Understanding the effect of contaminants on LSCF cathode performance

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Motivation

- Cathode durability is critical to long-term reliable SOFC performance for commercial deployment.
- Current state-of-the-art SOFC cathode materials are susceptible to degradation due to contaminants under realistic operating conditions (ROC).
- Mitigating the stability issues by design of new materials or electrode structures will reduce the cost of SOFCs and help to meet DOE cost and performance goals.

Project Objectives

- To characterize the electrochemical behavior of LSCF exposed to contaminants under realistic operating conditions (ROC);
- To probe the surface species/phases of LSCF cathodes exposed to contaminants under ROC using in situ and ex situ measurements performed on specially-designed cathodes;
- To unravel the degradation mechanism of LSCF cathodes by correlating the changes in performance with the surface chemistry, microstructure, and morphology under ROC;
- To establish scientific basis for rational design of new catalysts of high tolerance to contaminants;
- To validate the long term stability of modified LSCF cathodes in commercially available cells under ROC.
Accomplishments to Date

- Characterized **electrochemical behavior** of **porous** and **dense** thin-film LSCF cathodes exposed to H$_2$O, CO$_2$ and Cr under ROC;

- Probed and mapped **surface species/phases** of LSCF cathodes exposed to contaminants using SERS;

- Designed and implemented an **in operando SOFC testing assembly** capable of probing **thin-film** LSCF cells using **synchrotron-based X-ray techniques**.

Cell Configurations

- For electrochemical testing of **porous**, **dense** thin-film, and **patterned** LSCF electrodes under realistic operational conditions.
**Effect of H₂O on porous LSCF cathodes**

- Performance change is relatively small with addition up to 10% H₂O, regardless of electrical polarization (including OCV).
- The small effect is reversible upon H₂O removal.

**Effect of CO₂ on porous LSCF performance**

- Performance change is visible at 5% CO₂ under OCV and 3% CO₂ under polarization.
- The small effect is reversible upon CO₂ removal.
Effect of Cr and H2O on porous LSCF performance

- Severe degradation when the LSCF is in direct contact with the Cr-containing alloy
- H2O can exacerbate the degradation

Polarization Behavior of porous LSCF cathode in contact with Cr at H2O

- Gradual degradation when water is added.
- In contrast, relatively stable performance was observed without water.
Test Cells with thin-film or pattern electrodes

- A dense thin-film or patterned electrode with well-defined geometry, ideally suited for fundamental study.
- The top surface is open to \textit{in situ} or \textit{in operando} Raman and X-Ray analysis.
- No need for reference electrode because $R_{\text{WE}} \gg R_{\text{CE}}$
- Sheet resistance is not a problem since a Pt mesh was used as CC

Adjust the stoichiometry of LSCF Film

The sputtering parameters determine the stoichiometry of LSCF films; e.g., the partial pressure of O$_2$ in the chamber plays an important role. We optimized the pO$_2$ to obtain LSCF film with A/B ratio close to 1:1

<table>
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<tr>
<th>Parameter</th>
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<tr>
<td>Pressure</td>
<td>$2.2 \times 10^{-2}$ mBar</td>
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<tr>
<td>Temperature</td>
<td>Room Temp</td>
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<tr>
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<td>Target Size</td>
<td>1 inch</td>
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<tr>
<td>Power</td>
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![Graph showing AB ratio vs. O2 composition](image)
The sputtered LSCF film with 1:1 A/B ratio is annealed in air at 800°C for 1hr, and cross-sectional view was taken to determine the sputtering rate (~30 nm/hr) and surface morphology.

Thin Film LSCF cathode exposed to contaminants

Stability of thin film

- With H₂O
  - 0% H₂O
  - 3% H₂O
  - 5% H₂O

- With CO₂
  - 10% CO₂
  - 1% CO₂
  - 3% CO₂
  - 5% CO₂
  - 10% CO₂

- With Cr+H₂O
  - 6h
  - 1h
  - 2h
  - 3h
  - 24h
Accomplishments to Date

- Characterized electrochemical behavior of porous and dense thin-film LSCF cathodes exposed to H₂O, CO₂ and Cr under ROC;
- Probed and mapped surface species/phases of LSCF cathodes exposed to contaminants using SERS;
- Designed and implemented an in operando SOFC testing assembly capable of probing thin-film LSCF cells using synchrotron-based X-ray techniques.

Surface Characterization

To characterize changes in surface chemistry, structure, and morphology of LSCF cathodes, with or without exposure to contaminants, using Raman spectroscopy and synchrotron-based X-ray analyses under in situ or ex situ conditions.

*in situ and ex situ Raman:*

monitor the surface chemistry, e.g., interactions between LSCF and CO₂, water vapor, or Cr. The reaction products (e.g., SrCO₃) are Raman-active.
**Surface Enhanced Raman Spectroscopy (SERS)**

Li, Mostafa, Bottomley, Liu et al., PCCP, 14, 5919, 2012.

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**SERS Analysis of LSCF Surfaces**

**Raman:** Fingerprints the surface chemicals on the LSCF cathodes.

**Surface Enhanced Raman Spectroscopy (SERS):** Enhances the sensitivity to contaminants of low concentrations.

**Accelerated Degradation Tests:**
LSCF pellets, thin films, and patterned electrodes exposed to CO₂, H₂O containing atmospheres at 750°C.

**Probed** surface contaminants that is related to degradation
**Mapped** the spatial distribution of contaminants.
Typical Raman Spectra of LSCF

- 310, 540 and 720 cm\(^{-1}\) are associated with the rhombohedral (r3c) group of LSCF

SERS features of LSCF Degradation

- The emerging of peaks on 930 cm\(^{-1}\) and 980 cm\(^{-1}\) indicates the formation of orthorhombic (pbmn) perovskite phase, which could be La(Co, Fe)O\(_3\) that is related to SrO segregation. [1]

- 810 cm\(^{-1}\) and 860 cm\(^{-1}\) peaks are related to SrCrO\(_4\)

- 340 cm\(^{-1}\) peak is related to Cr\(_2\)O\(_3\) deposition on LSCF surface. [2]

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Patterned Electrode Study

- **LSCF Patterned Electrodes**
- **Cr Alloy**
- **GDC**
- **Porous LSCF Counter Electrode**

To study the spatial distribution of surface Cr species

To evaluate the effect of bias on the distribution of Cr species.

- Tested in the Raman Chamber at 550°C
- in air with 3% water vapor
- at a cathodic bias of 1.0 V
- for a duration of 12 hrs

Cr Deposition on LSCF Electrodes

- Mapping of Cr containing species assisted by SERS
- SrCrO₄ preferentially deposits on LSCF-GDC interface
- Bias has no impact on the SrCrO₄ deposition.
TEM images showing core-shell nanoparticles.
Size of the silver NPs: 50nm Thickness of the SiO₂: 5nm

SEM images. High temperature treatment did not change the shape and distribution.

Accomplishments to Date

- Characterized electrochemical behavior of porous and dense thin-film LSCF cathodes exposed to H₂O, CO₂ and Cr under ROC;
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In Operando XAS for SOFCs

- Working electrode: 200 nm thin film LSCF (sputter deposited)
- Electrolyte: single crystal YSZ
- Counter electrode: porous tape-cast LSCF with GDC buffer layer

Slight glancing angle to limit information depth to surface
Use glass pipet to inject contaminant gas directly over cell
Polyimide films used as high temperature, durable x-ray windows and also contain atmosphere

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Co K-edge of LSCF

OCV
Polarization

Oxidative effect at OCV
Reduced Oxidative effect with elevated temp. at OCV
Reduced Oxidative effect with elevated temp. at polarization
Fe K-edge of LSCF

Summary: Operando XAS for SOFCs

**Trends**
- At 400°C, Co and Fe tend to be oxidized by the CO2 and H2O, regardless of cathodic polarization
- At 700°C, the oxidative effect of CO2 is largely diminished

**Correlation:** Performance change caused by CO2 and H2O tends to be greater at lower temperatures

**Proposed Mechanisms:**
- CO2 may be forming a carbonate bond with Co and Fe, which is stable at lower temperatures
- Carbonate bond impedes oxygen vacancy migration paths, which depend on Co
Studying Surface Reactions of H$_2$O/CO$_2$ with XPS

Parameters of study
- Temperatures
  - 25°C (reference)
  - 400°C
  - 750°C
- Backfill atmospheres
  - UHV (reference)
  - H$_2$O
  - CO$_2$
  - H$_2$O+CO$_2$

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1. C 1s (SrCO$_3$)$_1$
2. C 1s (adventitious carbon) (BE=284.7 eV)
3. Sr 3p1/2 (SrCO$_3$)$_2$

Summary: Studying Surface Reactions of H2O/CO2 with XPS

**Trends**
- Cooling in the presence of CO2 and H2O from 750°C causes the formation of SrCO3, based on the new peaks observed and matched to C 1s in –CO3 and Sr 3p1/2.
- In pristine LSCF, only adventitious carbon and a slight amount of carbonates are detected at first.
- In LSCF annealed in 10% H2O for 60 h, a greater amount of “adventitious” carbonates was observed; more Sr appears on the surface after cooling in CO2 and H2O.

**Proposed mechanisms:**
- Sr segregation into SrCO3 on the surface seems to be mediated by both CO2 and H2O.
- H2O exposure may expose the Sr by bonding as a hydroxide, which then becomes more likely to bond with CO2 (if present) to form carbonates.

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**Conclusions - 1**
- **Dense** LSCF thin films are successfully fabricated with desired composition and thickness.
- **Small changes** in performance were observed for LSCF cathodes (porous or dense) when exposed to up to 10% H2O and/or 5% CO2 at 750°C. The small effect is reversible upon removal of contaminants.
- The LSCF electrodes in direct contact with a Cr-containing interconnect material displayed much more severe degradation than the one that was not in direct contact, implying that solid-state and/or surface diffusion of Cr contribute(s) much more than gas phase diffusion to Cr poisoning. Further, the presence of H2O can exacerbate the LSCF degradation, especially in the presence of other contaminants (e.g., Cr).
Conclusions - 2

- SERS results reveal that i) H₂O and CO₂ could have influences on the segregation of SrO; 2) the contamination of Cr species presents in two forms, Cr₂O₃ and SrCrO₄; 3) SrCrO₄ preferentially deposits on LSCF-GDC interface and bias has little effect on SrCrO₄ deposition.
- *In situ* XAS results show that Co and Fe tend to be oxidized by the CO₂ and H₂O at 400°C, regardless of cathodic polarization. At 700°C, the oxidative effect of CO₂ is largely diminished.
- XPS results indicate that H₂O may accelerate Sr segregation.

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