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In Situ X-Ray Studies of Segregation and Activity in SOFC Cathode Materials

Paul Fuoss, Tim Fister, Hoydoo You, Kee-Chul Chang, Dillon Fong, Jeff Eastman and Matt Highland
Materials Science Division
Argonne National Laboratory

Brian Ingram
Chemical Sciences and Engineering Division
Argonne National Laboratory

Kavaipatti Balasubramaniam and Paul Salvador
Department of Materials Science and Engineering
Carnegie Mellon University

Principal Results

A-site segregation in SOFC cathode materials including LSM, LSC and LSCF was measured as a function of pO_2, temperature and electrochemical state.

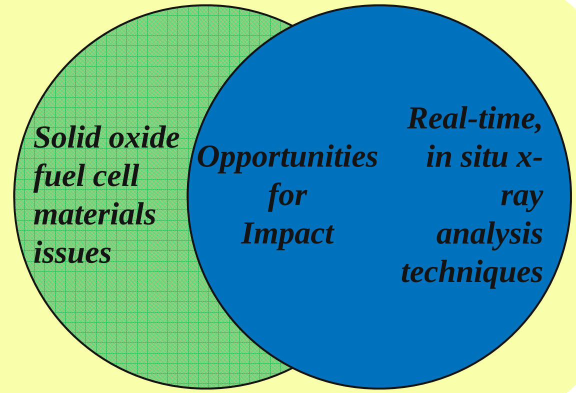
- Strontium surface segregation occurs in (001)-oriented $La_{0.7}Sr_{0.3}MnO_3$ thin films over a wide range of temperatures (25–900ºC) and oxygen partial pressures (pO_2=0.15–150 Torr).
  - The strontium surface concentration increases with decreasing pO_2.
  - A cathodic potential reduces strontium segregation in (110)-oriented LSM films.
- Strong segregation is also found in (001)-oriented LSC and LSCF films
  - little dependence on pO_2.
- The different pO_2 dependence is consistent with much smaller oxygen vacancy gradients in materials with high vacancy mobilities and concentrations.

Overview

- **High Level View**
  - Motivation and Approach
  - Overview of In Situ X-Ray Techniques
- **Film Structure, Composition versus Environment**
- **Chemical and Electronic Structure**
- **Conclusions**

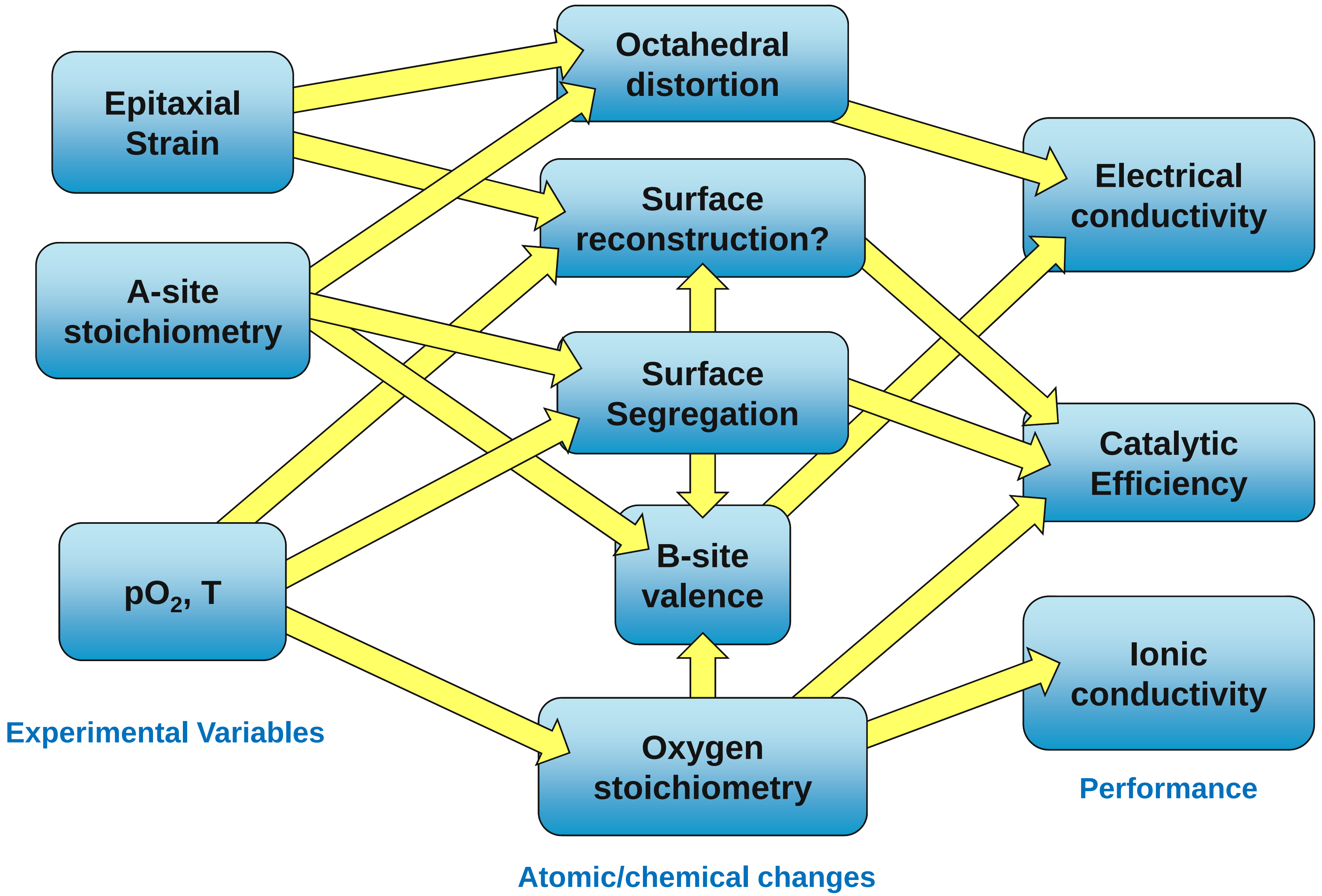
Synchrotron Studies - Goals and Objectives

Develop molecular-level models of SOFC cathode materials to stimulate rational design and development of high-performance cathode materials.

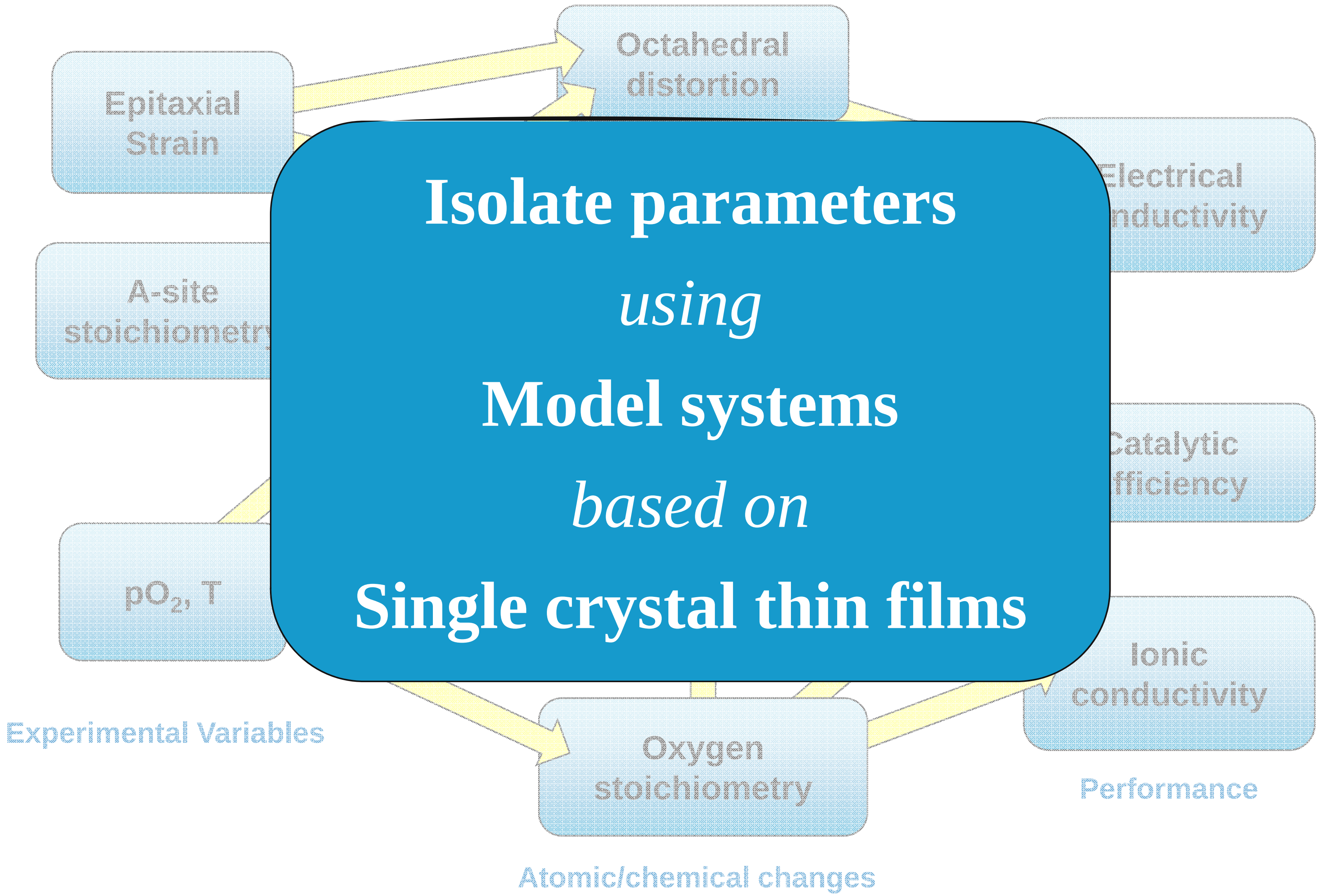


- **In Situ Controlled Atmosphere Studies**
  - Equilibrium structure in controlled atmosphere (e.g. variable pO_2).
  - Identify driving forces for structural and chemical rearrangement
- **In Situ Electrochemical Studies (Hoydoo You - poster yesterday)**
  - Determine dynamic changes of cathode occurring in SOFC half-cell
  - Correlate with equilibrium structures and ex situ measurements
- ***In Situ Studies of Operating Fuel Cells***
  - *Focus on cathode side of fuel cell*
  - *Examine atomic structure and chemical state of individual constituents*
  - *Correlate with ex situ measurements and performance data*

LSM, LSC, LSCF: Complicated Interactions



LSM, LSC, LSCF: Complicated Interactions



Isolate parameters

using

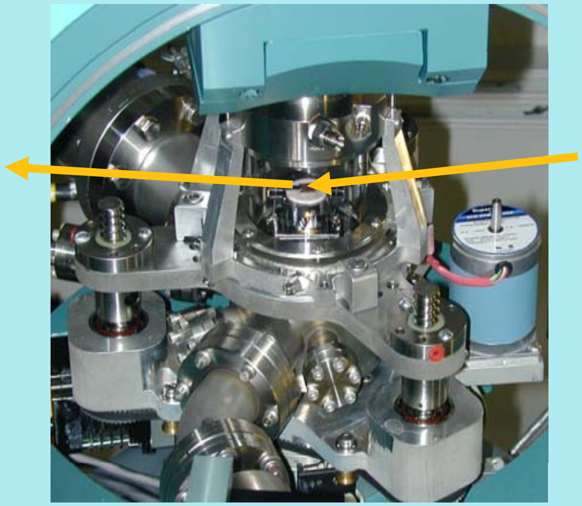
Model systems

based on

Single crystal thin films

Approach

- **LSM, LSC and LSCF epitaxial films grown by Pulsed Laser Deposition (PLD) at Carnegie Mellon University**
  - Growth: 750°C, 50 mTorr O_2, $La_{0.7}Sr_{0.3}MnO_3$, $La_{0.7}Sr_{0.3}CoO_3$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$
  - Cooled in 300 Torr pO_2
  - (001) $SrTiO_3$ (STO), (110) $NdGaO_3$ (NGO) & $DyScO_3$ (DSO) substrates provide different epitaxial strain conditions
  - Yittria-Stabilized Zirconia (YSZ) (111) and (001) single crystal substrates for electrochemical measurements
- **In situ synchrotron x-ray studies**
  - Probes atomic-scale processes during realistic SOFC conditions
  - Studies performed at the Advanced Photon Source
  - Total reflection x-ray fluorescence (TXRF) to determine surface composition
  - Grazing incidence & high angle diffraction to determine surface and film structure



- Portable environmental chamber; mounts on 6-circle diffractometer @ APS Sectors 12 or 20
- Base pressure ~10^{-7} Torr; pO_2 control by precise mixing of purified gases; monitor with RGA
- 24 keV x-rays
- T ≤ 1000°C

Synchrotrons Have Revolutionized X-Ray Analysis

- **The Advanced Photon Source is nine orders of magnitude brighter than laboratory sources.**
- **Brightness has enabled:**
  - Scattering from single layers of atoms
  - Nanometer resolution imaging
  - Realtime, *in situ* measurements from all types of surfaces and ultra-thin films
  - Structure determination of buried interfaces
- **Great potential for advancing understanding of complex industrial processes.**

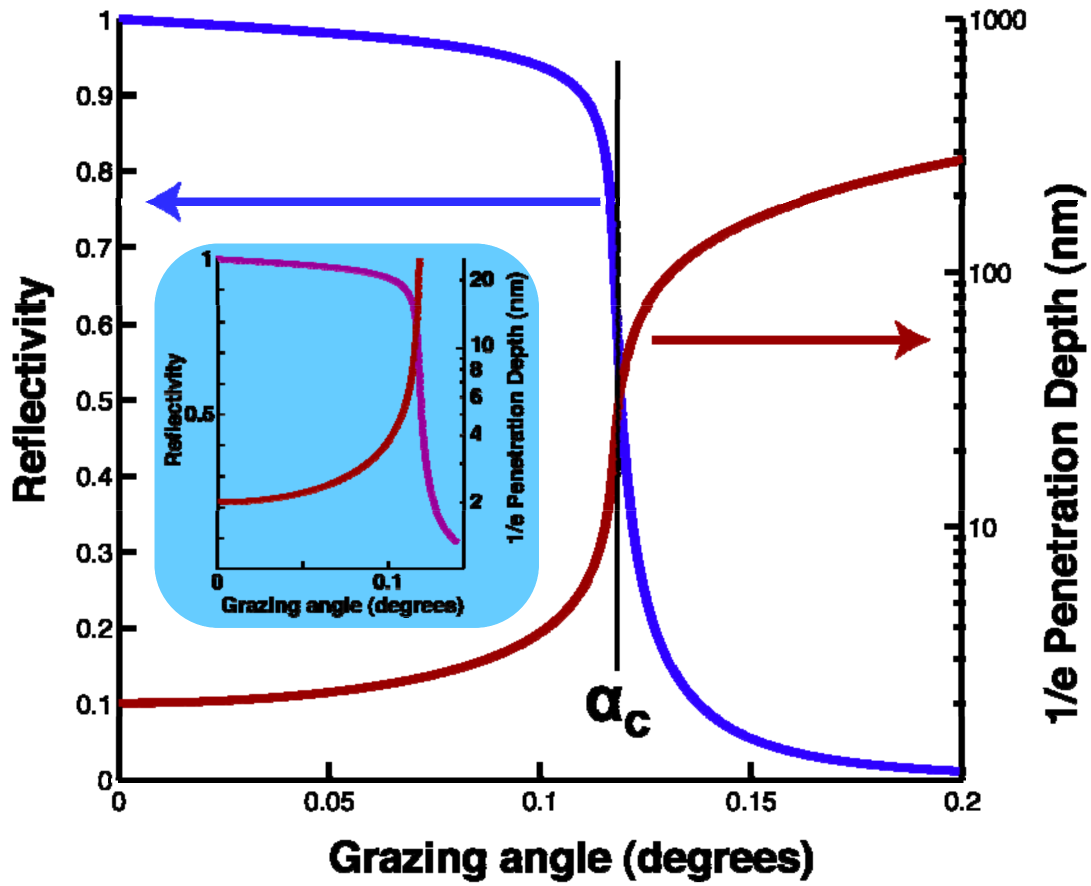
Typical X-Ray Measurements

Example from $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ Studies

- **Composition fluctuations: Strontium surface segregation?**
  - Total reflection x-ray fluorescence (TXRF)
- **Chemistry induced ordering: Surface reconstructions?**
  - Grazing incidence x-ray diffraction
- **Are there structural changes with pO_2?**
  - Diffraction, reflectivity
- **Chemical changes with pO_2?**
  - Resonant scattering techniques
  - X-ray absorption spectroscopy (XANES)

Total Reflection - Making X-rays Surface Sensitive

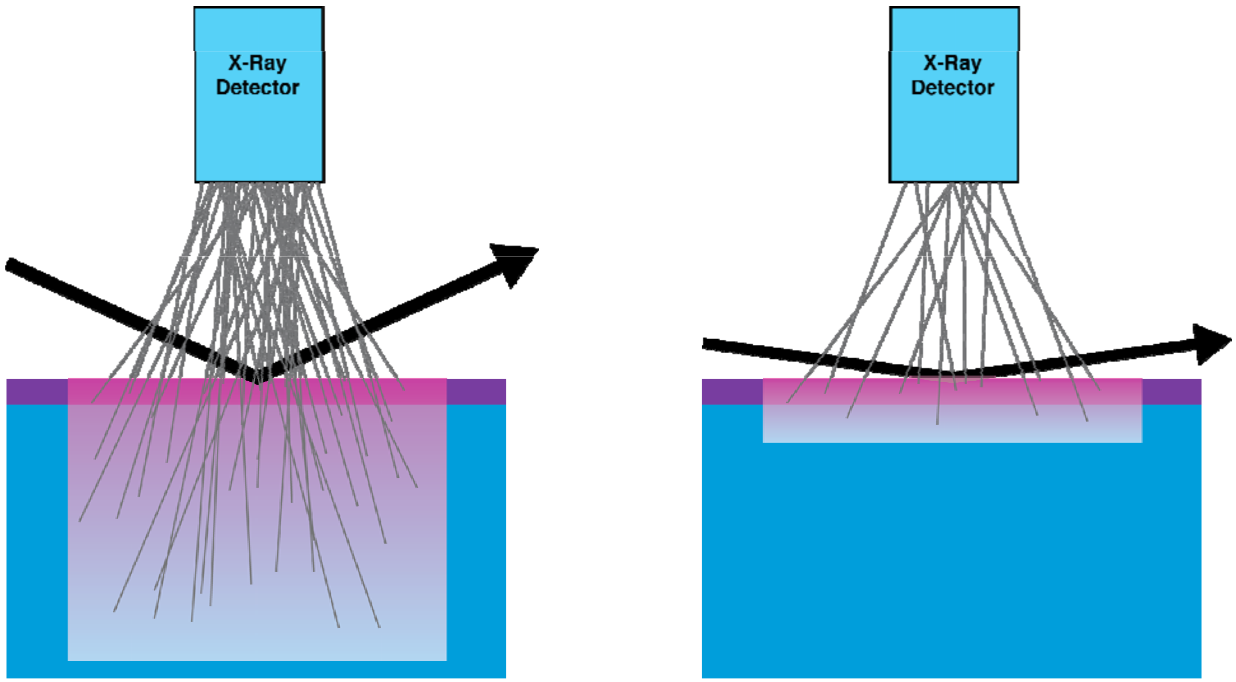
$La_{0.7}Sr_{0.3}MnO_3$ using 24 keV Photons



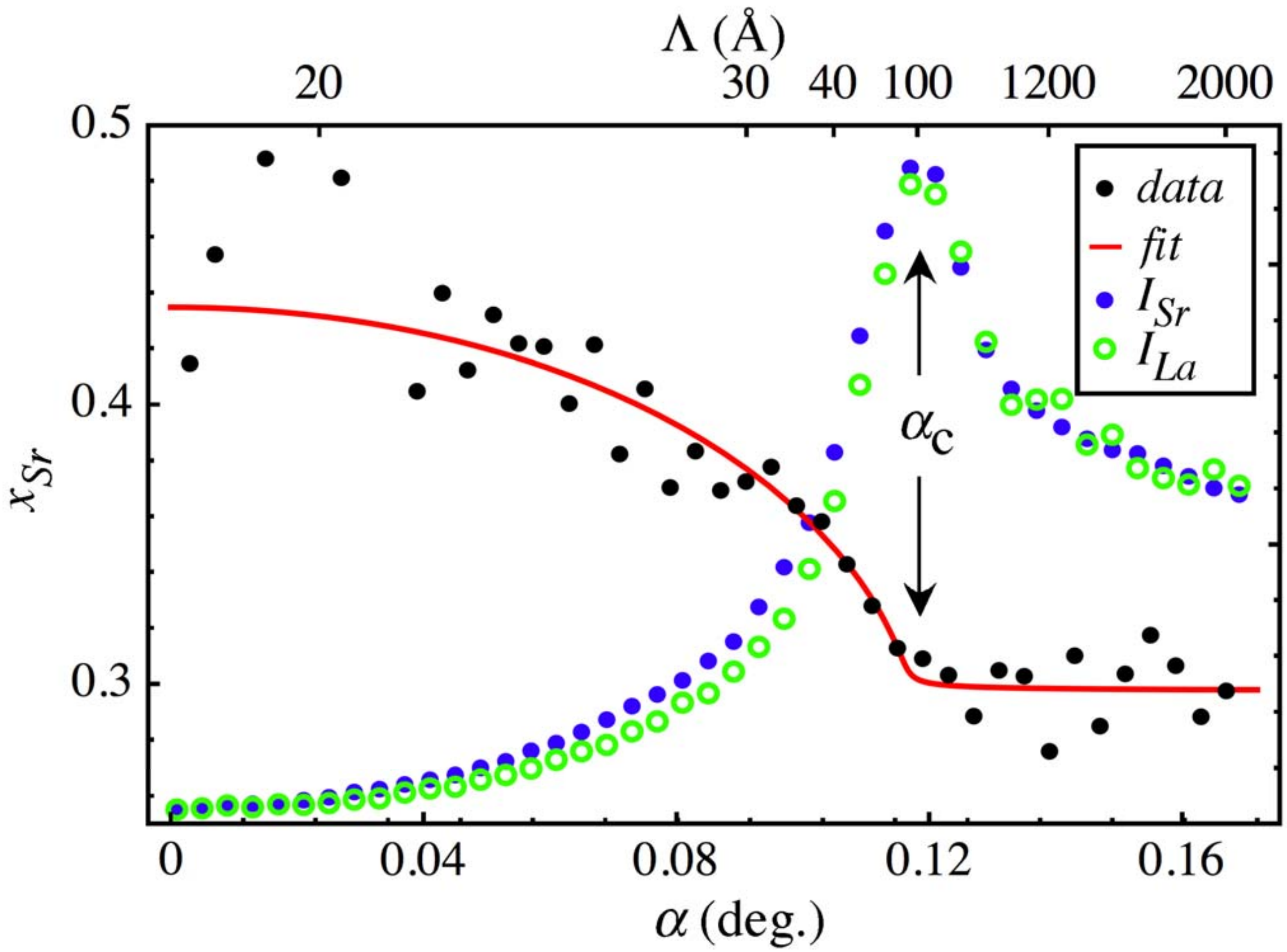
Total Reflection X-Ray Fluorescence (TXRF)

TXRF is a standard technique for analyzing impurities on semiconductor substrates since each element has a standard spectra.

We've extended it to quantitative studies of nanometer composition gradients at surfaces and buried interfaces.



Typical Analysis of TXRF



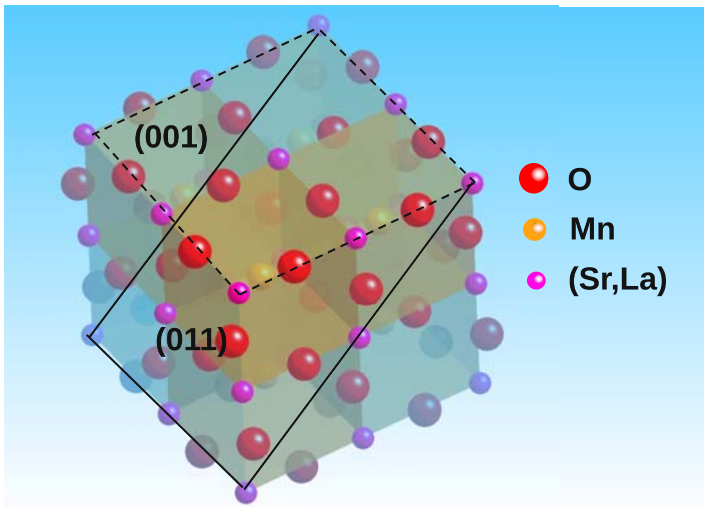
Overview

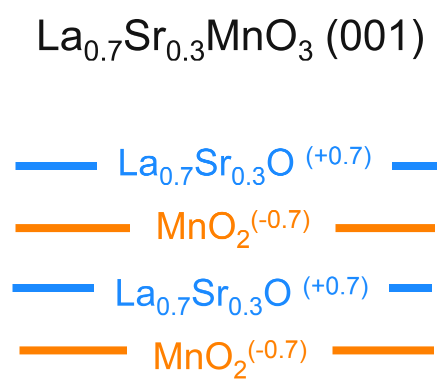
- **High Level View**
- **Film Structure, Composition versus Environment**
  - TXRF Measurements of Surface Segregation
  - Surface Structure
- **Chemical and Electronic Structure**
- **Conclusions and Future Directions**

Why look for segregation?

- **Structure of surfaces are crucial for determining catalytic performance.**
- **$La_{1-x}Sr_xMnO_3$ surfaces tend to be polar.**

LSM Pseudocubic Unit Cell

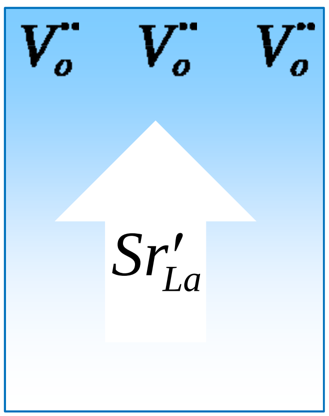


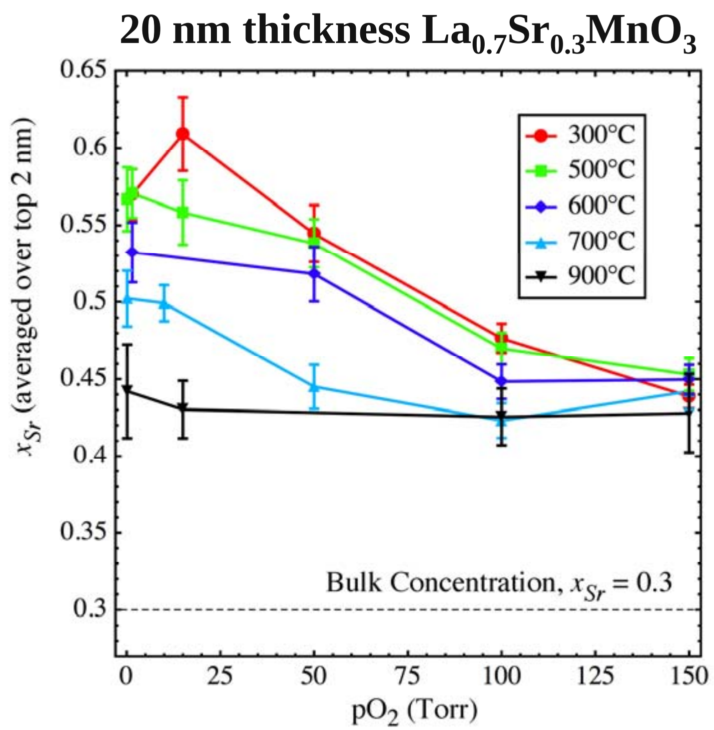


Polar surfaces are not stable!

LSM on DSO: Where we were last year

- **Applied Physics Letters 93, 151904 (2008):**
  - pO_2-dependence in Sr surface segregation
  - Possibly driven by surface oxygen vacancies
  - Possible implications for growth, SOFC performance



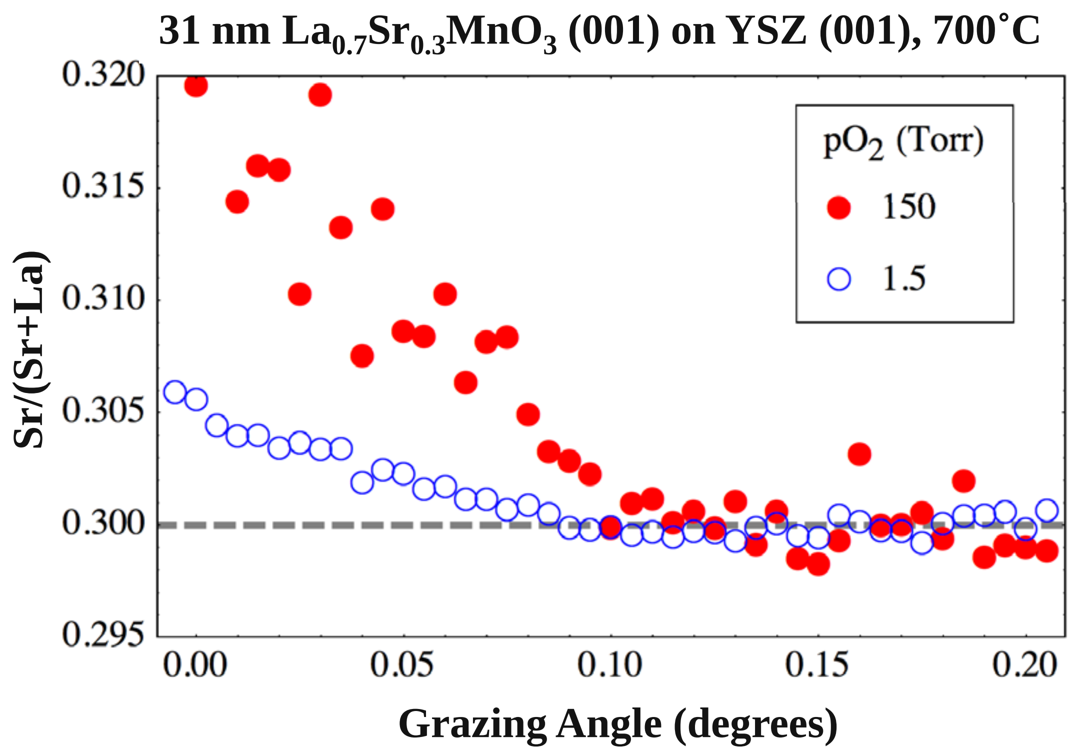


Change in Sr concentration from bulk

	Operating T (700-1000 C)	Low T (300 C)
Low pO_2 (mTorr)	+35%	+50%
Operating pO_2 (atmospheric)	+21%	+25%

$La_{0.7}Sr_{0.3}MnO_3$ on YSZ

- Reduced segregation compared with LSM/DSO
- Grain boundary segregation may limit surface concentration
- pO_2-dependence is opposite



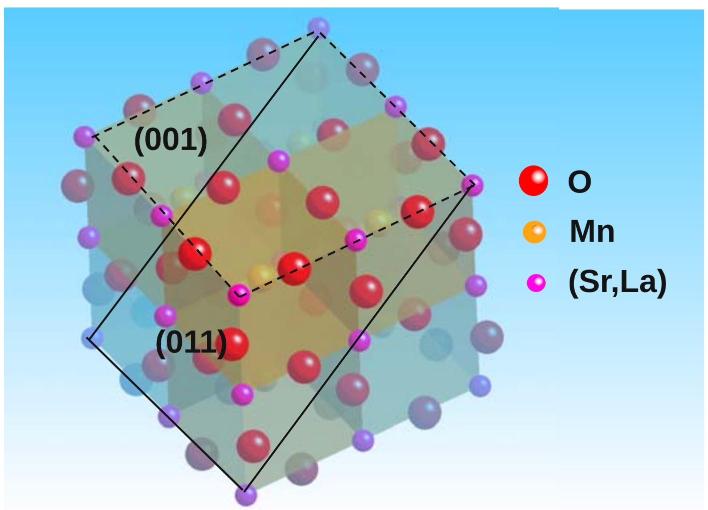
Do more oxygen vacancies in YSZ increase Sr segregation at the YSZ interface?

Orientation Dependence of Segregation

Substrate orientation changes

- film orientation
  - LSM(011) and LSC(011) grow on YSZ(111)
- the degree of epitaxy
- magnitude of surface polarity.

LSM Pseudocubic Unit Cell



$La_{0.7}Sr_{0.3}MnO_3$ (001)

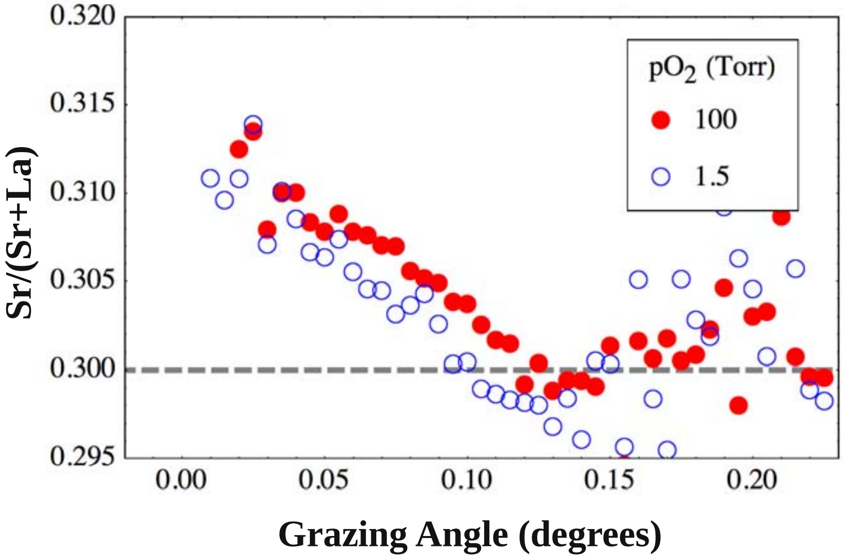
$La_{0.7}Sr_{0.3}O^{(+0.7)}$
$MnO_2^{(-0.7)}$
$La_{0.7}Sr_{0.3}O^{(+0.7)}$
$MnO_2^{(-0.7)}$

$La_{0.7}Sr_{0.3}MnO_3$ (011)

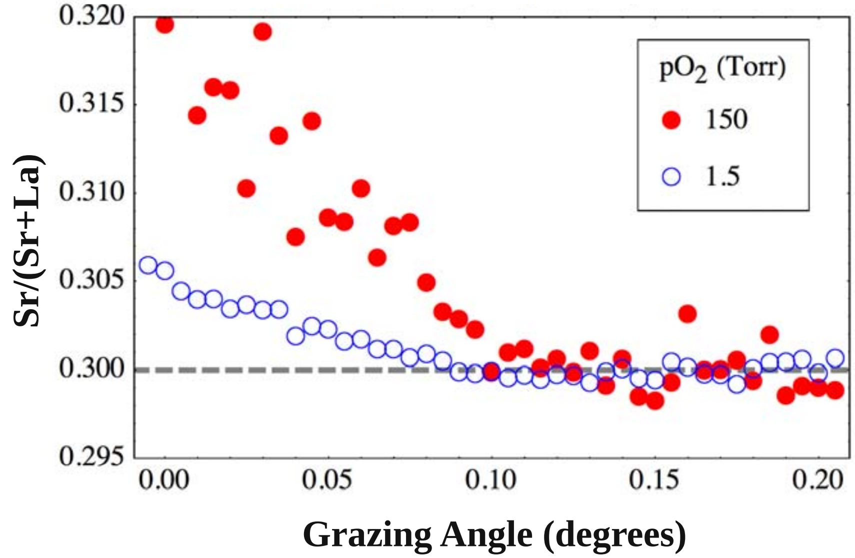
$La_{0.7}Sr_{0.3}MnO^{(+4)}$
$O_2^{(-4)}$
$La_{0.7}Sr_{0.3}MnO^{(+4)}$
$O_2^{(-4)}$

$La_{0.7}Sr_{0.3}MnO_3$ on YSZ: Orientation Dependence

20 nm $La_{0.7}Sr_{0.3}MnO_3$ (110) on YSZ (111)



31 nm $La_{0.7}Sr_{0.3}MnO_3$ (001) on YSZ (001)

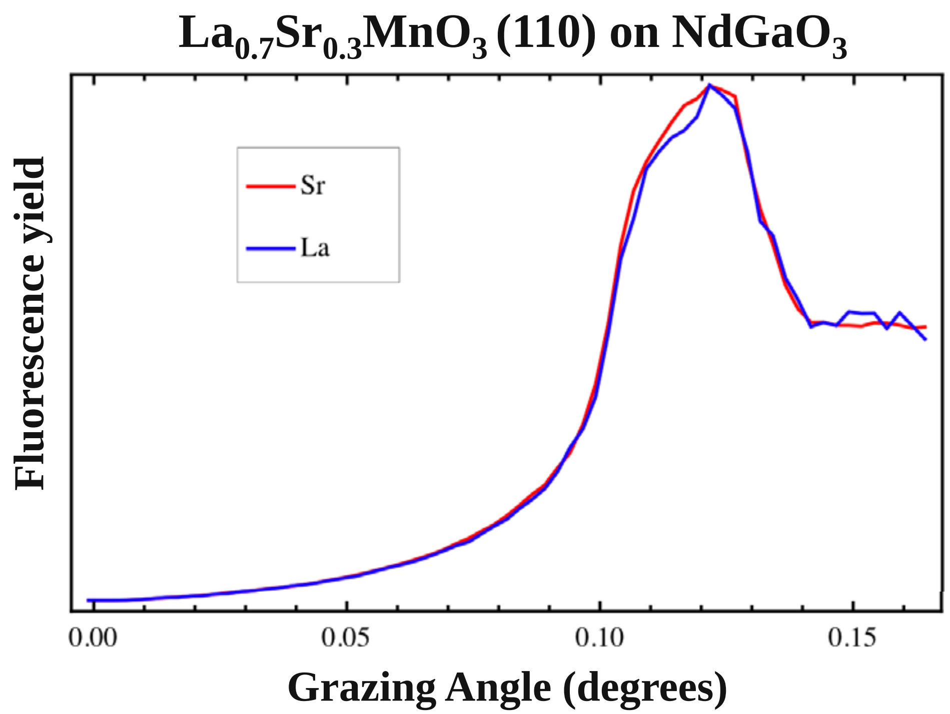


Segregation is observed for both orientations but is not significantly stronger for (110) surface.

Segregation: (110)-oriented $La_{0.7}Sr_{0.3}MnO_3$

- **We found Sr segregation for (100) $La_{0.7}Sr_{0.3}MnO_3$ on $NdGaO_3$**
  - at 700˚C and 300˚C
  - pO_2 = 0.15 – 150 Torr.

- **No evidence for Sr segregation at similar conditions for (110) $La_{0.7}Sr_{0.3}MnO_3$ on $NdGaO_3$**

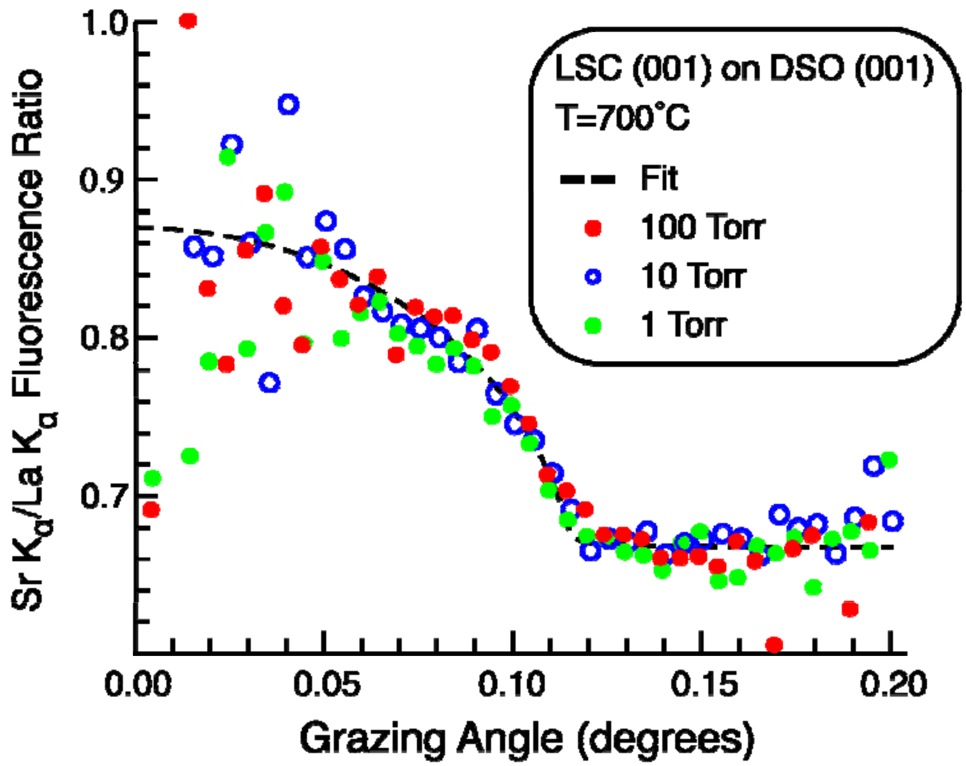


Do other mechanisms (perhaps reconstructions) start compensating the polarity?

$La_{0.6}Sr_{0.4}CoO_3$ (001) on $DyScO_3$

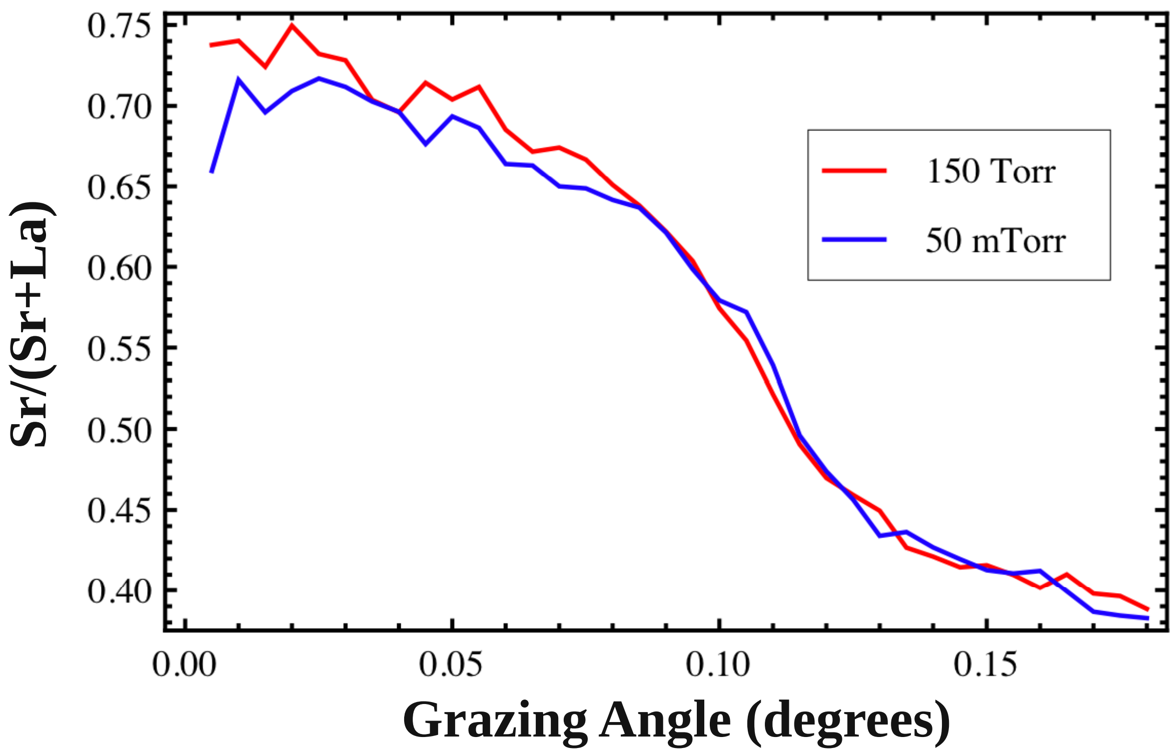
Strontium segregation

- Similar to LSM/DSO in magnitude
- No pO_2 dependence at this relatively high temperature.



Strontium concentration approaches 50% at the near surface. Will this high concentration drive oxygen vacancy ordering?

LSCF (001) Surface Segregation



- Segregation larger than LSC/DSO measured at 700˚C
- No apparent pO_2-dependence

Summary so far

- **Strontium segregation is usually found**
  - but there is evidence of other mechanisms suppressing segregation in a few cases

- **The pO_2 dependence is correlated with the ability of the film to support an oxygen vacancy gradient**

Are there other changes in surface structure that play an important role?

Overview

- **High Level View**

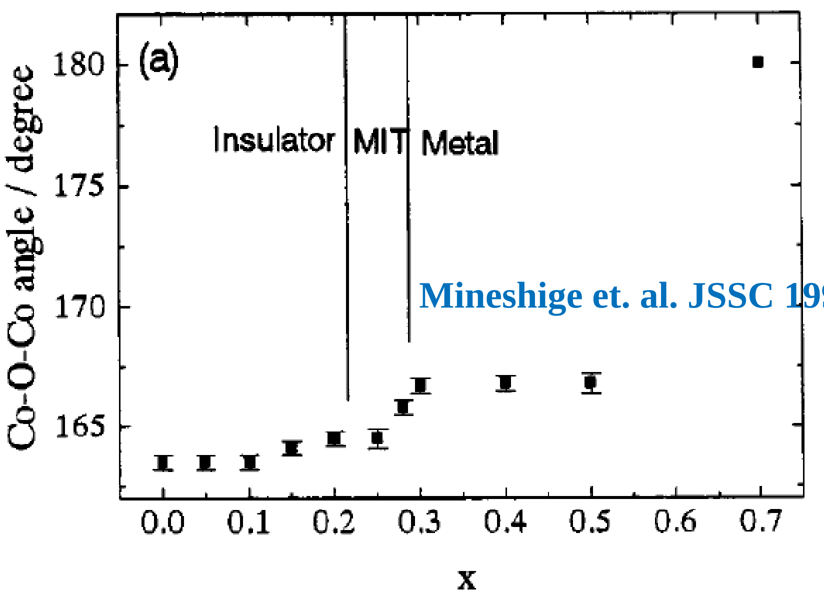
- **Film Structure, Composition versus Environment**
  - TXRF Measurements of Surface Segregation
  - Surface Structure

- **Chemical and Electronic Structure**

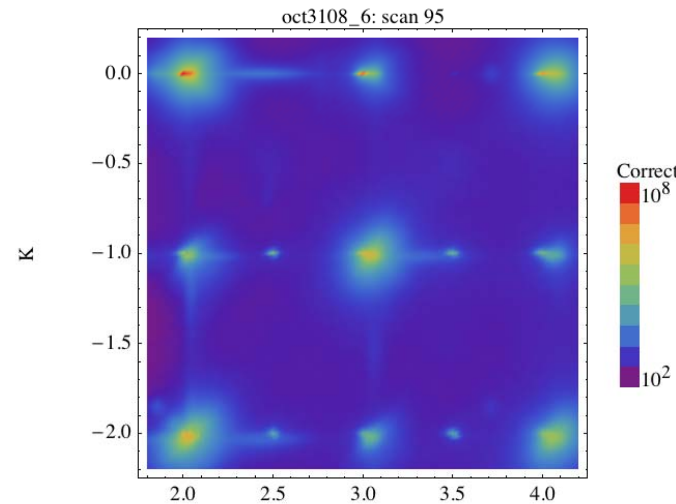
- **Next Steps and Directions**

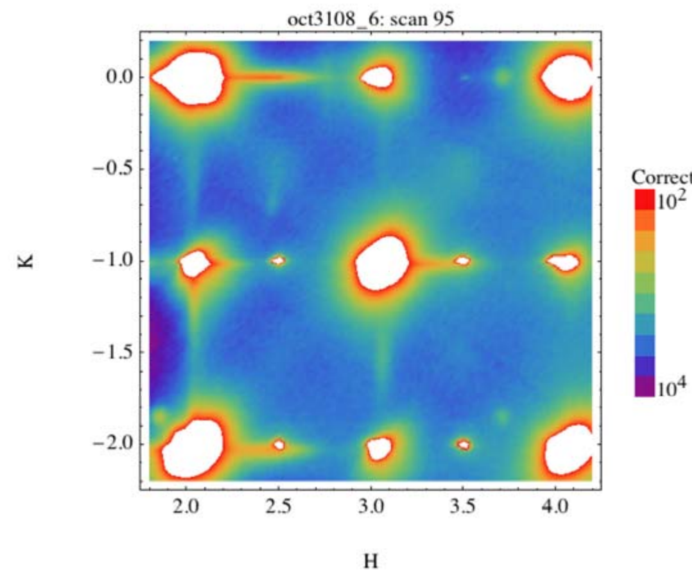
$La_{0.6}Sr_{0.4}CoO_3$ on $DyScO_3$ (110)

- **Search for reconstructions**
- **Strength of ½ order peaks related to degree of CoO_6 octahedral tilting. (related to O 2p/Co 3d overlap).**
  – Octahedral tilting in LSCO corresponds to electronic conductivity



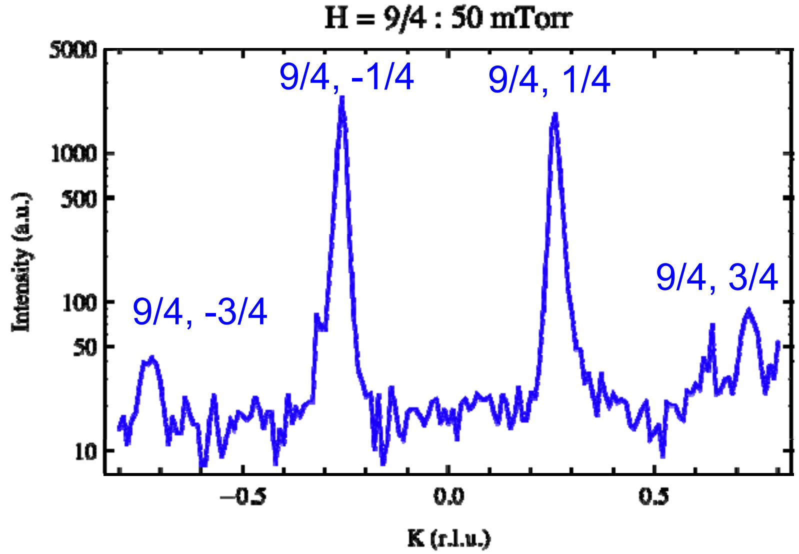
Mineshige et. al. JSSC 1999

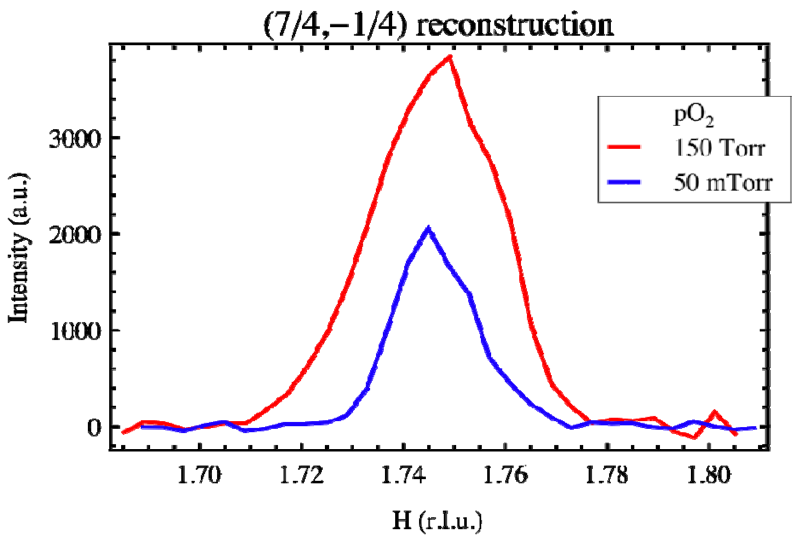


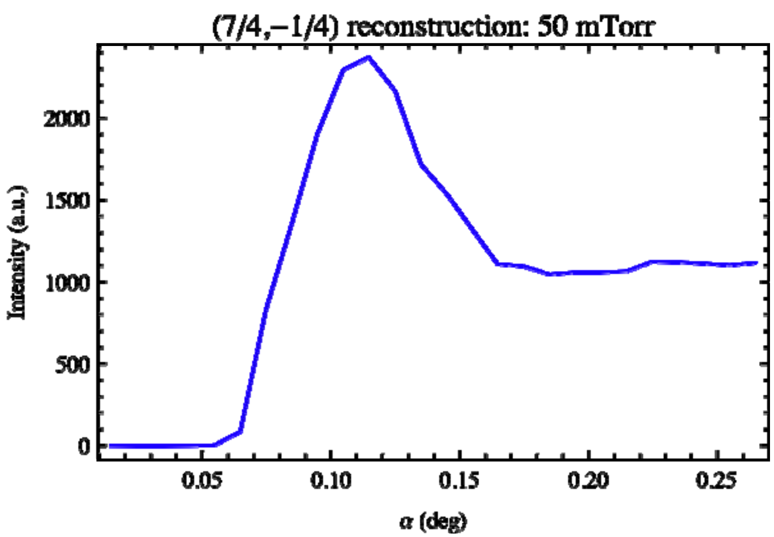


LSCF surface structure: reconstructions

- Superlattice peaks present at quarter order positions (but not half)
- Intensities of superlattice peaks are dependent on pO_2.
- Preliminary results, more data needed to determine structural parameters.





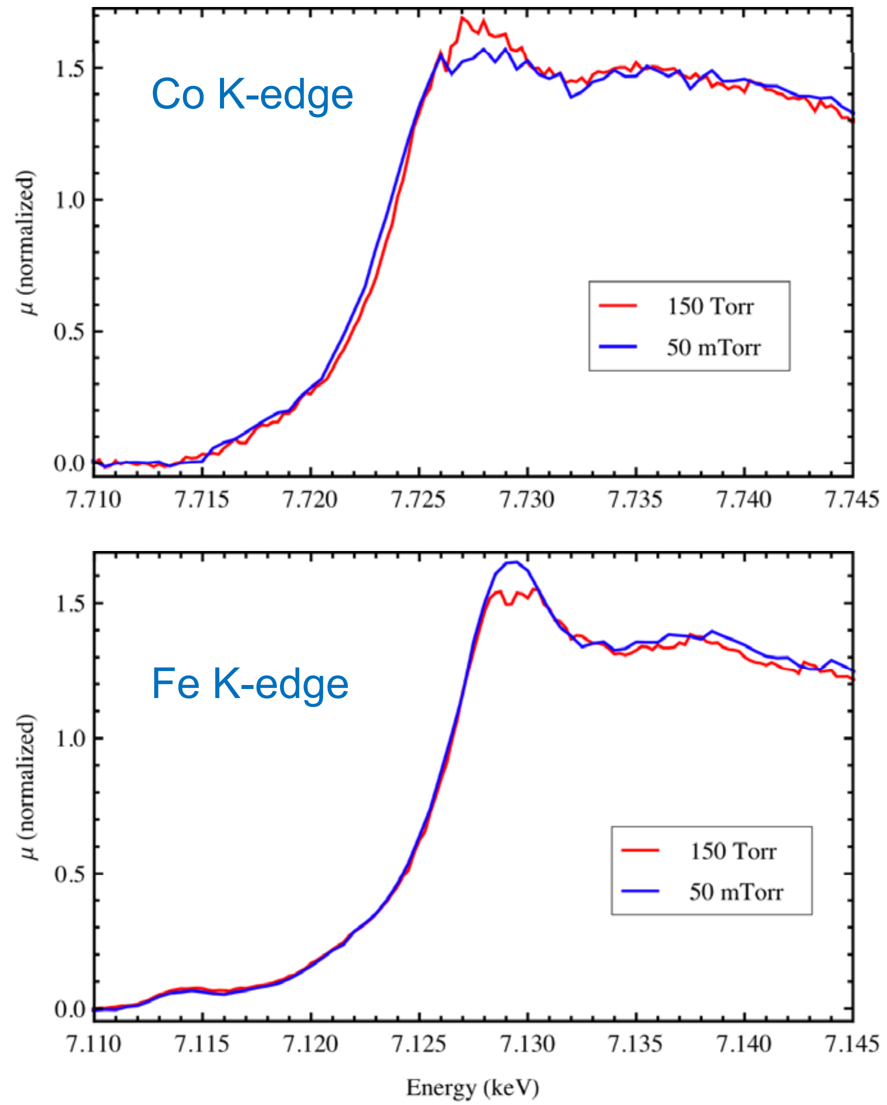


Overview

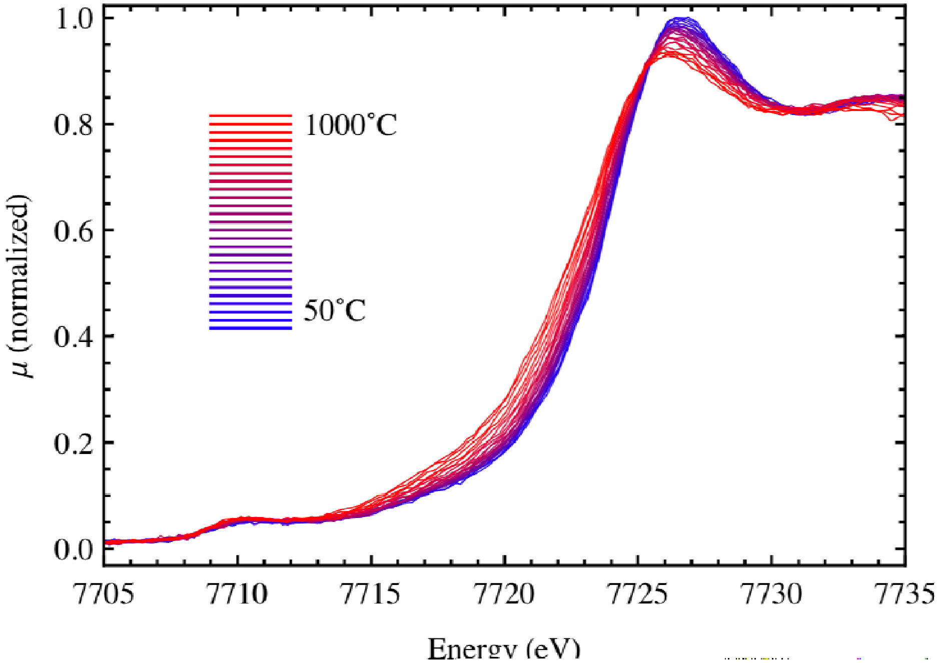
- **High Level View**
- **Film Structure, Composition versus Environment**
- **Chemical and Electronic Structure**
  - X-Ray Absorption Near Edge Structure (XANES)
  - ~~*Total Reflection Inelastic X-Ray Scattering (TRIXS)*~~
  - ~~*Resonant Anomalous X-Ray Reflectivity (RAXR)*~~
- **Summary and Conclusions**

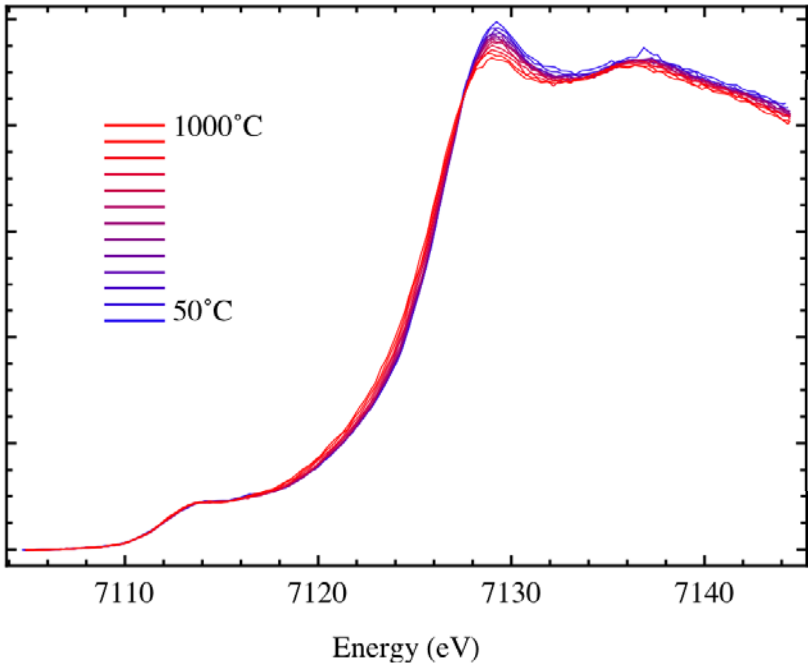
Measuring the local defect chemistry of LSCF

- **Goal: Correlate B-site oxidation state with vacancy concentrations**
  - T = 25-1000˚C. Measure bulk $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ in air and flowing argon
  - Measure changes in Fe and Co oxidation state with XANES
  - Measure local oxygen vacancy concentration by changes in oxygen coordination from Co and Fe EXAFS (number of nearest neighbors)
- **Question: Do oxygen vacancies prefer to sit adjacent to cobalt sites?**



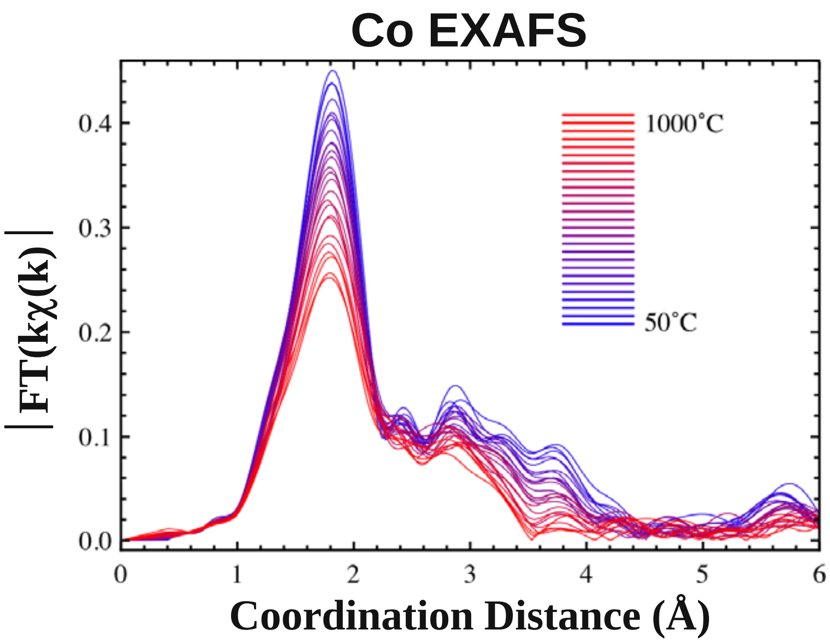
B-site reduction: Co vs. Fe XANES

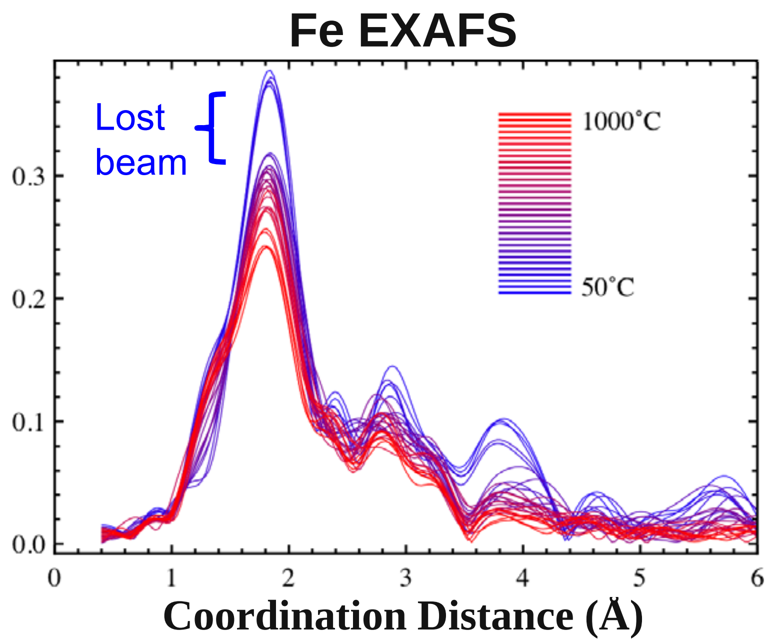




- **Shown: 9 hour ramp from 50 to 1000˚C in flowing argon.**
- **Negative edge shift indicates increasing reduction during heating.**
- **Much larger edge shift in Co edge than Fe K-edge**
  - Co preferentially reduces

B-site coordination





- **Decrease in first shell amplitude with temperature**
  - Due thermal disorder and, possibly, drop in coordination
  - No significant change in (Co,Fe)-O bond length
  - Thermal Debye Waller factors can be fit using T-dependence
- **Assuming similar thermal Debye-Waller factors, cobalt sees a larger drop in coordination**
  - consistent with higher local oxygen vacancy concentration at Co site

Summary of Principal Results

- **Strontium surface segregation occurs in (001)-oriented $La_{0.7}Sr_{0.3}MnO_3$ thin films over a wide range of temperatures (25–900ºC) and oxygen partial pressures (pO_2=0.15–150 Torr).**
  - The strontium surface concentration increases with decreasing pO_2.
  - A cathodic potential reduces strontium segregation in (110)-oriented LSM films.
- **Strong segregation is also found in (001)-oriented LSC and LSCF films**
  - little dependence on pO_2.
- **The different pO_2 dependence is consistent with much smaller oxygen vacancy gradients in materials with high vacancy mobilities and concentrations.**
- **Oxygen vacancies in LSCF appear to be preferentially associated with cobalt sites.**
  - defect models should account for this possibility

Acknowledgements

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We'd like to thank Wayne Surdoval and Briggs White of NETL for important discussions of SOFC science and technology.

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The End