Direct Simulation of Transport Properties from Three-Dimensional (3D) Reconstructed Solid-Oxide Fuel-Cell (SOFC) Electrode Microstructures

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Abstract. A well-known approach to develop a high efficiency solid-oxide fuel-cell (SOFC) consists of extracting the microstructure and transport properties such as volume fractions, internal surface area, geometric connectivity, effective gas diffusivity, effective electronic conductivity and geometric tortuosities from three-dimensional (3D) microstructure of the SOFC electrodes; thereafter, performing the SOFC efficiency calculations using previously mentioned quantities. In the present work, dual-beam focused ion beam - scanning electron microscopy (FIB-SEM) is applied on one of the SOFC cathodes, a lanthanum strontium manganite (LSM) electrode, to estimate the aforementioned properties. A framework for calculating transport properties is presented in this work. 3D microstructures of LSM electrode are reconstructed from a series of two-dimensional (2D) cross-sectional FIB-SEM images. Volume percentages of connected, isolated and dead-ends networks of pore and LSM phases are estimated. Different networks of pore and LSM phases are discretized with tetrahedral elements. Finally, the finite element method (FEM) is applied to calculate effective gas diffusivity and electronic conductivity of pore and LSM phases, respectively. Geometric tortuosities are estimated from the porosity and effective transport properties. The results obtained using FEM are compared with the finite volume method (FVM) results obtained by Gunda et al. [J. Power Sources, 196(7), 35929(2011)] and other numerical results obtained on randomly generated porous medium. Effect of consideration of dead-ends and isolated-ends networks on calculation of effective transport properties is studied.

1. Introduction
A solid-oxide fuel-cell (SOFC) is an electrochemical conversion device that produces electricity by oxidizing a fuel directly [1]. Fuel cells are typically characterized by their electrolyte material; the SOFC having a solid-oxide or ceramic electrolyte.
Understanding the microstructure properties \([2, 3, 4, 5, 6, 7, 8, 9, 10, 11, 12]\) and computing the transport properties \([3, 4, 5, 13]\) in such solid-oxide electrolytes provides the information to improve the SOFC performance. Typically, these solid-oxide electrolytes are porous in nature and composite in material. Scanning electron microscopy (SEM) is a powerful technique for extracting two-dimensional (2D) images of the microstructures but it does not provide the third component (i.e. depth) of the sample which is important to find interconnected regions and pore volumes, shapes and sizes \([13]\). In the last decade, extensive use of tomography \([14]\) techniques like X-ray micro or nano computed tomography \([11]\) and focused ion beam - scanning electron microscope (FIB-SEM)\([6, 7, 13]\) tomography has been applied to extract series of cross-sectional images of porous samples in order to generate 3D structures. These 3D structures are used to understand the microstructural parameters (porosity, surface area, etc.) to calculate the effective transport properties (effective gas diffusivity, electronic conductivity, permeability, etc.).

The main focus of this paper is to provide a framework of calculating the effective transport properties of SOFC electrodes from the point of preparing a sample to solving the diffusion equation in 3D reconstructed structures using the finite element method (FEM). Significant amount of qualitative and quantitative information for measuring the microstructural parameters as well as the transport properties from the porous materials is provided. In this work, a SOFC cathode electrode, lanthanum strontium manganite (LSM), is investigated using a dual-beam FIB-SEM system and the transport properties are computed using the FEM. Section 2 explains the materials and methods used to prepare the LSM sample, collecting the cross-sectional images, 3D reconstruction from the collected images, and the solution methodology to calculate the transport properties. In section 3, results are discussed. Finally, in section 4, important points are pointed out to conclude the paper.

2. Materials and Methods

2.1. Sample Preparation

The SOFC cathode, LSM, was prepared by pulse spraying \((\text{La}_{0.8}\text{Sr}_{0.2})_{0.95}\text{MnO}_3\pm\delta\) powder (LSM, Praxair) onto a thick electrolyte disk \(((\text{Y}_{2}\text{O}_3)_{0.08}(\text{ZrO}_2)_{0.92}\text{ (YSZ, Tosoh}))\) using an automated air-brush. Interested readers can refer Gunda et al. \([13]\) for further details of sample preparation. Fig. 1 explains the step-by-step procedure of preparing the LSM sample.

2.2. Collection of 2D cross-sectional images

The methodology involves taking a 2D cross-section SEM image of the LSM cathode and then etching a thin layer from the LSM sample using the FIB to take subsequent SEM cross-section images. A series of cross-sectional images of LSM sample was collected using a dual beam FIB-SEM system (Zeiss N-Vision 40 crossbeam workstation). Figure 2(a) shows the FIB-SEM system (Zeiss N-Vision 40 crossbeam workstation) and Fig. 2(b) shows the set of cross-section images of the LSM sample. The detailed procedure of collecting the LSM sample using the FIB-SEM system can be obtained in Gunda et al. \([13]\). The collected images are \(10.94nm \times 10.94nm \times 40nm\) each in voxel size. LSM has two phases, one is solid phase and other is pore phase.
**Figure 1.** Step by step procedure of LSM sample preparation

**Figure 2.** Collection of 2D cross-sectional images using FIB-SEM; (a) FIB-SEM system Zeiss N-Vision 40 crossbeam workstation; (b) set of cross-section images of the LSM sample
2.3. 3D reconstruction of LSM sample

Image processing of the collected images was performed using Avizo Fire edition version 7 (VSG, Visualization Sciences Group, Inc., Burlington, MA), before reconstructing the images. The details of different image processing steps and the reconstruction method applied to such series of images for 3D reconstruction can be found in Gunda et al [13]. A volume of 9.12 \( \mu m \times 4.75 \mu m \times 4.08 \mu m \) was selected from the 3D data which is shown in Fig. 3.

2.4. Computational Domain and Solution Methodology

The reconstructed 3D microstructures were used for computing the transport properties of the LSM sample. A computational domain of 2.74 \( \mu m \times 1.22 \mu m \times 1.43 \mu m \) was selected for calculating these transport properties. Based on computational source availability, we have restricted the computational domain for these dimensions. There is no thumb rule to take these dimensions. We have taken the domain from the middle of the reconstructed sample where there is no crater and no interface of electrode and electrolyte. Since we have taken the domain from the middle of the electrode, we assumed the transport process is taking place due to diffusion [15]. The concentration gradient is
the driving force to the diffusion. Dead-ends are the pores cannot be flushed, but they can cause fluid movement by release of pressure like gas expansion. Isolated-ends are the excluded closed pores (or non-connected cavities). Avizo Fire has the capability of removing these dead-ends and isolated-ends from the 3D reconstructed microstructures.

For each phase, the relevant potential field $\phi$ is governed by the diffusive process as follows:

$$\nabla \cdot (\alpha \nabla \phi) = 0, \quad \phi \in \Omega_{\text{phase}}, \quad (1)$$

where $\alpha$ denotes the bulk diffusion coefficient and $\Omega_{\text{phase}}$ is the computational volume of each phase. Note that each phase volume ($\Omega_{\text{phase}}$) is embedded in the electrode sample volume ($\Omega$) such that $\Omega = \Omega_{\text{LSM}} \cup \Omega_{\text{pore}}$. Dirichlet (fixed value) boundary conditions are imposed on the top and bottom boundaries of each phase, i.e., $\phi_{\text{top}} = 1$ and $\phi_{\text{bot}} = 0$. Symmetry (zero gradient) boundary conditions, i.e., $\frac{\partial \phi}{\partial n} = 0$, are presumed on the sides of the boundaries of each phase as well as the solid and pore phase interfaces.

In the present work, FEM based commercial software COMSOL Multiphysics Version 4.2a (COMSOL, Inc., Burlington, MA) was used to compute the effective gas diffusivity ($D_{\text{eff}}$) and the electronic conductivity ($\kappa_{\text{eff}}$) by solving the diffusion equation, shown in Eq.(1). Dead-ends and isolated-ends were removed from the 3D structures before discretizing the computational domain into tetrahedral elements. Computational domain
considered in this work is depicted in Fig. 4.

The local transport flux $q$ for each phase can be related to the generalized local concentration gradient such that:

$$ q = \alpha \nabla \phi, \tag{2} $$

where the potential field $\phi$ is calculated from Eq.(1). The average (surface integrated) local flux across the surface boundary of each phase should be satisfied such that:

$$ \int_{\partial \Omega} \alpha_{\text{eff}} \frac{\partial \phi}{\partial n} dS = \int_{\partial \Omega_{\text{phase}}} \alpha \frac{\partial \phi}{\partial n} dS. \tag{3} $$

Hence, the normalized effective transport coefficient can be evaluated by:

$$ \frac{\alpha_{\text{eff}}}{\alpha} = \frac{\int_{\partial \Omega_{\text{phase}}} \frac{\partial \phi}{\partial n} dS}{\frac{\Delta \phi}{L S}}, \tag{4} $$

where $\Delta \phi$ represents the potential difference, $L$ is the selected height of the computational domain and $S$ denotes the selected boundary surface area of each phase. Note that $\frac{\alpha_{\text{eff}}}{\alpha} = \frac{D_{\text{eff}}}{D}$ represents molecular diffusion ratio for the pore phase and $\frac{\alpha_{\text{eff}}}{\alpha} = \frac{k_{\text{eff}}}{k}$ represents electrical conductivity ratio for the LSM phase.

3. Results and Discussions

Figure 3 represents the 3D reconstructed microstructure obtained after stacking the FIB-SEM 2D cross-sectional images. The coloured part in the Fig. 3 is the LSM solid phase and the transparent part is the pore phase. In this 3D structure, volume fraction of the pore phase is 49.4\% and volume fraction of the LSM phase is 50.6\%.

The volume fractions of pore phase after removing the dead-ends and isolated-ends, is found to be 47.8\% (approx.) which tells that around 5.53\% of total pore phase contains the dead-ends and isolated-ends. Dead-ends contribute some error in the calculating effective transport properties whereas isolated ends do not change the effective transport values. But, the dead-ends and isolated-ends contribute to convergence problems while calculating the effective transport properties. Here in this work, we have removed the dead-ends and isolated-ends to compute the exact effective transport properties.

A computational domain of 2.74 $\mu$m $\times$ 1.22 $\mu$m $\times$ 1.43 $\mu$m was selected from the volume of 9.12 $\mu$m $\times$ 4.75 $\mu$m $\times$ 4.08 $\mu$m for calculating the transport properties. Figure 4 shows the computational domain considered. The 3D computational domain shown in Fig. 4 was discretized by the finite element tetrahedral elements (108,376 elements). The normalized effective gas diffusivity and electronic conductivity are computed by Eq.(4) for this 3D computational domain. Table 1 summarizes the normalized effective properties in $x$, $y$, and $z$-directions calculated for this computational domain as well as the values obtained by the finite volume method (FVM)[13]. Gunda et al. computed normalized effective transport properties on computational domains reconstructed by the FIB-SEM as well as by a numerical model. Numerical models are generated based on the assumption of the same sample size and porosity of FIB-SEM reconstructed microstructure. The values for effective transport properties obtained
in the present work using FEM after removing dead-ends and isolated-ends are 10% lesser than the values obtained by Gunda et al.\cite{13}. Lesser size of the sample might be the reason for this low values. The present method is more efficient for smaller microstructures but not for bigger ones.

| Sample Volume | FVM of Gunda et al. \cite{13} | Present Work |
|---------------|-----------------------------|--------------|
| Technique     | FIB-SEM | Numerical | FIB-SEM | Numerical | FIB-SEM |
| $D_{eff}^x/D$ | 0.304   | 0.298    | 0.276   | 0.265    | 0.243 |
| $D_{eff}^y/D$ | 0.297   | 0.305    | 0.284   | 0.270    | 0.212 |
| $D_{eff}^z/D$ | 0.225   | 0.312    | 0.211   | 0.290    | 0.189 |
| $k_{eff}^x/k$ | 0.242   | 0.159    | 0.265   | 0.184    | 0.211 |
| $k_{eff}^y/k$ | 0.225   | 0.176    | 0.294   | 0.207    | 0.197 |
| $k_{eff}^z/k$ | 0.146   | 0.174    | 0.165   | 0.214    | 0.122 |

Table 1. Normalized effective properties in $x$, $y$, and $z$-directions based on the present work and Gunda et al.\cite{13}.

4. Conclusion
This paper presented a framework of calculating the effective transport properties of solid-oxide fuel-cell porous electrodes. The framework explained in this work has significant potential to extend into computation of other transport properties like permeability, hydraulic conductivity, etc. It can be used to compute transport properties of reservoir core samples. The information obtained in this work will be helpful to elucidate the microstructure/performance relationship of SOFC cathodes such as the influence of internal surface area on oxygen gas adsorption and electrochemical performance of the cathode. In addition, it will give a better understanding of transport through porous media as it applies to sintered SOFC cathodes with non-uniform particle sizes and perhaps, non-spherical shapes.

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6. References
[1] Huang K and Goodenough J B 2009 Solid oxide fuel cell technology: principles, performance and operations (Woodhead Publishing)
[2] Giannuzzi L A and Stevie F A 2005 Introduction to Focused ion beams: Instrumentation, Theory, Techniques and Practice (Springer)
[3] Choi H W, Berson A, Kenney B, Pharoah J G, Beale S and Karan K 2009 ECS Transactions vol 25 pp 1341–1350
[4] Wilson J R, Cronin J S, Rukes S, Duong A, Mumm D and Barnett S 2009 ECS Transactions vol 25 pp 2283–2292
[5] Wilson J R, Duong A T, Gameiro M, Chen H Y, Thornton K, Mumm D R and Barnett S A 2009 Electrochemistry Communications 11 1052–1056
[6] Wilson J R, Kobsiriphat W, Mendoza R, Chen H Y, Hines T, Hiller J M, Miller D J, Thornton K, Voorhees P W, Adler S B, Mumm D and Barnett S A 2007 ECS Transactions vol 7 pp 1879–1887
[7] Wilson J R, Kobsiriphat W, Mendoza R, Chen H Y, Hiller J M, Miller D J, Thornton K, Voorhees P W, Adler S B and Barnett S A 2006 Nature Materials 5 541–544
[8] Iwai H, Shikazono N, Matsui T, Teshima H, Kishimoto M, Kishida R, Hayashi D, Matsuzaki K, Kanno D, Saito M, Muroyama H, Eguchi K, Kasagi N and Yoshida H 2010 Journal of Power Sources 195 955–961
[9] Kenney B, Valdmanis M, Baker C, Pharoah J G and Karan K 2009 Journal of Power Sources 189 1051–1059
[10] Shearing P, Golbert J, Chater R and Brandon N 2009 Chemical Engineering Science 64 3928–3933
[11] Shearing P R, Gelb J and Brandon N P 2010 Journal of the European Ceramic Society 30 1809–1814
[12] Ostadi H, Rama P, Liu Y, Chen R, Zhang X X and Jiang K 2010 Journal of Membrane Science 351 69–74
[13] Gunda N S K, Choi H W, Berson A, Kenney B, Karan K, Pharoah J G and Mitra S K 2011 Journal of Power Sources 196 3592 – 3603
[14] Ritman E L 2004 Annual Review of Biomedical Engineering 6 185–208
[15] Bove R and Ubertini S 2008 Modeling solid oxide fuel cells: methods, procedures and techniques vol 1 (Springer Verlag)