Synchrotron X-Ray Studies of SOFC Cathodes

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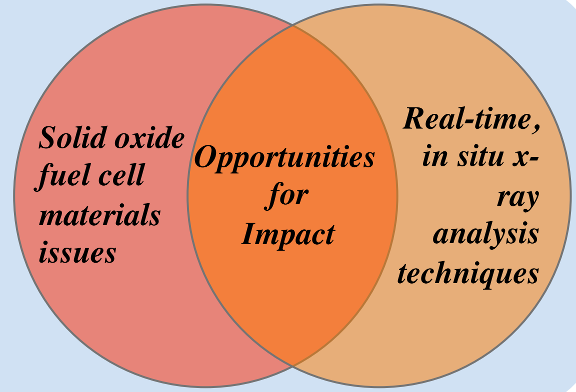
Overview

- **Background**
- Strontium Segregation Studies
- LSCF Reconstructions
- Lattice Parameter, Conductivity and Overpotential
- Plans for the Future

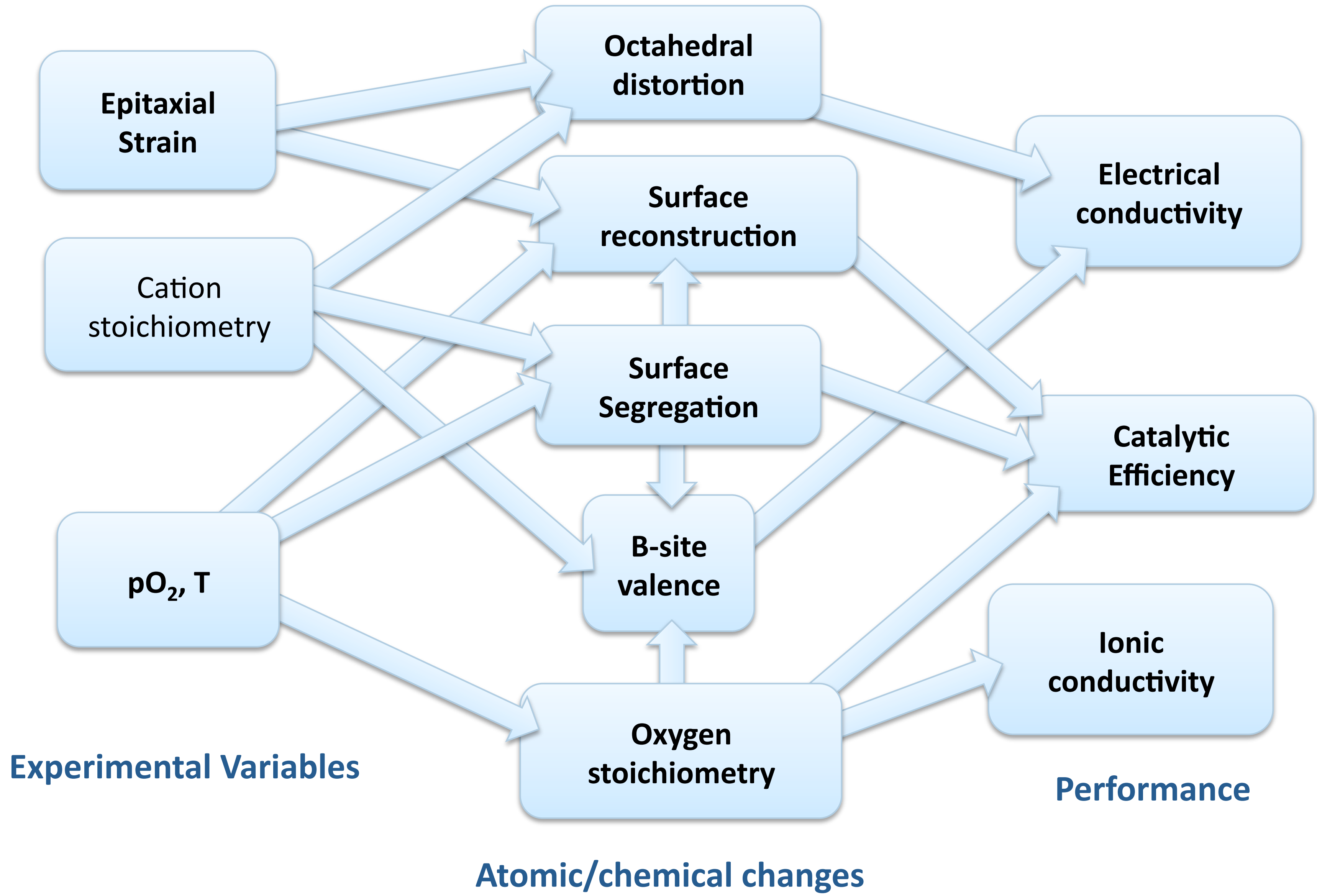
Synchrotron Studies - Goals and Objectives

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



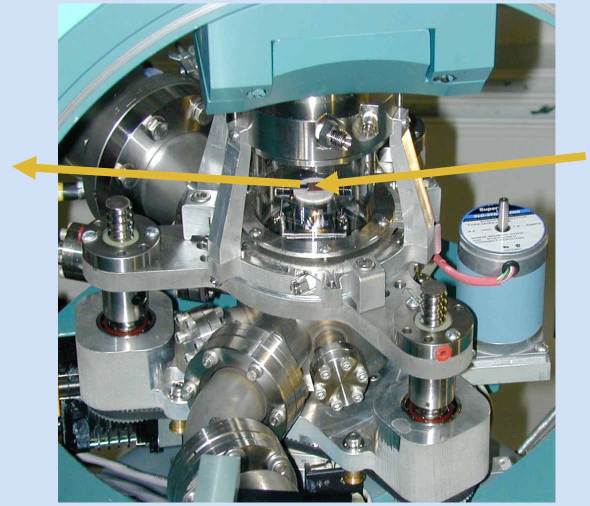
- **In Situ Controlled Atmosphere Studies**
  - Equilibrium structure in controlled atmosphere (e.g. variable pO_2).
  - Identify driving forces for structural and chemical rearrangement
- **In Situ Electrochemical Studies**
  - Determine dynamic changes of cathode occurring in SOFC half-cell
  - Correlate with equilibrium structures and ex situ measurements
- **Bridging between Synchrotron Measurements and Fuel Cells**
  - Compare model systems with “real” systems
  - Correlate with ex situ measurements and performance data

Correlate performance with atomic-scale processes



Approach

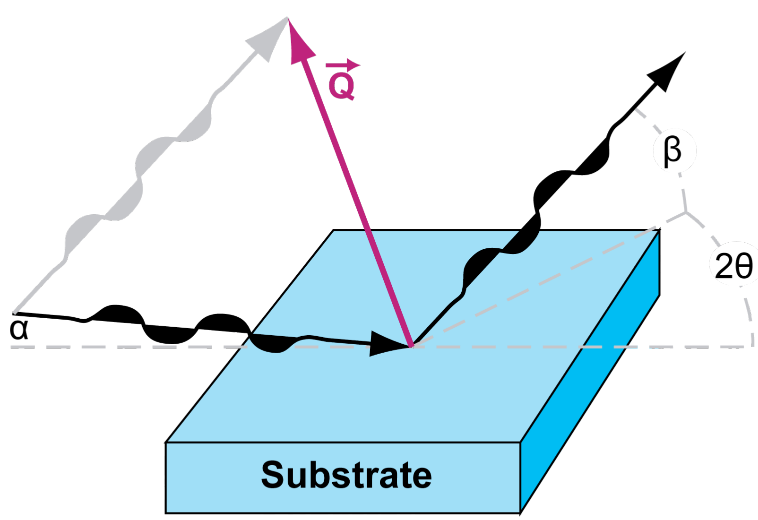
- LSM, LSC and LSCF epitaxial films grown by Pulsed Laser Deposition (PLD) at Carnegie Mellon University
  - Growth: 750°C, 50 mTorr O_2, $La_{0.7}Sr_{0.3}MnO_3$, $La_{0.7}Sr_{0.3}CoO_3$ and $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$
  - Cooled in 300 Torr pO_2
  - (001) $SrTiO_3$ (STO), (110) $NdGaO_3$ (NGO) & $DyScO_3$ (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

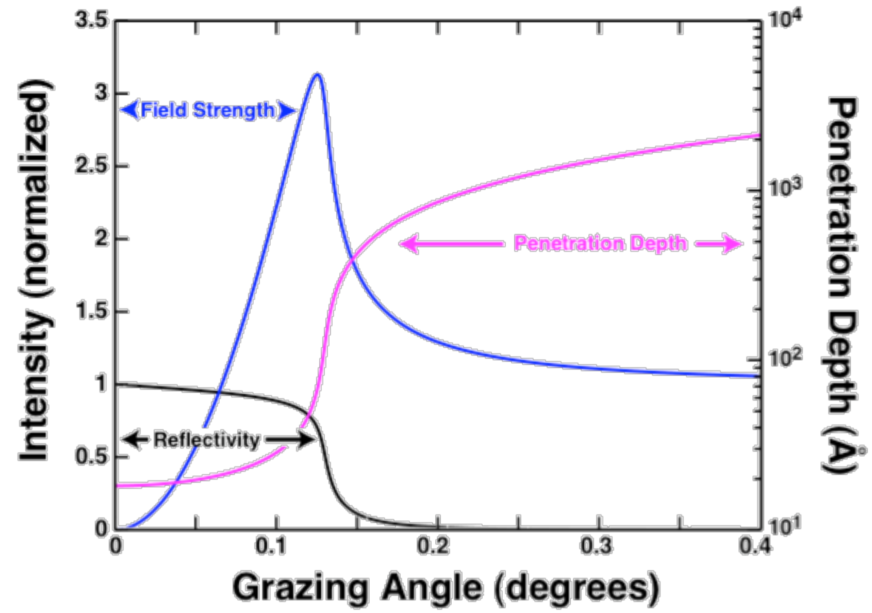


- Portable environmental chamber; mounts on 6-circle diffractometer @ APS Sectors 12 or 20
- Base pressure ~10^{-7} Torr; pO_2 control by precise mixing of purified gases; monitor with RGA
- 24 keV x-rays
- T ≤ 1000°C

X-Rays, Grazing Incidence and Surface Sensitivity

Penetration depth is tunable from ≈20Å to microns





Couple grazing incidence with x-ray scattering and spectroscopy techniques to create surface sensitivity.

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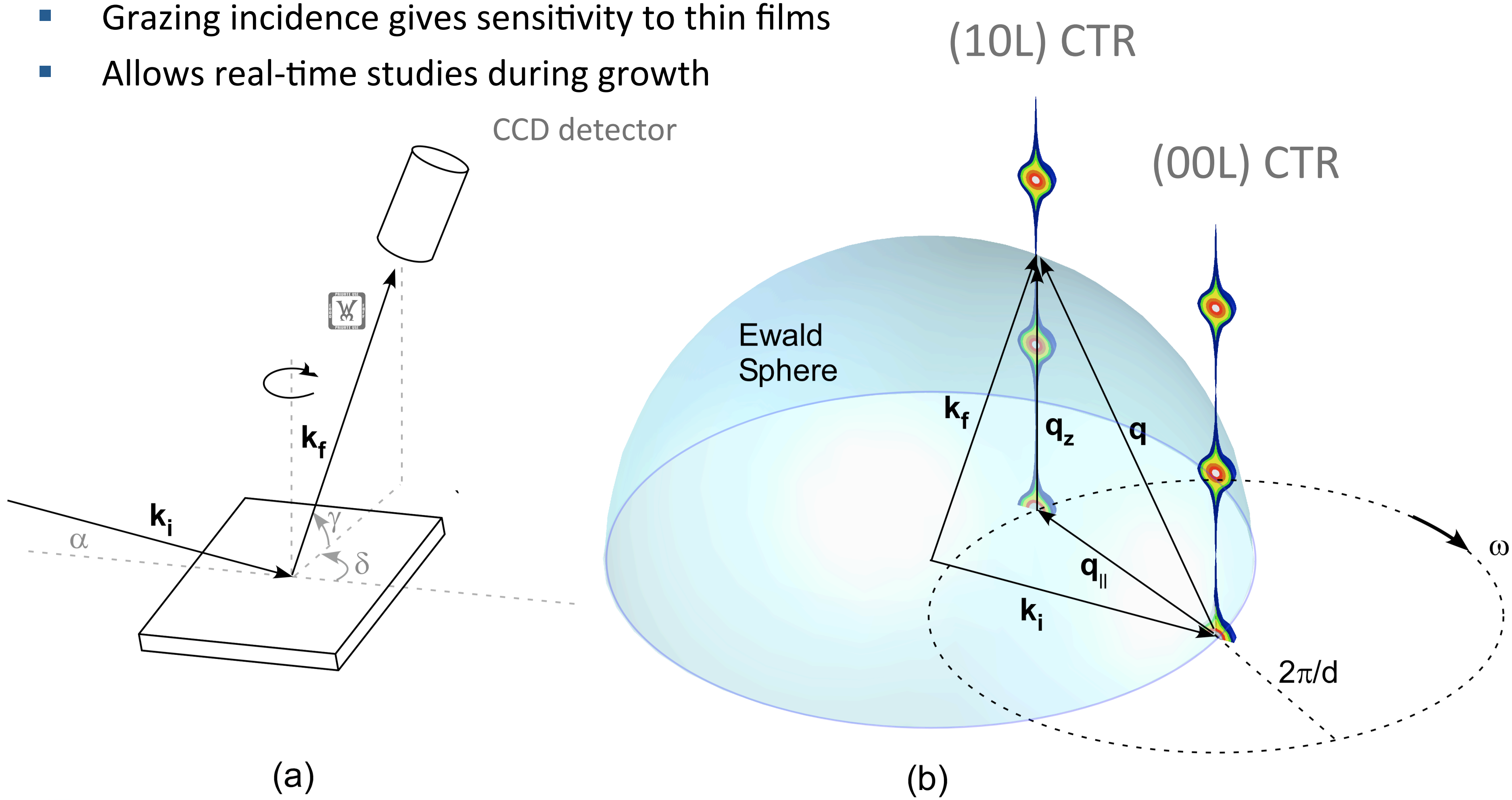
Reciprocal Space Mapping using Grazing-Incidence Scattering

- Use area detector and repeated theta scans to rapidly map reciprocal space volumes (e.g. 30 seconds per map)
- Grazing incidence gives sensitivity to thin films
- Allows real-time studies during growth



Typical X-Ray Measurements

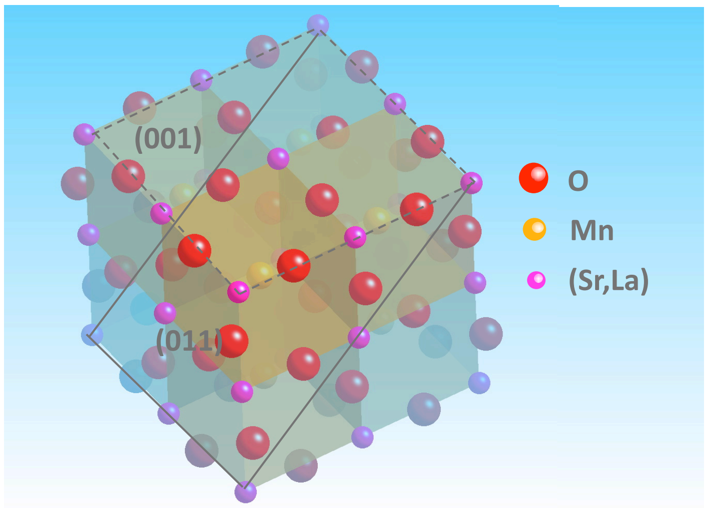
Example from $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ Studies

- **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)**

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



La0.7Sr0.3MnO3 (001)

Polar surfaces are not stable!

Strontium surface segregation: previous results

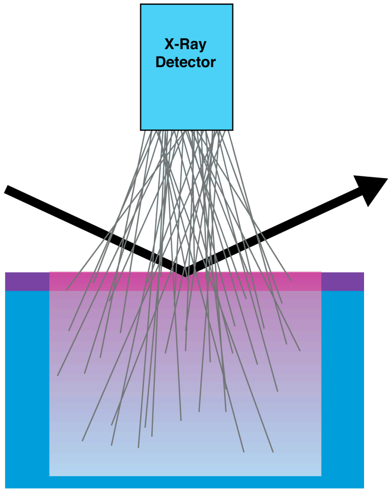
- **Multiple reports of strontium surface segregation in LSMO using UHV techniques.**
  (Bertacco Sur. Sci. 2002; Dulli et. al. PRB, 2001; Caillol et. al. App. Sur. Sci. 2007; de Jong et. al. J. App. Phys. 2003; Kumigashira et. al. APL 2003; Ponce App. Cat. B 2000; Wu et. al. J. Phys. D 2007)

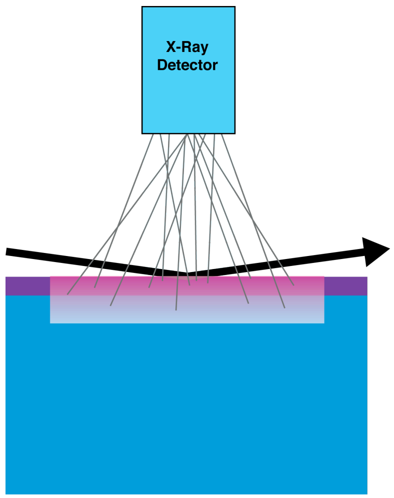
- **Some reports of concurrent Mn valence change near surface.**
  (de Jong et. al. PRB 2005, 2007)

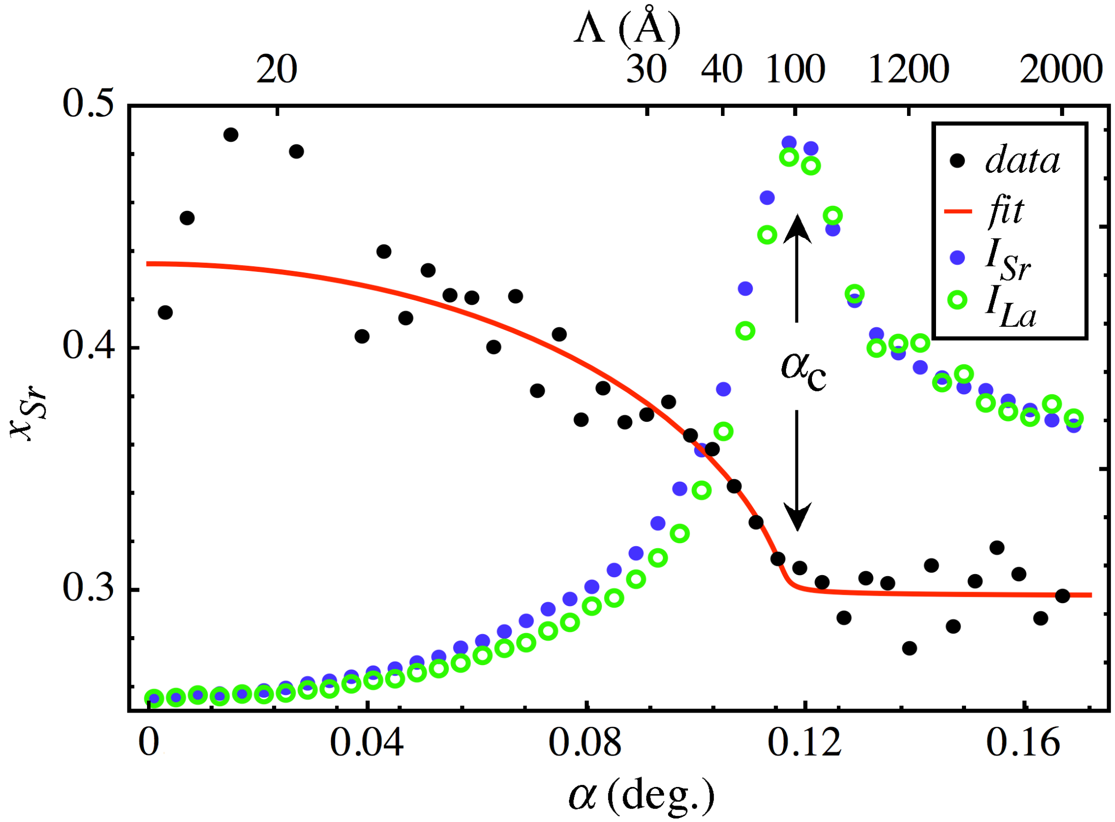
- **Recent room-temperature diffraction by Herger et. al. (PRB, 2007) confirms this picture.**

All of these measurements were done in non-equilibrium conditions.

Total Reflection X-Ray Fluorescence

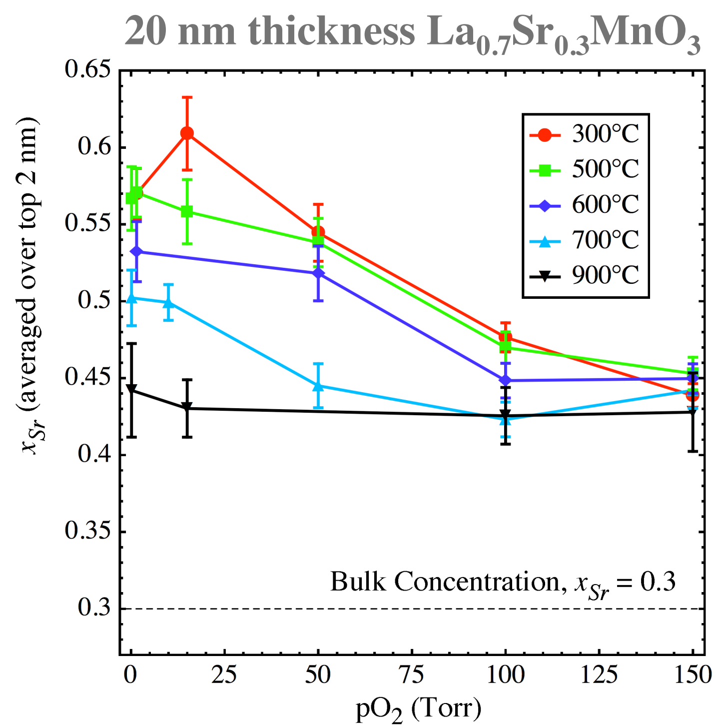






pO_2 Dependence of Sr Surface Segregation

- **Observe that Sr segregation depends on both T and pO_2**
  - plot shows average Sr composition in ~3 nm surface region (bulk composition = 0.3)
- **Charged vacancies are often not considered in surface segregation studies. The concentration of these defects depends strongly on temperature *and* pO_2.**
- **A gradient of $V_O^{\bullet\bullet}$ near the surface could drive Sr segregation.**
  - Lowering pO_2 increases the concentration of $V_O^{\bullet\bullet}$ at the surface.
  - $V_O^{\bullet\bullet}$ have a net +2 charge; substituting Sr for La results in net -1 charge
  - Segregation of strontium ions can provide necessary charge compensation in the surface region.



Change in Sr concentration from bulk

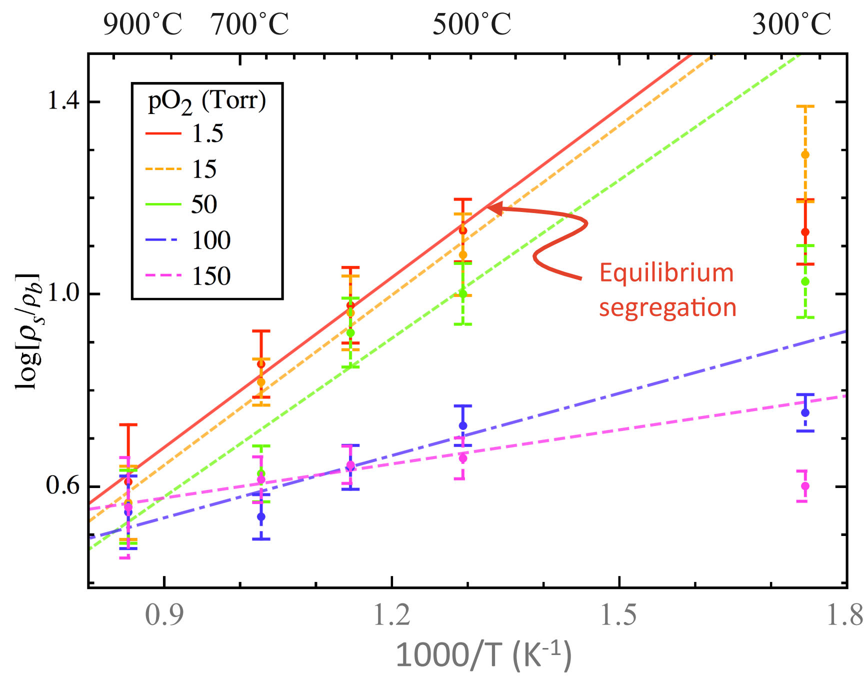
	Operating T (700-1000 C)	Low T (300 C)
Low pO_2 (mTorr)	+35%	+50%
Operating pO_2 (atmospheric)	+21%	+25%

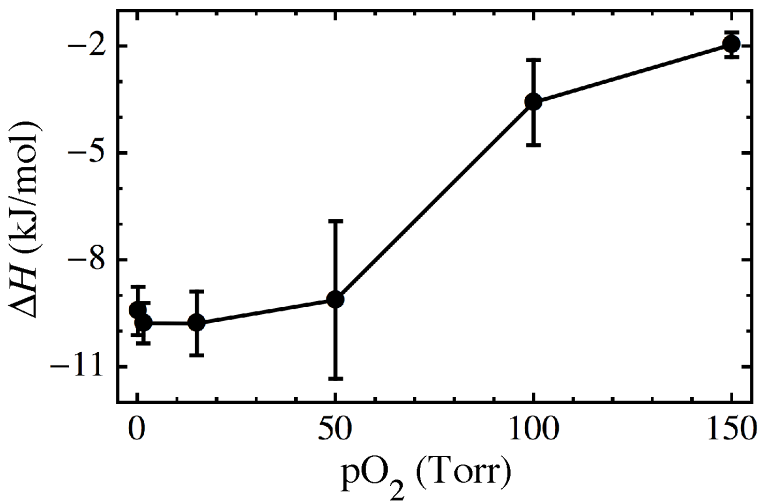
Extracting Thermodynamic Parameters

- Equilibrium segregation:

$$\frac{x^s_{Sr}}{x^s_{La}} = \frac{x^b_{Sr}}{x^b_{La}} e^{-\Delta H_{seg}/kT}$$

- Linearity at high T (above 500˚C) indicates equilibrium segregation.



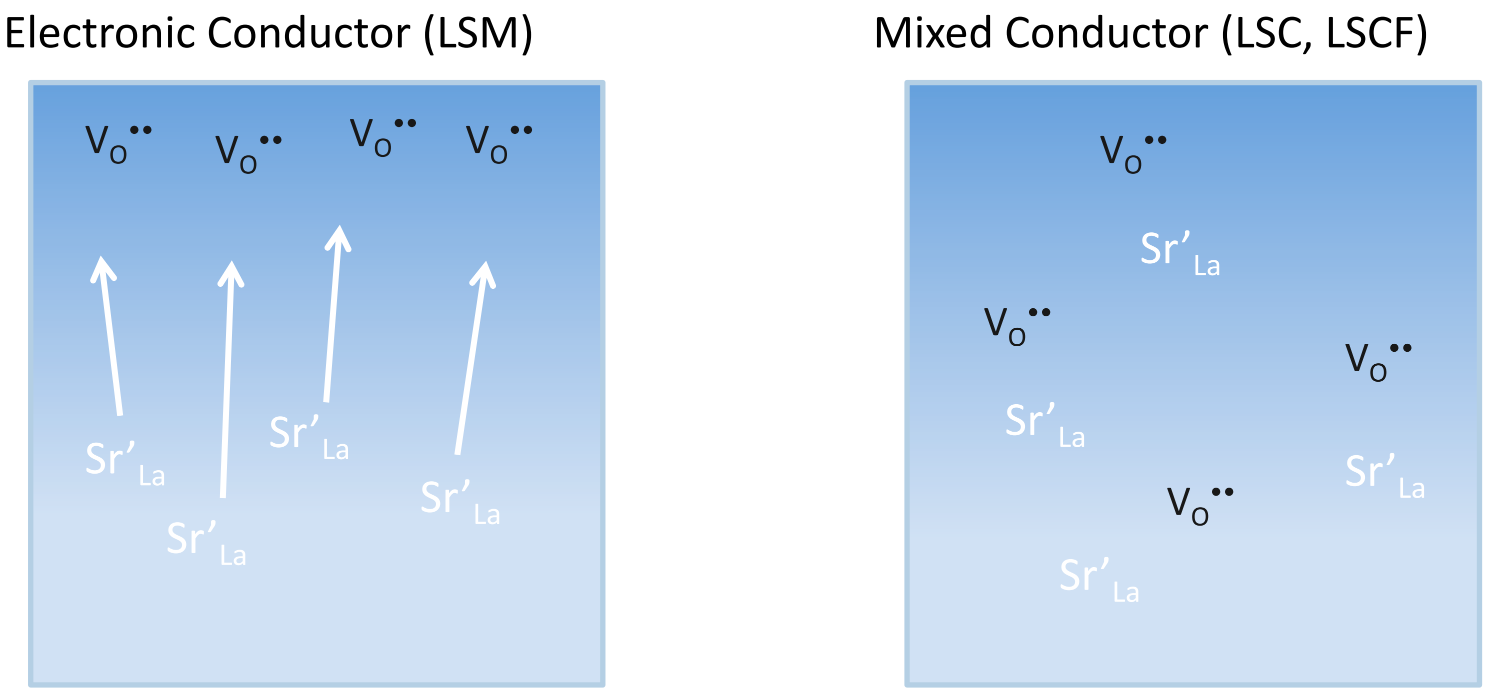


- Previous room-temperature measurements likely depended on thermal history

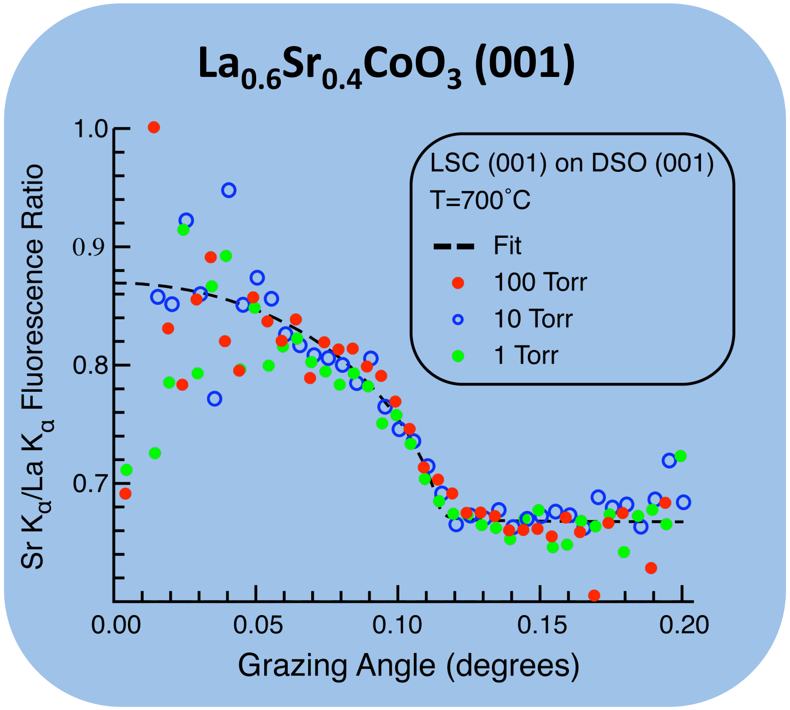
- **Further details: T.T. Fister et al. APL 93, 151904 (2008).**

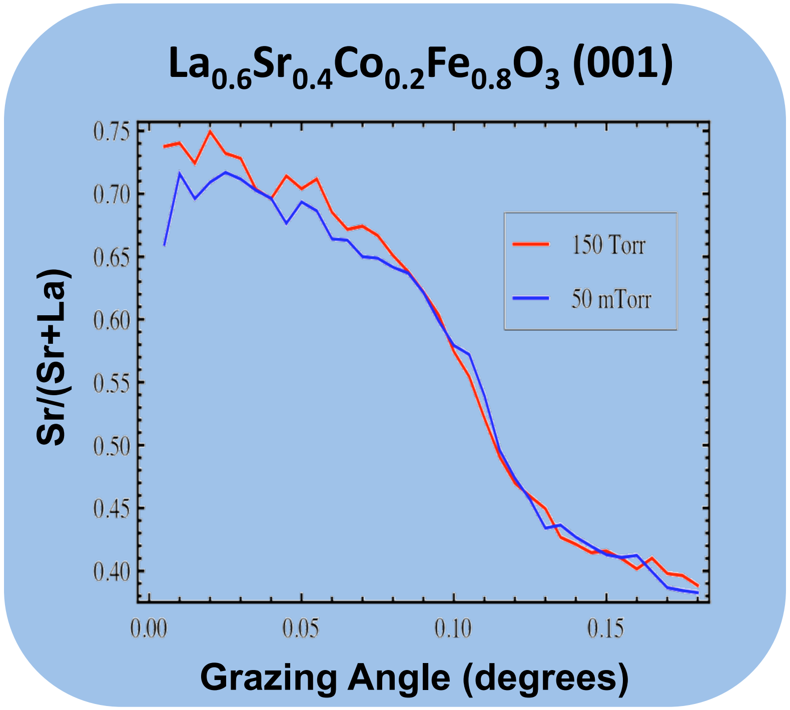
Mixed Conductor versus Electronic Conductor

- **LSM: surface oxygen vacancies**
- **$La_{0.6}Sr_{0.4}CoO_3$ (LSC) & $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) : bulk oxygen vacancies**



Strontium Segregation in Mixed Conductors





- Similar magnitude of strontium segregation as in LSM/DSO
- No pO_2 dependence at these relatively high temperature.

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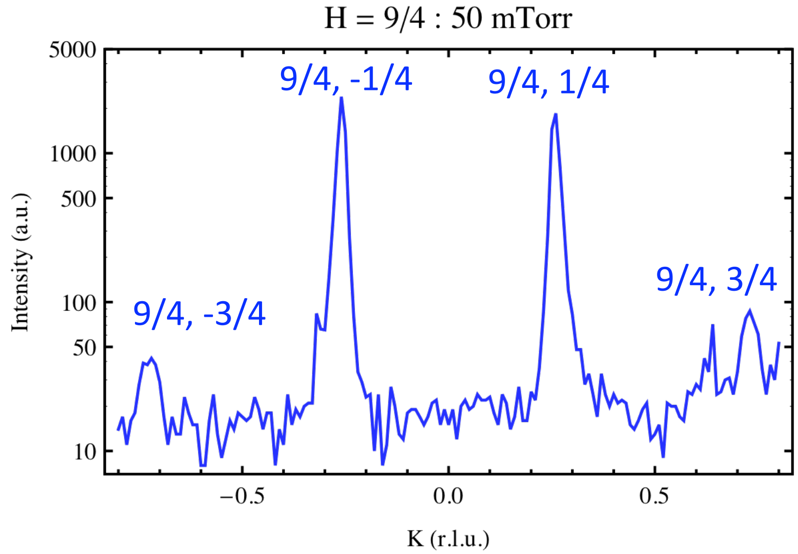
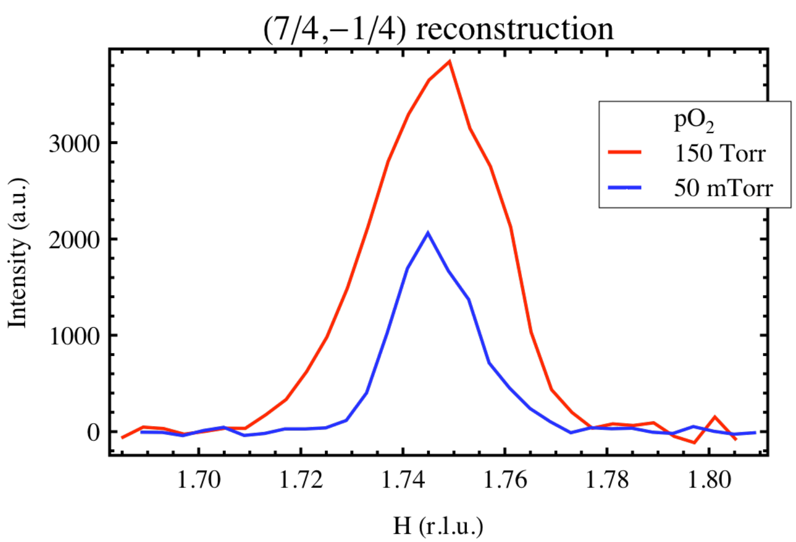
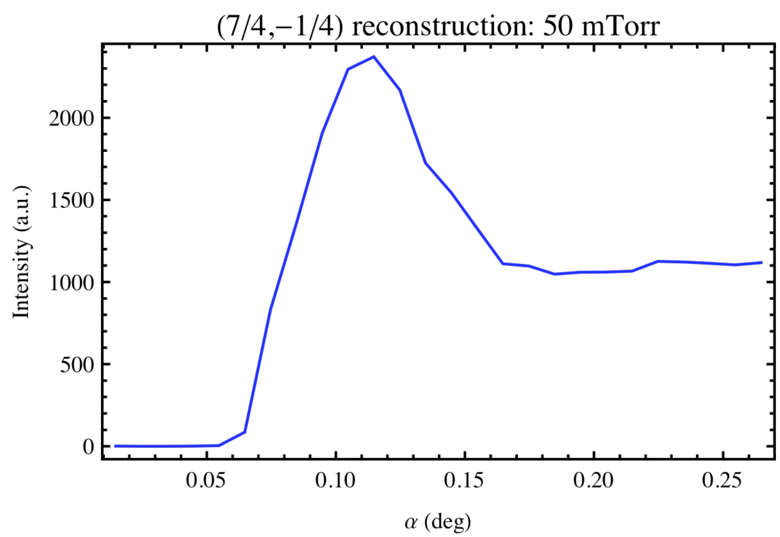
LSCF on NGO Reconstructs!

- 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.

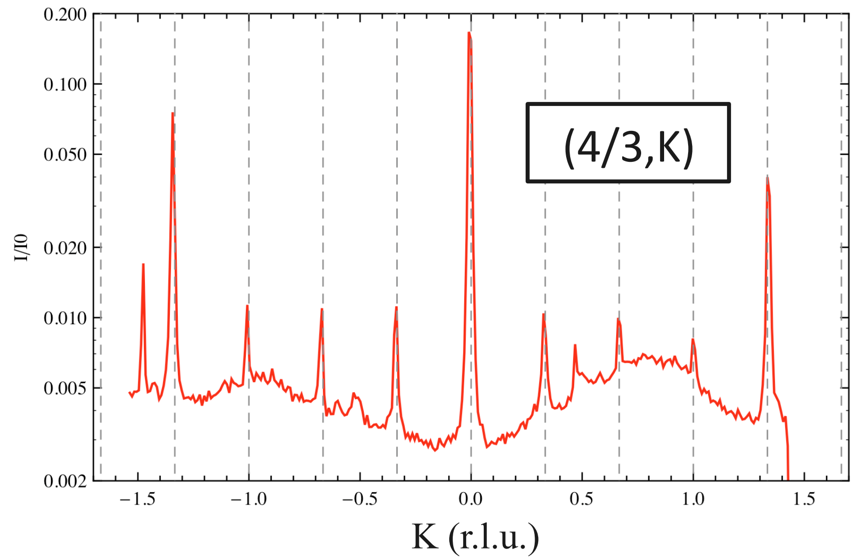


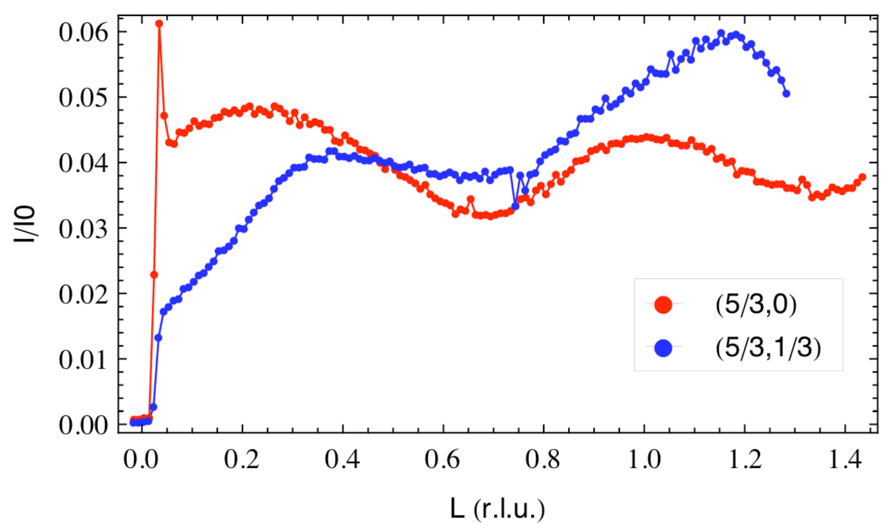




LSCF (001) on STO Surface Reconstruction

- Sample: 5 nm LSCF on Nb-doped $SrTiO_3$ (001)
- 1/3 order reconstruction peaks
- L-dependence indicates a roughly two monolayer thick reconstruction
- See ¼ order reconstruction peaks on opposite strain state (NGO)





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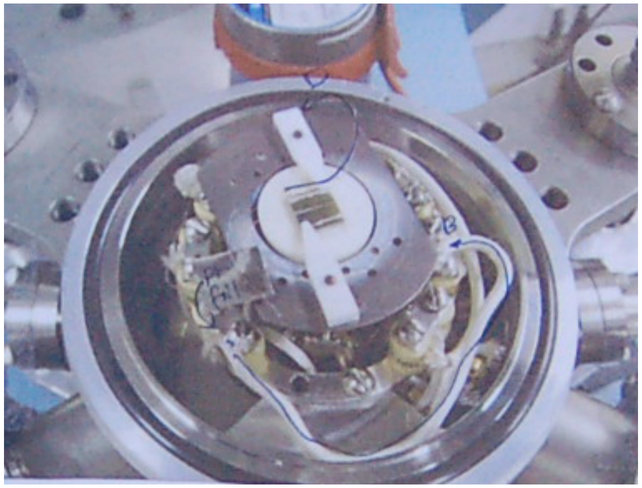
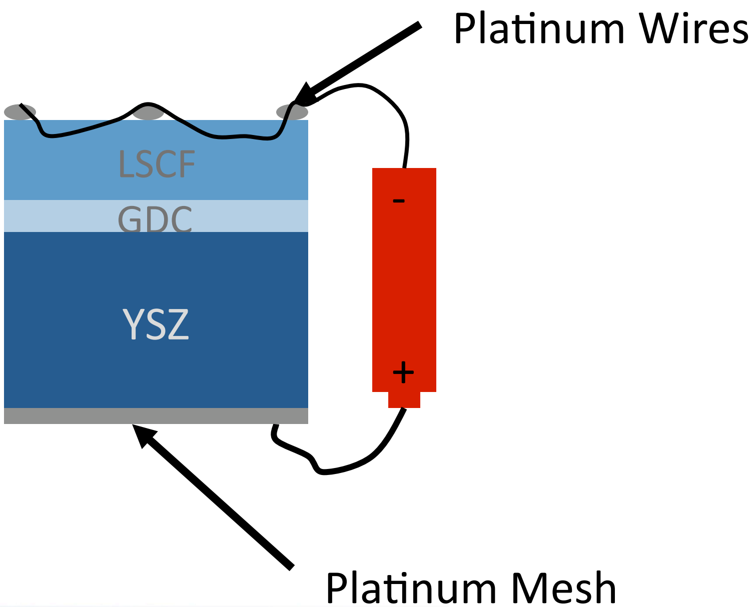
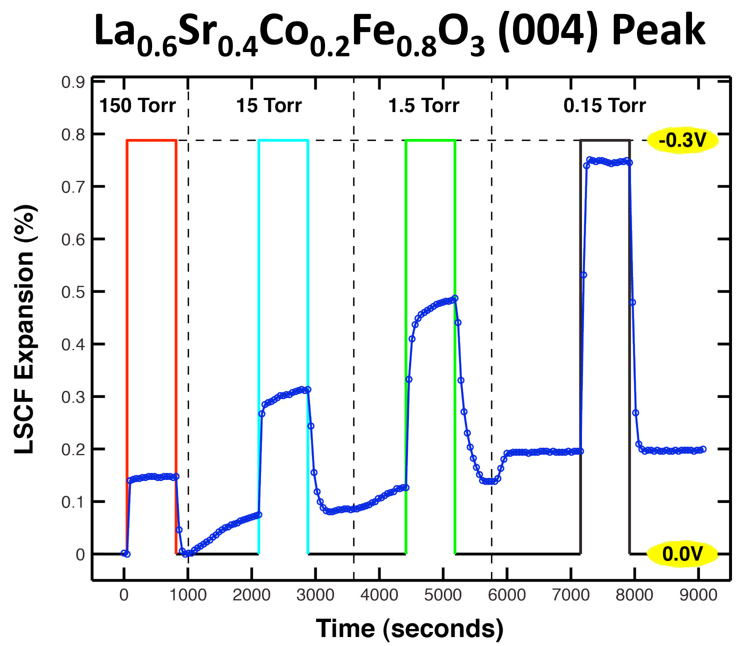
Overview of Electrochemical Measurements

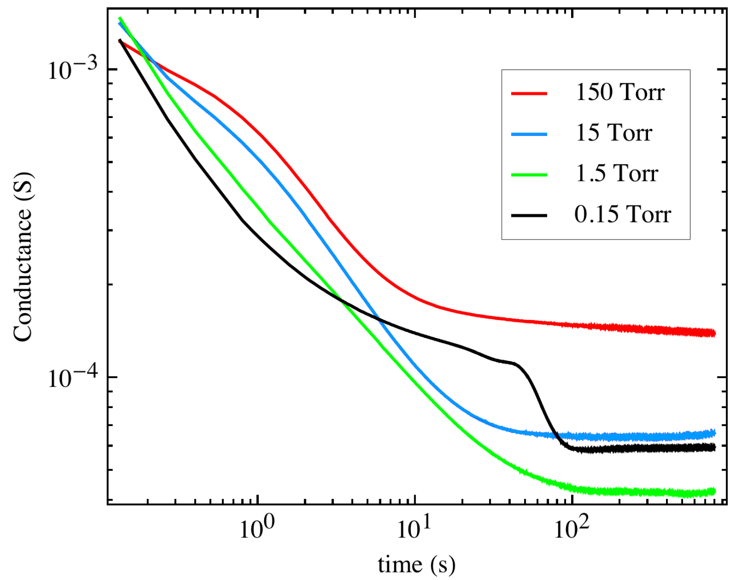
- Measure the response of a LSCF/GDC/YSZ stack (20 nm of LSCF) with platinum electrodes as a function of pO_2 and electrochemical potential.
- Measure the location of the LSCF (004) peak to determine the lattice parameter of the film.
- Monitor the YSZ and GDC diffraction peaks to correct for systematic effects.
- Systematically change the oxygen partial pressure and the applied cathodic potential while monitoring current through the sample.





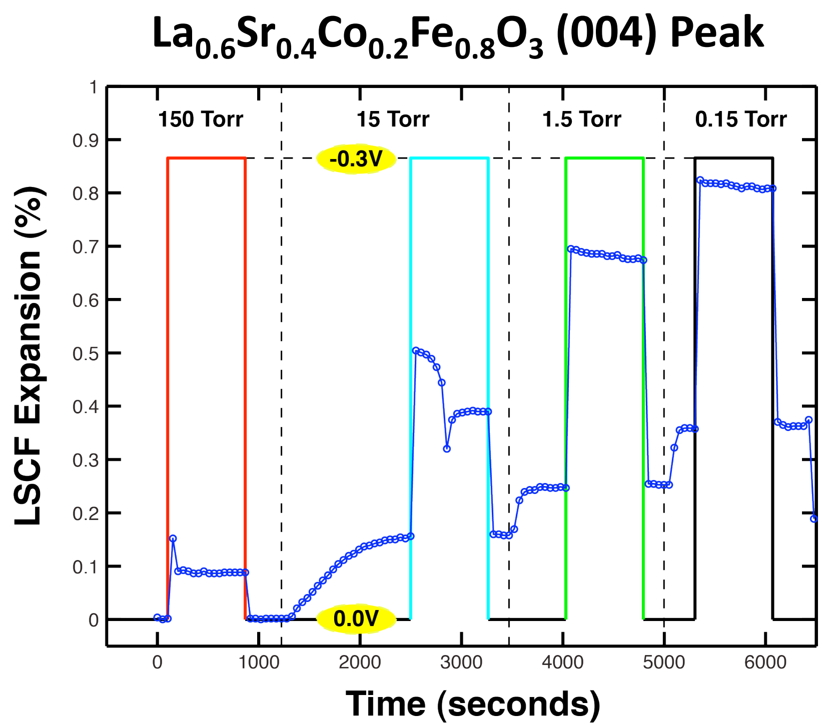
Correlate Lattice Parameter with Conductivity: 500°C

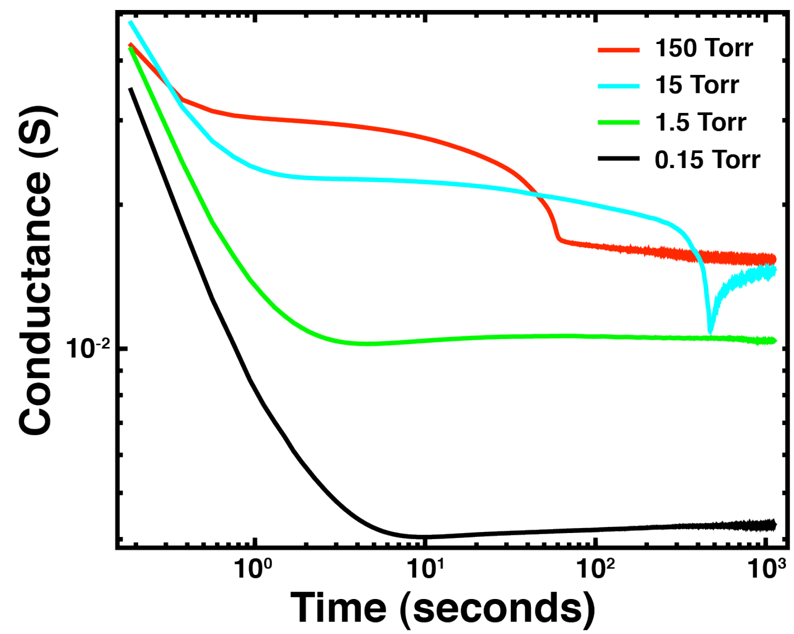




- L decreases with pO_2 and with cathodic overpotential (-0.3 V)
- Effect of overpotential is amplified at lower pO_2
- Kinetics of lattice expansion vary with pO_2
- Faster kinetics at 0.15 Torr correlates with a “kink” in conductance data.

Correlate Lattice Parameter with Conductivity: 700°C





- The "kink" is now at higher pO_2.
- Note the kink in the c-lattice parameter mirrors the kink in the conductivity.

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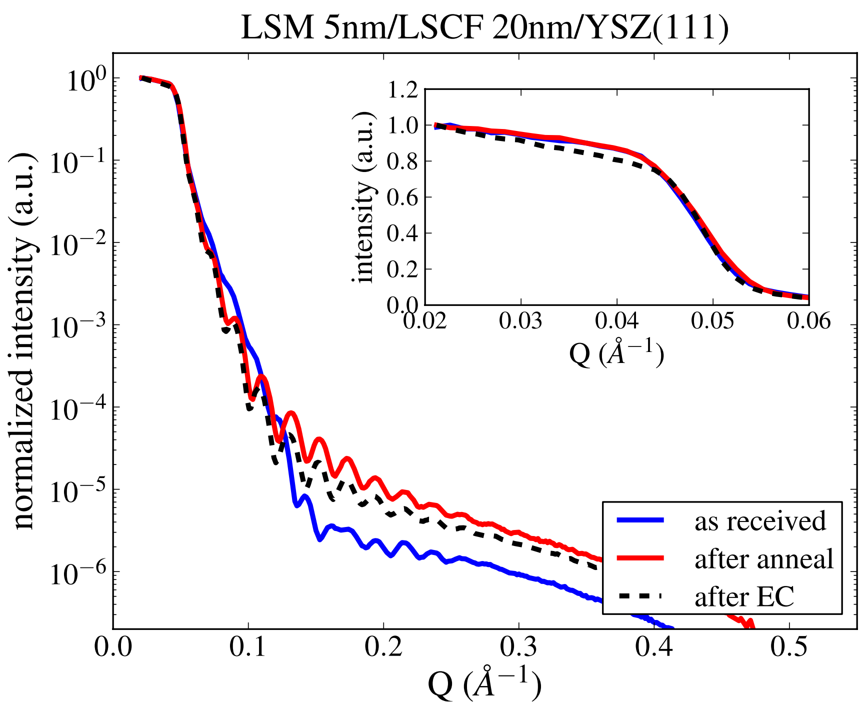
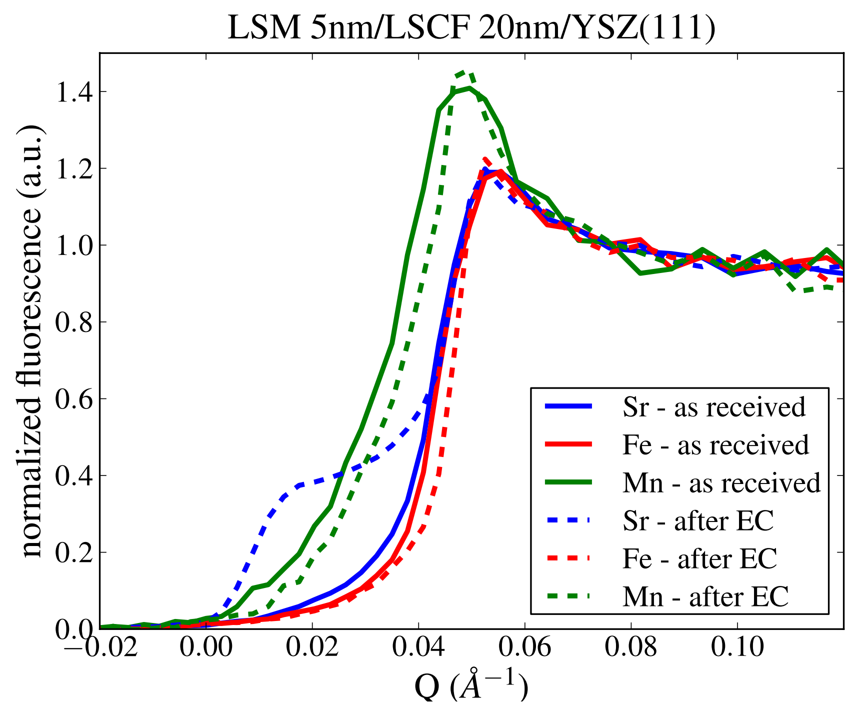
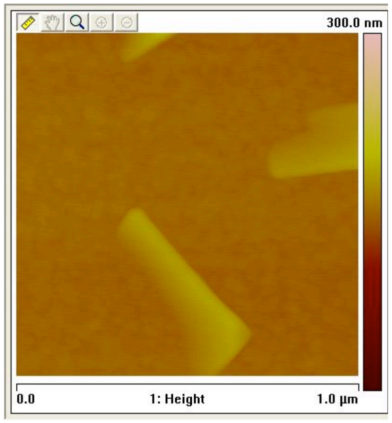
Effect of LSM capping layer on LSCF/YSZ(111)





- No critical angle shift for LSM capping layer after annealing
- Interfaces more stable with the LSM overlayer
- TXRF shows no Mn intermixing after 36 hours at 800C



Overall conclusions

- **Surface Reduction**
  - LSM (electronic conductor): Strontium surface segregation driven by surface oxygen vacancies
  - LSC, LSCF (mixed conductors): SrO formation at intermediate temperatures (700˚C)
  - LSCF: surface reconstruction varies with temperature and strain
- **Oxygen Exchange**
  - LSCF: large changes in cobalt edge position (valence state)
  - Total reflection inelastic x-ray scattering: new window on O K-edge, low energy cation states
- **Electrochemical potential introduces features in c lattice expansion**
  - Is a phase transition occurring?
  - Is it correlated with valence changes in the Fe or Co?
- **Future Research**
  - Develop better surface defect models and their relationship with catalytic activity
  - Correlate these effects with fuel cell performance
  - Study model intercalant systems (e.g. LSM deposited on LSCF)

The End