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Thermal aging stability of infiltrated solid oxide fuel cell electrode microstructures: A three-dimensional kinetic Monte Carlo simulation

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HIGHLIGHTS

- The KMC model is generic for the coarsening of infiltrated SOFC electrodes.
- The 3D microstructure and its evolution during thermal aging are simulated.
- Effects of materials properties and initial microstructure are studied.
- The evolutions of key geometric parameters are calculated.
- Strategies to enhance the thermal aging stability are suggested.

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ABSTRACT

Nanostructured electrodes are widely used for low temperature solid oxide fuel cells, due to their remarkably high activity. However, the industrial applications of the infiltrated electrodes are hindered by the durability issues, such as the microstructure stability against thermal aging. Few strategies are available to overcome this challenge due to the limited knowledge about the coarsening kinetics of the infiltrated electrodes and how the potentially important factors affect the stability. In this work, the generic thermal aging kinetics of the three-dimensional microstructures of the infiltrate electrodes is investigated by a kinetic Monte Carlo simulation model considering surface diffusion mechanism. Effects of temperature, infiltration loading, wettability, and electrode configuration are studied and the key geometric parameters are calculated such as the infiltrate particle size, the total and percolated quantities of three-phase boundary length and infiltrate surface area, and the tortuosity factor of infiltrate network. Through parametric study, several strategies to improve the thermal aging stability are proposed.

1. Introduction

Microstructures of solid oxide fuel cell (SOFC) electrodes play a significant if not dominant role in determining the electrochemical performance and the stability of SOFCs. Plenty of research validates the postulation that the cell performance scales with the volumetric densities of electrochemically hot spots, such as the heterogeneous surfaces and the three-phase boundaries (TPBs) where surfaces of gas phase, ionic phase and electronic phase meet with interface [1]. For the composite electrodes consisting of a predominately electronic conductor and a predominately ionic conductor, such as Ni -YSZ ($Zr_{0.84}Y_{0.16}O_{1.92}$) anode, Ni -LSGM ($La_{0.80}Sr_{0.20}Ga_{0.80}Mg_{0.2}O_{3-x}$) anode and LSM ($(La_{0.8}Sr_{0.2})_{0.98}MnO_{3-\delta}$) - YSZ cathode, the electrochemical reactions are constrained to the vicinity of TPBs [2–5]. For the electrodes containing mixed ionic and electronic conductors (MIECs), such as LSCF ($La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$) and BSCF ($Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$), the reaction sites extend to the MIEC surfaces [6]. Under specific conditions where resistance of transport of electrons and ions within the bulk of conducting networks becomes notable, the tortuosity factor of conducting network comes into

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play [7].

In the last decade, major interest in developing high-performance SOFCs has focused attention on advanced electrode microstructures with high densities of heterogeneous surface areas and TPB length and low tortuosity factors of conducting networks. Infiltration/impregnation is a well-established technology to prepare highly active SOFC electrode [2,8–10]. Compared to the composite electrodes consisting of randomly packed and micron-sized particles by mechanically mixing and co-sintering processes, the infiltrated electrodes are constructed by nano-sized catalyst particles anchoring onto the inner surface of porous electrolyte backbone or vice versa. Thus, the infiltrated electrodes have higher densities of surface areas and TPB length [11]. In addition, the tortuosity factors of the conducting networks of electrons and ions can be decreased pronouncedly by the optimization of backbone and infiltrate networks [12]. As a result, SOFCs with infiltrated electrodes have demonstrated significantly improved performance compared to conventional SOFCs with composite electrodes [8]. However, one major concern of the infiltrated electrodes is the stability during high temperature (500 °C – 800 °C) operations [13]. The nanostructures usually undergo coarsening and thus leading to the degradation in performance. For rational design of infiltrated electrodes with improved stability, it is essential to understand how the infiltrated microstructures change with thermal aging. However, only few studies are reported in the literature. Shah et al. developed an empirical equation for the coarsening of infiltrated nanoparticles with time and applied the model to the LSCF-infiltrated GDC ($Gd_{0.1}Ce_{0.9}O_{1.95}$) electrode [14]. Recently, a phase field model is developed to simulate the coarsening of a generic infiltrate within a LSM-YSZ composite backbone and effects of the initial particle size and loading of the infiltrate phase are studied [15]. However, many issues are still open questions, for example the effects of materials properties and the evolution kinetics of tortuosity factors of infiltrate network and percolation geometric properties such as active TPB length and active surface area of infiltrate.

In this paper, we report a systematic study on the thermal aging kinetics of infiltrated electrodes by a kinetic Monte Carlo (KMC) simulation. The three-dimensional (3D) microstructure evolution of the infiltrated electrodes is recorded during the simulation of thermal aging. The key geometric factors including infiltrate particle size, active TPB length, active surface of infiltrate, and tortuosity factor of infiltrate network are calculated as a function of KMC time. Effects of KMC temperature, infiltrate loading, wetting between infiltrate and backbone, and electrode configuration on these geometric factors are studied. Feasible strategies to improve the thermal aging stability of infiltrated electrodes are suggested based on the parametric study.

2. The kinetic Monte Carlo simulation model

The simulation begins with the generation of the initial 3D microstructure of the infiltrated electrode. Experimentally, the infiltrated electrode is fabricated by coating the nano-sized particles onto the surface of the sintered backbone via multiple repeats of infiltration–calcinations processes [2]. In this work, the initial 3D microstructure of the infiltrated electrode is generated by a numerical infiltration methodology. First, the backbone is generated by a random packing procedure of spherical submicron-sized particles within a 3D simulation domain with dimensions of 1 μm × 1 μm × 1 μm. The sintering of backbone is simulated by allowing contacting angles between particles. Second, the nano-sized particles of infiltrate are coated randomly onto the exposed surface of the backbone or the surface of the infiltrate particles. The aggregation of the infiltrate particles is simulated by tailoring the probability of the infiltrate particles coating onto the exposed surface of the backbone, given by,

$$P_{BBS} = wArea_{BBS}/[wArea_{BBS} + (1-w)Area_{IPS}] \quad (1)$$

where w is the aggregation factor, a constant between 0 and 1; $Area_{BBS}$ is the exposed surface area of the backbone; $Area_{IPS}$ is the surface area of infiltrate particles. The numerical infiltration is terminated when the expected infiltration loading is achieved. The simulation domain is discretized into a 3D digital image consisting of cubic voxels with a side length of 5 nm. The detail description of the methodology is presented in our previous study [11].

The microstructure evolution of the infiltrated SOFC electrodes is induced by many factors such as thermal aging effect [7,14,16–19], polarization effect [20] and other potential factors not yet known. Although these factors have not been understood quantitatively, the thermal aging effect is postulated as the dominant factor governing the kinetics of the microstructure evolution. Under typical operation temperatures of 500 °C – 800 °C, the nano-sized particles, especially of materials with low melting points (say lower than 2000 °C) exhibit high sinterability and thus may be coarsened by the various sintering mechanisms, such as grain-boundary diffusion, lattice diffusion, surface diffusion, viscous flow, and evaporation condensation. In our previous studies [21,22], the co-sintering kinetics of LSM-YSZ composite electrodes with randomly packed micron-sized particles are simulated by a KMC simulation model and an analytic sintering kinetics model. Therein, the simulations are conducted for the sintering temperatures of 1100 °C and 1200 °C, under which the micron-sized LSM particles with melting point of 1880 °C are postulated to be sinterable, and the sintering of YSZ particles with melting point of 2680 °C is too sluggish to be notable. It has been confirmed that the sinterability of particles can be increased significantly by decreasing the particle size. Validated by experimental results, these models provide a fundamental framework to extrapolate to infiltrated electrodes with nano-sized particles. The mechanisms of the co-sintering process are postulated to be the surface diffusion (responsible for coarsening), and the grain boundary diffusion (responsible for shrinkage). While for the thermal aging of the infiltrated electrodes at relatively low temperatures, the grain boundary diffusion could be neglected because the shrinkage of the electrode is not detectable. Thus, surface diffusion is considered as the only mechanism for the thermal aging of infiltrated electrodes.

The KMC simulation is then applied to the initial 3D microstructure of the infiltrated electrode. The surface diffusion is driven by the decrease in the system free energy, which is given by,

$$E = \frac{1}{2}\sum_i \sum_j J_{q_i,q_j} w_{i,j}\left[1 - \delta_{q_i,q_j}\right] \quad (2)$$

where i and j denote the index of voxels, which loop through all the voxels of the 3D microstructure; q_i denotes the phase index of the voxel i, which can be the backbone phase, or the infiltrate phase, or the pore phase; J_{q_i,q_j} denotes the interaction energy between two voxels with phase indexes of q_i and q_j; $w_{i,j}$ is a weighting parameter representing the effect of distance between voxels i and j on their interaction strength, which is 1 for the two voxels sharing one facet, and $1/\sqrt{2}$ for the two voxels sharing one edge, and 0 for the others; δ_{q_i,q_j} is the Kronecker delta function with $\delta_{q_i=q_j} = 1$ and $\delta_{q_i \neq q_j} = 0$. Thus, the system free energy actually consists of three parts of contributions, that is the surface of backbone, the surface of infiltrate, and the interface between backbone and infiltrate. The surface diffusion is conducted by migrating the voxels of the infiltrate phase and/or the backbone phase at the surfaces to the nearest vacant site. For each attempt of migration, a transition probability is