Comparison of SOFC cathode microstructure quantified using X-ray nanotomography and focused ion beam–scanning electron microscopy

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A B S T R A C T

X-ray nanotomography and focused ion beam scanning electron microscopy (FIB–SEM) have been applied to investigate the complex 3D microstructure of solid oxide fuel cell (SOFC) electrodes at spatial resolutions of 45 nm and below. The application of near edge differential absorption for x-ray nanotomography and energy selected backscatter detection for FIB–SEM enable elemental mapping within the microstructure. Using these methods, non-destructive 3D x-ray imaging and FIB–SEM serial sectioning have been applied to compare three-dimensional elemental mapping of the LSM, YSZ, and pore phases in the SOFC cathode microstructure. The microstructural characterization of an SOFC cathode is reported based on these measurements. The results presented demonstrate the viability of x-ray nanotomography as a quantitative characterization technique and provide key insights into the SOFC cathode microstructure.

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1. Introduction

Solid oxide fuel cell electrodes are heterogeneous functional systems that may be further advanced through micro- and nanoscale design [1]. Recent developments in three-dimensional imaging techniques [2–6] allow for the exploration of SOFC electrode microstructure and composition at resolutions below 50 nm. Several of these three-dimensional imaging techniques have involved the use of SEM images obtained through serial sectioning [2–4], Wilson et al. [2] used focused ion beam–scanning electron microscopy (FIB–SEM) to quantify the pore, nickel, and yttria-stabilized zirconia (YSZ) phases of a SOFC anode and have since applied FIB–SEM in imaging and reconstructing the cathode microstructure [3]. Using similar techniques, Faes et al. [4] developed a model of SOFC degradation based on the growth of Ni particles within the anode, which was applied to micro-scale transport models to predict performance degradation [9].

Sample integrity can be preserved using x-ray computed tomography (XCT) [5,8,10]. X-ray nanotomography using a transmission x-ray microscope (TXM) has been applied to discern the solid and pore phases of SOFC anodes [5]. Near edge differential absorption imaging techniques, taking advantage of the energy tuning capability of the synchrotron x-rays, have enhanced anode imaging efforts by enabling the elemental mapping and microstructural characterization of the distinct nickel and YSZ solid phases [8].

The present work compares x-ray nanotomography and FIB–SEM serial sectioning for quantification of the SOFC cathode microstructure. Near edge differential absorption contrast for nanotomography and energy-selected backscatter (EsB) detection for FIB–SEM permits microstructural characterization and elemental mapping of distinct lanthanum strontium manganese (LSM), YSZ, and pore phases within the cathode. Digitized reconstructions are produced from TXM images taken at 45 nm spatial resolution and from FIB–SEM images taken at 10 nm voxel size. Elemental mapping capabilities of these techniques are used to determine the distributions of phases within the cathode and compare predictions of critical microstructural parameters.

2. Experimental

Samples were taken from a composite cathode produced from lanthanum strontium manganese (La0.7Sr0.3)0.9MnO3±δ (Fuel Cell...
Materials, Lewis Center, Ohio, U.S.) and 8 mol% yttria-stabilized zirconia (Tosoh, Tokyo, Japan) base powders. For the x-ray nanotomography measurement a cylindrical sample with 10 μm diameter and 15 μm height was sectioned from the cathode using FIB milling. The use of a cylindrical sample provides a uniform cross-section for x-ray transmission. A sample from the same bulk cathode was also imaged using FIB–SEM serial sectioning.

X-ray nanotomography measurements of the SOFC cathode were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline BL6-2c and the Advanced Photon Source (APS) beamline 32-ID-C. A schematic of the TXM configuration used for these measurements is shown in Fig. 1, with additional details provided in the literature [6,8]. Nanotomography measurements were carried out, at a fixed x-ray energy, by collecting a series of projection images over a 180° rotation range with a data acquisition time of 1–5 s per projection image. Projection images were aligned and reconstructed using an iterative algebraic reconstruction technique (i-ART) algorithm [11] to produce 3D volumetric data sets. Consistent image quality was observed after 20 iterations. Volumetric data sets were collected around the Mn K-edge (6539 eV) at four energy levels. Data from two of these energy levels, 6528 and 6546 eV, was selected for segmentation and further analysis. A spatial resolution of 45 nm was achieved in these measurements, based on the zone plate characteristics.

To verify the findings obtained by TXM, cathode images were taken using a FIB–SEM serial sectioning approach similar to Wilson et al. [2]. Images were obtained with a Zeiss NVision 40 Crossbeam FIB–SEM at the Interdisciplinary Center for Electron Microscopy (CIME) at Ecole Polytechnique Fédérale de Lausanne (EPFL). The energy filtering capabilities of the EsB detector on this system enable contrast imaging between the LSM and YSZ phases of the sample. A rectangular volume 10 μm × 7 μm × 6 μm was imaged using an accelerating voltage of 1.87 kV. Application of this low accelerating voltage maintained the escape depth of backscattered electrons below 10 nm. The image pixel size was 10 × 10 nm and a slice thickness of 10 nm was used to obtain an isometric voxel of 10 nm.

The reconstructed nanotomography and FIB–SEM data sets were segmented and processed using the ImageJ software [12]. The volumetric data taken above the Mn K-edge was segmented to separate the LSM phase from the pore and YSZ phases. Comparable steps were taken to isolate the pore phase in the below edge data. The intersection of the non-LSM phase in the above edge data and the solid phase in the below edge data distinguished the YSZ in the sample. A similar approach was applied to the images obtained using FIB–SEM serial sectioning. The reconstructed volumes, shown in Fig. 2a–b, are comparable. However, it should be noted that the FIB–SEM imaging provided superior pore contrast due to resin impregnation of the FIB–SEM sample.

3. Results and discussion

The segmentation process produces a digitized representative volume element (RVE) that delineates the LSM, YSZ, and pore phases with unique integer identifiers. The digitized RVE facilitates computational characterization of the microstructure including phase sizes, volume fraction, interfacial characteristics, and phase contiguity. This characterization provides a means of quantitatively comparing the results of the x-ray nanotomography and FIB–SEM measurements.

Initial comparisons of the nanotomography and FIB–SEM imaging results were conducted in terms of the phase size distributions (PSD). The PSD were calculated using a ray-shooting routine based on a three-dimensional lattice Boltzmann method (LBM) formalism using 19 lattice directions (D3Q19) [13]. Each PSD provides a discrete histogram outlining the volumetric contribution specific phase diameters make to the overall phase volume. A cumulative size distribution (CSD) is also calculated, providing a continuous function that characterizes microstructural features. This continuous form enables calculation of mean phase size distributions through the averaging and subsequent numerical differentiation of the CSD data from multiple RVEs.

The calculated PSD for the x-ray nanotomography and FIB–SEM imaging are shown in Fig. 2c–e. The solid lines in each plot represent the mean PSD calculated from nanotomography data taken from two separate 5 μm × 5 μm × 5 μm (125 μm³) cubic sub-volumes. The symbols represent the PSD calculated from one cubic FIB–SEM sub-volume of ~43 μm³. Volume independence studies were performed to ensure that the RVEs sufficiently characterized the bulk cathode microstructure, and binning applied in the PSD calculations was set to ensure bin size independence of the mean phase diameters. The voxel size of the FIB–SEM phase size data in Fig. 2c–e is 10 nm. The predicted size distributions match well, particularly considering that the imaged samples were taken from distinct locations within the bulk cathode. These locations were not adjacent to each other, which leads to some discrepancy in the results because the volumes examined by TXM and FIB–SEM do not originate from the same exact location within the cathode. However, the results from both locations are generally representative of the bulk cathode microstructure, as supported by volume independence seen for the measurements. The agreement between these results suggests both techniques capture the microstructural characteristics of the samples at their respective resolutions.

Further comparison of the x-ray nanotomography and FIB–SEM imaging was made with respect to volume fraction, two phase interfacial area, triple phase boundary length, and phase contiguity. These parameters were determined by applying search algorithms to analyze the digitized RVEs [14]. The results of this analysis are

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**Fig. 1.** Schematic of the transmission x-ray microscope (TXM) used for x-ray nanotomography measurements. The x-ray beam is gathered onto the sample by a capillary condenser and pinhole, transmitted through the sample, and focused on to an optically coupled CCD using a Fresnel zone plate objective.

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outlined in Table 1. For the nanotomography data, average values were computed for two segmented RVEs. The data for the FIB–SEM results was down-sampled using 3×3×3 binning, which produced a volumetric data set with an effective sampling resolution of 30 nm. This binning produces a pixel size comparable to the pixel resolution of the CCD system for x-ray nanotomography data, so that the two data sets can be compared with a similar sampling resolution. Reasonable agreement is seen for most of the parameters investigated, with the exception of the LSM contiguity value and the effective YSZ–LSM interfacial area, which is directly influenced by the LSM contiguity. This difference in contiguity may be related to the difference in resolution of the imaging approaches. Such effects may warrant further investigation. However, the characterization results presented suggest that both techniques provide sufficient resolution and capability to accurately describe cathode microstructure and composition.

4. Conclusions

X-ray nanotomography and focused ion beam scanning electron microscopy have been applied to investigate the complex 3D microstructure of SOFC cathodes. Using the chemical sensitivity of x-ray absorption for x-ray nanotomography, and EsB detection for FIB–SEM, non-destructive x-ray nanotomography and FIB–SEM serial

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**Table 1**

<table>
<thead>
<tr>
<th>Parameters and phases</th>
<th>X-ray nanotomography</th>
<th>FIB–SEM</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mean phase diameter (μm)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>0.34 (±0.045)</td>
<td>0.27 (±0.030)</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.27 (±0.045)</td>
<td>0.28 (±0.030)</td>
</tr>
<tr>
<td>LSM</td>
<td>0.42 (±0.045)</td>
<td>0.40 (±0.030)</td>
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<tr>
<td><strong>Volume fraction</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>0.34</td>
<td>0.34</td>
</tr>
<tr>
<td>YSZ</td>
<td>0.32</td>
<td>0.33</td>
</tr>
<tr>
<td>LSM</td>
<td>0.34</td>
<td>0.33</td>
</tr>
<tr>
<td><strong>Contiguity (%)</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pore</td>
<td>99.6</td>
<td>99.8</td>
</tr>
<tr>
<td>YSZ</td>
<td>99.8</td>
<td>99.4</td>
</tr>
<tr>
<td>LSM</td>
<td>98.2</td>
<td>94.3</td>
</tr>
</tbody>
</table>

**Interfacial characteristics**

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<th>Total</th>
<th>Effective</th>
<th>Total</th>
<th>Effective</th>
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<tr>
<td>TPB length (m m⁻¹)</td>
<td>6.6E+13</td>
<td>6.0E+13</td>
<td>8.3E+13</td>
<td>7.0E+13</td>
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<tr>
<td>Interfacial area (m²)</td>
<td>7.7E+06</td>
<td>7.6E+06</td>
<td>7.4E+06</td>
<td>7.3E+06</td>
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<tr>
<td>Pore-YSZ</td>
<td>2.0E+06</td>
<td>2.7E+06</td>
<td>3.4E+06</td>
<td>3.1E+06</td>
</tr>
<tr>
<td>YSZ-LSM</td>
<td>6.4E+06</td>
<td>6.1E+06</td>
<td>5.7E+06</td>
<td>4.9E+06</td>
</tr>
</tbody>
</table>

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Fig. 2. Reconstructed volumes from (a) x-ray nanotomography and (b) FIB–SEM data are analyzed to quantify microstructural characteristics. Phase size distributions for the (c) pore, (d) YSZ, and (e) LSM phases of a solid oxide fuel cell cathode estimated from x-ray nanotomography (solid lines) and FIB–SEM (symbols) provide comparable assessments of the microstructure.

sectioning have been applied to obtain three-dimensional elemental mapping of the LSM, YSZ, and pore phases in the SOFC cathode microstructure. The reported measurements include size distributions of the phases; two-phase and three-phase boundary areas (nominal and effective); phase volume fractions; and phase contiguities. Microstructural characterization of an SOFC cathode based on these measurements is compared for each technique with general agreement found between predictions of phase size distributions and key microstructural parameters. The effects of instrument resolution on microstructural characterization were primarily evident in predictions of phase contiguity. Measurements from both techniques agree reasonably well, demonstrating the viability of x-ray nanotomography as a quantitative characterization technique and provide key insights into the SOFC cathode microstructure.

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