



# Numerical evaluation of oxide growth in metallic support microstructures of Solid Oxide Fuel Cells and its influence on mass transport



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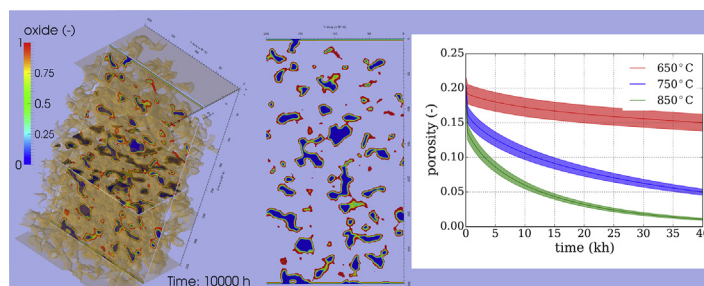
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## HIGHLIGHTS

- Examination of X-ray CT scanned and reconstructed metallic support microstructures.
- Development and implementation of a corrosion model for complex microstructures.
- Simulation of pore volume changes and decreased mass-diffusion due to oxide growth.
- Possibility to determine transient corrosion influence on mass-transport parameters.
- Analytical frame-work to determine diffusion resistance change based on weight-gain.

## GRAPHICAL ABSTRACT



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## ABSTRACT

Metal-supported Solid Oxide Fuel Cells (SOFCs) are developed as a durable and cost-effective alternative to the state-of-the-art cermet SOFCs. This novel technology offers new opportunities but also new challenges. One of them is corrosion of the metallic support, which will decrease the long-term performance of the SOFCs.

In order to understand the implications of the corrosion on the mass-transport through the metallic support, a corrosion model is developed that is capable of determining the change of the porous microstructure due to oxide scale growth. The model is based on high-temperature corrosion theory, and the required model parameters can be retrieved by standard corrosion weight gain measurements.

The microstructure is reconstructed from X-ray computed tomography, and converted into a computational grid. The influence of the changing microstructure on the fuel cell performance is evaluated by determining an effective diffusion coefficient and the equivalent electrical area specific

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resistance (ASR) due to diffusion over time. It is thus possible to assess the applicability (in terms of corrosion behaviour) of potential metallic supports without costly long-term experiments.

In addition to that an analytical frame-work is proposed, which is capable of estimating the porosity, tortuosity and the corresponding ASR based on weight gain measurements.

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## 1. Introduction

In recent years metal-supported Solid Oxide Fuel Cells (SOFCs) have been developed, as it is believed that the technology has the potential of improved mechanical strength, higher thermal conductivity and higher re-oxidation tolerance compared to state-of-the-art ceramic based anode and support (e.g. yttrium stabilised zirconia with nickel (Ni-YSZ)). The reasons are that these cells in SOFC stacks are brittle and thermal gradients over the stack together with thermal-cycling may lead to cracks and thus to failure of the stack, whereas the metallic supports show substantial yielding before failure [1,2]. In addition to that, the volume expansion of the nickel phase in the nickel/zirconia cermet during re-oxidation can induce cracks [3]. Not only advantages in mechanical stability, but also the overall electro-chemical performance of metal-supported SOFCs have shown, that this technology is a promising alternative to the state-of-the-art Ni-YSZ cermet SOFCs [4–9].

However, the porous metallic substrate is prone to other failure mechanisms, which are unique for this technology: Creep of the metallic support and contacting with interconnects might lead to failure of the electrolyte as the support might be too compliant [1]. Another problem, which is specific to metal-supported SOFCs, and is not prevailing in Ni-YSZ supports, is corrosion. In the temperature range between 650 and 750° (typical operation) the porous metallic support will form a chromia oxide scale, due to its high chromium content even at low water vapour partial pressures. In order to understand the implications of corrosion on the metallic support, experiments were conducted to determine the weight gain of potential substrate materials [10–13]. In these studies the weight gain of the samples was measured over time in a predefined atmosphere and temperature. The applicability of a potential material was then assessed based on its weight gain. However, it is hard to predict the impact on the performance due to changes in the microstructure such as blocking of pores, which will influence mass-diffusion and electrical performance.

It is thus desirable to assess the impact of corrosion on the electro-chemical performance of metal-supported SOFCs. It is however expensive, very cumbersome and practically unfeasible in a development process to test all possible material compositions because of the circumstantial modifications to the processing route for even the most promising metal-supported SOFCs, as these have to be exposed to thousands of hours of operation to assess the impact of corrosion.

The typical approach for determining performance loss contributions is by impedance measurement and analysis, see e.g. Ref. [14]. In this approach the distribution of relaxation times allows for the identification of the individual loss contributions. Taking into account their dependence on water vapour partial pressure, a part of the loss contributions can be related to gas diffusion processes, and thus the effective diffusion coefficient of the porous layer may be estimated. Nevertheless, the outcome of this approach relies on the feasibility of separating the convoluted response of the measurements by a relatively simple and suitable model. It is currently not possible to separate the gas diffusion loss

in the metal-supported SOFCs, as the relaxation times overlap with a process related to hydrogen electro-oxidation [15].

An often applied alternative for determining mass-transport parameters is the simulation of this process in the real microstructure. The microstructure can be depicted by either FIB-SEM or X-ray tomography, and the simulations are carried out on the reconstructed computational grid [16–23]. The simulations on the microstructure can be used to obtain the macroscopic homogenised parameters for simulations of cells and stacks. In order to minimise the needed size of a stochastic equivalent representative volume (SERVE) periodic boundary conditions for this type of simulations can be used with a significant gain as shown in Ref. [15].

Once the homogenised material parameters (e.g. effective diffusion coefficient) have been obtained for the SERVE, these can be used to compute the multi-physical behaviour inside an SOFC. This has in particular been pursued more often in recent years, as it offers the opportunity to understand the interplay between the processes inside the entire SOFC in greater detail. Multi-physics models that describe these various phenomena are available in literature [24], and a lot of research is carried out in this field [25,26]. Due to limitations in computational capacity all cell and stack-models resort to models, where the complex microstructure of the porous substrate and electrodes is modelled as pseudo-homogeneous materials with constant porosity and tortuosity [27–32]. The results of the computation depend on these properties, and therefore, it is important to use values, which accurately describes the porous structure.

However, the performance of most SOFCs is affected by microstructural changes, e.g. by nickel agglomeration [33] or corrosion, and it thus interesting to study the impact on the performance by combining imaging methods and microstructural simulations. Obtaining consecutive images of an evolving microstructure requires in-situ 3-D imaging methods, which is quite challenging [34], and the referenced microstructural simulation studies do thus rely on a microstructure obtained at a single point in time. In this study a 3-D image obtained at a single point in time is used as a reference, and the evolution of the microstructure is simulated by a developed corrosion model.

The corrosion model is based on Wagner's theory of oxidation of metals at high temperatures, where the diffusion of either metal or oxygen ions through the oxide film is the rate-limiting step of the electro-chemical reactions, and thus the growth of the oxide film obeys parabolic kinetics [35]. Many metals exhibit a parabolic kinetic behaviour when corroding, as long as the film is sufficiently thick (e.g. >1 µm for temperatures above 500°) [36]. During early stages of oxidation, Wagner's theory is not valid because of a high electric field, which influences the ion migration. The theory of Cabrera and Mott [37] identified inverse-logarithmic kinetics for thin films (<20 nm). Recently, it was found out that the intermediate region, between the Cabrera and Mott theory and Wagner's theory, shows direct logarithmic behaviour for temperatures below 200 °C [38]. However, at higher temperatures the oxidation rate may show linear behaviour, and as the film thickens a transition to parabolic kinetics can be observed [39].

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