Understanding the effect of contaminants on LSCF cathode performance

Project Number: FC FE0009652
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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 H2O, CO2 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 H₂O, CO₂ 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.
Understanding the effect of contaminants on LSCF Cathodes

**Typical Effect of H₂O/CO₂ on LSCF Cathodes**

• The degradation effect of H₂O and CO₂ is relatively small (when alone).
• The degradation effect is more pronounced at lower temperatures.
• As the concentrations of H₂O and CO₂ 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.
Understanding the effect of contaminants on LSCF: FE0009652

Accomplishments to Date

- Characterized electrochemical behavior of porous and dense thin-film LSCF cathodes exposed to H₂O, CO₂ 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

Intensity variation: 3%

Reliable for semi-quantitative analysis

In Operando SERS of Electrode Surfaces
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.

SEM as deposited | SEM after 450°C 1hr in 4%H2

In situ SERS for Identification of Surface Functional Groups

• 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.

In-situ SERS with core-shell nano probes

Detection of Coking on nickel surface

Detection of Surface defects on CeO2 powders

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.

Study of Cr poisoning with respect to H$_2$O concentration

SERS Analysis of Cr Poisoned Samples (Direct Contact)

- Cr$_2$O$_3$ and SrCrO$_4$ observed on poisoned porous LSCF surface.
- Increasing the H$_2$O concentration makes the Cr poisoning more severe.
Accomplishments to Date

- Characterized electrochemical behavior of porous and dense thin-film LSCF cathodes exposed to H₂O, CO₂ 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.

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
In situ CO₂ exposure, 400 °C

- Exposure to CO₂ causes oxidation
- Cathodic bias causes CO₂ 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

**XANES (a, b)**
- Fe + CO₂: oxidized
- Fe + H₂O: oxidized
- Co + CO₂: oxidized
- Co + H₂O: oxidized

**EXAFS (c, d)**
- Local structures reflect oxidation
XANES/EXAFS at 700°C

XANES (a, b)
- Fe + CO$_2$: oxidized
- Fe + H$_2$O: reduced
- Co + CO$_2$: oxidized
- Co + H$_2$O: no shift

EXAFS (c, d)
- Fe local structure stable
- Co local structure distorts under H$_2$O

In situ vs. operando

- Cathodic bias facilitates the oxidation Fe and Co in LSCF by CO$_2$ at both low and high temperatures
Understanding the effect of contaminants on LSCF & Effective strategies to mitigate their effects

**EIS-XANES Correlation Data**

- **Warm colors:** CO₂
- **Cool colors:** H₂O

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td>400°C</td>
<td>Co and Fe tend to be oxidized by CO₂ and H₂O, but cathodic bias enhances oxidation by H₂O/CO₂</td>
</tr>
<tr>
<td>700°C</td>
<td>Observed effects caused by H₂O and CO₂ is less significant, suggesting that the electrical effect is more prominent.</td>
</tr>
<tr>
<td></td>
<td>Local structure of Co is less stable than Fe, particularly at 700°C under H₂O</td>
</tr>
</tbody>
</table>

**Proposed Mechanisms:**

- CO₂ 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.

**Summary: Operando XAS for SOFCs**

- Increased polarization resistance under CO₂, H₂O
- Higher *Rp* correlates well with **stronger** oxidation

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

**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$_2$O/CO$_2$

**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
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

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 H₂O/CO₂
- 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 $\text{H}_2\text{O}$, $\text{CO}_2$ and Cr under ROC;
- Probed and mapped **surface species/phases** of LSCF cathodes exposed to contaminants using SERS;
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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.](image)

Tested at 750°C, 10% $\text{H}_2\text{O}+1%\text{ CO}_2$ 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% H₂O and 1% CO₂ at 750°C/75 h

Observation:
- No SrCrO₄ in the catalyst coated sample
- Accelerated experiment suggested that PNM coating should have powerful contaminant tolerance
- Adsorbed H\(_2\)O 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\(_2\)O and CO\(_2\).
- Both H\(_2\)O 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.

**Implications**

**Acknowledgement**

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

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

Brookhaven National Laboratory

DOE Basic Energy Science Energy Frontier Research Center