Sr out-diffusion and spatially mapped Co valence for operational LSCF cathodes

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Research Thrusts

1. Directed SOFC materials development thru rapid X-ray characterization.

2. Identification of interfacial barriers to oxygen ion formation and diffusion.

3. X-ray characterization under operational conditions.
Example – Map Sr out-diffusion

How do operational conditions affect Sr mobility?
X-ray Absorption Spectroscopy (XAS)

Co L edge XAS

Cobalt in CoO

Cobalt metal

Area Normalized XAS Intensity

Photon Energy (eV)
Soft x-rays are ideal for buried interfaces!

- strong resonant interaction
- elemental selectivity
- valence sensitivity

Fe absorption

spatially map elemental valence at buried interfaces under operational conditions
Example – Map Sr out-diffusion

Two problems

Sr is both on the surface and in bulk.

Sr remains as Sr\(^{2+}\)!

No change
Solution – Elemental tagging

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

Sr modifies Cr valence!
Oxygen ion flow direction modifies Cr valence!

Bias driven symmetric cell (2 half cells)
Oxygen ion flow (and bias)

Bias modified Cr valence

Cr$^{3+}$ (oxygen outflow)
Cr$^{6+}$ (oxygen inflow)

after reverse bias

O$_2^-$ flow

Oxygen ion flow reverses Cr valence!
1.1 mm electrolyte
850 °C 100 mV
Electrochemical Environment

solid – anode empty - cathode

Bias driven Sr out-diffusion ($V^{O2-}$)
PLD samples
(symmetric depositions)

- Substrate 0.5 mm single crystal YSZ (polished)
- Sintered GDC and LSCF targets
- 2 types of samples:
  - LSCF/YSZ/LSCF
  - LSCF/GDC/YSZ/GDC/LSCF
- Thickness: LSCF = 10 nm; GDC = 20 nm
- GDC interlayer to prevent secondary phase formation
SEM Sr segregation
Pulse laser deposited LSCF/GDC

As grown

particulates

100 hr 800 °C 500 mV

crystallites
EDS line-scans

- Line-scan shows *increase* in Sr
- Reduction in Zr and Ce
- XPS shows Sr present as SrO and LSCF

→ Surface segregated Sr
Co valence shift from Sr segregation

Removing Sr also increases Co\(^{3+}\) and decreases Co\(^{2+}\) concentrations

Measure of surface Sr

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Co L₃-edge valence reference spectra
Co valence map

Co present as $\text{Co}^{2+}$ (10% variation)

LSCF oxygen deficient (PLD vacuum cool down)

Reproduced with vacuum anneal
Co valence map

Air anneal @ 850 °C

Co present as Co$^{3+}$
(40% variation)

Circular pattern
Electrical Potential Testing Rig

- Entire ceramic and gold assembly is inserted into tube furnace.
- Symmetric SOFC half cells

Ceramics machined by water jet cutting.

Air/Oxygen flows in through tube

Sample sandwiched in assembly
Co valence map

Co present as $\text{Co}^{3+}$
(40% variation)

Circular pattern

Matches air inlet
Co valence map

Co present as $\text{Co}^{3+}$ and $\text{Co}^{4+}$ (130% variation)

Circular pattern

Matches air inlet

-500 mV Potential bias
Co valence map

Co present as Co$^{3+}$ and Co$^{4+}$ (130% variation)

Circular pattern

Matches air inlet

SEM$^2$

y-position (mm)

-500 mV Potential bias

Area Normalized XAS

Referenced Photon Energy (eV)
SrO formation correlated to Co$^{4+}$

Co$^{4+}$ valence

Co$^{3+}$ valence

100 μm  100 hr.  800 °C  500 mV

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Co valence map

Co present as $\text{Co}^{2+}$ and $\text{Co}^{3+}$ (30% variation)

LSCF oxygen deficient (PLD vacuum cool down)

$+500 \text{ mV Potential bias}$
New Testing Rig Design

- Air/Oxygen delivery tube
- Sample
- Ceramic insulators
- Stainless metal mat (electrical contact and gas distribution medium)
  * Tested against corrosion at operating temperatures
Co valence map

Co present as $\text{Co}^{3+}$ (30% variation)

LSCF oxygen deficient (PLD vacuum cool down)

Matches air inlet

+500 mV Potential bias
Co valence mapping

This type of mapping cannot be done at any other facility

Requires full XAS scans performed in 1-3 minutes (not 15-30 minutes)
Diffuse X-ray Resonant Scattering

Specular vs. Diffuse Int. → Perp. Roughness ($\sigma$)
Width of Diffuse → In-plane Corr. Length ($\xi$)
Soft x-rays scattering

- single interface

sensitivity!

- At grazing incidence → 15 Å penetration depth
- specular scans → structure along z, “bulk” properties
- rocking scans (diffuse scattering) → lateral structure
  structural (chemical) roughness
  in-plane roughness
  perpendicular roughness
Oxygen ion flow - cation diffusion

Oxygen ion flow redistributes La at interface! (Sr removal)

La M$_5$ edge (841 eV)
$\theta = 4^\circ$

Sample Current (A/cm$^2$)

0.6
0.5
0.4
0.3
0.2
0.1
0.0

0 20 40 60 80 100

Time (Hours)

LSCF/GDC

log Scattered Intensity

1000
100
10

$\sigma$

$\sigma$

Start ($\sigma = 13$ Å)
End ($\sigma = 22$ Å)
diffuse fit

$\sigma$

0.1

2 3 4 5 6

Sample Angle (deg.)

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Ion flow modified interface width

Start
σ = 13 Å

σ = 12 Å
σ = 18 Å
σ = 15 Å
σ = 20 Å
σ = 22 Å
La Distribution in La$_{2/3}$Sr$_{1/3}$TMO$_3$
from XRS diffuse scans

Increasing Mismatch

$A_0$ from fits

LSFO - 33.4 Å
LSCO - 41.3 Å
LSMO - 49.5 Å

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La Distribution in $\text{La}_{2/3}\text{Sr}_{1/3}\text{TMO}_3$
from XRS diffuse scans

$\lambda$ from fits

- LSCO - 17.9 Å
- LSFO - 22.2 Å
- LSMO - 38.5 Å

Increasing Stiffness?

$\exp(-t/\lambda)$ fits
Summary

Surface potential drives Sr surface segregation
- oxygen vacancy concentration.
- Cr trace tagging does not affect Sr segregation.

Increased oxygen vacancies results in Sr out-diffusion.
- modifies Co valence (surface mapped)

Implies *in-situ* cell without oxygen partial pressure will **NOT** be representative of surface chemistry and electronic structure.
Future Directions

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

Additional Dependencies
- oxygen gas flow dependence
- temperature dependence

Industrial Interactions (valence mapping)
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Testing rig(s)

- Seal-less design
- Contact paste-less tests