

# Electrochemical impedance modeling of gas transport and reforming kinetics in reformato fueled solid oxide fuel cell anodes



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## ABSTRACT

An approach to the understanding of the gas transport properties within reformato fueled Ni/YSZ solid oxide fuel cell anodes is presented. For this purpose, a transient finite-element model is developed and implemented in the software package COMSOL. Aim of our model is the simulation of electrochemical impedance spectra of reformato fueled anode-supported solid oxide fuel cells.

The isothermal model represents one-dimensional gas transport and reforming chemistry through the two-layer anode toward the electrolyte interface. Porous-media transport within the anode support structure is represented by the Stefan–Maxwell model. Heterogeneous (catalytic reforming) chemistry on the Ni-surfaces is modeled with a global reaction mechanism. Charge-transfer chemistry at the electrode–electrolyte interface is modeled with a simple time-dependent rate equation.

Output of the model is the transient, space-resolved prediction of the gas composition within the two-layer anode, from which impedance spectra can be simulated. As the model is capable to coherently calculate the complex coupling of species transport phenomena and reforming kinetics, the characteristics of the impedance spectra measured under reformato operation can be reproduced. After validation against experimental data, the simulation results are used to analyze the coupling of reforming chemistry and gas transport.

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## 1. Introduction

Due to the remarkable fuel flexibility, solid oxide fuel cells (SOFC) are very attractive for energy conversion systems that require reformato fuels [1]. However, there is no comprehensive understanding of the electrochemical polarization processes which determine the performance of SOFC anodes under operation with reformato fuels provided in literature yet. In particular the polarization processes related to the fuel gas transport at the anode exhibit a high complexity: the low-frequency impedance response is observed to consist of multiple arcs, presumably linked to the complex coupling of multi-component diffusion and reforming chemistry [2–6].

In our previous work, the electrochemical oxidation mechanism of reformato fuels (gas mixtures of H<sub>2</sub>, H<sub>2</sub>O, CO, CO<sub>2</sub> and N<sub>2</sub>) within a two-layer Ni/YSZ anode was investigated via electrochemical impedance spectroscopy (EIS) [4]. The kinetic analysis has

demonstrated that for reformato fuels, exclusively H<sub>2</sub> is electrochemically oxidized at the triple-phase boundary (TPB) as



whereas CO is thermally converted via the water–gas shift (WGS) reaction on the catalytically active Ni-surface within the anode substrate as



This is valid for typical reformato compositions (steam reforming of natural gas, partial oxidation of diesel) where the amount of hydrogen is usually exceeding the amount of carbon monoxide. In case of pure CO/CO<sub>2</sub> mixtures as well as very high CO:H<sub>2</sub> ratios, the direct electrochemical oxidation of CO at the TPB is taking place [7,8]. The resulting gas transport properties of reformato fueled Ni/YSZ anodes are illustrated in Fig. 1. The fuel is transported via two pathways (H<sub>2</sub>/H<sub>2</sub>O and CO/CO<sub>2</sub>), which are coupled by the WGS reaction.

Numerical simulation can be a valuable tool in understanding the processes inside porous electrode structures, which generally exhibit coupling of various physical phenomena. In SOFC literature, numerical modeling has been broadly applied in the field of internal reforming, accurately computing the coupling of reforming chemistry, gas transport and charge transfer chemistry within cermet

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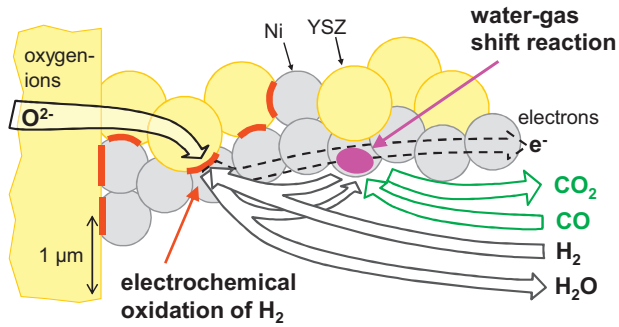


Fig. 1. Illustration of the reaction and transport processes for Ni/YSZ anodes in anode-supported SOFCs operating with reformat fuels (adapted from Ref. [9]).

anodes [10–15]. Also transient impedance modeling has proven to give interesting insights into the underlying coupled electrochemical reactions and species transport [3,16,17]. An implementation of the schematic model illustrated above (Fig. 1) in numerical simulation is hence promising to contribute to the understanding of the measured low-frequency polarization processes.

In this work, a transient finite element method (FEM) model is set up representing the reaction and transport processes for anode-supported SOFC operating with reformat fuels as depicted in Fig. 1: (i) electrochemical oxidation of  $H_2$ , (ii) CO-conversion via the WGS reaction and (iii) gas transport via the  $H_2/H_2O$  and  $CO/CO_2$  pathways. With the developed FEM model, it is aimed to investigate the relation between the reported characteristics of measured impedance response and the underlying gas transport and reforming processes within reformat fueled Ni/YSZ anodes.

## 2. Experimental

The experimental results reported in our previous work [4] have been taken as basis for the comparison and validation of the modeled results presented herein. The anode-supported cells (ASC) used in a solid oxide fuel cell and analyzed for this study are based on  $50 \times 50 \text{ mm}^2$  anode substrates made of a mixture of nickel and 8 mol% yttria-stabilized zirconia (Ni/8YSZ) with an average thickness of about  $1000 \mu\text{m}$ . On these substrates, an anode functional layer (AFL: Ni/8YSZ, approx.  $7 \mu\text{m}$  thick) and an electrolyte (8YSZ, approx.  $10 \mu\text{m}$  thick) are deposited and co-fired at  $1400^\circ\text{C}$ . A  $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  (CGO) interlayer with lateral dimensions of  $12 \times 30 \text{ mm}^2$  is screen-printed and sintered on the electrolyte (approx.  $7 \mu\text{m}$  thick). On top of this interlayer a  $\text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  (LSCF) cathode is applied by screen-printing, resulting in a thickness of approximately  $45 \mu\text{m}$  after sintering. Details regarding the manufacturing procedures can be found elsewhere [18]. The active area of the working cathode was  $10 \times 10 \text{ mm}^2$ . Two auxiliary electrodes in gas flow direction in front of and behind the cathode were applied for open circuit voltage (OCV) control. This layout is described in detail in Ref. [4].

With the single cells mounted into ceramic housings, the cathode is contacted by a gold mesh. On the anode side, an area of  $10 \times 10 \text{ mm}^2$  aligned with the cathode is contacted by a nickel mesh. Accordingly, both electrodes have an active electrode area of  $10 \times 10 \text{ mm}^2$  in the applied test setup. Gold rings are used for sealing. The cells are operated under ambient pressure with air at the cathode side. On the anode side, a simulated reformat gas mixture of  $H_2$ ,  $H_2O$ ,  $CO$ ,  $CO_2$  and  $N_2$  at chemical equilibrium was applied as fuel. The equilibrium gas composition was calculated with the thermodynamic database MALT [19]. The total anode and cathode gas flow rates were maintained at a constant value of 250 sccm during all experiments. All experiments have been performed at an operation temperature of  $800^\circ\text{C}$ . The operation with simulated reformat

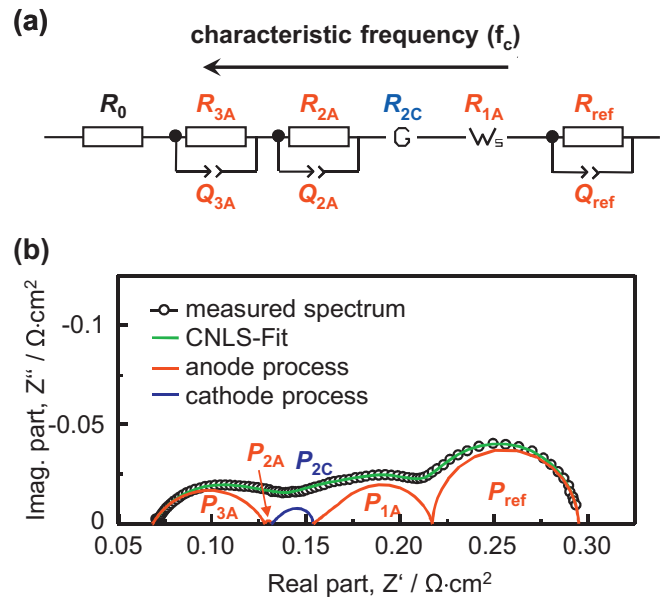


Fig. 2. (a) Equivalent circuit model used for the CNLS-fit of the measured impedance data. (b) CNLS-fit of an impedance spectrum recorded for  $x_{H_2} = 0.15$ ,  $x_{H_2O} = 0.05$ ,  $x_{CO} = 0.15$ ,  $x_{CO_2} = 0.05$ , balance  $N_2$ ; cathode: air;  $T = 800^\circ\text{C}$  [4].

fuels at chemical equilibrium has the advantage that the exact gas composition within the anode is known for every measuring point. Hence a highly accurate characterization of the electrochemical impedance spectra, which exhibit a notable sensitivity on the gas compositions at the electrodes, is guaranteed.

The electrochemical impedance spectra were recorded at open circuit conditions (OCC), using a SOLARTRON 1260 frequency response analyzer in a frequency range from 30 mHz to 1 MHz. The amplitude of the current stimulus was chosen in order to achieve a voltage response not higher than 12 mV. Details regarding the cell testing are reported in Ref. [4].

The measured impedance spectra were evaluated by fitting of a physically meaningful equivalent circuit (Fig. 2). The fit proceeds via a complex nonlinear least-squares (CNLS) method. The CNLS-fit of the impedance data was carried out with the commercial program ZView [20]. The equivalent-circuit models used for this procedure were developed by a pre-identification of the impedance response by calculating and analyzing the corresponding distribution of relaxation times (DRT). For a more detailed description of the DRT method and its application, we refer the reader to Refs. [21–23].

Figure 2 depicts the physically meaningful equivalent circuit model applied in this study. It was developed for reformat operation of the same type of anode-supported cells with two-layer Ni/YSZ anodes [4] and consists of the following serial elements representing the physical polarization processes (cf. Table 1 for details): (i) an ohmic resistor (overall ohmic losses), (ii) 2 serial RQ elements ( $P_{2A}$  and  $P_{3A}$ : gas diffusion coupled with charge transfer reaction and ionic transport within the AFL), (iii) a Gerischer element ( $P_{2C}$ : activation polarization of the LSCF-cathode) (iv) a generalized finite length Warburg element (G-FLWS) ( $P_{1A}$ : gas diffusion of  $H_2/H_2O$  within the anode substrate). In order to represent EIS spectra measured under reformat operation with the additional low-frequency polarization process ( $P_{ref}$ : presumably linked to WGS reaction and gas diffusion of  $CO/CO_2$  within the anode substrate), the equivalent circuit additionally contains (v) an RQ element at low characteristic frequencies [4].

With the help of the equivalent-circuit model and the numerical accuracy of the CNLS-fit, an accurate separated analysis of the single

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