

Hsiang-Jen Wang<sup>1</sup>, Mark R. De Guire<sup>1</sup>, Richard Goettler<sup>2</sup>, Zhien Liu<sup>2</sup>, and Arthur H. Heuer<sup>1</sup>

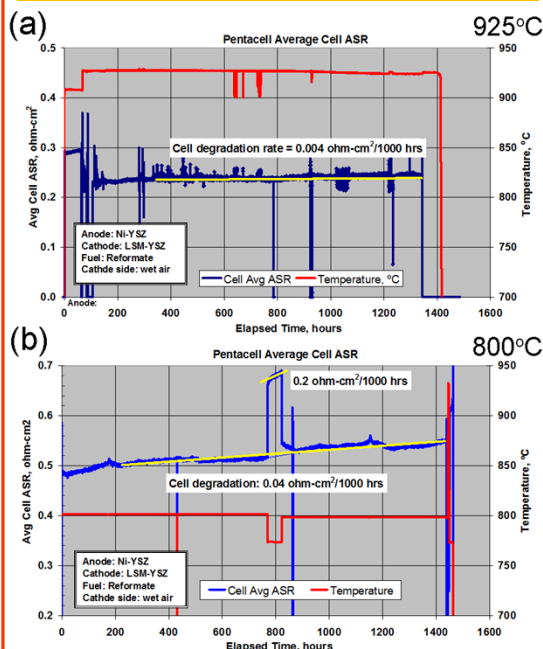
<sup>1</sup>) Dept. of Materials Science and Engineering, Case Western Reserve University, Cleveland, OH 44106;

<sup>2</sup>) Rolls-Royce Fuel Cell Systems (US) Inc., North Canton, Ohio 44720

## Abstract

In solid oxide fuel cells (SOFC) with lanthanum strontium manganite (LSM)-based cathodes and zirconia-based electrolytes, excess Mn is often added to the LSM to prevent the formation of lanthanum zirconates. The degradation rate (increase of area specific resistance (ASR) with time) in such cells is significantly higher at lower temperatures (e.g. 800°C) than at higher temperatures (e.g. 925°C), with 1-3% moisture present in the cathode environment. Therefore, a detailed study of microstructural changes at the cathode-electrolyte interface was performed on SOFCs after long-term operation at different temperatures with some steam applied in the cathode gas. 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 (EDS) was used to determine concentration profiles and to detect and identify secondary phases. Electron energy-loss spectroscopy (EELS) was employed to measure Mn valence state. This technique has been validated by X-ray photoelectron spectroscopy (XPS). Submicron manganese oxide particles were detected near the cathode-electrolyte interface: Mn<sub>2</sub>O<sub>3</sub> in cells operated at 925°C, and both Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>2</sub>O in cells operated at 800°C.

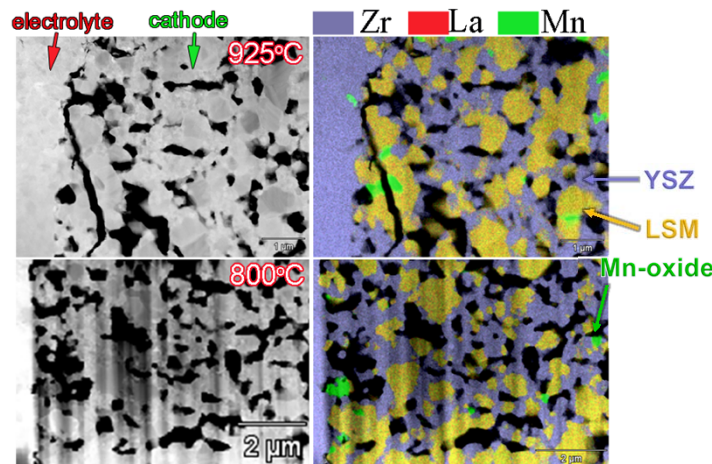
## Cell Performance vs. Temperature



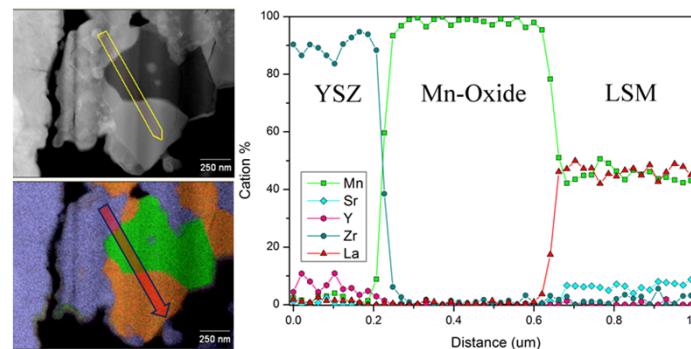
**Figure 1.** (a) Cell ASR with H<sub>2</sub>O in cathode environment as a function of operating temperature: (a) 925°C (1340 hrs) and (b) 800°C (1450 hrs).

© 2011 Rolls-Royce Fuel Cell Systems (US) Inc. This material is based upon work supported by the U.S. Department of Energy under Award Number DE-EE0000303. Used with permission.

## Chemical Analysis

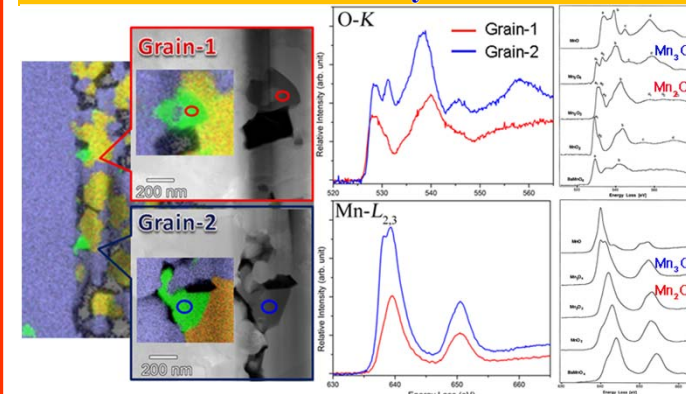


**Figure 2.** Left: STEM images of cells in Figure 1 across electrolyte (YSZ)/cathode (LSM+YSZ) interface of SOFCs operated at 925°C (top) and 800°C (bottom). Right: Corresponding elemental maps, constructed by superimposing Zr, Mn, and La maps.



**Figure 3.** STEM bright-field image (upper left), EDS elemental map (lower left), and the elemental concentration profiles (right) acquired across YSZ/Mn-oxide/LSM phases along the indicated arrow, in a cell operated at 925°C.

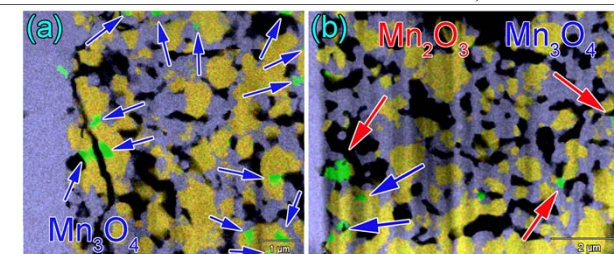
## EELS Analysis



**Figure 4.** EELS fine structure of O-K and Mn-L<sub>2,3</sub> edges from two Mn-oxide grains at the cathode-electrolyte interface of an SOFC operated at 800°C. Comparison to reference spectra (from [1]) indicates that grain 1 is Mn<sub>2</sub>O<sub>3</sub> and grain 2 is Mn<sub>3</sub>O<sub>4</sub>.

**Table 1.** Quantitative EELS data of Mn-L<sub>2,3</sub> edge from grain 1 and grain 2 (Figure 4) compared to reference values for Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub>. [2]

|   | Grain-1(Mn <sub>2</sub> O <sub>3</sub> ) | Mn <sub>2</sub> O <sub>3</sub> | Grain-2(Mn <sub>3</sub> O <sub>4</sub> ) | Mn <sub>3</sub> O <sub>4</sub> |
|---|--|--------------------------------|--|--------------------------------|
| L <sub>2</sub> (eV)                       | 639.7                                    |                                | 639.4                                    |                                |
| L <sub>3</sub> (eV)                       | 650.5                                    |                                | 650.5                                    |                                |
| ΔE (L <sub>2</sub> -L <sub>3</sub> ) (eV) | 10.8                                     | 10.8[2]                        | 11.1                                     | 11.2[2]                        |
| L <sub>3</sub> /L <sub>2</sub>            | 2.5                                      | 2.4(0.1)[2]                    | 3.0                                      | 2.8(0.2)[2]                    |
| Valence state                             | +3                                       |                                | +3,+2                                    |                                |



**Figure 5.** EDS maps of LSM-YSZ cathodes. EELS analysis (as in Figure 4) indicated that Mn-oxides in cells operated at 925°C were Mn<sub>3</sub>O<sub>4</sub> (a), whereas cells operated at 800°C contained Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> grains (b).

## Summary

1. Operation of the SOFC increased the ASR (Figure 1) more rapidly at 800°C than at 925°C when H<sub>2</sub>O is present in the cathode environment.
2. EDS mapping results revealed Mn-rich phases in the LSM-YSZ cathode after testing in both cells (Figure 2).
3. STEM-EDS showed that the Mn-rich phases contained little or no other metal elements, indicating they were Mn-oxides (Figure 3).
4. EELS showed that for the cell operated at 925°C, all Mn-oxide phases were Mn<sub>3</sub>O<sub>4</sub>. In contrast, both Mn<sub>2</sub>O<sub>3</sub> and Mn<sub>3</sub>O<sub>4</sub> were present in the cell operated at 800°C (Figures 4 and 5).

## References

1. H. Kurata and C. Colliex, *Phys. Rev. B*, **48** (1993) 2102-2108.
2. H. K. Schmid, W. Mader, *Micron* **37** (2006) 426-432.

## Financial Support

Solid State Energy Conversion Alliance Program, U.S. Department of Energy