Microstructural Evolution in LSM-YSZ Cathodes over Two Years of SOFC Operation

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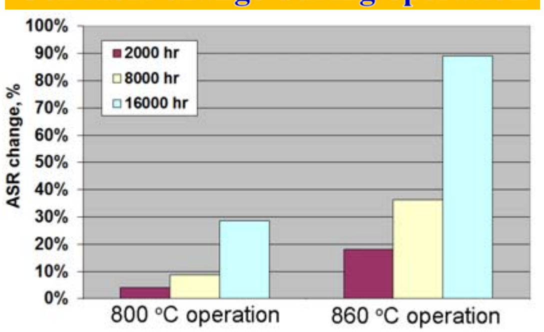
Abstract

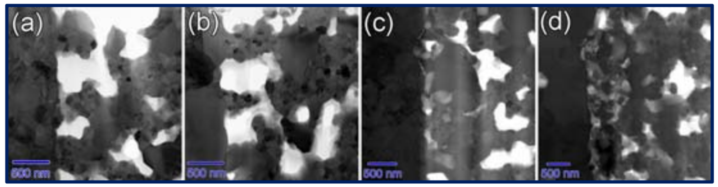
(La,Sr)MnO_3–yttria-stabilized zirconia (LSM–YSZ) SOFC cathodes gradually degrade during prolonged operation. Detailed studies of microstructural evolution at the cathode-electrolyte interface were performed on SOFCs after operation for up to 17,400 hours at different operating temperatures. Thin foils from the cathode/electrolyte interface were prepared using a focused-ion beam (FIB) milling technique. Transmission electron microscopy (TEM) with energy-dispersive x-ray spectroscopy (EDXS) was employed for chemical analysis and to detect and identify secondary phases. Three-dimensional (3D) reconstruction of the microstructures was performed using the FIB "slice and view" technique, in conjunction with TEM, to document and understand changes in the distribution and volume fractions of phases during long-term testing. Microstructural changes, including densification of the LSM phase near the cathode-electrolyte interface, were observed after two years of testing at 860 °C. Formation of manganese oxides was also detected, tending to concentrate near the cathode-electrolyte interface after one to two years of operation, especially at 860 °C.

Cell ASR change during operation

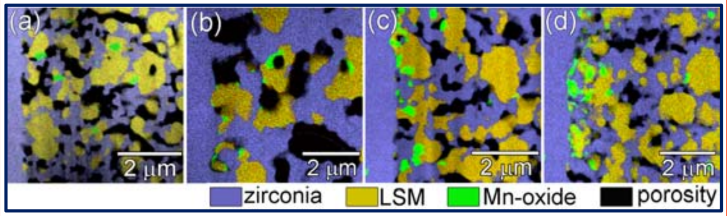


➢ **Figure 1.** Average Cell ASR change (from t=0) as a function of testing duration for the cells tested at 800°C (left) and 860°C (right).

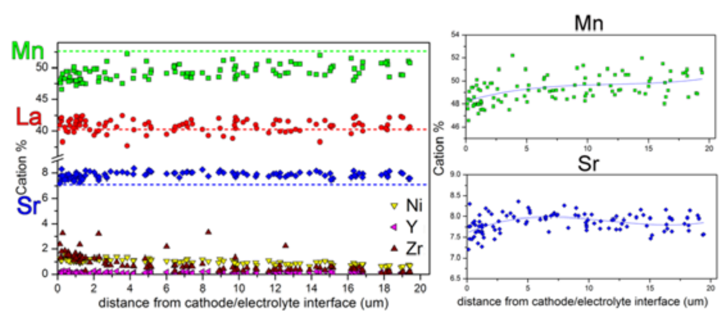
Microstructural change at 800°C



➢ **Figure 2.** TEM bright-field images acquired across the cathode-electrolyte interface for (a) the as-fired cell, (b) the 800 °C-2000 h cell (c) the 800 °C-8000 h cell, and (d) the 800°C-16000 h cell. (The electrolyte is at the left edge in each image.)

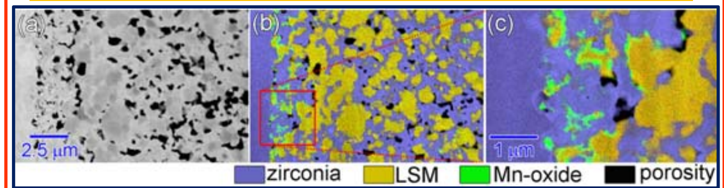


➢ **Figure 3.** EDXS elemental maps acquired across the cathode-electrolyte interface for (a) the as-fired cell, (b) the 800 °C-2000 h cell (c) the 800 °C-8000 h cell, and (d) the 800°C-16000 h cell. (The electrolyte is at the left edge in each image.)

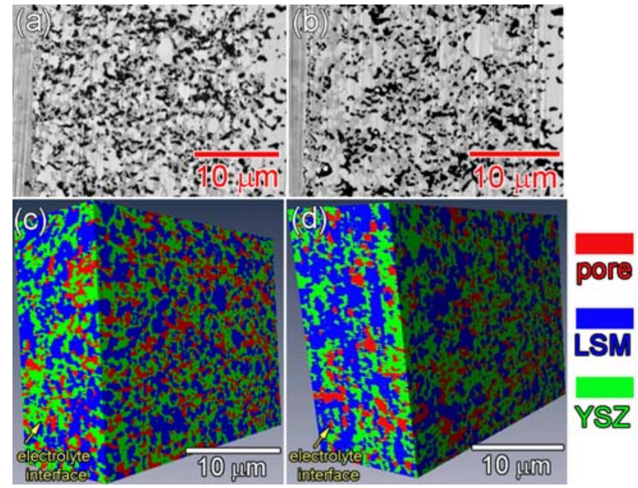


➢ **Figure 4.** Left: EDXS concentration profile of Mn, La, Sr, and other elements in the LSM (spot analyses) as a function of distance from the cathode-electrolyte interface for the 800°C-16000 h cell. Dashed line: nominal concentration of Mn, La, and Sr. Right: Scaled-up profile for Mn and Sr.

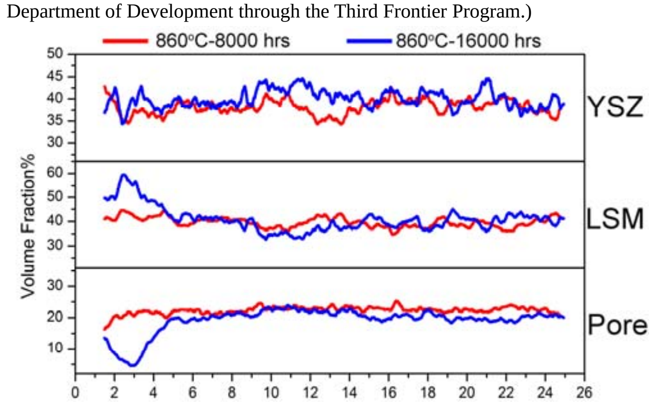
Cathode densification at 860°C



➢ **Figure 5.** (a) STEM dark-field image and (b) the corresponding EDS elemental map for the cell tested at 860°C for 16000 h. (c) is the magnified map acquired from the red box region in (b) showing the microstructural change near the electrolyte interface. (The electrolyte is at the left edge in each image.)



➢ **Figure 6.** SEM images of the cathode (electrolyte at left) for the 860 °C cells after testing for (a) 8000 h and (b) 16000 h. The 3D reconstruction of these cathodes are in (c) and (d) respectively. (The 3D work was supported by the Ohio Department of Development through the Third Frontier Program.)



➢ **Figure 7.** Comparison of volume fraction profile including the YSZ, LSM, and pore phases in cells tested at 860 °C for 8000 h (red) and 16000 h (blue).

Summary

1. Operation of SOFCs at 800°C and 860°C for prolonged durations increases the ASR (Figure 1).
2. TEM analyses revealed formation of Mn-oxide and LSM densification primarily near the cathode-electrolyte interface with increasing testing time at both 800 °C and 860 °C. (Figures 2, 3, and 5).
3. The Mn content in the bulk LSM decreased near the cathode-electrolyte interface after two years SOFC operation at 800 °C (Figure 4).
4. 3D reconstruction revealed a decreasing pore volume fraction, and an increasing LSM volume fraction, near the cathode-electrolyte interface. This verified that LSM densification occurred during two years of SOFC operation at 860 °C (Figures 6 and 7).

This research is based upon work supported by the Department of Energy, National Energy Technology Laboratory under Award Number DE-FE0000303. This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.