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Prediction of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode microstructures during sintering: Kinetic Monte Carlo (KMC) simulations calibrated by artificial neural networks

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HIGHLIGHTS

- Kinetic Monte Carlo simulations can capture the all stages of sintering.
- Input parameters calibration is vital for accurate Kinetic Monte Carlo simulations.
- A rigorous and efficient calibration is achieved via Artificial Neural Networks.
- The calibration method proposed is validated by experiment.

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ABSTRACT

The Potts Kinetic Monte Carlo (KMC) model, proven to be a robust tool to study all stages of sintering process, is an ideal tool to analyze the microstructure evolution of electrodes in solid oxide fuel cells (SOFCs). Due to the nature of this model, the input parameters of KMC simulations such as simulation temperatures and attempt frequencies are difficult to identify. We propose a rigorous and efficient approach to facilitate the input parameter calibration process using artificial neural networks (ANNs). The trained ANN reduces drastically the number of trial-and-error of KMC simulations. The KMC simulation using the calibrated input parameters predicts the microstructures of a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode material during sintering, showing both qualitative and quantitative congruence with real 3D microstructures obtained by focused ion beam scanning electron microscopy (FIB-SEM) reconstruction.

1. Introduction

Microstructural characteristics such as triple phase boundary (TPB) density, specific surface areas and tortuosity factors of different phases in the electrodes can strongly affect the performance of solid oxide fuel cells (SOFCs). Sintering phenomenon plays an important role in microstructural changes of the electrodes during the firing process as well as under the operation condition. For example, degradation of electrodes is partially attributed to the coarsening of electrode materials at an elevated operation temperature. In recent years, intensive efforts have been dedicated to addressing this issue in both experiments and simulations. X-ray computed tomography [1,2] and focused ion beam scanning electron microscopy (FIB-SEM) 3D reconstruction [3,4] were used to reveal the 3D microstructures in SOFC electrodes.

Recently, some numerical simulation techniques are emerging as alternative tools that can provide complementary insights to this study. Some established simulations can even study microstructure changes in a long term scale [5], whereas experiments usually fall short. Molecular Dynamic (MD) method which works at the atomic scale can handle sintering of a few or tens of nanoparticles [6–9]. Discrete Element Method (DEM) as a particle-based method is very suited for studying sintering of powders as it considers the particular nature of materials [10]. It can be used for the study of

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the particle slides and rearrangements and the derivation of stress and strain [11]. Martin et al. [12,13] and Kraft et al. [14] utilized DEM simulations to study constrained sintering of layered systems. Liu et al. [15] studied the microstructures of partially sintered NiO/YSZ and LSM/YSZ electrodes using spherical particles. However, when a particulate material is densified to a density above 0.85, the DEM model loses its confidence. What is more, grain coarsening during sintering is still a challenging aspect for DEM. Finite Element Method (FEM) established on a continuum theory has been used to study the stress and strain in layered systems during sintering by taking into account implicitly the pore effect, but the microstructures are usually ignored [16,17].

The Potts Kinetic Monte Carlo (KMC) method is recently emerging as a powerful tool at the mesoscale to mimic microstructure change caused by sintering [18–20]. It has been proven to be a robust method to deal with the entire sintering process from initial to final stages. Being coupled with FEM, it can consider the effect of stress imposed by constraints on the sintering in the constrained sintering scenarios [21]. Especially, the KMC method can handle arbitrarily shaped particles while it is so simple to code. Hara et al. [22] predicted the microstructures of sintered sub-micrometer nickel powders by KMC simulations which were verified by FIB-SEM tomography characterizations. Zhang et al. [23–25] and Hara et al. [26] modeled the sintering of dual-phase anodes using KMC simulations to study their thermal stability during operation. While having great potential to predict and to optimize microstructures of SOFC electrodes, the KMC model, based on a phenomenological description, is described using some parameters whose values are difficult to identify. For instance, there are sintering temperatures and frequencies for sintering mechanisms such as grain growth, pore migration, vacancy formation and annihilation. To achieve reliable and quantitative predictions using KMC simulations, the determination of these input parameters is crucial.

Although some researchers tried to relate the frequency parameters to the atomic diffusivity [23], further parameter calibration is still needed. In fact, physical model parameter calibration is a common concern for molders. A practical way is to calibrate the material parameters in the model by comparing the numerical simulations with the experimental observations. Usually, simulations under various combinations of input parameters are carried out for the comparison with experiments. This trial-and-error approach is usually very lengthy and time-consuming, especially when parameters interact with each other. In this context, the artificial neural networks (ANNs) method is a rigorous and efficient tool to calibrate the input parameters for KMC sintering simulations. To the authors' knowledge, this study is the first to report on the methodology of input parameter calibration for KMC simulations using ANNs.

The artificial neural network, as a “biologically inspired” computational model, is widely used in different fields for its excellent capability of handling multivariate and non-linear systems. Good examples can be found for predicting SOFCs performance [27–33] and microstructural properties of sintered materials [34–37] based on ANNs trained with a finite amount of experimental or simulation data. Particularly, ANNs have been used as inverse techniques to identify or optimize input parameters for different systems [38–41]. Chamekh et al. identified material's Hill anisotropic parameters [42] using an inverse ANN model trained by FEM simulation results of deep drawing tests. Benvenuti et al. [43] used ANNs trained by DEM simulation data to identify granular material properties in combination with granular mechanic tests.

2. Experimental

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) pellet samples were sintered and 3D microstructures were reconstructed using FIB-SEM tomography to calibrate input parameters for KMC sintering simulation and to validate the simulation.

2.1. Sample preparation

A commercial $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) powder (fuelcellmaterials Inc., USA) with a nominal diameter size D_{50} = 1.0 μm, ranging from 200 nm to 10 μm, was used as the starting powder. LSCF powder of 0.1 g was sampled and compressed for 30 s in a closed die (Φ = 5 mm) using a hand press (Newton press, Sansho Industry Co., Ltd., Japan) at a loading of 2 kN. Green pellet samples were formed with a green density (volume fraction of LSCF) of 0.602 ± 0.005. Pellet samples were heated up at 100 °C min^{-1} in an image furnace (SVF-QP2-6, Motoyama Co., Ltd, Japan) and sintered for 10 min and 60 min at 1000 °C. Several repeats for each condition were conducted by examining the shrinkage to secure that the sintering behavior of these samples was reproducible.

2.2. FIB-SEM reconstruction

A green sample (sample S0), a sample partially sintered at 1000 °C for 10 min (sample S1) and a sample sintered at 1000 °C for 60 min (sample S2) were impregnated with epoxy resin under vacuum, which allows LSCF and pore phases to be easily distinguished from images. Cross-sections of pellet samples were prepared by sand paper grinding followed by a fine polishing using an argon-ion beam cross-section polisher (SM-09010, JEOL Ltd., Japan). Cross-sections were carbon coated before FIB-SEM sectioning and imaging (Fig. 1(a)). A dual-beam FIB-SEM system (JIB-4600F, Hitachi, Ltd., Japan) was used to acquire a cross-sectional image sequence (Fig. 1(b) and (c)) under a voltage of 5 keV at a lateral resolution of 25 nm and a slicing pitch of 25 nm.

The acquired images in sequences were aligned, de-shadowed, and filtered following the detailed image processing procedures [44]. Fig. 1(d), (e) and (f) show the 3D microstructures of the three samples reconstructed by FIB-SEM with 300 × 300 × 300 voxels. Thanks to the impregnation, samples S0 and S1 have very good LSCF/pore contrast, with the gray regions being the LSCF and the dark regions being the resin-filled pores. However, due to the fact that sample S2 (Fig. 1(f)) was sintered to a very dense state ($\rho = 0.930$) and that most pores were isolated and closed, the resin failed to penetrate the pores. We have observed the “back-effect” of the pores, so cautions need to be taken when binarizing the raw images. Some manual checks and corrections were made to encounter these artifacts. The threshold value was decided by letting the relative density based on images to be equal to the real density of sample S2 (ρ = 0.930). We also verified the threshold value of the image stacks for sample S0 ($\rho = 0.602$) and sample S1 ($\rho = 0.806$) against the real density.

2.3. Microstructural characteristics

Based on binary images, microstructural characteristics such as specific surface area, sizes of LSCF and pore phases, and tortuosity factors of LSCF and pores can be quantified. The volume-specific surface area is also known as the surface-area-to-volume ratio, defined as $S_{a:v} = S_a/V$ ($\mu m^2\ \mu m^{-3}$), where S_a is the total surface area of solid, and V is the total volume of both solid and pore phases. In the present study, the surface area S_a was calculated using a marching cube method [45]. This advanced algorithm allows the surface curvatures to be considered even the microstructures are based on voxels. Phase sizes of LSCF and pores were measured using the linear intercept method and averaged over the entire image stack. Tortuosity factors (τ) of LSCF and pore phases were calculated