Infiltrated solid oxide fuel cell (SOFC) electrodes offer numerous advantages over conventional co-sintered electrodes. First, a broader choice of electrode materials is possible because materials that melt or chemically react with the electrolyte at conventional sintering temperatures can be considered. Second, a higher three-phase boundary (TPB) density can be achieved, which is attributed to the smaller particle sizes. These two advantages result from a lower processing temperature of the infiltrated phase compared to conventional sintering temperatures required of co-sintered electrodes.

Three additional advantages of infiltrated electrodes are associated with the unique morphology created by coating the surface of a presintered porous scaffolding with an infiltrated phase. The first morphological advantage is a mitigation of the coefficient of thermal expansion (CTE) mismatch between the electrolyte and the electrode. The second advantage is a stabilization of the electrode mechanical properties during redox cycling. Finally, less material is needed to form an interconnected network of the infiltrated phase throughout the electrode.

Although the benefits of infiltrated electrodes have been clearly demonstrated experimentally, researchers suggest that the electrode designs are not optimized. This is understandable because it is laborious to consider all of the combinations and permutations of the sizes and shapes of infiltrate particles, scaffold particles, and pores as well as the wide range of possible porosities. In order to more effectively and efficiently design electrodes, several computational models have been recently reported. Zhang et al. utilized a particle-layer model to estimate the TPB density, effective thickness of the electrochemically active region, and polarization resistance of cathodes. A more recent report by Zhang et al. utilized a numerically simulated to create our three-dimensional electrode geometry. The fabrication steps included (1) creating a mixture of scaffold particles, pore former, and binder, (2) removal of the binder and pore former during heating followed by sintering of the scaffold particles, and (3) repeated infiltration of electronically conductive particles. The results were reported in dimensionless form to allow one to consider any set of input parameters. Our results showed that scaffold:infiltrate particle size ratio had the largest impact on effective conductivity; porosity had less impact and the pore:infiltrate particle size ratio had a negligible impact on effective conductivity. We also showed that the percolation threshold is directly linked to the initial specific surface area of the scaffold.

In this paper we report on an extension of our model capabilities that include prediction of total and active TPB density as well as active infiltrate-scaffold, active infiltrate-pore, and scaffold-pore interfacial areas as a function of scaffold/infiltrate particle diameter ratio, pore:infiltrate particle diameter ratio, porosity, and infiltrate loading. The results are all non-dimensionalized by the characteristic size of the infiltrate particle. We show that the range of optimal infiltrate loading that maximizes the active TPB density is broad at high scaffold sizes.
scaffold:infiltrate particle diameter ratios and approaches a singular value as the scaffold:infiltrate particle diameter ratio approaches 1:1. A key insight provided by our work is the relationship between the active TPB density and the interfacial areas among each of the phases (active infiltrate-scaffold, active infiltrate-pore, and scaffold-pore). In addition, we have linked our TPB density results with our previous effective conductivity results and present a key range of effective conductivities predicted over a range of maximized TPB densities. These new insights have important implications for rational design of infiltrated electrodes.

The remainder of this work is outlined as follows. First, the model foundations are reviewed from our previous work, and further explanation for TPB density and surface area calculations are provided. Next, results are presented with the impact of the model parameters on overall and active TPB density. Particular attention is given to the maximum TPB density as a function of the model input parameters and its relation to the interfacial areas of each phase. Finally, our results are compared to experiment and implications of the results with respect to the design of SOFCs are considered.

Model Foundations

As previously stated, this work uses an identical model development to that in our previous work; however, several additional calculations are performed to provide the framework for this work. This section of the paper first summarizes the computational cell development and then the resulting cell property calculations are presented.

Modeled infiltrated electrode fabrication.—The overall framework of mechanistic modeling used here is to computationally mimic the experimental fabrication process. The method is meant to include sufficient detail to provide valuable insight into the design of infiltrated SOFC electrodes, but not add more complexity than necessary to capture that insight. Thus, the model can be run relatively quickly (less than a day for a singular fabrication) to synergistically be run in concert with the designing experimentalist. Based upon the demonstrated accuracy of previous calculations regarding effective conductivity, no complexity was added to the model beyond the calculation of additional properties.

The model is set up as a hexagonal packed array with each node in the array taking on one of the three characters: the scaffold, the porous space or the electronically conductive infiltrate. The first step in the modeling process mimics the creation of a film that contains randomly positioned pore former and scaffold particles leaving the remainder of the nodes as empty binder. Identically to our previous work, the shape of the initial pore formers and scaffold particles are spherical. Next, the model mimics heating of the film that first removes the binder and the pore former particles leaving nodes of unoccupied porous space behind. Further heating of the film provides sintering of the remaining scaffold particles which is achieved in the model by treating each node independently and moving them toward the center of the cell, maintaining the overall geometry until the target porosity is reached. Thirdly, the model mirrors the infiltration of the electronically conductive particles by sequentially placing them adjacent to scaffold or previously placed infiltrate. This set of sequential steps then can be run for a variety of cell formulations as well as with many trials at each formulation to yield statistically significant results.

For each iteration of each formulation, a series of resulting cell properties including percolation threshold, effective conductivity, three phase boundary (TPB) density and surface areas are desired. The percolation threshold, the loading of infiltrate particles above which a cell of infinite size will always conduct, was a large focus of the previous work and is not considered further here. The calculation of each of the remaining three properties is outlined in the following three paragraphs.

In order to calculate the effective conductivity, the first step is to determine the electric potential, \( \phi \), at each point in the conducting network. Assuming charge-transfer can be neglected (i.e. the difference in local electric potential between the ion conducting phase and the electron conducting phase has a negligible impact on effective conductivity), the electric potential can be found by solving

\[
\nabla \cdot (\sigma \nabla \phi) = 0
\]

Where \( \sigma \) is the bulk conductivity of the conducting material. Since the conducting particles are each specified to have identical contacts with one another, the system is discretized at the level of determining the average electric potential at each conducting particle node. The system of equations is solved by applying a set of boundary conditions, which are independent of the results since only effective conductivities are desired. Given the calculated electric potential throughout the cell, the electron flux, \( J_e \), normal to the top or bottom of the cell can be calculated as

\[
J_e = \int_{\partial \Omega_{\text{top}}} \sigma^n \cdot \nabla \phi \, dA = \int_{\partial \Omega_{\text{bot}}} \sigma^n \cdot \nabla \phi \, dA
\]

Where \( \partial \Omega_{\text{top}} \) and \( \partial \Omega_{\text{bot}} \) represent the conductors covering the top and bottom of the cell respectively. Finally, the effective conductivity is calculated as a ratio of \( J_e \) for the cell of interest to the same value for a cell filled with conductor particles. Three phase boundaries occur at the intersection of porous void space, scaffold and infiltrated conductor particles. Thus, each of these boundaries is a one dimensional curve in three dimensional space. Our model provides for groups of scaffold nodes to fully occupy space with scaffold structure. Our model also allows for adjacent conductor particles and groups of conductor particles to similarly fill space. Thus, a monolayer of infiltrate would fully cover the scaffold surface. This allows us to treat each node as a cube for the purposes of the TPB density calculation, rather than function as a hexagonal array of scaffold and conductor with significant void between them. Thus, the specific wetting of an individual conductor particle on the scaffold surface is not considered. The inclusion of such detail similar to that of other work could be included with a packing or wetting factor which would allow for a slightly higher proportion of TPB density in each case; however, the trends presented would not change. In this work, we chose to leave the model to be as predictive as possible without adding any such potentially adjustable parameters. The actual calculation of total TPB density then just sums the total linear intersection of nodes that have each of scaffold, pore space and infiltrate adjacent to one another. For calculation of active TPB density, the same calculation is repeated except the infiltrate particles which are not in a connected network are neglected.

Similar to our previous work, here we consider surface areas to help provide understanding with regards to the trends seen in the resulting data. In this work, the surface areas are calculated using the same geometric structure as that in the TPB density; however, interfacial areas for each of the infiltrate-pore, infiltrate-scaffold, and scaffold-pore are determined. Again, the calculation is repeated for considering only infiltrate particles in the conducting network thus determining active infiltrate-pore and active infiltrate-scaffold surface areas. It is important to note that the surface area calculation described here is slightly different than that in our previous work. In our previous work, a specific surface area was calculated as the amount of surface area available for the initial deposition of infiltrate particles. In some cases, particularly for small scaffold sizes and low porosities, several scaffold particle surfaces could be covered by the deposition of one infiltrate particle. In such an instance, only one of the surfaces was counted in determining the initial surface area available for infiltrate deposition. That initial surface area available for infiltrate deposition, counting each node location with one of the adjacent surfaces, made the most sense in explaining the percolation threshold results. In this work, the entirety of the surface areas are included which allows for the insights relating surface areas of the respective phases to that of the three phase boundary density.

Results

For all of the results presented, infiltrate loadings are specified as a volume fraction of the entire sintered electrode. The reported
porosities correspond to the porosity of the sintered electrode prior to infiltration. The total TPB density values account for all infiltrate-scaffold-pore intersections. The active TPB density values only take into account infiltrate-scaffold-pore intersections where the infiltrate is part of an interconnected network of infiltrate that spans from the top to the bottom of the electrode. The number of trials used to determine the TPB density values, interfacial areas, and effective conductivities were chosen such that the standard deviation for each data point did not decrease with an increase in the number of trials. Furthermore, the cell size was chosen to be large enough such that at least 90% of trials conducted for infiltrate loadings above the percolation threshold and less than 10% of trials conducted below the percolation threshold.

The scaffold and pore sizes are specified as a scaffold:infiltrate particle diameter ratio and a pore:infiltrate particle diameter ratio, respectively. Both the scaffold:infiltrate and the pore:infiltrate ratios are pre-sintered diameter ratio specifications. The particle diameter ratios were varied from 1:1 to 21:1. Porosity values were varied between 35% and 85%. The initial cell formulation, prior to removal of binder in the initial scaffold-pore former-binder mixture, was 10% scaffold-12% pore former-78% binder by volume (note that the total space occupied by the pore former and binder reduces to the desired porosity upon sintering). This initial cell formulation closely matches the experimental formulation we typically use. The dimensionless input specification also leads to dimensionless results, which allows all of the results to be relevant for any infiltrate particle size of interest. Results for the TPB density are reported as “units·units⁻³”, where a “unit” corresponds to the characteristic length of the infiltrate particle. Thus, if a TPB density value is 0.7 units·units⁻³ and the characteristic length of your infiltrate particles is 40 nm, the TPB density value would be (0.7)·(40 nm)·(40 nm)⁻³ = 4.38 × 10⁻⁶ nm·nm⁻³ = 438 μm·μm⁻³. Likewise results for surface areas are reported as “units²·units⁻³”, where a “unit” corresponds to the same infiltrate particle characteristic length. Thus, if a surface area is 0.8 units²·units⁻³ and the characteristic length of your infiltrate particles is 40 nm, the surface area value would be 0.8·(40 nm)²·(40 nm)⁻³ = 2.0 × 10⁻² nm²·nm⁻³ = 20.0 μm²·μm⁻³.

The effect of scaffold:infiltrate particle diameter ratio on TPB density.—Figure 1 shows total TPB density, active TPB density, and fraction of TPB sites that are active as a function of infiltrate loading for various scaffold:infiltrate particle diameter ratios. The pore:infiltrate particle diameter ratio was held constant at 1:1 and the porosity was held constant at 65%. It is important to remember that the TPB density is reported as a non-dimensionalized length of TPB per volume of the electrode. Therefore, with Figure 1 you can obtain a TPB density value for any combination of infiltrate particle size and scaffold:infiltrate particle diameter ratio you choose.

As seen in Figure 1a, the scaffold:infiltrate particle diameter ratio has a significant impact on the overall TPB density. As the scaffold:infiltrate particle diameter ratio increases, the overall TPB density decreases. This is expected because there is less scaffold particle surface area available to form TPB sites as the scaffold particles become larger. Compared to Figure 1a, the shape of the active TPB density curves in Figure 1b are similar at high infiltrate loadings, but significantly different at low infiltrate loadings. Figures 1a and 1b are similar at high infiltrate loadings because all of the infiltrate particles are participating in an interconnected conductive network that spans the cell. At low loadings, however, many infiltrate particles are not participating in an interconnected network and zero infiltrate particles participate in an interconnected network below the percolation threshold. Figure 1c shows that the fraction of infiltrate particles participating in such an interconnected network is impacted significantly by the scaffold:infiltrate particle diameter ratio. Here the fraction of infiltrate particles participating in an interconnected network increases as the scaffold:infiltrate particle diameter ratio increases. This trend is expected because the fraction of particles participating in an interconnected network is directly related to the percolation threshold (and the percolation threshold is known to decrease with increasing scaffold:infiltrate particle diameter ratio).

Figure 1. (a) Total TPB density, (b) active TPB density, and (c) fraction of total TPB sites that are active, as a function of infiltrate loading for various scaffold:infiltrate particle diameter ratios. The porosity and the pore:infiltrate particle diameter ratio were held constant at 65% and 1:1, respectively.
For a scaffold:particle diameter ratio of 1:1, there is a singular optimal infiltrate loading that will result in a maximum active TPB density. The optimal infiltrate loading occurs at \( \sim 34 \) vol\%, Figure 1b. As the scaffold:particle diameter ratio increases, the window of optimal infiltrate loadings that will result in maximizing the active TPB density continuously broadens. At a scaffold:infiltrate particle diameter ratio of 7:1, the optimal infiltrate loading is in the range of 25 vol\% to 34 vol\%. For a ratio of 21:1, any infiltrate loading between 13 vol\% and 31 vol\% will result in active TPB density within 10\% of the maximum. Clearly the sensitivity of infiltrate loading on active TPB density dramatically changes with the relative particle size of scaffold and infiltrate. This is another important factor to consider in electrode design. If the scaffold is similar in size to the infiltrate, careful infiltrate loading selection is critical for optimization of TPB density. However, if the scaffold is much larger than the infiltrate, a wide range of infiltrate loadings will result in similar TPB densities, which may allow infiltrate loading selection to focus on an electrode property other than TPB density.

The effect of pore:infiltrate particle diameter ratio on TPB density.— The total TPB density, active TPB density, and fraction of TPB sites that are active as a function of infiltrate loading for various pore:infiltrate particle diameter ratios is shown in Figure 2. The scaffold:infiltrate particle diameter ratio was held constant at 1:1 and the porosity was held constant at 65\%. As the pore size increases, the TPB density decreases. Comparing the maximum active TPB density values in Figure 2b, the active TPB density drops by \( \sim 10\% \) when the pore:infiltrate particle diameter ratio increases from 1:1 to 21:1.

We have previously shown that larger pores result in a smaller initial scaffold surface area, and we know that less initial scaffold surface area results in a lower TPB density. Therefore, the effect of pore size on TPB density can be explained by considering the impact of pore size on the initial scaffold surface area.

As shown in our previous work, the percolation threshold was only slightly impacted by the pore size, falling within a range of 16 vol\% to 20 vol\% infiltrate loading over the entire range of pore sizes investigated. Since the percolation threshold has a direct impact on the fraction of TPB sites that are active, the fraction of total TPB sites that are active is nearly independent of pore size as shown in Figure 2c. Thus, the impact on the active TPB density across the range of loadings seen in Figure 2b is most strongly related to the overall TPB density at a given loading rather than the fraction of sites in the conductor network.

The effect of porosity on TPB density.— Figure 3 shows total TPB density, active TPB density, and fraction of TPB sites that are active as a function of infiltrate loading for various porosity values. The scaffold:infiltrate particle diameter ratio and the pore:infiltrate particle diameter ratio were both held constant at 1:1. The most important observation in Figure 3 is that an optimal porosity exists for maximizing TPB density. The TPB density increases as the porosity increases from 45\% to 65\%. A maximum TPB density is reached at a porosity of 65\%. Then, the TPB density decreases as the porosity is further increased from 65\% to 85\%. This optimal porosity is directly linked to the interfacial areas of the various phases within the electrode, which we describe in the next section.

Similar to Figure 2, the fraction of TPB sites that are active in Figure 3c are nearly independent of porosity. The explanation, again, is the narrow percolation threshold range. In this case, the percolation threshold range is narrow because the initial scaffold surface area available for the deposition of infiltrate particles is not significantly impacted by a change in porosity. We also considered the effect of porosity for a larger scaffold:infiltrate particle diameter ratio, Figure 4. In this case, the scaffold:infiltrate particle diameter ratio was held constant at 21:1 and the pore:infiltrate particle diameter ratio was held constant at 1:1. Note that an optimal porosity for maximizing TPB density is still observed; however, the optimal porosity is different from that with the 1:1 scaffold:infiltrate ratio. Also, varying the porosity has a smaller effect on TPB density when the scaffold particle size is much

![Figure 2](image-url)

Figure 2. (a) Total TPB density, (b) active TPB density, and (c) fraction of total TPB sites that are active, as a function of infiltrate loading for various pore:infiltrate particle diameter ratios. The porosity and the scaffold:infiltrate particle diameter ratio were held constant at 65\% and 1:1, respectively.
Figure 3. (a) Total TPB density, (b) active TPB density, and (c) fraction of total TPB sites that are active, as a function of infiltrate loading for various porosities. The scaffold:infiltrate and the pore:infiltrate particle diameter ratios were both held constant at 1:1.

Figure 4. Active TPB density as a function of infiltrate loading for various porosities. The scaffold:infiltrate particle diameter ratio was held constant at 21:1. The pore:infiltrate particle diameter ratio was held constant at 1:1.

Linking interfacial area and TPB density.— All of the trends observed in Figures 1–4 can be explained by considering the interfacial areas of the various phases in the electrode. For the purposes of this discussion, we will focus on active TPB density and the following interfacial areas: active infiltrate-pore, active infiltrate-scaffold, and scaffold-pore. In order to clearly demonstrate the link between active TPB density and interfacial area, we compared the active TPB densities and interfacial areas for three porosities: 45% (Figure 5a), 65% (Figure 5b), and 85% (Figure 5c). In this case, the scaffold:infiltrate and pore:infiltrate particle diameter ratios were both held constant at 1:1. This data thus corresponds to a subset of the active TPB density data considered in Figure 3.

For each plot in Figure 5, the interfacial area that corresponds to the maximum TPB density is identified. A key insight is that the maximum active TPB density is regulated by the infiltrate loading where the smallest of the three types of interfacial areas: active infiltrate-pore, active infiltrate-scaffold, and scaffold-pore is the largest. For example, for a porosity of 45% the maximum active TPB density occurs at an infiltrate loading of 28 vol%, see Figure 5b. For that same porosity of 45%, the minimum interfacial area, among the three types of interfacial areas, is also largest at the same infiltrate loading of 28 vol%. Similarly, for a porosity of 65%, the maximum active TPB density and largest minimum interfacial area both occur at an infiltrate loading of 34 vol%. Finally, for a porosity of 85% the maximum active TPB density and the largest minimum interfacial area both occur at an infiltrate loading of 43 vol%.

Interestingly, Figure 5 demonstrates that the type of interfacial area constricting the active TPB density changes with porosity. At 45% porosity, the active infiltrate-pore interfacial area is the limiting interfacial area. At 85% porosity, the scaffold-pore interfacial area constrains the active TPB density. At 65% porosity, all three types of interfacial areas are nearly equal. This also happens to be the optimal porosity for maximizing TPB density.

The link between active TPB density and interfacial areas also exists when varying other electrode parameters. In Figure 6, three interfacial area plots are shown. Figure 6a shows interfacial areas for the base case of a scaffold:infiltrate particle diameter ratio of 1:1, a pore:infiltrate particle diameter ratio of 1:1, and a porosity of 65%. In Figure 6b, only the scaffold particle size is increased compared to the base case. In Figure 6c, only the pore size is increased compared to the base case.

larger than the infiltrate. In both Figure 3 and Figure 4, while data is presented in porosity increments of 10% for clarity, the maximum was determined at increments of 5%.
Figure 5. Interfacial area per volume as a function of infiltrate loading for various porosities. (a) 45% porosity, (b) 65% porosity, and (c) 85% porosity. The scaffold:infiltrate and pore:infiltrate particle diameter ratios were both held constant at 1:1. The highest minimum interfacial area indicated in each plot corresponds to the infiltrate loading at which the maximum active TPB density occurs.

Figure 6. Interfacial area per volume as a function of infiltrate loading for scaffold:infiltrate particle diameter ratio, pore:infiltrate particle diameter ratio, and porosity of (a) 1:1, 1:1, 65%, (b) 21:1, 1:1, 65%, and (c) 1:1, 21:1, 65%. The highest minimum interfacial area indicated in each plot corresponds to the infiltrate loading at which the maximum active TPB density occurs.
In Figure 6a, the electrode system is optimally designed to maximize the active TPB density because all three interfacial areas are equal. Indeed, this combination of parameters leads to not only a maximum feasible surface area, but also the maximum feasible active TPB density. As shown in Figure 6b, when the scaffold particle size is much larger than the infiltrate, the scaffold-pore interfacial area is limiting the maximum active TPB density. In Figure 6c, we can see that changing the pore size slightly shifts the interfacial areas away from the optimum, and the active infiltrate-scaffold interfacial area is limiting the TPB density. As discussed in our previous work, as pore size becomes larger the scaffold particles are more likely to be in contact with other scaffold particles, which decreases the overall scaffold surface area. This effect is also evident in our current work by comparing the scaffold-pore interfacial area in Figures 6a and 6c for a given infiltrate loading, and explains the interfacial area shift we observe in Figure 6c.

Comparison of model to experimental results.— There are numerous reports that provide experimental data for effective conductivity of infiltrated SOFC electrodes, but we have only found one report that provides experimentally measured TPB density values. In the work by Zhan et al, Ni-infiltrated LSGM anodes were studied. The porosity of the LSGM scaffolding prior to infiltration of the Ni phase was 30%, the average feature size of the LSGM phase was 1.5 μm, and the Ni infiltrate loading was 2.5 vol%. The average initial characteristic size of the infiltrated Ni particles was estimated to be 30 nm. Due to agglomeration of the Ni infiltrated particles upon multiple infiltrations, the characteristic size of the Ni agglomerations was estimated to be 90 nm on average for the 2.5 vol% loading. The infiltrate size input for our model corresponds to the size of individual infiltrate particles deposited into the scaffold. Since infiltrate particles are allowed to deposit onto existing infiltrate particles, our model naturally accounts for agglomerations. In order to compare our model predictions to Zhan’s experimental data, we predicted the TPB density for an initial scaffold porosity of 30%, an infiltrate loading of 2.5 vol%, and a scaffold:infiltrate particle diameter ratio of 50:1. For this set of inputs, our model predicted a total TPB density of 48 μm·μm⁻³. Zhan experimentally measured a total TPB density of 37.1 μm·μm⁻³. These singular results are quantitatively similar; however, conclusive prediction is harder to demonstrate with only one data point of comparison. Nonetheless, the power of the modeling work is rooted in the design of cells, experimental conditions, and a fundamental understanding of the impact of the input parameters relative to the design. Thus, while such experimental data to validate the model, which is difficult and expensive to obtain, is understandably lacking, the impact of the conclusions of this work remain undiminished.

Linking active TPB density and effective conductivity.— In this work, we also linked our TPB density results to our previous effective conductivity work. Figure 7 shows effective conductivity as a function of infiltrate loading for various scaffold:infiltrate particle diameter ratios. The porosity was held constant at 65% and the pore:infiltrate particle diameter ratio was held constant at 1:1. The effective conductivity values indicated by the open symbols correspond to the infiltrate loading at which the maximum active TPB density occurs. Over the entire range of scaffold particle sizes considered, the effective conductivity that corresponded to the maximum active TPB density ranged from 0.03 to 0.06 (i.e. 3% to 6% of the bulk conductivity of the electronic conducting material used in the electrode). Our results are consistent with previous infiltrated electrode experimental work, which has reported the conductivity of infiltrated electrodes to be approximately 2% to 5% of the bulk conductivity.

Discussion

When thinking about scaffold-pore and active infiltrate-scaffold interfacial areas, you can see in Figures 5 and 6 that they are competing interfacial areas. In other words, they are directly inversely proportional to one another. This is because you start with a porous scaffold and then cover the scaffold surface with infiltrate. Initially, the scaffold-pore interfacial area is at a maximum because all of the scaffold surface is in contact with the pores. As infiltrate is deposited onto the surface of the scaffold, the scaffold-pore interfacial area decreases and the active infiltrate-scaffold interfacial area increases. As the scaffold surface approaches complete coverage by infiltrate, the active infiltrate-scaffold interfacial area approaches the initial surface area of the scaffold. For a scaffold:infiltrate 1:1 ratio, the scaffold-pore and active infiltrate-scaffold interfacial areas are optimized when half of the initial scaffold surface area is covered with infiltrate (i.e. the scaffold-pore and active infiltrate-scaffold interfacial areas are equal). For a scaffold:infiltrate 1:1 ratio, filling half of the porosity with infiltrate (a loading equal to approximately half of the porosity value) will result in equal scaffold-pore and active infiltrate-scaffold interfacial areas. For large scaffold:infiltrate ratios, the infiltrate loading that corresponds to the optimum active TPB density is lower (a loading that is equal to less than half of the porosity value). This is expected because the percolation threshold is significantly lower for larger scaffold:infiltrate ratios resulting in significant porosity after infiltration.

Many research efforts in SOFC electrode development have focused on making smaller and smaller infiltrate particles at the nanoscale. Continuing to decrease the infiltrate particle size can dramatically increase TPB density. For example, decreasing the infiltrate particle size from 100 nm to 25 nm will increase the TPB density by a factor of 16 (100 nm · 100 nm⁻³ = 1.00 × 10⁻⁴ mm · mm⁻³ = 100 μm · μm⁻³ and 25 nm · 25 nm⁻³ = 1.60 × 10⁻³ mm · mm⁻³ = 1600 μm · μm⁻³). With this approach, however, one must be careful of the inherent thermal stability issues associated with maintaining the size of the nanoparticles during operation. Infiltrate particle coarsening over time is a major concern, even at “intermediate” temperatures (i.e. 500°C–700°C). The work we present here makes a strong case that we should also be thinking about how to decrease the characteristic particle size, and increase the initial surface area, of the scaffold. Our results show that the active TPB density can be increased by an order of magnitude with this approach. As shown in Figure 3, decreasing the scaffold size from a scaffold:infiltrate size ratio of 2:1 to 7:1 will increase the active TPB density by a factor of 3. Further decreasing the scaffold size to a scaffold:infiltrate size ratio of 1:1 will increase the active TPB density by a factor of 10. Eventually, increasing the scaffold surface area will begin to approach similar thermal stability issues, but there is certainly room for significant improvement.

Figure 7. Effective conductivity as a function of infiltrate loading for various scaffold:infiltrate particle diameter ratios. The porosity and pore:infiltrate particle diameter ratio were held constant at 65% and 1:1, respectively. The effective conductivity values indicated by the open symbols correspond to the infiltrate loading at which the maximum active TPB density occurs.
It is interesting to note, as shown in Figure 7, that the effective conductivity corresponding to the maximum active TPB density falls within a narrow range (3% to 6% of the electronic conductor bulk conductivity) over a large range of scaffold:infiltrate particle size ratios. With our previous work on effective conductivity, we found that the practical upper limit of achievable effective conductivity is approximately 7% of the bulk conductivity. Considering the effective conductivity that corresponds to the maximum active TPB density is so close to the practical upper limit of effective conductivity, our model suggests that one should focus on maximizing TPB density when designing an electrode rather than electronic conductivity. The exception would be when the electronic conductor you are trying to use in the electrode has such poor conductivity that a very high infiltrate loading is critical to achieve acceptable electrode conductivity. It should be recognized for such a scenario that the active TPB density will be significantly hindered.

There are many parameters and factors one must consider when designing a robust and high performing electrode. Depending on the combination of materials used in the electrode, there may be one particular design consideration that becomes the most important. For materials with poor redox stability or materials with widely different CTEs, one will want to focus on minimizing mechanical instabilities. If the electronic conductor is a poor conductor, the designer will want to consider how to optimize the conductivity of the composite electrode. For electrochemical activity, we have shown in this work that the combination of scaffold size, infiltrate size, pore size, porosity, and infiltrate loading that one chooses can change the active TPB density by orders of magnitude. Our results serve as a useful and practical guide for optimizing electrode activity.

Conclusions

The effects of scaffold size, pore size, and porosity on TPB density as a function of infiltrate loading were investigated. Varying the scaffold size had the largest effect on TPB density, followed by porosity and then pore size. Increasing the scaffold size substantially decreased the TPB density and increasing the pore size resulted in a small decrease in TPB density. The range of optimal infiltrate loading that maximizes the active TPB density is broad at high scaffold:infiltrate particle diameter ratios and approaches a singular value as the scaffold:infiltrate particle diameter ratio approaches 1:1. There is clearly an optimal porosity for maximizing active TPB density, and that porosity value depends on the scaffold and pore sizes. All of the TPB density trends observed as each parameter was varied can be explained by the interfacial areas of the various phases within the electrode. A key insight is that the active TPB density is regulated by the lowest interfacial area value among the active infiltrate-scaffold, active infiltrate-pore, and scaffold-pore interfacial areas. The type of interfacial area limiting the TPB density changes, depending on the combination of input parameters chosen. Finally, designing an electrode for maximum active TPB density always resulted in an effective conductivity in the 0.03 to 0.06 range. The results presented here provide useful and practical insights into optimizing future designs of SOFC infiltrated electrodes.

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