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Numerical evaluation of micro-structural parameters of porous supports in metal-supported solid oxide fuel cells

Georg Reiss [a, *], Henrik Lund Frandsen [b], Wilhelm Brandstätter [c], André Weber [d]

[a] ICE Strömungsforschung GmbH, Hauptplatz 13, 8700 Leoben, Austria
[b] Technical University of Denmark, Department of Energy Storage and Conversion, Frederiksborgvej 399, 4000 Roskilde, Denmark
[c] Montanuniversität Leoben, Lehrstuhl für Petroleum and Geothermal Energy Recovery, Franz-Josef-Straße 18, 8700 Leoben, Austria
[d] Karlsruher Institut für Technologie (KIT), Institut für Werkstoffe der Elektrotechnik (IWE), Adenauerring 20b, D-76131 Karlsruhe, Germany

HIGHLIGHTS

- Improved method to determine averaged transport parameters e.g. porosity, tortuosity.
- Based on reconstruction of 3D micro-structures of a metal-supported SOFC.
- Correct lateral boundary conditions change state-of-the art approach with 47%.
- Assessment of anisotropic micro-structures by determining the porosity distribution.
- Transport parameters for different dense layers are computed separately.

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ABSTRACT

Metallic supported Solid Oxide Fuel Cells (SOFCs) are considered as a durable and cost effective alternative to the state-of-the-art ceramic supported cell designs. In order to understand the mass and charge transport in the metal-support of this new type of cell a novel technique involving X-ray tomography and micro-structural modelling is presented in this work. The simulation technique comprises a novel treatment of the boundary conditions, which leads to more accurate effective transport parameters compared to those, which can be achieved with the conventional homogenisation procedures. Furthermore, the porosity distribution in the metal-support was determined, which provided information about the inhomogeneous nature of the material. In addition to that, transport parameters for two identified, different dense layers of the metal-support are evaluated separately.

The results of the evaluation show three significant findings. Firstly, that the effective transport parameters are up to a factor of 20 lower compared to other SOFC anodes. Secondly, that the micro-structure can have regions, which are much denser, especially the first 100 μm of the interface between gas-channel and support-structure. Thirdly, that the calculation of the transport parameters depends on the correct application of boundary conditions.

1. Introduction

The solid oxide fuel cell (SOFC) technology offers effective conversion of chemical stored energy to electricity. The state-of-the-art SOFC-stack is based mainly on all-ceramic cells, which are brittle and thus challenging to operate. During the operation of the SOFCs heat is generated, which must be transported out of the stack resulting in thermal gradients. These thermal gradients will cause thermal stresses, which may induce cracks in the ceramic cells. A second failure mechanism in state-of-the-art cells is the re-oxidation of the nickel/zirconia cermet anode and substrate. A re-oxidation of the nickel will result in a volume expansion and thus the formation of cracks. To overcome these drawbacks, alternative types of SOFCs based on porous metallic supports have been developed, exhibiting a number of advantages as an improved mechanical strength, a higher thermal conductivity of the substrate and a higher re-oxidation tolerance of the applied alloys. The actual cell and stack developments performed worldwide have shown very promising results compared to the state-of-the-art cells [1–9].

In order to avoid failures and optimise the cells further, experiments are carried out to study their behaviour [1,10], but the

* Corresponding author. Tel.: +43 3842 9828259; fax: +43 3842 9828212.
E-mail address: georg.reiss@ice-sf.at (G. Reiss).
URL: http://www.ice-sf.at

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theoretical foundation to understand their behaviour must also be developed. To this end, multi-physics models describing the variety of physics are being developed see e.g. Refs. [11–13]. The physics involved are: electronic and ionic charge transfer; solid mechanics; heat transfer; gas diffusion and flow. The parameters used in these multi-physics models can either be measured or deducted by micro-structural modelling. The measurements are typical on the cell level, why a convoluted response is measured and the physically meaningful parameters can only be determined by a reverse engineering approach if an appropriate electro-chemical model is existing [14]. In addition to that, if a component is modified or a new component is developed all physical parameters have to be re-measured. Therefore, a novel route based on micro-structural modelling of the material parameters is pursued in this work.

The various physical phenomena occurring in a SOFC take place on a large span of length scales from sub-micron to centimetres. Thus, in order to obtain meaningful computational results, the material properties and the material structure of the SOFC under investigation have to be represented in detailed micro-structural models. However, a high spatial resolution of the electrode structure will result in a computational model containing a tremendous amount of mesh cells, and will thus lead to impractical calculation times. Calculations of an entire SOFC-stack (12 cm × 12 cm × 10 cm) with a resolution of 1 μm^3 would result in approx. 1×10^{15} computational cells, which would require memory capacities exceeding most of the available supercomputers.

Often the details occurring on smaller scales are indirectly included through the applied material models or so-called constitutive models, in which the material parameters are fitted to experimental results. With the many interacting physics in SOFC, the modelling entails a large number of unknown parameters. The combined response of the cell can to some degree be decoupled by electrochemical impedance spectroscopy and e.g. by controlling the gas composition on the anode and the cathode side, such that parameters related to phenomena occurring either side can be determined. However, the combined response is a convolution of all the parameters, which makes the fitting task quite difficult.

This was successfully performed and shown in Ref. [14] at elevated temperatures (>800 °C). However, at lower temperatures the gas diffusion process in the anode substrate is overlapped by a process related to the hydrogen electro-oxidation in the impedance spectra, and deconvolution is thus not possible. The cell studied in this work has limited stability at these temperatures, and thus so far it has not been possible to determine the mass transport resistance with electrochemical impedance spectroscopy. Alternatively, one of the processes, e.g. the gas diffusion, could be studied separately allowing for a better deconvolution of the overall response. It should, however, be noted that the deconvolution approach only allows for determining the integrated diffusion resistance of all layers on either side of the electrolyte. Thus, for a direct study of the implication of variation of the composition and thickness of the individual layers other methods must be applied. Furthermore, it is given that the usage of this measurement/fitting approach will only re-produce the experiments that they rely on, but the impact of variations of micro-structure or maybe even layer thicknesses requires new experiments. In the spirit of John von Neumann, a mathematician and computer scientist:

> With four parameters I can fit an elephant, and with five I can make him wiggle his trunk;

computational attempts to reduce the level of uncertainty about these parameters should be undertaken.

The possibility to analyse the micro-structure of the electrodes by e.g. focused ion beam – scanning electron microscope (FIB-SEM) or X-ray computed tomography (CT) has therefore lead to a number of modelling studies of the phenomena occurring on the micro-scale [15–21]. The established methodology is to apply FIB-SEM measurements for regions, where a high resolution is needed see e.g. Ref. [22]. Only a small part of the electrode can be investigated with this method, whereas CT-scanning can be used to analyse larger volumes of the micro-structure. Nevertheless, X-ray nano-tomography yields comparable results to FIB-SEM [23,24]. The two approaches compliment and overlap each other in their regime of use. Common for both is that the data obtained is a sequence of two dimensional pictures, which has to be transformed into a three-dimensional voxelised picture of the micro-structure. This is used to reconstruct a computational geometry, after image processing with an in-house algorithm based on [25–28]. Subsequently, effective transport properties are calculated using numerical models. This approach has been used a number of times for SOFC anodes and cathodes [15–21], but was, to the author's knowledge, not yet applied to the porous metal-support. The new technology of a metallic porous support for the SOFC implicates a change of the micro-structure due to corrosion during operation. This is a very important issue in the development of durable metal-supports and is object to many experiments [29–32]. While improving the stability of the cells, a theoretical study of the influence of the changing micro-structure on the mass transport is needed to study the feasibility of this new technology. This could be done by such a micro-structural model which is capable of determining effective transport parameter that can be used for multi-physics models in cell simulations.

The diffusion through the micro-structure of the porous support can be determined by use of a numerical method, e.g. computational fluid dynamics (CFD), Lattice Boltzmann method (LBM) or the finite element method. However, it would be unfeasible with current computational power to represent a full SOFC stack for that sake by this approach. Thus, in a multi-scale modelling approach the accurate micro-structural models can be utilised to determine the response of the smaller scale model. The results can be represented through homogenised material parameters in homogenised continuum models [33]. Hereby an accurate description of the flow is ensured together with a reduction of computational cells and required computer time by a factor of 10^5 or more. By this approach more fundamental knowledge about the material parameters and the occurring physical phenomena are obtained.

In homogenisation a boundary value problem is posed and solved to obtain the homogenised material parameters [34–36]. The boundary conditions for the flow problem can either be the flux, concentration or a periodic boundary condition. It has become customary to compute the effective diffusion coefficient for diffusion through the thickness of the cell by applying symmetry condition (concentration gradient perpendicular to the boundary equals zero) for the lateral boundary (parallel to the main diffusion path) [15–19]. This effectively introduces dead-end pores, or in other words blocks tortuous paths involving diffusion in and out of the domain in the vicinity of the lateral boundary. The only workaround so far is to perform the simulation on a sufficiently large volume that suppresses any impact of the lateral boundaries, but requires a much larger volume to be reconstructed and more computing power and time to perform the simulation. In Ref. [16] it was shown that with increasing size of the base area the values of interest converge because the error due to the transport via the lateral boundaries decreases. Nevertheless, no comparison between periodic and zero gradient boundary conditions and their influence was made. So far the effect of different boundary conditions for the top and bottom boundaries is analysed by Ref. [20], but not for the lateral faces.