Synchrotron Studies of Cathode Materials

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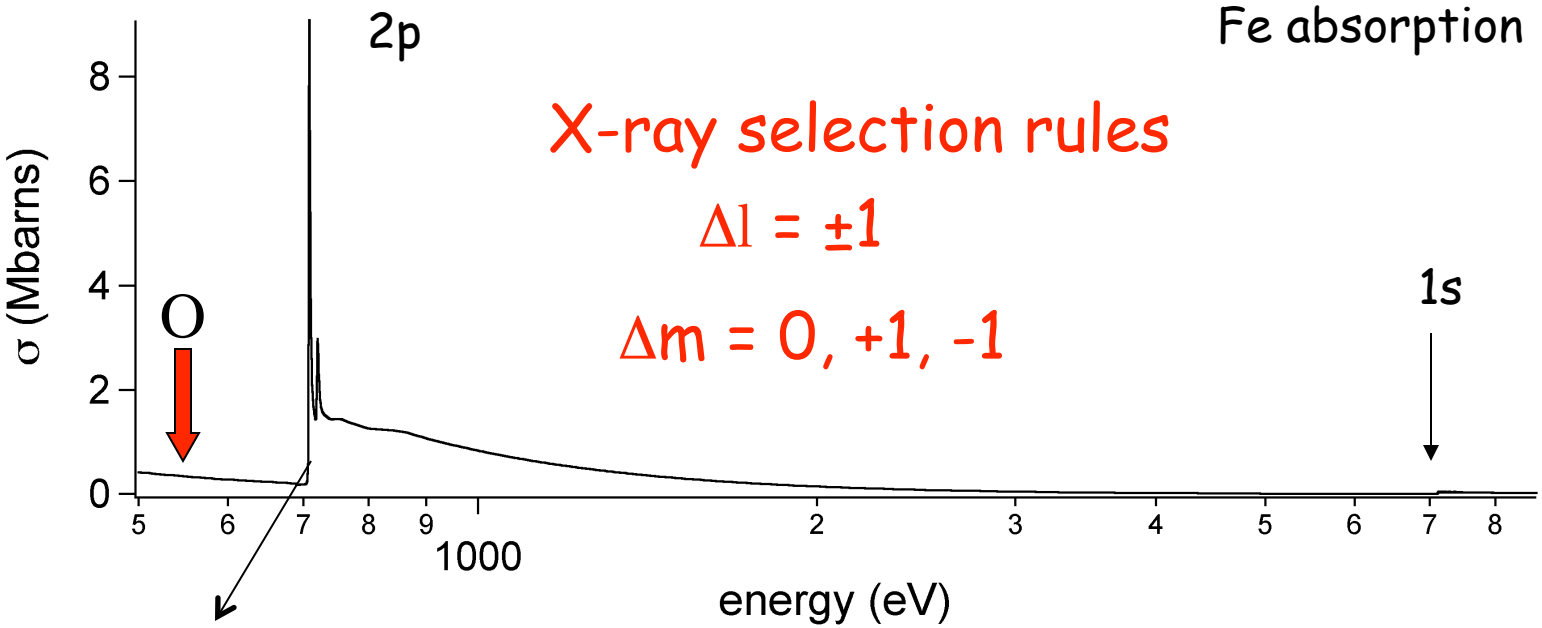
Material Issues

1. Electrode (YSZ/LSTMO) alloying
2. Modifying TM valence with ion flow
3. A-site/B-site occupancy
4. Quantifying O vacancy concentration

Soft x-rays are ideal for buried interfaces!

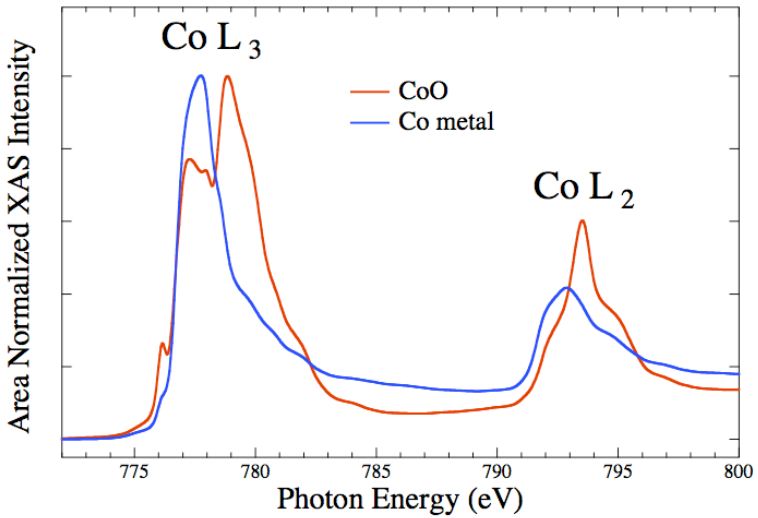


X-ray selection rules

$\Delta l = \pm 1$

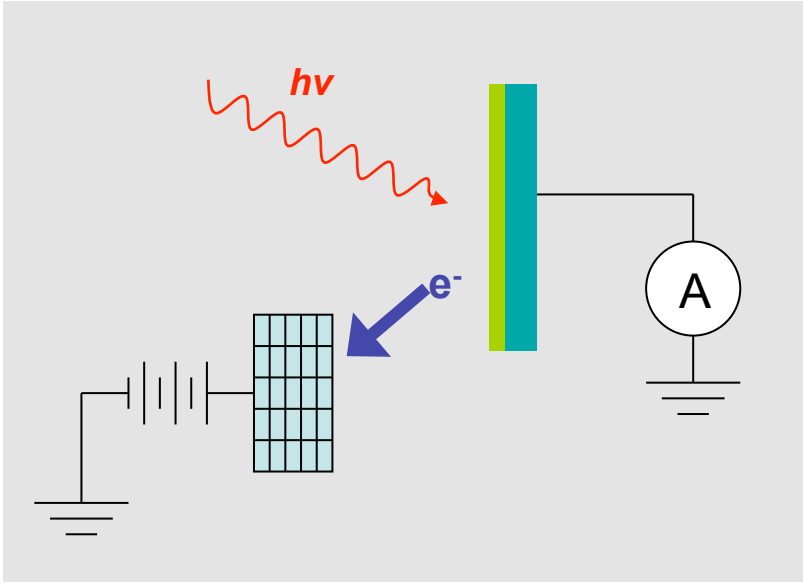
$\Delta m = 0, +1, -1$

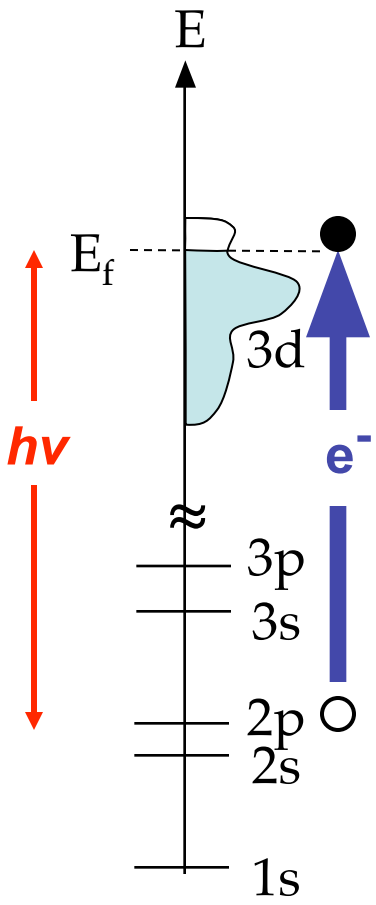
Co L edge XAS

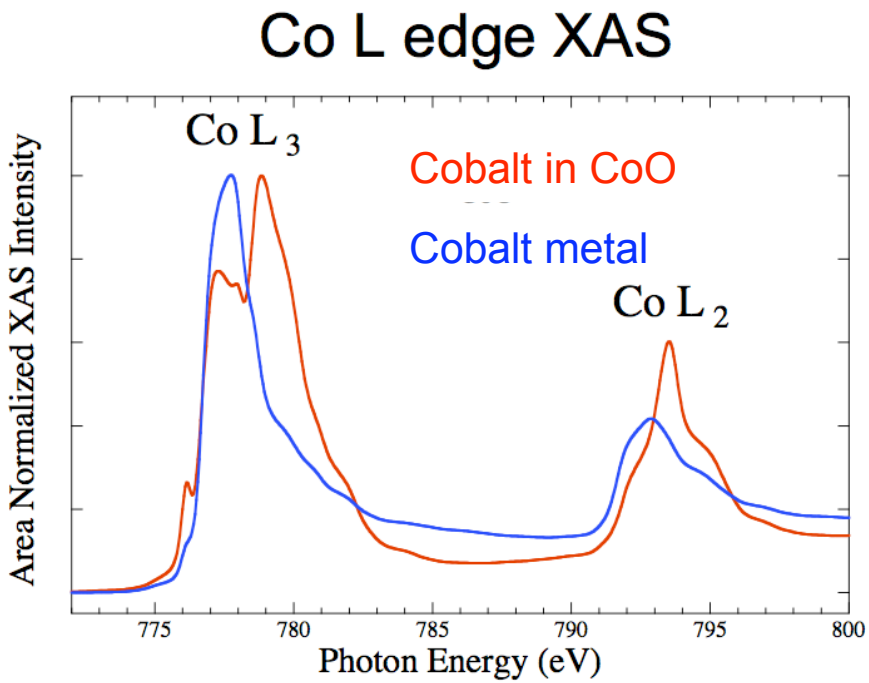


- strong resonant interaction
- elemental selectivity
- valence sensitivity
- probe different 3d states

X-ray Absorption Spectroscopy (XAS)



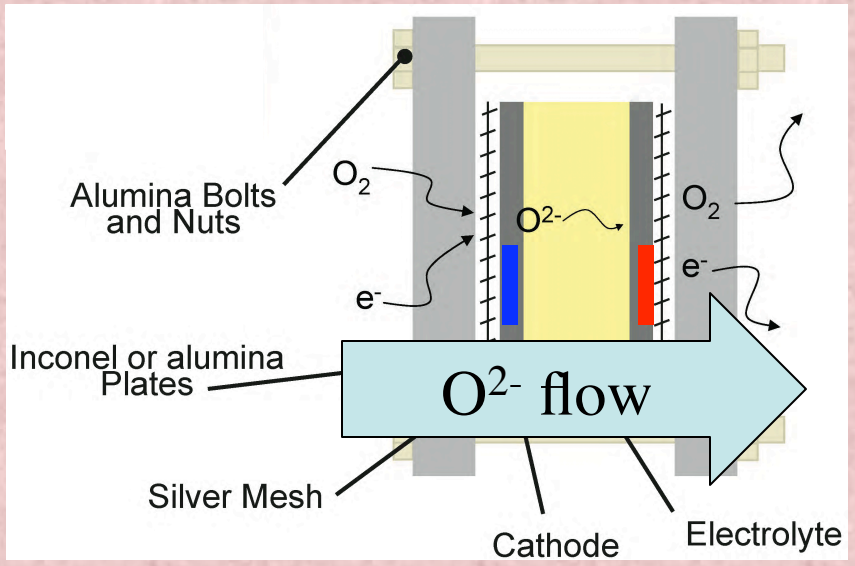


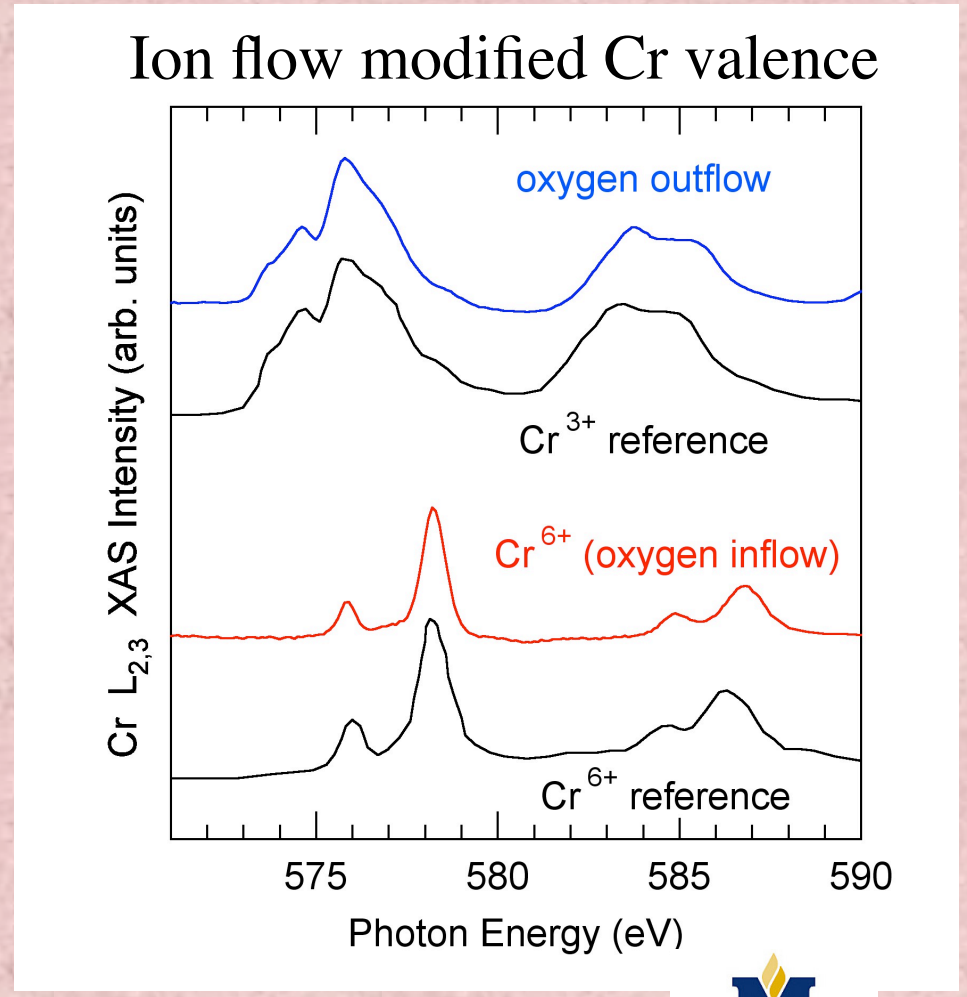


MOTIVATION - Oxygen ion flow

Oxygen ion flow modifies Cr valence!

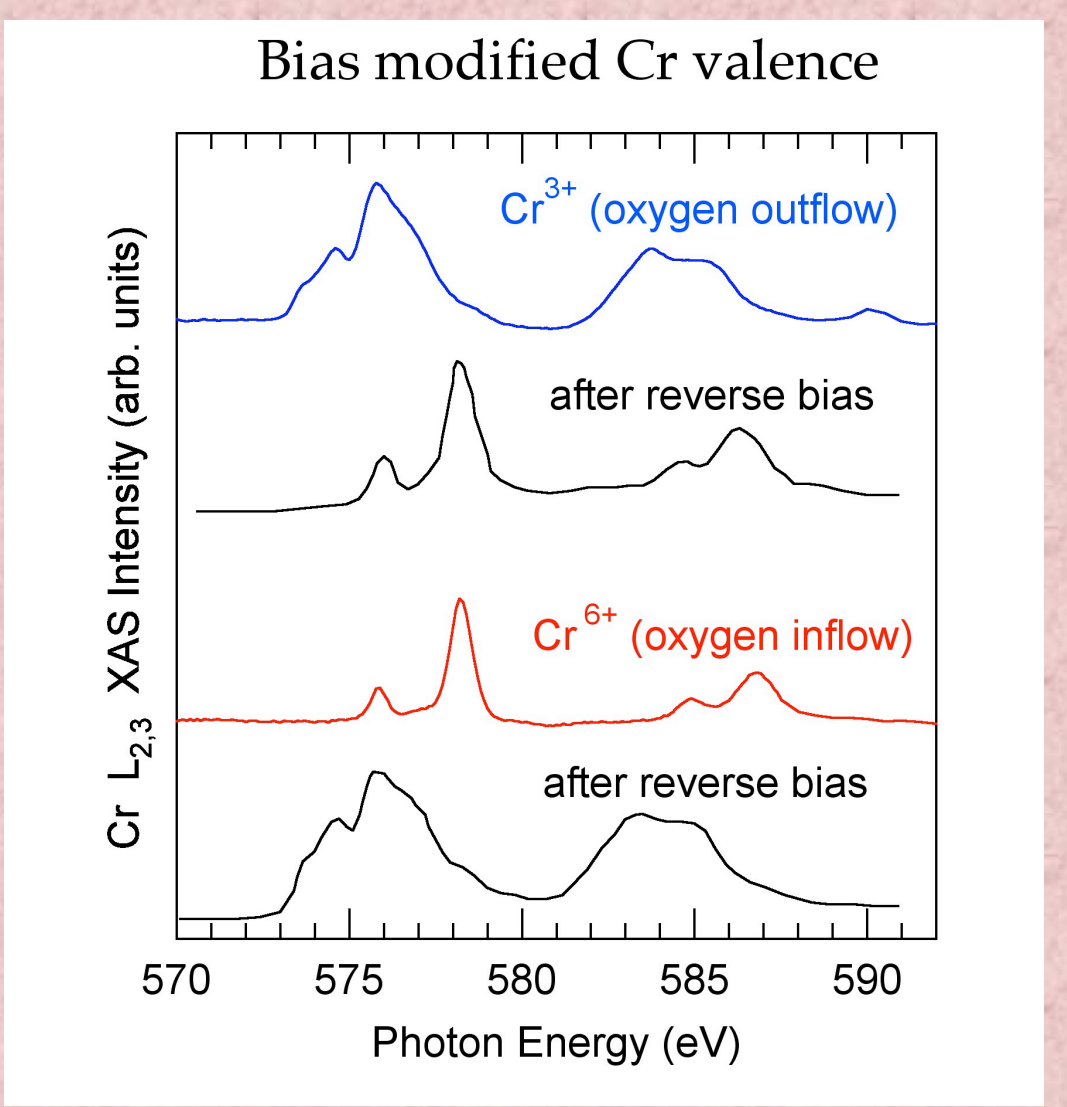
Bias driven symmetric cell (2 half cells)



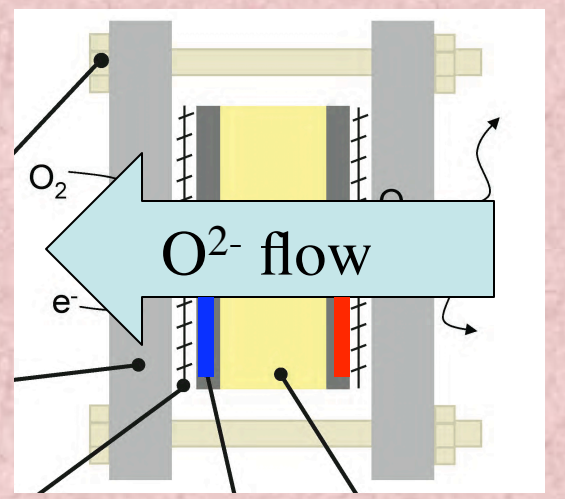


REF: Liu et al., Interfacial and Processing Science Annual Report (1999).

Oxygen ion flow (and bias)

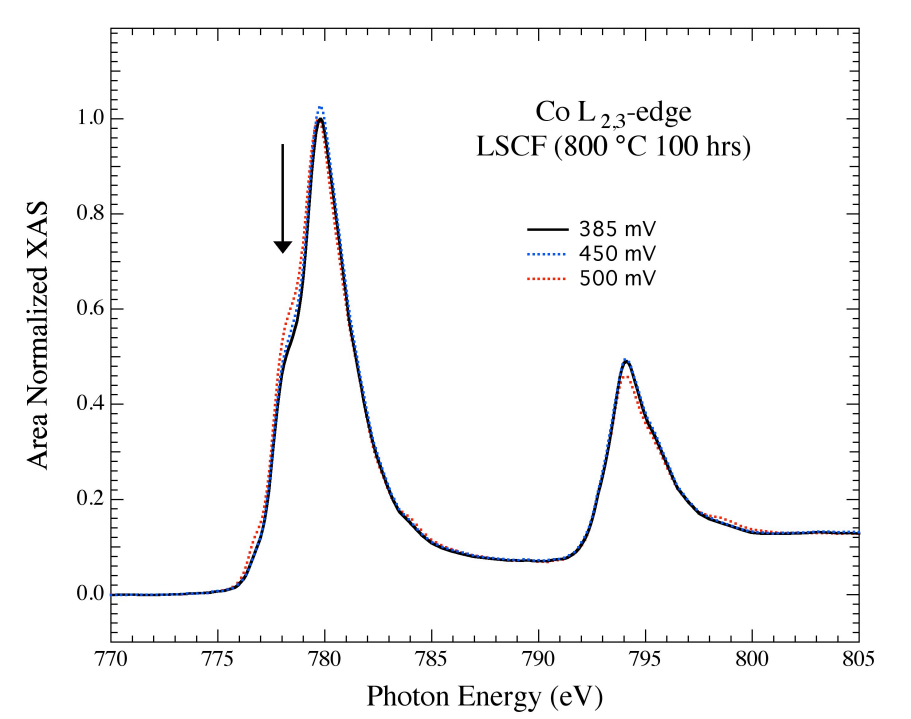


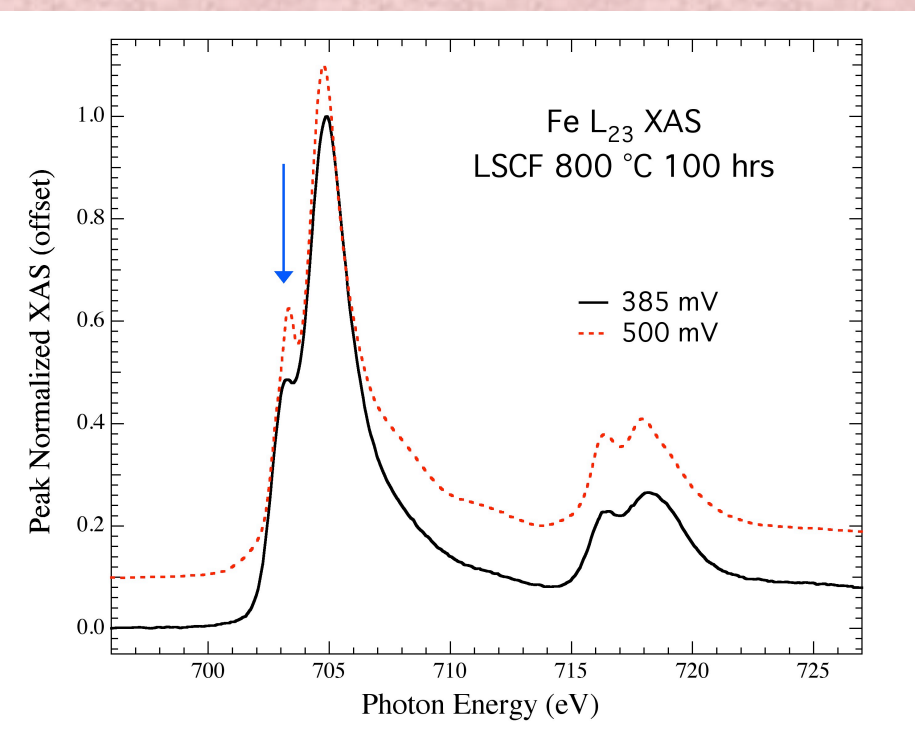
reverse bias



Oxygen ion flow reverses Cr valence!

Fe and Co electronic structure (in-flow, no change for out-flow)

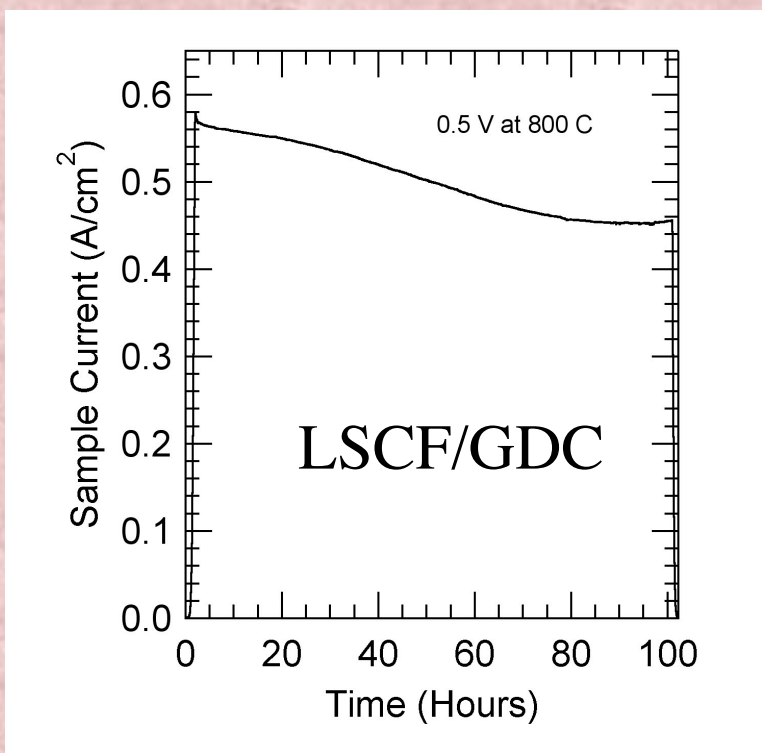




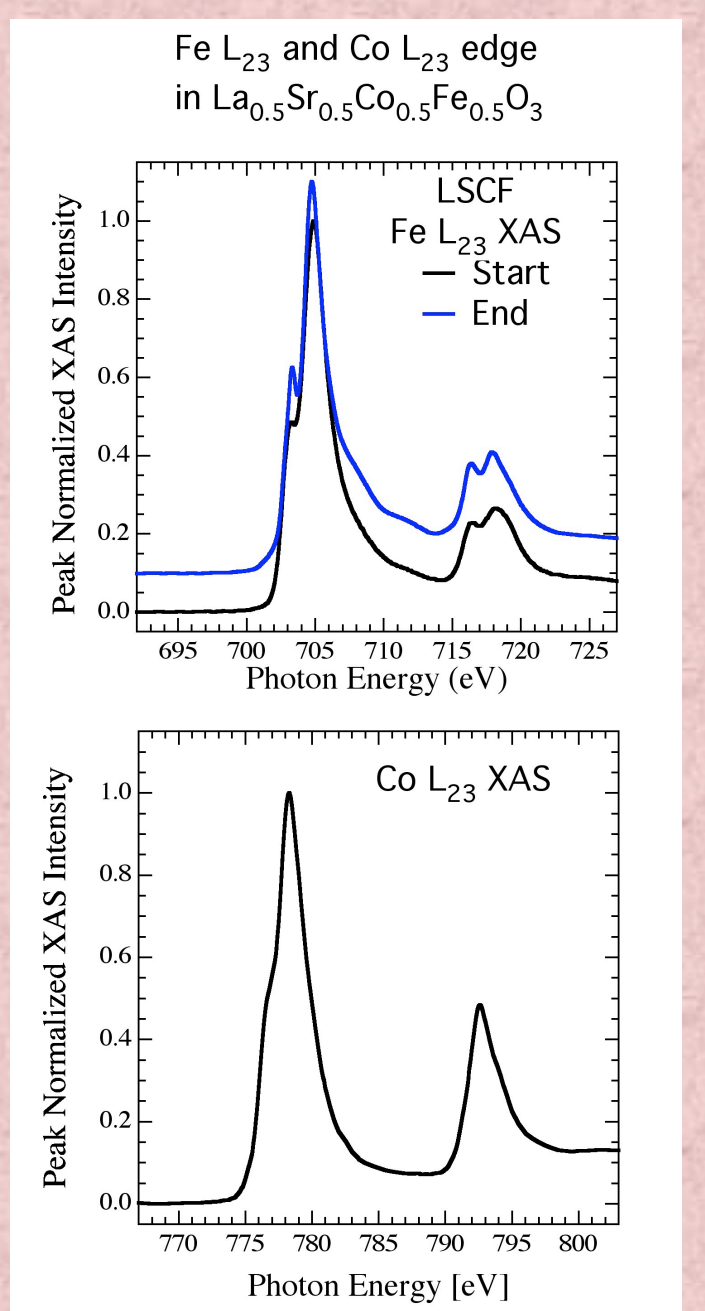
Increased oxygen co-ordination

Octahedral vs. tetrahedral O-Fe coordination

Oxygen ion flow



Oxygen ion flow modifies Fe valence!



A-site vs. B-site occupancy

Y-doped $SrTiO_3$ (stable to 12%)

(Sr^{2+}, Ti^{4+} and Y^{3+} - substitution site for Y?)

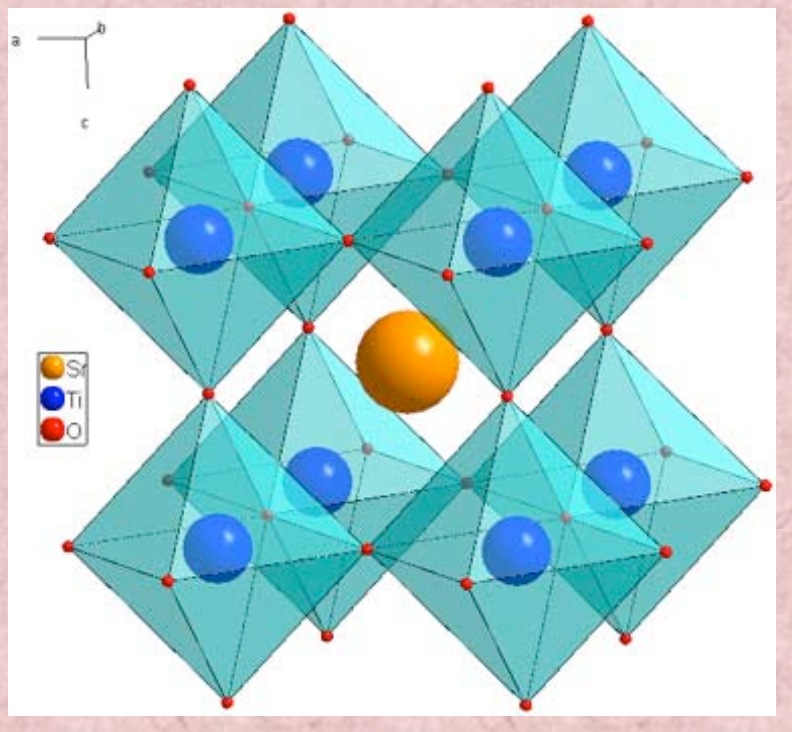
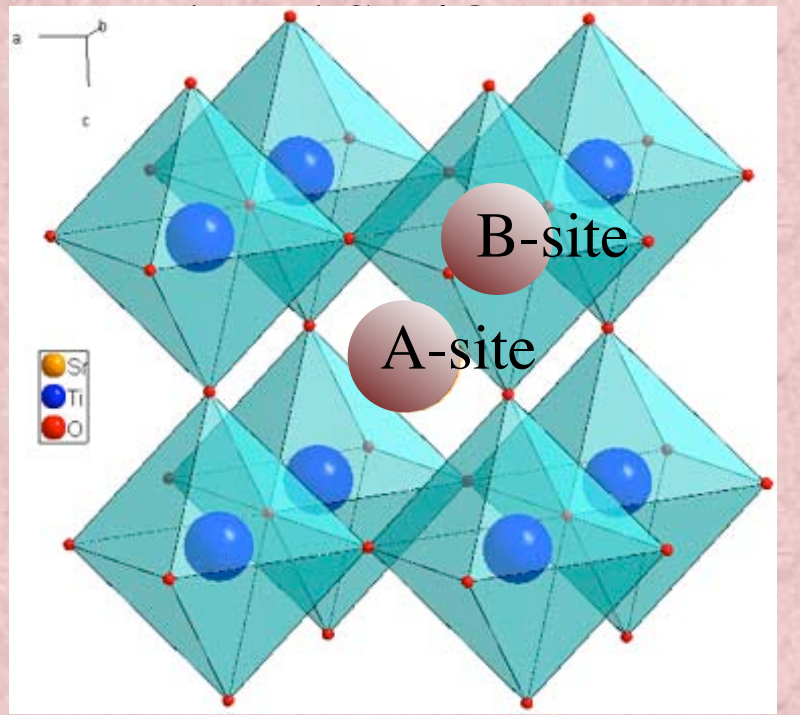


Image from webelements.com



Charge neutrality?

A-site vs. B-site occupancy

Y-doped $SrTiO_3$

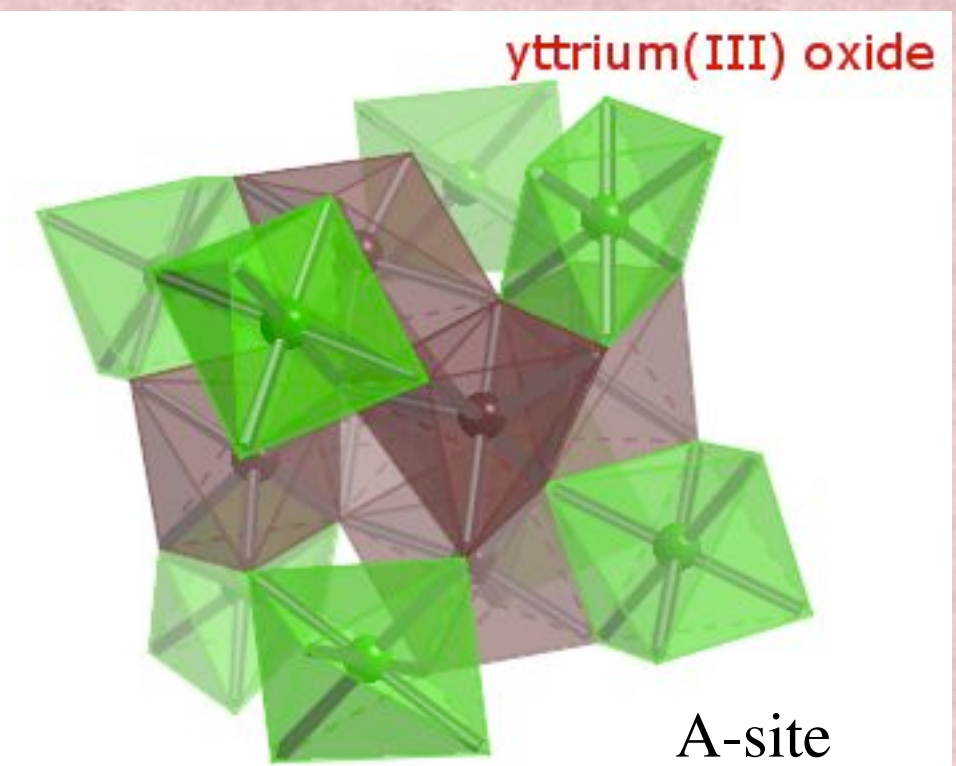
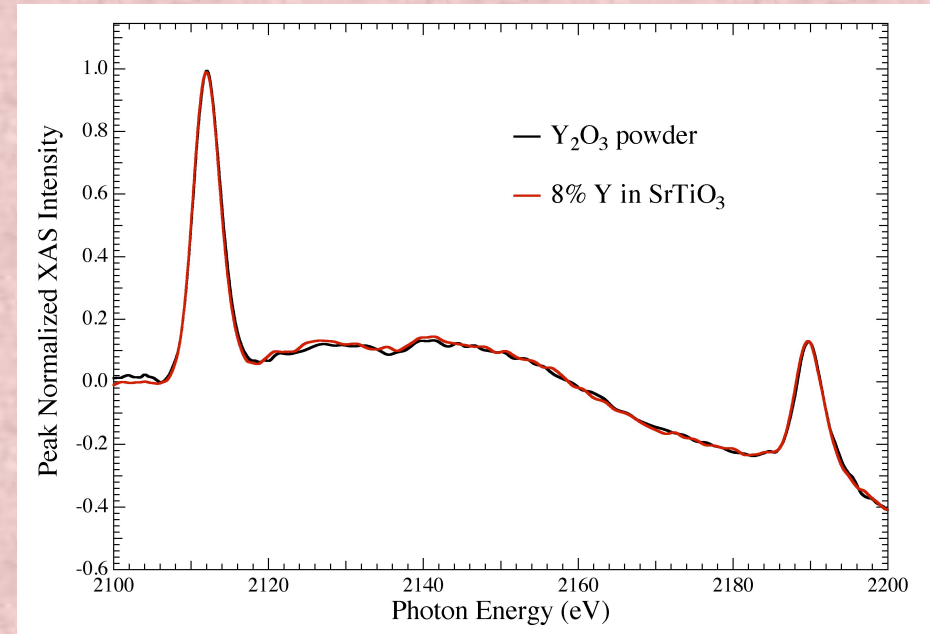


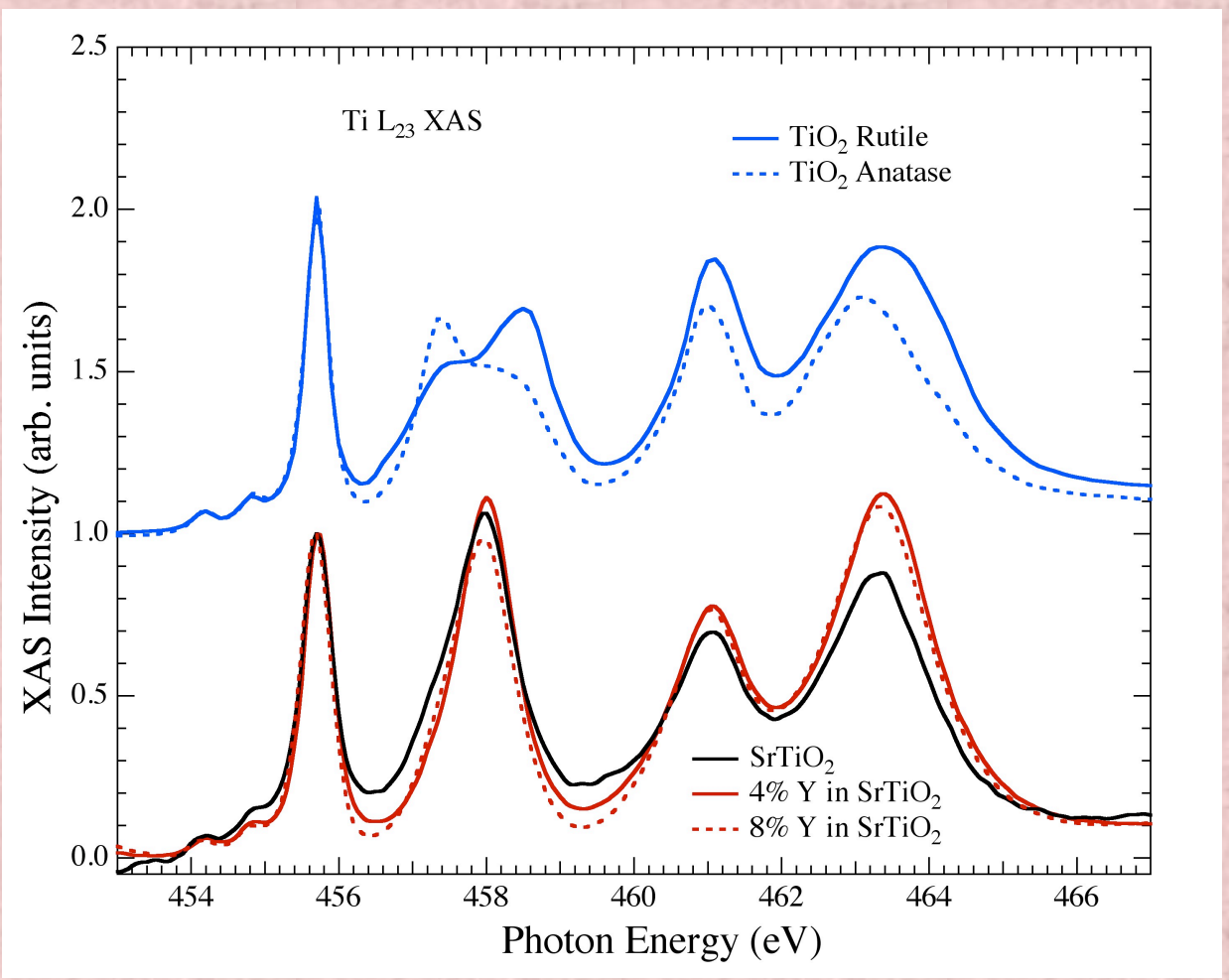
Image from webelements.com

Y^{3+} in A-site for Y_2O_3



Y is Y^{3+} in A-site
(Sr substitution)

A-site vs. B-site occupancy



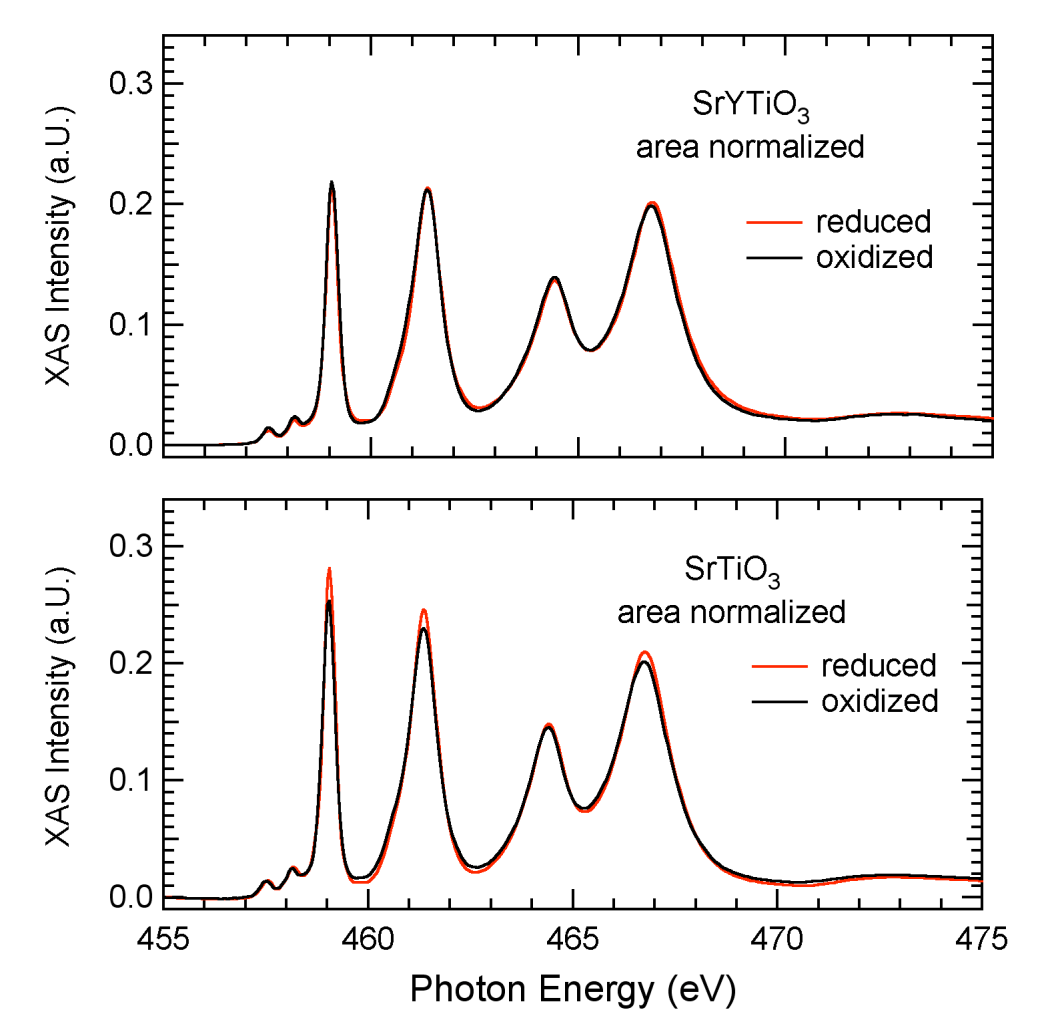
Y in A-site as Y^{3+}

Sr^{2+} spectra unchanged

Ti^{4+} spectra evolves suggesting changing oxygen coordination

Oxygen vacancy formation

Y-doped STO (with bias)



Y in A-site as Y^{3+}

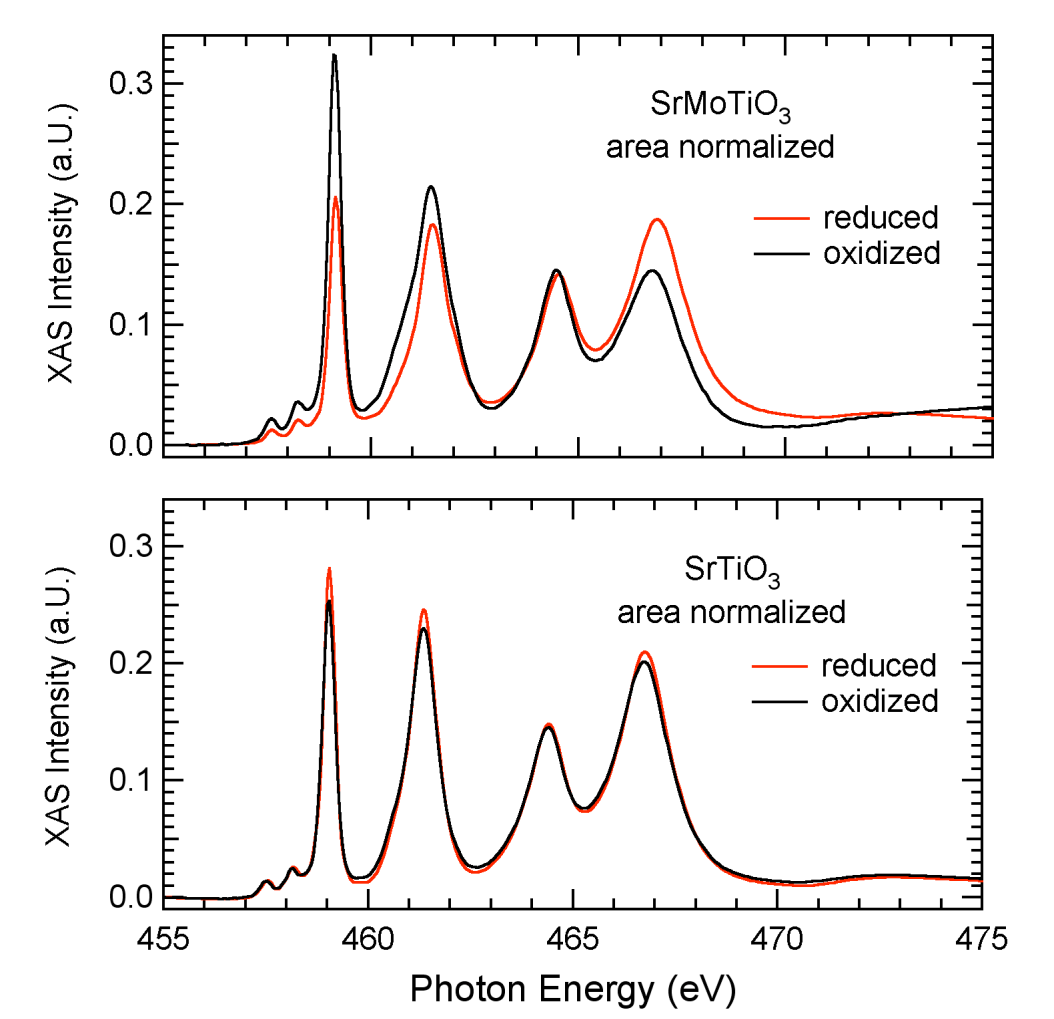
Sr^{2+} spectra unchanged

Ti^{4+} spectra evolves suggesting changing oxygen coordination

Oxygen vacancy concentration unaffected by bias

*Topic of Poster

Mo-doped STO (with bias)



Mo valence and site?

Sr^{2+} spectra unchanged

Ti^{4+} spectra evolves suggesting changing oxygen coordination

Oxygen vacancy concentration affected by bias

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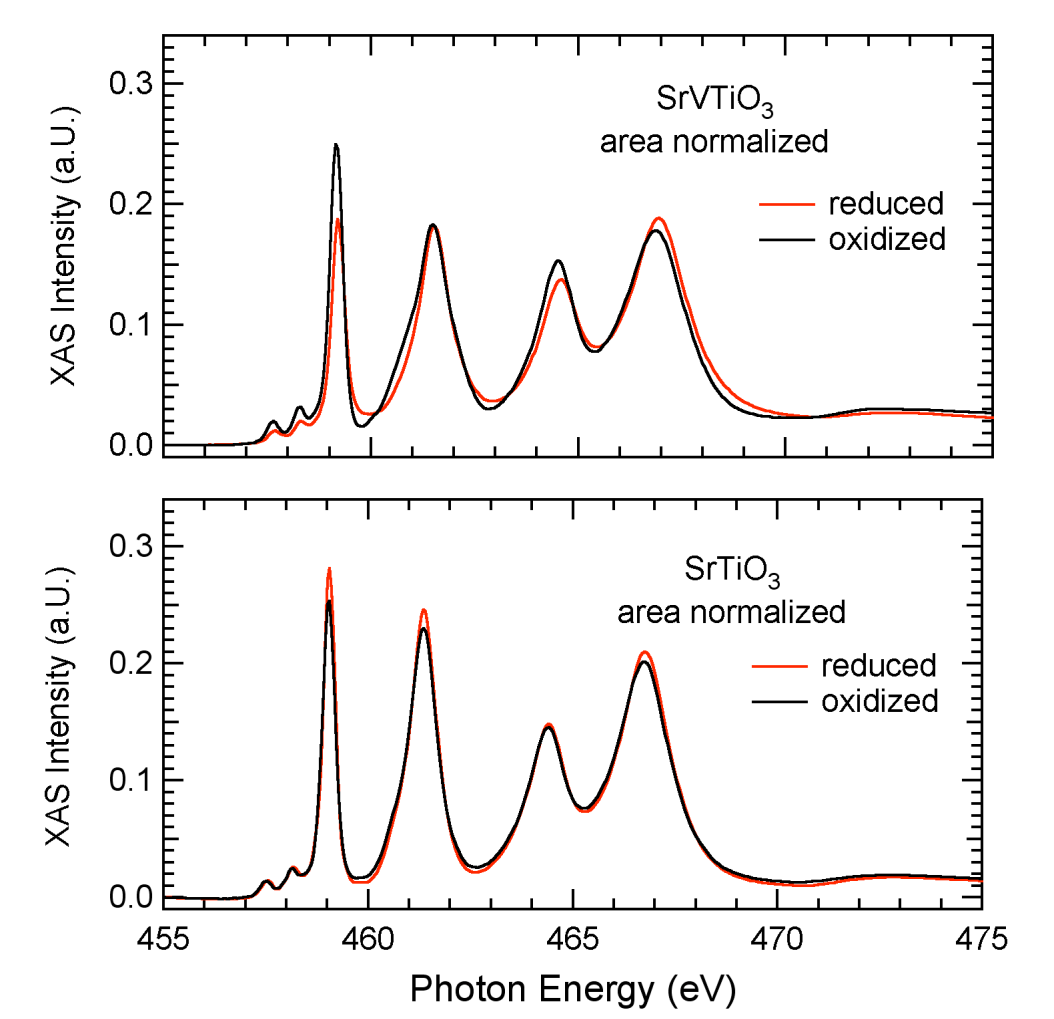
V-doped STO (with bias)



V valence and site?

Sr^{2+} spectra unchanged

Ti^{4+} spectra evolves suggesting changing oxygen coordination

Oxygen vacancy concentration affected by bias

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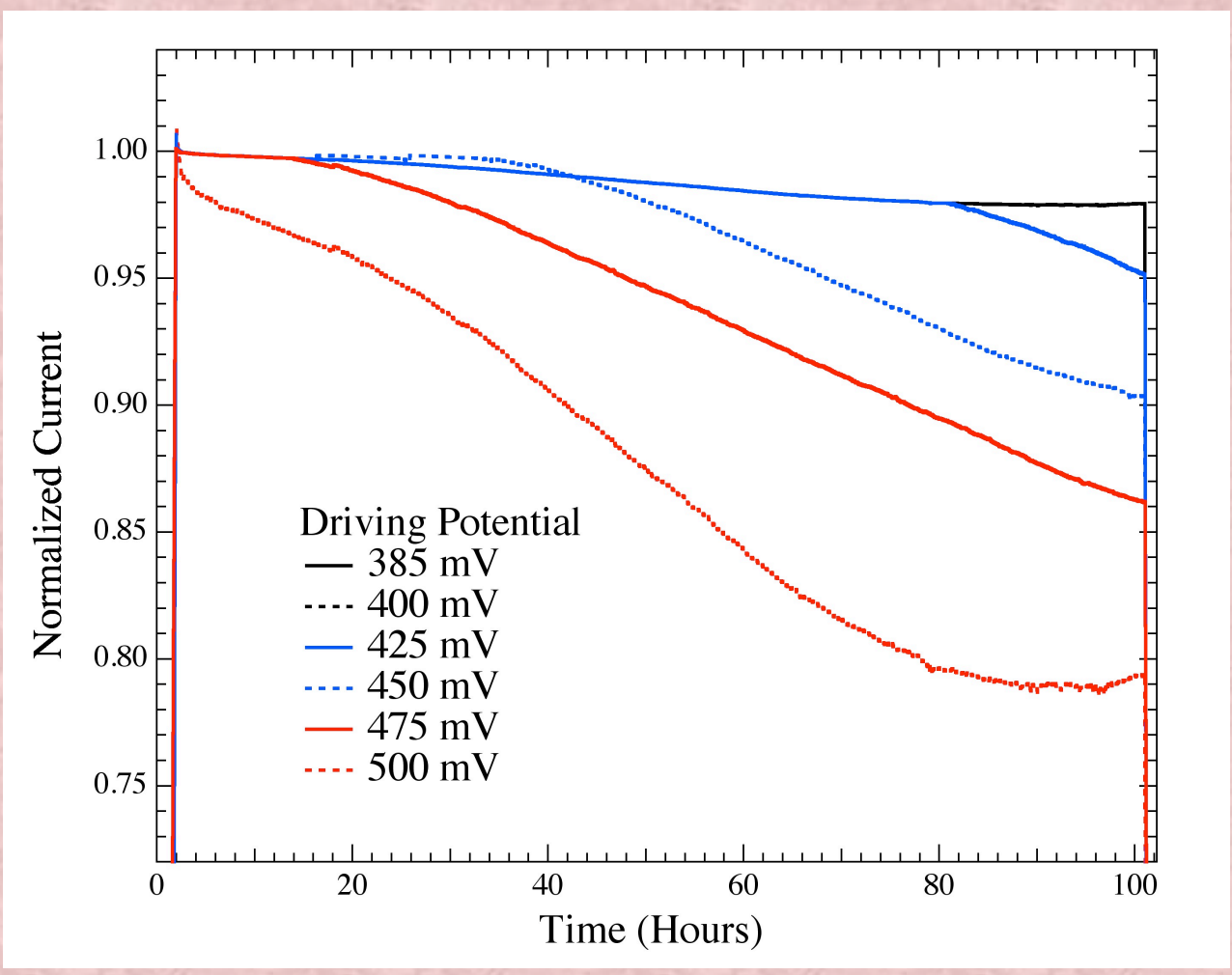
Onset of Degradation (425 mV @ 800 °C)



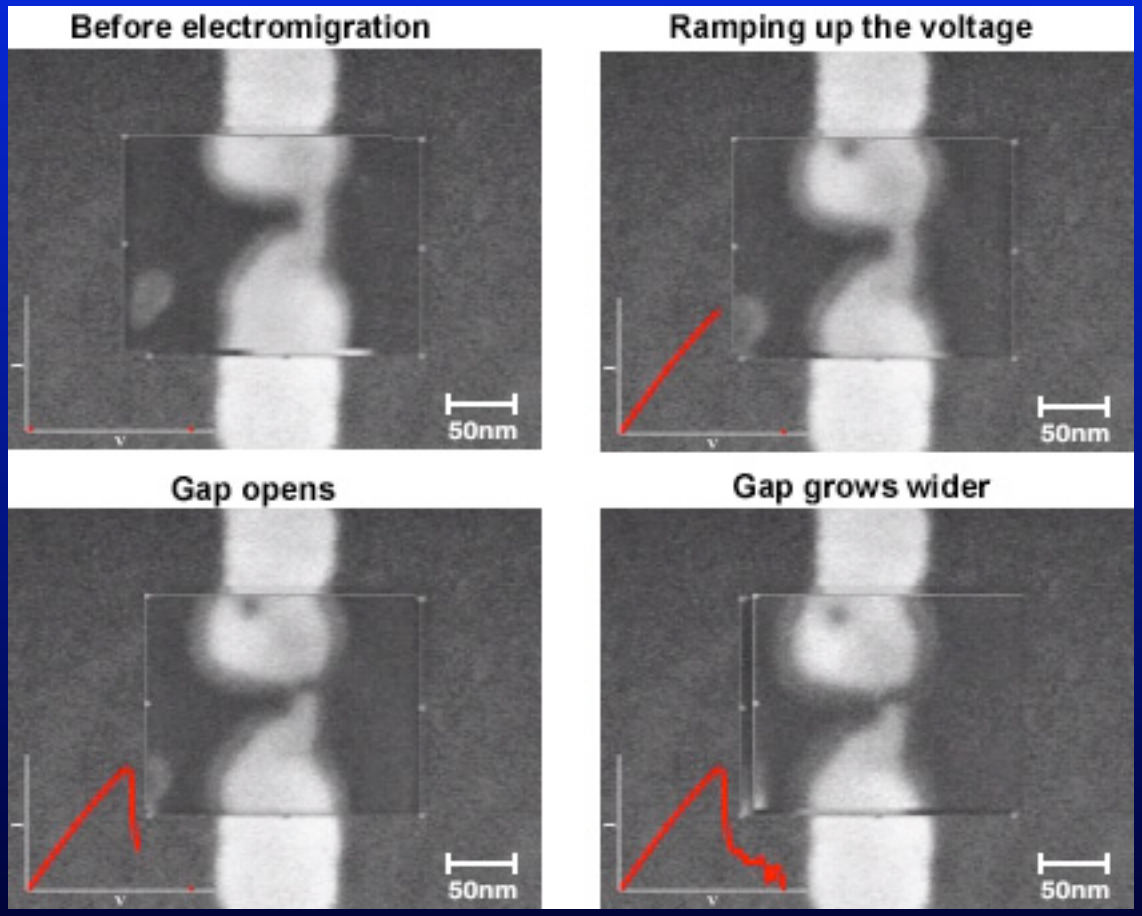
LSFC/GDC in air
Symmetric cells

Onset varies (V_{drive})

Similar slopes

Equilibrium value?

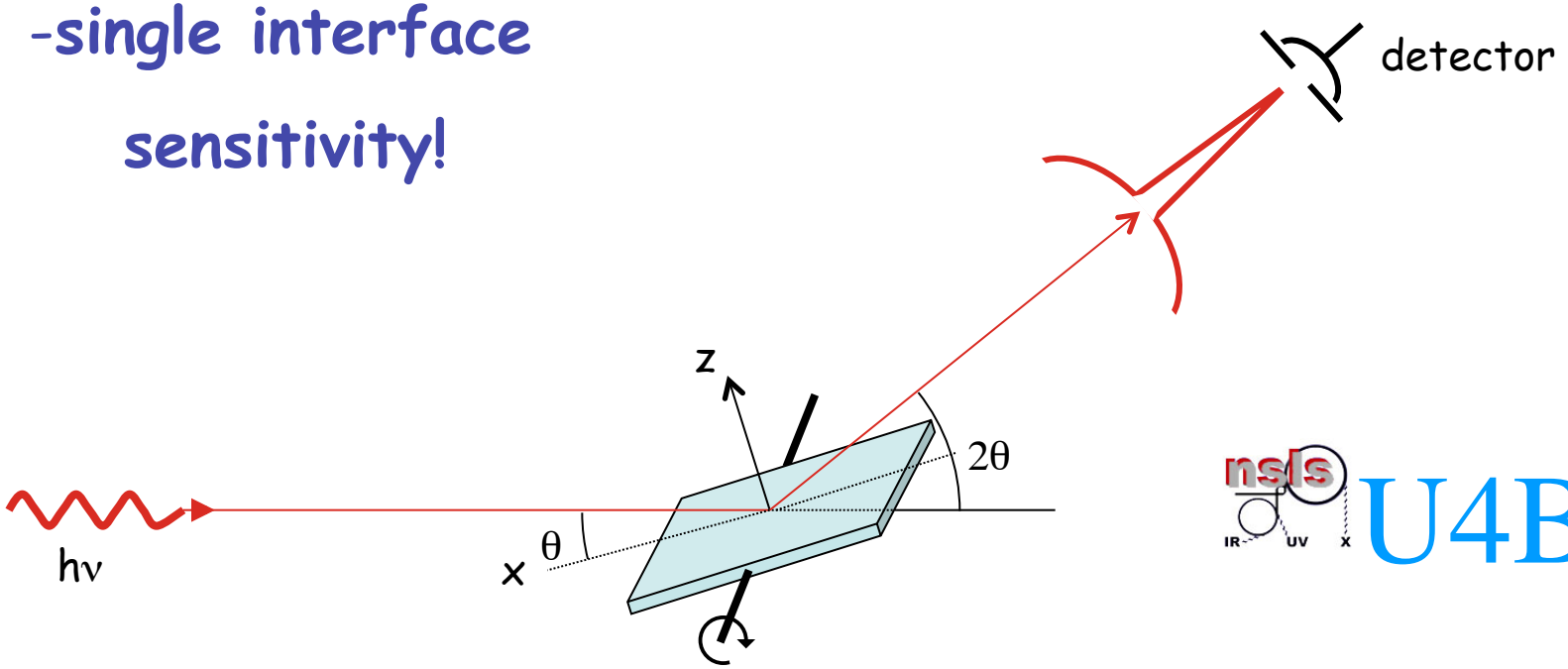
Electromigration



From: D. Ralph, Cornell Univ.

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

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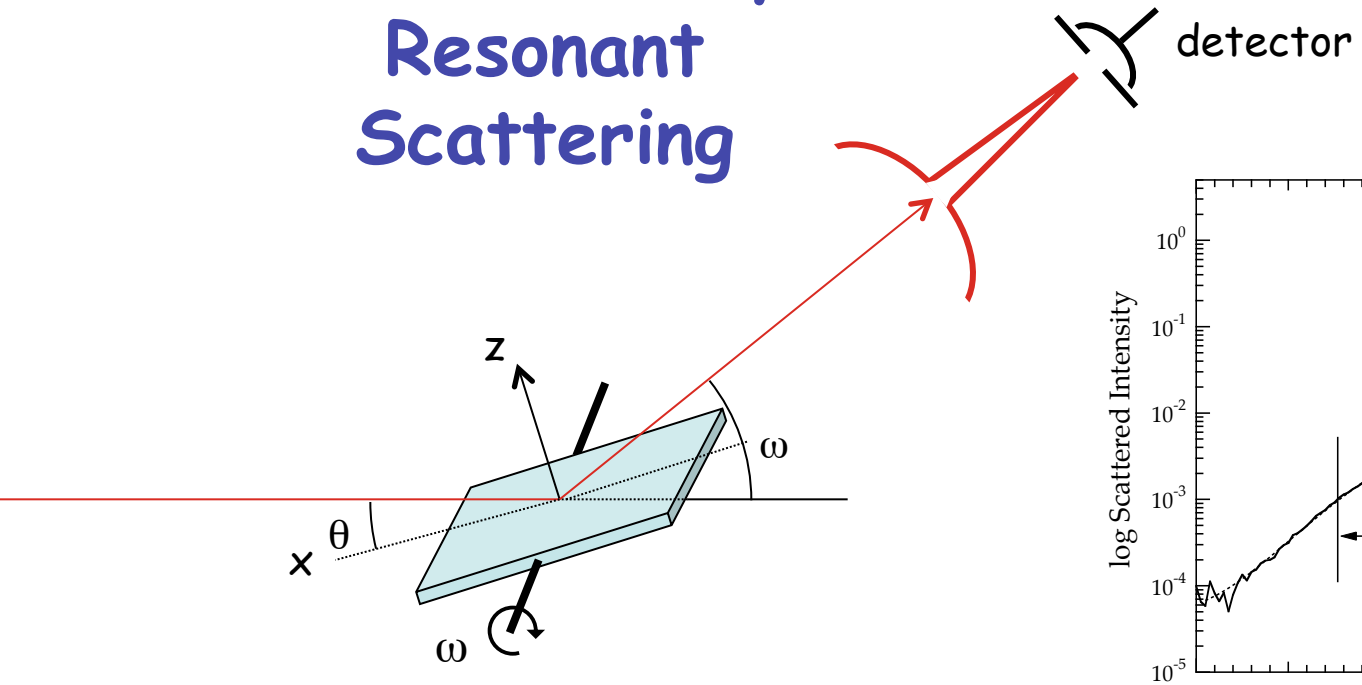
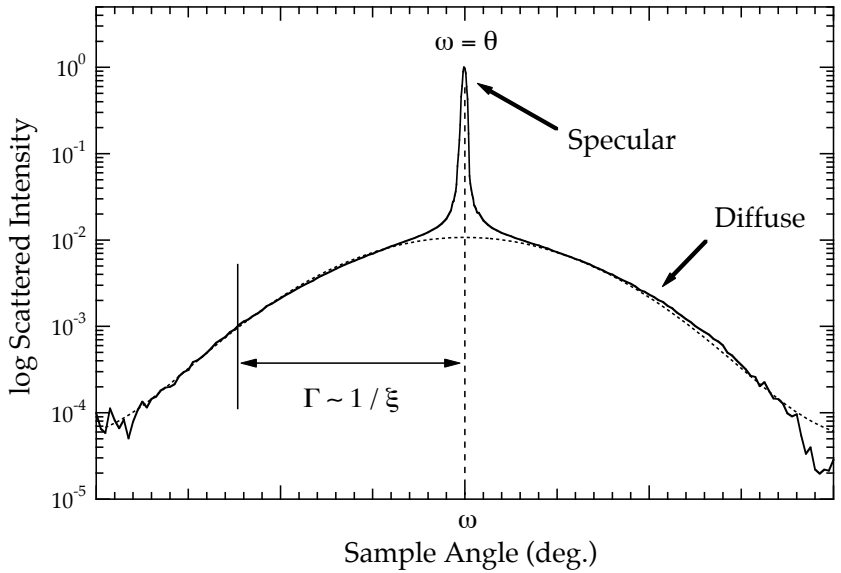
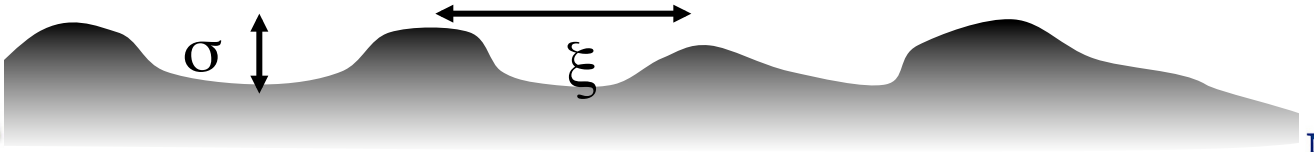
Diffuse X-ray Resonant Scattering





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

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



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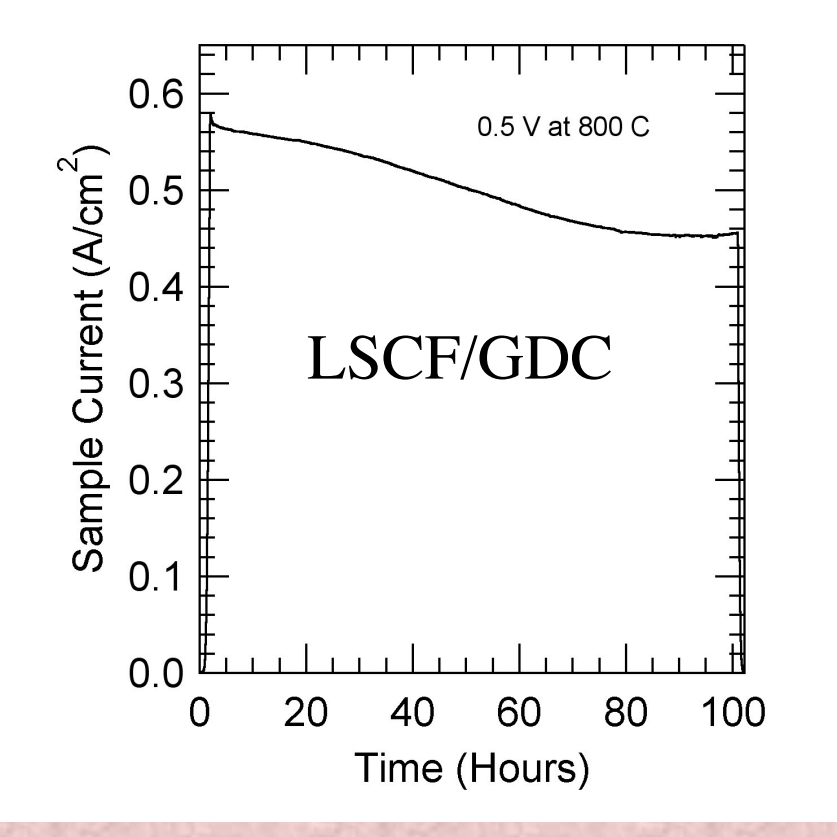
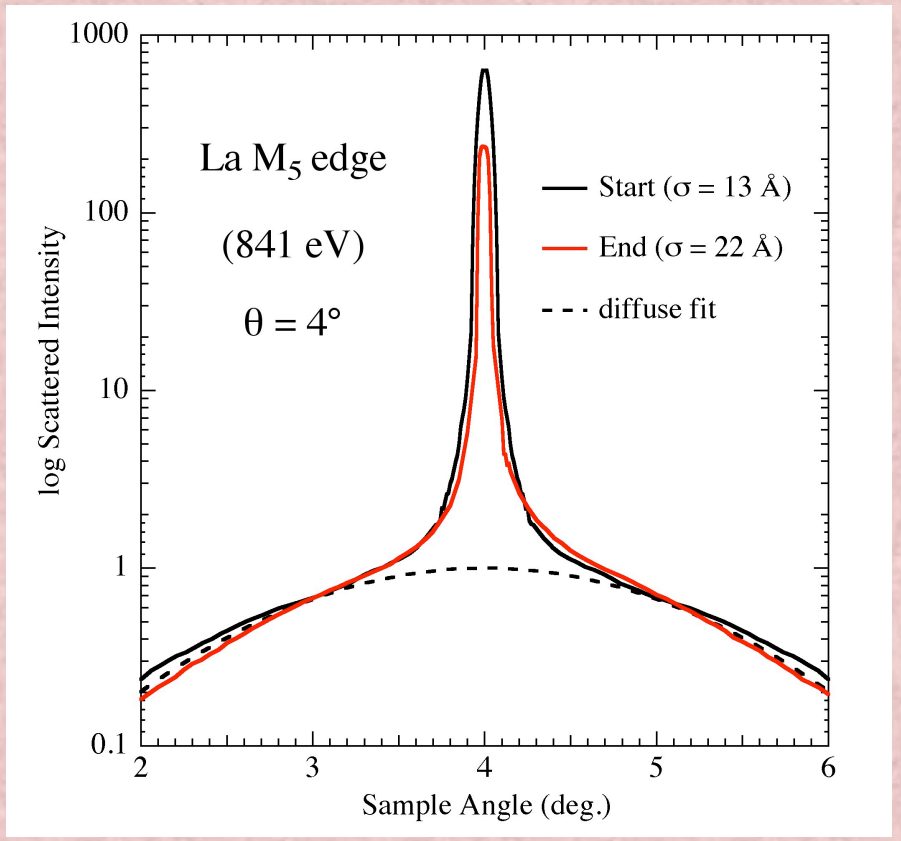
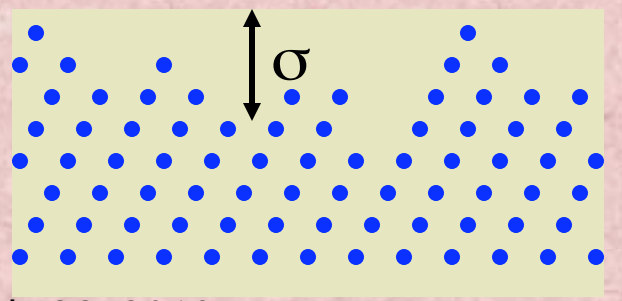
Oxygen ion flow - cation diffusion



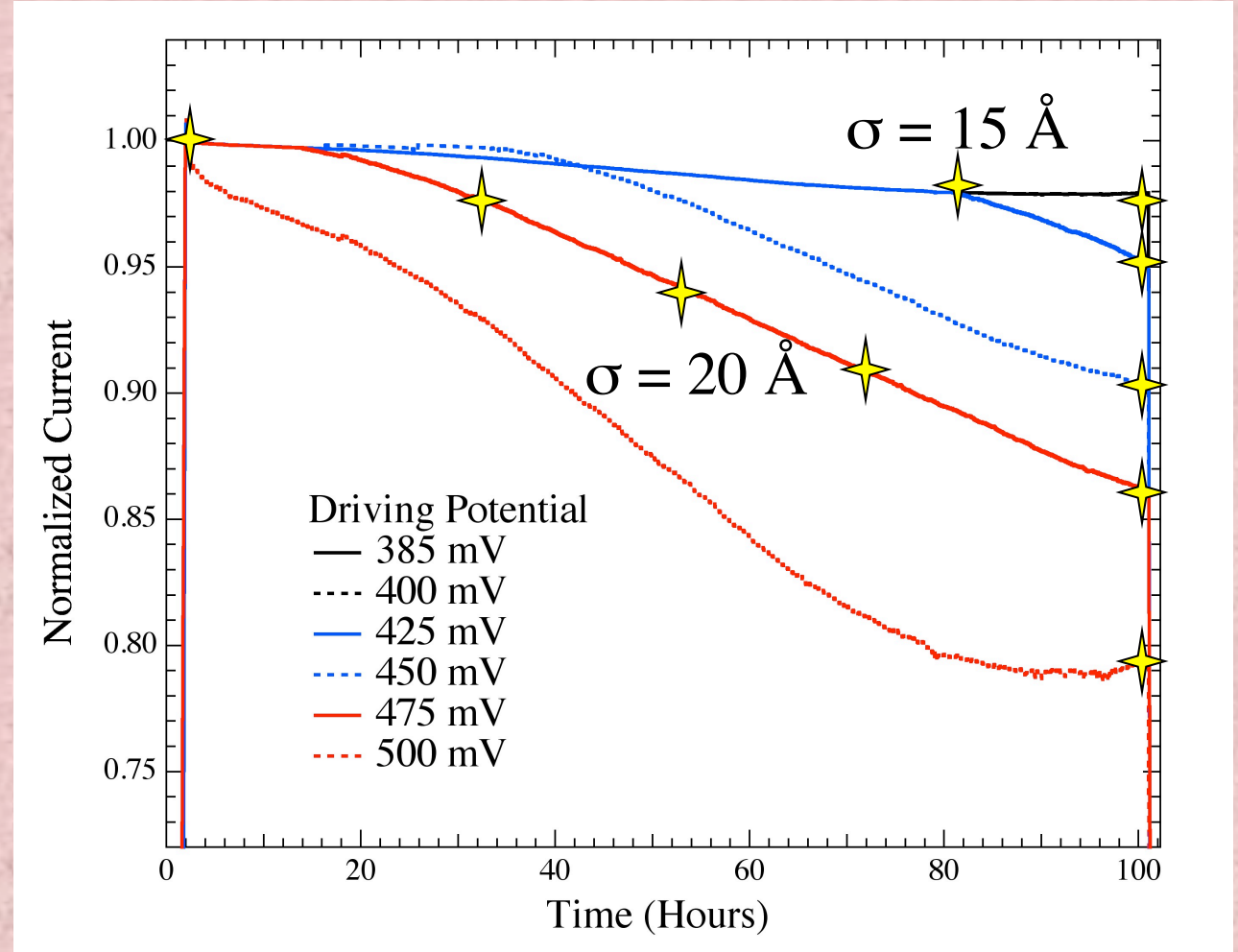


Oxygen ion flow removes La from interface!



Ion flow modified interface width

Start
σ = 13 Å



σ = 12 Å
σ = 18 Å
σ = 15 Å
σ = 20 Å
σ = 22 Å

Summary

Oxygen ion flow and/or surface potential modifies
- oxygen vacancy concentration.
- interfacial width.

Doping $SrTiO_3$ with V, Mo, and Y changes oxygen vacancy concentration.

Doping $SrTiO_3$ with V, Mo, and Y affects material response to oxidation and reduction.

Acknowledgements

Post-doctoral Fellow

Alex Lussier (FT)

Ezana Negusse (1/3)

Graduate Students

Martin Finsterbusch (FT)

Beamline U4-B

National Synchrotron Light Source (BNL)

Dr. Dario Arena (BNL scientist)