Developing micro-scale heterogeneous numerical simulation of a solid oxide fuel cell anode

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Abstract. In this article a fully three dimensional, multiphase, meso-scale Solid Oxide Fuel Cell (SOFC) anode transport phenomena model is described. The Butler-Volmer model is combined with empirical relations for conductivity and diffusivity - notably the Fuller-Shetler-Giddings equation - for transport of gas reagents. Numerical simulation is used to obtain partial pressure and electric potential fields for each phase, accounting for activation and concentration overpotential as well as ohmic losses. Mesh generator and a solver have been developed to provide an in-house code for the computations. The findings are presented alongside a parametric study of a specific YSZ electrolyte-based SOFC anode microstructure. Despite high dependence of SOFC anode performance on the geometry of its anisotropic, three-phase microstructure, meso-scale numerical models simulating transport phenomena within these electrodes are not very common.

1. Introduction

Fuel cells are devices capable of direct conversion of chemical energy to electrical energy. Lack of combustion chambers and heat engines facilitates elimination of irreversibility sources from the system which in turn results in a highly improved efficiency. This is accomplished by separating oxidation and reduction half-reaction, which occur on the anode and the cathode respectively. The conduction of ions between the separate electrodes takes place in the electrolyte. Solid Oxide Fuel Cell is a type of fuel cell where the electrolyte is composed of a ceramic material and its electrodes are made of ceramic-metal composites. Each phase of the composite performs a peculiar transport function. In an Yttrium-Stabilized Zirconia SOFC anode, the ion conduction takes place in the oxide phase, the electron transport is carried out in the metallic phase and gaseous reagents are delivered via a network of pores. This results in a highly complex microstructure which impacts the performance of SOFC devices (see Fig. 1). Thus, SOFC technologies have become a prominent subject of research in the field of energy engineering [1–8]. Attempts at modelling three dimensional transport phenomena in the depth direction of the cell have been relatively rare [9–11]. Yet, as we have discussed in our previous publication, this may be the most comprehensive method of investigating the impact of heterogeneity in a complex SOFC microstructure [12]. At the same time, the impact of the microstructure on the SOFC device performance still remains a subject of the contemporary research [13]. Such a state of affairs justifies attempts at increasing insight into SOFC anode transport phenomena, including gas diffusion within the porous medium. In this research, a fully three dimensional, multiphase, micro-scale (pore-scale), heterogeneous (non-continuous) SOFC anode model is proposed and verified using a semi-analytical approach. The Butler-Volmer model is combined with recently
developed empirical relations for conductivity and aspects of Maxwell-Boltzmann kinetic theory to describe the transport of mass within the porous medium. The numerical mesh construction is based on the data acquired using FIB-SEM tomography. Methods for localized quantification of electrode morphology parameters (such as Triple Phase Boundary length) are implemented and tested. Exchange current distribution in both electrodes, partial pressure and electric potential fields for each phase are computed numerically. The method of verification relies on a comparison of a three-dimensional, numerical solution to an analytical solution of a one-dimensional case within the range of its applicability. A predictive, parametric study involving localized second-law analysis is performed to predict activation, concentration and ohmic losses, as well as overpotentials at different working conditions of an SOFC stack. Furthermore, the paper contains a parametric study in which different kinds of heterogeneity (varying in placement and the material type of the introduced disturbance) have been introduced.

2. Mathematical model
The mathematical model is based on a set of Poisson equations, describing the transfer of charge and mass in the system. Transport of each of the substances - oxygen ions, electrons, gaseous species - is considered in the following set of equations:

\[
\begin{align*}
0 &= -i + \frac{\partial}{\partial x} \left( \sigma_{\text{el}} \frac{\partial \phi_{\text{el}}}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_{\text{el}} \frac{\partial \phi_{\text{el}}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \sigma_{\text{el}} \frac{\partial \phi_{\text{el}}}{\partial z} \right), \\
0 &= i + \frac{\partial}{\partial x} \left( \sigma_{\text{ion}} \frac{\partial \phi_{\text{ion}}}{\partial x} \right) + \frac{\partial}{\partial y} \left( \sigma_{\text{ion}} \frac{\partial \phi_{\text{ion}}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \sigma_{\text{ion}} \frac{\partial \phi_{\text{ion}}}{\partial z} \right), \\
0 &= -i + \frac{\partial}{\partial x} \left( \frac{2FD}{RT} \frac{\partial p_{\text{H}_2}}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{2FD}{RT} \frac{\partial p_{\text{H}_2}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \frac{2FD}{RT} \frac{\partial p_{\text{H}_2}}{\partial z} \right), \\
0 &= i + \frac{\partial}{\partial x} \left( \frac{2FD}{RT} \frac{\partial p_{\text{H}_2O}}{\partial x} \right) + \frac{\partial}{\partial y} \left( \frac{2FD}{RT} \frac{\partial p_{\text{H}_2O}}{\partial y} \right) + \frac{\partial}{\partial z} \left( \frac{2FD}{RT} \frac{\partial p_{\text{H}_2O}}{\partial z} \right),
\end{align*}
\]

where \( i \) is charge transfer rate, \( \phi_i \) is electric potential at ion-conducting or electron-conducting phase, \( p_i \) is pressure of species \( i \) in the gas mixture. \( T \) is temperature in Kelvins, \( F \) is the
Table 1. Scheme of boundary conditions

| $z = 0$ | $z = z_b$ | Vertical boundaries |
|---------|-----------|---------------------|
| $p_{H_2} = p_{H_2,b}$ | $\frac{\partial p_{H_2}}{\partial z} = 0$ | No transfer |
| $p_{H_2O} = p_{H_2O,b}$ | $\frac{\partial p_{H_2O}}{\partial z} = 0$ | |
| $\phi_{el} = \phi_{el,b}$ | $\frac{\partial \phi_{el}}{\partial z} = 0$ | |
| $\frac{\partial \phi_{ion}}{\partial z} = 0$ | $\phi_{ion} = \phi_{ion,b}$ | |

Faraday constant $R$ is the universal gas constant, while $\sigma_i$ and $D_i$ signify conductivities and diffusivities respectively. The values of conductivities are obtained with the following semi-empirical relationships by Anselmi-Tamburini et al. [14] and Bessette et al. [15], while $D_i$ is obtained from Fuller-Schettler-Giddings correlation [16]:

$$
\begin{align*}
\sigma_{el} &= 3.27 \cdot 10^6 - 1065.3T \\
\sigma_{ion} &= 3.4 \cdot 10^4 \cdot \exp\left(-\frac{10350}{T}\right) \\
D &= 10^2 \frac{T^{1.75} \left( \frac{1}{M_{H_2}} + \frac{1}{M_{H_2O}} \right)}{p \left( V_{1/3}^{H_2} + V_{1/3}^{H_2O} \right)},
\end{align*}
$$

(2)

The charge transfer rate is derived from the Butler-Volmer model. Additionally, empirical relationship for equilibrium charge transfer rate $i_0$ has been employed.

$$
i = i_0 l_{tpb} \left[ \exp \left( \frac{\alpha F \eta_{act}}{RT} \right) - \exp \left( -\frac{\alpha F \eta_{act}}{RT} \right) \right],
$$

(3)

$$
i_0 = 31.4 \cdot p_{H_2}^{-0.03} \cdot p_{H_2O}^{0.4} \cdot \exp \left( -\frac{152155}{RT} \right),
$$

(4)

where $i_0$ (A m$^{-1}$) is exchange current density derived from the data by de Boer [17], $l_{tpb}$ (m m$^{-3}$) is local TPB length density and $\eta_{act}$ is activation overpotential defined as follows:

$$
\eta_{act} = \phi_{el} - \phi_{ion} - \eta_{conc},
\eta_{conc} = \frac{RT}{2F} \ln \left( \frac{p_{H_2}^{bulk} p_{H_2O}^{bulk}}{p_{H_2}^{H_2O} p_{H_2O}^{H_2}} \right),
$$

(5)

where $\eta_{conc}$ (V) is concentration overpotential.

The model is discretized using Finite Volume Method and the resulting set of equations is solved using Successive Over-Relaxation method with local linearization of the source term.

2.1. Analytical approach

The performance of an anode can be described by a discussion of potential fields present in its interior, as well as electronic losses occurring during its operation. These values may, under some assumptions and approximations be obtained by means of analytical modelling. If the transport phenomena for a given case may be considered as one-dimensional, the problem can be described by the Set of Equations 7. The general scheme of case boundary conditions is presented in Table 1.

$$
\begin{align*}
\frac{\partial j}{\partial z} &= i_0 l_{tpb} \left[ e^{\frac{\alpha F \eta}{RT}} - e^{-\frac{\alpha F \eta_{act}}{RT}} \right] \\
j &= \frac{V_{ion}}{\tau_{ion}} \frac{\partial \eta}{\partial z},
\end{align*}
$$

(6)
Figure 2. Verification. Ionic potential and exchange current density fields. Boundary conditions: $\phi_{el,b} = 0.05$ V, $p=100000$ Pa, $p_{H_2O} = 3000$ Pa, $p_{H_2} = p - p_{H_2O}$, thickness: $62.6 \mu$m, $T = 1073$ K

where $V_{ion}$ is ion-conducting phase volume fraction, and $\tau_{ion}$ is ion-conducting phase tortuosity. For small effective conductivity and large anode thickness, the following solution holds true:

$$
\begin{align*}
\phi_{ion} &= \frac{RT}{\alpha F} \cdot \sinh \hat{\eta}_b \cdot \left( 1 - \frac{\cosh \hat{z}}{\cosh \frac{1}{\hat{\varepsilon}}} \right) \\
j &= \frac{V_{ion} \sigma_{ion} RT}{\tau_{ion} L \alpha F} \cdot \sinh \hat{\eta}_b \cdot \frac{\sinh \hat{z}}{\cosh \frac{1}{\hat{\varepsilon}}} \\
\end{align*}
$$

(7)

where $\hat{\eta} = \frac{\alpha F \eta}{RT}$, $\hat{\varepsilon} = \sqrt{\frac{V_{ion} \sigma_{ion} RT}{2 \tau_{ion} \alpha F \hat{\eta}}} \hat{z}$, and $\hat{z} = \frac{z}{\hat{\varepsilon}}$. $j$ $(Am^{-2})$ signifies current density at the ion-conducting phase. The ionic potential and mean exchange current density obtained from the numerical simulation have been compared to the analytic solution showing good agreement within the common range of applicability. The analytical solution does not account for concentration losses in thick anodes and is accurate when large currents are considered. Furthermore, it appears that at lesser depths, convergence occurs at a much slower rate - this is caused by small values of $\phi_{ion}$ gradient and barely significant difference between $\phi_{el}$ and $\phi_{ion}$. Since mean values of macroscopic overpotential and ohmic losses arise from the product of the local potential differences and the local exchange current density, resulting error should be very small. Verification has also been performed for other sets of boundary conditions. The numerical model appears to match the analytical solution in other applicable cases not presented in this paper (similar consistency is observed).

3. Results and discussion

The simulation has allowed to determine active layer thickness as well as current density for a number of boundary condition sets, allowing for a parametric analysis (see Fig. 3). In the presented example, it can be noted that when the electrode’s thickness is lower, the distribution of the potential fields is more uniform. This is related to the fact that, as the thickness increases, charge transfer rate is concentrated closer to the electrolyte, while a significant part of the anode experiences very small reaction rate. This is consistent with the experimental data on active thickness reported in the literature [18]. The uneven distribution of charge transfer rate is also related to variations in the local TPB density.
**Figure 3.** Electric potential field and exchange current distribution in oxide phase of a Solid Oxide Fuel Cell anode for electrodes of different thickness. Boundary conditions: $\phi_{el,b} = 0.05$ V, $p=100000$ Pa, $p_{H_2O} = 3000$ Pa, $p_{H_2} = p - p_{H_2O}$, $T = 1073$ K

**Figure 4.** Electric potential field and exchange current distribution in oxide phase of a Solid Oxide Fuel Cell anode at different depths of the electrode. Boundary conditions: $\phi_{el,b} = 0.05$ V, $p=100000$ Pa, $p_{H_2O} = 3000$ Pa, $p_{H_2} = p - p_{H_2O}$, Thickness: $62.6 \mu$m, $T = 1073$ K
4. Conclusions
It has been concluded that, in the case of a homogeneous electrode, the problem may be treated as one-dimensional, however only a three-dimensional, heterogeneous model offers an opportunity to address local phenomena within the electrode. The results support the claim that, in a non-homogeneous electrode, the local, microscopic morphology (visible in Fig. 3) may impact the macroscopic parameters of the microstructure. This is evident from irregularities in the potential and current distribution (see Fig. 4). The model provides a useful tool for analysis of cell degradation over its operation period, as well as other phenomena dependent on electrode heterogeneity.

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Matplotlib [19] library for Python programming language and Blender open source 3D graphics software were used for the result visualization.

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