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

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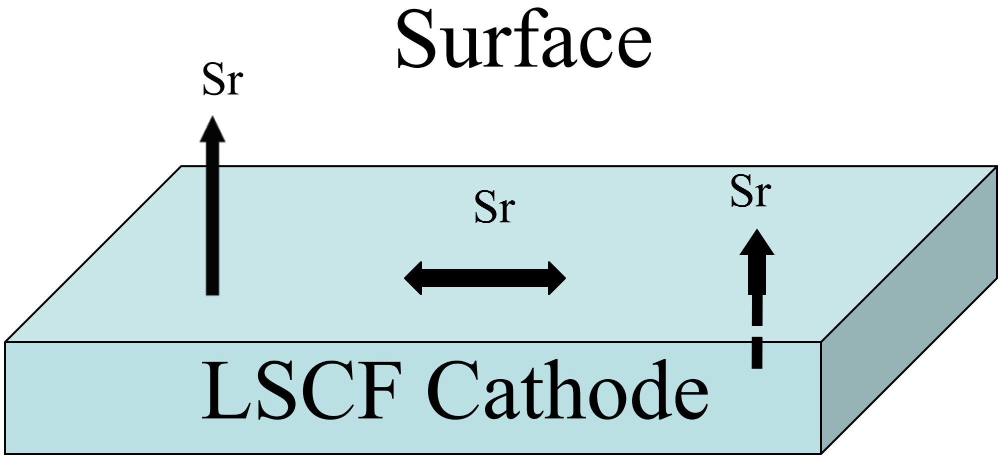
Research Thrusts

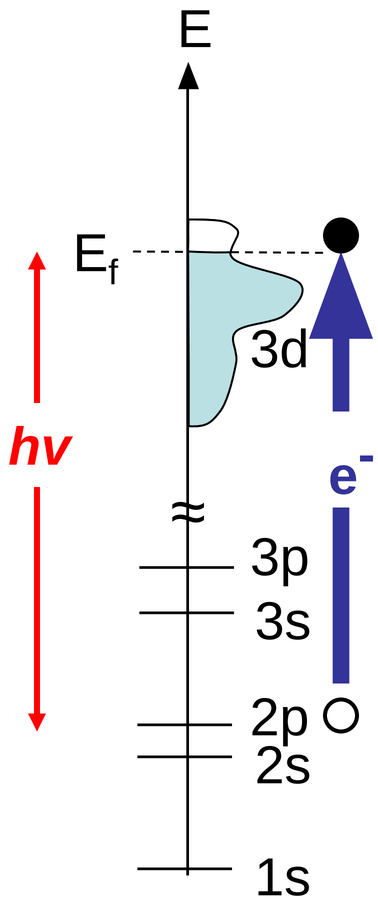
1. Directed SOFC materials development thru rapid X-ray characterization.
2. Identification of interfacial barriers to oxygen ion formation and diffusion.
3. X-ray characterization under operational conditions.

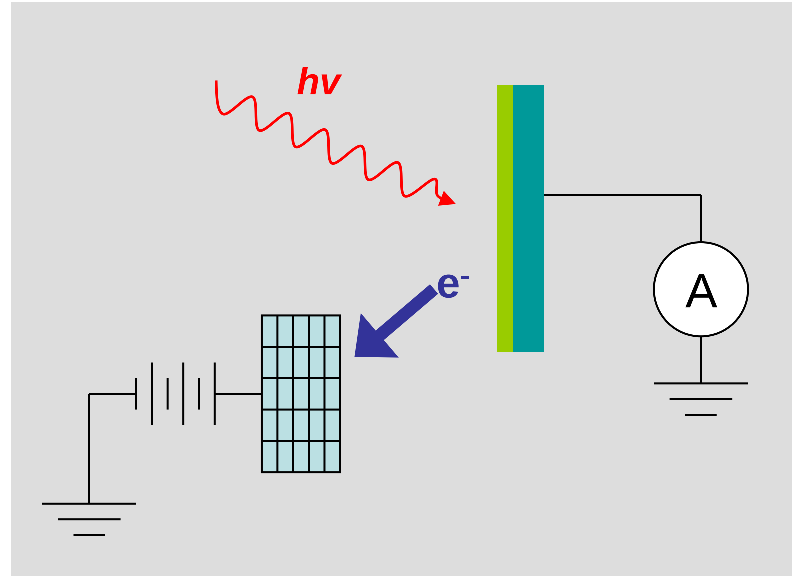
Example – Map Sr out-diffusion



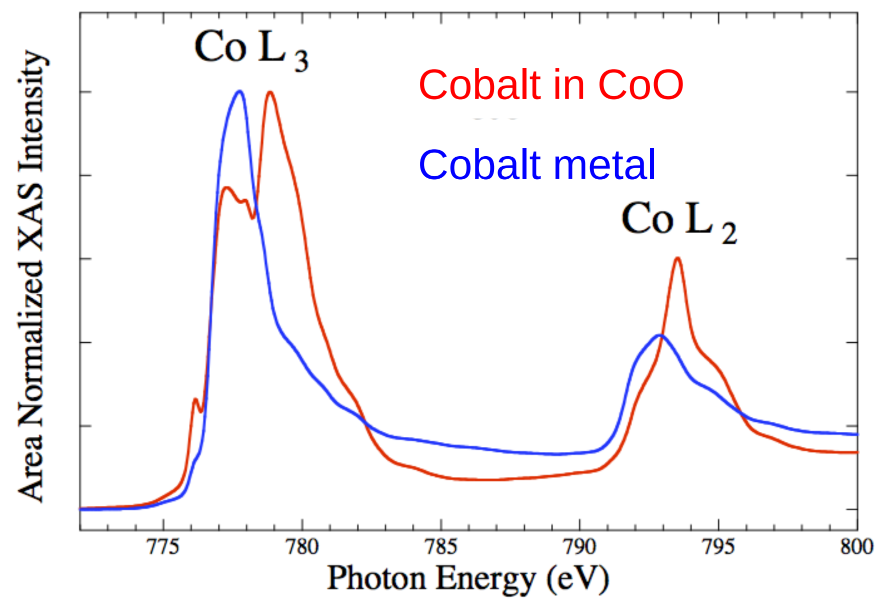
How do operational conditions affect Sr mobility?

X-ray Absorption Spectroscopy (XAS)

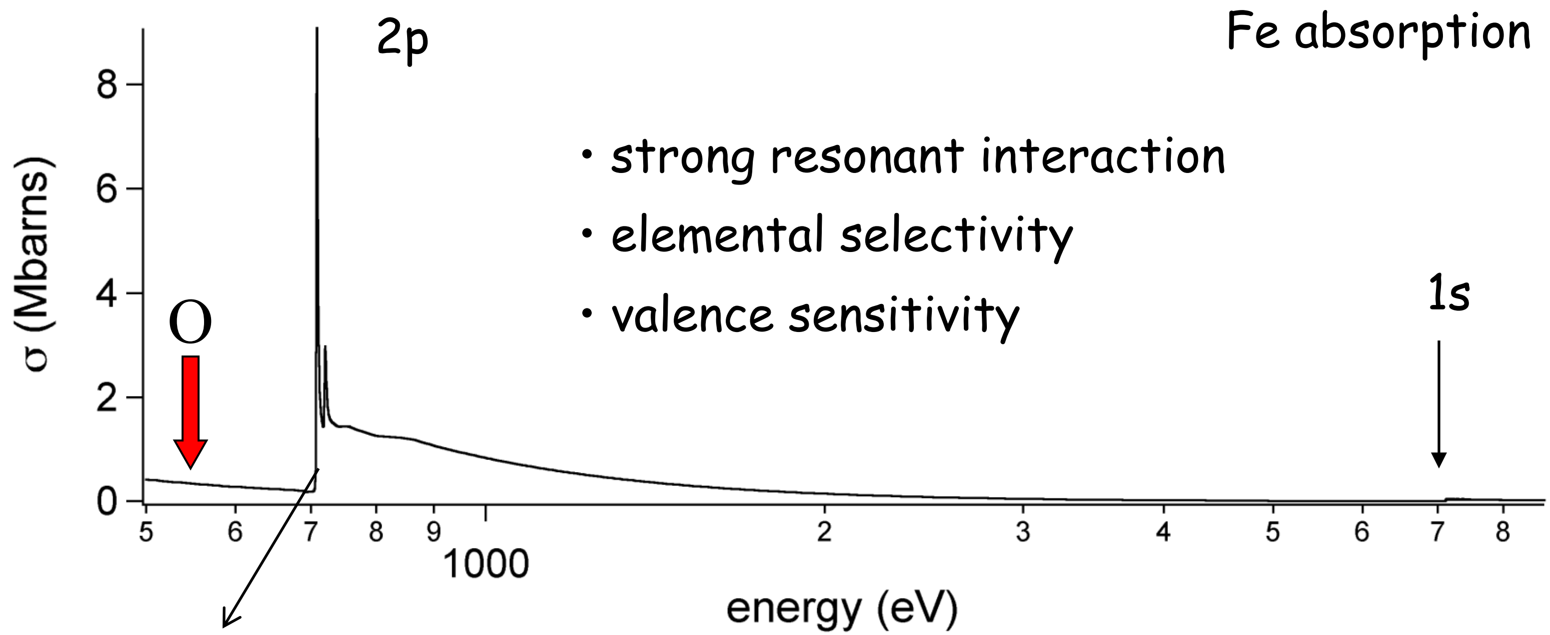




Co L edge XAS

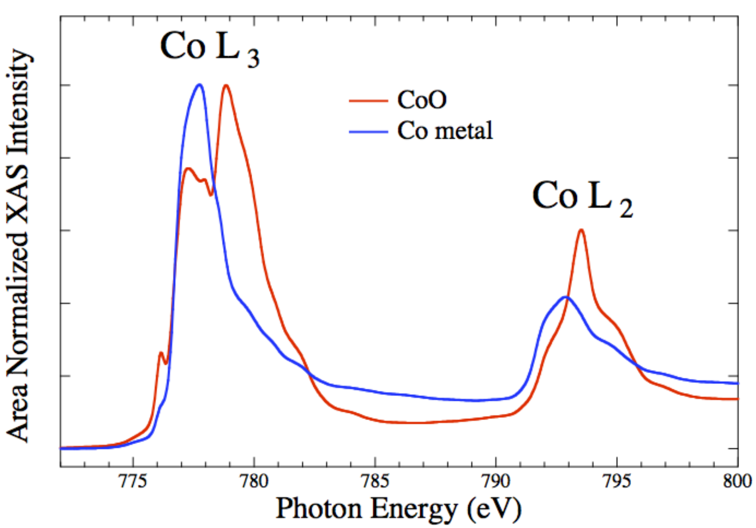


Soft x-rays are ideal for buried interfaces!



- strong resonant interaction
- elemental selectivity
- valence sensitivity

Co L edge XAS



spatially map elemental valence at buried interfaces under operational conditions

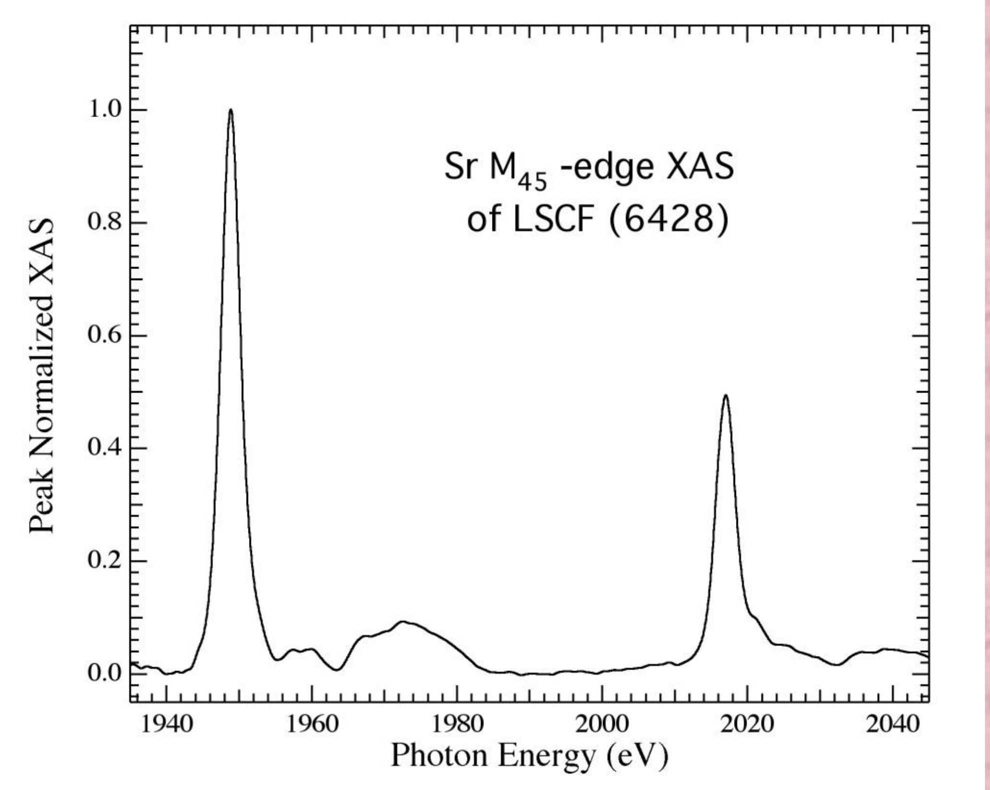
Example – Map Sr out-diffusion

Two problems

Sr is both on the surface and in bulk.

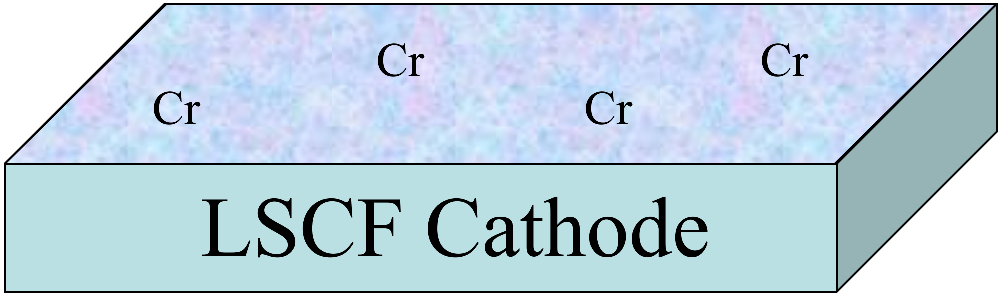
Sr remains as Sr^{2+}!

No change



Solution – Elemental tagging

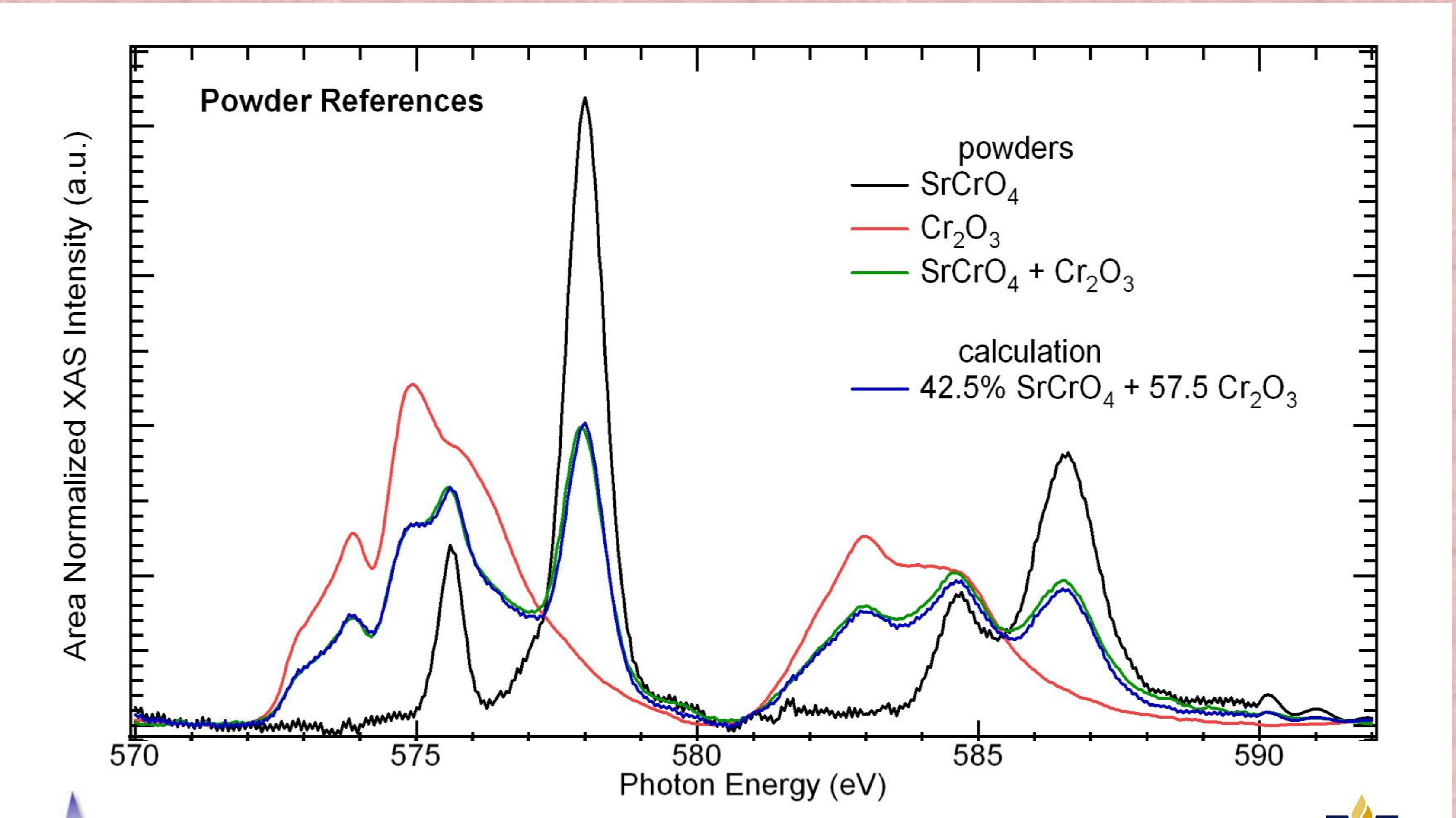
Introduce surface Cr



Cr present as Cr_2O_3 (Cr^{3+})
or
(in the presence of SrO) as $SrCrO_4$ (Cr^{6+})

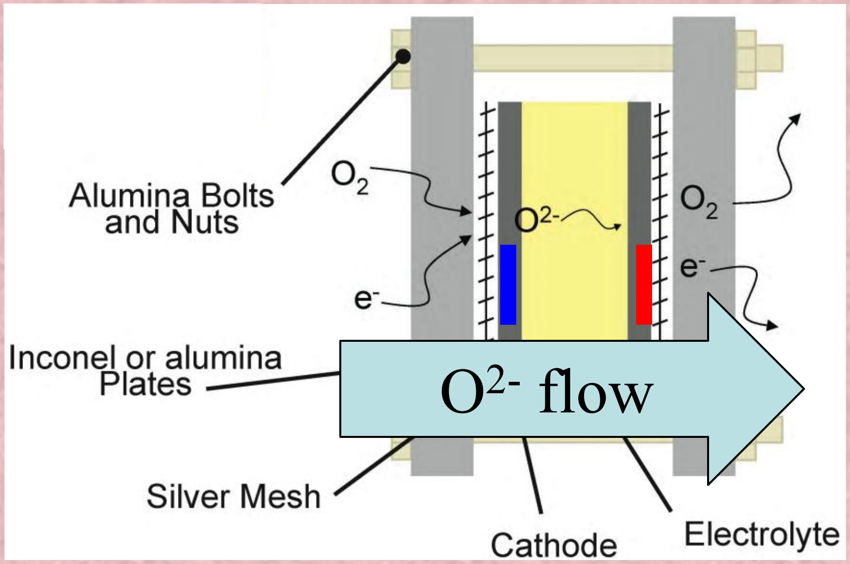
EXAMPLE – Sr out-diffusion

Sr modifies Cr valence!

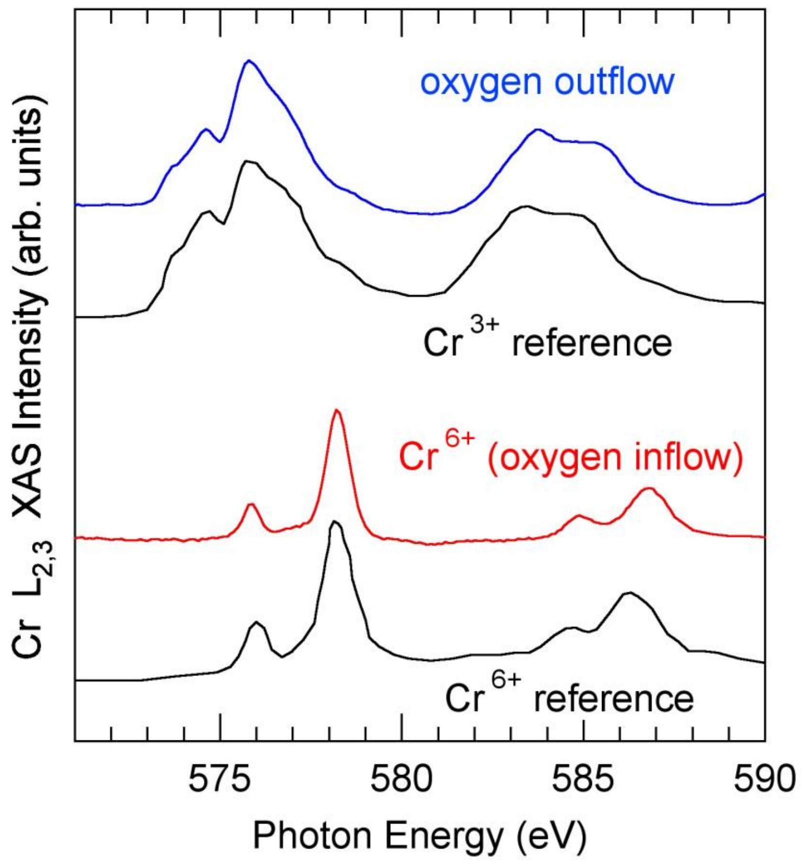


Oxygen ion flow direction modifies Cr valence!

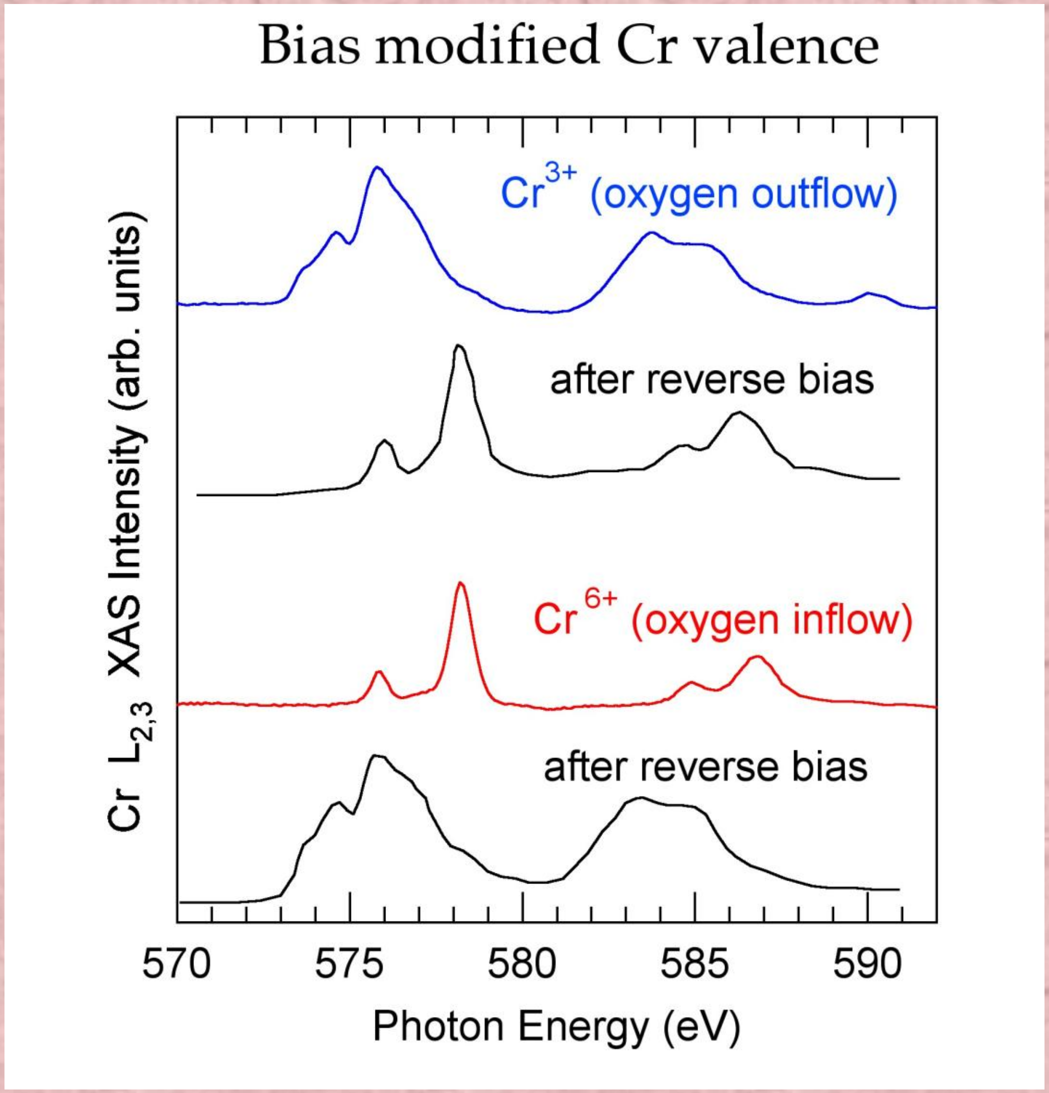
Bias driven symmetric cell
(2 half cells)



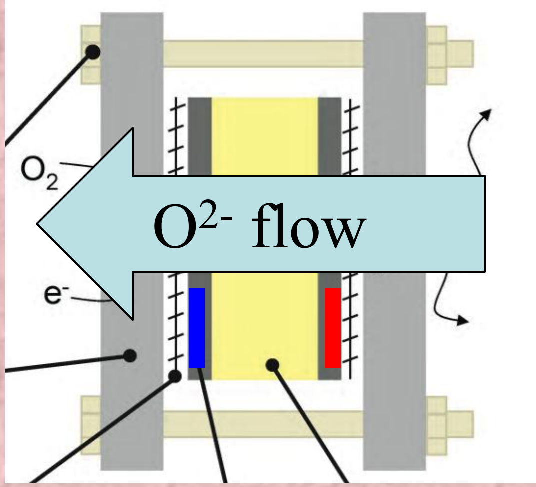
Ion flow modified Cr valence



Oxygen ion flow (and bias)

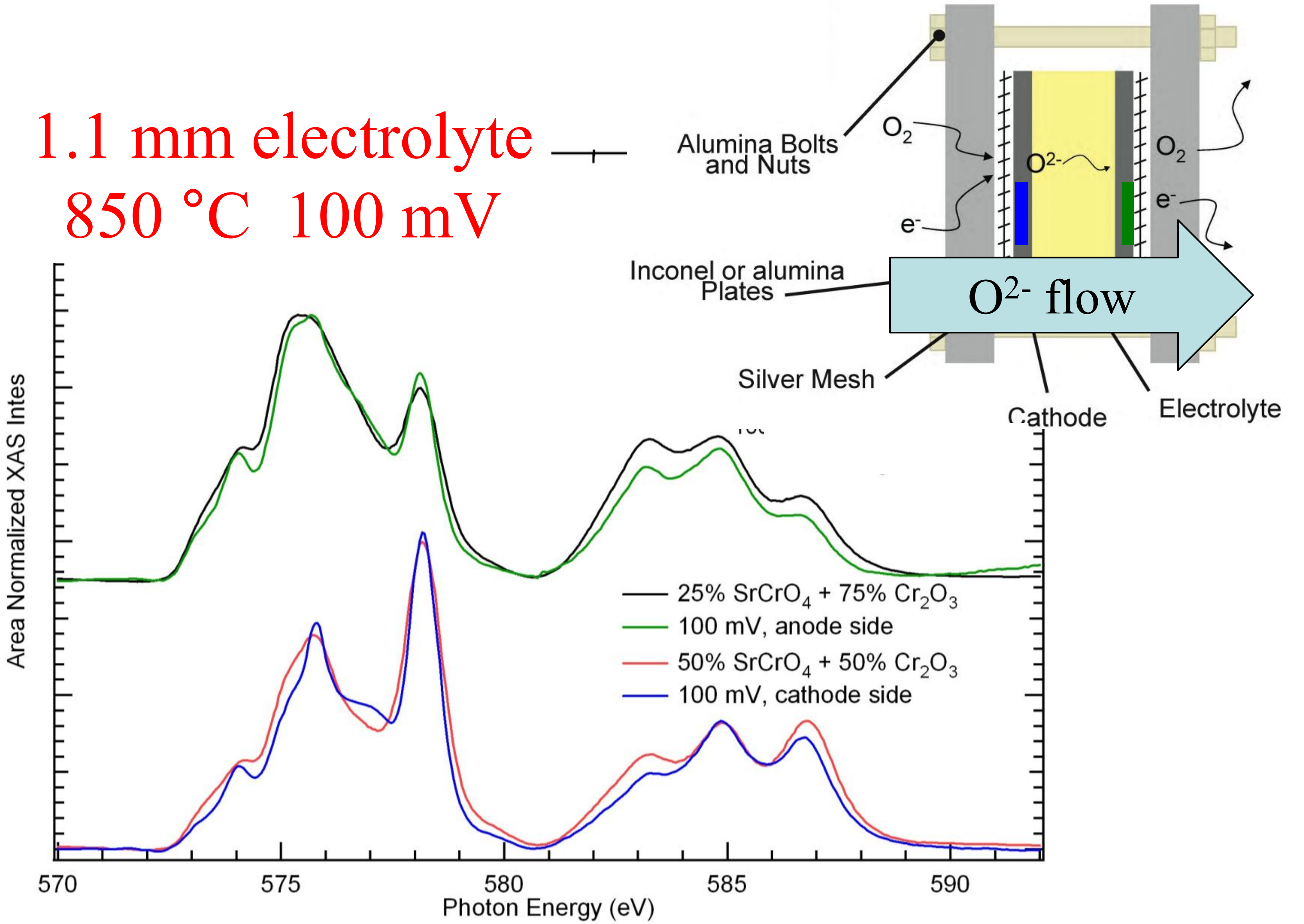


reverse bias



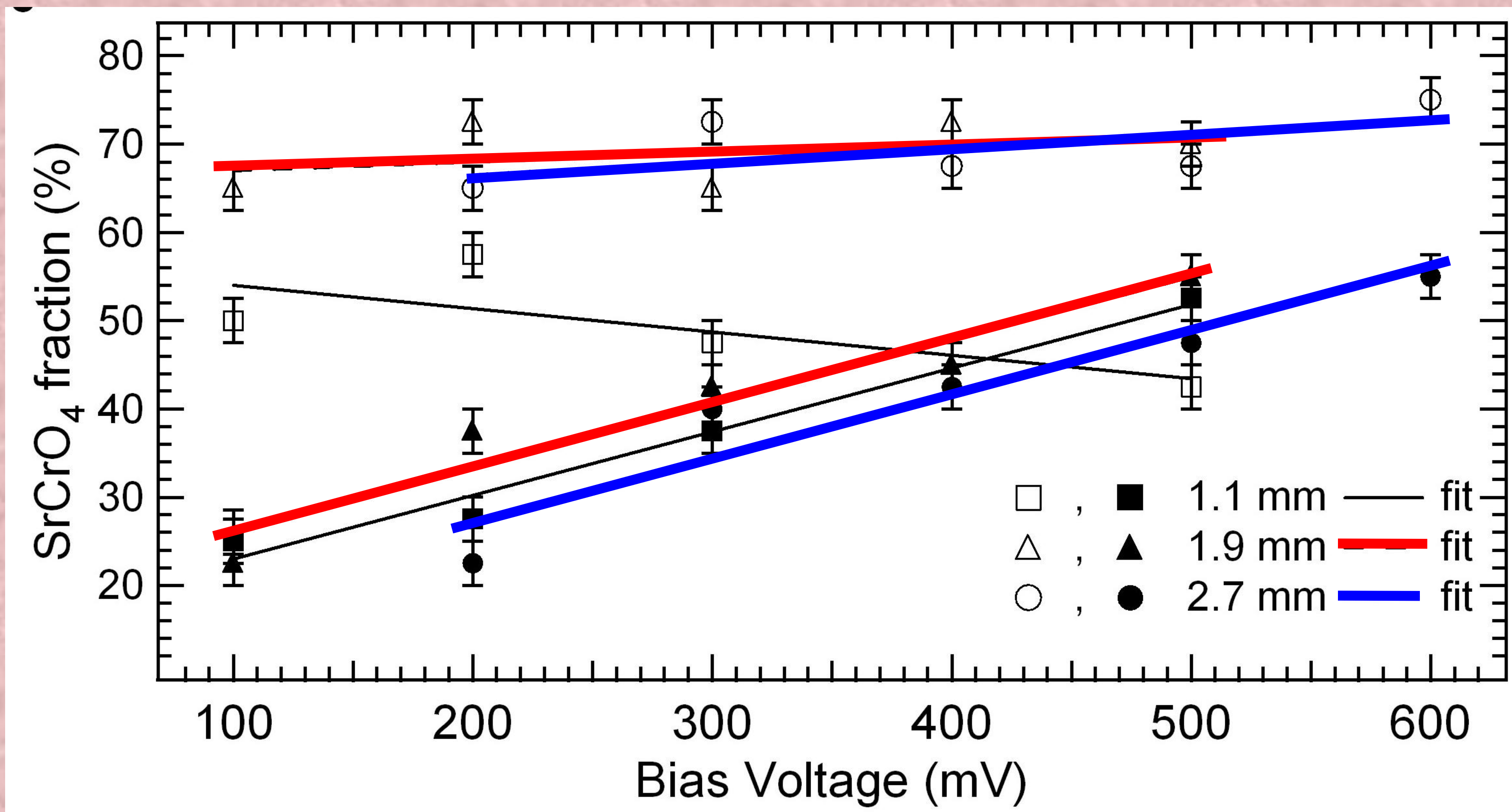
Oxygen ion flow reverses Cr valence!

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)

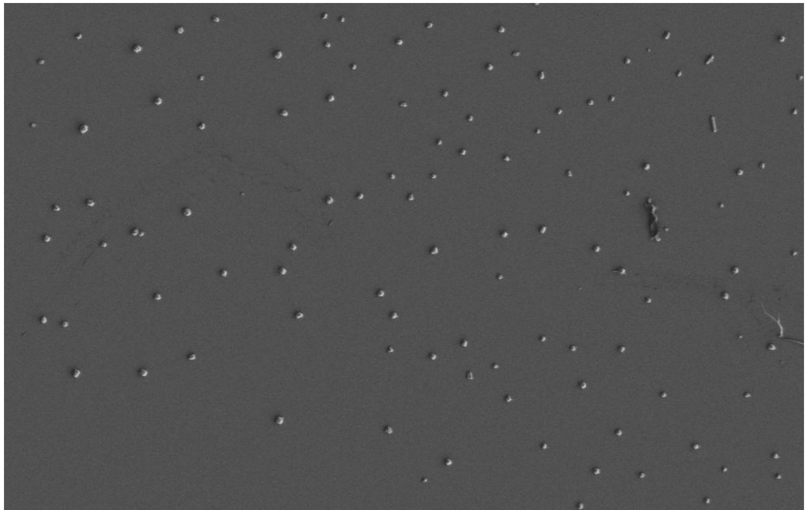
- Substrate 0.5 mm single crystal YSZ (polished)
- Sintered GDC and LSCF targets
- 2 types of samples:

  LSCF/YSZ/LSCF

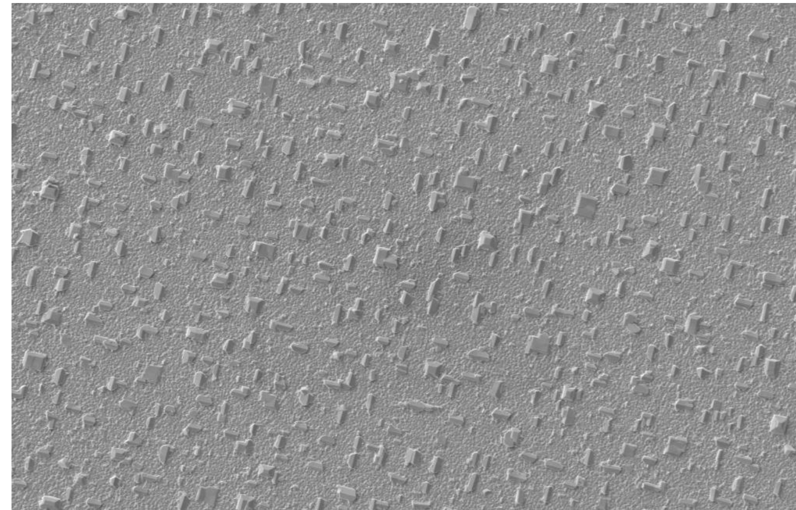
  LSCF/GDC/YSZ/GDC/LSCF
- Thickness: LSCF = 10 nm; GDC = 20 nm
- GDC interlayer to prevent secondary phase formation

SEM Sr segregation

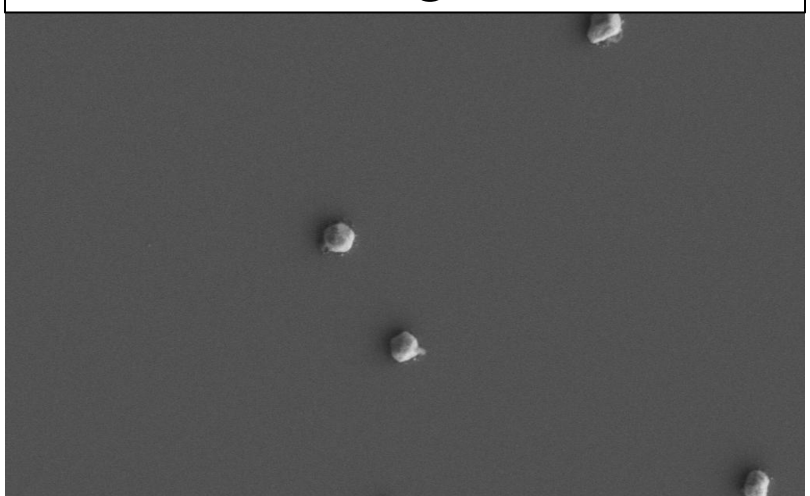
Pulse laser deposited LSCF/GDC



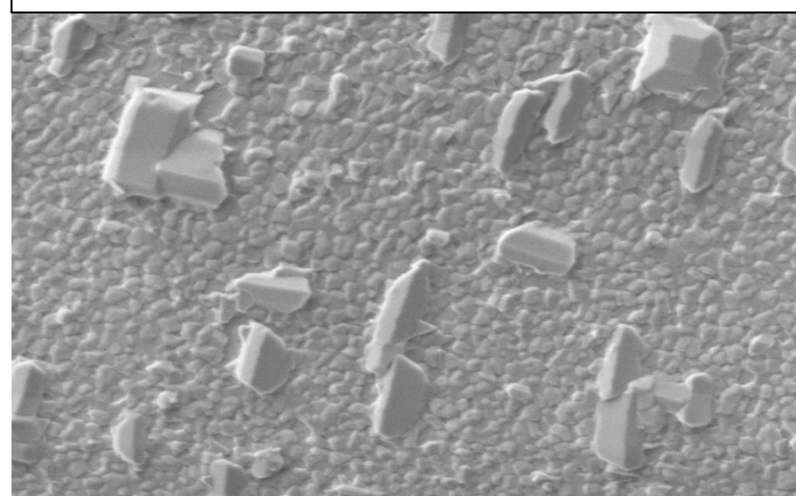
2 μm As grown



2 μm 100 hr 800 °C 500 mV

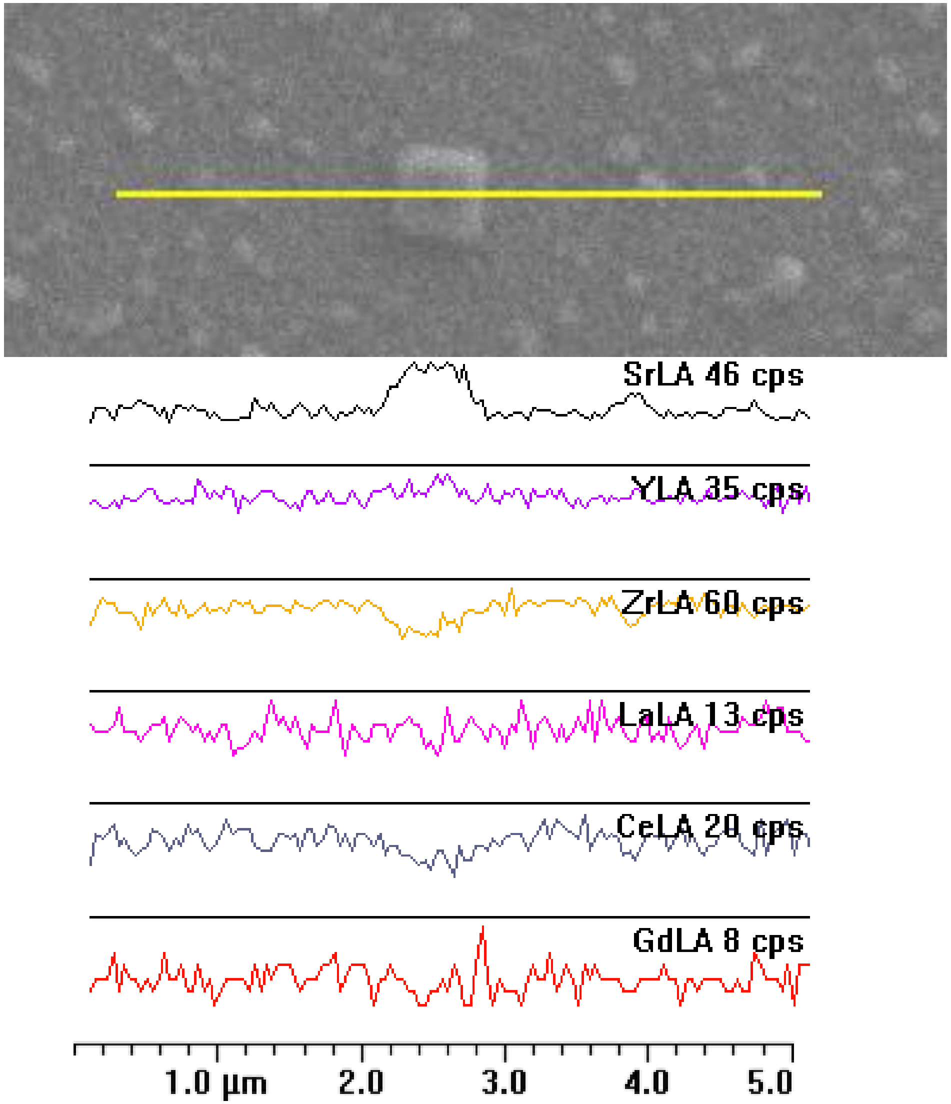


1 μm particulates



1 μm crystallites

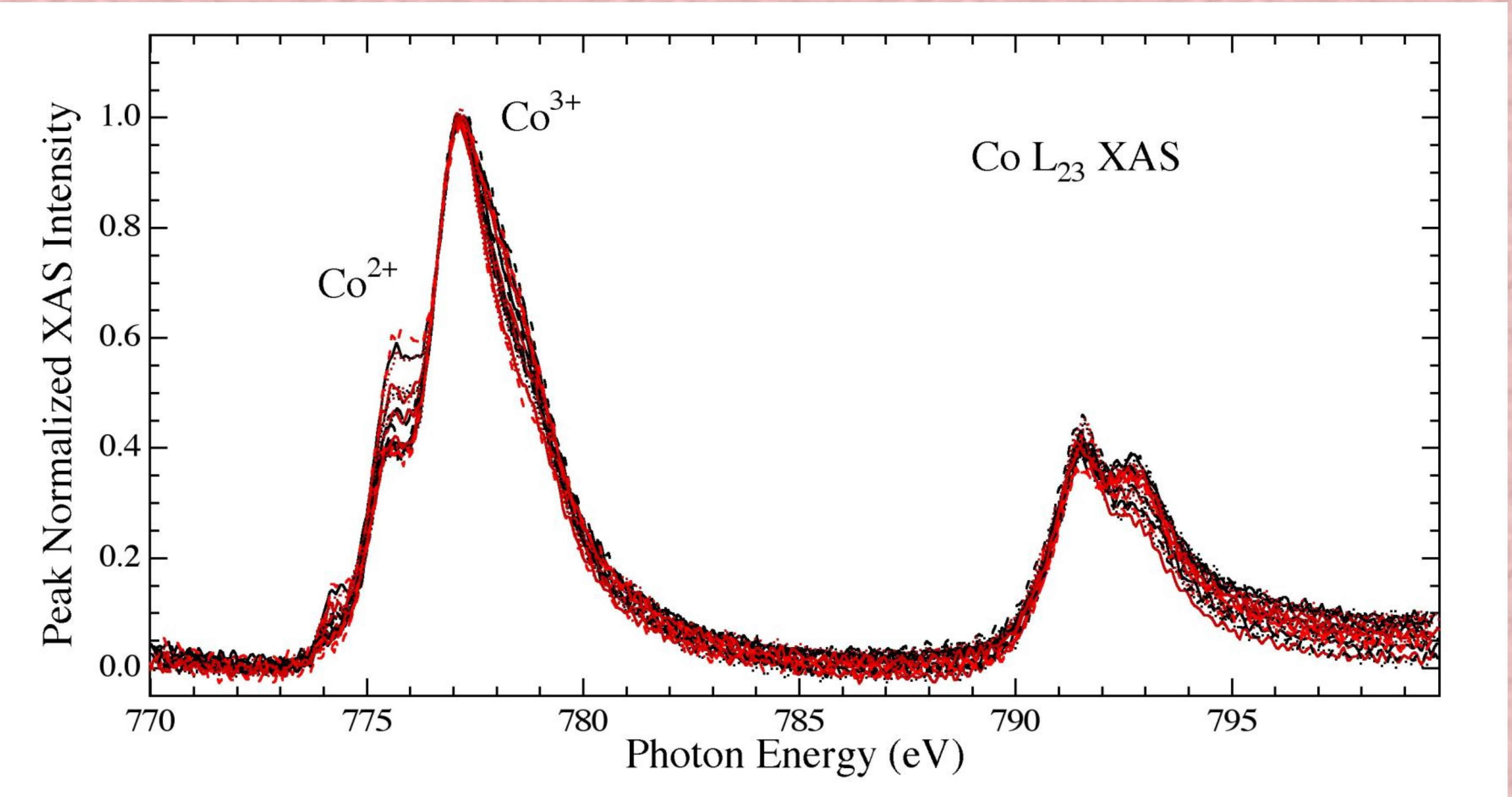
EDS line-scans



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

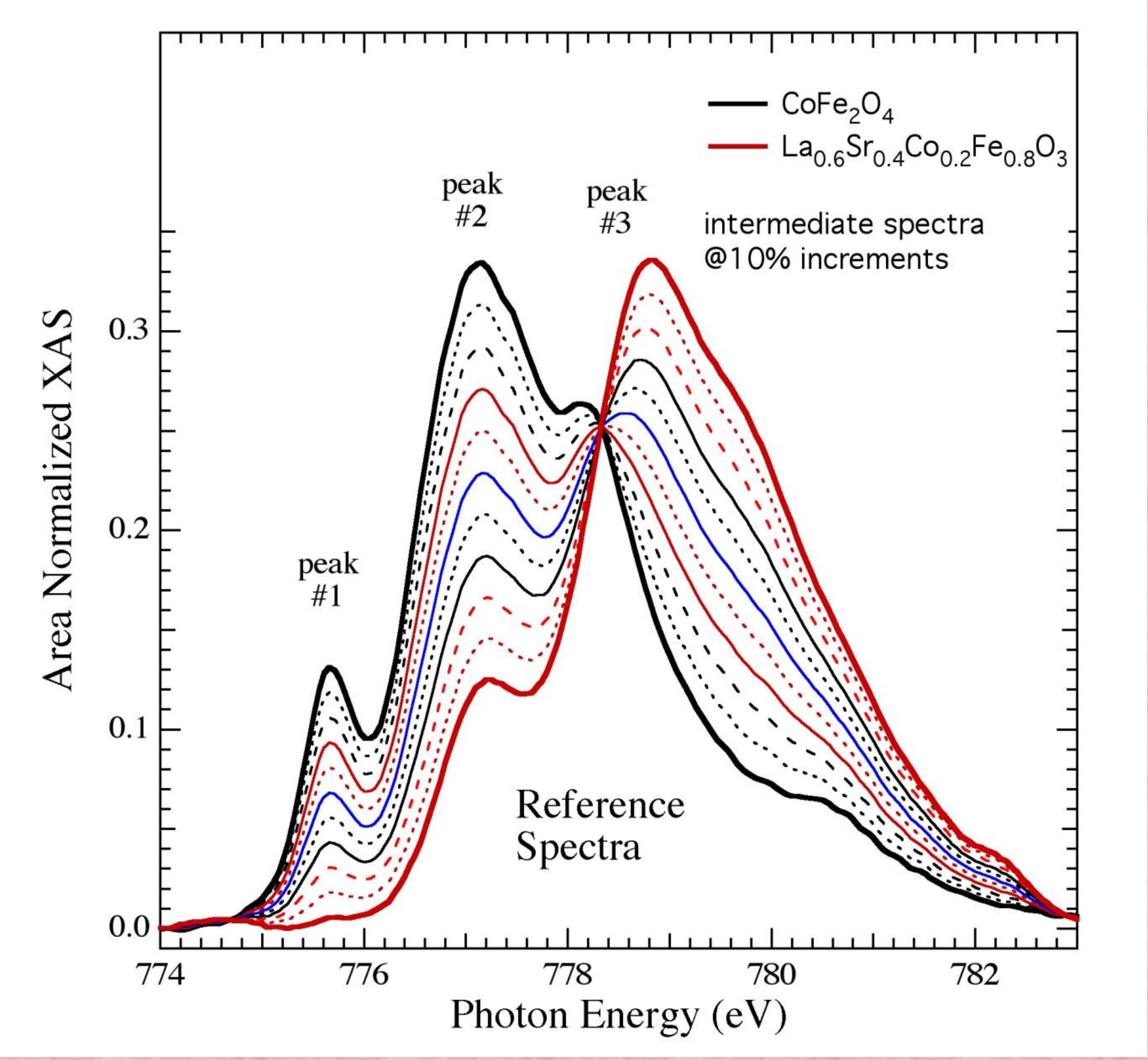
→Surface segregated Sr

Co valence shift from Sr segregation



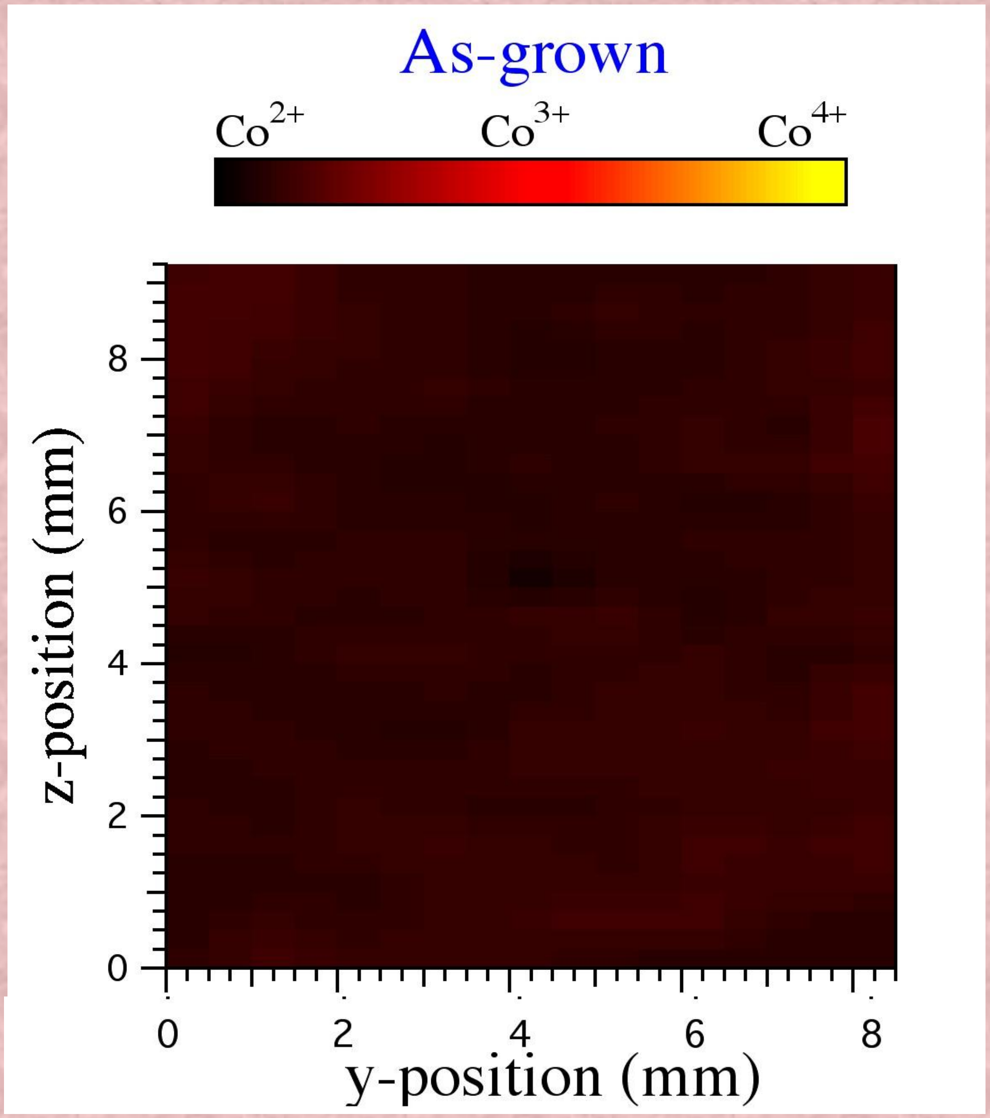
Removing Sr also increases Co^{3+} and decreases Co^{2+} concentrations

Measure of surface Sr



Co L_3-edge valence reference spectra

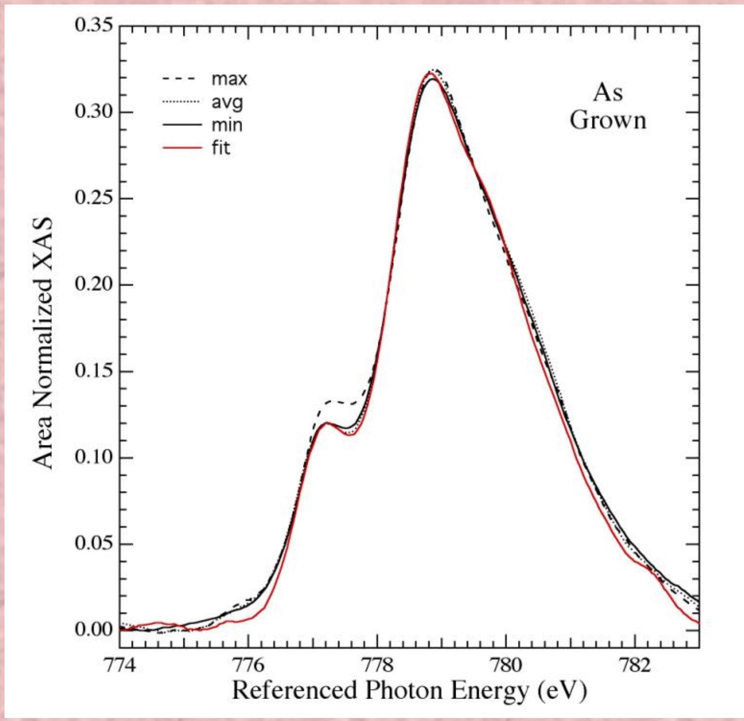
Co valence map



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

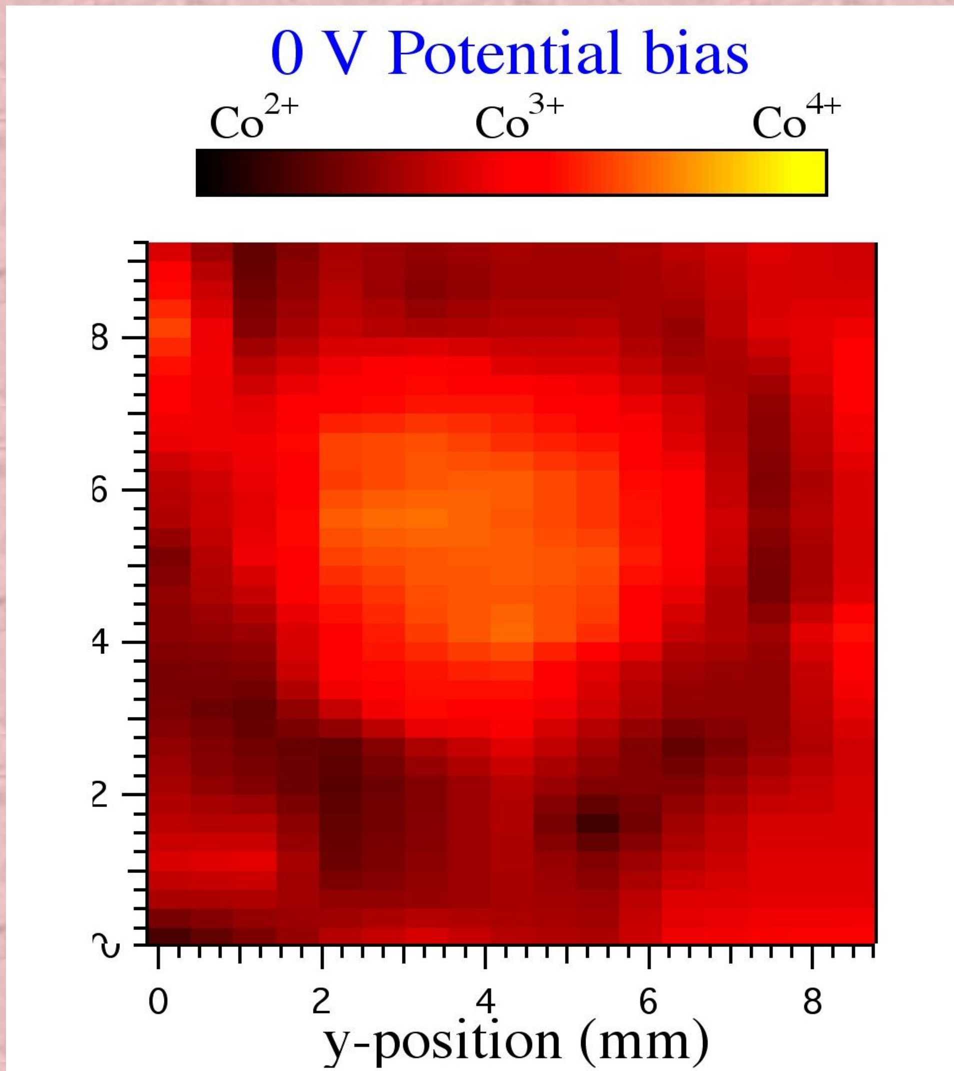
LSCF oxygen deficient
(PLD vacuum cool down)

Reproduced with
vacuum anneal



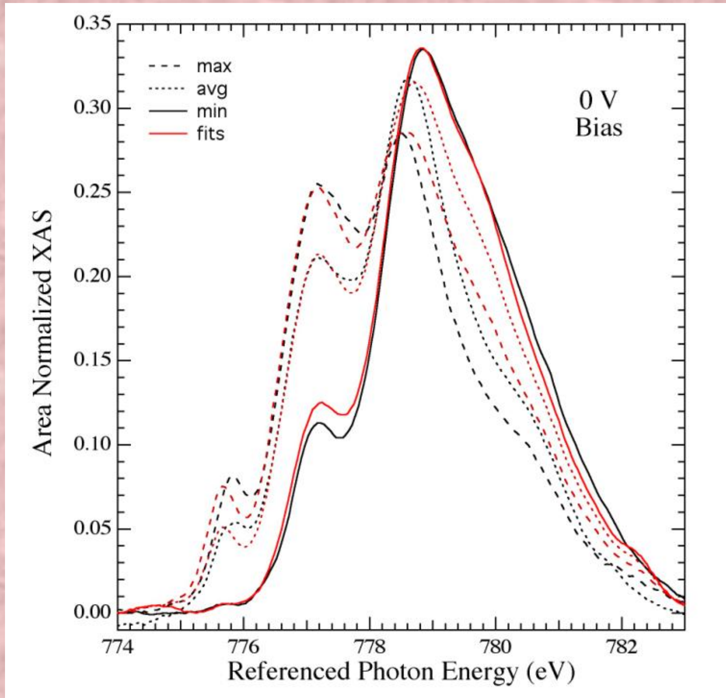
Co valence map

Air anneal @ 850 °C

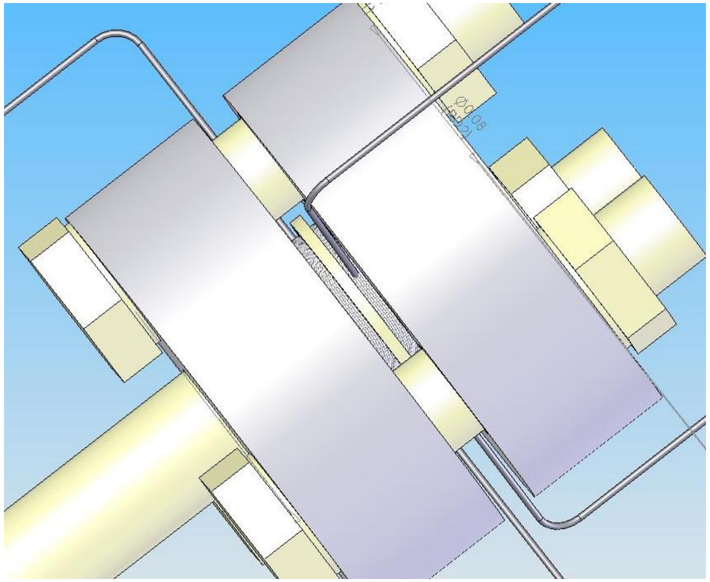


Co present as Co^{3+}
(40% variation)

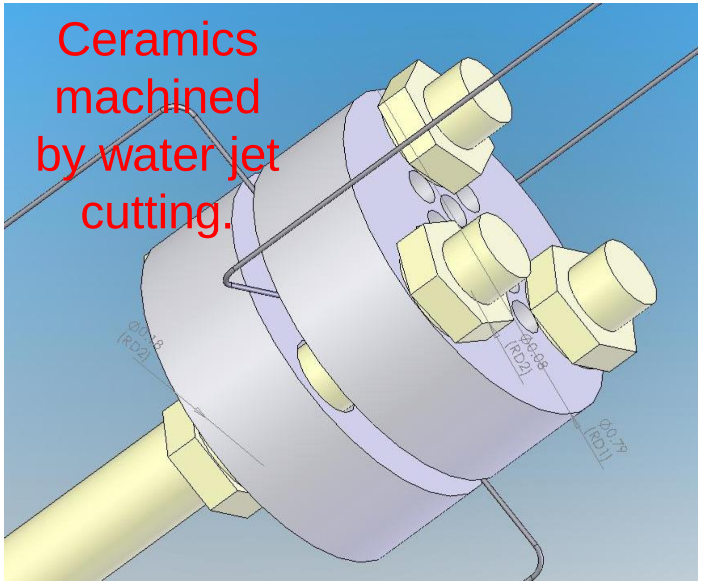
Circular pattern

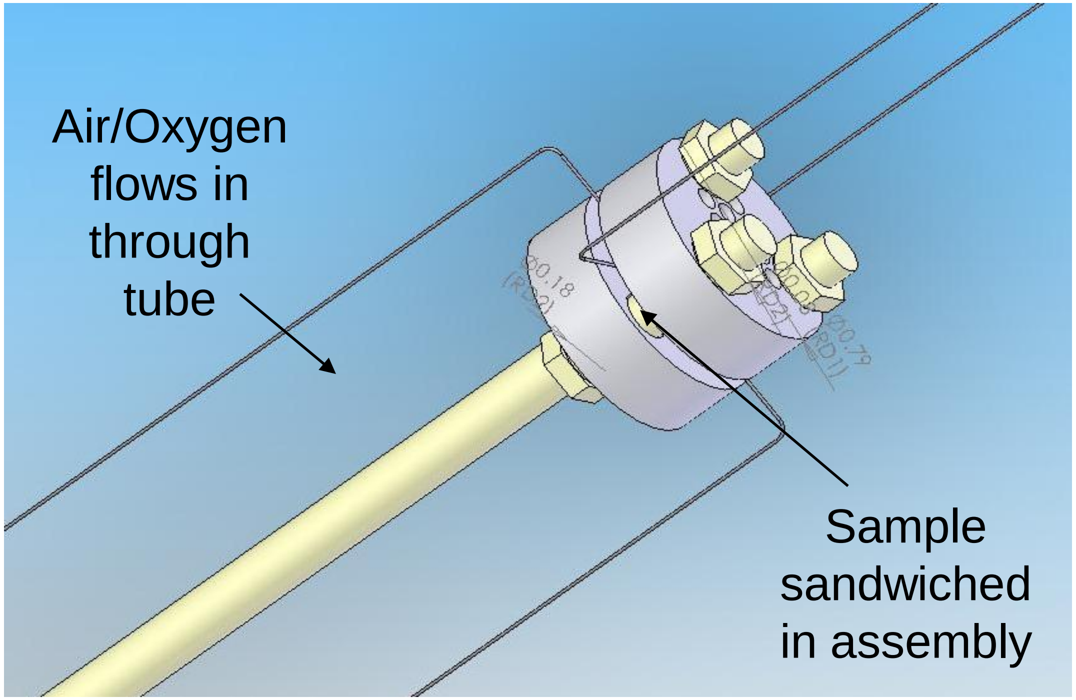


Electrical Potential Testing Rig



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



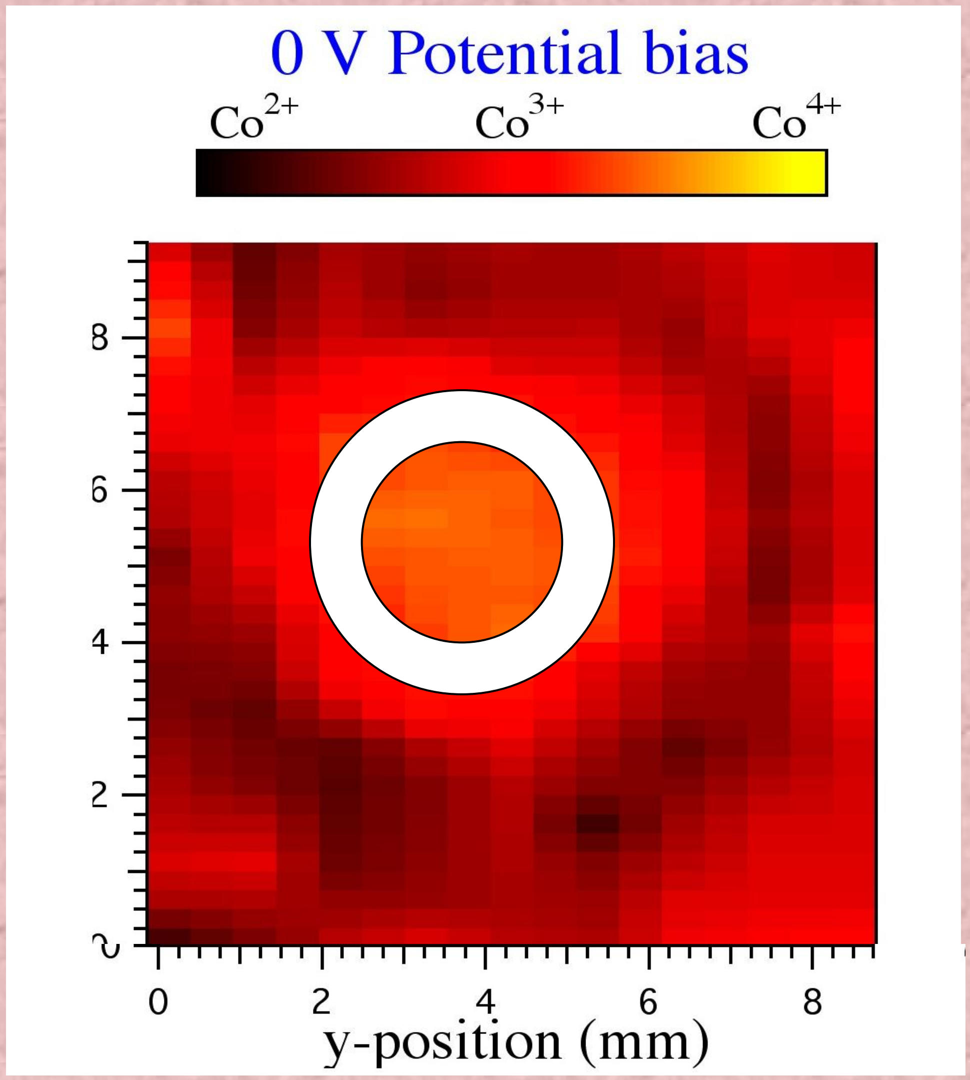


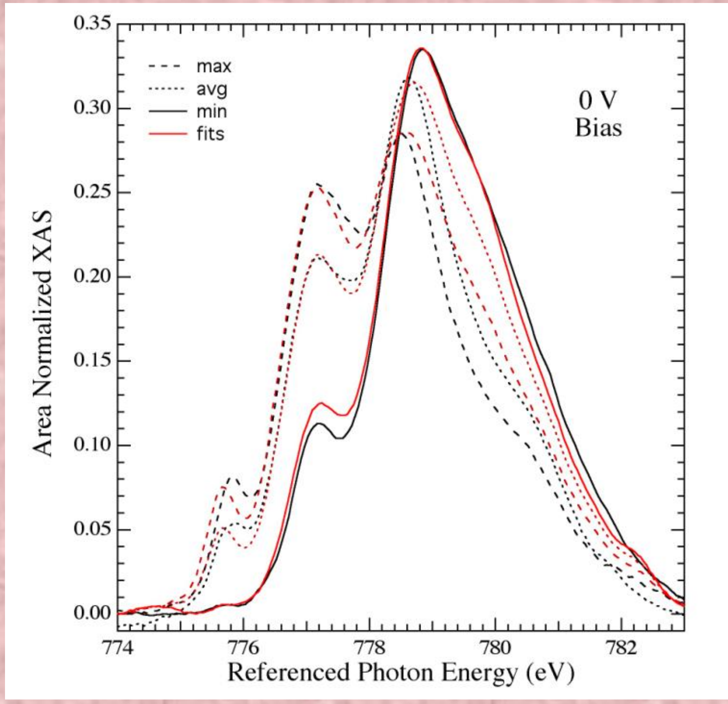
Co valence map

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

Circular pattern

Matches air inlet



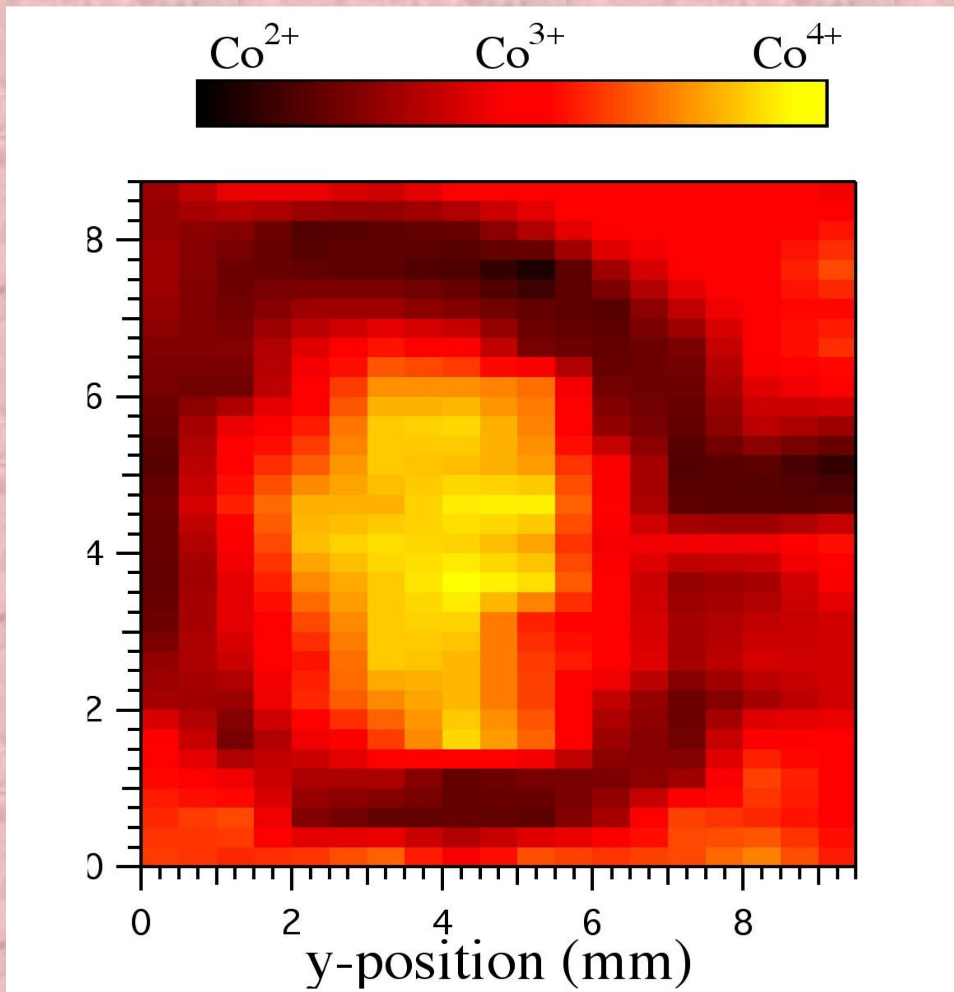


Co valence map

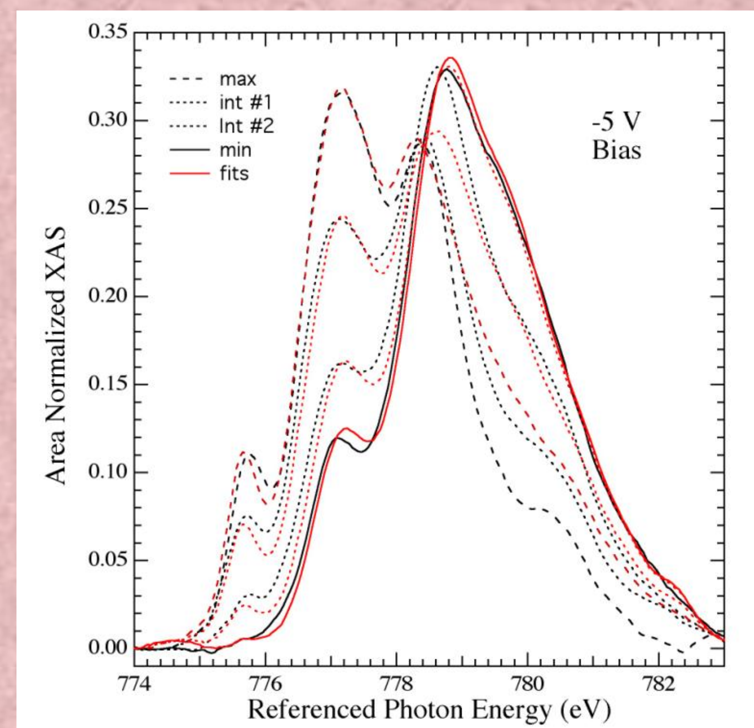
Co present as Co^{3+} and Co^{4+} (130% variation)

Circular pattern

Matches air inlet



-500 mV Potential bias

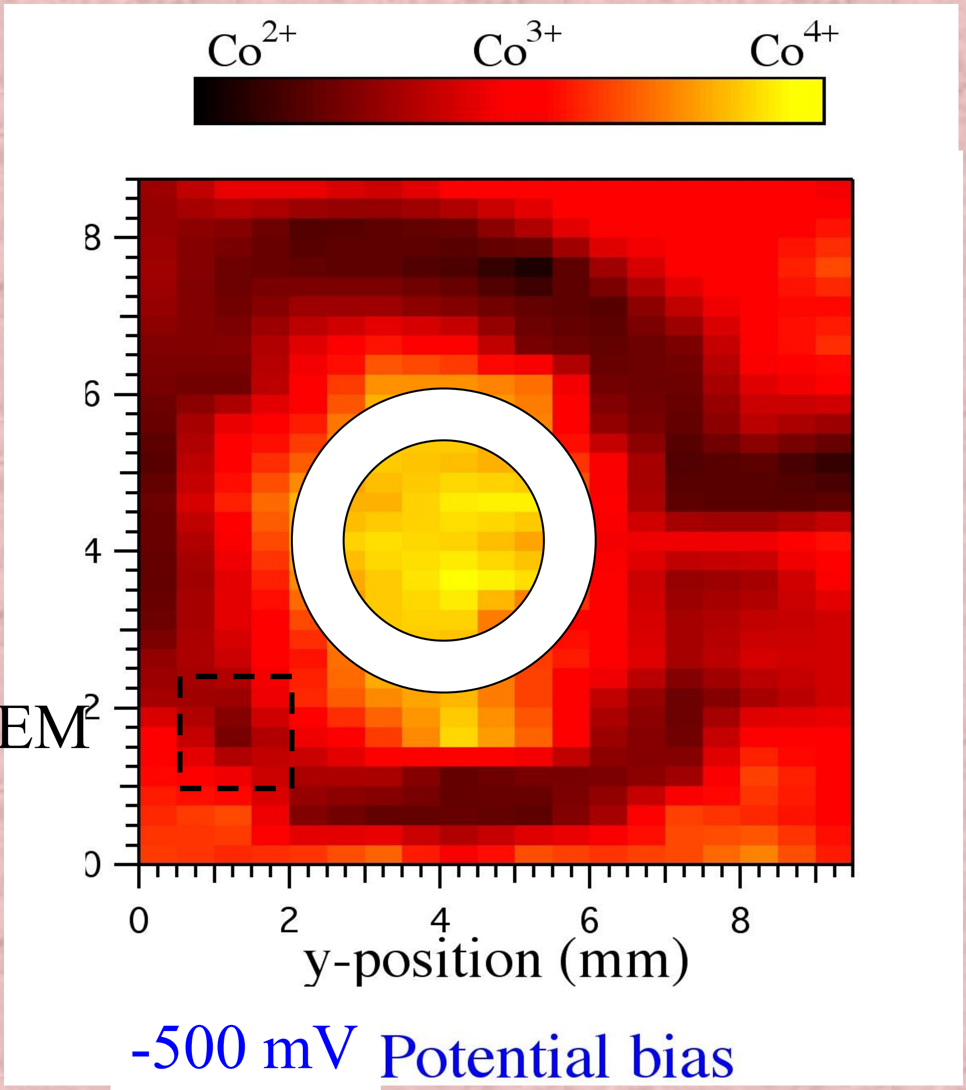


Co valence map

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

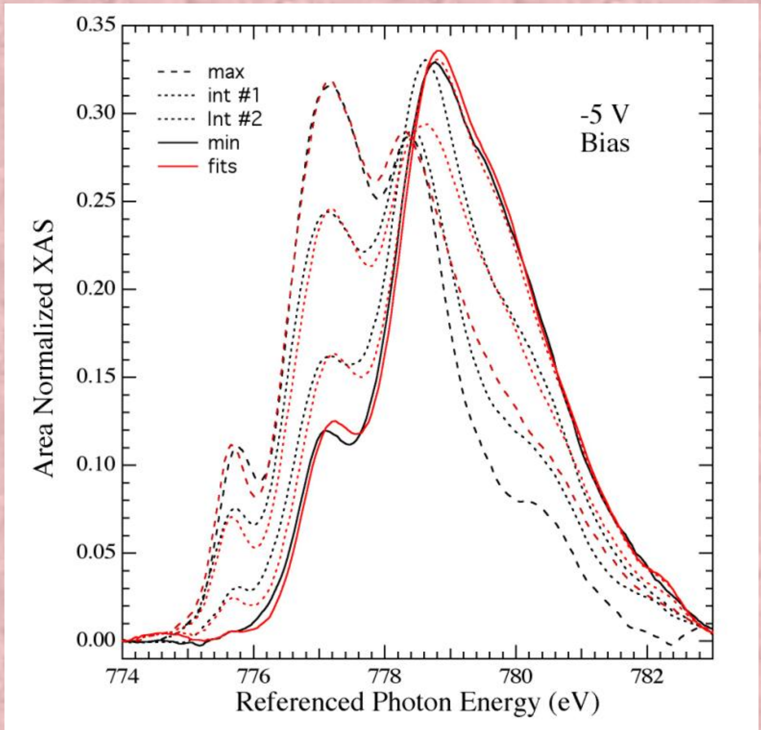
Circular pattern

Matches air inlet

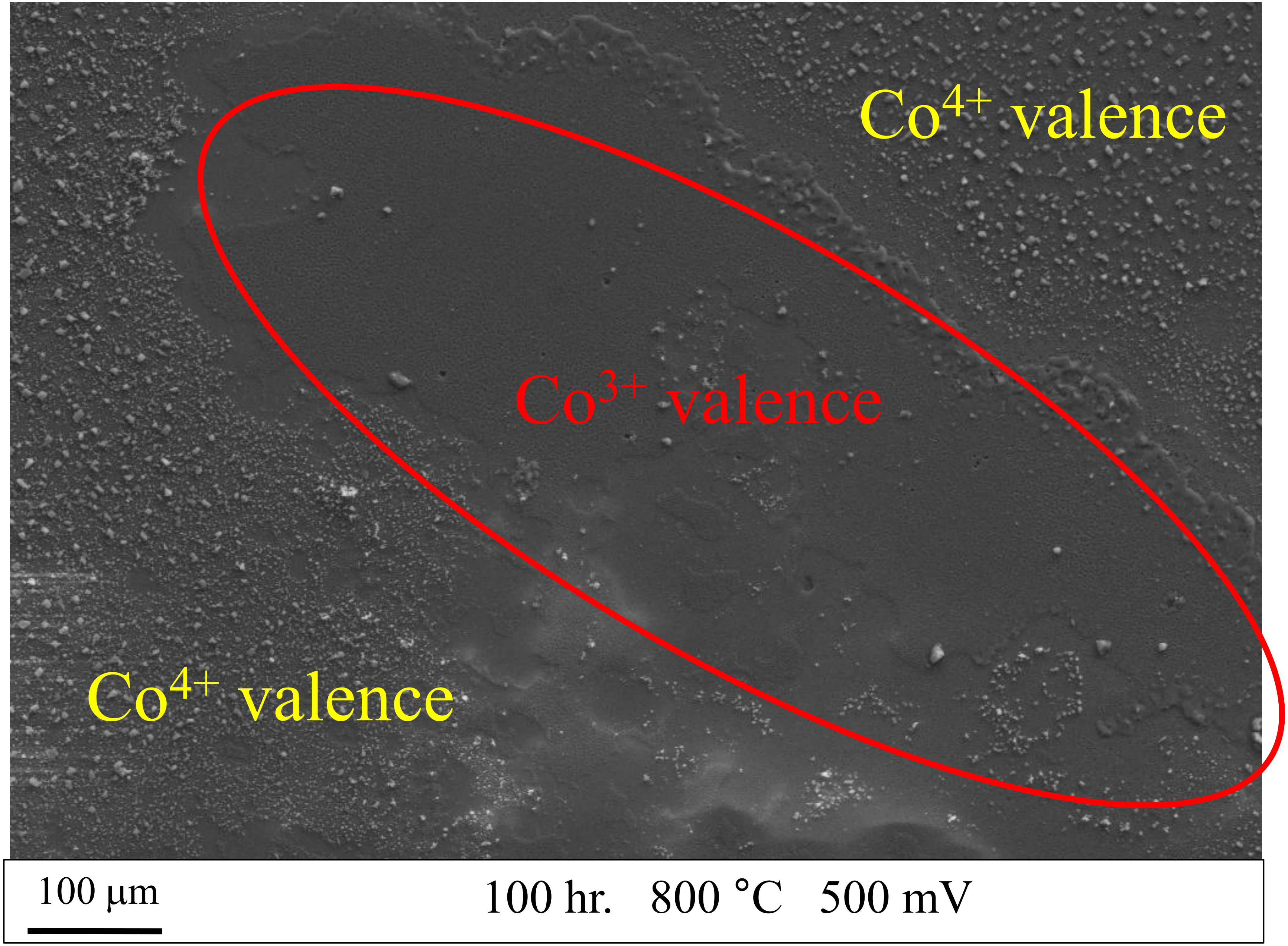


SEM

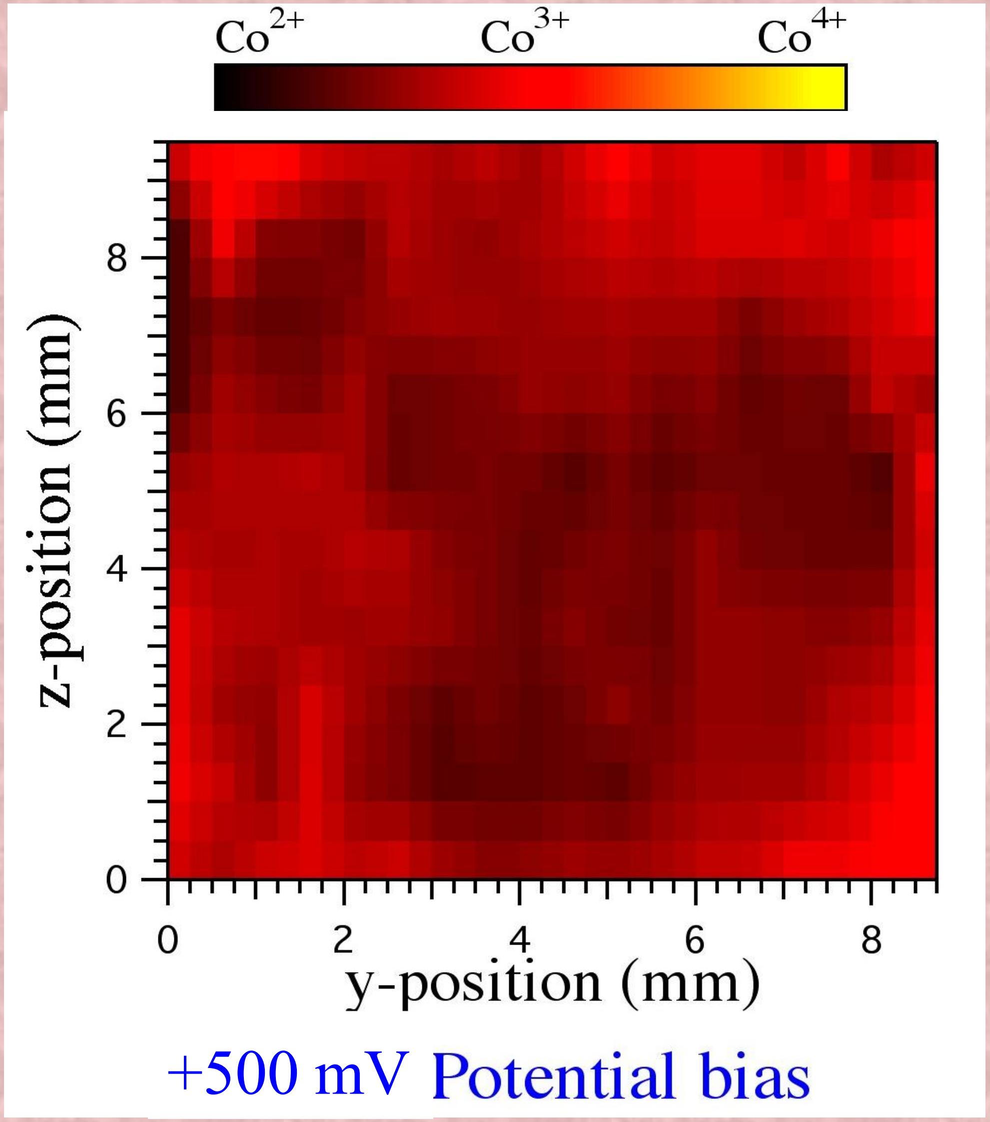
-500 mV Potential bias



SrO formation correlated to Co^{4+}

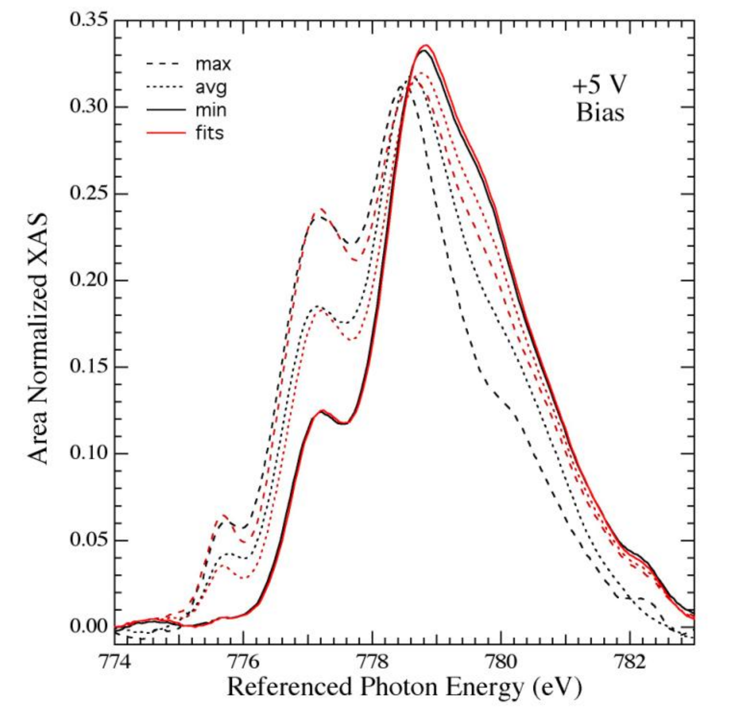


Co valence map

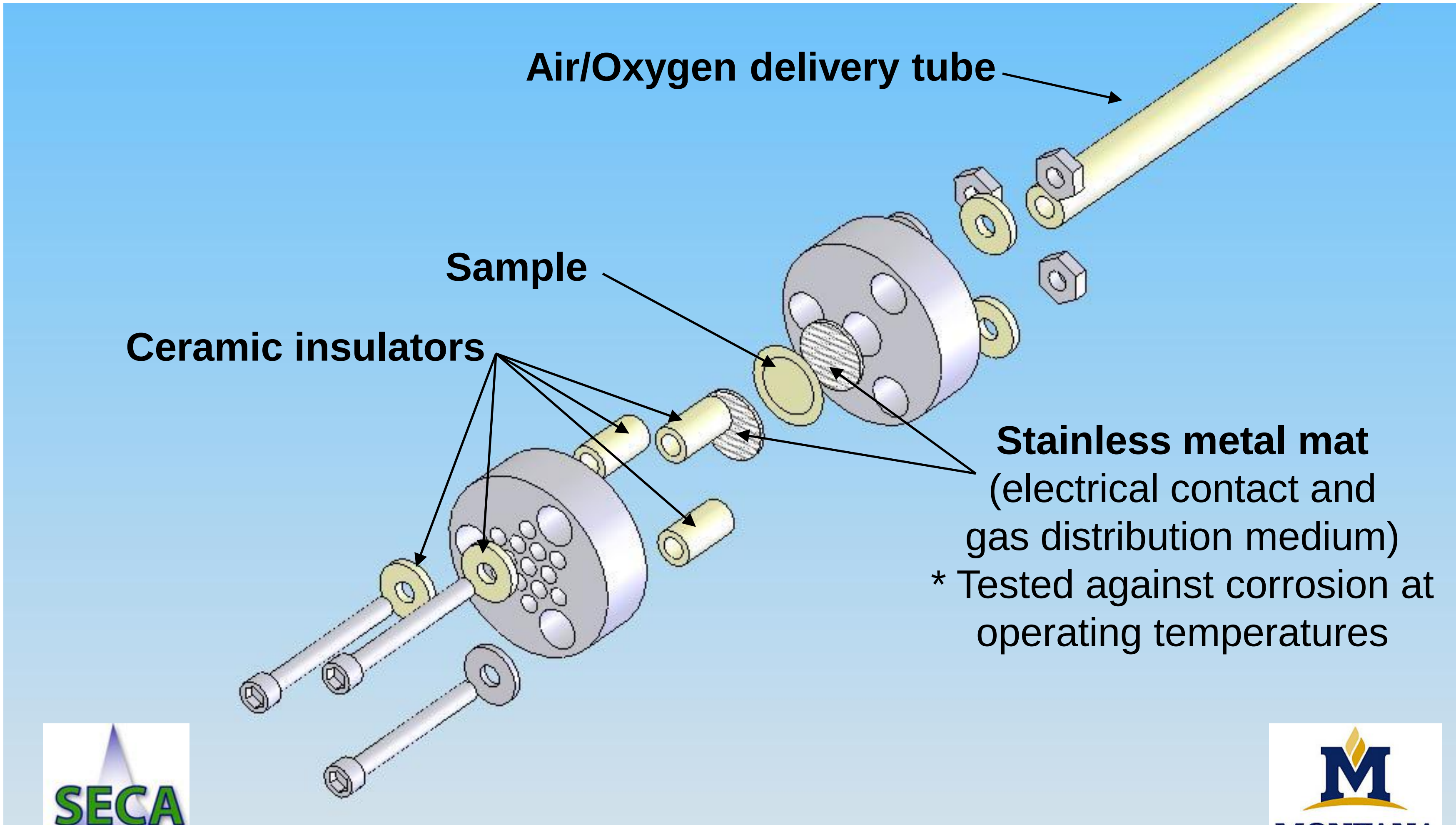


Co present as Co^{2+} and Co^{3+}
(30% variation)

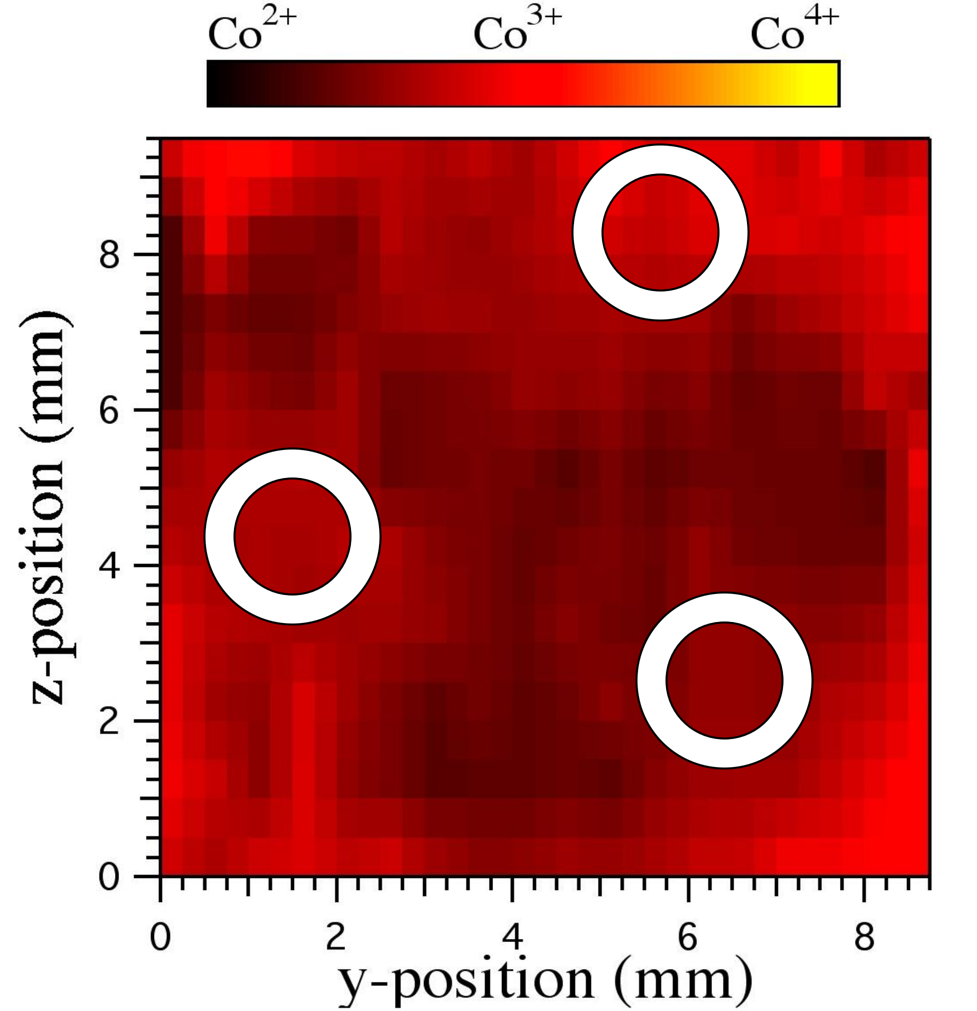
LSCF oxygen deficient
(PLD vacuum cool down)



New Testing Rig Design



Co valence map

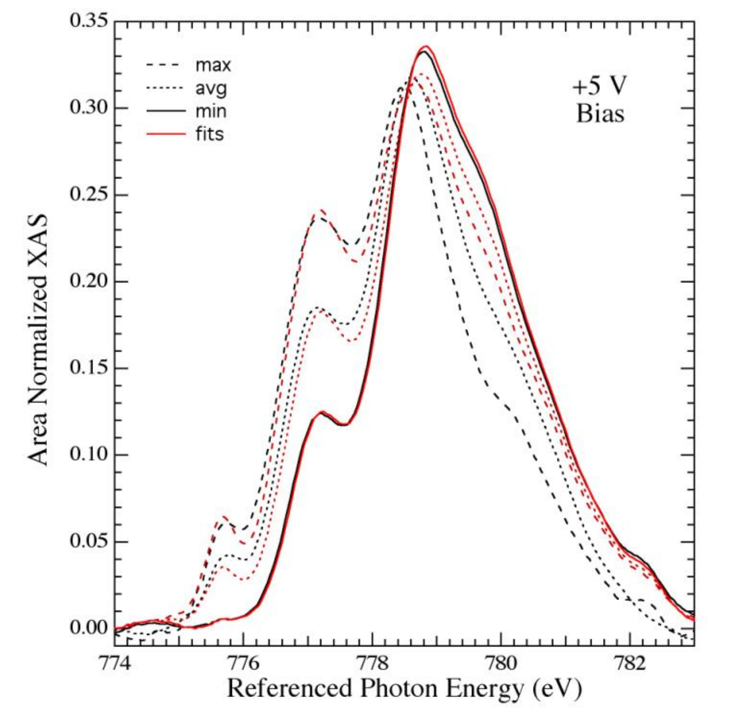


+500 mV Potential bias

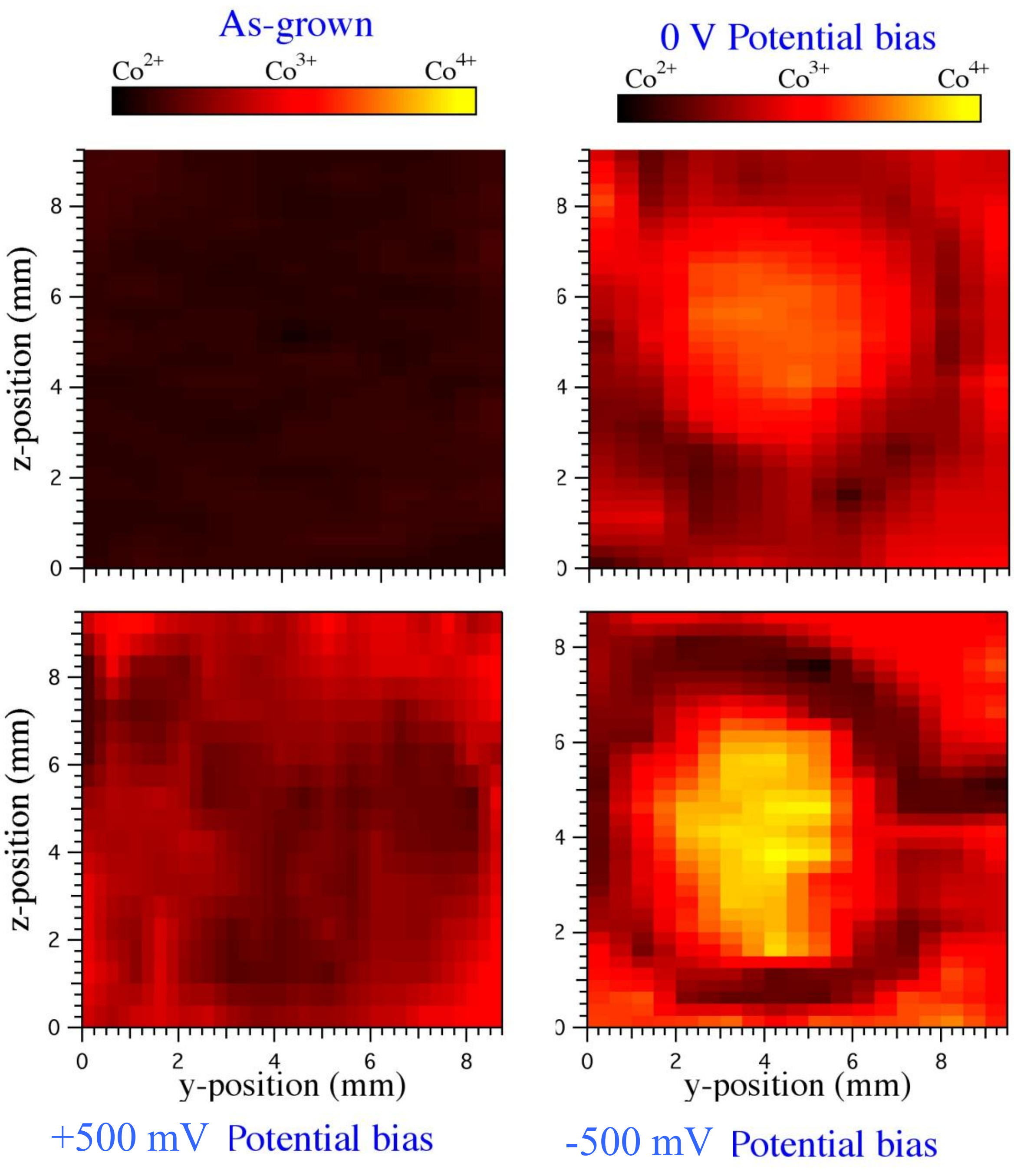
Co present as Co^{3+}
(30% variation)

LSCF oxygen deficient
(PLD vacuum cool down)

Matches air inlet



Co Valence variation LSCF/GDC/YSZ



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)

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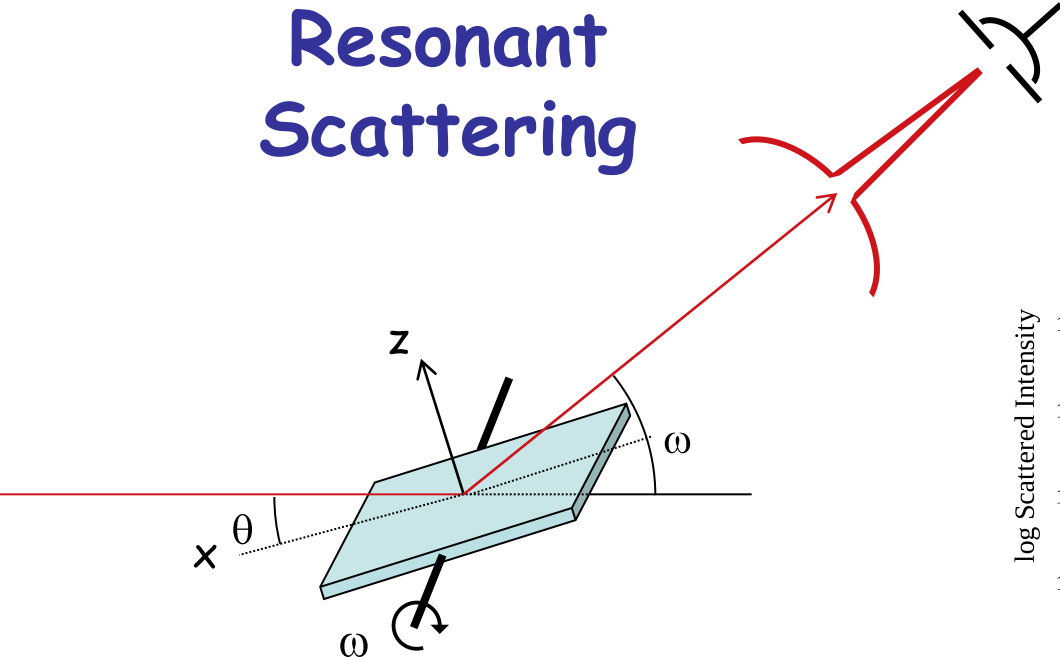
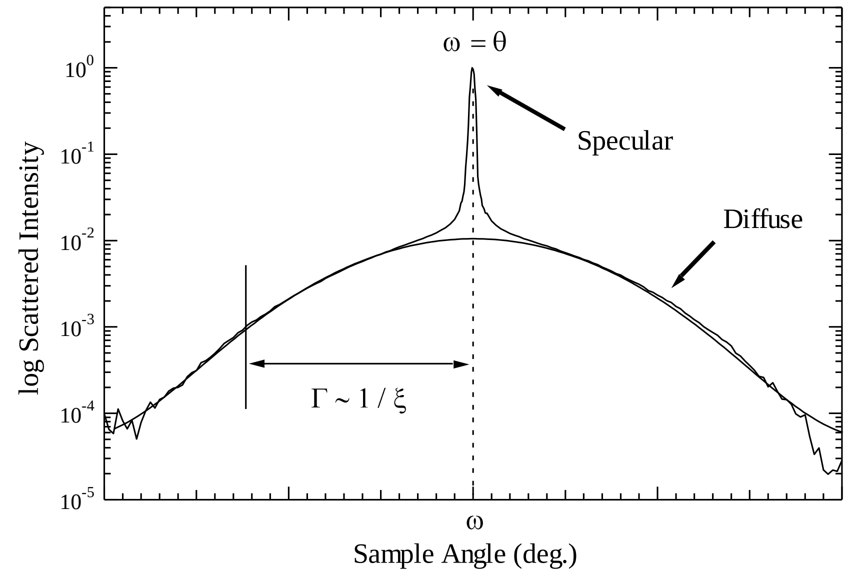
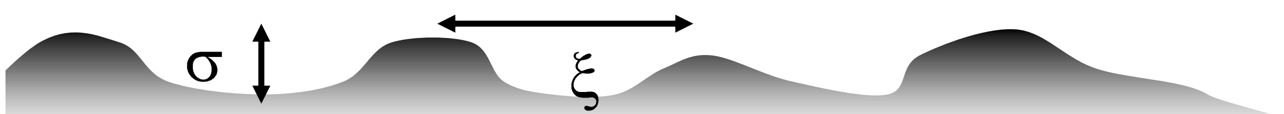
Diffuse X-ray Resonant Scattering





Specular vs. Diffuse Int. ➡ Perp. Roughness (σ)

Width of Diffuse ➡ In-plane Corr. Length (ξ)



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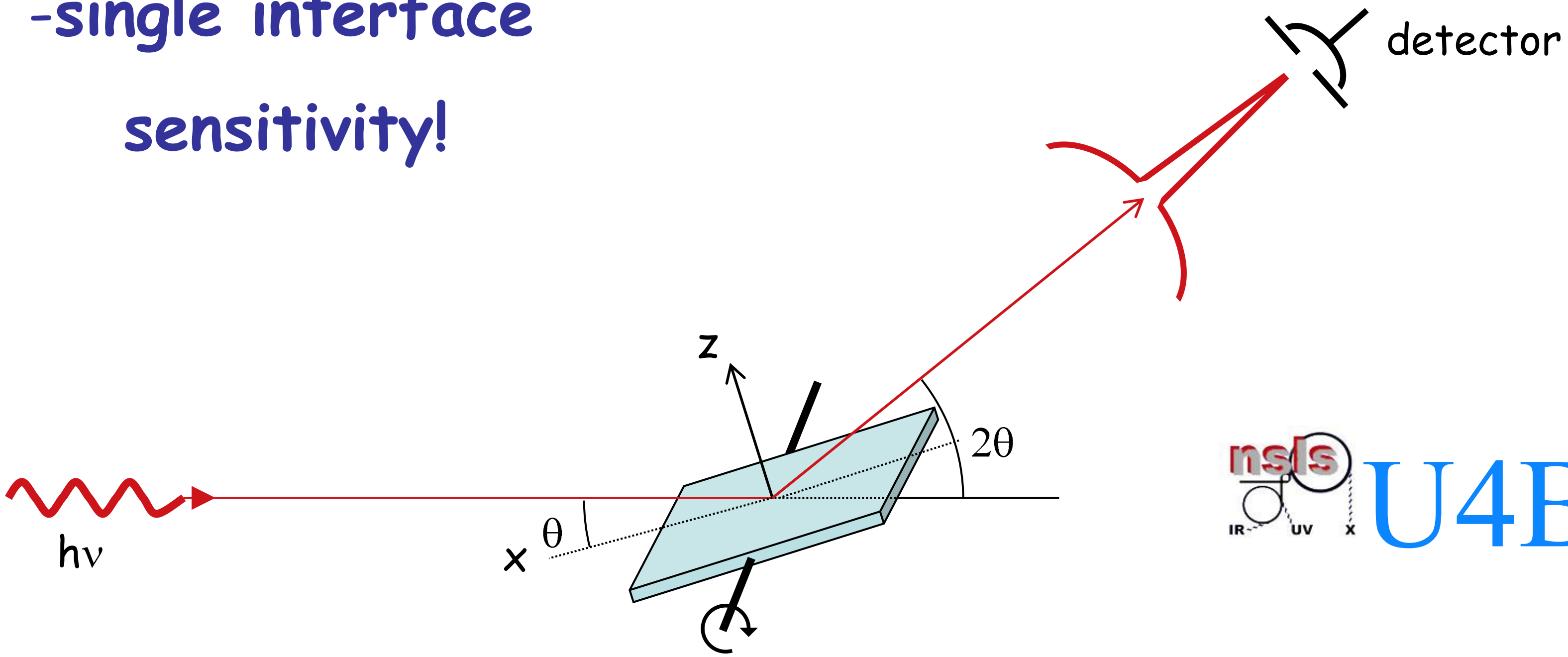
Soft x-rays scattering

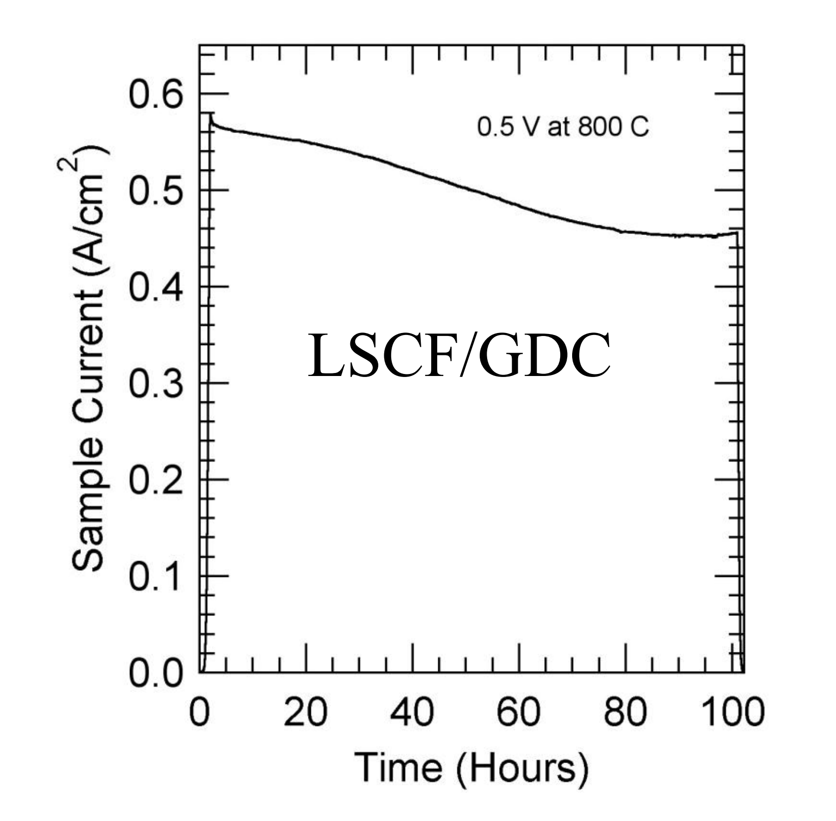
-single interface sensitivity!

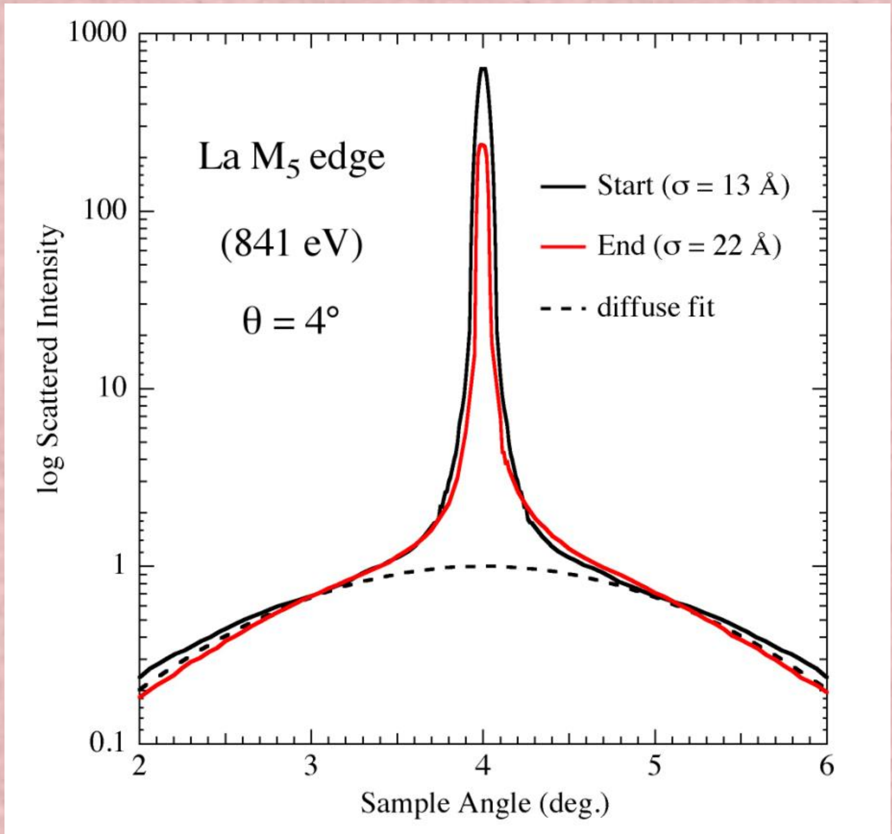


U4B

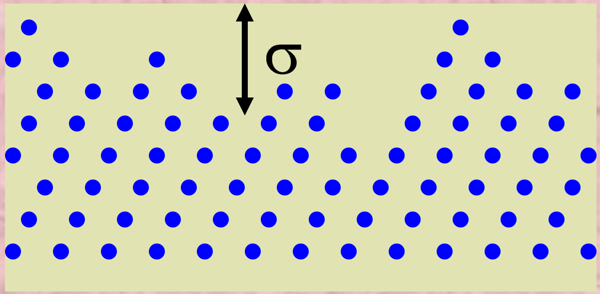
- At grazing incidence -> 15 Å penetration depth
- specular scans -> structure along z, “bulk” properties
- rocking scans (diffuse scattering) -> lateral structure
  structural (chemical) roughness
  in-plane roughness
  perpendicular roughness

Oxygen ion flow - cation diffusion



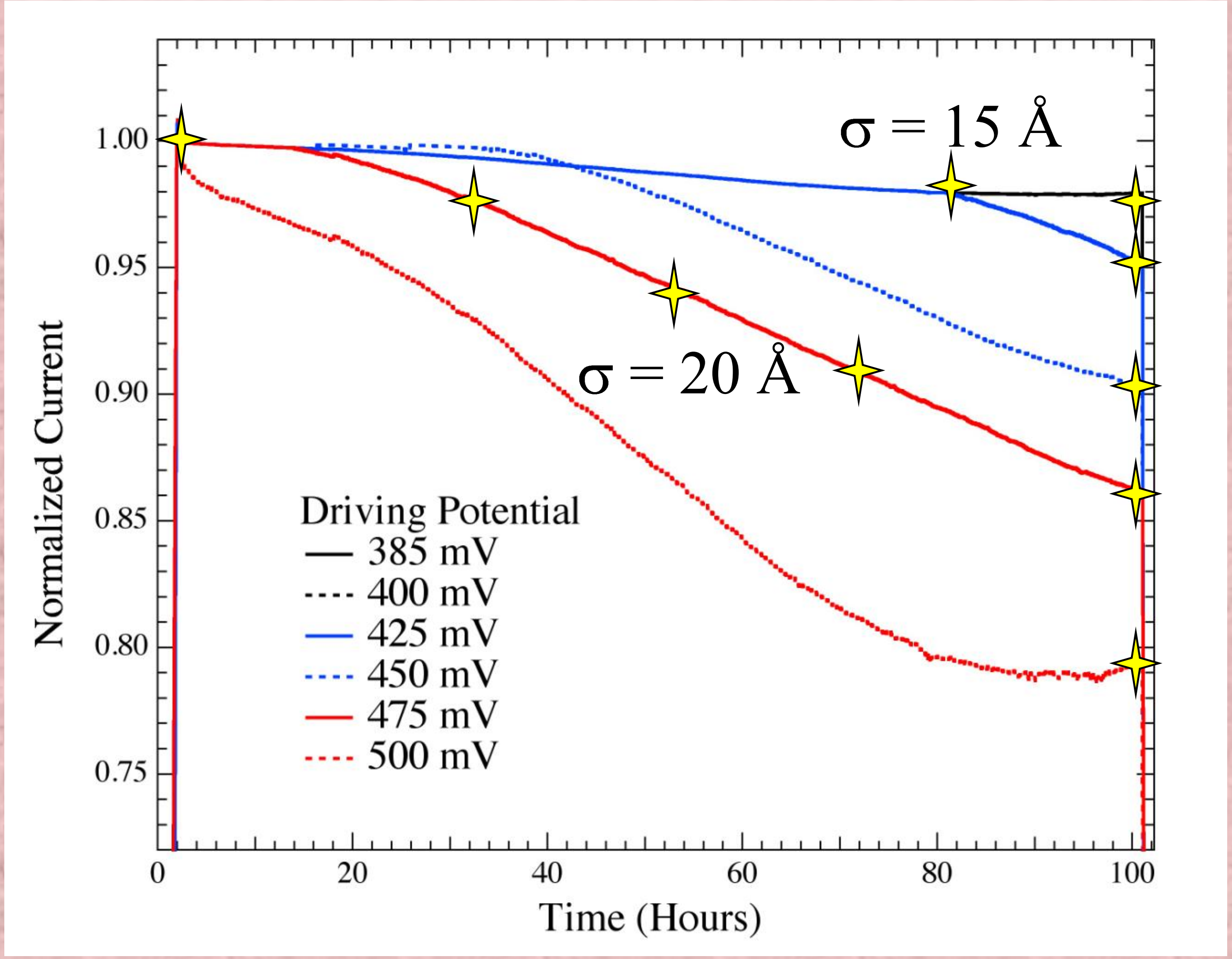


Oxygen ion flow redistributes La at interface! (Sr removal)



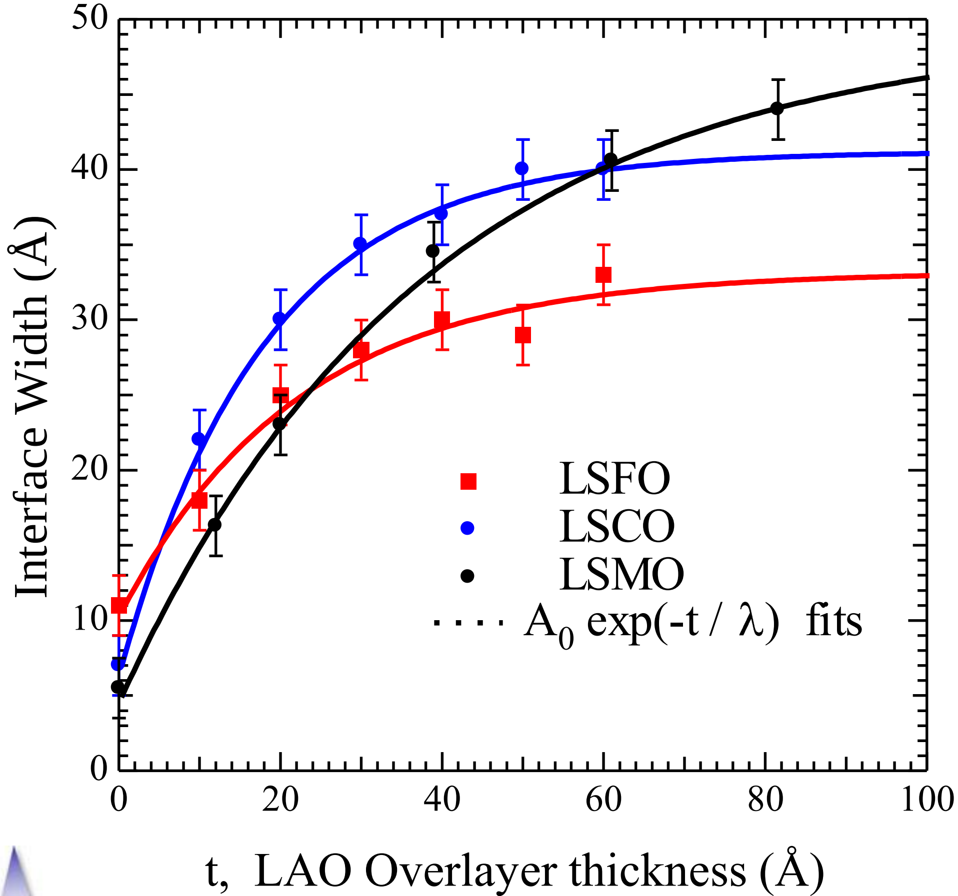
Ion flow modified interface width

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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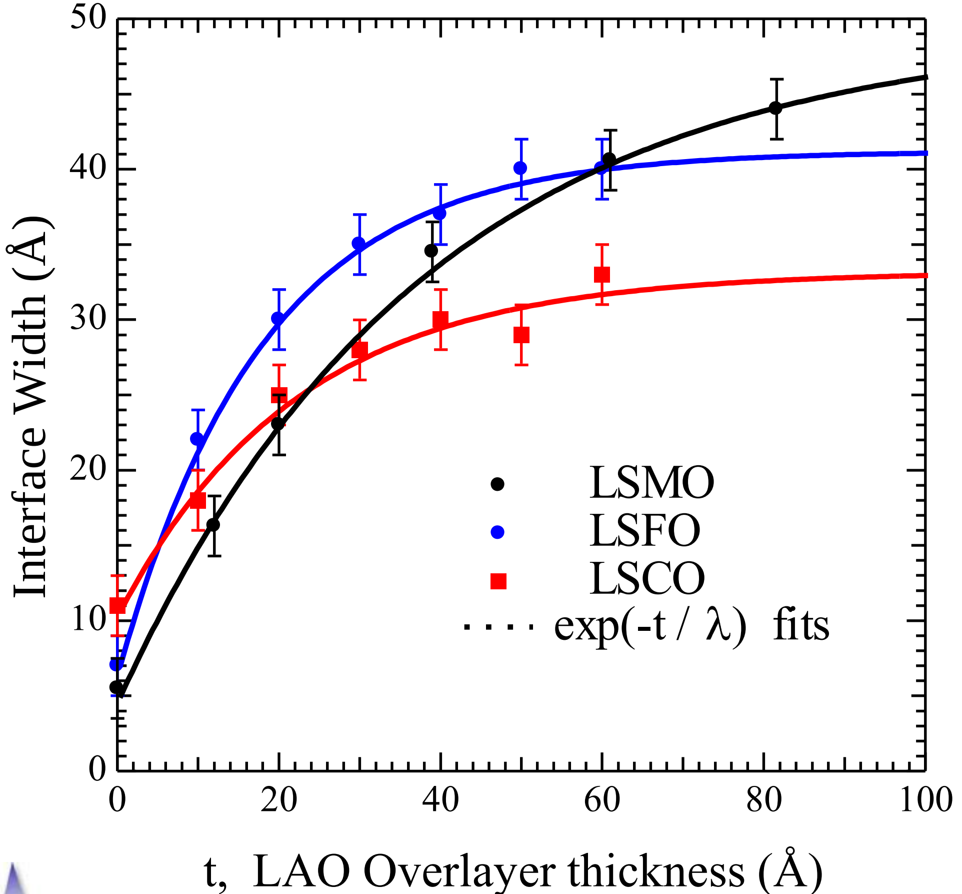
La Distribution in $La_{2/3}Sr_{1/3}TMO_3$ from XRS diffuse scans



λ from fits

LSCO - 17.9 Å

LSFO - 22.2 Å

LSMO - 38.5 Å

Increasing Stiffness?

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)

Acknowledgements

Post-doctoral Fellow

Alex Lussier

Graduate Students

Martin Finsterbusch

Vanessa Pool

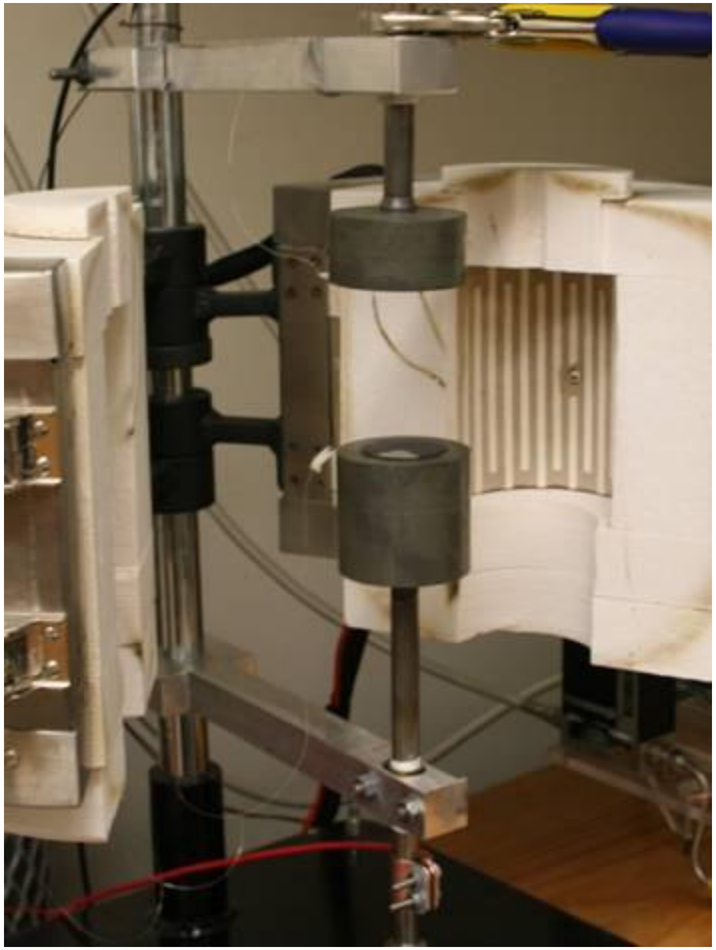
Adam McClure

Beamline 6.3.1

Advanced Light Source (ALS)

Dr. Elke Arenholz (ALS scientist)

Testing rig(s)



- Seal-less design
- Contact paste-less tests