Low cost, Durable, Contaminant-Tolerant Cathodes for SOFCs

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DOE-NETL SECA-CTP

Outline

- **Project information**
- **Project objectives**
- **Technical Approaches**
- **Project structure**
  - o **Tasks to be performed**
  - o **Milestones and Schedule**
- **Preliminary Results**

Project information

- **Team members**
  – Georgia Tech (and an Industry partner for Phase II)
- **Project description**
  – Modify LSCF cathodes for long-term stability under *realistic conditions* to enhance activity and stability
  – Enhance stability against B, S, and combined effect of contaminants;
- **What do we expect?**
  – Unravel LSCF cathode degradation mechanism when exposed to Cr, B, S and formulate strategies to mitigate degradation against contaminants (B, S, Cr, and combined effect);
  – Develop robust and electro-active catalysts against contaminants
  – Enhance the performance and durability of LSCF-based cathodes by application of a thin-film coating of robust electro-catalysts.

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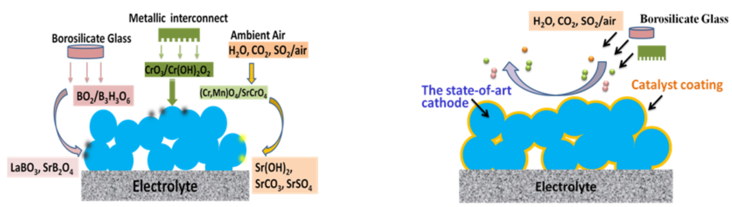
Motivation



- 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**.

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Critical questions to be answered

- How does the electrode ***surface*** differ from the ***bulk*** **chemically** and **structurally** when exposed to air with contaminants (S, B, Cr, etc.) under operating conditions?
- How do specific **elements** on electrode surface ***change chemically*** and ***structurally*** under operating conditions (w/o contaminants)?
- How are these phenomena related to the observed electrode **kinetics**, **catalytic** properties, and **durability**?

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Project Objectives

- To identify/develop new catalysts 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.

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Tasks and Schedule

Task 1: Project Management and Planning; Chemical compatibility
Task 2: Charactering the electrochemical behavior under realistic conditions
Task 3: Understanding the mechanism of contamination tolerance
Task 4: Modeling and rational design of new materials and electrode structures
Task 5: Perfecting enhanced performance in button cells

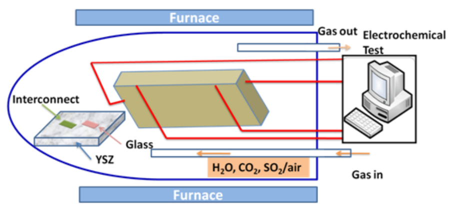
Task	FY2015	FY2016				FY2017
	Q4	Q1	Q2	Q3	Q4	Q1
1						
2						
3						
4						
5						

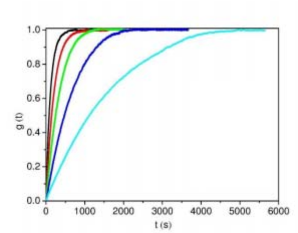
Task 1: PMP and Chemical compatibility

- Finalize Project Management Plan (PMP) in order to meet all technical, schedule, and budget objectives of the project;
- Coordinate activities 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.
- Use phase equilibria databases to guide the selection of highly-active and robust catalysts.
- Evaluate the chemical compatibility of each catalyst with these contaminants using XRD and Raman spectroscopy.

Task 2 Charactering the electrode behavior 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.

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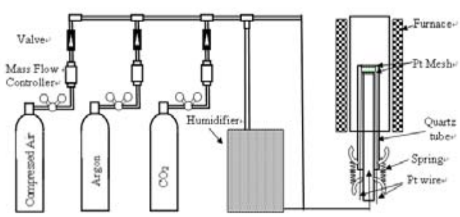
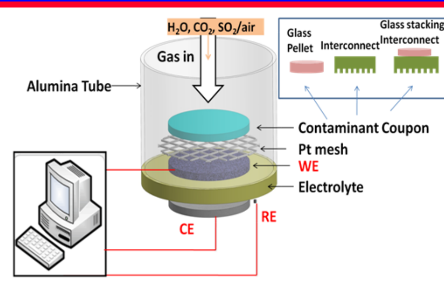
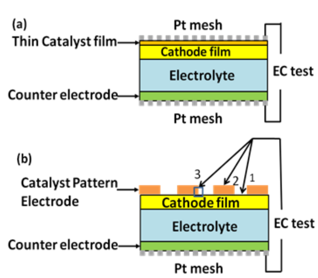
Evaluate electrochemical stability of catalyst-coated cathodes







Two types of cells:

- Symmetrical cells of porous LSCF cathode with 3-electrode configuration;

  Objective: To determine the sensitivity of cathode performance to the type and concentration of contaminants (S, B and Cr) under various testing conditions

- Thin-film dense LSCF electrode or patterned electrode with an asymmetrical electrode configuration;

  Objective: To facilitate the interface analysis and correlate the degradation mechanism with the geometric factors, revealing the major path of surface reaction on the cathodes

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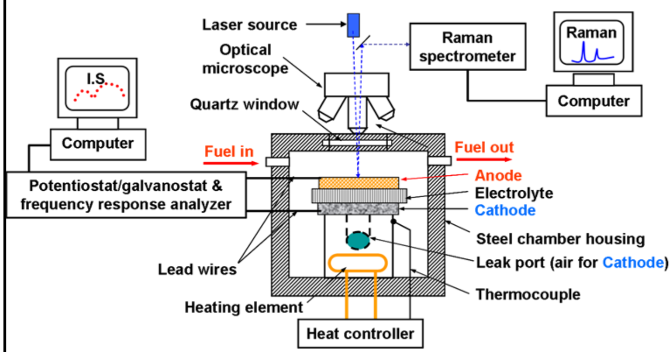
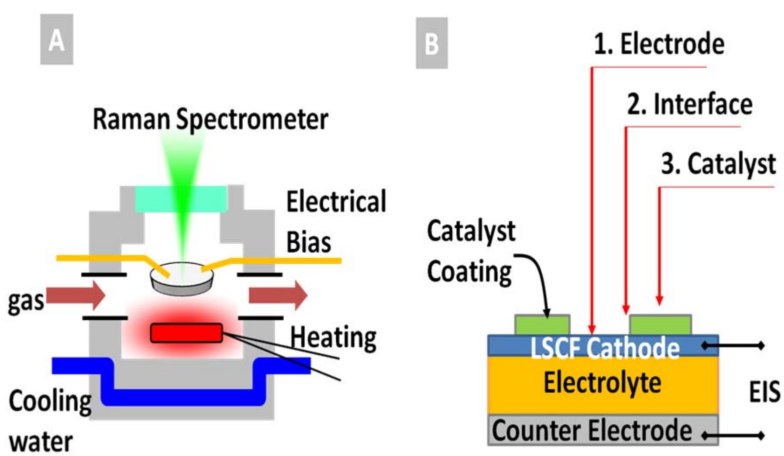
Task 3: Understanding the mechanism of contamination tolerance Surface Characterization

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. The reaction products are Raman-active.

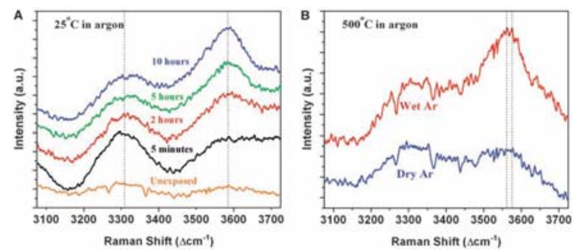
Surface of Cathode contamination study



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

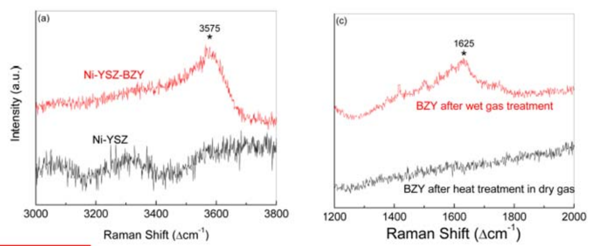
Yang *et al.*, Science, **326** (5949) 126, 2009.

BZCYYb



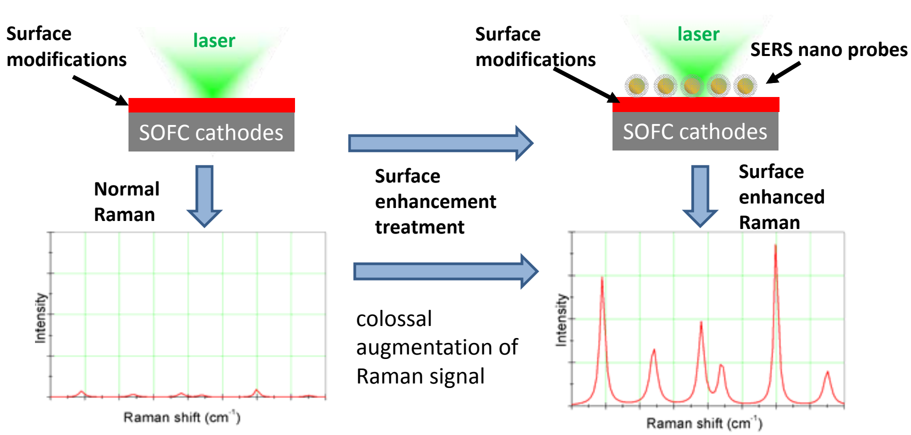
Liu *et al.*, Nano Energy, **1,** 448-455, 2012.

BZY



Understand the performance characteristics - Raman spectroscopy + Surface enhancement

- Combination of Raman spectroscopy with surface enhancement technique



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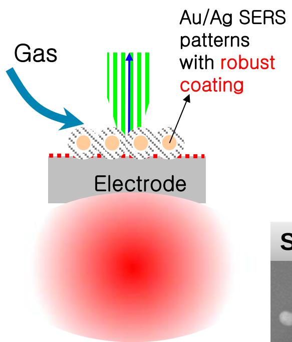
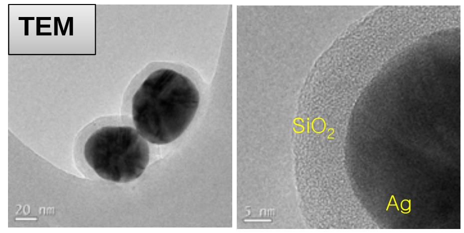
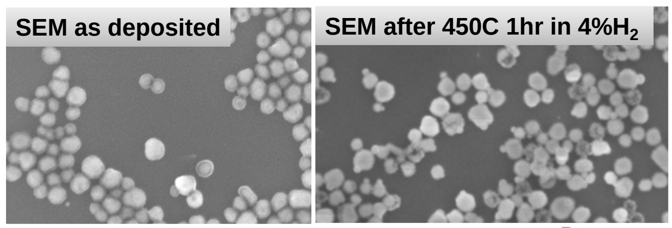
in situ SERS with Ag@SiO_2 Particles

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



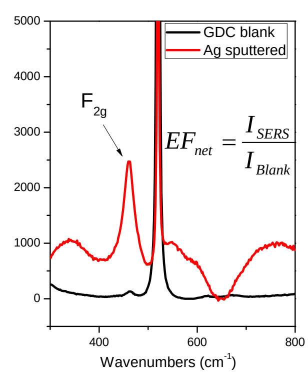


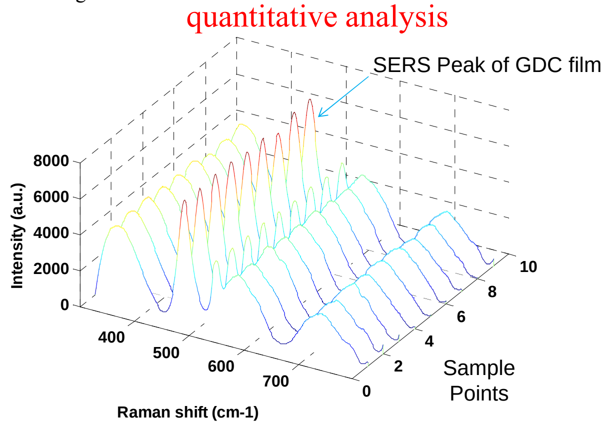
SEM images . High temperature treatment did not change the shape and distribution.



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





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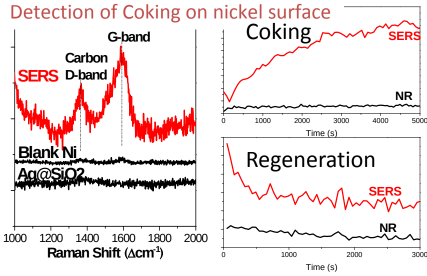
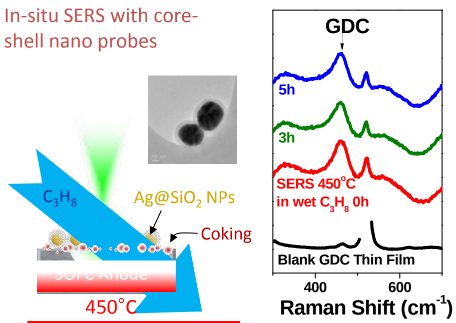
In situ SERS for Identification of Surface Species

- 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

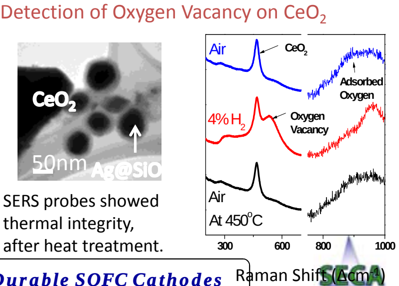


In-situ SERS with core-shell nano probes



Detection of Surface defects on CeO_2 powders

Detection of Oxygen Vacancy on CeO_2



SERS probes showed thermal integrity, after heat treatment.

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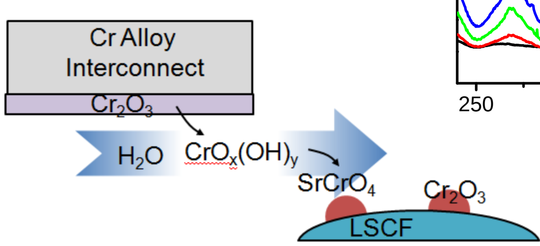
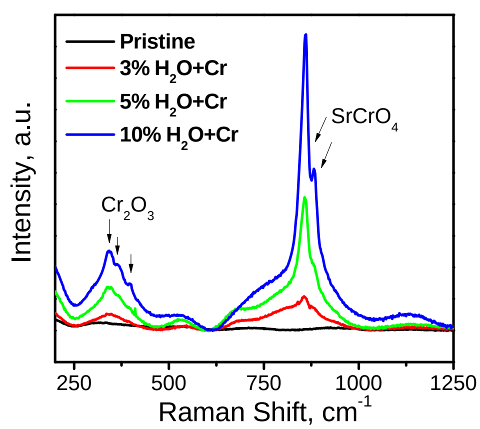
SERS Analysis of Cr Poisoned Samples (Direct Contact)

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





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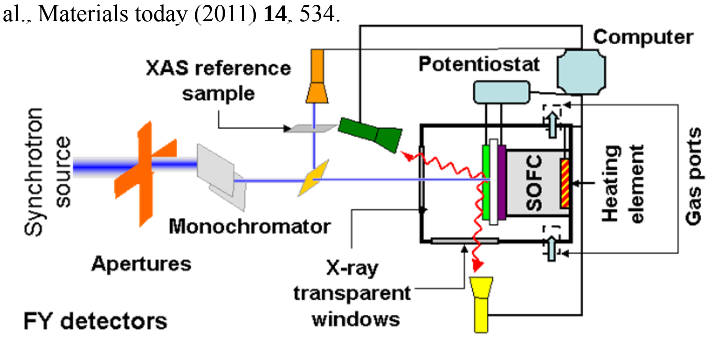
Synchrotron-Enabled XRD, XAS, & XPS

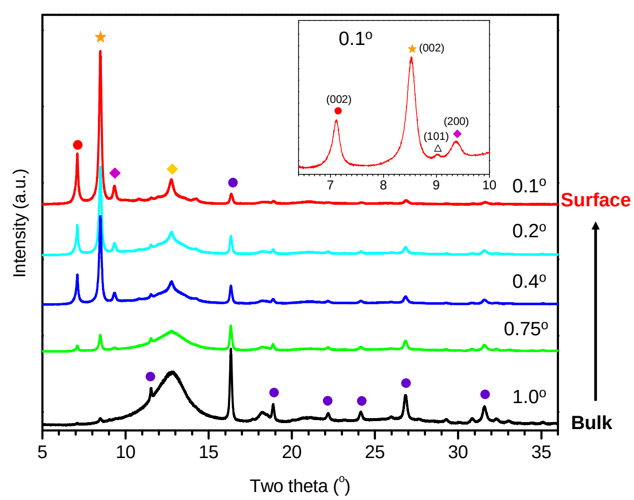
Liu et al., Materials today (2011) **14**, 534.



- 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

Glancing-Angle XRD

"Surface" is structurally quite different from that of "bulk"



A gradient in oxidation state of cation along the thickness direction.

Nano Lett., 2012, 12 (7) 3483; **dx.doi.org/10.1021/nl300984y**

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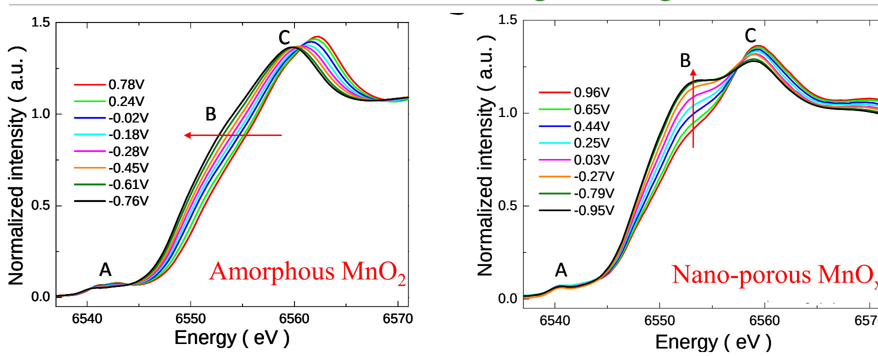
Effect of Electrical Polarization

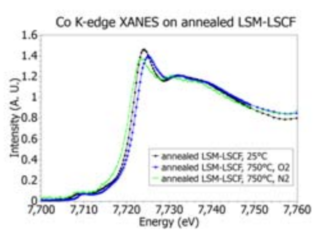
In-situ XANES during discharge



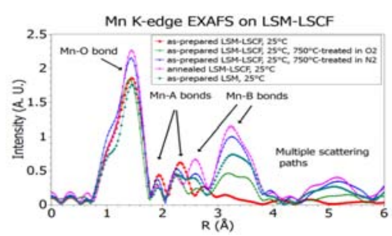
(a) In-situ XANES spectra showed an entire edge shift towards lower energy in a continuous manner, suggesting that the charge storage is mostly associated with the Mn^{3+}/Mn^{4+} redox reactions as conventionally believed. (b) The behavior of the nano-porous MnOx is different.

Nano Lett., 2012, 12 (7) 3483; **dx.doi.org/10.1021/nl300984y**

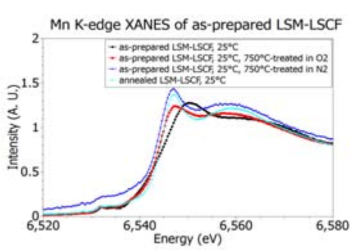
Synchrotron-Enabled XRD, XAS, & XPS



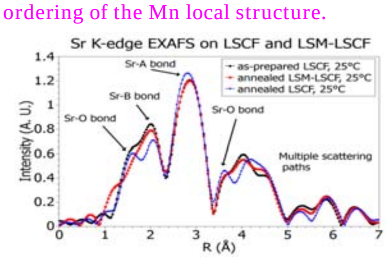
Reversible changes in oxidation state



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



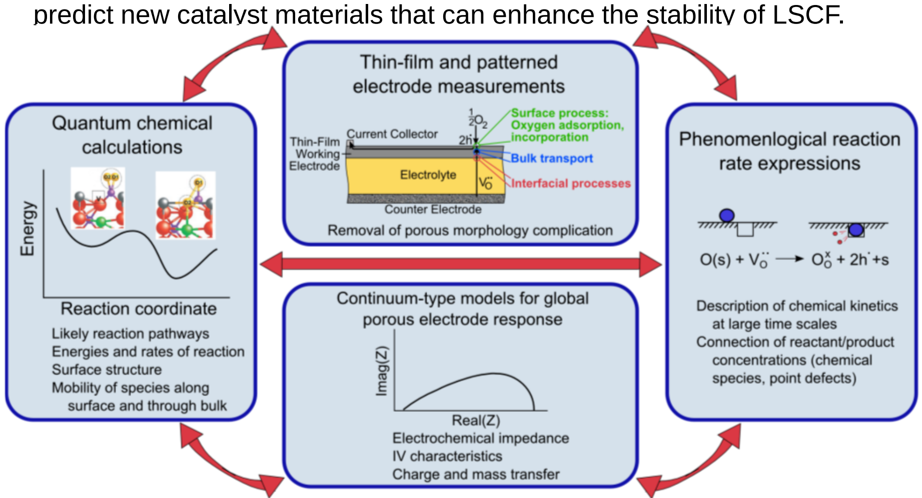
Mn is reduced at High Temp.



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

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.



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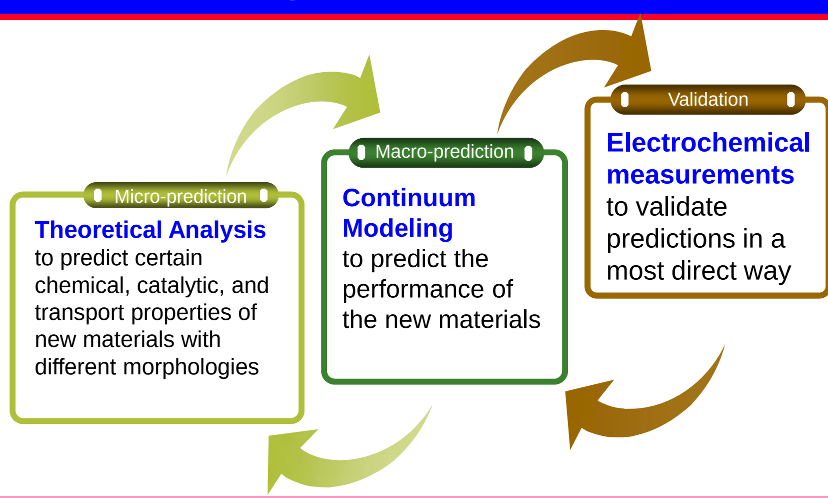
Design of new materials



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.

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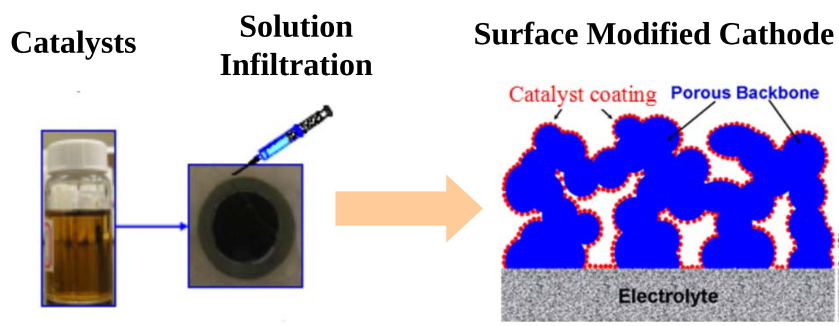
Surface modification

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



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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)
- A single cell with dimensions of 4”x4” (~100 cm^2 active electrode area) with the help of an industry partner

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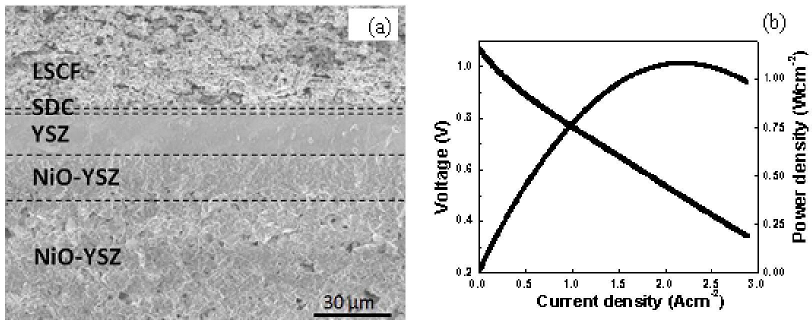
Validation in actual fuel cells



- 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

Preliminary Results

- **Chemical compatibility of catalysts with contaminant (Cr, B, S), using XRD**
- ECR measurement for blank LSCF
- Preparation of LSCF thin films and patterned electrodes

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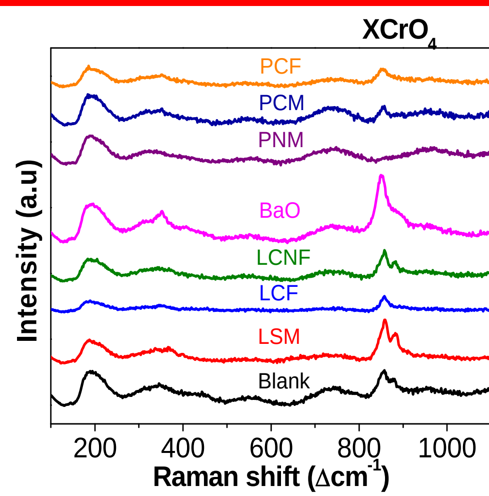
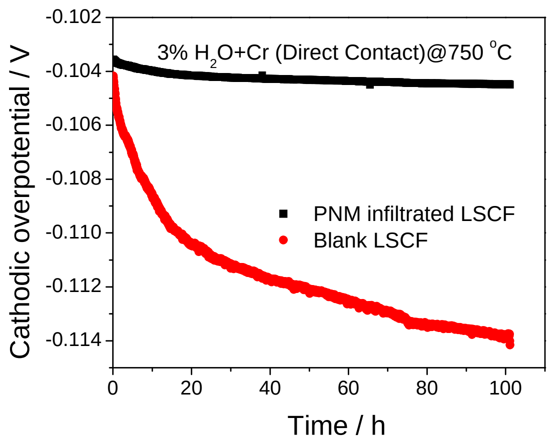
Screening of Catalysts using Raman Spectroscopy



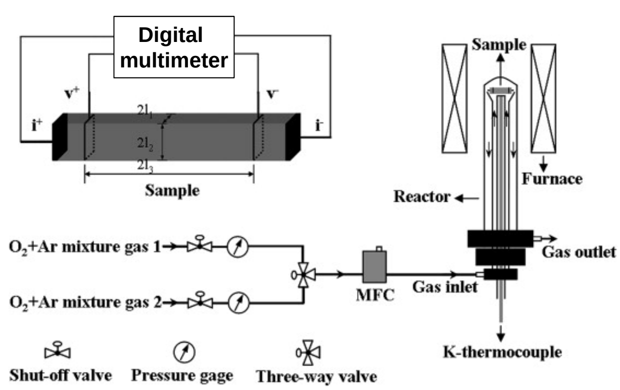
Conditions: Crofer 22 APU, 750 °C for 75 h, with air containing 3 % H_2O

Catalyst coating enhances Cr tolerance



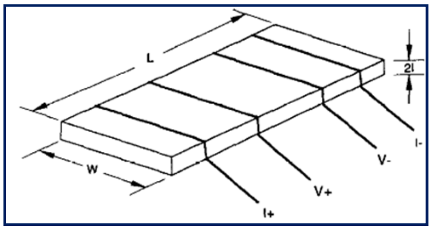
Cathodic overpotentials of a catalyst -infiltrated LSCF and blank LSCF cathode in contact with Cr materials at 3% H_2O+1% CO_2, measured at 750°C at a constant voltage of 0.40 V and 0.25 V at 750°C, respectively.

Experimental conditions



- 4-probe DC method
- Standard gas mixtures of O_2 and Ar
- Flow rate: 300mL/min
- Temperature: 550-800°C

In progress



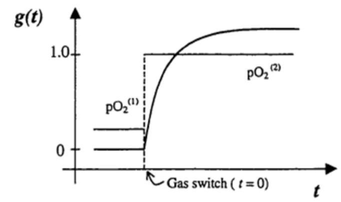


Figure 3.2. Schematic drawing of an ideal conductivity relaxation experiment.

$$g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = 1 - \sum_{m=1}^{\infty} \frac{2C^2 \exp(-\alpha_{1m}^2 D_{chem} t / l^2)}{\alpha_{1m}^2 (\alpha_{1m}^2 + C^2 + C)}$$

D_{chem} and k_{chem} were extracted with fitting by a least square method to an analytical solution of Eq. g(t)

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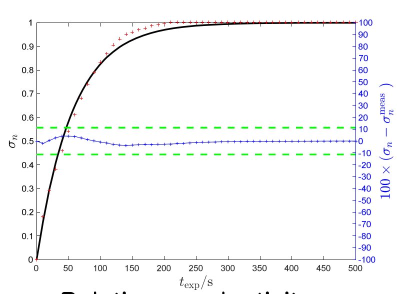
In progress: ECR test for Blank LSCF

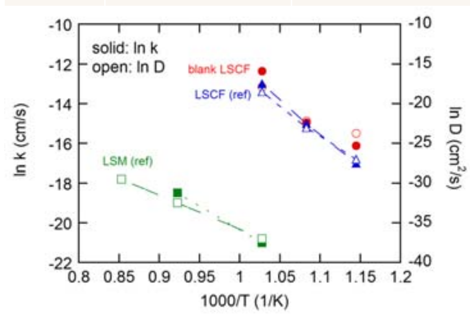
Experiment condition

- Temperature range: 600,650,700°C
- pO_2 range: 1 atm to 0.01 atm
- Flow rate: 300mL/min
- O_2 and Ar mixture gas
- Current: 10mA

PBSCF Temp.	k (cm/s)	D (cm²/s)
600°C	1.00±0.0188 x 10^{-7}	4.87±0.0188 x 10^{-11}
650°C	3.22±0.0188 x 10^{-7}	2.28±0.0188 x 10^{-10}
700°C	4.26±0.0188 x 10^{-6}	1.73±0.0188 x 10^{-8}



Relative conductivity



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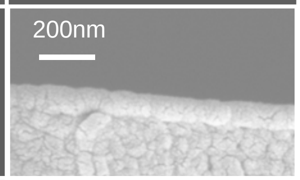
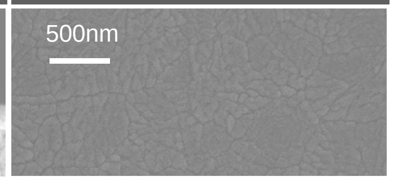
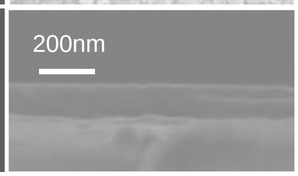
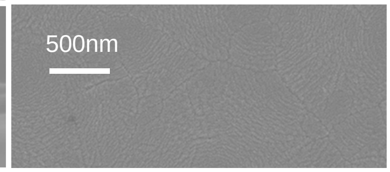
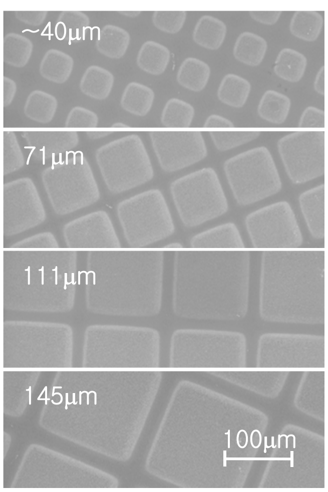
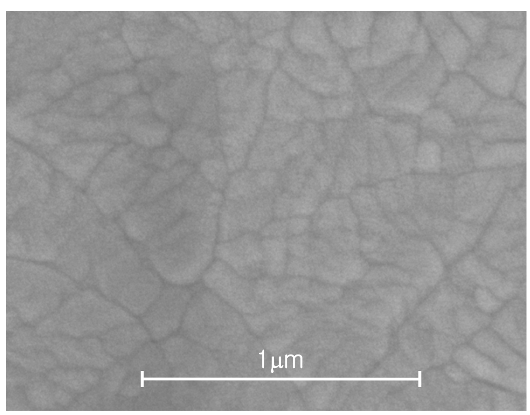
SEM Images of LSCF Films

Substrate	Cross Section	Surface
Polycrystalline GDC		
Single Crystal Si		

The sputtered LSCF film with 1:1 A/B ratio is annealed at 800ºC for 1hr, and SEM characterization is performed to identify the sputtering rate (~30nm/hr) and surface morphology.

SEM Images of the Patterned Electrodes





Top: high magnification, at the middle of an electrode

Right: low magnification, various electrode sizes

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