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Electrochemical fields within 3D reconstructed microstructures of mixed ionic and electronic conducting devices

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HIGHLIGHTS

- A thermodynamics model conform to local equilibrium postulation is developed.
- It is generic to calculating electrochemical fields within 3D MIEC devices.
- The cell-level performance and the stability of MIEC devices can be calculated.
- The calculation method is efficient for big size 3D tomographic microstructures.

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ABSTRACT

The performance and stability of the mixed ionic and electronic conducting (MIEC) membrane devices, such as solid oxide cells (SOCs) and oxygen separation membranes (OSMs) interplay tightly with the transport properties and the three-dimensional (3D) microstructure of the membrane. However, development of the MIEC devices is hindered by the limited knowledge about the distribution of electrochemical fields within the 3D local microstructures, especially at surface and interface. In this work, a generic model conforming to local thermodynamic equilibrium is developed to calculate the electrochemical fields, such as electric potential and oxygen chemical potential, within the 3D microstructure of the MIEC membrane. Stability of the MIEC membrane is evaluated by the distribution of oxygen partial pressure. The cell-level performance such as polarization resistance and voltage vs. current curve can be further calculated. Case studies are performed to demonstrate the capability of the framework by using X-ray computed tomography reconstructed 3D microstructures of a SOC and an OSM. The calculation method demonstrates high computational efficiency for large size 3D tomographic microstructures, and permits parallel calculation. The framework can serve as a powerful tool for correlating the transport properties and the 3D microstructure to the performance and the stability of MIEC devices.

1. Introduction

Mixed ionic and electronic conductors (MIECs) have been widely used as the functional components of various electrochemical devices, such as solid oxide fuel cells (SOFCs) [1], solid oxide electrolyzer cells (SOECs) [2], and oxygen separation membranes (OSMs) [3]. The transport properties (e.g., ionic and electronic conductivities and surface exchange coefficients) and the

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three-dimensional (3D) microstructure of MIECs in these devices play critical roles in determining the performance and stability. The transport processes within the SOFCs, SOECs, and OSMs membranes are essentially: 1) the transport of oxygen ions within the MIEC bulk, 2) the transport of electrons within the MIEC bulk, 3) the surface exchange of oxygen molecules at the MIEC surface, 4) the charge transfer of oxygen ions and electrons across the MIEC interface, and 5) gas transport within the pores if any. Electrochemical fields such as oxygen chemical/electrochemical potential, electrostatic/electric potential, ionic and electronic current densities may vary significantly across micro/nano-scale features, such as surfaces and interfaces. This is particularly obvious for many MIEC materials whose conductivity is dominated by either oxygen ions or electrons, for example yttria-stabilized zirconia (YSZ), gadolinia-doped ceria (GDC), Sr-doped $LaMnO_3$ (LSM), etc. The electrochemical reaction for these MIECs is constrained to the three-phase boundary (TPB) where the surface meets with the interface. The reaction zone extends to the MIEC surface when the MIEC for example $(La,Sr)(Co,Fe)O_3$ (LSCF) has pronounced conductivities of both oxygen ions and electrons [4]. For the rational design of these MIEC membranes, it is essential to understand how the transport properties and 3D microstructures affect the performance. However, this is still challenging because the pronounced interplay between MIEC properties and 3D microstructures is complex. Many theoretical models have been developed to correlate MIEC properties and 3D microstructures to the performance of MIEC devices, for instance the electrode polarization resistance models based on porous electrode theory [5–7], and the multi-physics models based on averaged microstructures [8–10]. However the validity of these models is limited by MIEC properties and operation conditions. In addition, difficulties in eliminating the uncertainty of averaged microstructure factors raise critical concerns about the prediction accuracy. Thus, the microstructure - performance relationship is understood mostly in an empirical way. So far, it is not clear about the degree to which the performance of SOFCs, SOECs, or OSMs can be further enhanced by microstructure optimization. Compared with the continuum models based on immeasurable parameters (chemical potentials of electrons and oxygen ions, and electrostatic potential) [11,12], a model based on measurable parameters (chemical potential of O_2 and electric potential) is more useful from an experimental standpoint. Especially, the models solving numerically the simple governing equations for the transport processes with the complex 3D microstructures of the MIEC device could show a unique capability of studying the electrochemical field distributions within the 3D local microstructures (e.g. surface and interface) and correlating materials properties and 3D microstructures with performance in an unambiguous manner.

The 3D imaging of microstructures by X-ray computed tomography (XCT) and focused ion-beam (FIB) serial sectioning permits the calculation of the multi-physics with the reconstructed 3D structures [13], and thus the accurate microstructure - performance relationship. To this end, several attempts have been made on an electrode level. For instance the Ni-YSZ electrode, the multi-physics including the transport of ions within YSZ, transport of electrons within Ni, charge transfer at TPB, and gas diffusion within pores have been calculated by finite volume method (FVM) [14], and lattice Boltzmann method [15,16]. The MIEC air electrodes such as LSCF [17–20] and LSM [21] have also been studied by incorporating governing equations of ions transport and surface exchange into the 3D reconstruction microstructures. However, all the above-mentioned models consider only one charge carrier, while neglecting the others to calculate charge transport within each individual phase, especially within the electrolyte. The thermodynamic analysis by Virkar suggests that the transport of both electrons and oxygen ions should be considered, so that the formulation is consistent with the postulation of local thermodynamic equilibrium and the oxygen chemical potential within MIECs concerning the stability can be calculated correctly [22,23]. Combining with the transport of electrons and ions within each phase, a complete formulation can be achieved by choosing a proper description of the oxygen surface exchange on the surface of each phase. The transport of ions and electrons as well as surface exchange have been characterized by well-defined properties, such as ionic and electronic conductivities, and surface exchange coefficient. Although the transport properties for many MIECs have been reported by a huge volume of studies, such a complete formulation using electronic conductivity, ionic conductivity and surface exchange coefficient of each phase of the MIEC device has never been used. Idealizations beyond irreversible thermodynamics, such as purely ionic conduction of electrolyte, uniform Fermi level (electrochemical potential of electrons) within predominantly electronic conductors and equilibrium state of surface exchange are usually used to obtain mathematically accessible solutions. These idealizations however challenge the postulations of steady-state thermodynamics, such as the existence of local equilibrium and the thermodynamic equation of motion. Thus, it is misty how the materials properties correlate to performance and stability. Accordingly, the quantitative linkage between the materials properties, 3D microstructures and performance is urgently needed in this regard. Actually, such a complete formulation is universal to SOFCs, SOECs, and OSMs on a cell level.

In this study, we have developed a complete formulation based on linear non-equilibrium thermodynamics for the transport of ions and electrons, and surface exchange within the 3D microstructure of MIEC membrane. The calculation of the multi-physics within the 3D MIEC microstructure is accomplished by home-built Matlab codes. The computational framework is dedicated to calculating the distributions of experimentally measurable variables, including electric potential and chemical potential of oxygen within the 3D microstructure. Post-processing permits calculation of electronic/ionic current distributions, oxygen partial pressure distribution, overpotential distributions, voltage vs. current curve, oxygen permeation flux, and area specific resistance (ASR). The calculation is free from empirical/fitting parameters. All computational inputs are based on well-studied properties which can be measured by well-established experiments. In addition, the complexity of the 3D tomographic microstructure can be substantial. For example, the membrane can contain many sub-phases and multi-layers, e.g. (porous/composite) air/fuel, electrode/electrolyte half cells, (polycrystal/composite) electrolytes, and single cells. We have also developed an effective strategy to improve the computational efficiency. The algorithm can tackle ~40 million voxels on a 16 GB RAM personal computer, while the reported domain size in the literature is 0.025–9 million voxels, sometimes with the aid of a high performance computing cluster [14–21]. Demonstrative calculations on a cell level are conducted using the simulated microstructures of patterned LSM/YSZ/LSM symmetric cell, LSCF/YSZ/LSCF symmetric cell, the XCT reconstructed 3D microstructures of GDC-CFO ($CoFe_2O_4$) OSM, and GDC-Ni/GDC/GDC-SSC ($Sm_{0.5}Sr_{0.5}CoO_3$) SOFC/SOEC. Classic insight is consolidated and new insight is provided into the correlation between local electrochemical field distributions and cell-level performance and stability of the MIEC devices.

2. Irreversible thermodynamics formulation

Although the transport equations are not entirely new, their derivations are provided here in a unified and comprehensive manner. Beginning with the Onsager equations, the transport