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Connecting microstructural coarsening processes to electrochemical performance in solid oxide fuel cells: An integrated modeling approach

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HIGHLIGHTS

- Integrated model: a phase-field model and an electrochemical cell one are linked.
- Using the integrated model, we study the role of Ni coarsening on SOFC performance.
- Simple scaling laws describe the evolution of key microstructural features.
- Ni particle size strongly affects morphological evolution in Ni–YSZ SOFC anodes.
- Integrated approach facilitates identification of parameters associated with stable microstructures and/or optimal performance.

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ABSTRACT

In solid oxide fuel cells (SOFCs), Ni coarsening in porous anodes that are comprised of Ni and yttria stabilized zirconia (YSZ) leads to changes in several microstructural attributes, which affect the electrochemical performance. Herein we present an integrated modeling approach, where a dynamic mesoscale phase field model is linked with a stationary macroscale electrochemical cell level model in order to assess the role of Ni coarsening on the performance of SOFCs. The phase field model is capable of capturing the morphological evolution of Ni and accounting for its polycrystalline nature, while the electrochemical model encompasses the entire set of processes of gas transport, electronic and ionic conduction as well as the electrochemical reactions. Microstructural features are extracted from the phase field model as anode systems evolve over time and employed as effective properties in the electrochemical model. Simulation results highlight the importance of Ni and YSZ particle size and ratio on both the microstructural stability and electrochemical performance of SOFCs. In particular, it is shown that, for the classes of microstructures employed in this work, coarsening of Ni particles can either improve or diminish the maximum power density relative to the as-sintered ones, depending on the initial particle size.

1. Introduction

Solid oxide fuel cells (SOFCs) are regarded as alternative devices for cleaner and more efficient energy conversion [1–3]. With the advantages of high efficiency of 60%–80% [4,5] and reduced carbon emissions [6], SOFCs are being developed for various stationary and auxiliary commercial power applications with a desired lifetime of 40,000 h or more [7]. In conventional SOFCs, which operate at temperatures in the range 800–950 °C [8,9], a thin film of yttria-stabilized zirconia (YSZ) is utilized as the oxygen ion conducting

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ceramic membrane. A porous composite of lanthanum strontium manganate (LSM) and YSZ is typically used for the cathode and a state-of-the-art anode is a porous Ni–YSZ composite [10].

In SOFCs, oxygen is electrochemically reduced at the cathode, from which the oxygen ions subsequently diffuse through the electrolyte and react with the oxidized fuel at the anode. The anode in turn is a porous, complex three phase material, within which all phases (pore, conducting metal, and ceramic oxide) percolate. The contiguity of the pore phase ensures effective transport of the fuel to the catalytic sites, while contiguous metallic and ceramic oxide phases serve as conduits of the charges (electrons and oxygen ions) involved in the electrochemical reactions taking place in the vicinity of three-phase boundaries (TPBs), which constitute the electrochemically active regions [11]. The anode must maintain a stable microstructure over extended periods of time at elevated temperatures, as well as high electron and ion conductivity and catalytic activity.

Electrochemical performance degradation in SOFC cermet anodes is usually attributed to several phenomena and processes at the microstructural level, such as poisoning by fuel impurities, coking, thermal and redox cycling [11–16], as well as microstructural coarsening processes associated with Ni particles in Ni-based cermet anodes [9,17,18]. Coarsening is a competitive growth process, which leads to a reduction in the total interfacial energy. Spatial variations in the mean interface curvature induce diffusional fluxes, which transfer material from regions of high mean curvature to ones associated with lower mean curvature. In the case of isotropic interfacial energies, coarsening leads to a reduction in the total interfacial area [19,20].

Indeed, Ni coarsening in SOFC anodes has been the subject of several experimental investigations in recent years [11,21–24]. These studies have revealed that performance degradation can be directly linked to changes in several microstructural features associated with coarsening processes, such as extent of TPBs, total interfacial areas, and contiguity of anode phases. In particular, the density of TPB lines, which is often employed as a simple metric to predict electrochemical performance, is found to decrease due to Ni coarsening [23]. Simwonis et al. [21] studied Ni–YSZ composite anodes under operating environments and observed a decrease in the electrical conductivity due to Ni coarsening. Moreover, Ni phase coarsening is found to affect phase contiguity [25]. A recent study by Cronin et al. [26] revealed that Ni coarsening affects several microstructural attributes, such as pore percolation, and total pore and Ni-pore interfacial areas.

While the aforementioned experimental studies have provided important insights to the evolution of anode microstructures in operating environments, they do not examine the effects of interrelated physical phenomena on coarsening rates. Computational models on the other hand are ideally suited for exploring the various hypothesized mechanisms that control microstructural evolution processes in SOFC anodes. Existing computational studies of Ni coarsening in SOFC anodes include two-particle systems [27], phase field models [28,29], and multi-scale frameworks [30]. Our approach builds on and significantly extends these previous computational studies by incorporating the coupling between microstructural evolution and electrochemical performance while accounting for the polycrystalline nature of the Ni phase.

In this work, we focus, in a parametric study, on the role of anode microstructure, characterized by Ni particle size and Ni to YSZ particle size ratio, on the topological evolution of SOFC anodes and its impact on electrochemical performance. More specifically, we present an integrated modeling approach to examine the impact of Ni phase coarsening in Ni–YSZ porous anodes on the performance of SOFC cells. In this approach, several representative anode microstructures with tunable features (such as phase volume fractions and particle sizes) are first generated "virtually". Next, a mesoscale diffuse-interface model, which is capable of capturing Ni–YSZ interaction, and accounting for the polycrystalline nature of Ni, is employed to quantitatively investigate the coarsening of Ni phase particles in said microstructures. Then, morphological features are extracted from the phase field model as the anode systems evolve over time and employed as effective input parameters to a recently developed macroscale cell level model to quantitatively evaluate the time-dependent electrochemical performance [31]. Here, we note that while the electrochemical model itself is time-independent, its input parameters, which represent effective properties that depend on the anode microstructure, are evolving in time and tracked via the phase field model.

Starting from a binary mixture of numerically sintered Ni and YSZ particles, our simulation results conclusively demonstrate that the overall TPB length decreases monotonically during coarsening. Furthermore, the reduction in the overall TPB length obeys a simple scaling law in time. In addition, the contiguity of the Ni phase, which also monotonically decreases during coarsening, displays an interesting size effect, such that systems with initially small Ni particles lose contiguity faster. Finally, the overall electrochemical performance can display a non-monotonic time-dependence during coarsening, and even improve over time. For initially coarse microstructures, the electrochemical performance is dominated by the electrochemical reactions taking place in the vicinity of TPBs, the length of which decreases monotonically. For initially fine microstructures, on the other hand, electrochemical performance is dominated by gaseous transport processes through the pore phase, leading to an increase in the maximum power density over time as the average pore size increases due to coarsening.

More broadly speaking, simulation results highlight the importance of initial anode microstructure on the stability and performance of SOFC anodes. Our modeling approach can be used as a design tool to identify combinations of morphological parameters, such as Ni and YSZ particle size and ratio that yield porous anode systems with optimal microstructural stability and electrochemical performance characteristics.

The rest of the manuscript is organized as follows. In Section 2 we first outline both the continuum modeling framework and the cell level approach to evaluate the electrochemical performance based on microstructural parameters. Then, in Section 3 we describe how the initial microstructures are generated and characterized. Quantitative results from coarsening studies and their

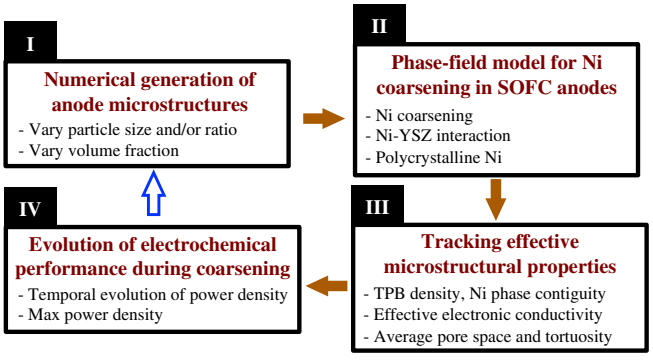

Fig. 1. A block diagram illustrating the integrated modeling approach that is used to examine the role of Ni coarsening in Ni–YSZ porous anodes on the electrochemical performance of SOFCs. The arrow outlined in blue represents the feedback from the electrochemical model to the input microstructures, which in turn closes the design iteration loop. This step is not implemented in the work presented here. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)