

3D microstructural characterization of the triple phase boundary length in solid oxide fuel cell/electrolyzer devices

Authors

Chengge Jiao, Bart Winiarski, Patrick Barthelemy, Dirk Laeveren, Ernst Jan Vesseur, and Scott Barnett*

* Northwestern University

Introduction

Solid oxide electrolyzer cells (SOECs) and solid oxide fuel cells (SOFCs) could enable decarbonization in a range of sectors and are therefore promising components of a sustainable future. SOFCs can use hydrogen and air to produce electrical power with only water steam as exhaust gas, while SOECs produce hydrogen with electrical power through water splitting. SOECs can also be used for the conversion of CO_2 into CO and O_2 . In practice, electrolysis and power generation are both supported by the same solid oxide cell (operated either as an electrolyzer or fuel cell), which is constructed as a composite of ceramic materials containing nickel. Whether it is for sustainable hydrogen production, the generation of ammonia, hydrocarbon production with CO_2 electrolysis, or power generation for the grid, it is vital that solid oxide devices are efficient and robust.¹

These properties are closely related to the micro- and nano-structure of the electrodes and electrolyte in the cell. Operating at high temperatures, solid oxide devices can suffer from cracking, nickel migration, or poisoning. It is important to characterize these degradation mechanisms to improve device lifetime. In this application note, advanced imaging techniques were employed to gain insights into these intricate 3D microstructures, utilizing the Thermo Scientific[™] Helios Hydra[™] Plasma Focused Ion Beam Scanning Electron Microscope (PFIB-SEM) and multi-detector image acquisition. Sophisticated software and deep learning techniques provided image processing and segmentation for the accurate analysis of material connectivity and voids. This comprehensive approach not only advances our understanding of triple-phase-boundary dynamics but also paves the way for the optimization of electrode materials and microstructures in SOECs and SOFCs, contributing to the development of more efficient and sustainable energy systems.





Figure 1. Solid oxide fuel cell cross-section. Hydrogen gas is added at the fuel electrode (anode) of the cell, while air (oxygen gas) is supplied at the cathode side. Through the electrochemical reactions, hydrogen is oxidized at the anode, and oxygen is reduced at the cathode, resulting in the generation of electrical energy and water as a byproduct. Oxygen, oxygen ions, water, hydrogen, and electrons all need to be transported in the cell. This depends on the porosity and interconnectivity of the ceramic (YSZ/LSCF) and nickel.

Fuel electrode structure in solid oxide cells

A solid oxide cell is composed of an air electrode, electrolyte, and fuel electrode. This application note focuses on the fuel electrode, which typically consists of three phases: metal (nickel), ceramic (YSZ), and voids. These phases are required for conducting electric current, ions (O₂-), and gases, respectively. The nickel has an additional function as a reaction catalyst at the fuel electrode, which only functions well if the nickel forms a continuous network that allows effective current distribution. Nickel can also exist as isolated clusters (so-called non-percolating nickel); increased amounts of these isolated nickel islands reduce electrode activity and performance. Non-percolating voids, similar to non-percolating nickel, disrupt pathways for gas diffusion, leading to uneven current distribution and reduced efficiency.

If nickel, ceramic, and voids are properly interconnected, they bring electrons, O_2 - ions, H_2 , and H_2O together for the reduction or oxidation reaction, depending on the operating mode of the cell. The place where these three phases meet is called the triple-phase boundary (TPB), and it is only here that the reaction takes place. This makes TPB length a crucial parameter in the optimization of a solid oxide cell.

Fabrication processes for solid oxide devices strive to optimize the TPB length by creating a well-distributed network of nickel, ceramic, and voids, which requires advanced materials engineering and characterization techniques. This application note explores an improved 3D characterization method for solid oxide cells. The active TPB length is measured by determining the relative volume fractions of the different phases, and the interconnectivity between these materials.





Figure 2. a) Schematic of a solid oxide cell sample, as prepared for 3D acquisition. The dashed rectangle indicates where PFIB slicing is performed. b) SEM image showing a cross section of the cell, corresponding to the dashed rectangle in (a). The red box indicated in (b) shows the area that is processed for segmentation and analysis of TPB length.

Method

The solid oxide cell studied in this application note incorporates yttria-stabilized zirconia (YSZ) as the solid electrolyte, while both electrodes are constructed using Ni-YSZ materials (this test cell utilizes two fuel electrodes in order to focus on phenomena in the Ni-YSZ).² The sample preparation prior to imaging consisted of filling the pores with high-pressure conductive resin, followed by a mechanical polish.

The Helios Hydra PFIB-SEM was used for large-volume 3D characterization. First, a capping layer was deposited onto the top surface using ion-beam induced deposition (IBID) of Pt + C precursor gases flowing through a Thermo Scientific™ MultiChem[™] Gas Delivery System. Then, a stack of images was acquired using Thermo Scientific Auto Slice and View™ (AS&V) 5 Software. AS&V Software allows Thermo Scientific™ DualBeam[™] Instruments (FIB-SEMs) to automate the acquisition of high-resolution images for the creation of 3D image data. Here, the PFIB used a 60 nA Xe ion beam for milling of serial sections (50-nm-thick slices), including a rocking polish approach and perpendicular imaging. Each slice was imaged with a field of view that included the electrolyte and the support layer on each side. The chosen pixel size was 32 nm, so that a typical Ni feature was sampled by 5-10 pixels. In total, a volume of 184 x 117 x 30 μ m³ was acquired, and a 18 x 98 x 21 μ m³ sub-volume was selected for subsequent image analysis. For each slice of the dataset, two images were simultaneously taken using a retractable backscatter electron (BSE) detector and a through-the-lens detector (TLD) for secondary electrons (SE).

The simultaneous acquisition of BSE and SE images, pixel by pixel, facilitated the identification of voids, YSZ, and Ni components using automatic segmentation and deep learning in Thermo Scientific[™] Avizo[™] Software. While the BSE images (Figure 3a) provide good porosity contrast, the SE images (Figure 3b) are combined for Ni and YSZ identification, allowing for the correct detection of unfilled or partially filled voids.

From these slices, a virtual 3D volume was reconstructed and segmented for these three materials. Based on this segmentation, the respective volume fractions and percolating/ non-percolating ratios were computed.



Figure 3. Simultaneously collected (a) BSE images and (b) SE images along with (c) segmentation performed in Avizo Software. Nickel: red, YSZ: dark blue, voids: light blue.

Results

Representative region-of-interest images are shown in Figure 3a and 3b, showing a clear contrast between all materials without FIB artifacts such as curtaining, resulting in a highquality segmentation between nickel, YSZ, and voids (Figure 3c). The images in Figure 4 also shows that unfilled or partially filled voids were correctly identified.



Figure 4. Identification of nickel, ceramic, and void. A) Backscattered electron image. B) Secondary electron image. C) Segmentation based on the combination of BSE and SE. Nickel: red (32%), YSZ: dark blue (50%), voids: light blue (18%).

The 3D virtual volume data can be used to further segment the percolating and non-percolating fractions, separately showing the percolating nickel and isolated nickel features (Figure 5a and 5b, respectively). Additionally, the area of each phase can be plotted in cross-sections parallel to the electrolyte (Figure 5c), with the direction indicated by the arrow in 5a. The results show that most of the nickel is well connected – the volume fraction of non-percolating nickel is about 1.2%. The concentrations of nickel, YSZ, and voids remain relatively constant as a function of distance from the electrolyte.



Figure 5. Phase areas in cross-sections throughout the 3D volume. a) Connected nickel. b) Isolated fractions.

Finally, TPB lines were extracted from the 3D percolating volume (Figure 6), and phase-to-phase contact areas (Table 1) were evaluated.







Figure 6. TPB lines (b) after extraction from the 3D percolating volume (a).

TPB 1.22 μm/μm ³	Pores	YSZ	Ni
Surface µm²/µm ³	1.02	2.11	1.40
Pores µm²/µm³		0.77	0.19
YSZ µm²/µm³	0.77		1.03
Ni µm²/µm³	0.19	1.03	

Table 1. Evaluation of phase-to-phase contact areas in a fuel electrode.

These results show that the electrode had a relatively low active TPB density, due in part to a large feature size arising from the relatively high firing temperature of 1,400°C. Although Ni connectivity was good, ~20% of pores were isolated, reducing the active TPB density. Thus, the electrode could be improved by reducing firing temperature, thereby decreasing feature size and increasing porosity.

Conclusion

This application note demonstrates that the 3D structure of solid oxide electrolyzers and fuel cell devices can be analyzed using PFIB milling and subsequent SEM imaging (slice-and-view). The PFIB allows a large sample volume to be measured, providing better statistics for the measured values. The measurements are made with multiple detectors, allowing clearer identification of Ni, YSZ, and pore phases, while artifacts such as curtaining are eliminated. Advanced segmentation eliminates other artifacts such as incomplete epoxy filling of pores. Both percolating and isolated volumes of nickel, ceramic, and voids were measured, and this data was then used to calculate the density of triple phase boundaries in relation to their distance from the electrolyte. This information is valuable for researchers and developers of novel electrolyzers and fuel cells, as it enhances their understanding of how these devices perform and/or degrade.

References

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