Modeling of Transport, Chemical and Electrochemical Processes in Solid Oxide Fuel Cells

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Dissertation for the degree philosophiae doctor (PhD) at the University of Bergen

2009

Acknowledgements

First and foremost I would like to thank my supervisor, Professor Alex C. Hoffmann from the Department of Physics and Technology for his continuous support and kindness during my time being with his group. He accepted me into his group and that enabled me to go to Norway and perform this thesis. Moreover, he was always beside me and even sometimes pushed me to go ahead when I met difficulties by his friendly guidance. I would also like to thank Dr. Pawel Kosinski, my co-supervisor, for his useful guidance. He has also been very kind to me right from the beginning when I first came to Norway.

I am highly indebted to the staff at Prototech for accepting me as a PhD student and always being kind to me during my time with them. I would especially like to thank Mr. Arild Vik, the technical director of Prototech AS, who brought me to a very interesting world of fuel cells and gave me a lot freedom in doing the PhD project. Many thanks go to Tor Monsen, amongst many others, who forced me to speak Norwegian but was always kind to me even I could not.

My sincere gratitude goes to the Department of Physics and Technology for accepting my enrollment for PhD studies and offering me excellent working conditions, even though most of the work was carried out at Prototech AS.

My friends and colleagues within the group of Multiphase Process at the Department are highly appreciated for exchanging experiences and ideas with me, especially during our CFD meetings, and for creating a highly supportive working environment and also for joyful moments over the last four years that I have had in Norway.

I would like to thank my parents, my grandmother and my father-in-law for their love and mental support.

Finally, I want to thank my wife, Loan, and my son, Vinh for being with me. My wife has given up her job in Vietnam to be with me and shared with me very many

things. My wife and my son were always supportive to me even during my most stressful time! Without their love, patience and understanding, I definitely could not finish this thesis. Thank you very much Loan and Vinh!

Contents

Abstract

The working of solid oxide fuel cells (SOFCs) involve fluid dynamics, chemical reactions and electrochemical processes. These phenomena happen simultaneously in complex and sophisticated structures of the SOFC main components consisting of gas channels, porous electrodes, dense electrolyte and interconnects. Therefore, modeling of SOFCs with consideration of the detailed processes, which is indispensably important in the development of the fuel cells, is not always an easy task.

The chemical reactions include the steam reforming of methane and the water–gas shift reaction. The former occurs heterogeneously on the anode surface and homogeneously in the fuel channel while the later occurs homogeneously everywhere in the anode compartment. The electrochemical reactions are oxidation of hydrogen and/or carbon monoxide and reduction of oxygen, which take place at the so-called "three-phase boundaries" (TPBs) formed by the presence of all three of the electrode, the electrolyte and the gas phase. When ionic–electronic conducting composite electrodes are used, the TPBs extends from electrode–electrolyte interfaces into the electrodes forming an electrochemically active layer with finite thickness.

A numerical model for the detailed processes happening in SOFCs is always needed. Advantage of a model is that it can provide detailed insights into the cells that can not be gained by experiments. Additionally, it helps investigating impacts of each process parameter and their interaction, giving information for cell optimization. Modeling of SOFCs has been increasing rapidly during the last two decades, especially the last few years. However, models considering detailed processes taking place at TPBs or considering effects of the composite electrodes are still relatively rare.

This thesis develops a detailed numerical model for planar solid oxide fuel cells. In this model, the electrochemical reactions are assumed to take place in the electrochemically active (functional) layers of finite thickness. The thickness of these

functional layers is up to 50μm, and depends among other things on the size of the particles from which the electrodes are made. The heat of the electrochemical reactions is assumed to be released on the anode side. Moreover, steady-state electrical field-driven transport of electrons and oxygen-ions in the composite electrodes–electrolyte assembly are modeled using an algorithm for Fickian diffusion built into the commercial CFD package Star-CD.

Moreover, in the developed model, one single computational domain includes the air and fuel channels, the electrodes–electrolyte assembly and/or the interconnects, and thus constitutes a single and continuous domain in which balances of mass, momentum, chemical species and energy associated with chemical and electrochemical processes are solved simultaneously.

The model is firstly applied to an anode-supported cell with co- and counter-flow configurations. The oxidation of carbon monoxide is included in this application, however, results show insignificant impact of it on performance of the cell. It is then applied to a cathode-supported cell, which showed a better performance in terms of temperature and current density distributions compared to the anode-supported design. In these applications, the computational domain does not include the interconnects and only variation along two directions (along the cell length and direction normal to the electrolyte surface) are captured.

The model is then applied to fully three-dimensional modeling of an anode-supported cell. In this investigation, the interconnects are included, therefore, their effects on the cell performance are observed.

In addition to the studies mentioned above, a discussion on transport of oxygen ions in the electrolyte is carried out. Some scenarios relating to ion fluxes are proposed, in which the Nernst–Planck and Poisson equations are solved for concentration of ions and potential distribution in the electrolyte.

Chapter 1

Organization of the thesis

This thesis is written in a paper form, which consists of an introductory section followed by a section with scientific papers. The introductory part consists of chapters 2, 3, 4 and 5 while the scientific papers includes papers published or accepted for publication in international journals, papers presented at conferences, and technical reports which will be submitted for publication later on.

In the introductory part, chapter 2 presents a relatively short introduction to solid oxide fuel cells (SOFCs). A brief description of state-of-the-art SOFC components is also given in this chapter. Chapter 3 gives a literature review on modeling of SOFCs.

The papers, which are included in this thesis, will briefly be summarized in chapter 4. Finally, concluding remarks and further work are presented in Chapter 5.

The following sections represent a list of papers that are included in the thesis and added after the introductory part. Papers which are not included in the thesis are named as well.

1.1   Papers included in the thesis

1. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2008. Numerical modeling of solid oxide fuel cells. *Chemical Engineering Science* 63 (21), 5356–5365.

2. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2008. Numerical study of an SOFC with direct internal reforming using charge diffusion-based model. *Proceedings of The 8th European SOFC Forum*, 30th June–4th July, Lucerne, Switzerland.

3. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Numerical analysis of a planar anode-supported SOFC with composite electrodes. *International Journal of Hydrogen Energy* 34, 3488–3499.

4. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Modeling of transport, chemical and electrochemical phenomena in a cathode-supported SOFC. *Chemical Engineering Science*, doi:10.1016/j.ces.2009.03.043.

5. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Numerical modeling of SOFCs using a fully three-dimensional approach. *Technical report*.

6. Ho TX, Kosinski P, Hoffmann AC, 2009. Discussion on the transport of oxygen-ions in an SOFC electrolyte. *Technical report*.

1.2 Papers not included in the thesis

1. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Fully three-dimensional modeling of solid oxide fuel cells. *The Sixth Symposium on Fuel Cell Modelling and Experimental Validation*, 25th–26th March, Bad Herrenalb, Karlsruhe, Germany (oral presentation).

2. Ho TX, Kosinski P, Hoffmann AC, Vik A, 2008. Numerical study of a SOFC with direct internal methane reforming. *Norwegian Hydrogen Seminar*, 25th–26th September, Bergen, Norway (poster).

3. Ho TX, Kosinski P, Hoffmann AC, Wærnhus I, Vik A, 2007. Numerical simulation of electrochemical and transport processes in solid oxide fuel cells. *Proceedings of SOFC-X, The Tenth International Symposium on Solid Oxide Fuel Cells*, 3rd–8th June, Nara, Japan (oral presentation).

4. Ho TX, Kosinski P, Hoffmann AC, 2006. Direct numerical simulation of particle-fluid flow: The state-of-the-art. *Proceedings of WCPT5, The Fifth World Conference on Particle Technology*, 23rd–27th April, Orlando, Florida, USA (oral presentation).

Chapter 2

General Introduction

Fuel cells are energy conversion devices, which directly convert chemical energy into electrical energy with high efficiency, low pollution and low noise. The process of combining hydrogen and oxygen to generate water and electricity is indeed a reversion of an electrolysis process, and was found by William Grove during his experiment in 1839 [1]. A typical fuel cell consists of a dense electrolyte, porous anode and cathode electrodes, fuel and oxidant channels and interconnects as main components. Fuel is oxidized at the anode releasing electrons, which then transport to the cathode via an external circuit. At the cathode, oxidant (mostly oxygen) is reduced consuming the transported electrons. The electrolyte allows ions to flow through in order to complete the overall electrochemical reactions. Depending on the nature of the electrolyte used, fuel cells are categorized in different types. Figure 2.1 represents the working principles of different types of fuel cells. Common types of fuel cells currently under development include [1, 2]:

- – Alkaline fuel cells (AFCs),

- – Polymer electrolyte membrane fuel cells (PEMFCs),

- – Phosphoric acid fuel cells (PAFCs),

- – Direct methanol fuel cells (DMFCs),

- – Molten carbonate fuel cells (MCFCs),

- – Solid oxide fuel cells (SOFCs).
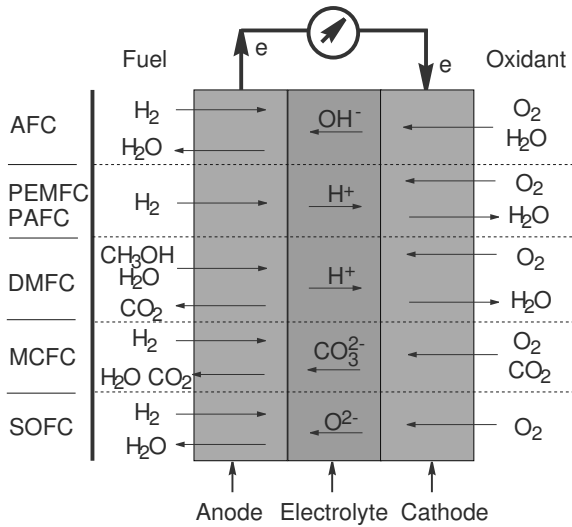
Figure 2.1: Principle of different types of fuel cells.

The first four types of fuel cells are known as low- and medium-temperature fuel cells, which operate at temperatures ranging from room temperature up to around 220°C. The last two types are high-temperature fuel cells operating at temperatures of 500–1000°C. These cells differ in many aspects such as their constituent materials, fuels, operating conditions and performance characteristics. Table 2.1 represents characteristics of different types of fuel cells. The focus of this thesis is on the last type of fuel cells, SOFCs, which is described in the following sections.

Table 2.1: Types of fuel cells and their characteristics [1–4]

| Type	Mobile ion	Operating temperature	Application and notes
AFC	OH^-	50–220°C	Military, space, e.g. Apollo and Shuttle
PEMFC	H^+	30–100°C	Vehicles and mobile application, low power CHP systems
PAFC	H^+	150–220°C	Large CHP systems
DMFC	H^+	20–90°C	Portable electronic systems
MCFC	CO_3^{2-}	600–700°C	Medium to large CHP systems
SOFC	O^{2-}	500–1000°C	Stationary electric power, small to large CHP systems

CHP: Combined heat-and-power

2.1 Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) use a solid-ceramic electrolyte and operate at high temperatures (500–1000°C). The electrolyte allows oxygen ions to transport through its crystal lattice via available vacancies. SOFCs possess a number of interesting features due to their high operating temperature and have therefore been receiving worldwide attention during the last two decades.

Solid oxide fuel cells may yield an electrical efficiency as high as 55%. Moreover, they are capable of working in hybrid systems with gas turbines and combined heat-and-power (CHP) generation, giving overal efficiencies up to 70% and 90%, respectively [5, 6]. Other advantages of SOFCs include:

– The capability of working with a relatively wide range of fuels, i.e. hydrogen, methane or natural gas and hydrocarbons.

– No expensive catalyst is needed for electrochemical reactions.

– The solid nature of the electrolyte gives geometrical flexibility of cell designs; planar, tubular and monolithic designs are known.
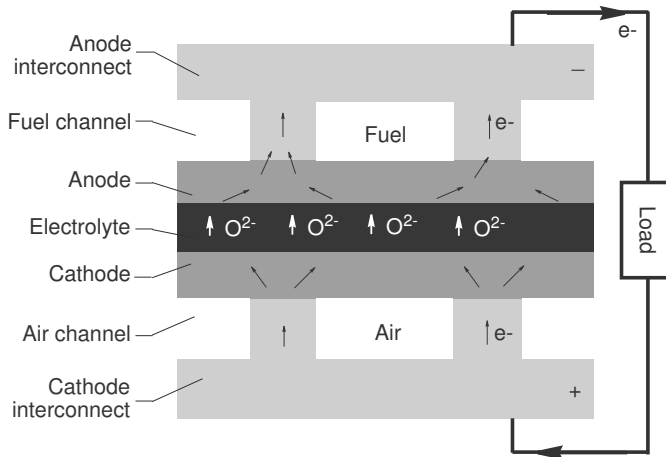
Figure 2.2: Diagram of part of a planar solid oxide fuel cell.

Figure 2.2 represents part of a planar solid oxide fuel cell. In the figure, the fuel and oxidant channels are parallel, which accommodates co- and counter-flow configurations. Cross-flow configuration is another option for flow arrangement in state-of-the-art SOFC manifolding.

Oxygen is oxidized in the cathode by electrons coming from the anode via the external circuit. Oxygen ions transport through the electrolyte to the anode where they combine with hydrogen and/or carbon monoxide to produce water and/or carbon dioxide and release electrons. The interconnects carry electrons from electrochemical reaction sites to the external circuit on the anode side and do the reverse on the cathode side. When stacking cells with planar geometry in series or parallel, they function as electrical connections between neighboring cells and as gas separators.

SOFCs are facing challenges which need to be solved due to the high operating temperature. High thermal stress in the fuel cells or fuel cell systems, for instance, accelerates the material degradation processes and has been shown to be the main cause of cell component breakages. Therefore, further research aiming at understanding the detailed processes or phenomena happening in the cells is needed. Amongst those, an accurate numerical approach, which enables modeling detailed physical and chemical processes and hence works as a numerical tool for optimizing cell performance, is the aim of this thesis.

2.1.1   Chemical and electrochemical reactions

Chemical Reactions
The high operating temperature (500–1000°C) of solid oxide fuel cells makes it possible for the cells to work directly with hydrocarbon fuels, reducing the need for a complex and expensive external fuel reforming. This is impossible for the low- and medium-temperature fuel cells.

It is common to use natural gas as fuel. With presence of nickel metal (Ni) in the anode, methane is strongly reformed producing CO and H_2. CO is then further transformed into CO_2 via a shift reaction. The reforming and shift reactions are described as

$$CH_4 + H_2O \rightleftharpoons CO + 3H_2, \tag{2.1}$$

$$CO + H_2O \rightleftharpoons CO_2 + H_2. \tag{2.2}$$
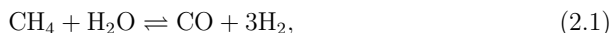
The reforming reaction is endothermic, therefore consuming heat generated by the exothermic electrochemical processes.

The Boudouard reaction: $2CO \rightleftharpoons CO_2 + C$ and the cracking reaction: $CH_4 \rightleftharpoons C + 2H_2$ are the main pathways for carbon formation in the anode at high temperature. This is a serious issue as carbon tars block active sites for chemical and

electrochemical processes and impede transport of the gas phase, therefore reducing cell performance. However, addition of excess steam to the fuel stream shifts the reactions away from carbon formation [7–9]. For SOFCs working with natural gas, steam-to-carbon ratios of 2.5–3 are common.

Electrochemical Reactions

In a typical SOFC, electrochemical reactions take place at three-phase boundaries (TPBs) formed by the presence of all three of the ionic phase, the electronic phase and the gas phase. These electrochemically active sites are mostly located at electrode–electrolyte interfaces. However, in case composite electrodes are used, the active sites can extend further into the electrodes up to a dept of $50\mu m$ [10–13].

Reduction of oxygen on the cathode side, and oxidation of hydrogen and carbon monoxide on the anode side are described, respectively, as

$$\frac{1}{2}O_2 + 2e^- \rightleftharpoons O^{2-}, \tag{2.3}$$

$$H_2 + O^{2-} \rightleftharpoons H_2O + 2e^-, \tag{2.4}$$

$$CO + O^{2-} \rightleftharpoons CO_2 + 2e^-. \tag{2.5}$$

Overall cell reactions are therefore

$$H_2 + \frac{1}{2}O_2 = H_2O, \tag{2.6}$$

$$CO + \frac{1}{2}O_2 = CO_2. \tag{2.7}$$

The overall cell reactions are exothermic, maintain the cell at the high temperatures required for reasonably high ionic conductivity of the electrolyte and reaction rates at the TPBs. Actually, CO mostly participates in the water-gas shift reaction of Eq. (2.2) rather than in the electrochemical processes [14]. In a system where H_2 and CO coexist, the rate of CO oxidation is around 2–3 times less than that of H_2 oxidation depending on the operating temperature [15].

2.1.2   The electrolyte

The SOFC electrolyte is a ceramic material sandwiched by the anode and cathode. The electrolyte functions as an ionic conductor enabling oxygen ions to flow from the three-phase boundaries on the cathode side to those on the anode side through its

crystal lattice. Moreover, with its dense solid nature, it also works as a gas separator, preventing gas species from penetrating into it. Additionally, the electrolyte can function as a mechanical supporting structure with thickness 100–200μm, i.e. in electrolyte-supported SOFCs [3, 16, 17]. However, more and more attention is given to electrode-supported designs with a very thin electrolyte of 5–20μm [16–18]. A thin electrolyte reduces ohmic resistance to ion transport in the electrolyte.

An SOFC electrolyte material must meet various requirements in order for the fuel cell to have a good performance and be stable over long time of operation. These include [1, 2, 9, 19, 20]:

- high ionic conductivity,

- negligible electronic conductivity,

- chemical stability in both reducing and oxidizing environments,

- thermodynamic stability over a wide range of temperature and oxygen partial pressure,

- thermal expansion compatibility with materials of electrodes and of other components, e.g. interconnects, sealants.

Common materials of SOFC electrolyte are zirconia, ceria fluorites and LaGaO$_3$-based perovskites [19].

Yttria-stabilized zirconia (YSZ) is currently the most commonly used material for SOFC electrolytes working at temperatures higher than 700°C since it fulfills the necessary requirements.

Scandia-stabilized zirconia (ScSZ) has higher ionic conductivity than the conventional YSZ material [21, 22]. However, a drawback of ScSZ is performance degradation over long-term exposure to high temperatures. Therefore, this type of material is mainly attractive for intermediate-temperature (600–800°C) SOFCs [19, 23, 24].

Doped-CeO$_2$ electrolytes, e.g. gadolinium doped ceria (GDC) are only attractive for low-temperature (< 600°C) SOFCs since they are partially reduced in hydrogen at temperatures above 600°C [3].

LaGaO$_3$-based electrolytes, typical lanthanum strontium gallate magnesite (LSGM), show high ionic conductivity and can be used for intermediate-temperature SOFCs. However, challenges remain in matching the thermal expansion coefficients, mechanical strength and chemical compatibilities [3].

2.1.3 The electrodes

The electrodes are in principle electronic conductors, forming together with the electrolyte and the gas phase the three-phase boundaries (TPBs) where electrochemical reactions take place. Therefore, they must be porous to allow gas species to transport in and out the TPBs. The electrodes also catalyze the electrochemical reactions.

However, electrode materials have to fulfill a number of conditions because of the high operating temperature. The anode material has to be chemically, morphologically, and dimensionally stable in the fuel gas environment, and likewise the cathode material in the air environment during cell operation. Moreover, the anode material has to be tolerant toward contaminants possibly available in fuel stream. Other conditions of the electrode materials include [3, 25–29]:

- high electronic conductivity,

- sufficient porosity to facilitate transport of reactants and/or products to and/or from the TPBs,

- chemically, thermally and mechanically compatibility with other cell component materials during fabrication as well as under operation.

Nickel can be used as anode material since nickel metal plays the dual role of hydrogen oxidation catalyst and electric current conductor. Additionally, nickel is also an excellent catalyst for cracking of hydrocarbons, e.g. *in situ* reforming of methane. However, the thermal expansion of nickel is considerably higher than that of the yttria-stabilized zirconia (YSZ) conventionally used for the electrolyte. Another problem with nickel is that it can sinter at the cell operating temperature, causing decreasing porosity and reduction of the TPB [26].

Strontium-doped lanthanum manganite (LSM) is the most widely used material for the cathode.

Composite electrodes made of a binary mixture of electronically and ionically conducting particles are more and more widely used in state-of-the-art SOFCs since they are superior to electrically conducting electrodes. An advantage of the composite electrodes is that the TPBs can extend into the electrodes, resulting in reduction of activation losses associated with the electrochemical processes. Figure 2.3 represents the TPBs in electrodes, which are made of electronically conducting, a binary

mixture of electronically and ionically conducting, and mixed-conducting particles, respectively [30]. As will become evident, cases b) and c) cannot be distinguished in the model developed in this thesis and they will both be referred to as "mixed-conducting electrodes". With mixed-conducting electrodes, the TPBs do, as the figure shows, extend into the electrodes from the electrode–electrolyte interfaces.
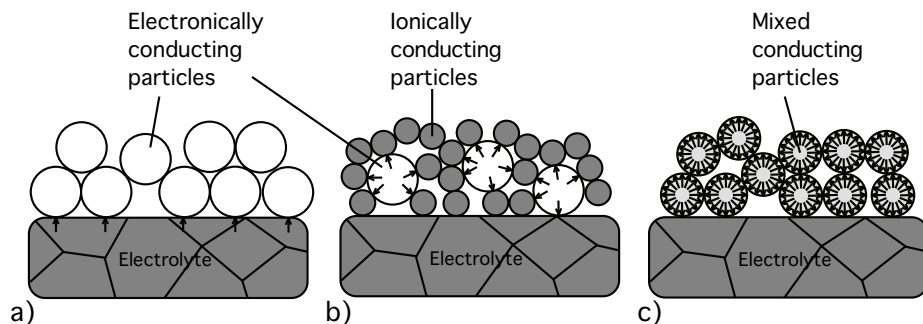
Figure 2.3: TPBs (arrowed) in a) electronically conducting, b) composite and c) mixed-conducting electrodes.

Common composite electrodes are Ni–YSZ and LSM–YSZ for the anode and cathode, respectively. Other advantages of the composite electrodes include:

– reduction of mis-matching of the thermal expansion: the thermal expansion coefficient of YSZ is closer to that of Ni–YSZ mixture than to that of pure Ni [5]. This also allows better anode–electrolyte adhesion;

– prevention of nickel sintering: the presence of YSZ particles between Ni particles in the Ni–YSZ mixture prevents agglomeration of the metal particles.

CeO_2 based materials, e.g. doped with Gd, Sm and Y, are typical mixed-conducting anodes [28, 31, 32]. Perovskite materials such as Sr-doped $LaCoO_3$ (LSC), $LaCoO_3$ co-doped with Sr and Fe (LSCF) are examples of mixed-conducting cathodes. These cathode materials are suitable for SOFCs operating at intermediate and low temperatures.

An electrode can be a mechanical supporting structure in a fuel cell, in which case it is the thickest component compared to that of the electrolyte and the other electrode; this is an electrode-supported cell. In anode-supported cells, the anode thickness is 0.5–1.5mm, while in cathode-supported cells, the cathode thickness is 0.3–1mm. The other electrode thickness is $\sim 50 \mu$m [3, 17].

2.1.4 The interconnect

The interconnect transports electrons between the electrochemically active sites (TPBs) and the external circuit. In a typical SOFC, the interconnect is in direct contact with both the anode and cathode and both the fuel and air. Therefore, requirements for interconnects are most severe of all cell components, namely [3, 33–36]:

 – good electrical conductivity,

 – chemical stability in both oxidizing and reducing environments at the cathode and anode, respectively, at high operating temperatures,

 – chemical stability with other cell components during cell operation and fabrication,

 – dimensional stability with changes in temperature and/or oxygen partial pressure,

 – thermal expansion matching that of the other cell components,

 – low permeability for oxygen and hydrogen (or fuel) minimizing their direct combination during cell operation, e.g. in planar geometrical designs,

 – adequate mechanical strength.

There are two types of materials for state-of-the-art SOFC interconnects, namely ceramic and metallic, with different features.

The ceramic lanthanum chromite is the most common material for SOFC interconnects working at high temperatures (900–1000°C) since it is stable in oxidizing environments at the cathode.

Metallic interconnects have a better electrical conductivity compared to ceramic ones, but are not stable in oxidizing conditions. Therefore, they are mainly suitable for lower temperatures [35]. Oxidation resistant alloys based on Cr or Ni are suitable for intermediate-high temperatures (800–900°C). For SOFCs working at intermediate temperatures (650–800°C) ferritic stainless steel is more favorable [3, 33].

Moreover, metallic interconnects have an interesting feature, which is of mechanical strength. Therefore, they can be used as mechanical support in planar SOFCs, in so-called interconnect-supported cells. This makes it possible to use thin electrolytes (5–15μm) and electrodes ($\sim50\mu$m), reducing ohmic losses considerably, and hence increasing cell performance.

2.2 Aim of the current study

The main aim of this work is to develop a numerical model for solid oxide fuel cells (SOFCs). This model can be used to study detailed phenomena taking place in complex geometries consisting of the gas channels, the porous electrodes, the dense electrolyte and the interconnects.

To be able to capture all the detailed processes including mass, heat and charge transports and chemical and electrochemical reactions occurring in the cell, the model should be three-dimensional. A single computational domain covering a whole unit cell will be used in order to avoid problems arising due to manually coupling solutions in separate domains, as in quasi-two or three dimensional models in the literature. In this single computational domain, equations describing the detailed processes are therefore resolved simultaneously.

Another aim of the thesis is to numerically investigate performance of SOFCs using the developed model. Simulation results can give detailed insights such as distributions of temperature, chemical species, current density and electrical potential in the fuel cells, therefore help optimizing the cell design and performance. Such insights can not be gained by experiments. Different geometries and flow configurations will be investigated. Experimental validation of the model are given where possible in the papers attached to this thesis, though this task is rather difficult because of lack of standardization - insufficient details and/or different data are used in different works in the literature.

Chapter 3

Modeling of Solid Oxide Fuel Cells: Review

Numerical modeling plays an critical role in the development of solid oxide fuel cells. The performance of an SOFC is directly related to processes taking place both in series and in parallel within the cell. Therefore, accurate modeling of the detailed processes is an essential task, which would never be easy because of a large number of physical, chemical and electrochemical processes occurring simultaneously in a complex and sophisticated geometrical system of SOFCs.

Modeling work can give detailed insights into the cell such as the distributions of temperature field, chemical species and electrical current and potential that can not easily be experimentally determined. Moreover, a numerical model or a computer code can help understanding impacts of a process parameter on the other, therefore, it can be used as a numerical tool for cell design and optimization.

This chapter gives a brief review on numerical models of different dimensional scales published in the open literature. A description of heat sources involved in SOFCs is undertaken and introduced as well since they are crucial in SOFC modeling.

3.1 Modeling approaches

Modeling approaches for SOFCs can be broadly classified into two types, namely transport approaches and system approaches [37]. The transport approaches consider more details of transport phenomena happening in the fuel cells while the

system approaches look at behaviors of the cells as a whole within a power generating system.

The system approaches are also known as zero-dimensional approaches or box approaches [38]. With these types of approaches, spatial variations are not taken into account and spatial averaging in all directions is performed. Impact of fuel and/air inlet conditions, utilization factors and overpotentials on cell performance is normally carried by them. The work of Campanari [39] and Lin et al. [40] are typical examples of system approaches. Lin et al. analyzed the effect of interconnect-rib size on the cell concentration polarization in planar SOFCs. The optimal rib design was obtained by minimizing the overall ohmic and concentration polarization of the ribs. It was found that for realistic electrical resistance, the rib width fraction is expected to be between 1/3 and 2/3 of the channel width.

Transport models range from one-dimensional (1D) to three-dimensional (3D) models, which consider the transport processes, hence providing more reliability than system models do. Therefore, they have received much attention during the last two decades.

The transport models can be used to model processes occurring within cell components, e.g. electrodes, interconnects. Thus they help understanding effects of various design parameters and give optimization for the cell components. Additionally, these types of models can be used for modeling of SOFCs at cell and/or stack level. A literature review of transport models is briefly given in the following subsections.

3.1.1 Cell-component level

A large number of papers focusing on cell components has been published in the last decade, including numerical investigations [12, 13, 41–62] and experimental investigations [63–69].

Cannarozzo et al. [42] presented a model for composite anode, taking into account mass transport effects. It was found that the electrode losses display a minimum for a well-defined radius of the electrode particles, which is related to a trade-off between activation and concentration losses. The electrode performance is a function of its composition, thickness and microstructure. Additionally, operating conditions should be taken into account in the optimization process since they significantly influence the electrode performance.

Costamagna et al. [44] modeled performance of solid oxide fuel cell electrodes. The model took into account electronic and ionic transport together with the electrochemical reaction, while mass transport phenomena in the macropores of the electrode was neglected. Assumptions of the model were: steady state, uniform temperature and pressure throughout the electrode and 1D. Also each of the two conducting phases were considered continuous and homogeneous, having a constant resistivity. It was found that the reciprocal electrode resistance (conductance) reaches a maximum in correspondence to a composition near the percolation threshold of the electronic conducting phase. The percolation threshold is the minimum volume fraction of the electronically/ionically conducting particles required to form continuous chains of the same type of particles in the composite electrodes. The chains work as pathways for electronic/ionic conduction.

Lehnert et al. [13] investigated gas transport phenomena in SOFC anodes using a 1D numerical model. The electrochemical conversion of H_2 and CO was known to take place in a zone of about $50\mu m$ thick near the anode–electrolyte interface. However, this zone is small compared to the anode thickness of 2mm, therefore it was treated as a boundary condition in the model. The system was under isothermal conditions with 30% pre-reformed CH_2 as fuel. It was found that a lower porosity-to-tortuosity ratio gives a lower overall conversion of CH_4 in the anode cermet, due to diffusion limitations. A decrease in pore average size also results in lowering the CH_4 conversion.

Kenney and Karan [52] presented a numerical 1D micro-model for investigating impacts of microstructure (porosity, composition and particle size) on the charge-transfer reaction and mass transport processes in a composite cathode of LSM–YSZ. It was found that the TPB line length is maximized at a composition of 50 vol% LSM, and the lower the porosity, the longer the TPBs. The composition of 50 vol% LSM, 50 vol% YSZ and 20% porosity was found to give the best performance.

In their subsequent study [53], a 2D model for composite cathode was introduced, which captures the influence of geometric parameters such as interconnect coverage in addition to microstructural parameters being considered in the 1D model [52]. It was found that a cathode of 0.3 porosity gives a current density higher than the electrode of higher porosities. This was explained by the fact that low porosity means high volume fraction of conducting solid phases, hence high ionic and electronic conductivities and large TPB, which results in good performance of the cathode. However, low porosity limits gas transport into the area under the interconnect, reducing the local current density in this region. Moreover, addition of a current

collector layer covering the functional layer results in an increase in the average current density because the current is higher underneath the interconnect. It was also found that for LSM–YSZ cathode an optimal electrode–interconnect fractional contact area is at around 25%.

Tanner et al. [12] examined numerically and analytically effects of porous composite electrode structure on SOFC performance. Parameters such as electrolyte thickness, charge-transfer resistance, electrode thickness and porosity were under investigation. The activation overpotential as a function of current density was assumed to be ohmic, thus an effective charge-transfer resistance was defined (This is applicable at low activation overpotential/current density, while the relationship between the overpotential and current density is linear). It was found that the resistance decreases as the thickness of the composite electrode increases, eventually to an asymptotic minimum. Moreover, the finer the microstructure of the electrode, the lower is the value of the electrode thickness at which the asymptotic minimum of the resistance is reached, and the lower is the minimum itself.

Suwanwarangkul et al. [70] performed comparison Fick's, Dusty-gas and Stefan–Maxwell diffusion models in predicting concentration overpotential of an SOFC anode. The model used is 1D, i.e. diffusion across the anode thickness.

3.1.2   Cell and/or stack level

One-dimensional models

In 1D models the PEN structure is considered as a thin layer separating the fuel and the air channel flows. Moreover, the cell is represented as a line. Examples of 1D models are references [11, 71–76].

Aguiar et al. [71] investigated the performance of an anode-supported SOFC with direct internal reforming for co- and counter-flow configurations. The results showed that with the same fuel and air inlet conditions, the counter-flow configuration gave rise to the least optimal operation due to steep temperature gradients and uneven current density distributions. However, the model used was one-dimensional and was for the cell working at intermediate temperatures (650–800°C).

Recently, Zhu and Kee [11] focused on the chemical reactions and the transport within the MEA (membrane–electrode assembly) of a planar anode-supported cell.

The charge-transfer process took place over a few tens of micrometers in the composite electrodes close to the electrolyte. On the anode side, a 50μm thick functional layer of different particle sizes was investigated. It was found that smaller particles (a binary mixture of Ni and YSZ particles) generally improve the cell performance as a result of an increased three-phase-boundary length. Zhu and Kee showed the distributions of chemical species, current density, electric potential and activation overpotential across the MEA. However, though the employed model considered the detailed chemistry and electrochemistry, it was one-dimensional such tha only the transverse transport within the MEA was considered. Variations along the cell length was not considered. Additionally, effects of interconnects could not been taken into account either with the 1D model.

Two-dimensional models

In this type of models, one geometrical dimension is neglected by making assumptions or simplifications and variations along the other two dimensions are considered. 2D models are generally used for unit cell simulations. Figure 3.1 presents a schematic diagram of a planar SOFC with three directions indicated.

Two-dimensional models are commonly applied to tubular solid oxide fuel cells because of their axial symmetry [77–80]. Quasi-2D models are also popular since they reduce computational efforts. In such models, 1D gas flows in the gas channels, i.e. x-direction, are coupled with the transverse transport of gas in the porous electrodes, i.e. y-direction, by boundary conditions at the channel–electrode interfaces. Examples of quasi-2D models can be found in [81, 82]. Other 2D models are for instance [83, 84].

Klein et al. [78] presented a 2D model for tubular electrolyte-supported SOFC with methane internal reforming, using the commercial package CFD-Ace. Electrochemical reactions were assumed to take place throughout the composite electrodes (200 and 100μm for the anode and cathode, respectively). Small amounts of steam were used to slow down the reforming reaction. Results showed that cooling effects due to the endothermic reforming could be avoided. However, solid carbon was deposited on the anode surfaces due to Boudouard and methane cracking reactions. This is often a hazard when the ratio steam-to-carbon is lower than unity, reducing the performance, and shortening the cell life.

In the quasi-2D model for an anode-supported SOFC with co-flow configuration
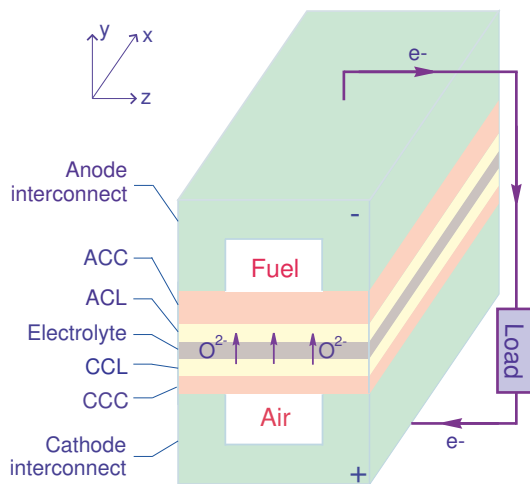
Figure 3.1: Schematic diagram of a repeating unit planar SOFC. ACC/CCC: anode/cathode current collectors; ACL/CCL: anode/cathode catalyst (active) layers.

proposed by Zhu et al. [82], attention was paid to the heterogeneous chemistry and electrochemistry. Results for chemical species fractions and surface species coverages showed the capability of implementing elementary heterogeneous chemical kinetics in the form of multi-step reaction mechanisms into the SOFC model. However, a limitation of the model is that constant temperature was assumed throughout the cell. The impact of the sub-cooling effects on the cell performance therefore was not observed. Carbon formation was not evaluated either.

Janardhanan and Deutschmann [81] later used a similar approach, but removing the isothermal assumptions, for a planar anode-supported cell fueled by humidified methane (3%vol. H_2O). For this, both steam and dry reforming reactions were considered. Drops in temperature along the cell length in the membrane–electrode assembly (MEA) were found near the inlets for the co-flow configuration due to the endothermic reforming reactions. Additionally, the problem of coking was qualitatively evaluated along the three-phase boundary and it shown that coking can occur near the fuel inlet.

Pramuanjaroenkij et al. [85] recently presented a 2D model for analyzing the performance of a planar SOFC fed by H_2 mixed with H_2O to the anode channel. The co-flow configuration was considered. With the electrolyte material of YSZ, a cell with anode-supported design was shown to give higher power density in the high current density range than that with electrolyte-supported design at 800°C.

Liu et al. [86] introduced a 2D numerical model to investigate the interconnect rib resistance on the performance of planar SOFC stack and for the rib design optimization. The interconnect rib affects the stack performance mainly through the intrinsic ohmic polarization due to the rib surface contact resistance, the increased cathode concentration polarization due to oxygen depletion in the area underneath the rib and the increased cathode ohmic polarization due to unfavorable current distribution.

Three-dimensional models

In 3D models the impact of the configuration and operating conditions, e.g. fuel and air inlets, on the overall performance of the cell/stack is one of the most common objectives. However, micro processes or phenomena occurring within the ensemble of positive electrode-electrolyte-negative electrode (PEN) are grossly simplified. Examples of three-dimensional models are [87–100]

Ferguson et al. [89] introduced a 3D model for SOFCs, which allows computation of local distributions of electrical potential, temperature and concentration of chemical species. Electrochemical reactions were considered to take place at electrode–electrolyte interfaces and the associated heat was implemented as a boundary condition at the anode–electrolyte interface. It was found that the counter-flow configuration is optimal (with H_2 as a fuel) in terms of electrical efficiency in comparison with the co- and cross-flow configurations.

Recknagle et al. [95] presented a model based on the commercial CFD package Star-CD for predicting the distribution of the gas species, temperature and current density in a planar SOFC stack working with H_2 as fuel. It was found that the co-flow configuration generates the most uniform temperature and thus the smallest temperature gradients compared to the other configurations. However, detailed transport processes in the porous electrodes and electrolyte were not simulated numerically as the PEN (positive electrode–electrolyte–negative electrode) structure was treated as a single solid layer. Mass production and consumption was implemented as boundary conditions at the PEN–channel interfaces.

Nikooyeh et al. [92], using a numerical approach, investigated thermal and electrochemical behaviors of an anode-supported cell working under direct internal reforming conditions. Distribution of temperature and chemical species along the cell length was shown. However, the paper does not make it entirely clear how trans-

port and chemical and electrochemical phenomena were modeled. The cell voltage was derived from the Nernst potential while neglecting concentration overpotential. Ohmic heat losses were not taken into account. The heat generated by the electrochemical reactions was assumed to be generated throughout the whole anode, which was 1000μm thick, rather than in a thin active layer of TPBs next to the electrolyte.

Chaisantikulwat et al. [91] developed a 3D dynamic model for an anode-supported planar SOFC working with hydrogen as fuel. In the model, heat associated with the electrochemical reactions was given in terms of entropy change and implemented only at electrode–electrolyte interfaces. It was found that the cell needed about 400s to settle down after sudden changes of both current density and concentration of hydrogen.

Recently, Suzuki et al. [90] studied heat and mass transfer with electrochemical reaction in an anode-supported flat-tube SOFC using a 3D numerical model. Half of a unit cell working with H_2 as fuel was investigated. Computational mesh was generated in the air channel, the fuel channel and the anode, but not in the other solid components of the cell as the electrolyte, the cathode and the interconnect were treated as solid boundaries, and the temperature was assumed to be constant in those domains. Heat released by electrochemical reaction was implemented as a boundary condition at the electrode-electrolyte interfaces.

Finally, Bessler et al. [100] presented an isothermal cell-level model covering three length scales: gas-phase flow in the gas chambers; gas-phase and charge transport within the porous electrodes and surface transport toward the three-phase boundaries. Each length scale was modeled one-dimensionally and the transport processes in the three scales were coupled through boundary conditions. Thus the model functioned as quasi-3D. Results of potential distribution within the porous electrodes and solid electrolyte were shown.

3.2 Heat sources

Modeling of heat sources/sinks in SOFCs is one of the most important task in order to accurately predict temperature distribution in the cells. This is due to the fact that temperature strongly affects chemical and electrochemical processes happening in the fuel cells, and therefore cell performance. Heat sources in SOFCs mainly include

– radiation,

– heat associated with chemical and electrochemical reactions, and

– Joule heating.

3.2.1 Radiation

Modeling of radiation in SOFCs of different geometrical designs has been done during the last few years, in monolith cells [101], planar cells [102–104] and tubular cells [77, 105–110]. Examples of models in which radiative heat transfer is considered can be found in references [71, 81, 87, 111–116].

To be able to model the radiative heat transfer in SOFCs, exact knowledge of phenomenological properties like absorption coefficients, refractive indices, scattering coefficients, emissivities and reflectivities are required. However, these properties are difficult to determine accurately.

In an analysis of radiation in planar SOFC electrodes, Damm and Fedorov [102] showed that the radiation effects in SOFC electrodes are minimal and can safely be neglected.

Daun et al. [103] characterized thermophysical and radiative properties of the electrode and electrolyte layers, which were then used to define a simple two-dimensional model incorporating the heat transfer characteristics of the electrode and electrolyte layers of a typical planar SOFC. It was found that radiative heat transfer has a negligible effect on the temperature field within these components, and does not need to be accommodated in comprehensive thermal models for planar SOFCs.

However, for tubular designs Calise et al. [105] showed that radiation is very significant in SOFCs. By using a finite volume approach they found that the radiative heat transfer contributes about 70% to the radial transfer between the SOFC tube and its air injection tube.

There are also some studies of radiative heat transfer around cells and stacks. Iwata et al. [117] investigated the radiative heat exchange between the outer surface of interconnects with a surrounding furnace. Modeling of thermal insulations of stack can be found, for example, in references [118, 119], in which radiation in the multilayer insulations was considered. Achenbach [88] investigated effects of

radiation between outer stack surfaces to surroundings on stack performance using a three-dimensional and time-dependent model. A good review on works modeling radiation in and around SOFCs can be found in [115].

We do not take the radiation effects into account in this work. This is supported by the fact that these effects are found to be negligible in planar SOFCs [102, 103].

3.2.2 Heat of chemical and electrochemical reactions

Heat of chemical reactions

Chemical reactions taking place in SOFCs working under direct internal reforming conditions are mainly methane reforming and water–gas shift reactions. The reforming reaction is endothermic, mostly taking place on the nickel surfaces available in the anode. Additionally, it can probably partly take place in the gas phase of the anode channel at high operating temperatures (800–1000°C). The shift reaction is slightly exothermic and takes place everywhere in the anode compartment.

Heat consumed or released by these reactions can be easily accounted for and modeled via enthalpy changes.

Reaction zones

Composite electrodes consist, as mentioned, of a binary mixture of electronically and ionically conducting particles (phases). The porous nature of the composite electrodes allows three-phase boundaries (TPBs) to be formed where the two solid phases and the gas phase are in contact. The TPBs are therefore present throughout the electrodes rather than only at electrode–electrolyte interfaces when electronically conducting electrodes are used. The electrochemical reactions take place at the TPBs accessible for all three of ions, electrons and gaseous reactants.

These active sites are commonly assumed to be continuously and homogeneously distributed throughout the electrodes. However, the actual zones where the electrochemical reactions take place remain close to the electrolyte, probably due to ionic resistances in the electrodes. Physically, the thickness of these active zones can be up to 50μm depending on the particle size [10–13, 41, 42, 120]. In this thesis, we assume these layers to be 30μm on the anode side and 25μm on the cathode side.

However, in some numerical models [121, 122] the TPBs were regarded as an infinite thin layer between the electrode and the electrolyte interface. As a result, mass consumption and/or production and heat associated with the electrochemical reactions were simplified and applied to the electrode–electrolyte interfaces as boundary conditions. This is common in SOFC modeling, examples are references [13, 89, 90].

Heat of electrochemical reactions

Ubertini and Bove [123] modeled heat associated with the electrochemical reactions as entropy changes at both anode and cathode active regions. Daun et al. [103] defined the entropy changes based on the experimental data available in Kanamura et al. [124]. The entropy change of the anode reaction was given as a function of hydrogen partial pressure, and was calculated by subtraction of the entropy change of the cathode reaction from that of the total electrochemical reaction [103]. Ito et al. [125, 126] proposed a procedure for calculating the entropy changes based on Seebeck coefficients. However, Seebeck coefficients for SOFC materials are still not fully available in open literature [123].

Fischer and Seume [114] made an analysis of the location and magnitude of heat sources in SOFCs. A method for estimation of the required single-electrode entropy changes from Seebeck coefficient data was presented and applied to a tubular SOFC with direct internal reforming of methane. The entropy changes were assigned to the electrode–electrolyte interfaces. Two cases were considered: a case where the entropy changes were assigned only on the anode side and one case where the entropy changes of the two half-cell reactions were implemented on both the anode and the cathode sides. It was found that the temperature profiles computed for the two cases showed only a small difference of less than 1 K in the absolute temperature values. However, the location of the heat sources was found to have a strong effect on the radial temperature gradient in the electrolyte. While the cathodic half-cell reaction is exothermic, the anodic reaction is endothermic [103, 114].

Other examples of works in the literature in which heat associated with the electrochemical reactions is calculated as entropy changes are [81, 91, 121]. In a one-dimensional dynamic model presented by Cheddie and Munroe [37], heat associated with the electrochemical reactions was determined as the entropy change of the total cell reaction, which was given as a function of temperature and applied to the electrodes–electrolyte assembly as an infinitely thin layer.

Alternatively, the heat generated by the electrochemical reactions can be evaluated by enthalpy changes. The electrochemical heat source therefore consists of the enthalpy changes of the overall cell reactions and the electrical work. Works in the literature using this approach for implementing the electrochemical heat source are [71, 72, 78, 90, 92, 112, 116, 117, 122, 127–131] and this thesis.

3.2.3   Joule heating

Resistances to flow of ions and electrons in solid parts known as electrodes, electrolyte and interconnects of SOFCs generate heat, increasing cell temperature. The heat loss associated with these resistances is called ohmic heat loss or Joule heating.

The Joule heating is determined as [11, 38, 78, 89, 91, 114, 121, 132–134]

$$Q_{\mathrm{Ohm}} = \sigma \nabla \phi \cdot \nabla \phi = \frac{i^2}{\sigma} \tag{3.1}$$

where Q_{Ohm} is the Joule heating rate per unit volume ($\mathrm{Jm^{-3}s^{-1}}$), σ is the conductivity of materials ($\Omega^{-1}\mathrm{m}^{-1}$), ϕ is the local potential (V) and i is the current density ($\mathrm{Am^{-2}}$). The conductivity is the reciprocal of the resistivity r ($\Omega\mathrm{m}$), i.e. $\sigma = 1/r$.

The electric conductivity of cell components such as a Ni–YSZ composite anode, an LSM–YSZ composite cathode and an LSC (strontium-doped lanthanum chromite) interconnect is large. Therefore, heat loss due to ohmic resistances to flow of electrons in these components may be negligibly small [135, 136]. As a consequence, Joule heating due to the flow of oxygen ions in the composite electrodes and electrolyte is the main contribution. We take into account this part of the Joule heating in some papers in this thesis.

Zhang et al. [122] found that the ohmic heat loss is about 2.37–4.1% of the total heat released in a planar electrolyte-supported cell. The high limit conresponds to the cell working under direct internal reforming of CH_4, the low limit to the cell working with H_2 as fuel. It was found to constitute about 8.0% of the total heat release for a tubular cathode-supported cell working with H_2 as fuel.

Chapter 4

Summary of papers included in the thesis

4.1 Paper 1

Ho TX, Kosinski P, Hoffmann AC, Vik A, 2008. Numerical modeling of solid oxide fuel cells. *Chemical Engineering Science* 63 (21), 5356–5365.

In this paper, a numerical model has been developed and introduced. Transport of mass and heat and chemical and electrochemical processes happening in solid oxide fuel cells was formulated. The application of Fickian algorithm built in the commercial CFD package Star-CD to steady-state charge transport was proposed. A single computational domain covering gas channels, porous electrodes and dense electrolyte was used, in which all phenomenological equations were solved simultaneously using in-built algorithms augmented with subroutines developed in-house. Using a single domain avoid problems due to couplings between separate domains as in the quasi-two or three dimensional models in the literature.

A planar anode-supported cell working under direct internal reforming conditions was investigated as an example of application of the model. Results for concentration of chemical species, temperature and current density distributions were shown, showing the possibility of using it as a numerical tool to study impact of detailed processes on performance of SOFCs.

4.2 Paper 2

Ho TX, Kosinski P, Hoffmann AC, Vik A, 2008. Numerical study of an SOFC with direct internal reforming using charge diffusion-based model. *Proceedings of the 8*th *European SOFC Forum*, **Lucerne, Switzerland.**

This proceeding paper investigated performance of an anode-supported fuel cell using the model developed in Paper 1. Effects of nickel load in the composite anode were observed, that the lower the nickel load, the less severe sub-cooling effect and hence the better the cell performance is. Effects of air inlet conditions were also investigated for counter-flow configuration. Some ideas of the paper were further developed with different fuel and gas inlet conditions in Paper 3.

4.3 Paper 3

Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Numerical analysis of a planar anode-supported SOFC with composite electrodes. *International Journal of Hydrogen Energy* **34, 3488–3499.**

This paper investigated an anode-supported solid oxide fuel cell in detail using the developed model. The cell worked under conditions of direct internal reforming of methane. However, in this paper, carbon monoxide was assumed to be electrochemically oxidized at the cathode active layer. Therefore, the model was modified to be able to include the oxidation of carbon monoxide in addition to that of hydrogen.

The computational domain remained the same as in Paper 1, and did not include interconnects. However, co- and counter-flow configurations were investigated.

Results for temperature, chemical species and current density distribution were shown and discussed. It was found that for co-flow configuration, a sub-cooling effect manifests itself in the methane-rich region near the fuel entrance, while for counter-flow configuration a super-heating effect manifests itself somewhat further downstream, where all methane is consumed. It was also found that there is no significant difference in temperature distribution and cell performance between systems with and without CO oxidation.

4.4   Paper 4

Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Modeling of transport, chemical and electrochemical phenomena in a cathode-supported SOFC. *Chemical Engineering Science*, **doi:10.1016/j.ces.2009.03.043.**

In this paper the developed model was adapted to a cathode-supported solid oxide fuel cell. The main features of the model were kept the same. However, in this paper, heat losses due to resistances to flow of charges were included as an improvement of the model. The objectives of the paper were to demonstrate the flexibility of the model in applying it to different cell geometries, and to analyze the performance of the cathode-supported fuel cell, demonstrating advantages and disadvantages compared to the more common anode-supported cell design.

Results for temperature, chemical species, current density and electric potential distribution were shown and discussed. It was found that the sub-cooling effect observed in anode-supported cells is almost eliminated, making the cathode-supported cell favorable from the viewpoint of material stability.

4.5   Paper 5

Ho TX, Kosinski P, Hoffmann AC, Vik A, 2009. Numerical modeling of SOFCs using a fully three-dimensional approach. *Technical report.*

The model used in the above four papers was two-dimensional, i.e. it considered variations along the cell length and along direction perpendicular to the electrolyte surface, while transversal variations were ignored precluding the inclusion of ribbed interconnects.

In this paper, the interconnects were included. To do this, variations in all three directions were taken into account and the model was fully three-dimensional. Joule heating was included. An anode-supported cell with the same component dimensions (except for the cell width), and properties as in Paper 3 was investigated.

Another new feature of this version of the model is that electric potential was fixed at the top and the bottom of the interconnects, rather than at the electrodes as applied in the above papers. This is physically more realistic though modeling results showed insignificant difference in cell performance because of the only slight

difference observed in potential at the outermost surface of the interconnects and at the electrodes.

Results of temperature, chemical species, current density and electric potential distribution were presented and discussed. Effects of interconnect ribs manifest themselves clearly. The results presented in this paper are supposed to be published later on.

4.6 Paper 6

Ho TX, Kosinski P, Hoffmann AC, 2009. Discussion on the transport of oxygen-ions in an SOFC electrolyte. *Technical report.*

This paper presented an analysis of the transport of oxygen ions in an yttria-stabilized zirconia (YSZ) SOFC electrolyte. The transport of oxygen ions is equivalent to an equal and opposite transport of oxygen vacancies. The Nernst–Planck equation for the ion/vacancy transport and the Poisson equation for electric potential–charge density relationship were solved using a finite difference method.

Empirical correlations for the ionic conductivity were proposed as functions of vacancy concentration at isothermal conditions. Results of the electric potential and vacancy distribution were shown and discussed. Non-linear distribution of the potential was observed in case the local neutrality condition is not met everywhere.

Chapter 5

Concluding remarks and further work

Numerical modeling of solid oxide fuel cells (SOFCs) is indispensably important for the development of the fuel cells. Advantages of SOFC numerical modeling are obvious. Amongst those, a modeling tool can provide detailed insights such as temperature field, chemical species, electrical potential and current density distribution in the cells, which are certainly difficult or impossible to be determined experimentally. Another advantage that a numerical approach can offer is that it helps investigating impacts of the process parameters and their interaction, giving information for cell design and optimization. This is difficult and costly to do by experiments.

The aim of this work was to develop a numerical tool for modeling detailed physical, chemical and electrochemical processes taking place in solid oxide fuel cells. The developed model took into account the following processes:

- – fluid flows in the gas channels and gas diffusion in the porous electrodes,

- – chemical reactions in the anode cermet as well as in the fuel channel,

- – electrochemical reactions in the electrochemically active layers, which have a finite thickness,

- – charge transport in the electrodes–electrolyte assembly and the interconnects,

- – heat transfer in the gas phase in considering heat sources due to the reactions and resistances to the charge transport.

All equations describing the mentioned processes were formulated in three dimensions. Therefore the model can be used for both 2D and 3D applications with minute changes. The commercial CFD (computational fluid dynamic) package Star-CD was employed along with Fortran-based subroutines built in-house to solve the equations. It is interesting to note that the steady-state charge transport in the solid parts was mimicked by making use of an algorithm for Fickian diffusion in Star-CD.

The operating voltage of the cell was fixed constant along the cell by applying constant potential on both sides of the electrolyte. In other words, the Nernst potential was not used to derive the cell output potential in our model. Another feature of the developed model was that it used a single computational domain covering all necessary cell components, therefore, no need was required for manual couplings as in quasi-2D or 3D models.

The model capabilities have been shown when applying it to the modeling SOFCs of different geometries (anode- and cathode-supported cells) and dimensions (2D and 3D) though further experimental validation of the model in addition to those presented in the papers included in this thesis is needed.

In an anode-supported cell, sub-cooling effect and super-heating effect occur near the fuel entrance with co- and counter-flow configurations, respectively. The extreme thermal effects cause temperature gradients to increase, which is unfavorable from the material viewpoint. However, the super-heating effect can be mitigated by using appropriate inlet conditions for the air.

A cathode-supported cell with a very thin composite anode working under the conditions of direct internal reforming of methane has shown to be superior to the anode-supported cell in terms of temperature and current density uniformity.

Three-dimensional simulations where interconnects were included have shown quite clear effects of the interconnects on the distribution of chemical species, temperature and current density.

The model in the thesis can be extended to model the whole cell within a reasonable computational effort. Modeling of the whole cell can be a future work. This is attractive and will probably provide more accurate results than with a repeating unit cell representing the whole cell, due to the fact that effects of the side-faces of the cell can be taken into account.

Implementing of radiative heat transfer into the model would be another work for

the future, though it has been shown in the SOFC literature that the radiation can be neglected within the components of planar SOFCs [102, 103].

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