

EBSD Analysis of Undesired Phase Development in Solid Oxide Fuel Cell (SOFC) Lanthanum Strontium Manganese Oxide (LSM) / 8 mol% Yttrium Zirconium Oxide (8YSZ) Cathodes During Long-Term Thermal Anneal

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SOFC's were prepared from four LSM-8YSZ based compositions: LSM-20-98 [(La_{0.8}Sr_{0.2})_{0.98}MnO_{3-δ} - (Y₂O₃)_{0.08}(ZrO₂)_{0.92}], LSM-20-95 [(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ} - (Y₂O₃)_{0.08}(ZrO₂)_{0.92}], LSM-10-98 [(La_{0.9}Sr_{0.1})_{0.98}MnO_{3-δ} - (Y₂O₃)_{0.08}(ZrO₂)_{0.92}], and LSM-20-90 [(La_{0.8}Sr_{0.2})_{0.90}MnO_{3-δ} - (Y₂O₃)_{0.08}(ZrO₂)_{0.92}]. A fifth set of cells was procured with cathodes prepared by a commercial vendor, Fuel Cell Materials [Lewis Center, OH] LSM-20-95 FCM [(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-δ} - (Y₂O₃)_{0.08}(ZrO₂)_{0.92}].

Cells of each composition were placed into furnaces and heated to 800°C, 900°C, or 1000°C. One cell of each composition was then removed from the furnaces at each temperature after 1000, 2000, 4000, 8000, 12000, and 16000 hours for EBSD analysis. For cells thermally annealed to 800°C, regardless of time, no undesired phases were noted. There were two undesired phases found in cells thermally annealed to 1000°C – monoclinic zirconia (MZrO) and strontium chromate (SrCrO₄). For cells thermally annealed at 900°C, only LSM-20-90/YSZ showed a very small (0.5%) concentration of SrCrO₄. Therefore, only the cells thermally annealed at 1000°C will be discussed.

Chemical characterization of all cells using EDS did not find any unexpected phases in the LSM/YSZ cathodes. MZrO would not be detected by EDS, because this phase has the same elemental composition as the YSZ in the cathode. For SrCrO₄, it is likely that the large beam interaction volume with the sample, and the small concentration of Cr in that volume, detection limits preclude distinguishing Cr from background. However, due to the superior spatial resolution and very shallow surface sampling depth of EBSD, detection of the MZrO and SrCrO₄ phases was easily achieved.

Figure 1 shows the concentration of MZrO and SrCrO₄ as a function of thermal annealing time for each cathode composition. Figure 1a shows that MZrO concentration varies widely with time for all LSM/YSZ compositions at 1000°C. Figure 1b shows a generally increasing trend in SrCrO₄ content for the three prepared LSM20/YSZ cathodes (i.e. LSM20-98, 20-95, and 20-90). The LSM20-95/YSZ FCM commercial cathode showed no SrCrO₄ concentration until 16000 hrs at 1000°C. The LSM10-98/YSZ cathode material showed no SrCrO₄ phase development up to 16000 hrs.

The SrCrO₄ appears to be most prevalent in the LSM20-90/YSZ, while the LSM20-95 and LSM20-98/YSZ appear to have far less of the SrCrO₄ phase – possibly indicating that decreasing Lanthanum and Strontium concentration relative to Manganese could potentially promote SrCrO₄ formation. Furthermore, the LSM-10-98/YSZ cathode has reduced Strontium content relative to Lanthanum compared to LSM-20-98/YSZ, which resulted in the least/no SrCrO₄ formation.

Discovery of SrCrO₄ in the cathode materials requires a source of Cr contamination. The most likely source is exposed Ni80Cr20 heating elements in the furnaces used for thermal annealing of the cells.

FactSage was used to calculate Cr species vapor pressures based on local average relative humidity of 80.4% and average temperature of 52.9°F, which equates to an average water partial pressure of 0.0109 atm. Assuming either NiCr_2O_4 or Cr_2O_3 scale formation on the Ni80Cr20 elements, the Cr vapor pressure would fall within a range of $4.03\text{E-}7$ to $7.00\text{E-}4$ atm at 1000°C .

Unfortunately, for samples with thermal annealing times up to 12000 hours, furnace locations of cells were not tracked. Therefore, variability in concentration of SrCrO_4 as a function of time are thought to be due to differing proximity of the cells to the heating elements causing differences in the Cr concentration in the local environment of each cell. For instance, if the cells extracted from the furnace after 8000 hour cells for the LSM20-98 and LSM20-95/YSZ cells were substantially closer to the heating elements than similar cells extracted after 12000 hours, it is reasonable to assume that more SrCrO_4 could have formed in the 8000 hour sample than in the 12000 hour sample. Variation in MZrO content in the cathodes appears quite random, and may be due to destabilization of the YSZ, as the sole purpose of the 8mol% yttrium addition to the zirconium oxide is to lock the cubic phase of the lattice and prevent phase changes with temperature. Monoclinic is the stable phase of unstabilized zirconium oxide at room temperature.

Additional cells are continuing to run beyond 16000 hours for each composition, and locations of each cell will be tracked to attempt to validate this hypothesis, and to see how undesired phase development continues with additional thermal annealing time for all cathode compositions. It is hoped that these additional tests will lead to a more complete understanding of SrCrO_4 formation in LSM/YSZ cathodes.

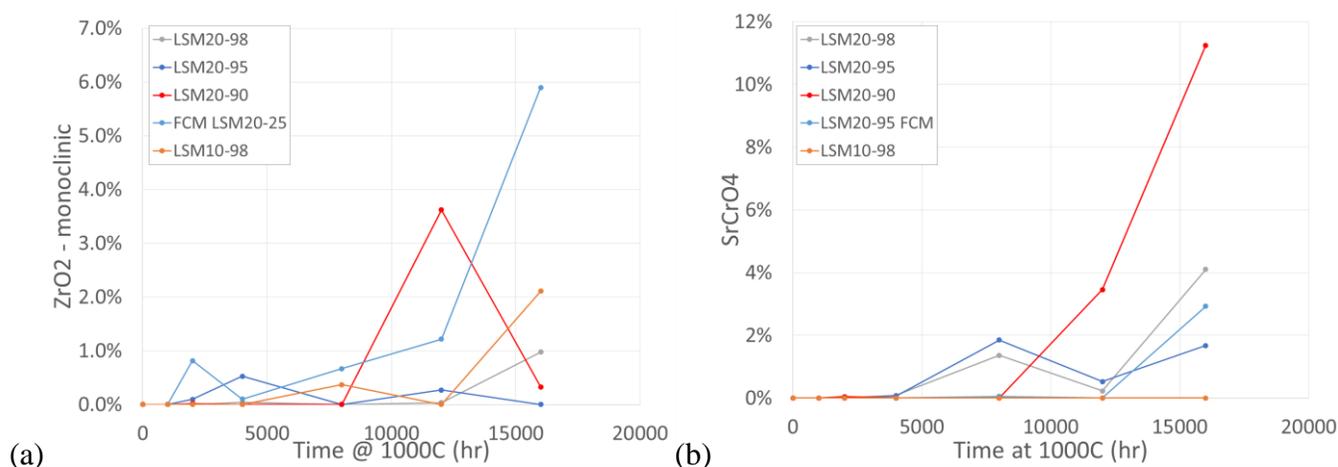


Figure 1. Concentrations of (a) monoclinic zirconia and (b) strontium chromate discovered by EBSD in LSM/YSZ cathodes after thermal annealing at 1000°C for various times.