated sintering of CGO

We found that constant heating rate as well as isothermal sintering experiments on 1 mol% cobalt oxide doped CGO give evidence for a liquid phase sintering process. DTA-TG and elemental mapping (STEM) on calcined powder have proven that cobalt nitrate precipitates on the surface of CGO and decomposes at temperatures below 400°C. The cobalt oxide is then homogeneously distributed on the surface of the CGO nanocrystals. TEM micrographs taken at different sintering stages show that a cobalt rich 1-2 nm thick amorphous grain boundary phase is present in samples sintered for short time at temperatures as low as 900°C. This amorphous film facilitates rearrangement in state II and III of the densification process. The layer vanishes at higher sintering temperatures and cobalt dissolves in the CGO lattice.

From these findings we can distinguish mainly four different sintering stages (Fig. 4.26):

Stage I, T<400°C:
Water is liberated and nitrate decomposed. Cobalt oxide (CoO and Co$_2$O$_3$) is formed and homogeneously distributed on the nanoparticle surface. Only little shrinkage occurs.
Stage II, 400 >T< 750°C:
The cobalt rich grain-boundary layer facilitates particle rearrangement and shrinkage starts.

Stage III, 750 >T< 1000°C:
An about 2 nm thick cobalt rich amorphous grain boundary layer is formed. Shrinkage occurs due to particle rearrangement facilitated by liquid phase sintering to full density. The incorporation of cobalt within the cerium oxide lattice is determined by the sintering temperature and time.
Stage IV, T>1000°C: Final stage of solid state sintering. Densification is finished and grain coarsening occurs. Cobalt is incorporated in the ceria lattice and no grain-boundary phase can be observed.

We found the highest sintering performance in terms of low sintering temperature and high shrinkage rate was achieved when adding 0.5 - 5 mol% of cobalt oxide to CGO. At dopant levels below 0.5 mol% solid state sintering is predominant and sintering temperatures above 1200°C are required to obtain dense sintered CGO. Adding more than 5 mol% cobalt oxide leads to decreased sintering performance and poor densification of the material (Fig. 4.27).

Factors affecting solid solution formation include ionic radius, valency, chemical affinity and structural similarity. For wide ranges of solid solubility,
4.5 Summary and Conclusions

both components must have comparable properties, i.e., similar ionic radii, iso-
valency, similar structures and a low chemical affinity (i.e. they do not form com-
 pounds) [23]. The solubilities of various divalent and trivalent alkaline-earth and
rare-earth metal oxides in CeO$_2$ have been tabulated in literature [1] but only little
data were given for transition metal oxides such as cobalt oxide. It is known how-
ever, that CeO$_2$ and CoO do not react to form a compound, and that the ionic
radius of Co$^{2+}$ is 0.90 Å, close to that of Ce$^{4+}$ with 0.97 Å. From this we expect
a high solubility of Co within the CeO$_2$ lattice which has been confirmed by our
results. This agrees well with results from literature where a solubility of 30 mol% 
at 1600°C [39] and of 10 mol% after sintering at 1127-1397°C [40] has been
reported. Table 4.5 (4-A.1) lists ionic radii and the solubility of several MO$_x$ in
CeO$_2$ taken from literature.

4.5 Summary and Conclusions

The results show that sintering of CeO$_2$ and CeO$_2$-solid solutions in presence
of transition metal oxides has a profound effect on densification and microstruc-
ture. It has been shown that doping of CGO with 1 mol% CoO gives rise to >99%
dense ceramic material with grain sizes in the 100 nm range when sintered at tem-
peratures as low as 900°C for 2 hrs. We found that precipitation of Co-nitrate on
the CGO nanocrystallite surface leads to a thin CoO coating after decomposing
the nitrates at 350°C.

TEM analysis on CoO containing CGO powders calcined for a short time
(~10 min) at 900°C revealed a several nm thick amorphous cobalt rich grain-
boundary film. This layer facilitates densification via liquid phase sintering at
these low temperatures with a minimum of grain growth. Consequently, rear-
rangement of the CGO nanoparticles and accelerated mass transport through this
intergranular, subeutectic amorphous film occurs. It also provides capillary pres-
sure which is responsible for activated sintering in this system.

Further heat treatment at temperatures higher than 900°C and/or increasing
annealing time results in the formation of a solid solution of CoO in the CGO lat-
tice and grain coarsening. The amorphous or liquid grain boundary film disap-
pears. No additional phases could be detected up to a temperature of 1644°C.
where we determined the eutectic temperature of the CeO$_2$-CoO system when using μm or nm sized powders (see 4-A.1).

Due to the small average grain size of ~100 nm in the sintered material we can expect ceramics with improved mechanical properties. In addition, by appropriate selection of doping level, sintering temperature and heating rate the opportunity is given to co-sinter cathode, anode and electrolyte in solid oxide fuel cell applications in a single step thereby reducing thermal stresses, chemical reactions of the components and fabrication costs.

References

4.5 Summary and Conclusions

[24] in [23], pp. 448
4 Activated Sintering of Cerium Oxide


Appendix

4-A.1 Phase diagram of the cerium oxide / cobalt oxide system

According to our knowledge there is no phase diagram of the CeO₂/CoO system available in literature. We performed DTA measurements on a mixture of 20 mol% CeO₂ and 80 mol% CoO powders with a heating rate of 10°C/min up to a temperature of about 1720°C. We found an endothermic melting peak during heating and an exothermic solidification peak on cooling at 1650 and 1640°C, respectively (Fig. 4.28). EDX analysis of the solidified eutectic melt revealed a very small solid state solubility of CeO₂ in CoO (<1 mol%) but a high solubility of CoO in CeO₂ of about 35 mol%. However, the two oxides are miscible in the liquid state with an eutectic composition of ~20/80 mol% (CeO₂/CoO). The eutectic temperature at 1644±10°C is much lower than the melting points of the two pure oxides. The phase diagram derived for the CeO₂-CoO system is shown in Fig. 4.29.

Fig. 4.28 DTA of the 20 mol% CeO₂ / 80 mol% CoO sample. The arrows indicate the heating cycle.
Fig. 4.29 Calculated phase diagram of the CeO$_2$/CoO system. Point (A) is taken from [40], (B) from [39], (C) and (D) from DTA and EDX measurements.
### 4-A.1 Ionic radius and solubility of MeO$_x$ in CeO$_2$

<table>
<thead>
<tr>
<th>element</th>
<th>ionic radius$^a$ [Å]</th>
<th>solubility [mol%] (°C)</th>
<th>reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg$^{2+}$</td>
<td>0.89</td>
<td>2 (1600)</td>
<td>[1]</td>
</tr>
<tr>
<td>Ca$^{2+}$</td>
<td>1.12</td>
<td>9 (1600)</td>
<td>[43]</td>
</tr>
<tr>
<td>Sr$^{2+}$</td>
<td>1.26</td>
<td>9 (1600)</td>
<td>[43]</td>
</tr>
<tr>
<td>Sc$^{3+}$</td>
<td>0.87</td>
<td>9.5 (1750)</td>
<td>[1], [44]</td>
</tr>
<tr>
<td>Yb$^{3+}$</td>
<td>0.99</td>
<td>40 (1400)</td>
<td>[44]</td>
</tr>
<tr>
<td>Y$^{3+}$</td>
<td>1.02</td>
<td>48.6 (1400)</td>
<td>[1], [44]</td>
</tr>
<tr>
<td>Gd$^{3+}$</td>
<td>1.05</td>
<td>100 (1400)</td>
<td>[44]</td>
</tr>
<tr>
<td>La$^{3+}$</td>
<td>1.16</td>
<td>45 (1600)</td>
<td>[44]</td>
</tr>
<tr>
<td>Ti$^{4+}$</td>
<td>0.74</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Zr$^{4+}$</td>
<td>0.84</td>
<td>30 (1400)</td>
<td>[44]</td>
</tr>
<tr>
<td>Nb$^{5+}$</td>
<td>0.74</td>
<td>0.6 (1320)</td>
<td>[20]</td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.73$^b$</td>
<td>&lt;15 (611)</td>
<td>[25]</td>
</tr>
<tr>
<td>Co$^{2+}$</td>
<td>0.90</td>
<td>0.5 (1400) 10 (1127) 10 (1500) 30 (1600)</td>
<td>[42] [40] [9] [39]</td>
</tr>
<tr>
<td>Ce$^{4+}$</td>
<td>0.97</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

*Tab. 4.5 Ionic radius [41] and solubility of MO$_x$ in CeO$_2$ taken from literature.*

a. for 8-fold coordination

b. for 6-fold coordination.
4 Activated Sintering of Cerium Oxide
Abstract

The effect of small amounts (<5 mol%) of cobalt oxide on the electrical properties of cerium oxide solid solutions has been evaluated. Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ (CGO) powder with an average crystallite size of 20 nm served as a model substance for the electrolyte material with a high oxygen ion conductivity and low electronic conductivity in its densified state. Doping the CGO powder by transition metal oxides (MeO) with concentrations below 2 mol% did not change the ionic conductivity nor the electronic domain boundary. After long sintering times (2 hrs) at temperatures above 900°C these MeO form CeO$_2$ solid solutions. However, short sintering times or high dopant concentrations lead to an electronic conducting grain boundary phase short circuiting the ionic conductivity of the CGO grains. Choosing proper doping levels, sintering time and temperature allows to tailor mixed conducting oxides based on CGO. These materials have potential use as electrolytes and/or anodes in solid oxide fuel cells and ion separation membranes.

Keywords: ceria solid solutions, mixed ionic electronic conductivity, nanosized ceramic, transition metal oxides, cobalt oxide, brick layer model.

1. parts of this chapter have been published in Solid State Ionics [19].
5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

5.1 Introduction

5.1.1 General

Solid electrolytes exhibiting high oxygen ion conductivity are of special interest for their application in electrochemical devices such as solid oxide fuel cells (SOFCs), oxygen separation membranes and methane gas conversion reactors. In the case of SOFCs, the state-of-the-art material is yttria stabilized zirconia which exhibits sufficient ionic conductivity at an operating temperature of 900°C to 1000°C [1]. This high temperature requires expensive materials for interconnectors, heat exchangers, and structural components. It is therefore desirable to lower the operating temperature to intermediate temperatures of about 700°C. This requires either new system concepts such as thin-film electrolyte SOFCs [2,3,4] or new electrolyte materials with higher oxygen ion conductivity [5,6,7]. Ceria solid solutions have been shown to exhibit 4 to 5 times higher ionic conductivities at intermediate temperatures [8] compared to zirconia. Although ceria based electrolytes are slightly reduced at low oxygen partial pressures and develop increasingly electronic conductivity [9], it has been shown that CGO based SOFC can be operated at temperatures as low as 700°C with high power output and high efficiency [10,11]. Therefore, CeO$_2$ss are attractive electrolytes in SOFCs. In a recent paper [12] it was also shown that CeO$_2$ containing anodes exhibit catalytic activity that allow to operate SOFC below 700°C with natural gas without carbon deposition.

One problem arising from ceria based electrolytes for SOFCs is that conventional sintering to full density needs temperatures exceeding 1300°C [13,14,15,16,17,18]. As consequence, high grain growth rates and large grains of several µm were observed resulting in poor mechanical stability of the ceramic component. This characteristic is one of the major reason which hinders the use of CeO$_2$ss in SOFC applications despite its superior electrochemical performance.

5.1.2 Aim of the study

In Chapter 4 we have shown that sintering of cerium oxide solid solutions with initial grain sizes in the nanometer range is strongly promoted when adding small amounts (~1 mol%) of transition metal oxides (e.g. cobalt oxide) [19,20]. We succeeded in obtaining >99% dense electrolytes with grain sizes of ~120 nm
5.2 Experimental Procedures

after sintering at temperatures as low as 900°C. It was also observed that when interrupting sintering of a cobalt oxide doped cerium oxide sample an about 2 nm thick amorphous cobalt rich grain-boundary layer was present. This layer disappears after thermally equilibrating the dense sample for longer sintering times or when higher sintering temperatures are used.

Now the question arises whether these low sintered and nanosized cerium oxide based ceramics still exhibit electrochemical properties suitable for using them as electrolytes or electrodes in intermediate temperature solid oxide fuel cells. Of particular interest is the influence of cobalt incorporated within the ceria lattice on the mixed ionic/electronic conductivity as well as the properties of CGO with cobalt oxide rich grain-boundary films. We want to investigate the formation as well as the dissolution of the cobalt rich grain-boundary layer and its effect on the grain/grain-boundary conductivity. The sample composition and also the sintering program have been varied in order to show the relation between the microstructures and the electrochemical behavior.

5.2 Experimental Procedures

5.2.1 Sample preparation

Ce_{0.8}Gd_{0.2}O_{2-x} (denoted CGO; #595250A, Rhodia GmbH, Frankfurt, FRG) with a crystallite size of 20 nm and a specific surface area of about 24 m²/g was used as starting powder to which the dopant was added in form of the nitrate (Co(NO₃)₂·6 H₂O, Fluka AG, Buchs, CH). Doping of CGO with different concentrations of cobalt oxide (0-5 mol%) was performed by first dispersing the CGO powder in ethanol (Fluka, puriss.p.a.), using an agate mortar. A desired amount of the dissolved dopant nitrate was then added. After drying at 120°C for two hours the powders were first uniaxially dry pressed at 50 MPa into pellets with a diameter of 10 mm followed by isostatic pressing at 840 MPa for 3 min.

Sintering of the pressed pellets has been conducted in air on magnesium oxide plates. The heating rate was fixed to 1 K/min up to 400°C followed by 3 K/min up to the desired temperature. After annealing at the sintering temperature the samples were cooled at 5 K/min to room temperature. The final densities of
5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

the sintered pellets were determined following the Archimedes method. For these data we refer to Chapter 4, Section 4.2.

5.2.2 Impedance spectroscopy and 4-point conductivity measurements

Both sides of a polished sample pellet were contacted by sputtering first a ~50 nm Pt layer (model SCD 040, Baltec, Balzers, FL) followed by fixing platinum wires (0.35 mm diameter) with a ceramic two-component binder (type 1500, Friag, Ebmatingen, CH) and finally coating with platinum paste (C 3605 P, Heraeus GmbH, Hanau, FRG). The electrodes were then heat treated at 700°C for two hours to burn out the binder of the platinum paste and to ensure good contact of the electrodes with the ceramic pellet. A.C. impedance spectroscopy was performed on each of the pellets in a temperature range from 150°C to 700°C using a Zahner FRA (model IM6, Zahner GmbH, Kranach, FRG) in the range 0.1 Hz - 2 MHz with an excitation voltage of 50 mV at T < 400°C and 10 mV at temperatures above. The measurements were carried out in air and in different gas mixtures (N2, CO/CO2, N2/H2) over a p(O2) range from 0.21 to 10^-27 atm. The p(O2) value was recorded using a zirconia based probe located close to the sample.

4-point conductivity measurements have been carried out on test bars of 30 x 4 x 4 mm (length x width x height) contacted by applying platinum paste and fixing platinum wires with ceramic two-component binder. Measurements were taken in air during heating up to 900°C as well as during annealing and cooling to room temperature to confirm the reproducibility.

5.2.3 Microstructural modelling

In order to correlate the measured electrical properties with the sample microstructure the so called “brick layer model”, hereafter referred to as the BLM, has been applied. The BLM was first proposed by Beekmans and Heyne [27] and further refined by Dijk and Burgraaf [22]. Their models are based on the work of Bauerle [23] who first developed an equivalent circuit model for conductive ceramics with resistive grain boundaries. Most recently, Hwang, et al. [24] applied the BLM to nanocrystalline CeO2 with enhanced conduction at grain boundaries discussing the limitations of this model for complex electroceramic microstructures. A general representation of the BLM is shown in Fig. 5.1. The grains are modeled as cubes of equal size and edge length, D, surrounded by a grain bound-
ary of a specific thickness, $\delta_{gb}$. For the apparent grain size it follows then: $<D> = D + \delta_{gb}$. The current flow is assumed to be one-dimensional, and the curvature of the current paths at the corners of the grains is neglected. Depending on the relative magnitudes of the conductivities $\sigma_{gr}$ and $\sigma_{gb}$, the current flows either through grains and across grain-boundaries (Fig. 5.2, path 1) or along grain-boundaries (Fig. 5.2, path 2).

![Fig. 5.1 Sketch of the brick-layer-model, BLM, indicating grain diameter, $D$, grain-boundary thickness, $\delta_{gb}$, sample thickness, $l$, cross-sectional area, $S$ and electrodes, $E$.](image)

**Case I: $\sigma_{gb} \ll \sigma_{gr}$ and $\delta_{gb} \ll <D>$**

If the grain boundary conductivity, $\sigma_{gb}$, is much smaller than the conductivity of the grain interior, $\sigma_{gr}$, and/or the grain boundary thickness is small compared to the grain size ($\delta \ll <D>$), then for an electric field applied only contributions from
Path 2: Short circuiting grains, current flows along parallel grain-boundaries. $R_1$ represents the ohmic contribution of current leads and contacts; $R_2$ and $C_2$ are representing the electrode response.

Fig. 5.2 Equivalent circuit representation of microstructures according the BLM. Two current paths are possible. Path 1: crossing grain and grain-boundary perpendicular. Path 2: Short circuiting grains, current flows along parallel grain-boundaries. $R_1$ represents the ohmic contribution of current leads and contacts; $R_2$ and $C_2$ are representing the electrode response.

Grain boundaries vertical to the electric flux have to be considered. Contributions from grain boundaries parallel to the electric flux, i.e. short-circuiting the grain contribution, can be neglected. This situation results in a Bauerle-type equivalent circuit consisting of two parallel RC (resistor-capacitor) elements in series representing the grain and grain-boundary contribution, respectively (Fig. 5.2, path 1).

From impedance spectra in which the imaginary part $\text{Im}(Z)$ is plotted against the real part $\text{Re}(Z)$ of the impedance, the grain resistance, $R_{gr}$, and the total grain-boundary resistance, $R_{gb}$, can be obtained from the intersections on the real axis.
5.2 Experimental Procedures

of the corresponding semicircular arcs. As the frequency peak of each semicircle is given by

$$\omega_{0_i} = \frac{1}{R_iC_i}$$  \hspace{1cm} (5.1)

the specific capacitances, \(C_i\), can be calculated. We also know that \(C_i\) is defined as \(C_i = \varepsilon_i \varepsilon_0 S/l\) and using \(\sigma_i = l/S/R_i\) it follows that

$$\frac{1}{\omega_{0_i}} = R_iC_i = \frac{1}{\sigma_i} \varepsilon_i \varepsilon_0$$  \hspace{1cm} (5.2)

where \(\varepsilon_i\) denotes the specific relative dielectric constant, and \(\varepsilon_0\) the permittivity of free space. \(S\) corresponds to the electrode area and \(l\) to the thickness of the sample. It is important to note that \(\omega_{0_i}\) is an intrinsic material property, independent of geometric considerations. Since the dielectric constants in sintered materials do not vary significantly compared to the conductivity, it is reasonable to make the usual assumption that \(\varepsilon_{gr} \approx \varepsilon_{gb}\) [25,26]. This holds also for cobalt doped cerium oxide since \(\varepsilon_\tau\) for cerium oxide is about 30 and for cobalt oxide about 40 [27,28]. However, the conductivity may easily change orders of magnitude as we will show lateron. Therefore, distinct arcs for grain and grain-boundary contributions in an impedance spectra can only be observed if \(|\sigma_{gr} - \sigma_{gb}| \gg 0\), which is true for the present case.

From this follows that the capacitance ratio of the two components is:

$$\frac{C_{gb}}{C_{gr}} = \frac{\varepsilon_{gb}}{\varepsilon_{gr}} \cdot \frac{<D>}{\delta_{gb}}$$  \hspace{1cm} (5.3)
where the total bulk capacitance, \( C_{gb}^T \), and the total grain-boundary capacitance, \( C_{gr} \), are given by

\[
C_{gr} = \frac{\varepsilon_{gr} \varepsilon_0 \cdot S}{l} \tag{5.4}
\]

\[
C_{gb}^T = \frac{\varepsilon_{gb} \varepsilon_0 \cdot S}{l} \tag{5.5}
\]

\( \varepsilon_{gr} \) is the bulk relative dielectric constant and \( \varepsilon_{gr} \) the grain-boundary relative dielectric constant. Eqn. (5.3) establishes a connection between microstructure and electrical properties allowing to relate the microscopically observed grain-boundary thickness estimated from electrical properties.

Furthermore, the grain conductivity, \( \sigma_{gr} \), and the total grain-boundary conductivity, \( \sigma_{gb}^T \), are given by:

\[
\sigma_{gr} = \frac{1}{R_{gr} S} \tag{5.6}
\]

\[
\sigma_{gb}^T = \frac{1}{R_{gb} S} \tag{5.7}
\]

and we can then define the specific grain-boundary conductivities as

\[
\sigma_{gb}^{sp} = \frac{\sigma_{gb}^T \delta_{gr}}{<D>} \tag{5.8}
\]

The interpretation of the impedance spectra in the case discussed above is straightforward. In a two arc spectrum (we do not consider electrode effects here) one can interpret the highest frequency arc representing the bulk response followed by the grain-boundary signal at lower/lowest frequency.

It is important to note that for impedance spectra which exhibit two clearly separated arcs, one can immediately deduce that \( \sigma_{gb} < \sigma_{gr} \) since only a difference
5.2 Experimental Procedures

Fig. 5.3 Sketch of a Niquist plot representing path 1 of Fig. 5.1. Grain and grain-boundary arcs are separated.

In conductivities of grain and grain-boundary can give a difference in characteristic frequencies.

**Case II: \( \sigma_{gb} \gg \sigma_{gr} \) and \( \delta_{gb} \ll \langle D \rangle \)**

In this particular case the grain-boundary width is small compared to the apparent grain-size \( \langle D \rangle \), but the grain-boundary conductivity, \( \sigma_{gb} \), is much higher compared to the grain conductivity, \( \sigma_{gr} \). Therefore the current flows mainly along grain boundaries, i.e. short circuiting the grain current, and the above discussed BLM is then reduced to one single RC circuit (c.f. Fig. 5.2, path 2). A ceramic sample will then show only one arc in the impedance plot and little information will be gained about the microstructure. However, if some microstructural data are available such as grain-boundary thickness, \( \sigma_{gb} \) may be estimated and some information about the composition of the grain-boundary and its specific properties can be deduced.

*Previously reported applications of the BLM on single-crystalline and polycrystalline materials*

Using impedance spectra alone allows to distinguish between conducting grains with blocking grain boundaries on the one hand and poorly conducting grains with highly conducting grain-boundaries on the other. Other work-groups have extensively used the BLM on doped and undoped cerium oxide single crys-
5.2.4 Defect chemistry of gadolinium doped cerium oxide containing ions of variable charges

Introduction of electronic conductivity in solid electrolytes by heavy doping with transition metal or rare earth ions has been widely discussed in terms of e.g. enlarging the triple phase boundary at electrode/electrolyte interfaces [31,32], enhancement of the oxygen exchange coefficient at the electrolyte surface [33], increasing the oxygen exchange coefficient and the electrocatalytic activity at electrolyte surfaces [34,35,36]. For doping of yttria stabilized zirconia single crystals with transition metals and rare earth ions of variable charges, Sasaki showed that the equilibrium concentrations of electrons and holes are not effected as long
as the dopant level of the redox active species is kept low and equilibrium conditions being present [37].

In the following, we will show that low level (~1 mol%) doping of cerium gadolinium oxide with transition metal oxides such as cobalt oxide does not significantly effect the overall conductivity of the bulk material. First, we will consider conditions in temperature and p(O_2) where ceria based solid electrolytes exhibit an ionic transference number close to unity, i.e. they are mainly oxygen ion conducting. Secondly, we will use operation regimes where Ce^{4+} becomes partially reduced to Ce^{3+} thus showing an increase in \( \sigma_c \) and consequently exhibiting an ionic transference number less than one.

**Defect chemistry of cerium gadolinium oxide assuming no partial reduction of cerium**

The defect chemistry, described in Kroger-Vink notation, is considered only for situations where \( [V^{\text{V}}_O] \gg [h^\text{e}'], [e^\text{e}'] \) and \( [V^{\text{V}}_O] \gg [M] \). \( c_M \equiv [M] \) denotes the concentration of dopant with variable charges.

The equilibrium defect chemistry at a temperature, \( T \), and an oxygen partial pressure, \( p(O_2) \), is described by the oxygen incorporation equilibrium:

\[
[V^{\text{V}}_O] + (1/2)O_2 \leftrightarrow [O^{x}_O] + 2[h^\text{e}']
\]  
(5.1)

giving the mass action constant \( K_1 \) as:

\[
K_1(T, p_{O_2}) = \frac{[h^\text{e}']^2 \cdot [O^{x}_O]}{[V^{\text{V}}_O] \cdot p_{O_2}^{1/2}}
\]  
(5.2)

Herein \( [O^{x}_O] \) can be assumed as constant.

Since \( [V^{\text{V}}_O] \gg [h^\text{e}'], [e^\text{e}'], [M^{\text{V}}_{Ce}], [M^{\text{V}}_{Ce}'] \) the overall electroneutrality condition

\[
2[V^{\text{V}}_O] + [h^\text{e}'] - [Gd^{\text{e}'}_{Ce}] - [e^\text{e}'] - [M^{\text{V}}_{Ce}] - 2[M^{\text{V}}_{Ce}'] = 0
\]  
(5.3)
is then reduced to:

$$2[V^*] \equiv [Gd^*]_e.$$  \hspace{1cm} (5.4)

From this, we can deduce the electron and the hole concentration which are fixed by $T$, $p(O_2)$, $[Gd^*]_e$ and $K_1$, $K_2$ respectively:

$$[h^*] = K_1^{1/2} [V^*]^{1/2} \cdot p_{O_2}^{1/4} \equiv K_1^{1/2} \cdot \left( \frac{[Gd^*]_e}{2} \right)^{1/2} \cdot p_{O_2}^{1/4}$$  \hspace{1cm} (5.5)

and

$$[e^*] = K_2/[h^*] = K_1^{-1/2} \cdot K_3 \cdot \left( \frac{[Gd^*]_e}{2} \right)^{-1/2} \cdot p_{O_2}^{-1/4}$$  \hspace{1cm} (5.6)

using $[e^*] \cdot [h^*] = K_2(T, p_{O_2})$ which refers to the band-band equilibrium.

Impurity equilibria such as:

$$M^{(n+1)+} \leftrightarrow M^{n+} + h^*$$  \hspace{1cm} (5.7)

with an equilibrium constant $K_3$ given by

$$K_3(T, p_{O_2}) = \frac{[M^{n+}] \cdot [h^*]}{[M^{(n+1)+}]}$$  \hspace{1cm} (5.8)

are not of influence on $[h^*]$, $[e^*]$, rather the ratio of $[M^{n+}] / [M^{(n+1)+}]$ is fixed through Eqn. (5.5) and Eqn. (5.6), respectively. This means that the electron and hole concentrations in cerium oxide are not affected by the redox-active species, as long as the simplification of the overall electroneutrality condition (Eqn. (5.3) and Eqn. (5.4)) is valid. Using the mass conservation condition,

$$c_M = [M^{(n+1)+}] + [M^{n+}],$$  \hspace{1cm} (5.9)
the concentrations \([M^{n+}]\) and \([M^{(n+1)+}]\) can be easily calculated. It follows for low \(p(O_2)\):

\[
[M^{n+}] \equiv c_M \text{ and } [M^{(n+1)+}] \equiv c_M \cdot K_1^{1/2} K_2^{-1} \cdot \left(\frac{[Gd'_{Ce}]}{2}\right)^{1/2} \cdot p_2^{1/4} \quad (5.10)
\]

and for high \(p(O_2)\):

\[
[M^{(n+1)+}] \equiv c_M \text{ and } [M^{n+}] \equiv c_M \cdot K_1^{-1/2} K_2 \cdot \left(\frac{[Gd'_{Ce}]}{2}\right)^{-1/2} \cdot p_2^{-1/4} \quad (5.11)
\]

These defect chemistry relations are, of course, different if the total M-concentration, \(c_M\), becomes comparable with \([Gd'_{Ce}]\) (Eqn. (5.4) invalid). Moreover, at much higher M-concentrations, the hopping electron conduction between \([M^{n+}]\) and \([M^{(n+1)+}]\) may not be negligible [38]. However, as in our study we are dealing with transition metal oxide concentrations as low as \(\approx 1\) cat\% compared to 20 cat\% of gadolinium incorporated in cerium oxide, this effect has not to be considered.

**Defect chemistry of cerium gadolinium oxide taking into account partial reduction of cerium oxide**

Ceria and ceria solid solutions are reduced and become nonstoichiometric under low oxygen partial pressures, e.g. on the anode side of solid oxide fuel cells (SOFC). The reduction of ceria introduces free electrons responsible for mixed ionic electronic conductivity [9,39,40,41]. The oxygen content in nonstoichiometric ceria is then changed by the electrochemical reaction

\[
2Ce^{x}_{Ce} + O^{x}_{O} \leftrightarrow 2Ce'_{Ce} + V_O' + \frac{1}{2}O_2 \quad (5.12)
\]
5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

giving:

\[ K_d(T) = \frac{[Ce_{Ce}']^2 \cdot [V_{O}^{\bullet \cdot}] \cdot p_{O_2}^{1/2}}{[Ce_{Ce}^x]^2 \cdot [O_{O}^\bullet]} \]  

(5.13)

Herein \([Ce_{Ce}^x],[O_{O}^\bullet]\) and \([V_{O}^{\bullet \cdot}]\) can be assumed as constant. Since \([e'] = [Ce_{Ce}']\) an n-type electronic conductivity giving a slope of -0.25 in a \(\log(\sigma)\) versus \(\log(p(O_2))\) plot can be found [42]. Under these conditions it is assumed that the concentrations of electrons generated is large compared to the concentration of dopants \(([e'] > [M])\). This means that the reduction of cerium oxide is the dominating effect under these conditions, and does not significantly influence the above derived electron and hole concentrations in (Eqn. (5.5)) and (Eqn. (5.6)). Therefore, we can note that the electronic and oxygen ionic conductivity in CeO\(_2\) is determined by the 20 mol\% Gd\(_2\)O\(_3\) concentration and a 1 mol\% doping of e.g. CoO will have no effect on the conductivity.

5.3 Results

5.3.1 Total conductivity

To investigate the influence of CoO dopant on the oxygen ionic conductivity, \(\sigma_i\), of CGO we first performed 4-pot measurements to determine the total electrical conductivity \(\sigma_{tot}\) (the sum of \(\sigma_i\) and the electronic conductivity \(\sigma_e\)). The activation energy, \(E_A\), was then derived from the slope in the \(\ln(\sigma_{tot})\) versus 1/T plot. Furthermore, we carried out conductivity measurements in different gas atmospheres and at different temperatures to find the electrolytic domain boundary, i.e. where \(\sigma_i\) equals \(\sigma_e\).

The total conductivity, \(\sigma_{tot}\), of CGO as a function of CoO concentration at 600°C, 700°C, and 800°C in air is plotted in Fig. 5.5. The sintering temperatures (two hours annealing time each) were as follows: 1400°C for pure, 0.01 and 0.1 mol\% doped, 1100°C for 0.5 mol\%, and 1000°C for >1 mol\% of cobalt oxide. The sintering temperatures and dwell times have been fixed following the results from Chapter 4 to obtain >98\% dense samples. We found that the conductivity \(\sigma_{tot}\)...
remains unchanged for concentrations ranging from 0 to 2 mol% compared to pure CGO. Exceeding 2 mol% of dopant a somewhat lower $\sigma_{\text{tot}}$ was noticed.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{fig5.5.png}
\caption{Total conductivity, $\sigma_{\text{tot}}$, for Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ doped with different concentrations of CoO at 600, 700 and 800°C in air (sintered at 1000°C for 2 hrs).}
\end{figure}

Sintering of 5 mol% CoO doped CGO sample at 1000°C for two hours does not lead to a fully equilibrated sample. This can be seen from Fig. 5.6 where $\log(\sigma_{\text{tot}})$ is plotted versus $1/T$ for CGO samples with dopant concentrations of 0.5, 2 and 5 mol%. The conductivity shown was recorded during heating and cooling. We found a hysteresis at temperatures below 400°C indicating a higher conductivity for the as-sintered sample. After a second cycle up to 900°C the conductivity was similar to pure and < 5 mol% doped samples. This suggests that a highly conducting phase is present which increases the total conductivity about two orders of magnitude at 250°C. This phase vanishes after two heating cycles as well as with increasing sintering time or increasing sintering temperature resulting in $\sigma_{\text{tot}}$ comparable to pure CGO. In the following subsection (5.3.2) we will further analyse this behavior in terms of grain/grain-boundary conductivity contributions.
Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

![Graph showing conductivity vs. temperature](image)

**Fig. 5.6** Total conductivity, $\sigma_{tot}$, of CGO doped with CoO (0, 0.5, 2, 5 mol%) after sintering at 1000°C for 2 hrs. The arrows indicate the heating and cooling cycle of the 5 mol% sample.

Fig. 5.7 shows a comparison of the total electrical conductivities in air determined by impedance spectroscopy and by 4-pt measurements for 1 mol% CoO doped samples sintered at 1000°C for two hours. We also plotted results reported earlier [42] determined by 4-point measurement. The actual measurements are in very good agreement with our previous ones, only at temperatures above 700°C slightly higher values were obtained for the actual samples.

It may be argued that there is a contribution to the total conductivity via a percolating semi conducting cobalt oxide grain boundary layer which equals the loss in $\sigma_i$. This contribution seems to be evident for the 5 mol% and 2 hrs sintered sample (c.f. Fig. 5.6) but perhaps it is also present in the samples containing lower dopant concentrations.

To elucidate this point, we conducted further measurements on the p(O$_2$) dependence of the total conductivity, $\sigma_{tot}$. In Fig. 5.8, $\sigma_{tot}$ for CGO doped with 1 mol% CoO ($T_s$ = 1000°C for two hours) is plotted as a function of p(O$_2$) ranging from 0.21 to $10^{-27}$ atm. We found at high p(O$_2$) the conductivity is predominantly
5.3 Results

Fig. 5.7  Arrhenius plot of the total conductivity, $\sigma_{tot}$, of CGO doped with 1 mol% CoO determined with 4-point and impedance spectroscopy. For comparison the results of [42] are added.

Ionic and at lower $p(O_2)$ the material becomes a mixed ionic/electronic conductor due to partial reduction of Ce$^{4+}$ to Ce$^{3+}$ (c.f. Eqn. (5.12)). The solid lines are fits to $\sigma_e \sim p(O_2)^{-1/m}$ where $1/m$ was fixed to 0.25, which means that the number of oxygen vacancies can be assumed as constant (c.f. 5.2.4). Activation energies $E_A$ obtained from the $\ln(\sigma_{tot}T)$ versus $1/T$ plot (c.f. Fig. 5.7) as well as data for the ionic conductivity ($\sigma_i$) and the electrolytic domain boundary (EDB) are listed in Table 5.1. These results compare well with our former results and with literature data (c.f. Table 5.1).

We can further calculate from the formation enthalpy of cobalt oxide [43] that e.g. at 700°C it will be reduced to metallic cobalt at a $p(O_2)$ below $10^{-22}$ atm. This is much higher than the $p(O_2)$ reached during the measurement which was
about $\sim 10^{-26}$ atm but we have not found an increase in $\sigma_e$ which can be attributed to a percolating cobalt metal grain boundary layer.

<table>
<thead>
<tr>
<th>Material</th>
<th>$\sigma_i [S/m]$ at 700°C</th>
<th>$EDB [atm pO_2]$ at 700°C</th>
<th>$E_A [eV]$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO</td>
<td>4.5</td>
<td>1.78 \cdot 10^{-19}</td>
<td>0.73</td>
</tr>
<tr>
<td>CGO + 1 mol% CoO</td>
<td>4.8</td>
<td>2.2 \cdot 10^{-19}</td>
<td>0.73</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9-x}$ [9]</td>
<td>3.62</td>
<td>1.14 \cdot 10^{-20}</td>
<td>0.73</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9-x}$ [44,45]</td>
<td>4.7</td>
<td>1.24 \cdot 10^{-19}</td>
<td>0.75</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9-x}$ [46]</td>
<td>2.8</td>
<td>3.5 \cdot 10^{-19}</td>
<td>-</td>
</tr>
</tbody>
</table>

Tab. 5.1 Ionic conductivity, $\sigma_e$, electrolytic domain boundary, EDB, and activation energy for ionic conductivity, $E_A$, for doped and undoped CGO. For comparison literature data are given.

Fig. 5.8 Total conductivity of Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ doped with 1 mol% CoO as a function of $p(O_2)$ at different temperatures. The sample was sintered at 1000°C for 2 hrs.
5.3 Results

We further analysed the long term conductivity behavior of a 1 mol% CoO doped CGO sample sintered at 900°C for 2 hrs. The measurement has been conducted in atmospheres present at SOFC anodes under fuel cell operation conditions, i.e., in a mixture of hydrogen/nitrogen containing 3% of water. The oxygen partial pressure was about \(10^{-23}\) atm (700°C). The result is plotted in Fig. 5.9. We found that a total conductivity of about 5.37 S/m is obtained after heating up to 700°C. From then on, the conductivity did not change during the whole measurement which was terminated after 420 hrs.

\[\text{Fig. 5.9 Total conductivity, } \sigma_{\text{tot}} \text{ versus time, } t, \text{ of CGO doped with 1 mol\% CoO sintered at 900°C for 2 hrs. The measurement has been carried out in a mixture of } N_2/H_2 \text{ humidified with 3\% } H_2O \text{ giving an oxygen partial pressure of about } 10^{-23} \text{ atm at 700°C.} \]

From these results we deduce that there is no cobalt oxide rich grain boundary layer formed which may block oxygen ions in samples of doping levels below 5 mol% after sintering at 900°C for dwell times \(\geq 2\) hrs or at temperatures \(\geq 1000°C\). At higher doping levels (~5 mol%) we found a strong indication of a cobalt oxide rich phase forming a percolating network thus increasing the electronic conductivity. However, this electron conducting layer vanishes after further
Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

heat treatment implying the dissolution of the cobalt cations within the ceria lattice.

This experimental result is consistent with the model described above (subsection 5.2.4) where we showed that doping of CGO with multivalent transition metal will not introduce electronic conductivity by electrons or holes as long as the dopant level is kept low compared to the gadolinium concentration.

In the following subsection we will further analyse the conductivity behavior of a cobalt rich grain boundary in CGO. With impedance spectroscopy the grain and grain-boundary contributions to the overall conductivity have been separated and their evolution with sintering time was recorded.

5.3.2 Impedance analysis of grain/grain-boundary contribution to total conductivity

To further analyse the conductivity behavior of the cobalt rich grain boundary layer in doped CGO we used impedance spectroscopy on 1 mol% CoO doped CGO sintered at 900°C with dwell times of 10 min, 2 and 50 hrs. Nyquist and Bode plots are shown in Fig. 5.10 and Fig. 5.11, respectively. We found that the 10 min sintered sample exhibits what appears to be a single arc which is centered on the real axis (Fig. 5.10(a)) giving a single plateau behavior in the bode plot (Fig. 5.11(a)). However, a slight distortion of the ideal ‘one relaxation time process’ behavior indicates that there might be a second process present which could not be resolved due to a similar characteristic relaxation frequency, \( \omega_0 \).

In contrast, samples sintered with 2 hrs dwell time exhibited two overlapping arcs (Fig. 5.10(b)) leading to a dual plateau behavior in the Bode plot (Fig. 5.11(b)). This indicates that a change in conductivity, i.e. a second conductivity mechanism contributes significantly to the overall impedance. Further increasing the dwell time up to 50 hrs gives two clearly separated high frequency arcs and an additional distinct third arc (marked ‘C’) at low frequency (Fig. 5.10(c) and Fig. 5.11(c)). From the model discussed in subsection 5.2.3 it becomes evident that the arcs ‘A’, ‘B’, and ‘C’ are representing the grain, grain-boundary and electrode contribution to the total impedance. We can further note that \( \omega_0 \) of the rising second arc (marked ‘B’ in Fig. 5.11) shifts continuously to lower frequencies with increasing dwell time. This clearly indicates that the conductivity of the corre-
5.3 Results

Fig. 5.10 Complex plane plot of the electrochemical response for different CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ samples sintered at 900°C with varying dwell times (10 min, 2 and 50 hrs). The results were obtained at 200°C in air. Plots have been normalized to the data of the specimen sintered at 900°C/10 min and corrected for ohmic contributions to illustrate the change in grain, grain boundary and contact contributions. Frequency increases from right to left.

The corresponding process decreases (c.f. Eqn. (5.2)). In contrast, the characteristic frequency of the first arc (marked 'A' in Fig. 5.11) remains constant with increasing dwell time implying a constant conductivity.

To investigate the temperature dependence of the conductivity of the samples we recorded the impedance at 150, 200, and 250°C (Fig. 5.12-5.14). The spectra reflect the temperature dependence of $\sigma_{gr}$ and $\sigma_{gb}$, i.e. an increase of $\sigma$ with increasing temperature. It is clear that the characteristic frequencies, $\omega_0$, are shifting to higher frequencies (arrows in Fig. 5.12-5.14). From spectra recorded at higher temperatures (>250°C) the grain/grain-boundary contribution could not be clearly resolved any more and only the total contribution of both processes has been recorded.
Fig. 5.11 Bode plot of 1 mol% CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ sintered at 900°C with varying dwell times (10 min (a), 2 hrs (b) and 50 hrs (c)). The spectra were recorded at 200°C. $|Z|$ is indicated by lines; phase angle $\phi$, by open symbols.

110
5.3 Results

Fig. 5.12 Bode plots of 1 mol% CoO doped CeₐGd₀₂₋ₓ sintered for short time (10 min) recorded at different temperatures.

Fig. 5.15 shows an Arrhenius plot of the conductivity values obtained from the impedance spectra. The grain-boundary conductivity, $\sigma_{gb}$, is shown in the temperature range from 150 to about 400°C and the total conductivity, $\sigma_{tot}$, above 400 up to 700°C. Sintering at 900°C for 10 min leads to an increase of $\sigma_{gb}$ as well as to a decrease in activation energy, $E_A$, from about 0.81 to 0.54 eV compared to pure CGO. With dwell times longer than 2 hrs a higher $\sigma_{gb}$ with $E_A = 0.54$ eV was still observed. However, the temperature where the slope changes to higher $E_A$ which means when $\sigma_{gr}$ equals $\sigma_{gb}$ shifts from about 400°C to 300°C. Further increase of dwell time up to 50 hrs leads to $\sigma_{tot}$ and $E_A$ comparable to pure CGO.

A similar influence on conductivity has been found for 5 mol% doped samples as shown in the previous section (c.f. Fig. 5.6). It becomes clear that for short sintered samples as well as for high doping levels there exists a highly conducting
5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide

figure 5.13 Bode plots of 1 mol% CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ sintered for intermediate time (2 hrs) recorded at different temperatures. Arrows indicate the characteristic frequency, $\omega_n$, of the grain-boundary contribution.

From these findings we deduce that below 400°C the conductivity is dominated by the amorphous about 2 nm thick cobalt oxide grain boundary layer identified by microstructural analysis (c.f. subsection 4.3.2). The ionic conductivity is nearly blocked at the grain-boundary at temperatures below $T_b$, which indicates
Fig. 5.14 Bode plots of 1 mol% CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ sintered for long time (50 hrs) recorded at different temperatures. Arrows are indicating the characteristic frequency, $\omega_0$, of the grain-boundary contribution

the point of intersection, where the grain-boundary conductivity equals the grain contribution. With increasing sintering temperature and time the conductivity changes to lower values with an activation energy of about 0.8 eV corresponding to $E_A$ of pure CGO. Consequently, $T_b$ shifts to lower temperatures. During annealing the cobalt cations from the CoO rich grain boundary layer that first introduced electronic grain boundary conductivity are now incorporated in the CGO lattice. As their concentration is low, this will not give rise to electronic conductivity in the CGO bulk material. On the other hand conductivity of oxygen ions now becomes predominant with clearly separated grain and grain-boundary contributions. Since the conductivity of the long-time sintered sample is now mainly ionic, an electrode response is found also in the low frequency region.
Fig. 5.15 Arrhenius plot of grain, grain-boundary and total conductivity of Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ doped with 1 mol% CoO. The samples were sintered at 900°C for 10 min, 30 min, and 2 hrs respectively. The slopes, m, of the curves in the $\ln(\sigma_{\text{tot}}T)$ versus $1/T$ were obtained from least-square fits of the experimental data. $T_b$ is the point of intersection where grain-boundary conductivity (dashed lines) equals grain conductivity (dotted line). Conductivity and activation energy of cobalt oxide taken from [47] is also shown.

CeO$_2$ is known to have a high solid solubility for many dopants [50,51,52]. The cobalt cations are dissolved in the ceria crystal structure during the later stage of sintering. They neither form an ion blocking grain boundary layer nor do they lead to a significant increase in the electronic conductivity of the host material.

The high solubility of cobalt within the CGO lattice observed agrees well with the results of Dontsov et al. who found that the solubility limit of cobalt in the CeO$_2$ lattice to be 30 mol% at 1600°C [53]. Also Naumovich et al. reported a solubility limit of cobalt in CGO around 10 mol% [54] after sintering at 1127-1397°C for 50 hours. This is in contrast to Sirman et al. who used dynamic SIMS in combination with XRD and determined a solubility limit of about 0.5 mol%
5.3 Results

after sintering at 1400°C for 50 hours [55]. No reaction products between CeO$_2$ and cobalt oxide in the above mentioned temperature range are reported in literature.

5.3.3 Correlation of conductivity data with microstructure

Following the BLM introduced in subsection 5.2.3 we can now calculate the specific grain-boundary conductivity, $\sigma_{gb}^{sp}$, from the data obtained in the impedance spectra (Eqn. (5.8)). The grain-boundary thickness, $\delta_{gb}$, is derived by means of Eqn. (5.2) and Eqn. (5.3). Values for apparent grain sizes are taken from Chapter 4. The results are listed in Table 5.2 determined from measurements taken at different temperatures, T.

<table>
<thead>
<tr>
<th>sintering time</th>
<th>$T$ [°C]</th>
<th>$\langle D \rangle$ [nm]</th>
<th>$\sigma_{gb}^{sp}$ [S/m]</th>
<th>$\delta_{gb}$ [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 min</td>
<td>150</td>
<td>120</td>
<td>1.2·10^{-6}</td>
<td>4.8</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td></td>
<td>8·10^{-6}</td>
<td>3.1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
<td>5.2·10^{-5}</td>
<td>2.8</td>
</tr>
<tr>
<td>2 hrs</td>
<td>150</td>
<td>160</td>
<td>5.4·10^{-7}</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td></td>
<td>3·10^{-7}</td>
<td>0.37</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
<td>5.5·10^{-5}</td>
<td>0.47</td>
</tr>
<tr>
<td>50 hrs</td>
<td>150</td>
<td>240</td>
<td>3.2·10^{-8}</td>
<td>0.42</td>
</tr>
<tr>
<td></td>
<td>200</td>
<td></td>
<td>2.9·10^{-7}</td>
<td>0.31</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td></td>
<td>1.6·10^{-6}</td>
<td>0.24</td>
</tr>
</tbody>
</table>

Tab. 5.2 Calculated grain boundary thickness, $\delta_{gb}$, and specific grain boundary conductivity, $\sigma_{gb}^{sp}$, for 1 mol% CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ samples sintered at 900°C, for times ranging from 10 min to 50 hrs. The apparent grain sizes, $\langle D \rangle$, are taken from Chapter 4 (Table 4.2).

The highest specific grain boundary conductivity ($\sigma_{gb}^{sp}$) was found for the 10 min sintered sample, it decreases with longer sintering times. We want to point out that $\sigma_{gb}^{sp}$ changes more than one order of magnitude (e.g. 8·10^{-6} to 2.9·10^{-7} S/m at 200°C) with increasing annealing time whereas the apparent grain size, $\langle D \rangle$,
changes only by factor of 1.7. The grain-boundary width calculated for the 10 min sintered sample using the BLM gave an average value of 3.6 nm. This agrees well with microstructural data reported in Chapter 4 where TEM analysis revealed a 2-4 nm thick grain-boundary film being present in short time sintered CGO. The thickness of this grain-boundary film decreases for longer sintering times. The calculated grain-boundary thickness from the BLM was 0.56 nm after 2 hrs and of 0.32 nm after 50 hrs annealing. This also agrees well with our TEM results which show no indication of a cobalt rich grain-boundary phase after these long-time sintering conditions [Chapter 4].

Conductivity data of grain-boundaries as a function of grain-size for Ce_{0.8}Gd_{0.2}O_{1.9} have been reported by Christie et al. [27]. They found that $\sigma_{gb}$ for grain sizes exceeding about 1 μm correlates well with the BLM, i.e. little increase of $\sigma_{gb}$ with increasing grain size. For smaller grain sizes in the range of 0.4 to 0.8 μm they found an abnormally high conductivity which they did not attribute to the presence of a grain-boundary phase. A further explanation has not been given by them. Comparing our results with their data we note that $\sigma_{gb}$ of the 10 min sintered material differs only by a factor of 2-3 from their values. $\sigma_{gb}$ of 50 hrs sintered material agrees very well with the data of Christie, et al. on samples having several μm sized grains.

5.4 Summary and Conclusions

It was shown in Chapter 4 that doping of CGO with 1 mol% CoO gives rise to dense ceramic material with grain sizes in the 100 nm range with a several nm thick amorphous cobalt rich grain boundary film when interrupting sintering at 900°C after 10 min. At higher temperatures and/or with increasing annealing time we found that cobalt oxide dissolves in the ceria lattice and the amorphous film vanishes.

In the study presented here we analysed the electrochemical behavior of CGO doped with different concentrations of CoO and sintered under various conditions. We found that in thermally equilibrated material the electrochemical performance in terms of oxygen ion conductivity and electrolytic domain boundary remains unchanged compared to pure CGO.
4-point conductivity data and impedance spectra allowed to discriminate between different conductivity mechanisms in non equilibrated samples. Mainly electronic conductivity along a percolating cobalt rich grain-boundary layer was found in the short (10 min) sintered material in comparison with oxygen ion conductivity across grains and grain-boundaries in the long-time (50 hrs) sintered samples. In addition, we were able to calculate the cobalt rich grain boundary layer thickness to be 2-3 nm in 1 mol% CoO doped samples sintered at 900°C for 10 min with ceria grains of 120 nm in diameter, which is in good agreement with our previously reported TEM results. CoO doped CGO represents also a model system where limitations of the BLM can be demonstrated and analysed.

Due to the small ceria grain size of <120 nm in the sintered material we can expect high mechanically stable electrolytes for SOFC applications with improved mechanical properties. In addition, the low sintering temperature of 900-1000°C gives us the opportunity to co-sinter cathode, anode and electrolyte in a single step thereby reducing thermal stresses, chemical reactions of the components and fabrication costs.

CoO doped Ce$_{0.8}$Gd$_{0.2}$O$_{2-x}$ ceramics sintered at temperatures as low as 900-1000°C are promising candidates for electrolytes in SOFCs which can be operated at intermediate temperatures with high power output. By choosing the appropriate cobalt oxide concentration and sintering time/temperature we also expect to increase the electrode/electrolyte triple phase boundary length thereby lowering the electrode overpotential.

References

5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide


5.4 Summary and Conclusions


5 Mixed Electronic-Ionic Conductivity of Cobalt Doped Cerium Gadolinium Oxide


Outlook

General

Solid oxide fuel cells (SOFCs) offer an opportunity for a highly efficient and cleaner fossil energy conversion. At the present time the state-of-the-art SOFC system based on zirconia electrolytes have almost passed the system prototype demonstration state and are close to market entry. The materials in this system have mostly been optimized in terms of long-term stability and cost.

This thesis is focused on the next generation SOFCs that can be operated at temperatures as low as 600-700°C. At this low operation temperature we expect less degradation and lower cost for interconnector materials and insulation. Further work and good ideas are needed in the following areas.

Electrode supported thin-film electrolyte solid oxide fuel cells

Preparation of cathode substrates for electrolyte thin-film deposition by reactive magnetron sputtering (PVD) was one of the aims of this work. However, it turned out that the substrate quality in terms of microstructure, surface roughness and pore size is very critical. To achieve a thin and dense electrolyte layer by PVD, small pore sizes in the substrate resulting in low open porosity are required. We found that this mainly limits the cathode performance at high current densities and at low operation temperature. Other thin-film electrolyte deposition techniques such as electrophoretic deposition, transfer printing, and spray pyrolysis might be more tolerant to variations in substrate quality. Electrophoretic deposition and transfer printing require a high temperature sintering step (>1200°C) of the electrolyte layer and are therefore difficult to apply to cathode substrates. However, by spray pyrolysis dense and adherent electrolyte layers are already formed at substrate temperatures of about 300°C. Currently a new research program has been initiated in our laboratory dealing with the development and application of this technique to SOFCs.
Outlook

Activated sintering and mixed electronic-ionic conductivity of cerium oxide

As shown in the present work the sintering, microstructure and mixed electronic/ionic conductivity of cerium oxide solid solutions can be strongly influenced by transition metal doping. The effect of cobalt oxide has been investigated in detail. Further work should apply this concept of transition metal oxide doping to other nano-sized materials such as ZrO₂, Bi₂O₃, SnO, and ZnO. To produce these nano-grain sized powders, spray pyrolysis followed by precipitation of the transition metal oxides onto the particle surface should be investigated. The microstructural as well as the electrochemical properties can then be varied from nano-porosity to fully dense material and from electronic to pure ionic conductivity by proper selecting the sintering conditions and doping levels. This will lead to better material properties, improved stability, reduced cost, and possibly new opportunities for existing and newly developed ceramics. Based on the results of this work, a new research project has been initiated dealing with the electrical properties of nano-scaled mixed electronic-ionic conductors.
# Abbreviations

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BLM</td>
<td>Brick Layer Model</td>
</tr>
<tr>
<td>CBED</td>
<td>Convergent-Beam Electron Diffraction</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CGO</td>
<td>$\text{Ce}<em>{0.8}\text{Gd}</em>{0.2}\text{O}_{2-x}$</td>
</tr>
<tr>
<td>CYO</td>
<td>$\text{Ce}<em>{0.9}\text{Y}</em>{0.1}\text{O}_{2-x}$</td>
</tr>
<tr>
<td>DTA</td>
<td>Differential Thermo Analysis</td>
</tr>
<tr>
<td>EDX</td>
<td>Electron Diffraction Analysis</td>
</tr>
<tr>
<td>FRA</td>
<td>Frequency Response Analyser</td>
</tr>
<tr>
<td>HEXIS</td>
<td>Heat Exchanger Integrated Stack</td>
</tr>
<tr>
<td>HRTEM</td>
<td>High Resolution Transmission Electron Microscope</td>
</tr>
<tr>
<td>IT</td>
<td>Intermediate Temperature (600-700°C)</td>
</tr>
<tr>
<td>LSCF</td>
<td>$\text{La}<em>{0.8}\text{Sr}</em>{0.2}\text{Co}<em>{0.2}\text{Fe}</em>{0.8}\text{O}_{3}$</td>
</tr>
<tr>
<td>LSM</td>
<td>$\text{La}<em>{0.85}\text{Sr}</em>{0.15}\text{MnO}_{3}$</td>
</tr>
<tr>
<td>Ni-YSZ</td>
<td>Mixture of Nickel and YSZ</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>PEELS</td>
<td>Parallel Electron Energy Loss Spectroscopy</td>
</tr>
<tr>
<td>PEN</td>
<td>Positive Electrode, Electrolyte, Negative Electrode</td>
</tr>
<tr>
<td>PPI</td>
<td>Pores per Linear Inch</td>
</tr>
<tr>
<td>SAD</td>
<td>Selected Area Diffraction Analysis</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscope</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary Ion Mass Spectroscopy</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cell</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscope</td>
</tr>
<tr>
<td>TG</td>
<td>Thermo Gravimetry</td>
</tr>
<tr>
<td>TZP</td>
<td>Tetragonal Stabilized Zirconia</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
<tr>
<td>XRD</td>
<td>X-Ray Diffraction</td>
</tr>
<tr>
<td>YSZ</td>
<td>8 mol% Yttria stabilized ZrO$_2$</td>
</tr>
</tbody>
</table>
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Publications


Patent


Presentations and Posters


