Mixed ionic electronic conductors for solid oxide fuel cells

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Mixed Ionic Electronic Conductors for Solid Oxide Fuel Cells

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1. Mixed Conductors for Solid Oxide Fuel Cells

Summary

Current solid oxide fuel cells (SOFC) employ stabilized zirconia as electrolyte. However, due to its high resistivity to ionic current, fuel cells with this material have to be operated at temperatures of 900 °C and higher. Decreasing the operation temperature to 700 °C would reduce system cost and enhance the reliability. To achieve this, the ionic resistance of the fuel cell has to be lowered e.g. by application of an electrolyte material with a lower resistivity.

Ceria based ionic conductors are promising candidates for such alternative electrolytes. They exhibit an ionic conductivity which is 3 to 5 times higher than that of zirconia electrolytes. However, at low oxygen partial pressures, such as they prevail at the anode side of SOFC, ceria is slightly reduced and develops additional n-type electronic conductivity. Thus, under SOFC operating conditions it is a mixed ionic electronic conductor and was not considered as fuel cell electrolyte up to now.

The scope of the present study is to show the possibility to apply mixed ionic electronic conducting ceria based materials as electrolyte to SOFC and to investigate the physical and electrochemical properties of such systems. Electrical conductivity, oxygen nonstoichiometry and thermal expansion are investigated under varying oxygen chemical potentials. Electrochemical measurements of fuel cells with ceria based membranes as electrolyte and different cathode and anode materials are interpreted by a novel model for mixed ionic electronic conductors. It is thereby important to consider the cathode/electrolyte/anode compound as a materials system to model its electrical and electrochemical properties.

The model gives a consistent description with explicit expressions for the oxygen transport properties of SOFC.
systems with mixed ionic electronic conductors as electrolyte. Partial electronic and ionic currents within this SOFC system are described as a function of the operating conditions under consideration of the defect chemistry of the electrolyte and the electrochemical performance of the electrodes. This information provides the base for design and construction of fuel cells operating with mixed ionic electronic conducting electrolytes. For the electrochemical reactions the model employs a straightforward technical interpretation considering a basic concept of a superposition of diffusion and charge transfer overpotential.

Fuel cells with ceria based electrolytes exhibit a power output at 700 °C which is comparable to state of the art of zirconia based systems at 900 °C. However, due to its mixed ionic electronic conductivity the electrical conversion efficiency is slightly lower compared to pure ionic conductors. The lower operating temperature and the lower electrical conversion efficiency favor ceria based SOFC systems after all for small combined heat/power plants.

From a systems engineering point of view, mixed conductors are more difficult to handle. They exhibit a small operating range between a maximum in efficiency at relatively high current densities and the maximum power output. Additionally, the thermal expansion coefficient of ceria based materials is dependent on oxygen partial pressure. Ceria based materials are therefore preferably used at temperatures below 800 °C.

Zusammenfassung

In heutigen Festelektrolyt-Brennstoffzellen findet stabilisiertes Zirkonoxid als Elektrolyt Verwendung. Wegen des hohen ionischen Widerstands dieses Materials müssen sie allerdings bei Temperaturen von über 900 °C betrieben werden, was ihre Lebensdauer beeinträchtigt und die Systemkosten erhöht. Diese Nachteile könnten durch eine
Senkung der Betriebstemperatur behoben werden. Dafür muss allerdings der Widerstand der Zellen gesenkt werden, was durch die Verwendung von alternativen Elektrolytmaterialien mit größerer Leitfähigkeit erreicht werden kann.


Ladungstransfer- und einer Diffusions-überspannung behandelt werden.


2. Introduction to Mixed Ionic Electronic Conductors in Solid Oxide Fuel Cells

1. Solid oxide fuel cells

Fuel cells are energy conversion devices which convert chemical energy directly to electrical energy and heat by electrochemical combination of a fuel with an oxidant. Fuel cells offer substantially higher conversion efficiencies and lower emission of pollutants \(^1\), \(^2\) than other energy conversion systems. There exist a number fuel cell types which differ in electrode and electrolyte materials used, in the requirements on fuel and oxidant purity, and in operating temperature \(^2\).

Solid oxide fuel cells (SOFC) have several advantages over other fuel cell types. Due to their operation temperature of more than 900 °C they are flexible in the use of fuel and offer the possibility of cogeneration of electrical power and heat. The high operating temperature enables to operate the fuel cell without precious electrocatalysts at the electrodes. The use of solid oxygen conductors as electrolyte eliminates corrosion and electrolyte management problems as they are present in other fuel cell types \(^1\).

Solid oxide fuel cells consist of two electrodes and an electrolyte. To the anode fuel is (e.g. hydrogen or hydrocarbons) supplied continuously. Oxidant (air or pure oxygen) is fed to the cathode. The electrolyte of SOFC is an oxygen ion (\(O^\text{-}\)) conductor. The working principle of this type of fuel cell is described as follows:

Oxygen is fed to the cathode where it adsorbs and is reduced according to

\[ O_2 + 4e \rightarrow 2O^\text{-} \quad (2-1) \]

These oxygen ions enter the electrolyte and react at the anode with the fuel gas, e.g. hydrogen:

\[ 2H_2 + 2O^\text{-} \rightarrow 2H_2O + 4e \quad (2-2) \]

The overall fuel cell reaction is given as
The overall fuel cell reaction can therefore be regarded as a spatially separated combustion reaction of hydrogen with oxygen, where the electrons which are transferred in the reaction are used as electrical energy in an external circuit. The driving force for the oxygen ions is the chemical potential difference between anode (low oxygen chemical potential) and cathode (high oxygen chemical potential). These electrode/electrolyte compounds are assembled to fuel cell stacks, i.e. they are connected in series with an interconnector between the single cells. This interconnector separates the gas room of fuel and oxidant and must be electrically conducting. It is important to treat this interconnector - single cell compound as one functional materials system, since all materials have to be chemically and mechanically compatible and the weakest link of the chain determines the performance of the whole system. Traditionally, this systems engineering point of view has not always been considered with the result, that until today no really competitive SOFC system is available.

State of the art SOFC are based on the standard materials yttria stabilized zirconia for the electrolyte, $\text{La}_{(1-x)}\text{Sr}_x\text{MnO}_3$ for the cathode, La-chromite for the interconnect and Ni-ermets for the anode \cite{3, 4}. These fuel cells operate at temperatures from 900 - 1000 °C, due to the thermally activated ionic conductivity of zirconia and the thermally activated electrochemical reactions at the electrodes.

For smaller combined heat power systems lower operation temperatures are of advantage as some cell components could be fabricated from less expensive materials (e.g. metallic interconnects). For this purpose, the operation temperature has to be lowered to temperatures of 700 - 800 °C \cite{5}. In the following sections an overview over electrolyte, cathode, anode and interconnector materials is given, and
the requirements to the single materials to act as one materials system are formulated.

2. Solid electrolytes

The electrolyte for SOFC is an oxygen ionic conductor. Basically, its thickness and ionic conductivity are a necessary but not sufficient criterion to define the operating temperature of the fuel cell. The electrolyte has to be stable under the oxidizing atmosphere prevailing at the cathode and under the reducing atmosphere at the anode. High oxygen ionic conductivity has been found in oxides which possess an open crystal structure, such as fluorites and related structures and perovskites [6, 7].

Most of the good ionic conductors exhibit fluorite related structures. This structure is relatively open and has an exceptional tolerance for high levels of atomic disorder introduced either by doping, or nonstoichiometry due to oxidation or reduction [7 - 9]. By doping with divalent or trivalent oxides oxygen vacancies are created which give rise to oxygen ionic conductivity. As the atomic disorder, however, extents on the anion lattice only, the mobility of the cations in the fluorite structure is orders of magnitude lower. Examples of oxides with the fluorite structure and high ionic conductivity are doped CeO$_2$ [10-11], doped ZrO$_2$ [7, 13] or PuO$_2$ [14]. Additionally, the $\delta$-Bi$_2$O$_3$ phase possesses an anion deficient fluorite structure for which the highest oxygen ionic conductivities have been reported so far [6].

In perovskite related structures comparable ionic conductivities have been reported only recently for doped LaGaO$_3$ [15]. High ionic conductivities have also been found for the perovskite related brownmillerite structure in which high oxygen ionic conductivity is introduced by an order-disorder transition, an example for this is doped Ba$_2$In$_2$O$_5$ [14].
Most of these compounds have been found to be unstable under the reducing atmosphere prevailing at the anode side of SOFC, e.g. Bi$_2$O$_3$ is reduced completely and forms a metallic melt when exposed to hydrogen at high temperatures. Also PuO$_2$ is disqualified for obvious reasons. The only compounds with sufficient stability under oxidizing as well as reducing conditions are doped ZrO$_2$ and doped CeO$_2$. Also doped LaGaO$_3$ seems to be stable, however, only very little is known up to now about this new compound.

Compositions with scandia or yttria exhibit the best ionic conductivities among the zirconia systems [13, 17, 18]. For its high price scandia is also disqualified and most SOFC systems rely on zirconia doped with 8 to 10 mole% of Y$_2$O$_3$. This fact is interesting if one considers the ionic conductivity of doped ceria for comparison. Ceria doped with 20 mol% of GdO$_{1.5}$ or SmO$_{1.5}$ is reported to have an oxygen ionic conductivity which is 3 to 5 times higher than the conductivity of yttria doped zirconia and has been suggested as an alternative to the latter [10, 19 - 20][21]

3. Mixed ionic electronic conductors

Under reducing conditions, as on the anode side of solid oxide fuel cells, ceria is partially reduced giving rise to mixed ionic electronic conductivity [9, 10]. This leads to a considerable ionic conductivity of the electrolyte material under fuel cell operating conditions. It is a common belief that electrolytes for SOFC have to be pure ionic conductors with an electronic conductivity level which has to be below 1% of the total electrical conductivity. Therefore, ceria has normally not been considered as SOFC electrolyte.

Despite this belief, ceria is an interesting candidate to replace zirconia in attempting to reduce the operating temperature of SOFCs due to its high ionic conductivity. The main emphasis of this dissertation is to identify the
advantages and limitations of the use of ceria which is a mixed ionic electronic conductor as electrolyte in a SOFC system.

The idea of applying mixed conductors to electrochemical systems is of course not new. Relying on Wagner's theory for mixed ionic electronic conductors \([23, 24]\), the possibility to use mixed ionic electronic conductors as SOFC electrolytes was pointed out by several authors \([25-26, 27, 28]\). However, these considerations were of pure theoretical nature, assuming an ideal system with no electrolyte/electrode interactions. Despite the high operation temperature of solid oxide fuel cells, their electrodes are not reversible, i.e. massive changes in oxygen chemical potential occur at the electrodes. This change in oxygen chemical potential affects the conductivity of mixed ionic conductors (MIEC) and influences the \(I-V\) relations and the efficiency of the system.

It is the aim of this thesis to quantify the changes in oxygen chemical potential at the electrode/MIEC interfaces and to determine the resulting partial ionic and electronic currents within the electrochemical system. From these considerations optimum system design and operating conditions are derived to yield a high electrochemical conversion efficiency and a high electrical power output. These electrochemical and system engineering considerations are presented in chapters 8 to 11.

4. Cathode

The electrochemical performance of SOFCs is controlled to a great extent by electrode processes. It is therefore important for the cathode to find materials with a high electrochemical activity for the oxygen reduction reaction. To prevent limitations due to supply of oxygen to the electrolyte, it is necessary to tailor the microstructure
of the electrodes in terms of thickness and porosity with respect to their electrical and electrochemical properties. State of the art zirconia based SOFC systems employ La_{1-x}Sr_xMnO_3 (LSM) as cathode material [3, 4]. This material is an electronic conductor and is chemically compatible with zirconia electrolytes. It has a high activity for the dissociative adsorption of oxygen on the surface, however it possesses only very limited oxygen ionic conductivity [29]. For this reason, the transfer of oxygen from the electrode into the electrolyte is restricted to the contact area of the gas phase with the electrolyte and the cathode, the so called triple phase boundary. There exist also potential cathode materials with mixed ionic electronic conductivity allowing the oxygen ions to pass across the whole electrode/electrolyte cross section. An example for such a material is La_{1-x}Sr_xCoO_3 (LSC) and related perovskite structures doped with Fe or Ni [30 - 32]. However, these materials react with zirconia based electrolytes and form insulating phases at the cathode/electrolyte interface [33].

Ceria based electrolytes on the other hand, are chemically compatible with LSC. This allows the construction of a mixed ionic electronic conducting cathode/electrolyte compound with a gradually changing ratio of ionic to electronic conductivity. The effect of the electrical transport properties of the cathode on cell performance is discussed for several cathode materials in chapter 9.

5. Anode

SOFC anodes should exhibit a good electrical conductivity and a high activity for the oxidation of the fuel gas. For state of the art SOFC systems a Ni-cermet, i.e. a mixture of metallic nickel and a ceramic component are used. The ceramic component normally is yttria-doped zirconia [2, 3]. The ceramic compound is added to the cermet to adjust the thermal expansion coefficient of the anode to the electrolyte and to prevent the nickel particles in the
porous structure from coalescence. Since nickel is a metallic conductor and zirconia is an oxygen ionic conductor, this anode can also be regarded as a mixed ionic electronic conductor. An obvious alternative to Ni-cermet anodes based on zirconia are Ni-ceria cermet anodes in case ceria is used as electrolyte. The use of Ni-ceria cermet, LSC as cathode and ceria as electrolyte allows now to construct an electrode/electrolyte systems consisting only of mixed conductors.

6. Interconnector

For the interconnector basically the same properties are required as for the electrolyte. Except, its conductivity should be of pure electronic nature. Today's SOFC employ either ceramic interconnectors such as La_{(1-x)}Sr_xCrO_3 or Cr-based oxide dispersion strengthened alloys [2, 3, 4]. These materials are extremely costly for machining and for their high chromium content. An inexpensive alternative to these materials would be the use of conventional ferritic chromium steels. These steels can withstand SOFC conditions only up to temperatures of about 750 °C, therefore, a basic need for fuel cells operating only up to this temperature is obvious.

Most electrochemical measurements of the present study were carried out on single cells avoiding the use of an interconnector. However, the properties of ferritic steels as interconnector were taken as boundary conditions for the development of a fuel cell system operating in the intermediate temperature range (600 to 800 °C).

7. Compatibility of the materials system

In today's SOFCs the electrolyte is the supporting and load bearing structural element in the single cell with a thickness of 150 to 250 µm. It supports the thin (10 to
Introduction

30 µm) electrodes. The interconnector used for stacking the single cells is also a thick, stiff structure with a thickness of about 2 to 5 mm. The compatibility requirements for the materials system can be summarized as follows:

- The thermal expansions of the single components of the cell have to match. This is after all important for the thermal expansion of the load bearing structural elements. Except the thermal expansion of the porous thin electrodes might be somewhat different from the electrolyte without causing problems.
- Chemical compatibility is necessary. No intermediate phases should be formed at the interfaces during manufacturing and operation.
- The electrode performance should allow intermediate temperature operation.
- High ionic conductivity of the electrolyte is necessary. The electrode performance alone is not sufficient for good performance of the whole system.

8. System efficiency and fuel cell design

In fuel cells with mixed conducting electrolytes a part of the ionic current through the electrolyte is compensated by an internal electronic short circuit current. For this reason not the entire chemical energy fed to the system as fuel is converted to useful electrical energy, in addition to the already existing losses by electrical resistance of electrolyte and electrodes. Under open circuit conditions, i.e. zero external load current, ionic and electronic current through the electrolyte are equal. The ratio of ionic to electronic current through the electrolyte, however, increases with decreasing cell voltage. This leads at fairly high ionic current densities to a maximum in conversion efficiency. Fuel cell systems with mixed conducting electrolytes have therefore to be operated under
somewhat different conditions compared to solid oxide fuel cells with pure ionic conductors.
The amount of ionic and electronic currents depends on the gradient of the electrochemical potential across the electrolyte. For very thin electrolytes it is obvious, that these partial currents increase. This leads to additional losses due to higher electrode polarization and to a lower fuel cell conversion energy. In chapter 11 the effects of mixed ionic electronic conductivity on the efficiency and its influence on fuel cell operation and design are discussed.

9. Terminology

In electrochemistry several terms are defined for materials with special properties and well defined abbreviations are used in general. However, most of the present work deals with materials which are difficult to describe in traditional electrochemical terms. To prevent confusion, some of the terms used throughout this work will now be defined.

Traditionally the term "electrolyte" is used for a material or a solution with mobile ions which exhibits only ionic conductivity or at least an ionic conductivity which is orders of magnitude higher than its electronic conductivity. In this work the term "electrolyte" is also used for mixed ionic electronic conductors (MIECs), if it describes the structural element of a SOFC.

The "electromotive force" of an electrochemical system is normally defined as the electrical voltage measured between cathode and anode of an electrochemical system. If the electrolyte is a pure ionic conductor this voltage \( E \) corresponds to the difference in chemical potential between cathode and anode and is given by the Nernst equation

\[
E = -\frac{\Delta G}{zF}
\]  
\( (2-4) \)
where $\Delta G$ is the difference in chemical potential, $z$ is the amount of electrons transferred per formula unit and $F$ is the Faraday constant. For a MIEC as "electrolyte" this voltage is lowered by the internal electronic short circuit within the MIEC. To avoid confusion the voltage on the MIEC is defined further as $V(MC)$ and the (hypothetical) voltage given by the (applied) chemical potential difference between cathode and anode is defined as $V_{th,app}$.

An additional problem arises when measuring the electrode overpotential of electrodes on MIECs directly. As will be described in chapter 8, the measured overpotential is lower than the effective one. Traditionally the measured electrode overpotential is abbreviated as $\eta$ or $\pi$. In the further descriptions $\eta$ is used for the measured overpotential, the real effective overpotential is however different from the measured one and is abbreviated as $\delta V_{th}$, i.e. as the deviation from the voltage $V_{th,app}$ given by the applied chemical potential.

10. Structure of the thesis

This dissertation deals with mixed ionic electronic conductors in SOFC systems. The main emphasis is put on the understanding and description of the nature of the electrode/electrolyte system in terms of electrochemical behavior using MIECs.

Processing and physical properties of these materials are discussed in chapters 4 to 7.

The electrochemical properties of fuel cells with MIECs are discussed in chapters 8 to 10.

In chapter 11 principles for fuel cell design and system engineering are derived.

All chapters of this thesis are stand alone pieces of information. For each chapter the necessary experimental and theoretical background as well as the literature is included separately as some chapters are already submitted
for publications. Due to this structure of the work repetitions and redundancy can not be avoided.

1. References

3. Aim of the Study

The aim of this dissertation is to demonstrate the feasibility of mixed ionic electronic conductors (MIECs) with a high ionic and a moderate electronic conductivity as electrolytes for solid oxide fuel cells operating at intermediate temperatures.

As model substance for such a material ceria solid solutions are selected. The electrical and electrochemical properties of solid oxide fuel cells (SOFCs) with ceria based electrolytes should be characterized. For this characterization the physical properties of the electrolyte and the electrochemical behavior of the electrode/electrolyte system should be established by appropriate means.

To describe the cell current-voltage characteristics and electrode overpotentials a model should be proposed which correlates electrochemistry and defect chemistry under all operating conditions considering non-reversible electrodes. With this model it should be possible to determine the partial electronic and ionic currents in order to find the electrode overpotential - ionic current relations for cathode and anode. Guidelines for design of the subsystem cathode/electrolyte/anodes should be established and the optimum operating conditions are expected to be derived by this model.
4. Processing of Ceria Powders and Membranes

Abstract

Ceria solid solutions with 20% Sm$^{3+}$ and 10% Ca$^{2+}$ were prepared by wet chemical coprecipitation of the corresponding nitrates or chlorides with ammonium hydroxide and ammonium oxalate. After calcination in air the solid solutions exhibited the cubic fluorite structure which was verified by X-ray diffraction analysis. Precipitation with ammonium hydroxide resulted in agglomerated powders which were not sinterable, whereas precipitation with ammonium oxalate produced homogeneous powders with good sinterability. From these powders ceramic membranes with a thickness of 220±40 µm were prepared by tapecasting and sintering in air at 1600 to 1700 °C. The density of sintered ceria membranes was larger than 95% of the theoretical density (TD).

1. Introduction

Ceria solid solutions with Sm, Gd, Y and Ca belong to the best solid conductors for oxygen ions. They are relatively stable under oxidizing as well as under reducing atmospheres and are therefore considered as electrolytes for solid oxide fuel cells (SOFC) \cite{1-23}. Ceria solid solutions can be prepared by mixing the powders of the corresponding oxides in a ball mill, pressing, and calcining at temperatures between 1700 and 1800 °C. This procedure yields a powder with low sinterability and usually results in sintered compacts with densities around 90% of TD \cite{4, 5}. This density is too low for SOFC electrolyte applications, since the electrical conductivity is low and gas tightness can usually not be guaranteed for samples with less than 95% of TD. Moreover, the mechanical stability is reduced in porous materials.
An alternative approach described in the present chapter is the one of chemically coprecipitated powders of ceria solid solutions starting with ceria and rare earth salts by adding e.g. ammonium hydroxide or ammonium oxalate. This procedure results in homogeneous fine powders. After calcination at temperatures between 400 and 800 °C for 2 h these powders decompose into high purity CeO₂ - solid solutions with a high surface area and good sinterability. The preparation of powders and their characterization by surface area analysis (BET), X-ray diffraction and particle size distribution is subject of section 2.

Most solid oxide fuel cell designs rely on the planar concept with the electrolyte as load bearing element in the cathode/electrolyte/anode compound [6, 7]. The most efficient method for the preparation for these relatively thick (~200 µm) membranes is tape-casting [8, 9]. This process starts with a slurry of inorganic ceramic materials dispersed in a liquid containing dissolved organic binders and plasticizing modifiers and dispersants. The slip is spread on a surface by means of a doctor blade and the solvent is allowed to evaporate. After drying the tape is removed from the surface and is sintered. This tape-casting process is well established and used in the microelectronics industry, however, a crucial point for the application of this process using a new powder is the composition of the organic slurry. After all the choice of dispersants - "wetting agents" for the dispersion of ceramic powders in a liquid - is important to achieve a slurry with a low viscosity and a high solids loading. In section 3 the tapecasting process for ceria solid solutions is illustrated and recipes for the preparation of ceramic tapes with a green thickness of 300 to 400 µm are given.

In section 4 the sintering of ceria-based membranes is described. For the sintering of ceramic tapes commonly alumina substrates are employed. Ceria solid solutions, however, tend to react with alumina at temperatures above 1450 °C to form cerium aluminate [10]. Therefore, magnesia or zirconia substrates were employed for the sintering of
ceria membranes in this work. Ceria tapes with a density of >95% TD were obtained from sintering at temperatures above 1600 °C.

The intention of this chapter is to describe the processing route from the nitrate precursors over the ceramic powder to the sintered ceramic membrane. It is thought as a collection of recipes for powder preparation and tapecasting.

2. Powder preparation

2.1 Hydroxide coprecipitation

Ceria solid solutions with 20% Sm³⁺ were prepared by coprecipitation with ammonium hydroxide. A solution of Ce(III)(NO₃)₃·6H₂O (>99%, Fluka, Buchs, CH) and Sm₂O₃ (>99%, Rhône-Poulenc, La Rochelle, F) dissolved in HCl was added dropwise to a ammonium hydroxide solution at 25 °C. The concentration of the of the ammonium hydroxide solution was 1 M and the solution of cerium nitrate and SmCl₃ was 1 M in Ce³⁺ and 0.25 M in Sm³⁺. After precipitation the solution was stirred for 15 min and subsequently filtered through filter-paper (5893 Schleicher & Schüll, Feldbach, CH). The filtrate was washed 3 times with distilled water. For coprecipitation and washing the pH of the solution was controlled and adjusted to a pH-value of 8.

The precipitate had a pink color which turned brownish when exposed to air. This change in color is attributed to an oxidation from Ce³⁺ to Ce⁴⁺ [1]. The gel-like precipitate was difficult to filter due to its high viscosity. After filtration the filtrate was dried overnight at 200 °C and calcined at temperatures of 500 to 1200 °C.

The calcined powders were die-pressed into pellets with a diameter of 30 mm and 10 mm in height at an axial pressure of 200 MPa. The pellets were sintered at 1600 °C/2 hrs with a heating rate of 2 °C/min. It was impossible to obtain dense crack-free pellets from this powders when sintered in
air. Only sintering in argon (99.95% pure) resulted in crack-free samples. After cooling to ambient temperature these samples were dark blue and had a density of <80% of TD.

The poor sinterability was attributed to strong agglomeration of the very reactive ceric oxide hydrate [9] which is formed by precipitation with ammonium hydroxide.

2.2 Ammonium oxalate coprecipitation

Upon thermolysis oxalates $\text{Me}^{n+}(\text{C}_2\text{O}_4)^{n/2}$ decompose into $\text{MeO}_{n/2}$ and $2\text{CO}_2$. Thereby a large quantity of carbon dioxide is liberated, preventing the particles from agglomerating. It is expected that those powders will sinter to dense materials.

The starting materials used were $\text{Ce}^{\text{III}}(\text{NO}_3)_3\cdot6\text{H}_2\text{O}$ (>99%, Fluka, Buchs, CH), $\text{Sm}_2\text{O}_3$ (>99%, Rhône-Poulenc, La Rochelle, F) dissolved in $\text{HCl}$, and $\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O}$ (>99%, Merck, Darmstadt, FRG). Ammonium oxalate $(\text{NH}_4)_2(\text{C}_2\text{O}_4)$ (>98% Fluka, Buchs, CH) was used for precipitation of the metal cations. Ammonium oxalate was dissolved in 3 l of distilled water to obtain a solution with a concentration of 0.52 M. Due to the low solubility of ammonium oxalate at room temperature this solution was heated to 43 °C. The pH of the solution was adjusted to 7.5 by addition of small amounts of NH$_3$.

The nitrate precursor solution was prepared by dissolving 0.6 mol of $\text{Ce}^{\text{III}}(\text{NO}_3)_3\cdot6\text{H}_2\text{O}$ plus 0.067 mol of $\text{Ca(NO}_3)_2\cdot4\text{H}_2\text{O}$ in 0.6 l of distilled water. Samarium chloride was used instead of calcium nitrate for the preparation of Sm-doped ceria. The salt solution was added dropwise (2 - 3 drops/s) to the ammonium oxalate solution while the precipitation bath was heavily stirred. Immediately a white precipitate was formed upon dropping into the ammonium oxalate solution. Subsequently, the suspension was stirred for another 15 min to assure complete precipitation and was then cooled down to room temperature. The precipitate was filtered with filter paper (589)
Feldbach, CH) and washed twice with distilled water at a pH = 7.5.
The oxalate powders were dried evaporating H$_2$O at a pressure of 10$^4$ Pa and a temperature of 80 °C (Rotavap RE 111, Büchi, Flawil, CH). After drying the powders were calcined at temperatures of 400 to 1200 °C in air for 2 h to form the mixed oxides from the oxalate precipitates. During calcination traces of cyanides were formed due to reaction of oxalate and traces of NH$_3$.
The precipitation conditions for hydroxide and oxalate coprecipitation are listed in Tab. 4-1.

| Precursor | 90% CeO$_2$ | 80% CeO$_2$ | 80% CeO$_2$
|-----------|-------------|-------------|-------------
|           | 10% CaO | 20% SmO$_{1.5}$ | 20% SmO$_{1.5}$ |
| Volume    | 600 ml | 600 ml | 600 ml |
| Ce(NO$_3$)$_3$·6H$_2$O | 1 M | 1 M | 1 M |
| Ca(NO$_3$)$_2$·4H$_2$O | 0.11 M | | |
| SmCl$_3$ | 0.25 M | 0.25 M |
| Temperature | 24 °C | 23 °C | 23 °C |
| pH        | 2.8   | -   | -   |
| Precipitation bath | | | |
| Volume    | 3000 ml | 3000 ml | 3000 ml |
| (NH$_4$)$_2$C$_2$O$_4$·H$_2$O | 0.47 M | 0.52 M |
| NH$_4$OH | | 1 M |
| Temperature | 45 °C | 43 °C | 25 °C |
| pH        | 7.7   | 8   | 9   |

**Tab. 4-1** Precipitation parameters for Sm and Ca doped ceria.

Ceramic powders with small crystallite sizes (~20 - 30 nm) and high surface area exhibit the highest sintering activity. For ceramic forming on the other hand large amounts of organic additives are needed to handle very fine powders. Therefore, a compromise between sintering activity and the amount of organic additives is aimed for. For tapecasting of ceramic powders with organic slurries a
surface area of the ceramic powders of ~10 m²/g was found to be desirable. The dependence of the specific surface area of calcined powders on the calcination temperature was followed by BET surface analysis (Area-Meter II, Ströhlein, Leonberg, FRG) for 20% samaria doped ceria (CSO), 10% calcia doped ceria (CCO) and a commercial 20% gadolinia doped ceria powder (CGO, Rhône-Poulenc, La Rochelle, F). The BET-surface area of CCO depending on the calcination temperature is presented in Fig. 4-1.

![Fig. 4-1 Bet surface area $S_{\text{BET}}$ versus calcination temperature (left scale) and corresponding crystallite size d assuming spherical particles (right scale) for CCO.](image)

Upon calcination at 400 °C the specific surface area of the samples increases from 1.77 m²/g (specific surface of the oxalate) to 82.8 m²/g. It decreases continuously to 0.74 m²/g at a calcination temperature of 1200 °C. After calcination at 750 °C the powder exhibits a specific surface area of 10.50 m²/g with a corresponding crystallite diameter of 85.2 nm. The decomposition of the oxalate was monitored by differential thermal analysis (DTA) in air (STA 501, Bähr, Hüllhorst, FRG) at a heating rate of 5 °C/min. In Fig. 4-2 the DTA signal versus temperature is shown for CCO. In the temperature range between 100 and
200°C the adsorbed water is removed (endothermic process) and the oxalate is completely decomposed to the corresponding mixed oxide (exothermic process) between 300 and 350 °C.

The specific surface area of CSO prepared by coprecipitation of samarium chloride and cerium nitrate is presented in Fig. 4-3. The CSO powder shows a similar dependence of the surface area and crystallite size on calcination temperature as observed for CCO (Fig. 4-1). For hydroxide precipitated CSO the surface area decreases only slowly to 40 m²/g by calcination at 1000 °C, followed by a rapid decrease in specific surface at higher calcination temperatures. After calcination the powders were white to yellowish (CSO) or had a slightly brownish color (CCO).

Fig. 4-2  Differential thermal analysis of the decomposition of CCO. The removal of adsorbed water is observed in the temperature range of 100 to 200 °C. Between 300 and 350 °C the oxalate is decomposed to the oxide solid solution.
As verified by X-ray diffraction measurements all powders exhibited the cubic fluorite structure. The cubic lattice constants of the different ceramic powders were measured with an X-ray diffractometer (D5000, Siemens, FRG) with CuK$_\alpha$ radiation using a step width of 0.003° and a measuring time of 5 s per step between 2θ = 25 to 60°. Silver was used as an internal standard for calibration. As an example the XRD spectrum of CGO is given in Fig. 4-4. The composition of the samples was measured with microprobe analysis or EDX. Cubic lattice constants and sample composition with respect to Ce and Sm, Ca or Gd are summarized in Tab. 4-2.
Fig. 4-4 XRD spectrum of CGO at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Compositio[n [atom %]</th>
<th>Cubic lattice constant [Å]</th>
<th>Ionic radius [Å] of dopant [12]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.8}$Sm$</em>{0.2}$O$_{1.9}$</td>
<td>18.82$^X$</td>
<td>5.4341±0.0008</td>
<td>1.079</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9}$</td>
<td>19.96$^X$</td>
<td>5.4312±0.0034</td>
<td>1.053</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Ca$</em>{0.1}$O$_{1.9}$</td>
<td>10.02$^E$</td>
<td>5.4177±0.0014</td>
<td>1.12</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

$^X$ by microprobe (Sulzer Innotec, Winterthur, CH), $^E$ by EDX (Tracor Northern Z-max 30)

Tab. 4-2 Composition and cubic lattice constant of sintered ceria-based membranes. The ionic radius of the host cation Ce$^{4+}$ is 0.97 Å [12].

3. Tapecasting
3.1 Slurry preparation

A specific powder surface area of ~10 m²/g was regarded as a good compromise between sinterability and amount of organic additives needed for the slurry. Therefore, the precipitated powders were calcined at 750 °C for 2 h. The particle size distributions of the powders were measured by sedigraphy (Sedigraph, Micromeritics®, Norcross GE, USA). The results are shown in Fig. 4-5.

The specific surfaces of the powders are listed in Tab. 4-3.

<table>
<thead>
<tr>
<th>Material</th>
<th>$S_{BET}$ [m²/g]</th>
<th>$d_{50}$ [µm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSO</td>
<td>11.94</td>
<td>1.2</td>
</tr>
<tr>
<td>CGO</td>
<td>8.10</td>
<td>1.1</td>
</tr>
<tr>
<td>CCO</td>
<td>10.50</td>
<td>2.5</td>
</tr>
</tbody>
</table>

Tab. 4-3 Specific surface area $S_{BET}$ from BET and mean particle size $d_{50}$ from Sedigraph.

For a similar specific surface area CCO shows a slightly higher $d_{50}$ compared to CSO and CGO. A possible explanation of this finding is the formation of larger agglomerates in the CCO powder compared to CSO. The commercial CGO powder contained the largest fraction of sub-micron particles.
Tapecasting slurries normally consist of a liquid, several plasticisers, a dispersant and a polymeric binder. In the present study ethanol was used as solvent. As plasticisers polyethylene glycol (PEG 400, Fluka AG, Buchs, CH) and dioctyl phthalate (C\textsubscript{24}H\textsubscript{38}O\textsubscript{4}, >97%, Fluka) were used. As binder in most commercial tapes PVB is employed \cite{13}, in the present study PVB (B 20H, Hoechst, Frankfurt, FRG) was used.

The proper choice of dispersants turned out to be the crucial point for the preparation of tapecasting slurries. Two different organic additives were used as dispersants, glycerol trioleate (\((\text{C}_{17}\text{H}_{33}\text{COOCH}_2)\text{CHOCO(CH}_2)\text{}_5, >99\%, \text{Fluka}\)) and triethanol amine (\((\text{HOCH}_2\text{CH}_2)\text{}_3\text{N}, >99\%, \text{Fluka}\)). Whereas both dispersants worked satisfactorily with the ceramic powders prepared in our laboratory (CSO and CCO), the dispersants were not optimal for the commercial powder (CGO). Tapes prepared from this powder always were brittle and cracked during drying into pieces of approx. 5 x 5 cm. This brittleness could also be traceable to the high sub-

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{fig4-5.png}
\caption{Particle size distribution of the powders used for tape-casting.}
\end{figure}
micron particle content of this powder consuming a large amount of the dispersants and binders. The composition of the tapecasting slurry was related to the surface area of the ceramic powder ($S_{\text{BET}} \times \text{weight of powder}$). It is given in Tab. 4-4.

<table>
<thead>
<tr>
<th>Additives</th>
<th>Additives per surface area of the ceramic powder [$10^{-3}$ g/m$^2$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Glycerol triooleate or triethanol amine</td>
<td>1.44</td>
</tr>
<tr>
<td>PEG 400</td>
<td>4.9</td>
</tr>
<tr>
<td>Dioctyl phthalate</td>
<td>4.23</td>
</tr>
<tr>
<td>PVB</td>
<td>6.83</td>
</tr>
<tr>
<td>Ethanol</td>
<td>28 - 42</td>
</tr>
</tbody>
</table>

**Tab. 4-4** Organic additives for the tapecasting slurry per surface area of the ceramic powder.

For the slurry 100 g ceramic powder were added into a mixture of ethanol and the dispersant. If the viscosity of this slurry was too high, i.e. homogeneous mixing could not be obtained, small amounts of ethanol were added until the slurry had a creamy consistence. The slurry was transferred into a zirconia beaker of 300 ml internal volume and 10 zirconia balls (15 mm in diam.) were added. The beaker was closed with a zirconia lid and placed in a planetary mill (Retsch, Haan, FRG). The slurry was homogenized during 4 h at 200 rpm. Subsequently the plasticisers and the binder were added to the slurry and the mixture was homogenized for additional 2 h. The treatment in the planetary mill led to a heating of the slurry to approx. 35 °C. The slurry was cooled to room temperature and degassed at $10^4$ Pa for 15 min to remove small gas bubbles. The optimal viscosity
of the slurry for tapecasting was found to be between 3.5 and 4 poise.

3.2 Tape-casting

A tape-casting equipment of EPH Associates Inc. (Orem, Utah, USA) was used for casting. The slurry was poured on a dry float glass plate and spread with a doctor blade with an opening of 350 to 700 µm between blade and glass plate at a speed of 30 cm/min. The slurry was dried at ambient temperature for 2 h and the resulting green tape was removed from the glass plate. The consistency of the tape was leathery in case of CCO and CSO but very brittle in case of CGO powders. The upper surface of the tape was smooth (CCO and CSO) whereas in case of CGO the tape exhibited microcracks parallel and perpendicular to the pulling direction. The bottom surface of the tape was very smooth and reflecting mirror-like.

After drying the tapes had a green density of 30 to 40% in relation to the ceramic powder (i.e. percent of TD of the ceramic) and a thickness of 300 to 500 µm. The green densities of the tapes determined after burnout of the binder at 600 °C for 2 h are summarized in Tab. 4-5 together with the green densities, blade openings and the thicknesses of the sintered tape.

<table>
<thead>
<tr>
<th>Sample</th>
<th>green density [% of TD]</th>
<th>blade opening [µm]</th>
<th>thickness after drying [µm]</th>
<th>thickness after sintering [µm]</th>
<th>lateral shrinkage [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>CCO</td>
<td>29</td>
<td>700</td>
<td>365</td>
<td>260</td>
<td>25</td>
</tr>
<tr>
<td>CSO 1</td>
<td>30</td>
<td>700</td>
<td>345</td>
<td>239</td>
<td>25</td>
</tr>
<tr>
<td>CSO 2</td>
<td>38</td>
<td>500</td>
<td>320</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CSO 3</td>
<td>37</td>
<td>700</td>
<td>295</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CGO 1</td>
<td>39</td>
<td>600</td>
<td>300</td>
<td>220</td>
<td>25</td>
</tr>
<tr>
<td>CGO 2</td>
<td>26</td>
<td>700</td>
<td>365</td>
<td>240</td>
<td>28</td>
</tr>
</tbody>
</table>
Although it seems to be favorable to have a high green density in the dried tape to minimize shrinkage, it turned out that tapes with green densities between 26 and 39% exhibited almost the same lateral shrinkage. Moreover, tapes with a higher green density were brittle and therefore difficult to handle.

4. Sintering of Tapes

4.1 Substrates

Ceria needs sintering temperatures higher than 1500 °C. The most commonly used substrate for sintering is alumina. Ceria, however, is known to react with alumina to form CeAlO$_3$ at temperatures above 1450 °C [10]. In order to check the compatibility with different polished substrates, ceria tapes were sintered on MgO plates (Metoxit, Thayngen, CH), Al$_2$O$_3$ plates, 3 mol% yttria stabilized zirconia (TZP, Tosoh) and fully stabilized zirconia (YSZ). Upon sintering at 1650 °C the tapes reacted with alumina substrates forming a yellow melt (CGO) or a dark green melt (CSO). CCO was laminated onto these substrates. Also on MgO and TZP, the tapes could not be removed without destruction. The only feasible substrate was fully stabilized zirconia (YSZ).

To ensure flatness of the tapes after sintering, the tapes were loaded uniformly with 1.5 - 2 g powder per cm$^2$. For the powder loading CGO powder was sintered at 1700 °C for 6 h to obtain a coarse inactive powder of the same composition. Care was taken to avoid contamination with alumina powders, since even smallest amounts of alumina formed highly reactive melts, which destroyed the ceria tapes.

4.2 Sintering and Microstructure
The tapes were sintered at temperatures between 1200 and 1700 °C. The samples were heated with 1 °C/min to 600 °C to burn out the organic additives followed by heating with 3 °C/min to temperatures of 1600 to 1700 °C with a dwell time of 2 h at the maximum temperature. The cooling rate to room temperature was 5 °C/min. After sintering the tapes were light orange to brownish and were translucent.

For CCO a sintering temperature of 1600 °C was high enough to form dense tapes. CSO and CGO were found to be less active. For these powders a sintering temperature of at least 1650 °C during 2 h was necessary to form tapes with a density of >95% TD. Moreover, sintered samples of CGO powder always exhibited spots of the size of one to several millimeters which were not translucent. SEM investigations revealed a slightly higher porosity in these spots (6 to 7% of porosity instead of 5%).

In Fig. 4-6 to 4-8 SEM micrographs of the development of the microstructure as a function of maximum sintering temperature (without dwell time) is presented for CSO. In Fig. 4-9 the surface of a CSO tape sintered at 1650 °C with a dwell time of 2 h is shown.

At 1200 °C the microstructure consists of grains with an average crystallite size of 0.25 µm agglomerated to rectangular platelets of ~1.5 to 2 µm with a thickness of 0.25 to 0.5 µm. These platelets form spherical grains with a diameter of 0.5 µm during sintering at 1400 °C to 1600 °C. The grain size for all three compositions as a function of maximum sintering temperature is presented in Fig. 4-10. CCO exhibited the rapidest grain growth of all compositions.

The average grain size of the sintered tapes and the (closed) porosity determined by line intersection method from fracture surfaces of the tapes are summarized in Tab. 4-6.
Fig. 4-6  Microstructure of a CSO tape sintered at 1200 °C. The crystallite size is 0.25 µm. The particles are agglomerated to platelets of ~1.5 x 2 x 0.5 µm.

Fig. 4-7  Microstructure of a CSO tape sintered at 1400 °C. The average grain size is 0.5 µm.
Fig. 4-8  Microstructure of a CSO tape sintered at 1600 °C. The average grain size is 2.1 µm.

Fig. 4-9  Surface of a CSO tape sintered at 1650 °C for 2 h.
Fig. 4-10  Average grain size of CSO, CCO and CGO as a function of sintering temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>average grain size</th>
<th>closed porosity</th>
</tr>
</thead>
<tbody>
<tr>
<td>CSO</td>
<td>7.7 µm (1650 °C/2 h)</td>
<td>3.1%</td>
</tr>
<tr>
<td>CGO</td>
<td>6.7 µm (1650 °C/2 h)</td>
<td>5%</td>
</tr>
<tr>
<td>CCO</td>
<td>7.5 µm (1600 °C/2 h)</td>
<td>1.3%</td>
</tr>
</tbody>
</table>

Tab. 4-6  Average grain size and closed porosity of sintered ceria tapes.

5. Summary
Ceria solid solutions with 20% Sm$^{3+}$ or Gd$^{3+}$ and compositions with 10% Ca$^{2+}$ were prepared by coprecipitation.
Precipitation with ammonium hydroxide led to very reactive cerium oxide hydrate which cracked during sintering. Precipitation with ammonium oxalate on the other hand produced fine, sinterable ceramic powders. By adequate choice of the calcination conditions the surface area of these powders was tailored to obtain a specific surface area of about 10 m²/g which was found suitable for tape-casting.

Tape-casting was carried out using organic slurries with homogeneously dispersed ceramic powders. The proper choice of the dispersant proved to be the crucial point for this process. Whereas the powders prepared in our institute (CSO and CCO) did not cause difficulties, the commercial CGO powder (Rhône-Poulenc, La Rochelle, F) was not fully compatible to the employed dispersants. These tapes were always very brittle and difficult to handle.

Sintering of the tapes at temperatures of 1600 to 1650 °C led to tapes with an average grain size of ~7 µm and a closed porosity of <5%. To ensure flatness of the tapes they were sintered under a powder load of 1.5 to 2 g/cm² of coarse ceria powder. The lateral shrinkage during sintering was around 25% and was found to be nearly independent of the green density of the tapes in the range of 26 to 39% of the theoretical density.

6. References


5. Mixed Ionic Electronic Conductivity in Ceria-based Ceramic Membranes

Abstract

The electrical conductivity of tapecast membranes of ceria solid solutions with calcia (10 at. %), samaria and gadolinia (20 at. %) was measured in the temperature range from 400 to 850 K by impedance spectroscopy in air and by DC 4-pt measurements in an oxygen partial pressure range from 0.21 to $10^{-25}$ atm over a temperature range from 873 K to 1073 K. These measurements were performed in a Ca-stabilized zirconia cell in which the oxygen partial pressure was adjusted by pumping out oxygen electrochemically.

At high oxygen partial pressure the conductivity is mainly ionic with an activation energy from 0.98 eV (Ca-doped) to 0.93 eV (Sm-doped) in the temperature region up to 670 K and an activation energy of 0.83 eV (Ca-doped) to 0.70 eV (Sm-doped) in the temperature region of 670 to 1073 K.

All samples exhibited mixed conduction at low oxygen partial pressures. The electrical domain boundary ($\sigma_e = \sigma_i$) at 973 K is at $1.5 \times 10^{-20}$ atm for Sm-doped ceria, $10^{-20}$ atm for Gd-doped ceria and $6 \times 10^{-18}$ atm for Ca-doped ceria. Combination with nonstoichiometry data (chapter 6) electronic mobilities in Sm, Gd and Ca doped ceria were calculated. The mobility was $1.76 \times 10^{-3}$ for Sm-doped, $3 \times 10^{-3}$ for Gd-doped and $4.22 \times 10^{-3}$ for Ca-doped ceria at 973 K.

1. Introduction

Oxygen ion conducting solid electrolytes have been studied extensively for technological applications which include oxygen sensors, oxygen pumps and solid oxide fuel cells (SOFC). To minimize the electrolyte resistivity losses in devices such as oxygen pumps and fuel cells there is a need for solid electrolytes having a high ionic conductivity. A beneficial effect of a lower resistivity is also the possibility to decrease the operation temperature from today's 1173 to 1273 K (mainly using yttria-stabilized zirconia) to the intermediate temperature range of 873 to 1073 K.

Doped CeO$_2$, $\delta$-Bi$_2$O$_3$ and certain perovskites such as the only recently discovered LaGaO$_3$ [1] have been proposed as electrolytes in intermediate temperature SOFCs. The higher ionic conductivity of these materials compared to yttria-stabilized zirconia enables to operate fuel cells in the intermediate temperature range (873 - 1073 K).
Electrical Conductivity

Among these alternative materials ceria solid solutions are of special interest due to their mechanical and thermodynamic stability. Several authors [2-3456789] pointed out the possible usefulness of ceria as fuel cell electrolyte.

Ceria possesses the cubic fluorite structure. It can dissolve up to 15 mole% of CaO and more than 50 mole% of different rare earth oxides such as SmO\(_{1.5}\), GdO\(_{1.5}\) or YO\(_{1.5}\) [10]. Ceria solid solutions are of special scientific interest, since they offer the possibility to investigate ionic conductivity in a solid oxygen ion conductor over a wide range of dopant concentrations without changing the lattice crystal structure.

The ionic conductivity of pure ceria and ceria solid solutions has been investigated extensively in the last 20 years. The ionic conductivity of calcia doped ceria has been studied by several authors [11-12131415]. The conductivity of rare earth doped ceria was investigated by Kudo and Obayashi [4, 16] for ceria solid solutions with up to 50 mole% of LnO\(_{1.5}\) (Ln = lanthanide cation). It is generally agreed upon, that doping with divalent or trivalent cations results in substitution of Ce\(^{4+}\) in the lattice compensated by oxygen vacancies. The highest conductivities were found for a dopant level introducing 5% of vacant oxygen sites in the lattice, e.g. for a dopant level of 20 mole% of SmO\(_{1.5}\) and GdO\(_{1.5}\) [1718 - 19].

Whereas at high oxygen partial pressures doped ceria is an ionic conductor, at low oxygen partial pressures it is partially reduced and develops electronic conductivity. It is therefore denoted as a mixed ionic electronic conductor where unlike e.g. in yttria-stabilized zirconia only n-type electronic conductivity has been reported to date. Electronic conductivity studies of ceria solid solutions with YO\(_{1.5}\) [5] and CaO [11] at low oxygen partial pressures revealed n-type electronic conductivity, where the electronic conductivity was confirmed by Naik and Tien [20] and Tuller and Nowick [21] to proceed by a small polaron transport mechanism.

Whereas for calcia and yttria doped ceria there exist reliable studies on the mixed ionic and electronic conductivity, for samaria and gadolinia doped ceria only preliminary and contradictory data are available. Kudo and Obayashi [4] studied the ionic transference number of oxygen by EMF studies. They found the electrical domain boundary (EDB), where ionic and electronic conductivity are equal at 1.24\( \times \)10\(^{-19}\) atm at 700 °C. This method, however, is problematic since it generates values which are only system parameters, because the influence of the electrodes on the ionic transport number cannot be separated (see e.g. chapter 8&9). Maricle et al. [6] studied the ionic and electronic conductivity of Gd-doped ceria as a function of oxygen partial pressure and found the EDB at 3.5\( \times \)10\(^{-19}\) atm. For small additions of Sm or Pr (1 to 3%) to gadolinia doped ceria they reported a lowering of the EDB of two orders of magnitude.

The aim of the present study was to investigate the ionic and electronic conductivity of calcia, samaria and gadolinia doped ceria. The measurements were performed on
tapecast membranes of solid solutions with 10 mole% CaO and 20 mole% of SmO$_{1.5}$ or GdO$_{1.5}$. Microstructural aspects such as grain size and porosity greatly influence the electric conductivity of polycrystalline materials. Impedance spectroscopy measurements were carried out in the temperature range from 400 to 850 K and in the frequency range from 40 Hz to 1 MHz in order to evaluate grain boundary and intragrain conductivities. The specific grain boundary resistivity was evaluated by using the brick-layer model. The electrical conductivity as a function of oxygen partial pressure was measured by 4-pt measurements in the temperature range from 873 to 1073 K and at oxygen partial pressures ranging from 0.21 to $10^{-25}$ atm. In section 2 of this chapter the theory that describes the ionic and mixed ionic electronic conductivity is summarized. The sample preparation and the experimental setup are presented in section 3. Section 4 presents the results of the impedance spectroscopy study in air. The oxygen partial pressure dependent measurements are presented in section 5. Summary and conclusions are given in section 6.

2. Ionic and electronic conductivity

2.1 Ionic conductivity

The ionic conductivity is expressed as

$$\sigma_i = N(2q)v_i$$

(5-1)

where $\sigma_i$ denotes the ionic conductivity, $(2q)$ the charge of an oxygen vacancy, $N$ their concentration and $v_i$ the ionic mobility. According to [22] the ionic mobility can be expressed as

$$v_i = \frac{B}{T} \exp\left(-\frac{\Delta H_m}{kT}\right)$$

(5-2)

where $k$ the Boltzmann constant and $\Delta H_m$ is the enthalpy of migration of an oxygen vacancy, the pre-exponential factor $B$ contains geometrical terms and the jump attempt frequency. From Eqs. (5-1) and (5-2) the ionic conductivity is expressed as

$$\sigma_i = 2q \frac{BN}{T} \exp\left(-\frac{E_A}{kT}\right)$$

(5-3)

Where $E_A$, the activation energy of the ionic conductivity contains the enthalpy of migration $\Delta H_m$ and additional terms due to association of oxygen vacancies with dopant cations. This association is mainly due to coulombic attraction of dopant cations and oxygen vacancies. For association of oxygen vacancies with divalent cations such as Ca$^{2+}$ the activation energy is given as $E_A = \Delta H_m + \Delta H_A/2$. For associates with trivalent
Electrical Conductivity

dopants the association energy can be expressed as $E_A = \Delta H_{m+} + \Delta H_{A2}$ where $\Delta H_{A1}$ and $\Delta H_{A2}$ are the association enthalpies for divalent and trivalent associates, respectively [24]. Usually two different ranges of the ionic conductivity are distinguished. In the low temperature range ($T < 1200 \text{ K}$) almost all oxygen vacancies are associated and the activation energy for the ionic conductivity is of the order of 0.8 to 0.9 eV. At temperatures above 1200 K the charge carriers are almost unassociated and the activation energy is of the order of 0.6 to 0.7 eV [22].

2.2 Electronic conductivity

At low oxygen partial pressures ceria is partially reduced and develops n-type electronic conductivity according to

$$O^{x}_O \leftrightarrow V^{**}_O + 2e + \frac{1}{2}O_2 \quad (5-4)$$

With the law of mass action it follows, that

$$n = K_e N_{\text{inir}} p(O_2)^{-1/4} \quad (5-5)$$

where $n$ denotes electron concentration and $K_e$ is a constant. $N_{\text{inir}}$ is the number of additional oxygen vacancies introduced by partial reduction.

Similar to the ionic conductivity, the electronic conductivity is expressed as

$$\sigma_i = n q v_e \quad (5-6)$$

and the dependence of the electronic conductivity on the oxygen partial pressure is given as (Eqs. (5-5) and (5-6))

$$\sigma_e \propto p(O_2)^{-1/m} \quad (5-7)$$

The exponent $1/m$ in Eq. (5-7) is equal to 0.25, if the number of oxygen vacancies $N$ can be assumed as constant. If the number of oxygen vacancies introduced by reduction increases at very low oxygen partial pressures, $1/m$ approaches 1/6. For association of quasifree electrons with oxygen vacancies, the exponent $1/m$ can increase up to 1/2 (chapter 6).

3. Experimental
3.1 Sample preparation

Ce$_{0.9}$Ca$_{0.1}$O$_{1.9-x}$ (CCO) was prepared by wet-chemical coprecipitation from nitrate precursors. An aqueous solution ([Ce$^{3+}$] = 1 M, [Ca$^{2+}$] = 0.11 M) of Ce$^{III}$(NO$_3$)$_3$·6H$_2$O (>99%, Fluka, Buchs, CH) and Ca(NO$_3$)$_2$·4H$_2$O (>99%, Merck, Darmstadt, FRG) was precipitated with a 0.47 M solution of ammonium oxalate (>99.5%, Fluka) at 45 °C. This solution was washed three times with water at a pH of 8 and calcined at 750 °C for 2 hrs. Ce$_{0.8}$Sm$_{0.2}$O$_{1.9-x}$ (CSO) was prepared under the same conditions with a Sm-nitrate solution prepared from Sm$_2$O$_3$ (>99%, Rhône-Poulenc, La Rochelle, F) dissolved in nitric acid. Ce$_{0.8}$Gd$_{0.2}$O$_{1.9-x}$ (CGO) powder was obtained from Rhône-Poulenc (Lot. NR. 94007/99, La Rochelle, F). The exact procedure for the powder preparation is given in chapter 4. All samples had the cubic fluorite structure as was verified by XRD. The composition was analyzed by microprobe analysis and by EDX. Composition with respect to Ce$^{4+}$ and dopant as well as lattice constants and ionic radii are given in Tab. 5-1. As minor impurities SiO$_2$ and ZrO$_2$ were found (below 0.1% wt.).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition [atom %]</th>
<th>Cubic lattice constant [Å]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.8}$Sm$</em>{0.2}$O$_{1.9}$</td>
<td>18.82$^x$</td>
<td>5.4341</td>
</tr>
<tr>
<td></td>
<td>81.18$^x$</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9}$</td>
<td>19.96$^x$</td>
<td>5.4312</td>
</tr>
<tr>
<td></td>
<td>80.04$^x$</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Ca$</em>{0.1}$O$_{1.9}$</td>
<td>10.02$^e$</td>
<td>5.4177</td>
</tr>
<tr>
<td></td>
<td>89.98$^e$</td>
<td></td>
</tr>
</tbody>
</table>

$^x$ by microprobe (Sulzer Innotec, Winterthur, CH), $^e$ by EDX (Tracor Northern Z-max 30)

Tab. 5-1 Composition and cubic lattice constant of sintered ceria-based membranes. The ionic radius of the host cation Ce$^{4+}$ is 0.97 Å [23].

3.2 Tapecasting and sintering

100 g of ceria powder was mixed into a organic slurry using ethanol as solvent (30 g), polyethylene glycol 400 (2.95 g) (pract., Fluka) and dioctyl-phthalate (2.8 g) (>97%, Fluka) as plasticisers, triethanolamine (>99% Fluka) as dispersant (0.38 g), and PVB (Mowital B 20H, Hoechst, Frankfurt, FRG) as binder (5.8 g). The slurry was homogenized in a planetary mill, degassed at a pressure of 100 mbar for 15 min and cast into green ceramic tapes by use of a doctor blade technique.
Samples were cut from the green tapes and sintered at 1650 °C. To ensure flatness of the samples they were sintered on polished yttria-stabilized zirconia plates and covered with ~1.5 to 2 g cm\(^{-2}\) of a coarse powder with the same composition. For the impedance spectroscopy study three layers of tape (1 x 1 cm\(^2\)) were laminated with ethanol and sintered together. For the 4-pt conductivity study strips of 0.5 to 3 cm were sintered. The sample had a density of more than 95% of the theoretical density and an average grain size of 3.6 to 6.1 µm. Average grain size and density were determined from scanning electron micrographs (Jeol, JEM-6400). Density and average grain size of the samples used in this study are summarized in Tab. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theor. density [g/cm(^3)]</th>
<th>% of TD measured</th>
<th>Av. grain size [µm]</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce(<em>{0.8})Sm(</em>{0.2})O(_{1.9})</td>
<td>7.14</td>
<td>98 ± 1</td>
<td>6.1</td>
<td>impedance study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>97 ± 2</td>
<td>7.7</td>
<td>4-pt measurement</td>
</tr>
<tr>
<td>Ce(<em>{0.8})Gd(</em>{0.2})O(_{1.9})</td>
<td>7.21</td>
<td>99 ± 1</td>
<td>5.2</td>
<td>impedance study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>95 ± 3</td>
<td>6.2</td>
<td>4-pt measurement</td>
</tr>
<tr>
<td>Ce(<em>{0.9})Ca(</em>{0.1})O(_{1.9})</td>
<td>6.73</td>
<td>96 ± 2</td>
<td>3.6</td>
<td>impedance study</td>
</tr>
<tr>
<td></td>
<td></td>
<td>99 ± 2</td>
<td>5.6</td>
<td>4-pt measurement</td>
</tr>
</tbody>
</table>

**Tab. 5-2**  Theoretical density, measured density and average grain size of the samples used for the impedance and 4-pt conductivity studies.

Typical microstructures of sintered tapes are shown in Figs. 5-1 (as sintered surface of a CSO tape) and 5-2 (fracture surface of CSO).

### 3.3 Impedance spectroscopy

Complex impedance spectroscopy in the frequency range from 40 Hz to 1 MHz was used to distinguish between the intragrain and the grain boundary contribution to the charge transport. The total impedance of polycrystalline ceramic specimens originates from the impedance contribution of the grains and from interfacial effects on grain boundaries and electrodes.
Fig. 5-1  SEM micrograph of the surface of a sintered CSO tape (1650 °C, 2 h).

Fig. 5-2  SEM micrograph of the fracture surface of a sintered CSO tape (1650 °C, 2 h).
Complex impedance measurements using a PC-controlled HP Precision LCR meter 4284A were carried out between 400 and 1100 K in air on rectangular samples with a thickness of 0.8 to 1 mm and an area of ~1 cm² using a two-probe method with separate wires for current and voltage. Platinum electrodes were applied by sputtering (Union SCD-040, Balzers, FL) a layer of 0.5 µm of platinum onto the polished surface of the specimens. Pt-mesh (Aldrich 99.9%, 52 mesh, Aldrich, Milwaukee, USA) was attached by platinum paste (Heraeus C3605 P, Heraeus, Hanau, FRG) on these sputtered electrodes. The temperature was controlled to ± 2 °C close to the specimen. The data were analyzed using the NLLS-fit program of Boukamp [24].

The specific resistivity of the grain boundaries was evaluated by use of the brick-layer model [14, 25]. According to this model, it is assumed that the bulk material consists of conducting grains, approximated by cubes with an edge length \( a \), separated by a thin homogeneous grain boundary layer of thickness \( \delta_{GB} \). For \( \delta_{GB} \ll a \) and \( \sigma_{GB} \ll \sigma_{G} \), the parallel conduction along the grain boundaries is negligible. The equivalent circuit model of the sample then consists of a simple series combination of three RC-elements (grain, grain boundary and electrodes). An idealized schematic picture of the observed impedance plot in the complex plane is given in Fig. 5-3. The spectrum in Fig. 5-3 consists of three semicircles which may be tilted below the real axis \( Z' \), since the sample reacts not as an ideal RC element. The frequency \( \omega \) increases with decreasing resistance. Below the schematic impedance plot, the equivalent circuit is given with the corresponding resistors and capacitors for grain (\( R_G, C_G \)), grain boundary (\( R_{GB}, C_{GB} \)) and electrode dispersions (\( R_E, C_E \)). The resistance of the electrode in this case corresponds to the charge transfer resistance and the capacitance to the electrochemical double layer capacity. The relaxation time \( \tau \) of the single processes can be determined from the crest of the semicircles were \( \omega \tau = 1 \).

The total (DC) resistance of the ceramic material \( R_T = R_G + R_{GB} \), is the sum of the resistance of grains \( R_G \) and grain boundaries \( R_{GB} \). Usually macroscopic specific conductivities \( \sigma_T', \sigma_G' \) and \( \sigma_{GB}' \) are calculated from resistivity values using the relation

\[
\sigma_i' = \left( \rho_i' \right)^{-1} = \left( R_i L_T A_T \right)^{-1}
\]

(5-8)

where \( L_T = L_G + L_{GB} = n(a+\delta_{GB}) \) is the total length of the sample, \( n = L_T/a \) is the number of grain boundaries perpendicular to the current direction, and \( A_T = A_G + A_{GB} \) is the total cross-sectional area of the sample. Since \( L_{GB}/L_T = \delta_{GB} / (a + d_{GB}) \), it can be shown that the length fraction of grain boundaries \( L_{GB} \) amounts to \( L \delta_{GB} / (a + \delta_{GB}) \approx L_T \delta_{GB} / a \) and the length fraction of grains \( L_G \) to \( L_T a / (a + \delta_{GB}) \approx L_T \).

For the cross section of the current path through the area fractions of grains \( A_G \) we obtain:
If the grain boundary conduction path along the length of the sample can be omitted, the microscopic specific conductivity of grain and grain boundary is given by

\[ \sigma_G = \sigma_G' \quad \text{and} \quad \sigma_{GB} = \sigma_{GB}' \frac{\delta_{GB}}{a} \]  

In order to eliminate the size effect of ceramic grains, the macroscopic specific grain boundary resistivities, \( \rho_{GB}' = R_{GB} A_T / L_T \), have to be converted to the normalized macroscopic resistivities \( r_{GB} \) per unit area of the grain boundary surface, according to the relation

\[ r_{GB} = \rho_{GB}' a = \rho_{GB} \delta_{GB} \]  

where \( a = 1.5 l \) is the corresponding cube edge length derived from the linear average grain size \( l \) of the ceramic sample [26].

Fig. 5-3  
Idealized complex plane impedance plot schematically showing the observed semicircles for grain, grain boundary and electrodes. Below the impedance plot the equivalent electronic circuit is given.

3.4 Four-point electrical conductivity measurements
4-pt conductivity measurements were carried out on sintered strips of 0.5 x 3 cm with a thickness of 250 µm. On these strips Pt electrodes were painted and sintered at a temperature of 800 °C for 2 hrs. The length of the sample between the inner electrodes (voltage probes) was 1 cm.

The specific resistance of the samples was measured as a function of oxygen partial pressure in the p(O2) range from 10^{-25} to 0.21 atm at 600, 650, 700, 750 and 800 °C. The measurement setup is shown schematically in Fig. 5-4. The samples were placed in a Ca-stabilized zirconia tube which was closed at one end by a brass flange and a polymer (PMMA) lid. Between the flange and the lid vacuum grease was applied to ensure gastightness. Within the zirconia tube the oxygen partial pressure was adjusted by pumping out oxygen electrochemically by application of a voltage between the lower electrodes with a laboratory power supply (GPR 3030D, G.W. Instruments, Taiwan). The pumping current was adjusted to 6 - 10 mA and the oxygen partial pressure was calculated from the EMF of the upper electrodes by the Nernst equation measured with an electrometer (Keithley 517 programmable electrometer).

For the conductivity measurements oxygen was removed from the cell until a p(O2) of about 10^{-25} atm was reached. Subsequently, the current was switched off and the resistivity of the sample was measured with a micro-ohmmeter (Keithley 580). Leakage through the seals on top of the cell led to a slow increase of p(O2) corresponding to an increase in EMF of about 0.025 V/hr. The resistivity of the sample, the EMF of the upper electrodes and the temperature close to the sample were recorded with a pen-chart recorder (SE120, ABB Metrawatt) connected to the analog output of the respective devices. The EMF varies very quickly with time in an oxygen partial pressure range from 10^{-15} to 10^{-5} atm for a constant oxygen leakage current. Therefore, in this oxygen partial pressure range the samples were not in equilibrium with the surrounding atmosphere and were not included. Only for CSO at 873 K special care was taken to determine the conductivity also in this range.

By 4-pt measurements the total conductivity of the sample, \( \sigma_t \), is measured. It is the sum of electronic, \( \sigma_e \), and ionic, \( \sigma_i \), conductivities. The total conductivity in air was assumed as the ionic conductivity and the electronic conductivity of the samples was calculated as

\[
\sigma_e = \sigma_i - \sigma_{tot}(\text{air})
\]  

(5-12)

since for high level doping the ionic conductivity of the sample can be assumed to be constant over a wide range of oxygen partial pressures.
1 PMMA lid  
2 brass flanges  
3 upper electrodes for EMF sensing (Pt)  
4 lower electrodes for p(O_2) adjustment (Pt)  
5 thermocouple (type K, Interstar, Cham, CH))  
6 sample in 4-pt setup (Pt electrodes)  
7 Ca-stabilized zirconia tube (Zr 23, Degussa, Baar, CH)

A Micro-Ohmmeter (Keithley 580)  
B Furnace controller (CRL455, Thermotronic, Bern, CH)  
C Digital multimeter (Keithley 517 Programmable Electrometer)  
D Digital multimeter (Keithley 179A)  
E Power supply (GPR-3030D, G.W. Instruments Co., Taiwan)  
F Electrical furnace

Fig. 5-4 Schematic setup for the 4-pt electrical conductivity measurements as a function of temperature and oxygen partial pressure. The cell volume was 13.9 cm^3.
4. Results and discussion

4.1 Impedance spectroscopy

Impedance spectroscopy measurements were carried out in the frequency range of 40 Hz to 1 MHz. For this reason only a small window of the grain, grain boundary and electrode resistances as depicted schematically in Fig. 5-3 is visible at a given temperature. The intragrain conductivity of CSO, CGO and CCO can be measured up to a temperature of 850 K. Total conductivity of the samples and grain boundary resistance can be measured accurately up to temperatures of 900 K. In Fig. 5-5 a plot of log(frequency) versus real part of the resistivity is shown for CGO in the temperature range from 559 to 1122 K. In this plot the dispersions on grain, grain boundary and electrodes are visible for different temperature regimes. Small numbers indicate the temperature in Kelvin.

![Figure 5-5](image_url)

**Fig. 5-5** Grain, grain boundary, and electrode dispersions of the real part of complex specific impedance for CGO in air.

A typical impedance plot with real and imaginary part of the specific resistivity is given in Fig. 5-6 for a CSO sample consisting of three laminated tapes at 481 K. Small numbers indicate the corresponding frequency in Hertz.
Fig. 5-6  Complex impedance diagram at 481 K (CSO, three laminated tapes) in air.

By using a NLLS-fit program ("Equivalent circuit", Boukamp [24]) the specific intragrain conductivity was determined in the temperature range from 400 to 850 K in air. The activation energy of the ionic conductivity of CSO, CGO and CCO in this temperature range was found to vary from 0.93 - 0.98 eV in the temperature range of 400 to 673 K to 0.77 - 0.83 eV in the temperature range from 673 to 850 K. The ionic conductivity of the three compositions is shown in Fig. 5-7 as $\sigma_i T$ versus $10^3/T$. The corresponding activation energy and the ionic conductivity are summarized in Tab. 5-3. These measurements were carried out on laminated tapes and are slightly lower than the conductivities measured for single tapes as well as for the 4-pt conductivity measurements. It was found for these samples, that not the entire cross-section of the tapes were well laminated and therefore the effective microscopic cross-section was slightly smaller than the macroscopic one. However, this does not influence the activation energy. The activation energy is found to decrease with increasing temperature. Assuming a concept of association of oxygen vacancies with dopant cations, this can be explained with a decreasing degree of association at higher temperature leading to a higher mobility of oxygen vacancies.
Electrical Conductivity

Fig. 5-7 Specified intragrain conductivity measured by impedance spectroscopy of CSO, CGO and CCO depicted as $\sigma_T$ vs. $10^3/T$.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Intragrain conductivity at 800 K [S/m]</th>
<th>Activation energy 400........673 K</th>
<th>Activation energy 673........850 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ce}<em>{0.8}\text{Sm}</em>{0.2}\text{O}_{1.9}$</td>
<td>0.32</td>
<td>0.93 eV</td>
<td>0.78 eV</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.8}\text{Gd}</em>{0.2}\text{O}_{1.9}$</td>
<td>0.28</td>
<td>0.97 eV</td>
<td>0.77 eV</td>
</tr>
<tr>
<td>$\text{Ce}<em>{0.9}\text{Ca}</em>{0.1}\text{O}_{1.9}$</td>
<td>0.12</td>
<td>0.98 eV</td>
<td>0.83 eV</td>
</tr>
</tbody>
</table>

Tab. 5-3 Intragrain ionic conductivity at 800 K and activation energies for the intragrain conductivity estimated following Eq. (5-3) for CSO, CGO and CCO.

The activation energies compare well to values given by Arai et al. [15], who found an average activation energy of 0.89 eV (660 to 1100 K) for $\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9}$. Kudo and Obayashi [16] found activation energies of 0.98 eV for $\text{Ce}_{0.7}\text{Sm}_{0.3}\text{O}_{1.85}$ in the temperature range from 700 to 900 K and 0.78 eV for 900 to 1100 K. For $\text{Ce}_{0.7}\text{Gd}_{0.3}\text{O}_{1.85}$ they found activation energies of 1.05 and 0.84 eV for the low and high temperature range, respectively.

The normalized macroscopic grain boundary resistance $r_{GB}$ of the samples was determined from the macroscopic specific grain boundary resistivity according to the
Electrical Conductivity

brick-layer model (Eqs.(5-9) to (5-11)) to eliminate the size effect of the grain size of the samples. It is equal to the product of specific grain boundary resistance $\rho_{\text{GB}}$ and the thickness of the grain boundaries $\delta_{\text{GB}}$. In Fig. 5-8 $\rho_{\text{GB}}\delta_{\text{GB}} T$ is shown versus $10^3/T$ for the three investigated materials CSO, CGO, and CCO. The activation energy of the grain boundary conductivity was determined from this plot as 1.18 eV for CSO, 1.11 eV for CGO and 1.02 eV for CCO. Unlike for the intragrain conductivity no different activation energies were found for the low and high temperature range.

![Graph showing $\rho_{\text{GB}}\delta_{\text{GB}} T$ vs. $10^3/T$.]

Fig. 5-8  Macroscopic specific grain boundary resistivity of CSO, CGO and CCO as $\rho_{\text{GB}}\delta_{\text{GB}} T$ vs. $10^3/T$.

For CSO the highest macroscopic specific grain boundary resistivity was found followed by CGO and CCO which exhibited only small differences. The values of the activation energy of $\rho_{\text{GB}}\delta_{\text{GB}} T$ versus $10^3/T$ compare well to values found by El Adham and Hammou [14] who found an activation energy for the grain boundary resistance of 0.96 to 1.2 eV for polycrystalline samples of calcia doped ceria. Maricle et al. reported an activation energy for the grain boundary conductivity of 1.16 eV for Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$. For the electrochemical characterization of various electrodes on ceria-based electrolytes by current interruption measurements (chapters 8 to 10) it is important to know in which time scale the polarization of the electrolyte under load relaxes. Therefore, the relaxation time of the slowest process taking place in the bulk, i.e. the relaxation time of the grain boundaries, was estimated from the frequency on the crest.
Electrical Conductivity

of the semicircles observed in the impedance measurements (see Fig. 5-3). For the small frequency window, the relaxation time was only observed in the temperature range from 400 to 670 K. The relaxation time of the grain boundaries for CSO, CGO and CCO is plotted versus $10^3/T$ in Fig. 5-9 and extrapolated to values up to 1000 K. In the intermediate operating temperature range the present ceria-based SOFC are designed for (873 to 1000 K), the grain and grain boundary polarization exhibits relaxation times below 0.1 $\mu$s for all investigated samples.

![Graph](image)

**Fig. 5-9** Grain boundary relaxation times versus inverse temperature estimated from the frequency on top of the observed semicircles in impedance spectroscopy.

5. Four point measurements

5.2 Total and ionic conductivity

4-pt resistivity measurements were carried out in the temperature range from 873 to 1173 K in steps of 50 K as a function of oxygen partial pressure. Fig. 5-10 shows the total electrical conductivity $\sigma_{tot}$ of CSO, CGO and CCO as a function $10^3/T$ at an oxygen partial pressure of 0.21 atm. The corresponding activation energies calculated from $\sigma_{tot}T$ vs. $1/T$ are 0.70 eV for CSO, 0.73 eV for CGO and 0.83 eV for CCO. Fig. 5-11 shows a comparison of the total electrical conductivities in air determined by impedance spectroscopy on single tapes of 250 $\mu$m thickness and 4-pt measurements on
tape strips of 250 µm thickness as a function of inverse temperature. Open symbols represent 4-pt measurements, closed symbols impedance spectroscopy measurements. The measurements are in good agreement, only for CSO slightly higher values were gained from 4-pt measurements.

![Graph showing electrical conductivity as a function of inverse temperature](image)

**Fig. 5-10** Total electrical conductivity of CSO, CGO and CCO in air determined by 4-pt measurements on sintered polycrystalline tape strips.
The total electrical conductivity of ceria solid solutions is the sum of the ionic and n-type electronic conductivity. At low oxygen partial pressures the electronic conductivity increases due to partial reduction of $\text{Ce}^{4+}$ to $\text{Ce}^{3+}$. The total electrical conductivity of $\text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-x}$ (CSO) is plotted in Fig. 5-12 as a function of oxygen partial pressure for 873, 973 and 1073 K. In Fig. 5-13 and 5-14, the total electrical conductivity as a function of $p(O_2)$ is shown for $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9-x}$ and $\text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9-x}$, where $x$ indicates the deviation from the stoichiometric oxygen content due to partial reduction according to Eq. (5-4). The solid lines are fits to Eq. (5-7) where $1/m$ was fixed to 0.25.

From these fit curves the electrical domain boundaries (EDB) for CSO, CCO and CGO, i.e. the oxygen partial pressure where the ionic conductivity equals the electronic conductivity, were determined. These EDB values are given in Fig. 5-15 as a function of inverse temperature. Arrhenius plots of the EDB versus $1/T$ revealed activation energies of 6.38 eV for CSO, 5.78 eV for CGO and 6.58 eV for CCO.

**Fig. 5-11** Arrhenius plot of the total electrical conductivity determined from 4-pt measurements (open symbols) and impedance spectroscopy (closed symbols).
Fig. 5-12  Total electrical conductivity of CSO as a function of oxygen partial pressure.

Fig. 5-13  Total electrical conductivity of CGO as a function of oxygen partial pressure.
Fig. 5-14 Total electrical conductivity of CCO as a function of oxygen partial pressure.

Fig. 5-15 Arrhenius plot of the electrolytic domain boundary (EDB) of CSO, CGO and CCO.
The electrical domain boundary and the ionic conductivity at 973 K, the activation energy of the EDB and the ionic conductivity are summarized in Tab. 5-4 and compared to literature values.

The activation energy of the ionic conductivity found by 4-pt measurements in this work compares well to literature values of Kudo and Obayashi [4] and Maricle et al. [6]. The electrolytic domain boundary for CSO and CGO was one order of magnitude lower than that found in the literature, but the activation energy of the EDB compares well with values of [4]. The activation energy of the EDB includes the activation energy of the ionic mobility, the activation energy of the electronic mobility and the partial enthalpy of reduction for CSO, CGO and CCO, respectively. For CCO the lowest EDB-value of \(5.99 \times 10^{-18}\) was found at 973 K in this study. Maricle et al. found an increase of the electrolytic domain boundary by two orders of magnitude for small additions of samaria or praseodymia (1 to 3 atomic percent) compared to their \(\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9}\). In this work the mechanism for the lowering of the EDB by small additions of Sm or Pr is however unclear. A possible explanation is a trapping of the electronic charge carriers introduced by partial reduction of the Sm or Pr cations.

<table>
<thead>
<tr>
<th>Material</th>
<th>(\sigma_i) [S/m] at 973 K</th>
<th>(E_A) of (\sigma_i) [eV]</th>
<th>EDB [atm] at 973 K</th>
<th>(E_A) of EDB [eV]</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{Ce}<em>{0.8}\text{Sm}</em>{0.2}\text{O}_{1.9-x})</td>
<td>3.45</td>
<td>0.70</td>
<td>1.48 \times 10^{-20}</td>
<td>6.38</td>
</tr>
<tr>
<td>(\text{Ce}<em>{0.8}\text{Gd}</em>{0.2}\text{O}_{1.9-x})</td>
<td>3.62</td>
<td>0.73</td>
<td>1.14 \times 10^{-20}</td>
<td>5.78</td>
</tr>
<tr>
<td>(\text{Ce}<em>{0.9}\text{Ca}</em>{0.1}\text{O}_{1.9-x})</td>
<td>1.99</td>
<td>0.83</td>
<td>5.99 \times 10^{-18}</td>
<td>5.52</td>
</tr>
<tr>
<td>(\text{Ce}<em>{0.8}\text{Gd}</em>{0.2}\text{O}_{1.9-x}) [4]</td>
<td>4.7</td>
<td>0.75</td>
<td>1.24 \times 10^{-18}</td>
<td>5.99</td>
</tr>
<tr>
<td>(\text{Ce}<em>{0.8}\text{Gd}</em>{0.2}\text{O}_{1.9-x}) [6]</td>
<td>2.8</td>
<td></td>
<td>3.5 \times 10^{-19}</td>
<td></td>
</tr>
<tr>
<td>(\text{Ce}<em>{0.8}\text{Gd}</em>{0.17}\text{Pr}<em>{0.03}\text{O}</em>{1.9-x}) [6]</td>
<td>4.3</td>
<td>0.73</td>
<td>1.1 \times 10^{-21}</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 5-4 Ionic conductivity activation energy for ionic conductivity, electrolytic domain boundary (EDB) and activation energy of the EDB for CSO, CGO and CCO determined from 4-pt measurements. For comparison literature data of Kudo and Obayashi [4] and Maricle et al. [6] are given.
5.2 **Electronic conductivity and mobility**

The dependence of the electronic conductivity of ceria solid solutions on $p(O_2)$ should follow a power law with an exponent $1/m$ (Eq. (5-7)) which is $\sim 1/4$ for small deviations from stoichiometry and $\sim 1/6$ for large deviations from stoichiometry. However, if oxygen vacancies associate with Ce$^{3+}$, the slope of $\sigma_e$ vs. $p(O_2)$ can increase to values of $\sim 1/3$ to $1/2$ (chapter 6). The electronic conductivity was calculated according to Eq. (5-14) from the total conductivity vs. $p(O_2)$. In Fig. 5-16 the dependence of the electronic conductivity of CSO on the oxygen partial pressure is given for 873, 973 and 1073 K. The slopes indicate the possible $\sigma_e$ vs. $p(O_2)$ dependencies as explained in chapter 6. The location of the EDB is also shown.

*Fig. 5-16* Dependence of the electronic conductivity on the oxygen partial pressure for CSO at 873, 973 and 1073 K. Solid lines indicate the slope $1/m$ (Eq. (5-7)).

From Fig. 5-16 it can be seen, that the electronic conductivity follows a $p(O_2)^{-1/4}$ law over wide ranges of the oxygen partial pressure. A fit of $\sigma_e$ vs. $p(O_2)^{-1/4}$ can therefore be regarded as a reasonable approximation.

In Fig. 5-17 the electronic conductivity of CSO, CGO and CCO is given as a function of oxygen partial pressure at 973 K. The values for CSO and CGO are more or less
identical whereas CCO exhibits a significantly higher electronic conductivity. Therefore, CSO and CGO are regarded as suitable electrolyte materials for SOFC. CCO, due to its sufficiently high ionic conductivity and its higher electronic conductivity compared to CSO and CGO might be considered as an interesting material for SOFC anodes, since it is operated thereby at low p(O_2) and can profit from its high ionic and electronic conductivity. By combination of these electronic conductivity values vs. oxygen partial pressure, with nonstoichiometry data, the electronic mobilities in ceria solid solutions with CSO, CGO and CCO can be determined. Fig. 5-18 shows the oxygen nonstoichiometry x vs. p(O_2) at 973 K. The data are taken from chapter 6 and were obtained by coulometric titration.

![Dependence of the ionic conductivity on -log(p(O_2)) for CSO, CGO and CCO at 973 K.](image)

**Fig. 5-17** Dependence of the ionic conductivity on -log(p(O_2)) for CSO, CGO and CCO at 973 K.
Fig. 5-18 Oxygen nonstoichiometry \( x \) of \( \text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-x} \), \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9-x} \) and \( \text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9-x} \) as a function of \(-\log(p(\text{O}_2))\).

Fig. 5-17 and Fig. 5-18 exhibit approximately the same oxygen partial pressure dependence. From the \( \sigma_e \) vs. \( p(\text{O}_2) \) and \( x \) vs. \( p(\text{O}_2) \) measurements electronic mobility \( \nu_e \) data were calculated according to (with Eq. (5-6))

\[
\nu_e = \frac{a^3}{4q} \frac{\sigma_e}{x} \left[ \frac{\text{cm}^2}{\text{Vs}} \right] 
\]

In Eq. (5-13) \( a \) signifies the cubic lattice constant (Tab. 5-1), \( q \) is the elementary charge and \( x \) is the nonstoichiometry. The factor 4 comes from the fact that an elementary cell of the fluorite lattice contains two formula units of ceria solid solution and that the electron concentration \( [e] = 2x \).

Similarly the ionic mobility \( \nu_i \) is calculated from the ionic conductivity as

\[
\nu_i = \frac{a^3}{2q} \frac{\sigma_i}{y} \left[ \frac{\text{cm}^2}{\text{Vs}} \right] 
\]

where \( y \) is the number of oxygen vacancies per formula unit. For the given compositions \( \text{Ce}_{0.8}\text{Sm}_{0.2}\text{O}_{1.9-x} \), \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{1.9-x} \), and \( \text{Ce}_{0.9}\text{Ca}_{0.1}\text{O}_{1.9-x} \) \( y = 0.1 \). Since \( y \gg x \) the influence of nonstoichiometry was neglected for the calculation of \( \nu_i \). The ionic
mobility values are not discussed in further detail here, since they are proportional to the ionic conductivity values already discussed in section 5.1. Ionic mobility values and electronic mobilities at an oxygen nonstoichiometry $x = 0.01$ are summarized in Tab. 5-5. It should be noted that these values exhibit a large uncertainty since they were determined by two different measurements. However, they compare well with electronic mobility values for pure ceria given by Blumenthal and Panlener [27] who found electronic mobilities of $5.6 \cdot 10^{-3}$ to $7.28 \cdot 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ at 1073 K. Considering an activation energy of 0.1 to 0.5 eV for the electronic mobility as it is typical for a small polaron hopping mechanism which is reported for the electronic conductivity of ceria, these values compare also well to electronic mobilities at 1273 K reported by Tuller and Nowick [21] of $8.1 \cdot 10^{-3}$ cm$^2$V$^{-1}$s$^{-1}$ at $x = 0.008$ on ceria single crystals. Naik and Tien [20] found slightly higher mobility values of $2 \cdot 10^{-2}$ cm$^2$V$^{-1}$s$^{-1}$ at 1273 K and $x = 0.025$.

From Tab. 5-5 it can be seen that the electronic mobilities are one order of magnitude higher than the ionic mobilities. Assuming an activation energy for the electronic mobility of $\sim 0.4$ eV (small polaron hopping) and an activation energy for the ionic mobility of $\sim 0.8$ eV, it is obvious that the ratio of $\nu_i/\nu_e$ decreases with rising temperature. Moreover, the reducibility of ceria increases with temperature. Therefore, ceria-based materials can be regarded as suitable SOFC electrolytes in a temperature range below 1073 K only. Preferably they are operated at 800 to 1000 K.

<table>
<thead>
<tr>
<th>Material</th>
<th>$T$ [K]</th>
<th>$\nu_e$ [cm$^2$V$^{-1}$s$^{-1}$]</th>
<th>$\nu_i$ [cm$^2$V$^{-1}$s$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.8}$Sm$</em>{0.2}$O$_{1.9-x}$</td>
<td>973</td>
<td>$1.76 \cdot 10^{-3}$</td>
<td>$1.73 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>$5.01 \cdot 10^{-3}$</td>
<td>$3.61 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9-x}$</td>
<td>973</td>
<td>$3.00 \cdot 10^{-3}$</td>
<td>$1.81 \cdot 10^{-4}$</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>$3.00 \cdot 10^{-3}$</td>
<td>$3.84 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>Ce$<em>{0.9}$Ca$</em>{0.1}$O$_{1.9-x}$</td>
<td>973</td>
<td>$4.22 \cdot 10^{-3}$</td>
<td>$9.89 \cdot 10^{-5}$</td>
</tr>
<tr>
<td></td>
<td>1073</td>
<td>$5.22 \cdot 10^{-3}$</td>
<td>$1.09 \cdot 10^{-4}$</td>
</tr>
<tr>
<td>CeO$_{2-x}$ [21]</td>
<td>1273</td>
<td>$8.1 \cdot 10^{-3}$ $x = 0.008$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$2.2 \cdot 10^{-3}$ $x = 0.025$</td>
<td></td>
</tr>
<tr>
<td>CeO$_{2-x}$ [20]</td>
<td>1200</td>
<td>$2 \cdot 10^{-2}$ $x = 0.025$</td>
<td></td>
</tr>
<tr>
<td>CeO$_{2-x}$ [27]</td>
<td>1073</td>
<td>$7.28 \cdot 10^{-3}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1273</td>
<td>$9.19 \cdot 10^{-3}$</td>
<td></td>
</tr>
</tbody>
</table>

Tab. 5-5 Ionic mobilities and electronic mobilities of ceria solid solutions (this work) at $x = 0.01$ compared to electronic mobilities reported in literature.
The highest electronic mobilities were found for CCO compared to CSO and CGO, however, even these are slightly lower than any data reported in literature. Possibly the electron mobility in ceria solid solution is diminished by association of electrons and oxygen vacancies. This is also seen from results of Tuller and Nowick [21] who found a decreasing electronic mobility with increasing defect concentration in pure ceria at 1273 K. Since the number of oxygen vacancies in ceria solid solutions is considerably higher than in pure ceria (due to nonstoichiometry and doping) an association would lower the electronic mobility compared to pure ceria.

6. Summary and conclusions

The electrical conductivity of tapecast membranes of ceria solid solutions with calcia (10 at.%), samaria and gadolinia (20 at.%) was measured in the temperature range from 400 to 850 K by impedance spectroscopy in air. From these measurements activation energies for the ionic conductivity in the bulk of 0.98 eV (Ca-doped) to 0.93 eV (Sm-doped) in the temperature region up to 670 K and an activation energy from 0.83 eV (Ca-doped) to 0.70 eV (Sm-doped) in a temperature region of 670 to 1073 K were determined. The activation energy for the grain boundary resistance was 1.02 eV (Sm-doped) to 1.18 eV (Ca-doped) over a temperature range from 450 to 900 K.

By DC 4-pt measurements in an oxygen partial pressure range from 0.21 to 10^{-25} atm over a temperature range from 873 K to 1073 K, electronic and ionic conductivities were determined. These measurements were performed in a Ca-stabilized zirconia cell in which the oxygen partial pressure was adjusted by pumping out oxygen electrochemically.

At high oxygen partial pressure, the conductivity is mainly ionic, but all samples exhibited mixed conduction at low oxygen partial pressures. The electrical domain boundary (σ_e = σ_i) at 973 K is at 1.5·10^{-20} atm for Sm-doped ceria, 10^{-20} atm for Gd-doped ceria and 6·10^{-18} atm for Ca-doped ceria. Combination with nonstoichiometry data (chapter 6) revealed electronic mobilities in Sm, Gd and Ca of 1.76·10^{-3} for Sm-doped, 3·10^{-3} for Gd-doped, and 4.22·10^{-3} for Ca-doped ceria at 973 K. The ratio of ionic to electronic mobility decreases with increasing temperature in favor to higher electronic conductivity. Therefore, it is concluded, that ceria solid solutions are suitable SOFC electrolytes in the temperature range below 1000 K only.
7. References


7. C. Milliken, S. Elangovan, and A.C. Khandkar, in Ref. [1], p. 1049.


6. Nonstoichiometry and Defect Chemistry of Ceria Solid Solutions

Abstract

The nonstoichiometry $x$ of $\text{CeO}_{2-x}$ solid solutions with 20% of $\text{SmO}_{1.5}$ or $\text{GdO}_{1.5}$ and 10% of $\text{CaO}$ was investigated by isothermal coulometric titration using a solid electrolyte zirconia cell in the temperature range from 700 to 900 °C and in the oxygen partial pressure range from $10^{-12}$ to $10^{-25}$ atm.

The nonstoichiometry of the 3 different compositions at 900 °C is comparable to pure ceria. At lower temperatures, however, pure ceria is more stable against reduction than ceria solid solutions. The dependence of nonstoichiometry on oxygen partial pressure suggests a defect model with oxygen vacancies and their associates with reduced cerium cations and dopant cations. At conditions prevailing on the anode side of solid oxide fuel cells the nonstoichiometry of ceria solid solutions is $x = 0.005$ to 0.03 at temperatures of 700 °C to 800 °C.

1. Introduction

Ceria and ceria solid solutions are reduced and become nonstoichiometric under the conditions prevailing at the anode side of solid oxide fuel cells (SOFC). The reduction of ceria introduces free electrons responsible for mixed ionic electronic conductivity. Furthermore, it leads to an isothermal expansion of the material which can cause mechanical failure of ceria-based SOFC membranes and delamination of the electrodes.

The nonstoichiometry of pure undoped ceria was investigated intensively [1 - 21]. Most of these studies were carried out using thermogravimetical methods [1-5] or solid state
coulometric titration [8, 9] to determine the extent of nonstoichiometry. For ceria solid solutions on the other hand only limited nonstoichiometry studies exist. Garnier et al. [10] and Park et al. [11] measured the reducibility of Ca substituted ceria at 800 - 1500 °C by thermogravimetry and at temperatures between 850 and 920 °C by coulometric titration, respectively. For Gd substituted ceria, the nonstoichiometry at 1000 °C was investigated by Zachau-Christiansen et al. [12].

It was shown by Bevan and Kordis [1], that pure ceria retains its cubic fluorite structure up to a nonstoichiometry of $x = 0.22$ at temperatures above 685 °C. The partial enthalpy of oxygen, $\Delta H(O_2)$, was calculated as $\sim -9.8$ eV for small nonstoichiometries ($\log x = -2.6$) of pure ceria by Sorensen [4]. This is in good agreement with values found by Panlener et al. [2], who found values around $-10$ eV for small deviations from stoichiometry ($\log x = -2.8$). For 10% calcia substituted ceria on the other hand a partial enthalpy of oxygen of $-8.64$ eV at $\log x = -2.59$ was found by Park et al. [10]. Different defect chemical models were suggested to describe the dependence of the nonstoichiometry on the oxygen partial pressure [2, 8, 13]. Panlener et al. [2] and Panhans et al. [8] suggested a model considering only doubly ionized oxygen vacancies without consideration of defect interactions. Tuller and Nowick [13] used a model including interactions between oxygen vacancies and quasi-free electrons introduced by deviation from nonstoichiometry also.

The purpose of this study is to determine the nonstoichiometry of ceria solid solutions under SOFC operating conditions and to elucidate the dependence of nonstoichiometry on the oxygen partial pressure by a defect chemical model. The extent of reduction is also needed for the proper description of solid oxide fuel cells based on an electrolyte with mixed ionic electronic conductors over
Nonstoichiometry data of ceria solid solutions are obtained by solid state coulometric titration with a glass-sealed solid electrolyte coulometric titration cell. The experimental setup is described in section 2. In section 3 and 4 the results are presented and interpreted by a defect chemical model considering also defect interactions. A summary is given in section 5.

2. Experimental

2.1 Powder Preparation

Ce$_{0.9}$Ca$_{0.1}$O$_{1.9-x}$ was prepared by wet-chemical coprecipitation from nitrate precursors. An aqueous solution ([Ce$^{3+}$] = 1 M, [Ca$^{2+}$] = 0.11 M) of Ce$^{III}$(NO$_3$)$_3$·6H$_2$O (>99%, Fluka, Buchs, CH) and Ca(NO$_3$)$_2$·4H$_2$O (>99%, Merck, Darmstadt, FRG) was precipitated with a 0.47 M solution of ammonium oxalate (>99.5%, Fluka) at 45 °C. This solution was washed three times with water at a pH of 8 and calcined at 750 °C for 2 hrs. Ce$_{0.8}$Sm$_{0.2}$O$_{1.9-x}$ was prepared under the same conditions with a Sm-nitrate solution prepared from Sm$_2$O$_3$ (>99%, Rhône-Poulenc, La Rochelle, F) dissolved in hydrochloric acid. Ce$_{0.8}$Gd$_{0.2}$O$_{1.9-x}$ powder was obtained from Rhône-Poulenc (Lot. No. 94007/99, La Rochelle). The exact procedure for the powder preparation is given in chapter 4. The composition was verified by microprobe analysis and by EDX. Composition of the samples is given in Tab. 6-1. Pure ceria powder was obtained from a commercial source (>99.9%, Aldrich, Milwaukee, WI, USA).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Composition [atom %]</th>
<th>Specific surface BET [m$^2$/g]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce$<em>{0.8}$Sm$</em>{0.2}$O$_{1.9}$</td>
<td>18.8 Sm 81.2 Ce</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{1.9}$</td>
<td>19.6 Gd 80.2 Ce</td>
<td>16.6</td>
</tr>
</tbody>
</table>
Nonstoichiometry

<table>
<thead>
<tr>
<th></th>
<th>0.2 La</th>
<th>9.9 Ca</th>
<th>10.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ce₀.₉Ca₀.₁O₁.₉</td>
<td>88.9 Ce</td>
<td>1.2 Zr</td>
<td></td>
</tr>
</tbody>
</table>

**Tab. 6-1** Composition and specific surface area of the powder samples used for coulometric titration.

2.2 Solid-state coulometric titration

2.2.1 Experimental setup. The experimental setup with the coulometric titration cell is shown in Fig. 1. The cell consists of an alumina tube 14.5 mm in diameter 20.8 mm high, which is closed at one end. The top of the cell is an 8 mole% yttria stabilized zirconia (YSZ) solid electrolyte disk with a thickness of 1 mm. On both sides of the electrolyte platinum paste (Heraeus C 3605 S) was applied as electrodes. The inner electrode was connected to the measurement circuit through the seal. Ceria solid solutions were filled into the cavity. It is well known, that Ce³⁺ tends to react with alumina to form cerium aluminate CeAlO₃ \[1\], however this reaction is only observed at temperatures above 1450 °C.

The measurement setup consists of a programmable power supply (GPM 6030, Good Will Instrument CO., Taiwan) and a scanning digital multimeter (Keithley, DMM 2001) equipped with a 10 channel scanning card for the detection of electrical current and EMF. The measurement is controlled by an IBM compatible personal computer connected to the measurement devices by an IEEE-bus. The measurement of the EMF and the integration of current after time was accomplished by the measurement program written in Basic™. The sample was placed in an electrically heated furnace and the temperature was controlled by a thermocouple placed on top of the solid electrolyte. The solid electrolyte with
the platinum electrodes (Fig. 1) served as both oxygen pump and EMF sensor.

![Diagram of solid electrolyte coulometric titration cell](image)

**Fig. 6-1** Solid electrolyte coulometric titration cell for the nonstoichiometry measurements.

2.2.2 Measurement. Approximately 4 g of sample powder was weighted into the cell. To seal the cell an organic slurry containing a glass (Cerdec 90016, Degussa, Frankfurt, FRG) with a good wettability [15] for zirconia as well as for alumina was applied between the alumina crucible and the electrolyte. The slurry consisted of a mixture of ethanol (23 wt.%) PVB (2 wt.% Mowital B20H, Hoechst, Frankfurt, FRG) and the glass powder (75 wt.%). The cell was heated to 920 °C and then slowly cooled down to 900 °C. In a first coulometric titration run oxygen was removed from the cell. The gas-tightness of the cell was verified by following the EMF vs. time. When a steady state was reached, i.e. the EMF decreased by less than 0.3 mV/min the cell was judged to be sufficiently gas-tight. If the EMF change was higher the cell was again cooled down to
room-temperature and another layer of glass paste was applied. This procedure was repeated until a gas-tight cell was obtained. For this easy cell assembly only about 20% of the cells were gas-tight for the first time and the sealing procedure had to be performed up to 5 times to obtain gas-tight cells.

The oxygen content in nonstoichiometric ceria is changed by the electrochemical reaction

\[ \text{CeO}_2 - x \cdot O^\oplus \leftrightarrow \text{CeO}_{2-x} + 2e^- \]  

(6-1)

where the oxygen content of the sample can be changed by electrochemically pumping out oxygen from or to the solid electrolyte cell (Coulometric titration). The electrical charge \( Q \) which is exchanged during the titration is given as

\[ Q = I \cdot t \]  

(6-2)

where \( I \) is the electrical current across the solid electrolyte. By integration of this current over time the total electrical charge is obtained. However, in this calculation we neglect the charge which might be exchanged due to the minor n and p type electronic conductivity of the YSZ solid electrolyte. From the exchanged electrical charge the exchanged amount of oxygen is calculated as

\[ n(O^\oplus)_{\text{tot}} = \frac{I \cdot t}{2 \cdot F} \]  

(6-3)

where \( F \) is the Faraday constant. From this value \( n(O_2) \), the amount of gaseous oxygen which is contained in the titration cell before measurement has to be subtracted and the amount of oxygen removed from the sample is then given as

\[ n(O^\oplus) = n(O^\oplus)_{\text{tot}} - 2 \cdot n(O_2) \]  

(6-4)

where oxygen is treated as an ideal gas. The nonstoichiometry of the material is expressed as

\[ x = \frac{n(O^\oplus)}{\delta \cdot \frac{m}{M}} \]  

(6-5)
In Eq. (5) $\delta$ denotes the stoichiometric composition of ceria solid solutions, i.e. $\delta = 2-y/2$ for trivalent dopants (Sm, Gd) and $\delta = 2-y$ for divalent dopants (Ca). $M$ is the weight of the sample material per formula unit (g/mol) and $m$ is the sample mass (g). By measuring the electromotive force of the titration cell the corresponding equilibrium oxygen partial pressure is determined by the Nernst equation.

The cell was cooled down to measurement temperature at 0.5 °C/min. Cooling rates higher than this value led to cracking of the glass seal, especially at temperatures below 800 °C. After reaching the measuring temperature of 700, 800 or 900 °C, the cells were held at this temperature for at least 30 min to allow for temperature stabilization. The cells were short circuited until the EMF was zero, i.e. the oxygen partial pressure at the inner electrode corresponded to the one at the outer electrode. The composition of the samples was assumed to be stoichiometric under these conditions.

For the nonstoichiometry measurements oxygen was removed from the cell at a current of 5 to 15 mA, where the exact amount of oxygen was determined by integration of the electrical current over time. After a preset time the current was switched off and the stabilization of the EMF over time was observed until equilibrium was reached. An equilibrium criterion was introduced, where a change of EMF of less than 0.2 - 0.3 mV per minute was taken as equilibrium criterion. Normally the equilibrium criterion was fulfilled after 60 - 200 min at 700 °C and 40 - 80 min at 900 °C.

Measurements were carried out with Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$, Ce$_{0.8}$Gd$_{0.2}$O$_{1.9}$ and Ce$_{0.9}$Ca$_{0.1}$O$_{1.9}$ at 700, 800 and 900 °C. A typical example of the time needed for equilibration is given in Fig. 6-2 for a Ce$_{0.8}$Gd$_{0.2}$O$_{1.9-x}$ sample at 700 °C. A measurement run with the titration period (a) and the equilibration period (b) is given in Fig. 6-3 for Ce$_{0.9}$Ca$_{0.1}$O$_{1.9-x}$ at 700 °C.
Fig. 6-2  EMF measured over the YSZ-electrolyte after the titration current was switched off (t =0) for different titration runs (Ce$_{0.8}$Gd$_{0.2}$O$_{1.9-x}$ at 700 °C).
3. Results and discussion

The dependence of the nonstoichiometry on the oxygen partial pressure was calculated according to Eqs. (6-3 - 6-5). The nonstoichiometry, \( x \), versus \( p(O_2) \) is shown in Figs. 6-4 a to c for 900, 800, and 700 °C. For comparison literature data [2] for pure CeO\(_{2-x}\) are given also. Among the different ceria solid solutions only small differences in nonstoichiometry are found. The difference between the ceria solid solutions and pure ceria, however, increases with decreasing temperature. At 900 °C pure ceria and ceria solid solutions show the same stability against reduction. At lower temperatures pure ceria is more stable than ceria solid solutions, i.e. the partial enthalpy of oxygen is higher for pure ceria than for its solid solutions. This finding is in accordance with findings of Sorensen [4], and Park et al. [2], who found a partial enthalpy of oxygen of -9.8 to -10 eV at \( \log(x) = 2.6 \) for pure ceria, and Garnier [10] or Park [11], who found a partial enthalpy of oxygen of -8.64 eV for 10% CaO doped ceria (\( \log(x) = 2.6 \)).

Assuming a simple defect model as presented in section 4 of this chapter (see Eq. (6-12) to (6-15)) a partial enthalpy of oxygen \( \Delta H(O_2) \) of -7.45 eV is found for Ce\(_{0.8}Gd_{0.2}O_{1.9-x}\), -7.26 eV for Ce\(_{0.9}Ca_{0.1}O_{1.9-x}\), -7.24 eV for Ce\(_{0.8}Sm_{0.2}O_{1.9-x}\) at \( \log x = -2.6 \).

For comparison coulometric titration measurements with pure CeO\(_{2-x}\) were carried out at 900 °C and compared to literature data obtained by thermogravimetric measurements. Fig. 6-5 shows a plot of nonstoichiometry against oxygen partial pressure for pure CeO\(_{2-x}\). The data obtained for pure ceria in this work are in good agreement with the literature data [2, 4]. The slope of the curves in fig. 6-5 was found to increase from \(-1/5\) at higher oxygen partial pressures to \(-1/2\) at
p(O_2) around 10^{-16} atm. At oxygen partial pressures lower than 10^{-18} atm the slope decreases again. In Fig. 6-6 the reciprocal of the slope of log(x) vs. -log(p(O_2)) is plotted at 900 °C. It is given as 
\[ m(x) = \frac{d\log p(O_2)}{d\log(x)} \]. For pure ceria (Ref. [2]) and Ce_{0.9}Ca_{0.1}O_{1.9-x} a minimum of m(x) is observed at x 0.02 and x 0.05, respectively. For Ce_{0.8}Gd_{0.2}O_{1.9-x} m(x) increases from 4 at lower nonstoichiometries to values comparable to pure ceria and Ce_{0.9}Ca_{0.1}O_{1.9-x}. In the next section defect chemical modes are presented to explain this behavior. Values for Ce_{0.8}Sm_{0.2}O_{1.9-x} are not included, since due to the lack of enough data points, they show considerable scattering.

![Graph showing the dependence of nonstoichiometry of ceria solid solutions and pure ceria at 900 °C.](image_url)

**Fig. 6-4a** Dependence of nonstoichiometry of ceria solid solutions and pure ceria at 900 °C.
**Fig. 6-4b** Dependence of nonstoichiometry of ceria solid solutions and pure ceria at 800 °C.

**Fig. 6-4c** Dependence of nonstoichiometry of ceria solid solutions and pure ceria at 700 °C.
Fig. 6-5  Dependence of nonstoichiometry on oxygen partial pressure compared to literature data from thermogravimetric measurements at 900 °C.

Fig. 6-6  Slope of $m(x) = d \log p(O_2) / d \log(x)$ for pure CeO$_{2-x}$ [2], Ce$_{0.8}$Gd$_{0.2}$O$_{1.9-x}$ (CGO) and Ce$_{0.9}$Ca$_{0.1}$O$_{1.9-x}$ (CCO) at 900 °C.
4. Defect models

In this section defect models are derived for pure ceria and ceria solid solutions with divalent or trivalent dopants. First a simple defect model is presented which, however, cannot explain the different slopes of the nonstoichiometry curves presented in Fig. 6-5 in section 3. Therefore, in a second step the simple model is extended to a more complex model allowing also defect interactions.

4.1 Simple Defect Model

The overall reduction reactions for ceria solid solutions are for divalent dopants (e.g. Ca$^{2+}$)

\[
Ce_{1-y}Ca_yO_{2-y} \leftrightarrow Ce_{1-y}Ca_yO_{2-y-x} + \frac{x}{2}O_2(g)
\]  
(6-6)

For trivalent dopants (e.g. Sm$^{3+}$) this reaction is

\[
Ce_{1-y}Sm_yO_{2-y} \leftrightarrow Ce_{1-y}Sm_yO_{2-y-x} + \frac{x}{2}O_2(g)
\]  
(6-7)

The site fractions of the different species can be expressed as follows:

\[
[Ce_Ce^x] = 1 - y - 2x
\]  
(6-8)

\[
[Ce_Ce'] = 2x
\]  
(6-9)

\[
[O_\theta^y] = \frac{1}{2}(2 - x - y) \quad \text{and} \quad [V_{\theta}^{**}] = \frac{1}{2}(x + y) \quad \text{for divalent dopants}
\]  
(6-10a)

\[
[O_\theta^y] = \frac{1}{2}(2 - x - \frac{y}{2}) \quad \text{and} \quad [V_{\theta}^{**}] = \frac{1}{2}(x + \frac{y}{2}) \quad \text{for trivalent dopants}
\]  
(6-10b)

The reduction reaction in Kröger-Vink notation is

\[
2Ce_Ce^x + O_\theta^y \xrightarrow{K_I} 2Ce_Ce' + V_{\theta}^{**} + \frac{1}{2}O_2(g)
\]  
(6-11)

The mass action constant associated with the above reaction for divalent dopants is given as

\[
K_I(Ca) = \frac{4x^2 \cdot (x + y)}{(1 - y - 2x)^2 \cdot (2 - y - x)} \cdot p(O_2)^{1/2}
\]  
(6-12)
For trivalent dopants the mass action constant is given as
\[ K_f(Sm) = \frac{4x^2 \cdot (x + \frac{y}{2})}{(1 - y - 2x)^2 \cdot (2 - \frac{y}{2} - x)} \cdot p(O_2)^{1/2} \]  
(6-13)

The corresponding relative Gibb's free energy of oxygen \( \Delta G(O_2) \) can be given as
\[ \Delta G(O_2) = 2kT \ln(K_f) \]  
(6-14)

From a fit of \( \ln(K_f) \) against \( 1/T \) one can obtain the corresponding relative enthalpy and entropy of oxygen according to
\[ \Delta G(O_2) = \Delta H(O_2) - T \Delta S(O_2) \]  
(6-15)

Values for the relative enthalpy of oxygen are given already in section 3, but since only three temperatures were measured they are not very accurate.

Simplifying the relation between \( p(O_2) \) and \( x \) (Eq. (6-13) under the assumption that doubly ionized vacancies are dominating and defect interaction can be neglected we get
\[ x \propto p(O_2)^{-1/m(x)} \]  
(6-16)

where \( m(x) \) is the reciprocal slope in the plot \( \log(x) \) vs. - \( \log(p(O_2)) \) for di-valent dopants
\[ m(x) = \frac{d \log(p(O_2))}{d \log(x)} = 4 + \frac{2x}{x + y} + \frac{8x}{1 - y - 2x} + \frac{2x}{2 - y - x} \]  
(6-17)

and for trivalent dopants
\[ m(x) = \frac{d \log(p(O_2))}{d \log(x)} = 4 + \frac{2x}{x + \frac{y}{2}} + \frac{8x}{1 - y - 2x} + \frac{2x}{2 - \frac{y}{2} - x} \]  
(6-18)

From Eqs. (6-17) and (6-18) it follows, that for small deviations from stoichiometry the slope \( \log(x) \) vs. \( \log(p(O_2)) \) is \( 1/m(x) \) = 1/6 for pure CeO\(_{2-x}\) and 1/4 for ceria solid solutions with divalent and trivalent dopants (\( y >> x \)). In Fig. 6-7 the calculated reciprocal slopes \( m(x) \) for pure and doped ceria are shown. Using the simple defect model an increasing reciprocal slope \( m(x) \) is expected for increasing nonstoichiometry. This is in contradiction to