Mitigation of Degradation associated with Elevated Steam Content in SOFC cathode oxidant by Surface Modification

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Introduction
Moisture content in cathode feed air is postulated to lead to performance degradation in LSM and LSCF cathodes.

- PNNL: Humidity causes degradation in the performance of LSM/YSZ cathodes. It is more pronounced at lower temperature, partially reversible.
- Case Western Reserve Univ.: Abrupt rise in ASR was observed upon 3% steam introduction.
- Kyushu Univ.: Steam decomposes LSM to form MnO on the LSM surface rather than at cathode / electrolyte interface (Lu et al.) / Power Sources, 20k (2002) 7909.

Proposed degradation mechanism:
\[
\text{LaMnO}_3 + \frac{1}{2} \text{H}_2\text{O} = \text{La(OH)}_2 + \frac{1}{2} \text{Mn}_2\text{O}_3
\]
\[
2 \text{La(OH)}_2 + \text{H}_2\text{O} = \text{La}_2\text{O}_3 + 3\text{H}_2\text{O}
\]
The group observed Mn$_2$O$_3$ possibly due to further reduction of MnO$_x$.

Steam Content (10 % vs. 20 %) Effect

Cell voltage under 0.25 A/cm$^2$

- Steaming under 10% steam:
  - No noticeable degradation was observed for the cells tested under 10% steam.
  - Cell performance was severely degraded under 20% steam, particularly within 100 h after current loading.

Surface Modification with Mn

Possible degradation mechanisms under high steam content

- Accelerated removal of Mn from LSM/YSZ interface and eventual decomposition of LSM
- Prevent Mn deficiency (LSM decomposition)

Deactivation of surface near TPB due to absorption of steam-originated functional groups

1. No noticeable degradation was observed for the cells tested under 10% steam.
2. Cell performance was severely degraded under 20% steam, particularly within 100 h after current loading.
3. The observed degradation is analyzed to be related with surface oxygen exchange and/or oxidant gas concentration at cathode.

- Mn infiltrate on LSM/YSZ cathode were coarsened with operation period.

Purpose of the Study

- Determine the effects of high steam on cathode performance;
- Identify the underlying mechanisms responsible for cathode degradation;
- Improve long-term stability of SOFC by modifying cathode structure (surface composition) based on mechanistic understanding of cathode degradation.

NETL Operating Parameters

- Commercially available MSR anode supported cells
- Cathode: LSM/La$_{0.2}$Sr$_{0.8}$CoO$_{3}$ / YSZ active layer
- Electrolyte: YSZ; Anode: Ni-YSZ

Steam Generation:
- Saturated steam is pressure/temperature controlled and injected through a restrictive flow orifice at choked flow conditions.

Operating Conditions:
- 800°C, 0.75 A/cm$^2$ or 0.25 A/cm$^2$
- 10 or 20% steam content / balance air

Operating Current (0.25 A/cm$^2$ vs. 0.75 A/cm$^2$) Effect

Cell voltage under 10% steam

- 0.25 A/cm$^2$:
  - No noticeable degradation was observed for the cells tested under 0.25 A/cm$^2$.
  - Cells were severely degraded when tested under higher current density (0.75 A/cm$^2$).
  - Degradation rates were relatively independent on operation time (linear relationship) over all the test period.

Mn infiltrate on LSM/YSZ cathode were coarsened with operation period.

Summary & Conclusion

- Steam content in air matters to cell degradation rate at low current density (0.25 A/cm$^2$): (1) Essentially no degradation with 10% steam; and (2) Rapid initial degradation followed by a slower, more linear degradation at extended time with 20% steam.
- Current density matters to cell degradation rate at relatively low steam content (10%): Accelerated degradation was observed for the cells tested at the higher current density, 0.75 A/cm$^2$.
- Mn was introduced into LSM/YSZ cathode by solution infiltration method to modify surfaces of the composite cathode with the expectation that it prevents Mn deficiency from LSM/YSZ interface and extend effective three-phase boundary (TPB) under high steam condition.
- Mn-infiltrated cells showed performance improvement initially, and maintained lower degradation rates compared to uninfiltrated cells.

This study demonstrates the effects of steam content and operating current density on cathode degradation rate, and suggests that surface modification by infiltration is a technique to mitigate electrode degradation.