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Electrochemical properties of $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ in reducing and oxidizing conditions

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*Dedicated to my brother Alexander,
for showing me the beauty of science.*

Abstract

$La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF64) is a mixed ionic electronic conductor with a potential use as electrode material in solid oxide fuel and electrolysis cells. Due to its comparatively high thermo-chemical stability over a wide oxygen partial range, it can not only be used under oxidizing, but also under reducing conditions.

In this thesis the impact of oxidizing and reducing atmospheres on LSF64 was characterized using well-defined electrodes in impedance spectroscopy, oxygen isotope exchange and subsequent time-of-flight secondary ion mass spectrometry (TOF-SIMS) as well as high temperature *in-situ* powder X-ray diffraction (XRD).

Impedance spectra of well-defined thin film LSF64 microelectrodes revealed an electronic sheet resistance under reducing conditions. However, this sheet resistance can be overcome by the use of an additional current collector. In analogy to *Ni/YSZ* cermet, the ion conducting LSF64 is combined with an electronic conducting current collector. In this work well-defined platinum current collector structures were applied. Different geometries of current collectors as well as their positioning on top and beneath the film are discussed. Astonishingly, with the sheet resistance being compensated the electrode resistance and accordingly the oxygen exchange kinetics, is similar in both atmospheres. In air rather fast degradation of the electrochemical activity is found. Impedance measurements under cyclic gas change on micro- as well as macroscopic electrodes show that the gas change to reducing atmosphere can regenerate the surface to a state of higher oxygen exchange kinetics, i.e. H_2/H_2O can annihilate the previous degradation in air. The chemical capacitance, from the measured

thin-film electrodes, is in good accordance with that calculated from the defect model, using the relationship between oxygen partial pressure (p_{O_2}) and oxygen non-stoichiometry (δ) as found in literature. Despite the high thermo-chemical stability of LSF64, all electrodes show a long-term degradation in surface kinetics.

The degradation was investigated by additional *in-situ* high temperature X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) measurements. XRD on LSF64 powder was performed under different atmospheres with temperatures up to 800 °C. The diffraction patterns show decomposition in dry hydrogen and the formation of a small amount of secondary phases under reducing conditions: iron oxides and Ruddlesden-Popper phases. XPS measurements on LSF64 thin films on yttria stabilized zirconia (YSZ) suggest a slight enrichment of strontium towards the surface.

Oxygen isotope exchange confirmed the findings from the electrochemical measurements, namely that the oxygen exchange kinetics is similar under oxidizing and reducing conditions. The oxygen diffusivity was found to be higher under reducing conditions, which is to be expected due to a higher concentration of oxygen vacancies.

Kurzfassung

$La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF64) ist ein gemischt ionisch-elektronisch leitendes Material mit hoher Stabilität über einen weiten Temperatur und Sauerstoffpartialdruckbereich. Diese hohe Stabilität ermöglicht den Einsatz von LSF64 in oxidierenden als auch reduzierenden Bedingungen. Diese Eigenschaften machen es interessant für den Einsatz als Elektrodenmaterial in Festoxidbrennstoffzellen oder auch Elektrolysezellen.

In dieser Arbeit wurden die Eigenschaften von LSF64 in oxidierender und reduzierender Atmosphäre untersucht. Hierfür wurden Impedanzmessungen und Sauerstoff-Isotopen-Austauschexperimente an definierten Dünnschichtelektroden und Röntgenstreuung an LSF64 Pulver durchgeführt.

Für die elektrochemische Untersuchung wurden definierte mikroskopische und makroskopische Dünnschichtelektroden mittels Laserablation hergestellt. Es wurde festgestellt, dass unter reduzierender Atmosphäre die Elektroden nicht vollständig polarisiert werden, da die elektrische Leitfähigkeit unter diesen Bedingungen zu gering ist. Um den Schichtwiderstand zu kompensieren wurden definierte Platin-Gitter als Stromsammler verwendet. Die Kombination aus einem ionisch leitenden Material und elektronisch leitenden Stromsammlern ist den in der Praxis unter reduzierenden Bedingungen verwendeten Ni/YSZ Cermet Elektroden ähnlich. In den Messungen wurde die Geometrie und die Positionierung der Stromsammler (über oder unter den Dünnschichtelektroden) variiert, um möglichst viele Informationen über den Effekt des metallischen Stromsammlers auf das Impedanzspektrum sowie über die elektrochemischen Vorgänge an der Elektrode zu erfahren. Es konnte

gezeigt werden, dass mittels Stromsammler zumindest ein großer Teil der Elektrode polarisiert wird. Die kinetischen Parameter einer Elektrode mit Stromsammler in reduzierenden Bedingungen sind sehr ähnlich den gemessenen Parametern einer vergleichbaren Elektrode in Luft. Die aus den Impedanzspektren bestimmte chemische Kapazität wurde mit der aus dem Defektmodel berechneten Kapazität verglichen. Dabei stellte sich heraus, dass es eine gute Übereinstimmung zwischen diesen Werten gibt. Bei Versuchen mit zyklischen Gasaustausch zwischen synthetischer Luft und befeuchteten Wasserstoff zeigte sich, dass die Elektrodenoberfläche in Luft stark degradiert. Diese Degradation kann durch den Gaswechsel zu reduzierenden Bedingungen wieder rückgängig gemacht werden. Ein leichter Drift zu höheren Elektrodenwiderständen bleibt allerdings erhalten.

Die Gründe für die Degradation der Elektroden wurden mittels *in-situ* Hochtemperatur-Röntgenbeugung untersucht. Dabei wurde gasumspültes LSF64 Pulver auf bis zu 800 °C in verschiedenen Atmosphären erhitzt. Während sich LSF64 in trockenem Wasserstoff zersetzt, bildet es in befeuchtetem Wasserstoff lediglich kleinere Anteile an Sekundärphase, Eisenoxide und eine Ruddlesden-Popper-Phase, aus. In trockenem Wasserstoff kommt es zu einer Zersetzung des Perovskits. Zusätzliche Röntgenphotoelektronenspektroskopie an LSF64 Dünnschichten deutet auf eine Anreicherung der Oberfläche mit Strontium nach längeren Temperaturen unter reduzierenden Bedingungen hin.

Zusätzlich wurde die Sauerstoffaustauschkinetik mittels Sauerstoffisotopenaustausch untersucht. Dabei wurden die Ergebnisse der Impedanzmessungen, dass die Austauschkinetik unter reduzierenden und oxidierenden Bedingungen etwa gleich schnell ist, weitgehend bestätigt. Zusätzlich wurde festgestellt, dass wegen einer erhöhten Sauerstoffleerstellenkonzentration unter reduzierenden Bedingungen die Sauerstoff Diffusivität höher ist als in oxidierenden Bedingungen.

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Motivation

Solid oxide fuel cells (SOFCs) transform chemically bound energy from a fuel into electrical power. Due to their high efficiency and fuel flexibility SOFCs are among the most attractive and versatile power generation systems [1]. As fuel not only hydrogen but also hydrocarbons can be fed into the cells directly [2]. Solid oxide electrolysis cells (SOEC) are in principal SOFCs operated in the opposite direction, to produce fuel from electrical energy. As fuel can be stored easily, SOECs are ideal candidates as complementary technology for future energy systems as they can transform exhaust energy from the grid into easily storable fuel. Upon demand this fuel can be transformed into electrical energy by SOFCs. The trend towards SOFCs and SOECs can also be seen in an exponential increase in research activities since the 1990's [3].

Much research is focused on explaining the ongoing electrochemical reactions and finding new electrode materials as those are the weak point of commercially available SOFCs. Currently Ni/YSZ cermet is the standard material for electrodes in reducing conditions. However, Ni/YSZ electrodes suffer from sulphur poisoning, sintering, cycle stability, etc. [4], [5]. Thus it would be highly favourable to find an alternative electrode material for the use under reducing conditions.

In contrast to Ni/YSZ, where only the triple phase boundary (TPB) is active, mixed ionic electronic conductors (MIECs) show a higher active surface area for the oxygen exchange reaction [6], [2]. Accordingly, finding a MIEC with a high catalytic activity towards the oxygen exchange reaction

as alternative for Ni/YSZ would be advantageous. Such a material would further need a high thermochemical stability over a wide oxygen partial pressure range.

State of the art SOFC/SOEC commonly use perovskite type materials under oxidizing conditions, as many of them exhibit a mixed ionic electronic conductivity and a high catalytical activity. However, many of these oxides are not stable under reducing conditions, like Sr-doped $LaMnO_{3-\delta}$ or $LaCoO_{3-\delta}$ [7], [8], [9]. Several stable perovskite type oxides have been tested under reducing conditions [6], like $(La, Sr)(Mn, Co)O_3$ [10], [11], [12], [13], $(La, Sr)(Co, V)O_3$ [14], [15], $(La, Sr)(Cr, Ru)_3$ [16], [17] or La and Fe doped $SrTiO_3$ (STO) [18], [19].

Lanthanum ferrites, due to their electronic configuration, are expected to be more stable than the cobaltite perovskites [6]. The composition $La_{0.6}Sr_{0.4}FeO_{3-\delta}$ (LSF64), for example, is highly stable over a wide temperature and oxygen partial pressure range [20] [21], [22]. Further, temperature expansion coefficients (TECs) in ferrite perovskites are relatively similar to those of YSZ and gadolinium-doped ceria (CGO) electrolyte [6], [20], [23]. Strontium doped lanthanum ferrites (LSF) only react with the YSZ electrolyte above 1100 °C under formation of $SrZrO_3$ [24]. Owing to its potential use in air LSF has already been investigated intensively [25], [26], [27], [28], [29], [30], [31], [32], [33], [34], [35]. However, it has a high potential for the use in reducing conditions in SOF/ECs and as oxygen membrane material [27]. Also, first tests in a SOEC were performed [36]. However, a thorough study on the impact of reducing atmospheres as well as the effect of gas changes between oxidizing and reducing atmospheres on the properties of LSF64 has not been performed yet.

In this work, impedance spectroscopy on well-defined thin film electrodes was employed to characterize the electrochemical properties under different conditions with emphasis on LSF64 in H_2/H_2O gas phase. A metallic current collector helps to overcome the sheet resistance under reducing atmosphere. A similar approach has already been made with ceria-based electrodes [37] and STO model thin film electrodes [38]. As surface chemistry can differ from the bulk and it is very likely to change under different

operational modes and/or atmosphere [39] high-temperature *in-situ* powder X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) was used to identify the possible sources of fast oxygen exchange kinetics as well as degradation effects. The electrochemical properties were also probed by oxygen isotope exchange experiments. For the isotope exchange under reducing conditions a tracer back-exchange as well as isotope incorporation from tracer marked water are used.

Fundamentals

2.1 Defects in solids

Defects in crystals significantly influence many properties like conductivity, mechanical stability and optical properties. They appear even in the purest crystals and therefore have to be considered whenever investigating a crystalline material. Understanding the nature of these defects can be used to optimize a material for its application and will also help to prevent failure.

The different types of structural defects are classified according to their dimensionality:

- **zero-dimensional defects or point defects**
mistakes in the lattice like a missing atom
- **one-dimensional or linear defects**
dislocations
- **two-dimensional or planar defects**
external and internal surfaces and interfaces
- **three-dimensional or volume defects**
point defect clusters or precipitates, pores

From the above mentioned defect types, point defects are particularly important in perovskite-type SOFC/EC electrodes, as they can introduce conductivity and diffusion in these materials and are involved in electrochem-

ical surface reactions. Therefore point-defects are described in more detail in the next section.

2.1.1 Point defects

According to their origin, point defects subdivide in intrinsic and extrinsic defects. Intrinsic defects occur even in a pure crystal, while extrinsic defects are caused by impurities or dopands. Although several point defects are possible in a material, usually only a small number is present and determines the physical and chemical properties.

Due to their importance a notation for point defects was developed by Kröger and Vink[40]. The lattice of the pure, defect-free crystal is defined as the host lattice, so that each site in a lattice has a defined species and charge. Fig. 2.1 shows the general structure of the notation, table 2.1 gives the used symbols.

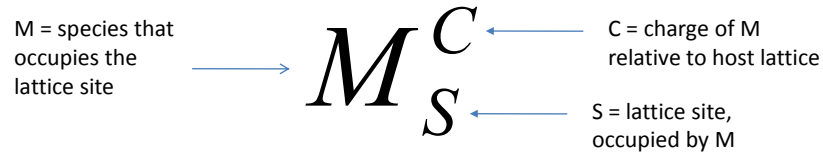


Figure 2.1: *Principle of Kröger Vink notation.*

M	symbol
ion	element symbol
vacant site	V
S	symbol
ion	element symbol
interstitial	i
C	symbol
relative positive charge	·
relative neutral charge	x
relative negative charge	/

Table 2.1: Symbols used in Kröger Vink notation: possible species (M) that occupies a lattice site (S) and its charge (C) relative to the host lattice.

Electrons and electron holes can be accounted for in two ways: either as e' and $h^\bullet$ or as an oxidation state of an ion. The latter form is usually used to emphasize if a charge is rather localized as is the case for polarons.

Intrinsic defects

The formation of defects is thermodynamically favoured since it increases configuration entropy. Consequently defect concentration rises with increasing temperature. Two common types of point defect formation in ionic crystals are shown in Fig. 2.2:

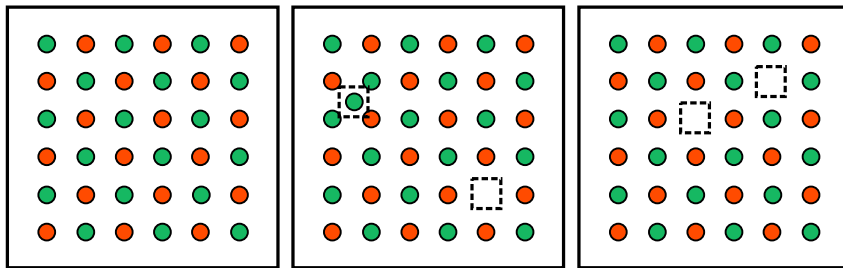


Figure 2.2: Schematic of (a) a perfect crystal lattice (b) Frenkel disorder and (c) Schottky disorder.

- Frenkel disorder: vacancies and interstitials of the same cation are formed; if vacancies and interstitials of an anion are formed the term anti-Frenkel disorder is used.
- Schottky disorder: cation vacancies are charge balanced by anion vacancies.

Each of these defects is charged relative to the lattice, however charge neutrality is ensured as they are created in pairs of opposite relative charge. The most common intrinsic defects are interstitials (atoms that occupy non-lattice sites) and vacancies (missing atoms). In addition to structural defects electronic defects, like electrons or electron holes, exist.

Charge transport in crystalline materials can be electronic, by electrons and electron holes, or ionic, by charged point defects like vacancies or interstitials. Even a combination of both types of conductivity is found in some materials, which is referred to as mixed ionic electronic conductivity (MIEC).

Extrinsic defects

Extrinsic defects are distinguished by their cause. If they are undesirable and/or added accidentally they are called impurities, but if they are added deliberately to manipulate the properties of a material, they are called dopands. In doped ceramics, where the dopand is usually added in the percentage range, the intrinsic defect concentration is often negligible compared to the extrinsic defect concentration.

In ceramics used in electrochemical cells doping is often used to enhance ionic or electronic conductivity. This is achieved by the addition of alio-valent ions, which are compensated by structural defects, incorporation of interstitials or vacancies, or by electronic defects (electrons or electron holes). Ionic compensation is typical for compounds with cations of fixed valence, while cations with more possible valence states also can compensate the dopands electronically.

There are two types of dopands

- **donor dopands:** the added ions are higher in valence than the host-lattice ions and therefore are relatively positive charged. Charge neutrality is reached by counterbalancing with electrons (enhancing n-type conductivity), cation vacancies or anion interstitials.
- **acceptor dopands:** the doping ions are lower in valence than the host-lattice ions, therefore the acceptor species is effectively negative charged. Balancing defects are electron holes (enhancing p-type conductivity), cation interstitials or anion vacancies.

Non-stoichiometry

Non-stoichiometry can result from a reaction with the surrounding atmosphere. Oxides will equilibrate with the atmosphere at sufficiently high temperatures.

For high oxygen partial pressures oxygen from the atmosphere is incorporated into the lattice:



At low oxygen partial pressures, on the other hand, oxygen is released from the lattice, leaving oxygen vacancies and electrons in the lattice:



In contrast to that, oxides with large interstitial sites can form oxygen interstitials under high oxygen partial pressures.

Ionic defects will change the volume of a crystal. Vacancies, although being missing atoms, can increase the lattice, due to repulsion of equal charges of ions and neighbouring sites. Also the reduction of the charge compensating cations increases their ionic radius. The formation of such defects depends upon temperature and the surrounding atmosphere, within the stability range of the oxide. The relative charge introduced by oxygen vacancies or interstitials is often balanced by electrons or electron holes. Accordingly, compounds with cations of multiple possible valence states are more likely to exhibit non-stoichiometry.

Brouwer diagram

Brouwer diagrams depict defect concentrations or conductivities as function of oxygen partial pressure for a fixed temperature. Concentrations instead of activities can be plotted if the assumption is made that there is no defect interaction. Further, only one defect reaction is considered to be dominant in any particular composition region ([41]).

Brouwer diagram for an undoped oxide

For a simple oxide $MO_{1-\delta}$, where oxygen vacancies $V_O^{\bullet\bullet}$ and cation vacancies $V_M^{\bullet\bullet}$ are the dominating ionic defects, the exact stoichiometric composition is given when $V_M^{\bullet\bullet} = V_O^{\bullet\bullet}$ (region (II) in Fig. 2.3). When the solid becomes non-stoichiometric, electrons e' (region (I)) or electron holes $h^{\bullet}$ (region (III)) help to maintain charge neutrality.

Towards lower oxygen partial pressures (region I), oxygen will be released from the lattice, forming electrons and oxygen vacancies (see reaction 2.2). Consequently, the concentration of electrons and oxygen vacancies rises in region I, while the concentration of cation vacancies decreases. The de-

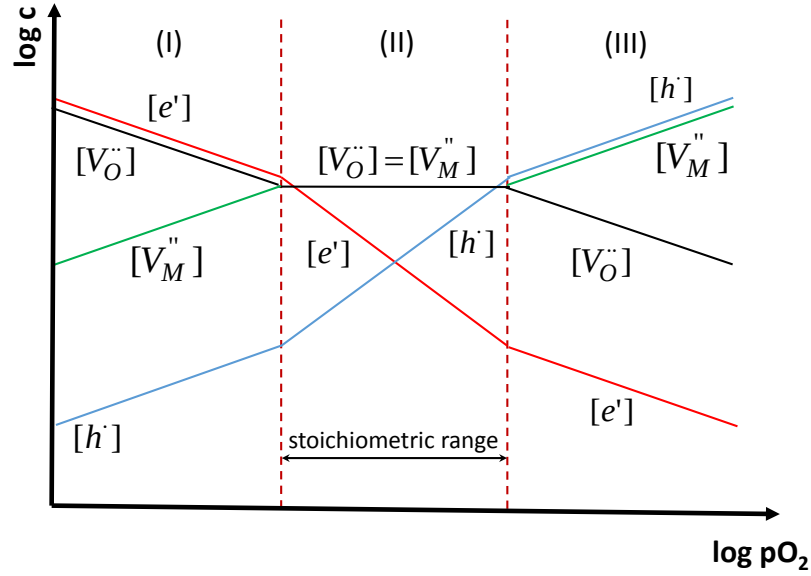
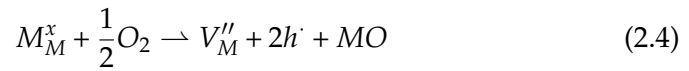


Figure 2.3: Schematic Brouwer diagram for an undoped $MO_{1\pm\delta}$.

crease in electron hole concentration is due to the annihilation of electron holes with electrons according to:



Towards higher oxygen partial pressures cationic vacancies and electron holes are formed, while oxygen vacancies are consumed



Brouwer diagram for a doped oxide

Brouwer diagrams can be extended to cover extrinsic defects, see Fig. 2.4. If we acceptor-dope the $MO_{1\pm\delta}$ from above with a monovalent A^+ cation, we obtain A_M' defects. This changes the condition of electroneutrality from

$$2[V_M''] + [e'] = 2[V_O'] + [h'] \quad (2.5)$$

to

$$2[V_M''] + [e'] + [A_M'] = 2[V_O'] + [h'] \quad (2.6)$$

The acceptor doping can be balanced by oxygen vacancies or electron holes $h^\cdot$.

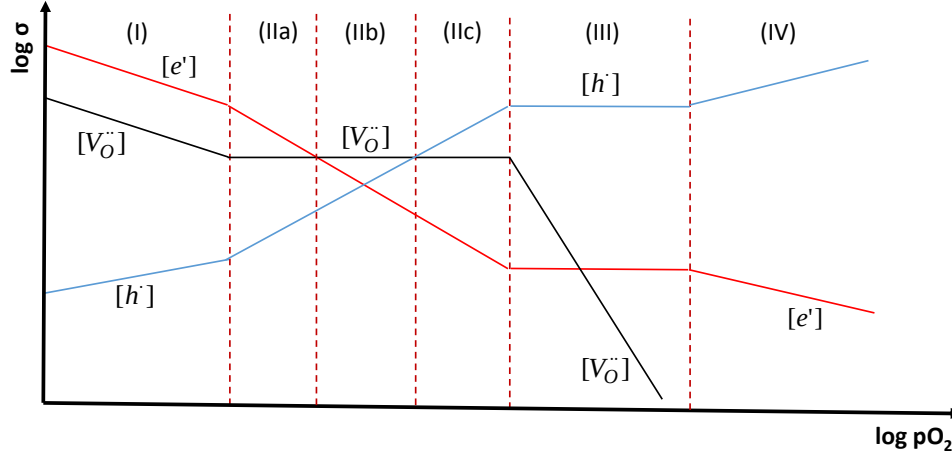


Figure 2.4: Brouwer diagram, showing conductivities, for A-doped $MO_{1-\delta}$.

For the acceptor doped oxide the conductivity at low oxygen partial pressures is given by electrons (region I in Fig. 2.4). Towards higher oxygen partial pressures the concentration of electrons, and hence the conductivity by electrons, decreases. In region II, the oxygen vacancies are the majority charge carrier. Nevertheless, as the mobility of electronic charge carriers is commonly higher than that of ionic charge carriers, the current is transported mainly electronically in region IIa and IIc. In region IIb the current is transported mainly by the oxygen vacancies. Under higher oxygen partial pressures (region III) the concentration (and therein the contribution to the conductivity) of oxygen vacancies declines. There the charge introduced by the doping is mainly compensated by electron holes [42].

The partial pressure range of the different regimes depends upon the material. Often oxides are not stable over a broad oxygen partial pressure range, many decompose at low oxygen partial pressures and high temperatures. Also the ionic conductivity regime (IIb) is not always present.

2.1.2 Mass and charge transport

For an oxide with oxygen vacancies ($V_O^{\bullet\bullet}$) the oxygen ions can diffuse through the crystal by hopping from an occupied to a vacant oxygen site. As the oxygen ion is charged not only mass, but also charge is transported,

resulting in a current. This hopping is often referred to as vacancy diffusion, for as the oxygen ions jump the vacant sites also moves through the lattice.

Equations of mass and charge transport

The likeliness for a particle i to change site or react is described by its chemical potential μ_i

$$\mu_i = \mu_0 + k_B \cdot T \cdot \ln(x_i) \quad (2.7)$$

where μ_0 is the chemical potential under standard conditions and x_i is the normalized concentration. For large concentrations μ_0 is concentration dependent, in such cases the activity a_i rather than the normalized concentration x_i has to be used. k_B is Boltzmann's constant and T is the temperature. Neutral particles are in equilibrium if their chemical potential is spatially constant: $\nabla\mu = 0$.

An electric potential changes the 'willingness' of a charged particle to move or react. Therefore the electrochemical potential, $\tilde{\mu}$ is introduced:

$$\tilde{\mu}_i = \mu_i + z_i \cdot e \cdot \varphi \quad (2.8)$$

where φ is the electric potential, z is the charge number and e the elementary charge.

In spatial equilibrium $\nabla\tilde{\mu}$ equals 0. A deviation from the equilibrium leads to a particle flux density J_i .

$$J_i = -\frac{\sigma_i}{z_i^2 e^2} \nabla \tilde{\mu}_i \quad (2.9)$$

For $\nabla\mu_i = 0$ the driving force of the particle flow is only the electric field $\nabla\varphi$. Putting equation 2.8 with $\nabla\mu_i = 0$ in equation 2.9 we obtain

$$J_i = -\frac{\sigma_i}{z_i \cdot e} \nabla \varphi \quad (2.10)$$

Using the electric current density $j_i = z_i \cdot e \cdot J_i = -\sigma_i \nabla \varphi$ Ohm's law of electric conduction can be derived:

$$\sum_i j_i = j = -\sum_i \sigma_i \cdot \nabla \varphi \quad (2.11)$$

In the other extreme case where $\nabla\mu \neq 0$ and $\nabla\varphi = 0$ the gradient in the chemical potential can cause a mass and charge transport.

$$J_i = -\frac{\sigma_i}{z_i^2 e^2} \nabla \tilde{\mu}_i = -\frac{\sigma_i}{z_i^2 e^2} (\nabla \mu_0 + k_B \cdot T \cdot \nabla \ln x_i) \quad (2.12)$$

In a homogenous material $\nabla \mu_0 = 0$ and $\nabla \ln x_i = \frac{\nabla c_i}{c_i}$, and therefore we obtain Fick's first law of diffusion [43].

$$J_i = -\frac{k_B \cdot T \cdot \sigma_i}{z_i^2 e^2 c_i} \nabla c_i = -D_i \cdot \nabla c_i \quad (2.13)$$

where D_i is the diffusion coefficient. Rearranging equation 2.13 to express D_i we obtain the *Nernst Einstein* equation [44] which connects conductivity and diffusion coefficient.

$$D_i = \sigma_i \cdot \frac{k_B \cdot T}{z_i^2 \cdot e^2 \cdot c_i} \quad (2.14)$$

Conductivity

At constant temperature the conductivity of the particle i , σ_i is given by

$$\sigma_i = |z_i| \cdot e \cdot u_i \cdot c_i \quad (2.15)$$

where $|z_i| \cdot e = q_i$ is the charge on the particle and u_i is its mobility, which is defined as $u_i = \frac{D_i \cdot z_i \cdot e}{k_B \cdot T}$ (equation 2.15 in 2.14).

For a mixed conducting material the electrical conductivity σ_{tot} can be calculated as the sum of the partial conductivities of the ionic and electronic charge carriers. This is valid if the charge carriers are transported independently from each other.

$$\sigma_{tot} = \sum_i \sigma_i = \sigma_{cation} + \sigma_{anion} + \sigma_{electrons} + \sigma_{holes} \quad (2.16)$$

In MIECs the conductivity usually increases with temperature. This dependence can be shown in an Arrhenius plot. In many cases (particularly for the ionic conductivity) one finds:

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (2.17)$$

where σ is the conductivity, the pre-exponential factor σ_0 is a constant and E_a is the activation energy of diffusion.

Logarithms of both sides give

$$\ln \sigma = \ln \sigma_0 - \frac{E_a}{k_B T} \quad (2.18)$$

Accordingly the activation energy E_a can be determined from the gradient of a plot of $\ln \sigma$ versus $\frac{1}{T}$, these graphs are known as Arrhenius plots.

2.2 The perovskites: structure and defect chemistry

Perovskites, i.e. materials crystallising in the perovskite structure, are a class of materials with the general formula of ABO_3 , where A is a large and B a smaller cation. The general structure of a perovskite is shown in 2.5. The idealized cubic symmetry is often broken to lower symmetry as already temperature leads to distortions of the BO_6 octahedra, so that many perovskites show tetragonal or orthorhombic symmetry instead of the cubic one [41].

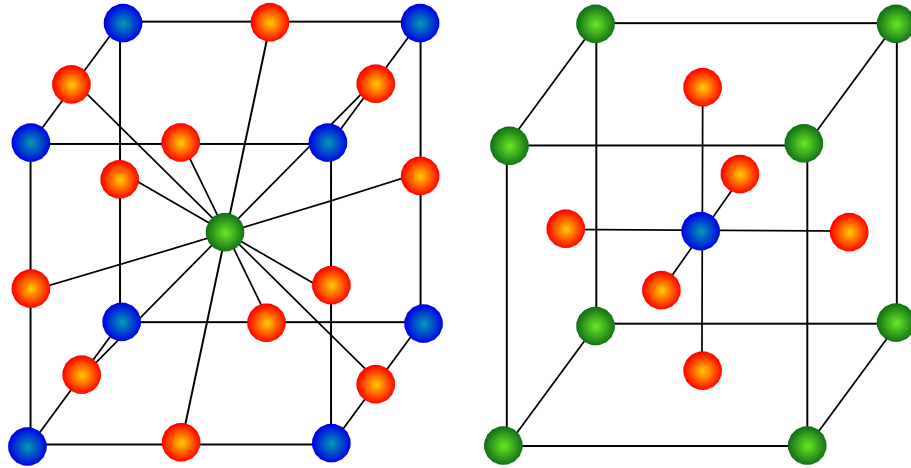


Figure 2.5: Schematic of the perovskite structure, A-centered (left) and B-centered (right) (green: A, blue: B, red: oxygen).

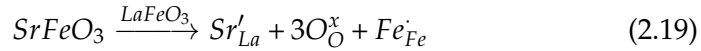
There are manifold possible combinations of cations and different cations can also occupy one cationic site (as is the case in doped perovskites). The properties vary strongly with the combination of cations in the perovskite, the temperature and the oxygen partial pressure. Accordingly, they are

used in a variety of applications. For example, lead zirconium titanate (PZT) $Pb(Zr, Ti)O_3$ is a ferroelectric material and is used in sensors and actuators. Lanthan strontium manganites (LSM), ferrites (LSF) and cobaltites (LSC) are electronically conducting and are therefore used as cathodes in SOFCs.

2.3 Defect chemistry in LSF

The main focus of this thesis is on the material $La_{0.6}Sr_{0.4}FeO_{3-\delta}$, therefore the defect chemistry of this material will be shown in detail here.

LSF is an acceptor-doped, perovskite-type material. Using Kröger - Vink notation, LSF64 can be described as the dissolution of $SrFeO_3$ in the host lattice of $LaFeO_3$

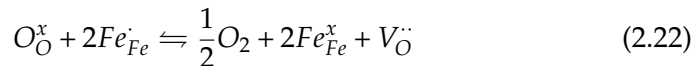


Lanthanum and strontium have a fixed valence state, the iron however can take several oxidation states. Accordingly, the charge introduced by the doping can be balanced electronically by an oxidation of the iron ($Fe_{Fe}^{\bullet}$), which equals the formation of electron holes $h^{\bullet}$. The iron can further undergo a disproportionation reaction,



$$K_i = \frac{[Fe_{Fe}^{\bullet}][Fe_{Fe}']}{[Fe_{Fe}^x]^2} \quad (2.21)$$

where K_i is the equilibrium constant for the disproportionation reaction K_i . Besides the electronic charge compensation, charges can also be compensated ionically, by oxygen vacancies $V_O^{\bullet\bullet}$ [20], [45], [46]. Electron holes and oxygen vacancies are connected by the interaction with the gas atmosphere.

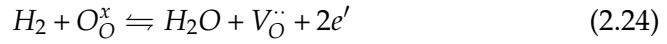


If we set up the equilibrium constant for the defect formation K_{defect} ,

$$K_{defect} = \frac{[O_O^x][Fe_{Fe}^{\bullet}]^2}{p_{O_2}^{\frac{1}{2}}[Fe_{Fe}^x]^2[V_O^{\bullet\bullet}]} \quad (2.23)$$

it becomes obvious that the defect equilibrium depends on the oxygen partial pressure (p_{O_2}). At high oxygen partial pressures [$Fe_{Fe}^\cdot$] mainly compensates the charge, accordingly conductivity is electronic [32], by electron holes [29] [27], [23], [25], [26]. For lower oxygen partial pressures the equilibrium is on the left side [27], [28]. Oxygen is released from the lattice, accordingly we find more $V_O^\cdot$ and less $h^\cdot$ in the LSF [20].

In hydrogen atmosphere the oxygen partial pressure is very low. In analogy to equation 2.22 the amount of oxygen vacancies and electrons in the LSF increases towards low p_{O_2} , however the reacting species are different.



2.4 Perovskite related structures

When working with perovskites it is important to take the perovskite related structures in consideration as perovskites can change their structure under different oxygen partial pressures and temperature. These structures may exhibit interesting properties like for example high temperature superconductivity in cuprate superconductors ($YBa_2Cu_3O_{7-x}$) [41]

Often the perovskite related structures are modular. They are frequently disordered so that many planar faults are usually found. Such structures are

- $A_2B_2O_7$ double perovskites like $Ca_2Nb_2O_7$
- A_2BO_4 Ruddlesden-Popper
- $KLaNb_2O_7$ Dion-Jacobson
- $Bi_4Ti_3O_{12}$ Aurivillius

In case of the double perovskite ($A_2B_2O_7$) two cations are ordered on the B site, thus the unit cell is twice that of a perovskite, see Fig. 2.6.

Ruddlesden-Popper, Aurivillius and Dion-Jacobsen phases are essentially layered perovskites.

The Ruddlesden-Popper phase consists of simple slabs of perovskite structure with the general formula $A_{n+1}B_nO_{3n+1}$, where n is the number of complete BO_6 octahedra in a slice (Fig. 2.7). Alternatively the structure can

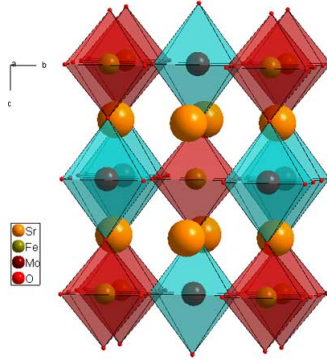


Figure 2.6: Double Perovskite structure for $(La, Sr)(Fe, W)O_3 - \delta$. Picture taken from Ref. [47].

simply be described as intergrowth of perovskite of varying thickness and sodium chloride structured layers, $[AO(A_nB_nO_{3n})]$. In practice synthesis of a ordered Ruddlesden-Popper phase is difficult, often disordered materials are obtained ([47]).

Aurivillius and Dion-Jacobson phases differ from Ruddlesden Popper phases in the interlayer between the perovskite layers, which is A_2O_2 in case of Aurivillius, giving the general formula: $(A_2O_2)(A_{n-1}B_nO_{3n+1})$ and an alkali metal interlayer in the case of Dion-Jacobson.

Perovskites with ordered defects

Another class of structures are perovskites with ordered point defects. Ordered defects are usually found only at low temperatures, as at high temperatures the entropy increases. Due to the ordering the unit cell is bigger although by its nature the material is still a perovskite. This ordering can have a significant impact on the material properties [41].

An example of a defect ordered perovskite structure is the brownmillerite phase: $A_2B_2O_5$ or $ABO_{2.5}$ [41]. This structure is found for example in $SrFeO_{3-\delta}$ below 900°C [48]. The oxygen deficiency is a function of oxygen partial pressure and temperature. For higher oxygen deficiency the sum formula approaches $Sr_2Fe_2O_5$. Thus the structure distorts so that half of the Fe cations are in octahedral sites, while the other half occupies tetrahedral sites, leaving the oxygen vacancies in ordered rows. Hence the structure can be described as a stack of octahedral and tetrahedral sites.

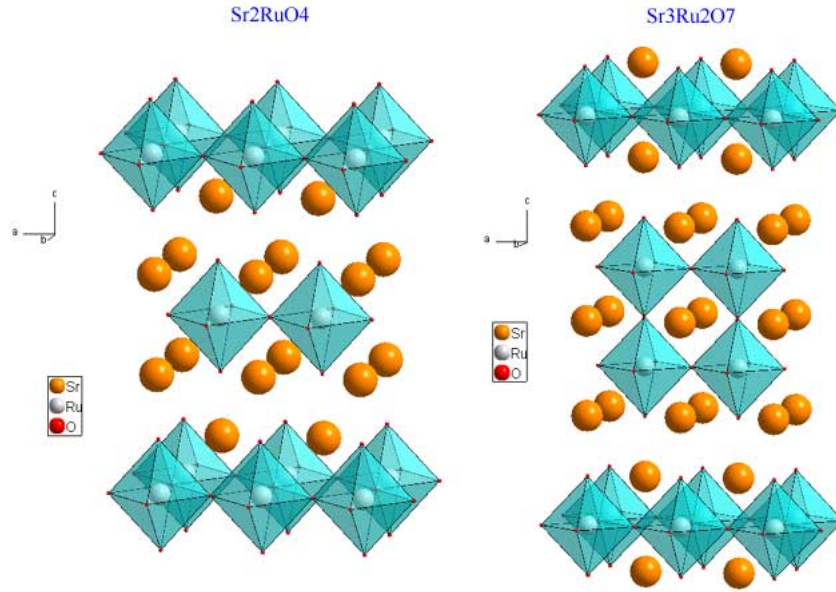


Figure 2.7: Examples for the Ruddlesden-Popper phases of the $n = 1$ (Sr_2RuO_4) and $n = 2$ ($\text{Sr}_3\text{Ru}_2\text{O}_7$) series. For these phases, Sr is the A cation, and Ru is the B cation. Picture taken from Ref. [47].

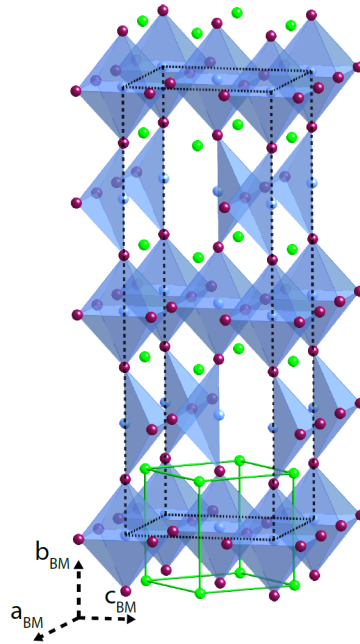


Figure 2.8: Idealized brownmillerite ($\text{ABO}_{2.5}$) unit cell. A cations are green spheres, B site blue spheres, and oxygen atoms are shown as red spheres. The corresponding perovskite unit cell is shown in green. Picture taken from Ref. [49].

Usually both - perovskite and brownmillerite - coexist in a wide temperature and pressure range, as already the formation of defect clusters in a perovskite lattice equals the formation of brownmillerite microdomains [41].

2.5 Phenomenological diffusion coefficients and oxygen surface exchange factors

In technical applications such as SOF/ECs or oxygen sensors the oxygen exchange with the gas phase and oxygen ion conductivity are important material parameters. The diffusion of oxygen in the crystal lattice is given by the oxygen diffusion coefficient, D . The oxygen exchange is described by the oxygen surface exchange factor, k .

2.5.1 The diffusion coefficients

Diffusion in a solid depends on several parameters: the concentration of the diffusion particles, the structure of the surrounding matrix and the present defects [41]. In case of an oxide the concentration of the diffusion particles as well as the predominant defect type may be changed by altering the oxygen partial pressure. Accordingly D can change with partial pressure. If the diffusing particle is charged, as is the case for oxygen ions, another particle also has to diffuse to maintain charge neutrality [50]. Accordingly, measurements don't probe the oxygen vacancy diffusion coefficient, but rather a phenomenological diffusion coefficient [51] [52].

Phenomenological diffusion coefficients can be measured by [51]

- conductivity experiment
- tracer exchange experiment
- partial pressure change experiment

The different methods to measure oxygen diffusion in solids are depicted in Fig. 2.9. To emphasize the difference between diffusion coefficients measured in different experiments, each gets a superscript: D^σ for the conductivity based diffusion coefficient, D^* for the tracer diffusion coefficient and D^δ for the chemical diffusion coefficient.

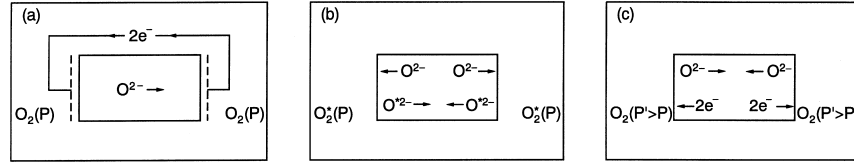


Figure 2.9: Comparison of different experiments for the evaluation of the oxygen diffusion coefficient, taken from [50]. a) conductivity experiment, b) tracer exchange experiment, c) partial pressure change experiment.

Conductivity based diffusion coefficient, D^σ

The diffusion coefficient D^σ can be calculated from conductivity measurements using the *Nernst-Einstein* relation (equation 2.14), with the restriction that the measured conductivity is caused by one mobile species alone $\sigma_{tot} = \sigma_i$. For the calculation of D^σ of oxygen the mobile species has to be oxygen ions.

The evaluation of the oxygen diffusion coefficient in a MIEC is difficult as typically ionic and electronic charge carriers contribute to σ_{tot} . One way to gain the ionic conductivity of a pure ion conductor is to measure the complex impedance and then use a fit that extracts the ionic conductivity (Fig. 2.9 a)).

Independently how the ionic conductivity was found, it accounts for all O^{2-} not only for fast diffusing defects. This can be seen in equation 2.15, where c_i is equal to the volume concentration of oxygen $c_{O^{2-}}$. Accordingly the gained D^σ is an average diffusion coefficient that accounts for all oxygen species in the lattice. Therefore it is sometimes also called the self-diffusion-coefficient. The diffusion coefficient of the mobile species D_i could be calculated if the ratio of mobile defects to the total amount of the species $\frac{c_i}{c_{O^{2-}}}$ was known.

$$D^\sigma = \frac{c_i}{c_{O^{2-}}} D_i \quad (2.25)$$

Tracer diffusion coefficient, D^*

Another possibility to obtain the diffusion coefficient is to incorporate tracer ions into a homogenous host and then measure their distribution in the lattice (Fig. 2.9 b)). Commonly for oxides an oxygen isotope is used, in combination with the detection by a Secondary Ion Mass Spectrometry

(SIMS).

One possibility to incorporate tracer into the sample is to anneal it at elevated temperatures in ^{18}O tracer gas. The tracer is incorporated into the crystal lattice due to the concentration difference of the tracer in the gas and in the crystal lattice (configurational entropy).

Once incorporated, the isotope will follow oxygen vacancy diffusion as it can only jump to vacant sites in the lattice. Nevertheless tracer diffusion and self diffusion are different, as the respective jump probabilities are different. A vacancy in a lattice site can jump to any neighbouring oxygen site. After a successful jump a vacancy can again, with equal probability, jump to any neighbouring site. In contrast to that a tracer-ion can only jump to a vacant site. After the jump the initial position is vacant, accordingly it is probable for the tracer to jump back to the initial position. Thus the tracer can only jump to a new position if the vacancy has diffused to an alternative neighbouring site or another vacancy comes around. Accordingly D^* is not directly comparable to the other diffusion coefficients. The *Haven ratio* H_R was introduced to account for this difference [51] [53] [54].

$$D^* = H_R \cdot D^\sigma \quad (2.26)$$

As the thermal tracer diffusion, D^* , is usually smaller than the self diffusion, D^σ : $H_R < 1$. Nevertheless H_R is expected to be close to unity in a perovskite-like lattice [30].

Chemical diffusion coefficient, D^δ

Also conductivity relaxation measurements can be used to calculate the diffusion coefficient. In such an experiment the sample is equilibrated in one p_{O_2} then the oxygen partial pressure is rapidly changed, see Fig. 2.9 c). The sample reacts to the change in p_{O_2} by a change in the non-stoichiometry, which is seen as a change in conductivity. As ionic and electronic defects are in equilibrium the experiment probes both, ionic and electronic, defects [51].

2.5.2 Surface exchange coefficient

Besides the diffusivity, the oxygen exchange at the surface of an electrode is an important parameter. The oxygen surface exchange coefficient, k , describes mass transfer of oxygen from the gas into the lattice. In analogy to the oxygen diffusion coefficients the k s receive a superscript, indicating the measurement method: k^* in case of tracer experiments and k^q in case of evaluation from resistances.

Tracer surface exchange coefficient k^*

In case of an oxide the sample is annealed in $^{18}\text{O}_2$. Subsequent SIMS analysis can be used to measure the tracer concentration in the sample close to the gas surface, c^x . From the tracer depth profiles k^* can be evaluated [55].

Conductivity based surface exchange coefficient k^q

The surface exchange coefficient k^q can be calculated using an equation similar to the *Nernst-Einstein* equation (equation 2.14):

$$k^q = \frac{1}{R} \cdot \frac{k_B \cdot T}{4 \cdot e^2 \cdot c_0} \quad (2.27)$$

The surface resistance R of an electrode and the total concentration of lattice oxygen c_0 are used in this calculation [56].

It is important that the resistance, used to calculate k^q , is only caused by the oxygen exchange reaction, other contributions will adulterate the value obtained for k^q .

Comparison of the surface exchange coefficients

Similar to the diffusion coefficients, the value obtained for the surface exchange coefficient depends on the type of experiment. Typically tracer (k^*) and electrical (k^q) measurements are expected to yield similar values for the surface exchange coefficient in case of a mixed conductor with predominant electronic conductivity ($k^* \approx k^q$) [57].

However, there is a possibility for the surface exchange coefficients to be distinct. In case of a surface species that exchanges oxygen with the surrounding atmosphere, electrons may flow only locally, but not over the

bulk. Consequently tracer can be incorporated, increasing k^* , while this exchange will be unnoticed by the electrical measurement, yielding $k^* \neq k^q$.

2.6 Solid oxide fuel/electrolysis cells

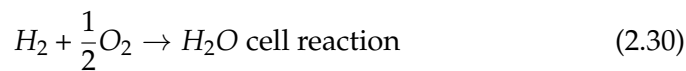
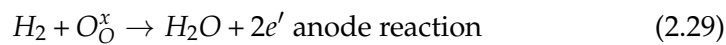
A solid oxide fuel cell (SOFC) converts chemically bound energy to electrical energy using a redox reaction with oxidation and reduction reaction being separated by an O^{2-} conducting ceramic. A solid oxide electrolyser cell (SOEC) is in principle the same, just that electrical energy is applied to generate chemically bound energy. In contrast to batteries, which already contain the chemical reactants, fuel or electrolysis cells only contain the means of conversion, the reactants are continuously supplied from external sources.

2.6.1 Working principle

An electrochemical cell consists of two electrodes and an electrolyte (see Fig. 2.10). In case of a SOFC the electrolyte is a solid oxide, from which the name - SOFC - derives. The electrolyte supports ionic but not electronic conduction.

The electrodes are exposed to different gases. On the cathode side oxygen (from air) is reduced and incorporated into the lattice see equation 2.28. The oxygen ions diffuse through the electrolyte driven by the partial pressure difference to react on the anode side with the fuel gas.

In a SOFC the high operating temperature allows for the use of different fuels, like CH_4 , CO or H_2 . In the case of hydrogen as fuel, the hydrogen will react with the oxygen ion leaving two electrons to form the exhaust water vapour (see equation 2.29). The electrons released from this reaction travel from the anode side to the cathode side via the outer circuit, performing electrical work. The sum reaction is given in equation 2.30.



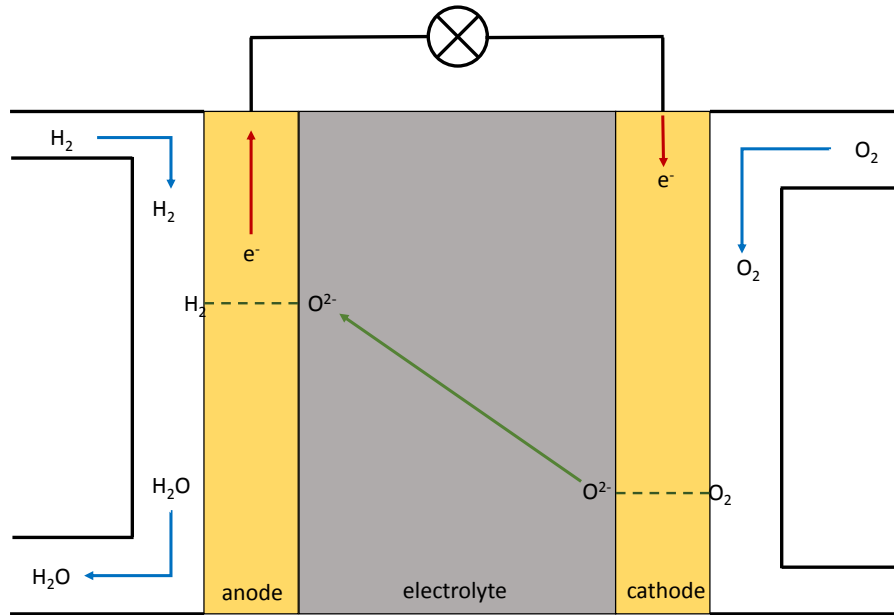


Figure 2.10: Schematic of a SOFC, with hydrogen fuel.

A main problem of SOFCs is that the oxygen exchange at the cathode is often sluggish. Therefore, cathode materials with a high catalytic activity are necessary. Perovskites, such as manganites, ferrites and cobaltites have already been intensively investigated [58].

A typical electrolyte material is yttria stabilized zirconia (YSZ), which shows a high ionic, but negligible electronic conductivity over a wide oxygen partial pressure range at elevated temperatures. Operation at intermediate temperatures would reduce stress on all components of the cell. Therefore, alternatives for YSZ that show a high ionic conductivity in a temperature range 500°C - 600°C are tested [59].

The typical anode material is porous Ni/YSZ-cermet (composite of ceramic and metal). However, this material has several problems like sintering, sulfur poisoning and other degradation issues. Finding electrode materials for reducing conditions has gained more attention going hand-in-hand with increasing research interest in SOECs [6], [60].

Commercial fuel cells are typically a stack of cells, connected in series. The material used for the connection is referred to as interconnect.

Finding new materials for the use in SOF/ECs is difficult as these materials are exposed to harsh conditions

- high temperature
- reducing and/or oxidizing conditions

Further they have to meet high demands

- sufficient electrical and/or ionic conductivity
- thermal expansion coefficients have to match sufficiently between different materials
- reaction between different cell compounds is undesirable

In this thesis the LSF64 material is tested for its use as electrode in reducing conditions.

2.6.2 Exchange kinetics and reaction pathways

A close look at the electrodes reveals the similarities and differences between solid electrochemistry and liquid electrochemistry. In liquid electrochemistry the electrolyte transports the charge carrying species, but it also offers the reactants. In solid electrochemistry the electrolyte only transports the charge carrying species, reactants are adsorbed from the gas phase. After the adsorption of the reactant different reaction paths (at different sites) are possible:

- **three phase boundary (TPB) path**

A schematic of the three phase boundary (TPB) path is shown in Fig. 2.11. This reaction path is often found in cases where the electrode is a good electronic but a weak or no ion conductor. After the adsorption of the reacting species (e.g. oxygen) on the electrode surface it probably dissociates and possibly gets (partly) ionized. Then the adsorbed species diffuses along the surface to the TPB, where electrode, electrolyte and gas phase meet. At the TPB the species is fully ionized and, in the case of a reduction reaction, oxide ions are incorporated into the electrolyte. Such a TPB path has been found for oxygen on platinum electrodes [61], [62]. Similar processes are assumed for reducing conditions.

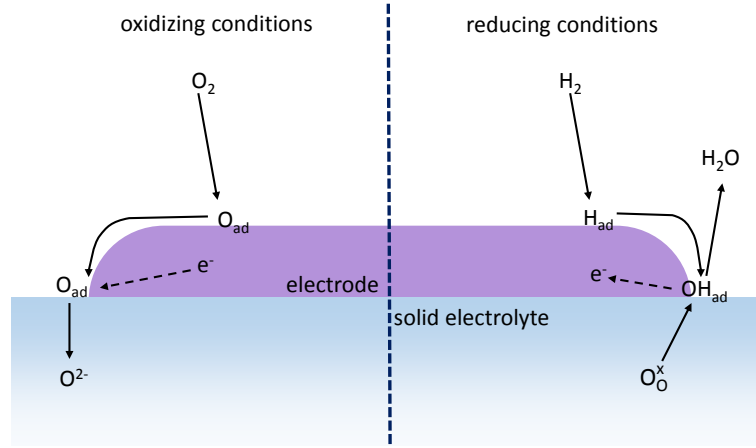


Figure 2.11: Schematic of TPB path under oxidizing and reducing conditions, with exemplary adsorbed species.

- **bulk path**

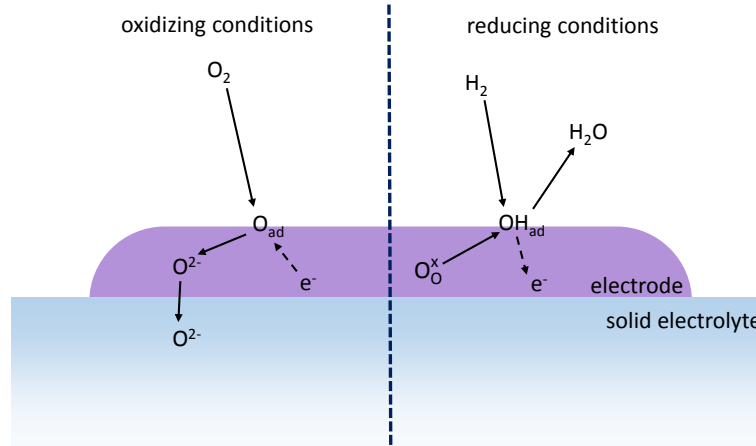
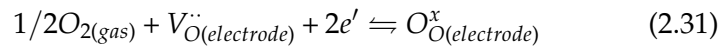


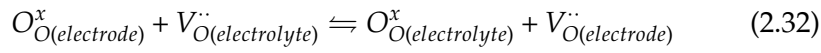
Figure 2.12: Schematic of bulk path under oxidizing and reducing conditions; exemplary adsorbed species.

A schematic of the bulk path is shown in Fig. 2.12. This path is typical for MIEC electrodes, giving the advantage of a larger active area in comparison to the TPB path.

The overall oxygen exchange reaction (equation 2.31) seems quite simple, but it consists of several consecutive steps [63].



After adsorption in case of the bulk path the oxygen probably dissociates and is ionized. A dissociative charge transfer step might be the rate limiting step of all the oxygen exchange reaction. The oxygen ion is incorporated into the electrode lattice. The uptake of oxygen into the lattice depends on the oxygen vacancy concentration close to the surface. The oxide ion diffuses through the electrode and is then transferred into the electrolyte.



In MIECs with sufficient ionic conductivity the transfer from the electrode to the electrolyte as well as the transfer into the electrolyte typically contribute little to the overall electrode resistance [64] [56].

A similar set of consecutive reaction steps is assumed for reducing conditions.

A distinction between the different pathways can be made by impedance spectroscopy if the electrode geometry is varied (TPB-length to surface ratio) or by oxygen tracer incorporation and consecutive tracer profile analysis [61] [62] [65]. Also a combination of both paths is possible as seen for example in LSM [66].

2.7 Impedance Spectroscopy (IS)

Impedance spectroscopy (IS) is a very powerful, non-destructive and yet simple method, where the impedance to the applied alternating current (ac) is measured. Due to its simplicity it is used in a broad range of applications, from measuring bodyweight, food safety, quality of coatings and semiconductor technology to characterizing fuel cells. The universal applicability results from describing the measured system with its different processes as a circuit of electrical elements. Some typical circuit elements and their respective spectra are shown in Fig. 2.14. However, finding and interpreting an equivalent circuit is the challenge of this method.

2.7.1 Measurement principle

The impedance Z is given by Ohm's law:

$$Z = \frac{\hat{U}(t)}{\hat{I}(t)} \quad (2.33)$$

where $\hat{U}(t)$ and $\hat{I}(t)$ are the alternating voltage and current, respectively. In an impedance measurement a frequency modulated commonly sinusoidal potential is applied to an electrochemical cell. The current through the cell $\hat{I}$ is measured. As the current is a response to the frequency modulated potential $\hat{U}$ it has to contain the excitation frequency and its harmonics but it can be shifted in phase (Fig. 2.13) [67].

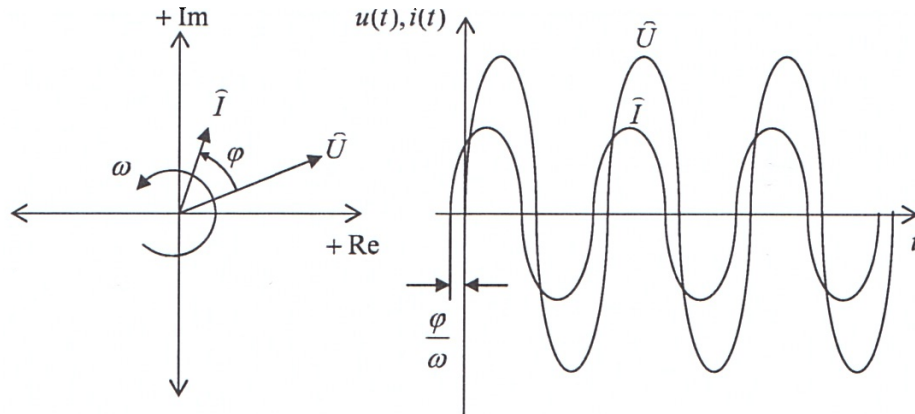


Figure 2.13: Schematic of the complex impedance plane showing a phase shift between voltage and current. Figure taken from [68].

Commonly the measurement is performed in the frequency domain, where consecutively single frequency sinus voltages are applied. Amplitude and phase shift of the current response ($\hat{I}$ and φ) are measured. Together with the input voltage $\hat{U}$ the complex impedance can be calculated.

$$u(t) = \hat{U} \cdot e^{j(\omega t + \varphi_1)} \quad (2.34)$$

$$i(t) = \hat{I} \cdot e^{j(\omega t + \varphi_2)} \quad (2.35)$$

Z can be separated in a real part Z' and an imaginary part Z'' .

$$\frac{\hat{U}}{\hat{I}} \cdot \exp(j \cdot \varphi) = Z = Z' + j \cdot Z'' \quad (2.36)$$

The frequency resistance and capacitance are given by:

$$Z_R = R \quad (2.37)$$

and

$$Z_C = \frac{1}{j\omega C} \quad (2.38)$$

where the angular frequency ω is given as $\omega = 2 \cdot \pi \cdot f$ and f is frequency in Hz .

There are a few requirements for a good impedance measurement [69] [70]:

- linearity: In a linear system the response is independent from the excitation amplitude.
- stability: electrochemical properties should stay constant during the measurement, after the excitation is removed the system should return to its initial state, accordingly the measured impedance is not time-dependent
- causality: Excitation causes response, before excitation no response can be measured - meaning that the system does not generate noise independent of the applied signal. Accordingly shielding of the sample from outside perturbations during measurement is important
- finiteness: a stationary state should be reached at low frequencies

Electrochemical cells, like SOF/ECs, usually behave far from linear. However, if the applied potential is small enough then the response can safely be assumed to be linear. Thus these systems are referred to as pseudo-linear systems.

Also measured electrode resistances are usually caused by electrochemical reactions or the transfer through space charge rather than the resistance of the electrode material itself.

Further stability is an issue. Electrochemical cells can degrade during measurement, therefore the measurement time (measured frequency range) is kept small.

2.7.2 Impedance spectra

There are two plots common in solid state ionics to show impedance measurements

- **Nyquist plot:** the real part of the impedance (Z') is plotted versus the imaginary part Z'' .

$$Z(\omega) = Z' + Z'' = |Z| \cdot \cos(\varphi) + j \cdot |Z| \cdot \sin(\varphi) \quad (2.39)$$

A simple RC element in a Nyquist plot gives a semicircle (see Fig. 2.14). On the vertex of the semicircle the characteristic frequency $\omega_P = \frac{1}{RC}$ can be read out.

- **Bode plot** The Bode plot actually consists of two plots: In one the absolute value of the impedance $|Z|$ is plotted versus the frequency f , in the other the phase angle φ is plotted versus the frequency f . The plots are usually shown on top of each other. The Bode plot explicitly shows the frequency dependence.

$$|Z| = \sqrt{(Z')^2 + (Z'')^2} \quad (2.40)$$

$$\varphi = \arctan \frac{Z'}{Z''} \quad (2.41)$$

A simple RC element in a Bode plot is shown in Fig. 2.14.

In principle both plots show the same data, however the different used axes highlight different aspects.

2.7.3 Equivalent circuits

A chemical reaction can be described by a reaction rate. This limiting reaction rate can also be interpreted as a resistance against the course of reaction. If such a reaction is linked to a current flow it can be measured by impedance spectroscopy and interpreted as a resistance.

Furthermore, the storage of charge or a reactant that can undergo a electrochemical reaction equals a capacitor. Hence, many materials and systems act like a combination of resistors (R) and capacitors (C). Resistive and capacitive processes can be in series or in parallel.

Accordingly, when an ac voltage is applied to a ceramic material of area A and thickness d 2 kinds of current flow simultaneously:

- **faradadic current:** transport of charge carrying species, described by conductivity σ

$$R = \frac{1}{\sigma} \cdot \frac{d}{A} \quad (2.42)$$

- **capacitive (dielectric) current:** involves displacement of bound charges e.g. core electrons of an ion

$$C = \epsilon \cdot \frac{A}{d} \quad (2.43)$$

with permittivity $\epsilon = \epsilon_0 \cdot \epsilon_r$.

Thus, in a very simple case a homogeneous material can be described by a parallel connection of R and C. The impedance of circuit elements in series can be calculated as the sum of the single impedances. In case of parallel connection the impedance is calculated as the sum of the reciprocal impedances of the single circuit elements. Accordingly, using 2.42 and 2.43, the impedance of a parallel connection of R and C (RC element) is given by

$$Z_{RC} = \frac{R}{1 + j\omega RC} \quad (2.44)$$

For parallel elements the branch with the smaller impedance carries the current. this means that in case of a RC element the current will be mainly capacitive at high frequencies and mainly resistive at low frequencies. The characteristic frequency ω_p of a RC element is the frequency where the current flow via the resistor and the capacitor are equal. At ω_p the imaginary part of the impedance reaches its maximum. Using 2.42 and 2.43 it becomes obvious that ω_p is a material constant.

$$\omega_p = \frac{1}{RC} = \frac{\sigma}{\epsilon} \quad (2.45)$$

Real electrochemical cells are not ideal, for example polycrystalline samples show a variation in grain size. Accordingly capacitances can deviate from

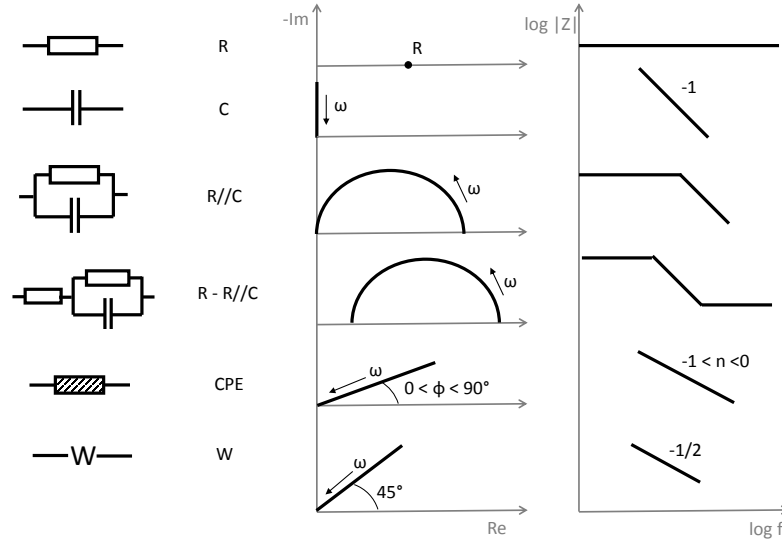


Figure 2.14: *Electrical circuit elements and their impedance spectra.*

ideality. These non-idealities can be accounted for by the use of a constant-phase element CPE, instead of an ideal capacitance C .

$$Z_{CPE} = \frac{1}{T(j \cdot \omega)^P} \quad (2.46)$$

where j and ω denote the imaginary unit and angular frequency, respectively. The corresponding capacitance is calculated using

$$C = (R^{1-P} \cdot T)^{\frac{1}{P}} \quad (2.47)$$

accordingly, in case of $P = 1$, the CPE becomes an ideal capacitance ($CPE = T = C$).

In an impedance measurement of an electrochemical cell processes can be separated if their time dependences are sufficiently different. If a single electrode is characterized by IS the different reaction steps (adsorption, dissoziation, charge transfer, diffusion) are probed. The impedance spectra will be dominated by the processes with the highest impedance. A variation in temperature, oxygen partial pressure and device geometry can help to assign the different parts of the impedance spectra to the different processes.

The equivalent circuits, used in this thesis, and their interpretation are given in the results part, together with the measurements to which the circuits were applied.

2.7.4 Microelectrodes

An impedance measurement always probes the whole electrochemical cell. For the investigation of one electrode, however, it would be advantageous to only measure processes on one electrode.

In liquid electrochemistry this problem is solved by the use of a reference electrode (RE). In solid electrochemistry the placement of the RE is problematic. An inappropriate placement can have an effect on the voltage drop between RE and working electrode (WE) under polarization of the counter electrode (CE).

A simple solution for this dilemma is to use microelectrodes in combination with macroscopic CEs. The large active area of the CE leads to a negligible voltage drop at the CE compared to the potential drop at the microelectrode.

If further the microelectrode is geometrically well defined dependences can be evaluated by varying the microelectrode size and form. For example a variation in geometry can reveal bulk or TPB path kinetics. If the electrode resistance scales with the surface area a bulk path is likely, while if it scales with the inverse TPB length the rate determining step is likely to be located on the TPB [61], [62].

2.8 Time of Flight - Secondary Ion Mass Spectrometry (ToF-SIMS)

In this thesis Time of Flight - Secondary Ion Mass Spectrometry (ToF-SIMS) was used to measure the lateral ion distribution as well as the depth profiles of the oxygen isotope ^{18}O in LSF thin films to investigate oxygen exchange kinetics in the electrode material. Therefore the principle of ToF-SIMS is explained here shortly.

The ToF-SIMS measurements were carried out by Katharina Langer-Hansel. Details concerning the ToF-SIMS measurements, the evaluation

of oxygen concentrations and the calculation of D^* and k^* can be found in her dissertation [71] and the publication [72].

2.8.1 Introduction and principle of TOF-SIMS

A schematic of the working principle of a TOF-SIMS is shown in Fig. 2.15.

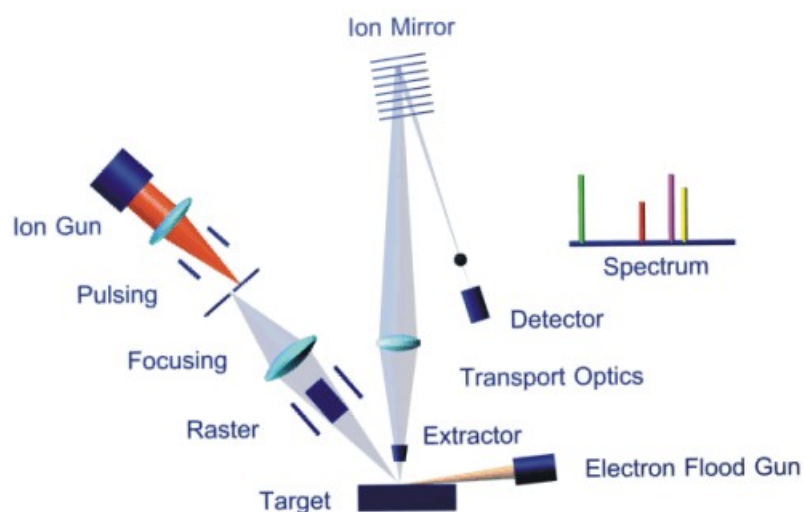


Figure 2.15: Working principle of a TOF-SIMS taken from Ref. [73].

A pulse of ions, called primary ion beam, bombards the sample with an energy of approximately 10 keV and sputters it. This produces a cloud of atoms, ions and clusters. Charged species originating from the sample within this cloud are referred to as secondary ions (see Fig. 2.16).

The composition of the secondary ions depends on several parameters: impact energy, mass and polarity of the primary ions as well as on the matrix of the sample itself. The impact energy is high so as to prevent preferential sputtering. As equal polarity repels, positive ions, like Cs^+ or Bi^+ , are more likely to extract positive secondary ions, while negative ions, like O^- , are used to extract chiefly negative ions. Extraction depth of ions is several nm. To detect the secondary ions voltage is applied to the extractor so that ions of one polarity are extracted and accelerated towards the detector. Lenses and an ion mirror focus the secondary ion beam before it hits the detector.

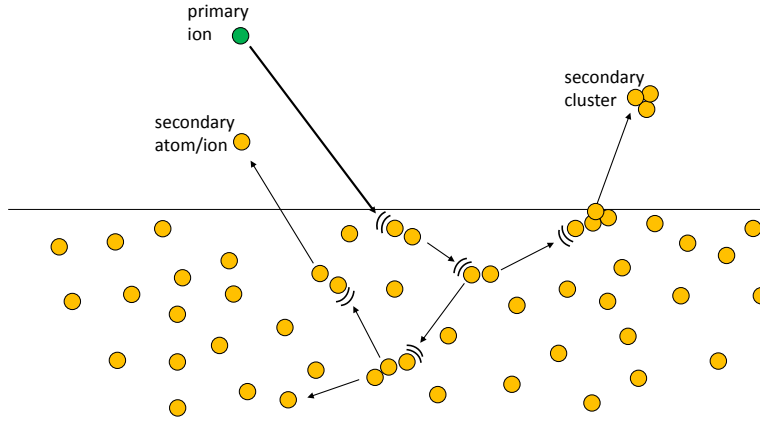


Figure 2.16: *Collision-cascade: a primary ion causes a cascade of subsequent collisions in the near surface region, secondary particles (ions/atoms/clusters) are ejected from the sample.*

Flight times differ between ions due to their distinct mass to charge ratio (m/z) if the distribution of kinetic energy is narrow.

$$E_{kin} = q \cdot U_e = \frac{m \cdot v^2}{2} \implies t_F = L_a \cdot \sqrt{\frac{m}{2 \cdot q \cdot U_A}} \quad (2.48)$$

with E_{kin} kinetic energy, t_F flight time, L_a specific length, q charge of the ion, U_A acceleration voltage, m mass of secondary ion, v velocity.

The detection relies on the different flight times, hence it is important that all secondary ions are extracted simultaneously, otherwise the spectral resolution degrades. Accordingly the primary pulse should be as short as possible. The time between extractions of secondary ions must be large enough so that even the heavy (and little charged) ions reach the detector. For a lateral ion profile the primary ion beam scans over the sample surface, while the secondary ions are recorded as a function of position. The spatial resolution depends on the focus of the primary ions - a smaller diameter of the primary ions will give a better resolution. However well the resolution an absolute quantification is difficult, as the ionization of the ions also depends upon the matrix.

For the recording of depth profiles the sample needs to be sputtered. In dynamic-mode SIMS the primary ion current is high enough to sputter the surface. In static-mode SIMS the primary ion current is low, so as to cause only a negligible excavation. Still static-mode SIMS can be used for depth

profiling, if the set-up is equipped with an additional sputter gun (typically caesium ions). At each depth lateral ion profiles are recorded. Depth profile resolution is limited by the focus of the sputter ions and by intermixing. Intermixing is caused by the impact of the ions (primary or sputter ions) on the surface and causes a mixing of the ions in the sample and a partial uptake of ions from the bombardment. Still, incorporation of sputter ions can be advantageous as is the case for Cs sputter ions when measuring oxygen ions. As the electro-positive nature of Cs increases secondary ion output for negatively charged ions like oxygen [74].

Bombardment of the sample surface of bad conducting materials with primary or secondary ions can lead to a charging of the surface, which in turn will repel the primary ions. To prevent charging of the surface electrons from a flood gun (heated wire) are accelerated towards the sample to neutralize the charges on the sample surface. The voltage in the flood gun is kept small (usually around 20 V) in comparison to the extractor voltage (kV range), so that the effect on the secondary ions is negligible.

2.8.2 Oxygen isotope profiles

In this thesis tracer exchange was used to characterize oxygen exchange kinetics in the perovskite-type LSF material.

Oxygen has three isotopes:

isotope	natural abundance
^{16}O	99.76%
^{17}O	0.039%
^{18}O	0.201%

The change in concentration of the ^{18}O to ^{16}O ratio was monitored. Due to the similarity between different isotopes it can safely be assumed that sputter rates and ionization of the isotopes is the same. From the detection of signal intensities S of the different isotopes the ratio can be calculated, which equals the concentration ratio.

$$f_{^{18}\text{O}} = \frac{S_{^{18}\text{O}}}{S_{^{16}\text{O}} + S_{^{18}\text{O}}} \quad (2.49)$$

Possible problems with oxygen detection

As doubly charged ions or clusters appear at half mass accordingly a doubly charged ^{32}S can give an interference with the oxygen signal. In our samples however sulphur is of negligible concentration.

Over an ionization pulse the probability for oxygen ions to be knocked out of the sample is constant. However, due to the high ^{16}O concentration in oxides, the detector gets clogged up. Therefore, oxygen ions that are knocked out in the first nanoseconds are detected preferentially and accordingly the signal is not box shaped. The obtained signal is more difficult to use for the Poission correction. The reader is referred to the dissertation of Katharina Langer-Hansel for more detail on the evaluation of oxygen tracer profiles.

2.8.3 Other profiles

The ToF-SIMS measurement is not limited to oxygen. Cation profiles, giving the ratio of cations in the sample, can give information on changes in the stoichiometry of the sample.

2.9 X-ray photoelectron spectroscopy (XPS)

In SOF/ECs often the main overpotential comes from the oxygen exchange reaction, but up to now little is known about the involved surface species. Also electrode degradation is often located at the surface by surface contamination or segregation of secondary phases. For example strontium containing perovskites can show a strontium enrichment towards the surface [75], [76], [77]. Accordingly an investigation of the surface is advantageous. X-ray photoelectron spectroscopy (XPS) is capable of quantitatively detecting surface species and surface composition.

In a XPS experiment the sample is irradiated with X-rays, causing the electrons of surface near (first nanometres of the sample) atoms to escape from the sample. The amount of electrons and their kinetic energy is measured. The kinetic energy gives information about the element and its binding state, while the amount of detected electrons is determined by the amount of the atoms in the probed sample volume. Ion sputtering can be used to clean the surface and to obtain depth profiles. A severe disadvantage of the technique is that it has to be performed under vacuum conditions as

the electrons are scattered by the gas molecules what adulterates the measurement result.

Efforts have been made to perform XPS measurements under ambient pressure. In ambient pressure XPS the path length of the electrons in the high-pressure regime is minimized by placing the sample close to a differential pumping system, behind which the pressure drops by orders of magnitude. This allows for measurements up to the millibar range [78]. However, catalytic activity may change as function of pressure and temperature [75], so that the information gained at low pressures may be considerably different from what occurs at high pressures [79].

Synchrotron based *in-situ* ambient pressure X-ray photoelectron spectroscopy (APXPS) can detect catalytic species, as was done on ceria [78], at higher pressures than standard XPS systems.

2.10 X-ray diffraction (XRD)

A beam of X-rays is diffracted on a crystalline sample according to Bragg's law (see Fig. 2.17)

$$n\lambda = 2d \sin \theta \quad (2.50)$$

where d is the distance between atomic layers in the crystal, λ wavelength of incident X-ray beam, θ angle of incidence and n is an integer.

The angular dependency of the intensity of the diffraction can be used to identify the material, to qualify its purity and to gain information on stress and strain in the lattice.

For thin films the angle of the impact beam is kept small (grazing incidence) so that the penetration depth of the X-ray beam is small. Therein the diffraction pattern is mostly generated in the first few hundred nm - allowing to gain information of thin films on substrates.

It is more common to use powders. Reaction chambers with beryllium windows allow for temperature and atmosphere dependent *in-situ* XRD measurements.

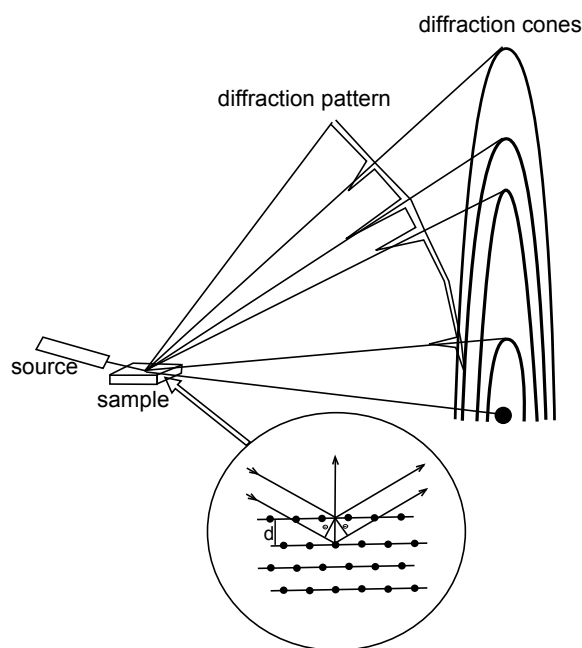


Figure 2.17: Schematic of XRD measurement.

2.11 Methods of sample preparation

Slightly different conditions during sample preparation can cause variations in samples and therefore in measurement results. Unfortunately for some sample preparation methods even under careful handling it is not possible to repeat the exact same conditions again and again. Therefore a few words on the most critical steps and methods of sample preparation are shed here.

2.11.1 Growing of thin layers by pulsed laser deposition (PLD)

Principle of PLD

Pulsed laser deposition (PLD) can be used to deposit materials of complex stoichiometry, like multi-element oxides. The principle is rather simple (Fig. 2.18): A high energy laser beam is used to evaporate a material from a rotating target. The vapour plume settles on a substrate which is in close vicinity, thus forming a thin film.

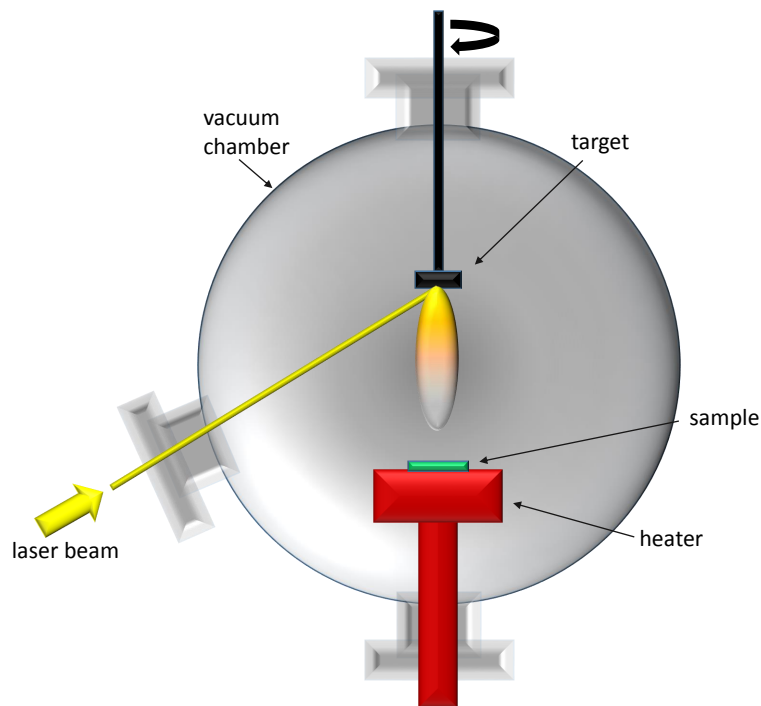


Figure 2.18: *Schematic of a pulsed laser deposition (PLD).*

The big advantage is that in contrast to classical thermal evaporation the evaporation energy is so high that the initial stoichiometry of the target material is preserved in the vacuum plume and accordingly in the thin film.

Parameters affecting thin layer growth

As simple as the principle of PLD is, thin layer growth is a rather complex topic, as it is influenced by various parameters:

- substrate temperature (diffusion of particles on the surface)
- absolute pressure in the deposition chamber (bumps of particles in the gas phase)
- partial pressure in case of a reactive component (p_{O_2} in case of oxides)
- frequency of laser (relaxation frequency of particles on the surface; lower frequency gives bigger grains)
- laser energy (energy of particles at the impact on the surface)

- substrate (material lattice parameters, crystallinity, surface roughness)
- heating and cooling rates (possibility of crack formation)
- distance between target and substrate (energy of particles on impact)

Thin layer growth by PLD is highly sensitive to a slight change in any of the above mentioned parameters. For example the variation of the substrate temperature alone gives highly different thin layers. In this thesis it was attempted to keep the parameters as equal as possible and therefore it is assumed that comparable thin films were gained.

2.11.2 Photolithography

Photolithography is a process used to pattern thin films (see Fig. 2.19). In case of positive photolithography first a photoresist polymer is coated on the sample usually by spin-coating. A mask is put on top of the photoresist, partly shading it from the light. Upon exposure to light of the correct wavelength the polymer will cross link therein getting insoluble. The developer is used to remove not hardened photoresist. Then the sample is etched, where the hardened photoresist protects the underlying layer. Then chemical or ion-beam etching is applied, according to the etchability of the sample. Afterwards organic solvents are used to remove the residual photoresist. For negative photolithography the process is slightly different. The to-be-structured layer is put on top of the structured photoresist. When the sample is put in an solvent the photoresist is removed, taking the covering layer with it.

In photolithography the quality of the photoresist is a critical issue. Other problems in photo-lithography are quite forgiving. But an old photoresist may not form a continuous layer, therefore during etching the area one is trying to protect might partly be etched. This can cause a different behaviour in a sample. An important difference between positive and negative photolithography is that negative photolithography typically pulls the edges of the thin film up.

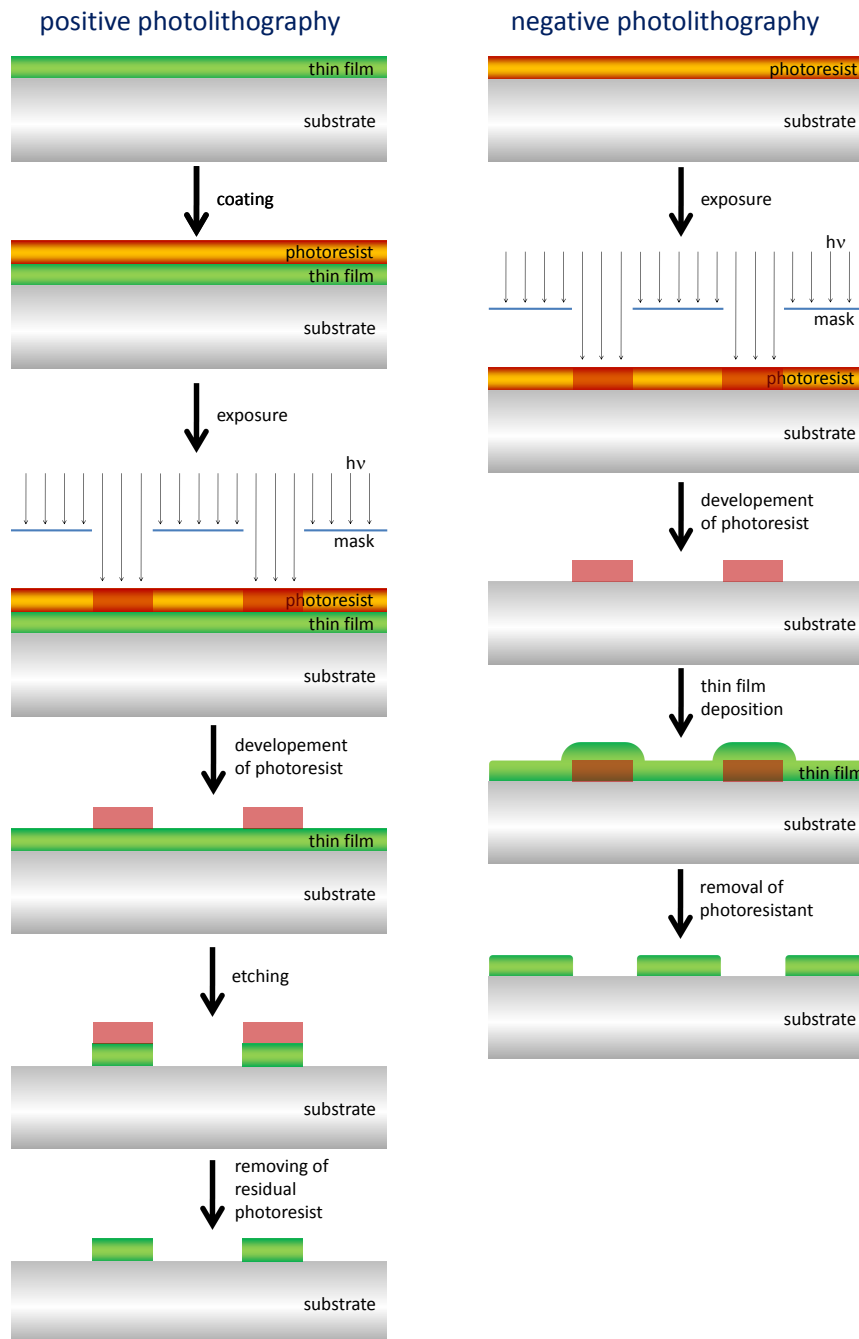


Figure 2.19: Principle of positive and negative photolithography.

2.11.3 Ion beam etching

In ion etching ions are accelerated towards the surface of the sample to be etched. The impact of the ions leads to a sputtering of the sample.

The ion etch machine, like the PLD, tends to drifting properties. Generally a good etching result is gained if the parameters give a plume with focus on the sample. This usually depends on experience not on equal set parameters. Anyhow the thin film of interest is protected by a polymer film (photoresist) so that the differences between samples due to ion-beam etching should only be the depth by which the electrolyte is etched.

General effects of ion etching on the thin layer:

- temperature increase, due to ion bombardment (danger of burning the photoresist, which then is difficult to remove)
- generation of defects in the crystal structure (reduction of YSZ)
- change of surface topography
- change in stoichiometry (especially in case of different compounds, with different sputter rates and different diffusion at elevated temperatures)
- implantation of gas atoms

Experimental

3.1 LSF64 powder

LSF64 powder was either synthesized or purchased (Sigma Aldrich). Synthesis was performed following Pecchini's method [80]. The cations are mixed in the desired stoichiometric ratio. In case of LSF, Fe_2O_3 (99.99%, Alfa Aesar), $SrCO_3$ ($\geq 99.99\%$, Aldrich) and La_2O_3 ($\geq 99.99\%$ Sigma-Aldrich) were used. The compounds were weighed according to the desired amount and dissolved in HNO_3 (65% extra pure, Merck). Citric acid was added in a ratio 1:1.1 so as to form complexes with the cations. The solution was concentrated to form a gel. The gel was heated until self-ignition took place. The obtained powder was then calcinated for 3 h at 900 °C and then at 1200 °C for 5 h. After calcination the powder was pressed into a pellet using a cold-isostatic press. Phase purity was controlled by X-ray powder diffraction (XRD).

3.2 Thin film deposition

The pressed LSF64 pellet was used as target for a pulsed laser deposition (PLD), as well as a target of commercially bought LSF64 powder (Sigma-Aldrich). A KrF-excimer laser (Compex Pro 201 F) with 248 nm wavelength was used for ablation. The intensity was set to 400 mJ/pulse. For impedance measurements YSZ (100) single crystalline substrates (9.5 mol – % Y_2O_3 , Crystec Germany) were used, while for isotope exchange measurements single crystalline MgO (100) substrates (Crystec Germany) were utilized [81]. The distance between target and substrate

was fixed at 6 *cm*. The substrate was heated to 650 °C, the temperature on the substrate was measured using a pyrometer (Heitronics KT 19.99). Oxygen partial pressure during ablation was held at $4 \cdot 10^{-2}$ *mbar*. Samples for impedance measurements were deposited using a frequency of 5 *Hz* for 35 *min* and 45 *min*, the obtained film thickness were 220 *nm* and 300 *nm*. Sample for oxygen isotope exchange were deposited using a rate of 10 *Hz* for 35 *min*, which yielded approximately 440 *nm* thick films. After deposition the sample was slowly cooled to room temperature, using a cooling rate of 15 °C.

Deviation of measurement results may partly be due to a slightly inhomogeneous thin film, caused by

- inhomogeneous heating of the substrate during ablation process and
- a focus of the vapour plume during PLD process to the center of the substrate leading to a thicker film in the center of the sample than on the edges of the substrate.

Both processes may as well slightly change the stoichiometry in the thin film towards the edges of the substrate.

3.3 Photolithography

LSF microelectrodes and bottom current collector structures were obtained by photolithography and subsequent Ar-ion beam etching. 100 μ l photoresist (N-1430 MicroResist Technology, Germany) were pipetted onto the spinning substrate. The spin-coater (SCC-200 KLM, Germany) rotated at a speed of 70 *rps* for 30 *sec*. The photoresist was dried for 2 *min* at 100 °C on a heating plate. The photo mask (Rose Germany) with the desired pattern was put on the sample, then the photoresist was crosslinked by illumination with a Hg UV-lamp (350 *W* for 40 *sec*)(USHIO 350DP Hg, Ushio, Japan). The undeveloped photoresist was removed by bathing the sample for approximately 45 *sec* in developer solution (MicroResist Technology, Germany). Subsequently, the sample was etched using Ar-ion beam etching (tectra GmbH, ionEtch Sputter Gun).

Top current collector structures were obtained by lift-off (negative) photolithography. The process is the same as for positive lithography, besides the etching step as it is not needed for negative photolithography, see section 2.11.2. Instead, the sample is put into ethanol to dissolve the remaining photoresist.

3.4 Metal deposition for current collectors

For the metallic current collectors, thin films of platinum (100 nm, 99.95% pure ÖGUSSA) on titanium (15 nm, BAL-TEC) were utilized. The titanium acted as a adhesion layer. For deposition a MED 020 Coating System machine (BAL-TEC Germany) was used. The distance between sample and target was set to 6 cm, a sputter current of 100 mA was applied. The argon pressure was $7 \cdot 10^{-3}$ mbar for the titanium layer and $2 \cdot 10^{-2}$ mbar for the platinum layer, yielding a sputter rate of 0.18 nm/sec (Ti) and 0.75 nm/sec (Pt), respectively. Current collectors were micro-structured using photolithography.

3.5 Sample geometry for impedance measurements

For impedance spectroscopy three different sample geometries were prepared.

- **circular LSF microelectrodes**

LSF64 thin films were structured using photolithography and ion beam etching. Circular microelectrodes (100 and 200 μm diameter) were prepared. Those microelectrodes were either without current collector, with current collector beneath the LSF electrodes (bottom geometry) or with current collector on top of the electrodes (top geometry). As counter electrode an approximately $1.5 \times 5 \text{ mm}^2$ sized LSF64 thin film stripe was used. Additionally platinum was brushed on the back side of the sample and connected to the counter electrode stripe. This causes a more homogeneous current distribution in the sample. Due to the much bigger size of the counter electrode in comparison to the working electrode, its contribution to the impedance spectra is negligible [82]. A schematic is shown in Fig. 3.1. In the typical current collector geometry the distance between

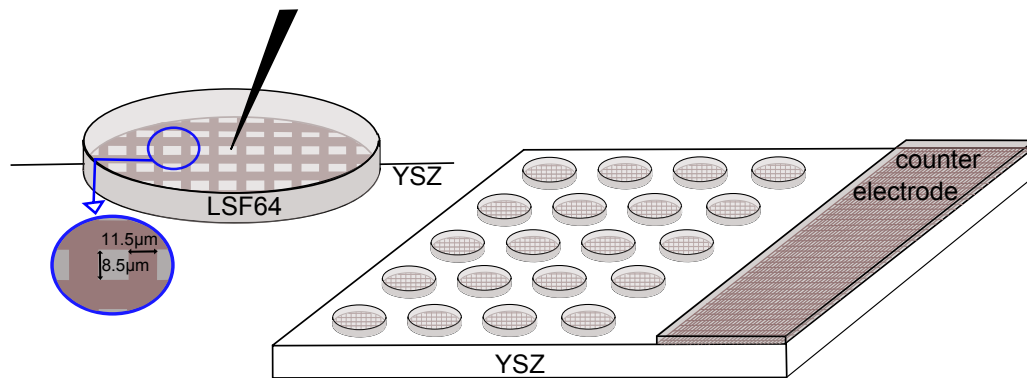


Figure 3.1: Schematic of a circular microelectrode with current collector. The zoom shows the dimensions of the current collector. Also a schematic of the entire sample with counter electrode stripe is shown.

stripes ($11.5 \mu\text{m}$) width is $8.5 \mu\text{m}$, if another current collector geometry was used it is explicitly mentioned.

Fig. 3.2 shows an SEM image of the $10 \times 10 \mu\text{m}^2$ top grid. Due to shading in the photolithographic process the structures are not ideally quadratic.

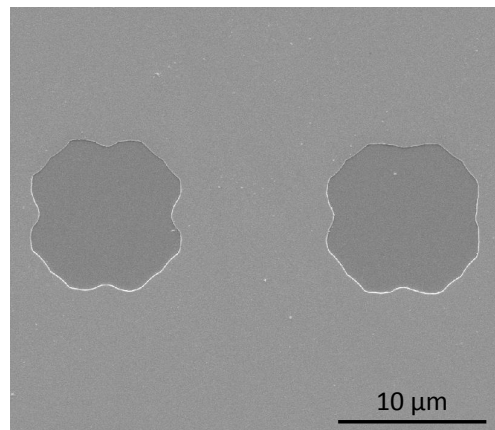


Figure 3.2: SEM image of LSF macroscopic sample with top grid, $10 \times 10 \mu\text{m}^2$ current collector.

- **microelectrodes with current collecting fingers**

For the microelectrodes with current collecting fingers the same preparation procedure as for circular microelectrodes with bottom

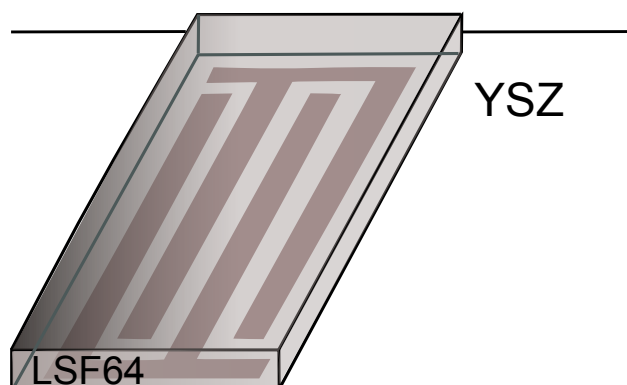


Figure 3.3: Schematic of a microelectrode with current collecting fingers. The dimensions of one electrode are $340 \times 140 \mu\text{m}^2$.

current collector is used. A schematic and a light-microscope image of the electrodes are shown in Figs. 3.3 and 3.4, respectively. Also the same counter electrode as for circular microelectrodes was applied.

- **macroscopic LSF electrodes**

A schematic of a macroscopic LSF64 thin film electrode ($5 \times 5 \text{ mm}^2$) is shown in Fig. 3.5. The current collecting fingers were put on top of the LSF64 thin film. Before thin film deposition the counter electrode was prepared. LSF64 was brushed on the unpolished side of the YSZ single crystalline substrate. After drying at 100°C platinum paste was brushed on top. Then the sample was annealed (3 h at 900°C). The resistances of such electrodes was measured using symmetrical cells. It was found that such counter electrodes had resistances of approximately $1.1 \Omega\text{cm}^2$ in air and $1.5 \Omega\text{cm}^2$ in humidified hydrogen at 683°C . Although the resistance of the counter electrode is lower than that of the working electrode its contribution is still seen in the impedance spectra. It can be identified by the relaxation frequency, which differs from that of the thin film electrode.

3.6 Needle fabrication and sharpening

For contacting the LSF electrodes Pt and Pt/Ir needles were used. The tip of the needles had to be very sharp to reduce cooling of the microelectrodes

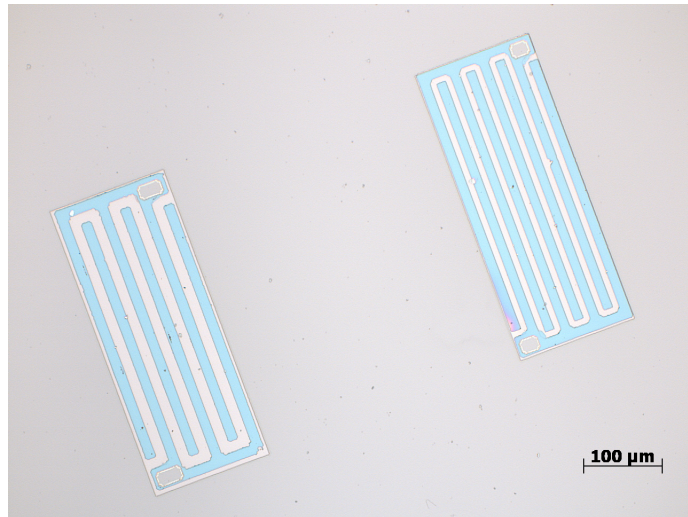


Figure 3.4: Light-microscope image a microelectrode with current collecting fingers. The dimensions of one electrode are $340 \times 140 \mu\text{m}^2$.

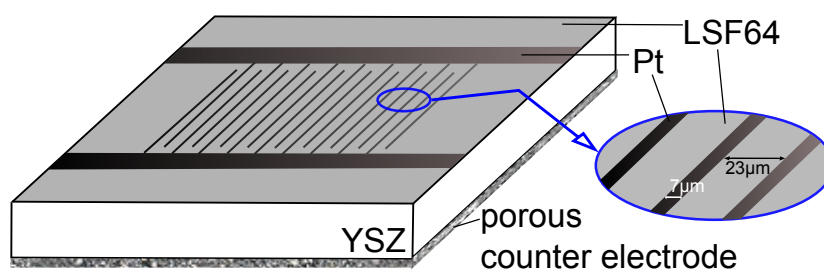


Figure 3.5: Schematic of a macroscopic ($5 \times 5 \text{ mm}^2$) electrode with current collecting fingers on top. The zoom shows the dimensions of the current collector. Also the porous counter electrode is indicated on the back side of the sample.

in case of inhomogenous heating. Therefore needles were fabricated electrochemically from Pt/Ir wires.

Two pieces of thick Pt wire ($d = 0.5 \text{ mm}$, approximately 1 cm length) were welded on a thin Pt/Ir wire ($d = 0.25 \text{ mm}$, approximately 2 cm length), so that the thin wire was in-between the thick wires. This wire was etched in the middle, using ac voltage (150 mA , 400 Hz , *sinus*) and a KCl, sat. electrolyte. Every half thus gives a needle with a sharp tip (see Fig. 3.6, left).

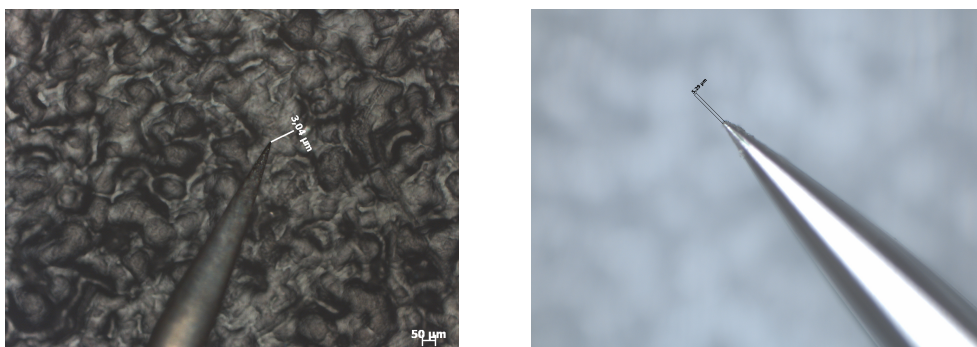


Figure 3.6: *Light microscope image of an electrochemically etched Pt/Ir needle (left) and a mechanically sharpened Pt/Ir needle (right).*

After a few measurements the needle tips blunt and needed re-sharpening. Sharpening the needles by hand on abrasive paper gives tolerable results, with tip diameters of approximately $5 \mu\text{m}$. However, mechanical sharpening gives far better results, with tip diameters of $2 - 2.5 \mu\text{m}$. For this abrasive paper was glued onto a pc hard-drive. During the rotation of the hard-drive the needle tip was put on the abrasive paper in a small angle. This method is very fast and gives sharp tips of approximately $3 \mu\text{m}$ diameter, see Fig. 3.6, right. Positioning of the contact needles on the microelectrodes was done with micromanipulators (Karl Suss) under an optical microscope.

3.7 Impedance measurements

Microelectrode samples were placed on a heating stage (Linkam, UK) in a vacuum chamber [66], macroscopic electrodes were put in a tube furnace (Gero, SR 40-200/12). Impedance measurements were carried out under air, synthetic air or hydrogen ($\text{H}_2 \text{ 2.5\%/Ar}$, Air liquide, ARCAL

10). Humidification of the gases was achieved by slowly bubbling the gas through a stainless steel bubbler filled with distilled water at room temperature (ca. 22 °C). The resulting water partial pressure was assumed to equal the vapour pressure of saturated water at room temperature, approximately 26 *mbar*.

Impedance spectra were recorded in a frequency range of $10^6 - 0.1/0.01$ Hz. with an rms of 10 *mV* using a Alpha-A impedance analyzer (Novocontrol).

3.8 Tracer exchange measurements

Thin films for tracer exchange experiments

All samples for tracer exchange were annealed after PLD in air at 700 °C for 10 *min*. For the tracer exchange experiments ^{18}O gas (Campro scientific GmbH, 99.7 *mol* – % = 97.1 *m* – % chemical purity) was used.

Three different types of tracer exchange were carried out:

- 1-step ^{18}O tracer exchange
- 2-step ^{18}O tracer exchange
- H_2^{18}O tracer exchange

1-step ^{18}O tracer exchange experiment

In case of the 1-step tracer exchange experiment the thin film is heated in a tracer containing atmosphere to a defined temperature and held there for a defined time.

For the tracer exchange the samples were placed in set-up with the heated area made up entirely of quartz. The oven can be pulled of the set-up for fast cooling. The sample temperature is controlled by a thermocouple type K placed close to the sample. First the sample is heated in air to the desired temperature (350 – 500 °C), with a heating rate of approximately 15 °C/*min*. Then the set-up is kept at temperature and evacuated down to $2 \cdot 10^{-2}$ *mbar*.

The time needed for evacuation depends strongly upon the residual adsorbates within the set-up, typically it took approximately 15 *min* to reach the low pressure. After that the set-up is filled with 200 *mbar* of ^{18}O tracer gas. The sample is kept under this atmosphere at the set temperature for the desired amount of time, which for the measurements shown is 20 *min*. Then the set-up is pulled out of the oven to ensure fast cooling, which can take several minutes. During the cooling the sample is still exposed to the tracer gas atmosphere. The sample is only taken out of the set-up once the temperature has fallen below 125°C, due to the low temperature the tracer from within the thin film with the surrounding atmosphere is negligible.

2-step ^{18}O tracer exchange experiment

In case of the 2-step ^{18}O tracer exchange experiment the LSF64 thin film is first 'filled' with a high amount of tracer, using the above described 1-step experiment. Then the tracer from the thin film is released under a defined atmosphere, generating a diffusion profile within the thin film.

First a 1-step tracer exchange is carried out: at 500°C for 20 *min* under 200 *mbar* ^{18}O . The tracer depth distribution is measured using a TOF-SIMS. Due to the high temperature and the long exchange time in the 1-step experiment the gained profiles in the LSF64 thin layers are box-shaped. This is a necessity for the 2-step experiment. For the second step the thin films are exposed to either reducing or oxidising conditions. For this the sample is placed on a Linkam heating stage (Linkam Scientific Instruments), a description of the set-up is given in [83]. For reducing conditions the set-up was filled with $\text{H}_2/\text{H}_2\text{O}/\text{Ar}$, the humidification of the gas was achieved by slow bubbling through deionized water. The set-up was 3-times filled with the desired gas and evacuated to $4 \cdot 10^{-2}$ *mbar*. For oxidizing conditions room air or synthetic air was used. Once the gas atmosphere was established the sample was heated to the desired temperature 350 – 500°C with a heating rate of 70°C/*min*. The temperature was then kept at the set temperature for 1 – 5 *min*. During this time tracer from within the thin film was released. After that the sample was cooled (70°C/*min*) under the gas atmosphere to below 125°C before it was removed from the set-up. The 70°C/*min* heating/cooling rate is a compromise of fast heating/cooling and still maintaining a controlled temperature profile.

$H_2^{18}O$ tracer exchange experiment

1-step tracer exchange experiments were also carried out using $H_2^{18}O$. These experiments are compared to the two step tracer exchange under reducing conditions. The tracer marked water was produced directly before the measurement in a reactor.

Building of the reactor for tracer marked water:

A thin quartz tube (outer diameter 5 mm, inner diameter 1 mm) of a length of 20 cm (both ends with KF15 flange) was filled with Pt wire and Pt paste, as Pt acts catalytically in the reaction of oxygen with hydrogen. Further this filling would also provide resistance towards the gas flow. For heating a Kanthal wire (0.5 mm diameter) was wrapped directly around the quartz tube, giving an resistance of approximately 20 Ω at room temperature. A thermoelement type K was mounted close to the heating wires. The wire was insulated towards the outside by applying multiple layers of oven wool, which were then fixed using a metallic net. A laboratory voltage source (Votcraft DPS-4005 PFC) was used to apply voltage to the heating wires. Approximately 9 V were needed to heat the reactor to 500 °C. The reactor was mounted on laboratory poles.

Generation of tracer marked water:

For the generation of tracer marked water the reactor was heated above 500 °C, to ensure that the equilibrium of reaction $\frac{1}{2}O_2 + H_2 \rightarrow H_2O$ is established. Massflow controllers (Rod-4 Aero) were used to apply ARCAL (2.5% H_2/Ar) (Air Liquide) and $^{18}O_2$ (Campro scientific GmbH, 99.7 mol - % = 97.1 m - % chemical purity). The gases were mixed with a stoichiometric surplus of hydrogen. The evolution of $H_2^{18}O$ was monitored using a mass spectrometer (Pfeiffer Vacuum, Omni StarTM Gas Analysis System). The resulting gas had a partial pressure ratio for $H_2 : H_2^{18}O$ of 1 and was used in the tracer exchange experiment.

Tracer exchange:

The sample was placed in the set-up described in Ref. [83] on a Linkam heating stage. The set-up was filled twice with $H_2 : H_2^{16}O = 1$ to 1050 mbar and evacuated to $4 \cdot 10^{-2}$ mbar, before it was filled with $H_2 : H_2^{18}O$

(1070 *mbar*). Then the sample was heated (70°C) to the desired temperature (350 – 500°C) and kept there for 1 – 5 *min*. Then the sample was cooled in the tracer atmosphere (70°C/*min*) to below 125°C. The gas was released over the mass spectrometer (Pfeiffer Vacuum, Omni StarTM Gas Analysis System).

SIMS measurements for tracer evaluation

Tracer profiles were measured using a ToF-SIMS V (ION-TOF GmbH, Germany). Primary ions from Bi/Mn Liquid Metal Ion Gun (LMIG) are accelerated with 25 *keV*. The LMIG is operated in CBA-mode (Collimated Burst Allignment) [84], [85]. In CBA mode the pulse is less than 65 *ns*, in order to minimize dead-time effects on the single ion counting detector. Thus enough ions for good resolution are extracted, while the amount is still low enough so as not to oversaturate the detector. The measurement raster was set to 512x512 *pixels* per area scan of 60x60 μm^2 . Cs^+ ions with 2 *kV* acceleration were used in the sputter gun (raster 310x310 μm^2). Primary ions and sputter ions were applied in a non-interlaced mode combined with low energy electron floodgun (20 *eV*). The flood gun is necessary to prevent charging effects on the LSF, due to weak conductivity at room temperature.

All TOF-SIMS measurements shown in this thesis were carried out by Katharina Langer-Hansel. For more detail on the TOF-SIMS measurements the reader is referred to [72] [71].

3.9 Powder XRD

LSF64 powder (Sigma Aldrich) was used in high temperature *in-situ* powder XRD to test the chemical stability of LSF64.

The measurement was performed using $\text{Cu} - K\alpha$ radiation. Ca. 1 *g* powder was put in the XRK 900 reaction chamber (Anton Paar). In this chamber the powder is placed on a frit. The gas is sucked through the frit, accordingly the gas flows through the powder, giving a maximum contact. Gas flow was applied 1 *h* before actual measurement, to ensure that the entire set-up was filled with the gas. To increase sensitivity the angular steps were small 0.008°/step and the measurement time was long 3 *hour*/scan. Diffraction

patterns were recorded in a range of $20^\circ - 80^\circ$ 2Θ (PANalytical, X'Pert Pro). Peak evaluation was done by comparison to ICDD database: 01-082-1961 for LSF64 ($La_{0.6}Sr_{0.4}FeO_{2.796}$), 00-001-1111 for Magnetite (Fe_3O_4), 00-002-1180 for Wustite (FeO), 00-029-1305 for $SrFeLaO_4$ (A_2BO_4 , Ruddlesden Popper), 00-057-0088 for $LaSrFe_2O_{5.5}$ ($A_2B_2O_{5.5}$ brownmillerite), 00-006-0696 for metallic iron and 04-015-5007 for La_2O_3

Results and discussion

4.1 Defect model and thermodynamic calculations

Highly doped materials often show a non-ideal thermodynamic behaviour [45]. However, for some materials, like LSF64, it is possible to apply simple mass action laws to describe the system. In literature a thermodynamic defect-chemical model was derived for LSF64 [20], [33], which fitted their experimental results over a wide oxygen partial pressure and temperature range.

Having the full defect chemical model allows to make predictions on other measurement results (here chemical capacitance and conductivity), and to draw mechanistic conclusions from them.

4.1.1 Calculation of the oxygen partial pressure

When applying a defect chemical model over a wide temperature and partial pressure range, it has to be taken into account that the partial pressure can be a function of temperature. This dependency can strongly affect the results gained from the model. The oxygen partial pressure calculated here from thermodynamic data [86] correlates to the atmosphere used in our impedance and tracer experiments (2.5% H_2 /Ar).

According to the reaction



ΔH_R^0 equals the standard formation enthalpy of water: $\Delta H_R^0 = \Delta_f H_{H_2O}^0$. The reaction entropy can be calculated as the difference of products minus reactants:

$$\Delta S_R^0 = S_{H_2O}^0 - (S_{H_2}^0 + S_{O_2}^0) \quad (4.2)$$

From the knowledge of ΔH_R^0 and ΔS_R^0 for a given temperature, we can calculate ΔG_R^0 . Equalising the expressions for ΔG_R^0 we obtain

$$\Delta G_R^0 = \Delta H_R^0 - T \cdot \Delta S_R^0 = -RT \ln K \quad (4.3)$$

From this relationship we can express the equilibrium constant K for the formation of water (equation 4.1), which is defined as:

$$K = \frac{p(H_2O)}{p(H_2) \cdot \sqrt{p(O_2)}} \quad (4.4)$$

From K the oxygen partial pressure for a given temperature can be calculated, if the partial pressures of water and hydrogen, or their ratio is known. For our calculations we assumed $p_{H_2O}/p_{H_2} = 1$. This is a reasonable assumption for the gas atmosphere in our measurements as, we have approximately 25 *mbar* water vapour and 25 *mbar* hydrogen. This values are obtained from the following considerations:

- When filling our set-up with gas, the gas is bubbled through water at room temperature. In case of slow bubbling, water vapour should reach its saturation pressure which is approximately 25 *mbar* at typical laboratory temperature (according to literature [87]: 23.393 *mbar* at 20 °C and 31.699 *mbar* at 25 °C). For the case of fast bubbling, the gas is over-saturated with water vapour, but this would cause the water to condensate at parts in the measurement set-up which are at room temperature. Therefore we would reach again approximately $p_{H_2O} = 25 \text{ mbar}$.
- For the estimation of the hydrogen partial pressure, we take into account that a total pressure of 1050 *mbar* of humidified 2.5% H_2/Ar is used, accordingly the partial pressure of hydrogen is approximately 26 *mbar*.

Plotting the calculated values from 25 – 1027°C, we observe a strong dependency of oxygen partial pressure on temperature for the fixed ratio of $p_{H_2O}/p_{H_2} = 1$, see Fig. 4.1.

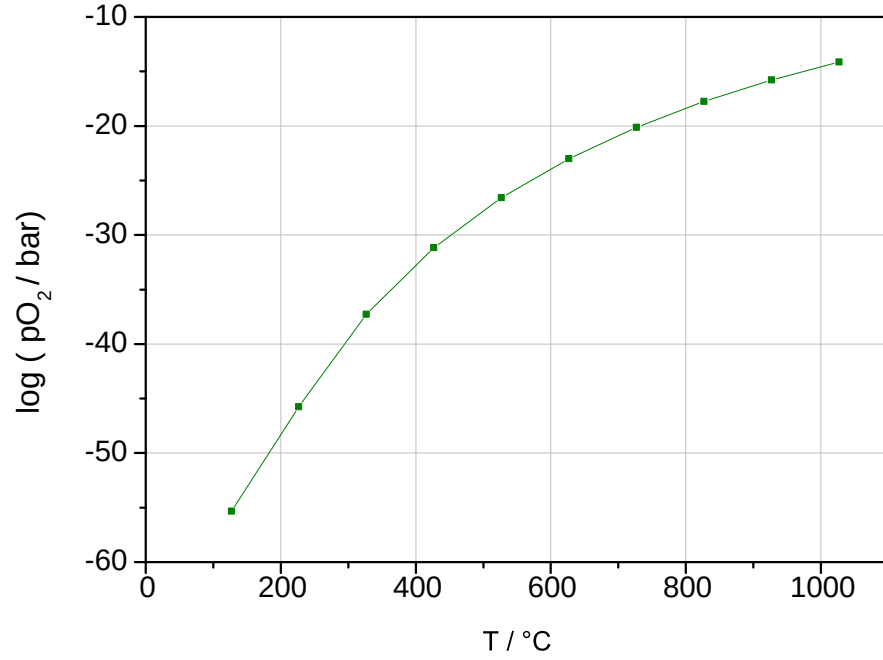


Figure 4.1: Calculated dependency of oxygen partial pressure on temperature, for $p_{H_2O}/p_{H_2} = 1$.

4.1.2 Calculation of the chemical capacitance and the charge carrier concentrations

The defect chemical model of LSF64 was already described in Sec. 2.3. There the oxygen exchange reaction (Eq. 2.22) and the disproportionation of the iron (electron-hole formation) (Eq. 2.20), with their corresponding mass action constants K_{defect} (Eq. 2.23) and K_i (Eq. 2.21) are given.

The mass action constants K_{defect} and K_i were calculated using

$$\ln K = \frac{-\Delta H}{RT} + \frac{\Delta S}{R} \quad (4.5)$$

with values for the standard enthalpy and entropy taken from Ref. [20]. From the defect model the correlation of p_{O_2} to the oxygen non-stoichiometry (δ) can be derived [20]:

$$p_{O_2} = \frac{1}{16} \left(-\frac{1}{K_{defect}^{1/2}} \frac{(2\delta - 0.4)(3 - \delta)^{1/2}}{(2\delta + 0.6)\delta^{1/2}} + \left(\frac{1}{K_{defect}} \frac{(3 - \delta)(2\delta - 0.4)^2}{\delta(2\delta + 0.6)^2} + \frac{K_i}{K_{defect}} \frac{4(3 - \delta)(1.4 - 2\delta)^{1/2}}{\delta(2\delta + 0.6)} \right)^{1/2} \right)^4 \quad (4.6)$$

which can be solved numerically. Kuhn et al. [20] proved the validity of this equation over several temperatures and a wide oxygen partial pressure range by the good agreement between their measurement data and the calculated oxygen non-stoichiometry. Also Bucher and Sitte used these defect chemical calculations to quantify electronic conductivity relaxation experiments of LSF46 [88].

From the knowledge of δ the concentration of the ionic charge carriers (oxygen vacancies) can be calculated:

$$[V_O^{\bullet\bullet}] = \delta \cdot \frac{c_0}{3} \quad (4.7)$$

where $c_0 = 4.994 \cdot 10^{22} \text{ cm}^{-3}$ is the number of available oxygen sites in the LSF64 lattice (not the concentration of occupied oxygen sites), which was calculated using lattice parameters taken from ICDD (01-072-8136). For the calculation of the electronic charge carriers we have to take the charge neutrality condition into account:

$$[Fe'_{Fe}] + [Sr'_{La}] = 2[V_O^{\bullet\bullet}] + [Fe^{\bullet}_{Fe}] \quad (4.8)$$

In reducing conditions the assumption can be made that the concentration of electron holes is negligible as is the concentration of electrons in oxidizing conditions. With these assumptions we obtain

$$[h^{\bullet}]^{ox} = (0.4 - 2\delta) \frac{c_0}{3} \quad \text{and} \quad [e']^{red} = (2\delta - 0.4) \frac{c_0}{3} \quad (4.9)$$

Also a more accurate solution is possible if the charge neutrality equation is put into equation 2.21. The obtained quadratic equation can then be solved

for the concentration of electrons, with which the electron hole concentration can be calculated.

$$[e'] \left([e'] - (2\delta - 0.4) \frac{c_0}{3} \right) = K_i \quad \text{and} \quad [h'] = [e'] - (2\delta - 0.4) \frac{c_0}{3} \quad (4.10)$$

The charge carrier concentrations in oxidizing conditions were calculated for $p_{O_2} = 0.2 \text{ mbar}$. Fig. 4.2 shows that in oxidizing conditions electron holes are the majority charge carrier. However, upon heating the concentration of electron holes declines, accompanied by a strong increase in oxygen vacancy concentration.

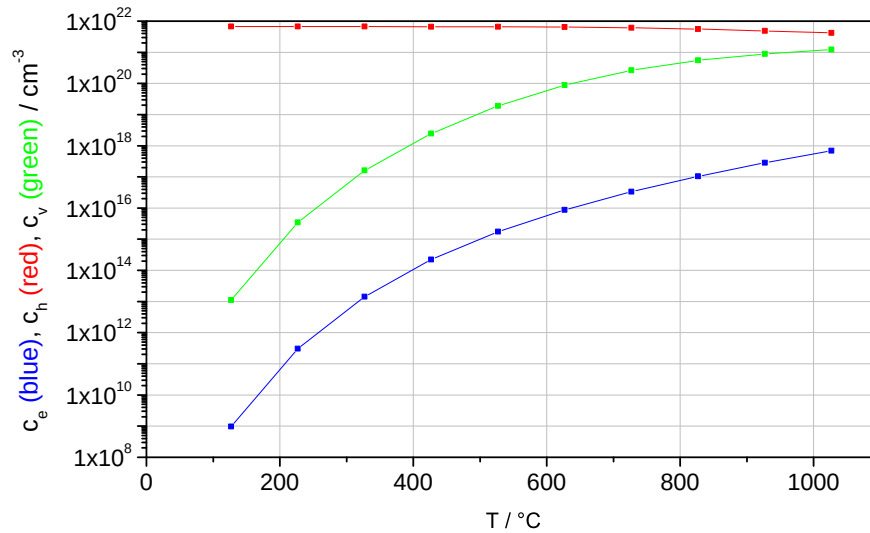


Figure 4.2: Calculated charge carrier concentrations for LSF64 at $p_{O_2} = 0.2 \text{ bar}$. Concentration of electrons $[e']$ (blue), concentration of holes $[h']$ (red) and concentration of oxygen vacancies $[V_O^{\bullet\bullet}]$ (green).

For reducing conditions the concentration of the charge carriers was calculated (see Fig. 4.3) taking into account the calculated dependency of p_{O_2} on T , see Fig. 4.1. In reducing conditions the oxygen vacancies are the majority charge carrier, but we observe a strong increase of the electron concentration upon heating.

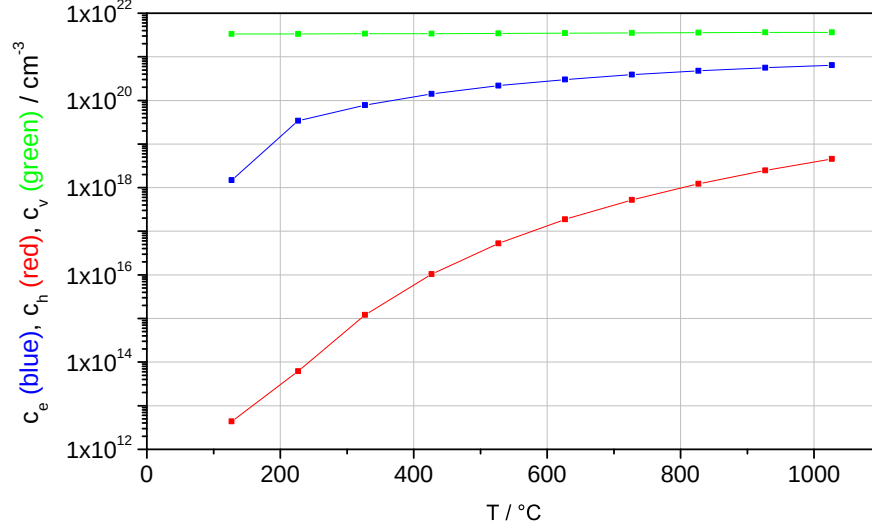


Figure 4.3: Calculated charge carrier concentrations for LSF64 in reducing conditions ($p_{H_2}/p_{H_2O} = 1$, using data from Fig. 4.1. Concentration of electrons $[e']$ (blue), concentration of holes $[h']$ (red) and concentration of oxygen vacancies $[V_{O\cdot}]$ (green).

With the concentrations of the ionic and electronic charge carriers, the chemical capacitance, C_{chem} , can then be calculated, under the assumption of diluted charge carriers and the absence of traps [89], [90]:

$$C_{chem} = \frac{e^2}{k \cdot T} \cdot A \cdot L \cdot \left(\frac{1}{z_{eon}^2 \cdot c_{eon}} + \frac{1}{z_{ion}^2 \cdot c_{ion}} \right) \quad (4.11)$$

c_{eon} and c_{ion} denote the concentrations of the main electronic and ionic defects, respectively. The chemical capacitance results from stoichiometric changes in the bulk of the material. In this model only the change in oxygen content in LSF64 is taken into account. However, as LSF64 is supposed to be highly stable, it is a good approximation. In oxidizing conditions the chemical capacitance shows a strong temperature dependency, with a strong incline in chemical capacitance from 500 to 900 °C (see Fig. 4.4). This incline is caused by the increase of oxygen vacancies in air upon heating (see Fig. 4.2).

In reducing conditions, however, the chemical capacitance is relatively stable from 400 to 1000 °C, see Fig. 4.5. This is also caused by the relationship

between p_{O_2} and T (Fig. 4.1): the increase in temperature leads to an increase in $[e']$, but causes a decrease in oxygen partial pressure which in turn decreases $[e']$. Due to these counteracting effects the overall change in $[e']$ is small and accordingly C_{chem} is relatively stable under reducing conditions.

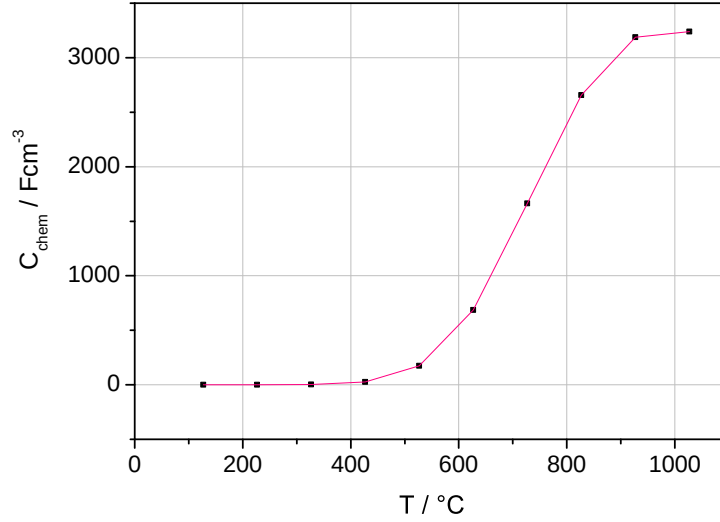


Figure 4.4: Calculated chemical volume specific capacitance for LSF64 in oxidizing conditions. Black squares are calculated neglecting the electrons. The pink lines shows the calculated chemical capacitance for $c_{eon} = [h'] + [e']$.

4.1.3 Calculation of the Brouwer diagram for LSF64

The defect model can also be used to calculate the Brouwer diagram for a fixed temperature, see Fig. 4.6. For the calculation we used $T = 650^\circ\text{C}$, as many impedance measurements were performed at this temperature. The horizontal lines set at $\log(p_{O_2}/\text{bar}) = 0.2$ and -22 indicate the atmosphere in which the impedance measurements were performed. A comparison to the Brouwer diagram given in the introduction (Fig. 2.4) shows that our measurement conditions lie in region (III) and (IIb) for oxidizing and reducing conditions, respectively.

4.2 Thin film characterization

Thin film quality is an critical issue for the reproducibility and the interpretation of measurement results. Thus different methods were applied for film characterization.

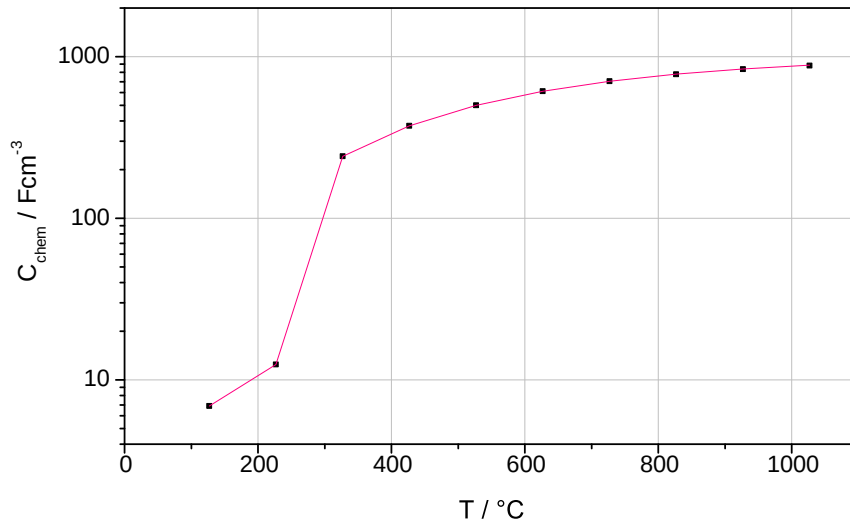


Figure 4.5: Calculated volume specific chemical capacitance for LSF64 in reducing conditions. Black squares are calculated neglecting the electron holes. The pink lines shows the calculated chemical capacitance for $c_{eon} = [h'] + [e']$.

- **Scanning electron microscope (SEM) and tunneling electron microscope (TEM)**

SEM was used to investigate the thin film surface. Fig. 4.7 shows a SEM image of a freshly deposited LSF64 thin film on YSZ (100) single crystalline substrate. The thin film consists of several grains of approximately 50 nm width. Under the given deposition parameters (see section 3.2) the LSF64 grows columnar as can be seen in the TEM image in Fig. 4.7. However no indication of pores was found.

- **X-ray diffraction (XRD)**

Grazing incidence X-ray diffraction patterns were recorded of a freshly deposited LSF64 thin film (220 nm) on a YSZ (100) single crystalline substrate. Despite the low incidence angle (2°) the main peaks correlate to the YSZ substrate. Peaks from LSF were merged with those from the ICDD database (PDF-Nr. 01-072-8137), no further peaks were detected. Literature reports a phase transition for LSF64 from rhombohedral to cubic at $850 \pm 50^\circ\text{C}$ in air for LSF64 [28].

- **Time of Flight - Secondary Ion Mass Spectroscopy (TOF-SIMS)**

The depth dependence of the cations in the sample was determined by TOF-SIMS measurements, see Fig. 4.9. These measurements

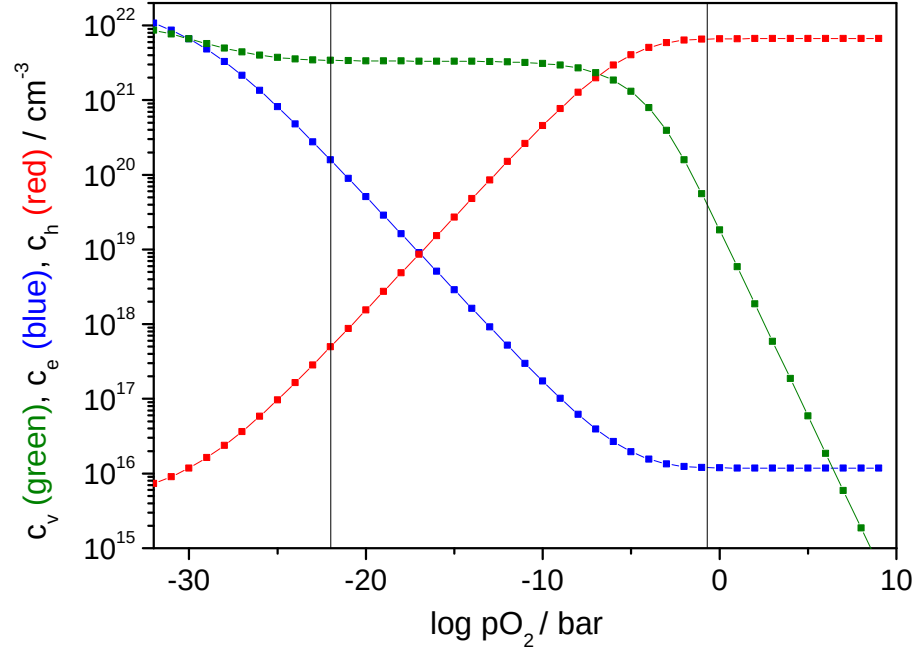


Figure 4.6: Calculated Brouwer diagram for LSF64 at $T = 650^\circ\text{C}$. Concentration of electrons $[e']$ (blue), concentration of holes $[h']$ (red) and concentration of oxygen vacancies $[V_{\text{O}}^{\bullet\bullet}]$ (green).

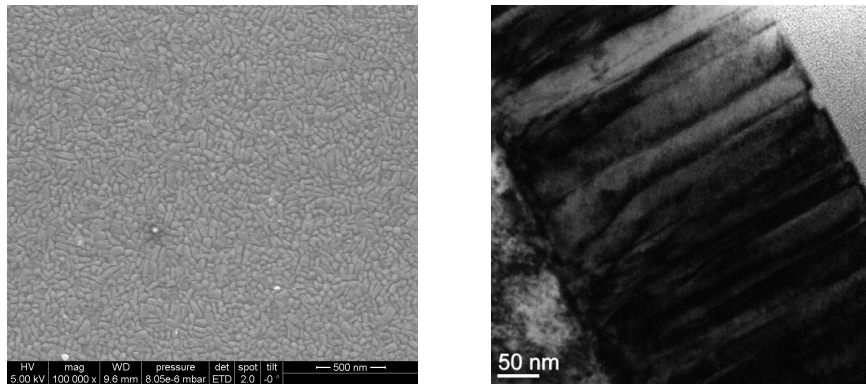


Figure 4.7: Left: SEM image of LSF64 thin film (220 nm) surface on YSZ (100) single crystalline substrate after PLD deposition. Right: TEM image of LSF64 thin film cutting edge.

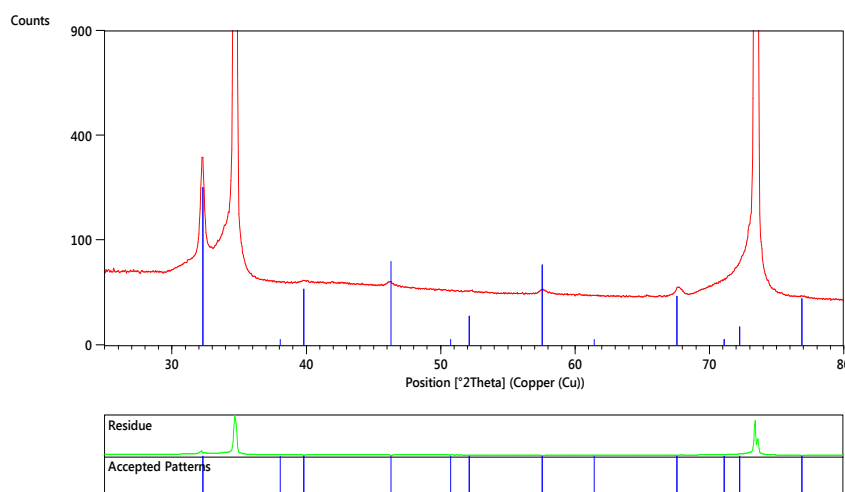


Figure 4.8: *Grazing incidence X-ray diffraction pattern of freshly deposited LSF64 thin layer (220 nm) on YSZ single crystalline substrate, comparison to 01-072-8137 (LSF64).*

showed that the cationic ratio is constant over the entire film thickness and does not undergo changes within the sensitivity limit of the TOF-SIMS upon annealing in air or humidified hydrogen for 72 h. Absolute ratios, however, cannot be determined by SIMS.

4.3 Impedance measurements

Several measurements shown in this section were also published in Ref. [91]. Each graph taken from the publication is indicated by a citation. The interpretation is naturally similar to that delivered in the publication.

4.3.1 Impedance measurements in oxidizing conditions

Well-defined LSF64 thin film microelectrodes were measured in air. Typical impedance spectra of circular microelectrodes (200 μm diameter) without current collector and with bottom current collector are shown in Fig. 4.10.

The spectra consist of

- a high frequency non-zero axis intercept (R_a), which is similar for both electrodes,

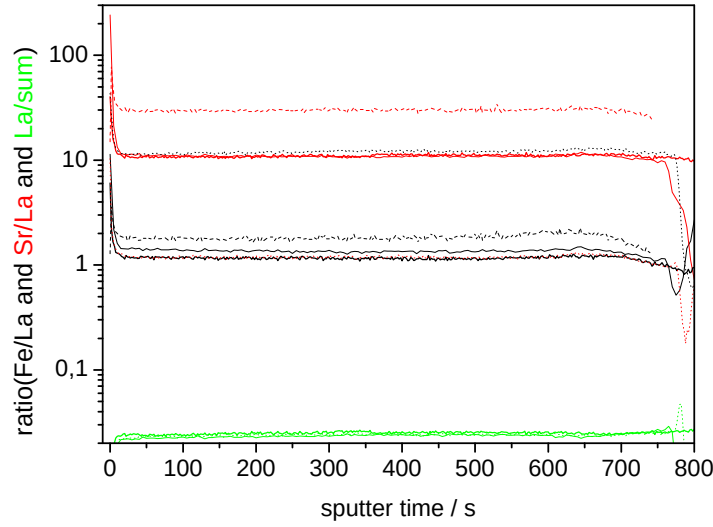


Figure 4.9: Secondary ion ratios (Fe/La (black), Sr/La (red) and La/sum (green)) in LSF64.

- an intermediate frequency depressed semicircle (R_b , C_b), which is pronounced in the case of the additional current collector and
- a low frequency dominant semicircle (R_c , C_c).

The high frequency axis intercept can consist of three contributions: the dc resistance of the electrolyte, the resistance of the contacts and a sheet resistance from the electrode. The contribution from the contacts is negligible in comparison to the contribution from the electrolyte. In air LSF64 is in a p -conducting regime, see Fig. 4.6, with an acceptable conductivity [27], accordingly, a contribution from a sheet resistance is not to be expected. Also in literature the high frequency intercept has been assigned to the dc resistance of the electrolyte[92], [56], [93]. It is typical that the electrolyte impedance consists only of a dc resistance, due to the small capacitance at high temperatures [56].

As the electrolyte resistance is a function of temperature, we can use the measured resistance to calculate the electrode temperature (T_{calc}) using the spreading resistance formula, which connects the ionic conductivity of the

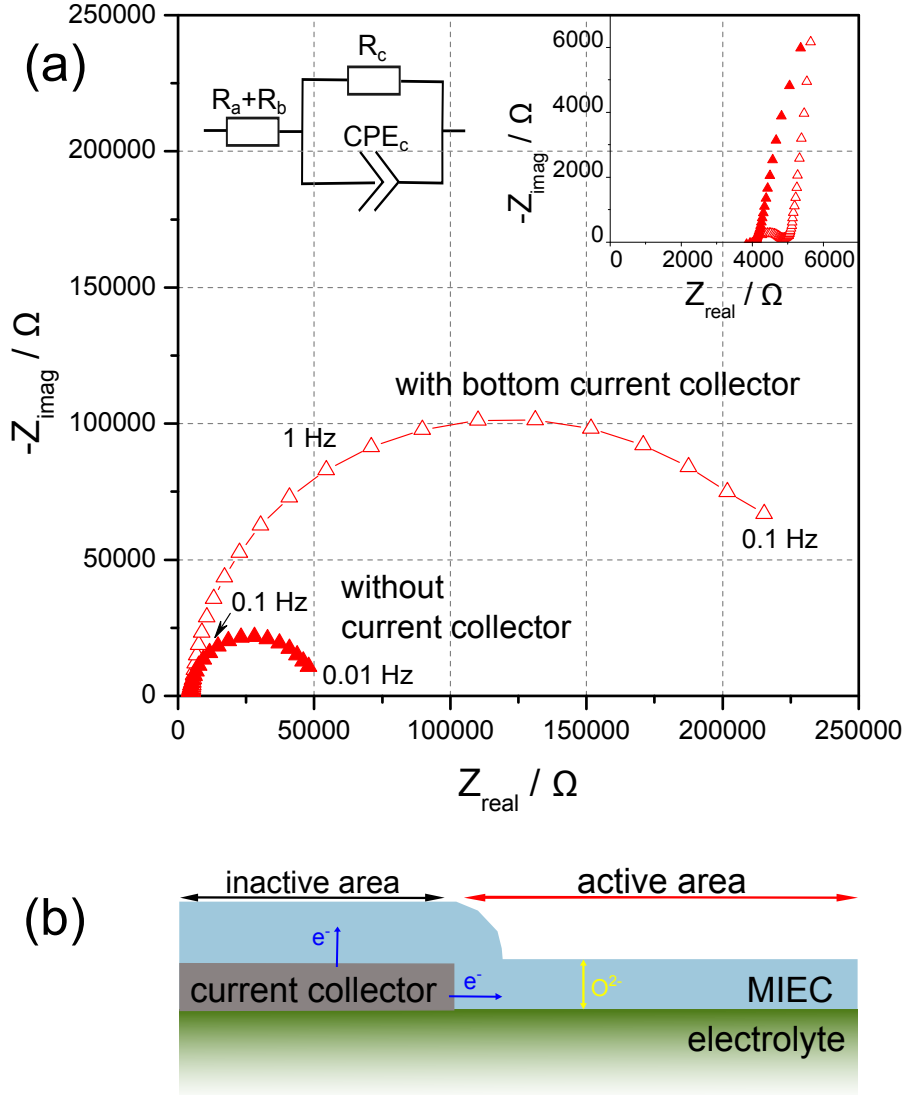


Figure 4.10: a) Impedance spectra of LSF64 microelectrodes (195 μm diameter) in air, with bottom (open triangles) and without (filled triangles) current collector. The electrode temperature T_{calc} , calculated from the high frequency offset R_a , is 619 $^{\circ}\text{C}$ for both measurements. Right inset: zoom on the high frequency range of the impedance spectra. Left inset: simple equivalent circuit, used to fit the low frequency arc in the impedance spectra. b) Schematic picture of active and inactive electrode surface areas for electrodes with (bottom) current collector. Taken from Ref. [91].

YSZ 9.5 *mol%* single crystal electrolyte (σ_{YSZ}) and the diameter of a circular LSF microelectrode (d_{ME}) [94] [82] [92].

$$\sigma_{YSZ} = \frac{1}{2R_a d_{ME}} \quad (4.12)$$

This formula together with a polynomial fit of the measured conductivity as function of temperature, allows to estimate the temperature of the microelectrodes. The evaluated temperature is not the surface temperature of the electrode, but rather a mean temperature of the electrolyte in vicinity of the electrode. However, it is important, as the sample temperature deviates strongly from the set temperature, due to heating from below and local cooling of the microelectrode by the contact tips. We observe that the calculated temperature can deviate from the set temperature by 80 – 90°C [66].

In Fig. 4.10 R_a has an almost identical value for both types of microelectrodes, which is due to the same set temperature, same electrolyte substrate and same total electrode size. Moreover, the same R_a value with and without current collector also confirms high in-plane electronic conductivity, cf. Ref. [95].

The intermediate frequency feature is assigned to the interfacial impedance [56]. Its capacitance is caused by stoichiometric changes at the electrode/electrolyte interface and/or charging of the interface similar to an electrostatic double layer. Values found for C_b are often bigger than those expected for an electrostatic double layer [96]. The interfacial resistance results from the charge transfer between electrode and electrolyte. In case of the electrode with additional current collector the intermediate frequency feature is pronounced, see Fig. 4.10 inset. This is very likely an effect of the different geometry. The current collector covers approximately 80% of the electrode/electrolyte interface, accordingly it is expected to increase by ca. a factor of 5. Also additional interfaces (electrolyte/current collector and current collector/electrode) may contribute to this capacitance. In the equivalent circuit used to fit the impedance spectra (see Fig. 4.10, inset) the interfacial capacitance is neglected and only the interfacial resistance (R_b)

is considered.

The capacitance of the dominant semicircle (C_c) is often referred to as chemical capacitance, it is caused by stoichiometric changes in the electrode bulk (see Eq. 4.11). In the equivalent circuit (see Fig. 4.10, inset) the chemical capacitance is represented by a constant phase element (CPE). Its impedance, Z_{CPE} is expressed by:

$$Z_{CPE_c} = \frac{1}{[T_c \cdot (j * \omega)^{P_c}]} \quad (4.13)$$

where j is the imaginary unit and ω represents the angular frequency. The chemical capacitance can then be calculated using

$$C_c = C_{chem} = \left(R_c^{1-P_c} \cdot T_c \right)^{\frac{1}{P_c}} \quad (4.14)$$

where P_c and T_c are fitting parameters [97]. For $P = 1$ the CPE describes an ideal capacitance. For the chemical capacitance P -values close to 1 are expected, and indeed, 0.98 and 0.94 are found for the samples shown in Fig. 4.10 without and with current collector, respectively.

As the chemical capacitance is a bulk property it is normalized to the thin film volume. The chemical capacitances evaluated from the spectra shown in Fig. 4.10 have values of 1293 F/cm^3 and 289 F/cm^3 for the sample without and with current collector, respectively. This order of magnitude is in accordance to what is expected for MIECs [57].

The main resistive process R_c , observed at low frequencies, is attributed to the oxygen exchange reaction at the surface of the electrode [56]. As LSF64 is a MIEC we expect the entire surface area to be active towards the oxygen exchange reaction. Accordingly the area specific resistance (ASR), referred to the entire electrode surface, is calculated to equal $13.6 \text{ } \Omega\text{cm}^2$ for the microelectrode without current collector and $68.2 \text{ } \Omega\text{cm}^2$ for the sample with current collector.

The surface resistance is highly sensitive to thermal history, segregation and contamination. The shown spectra (Fig. 4.10 a)) were recorded on fresh samples, thus their resistances should be similar, but they differ by a factor of 0.19. Almost the same difference (factor 0.22) is seen in

the chemical capacitance. As the chemical capacitance is generally more stable than the surface resistance, we conclude that this factor has to be caused by sample geometry. Indeed, the electrode surface with no current collector beneath is $A \cdot 0.18$. This indicates that the electrode volume on top of the current collector is not polarized (see schematic in Fig. 4.10 b)). From the calculated Brouwer diagram (see Fig. 4.6) we know that LSF64 in air is in a p-type conducting regime, simultaneously the concentration of oxygen vacancies is low. If we correct the gained values for the assumption that the volume above the current collector does neither contribute to the oxygen exchange nor to the chemical capacitance, we gain $12.3 \Omega\text{cm}^2$ and 1606 F/cm^3 for the sample with current collector. Both values are in good agreement with those found for the sample without current collector: $13.6 \Omega\text{cm}^2$ and 1293 F/cm^3 for R_c and C_{chem} , respectively. These values are somewhat lower than those found in literature (approximately $100 \Omega\text{cm}^2$ at 635°C) [98], which is probably due to a different thermal history. The values for the chemical capacitance are also in the range of the calculations (see Sec. 4.1.2), where 644 F/cm^3 were found.

The area related electrode resistances of a freshly prepared LSF64 microelectrode ($200 \mu\text{m}$ diameter, 220 nm thickness, no current collector) at different temperatures were used to evaluate the activation energy, see Fig. 4.11. Measurements were performed in dry synthetic air. At each temperature only two spectra were recorded to ensure a fast measurement progress, and therein minimize the effect of degradation in the evaluated data. Even with only this few measurements the points in the Arrhenius plot scatter. The activation energy of 1.74 eV is very similar to the findings by Baumann et al. where 1.8 eV were found [98]. However, microelectrodes in air usually show a strong degradation.

The corresponding chemical capacitances are depicted in Fig. 4.12. The chemical capacitance usually does not show much time dependent changes for microelectrode measurements in air. Thus the degradation observed in the electrode resistance (see Fig. 4.11) is very likely located on the electrode surface. The calculated chemical capacitance is also depicted in Fig. 4.12. It is proportional to the derivative of the chemical potential of oxygen vacancies with respect to their concentration [99]. Accordingly a larger chem-

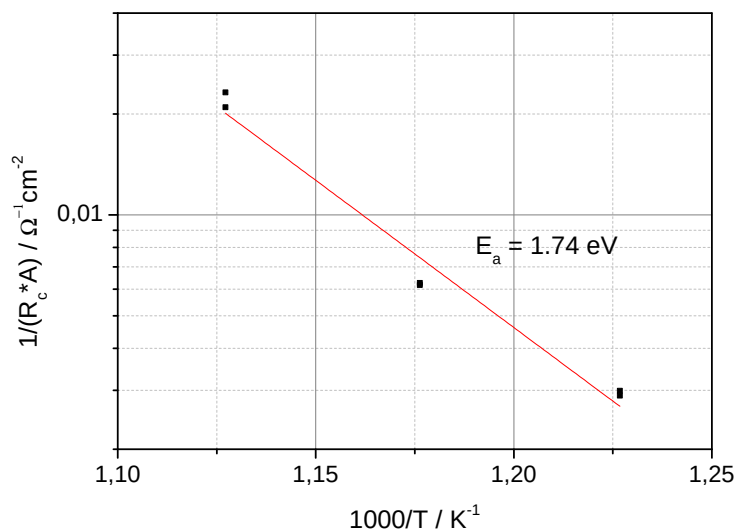


Figure 4.11: Arrhenius plot of the area related surface resistances of a LSF64 circular thin film electrode (200 μm diameter, 220 nm thickness) without current collector in synthetic air.

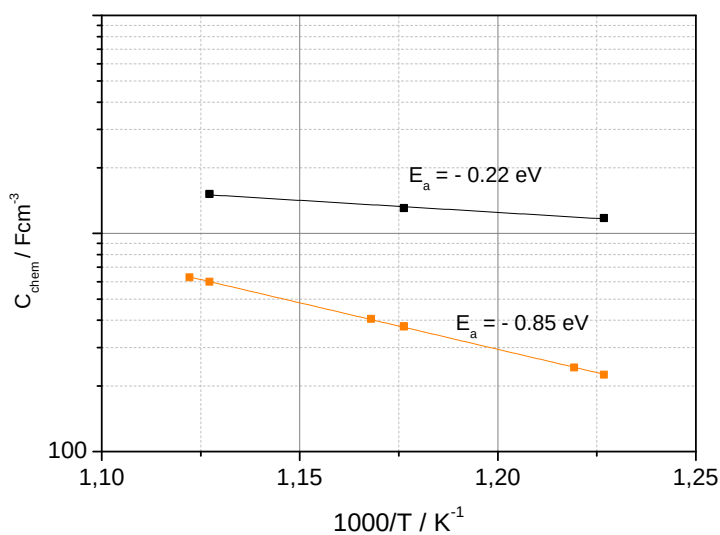


Figure 4.12: Arrhenius Plot of the chemical capacitances of a LSF64 circular thin film electrode (200 μm diameter, 220 nm thickness) without current collector in synthetic air (black) and chemical capacitances calculated from the defect chemical model (orange).

ical capacitance implies that a change in p_{O_2} has a stronger impact on the oxygen non-stoichiometry, than it would actually have at lower temperatures [57]. However, the measured chemical capacitance does not show the high activation energy expected from the calculation. For the calculated chemical capacitance an activation energy of -0.85 eV is found, while the measured values are activated with -0.22 eV . The difference between the calculated and the measured capacitance values is bigger at lower temperatures. On the other hand, the activation energy of the measured values is in accordance with literature where -0.27 eV were found [98]. Possibly this indicates some shortcomings of the defect chemical model of LSF64 at least for describing thin films.

Degradation in oxidizing atmosphere

Generally the electrodes degraded at elevated temperatures in air. Such a long-term degradation is exemplary shown, by the impedance measurement in air on a LSF64 microelectrode ($380 \times 146 \mu\text{m}^2$) with finger geometry ($13 \mu\text{m}$ spacing between the fingers, below the thin film) at $T_{set} = 650^\circ\text{C}$. Fig. 4.13 shows the area related surface resistance (calculated for the entire electrode surface area) and the chemical capacitance.

For this microelectrode, the resistance starts at a low initial value of approximately $2 \Omega\text{cm}^2$. After ca. 1.2 h a sudden degradation of electrode resistance sets in (to ca. $33 \Omega\text{cm}^2$), accompanied by a strong change in C_{chem} , indicating that this degradation affects both, the surface and the bulk, of the LSF64 microelectrode.

Later, at approximately 30 h another degradation sets in, first gradually and then stronger. At the same time the chemical capacitance grows slowly from 980 Fcm^{-3} to 1250 Fcm^{-3} , it seems to reach a plateau towards the end of the experiment. The measured chemical capacitance is in good agreement with the capacitance calculated from the defect model at 650°C (923 Fcm^{-3}). Except from the step after 1.5 h there is no clear correlation observable between R_c and C_{chem} .

The cause of the degradation is unclear, especially as the course of degradation did not always follow the one showed here. As LSF64 is supposed to be stable in air at 650°C a demixing of the material is highly improbable. The temperature gradient over the sample, due to the heating from

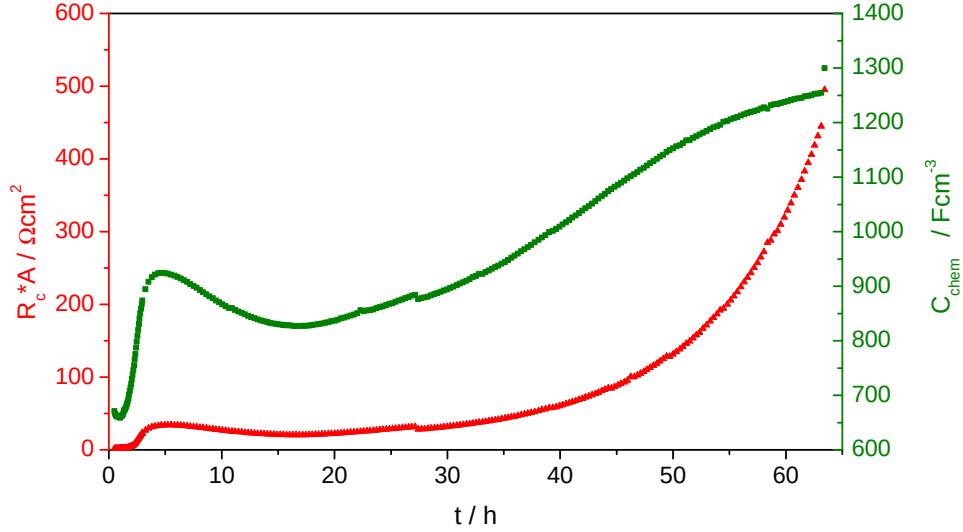


Figure 4.13: Area related electrode resistance (red) and chemical capacitance (green) of a LSF64 thin film microelectrode ($380 \times 146 \mu\text{m}^2$) with finger geometry ($13 \mu\text{m}$ spacing between the fingers) at a set temperature of 650°C over time.

below, might be involved in the degradation process. Degradation of the electrode surface can be caused by contamination with sulphur (from air), as was observed by Bucher et al. on $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ [100]. Also silicon-hydroxide may decompose on the surface, causing an enrichment of silicon on the surface [101].

Effect of humidity on electrode impedance

Water is part of the real reaction conditions, and therefore the impact of humidity on the electrode resistance was tested. Impedance measurements were again performed on well defined circular LSF64 thin film electrodes ($200 \mu\text{m}$ diameter, 220 nm thickness). The first spectra were recorded under air at $T_{\text{calc}} = 619^\circ\text{C}$, see Fig. 4.14. The spectra show the same features, as described above. The microelectrode shows a strong degradation as the electrode resistance increases with each consecutive measurement. The chemical capacitance is approximately 1500 Fcm^{-3} and increases with advancing degradation.

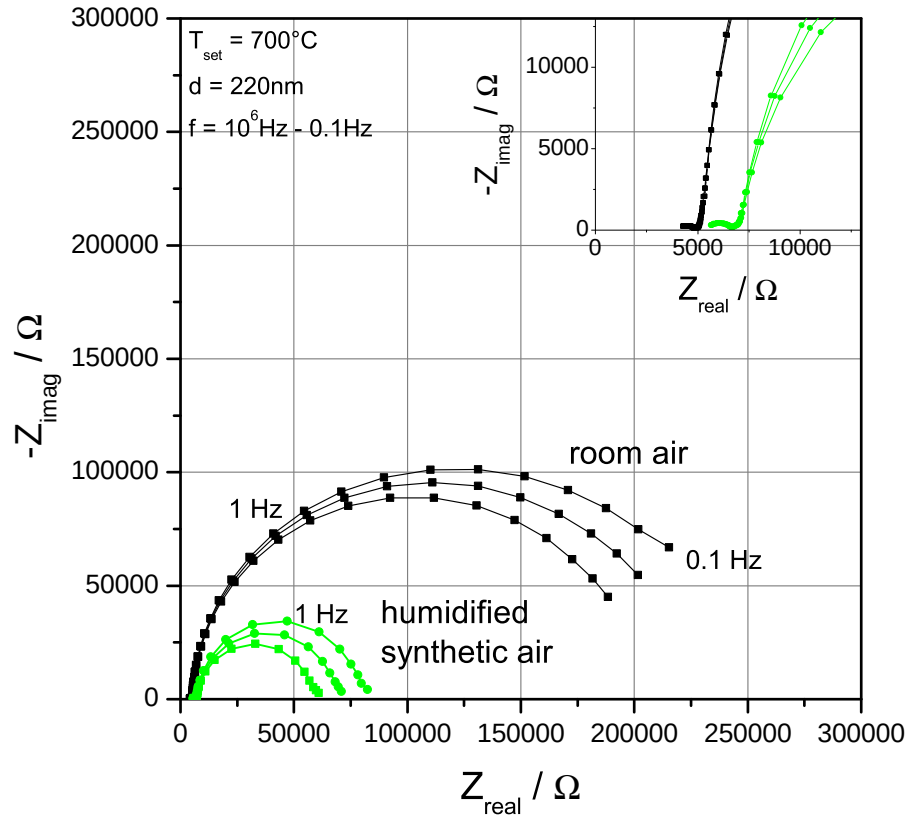


Figure 4.14: Impedance spectra of LSF64 microelectrode ($200\ \mu\text{m}$ diameter, $220\ \text{nm}$ thickness) with bottom current collector at $T_{\text{calc}} = 600^\circ\text{C}$ in humidified synthetic air (green) and at $T_{\text{calc}} = 619^\circ\text{C}$ in room air (black).

Upon gas change to humidified, synthetic air the impedance features are still those expected for a measurement in air, but the electrode resistance R_c drops dramatically (factor 1/3) and also the chemical capacitance is reduced to approximately 1000 Fcm^{-3} . The fast degradation observed in dry air, also continues in the humidified conditions and like in air it is accompanied by an increase in chemical capacitance. The calculated electrode temperature is 20°C lower for the measurement in humidified air.

The measurements in both atmospheres were taken consecutively on the very same microelectrode in the same measurement set-up, the only changed parameter was the gaseous atmosphere. The observed change in chemical capacitance could be a result of this difference in electrode temperature. The calculated chemical capacitance equals 506 Fcm^{-3} (at 600°C) and 637 Fcm^{-3} (at 620°C). Accordingly, the measured chemical capacitance is in both cases bigger than the chemical capacitance by a factor of ca. 2. The drastically reduced electrode resistance in humidified synthetic air suggests an enhanced oxygen exchange kinetics due to humidity.

To further investigate the impact of humidity on the electrode resistance, a macroscopic ($5 \times 5 \text{ mm}^2$) LSF64 thin film electrode on YSZ with current collecting fingers on top and a porous LSF64/Pt counter electrode on the back side, was heated in dry and humidified synthetic air. The use of synthetic air in both cases rules out an effect from other components (e.g. sulphur) in room air. Fig. 4.15 shows the area related surface resistances (calculated using the total free electrode area) as well as the corresponding chemical capacitances at temperatures of 599.6 , 649.9 and 700.9°C . Measurements taken in dry synthetic air are shown as red triangles, those recorded in humidified synthetic air are depicted as blue squares, see Fig. 4.15. The measurement time plotted on the x-axis refers to the first measurement taken at 600°C as starting point.

At 600°C the sample first degrades with a constant rate. The change to humidified gas leads to an increased degradation. Simultaneously the chemical capacitance is slightly bigger under humidified conditions. The calculated chemical capacitance for 600°C equals 506 Fcm^{-3} and is shown

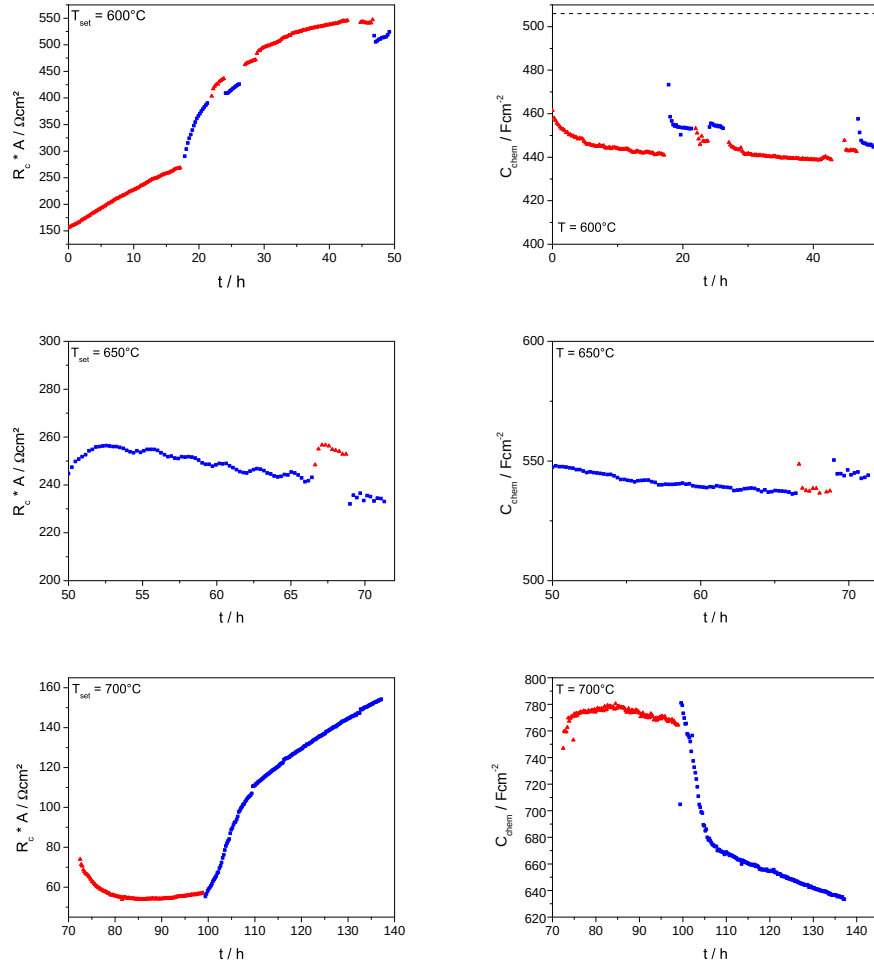


Figure 4.15: Measurement of a macroscopic (5x5 mm²) LSF64 thin film electrode at different temperatures: 599.6, 649.9 and 700.9°C in *dry* (red) and *humidified synthetic air* (blue). Left: area related resistance and right: chemical capacitance over time.

in the plot as dashed line. Upon further gas changes at 600 °C the chemical capacitance is always slightly enhanced in humidified conditions in comparison to wet conditions. This suggests that the effect by the humidity on the chemical capacitance is at least always the same. In contrast to that the electrode resistance decreases after the second and third gas change to humidified conditions. In general the electrode resistance seem to reach a constant level after ca. 40 *h*.

At 650 °C the electrode resistance declines. It is again higher in dry conditions, but also there it declines. The oscillations observed in R_c and C_{chem} are very likely simply caused by the pulsing of the oven. After change to dry synthetic air C_{chem} does not seem to be affected, nevertheless, upon change to humidified conditions the chemical capacitance is again slightly higher, a behaviour already seen at 600 °C.

At 700 °C the electrode resistance first declines in dry synthetic air and then seems to reach a constant value. Upon gas change to humidified conditions a fast degradation sets in. Interestingly at ca. 110 *h* the degradation suddenly turns to a slower rate. This behaviour is reflected in the chemical capacitance. In dry synthetic air C_{chem} is more or less stable, starting from 85 *h* it seems to decline slowly. This could hint towards a starting change in the bulk. Upon gas change, first the chemical capacitance is slightly higher. This was already observed at the two lower measurement temperatures. However, it then declines steeply until $t = 105$ *h*, when it suddenly changes to a slower decline. At first glance one would expect that the change in R_c and C_{chem} correlate, what they probably do, but the drastic change in C_{chem} stops 5 *h* before the fast degradation of the surface changes to a slower degradation rate.

The chemical capacitances from the measurements shown above are compared to those calculated from the defect model, see Tab. 4.1 and Fig. 4.16.

The measured chemical capacitance is again less strongly activated than calculated capacitance, see Fig. 4.16. However, the activation energy of the measured chemical capacitances equals 0.41 eV and is therefore by a factor 2 larger than that found in microelectrode measurements in air and than

temperature °C	C_{chem} -calculated Fcm^{-3}	C_{chem} -measured Fcm^{-3}
600	506	441
650	892	539
700	1393	779

Table 4.1: Comparison of chemical capacitances calculated from the defect model of LSF64 and those observed (Fig. 4.15) or different temperatures.

expected from literature [98].

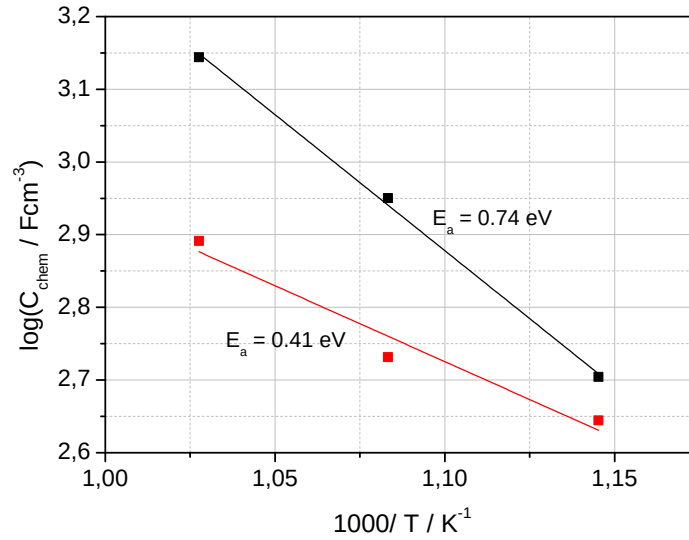


Figure 4.16: Arrhenius plot of calculated (black) and measured C_{chem} values (red) in dry synthetic air on macroscopic sample.

The effect observed for this macroscopic LSF64 thin film electrode is by no means as strong as the enhancement due to humidity observed for the LSF64 microelectrode. Further, humidity seems to be able to enhance degradation as well as oxygen exchange, indicating a dependency on the sample history. Similar findings were made on LSCM [102]: the oxygen surface exchange was measured in water and carbon dioxide containing atmospheres using a tracer exchange method. It was found that humidity leads to a more than twice as high k^* . However, if those samples were

pre-annealed in water or carbon dioxide systems k^* was decreased.

Horita et al. found an enhancement of the surface exchange factor in *LSF* cathodes under cathodic polarization, which they suspected may be due to water vapour [96]. Also on $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC64) impedance measurements showed a lower electrode surface resistance under humidified air [103]. The effect was stronger at lower temperatures, which indicates a relation to surface hydroxide coverage, which is higher at lower temperatures. However, the hydroxide coverage is probably low as on lanthanum oxide the hydroxyls are removed above 427 °C [104], and also in the case of $\alpha - Fe_2O_3$ the coverage with hydroxyls at higher temperature is low, approximately 0.01 ML at 700 °C. Consequently, already minor amounts of hydroxyls drastically increase the oxygen exchange rate or water causes other changes, which in turn lead to a high exchange rate. For example the adsorption of superoxide or peroxide on the surface, or an enhanced oxygen vacancy concentration due to those adsorbates could lead to the decrease in surface resistance [105].

The enhanced degradation under humid atmospheres was investigated by Bucher et al. [101]. They observed that in humid atmospheres *Si* poisoning (assuming a *Si* source in close vicinity) leads to an increase in degradation. In dry atmospheres degradation of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC64) at 600 °C is mainly caused by the formation of a *Sr* rich perovskite at the surface together with *La* oxide.

Humidity clearly shows an impact on the exchange kinetics not only in the case of *LSF*64. However, the underlying nature of the observed effects needs further investigation, especially as humidity is part of the real fuel/electrolysis cell operation conditions.

4.3.2 Impedance measurements in reducing conditions

Fig. 4.17 shows the impedance measurement of a circular (100 μm) *LSF*64 thin film electrode without current collector in humidified hydrogen. In comparison to the analog measurement in air (Fig. 4.10) the high frequency intercept (R_a) is shifted, the main arc is depressed and the

electrode resistance is drastically increased.

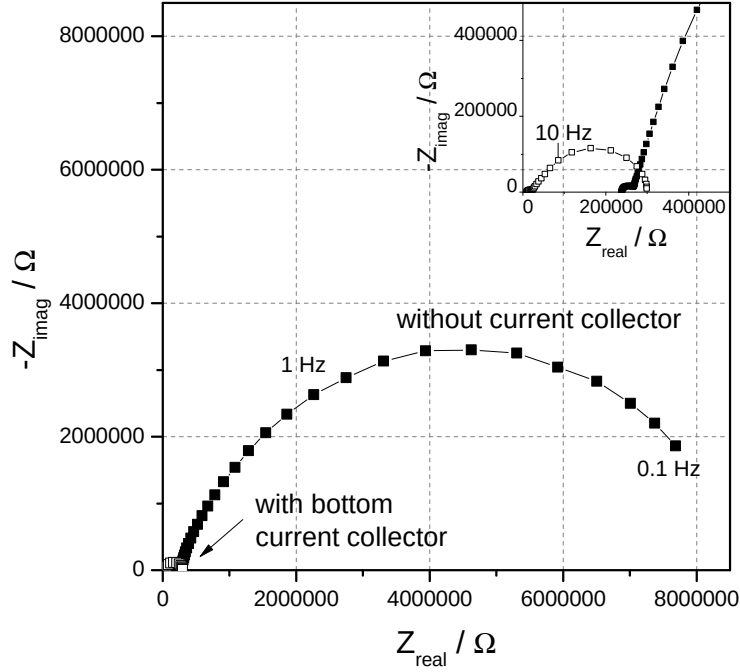


Figure 4.17: Impedance spectra of LSF64 microelectrodes (95 μm diameter) in humidified hydrogen, with bottom current collector (open squares) and without current collector (filled squares). Spectra were recorded at 700 $^{\circ}\text{C}$ set temperature, T_{calc} for the electrode with current collector is equal to 605 $^{\circ}\text{C}$. For the sample without current collector a meaningful temperature could not be calculated due to the sheet resistance. Taken from Ref. [91].

As mentioned above, R_a consists of three contributions: the electrolyte resistance, which in case of YSZ is only a function of temperature and not of partial pressure, the contact resistance and a sheet resistance. The contact resistance can be ruled out, as it is not observed in air, although using the very same contact needles. A sheet resistance is not only likely but also expected due to the decrease in electronic charge carriers towards lower oxygen partial pressures, see Fig. 4.6. Further a sheet resistance would also explain the very high electrode resistance, as it reduces the active surface area to the vicinity of the contact and simultaneously increases the YSZ bulk resistance due to geometrical reasons. If we compare R_a with that found for a 100 μm circular thin film electrode with current collector, we observe that the additional current collector leads to a R_a value in the

range expected for the set temperature. Also the electrode resistance is drastically reduced with the additional current collector.

With additional current collector we observe a small shoulder in the intermediate frequency range followed by an approximately 45° slope. Such an increase is typical for diffusion limited processes. This diffusion limitation is not caused by across-plane ionic conductivity, as the concentration of oxygen vacancies is high under reducing conditions (see Fig. 4.6) and as ^{18}O tracer exchange experiments using a tracer back-exchange show a fast D^* [72]. However, the lateral transport of oxide ions above the current collecting grid structure after oxygen incorporation could cause a complex transmission line (see Fig. 4.18) and thus slopes close to 45° [38]. Also lateral electron transport can cause a complex transmission line and of course a combination of both is conceivable.

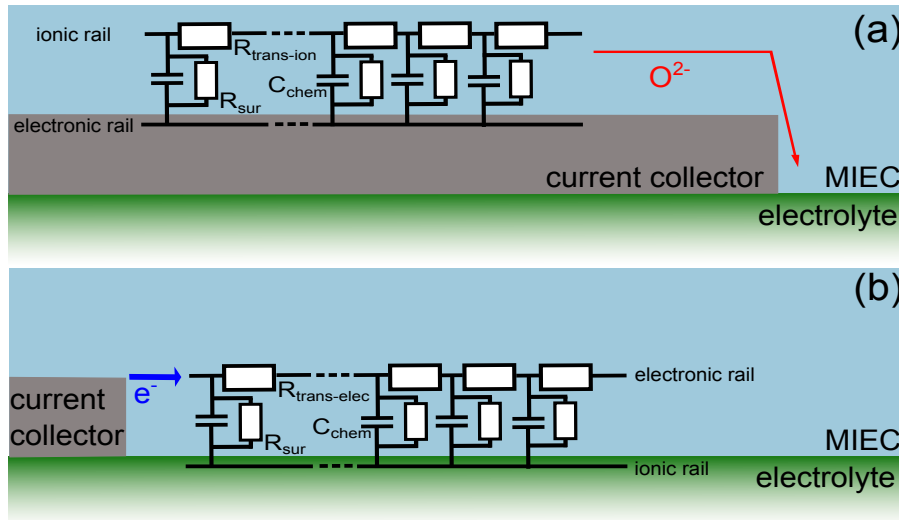


Figure 4.18: Possible transmission lines in a MIEC with current collector for the case of a) low lateral ionic conductivity resulting in an ionic transmission line in the MIEC, b) low electronic conductivity with ionic short circuit in the electrolyte and remaining electronic transmission line. Charge transport lines are set at the correct location, while the surface resistance R_{sur} has been moved inside the MIEC for reasons of clarity of the equivalent circuit, as R_{sur} and C_{chem} have to be in parallel. However, the actual surface resistance R_{sur} is located at the gas-MIEC interface. Taken from Ref. [91].

For the microelectrode with bottom current collector we obtain $C_{chem} = 103 \text{ F/cm}^3$, whereas from the defect chemical model calculation we expect a value of 545 F/cm^3 . However, taking into account that the measured sample is a thin film, the values are in reasonable agreement, and as expected much lower than in air. Still, the agreement between the measures and the calculated value is not good enough to estimate which parts of the microelectrode are actually active towards the oxygen exchange reaction.

Top vs. bottom current collector under reducing conditions

The positioning of the current collector on top or beneath the thin film (bottom geometry) has an impact on the electrode impedance. Fig. 4.19 shows a comparison of two circular ($100 \mu\text{m}$ diameter, 220 nm thickness) thin film microelectrodes with top and bottom current collector in humidified hydrogen. The spectra with top current collector look similar to those in air, with a high frequency non-zero axis intercept, a small intermediate frequency shoulder and a dominant low frequency semicircle. In contrast, spectra of samples with bottom current collector show an intermediate frequency shoulder followed by an approximately 45° slope. R_a is similar for both geometries, as the set temperature is the same and the current collectors compensate for the sheet resistance.

The features at intermediate frequencies are again assigned to the interfacial impedance. The higher electrode resistance in case of top current collector is simply caused by geometry, as the current collector covers large parts (approximately 80%) of the surface. This is also depicted in Fig. 4.20. In case of the bottom current collector substantial parts of the electrode surface above the current collecting structure might be active (area $A_1 + A_2$), while in case of top current collector only the area A_2 can contribute to the oxygen exchange reaction. Taking this into account the electrode surface resistances are similar. This also suggests that the platinum of the current collector does not act catalytically, although in literature platinum-coated nanostructured oxides have been used as catalysts for water splitting [106] and platinum is known to be catalytic towards the water forming reaction at high temperatures (1300 K) [107].

Using the simple equivalent circuit depicted as inset in Fig. 4.10 to fit only the low frequency arc, we obtain a chemical capacitance of 129 F/cm^3 in

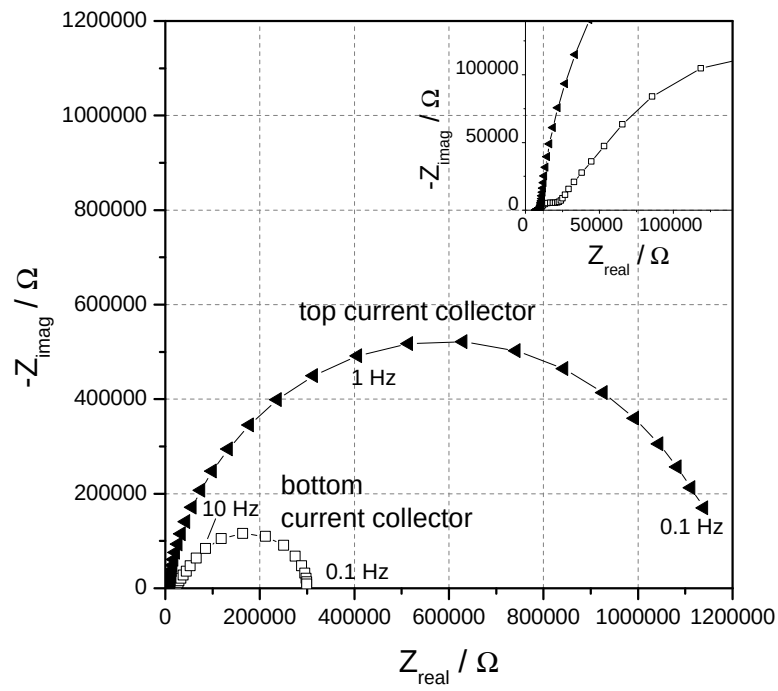


Figure 4.19: Impedance spectra of LSF64 microelectrodes (95 μm diameter) in humidified hydrogen with top (filled triangles, $T_{\text{calc}} = 623^\circ\text{C}$) and bottom (open squares, $T_{\text{calc}} = 605^\circ\text{C}$) current collector. Taken from Ref. [91].

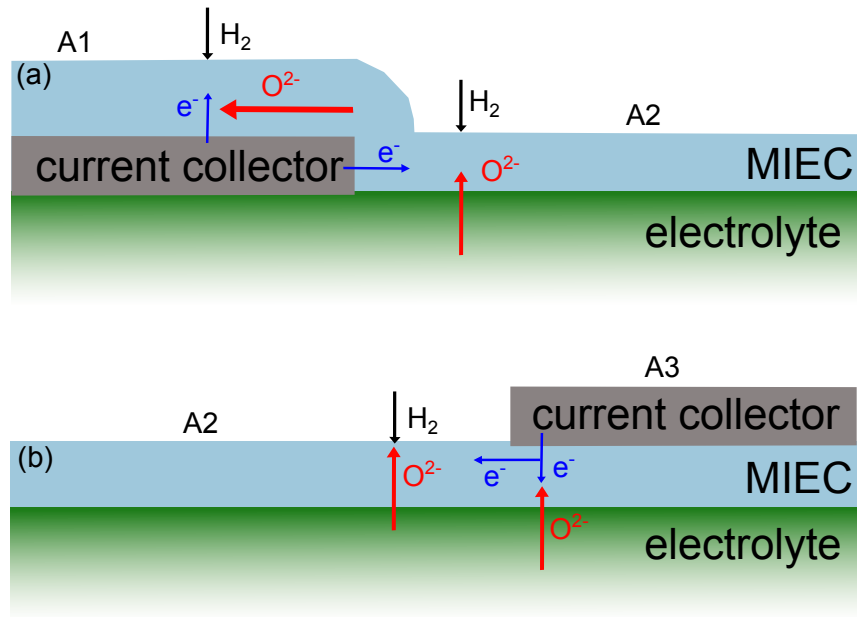


Figure 4.20: Schematic picture of ionic and electronic current and reaction pathways for bottom (a) and top (b) current collector. A2 represents the current collector free electrode surface area, while A1 and A3 describe the areas with bottom and top current collector, respectively. Taken from Ref. [91].

case of the top grid structure and 103 F/cm^3 for the bottom grid structure. In both cases the entire volume was used as reference. In case of the top current collector, the volume below the current collector (A3) is definitively polarized and probably large amounts of the free volume (A2). The similar chemical capacitance also for bottom current collector implies that also in this case large amounts of the electrode volume are polarized, and thus that the lateral charge transport indeed takes place.

Fig. 4.21 shows the impedance spectra of a $200 \mu\text{m}$ diameter electrode under the same conditions as the electrodes in Fig. 4.19. The impedance features are equal to that described above for a microelectrode with bottom current collector in humidified hydrogen. In contrast to the electrodes described above, this electrode has a current collector grid with $10 \mu\text{m}$ broad metallic stripes and $30 \times 30 \mu\text{m}^2$ holes in the grid. For this case the 45° feature is pronounced, indicating that the transport resistance is higher in this case. As the current collecting stripes still have the same width as those described above, this also hints towards an electronic in-plane transport limitation.

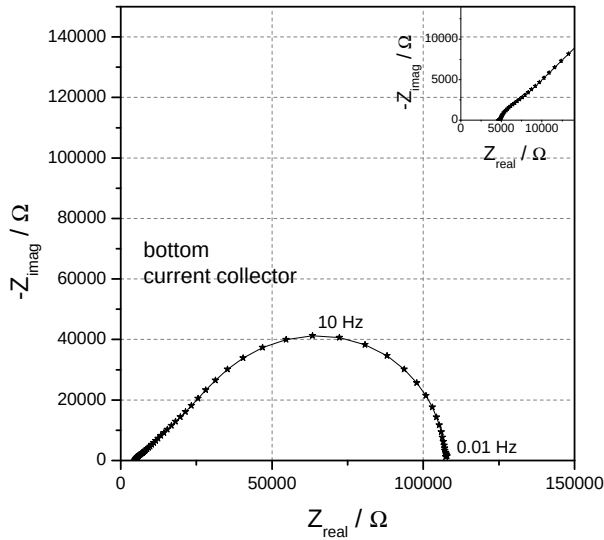


Figure 4.21: Impedance spectra of circular ($200 \mu\text{m}$ diameter) LSF64 thin film microelectrodes in humidified hydrogen with bottom (black stars) current collector with $30 \mu\text{m}$ spacing, $T_{\text{calc}} = 610^\circ\text{C}$.

The high electronic sheet resistance under reducing conditions is caused by the low concentration of electronic charge carriers, see Fig. 4.6, but also by their lower mobility [5]. The interruption of the $Fe - O - Fe$ chains by oxygen vacancies [29] [108], [109], [110] reduces the mobility of the electrons in the lattice. This might also be the reason for the measured chemical capacitance to be lower than the calculated chemical capacitance in reducing conditions.

An estimation of electrochemically active zone is very difficult, Zhang et al. tried to highlight these zones using XPS [79].

Evaluation of electrochemical properties by an impedance based analysis

For the evaluation of the electrochemical properties well defined thin film microelectrodes with metallic fingers beneath the thin film were used (see Fig. 3.3). Such microelectrodes allow for two different measurement modes: an in-plane measurement within the electrode (see Fig. 4.22) as well as an electrochemical measurement (out-of-plane) versus a counter electrode (see Fig. 4.23). In the in-plane measurement mode the metal finger combs are contacted separately, while during the electrochemical measurement the metallic fingers are short-circuited, therein acting as a current collector. Accordingly, the electrochemical measurement mode is comparable to the measurements shown above on circular microelectrodes with a grid structured current collector. This is also observed by the qualitatively same shape of the impedance spectra in electrochemical mode compared to that observed for circular microelectrodes. The typical shape of an in-plane spectrum is shown in Fig. 4.25.

The equivalent circuits used for the two measurement modes are shown in Fig. 4.24. A special fit procedure allows a simultaneous fit of both measurement modes, using the same parameter set giving an analytical solution. Details concerning the fitting procedure are given in Ref. [38]. A similar study was conducted on symmetrical cells (see Ref. [111]).

A fit of the measured impedance spectra is exemplarily shown in Fig. 4.25. For the in-plane measurement the fitting procedure gives a relatively well

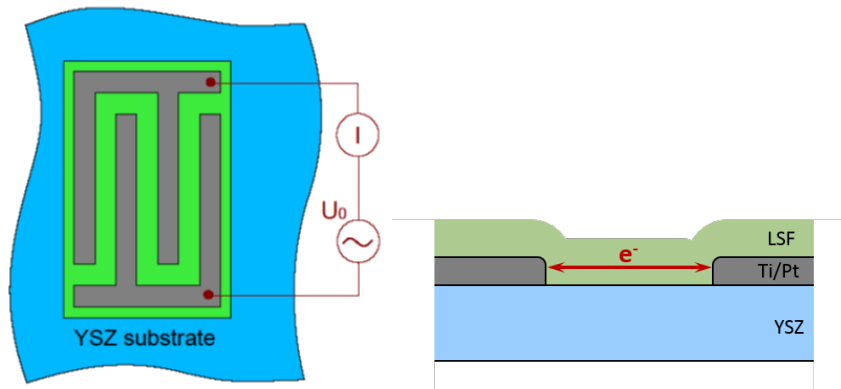


Figure 4.22: 'In-plane measurement': by contacting the metallic fingers on the microelectrode as shown on the left side a predominantly electronic measurement through the electrode (right) is possible [38].

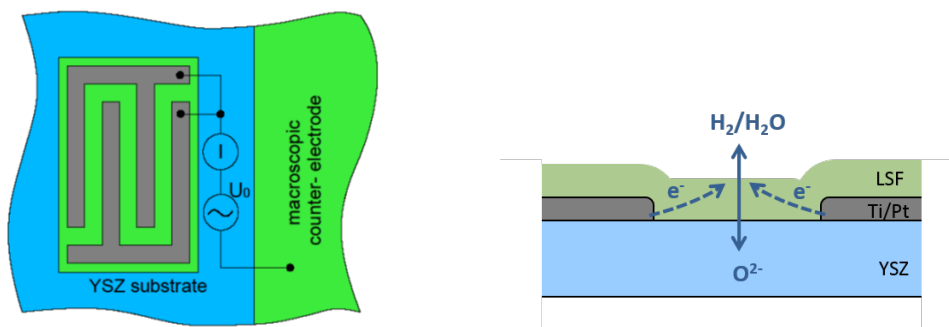


Figure 4.23: 'Out-of-plane measurement' (electrochemical mode): by shorting the metallic fingers on the microelectrode they act as current collector (left). Thereby an electrochemical measurement of the microelectrode versus a macroscopic counter electrode is possible. The current path is electrochemical [38].

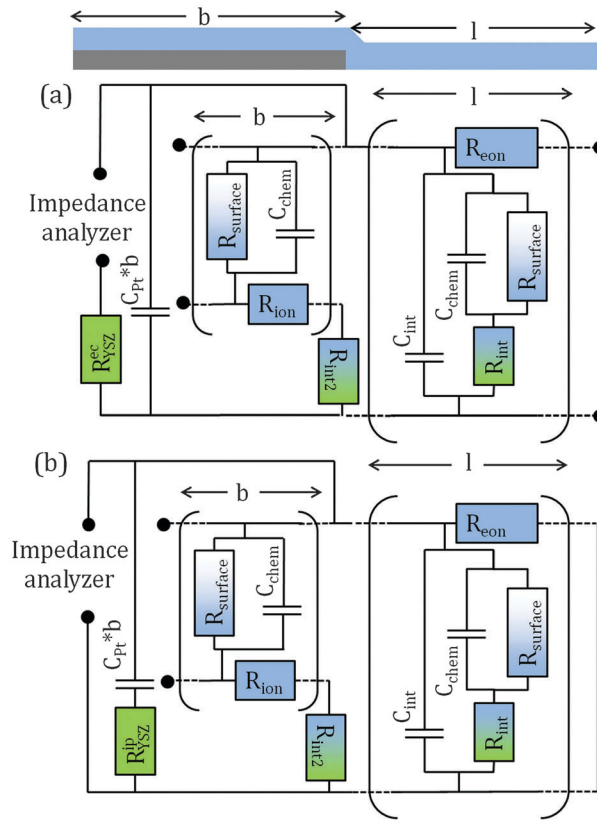


Figure 4.24: Equivalent circuit for an electrode deposited on top of the current collectors: (a) electrochemical mode, (b) in-plane mode. The elements R_{int} , C_{int} , C_{chem} and $R_{surface}$ reflect area-specific resistances and capacitances, R_{eon} and R_{ion} are electronic and ionic sheet resistance, respectively. Taken from Ref. [38].

fit. However, for the LSF64 thin film electrodes the fit was not applicable to the high and intermediate frequency range of the electrochemical measurement. Nevertheless, the fit gives good results for the main, low-frequency arc of the electrochemical measurement.

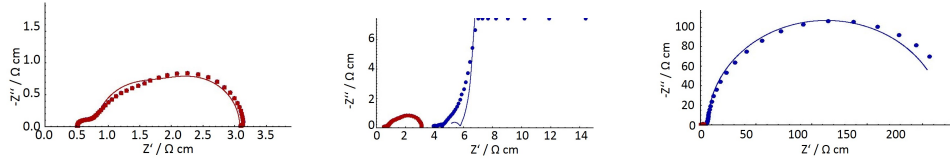


Figure 4.25: Measured spectra and fit of a LSF64 thin film microelectrode with metallic fingers (distance between fingers: $13 \mu\text{m}$) at 650°C set temperature in $\text{H}_2/\text{H}_2\text{O}$. Left: normalized in-plane spectrum (red points) with fit (red line); Right: out-of-plane spectrum (blue points) with fit (blue line); Middle: Zoom into the in-plane and the intermediate frequency range of the out-of-plane measurement.

From the described fitting procedure the following electrochemical parameters are evaluated: the chemical capacitance (C_{chem}), the surface resistance (R_{sur}), the sheet resistance (R_{eon}) and the ionic resistance (R_{ion}). From the measurement of microelectrodes with interdigitated fingers in both measurement modes (in-plane and electrochemical) at different temperatures and the subsequent analysis by the fitting procedure, the activation energy E_a of those parameters was determined (see Figs. 4.26, 4.27, 4.28 and 4.29).

Due to a variation between different microelectrodes the measured parameters scatter, nevertheless, mean values were calculated. Those mean values of C_{chem} and R_{sur} for different set temperatures are summarized in Tab. 4.2. These results are in good agreement with those observed for circular microelectrodes, as can be seen by a comparison to the measurement for a circular microelectrode with bottom current collector under reducing conditions (see Fig. 4.19), where 103 F/cm^2 and $85 \Omega\text{cm}^2$ were found at a set temperature of 650°C . Also, the activation energy of the chemical capacitance (0.23 eV) is similar to that expected from the defect chemical calculations (0.15 eV). Further, the decay length of the electronic $l_{eon} = \sqrt{\frac{R_{sur}}{R_{eon}}}$ and ionic charge carriers $l_{ion} = \sqrt{\frac{R_{sur}}{R_{ion}}}$ is longer than

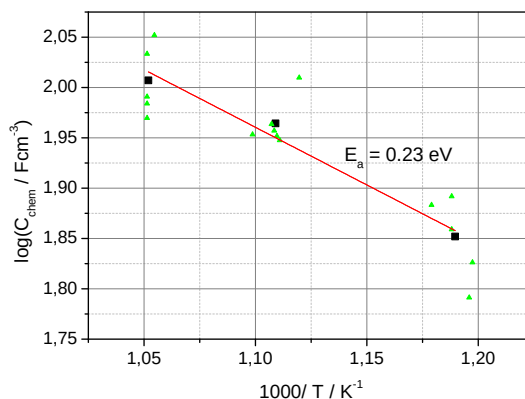


Figure 4.26: Arrhenius plot of C_{chem} for LSF64 thin film microelectrodes with interdigitating metallic fingers (distance between the metallic fingers was either 8 or 13 μm), evaluated using the fitting procedure from Ref. [38]. Green triangles show the actual measurement results, while black squares indicate mean values. The linear fit was applied to the mean values, giving an activation energy E_a of 0.23 eV.

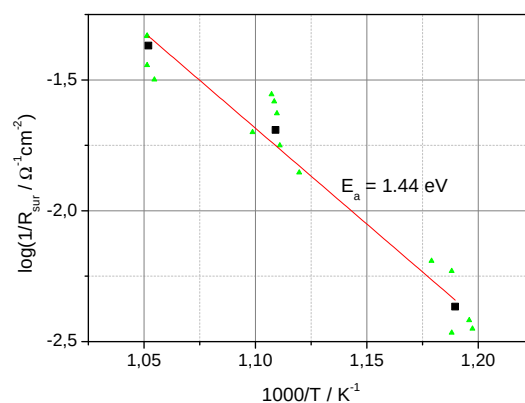


Figure 4.27: Arrhenius plot of R_{sur} for LSF64 thin film microelectrodes with interdigitating metallic fingers (distance between the metallic fingers was either 8 or 13 μm), evaluated using the fitting procedure from Ref. [38]. Green triangles show the actual measurement results, while black squares indicate mean values. The linear fit was applied to the mean values, giving an activation energy E_a of 1.44 eV.

the distance between the metallic fingers (either 8 or 13 μm) for all set temperatures (see Tab. 4.3), indicating that the LSF64 volume between the metallic fingers is fully polarized. Accordingly, the values for C_{chem} and R_{sur} evaluated from the fitting procedure can be considered as meaningful.

set temperature $^{\circ}C$	$R_{sur} \Omega cm^2$	$C_{chem} F cm^{-3}$
600	233	71
650	49	92
700	23	102

Table 4.2: Impedance parameters of LSF64 evaluated on thin film microelectrodes.

set temperature $^{\circ}C$	l_{eon}	l_{ion}
600	34.4	22.7
650	63.3	32.0
700	50.9	26.5

Table 4.3: Decay lengths of LSF64 evaluated on thin film microelectrodes.

From the sheet resistance (R_{eon}) and the ionic resistance (R_{ion}) the specific conductivities are calculated. Again, the results are shown in Arrhenius plots (see Figs. 4.28 and 4.29). The activation energies of the different electrochemical properties are summarized in Tab. 4.4.

	C_{chem}	R_{sur}	σ_{eon}	σ_{ion}
$E_a [eV]$	0.23	1.44	1.19	1.67

Table 4.4: Activation energies of LSF64 evaluated on thin film microelectrodes.

Degradation effects

Degradation was observed on macroscopic and microscopic LSF64 thin film electrodes. However, the degradation is different for these geometries.

Macroscopic samples

The positioning of the current collector on top or below (bottom) the thin film has also an impact on stability. A comparison of different grid

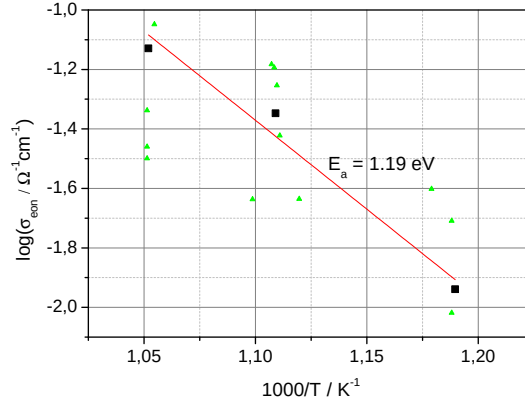


Figure 4.28: Arrhenius plot of σ_{eon} for LSF64 thin film microelectrodes with interdigitating metallic fingers (distance between the metallic fingers was either 8 or 13 μm), evaluated using the fitting procedure from Ref. [38]. Green triangles show the actual measurement results, while black squares indicate mean values. The linear fit was applied to the mean values, giving an activation energy E_a of 1.19 eV.

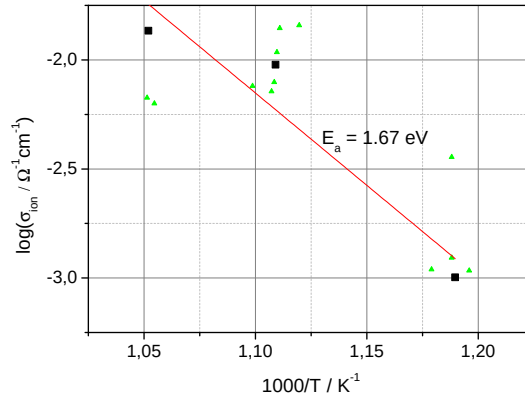


Figure 4.29: Arrhenius plot of σ_{ion} for LSF64 thin film microelectrodes with interdigitating metallic fingers (distance between the metallic fingers was either 8 or 13 μm), evaluated using the fitting procedure from Ref. [38]. Green triangles show the actual measurement results, while black squares indicate mean values. The linear fit was applied to the mean values, giving an activation energy E_a of 1.67 eV.

geometries on top and below the thin film was performed on macroscopic electrodes as their degradational behaviour is more reproducible than that of microelectrodes (see Fig. 4.35).

For this experiment symmetric electrodes were prepared on YSZ $5 \times 5 \text{ mm}^2$ single crystalline substrates. The thin films had a thickness of ca. 220 nm . The current collector structures had a net structure, where the width of the metallic parts was $10 \text{ }\mu\text{m}$ while the holes in the grid had the following dimensions: 10×10 , 35×35 and $100 \times 100 \text{ }\mu\text{m}^2$

Fig. 4.30 shows impedance measurements recorded at approximately 700°C . Spectra on the left correspond to top grid structure, those on the right are samples with bottom grid. In case of the top geometry we observe a degradation while those with bottom grid are almost constant. An interaction of the perovskite with the Ti or Pt from the current collector is unlikely. This degradation could be caused by residuals from the photolithographic process on the edges of the current collector. While such contaminations are trapped in the bottom grid case, they might spread over the surface in the top grid case.

For the samples with bigger holes in the current collector the high frequency offset is shifted to higher values, indicating that in those cases the sheet resistance of the film is not sufficiently compensated by the grid.

The electrode resistance is higher for samples with top current collector, which is simply caused by the covering of parts of the electrode surface. Taking this into account the area related electrodes resistances of fresh samples are similar for both geometries: for the $10 \times 10 \text{ }\mu\text{m}^2$ geometry $32.3 \text{ }\Omega\text{cm}^2$ for top grid and $36.9 \text{ }\Omega\text{cm}^2$ for the bottom grid are found at ca. 700°C . This similarity also suggests that there is no catalytic contribution from the platinum of the current collector.

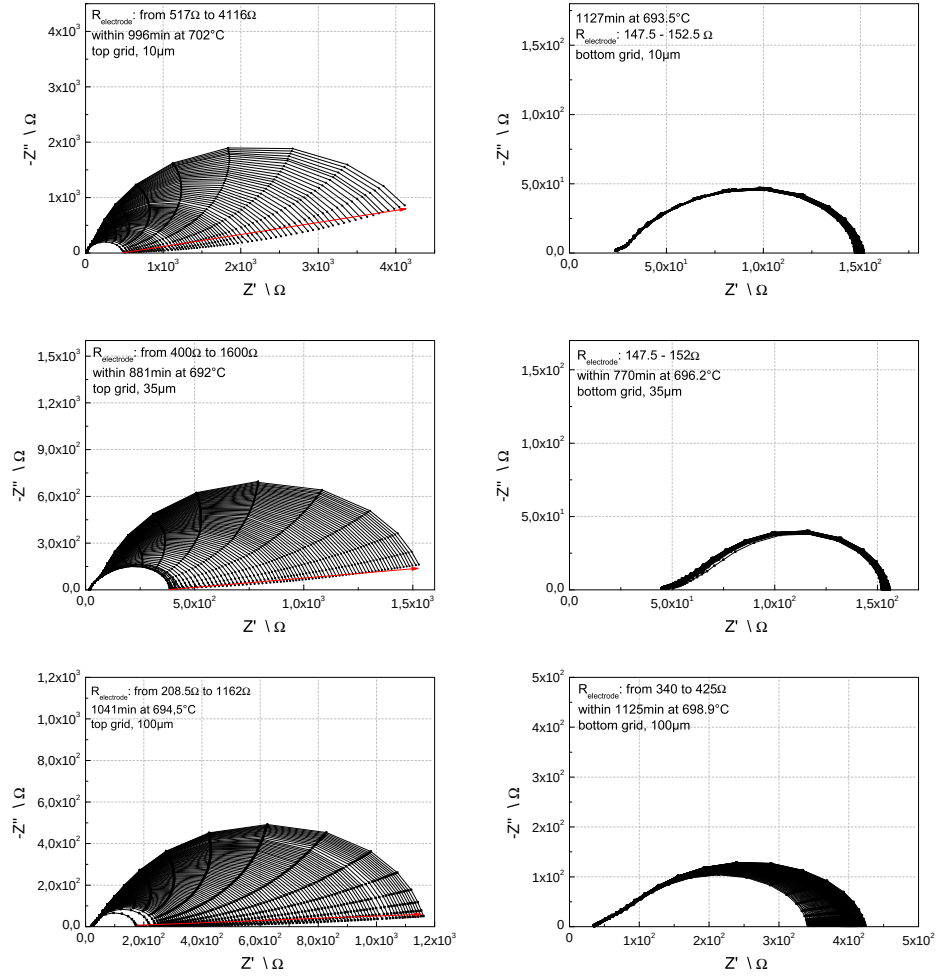


Figure 4.30: Degradation in H_2/H_2O of symmetric, macroscopic ($5 \times 5 \text{ mm}^2$) LSF64 thin layers on YSZ single crystalline substrates, with top and bottom current collector.

Microscopic electrodes

Microelectrodes, in contrast to macroscopic electrodes degrade strongly. In Fig. 4.31 the area related surface resistance ($R_c * A$) of microelectrodes with finger geometry (see Fig. 3.3) in H_2/H_2O is plotted for $T_{set} = 600, 650$ and 700°C . The electrode resistance decreases slightly in the beginning and then increases in all samples. However, this degradation is not similar, some samples show plateaus while others simply degrade continuously. Only within the first hours of the measurement the surface resistances are relatively stable (see inset Fig. 4.31). From the resistance values within this more or less stable period at the beginning an Arrhenius plot was constructed (Fig. 4.32). The fit through the mean values gives an activation energy of 1.62 eV .

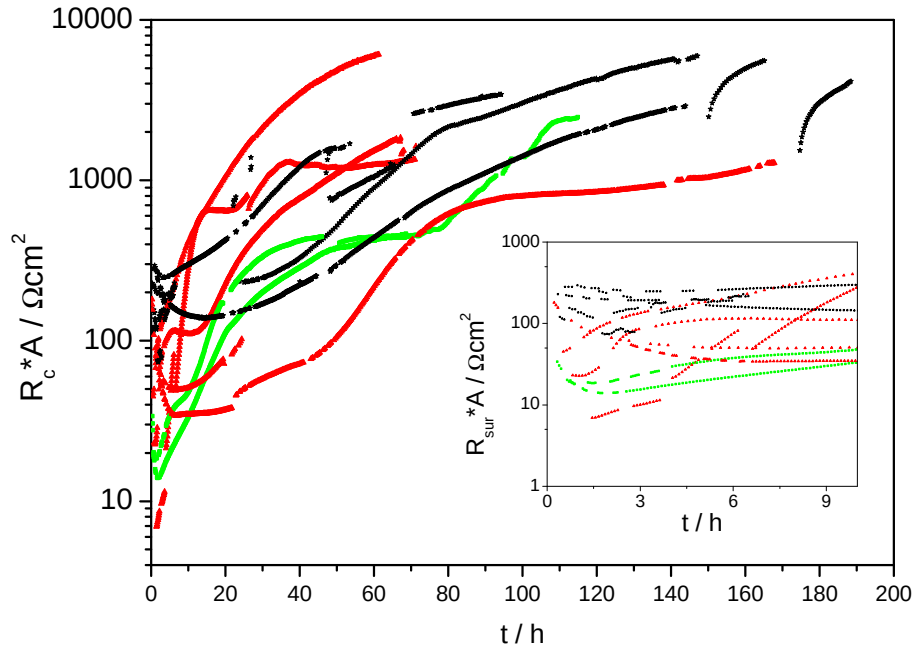


Figure 4.31: Area related resistances of LSF64 microelectrodes with interdigitating current collecting fingers (electrochemical mode) at 600°C (black), 650°C (red) and 700°C (green).

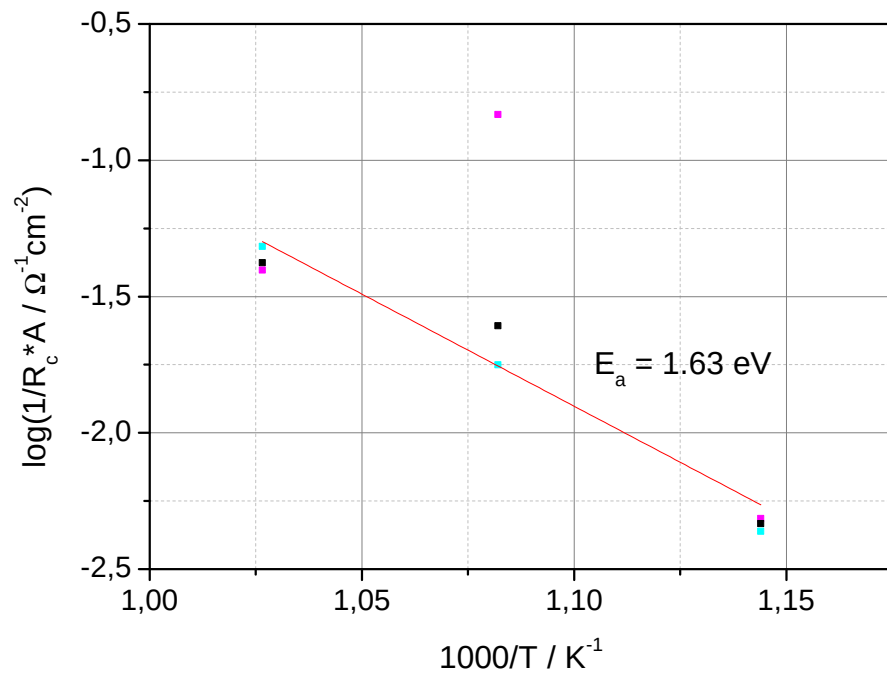


Figure 4.32: Arrhenius plot of the mean values (black) of the electrode resistances at the beginning of respective measurements shown in Fig. 4.31. Turquoise squares indicate mean values of samples with 8 and pink squares those with 13 μm spacing between the interdigitated fingers.

The corresponding in-plane conductivity is shown in Fig. 4.33 for $T_{set} = 650^\circ\text{C}$, for two geometries: spacing between the fingers $13\ \mu\text{m}$ (red) and spacing between the fingers $8\ \mu\text{m}$ (black). The in-plane resistance R_{ip} is, due to the geometry, higher in samples with larger distance between the current collecting fingers. Within the first hours of the measurement the in-plane resistance declines in all samples, then all show a degradation, but no clear degradation pattern can be observed.

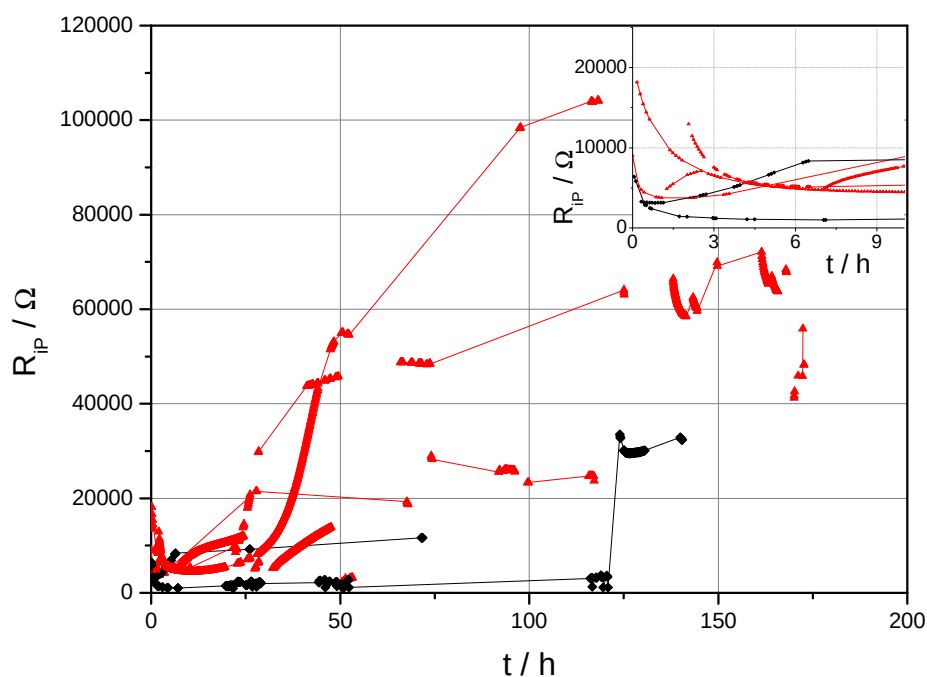


Figure 4.33: In-plane resistance (R_{ip}) of microelectrodes with interdigitated fingers ($8\ \mu\text{m}$ distance between the fingers) measured at 650°C set temperature in $\text{H}_2/\text{H}_2\text{O}$. Black squares and red triangles correspond to measurements on microelectrodes with a distance of $8\ \mu\text{m}$ and $13\ \mu\text{m}$ between the current collecting fingers.

The degradation of the in-plane conductivity suggests changes in the bulk of the LSF64 electrode. Such changes should also be reflected in the corresponding chemical capacitance. However, also between in-plane conductivity and chemical capacitance no clear correlation is observed.

Two examples are shown in Fig. 4.34. On the other hand this could suggest that there are changes in the grains and at the grain boundaries, as the chemical capacitance is only sensitive to the grains, while the in-plane conductivity depicts both, the changes in the grains and at the grain boundaries.

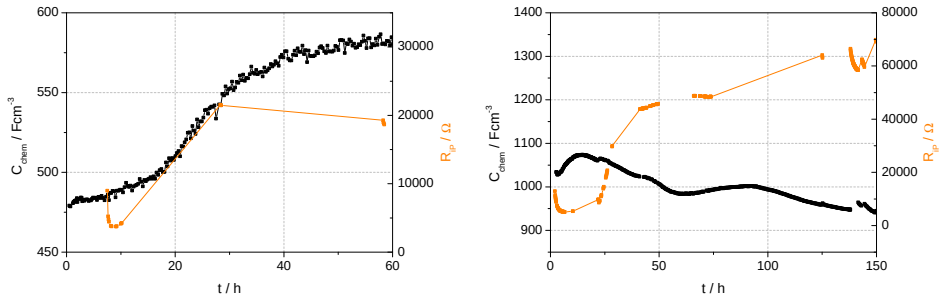


Figure 4.34: In-plane resistance (orange) and chemical capacitance (black) (per volume) of nominally identical microelectrodes with current collecting fingers with a distance of $13 \mu\text{m}$ in humidified hydrogen at 650°C set temperature.

A degradation behaviour similar to that at 650°C is also observed at $T_{set} = 600$ and 700°C . The minimum in-plane conductivity is reached at approximately $5h$ at 600°C , at 650°C at approximately $3h$ and at 700°C at approximately $0.5h$. Values at those times were collected and plotted in an Arrhenius plot to gain the activation energy, see Fig. 4.35. Again we observe a strong variation between the measurements. The fit over the mean values yields an activation energy of 2.00 eV . This is in accordance with the activation energy evaluated for the electronic conductivity from the simultaneous fit of the electrochemical and electronic measurement, see Tab. 4.4.

4.3.3 Impact of gas change on impedance measurements

The effect of the different atmospheres on the electrode impedance has already been discussed. In this section a comparison of impedance spectra in the different atmospheres as well as impedance measurements under gas change will be shown.

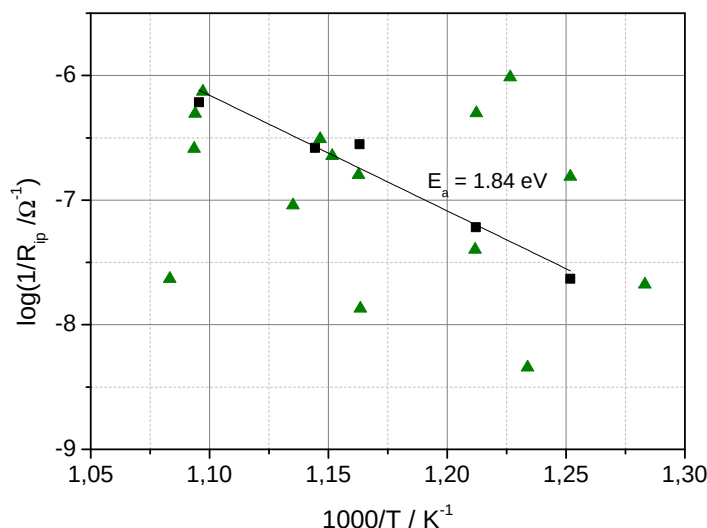


Figure 4.35: Green triangles show measurement values of in-plane resistance after approximately 3 h at temperature (from the measurements depicted in Fig. 4.33). The black squares are mean values, for which a fit was made.

Microscopic electrodes

Fig. 4.36 shows a comparison of 200 μm diameter circular LSF64 thin film electrodes. One electrode was measured in air the other in humidified hydrogen. For the reducing conditions an electrode with top current collector was used for the comparison as in reducing conditions the current collector is necessary to compensate the sheet resistance.

Due to the same set temperature the high frequency axis intercept R_a is similar for both electrodes. This is expected, as the conductivity of YSZ is essentially independent of the oxygen partial pressure [112], it is only a function of temperature. Accordingly, the same set temperature gives similar values for R_a . Again, the contribution of the contact resistance to R_a is negligible, and the sheet resistance under reducing conditions is accounted for by the current collector. From the calculation of the ASR ($R_c * A$) (taking into account the top grid under reducing conditions) we gain a remarkable result, namely that the ASR is similar in both atmospheres: 4.5 Ωcm^2 in reducing conditions versus 13.6 Ωcm^2 in oxidizing conditions.

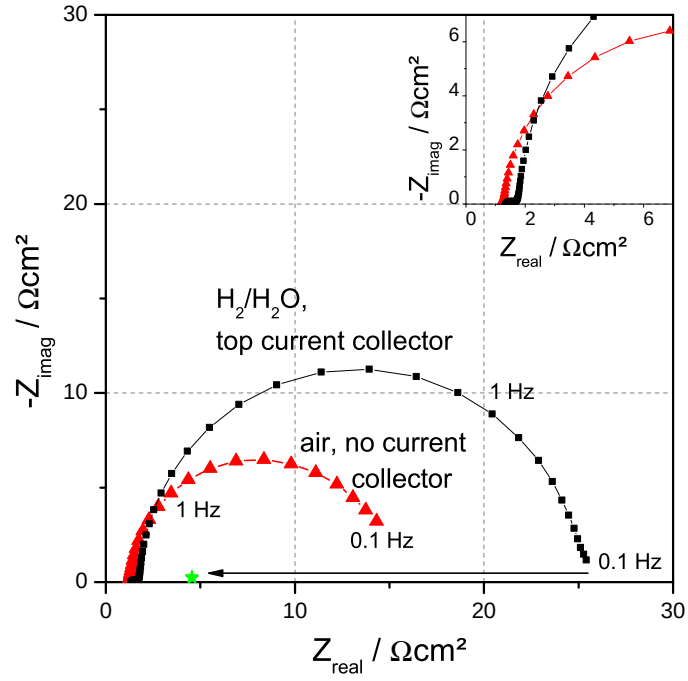
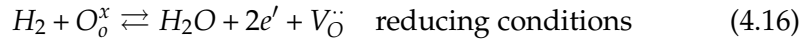
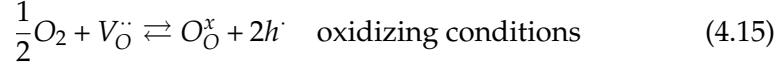


Figure 4.36: Comparison of impedance spectra of LSF64 microelectrodes ($195 \mu\text{m}$ diameter) in humidified hydrogen with top current collector (black squares, $T_{\text{calc}} = 609^\circ\text{C}$) and in air without current collector (red triangles, $T_{\text{calc}} = 619^\circ\text{C}$). Both spectra are normalized to the total electrode area A_{tot} . The top current collector covers large parts of the surface and the actual surface resistance in reducing conditions normalized to the free surface is therefore $4.5 \Omega\text{cm}^2$ (green star). Published in [91].

This result is very astonishing as the concentrations of the ionic and electronic charge carriers are highly different in the different atmospheres (see Fig. 4.6) and also the participating species are different:



A comparison of C_{chem} shows that it is bigger in oxidizing conditions than in reducing conditions. For the measurements in Fig. 4.36 1293 F/cm^3 and 149 F/cm^3 were found for oxidizing and reducing conditions, respectively.

Also measurements with gas change between air and humidified hydrogen on LSF64 thin film microelectrodes (220 nm thickness) were performed: Fig. 4.37 shows the ASR of such a measurement on a $380 \times 146 \text{ }\mu\text{m}^2$ microelectrode with interdigitated metallic fingers (13 μm finger width and 13 μm distance between fingers).

In oxidizing conditions the increase in $R_c \cdot A$, evaluated using the fit shown as inset in Fig. 4.10, with time (red guideline, Fig. 4.37), is rather slow. The resistance in reducing conditions does not show a clear trend. However, it declines directly after gas change. Measurements in air were kept short, as a strong degradation started after gas change. The corresponding chemical capacitance is shown in Fig. 4.38.

The chemical capacitance under air (red) is very stable. The chemical capacitance calculated from the defect chemical model of LSF64 at 600°C is 506 Fcm^{-3} in air (red line) and 246 Fcm^{-3} in reducing conditions (black line). The measured value in air is close to calculated value. In reducing conditions C_{chem} is high directly after the change and then declines. It seems to move toward the calculated value. The change in chemical capacitance in reducing conditions happens rather slow.

Microscopic electrodes with metallic fingers allow also measurements of the in-plane resistance (see Fig. 4.22). In air the in-plane resistance stays relatively constant at approximately $40 - 60 \text{ }\Omega$. This value also includes

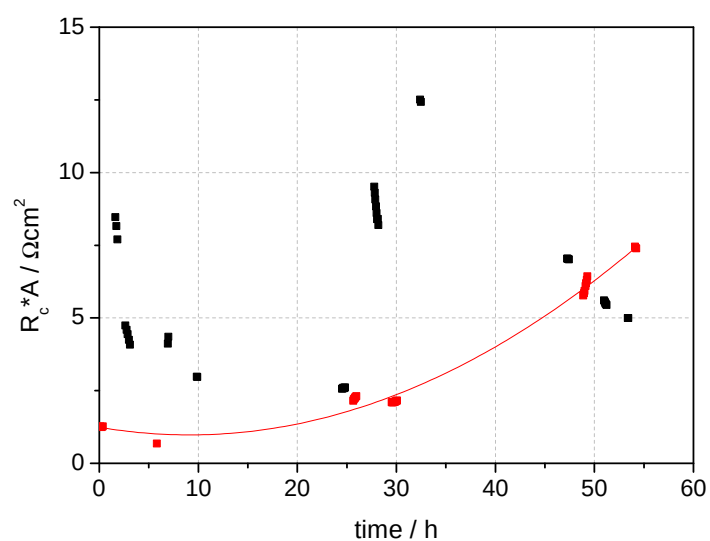


Figure 4.37: Area specific surface resistance ($R_c * A$) of a thin film microelectrode (220 nm thickness, area: $380 * 146 \mu\text{m}^2$) with interdigitating metallic fingers ($13 \mu\text{m}$ finger width and $13 \mu\text{m}$ distance between fingers) in a cyclic gas change between air (red) and humidified hydrogen (black) measured in the electrochemical mode at 650°C set temperature.

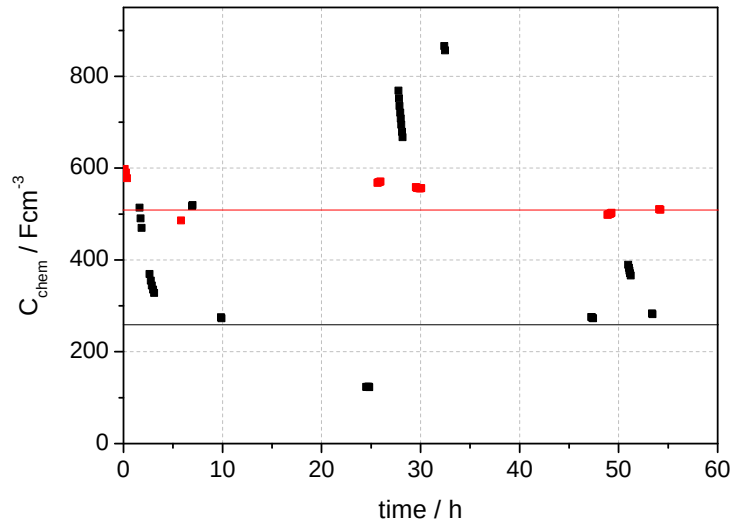


Figure 4.38: The chemical capacitance C_{chem} , corresponding to the area specific surface resistance shown in Fig. 4.37, in oxidizing (red) and reducing (black) conditions measured at a set temperature of 650 °C with guidelines for the eye. The calculated chemical capacitance for 600 °C is shown as for reducing and oxidizing conditions as red and black horizontal lines, respectively.

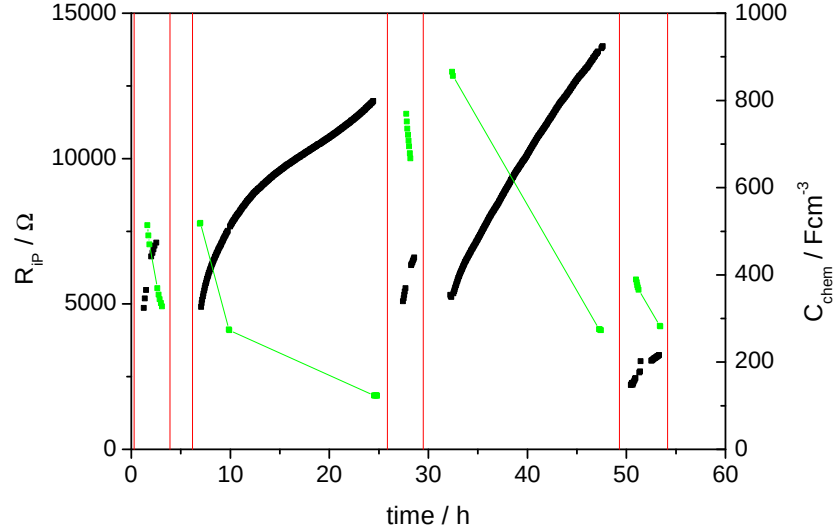


Figure 4.39: In-plane resistance R_{ip} (black) and C_{chem} (green) in reducing conditions. In air R_{ip} is lower than 100Ω , therefore measured values in air are not shown, but the measurements are indicated by red lines.

the contact resistance, which could make up for a significant part of that value.

Fig. 4.39 shows the in-plane resistance R_{ip} in reducing conditions. Red lines indicate measurements in air. After measurements in air the initial in-plane resistance is around 5000Ω , then the in-plane conductivity decreases, while simultaneously the chemical capacitance decreases. C_{chem} in reducing conditions is dominated by the concentration of electronic charge carriers, which is mostly electrons in humidified hydrogen. A loss in concentration in electronic charge carriers should cause the in-plane conductivity to rise and indeed this is observed.

Macroscopic electrodes

The same type of measurements as on microelectrodes, with cyclic gas change between oxidizing and reducing conditions, was repeated on macroscopic electrodes. $5 \times 5 \text{ mm}^2$ thin film electrodes with current collecting fingers on top (see Fig. 3.5) were used, where the fingers cover approximately 20% of the electrode surface. In the case of these macro-

scopic thin film electrodes much less of the electrode area than before is covered by Pt (approximately 20% vs. 80% for microelectrodes). The gas flow was changed every two hours from humidified hydrogen to dry synthetic air, while the temperature was kept constant at 668°C. Examples of impedance spectra of these measurements are shown in Fig. 4.40.

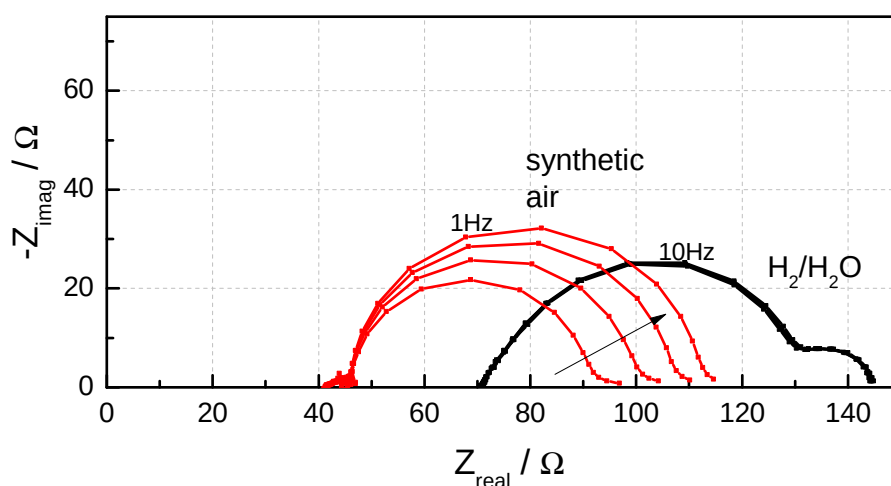


Figure 4.40: Spectra of samples with macroscopic LSF64 thin film electrodes recorded at 668°C with top current collector and porous LSF64/Pt counter electrode (see Fig. 3) in synthetic air (red) and humidified hydrogen (black). Published in [91].

During the gas cycling series impedance spectra were continuously recorded, measuring one spectrum took approximately 12 min. Examples of these spectra are shown in Fig. 4.40. The shapes of the spectra are similar to those observed for microelectrodes under the respective atmosphere (see Figs. 4.10 and 4.19). The contribution of the counter electrode to the measured spectra was identified by comparison with impedance spectra from symmetrical porous LSF64/Pt electrodes. A high frequency intercept with a small depressed intermediate frequency arc and a low frequency semicircle is found in oxidizing conditions. Here, the intermediate frequency shoulder could mainly be assigned to the counter electrode rather than to the thin film electrode. Its small additional resistance is within the $R_a + R_b$ part of the equivalent circuit (Fig. 4.10) and therefore does not influence the analysis of the main working electrode arc at low frequencies. In reducing conditions, a close to 45° slope of the

impedance at intermediate frequencies is followed by two semicircles. In this case, the counter electrode causes the second arc at low frequencies. Its impedance contribution is larger than in air, which is probably due to the increased electronic resistance of LSF64 in reducing atmosphere. Because of the different absolute chemical capacitances of the thin film electrode and the porous counter electrode, the impedance features are still rather well separated. In reducing conditions, only the main arc was considered in the fit procedure using the circuit of Fig. 4.10. Due to the overlap of this main arc with the slope at higher frequencies and the counter electrode arc at low frequencies, the fit includes some inaccuracies, but meaningful comparison of data is still possible.

The high frequency offset under reducing conditions is shifted to higher resistances compared to oxidizing conditions. This indicates different capacitively active areas: In air the electronic sheet resistance of the LSF64 film is low, therefore large parts of the film are involved in the charging and discharging of C_{chem} . Under reducing conditions mainly the area between the fingers and beneath the current collector is reached by the electronic charge carriers. This is confirmed by the numerical analysis of the chemical capacitances. In air C_{chem} has a value of 792 Fcm^{-3} if normalized to the entire electrode area and this is acceptably close to 1293 Fcm^{-3} found for microelectrodes without current collector at somewhat lower temperatures.

Normalizing C_{chem} for reducing conditions to the entire area leads to ca. 45 Fcm^{-3} and thus much less than the values of ca. $100 - 150 \text{ Fcm}^{-3}$ found for microelectrodes. However, normalization to the area covered by the current collector plus the area between the fingers, gives very reasonable 90 Fcm^{-3} . Hence, due to the high sheet resistance the area outside the current collectors is inactive (see Fig. 4.17). Moreover, the macroscopic sample has larger spacing between the current collecting fingers ($23 \mu\text{m}$) than the microelectrodes ($8.5 \mu\text{m}$, see Figs. 3.1 and 3.5) and it is likely that the center between the current collecting fingers is only partly polarized. The smaller capacitively active area in reducing conditions causes the larger R_a value compared to air. However, an exact analysis of this R_a increase would require numerical simulations due to the different active electrode areas

on the two sides of the sample (in H_2/H_2O).

These considerations also suggest the following normalization of the measured electrode resistances: For the samples in air the electrode resistance is related to the total surface area minus the area covered by the current collector since almost the entire free surface can be assumed to exchange oxygen. For reducing conditions the resistance was related to the area between the metal fingers as this area is assumed to be electrochemically active. The area of a supposedly active region outside the finger region was neglected. This normalization may slightly overestimates the active surface areas, cf. C_{chem} analysis given above. However, all main messages deduced from the experiments are not affected by this approximation.

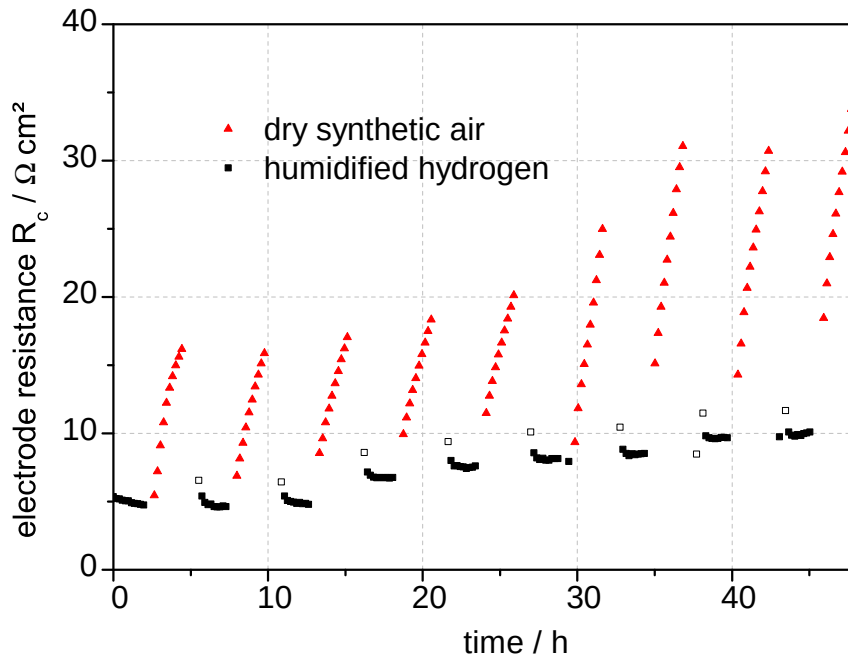


Figure 4.41: *Electrode resistance per area (normalized to the total free LSF surface in oxidizing conditions and the free LSF surface between current collector fingers in reducing atmosphere) over time, at 668 °C. Red triangles are measured in synthetic air, while black squares are measured under H_2/H_2O . Open symbols indicate that the measurement was taken while the atmosphere in the setup was not yet defined. Published in [91].*

Fig. 4.41 shows the change of these normalized electrode resistances R_c with time and gas phase. First of all, the finding from the microelectrode measurements is confirmed: the area specific electrode resistances in both atmospheres are similar. In the first gas cycle under reducing conditions the ASR is $5 \Omega \text{cm}^2$ and for the first measurement in oxidizing conditions it is approximately the same (Fig. 4.41). The electrode resistance rises steeply in dry synthetic air, while its stability under reducing conditions is comparatively high. Stability in $\text{H}_2/\text{H}_2\text{O}$ is in accordance with the fact that the humidified hydrogen used here has an oxygen partial pressure of ca. $1.4 \cdot 10^{-22} \text{ bar}$ at 668°C which is still in the range where LSF64 is supposed to be stable [20].

The strong changes in air are in contrast to the high phase stability of the LSF64 bulk material under oxidizing conditions [20]. Degradation could be caused by the formation of a less active surface termination or Sr segregation as was found for LSC [77] [113].

Interestingly, by changing back from oxidizing to reducing conditions the initial electrode resistance is again almost reached. This means that the variation of the electrode resistance under oxidizing conditions is not an irreversible degradation. Rather, exposure to reducing conditions again undoes the strong changes in air. Only on a longer time scale there is a slow degradation of the electrode resistance that affects both atmospheres. At present we can only speculate about the mechanisms behind this reversibility of the degradation in synthetic air. Possibly, a drastic, but fast chemical/structural reorganization of the LSF64 surface takes place in $\text{H}_2/\text{H}_2\text{O}$, irrespective of the degradation state in air.

This might even be the formation of a second phase: In Sec. 4.4.1 XRD results showing the fast formation of small amounts of Ruddlesden Popper like phases and iron oxides on LSF64 powder samples in $\text{H}_2/\text{H}_2\text{O}$ without decomposition of the entire bulk are shown. Assuming such a severe change of LSF64 film surfaces in $\text{H}_2/\text{H}_2\text{O}$ would explain the undoing of the degradation in air. This novel surface structure formed in reducing atmosphere seems to be much less prone to degradation than the LSF64

surface in air. Also humidity present in H_2/H_2O may play a role here.

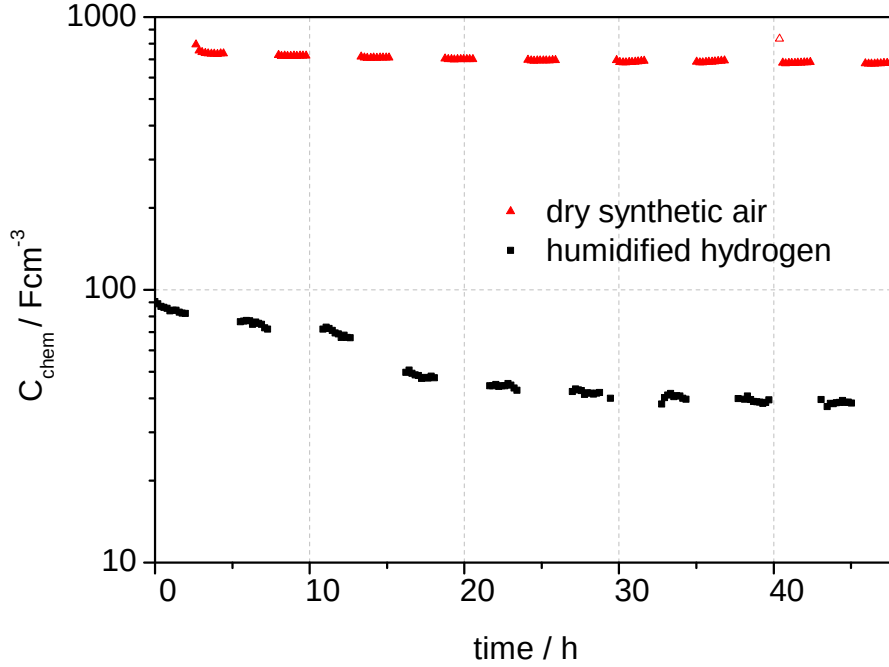


Figure 4.42: Chemical capacitance per area (normalized to the total electrode area for oxidizing conditions and to the sum of the areas below the entire Pt current collector and between current collector fingers in reducing conditions) over time, at 668 °C. Red triangles are measured in synthetic air, while black squares are measured under H_2/H_2O . Published in [91].

In the first cycle, the chemical capacitance is almost one order of magnitude higher in oxidizing conditions than in reducing conditions, in accordance with the findings from the microelectrode measurements (see Sec. 4.3.2).

Fig. 4.42 shows that in air the chemical capacitance is almost constant over the entire measurement, it is not affected by the gas cycling or temporal degradation. The chemical capacitance in reducing atmosphere slowly decreases from ca. 90 to 38 $F cm^{-3}$ within 48 hours. This process cannot be reversed by gas change to synthetic air. The chemical capacitance is a bulk property (in contrast to R_c) and the change indicates a variation on the level of the electronic charge carriers of LSF64 in H_2/H_2O . A lower concentration of electronic charge carriers would decrease C_{chem} and a lower electronic conductivity could reduce the effective area which contributes

to C_{chem} and thus also lowers the absolute value of C_{chem} . Interestingly, this change does not significantly affect the oxygen vacancy concentration in air, which can be deduced from the almost constant chemical capacitance in oxidizing conditions.

Moreover, comparing Figs. 4.41 and 4.42 indicates that the change in the bulk C_{chem} and the slow overall degradation of the surface resistance (R_c) in reducing atmosphere are possibly linked. Accordingly, the change of C_{chem} in H_2/H_2O might be related with a slow phase change or second phase formation affecting both the electronic conductivity in the bulk of our film and the surface reaction. In both graphs (Figs. 4.41 and 4.42) data points immediately after gas changes, marked with open symbols, seem to deviate from the general trend. However, from the peak frequencies in the impedance spectra (approximately 0.5 Hz in oxidizing and 10 Hz in reducing conditions, Fig. 4.40) we can conclude that the equilibration to the different atmospheres is fast. Hence, the deviation is most probably simply due to the slow gas change in the setup which leads to an undefined gas mixture in the first minutes of the measurement.

4.4 Diffraction patterns of LSF64 in different gas atmospheres

Due to the findings from impedance spectroscopy, we suspected a phase change of only a small amount of material close to the electrode surface. However, using grazing-angle X-ray diffraction we did not observe phase changes, see Sec. 4.2. Therefore we switched to high temperature *in-situ* powder XRD. The advantage of this method is that gas is flown through loosely packed powder during heating. Accordingly, the contact area of material with gas is enlarged in comparison to pressed pellets or thin films, what makes it more sensitive towards slight changes on the surface. These measurements were performed in dry hydrogen and air as well as in humidified hydrogen.

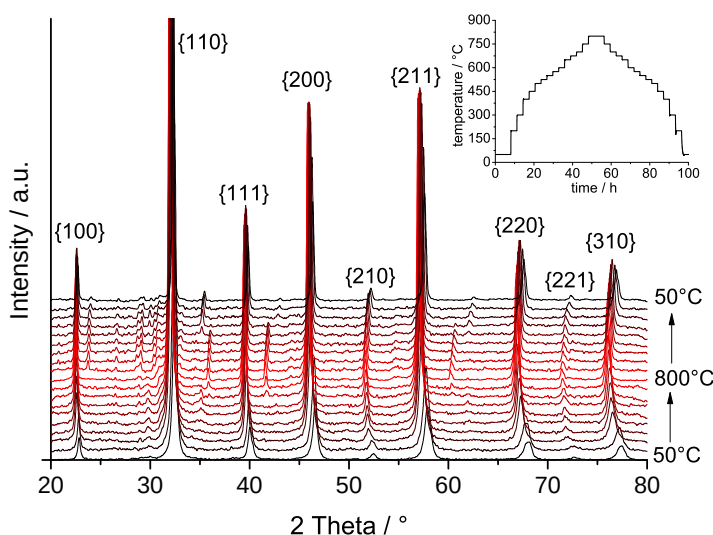


Figure 4.43: Diffraction pattern ($\text{Cu} - \text{K}\alpha$) of LSF64 powder in humidified hydrogen. Reflections of LSF are given with their respective (hkl) indices. Inset: Temperature profile; at each dwell temperature diffraction patterns were collected. Published in [91].

4.4.1 Diffraction patterns recorded in humidified hydrogen

Figs. 4.43 and 4.44 show the diffraction patterns of LSF64 powder in humidified hydrogen. The temperature profile is shown as inset in Fig. 4.43.

Diffraction patterns recorded below 200°C before heating only consist of LSF64 peaks. The peak area of these peaks changes upon heating, see Fig. 4.45. A change in peak area is typical for a chemical reaction. However, no secondary peaks occur. In this temperature range the reduction of LSF64 is supposed to occur [30]. Accordingly, the change in peak area may indicate the reduction of the LSF64 in humidified hydrogen.

Around 400°C new peaks start to appear (at 23.8° , 24.6° , 26.7° , 28.9° , 29.2° , 29.8° , 30.4° , 31.2° , 33.1° , 35.2° , 36.0° and 41.8°). Once formed their intensity does not further increase, as is seen by their constant peak height even during heating. These peaks are preserved over the entire

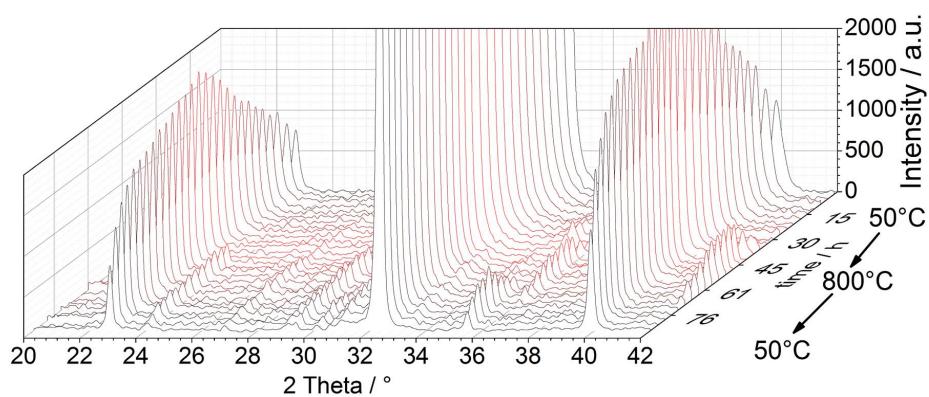


Figure 4.44: 3D plot of measured diffraction patterns (from Fig. 4.44) with time. Published in [91].

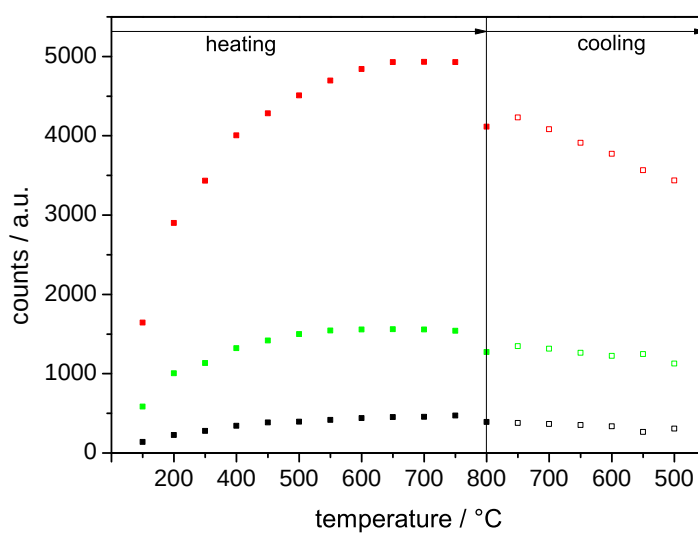


Figure 4.45: Change in peak area for the peaks at 22.8°, 32.5° and 46.5° with temperature.

measurement and do not vanish upon cooling. At around 550°C Fe_3O_4 starts to emerge ($2\Theta = 29.8^\circ$ and 35.2°). Upon heating Fe_3O_4 is further reduced to FeO , as can be seen by the vanishing of the peaks correlated to Fe_3O_4 while new peaks at ($2\Theta = 36.0^\circ$ and 41.8°). During cooling the back-transition from FeO to Fe_3O_4 occurs at 550°C. These different transition temperatures show that at least one transition is kinetically hindered. Also the formation of a Ruddlesden-Popper phase is observed. The main peak of the Ruddlesden-Popper phase is only seen as shoulder of the LSF64 (110) peak, but the peak at 23.8° could also be assigned to this phase. The peaks of the Ruddlesden-Popper phase grow during heating. Other peaks between 25° and 33° could not be assigned.

Reduction of the perovskite first causes a loss of iron from the lattice, which in turn leads to the formation of a Ruddlesden-Popper like phase. Ruddlesden Popper like phases in strontium ferrites have already been investigated [113], [114] [115] and the ternary phase diagram of $La_2O_3 - SrO - Fe_2O_3$ in air at 1100°C shows multiple Ruddlesden Popper phases [116]. Also in literature the loss of iron as well as the formation of Ruddlesden-Popper like phase was observed in LSF64 and LSF55 [20], [117].

Further, the formation of brownmillerite-like phases is possible. In literature brownmillerite-like structures were observed in LSF at 700°C only in stoichiometries with $x > 5$ in $La_{1-x}Sr_xFeO_{3-\delta}$ [30]. However, at lower temperatures oxygen vacancy ordering becomes more likely, so that brownmillerite-like phase may be found in LSF64. From the diffraction patterns, we cannot exclude the formation of brownmillerite-like phases in LSF64 as their respective peaks superimpose with those of LSF64 and the Ruddlesden-Popper phase. Indeed, the peak found at 33.1° suggests the formation of a brownmillerite-like phase.

These results show the formation of secondary phases in LSF64 although staying within the stability limit [20]. XRD measurements on pressed pellets [30] may not show these phase changes as there the gas/material inter-phase is smaller. A comparison of the peak area of the peak of highest intensity of LSF64 ($2\Theta = 32.2^\circ$) with that from Fe_3O_4 ($2\Theta = 35.2^\circ$) gives 1.7%

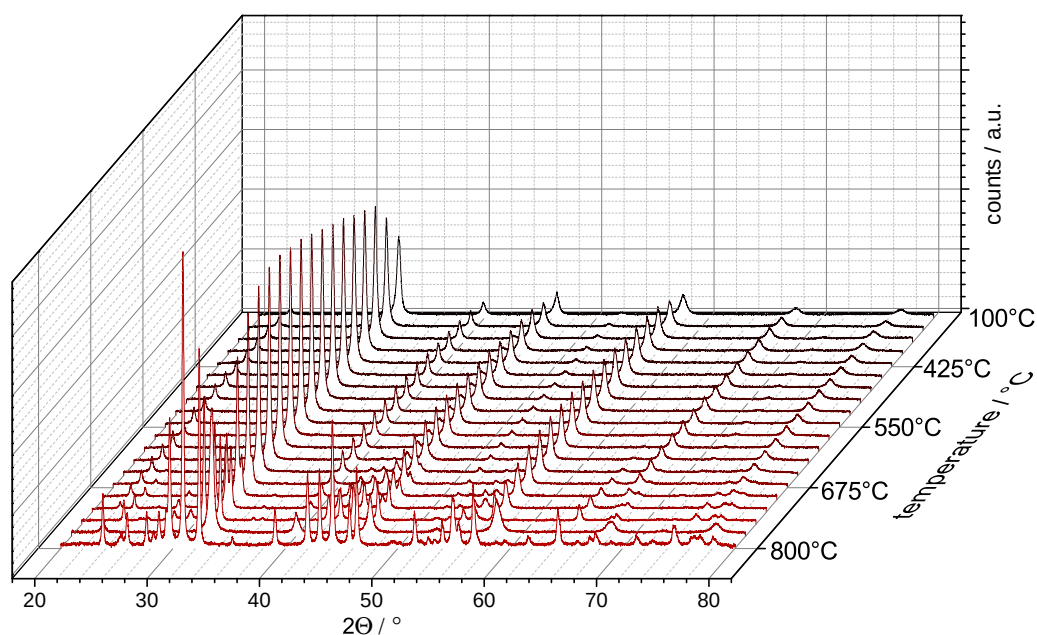


Figure 4.46: Diffraction patterns of LSF64 powder upon heating in dry hydrogen ($H_2(2.5\%)/Ar$).

iron oxides. We therefore estimate the total amount of secondary phases to be lower than 5%.

4.4.2 Diffraction patterns recorded in dry hydrogen and air

Fig. 4.46 shows the diffraction patterns of LSF64 powder during heating in dry $H_2(2.5\%)/Ar$. The temperature profile is depicted as inset in Fig. 4.47, where also the diffraction pattern at 50 °C before and after heating are compared.

At around 400 °C the formation of metallic iron is observed by the formation of a peak at 44.7°. The iron peak grows in intensity with increasing temperature. At around 650 °C $SrLaFeO_3$ forms, indicated by the occurrence of peaks at 29.6 30.9 42.6, 43.2 and 64.5. Those are shifted slightly due to temperature, but could be assigned nevertheless. $SrLaFeO_4$ seems to be stable up to 700 °C, where it decomposes to La_2O_3 and SrO , while the Fe peak keeps increasing its intensity. Upon cooling no change is observed, the assignment of the peaks to ICDD database is shown in Fig. 4.48.

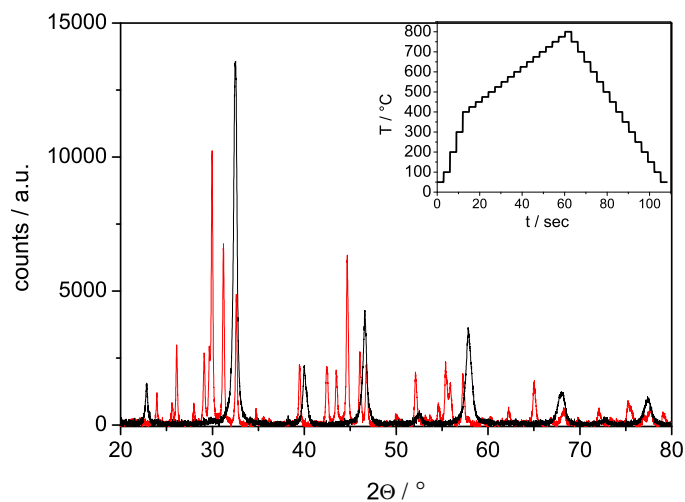


Figure 4.47: Diffraction patterns of LSF64 powder before (black) and after (red) heating to 800 °C in dry hydrogen. The temperature profile is shown as inset.

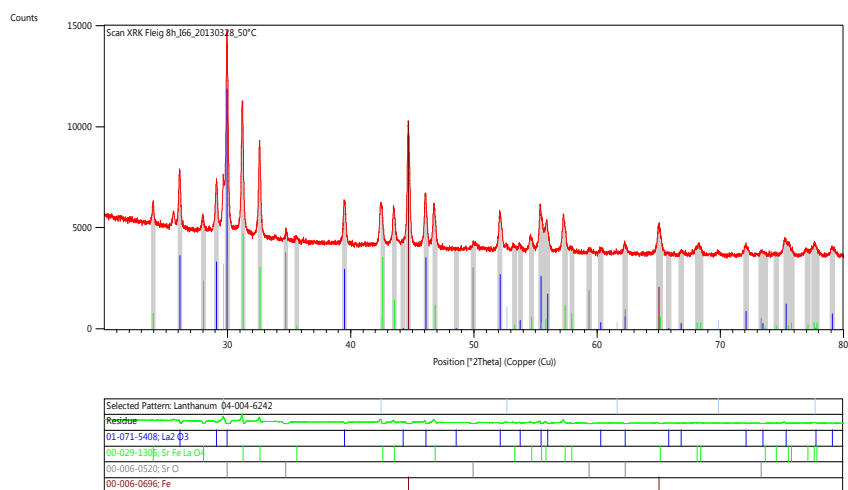


Figure 4.48: Diffraction patterns of LSF64 powder measured at 50 °C after heating to 800 °C in dry hydrogen. The patterns are assigned to patterns from ICDD database.

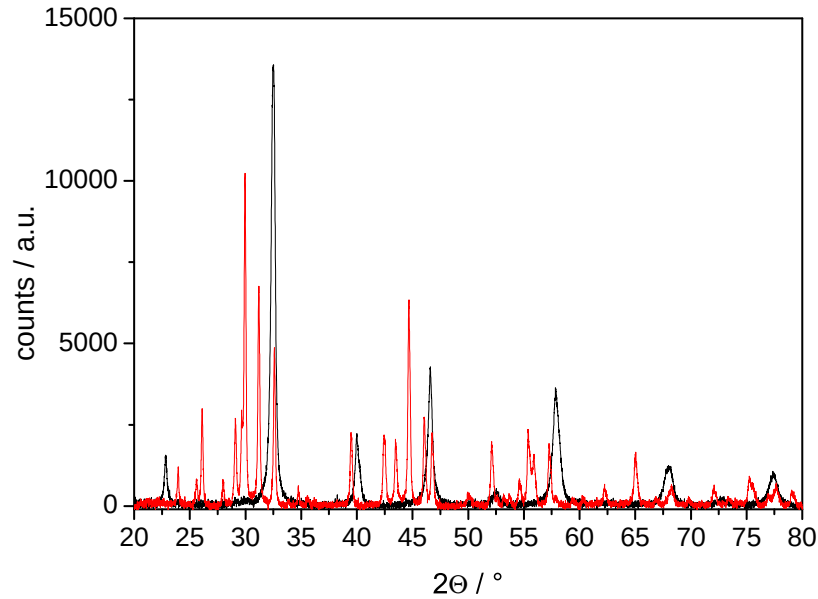


Figure 4.49: Comparison of LSF64 powder pre-annealed in dry hydrogen (red) and after subsequent heating in air (black) to 800 °C.

Fig. 4.49 shows diffraction patterns of the powder from the above measurement upon heating in air. Between 200 and 300 °C the iron peak vanished, while the formation of iron oxide is observed. Simultaneously also the formation of perovskite phase is observed. In principle this experiment equals a shake-and-bake synthesis of LSF64, where the formation of the perovskite from the oxides is not complete due too low temperature.

XRD diffraction on reduced LSF64 thin films

Fig. 4.51 shows the diffraction patterns of LSF64 thin films on (220 nm) YSZ. The samples were kept at a set temperature of 700 °C (Linkam oven) in H_2/H_2O atmosphere for different annealing times. Fig. 4.52 shows the measured X-ray reflectivity (XRR) of those samples.

The diffraction patterns show a shift of the (104), (111) peak from $2\theta = 32.5^\circ$ to smaller angles with increasing exposure time. This shift is also seen for the (024) and (300), (214) peaks. This indicates an increase in the lattice paramters in reducing conditions, which is due to the formation of oxygen

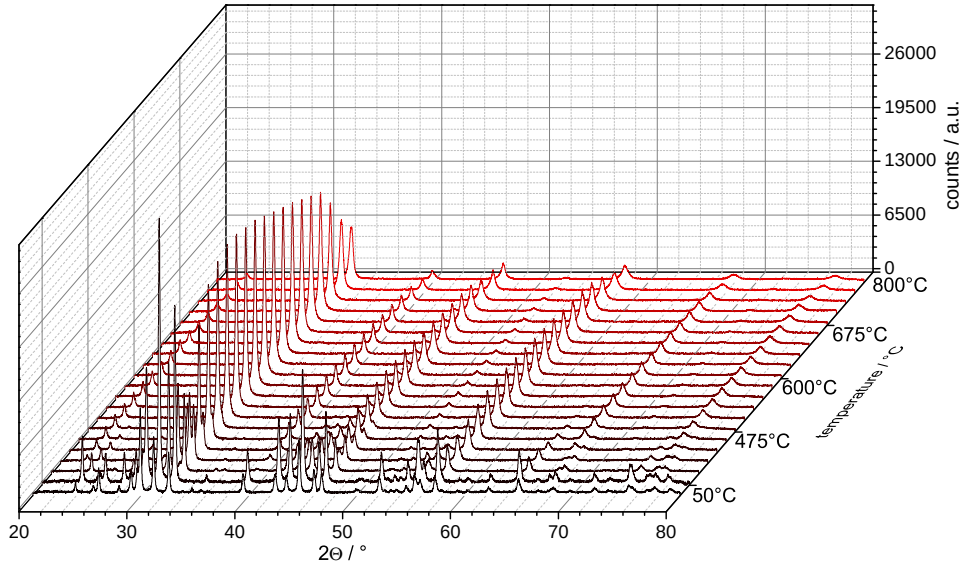


Figure 4.50: Diffraction patterns of LSF64 powder that has been pre-annealed in dry hydrogen at 800 °C upon heating in air.

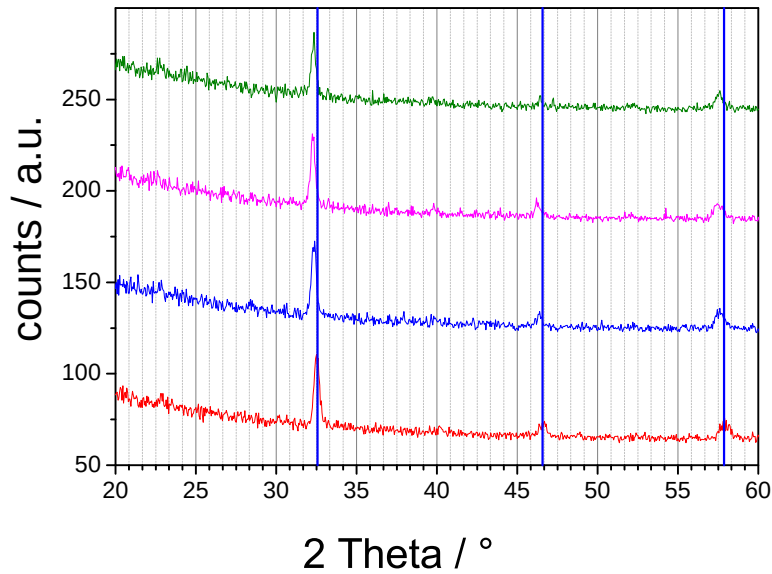


Figure 4.51: Diffraction patterns of LSF64 thin films (220nm) on YSZ substrates, with different annealing times at $T_{\text{set}} = 700^\circ\text{C}$ in reducing atmosphere: 0 min (pristine, red), 120 min (blue), 480 min (pink) and 3000 min (green). Measurement from a cooperation with Andreas Stierle, Hamburg.

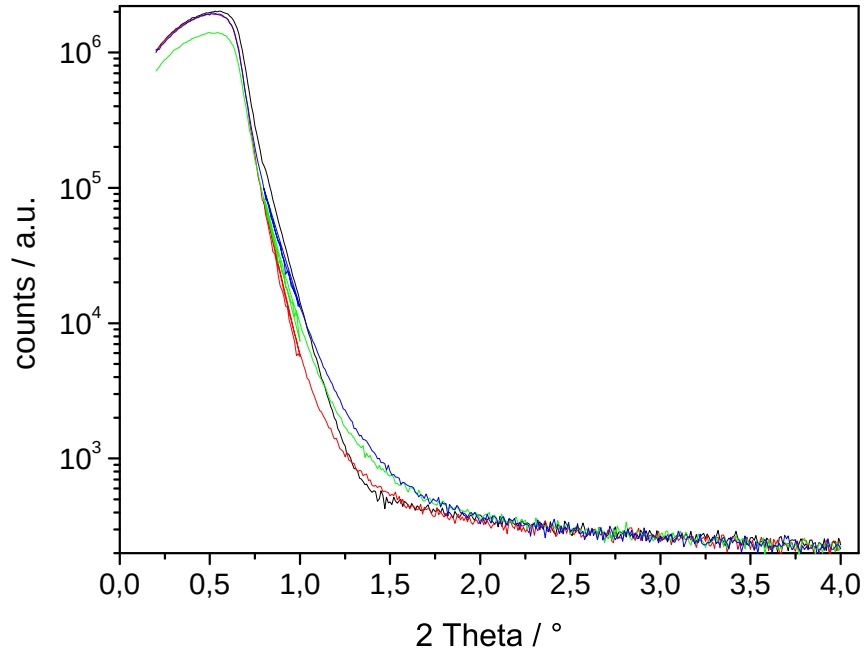


Figure 4.52: XRR patterns of LSF64 thin films (220nm) on YSZ substrates, with different annealing times at $T_{\text{set}} = 700^\circ\text{C}$ in reducing atmosphere: 0 min (pristine, red), 120 min (blue), 480 min (pink) and 3000 min (green). Measurement from a cooperation with Andreas Stierle, Hamburg.

vacancies. This can also be seen in entries of the ICDD database, where $a = b = 5.5273$ and $c = 13.4212$ are found for $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_3$ (01-082-1961) and $a = b = 5.5399$ and $c = 13.5600$ are found for $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{2.796}$ (01-072-8136).

XRR measurements (see Fig. 4.52) on the reduced LSF64 thin films show an intensity increase at $2\theta = 1.5^\circ$ for the longer annealed samples. This indicates a rough surface layer of approximately 6 nm thickness with increased electron density.

4.4.3 Results and discussion of XRD analysis

For LSF64 we observe the expected [30] rhombohedral lattice. The rhombohedral modification transforms into the cubic at high temperatures (in air LSF64 transforms at $850 \pm 50^\circ\text{C}$), in lower oxygen partial pressures the

transition to cubic crystal structure occurs at significantly lower temperatures, but the phase transition temperature observed for bulk materials also depends on the thermal history of the sample [118].

In dry hydrogen we observe the structural collapse of the perovskite under formation of metallic iron, this is also in accordance with literature [30]. Metallic Ni, Co and Fe was observed to precipitate from the corresponding perovskites in reducing conditions [2]. Heating of the decomposed powder in air again lead to the formation of the perovskite.

In humidified hydrogen the formation of secondary phases, mainly iron oxides and Ruddlesden-Popper like phase is observed. Also we speculate on the formation of brownmillerite-like phase. Oxygen ion conductivity in the brownmillerite phase $SrFeO_y$ was found to be about 0.1 S/cm , which is comparable to values found in YSZ, but lower than in the perovskite phase [119] [113]. Above 700°C the brownmillerite ($Sr_2Fe_2O_5$) transforms into the cubic perovskite by the formation of microdomains [120] [121]. LSF28 transformed into brownmillerite structure observed by Mössbauer spectroscopy at 700°C in air [122]. Strontium ferrites are often MIECs [123] [113].

4.5 Surface analysis using XPS

To investigate possible changes on the surface of the LSF64 thin film, thin films with 400 nm thickness on MgO were prepared and annealed in H_2/H_2O at $T_{set} = 700^\circ\text{C}$ for different times (0 h (pristine), 2 h , 7.9 h and 18.7 h). Annealing was done in the very same setup in which also the impedance measurements on microelectrodes were performed (heating from below, T_{calc} typically 80°C lower than set temperature). The surfaces of these films were then analysed by XPS. Measurements were performed by Andreas Nenning.

Fig. 4.53 shows the changes of signal intensity from ions on or close to the surface. The calibration was performed with reference to the library sensitivity factor for oxygen. The exact molar fraction could not be determined, but general trends can be evaluated.

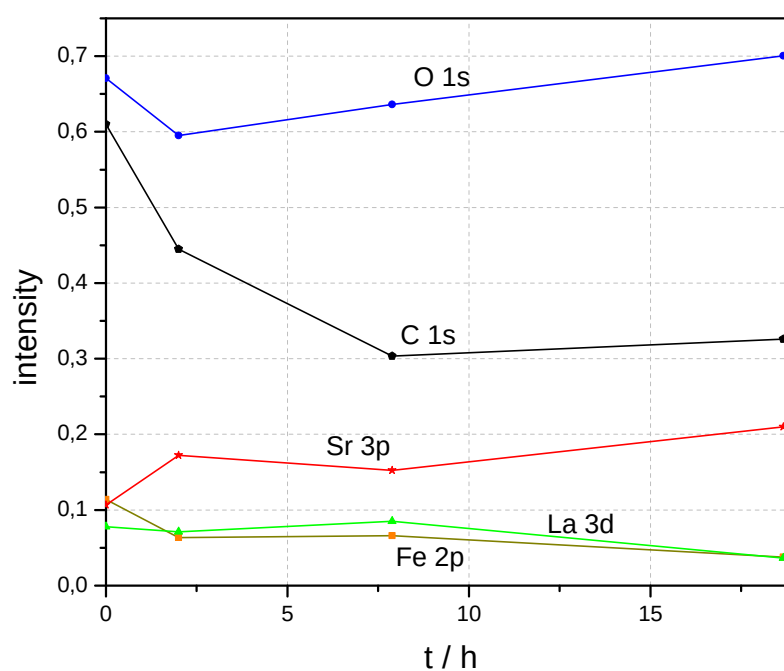


Figure 4.53: Changes of the intensity of the signals from ions on/close to the surface of a LSF64 thin layer (300 nm) on MgO. Fe (orange, squares), O (blue, circles), La (green, triangles), Sr (red stars), C (black, polygons).

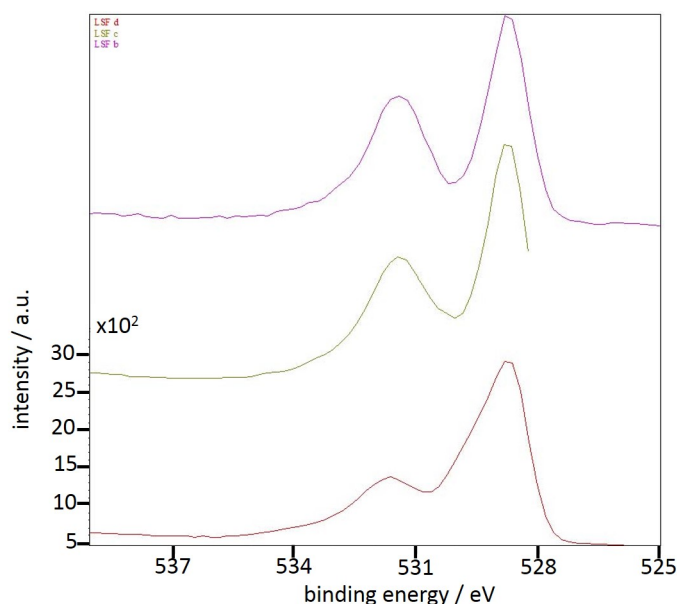


Figure 4.54: Oxygen 1s peaks of LSF64 thin films (300 nm) on MgO, pre-annealed in H_2/H_2O , corresponding to different annealing times 2 h (violet), 7.9 h (green) and 18.7 h (red).

With longer annealing time the surface becomes enriched with Sr, whereas the amount of Fe and La are slightly reduced. During XPS analysis a high amount of carbon was found on all samples, even the untreated ones. The carbon coverage is not necessarily on the surface during electrochemical studies, but could simply be adsorbed from air at room temperature. Such a high carbon coverage, also on treated and untreated samples, was already observed on LSCM [102]. The oxygen found on the surface could also originate from carboxides, accordingly a quantification of oxygen at the surface is not possible.

The oxygen 1s signal consists of two peaks, see Fig. 4.54. The peak on the high energy binding side originates from an oxygen species close to the surface. The intensity of this peak is similar for the samples that were annealed for 2 and approximately 8 h and was not evaluated for the others.

The enrichment of the surface with Sr could be due to a segregation of a Sr-rich secondary phase or the formation of a Sr termination of the perovskite. In literature an enrichment of the surface with Sr was found

for LSC, were it seemed to cause a degradation [124], [125]. It could be that a Sr termination is less active towards the oxygen exchange reaction. The other possibility, a secondary Sr containing phase, could simply act as a pollutant of the perovskite surface, thereby blocking otherwise catalytically active sites. In SOF/ECs the effect of surface pollution is pronounced as at the high operational temperatures the oxygen surface coverage is already low. At around 1000 K only approximately 10% of the surface are covered with oxygen [39]. Accordingly a loss of active surface area will decrease the cell efficiency. However a demixing of the perovskite due to loss of strontium is not likely, as literature predicts a perovskite-like structure for $La_{1-x}Sr_xFeO_{3-\delta}$ for all strontium contents [30].

Comparing the findings from XPS measurements with XRD measurements, the increased Sr on the surface could imply the formation of a Ruddlesden Popper like phase (A_2BO_4). These phases may preferentially form with Sr. The two oxygen species found in XPS spectra could also be a result of the increased Sr content at/close to the surface. Oxygen vacancies may prefer sites next to Sr. Due to this differentiation between A cations, two oxygen species with different binding energy might exist.

4.6 Tracer exchange experiments

All tracer exchange experiments were performed in cooperation with Katharina Langer-Hansel. Therefore, only the main results are depicted here. For more detailed information about the exchange experiments, the TOF-SIMS measurements as well as the fitting procedure the reader is referred to [71] and [72].

1-step tracer exchange experiment

1-step ^{18}O tracer exchange experiments, where a sample is exposed to a tracer enriched atmosphere at elevated temperatures, have been used to investigate oxygen exchange pathways on different SOFC electrode materials [77], [126], [61] and [127].

Such an experiment on LSF64 microelectrodes is shown in Fig. 4.55. The sample was heated to 400 °C and for 10 min exposed to 200 mbar $^{18}\text{O}_2$. The

distribution of the tracer was evaluated by subsequent TOF-SIMS analysis. The measurement shows a high amount of tracer in the LSF64 electrode and a lower amount in the YSZ electrolyte. From the tracer distribution in the sample the D^* and k^* values can be evaluated. However this method only gives information on the oxygen exchange under oxidizing conditions. For reducing conditions the experiment may be performed using tracer marked water ($H_2^{18}O$), as described below.

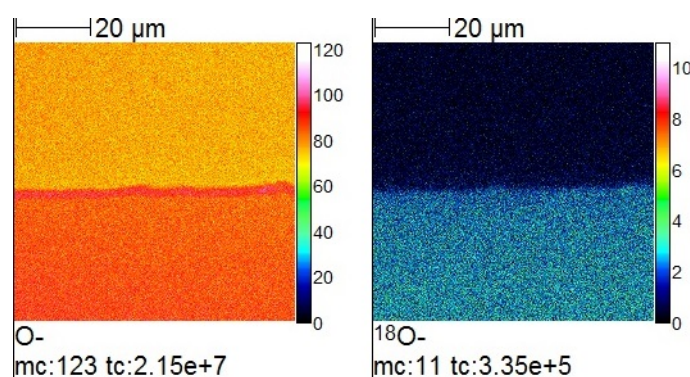


Figure 4.55: Lateral ^{18}O profile of LSF64 thin layer on YSZ single crystalline substrate, after $^{18}O_2$ exchange at $400^\circ C$ for 10 min. Left: oxygen ion and right: $^{18}O^-$ distribution, showing a high tracer concentration within the LSF64 electrode (lower part of the images) and a lower concentration in the YSZ electrolyte.

2-step tracer exchange experiment

Additionally, we used a simple 2-step method to investigate the tracer exchange under oxidizing and reducing conditions, that also allows for a direct comparison of the results. A schematic of this method is shown in Fig. 4.56. A similar method was already used on LSCF [102].

The method consists of 2 experimental steps and evaluation and fitting, as shown in Fig 4.56:

1. filling + SIMS analysis

A thin layer on an insulating substrate is heated in an ^{18}O -containing atmosphere. The temperature should be high and the time long enough to incorporate a large amount of tracer in the thin layer ('filling'). The diffusion of the tracer into the substrate is blocked, by its

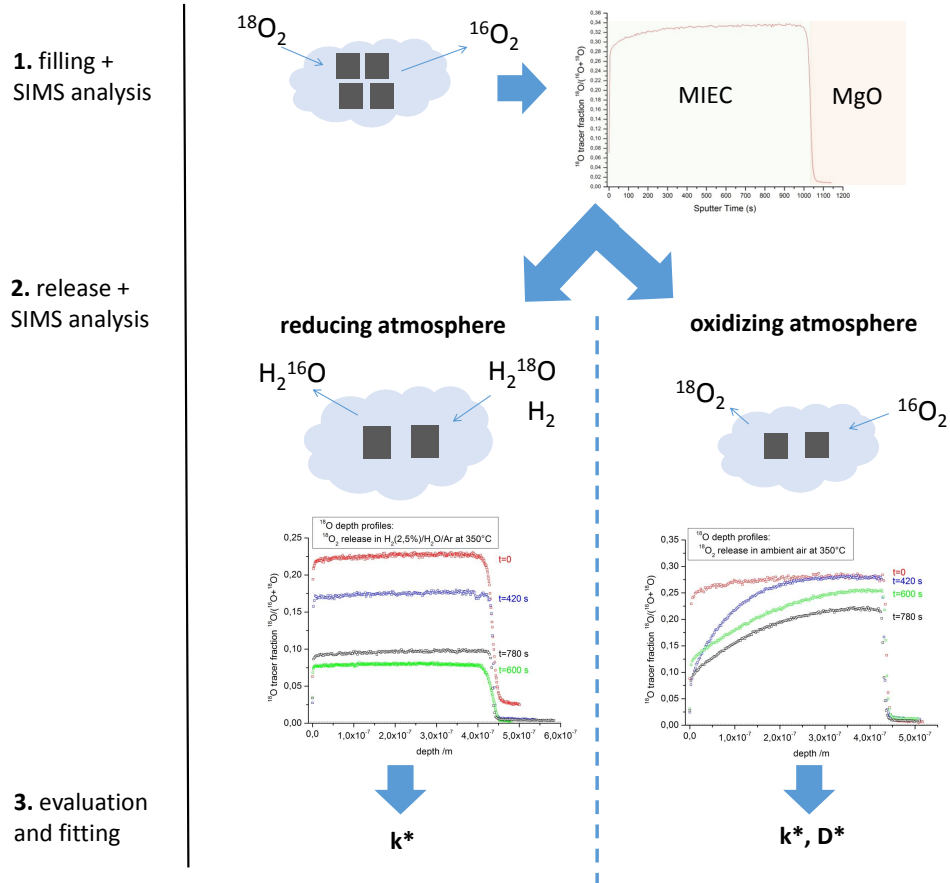


Figure 4.56: Schematic of 2-step tracer exchange experiment and resulting tracer depth profiles after tracer filling at 500°C for 20 min ($t = 0$) and subsequent tracer release at 350°C for 420, 600 and 780 s in $\text{H}_2/\text{H}_2\text{O}$ or air, respectively.

insulating nature, leading to a homogenous 'filling'. Therefore, a subsequent tracer depth profile, measured by TOF-SIMS, has to give a box shaped profile.

2. release + SIMS analysis

The 'filled' sample, with the defined distribution of tracer in the thin layer, is broken into pieces. Half of which are placed in a reducing atmosphere, while the other half is placed in an oxidizing atmosphere.

(a) *reducing atmosphere*

Each piece is heated in the reducing atmosphere for a defined time to a defined temperature. The reaction with the atmosphere leads to a release of tracer and incorporation of ^{16}O . For the 'release' step temperature and time are chosen in a way that some tracer will be released, but enough tracer stays inside the sample for subsequent TOF-SIMS analysis.

(b) *oxidizing atmosphere*

Tracer is released from the remaining pieces under exact the same conditions like for reducing atmosphere, but with oxidizing atmosphere.

After the 'release' the tracer distribution in the samples is again measured by TOF-SIMS analysis.

3. evaluation and fitting

The gained tracer profiles are used to evaluate D^* and k^*

This 2-step method gives several advantages:

- The experiment can be performed in oxidizing or reducing conditions, or in both. Therein a direct comparison of D^* and k^* for different atmospheres is possible.
- The amount of tracer in the sample before the actual experiment is well defined.
- The release with different times, allows to adjust to different temperatures (release at higher temperatures should be performed with shorter time to gain a reliable tracer profile).

- Using just one thin layer and braking it into pieces, rather than using several layers brings some advantages: the sample history and the deposition parameters are exactly the same, hence tracer distributions from each piece should be excellently comparable. If fast degradation plays a role, two pieces 'released' at equal conditions but different times, will show a difference in k^* .
- A loss of tracer due to a leaky set-up or the exchange of tracer with a part within the set-up will only have a negligible effect on the measurement result. During the 'filling' step a reduced amount of tracer will cause a reduced concentration of the tracer within the sample. This will have no impact on the 'release' step as the concentration after 'filling' is known from TOF-SIMS analysis and as the amount of tracer within the gas atmosphere at any rate is very low (natural abundance) and is not changed measurably by the release of tracer from the sample.
- Also from an economic point this 2-step method holds an advantage, namely that the ^{18}O tracer is cheaper than the H_2^{18}O tracer.

Experimental results for the 2-step tracer exchange experiment on LSF64 thin layers

We performed measurements using the above described 2-step tracer exchange method. We used PLD-deposited LSF64 thin films (440 nm) on blocking MgO substrates. The samples were annealed at 600 °C for 10 min in ambient atmosphere to guarantee equal starting conditions for all layers. Each sample (10x10 mm²) was broken into 4 pieces (4x(5x5 mm²)). To achieve a good comparability between the tracer exchange experiments and the impedance measurements, both were carried out either under air or humidified hydrogen. Tracer exchange was performed at 350, 400, 450 and 500 °C. Each temperature was measured several times, for the release step different times were used.

1. filling + SIMS analysis

The LSF64 thin layers were 'filled' with tracer at 500 °C for 20 min in $^{18}\text{O}_2$ at 200 mbar. The TOF-SIMS depth profiles yielded a homogeneous distribution of tracer over the entire film thickness (box-shaped profiles), with a tracer content of 40 – 60%

2. release + SIMS analysis

From every sample (4 pieces), two pieces were used for oxidizing (air) and two for reducing ($\text{H}_2/\text{H}_2\text{O}/\text{Ar}$) conditions. In each case the sample was heated from below on a Linkam oven (Linkam, Germany) in a closed set-up filled with the respective atmosphere. Heating and cooling rate was set to 70 °C/min. Tracer depth profiles for oxidizing and reducing conditions are shown in Fig. 4.56.

(a) *reducing atmosphere*

In reducing atmosphere the release of tracer from the sample leads to an overall lower concentration of tracer in the sample. However, the box-shape is conserved. This indicates a fast D^* , as expected, as ionic diffusion is fast under reducing conditions due to a high oxygen vacancy concentration. An accurate fit of D^* is not possible due to the box-shape of the tracer profile. The tracer exchange in reducing conditions is only limited by the surface tracer exchange.

(b) *oxidizing atmosphere*

The tracer depth profile taken under oxidizing conditions shows a drop of tracer concentration close to the surface, indicating a fast k^* . The depth profile is curved instead of box-shaped, indicating that D^* is slower than the oxygen release (k^*).

3. evaluation and fitting

Fig. 4.57 and Fig. 4.58 show the averaged k^* and D^* values in an Arrhenius-plot. The k^* values are highly similar for both atmospheres, which is rather surprising as a $p\text{O}_2$ sensitivity for k^* is to be expected as oxygen surface exchange also depends on the adsorption of oxygen on the surface [63].

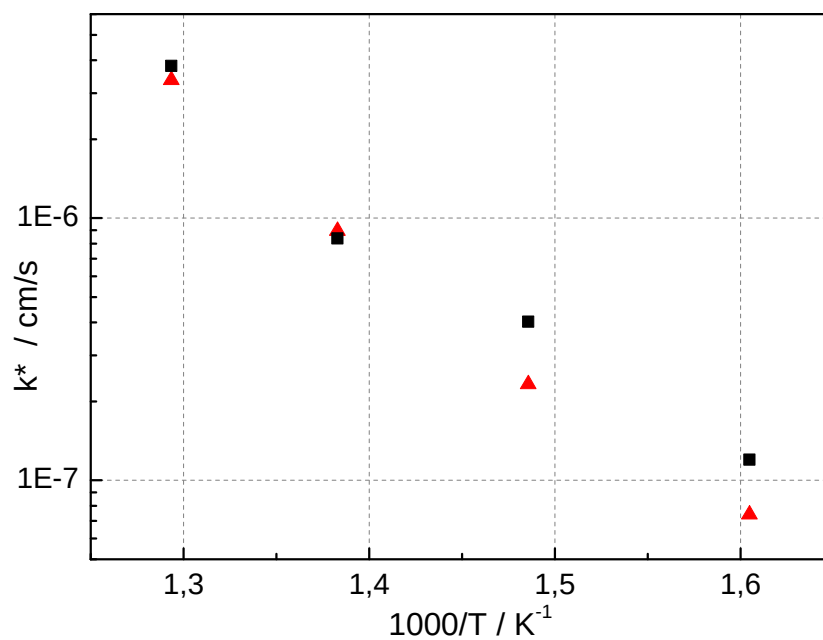


Figure 4.57: Arrhenius plot of k^* obtained in the two-step tracer exchange experiment for oxidizing conditions (red) and for reducing conditions (black).

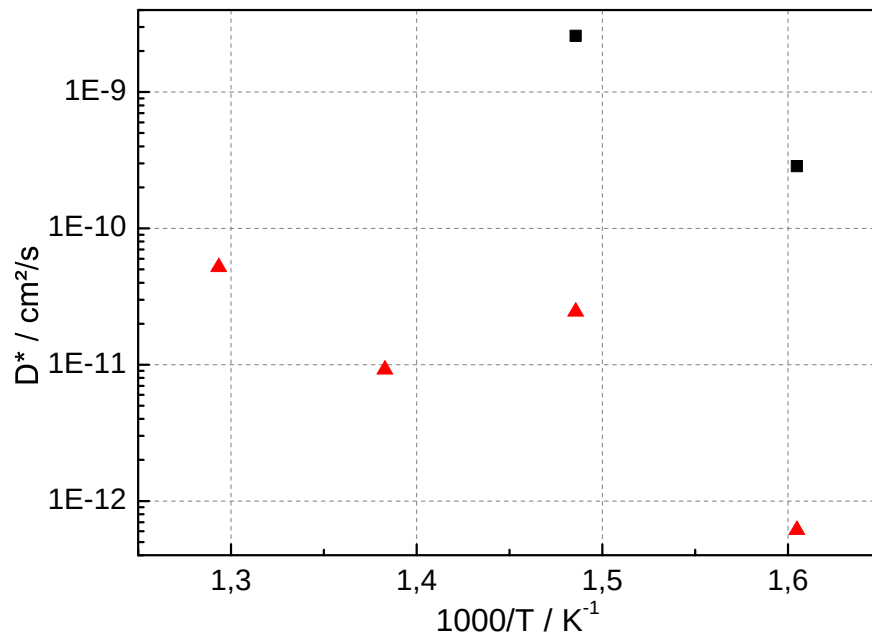


Figure 4.58: Arrhenius plot of D^* obtained in the two-step tracer exchange experiment for oxidizing conditions (red) and for reducing conditions (black), only rough estimates.

The values for k^* are slightly overestimated, as the tracer exchange will already occur during heating and cooling. With the applied heating/cooling rate the temperature changes 100 °C within 90 sec. The error due to the heating/cooling rate is more pronounced at higher temperatures, as the holding times are shorter and the time needed for heating and cooling is longer. For an estimate of the error we may assume a linearity between tracer concentration change and time and a constant k^* between 500 °C and 450 °C. Then the true diffusion time is increased by 1.5 minutes and the k^* at 500 °C is ca. $2.5/1 = 2.5$ times its true value. Accordingly all statements given here are not affected by this error.

The activation energy of the k^* values is similar for both atmospheres, 1.1 and 0.92 eV for oxidizing and reducing conditions, respectively. Also the D^* value in oxidizing conditions has an activation energy of 1.06 eV, when neglecting the point at 400 °C. Nevertheless, the error due to the heating rate can not explain the comparatively high values for k^* and D^* . For LSC82, which should give results at least in the same order of magnitude like LSF64, at 400 °C k^* is approximately $8 \cdot 10^{-9}$ cm/s and D^* is approximately $1 \cdot 10^{-14}$ cm²/s [128] and thus much smaller. Also tracer exchange experiments on LSF82 bulk samples [129] gave values (annealing temperature 800 °C, exchange duration 560 min: $k = 2.0 \cdot 10^{-7}$ cm/s and $D^* = 1.5 \cdot 10^{-9}$ cm²/s) that are considerably lower than those observed in our study. So far no explanation for the fast tracer exchange and diffusion in our LSF64 thin film samples has been found.

4.6.1 Tracer exchange experiments using $H_2^{18}O$

The experiments with tracer marked water were carried out in analogy to typical oxygen tracer exchange experiments. In a one-step experiment, the sample is annealed in the tracer gas atmosphere and then the tracer distribution is measured by TOF-SIMS analysis. For the tracer exchange the ratio of H_2 to $H_2^{18}O$ in the gas atmosphere was 1, so as to reflect the same conditions as used in the two-step tracer exchange experiment and the impedance measurements. The obtained diffusion profiles show, in

accordance with findings from the two-step experiment, a box shaped profile, due to the fast oxygen vacancy diffusion in reducing conditions.

Fig. 4.59 shows a comparison of the k^* values obtained in the tracer-marked water exchange experiment (blue) assuming 97.5% $H_2^{18}O$ in the gas and the k^* values from the 2-step tracer exchange experiment for oxidizing conditions (red) as well as for reducing conditions (black).

The values for k^* were estimated using [130]

$$k^* = -\frac{d}{t} \ln \frac{c^x - c^\infty}{c^0 - c^\infty} \quad (4.17)$$

where c^∞ is the concentration of tracer in the gas atmosphere and c^0 is the initial tracer concentration in the sample. This approximation is only applicable to box-shaped profiles.

k^* values obtained from the two-step experiment are faster than for the tracer marked water exchange experiment. The difference is bigger for higher temperatures. The atmosphere, temperature and holding time at temperature as well as the heating and cooling rate (70 °C/min) are equal. However, as exchange already occurs during heating and cooling, k^* values will be affected, see above. A new tracer exchange set-up was therefore constructed to minimize the heating and cooling times, see Section 'New tracer exchange set-up'. Unfortunately no measurements performed on the new set-up can be displayed here, as the finishing of the set-up was delayed until the end of this thesis.

One explanation for the difference between the observed k^* values is the loss of tracer in the one-step experiment due to tracer exchange with the set-up, which is likely due to hot oven-wool and aluminium oxide (from the heater). This loss of tracer would cause an underestimation of k^* from the one-step experiment. Still, even with this likely underestimation of k^* in the one-step experiment, the obtained values are faster than those for comparable materials found in literature [128] [129].

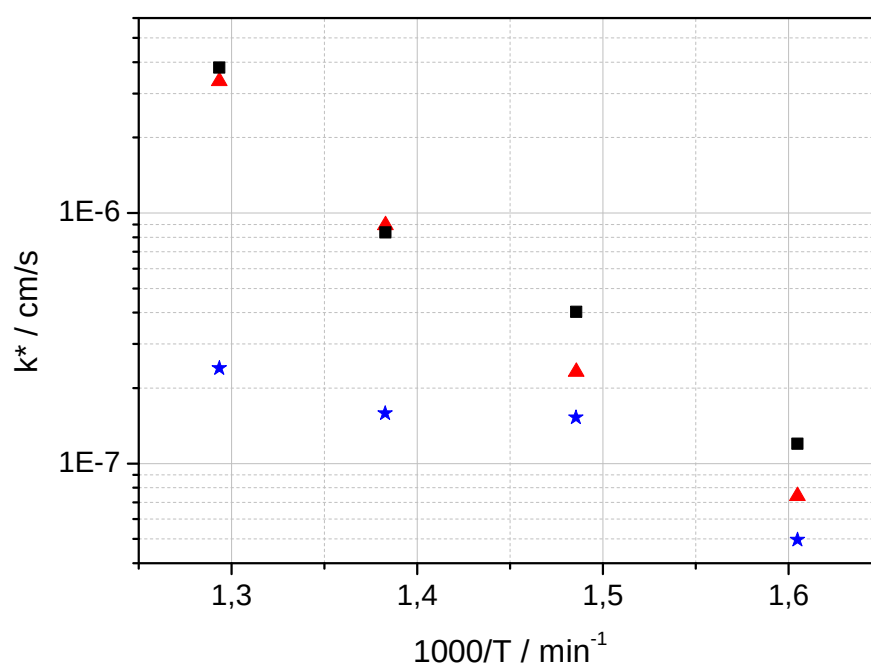


Figure 4.59: Arrhenius plot of k^* , for oxygen release in *oxidizing* (red) and *reducing* conditions (black) as well as k^* values determined from H_2^{18}O exchange experiments.

4.6.2 Impact of time, pre-reduction and humidity on k^*

Time-dependency of k^ :*

To evaluate a time-dependency of k^* a LSF64 thin layer (440 nm thickness) was deposited on MgO. The sample was annealed at 600 °C for 10 min in air and then broken into 4 pieces. Accordingly, every piece should have the exact same thin layer with the same history. Tracer was incorporated into three of the pieces at $T = 500^\circ\text{C}$, in 200 mbar $^{18}\text{O}_2$ for 8 min, 2 h and 24 h. The depth profiles, shown in Fig. 4.60 inset, were measured by TOF-SIMS analysis. The corresponding tracer profiles are flat, indicating that D^* is fast at 500 °C and does not hinder the tracer incorporation. Only in the 8 min-annealed sample a slight curve is visible, which indicates that some effect of D^* . From the depth profiles k^* was calculated and is plotted as function of tracer exchange time in Fig. 4.60. The samples with the short tracer exchange time (8 min and 2 h) give similar values for k^* , but the value obtained for the 24 h tracer exchange time is significantly slower.

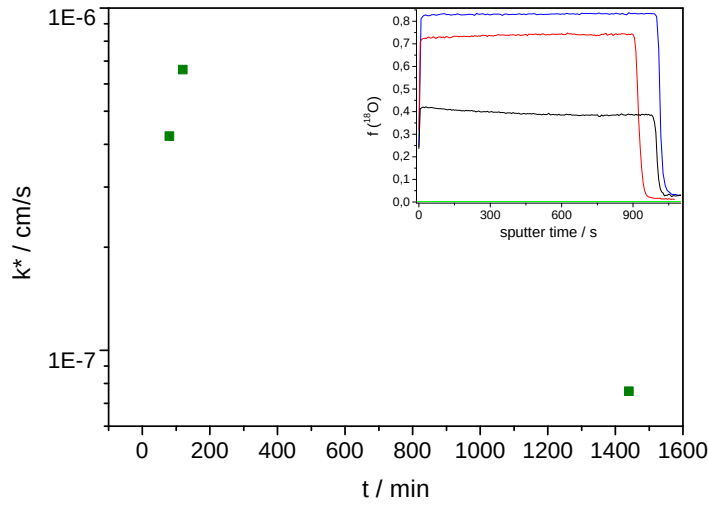


Figure 4.60: k^* values for a 367 nm thick LSF64 layers on MgO. The samples were annealed at 500 °C for different times (8 min, 2 h and 24 h). The inset shows the ^{18}O depth profiles after annealing, for 8 min (blue), 2 h (red) and 24 h (black).

In general the driving force decreases with the increasing amount of tracer in the sample or the decreasing amount of tracer in the gas atmosphere. The change of concentration of the tracer in the gas atmosphere due to

exchange with the sample is negligible, the 24 *h* exchange sample was expected to reach 97.5% of tracer in the thin layer. However, only 82% were found. Two explanations for the slow tracer uptake are possible. First, a loss of tracer from the gas atmosphere. The measurement set-up was gas tight, however, a exchange of tracer with parts from the set-up cannot be excluded even though. All parts of the set-up in the heated zone, except the thermocouple wires, are made from quartz and an exchange of tracer is unlikely. An erroneous outer concentration used in the data analysis may cause an apparent decrease of k^* . A degradation of the surface might further contribute to a decrease in k^* as in impedance measurements.

Pre-reduced thin layers:

As observed in XRD powder measurements, LSF64 forms Ruddlesden-Popper phases under reducing conditions. To test if these phase may act catalytically on the oxygen exchange reaction a LSF64 thin layer (440 *nm* thickness) on MgO was broken into pieces and put under reducing conditions for different times. One piece was reduced for 2 *h* the other for 24 *h* in humidified hydrogen at $T_{set} = 650^\circ\text{C}$. After the pre-reduction step the reduced samples as well as a pristine piece of the same thin layer were heated to 500 $^\circ\text{C}$ for 20 *min* in 200 *mbar* $^{18}\text{O}_2$. The obtained depth profiles are shown in Fig. 4.61.

The pristine (not pre-reduced) LSF64 thin film shows the highest amount of tracer (black curve). The pristine layer also shows a slight curvature in the depth profile, indicating a slight effect of D^* . The film that has been reduced for 2 *h* shows a very similar concentration of tracer in the film (red curve), while the concentration of tracer in the 24 *h* reduced sample is low (blue curve). This experiment indicates that the pre-reduction has not enhanced, but decreased the oxygen surface exchange. While the effect in the 2 *h* pre-reduced sample is almost negligible, it is dramatic in the 24 *h* reduced sample. Both pre-reduced thin films show a box-shaped profile.

Effect of humidity on tracer exchange:

Due to the very similar and very fast k^* values for oxidizing and reducing conditions we speculated that humidity might have an impact on the

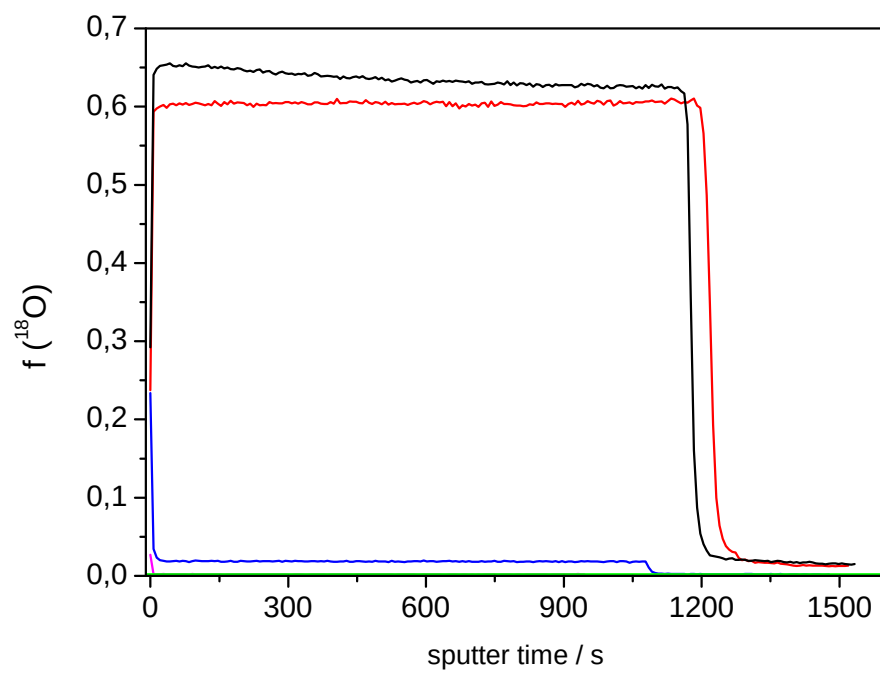


Figure 4.61: k^* values for a 440 nm thick LSF64 layers on MgO. The samples were annealed at 500°C for 20 min. (black) pristine, (red) 2h reduced, (blue) 24h reduced, (green) natural abundance.

oxygen exchange. Therefore we again performed a two-step experiment, as described in Section 4.6. The release was performed in 1050 mbar of (a) dry $^{16}\text{O}_2$, (b) dry $^{16}\text{O}_2/\text{N}_2$ (20%/80%), (c) humidified $^{16}\text{O}_2/\text{N}_2$ (20%/80%) and (d) humidified hydrogen at 350 °C, for 3 min, with a heating and cooling rate of 70 °C/min. Solid lines in Fig. 4.62 indicate the 'filled' depth profiles (step-1 of the 2-step experiment) and the dotted lines indicate the depth profiles after release under the respective atmosphere.

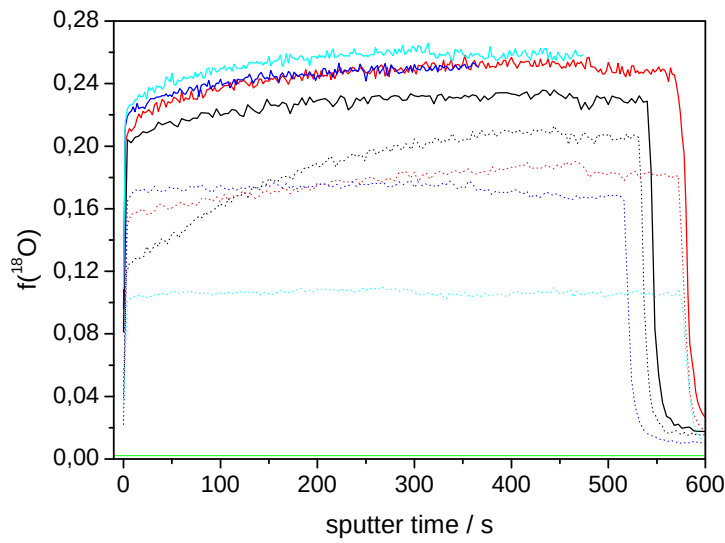


Figure 4.62: Oxygen tracer depth profiles of a 2-step tracer exchange experiment. Solid lines show the tracer distribution after the 'filling' step (500 °C, 20 min, 200 mbar $^{18}\text{O}_2$). The tracer release is performed in 1050 mbar of (a) dry $^{16}\text{O}_2$ (black), (b) dry $^{16}\text{O}_2/\text{N}_2$ (20%/80%) (red), (c) humidified $^{16}\text{O}_2/\text{N}_2$ (20%/80%) (violet) and (d) humidified hydrogen at 350 °C (blue), for 3 min, with a heating and cooling rate of 70 °C/min.

The depth profiles, although all pieces (a-d) originate from the same thin layer and were 'filled' together, show a slightly different tracer content from 20 – 24%. After release in (a) dry oxygen the thin film, shows a strongly curved profile, which indicates a slow oxygen diffusion in the bulk. This is expected for high oxygen partial pressures, as the oxygen vacancy concentration is low. Under dry, synthetic air (b) (red) the depth profile is flat and almost identical to that found for humidified synthetic air (violet). This is rather surprising since release in ambient air lead to curved profiles (see Fig. 4.56). Moreover, this suggests negligible effect of

water in oxygen atmosphere. The tracer depth profile for the sample with release in humidified hydrogen is also flat, but the amount of tracer in the sample is lower than for the other samples. In this measurement it seems that the oxygen surface exchange is even faster in humidified hydrogen than under air. In case of humidified hydrogen (d), (blue)) the oxygen surface exchange is faster than in the other three cases.

4.6.3 New tracer exchange set-up

In the tracer exchange experiments described above the heating and cooling rate is limited and the exchange times are short. Consequently the obtained tracer exchange profiles also contain the error of exchanged tracer fraction during heating and cooling. Therefore a new tracer set-up was assembled. As the completion of this set-up was delayed, only the set-up but no measurements conducted in the set-up are shown.

Marius Maier (technical staff) and Tobias Huber (PhD student) contributed to the building of the new set-up described here.

Requirements for an ideal tracer exchange set-up:

- heating and quenching: the sample should be heated and quenched as fast as possible. Thus the time and temperature of tracer exchange are better defined.
- material: the tracer exchange set-up must not exchange tracer itself, to guarantee a defined atmosphere
- volume: a small gas volume is advantageous as it spares tracer gas.
- temperature: temperature distribution has to be homogeneous.
- atmosphere: the sample should be at room temperature or lower during gas change, otherwise the sample will equilibrate with the atmosphere which, in case of a one-step experiment, will cause an error. This is especially a problem during gas change from non-tracer to

tracer, as the set-up needs to be evacuated. Accordingly, if the sample is already heated, it will release oxygen and upon filling the set-up with tracer it will incorporate tracer simply due to chemical equilibration.

The new set-up was designed to meet all above mentioned requirements. In order to prevent oxygen tracer exchange with the set-up only quartz was used in the heated volume of the oven. A quartz tube of 20 *cm* length, with KF40 flanges on each end was used. In order to minimize the volume the inner diameter of the tube was reduced to 15 *mm*, see Fig. 4.63.

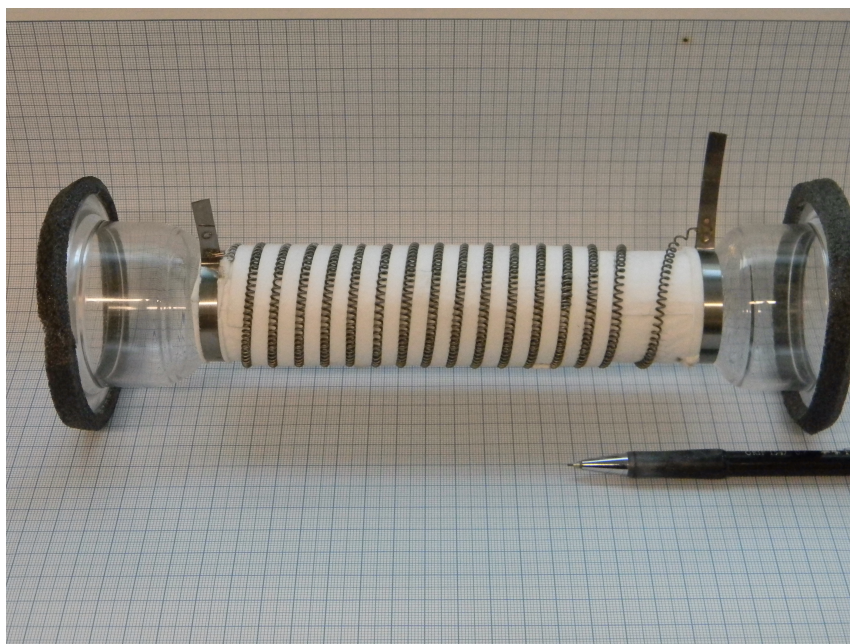


Figure 4.63: *Application of the heating wire.*

The inner parts of the tracer exchange oven consist of a moveable sample stamp and a thermocouple holder. For the sample stamp also quartz was used. The volume of the stamp, especially the part that carries the sample was kept small to allow a fast heat exchange between the stamp and the cooler. Further the shape of the stamp was sloped in a way that it would fit in the cooler, see Fig. 4.64. This is important as quartz is a weak heat conductor. The sample is placed on top of the stamp. To prevent the

sample from falling of the stamp quartz droplets were put on the edges of the stamp. The stamp can be moved up and down with the aid of a KF15 feed through (Pfeiffer Vacuum, type: DS 016A). The quartz stamp and the feed through are connected by a teflon connector (teflon cylinder with holes of the diameter of the quartz stamp and the feed-through pole).

The thermocouple holder consists of a quartz tube and a broad stamp-like top, see Fig. 4.64. The thermocouple wires (Pt/Rh and Pt - thermocouple type K) were put into the quartz tube. To prevent the wires from touching, one was isolated using a very thin quartz tube. Close to the stamp-like top the wires were pulled out from the quartz tube through a hole. The contact point of the wires was on top of the stamp-like top. The stamp-like shape allowed to bring the thermocouple holder in contact with the sample holder, were the quartz droplets would ensure that the thermocouple holder would not sit on the sample. Nevertheless, the thermocouple would touch the sample. When the sample is moved from the cooler into the heated area, the contact between thermocouple and sample can be seen by a drop in the measured temperature upon contact. To prevent a pressing force on the thermocouple and sample holder, the thermocouple holder was mounted free-hanging. When the sample holder is pushed up, the thermocouple holder will be moved upwards by the sample holder upon contact. When the sample holder was pulled down, the thermocouple would move down to its initial position, were two quartz droplets would prevent further down gliding. The quartz droplets were simply put on the the thermocouple holder above the cooling-unit. This mounting of the thermocouple has proven advantageous in comparison to a thermocouple connected to the sample stamp. In a first prototype the thermocouple was connected to the sample stamp, the moving of the wires would short circuit or lose contact every now and then.

The cooling units (see Fig. 4.65) were made from copper, to ensure a good heat exchange. They were equipped with a water in- and outlet, to allow for water cooling. The hoses were connected in counter current flow. The cooling units had KF-norm ends to connect them gas-tight to the quartz

tube. The lower cooling unit is needed for quenching the sample, the upper cooling unit prevents heat accumulation.

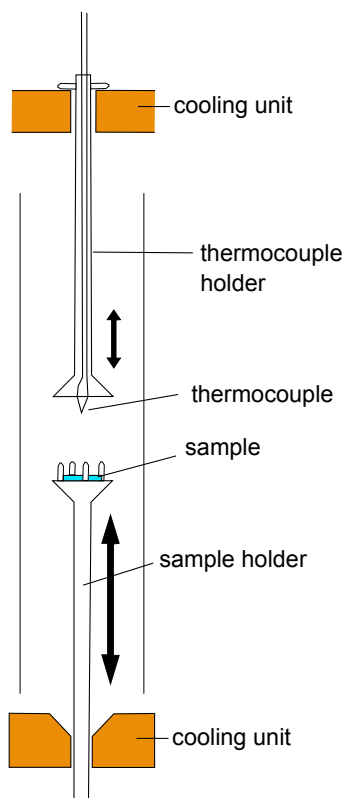


Figure 4.64: Schematic of sample and thermocouple holder.

The heating of the quartz tube was achieved by a Kanthal (0.7 mm diameter) heating wire. The inner resistance of the oven had to be $25\ \Omega$, so that it could be operated by a Eurotherm 3216 control unit. Accordingly, the heating wire used had to be a few meters long. Therefore the wire was spiralized, by winding it around a stick and then cautiously pulling it off. To prevent the heating wire from gliding on the quartz tube and hence causing a short-circuit, as well as to ensure a homogeneous heating, a layer of thermopaper (Si-paper, 1 mm thick) was put between the quartz tube and the heating wire. To further prevent the heating wire from gliding, stripes of the thermopaper were placed in between the wire, see Fig. 4.63. Broader stripes were used on the top side, so that the distance between the heating

wire would be greater and the heating in the top area therefore less. This inhomogeneity in mounting leads to a more homogeneous temperature distribution in the oven, as hot gas will diffuse upwards. The ends of the heating wire were connected to a metal sheet, for easier connecting them to the outer circuit.

For thermal shielding to the outside alternating layers of thermopaper and a thick alumina foil were used, see Fig 4.65.

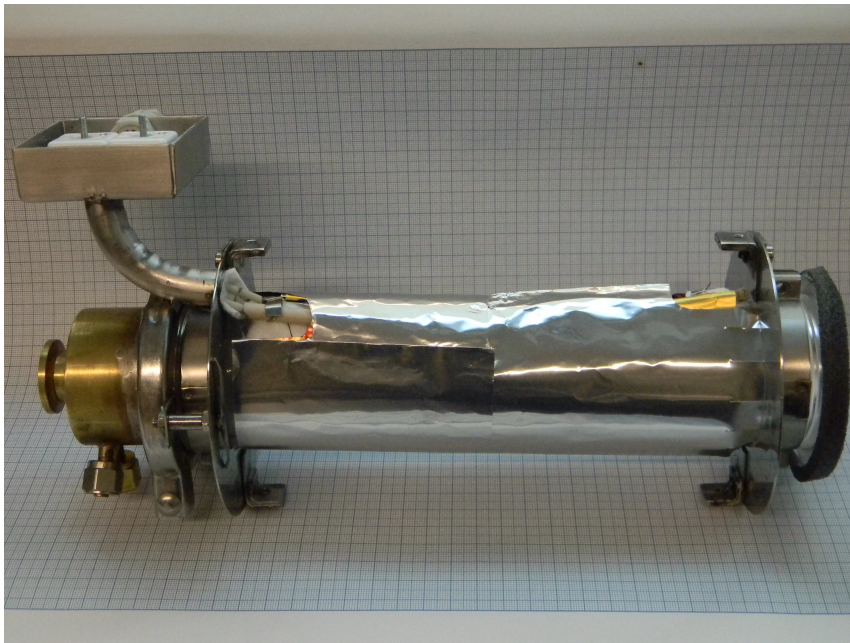


Figure 4.65: *Thermal shielding.*

The connection wires were feed through a metal tube to a connection box, see Fig. 4.66. In the tube, between the wires oven wool was stuffed, to prevent movement of the wires and hot air diffusion, which could heat up the connection box. Ceramic insulating screw joints were used for the connections. Also, to protect the oven from to high voltage, a fuse was used.

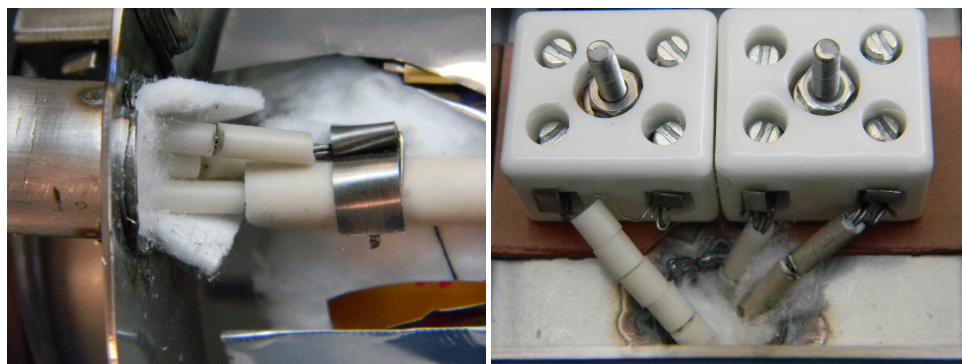


Figure 4.66: *Electrical connections.*

The KF flange clips (Edwards vacuum) are made from a rather elastic metal sheet, therefore the pressure on the quartz tube is more homogeneous than with typical KF flange clips. Also teflon foil was glued into the clips on the quartz-facing side, to further ensure no pressure points on the quartz tube, as those could cause a breaking of the tube.

The oven housing was connected to the KF40 clip on the top side of the quartz tube. Thereby a shifting of the quartz tube was further prevented. A pole was connected to the oven housing to allow for the mounting of the oven on a standard laboratory pole.

4.7 Final comparison of results

Oxygen exchange parameters of LSF64 are very similar in oxidizing and reducing conditions. This has been observed in impedance measurements as well as tracer exchange experiments. Although different substrates were used - YSZ for impedance measurements and MgO for tracer exchange experiments - there are no obvious differences between the films observable in SEM. Although, both methods lead to the same conclusion, there is no explanation why tracer exchange experiments yield oxygen exchange coefficients and diffusion coefficients that are approximately 2 orders of magnitude faster than what would be expected from impedance results or

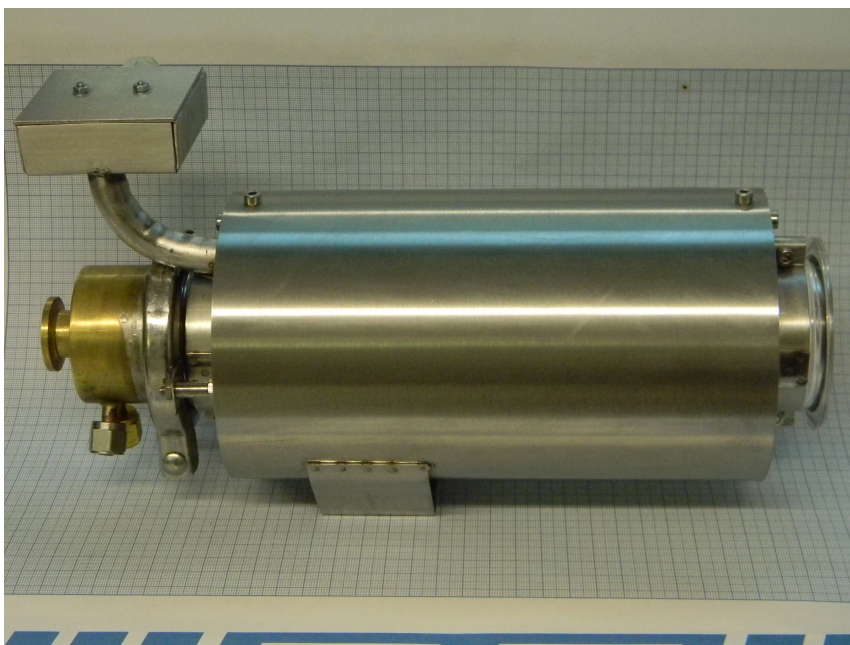


Figure 4.67: *Completed tracer exchange oven.*

what is found in literature.

Impedance measurements showed that humidity has an impact on the oxygen exchange and in most cases leads to an enhancement of the oxygen exchange rate. Sakai et al. found in their ^{18}O tracer exchange experiments on scandium stabilized zirconia (ScSZ) and iron doped (Fe-ScSZ) that the addition of water vapour enhances the oxygen exchange rate (500 times higher), but does not affect the oxygen isotope diffusivity [131]. This indicates that adsorbed water molecules support the oxygen exchange. A similar finding was made on gadolinia doped ceria (GDC) where the oxygen tracer exchange rate is enhanced by water vapour [132].

The catalytic effect of humidity, and the fact that it depends on thermal history indicate that a secondary phase could play a role in this process. In the XRD measurements on LSF64 powder in humidified hydrogen we see the formation of a Ruddelsten-Popper like phase and iron oxide. The increased amount of Sr on the electrode surface after exposure to reducing

conditions, observed in XPS, also points towards a formation of such phases on the thin film electrodes.

These results suggest that in the temperature range of our thin film studies LSF64 quickly forms small amounts of secondary phases in reducing conditions, despite nominally remaining within the stability limit found in Ref. [20]. Irrespective of these phase formations, the main LSF64 peaks remain by far the largest. Possibly, surfaces with their different energetics are already unstable in our reducing atmosphere and demix while the bulk remains perovskite-type.

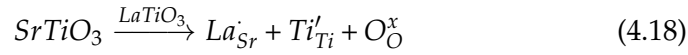
Transferring this interpretation to our thin film measurements thus means that iron oxide and a Ruddlesden Popper like phase might be formed on the electrode surface under reducing conditions. This could also happen for a degraded surface and thus might be the origin of the reactivation of the LSF64 surface in air after redox cycling, as suggested in Sec. 4.3.3. In LSC surface decorations with Ruddlesden Popper like phases lead to an increased oxygen exchange [133] [134]. This is most likely caused by fast oxygen incorporation paths along the hetero-phase interface [135], [136]. In humidified gas Ruddlesden-Popper phases can form oxyhydrates [137], these oxyhydrates on the surface could also be the cause for the enhanced oxygen exchange kinetics. Degradation in air after exposure to reducing conditions as observed in Sec. 4.3.3 could be caused by segregation of a Sr-rich phase or formation of a Sr-rich surface termination cf. processes for LSC [77], [113], the surface phases evolving in H_2/H_2O can undo these processes by forming the surface being most stable in the reducing atmosphere.

4.8 LST27 as anode material in SOFCs

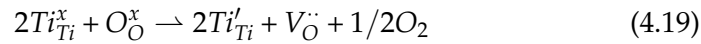
As part of this thesis also the diploma thesis of Gerhard Fritscher was supervised. In this diploma thesis the electrode material $La_{0.2}Sr_{0.7}TiO_{3\pm\delta}$ (LST27) was investigated by impedance spectroscopy and by a van der

Pauw set-up which was build-up for the measurement of thin films. A detailed description of the results will not be given here, but can be found in [138]. However, a few key points shall be noted here.

$La_{0.2}Sr_{0.706}TiO_{3\pm\delta}$ (LST27) is a perovskite-type material. It is special in a way that it not only has oxygen nonstoichiometry, but also that its composition is also cation non-stoichiometric, meaning that only 90% of the A-sites are occupied. The La doping will create $La_{Sr}^{\bullet}$ (see Eq. 4.18), the majority of this charge is balanced by the strontium vacancies V_{Sr}'' , leaving the material almost nominally undoped ($La_{Sr}^{\bullet} \rightarrow 20\%$ and $V_{Sr}'' \rightarrow 10\%$). The small surplus of lanthanum (0.2 instead of 0.188) is balanced by a reduction of the titanium, giving Ti_{Ti}' .



Under reducing conditions oxygen is released from the lattice, creating oxygen vacancies but also electrons, leading to an increase in n-type conductivity.



Thin films of LST27 on YSZ and MgO (approximately 200 nm) were investigated by impedance spectroscopy and van der Pauw measurements.

Fig. 4.68 shows the electrode resistance obtained from impedance measurements of a circular 200 μm diameter microelectrode with time. Within the first hours the electrode resistance slightly decreases, followed by a degradation. The effect of degradation can partly be reversed by sintering in reducing atmosphere (2% H_2 /Ar).

Fig. 4.69 shows the electronic conductivity as a function of temperature, measured for LST27 thin films on YSZ (blue), on MgO (green) and a

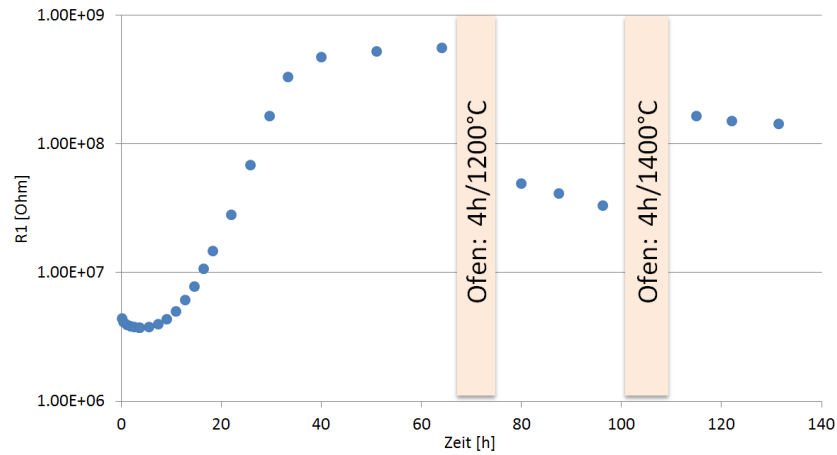


Figure 4.68: Change of electrode resistance at 600 °C with time and effect of sintering at 1200 °C and 1400 °C for 4 h. Taken from Ref. [138].

comparison to literature values for LST27 bulk conductivity (red dotted). The values found for LST27 on MgO are comparable to those from literature. Specific conductivity values for LST27 on YSZ, however, show an increase with increasing temperature, indicating an influence of the ionic conductivity of the YSZ substrate to the measurement.

Measurements were performed in different atmospheres (wet and dry hydrogen) at different temperatures, with different pre-annealing procedures. It could be shown that LST27 has an acceptable electrode resistance in reducing conditions. Van der Pauw measurements on the new set-up showed that thin film conductivity is comparable to literature bulk conductivity values. Both measurement types revealed that the conductivity is higher in dry hydrogen than in wet hydrogen and that pre-annealing temperatures and atmospheres had an impact on conductivity.

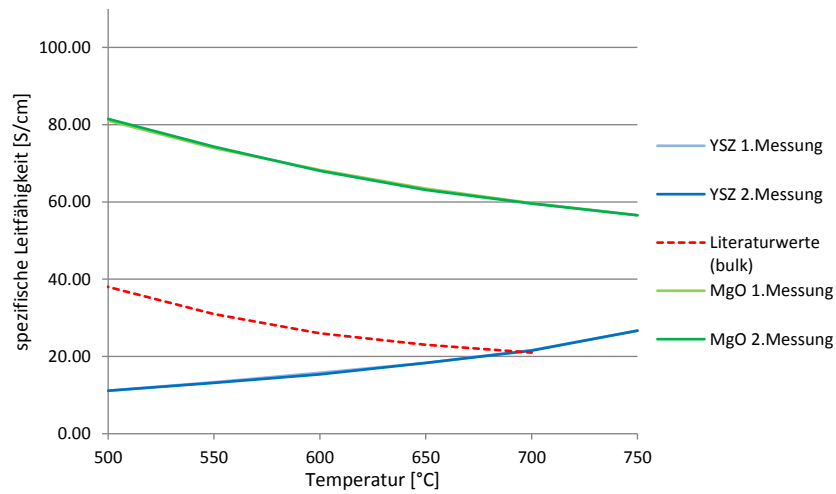


Figure 4.69: Specific conductivity of LST27 thin layers (200 nm thickness) as function of temperature: (blue) on YSZ single crystalline substrate, (green) on MgO single crystalline substrate and (red dotted) literature values for LST27 bulk conductivity. Taken from Ref. [138].

Summary of scientific achievements

Impedance measurements of well-defined LSF64 thin film microelectrodes were successfully carried out under oxidizing as well as reducing conditions. The low electronic conductivity of LSF64 thin film electrodes under reducing conditions leads to a high sheet resistance, which can be overcome by the use of an additional current collector. Interpretation of many findings required a detailed defect chemical model. Based on literature data (Ref. [20]) the p_{O_2} and T dependence of all relevant charge carriers were therefore calculated. Among others these calculations were used in the interpretation of chemical capacitances and electronic conductivities. Chemical capacitances (C_{chem}) are about one order of magnitude larger in air, compared to H_2/H_2O and in acceptable agreement with values predicted from the defect chemical model in literature. In both cases C_{chem} reflects the concentration of the minority charge carriers, which are oxygen vacancies in air and electrons in H_2/H_2O . The chemical capacitance even allows an estimation of the electrochemically active area and thus determination of area-specific electrode resistances for oxidizing and reducing conditions. Surprisingly similar specific resistances are found in both atmospheres.

Findings from the microelectrodes were also reproduced with macroscopic LSF64 electrodes that were exposed to a cyclic gas change. Further, the cyclic gas change shows that there is a continuous severe increase in the electrode resistance under oxidizing conditions after each exposure to re-

ducing conditions. In H_2/H_2O , the previous degradation under air could be reversed. As a reason we suggest reversible demixing of near-surface regions in H_2/H_2O with formation of a new stable surface, irrespective of previous surface degradation processes in air. The latter would be in line with high-temperature in-situ XRD measurements, where the formation of small amounts of iron oxides were observed in reducing conditions together with the formation of another phase which is probably Ruddlesden Popper-like. XRD measurements in dry hydrogen, on the other hand, showed the decomposition of the LSF64. Subsequent heating of the decomposed powder lead to the formation of the perovskite phase already at comparatively low temperatures.

Additional impedance studies made use of a special microelectrode geometry with interdigitating current collectors. This allowed measurements in two modes (in-plane, out-of-plane). A fitting procedures that fits both measurements simultaneously, was used to evaluate C_{chem} , R_{sur} , σ_{eon} and σ_{ion} . The chemical capacitance and surface resistance are in accordance with the findings from the circular microelectrodes with current collector under reducing conditions.

The findings of similar oxygen exchange kinetics under reducing and under oxidizing atmospheres could also be reproduced by tracer exchange measurements. For these measurements a 2-step tracer exchange was used that allowed for a direct comparison of the evaluated oxygen exchange parameters. Although the general trend found by impedance measurements that the oxygen exchange kinetics for LSF64 are similar in both atmospheres is confirmed, ^{18}O tracer exchange experiments lead to k^* values that are by approximately two orders of magnitude faster than what is expected from literature and than what would be estimated from the impedance measurements.

All together, the results show that LSF64 might be used in electrodes of solid oxide cells under reducing conditions if prepared with an additional current collector.

Nomenclature

ΔH_R^0	standard reaction enthalpy
ΔS_R^0	standard reaction entropy
$\Delta_f H^0$	standard formation enthalpy
λ	wavelength of incident X-ray beam
μ_0	chemical potential under standard conditions
μ_i	chemical potential
$\omega = 2\pi f$	angular frequency
ω_p	characteristic frequency
σ_i	conductivity (SI unit: $\Omega^{-1}m^{-1} = Sm^{-1}$, but $\Omega^{-1}cm^{-1}$ is more common)
θ	angle of incidence
φ	electric potential
c_0	concentration of oxygen sites
c_i	concentration of particle i
d	distance between atomic layers in the crystal
D^*	tracer diffusion coefficient (cm^2s^{-1})
D^δ	chemical diffusion coefficient (cm^2s^{-1})

D^σ	conductivity based diffusion coefficient (cm^2s^{-1})
D_i	diffusion coefficient
e	elementary charge
E_{kin}	kinetic energy
I	current
j	imaginary unit $\sqrt{-1}$
J_i	particle current
j_i	current density of particle i
k	surface exchange coefficient (cms^{-1})
k^*	tracer surface exchange coefficient (cms^{-1})
k^q	conductivity based surface exchange coefficient (cms^{-1})
k_B	Boltzmann's constant
L_a	specific length
m	mass of secondary ion
n	an integer
q	charge
q_i	charge of the particle ($z_i \cdot e = q_i$)
S^0	standard entropy
T	temperature
t_F	flight time
U	voltage(between two electrodes)
U_A	acceleration voltage
u_i	mobility of the particles ($m^2V^{-1}s^{-1}$)
v	velocity

$V_{\text{O}}^{\cdot\cdot}$	oxygen vacancy
Z	impedance
z_i	charge number
R	ideal gas constant
ac	alternating current
ASR	area specific resistance
C	capacitor
CGO	gadolinium-doped ceria
CPE	constant phase element
IS	Impedance Spectroscopy
K	equilibrium constant
MIEC	mixed ionic electronic conductivity
PLD	pulsed laser deposition
R	resistor
SOEC	solid oxide electrolysis cell
SOFC	solid oxide fuel cell
TEC	temperature expansion coefficient
TOF-SIMS	time of flight - secondary ion mass spectrometry
TPB	three phase boundary
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectivity
YSZ	yttria stabilized zirconia

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