Synchrotron X-Ray Studies of SOFC Cathodes

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SOFC Cathodes are Dynamic Objects

The goal is to convert energy, a lot of energy, between different forms.

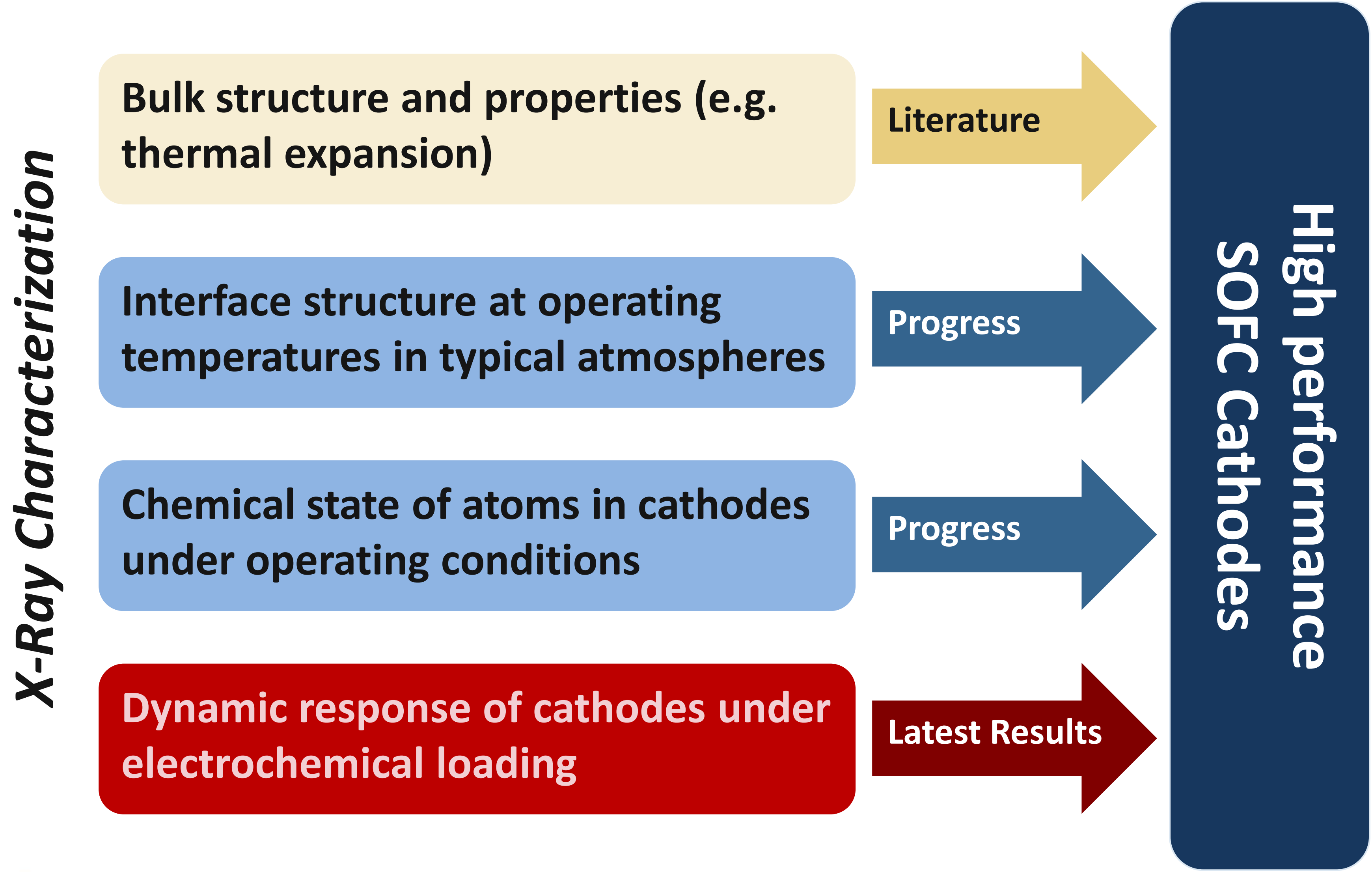
SOFCs Ionic Currents

0.5 amps/cm^2

1.6 × 10^{18} O/cm^2/second

2400 oxygen ions/unit cell/second

Overview of Synchrotron X-Ray Program



X-Ray Characterization

Bulk structure and properties (e.g. thermal expansion) → **Literature**

Interface structure at operating temperatures in typical atmospheres → **Progress**

Chemical state of atoms in cathodes under operating conditions → **Progress**

Dynamic response of cathodes under electrochemical loading → **Latest Results**

High performance SOFC Cathodes

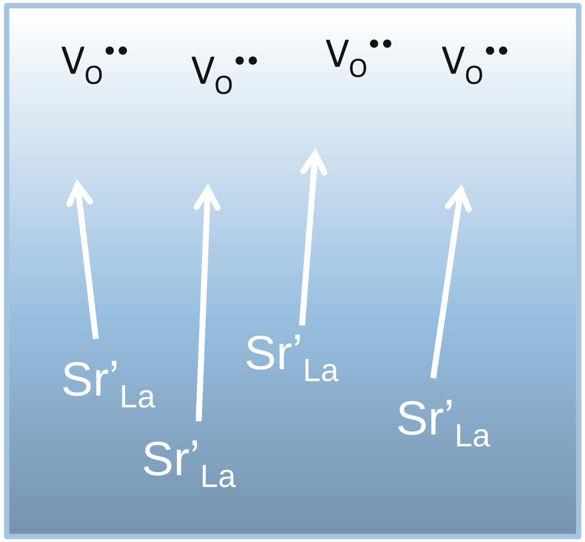
Presentation Plan

- Strontium Segregation
- Lattice Parameter, Conductivity and Overpotential
- ~~B-Site Chemistry and Distribution~~
  (see poster by Kee-Chul Chang, et al.)

Focus on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

LSM on $DyScO_3$

- Observe that strontium segregation depends on both T and pO_2
- 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.



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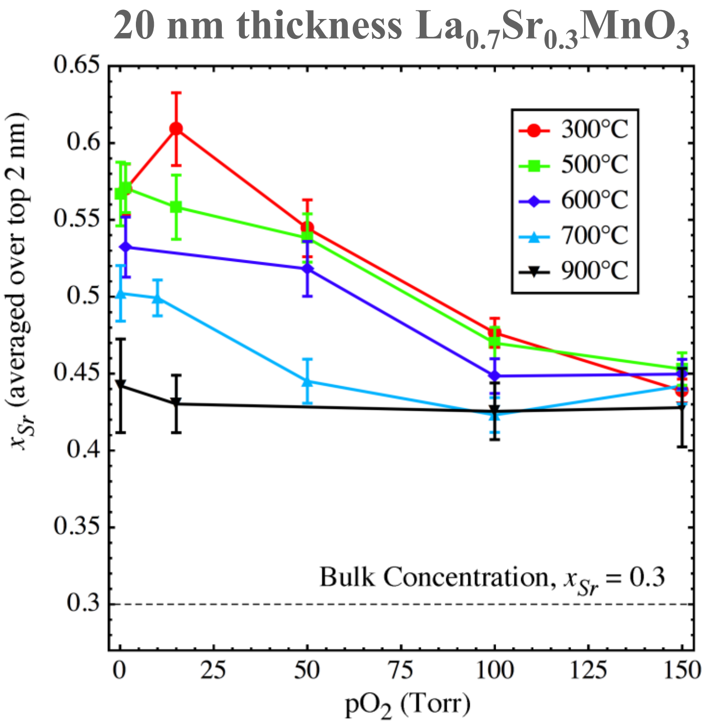
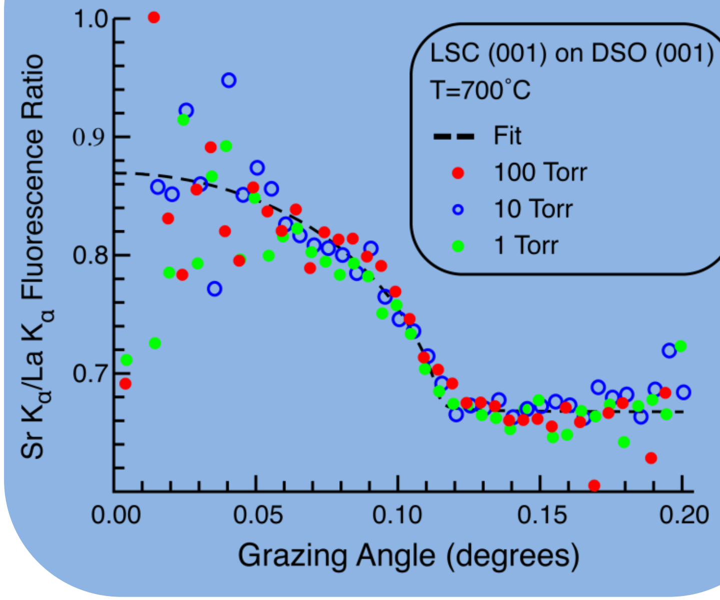


Change in Sr concentration from bulk

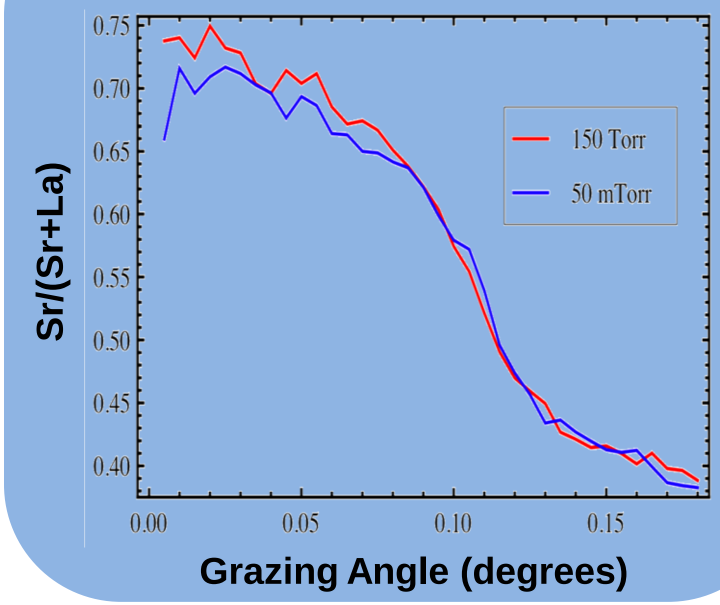
	Operating T (700-1000 C)	Low T (300 C)
Low pO_2 (mTorr)	+35%	+50%
Operating pO_2 (atmospheric)	+21%	+25%

Strontium Segregation in Mixed Conductors

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



$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (001)

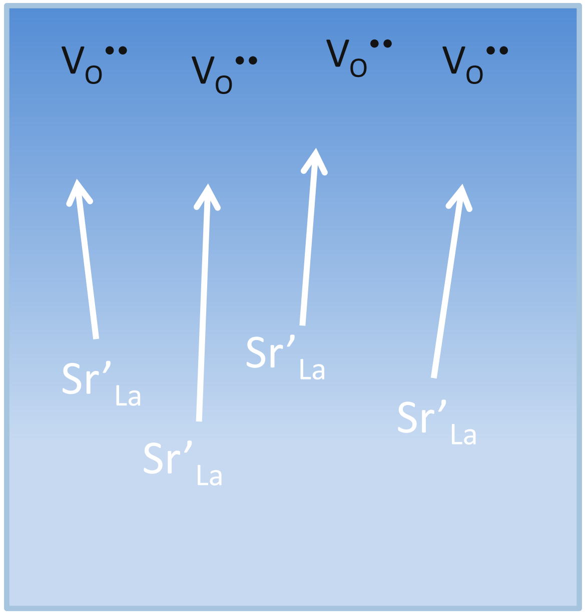


- **Similar magnitude of strontium segregation as in LSM/DSO**
- **No pO_2 dependence at these relatively high temperature.**

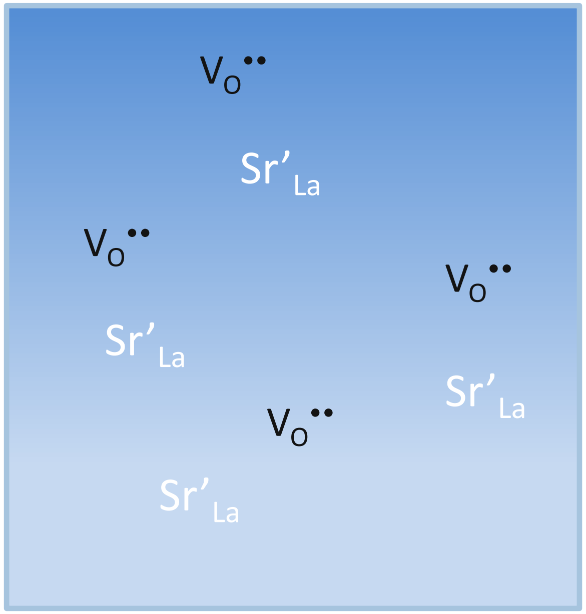
Mixed Conductor versus Electronic Conductor

- **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**

Electronic Conductor (LSM)

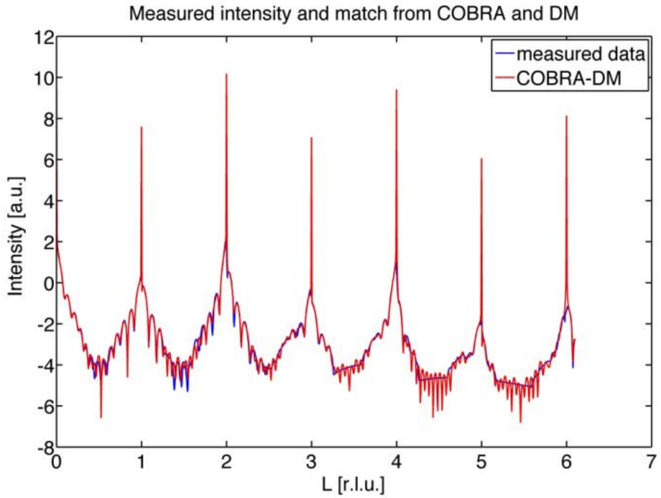


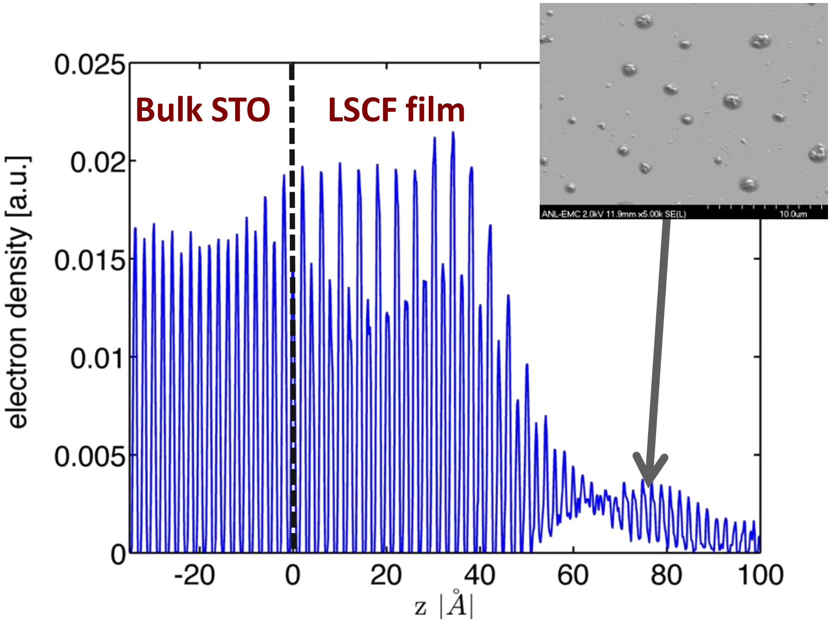
Mixed Conductor (LSC, LSCF)



Higher Resolution with Reflectivity Measurements

- The TXRF results have limited resolution normal to the surface (about 2-4 nm)
- Analysis of specular reflectivity can yield atomic resolution
- Use “direct methods” to interpret these complicated spectra



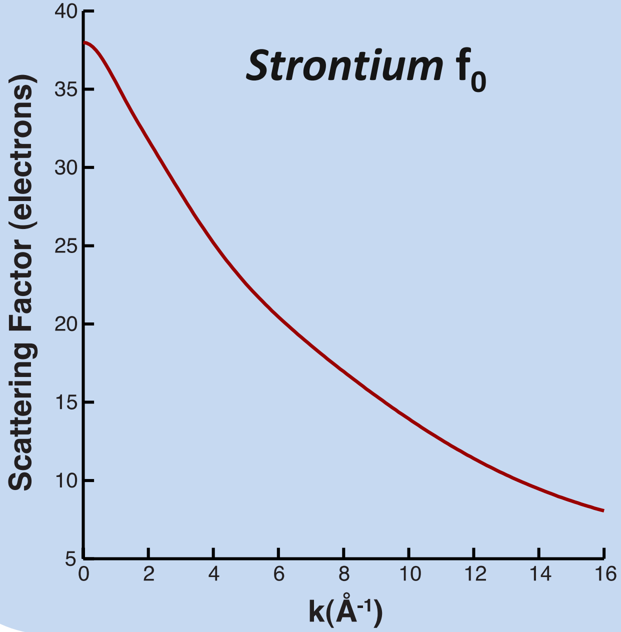


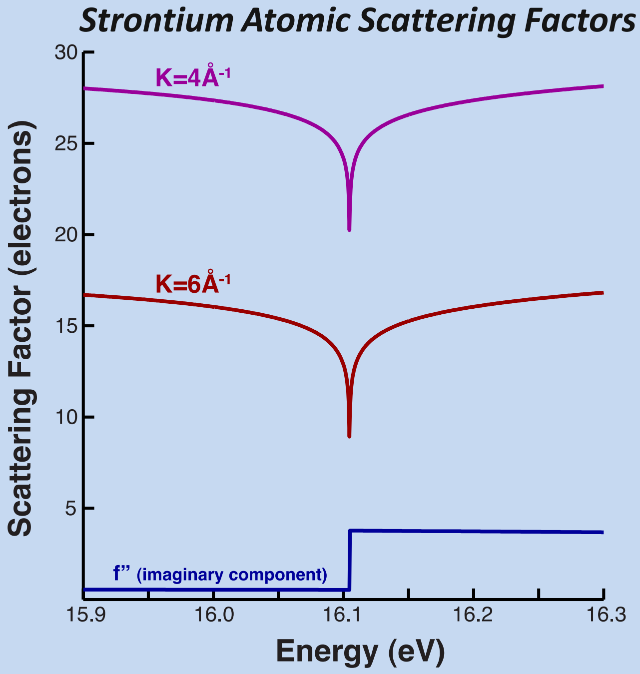
Atomic Scattering Factors

The scattering by an individual atom is dominated by the energy independent Fourier transform of its electron density plus real and imaginary resonant components that have a strong energy dependence unique to each element.

$$f(k,E) = f_0(k) + f'(E) + if''(E)$$

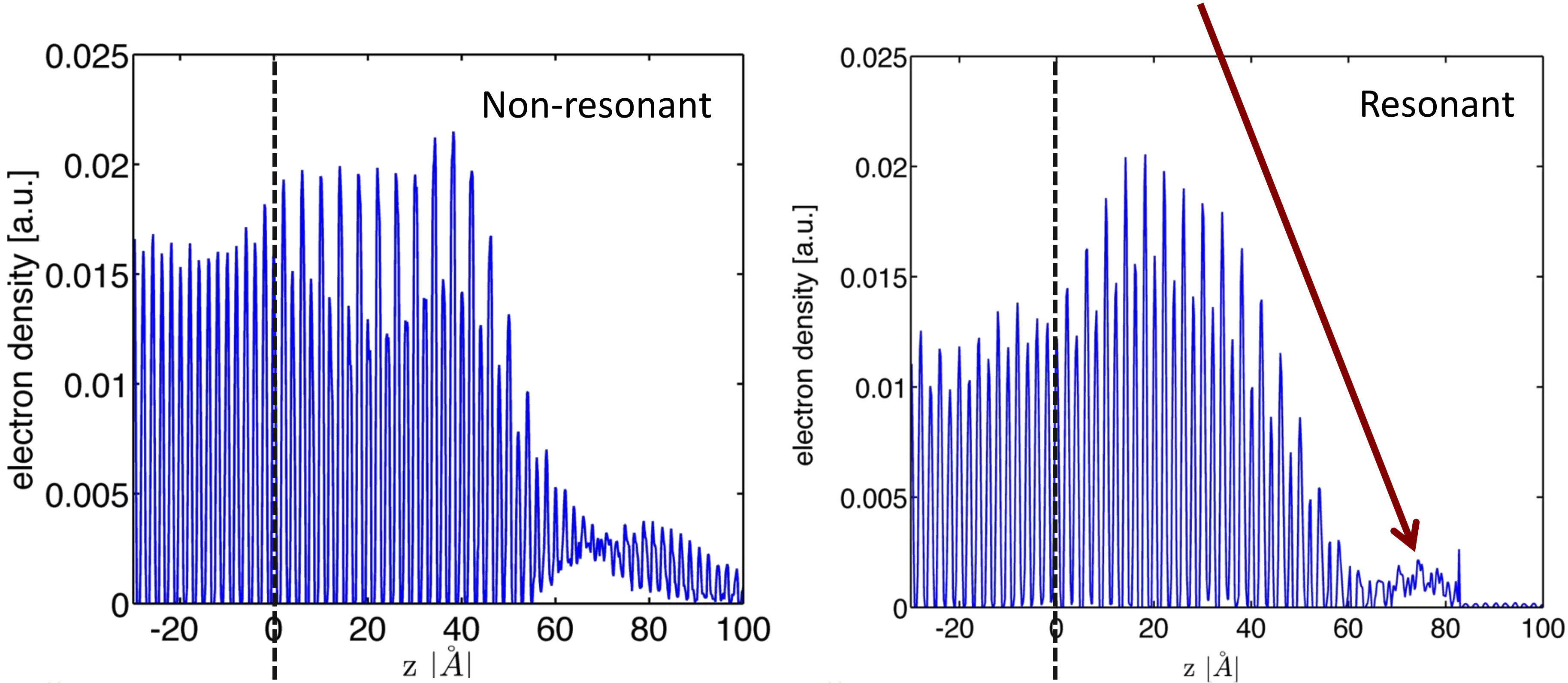
where $k = 4\pi\sin(\theta)/\lambda$ and E is the photon energy. The imaginary component $f''(E)$ is proportional to the atomic absorption coefficient.





Electron density: non-resonant (E=16.0 keV) and resonant (E=16.109 keV) at 750°C

Lower electron density in resonant case – particles consist of a large amount of Sr.



Bulk STO ← → **LSCF film**

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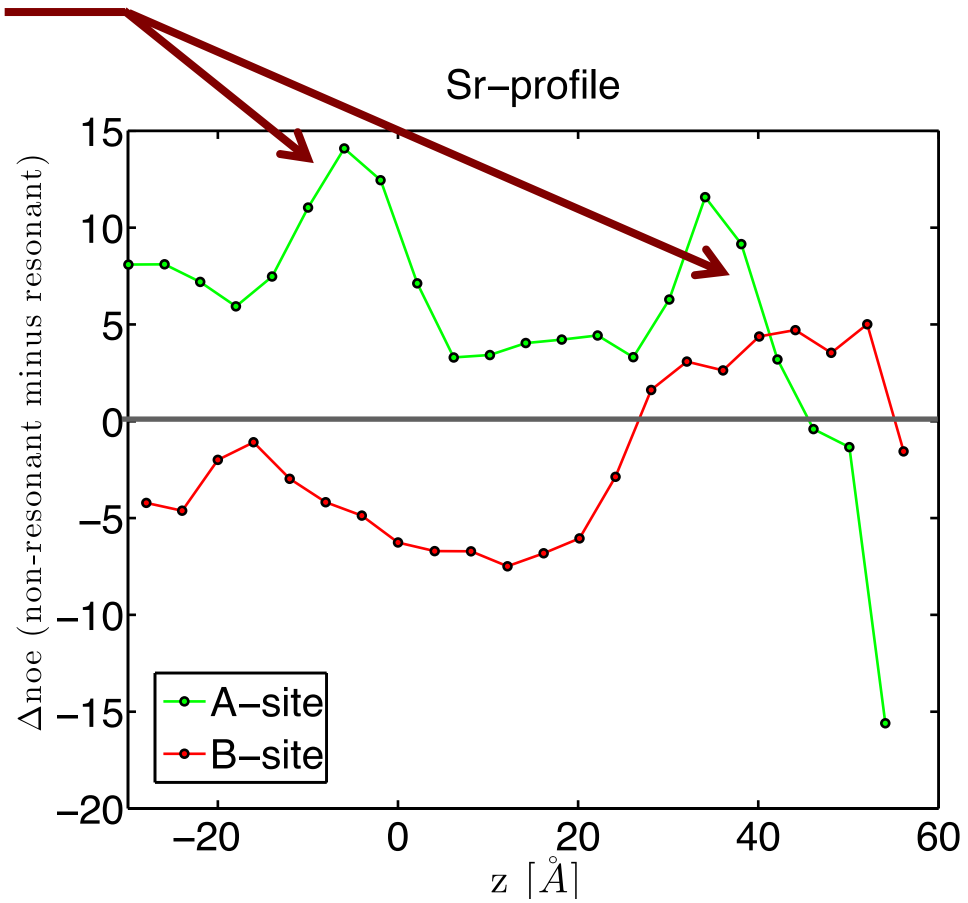
Segregation Profiles at 750°C

Strontium segregation is observed at the interface and at the LSCF surface



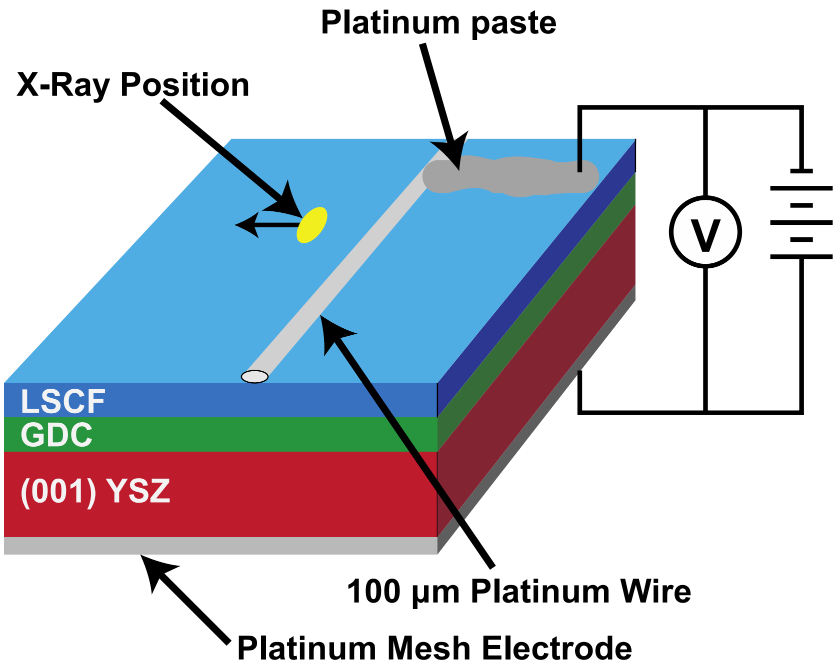
Presentation Plan

- **Strontium Segregation**
- **Lattice Parameter, Conductivity and Overpotential**

Focus on $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

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, electrochemical potential and x-ray position.
- Measure the location of the LSCF (004) peak to determine the lattice parameter of the film.
- Systematically change the oxygen partial pressure and the applied cathodic potential while monitoring current through the sample.

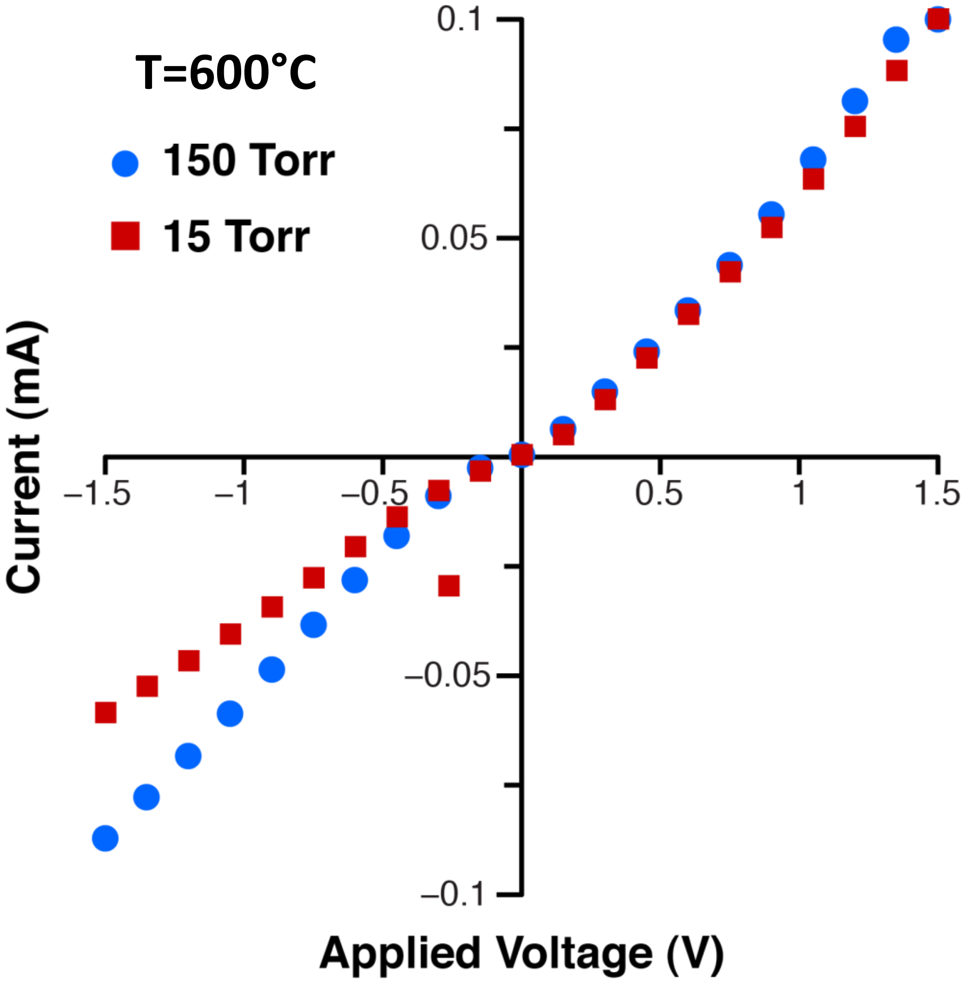


The incident X-ray beam was ~20 µm wide

i-V Curve at 600°C

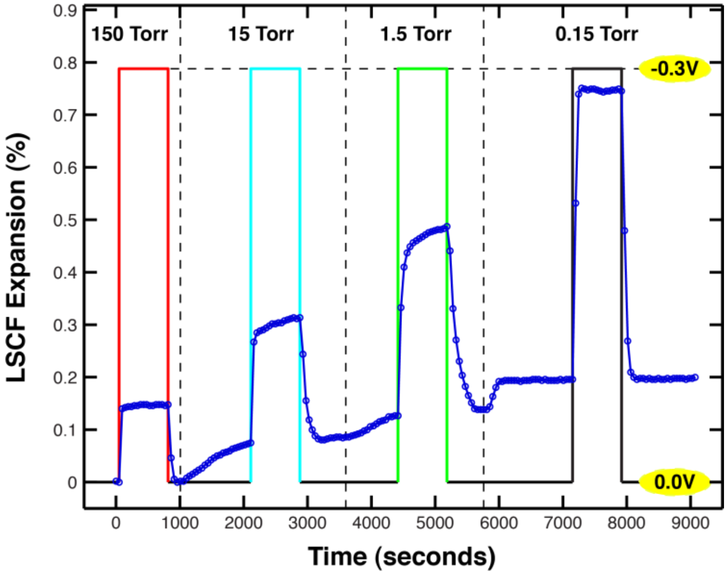
Oxygen reduction reactions are the limiting mechanism

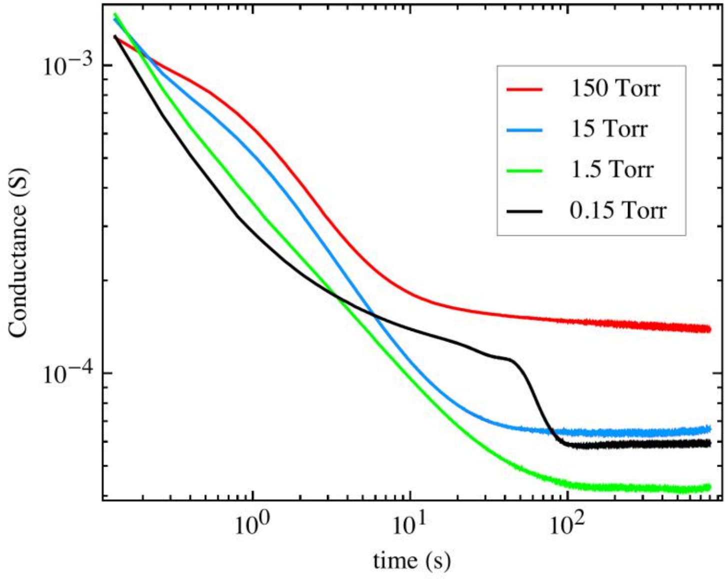
From other data, the active area is ≈0.1 cm^2 so -1V yields a current density of 0.5 mA/cm^2



Correlate Lattice Parameter with Conductivity: 500°C

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (004) Peak



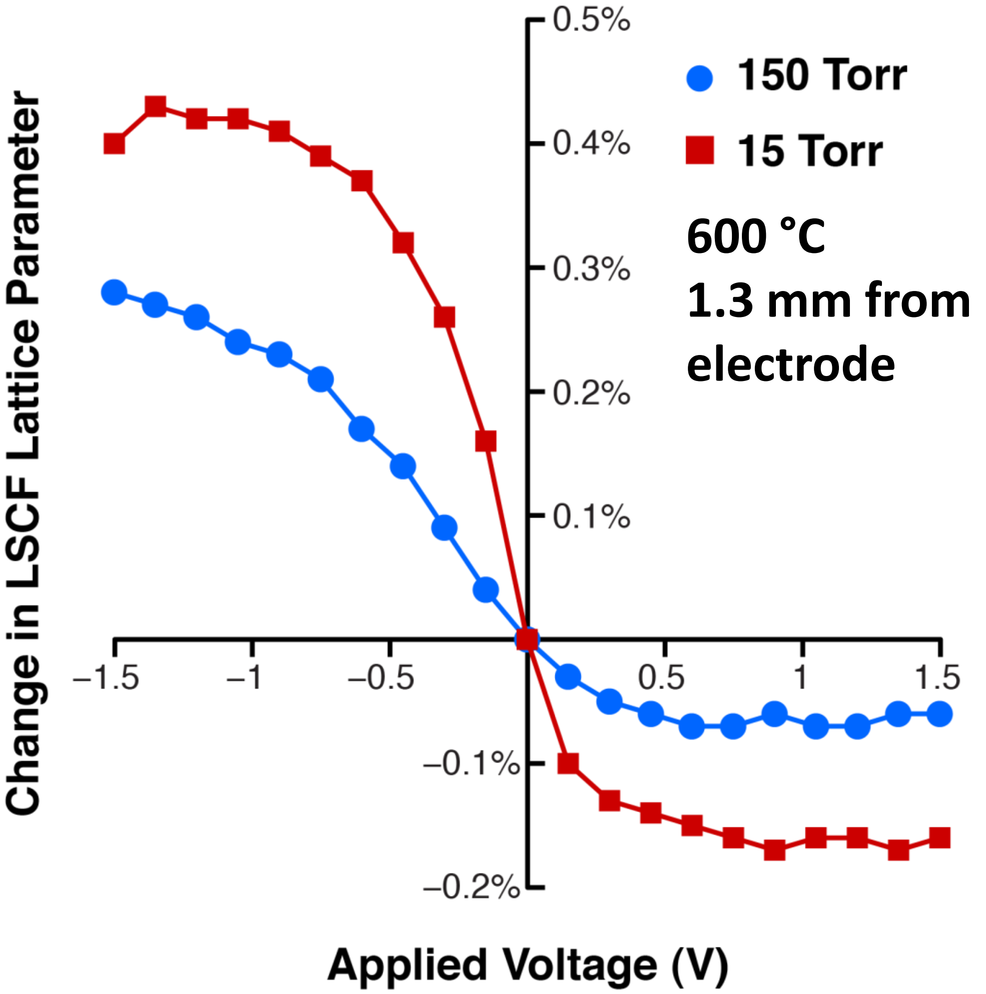


- **L decreases with pO_2 and with cathodic overpotential (-0.3 V)**
- **Effect of overpotential is amplified at lower pO_2**
- **Kinetics of lattice expansion vary with pO_2**
- **Faster kinetics at 0.15 Torr correlates with a “kink” in conductance data.**

LSCF Lattice Parameter Shift vs Applied Potential

Using Bishop[1], 0.4% strain corresponds to δ=0.13 or 4% oxygen vacancies.

The "odd" functional dependence limits models – not just current driving oxygen vacancies into the film.

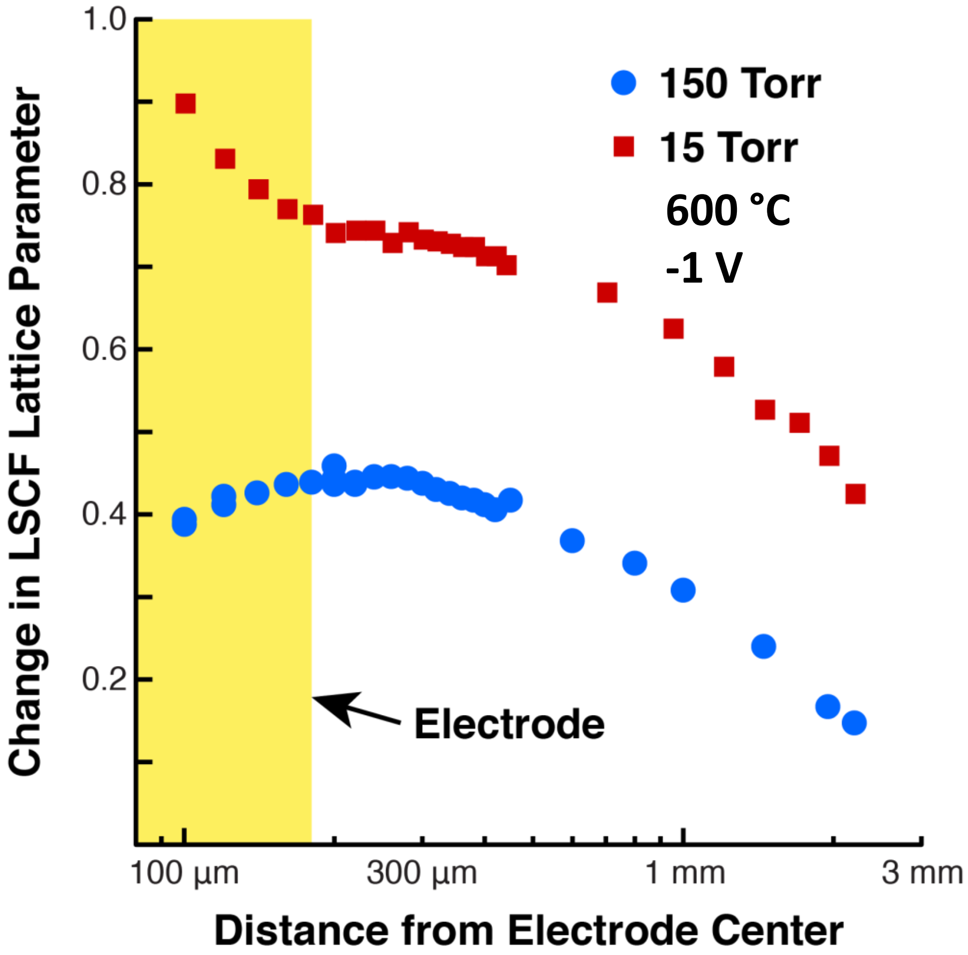


[1] S.R. Bishop, K.L. Duncan, E.D. Wachsman, *J. Am. Ceram. Soc. 93 (2010) 4115-4121.*

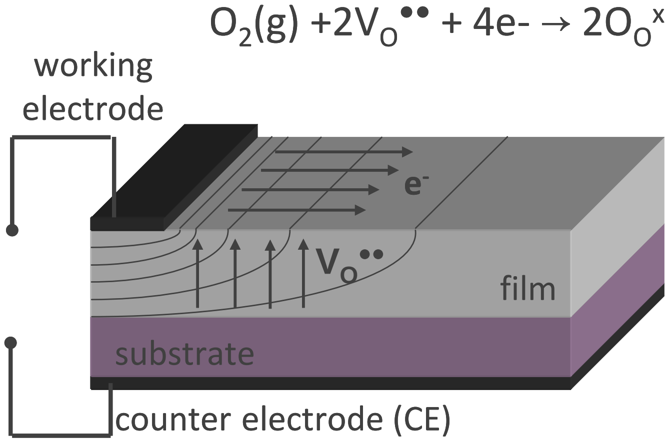
LSCF Lattice Parameter Change versus Position

The lattice parameter changes smoothly with distance from electrode.

The may be useful in mapping conductivity and potential profiles since the electrochemical potential dependence is simple.



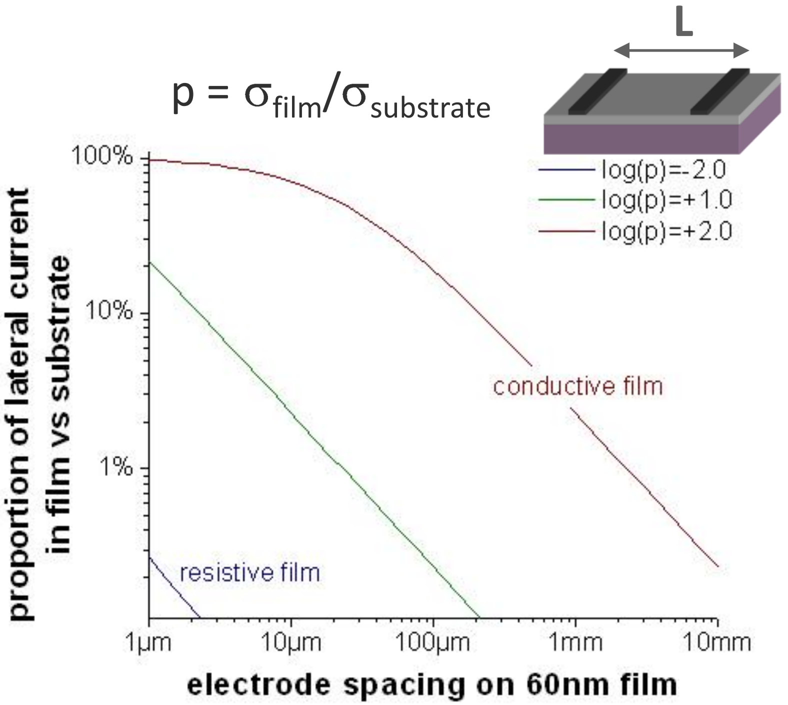
Current distribution in thin films



$$O_2(g) + 2V_O^{\bullet\bullet} + 4e^- \rightarrow 2O_O^x$$

- Electronic and ionic carriers required for oxygen reduction reaction
- Inhomogeneous electrochemical potential on MIEC film surface
  - High sheet resistance
  - Limited ionic conductivity
- Need to understand current flow and potential distributions, i.e., rate of oxygen reduction events

- Simple case: 2 parallel surface electrodes
- Similar situation witnessed in our electrochemical measurements
- Modified Farnell's equation* for measuring complex in-plane electrical properties of thin films



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* N. Kidner, et al., *Thin Solid Films* **496** (2006) 539-545.

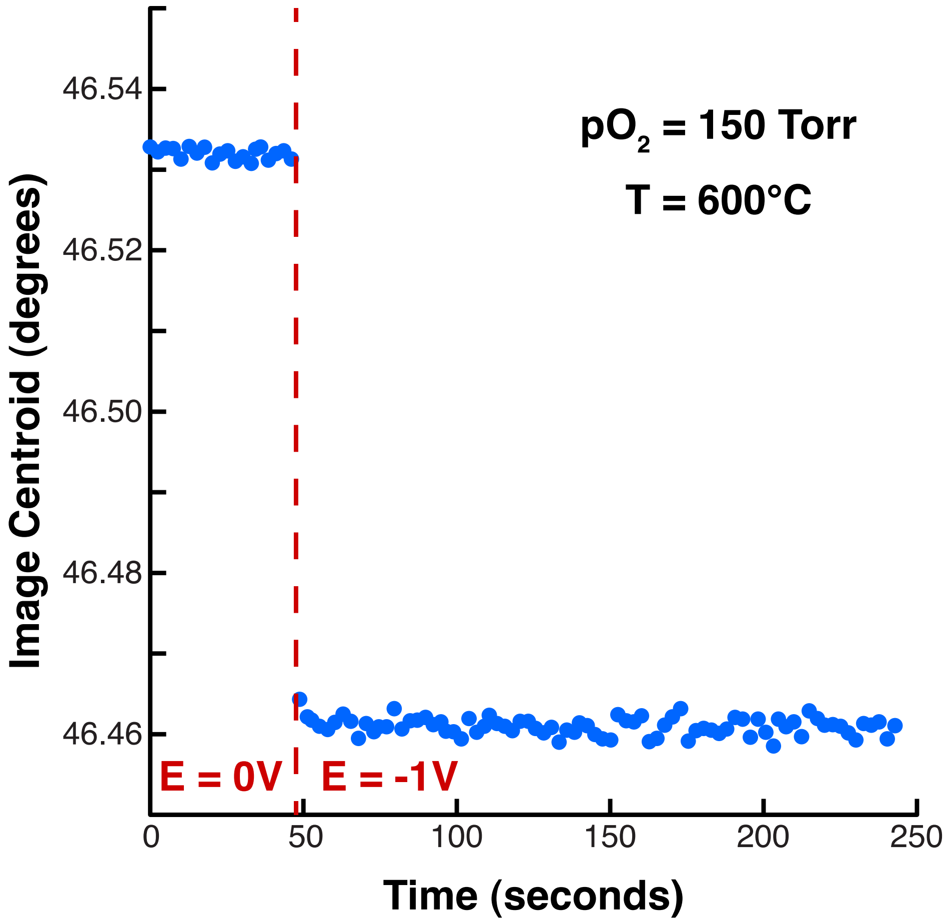
Time Dependence of Lattice Parameter Shift

Lattice expansion occurs in 1 second.

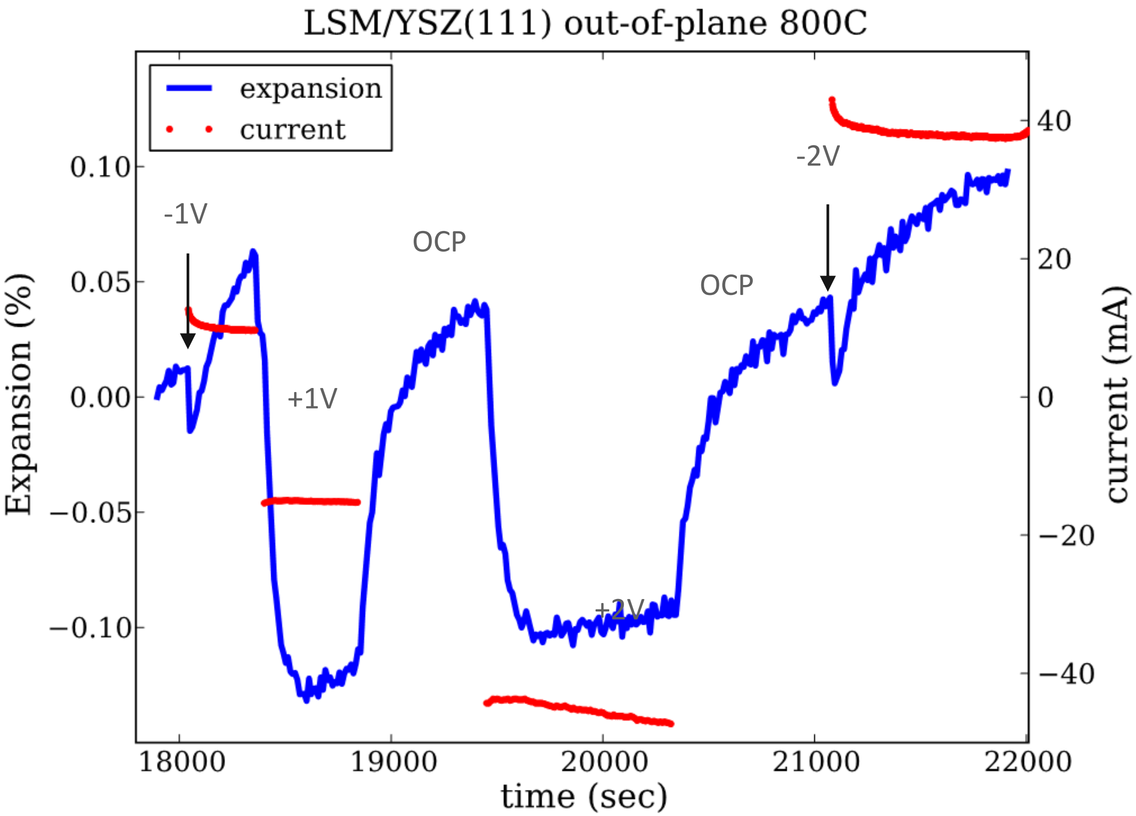
I ≈ 0.5 mA/cm^2

≈ 0.013 vac./unit cell/sec

δ = 0.013 is an order of magnitude smaller than predicted from Bishop chemical expansion data for 0.4% lattice expansion (δ = 0.13)



Chemical Expansion of LSM/YSZ(111) at 800C



LSM has smaller chemical expansion and slower kinetics compared to LSCF

LSCF Chemical Expansion Summary

- Range of chemical expansion for the LSCF is from -0.2% to 0.8% implying δ ~ 0.3 change in stoichiometry based on Bishop’s recent results

- High anodic potentials induce lattice expansions that may indicate the initial stages of phase change

- Working through defect models, e.g. those of Wachsman and coworkers, to develop better models of this process.

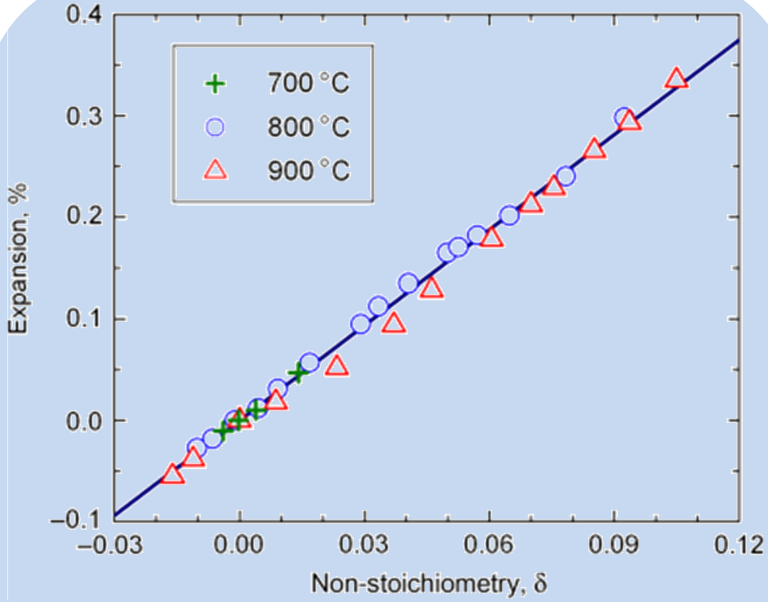


Fig. 5. Chemical expansion as a function of change in oxygen content using $P_{O_2} = 0.21$atm (air) at temperature as a reference point for zero expansion and change in stoichiometry. The solid line represents a linear fit of Eq. (2) to the data.

S.R. Bishop, K.L. Duncan, E.D. Wachsman, J. Am. Ceram. Soc. 93 (2010) 4115-4121.

Project Conclusions and Direction

- **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: significant 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-axis lattice expansion**
  - Effect is suggests very large vacancy concentrations
  - Time response is inconsistent with current densities and needed vacancies.
  - Lattice expansion is correlated with valence changes on Co.

- **Current Effort**
  - Develop better surface defect models and their relationship with catalytic activity
  - Correlate these effects with fuel cell performance
  - Study intercalation into porous backbone using atomic layer deposition (e.g. LSM deposited on LSCF)

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