Highly-Active and Contaminant-Tolerant Cathodes for Durable Solid Oxide Fuel Cells

Project Number: DE-FE0031201
DOE Project Manager: Dr. Arun Bose

Meilin Liu, Yu Chen, Ryan Murphy

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
DOE-NETL SOFC Kickoff Meeting
Nov. 29, 2017

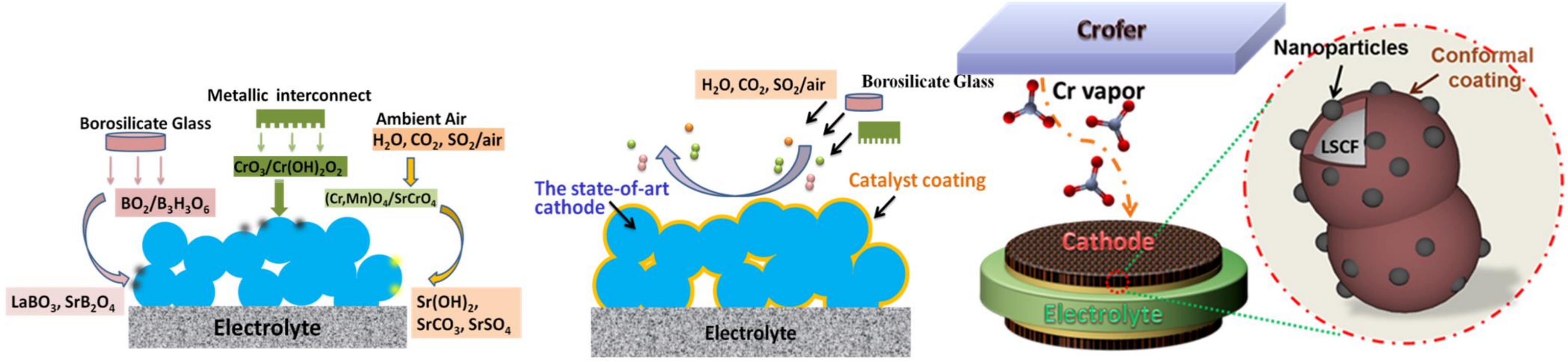
Outline

- Project information
- Background: Motivation, Critical Issues
- Project objectives
- Technical Approaches
- Project structure
    - Tasks to be performed
    - Milestones and Schedule
- Project budget
- Project Management Plan, including Risk Management
- Preliminary Results

Project information

- **Team members**
  - Georgia Tech (Meilin Liu, Yu Chen, Ryan Murphy)
- **Project description**
  - Modify LSCF cathodes for long-term stability under *realistic conditions* to enhance activity and stability
  - Enhance stability against Cr, H_2O etc, and combined effect of contaminants;
- **What do we expect?**
  - Unravel LSCF cathode degradation mechanism when exposed to Cr, H_2O, CO_2, etc, and formulate strategies to mitigate degradation against contaminants;
  - Develop robust and electro-active catalysts (**Alkaline-based oxide**) against contaminants
  - Enhance the performance and durability of LSCF-based cathodes by application of a thin-film coating of robust electro-catalysts.

Motivation



- Cathode durability is critical to long-term reliable SOFC performance for commercial deployment.
- 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 help to meet **DOE cost and performance goals**.

Project Objectives

- **To develop new catalysts (low-cost alkaline-earth metal oxide)** that are compatible chemically with the state-of-the-art cathode materials at high temperatures required for fabrication and with contaminates commonly encountered under operating conditions (Cr, S, B, and combined effect);
- **To evaluate the electro-catalytic activity** toward ORR of the chemically-stable materials when exposed to different types of contaminants using electrical conductivity relaxation measurements on bar samples and performance evaluation of catalyst-infiltrated cathodes;
- **To unravel the contamination-tolerant mechanisms** of the new catalyst coatings under realistic environmental conditions (with different types of contaminants) using powerful *in situ* and *in operando* characterization techniques performed on **model cells** with thin-film/pattern electrodes, as guided by modeling and simulation;
- **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.

Tasks and Schedule

Task 1: Project Management and Planning

Task 2: Charactering the EC Behavior of Catalyst-Coated LSCF under Realistic Conditions

Task 3: Understanding the Mechanism of Contamination Tolerance

Task 4: Development of Low-cost and Applicable Deposition Techniques for Cathode

Task 5: Development of Catalyst Coating on Porous Cathodes of Large Commercial Cells

Task 6: Verification of Catalyst Coating in a Subscale Stacks of Fuel Cell Energy

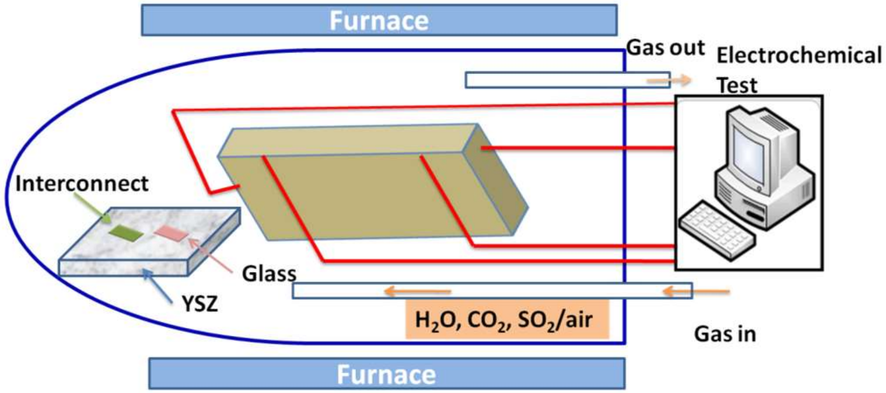
Task	FY2017	FY2018				FY2019		
	Q4	Q1	Q2	Q3	Q4	Q1	Q2	Q3
1	→							
2	→	→	→					
3		→	→	→	→			
4				→	→	→	→	
5						→	→	→
6							→	→

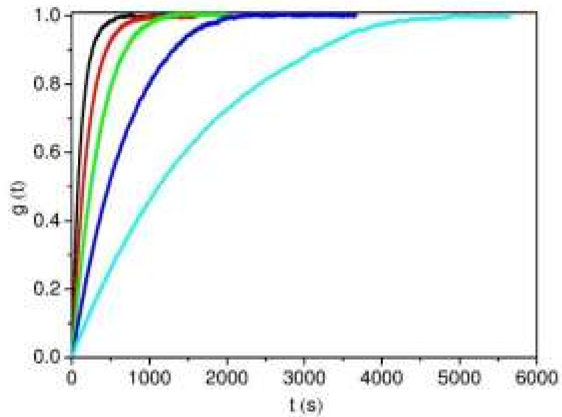
Task 1: Project Management Plan (PMP)

- Finalize the PMP in order to meet all technical, schedule, and budget objectives of the project;
- To ensure that all activities are well coordinated in order to effectively complete all tasks;
- Ensure that project plans, results, and decisions are appropriately documented and project reporting and briefing requirements are satisfied.

Task 2: Charactering EC behavior of cathodes under realistic conditions

- ECR (Electrical Conductivity Relaxation) measurement

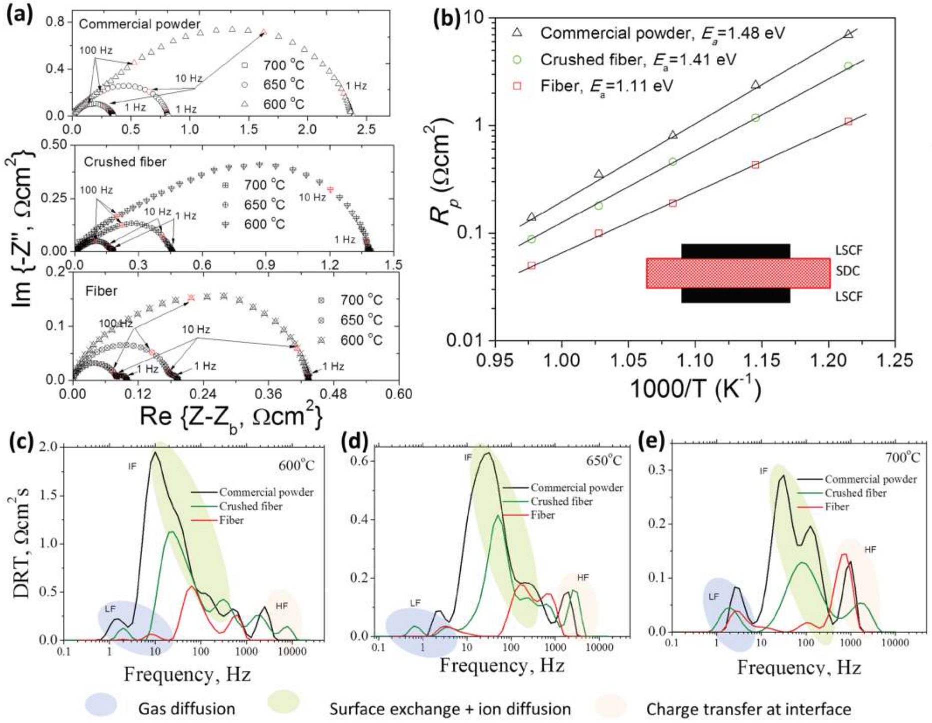




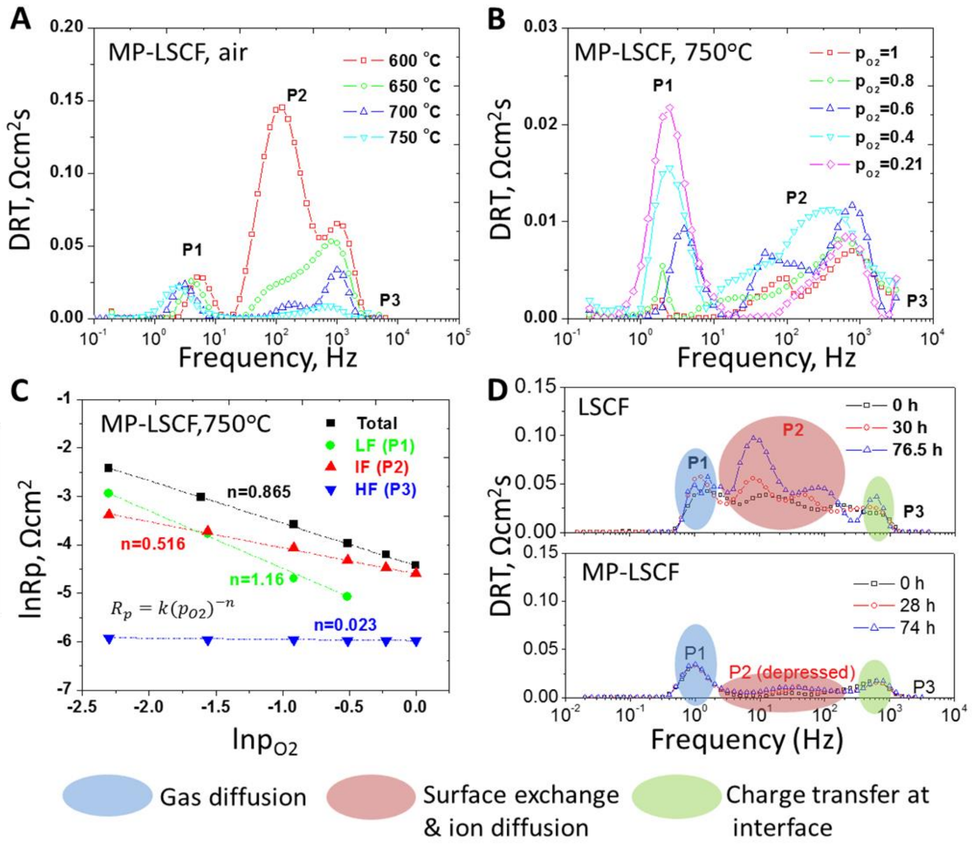
$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)}$$

- Performed by changing the oxygen partial pressure while recording the electrical relaxation curves of dense bar samples (w/o catalyst);
- Oxygen surface exchange rates of the cathode materials will be calculated from fitting the relaxation curves.

Distribution of Relaxation Time (DRT)



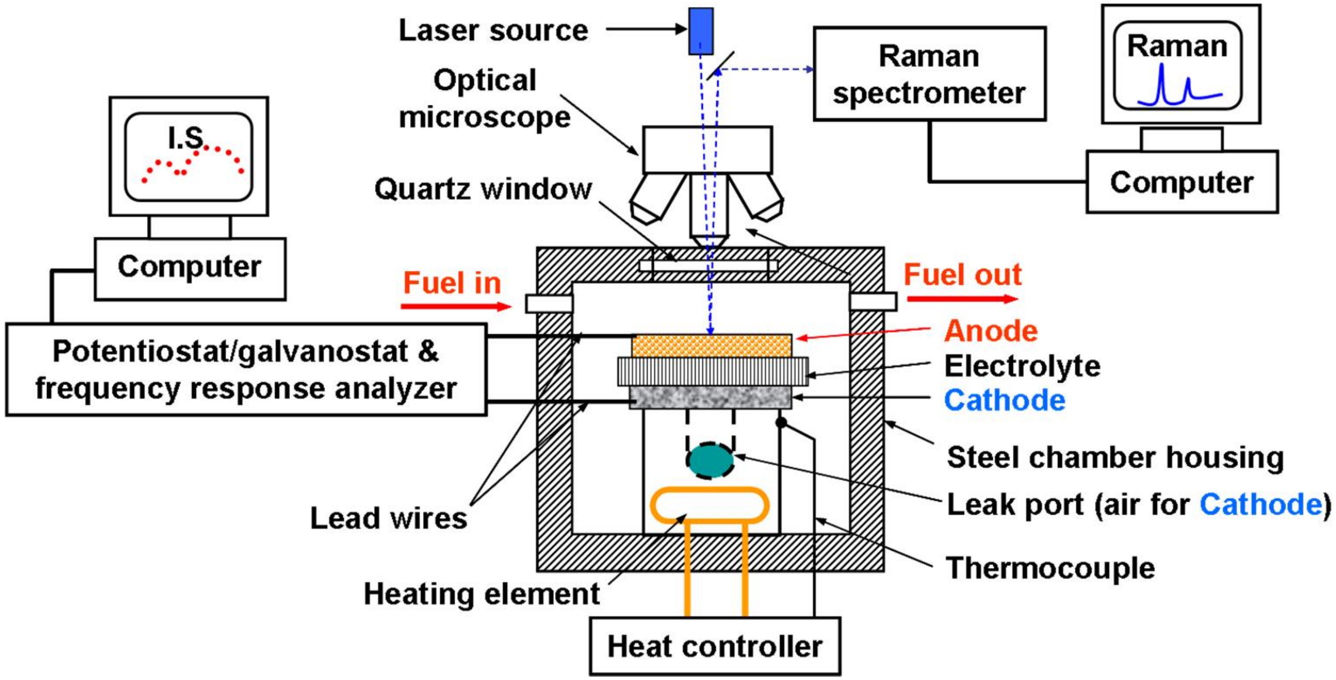
***Advanced Energy Materials* 2017, 7, 1601890.**



- ❑ DRT is a powerful tool for deconvoluting the impedance data of the complex ORR reactions, helping us to separate or isolate some of the key steps involved in the electrode reactions.

Task 3: Understanding the mechanism of contaminant tolerance

Changes in surface chemistry, structure, and morphology of LSCF cathodes, with or without exposure to various contaminants, will be characterized using SEM, AFM, EDX, XRD, Auger, XPS, **Raman (SERS)**, **synchrotron-based X-ray** analyses under *in situ* or *ex situ* conditions.

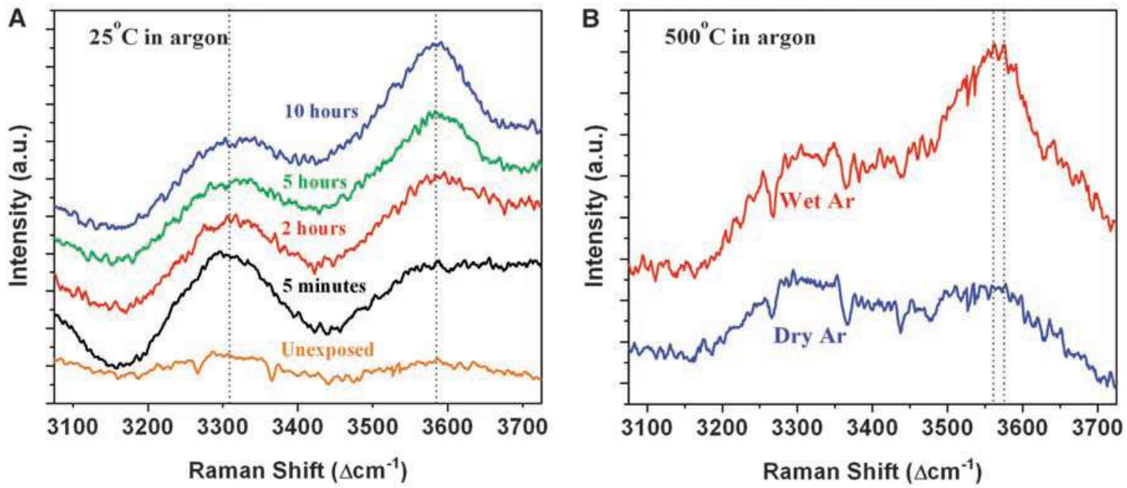


in situ and *ex situ* Raman: monitor the surface chemistry, e.g., interactions between LSCF and B, S and/or Cr. Many reaction products are Raman-active.

OH stretching (3300cm^{-1}) and water bending (1600cm^{-1})

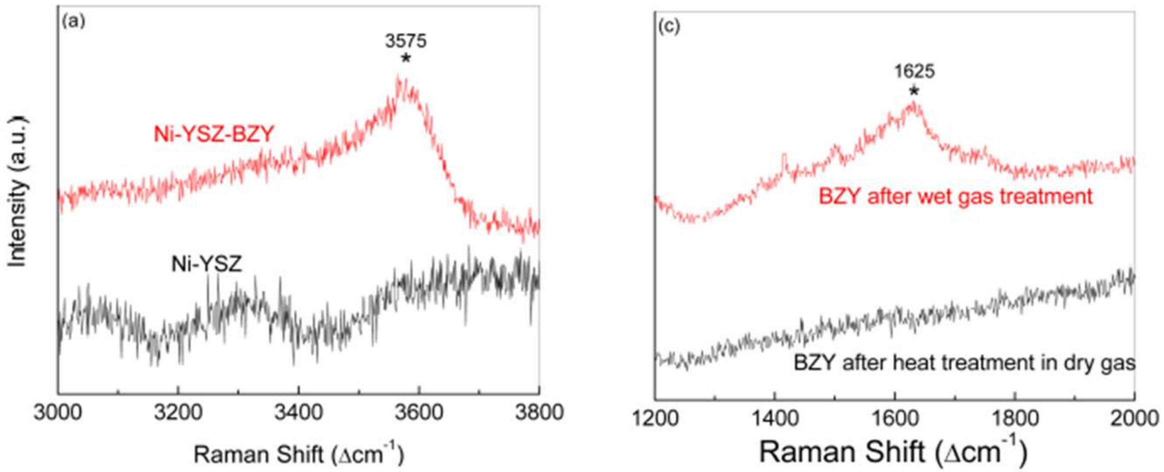
Yang *et al.*, Science, **326** (5949) 126, 2009.

BZCYYb



Liu *et al.,* Nano Energy, **1,** 448-455, 2012.

BZY



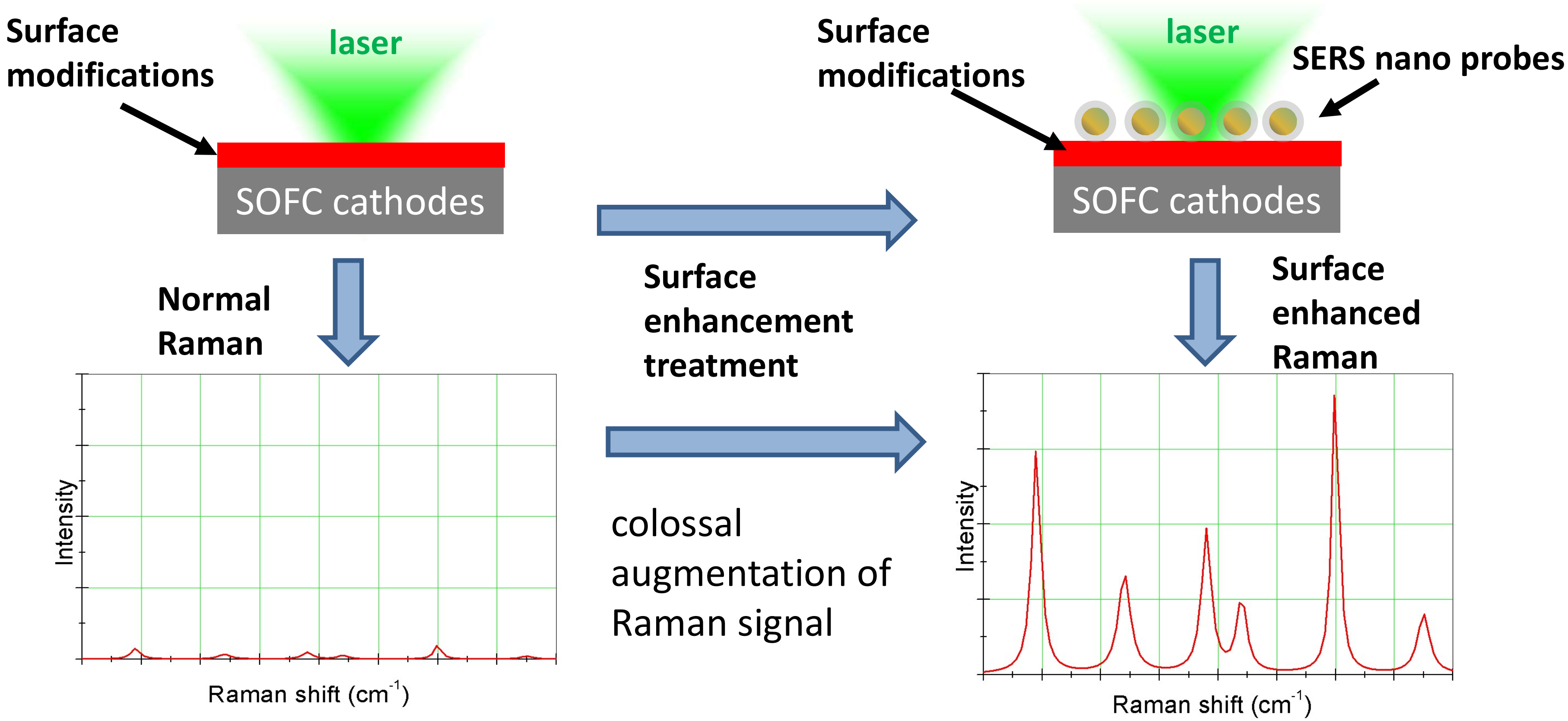
U.S. DEPARTMENT OF ENERGY

Highly Active and Durable SOFC Cathodes

SECA

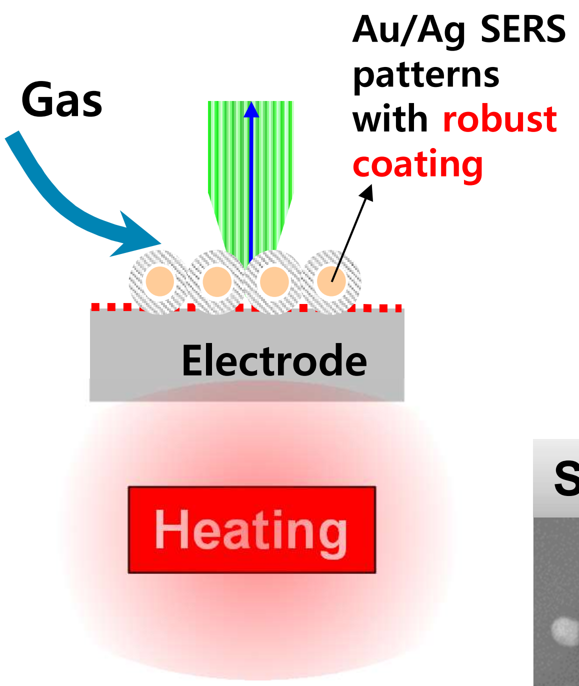
Surface Enhanced Raman Spectroscopy (SERS)

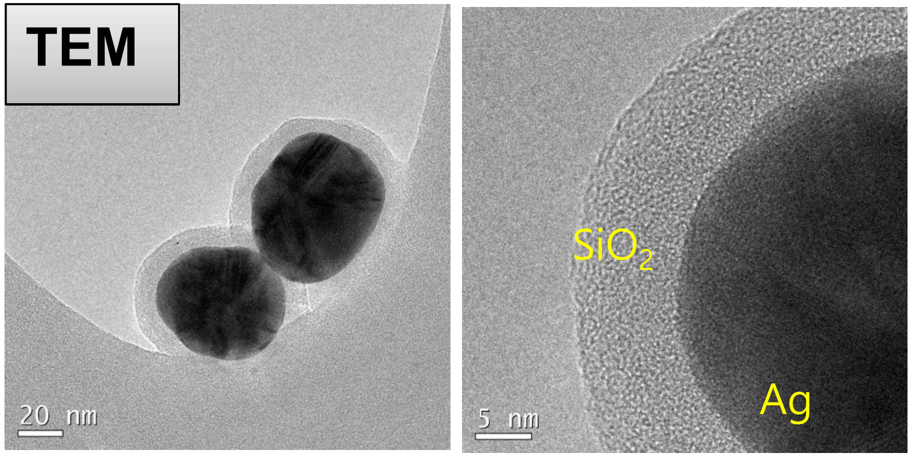
- Combination of Raman spectroscopy with surface enhancement technique



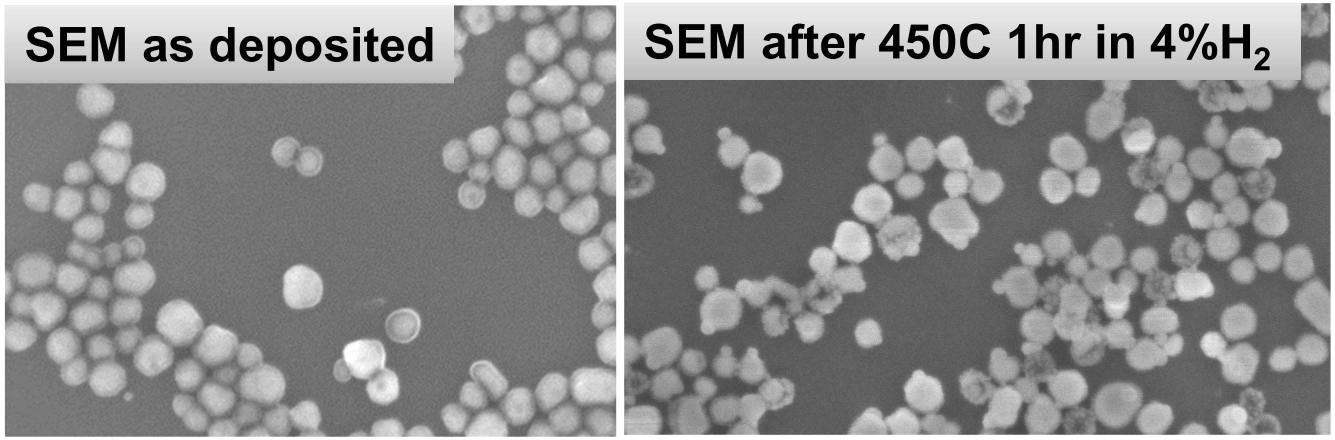
In situ SERS with Ag@SiO_2 Nanoparticles (NPs)

TEM images showing core-shell nanoparticles.
Size of the silver NPs: 50nm Thickness of the SiO2: 5nm



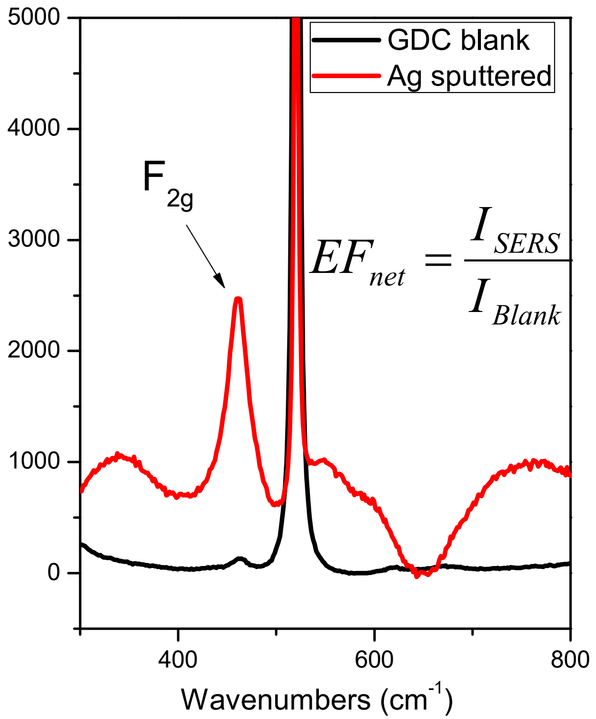


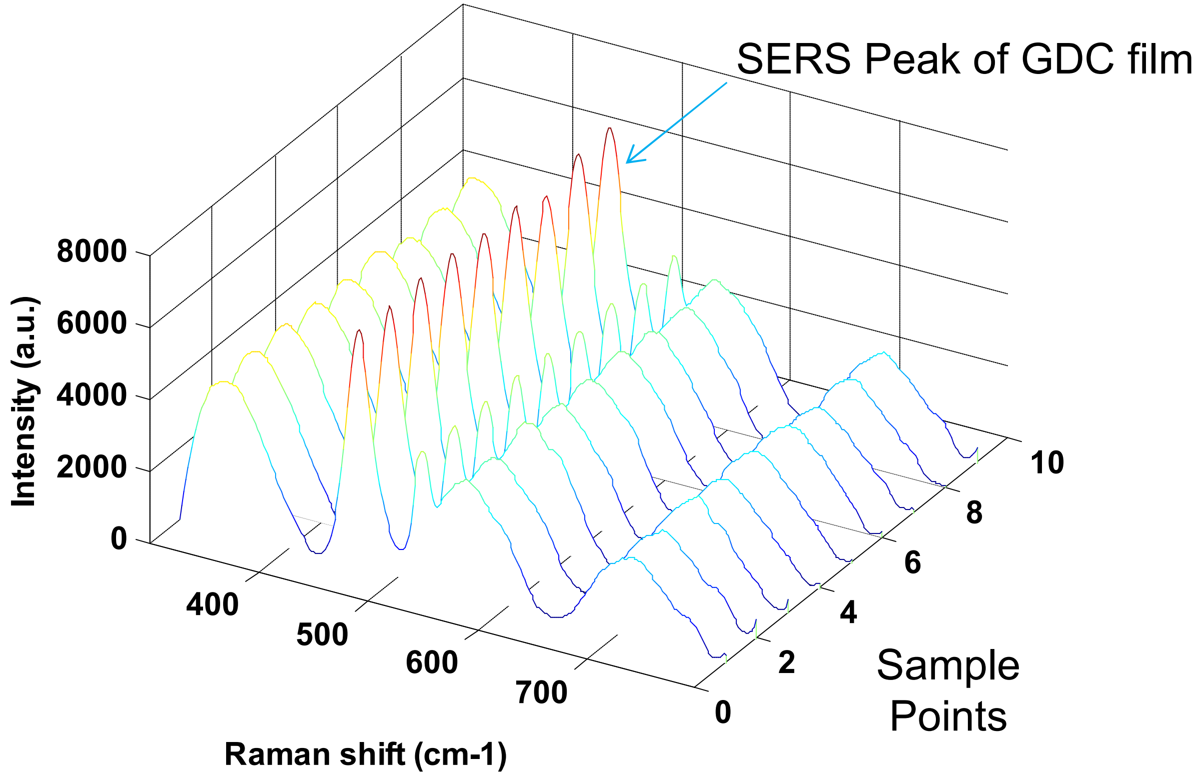
SEM images . High temperature treatment did not change the shape and distribution.



Confirmation of SERS with Ag NPs

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

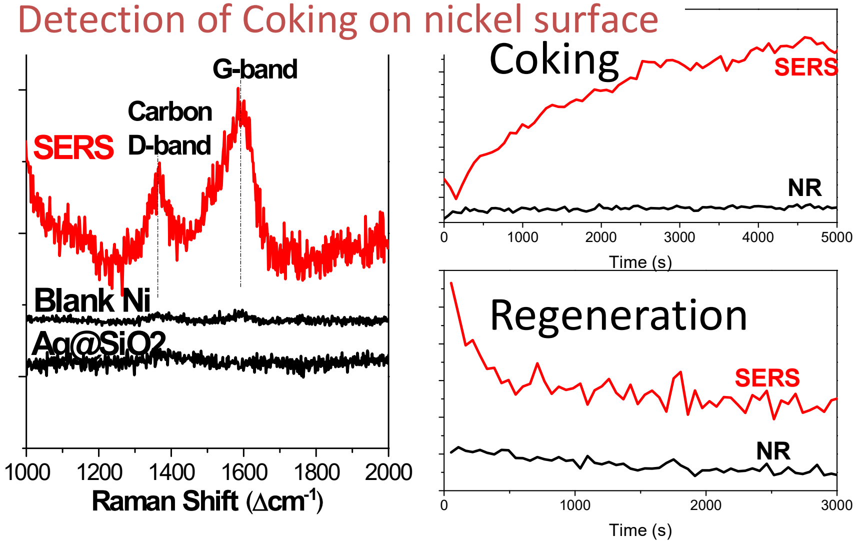




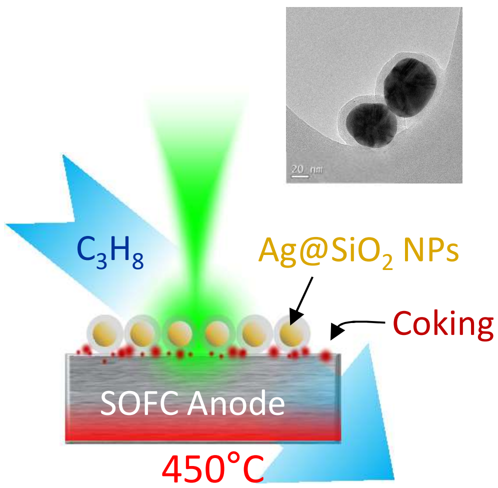
In situ SERS for Identification of Surface Species

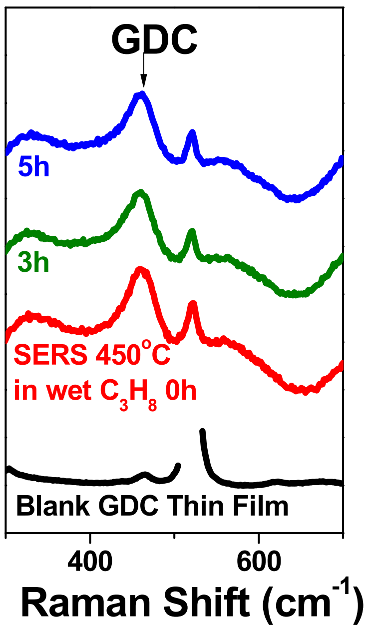
- •Developed thermally robust & chemically inert Ag@SiO_2 core-shell nanoparticles for in situ SERS at 450C.
- • Detected incipient stage carbon deposition on nickel.
- • Detected surface defects on CeO2 powders.

Detection of Coking on nickel surface



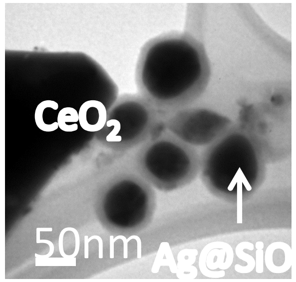
In-situ SERS with core-shell nano probes



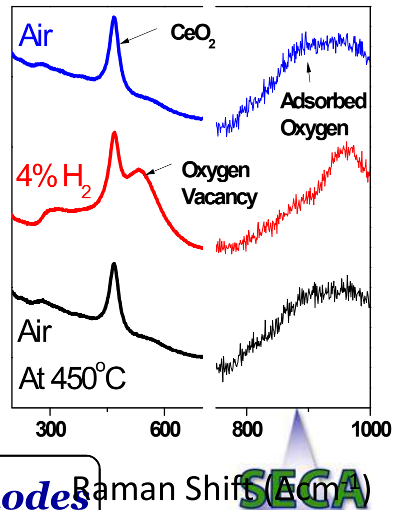


Detection of Surface defects on CeO_2 powders

Detection of Oxygen Vacancy on CeO_2



SERS probes showed thermal integrity, after heat treatment.

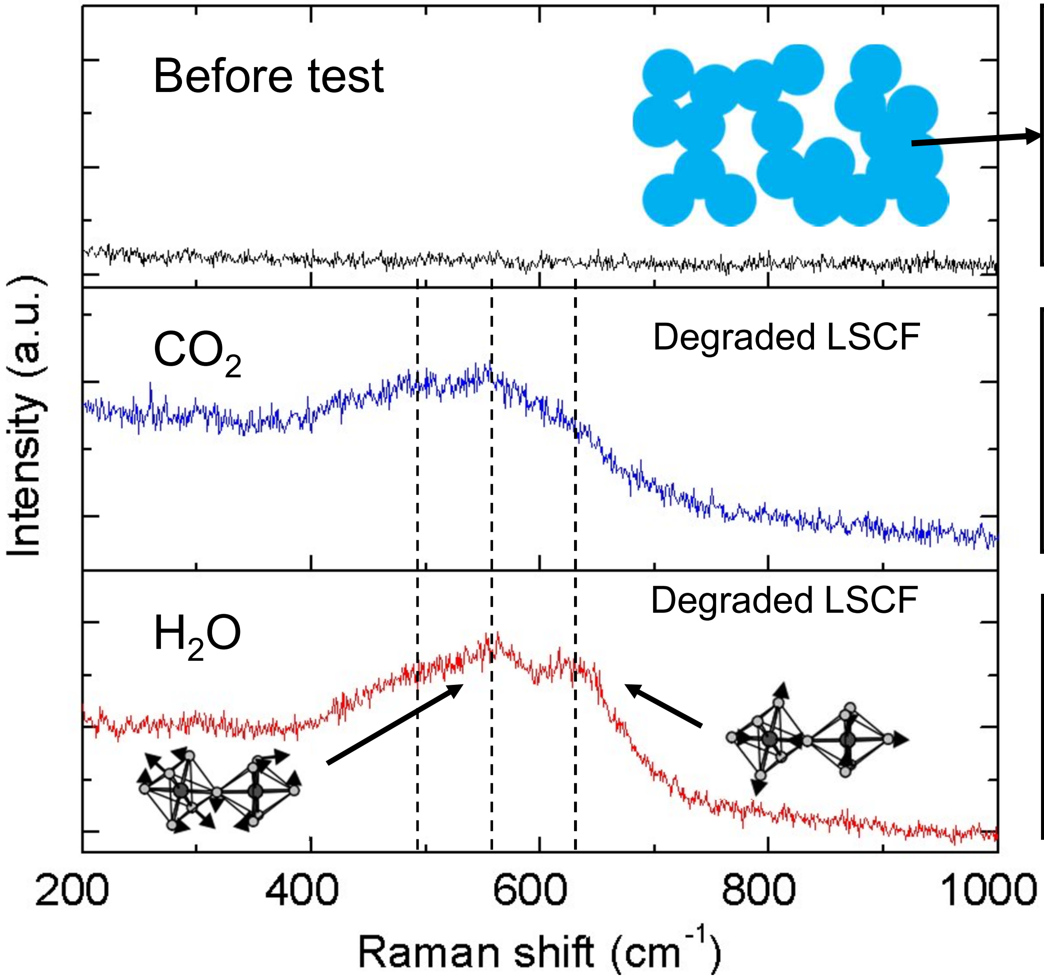


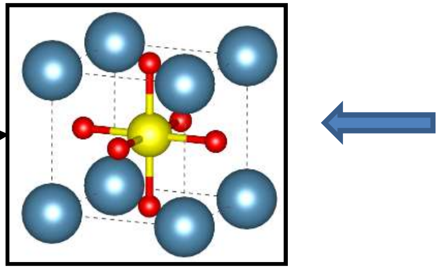
Highly Active and Durable SOFC Cathodes

U.S. DEPARTMENT OF ENERGY

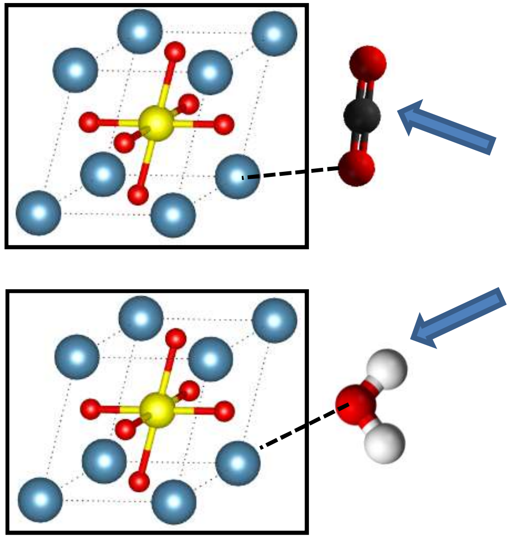
SECA

Effects of H_2O and CO_2 on Bare LSCF





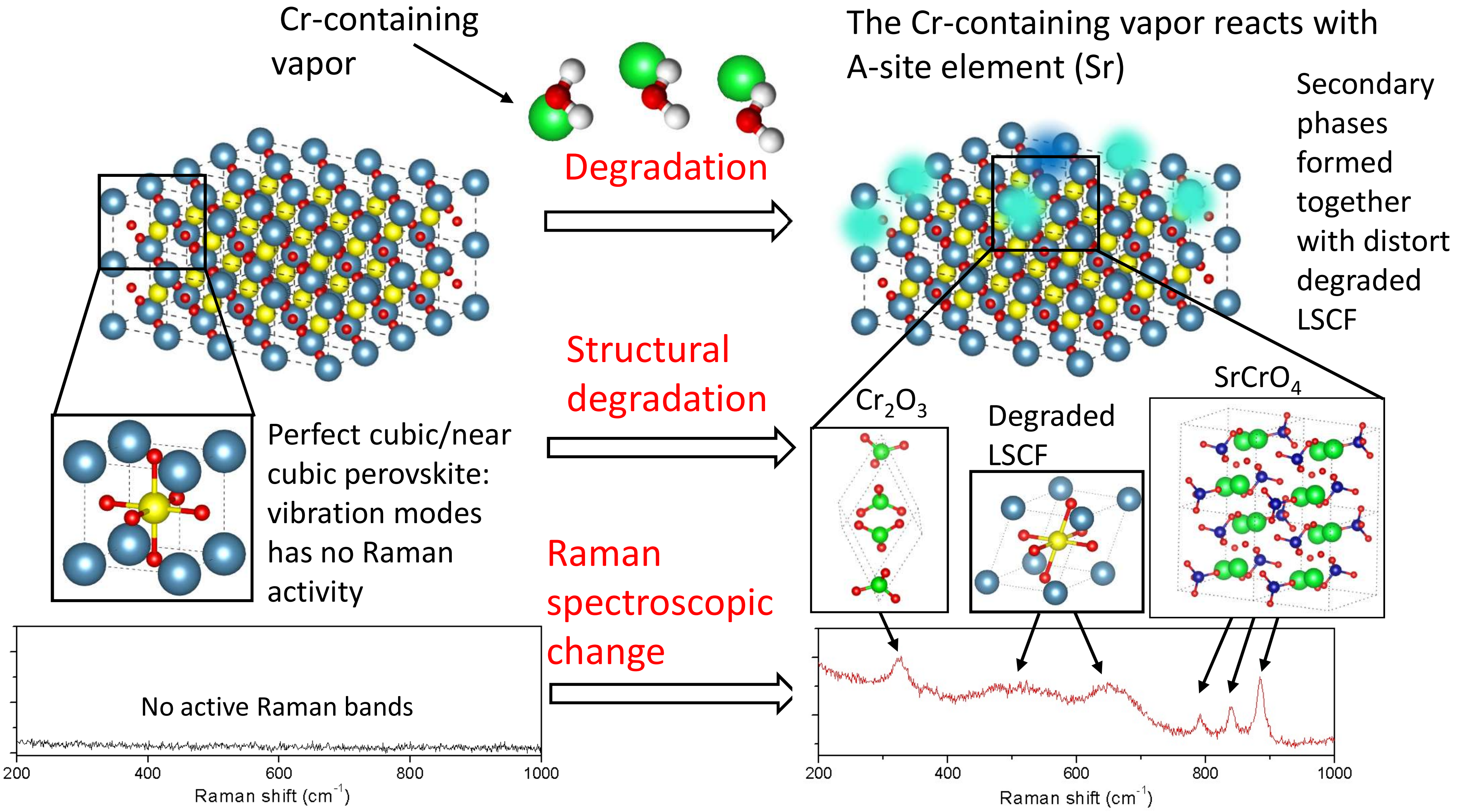
No visible Raman bands due to perfect cubic/near cubic structure



Both CO_2 and H_2O lead to considerable Raman bands of surface locally distorted degraded LSCF

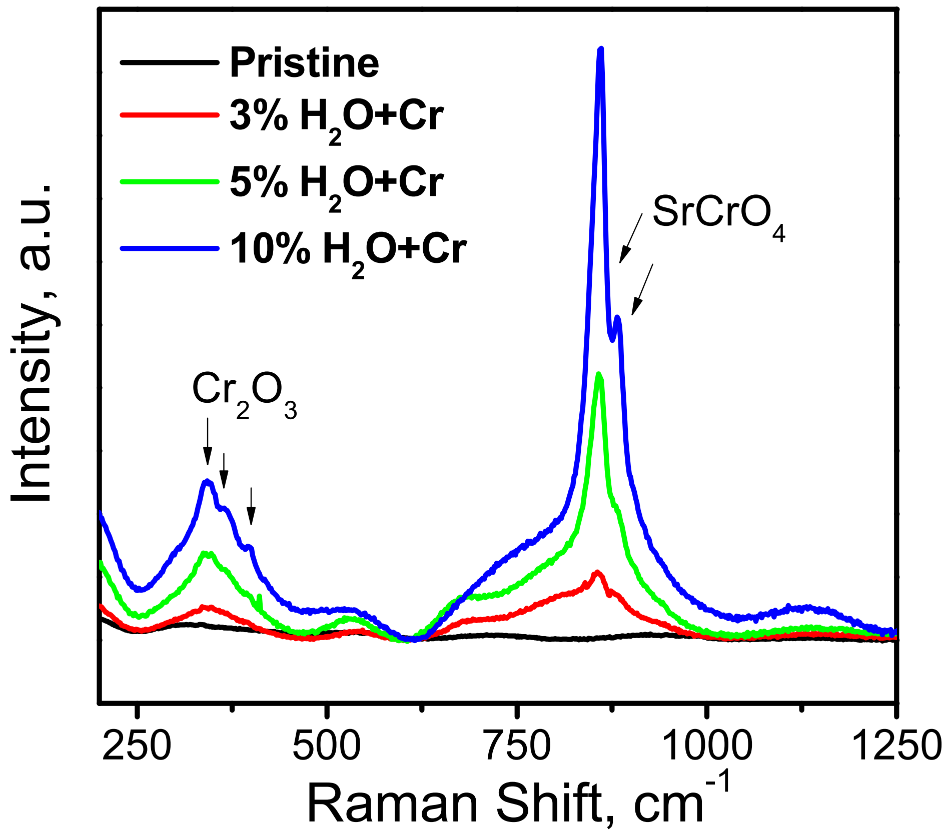
However, no **secondary phases** were observed, consistent with the fact that no serious performance degradation.

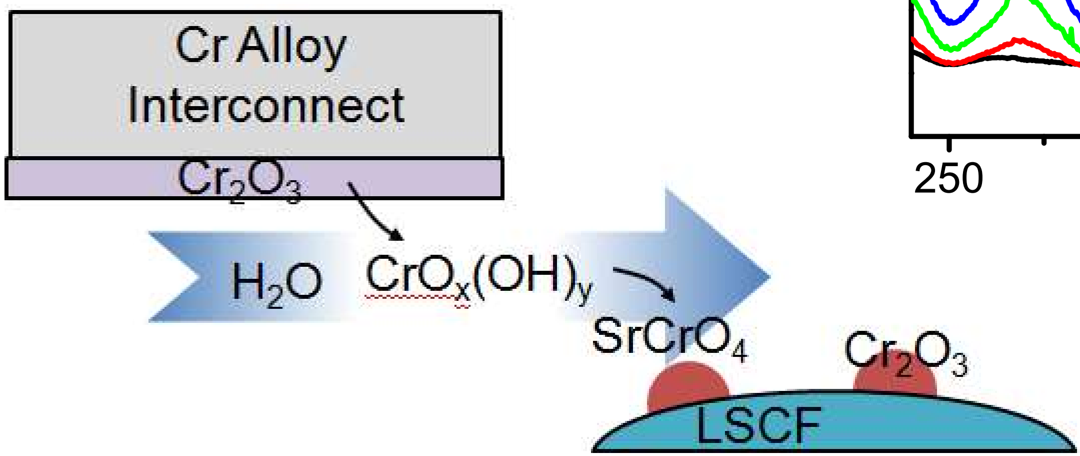
Effects of Cr on LSCF Raman spectra



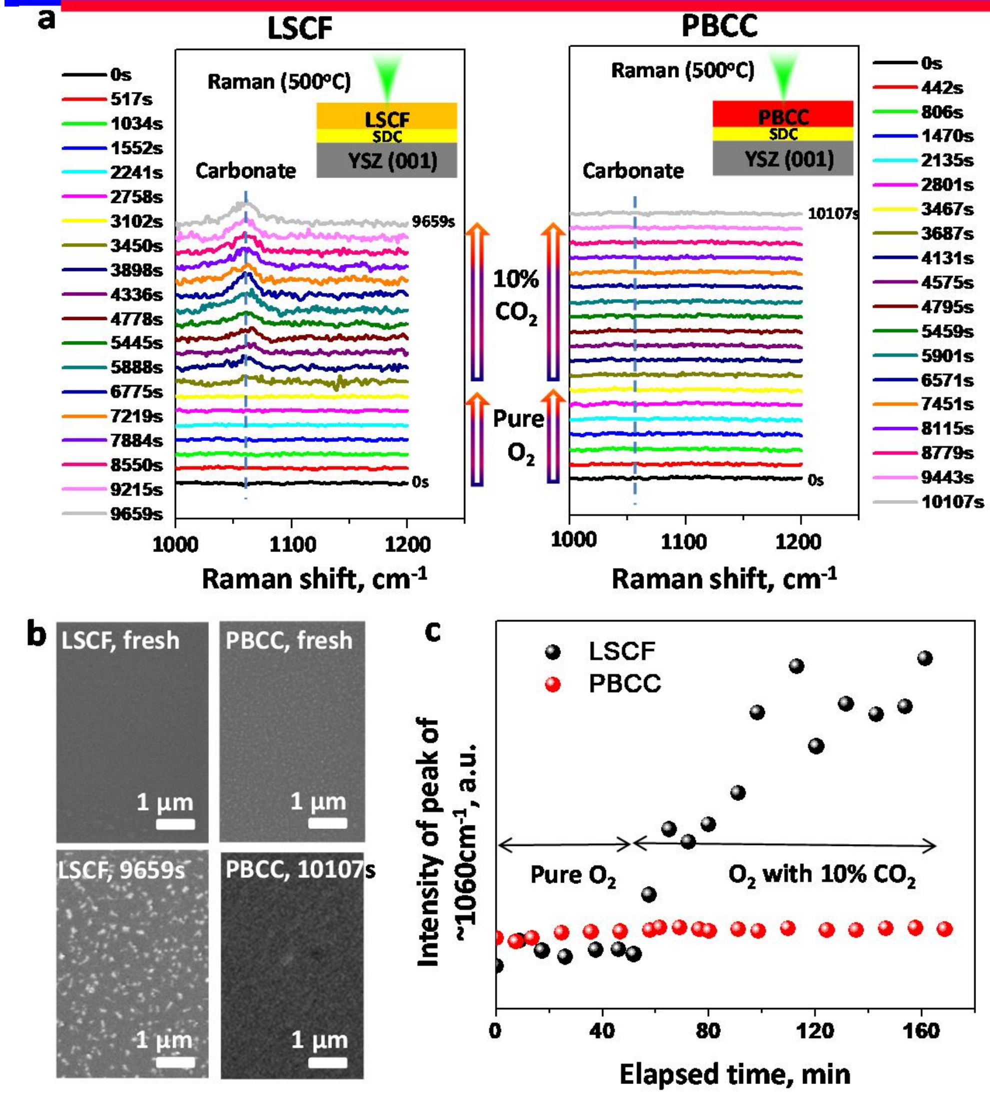
SERS Analysis of Cr Poisoned Samples (Direct Contact)

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





SERS Analysis of CO2 Poisoned Samples



***In situ* Surface enhanced Raman spectroscopic (SERS) study of thin film electrode prepared by PLD. (a)** *In situ* SERS spectra of LSCF and PBCC thin film at 500 °C in atmosphere of pure O_2 or O_2 with 10% CO_2; **(b)** SEM of fresh films and films after Raman testing in O_2 with 10% CO_2; **(c)** Intensity of peak of ~1060cm^{-1} observed from thin film LSCF and PBCC surface.

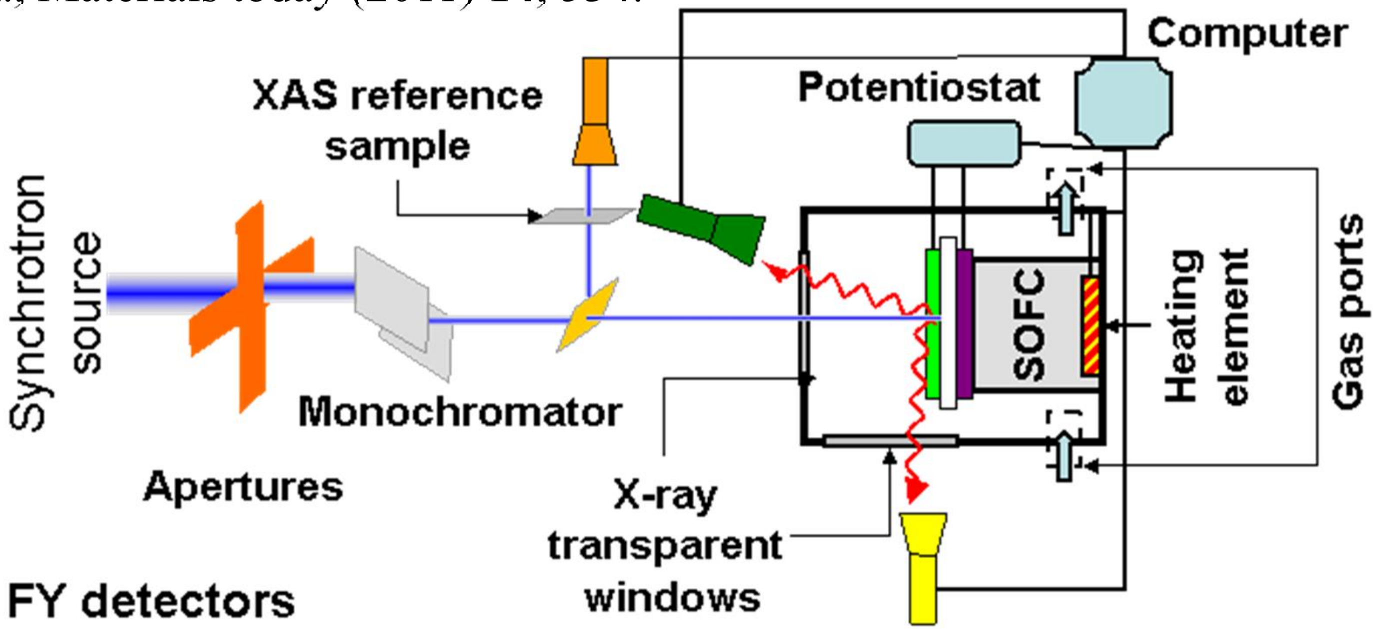
- **PBCC is more robust than LSCF**

U.S. DEPARTMENT OF ENERGY

SECA

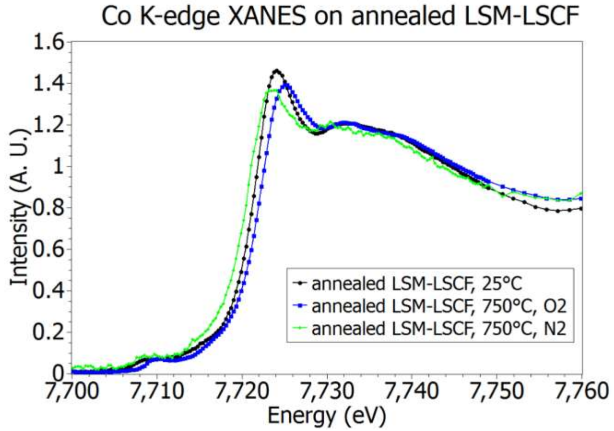
Synchrotron-Enabled XRD, XAS, & XPS

Liu et al., Materials today (2011) **14**, 534.

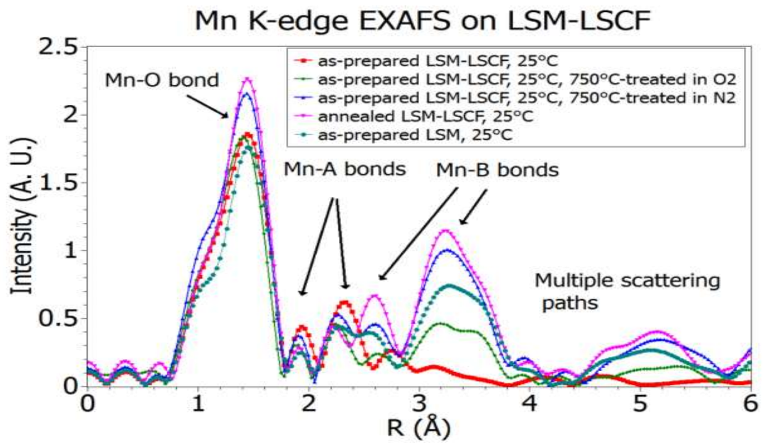


- Provides unique ability to study *bulk and surface structures* simultaneously via fluorescent X-ray absorption spectroscopy (XAS), Auger electron yield, and X-ray diffraction (XRD)
- Probe *near-surface* of electrode and identify surface composition, structure and chemical environment of specified element under *in situ* conditions: temperature, atmosphere, and bias
- Examine *interface reactions* between electrode and electrolyte under *in situ* conditions: temperature, atmosphere and bias

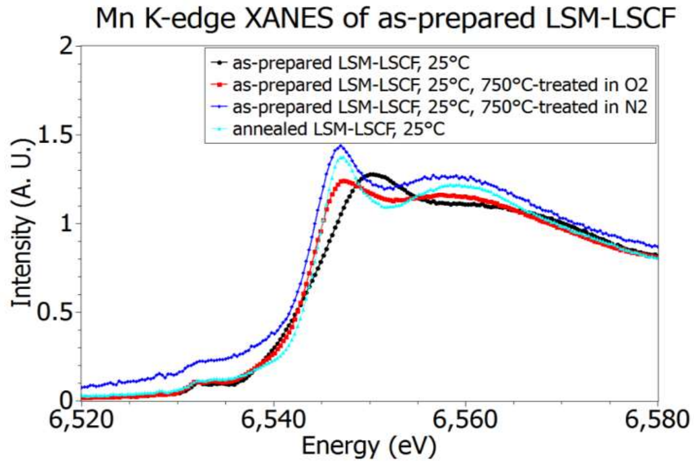
Synchrotron-Enabled XRD, XAS, & XPS



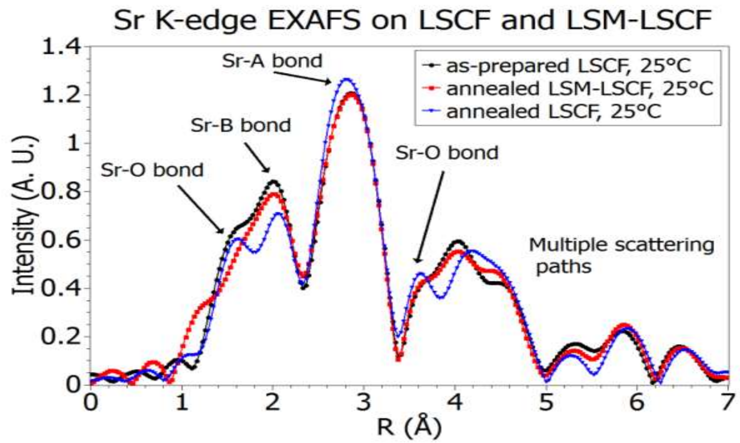
Reversible changes in oxidation state



The peak growth and new features indicate ordering of the Mn local structure.

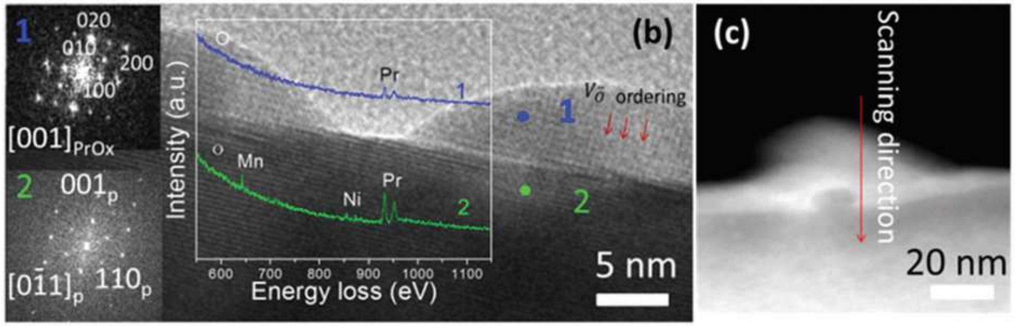


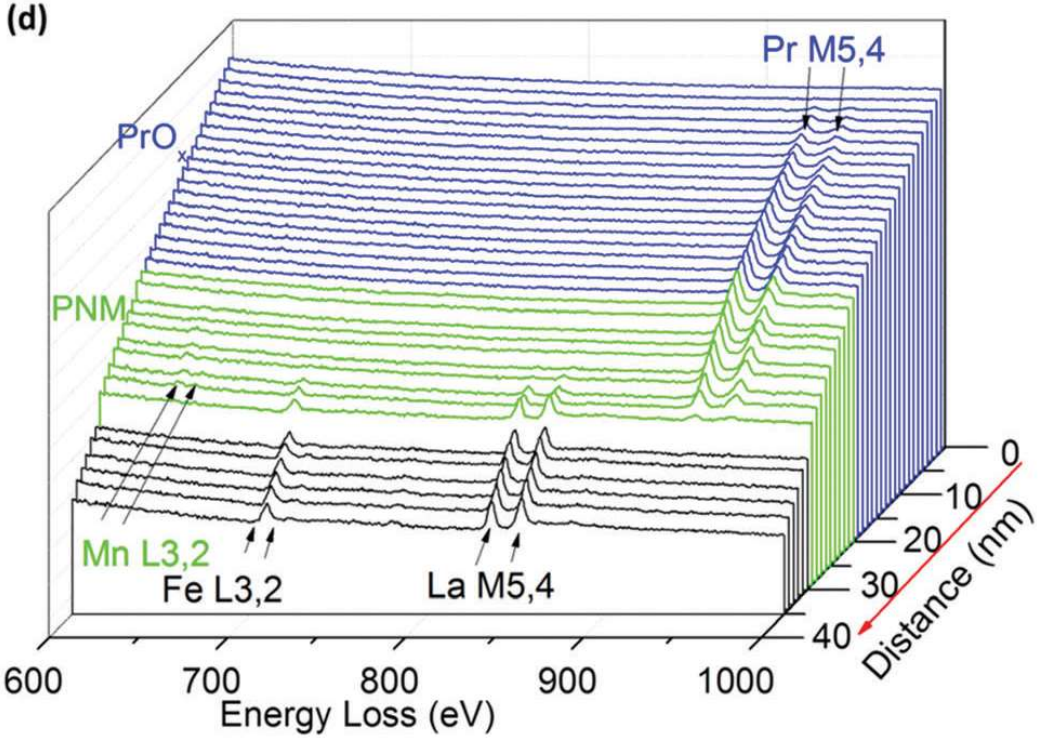
Mn is reduced at High Temp.



Peak splitting and shifting at 2.8 Å represent slight structural deformation.

Microstructure of Interface

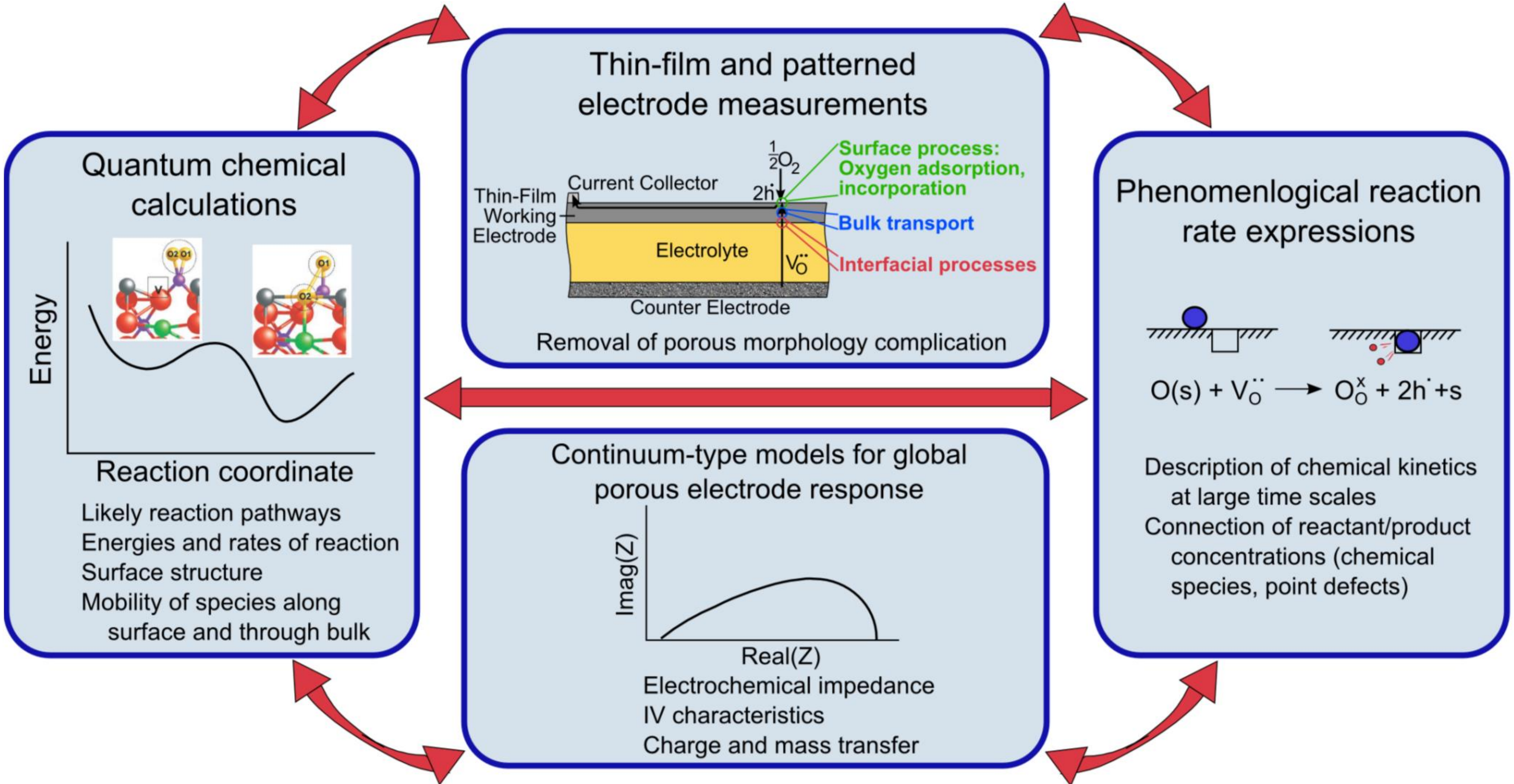




Energy Environ. Sci. 2017, 10, 964.

Task 4: Modeling/rational design of new materials/electrode structures

Modeling, simulation as well as prediction tools will be used to help in formulating an effective strategy to mitigate the stability issues and predict new catalyst materials that can enhance the stability of LSCF.



Design of new materials

Micro-prediction

Theoretical Analysis to predict certain chemical, catalytic, and transport properties of new materials with different morphologies

Macro-prediction

Continuum Modeling to predict the performance of the new materials

Validation

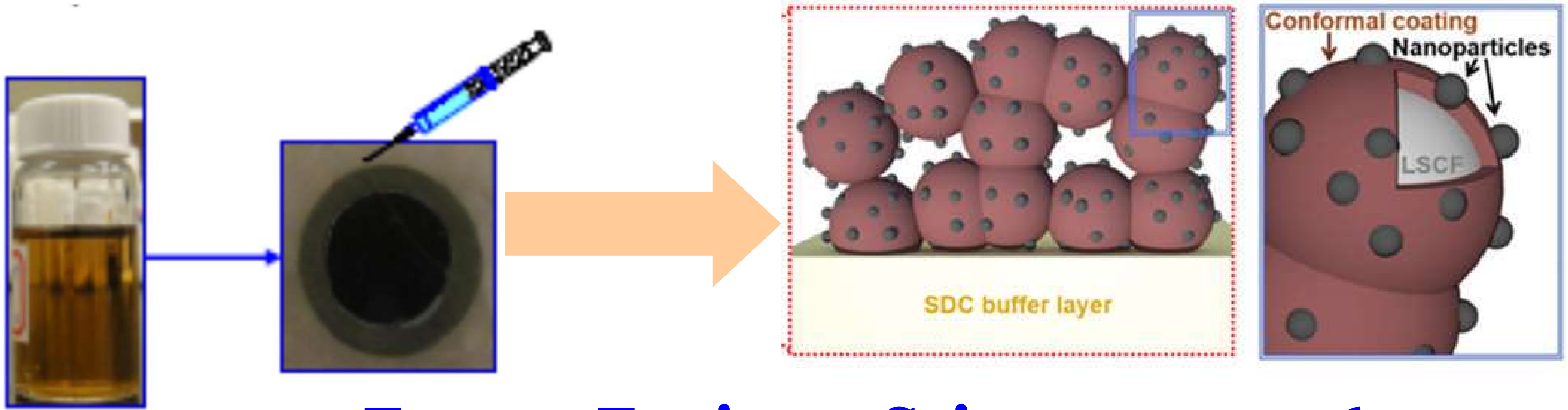
Electrochemical measurements to validate predictions in a most direct way

The combination of Theoretical/continuum models and the well-controlled experiments will lead to new materials and novel structures for cathode of low polarization resistance and high durability.

Surface modification

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

Catalysts | **Solution Infiltration** | **Surface Modified Cathode**

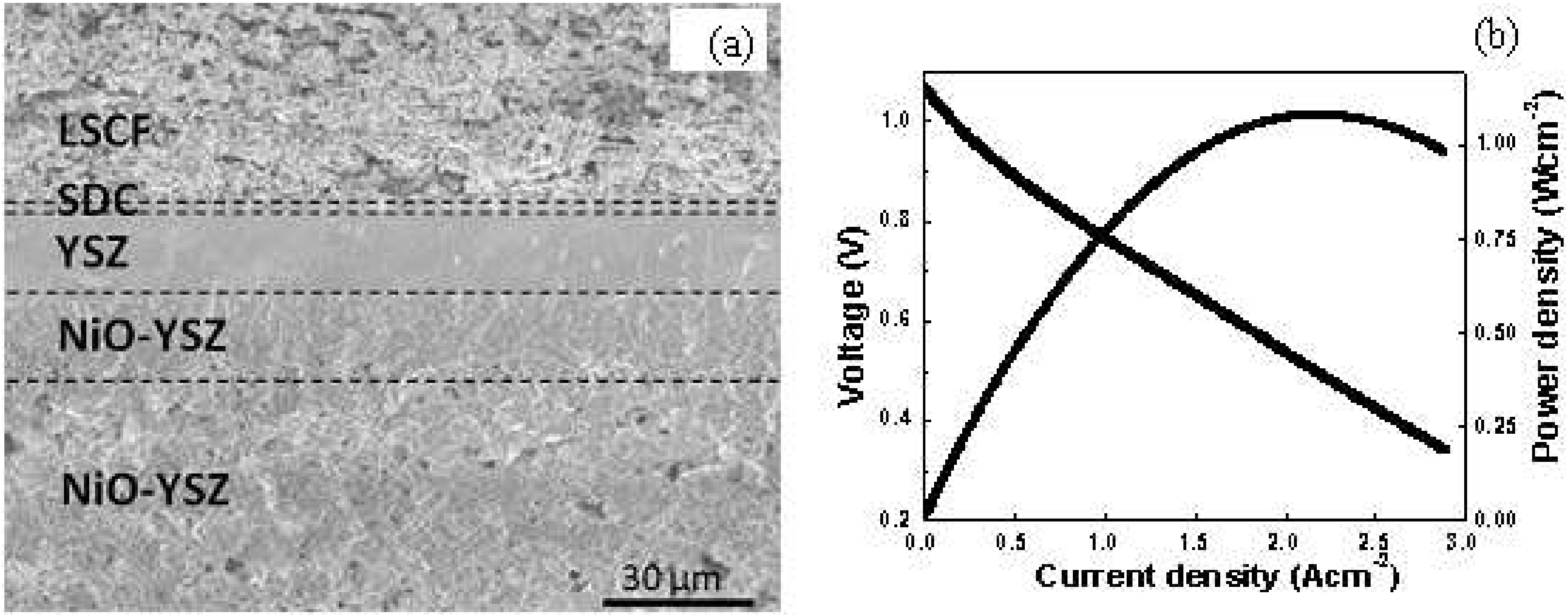


Energy Environ. Sci. 2017, 10, 964.

Task 5: Perfecting enhanced performance in button cells

- New catalysts or structures will be first examined in symmetric cells to characterize the electrochemical behavior of the modified LSCF cathode under ROC with different concentrations of S, B and/or Cr.
- Once enhanced tolerance to impurities is demonstrated, the detailed microstructure, morphology, and composition will be carefully characterized using various in-situ and ex-situ measurements.
- Proper fabrication processes will then be developed for implementation of the new catalysts/structure in actual cells.
- Button cells with a diameter of about 1” (~2 cm^2 active electrode area, for quick check)

Validation in actual fuel cells



- Fabrication of anode-supported cells of high performance;
- Demonstration of enhanced durability while maintaining high performance by infiltrating newly developed catalysts into porous LSCF cathode;
- Demonstration of enhanced durability in commercially available cells;
- Post-analysis of tested cells

Milestones

Task/ Subtask	Milestone Title	Planned Completion Date	Verification method
1.0	Project Management Plan	12/31/17	PMP file
1.0	Kickoff Meeting	09/30/17	Presentation file
2.2	Finish the electrochemical evaluation of alkaline-earth metal oxide coatings	12/31/17	Summary report
2.3	Finish the electrochemical testing of alkaline-earth metal oxide coatings under realistic conditions	03/31/18	Summary report
3.1	Complete the fabrication of model cells with thin-film electrodes or patterned electrodes; Complete the characterization of catalyst-LSCF with a variety of *in-situ* and *ex-situ* surface analysis;	06/30/2018 09/30/2018	Summary report
3.2	Atomic-level understanding of contaminates-tolerance enhancement	12/31/2018	Summary report
4.0	Develop the low-cost and applicable deposition techniques for large cathode s	03/31/2019	Summary report
5.0	Demonstration of catalyst coating on commercial large cells	06/30/2019	Summary report
5.0	Demonstration of catalyst coating on subscale SOFC stack	09/30/19	Test results provided to DOE in summary report

Risk management

The major potential risks include:

(1) achieving complete control of the morphology, composition, and thickness of the catalyst layer;

(2) eliminating the chemical reactions or inter-diffusion between the backbone (e.g., LSCF) and the catalyst coating, thus preventing any undesirable phases from formation at the interface between the catalyst and the backbone.

Risk management

To address risk # 1, we will develop well controlled infiltration process to quantify the thickness of the catalyst layer. We will determine the catalyst thickness by (a) measuring the specific area of porous cathode and the infiltration loading and (2) TEM examination. Ultimately, we will correlate the performance enhancement of the cells with the actual thickness of catalyst layers. **Other thin film deposition processes may be explored such as ALD and surface sol-gel process.**

To address risk #2, we must select materials that are immiscible with the backbone so that the key constituents will remain on the surface throughout the lifetime of cell operation. We will perform necessary microscopic analysis of the interfaces between the backbone and the catalyst coatings under various testing conditions to fully characterize the interactions between the materials and to develop approaches to minimize or eliminate any detrimental interactions.

Project Budget

Calendar Quarter	DOE Cost	Share Cost
Oct 2017	$12,500	$3,125
Nov 2017	$12,500	$3,125
Dec 2017	$12,500	$3,125
Jan 2018	$12,500	$3,125
Feb 2018	$12,500	$3,125
Mar 2018	$12,500	$3,125
Apr 2018	$12,500	$3,125
May 2018	$12,500	$3,125
Jun 2018	$12,500	$3,125
Jul 2018	$12,500	$3,125
Aug 2018	$12,500	$3,125
Sept 2018	$12,500	$3,125
Oct2018	$12,500	$3,125
Nov 2018	$12,500	$3,125
Dec 2018	$12,500	$3,125
Jan 2019	$12,500	$3,125
Feb 2019	$12,500	$3,125
Mar 2019	$12,500	$3,125
Apr 2019	$12,500	$3,125
May 2019	$12,500	$3,125
Jun 2019	$12,500	$3,125
Jul 2019	$12,500	$3,125
Aug 2019	$12,500	$3,125
Sept 2019	$12,500	$3,125

Relevant experience, capabilities, and responsibilities of team members

Team Member	Capabilities/Experience	Responsibility
Meilin Liu **PI, GT**	Electrochemistry, Solid state ionics, Electroceramics	Oversee all activities Theory and modeling of electrode materials and *in situ/operando* characterization of electrode materials
Yu Chen Postdoc	Cell design, ceramic processing; Fuel cell fabrication; Electrochemical measurements	Fabrication of cathodes and cells; SOFC Performance tests with controlled microstructures, structural characterization and electrochemical impedance spectroscopy
Seonyoung Yoo Postdoc	Solid state ionics, synthesis and characterization of nanostructured electrolyte and electrodes	Evaluation of chemical stability of new catalysts with contaminants (Cr, B, S, etc.); Fabrication and testing of cell components and single cells exposed to contaminants
JunHyuk Kim Ph.D. Student	Raman Spectroscopy; Electrochemical testing; Sputtering of thin films, AFM/STM; TEM Analysis	Fabrication and characterization of cathode materials; *In situ/operando* investigations into gas-solid reaction mechanism at interfaces using Raman spectroscopy, micro-impedance spectroscopy, and GC/MS
Ryan Murphy Ph.D. Student	X-ray diffraction and XPS; Synchrotron-based XRD, XAS, and XPS at BNL synchrotron facilities; TGA/DSC thermal analysis	Characterization of atomistic and electronic structures of cathode materials under in situ and ex situ conditions using synchrotron-based RXD, XAS, and XPS
Lei Zhang Ph.D. Student	Modeling and simulation of surface processes; Solid state electrochemistry; DFT calculation	Modeling and simulation of test cells with patterned electrodes or porous composite electrodes

Acknowledgement

Discussions with **Dr. Arun Bose**

SECA

DOE-SECA core technology program
Grant No. DE-FE0031201