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Effect of Porous Microstructural Properties on the Results of a Cell-level Model in Solid Oxide Fuel Cells

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A detailed micro-model framework is used for calculating effective microstructural properties for the porous anode and cathode electrodes in solid oxide fuel cells (SOFCs). The resulting microstructural parameters obtained from this detailed numerical approach are then applied to a macro-scale SOFC cell model. The performance of the SOFC cell model is determined by the geometric and effective transport microstructural properties which properly accounting for representative porous SOFC electrode structures.

Introduction

Proper characterization of the porous composite electrodes used in solid oxide fuel cells (SOFCs) is essential to design and optimize the cell, stack, and hot-box with mathematical models. It is imperative, not only to employ well-reconstructed microstructures, but also to access accurate data for effective physical and transport properties of the multi-phase and multi-layer electrodes used in SOFCs. The effective properties from such micro-scale porous media may readily be integrated into the macro-scale cell/stack/hot-box models used in SOFCs (2,3). Therefore, the accurate and reliable techniques for the micro-structural reconstruction and computation of relevant physical and transport properties will lead to improvement in the overall design of SOFCs.

In recent times, a number of micro-structural reconstruction techniques have been implemented to SOFC electrode design (10-15,19-25). In order to directly facilitate the above mentioned reconstruction techniques into porous electrode models used in SOFC applications, reliable techniques to evaluate the fidelity of the reconstructed microstructures are needed. To calculate effective physical and transport properties of microstructures, theoretical (5,16), numerical (4,6,7,13,19,25) and experimental (1,8) techniques have all been used.

Among many others, this paper follows the reconstruction technique by Kenney et al. (14) and is an adaptation of the techniques described in (4,6,7). The methodology involves the construction of the porous electrode microstructure based on measureable starting input parameters and the subsequent numerical evaluation of effective microstructural parameters. To this end, the anode and cathode electrodes of SOFCs are reconstructed as porous microstructures that are formed by randomly distributed particles with measured parameters such as particle size distributions, solid matrix compositions and porosities that match those of actual ceramic powders. The resulting 3-D

reconstructed volumes are converted into the computational domain based on the high-resolution body-fitted/cut-cell based finite volume meshes. We use a finite volume method (FVM) to enumerate effective micro-mechanical properties. The FVM is implemented through the open-source computational fluid dynamics (CFD) toolbox OpenFOAM[®] (18) written in the objected-oriented C++ language. The computed micro-structural properties obtained from above mentioned techniques are integrated into a single cell SOFC model (17) to analyze overall fuel cell performance.

Model Descriptions

Micro-scale Model

A particle-based numerical model developed in (14) was adapted to generate 3-D microstructures based on random distributions of spherical particles. Input parameters to the numerical model are the porosity and (uniform) particle size of each porous electrode layer as listed in Table 1, which is adapted from reference (17). The reconstruction procedure used follows a ‘drop-and-roll’ algorithm. A particle is randomly dropped into a sample box domain of specific dimensions. The particle is allowed to roll over other particles until it touches either three others or the bottom of box. Unlike conventional packed-bed type structures, SOFC electrode structures undergo particle sintering process during fabrication, creating percolation networks for each of the phases embedded in the electrode. The sintering was taken into account by manipulation of the particle-to-particle contact-angle. The numerical model provides as output, the centre co-ordinates and particle diameter. A Sample particle reconstruction is illustrated in Figure 1. The reconstructed volumes are converted into the computational domains to measure geometric quantities such as volume fractions and internal surface areas as well as to compute effective transport properties such as effective electronic conductivity and effective gas diffusivity and permeability. The computational domains are adapted into the body-fitted/cut-cell based finite volume meshes using MicroFOAM (7), which is a suitably modified version of the open-source CFD toolbox OpenFOAM[®].

Figure 1. Sample reconstructed microstructure consisting of randomly placed particles: a monosized electrode with diameter of $d=1\mu\text{m}$ and the porosity of $\varepsilon=0.3$.

Table 1: Geometry descriptions for porous anode and cathode electrode layers used in anode supported single cell model.

	anode support layer	anode functional layer	cathode current collector layer	cathode functional layer
porosity	0.47	0.36	0.47	0.35
particle size (μm)	2	1.3	12	0.5
layer thickness (μm)	1000	7	267	18

Transport phenomena of gas species in the pore space and electron-conducting phase in LSM of the sample electrode are predominately governed by diffusion. The governing diffusion equation for phase potential is written as follows:

$$\nabla \cdot (\alpha \nabla \phi) = 0 \text{ on } \Omega_{\text{phase}} \quad [1]$$

where α is the bulk transport coefficient, ϕ is the relevant potential and Ω_{phase} is the computational domain for each phase, respectively. Dirichlet boundary conditions are imposed on the top and bottom surfaces of the sample domain and symmetry (i.e. zero-flux Neumann) boundary conditions are applied on the electron-pore phase interfaces as well as side boundaries. The FVM is used to obtain solutions to Equation [1] using a preconditioned iterative conjugate-gradient (CG) solver. From the solution of Equation [1], the normalized effective transport coefficient for each phase as follows may be evaluated as follows:

$$\frac{\alpha^{\text{eff}}}{\alpha} = \frac{\int_{\Omega} \partial \phi / \partial n \, dS}{(\Delta \phi / L) S} \text{ on } \Omega_{\text{phase}} \quad [2]$$

where $\Delta \phi$ represents the applied potential difference, L is the selected length of the domain, and S denotes the selected boundary surface area for each phase. The tortuosity factor as defined in (9) is calculated as follows:

$$\tau = \frac{\varepsilon_{\text{phase}}}{\alpha^{\text{eff}} / \alpha} \text{ on } \Omega_{\text{phase}} \quad [3]$$

where $\varepsilon_{\text{phase}}$ is the volume fraction of each phase. In this study, the normalized effective transport coefficient and tortuosity factor is calculated for each co-ordinate direction (i.e., x , y , and z) of the sample electrode. The directional transport properties, often used to measure the anisotropy of the porous sample electrode, can be evaluated by changing the direction of the applied potentials.

In a denser particle packing of spheres for porous electrodes such as occurs for lower porosity cases (e.g. for $\varepsilon=0.35$ in Table 1), Knudsen diffusion effects must be taken into account, in order to properly evaluate the effective binary gas diffusivity. This paper follows the effective gas diffusivity formation including Knudsen diffusion as given in reference (4). The Bosanquet formation can be written in terms of the bulk diffusivity and Knudsen number such that:

$$\frac{D^{\text{eff}}(Kn)}{D} = \frac{\varepsilon}{\tau} \frac{1}{1+Kn} \quad \text{on } \Omega_{\text{pore}} \quad [4]$$

$$D = \frac{1}{3} \langle \lambda \rangle \langle v_T \rangle \quad \text{on } \Omega_{\text{pore}} \quad [5]$$

$$v_T = \sqrt{\frac{8k_B T}{m\pi}} \quad \text{on } \Omega_{\text{pore}} \quad [6]$$

where $D^{\text{eff}}(Kn)$ is the effective gas diffusivity for Knudsen diffusion, D is bulk diffusivity, Kn is the Knudsen number, and Ω_{pore} is the computational domain for the pore phase of each electrode layer. $\langle \lambda \rangle$ denotes the mean free path, $\langle v_T \rangle$ is the thermal velocity of gas molecules, k_B is Boltzmann constant, T is the gas temperature, and m is mass of gas particles.

The Knudsen number is the dimensionless number that accounts for the pore confinement for diffusion process applied in denser porous media:

$$Kn = \frac{\langle \lambda \rangle}{d_{CL}} \quad \text{on } \Omega_{\text{pore}} \quad [7]$$

$$\langle \lambda \rangle = \frac{k_B T}{P \sqrt{2\pi} d_g^2} \quad \text{on } \Omega_{\text{pore}} \quad [8]$$

where d_{CL} represents the characteristic length of pore confinement, d_g is the gas particle diameter, and P is the gas pressure. The characteristic length d_{CL} is defined by

$$d_{CL} = \left[\frac{\langle l^2 \rangle}{2\langle l \rangle^2} - \beta \right] \langle l \rangle \quad \text{on } \Omega_{\text{pore}} \quad [9]$$

where the first term in parenthesis depends on the first two moments of the chord length distribution, l is the chord length of pore domain, and β is the average cosine of the angle between particle trajectories separated by m wall collisions. Note that $\langle l^2 \rangle / 2\langle l \rangle^2 = 1$ for an exponential chord-length distribution. Knudsen's cosine law holds for $\beta = 4/13$ as given in (4). So Equation [7] reduces to $d_{CL} = 9\langle l \rangle / 13$. According to reference (9), the mean chord length can be defined by

$$\langle l \rangle = \frac{4V}{S} \quad \text{on } \Omega_{\text{pore}} \quad [10]$$

where S is the surface area of the pore domain and V is the volume of the pore domain.

The permeability, κ , can be determined by applying Darcy's law on given pore computational domain such that

$$\kappa = -\frac{\mu U}{\nabla p} = -\mu \frac{Q}{A} \frac{L}{\Delta p} \quad \text{on } \Omega_{\text{pore}} \quad [11]$$

where μ denotes the fluid viscosity, U is the average velocity, and ∇p is pressure gradient. Q is the volumetric flow rate and A is cross-sectional area to flow, and Δp is the pressure drop at a given distance L .

Single SOFC Cell Model

A single SOFC cell model used in this study is based on the continuum based computational fluid dynamics (CFD) model with electrochemical reactions. The model includes momentum transport for fuel and air flow fields, species transport for fuel-channel side gas species (hydrogen and water-steam) and for air-channel side gas species (oxygen and nitrogen), and thermal transport for all components within the cell. The heat transfer includes conduction and convection without radiation. The descriptions of governing equations and operating conditions can be found in (17).

Numerical Results

The micro-scale model results, which eventually feed to the macro-scale SOFC cell-level model, are given in this section. The brief example of the performance evaluation of a single cell SOFC cell-level model is demonstrated in Figure 3 for only illustration purpose. Nevertheless, detailed sensitivity analyze associated with a single cell- and stack- levels performance of SOFC will be addressed in forthcoming paper.

Table 2: Normalized effective gas diffusivities and tortuosity factors for multi-layer electrodes used in SOFC. Both effective properties and tortuosity factors are presented in terms of x -, y -, and z -directions. Those directional properties can be used to measure the degree of anisotropy.

	anode support layer	anode functional layer	cathode current collector layer	cathode functional layer
ε	0.467	0.36	0.473	0.35
D_x^{eff}/D	0.294	0.184	0.314	0.159
D_y^{eff}/D	0.291	0.183	0.313	0.159
D_z^{eff}/D	0.294	0.202	0.330	0.179
τ_x	1.587	1.97	1.51	2.21
τ_y	1.604	1.98	1.51	2.22
τ_z	1.509	1.79	1.43	1.97

Table 2 demonstrates effective transport properties and tortuosity factor evaluated by the solution of diffusion equations applied on each phase domain. The FVM through OpenFOAM solver is used to calculate these properties. The normalized effective gas diffusivities and tortuosity factors are given in terms of x , y , and z -directions. This directional normalized effective properties provide the local anisotropic measure of the given electrode layers. As clear shown in Table 2, the normalized effective properties in x - and y -directions, are in excellent agreement but they are slight smaller than the effective properties in z -direction. The tortuosity factor, which relates the effective transport properties inversely, in z -direction is smaller than that in x - and y -directions.

Again, the tortuosity factors in x - and y - directions are in good agreement. The Knudsen gas diffusivity, as given in Table 3, is calculated by using the Bosanquet's formation as well as geometric Knudsen number evaluation to properly account-for the Knudsen diffusion effect.

Table 3: Normalized Knudsen gas diffusivities and Kundsens number (Kn) for multi-layer electrodes used in SOFC. For the working fluid, oxygen for the cathode layers and hydrogen for the anode layers, at $P=1\text{atm}$ and $T=850^\circ\text{C}$, are considered.

	anode support layer	anode functional layer	cathode current collector layer	cathode functional layer
$\langle \lambda \rangle$ [nm]	598	598	372	372
$\langle l \rangle$ [μm]	1.989	0.675	1.985	0.671
d_{CL} [μm]	1.374	0.467	1.374	0.465
Kn	0.435	1.280	0.271	0.801
$\frac{D^{\text{eff}}(Kn)}{D} = \frac{1}{1+Kn} \frac{\varepsilon}{\tau}$	$0.697 \frac{\varepsilon}{\tau}$	$0.439 \frac{\varepsilon}{\tau}$	$0.787 \frac{\varepsilon}{\tau}$	$0.555 \frac{\varepsilon}{\tau}$

The permeability tensor in Equation [9] is computed by using the velocity and pressure fields obtained from Navier-Stokes equations applied in the pore phase domain. Stream tracer of the velocity field is demonstrated in Figure 2. Finally, the V-I performance curve for three flow configurations used in SOFC is given in Figure 3. Three flow configurations, i.e., co-flow, counter-flow, and cross-flow, are applied for a single cell-level model. Note that the micro-structural model properties have been applied in this case only illustration purpose. Nevertheless, further investigations related to design and optimization of a single cell and stack level SOFC applications using the detailed micro-scale model will be addressed in future papers.

Figure 2. Stream tracer of the velocity field (blue color lines) of pore phase domain. Note that grey-color indicates solid phase domain.

Figure 3. V - I performance curves of a single cell-level model using the detailed micro-model properties.

Conclusion

A detailed micro-model framework was presented for calculating effective micro structural properties for the porous anode and cathode electrodes in solid oxide fuel cells (SOFCs). The Knudsen diffusion effect was taken into account for the effective gas diffusivity. The resulting micro-structural parameters obtained from this detailed numerical approach were then applied to a single SOFC cell-level model. The performance of the single SOFC cell-level model was demonstrated for three flow configurations.

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