Transition metal valence mapping in LSCF cathodes

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Research Objectives

1. Identification of surface/interface species thru rapid X-ray characterization.

2. Determination of interfacial barriers to oxygen diffusion - pathways to mitigation.

3. X-ray characterization under operational conditions.
1. Electrode (YSZ/LSTMO) alloying
2. Maintaining TM multi-valence
3. A-site/B-site Sr occupancy
4. Quantifying O vacancy concentration
Performance has degraded.

How can I prove the surface/interface is responsible?
Soft x-rays are ideal for buried interfaces!

- $\lambda_{\text{attn}} \approx 100 \text{ nm off res.}$
- $\lambda_{\text{attn}} \approx 20 \text{ nm on res.}$
- $\lambda_{\text{attn}} \approx 15 \AA \text{ on res. grazing}$

• $\lambda \approx 20 \AA$
• strong absorption signal
• elemental selectivity
• valence sensitivity
• probe TM 3d states
X-ray Absorption Spectroscopy (XAS)

Co L edge XAS

Cobalt in CoO
Cobalt metal

Area Normalized XAS Intensity

Photon Energy (eV)
Interface Engineering

Pulsed Laser Deposition

Chemical Vapor Deposition

Collaboration with Prof. S. Stadler, LSU
Now available at MSU (ARO-DURIP)

PLD Plume

CVD at MSU
PLD Film Symmetric Half Cells for SOFC Studies

- PLD targets are $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{2-\delta}$, and LSCF (6428)
- 2 types of samples:
  
  \[
  \begin{align*}
  \text{LSCF/YSZ/LSCF} \\
  \text{LSCF/GDC/YSZ/GDC/LSCF}
  \end{align*}
  \]

- Thickness: LSCF = 10 nm; GDC = 20 nm (YSZ 0.5mm)
New Testing Rig Design

- Alumina Bolts
- Voltage Leads (now gold mesh)
- Current Collectors (now gold mesh)
- Alumina Plates
- Sample
- Gold Current Leads

13th SECA Workshop - July 24-25, 2012
Example – Sr out-diffusion

How do operational conditions affect Sr mobility?

XPS work (Sandia) provided a direct confirmation of Sr out-diffusion
Example – Map Sr out-diffusion

Can’t determine whether Sr at surface or in the bulk.

Surface Sr valence is same as bulk (Sr$^{2+}$)!

No change
Solution – Elemental tagging

Introduce surface Cr

Cr present as Cr$_2$O$_3$ (Cr$^{3+}$) or (in the presence of SrO) as SrCrO$_4$ (Cr$^{6+}$)
Determine TM valence as a function of operational conditions

Introduce surface Cr

Cr present as $\text{Cr}_2\text{O}_3$ ($\text{Cr}^{3+}$)

or

(in the presence of SrO) as $\text{SrCrO}_4$ ($\text{Cr}^{6+}$)
EXAMPLE – Sr out-diffusion

Surface Sr modifies Cr valence!
1.1 mm electrolyte
850 °C  100 mV

**Graph**: Area Normalized XAS Intes

*Lines:*
- Black: 25% SrCrO$_4$ + 75% Cr$_2$O$_3$
- Green: 100 mV, anode side
- Red: 50% SrCrO$_4$ + 50% Cr$_2$O$_3$
- Blue: 100 mV, cathode side

*Photon Energy (eV)*

570 to 590
Driven Sr out-diffusion

solid – anode empty - cathode

A major complication is the strong spatial valence variation. Averaging techniques miss the extremes.

+500 mV bias potential
Co valence map

Matches air inlet -500 mV Potential bias

Co present as Co$^{2+}$ thru Co$^{4+}$ (130% variation)

Circular pattern

Matches air inlet
Automated fitting reproduced data exactly.
Co valence mapping

Co valence variation due to oxygen and water vapor availability.

Requires full XAS scans performed in 1-3 minutes (not 15-30 minutes)

Spectra reproduced after 4 months in desiccator.
Distribution matches air inlets

Alumina Bolts

Gold Current Leads

Alumina Nuts
Humidity Control

Heated air-line bubbler installed

3 symmetric PLD samples created
LSCF (6428)/GDC/YSZ/GDC/LSCF (6428) pellets
±450 mV @ 850°C for 100 hrs
25%, 50%, 75% humidity
Humidity – Valence variation of Co

Co L_{23} electron valence variation
100 hrs @850°C and +450 mV at 75% humidity

Strong dependence on gas inlet configuration.

Improved with diffusive air flow.
Valence mapping of Co with humidity

-450 mV bias  Co$^{3+}$/Co$^{2+}$ ratios  +450 mV bias
Conclusions

Spatial variation of TM valence complicates the identification of degradation mechanisms.

Average values do not identify extremes in valence.

Areas with extremes in TM valence can be identified thru valence mapping and correlated with degradation.
Future Directions

Mitigation Strategy (Sr out-diffusion)
- higher Co doping (at surface only)
- co-doping with Mn (at surface only)

Additional Dependencies
- Improved Laminar gas flow
- $PO_2$ vs humidity dependence