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Lattice-Boltzmann modeling of gas transport in Ni-Yttria-stabilized zirconia anodes during thermal cycling based on X-ray computed tomography

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ABSTRACT

The thermal cycling treatment of Ni-Yttria-stabilized zirconia (Ni-YSZ) anodes strongly influences their three-dimensional (3D) microstructure, including their interior connectivity, phase size and three-phase boundary (TPB) density. In this paper, a nondestructive imaging technology based on X-ray computed tomography is used to obtain the 3D microstructure of Ni-YSZ anode samples after thermal cycling. The lattice Boltzmann method (LBM) is used to simulate gas transport in these 3D microstructures. The mole fraction distributions of gases through the 3D connected pore phase are obtained from the simulated results, enabling the concentration polarization to be calculated. Moreover, the active-TPB density is associated with an electrochemical reaction to simulate the mass diffusion. These results may elucidate the relationship between the microstructure and electrochemical properties.

1. Introduction

A solid oxide fuel cell (SOFC) is an electrochemical device that converts chemical energy to electrical energy with high efficiency. The commercial applications of SOFCs in stationary power sources require stable performance over long periods of time (>40,000 h). However, the electrochemical performance of SOFCs inevitably degrades due to structural changes that occur during long-term operation [1]. The performance degradation of SOFCs is associated with the electrode microstructure [2,3]. Therefore, understanding the relationship between the performance degradation mechanism of SOFCs and their 3D structure is important for improving their performance and stability.

To reveal the SOFC 3D microstructure, highly advanced 3D anode imaging techniques have been developed to study SOFC electrodes. For example, focused ion beam and scanning electron microscopy (FIB-SEM) has been developed to reconstruct the 3D microstructures of SOFC porous electrodes [3–10]. A nondestructive imaging method based on nano X-ray computed tomography (Nano-XCT) is a powerful tool when used to image porous SOFC electrodes [11–16]. The 3D microstructure of SOFCs was obtained using Nano-XCT, and parameters such as the grain size and shape distribution and the elemental composition of various SOFC materials were analyzed using the 3D microstructural data. The nano-tomography results indicated that the growth of Ni particle size causes the decreasing of Ni connectivity and results in a reduced conductivity of the Ni-YSZ anode during thermal cycling [17]. These microstructure changes affect the gas diffusion through the 3D structure of Ni-YSZ anode resulting in performance degradation [18,19]. Moreover, the exhaustion of reactants and the accumulation of products at the reaction sites can cause high levels of local concentration polarization in SOFCs [20]. Therefore, SOFC performance is related to gas diffusion in the anode. Consequently, numerical SOFC models should be developed to predict gas transport and cell performance during SOFC electrode optimization.

Methods such as Lattice Boltzmann method (LBM) were developed to simulate the gas diffusion and concentration polarizations in SOFC anodes to reveal the relationship between mass transport and concentration polarizations. The LBM model is a powerful tool that can be used to design and optimize SOFC electrodes without empirically modifying the diffusion coefficients using medium porosity and tortuosity when detailed imaged geometry data are used as input for the LBM model [21,22]. Therefore,

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information regarding the 3D anode microstructure is critical for improving the reliability of the LBM model that simulates gas diffusion in the SOFC anode. Grew KN. et al. developed a coupled electrochemical kinetic and LBM mass transfer model to study the interplay of the electrochemistry and mass transfer based on a single 2D pore; the active-TPB and porosity were discretely considered. These researchers also proposed that future studies should consider the details of the SOFC anode microstructure [23]. However, until now, few reports have focused on the effect of the actual 3D microstructure of the Ni-YSZ anode relative to the concentration polarization. The tight connection between the active- TPB density and the electrochemical reaction rates in Ni-YSZ anode are ignored because simulation results are difficult to relate to the actual SOFC performance; therefore, SOFC properties are difficult to predict. Nano-XCT can reveal the detailed 3D microstructure and active-TPB density of SOFCs as mentioned above. Combining the LBM model with the Nano-XCT data should simulate the gas diffusion, enabling the calculation of the concentration polarization and helping us to understand the effect of the microstructure on the theoretical electrochemical performance of the SOFCs.

In this paper, the 3D microstructures of several Ni-YSZ anodes subjected to different thermal cycles were collected via Nano-XCT. An LBM using 3D microstructural data and active-TPB density was applied to simulate the ternary gas diffusion (H_2, H_2O and N_2) in the connected pore channel. The effect of 3D microstructure and active-TPB density on the gas transport is discussed, and the concentration polarizations of the anodes during thermal cycling were calculated.

2. Experimental

NiO-YSZ ceramic samples were prepared using the tape-casting method with 56:44 wt% NiO (Nickel carbonate decomposed at 600°C, Sinopharm Chemical Reagent, Shanghai, China): YSZ (BQ-8Y, Jiaozuo Weina Fine Ceramic, Jiaozuo, Henan, China) before being sintered in air at 1,400°C for 5 h; afterward, the product was reduced under flowing Ar/4% H_2 gas at 800°C to obtain the Ni-YSZ anode substrate.

The thermal cycling procedure was as follows: the Ni-YSZ anodes were first heated to 750°C under N_2 gas, maintained for 4 h at 750°C with 50 ml min^{-1} H_2 and finally cooled to room temperature under hydrogen in a tubular quartz reactor. This heating-cooling process was considered one thermal cycle. Three anode samples were imaged after having undergone either 2, 4 and 6 thermal cycles; a Ni-YSZ anode that was not subjected to thermal cycling was used a reference. After the thermal cycling, we collected a small sample from the anode for imaging and analyzing the microstructure.

The 3D images of the samples were collected with a full-field transmission X-ray microscope (TXM) station that was installed at the U7A beamline at the National Synchrotron Radiation Laboratory [24]. In this study, four tomography data sets were collected from three Ni-YSZ anodes that were subjected to either 2, 4 or 6 thermal cycles and a non-cycle anode at 8.4 keV (above the Ni K-edge). Each tomography measurement consisted of 181 projections over a 180° angular range with a 50 nm spatial resolution and a 15-μm field of view. Subsequently, the 3D microstructures were reconstructed from 181 projected images via Xradia's reconstruction software. The experimental procedure was described in detail in our previous work [12]. The 3D reconstruction volume of each sample was cropped to the same cuboid size to eliminate the impact of size differences on gas diffusion. The voxel size of the reconstructed volume is 58.3 nm after 2 × 2 pixel binning.

3. Computations

The electrochemical reaction at the Ni-YSZ anode can be described using Eq. (1). The reaction site was at the three-phase boundary (TPB) where Ni, YSZ and the porous phase meet [3,25]. When the TPB site was positioned across (completely contiguous with) the networks for the Ni, YSZ and pore phases, it was labeled "active". The LBM model was applied to simulate the gas diffusion in the connected pores of the SOFCs.

$$H_2(pore) + O^{2-}(YSZ) \rightarrow H_2O(pore) + 2e^-(Ni) \quad (1)$$

3.1. LBM model

One of the LBM models, the D3Q19 velocity model, was used to simulate ternary gas diffusion (H_2, H_2O and N_2) through the connected pore channels in the Ni-YSZ anode. The D3Q19 model is a lattice with 19 discrete velocities in 3D space that represent higher symmetry, reliability and computational efficiency [26]. All 19 vectors start at the center of the lattice with six vectors pointing to the six face centers and twelve vectors pointing to the twelve edge centers. The whole process of simulating ternary gas (H_2, O_2 and N_2) diffusion in a 2D geometry by LBM has previously been introduced in detail in the literature [18,22,27,28]. Here, we give only a brief description of several of the main steps of the LBM method. The most vital and essential part of the LBM is the lattice Boltzmann equation, shown in Eq. (2).

$$f_i^\alpha\left(x + \delta e_i^\alpha, t + \delta\right) - f_i^\alpha(x + t) = \Omega_i^\alpha \quad (2)$$

In the D3Q19 model, there are 19 discrete directions $\mathbf{e}_i{}^\alpha$ at each lattice point $\mathbf{x}$. Where $i = 0, 1, 2. \ldots . .18$ represents different directions, and $\alpha = 1$, 2 and 3 represent the species, such as those of H_2, H_2O and N_2 gases. The particle distribution function (PDF) denoted by $f_i{}^\alpha$ is the number of molecules of that species moving in a specified direction. The species with higher molecular weights have a slower travelling speed when the gas diffuses at a constant temperature and the kinetic energy of all species is constant. The bilinear interpolation method was used to obtain the streamlined values for heavier species under these conditions. The term t represents the time; δ is the time step in the physical unit and is normally set as 1. The right-hand side of Eq. (2) is the collision term that reflects the interaction between particles arriving at the same lattice point. The particle density n_α and velocity $\mathbf{u}_\alpha$ can be obtained based on conservation of mass (see Eq. (3)) and the conservation of momentum (see Eq. (4)).

$$n_\alpha = \sum_{i=0}^{18} f_i^\alpha \quad (3)$$

$$n_\alpha u_\alpha = \sum_{i=0}^{18} f_i^\alpha e_i^\alpha \quad (4)$$

Gas is unable to diffuse to the TPB sites through isolated pores. Therefore, the isolated pore volume should be an impermeable solid obstacle for gas diffusion. The no-slip boundary particle-wall interaction model used in this paper indicates that particles that encounter a solid obstacle are reflected back in the opposite direction (bounce-back). The particle densities are assigned on the side with the gas inlet. Afterward, the velocity and the unknown PDF can be calculated from Eqs. (3) and (4) after being combined with the bounce-back rule for the non-equilibrium portion of the particle distribution [29]. This work will outline the impact of the microstructural evolution on the concentration polarization at the active-TPB sites. The detailed carriers, pathways, and potentials