Improved Cathode Performance via Infiltration

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Outline

- Major Conclusions
- Motivation: Economic Merit & Benefit
- Objectives and Technical Approach
- Results and discussion
  - Isolation of surface properties
    - The use of dense film electrode to eliminate effects of microstructure
    - Elimination of mass transfer limitations
  - Surface limitation of LSCF
    - Cells with dense LSCF films prepared by sputtering
  - Cells with surface-modified LSCF (sputtering and infiltration)
    - Improved performance and stability
- Conclusions
- Questions to be Answered
- Acknowledgment
Major Conclusions

• Demonstrated the feasibility that the stability and catalytic properties of LSCF-based cathodes can be enhanced by infiltration of a catalytically active coating.

• Developed a platform for reliably evaluating the surface catalytic properties of cathode materials.
Major Conclusions

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• Developed a platform for reliably evaluating the surface catalytic properties of cathode materials.
**Motivation**

- Since performance/reliability of SOFCs depends critically on the cathodes (more so at lower operating temperatures), reduction in cathode polarization resistance and improvement in stability will **reduce the cost of SOFCs** and help to meet **DOE cost goals**.

**Benefits**

- **Reduce the ASR** of the cathode to further enhance the performance and reduce the losses on cathodes
- **Improve the stability** and operational life of cathodes and SOFCs
- **Reduce the sensitivity to contaminants poisoning** (using a coating with tolerance to poisoning)
- Develop new approaches to **high performance cathodes** through new design of cathode architecture
Characteristics of an ideal cathode material

- High catalytic activity
- Fast Transport of ionic and electronic species

A porous MIEC backbone with a thin film coating of catalytically active materials for oxygen reduction
Objectives

• To demonstrate the concept feasibility that a highly conductive backbone coated with a catalytically active material makes a more efficient electrode;

• To determine if the surface catalytic property and/or stability of a state-of-the-art LSCF cathode can be enhanced by a catalytically active coating; and

• To gain insight into rational design of better or more efficient electrode structure or microstructure.
Technical Approach

- To develop a strategy for reliable testing of surface catalytic properties of a thin film cathode material without the limitation of geometry/microstructure of the electrodes;
- To modify the surface of an LSCF backbone (having high ionic and electronic conductivity) by a thin coating of a stable and catalytically active material for $\text{O}_2$ reduction;
- To select and modify the detailed microstructure of backbone and catalyst materials that create a better performing cathode.
How to determine the catalytic property of an electrode?

Little can be learn from the impedance spectra.
### Factors Influencing $R_P$

<table>
<thead>
<tr>
<th></th>
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<th>Electrode Polarization Resistance</th>
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<td>Continuum modeling</td>
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Challenges

• How to determine the intrinsic properties or how to eliminate the effect of electrode microstructure?

• How to separate charge transfer from the mass transfer processes?

• How to isolate different reaction sites and sort out the reaction sequence and mechanisms?

• How to extract the characteristic parameters of electrode materials?
Electrode of well-controlled geometry

- To eliminate the effect of microstructure of porous electrodes (or to decouple intrinsic from extrinsic properties)
- To correlate electrochemical performance with specific reaction sites (TPB, surfaces, etc…)
Schematic of oxygen reduction and the relevant transport processes in an SOFC.

Factors Influencing $R_P$

- The use of **dense MIEC films**

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**MIEC**

- electrolyte
- Pt mesh

**Continuum modeling**
The Simplest Case:

Surface reactions on a dense MIEC electrode

\[ \text{O}_2 \rightarrow \text{h}, e' \rightarrow v_o \]

MIEC

Electrolyte
Two competing influences:

- Top-to-bottom vacancy transport: $R_{\text{vac}} \propto L = \text{thickness}$
- Lateral transport of electrons/holes: $R_{\text{sheet}} \propto \frac{1}{L}$

As the thickness of the MIEC, $L$, decreases, ionic transport gets easier while electronic transport gets harder.
O\textsubscript{2} reduction involves electron and vacancy transport as well as surface reactions across the MIEC-air interface; thus, \( R_p \) depends on \( R_{\text{sheet}} \), \( R_v \), and \( R_{\text{surface}} \).

- By changing the thickness of the dense MIEC electrode
Effect of $L$ on $R_{\text{sheet}}$, $R_V$, $R_{\text{surface}}$

Electrode Polarization Resistance, $R_p$

$R_{\text{sheet}} \propto \frac{1}{L}$

$R_{\text{surface}}$ is independent of $L$

$V_0^{**} \uparrow$

Thickness (L, nm)
Factors Influencing $R_P$

- The use of a **dense MIEC film** of **sufficiently thin**

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Factors Influencing $R_P$

- The use of **dense** MIEC film of **sufficiently thick**

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Continuum modeling

![Diagram](image)
Factors Influencing $R_P$

- The use of **dense MIEC film of proper thickness**

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DFT: Density Functional Theory
Step 1: The optimal thickness of LSCF can be determined from its effect on cell performance → thickness window for surface study.

Step 2: A cell with proper thickness of LSCF as the current collector can then be used to evaluate the surface catalytic properties of the surface coating.
Effect of L on $R_{\text{sheet}}$, $R_V$, $R_{\text{surface}}$

$R_{\text{sheet}} \propto \frac{1}{L}$

$R_{\text{surface}}$ for LSCF

$R_{\text{surface}}$ for coated LSCF

$R_{\text{polarization resistance}} \propto L = \text{thickness}$

Thickness (L, nm)

Electrode Polarization Resistance, $R_p$
Morphology and thickness of LSCF

Annealed at 800°C for 1 hour; the desired phase was confirmed by XRD and Raman spectroscopy.
Raman spectra of LSCF

![Raman spectroscopy graph](image)

- **Intensities [Arb. Unit]**
- **Raman Shift [Cm\(^{-1}\)]**

- **LSCFFilm**
- **LSCFTarget**
- **Si**
Dependence of $R_p$ on LSCF film thickness

The electrode polarization resistance, $R_p$, is determined by:

\[ R_{V_0} \propto L = \text{thickness} \]

\[ R_{\text{sheet}} \propto \frac{1}{L} \], and

\[ R_{\text{surface}} \] is independent of $L$

The sheet resistance is no longer rate-limiting for LSCF films thicker than ~400 nm, where $R_p$ is limited by surface catalytic activity.
Improved Cathode Performance via Infiltration

Dependence of $R_P$ on $\rho O_2$ - Theory

In General

$$R_{ct,\text{surface}} = \frac{1}{(\alpha_a + \alpha_c)i_o \left( \frac{RT}{4F} \right)} \propto \frac{1}{p_{O_2}^\gamma} \downarrow \text{with} \uparrow p_{O_2} ; \text{ strong}$$

$$R_{V_{O\cdot\cdot}} \propto p_{O_2}^\gamma \text{ since } [V_{O\cdot\cdot}] \uparrow \text{ with } \uparrow p_{O_2} ; \text{ week}$$

$$R_{\text{sheet}} \text{ little dependence on } p_{O_2} ; \text{ very week}$$
Dependence of RP on $\rho$O$_2$ - Results

![Graph showing the interfacial resistances (Ω cm$^2$) as a function of overpotential (V) for different $\rho$O$_2$ values.

- 1 % O$_2$
- 21 % O$_2$

The graph indicates that as the overpotential increases, the interfacial resistances decrease for both 1 % O$_2$ and 21 % O$_2$. The interfacial resistances are higher at 1 % O$_2$ compared to 21 % O$_2$ at the same overpotential.
The $R_p$ appears to be limited by the surface catalytic activity, not by the bulk transport property for both 400 and 750 nm thick LSCF films; otherwise, $R_p$ should increase with $p_{O_2}$. 

$R_{\text{V}_o^{\bullet}}$ increases with $p_{O_2}$ 

$R_{\text{surface}}$ decreases with $p_{O_2}$
Effect of surface modification

![Graph showing interfacial resistance vs. voltage for Blank LSCF and LSM coated LSCF at 700 °C.](image-url)

- Interfacial Resistance (Ω cm²)
- Voltage (V)
Effect of surface modification

Improved Cathode Performance via Infiltration
Cell for performance evaluation

(a) WE, Electrolyte, RE

(b) CE, Electrolyte

(c) Pt current collector, WE, Electrolyte, RE, CE
Cross-sectional views of porous LSCF cathodes: (a) blank LSCF, (b) infiltrated with SSC (concentration of SSC solution: 1.44 mol/L), and (c) infiltrated with LSM (concentration of LSM solution: 0.0312 mol/L). 850°C/1hr
Typical Impedance Spectra

700°C
E=-0.5V

700°C
OCV

-\text{Zim}(\text{ohm.cm}^2)

Z_{re}(\text{ohm.cm}^2)
Effect of polarization on $R_p$

- Polarization resistance of porous LSCF and LSM infiltrated LSCF electrode
**Sm_{0.6}Sr_{0.4}CoO_{3-\delta} (SSC) infiltrated LSCF-6428**

- Comparison of polarization resistance ($R_p$) of the blank, LSCF infiltrated, and SSC infiltrated LSCF/GDC/LSCF symmetrical cells.
Performance stability of LSM/LSCF

$I=833\ \text{mA/cm}^2$
$T=825\ ^\circ\text{C}$

- LSM infiltrated cell
- Blank cell
Current-Voltage Characteristics

825 °C

- Blank cell
- LSM infiltrated cell

After testing for 100 h

Voltage (V)

Power Density (W/cm²)

Current Density (A/cm²)
Cell performance

![Graph showing cell performance at 700 °C]

- Blank cell
- LSM infiltrated cell

- Solid - initial performance
- Open - after stability testing

- Voltage (V) vs. Current Density (A/cm²)
- Power Density (W/cm²)

700 °C
- 87 h
- 66 h
Conclusions

- Developed a platform for reliably evaluating the surface catalytic properties of cathode materials;
- Fabricated high quality thin films of cathode materials for evaluating their intrinsic catalytic activities;
- Confirmed that the surface catalytic activity limits the performances of LSCF-based cathodes;
- Enhanced the stability and performance of LSCF-based cathodes by infiltration of a catalytically active coating (such as LSM and SSC); and
- Demonstrated the concept feasibility of the novel cathode design - highly conductive backbone coated with a highly active catalyst.
Several fundamental questions still remain:

- Why are the degradation rates of LSCF cathodes relatively high? What is the degradation mechanism?
- Why does a LSM coating improve the stability of LSCF cathodes? What is the mechanism?
- Are there other catalytically more active materials for the catalyst or more effective matrixes as the backbone?
- The long-term stability of the interfaces (e.g., LSM/LSCF) is yet to be determined.
Other questions to be Answered

- How the surface morphology, composition, and thickness of the coatings change under operating conditions?

- How these changes influence the electrochemical behavior of the cathodes?

- How to control the microscopic details of the coatings in order to optimize the performance?
The authors are grateful to Briggs White, Wayne Surdoval, and Lane Wilson for valuable discussions.

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