Evaluation of electrochemical reaction mechanisms of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$-$Gd_{0.1}Ce_{0.9}O_{2-\delta}$ composite cathodes by 3D numerical simulation

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ABSTRACT

In the present study, electrochemical reaction mechanisms of $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC)-$Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) composite cathodes for solid oxide fuel cell (SOFC) were evaluated by a Lattice Boltzmann Method (LBM) with 3D reconstructed cathode microstructures. Two electrochemical reactions, i.e. one which scales with the LSC surface area and the other with the triple phase boundary (TPB) length, were considered in the simulation. The exchange current density of the surface reaction was fitted with an experimental result of pure LSC cathode, and the TPB reaction exchange current density was fitted using the experimental results of LSC-GDC composites with various volume ratios. It is found for the LSC-GDC composite cathodes that the contribution from the TPB reaction dominates and that the effective reaction thickness elongates as the volume fraction of GDC is increased. It is considered that the performance enhancement of LSC-GDC composite cathode is attributed to both the improvement in effective ionic conductivity and the additional contribution from the TPB reaction.

1. Introduction

Composites of mixed ionic electronic conductors (MIECs) such as $La_{0.6}Sr_{0.4}CoO_{3-\delta}$ (LSC) and ceria based ionic conductors such as $Gd_{0.1}Ce_{0.9}O_{2-\delta}$ (GDC) or $Sm_{0.1}Ce_{0.9}O_{2-\delta}$ (SDC) are promising cathode materials for intermediate-temperature solid oxide fuel cells (IT-SOFCs). Addition of ceria based materials helps to overcome the practical issues of applying pure LSC cathode, since it can alleviate thermal expansion mismatch with the electrolyte and inhibits microstructure agglomeration due to sintering [1–10]. Recently, it is reported that GDC or SDC addition contributes not only for improving mechanical properties but also for enhancing electrochemical performance [8,9]. It is considered that the improvement of effective ionic conductivity contributes to the performance enhancement. On the other hand, there's a possibility of additional contribution from the triple phase boundary (TPB) reaction. Concrete performance enhancement mechanisms of LSC-GDC or LSC-SDC composite cathodes are not fully understood.

Three dimensional (3D) microstructures from which precise information of fine and complex electrode microstructures can be obtained are extremely valuable to overcome the difficulties in investigating the electrochemical reaction mechanisms [11–16]. In order to reconstruct the SOFC electrode microstructures, focused ion beam-scanning electron microscopy (FIB-SEM) has been widely used [13–20]. Several numerical simulation works based on 3D reconstructed microstructures have been reported. Cararro et al. [11] conducted 3D finite

element calculation of mixed electronic ionic conductor. Matsuzaki et al. [15] also investigated the electrochemical performance of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathode using 3D reconstructed microstructure.

In our previous work, electrochemical performances of LSC-GDC with different volume ratios were experimentally evaluated and correlated to the cathode microstructural characteristics using FIB-SEM [10]. The best performance was achieved at a target volume ratio of LSC:GDC = 30:70%. Based on the microstructure parameter calculations, it was found that neither surface reaction nor TPB reaction individually could explain the performance of LSC-GDC composite cathode. It is therefore meaningful to investigate the concrete electrochemical reaction mechanisms of LSC-GDC composite cathodes in detail with the help of numerical simulations.

In the present study, electrochemical reaction mechanisms of LSC-GDC composite cathode with different volume ratios are investigated by a lattice Boltzmann method (LBM). Overpotentials are calculated and compared with the experimental results. Two electrochemical reactions, i.e. one which scales with LSC surface area and the other which scales with the triple phase boundary (TPB) length, are both considered in the numerical simulation. The exchange current densities of the two reactions are fitted to the measured overpotentials. Finally, contributions from surface and TPB reactions are quantified. In addition, effect of GDC addition to the enhancement of effective ionic conductivity is quantitatively investigated.

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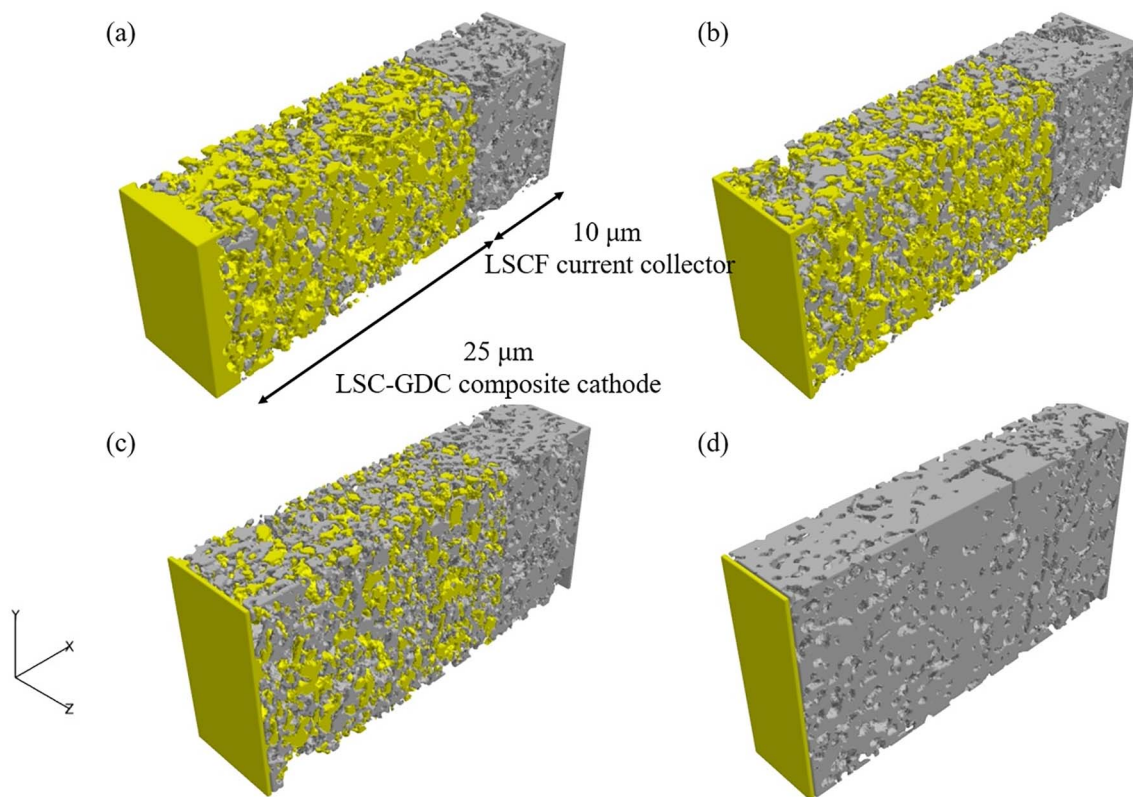 *E-mail address:* ytkim@iis.u-tokyo.ac.jp (Y.T. Kim).

Fig. 1. Computational domains of LSC-GDC composite cathodes. Volume ratios of LSC to GDC are (a) 30:70 vol%, (b) 50:50 vol%, (c) 70:30 vol%, and (d) 100:0 vol% (Yellow: GDC, gray: LSC). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Numerical simulation

2.1. Computational domain

In the present study, numerical simulations were conducted using the microstructures of LSC-GDC composite cathodes reconstructed by focused ion beam electronic scanning microscopy (FIB-SEM) [10]. The computational domains were elongated to 35 μm in the cathode thickness direction by mirroring the microstructures originally obtained by FIB-SEM. Then, the outer 10 μm thick region was just simply considered as pure LSCF current collection layer as the porosities of LSC-GDC composite and pure LSCF are close as reported in Refs [10,16]. Only for the case of pure LSC, the thickness of LSC was elongated to 25 μm, and then 10 μm LSCF microstructure which is taken from Ref. [16] was attached. This is because the porosity value of pure LSC in Ref. [10] is significantly lower than that of the pure LSCF described in Ref. [16]. Connectivity of LSC and LSCF at the interface is over 70%. Fig. 1 shows the computational domains of LSC-GDC composite cathodes. The LSCF layer contributes not only for current collection but also for electrochemical reaction. Therefore, surface reaction was also considered in the porous LSCF current collector, in which parameters shown in Table 1 are used [16].

A dense electrolyte and a dense electronic conductive layers with thicknesses of 5 μm were attached to both ends to give uniform ionic and electronic fluxes as boundary conditions for the simulation. For the

Table 1
Surface reaction parameters for the LSCF current collector $T = 973\,\mathrm{K}$, $p\mathrm{O}_2 = 1$ atm.

Properties	Values
Exchange current density (A/m^2)	4.088
Ionic conductivity (S/m)	0.474

electrolyte side, putting dense electrolyte make sense since there's physically a dense electrolyte in the real cell. But for the current collection side, this dense layer is just an artificial layer for the computation which gives uniform electronic flux outside the current collector. Computational grid was remeshed from FIB-SEM resolution (25 nm) to 100 nm due to the limitation of computational resource. The LSC:GDC = 20:80 vol% sample was excluded from the simulation runs because it did not converge, which might be attributed to the loss of LSC phase percolation. The unknown phases which appear at the boundaries of the domain but connect neither to the electrolyte nor to the dense electronic conductive layer are considered as non-conductive in the computation. Details of the phase segmentation can be found in Ref. [16].

2.2. Governing equations

In the present simulation, electrochemical potential of electron is assumed to be constant due to the high electronic conductivity of LSC [11,16]. In addition, oxygen pressure in the pore phase is fixed to $p\mathrm{O}_2 = 1$ atm and gas diffusion in the pore phase is neglected [15]. The governing equation of oxide ion electrochemical potential is written as follows:

$$\nabla \frac{\sigma_{\mathrm{O}^{2-}}}{2F} \nabla \widetilde{\mu}_{\mathrm{O}^{2-}} = -i_{\mathrm{reac}}, \tag{1}$$

where i_{reac} is the reaction current, $\widetilde{\mu}_{\mathrm{O}^{2-}}$ is the electrochemical potential of oxide ion, and $\sigma_{\mathrm{O}^{2-}}$ is the ionic conductivity. Ionic conductions in LSC and GDC phases were calculated using the ionic conductivity of each phase, and interfacial resistance between LSC and GDC was neglected.

Ionic conductivity of LSC was calculated from the chemical diffusion coefficient D_{chem} and oxygen nonstoichiometry δ, with $V_{\mathrm{mol}} = 35.17 \times 10^{-6}$ m3/mol [16, 22]. In the present study, two literature data for the LSC ionic conductivity [23,24] were considered, as shown