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Towards the 3D Modelling of the Effective Conductivity of Solid Oxide Fuel Cell Electrodes – Validation against experimental measurements and prediction of electrochemical performance

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ABSTRACT

The effective conductivity of thick-film solid oxide fuel cell (SOFC) electrodes plays a key role in their performance. It determines the ability of the electrode to transport charge to/from reaction sites to the current collector and electrolyte. In this paper, the validity of the recently proposed 3D resistor network model for the prediction of effective conductivity, the ResNet model, is investigated by comparison to experimental data. The 3D microstructures of Ni/10ScSZ anodes are reconstructed using tomography through the focused ion beam and scanning electron microscopy (FIB-SEM) technique. This is used as geometric input to the ResNet model to predict the effective conductivities, which are then compared against the experimentally measured values on the same electrodes. Good agreement is observed, supporting the validity of the ResNet model for predicting the effective conductivity of SOFC electrodes. The ResNet model is then combined with the volume-of-fluid (VOF) method to integrate the description of the local conductivity (electronic and ionic) in the prediction of electrochemical performance. The results show that the electrochemical performance is in particular sensitive to the ionic conductivity of the electrode microstructure, highlighting the importance of an accurate description of the local ionic conductivity.

1. Introduction

Solid oxide fuel cells (SOFCs) are high-efficiency energy conversion devices capable of operation on a wide range of fuels. SOFCs comprise a cathode, an anode, and a dense ceramic oxide ion conducting electrolyte. The electrodes have a porous and tortuous microstructure, within which electrochemical reactions take place at the meeting points of the ionic, electronic and gas phases, termed triple phase boundaries (TPBs). These TPBs have to be established by contact between percolated phases through which chemical species can be effectively transported to and from the TPBs. Alongside the requirement for fuels and products to be transported easily in the electrode pore space, there is also a need to provide a large TPB length in the electrode, as well as a large number of pathways for the transport of charge carriers in the solid phases. However, the number and lengths of the transport pathways is not sufficient to fully characterize an electrode microstructure; a comprehensive understanding of the percolated solid and pore networks is required, which can only be achieved by studying the three-dimensional (3D) microstructure. The capability to model the transport and electrochemical processes in these porous composites provides a link between the electrode performance and the underlying microstructure, and thus the design of electrodes with desirable microstructure.

Structural properties such as porosity, tortuosity factor and effective conductivity of SOFC electrodes have been used as performance indicators, and indeed provide a quantitative basis for a better understanding of highly heterogeneous microstructures. Of particular interest is the effective conductivity which is related to the electronic and ionic transport processes, and correlates strongly with the electrochemical performance of the electrodes. There have been growing efforts in developing models to predict the effective conductivities of SOFC electrodes because they can provide insights into the physics behind the measured

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conductivity, they can help to analyse the effects of microstructure change on conductivity over time, and support electrode design studies, for example using synthetically generated structures, to explore the effect of a wide range of microstructures on conductivity, and electrochemical performance. One of the approaches proposed to date is based on percolation theory and the simulation of the electrode as a random mixture of electronic and ionic conducting particles [1–3]. The approach depends upon an arbitrary coordination number (the number of contacts a particular particle makes with its neighbouring particles) and primary parameters such as particle radii, volumetric packing density and porosity. Resistor network models [4–7] have also been used to simulate the electrodes as resistor networks and derive the effective conductivities by applying Kirchhoff's current conservation law to the equivalent electronic circuits. The resistor network is often drawn from randomly packed electronic and ionic spherical particles in which one particle is essentially represented by one vertex in the resistor network, and each vertex is assigned a resistance to represent a particular phase in an SOFC electrode. Recently, the 3D imaging of experimental SOFC electrode microstructures has been made possible through focused ion beam-scanning electron microscope (FIB-SEM) or X-ray computed tomography (XCT) techniques [8–14,36]. This has in turn further promoted the development of modeling methods to derive effective conductivities based on complex real 3D microstructures. Examples of these include the lattice Boltzmann method (LBM) [9], finite-volume-based methods such as computational fluid dynamics (CFD) [13], and finite-element-based approaches such as COMSOL multiphysics [14]. These approaches have been used to investigate the effects of microstructural properties such as particle size and porosity on effective conductivities. However, in all the studies mentioned above, the computed effective conductivities were not validated against experimentally measured values.

The porous 3D microstructure of electrodes has been investigated in several modelling frameworks to predict electrochemical performance. Suzue et al. [15] used the LBM to model the transport phenomena and electrochemical reactions in 3D SOFC anode microstructures derived using stochastic correlation reconstruction, through which 3D distributions of potential and current were obtained. Gas diffusion was assumed to be due to the combination of binary Fickian diffusion of H_2 and H_2O and Knudsen diffusion, and the Butler–Volmer equation was used to describe the charge-transfer kinetics. Shikazono *et al.* [9] used LBM simulation of the anode overpotential in a 3D microstructure reconstructed by FIB-SEM. Kishimoto *et al.* developed a 3D simulation model based on the finite volume method combined with a sub-grid scale model which allows 3D overpotential analysis with a relatively coarse grid system [16,17]. Lynch *et al.* [14] developed a modelling framework based on COMSOL multiphysics to predict electrochemical performance including overpotential vs current density, area specific resistance (ASR) and impedance behavior for a 3D reconstructed microstructure using X-ray nanotomography.

Golbert *et al.* [18] used the volume-of-fluid (VOF) method to analyze 3D SOFC electrode microstructures and model the transport of electronic, ionic and gas phase species, as well as electrochemical reactions. The VOF method presents the advantages of being able to handle large microstructures and to solve the transport and reaction equations efficiently. This modeling framework has provided a platform to link electrode design parameters to microstructural properties and the electrochemical performance of the electrodes. The structure in question is discretized into small cubic elements called voxels, followed by an aggregation of these voxels into discrete volumes called VOF elements. Each VOF element contains volume fractions of the pore phase, the electronic and ionic conducting phases; a VOF element in which any single phase fraction lies between 0 and 1 contains a phase interface. This methodology can capture interface information through discrete volume data and enable the representation of complex multiphase structures alongside continuous phases, which are well-suited for modelling conduction/diffusion and reaction. In applications of the VOF approach to date [18–21], the relevant conductivities have been approximated by assuming uniformity of the microstructure within each VOF element. The conductivities of the materials within one VOF element were simply calculated by multiplying the conductivity of the pure material with its volume fraction in the VOF element. This approximation does not take into account local percolation limitations and the structural complexity within a given VOF element, raising concerns about model accuracy, especially close to the percolation threshold. We therefore improve the quality of the simulations by computing the effective conductivity of VOF elements.

A 3D effective conductivity model [22] has been developed separately to calculate the effective electronic and ionic conductivities of the microstructure (the entire electrode or the local VOF elements). The model is based on the resistor network approach (hereafter termed ResNet model). The methodology for analyzing a given structure can be summarized as follows: the 3D microstructure (real or synthetic) is initially discretized into small cubic elements (voxels), based on which a mixed resistor network is drawn. A potential difference is then applied to this network, the application of Kirchhoff's law of current conservation on the resistor network yields the corresponding currents entering and leaving the system, allowing for the equivalent resistance and hence conductivity of the entire structure to be determined. The model is simple and enables the integration of the conductivity model with a wide array of models and structures. In our previous work, the ResNet model was first validated against simple structures from which analytical effective conductivities could be extracted [22]. The model was also validated against more complex synthetic structures in a second paper [23], and was used to compute the effective conductivity of a Ni/10ScSZ reconstructed anode with a nickel content of 30% in the solid phase. It was shown that one needs to consider a sample large enough to be representative of each dimension for a meaningful analysis [23].

The primary objective of this paper is to validate the ResNet model by comparing the calculated electronic conductivities of regions of actual electrode structures measured using FIB-SEM techniques, with the measured electronic conductivities of the same electrodes. In order to ensure the reliability of the results, we first investigate in Section 2 the sample size required for the microstructure to be considered representative of an entire electrode for the purpose of calculating the effective conductivity. In Section 3, we describe the fabrication, characterization and imaging of several Ni/10ScSZ electrodes. In Section 4, the measured effective conductivities of some of these anodes are compared to those computed based on the reconstructed 3D microstructures of the same anodes. The effective conductivities of a set of synthetic anodes are also computed. This provides an opportunity to test the validity of the model and to analyze the variation of the effective electronic conductivity across the percolation threshold. With a view to assess the impact of errors in the electronic conductivities on the validity of the prediction of electrochemical performance of SOFC anodes, the ResNet model is then integrated with the VOF model of Golbert et al. [18].

2. Representative sample size for investigating the effective conductivity

In order to make a valid comparison between the predicted and experimentally measured effective conductivities, it is necessary to