Understanding the effect of contaminants on LSCF cathode performance

Project Number: FC FE0009652
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Outline

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  - **Goals and objectives**
  - **Technical Approaches**
- **Accomplishments to date**
  - Effect of H_2O, CO_2 and Cr on the electrochemical behavior of LSCF cathodes
  - Surface species of LSCF as probed and mapped by SERS
  - Synchrotron-based X-ray analysis of test cells based on LSCF thin films under ***in operando*** conditions
- **Summary**
- **Acknowledgement**

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.

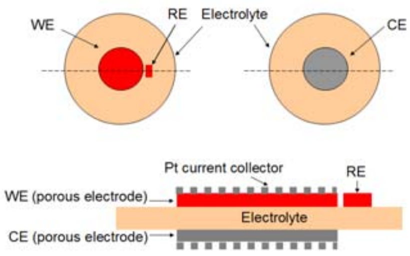
Accomplishments to Date

- ❖ Characterized **electrochemical behavior** of *porous* and *dense* *thin-film* LSCF cathodes exposed to H_2O, 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.

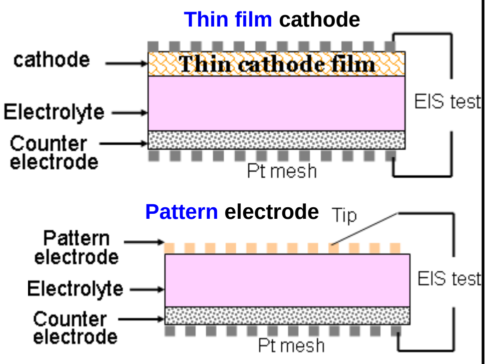
Cell Configurations

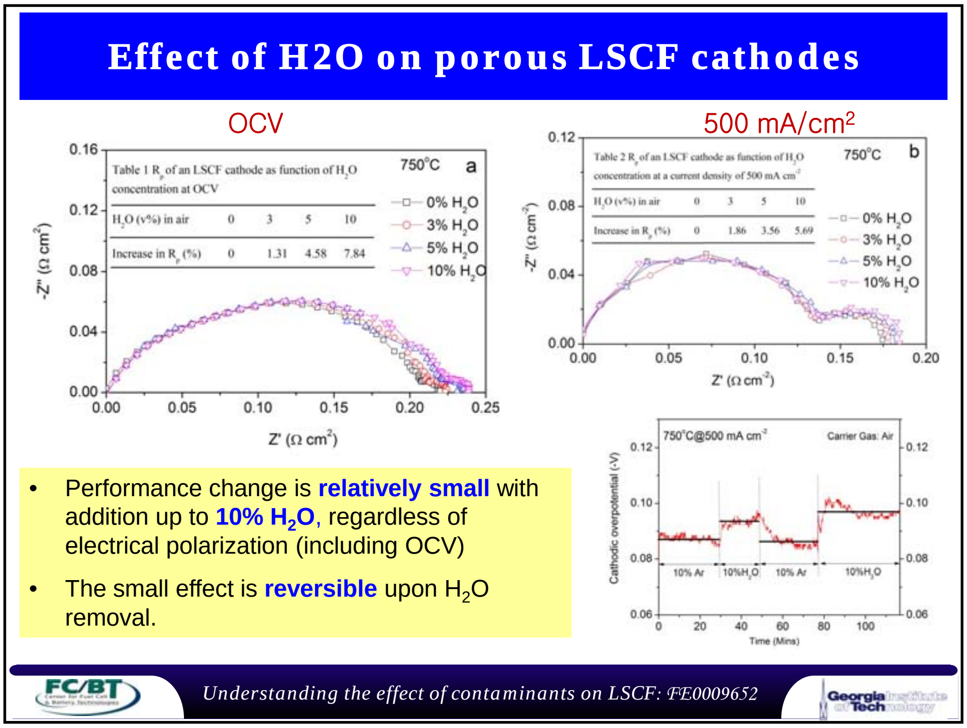
- ❖ For electrochemical testing of *porous*, *dense* thin-film, and *patterned* LSCF electrodes under realistic operational conditions.

3-electrode configuration for porous electrodes



2-electrode configuration





Effect of H2O on porous LSCF cathodes

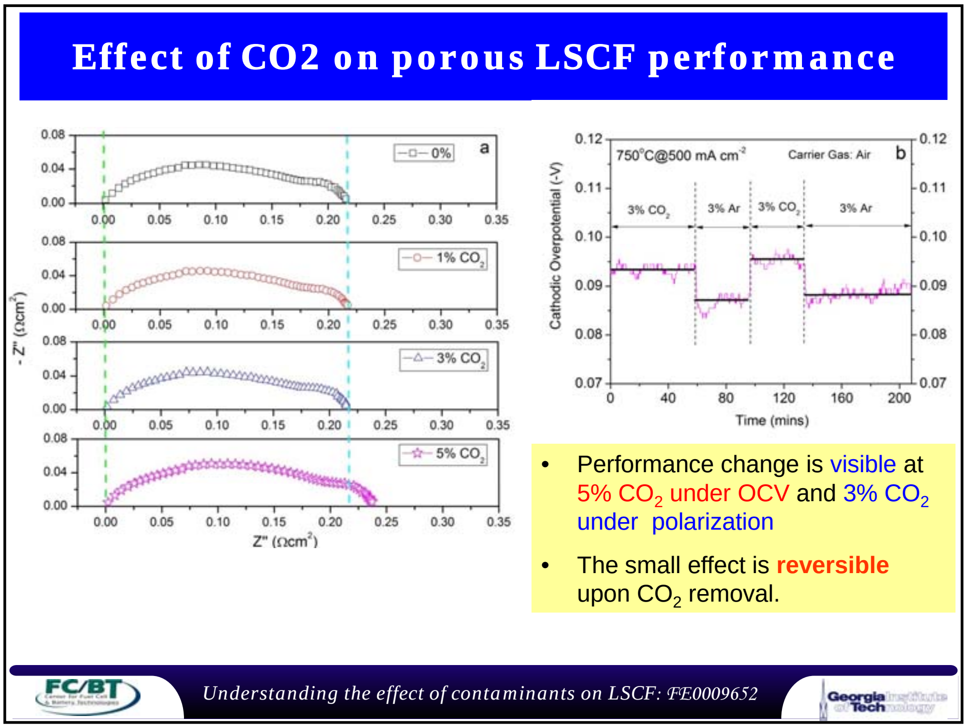
Table 1 R_p of an LSCF cathode as function of H_2O concentration at OCV

H_2O (v%) in air	0	3	5	10
Increase in R_p (%)	0	1.31	4.58	7.84

Table 2 R_p of an LSCF cathode as function of H_2O concentration at a current density of 500 mA cm^{-2}

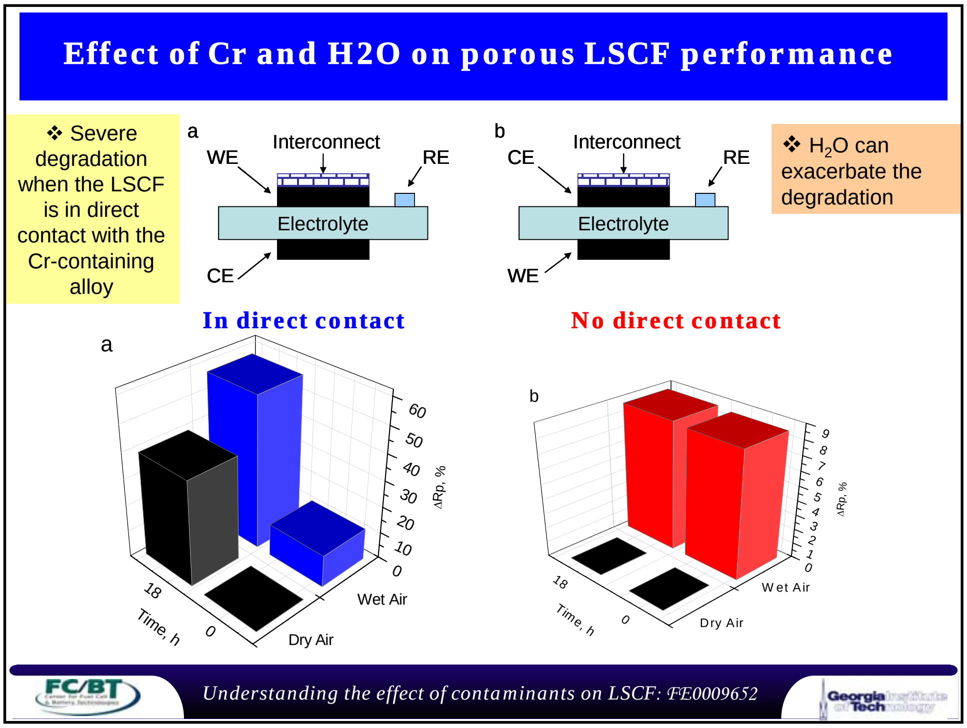
H_2O (v%) in air	0	3	5	10
Increase in R_p (%)	0	1.86	3.56	5.69

- Performance change is **relatively small** with addition up to **10% H_2O**, regardless of electrical polarization (including OCV)
- The small effect is **reversible** upon H_2O removal.



Effect of CO2 on porous LSCF performance

- Performance change is visible at 5% CO_2 under OCV and 3% CO_2 under polarization
- The small effect is **reversible** upon CO_2 removal.



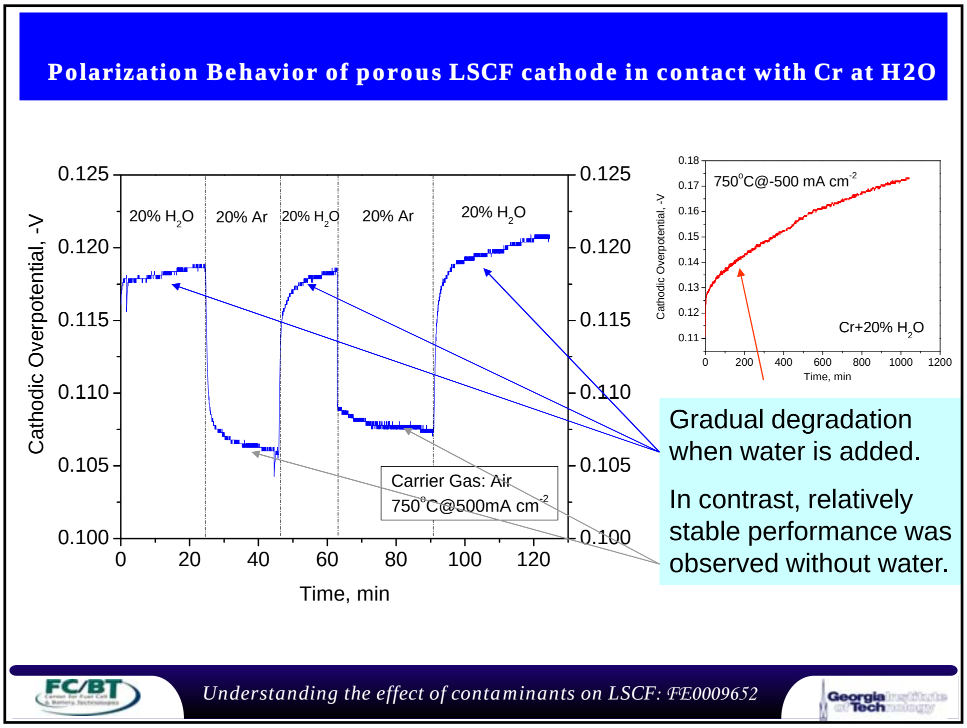
Effect of Cr and H2O on porous LSCF performance

- ❖ Severe degradation when the LSCF is in direct contact with the Cr-containing alloy

- ❖ H_2O can exacerbate the degradation

In direct contact

No direct contact

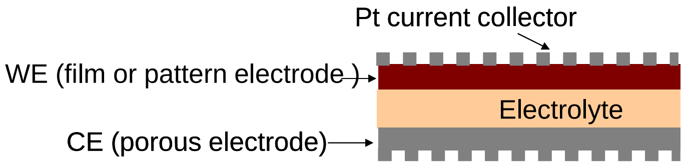


Polarization Behavior of porous LSCF cathode in contact with Cr at H2O

Gradual degradation when water is added.

In contrast, relatively stable performance was observed without water.

Test Cells with thin-film or pattern electrodes

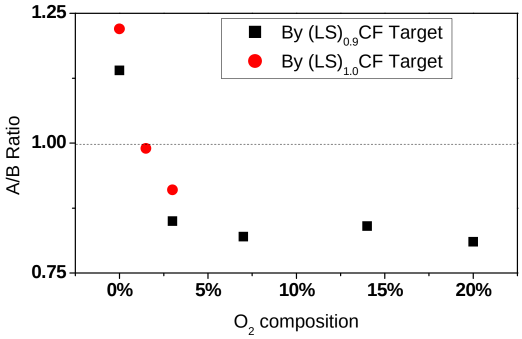


- A dense thin-film or patterned electrode with well-defined geometry, ideally suited for fundamental study.
- The top surface is open to *in situ* or *in operando* Raman and X-Ray analysis.
- No need for reference electrode because R_{WE}>>R_{CE}
- Sheet resistance is not a problem since a Pt mesh was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

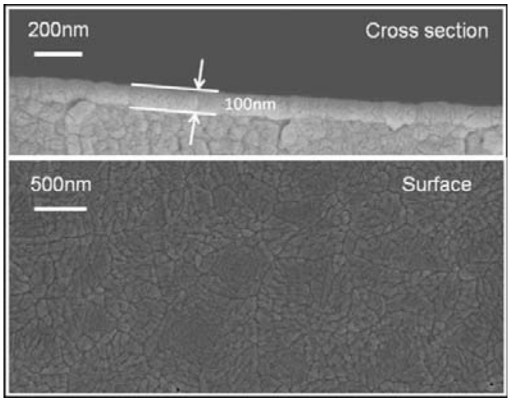
Adjust the stoichiometry of LSCF Film

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

Pressure	2.2×10^{-2} mBar
Temperature	Room Temp
Target A/B	0.9 and 1.0
Target Size	1 inch
Power	20W



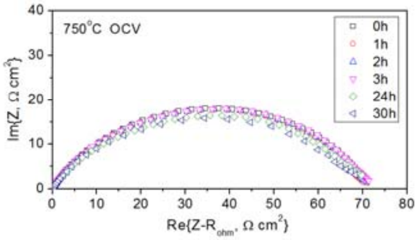
SEM Images of an LSCF Film



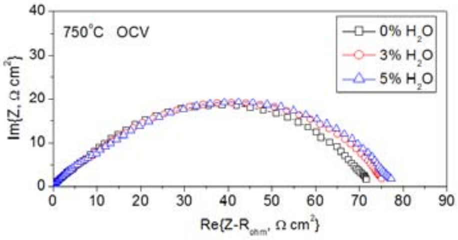
The sputtered LSCF film with 1:1 A/B ratio is annealed in air at 800ºC for 1hr, and cross-sectional view was taken to determine the sputtering rate (~30 nm/hr) and surface morphology.

Thin Film LSCF cathode exposed to contaminants

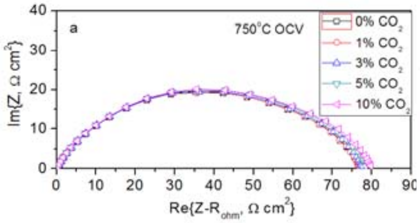
Stability of thin film



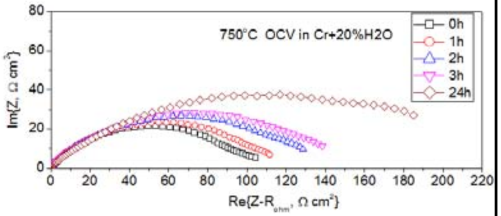
With H_2O

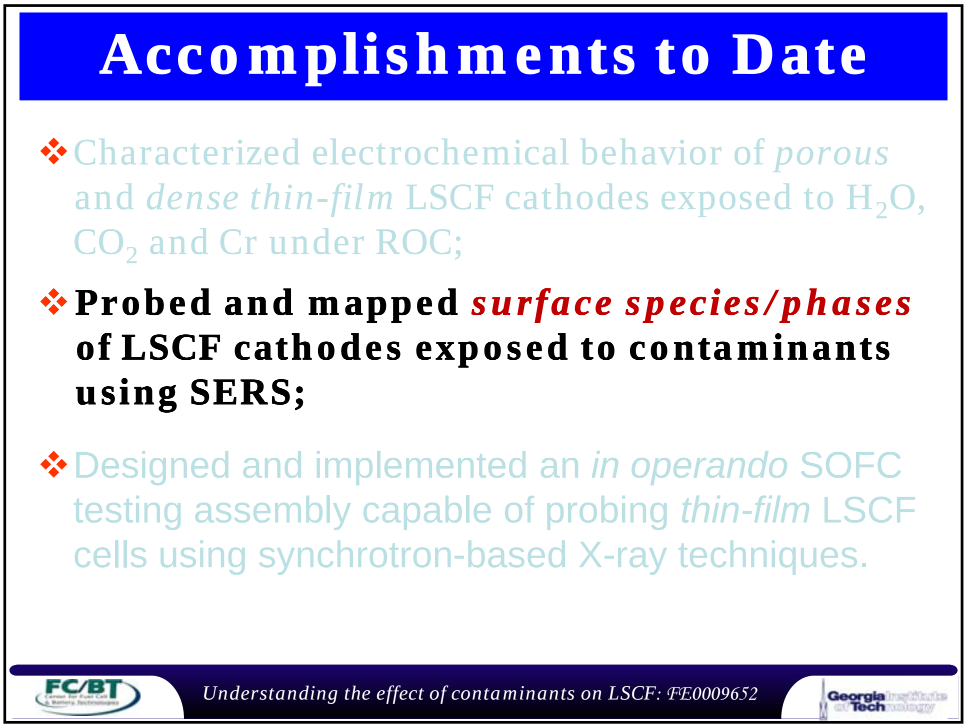


With CO_2



With $Cr+H_2O$





Accomplishments to Date

- Characterized electrochemical behavior of *porous* and *dense thin-film* LSCF cathodes exposed to H_2O, CO_2 and Cr under ROC;
- **Probed and mapped *surface species/phases* of LSCF cathodes exposed to contaminants using SERS;**
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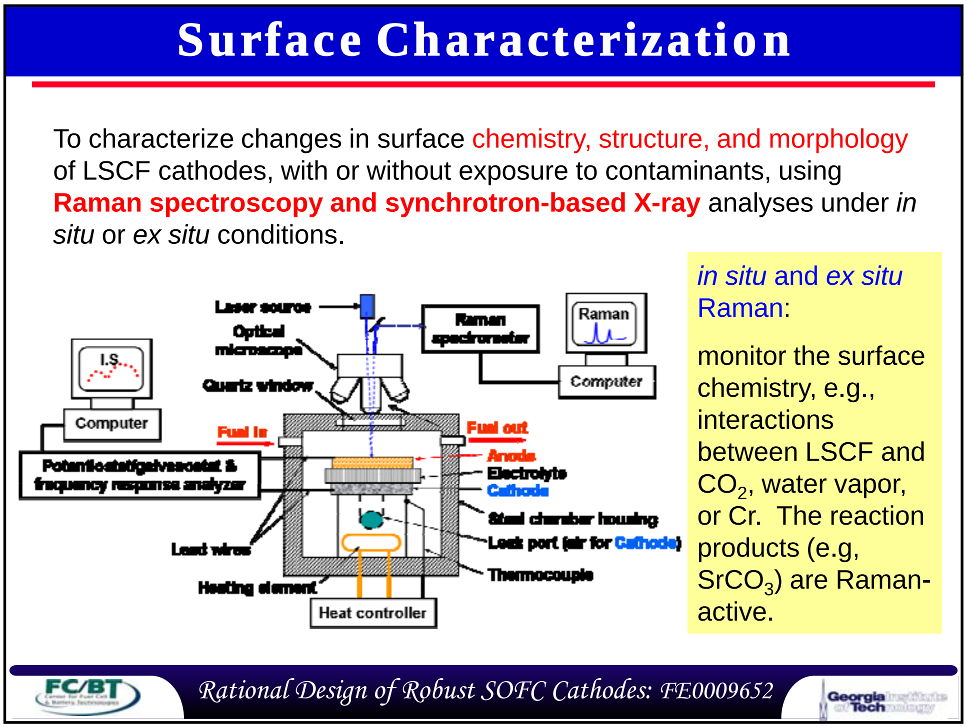
Understanding the effect of contaminants on LSCF: FE0009652



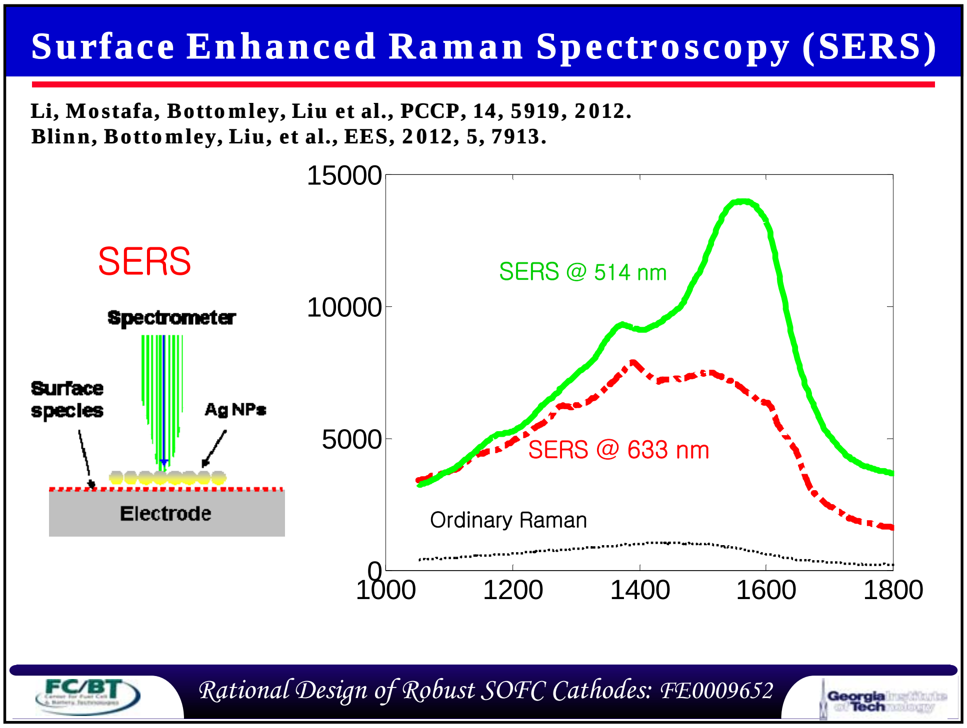
Surface Characterization

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 CO_2, water vapor, or Cr. The reaction products (e.g, $SrCO_3$) are Raman-active.

Rational Design of Robust SOFC Cathodes: FE0009652



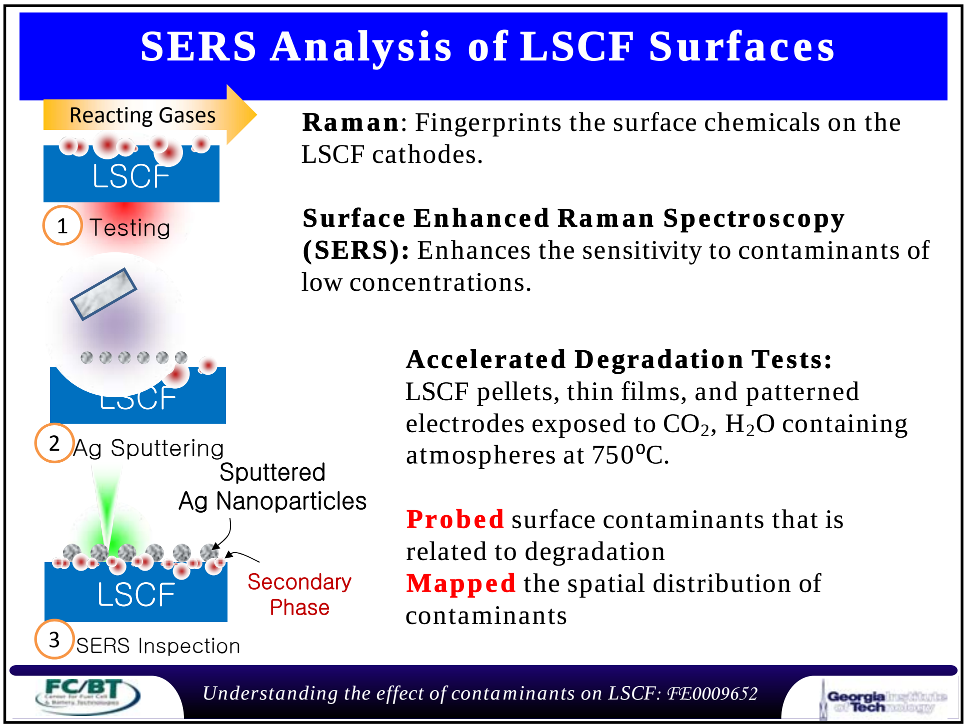
Surface Enhanced Raman Spectroscopy (SERS)

Li, Mostafa, Bottomley, Liu et al., PCCP, 14, 5919, 2012.
Blinn, Bottomley, Liu, et al., EES, 2012, 5, 7913.

FC/BT

Rational Design of Robust SOFC Cathodes: FE0009652

Georgia Institute of Technology



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 CO_2, H_2O containing atmospheres at 750°C.

Probed surface contaminants that is related to degradation
Mapped the spatial distribution of contaminants

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Understanding the effect of contaminants on LSCF: FE0009652

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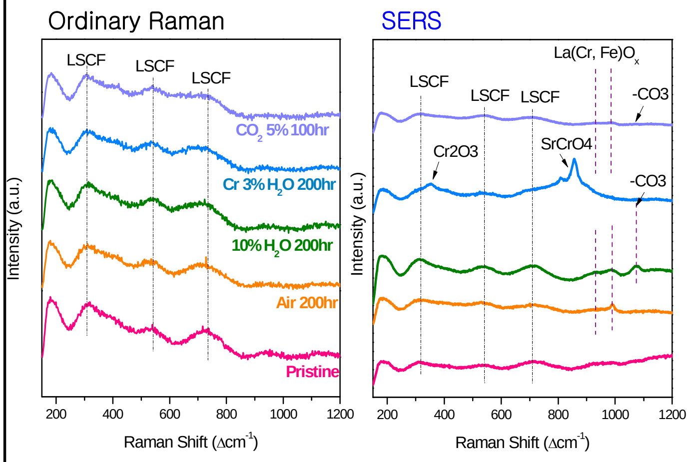
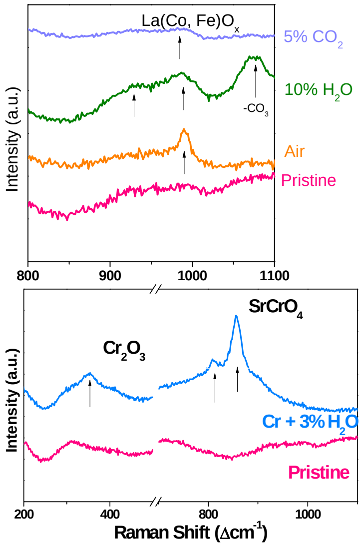
Typical Raman Spectra of LSCF



- Dramatic enhancement by **SERS**
- Indirect indication of **SrO** segregation, particularly after annealing in **10% H_2O**
- Contamination species of **Cr_2O_3 and $SrCrO_4$** as a result of annealing with **Cr Alloys**

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

SERS features of LSCF Degradation

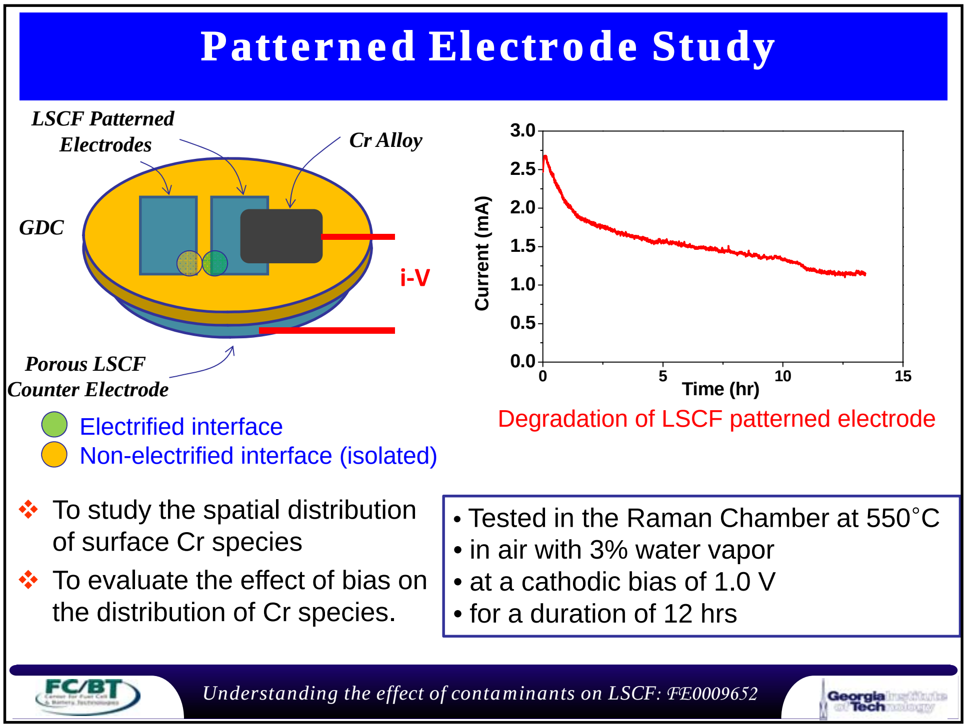


- The emerging of peaks on 930cm-1 and 980cm^{-1} indicates the formation of **orthorhombic (pbmn)** perovskite phase, which could be La(Co, Fe) O_3 that is related to **SrO segregation**. [1]

- 810cm^{-1} and 860cm^{-1} peaks are related to **$SrCrO_4$**

- 340cm^{-1} peak is related to **Cr_2O_3** deposition on LSCF surface.[2]

[1] B.P. Barbero, J.A. Gamboa, L.E. Cadus, Applied Catalysis B-Environmental, 65 (2006) 21-30.
[2] H.W. Abernathy, E. Koep, C. Compson, Z. Cheng, M.L. Liu, Journal of Physical Chemistry C, 112 (2008) 13299-13303.



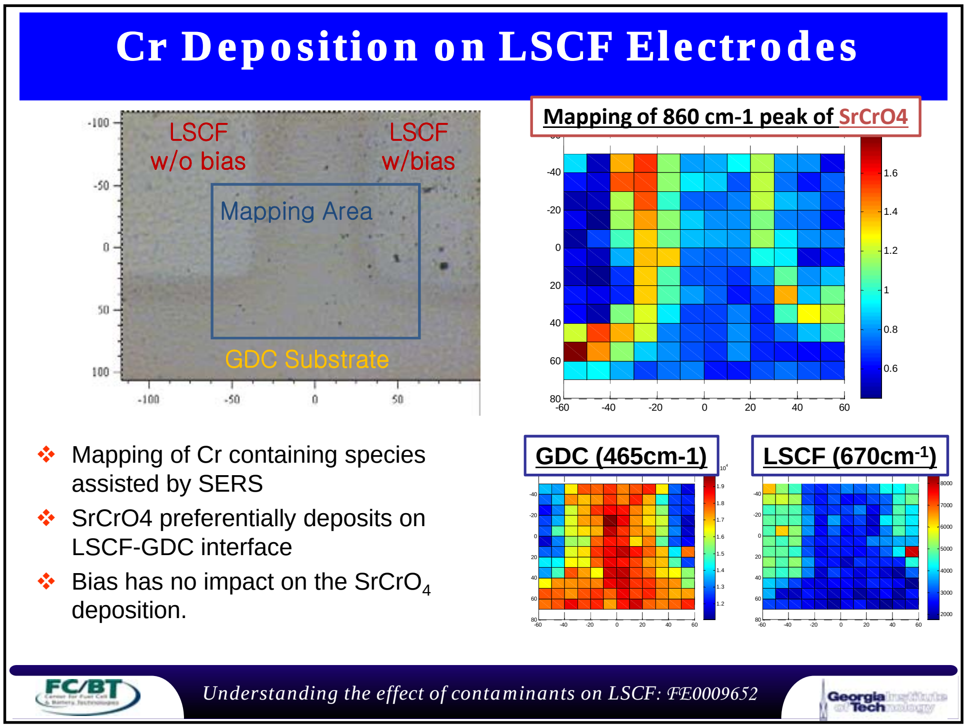
Patterned Electrode Study

🟢 Electrified interface
🟡 Non-electrified interface (isolated)

Degradation of LSCF patterned 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

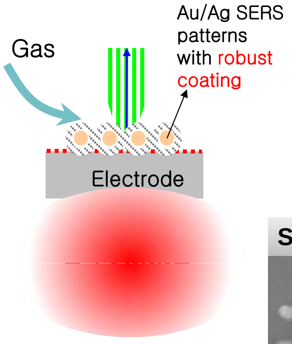
Mapping of 860 cm-1 peak of SrCrO4

GDC (465cm-1)

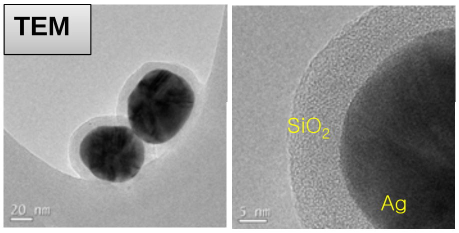
LSCF ($670cm^{-1}$)

- Mapping of Cr containing species assisted by SERS
- SrCrO4 preferentially deposits on LSCF-GDC interface
- Bias has no impact on the $SrCrO_4$ deposition.

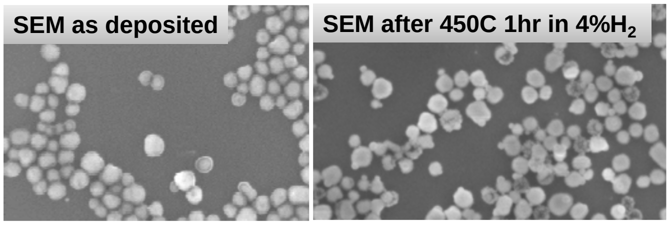
in situ SERS with Ag@SiO_2 Particles



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 H_2O, CO_2 and Cr under ROC;
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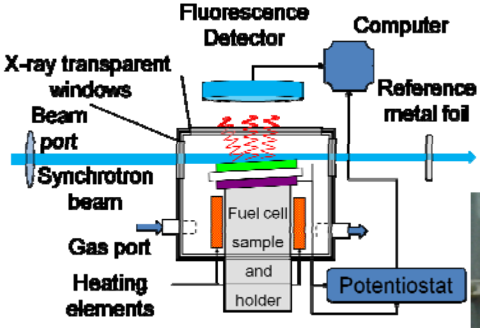
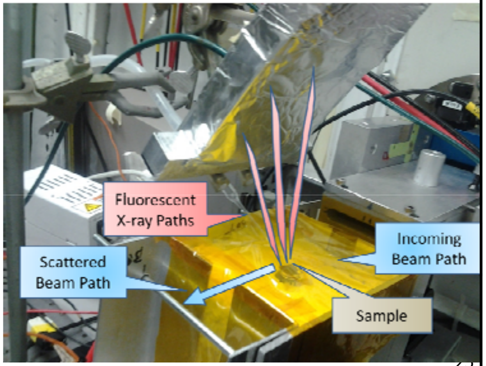
In Operando XAS for SOFCs



- 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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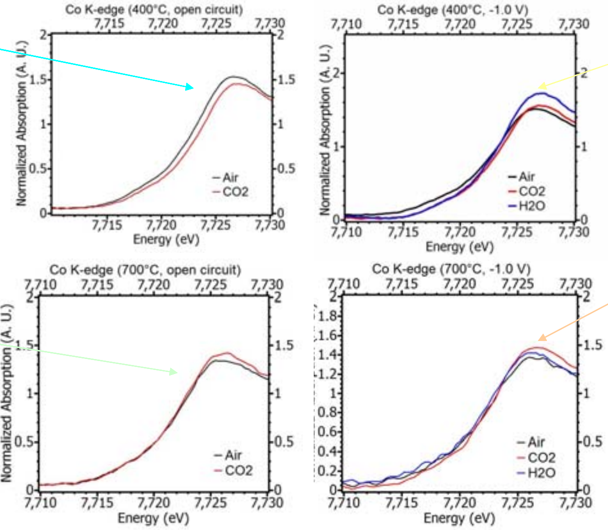
Co K-edge of LSCF

OCV

Polarization

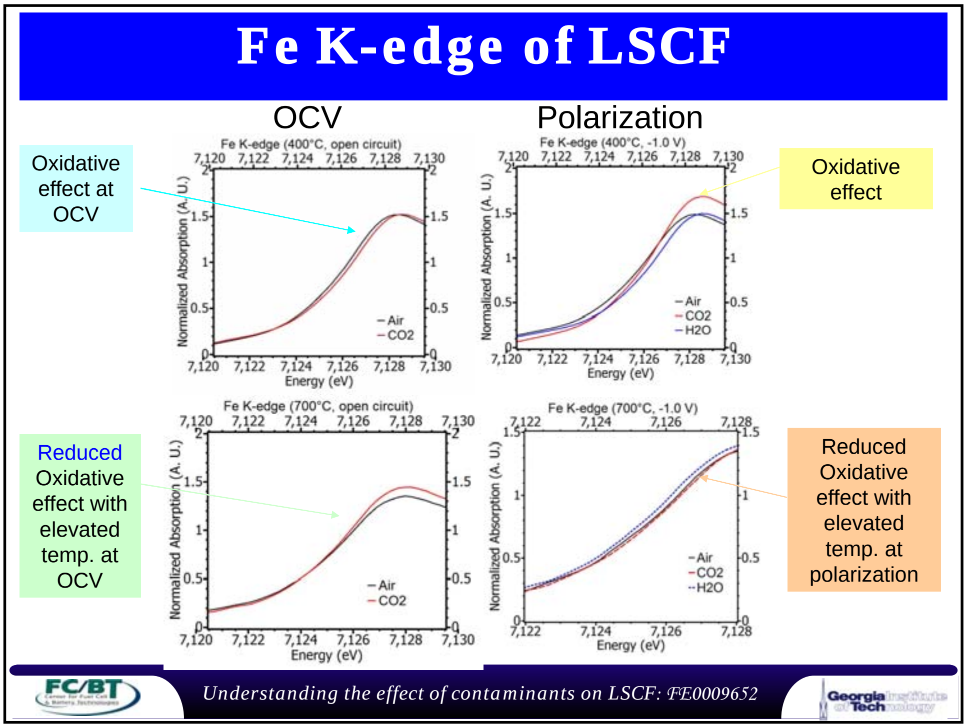


Oxidative effect at OCV

Oxidative effect

Reduced Oxidative effect with elevated temp. at OCV

Reduced Oxidative effect with elevated temp. at polarization



Fe K-edge of LSCF

OCV

Polarization

Oxidative effect at OCV

Oxidative effect

Reduced Oxidative effect with elevated temp. at OCV

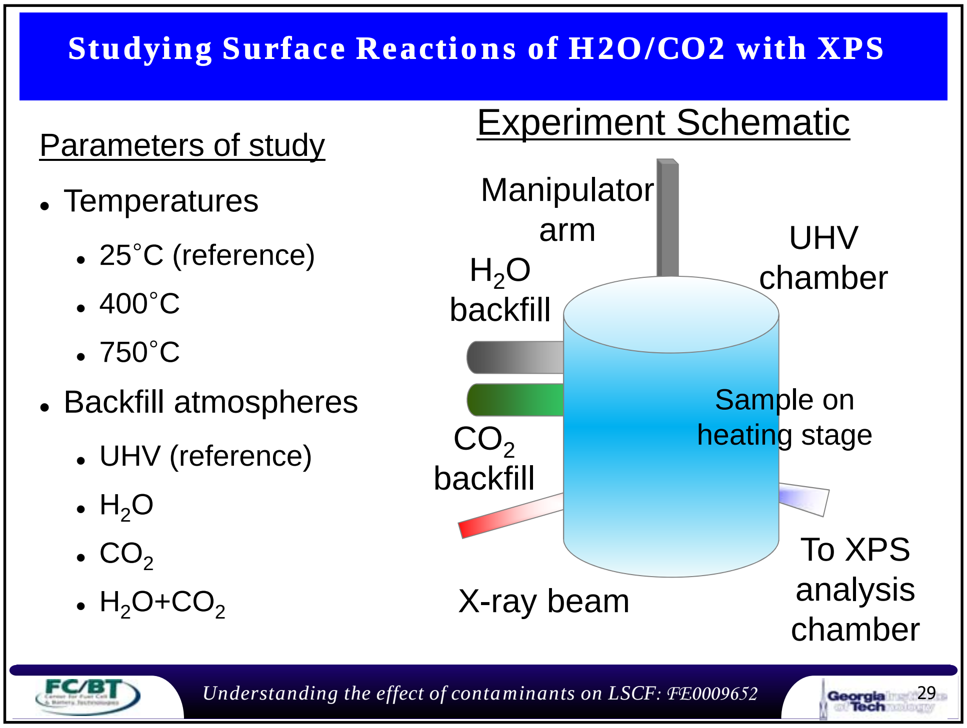
Reduced Oxidative effect with elevated temp. at polarization

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 CO_2 and H_2O tends to be greater at lower temperatures

Proposed Mechanisms:

- ✓ CO_2 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

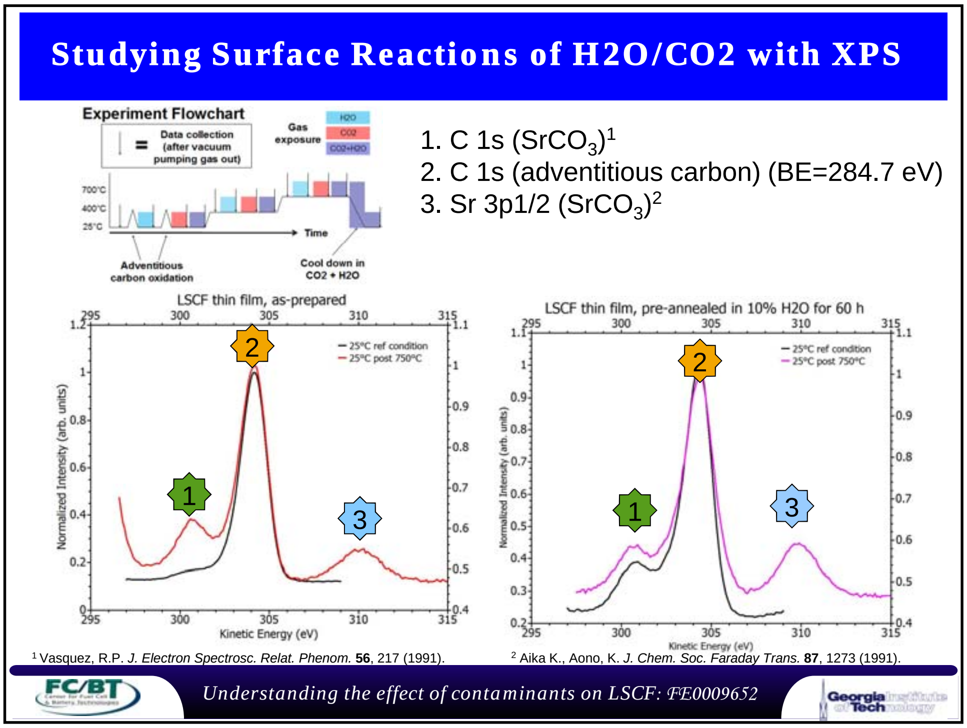


Studying Surface Reactions of H2O/CO2 with XPS

Parameters of study

- Temperatures
  - 25°C (reference)
  - 400°C
  - 750°C
- Backfill atmospheres
  - UHV (reference)
  - H_2O
  - CO_2
  - H_2O+CO_2

Experiment Schematic



Studying Surface Reactions of H2O/CO2 with XPS

1. C 1s $(SrCO_3)$[1]
2. C 1s (adventitious carbon) (BE=284.7 eV)
3. Sr 3p1/2 $(SrCO_3)$[2]

[1] Vasquez, R.P. *J. Electron Spectrosc. Relat. Phenom.* **56**, 217 (1991).

[2] Aika K., Aono, K. *J. Chem. Soc. Faraday Trans.* **87**, 1273 (1991).

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 CO_2 and H_2O

Proposed mechanisms:

- Sr segregation into $SrCO_3$ on the surface seems to be mediated by both CO_2 and H_2O
- H_2O 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% H_2O and/or 5% CO_2 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 H_2O can exacerbate the LSCF degradation, especially in the presence of other contaminants (e.g., Cr).

Conclusions - 2

- SERS results reveal that i) H_2O and CO_2 could have influences on the segregation of SrO; 2) the contamination of Cr species presents in two forms, Cr_2O_3 and $SrCrO_4$; 3) $SrCrO_4$ preferentially deposits on LSCF-GDC interface and bias has little effect on $SrCrO_4$ deposition.
- *In situ* XAS results show that Co and Fe tend to be oxidized by the CO_2 and H_2O at 400ºC, regardless of cathodic polarization. At 700°C, the oxidative effect of CO_2 is largely diminished.
- XPS results indicate that H_2O may accelerate Sr segregation.

Acknowledgement

Discussions with Joseph Stoffa, Briggs White, and other DOE management team members.

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