Microstructure evolution driven by thermal coarsening is an important factor for the loss of oxygen reduction reaction rates in SOFC cathode. In this work, the effect of an initial microstructure on the microstructure evolution in SOFC cathode is investigated using a recently developed phase field model. Specifically, we tune the phase fraction, the average grain size, the standard deviation of the grain size and the grain shape in the initial microstructure, and explore their effect on the evolution of the grain size, the density of triple phase boundary, the specific surface area and the effective conductivity in LSM-YSZ cathodes. It is found that the degradation rate of triple phase boundary density and specific surface area of LSM is lower with less LSM phase fraction (with constant porosity assumed) and greater average grain size, while the degradation rate of effective conductivity can also be tuned by adjusting the standard deviation of grain size distribution and grain aspect ratio. The implication of this study on the designing of an optimal initial microstructure of SOFC cathodes is discussed.

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Manuscript submitted April 25, 2017; revised manuscript received June 15, 2017. Published July 5, 2017. This paper is part of the JES Focus Issue on Oxygen Reduction and Evolution Reactions for High Temperature Energy Conversion and Conversion.
\( i \) is denoted by \( C_i = \eta_i' = 1 \), while the pore phase is denoted by \( C_i = \eta_i' = 0 \).

The total free energy functional of the system is chosen to be

\[
F \left( \{ C_i \}, \{ \eta_i' \} \right) = \int \left[ \sum_{i=1}^{M_c} \left( \frac{\kappa_i' M_c}{2} \nabla C_i \cdot \nabla C_i \right)^2 \right] dv
\]

\[ + \sum_{i=1}^{M_c} \sum_{j=1}^{M_c} \frac{\kappa_i' \kappa_j'}{2} \left( \nabla C_i \cdot \nabla C_j \right)^2 \right] dv \tag{1}
\]

where \( \kappa_i' \) and \( \kappa_j' \) are the gradient energy coefficients which need to be determined for a specific material system, and \( f_i(\{ C_i \}, \{ \eta'_i \}) \) is the bulk free energy density which is constructed to be

\[
f_0 \left( \{ C_i \}, \{ \eta'_i \} \right) = \sum_{i=1}^{M_c} \rho_i f_1(C_i) + \sum_{i=1}^{M_c} \rho_{12} f_1(C_i + C_2)
\]

\[ + \sum_{i=1}^{M_c} \chi_i \left[ f_2(C_i) + \sum_{j=1}^{M_c} f_3(C_i, \eta_j') \right]
\]

\[ + \sum_{i=1}^{M_c} \sum_{j=1}^{M_c} \sum_{k=1}^{M_c} \kappa_{ij} f_4(\eta_i' , \eta_j' , \eta_k') \tag{2}
\]

where

\[
f_1(C) = C^2 (1 - C)^2
\]

\[ f_2(C) = \frac{1}{4} C^4
\]

\[ f_3(C, \eta_i) = -\frac{1}{2} C^2 \left( 2 \eta_i^3 - 3 \eta_i^2 + \frac{1}{2} \eta_i \right)
\]

\[ f_4(\eta_i', \eta_j') = \frac{1}{2} (\eta_i')^3 (\eta_j')^2
\]

These polynomials in Eq. 3 are chosen so that \( f_0(\{ C_i \}, \{ \eta'_i \}) \) has local minima at \( C_i = \eta_i' = 0 \) and \( C_i = \eta_i' = 1 \) whereas the energetic parameters \( \rho_i, \rho_{12}, \chi_i \) and \( \kappa_{ij} \) are to be determined for a specific material system as well. A detailed discussion on the free energy functional and the relevant parameters has been given in Ref. 17.

The spatial-time evolutions of the COPs and GOPs are governed by the Cahn-Hilliard equation and the time-dependent Ginzburg-Landau equation respectively, i.e.

\[
\frac{\partial C_i}{\partial t} = \nabla \cdot \left[ M_{Ci} \nabla \left( \frac{\partial f_0}{\partial C_i} - \sum_{j=1}^{M_c} \kappa_{ij} \nabla^2 C_j \right) \right], \quad i = 1, 2 \tag{4}
\]

\[
\frac{\partial \eta_i'}{\partial t} = -M_{\eta i} \left( \frac{\partial f_0}{\partial \eta'_i} - \kappa_i' \nabla^2 \eta_i' \right), \quad i = 1, 2, j = 1, 2, \cdots, M_c \tag{5}
\]

where \( M_{Ci} \) and \( M_{\eta i} \) are the mobilities of COPs and GOPs respectively. These equations conserve the total fraction of each phase while allow grains to change from one crystallographic orientation to the other. The information on the densification in cathode is limited in the literature. Densification has been reported during sintering at relatively high temperature.\textsuperscript{22} Densification near the YSZ-LSM interface has also been reported at the temperature greater than 850°C.\textsuperscript{13} However, there are experiments showing that the porosity in LSM-YSZ cathode doesn’t have much temperature dependence up to 1200°C.\textsuperscript{21} An experiment on a very large reconstruction volume also shows that the porosity in LSM-YSZ cathode doesn’t have much temperature dependence up to 1200°C.\textsuperscript{21} An experiment on a very large reconstruction volume also shows that the porosity in LSM-YSZ cathode doesn’t have much temperature dependence up to 1200°C.\textsuperscript{21} Therefore, for simplicity we assume that the overall porosity in cathode does not change with time. A large number of GOPs, hence coupled Eq. 5, are essential to simulate the microstructure evolution of a polycrystal system. Therefore, the sparse data structure proposed in Ref. 20 is used to overcome this difficulty. Eqs. 4 and 5 are solved on a cubic mesh with the spatial resolution of 0.1 μm in all x, y and z directions. The fourth order Runge-Kutta method with time step of 10 second is used in the integration in time domain.

The microstructure evolution in the phase field model is driven by the reduction of interfacial energy in the system. Therefore, it is important to match the energy and mobility of the interfaces in the phase field model to that of the LSM-YSZ material system. In this work, the interfacial energy is assumed to be isotropic for simplicity. To our knowledge, report on the orientation dependence of interfacial energy in LSM-YSZ cathode is scarce in the literature. Once it is known, anisotropic interfacial energy can be incorporated via changing the gradient energy coefficients \( \kappa_i' \) and \( \kappa_j' \) from scalars to tensors. We use the energetic parameter sets for LSM-YSZ cathode developed in Ref. 17 which provide fairly good descriptions of the interfacial energy in the cathode. The same constant mobility in Ref. 17, which is comparable to the diffusivity and grain boundary mobility of LSM at 1000°C, is used for all three phases in the first 500 steps to equilibrate the profile of COPs and GOPs in the interface region. The diffusivity of cations in YSZ is 9 orders of magnitude lower than that in LSM.\textsuperscript{26,27} Therefore, the mobility of YSZ phase is set to zero after the equilibrium steps. In addition, the diffusivity of La and Sr in YSZ is much smaller than that in LSM.\textsuperscript{28,29} YSZ and pores are expected to block the diffusion path of cations in LSM. Despite that the exact diffusivity of LSM in YSZ and pore is unknown, our previous simulations in Ref. 17 show that setting the mobilities of Ni in YSZ and pore phases one and two orders of magnitude lower than that in Ni phase leads to prediction of TPB degradation rate in anode in good agreement with experiments. The same mobility setting is assumed in this work.

The initial microstructure used in this work is generated by DREAM.3D,\textsuperscript{30} in which the GSD is assumed to be log-normal. The model size is chosen to be 12.8 × 12.8 × 12.8 μm³, which is sufficiently large to reduce the error in effective conductivity by random sampling, to be less than ~5%.\textsuperscript{17} With such model size, the typical number of grains in each solid phase is more than 800 at the beginning and more than 300 at the end of simulations. To investigate the effect of the four attributes of the initial microstructure, i.e. the phase fraction, the average grain size, the standard deviation of GSD and the grain shape, we start from a baseline electrode with 35% YSZ, 35% LSM and 30% pore, in which the grain of all phases are assumed to be equiaxed with the average grain size of 0.53 μm and the standard deviation of GSD of 0.13 μm. Then we deviate each of the four attributes from the baseline electrode one by one and check their effect on the rate of grain coarsening and property degradation in the SOFC cathode. The effective conductivity \( \sigma_{eff} \) is defined as the ratio between the output current \( I \) and an applied voltage \( U \) on two opposing sides of the electrode in the corresponding direction, which is in turn normalized by the ratio between the cross-section area \( A \) and length \( L \) of the electrode, i.e.

\[
\sigma_{eff} = \frac{L}{U} \frac{A}{1} \tag{6}
\]

The output current is calculated by solving the Poisson’s equation on the cathode microstructure using the bound charge successive approximation algorithm.\textsuperscript{17,21} Five microstructures are used for each combination of the four attributes to quantify the uncertainty of the simulated grain coarsening and property degradation.

**Results**

**Microstructure evolution in the baseline cathode.**—The microstructure of one of the five baseline cathodes before and after the simulation is given in Figure 1, which shows increase in LSM grain...
size during coarsening. The static YSZ grains can also be observed. The average LSM grain size increases from 0.53 μm to 0.78 μm after 150 hours. This is followed by the reduction of the TPB density from 1.65 μm\(^{-2}\) to 1.42 μm\(^{-2}\), SSA of LSM from 0.74 μm\(^{-1}\) to 0.62 μm\(^{-1}\) and effective conductivity from 996 S to 947 S. The decrease in all ORR related properties due to coarsening is consistent with previous experiments and simulations, which demonstrates the necessity to reduce the coarsening rate in SOFC cathode.

**Effect of phase fraction.**—The effect of the phase fraction on the rate of coarsening and property degradation is investigated by changing the total phase fraction of YSZ (LSM) from 25% (45%) to 45% (25%) with step size of 5% while keeping the porosity to be 30%, so that the lowest phase fraction of YSZ (LSM) phase is slightly lower than the theoretical percolation threshold, i.e. ~30%. The time evolution of the average grain size of LSM and the normalized TPB density, SSA of LSM and effective conductivity are given in Figure 2. The first 500 equilibration steps are ignored so that the 0 hour corresponds to the 500th time step. The TPB density, SSA of LSM and effective conductivity are normalized by the corresponding property at 0 hour for the purpose of comparing the degradation rate in different cathodes. It is clear that both the growth rate of the average grain size of LSM and the degradation rate of TPB density and SSA of LSM in SOFC cathodes are greater when there is greater phase fraction of LSM. For the effective conductivity, despite that the degradation rate in the cathode with 30% LSM is slower than others at the early stage, its degradation rate after ~60 hours is still faster than the electrode with phase fraction of LSM greater than 30%. Therefore, it is anticipated that for long term behavior, the degradation rate of the effective conductivity would decrease with increased phase fraction of LSM. Starting from the same average LSM grain size at ~0.57 μm, the average LSM grain size reaches ~0.85 μm and ~0.67 μm after 100 hours in the cathode with 40% LSM and 25% LSM, respectively. This is consistent with the experiments on Ni-YSZ anode which shows that increasing the content of electrode phase leads to faster grain coarsening in the electrode.

![Figure 1](https://example.com/figure1.png) Figure 1. The microstructure of one of the five baseline cathodes at 0 hours and 150 hours. The red and green phases represent YSZ and LSM respectively.

![Figure 2](https://example.com/figure2.png) Figure 2. The time evolution of (a) LSM average grain size, (b) normalized TPB density, (c) normalized SSA of LSM and (d) normalized effective conductivity in the cathodes with five different initial fractions of LSM phase.
It notes that the effective conductivity increases in the first 15 hours in all the simulations then starts to decrease (Figure 2d). We find that this early stage is a result of the adjustment of GSD. As noted in the methodology section, the initial GSD is assumed to be log-normal. However, we find that the GSD in the later stage after 15 hours is no longer log-normal. During the first 15 hours, the standard deviation of the GSD rapidly increases from ∼20% to ∼30% of the average grain size, but remains at ∼30% after the first 15 hours. This indicates that the GSD is self-similar in the later stage, which is a typical feature of Ostwald ripening. Despite that there are two coarsening mechanisms, i.e., grain boundary motion and phase diffusion, in our simulations. Since the standard deviation increases in the early stage, it is anticipated that the relative amount of small grains increases in the cathode, which might lead to better connection between the LSM grains, hence the enhanced effective conductivity.

We quantify the rate of grain coarsening and property degradation by the relative changes in the average grain size and all three properties after 150 hours. These relative changes are plotted in Figure 3a as a function of the phase fraction of LSM. It again shows that the rate of grain coarsening and degradation of TPB density and SSA of LSM are all greater with more LSM phase. It clearly demonstrates that the slowly growing YSZ blocks the grain coarsening in the LSM phase, which reduces the degradation rate of the geometrical properties of the electrode as well. In contrast, the degradation of effective conductivity is slower with the increased fraction of LSM phase. Since the effective conductivity of the cathode comes from the percolated network of the LSM phase, it shows that the coarsening in SOFC cathode has limited effect on the percolation of the electrode phase when the phase fraction of the electrode phase is sufficiently greater than the percolation threshold, i.e., ∼30%.32

In addition to the effect on the rate of grain coarsening and property degradation, the phase fraction also affects the initial properties of the cathode. Figure 3b shows the initial TPB density, SSA of LSM and effective conductivity in the cathode with different LSM phase fraction normalized by the corresponding properties in the baseline cathode. It shows that the baseline cathode has the greatest initial TPB density, while the initial SSA of LSM and effective conductivity increases as the LSM phase fraction increases. Therefore, it is anticipated that the TPB density in the cathodes with LSM phase fraction greater than 35% will always be lower than the baseline electrode for that the degradation rate of TPB density is greater in these cathodes while they also have a lower initial TPB density. For the similar reason, the effective conductivity in the cathodes with higher LSM phase fraction will always be greater than the one with lower LSM phase fraction. On the contrary, the cathode with the greatest initial SSA of LSM may no longer have the greatest SSA of LSM after certain operation time, for that both the initial SSA of LSM and its degradation rate are greater in the cathode with greater LSM phase fraction. This implies that the interplay between the electrode initial properties and their degradation rate needs to be considered in the designing of an optimal initial microstructure in SOFC cathode.

**Effect of average grain size.**—We investigate the effect of average grain size on the rate of grain coarsening and property degradation in SOFC cathode by tuning the average grain size of LSM phase in the initial microstructure from ∼0.44 μm to ∼0.69 μm with step size of ∼0.06 μm, while the average grain size of YSZ phase is kept at ∼0.57 μm. The time evolution of the average grain size of LSM in cathode and the normalized TPB density, SSA of LSM and effective conductivity are given in Figure 4. Again, the first 500 steps are ignored and the properties are normalized by the corresponding property at 0 hours. The early increasing in effective conductivity due to GSD adjustment discussed in the last section can be seen here as well. Figure 4 shows that the grain coarsening and the degradation of all three properties are slower when the initial average grain size of LSM phase are greater. The TPB density degradation after 100 hours reduces from 15% to 10% when the initial grain size of LSM increases from ∼0.44 μm to ∼0.70 μm. Previous phase field simulations show that the TPB density degradation in anode after 100 hours reduces from 69% to 42% when the Ni grain size increased from 0.25 μm to 0.5 μm.16 Though a much slower degradation rate is obtained in this work due to the difference in interfacial energy and mobility, both simulations show that the average radius of electrode phase can affect the degradation rate of TPB in SOFC electrode.

The relative changes in the average grain size, TPB density, SSA of electrode phase and effective conductivity after 150 hours are given in Figure 5a as a function of the initial average grain size of LSM phase. Again, it shows that the evolution rate of all four properties is slower when the initial average grain size of LSM phase is greater. The relative change in SSA of LSM after 150 hours reduced from −20% to −13% as the initial grain radius increases from ∼0.44 μm to ∼0.69 μm. The degradation of effective conductivity in the cathode with initial grain radius of ∼0.69 μm is so slow that the effective conductivity even increases a little bit after 150 hours. It is clear that the smaller interface curvature in the cathode with greater grain size of LSM phase leads to lower driving force hence slows down the evolution of the microstructure.

The initial average grain size of LSM phase affects the initial electrode properties as well as their degradation rate. Figure 5b shows that the initial TPB density, SSA of LSM and effective conductivity all decreases with the increased LSM grain size. The differences in the initial properties are so great in this case that the cathode with smaller initial grain size of LSM always have greater properties up to 150 hours, in spite that the degradation rates of all properties are
greater. The property differences indeed decrease after 150 hours, e.g., the TPB density in the cathode with initial LSM grain size of \( \sim 0.44 \) \( \mu \)m is 10\% and 6\% greater than that in the baseline electrode at 0 and 150 hours respectively. But the difference in the degradation rate is not enough to change the order of the property up to 150 hours. More importantly, the difference in the degradation rate will decrease with time as the coarsening becomes slower and slower. Therefore, it is not clear whether the difference in the initial property will be reversed for longer time. This again demonstrates that the interplay between the initial electrode properties and their degradation rate needs to be considered to determine the optimal initial microstructure for SOFC cathode.

**Effect of the standard deviation of grain size distribution.**—We change the standard deviation of GSD of LSM phase from \( \sim 0.05 \) \( \mu \)m to \( \sim 0.22 \) \( \mu \)m with step size of \( \sim 0.04 \) \( \mu \)m to explore its effect on the

![Figure 4](image1.png)

Figure 4. The time evolution of (a) LSM average grain size, (b) normalized TPB density, (c) normalized SSA of LSM and (d) normalized effective conductivity in the cathodes with five different initial grain sizes of LSM phase.

![Figure 5](image2.png)

Figure 5. (a) The relative changes in the average grain size, TPB density, SSA of LSM and effective conductivity after 150 hours, and (b) the relative initial TPB density, SSA of LSM and effective conductivity with respect to the corresponding properties in the baseline electrode, as a function of initial average grain size of LSM phase.
rate of microstructure evolution in SOFC cathode. The average grain size of LSM phase is kept to be ~0.57 μm for all simulations. The corresponding difference in radius between the largest and the smallest grain ranges from 0.2 μm to 1.3 μm and the difference increases with increased standard deviation. The evolution of the average grain size of LSM phase and the normalized TPB density, SSA of LSM and effective conductivity are given in Figure 6. It shows that the rate of grain coarsening and degradation of effective conductivity has a strong dependence on the standard deviation, but the degradation rate of TPB density and SSA of LSM is much less sensitive to it. As shown in Figure 7a, the relative change in grain radius after 150 hours is 29% and 45% in the cathodes with the smallest and the
largest standard deviation respectively, while the loss of effective conductivity in these two cathodes is 0% and 7% respectively. Both show strong dependence on the standard deviation. On the contrary, the relative change in TPB density is −14% and −13% in the cathodes with the smallest and largest standard deviation, while the reduction in SSA of LSM in these two cathodes is 15% and 16% respectively. This basically means that the degradation rates of TPB density and SSA of LSM are independent of the initial standard deviation of GSD of LSM phase. Clearly, the larger difference in interface curvature caused by the greater standard deviation significantly speeds up the grain coarsening, but only slightly affects the degradation rate of TPB density and SSA of LSM.

With similar degradation rate of TPB density and SSA of LSM, the difference in the initial properties determines the performance of the cathode. In Figure 7b, it shows that the initial TPB density and SSA of LSM decrease with increased standard deviation of LSM GSD. This trend is the same for the entire simulation up to 150 hours, and is expected to remain after longer time. Therefore, tuning the standard deviation of LSM GSD can change the polarization resistance in the cathode without altering its degradation behavior. Moreover, our simulations show that the effective conductivity in the cathode with large standard deviation of LSM GSD is lower in the beginning and degrades faster. Thus, a narrower GSD of LSM is desired in the cathode for that the effective conductivity in it is expected to be greater than the cathode with broader GSD of LSM all the time.

**Effect of Grain Shape.**—The effect of the grain shape on the rate of grain coarsening and property degradation in SOFC cathode is investigated by tuning the relative length of three principal axes A, B, and C of the grains in the initial microstructure. In this work, we adjust the length of A-axis to be 1/5, 1/3, 1, 3, and 5 in the grains of both YSZ and LSM phase while keep B- and C-axis to be 1. And the pores are assumed to be equiaxed. The A-axis of all grains are assumed to be aligned in the z-direction. As mentioned in the methodology section, current phase field model assumes isotropic interfacial energy. Therefore, any anisotropy in the initial grains is anticipated to be eliminated after a certain simulation time if the grains are mobile. However, since the YSZ phase is static in our simulations, the anisotropy in YSZ grain would be kept during the simulation and we expect the resulting texture in the YSZ phase to alter the coarsening behavior of LSM phase.

The time evolutions of the average grain size of LSM phase and the normalized TPB density, SSA of LSM and effective conductivity in z-direction in the cathode with different grain shapes are given in Figure 8. The grain shape affects the rate of grain coarsening and degradation of SSA of LSM and effective conductivity, but its effect on TPB density degradation is very limited. Starting from the same grain size, the average radius of LSM phase after 150 hours in the baseline electrode is $\sim 0.77 \, \mu \text{m}$, while all the other electrodes with non-equiaxed initial grains show a greater final average grain size, i.e. $\sim 0.80 \, \mu \text{m}$ to $\sim 0.84 \, \mu \text{m}$. Since the average grain radius is assumed to be the same regardless of the length of A-axis value, the overall interface area, hence the driving force of grain coarsening, would be greater in the cathodes with non-equiaxed initial grains than that in the baseline electrode. Therefore, it is understandable that the baseline electrode has the lowest coarsening rate. On the contrary, the relative change in TPB density after 150 hours is all around −14%. It is clear

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**Figure 8.** The time evolution of (a) LSM average grain size, (b) normalized TPB density, (c) normalized SSA of LSM and (d) normalized effective conductivity in the cathode with five different initial length of A-axis of grains in solid phases.
that the A-axis length of grains in electrodes does not have much influence on the degradation rate of TPB density. The relative changes in the average LSM radius, TPB density, SSA of LSM and effective conductivity after 150 hours are given in Figure 9 as a function of the length of A-axis. Since the z-direction is no longer symmetric to x- and y-direction, the relative changes in the effective conductivity in x-direction are plotted as well. It shows that both the rate of grain coarsening and SSA degradation increase with increased anisotropy in the initial grains, while the degradation rate of TPB density is almost a constant. The degradation rate of effective conductivity in the z- and x-direction has different dependence on the length of A-axis. The former in general increases with increased length of A-axis, while the latter decreases with increased length of A-axis. The large uncertainty in the effective conductivity in z-direction in Figure 8d suggests that the exception at A = 1/5 for the effective conductivity in z-direction might be related to the finite size effect of the simulation cell, for that the grain size is expected to be greater in x- and y-direction, which requires greater cell in the x-y plane to obtain accurate estimation of the effective conductivity in z-direction. The exception at A = 5 for the effective conductivity in x-direction might be caused by the same effect. The relation between the length of A-axis and the effective conductivity is clearly a result of how the grains are packed in the initial microstructure. Since the A-axis of all grains is aligned in z-direction, it is anticipated that the connectivity of LSM phase is better in z-direction than in x-direction when A/B > 1, and better in x-direction when A/B < 1. But the anisotropy in the LSM grain is losing during coarsening, which largely reduces the effective conductivity in z- and x-direction when A/B > 1 and A/B < 1 respectively.

Besides the degradation rate, the grain shape also affects the initial properties of SOFC cathode. Figure 9b shows that the baseline cathode has the lowest initial TPB density but the initial SSA of LSM is almost the same in all cathodes. It also shows that the initial effective conductivity in z-direction increases with increased length of A-axis, while the initial effective conductivity in x-direction decreases. It is noted that the effect of grain shape on the initial electrode property also depends on how the grains are packed in the microstructure. With the A-axis of all grains aligned in z-direction, we find that the increased anisotropy in grains not only increases the total area of the interfaces, but also increases the area ratio between YSZ-LSM interphase boundary and the surface of LSM/YSZ. The increased total area of the interfaces tends to increase both the TPB density and SSA of LSM, but the increased area ratio between the interphase boundary and the surface partly cancelled this effect, which makes SSA of LSM almost the same in all cathodes.

To further understand how the grain alignment affects the grain shape effect, we perform a set of simulations on the cathode with randomly aligned non-equiaxed grains. The time evolution of the average LSM grain size and TPB density in the cathode with randomly aligned grains is compared to that in the cathode with fully aligned and the baseline cathode.
shows that the grain coarsening in the cathode with randomly aligned grains is slower than that in the cathode with fully aligned grains, but it is still faster than that in the baseline cathode. In contrast, all three curves of TPB density evolution are almost parallel to each other, indicating similar degradation rates. The TPB density in the cathode with randomly aligned grains is greater than that in the cathode with fully aligned grains, but both of them are greater than that in the baseline cathode. Our simulations show that the dependence of the degradation rate and initial value of TPB density and SSA of LSM on the length of A-axis is qualitatively the same in the cathode with randomly aligned grains and fully aligned grains. In addition, we find that the degradation rate of the effective conductivity in both x- and z-direction increases with increased anisotropy in grain shape. These results show that the cathode with equiaxed grains is favored regardless of grain alignment in the sense of minimizing degradation rate.

**Discussion**

The ORR rate in SOFC cathode is closely related to the TPB density and SSA of LSM. Large TPB density and SSA of LSM provide sufficient reaction sites for ORR, hence reduce the polarization resistance in cathode. In addition, the effective conductivity not only determines the ohmic resistance of the cathode, but also, as shown in our previous study, reveals the connectivity of the LSM phase, which is also important to ORR rate in SOFC cathode. Thus, it is essential to maintain all these three properties in SOFC cathode during operations. The results present in current work provide some insights on how to slow down the degradation of cathode performance in SOFC by manipulating the initial microstructure.

The effect of the four attributes of initial microstructure on the rate of property degradation in SOFC cathode is summarized in Table I. It shows that the low degradation rate of TPB density can be expected by lowering the LSM phase fraction and increasing the average grain size, and the low degradation rate of SSA of LSM can be expected by the same adjustment of these two attributes plus keeping a low anisotropy in grain shape. The low degradation rate of effective conductivity, however, requires enhancing the LSM phase fraction. Therefore, the relative slow degradation rate of both polarization resistance and ohmic resistance in cathode is likely to be found in an initial microstructure with relatively high LSM phase fraction and small average grain size, or relatively low LSM phase fraction and large average grain size. In addition, the degradation rate of effective conductivity can be lowered by reducing the standard deviation of GSD without altering the degradation rate of TPB density and SSA of LSM. So the GSD in the initial microstructure should be kept as narrow as possible to prevent the increasing in ohmic resistance.

<table>
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<tr>
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<th>Degradation rate of TPB density</th>
<th>Degradation rate of SSA of LSM</th>
<th>Degradation rate of Effective conductivity</th>
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<td>LSM Phase fraction</td>
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<td>+</td>
<td>+</td>
</tr>
<tr>
<td>Average grain radius</td>
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<td>−</td>
<td>−</td>
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<tr>
<td>Standard deviation of GSD</td>
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<td>+</td>
</tr>
<tr>
<td>Length of A-axis ($A&gt;B=C$)*</td>
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<td>−</td>
<td>−</td>
</tr>
<tr>
<td>Length of A-axis ($A&lt;B=C$)*</td>
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<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

*With the A-axis of all grains align along z-axis.

**Table II.** The change in initial electrode properties when one of the four attributes, i.e., LSM phase fraction, average grain radius, standard deviation of GSD and length of A-axis of grains, of the initial microstructure increases. The +, − and × sign means increasing, decreasing and limited effect respectively. The ↔ sign in the LSM phase fraction row means that maximum occurs when

<table>
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<tr>
<th>Attributes</th>
<th>Initial TPB density</th>
<th>Initial SSA of LSM</th>
<th>Initial Effective conductivity</th>
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<td>+</td>
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<tr>
<td>Average grain radius</td>
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<td>−</td>
</tr>
<tr>
<td>Standard deviation of GSD</td>
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<tr>
<td>Length of A-axis ($A&gt;B=C$)*</td>
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<td>−</td>
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<tr>
<td>Length of A-axis ($A&lt;B=C$)*</td>
<td>+</td>
<td>+</td>
<td>+</td>
</tr>
</tbody>
</table>

*With the A-axis of all grains align along z-axis.

However, the degradation rate of electrode properties is not the only concern. The cathode properties at a given time are determined by both their initial value and degradation rate. If the degradation rate of a property is faster in the cathode with lower initial value, then the order in the initial property would remain to be the same after coarsening. For example, the effective conductivity in the cathode with the least LSM phase would always be the smallest. But if the degradation rate of a property is faster in the cathode with higher initial value, the order in the initial property may be changed after coarsening. We find that the TPB density in the cathode with 40% LSM ($\sim 1.61 \mu m^{-2}$) is greater than that in the cathode with 30% LSM ($\sim 1.59 \mu m^{-2}$) initially, but the TPB density in the cathode with 40% LSM ($\sim 1.49 \mu m^{-2}$) becomes less than that in the cathode with 30% LSM ($\sim 1.51 \mu m^{-2}$) after 17 hours of coarsening, and the difference becomes even greater with further coarsening ($\sim 1.35 \mu m^{-2}$ to $\sim 1.38 \mu m^{-2}$ at 150 hours) due to the faster degradation rate in the former.

The effect of the four attributes of initial microstructure on the initial properties of SOFC cathode is summarized in Table II. It shows that although the electrode with greater average grain radius has smaller degradation rate, the initial value of TPB density, SSA of LSM and effective conductivity in it are all smaller, and they tend to be smaller up to 150 hours as shown in our simulations. Thus, it is better to tune the LSM phase fraction with a relative small average grain size for that both the polarization resistance and ohmic resistance are likely to be smaller in the cathode. It also shows that the cathode with smaller standard deviation of GSD is likely to have faster ORR rate, for that all three initial properties in Table II would be greater, while keeping a similar degradation behavior. In addition, both the phase fraction and grain shape can be used to tune the relative amount of TPB and SSA of LSM, which could be helpful in adjusting the relative amount of electrode surface pathway and bulk pathway in SOFC electrode.

The simulations in this work show that it is possible to tune the performance degradation rate by delicately designing the initial microstructure in SOFC cathode. However, to what extend these results are applicable to real SOFC electrodes is still pending more refined study and experimental verification. For example, though the SSA of LSM in the cathode with initial LSM grain size of 0.63 $\mu m$ is greater than that in the cathode with initial LSM grain size of 0.69 $\mu m$ up to 150 hours, a longer simulation up to 580 hours shows that the SSA of LSM in the former becomes less than that in the latter after around 400 hours. Longer simulations would be required to understand the coarsening effect over even more longer terms. Another example is that only individual effect of these four attributes in the initial microstructure has been investigated, whether there are cross effects between them is unknown either. Further simulations with longer simulation time and more complete set of initial microstructures are needed.
Conclusions

In this work, we investigated the effect of four attributes, namely, phase fraction, average grain radius, standard deviation of GSD and grain shape, of the initial microstructure on the rate of property degradation in SOFC cathode using a newly developed phase field model. The degradation rate of ORR related properties, i.e. the TPB density, SSA of LSM and effective conductivity, have been simulated. It is found that the degradation rate of both TPB density and SSA of LSM are affected by the LSM phase fraction (with constant porosity assumed) and average grain size in the microstructure, while the grain shape affects the degradation rate of SSA of LSM but not TPB density. The degradation rate of effective conductivity can be altered by tuning all four attributes, but it has an opposite dependence on LSM phase fraction as compared to that of TPB density and SSA of LSM.

Our simulations also show that the initial properties of SOFC cathode are also affected by these four attributes of the initial microstructure. The TPB density, SSA of LSM and effective conductivity are greater in the electrodes with smaller average grain size and standard deviation of GSD, and the grain shape can be used to tune the relative amount of TPB density and SSA of LSM. These results suggest that, in terms of the initial microstructure to minimize the degradation of cathode performance (the polarization and ohmic resistances), an initial microstructure with relatively low LSM phase fraction, small average grain size and narrow GSD of LSM is favored. It also suggests that grain shape can be used to tune the relative amount of electrode surface pathway and bulk pathway in SOFC cathode.

Acknowledgments

The authors are grateful to Professor Xingbo Liu (West Virginia University), Drs. Kirk Gerdes, Gregory Hackett, Harry Abernathy, Thomas Kalapos, William Epping and Jason Vielma (NETL) for valuable discussions. This project is supported in part by an appointment to the Internship/Research Participation Program at the National Energy Technology Laboratory, U. S. Department of Energy, administered by the Oak Ridge Institute for Science and Education. This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, make any warranty, express or implied, or assumes any legal liability of responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

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