Low cost, Durable, Contaminant-Tolerant Cathodes for SOFCs

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Outline

- Project information
- Project objectives
- Technical Approaches
- Project structure
  - Tasks to be performed
  - 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.

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.
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?

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.
Tasks and Schedule

Task 1: Project Management and Planning: Chemical compatibility
Task 2: Characterizing 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

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<th>Task</th>
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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**
  
  ![ECR Diagram](image)

  \[ \varepsilon(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} \]

  - 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.

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
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 \textit{in situ} or \textit{ex situ} conditions.

\textbf{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.
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Understand the performance characteristics - Raman spectroscopy + Surface enhancement

- Combination of Raman spectroscopy with surface enhancement technique

- Surface modifications + laser

- Normal Raman

- Surface enhancement treatment

- Colossal augmentation of Raman signal

- Surface enhanced Raman


**in situ SERS with Ag@SiO\textsubscript{2} Particles**

TEM images showing core-shell nanoparticles.
Size of the silver NPs: 50nm
Thickness of the SiO\textsubscript{2}: 5nm

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

SEM as deposited
SEM after 450°C 1hr in 4%H\textsubscript{2}

**SERS with Ag Nanoparticles (NPs)**

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

800 600 400

Raman shift (cm\textsuperscript{-1})

Sample Points

Wavenumbers (cm\textsuperscript{-1})

Intensity (a.u.)

SERS Peak of GDC film
**In situ SERS for Identification of Surface Species**

- Developed thermally robust & chemically inert Ag@SiO₂ core-shell nanoparticles for in situ SERS at 450°C.
- Detected incipient stage carbon deposition on nickel.
- Detected surface defects on CeO₂ powders.

**SERS Analysis of Cr Poisoned Samples (Direct Contact)**

- Cr₂O₃ and SrCrO₄ observed on poisoned porous LSCF surface.
- Increasing the H₂O concentration makes the Cr poisoning more severe.
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Synchrotron-Enabled XRD, XAS, & XPS

- 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
**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

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**Synchrotron-Enabled XRD, XAS, & XPS**

Reversible changes in oxidation state

Mn is reduced at High Temp.

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

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

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**Low Cost and Durable SOFC Cathodes**
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

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

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 cm² active electrode area, for quick check)
- A single cell with dimensions of 4”x4” (~100 cm² 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

Screening of Catalysts using Raman Spectroscopy

Conditions: Crofer 22 APU, 750 °C for 75 h, with air containing 3 % H₂O
Catalyst coating enhances Cr tolerance

Cathodic overpotentials of a catalyst-infiltrated LSCF and blank LSCF cathode in contact with Cr materials at 3% H₂O+1% CO₂, 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 O₂ and Ar
- Flow rate: 300mL/min
- Temperature: 550-800°C
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**In progress**

![Diagram](image)

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

\[
g(t) = \frac{\sigma(t) - \sigma(0)}{\sigma(\infty) - \sigma(0)} = 1 - \sum_{\alpha=1}^{\infty} \frac{2C^2 \exp(-\alpha^2 D_{\text{chem}} t / \tau^2)}{\alpha^4 (\alpha^4 + C^2 + C)}
\]

\(D_{\text{chem}}\) and \(k_{\text{chem}}\) 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
- \(p_O_2\) range: 1 atm to 0.01 atm
- Flow rate: 300mL/min
- \(O_2\) and \(Ar\) mixture gas
- Current: 10mA

<table>
<thead>
<tr>
<th>Temp.</th>
<th>(k) (cm/s)</th>
<th>(D) (cm²/s)</th>
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<tbody>
<tr>
<td>600°C</td>
<td>(1.00 \pm 0.0188 \times 10^{-7})</td>
<td>(4.87 \pm 0.0188 \times 10^{-11})</td>
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<tr>
<td>650°C</td>
<td>(3.22 \pm 0.0188 \times 10^{-7})</td>
<td>(2.28 \pm 0.0188 \times 10^{-10})</td>
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<tr>
<td>700°C</td>
<td>(4.26 \pm 0.0188 \times 10^{-6})</td>
<td>(1.73 \pm 0.0188 \times 10^{-8})</td>
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![Graph](image)
The sputtered LSCF film with 1:1 A/B ratio is annealed at 800°C for 1hr, and SEM characterization is performed to identify the sputtering rate (~30nm/hr) and surface morphology.

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**SEM Images of the Patterned Electrodes**

Top: high magnification, at the middle of an electrode
Right: low magnification, various electrode sizes
Acknowledgement

Discussions with **Dr. Briggs White**

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