Nondestructive Imaging and Analysis of Transport Processes in the Solid Oxide Fuel Cell Anode

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Three-dimensional reconstruction methods, such as the non-destructive transmission x-ray imaging with tomographic reconstruction, have enabled the micro- to nano-scale characterization of the porous solid oxide fuel cell electrode structures. This work provides an examination on the use of several methods being developed by the authors to quantitatively characterize and examine electrode structures in the SOFC. The porous Ni-YSZ cermet anode is used as a framework for this study. Specific attention is paid to the effect these types of structures may have on the functional electrochemical behavior that must be supported by the SOFC; including transport phenomena in the electrode structure in addition to accounts of the interfaces associated with the electrochemical and heterogeneous catalytic phenomena. Phenomenological structures are used to support these efforts. Further, a quantitative description of the characteristic lengths of the electrode structure is discussed in this work.

Background and Introduction

Numerous reviews within the SOFC literature, such as those by A. Atkinson et al., S. McIntosh et al., N. Brandon et al., and W. Z. Zhu and S. C. Deevi, on the performance, materials, and degradation of the solid oxide fuel cell detail the need for an improved understanding of the materials and structures that are used in the present SOFC (1-5). Advanced characterization tools and techniques, which are capable of providing scientific and engineering insights that are necessary to meet these challenges, are needed. Among the challenges facing the SOFC community, is the determination of materials and structures suitable for providing the necessary stability and durability while not compromising performance. This is especially true of attempts to stabilize the SOFC by lowering operational temperature and use alternative materials for the direct use of energy dense light hydrocarbon fuels and/or fuel reformates. The performance degradation observed in present SOFCs range from coking and poisoning of the electrocatalyst, redox instability, thermal and chemical materials instability, and microstructural aging/durability are among the most discussed and difficult issues to address (1-14).

Characterization methods that are capable of providing micro- to nano-scale accounts of the microstructure of the solid oxide fuel cell may serve in an enabling capacity for addressing these issues. Over the past few years, several methods have been reported within the literature that can provide these opportunities. The stereological imaging and
reconstruction using a dual beam focused ion beam mill in conjunction with a scanning electron microscope (FIB-SEM) has gathered considerable attention. This method has been used for a number of studies in the SOFC literature and has excellent capabilities in terms of resolution and elemental sensitivity (15-17). These groups have used the FIB-SEM based methods to provide advanced measurements and accounts of the three-phase-boundary (TPB) lengths, pore-tortuosity in the electrode structures, and the effects and importance of manufacturing and processing compositions and methods on these types of effects. A nondestructive alternative to the FIB-SEM is the direct x-ray imaging of segments of electrode structures using a transmission x-ray microscope. A series of incrementally rotated transmission images from a sample segment has been shown to provide detailed tomographic reconstruction of the imaged sample using computed tomography (CT) methods (18-20). Details on the characterization of porous SOFC anode samples at sub-50 nm spatial resolution through the use of x-ray computed tomography (XCT) have been previously reported (19).

Method of Approach

There have been several discussions on the experimental, reconstruction, and segmentation methods that have been used in this study in the open literature, and will note be repeated here. General x-ray imaging and computed tomography (18-20). The experimental methods used for the direct x-ray imaging and tomographic reconstruction that are driving this work have been previously reported (19). This work focuses on the characterization, analysis, and effects that these types of structures have on the processes that the SOFC must support, including those related to performance, degradation, and durability.

Monte Carlo Sphere-Packing Generation of Phenomenological Structures

The use of Monte Carlo, or sphere-packing, methods to artificially replicate heterogeneous electrode structures is an approach that has been explored by a number of groups. Works by the groups of S. Sunde, N. Brandon, and P. Costamagna are just a few examples within the SOFC community (21-24). These efforts have provided significant insights and contributions to the SOFC and broader scientific community; however, there is considerable uncertainty with regard to the ability of these methods to replicate real electrode structures despite claims otherwise. This uncertainty is a product of the non-linear processes that the real structures must support, permeations that are possible and limited methods available to uniquely validate these approaches. Assumptions that are required to condition the Monte Carlo routines are limited by our present understanding of the systems. Detailed reconstructions of real structures using XCT, FIB-SEM, and/or other stereological reconstruction and imaging methods can provide great insight into how to better replicate real structures using these types of artificial generation. S. Torquato’s review on the use of statistics and correlation functions to stochastically replicate the multifunctional structure and behavior of heterogeneous systems using correlation function is widely discussed in the literature (25).

Because of the difficulty in any attempt to generate and validate an artificial structure, we use a reverse approach here. The generated structures are considered phenomenological; they are used simply as a framework for the development and
demonstration of quantitative characterization and analysis tools and approaches. Once there is a comfort with the methods and the information that is obtained from them, they can be applied to the three-dimensional reconstructions of the electrode microstructures using XCT or FIB-SEM type imaging and reconstruction methods. The Monte Carlo sphere-packing routine that was used, considered the random placement of N_{YSZ} spherical YSZ particles and N_{Ni} spherical Ni particles of diameter, D_{YSZ} and D_{Ni}, respectively, in a cubic volume of L^3. To approximate XCT data, the cubic volume was broken down into cubic voxels of comparable dimensions. Voxels that are 50 nm/edge were considered in this study, with 100 voxels per edge for the total generated volume. The randomly generated YSZ particle placement within this volume occurred prior to the random Ni particle placement. Therefore, the Ni was permitted to overwrite the YSZ particles. To provide appropriate volumetric contributions of all three phases despite this overwrite process, nearly twice as many YSZ particles were initially placed. More sophisticated approaches are possible. Still, the heterogeneous structures generated using the described method is suitable for the purposes of this work. Details of the generated structure are provided in Table I. A three-dimensional segmentation rendering of a XCT reconstruction previously reported by the authors, the phenomenological sphere-packing structure generated, and the three-phase boundary (TPB) are rendered in Figure 1.

![Figure 1](image1.png)

Figure 1. The three-dimensional rendering of several structures considered in this study. These include, (a) a 6.3 µm x 6.3 µm x 6.3 µm (250 µm^3) cubic section of a porous Ni-YSZ cermet SOFC anode is shown where both the pore and dense regions of the anode are visible. This volume and XCT reconstruction methodology has previously been described in previous *Electrochemical Society* journals and meetings (19). Additionally, a (b) 5 µm x 5 µm x 5 µm (125 µm^3) phenomenological volume generated using a sphere-packing routine is shown. This volume is used to supplement the XCT measurements in this study for the development of quantitative characterization methods and routines. Finally, (c) a rendering the lines forming the three-phase boundary (i.e. union of the Ni, YSZ, and Pore regions) of the generated volume is shown.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Volume Fraction</th>
<th>Particle Diameter</th>
<th>Particles</th>
<th>Voxel Size</th>
<th>Voxels/Edge</th>
<th>Volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.34</td>
<td>1.0, µm</td>
<td>100</td>
<td>50^3 nm³</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.36</td>
<td>1.0, µm</td>
<td>200</td>
<td>50^3 nm³</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Pore</td>
<td>0.28</td>
<td>NA</td>
<td>NA</td>
<td>50^3 nm³</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>Volume</td>
<td>1.00</td>
<td>NA</td>
<td>NA</td>
<td>50^3 nm³</td>
<td>100</td>
<td>5^2 µm³</td>
</tr>
</tbody>
</table>

Representing Heterogeneous Structures with Homogeneous Properties

An important aspect of reporting volumetric properties of a heterogeneous structure is the recognition that a large enough volume needs to be considered if a true measure of the
sample can be considered. Depending on the property being measured, the nature of the heterogeneous structure, and the conditions that the sample has been exposed to (i.e. operational, environmental, physical, etc.), the properties of a localized region of a structure may differ greatly from those just a relatively small distance away. These types of effects can convolute the measurements and understanding of complex systems and it is important to be cognizant of them when characterizing these structures. Further, part of the ongoing efforts of these works are to identify and/or demonstrate if representing a heterogeneous structure with effective properties (i.e. as homogeneous) is sufficient.

To account for these effects, measurements are ideally made on several independent but neighboring regions of the sample. This can help ensure the accuracy and validity of the measurement. However, when a limited number of measurements are available, the individual measurements must be examined in greater detail. One approach is to consider the volumetric dependence of that measurement using subsequent but subsets of the same structure. By considering subsets of the same sample volume that is available, which incrementally increase in the size over the same region, the dependence of the property on the considered volume can be tracked. Metaphorically speaking, this approach is much like the Russian nesting dolls; only for the determination of structural properties. An asymptote on the measured properties (i.e. the derivative with respect to the volume size approach zero), the property may be considered as representative of the sample. This measurement does not guarantee that the property is representative of the entire sample. Additional and independent validation of (i.) the methods used, (ii.) reconstruction, and (iii.) additional regions of the sample are necessary to make sure a claim. To demonstrate the importance of these types of volumetric studies, several results from the generated structures will be shown for increasing sample volumes.

Phase-Contiguity/Percolation

One of the significant capabilities of the three-dimensional imaging and reconstruction methods that have been developed is a new found ability to examine the nature of the paths in these heterogeneous structures. Percolation theory has driven many of the discussed Monte Carlo and sphere-packing studies. The successes and usefulness of percolation theory, including those in the SOFC community, is certainly well documented. Evidence of this is the widespread use and discussion of percolation theory throughout the community; however, it can also be of limited in scope and breadth. It provides limited information regarding the underlying mechanisms and microstructural validation that are needed. Several examples of these types of effects that can be overlooked include: (i.) differences in transport coefficients for multifunctional materials, (ii.) parallel transport mechanisms such as homogeneous/surface/grain boundary, (iii.) mixed transport processes, (iv.) multiple phases/properties of a single material in the structure, and (v.) the effects of manufacturing/processing/environment on the structure (e.g. after sintering). An example of an SOFC application beyond what many would consider being the constraints of percolation theory has been demonstrated by several groups. P. Jasinski, H. U. Anderson and coworkers, among others, who have fabricated SOFC cermet anodes with very small Ni contents (i.e. 7.5-14% Ni by volume in a Ni-ceria cermet) that perform remarkably well and maintain impressive redox stability (26). This was achieved by the use of custom manufacturing method where the ceria oxide was used as rigid oxide skeleton to infiltrate the Ni, and thus providing high connectivity, surface area, and TPB regions.
To study the contiguity, or percent volumetric connectivity, previously demonstrated marching schemes are considered (19). By measuring the contiguity discretely, an improved understanding of the structures can be obtained. Effects from environment, operation, and manufacturing can be examined in more detail in future studies. In this study, contiguity measurements are made on the generated phenomenological structures. They are further extended to several other key measurements and estimates discussed and used. Namely, the two and three-phase interfaces. Volumetric dependence for making contiguity considerations is also reported.

**Phase-Tortuosity**

The tortuosity (i.e. the ratio of the effective to nominal transport paths) of the three phases of the generated structure is examined here. A method consistent with a previously reported method by A. S. Joshi et al. was used (27). To do so, the empirical diffusivity factor, $\Psi$, was equated to the ratio of the phase volume fraction to the tortuosity squared, $\Psi = \varepsilon / \tau^2$, where $\varepsilon$ is the volume fraction and $\tau$ is the tortuosity. The method was also extended to the Ni and YSZ phases in addition to the pore phase. This was done by making an analogy between the continuum forms of Laplace’s equation that are used for mass, electronic, and ionic transfer processes (i.e. Fick’s law and Ohm’s law respectively). The tortuosity of the Ni and YSZ phases in the SOFC electrode regions are typically not reported and/or considered; however, the concept is consistent. Additionally, the tortuosity should not be confused with the tortuosity factor which is the square of the tortuosity (28). Volumetric dependence studies were also considered with the examination of the phase tortuosities.

**Phase-Interfaces**

Both the two- and three-phase interfaces play a key role in the performance and stability of the SOFC electrode structures. The length of the three-phase boundary (TPB) is recognized as a measure of the electrocatalytic activity of the electrode structure. This is a result of the distinct function of each participating phase as a unique mass or charge carrier (i.e. Ni-electron, YSZ-ionic, pore-mass). The Ni-pore interface is often noted as a heterogeneous catalytic interface for light hydrocarbons and/or molecular hydrogen absorption/splitting during electro-oxidation. Conversely, the Ni-YSZ interfaces support the electronic/ionic double layer. Both the Ni and YSZ interfaces have been discussed as supporting spillover pathways (hydrogen and oxygen, respectively) from the TPB line for the oxidation kinetics (29). While approaches such as percolation theory can provide estimations of both the two and three-phase interfaces using geometric considerations, detailed experimental measurements are of considerable interest. Reconstruction of the sample structure using XCT or FIB-SEM can provide not-only the direct measurement of these interfaces, but also the effects of contiguity for the participating phases through the structure. When these measurements are combined, the true two and/or three-phase interface measurements can be determined. This provides a detailed account on the effective use of the available structure. The generated volumes are considered in the results of this study and the effects of the volume considered are also reported. All two and three-phase interface measurements are reported with respect to the volume considered so that they are provided in the form of a property.
Size Distributions

The volumetric distribution regions of a heterogeneous structure are of interest to understanding the electrode structure, design, and effects. This type of information can provide insights into aspects of the electrode, such as to the effects of structure on transport-related losses and the impact/result of different manufacturing and processing methods. Here, a ray-tracing type of analysis, which extends from the discretization of the generated structures, is used to examine the diameters in the system. The data is provided as a size distribution, normalized to the total volume fraction of each phase. A cumulative form of the distribution is also provided. A detailed development and validation of these methods extend beyond the scope of this manuscript and will be addressed in more detail at a later time. In effect, the distributions represent the total volume of a given phase that is described by a given diameter, within a finite differential region centered at that diameter. Qualitative validation can be provided by observation of a delta-peak at a diameter of 1 µm for the Ni and YSZ regions of the generated structure, representative of the particle sizes used. Additionally, grid dependence studies show a consistent distribution and cumulative form, demonstrating repeatability.

Results and Discussion

Select characterization results for the generated phenomenological structures are shown in Figures 2 and 3. Tabulated results for specific measurements are also provided in Tables II and III. In Figure 2, several grid dependence studies for the generated structure are considered. In Figure 2(a), a normalized representation of the absolute phase volume fraction and TPB lengths are shown. After some initial fluctuations, these measurements become representative of the structure when volumes larger than 3³ µm³ are considered. However, when the tortuosity is examined in Figure 2(b), the oscillations continue. This is particularly the case with the Ni regions that continues to increase with an increasing volume. This can be explained by Figure 2(c). To make tortuosity measurements that are based upon a Laplace’s equation type formulation, only the contiguous regions of the structure can be considered. Despite what appears to be a well behaved system in Figure 2(a), it is clearly evident in Figure 2(c) that there is a considerable region of the Ni phase that is disconnected from the rest. This effect is carried through in Figure 2(d), where the two and three-phase interfaces within the structure are reported. However, Figure 2(d) considers only those interfaces that have contiguous pathways through the structure. This provides insight into the scatter of the TPB and decreases in the Ni-Pore and Ni-YSZ interfaces. Once again, measurements of these properties for the full volume are available in Tables II and III. While the structures generated are artificial, the magnitude of the volume fractions, tortuosities, and interfaces are comparable to those reported by independent studies (15-16,21-24)

<table>
<thead>
<tr>
<th>Phase</th>
<th>Volume Fraction</th>
<th>Tortuosity</th>
<th>Mean Particle Size, µm</th>
<th>Contiguity, %Vol.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>0.34</td>
<td>2.8</td>
<td>1</td>
<td>83.3%</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.36</td>
<td>1.9</td>
<td>1.0</td>
<td>97.7%</td>
</tr>
<tr>
<td>Pore</td>
<td>0.28</td>
<td>1.7</td>
<td>N/A</td>
<td>100.0%</td>
</tr>
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</table>
Figure 2. Quantitative characterization results where the generated phenomenological structure is treated as a homogeneous medium. Increasing volumes from the same generated structure are examined in all subfigures. Specific grid dependence studies and results include, (a) a normalized representation of the TPB length and volume fractions of the individual Ni, YSZ, and pore phases. Each is normalized to their value corresponding to the full cube volume of $5^3 \mu m^3$. The mean tortuosity, not to be confused with the tortuosity factor, is shown in (b). The increase in the Ni tortuosity of the Ni phase with increasing volume size can be explained by disconnected regions within the structure. This is shown in (c), where the contiguity or percent volumetric connectivity of each of the three phases in the generated structure are considered. Finally, using the contiguity of the generated structures, the interfaces within the structure were examined in (d), where only the contiguous regions of the structure were considered.

As we turn our attention to Figure 3, size distributions for the generated structures are presented in Figure 3(a) and 3(b). In Figure 3(a) the delta-peak at a diameter of 1 $\mu m$ for the Ni and YSZ particles is both expected and a qualitative validation of the method since the sphere packing routine started with 1 $\mu m$ particles. This translates into a nearly vertical asymptote at a diameter of 1 $\mu m$ in Figure 3(b) for these same phases because of the large volume contained in these regions. Scatter and broadening near these regions represent volumes that have overlap, unique cross-sections, and assumptions built into the method to interpret the structure. As expected the pore regions maintain a broader spectrum of diameters because it represents arbitrarily void space. To demonstrate the consistency of the method, Figure 3(c) and 3(d) represent distributions determined for the
YSZ regions, where increasing regions of the same sample volume are considered, much like the volume dependence studies shown in Figure 2. While there is some inherent uniqueness, the consistency of the trends demonstrates the consistency and detail of the method.

Figure 3. Select results from analysis of three-phase volume generated using the described phenomenological structures. These include, (a) a volume fraction weighted distribution of diameters in the discrete phases. It is noted that 1 µm diameter Ni and YSZ spheres were used to generate the structure considered. When integrated over all diameters, (b) provides a cumulative distribution within the volume. To demonstrate that consistent results are obtained, (c) a grid dependence study on the normalized size distribution of the YSZ regions of the volume is considered. Subsets within the generated structure of different size are predominately independent of the volume considered. This study is also shown in cumulative form in (d) for completeness.

<table>
<thead>
<tr>
<th>Interface</th>
<th>Contiguous</th>
<th>Absolute</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni-YSZ (Area/Vol.)</td>
<td>0.94 x 10^6, m^-1</td>
<td>1.38 x 10^6, m^-1</td>
<td>0.67</td>
</tr>
<tr>
<td>YSZ-Pore (Area/Vol.)</td>
<td>1.91 x 10^6, m^-1</td>
<td>1.98 x 10^6, m^-1</td>
<td>0.97</td>
</tr>
<tr>
<td>Ni-Pore (Area/Vol.)</td>
<td>0.67 x 10^6, m^-1</td>
<td>1.00 x 10^6, m^-1</td>
<td>0.67</td>
</tr>
<tr>
<td>Ni-YSZ-Pore (TPB Length/Vol.)</td>
<td>3.20 x 10^12, m^-2</td>
<td>4.70 x 10^12, m^-2</td>
<td>0.67</td>
</tr>
</tbody>
</table>
Conclusions

This article presented several approaches to characterize the SOFC electrode structures. These characterization methods are designed for the interpretation of three-dimensional XCT reconstructions of heterogeneous SOFC electrode structures. The methods demonstrated in this study provide a pathway to interpretation of not only effective electrode properties but descriptions of the characteristic transport pathways in the system. Independence of the volume considered was shown; however, as noted for the contiguity and tortuosity of the Ni regions, volumetric independence is not always possible. Future studies will extend these processes to detailed studies in real systems and consider additional effects of the structure on the transport phenomena that must be supported.

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References