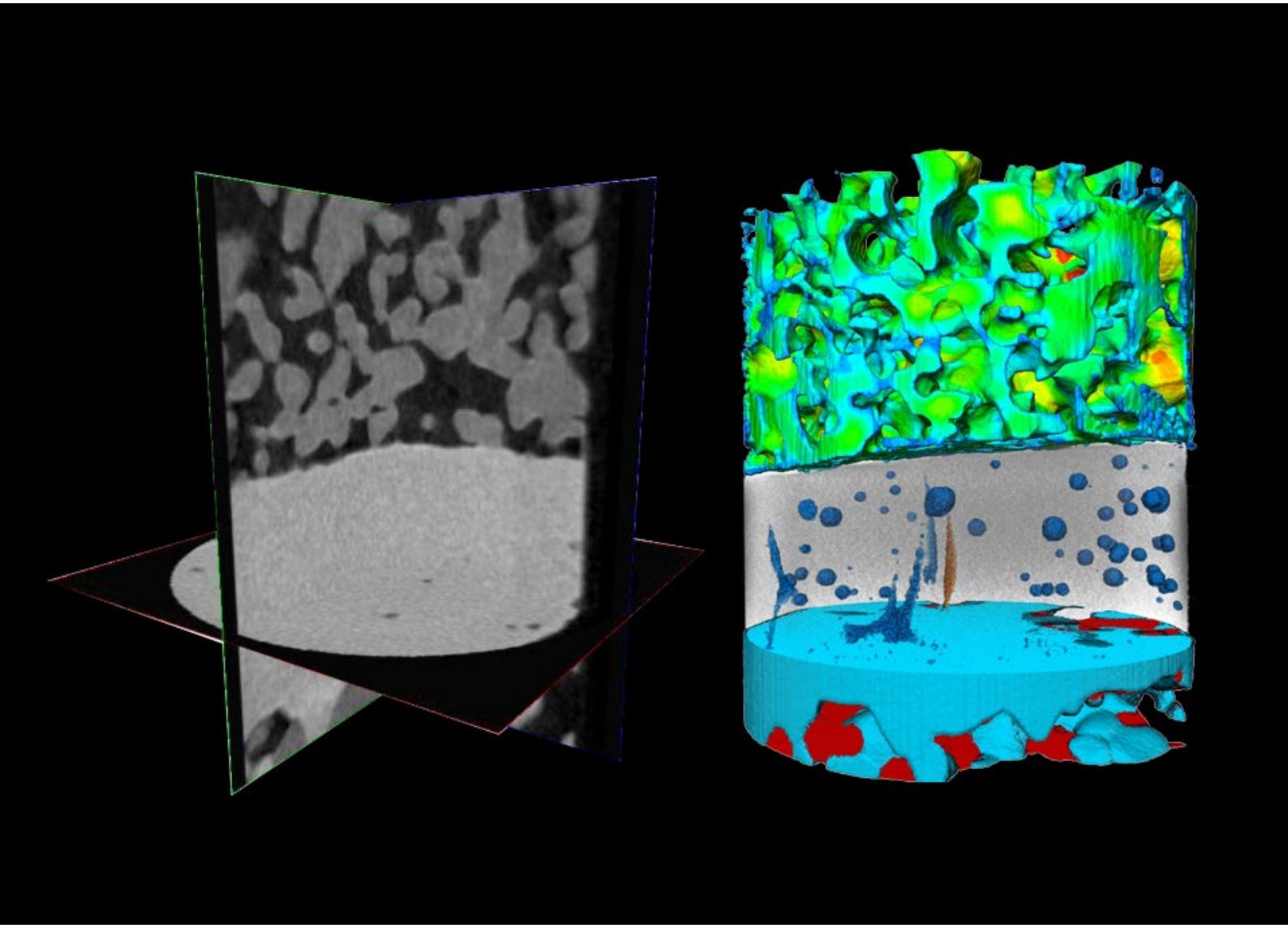
Application Note



ZEISS Xradia 810 Ultra

Characterizing Solid Oxide Fuel Cell Microstructures in 3D

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Solid Oxide Fuel Cells (SOFCs) provide efficient energy conversion with reduced carbon emissions by the electrochemical oxidation of a fuel at high temperature. Controlling and manipulating this electrochemical process places stringent requirements on material selection and cell design. Notably, the electrode and electrolyte materials must simultaneously support catalytic and transport activity while also maintaining long term stability at high temperature through extended operation. Moreover, the complex distribution of these multiple solid phases within the cell directly dictates the power density, motivating the need to understand the heterogeneous microstructure in 3D. In this application note, the ZEISS Xradia 810 Ultra X-ray microscope was used to examine internal structures of an SOFC down to 50 nm spatial resolution.

An anode-supported SOFC was obtained with a single-phase Lanthanum Strontium Manganite (LSM) cathode, yttria-stabilized zirconia (YSZ) electrolyte, and composite NiO-YSZ anode. The cell was obtained in the as-fabricated state, prior to operation and reduction of the NiO to metallic nickel.
A cylindrical sample (approximately 15 microns in diameter and 70 microns tall) containing all three components of the SOFC was extracted from the bulk material using a combination of laser milling and focused ion beam polishing techniques. The sample was examined using the Xradia 810 Ultra X-ray microscope to evaluate:

- The homogeneity of the porous anode and cathode structures, which is desirable to promote efficient transport processes as well as distributed electrochemical reactions
- The possible existence and geometry of undesired porosity in the electrolyte, which can lead to detrimental gas crossover effects

The sample was first examined in Xradia 810 Ultra's large field of view absorption contrast mode, as shown in Figure 1. Figure (a) shows a 2D radiograph, and (b) shows a virtual cross section through the reconstructed volume. This imaging mode provides 150 nm spatial resolution with a 65 µm field of view. The multi-layered structure of the cell components is clearly visible due to the density contrast between

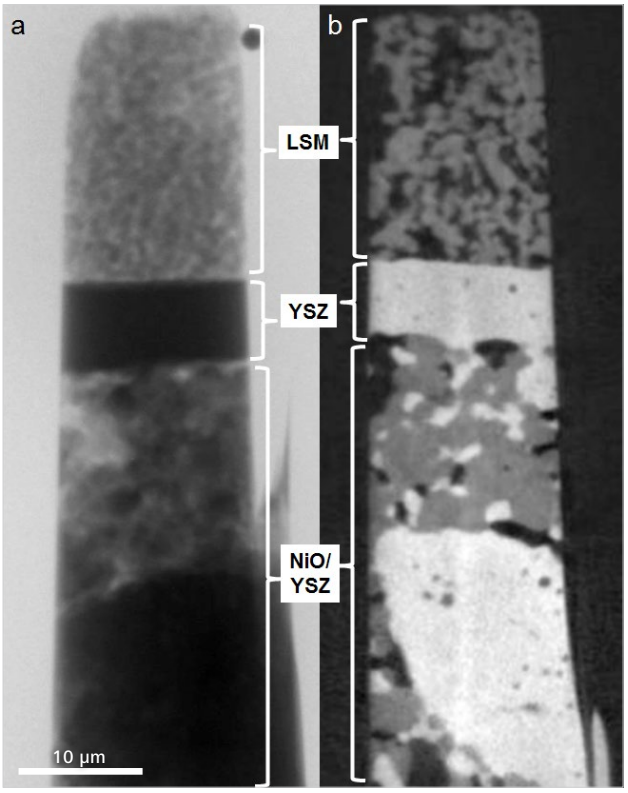

Figure 1 *Data collected on Xradia 810 Ultra in the large field of view absorption contrast mode. a) A 2D radiograph raw image. b) A virtual cross sectional slice through the interior of the reconstructed 3D volume. This data reveals the structure of all three of the primary components of the SOFC: LSM cathode (top), YSZ electrolyte (middle) and NiO-YSZ anode (bottom). The cathode exhibits a relatively uniform porous structure, while the anode contains a distinct, large YSZ particle.*

the different solid phases, with cathode on the top of the image, electrolyte in middle, and anode on bottom. There are numerous pores down to several hundred nm in size visible in the electrolyte. In addition, the cathode layer is seen to have a relatively homogeneous porous structure, while the anode contains an anomalous large YSZ particle. This large particle has the potential to be problematic as it could interrupt the local contiguity of the pore and NiO (soon-to-be metallic nickel following reduction) networks in this region of the anode close to the electrolyte, reducing the transport efficiency of these phases and ultimately decreasing the density of active triple phase boundary reaction sites.

To further visualize the pores within the electrolyte, a portion of the sample was imaged in Xradia 810 Ultra's high resolution mode (nondestructively, with no physical cutting of the sample), offering 50 nm spatial resolution and a 16 µm field of view. This sub-region is shown as the color inlay in Figure 2, with the large field of view data shown in grayscale. The high resolution imaging was performed in two modes: absorption contrast and Zernike phase contrast. Raw data results from each of these scans are shown side by side in Figure 3. These images represent 2D virtual cross sections of the data taken at equivalent locations. Figures (a) and (b) are cross sections along a vertical plane and reveal the cathode (top), electrolyte (middle), and anode (bottom) layers.
By comparing the two images, it is evident that the absorption contrast mode provides excellent grayscale contrast between the various materials based on their density differences. Conversely, the phase contrast image provides poorer differentiation of the materials, but improved sharpness and clarity of edges and small features, particularly the two elongated pores in the electrolyte. This is even more evident in (c) and (d) which show cross sections of a horizontal plane through the electrolyte. The phase contrast mode (d) helps to highlight the edges of numerous small voids which are visible, but not as distinct, in the absorption image.

The high resolution data was used to segment and label the volume, as shown in Figure 4. The electrolyte voids are seen in the center of the image colored blue and orange, surrounded by the relatively uniform grayscale representative of the bulk electrolyte material. While most voids are approximately spherical in shape, there are several elongated voids which appear to be the result of incomplete densification of the YSZ starting powder. In this sample it is likely that the

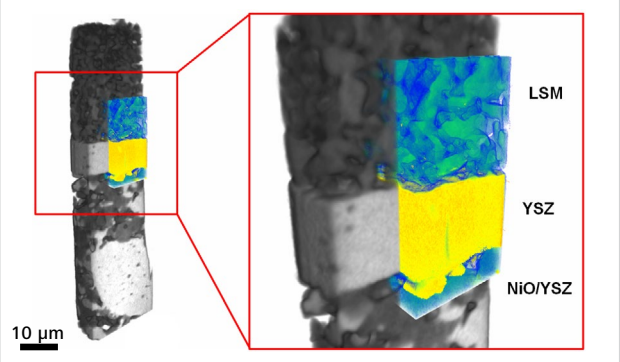

Figure 2 *To examine the electrolyte in greater detail, a region of the sample was imaged using the high resolution imaging mode, providing 50 nm spatial resolution. The location of the high resolution data (color inlay) relative to the large field of view result (grayscale) is shown here.*

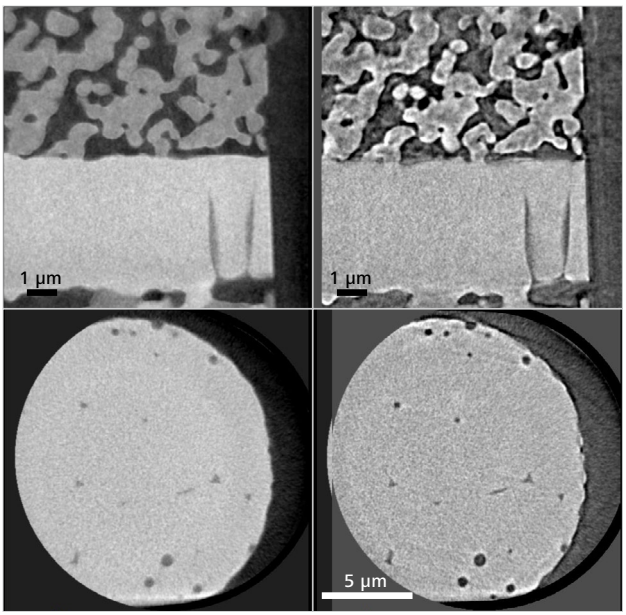

Figure 3 *High resolution imaging results. (a) and (b) show virtual sections of the sample along the long axis in absorption and phase contrast modes, respectively. The images reveal elongated pores in the electrolyte layer, which appear to nearly span the thickness of the electrolyte. (c) and (d) are virtual cross sections along an orthogonal plane through the center of the electrolyte region, again in absorption and phase contrast mode. The absorption mode provides superior contrast between different solid materials, while the phase contrast mode highlights edges and interfaces thereby helping small features to stand out.*

parameters and processes used in electrolyte sintering are worthy of further consideration. At least one such void, shown in orange, is connected with the pore network on the anode side. Within the resolution of the instrument, no voids were found which completely spanned the electrolyte thickness although several were very close. However, it is possible such passageways could exist on a smaller length scale, which would still be quite problematic as a point of gas crossover creating a short in the cell.

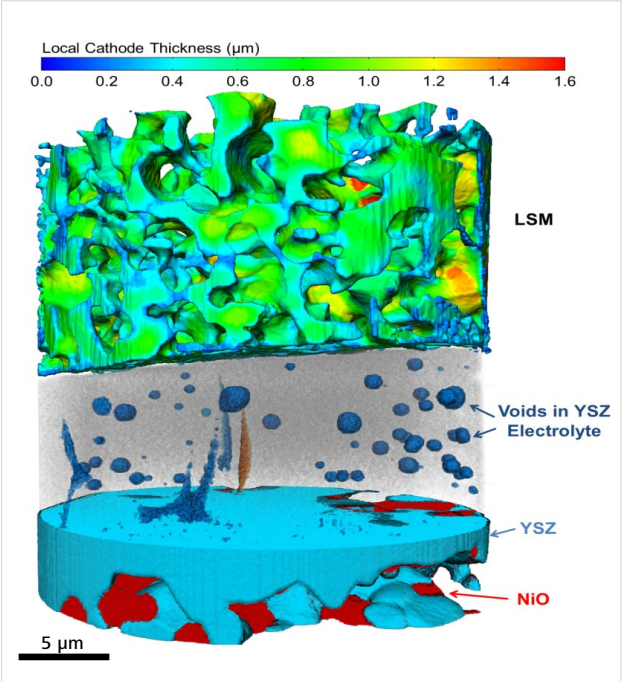

Figure 4 *The high resolution data was used to segment and analyze the volume. Pores and voids present in the electrolyte (seen in the middle of the figure in dark blue and orange) seem to belong to two categories: spherical and elongated. The isolated spherical voids are unlikely to be of concern; however the elongated voids are more problematic as they may connect with either or both sides of the electrolyte, providing a gas crossover pathway. The YSZ and NiO phases in the anode have been segmented based on gray-scale contrast, and in the LSM cathode the solid phase has been segmented from the pores and used to compute the local thickness of the LSM electronic conducting network. (Some artifacts can be observed on the exposed surface of the thickness map due to the artificial truncation of the data from its surrounding structure.) Note: the thickness colorbar at the top of the figure corresponds only to the cathode.*

Figure 4 also displays the anode, segmented into YSZ (blue) and NiO (red) phases, as well as the LSM cathode which has been segmented and analyzed to evaluate local thickness, an approximate measure of the local feature sizes. The thickness map corresponds to the colorscale shown at the top of the image, with LSM feature sizes reaching up to about 1.6 µm. However, it is clear that the feature sizes characterizing the cathode network are relatively uniform in the range of 0.5 – 1.5 µm. This type of measurement can be used to characterize the solid state transport processes in the LSM (electronic, and to a much lesser extent, ionic transport), and can also be easily performed on the complementary pore phase to correlate to gas diffusion behavior.

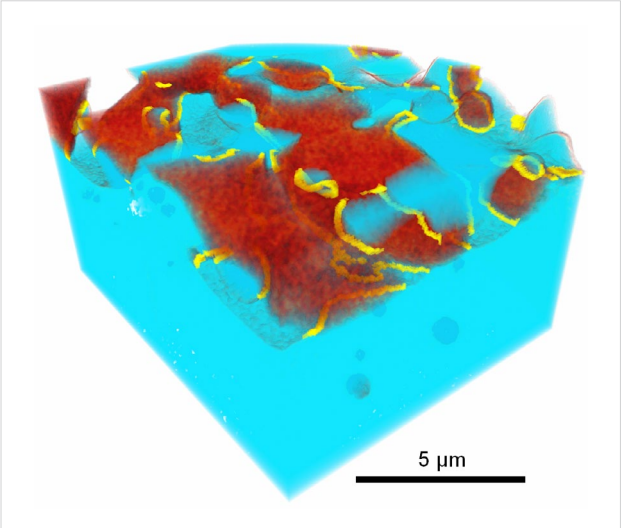

Figure 5 *The triple phase boundary of the anode was determined using a series of morphological operations performed on the segmented structure. Shown here are the TPB points (yellow) overlaid on partially transparent renderings of the NiO (red) and YSZ (blue).*

Additional analysis was performed on the anode to qualitatively evaluate the distribution of triple phase boundary (TPB) points. The TPB exists where the electronic, ionic, and gas conducting phases converge at a common point in space, providing the necessary pathways for species transport and thereby defining the locations of electrochemical reactions. (For this sample, evaluation of TPB is not rigorously meaningful as the anode is still in its oxide phase and has not yet been reduced to metallic nickel, but the analysis is nonetheless performed in the same fashion and is presented here as a demonstration of the concept.) To determine the TPB locations, a morphological dilation was performed sequentially on each of the segmented NiO, YSZ, and pore phases. The overlap of these dilations occurs at locations where these three phases are in immediate proximity, representing the TPBs. Figure 5 presents a visualization in which the Ni and YSZ phases have been rendered partially transparent to reveal the distribution of the TPB, shown in yellow. (This is the same anode region as shown in the bottom of Figure 4, but flipped upside-down for easier viewing). It is readily apparent the TPB lines are well distributed throughout the anode in this particular sample.

Conclusions

Nanoscale X-ray microscopy has been used in this work to examine the 3D microstructure of the three primary components of a solid oxide fuel cell: cathode, electrolyte, and anode. Imaging performed down to 50 nm spatial resolution, and employing Zernike phase contrast to highlight edges and small features, reveals the structures in great detail and with high contrast. Notably, numerous voids have been detected within the electrolyte, including several elongated voids nearly spanning the thickness between cathode and anode. The solid phases within each electrode have also been segmented, which can provide geometric microstructural properties such as porosity, volume fractions, size distributions, and triple phase boundary density.

References:

[1] Merkle, A. and Gelb, J., "The ascent of 3D X-ray microscopy in the laboratory," Microscopy Today, Vol. 21 (2013): 10–15.

[2] Cronin, J. et al., "Three-dimensional reconstruction and analysis of an entire solid oxide fuel cell by full-field transmission X-ray microscopy," J. Power Sources, Vol. 233 (2013): 174–179.

[3] Nelson, G. et al., "Three-dimensional microstructural changes in the Ni-YSZ solid oxide fuel cell anode during operation," Acta Materialia, Vol. 60 (2012): 3491-3500.

[4] Shearing, P. et al., "Exploring microstructural changes associated with oxidation in Ni-YSZ SOFC electrodes using high resolution X-ray computed tomography," Solid State Ionics, Vol. 216 (2012): 69-72.

[5] Shearing, P. et al., "X-ray nano computerised tomography of SOFC electrodes using a focused ion beam sample-preparation technique," J. Eur. Ceram. Soc., Vol. 30 (2010): 1809–1814.

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