Identification of the oxygen reduction at cathodes of solid oxide fuel cells

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Identification of the Oxygen Reduction at Cathodes of Solid Oxide Fuel Cells

A dissertation submitted to the
SWISS FEDERAL INSTITUTE OF TECHNOLOGY
ZURICH

for the degree of
Doctor of Technical Sciences

presented by
Andreas Mitterdorfer

Dipl. Werkstoff-Ing. ETH
born on February 19, 1966
citizen of Wiesendangen, ZH

accepted on the recommendation of
Prof. Dr. L.J. Gauckler, examiner
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Leer - Vide - Empty
SUMMARY

The high temperature reduction of oxygen at interfaces between solid oxide oxygen ion conductors and electronically conducting cathode materials consists of a number of elementary steps: transport of oxygen in the porous cathode network, adsorption of oxygen on the cathode, and electrochemical and chemical interfacial reactions. Steady-state current-voltage measurements and electrochemical impedance spectroscopy are the main electrochemical investigation techniques employed for electrode characterization. In order to be able to improve the electrochemical performance of cathodes the reaction mechanisms and the associated kinetic rate constants must be known. The purpose of the present study is to provide a general method for the identification of heterogeneous electrode reaction mechanism. The application of this method is demonstrated with two different systems.

A method is developed for dealing with micro-kinetic models. This methods allows for performing mathematical analysis of the equations, model implementation, steady-state and dynamic simulations, and parameter estimation (numerical optimization) within a single framework. The models are described by time-independent state-space equations from which the Faradaic admittance transfer function is obtained.

The Pt, O$_2$(g) $|$ ZrO$_2$ system is considered as a model system and is investigated for its identifiability of unknown parameters. Oxygen adsorp-
tion on Pt, surface diffusion of atomic oxygen, and the electrochemical reduction of adsorbed oxygen at the three-phase boundary is considered. It is shown that the unknown rate constants and parameters can be accurately estimated from a combination of mathematical analysis, electrochemical measurements, and numerical data analysis. Coverage dependent surface diffusion coefficients can be estimated from impedance spectroscopy measurements. The method of working demonstrated can be well applied to other metal electrode/solid electrolyte systems.

The relevant reaction steps in the $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3, \text{O}_2(\text{g}) \mid \text{ZrO}_2$ system are discriminated from an experimental study, comprising microstructural and electrochemical characterizations. The formation of the foreign phase $\text{La}_2\text{Zr}_2\text{O}_7$ at the cathode/electrolyte interface is investigated by means of high resolution transmission electron microscopy and atomic force microscopy. The manganese concentration in the perovskite affects the onset of nucleation and the growth rate of $\text{La}_2\text{Zr}_2\text{O}_7$. A-site deficiency in the perovskite may prevent $\text{La}_2\text{Zr}_2\text{O}_7$ formation. The electrochemical properties of the interfaces are strongly influenced by $\text{La}_2\text{Zr}_2\text{O}_7$ islands at the three-phase boundary. Charge transfer, dissociation of adsorbed molecular oxygen ions, and surface diffusion of atomic oxygen are discriminated from electrochemical impedance investigations.
ZUSAMMENFASSUNG


Als Modell-System wird das Pt, O$_2$(g) | c-ZrO$_2$-System betrachtet. Dieses wird bezüglich der Identifizierbarkeit von unbekannten Parametern untersucht. Es werden die Sauerstoffadsorption auf Pt, die Oberflächendiffusion von atomarem Sauerstoff auf Pt und die elektrochemische Reduktion von adsorbiertem Sauerstoff an der Dreiphasengrenze miteinbezogen. Es wird gezeigt, dass die unbekannten kinetischen Konstanten und Parameter aus einer Kombination von mathematischer Behandlung, elektrochemischen Messungen und numerischer Datenanalyse mit großer Genauigkeit ermittelt werden können. Der vom Bedeckungsgrad abhängige Diffusionskoeffizient von atomarem Sauerstoff auf Pt kann aus elektrochemischen Impedanzmessungen bestimmt werden. Die vorgestellte Methodik kann ohne weiteres auf andere Metall/Festelektrolyt-Systeme übertragen werden.

Der Mechanismus der Sauerstoffreduktion an Grenzflächen zwischen La$_{0.85}$Sr$_{0.15}$MnO$_3$ und c-ZrO$_2$ wird mit mikroskopischen und elektrochemischen Methoden charakterisiert. Die Bildung der Fremdphase La$_2$Zr$_2$O$_7$ an der Grenzfläche zwischen der porösen Kathode und dem Festelektrolyten wird mittels hochauflösender Transmissions-Elektronenmikroskopie und Atomkraftmikroskopie untersucht. Der Mangan-Gehalt vom Perowskit beeinflusst sowohl den Zeitpunkt als auch die Geschwindigkeit der La$_2$Zr$_2$O$_7$-Bildung. Die elektrochemischen Eigenschaften der Grenzfläche werden durch La$_2$Zr$_2$O$_7$-Inseln an der Dreiphasengrenze beträchtlich verschlechtert. Der Ladungstransfer-Schritt, die Dissoziation von adsorbierten molekularen Sauerstoffionen und die Oberflächendiffusion von atomarem Sauerstoff werden als relevante Reaktionsschritte aus Impedanzmessungen bestimmt.
Part I

Front Matter
Chapter 1

Introduction

Abstract The reader is introduced into the operating principles of solid state ionics electrochemical devices and into electrochemical kinetics. The differences between Solid Oxide Fuel Cells (SOFC), oxygen sensors, oxygen pumps, and oxygen separation membranes are presented. Some emphasis is given on the heterogeneous processes that occur at materials interfaces. The term "overpotential" is explained. The present status of knowledge about the oxygen reduction kinetics at SOFC cathodes is given. References to the most relevant literature in the field are given. It is assumed that the reader is familiar with most of the microscopic and spectroscopic techniques employed in this thesis.

1.1 Background

1.1.1 Solid State Ionics Electrochemical Devices

Solid state ionics electrochemical devices consist of two electronically conducting electrodes which are separated by a gas tight solid electrolyte. Y$_2$O$_3$-stabilized ZrO$_2$ (YSZ) has been employed by far most as oxygen ion conducting electrolyte for its relatively high ionic conductivity at high temperatures, its structural stability in both oxidizing and reducing atmospheres, its capability of being easily produced, and its relatively low price [1]. A number of other ionic conductors, such as doped CeO$_2$ [2], δ-Bi$_2$O$_3$ [3], or per-
ovskite-type LaGaO$_3$ [4] have been investigated for use as solid oxygen ion conductors. Neither of these materials has reached the role of YSZ up to the present time. The reader interested in new ceramic oxygen conductors is referred to recent literature (see e.g. [5, 6], and references therein). A profound review on the science and technology of solid oxide fuel cells (SOFC) can be found in the article and book of Minh [7, 8].

In the case of a current-producing device, such as a SOFC, the electrodes are exposed to atmospheres of different oxygen partial pressures. The electromotive force (emf) which develops across the cell under equilibrium conditions, i.e. if no current is flowing through the device, is given by the Nernst equation

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

where $p_{O_2}^{\text{high}}$ and $p_{O_2}^{\text{low}}$ are the oxygen partial pressures at the cathode and at the anode, respectively, $F$ is the Faraday constant, $T$ is the absolute temperature, $R$ is the gas constant, and where an ideal oxygen ion conductor is considered. Oxygen is reduced at the cathode/electrolyte interface and incorporated into the solid electrolyte according to the stoichiometric equation

$$\frac{1}{2} O_2(g) + 2e^- + \square = O^{2-}$$

where $\square$ denotes oxygen vacancies in the solid electrolyte, $O^{2-}$ denotes occupied oxygen lattice sites in the solid electrolyte, and $e^-$ denotes electrons from the electrode. In equilibrium the rate of the forward and backward reaction in Eq. (1.2) are equally fast. At the anode, oxygen ions are oxidized to form either oxygen molecules (backward reaction of Eq. (1.2)) or a different reaction product in the presence of a fuel gas, e.g. H$_2$O in the presence of hydrogen or CO$_2$ in the presence of CO.

The cell potential generally decreases when the cell produces a current. The deviation of the cell potential from the Nernst potential depends on the current and the internal resistance of the cell. This behaviour is typical for any

* Note that in electrochemistry the term "potential" is usually used to ascribe a "potential difference".
current-producing electrochemical device, i.e. galvanic cells. The internal resistances are due to the ohmic resistance of the electrolyte and electronic conductors, as well as due to interfacial resistances (generally non-ohmic). The understanding of these interfacial resistances has been a driving force for the science of electrochemical kinetics.

By contrast, current-driven devices, such as oxygen pumps or oxygen separation membranes, are operated by imposing an external load. This can either be accomplished by applying a constant current (galvanostatic mode) or by applying a constant potential (potentiostatic mode) across the cell. In the first case, a potential difference develops across the cell which is proportional to the cell conductivity, whereas in the second case, the current through the cell is proportional to the cell resistance (inverse conductivity). Accordingly, low cell resistances are desired to keep internal losses low.

The third type of solid state electrochemical devices, oxygen sensors, are neither producing a current nor are they driven by a current. Their purpose is to probe an oxygen partial pressure of interest (cf. Eq. (1.1)). One might therefore believe that the internal resistance of an oxygen sensor is of minor concern. However, if the response of $E_{\text{emf}}$ upon a change in the oxygen partial pressure must be fast, low electrode resistances are required.

So far we have briefly summarized the operating principles of solid state electrochemical devices from a macroscopic point of view. We have seen that internal cell resistances influence the properties of these cells. In the following we consider the interfacial processes in more detail. The reader is also referred to standard textbooks about electrochemical kinetics and electrochemical methods (see Chapters 8 and 9 of [9] as a starting point, as well as Refs [10–14]).

### 1.1.2 The Origin of Potential Differences

If two materials $\alpha$ and $\beta$ are brought into contact, in our case a noble metal and YSZ (Fig. 1.1), the electrochemical potential of the electrons within these two phases will generally not be the same, i.e. $\Delta^\beta \mu_e = \mu_e^\alpha - \mu_e^\beta$. Note that YSZ is not a pure oxygen ion conductor but that a small electronic (or hole) conductivity is always present [15]. As a consequence, electrons from one phase will flow to the other phase, leaving a positively charged phase behind. Accordingly, a potential difference develops between these phases, the equilibrium potential difference, $E_{\text{eq}}$. It is a fundamental property of materi-
als interfaces that their equilibrium potential differences can not be measured (see e.g. [9], p. 845). However, we can measure the potential difference between an interface apart from equilibrium and an interface at equilibrium, \( \eta = E - E_{eq} \). The quantity \( \eta \) is termed overpotential and plays a fundamental role in electrochemistry. This situation is accomplished by measuring the potential difference between two identical electrode/electrolyte interfaces, where one interface is at rest and the other distorted by an electrical current.

As known from chemical kinetics, equilibrium does not mean that no flow of electrons occurs, but that the forward and backward currents are equal. This equilibrium current is designated equilibrium exchange-current density \( i_0 \). Obviously, \( i_0 \) reflects the kinetic properties of the considered interface and thus can be rather different from one type of interface to another. As in the case of \( E_{eq} \), the quantity \( i_0 \) can not be directly measured. However, there are different possibilities to determine \( i_0 \), and some methods (and its limitations) will be discussed.

We can obtain a net current density \( i \) if the forward and backward currents, \( i_f \) and \( i_b \), become different in magnitude

\[
i = i_f - i_b.
\]  

(1.3)

It is easy to see that this implies that the interfacial potential difference must depart from \( E_{eq} \). The difference between the actual interfacial potential and \( E_{eq} \) is the overpotential \( \eta = E - E_{eq} \), as introduced above.

Let us briefly consider a platinum oxygen electrode to understand the physical significance of overpotentials (Fig. 1.1). The half-cell reaction is written as

\[
O^2-(\beta) | O_2, Pt(\alpha)
\]  

(1.4)

where the notations correspond to those given in Fig. 1.1. The potential is determined by the following reaction

\[
\frac{1}{2}O_2 + 2e^- \Leftrightarrow O^2-,
\]  

(1.5)

because the electrons are the only charge-carriers that can exist in both phases. Note that the activity of electrons \( e^- \) in the electrolyte is related with \( O^2-(\beta) \) through the reaction \( O^2-(\beta) = O(\beta) + 2e^- (\beta) \). Similarly, the activity of oxygen at the interface between Pt and YSZ, \( a_O \), is determined by the oxygen partial pressure. Accordingly, the oxygen partial pressure \( p_{O_2} \) deter-
mines the electrochemical potential of the oxygen ions in the YSZ, \( \tilde{\mu}_{O^2} (\beta) \), and therefore the equilibrium potential. Note that in equilibrium all activities of the species involved in the overall reaction exhibit its equilibrium value.

As soon as a current flows through an external circuit, oxygen is removed from the cathode side (the direction of the current is so that oxygen ions migrate from the cathode side to the anode). On the anode side hydrogen is consumed and water is produced. Thus, the activities of oxygen \( a_O \) on both electrode sides change near the tpb (cf. Fig. 1.1). This change of \( a_O \) with respect to the equilibrium value, \( a_O (E_{eq}) \), is the origin of \( \eta \). If the supply of atomic oxygen on the cathode side was infinitely fast, the interface would remain at equilibrium even if a large net currents flows. However, there are two fundamental barriers for this not to occur:

(i) Molecular oxygen from the gas phase must pass a number of reaction steps until it arrives as atomic oxygen near the tpb. Because every elementary reaction proceeds with a finite rate, the concentrations of the species involved in the reaction

\[
\begin{align*}
\text{Pt} & \quad | \quad \text{Pore} \\
\quad & \quad | \quad O_2(g) \\
\alpha & \quad | \quad O(\text{ad}) \\
\text{YSZ} & \quad | \quad \beta \\
O^2-(\beta) = O(\beta) + 2e^- 
\end{align*}
\]

**Fig. 1.1** Schematics of a half cell with Pt and an ionic conductor in contact. \( \alpha \) denotes the Pt phase and \( \beta \) denotes the solid oxide ion conductor. Electrons may exist in the Pt and the ion conductor. Gaseous oxygen is contained within the gas phase. Note that \( O_2(g) \) may undergo heterogeneous chemical reactions with the Pt and YSZ surface. In addition, adsorbed atomic oxygen may be incorporated in the electrolyte. In equilibrium, all elementary reactions are equally fast. The triple phase boundary (tpb) is the line where YSZ, Pt, and the gas phase are in contact.
mechanism will deviate from its equilibrium concentrations. The term concentration overpotential, $\eta_c$, is used to ascribe for these phenomena. Furthermore, it is clear from the above that $\eta_c$ may be further split into contributions from the elementary reactions, e.g. gas phase diffusion, adsorption, dissociation, and surface diffusion.

(ii) Once the atomic oxygen arrived at the tpb it must be electro-nated and incorporated into the solid electrolyte. Certainly, an activation energy is necessary to incorporate an oxygen ion into the YSZ lattice. In addition, electrostatic forces act on the oxygen ion which must be overcome. The term charge-transfer (or activation) overpotential, $\eta_{ctr}$, is used to ascribe for these phenomena. It is readily seen that an applied potential difference influences the rate of oxygen transfer, because the oxygen species are negatively charged.

1.1.3 Oxygen Reduction

Fig. 1.2 shows a typical interface between a porous cathode and a solid electrolyte. The porosity of the cathode is in the order of 45% and the mean pore size is $\sim$1 $\mu$m. The cathode material should exhibit a good electronic conductivity at high temperatures and it must be stable under oxidizing conditions. Therefore, noble metals, such as Pt, Au, or Ag, and oxide materials, such as Sr-doped LaMnO$_3$ or LaCoO$_3$, have been considered (see e.g. [7, 16–19]). The overall reaction of the oxygen reduction at SOFC cathodes is given by Eq. (1.2). This reaction is made up of a couple of elementary reactions, some of them occur on the surface of the cathodes, others take place near the interface between the cathode and the electrolyte, i.e. at the triple-phase boundary (tpb) (cf. Fig. 1.2). Which processes in detail occur depends on the type of cathode material and electrolyte material considered. We start our considerations at the tpb and work along the cathode surface. Three main types of heterogeneous elementary reactions can be distinguished (Fig. 1.3):

(i) Charge transfer of electrons from the metal to adsorbed atomic oxygen species and subsequent incorporation of oxygen ions into YSZ near the tpb. This reaction is certainly con-
fined to the vicinity of the tpb [17, 20, 21]. An almost linear
dependence of the electrode resistance with the length of the
tpb is generally found [22, 23]. In contrast, there is no experi¬
mental evidence about the actual mechanism of electron
transfer. Two one-electron transfer steps to atomic oxygen are
more probable than a single two-electron transfer step. In
addition, there is also relatively little known about the actual
charge of any adsorbed oxygen species.
The atomic oxygen is supplied by either of two processes:
adsorption and subsequent dissociation of oxygen molecules
or surface diffusion of atomic oxygen. Note that the
charge-transfer process and the supply of atomic oxygen are
series processes. Therefore the slower of the processes will
control the electrode behaviour.

Fig. 1.2 Interface between cathode and solid electrolyte surface.—Secondary Electron
Micrograph (SEM) of porous La$_{0.85}$Sr$_{0.15}$MnO$_3$ cathode on YSZ polycrystal. The cathode
was applied by screen-printing and subsequent sintering at 1373 K (1100°C) in air. Oxy-
gen molecules may diffuse through the porous network towards the triple phase
boundary (tpb), i.e. the location where the cathode, the solid electrolyte, and the gas
phase are in contact.
(ii) Adsorption of oxygen on the cathode surface. This may either occur dissociatively (such as on Pt [24]), or associatively (such as on Au [25] or Sr-doped LaMnO₃ [16]). However, it is of fundamental difference whether the bonding of the oxygen molecule is broken upon adsorption or not and the overall behaviour of the electrode is expected to be different. Obviously, the adsorption/dissociation process occurs on the entire cathode surface. It can be taken as a general rule that, at least for Pt and Sr-doped LaMnO₃ cathodes, the supply rate of adsorption/dissociation is too low to account for the relatively high current-densities measured. A further process must therefore be responsible for the supply of atomic oxygen.

Fig. 1.3 Schematic diagram of predominant reaction steps at electrode/electrolyte interface.—(1) O₂(g) is supplied by gas phase diffusion through the pores of the cathode. (2) The oxygen molecules may adsorb on the entire cathode surface. (3) the adsorption process can be accompanied by an electron transfer and it can be followed by an immediate dissociation of the molecule. (4) Atomic oxygen species are considered to diffuse along the cathode surface. (5) The final charge transfer and incorporation step is believed to take place at the tpb, where O⁺ denotes occupied oxygen lattice sites in YSZ and □ denotes oxygen vacancies. Similar processes on the YSZ surface are not believed to be of comparable relevance.
(iii) Diffusion of atomic oxygen on the cathode surface. This process may generally deliver atomic oxygen towards the tpb with a high transport rate. Because the adsorption/dissociation reaction and surface diffusion occur in parallel on the cathode surface, the faster process will control the electrode behaviour*. At temperatures above \( \sim 500^\circ \text{C} \) this is usually the surface diffusion process (see e.g. [26–29]).

Obviously, further processes may be important, such as the diffusion of oxygen through the gas phase, or the interaction of oxygen with the YSZ surface. However, it is generally accepted that these types of interactions can be neglected under most operating conditions.

Although there is general agreement about the reaction pathway of oxygen at interfaces between electronically conducting cathodes and YSZ, there is still little known about the reaction mechanisms. Even less is known about the kinetic constants of the elementary reactions involved in the overall kinetics. There are two main reason for this. First, experimental electrochemical results are difficult to interpret and the mean variation of the results is generally large. Furthermore, rarely an operating condition of the cell is found where the mechanism is dominated by a single step. Second, the reaction mechanisms are relatively complicated and, therefore, they are difficult to treat mathematically in analytical form. However, it is not always necessary to run through all the mathematics, and a combination of both analytical analysis and numerical simulation may help to solve a particular problem.

1.2 Aim of the Thesis

The aim of this thesis is to provide a general method for the identification of heterogeneous reaction mechanisms at solid state oxygen electrodes. Identification on the one hand includes the discrimination of the relevant reaction steps, and on the other hand the quantitative estimation of (electro-) kinetic parameters.

*) It is worth to think about this statement and the corresponding statement in (i).
1 INTRODUCTION

The following sub-goals will be followed:

(i) development of a general framework for modelling, structural investigation, and implementation of reaction mechanisms;

(ii) exemplary validation of the proposed method with the Pt, O₂(g) | YSZ system;

(iii) discrimination of the relevant reaction steps of La₀.₈₅Sr₀.₁₅Mn₂O₃ cathodes on YSZ near equilibrium potential; proposal of reaction mechanism;

(iv) assessment of the MATLAB/SIMULINK programming environment for the numerical treatment of models of reaction mechanisms.

1.3 Structure of the Thesis

The main part of the thesis is enclosed by an introductory chapter and the outlook chapter. In the outlook we give a concise summary of our conclusions and we give some ideas for further studies in the field of high temperature electrode reaction kinetics. The main part consists of three chapters, each of them intended for publication in the present form or in a similar form. They are organized in the usual way, starting with an abstract, followed by an introduction, an experimental section, a results section, a discussion section, and the corresponding list of references. Nevertheless, redundancy and repetition are kept to a minimum.

Following, a brief summary of the contents of the three main chapters:

Chapter 2. The general framework for modelling and structural identification of reaction mechanisms is developed. The terms “structural identification” and “state-space modelling” are explained. The theoretical concepts are exemplified by a thorough treatment of a kinetic model describing the Pt, O₂(g) | YSZ system.
Chapter 3. The system explored in Chapter 2 is implemented in MATLAB and SIMULINK. Step-by-step instructions are given in the appendix. Simulations for the steady-state current–voltage behaviour and the small-signal frequency dependent behaviour are obtained. The results are discussed with respect to reported experimental and simulated data. A procedure for the identification of unknown parameters in the model is proposed.

Chapter 4. The interface between porous $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_y\text{O}_3$ cathodes and YSZ single crystal surfaces is investigated by a number of microscopic techniques and by electrochemical impedance spectroscopy. The formation of the foreign phase $\text{La}_2\text{Zr}_2\text{O}_7$ between YSZ and $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_y\text{O}_3$ is investigated on the sub-micron to nanometer scale. The influence of $\text{La}_2\text{Zr}_2\text{O}_7$ at the interface upon the electrochemical properties is clarified. The relevant reaction steps in the overall process of oxygen reduction are discriminated.

References


1 INTRODUCTION


1 INTRODUCTION
Part II

Theoretical Analysis of the Pt, $O_2(g)$ | YSZ System
Chapter 2

General Framework, Modelling, and Structural Investigation

Abstract This study aims to provide a general framework for modelling and structurally investigating complex heterogeneous electrode reaction mechanisms. The necessary theory is derived from classical systems and control theory. Relationships between abstract expressions and measurable electrochemical quantities are established. The procedure is illustrated by means of the oxygen reduction at the interface between platinum electrodes and yttria-stabilized zirconia solid electrolytes. Dissociative adsorption of oxygen on the platinum surface, surface diffusion of atomic oxygen, and a two-electron transfer step near the triple phase boundary are considered. The first model includes the adsorption/desorption step and the electron transfer step, whereas the second model also incorporates surface diffusion. The finite-difference approach is used for modelling mass transport. The surface concentrations of adsorbed atomic oxygen are considered as the time dependent state-variables within each ele-

*) Submitted to J. Electrochem. Soc.
ment. The mass-balance equations are obtained for the state-variables. The reaction mechanisms are formulated in state space form and structural investigation of the resulting set of equations is performed on the corresponding transfer functions. The concept of structural identifiability, which is well accepted in some domains of mathematical modelling, is demonstrated. Expressions describing the steady-state current-voltage behaviour and the frequency response behaviour are derived. It is shown that both models are globally structurally identifiable under the given assumptions. It is emphasized that modelling and testing model structures for identifiability must be accomplished prior to experimental work. In combination with Part II of this publication, a complete tool for the identification of heterogeneous reaction mechanisms is provided.

**Keywords.** Electrochemical kinetics, state space modelling; structural investigation; electrochemical impedance; oxygen reduction; solid oxide fuel cell.

### 2.1 Introduction

Metal electrodes play an important role in high temperature electrochemical devices such as Pt in oxygen sensors or oxygen pumps, or Ni in anodes of solid oxide fuel cells. The reduction of electrode resistances has been a major driving force for the investigation of these interfaces during the past 25 years. The design of electrodes with desired properties necessitates knowledge about the micro-kinetics of the overall electrode process. Although this field has been extensively examined and general agreement exists on the reaction pathway of oxygen at noble metal electrodes, there remains little knowledge and uncertainty about the relevant elementary processes and their kinetic parameters [2, 3]. But, it is this information about the micro-kinetics that makes a prediction of electrode properties under different operating conditions possible. The reason for this situation is probably due to the interdisciplinary of high temperature electrochemistry, where a number of problems must be solved in depth individually, in order to be able to identify a particular reaction mechanism. First, models taking into account the relevant electrode processes are mathematically difficult. Second, the characterization of high temperature electrodes with electrochemical methods needs experience
and special equipment. Finally, sample preparation and characterization requires knowledge about ceramic materials and its processing. However, modelling is often considered as the most difficult step and is, therefore, put at the end of an investigation. It is one aim of this study to make clear that modelling, structural investigation of the associated set of equations, and digital simulation should be accomplished prior to any experimental work.

A large number of authors have studied the behaviour of the Pt, O\textsubscript{2}(g) | solid electrolyte system. Generally, analyses include an experimental investigation combined with a certain extent of modelling. The methods of modelling have been strongly related to the experimental methods employed for studying this electrode system and can be grouped into (i) steady-state current-voltage investigations \([4-12]\) and (ii) electrochemical impedance spectroscopy (EIS) investigations \([11, 13-18]\). In addition, there are reports of transient-signal (small and large) analyses \([19-22]\). In all cases, the starting points of a model formulation are the mass and charge balances describing the dynamic properties of a proposed reaction mechanism. These equations are obtained from ordinary chemical kinetics considerations. Steady-state models relate a constant overpotential as the input quantity to a constant current as the output quantity (potentiostatic mode). The equations then may be independent of time and therefore facilitating the mathematical treatment of the equations. As soon as the reaction mechanism is assumed to consist of more than a single reaction step, it becomes difficult to find analytical solutions to the emerging system of equations. To circumvent these difficulties, simplifying assumptions are introduced. The most popular, introduced by Bockris and Reddy \([23]\), assumes quasi-equilibrium for all steps except the rate determining one. With this method, Butler-Volmer type relations are obtained relating the current \(I\) to the overpotential \(\eta\)

\[
I = i_0 \cdot A \cdot \left[ \exp \left( \frac{\alpha_a F}{RT} \cdot \eta \right) - \exp \left( \frac{\alpha_c F}{RT} \cdot \eta \right) \right]
\]  

(2.1)

where \(i_0\) is the exchange current density, \(\alpha_a\) and \(\alpha_c\) are the apparent charge transfer coefficients \([23]\), \(A\) is the active electrode area, and the remaining symbols have their usual meaning. If \(A\) is known, \(i_0, \alpha_c,\) and \(\alpha_a\) can be uniquely estimated from a Tafel plane plot (log \((I)\) versus \(\eta\)). It is further possible to include mass transport processes in the models, although only the most simple situations and boundary conditions can be treated \([7, 8, 9, 24, 25]\). In addition, the steady-state method offers the possibility of predicting the qualitative dependence of the exchange current density, \(i_0\), or the limiting
current, $I_1$, on external parameters, such as oxygen partial pressure, temperature, or overpotential [8, 10, 14, 15, 25]. However, steady-state methods do not provide any information about the dynamic behaviour of electrode systems, and rarely give unique access to the kinetic constants of the elementary processes involved in the overall electrode reaction. For this purpose, dynamic methods are indispensable. Furthermore, the use of steady-state methods is limited to investigation of relatively simple reaction mechanism, i.e. where one reaction step dominates the overall electrode behaviour. Unfortunately, heterogeneous reaction mechanisms at gas electrode of solids state ionics devices involve a number of elementary steps, neither of them dominating the overall characteristics. Although the current-voltage characteristics may exhibit an apparent Tafel behaviour, numerical estimates of the Tafel parameters ($\beta$, and $i_0$) may contain large errors. Interpreting these data might lead to wrong conclusions (see also [1, 12, 26, 27]).

The power of electrochemical impedance spectroscopy (EIS) lies in the fact that it is a small-signal perturbation method which reveals both the relaxation times and the relaxation amplitudes of a system over a wide range of frequencies [28]. EIS gives information about the static and dynamic properties of a system. However, the complexity in obtaining expressions describing the frequency response increases. This has led many researchers to interpret experimental data only in terms of circuits of electrical elements [cf. e.g. 16, 17, 29]. Recently, a method developed by Gabrielli and coworkers [30] for dealing with aqueous electrochemical systems, was applied by van Hassel et al. to describe the Au, $O_2(g)$ \rvert YSZ system with a second-order reaction mechanism [12, 31]. This approach has been increasingly used to model complicated reaction mechanisms [32, 33]. The method is based on a Tailor series expansion of the charge balance equation, from which the current modulation and finally an expression for the impedance is obtained [30]. Recently, Gabrielli and coworkers provided a general framework for dealing with electrochemical reaction kinetics of heterogeneous aqueous systems [34–36]. The method allows for the treatment of multi-step reaction mechanisms. But the multi-step treatment of the electrode reaction must be abandoned, as soon as mass transport processes become relevant (see e.g. [12] and references therein). Furthermore, the fact that both type of processes (mass transport and heterogeneous reactions) occur in parallel on the electrode surface, drastically increases the complexity to solve the equation system. It is, therefore, often assumed that only mass transport being relevant within a characteristic length (often over the Nernst diffusion layer length $\delta$, or a multiple of $\delta$; see
A quasi-equilibrium approach is employed for the treatment of the boundary concentrations at distances larger than $\delta$. However, these simplifications may give different solutions for the frequency-dependent behaviour, as well as for the limiting behaviour (see e.g. [37] p. 73, for the problem of surface diffusion of an atomic species which occurs in parallel with dissociative adsorption).

We propose to employ numerical simulation techniques in combination with an analytical treatment to overcome the mentioned problems. The general system behaviour is obtained from analytical expressions. Approximate solutions can be obtained from simulations of state space models. To the best of our knowledge, the notion "state space" has not been used in the electrochemical literature. We give a brief description in appendix 2-A.1.

In Part I of this paper we provide a general framework for modelling electrochemical reaction mechanisms in state space form, which makes structural investigation, simulation, and parameter estimation of heterogeneous reaction mechanism possible. First, some general theoretical background about state space modelling is given, and the link between the theoretical concepts and electrochemical quantities is accomplished. Second, we illustrate the procedure using a fairly well known reaction mechanism that describes the oxygen reduction at interfaces between Pt and Yttria-Stabilized Zirconia (YSZ). We particularly investigate the influence of surface diffusion on the steady-state and the small-signal electrode behaviour. In the first model (M1) we consider dissociative adsorption of oxygen molecules and reduction of adsorbed atomic oxygen within the active electrode area. In a second model (M2), surface diffusion of atomic oxygen on the Pt surface is included. In Part II we report the computer implementation of the equations, we give various simulation results, and we discuss the results with respect to some of the experimental results from literature [1]. We have found that it is extremely helpful for a better understanding of a particular reaction mechanism, if time and frequency dependent behaviour can be studied by simulation. It should be mentioned that the method of state space modelling is widely used in control and systems theory as well as in chemical engineering (see e.g. [38] or [39]). Nevertheless, we briefly present the necessary theoretical tools and we focus on the peculiarities of electrochemical modelling.
2.2 General Framework

2.2.1 The Process of Modelling

The form and detail of a mathematical model is basically determined by the purposes for which the micro-kinetic model is required. In kinetics three categories are generally distinguished for structure identification, parameter estimation, and prediction purposes. Although there is general agreement about the reaction pathways at high temperature SOFC electrodes [2, 3, 40], we still have very little a priori knowledge of the actual electrode mechanism. Our interest has to be primarily focused on the identification of the overall process structure; therefore we first need a qualitative understanding of the overall process and the corresponding elementary processes. Experimental results obtained from various electrochemical techniques provide such information. In addition, information is obtained from other physico-chemical investigations, in particular from surface science. From those, we develop a qualitative picture of the overall electrode reaction that considers the essential elementary processes as well as their interactions. Last, we translate the qualitative ideas into a quantitative description of the model. Here three different types of equations emerge: mass balance equations, physical relations, and equations describing the geometry. The final mathematical realization is obtained by casting the equations into a form suitable for further analysis and implementation in a computer.

Often, uncertainties remain in the structure of the model and its parameters. Then simulation is only possible by assuming values for the parameters and the identification of the model from input/output data must be made. Experiments must be designed in which the system is perturbed, thus providing input/output data. In some cases static analyses, such as current-voltage measurements, may be adequate. More often the dynamic response of the system is required that can be obtained from EIS measurements. The relation between the input/output data of the physical system are then compared with the corresponding input/output data from the model and the structure and/or parameters of the model are adjusted until a certain optimization criteria is fulfilled.

At all levels within the modelling process, model validation should be applied. Obviously the model should contain no contradictions and the simulation should be verified. In addition, simulations should correspond to available data and the model should be consistent with accepted theories.
2.2.2 General Considerations and Hypotheses

**Electrode microstructure.** For noble metal electrode general agreement exists on the dissociative adsorption of oxygen molecules and surface diffusion towards the triple-phase boundary (tpb) (cf. Fig. 2.1) [7, 8, 12]. The direct reaction of molecular oxygen from the gas phase with the electrolyte surface (at least with YSZ) or the solid state transport of oxygen ions in Pt or Au electrodes is generally ruled out [3, 41, 42]. For modelling purposes quantitative data for the tpb length $l_{tpb}$ are needed. These values can vary over more than two orders of magnitude (0.1–10 μm/μm²), depending on the preparation procedure as well as on the operating conditions of the electrode. Although estimates for $l_{tpb}$ and the mean pore diameter can be obtained from microscopic data, modelling is complicated by the morphology of the porous electrode and therefore simplified electrode geometries are employed (see Fig. 2.1).

![Fig. 2.1](image-url) Schematic view of the oxygen reduction process at interfaces between noble metals and solid oxide ion-conducting electrolytes.—The case of platinum is taken as an example. The oxygen molecules adsorb dissociatively (1) on the metal surface. Adsorbed atomic oxygen diffuses (2) towards the triple phase boundary (tpb). The electronation reaction (3) near the tpb may be considered as a single-step or a multi-step reaction. The concentrations of oxygen vacancies $V_O^-$, oxygen ions $O_O^x$, and electrons $e^-$, as well as the oxygen partial pressure $p_{O_2}$ facing the noble metal are considered to be constant over a wide range of operating conditions.
appendix 2-A.1). Fig. 2.2 shows a SEM of a Pt electrode on a YSZ single crystal surface. It is readily seen that a description of the microstructure can be accomplished with a few simple quantities (see appendix 2-A.2). However, an uncertainty remains and large errors may be introduced into a model description. Moreover, there is still little information about the question of how large the spatial extension of the tpb is. It is easy to demonstrate that there must be a spatial extension of the electrochemical active area around the tpb to accommodate the high current densities experimentally found (see e.g. [2, 40, 43]). We will give more account on this question below.

**Adsorption.** The adsorption of oxygen is the first process taking place on the noble metal surface. Depending on the noble metal and its surface orientation, oxygen adsorption is generally an activated process which proceeds through a sequence of precursor states (see e.g. for Pt(111): [44, 45]). The elementary steps of the oxygen adsorption and desorption are rather well dis-

---

**Fig. 2.2** Secondary Electron Micrograph (SEM) of porous Pt on a (001) YSZ single crystal surface.—The YSZ surface was dc-sputtered with Pt during 10 min, additionally painted with Pt paste, and subsequently fired in air at 1223 K (950°C) for 4 h. The SEM shows the boundary between the sputtered area and the painted area (lower right). Estimates of the length of the tpb and the pore sizes may be obtained from quantitative image analysis.
2.2 General Framework

criminated for Pt(111) surfaces [44–47]. However, care is necessary when employing these data in simulations because they were almost exclusively obtained from single crystal studies under low partial pressures and at relatively low temperatures. Real noble metal electrodes are polycrystalline and are operated at high temperatures under ambient pressures. Furthermore, it is well accepted that low amounts of impurities may drastically influence the adsorption behaviour of oxygen on metals [48]. We should also be aware of the fact that available experimental data show some scatter and some parameters, such as most frequency factors, are even not known. Nevertheless, information about the adsorption and desorption of oxygen on noble metal surfaces constitutes basically the only a priori knowledge we have for modelling the oxygen exchange reaction at noble metal/YSZ interfaces.

Diffusion. There are two different types of diffusion which may be relevant when modelling high temperature oxygen electrodes. First, binary gas phase diffusion of the oxygen through the pore network of the cathode. Second, surface diffusion of adsorbed oxygen intermediates. The first type of diffusion can generally be ruled out in these systems at high to moderate oxygen partial pressures \( p_{O_2} > 10^{-3} \) atm because of the very high diffusivities through the large pores even at high temperatures [14]. For modelling purposes, the partial pressure of oxygen is therefore assumed to be uniform over space and time. However, at oxygen partial pressures below \( 10^{-3} \) atm, gas phase diffusion may become apparent at porous SOFC cathodes at high temperatures [49].

In contrast, diffusion of adsorbed oxygen intermediates due to a gradient of the chemical potential along the metal surface can generally not be considered to be either infinitely fast or absent. It is important to recognize that these limiting cases result in completely different dynamic behaviour of the electrodes. In the first case, concentration gradients are absent and the system can be modelled using one single compartment where different species are distributed homogeneously. The concentration of adsorbed species would remain constant with time and would further be independent of the applied overpotential (i.e. the resulting current). Therefore, the overall electrode reaction would be entirely charge-transfer controlled. In the second case, diffusive transfer of adsorbed oxygen over the electrode surface is absent and therefore only the reaction zone must be considered [12]. The rate-controlling mechanisms may either be the adsorption process, the charge transfer process, or a combination of both. Both types of problems lead to systems of ordi-
nary first-order differential equations, the state equations, which are generally non-linear.

Electrochemical reactions. The rates of electron transfer processes are indirectly influenced by a change of the electrode stoichiometry or by a change of the electrochemical potential of the reacting species, whereas the rates are directly influenced by a change of the work function of the electrode material. It is usually assumed that the rate constants of the electron transfer reactions depend exponentially on the applied potential [23, 30, 50].

2.2.3 Modelling Reaction Mechanisms

State space model. We consider the noble metal, $O_2 \mid YSZ$ high temperature electrode as an open time-invariant system [38] which can be described in the form (see also appendix 2-A.1)

$$\dot{x}(t, p) = f[x(t, p), u(t), t; p]$$

subject to the initial conditions

$$\dot{x}(0, p) = \dot{x}_0(p).$$

In Eq. (2.2) the vector $x(t) \in \mathbb{R}^n$ represents the state variables of the model, usually the concentrations of adsorbed species; $u(t) \in \mathbb{R}^m$ is some external variable or input that can be varied during the experiment, e.g. the potential difference the temperature or the pressure; $p$ is the vector of the unknown parameters.

In addition to the differential Eqs. (2.2), the model consists of the observation functions

$$y(t, p) = g[x(t, p); p],$$

where $y(t) \in \mathbb{R}^p$ denotes the observed quantities and is referred to as the model output or response function (most often the current). We assume that the parameters are a priori independent and that $f$ and $g$ are (generally non-linear) real analytic functions for all possible sets of parameters.

It is generally difficult or impossible to obtain analytical solutions of this set of differential equations, that would describe the large-signal dynamic behaviour. Although non-linear studies are more general and yield more information, small signal methods are more often employed for they rely on a
2.2 General Framework

Linearisation of the model around some steady-state operating point that is associated with constant external variables. This procedure makes further mathematical treatment much easier.

**Linearized state space model.** Linearisation of Eqs. (2.2) and (2.4) yields

\[
\delta x(t, p) = A(p)\delta x(t, p) + B(p)\delta u(t) \tag{2.5}
\]

\[
\delta y(t, p) = C(p)\delta x(t, p) + D(p)\delta u(t) \tag{2.6}
\]

where \( A, B, C, \) and \( D, \) are the system matrices describing the system properties entirely. The matrices are given as

\[
A = \frac{\partial f}{\partial x} \mid _* \in R^{n \times n},
\]

\[
B = \frac{\partial f}{\partial u} \mid _* \in R^{n \times m},
\]

\[
C = \frac{\partial g}{\partial x} \mid _* \in R^{p \times n},
\]

\[
D = \frac{\partial g}{\partial u} \mid _* \in R^{p \times n},
\]

where the star (*) denotes a particular operating point. The intrinsic dynamic behaviour of a system is given by the eigenvalues of matrix \( A. \) For intrinsically linear systems, \( \delta x \) and \( \delta u \) are replaced by \( x \) and \( u. \) However, in electrochemistry we are dealing with intrinsically non-linear systems due to the exponential dependence of the electrochemical rate constants on the overpotential [23]. In the following we will write \( x \) and \( u \) instead of \( \delta x \) and \( \delta u, \) keeping in mind that we only mean small deviations around an operating point.

**Transfer function description.** An equivalent representation of the linearized state space description can be obtained by Laplacian transforms of Eqs. (2.5) and (2.6) with \( x_0 = 0: \)

\[
Y(s, p) = G(s, p) U(s) \tag{2.11}
\]

where
\[ G(s, p) = C(sI - A)^{-1}B + D. \]  

(2.12)

\( U(s) \) and \( Y(s, p) \) are the Laplace transforms of the input \( u \) and the output signal \( y \); \( G(s, p) \) is the transfer function and \( I \) is the appropriate identity matrix. This description is either called "transfer function description" or "Laplace transform description".

\( G(s, p) \) is generally a three-dimensional matrix in case of a multi-input multi-output (MIMO) system. In case of single-input multi-output systems (SIMO), \( G(s, p) \) reduces to a two-dimensional matrix, and in case of a single-input single-output (SISO) system, \( G(s, p) \) results in a fraction. In this case, \( G(s, p) \) can be easily obtained by means of Eq. (2.12) or by Laplace transforming, in the linear (or linearized) case, the input and output

\[
G(s, p) = \frac{Y(s, p)}{U(s)} = \frac{b_{k}s^{k} + b_{k-1}s^{k-1} + \ldots + b_{1}s + b_{0}}{s^{n} + a_{n}s^{n-1} + \ldots + a_{1}s + a_{0}} \quad (k \leq n)
\]  

(2.13)

where \( s \) is the Laplace variable and \( b_{i}(p) \) and \( a_{i}(p) \) are constant coefficients of the transfer function. Eqs. (2.12) and (2.13) are fundamental results from systems and control theory (see e.g. [38]). Gabrielli and Tribollet first used a similar description as presented above for the treatment of aqueous electrochemical systems [35].

The state space representation is the most reliable linear time-independent (LTI) model to use for computer analysis. Stable computer algorithms for eigenvalues, frequency response, time response, and other properties of the \((A, B, C, D)\) quadruple are known [51]. Transfer function models are numerically more difficult to handle, and tend to be inherently ill-conditioned. Nevertheless, this representation is often used for testing the identifiability of low-order LTI systems (see e.g. [52, 53] and references therein).

2.2.4 Identifying \( G(s) \) with Electrochemical Quantities

Faradaic admittance and impedance. Classical electrochemistry deals with electrochemical systems as SISO systems. Specifically, in potentiostatic mode \( I_{F}(t, p) = y(t, p) \) and \( \eta(t) = u(t) \), where \( I_{F} \) is the Faradaic current and the overpotential \( \eta = E - E_{eq} \) is defined as the deviation of the potential \( E \) from the equilibrium potential \( E_{eq} \). We would like to point out that this approach is by no means limited to the treatment of SISO systems, but that it
is applicable to the treatment of SIMO systems in much the same way (cf. [36, 54]). The linearized state space description is obtained as

\[
\dot{x}(t) = Ax(t) + B\eta(t)
\]  
(2.14)

\[
I_F(t) = Cx(t) + D\eta(t)
\]  
(2.15)

where \(D\) has become a scalar quantity. In accordance with Eq. (2.11) and (2.12) we further obtain

\[
I_F(s, p) = Y_F(s, p)\eta(s)
\]  
(2.16)

\[
Y_F(s) = C(sI-A)^{-1}B + D
\]  
(2.17)

which is obviously the Faradaic admittance transfer function. Accordingly, we find for the Faradaic impedance transfer function

\[
Z_F(s) = \frac{1}{Y_F(s)}.
\]  
(2.18)

**Frequency response.** Electrochemical impedance spectroscopy (EIS) imposes a harmonically oscillating overpotential with frequency \(\omega\) and amplitude \(\hat{\eta}\) at the input of the system [30]

\[
\eta(t) = \hat{\eta}\cos(\omega t).
\]  
(2.19)

It can be shown for stable LTI systems [38] that the output signal in time domain is given by

\[
y(t) = \hat{y}\cos(\omega t + \phi)
\]  
(2.20)

where

\[
\frac{\hat{y}}{x} = |Y_F(j\omega)| \quad \text{and} \quad \phi = \angle y - \angle \eta = \arg\{Y_F(j\omega)\}.
\]  
(2.21)

The complex function \(Y_F(j\omega)\) is known as the frequency response, \(|Y_F(j\omega)|\) as the magnitude and \(\arg\{Y_F(j\omega)\}\) as the phase of \(Y_F(j\omega)\), i.e. we have a relationship between the measurable frequency response and the model in a state space or transfer function description. Note that it would be more natural to use the admittance data than the impedance data because EIS is nor-
mally carried out by imposing an alternating voltage across the interface, thereby measuring the admittance rather than the impedance.

We must also keep in mind that the method relies on the linearisation of the equation system and on small-signal excitation. If the non-linear physical system is excited with large input signals, the output might contain frequencies other than the input frequency and the output magnitude might be dependent on the input magnitude. This can easily be checked with EIS by exciting a sample with increasing input amplitudes. The validity of linearity prevails as long as $|Y_F(j\omega)|$ and $\arg\{Y_F(j\omega)\}$ do not depend on the input amplitude. Additionally, the system matrices should not be used to calculate any large-signal response since the non-linear model equations must be employed for these purposes. Let us identify some useful quantities that can be generally obtained from the state-space description of an electrochemical system.

**Charge transfer resistance.** The charge transfer resistance $R_t$ is defined by

$$1/R_t = \left( \frac{\partial i_F}{\partial \eta} \right)_{x_i} \tag{2.22}$$

which becomes with Eq. (2.15)

$$1/R_t = D = \lim_{\omega \to \infty} Y_F(j\omega), \tag{2.23}$$

i.e. $R_t$ is a scalar quantity which can be found on the real axis at high frequencies of the complex plane plot of $Z_F(j\omega) = 1/Y_F(j\omega)$ (cf. Fig. 2.3).

Accordingly, $1/D$ is the most general description for $R_t$ taking the non-reversibility of the elementary reactions into account. Note that only in the case where the concept of the rate determining step applies, we obtain from Eq. (2.1)

$$R_t^{-1} = i_0 \cdot A \cdot \left[ \exp\left(\frac{\alpha_a F}{RT} \eta \right) - \exp\left(\frac{\alpha_c F}{RT} \eta \right) \right] \tag{2.24}$$

where $\bar{\eta}$ is the overpotential at the corresponding operating point. At zero overpotential we find the well known result

$$R_t^{-1} = i_0 \frac{F}{RT} (\alpha_a + \alpha_c) = i_0 \left( \frac{F}{RT} \right) \bar{\eta} = D \tag{2.25}$$
2.2 General Framework

Fig. 2.3 General Faradaic frequency response $Z_F(j\omega)$ of first-order electrochemical systems.—(a) Complex plane plot of $Z_F(j\omega)$ data and (b) Bode plot of the same data. (—) denotes $|Z_F|$ and (- -) denotes the phase $\phi$. The numbers in the complex plane plot denote the frequencies in Hz. The data were obtained from a simulation of model M2 (fully described in Part II of the present paper [1]). $R_p$ denotes the polarization resistance, $R_t$ is the transfer resistance, and $R_g = R_c = R_p - R_t$ denotes the concentration resistance. $Z_g(j\omega)$ denotes the frequency dependent part of the Faradaic impedance $Z_F(j\omega)$. 

33
where \( n \) is the number of electrons which were transferred in the rate-determining step, and \( v \) is the stoichiometric number (see [23], p. 1006). Eq. (2.25) is of importance as it gives a relation between the exchange-current density \( i_0 \), which can be obtained from steady-state current–voltage measurements, and \( R_t \), which can be obtained from EIS measurements (see below).

**Polarization resistance.** The *dc* gain of a system is the ratio of the output to its (constant) input after all transients have decayed. To find the *dc* gain of an asymptotically stable system we put \( s = j\omega = 0 \) in Eq. (2.17) and obtain for the polarization resistance \( R_p \)

\[
\frac{1}{R_p} = Y_F(0) = D - CA^{-1}B.
\]  

(2.26)

Obviously, \( R_p \) depends also on \( \bar{n} \) at the operating point as well as on the experimental parameters \( (T, p_{O_2}) \). \( R_p \) is also a scalar quantity which can be found on the real axis at low frequencies of a complex plane plot of \( Z_F(j\omega) \) (see Fig. 2.3).

**Concentration admittance.** For reasons which will become clear later, we write the Faradaic impedance \( Z_F(s) \) as the sum of the charge transfer resistance \( R_t \) and the concentration impedance \( Z_e(s) \), an impedance due to the time dependence of the concentrations of the adsorbed species

\[
Z_F(s) = R_t + Z_e(j\omega).
\]  

(2.27)

From Eq. (2.17) we obtain

\[
Y_F(s) = D \left[ 1 + \frac{C(sI - A)^{-1}B}{D} \right]
\]  

(2.28)

and from \( Z_F(s) = Y_F^{-1}(s) \) we further have

\[
Z_F(s) = \frac{1}{D} \left[ \frac{D}{D + C(sI - A)^{-1}B} \right] = \frac{1}{D} \left[ \frac{D - (D + C(sI - A)^{-1}B) + 1}{D + C(sI - A)^{-1}B} \right].
\]  

(2.29)

From Eq. (2.29) we obtain

\[
Z_F(s) = \frac{1}{D} \left[ 1 - \frac{C(sI - A)^{-1}B}{D + C(sI - A)^{-1}B} \right]
\]  

(2.30)
2.2 General Framework

which is equivalent to

\[ Z_F(s) = R_t - R_t \cdot \frac{Y_F(s) - D}{Y_F(s)}. \] (2.31)

By comparing Eqs. (2.27) and (2.31) we finally obtain

\[ Z_\theta(s) = -R_t \cdot \frac{Y_F(s) - D}{Y_F(s)}. \] (2.32)

and by definition (cf. Fig. 2.3)

\[ Z_\theta(0) = R_\theta = -R_t \cdot \frac{1/R_p - 1/R_t}{1/R_p} = R_p - R_t. \] (2.33)

From Eqs. (2.23) and (2.26) we see that \( Z_F(j\omega) \) is limited by \( R_t \) at high frequencies and by \( R_p \) at low frequencies. The frequency response \( Z_F(j\omega) \) in between these limits is described by the concentration impedance \( Z_q(j\omega) \) (Eq. (2.32)). Note that the concentration resistance \( R_\theta \) not simply depends linearly on the charge transfer resistance \( R_t \), but that a rather complicated relationship exists. Thus, it is expected that the dependence of \( R_\theta \) (or of \( R_p \) if \( R_p >> R_t \)) on temperature and on oxygen partial pressure shows a rather complicated behaviour.

2.2.5 Working with Frequency Responses

**Bode plots.** If linear time-independent systems are put in series, the frequency response of the new system is simply the product of the individual frequency responses, the magnitude is the product of the individual magnitudes, and the phase is the sum of the individual phases. It is therefore convenient to draw the magnitude in a logarithmic plot and the phase in a linear plot. Together, these two curves comprise a Bode plane plot of the system. There are some important quantities that can be directly obtained from the Bode plot (or from the Nyquist plot) of a system. It is important to be able to hand-plot frequency responses for several reasons: simple problems can be dealt with directly and computer results for more complicated cases can be checked. Hand-plotting is especially useful in interpreting frequency response data that have been obtained experimentally.
We will illustrate this procedure later. The interested reader is referred to a common textbook about control theory (see e.g. [38, 39]).

Admittance vs. Faradaic admittance. It is emphasized that $Z_F$ describes the intrinsic electrode dynamics. In contrast, EIS measurements yield the total impedance $Z$, i.e. $Z_F$ obscured by a double layer capacitance $C_{dl}$. A rigorous treatment of the electrode impedance must include coupling between Faradaic processes and the charging of the double layer. If, and only if, the origin of $C_{dl}$ can be attributed to a space charge at the interface between the noble metal grains and the YSZ [12, 50, 55], can it be assumed that $C_{dl}$ is associated in parallel with $Z_F$ and therefore:

$$Z(j\omega) = \frac{Z_F(j\omega)}{1 + j\omega C_{dl} Z_F(j\omega)}.$$  \hspace{1cm} (2.34)

In addition, there is always a finite un-compensated electrolyte resistance $R_e$ present. Therefore, the total electrode system can be represented by the "equivalent circuit" shown in Fig. 2.4.

![Fig. 2.4 "Equivalent circuit" of an noble metal/electrolyte system.—The Faradaic impedance $Z_F(s)$ is obscured by an electrical double layer capacitance $C_{dl}$ (transfer function: $C_{dl}(s) = 1/(sC_{dl})$) in parallel and an electrolyte resistance $R_e$ in series. $Z_F(j\omega)$ comprises a series combination of the transfer resistance $R_t$ and the concentration impedance $Z_0(j\omega)$. Note that the (measurable) frequency response $Z(j\omega)$ depends on $Z_F(j\omega)$, $C_{dl}$, and $R_e$ and that the intrinsic dynamic behaviour of the electrochemical interface is exclusively described by its Faradaic frequency response $Z_F(j\omega)$ (not directly measurable).]
The various possible frequency responses depend on the actual electrochemical reaction mechanism as well as upon the values of $C_{dl}$ and $R_e$. We will expand this point in part II. However, we would like to point out here that $Z_F(i\omega)$ is entirely dependent on our kinetic model and that $R_e$ and $C_{dl}$ are (measurable!) external quantities. It is well known that $R_e$ can be determined experimentally with EIS [56] or with the current interruption technique [57]. But it is less known that $C_{dl}$ can be almost equally well determined from EIS data, if the general "equivalent circuit" of Fig. 2.4 applies, even without making any assumptions on the Faradaic impedance [58]. There are examples in literature where values for $C_{dl}$ are reported from equivalent circuit analyses ([17, 18, 59] and references therein). Always, an a priori choice of an equivalent circuit was made. Obviously, the values determined for $C_{dl}$ from fitting impedance data to equivalent circuits largely depend on the choice of the circuit. We believe that the interpretation of these data is doubtful.

2.2.6 Identifiability of Linear Reaction Models

Testing model structures for identifiability and distinguishability has become a well accepted practice in identification of metabolic systems [60, 61]. The notion of identifiability is most easily understood by considering the problems often encountered in equivalent circuit fitting. There, identical simulation results may be either obtained with different sets of parameters for the same equivalent circuit (problem of structural global identifiability), or the same simulation results may be obtained with different model structures (with the same number and type of electrical elements) but the same set of parameters (problem of structural model distinguishability). Note that structural global identifiability is a property of the model itself that is assessed. It has nothing to do with the accuracy of measurements and data. There are currently many methods available for analysing the identifiability of LTI systems. In contrast, efficient methods to analyse the identifiability of non-linear systems have only recently been introduced [62, 63]. The interested reader is referred to the cited literature and references therein.

It is only recently that the concepts of model identifiability and model distinguishability have been introduced in the field of aqueous electrochemistry [64, 65]. It is not our intention to present the theory, for the literature on it is substantial, although mostly concerned with pharmaceutical kinetics [61] or mechanical systems [62]. A reaction mechanism is said to be globally structurally identifiable if, and only if, a unique set of parameters $p$ can be deter-
mined for a given input. The mechanism is said to be locally identifiable if a finite (and hopefully small) number of parameter sets is estimated from experimental data (very often encountered in equivalent circuit fitting). Non-identifiable mechanisms give identical outputs for a given input for any set of parameters. We will encounter all three situation while investigating our proposed models of the Pt, O₂(g) | YSZ system.

2.3 Reaction Models of the Pt, O₂(g) | YSZ System

2.3.1 Introduction

The problem associated with the use of numerical methods may, in our opinion, best be elucidated using simple examples. This section illustrates this idea by considering a simple reaction mechanism of the Pt, O₂(g) | YSZ system, which is by far the most thoroughly studied electrode system in high temperature electrochemistry (see e.g. [5, 11, 13, 66]). Dissociative adsorption of oxygen on Pt, surface diffusion of atomic oxygen, and electrochemical reduction of adsorbed oxygen in a two-electron transfer step near the tpb line is considered [25, 66].

In our first model (M1), mass and charge balances are formulated and the complete model structure is developed. For illustration purposes, surface diffusion is first neglected, i.e. we assume that any diffusive transfer of adsorbed atomic oxygen is slow (which is the case for temperatures below ~723 K (~450°C) [11]) and therefore the oxygen is only delivered by the direct adsorption process near the tpb. The model M1 is tested for structural identifiability in the steady-state as well as for electrochemical impedance spectroscopy. In our second model (M2) we include surface diffusion. The finite-difference approach is employed for the treatment of surface diffusion. Considering one-dimensional, first-order coupled differential equations, the finite-difference method is the most straightforward method of numerical solution. Computer implementation and simulation results of both models are illustrated in part II [1]. A more realistic model of the Pt, O₂ | YSZ system (M3), accounting for the step-wise adsorption/desorption dynamics of O₂ on Pt surfaces, will be the subject of a forthcoming publication [67].
2.3 Reaction Models of the Pt, O₂(g) | YSZ System

2.3.2 Basic Equations and Assumptions

**Model equations.** We consider the electrochemical exchange of oxygen at the Pt/YSZ interface which is described by the overall reaction

\[
\frac{1}{2}O_2 + V^-_O + 2e^- = O^x_O
\]  

(2.35)

where, in Kröger-Vink notation, \( V^-_O \) represents the oxygen vacancies, \( O^x_O \) represents occupied oxygen lattice sites in the electrolyte, and \( e^- \) represents the electrons within the Pt.

The overall reaction is considered to consist of several elementary reactions [5, 8]. Oxygen adsorbs dissociatively on the Pt surface, diffuses linearly in the direction perpendicular to the electrode surface, and is electronated and incorporated near the thp in the active area of width \( w \) (cf. Fig. 2.1 and Fig. 2.5):

\[
O_2(g) + 2s \leftrightarrow 2O_{ad}
\]

\( k_{ad} \)

(2.36)

\[
\frac{\partial c}{\partial t} = \frac{\partial}{\partial z}D(c)(\frac{\partial c}{\partial z})
\]

(2.37)

\[
O_{ad} + V^-_O + 2e^- \leftrightarrow O^x_O + s
\]

\( k_1 \)

\( k_1^- \)

(2.38)

where \( k_{ad} \) and \( k_{des} \) are the rates for adsorption and desorption of oxygen on polycrystalline Pt; \( c \) is the surface concentration of \( O_{ad} \); \( D(c) \) is the chemical diffusion coefficient of \( O_{ad} \) on the Pt surface; \( k_1 \) and \( k_1^- \) are the electrochemical rate constants; and \([s]\) is the concentration of vacant surface sites.

**Assumptions.** We will base M1 on the following assumptions:

(i) The adsorption of oxygen occurs dissociatively and obeys a Langmuir isotherm;

(ii) The maximum number of surface sites per unit area which can be occupied by \( O_{ad} \) is characterized by \( N_0 \);
(iii) The rate of adsorption \( k_{\text{ad}} \) and desorption \( k_{\text{des}} \) are independent of surface coverage and are known from the literature;

(iv) The concentrations of \( V_O^- \) and \( O_O^x \) in the YSZ surface are constant;

(v) The electrochemical rate constants are exponentially dependent on the potential difference \( E \)

\[
\begin{align*}
  k_1 &= k_{1c}(T) \cdot \exp[-n\beta_c F E/(RT)] \\
  k_{-1} &= k_{-1c}(T) \cdot \exp[n\beta_a F E/(RT)]
\end{align*}
\]

(2.39)

where \( k_{1c}(T) \) and \( k_{-1c}(T) \) are potential independent chemical rate constants; \( \beta_c \) and \( \beta_a \) are the cathodic and anodic transfer coefficients of the electrochemical reaction; \( n \) is the number of electrons transferred in the reaction step (in our case \( n = 2 \)); \( E = E_{eq} + \eta \) where \( E_{eq} \) is the equilibrium potential and \( \eta \) is the overpotential.

For M2 we make the additional assumption:

(i) Surface diffusion depends only on concentration gradients. No interaction of adsorbed species is considered;

(ii) The surface diffusion coefficient \( D \) is known from literature data;

(iii) \( D \) is independent of the local surface concentration.

**Mass and charge balances.** For M1 mass and charge balance give

\[
\frac{d}{dt}[O_{\text{ad}}] = 2k_{\text{ad}}pO_2[s]^2 - 2k_{\text{des}}[O_{\text{ad}}]^2
\]

\[
-k_1[O_{\text{ad}}][V_O^-] + k_{-1}[s][O_O^x]
\]

\[
I_F = 2FA_a[k_1[s][O_O^x] - k_1[O_{\text{ad}}][V_O^-]]
\]

(2.41)

where \( A_a = tpb \times w \) is the area of the active region extending from the tpb line under the electrolyte grains, and/or along the electrolyte surface. For the moment we make no speculations as to the physical basis of this extension. From the modelling point of view, the active region is simply regarded as a
Fig. 2.5 Schematic view of the active electrode area near the tpb.—Regardless of the physical extension of the active area around the tpb, \( w \), from a conceptual point of view only the electron transfer rate in the active area \( A_{ar} \) and not the location of the reaction, determines the electrochemical properties of the interface. Accordingly, we can \( A_{ar} \) consider to extend from the tpb towards the Pt electrode.

strip extending from the tpb line along the noble metal surface towards the electrode (cf. Fig. 2.5). We assume for the moment that \( A_{ar} \) is a priori known. For M2 a further term must be added to Eq. (2.40) accounting for the surface diffusion.

**Complete model structure.** The mathematical model should first be normalized or scaled to improve its numerical conditioning. This is accomplished by replacing the surface concentration by its fraction of surface coverage. By expressing \([O_{ad}] = N_{0} \cdot \theta \) and \([s] = N_{0} \cdot (1 - \theta)\) Eqs. (2.40) and (2.41) are rewritten

\[
\frac{d\theta}{dt} = 2k_{ad}p_{O_{2}}N_{0} \cdot (1 - \theta)^2 - 2k_{des}N_{0} \cdot \theta^2 - k_{1} \cdot [V_{o}] \cdot \theta + k_{1} \cdot [O_{O}^{x}] \cdot (1 - \theta)
\]  

(2.42)
which is simply a representation of Eqs. (2.2) and (2.4) with the state vector $x(t, p)$, the input scalar $u(t)$, and the output scalar $y(t)$:

$$\theta(t, p) = x(t, p), \eta(t) = u(t), \text{ and } I_F(t, p) = y(t, p).$$  \hspace{1cm} (2.44)

The vector with the unknown parameters is given by

$$p = [k_{lc}(T), \beta_c, k_{ic}(T), \beta_a].$$  \hspace{1cm} (2.45)

Eqs. (2.42) and (2.43) generally describe the dynamic behaviour of the reaction mechanism $M_1$.

To complete $M_1$, we have to consider all additional and independent algebraic equality or inequality constraints relating $\theta, \eta,$ and $p$ or any combination of these, known a priori. The relationships are generally written as

$$h[\theta(t, p), \eta(t), p] \leq 0.$$  \hspace{1cm} (2.46)

The equation system of Eqs. (2.42) to (2.46) is defined as the constrained structure, which completely describes our model structure $M_1$. In our particular case we have the two following equality constraints (cf. e.g. [23]).

$$\beta_a + \beta_c - 1 = 0 \text{ and } I_F(E_{eq}) = 0.$$  \hspace{1cm} (2.47)

The number of independent parameters is therefore reduced by the number of equality constraints. Accordingly, the number of parameters to be determined in Eq. (2.45) is reduced to one rate constant and one transfer coefficient, e.g. $p = [k_{lc}(T), \beta_c]$. In the following we will simply write $\beta$ instead of $\beta_c$.

### 2.3.3 Electrode Overpotential

Let us consider a cell of the type shown in Fig. 2.6. Electrochemical measurements are performed in a three-terminal configuration where the working electrode (WE), reference electrode (RE), and counter electrode (CE) are exposed to the same atmosphere. We should be aware of how a polarisation device interacts with the electrochemical cell. In potentiostatic mode a reference potential difference between the WE and CE is set by the experimenter.
Negative feedback of the actual potential difference ensures control of the reference potential. A polarisation is imposed on the CE side. As a consequence, the electrode reaction on the CE departs from its equilibrium point and the electrochemical potential of oxygen ions, $\mu_{O^2-}(\beta"')$, in the surface of the solid electrolyte is altered. This causes a current through the electrolyte and, therefore, a net current flows through the WE. If the electrode reaction is not infinitely fast, $\mu_{O^2-}(\beta')$ deviates from its equilibrium value, whereas $\mu_{O^2-}(\beta)$ remains at its equilibrium value. $\mu_{O^2-}(\beta')$ is somehow related to the oxygen partial pressure and the current. The question which emerges is the following: what is the physical significance of the potential difference between WE and CE that can be measured?

We therefore consider the following half-cell reaction

$$O^{2-}(\beta)|O_2, \text{Pt}(\alpha)$$

(2.48)

where $\beta$ denotes the solid electrolyte and where the electrode material Pt (phase $\alpha$) seems not to be involved in the electrochemical reaction. The potential is determined by the following reaction

$$\frac{1}{2}O_2 + 2e^- \leftrightarrow O^{2-},$$

(2.49)

i.e. the electrons are the only charge carrying species which are common in phase $\alpha$ and $\beta$. For the equilibrium of reaction Eq. (2.49) we have

![Fig. 2.6 Schematics of a three-electrode cell with identical porous Pt electrodes.—The notations used in subsection 2.3.3 are indicated.](image)
With the definition of the electrochemical potential of species \( i \) in phase \( \gamma \), 
\[
\mu_i(\gamma) = \mu_i^{\circ}(\gamma) + z_i F \phi(\gamma),
\]
and the definition of the chemical potential, 
\[
\mu_i(\gamma) = \mu_i(\gamma) + RT \ln a_i(\gamma)
\]
where \( a_i(\gamma) \) is the activity and \( \mu_i^{\circ}(\gamma) \) is the standard chemical potential of species \( i \), we can calculate the equilibrium potential difference (Galvani potential) between the metal and the solid electrolyte at the reference electrode as follows

\[
\Delta \phi^{\text{eq}} = \varphi(\alpha) - \varphi(\beta) = \frac{\mu^{\circ}(\alpha) - \mu^{\circ}(\beta)}{F} - \frac{RT}{F} \ln a_e(\beta).
\]

where we used \( a_e(\alpha) = 1 \). The activity of the electrons in the solid electrolyte, \( a_e(\beta) \), can be expressed in terms of the equilibrium in which they are involved

\[
K(O|O^{2-}) = \frac{a_{O^{2-}}(\beta)}{a_{O}(\beta) \cdot [a_e(\beta)]^2}.
\]

At the reference electrode, the gas phase (g) is in equilibrium with the solid electrolyte surface (\( \beta \)), thus \( \Delta \mu_O = \mu_O(\g) - \mu_O(\beta) = 0 \) and accordingly \( a_O(\beta) = a_O(\g) = \sqrt{p_O}/\sqrt{p^\circ} \) where we conveniently set \( p^\circ = 1 \) atm. Using this result and solving Eq. (2.52) for \( a_e(\beta) \) we obtain for the equilibrium potential difference

\[
\Delta \phi^{\text{eq}} = \Delta \varphi^\circ + \frac{RT}{2F} \ln(\sqrt{p_O^2}) - \frac{RT}{2F} \ln[a_{O^{2-}}(\beta)]
\]

where we used \( \Delta \varphi^\circ = \Delta \mu^\circ + \frac{RT}{F} \ln[K(O_2|O^{2-})] \) for the concentration independent terms.

The overpotential \( \eta \) is defined as the deviation of the interfacial potential difference \( \Delta \varphi \) from the equilibrium potential difference \( \Delta \phi^{\text{eq}} \), 
\[
\eta = \Delta \varphi - \Delta \phi^{\text{eq}}.
\]

If a current flows through the interface between the electrode (\( \alpha' \)) and the solid electrolyte (\( \beta' \)), the equilibrium situation no longer prevails for polarizable electrodes. Analogous to the derivation of \( \Delta \phi^{\text{eq}} \) we obtain for the non-equilibrium potential difference

\[
\Delta \varphi = \Delta \varphi^\circ + \frac{RT}{2F} \ln[a_O(\beta')] - \frac{RT}{2F} \ln[a_{O^{2-}}(\beta')].
\]
2.3 Reaction Models of the Pt, $O_2(g)$ / YSZ System

With the definition of the electrochemical potential for $O^{2-}$ we obtain

$$\frac{RT}{2F} \ln[a_{O^{2-}(\beta')}] = \frac{1}{2F} [\mu_{O^{2-}}(\beta') - \mu_{O^{2-}}(\beta') - \mu_{O^{2-}}(\beta)] + \varphi(\beta') \quad (2.55)$$

and a similar result for $a_{O^{2-}(\beta)}$ by replacing $\beta'$ with $\beta$. With $\mu_{O^{2-}}(\beta) = \mu_{O^{2-}}(\beta')$ we obtain for the overpotential

$$\eta = \Delta \varphi - \Delta \varphi^{eq} = \frac{1}{2} [\mu_{O^{2-}}(\beta) - \mu_{O^{2-}}(\beta')] + [\varphi(\beta) - \varphi(\beta')] \quad (2.56)$$

$$+ \frac{RT}{2F} \ln \left[ \frac{a_{O}(\beta')}{\sqrt{p_{O_2}}} \right]$$

Eq. (2.56) shows that the overpotential is attributed to the ohmic drop due to the ionic current in the solid electrolyte (first term: ohmic potential drop), to the (ohmic) potential drop due to charge transfer (second term: charge-transfer overpotential), and to the deviation of $a_{O}(\beta')$ from the equilibrium value at the electrode/solid electrolyte interface (third term: concentration overpotential). Accordingly, Eq. (2.56) can be used to validate simulation results.

2.3.4 Structural Properties of the Models

Model Identification. Identification is concerned both with determining the structure of a physical process and with estimating the unknown parameters. The structure of a mathematical model is reflected in its set of (coupled) differential equations. The question of identification addresses the question of whether it is possible to obtain a unique solution for the unknown parameters of interest on the basis of data collected in a particular experiment. This question is often referred to as that of theoretical or structural identifiability. If the parameters of M1 and M2 can be theoretically identified uniquely, the parameters estimation problem is theoretically well posed and the actual experiment can be carried out to provide real data for parameter estimation. This assumes, however, that the experimental test data used for identification are noise-free and that the structure of the proposed model is not in error (question of practical identifiability). Indeed, the second assumption is often not fulfilled and therefore postulating a false of (partly) inappropriate model structure constitutes an important source of error.
**Equilibrium potential** $E_{eq}$. We first show that the unknown parameters $p$ of the model structures $M_1$ and $M_2$ can be uniquely obtained from current-overpotential measurements. We first rigorously develop the expression describing the steady-state $I_F(\eta)$ behaviour. Starting from this result we prove in a second step the global structural identifiability of the mechanisms in the steady-state.

Under steady state the condition $d\vartheta/dt = 0$ must apply. By solving Eq. (2.43) for $I_F(E_{eq}) = 0$, we obtain for the equilibrium potential

$$E_{eq}(T, p_{O_2}) = \frac{1}{2f} \cdot \ln \left[ \frac{k_{1c}(T)}{k_{1c}(T)} \cdot \frac{[V_o]}{[O_O^x]} \cdot \frac{\theta_0(T, p_{O_2})}{1 - \theta_0(T, p_{O_2})} \right]$$

(2.57)

where $f = F/(RT)$. Note that in this way $E_{eq}(T, p_{O_2})$ depends on the temperature as well as on the oxygen partial pressure. $\theta_0(T, p_{O_2})$ denotes the equilibrium surface concentration of $O_{ad}$ which is obtained from the mass action relation (Eq. (2.36))

$$\frac{\theta_0(T, p_{O_2})}{1 - \theta_0(T, p_{O_2})} = K(T) \cdot \sqrt[p_{O_2}]{Q_0(T, p_{O_2})}$$

(2.58)

with the equilibrium constant $K(T) = k_{ad}(T)/k_{des}(T)$. By putting Eq. (2.58) in Eq. (2.57) we obtain

$$E_{eq}(T, p_{O_2}) = \frac{1}{2f} \cdot \ln \left[ \frac{k_{1c}(T)}{k_{1c}(T)} \cdot \frac{[V_o]}{[O_O^x]} \cdot K(T) \right] + \frac{1}{4f} \cdot \ln(p_{O_2})$$

(2.59)

and, accordingly, $E_{eq}(T, p_{O_2}) = E_{eq}(T) + E_{eq}(p_{O_2})$.

Eq. (2.59) is simply an expression of the Nernst form. We arbitrarily set the equilibrium potential which evolves at $T = T^o$ and $p_{O_2} = p_{O_2}^o$ equal to zero. In this way the electrode potential, and therefore also the electrochemical rate constants, are defined relative to this reference state.

For temperatures not too far from $T^o$ we make the following formulation for the temperature dependence of the chemical rate constants:

$$k_{1c}(T) = k_{1c} \cdot \exp \left[ -E_{a}^1/(RT) \right]$$

$$k_{1c}(T) = k_{1c} \cdot \exp \left[ -E_{a}^1/(RT) \right]$$

(2.60)
where the pre-exponential factors, $k_{1c}$ and $k_{1c}^-$, and the activation energies, $E_a^1$ and $E_a^1$, are assumed to be temperature independent. Accordingly, we find in the reference state

$$E_{eq} \equiv 0 = \frac{1}{2f} \ln \left( \frac{k_{1c}^0 \cdot [V_0] \cdot K(T^0)}{k_{1c}^0 \cdot [O_0]^x} \right) + \frac{1}{2f} \ln(\sqrt{p_{O_2}^o}) \quad (2.61)$$

where, by definition, $k_{1c}^o = k_{1c}(T^0)$ and $k_{1c}^- = k_{1c}^-(T^0)$.

With $p_{O_2}^o = 1$ atm we find $k_{1c}^o$ at $T^0$ from Eq. (2.61) as

$$k_{1c}^o = k_{1c}^o \cdot \frac{[V_0]}{[O_0]^x} \cdot K(T^0) \quad (2.62)$$

The values for the forward and backward electrochemical rate constants at equilibrium, $k_1(T, p_{O_2})$ and $k_1^-(T, p_{O_2})$, are finally obtained from Eq. (2.39) by use of Eqs. (2.59) to (2.62).

In principle, we are free to choose the reference state. For obvious reasons, it is advantageous to take it at $p_{O_2}^o = 1$ atm. The reference temperature can be taken anywhere, but once this temperature is fixed, the chemical rate constants must be described by Eq. (2.60) and (2.62). For simulation purposes we need to assign the activation energies $E_a^1$ and $E_a$ some (reasonable) values. In principal, it is possible to determine these values experimentally. We will return to this point below. Finally, it is important to recognize that by defining the equilibrium potential in this way, a change in the oxygen partial pressure influences both the forward and backward rate constant through the change in $E_{eq}^0$.

**Steady-state $I_F(\eta)$ behaviour.** In the following we derive the expressions for the steady-state $I_F(\eta)$ behaviour and the exchange current density as a function of $p_{O_2}$ at $T^0$. By substituting Eqs. (2.39), (2.60) and (2.62) in the expression for the Faradaic current (Eq. (2.43)) we obtain

$$I_F(\eta, T^0, p_{O_2}) = 2N_0F a_1 k_{1c}^o [V_0^-] \cdot K(T^0) \cdot (1 - \hat{\theta}) \cdot e^{2(1 - \beta f(E_{eq} + \eta))} - \hat{\theta} \cdot e^{-2\beta f(E_{eq} + \eta)}$$

where $\hat{\theta} = \theta(\eta, p_{O_2}, T^0)$, i.e. the steady-state surface coverage of $O_{ad}$ at the corresponding operating point. Eq. (2.63) is the general description of the
steady state current–voltage behaviour of the proposed reaction mechanism (valid for M1 and M2). As long as $\hat{\theta}$ is independent of $\eta$, either because the adsorption flux or the surface diffusion flux is much larger compared to the electrochemical reaction step, we simply have to deal with a charge transfer-controlled reaction and $\hat{\theta}$ is obtained from Eq. (2.58)

$$\hat{\theta} = \theta_0(T^\circ, p_{O_2}) = \frac{K(T^\circ) \cdot \sqrt{p_{O_2}}}{1 + K(T^\circ) \cdot \sqrt{p_{O_2}}}.$$  

(2.64)

The anodic and cathodic exchange currents densities are therefore given as

$$i_0 = i_{0a} = 2N_0Fk_{1c}^o[V_O^-]K(T^\circ)\cdot(1-\theta_0)\cdot e^{2(1-\beta)fE_{eq}}$$ and \hspace{1cm} (2.65)

$$i_0 = i_{0c} = 2N_0Fk_{1c}^o[V_O^-] \cdot \theta_0 \cdot e^{-2\beta fE_{eq}}.$$  \hspace{1cm} (2.66)

By taking the product of Eqs. (2.65) and (2.66) we obtain for the exchange current density (note that we do not (!) assume that $\beta = 0.5$)

$$i_0 = 2N_0Fk_{1c}^o[V_O^-] \cdot [\theta_0(1-\theta_0)]^{1/2} \cdot \sqrt{K(T^\circ)} \cdot e^{(1-2\beta)fE_{eq}}.$$  \hspace{1cm} (2.67)

By using Eq. (2.64) for expressing $\theta_0$ and by replacing $E_{eq}(T^\circ, p_{O_2})$ with $1/(2f) \cdot \ln(\sqrt{p_{O_2}})$, we finally obtain

$$i_0(T^\circ, p_{O_2}) = 2N_0Fk_{1c}^o[V_O^-] \cdot \frac{K(T^\circ)}{1 + K(T^\circ) \cdot \sqrt{p_{O_2}}} \cdot p_{O_2}^{(1-\beta)/2}.$$  \hspace{1cm} (2.68)

With $\beta = 1/2$, the well known $p_{O_2}^{1/4}$ and $p_{O_2}^{-1/4}$ dependence of $i_0$ is obtained at low and high oxygen partial pressures, respectively [8, 68]. This behaviour is generally explained with the Langmuir adsorption of oxygen (Eq. (2.58)). Our result is more general.

The oxygen partial pressure where the maximum of $i_0(T^\circ, p_{O_2})$ occurs is given by

$$p_{O_2}^*(T^\circ) = \frac{1 - 2\beta + \beta^2}{\beta^2 \cdot [K(T^\circ)]^2}.$$  \hspace{1cm} (2.69)

The expression for the exchange current at arbitrary temperatures and oxygen partial pressures can be similarly calculated and is given by
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\[ i_0(T, p_{O_2}) = 2N_0Fk_{1e}^p[V_O] \]

\[ \times \left[ \frac{(1-2\beta)\left(\frac{1}{T^0} - \frac{1}{T}\right)\left(\frac{\Delta E + (\Delta H_{ad})/2}{R}\right)}{\frac{1}{T^0} - \frac{1}{T}\left(\frac{E_1^{1} + E_1^{1}}{R}\right)} \right]^{1/2} \]

\[ \times \frac{\sqrt{K(T^0)K(T)}}{1 + K(T) \sqrt{p_{O_2}}} \times p_{O_2}^{(1-\beta)/2} \]  

(2.70)

where we used \( \Delta H_{ad} = E_{ad} - E_{des} \) for the adsorption enthalpy, and where \( \Delta E = E_1^{1} - E_2^{1} \). It is seen that the temperature dependence of \( i_0 \) at a fixed oxygen partial pressures shows a rather complicated behaviour and no straight line can be expected in an Arrhenius plot of \( i_0 \). Let us finally note that Eq. (2.69) is generally valid for arbitrary temperatures and not only for \( T = T^0 \).

By use of Eq. (2.70), Eq. (2.63) simplifies to the well known Butler–Volmer equation

\[ I_F(\eta, T, p_{O_2}) = i_0(T, p_{O_2}) \cdot A_a \cdot \left[ e^{2(1-\beta)f\eta} - e^{-2\beta f\eta} \right]. \]  

(2.71)

As soon as \( \hat{\theta} \) deviates from its equilibrium value \( \hat{\theta}_0 \) (due to an applied over-potential), then \( I_F(\eta) \) will deviate from the ideal Butler–Volmer behaviour described by Eq. (2.71) and the reaction can not be considered as charge-transfer controlled. The actual behaviour depends on the relative magnitudes of the electrochemical rate constants to the rate constants of the source terms of O\(_{ad}\) (adsorption and surface diffusion).

**Identifiability in the steady-state.** We now use the result of Eq. (2.71) to give an intelligible prove of structural identifiability. The mechanisms M1 and M2 are said to be globally structurally identifiable from steady-state \( I_F(\eta) \) measurements when for all \( \eta \)

\[ I_F(p) = I_F(p^*), \text{ if and only if } p = p^*. \]  

(2.72)

It is well-known that purely charge-transfer controlled reactions are described by only two parameters—the exchange current density \( i_0 \) and the apparent transfer coefficient \( \alpha \) (note that we deliberately use the symbol \( \alpha \)
instead of $\beta$, which we use for elementary reactions)—which can be uniquely determined by a Tafel-analysis ($\log(I_F) \text{ vs. } \eta$) (see e.g. [23], p. 888). Thus, in our case, $k_{1c^o}$ and $\beta$ can be uniquely determined if the reaction is entirely charge-transfer controlled.

It is rather troublesome to show analytically that $M_1$ is globally structurally identifiable in the general case, because the (non-linear) analytical expression for $\theta(\eta, p_{O_2}, T)$ (which is obtained by solving $d\theta/dt = 0$) must be substituted in Eq. (2.63). For the case where Tafel behaviour should prevail ($|\eta| > RT/(2F)$) the problem reduces to show that the following must hold for all $\eta$

$$\hat{\theta}(p) = \hat{\theta}(p^*), \text{ if and only if } p = p^*. \quad (2.73)$$

It can be shown, by means of a symbolic computer program such as Mathematica or MAPLE, that Eq. (2.73) holds and that therefore the problem is uniquely identifiable in the steady-state, even if the reaction is not charge-transfer-controlled. (We do not give these results because they can be easily reproduced on the computer and it takes some space to present them.)

Keep in mind that in this case the unknown parameters can not be estimated from a Tafel analysis, but can be obtained from a least-square fit of Eq. (2.63) to the experimental data. A Tafel-analysis of experimental data would give incorrect values for the unknown parameters.

We use these results to infer the identifiability of reaction mechanism $M_2$. We can expect that $M_2$ is also globally structurally identifiable in the steady-state, because the model structures of $M_1$ and $M_2$ are similar. In addition, the surface diffusion coefficient of $O_{ad}$ on Pt was assumed to be known. Therefore, we have not introduced any new parameter into the problem. Note that the steady-state concentration of $O_{ad}$ near the tpb line, $\hat{\theta}$, is strongly influenced by the surface diffusion of adsorbed species. We therefore expect this concentration to remain approximately constant up to much higher overpotentials as in the case where surface diffusion is absent ($M_1$). This means that such an electrode is much more likely to exhibit a charge-transfer dominated behaviour, which allows for parameter estimation from an $I_F(\eta)$ analysis.

**Linearized state space description.** We will first rewrite the non-linear state space model from Eqs. (2.42) and (2.43) using the definitions of the rate constants from Eqs. (2.39) and (2.60). With the abbreviations
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\[
\begin{align*}
    k_1^\text{eq} &= k_1^c \cdot e^{-E_1^\text{eq} / (RT)} \cdot e^{-2\beta \eta E_{\text{eq}}} \\
    k_2^\text{eq} &= k_1^c \cdot e^{-E_2^\text{eq} / (RT)} \cdot e^{2(1-\beta) \eta E_{\text{eq}}}
\end{align*}
\]

we obtain

\[
\begin{align*}
    f_1: \quad \frac{d}{dt} \theta(t, p) &= 2k_{\text{ad}} p_{O_2} N_0 \cdot [1 - \theta(t, p)]^2 - 2k_{\text{des}} N_0 \cdot \theta(t, p)^2 - [V_O^{-}] \cdot \theta(t, p) \cdot k_1^\text{eq} \cdot e^{-2\beta \eta n(t)} \\
    &+ [O_O^x] \cdot [1 - \theta(t, p)] \cdot k_1^\text{eq} \cdot e^{2(1-\beta) \eta n(t)}
\end{align*}
\]

\[
\begin{align*}
    g_1: \quad I_F &= 2N_0 F A_a \times [-[V_O^{-}] \cdot \theta(t, p) \cdot k_1^\text{eq} \cdot e^{-2\beta \eta n(t)} \\
    &+ [O_O^x] \cdot [1 - \theta(t, p)] \cdot k_1^\text{eq} \cdot e^{2(1-\beta) \eta n(t)}]
\end{align*}
\]

Note that $k_1^\text{eq}$ must be expressed through $k_1^\text{eq}$. The linearized state space description of M1 is obtained by linearisation of Eqs. (2.75) and (2.76), using the steady state values for the rate constants, $\hat{k}_1 = k_1(E, T)$ and $\hat{k}_1 = k_1(E, T)$, and the surface coverage, $\hat{\theta} = \theta(p, T, p_{O_2})$, at the corresponding operating point. We obtain

\[
\begin{align*}
    \frac{\partial f_1}{\partial \theta} \bigg|_* &= a(p) = -4k_{\text{ad}} p_{O_2} N_0 \cdot (1 - \hat{\theta}) - 4k_{\text{des}} N_0 \cdot \hat{\theta} - [V_O^{-}] \cdot \hat{k}_1 - [O_O^x] \cdot \hat{k}_1 \\
    \frac{\partial f_1}{\partial \eta} \bigg|_* &= b(p) = [V_O^{-}] \cdot 2\beta f \cdot \hat{k}_1 \cdot \hat{\theta} + [O_O^x] \cdot 2(1-\beta) f \cdot \hat{k}_1 \cdot (1 - \hat{\theta}) \\
    \frac{\partial g_1}{\partial \theta} \bigg|_* &= c(p) = -2N_0 F A_a \times [[O_O^x] \cdot \hat{k}_1 + [V_O^{-}] \cdot \hat{k}_1]
\end{align*}
\]
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\[ \frac{\partial g_1}{\partial \eta} = d(p) = 2N_0FA_a \times \left[ [O^*_O] \cdot 2(1-\beta) f \cdot \hat{k}_1 \cdot (1-\hat{\theta}) + [V^*_O] \cdot 2\beta f \cdot \hat{k}_1 \cdot \hat{\theta} \right] \quad (2.80) \]

which finally may be written compactly

\[ \begin{align*}
\dot{\theta}(t, p) &= a(p)\theta(t, p) + b(p)\eta(t) \\
I_F(t, p) &= c(p)\theta(t, p) + d(p)\eta(t),
\end{align*} \quad (2.81) \]

where we used lowercase letters for the (A, B, C, D) quadruple to denote that we are dealing with scalars (first-order SISO system) instead of matrices.

Following the procedure described in subsection 2.2.4 we obtain the Faradaic impedance \( Z_F(s, p) \) in transfer function representation (cf. Eq. (2.30)):

\[ Z_F(s, p) = \frac{R_t}{1 - \left( [O^*_O] \cdot \hat{k}_1 + [V^*_O] \cdot \hat{k}_1 \right) / s + 4k_{ad}N_0P_{O_2} \cdot (1-\hat{\theta}) + 4k_{des}N_0 \cdot \hat{\theta}} \quad (2.82) \]

where \( R_t(p) = 1/d(p) \) by definition (cf. Eq. (2.23)). It can be shown that the result for \( R_t(p) \) and the expression for the exchange current density \( i_0 \) (Eq. (2.68) or (2.70)), satisfy relation (2.25).

Identifiability with electrochemical impedance spectroscopy. This model structure is globally identifiable at \( p^* \) if the equations in \( p \) that arise from the equivalence \( Z_F(s, p) = Z_F(s, p^*) \) \( \forall s \) have the only solution \( p = p^* \). This is determined by seeking solutions of the following system of equations for any \( E \):

\[ \begin{align*}
R_t &= R_t^* \\
[O^*_O] \cdot \hat{k}_1 + [V^*_O] \cdot \hat{k}_1 &= [O^*_O] \cdot \hat{k}_1^* + [V^*_O] \cdot \hat{k}_1^* \\
4k_{ad}N_0P_{O_2} \cdot (1-\hat{\theta}) + 4k_{des}N_0 \cdot \hat{\theta} &= 4k_{ad}N_0P_{O_2} \cdot (1-\hat{\theta}^*) + 4k_{des}N_0 \cdot \hat{\theta}^*
\end{align*} \quad (2.83) \]

Keep in mind that \( \hat{\theta} = \theta(p, T, P_{O_2}) \), \( \hat{k}_1 = \hat{k}_1(c(\eta, T, P_{O_2})) \), and that \( \hat{k}_1 \) should be expressed in terms of \( \hat{k}_{1c} \). The problem is solved for illustration purposes at \( T = T^\circ \) and \( P_{O_2} = p_{O_2}^\circ \). We obtain (by substituting the backward rate constant and with \( \dot{E} = 0 \)) for the second relation in Eq. (2.83)
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\[ k_{1c^o} \cdot [K(T^o) + 1] = (k_{1c^o})^* \cdot [K(T^o) + 1] \]  

(2.84)

which has obviously a single solution for \( k_{1c^o} \). The value for \( \beta \) can now be uniquely obtained from the first relation. Accordingly, M1 is globally structurally identifiable by impedance spectroscopy at least under equilibrium conditions, i.e. we could estimate a unique set of parameters from EIS data obtained at the reference condition and zero overpotential. Obviously, it becomes much more difficult to prove the structural identifiability of M1 apart from the reference state or for \( \eta \neq 0 \) and we do not intend to do so analytically.

Let us now consider M2. We approximate the surface diffusion by a first-order process (Fig. 2.7) and keep the surface concentration at \( z = \delta \) as constant (boundary condition). We obtain for the surface diffusion flux (cf. Fig. 2.7)

![Fig. 2.7 Two-compartment model for structural investigation of reaction mechanism M2. — The electrochemical reaction takes place in the tpb compartment \( (i = 1) \). The concentration of adsorbed atomic oxygen is considered to be homogeneous within a compartment. At a distance \( z \geq \delta \), \( \theta \) is considered to be time-independent. The surface diffusion flux is proportional to the concentration gradient.](image)

53
\[ j_1(t) = D \cdot \left[ \frac{\theta_0 - \theta(t)}{\delta} \right] \quad \text{and} \quad j_1'(t) = D \cdot \left[ \frac{\theta(t) - \theta_0}{\delta} \right]. \] (2.85)

The mass balance for the tpb compartment is obtained from

\[ (l_{tpb} \delta) \cdot \frac{d}{dt} \theta(t) = (j_1 - j_1') \cdot l_{tpb} \] (2.86)

which results in

\[ \frac{\delta^2}{2D} \frac{d}{dt} \theta(t) = \theta_0 - \theta(t) \] (2.87)

where \( T_d = \frac{\delta^2}{2D} \) is the time constant of the considered surface diffusion process (\( \delta \) is often called the average diffusion length of \( O_{ad} \) [25] or the penetration depth [7]). We include this term in the mass balance of Eq. (2.75) and re-evaluate \( Z_F(s, p) \). The result is given by

\[ Z_F(s, p) = R_t \left[ 1 - \frac{-([O^*] \cdot \hat{k}_1 + [V^*] \cdot \hat{k}_1)}{s + \frac{1}{T_d} + 4k_{ad}N_0P_{O_2} \cdot (1 - \hat{\theta}) + 4k_{des}N_0 \cdot \hat{\theta}} \right] \] (2.88)

which means that the existence of surface diffusion has no negative influence upon the identifiability of \( M_2 \). Furthermore, we can expect to estimate \( T_d \) from an impedance analysis under the experimental conditions where the simplifications are justified (at high cathodic overpotential and low oxygen partial pressure, i.e. under limiting current conditions).

From these examples it might seem that the proof of unique identifiability is mathematically straightforward. But the mathematical effort necessary to test for identifiability increases with model complexity and the problem of whether \( Z_F(s, p) = Z_F(s, p^*) \quad \forall s \) implies that \( p = p^* \) is generally a difficult one. Berthier and coworkers [58, 64, 65] have proven the identifiability for a number of reaction mechanisms under different experimental conditions. The reader interested in more elaborated examples is referred to their work and the references therein. Fortunately, computer implementations of efficient algorithms for testing structural identifiability are becoming increasingly available [62], and the field is growing rapidly.
Vagueness of \( w \)—its consequences to identifiability. In the following we will address our attention to the question, what consequences will it have upon the identifiability of \( M_1 \) or \( M_2 \), when we skip our assumption that the width \( w \) of the \( \text{tpb} \) is known, i.e. when we assume that \( w \) is unknown and that we would like it to estimate it from experimental data. Indeed, as mentioned before, there is no plausible argument to assume that the width of the \( \text{tpb} \) can be considered as a known quantity.

Let us first consider the simplest case of a charge-transfer controlled reaction under steady-state investigation. The \( I_F(\eta) \) behaviour is given by Eq. (2.71) where we put \( A_a = I_{\text{tpb}} \cdot w \). Thus, from a Tafel-analysis, \( \beta \) and the parameter product \( k_{1c}^o \cdot w \) are uniquely identifiable, but \( k_{1c}^o \) and \( w \) are not individually identifiable. Thus, \( M_1 \) with \( p = [\beta, k_{1c}^o, w] \) is un-identifiable in the steady-state.

An important point to note is that, for a classical EIS experiment on a system with \( n \) states, there are, at most, \( 2n + 1 \) equations in the parameters. This fact is easily seen by looking at a complex plane plot where every loop provides two quantities: one time constant and one resistance. The number of states \( n \) determines, at most, the number of loops. The additional equation is given by the expression for the charge transfer resistance (cf. Eq. (2.83)). Thus, we could expect that EIS might be capable to give us unique estimates of \( \beta \), \( k_{1c}^o \) and \( w \).

We answer our conjecture as follows: From a Tafel-analysis, estimates for \( \beta \) and \( k_{1c}^o \cdot w \) can be obtained. Obviously, \( k_{1c}^o \) can still be uniquely determined from an impedance analysis. Accordingly, all parameters can be obtained uniquely from a combined analysis. Note that an impedance analysis alone can not solve the problem, because the last expression in Eq. (2.83) does not contain any unknown parameter (at least at \( E = 0 \)). Because \( R_t \propto i_0^{-1} \) and \( R_t(k_{1c}^o, w, \beta) \), we are left with similar problems as in the steady-state. We see from this example that it is important to have as much as possible \textit{a priori} knowledge of a system available at an early stage of experimental design.

Let us close this section by touching on a problem which occurs in practical parameter estimation. A reliable quality measure of an obtained parameter estimate is a prerequisite for any reasonable use of the results. It is also necessary for experimental design, in particular for determination of optimal input signals. To obtain accurate parameter estimates, it is a necessary requirement that the object function is highly sensitive on the individual parameters. This requirement is not sufficient, however, as the sensitivity of a combination of two or more parameters may be much smaller than the individual sensitivi-
ties, indicating a high correlation between the parameters [69]. We will illustrate this point in part II.

2.3.5 Qualitative Analysis of Frequency Response Behaviour

Nyquist plot properties. The expression for \( Z_F(s, p) \) (Eq. (2.82)) is a first-order rational fraction in \( s \)

\[
Z_F(s, p) = R_t(p) \cdot \left[ 1 - \frac{b_0(p)}{s + a_0(p)} \right]
\]  

(2.89)

which can be rearranged to the general form of Eq. (2.13):

\[
Z_F(s) = R_t \cdot \left[ \frac{s + (a_0 - b_0)}{s + a_0} \right].
\]  

(2.90)

where we actually mean that \( Z_F, R_t, \) and the polynomial coefficients depend on the set of parameters \( p \). The polarization resistance is found to be

\[
R_p(j\omega) = \lim_{j\omega \to 0} Z_F(j\omega) = R_t - R_t \cdot \frac{b_0}{a_0} = R_t \cdot \frac{(a_0 - b_0)}{a_0}.
\]  

(2.91)

We also immediately see by comparing Eq. (2.32) and Eq. (2.89) that

\[
Z_0(s) = -R_t \cdot \frac{b_0}{s + a_0}
\]  

(2.92)

which is the transfer function of an electrical circuit made up of a resistance \( R \) and a capacitance \( C \) in parallel where \( R = -R_t b_0 / a_0 \) and \( C = 1 / a_0 \).

The frequency response \( Z_F(j\omega, p) \) shown in the Nyquist plane is a semicircle in the fourth quadrant ("capacitive" behaviour) (Fig. 2.8) with the high frequency intercept at \( R_t \), the low frequency intercept at \( R_p \), the angular frequency of the apex at \( \omega_0 = a_0 \), and \( R_p \geq R_t \). We can further see that if the denominator in Eq. (2.82) (or Eq. (2.89)) is much larger than the numerator, i.e. if the adsorption and desorption process (or surface diffusion) is much faster than the electrochemical reaction step, then this second term will almost disappear and the overall reaction is charge-transfer controlled with
Fig. 2.8 Qualitative frequency response of M1 shown in the complex plane. —The impedance data are standardized with $R_p(a_0,b_0)$. We have $(R_t \leq R_p) \forall (j\omega)$. The numbers within the figure denote the frequencies in Hz. The simulations were obtained with increasing values for the forward electrochemical rate constant. Note that by doing so the values of $b_0$ as well as $R_t$ are influenced. With increasing values for $k_1$, $R_t$ decreases and $|b_0|$ increases.

$R_p = R_t$ (curve (1) in Fig. 2.8). In the limiting case the frequency response $Z(j\omega)$ would exhibit as a single point on the real axis at $R_p = R_t$.

**Bode plot behaviour.** By introducing $\tau_1^{-1} = \omega_1 = a_0 - b_0$ and $\tau_2^{-1} = \omega_2 = a_0$ in the expression of $Z_F(j\omega)$ we obtain

$$Z_F(j\omega) = \frac{R_t \tau_2}{\tau_1} \frac{j\omega \tau_1 + 1}{j\omega \tau_2 + 1} \quad (2.93)$$

which is a well known transfer function in control theory [39]. We have for the phase

$$\angle Z_F(j\omega) = \angle R_t \frac{\tau_2}{\tau_1} + \angle (j\omega \tau_1 + 1) - \angle (j\omega \tau_2 + 1) \quad (2.94)$$

and the magnitude can be written as
\[
\log|Z_F(j\omega)| = \log\left|\frac{R_2}{R_1}\right| + \log(|j\omega\tau_1 + 1|) - \log(|j\omega\tau_2 + 1|).
\] (2.95)

We can identify three kinds of terms, where the first term is independent of the frequency. The behaviour of the frequency dependent terms is shown in Fig. 2.9.

Note that the frequency where the maximum of \(\angle Z_F(j\omega)\) occurs is not given by the inverse relaxation time of the process, \(1/\tau^*\), but that this frequency is

![Graph showing qualitative frequency response of \(M1\) shown in Bode representation.](image)

Fig. 2.9 Qualitative frequency response of \(M1\) shown in Bode representation.—(a) \(|Z_F|\) scaled with \(R_p\) and (b) phase of \(Z_F(j\omega)\). Note that the overall magnitude and overall phase can be simply obtained by adding the individual terms (curves (1), (2), and (3)) in a Bode plot. The break frequencies \(1/\tau_1\) and \(1/\tau_2\) are obtained where a phase shift of \(\pm45^\circ\) occurs. The phase peak is at \(\omega_0 = \sqrt{\omega_1\omega_2}\) where \(\omega_1 = 1/\tau_1\) and \(\omega_2 = 1/\tau_2\). Note that \(\omega_0\) does not correspond to the relaxation frequency of the overall electrode reaction.
Fig. 2.10 Frequency responses of M1 in Bode representation.—(a) Magnitudes and (b) phases of $Z_F(j\omega)$ data with different ratios of $a_0/b_0$. Note that the slope of $Z_F(j\omega)$ only emerges clearly as $-1$ if $\omega_1$ and $\omega_2$ are different by about one order of magnitude.

given by $\sqrt{\omega_1 \cdot \omega_2}$ (cf. Fig. 2.9). The imaginary part of the Faradaic admittance, $\text{Im}[Y_F(j\omega)]$, has its maximum at the relaxation frequency of the overall process. This fact must be kept in mind when discussing experimental data.

We can see a further important property of Bode plots by considering the high frequency behaviours of the terms in Eq. (2.95). The magnitudes of these terms approach an asymptote at frequencies $\omega r_i >> 1$. The slope of these terms in a Bode plot is either $+1$ or $-1$, i.e. it is possible to get information about the order of an electrochemical process by examining the slope of the magnitude in the Bode plot. But at the same time we draw attention to the fact that the polynomial coefficients $a_0$ and $b_0$ have to be different by at least one order of magnitude (in our particular example). Otherwise, both curves will overlap and the slope of the total curve will always be flatter than minus
one. Note that the ratio of the relaxation frequencies as introduced in Eq. (2.93), is given by $\omega_1/\omega_2 = 1 - b_0/a_0$. These facts are envisaged in Fig. 2.10 where the same data as in Fig. 2.8 are given in a Bode plot.

### 2.4 Conclusions

The present study, comprising of this and a second part, was undertaken to provide a tool to treat heterogeneous reaction mechanisms within a uniform framework. The concepts were presented by investigating the reaction mechanism of the rather well understood Pt, $O_2(g)$ $|$ YSZ system. We showed that the electrochemical kinetics can be conveniently represented in (non-linear) state space models. In the cases where the reaction mechanisms are simple, analytical solutions for the steady-state and frequency response behaviours can be obtained. Otherwise, numerical solutions can be found for any input/output behaviour, which we will present in part II of this study. Although state space models can accommodate any degree of complexity, the need for testing the structural properties demands rather simple equations. We showed how problems can be simplified without losing too much general validity. There is certainly a need for a widely available and easy-to-use method to carry out the task of testing model identifiability and model distinguishability and the lack of such a method is the reason why we feel some discomfort at the present time. However, it is obvious that these problems must be tackled before experiments are carried out to make certain that the experimental work gives the most possible information. We have also shown that it is extremely important to have (and use) as much a priori knowledge of a reaction mechanism as possible to be able to estimate unknown kinetic parameters from measurements. Despite these difficulties, the power of the proposed method is the fact that state space models can be treated on the computer efficiently and in a straightforward way.

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References


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Appendix

2–A.1 State Space Description of an Electrical Circuit

The notion "state space" is best introduced by means of a simple example. Consider the electrical circuit shown in Fig. 2–A.1. The circuit should be familiar to electrochemists. Let us derive the state space model for this particular circuit. In the appendix of Part II of this publication, a more complicated system is treated.

The dynamic properties of this system are entirely described for times \( t \geq t_0 \), if the voltage \( U_y(t_0) \) and the current \( I(t_0) \), as well as the input voltage \( U_u(t) \) for \( t \geq t_0 \) is known. From this information, \( I(t) \) and \( U_c(t) \) can be determined for \( t \geq t_0 \). However, \( I(t) \) and \( U_c(t) \) characterize the "state" of the electrical circuit and are therefore called state variables. From a node analysis for node 1 we find

\[
\frac{1}{R_1} \cdot [U_u(t) - U_1(t)] + C \cdot \frac{d}{dt} [U_y(t) - U_1(t)] + \frac{1}{R_2} \cdot [U_y(t) - U_1(t)] = 0
\]

and

\[
I(t) = \frac{1}{R_1} \cdot [U_u(t) - U_1(t)].
\]

![Fig. 2–A.1](Image)

Fig. 2–A.1  RC electrical circuit.—The notations are given within the text.
We put $U_y(t) = 0$ (ground). We solve Eq. (2-A1.1) for $U_1(t)$ and sort the different terms to obtain

$$\frac{d}{dt}U_1(t) = -\frac{1}{C} \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \cdot U_1(t) + \frac{1}{CR_1} \cdot U_u(t) \quad (2-A1.3)$$

and similarly for Eq. (2-A1.2)

$$I(t) = -\frac{1}{R_1} \cdot U_1(t) + \frac{1}{R_1} \cdot U_u(t). \quad (2-A1.4)$$

Eq. (2-A1.3) is called state equation and Eq. (2-A1.4) is called output equation. Form Eq. (2-A1.4) it is clearly seen that $I(t)$ depends on the input $U_u(t)$ and the present value of $U_1(t)$. Because the circuit is a linear and time independent system, we can easily write Eqs. (2-A1.3) and (2-A1.4) in matrix form as

$$\dot{x} = Ax + Bu \quad (2-A1.5)$$

$$y = Cx + Du \quad (2-A1.6)$$

where we used $x = U_1(t), y = I(t), u = U_u(t)$, and the state space matrices $(A, B, C, D)$ are obtained by comparing the coefficients of Eqs. (2-A1.3) to (2-A1.6)

$$A = \left[ -\frac{1}{C} \cdot \left( \frac{1}{R_1} + \frac{1}{R_2} \right) \right] \quad B = \left[ \frac{1}{CR_1} \right]$$

$$C = \left[ -\frac{1}{R_1} \right] \quad D = \left[ \frac{1}{R_1} \right] \quad (2-A1.7)$$

State-space systems are easily treated numerically (see Part II of this publication). The dynamic properties of a system are entirely described by the $(A, B, C, D)$ quadruple and the starting conditions.
2–A.2 Calculation of tpb length from microstructural data

We intend to describe the electrode morphology mathematically in terms of measurable microstructural data. From SEM images (see Fig. 2.2) the total coverage of the electrolyte surface, $A_{cov}$, as well as the average pore size, $d_p$, can be obtained from image analysis. We will express the length of the tpb, $l_{tpb}$, as a function of these two parameters.

We assume that the electrode microstructure facing the solid electrolyte can be regarded as a mesh of metal strips (Fig. 2–A2.1). A characteristic length, $l_{char}$, is introduced, which reflects the size of the unit cell as defined in Fig. 2–A2.1. Let us consider $l_{char}$ as constant for the moment and let $d_p$ be the only free parameter. Then we obtain for the length of the triple phase boundary

$$l_{tpb} = 4d_p \cdot \frac{A_{cov}}{l_{char}^2}$$

Fig. 2–A2.1 Simplified morphology of noble metal/electrolyte interface.—A mesh of noble metal strips is arranged in a regular lattice. The unit cell size is characterized by its characteristic length $l_{char}$ and $d_p$ is the pore size. The length of the triple phase boundary is parametrized in terms of the surface coverage $A_{cov}$ of the solid electrolyte and the characteristic length $l_{char}$. Both quantities can be estimated with satisfactory accuracy from SEM image analysis.
where $A_\phi$ is the apparent electrode area. With the definition of the surface coverage $A_{cov} = (l_{char}^2 - d_p^2)/l_{char}^2$ which we solve for $d_p$ we find

$$l_{tpb} = 4 \frac{A_\phi}{l_{char}} \sqrt{1 - A_{cov}}.$$  (2-A2.2)

Typical values for noble metal electrodes are in the range of 2–10 $\mu$m for $l_{char}$ and in the range of 0.4–0.85 for the coverage $A_\phi$ (cf. Fig. 2.2 and e.g. [7, 10, 17, 20]).
2 General Framework, Modelling, and Structural Investigation
CHAPTER 3

COMPUTER IMPLEMENTATION, SIMULATION, AND VALIDATION *

Abstract In part I of this paper a nonlinear state-space model of the Pt, O$_2$(g) | ytrria-stabilized zirconia system was proposed and the structure of the equations was investigated. In this part one dimensional finite-element representation of the model is given. The computer implementation of the heterogeneous chemical and electrochemical kinetics and the surface mass transport is developed. The origin of the double layer capacitance and its influence upon the electrochemical impedance (EIS) is discussed. The problems of the space discretization of the electrode surface, the extension of the triple phase boundary (tpb), and numerical aspects are considered. The simulation method is described in detail. The steady-state current–voltage behaviour and the Faradaic impedance is simulated for temperatures from 773 K (500°C) to 1173 K (900°C), and oxygen partial pressures from 1 Pa to $10^5$ Pa. Three different reaction regimes are discriminated. Above 1123 K (850°C), high $p_{O_2}$, and low cathodic overpotentials the reaction kinetics is essentially determined by the charge-transfer step. With increasing cathodic overpotentials, and/or decreasing $p_{O_2}$ surface diffusion is in competition with charge-transfer. At tem-

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peratures between 773 K and 1073 K the reaction is essentially dominated by the supply of atomic oxygen (O_{ad}) via surface diffusion and dissociative adsorption of O_2(g) near the tpb. The charge-transfer coefficient, the electrochemical rate constants, and the activation enthalpy of the charge-transfer reaction can be uniquely estimated from EIS data. The activation enthalpy of the dissociative oxygen adsorption on Pt can be estimated. With electrodes of well known geometry the surface diffusion coefficient of chemisorbed atomic oxygen on Pt and its concentration dependence can be obtained. It is demonstrated that the simulation of micro-kinetic models is a powerful technique in order to obtain a deeper understanding of reaction mechanism.

**Keywords.** Reaction mechanism, electrochemical impedance (EIS), state-space model, double layer capacitance, digital simulation, MATLAB/SIMULINK.

### 3.1 Introduction

In part I of the present paper we have presented a general framework for modelling reaction mechanisms at noble metal electrodes in solid state electrochemistry [1]. We illustrated the process of modelling and structural investigation by means of a well known reaction mechanism describing the Pt, O_2(g) \r Yttria-Stabilized Zirconia (YSZ) interface. In a first model (M1), we considered the dissociative adsorption of oxygen on the Pt surface and the reduction of atomic oxygen near the triple phase boundary (tpb) line. In a second model (M2), surface diffusion of atomic oxygen on the Pt surface was included. It was assumed that only one electrochemical rate constant and one charge-transfer coefficient are unknown, whereas the remaining model parameters, such as activation energies or the rate of adsorption and desorption, were assumed to be *a priori* known. We investigated the structure of the models in detail, showed the condition for their identifiability, and presented a rigorous treatment of the steady-state behaviour in the case of a charge transfer controlled reaction. Expressions describing the steady-state I(\eta) behaviour as well as the small-signal frequency response behaviour were also given. However, we have not yet described how the theoretical results from part I can be used to obtain more insight into the reaction kinetics of the Pt, O_2(g) \r YSZ system. In addition, the implementation and simulation proce-
It is one of the aims of this part to present the computer implementation of the model equations and to show how simulations can be obtained. We use the high level programming environment of MATLAB and SIMULINK [2], which is widely available for many computer hardware platforms. Detailed instructions for the implementation are given in the appendix, in order to facilitate the re-implementation of the models and to encourage the reader to use these computer tools for the investigation of reaction mechanisms. We introduce block diagrams for the description of dynamic electrochemical systems. The steady-state and dynamic behaviour of model M2 is simulated and the simulation results are compared with experimental results from the literature. We further propose a procedure for the estimation of many of the parameters employed in M2. It is shown that almost any parameter can be estimated from a combination of different measurements and analyses. The difference between theoretical identifiability, as introduced in part I, and practical identifiability are enlightened. The limitations of M2 are discussed and improvements are proposed.

3.2 Model Implementation

3.2.1 Computer Tools and General Procedure

We have chosen MATLAB and SIMULINK as primary software tools for the implementation and simulation of models [2], instead using an ordinary programming language, such as C or Fortran. MATLAB is an efficient tool for dealing with numerical analysis, matrix computation, signal processing, and visualization. MATLAB has become a widely used computer tool in engineering science and is available on a large number of computer hardware platforms. There are two basically different approaches to implement the set of equations into an executable MATLAB code. The first method makes use of the graphical programming extension SIMULINK in MATLAB [3], where the dynamic system is represented as a block diagram. Single SIMULINK models can be converted to subsystems which can itself be further built to larger systems; a property which is particularly useful when treating finite-difference models for dealing with mass transport processes. From a SIMULINK function, the
dynamic behaviour of a system can be investigated in time and frequency domain. Linear time invariant (LTI) models can be converted between state-space and transfer function representations.

The second approach, which is commonly used in ordinary programming languages, uses the system of equations directly. Explicit state-space descriptions are obtained by linearization of the state equations as described in part I. Each methods offers specific advantages; in fact both approaches are useful and are best employed in conjunction. When dealing with small models (i.e. if the number of state variables is below ~50), model implementation in Simulink is considerably faster and more intuitive. In addition, the loss in performance during simulation is negligible. We mainly use the graphical programming environment.

The overall strategy to solve a problem can be summarized as follows:

(i) Implement the model either by building a block diagram in Simulink or by writing ordinary (C like) MATLAB functions.

(ii) Make the physical and kinetic constants available to the MATLAB workspace. Estimate some reasonable values for the unknown parameters.

(iii) Determine the steady-state values for the state variables from the condition $dx(t)/dt = 0$ (initial conditions).

(iv) Run large-signal simulations in the time domain of the non-linear model (Simulink or MATLAB function), or

(v) generate a (linearized) state-space model of the non-linear model and compute the frequency response or the small-signal time dependent behaviour.

3.2.2 Heterogeneous Chemical and Electrochemical Kinetics

The primary objective of these procedures is to implement the mass and charge balance equations into the computer suitable for simulation. There is no need to concern about the time discretization of the equations for MATLAB takes entirely care of that. It is, therefore, not necessary to know precisely the
3.2 Model Implementation

nature of the numerical integration techniques, although a basic knowledge may be helpful in choosing the appropriate algorithms for simulations in time domain. Basic details can be found within the handbooks of the programming environment or in textbooks about numerical mathematics [3-5]. As it is the first time where electrochemical systems are treated with this programming environment we put some emphasis on the actual implementation process in order to facilitate the re-implementation of the model. Implementation details specific for MATLAB and SIMULINK will be given in the appendices 3-A.3 and 3-A.4.

We use the non-linear state-space model M1 developed in part I of this publication as the starting point for the implementation [1]. The mass and charge balances were obtained as

\[ f_1: \quad \frac{d}{dt} \theta(t, p) = 2k_{ad}pO_2N_0 \cdot [1 - \theta(t, p)]^2 - 2k_{des}N_0 \cdot \theta(t, p)^2 \]
\[ = [V_0] \cdot \theta(t, p) \cdot k_1^{eq} \cdot e^{-2\beta f\eta(t)} \]
\[ + [O_0^x] \cdot [1 - \theta(t, p)] \cdot k_1^{eq} \cdot e^{2(1 - \beta)f\eta(t)} \]

\[ g_1: \quad I_F = 2N_0FA\times [- [V_0^x] \cdot \theta(t, p) \cdot k_1^{eq} \cdot e^{-2\beta f\eta(t)} \]
\[ + [O_0^x] \cdot [1 - \theta(t, p)] \cdot k_1^{eq} \cdot e^{2(1 - \beta)f\eta(t)}] \]

with the vector of the unknown parameters \( p = [k_{1c}, \beta] \), and \( k_1^{eq} = k_{1c} \cdot \exp[-E_a/RT] \cdot \exp[-2\beta fE_{eq}] \); the definition of the remaining symbols was explained in part I or can be found in Table 3.1 of appendix 3-A.1. Let us rewrite Eq. (3.1) with \( x = \theta(t, p) \) (state variable), \( u = \eta(t) \) (input quantity), \( k_f = [V_0] \cdot k_1^{eq} \), and \( k_b = [O_0^x] \cdot k_1^{eq} \) as

\[ \dot{x} = 2k_{ad}pO_2N_0 \cdot (1 - x)^2 - 2k_{des}N_0 \cdot x^2 \]
\[ - k_f \cdot x \cdot \exp[-2\beta f u] + k_b \cdot (1 - x) \cdot \exp[2(1 - \beta)f u] \]

The first two terms are related with the adsorption and desorption of oxygen on the platinum surface. These reactions takes place on the entire cathode surface and are not restricted to the \( tpb \) area as the electron transfer reaction is (terms three and four of Eq. (3.3)). The model M1 is completed by adding the equation for the charge balance. Using \( y = I_F(t, p) \) and the same abbreviations as in Eq. (3.3) we write
\[ y = 2N_0FA_a \left[ -k_f \cdot x \cdot e^{-2\beta f_u} + k_b \cdot (1 - x) \cdot e^{2(1-\beta)f_u} \right]. \] (3.4)

Eqs. (3.3) and (3.4) can be implemented into a MATLAB function or into a SIMULINK block diagram. Appendix 3-A.3 gives more detailed information about the SIMULINK implementation of model M1 and most of the MATLAB commands used for simulation. The following gives an overview of the capabilities of the method.

The initial condition for the state variable, \( x = x_0 \), is obtained by solving Eq. (3.3) numerically for \( \dot{x} = 0 \). If \( u = 0 \), only the first two terms must be taken into account and the well known analytical solution of the Langmuir equation is obtained (cf. 3-A.3). The time dependent behaviour of the system from any starting point towards the steady-state point can be followed by choosing an appropriate simulation algorithm and appropriate step sizes. Simulation results can either be followed directly within the SIMULINK environment or by writing the simulation results into the MATLAB workspace. Linearized state-space descriptions of the models can be obtained by following either of two routes. First, analytical expressions for the state-space matrices \( A, B, C, \) and \( D \) can be obtained by linearization of Eqs. (3.3) and (3.4) as described in part I. This can be done for both M1 and M2, although it becomes tedious doing so for multi-compartment models. From linearized state-space models (SSM) the frequency response and the small-signal time dependent behaviour can be obtained at the corresponding operating point. Note that the linearized SSM can not be used to simulated the large-signal time dependent behaviour, such as potential-step responses or cyclic voltammetry. The second approach circumvents these limitations. The function "linmod" from SIMULINK is used to extract numerical estimates of the state-space matrices from the non-linear SIMULINK block diagram (cf. 3-A.3). This approach has the advantage that both the large-signal behaviour and small-signal behaviour of the model can be analysed with one representation and without the need to obtain (lengthy) analytical expressions for the state-space matrices. However, during the early implementation stage it is often useful to follow both routes simultaneously in order to validate the model implementation. In addition, SIMULINK offers the function "trim" which enables to determine steady-state equilibrium points from (non-linear) systems in block diagram representation (cf. 3-A.3). This is especially useful when the steady-state values for the state variables are needed under the condition where an overpotential is applied, i.e. when a current flows. Under
these conditions it is generally not possible to solve equations or systems of
equations of the type such as Eq. (3.3) for \( x = 0 \) analytically. The complete
Simulink block diagram of M1 is given in appendix 3-A.3.

3.2.3 Surface Mass Transport

There are basically two different methods to deal with partial differential
equation (PDE) systems numerically. The first is the collocation method [6].
The second method, which we use in this paper, is the method of the
finite-difference approach [7]. Whereas the first technique is more elegant, it
generally requires more mathematical treatment.

We employ the simplified model of the electrode morphology developed in
part I. The height of the Pt strips is assumed to be equal to the thickness of the
electrode layer (Fig. 3.1a). The z axis is divided into compartments of increasing
size directed away from the tpb line (Fig. 3.1b). However, there is no need
to discretize the electrode surface over its entire thickness, but only to a certain
extent which is in the order of the Nernst diffusion layer (see below). The
concentration of \( O_{ad} \) is considered to be homogeneous within the compartments.

For digital simulation it is convenient to rewrite Fick's second law for diffusion
along the z-coordinate in the form [8]

\[
\frac{dc}{dt} = \frac{\partial D(c) \partial c}{\partial z} + D(c) \frac{\partial^2 c}{\partial z^2} = \frac{\partial D(c)}{\partial c} \left( \frac{\partial c}{\partial z} \right)^2 + D(c) \frac{\partial^2 c}{\partial z^2}.
\]  

(3.5)

In part I we assumed that \( D \) does not depend on the concentration. Accord¬
ingly, the first term in Eq. (3.5) vanishes and we are left with the second term.
However, it is obvious that Eq. (3.5) is the starting point for a refined treatment
of surface diffusion. The space derivatives are approximated with central differences (see e.g. [7]). The diffusional flow \( j \) (mol/(m·s)) of \( O_{ad} \) into
and out of a compartment is obtained from

\[
j_{i-1,i} = D \frac{N_0}{N_A} \left( \frac{x_{i-1} - x_i}{\Delta z_{i-1} + \Delta z_i} \right) \quad \text{and} \quad j_{i,i+1} = D \frac{N_0}{N_A} \left( \frac{x_i - x_{i+1}}{\Delta z_i + \Delta z_{i+1}} \right),
\]

(3.6)
Fig. 3.1 Simplified electrode geometry and one-dimensional finite element model.—
(a) 3-dimensional view of porous Pt on solid electrolyte according to the 2-dimensional model developed in the appendix of part I. $d_p$ is the pore diameter and $l_{\text{char}}$ is the characteristic length. Gas mass transport is considered to be infinitely fast in the Pt pores. (b) The plane (ABCD) is discretized in compartments of increasing size starting with the $tpb$ compartment of width $w$ ($= \Delta z_1$). Mass balances are formulated for every compartment. In addition, for the $tpb$ compartment the charge balance is formulated.
3.2 Model Implementation

where $x_i$ is the surface coverage of $O_{ad}$ in compartment $i$, $N_0$ is the number of surface sites on Pt (atoms/m$^2$), $N_A$ is the Avogadro constant (mol$^{-1}$), and $\Delta z_i$ is the width of compartment $i$ (m). The mass balance (mol/s) for compartment $i$ is obtained as

$$A_i \frac{dc_i}{dt} = t \cdot (j_{i-1,1} - j_{i,i+1})$$  \hspace{1cm} (3.7)

where $A_i = t \cdot \Delta z_i$ is the area of compartment $i$, $t$ is the width of the pore, and $c_i$ is the surface concentration of $O_{ad}$ in compartment $i$. With $c_i = N_0 / N_A \cdot x_i$ we finally find for the mass balance of compartment $i$

$$\Delta z_i \cdot \frac{dx_i}{dt} = \frac{D}{\Delta z_i/2} \times \left[ \frac{1}{\Delta z_{i-1} + 1} x_{i-1} - \left( \frac{1}{\Delta z_{i-1} + 1} + \frac{1}{\Delta z_i + 1} \right) x_i + \frac{1}{\Delta z_{i+1} + 1} x_{i+1} \right]$$  \hspace{1cm} (3.8)

or in short form

$$\frac{\Delta z_i^2}{2D} \cdot \frac{dc_i}{dt} = T_i \cdot \frac{dx_i}{dt} = a_{i-1,i} x_{i-1} - a_{i,i} x_i + a_{i,i+1} x_{i+1}$$  \hspace{1cm} (3.9)

where $T_i = \Delta z_i^2 / (2D)$ is the time constant of the diffusion process in compartment $i$, and the $a_{i,j}$ are numerical factors which depend on the geometry and the boundary conditions.

The state-space model is realized by writing the mass and charge balance equation for every compartment using the following initial and boundary conditions:

(i) Initial conditions: the surface concentration of $O_{ad}$ is homogeneous before establishing an external disturbance.
(ii) Boundary conditions at an infinite distance \( \omega \) from the electrode/electrolyte interface: at a sufficiently large distance from the interface the concentration of \( O_{\text{ad}} \) is equal to the equilibrium surface concentration \( x_0 \) determined by the adsorption/desorption equilibrium \( (c_{\omega + 1} = x_0 \) and \( \Delta z_{\omega + 1} = 0 \)).

(iii) Boundary conditions in the tpb compartment: the interface is blocking for surface diffusion; the Faradaic current is equal to the charge balance; the electron transfer reaction can only take place in this compartment; i.e. \( c_{\text{tpb}-1} = 0 \) and \( \Delta z_{\text{tpb}-1} = \infty \).

Note that the \( a_{i,j} \) of the boundary compartments can be conveniently obtained from the following argument: if the boundary is blocking we put either \( \Delta z_{i-1} = \infty \) or \( \Delta z_{i+1} = \infty \), depending on which boundary is blocking. If the concentration of a neighbouring compartment is taken to be constant with time, we put \( \Delta z_{i+1} = 0 \). Starting from the tpb compartment we increase the size of every successive compartment by a factor of \( q \). Accordingly, we obtain an approximate state-space description of \( M_2 \):

\[
\frac{dx_{\text{tpb}}}{dt} = 2k_{\text{ad}}P_{O_2}N_0 \cdot (1-x_1)^2 - 2k_{\text{des}}N_0 \cdot x_1^2 \\
- k_i \cdot x_1 + k_b \cdot (1-x_1) + \frac{1}{T_1} \left( \frac{1}{1+q} x_1 + \frac{1}{1+q} x_2 \right)
\]

\[
\frac{dx_i}{dt} = 2k_{\text{ad}}P_{O_2}N_0 \cdot (1-x_i)^2 - 2k_{\text{des}}N_0 \cdot x_i^2 + \\
\frac{1}{T_1} \left( \frac{q}{1+q} x_{i-1} - x_i + \frac{1}{1+q} x_{i+1} \right)
\]

\[
\frac{dx_{\omega}}{dt} = 2k_{\text{ad}}P_{O_2}N_0 \cdot (1-x_{\omega})^2 - 2k_{\text{des}}N_0 \cdot x_{\omega}^2 + \\
\frac{1}{T_\omega} \left( \frac{q}{1+q} x_{\omega-1} - \frac{2q+1}{1+q} x_{\omega} + x_{\omega+1} \right)
\]

where \( \omega \) denotes the outmost compartment facing the region with \( x_{\omega + 1} = x_0 \).
3.3 Simulation Procedures

3.3.1 Model Initialization and Sensitivity

The models are initialized by making the numerical values of all constants and parameters available to the MATLAB workspace. The values for the parameters which are (assumed to be) a priori known are given in Table 3.1 (appendix 3–A.1). These values are used for the simulations if not otherwise stated. It should be mentioned that there is much information available in the literature about the adsorption and desorption dynamics of O\(_2\)(g) on Pt surfaces (see model M3 in [33]). The kinetic rate constants were chosen while taking into account most of this available information (see references cited in Table 3.1 of Appendix 3–A.1). Note that the activation enthalpy of the electrochemical reaction is also reasonably known [9, 10].

In order to be able to run simulations, some values must also be chosen for the unknown parameters \(p = \{k_{1e}, \beta\}\). Often one can obtain reasonable estimates of unknown parameters by considering the static properties of the system. This is exemplified in the following. Assume that we would like to obtain an estimate for \(k_{1e}^{eq}\) at \(T = 1000\) K and \(p_{O_2} = 1\) atm. Assume that \(R_t\) has been determined experimentally as \(R_t = 10 \Omega \cdot \text{cm}^2\) for an electrode of 1 cm\(^2\) of apparent area. From the relation \(R_t = RT/(2F) \cdot 1/i_0\) we find \(i_0 = 4.3\) mA/cm\(^2\). This value should be close to \(2N_0FA_a \cdot [V_{O}^\cdot] \cdot k_f \cdot x\). Using the parameters given in Table 3.1 and with \(A_a = w \cdot l_{tpb}\), where \(w\) is the width of the tpb compartment and \(l_{tpb}\) is the length of the triple phase boundary, a numerical estimate of \(k_{1e}^{eq}\) is obtained if \(x\) is calculated for the temperature and \(p_{O_2}\) considered. Other reaction rates can be estimated in a similar way.
Once the \textit{a priori} known parameter values and the approximate parameter estimates are made available to the MATLAB workspace, simulations can be obtained. If the goal of a study is to determine accurate estimates of unknown model parameters, it is generally not sufficient to test for (theoretical) identifiability of the model (cf. [1]). Obviously, a further necessary condition for accurate parameter estimates is that the model frequency response shows a high sensitivity with respect to the parameters [11]. The relative parameter sensitivity of the magnitude of $Z_F(j\omega)$ to each parameter $p_i$ is easily obtained numerically [11]

$$S_i(\omega) = \text{abs}\left(\frac{d}{dp_i}|Z_F(j\omega)| \cdot \frac{p_i}{|Z_F(j\omega)|}\right).$$ \hspace{1cm} (3.13)

In addition, the correlation between the parameters must be low in the investigated frequency range.

### 3.3.2 Penetration Depth and tpb Width

Consider a porous Pt electrode of thickness $L$ (cf. Fig. 3.1a). So far we have only stated that the finite difference approach will be employed for the treatment of the diffusion equation [12-14]. But we have neither fixed the distance up to which we intend to discretize the surface nor have we fixed the width of the surface compartments (especially the tpb compartment). We have also not yet decided how many compartments we should use for this purpose. The first question is generally treated with the concept of the Nernst diffusion layer thickness or penetration depth, $\delta$ [14-16], whereas the remaining questions must be treated with intuition and physical insight.

It was stated above that there are two concentration boundary values, not determined by surface diffusion: $x_1(t)$ at $z = 0$ and $x_0$ at $z \to \infty$. In a strictly mathematical sense, concentration perturbations at the interface, i.e. due to an applied overpotential, have an effect up to an infinite distance from the interface. In practice, however, there is a limit beyond which changes can be neglected. This value is generally set to $6\delta$ where $\delta = \sqrt{D\tau}$ and $\tau$ is the experimental time interval [14, 16]. This approach works fine for time-domain simulations but may it also help for simulations in the frequency-domain, i.e. for electrochemical impedance simulations?
3.3 Simulation Procedures

Fig. 3.2 Temperature dependence of $\omega_{\text{max}}$. —The definition of $\omega_{\text{max}}$ can be seen in the inset of the figure. The maximum of $-\text{Im}[Z_F(j\omega)]$ was determined as a function of $T$ and $p_{O_2}$. The quantitative relation between $\omega_{\text{max}}$ and $T$ is given within the figure. The parameters given in Table 3.1 were used. The inset shows a typical Faradaic impedance in the complex plane obtained at $T = 973$ K and $p_{O_2} = 10^5$ Pa. A perfect $p_{O_2}^{1/2}$ dependence is found for $\omega_{\text{max}}$ at constant temperatures from 773 K (500°C) to 1073 K (800°C) (not shown).

\[
\omega_{\text{max}}/(\text{rad}\cdot\text{s}^{-1}) = \exp[21.11 - 117.6 \times 10^3 \text{ K}/(RT)]
\]

$p_{O_2} = 10^5$ Pa
Analytical solutions for the Faradaic impedance are available if one-dimensional surface diffusion (semi-infinite medium; without adsorption) is present [15]. A classical Warburg impedance is obtained at high frequencies and a perfect semi-circle is found at low frequencies in the complex plane (see inset of Fig. 3.2). The frequency of the maximum value of the imaginary component, $\omega_{\text{max}}$, is related to $\delta$ by the expression $2/\sqrt{\pi} = \delta \cdot \sqrt{\omega_{\text{max}}/(2D)}$ [15]. We have obtained simulations for $Z_F(j\omega)$ with the parameters given in Table 3.1 from $T = 773 \text{ K (500°C)}$ to $1173 \text{ K (900°C)}$ and $p_{O_2} = 10^5 \text{ Pa to 1 Pa}$ for a fixed value of $w = 10 \text{ nm}$. The temperature dependence of $\omega_{\text{max}}$ is shown in Fig. 3.2. A $p_{O_2}^{1/2}$ dependence of $\omega_{\text{max}}$ is found by simulation over the temperature range, which was found by others experimentally [15, 17]. Thus having found an expression for $\omega_{\text{max}}$ and $\delta$, we limit the space discretization to $6\delta$ as described above.

Once $\delta$ is determined, we are left with the question about the number of compartments and the size of the tpb compartment. The number of space elements required for a successful simulation can be reduced drastically by using a space grid with small space elements in the region near the electrode/electrolyte interface. Joslin and Pletcher [14] and Feldberg [18] have discussed some suitable transformation functions for the space variable with regards to computing time. The function of Feldberg is an exponentially expanding sequence of box widths. We use increasing compartment sizes which expand according to a geometric series with a constant factor $q$. With $1.5 \leq q \leq 2$ this transformation is close to the proposed transformations from Feldberg and Joslin and Pletcher, but without making the implementation more difficult. Thus, as soon as we fix the value for the tpb compartment, the number of compartments can be determined from the length $6\delta$ and the condition for $q$.

There has been much debate about the extension of the tpb of Sr-doped LaMnO$_3$ cathodes on YSZ (see e.g. [19, 20]). There is agreement that the electrode conductivity of these electrodes is approximately proportional to the length of the tpb at zero or low overpotentials. For higher cathodic overpotentials, the extension of the tpb is believed to increase due to the occurrence of mixed conductivity of the cathode at the interface [21]. Similarly, a proportionality between the electrode conductivity $\sigma_e$ and the length of the tpb has been determined for porous Pt electrodes on YSZ [22, 23]. It is clear that mixed conduction in noble metals can be ruled out. However, the ideas about the extension of the tpb of electronically conducting electrodes (LaMnO$_3$ at equilibrium potential and noble metals) are sparse. Wang and Nowick [24]
proposed a model where oxygen is supplied by surface diffusion towards the tpb and subsequently diffuses laterally in the two-phase region between the electrode and electrolyte. But, from the rather low solubility and diffusion coefficient of oxygen in bulk Pt [25], we expect this contribution to be negligible at bonded (i.e. sintered) interfaces between Pt particles and YSZ. In addition, this model is rejected by others [15, 26]. Thus, we are left with the picture that adsorbed oxygen is reduced and incorporated near the tpb.

From the modelling point of view it can be assumed that the electron transfer reaction takes place in the tpb compartment of width $w$. It is thereby not relevant whether the real process takes place on the Pt surface, between the Pt grain and the YSZ surface, on the YSZ surface, or whether a combination of these possibilities takes place. The model accounts for the reaction irrespective of its location. However, the Faradaic current $I_F$ is proportional to the active area $A_a = l_{tpb} \cdot w$ and to the electrochemical rate constants. We feel intuitively that doubling $w$ should doubling the current, and therefore halve the polarization resistance $R_p$. But what happens, if we keep the product $w \cdot k_{1c}$ constant and change, for example, the value for $w$ in a certain range? If the Faradaic impedance $Z_F(j\omega)$ was independent of the choice of $w$ (at least for a certain range and when the constraint is applied), we would be released from the task to assign a value to $w$. In this case we would state that there exists a strong correlation between $w$ and $k_{1c}$. Let us first consider $Z_F(j\omega, p)$ of model M1 [1]

$$Z_F(j\omega, p) = R_t \left[ 1 + \frac{k_f + k_b}{j\omega + 4k_{ad}N_0P_{O_2}\cdot(1 - \hat{x}) + 4k_{des}N_0\cdot\hat{x}} \right]$$

(3.14)

where

$$R_t^{-1} = 4N_0F \cdot w \cdot l_{tpb} \cdot [(1 - \beta)f \cdot k_b \cdot (1 - \hat{x}) + \beta f \cdot k_f \cdot \hat{x}]$$

(3.15)

It is immediately seen that $R_t$ is insensitive to changes of $w$, if the product $w \cdot k_{1c}$ is kept constant (note that $k_b$ is expressed in terms of $k_f$ and remember the definition of $k_f$). However, the fraction within Eq. (3.14) is strongly sensitive to changes of $w$ if $w \cdot k_{1c} = const$. It is not a priori clear how the behaviour of model M2 will be. Certainly, $R_t$ will exhibit the same properties as in M1. The sensitivity of $Z_F(j\omega)$ with respect to $w$ should be investigated numerically.
In absence of detailed information we set \( w = 10 \) nm for the moment. We assume \( w \) to be independent of temperature and oxygen partial pressure. With \( l_{\text{tpb}} \) in the order of \( 1 \mu m/\mu m^2 \), the active area will be in the order of 1% of the apparent electrode area which seems to be in a reasonable range. The problem will be examined numerically below.

### 3.3.3 The Double Layer Capacitance

While it is clear that electrodes in SOFC do exhibit capacitive behaviour, little attention has been paid to the nature and the magnitude of the double layer at the electrode/solid electrolyte interface. In addition, there has been some confusion in the literature about the terms ‘double layer capacitance’ and ‘pseudo-capacitance’. We believe that equivalent-circuit models have contributed to this confusion. We will give a brief description of the physical phenomena which lead to the occurrence of “capacitive” behaviour and we will estimate its order of magnitude for a real porous Pt cathode.

First, we expect a double layer capacitance at the metal/solid electrolyte interphase. For the moment, we consider the interface as blocking for electrons and oxygen ions. It is generally agreed that the measured capacitance \( C_{\text{dl}} \) of metal/solid electrolyte interphases is a series combination of a diffuse layer capacitance \( C_d \) and an inner layer capacitance \( C_i \), since there is a minimal distance between the oxygen ions and the Pt ions (assuming a sharp boundary between the metal and the electrolyte) [27–30]. The inner layer capacitance is generally estimated from [28]

\[
C_i = A_\phi \cdot A_{\text{cov}} \cdot \varepsilon_0 \varepsilon / r \quad (3.16)
\]

where \( A_\phi \) is the apparent electrode area, \( A_{\text{cov}} \) is the electrolyte coverage with electrode material, \( \varepsilon_0 \) is the permittivity of vacuum, \( \varepsilon \) is an effective dielectric constant (of order 1), and \( r \) is the distance between the metal electrode and the centres of the oxygen ions (a few tenth of a nanometer). \( C_i \) should therefore be between (1 to 10) \( \mu F/cm^2 \). It is expected to be independent, or a slowly varying function, of interfacial potential. Since the concentration of oxygen vacancies in YSZ is fixed by the content of yttrium, the effect of temperature is to increase the ionic mobility. However, \( \varepsilon \) and \( r \) could be dependent on the potential and/or the temperature.
For the case of completely blocking electrodes without specific adsorption (of oxygen ions at the metal–solid electrolyte interface), the diffuse double layer is described by \( z^+ = z^- \) \[ 31 \]

\[ c^- A - 4 - ° \cdot \cdot \cdot - m) \] \( 3.17 \)

where \( \Phi_0 \) is the potential at the interface \((x = 0)\) measured relative to \( \Phi \) at \( x = \infty \), \( L_D \) is the Debye length (i.e. the extension of the perturbation in concentration into the electrolyte due to the electric field), and the other symbols have their usual meaning. The Debye length is given by

\[ L_D = \left( \frac{\varepsilon \varepsilon_0 RT}{2z^2 F^2 c_i^0} \right)^{1/2} \] \( 3.18 \)

where \( c_i^0 \) is the concentration of mobile ions. However, the theory of diffuse double layers assumes mobile point charges and relatively low concentrations of ionic species. Robertson and Michaels \[ 32 \] have discussed the possibility of a diffuse double layer in YSZ in terms of Eqs. (3.17) and (3.18). They estimated values for \( L_D \) between 2.85 nm at 968 K (695°C) and 15.4 nm at 828 K (555°C). The authors stated that their experimental results were in disagreement with this theory. In addition, since the concentration of oxygen ions in YSZ is high, it is unlikely that any diffuse layer effects will contribute to \( C_{dl} \). Using a typical oxygen vacancy concentration of \( 4.6 \cdot 10^3 \) mol/m\(^3\) we obtain a Debye length of \( \approx 0.015 \) nm at \( T = 1000 \) K. Thus it is assumed that \( C_{dl} \) is essentially determined by the inner layer capacitance. This implies that the value of \( C_{dl} \) should be basically independent of temperature, oxygen partial pressure, and applied overpotential. \( C_{dl} \) should, however, be dependent on the coverage of the electrolyte surface with the noble metal. In addition, there may be some specific adsorption of oxygen ions at the metal/solid electrolyte interface be present.

There are few reports on the investigation of double layer capacitances of porous metal electrodes on YSZ solid electrolytes. Robertson and Michaels \[ 32 \] have given a summary of the values which can be found for Pt electrodes in the literature. The values are in the range of 30 \( \mu F/cm^2 \) to 350 \( \mu F/cm^2 \) at temperatures between 673 K (400°C) to 1073 K (800°C). These values were obtained by fitting equivalent circuits to experimental EIS data. Obviously,
these values are too high to account for pure inner layer capacitances. In contrast, Robertson and Michaels itself have reported rather low values between 0.3 µF/cm² and 1.3 µF/cm² from potential step chronoamperometry [32]. They fitted experimental current-decay curves to the equivalent circuit shown in Fig. 3.3a. The authors have claimed that the initial current after a potential step should decay exponentially with a time constant of \( \tau = \frac{C_{dl}R_e}{R_p} \) when the polarization resistance of the electrode, \( R_p \), is much larger than the uncompensated electrolyte resistance \( R_e \). From an evaluation of the eigenvalues of the equivalent circuit shown in Fig. 3.3a and Fig. 3.3d we see that the proposed relation between \( \tau \) and \( C_{dl} \) is approximately met if \( R_t \geq 2R_e \) (cf. 3-A.2). The condition \( R_p \gg R_e \) is a necessary one. Unfortunately, the first condition is rarely fulfilled experimentally even at relatively low temperatures [33]. We believe that the estimated \( C_{dl} \) values from Robertson and Michaels are a factor of 2 to 10 too low (see 3-A.2).

Higher electrode capacitances (between ~0.1 mF/cm² to 1 mF/cm², usually termed "pseudo-capacitances" [19]) are usually obtained by fitting experimental data to equivalent circuits of the type shown in Fig. 3.3b (see also Tab. 1 in [32], and [19, 34]). These high values have been attributed to the presence of a double layer between the metal surface and an adsorbed layer of oxygen atoms or ions. Assuming a complete coverage of the metal surface with atomic \( O_{ad} \) species of radius ~0.06 nm, we obtain (Eq. (3.16)) a capacitance of ~18 µF/cm². Smaller coverages imply smaller values. Note that for this capacitance contribution the Pt surface area is of relevance. Typical values for porous Pt electrodes are in the range of few cm² (thickness < 50 µm).

Vayenas et al. have proposed that an "effective electrochemical double layer" is established due to backspillover of oxygen ions \( O_{ad}^{-} \) from the tpb [35]. These ions spread over the metal surface and are accompanied by their compensating (screening) charge in the metal, thus forming surface dipoles [36]. With XPS the authors found two types of chemisorbed oxygen on Pt surfaces, subject to a prolonged anodic current treatment. If these surface ions contribute to the double layer capacitance, experimentally determined values for \( C_{dl} \) should be dependent on the surface area of the porous electrode (i.e. its thickness and microstructure), on the applied overpotential, and on the temperature, because the equilibrium concentration of adsorbed atomic oxygen on Pt strongly decreases with increasing temperature. However, values below 100 µF/cm² are expected for typical porous Pt electrodes.

There is considerable experimental and theoretical evidence that capacitance values above 100 µF/cm² are almost exclusively caused by Faradaic proc-
3.3 Simulation Procedures

Fig. 3.3 Electrical equivalent circuits for fitting experimental EIS data.—(a) Simplest circuit to account for the electrolyte resistance $R_e$, the electrode resistance $R_p$ and the double layer capacitance. (b) Circuit often found in the literature to fit experimental impedance data where two semi-circle or one broad semi-circle is observed. Numerical fit leads to capacitances in the order of (0.1 to 1) mF. (c) “Equivalent circuit” proposed to determine $C_{dl}$, $R_e$, and $R_t$. No assumptions are necessary for the concentration impedance $Z_c(j\omega)$. (d) Simplified version of circuit shown in (c). The circuit may account for depressed semi-circles or broad semi-circles in the complex plane.
esses [37, 38]. The occurrence of this behaviour can be easily understood in terms of the dynamic properties of these cathode/solid electrolyte systems, as we have shown in part I [1]. These Faradaic processes take place on the metal surface and near the tpb, i.e. they occur in parallel to the double layer charging. This justifies the proposed general equivalent circuit shown in Fig. 3.3c. A blocking interface would simply consist of the electrolyte resistance in series with the double layer capacitance. The splitting of $Z_F(j\omega)$ into a series combination of the charge-transfer resistance $R_t$ and the concentration impedance $Z_\theta(j\omega)$ has been justified in part I. In model M1 we determined a capacitance

$$C = \left(4k_{ad}N_0p_{O_2}(1 - \hat{\theta}) + 4k_{des}N_0\hat{\theta}\right)^{-1},$$

which obviously depends on the rates of adsorption and desorption, as well as on the steady-state concentration of adsorbed atomic oxygen, $\hat{\theta}$. We immediately see that $C$ increases with decreasing oxygen partial pressure which is in contradiction to the idea of "pseudo-capacitances" (decreasing $p_{O_2}$ lead to lower surface coverages). Note that the occurrence of this capacitive behaviour is entirely caused by the dynamics of the oxygen reduction at the interface. However, if experimental data are fitted with an equivalent circuit of the type shown in Fig. 3.3b it is expected that high values for $C_{dl}$ will be estimated. But, as we stated in part I, parameter estimation requires that the proposed model may reasonably well describe the behaviour of the real system. Fitting inappropriate model structures to experimental data will give erroneous parameters or even parameters without any physical relevance, even if the "fit quality" is excellent! The use of equivalent circuits of the type shown in Fig. 3.3b is discouraged.

We have put some emphasis on this point for two important reasons.

(i) We must be aware of the fact the dynamic properties of the electrode/electrolyte interface are reflected by the Faradaic impedance $Z_F(j\omega)$. The experimentally determined impedance $Z(j\omega)$ is always obscured by the double layer capacitance, as we have shown above. For a discussion of the properties of the interface it is therefore required to obtain $Z_F(j\omega)$ from $Z(j\omega)$. Fitting experimental data to an equivalent circuit may give completely wrong estimates for $C_{dl}$ and
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$R_t$, because we first have to choose an equivalent circuit. Unfortunately, we do not know whether the structure of the chosen circuit is appropriate or not. In addition, simple equivalent circuits can never fully account for the complex reaction mechanism which is a further source of error. We have already mentioned that Berthier et al. [39] have proposed a method which allows for the determination of $C_{dl}$ without assuming an equivalent circuit.

(ii) The second important point is to recognize that an accurate estimation of $C_{dl}$ is a mandatory prerequisite to obtain accurate values for the charge-transfer resistance $R_t$. An accurate estimate of $R_t$ is required if one aims to carry out a parameter estimation on the experimental data. For M1 and M2 we have shown that these models are not globally identifiable with EIS if $R_t$ is not known [1]. This statement can be generalized as follows: if $R_t$ can not be determined independently, we are losing one (important) equation in the parameters. This fact generally drastically decreases the global identifiability of a system. We will illustrate these points in the following section.

3.3.4 Digital Simulation and Numerical Aspects

The simulations were obtained by running version 4.2c of MATLAB and version 1.3c of SIMULINK on a Sun SPARCstation 20 running the Solaris 2.4 operating system. The MATLAB Optimization and Control System Toolboxes were used in addition. However, most of the simulations can be run with reasonable speed on a mid-range personal computer using the student editions of MATLAB and SIMULINK. It is beyond the scope of this paper to discuss in depth the details of MATLAB and SIMULINK. However, with a basic familiarity of the programs and together with the information given in the appendices 3-A.3 and 3-A.4 it should be possible to re-implement the models and to run simulations. We believe that this is a good starting point to write own programs. The following information is addressed to the reader familiar with the programming environment.
We encountered stability problems during simulation of the time dependent behaviour when using an inappropriate integration (e.g. Runge-Kutta or Euler method) algorithm due to the stiffness of the mass balance equation. By using the “gear” method with appropriate step sizes we were able to circumvent these problems. Steady-state values for the state variables were reliably determined with the Simulink function “trim” for any physically reasonable values of the overpotential $\eta$. Appropriate starting values for $x$ and $y$ were given while $u$ was fixed. The state-space vector determined with “trim” was used for the extraction of linearized state-space models with the Simulink function “linmod” at the corresponding operating point. The default perturbation level of $10^{-5}$ was used. Different levels could be set to probe for the validity of the linear regime. The conditioning of the system was achieved through the scaling of the state variables with the maximum number of adsorption sites, $N_0$. The values for the input and output quantities were in the range of unity for the chosen geometry, thus no further scaling of these values was necessary. The condition number of matrix $A$ obtained with the MATLAB function “cond” was generally below $10^4$, indicating that the problem was well conditioned ([40], p. 1–66). Frequency response data were obtained with the MATLAB functions “bode” or “nyquist”. Numerical estimates for the inverse polarization resistance $R_p^{-1}$ were conveniently obtained with the Control Toolbox function “dcgain”.

### 3.4 Simulation Results

#### 3.4.1 Charge-Transfer Controlled Kinetics

**Exchange current density $i_0$.** Experimental results obtained on the system Pt, O$_2$(g) | YSZ at high temperatures (above ~1123 K (850°C)), high $p_{O_2}$, and zero to moderate cathodic overpotentials indicate that the oxygen reduction under these conditions is charge transfer controlled [9, 10, 41, 42]. We can expect such a behaviour if the concentration of adsorbed atomic oxygen near the tpb is independent of the current through the interface. This occurs if the rate of surface diffusion and/or the rate of dissociative adsorption is fast compared to the electron transfer rate near the tpb. We assume for the moment that the electrode kinetics is charge-transfer controlled over a broad range of temperatures.
If, and only if, the electrode reaction is dominated by the charge-transfer process at the tpb, then the following holds (with \( n = 2 \) and \( v = 1 \) [1])

\[
i_0 = \frac{RT}{2F} \cdot \frac{1}{R_t(\eta = 0)}
\]  

(3.20)

where \( R_t(\eta = 0) \) is the charge transfer resistance at equilibrium potential. If Eq. (3.20) applies, the electrode properties can either be described by \( R_t \) or \( i_0 \). A quantitative expression relating the exchange current density \( i_0 \) with the oxygen partial pressure at \( T = T^\circ \) as well as at arbitrary temperatures is given in part I of this paper [1]. At \( T = T^\circ \) the expressions reads as

\[
i_0(T^\circ, p_{O_2}) = 2N_0Fk_1c^o[V_0] \cdot \frac{K(T^\circ)}{1 + K(T^\circ) \cdot \sqrt{p_{O_2}}} \cdot p_{O_2}^{(1-\beta)/2}.
\]  

(3.21)

Fig. 3.4 shows the calculated dependence of \( i_0 \) on oxygen partial pressure and on temperature. A similar behaviour was obtained experimentally by a number of authors [9, 43, 44]. They found approximately a \( p_{O_2}^{1/4} \) dependence of \( i_0 \) at low oxygen partial pressures and a \( p_{O_2}^{-1/4} \) dependence at high oxygen partial pressures. This follows immediately from Eq. (3.21) with \( \beta = 1/2 \). The one-quarter dependence of \( i_0 \) on \( p_{O_2} \) was first analytically obtained by Wang and Nowick [9]. However, they assumed \( \beta = 1/2 \) and they considered the Langmuir equation \( \theta/(1-\theta) = K(T)\sqrt{p_{O_2}} \) under the limiting conditions of \( \theta \to 0 \) and \( \theta \to 1 \) (see [9] for details). From the available data on oxygen adsorption on Pt it is questionable whether these limiting conditions are reached under the experimental situations considered [33]. However, the one-quarter dependence is also obtained without the simplifications of the Langmuir equation, as we have shown in part I. Note that the \( p_{O_2} \) dependence is also a function of the charge-transfer coefficient \( \beta \). This property has not yet been stated in the literature. A measurement of \( i_0(p_{O_2}) \) may reveal the value of \( \beta \) accurately and uniquely.

The oxygen partial pressure where the maximum of \( i_0 \) occurs, \( p_{O_2}^* \), decreases with decreasing temperature (Fig. 3.5). It is given by [1]

\[
p_{O_2}^* = \frac{1 - 2\beta + \beta^2}{\beta^2K(T)^2} = \left[ \frac{1 - \beta}{\beta K(T)} \right]^2.
\]  

(3.22)
It is seen that the temperature dependence of $p_{O_2}^*$ is determined by $K(T) = \sqrt{k_{ad}(T)/k_{des}(T)}$ as long as $\beta$ remains constant over the temperature range considered. It is also seen that the value of $p_{O_2}^*$ is rather sensitive

![Graph showing the relation between the exchange current density $i_0$ and the oxygen partial pressure. The temperatures (K) are given within the figure. The parameters and rate constants given in Table 3.1 (appendix 3-A.1) were used for the simulation. Note that $\beta = 0.62$.](image)

Fig. 3.4  Relation between the exchange current density $i_0$ and the oxygen partial pressure.—The temperatures (K) are given within the figure. The parameters and rate constants given in Table 3.1 (appendix 3-A.1) were used for the simulation. Note that $\beta = 0.62$. 
3.4 Simulation Results

Fig. 3.5 Dependence of $i_0$ on the charge transfer coefficient $\beta$. The simulation was obtained for $T = 900$ K with the same parameters as in Fig. 3.4. $p_{O_2}^*$ denotes the oxygen partial pressure where the maximum value of $i_0$ occurs.

The dependence of $i_0$ on $p_{O_2}$ for different values of $\beta$ is shown in the figure. The equation $p_{O_2}^* = \frac{(1 - \beta)^2}{\beta^2 K^2}$ is used to determine the oxygen partial pressure where the maximum value of $i_0$ occurs.

To the value of $\beta$ (cf. Fig. 3.5), Eq. (3.22) simplifies to the well known result of $p_{O_2}^* = K(T)^{-2}$ with $\beta = 1/2$ [44].

In the literature, the experimentally obtained temperature dependence of $p_{O_2}^*$ was employed for the determination of the heat of oxygen adsorption $\Delta H_{ad} = E_{ad} - E_{des}$ [44, 45]. Note that $E_{ad}$ and $E_{des}$ are strongly dependent on the surface coverage of Pt with atomic oxygen (see e.g. [46]). From the Langmuir equation it is easily seen that the surface coverage where the maximum of $i_0$ occurs is given by

$$\theta^* = \frac{K(T)\sqrt{p_{O_2}^*}}{1 + K(T)\sqrt{p_{O_2}^*}}$$

(3.23)

which gives by use of Eq. (3.22) the simple result of

$$\theta^* = 1 - \beta.$$  

(3.24)
Only in case where $\beta = 1/2$ we have $\theta^* = 0.5$ [47]. However, if $\theta \geq 0.2$, $\Delta H_{ad}$ becomes almost independent of surface coverage [48] and we can consider the activation energy obtained from an Arrhenius plot of $p_{O_2}^*$ as a good estimate of the oxygen adsorption enthalpy $\Delta H_{ad}$ at high Pt surface coverages, i.e. at $\theta = \theta^*$. We would like to mention that the values determined for $\Delta H_{ad}$ by Okamoto et al. [44] and Mizusaki et al. [45] differ by about 50 kJ/mol. It is important to note that Eq. (3.22) was derived from an expression relating $i_0$ with experimental quantities (Eq. (3.21)). Mizusaki et al. determined $\Delta H_{ad}$ from the electrode conductivities $\sigma_e = R_p^{-1}$, whereas Okamoto et al. based their analysis on measured exchange current densities. We will show below that $i_0^*$ is generally not located at the same $p_{O_2}$ as $\sigma_e^*$, therefore an Arrhenius plot of $p_{O_2}(\sigma_e^*)$ will not yield $\Delta H_{ad}$.

Finally, the temperature dependence of $i_0$ is investigated. Fig. 3.6 shows isobaric Arrhenius plots of $i_0$. With decreasing temperature, the isobars show breaks to steeper slopes, which occur at a higher temperature the higher the $p_{O_2}$. Note that only $i_0(p_{O_2}^*)$ shows a straight line and that the corresponding activation enthalpy for charge transfer is given by

$$\Delta H_{ct}^* = (1 - \beta) \cdot E_a^1 + \beta \cdot E_a$$

(3.25)

where $E_a^1$ and $E_a$ are the activation energies for the forward and backward electrochemical reaction, respectively. The result in Eq. (3.25) is easily obtained from the general expression $i_0(T, p_{O_2})$ given in part I by replacing $p_{O_2}$ with the expression given in Eq. (3.22). For arbitrary $p_{O_2}$ we find a limiting apparent activation enthalpy at low $p_{O_2}$ with $K(T)\sqrt{p_{O_2}} << 1$, and similarly at high $p_{O_2}$ with $K(T)\sqrt{p_{O_2}} >> 1$. In the first case we obtain

$$\Delta H_{\phi, ct}^{low} = \Delta H_{ct}^* - \frac{(1 - \beta)}{2} \cdot \Delta H_{ad}$$

(3.26)

whereas in the second case

$$\Delta H_{\phi, ct}^{high} = \Delta H_{ct}^* + \frac{\beta}{2} \cdot \Delta H_{ad}.$$  

(3.27)

The transition between the limiting $p_{O_2}$ regimes, as well as the limiting behaviour of $i_0(p_{O_2})$ is clearly seen in Fig. 3.6. With $\beta = 1/2$ we obtain the same results as developed by Wang et al. and by Velle et al. [9, 10]. A behav-
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The behaviour of \( i_0(p_{O_2} = \text{const}) \) with temperature similar to the one shown in Fig. 3.6 was found experimentally [9, 49]. With the parameters given in Table 3.1 we obtain \( \Delta H_{ct}^* = 131 \text{ kJ/mol} \), \( \Delta H_{\phi, ct}^{\text{low}} = 99 \text{ kJ/mol} \), and \( \Delta H_{\phi, ct}^{\text{high}} = 183 \text{ kJ/mol} \). Wang et al. [9] found \( \Delta H_{\phi, ct} = 96 \text{ kJ/mol} \) from the temperature dependence of \( i_0(p_{O_2}) \), and Velle et al. [10] determined \( \Delta H_{\phi, ct}^{\text{high}} = 199 \text{ kJ/mol} \) from the temperature dependence of \( R_t(p_{O_2}, T) \) (equivalent circuit fitting of EIS data was used). Both authors used a relatively high value for the adsorption enthalpy, \( \Delta H_{ad} = 294 \text{ kJ/mol} \). However, a relatively large discrepancy exists between the reported values for \( \Delta H_{ct}^* \) (Ref. [9]: 170 kJ/mol; Ref. [10]: 126 kJ/mol) which is attributed to the large value used for \( \Delta H_{ad} \). Using a more probable value for the adsorption enthalpy \( \Delta H_{ad} \) in the range of \( \sim 180 \text{ kJ/mol} \) [48], this discrepancy diminishes and \( \Delta H_{ct}^* \) is obtained in the order of 140 kJ/mol.

In summary, \( \Delta H_{ct}^* \) can be obtained experimentally. The charge-transfer coefficient \( \beta \) can be obtained from \( i_0(p_{O_2}) \) data at high temperatures (cf. Fig. 3.4). Unfortunately, Eq. (3.25) is now not sufficient to estimate uniquely the activation energies of the charge-transfer reaction, \( E_a^1 \) and \( E_a^1 \). It is expected, however, that both values are not too far apart. Estimates of \( \Delta H_{ad} \) are available through Eqs. (3.26) and (3.27). For reasons which will become clear below it is suggested that \( R_t \) data are employed rather than \( i_0 \) estimates.

Electrode polarization and experimental determination of \( i_0 \). So far we have assumed that the reaction is charge-transfer controlled over a broad range of temperatures. In this case, the exchange current density \( i_0 \) and the charge-transfer coefficient \( \beta \) determine the overall electrode characteristics. In solid state electrochemistry it has been common practice to obtain both values from a Tafel-plot analysis of \( I_p(\eta) \) data. However, the parameters obtained from this analysis are only meaningful, if one charge-transfer (or one chemical) step is actually rate determining the overall electrode reaction [1, 50, 51]. But how can we test whether this requirement is fulfilled under the experimental conditions considered? The problem will be examined below and we will propose a method in the following subsection which may uniquely clarify whether an electrode reaction is controlled by a charge-transfer step or not. We use the parameters of Table 3.1 with two important modifications: \( k_{1c} = 2 \cdot 10^5 \text{ m}^3/(\text{mol} \cdot \text{s}) \) and \( E_d = 110 \text{ kJ/mol} \).
Fig. 3.6  Isobaric Arrhenius plot of $i_0$ at different oxygen partial pressures. —Analytical expressions for the charge transfer activation enthalpy at $p_{O_2}^* = \Delta H_{ct}^*$, and the apparent activation enthalpies at low and high $p_{O_2}$, $\Delta H_{\phi,ct}^{low}$ and $\Delta H_{\phi,ct}^{high}$, are given in the text. The parameters of Table 3.1 were used. Note that $p_{O_2}^*(1100 \, K) = 10^5 \, \text{Pa}$. Compare with the simulations of Fig. 3.4.
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First, remember the general definition of the charge transfer resistance

\[ R_t^{-1} \equiv \left( \frac{\partial I_F}{\partial \hat{\eta}} \right) \hat{x}_i \quad (3.28) \]

where \( \hat{x}_i \) denotes the steady-state surface concentrations at the corresponding operating point (defined by \( \eta, T, \) and \( p_{O_2} \)). It is seen that \( R_t \) can be obtained at arbitrary operating points, whereas \( i_0 \) (Eq. (3.20)) gives only a description of an equilibrium situation (i.e. where \( \eta = 0 \) and therefore \( I_F = 0 \)). By considering Eq. (3.28) it seems that \( R_t \) could be obtained experimentally from a small-signal dc analysis around \( E_{eq} \) or around a steady-state overpotential, as it was done in the literature [44]. This is not generally the case, as Eq. (3.28) requires that the surface concentrations \( x_i \) remain constant. Such an analysis will reveal the polarization resistance \( R_p \) which is only equal to \( R_t \) if the reaction is charge transfer controlled. Similarly, we can strictly speak of a pure Tafel behaviour only if the concentration of surface species (in our case only \( O_{ad} \)) remains constant over the overpotential range where the analysis is conducted. However, surface concentrations can not be measured directly and therefore it is difficult to draw conclusions about the reaction mechanism from \( I_F(\eta) \) curves alone. In addition, it has been shown that an apparent Tafel behaviour may be caused by a competition between surface mass transport and charge transfer, if some requirements are satisfied [38].

Fig. 3.7 shows the simulated \( I_F(\eta) \) curves of M2 at 1123 K (850°C). It is seen that the \( I_F(\eta) \) behaviour at high \( p_{O_2} \) follows an ideal Tafel behaviour up to relatively low cathodic overpotentials of approximately \(-0.15\) V. Strong deviations from the purely charge-transfer controlled behaviour occur at larger overpotentials. The deviation from Tafel behaviour is shifted to lower cathodic overpotentials with decreasing \( p_{O_2} \). It is further seen that the \( I_F(\eta) \) curves follow an apparent Tafel behaviour at low cathodic overpotential (with apparently lower \( \beta \) than used for the simulation), indicating a competition between the charge-transfer process and a further reaction.

The reason for the deviation is easily found in the deviation of the surface concentration \( x \) from its equilibrium \( x_0 \) value near the \( tpb \). Fig. 3.8 shows the high \( p_{O_2} \) curve from Fig. 3.7 in a linear plot. Although the deviation from the Tafel behaviour is obvious, it would be difficult to recognize this without the given curve. The inset of Fig. 3.8 shows the behaviour of three surface concentrations at different distances from the \( tpb \). It is seen that the concentration
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of $O_{ad}$ near the tpb strongly decreases with increasing cathodic overpotential. This is the reason for the deviation from the ideal Tafel behaviour and for the occurrence of a concentration polarization. Note that we used a very high value for the surface diffusion coefficient to obtain this behaviour ($D = 3.55 \times 10^{-9} \text{ m}^2/\text{s}$). This also causes a very large diffusion layer of $\sim 10 \mu\text{m}$. Real values for $D$ are expected to be one to two orders of magnitude below this value at $T = 1123 \text{ K}$ [52]. In contrast to the simulations shown in Fig. 3.7, the real porous electrode/electrolyte system does not exhibit a limiting $I_F(\eta)$.
behaviour under the considered conditions. This is due to the fact that model M2 does not account for the strong coverage dependence of the adsorption and desorption rate. The sticking coefficient of O₂(g) on Pt may vary many orders of magnitude with surface coverage [46]. Accordingly, the adsorption rate should strongly increase with cathodic overpotential [33].

Let us, as it is often done in practice, perform a Tafel analysis on the simulated \( I_F(\eta) \) curves from \( \eta = -0.15 \) V to \(-0.35\) V. Fig. 3.9 shows some of the results. It is seen that the simulated \( I_F(\eta) \) curves follow an apparent Tafel

![Graph](image)

**Fig. 3.8** Deviation of \( I_F(\eta) \) from theoretical Tafel behaviour.—Linear plot of the data shown in Fig. 3.7 at \( p_{O_2} = 10^5 \) Pa. The filled circles show the simulated behaviour of M2 and the solid line denotes the ideal Tafel behaviour. The inset shows the corresponding surface concentrations as a function of the distance from the tpb and the applied overpotential \( \eta \). Note that the surface concentration gradient extends over \( \sim 10 \) μm.
line over the range of overpotentials considered. However, the estimated value for the charge-transfer coefficient $\beta$ decrease with $p_{O_2}$ and are all below the actual value of $\beta = 0.62$. Fig. 3.10 compares the theoretical results for $i_0$ with the ones estimated from the Tafel analysis. It is seen, although the values are rather close to each other, that the $p_{O_2}$ dependence of $i_0$ estimated from the Tafel analysis is completely different to the expected (theoretical) $p_{O_2}$ dependence. It can be further seen that a relative large number of measurements (or simulations) are necessary to reveal the $p_{O_2}$ dependence. It

![Figure 3.9](image.png)

**Fig. 3.9** Simulated $I_F(\eta)$ behaviour and Tafel analysis.—The Tafel analysis was obtained from the simulated $I_F(\eta)$ data from $\eta = -0.15$V to $-0.35$V. The results are given as $(\beta, i_0/\text{mA}\cdot\text{cm}^{-2})$ pairs within the figure. The value for $\beta$ in the simulation was 0.62. The same parameters as for the simulations in Fig. 3.7 were used.
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should be mentioned that the estimated values of $i_0$ are rather sensitive to the number of simulated data points used for the Tafel analysis.

We end this subsection with the following conclusions: first, an apparent Tafel behaviour of the $I_F(\eta)$ curve does not assure that the reaction kinetics is charge-transfer controlled. Second, Tafel parameters ($\beta$ and $i_0$) obtained from a Tafel analysis of $I_F(\eta)$ data may be far apart from the real values and an interpretation of these parameters will be questionable. Third, measurements of the $I_F(\eta)$ behaviour impose a large perturbation to the electrode/electrolyte system which may cause irreversible changes to the microstructure and/or the interfacial structure. Finally, $I_F(\eta)$ measurements reveal the least possible amount of information about an electrode/electrolyte system, which nevertheless, might be needed in combination with further electrochemical

Fig. 3.10 Comparison of theoretical and estimated $i_0$ values at $T = 1123$ K.—The open circles represent the estimated $i_0$ values from the Tafel analysis as described in Fig. 3.9. Note that the $i_0$ can not be compared with the data in Fig. 3.4 because the electrochemical rate constants differ by a factor of 10. The same parameters as for the simulations in Fig. 3.7 were used.
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methods, such as electrochemical impedance spectroscopy (cf. part I of this publication [1]).

Electrode impedances—determination of $R_t$ and $C_{dl}$. As mentioned above, electrochemical impedance measurements do not directly reveal the Faradaic impedance $Z_F(j\omega)$, but $Z(j\omega)$ which is concealed by a double layer capacitance $C_{dl}$ in parallel and the electrolyte resistance in series. However, EIS might be a way of assessing if there is only one, or if there are more rate limiting steps [51, 53]. Mogensen et al. have claimed that the presence of one semicircle (which is not too depressed), indicates that the rate of an electrode reaction is dominated by one single reaction step. Let us elaborate this statement by means of the reaction kinetics of model M2 at high temperatures and high oxygen partial pressures.

In Fig. 3.8 the simulated $I_F(\eta)$ behaviour of M2 at $T = 1123$ K and $p_{O_2} = 10^5$ Pa was shown. The corresponding simulated EIS spectra obtained at different operating points of the $I_F(\eta)$ curve are shown in Fig. 3.11. The $Z(j\omega)$ spectra at low to moderate cathodic overpotentials exhibit a (almost perfect) semicircle in the complex plane (Fig. 3.11a). With increasing cathodic $\eta$ the semicircle becomes depressed and finally, at $\eta < -0.3$ V, a second semicircle appears (Fig. 3.11b). Note that $Z_F(j\omega)$ can hardly be observed in the $Z(j\omega)$ plot (cf. inset of Fig. 3.11a). One should be aware of the fact that EIS measurements only reveal the $Z(j\omega)$ curves and that the information contained within $Z_F(j\omega)$ is not accessible immediately. For the simulation of the spectra in Fig. 3.11 we have assumed that a double layer capacitance is in parallel to the Faradaic impedance. We have taken a value of $C_{dl} = 20 \mu$F/cm$^2$. Obviously, if these spectra were measured and if we were interested in the reaction kinetics, we could analyse the spectra with a simple equivalent circuit and interpret the values obtained for the resistances and the capacitances. This might work well in this simple case, but it will certainly fail in more complicated cases. We therefore propose to continue as described below.

Fig. 3.12 shows two series of spectra, each series taken at different operating points of M2 but with different values for the double layer capacitance $C_{dl}$. The spectra show the Faradaic impedances $Z_F(j\omega)$ (thick lines) of a purely charge-transfer controlled reaction kinetics (figures on the left), a kinetics where charge-transfer is in competition with surface diffusion (figures in the centre), and a kinetics where surface diffusion is rate limiting (figures on the right). It is readily seen that it is almost impossible to come to these conclu-
Fig. 3.11  Simulated $Z(j\omega)$ of M2 shown in the complex plane.—The spectra were simulated at $T = 1123$ K and $p_{O_2} = 10^5$ Pa at the overpotentials given within the figure. The results can be directly compared with the $I_{F}(\eta)$ simulations given in Fig. 3.8. The numbers within the figure denote the frequency in Hz. The same parameters as for the simulation of the $I_{F}(\eta)$ curve in Fig. 3.7 were used. A double layer capacitance of $C_{dl} = 20 \mu F/cm^2$ was assumed. Note that the Faradaic impedances $Z_{F}(j\omega)$ at low cathodic overpotentials are almost invisible because $R_t \approx R_p$ (see inset of upper figure).
Fig. 3.12  Influence of double layer capacitance on appearance of \(Z(j\omega)\) spectra.—The bold curves show the Faradaic Impedance \(Z_F(j\omega)\) and the thin curves show the corresponding impedance \(Z(j\omega)\). The numbers within the figure denote the frequency in Hz. The high frequency intercept of \(Z_F(j\omega)\) with the real axis corresponds to the charge transfer resistance \(R_t\) and the low frequency intercept corresponds to the polarization resistance \(R_p\). The data are scaled with \(R_p\). The difference between the spectra in the upper row and the spectra in the lower row is the value of \(C_{dl}\). No electrolyte resistance was added.
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Fig. 3.13 Complex plane plot of simulated impedance data.—The parameters as given in Table 3.1 were used at $T = 1000$ K with $C_{dl} = 28 \mu F/cm^2$ and $R_e = 1.3 \Omega cm^2$. Weighted ($1/|Z|$) random noise of a maximum amplitude of 1% was added to the data. The inset shows the high frequency part of the spectra for decreasing values of $C_{dl}$.

sions from the impedance $Z(j\omega)$ spectra (thin lines). We further see that the actual value of $C_{dl}$ strongly influences the appearance of $Z(j\omega)$ and that the appearance of a single semicircle in the complex plane is by far not a sufficient condition that the reaction kinetics is governed by a single step (see [51]). We feel that it is necessary to determine the Faradaic impedance $Z_F(j\omega)$ rather than just the impedance $Z(j\omega)$, i.e. we need to know $C_{dl}$. We demonstrate a promising procedure in the following.

Fig. 3.13 shows a simulated impedance of M2 in the complex plane. A random noise is added to the spectra. The problem is to extract the Faradaic impedance from the given data without fitting the data to an equivalent circuit. The inset of Fig. 3.13 clearly shows the influence of a double layer capacitance on the $Z_F(j\omega)$. $R_t$ is expected to be in the order of 7 $\Omega$-cm$^2$ and $R_e$ is $\sim 1.3 \Omega$-cm$^2$. We apply the method proposed by Berthier et al. [39] on the impedance data. Fig. 3.14 shows the final result. The Faradaic impedance is obtained by subtracting $C_{dl}$ and $R_e$ from the impedance data. Once $C_{dl}$ is
Fig. 3.14 Determination of $Z_F(j\omega)$ from simulated noisy $Z(j\omega)$ data.—The method from Berthier et al. is used [39]. The electrolyte resistance is subtracted from the data. With $R_e = 1.3 \ \Omega \cdot \text{cm}^2$ a value of $C_{dl} = 28 \ \mu F/cm^2$ is estimated. The inset shows the "equivalent circuit" which describes $Z(j\omega)$. Note that $Z_\theta(j\omega)$ cannot be represented by an electric circuit.

estimated, $R_p$ and $R_t$ can be accurately estimated from the function $S'$ (equation (26) in [39]). $S'$ for the data set considered is shown in Fig. 3.15a. However, the method requires an accurate estimate of the electrolyte resistance $R_e$, as was also mentioned by Berthier et al. [39]. In practice $R_e$ is often not accurately known and it is estimated by extrapolating the high frequency impedance data towards the real axis. This may cause large errors in $C_{dl}$ and, therefore, in $R_t$ as shown in Fig. 3.15b. If $R_e$ is only approximately known one can run the algorithm for a series of electrolyte resistances around the expected value (Fig. 3.15b). We have done so for a large number of experimental [54] and simulated data and we have found that the shape of the $C_{dl}(R_e)$ function always looks like the one shown in Fig. 3.15b. Furthermore, from simulations we have found that the "true" value for $R_e$ is always located near to the maximum of the curve towards higher electrolyte resistances. This procedure helps to obtain a starting guess for $R_e$. Further refinement is achieved through an iterative search of the "optimal" $(C_{dl}, R_e)$ pair.
by optical inspection of the resulting spectra. In the following we will always give both the Faradaic impedance $Z_F(j\omega)$ and the impedance $Z(j\omega)$.

In conclusion, a Tafel analysis may give only meaningful parameters if the reaction kinetics is dominated by a single reaction step. Interpreting $\beta$ and, especially, $i_0$ is doubtful. EIS spectra alone do not generally help to clarify the question of single-step control. The double layer capacitance $C_{dl}$ must be determined and extracted from the EIS raw data. $R_e$ and, more importantly, $R_t$ are obtained with reasonable accuracy, where $R_t$ is related through $i_0 = (RT)/(2F) \cdot R_t^{-1}$ with the exchange current density $i_0$ (at arbitrary operating points). A discussion of $i_0$ data obtained in this way seems reasonable. Much information is contained within the Faradaic impedance, as further illustrated in the following section.

3.4.2 Competition Between Surface Diffusion and Adsorption

**Electrode conductivities.** At temperatures below $\sim 1073 \text{ K} (800^\circ \text{C})$ to $\sim 773 \text{ K} (500^\circ \text{C})$ and at oxygen partial pressures above $\sim 100 \text{ Pa}$, surface diffusion of atomic oxygen on the Pt surface is believed to be rate determining the overall electrode kinetics [10, 15, 45, 47, 55, 56]. Various analytical expressions describing the electrode conductivity, the $I_F(\eta)$ characteristics, and the electrochemical impedance have been presented in the literature. However, it has been always assumed that no adsorption takes place in parallel to the surface diffusion process. Under this assumption, a $p_O^1/2$ dependence has been derived for the electrode conductivity $\sigma_e = R_p^{-1}$ at low $p_O$. In the following we will obtain simulations for $R_t$ and $R_p$ as a function of $p_O$ and $T$ and compare the results with the preceding experimental results.

The relation between $R_t^{-1}$ and $R_p^{-1}$ as a function of $p_O$ is shown in Fig. 3.16 for temperatures from 773 K (500°C) to 1073 K (800°C). By use of Eq. (3.20) the exchange current densities $i_0$ can be obtained from $R_t$. The $i_0$ values correspond to those given in Fig. 3.4. The simulations give a picture which is in reasonable qualitative and quantitative agreement with the measurements of Mizusaki et al. (see Fig. 7 in [45]). The maxima of the log($R_p^{-1}$) versus log($p_O$) curves shift to lower $p_O$ with decreasing temperature. However, there are some differences that attain further attention.

First, the $p_O$ dependence of $R_p^{-1}$ is considerably stronger in the low $p_O$ region than in the high $p_O$ region. Fig. 3.17 shows the $p_O$ dependencies of $R_p^{-1}$ and $R_t^{-1}$. Note that not a clear $p_O$ is found for the conductivities, but
Fig. 3.15 Determination of $R_p$ and $R_t$ after subtraction of $C_{dl}$.—(a) Cost function $S'$ showing two maxima for $R_t$ and $R_p$. The definition of the function $S'$ can be found in [39] (Eq. (26)). (b) Dependence of $C_{dl}$ on the initial value of the uncompensated electrolyte resistance $R_e$. 
that the dependence varies continuously over more than one decade of $p_{O_2}^{-1}$. It is clearly seen that a $p_{O_2}^{3/4}$ dependence of $R^{-1}$ is found at low oxygen partial pressures. The reason for this can be found in the fact that dissociative oxygen adsorption of oxygen molecules and surface diffusion of atomic oxygen occur in parallel, even near the tpb. Analytical solutions describing the $p_{O_2}$

Fig. 3.16 Electrode conductivities as a function of temperature and oxygen partial pressure.—The temperatures (K) where the simulations were obtained are given within the figure. The data for $R_t$ and $R_p$ were obtained from the linearized state-space model M2 ((A, B, C, D) quadruple) at the corresponding operating point. The parameters given in Table 3.1 were used.
dependence of $Z_F(j\omega)$, and therefore also of $R_p$, can be found in [57]. Similarly at high oxygen partial pressures a minus one-quarter $p_O^2$ dependence of $R_p^{-1}$ is obtained, as can be seen in Fig. 3.17. It is further found (but not shown) that $R_p^{-1}(p_O^2)$ is almost independent of the charge transfer coefficient $\beta$, where in contrast, $R_t^{-1}(p_O^2)$ strongly depends on $\beta$ (cf. Fig. 3.5). Taking a closer look at the experimental $\sigma_e(p_O^2)$ data from Mizusaki et al. reveals that the $p_O^2$ dependence tends to be stronger than 1/2, especially at high temperatures (cf. Fig. 7 in [45]). Similar observations can be made on the early results from Fabry and Kleitz [58]. We again see that a relatively large number of measurements is necessary to reveal the $p_O^2$ dependence of the electrode conductivities, otherwise the information might get lost in the experimental errors.

A $p_O^2$ dependence of $R_p^{-1}$ has been reported for oxygen partial pressures below (10 to 100) Pa by a number of authors [59–61]. This is generally attrib-
3.4 Simulation Results

uted to gas phase diffusion of oxygen in the porous electrode network. Our model M2 can not account for this.

It has been claimed by Mizusaki et al. that the activation energy for O$_{ad}$ diffusion on Pt can be obtained from an Arrhenius plot of $R_p^{-1}(p_{O_2}^\dagger)$, if surface diffusion of O$_{ad}$ is determining the electrode kinetics. The authors have argued that $R_p^{-1}(p_{O_2}^\dagger)$ is where $\theta = 1/2$ and therefore the temperature dependence of the concentration term should be excluded. However, we have shown above that $R_t^{-1}(p_{O_2}^\star)$ results at $\theta^* = 1 - \beta$ and we see that $R_p^{-1}(p_{O_2}^\dagger)$ is located at higher $p_{O_2}$ than $R_t^{-1}(p_{O_2}^\star)$. From the simulations shown in Fig. 3.16 it is seen that the log($p_{O_2}$) difference between the two maxima is almost independent of temperature. Because $R_p^{-1}$ is virtually independent of $\beta$ and $p_{O_2}^\star$ for $R_t^{-1}$ is given by Eq. (3.22) (see also Fig. 3.5), we find that this distance decreases with decreasing values for $\beta$ (we find by simulation that $p_{O_2}^\star = p_{O_2}^\dagger$ at $\beta = 1/4$ for M2 and the other parameters as given in Table 3.1.

Fig. 3.18 shows the temperature dependence of $1/R_p$ at different $p_{O_2}$ from 723 K (450°C) to 1073 K (800°C). Note that $p_{O_2}^\dagger > 10^5$ Pa for $T > 1000$ K. It is seen that the slope of the log[$R_p^{-1}(p_{O_2}^\dagger)$] versus $1/T$ plot is approximately independent of temperature and the value of $\beta$ (not shown). We find an apparent activation energy of ~152 kJ/mol at high temperatures and a value of ~167 kJ/mol at lower temperatures. Mizusaki et al. determined a value of ~171 kJ/mol experimentally (see Fig. 10 in [45]). We assumed $E_d = 155$ kJ/mol and it is seen that the activation enthalpy of $R_p^{-1}(p_{O_2}^\dagger)$ does not correspond to the activation energy of surface diffusion. This becomes even more pronounced if a larger value for $\Delta H_{ad}$ in the simulation is used. It shows that the apparent activation enthalpy of $R_p^{-1}(p_{O_2}^\dagger)$ comes close to $\Delta H_{ad}$ at temperatures below ~873 K (600°C). The apparent activation energy of $R_p^{-1}(10^5$ Pa) is obtained as ~200 kJ/mol at lower temperatures (high surface coverage regime) and it changes to ~140 kJ/mol at higher temperatures. At low $p_{O_2}$ and high T (low surface coverage regime) we find a very low apparent activation energy of ~45 kJ/mol.

These simulation results can be easily explained by considering the temperature dependence of the concentration impedance $Z_\theta(j\omega)$ as introduced in

*) $p_{O_2}^\dagger$ is the oxygen partial pressure where the maximum of $\sigma_e$ is obtained; we use this notation in order to avoid confusions with $p_{O_2}^\star$ where the maximum of $R_t^{-1}$ is obtained. Note that Mizusaki et al. use the notation $\sigma_e^\star$ for expressing $p_{O_2}^\dagger$. 113
part I. From the two-compartment $Z_F(j\omega)$ transfer function of M2 we find the concentration resistance [1]

$$R_c = Z_\theta(\omega = 0) = R_t \cdot \frac{k_f + k_b}{\frac{1}{T_d} + 4k_{ad}N_0p_{O_2} \cdot (1 - \hat{x}) + 4k_{des}N_0 \cdot \hat{x}}.$$  \hspace{1cm} (3.29)

Remember the definitions of $T_d = S_2/(2D)$, $D = D_0\exp\left[(-E_d)/(RT)\right]$, $k_{ad} = \nu_{ad}\exp\left[(-E_{ad})/(RT)\right]$, and $k_{des} = \nu_{des}\exp\left[(-E_{des})/(RT)\right]$. Again, by expressing $k_b$ in terms of $k_f$ (see part I) it is seen that the temperature dependence of the product $R_t \cdot (k_f + k_b)$ cancels and we are left with a simple expression for the temperature dependence of $R_c$. We consider two limiting cases:

(i) low $T$ and high $p_{O_2}$ (high coverage: $(1 - x) \to 0$): surface diffusion vanishes (1. term of the denominator in Eq. (3.29)). We expand the remaining fraction of Eq. (3.29) with $1/k_{des}$ and obtain with $K(T) = \sqrt{k_{ad}/k_{des}}$ and $(1 - x) \to 0$ the following result:

$$\Delta H^h_\phi = E_{des}$$  \hspace{1cm} (3.30)

and with the parameters given in Table 3.1 $\Delta H^h_\phi = 200$ kJ/mol.

(ii) high $T$ and low $p_{O_2}$ (low coverage: $x \to 0$): proceeding as above and with $x \to 0$ we obtain:

$$\Delta H^1_\phi = E_{des} - E_d$$  \hspace{1cm} (3.31)

and, accordingly, $\Delta H^1_\phi = 45$ kJ/mol.

The simulation results are in excellent agreement with Eqs. (3.30) and (3.31). Obviously, the apparent activation energy may vary in between these two limiting values, as seen in Fig. 3.18 for the simulations of $R^{-1}_{p}(10^3$ Pa).

Let us finally consider the temperature dependence of $p_{O_2}^\dagger$ (cf. Fig. 3.19). An average apparent activation enthalpy of $\sim$150 kJ/mol is obtained over the temperature range considered. The value is slightly higher at lower tempera-
Fig. 3.18 Isobaric Arrhenius plots of electrode conductivity $R_p^{-1}$.—The parameters given in Table 3.1 were used for the simulation. The values for $R_p^{-1}$ were obtained from the linearized SSM at the corresponding operating point. The apparent activation enthalpies $\Delta H_\phi$ are given within the figure.

tures (158 kJ/mol) and decreases with increasing temperatures (~140 kJ/mol). The surface coverage of Pt is relatively high and remains not constant in the temperature range considered. Mizusaki et al. [45] determined an apparent activation enthalpy of ~220 kJ/mol for the maximum value of the electrode conductivity. Accordingly, a large discrepancy exists between our simulations and these experimental results. However, the reported result was obtained from a number of different measurements.
which itself exhibited a rather large mean variation (see Fig. 9 in [45]). It is questionable whether this large value can be attributed to $\Delta H_{ad}$, as was done by the authors.

We would like to point out two important differences between our model M2 and the model investigated by Mizusaki et al. [45, 47]. First, Mizusaki et al. assumed that the charge-transfer reaction was infinitely fast. However, we show below that this influence is significant in the temperature range consid-

![Graph](image)

**Fig. 3.19** Simulated temperature dependence of the oxygen partial pressure where the maximum of the electrode conductivity occurs.—The data were obtained from $R_p^{-1}(p_{O_2}, T)$ simulations by determining the maximum value for $R_p^{-1}$. The inset shows the corresponding equilibrium surface concentrations of adsorbed atomic oxygen.
3.4 Simulation Results

erved and at high oxygen partial pressures. Second, Mizusaki et al. made the following formulation for the surface diffusion coefficient: 

\[ D_0(\theta) = D_0 \theta (1 - \theta) \]

By use of this formulation we obtain simulation results which are in qualitative agreement with the results obtained before with the difference that the \( pO_2 \) dependence of \( R_p^{-1} \) vanishes at low temperatures \( T < 773 K (500°C) \) and high \( pO_2 \), as experimentally observed by Mizusaki et al. [45]. However, there can be no data found in the literature concerning the concentration dependence of the surface diffusion coefficient of \( O_{ad} \) on Pt. Accordingly, the proposed formulation seems rather arbitrary.

Electrode polarization. Fig. 3.20 shows simulation results for the \( I_F(\eta) \) behaviour at 973 K (700°C) at low cathodic and anodic polarizations. The results can be directly compared with the simulations and the experimental results of Mizusaki et al. (see Fig. 8 in [47] and Fig. 11 in [45]). There is good agreement between our simulations and reported results. We find limiting cathodic currents in the simulations at relatively high \( pO_2 \) of \( 10^3 \) Pa to \( 10^4 \) Pa. The reason for this can be found in the strong \( pO_2 \) dependence of the equilibrium concentration of \( O_{ad} \) in the model M2. To improve the model, the rate constants for the adsorption and desorption should be taken as a function of the surface coverage. It is known from adsorption studies that the initial sticking coefficient of \( O_2(g) \) on Pt surfaces may vary many orders of magnitude, depending on the Pt surface coverage (see e.g. [46,48]).

The inset of Fig. 3.20 shows the \( I_F(\eta) \) relation at small overpotentials and compares with the behaviour we would obtain if the reaction was charge transfer controlled. A large difference between these curves is seen even at these low overpotentials. Evaluating the slope of small signal dc curves at low overpotentials will therefore reveal the electrode conductivity \( R_p^{-1} \) and not the inverse charge-transfer resistance \( R_t^{-1} \). Only if the reaction kinetics is charge transfer controlled, i.e. \( R_t = R_p \), small signal dc analyses reveal \( R_t \). The difference between the two curves is attributed to a concentration polarization which can be clearly seen in the Faradaic impedance which is shown below.

More information about the rate limiting process is obtained from the \( pO_2 \) dependence of the limiting-current \( I_1 \). For the system Pt, \( O_2(g) \) | YSZ at high cathodic overpotentials, \( pO_2^1 \) and \( pO_2^{1/2} \) dependencies of \( I_1 \) have been found [9, 59, 61]. The stronger dependence is generally attributed to gas mass transport limitation whereas the weaker dependence is attributed to a surface diffusion limitation. However, clear relationships become apparent only at oxygen par-
tial pressures below $\sim 10^3$ Pa. Fig. 3.21 shows the simulated $I_\ell(p_{O_2})$ behaviour of M2 from 873 K (600°C) to 1073 K (800°C). A clear $p_{O_2}^{3/4}$ dependence is obtained at lower oxygen partial pressures. At higher $p_{O_2}$ the slope of $\log[I_\ell(p_{O_2})]$ versus $\log(p_{O_2})$ decreases towards $\sim 3/5$. This behaviour is

![Graph showing simulated $I_\ell(p_{O_2})$ relationships under different oxygen partial pressure conditions at 973 K (700°C). The $p_{O_2}$ is given within the figure. The solid line shows the theoretical Tafel behaviour at $p_{O_2} = 10^5$ Pa. The inset shows the results for $p_{O_2} = 10^5$ Pa (real and Tafel behaviour) and at small overpotentials of $\pm 10$ mV, as usually employed in EIS. From a dc analysis of the small-signal data in the inset the following results are obtained: $R_t = 10.5 \, \text{\Omega cm}^2$, $R_p = 29.9 \, \Omega \text{cm}^2$. Compare these results with the impedance spectra in Fig. 3.22 at the same conditions.]

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explained as follows: at high cathodic overpotentials, the charge transfer resistance $R_t$ decreases to very low values and the entire electrode polarization is caused by the surface diffusion of $O_{ad}$ and the adsorption of $O_2(g)$. Because the later two processes occur in parallel, a $p_{O_2}^{3/4}$ dependence of $I_1(p_{O_2})$ is found. This is consistent with the simulation results for the $R_p(p_{O_2})$ behaviour as shown above (Fig. 3.16). If $R_p \gg R_v$, then the electrode reaction is dominated by the concentration polarization and therefore a $p_{O_2}$ dependence is also found for $I_1$. However, such a $p_{O_2}$ has not yet been observed experimentally, probably because most of the studies were performed with porous electrodes. We would expect the described behaviour at Pt pattern electrodes where the Pt strip width is in the order of (10...100) µm, i.e. considerably larger than the Nernst diffusion layer width $\delta$.

One might expect that further information is obtained from the temperature dependence of the limiting current. The temperature dependence of $I_1(p_{O_2})$ is directly obtained from the data shown in Fig. 3.21. For the limiting behaviour at low $p_{O_2}$ we find an average apparent activation energy of $\Delta H^\theta = 64$ kJ/mol, where a value of $\sim 76$ kJ/mol is found at low temperatures and the value decreases to $\sim 54$ kJ/mol at high temperatures. To the best of our knowledge, no corresponding experimental data are reported in the literature (note that the results must be from non-porous electrodes, otherwise gas diffusion could be the limiting process). By consideration of Eq. (3.29), and with $k_b \to 0$ it is seen that a rather complicated temperature dependence of $I_1(p_{O_2})$ results, where the activation energies of surface diffusion, adsorption, and desorption have an influence, although an analytical expression can not be derived for a limiting case.

**Electrode Impedances.** It has been often experimentally found that the impedance $Z(j\omega)$ in the complex plane exhibits as a single (depressed or Warburg-like) semi-circle at intermediate temperatures and at high $p_{O_2}$ [15, 42, 45, 55, 56, 61, 62]. With decreasing $p_{O_2}$ a second semi-circle generally appears [15, 41]. There can no study be found where EIS spectra were recorded under a cathodic or anodic polarization of the cell. The interpretation of the spectra has been generally difficult and is further complicated by the presence of the double layer capacitance $C_{dl}$. As we have shown in the previous section, it is necessary to consider the Faradaic impedance $Z_F(j\omega)$ which can be obtained from the measured impedance $Z(j\omega)$ by subtracting the double layer capacitance and the electrolyte resistance. In the following we will give both the Faradaic impedance and the impedance, assuming that

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Fig. 3.21 Simulated cathodic limiting-current behaviour of M2. — The temperatures (K) are given within the figure. The same parameters as in Fig. 3.20 were used. The $I_F(\eta)$ behaviour was simulated to $-0.6$ V and the corresponding current was taken as $I_1$. The inset shows the concentration gradient (surface coverage $\theta$) of $O_{ad}$ near the $t_{pb}$ at $T = 973$ K, $\eta = -0.6$ V, and $p_{O_2} = 10^5$ Pa.

a constant double layer capacitance $C_{dl}$ of $20 \mu F/cm^2$, as well as a temperature dependent electrolyte resistance $R_e$ in series is present.

To obtain a complete picture of the electrode behaviour at 973 K (700°C) we simulate the frequency response at different overpotentials and compare the results with the $I_F(\eta)$ behaviour. Fig. 3.22 shows simulated EIS spectra for two different $p_{O_2}$ at low cathodic overpotentials in the complex plane. It is readily seen that an interpretation of the impedance alone is difficult. In contrast, the information is contained within the Faradaic impedance. From the
3.4 Simulation Results

Fig. 3.22 Simulated impedances at $T = 973 \, \text{K} (700^\circ \text{C})$ at different overpotentials $\eta$. The same parameters as for the simulation of the $I_F(\eta)$ curves in Fig. 3.20 were employed. Spectra at (a) $p_{O_2} = 10^5 \, \text{Pa}$ and (b) $p_{O_2} = 10^3 \, \text{Pa}$ for different overpotentials as given in the figure.
knowledge of $R_t$ with respect to $R_p$ and the shape of the impedance arc, we can immediately infer the reaction mechanism. At high $p_O_2$, $R_t = R_c$ (where $R_c = R_p - R_t$) and we find that a competition exists between the charge transfer process and the chemical processes. From the shape of the $Z_F(j\omega)$ arc we conclude that the surface diffusion process causes $R_c$. From a comparison of the $Z_F(j\omega)$ and $I_F(\eta)$ data at high $p_O_2$ (Fig. 3.22 and Fig. 3.20) it can be well understood why the $I_F(\eta)$ behaviour resembles a Tafel behaviour. The overall kinetics is still influenced by the relatively large charge transfer resistance $R_t$. If the $p_O_2$ is lowered, the reaction kinetics is almost completely dominated by the surface diffusion process ($R_t \ll R_p$). In both cases, the concentration polarization increases with increasing cathodic overpotential, which can be readily explained with the decrease of $R_t$ with cathodic overpotential (as long as $O_{ad}$ near the tpb is not too far from the equilibrium concentration). Note that the values for $R_t$ and $R_p$ obtained at high $p_O_2$ and zero overpotential (Fig. 3.22a) are in full agreement with the values obtained from the small-signal dc analysis in Fig. 3.20.

It was said above that the parallel process of $O_2(g)$ adsorption and $O_{ad}$ surface diffusion was responsible for the limiting-current behaviour. This can be seen from the $Z_F(j\omega)$ at high cathodic overpotentials (see inset in Fig. 3.22). However, more information is obtained from a Bode plot of the $Z_F(j\omega)$ data and the slope of the log|$Z_F|$ versus log($\omega$) curve (Fig. 3.23). We have discussed some properties of frequency response data in Bode plot representation in more detail in part I of this publication [1]. With increasing cathodic overpotential the influence of the adsorption process can be seen in the high frequency part of the spectra: the $\omega$ dependence of |$Z_F$| changes from $-1/2$ to $-1$. This behaviour becomes more pronounced with decreasing temperatures. However, we believe that this behaviour is particular to the modelling of the adsorption process and that real electrodes should not show a first-order dependence of |$Z_F$| at such high frequencies. Remember that the adsorption of $O_2(g)$ was assumed to occur directly from the gas phase on the Pt surface. Relatively high rate constants for the adsorption and desorption were chosen. This causes short relaxation times for this process which can be observed in the spectra. It is well known that the chemisorption of oxygen proceeds via one or more physisorbed precursor states [63, 64]. Accordingly, these precursors act as a reservoir. A more refined model should include this dynamic behaviour [33].
3.4 Simulation Results

Fig. 3.23 Simulated impedances at $T = 973$ K (700°C) and different cathodic overpotentials. $p_{O_2} = 10^3$ Pa. (a) Magnitude of the Faradaic impedance $Z_F(j\omega)$ and the impedance $Z(j\omega)$. (b) Phase angle of the corresponding data. Note the change of slope in the log[|$Z_F$|] versus log($\omega$) plot from $-1/2$ towards $-1$ at high frequencies with increasing cathodic overpotential.
3.4.3 Sensitivity Analysis and Practical Identifiability

Sensitivity of $Z_F$ with respect to the unknown parameters. The sensitivity of the Faradaic impedance, $S$, with respect to the unknown parameters, $p$, should be high in order to obtain accurate quantitative parameter estimates from experimental data. For model M2 we assumed that only the charge-transfer coefficient, $\beta$, and the forward electrochemical rate constant, $k_1^{\text{eq}}$, are unknown. The remaining parameters were assumed to be known with high accuracy. Fig. 3.24 shows the sensitivity of $|Z_F|$ with respect to $\beta$ and $k_1^{\text{eq}}$. $S(\beta)$ is relatively low compared to $S(k_1^{\text{eq}})$. We may infer that the higher the frequency the better. However, at high frequencies the influence of the electrical double layer becomes dominant and $Z_F(j\omega)$ must be first obtained from $Z(j\omega)$ raw data. This procedure generally introduces relatively large errors in the high frequency part of the $Z_F(j\omega)$ data. Therefore, $\beta$ can not be estimated accurately from EIS measurements. However, as shown above, $\beta$ can be obtained from the dependence of the charge-transfer resist-

Fig. 3.24 Sensitivity of $|Z_F|$ with respect to the unknown parameters.—The simulations were obtained for $T = 973 \text{ K}$ in oxygen (cf. simulations in Fig. 3.22a). The magnitude of $Z_F(j\omega)$ is also shown. Eq. (3.13) was used to calculate the individual sensitivities $S(\beta)$ and $S(k_1)$. 

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ance, \( R_t \), on the oxygen partial pressure, \( p_{O_2} \) (cf. Fig. 3.4). Once \( \beta \) is known, \( k_1^{\text{eq}} \) is accurately obtained from EIS measurements.

This method works well for the considered system if, and only if, the remaining parameters are well known (as we have assumed so far). However, in real porous electrode/electrolyte systems the length of the tpb, \( l_{\text{tpb}} \), can be only estimated to \( \pm 10\% \) or even less. Similarly, we have no estimate for the width of the active area, \( w \) (see above). Unfortunately, the sensitivity of \( |Z_F| \) is large with respect to \( w \) and \( l_{\text{tpb}} \) (cf. Fig. 3.25), which can be easily understood: the larger the length of the tpb and/or the larger the width of the active area, the higher the rate of the electrochemical reaction is and therefore the lower \( R_t \) and \( R_p \) becomes. Accurate estimates of \( l_{\text{tpb}} \) and \( w \) are therefore a mandatory prerequisite to obtain accurate estimates of \( k_1^{\text{eq}} \) from EIS measurements. This means that pattern electrodes of noble metal electrodes on (preferably single crystal) solid electrolytes must be employed instead of porous electrodes if one seeks for the electrochemical rate constants. This allows to fix \( l_{\text{tpb}} \) experimentally to a certain value within a small range, as long as the

![Graph](image)

**Fig. 3.25** Sensitivity of \( |Z_F| \) with respect to the length of the tpb and the width of the active area.—The same parameters as for the simulations in Fig. 3.24 were used with \( w = 10 \text{ nm} \).
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microstructure remains stable at high temperatures. We are, therefore, left with the question of how to obtain the width of the active area \( w \).

While discussing Eqs. (3.14) and (3.15) we found that \( R_t \) is insensitive to changes in \( w \) if the product \( w \cdot k_{1c} \) is kept constant (remember the definition of \( k_{1c} \)). We now choose a reference value for \( w \) as \( w_N = 10 \text{ nm} \) and express the forward chemical rate constant by \( k_{1c} \cdot w_N/w \). The simulations of \(|Z_F| \) for different values of \( w \) are somewhat surprising (cf. Fig. 3.26). We find that \(|Z_F| \) is rather insensitive to \( w \), if \( w \) is in the order of \((1...10) \text{ nm} \). As already stated, \( R_t \) does not depend on \( w \) if \( w \cdot k_{1c} = \text{const} \). Surprisingly, \( R_p \) is only slightly depending on \( w \) (cf. Fig. 3.26a). However, we find that the frequency dependence of \(|Z_F| \) depends on the width of the active area \( w \). At low values of \( w \), \( Z_F \) follows an almost perfect -45° line with respect to the real axis in the complex plane, indicating surface diffusion limitation. This behaviour diminishes at high frequencies with increasing size of \( w \) where a \( \omega^{-1} \) dependence of \(|Z_F| \) is found (see also Fig. 3.23a for \( w = 10 \text{ nm} \)). Obviously, this effect is caused by the space discretization and is not a structural property of the model. However, due to the low sensitivity of \(|Z_F| \) with respect to \( w \) (if \( w \cdot k_{1c} = \text{const} \)) we can obtain rather accurate estimates of \( k_{1c} \) from EIS measurements if a value of \((1...10) \text{ nm} \) is assumed for the width of the active area \( w \). This is close agreement with what we would expect intuitively for \( w \).

Practical identifiability. In part I of this publication we proved the theoretical identifiability of the model parameters of model M1 and M2 with EIS. However, we have shown above that the feature of sensitivity must be also considered. Unfortunately, theoretical identifiability and high sensitivities are only necessary requirements for an accurate parameter estimation. If a correlation between parameters exists, a numerical parameter estimation can become impossible as we show now.

Let us produce \( Z_F(j\omega) \) data at \( T = 973 \text{ K} \), \( p_{O_2} = 10^5 \text{ Pa} \), and with the remaining parameters given in the appendix (Table 3.1). It is now the objective to estimate the unknown parameters from the generated data and the model M2, while different values for \( p = \{\beta, k_{1c} \} \) should be used as starting guesses than for the generation of \( Z_F(j\omega) \) were used. This problem is well known from numerical optimization methods. We consider the weighted sum of squared terms (see appendix 3–A.4 for more mathematical and computer implementation details)
Fig. 3.26 Sensitivity of $|Z_F|$ with respect to $w$ with under the condition $w \cdot k_{lc} = \text{const.}$

(a) $Z_F$ shown in the complex plane for different values of $w$ from 2 nm to 20 nm (see text in the figure). The inset shows the high frequency part of $Z_F$. (b) Sensitivity of $|Z_F|$ at different levels of $w$. (----) corresponds to $|Z_F|$ at $w = 10$ nm.
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Fig. 3.27 Correlation between $\beta$ and $k_{1c}$.—The parameters given in Table 3.1 were used to calculate $f(p)$ (Eq. (3.32)). The bold line denotes the minima of the function $f(p)$.

\[
f(p) = \frac{1}{|Z_F|} \sum_i (Z_F(p, i) - Z^*_F(p, i))^2 \tag{3.32}
\]

where $Z^*_F(i)$ denotes the generated data. Fig. 3.27 shows the function $f(p)$ for this particular problem. There are a few things worth to note. First, the sensitivity of $f(p)$ with respect to $k_{1c}$ is considerably larger as to $\alpha$ (as already mentioned above). Second, there exists a strong correlation between $\alpha$ and $k_{1c}$ which is reflected in the fact that the cost function $f(p)$ exhibits a shallow minimum. Although the absolute minimum can be found numerically at $\beta = \beta_N$ and $k_{1c} = k_{1cN}$ for these noise free data, this is generally not the case for experimental (and therefore noisy) data. It becomes clear that the numerical estimates of $\alpha$ from EIS data may be completely wrong. Accordingly, $\alpha$ must be obtained from different measurements than EIS measurements, even if $S(\beta)$ was high (but which is not the case as shown in Fig. 3.24). Once $\beta$ is determined, $k_{1c}$ can be obtained accurately.

We have shown that the electrode reaction of the Pt, O$_2$(g) | YSZ system is dominated by surface diffusion of atomic oxygen species over a large range.
3.5 Summary and Conclusions

It has been the purpose of this paper to demonstrate the computer implementation of a kinetic model describing the oxygen reduction at interfaces between Pt and YSZ. The simulated steady-state and small-signal behaviour have been compared with reported data. A procedure for the identification of the rate constants of the considered model has been attempted.
Although the considered Pt, \( \text{O}_2(\text{g}) \mid \text{YSZ} \) seems to be a quite well understood electrode/solid electrolyte system, the actual procedure for the identification of the reaction mechanism is by far not a straightforward and easy task. From the theoretical analysis we determined the conditions for the unique identifiability of the unknown parameters which proved to be only of limited usefulness for the practical identifiability.

We suggest the following procedure for the estimation of the model parameters of model M2 describing the Pt, \( \text{O}_2(\text{g}) \mid \text{YSZ} \) system:

(i) Determine the charge transfer coefficient \( \beta \) from \( \log(R_t^{-1}) \) versus \( \log(p_{O_2}) \) plots at \(-1000\) K. The \( R_t(p_{O_2}) \) values should be obtained from electrochemical impedance measurements by subtracting the double layer capacitance.

(ii) Determine the activation enthalpy of the charge transfer reaction, \( \Delta H_{ct}^\ast \), from an \( \ln[i_0(p_{O_2}^\ast)] \) versus \( 1/T \) plot. Note that \( i_0(p_{O_2}^\ast) \) is accurately obtained from \( R_t \) data which can be obtained as described in (i). The relation \( i_0 = (RT) / (2F) \cdot R_t^{-1} \) can be used to obtain \( i_0 \).

(iii) Determine the oxygen adsorption enthalpy \( \Delta H_{\text{ad}} \) for high surface coverages from a \( \ln(p_{O_2}^\ast) \) versus \( 1/T \) plot either at high \( p_{O_2} \) and low \( T \) (high surface coverage), or at low \( p_{O_2} \) and high \( T \) (low surface coverage). Note that a large amount of data is available in the literature for \( E_{\text{ad}} \) and \( E_{\text{des}} \), as well as \( k_{\text{ad}} \) and \( k_{\text{des}} \).

(iv) From electrode with well known geometry (e.g. strip electrodes with well known length of \( tpb \), no porosity, and known Pt surface area), obtain impedance spectra. Use the parameter estimates obtained in (i) to (iii) and estimate \( k_{1c} \) with the numerical method described.

(v) Estimate \( D(O_{\text{aq}}) \) and \( E_d \) from EIS measurements of electrodes described in (iv).

It is clear that a validation of experimental data and model parameters should be carried out continuously.
Model M2 accounts for the adsorption and desorption of oxygen on the Pt surface, the surface diffusion of atomic oxygen, and for a two-electron transfer reaction near the tpb. However, much information is available about the interaction between $O_2(g)$ and Pt surfaces which could be included in a refined model. First, the adsorption/desorption dynamics of $O_2(g)$ on the Pt surface should be modelled in more detail, as the kinetic constants may vary several orders of magnitude over the $p_{O_2}$ range considered. To fully describe the behaviour of porous electrodes, gas mass diffusion (binary diffusion and Knudsen diffusion) should be taken into account. This can be easily accomplished with the numerical method presented in this paper. Finally, the concentration dependence of the surface diffusion coefficient of $O_{ad}$ could be accounted for in the model.

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### 3–A.1 Reaction Model Constants and Parameters

**Table 3.1** Parameters and Constants used in Model M1 and M2

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<th>Ref.</th>
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<td>kJ/mol</td>
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Table 3.1 Parameters and Constants used in Model M1 and M2

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</table>

3–A.2 Determination of $C_{dl}$ by Potential Step Chronoamperometry

Let us assume that the electrochemical impedance of a Pt, $O_2(g)$ | YSZ system can be reasonably well described by the equivalent circuit shown in Fig. 3.3d. The only difference to the equivalent circuit of Fig. 3.3c is that we assume that the Faradaic impedance $Z_F(j\omega)$ can be approximated by a conventional parallel circuit of a capacitance $C$ and a concentration resistance $R_c$. From a node analysis (see, for example, any textbook about electrical engineering) of this circuit we obtain the following state-space description for the circuit in Fig. 3.3d

$$A = \begin{bmatrix} -1/C_{dl} \cdot (1/R_e + 1/R_t) & 1/(C_{dl}R_t) \\ 1/(CR_t) & -1/C \cdot (1/R_t + 1/R_c) \end{bmatrix}$$

$$B = \begin{bmatrix} 1/(C_{dl}R_e) \\ 0 \end{bmatrix}^T$$

$$C = \begin{bmatrix} -1/R_e \\ 0 \end{bmatrix}$$

$$D = [1/R_e]$$

(3–A2.1)

with $x(t) = [u_1(t) \ u_2(t)]^T$, $u_0 = u(t)$, and $y(t) = 1/R_e \cdot (u(t) - u_1(t))$, and where $T$ denotes vector transposition. Two relaxation times $\tau_1$ and $\tau_2$ are
obtained from the eigenvalues of the matrix A (use a symbolic mathematics program such as Mathematica or Maple). Quite lengthy expressions for \( \tau_1 \) are obtained. The faster relaxation time is associated with the double layer capacitance, although in a rather complicated form. Can we simplify the analytical expression for \( \tau_1 \)? At temperatures around \( \sim 950 \) K we find typical values for \( R_c \) in the order of 100 \( \Omega \)-cm\(^2\) and \( C \) is typically in the order of 1 mF-cm\(^{-2}\). The values for \( R_t, R_e, \) and \( C_{dl} \) are at least one order of magnitude lower. This makes a simplification to a certain extent of the expression for \( \tau_1 \) possible. In addition, if \( R_t \gg R_e \) we can finally derive

\[
\tau_1 \approx \frac{C_{dl}R_eR_t}{R_e + R_t}. \tag{3-A2.2}
\]

Let us now analyse the relative error we make in the estimation of \( C_{dl} \) when experimental potential step chronoamperometry data are evaluated with the expression \( \tau^* = R_eC_{dl} \) instead of the expression derived above (note that the exact value for \( \tau \) of the equivalent circuit shown in Fig. 3.3a is easily obtained from a node analysis as \( \tau = (C_{dl}R_eR_t)/(R_e + R_t) \) which corresponds to Eq. (3-A2.2)). The result is shown in Fig. 3-A2.1 for \( C = 1 \) mF, \( R_c = 100 \) \( \Omega \), \( C_{dl} = 1 \) \( \mu \)F, and \( R_e = 10 \) \( \Omega \). It is seen that the expression \( \tau^* = R_eC_{dl} \) is only a good approximation for \( \tau \) if \( R_t \geq (5...10) \cdot R_e \). If \( R_t \leq R_e \), the values for \( C_{dl} \) are estimated too low if the step response data are evaluated with the expression for \( \tau^* \) instead of \( \tau \). In addition, the expression derived above for \( \tau_1 \) (Eq. (3-A2.2)) is a very good approximation down to very low values of \( R_t \).

We conclude that the true values for \( C_{dl} \) of Pt/YSZ interfaces can be obtained from potential step chronoamperometry experiments if the current decay curves are evaluated with Eq. (3-A2.2) if \( R_t >> R_e \), which is generally fulfilled at low temperatures. However, numerical estimates of \( R_t \) (and \( R_e \)) are required. But, as we show in the main text, \( R_t \) is related with the exchange current density \( i_0 \) which itself can be obtained from a Tafel analysis. Unfortunately, a Tafel analysis only gives reasonable values for \( i_0 \) if the reaction is charge-transfer controlled, which is certainly not the case for the Pt, \( O_2(g) \mid YSZ \) system at temperatures below 1000 K. On the other hand, at high temperatures the reaction would be charge-transfer controlled which implies that \( R_t \approx R_p \) (i.e. \( R_c \approx 0 \)), thus making a simplification of the equation describing the relaxation time impossible. We propose to employ the method of Berthier et al. [39] for estimating \( C_{dl} \) from impedance data, as demonstrated in the text.

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Fig. 3–A2.1 Comparison of potential step responses of equivalent circuits.—The ratio \(\tau/\tau^*\) is shown (relative error). Only if \(R_t > R_e\), the error is below a factor of 2. The following parameters were taken (see equivalent circuit of Fig. 3.3d): \(R_e = 10 \Omega, R_t = 10 \Omega, R_c = 100 \Omega, C_{dl} = 10 \mu F, C = 1.5 \text{ mF}\). We obtain \(\tau^* = 0.1 \text{ ms}\) and \(\tau = 0.045 \text{ ms}\). The relative error is a factor of \(~2\) for these parameters (see figure). The inset shows the current response to a +10 mV potential step input.

3–A.3 Implementation and Simulations of Model M1

General. In this example the implementation and simulations of model M1 in Simulink and in Matlab is shown. Only a basic familiarity with the programs is assumed which can be obtained by working through the introductory chapters of the handbooks [3, 4]. A very good introduction to block diagrams can be found in the textbook from Franklin [65]. The reader is encouraged to try the implementation for himself and to experiment with the model. All the examples shown below can be worked through with the student version of the software (Matlab: version 4.2; Simulink: version 1.3). The parameters used for simulations are taken from Table 3.1 in appendix 3-A.1 and evaluated at \(T = 1000 \text{ K}\) and \(p_{O_2} = 1 \text{ atm}\). There is no need to concern about the parameters for the moment.
Fig. 3−A3.1 Simulink block diagram for the adsorption/desorption dynamics.—The initial value of the integrator block is set to \( x_0 \). The simulation can be followed within the Simulink window by connecting an Auto-Scale Graph from the Sinks Block Library to any connection line (although it will be most interesting to follow \( x(t) \)). Set the parameters in the Simulation:Parameters... sub-menu and start the simulation. This possibility is convenient in the early stage of model testing and debugging.

**Adsorption dynamics.** First, the adsorption and desorption dynamics is implemented in a block diagram (Fig. 3−A3.1; filename: simads1.m). The parameters are defined as

\[
\begin{align*}
p_0 &= 1; & \text{in units of } (10^5 \text{ Pa}) \\
n_0 &= 1.6e-5; \\
\text{kad} &= 1.8888e7; \\
\text{kdes} &= 4.3007e6;
\end{align*}
\]

The initial value of \( x \) is set to \( x_0 = 0.65 \). The rk45 (Runge-Kutta fifth order) integration methods is used with

\[
\begin{align*}
tol &= 1e-3; \text{ minstep } = 1e-6; \text{ maxstep } = 1e-3; \\
\text{options} &= [\text{tol}, \text{minstep}, \text{maxstep}]; \\
x_0 &= 0.65; \\
[t,x] &= \text{rk45('simads1', 1.5e-2, x0, options}); \\
\text{subplot(221), plot(t,x), xlabel('t/s'), ylabel('x')}
\end{align*}
\]
Fig. 3–A3.2 Simulation results for model M1 at reference conditions. —The parameters from Table 3.1 were evaluated at \( T = 1000 \) K and \( p_{O_2} = 1 \) atm. subplot (221) shows the time response of \( x(t) \) for a small deviation from the equilibrium value \( X_0 \). subplot (222) shows the Faradaic impedance and the impedance at \( \eta = 0 \) V (larger semicircle) and \( \eta = -0.8 \) V (smaller semicircle). A double layer capacitance of \( C_{dl} = 10^{-6} \) was assumed. subplot (223) shows the charge transfer resistance \( R_t \) and the polarization resistance \( R_p \) as a function of the overpotential \( \eta \). subplot (224) shows the current–voltage behaviour of M1.

The subplot (221) of Fig. 3–A3.2 shows the time dependence of the surface concentration. The simulation can also be followed within Simulink on the Auto-Scale Graph block which can be found in the Sinks Block Library. The integration parameters can be set directly in the Simulation:Parameters... submenu.

The surface concentration attains its equilibrium value

\[
x_0 = \frac{K \cdot \sqrt{p_{O_2}}}{1 + K \cdot \sqrt{p_{O_2}}}
\]
where

\[ K = \sqrt{\frac{k_{ad}}{k_{des}}} \]

(cf. part I). The relaxation time for small perturbations is given by [66]

\[ \tau = \frac{1}{4k_{des}X_0 + k_{ad}}. \]

Note that the result for the relaxation time is based on the assumption that the perturbation is small. If the starting value is far from the equilibrium value, the simulated values for the relaxation time will deviate from the small-signal value.

**Electrochemical reaction.** We now include the electrochemical reaction. Fig. 3-A3.3 shows the corresponding Simulink block diagram (filename: simmodla.m). See the main text and Table 3.1 for a detailed description of \( k_f, k_b \) and the remaining parameters. Non-linearities are due to the exponential dependence of \( k_f \) and \( k_b \) on the overpotential. The Fcn block in the Nonlinear Block Library is best used for this purpose. Note that the \( \eta(t) \) block corresponds to an inport block and that the IF(t) block corresponds to an output block from the Connections Block Library. From this block diagram we can easily obtain the Faradaic admittance \( Y_F(j\omega) \) at equilibrium potential. We define the following constants

\[ \text{ac} = 0.62; \text{A} = 2.73e-7; \text{R} = 8.314; \text{T} = 1000; \text{F} = 96487; \]
\[ f = \frac{F}{(R \times T)}; \]
\[ k_f = 2.7474e3; \quad k_b = 5.7577e3; \]

Note that the electrochemical rate constants can not be chosen independently (cf. part I). It is a good idea to check the time dependent behaviour now. If \( x_0 \) is set to a different value than the equilibrium one, the system will relax towards the equilibrium state within a short time. The current should decrease to zero (or very low values) due to the constraint \( I_f(E_{eq}) = 0 \). The linearized state-space model (SSM) is obtained as follows:

\[ x_0 = \frac{K \times \sqrt{p_0^2}}{1 + K \times \sqrt{p_0^2}} \]
\[ [a,b,c,d] = \text{linmod('simmodla', x0, 0);} \]
Appendix

Fig. 3-A3.3 Simulink block diagram of M1 in order to extract linearized state-space models.—The integrator block is set either to 0 (zero) or to X0.

where the a, b, c, d quadruple denotes the linearized state-space matrices. It is important to recognize that X0 is given as an argument to the function linmod. If no argument was given, the function linmod would take zero for the surface concentration which would result in a wrong SSM. See also the on-line help (help linmod) for a description of the purpose of the function and its arguments. Note that we have the SSM in admittance form rather than in impedance form, because “simmod1a” defines a model of the form $I_F(s) = Y_F(s) \cdot \eta(s)$ where $s$ is the Laplace variable, $\eta(s)$ is the Laplace transform of the input, $I_F(s)$ is the Laplace transform of the output, and $Y_F(s)$ is the Laplace transform of the Faradaic admittance.

We continue with the transfer function to obtain the electrochemical impedance (we use deliberately “electrochemical impedance” and not just “impedance” because, as it should have become clear, we could analyse different
input/output relationships (e.g. the oxygen partial pressure as input and the current as output)

\[
[numYf, denYf] = \text{ss2tf}(a, b, c, d);
\]
\[
w = \text{logspace}(-1, 5, 100);
\]
\[
[reZf, imZf] = \text{nyquist}(denYf, numYf, w);
\]
\[
Zf = reZf + j*imZf;
\]

where \(Zf\) denotes the Faradaic impedance. Note that we changed the variables for \(denYf\) and \(numYf\) in the input of the \text{nyquist} function to obtain the result for the impedance (see \text{help nyquist}). A simple calculation reveals the electrochemical impedance \(Z\) including a double layer capacitance \(Cdl\) and an electrolyte resistance \(Re\)

\[
Cdl = 10e-6; Re = 10;
\]
\[
w = w'; % transpose the frequency vector!
\]
\[
Y = j*w*Cdl + 1./Zf; Z = Re + 1./Y;
\]

Let us plot the results (Fig. 3-A3.2)

\[
\text{subplot}(222), \text{plot}(\text{real}(Zf) + Re, -\text{imag}(Zf), '-',...)
\]
\[
\text{real}(Z), -\text{imag}(Z), '-');
\]
\[
\text{axis equal}; \text{axis}([0 500 -100 300]),...
\]
\[
\text{xlabel('Real(Z,Zf)'), ...}
\]
\[
\text{ylabel('-imag(Z,Zf)'), grid};
\]

The low frequency intercept of \(Zf\) and \(Z\) correspond to the polarization resistance,

\[
Rp = 1/(d-c/a*b),
\]

the high frequency intercept of \(Zf\) corresponds to the charge transfer resistance,

\[
Rt = 1/d,
\]

and the high frequency intercept of \(Z\) corresponds to the electrolyte resistance, \(Re\) (see part I of this publication for further details). It is seen that the
reaction kinetics is almost entirely controlled by the adsorption of oxygen. The charge transfer resistance is low compared with the polarization resistance. It is generally a good idea to validate the simulations with analytical results. In part I of this publication we give the linearized SSM in analytical form

\[
\begin{align*}
    a_1 &= -4k_{ad}pO_2N_0(1-X_0) - 4k_{des}N_0X_0 - k_f - k_b; \\
    b_1 &= 2a_1f_kfX_0 + 2(1-a_1)f_kb(1-X_0); \\
    c_1 &= -2N_0F*A*(k_b + k_f); \\
    d_1 &= 2N_0F*A*(2(1-a_1)f_kb(1-X_0) + 2a_1f_kfX_0);
\end{align*}
\]

which are equal to the \(a, b, c, d\) matrices obtained with the function \texttt{linmod}. Let us now obtain simulations at a cathodic overpotential of \(\eta = -0.08\).

With

\[
\begin{align*}
    \eta &= -0.08; \\
    [X, U, Y] &= \text{trim('simmodla', \(X_0\), \(\eta\), [], [], [1], [ ])}; \\
    [a_2, b_2, c_2, d_2] &= \text{linmod('simmodla', \(X\), \(U\)});
\end{align*}
\]

and with the same calculations as in the equilibrium case we obtain the impedances \(Z_f\) and \(Z\) at an overpotential of \(-80\) mV which are also shown in \texttt{subplot(222)} of Fig. 3-A3.2 (use \texttt{subplot(222)}, \texttt{hold on}, and the same procedure as in the first case). There are a few things which are noteworthy about these three lines of \texttt{MATLAB} code. If an overpotential is imposed at the input, the system state will change to a new steady state. The value for the state variable \(X\) will be lower than the equilibrium value \(X_0\) (cathodic overpotential). The corresponding current is given by \(Y\). The output of \texttt{trim} is used as the input of the function \texttt{linmod} which give the linearized SSM at the new operating point. Note that \(R_p\) decreases with increasing \(\eta\). However, increasing \(\eta\) to much higher values will increase \(R_p\) drastically because the steady-state values for \(X\) decrease. We find that the reaction is limited by the rate of adsorption.

If we wanted to obtain simulations at overpotentials with the analytical model, we had to substitute the state variable \(X_0\) with the actual state variable \(X\) (depending on \(\eta\)) in the analytical expressions of the state-space matrices. This requires either an analytical solution of the mass balance equation, or that we solve this equation numerically. This can be done with the \texttt{Simulink} function \texttt{constr} (or, if available, with the function \texttt{fsolve} from
the Optimization Toolbox). We see that it is much more convenient to find the steady-state point with the function trim. The function constr may solve a number of different problems and it will be needed for parameter estimation (fitting). The function trim makes use of constr. It is worth to know the abilities and limitations of trim and constr in some depth.

Let us consider the behaviour of $R_t$ and $R_p$ over a range of overpotentials from $-0.2$ V to $0.1$ V. We run the following commands:

```matlab
etaList = [-0.2:0.04:0.1];
for m = 1:length(etaList),
    eta = etaList(m);
    [X(m),U(m),Y(m)] = trim('simmod1a',x0,eta,[],[],...
        [1],[1]);
    [a2(m),b2(m),c2(m),d2(m)] = linmod('simmod1a', ...
        X(m), U(m));
    Rt(m) = 1/d2(m);
    Rp(m) = 1/(d2(m)-c2(m)/a2(m)*b2(m));
end
```

Occasionally, the following warning message may appear

```
Maximum number of iterations exceeded
increase OPTIONS(14)
```

In this case trim has not found a solution after a default number of iterations (OPTIONS(14)). For more details about the OPTIONS vector and the function trim, refer to the manuals or the on-line help (help foptions; help trim). We would like to point out that any warning message should be taken seriously and the reason for it should be found (and eliminated). The results are finally plotted in a semilogy plot

```matlab
subplot(223), semilogy(etaList, Rp, 'o', ...
    etaList,Rt,'*'), grid
xlabel('eta/V'), ylabel('(Rp,Rt)/Ohm')
```

where the exponential dependence of $R_t$ on $eta$ is readily seen.

Finally, we look at the steady-state current-voltage curve of model M1. All blocks in the model simmod1a are selected and grouped. A Repeating
Sequence block from the Sources Block Library is used as input and a second output is used for the feed-through of the input (cf. Fig. 3–A3.4; filename: `simmodlb.m`). The vector \([0 \ \text{dt} \ 2*\text{dt} \ 3*\text{dt} \ 4*\text{dt}]\) is used as time value and \([0 \ -\text{du} \ 0 \ \text{du} \ 0]\) is used as output value in the Repeating Sequence block. We scan with 6 mV/s (which is almost zero for the system under consideration).

\[
\begin{align*}
\text{dt} &= 100; \ \text{du} = 0.3; \ \text{TF} = 4*\text{dt}; \\
[T1,X1,Y1] &= \text{gear('simmodlb', TF, X0, ..., [1e-3, TF/1000, TF/20])}; \\
\text{If} &= Y1(:,1); \ \text{V} = Y1(:,2); \\
\text{subplot}(224), & \text{plot(V,If), grid}
\end{align*}
\]

The results can be found in `subplot(224)` of Fig. 3–A3.4. Note that a limiting cathodic and anodic behaviour is found at relatively low overpotentials. The step response to an potential step at the input can be simulated as shown in 3–A.2. Because \(\text{cdl}\) and \(\text{Re}\) play a significant role in the time-dependent behaviour we must include them in the model.

We learn from the EIS spectra and the I–V curve that further processes, not just the dissociative oxygen adsorption near the \(tpb\), must play a significant role in the supply of atomic oxygen. Surface diffusion of atomic oxygen towards the \(tpb\) must be taken into account when investigating the kinetics of high temperature oxygen gas electrodes.
3–A.4 Implementation and Simulations of Model M2

General. In this appendix we present the implementation of model M2 in MATLAB and SIMULINK. Special emphasis is given on the implementation of the mass transport phenomena in SIMULINK. Note that the full version of SIMULINK is required to perform the simulations (the student version is limited to 40 blocks per model). The parameters used for the simulations are taken from Table 3.1 of appendix 3–A.1 and evaluated at $T = 973$ K and $p_{O_2} = 10^3$ Pa. MATLAB version 5.1 and SIMULINK version 2.1 on a SPARCstation 5 operating under Solaris 2.5.1 were used for the simulations.

Programme initialization. We first define the model constants and parameters (see also appendix 3–A.1).

\begin{verbatim}
Aelectrode = 1e-4; % apparent electrode area
Acov = 0.7; % electrolyte coverage
Lchar = 2e-6; % characteristic length
tpb = 4*Aelectrode/Lchar * sqrt(1-Acov); % Eq. (2-A2.2)
R = 8.314; % gas constant
F = 96487; % Faraday constant
Na = 6.023e23; % Avogadro constant
T = 973; % temperature in units of K
pO2 = 1e-2; % in units of (10^5 Pa)
Voo = 4.65e3; % oxygen vacancy concentration
Oox = 4.45e4; % oxygen ion concentration
\end{verbatim}

The penetration depth $\delta$ is obtained as described in subsection 3.3.2:

\begin{verbatim}
D0 = 4.65e-4; % surface diffusion constant
Ediff = 155e3; % activation energy
D = D0*exp(-Ediff/(R*T)); % surface diffusion coefficient
wmax = exp(21.11-14150/T);
Wmax = wmax*(pO2)^(1/2); % cf. Fig. 3.2
delta = 6*2/sqrt(pi)*1/(sqrt(Wmax/(2*D)));
\end{verbatim}

Having determined the penetration depth we can divide $\delta$ in compartments of increasing size according to a geometric series (note that we fix the width of the $tpb$ compartment to 10 nm):
Appendix

dz = 10e-9; % width of tpb compartment
q0 = 2; % starting guess
n = 10; % number of compartments;
dz = 10e-9; % width of tpb compartment
A = dz*tpb; % active area around tpb
q = fzero('compart', q0,...
[],[],dzl,delta,n); % find series factor q
dz =[]; % width of compartments
for k=1:n,
   dz(k) = dzl*q^(k-1);
end

where 'compart' is a small M-file called compart.m:

function f = compart(x,dxl,delta,n)
   f = dzl/delta - (1-x)/(1-x^n);

The midpoints of the compartments are obtained from:

for pp=1:length(dz),
   Zaxis(pp) = sum(dz(1:pp-1)) + dz(pp)/2;
end

and the time constants for surface diffusion (Eq. (3.9)) are obtained as

Tdiff = dz.^2./(2*D);

We continue with the constants for the adsorption and desorption:

N0 = 1e19/Na; % number of adsorption sites
nad0 = 1e9; % freq. factor of adsorption
ndes0 = 2e12/N0; % freq. factor of desorption
Ead = 33e3; % activation energy for adsorption
Edes = 200e3; % activation energy for desorption
DH = 1/2*(Edes-Ead); % activation enthalpy

We now determine the electrochemical quantities:
Elf = 125e3;  % activation energy of forward reaction
Elb = 135e3;  % backward reaction
De = Elf - Elb;
ac = 0.62;  % charge transfer coefficient
kad = nad0*exp(-Ead/(R*T));
kes = ndes0*exp(-Edes/(R*T));
K = sqrt(kad/kdes);
ff = F/(R*T);
T0 = 1000;  % reference temperature in K
k1fChem = 2e6;  % forward chemical rate constant
k1fT0 = k1fChem*exp(-Elf/(R*T0));  % cf. Eq. (2.60)
K0 = sqrt(nad0*exp(-Ead/(R*T0))/*...
(ndes0*exp(-Edes/(R*T0))))
k1bT0 = k1fT0*Voo/Oox*K0;  % cf. Eq. (2.62)
k1bChem = k1bT0*exp(E1b/(R*T0));

Note that the backward chemical rate constant \( k_{lc} \) (k1bChem) must be expressed in terms of the forward chemical rate constant \( k_{lc} \) (k1fChem). This must be accomplished via Eq. (2.62).

The equilibrium potential is obtained as follows (cf. Eq. (2.59)):

\[
E_{eqT} = \frac{1}{2*ff} \log\left(\frac{k1fChem}{k1bChem*... \exp\left(-\frac{(Elf-Elb)}{(R*T0)}\right) Voo/Oox*K}\right);
\]
\[
E_{eqP} = \frac{1}{4*ff} \log(pO2);
\]
\[
Eeq = E_{eqT} + E_{eqP};
\]

and finally (cf. Eq. (2.74)):

\[
k1fEq = k1fChem*exp(-Elf/(R*T0))*exp(-2*ac*ff*Eeq);
k1bEq = k1bChem*exp(-Elb/(R*T0))*exp(2*(1-ac)*ff*Eeq);
\]

We finally add some electrolyte resistance (thickness: 0.5 mm; area: 1 cm\(^2\)) and further assume that one half of the electrolyte thickness is contributing to the electrolyte resistance (three-terminal measurement):

\[
sigma = 1.63e2*exp((-0.78*1.602e-19*Na)/(R*T))*1e2;
Re = 0.5 * 1/sigma*0.5e-3/1e-4;
\]
At zero current the surface coverage is given by (cf. Eq. (2.58)):

\[ x_0 = \frac{K\sqrt{p_{O2}}}{1+K\sqrt{p_{O2}}}; \]
\[ x = \text{ones}(n,1)*x_0; \quad \% \text{surface concentration vector} \]

The last command generates a vector of length equal to the number of compartments. Under zero current conditions there will be no concentration gradient, therefore, all components of the vector \( x \) will be equal.

It is generally useful to keep all these parameters and constants within a different parameter M-file, except the temperature and oxygen partial pressure. The parameters are loaded into the workspace from within the main program where appropriate.

**Simulink block diagram.** In Eqs. (3.10) to (3.12) the mass balances were given for the various compartments. We start our considerations with the block diagram of M1 (cf. Fig. 3–A3.3). The block diagram of the tpb compartment of M2 is obtained by adding the blocks for surface diffusion (last term in Eq. (3.10)). The resulting diagram is shown in Fig. 3–A4.1. Note how we added the terms for surface diffusion and that the electrochemical rate constants are defined slightly different than in Fig. 3–A3.3. In M1 the results for \( kf \) and \( kb \) were obtained from:

\[ kf = k_{1f}\text{Eq*V}_{oo}; \quad kb = k_{1b}\text{Eq*}0_{ox}; \]

Using \( T = 1000 \) K and \( p_{O2} = 1 \) we obtain the same results for \( kf \) and \( kb \) as in appendix 3–A.3. Note also that the initial value of the integrator block must be set correctly, this is best accomplished by introducing a vector \( x \) of appropriate length (equal to number of compartments) and setting the initial conditions of each individual compartment to \( x(i) \). The same applies to the time constants of the surface diffusion process (compare the multiplication block with \( 1/T_{diff}(1) \)).

Similarly we obtain the block diagrams for the other compartments. The complete block diagram for M2 is obtained by packing every compartment into a subsystem and by connecting these subsystems appropriately. Fig. 3–A4.2 shows an example with four compartments and the notation introduced in Eqs. (3.10) to (3.12). The entire block diagram can be easily extended to more than four compartments by copying and pasting an intermediate subsystem and connecting it with the remaining part. Note that the initial condi-
Fig. 3–A4.1 Simulink block diagram for the tpb compartment of M2.—We used the block diagram from M1 (Fig. 3–A3.3 ) and added the blocks for the surface diffusion process (marked with dropped shadows). $\eta(t)$ is the system input quantity and $IF(t)$ is the system output quantity. The concentration of adsorbed oxygen atoms in compartment two ($O_{ad}(2)$) is fed into this compartment and $O_{ad}(1)$ is fed into compartment two.

Fig. 3–A4.2 Simulink block diagram of M2 with four compartments.—The tpb subsystem corresponds to the block diagram shown in Fig. 3–A4.2.
tions of the integrator blocks and the $1/T_{\text{diff}}(i)$ blocks must be set appropriately for every subsystem. For clarity the block diagram of subsystem 2 is given in Fig. 3–A4.3. Obviously, only the blocks representing the surface diffusion process and the adsorption/desorption process are present. The initial condition for the integrator block is set to $x(2)$ and the time constant for the surface diffusion is set to $T_{\text{diff}}(2)$ (note how we defined the vector of $T_{\text{diff}}$).

**Simulations.** In order to be able to run simulations of M2 we create a Simulink block diagram with ten ($n = 10$) compartments. We save this file under the name `model2.m`. We show in detail how the results from Fig. 3.22b can be obtained.

We begin with the Faradaic impedance at zero overpotential (note that we defined $T = 973$ and $pO_2 = 0.01$ above):

```matlab
[a,b,c,d]=linmod('model2', x, 0);
[numYf,denYf] = ss2tf(a,b,c,d);
w = logspace(-1,5,100); w = w';
[reZf,imZf] = nyquist(denYf,numYf,w);
Zf = reZf + j*imZf; Cdl = 20e-6;
Y = j*w*Cdl + 1./Zf; Z = Re + 1./Y;
```

![Simulink block diagram](image)

**Fig. 3–A4.3** Simulink block diagram for compartment two of M2 (subsystem).—See main text for further explanations.
subplot(221), plot(real(Zf) + Re, -imag(Zf), 'b-',...
real(Z), -imag(Z), 'g-');
axis equal; xlabel('Real(Z,Zf)'), ylabel('-imag(Z,Zf)')

which should give the curve shown in Fig. 3.22b for \( \eta = 0 \). Note that the value for the polarization resistance \( R_p = 1/dcgain(a,b,c,d) \) of \( R_p = 82.52 \) should also be in agreement with the simulation results given in Fig. 3.16 for \( T = 973 \) and \( p_{02} = 0.01 \).

It is more interesting to consider a situation where a cathodic overpotential \( \eta \) is imposed to the system. Note that we cannot simply repeat the calculations from above with \([a,b,c,d]=\text{linmod('model2', x, eta})\), because \( x \) does not contain the actual steady-state values. We first have to determine the steady-state equilibrium point:

\[
\eta = -0.035; \quad \% \text{ as in Fig. 3.22b}
\]
\[
\text{options}(2) = 1e-6;
\]
\[
\text{options}(4) = 1e-8;
\]
\[
\text{options}(10) = 1e3; \; \text{xtemp} = x;
\]
\[
\text{while} \; \text{options}(10) \geq 100,
\]
\[
\quad \text{options}(14) = 100;
\]
\[
\quad [X,U,Y,DX,\text{options}] = \text{trim('model2',...}
\]
\[
\quad \text{xtemp,eta,[],[],[1],[[],[],[],[],[]],options});
\]
\[
\quad \text{xtemp} = X*(1+\eta*\text{randn}(1));
\]

Type \text{help} \text{ foptions} to get more information about the \text{options}. We use the while loop because the function \text{trim} does not always find a solution within a reasonable number of iterations. The result of \text{trim} is the state vector \( X \), the input \( U \) and the output \( Y \). Check these results by typing:

\[
>> X
\]
\[
X =
\begin{align*}
0.1151 \\
0.1202 \\
0.2165 \\
0.2141 \\
0.1278 \\
0.1388
\end{align*}
\]
Note that \( U \) corresponds to the input overpotential of -35 mV and that \( Y \) corresponds to an output current of -0.32 mA/cm\(^2\). The sort order of the \( X \) vector seems somewhat strange, but the necessary information can be obtained from the variable \textit{info} which is obtained as follows:

```matlab
>> [str, xo, info] = model2;
```

```matlab
>> info

'\textit{model2/Subsystem1/Oad}'
'\textit{model2/Subsystem2/Oad}'
'\textit{model2/Subsystem10/Oad}'
'\textit{model2/Subsystem9/Oad}'
'\textit{model2/Subsystem3/Oad}'
'\textit{model2/Subsystem4/Oad}'
'\textit{model2/Subsystem5/Oad}'
'\textit{model2/Subsystem6/Oad}'
'\textit{model2/Subsystem7/Oad}'
'\textit{model2/Subsystem8/Oad}'
```

This order is obviously in agreement with the order of \( X \). The concentration profile of adsorbed oxygen is easily obtained with:

```matlab
plot(Zaxis, sort(X));
```

We can now obtain the linearized SSM as follows:

```matlab
[a1, b1, c1, d1] = linmod('\textit{model2}', X, eta);
```
Note that not the initial values within the integrator blocks are used by the function `linmod`, but that the state vector $x$ is evaluated. The initial values are contained within the vector $x_0$. The same procedure as above can be used to plot the results. Compare again with the curves shown in Fig. 3.22.

Similarly, current–voltage simulations can be obtained as described in appendix 3-A.3. Limiting currents are determined with `trim` using high cathodic overpotentials (cf. Fig. 3.21).
Part III

The Interface between $\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_y\text{O}_{3+\delta}$ and Yttria-Stabilized Zirconia
Abstract

Nucleation and growth of lanthanum zirconate (LZO) between (001) single crystals of 9.5 mol% \( Y_2O_3 \)-stabilized \( ZrO_2 \) (YSZ) and porous \( La_{0.85}Sr_{0.15}Mn_yO_{3\pm\delta} \) \( (y = 0.95...1.10) \) perovskites were investigated. The perovskites were screen-printed on the solid electrolyte and sintered in air at 1373 K for short periods. High resolution transmission electron microscopy, electrochemical impedance spectroscopy, and atomic force microscopy were employed for interface characterization. The manganese concentration in the perovskite affect the onset of nucleation and the growth rate of lanthanum zirconate. Excess lanthanum oxide within the perovskite reacts immediately with YSZ to form dense LZO layers. Layer growth kinetics is controlled by bulk diffusion of cations. Stoichiometric perovskite leads to the reductive formation of cubic LZO islands at the cathode/electrolyte interface after a few minutes of sintering. The A-site deficient perovskite is characterized by the reductive dissolution of Mn into YSZ in the early
sintering stage and by a pronounced surface diffusion of cations. After the critical Mn concentration in the perovskite is reached, reductive nucleation of LZO originates. Island growth is controlled by surface diffusion of cations and the supply of lanthanum. The electrochemical properties of the cathode/YSZ interfaces are strongly influenced by the formation of LZO at the triple phase boundary. Charge transfer, dissociation of adsorbed molecular oxygen ions, and surface diffusion of atomic oxygen are discriminated from electrochemical impedance data.

**Keywords.** Lanthanum zirconate (La$_2$Zr$_2$O$_7$); lanthanum strontium manganite; oxygen reduction; electrochemical kinetics; electrochemical impedance; solid oxide fuel cell (SOFC).

### 4.1 Introduction

#### 4.1.1 General

Oxygen ion conducting Yttria-Stabilized Zirconia (YSZ) and perovskite-type Sr-doped LaMnO$_{3.5}$ (LSM) have been widely used as electrolyte and cathode materials in Solid Oxide Fuel Cells (SOFC). The target operating temperatures of SOFC have been markedly reduced from ~1273 K (1000°C) to ~1173 K (900°C) or even less over the past ten years. A further reduction of the operating temperatures seems required to circumvent the use of expensive interconnect materials, such as lanthanum chromite or nickel base alloys. But lower operating temperatures cause an increase of the electrode and electrolyte resistances, thus, the overall power output of the cell decreases. These circumstances have heightened the need for a better understanding of the factors influencing the electrochemical properties of SOFC electrodes. Of particular interest is the interface between the cathode and the electrolyte, i.e. the triple phase boundary (tpb) region, where the reduction and incorporation of adsorbed oxygen species is supposed to take place [1]. Nowadays, it is generally accepted that the electrochemical properties of LSM cathodes depend to a larger extent on the nanostructure and the phase composition of the interface, than on the microstructure of cathode layer. The formation of badly conducting foreign phases during heat treatment and/or operation is believed to be the main factor for a degradation of the electrochemical properties of per-
4.1 Introduction

Lanthanum zirconate (La$_2$Zr$_2$O$_7$, abbr. LZO) and strontium zirconate (SrZrO$_3$, abbr. SZO) are well known to form under certain conditions. The successful employment of Co and Fe containing perovskites with high electrochemical activity for SOFC operation at intermediate temperatures will depend to a large extent on the ability to control or inhibit the formation of foreign phases.

4.1.2 Microstructure and Chemistry

Lau and Singhal [2] first reported pyrochlore-type La$_2$Zr$_2$O$_7$ formation between diffusion couples of dense La$_{0.9}$Sr$_{0.1}$MnO$_3$ and (ZrO$_2$)$_{0.8}$(YO$_{1.5}$)$_{0.2}$ single crystals. La$_2$Zr$_2$O$_7$ and perovskite-type SrZrO$_3$ have been found to form at interfaces between YSZ and (La,Sr,Ca)MnO$_3$ at high temperatures in air [3–4]. The amount of LZO has been found to decrease with increasing Sr or Ca substitution for La [5, 6, 7], and to increase with longer reaction periods or higher sintering temperatures, respectively. Formation of SrZrO$_3$ has been found to occur between heavily doped La$_{1-x}$Sr$_x$MnO$_3$ (x > 0.3) and YSZ [8,4,9,10]. A-site deficiency in (La,Sr)$_{1-y}$MnO$_3$ has been shown to decrease or even prevent zirconate formation during high temperature treatment. Yamamoto et al. [11] found no reaction product by X-ray diffraction analysis for the mixture of La$_{0.8}$MnO$_3$ and (ZrO$_2$)$_{0.84}$(YO$_{1.5}$)$_{0.16}$ after sintering at 1473 K (1200°C) for 192 h; however, when the temperature was raised to 1573 K (1300°C), lanthanum zirconate was detected after 50 h of heat treatment. (La,Sr)$_{0.9}$MnO$_3$ was found to be considerably less reactive than the stoichiometric material [5]. In addition, an induction period for zirconate formation was observed when A-site deficient LSM was used [5, 12]. The following explanation [12] was given: Mn diffuses in larger quantities than La, therefore lanthanum manganite depletes in Mn which further leads to La$_2$O$_3$ precipitation, which itself immediately reacts with YSZ to form LZO.

These experimental findings are in good agreement with the chemical equilibria calculations of mixtures of (La$_{1-x-y}$Sr$_x$Ca$_y$)MnO$_3$ and (ZrO$_2$)$_{0.87}$(YO$_{1.5}$)$_{0.13}$ by Yokokawa et al. [13, 14]. The reaction of LaMnO$_3$ with ZrO$_2$ has been characterized as a combination of the LZO formation and a reduction of the Mn ion [15]. The thermodynamic origin of the driving force of this reaction has been attributed to the destabilization of the unusual valence state of Mn$^{3+}$ in the perovskite in presence of zirconia. Thermodynamic studies showed for the case of LaMnO$_3$ that the relatively stable tetravalent manganese ions in the perovskite give rise to the lanthanum...
nonstoichiometry. It was pointed out [15-16] that when La$_2$Zr$_2$O$_7$ is formed between La$_{y}$MnO$_{3+\delta}$ and YSZ, a small number of the manganese ions may be oxidized in the perovskite structure. In contrary, the dissolution of manganese is reductive. This seems to originate from the size of manganese ions: the ionic radius of the tetravalent state is small, and this makes it easy to accommodate the La nonstoichiometry in the perovskite phase, whereas the relatively large size of the divalent ions ensures the large solubility into YSZ (see [16] and references therein).

Manganese, a major constituent of doped LaMnO$_3$, is known to be a mobile species at high temperatures and can easily dissolve from lanthanum manganites into YSZ, thereby changing the properties of the cathode and electrolyte surface [2, 3, 8, 12, 17, 18]. Diffusion coefficients of Mn in (ZrO$_2$)$_{0.8}$(YO$_{1.5}$)$_{0.2}$ single crystals were reported to be (10$^{-13}$ to 10$^{-12}$) cm$^2$/s at 1673 K (1400°C) and two orders of magnitude higher in polycrystalline YSZ [2]. This large difference has been attributed to fast diffusion paths through grain boundaries [3, 6, 19]. Total solubilities of manganese oxides were calculated from chemical equilibria calculations by Yokokawa et al. [20]. It was shown that manganese can be dissolved up to 11.4% (2.1% as Mn$^{3+}$ and 9.3% as Mn$^{2+}$) in (ZrO$_2$)$_{0.85}$(YO$_{1.5}$)$_{0.15}$ at 1573 K (1300°C) in air. At 1273 K (1000°C), calculated solubility is lowered to 5.1% (1.4% and 3.7% for Mn$^{3+}$ and Mn$^{2+}$, respectively). This contradicts the observations of Roosmalen and Cordfunke [4] who found no diffusion of manganese from La$_{1-x}$Sr$_x$MnO$_3$ (x = 0, 0.15, 0.3, 0.5) into YSZ from diffusion couple experiments. They observed a mass transport of lanthanum and strontium from the perovskite into YSZ. However, the previously mentioned studies were performed under different experimental conditions and employed different sample preparation and characterization methods, which may be the basis to discrepancies and disagreement concerning the reaction mechanism of YSZ with LaMnO$_3$ based cathode materials. This conjecture is supported by Yokokawa et al. [21] who pointed out that oxygen plays an important role in the reductive dissolution of manganese from the perovskite phase in YSZ:

$$\text{MnO}_{n(p)} = \text{MnO}_{n'(YSZ)} + (n' - n)/2 \cdot \text{O}_2(g).$$  \hspace{1cm} (4.1)

Oxygen removal may be hindered in dense diffusion couples, therefore retarding manganese dissolution. In contrast to Mn, diffusion and solubility of La from the perovskite phase in YSZ has generally found to be much
smaller, whereas Sr diffusion and solubility in YSZ have been found to be almost completely absent [2, 8, 11, 12, 18]. Also migration of Zr and Y into the perovskite was observed [6, 8].

4.1.3 Influence on Electrochemical Properties

The literature on the relation between electrode characteristics and the type and amount of foreign phases is far less extensive in comparison to thermodynamic studies. Yamamoto et al. [9] first showed the influence of annealing La$_{1-x}$Sr$_x$MO$_3$ (M = Cr, Mn, Fe)/YSZ interfaces at 1273 K (1000°C) on the current–overpotential behaviour at 1073 K (800°C). The overpotential of these cathodes was not significantly affected with the annealing process. However, at annealing temperatures of 1373 K (1100°C) the overpotential increased rapidly with annealing time. This was attributed to the formation of large amounts of SrZrO$_3$ which was detected with X-ray diffraction. On the other hand, the overpotential for rf-sputtered LaCoO$_3$ cathodes increased rapidly with annealing time, which the authors explained by the chemical reaction of YSZ and LaCoO$_3$ to form lanthanum zirconate. Similar results were found by Ivers-Tiffeé et al. [22]. Kaneko et al. [12] followed the change of the electrochemical impedance during sintering at 1673 K (1400°C) in air and investigated the interfaces after sintering with EDX. Both the high frequency resistance and the low frequency resistance increased markedly with time and a the presence of LZO was observed after sintering. The authors explained this increase in electrode resistance with the formation of a LZO layer at the interface, but they did not attribute any relaxation frequency to a particular electrode process. They noted that the cathodes were almost dense after the experiment and the low frequency losses were in the range of (0.01 to 1) Hz. From this it seems unlikely that the increase in cathode resistance was caused entirely by the LZO layer, rather gas phase diffusion through the almost dense cathode must have been mainly responsible for the low frequency losses. Electrochemical impedance spectroscopy (EIS) was also employed by Elangovan et al. [23] to study the La$_0.89$Sr$_{0.1}$MnO$_3$, air \ YSZ system. The authors found significant changes in the high frequency part of the spectrum during operation at 1273 K (1000°C). Although they failed to prove the existence of foreign phases at the interface by means of SEM in this work, they concluded from diffusion couple studies [3] that lanthanum zirconate must have formed at the interface. Similar experiments were carried out by Kenjo et al. [24] who conducted polarization measurements at 1173 K (900°C)
on YSZ–LaMnO$_3$ cathodes mixtures sintered at 1273 K (1000°C) to 1573 K (1300°C) in air. They detected traces of lanthanum zirconate at the cathode/electrolyte interface by means of XRD after removing the cathode. Although, a general correlation between the amount of LZO and polarization resistance $R_p$ was found, no detailed explanations were given for the increase in $R_p$. It was argued that a layer of badly conducting LZO simply increases the ohmic resistance of the cathode. We note that those studies were carried out at high operating temperatures of ~1273 K (1000°C) where cathode resistances are generally low (< 1 Ω·cm$^2$) and where it is experimentally difficult to obtain accurate electrochemical impedance measurements up to high frequencies. Using lower temperatures for cathode characterization would yield more information about the oxygen reduction reaction mechanism [25, 26].

We will give a brief review on the present knowledge of the oxygen reduction reaction mechanism in the discussion section.

Recently, transmission electron microscopy (TEM) studies were performed by Tricker and Stobbs [17] on porous La$_{0.85}$Sr$_{0.15}$MnO$_3$/YSZ reaction couples which were sintered at 1573 K (1300°C) and operated at 1273 K (1000°C) in air. The authors were able to detect grains of lanthanum zirconate in an early stage of growth. Growth of LZO was predominantly epitaxial and directed away from the parent YSZ into the abutting LSM. Similarly, Clausen et al. [18, 27] performed TEM studies on diffusion couples as well as on pressed and sintered mixtures with different ratios of manganese excess LSM and YSZ. They concluded from their measurements that nucleation of LZO occurred at the interface between LSM and YSZ grains with supply of material from both the cathode and the electrolyte. According to these authors, the diffusion of manganese into YSZ causes manganese depletion of the LSM and in the case of stoichiometric LSM chemically active La$_2$O$_3$ is formed at the interface, whereas this process is impeded or delayed by an excess of Mn in the LSM. They further showed, that the extra manganese does not have to be contained within the manganite structure, but that it is sufficient to increase the manganese activity by means of doping the cathode with Mn ions. Although these TEM measurements gave a rather detailed picture of the microstructure and microchemistry of the YSZ/YSZ/LZO interface, the authors gave no answer on the question of how the electrochemical properties of cathodes are influenced by the presence of LZO at cathode/electrolyte interfaces. Østergård et al. [28] performed electrochemical measurements at 1273 K (1000°C) on slurry coated and screen printed LSM–YSZ composite cathodes. Unfortunately they carried out TEM not on these samples but on
4.1 Introduction
dense pellets of mixtures between LSM$_y$ and YSZ. Nevertheless, the polarization resistance $R_p$ for the oxygen reduction at 1273 K showed decreasing values upon increasing the length of the triple phase boundary, i.e. by increasing the volume amount of YSZ in the composite cathode, and $R_p$ decreased with increasing manganese excess. In parallel, samples with manganese excess and low amounts of YSZ developed no lanthanum zirconate, whereas stoichiometric cathodes and cathodes with large amounts of YSZ showed the presence of lanthanum zirconate after sintering at 1573 K. The performance increase of the cathodes has been explained with the increase of the length of the tpb and an improved electrode adhesion. Mn dissolution was considered as the controlling factor for LZO formation; however, the authors did not quantify the different factors which influence $R_p$.

4.1.4 Open Questions and Aims of the Study
Despite the fact that a large number of experimental and theoretical studies have been performed, important questions are not yet answered. First and most important, it is unclear how the oxygen reduction at LSM/YSZ interfaces is influenced by the presence of LZO and the microchemistry of the interface. Second, Mn seems to play an important role in the kinetics of the LZO formation. But, does A-site deficiency in LSM$_y$ lead to an incubation time in LZO formation and to a decrease in LZO growth, or were these conclusions drawn due to the detection limits of the experimental apparatus employed? And finally, can we circumvent the formation of detrimental foreign phases by lowering both the fabrication temperature and operating temperature, and/or by choosing appropriate cathode stoichiometries?
The purpose of our work was to investigate the influence of the manganese stoichiometry in La$_{0.85}$Sr$_{0.15}$Mn$_y$O$_3$ (LSM$_y$) upon the nucleation and the growth of lanthanum zirconate at 1373 K (1100°C) in air at electrode/electrolyte interfaces, and to simultaneously determine the electrochemical properties of these interfaces. The study was performed with porous screen-printed cathodes on (001) YSZ single crystals. After sintering, the cathode layers were first removed before any further microstructural investigation was performed. Atomic force microscopy (AFM) and X-ray photoelectron spectroscopy (XPS) were used for analysing the YSZ surfaces. High resolution (HR) TEM was employed for structural analysis and phase analysis of the YSZ surfaces after heat-treatment. Electrochemical impedance spectroscopy (EIS) was employed to monitor the frequency response of cathodes during the
heat-treatment process. Distinct differences in nucleation and growth of LZO were found depending on the stoichiometry of LSM$_y$. Surface diffusion of cations was predominant in case of near-stoichiometric and A-site deficient LSM$_y$. LZO islands formed predominantly at the tpb which caused an increase of the cathode resistance. The charge-transfer reaction was found to be not rate determining at temperatures below 1173 K (900°C). The electrode resistance was attributed to the dissociation of adsorbed oxygen and the surface diffusion of atomic oxygen.

4.2 Experimental Procedures

4.2.1 Sample Preparation

Reaction couples were prepared from dense YSZ substrates and porous perovskite layers. Single crystals of 9.5-mol% Y$_2$O$_3$-stabilized ZrO$_2$ (25x25x0.5 mm, (001) orientation, polished on both sides) (Zirmat Corp., N. Billerica, MA, USA) were obtained. The impurity content of the raw materials for single crystal fabrication is low, and the impurity concentration of the single crystals is expected to be even 1 to 2 orders of magnitude lower than of the raw materials due to the single crystal fabrication process (skull melting). The primary crystallite size of the perovskite powders (ball milled after calcining at 1223 K (950°C) for 2 h) (SSC Inc., Woodinville, WA, USA) was ~250 nm. The powders were strongly agglomerated. The powder compositions were verified with inductively coupled plasma (ICP) atomic absorption spectroscopy (AAS). Two powders with nominal stoichiometries of La$_{0.85}$Sr$_{0.15}$Mn$_{0.95}$O$_3$ (LSM$_{0.95}$) and La$_{0.85}$Sr$_{0.15}$Mn$_{0.98}$O$_3$ (LSM$_{0.98}$) were used in this study.

Pastes of perovskites were prepared by mixing appropriate amounts of powder (71.9 wt%) with a solvent (24.5 wt%) (diethylene glycol monobuthyl ether acetate, Fluka AG, Buchs, CH), a binder (0.9 wt%) (Ethyl cellulose, Ethoxyl content 48%, Aldrich, Inc., Milwaukee, WIS, USA), and a dispersant (2.7 wt%) (Furan-2-carboxylic acid, Fluka AG, Buchs, CH) in an agate mortar. Screen printing pastes with higher manganese contents (0.98<y<1.10) were prepared by adding Mn(NO$_3$)$_2$·4·H$_2$O (Fluka AG, Buchs, CH) (dissolved in ethanol) in appropriate amounts to the LSM$_{0.98}$ powder before preparing the paste. This procedure ensures that the additional manganese is homogeneously distributed on the powder surface and within the organic paste. Table 1
Table 4.1 Characteristics of the screen-printing pastes used in this study. —Note that the cation ratio (column 3) refers to the nominal cation composition of the screen-printing paste. LSM$_y$ ($y \geq 1.02$) screen-printing pastes consist of the La$_{0.85}$Sr$_{0.15}$Mn$_{0.98}$O$_3$ powder with additions of manganese nitrate.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Description</th>
<th>$n_{\text{Mn}}/(n_{\text{La}} + n_{\text{Sr}})$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM$_{0.95}$</td>
<td>SSC, Inc., calcined 1223 K for 2 h, ball milled</td>
<td>0.95</td>
</tr>
<tr>
<td>LSM$_{0.98}$</td>
<td>SSC, Inc., calcined 1223 K for 2 h, ball milled</td>
<td>0.98</td>
</tr>
<tr>
<td>LSM$_{1.02}$</td>
<td>LSM$_{0.98}$ with additions of Mn(NO$_3$)$_2$·4H$_2$O</td>
<td>1.02</td>
</tr>
<tr>
<td>LSM$_y$ ($y &gt; 1.02$)</td>
<td>LSM$_{0.98}$ with additions of Mn(NO$_3$)$_2$·4H$_2$O</td>
<td>$&gt; 1.02$</td>
</tr>
</tbody>
</table>

summarizes the screen-printing pastes used in this study. Note that doped powders were not calcined before use, i.e. the additional manganese is supposed to be on the particle surface, as well as within the organic paste. Perovskite layers were screen printed (325 mesh) on YSZ substrates. The samples were sintered at 1373 K (1100°C) in flowing air for periods from 15 min to 12 h using a chamber furnace (Nabertherm HT10/18, Naber GmbH, FRG). The temperature was controlled by means of a thermocouple which was located close to the samples. The samples were held at 1073 K (800°C) before and after sintering in an supplementary furnace. The heating rate was 1 K/min from room temperature to 873 K (600°C) with a dwell time of 4 h at this temperature followed by a heating rate of 3K/min to 1073 K. The samples were taken from the supplementary furnace, put into the sintering furnace for the desired period, and subsequently put back into the furnace held at 1073 K. The cooling rate from 1073 K to room temperature was 3 K/min. Home-made high purity alumina crucibles (CERALOX HPA-0.5 Mg, Condea, Tucson, AR, USA) were employed as sintering supports. The pore size distributions and porosities of cathodes were obtained from mercury-intrusion measurements (model 2000, Carlo Erba, Italy) on ~0.12 g of sintered screen-printing paste. The cathode layer thickness was ~20 µm after sintering. In order to examine the YSZ surface and the reaction products on the YSZ surface after sintering, the sintered porous perovskite layers were dissolved with concentrated hydrochloric acid in an ultrasonic bath at room
temperature. Finally, the samples were cleaned with water and ethanol. YSZ and lanthanum zirconate are stable against hydrochloric acid whereas LSM$_y$ dissolves rapidly.

4.2.2 Investigation of Surfaces and Interfaces

Topographic observations of YSZ single crystal surfaces were conducted with AFM (TMX 2010, TopoMetrix, Santa Clara, CA, USA). All the AFM experiments were conducted in air using a constant force mode. A square pyramidal Si$_3$N$_4$ tip with radius of curvature of ~100 nm, produced lateral and vertical resolutions of 2 nm and 0.5 nm, respectively. The base of the pyramid consisted of a square with sides ~5 µm long. The aspect ration was about 1:1. A tripod scanner (70 µm scan range) was used for scanning large ranges. Higher resolution was obtained with a tubular scanner (7 µm scan range). Five images from each sample were analysed quantitatively, with each image consisting of 1024 lines with 1024 points. The quality of the silicon nitride tip was regularly checked with a sample of known surface structure. Numerical analysis of surface data was carried out with the AFM software package (version 3.08) on a windows compatible (486) personal computer. Raw data were first corrected for sample tilt before conducting numerical analysis. Quantitative estimates of the volume amount of surface phase, its average height, the YSZ surface coverage, and the length of the tpb between the YSZ surface and any surface foreign phases were obtained.

HRTEM analyses were conducted on YSZ surfaces. Electron transparent samples were prepared by dividing, polishing, and argon-ion-thinning. Following standard procedure of mechanical pre-thinning of cross-sectional specimens, two slices from the sample were epoxy bonded in a metallic tube face to face. This composite was sliced, mechanically thinned, and polished to a thickness of (20...30) µm. Plan-view samples were cut into disks of 3 mm diameter using an ultrasonic disc cutter and then dimpled from the substrate side to a final thickness of 20 µm. In both instances, final thinning to electron transparency was done by argon-ion beam thinning. Micrographs were obtained with a HRTEM (model CM30, Philips) operating at 300 kV. Energy-dispersive X-ray analysis (EDX) (VOYAGER III, Noran Instruments, Middleton, WI, USA) was used for elemental analyses of foreign phases on the YSZ surface.
4.2 Experimental Procedures

XPS sputter depth profiles were recorded in a Perkin-Elmer PHI 5400 ESCA system using Mg Kα excitation (hv = 1253.6 eV). Using an electron take-off angle of 43°, the analysed surface area was 1.5 mm². Sputter depth profiling was performed using argon ions at 3.3 keV. The sputter rate was calibrated with reference films to 3.7 nm-min⁻¹ for SiO₂. The sputter rate ratio between ZrO₂ and SiO₂ is 0.46 therefore giving a sputter rate of 1.7 nm-min⁻¹ for ZrO₂. The depth profiles were acquired as a set of discrete sputter cycles interrupted by XPS measurements of the Zr 3d, Y 3d, La 3d, Sr 3d and O 1s core-level lines. The atomic concentrations reported here were calculated using PHI sensitivity factors.

4.2.3 Electrochemical Investigation

Perovskite working electrodes (1x1 cm, ~20 μm thickness) and reference electrodes were applied to YSZ single crystals by screen printing. Platinum gauzes (52 mesh, Fisher Scientific, Pittsburgh, PA, USA) were pressed by hand into the freshly printed perovskite layers. The gauze was fixed at the edges with a ceramic two-component binder (type 1500, Firag, Ebmatingen, CH), and further coated with diluted screen printing paste in order to have a good electrical contact between the cathode layer and the gauze. Platinum wires (0.35 mm diameter) were used to contact the gauzes. The counter electrodes were prepared from Pt paste (C 3605 P, Heraeus GmbH, Hanau, FRG) where we first dc-sputtered ~50 nm of Pt on the YSZ surface (model SCD 040, Bal-tec, Balzers, FL). The in-plane conductivity of unsintered and sintered cathode layers, as well as the conductivity of dense cathode material, was measured with four-probe measurements. The layers were screen printed on polished alumina rods (3x3x40 mm). Pt wires were used as current leads and potential probes.

Electrochemical measurements were conducted in air atmosphere over the temperature range of 723 K (450°C) to 1373 K (1100°C) during heating and cooling cycles. Steady-state current–potential curves and electrochemical impedance spectra were obtained (Model IM6, Zahner GmbH, FRG) in a three-electrode, four-lead configuration. The measurements were carried out in air or O₂/N₂ mixtures (5 Pa ≤ pO₂ ≤ 10⁵ Pa). Impedance measurements were carried out at equilibrium potential E_eq (if not otherwise stated) in potentiostatic mode over a frequency range of 10 mHz to 100 kHz or less. The excitation voltage was 20 mV at T ≤ 873 K (600°C) and 10 mV at temperatures above. Short electrical wires were used to minimize inductive errors at high
frequencies and high temperatures due to low electrode impedances. The uncompensated electrolyte resistance $R_e$ was determined from the high frequency intercept of the impedance data in a complex plane plot. The polarization resistance $R_p$ was obtained from the low frequency intercept in the complex plane plot. The dc resistance was obtained from the slope of the steady-state $I(\eta)$ curve at $\eta = 0$. A further analysis of impedance data will be described in the discussion section.

## 4.3 Results

### 4.3.1 Cathode Microstructure and Electrical Conductivity

A scanning electron micrograph of a fractured cross section of a porous cathode layer on a YSZ single crystal is shown in Fig. 4.1. The micrographs show the typical morphology of the La$_{0.85}$Sr$_{0.15}$Mn$_y$O$_3$ layers obtained in this study. The cathodes were without cracks and adhered well to the YSZ substrate, even after only 15 min of sintering. The average grain size of the cathodes was in the range of 0.3 µm to 0.8 µm, depending on the sintering period.

![SEM of sintered LSM$_{1.02}$ cathode on YSZ single crystal.](image)

The sample was sintered at 1373 K (1100°C) in air for 2 h. (a) Overview of the microstructure. (b) Necks around the LSM grains and at the contacts between the YSZ surface and the LSM$_{1.02}$ grains formed during sintering.
Neck formation between the cathode grains, as well as at the interface between the cathode grains and the YSZ electrolyte surface, can be observed (Fig. 4.1b). SEM-EDX gave no indication of formation of foreign phases (irrespective of the composition of the cathode) at the interface or for interdiffusion of cations. The porosity of La$_{0.85}$Sr$_{0.15}$Mn$_y$O$_3$ cathodes changed from...
-55% in the green state to ~42% after 12 h of sintering at 1373 K (1100°C), where the mean pore diameter increased from $d = 0.32 \mu m$ to $d = 0.5 \mu m$. We observed by SEM that cathodes densified faster the higher their manganese content was. Nevertheless, the porosity did not decrease to values less than 40% at sintering temperatures of 1373 K for cathodes with 10% manganese excess. The cathode materials in our study with $y = 0.95$ to 1.10 were single phase perovskites of rhombohedral structure. We could not detect any further phase in sintered cathodes by X-ray diffraction; however, cathodes with higher amounts of manganese ($y = 1.16$) showed the presence of Mn$_3$O$_4$ grains in the TEM.

The electrical conductivity of the cathode layers followed the general dependence for small polaron conductivity. Fig. 4.2 shows the variation of $\log(\sigma \cdot T)$ vs. $1/T$ of freshly screen-printed porous layers of LSM$_{0.98}$ and LSM$_{1.02}$ on polished alumina substrates and compares the results of porous and dense LSM$_{0.98}$. Note that the cathode layers were not heated to 1373 K but only to 1223 K (950°C). Nevertheless, the cathode layers cracked during cooling below 723 K (450°C) due to the thermal expansion mismatch between alumina and slightly sintered porous LSM$_y$. Note that the electrical conductivity of unsintered cathode layers is relatively high after the heat treatment at 1223 K in comparison with sintered cathodes. The addition of Mn ions to the screen printing paste has a beneficial influence on the electrical conductivity of unsintered cathodes at lower temperatures during heating. There is no significant difference in the conductivity of undoped and doped (+4% Mn) LSM$_{0.98}$ after heat treatment at 1223 K.

### 4.3.2 Interface Development During Sintering

**Manganese Deficient Perovskite ($y = 0.95$).** Fig. 4.3 depicts a XPS sputter depth profile from a YSZ surface which was sintered with a porous La$_{0.85}$Sr$_{0.15}$Mn$_{0.95}$O$_3$ (LSM$_{0.95}$) cathode layer at 1373 K in air for 2 h. The YSZ single crystal was completely transparent after removal of the cathode. The surface layer (after 30 sec of Ar$^+$ sputtering) of this sample is seen to contain primarily Zr, La, and O. The concentration of Sr decreases from ~1% at the surface to less than 0.5% after 30 nm of sputtering. In comparison, Y is present at the surface and its concentration increases to the nominal value of YSZ after ~30 nm of sputtering. Mn is below the detection limit of the XPS method (~0.1%). The composition of the surface layer is seen to remain
4.3 Results

Fig. 4.3 XPS sputter depth profile of a La-rich surface layer on YSZ single crystal. The first few nanometers of the surface show a La/Zr ratio of ~1.35. The atomic concentration of Sr is below 1%. Beyond a sputter depth of ~40 nm the composition corresponds to the nominal composition of (Y0.15)0.19(Zr0.81)0.81. The sample was first sputtered with Ar+ during 30 s for removal of carbon (composition of 'as received' sample surface not shown) [32].

approximately constant over the first 20 nm and the La/Zr atomic ratio is ~1.35 within the topmost 15 nm. During depth sputtering, electrostatic charging of the sample surface occurred after ~15 nm of sputtering. The La/Zr ratio before Ar+ sputtering of the sample was ~0.65, i.e. the Zr4+ concentration within the first (0.5...1) nm was distinctly higher than the La3+ concentration. However, the carbon concentration before sputtering (as received sample) was ~50% and, therefore, care must be taken in interpreting this result.

TEM images of a cross-section of the YSZ surface studied with XPS as described above, are shown in Fig. 4.4 Even under low magnification (Fig. 4.4a) it is clear that the YSZ surface contains grains of a new phase which cover the YSZ surface entirely. Fig. 4.4b shows the Selected Area Elec-
Fig. 4.4 TEM images of lanthanum zirconate islands grown on a (001) YSZ single crystal surface.—(a) Bright field image of LZO grains of uniform thickness and size. (b) Simulated (right side) and experimental (left) [011] SAED of epitaxial LZO on (001) YSZ surface. The filled circles in the simulated pattern represent the YSZ reflexes where the open circles represent the LZO reflexes. Given (hkl) refer to LZO. The structural data from Deiseroth [29] were used for simulation (oxygen parameter: $x = 0.295$).
4.3 Results

Fig. 4.4 (continued) (c) High resolution image of lanthanum zirconate grain in [011] direction. The inset shows a magnified selection of the top of the island. An experimentally obtained HR image of YSZ in [011] direction is pasted into the inset for comparison (darker square).

Electron Diffraction (SAED) pattern of the surface region and compares with simulations for YSZ and La$_2$Zr$_2$O$_7$ with a zone axis of [011]. The wide and intense diffraction spots are caused by the YSZ substrate whereas the weak diffraction spots index perfectly as fcc with a unit cell parameter which is ~2.08 times the lattice parameter of the YSZ substrate (9.5 mol% Y$_2$O$_3$-stabilized; $a_0$ = 0.5142 nm [30]).

These findings are consistent with the reaction product on the surface being lanthanum zirconate, La$_2$Zr$_2$O$_7$, which has a lattice parameter of $a_0$ = 1.0786 nm [29, 31]. The diffraction spots $n\{hkl\}$ ($n$ being an integer) of LZO are weak when $n$ is odd and strong when $n$ is even [31]. Although the [200] reflections are not allowed with [011] beam direction, they are present in the SAED pattern. This was also observed by Clausen et al. [18] and is

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explained by double diffraction, \((1\bar{1}1) + (1\bar{1}1) = (200)\). The diffraction pattern also reveals that the LZO grains shown in Fig. 4.4a grew epitaxially on the (001) YSZ surface

\[
\{001\}_{\text{LZO}} \parallel \{001\}_{\text{YSZ}} \\
\langle 100\rangle_{\text{LZO}} \parallel \langle 100\rangle_{\text{YSZ}}
\] (4.2)

which is in agreement with previous results [17]. Finally, the splitting of the LZO reflections reveals that the epitaxy is not perfect, but that a slight misorientation exists between the YSZ substrate and the LZO grains. It was not possible to determine the cation concentration of the LZO grains reliably with TEM-EDX due to the size of the grains; however, the concentrations of La and Mn in the YSZ adjacent to the lanthanum zirconate grains were below the detection limit of our TEM-EDX. In addition, Mn could not be detected in the surface layer. Fig. 4.4c shows a HRTEM in [011] direction of a single LZO

Fig. 4.5 AFM of a lanthanum zirconate layer covering a YSZ single crystal surface.—
(a) 2-dimensional view of a (800x800) μm area. Note the preferential orientation of the LZO grains [32].
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Fig. 4.5 (continued) (b) Lower right part of (a) shown in a surface plot to depict the variations in layer height. Note that Fig. 4.3 and Fig. 4.4 show the XPS profile and HRTEM images of the same sample surface, respectively.

...grain. Note that the surface of the grain shows a high-resolution (HR) pattern which is apparently equal to the pattern of the YSZ substrate (cf. inset of Fig. 4.4c). We found that every investigated LZO grain was covered with a few atomic layers of this phase. Note that the transition from the LZO high resolution contrast to the high resolution image of the surface phase is seen to be continuous. No dislocations can be seen.

Fig. 4.5 shows the topography of the same YSZ sample surface. It is seen from the AFM image in Fig. 4.5a that the lanthanum zirconate grains are preferentially orientated with respect to the <100> axes of the (001) YSZ surface. The average height of the surface layer shown in Fig. 4.5b is (18 ± 3) nm, which is in agreement with the XPS results reported in Fig. 4.3. The average grain size of the LZO grains is about (120 ± 40) nm. Nucleation of LZO grains occurred around the contact between the LSM grains facing the YSZ surface. Even after sintering periods of less than 15 min, the YSZ surface was almost completely covered with islands of LZO of considerable thickness (~5 nm). The growth constant $D$ of the reaction layer was evaluated through the Wagner equation, $x^2 = D \cdot t$, where $x$ is the average thickness as a function of the sintering time $t$. With $x = (18 \pm 3)$ nm and $t = 2$ h we estimate $\log D/(m^2 \cdot s^{-1}) = -(19.35 \pm 0.15)$ at 1373 K.
Slight Manganese Deficient Perovskite \((y = 0.98)\). Fig. 4.6 shows AFM images of the development of lanthanum zirconate islands during sintering at 1373 K (1100°C) in air between cathode layers of \(\text{La}_{0.85}\text{Sr}_{0.15}\text{Mn}_{0.98}\text{O}_3\) and YSZ. It is discernible that the islands grow in between the cathodes grains and the YSZ surface towards the cathode. The shape of the islands is cube-like and the islands show a preferential orientational relationship with the YSZ substrate. By looking closely at the islands in Fig. 4.6a it can be seen that the large islands are made up of four smaller islands (embryos). During sintering the embryos grew in diameter and height until they faced each other and therefore formed a single island. These islands further grew in height and diameter until most of the YSZ surface was covered by a relatively thick layer.

Fig. 4.6 AFM images of a (001) YSZ single crystal surface covered with cube-shaped islands of lanthanum zirconate. —The colourbar on the right denotes the \(z\) scale. (a) Epitaxial LZO grains (1) on top of the YSZ surface after 30 min of sintering at 1373 K (1100°C) in air. The average island size is \((0.5\pm0.1)\ \mu\text{m}\) and the average height is \(-35\ \text{nm}\) after 30 min. Note that the YSZ level is approximately at \(z = 60\ \text{nm}\) and that there is an obvious orientation relationship between the LZO grains with the parent YSZ. (2) denotes the \(tpb\) between YSZ, LZO, and the gas phase.
of cube-shaped lanthanum zirconate islands (Fig. 4.6b). Note also the differences in the $z$ scale of these two figures and compare with Fig. 4.5. The initial surface coverage after 15 min was estimated numerically from AFM images to be $\sim 50\%$ (Fig. 4.7b). This value increased to $\sim 90\%$ after 12 h of sintering period. The length of the $tpb$, $l_{tpb}$, was obtained by estimation of the perimeter between the LZO grains and the YSZ surface numerically. The length of the $tpb$ increases rapidly within the first 30 min of sintering and slowly decreases with increasing sintering time. A clear correlation between $l_{tpb}$ and $A_{cov}$ is seen. Fig. 4.7c shows the average height of the LZO islands, $h_{av}$, which was obtained from the estimated volume amounts of LZO on the YSZ surface, standardized with the corresponding surface coverage. In this way $h_{av}$ corresponds to an apparent LZO layer thickness and the results can be compared with those of LSM$_{0.95}$. The growth rate of the island height follows a different law as in the case where the LZO layer is dense.
Fig. 4.7 LZO island growth kinetics at 1373 K between $\text{LSM}_{0.98}$ and YSZ.—(a) Length of tpb shown versus sintering time at 1373 K in air. The region marked contains at least 50% of the predictions. (b) Length of tpb shown versus YSZ surface coverage with LZO islands.
Fig. 4.7 (continued) (c) Apparent layer growth kinetics. The data were obtained by numerically estimating AFM images.

Fig. 4.8 shows a bright field TEM of a LZO island. A sharp boundary between the YSZ and the lanthanum zirconate, as well as a dislocation network around the grain boundary, can be seen. The LZO island grew completely towards the cathode side and not into the YSZ. The boundary is remarkably flat. The lattice constant of LZO was estimated from a [011] SAED pattern as $a_0 = 1.077$ nm. The cation concentration in the islands (averaged over 6 islands) was determined with TEM–EDX. We obtained $(40.3 \pm 0.1)\%$ for La, $(6.5 \pm 0.2)\%$ for Y, and $(53.2 \pm 0.2)\%$ for Zr. The Zr/(La + Y) ratio is therefore equal to 1.14 at a Zr concentration of 19.3%. The Zr/Y ratio in the LZO islands is 8.1, which is larger than in the YSZ (nominal 4.26). The amount of Sr and Mn in the LZO islands was below the detection limits. The amounts of Mn detected in the topmost YSZ surface near and below the LZO islands was very low, generally less than 0.3%. Sr and La could not be detected in the YSZ. Note that the YSZ surface near the LZO grain is lowered by a few nanometers compared with the original level (cf. Fig. 4.8). This was also
observed in the AFM investigations. In addition, the YSZ surfaces were often faceted after the high-temperature treatment. Again, as in the case with LSM$_{0.95}$, we found from HRTEM (Fig. 4.9) that all investigated LZO islands were covered with a thin layer (< 10 nm) of material of cubic symmetry with a unit cell parameter of ~0.5 times the lattice parameter of LZO. The layers are found to be inhomogeneous in thickness. Relatively thick zones (up to 10–15 atomic layers) are found at the top of the islands where the contact between the LSM grains and the LZO islands is supposed to be. Very thin regions (1–3 atomic layers) can be observed at the side walls of the islands. Note again that the transition from the LZO phase to the surface layer is continuous and that no dislocations can be seen.

**A-Site Deficient Perovskite ($\gamma = 1.02$).** Fig. 4.10a shows an AFM image of a YSZ surface which was sintered with a porous La$_{0.85}$Sr$_{0.15}$Mn$_{1.02}$O$_3$ cathode at 1373K (1100°C) in air for 2 h. The surface topography is dominated by evenly distributed rings [32]. The thickness as well as the height of the rings increase rapidly with increasing sintering time. No distinct changes in mor-
Fig. 4.9  HRTEM of LZO island surface.—The image shows the upper right area of the island shown in Fig. 4.8 (rotated clockwise by 90°). The entire LZO island is covered with a thin layer of a cubic phase with a lattice constant of ~0.5 times the lattice constant of LZO.
Phology can be noted with AFM up to 4 h of sintering. From XPS measurements and HRTEM investigations we found that the rings which formed at early sintering times consisted of Mn-doped YSZ with a high defect density. The atomic concentrations of the islands were estimated with TEM-EDX. We obtained (13.8 ± 0.8)% Y, (78.7 ± 1.6)% Zr, and (7.4 ± 1.0)% Mn (average over 6 islands, sample sintered for 2 h at 1373 K). Note that the surface of the YSZ substrate shows steps near the islands which is clearly seen in Fig. 4.10b. Around the island the surface of the YSZ is lowered with increasing sintering time (cf. z scale bar in Fig. 4.10b). The step size in the YSZ was typically ~5 nm. After prolonged sintering (> 4 h), we found again cube-shaped islands on top of the zirconia rings (Fig. 4.11). The change in morphology towards the cube-shaped islands can be well observed from this image. After nucleation, these islands further grew and exhibited a characteristic cube shape as observed in the case of the manganese deficient perovskite (y = 0.98). The rate of growth of these cube shaped islands was about one to

![AFM images of (001) YSZ surface after sintering with a La$_{0.85}$Sr$_{0.15}$Mn$_{1.02}$O$_3$ cathode.](image)

Fig. 4.10  AFM images of (001) YSZ surface after sintering with a La$_{0.85}$Sr$_{0.15}$Mn$_{1.02}$O$_3$ cathode. —Mn nitrate was added to the starting powder (LSM$_{0.98}$) to obtain the nominal composition. (a) AFM image of larger YSZ surface area. The cathode was sintered for 2 h.
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Fig. 4.10 (continued) (b) AFM image of single island after 4 h of sintering. Note the slope down of the YSZ surface towards the island. The original YSZ level is at $z = 0$ nm.

Two orders of magnitude lower than that of the LZO islands in the case of LSM$_{0.98}$. From the morphological information obtained from the AFM images we supposed that these cubic islands consist of lanthanum zirconate. To prove this hypothesis, we investigated some of these samples with the HRTEM. Plan-view TEM of a sample sintered for 4 h reveals that every large island consists of several smaller islands (Fig. 4.12), which is in agreement with the AFM investigations. In addition, the stepped YSZ surface can be clearly seen in this image. The [001] SAED pattern of this sample shows intense diffraction peaks from the YSZ parent material (Fig. 4.12). The weak reflections index as fcc with a lattice parameter $\sim 1.98$ times the lattice parameter of YSZ. XPS measurements of this sample revealed about 4 atomic percent of La within the surface. The La concentration diminished within 15 nm of sputtering. Note that XPS probes the entire surface which was in this case only partially covered with islands. Fig. 4.13a shows a cross-sectional bright field TEM of a ring-shaped island which formed during 12 h of sintering. Both island tips show a sharp boundary at the top and a different contrast.
From HRTEM images (Fig. 4.13b) it is seen that the tip consist mainly of lanthanum zirconate with small inclusions of $c$-$\text{ZrO}_2$. This was also confirmed from the [011] SEAD patterns of the islands. The lattice constant of the LZO phase was determined as $\sim 2.09$ times the lattice constant of the YSZ parent material. The deviation from perfect epitaxy was $\sim 1\text{"}$. Note also the difference in the LZO lattice constant of the samples sintered for 4 h and 12 h, respectively.

In addition, we investigated the behaviour of interfaces between (001) YSZ and LSM$_y$ ($y > 1.02$). AFM investigations of YSZ surfaces after sintering with LSM$_{1.10}$ and LSM$_{1.16}$ showed almost no indication for LZO formation up to 12 h of sintering at 1373 K. Occasionally, cube-shaped islands could be detected after 12 h. HRTEM and SAED gave no indication for LZO formation.

![Density sliced AFM image of YSZ surface after long-term sintering. —The LSM$_{1.02}$ cathode was sintered for 10 h. Note the typical square-like morphology of the areas at the $z$ level above $\sim 250$ nm. These areas also exhibit a typical orientation relationship with the (001) YSZ single crystal surface.](image-url)
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Fig. 4.12  Plan-view TEM of YSZ surface.—The sample was sintered for 4 h at 1373 K. The dark horizontal lines are Bragg contours. The \( c-ZrO_2 \) islands show as clusters of dark rings. Note how the steps on the YSZ surface can be clearly seen (marked with the white arrow). The inset shows the corresponding SAED pattern.

Fig. 4.13  (next pages) Bright-field TEM of cross section of ring-shaped island.—The sample was sintered for 12 h at 1373 K in air. (a) The lower part of the islands consist of \( c-ZrO_2 \) which contains \( \sim 7\% \) Mn (referred to the cation concentration). (b) HRTEM of left tip shown in (a).
La$_2$Zr$_2$O$_7$ Formation and O$_2$ Reduction Kinetics
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![Image of a material sample with a scale bar of 20 nm]
4.3.3 Electrochemical Properties LSM$_{0.98}$ Cathodes

Electrochemical impedance spectra were recorded during the heat treatment of La$_{0.85}$Sr$_{0.15}$Mn$_{0.98}$O$_3$ (LSM$_{0.98}$) cathodes on (001) YSZ single crystal electrolytes. The spectra were taken at the same temperature during heating and cooling. In Fig. 4.14 a typical electrochemical impedance of the La$_{0.85}$Sr$_{0.15}$Mn$_{0.98}$O$_3$, air|YSZ system before and after sintering at 1373 K (1100°C) is shown in the complex plane. The frequency response of unsintered cathodes is similar in the complex plane over the temperature range of 773 K (500°C) to 1273 K (1000°C). Also the frequency response of sintered cathodes is similar in the complex plane.

In contrast, the frequency response of unsintered and sintered cathodes was completely different. Fig. 4.15 compares the frequency responses of unsintered and sintered LSM$_{0.98}$ cathodes in air taken at the same temperatures. It is clear that the phase maxima shifts to higher frequencies with increasing temperature. Note the marked broadening of the dispersion due to sintering, which becomes more pronounced at lower the temperatures [25]. The polarization resistance $R_p$ is increasingly dominated by the low frequency losses.

![Fig. 4.14 Typical complex plane plot of the electrochemical impedance of a LSM$_{0.98}$|YSZ interface during heat treatment in air.—The shown measurements were obtained at 973 K (700°C) in air. (a) Cathode impedance before sintering.](image-url)
Fig. 4.14 (continued) (b) Cathode impedance after sintering at 1373 K (1100°C) for 2 h. The numbers within the figures denote the frequencies in Hz. The frequency range was limited to (0.1...10^5) Hz. No inductive behaviour was observed at high frequencies. \( R_e \) denotes the uncompensated electrolyte resistance and \( R_p \) is the polarization resistance of the electrode.

with decreasing temperature. The resistances from small-signal dc measurements at equilibrium potential were in accordance with the \( R_p \) determined from EIS measurements, indicating that no polarization losses occurred below the probed frequency range.

Fig. 4.16 shows an Arrhenius plot of the cathode conductivity, \( \sigma_e = R_p^{-1} \), from 773 K to 1373 K in air. The apparent activation enthalpies, \( \Delta H_\phi \), below ~1000 K are significantly lower than \( \Delta H_\phi \) above 1100 K. Note also that \( \Delta H_\phi \) of \( \sigma_e \) of unsintered and sintered cathodes are comparable at high temperatures but that they are rather different at lower temperatures. The temperature dependence of \( R_p \) of different samples was similar to the one shown in Fig. 4.16, although the absolute values of \( \sigma_e \) varied within a factor of two.

The influence of the oxygen partial pressure \( p_{O_2} \) on \( \sigma_e \) is shown in Fig. 4.17. These data were obtained from impedance measurements and dc measurements on one sample during its heat treatment. The temperatures were chosen in order to obtain the \( p_{O_2} \) dependencies where \( \sigma_e \) exhibited different activation energies. The oxygen partial pressure dependencies of \( \sigma_e \), i.e.
Fig. 4.15 Bode plots of LSM$_{0.98}$ cathodes on YSZ during heat treatment. The spectra were recorded at the same temperature during heating and cooling while keeping the temperature constant during the measurement. Electrochemical impedances shown at (a) $T = 779$ K ($506^\circ$C), (b) $T = 974$ K ($701^\circ$C), and (c) $T = 1173$ K ($900^\circ$C). (—) $|Z|$ before sintering; (— —) $|Z|$ after sintering; (o) phase angle before sintering; (*) phase angle after sintering.
4.3 Results

![Arrhenius plot of conductivity $\sigma_e$ of LSM$_{0.98}$ cathode.](image)

$\Delta H_\phi = 182 \text{ kJ/mol}$

$\Delta H_\phi = 190 \text{ kJ/mol}$

$\Delta H_\phi = 90 \text{ kJ/mol}$

$\Delta H_\phi = 125 \text{ kJ/mol}$

**Fig. 4.16** Arrhenius plot of conductivity $\sigma_e$ of LSM$_{0.98}$ cathode. —The sample was heated from room temperature to 1373 K, held for 2 h, and subsequently cooled.

$\sigma_e \propto p_{O_2}^m$, for the different temperatures are given within the figure. Note the change of the slopes, $m$.

A selection of the corresponding impedance data of unsintered and sintered cathodes is given in Fig. 4.18. With decreasing $p_{O_2}$ the low frequency losses of the cathode increase, independent of the temperature.
Fig. 4.17  Oxygen partial pressure dependence of electrode conductivity of LSM$_{0.98}$ cathode.—(a) Results obtained during heating of unsintered cathode. (b) Results obtained during cooling from 1373 K. The measurements were obtained with a sample different from the one which results are shown in Fig. 4.15 and Fig. 4.16. The slopes of the curves in the log($R_p^{-1}$) versus log($p_{O_2}$), $m$, were obtained from least-square fits of the experimental data over the range indicated with the line.
Fig. 4.18 Oxygen partial pressure dependence of the electrochemical impedance of LSM$_{0.85}$ thin films. —Unsintered cathodes at (a) 873 K (600°C) and (b) 1123 K (850°C).
Fig. 4.18 (continued) After sintering at 1373 K (1100°C) for 2 h in air at (c) 1123 K (850°C) and (b) at 893 K (620°C). The oxygen partial pressures of the measurements are given within the figures.
4.4 Discussion

4.4.1 General

Earlier investigations of lanthanum zirconate formation between LSM and YSZ led to the conclusion that a low conducting dense layer of lanthanum zirconate causes the deterioration of the oxygen reduction properties of the cathode. It was concluded from XRD measurements that A-site deficiency in LSM\textsubscript{y} may prevent, or at least retard lanthanum zirconate formation between LSM\textsubscript{y} and YSZ. It was the main purpose of this study to identify the influence of lanthanum zirconate at the triple phase boundary (tpb) upon the oxygen reduction kinetics of LSM\textsubscript{y}/YSZ interfaces. We further wanted to answer the questions of the incubation time and the role of the manganese content in the LSM\textsubscript{y}.

We would like to point out here that our experimental approach differs on a number of points from earlier investigations. First, we studied the behaviour of porous cathodes on single crystal YSZ. Using single crystals has the advantage, that the influence of impurities usually present in polycrystalline YSZ (e.g. SiO\textsubscript{2}, see e.g. [33]), can be eliminated. Porous cathodes are representative of the actual cathode/electrolyte interface in SOFC. Second, actual sintering temperatures and periods were employed, in order to be able to study the electrochemical properties of the (well performing) interfaces. Last, we employed a number of sensitive surface and interface investigation techniques in parallel to obtain a conclusive interpretation of the nucleation and growth mechanism of lanthanum zirconate between YSZ and La\textsubscript{0.85}Sr\textsubscript{0.15}Mn\textsubscript{y}O\textsubscript{3}.

Our findings have clearly supported the hypothesis of an incubation time [6] with increasing Mn content. Additionally, we have found that the Mn content in LSM\textsubscript{y} drastically influences both the nucleation and the growth kinetics of LZO at the cathode/electrolyte interface. From the electrochemical impedance measurements we have demonstrated that the presence of LZO at the tpb drastically influences the oxygen reduction properties of the electrochemical interface. For the first time it has been shown that the AFM can be successfully employed to obtain information about the nanostructure of the cathode/electrolyte interface.
4.4.2 Lanthanum Zirconate Formation

**Bulk diffusion limited growth.** Sintering of porous LSM$_{0.95}$ cathodes on (001) YSZ single crystals at 1373 K (1100°C) in air results almost immediately in fine-grained, homogeneous layers of La-rich LZO on the YSZ surface (Fig. 4.4a). The reason for the low activation energy for La$_2$Zr$_2$O$_7$ nucleation can be found in the close lattice match of the (001) surfaces of YSZ and La$_2$Zr$_2$O$_7$. The pyrochlore structure may be compared to a fluorite structure with one out of every eight oxygen ions missing. If these vacant sites were also occupied, the formula type would be A$_2$B$_2$O$_8$ instead of A$_2$B$_2$O$_7$ [31].

From the [011] SAED pattern (Fig. 4.4b) we find that the lattice constants of the LZO grains in [001] and [010] direction agree with those of pure La$_2$Zr$_2$O$_7$ from the literature [31, 29, 34]. We find a misalignment of the [100]$_{LZO}$ axis referred to the [100]$_{YSZ}$ axis of ~1°.

Although we found from powder XRD measurements that the LSM$_{0.95}$ was single phase, we suppose that traces of La$_2$O$_3$ were present in the powder. It is well known that the detection limit of the XRD method is ~3 vol%. Excess La$_2$O$_3$ from the Mn-deficient LSM$_y$ is chemically active and reacts immediately at high temperatures with YSZ to form LZO. Nucleation and growth of LZO is facilitated by the use of porous cathodes which allows surface diffusion of cations and unhampered oxygen exchange with the surrounding atmosphere. From this information, certain conclusions can be drawn about the mechanism of LZO nucleation and growth (cf. Fig. 4.19).

Let us first consider the phase diagram of the ZrO$_2$–La$_2$O$_3$ system [34]. At temperatures below 2100 K, La$_2$Zr$_2$O$_7$ exists and has a wide solid solution (ss) range. At lower La$_2$O$_3$ concentrations, pyrochlore co-exists with ZrO$_2$, where a hexagonal lanthanum oxide ss appears at higher La$_2$O$_3$ concentrations. Cubic ss of both the CaF$_2$ and Ti$_2$O$_3$ type exist at temperatures above 2200 K. With increasing temperatures, excess La$_2$O$_3$ may be transported to the interface either by surface diffusion of cations or by a vaporization–condensation mechanism. The hypothesis of the second mechanism is supported by the fact that the YSZ surface was rapidly covered with LZO grains at the beginning of the sintering process. The presence of Mn within the LZO layer and/or the YSZ surface adjacent to the LZO grains was not demonstrated and its presence is not expected, because the La is provided from the excess La$_2$O$_3$. Obviously, once a dense layer forms, further layer growth is limited by bulk and/or grain boundary diffusion of Zr$^{4+}$ and/or La$^{3+}$ across the LZO layer. From our AFM and HRTEM measurements we found that the
LZO layer grew almost exclusively towards the cathode and only to a minor extent (ratio ~10:1) into the YSZ. Is this tantamount to the statement that the bulk (or grain boundary) diffusion rate of $\text{Zr}^{4+}$ is controlling the LZO layer growth kinetics in the early growth state?

Brugnoni et al. [35] investigated the LZO layer growth kinetics at the interface between porous $\text{La}_{0.85}\text{Sr}_{0.15}\text{MnO}_3$ and YSZ polycrystals at temperatures between 1573 K (1300°C) and 1773 K (1500°C). By interpolating their data to 1373 K (1100°C) we obtain for the layer growth constant $\log D_{1373K}^1/(\text{m}^2 \cdot \text{s}^{-1}) = -19.9$, which is in rather close agreement with the result we obtained. Nevertheless, they measured the LZO growth kinetics at significantly higher temperatures than we did, and they obtained layer thicknesses in the range of micrometers. Brugnoni et al. [35] concluded from their

Fig. 4.19 Schematic view of the LZO layer formation at the interface of $\text{LSM}_{0.95}$ and YSZ.—(a) Nucleation of epitaxial LZO islands starts near the $\text{LSM}_{0.95}$ grains. Growth of LZO islands takes place along the YSZ surface until a dense layer is obtained. (b) Subsequent layer growth is limited by bulk diffusion of $\text{Zr}^{4+}$ and surface diffusion of $\text{La}^{3+}$, depending on the distance to the nearest $\text{LSM}_{0.95}$ grain.
SEM-EDX measurements of the interfacial region that the diffusion of La\(^{3+}\) through the reaction layer is the rate determining step, as was concluded by others [4] (though these authors used dense diffusion couples), but which is in contradiction to our experimental findings. Both authors found reaction layers which almost completely grew towards the YSZ.

Our XPS measurements of the freshly prepared sample (before Ar\(^+\) sputtering) showed that the topmost surface layer was strongly enriched in Zr\(^{4+}\). In addition, HRTEM images indicated the presence of a few atomic layers of a cubic phase on top of the LZO grains (cf. Fig. 4.4c). From the phase diagram and a comparison of the high resolution images of this surface region with experimentally obtained high resolution images of YSZ, we conclude that the surface layer consists of cubic-stabilized ZrO\(_2\) (c-ZrO\(_2\)). It is known that La can be dissolved in YSZ up to a few at\% [5], which leads to a slight increase of the lattice constants. However, La is not known to stabilize ZrO\(_2\) in cubic symmetry [34] but it is likely that La\(^{3+}\) and Mn\(^{2+/3+}\) are present in the topmost layer. The cubic stabilization may be due to these doping elements and the influence of the cubic LZO lattice facing the c-ZrO\(_2\) layer.

Let us come back to the question whether the LZO layer growth is determined by the Zr\(^{4+}\) diffusion through the layer. It is probable that the Zr\(^{4+}\) transport takes place predominantly through the grain boundaries, which are generally 3–5 times thinner than the LZO grains (cf. Fig. 4.5b). Subsequent distribution of Zr\(^{4+}\) takes place by surface diffusion. The mean distance between the LSM grains is of the order of 1 \(\mu\)m (cf. Fig. 4.1), which is about 10 times the mean LZO grain size. Accordingly, the supply of Zr\(^{4+}\) is supposed to be much faster than the supply of La\(^{3+}\) by surface diffusion. This may explain the appearance of the c-ZrO\(_2\) layer found on the LZO grains: excess Zr\(^{4+}\) reacts with oxygen to intermediate c-ZrO\(_2\) and later transforms to LZO when sufficient La\(^{3+}\) is present. From the present experimental data it is not possible to make predictions about the layer growth mechanism at higher temperatures or in a later growth stage. It may be that the mechanism changes as soon as the excess La\(_2\)O\(_3\) is consumed and, therefore, La\(^{3+}\) must be supplied by a different mechanism.

**Surface diffusion limited growth.** Sintering of porous LSM\(_{0.98}\) cathodes on (001) YSZ single crystals at 1373 K (1100°C) in air results after a few minutes in epitaxial, cube-shaped LZO grains on the YSZ surface. From the AFM and the TEM images we conclude that the LZO islands grow as an interphase between the LSM\(_{0.98}\) grains and the YSZ surface. The most striking feature of
the LZO islands is its very clearly visible cube shape on the (001) YSZ single crystal surface. It is likely that the orientation of the cube axes of the LZO grains are parallel to the [100] and [010] axes of the YSZ surface. The appearance of the island did not depend on the relative orientation between the sample and the scan direction of the AFM probe, i.e. it can not be considered as an artifact. We would also like to mention that we obtained similar results with polished YSZ polycrystalline samples and that these observations can also be carried out with the SEM. In contrast, Tricker and Stobbs [17] observed epitaxy only when the LZO was formed during operation, otherwise LZO formed incoherently. They concluded that an oxygen ion flux in the vicinity of the interface during operation must be controlling LZO nucleation process. Our observations contradict these conclusions.

From the shape of the LZO islands and the sharp boundary between the islands the YSZ parent material we conclude that the growth of the LZO islands is controlled by surface diffusion of Zr$^{4+}$ along the LZO side walls towards the top of the LZO islands. This explains the growth law obtained for the apparent LZO layer thickness, $h_{av}$, which is clearly different from the growth law of dense layers. An exponent of 2 is expected in Wagner’s law, if volume diffusion is rate limiting. Higher exponents are indicative for surface diffusion [36]. LZO islands growth is, therefore, expected to be much faster as in the case where an initial dense layer forms. But even after 12 h of sintering at 1373 K, the LZO layer is not dense and Zr$^{4+}$ transport can still take place by surface diffusion. As soon as the YSZ surface is entirely covered with LZO, further growth is bulk diffusion limited and the mechanism is similar as in the case with LSM$_{0.95}$, with the important difference that in this case dense layer growth starts at a layer thickness which is about two orders of magnitude larger (~200 nm) compared with dense LZO layers obtained with LSM$_{0.95}$.

Nucleation of the LZO islands does not, as one would expect, occur where the LSM$_{0.98}$ grain and the YSZ surface are in immediate contact but it occurs at the tpb (cf. Fig. 4.20). Similarly, Clausen et al. [18] has found from TEM investigations of YSZ–LSM phase boundaries that LZO nucleation takes place at the interface. This does not agree completely with our findings, but they observed LZO islands in a late state of growth (after sintering at 1573 K) where the actual location of nucleation can not be observed. We typically find four LZO embryos around the contact sites. The reason for this phenomena can be explained as follows: because the region near the tpb of unsintered LSM grains on YSZ surfaces is highly curved, the free surface energy can be
La$_2$Zr$_2$O$_7$ Formation and $O_2$ Reduction Kinetics

Fig. 4.20 Schematic view of LZO island formation and growth at the interface between LSM$_{0.98}$ and YSZ.—(a) Nucleation near the tpb. (b) Growth is limited by surface diffusion of Zr$^{4+}$ along the LZO islands. La$^{3+}$ is supplied from the LSM$_{0.98}$ grain.

diminished by decreasing the curvature of the contact. At relatively low sintering temperatures this occurs predominantly by surface diffusion of cations (see a textbook about sintering, e.g. [37] and references therein). Because Zr$^{4+}$ and La$^{3+}$ are likely to form LZO in presence of oxygen, nucleation of LZO nuclei takes place in this convex interface region (cf. Fig. 4.20). Supporting this hypothesis is the experimental fact that the YSZ surfaces were stepped after a heat treatment (even at low temperatures as 1373 K) and that the YSZ surface sloped down towards the LZO islands. The first fact is due to the slight misorientation of the (001) single crystals, where the second fact is clearly related to the surface diffusion of cations from the YSZ parent material. Further support is given by the HRTEM observation of the LZO islands. These were covered with a few atomic layers of $c$-ZrO$_2$. Although the samples were not quenched to room temperature from 1373 K (but only to 1073 K, cf. the experimental description), it seems that the high temperature
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situation was preserved. A few atomic layers of $c$-$ZrO_2$ are seen on the side walls of the LZO grains, whereas a relatively thick region of $c$-$ZrO_2$ is seen on top of the island. By closer examination of HRTEM images of the island shown in Fig. 4.8 we find that the thickness of the $c$-$ZrO_2$ layer on the side wall does not depend on the crystallographic orientation of the habitus plane. We further observe that the LZO cube surface, which is supposed to be in contact with the LSM$_{0.98}$ grains during sintering, is covered with $c$-$ZrO_2$ of $\sim$10 atomic layers (Fig. 4.9) as well.

From these experimental findings we would expect that the LZO island growth rate would decrease with increasing time, because the manganese activity is supposed to increase markedly in the vicinity of the growth front of the LZO islands. The concentration of Mn in the YSZ surface near the LZO islands was distinctly below 1% and we could not detect any Mn in the LZO islands with TEM-EDX. We could also find no manganese containing precipitations, either by TEM or AFM (although they could have disappeared during the removal of the porous cathode). These findings can be explained with the reductive formation of $La_2Zr_2O_7$ [21]

$$\text{(La}_{1-x}\text{Sr}_y\text{)}\text{MnO}_{3-\delta} + z\text{ZrO}_2 + [(\delta - \delta')/2 + 3z/4]\text{O}_2(g) = (\text{La}_{1-x}_{-x}\text{Sr}_y\text{)}\text{MnO}_{3-\delta} + (z/2)\text{La}_2\text{Zr}_2\text{O}_7$$

(4.3)

where the reaction originated from the A-site nonstoichiometry. In order to lower the A-site occupancy and to oxidize the manganese ions ($\text{Mn}^{3+} \rightarrow \text{Mn}^{4+}$) in the perovskite, La in the perovskite reacts with ZrO$_2$ to form $La_2Zr_2O_7$. In addition, the reductive dissolution of manganese ions in YSZ (cf. Eq. (4.1)) seems to play to a certain extent. Due to the relatively large manganese deficiency in LSM$_{0.98}$ rather substantial amounts of LZO can be expected. Additionally, supply of manganese deficient LSM$_{0.98}$ is ensured because the LZO islands grow towards the unreacted LSM$_{0.98}$. Accordingly, a decline of the growth rate is not expected until a dense LZO layer forms and further supply of Zr$^{4+}$ is controlled by grain boundary or bulk diffusion through the LZO layer.

Our findings about the stoichiometry of the LZO islands are in excellent agreement with the results of Clausen et al. [18]. Y substitutes for La in the LZO in significant amounts. This is known to enhance the concentration of oxygen vacancies [38] which increases the conductivity (approximately one order of magnitude at 1173 K) and ionic transport numbers. Y-doped LZO is
considered as a mixed p-type and ionic conductor in air at temperatures above \(\sim 1000\) K [38]. In addition, the Zr/Y ratio in the LZO is about two times higher than in the YSZ, indicating that the YSZ facing the LZO must be enriched in Y.

Let us finally compare the behaviour of LSM\(_{0.95}\) and LSM\(_{0.98}\). In the first case, thin and dense LZO layers are obtained after short sintering periods, whereas in the second case large islands are obtained. We want to address the question why LSM\(_{0.98}\) does not form dense layers immediately, too? This might be due to traces of La\(_2\)O\(_3\) in the original powder which reacted immediately with hardly any inhibition with the YSZ surface to form LZO. In the case of LSM\(_{0.98}\), only solid state reactions between manganese deficient LSM and YSZ or LZO occur. Accordingly, higher amounts of Mn should further inhibit the formation of LZO.

**Retardation of nucleation and delayed growth.** Keep in mind that the LSM\(_{1.02}\) was prepared from LSM\(_{0.98}\) powder by adding the appropriate amount of manganese nitrate, i.e. the additional manganese is expected to be distributed on the LSM\(_{0.98}\) surface and within the organic part of the screen-printing paste. It is expected that the incorporation of excess manganese into the perovskite phase takes place to a certain extent when the temperature is raised. Accordingly, the manganese deficient perovskite grains are doped with manganese and change stoichiometry. Certainly, manganese also diffuses into the YSZ single crystal surface at elevated temperatures. In any case, the manganese activity is raised at the interface between the cathode grains and the YSZ. Similar arguments were given by Clausen et al. [18] who stated that the excess Mn must not to be contained within the perovskite to develop its efficiency in suppressing LZO formation (cf. Fig. 4.21). Although we know from the previous results that Zr\(^{4+}\) heavily diffuses on the YSZ surface towards the tpb to decrease the free surface energy of the interface, it is surprising to see how the magnitude of transported YSZ even after only (2 to 4) h at 1373 K (cf. Fig. 4.10a). The result of Zr\(^{4+}\) surface diffusion is excellently seen in Fig. 4.10b. The YSZ diffused towards the sintering neck which formed between the LSM particle and the YSZ surface, leaving behind a lowered and faceted YSZ surface. It is also easily imaginable that a single LSM\(_{1.02}\) grain was positioned within the zirconia ring before dissolution. This can also be seen in SEM images of the interface (cf. Fig. 4.1b). The Zr/Y ratio within the formed Mn-doped YSZ rings is almost equal to the nominal ratio of the YSZ, indicating that the surface diffusion of Y is not sig-
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Fig. 4.21 Schematic view of LZO island formation and growth at the interface between LSM$_{1.02}$ and YSZ. (a) Nucleation of epitaxial (Mn)-YSZ starts near the LSM$_{1.02}$ grains. Zr$^{4+}$ and Y$^{3+}$ diffuse along the surface of YSZ. Excess Mn from the LSM$_{1.02}$ is incorporated into the sintering necks until La$_2$O$_3$ forms which (b) reacts with the YSZ tip necks to form LZO. (c) Further growth of LZO islands is retarded.

Significantly hindered, as one could have concluded in the previous case where the LZO islands contained no Y. Cubic stabilization of the rings is explained with the presence of Y. In contrast to the situation with LSM$_{0.98}$, manganese dissolution from the perovskite into the YSZ heavily takes place (cf. Eq. (4.1)). The concentration of $\sim$7.4% Mn is close to the value which can be expected ($\sim$7% at 1373 K in air) from the thermodynamic calculations of

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Yokokawa [20]. These large amounts of Mn at the tpb may have a beneficial effect upon the oxygen reduction and incorporation properties of the interface. Note that the Mn concentration corresponds to the equilibrium concentration. Higher concentrations could only be obtained by increasing the sintering temperature (which would adversely increase the LZO formation tendency) or with non-equilibrium methods, such as ion-implantation [39].

The topographic information obtained from plan-view TEM is in full agreement with the AFM measurements. Nucleation of LZO islands is also confirmed from the [001] SAED pattern from the plan-view TEM sample (Fig. 4.12). The SAED pattern shown in Fig. 4.12b shows a superposition of the SAED patterns from the YSZ matrix, the Mn–YSZ islands, and the LZO nuclei. The strong reflections are due to YSZ. Its variation of the reflection intensity is characteristic for the fluorite structure type. It further is known that Mn-doping of YSZ contracts the YSZ unit cell slightly. From the results given by Yamamoto et al. [5] we estimate a decrease of $a_0 = 0.514 \text{ nm}$ to $\sim 0.513 \text{ nm}$. This change does not become apparent in the SAED pattern. Surprisingly, the lattice constant of the LZO nuclei is only $\sim 2$ times larger than the lattice constant of YSZ (instead of 2.09 times). From the [001] SEAD pattern shown in Fig. 4.12b, an almost perfect overlay of both the YSZ and LZO pattern can be seen; however, the misorientation can be observed. This indicates that the interface between YSZ and LZO nuclei is fully coherent, although not strain-free. The minimization of the interfacial energy is probably achieved through the slight misorientation of both lattices. The misfit between the two lattices is obtained as $\delta = (a_{\text{LZO}}/2 - a_{\text{YSZ}})/a_{\text{YSZ}} = 4.88\%$. This value is small, and accordingly, the mean distance between misfit dislocations is expected to be large. Indeed, misfit dislocations can be observed in the cube-shaped LZO grains (cf. Fig. 4.8). But in this case, the lattice constant of the LZO islands was estimated to be close to the theoretical value.

During sintering at 1373 K, the zirconia rings grow in diameter and height. This leads to a further decrease of the Mn concentration in the perovskite. As soon as the critical Mn concentration is attained, a further Mn supply can only be maintained by the reductive decomposition of the perovskite (cf. Eq. (4.3)). This leads to the nucleation of LZO grains on top of the Mn-YSZ rings, as observed in the AFM (Fig. 4.11) and HRTEM (Fig. 4.13). The further growth of these LZO islands was significantly retarded with respect to the LZO islands in the case of LSM$_{0.98}$. This can be explained with the rate controlling factor which in this case must be the reductive decomposition of the
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perovskite, i.e. the supply of La. This is also supported by the HRTEM images of the tips of the Mn-YSZ rings (Fig. 4.13b). Although LZO formation took place at the tips, relatively large regions of c-ZrO$_2$ can be seen.

4.4.3 Oxygen Reduction Kinetics at LSM$_{0.98}$/YSZ Interfaces

General. Although a number of experimental studies (see e.g. [28, 40-46] on the oxygen reduction of Sr- or Ca-doped LaMnO$_3$ cathodes on YSZ have been performed, there is still relatively little known about the actual reaction mechanism at equilibrium potential. It is generally accepted that the overall reaction is composed of a multi-step reaction [45-47]. Adsorption of oxygen [46], dissociation of adsorbed molecular oxygen [40, 45, 48] and surface diffusion of oxygen species [42, 45, 49] have been considered to be rate determining the overall reaction rate. It has been found that the kinetics of the oxygen reduction is literally independent of the morphology of perovskite cathodes, whereas the reaction rate has been found to be essentially proportional to the length of the tpb [42]. It has also been argued that the electrode behaviour of LSM cathodes on YSZ is similar to the behaviour of the Pt, O$_2$(g) | YSZ system [1], where it has been shown that the dissociative adsorption of oxygen molecules and/or the surface diffusion of atomic oxygen are rate limiting [50], depending on the operating conditions. However, care must be taken when comparing these two systems, because the oxygen adsorption process on oxide materials at high temperatures is completely different from that on Pt [51].

Our electrochemical impedance measurements of the LSM$_{0.98}$, O$_2$(g) | YSZ system show that $R_p$ increases due to sintering at 1373 K in air and that the frequency response changes markedly (Fig. 4.15 and Fig. 4.16). From the temperature dependence of the electrode conductivity, $\sigma_e = R_p^{-1}$, we conclude that the rate-limiting reaction steps are different at low and high temperatures. It is suggested that the formation of the LZO islands at the tpb due to sintering is the main cause for the change of the electrode properties. The oxygen partial pressure dependence of $\sigma_e$ may therefore provide more information about the reaction mechanism.

Cathode microstructure, conductivity, and tpb length. From the SEM images of the cathode microstructure (Fig. 4.1) we see that the perovskite/YSZ interface corresponds to an actual cathode/electrolyte interface of a SOFC. The oxygen activity at the interface can therefore be compared to a
real cell. One might expect that the electronic conductivity of unsintered cathodes is insufficient and orders of magnitude below the electronic conductivity of sintered cathodes; therefore, it is expected that the polarization resistance of unsintered cathodes are below those of sintered cathodes. First, we have shown that the difference in electronic conductivity of unsintered and sintered LSM$_x$ cathodes is considerably less than one order of magnitude (cf. Fig. 4.2). Second, from the conductivity measurement we can see that even a heat treatment at temperatures as low as 1223 K (950°C) is sufficient to increase the electronic conductivity compared to unsintered cathodes. We conclude that the electronic conductivity has only a minor influence on the electrochemical properties, because the polarization resistance $R_p$ of sintered cathodes is markedly higher than the polarization resistance of unsintered cathodes, in contrast to what might be expected.

Our numerical estimates of the $tpb$ length are in agreement with results reported in the literature from comparable cathode microstructures [42, 49]. We would like to point out, however, that the approach we employed permits a rather accurate estimation of the $tpb$ length. Similarly, the SEM can be used to obtain this information from electrolyte surfaces, as recently shown by others [52]. It is surprising that the $tpb$ length of LSM$_{0.98}$|YSZ interfaces reaches its maximum value (~$5 \times 10^6$ m/m$^2$) already after ~30 min of sintering (cf. Fig. 4.7a). We have observed a similar behaviour for the LSM$_{1.02}$ cathodes. With increasing sintering time at 1373 K (1100°C) the $tpb$ length decreases, although only by about a factor of two within 10 h. There have been some attempts in the literature to demonstrate a correlation between the length of the $tpb$ and the polarization resistance of perovskite cathodes (see e.g. [52–54]). Despite it is experimentally very difficult to obtain samples where the only difference is the length of the $tpb$. From the results discussed above we see that increasing sintering times or increasing sintering temperatures not only influence the microstructure, but also lead to second phase formation with altered microchemistry at the interface. In addition, one must be aware of the fact that slight differences in the stoichiometry of the LSM$_y$ (as it might be the case when using different powders of different grains sizes) may have a pronounced and unexpected (and unnoticed) effect, as we see from the comparison of the three perovskite compositions. It is, therefore, important to characterize the raw materials sufficiently.
Towards a reaction mechanism of unsintered interfaces. At $T = 873\, \text{K}$ (600°C) we find a $p_{O_2}^{1/4}$ dependence of $\sigma_e$ for the unsintered LSM$_{0.98}$ cathode (cf. Fig. 4.17a). In the literature a variety of $p_{O_2}$ dependencies can be found (values from 1/4 to 1 have been found for the oxygen pressure exponent; see references cited above). Most reported measurements were obtained at temperatures between 1073 K (800°C) and 1273 K (1000°C). A one-quarter power $p_{O_2}$ dependence is generally attributed to a charge transfer controlled reaction, where the dissociative oxygen adsorption obeys the Langmuir isotherm [55]. The same $p_{O_2}$ dependence has been often found with Sr-doped LaCoO$_3$ perovskites (see e.g. [40]). In contrast to these conclusions we have to assume from our EIS measurements that the cathodic reaction at 873 K (600°C) is not charge transfer controlled, but that it is controlled by a surface diffusion process. Let us analyse our experimental results presented in Fig. 4.18a in more detail.

In the theory of the electrochemical impedance spectroscopy of solids it is often assumed that a double layer capacitance $C_{dl}$ is associated in parallel with the Faradaic impedance $Z_F(j\omega)$ (cf. Fig. 4.22 and e.g. [56, 57]). We have discussed the possible reasons for the occurrence of $C_{dl}$, its consequences on the electrochemical impedance, and its order of magnitude elsewhere [58]. Typical values for $C_{dl}$ are in the range of (1...20) $\mu$F/cm$^2$. Usually, $C_{dl}$ is estimated by fitting equivalent circuits to experimental data. Unfortunately, this procedure requires an a priori choice of such a circuit which itself influences the result of $C_{dl}$. Berthier et al. [59] have presented a method for estimating $C_{dl}$ without the need to assume an equivalent circuit for the electrode reaction. The authors have also presented some illustrative examples. We briefly summarize the main concepts in the following.

Electrochemical impedance spectroscopy has been considered as a promising tool for identifying complex reaction mechanisms in solid state electrochemistry (see e.g. [56] and references therein). However, the interpretation of spectra is generally difficult and it is further complicated by the influence of the double layer capacitance. There is nowadays no generally accepted method for dealing with this problem. EIS spectra of electrode processes have been interpreted for a long time in terms of equivalent electrical circuits and it has been only recently, where micro-kinetic models have been employed to
Fig. 4.22 "Equivalent circuit" of an electrode/solid electrolyte system and corresponding frequency responses.—(a) Equivalent circuit which may give rise to the spectra shown in (b). The Faradaic impedance $Z_F(s)$ is obscured by an electrical double layer capacitance $C_{dl}$ in parallel and an electrolyte resistance $R_e$ in series. $Z_F(j\omega)$ comprises a series combination of the transfer resistance $R_t$ and the concentration impedance $Z_\theta(j\omega)$. $Z_\theta(j\omega)$ often depends in a complicated way on the frequency. Only in very simple cases $Z_\theta(j\omega)$ can be approximated with an electrical equivalent circuit. Note that the (measurable) frequency response $Z(j\omega)$ depends on $Z_F(j\omega)$, $C_{dl}$, and $R_e$ and that the intrinsic dynamic behaviour of the electrochemical interface is exclusively described by its Faradaic impedance $Z_F(j\omega)$ (which is not directly measurable).

describe the dynamic properties electrodes in solid state electrochemistry [58, 60–62]. In the general theory of EIS a number of quantities are of interest and some important relations can be derived [63, 64]:

(i) the polarization resistance $R_p$ of an electrode is a characteristic measure of electrode performance. Its value corresponds to the small-signal dc resistance of the considered electrode/electrolyte system. Accordingly, there is no need to obtain impedance spectra if one is only interested in the polarization resistance. $R_p$ is defined for arbitrary operating points on the current–overpotential curve, $I_F(\eta)$. $R_p$ shows as the low frequency intercept with the real axis in a complex plane plot of impedance data $Z(j\omega)$ (cf. Fig. 4.23).
Fig. 4.23 Complex plane plot of Impedance $Z$ and Faradaic impedance $Z_F$ of unsintered LSM$_{0.98}$YSZ interface at 873 K (600°C). $p_{O_2} = 10^5$ Pa. The double layer capacitance $C_{dl}$ is obtained by applying the method from Berthier et al. [59]. We estimate $C_{dl} = 1.34 \mu F/cm^2$, $R_t = 7.32 \Omega \cdot cm^2$, $R_e = 3.42 \Omega \cdot cm^2$, and $R_p = 141 \Omega \cdot cm^2$. Both $Z$ and $Z_F$ are shown with the electrolyte resistance $R_e$ subtracted.

(ii) The charge-transfer resistance $R_t$ is a further important quantity. The well known exchange-current density, $i_0$, is related to $R_t$ by $i_0 = RT/(2F) \cdot 1/R_t$. However, $R_t$ is defined for arbitrary operating points, i.e. overpotentials, whereas $i_0$ must be considered as a steady-state quantity [58]. Unfortunately, $R_t$ is not directly accessible from electrochemical measurements, but it must be extracted from EIS data by estimating the associated double layer capacitance $C_{dl}$ (see Fig. 4.23 and Refs [58, 59]).

(iii) The difference between the polarization resistance and the charge-transfer resistance is attributed to the concentration polarization, $R_c = R_p - R_t$. The origin of $R_c$ can be attributed to chemical processes on the electrode surface, or to mass transport processes on the electrode surface or in the gas phase.
(iv) Once $C_{dl}$ and $R_t$ are known, the Faradaic impedance $Z_F(j\omega)$ can be obtained from the $Z(j\omega)$ raw data. It is important to understand that the dynamic properties of an electrode/electrolyte system are entirely described by $Z_F(j\omega)$, and not by $Z(j\omega)$. A discussion of EIS data should, therefore, always be performed on the $Z_F(j\omega)$ data (cf. Fig. 4.23).

We now apply these concepts to the present data. Fig. 4.23 shows both the electrochemical impedance $Z(j\omega)$ and the Faradaic impedance $Z_F(j\omega)$ of the LSM$_{0.98}$ cathode in oxygen at 873 K. It is readily seen that the polarization resistance $R_p$ is not dominated by the transfer resistance $R_t$, but that $R_p$ is controlled by a concentration polarization $R_c$. Therefore the idea of a charge transfer controlled reaction must be abandoned. The value for $C_{dl}$ was estimated as $\sim 1.3 \mu F/cm^2$ and it was virtually independent of the oxygen partial pressure. This result is in agreement with what we expect for an unsintered (i.e. unbonded) interface, where we guess the actual electrode/electrolyte coverage to be less than $\sim 10\%$. After sintering, i.e. when the contact area is about 70\% (cf. Fig. 4.7a), we expect the value for $C_{dl}$ to be about one order of magnitude higher. We would like to point out that we understand the origin of the double layer capacitance to be entirely caused by the contact of an electronic conductor (the perovskite grains) and a dielectric material (the YSZ single crystal). We neither interpret the double layer capacitance as a "pseudo-capacitance" [65], nor is it ascribed to the heterogeneous electrode reaction [1]. The dynamics of the oxygen reduction are completely described by the Faradaic impedance, and it is this contribution in which we are actually interested [64].

More information about the type of the concentration polarization is therefore obtained by looking at the frequency dependence of $|Z_F|$. In the $\log(|Z|)$ vs. $\log(\omega)$ plot of Fig. 4.18a a slope close to $-0.5$ is found. This is better seen from the numerical derivatives of $\log(|Z|)$ and $\log(|Z_F|)$ with respect to $\log(\omega)$ (Fig. 4.24). $|Z_F|$ is approximately proportional to $\omega^{-1/2}$ over a broad range of frequencies even in pure oxygen atmosphere. With decreasing $p_{O_2}$ the concentration polarization increases and $|Z_F|$ is almost perfectly proportional to $\omega^{-1/2}$ from 10 Hz to $\sim 5$ kHz at $p_{O_2} = 8$ Pa (Fig. 4.24).

It is well known that at high frequencies under surface diffusion control of atomic species, the following holds (see e.g. [66], or [67])
4.4 Discussion

Fig. 4.24 Frequency dependencies of $|Z|$ and $|Z_F|$ of the unsintered LSM$_{0.98}$|YSZ interface at 873 K (600°C).—The Faradaic impedance $Z_F$ is obtained as described in the text and the legend of Fig. 4.22. The oxygen partial pressures are given within the figure. Note the decreasing accuracy of the impedance measurements with increasing frequency. At high frequencies $|Z_F|$ should reach its limiting value $R_t$ and therefore the frequency dependence of $|Z_F|$ should diminish. Generally, this is only partially the case due to the influence of the electrolyte impedance upon the electrode impedance at high frequencies.

$$Z_F(j\omega) = K_w \omega^{-1/2} \times (1 - j) = \left(\frac{RT}{n^2 F^2} \cdot \frac{1}{C_0 \sqrt{2D}}\right) \omega^{-1/2} \times (1 - j) \quad (4.4)$$

where $D$ is the surface diffusion coefficient of the mobile species, $C_0$ is its equilibrium surface concentration, $K_w$ is called the Warburg constant, and the other symbols have their usual meaning. Obviously, the experimentally determined $\omega^{-1/2}$ dependence of $|Z_F|$ supports the hypothesis of a surface diffusion controlled kinetics. By contrast, it has been argued that $\sigma_e$ should follow a $pO_2^{1/2}$ dependence if surface diffusion is rate limiting [40, 68]. But at the same time it should be mentioned that those results were obtained for the
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Pt, O$_2$(g) | YSZ system. We know that it is misleading to use results obtained for noble metal/solid electrolyte systems directly for the interpretation of perovskite cathodes. At higher temperatures, e.g. at 1123 K (850°C), we find almost a $p^{3/8}_{O_2}$ dependence of $\sigma_e$ at $p_{O_2}$ above $\sim 10^2$ Pa (Fig. 4.17a). By consideration of $Z_F(j\omega)$ and $Z(j\omega)$ at $p_{O_2} = 10^5$ Pa it is seen that the polarization resistance $R_p$ is to a large extent due to the charge transfer resistance $R_t$ (Fig. 4.25). With decreasing $p_{O_2}$, the concentration polarization $R_c$ increases, but the contribution from $R_t$ remains significant. At $p_{O_2}$ lower than $10^2$ Pa, surface diffusion becomes dominant as described above, although less pronounced in contrast to the situation at 873 K (600°C). At $p_{O_2} = 5$ Pa a $\omega^{-1/2}$ dependence of $|Z_F|$ is found from $\sim 100$ Hz to $\sim 5$ kHz. The $p^{1/4}_{O_2}$ dependence of $\sigma_e$ at low oxygen partial pressures is in agreement with this observation. We conclude that a competition between charge transfer and surface diffusion dominates the electrode behaviour at oxygen partial pressures between $(10^3...10^5)$ Pa and tempera-

![Fig. 4.25 Complex plane plot of Impedance Z and Faradaic impedance Z_F of the unsintered LSM$_{0.98}$ | YSZ interface at 1123 K (850°C).—We obtain $C_{dl} = 5.1 \mu F/cm^2$, $R_t = 2.17 \Omega \cdot cm^2$, $R_e = 0.32 \Omega \cdot cm^2$, and $R_p = 4.88 \Omega \cdot cm^2$. Both Z and Z_F are shown with the electrolyte resistance $R_e$ subtracted.](image-url)
tures above ~1100 K. At oxygen partial pressures below $10^2$ Pa, surface diffusion of atomic oxygen becomes rate determining again, as at lower temperatures over the entire oxygen partial pressure range.

Note that we have assumed that atomic oxygen species are diffusing and that the preceding reaction steps, i.e., adsorption and dissociation, are not playing a significant role in the overall reaction path. Let us consider the consequences of these assumptions. Only if the elementary reactions are in sequence, can we expect that the slowest reaction step determines the overall reaction rate. But, surface diffusion of atomic oxygen and dissociation of oxygen molecules occur in parallel on the perovskite surface. Obviously, if the dissociation rate near the tpb is much slower than the surface transport rate towards the tpb (which is normally the case at high temperatures), the overall reaction will be dominated by the faster supply rate, i.e., the surface diffusion step. This is in agreement with the results obtained with unsintered LSM$_{0.98}$ cathodes on YSZ. By contrast, if we assumed that molecular oxygen species were diffusing on the perovskite surface, we would expect that the necessary dissociation step near the tpb (before the incorporation step) would be rate limiting, which is experimentally not observed. It is finally seen from the complex plane plot in Fig. 4.14a that the low frequency part has no circular shape, but that the impedance starts as a straight line with almost a $-135^\circ$ angle with respect to the real axis. This is observed over a broad range of temperatures and may be explained with the phenomenon of spherical surface diffusion [69].

**Influence of sintering on electrochemical properties.** After sintering at 1373 K for 2 h in air, we still find almost a $P_{O_2}^{3/8}$ dependence of $\sigma_e$ at 1223 K (950°C) (Fig. 4.17b). The change of the oxygen partial pressure dependence towards $P_{O_2}$ is readily explained by oxygen gas diffusion in the electrode pores [41]. In the complex plane a second semi-circle develops (Fig. 4.26) at low frequencies (from 1 mHz to ~1 Hz) with decreasing $P_{O_2}$. The resistance related with this low frequency dispersion was proportional to $P_{O_2}$ and showed almost no temperature dependence from 1223 K to 1273 K, which is distinctive for gas diffusion limitation. The contribution from gas diffusion was shifted to lower oxygen partial pressures with decreasing temperatures. At $T = 1123$ K (850°C) it became apparent (but not significant) at $P_{O_2} \leq 10$ Pa. At $T = 1123$ K (850°C) and $T = 1093$ K (820°C) a $P_{O_2}^{0.44}$ dependence of $\sigma_e$ is found at high oxygen partial pressures. With decreasing $P_{O_2}$, a slight change towards a $P_{O_2}^{3/8}$ dependence is found. This change is also shifted to lower
oxygen partial pressures with decreasing temperatures (cf. Fig. 4.17b). It would be most straightforward to conclude from the $p_{O_2}^{3/8}$ dependence of $\sigma_e$ that a competition between charge transfer and surface diffusion exists, as is the case for the unsintered interface. However, we have shown that islands of lanthanum zirconate formed during sintering (cf. Fig. 4.6) and we know that the frequency response of sintered LSM$_{0.98}$/YSZ interfaces is significantly different from that of unsintered interfaces (Fig. 4.15). It is, therefore, obvious to ascribe these changes to the presence of the LZO islands. Based on this idea, we further analyse and discuss the impedance results of the sintered interface.

Towards a reaction mechanism of sintered interfaces. Fig. 4.27 shows a complex plane plot of both the impedance and the Faradaic impedance of a sintered LSM$_{0.98}$/YSZ interface at 893 K (620°C) in oxygen. The spectrum shows almost a perfect semi-circle at low frequencies (< 20 Hz). At high frequencies, $Z_F$ displays a $-45^\circ$ angle with the real axis (cf. inset in Fig. 4.27). $R_t$,
is extremely low, therefore the overall reaction rate is limited by concentration polarization, as in the case before sintering at 873 K (600°C) (cf. Fig. 4.23). Let us now again analyse the $\omega$ dependence of $|Z_F|$. If the reaction was surface diffusion limited, a clear $\omega^{-1/2}$ dependence should be noticeable. From Fig. 4.28 it is seen that this is not undoubtedly found. Nevertheless, a $\omega^{-1/2}$ can be observed from $\sim 1$ kHz to $\sim 10$ kHz, which is also reflected in the $-45^\circ$ angle between $Z_F$ and the real axis in this frequency range. It seems that the $\omega$ dependence from the unsintered cathode is contained within the spectrum of the sintered cathode (compare from $\omega = 1$ kHz to $20$ kHz). The stronger frequency dependence of $|Z_F|$ between 10 Hz and 500 Hz indicates that a different process than surface diffusion must be contributing to the overall electrode resistance.

A slope of $-1$ in the $\log(|Z_F|)$ versus $\log(\omega)$ plot is a clear indication of a first-order (electro-) chemical reaction on the perovskite surface [64]. "First-order" means that a single adsorbed species is relevant and responsi-

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**Fig. 4.27** Complex plane plot of Impedance $Z$ and Faradaic impedance $Z_F$ of the sintered LSM$_{0.98}$|YSZ interface at 893 K (620°C) in oxygen.—The interface was sintered in air at 1373 K for 2 h before cooling to measuring temperature. A Bode plot of the same data set is shown in Fig. 4.18d. We obtain $C_{dl} = 5.5$ µF/cm$^2$, $R_i = 4.5$ Ω·cm$^2$, $R_e = 2.5$ Ω·cm$^2$, and $R_p = 455$ Ω·cm$^2$. 

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In the case of the electrode dynamics, due to a coupling between surface diffusion and the chemical reaction, i.e., the relaxation frequencies are too close, slopes between -1 and \(-1/2\) are expected. This is what is seen in Fig. 4.28a and what gives rise to the "depressed" semi-circle, i.e., that the semi-circle has its centre below the real axis (cf. Fig. 4.27). We now would expect that a slope of -1 could be reached upon lowering the oxygen partial pressure. Fig. 4.28b shows the analysis for \(p_{O_2} = 10\) Pa. It is clearly seen that a \(\omega^{-0.8}\) behaviour predominates over more than one order of frequency magnitudes. This supports the hypothesis that surface diffusion is in competition with a chemical reaction on the cathode surface. In addition, by comparing the graphs in Fig. 4.24 with the graphs in Fig. 4.28 it is seen that the relaxation frequencies contained within the surface diffusion process are spread over a wide range of frequencies, in particular at low \(p_{O_2}\). It is concluded therefore that the surface diffusion process interferes with the chemical process in the spectrum and therefore neither a distinct \(\omega^{-1}\) dependence nor a distinct \(\omega^{-1/2}\) depend-

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**Fig. 4.28** Frequency dependence of \(|Z|\) and \(|Z_F|\) of the sintered \(\text{LSM}_{0.98}\)/YSZ interface at 893 K (620°C) at different oxygen partial pressures. — (a) \(p_{O_2} = 10^5\) Pa and (b) \(p_{O_2} = 10\) Pa.
ence of $|Z_F|$ is measured. We find a similar behaviour of the sintered interface at higher temperatures. However, the $\omega$ dependence is closer to a $\omega^{-1/2}$ dependence than to a $\omega^{-1}$ dependence. This indicates that the surface diffusion process predominates and that the supply of oxygen by the chemical process plays a minor role. Using the same arguments as above concerning the nature of the chemical step we conclude that the dissociation step, and not the associative adsorption step, is responsible for the concentration impedance seen in the spectra. It is, however, not yet clear why the electrochemical behaviour of unsintered and sintered LSM$_{0.98}$ cathodes differs so strongly, especially at low temperatures, and we will finally address this question.

**Discrimination of reaction steps.** We have seen that the overall reaction of unsintered LSM$_{0.98}$ cathodes is limited by surface diffusion of an atomic oxygen species at $T \leq 1123$ K (850°C). With increasing $T$, a competition between charge-transfer and surface diffusion develops. This is easily explained with the difference in activation enthalpies of surface diffusion, $\Delta H_d$, and
charge-transfer, \( \Delta H_{ct} \). From the experimental results it is concluded that \( \Delta H_d \) is higher than \( \Delta H_{ct} \), which is comparable to the situation in the Pt, \( \text{O}_2(\text{g}) \) | YSZ system (see e.g. [55, 70]). Obviously, the adsorption and dissociation processes take place in parallel to surface diffusion on the cathode surface close to the tpb [42]. Furthermore, the surface diffusion rate of \( \text{O}_{ad}^{\delta-} \) towards the tpb is much larger than the direct supply rate of \( \text{O}_{ad}^{\delta-} \) from the adsorption/dissociation near the tpb (Fig. 4.29a). We assume that the surface diffusion coefficient of \( \text{O}_{ad}^{\delta-} \) on LSM is in the same order of magnitude as for \( \text{O}_{ad} \) on Pt [66]. Accordingly, we find that the Nernst diffusion layer thickness \( \delta \), i.e. the distance where perturbations of \( \text{O}_{ad}^{\delta-} \) near the tpb are propagated, is in the order of \((50 \text{ to } 150) \text{ nm}\) at temperatures between 823 K (550°C) and 1273 K [58]. The supply of \( \text{O}_{ad}^{\delta-} \) within \( \delta \) is realized by the surface diffusion process of atomic species and to a

![Fig. 4.29 Model of the oxygen reduction at unsintered and sintered LSM0.98/YSZ interfaces.—(a) Oxygen adsorbs (1) on the LSM surface. The dissociation step (2) is expected to be slow. Both the adsorption and dissociation step are coupled with charge transfer. The LSM surface above the tpb acts as a reservoir for atomic oxygen species. \( \text{O}_{ad}^{\delta-} \) are supplied by surface diffusion (3) and finally electronated and incorporated (4) at the tpb. Note that the Nernst diffusion layer \( \delta \) is in expected to be in the order of 100 nm.](image-url)
Fig. 4.29 (continued) (b) LZO islands at the tpb hinder both the dissociation step and the final electron-transfer step (denoted with the smaller arrows). In consequence, the equilibrium concentration of $O^{\delta-}$ on the LZO is smaller compared to the concentration of $O^{\delta-}$ on the LSM above. Surface diffusion of $O^{\delta-}$ from the LSM surface towards the tpb is considerably retarded, because the thickness of the LZO islands is in the order of $\delta$. Accordingly, the direct supply of $O^{\delta-}$ via the adsorption/dissociation process becomes dominant. See the main text for further explanations.

minor part by the adsorption/dissociation process. Note that the adsorption/dissociation process also takes place near the tpb, but the rate of this supply is generally far below the surface transport rate (compare with the Pt, $O_2(g)\mid$YSZ system [50, 58, 64]). It is furthermore important to recognize that the electrode material completely determines the rate (and type) of oxygen adsorption and dissociation and that the rates may vary many orders of magnitude for different cathode materials (see e.g. for Pt: [71], Au: [72], Oxides: [51, 73]).

In the case of sintered LSM$_{0.98}$ cathodes, $\delta$ is in the order of the thickness of the lanthanum zirconate (LZO) islands which formed between the LSM$_{0.98}$ grains and the YSZ surface after 2 h sintering (see Fig. 4.6a and Fig. 4.7c). Accordingly, surface diffusion and adsorption/dissociation take place predominantly on the lanthanum zirconate surface after sintering (see
Fig. 4.29b. From YSZ it is known that it has a low surface exchange coefficient of $\text{O}_2(\text{g})$ [74]. It is expected that the surface exchange properties of LZO are comparable with those of YSZ, because LZO and YSZ are of similar structure. Accordingly, the rate of adsorption/desorption near the tpb decreases due to the presence of LZO. We suppose that the surface diffusion coefficient of adsorbed atomic oxygen is not altered drastically. However, because the large reservoir of $\text{O}_{\text{ad}}^{\delta-}$ on the LSM$_{0.98}$ surface is $\sim$ 100 nm apart from the tpb it is expected that the $\text{O}_{\text{ad}}^{\delta-}$ supply by surface diffusion strongly decreases. Accordingly, the direct supply of $\text{O}_{\text{ad}}^{\delta-}$ through the adsorption/dissociation process becomes increasingly significant. This interpretation is in agreement with the experimental observations. It is further supported by the fact that the differences in $\sigma_e$, unsintered and sintered cathodes, increase with decreasing temperatures (Fig. 4.16). This can be explained with the decreasing supply rate of $\text{O}_{\text{ad}}^{\delta-}$ by surface diffusion, because $\delta$ decreases with decreasing temperature.

Having discriminated the relevant reaction steps of the oxygen reduction at LSM/YSZ interfaces, we give the following model description

(i) $\text{O}_2(\text{g})$ adsorbs on the LSM surface according to [73]

$$\text{O}_2(\text{g}) + e^- + s \Leftrightarrow \text{O}_2^{\text{ad}}$$  \hspace{1cm} (4.5)

where $s$ denotes free adsorption sites, and $e^-$ electrons from the electrode.

(ii) The adsorbed $\text{O}_2^{\text{ad}}$ species subsequently turns into $\text{O}^-$

$$\text{O}_2^{\text{ad}} + e^- \Leftrightarrow 2\text{O}^-(\text{ad})$$  \hspace{1cm} (4.6)

(iii) and may diffuse on the LSM (or LZO) surface, before it is finally incorporated in the charge-transfer reaction near the tpb according to

$$\text{O}^-(\text{ad}) + e^- + V_O^- \Leftrightarrow \text{O}_O^x + \text{ad}.$$  \hspace{1cm} (4.7)

Although the structure of this model complies with our experimental findings, we know very little about the rate constants and activation enthalpies involved. However, investigating the properties of this micro-kinetic model similarly as described elsewhere [64], could help to obtain more information from experimental data (cf. [58, 64]).
4.5 Conclusions

The thermodynamic study was limited to the investigation of La$_{0.85}$Sr$_{0.15}$Mn$_{y}$O$_3$/YSZ interfaces under equilibrium conditions, i.e. where no current through the interface was flowing. It is well known [21] that current-produced overpotentials at the cathode influence the oxygen chemical potential in the electrolyte in particular in the vicinity of the cathode grains. It is also known from recent TEM studies that the reverse reaction of Eq. (4.3) can take place to some extent, and that therefore initially formed LZO islands may disappear during cell operation [75]. However, we have shown that the formation of lanthanum zirconate can be effectively suppressed by reducing the sintering temperatures to ∼1373 K and by doping the La$_{0.85}$Sr$_{0.15}$MnO$_3$ with excess manganese. We have demonstrated how the excess manganese controls the nucleation and growth of the lanthanum zirconate.

From the electrochemical investigation of the LSM$_{0.98}$, O$_2$(g) | YSZ system we were able to discriminate the relevant reaction steps of the oxygen reduction mechanism at LSM$_y$/YSZ interfaces. Dissociation adsorbed oxygen ions, surface diffusion of atomic oxygen, and the charge transfer contribute to the polarization resistance, depending on the operating and fabrication conditions. We believe that a successful identification of a reaction mechanism requires first a detailed microstructural investigation of the cathode/electrolyte interface. We have also shown that the interpretation of the frequency dependence of $\sigma_\epsilon$ alone is not straightforward and may lead to ambiguous conclusions. We, therefore, suggest that impedance data not be analysed in terms of equivalent circuits but from a more fundamental perspective.

However, we believe that we are still far from a state and parameter estimation of the LSM$_y$, O$_2$(g) | YSZ system, mainly because little physico-chemical data are available on the interaction of oxygen with perovskite surfaces. Further work in this area is even more necessary than further electrochemical investigations.

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References


4 La$_2$Zr$_2$O$_7$ FORMATION AND O$_2$ REDUCTION KINETICS


Part IV

End Matter
Chapter 5

Outlook

5.1 General

Solid State Ionics Devices (SSID) have found application in a large number of different areas. For the future, solid oxide fuel cells (SOFC) are believed to offer an opportunity for a cleaner and more efficient way of energy production. However, at the present time SOFC technology is still in development and in initial system prototype demonstration state. This is, to our opinion, due to the history of development: a large number of experimental studies have been performed, but most of them were related with the optimization of materials or processing routes, and materials characterization. Considerably less basic studies have been performed, and accordingly, still relatively little is known about the electrode reaction mechanisms, the factors responsible for electrode degradation, and how the electrochemical behaviour depends on the processing steps. This thesis has been concerned with the latter type of questions. Following, a summary of conclusions and some ideas for further work in this area.
5.2 Identification of Reaction Mechanisms

The identification of reaction mechanisms is just as an art as a science. Apart from intuition, persistence, and luck we found that following a certain route may help finding the solution faster. We would give the novice the following advice:

(i) Collect as much information as possible related with the system before any experimental work is carried out. Note that much information can often be found in the literature which is not directly related with SOFCs or SSIDs. Try to understand what people have done before and realize the essence. This might be difficult at the beginning, but ask people.

(ii) Do not hesitate to translate your ideas into models. Implement your ideas into the computer and run simulations. Re-implement the models of others as a starting point. Study the behaviour of the models by simulation. Play!

(iii) Start modelling seriously. Define what your models should account for and what is beyond. Collect the a priori known information. Obtain a qualitative understanding from the overall process and recognize the relevant elementary steps. Translate your qualitative models into a quantitative models. Transform the quantitative models into a form suitable for structural investigation and computer implementation. Implement the models into the computer.

(iv) Investigate the structure of the models. Obtain analytical expressions describing the steady-state and dynamic behaviour, as well as the behaviour under limiting conditions, such as high overpotentials, low oxygen partial pressures, and low or high temperatures. Compare your results with those reported in the literature. From simulations, further relationships may become apparent. Use simulations also in order to check your analytical results (and the implementation). Is the model structure in agreement with the reported data? If not, why?
5.3 Modelling and Simulation

(v) Design your experiments according to the information obtained above. Estimate unknown parameters in the models from experimental data. Validate your results. Refine or reject the models.

Note that steps (i) to (iv) consume most of the time available. The ideal experiment needs no more than a single sample. Let us consider some of the thoughts mentioned more closely.

5.3 Modelling and Simulation

Modelling and model implementation are probably considered as the most difficult steps for an experimentalist. However, the pain necessary when learning these tasks is worth the results which can be obtained. We believe that the method developed in this thesis can be applied without an extraordinary mathematical background.

Although the method of digital simulation of electrochemical systems was introduced more than 30 years ago, the method has not found its wide application as it was supposed in the early days. The reason for this might lie in the fact that considerable programming skills of a low level programming language have been necessary (e.g. FORTRAN). This has changed these days. The programming environment of MATLAB and SIMULINK offers a high level programming environment which requires only moderate programming knowledge, as every chemist or materials scientist should possess. This enables to focus on the actual problems. The straightforward implementation of model equations, the extendability of the SIMULINK models, the possibility to reuse programming blocks, and the numerical environment of MATLAB, make a strong tool. The complete process of modelling, simulation, and parameter estimation can be accomplished within one single environment, as we have presented. However, the process of modelling, structural investigation, and simulation must be considered as the first (and mandatory) step of an investigation.
5.4 Materials and Samples

Sintered, porous electrodes have been widely employed for kinetic studies. However, a number of unknown (or badly known) parameters are introduced in this way. First, the microstructure, i.e. the length of the triple phase boundary (tpb) and the porosity, cannot be determined with reasonable accuracy. This makes quantitative parameter estimation difficult, as we have shown. Second, during sintering a number of undesired processes may occur. It is therefore very important to monitor every single step in sample fabrication. If one is not interested in these reactions, they must be avoided which is not always possible. Third, even if a large number of "identical" samples is prepared, their polarization resistance will hardly scatter below a factor of two. This is due to the factors mentioned above.

To circumvent these problems, a number of routes have been proposed. The most popular of them is the use of cone shaped or wire electrodes. However, it is doubtful whether a perfect contact is obtained with a defined length of the tpb. We propose to employ electrodes with simple geometries, i.e. pattern electrodes. This should work without larger problems for metal electrodes which can be sputtered and subsequently etched. The length of the tpb is determined to high accuracy and the influence of porosity (gas phase diffusion) rules out. However, one must be aware of the limitations of this type of electrode. First, the electrochemical investigation is limited to potentials near the equilibrium potential, because of the relatively high electronic resistance of the thin metal strips. Second, the temperatures of investigation must be somewhat low, in order to avoid a drastic microstructural change of the metal pattern. However, the use of one or another type of electrode is determined by the kind of information one is seeking for. Starting with simpler geometries is good advice. In addition, use single crystal material if ever available and use high quality materials with well known levels of impurities. Always check powders for composition.

5.5 Electrochemical Investigation Techniques

Once one has a sound understanding of the materials and their interactions during preparation and operation, electrochemical measurements should be attempted. There has been much praise for electrochemical impedance spectroscopy (EIS) as the tool for identification of electrode reaction mechanism.
However, there has been made no significant progress in the investigation of SSID electrodes. We believe that the reason for this lies in the fact that the theoretical basis of EIS is not sufficiently understood by the experimentalists. Therefore, it is generally concluded that the interpretation of experimental data is difficult. Furthermore, fitting data to equivalent electrical circuits does not help to understand the physical processes involved in the electrode reaction mechanism.

In order to make use of the powers of EIS, micro-kinetic models of the assumed electrode reaction mechanism must be employed. In addition, the actual system response must be extracted from raw data, as we have shown. Any further interpretation and modelling must be based on the system response. However, one should be aware that EIS can not give answers to any question, and that even conventional steady-state current-voltage investigations may give some useful and complementary (and possibly accurate) information. But, be aware of the requirements necessary for a successful application of this method. We propose to consider always a number of different experimental techniques. Certainly, the choice depends on the preceding theoretical analysis.
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[6] A. Mitterdorfer and L. J. Gauckler. La$_2$Zr$_2$O$_7$ formation and oxygen reduction kinetics in La$_{0.85}$Sr$_{0.15}$Mn$_{0.9}$O$_3$ O$_2$(g) | YSZ systems. *Solid State Ionics*, submitted.


Presentations


