ECS Transactions, 35 (1) 2417-2421 (2011)
10.1149/1.3570238 ©The Electrochemical Society

Comparison of X-ray Nanotomography and FIB-SEM in Quantifying the Composite LSM/YSZ SOFC Cathode Microstructure

George J. Nelson[1], William M. Harris[1], Jeffrey J. Lombardo[1], John R. Izzo, Jr.[1]
Wilson K. S. Chiu[1], Pietro Tanasini[2,4] , Marco Cantoni[3], Jan Van herle[4]
Christos Comninellis[2], Joy C. Andrews[5], Yijin Liu[5], Piero Pianetta[5], Yong S. Chu[6]

[1]Department of Mechanical Engineering, University of Connecticut, Storrs, CT, USA
[2]Electrochemical Engineering Group (GGEC), [3]Centre for Interdisciplinary Electron Microscopy, [4]Industrial Energy Systems Laboratory
École Polytechnique Fédérale de Lausanne, Lausanne, Switzerland
[5]Stanford Synchrotron Radiation Lightsource, Stanford Linear Accelerator Center
Menlo Park, CA 94025, USA
[6]National Synchrotron Light Source II, Brookhaven National Laboratory
Upton, NY 11973, USA

X-ray nanotomography and focused ion beam scanning electron microscopy (FIB-SEM) provide unique opportunities to interrogate the 3D microstructure of solid oxide fuel cell (SOFC) electrodes with unprecedented spatial resolution with elemental specificity. Using x-ray nanotomography with differential absorption imaging across the Mn K-absorption edge (6539 eV), and energy selected backscatter detection for FIB-SEM, these two techniques have been applied to obtain 3D elemental mapping of the LSM, YSZ and pore phases in the cathode microstructure. Measurements taken by non-destructive x-ray imaging and FIB-SEM serial sectioning include three-phase boundary areas (nominal and effective); phase volume fraction; and phase contiguity. The results presented demonstrate the viability of nanotomography as a characterization technique and provide key insights into the SOFC cathode microstructure. The effects of instrument resolution on microstructural characterization are addressed and the roles of FIB-SEM and x-ray nanotomography in future SOFC microstructural characterization efforts are discussed.

Introduction

Composite SOFC electrodes contain multiple distinct phases that support gaseous reactant transport, and chemically active interfaces at the junctions of these phases. An enhanced understanding of the structure and composition of SOFC electrodes at the micro- and nano-scales is critical to the further development of SOFCs. Recent developments in three-dimensional imaging techniques (1-6) allow for the exploration of SOFC electrode microstructure and composition at resolutions below 50 nm. Several of these microstructural analysis developments have involved use of SEM images obtained through serial sectioning techniques (1, 2, 7). Wilson et al. (1) used focused ion beam-scanning electron microscopy (FIB-SEM) to reconstruct the pore, nickel, and yttria-stabilized zirconia (YSZ) phases of a SOFC anode and predict the concentration of triple-

phase boundaries. This work has since been expanded through the application of FIB-SEM in imaging and reconstructing cathode microstructure (2). Using similar techniques, Faes et al. (7) 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 (8).

While FIB-SEM serial sectioning techniques can provide a detailed three-dimensional understanding of electrode microstructure, these methods result in the destruction of the imaged sample. Sample integrity can be preserved by the application of x-ray nanotomography (3, 6). In particular, full-field x-ray nanotomography has been applied to discern the solid and pore phases of SOFC anodes (3). The application of near edge differential absorption imaging techniques have enhanced anode imaging efforts by enabling the elemental mapping and microstructural characterization of the distinct nickel and YSZ solid phases (6).

The application of x-ray nanotomography and FIB-SEM serial sectioning for the characterization of SOFC cathode microstructure is demonstrated. Nanotomography with near edge differential absorption imaging and energy selected backscatter (EsB) detection for FIB-SEM permit the microstructural characterization and elemental mapping of lanthanum strontium manganite (LSM), YSZ, and pore phases within the cathode. Digitized reconstructions are produced from transmission x-ray microscope (TXM) images taken at 45 nm spatial resolution and from FIB-SEM images taken at 10 nm spatial resolution. Elemental mapping capabilities of these techniques are used to determine the distributions of phases within the cathode and compare predictions of critical microstructural parameters.

Experimental

Samples were taken from a composite cathode produced from lanthanum strontium manganite $(La_{0.7}Sr_{0.3})_{0.9}MnO_{3\pm\delta}$ (Fuel Cell Materials, U.S.) and 8% yttria-stabilized zirconia (Tosoh, Japan) base powders. Inks composed of these powders were screen-printed onto an YSZ substrate in multiple layers to a thickness of 100-150 μm and sintered at 1050°C for 1 hour. The sintered cathodes were then sectioned to produce stock pieces for the production of smaller samples. Samples imaged using nanotomography were produced from these larger stock pieces using traditional sectioning methods and FIB milling. The nanotomography results presented are for a cylindrical sample with a 10 μm diameter and height of 15 μm cut from a larger cathode segment using FIB milling and subsequently mounted on a sample holder. 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. This sample was taken from the cathode using traditional sectioning methods, impregnated with resin, and polished prior to imaging.

Full-field x-ray nanotomography measurements of the SOFC cathode were conducted at the Stanford Synchrotron Radiation Lightsource (SSRL) beamline BL6-2c and beamline 32-ID-C of the Advanced Photon Source (APS) at Argonne National Laboratory. The sample is illuminated by monochromatic x-rays from the synchrotron source that are collected using a capillary condenser optic prior to passing through a

pinhole. The sample is mounted on a stage capable of rotation about the vertical axis and translation on three axes. The x-rays penetrate the sample and are focused by a Fresnel zone plate objective lens prior to being captured by a high resolution charge couple device (CCD) (4). Additional details of this TXM configuration are provided by Grew et al. (6). The field of view for the images discussed in the present work ranges from 5-30 μm. However, with the current apparatus the capability exists to capture images with a field of view over 100 μm by using stitching methods. For each nanotomography measurement the x-ray energy level was fixed and the sample was rotated through 180°. Sample projection images were taken at 1° intervals for a total of 181 projections. These projection images were then aligned and reconstructed using the iterative algebraic reconstruction technique (i-ART) algorithm (9).

The tomographic imaging of the SOFC cathode was completed by first calibrating the TXM and then taking tomographic scans. X-ray absorption characteristics of the cathode sample analyzed were examined using a series of transmission images taken around the Mn K-edge (6539 eV). This initial investigation was followed by tomography measurements completed at four energy levels: 6510, 6528, 6546, and 6550 eV. A spatial resolution of 45 nm was achieved in these measurements, based on the zoneplate characteristics. Volumetric data sets at 6528 and 6546 eV were selected for segmentation and microstructural analysis.

To verify the findings obtained by x-ray nanotomography, the cathode's microstructure was characterized by serial sectioning using a Zeiss NVision 40 Crossbeam FIB-SEM at the Interdisciplinary Center for Electron Microscopy (CIME) at Ecole Polytechnique Fédérale de Lausanne (EPFL). A rectangular volume $10\times7\times6$ μm^3 was imaged using an accelerating voltage of 1.87 kV. A resolution of 10 nm was achieved. The energy filtering capabilities of the energy selected backscatter detector on the FIB-SEM system enable contrast imaging between the LSM and YSZ phases of the sample.

Prior to analysis, the reconstructed x-ray nanotomography and FIB-SEM data was segmented using the ImageJ software (10). The volumetric data was cropped to produce a representative volume element (RVE). The above edge x-ray nanotomography data set was segmented to distinguish the LSM phase from the pore and YSZ. Comparable steps are 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 delineates the YSZ. A similar processing approach was applied to the images obtained by FIB-SEM serial sectioning. The FIB-SEM data was down-sampled using 3×3×3 binning to enable microstructural characterization based on similar pixel sizes.

Results and Discussion

Segmentation of the volumetric data produces a digitized version of the RVE that delineates the LSM, YSZ, and pore phases with unique integer identifiers. This form of the data is amenable to computational characterization of the microstructure including phase sizes, volume fraction, two phase interfacial area, triple phase boundary length, and phase contiguity. Further details outlining the methods applied in the microstructural

characterization are provided by Grew et al. (11). This characterization enables quantitative comparison of the x-ray nanotomography and FIB-SEM measurements.

Comparison of the microstructural characterization based on x-ray nanotomography and FIB-SEM measurements was made with respect to volume fraction, triple phase boundary length, and phase contiguity. These parameters can be readily determined from straightforward search algorithms used to analyze the digitized structure produced from the image processing steps (12). The results of this analysis are outlined in Table I. For the nanotomography data average values were computed for two RVEs segmented from the full sample image stack. As noted, the data for the FIB-SEM RVE was down-sampled using 3×3×3 binning, which produced a 3D image with an effective resolution of 30 nm. This step was taken as a means of comparing data based on comparable pixel sizes. Close agreement is seen for most of the parameters investigated, with the exception of the LSM contiguity value. This difference in contiguity may be related to the difference in resolution of the imaging approaches.

TABLE I. Microstructural characterization measurements for the cathode samples imaged using x-ray nanotomography and FIB-SEM. The FIB-SEM results were down-sampled using 3×3×3 binning to produce a pixel size similar to that used in the x-ray nanotomography measurements.

Parameters and Phases	**X-ray Nanotomography**		**FIB-SEM**	
Volume Fraction				
YSZ	0.32		0.33	
LSM	0.34		0.33	
Contiguity (%)				
YSZ	99.8		99.4	
LSM	98.2		94.3	
TPB Length (m/m^3)	Total	Contiguous	Total	Contiguous
	6.6E+13	6.0E+13	8.3E+13	7.0E+13

Conclusions

X-ray nanotomography and focused ion beam scanning electron microscopy have been applied to investigate the complex 3D microstructure of composite SOFC cathodes. Using near edge differential absorption imaging for x-ray nanotomography and energy selected backscatter detection for FIB-SEM, non-destructive x-ray imaging and FIB-SEM serial sectioning have been applied to obtain three-dimensional elemental mapping of the LSM, YSZ, and pore phases in a SOFC cathode. The reported measurements three-phase boundary areas (nominal and effective); phase volume fraction; and phase contiguity. Microstructural characterization of an SOFC cathode based on these measurements revealed between predictions of key microstructural parameters. The effects of instrument resolution on microstructural characterization were primarily evident in predictions of phase contiguity. The agreement found in the results presented demonstrates the viability of x-ray nanotomography as a method for characterizing the SOFC cathode microstructure.

Acknowledgments

Financial support from an Energy Frontier Research Center on Science Based Nano-Structure Design and Synthesis of Heterogeneous Functional Materials for Energy Systems (HeteroFoaM Center) funded by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences (Award DE-SC0001061), the National Science Foundation (Award CBET-0828612), and the ASEE National Defense Science and Engineering Graduate Fellowship program are gratefully acknowledged. The authors would like to thank Dr. Roger Ristau for his assistance in preparation of x-ray nanotomography samples. Portions of this research were carried out at the Advanced Photon Source supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract No. DE-AC02-06CH11357, the Stanford Synchrotron Radiation Lightsource, a national user facility operated by Stanford University on behalf of the U.S. Department of Energy, Office of Basic Energy Sciences, and by the Brookhaven Science Associates, LLC under Contract No. DE-AC02-98CH10886.

References

1. J. R. Wilson, W. Kobsiriphat, R. Mendoza, H. Chen, J. M. Hiller, D. J. Miller, K. Thornton, P. W. Voorhees, S. B. Adler and S. A. Barnett, *Nature Materials,* **5**(7), 541 (2006).
2. J. R. Wilson, A. T. Duong, M. Gameiro, H. Chen, K. Thornton, D. R. Mumm and S. A. Barnett, *Electrochemistry Communications,* **11**(5), 1052 (2009).
3. J. R. Izzo Jr, A. S. Joshi, K. N. Grew, W. K. S. Chiu, A. Tkachuk, S. H. Wang and W. Yun, *Journal of the Electrochemical Society,* **155**(5), B504 (2008).
4. Y. S. Chu, J. M. Yi, F. De Carlo, Q. Shen, W. Lee, H. J. Wu, C. L. Wang, J. Y. Wang, C. J. Liu, C. H. Wang, S. R. Wu, C. C. Chien, Y. Hwu, A. Tkachuk, W. Yun, M. Feser, K. S. Liang, C. S. Yang, J. H. Je and G. Margaritondo, *Applied Physics Letters,* **92**(10), (2008).
5. Y. -. Chen, T. Lo, Y. S. Chu, J. Yi, C. Liu, J. Wang, C. Wang, C. Chiu, T. Hua, Y. Hwu, Q. Shen, G. Yin, K. S. Liang, H. Lin, J. H. Je and G. Margaritondo, *Nanotechnology,* **19**(39), (2008).
6. K. N. Grew, Y. S. Chu, J. Yi, A. A. Peracchio, J. R. Izzo Jr, Y. Hwu, F. De Carlo and W. K. S. Chiu, *Journal of The Electrochemical Society,* **157**(6), B783 (2010).
7. A. Faes, A. Hessler-Wyser, D. Presvytes, C. G. Vayenas and J. Vanherle, *Fuel Cells,* **9**(6), 841 (2009).
8. P. Tanasini, M. Cannarozzo, P. Costamagna, A. Faes, J. Van Herle, A. Hessler-Wyser and C. Comninellis, *Fuel Cells,* **9**(5), 740 (2009).
9. Y. J. Liu, P. P. Zhu, B. Chen, J. Y. Wang, Q. X. Yuan, W. X. Huang, H. Shu, E. R. Li, X. S. Liu, K. Zhang, H. Ming and Z. Y. Wu, *Physics in Medicine and Biology,* **52**(12), (2007).
10. W. S. Rasband, ImageJ, U.S. National Institutes of Health, Bethesda, MD, USA (http://rsb.info.nih.gov/ij/).
11. K. N. Grew, A. A. Peracchio and W. K. S. Chiu, *Journal of Power Sources,* **195**(24), 7943 (2010).
12. K. N. Grew, A. A. Peracchio, A. S. Joshi, J. R. Izzo Jr. and W. K. S. Chiu, *Journal of Power Sources,* **195**(24), 7930 (2010).