Synchrotron X-Ray Studies of SOFC Cathodes

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Overview

- **Motivation and Background**
- Current Results
  - Segregation
  - Lattice parameter vs. electrochemical state
- Summary

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

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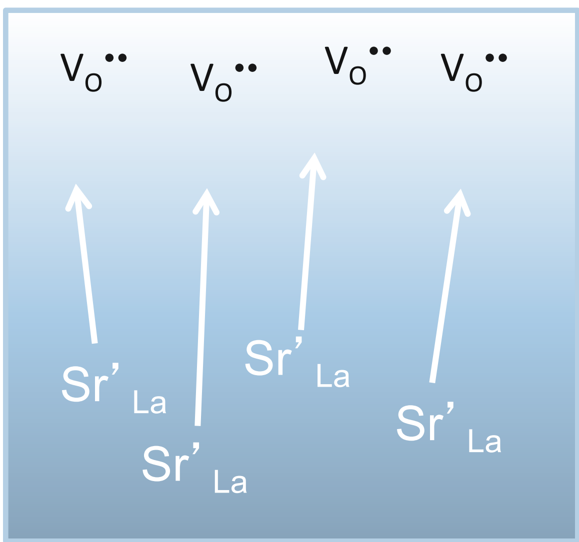
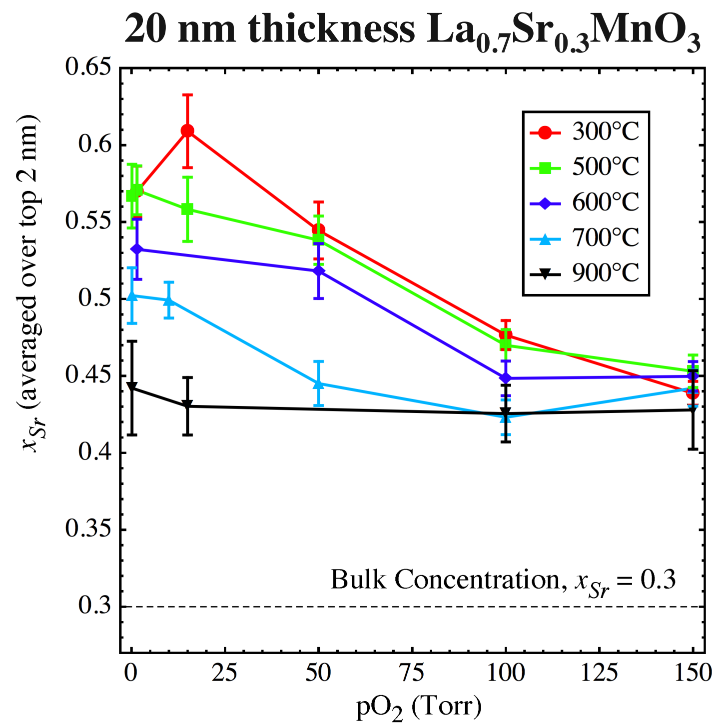
LSM on $DyScO_3$

- 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.



Applied Physics Letters 93, 151904 (2008)



Change in Sr concentration from bulk

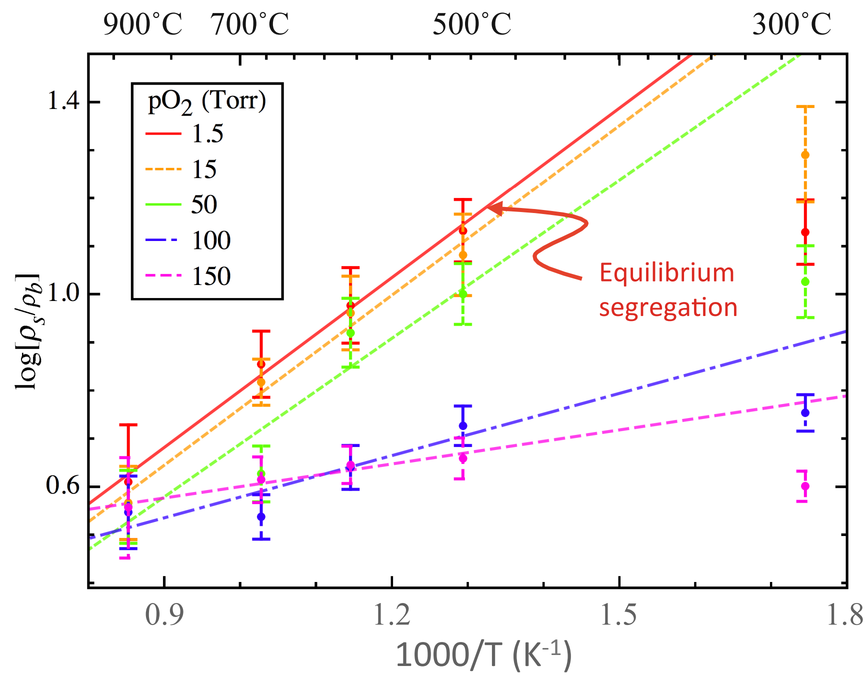
	Operating T (700-1000 C)	Low T (300 C)
Low pO_2 (mTorr)	+35%	+50%
Operating pO_2 (atmospheric)	+21%	+25%

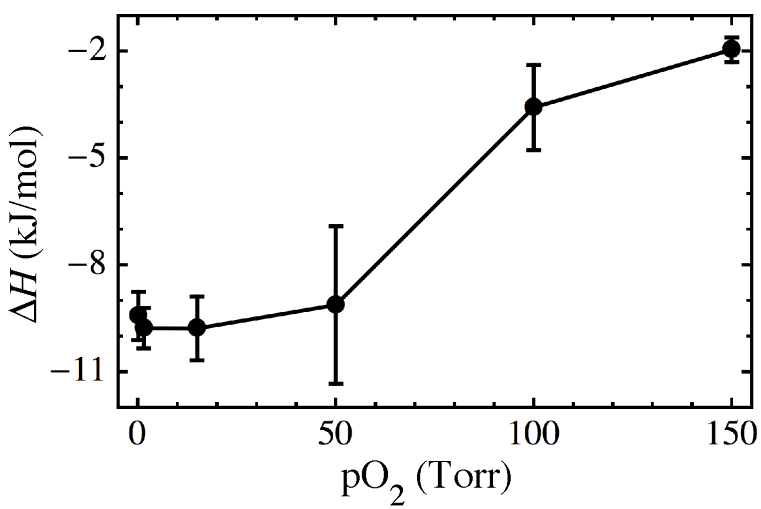
Kinetic limitations

- 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.



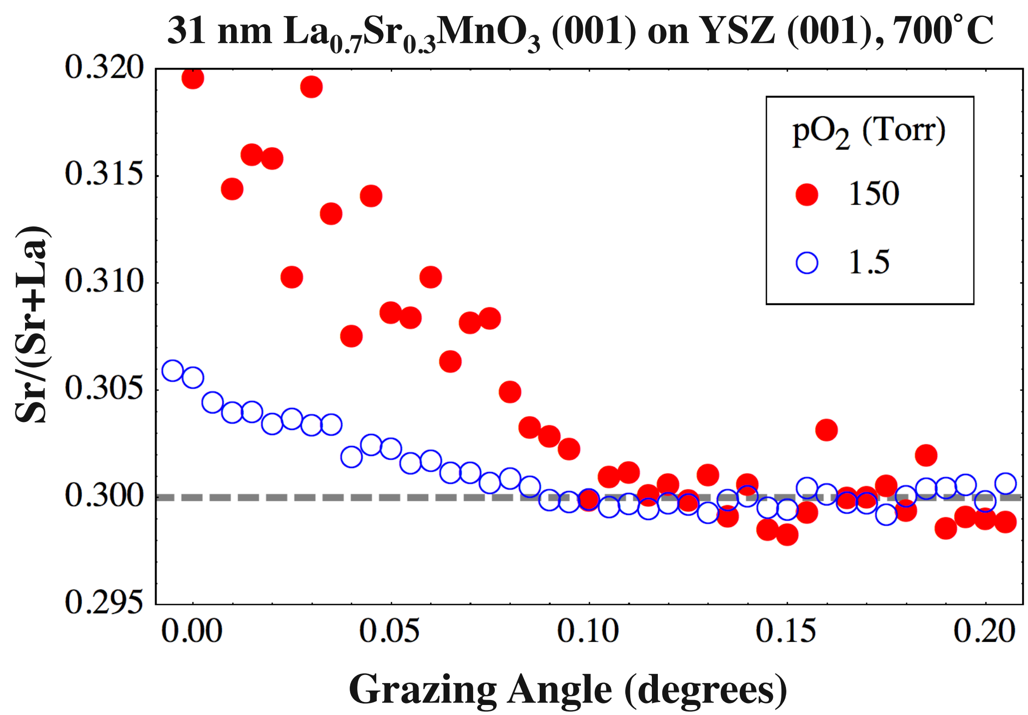


→ Previous room-temperature measurements likely depended on thermal history

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

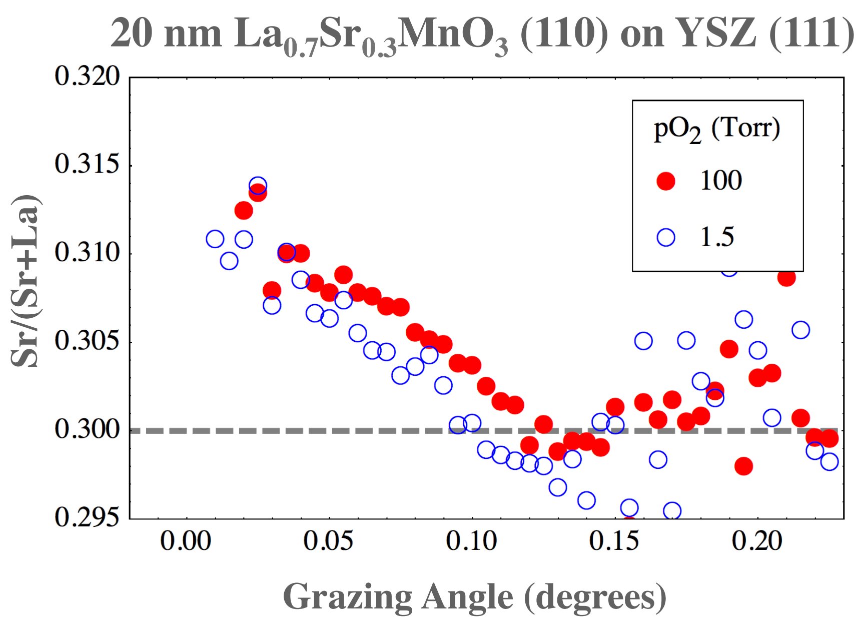
$La_{0.7}Sr_{0.3}MnO_3$ on YSZ

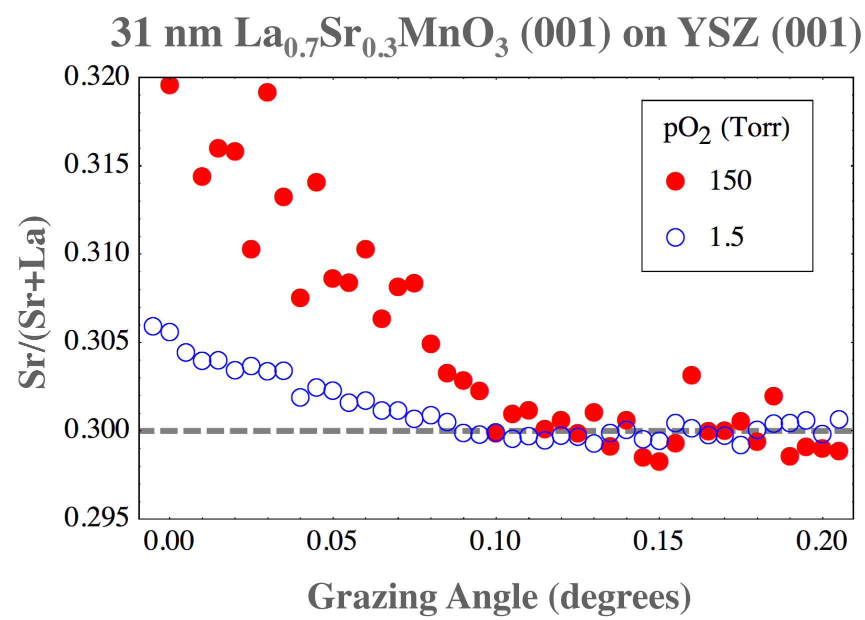
- Reduced segregation compared with LSM/DSO
- Grain boundary segregation may limit surface concentration
- pO_2-dependence is opposite



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

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

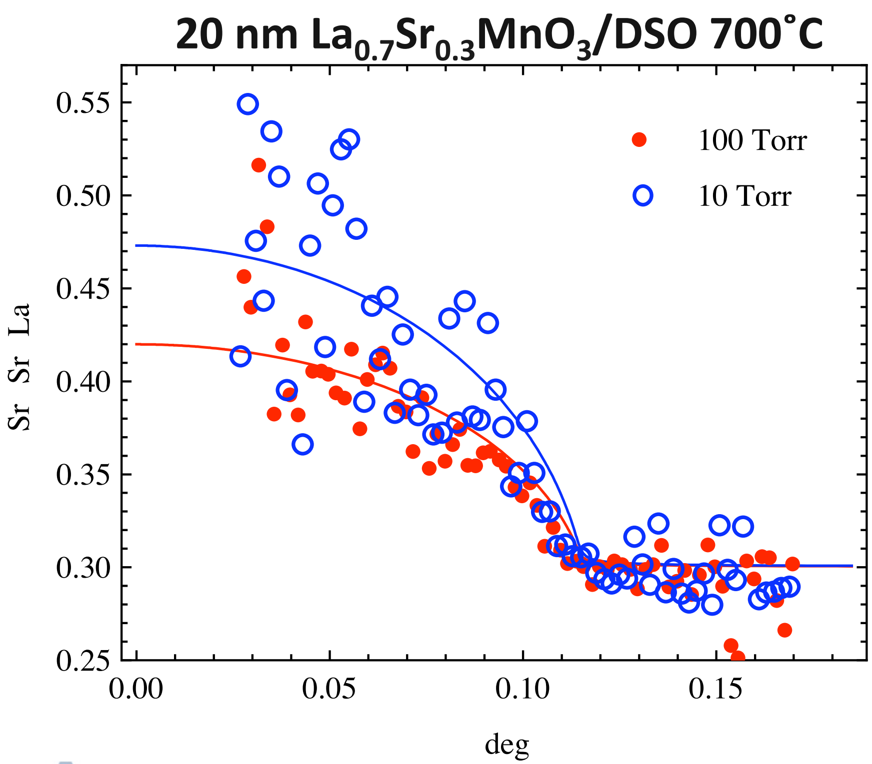


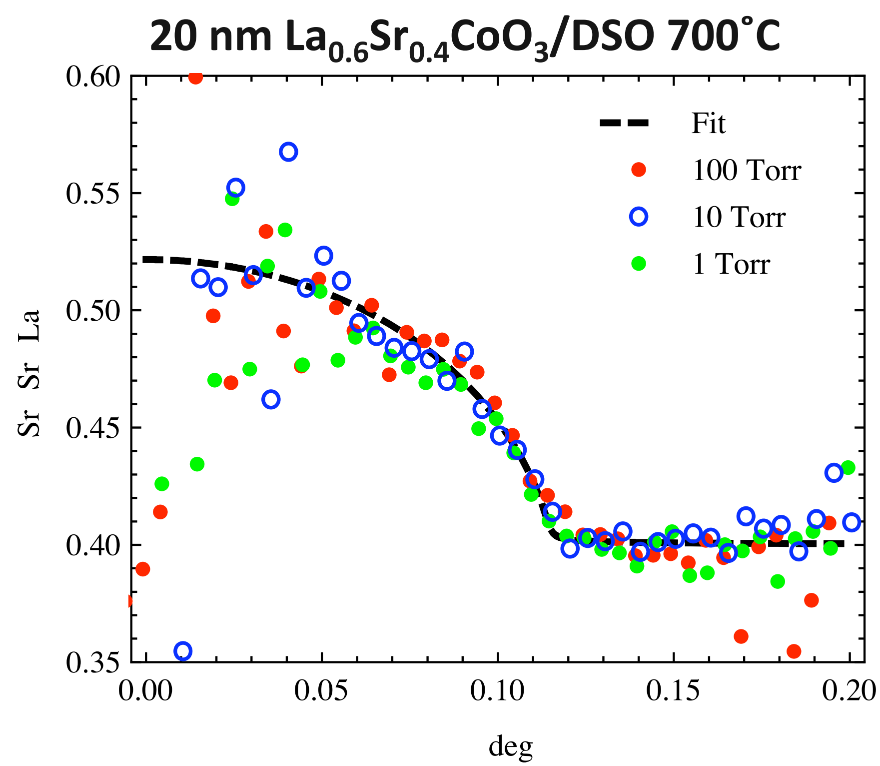


Segregation is observed for both orientations but is not significantly stronger for (110) surface.

LSC Behaves Differently Than LSM

- LSM: surface oxygen vacancies
  - pO_2-dependent strontium surface segregation
- $La_{0.6}Sr_{0.4}CoO_3$ (LSC) & $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (LSCF) : bulk oxygen vacancies
  - Surface strontium enrichment, but no pO_2 dependence





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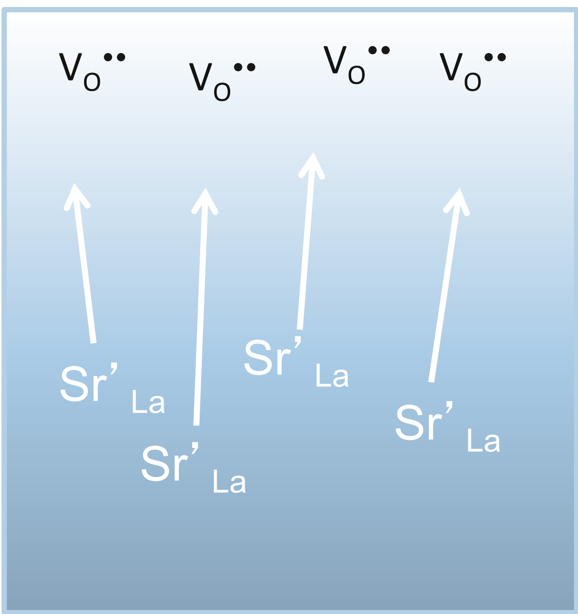
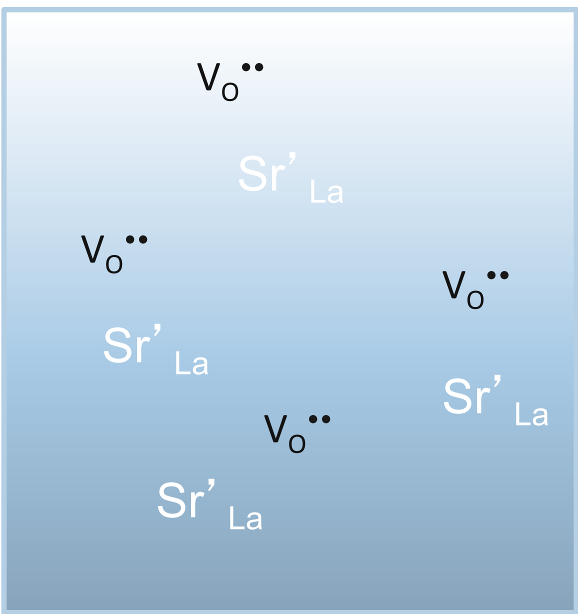
Electronic Conductor (LSM)



Mixed Conductor (LSC, LSCF)



Summary of Strontium Segregation

- For nearly all samples, strontium surface segregation is observed.
- The strontium segregation:
  - Is approximately independent of strain state (i.e., substrate) and film-thickness
  - Depends on pO_2 for LSM but not for LSC and LSCF
    - Behavior may dependent on mobility of oxygen vacancies
  - Depends on temperature and crystal orientation.

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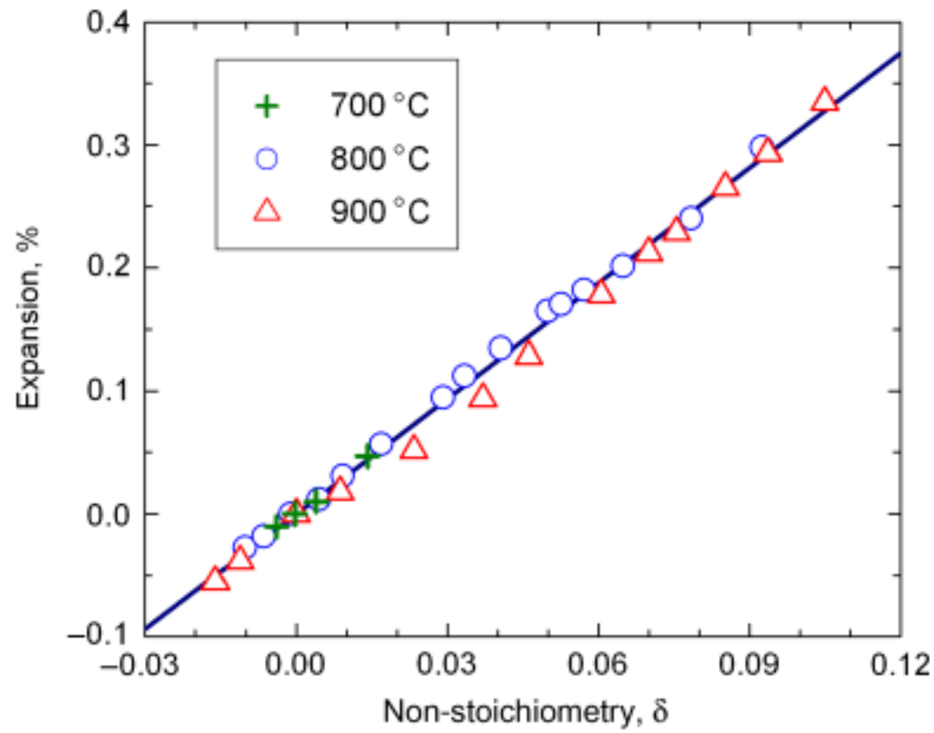
Effect of oxygen stoichiometry on lattice parameter

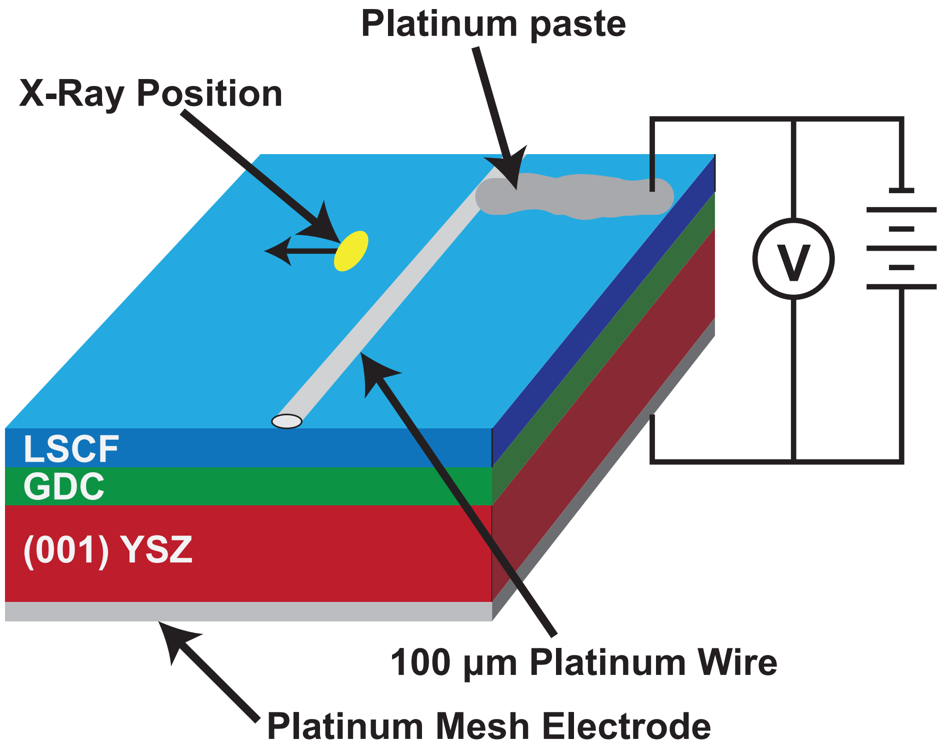
- Volume expansion of LSCF lattice is linearly proportional to deviation from ideal stoichiometry
- Literature curve is for bulk samples expanding in all three dimensions (have to account for one-dimensional expansion of our constrained films)
- Estimate that 1 V cathodic potential at 600° and pO_2 = 150 Torr gives rise to approximately Δd = 0.05 (initial d was not determined)
  - corresponds to ~1 new oxygen vacancy per 20 unit cells



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

Experiment

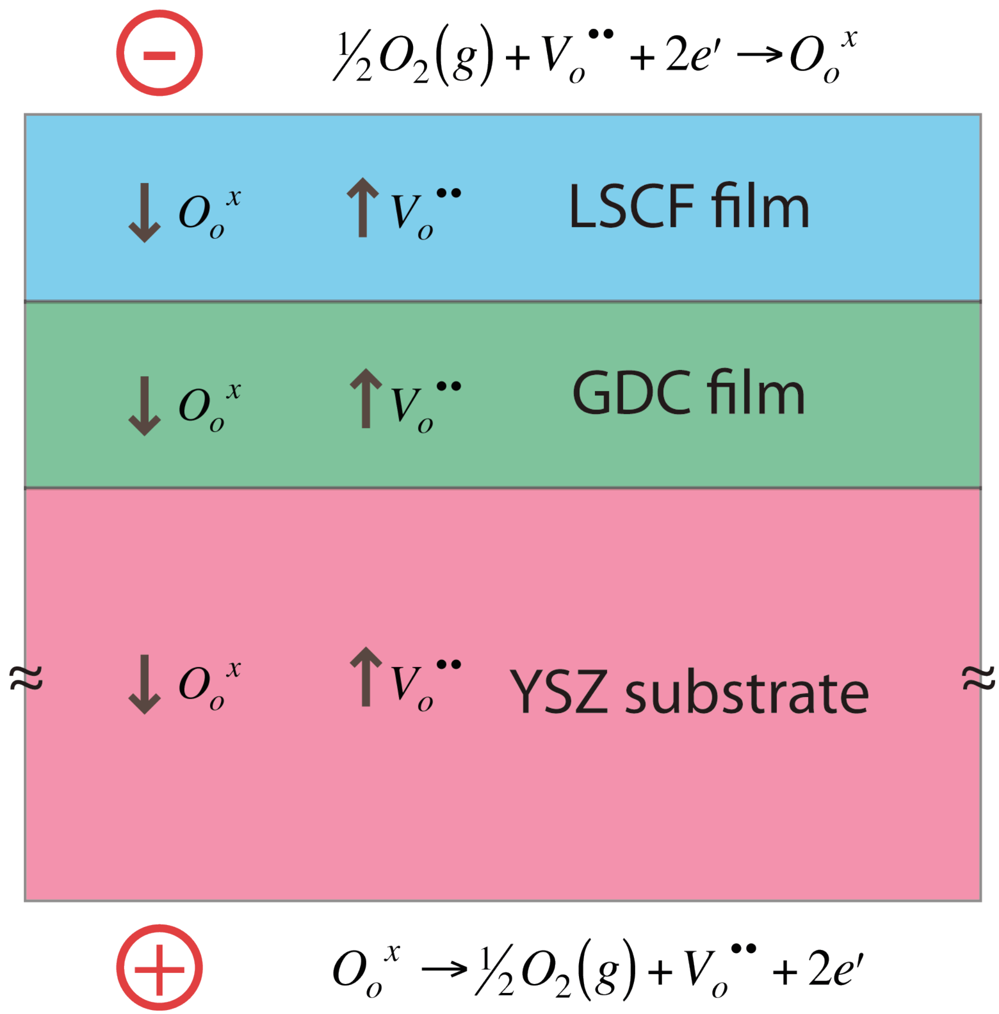
- ~20 nm thickness LSCF and Gd_2O_3-doped CeO_2 (GDC) layers by PLD on (001) YSZ; GDC prevents reactions between LSCF and YSZ
- Examined effects of applied DC potential, pO_2, and T
- Monitored changes in both current (conduction) and out-of-plane lattice parameter (of all three materials)
- Investigating ionic component of LSCF conductivity (YSZ blocks electronic component)



~20 µm wide incident X-ray beam

Expected behavior

- Applying a cathodic (anodic) potential drives oxygen into (out of) the LSCF film at the LSCF/gas interface
- Also drives oxygen into (out of) the GDC film at the LSCF/GDC interface
- If barriers to oxygen vacancy transport across these two interfaces are equal, expect <u>no</u> change in lattice parameter or conduction when field is applied
- If changes in lattice parameter and conduction <u>are</u> observed, we can determine which interface is rate limiting



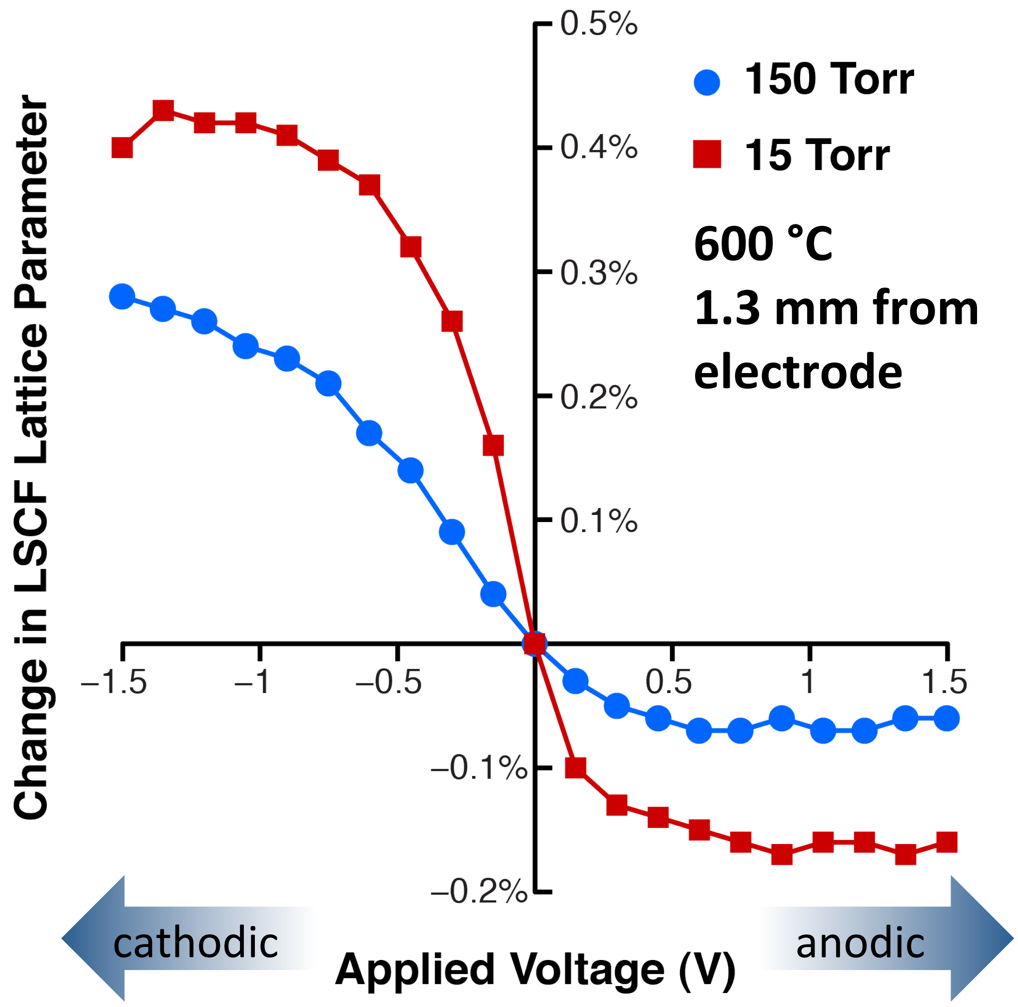
Cathodic potential condition

LSCF lattice parameter shift vs applied potential

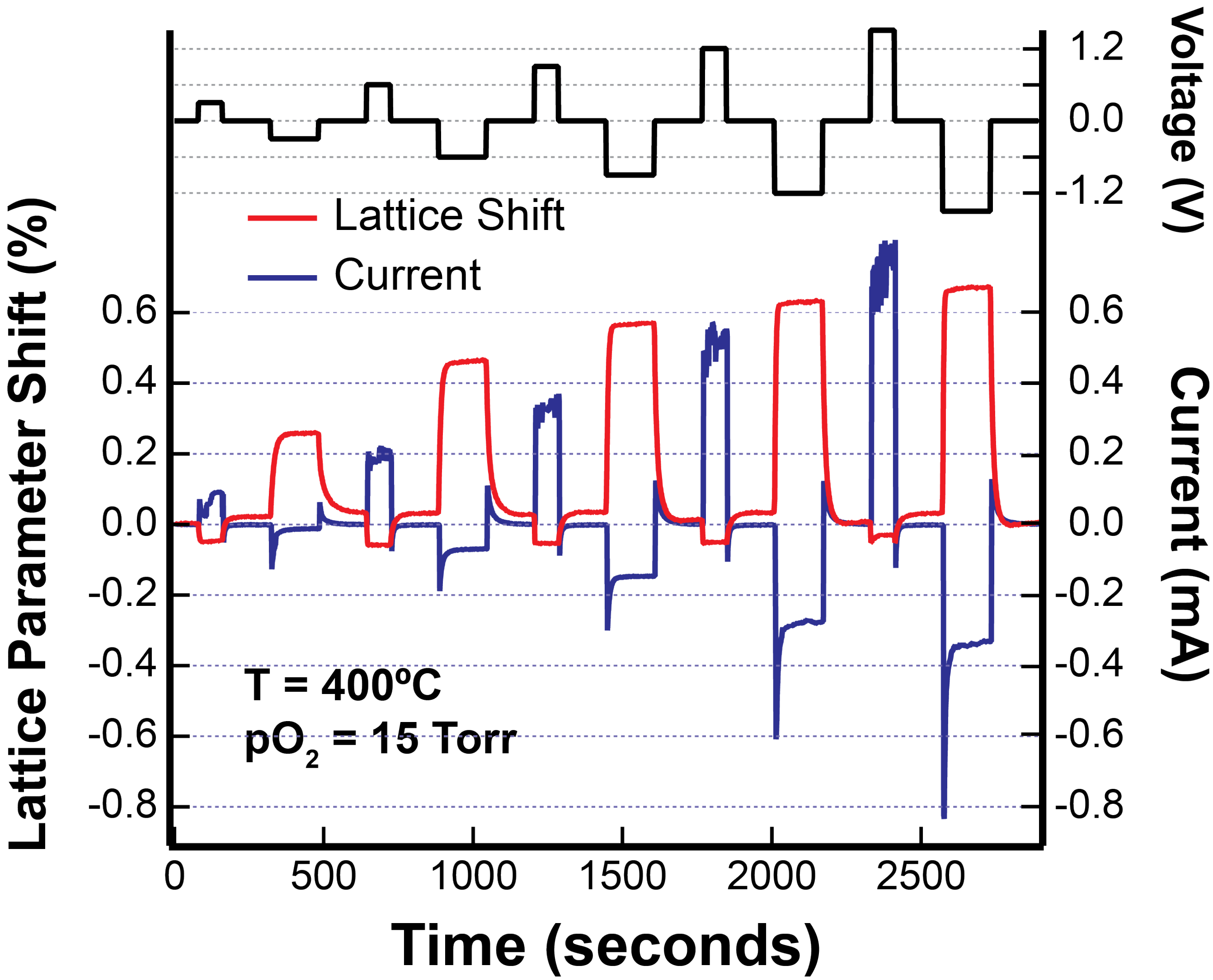
- Oxygen transport across the LSCF/gas interface is rate-limiting under both anodic and cathodic conditions

- Cathodic potentials result in larger Δd than anodic potentials
  - larger barrier to oxygen reduction at the LSCF/GDC interface under cathodic conditions than to reverse reaction under anodic conditions

- Stoichiometry changes increase with decreasing pO_2
  - O_2 reduction barrier increases with decreasing pO_2



Time Dependence of Electrochemical Response



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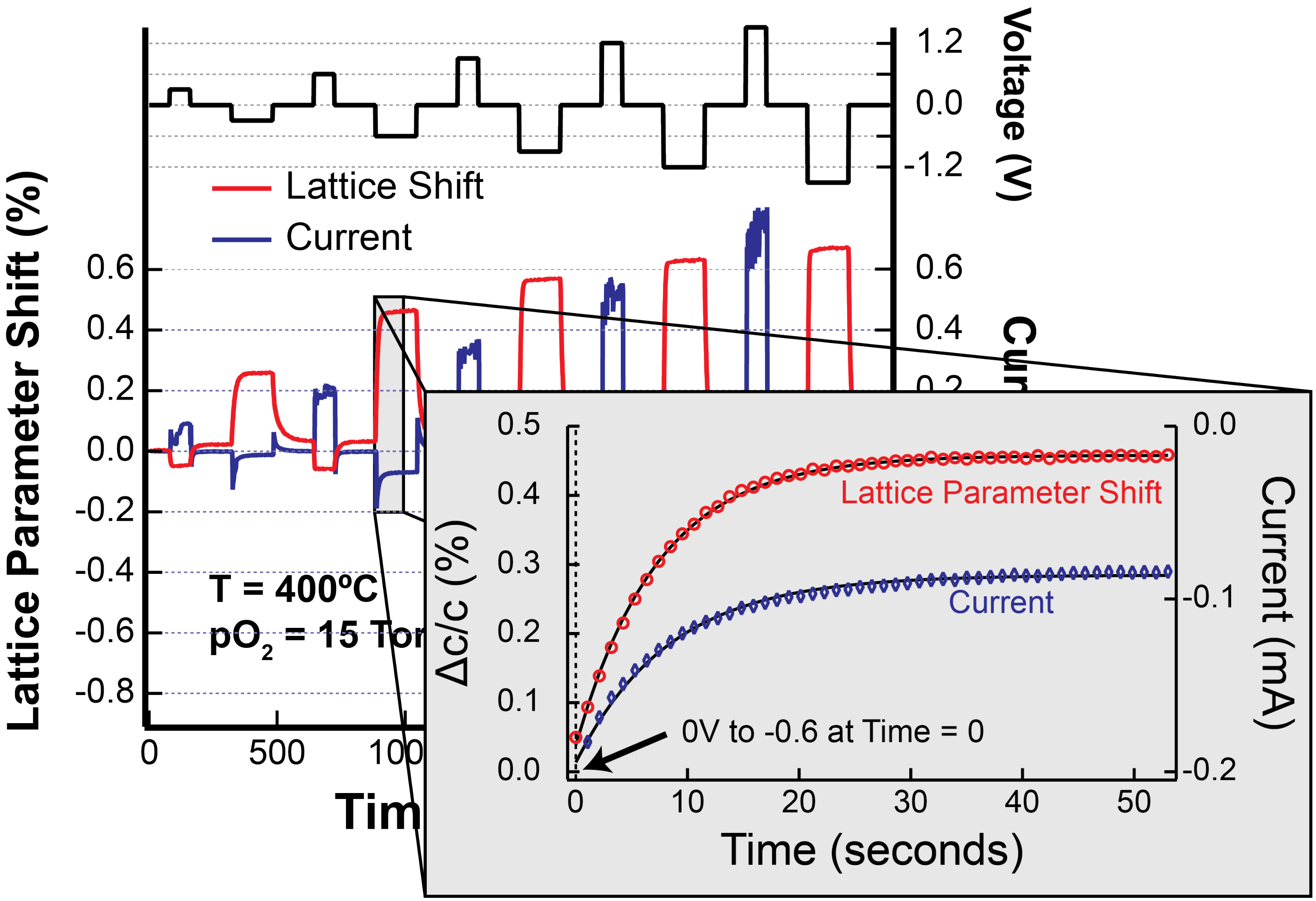
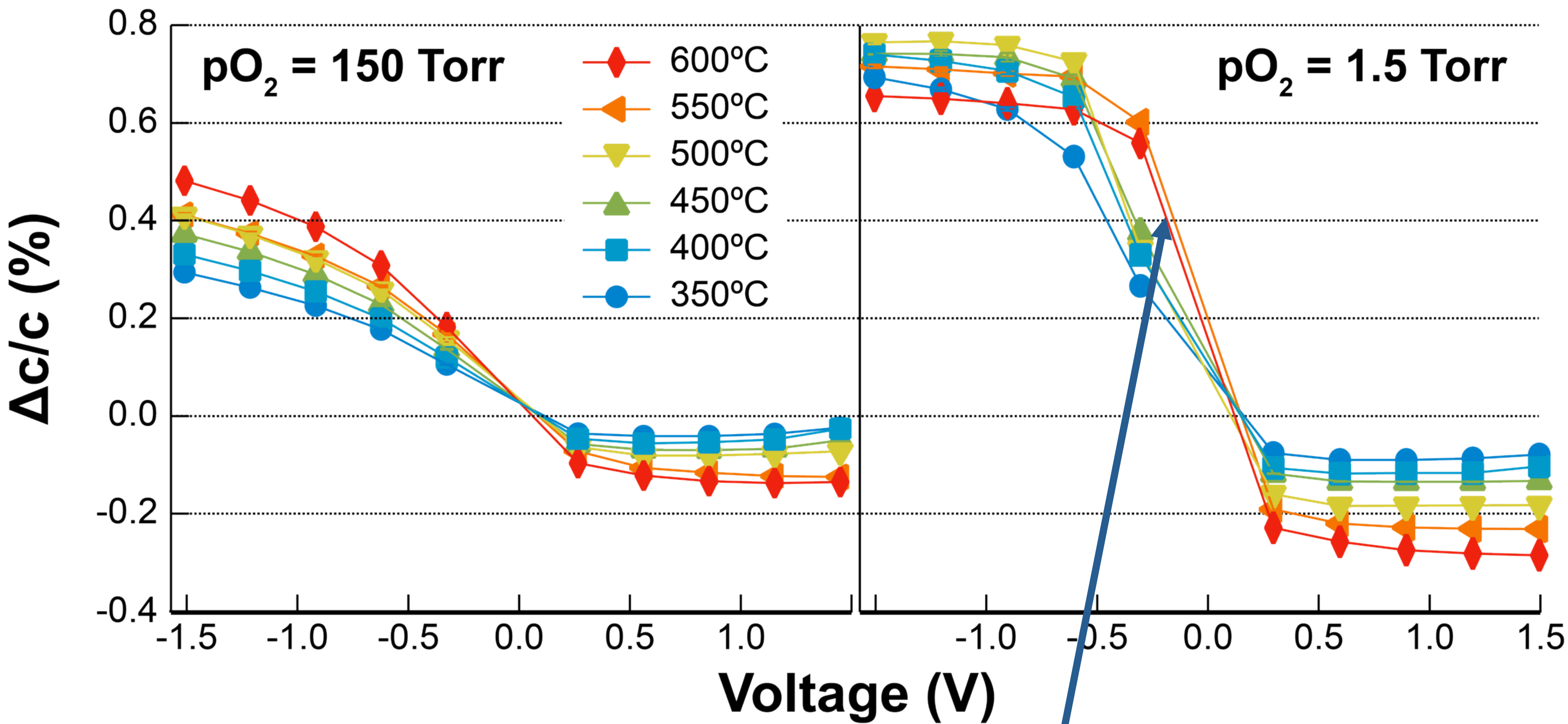


C-Lattice Shifts versus Voltage and Temperature



Explanation: LSCF phase change from rhombohedral to cubic between 400-550°C

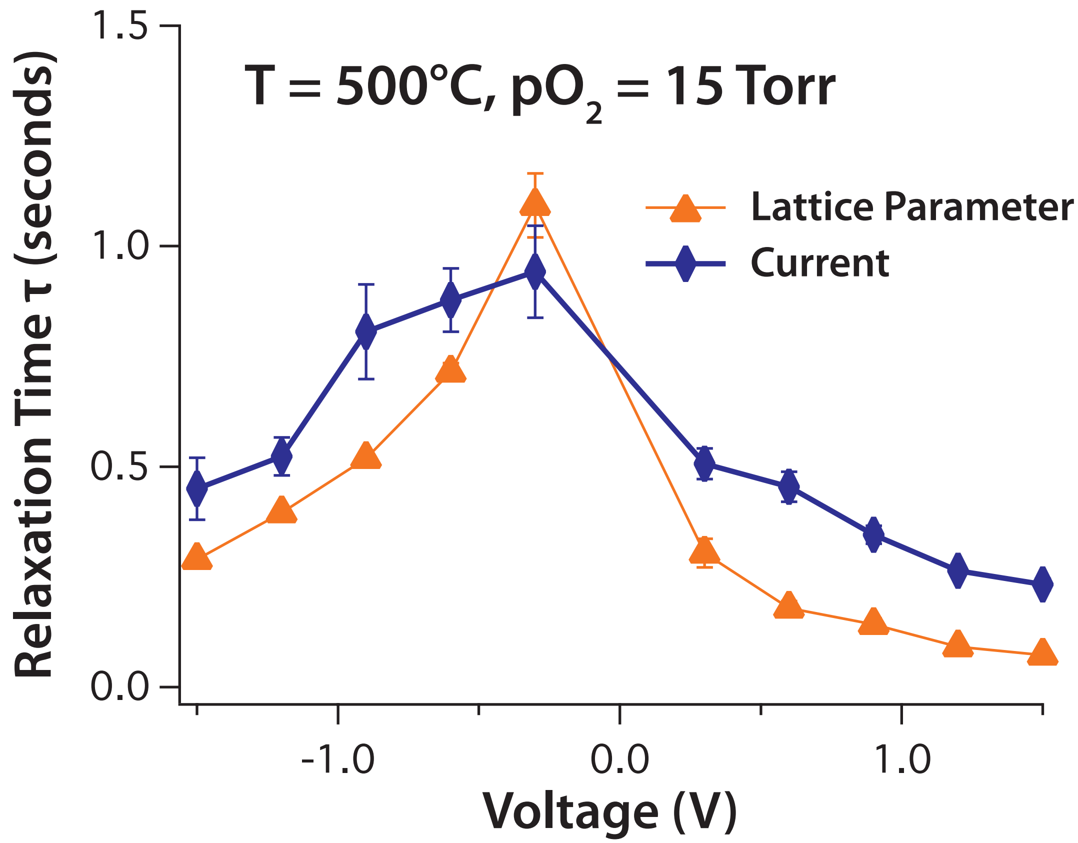
Solid State Ionics 159 (2003) 71–78

Applied Catalysis B: Environmental 103 (2011) 318–325

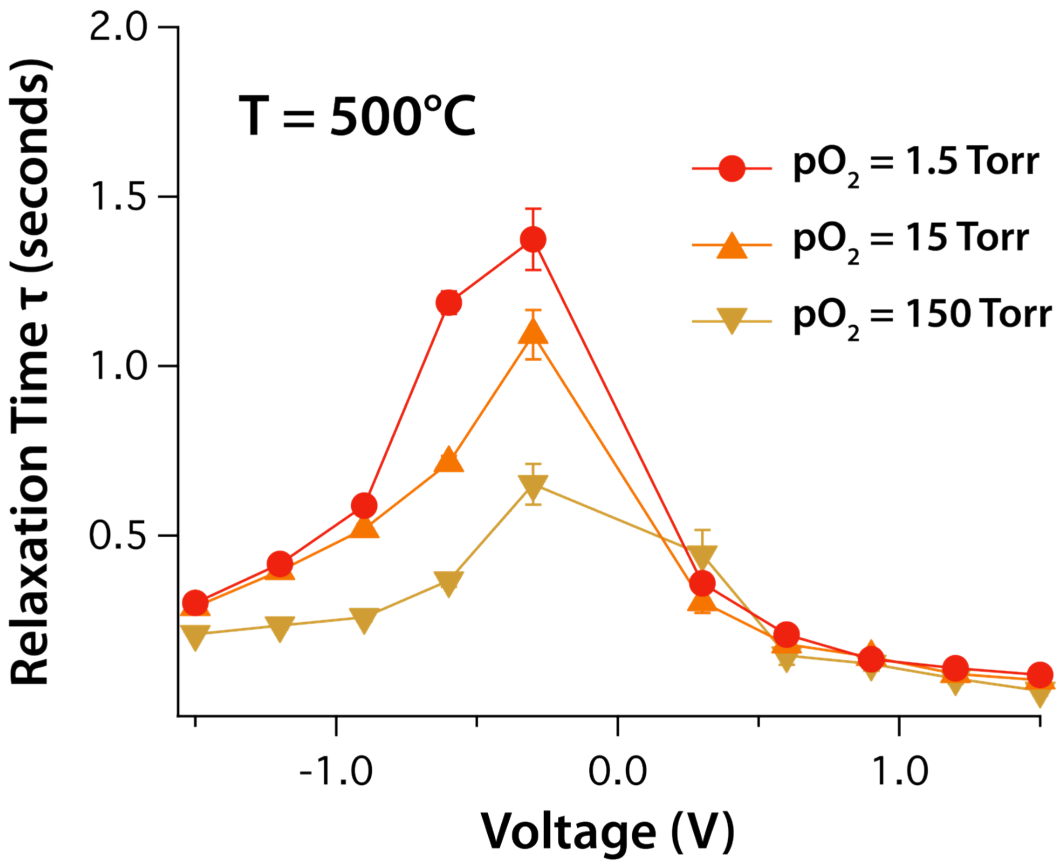
Comparing Current and Lattice Relaxation

Current averages over the entire sample.

X-rays sample a very small area responds more quickly.

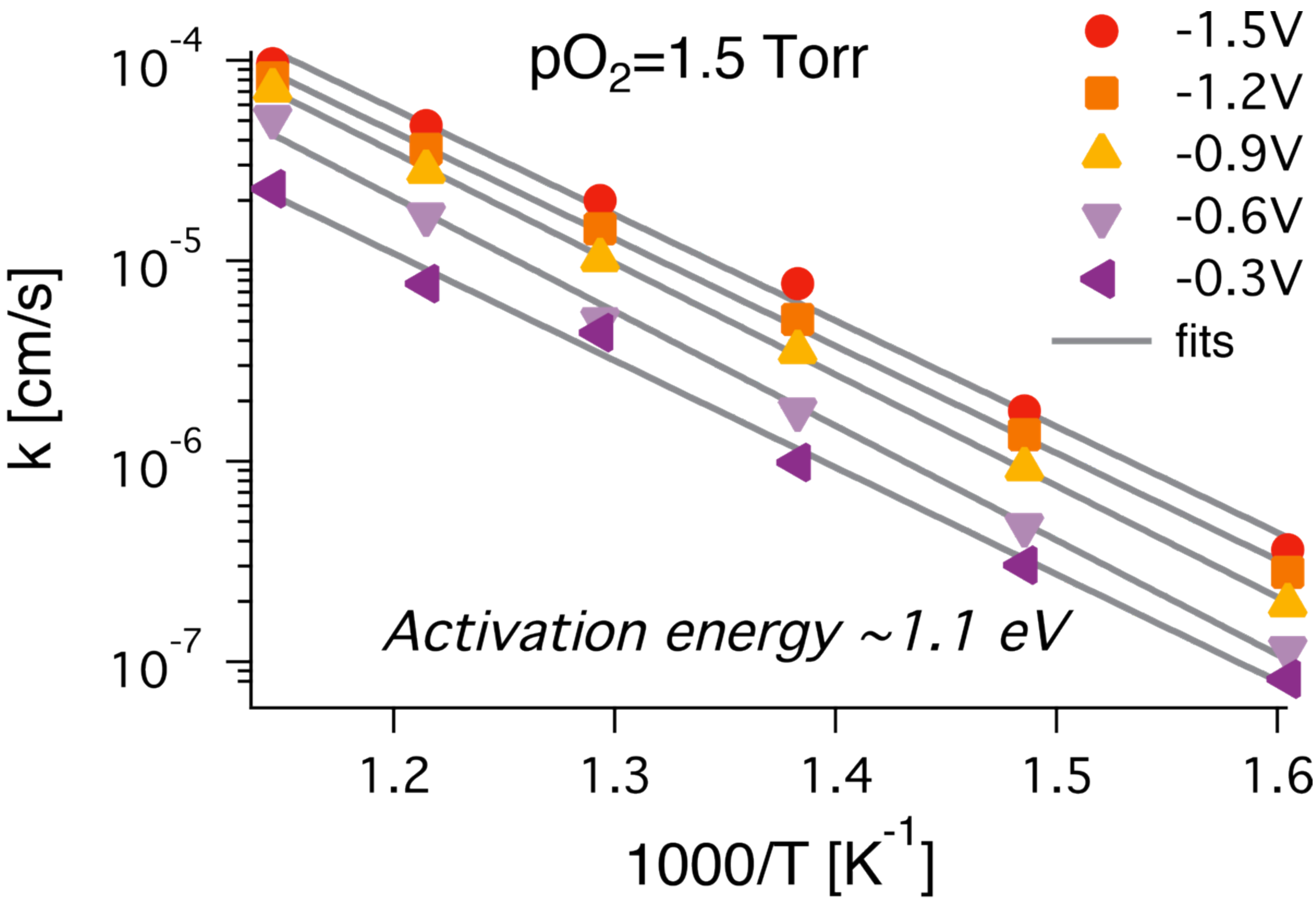


Effect of pO_2 on Lattice Relaxation



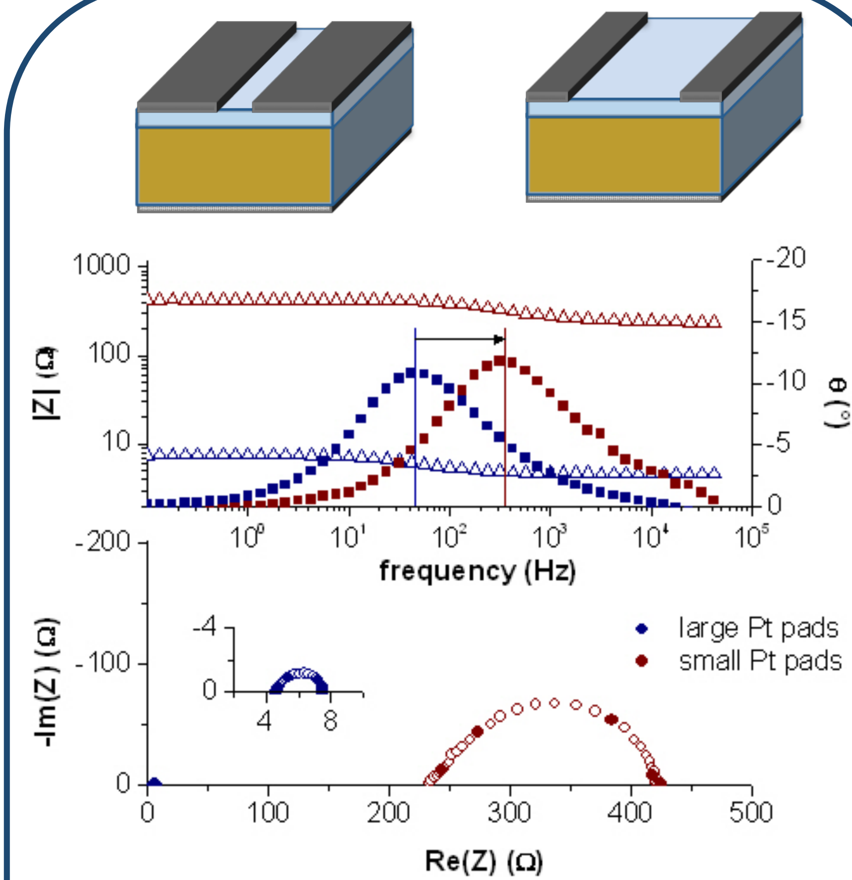
Not surprisingly, the lattice responds more quickly at higher oxygen partial pressures.

Activation Energy for Oxygen Exchange



Electrochemical variation due to current collector geometry and morphology

- Current collector geometry is critical
  - Macroscopic area is not linearly related to impedance
- Current collectors affect electrical property measurements (active area)
- Inconsistency in “painting” Pt-paste
  - Area coverage
  - Contact area with film
- Sputtered Pt de-wets film surfaces
  - Contact is lost as Pt loses continuity



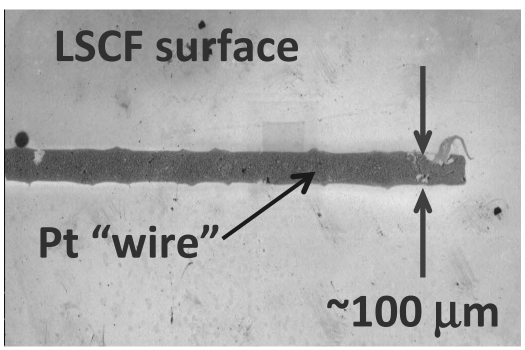
Typical performance variability using:

- sputtered Pt working electrode
- Pt paste counter electrode

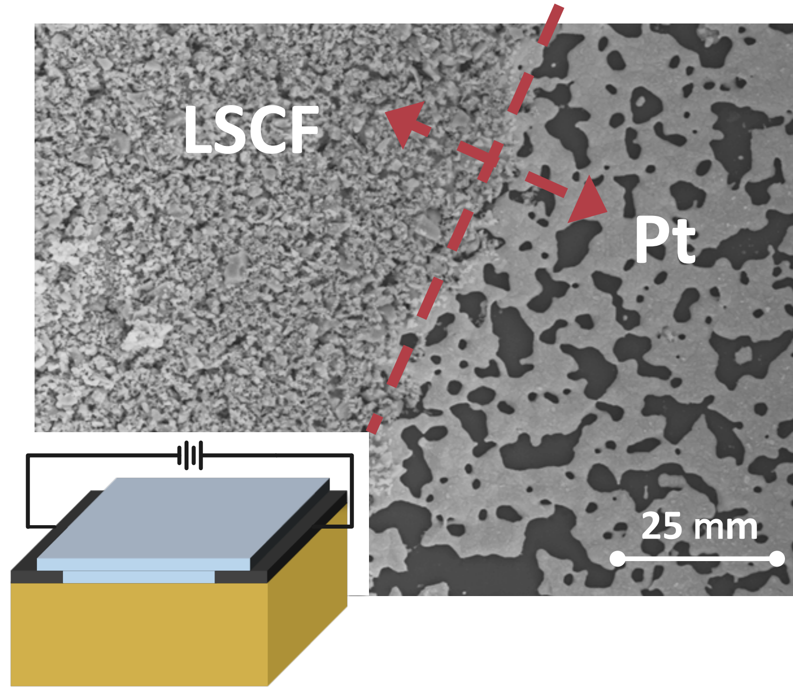
Screen-Printing of SOFC Materials

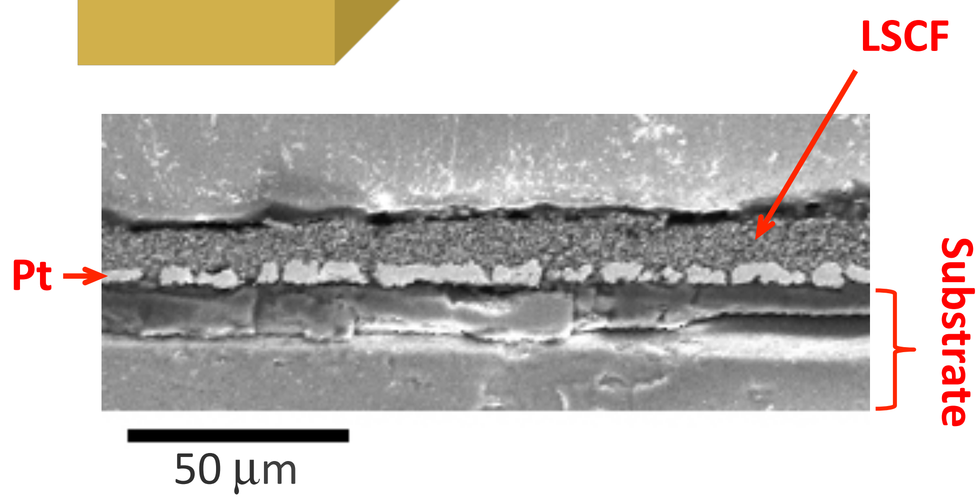
Screen-printed electrodes provide enhanced performance

- Total thickness variation < 10%
- Accurate lateral positioning and sizing
- Electrically continuous "wires"
- Complex geometries are possible
- High process control and repeatability

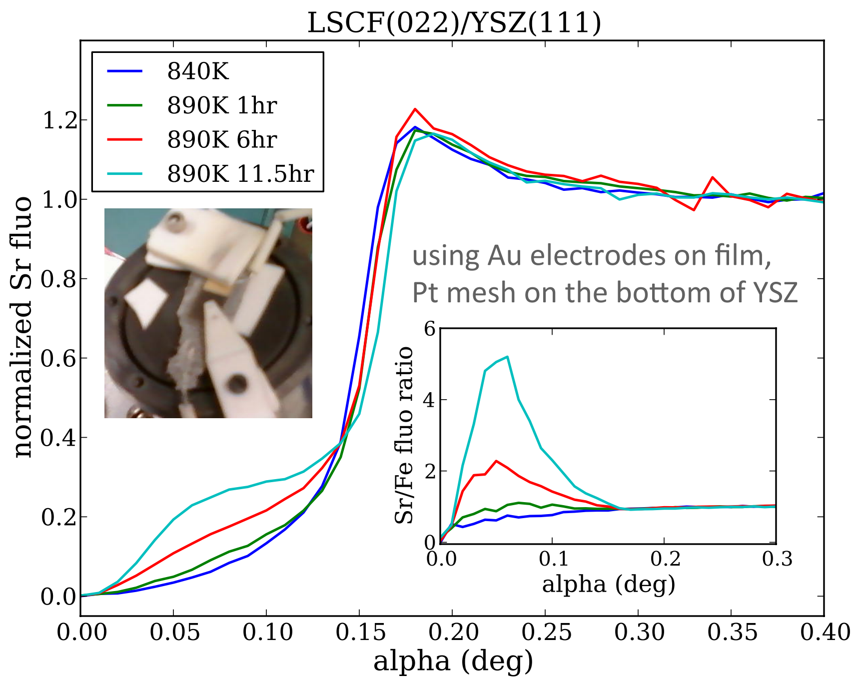


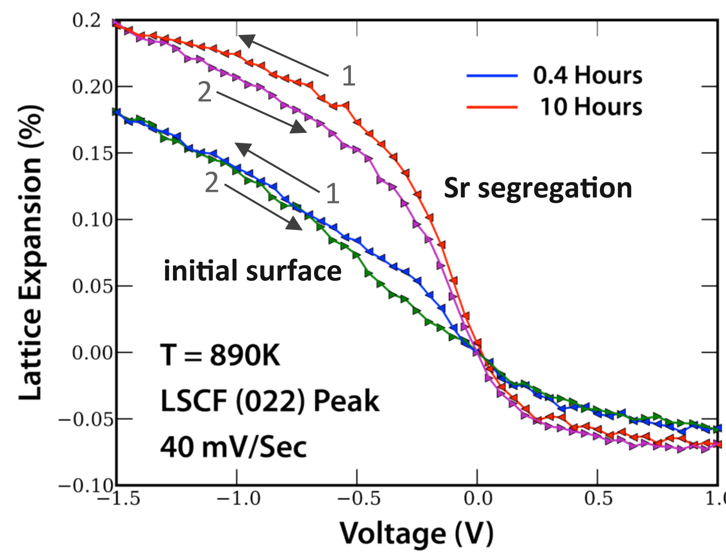
- Buried Pt electrodes / porous LSCF
- Stable microstructure after anneal

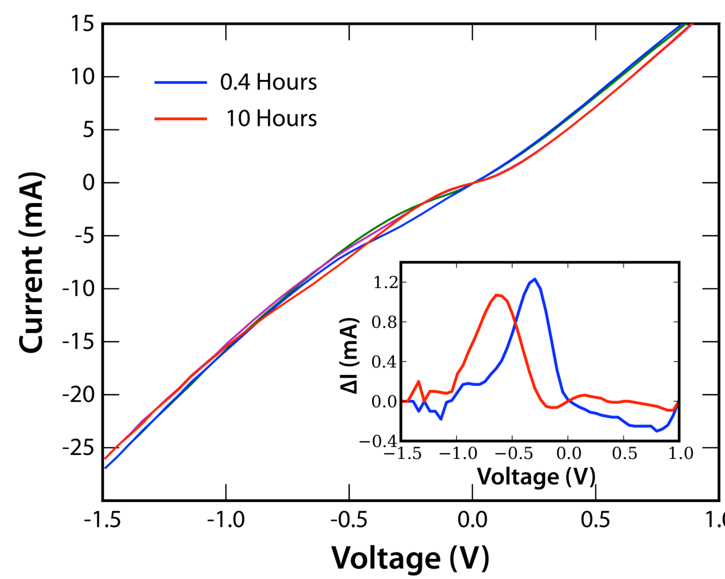




Impact of Sr Segregation on Oxygen Exchange







- Slow increase in Sr segregation during annealing at ~620°C in air
- Lattice expansion is higher and shows more hysteresis on the Sr segregated surface
- IV curve shows only small difference between the initial and Sr segregated surface

Summary

- In-situ x-ray techniques provide opportunity to understand relationships between film / interface structure and electrical behavior

- Application of DC fields across LSCF/GDC/YSZ heterostructures results in rapid (< 1 sec) changes in LSCF (but not GDC or YSZ) out-of-plane lattice parameters
  - Indicates that oxidation / reduction reactions at the LSCF / gas interface are rate-limiting

- The activation energy is in the order of 1.1eV for the currents and c-lattice parameter shifts.

- The tau values extracted from the current are larger than the ones from the c-shift for high pO_2 and high T.

The End