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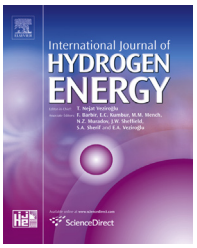

Effect of powder morphology on the microstructural characteristics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode: A Kinetic Monte Carlo investigation

Zilin Yan [a,*], *Shotaro Hara* [b], *Naoki Shikazono* [a]

[a] *Institute of Industrial Sciences, The University of Tokyo, 4-6-1, Komaba, Meguro-ku, Tokyo 153-8505, Japan*
[b] *Department of Mechanical Engineering, Faculty of Engineering, Chiba Institute of Technology, 2-17-1, Tsudanuma, Narashino, Chiba 275-0016, Japan*

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ABSTRACT

Microstructural parameters such as triple phase boundary (TPB) density, surface area density, connectivity and tortuosity of different phases strongly influence the performance of solid oxide fuel cells (SOFCs). In this study, the effect of the powder morphology on the microstructural parameters of a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) cathode is comprehensively examined using Kinetic Monte Carlo (KMC) simulations. A number of numerical samples consisting of spheres or clumped spheres are created using a Discrete Element Method (DEM), taking into account the powder morphology such as particle size, particle size distribution, particle aspect ratio and sphericity, and particle orientation. The DEM-generated numerical structures with different particle morphologies are submitted to the KMC simulations. Their effects on relative density, densification rate, surface area density, tortuosity factor of LSCF phase and tortuosity factor and connectivity of the pore phase are compared and analyzed.

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Introduction

Solid oxide fuel cells (SOFCs) are promising energy conversion systems for their excellent energy efficiency and fuel flexibility [1]. Microstructural parameters such as triple phase boundary (TPB) density, surface area density and tortuosity factors of different phases in electrodes strongly affect the performance of SOFCs [2–8]. The microstructures of electrodes need to be porous but highly percolated to provide sufficient electrochemical reaction sites and conduction of ion/electron/gas. On the other hand, the electrolyte requires very dense microstructures to prevent gaseous fuel permeation. These microstructures are supposed to possess good thermal stability under long-term operations. Therefore, the design and tailoring of the microstructures (especially the electrodes) in SOFCs is a key technology in the development of the SOFCs [9]. Sintering phenomenon plays an important role in microstructural change of the electrodes during the firing process [10–12] as well as under the operation condition [13–17]. For example, one of the reasons that cause the degradation of electrodes is the coarsening of electrode

* *Corresponding author.*
E-mail addresses: zilinyan@gmail.com, zilin@iis.u-tokyo.ac.jp (Z. Yan).
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materials at an elevated operation temperature, typically in the range of 750–900 °C for Nickel (Ni)-Yttria stabilized Zirconia (YSZ)|$Gd_{0.1}Ce_{0.9}O_{1.95}$ (GDC)|$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) SOFCs. These layered structures are usually made initially using tape-casting or screen-printing of slurry consisting of powder and organics, followed by drying and sintering or co-sintering processes [18–21]. It is well known that the final microstructures of a sintered body depends on the powder properties in green state and processing parameters such as sintering temperature and sintering time [22]. The initial configuration of particles in the green body involves many variables such as crystallite size, particle size, particle size distribution (PSD), particle shapes, and packing condition. Understanding the effects of these factors on the microstructural evolution is crucial for the electrode design of SOFCs.

In recent years, the correlations between microstructures and powder morphologies have been intensively explored both experimentally and numerically for SOFC materials. Zhang et al. [23] showed that YSZ powder with a small particle size and a narrow PSD can obtain dense YSZ electrolyte while YSZ powder with high aggregates resulted in very porous YSZ electrolyte. Song et al. [24] studied the effect of size of $La_{0.7}Sr_{0.3}MnO_3$ (LSM) powder on cathodic performance of nonporous LSM/YSZ composite cathode. They found smaller nano-sized LSM particles were more sinterable and undergo excess grain growth to inhibit TPB formation. Prasad et al. [25] revealed in dilatometric studies that the sintering behavior of GDC powder was a cumulative function of various powder morphologies and, in particular, strongly influenced by the agglomeration. Li et al. [26] found that the Nickel (Ni) – Samaria-doped ceria (SDC) anode electrical conductivity depended strongly on the NiO powder morphology and particle sizes. Fukui et al. [27] showed from the experiments that the morphology of the resultant Ni-YSZ cermet anode was strongly influenced by the particle size and the shape of the powder mixture of NiO and YSZ. Völker et al. [28] suggested that under certain conditions the performance of composite cathodes can be enhanced by using electronic conducting particles of size different from that of the ionic conducting particles when compared to the best possible configuration of monodisperse particles. Sato et al. [29] showed that nanostructured LSM/YSZ formed a large amount of TPBs, giving rise to high-performance of intermediate temperature (IT) – SOFCs. Pharoah et al. [30] found that with respect to close-packed structures, the TPB length, the effective solid phase conductivity and the electrode performance increased with increasing base particle aspect ratio, while the pore phase effective diffusivity decreased with the increase of the base particle aspect ratio. Murata et al. [31] showed in experiments that an LSCF cathode fabricated with finer powder provided better SOFC performance.

Alternatively, a number of numerical simulation models have been developed to investigate the relationship between SOFC performance and microstructures. The discrete element method (DEM) [32–36] is widely used to model the electrodes as 3-dimensional (3D) random packing structures composed of electronic and ionic particles. The effective conductivity is calculated by using a resistor network model [32], where the overpotential is obtained using Kirchhoff's current law. However, none of these references ever reported the impacts of powder morphology on the microstructural characteristics after sintering. Thus, simply assumption the electrode microstructures as overlapped spheres may be not sufficient for quantitative prediction. Wonisch et al. [37] showed in DEM simulations of sintering of alumina powder that the densification rate declined significantly as the width of the PSD increases. Martin et al. [38,39] demonstrated in DEM simulations that the microstructures can be affected by green packing density, packing conditions and agglomeration of powders. With recent advances in the DEM method, irregularly shaped particles can be represented using multisphere approach [40]. This opens up a possibility to consider realistic particles for the DEM modeling of sintering. However, when dealing with the last stage of sintering, the DEM sintering simulation will be fallacious as grain coarsening and contact impingement are hardly captured [39]. The Potts Kinetic Monte Carlo (KMC) method is recently emerging as a powerful tool at the mesoscale to simulate the microstructural evolution caused by sintering [41–43]. It has been proven to be a robust method to deal with all stages of sintering process. Particularly, the KMC method can handle arbitrarily shaped particles while it is so simple to code. Bjørk et al. [44] found that the densification rate and the final density obtained were inversely proportional to the distribution width using KMC simulations. Hara et al. [45] predicted the microstructural characteristics of sintered sub-micrometric Ni powder using KMC simulations, which were verified by focused ion beam-scanning electron microscopy (FIB-SEM) tomography characterizations of sintered real microstructures. Zhang et al. [46] utilized the KMC method to study the thermal stability of LSM/YSZ composite electrode composed of overlapped spheres. They showed that the evolutions of TPB length, porosity, and tortuosity factor of pores are faster for the samples with smaller particles than for the samples with larger particles. In addition, they found that high TPB density can be obtained by using small particles. Yan et al. [47] showed that with calibrated input parameters, the KMC model can predict the microstructural characteristics of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode during sintering in a real-time scale.

In this study, we combine the strengths of both DEM and KMC methods to study the influence of the powder morphology on the microstructure of LSCF cathode as a case study during sintering process. In addition, we will describe the workflow for a typical sintering simulation by combining the DEM and KMC models. In Section Results and Discussions, we will address the effect of the morphological factors on the microstructural parameters. And finally, we will summarize this research and point out some directions to future explorations.

Methodologies

Workflow in this study

In this study, we bridge from the DEM simulations for power packing to the KMC simulations for powder sintering. The workflow in this study is shown in Fig. 1. First, a serial of powder samples with random packings are generated using

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