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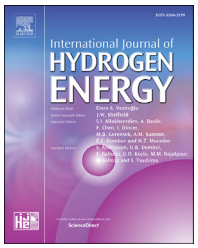

A three-dimensional heterogeneity analysis of electrochemical energy conversion in SOFC anodes using electron nanotomography and mathematical modeling

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ABSTRACT

In this paper a fully three dimensional, multiphase, micro-scale solid oxide fuel cell anode transport phenomena numerical model is proposed and verified. The Butler-Volmer model was combined with empirical relations for conductivity and diffusivity - notably the Fuller-Shetler-Giddings equation, and the Fickian model for transport of gas reagents. FIB-SEM tomography of a commercial SOFC stack anode was performed and the resulting images were processed to acquire input data. A novel method for estimating local values of Triple Phase Boundary length density for use in a three-phase, three-dimensional numerical mesh was proposed. The model equations are solved using an in-house code and the results were verified by comparison to an analytical solution within the range of its applicability. A limited parametric study was performed to qualitatively assess simulation performance and impact of heterogeneity. Despite the high dependence of the SOFC anode performance on the geometry of its anisotropic, three-phase microstructure there are very few micro-scale numerical models simulating transport phenomena within these electrodes.

Introduction

Fuel Cells are energy conversion devices capable of converting chemical energy directly into electrical energy. Solid Oxide Fuel Cells (hereafter SOFC) - excelling in terms of efficiency, magnitude of power output and relative affordability - are defined as fuel cells, where the electrolyte is composed of a solid-state ceramic material. Despite the progress of SOFC technology in recent years, devices of this type face several challenges [1]. Since commercial fuel cells include very thin ceramic and ceramic-metal composite elements, their

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Nomenclature

Abbreviations

FIB	Focused Ion Beam
SEM	Scanning Electron Microscopy
SOFC	Solid Oxide Fuel Cell
TPB	Triple Phase Boundary
YSZ	Yttrium Stabilized Zirconia

Roman symbols

C	Integration constant
D	Binary diffusion coefficient ($m^2\ s^{-1}$)
F	Faraday constant ($A\ s\ mol^{-1}$)
i	Charge tranfer rate ($A\ m^{-3}$)
j	Mean charge tranfer rate ($A\ m^{-2}$)
l_{tpb}	Sample average TPB density ($m\ m^{-3}$)
$\hat{l}_{tpb}$	Local TPB density ($m\ m^{-3}$)
n_{tpb}	Mesh TPB edges in a node
N_{tpb}	Mesh TPB edges in a mesh
p	absolute pressure (Pa)
p_i	partial pressure of substance i (Pa)
R	Universal gas constant ($J\ mol^{-1}\ K^{-1}$)
T	Temperature (K)
V	Phase volume fraction
x, y	Planar coordinates (m)
z	Depth (m)

Greek symbols

α	Charge transfer coefficient
$\hat{\eta}$	Dimensionless potential losses (V)
$\hat{\varepsilon}$	Dimensionless constant
η	Local overpotential (V)
$\overline{\eta}$	Mean overpotential (V)
ϕ	Electrical potential (V)
$\overline{\Phi}$	Mean potential difference (V)
σ	Electrical conductivity ($\Omega^{-1}\ m^{-1}$)
τ	Tortuosity

Subscripts

tpb	Triple phase boundary
H_2	Hydrogen
H_2O	Water vapor
act	Activation
an	Analytical
b	Boundary (bulk)
conc	Concentration
eff	Effective, homogeneous model value
ion	oxide ion conducting phase
ohm	ohmic
P	In the processed node

Superscripts

tpb	Nodes neighboring TPB

production and design is demanding. They are also subjected to material fatigue and damage stemming from thermal expansion and composition changes occurring at large temperatures, making operation and control more difficult: users face long warm-up times, high latency and limitations regarding the maximum number of shutdowns. Large gains in efficiency are yet to be made by better utilization of fuel [2]. Alleviation of these difficulties is impeded by the fact that a comprehensive understanding of SOFC processes, as of yet, has not been achieved. Therefore, in spite of promising results, SOFC technologies require more research to achieve their full potential. This commercial and academic interest has produced demand for increasingly sophisticated models of transport phenomena within the SOFC electrode microstructure. The SOFC anode is formed from a highly porous ceramic-metal composite. The pores allow hydrogen molecules to penetrate the electrode. When the molecules encounter oxygen ions transported through the solid oxide phase, oxidation half-reaction occurs. The metallic phase functions as a drain for the excess electrons, while the pore network forms pathways for the produced water vapor. Within this complex microstructure, the anodic reaction may only occur in the presence of all the aforementioned transport routes - at the boundary of all the three phases, known as Triple Phase Boundary (hereafter referred to as TPB). The resulting geometric complexity is a major obstacle in SOFC anode design. There has been a number of approaches to describing gaseous, ionic and electronic transport within porous SOFC electrodes. It is common to use the continuous electrode theory - assuming homogeneous distribution of small morphological features within the sample and modeling it as a continuous medium. This requires the introduction of macroscopic coefficients, reflecting the influence of case-specific microstructure. These include phase volume ratio, surface area, pore tortuosity and TPB length. Since SOFC thickness tends to be small compared to its surface area, research - including its more recent iterations - has relied on two-dimensional [3–8] or one-dimensional [9–11] models. Three-dimensional models have also been proposed [12–17]. Quantitative analyses of anodic charge transport have generally been based on the relations derived from empirical data and employed, for example, in order to estimate temperature-dependent conductivity coefficients peculiar to the materials used in the analyzed electrode [9,12,18,19]. The diffusion models commonly employed in the quantitative descriptions of SOFC electrode performance include: models prioritizing the Fickian or Knudsenian diffusion, the dusty gas model, as well as more sophisticated variations of the Stefan-Maxwell Model [5,13,20]. Notably, the Lattice Boltzmann Method for diffusion simulation has gained particular prominence [4,9,15,16,21], as - based on mesoscopic kinetic fluid equations and microscopic models [22] - it shows particular utility in the modeling of flows of small characteristic length within complex geometry. According to Jeong et al. [23], the Lattice Boltzmann Method is computationally more efficient than the lattice gas automata model, or the direct simulation Monte Carlo method. Some, however, consider Fick's model with corrected diffusivity coefficient to perform better than LBM [24]. It is worth noting that, due to the operating conditions and microstructure of SOFC devices it may be observed that the mean free path of molecules in the gaseous phase is often of comparable magnitude to a pore's specific length (i.e. its diameter) - thus, as Yang has proposed [25], macroscopic models relying solely on Fickian diffusion may be laden with error due to the *de facto* non-negligible Knudsen's diffusion coefficient. However,