Homogeneity and representativeness analyses of solid oxide fuel cell cathode microstructures

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ABSTRACT

Microstructural properties such as relative density, triple phase boundary length, specific surface area, tortuosity factors are often calculated for microstructure-based analysis and modeling of solid oxide fuel cells (SOFCs). A realistic representation of the microstructure is a challenging and important issue for both experiments and modeling. In the present study, statistical correlation functions and a volume expansion method are used to determine the representative volume element size for the analyses of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathode microstructures in SOFCs.

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Introduction

Solid oxide fuel cells (SOFCs) are considered as one of the most promising future clean energy systems for their high conversion efficiency, fuel flexibility and low emissions [1]. It is widely recognized that the electrochemical performance of SOFCs strongly depends on the microstructures of the porous electrodes [2—8]. In recent years, three-dimensional (3D) microstructure characterization techniques such as X-ray computed tomography (XCT) [9,10] and focused ion beam-scanning electron microscopy (FIB-SEM) [11,12] have enabled the acquisition of 3D microstructure information of SOFCs. Based on the 3D microstructures, microstructural properties such as triple phase boundary length (L_{TPB}), specific surface area ($S_{a:v}$), and tortuosity factors (τ) of different phases can be calculated and correlated to the electrochemical performance of SOFCs [12—15]. Accordingly, 3D numerical simulations such as discrete element method (DEM) [16,17], phase field method (PFM) [18,19], and Potts kinetic Monte Carlo (KMC) [20—23] method have attracted more and more attentions for modeling of microstructures in the SOFCs. The experimentally or numerically acquired 3D microstructures can be coupled with other numerical methods such as finite element method (FEM) [24,25] and computational fluid dynamics (CFD) [15] modeling to assess some important mechanical and electrochemical properties [26,27] in the porous structures of SOFCs. In order to obtain reliable results from these 3D microstructure characterizations and microstructure-based numerical simulations, the sample volume size for the

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evaluations needs to be sufficiently large to represent the macroscopic properties of the heterogeneous electrode microstructures. On the other hand, there are often limitations on the sample size in both experiments and simulations. For example, the experimentally acquired volume is usually limited by the field of view (FOV) which is related with resolutions of the X-ray microscope and FIB-SEM. In the FIB-SEM 3D reconstructions, the final useful sample volume is compromised by image drifting and shadow issues. In numerical simulations, the size of the simulation samples that are digitally represented by 3D arrays is usually restricted by the capability and the efficiency of the dedicated computational resource. In this context, to determine a minimum volume size, or referred to as representative volume element (RVE) that can capture the macroscopic properties is very crucial for both 3D imaging-based microstructure analysis and modeling of SOFCs.

The RVE concept is originally proposed by Hill [28] in 1963 for continuum mechanics. The RVE is usually regarded as a volume of heterogeneous material that is sufficiently large to statistically represent the whole material [29]. Many procedures have been proposed to determine the RVE size for various heterogeneous materials in the literature [28—35]. In general, there are two main indices to determine the RVE size of a heterogeneous material. First is based on the geometric microstructural properties [30,34,35]. This is carried out by an image-based analysis, in which the features of the microstructure are measured quantitatively by successively increasing the sample size until the variation in the microstructural features reaches an asymptotic limit. Second is based on the material properties [31,32,36]. In this approach, material properties are measured from a population of samples with a successively expanding sample size. When the variation of the measured material properties converges to a stagnant value, the sample size is assumed to be representative of the bulk material. Usually, a volume expansion method [37—40] is used to determine the RVE size, and the RVE decided in this method is also called "deterministic" RVE [34].

There are a few factors that can influence the determination of the RVE size:

(1) The nature of homogeneity in the microstructure. For example, the size and shape distributions of particles, inclusions, pores, or agglomerates will intrinsically influence the homogeneity of the microstructures [35,41,42].
(2) The physical or microstructural properties to measure. Al-Raoush et al. [35] revealed that the RVE for porosity may not be adequate to be considered as a RVE for parameters such as particle size distribution, local void ratio and coordination number.
(3) The criteria of error acceptance which is based on the variations in the measurement data [36,43].

Despite the fact that the different RVE sizes will be obtained due to different definitions and criteria, they all respect the separation scale $l_{micro} \ll l_{RVE} \ll l_{macro}$, where l_{micro}, l_{RVE} and l_{macro} represent, respectively, the characteristic length at the microscale, the representativity, and the macroscale [34]. This separation of scales is also known as the Micro-Meso-Macro principle [44].

In the field of SOFCs, many researchers [40,45—52] have investigated the RVE size for different electrode microstructures obtained either by tomography techniques (XCT and FIB-SEM) or by simulations (particle packing and artificial sintering). Some researchers [40,52] determined the RVE size for Ni/YSZ microstructures simply by volume expansion until the variation in porosity became stable. The RVE size determined only by porosity may not be appropriate for other microstructural properties. In support of this assertion, Joos et al. [46] found different RVE sizes for analyses of porosity, tortuosity, specific surface area, and area specific resistance (ASR) of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ cathode. Table 1 summarizes the typical findings of RVE sizes for SOFC materials. From these studies, it is concluded that the RVE size can be different, depending on the properties to examine and the desired error tolerance. It is shown that the RVE size is typically around 10—20 times the average particle size.

As is known, during the fabrication processes of SOFCs, the green body of the electrode undergoes a sintering process, usually taking place in the temperature range of 1100—1500 °C, during which the microstructures of the electrodes are being coarsened and densified. In addition, under the operation conditions (usually in the temperature range of 600—1000 °C), the microstructures further evolve and densify through the sintering mechanism. Due to the microstructure coarsening during sintering, the RVE size will change correspondingly [50], [53]. Okuma et al. [53] showed that a larger RVE size is required for the relative density, specific surface area and sintering stress analyses of densified alumina samples, based on the microstructures obtained by XCT. Jiao et al. [50] showed that the RVE size must be larger for the microstructure analysis of Ni/YSZ anode after operation due to microstructure coarsening. Harris et al. [48,49] showed in theoretical and experimental analyses that RVE sizes for volume fraction, particle size distribution and phase contiguity had strong dependency on the phase volume fraction. As is known, the phase volume fraction is a variable which is directly related with the densification process during sintering.

In this study, we reconstruct the 3D microstructures of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode samples for solid oxide fuel cells which are sintered to different densities. We propose two methods to determine the RVE size for the 3D microstructures of LSCF cathode. First one is a statistical correlation function method which uses two-point function and lineal-path function to characterize the heterogeneities of these porous microstructures, where the RVE size is determined as the critical distance at which the correlation function begins to converge. Second method is based on a volume expansion method, in which the variations in microstructural properties such as LSCF phase volume fraction, or termed relative density (ρ), specific surface area ($S_{a:v}$), tortuosity factor of LSCF phase (τ_{LSCF}) and pore phase (τ_{pore}) are analyzed for different chosen volume sizes. The RVE sizes are decided for each microstructural property within 5% errors. The effects of volume fraction, particle size distribution of LSCF phase and error tolerance on the RVE size are also discussed.