Transition metal valence mapping in LSCF cathodes

H. Bhatkar and Y. Idzerda

Montana State Univ., Bozeman, MT

Acknowledgements

Current Student

Harsh Bhatkar

PhD completed

Martin Finsterbusch

Beamline 6.3.1

Advanced Light Source (ALS)

Dr. Elke Arenholz (ALS scientist)

MONTANA STATE UNIVERSITY

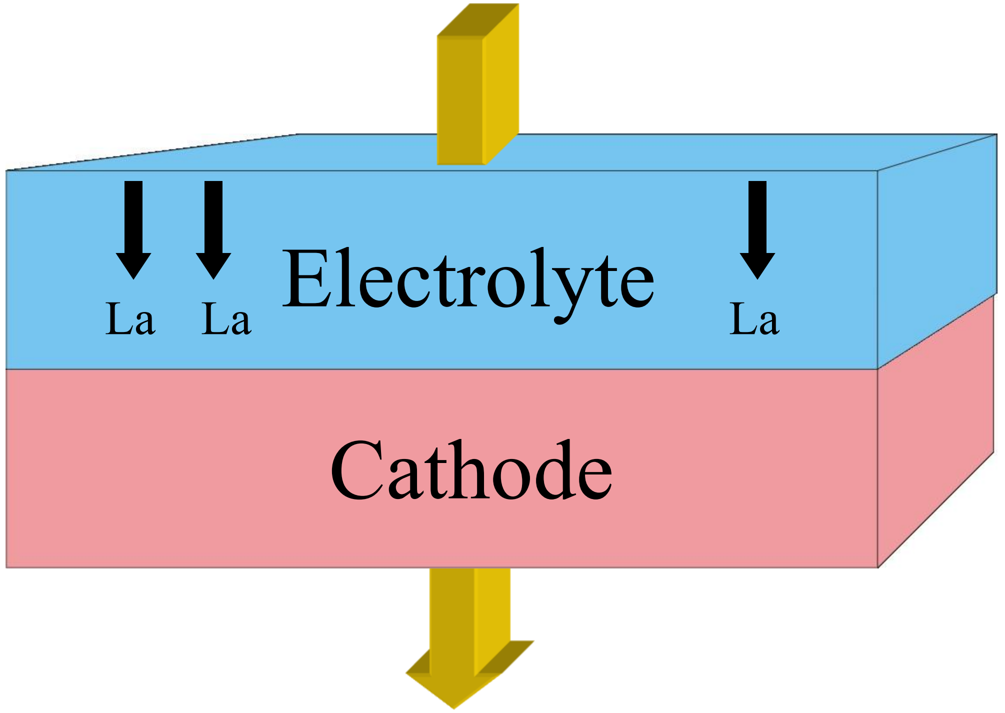
Research Objectives

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.

TM Valence Utility

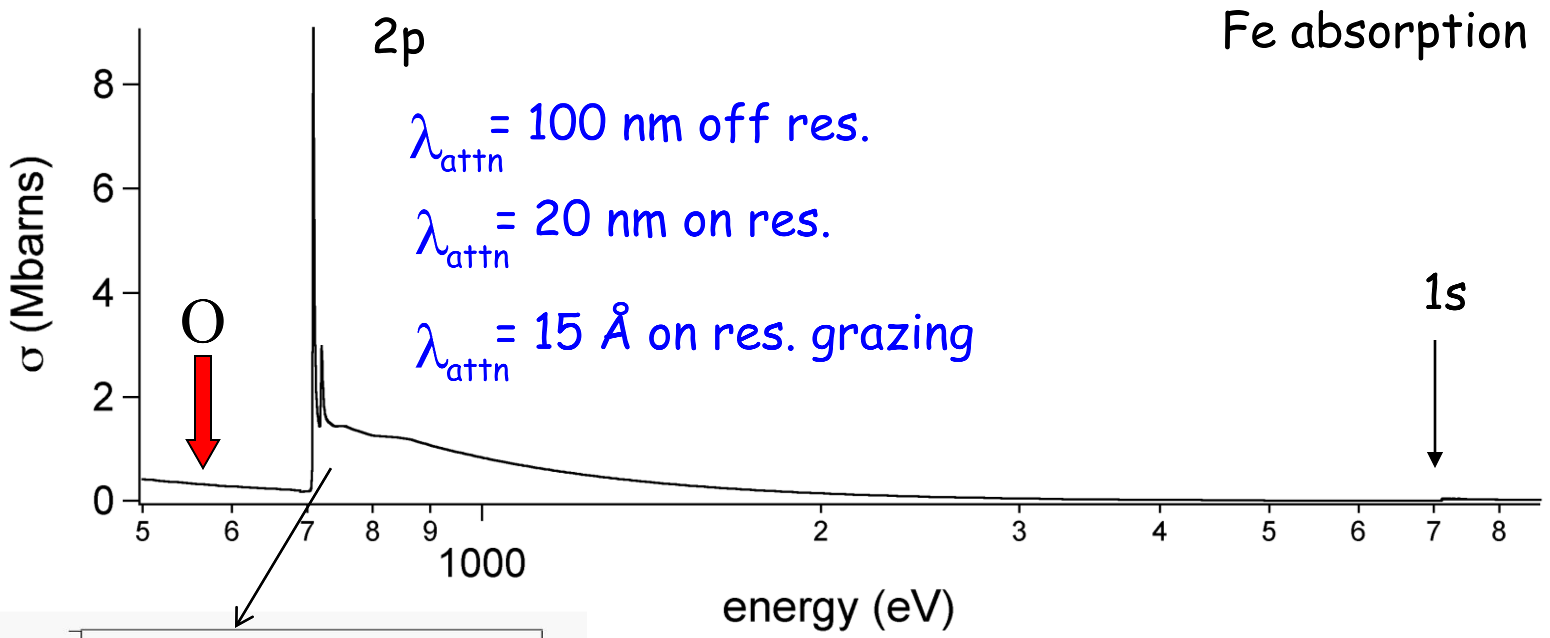
1. Electrode (YSZ/LSTMO) alloying
2. Maintaining TM multi-valence
3. A-site/B-site Sr occupancy
4. Quantifying O vacancy concentration

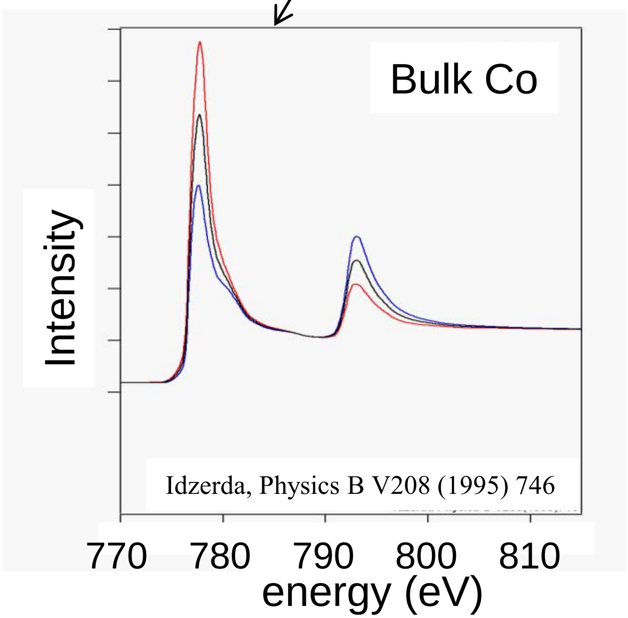
Performance has degraded.



How can I prove the surface/interface is responsible?

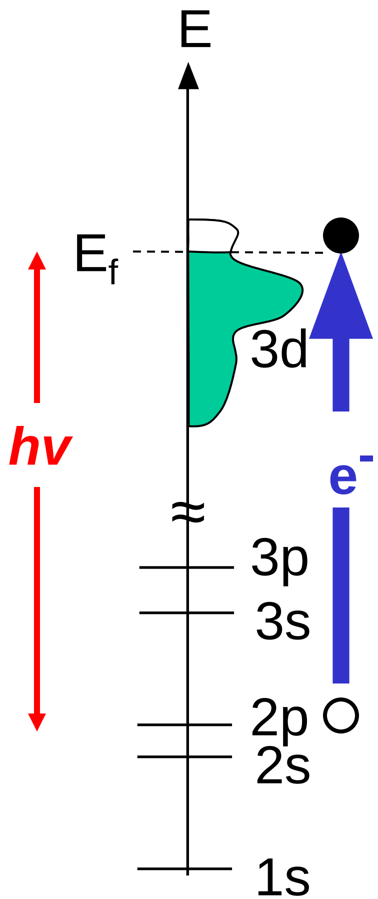
Soft x-rays are ideal for buried interfaces!

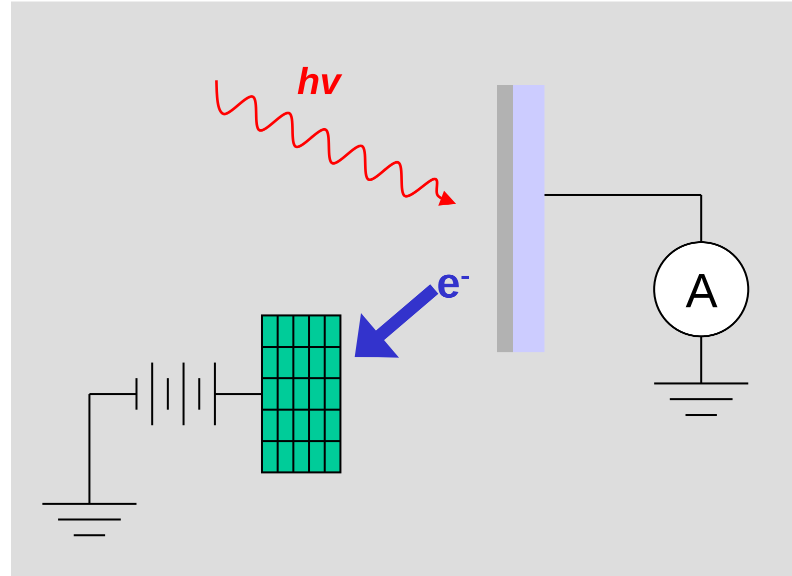


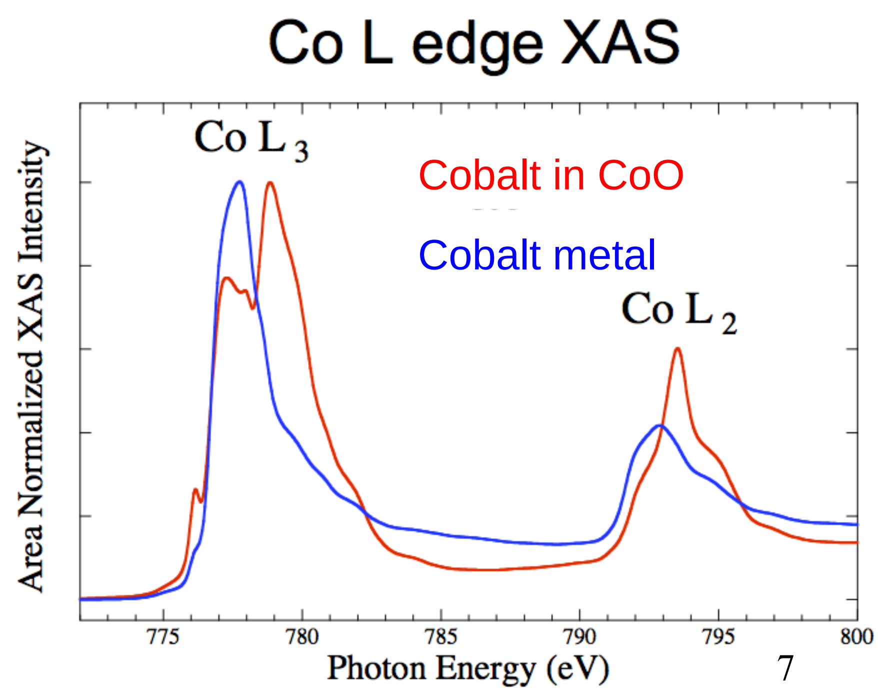


- λ ~20 Å
- strong absorption signal
- elemental selectivity
- valence sensitivity
- probe TM 3d states

X-ray Absorption Spectroscopy (XAS)

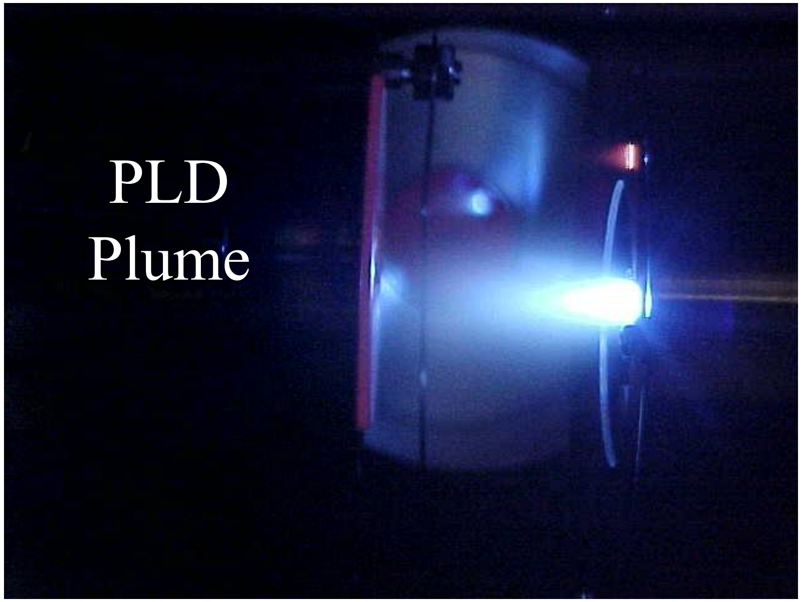






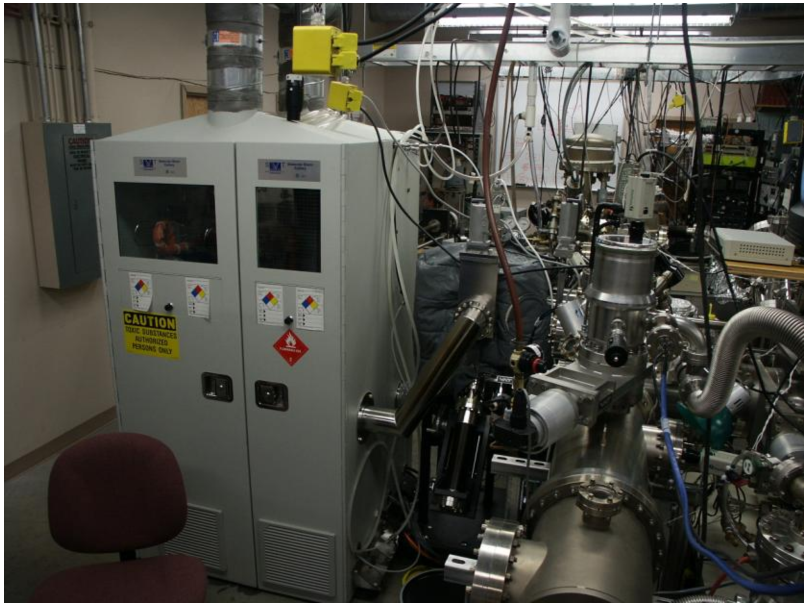
Interface Engineering

Pulsed Laser Deposition



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

Chemical Vapor Deposition



CVD at MSU

PLD Film Symmetric Half Cells for SOFC Studies

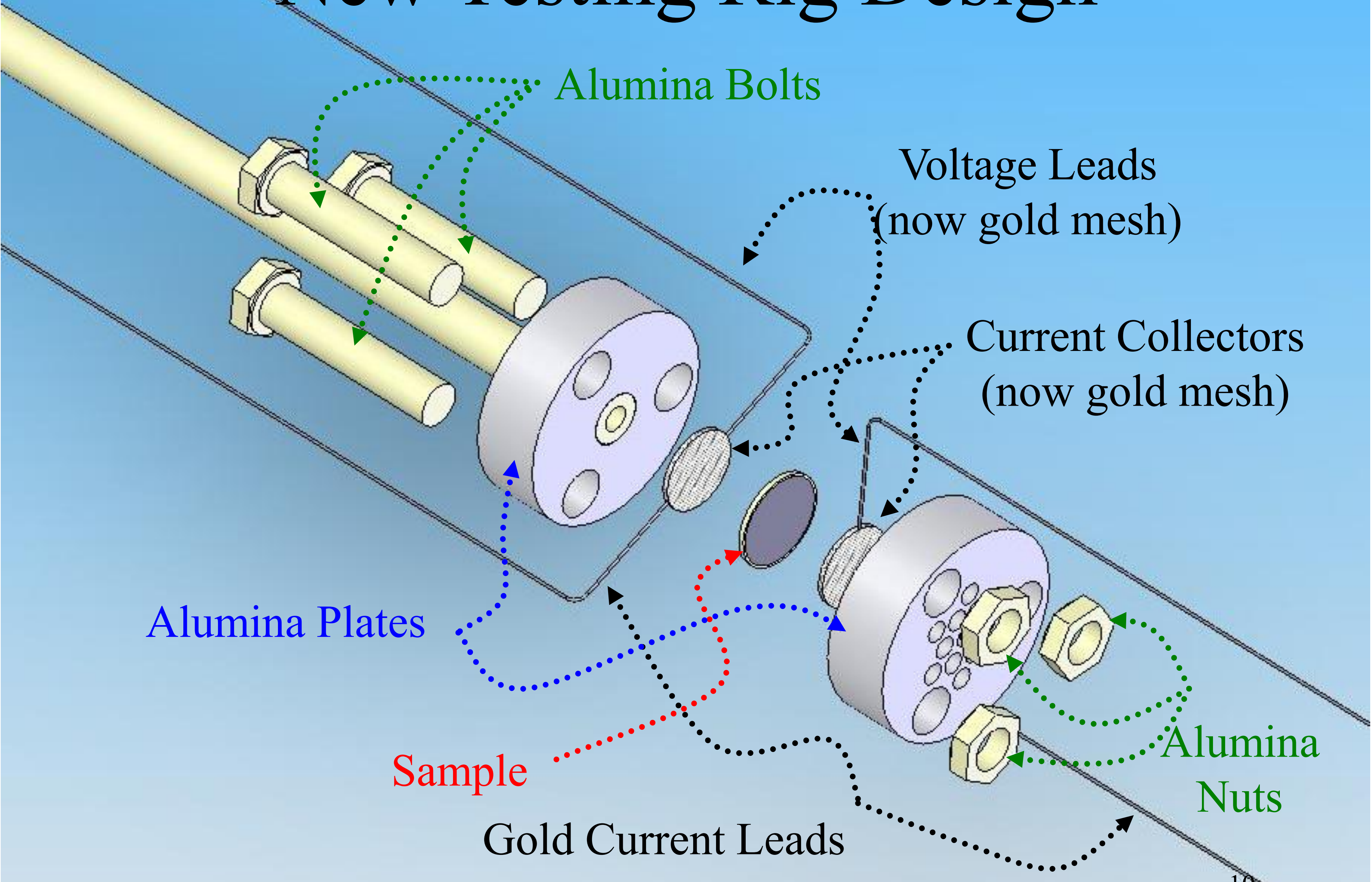
- PLD targets are $Gd_{0.1}Ce_{0.9}O_{2-\delta}$, and LSCF (6428)
- 2 types of samples:

LSCF/YSZ/LSCF

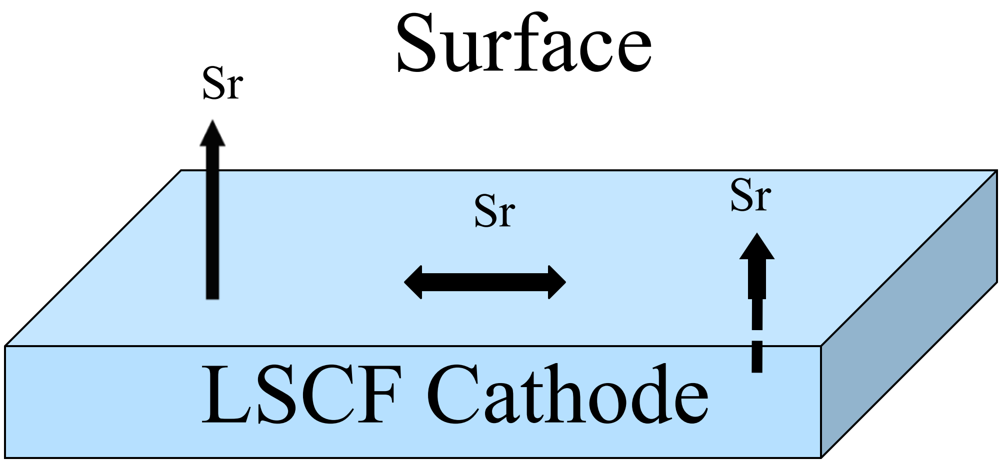
LSCF/GDC/YSZ/GDC/LSCF

- Thickness: LSCF = 10 nm; GDC = 20 nm (YSZ 0.5mm)

New Testing Rig Design



Example – Sr out-diffusion



How do operational conditions affect Sr mobility?

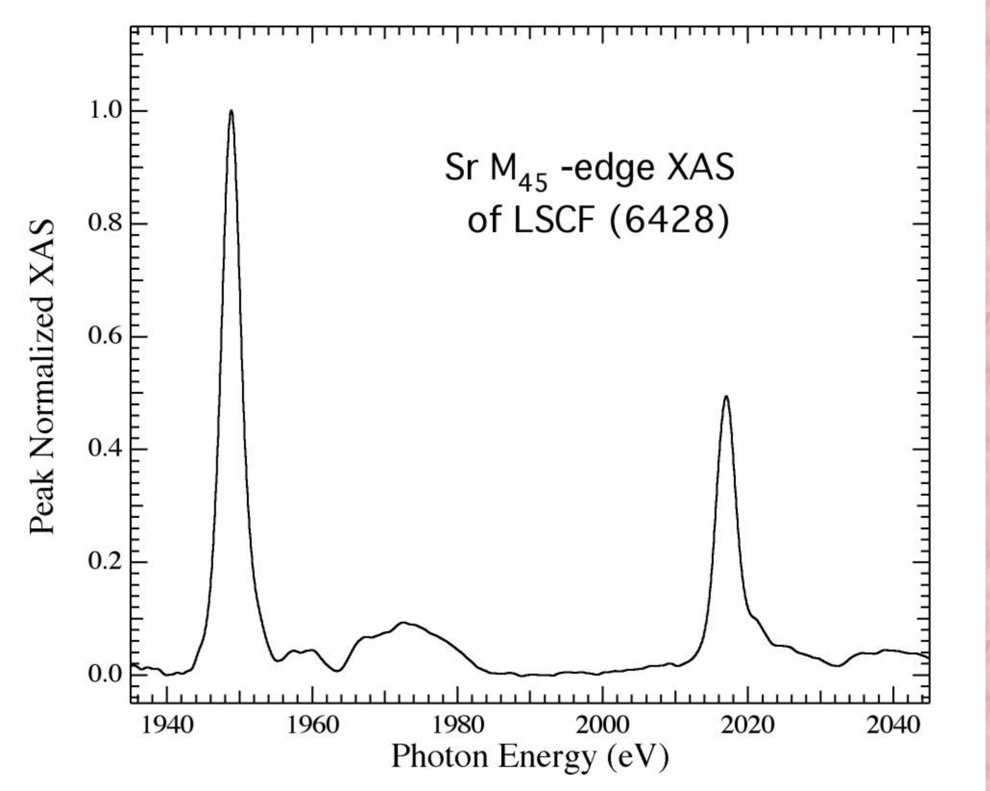
XPS work (Sandia) provided a direct confirmation of Sr out-diffusion

Example – Map Sr out-diffusion

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

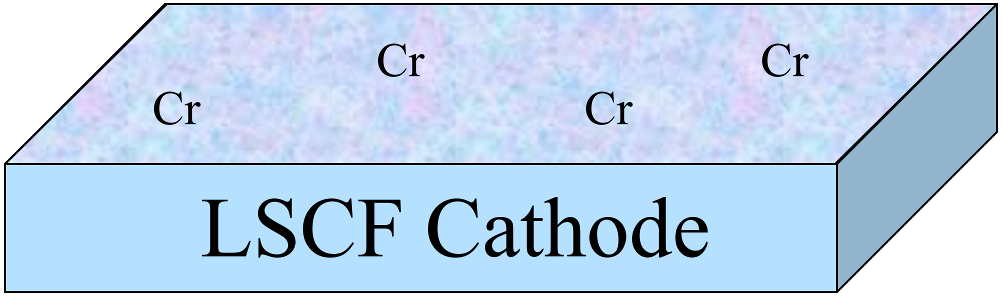
Surface Sr valence is same as bulk (Sr^{2+})!

No change



Solution – Elemental tagging

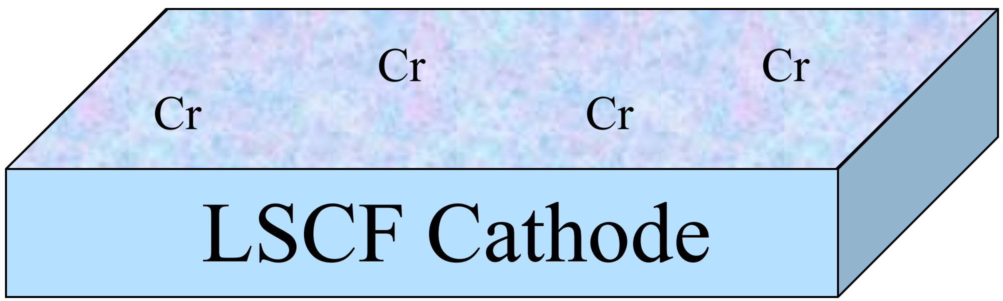
Introduce surface Cr



Cr present as Cr_2O_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



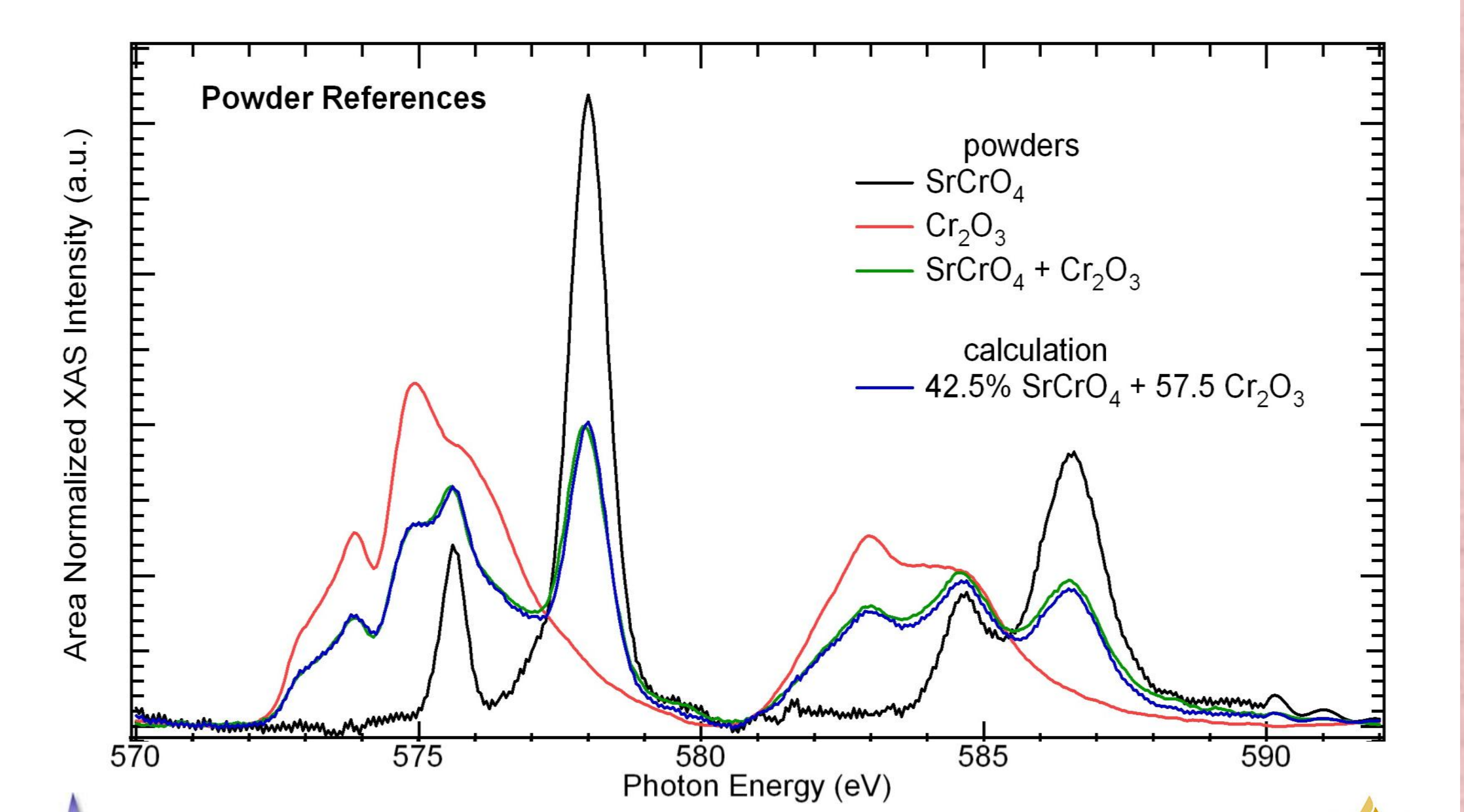
Cr present as Cr_2O_3 (Cr^{3+})

or

(in the presence of SrO) as $SrCrO_4$ (Cr^{6+})

EXAMPLE – Sr out-diffusion

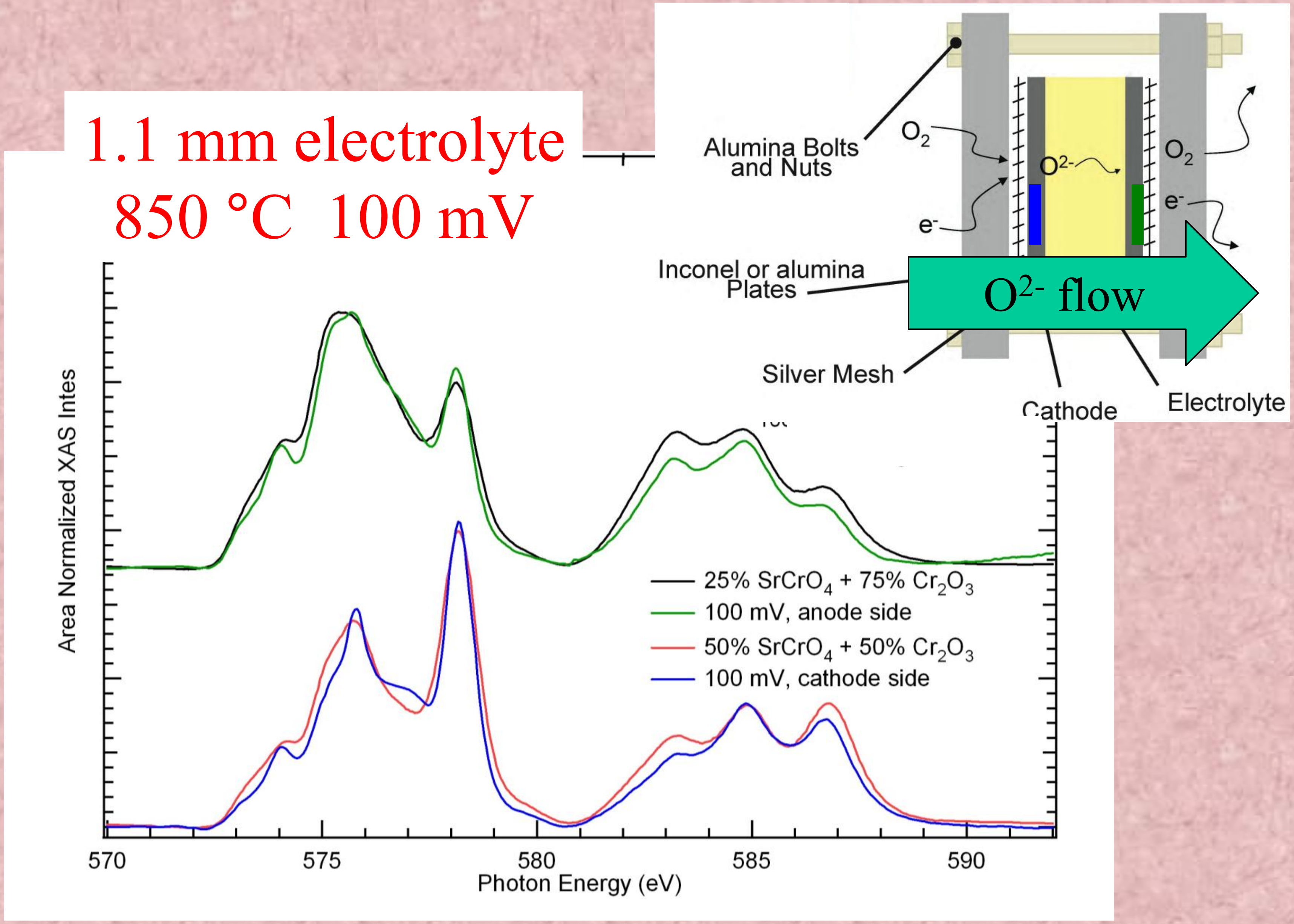
Surface Sr modifies Cr valence!



SECA

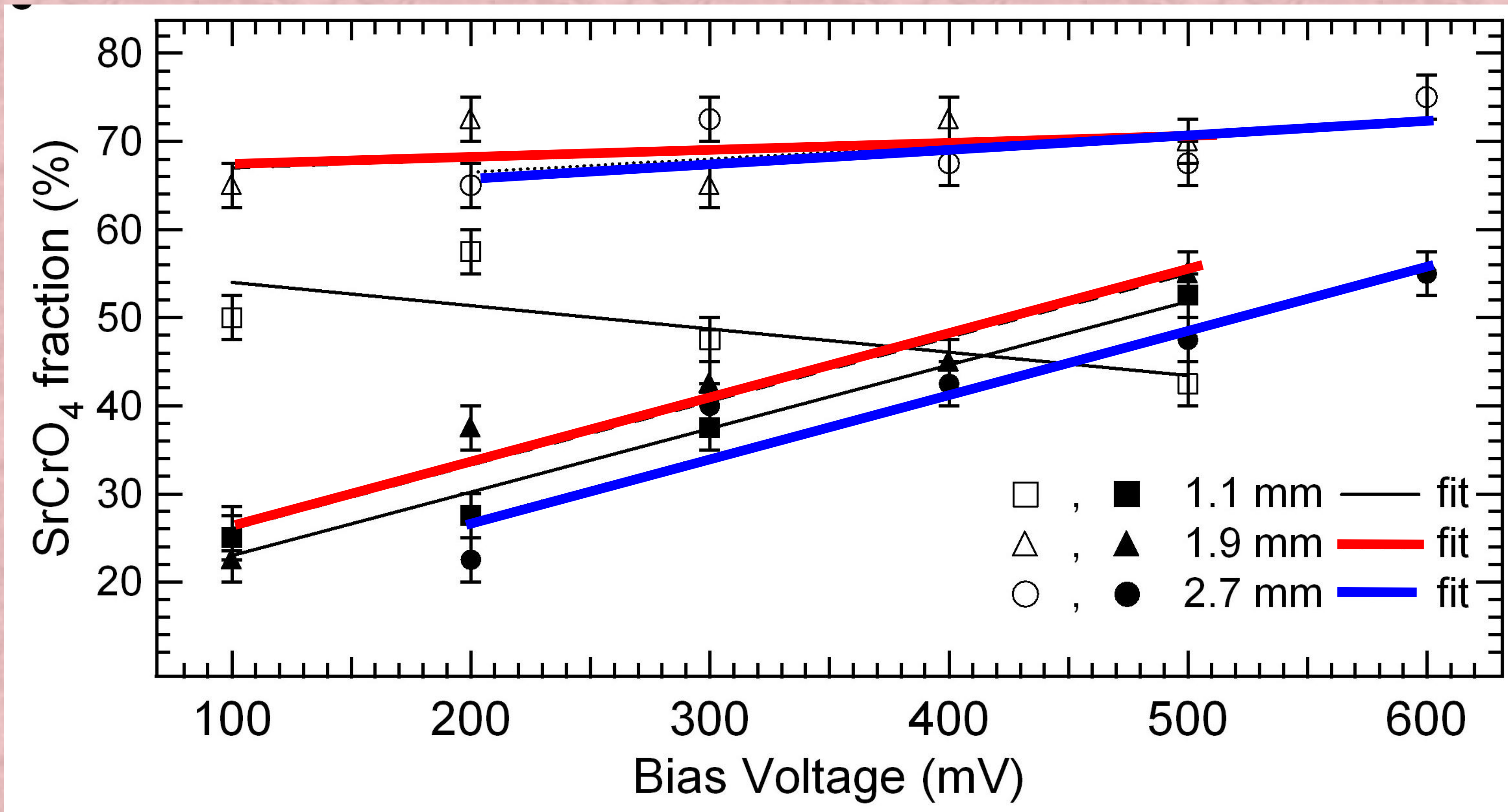
MONTANA STATE UNIVERSITY

1.1 mm electrolyte
850 °C 100 mV



Driven Sr out-diffusion

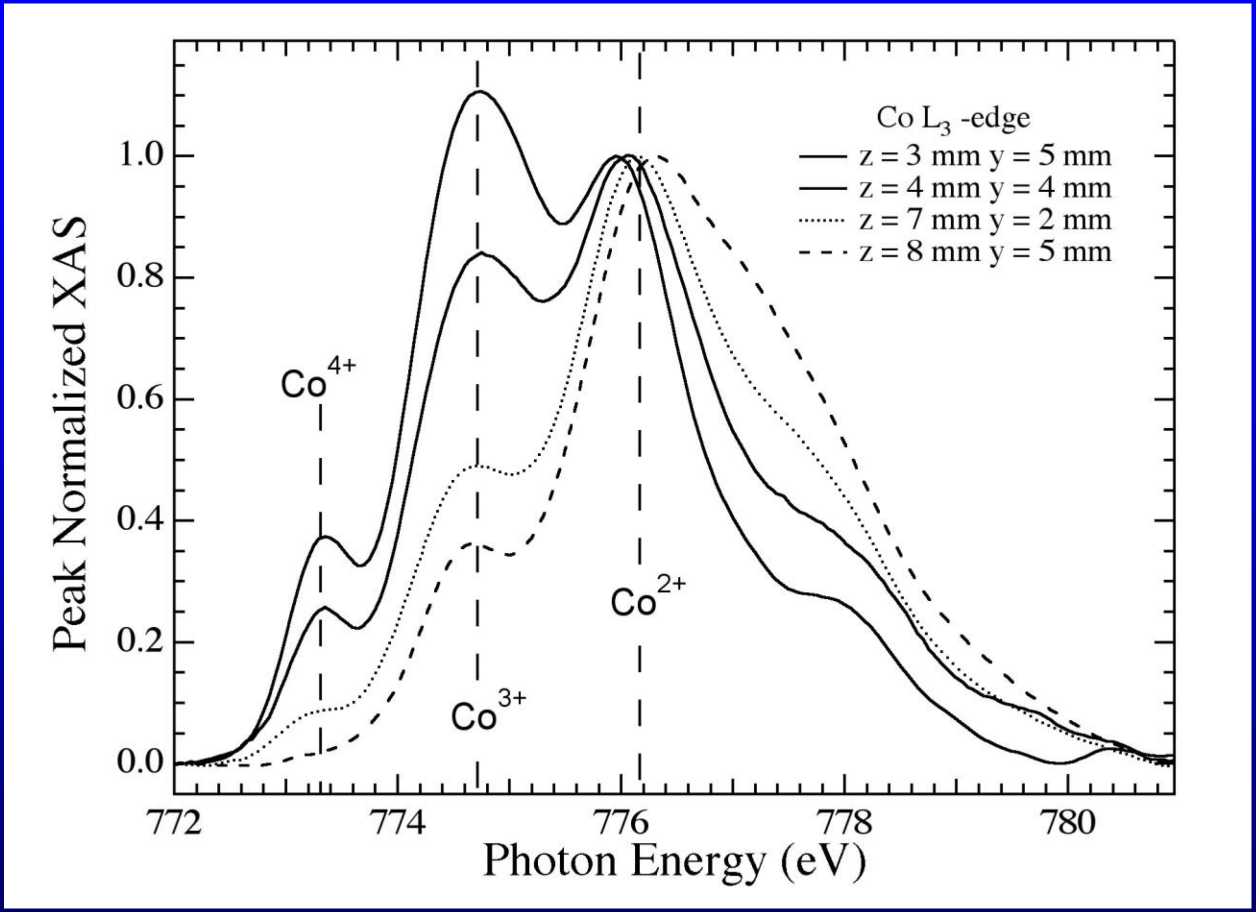
solid – anode empty - cathode



Solid State Ionics ***212****, 70 (2012).*

MONTANA STATE UNIVERSITY

Major complication



Strong spatial valence variation

Averaging techniques miss the extremes.

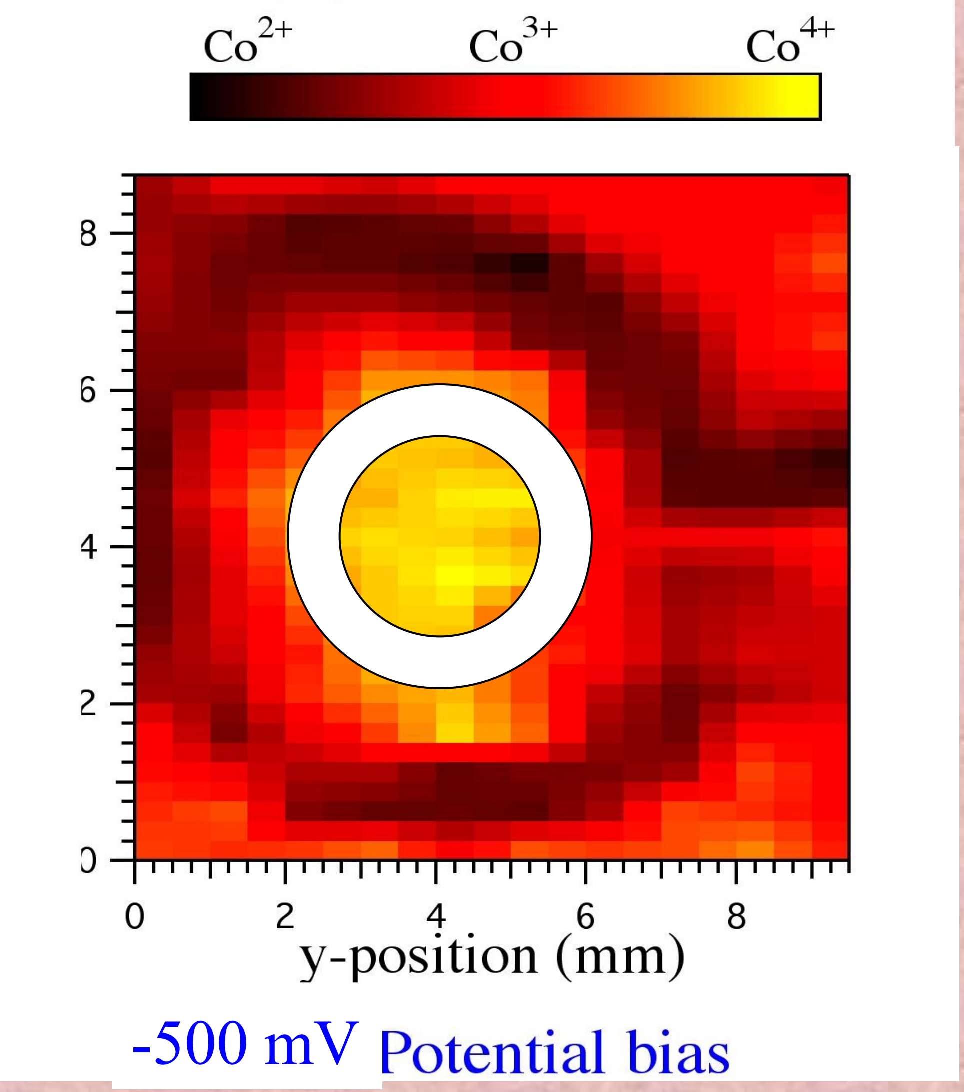
+500 mV bias potential

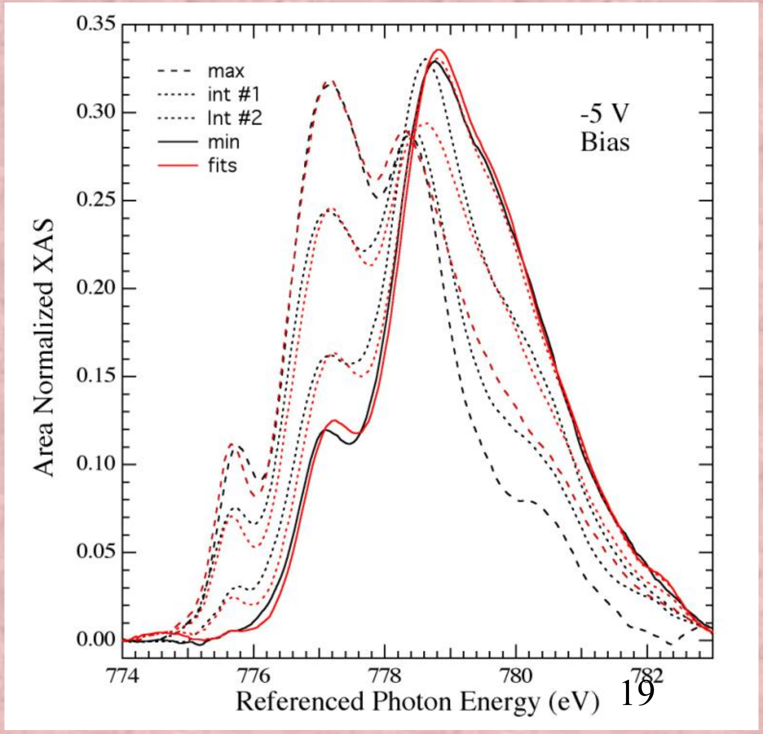
Co valence map

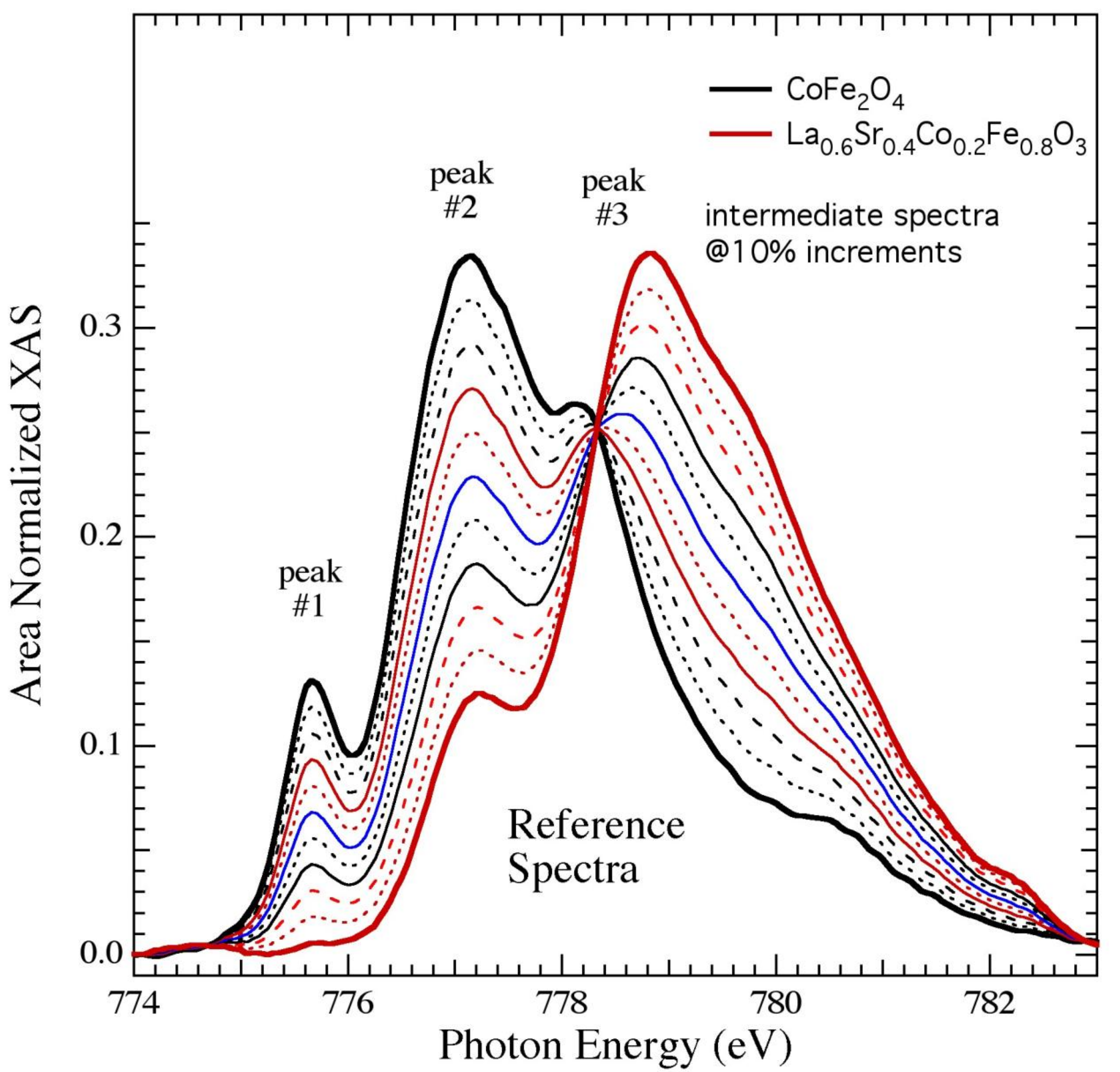
Co present as Co^{2+} thru Co^{4+} (130% variation)

Circular pattern

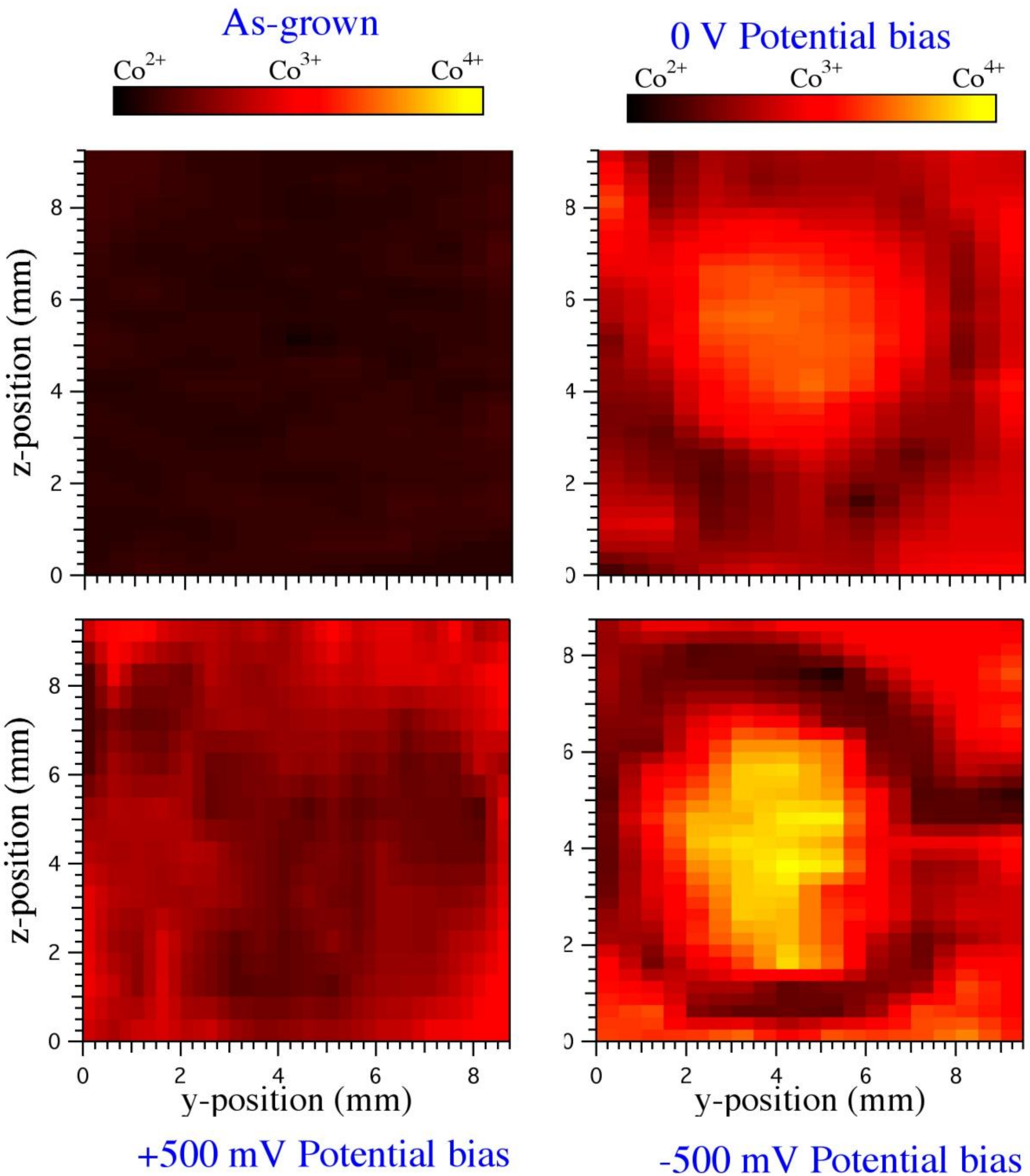
Matches air inlet







Automated fitting reproduced data exactly.



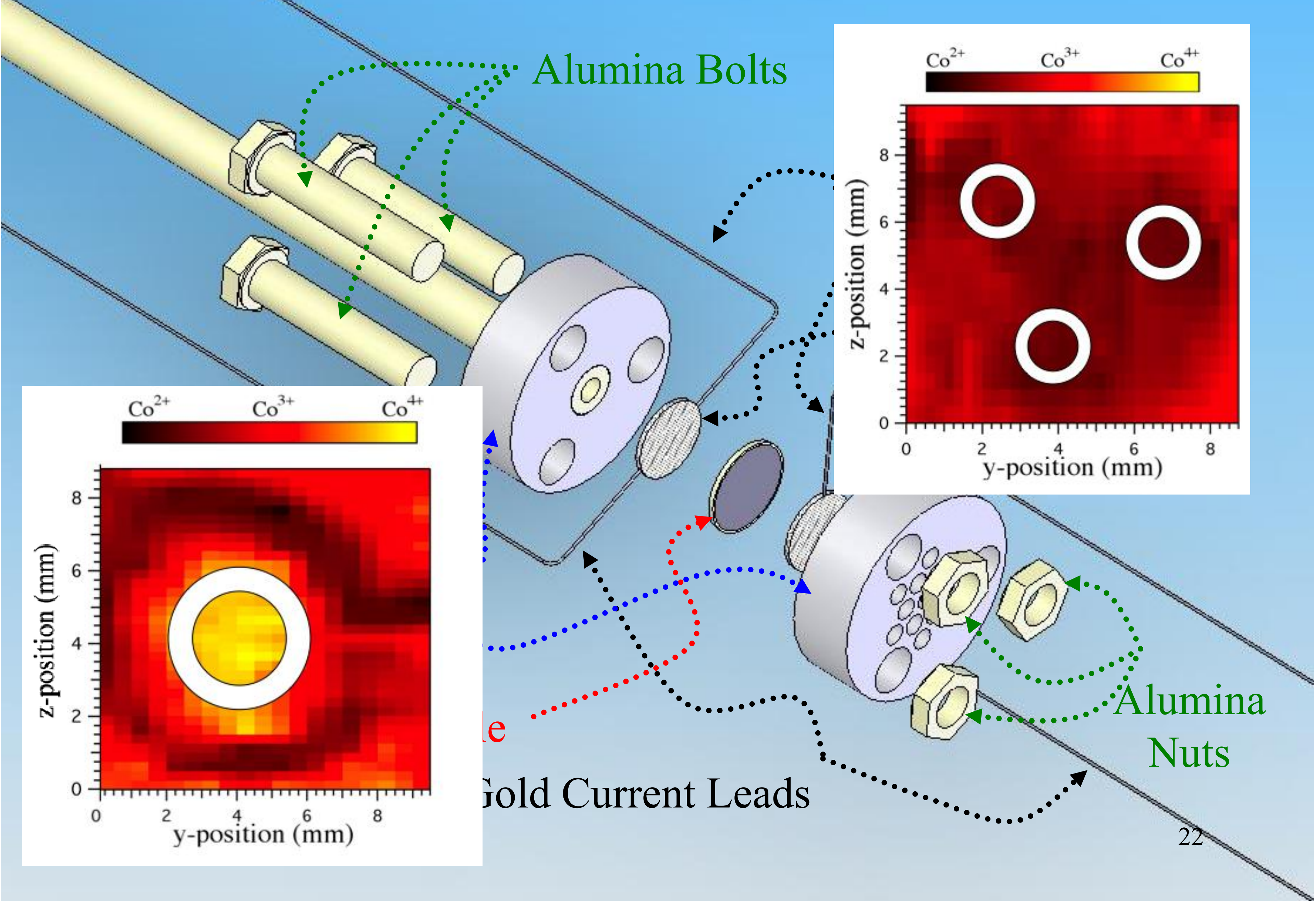
Co valence mapping

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



Humidity Control

Heated air-line bubbler installed

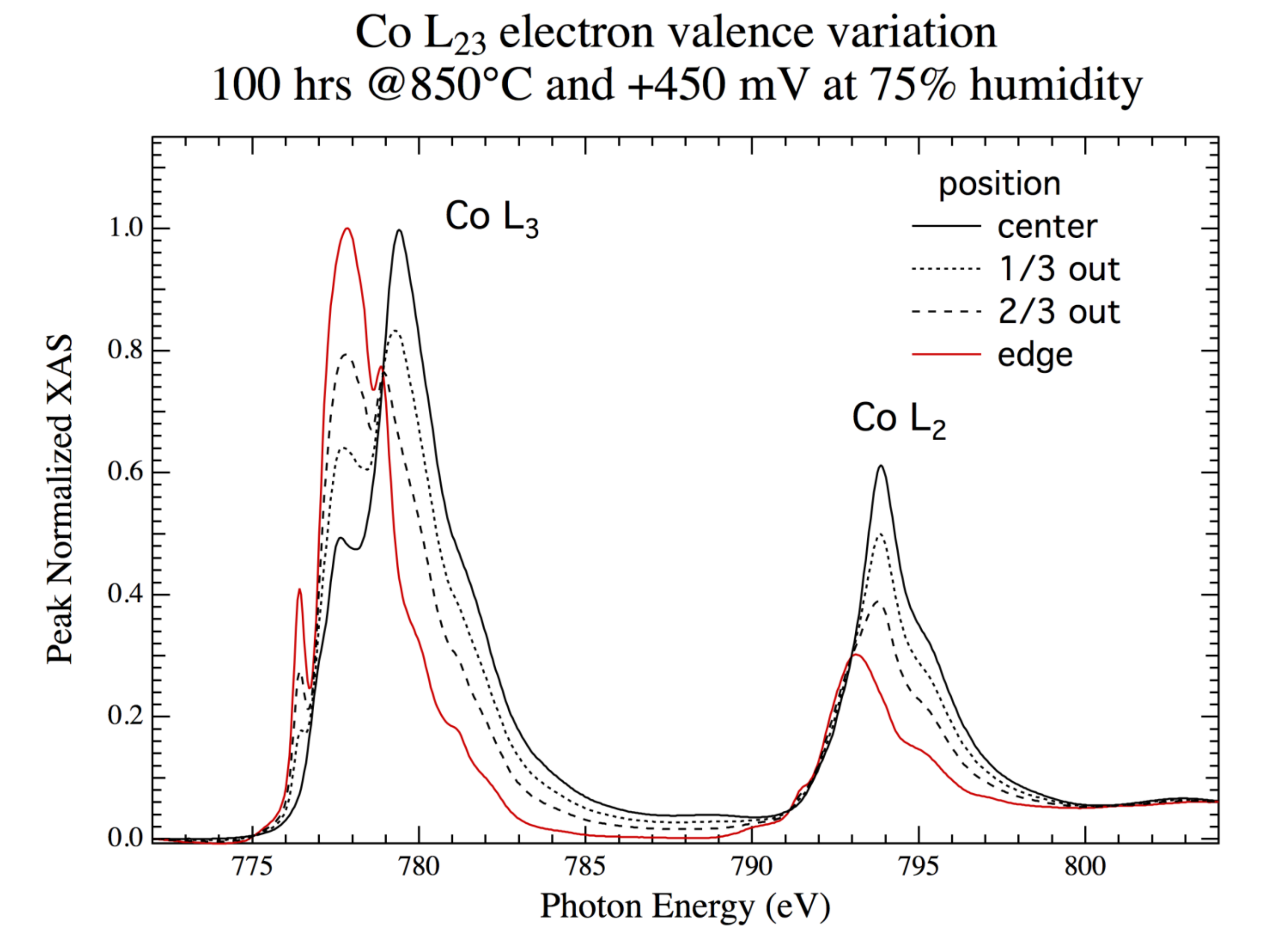
3 symmetric PLD samples created

LSCF (6428)/GDC/YSZ/GDC/LSCF (6428) pellets

±450 mV @ 850°C for 100 hrs

25%, 50%, 75% humidity

Humidity – Valence variation of Co

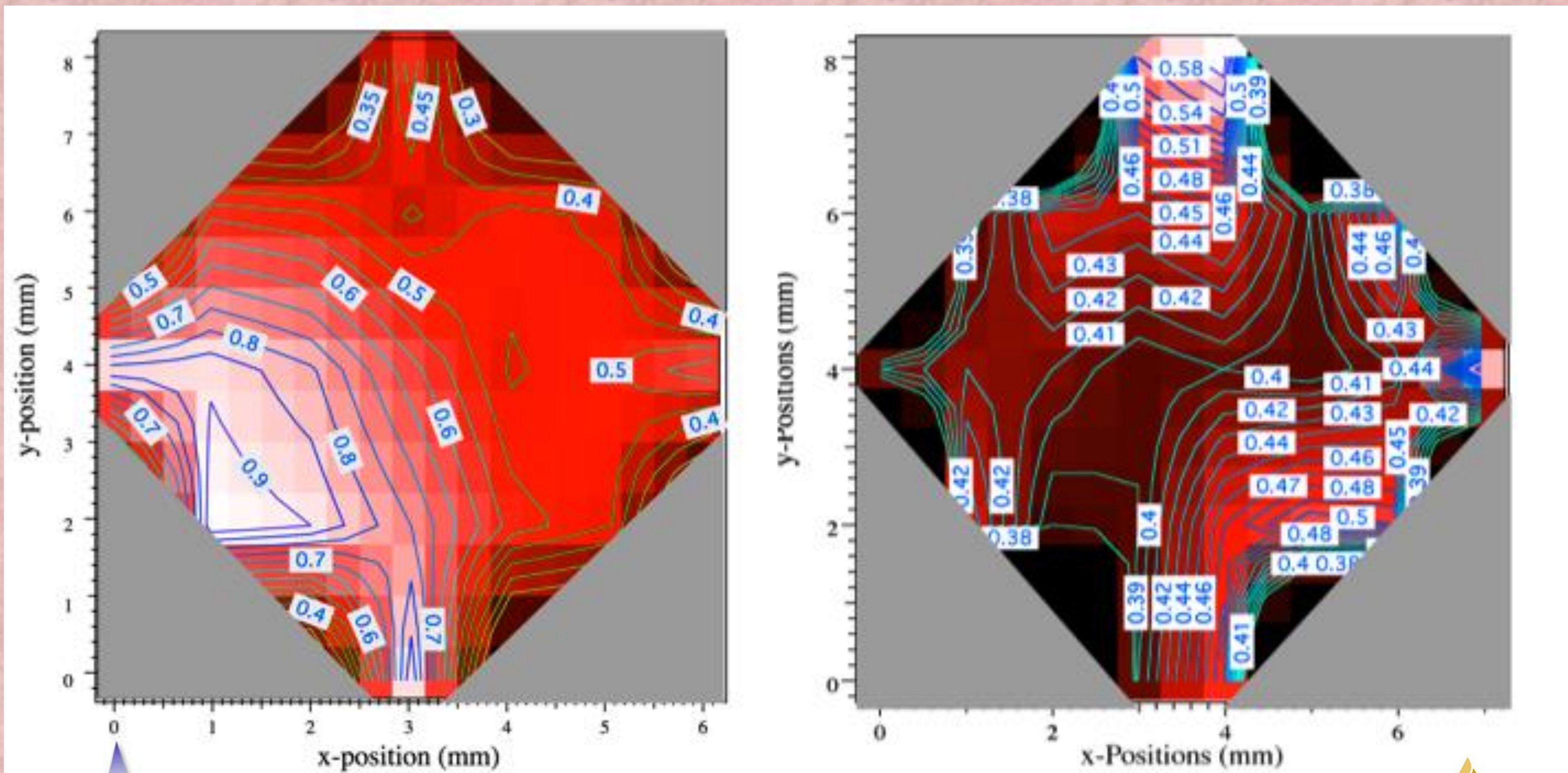


Strong dependence on gas inlet configuration.

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