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A comprehensive micro-scale model for transport and reaction in intermediate temperature solid oxide fuel cells

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Abstract

A comprehensive model for detailed description of micro-scale transport and electro-chemical reaction in intermediate temperature SOFCs (solid oxide fuel cells) was developed by combining many relevant theoretical and experimental researches. Dependence of electro-chemical performance of PEN (positive electrode/electrolyte/negative electrode) on micro-structural parameters of electrodes was investigated through numerical simulation. Spatial distribution of transfer current density confirmed that TPBs (three phase boundaries) at electrode/electrolyte interface were most active for electro-chemical reaction and its contribution to overall reaction increased at higher current densities. Spatial gradient of total pressure in cathode was found to facilitate oxygen transport while that in anode hinder hydrogen transport. Among various micro-structural parameters for electrodes, particle diameter was found to be the most important one that governs the PEN performance; smaller particle diameter decreased activation overpotential with larger TPB length, while increasing mass transport resistance and concentration overpotential with smaller pore diameter. The proposed micro-model was found successful in micro-structural characterization of PEN performance, and thus believed to serve as a bridge connecting micro-scale models and macro-scale calculations.

Keywords: Fuel cell; SOFC (solid oxide fuel cell); PEN (positive electrode/electrolyte/negative electrode); Micro-scale model; TPB (three phase boundary)

1. Introduction

SOFC (solid oxide fuel cell) is an energy conversion device that directly converts chemical energy of gaseous fuel to electricity [1,2]. Electro-chemical reaction in SOFC is completed in PEN (positive electrode/electrolyte/negative electrode); oxygen reduction reaction occurs in the cathode, detached oxygen ions migrate from cathode to anode through the electrolyte, and hydrogen oxidation reaction occurs in the anode. Typically, PENs are made of a solid electrolyte made of YSZ (yttria-stabilized zirconia), a cermet anode made of Ni/YSZ (nickel and YSZ), and a composite cathode made of LSM/YSZ (strontium-doped lanthanum manganite and YSZ).

The output potential of SOFC φ^{FC} may be expressed as

$$\varphi^{FC} = \varphi^{o} - \Delta\varphi^{PEN} - \Delta\varphi^{BP} - \Delta\varphi^{FF}, \quad (1)$$

where φ^{o} is the Nernst potential or OCP (open circuit potential)

$$\varphi^{o} = -\frac{\Delta g_f^{o}}{2F} + \frac{R_g T}{2F} \ln\left(\frac{p_{H_2,\infty}}{p_{H_2O,\infty}}\left(\frac{p_{O_2,\infty}}{100{,}000}\right)^{1/2}\right)$$

(pressures are in Pa) (2)

and $\Delta\varphi^{PEN}$, $\Delta\varphi^{BP}$ and $\Delta\varphi^{FF}$ denote the potential loss in PEN, the potential loss due to bipolar plates, and that due to flow field effects, respectively. Main part of $\Delta\varphi^{BP}$ is contact resistance and non-uniform current generation due to interconnect rib geometry. Variation of channel conditions along the flow direction comprises $\Delta\varphi^{FF}$ ($\Delta\varphi^{BP}$ and $\Delta\varphi^{FF}$ were not considered in this study). Note that the present model is not limited to planar geometries and can be implemented in radial coordinates to represent tubular SOFCs. The potential loss in PEN $\Delta\varphi^{PEN}$ can be decomposed as

$$\begin{aligned}\Delta\varphi^{PEN} &= \Delta\varphi_E + \Delta\varphi_A + \Delta\varphi_C \\ &= (\Delta\varphi_{ohm})_E + (\Delta\varphi_{ohm} + \Delta\varphi_{act} + \Delta\varphi_{conc})_A \\ &\quad + (\Delta\varphi_{ohm} + \Delta\varphi_{act} + \Delta\varphi_{conc})_C \end{aligned} \quad (3)$$

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Here $\Delta\varphi_{ohm}$ are ohmic losses due to ionic and electronic resistances of the electrolyte and electrodes, $\Delta\varphi_{act}$ are activation losses due to irreversibility of electro-chemical reaction at TPBs (three phase boundaries), and $\Delta\varphi_{conc}$ are concentration losses due to mass transport resistance in the electrodes. Because of complicated interaction between those losses, it is rather difficult to determine what fraction of anodic or cathodic loss is due to ohmic, activation or concentration polarizations.

High performance of SOFC largely relies on the optimal transport and the electro-chemical reaction in porous electrodes, which in turn requires the optimal design of micro-structures of porous electrodes. Detailed micro-scale models for transport and reaction in SOFC is indispensable to understand the phenomena, and to predict and enhance its electro-chemical performance.

Micro-structures of porous electrodes are generally modeled as random packing systems made of electronic particles for transport of electrons, ionic particles for transport of ions, and interstitial pores for transport of gas species, as shown in Fig. 1a. The porosity ε, the volume fraction of electronic phase ϕ_{el}, and the diameters d_{el}, d_{io} of the electronic and ionic particles affect the effective electronic and ionic conductivities (ohmic loss), the effective TPB length (activation loss), and the effective mass transport properties (concentration loss) through the percolation for the continuity of each electronic, ionic and gas phase. Listed below are the related previous researches, adopted in this study.

- Monte-Carlo resistor network simulations for SOFCs based on lattice or random packing of binary spherical particles [3–7];
- Studies on statistical properties of random packing of binary spherical particles [8–10];
- Continuum micro-scale models for SOFCs based on the statistical properties [11–16];
- Experimental observations on anodic activation overpotential for Ni/YSZ cermet anodes [17–23] and cathodic activation overpotential for LSM/YSZ composite cathodes [24–29];
- Dusty-gas model for parallel flow and diffusion through porous media [30–32].

In Monte-Carlo simulations by Sunde [3–5] and others [6,7], individual particle location and connection to other particles were stored and used to construct resistor networks, followed by calculation of electrical potential at each particle location. In spite of its advantages in predicting the percolation behaviors of binary particle systems, the use of resistor network models were limited to problems with small specimen size due to high computational costs, primarily to estimate macro-scale properties of porous electrodes.

In continuum micro-scale models [11–16], the effective properties of porous electrodes were estimated based on the statistical properties of random packing systems of binary spherical

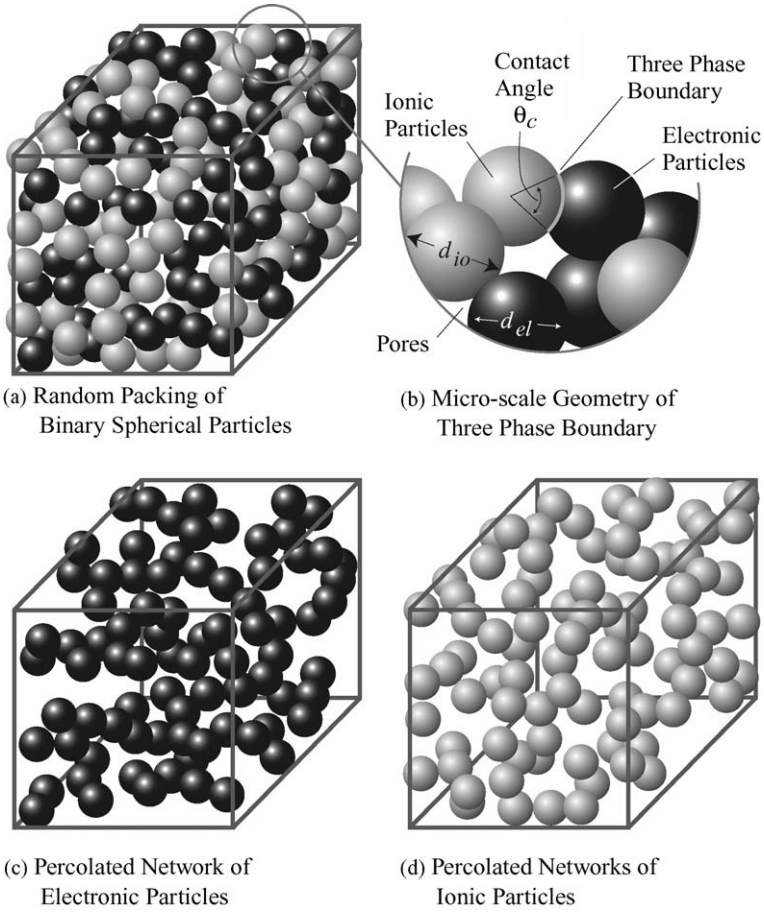

Fig. 1. Micro-structural modeling of a porous electrode as a random packing system of binary spherical particles.