BOSTON UNIVERSITY

SURFACE SEGREGATION AND PHASE FORMATION IN SOFC CATHODE THIN FILMS

Jacob Davis, Yang Yu, Deniz Cetin, Heng Luo, Xi Lin, Karl Ludwig, Uday Pal, Srikanth Gopalan, and Soumendra Basu

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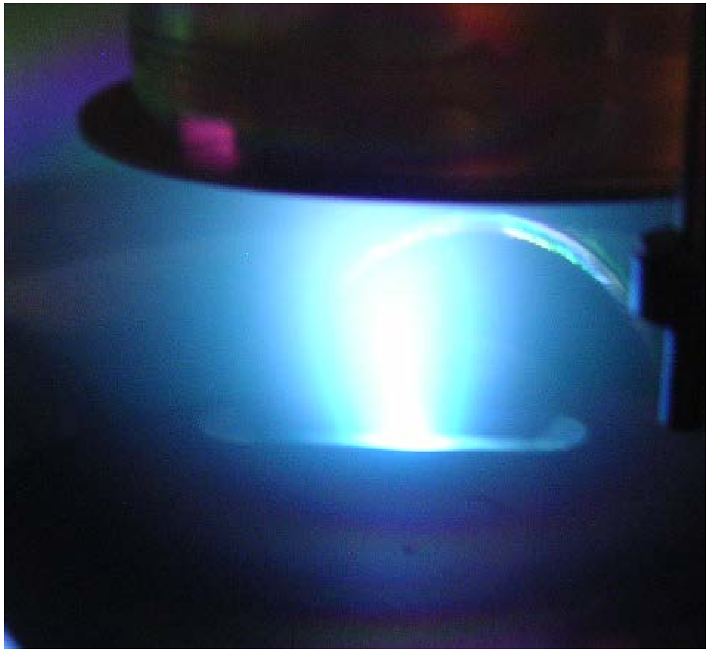
Current Research Thrusts

- Surface studies
  - Jacob Davis, Yang Yu, Karl Ludwig, Soumendra Basu
- LSM 20, LSCF 6428, LSCF 7328
- Flat surfaces needed for glancing incidence x-ray experiments
- Heteroepitaxial thin films on LAO and NGO as model systems

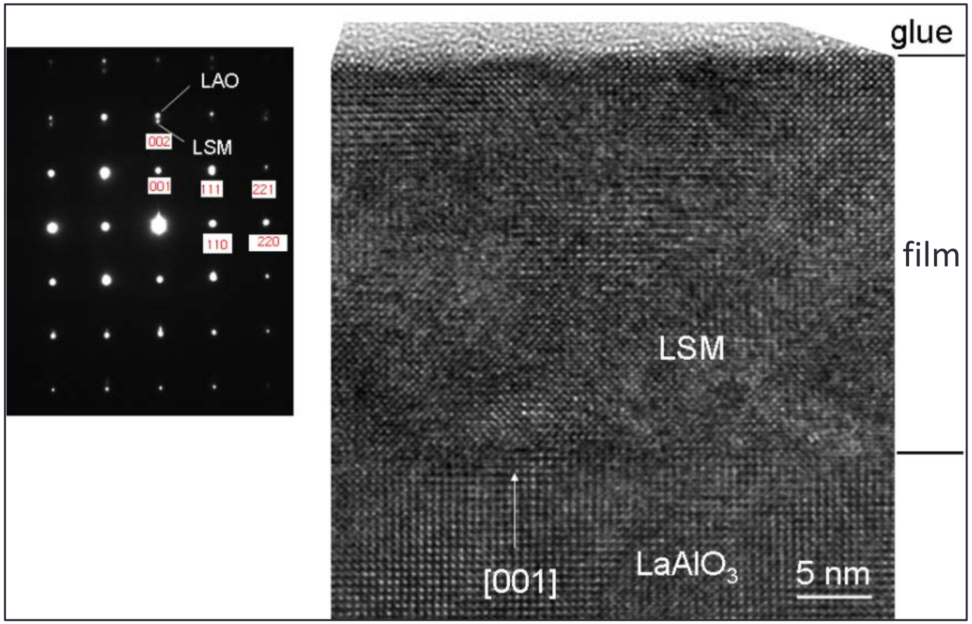
- DFT calculations
  - Heng Luo, Xi Lin

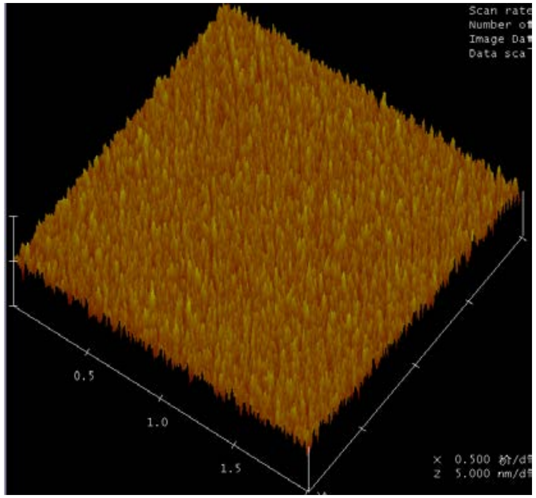
- Patterned electrode experiments
  - Deniz Cetin, Uday Pal, Srikanth Gopalan

$(La_{0.8}Sr_{0.2})_{0.95}MnO_3$ (LSM-20) Thin Films on LAO, NGO

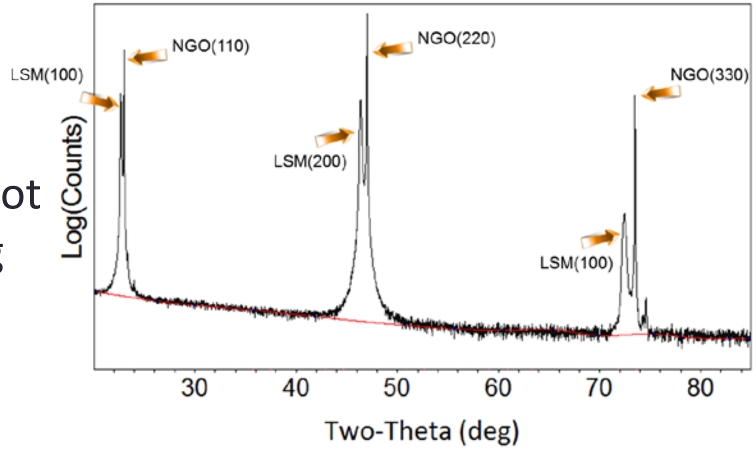


PLD at EMSL at PNNL

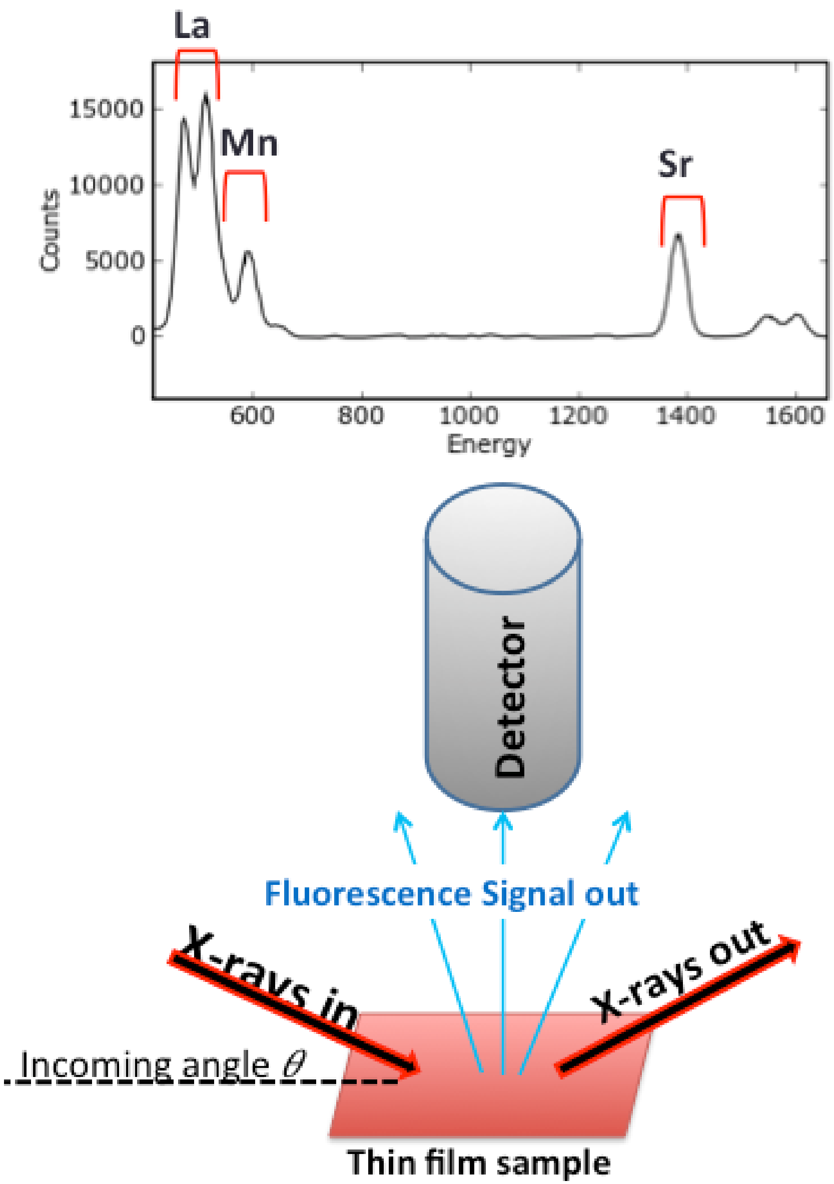


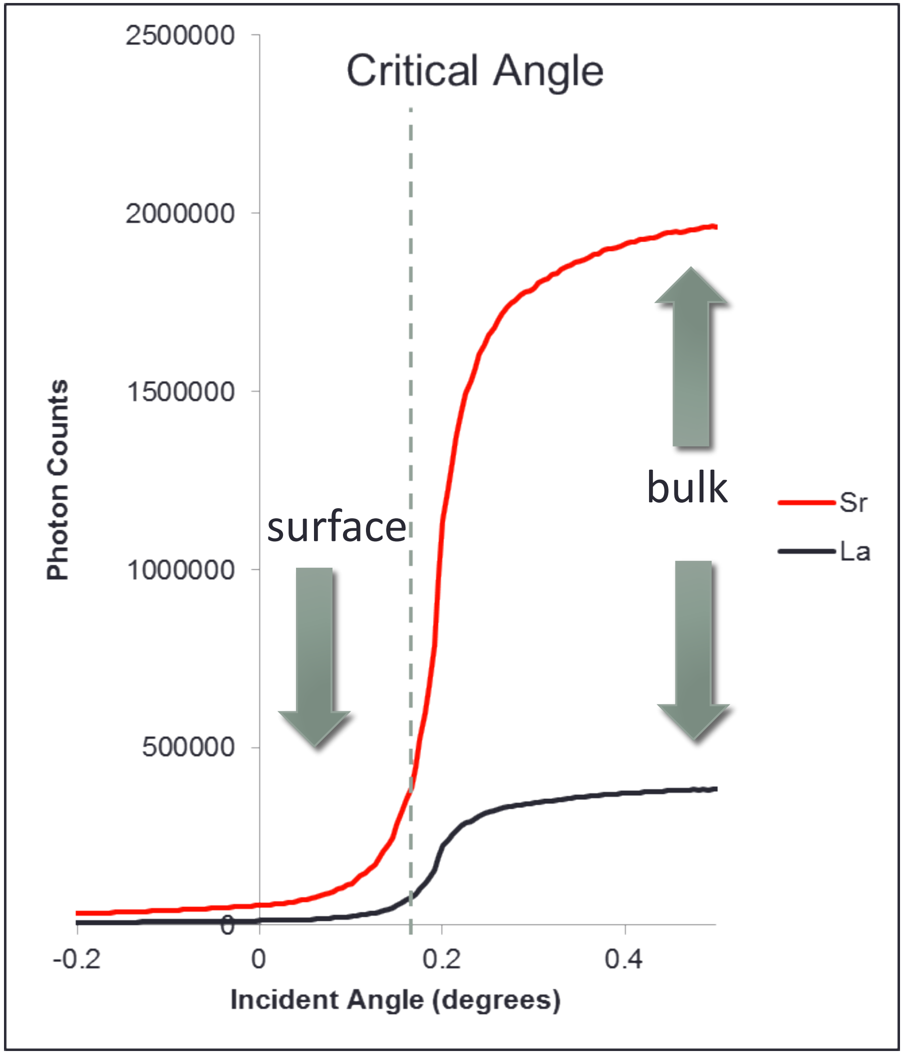


- RMS of surface roughness = 0.522 nm
- RMS roughness does not change after annealing 12 hours at 800°C
- **No surface phase formation observed**

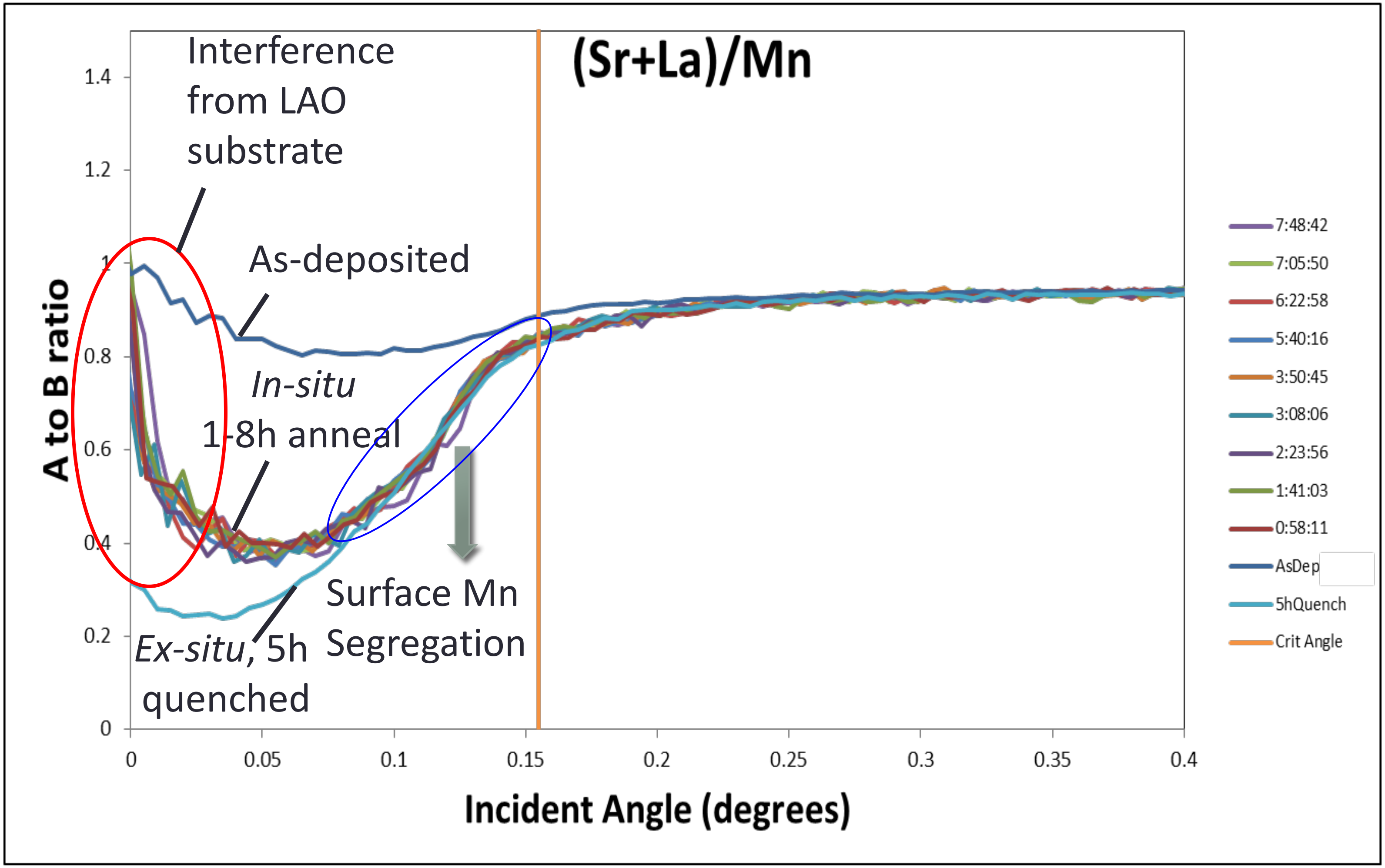


Total Reflection X-ray Fluorescence (TXRF)

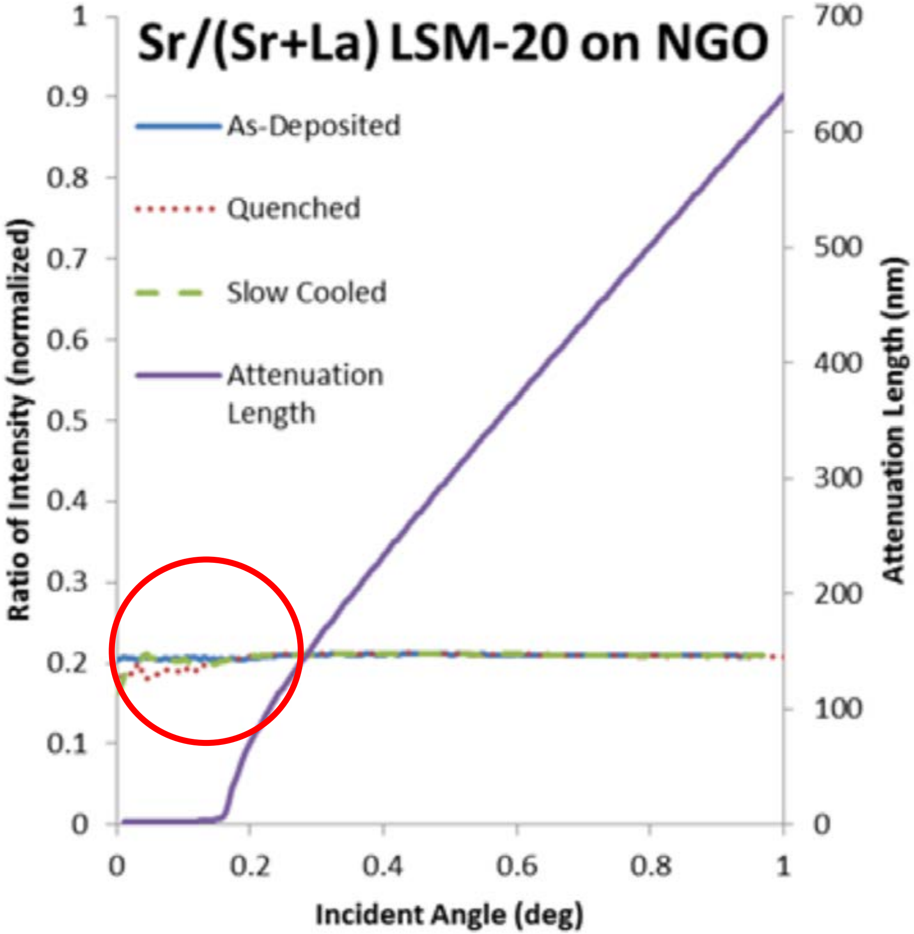


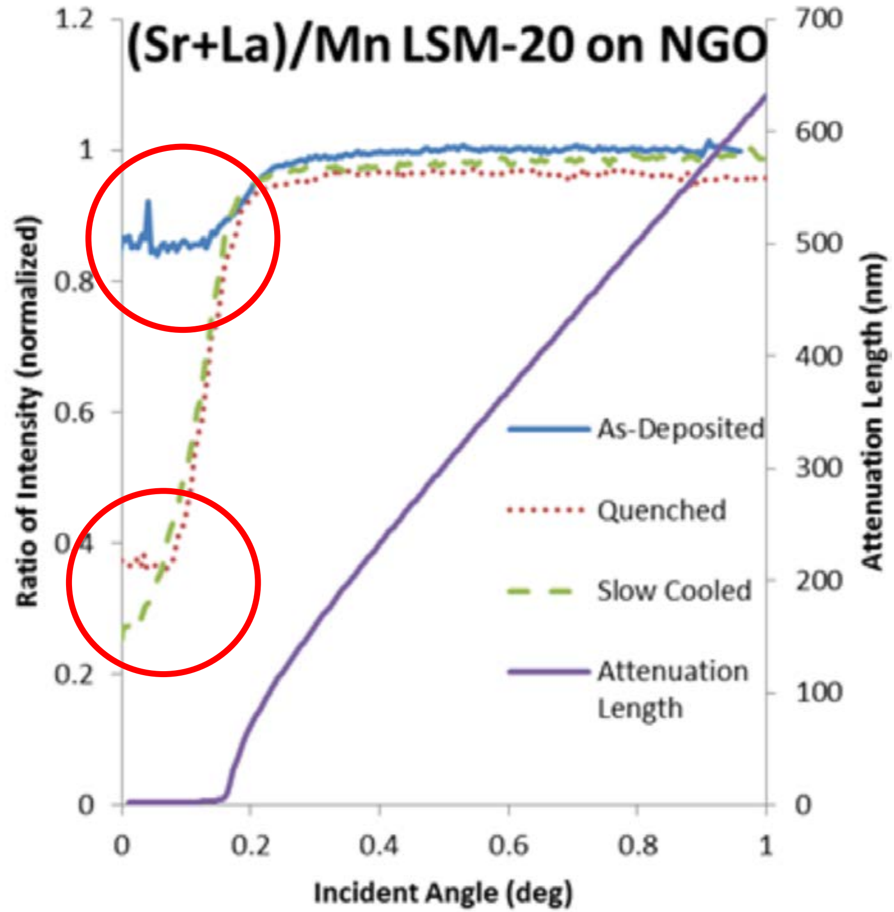


LSM-20 on LAO, TXRF *in-situ* Study, 800°C in Air



LSM-20 on NGO, Annealed 5h at 800°C in Air



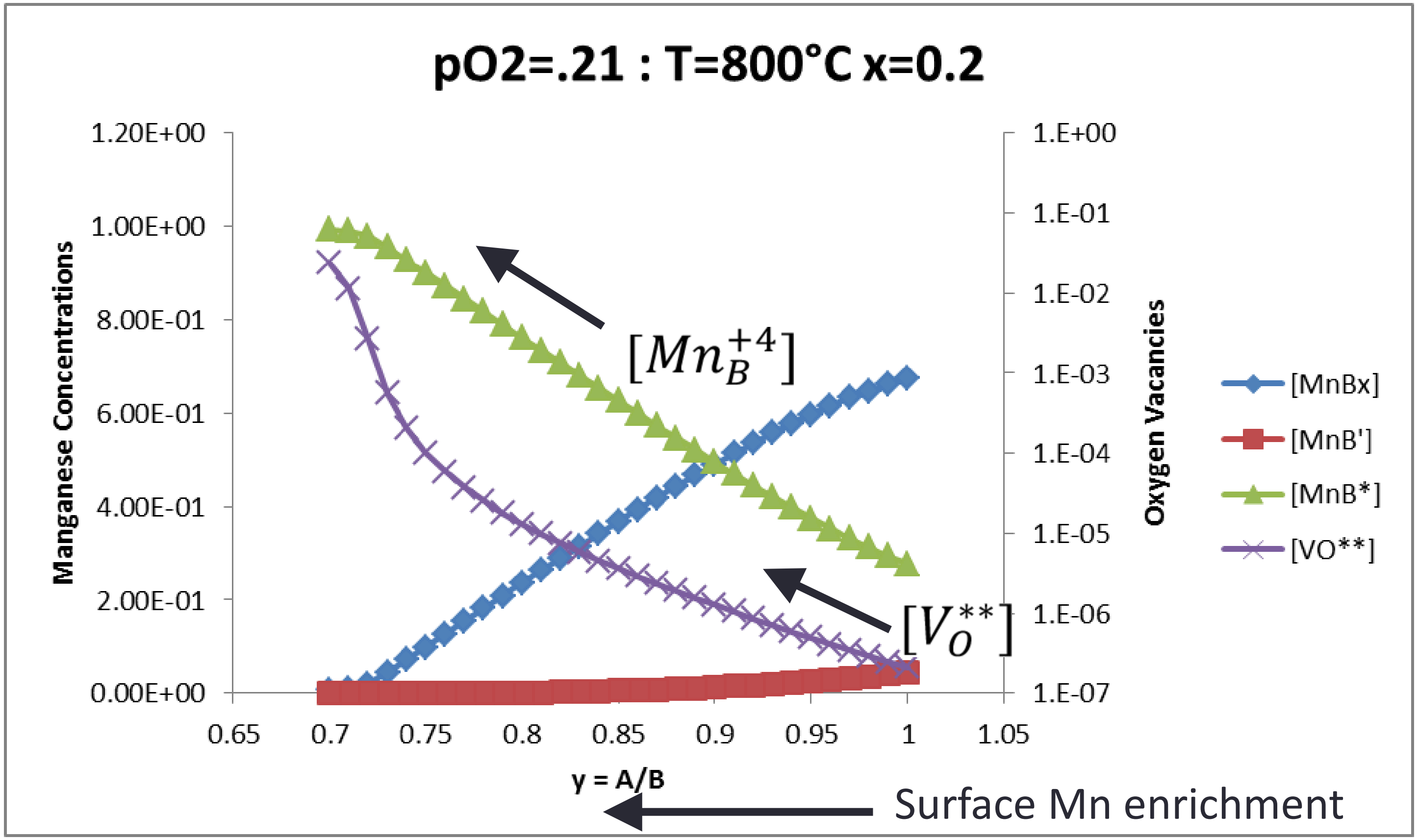


No change in A-site cation ratios on annealing

B-site cation (Mn) surface enrichment on annealing with no new phase formation

Effect of Mn Surface Segregation in LSM

F. W. Poulsen, *Solid State Ionics* **129**, pp 145-162 (2000)

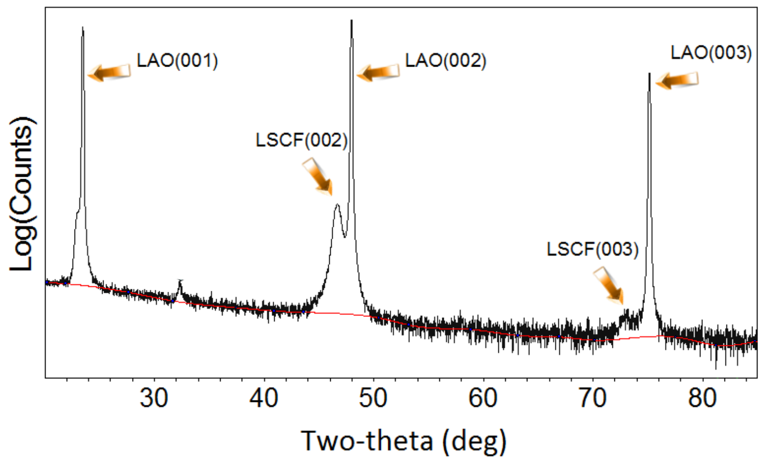


LSM-20 Conclusions

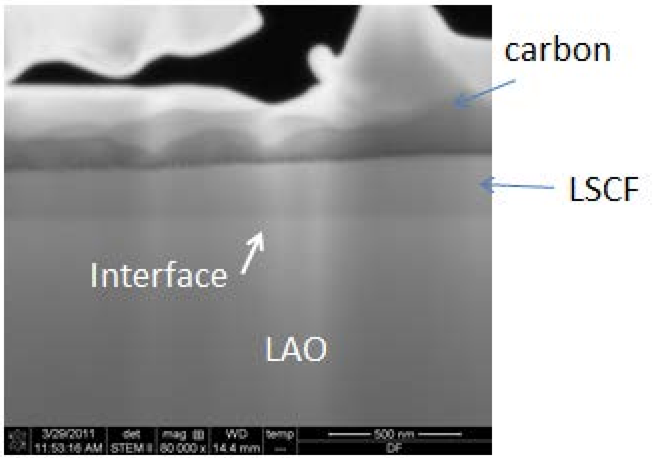
- TXRF shows increased surface manganese segregation
- AFM shows no surface phase formation
- At 800°C, Mn surface enhancement is complete within 1h
- Quenching preserves the surface state, allowing *ex-situ* studies
- Surface segregation of Mn in LSM increases the oxygen vacancy concentration, and the concentration of Mn^{+4} at the surface.
- Both effects should aid the ORR process at the cathode surface.

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF-6428) on LAO and NGO

XRD



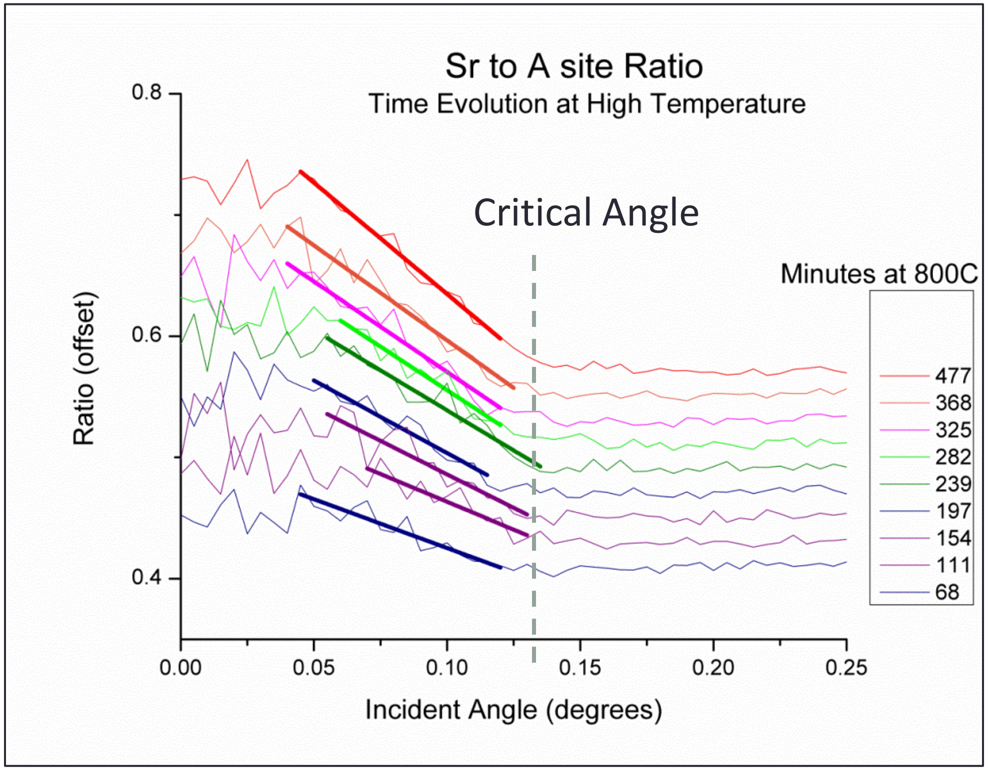
FIB-SEM



X-ray diffraction shows good alignment and the SEM image shows uniform thickness.

LSCF-6428 – TXRF *in-situ* Measurements

- Above the critical angle the bulk value is unchanging.
- Below the critical angle an increase in the ratio value indicates a higher strontium content.
- At 800°C the surface is still evolving over eight hours.



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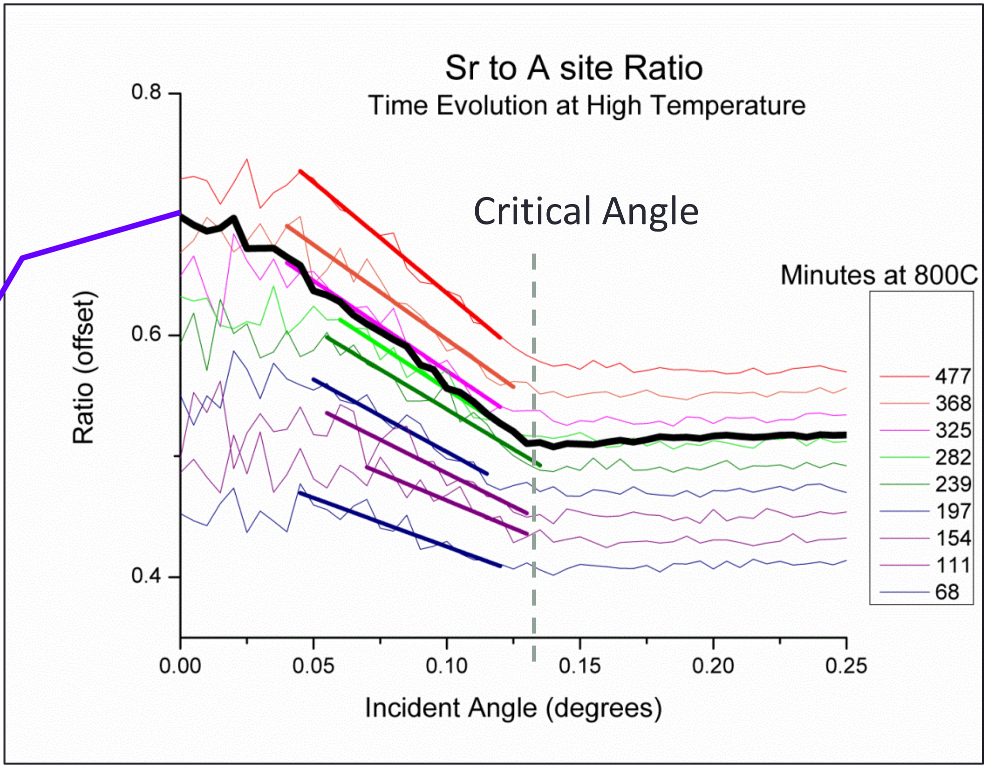
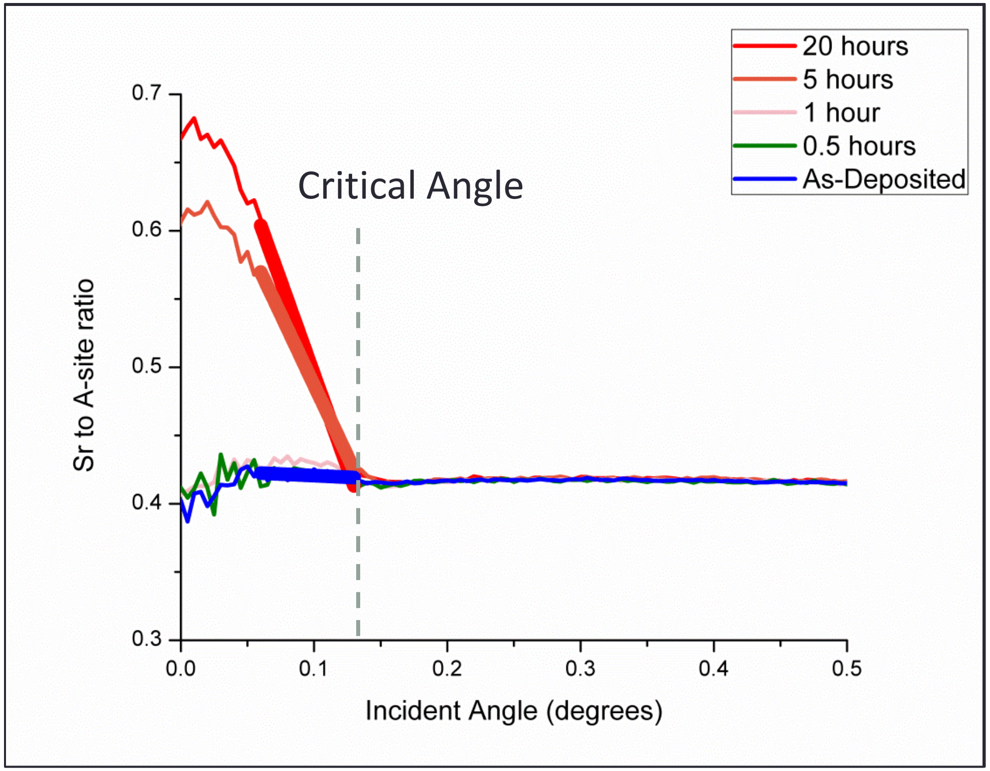


- Quenched after 5 hours. Measured at room Temperature.
- Consistent with high temperature measurement.
- *ex-situ* enables longer count times, better statistics.

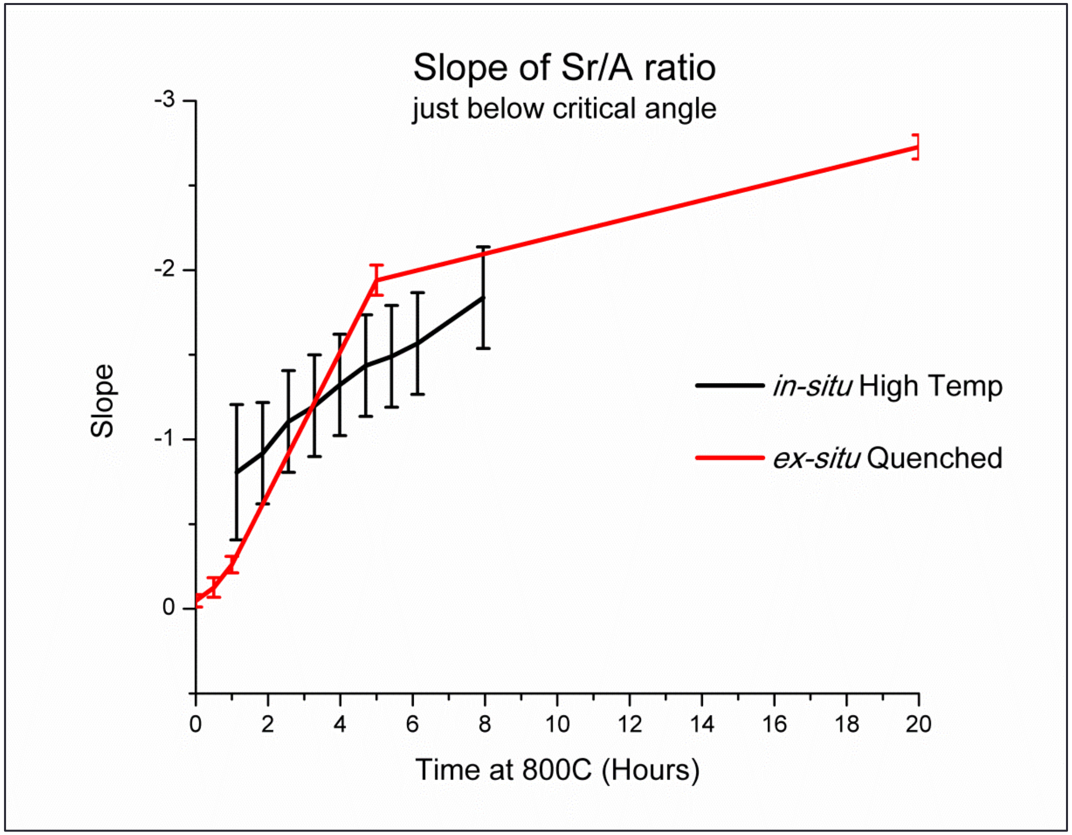
LSCF-6428 – TXRF *ex-situ* Measurements

- Samples quenched from 800°C after various time.
- *Ex-situ* allows for longer measurement times and better counting statistics.
- Use slope below just below the critical angle as a metric for surface enhancement.



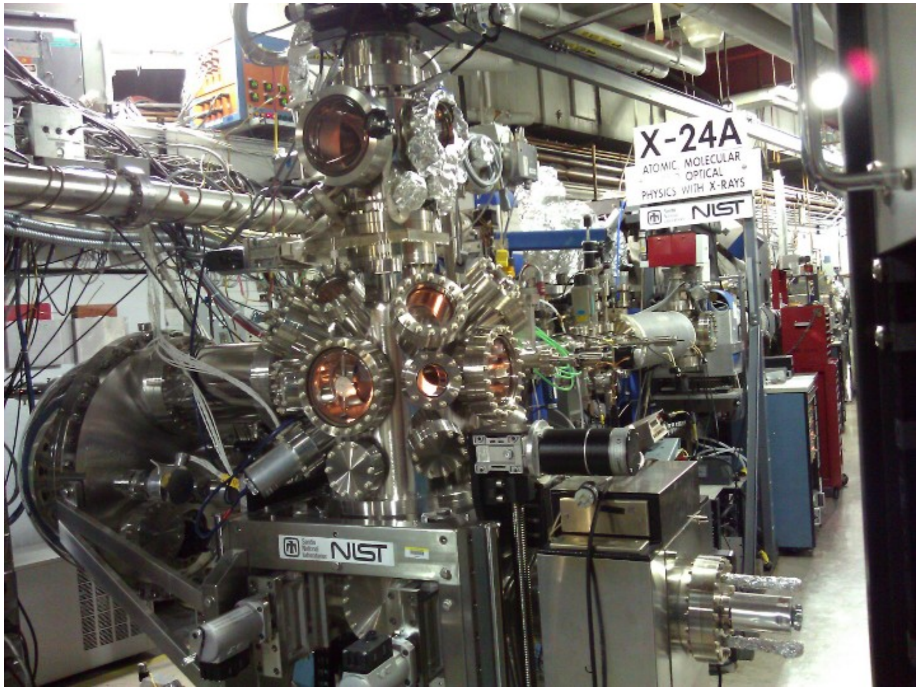
LSCF-6428 TXRF Conclusions

- Quenching preserves high temperature state.
  - *ex-situ* more reliable.
- Strontium surface enrichment rapid over 5 hours at 800°C.
- Still evolving at 20 hours, but at slower rate.
- Need to investigate what the surface strontium is…



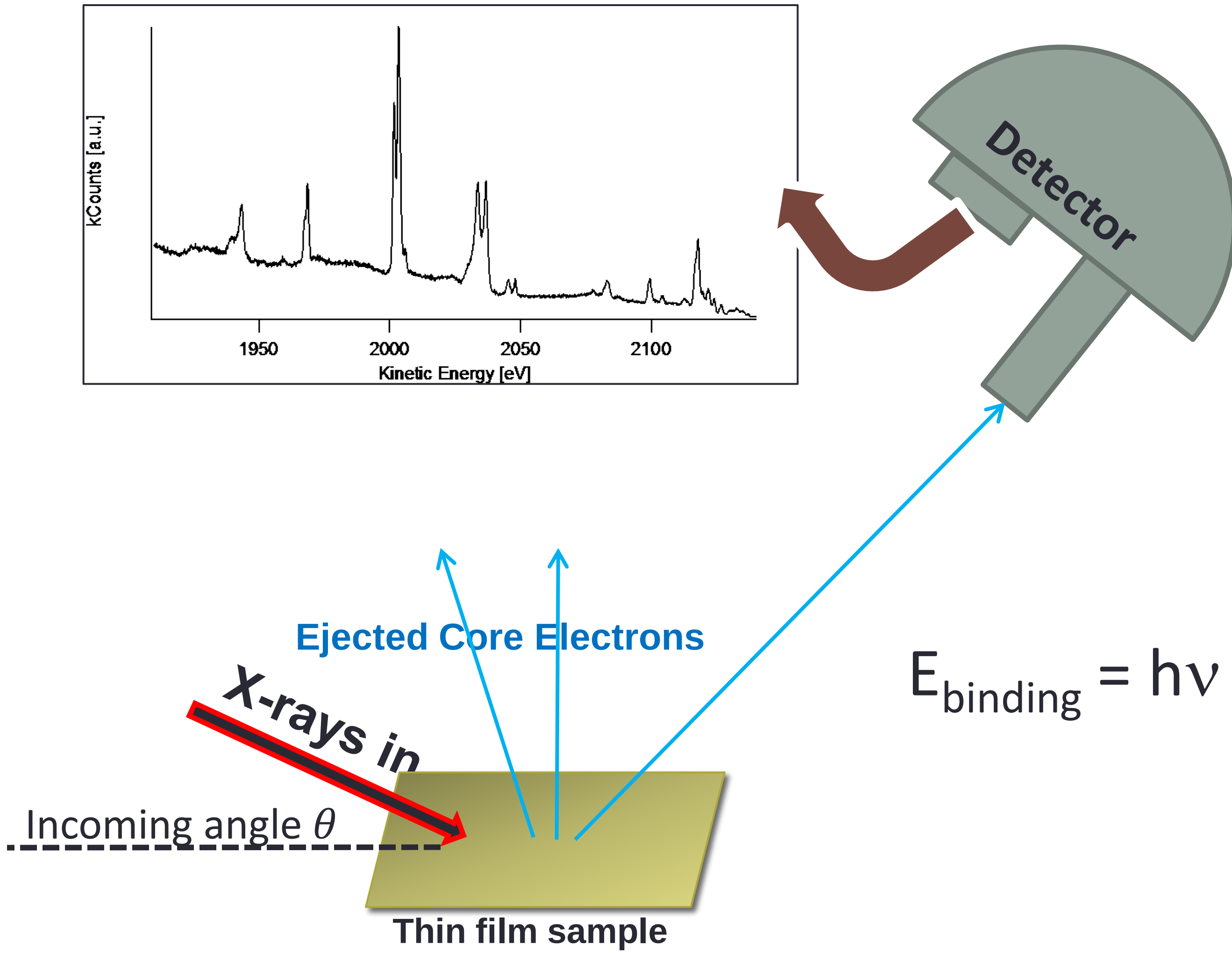
HArd X-ray PhotoElectron Spectroscopy (HAXPES)

- 2000 - 4000 eV photon energies
- Overcomes surface contamination problems of soft x-ray spectroscopies



New HAXPES endstation on NIST beamline X24A.

X-ray Photoelectron Spectroscopy

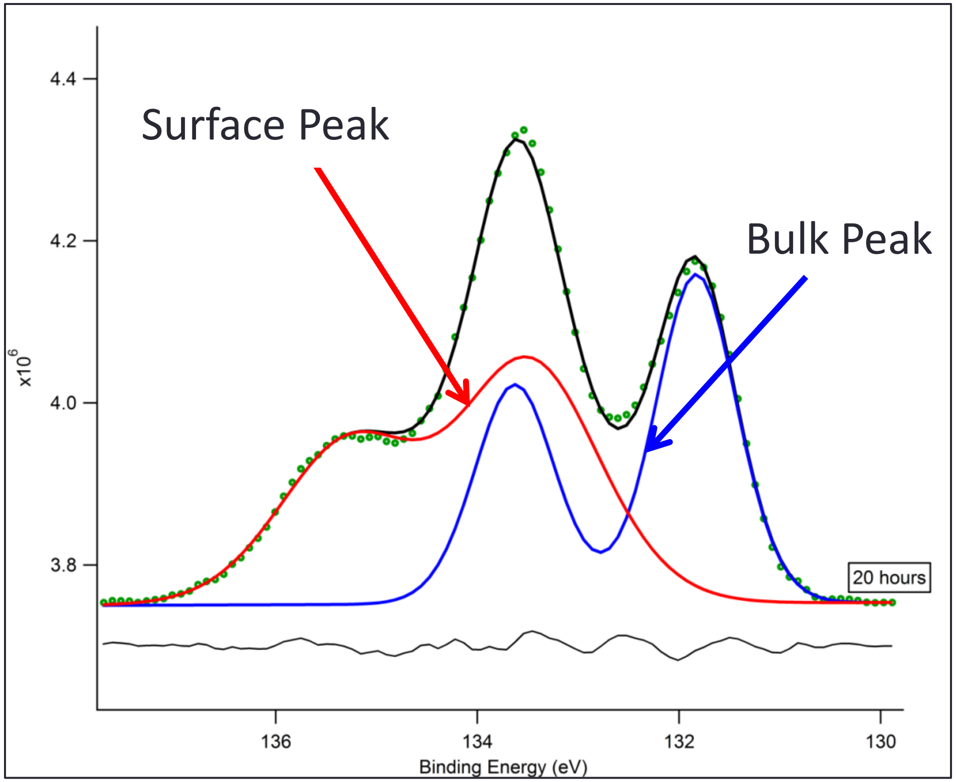


$$E_{binding} = h\nu - (E_{kinetic} + \phi)$$

$Sr3d_{3/2}$ & $Sr3d_{5/2}$ Fit Results (20 h, 800°C anneal)

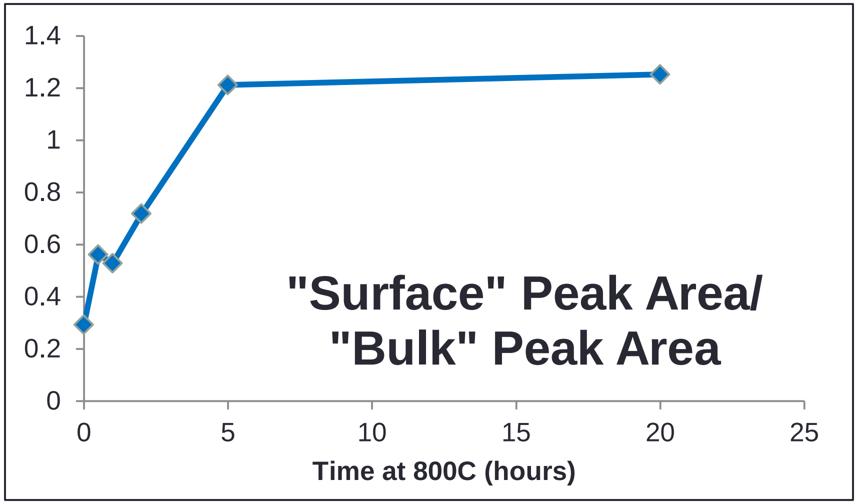
- hv=2140eV.
- Doublet from spin orbit splitting
- Surface Sr $3d_{5/2}$ signal consistent with:

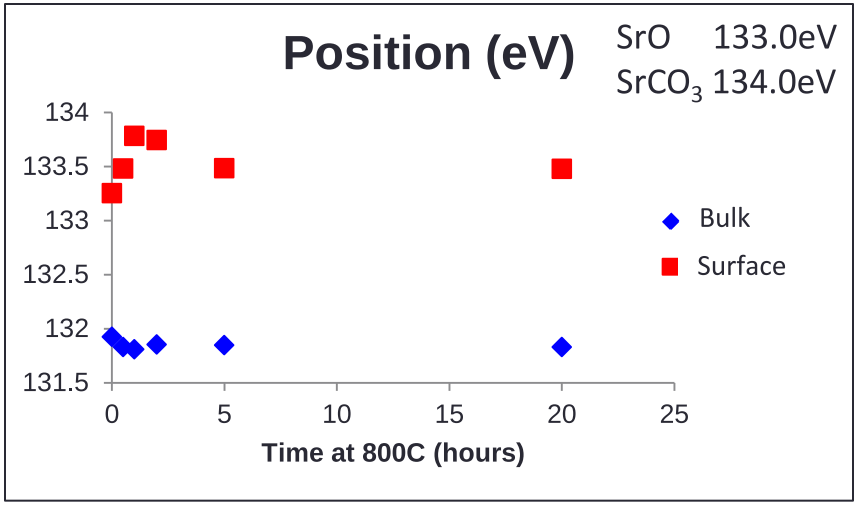
SrO	133.0eV
$SrCO_3$	134.0eV*

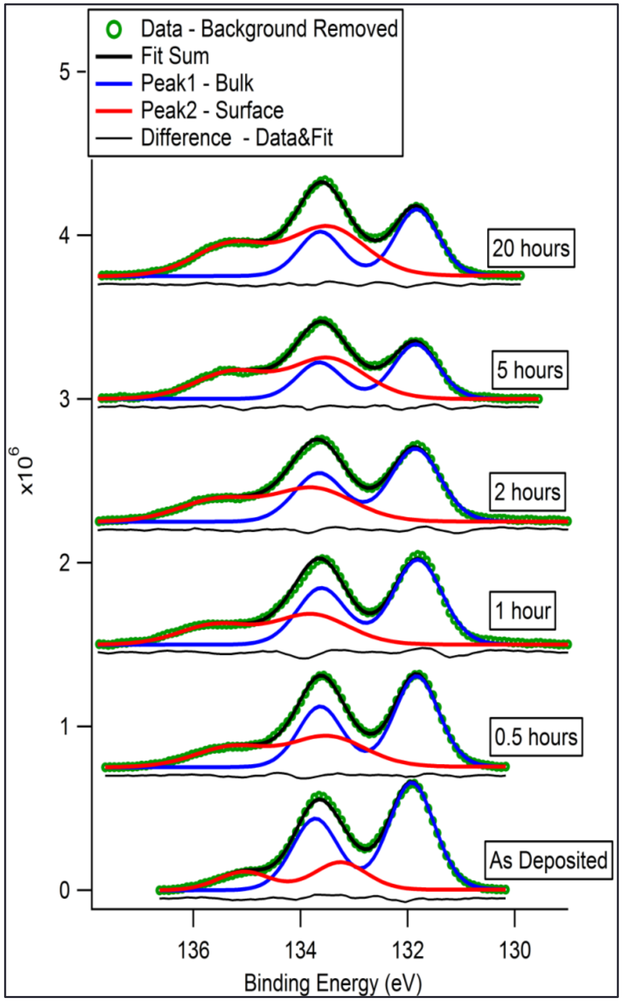


*P.A.W van der Heide, *Surf. Interface Anal.* 2002

LSCF-6428 Sr3d hv=2140 eV – Peak Evolution







Thermodynamics of $SrCO_3$ Formation

- Standard Gibbs free energy change for $SrO + CO_2 \rightarrow SrCO_3$ is given by, $\Delta G^0 = -230{,}290 + 161.43T$ (J/mol)*
- pCO_2 (atm) = 390 ppm = 390×10^{-6} atm
- T(cr) = 1015 K = 742°C
- At 800°C, SrO is stable in air.
- However, during the quench we pass T(cr).
  - formation of $SrCO_3$ increasingly favored at lower temperatures.

*I. Barin, *Thermodynamic Data of Pure Substances,* 1989

Implications of Surface Instability in LSCF-6428?

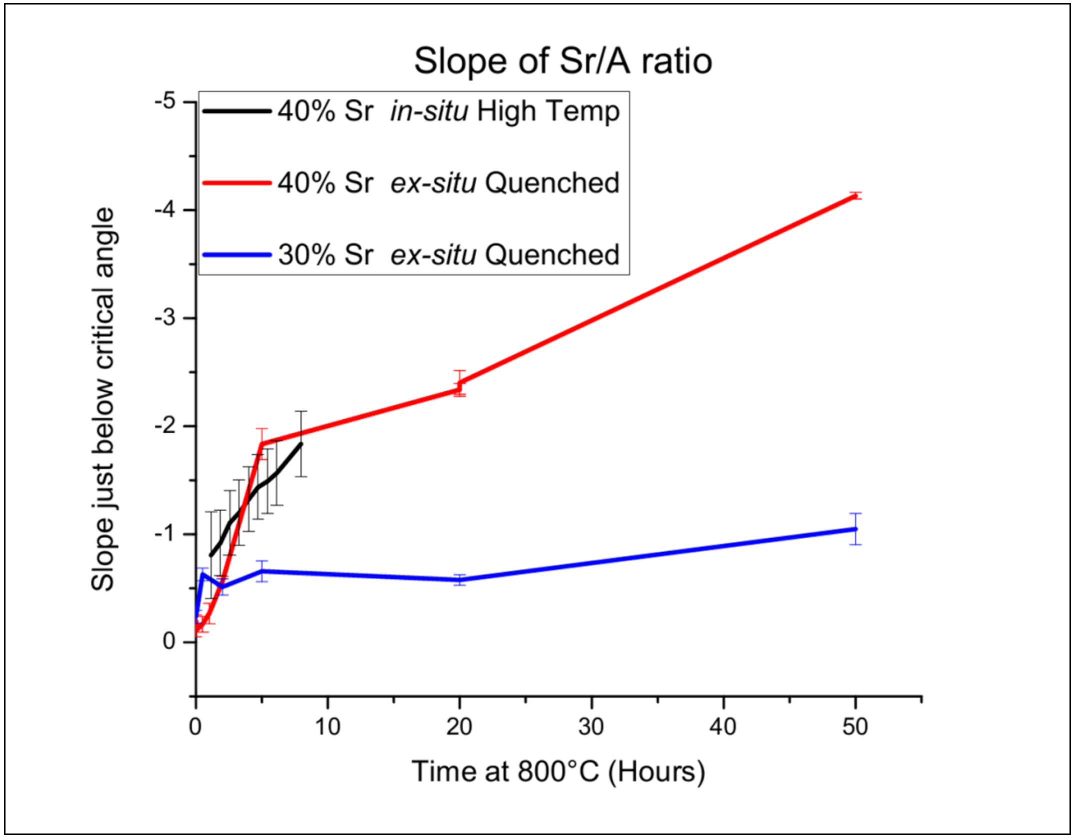
- LSCF-6428 is a commercially available cathode material. However, its surface appears to be unstable.

- Is surface phase formation deleterious to cathode performance due to reduced cathode surface area exposed?

- Will lowering strontium dopant concentration reduce segregation? **$La_{0.7}Sr_{0.3}Co_{0.2}Fe_{0.8}O_3$ (LSCF-7328)**

LSCF-7328 – TXRF *ex-situ* Measurements

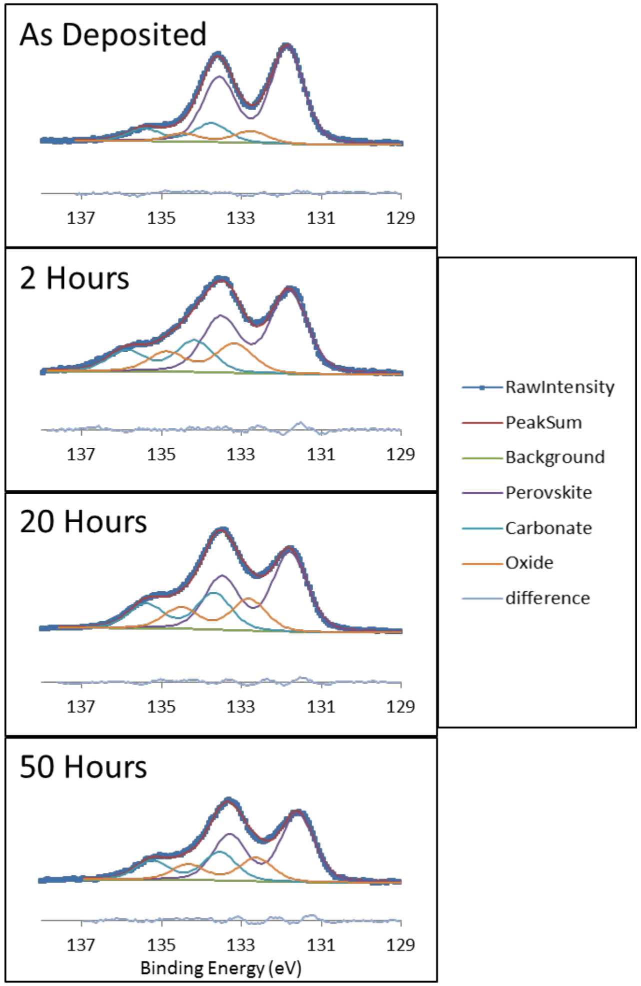
- Less migration of strontium to the 7328 surface.
- Sr Migration is not entirely eliminated.



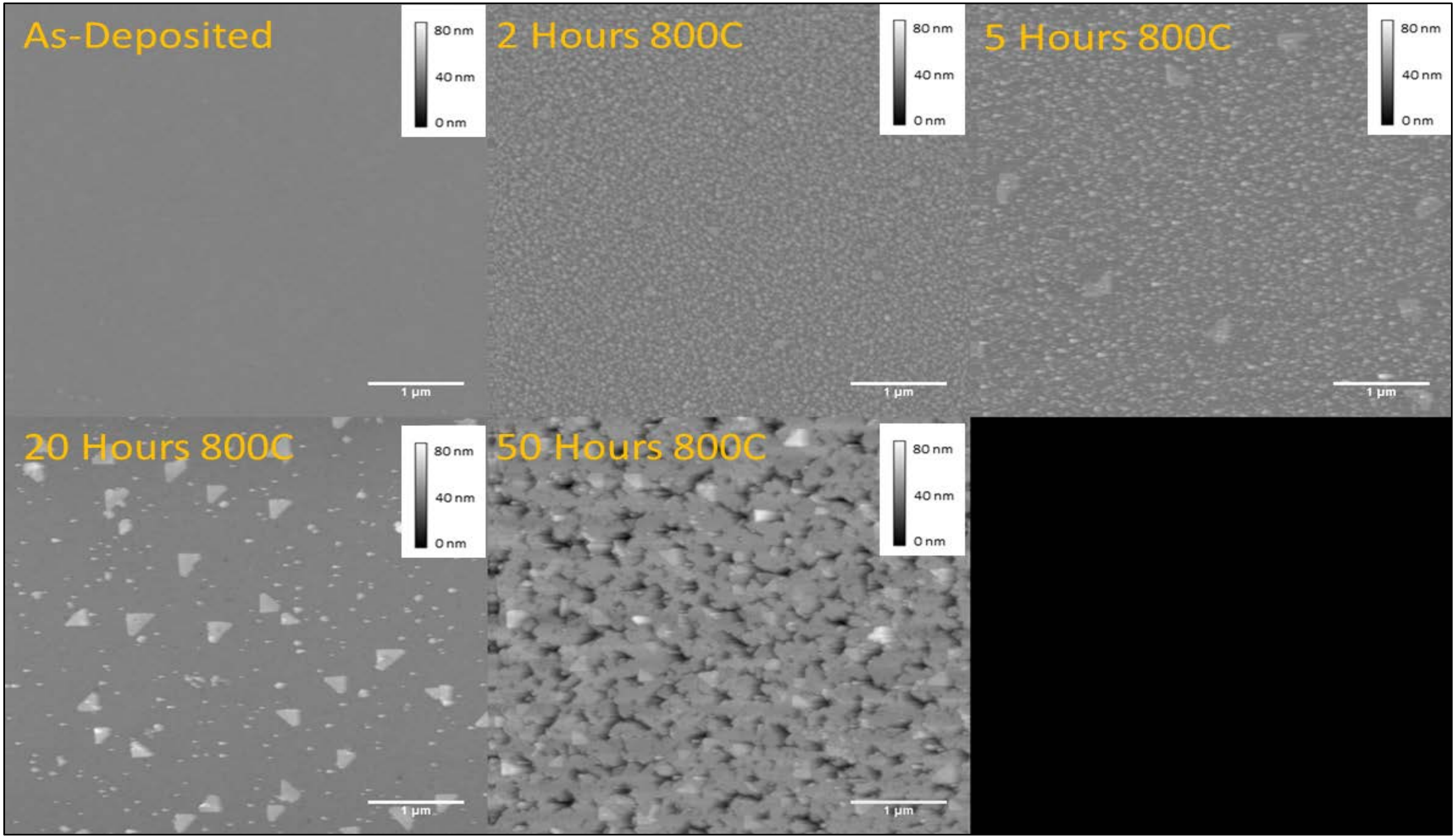
LSCF-7328 – Sr 3d HAXPES Measurements

- Fit Sr 3d to a bulk perovskite and 2 surface peaks (oxide, carbonate).
- Better resolution than LSCF-6428.

	Bulk	Oxide	Carbonate
As deposited	76.1%	9.2%	14.7%
2 Hours	57.6%	20.5%	21.9%
20 Hours	53.6%	21.5%	24.8%
50 Hours	56.9%	19.5%	23.6%



LSCF-7328 Surface Phase Evolution



LSCF Conclusions

- TXRF shows increased surface strontium segregation with time
- AFM shows phase formation at surface
- HAXPES shows different strontium binding environment at surface consistent with SrO, $SrCO_3$ formation
- The amount of surface Sr segregation for $La_{1-x}Sr_xCo_{0.2}Fe_{0.8}O_3$ materials is related to the amount of strontium dopant of the bulk
  - Lowering x from 0.4 to 0.3 reduces, but does not eliminate Sr migration to the surface
- The surface morphology shows significant evolution
  - General roughening, triangular shaped precipitate development, and pore formation appear over longer time scales at temperature

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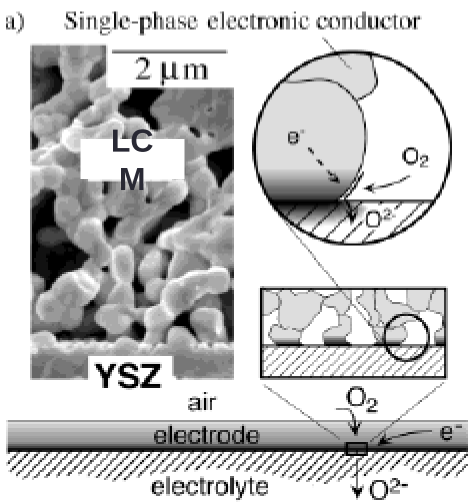
Ongoing Research

- Effect of atmospheric CO_2 partial pressure on surface segregation
- Understand thermodynamics of surface segregation and phase formation based on DFT calculations
- Connect the effect of surface segregation on the ORR reaction by impedance measurements on patterned electrodes

Pathways for Oxygen Reduction Reaction



The "Surface Path"
LCM/LSM

Gas Phase Diffusion

↓

Surface Adsorption

↓

Dissociation

Surface Path:

Surface Diffusion to Triple Phase Boundary (TPB)

↓

Electronation and Incorporation to electrolyte at TPB

Bulk Path:

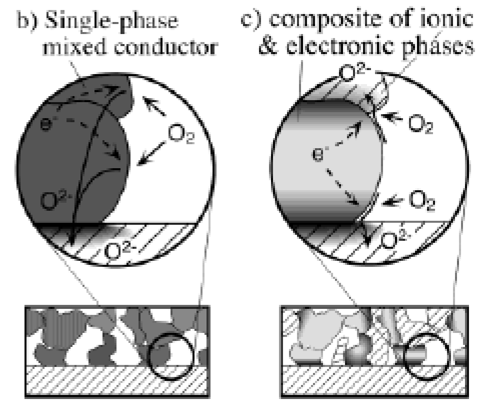
Electronation and Incorporation to cathode

↓

Bulk Diffusion to Electrolyte

↓

Incorporation into Electrolyte

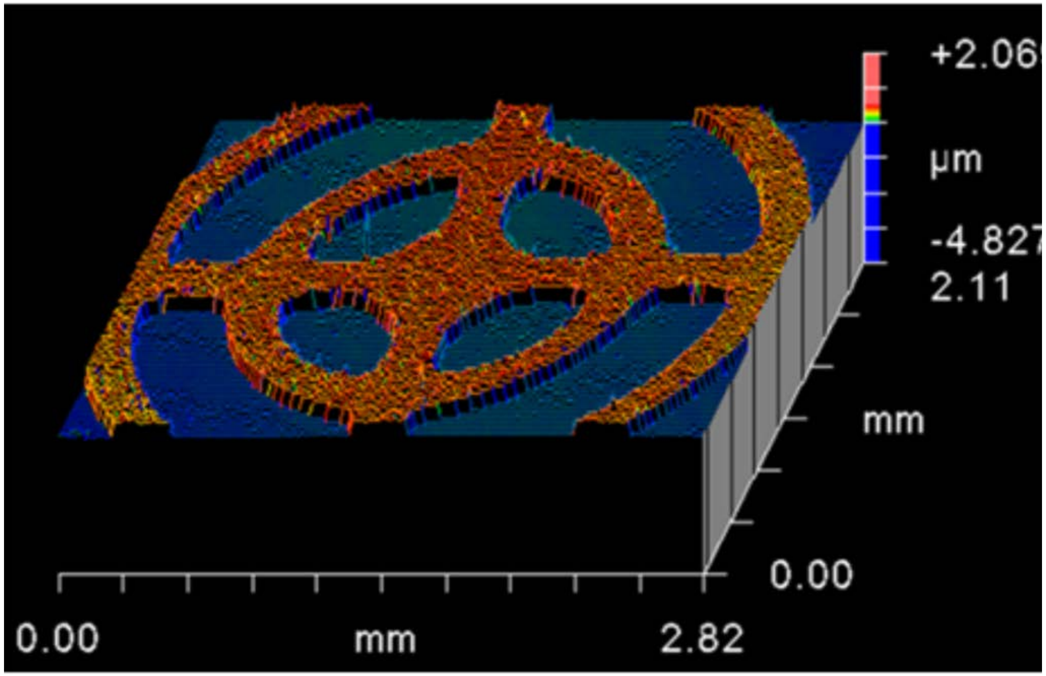


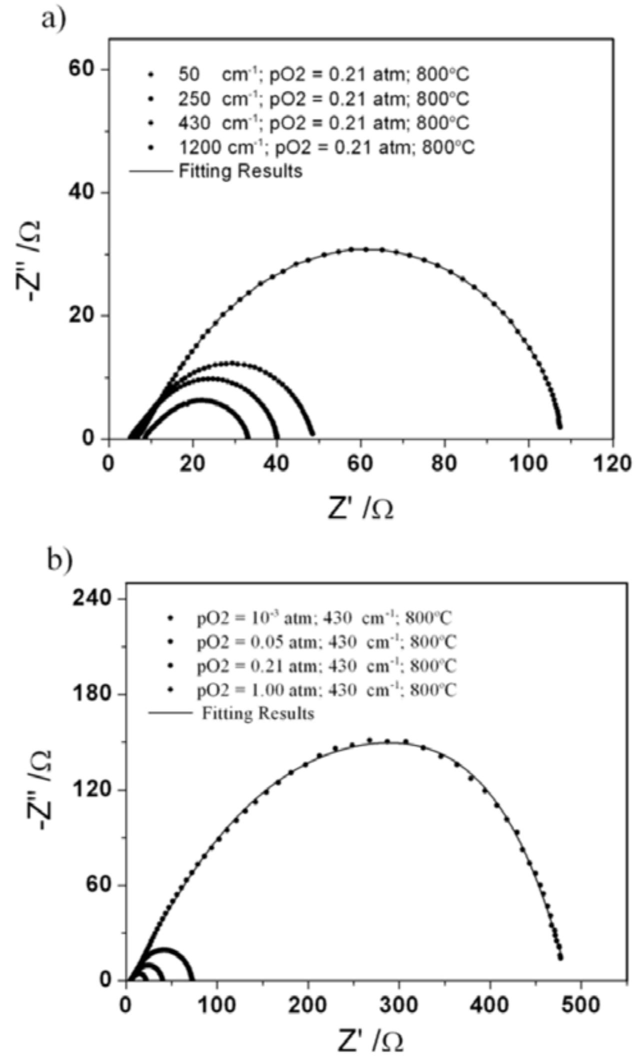
The "Bulk Path"
LSCF-6428

Previous Patterned Electrode Studies

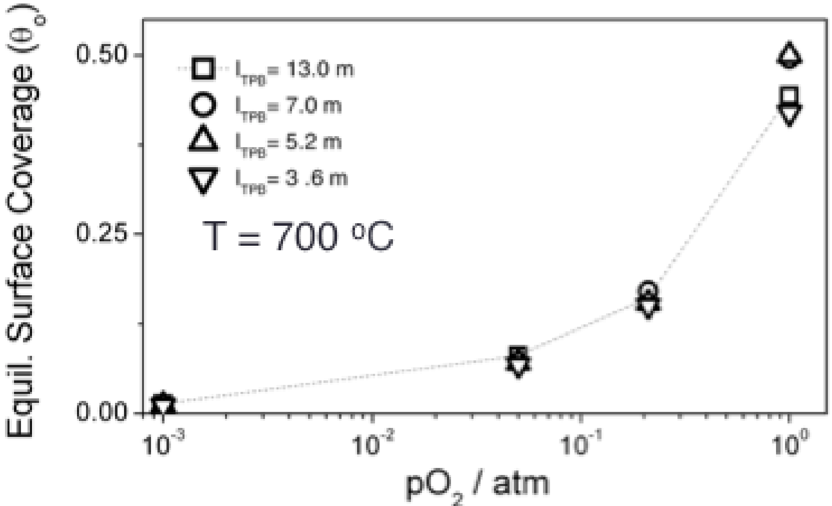
<u>Generated Patterns:</u>

- TPB length = 450 – 1600 cm cm^{-2}
- Cathode/electrolyte area = constant

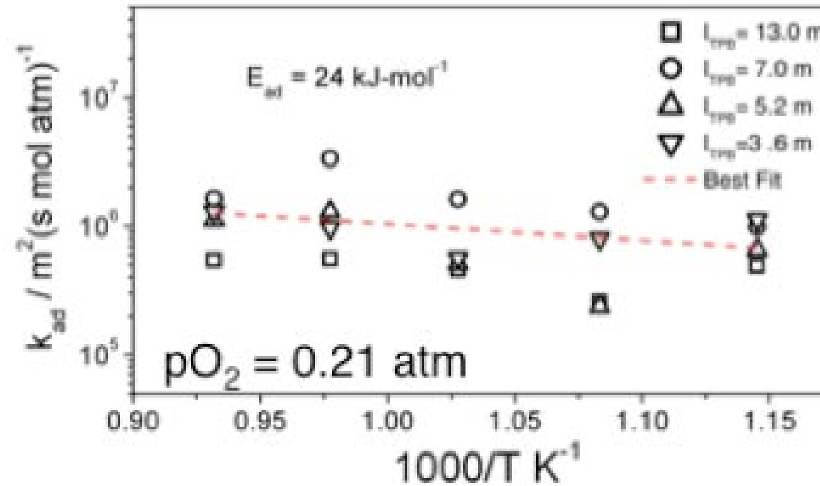




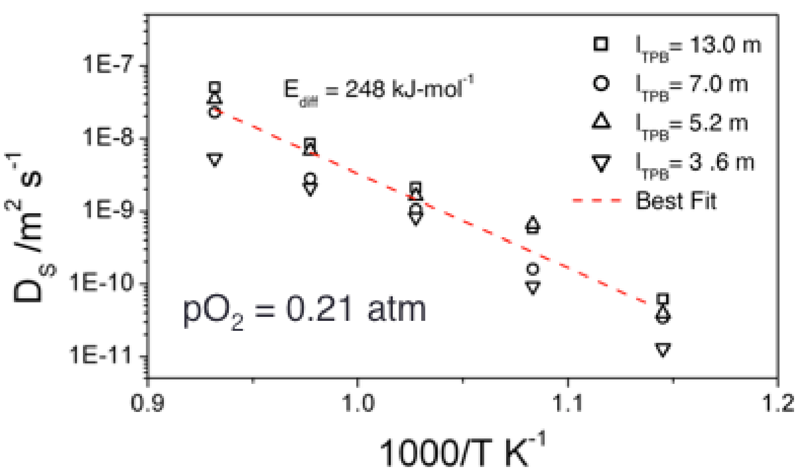
Insight into ORR Mechanism



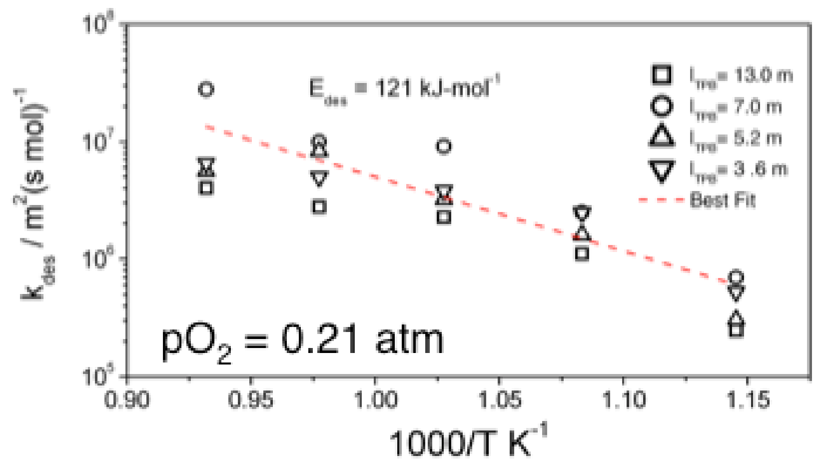
Surface Coverage



Adsorption Constant



Surface Diffusivity



Desorption Constant

How does surface segregation/phase formation affect these constants?

Acknowledgements

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Questions?