Understanding the effect of contaminants on LSCF cathode performance

Project Number: FC FE0009652
DOE Project Manager: Joseph Stoffa

Presenter: M. Liu
Co-authors: D. Ding, S. Lai, X. Li, and F. Alamgir

School of Materials Science and Engineering
Center for Innovative Fuel Cell and Battery Technologies
Georgia Institute of Technology, Atlanta, GA 30332-0245, USA

Presented to
15th SECA Workshop
July 23, 2014

DOE-NETL SECA-CTP

Outline

- **Project Information**
  - **Motivation**
  - **Goals and objectives**
  - **Technical Approaches**
- **Accomplishments to date**
  - Characterized **electrochemical behavior** of LSCF cathodes exposed to H_2O, CO_2 and Cr under ROC;
  - Probed **surface species** of LSCF using *in operando* **SERS**
  - Characterized **local atomistic** and **electronic structures** of active ions by *in operando* **synchrotron-based X-ray** analysis
  - Identified **efficient catalysts** for enhancing **ORR activity** and **durability**
- **Summary**
- **Acknowledgement**

Motivation

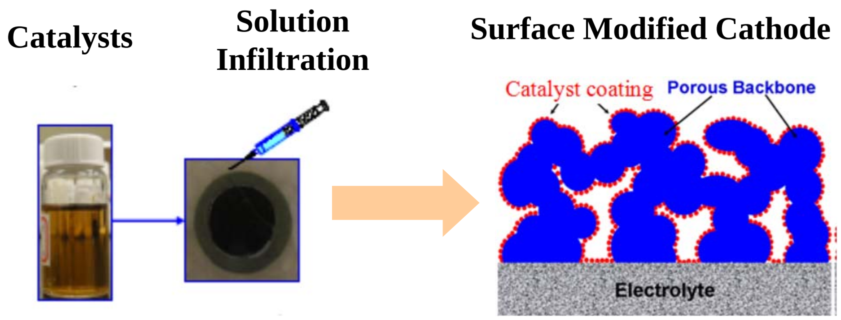
- Cathode durability is critical to long-term reliable SOFC performance for commercial deployment.
- Current state-of-the-art SOFC cathode materials are susceptible to degradation due to contaminants under realistic operating conditions (ROC).
- Mitigating the stability issues by design of new materials 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.

Surface modification

- Develop catalysts of high activity and durability
- Infiltrate catalysts into porous cathode backbones to mitigate the effect of contaminants



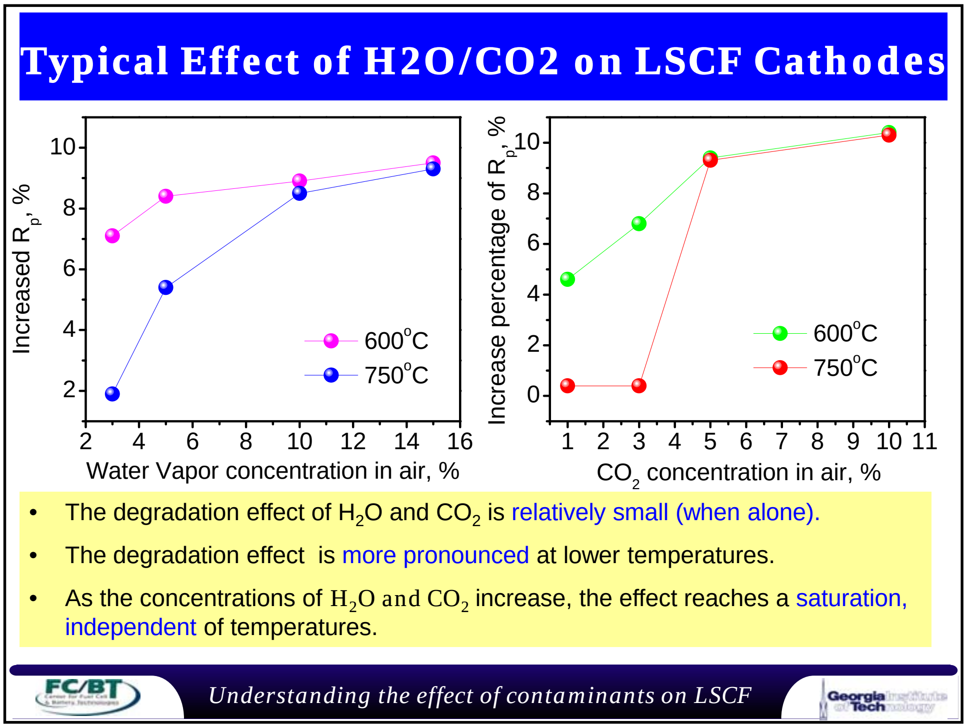
Accomplishments to Date

❖ **Typical 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;

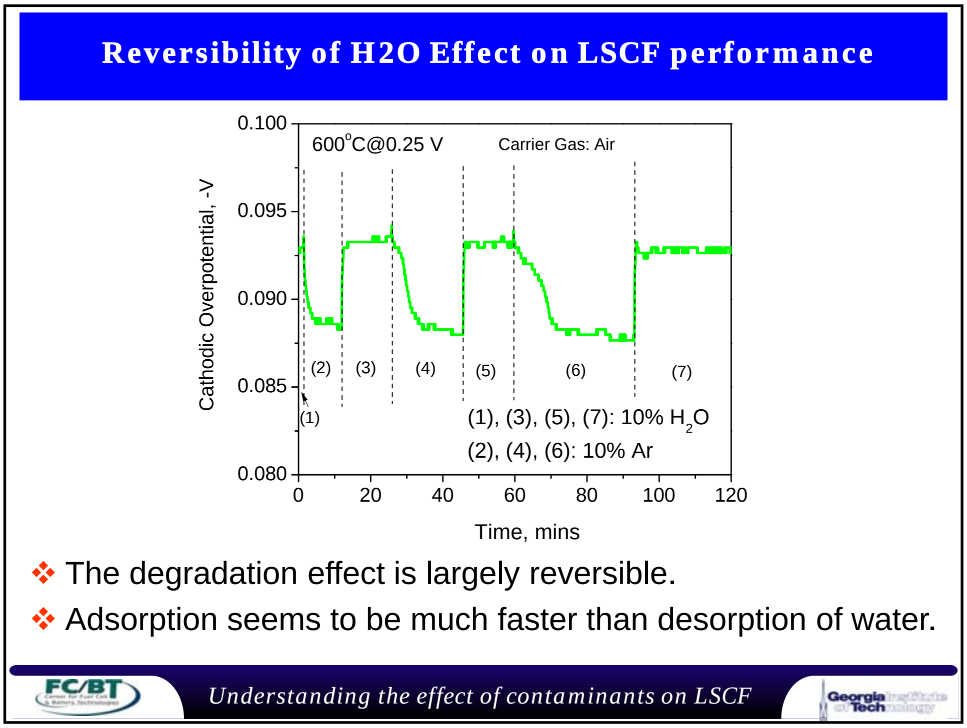
❖ Designed and implemented an *in operando* SOFC testing assembly capable of probing *thin-film* LSCF cells using synchrotron-based X-ray techniques.

❖ Identified efficient catalysts for enhancing **ORR activity** and **durability** .



Typical Effect of H2O/CO2 on LSCF Cathodes

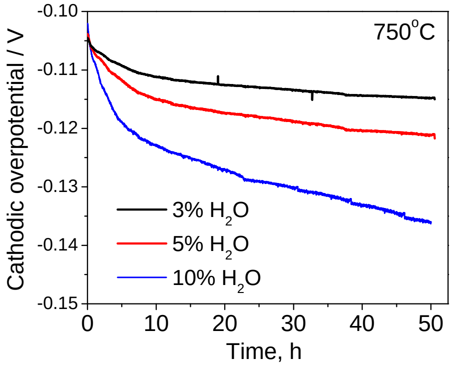
- The degradation effect of H_2O and CO_2 is relatively small (when alone).
- The degradation effect is more pronounced at lower temperatures.
- As the concentrations of H_2O and CO_2 increase, the effect reaches a saturation, independent of temperatures.



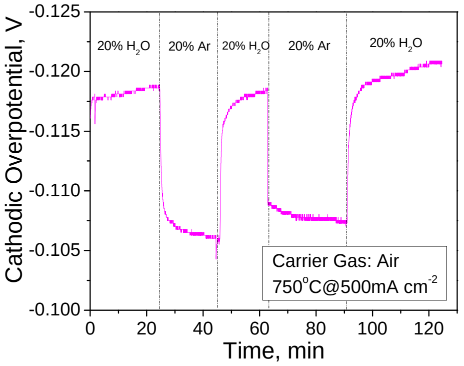
Reversibility of H2O Effect on LSCF performance

- ❖ The degradation effect is largely reversible.
- ❖ Adsorption seems to be much faster than desorption of water.

Polarization Behavior of porous LSCF cathode in contact with Cr w/o H_2O



The effect of water concentrations

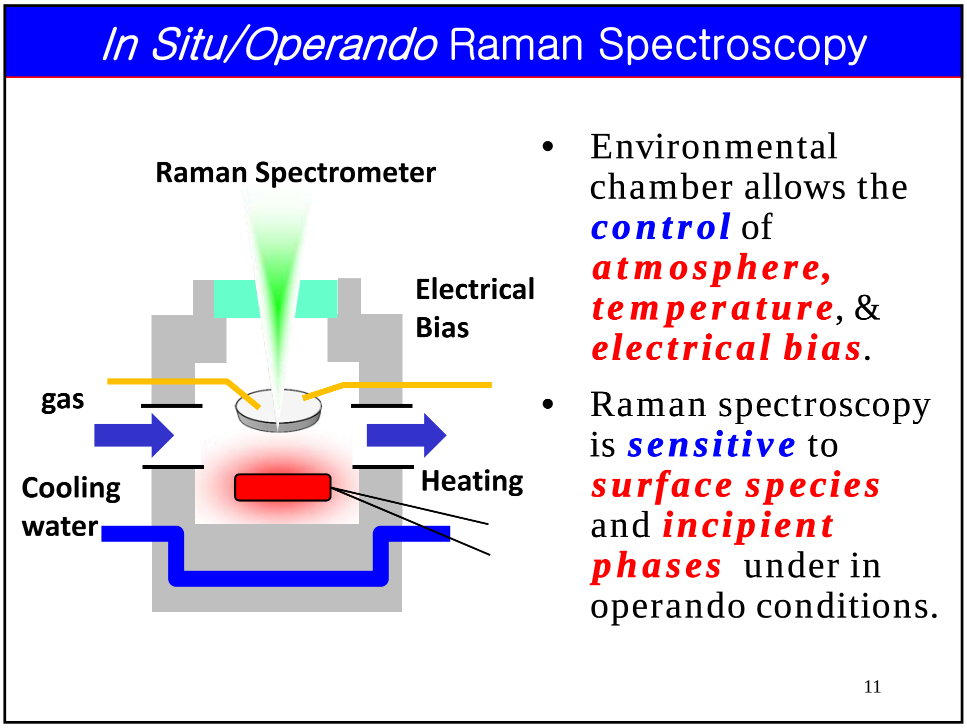


The early stage of Cr-poisoning seems to be reversible; it may involve adsorption of some reaction intermediates

---

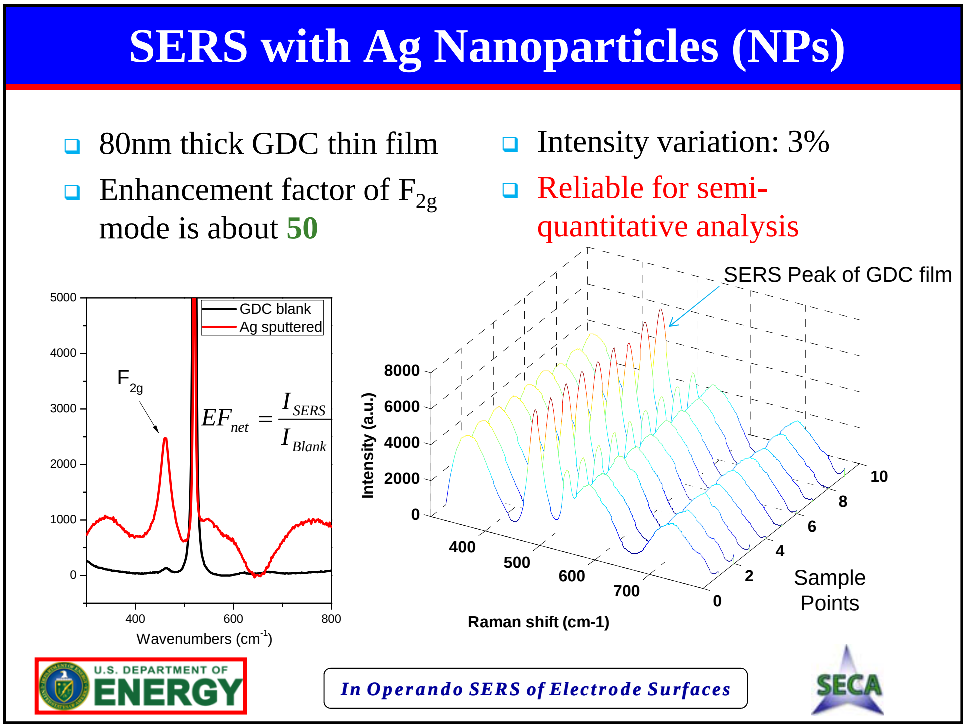
Accomplishments to Date

- Characterized **electrochemical behavior** of *porous* and *dense thin-film* LSCF cathodes exposed to H_2O, CO_2 and Cr under ROC;
- ***Typical surface species/phases* on LSCF cathodes exposed to contaminants as probed by *in operando* SERS;**
- Designed and implemented an *in operando* SOFC testing assembly capable of probing *thin-film* LSCF cells using synchrotron-based X-ray techniques.
- Identified efficient catalysts for enhancing **ORR activity** and **durability** .



In Situ/Operando Raman Spectroscopy

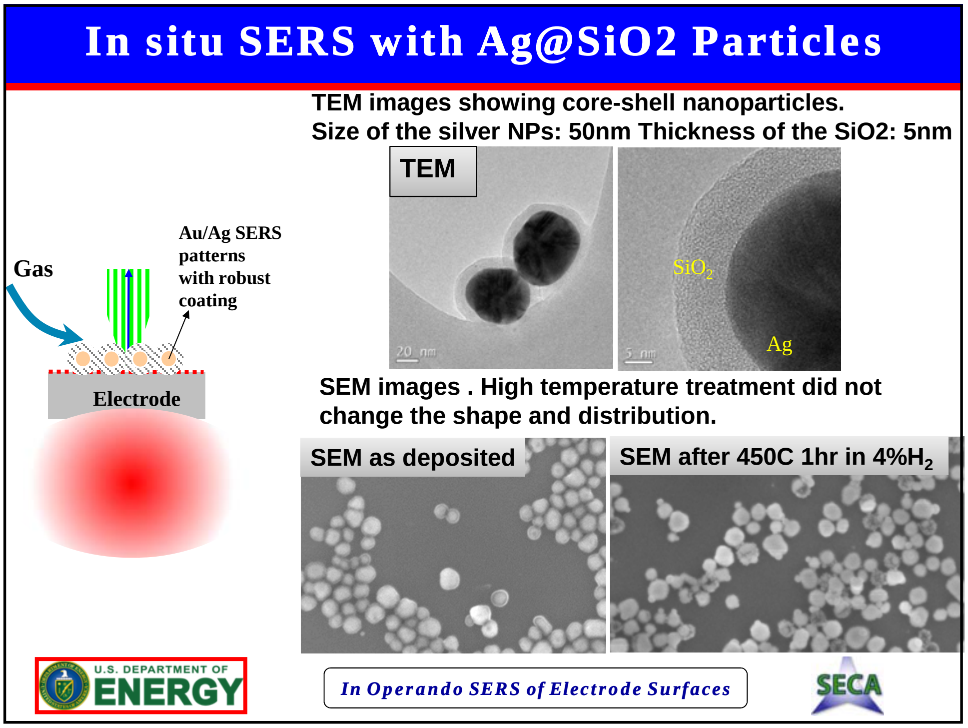
- Environmental chamber allows the ***control*** of ***atmosphere***, ***temperature***, & ***electrical bias***.
- Raman spectroscopy is ***sensitive*** to ***surface species*** and ***incipient phases*** under in operando conditions.



SERS with Ag Nanoparticles (NPs)

- ❑ 80nm thick GDC thin film
- ❑ Enhancement factor of F_{2g} mode is about **50**
- ❑ Intensity variation: 3%
- ❑ Reliable for semi-quantitative analysis

$$EF_{net} = \frac{I_{SERS}}{I_{Blank}}$$

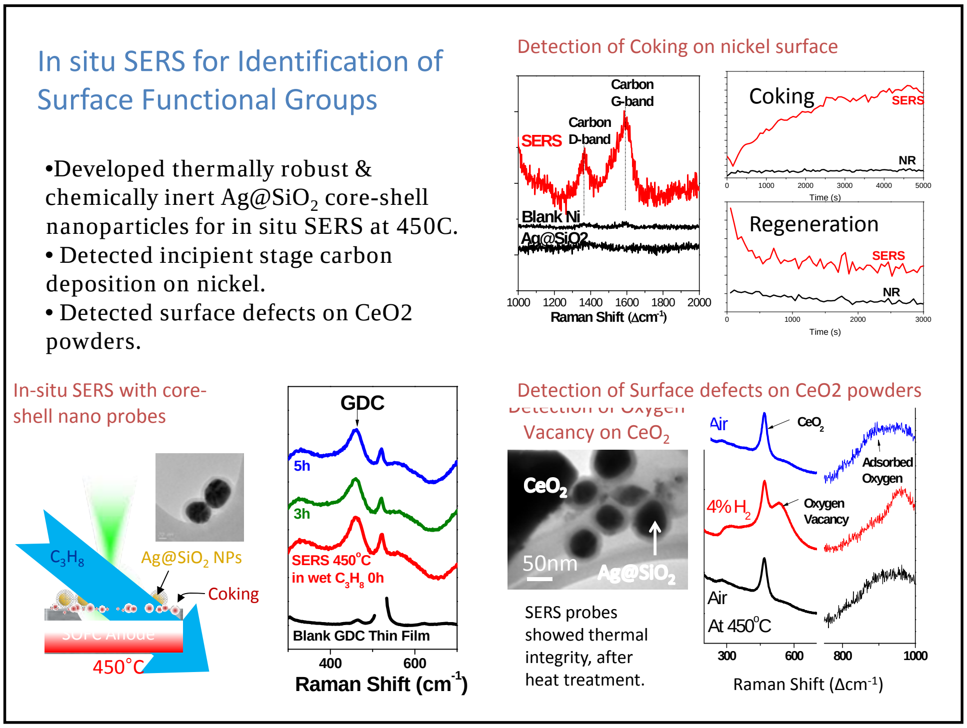


In situ SERS with Ag@SiO2 Particles

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.

In Operando SERS of Electrode Surfaces



In situ SERS for Identification of Surface Functional Groups

- Developed thermally robust & chemically inert Ag@SiO_2 core-shell nanoparticles for in situ SERS at 450C.
- Detected incipient stage carbon deposition on nickel.
- Detected surface defects on CeO2 powders.

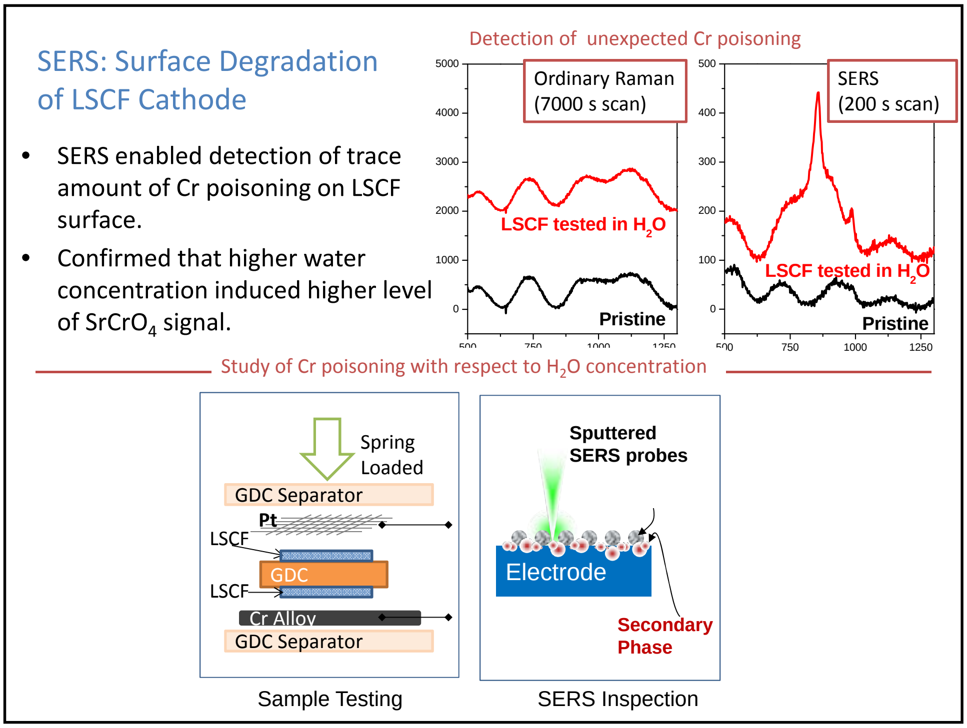
In-situ SERS with core-shell nano probes

Detection of Coking on nickel surface

Detection of Surface defects on CeO2 powders

Vacancy on CeO_2

SERS probes showed thermal integrity, after heat treatment.



SERS: Surface Degradation of LSCF Cathode

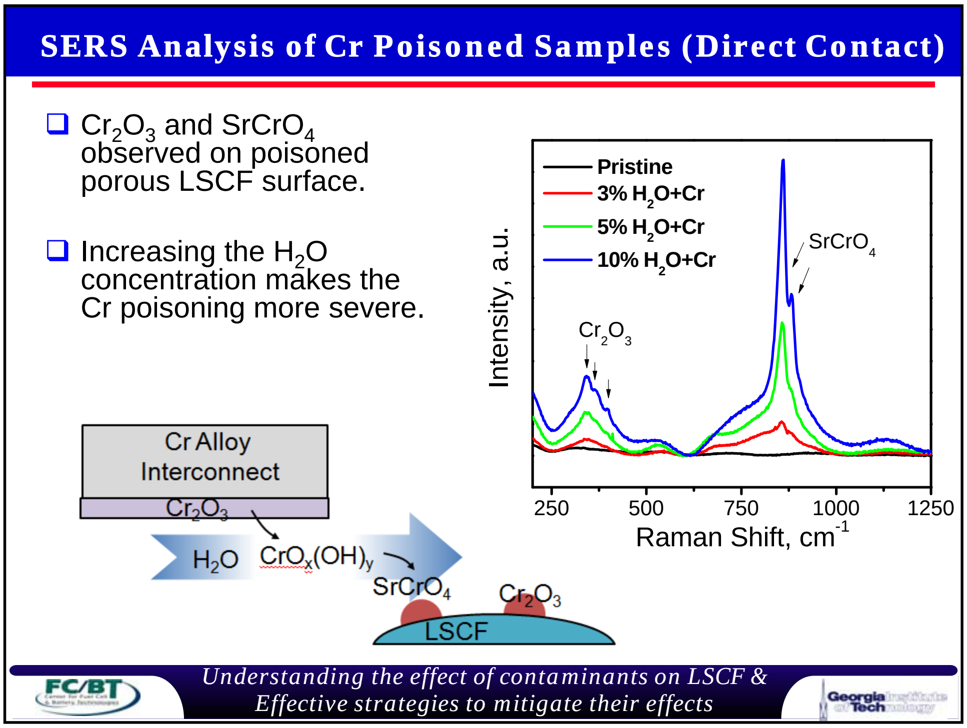
- SERS enabled detection of trace amount of Cr poisoning on LSCF surface.
- Confirmed that higher water concentration induced higher level of $SrCrO_4$ signal.

Detection of unexpected Cr poisoning

Study of Cr poisoning with respect to H_2O concentration

Sample Testing

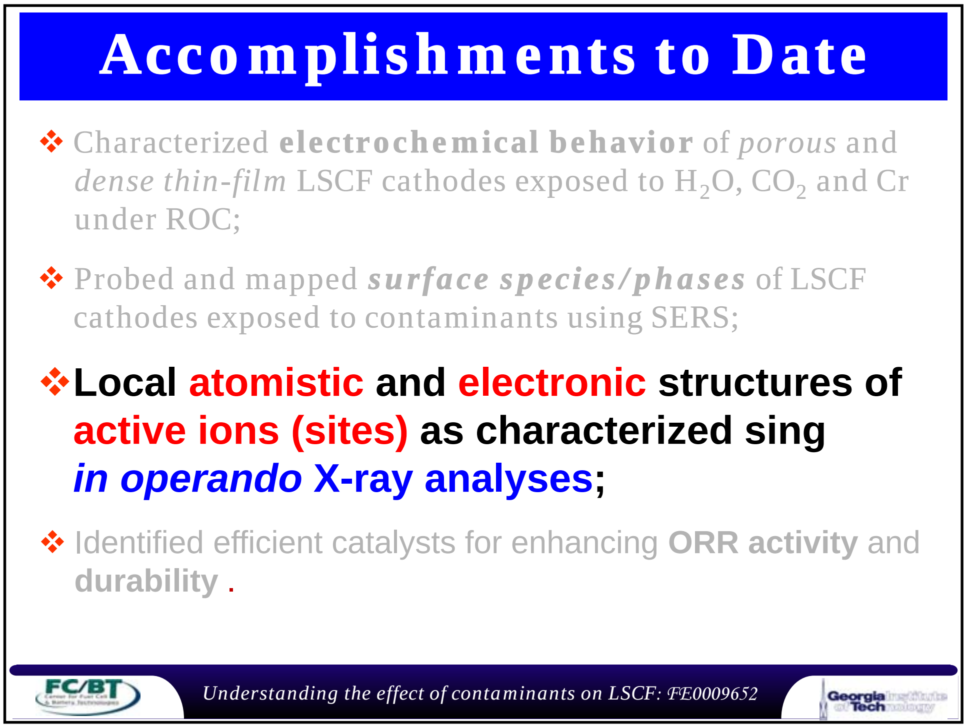
SERS Inspection



SERS Analysis of Cr Poisoned Samples (Direct Contact)

- ☐ Cr_2O_3 and $SrCrO_4$ observed on poisoned porous LSCF surface.
- ☐ Increasing the H_2O concentration makes the Cr poisoning more severe.

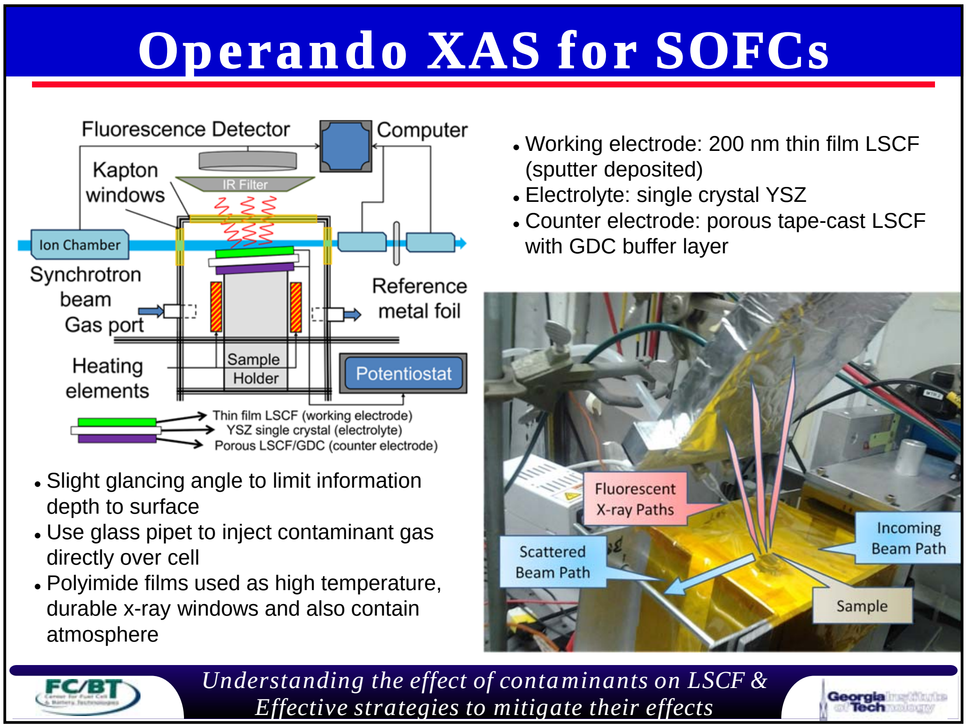
Understanding the effect of contaminants on LSCF & Effective strategies to mitigate their effects



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;
- ❖ **Local atomistic and electronic structures of active ions (sites) as characterized sing *in operando* X-ray analyses;**
- ❖ Identified efficient catalysts for enhancing **ORR activity** and **durability** .

Understanding the effect of contaminants on LSCF: FE0009652

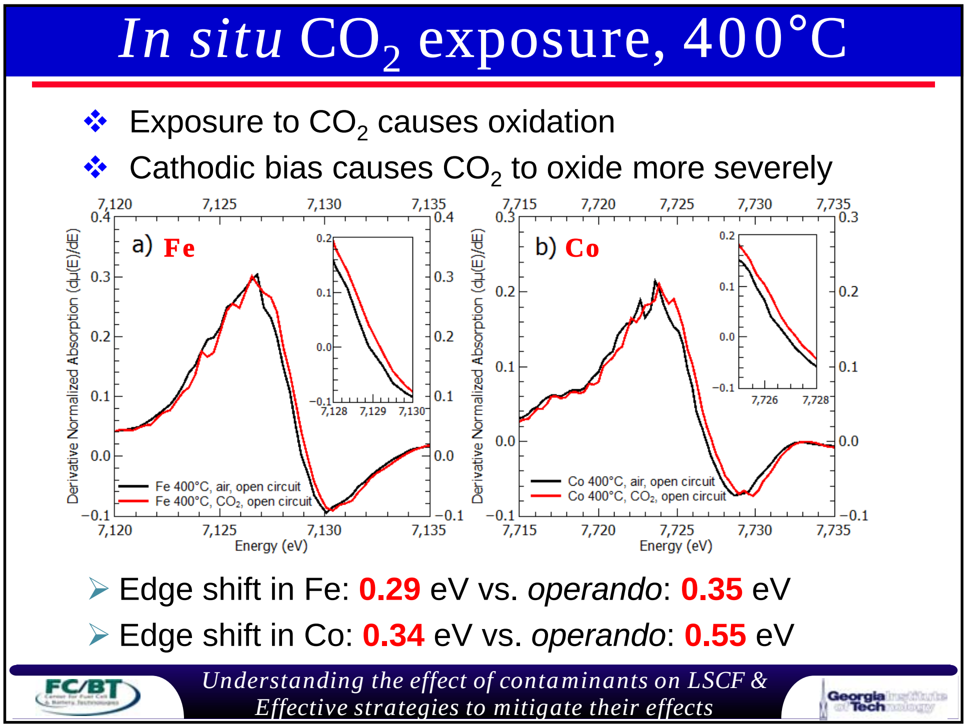


Operando XAS for SOFCs

- 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

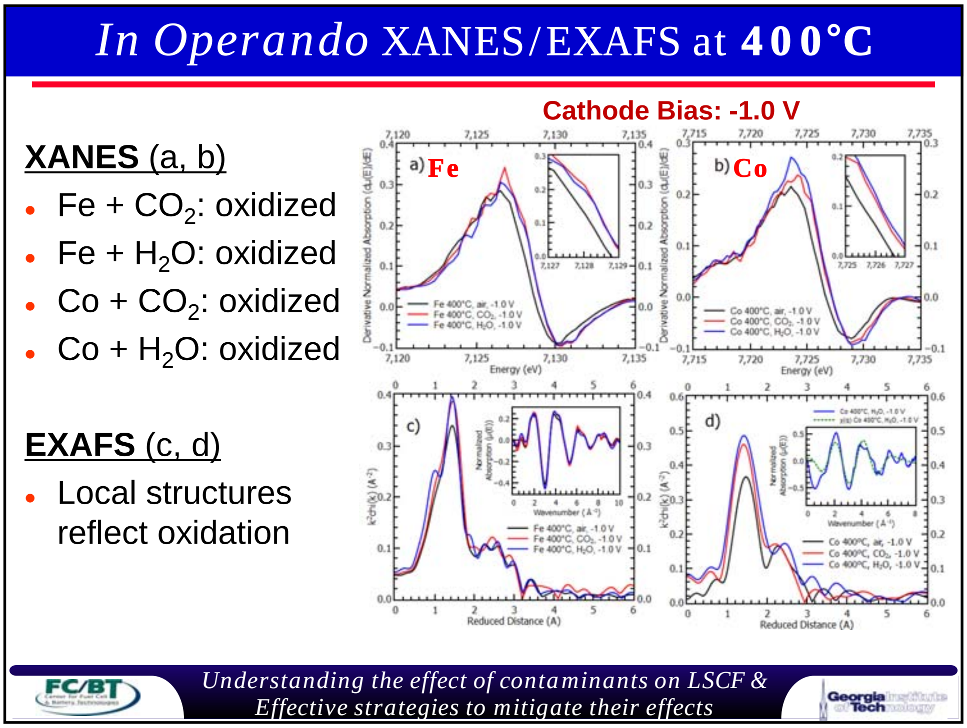
Understanding the effect of contaminants on LSCF & Effective strategies to mitigate their effects



In situ CO_2 exposure, 400°C

- Exposure to CO_2 causes oxidation
- Cathodic bias causes CO_2 to oxide more severely

- Edge shift in Fe: **0.29** eV vs. *operando*: **0.35** eV
- Edge shift in Co: **0.34** eV vs. *operando*: **0.55** eV



In Operando XANES/EXAFS at **400°C**

Cathode Bias: -1.0 V

XANES (a, b)

- Fe + CO_2: oxidized
- Fe + H_2O: oxidized
- Co + CO_2: oxidized
- Co + H_2O: oxidized

EXAFS (c, d)

- Local structures reflect oxidation

XANES/EXAFS at **700°C**

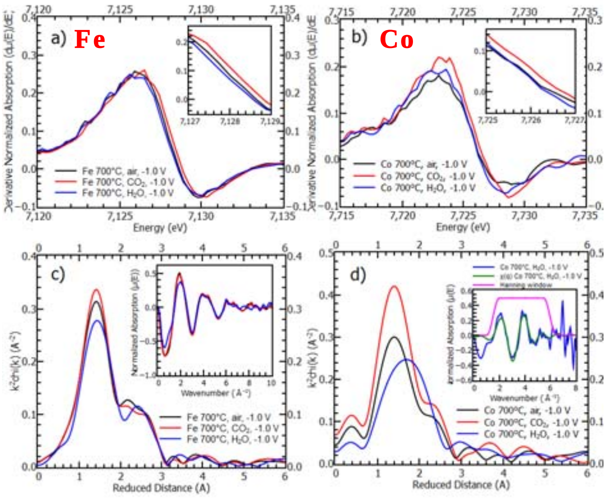
Cathode Bias: -1.0 V

XANES (a, b)

- Fe + CO_2: oxidized
- Fe + H_2O: reduced
- Co + CO_2: oxidized
- Co + H_2O: no shift

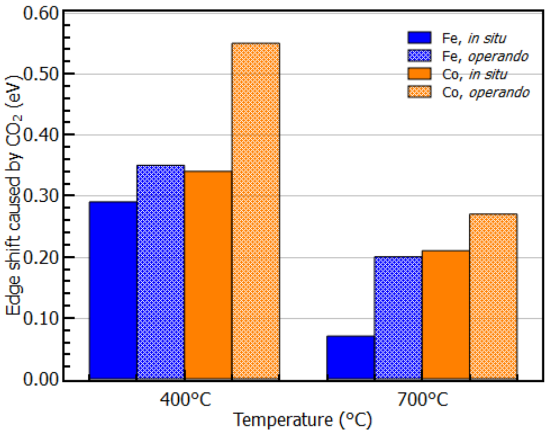
EXAFS (c, d)

- Fe local structure stable
- Co local structure distorts under H_2O



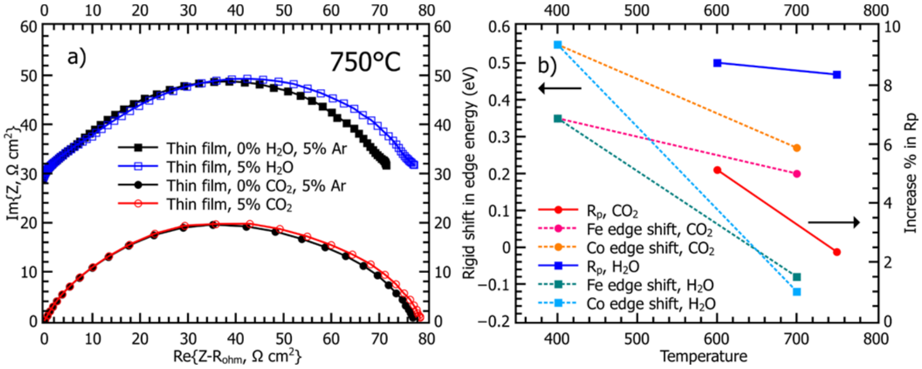
In situ vs. *operando*

- Cathodic bias facilitates the oxidation Fe and Co in LSCF by CO_2 at both low and high temperatures



EIS-XANES Correlation Data

Warm colors: CO_2 Cool colors: H_2O



- Increased polarization resistance under CO_2, H_2O
- Higher ***Rp*** correlates well with **stronger** oxidation

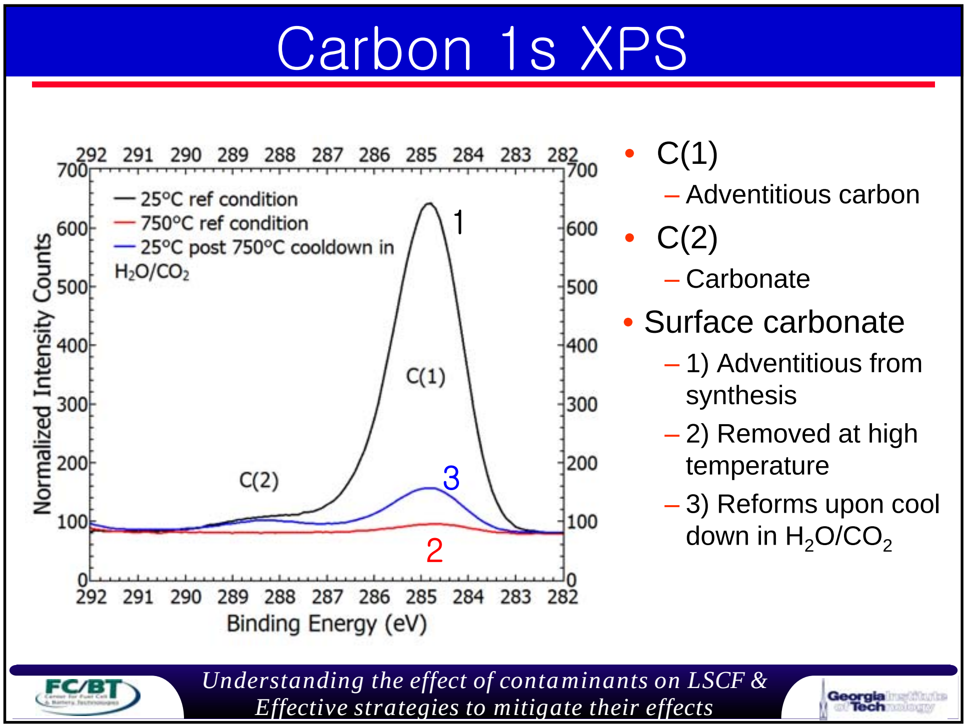
Summary: Operando XAS for SOFCs

Trends

- At **400˚C**, Co and Fe tend to be oxidized by CO_2 and H_2O, but cathodic bias enhances oxidation by H_2O/CO_2
- At 700˚C, observed effects caused by H_2O and CO2 is less significant, suggesting that the electrical effect is more prominent.
- Local structure of Co is less stable than Fe, particularly at 700˚C under H_2O

Proposed Mechanisms:

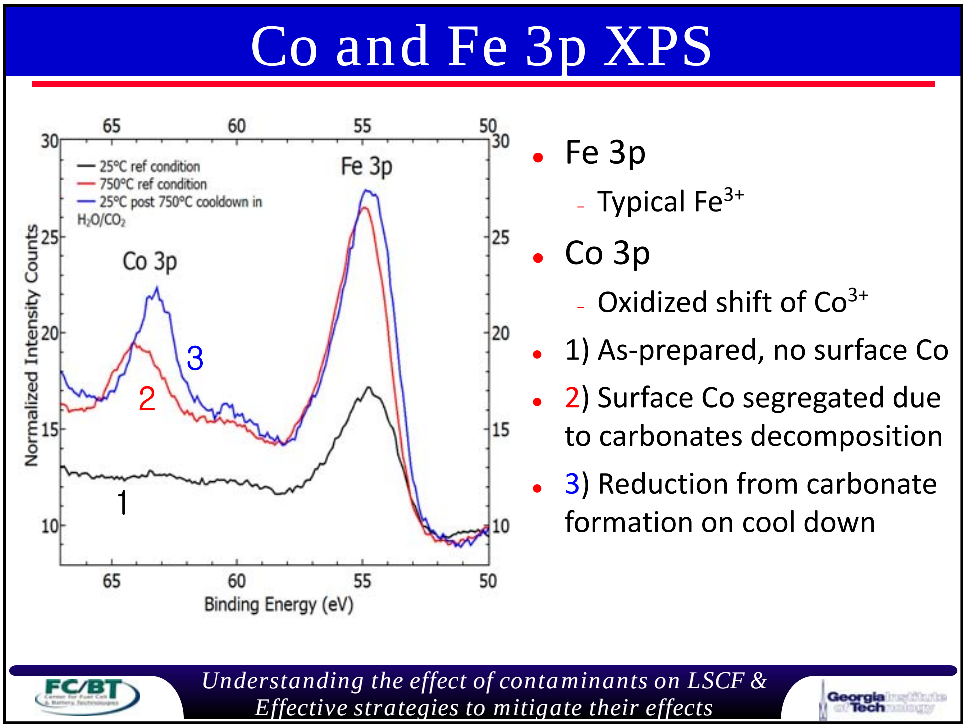
- ✓ CO_2 may form a carbonate bond with Co and Fe, which is more stable at lower temperatures
- ✓ Cathodic bias accelerates carbonate formation by creating more oxygen vacancies, causing stronger oxidation of Co and Fe, and more rapid degradation



Carbon 1s XPS

- C(1)
  - Adventitious carbon
- C(2)
  - Carbonate
- Surface carbonate
  - 1) Adventitious from synthesis
  - 2) Removed at high temperature
  - 3) Reforms upon cool down in H_2O/CO_2

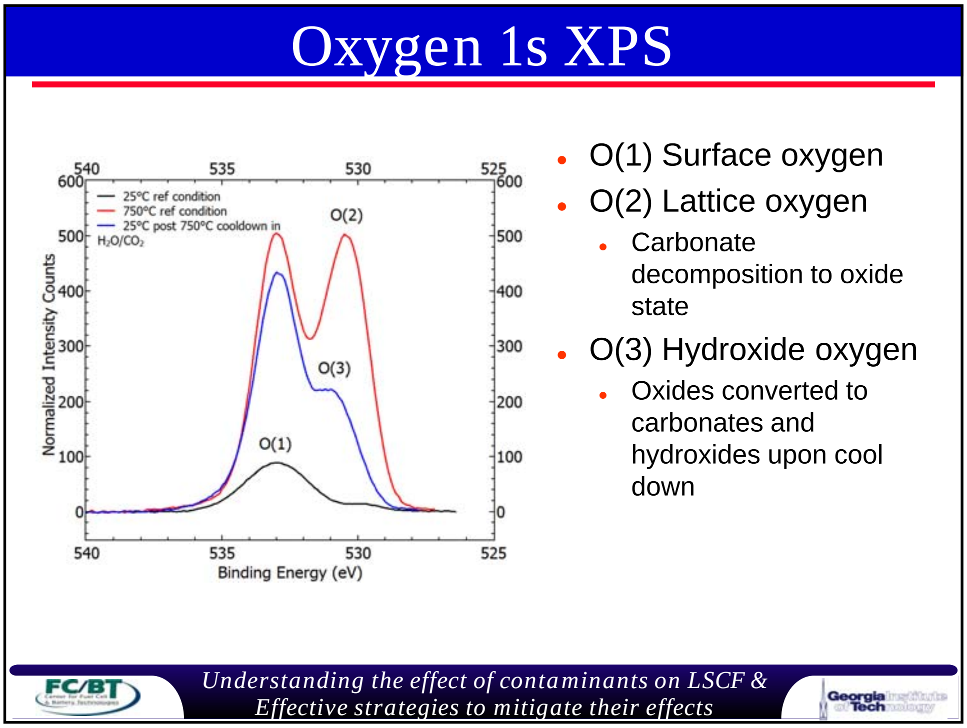
Understanding the effect of contaminants on LSCF &
Effective strategies to mitigate their effects



Co and Fe 3p XPS

- Fe 3p
  - Typical Fe^{3+}
- Co 3p
  - Oxidized shift of Co^{3+}
- 1) As-prepared, no surface Co
- 2) Surface Co segregated due to carbonates decomposition
- 3) Reduction from carbonate formation on cool down

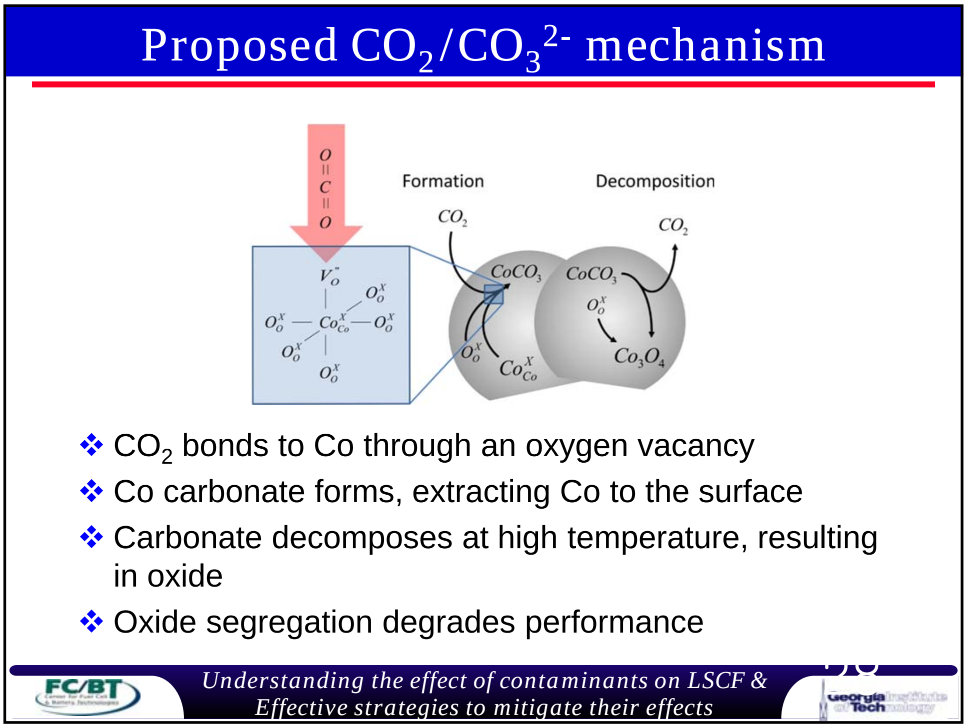
Understanding the effect of contaminants on LSCF &
Effective strategies to mitigate their effects



Oxygen 1s XPS

- O(1) Surface oxygen
- O(2) Lattice oxygen
  - Carbonate decomposition to oxide state
- O(3) Hydroxide oxygen
  - Oxides converted to carbonates and hydroxides upon cool down

Understanding the effect of contaminants on LSCF &
Effective strategies to mitigate their effects



Proposed CO_2/CO_3^{2-} mechanism

- CO_2 bonds to Co through an oxygen vacancy
- Co carbonate forms, extracting Co to the surface
- Carbonate decomposes at high temperature, resulting in oxide
- Oxide segregation degrades performance

Understanding the effect of contaminants on LSCF &
Effective strategies to mitigate their effects

Summary: Studying Surface Reactions of H2O/CO2 with XPS

Trends

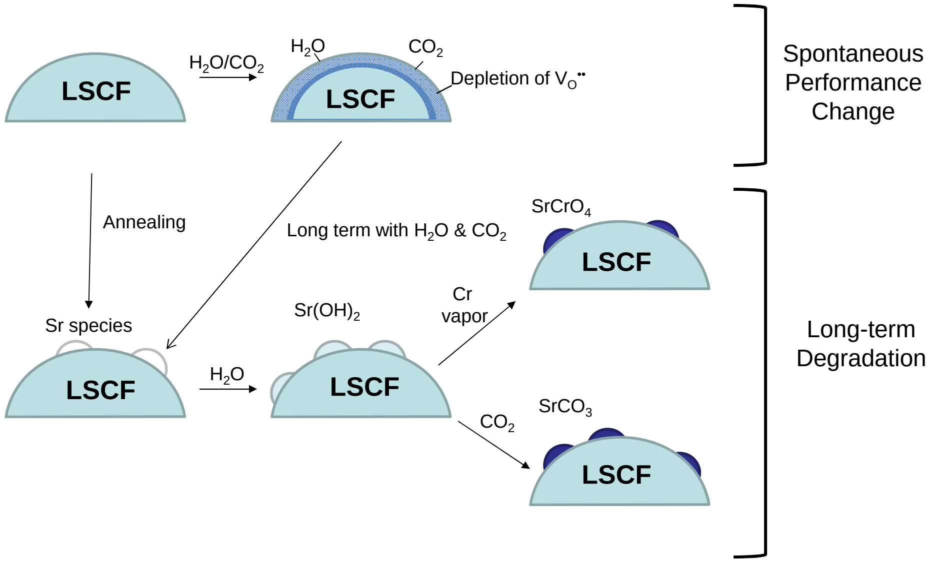
- Carbonate formation occurs adventitiously but decomposes at high temperature, which presumably results in oxide formation
- Carbonates can form from cooling down in an environment of H_2O/CO_2
- Co cations are absent initially from the surface but segregate to the surface at high temperature and irreversibly remain there
- Oxygen photoemission at high temperature confirms oxide species on surface

Proposed mechanisms:

- Co appears to be more susceptible to segregation through carbonate formation and decomposition
- Fe is more stable because of its electron bonding orbital occupancy
- Surface hydroxide formation may play a mediating role in continued segregation of Co

---

Proposed degradation mechanisms of LSCF with H2O, CO2 & Cr

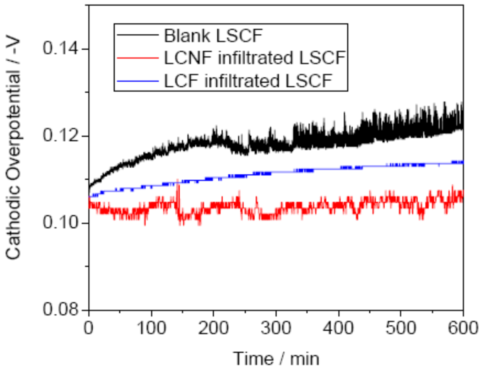


Accomplishments to Date

- ❖ 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.
- ❖ **Identified efficient catalysts for enhancing ORR activity and durability .**

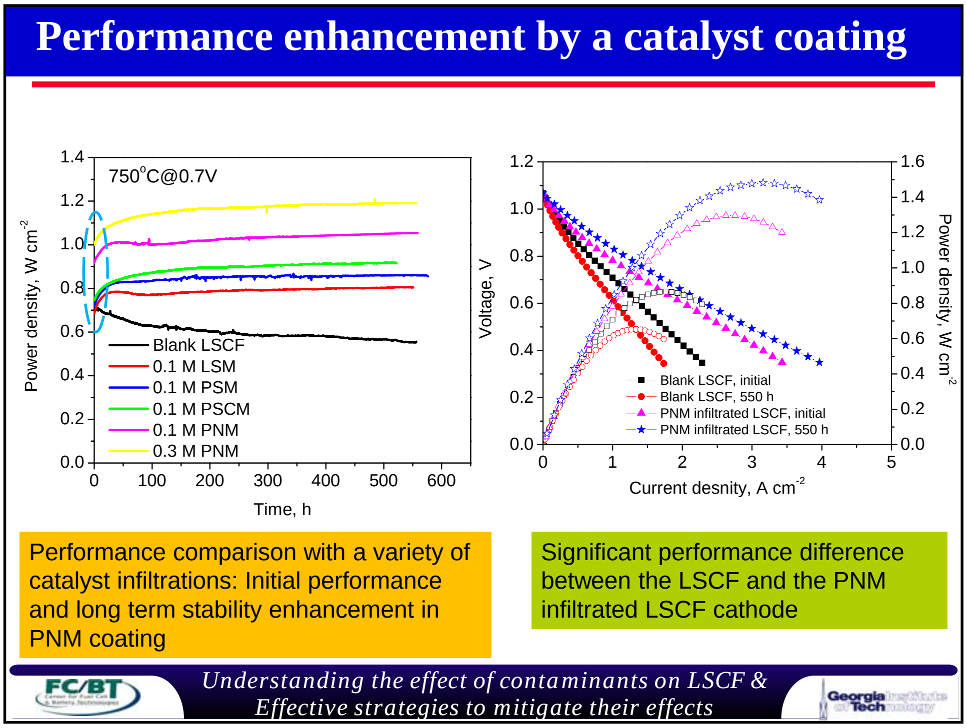
Cr Resistance by Surface Coating

- $(La, Ca)(Ni,Fe)O_{3-d}$ and $(La, Ca)NiO_{3-d}$ were infiltrated into the LSCF porous electrode.
- Infiltrated electrodes showed smaller cathode overpotential.



Symmetric cell with porous LSCF electrode.

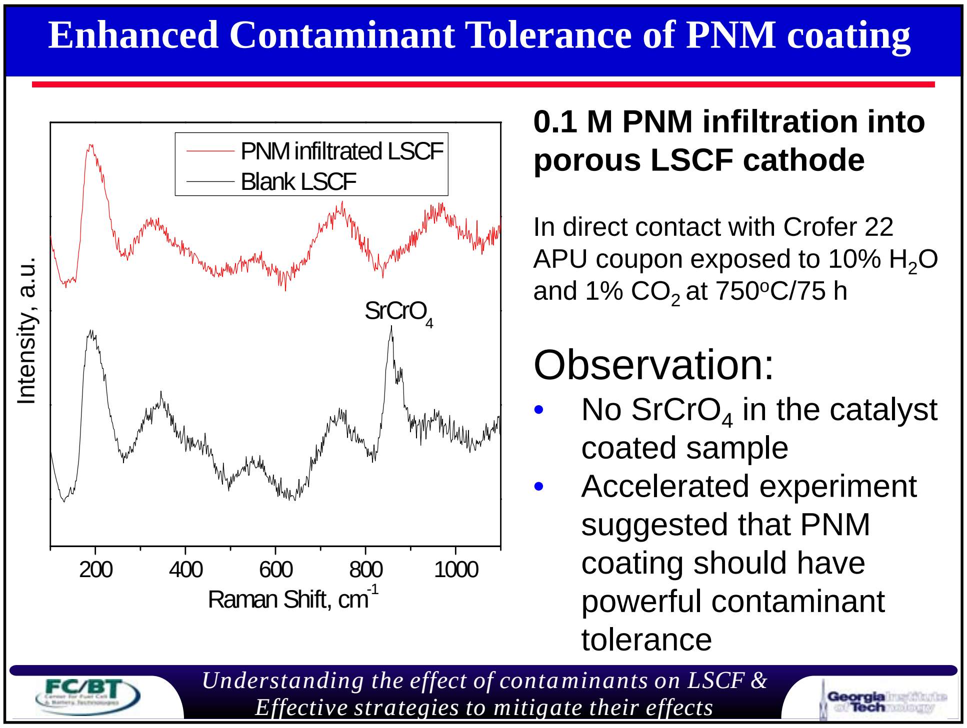
Tested at 750ºC, 10% H_2O+1% CO_2 in contact with Cr alloy.



Performance enhancement by a catalyst coating

Performance comparison with a variety of catalyst infiltrations: Initial performance and long term stability enhancement in PNM coating

Significant performance difference between the LSCF and the PNM infiltrated LSCF cathode



Enhanced Contaminant Tolerance of PNM coating

0.1 M PNM infiltration into porous LSCF cathode

In direct contact with Crofer 22 APU coupon exposed to 10% H_2O and 1% CO_2 at 750°C/75 h

Observation:

- No $SrCrO_4$ in the catalyst coated sample
- Accelerated experiment suggested that PNM coating should have powerful contaminant tolerance

Implications

- Adsorbed H_2O and CO_2 may react with segregated Sr to form hydroxide and then carbonate. Since carbonate may be more stable thermodynamically, Sr segregation is exacerbated in the presence of H_2O and CO_2.
- Both H_2O and CO_2 promote the formation of A-site deficiency which is very likely to accelerate (a) surface segregation of Sr from LSCF (intrinsic degradation mechanism) and (b) the increased formation of Cr-containing surface species (e.g. $SrCrO_4$) (extrinsic degradation mechanism).
- New catalyst coatings through solution infiltrations are effective approaches to enhance ORR activity and durability, effectively mitigating the effect of contaminants.

Acknowledgement

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

SECA

DOE-SECA core technology program (Grant No. FE0009652)

BROOKHAVEN NATIONAL LABORATORY

Brookhaven National Laboratory

HeteroFoaM CENTER

DOE Basic Energy Science Energy Frontier Research Center