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Mesoscale characterization of local property distributions in heterogeneous electrodes

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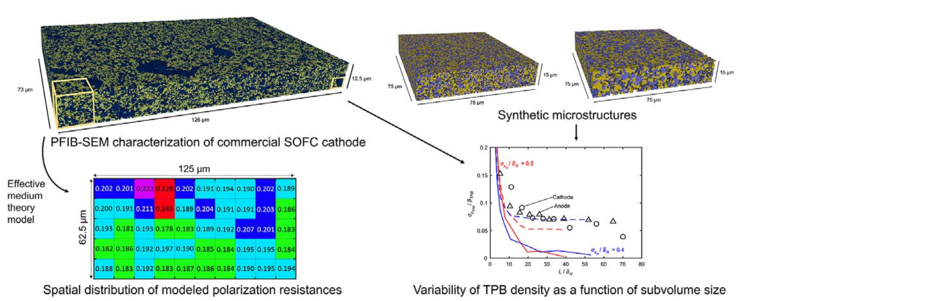
HIGHLIGHTS

- Large volume 3D reconstructions of SOFC electrodes are achieved using Xe PFIB-SEM.
- PFIB reconstructions enable scale-bridging characterization of properties.
- Significant variation exists in microscale structural values over the mesoscale.
- Synthetic microstructures model origin of high-frequency microstructural variation.
- Significant variation in microscale electrochemistry expected over the mesoscale.

GRAPHICAL ABSTRACT



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ABSTRACT

The performance of electrochemical devices depends on the three-dimensional (3D) distributions of microstructural features in their electrodes. Several mature methods exist to characterize 3D microstructures over the microscale (tens of microns), which are useful in understanding homogeneous electrodes. However, methods that capture mesoscale (hundreds of microns) volumes at appropriate resolution (tens of nm) are lacking, though they are needed to understand more common, less ideal electrodes. Using serial sectioning with a Xe plasma focused ion beam combined with scanning electron microscopy (Xe PFIB-SEM), two commercial solid oxide fuel cell (SOFC) electrodes are reconstructed over volumes of $126 \times 73 \times 12.5$ and $124 \times 110 \times 8\,\mu m^3$ with a resolution on the order of $\approx 50^3\,nm^3$. The mesoscale distributions of microscale structural features are quantified and both microscale and mesoscale inhomogeneities are found. We analyze the origin of inhomogeneity over different length scales by comparing experimental and synthetic microstructures, generated with different particle size distributions, with such synthetic microstructures capturing well the high-frequency heterogeneity.

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Effective medium theory models indicate that significant mesoscale variations in local electrochemical activity are expected throughout such electrodes. These methods offer improved understanding of the performance of complex electrodes in energy conversion devices.

1. Introduction

Electrodes in energy conversion devices, such as fuel cells or batteries, have complex microstructures that improve performance [1–7]. Solid oxide fuel cell (SOFC) electrodes are composites of an electron-conducting phase (ECP), an ion-conducting phase (ICP), and gas permeable pores (GPP) [1–3,5]. Electrochemical reactions occur readily at the intersection of these three phases (triple-phase boundaries or TPBs) [1–4]. High-performance electrodes have all three phases interconnected in three dimensions (3D) with characteristic feature diameters, *a*, on the scale of hundreds of nanometers, resulting in a high density of TPBs and fast transport of ions, electrons, and gas to the TPBs [1–5,8–16]. Owing to the discrete nature of the three phases, SOFC electrodes are inherently inhomogeneous at the nanoscale (hundreds of nm) [16]. SOFC electrodes built from uniformly distributed monodisperse nanoscale powders become homogeneous in their microstructure and electrochemical activity over the microscale (tens of microns), typically $\geq 10a$ to $15a$ (or ≥ 5 to 15 μm) [16]. Over the past decade [4], methods to quantify the 3D distribution of phases over the microscale have been developed, primarily using serial sectioning with a Ga focused ion beam (Ga FIB) combined with scanning electron microscopy (SEM) [4,9–11,13,14,17–30] or using nanoscale x-ray computed tomography (nano-CT) [8,15,19,24,31–39]. These microscale distributions have been used to inform effective medium theory models of average electrochemical activity, and model results compare favorably with experimental results [9–12,15,17,23,33,34,36,40,41]. The microstructures of SOFC materials have also been simulated using packed spheres or shapes based on expected microscale distributions [42–45], and such synthetic microstructures have been used to predict electrochemical parameters [42,44]. Thus, average electrochemical activity of a uniform SOFC electrode is thought to be well-defined by the 3D microscale distribution of phases.

Electrode microstructures are also related to the three key issues that impede widespread implementation of SOFCs— reliability, durability, and cost [1,3,5,12,14,27–29,46–49]. Several groups have specifically investigated the relationship between cell operation, microstructural change, and resulting performance loss [12,14,25,27–29,49]. When electrodes are fabricated using methods or materials that do not produce an ideal uniform electrode, which are likely for mass-produced low-cost SOFCs, variations in the local microstructure are expected over the mesoscale (several tens to hundreds of microns) [26,39]. Mesoscale variations in local structure will result in distributions of electrochemical activity throughout the cell that impact both reliability and durability. This impact may be significant, arising for example from locally high overpotentials or thermal gradients near zones of poor performance. However, while earlier groups have examined the links between overall microstructure, performance, and degradation, to our knowledge the impact of microstructural variations has not been explicitly investigated. We have previously reported on 3D microstructural inhomogeneities in commercial fuel cells using both Ga FIB-SEM [26] and x-ray CT methods [39], but these are unable to capture large enough volumes at high enough resolutions to fully quantify mesoscale distributions.

Herein we use a Xe Plasma (P) FIB-SEM to capture volumes over an order of magnitude larger (≈ 100 μm in linear dimensions) than what is typical using a Ga FIB-SEM or nano-CT while maintaining a resolution on the order of tens of nm. We characterize the mesoscale 3D distributions of local property values in a pair of SOFC electrodes and compare the results quantitatively to those of synthetic microstructures having varying particle size distributions (*PSD*s). While variations over the microscale appear to be well-captured using *PSD* models, variations over the mesoscale (or higher) originate from differences in local volume fractions within distinct microscale volumes. Finally, we discuss the impact on local electrochemical performance, using effective medium theory, for tens to hundreds of those microscale volumes. These results provide a path to accelerate the development of reliable, durable, low-cost SOFCs.

2. Experimental and computational methods

2.1. Sample description

A standard 25 mm anode supported SOFC button cell obtained from a commercial supplier (Materials and Systems Research, Inc. (MSRI), Salt Lake City, UT) was used in this work. The compositions of the MSRI cells for the current collector (*CC*), active cathode (*C*), electrolyte (*E*), active anode (*A*), and the anode support (*AS*) were respectively: (La,Sr) MnO_3 (LSM)/Macro-pores, LSM/yttria-stabilized zirconia (YSZ)/Pore, Dense YSZ, YSZ/Ni/Pore, and YSZ/Ni/Macro-pores. The performance of related MSRI cells is reported elsewhere [50,51]; cells from this batch were similar to those, exhibiting a voltage of ≈ 0.8 V at 0.5 A/cm^2. We previously reported on microstructural heterogeneities in such cells using laboratory nano-CT and synchrotron micro-CT methods [39] and the potential of PFIB-SEM for their characterization [52]. Pillar samples were prepared in identical fashions to those reported elsewhere [52].

2.2. PFIB-SEM data collection

We used a DualBeam Helios PFIB-SEM (FEI Company, Hillsboro, OR) and the commercial 3D acquisition package "AutoSlice and View" (FEI Company, Hillsboro, OR) [52]. Images were collected using the through-lens detector (TLD) at a short working distance (4 mm) that lead to the SE1 (secondary electron 1) signal, which is sensitive to the electronic properties of the solid, contributing primarily to the image contrast [52]. The positive correlation between grayscale and chemistry is shown in Fig. S1. Specific milling parameters were: an ion current of 59 nA at 30 kV accelerating voltage, with a ± 5° rocking mill; specific cleaning parameters were a 19 pA ion current at 5 kV voltage; specific imaging parameters were an electron beam current of 172 pA, an accelerating voltage of 5 kV, and a 3 μs dwell time per pixel. The slicing distance, or the distance between slice images, was 50 nm. The slice and imaging time was ≈ 4 min to complete the entire slice and view for an individual slice. The overall collection time was about three to four days each for both the cathode and anode.

2.3. Data processing and segmentation

Stacks of SEM images (tif images) from PFIB scans were reconstructed in the 3D visualization and analysis software Avizo (FEI Version 9.1.1), similar to previously reported for the *CC* layer for an MSRI button cell [52]. The reconstruction involves cropping and aligning the image slices in the stack. The output is a 3D, grayscale dataset, represented by a voxel-defined 3D matrix. The grayscale microstructure contains phase information in the different levels of contrast. The image slices in the reconstructed volume were then filtered using non-local means [53] and adaptive histogram equalizer filters [54]. This improved the grayscale contrast between phases in the 3D dataset. Next, the data was segmented into the phases using a watershed segmentation method built into Avizo, in which the grayscale data was converted into a more meaningful 3D matrix with the three