# Effect of Carbon Dioxide on the Cathodic Performance of Solid Oxide Fuel Cells

**S.Gopalan**, Y.Yu, H.Luo, D.Cetin, K.Ludwig, X.Lin, S.N.Basu, and U.B.Pal

Division of Materials Science and Engineering

Boston University, Boston, MA -2215

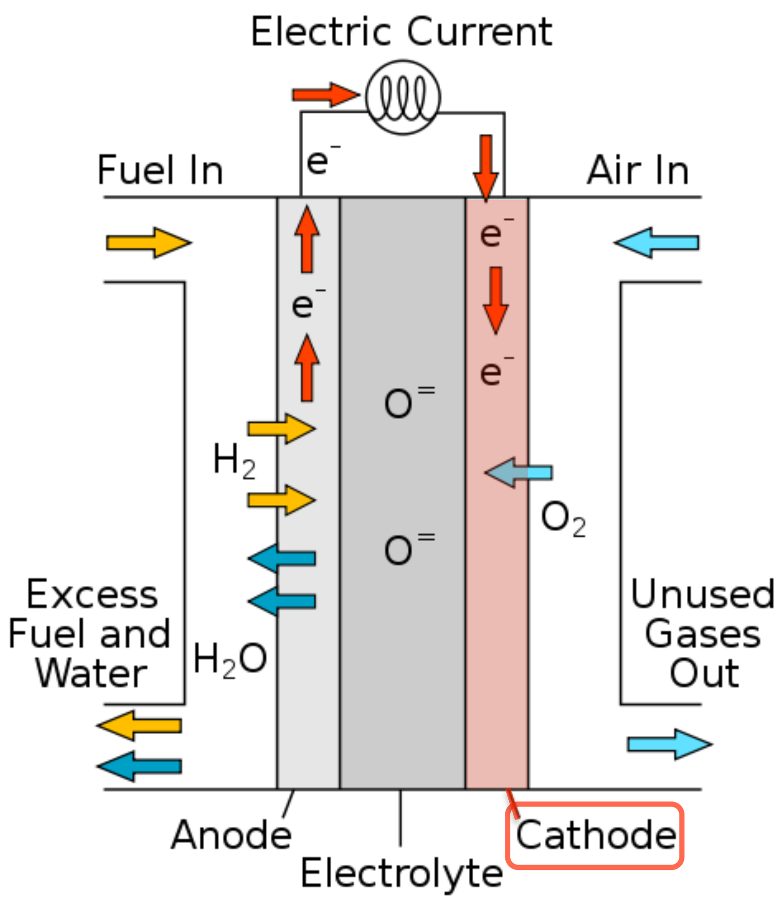
Presented at the 2014 SECA Meeting, Pittsburgh PA

July 23, 2014

# Outline

- Motivation
- Experimental
  - Sr surface segregation
  - Effect of $CO_2$ on Sr segregation in LSCF
- DFT results
- Implication for SOFC cathodes

# Motivation




Scheme of an SOFC

Advantages

- Long operation: >50,000 hours
- High Efficiency: >65% with cogeneration
- Fuel Flexibility

Challenges

- High temperature operation
- Thermal expansion mismatch
- Sealing difficulty – cross leaks
- Degradation of stack components

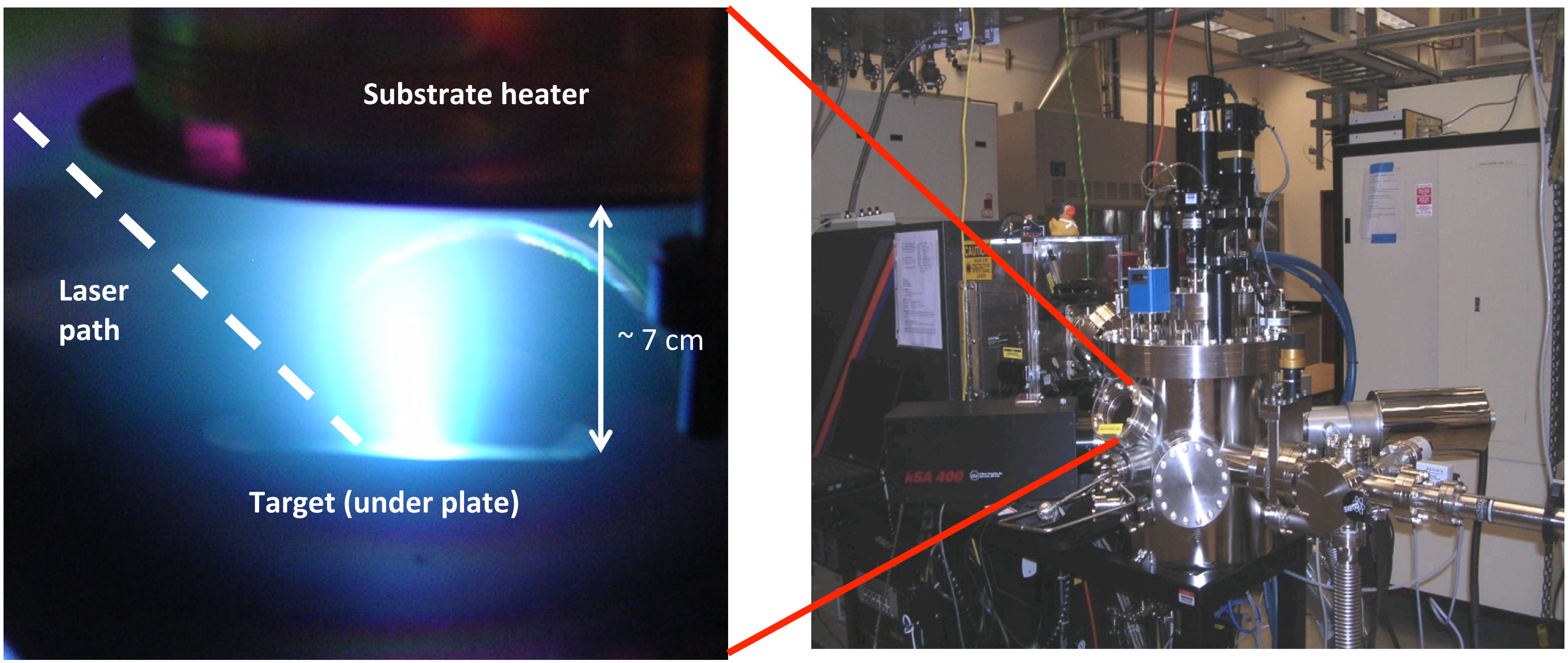
One potential degradation mechanism is degradation of cathode materials (eg, LSCF.) by gas phase impurities such as $CO_2$ and $H_2O$, including from cross leaks.

# Questions

- What happens to the surface of the LSCF cathode upon exposure to air side impurities such as $CO_2$ and $H_2O$ present in trace quantities?
- What happens to the cathode when there are larger scale accidental cross-leaks from the anodic side due to compromised seals and/or leaks from large numbers of pinholes?
- What are the implications for cell performance including long term performance?

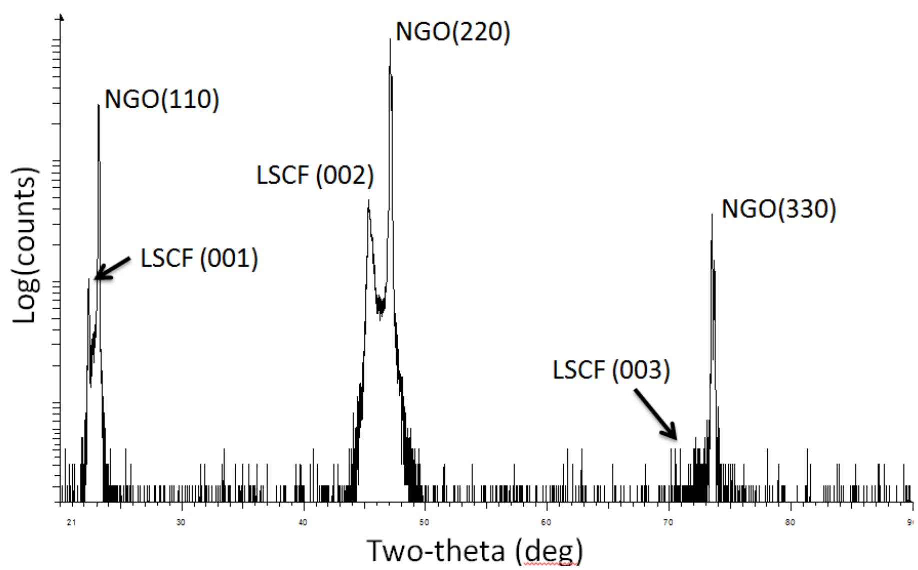
# Experimental: Thin Film Deposition LSCF-6428 on $NdGaO_3$ (NGO)

- Pulsed Laser Deposition (PLD) at Environmental Molecular Sciences Laboratory (EMSL) at Pacific Northwest National Laboratory (PNNL).

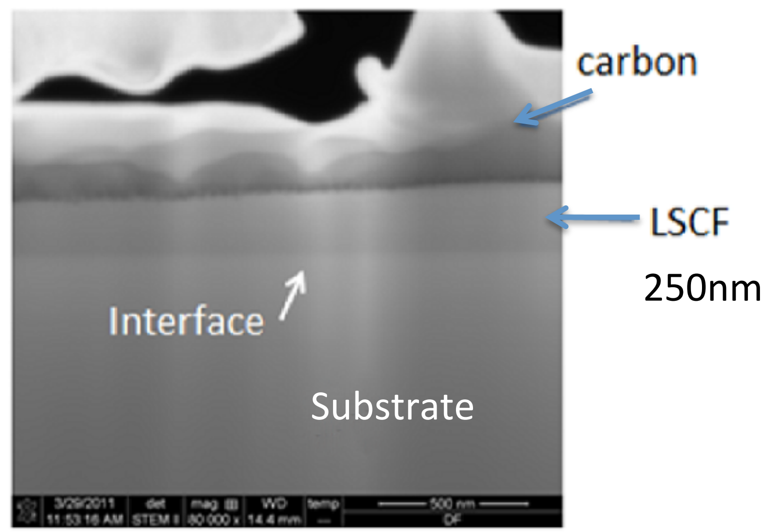


# Thin Film Characterization LSCF-6428 on NGO

## XRD

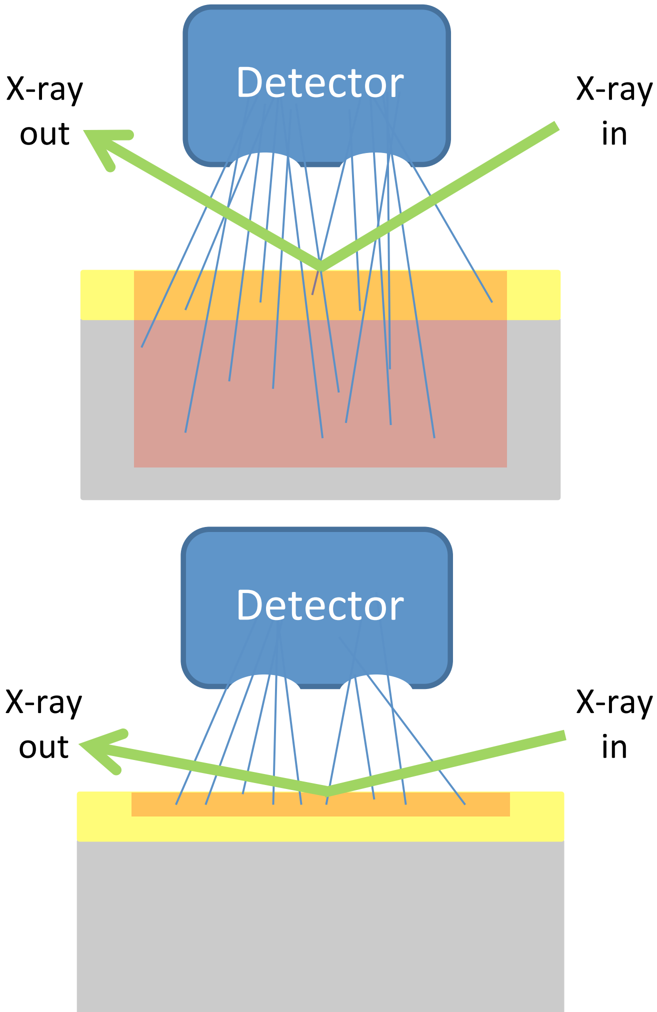



## FIB-SEM

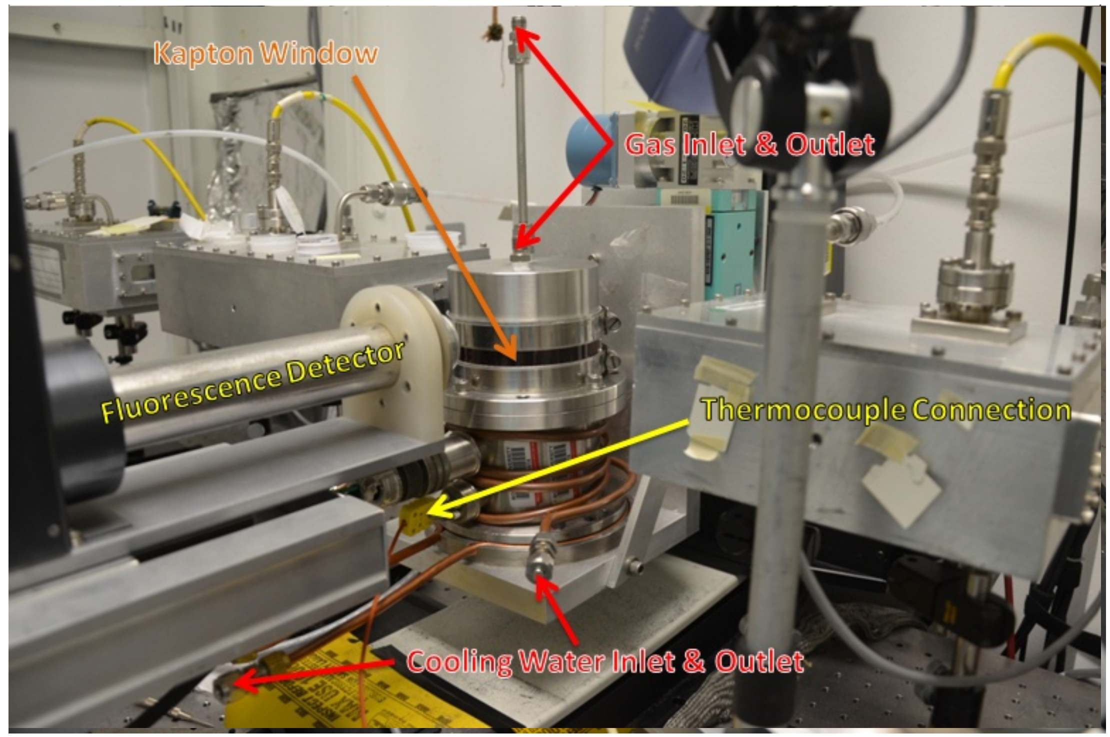



X-ray diffraction shows good alignment and the SEM image shows clean interfaces at the film/substrate.

# Total Reflection X-ray Fluorescence (TXRF)

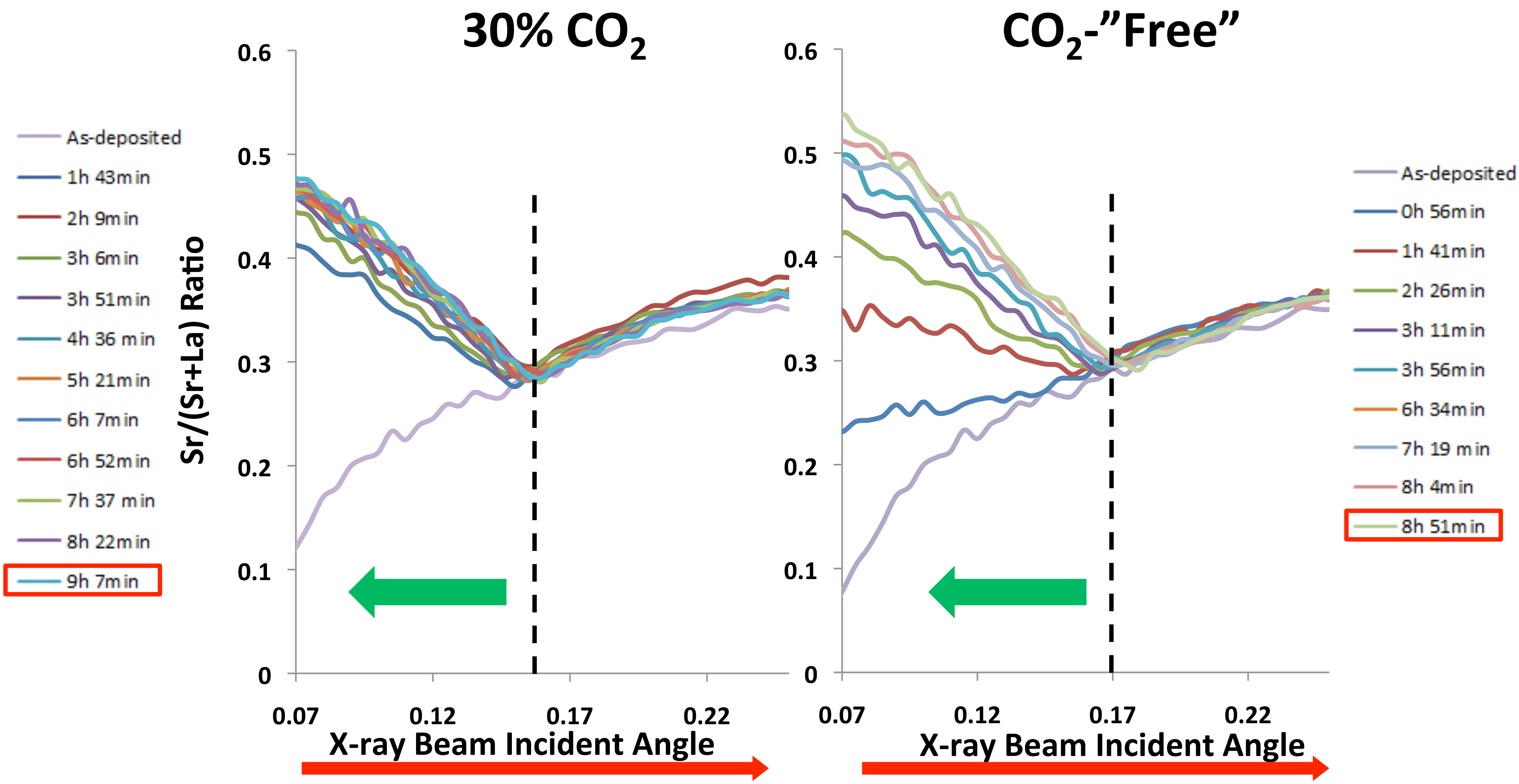



TXRF working principle




TXRF Setup at X23A2,
National Synchrotron Light Source-I,
Brookhaven National Laboratory

# Real-Time TXRF Analyses of LSCF-6428




800°C 30%$CO_2$-21%$O_2$-49%$N_2$

800°C 21%$O_2$-79%$N_2$

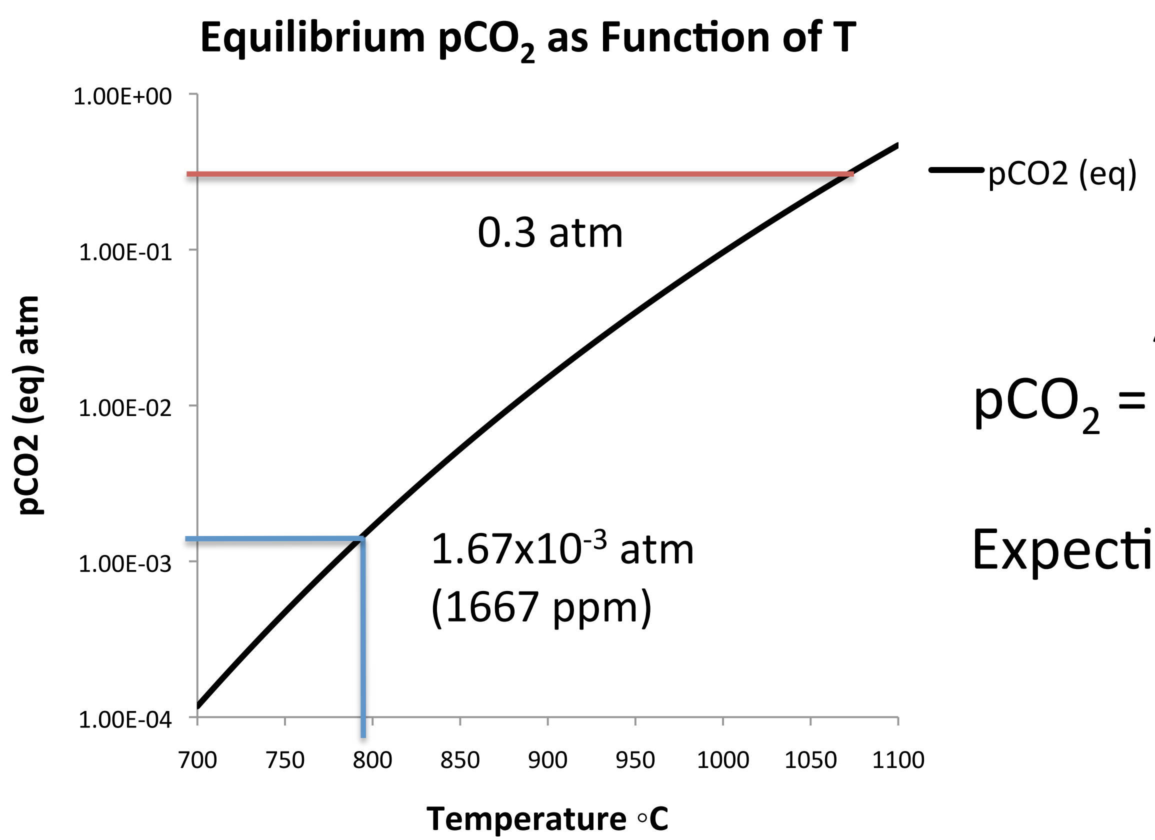
Both annealed at 800°C

Total Pressure = 1atm

$pO_2$=0.21atm

# Mechanisms of Enhanced Kinetics of Sr Surface Segregation

- Step 1. $\text{Sr from LSCF lattice} + \frac{1}{2}O_2 \rightarrow SrO$ (by Sr Surface Segregation)
- Step 2. $SrO + CO_2 \rightarrow SrCO_3$ $\Delta G^\circ = -230{,}290 + 161.43T\ (J/mol)$

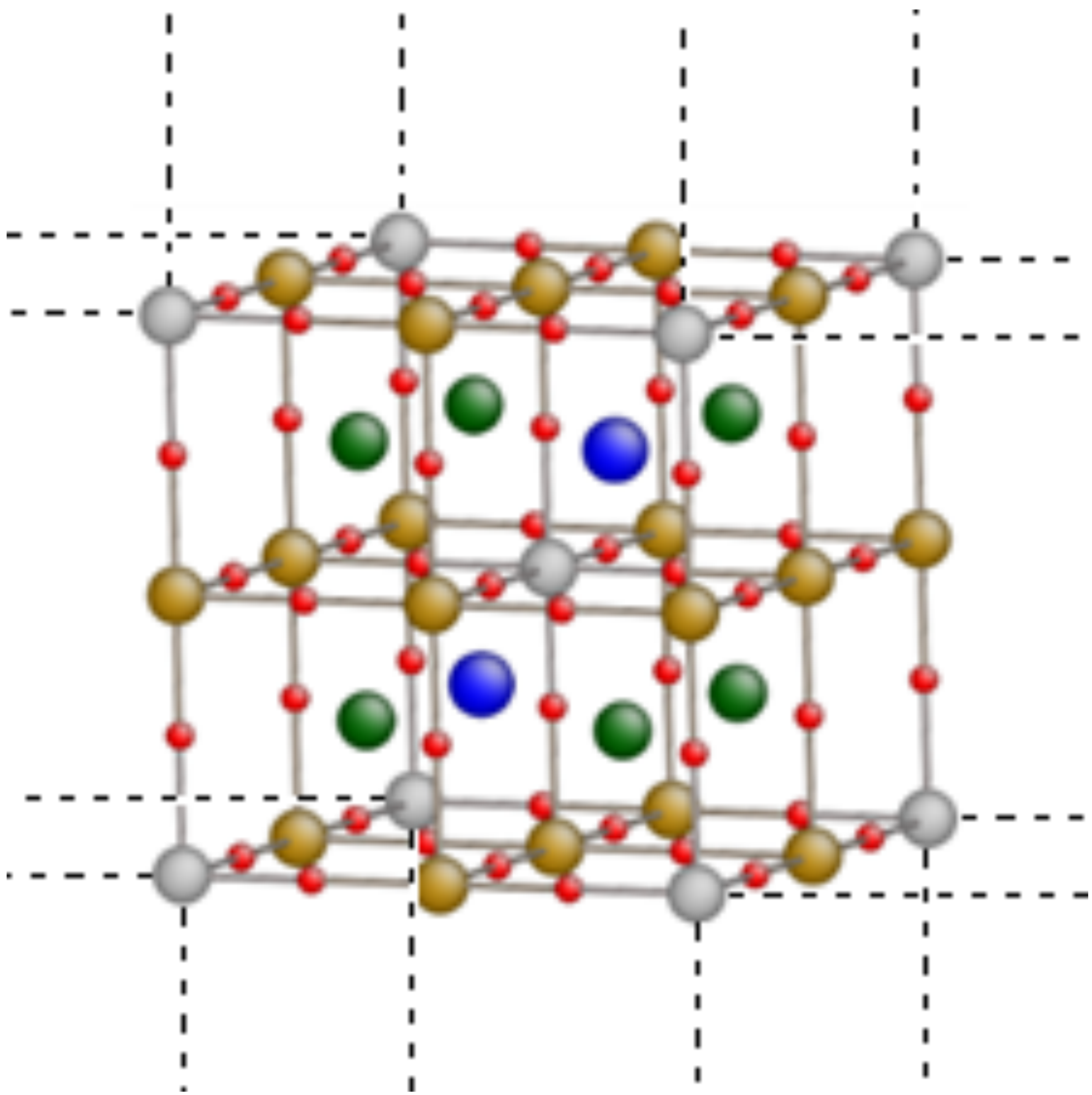



At T = 800 °C

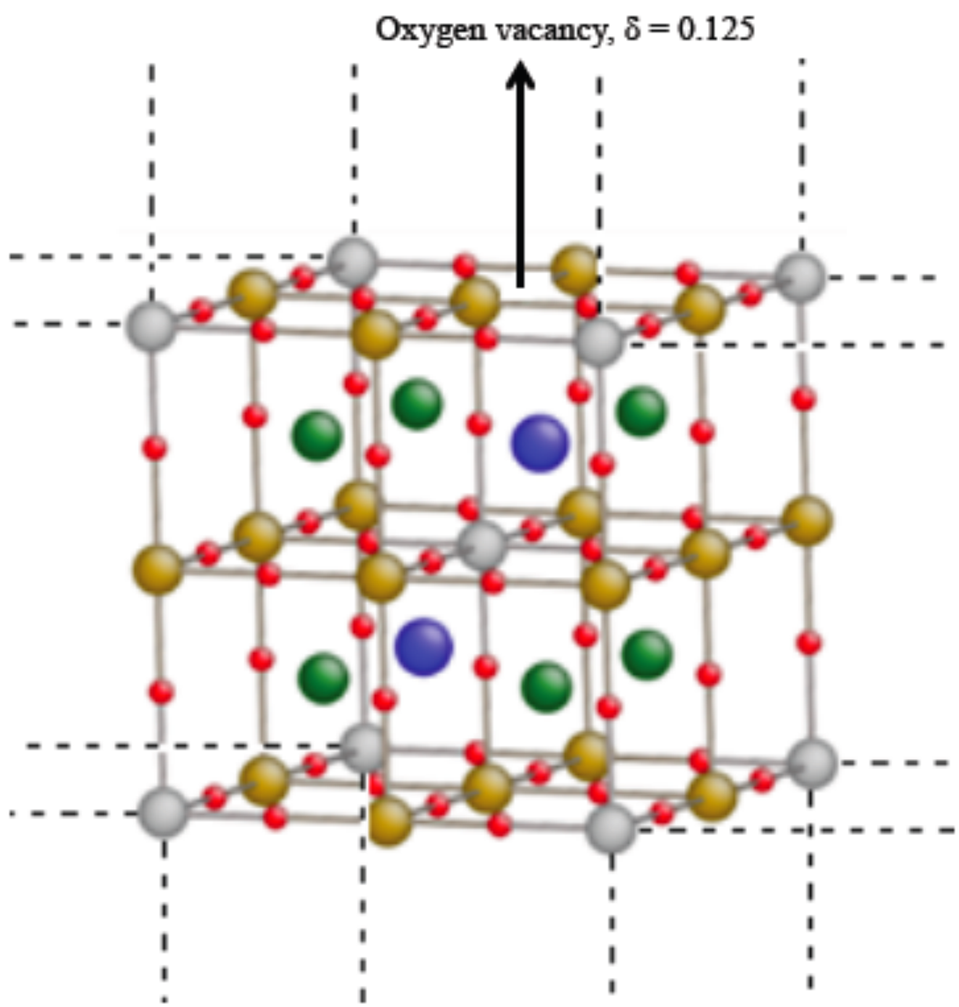
$pCO_2 = 0.3atm >> pCO_2(eq)$

Expecting the formation of $SrCO_3$

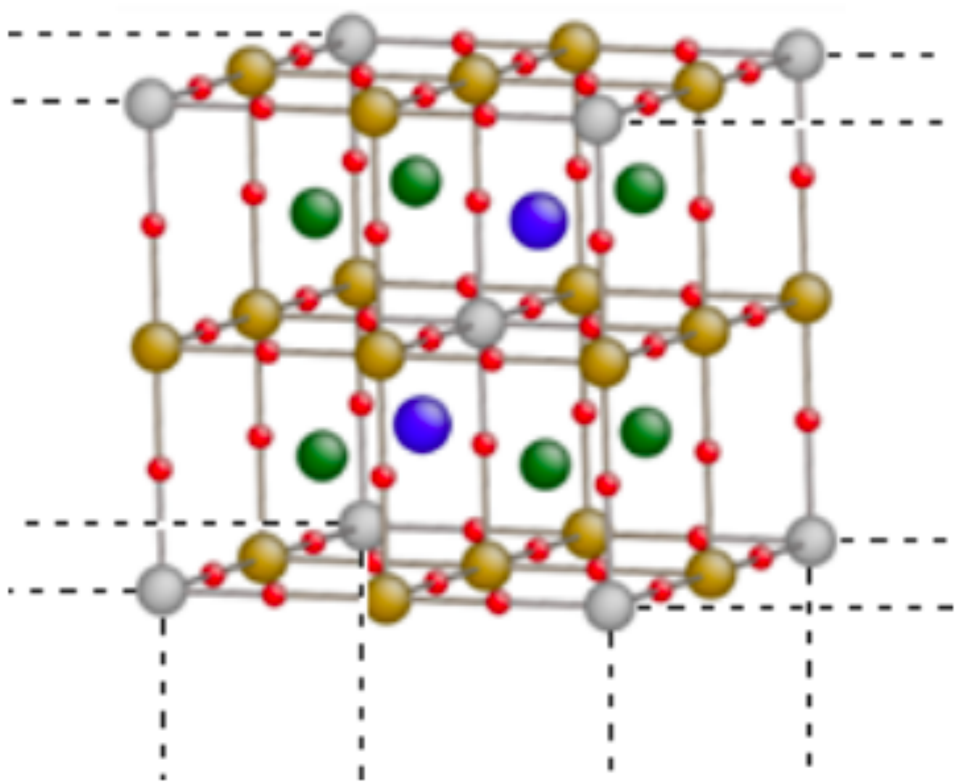
Bulk Phase



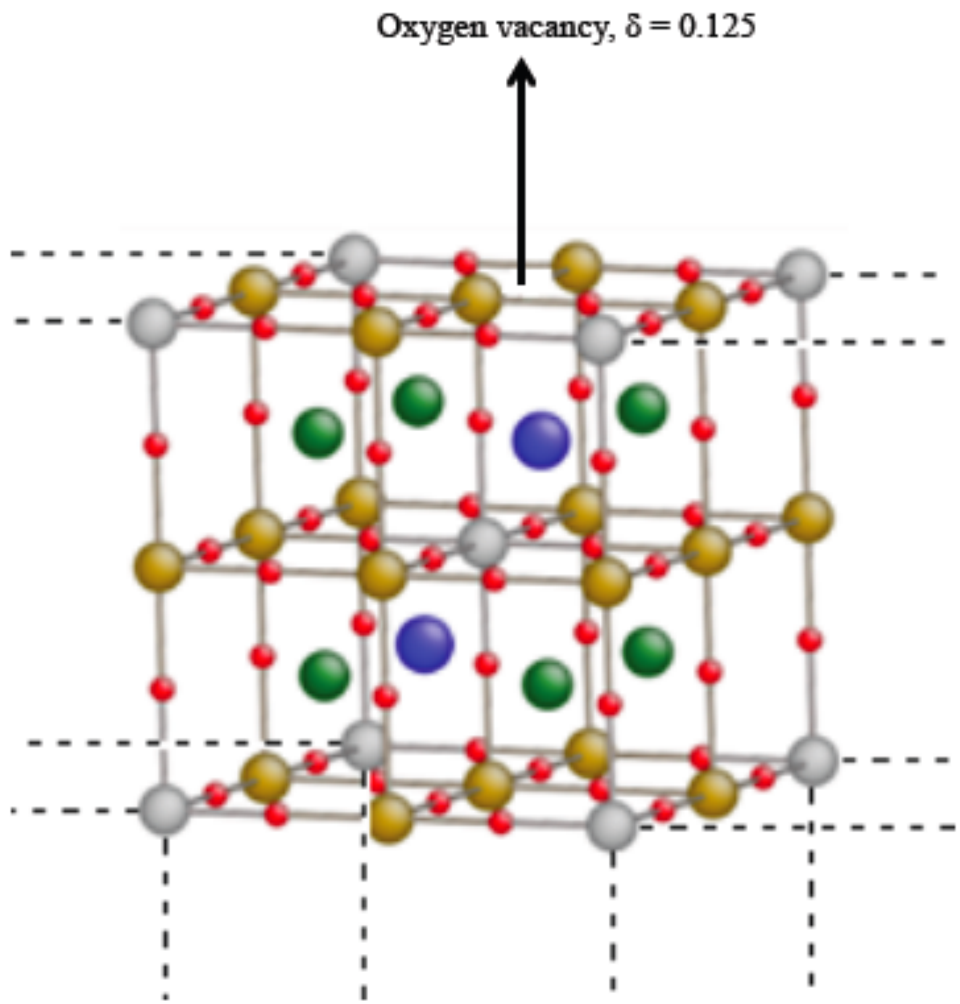
# Bulk Phase with Oxygen Vacancy

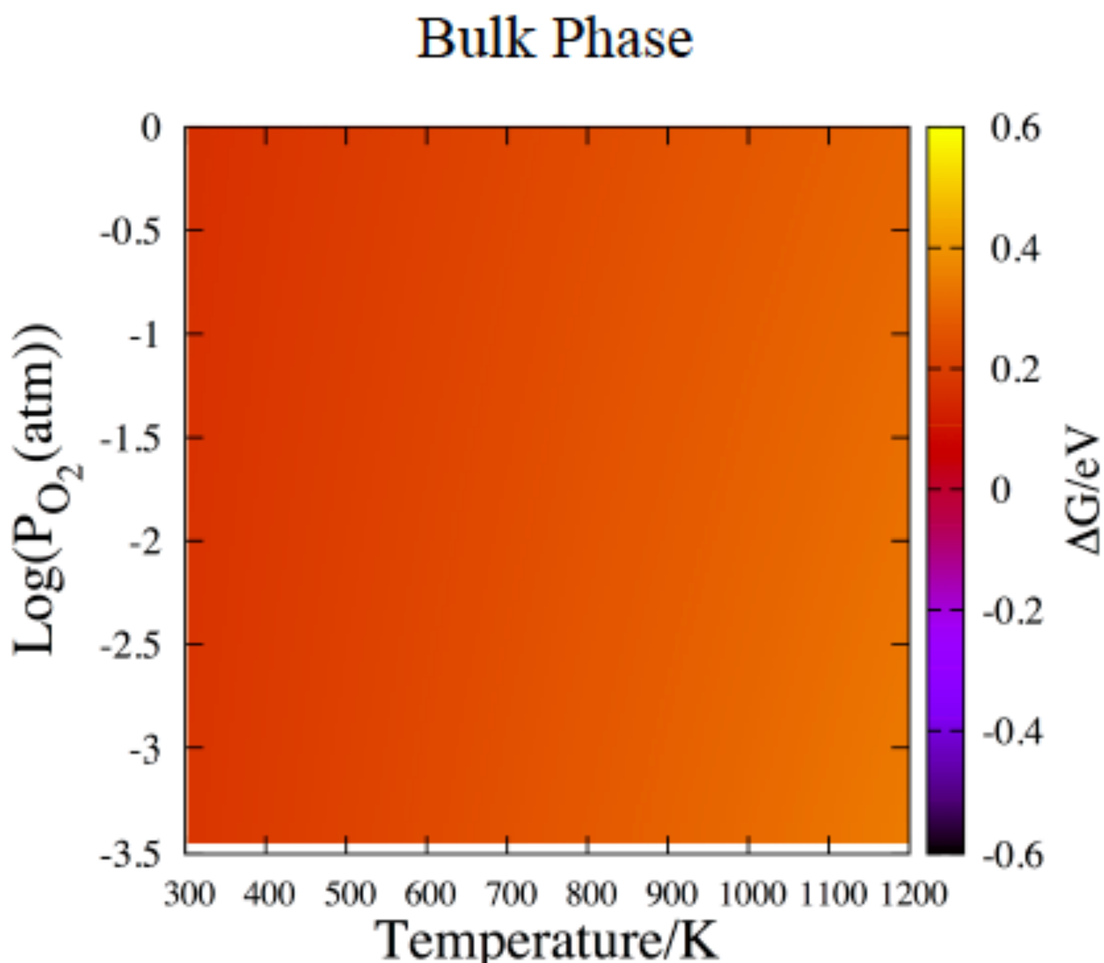


Surface Phase

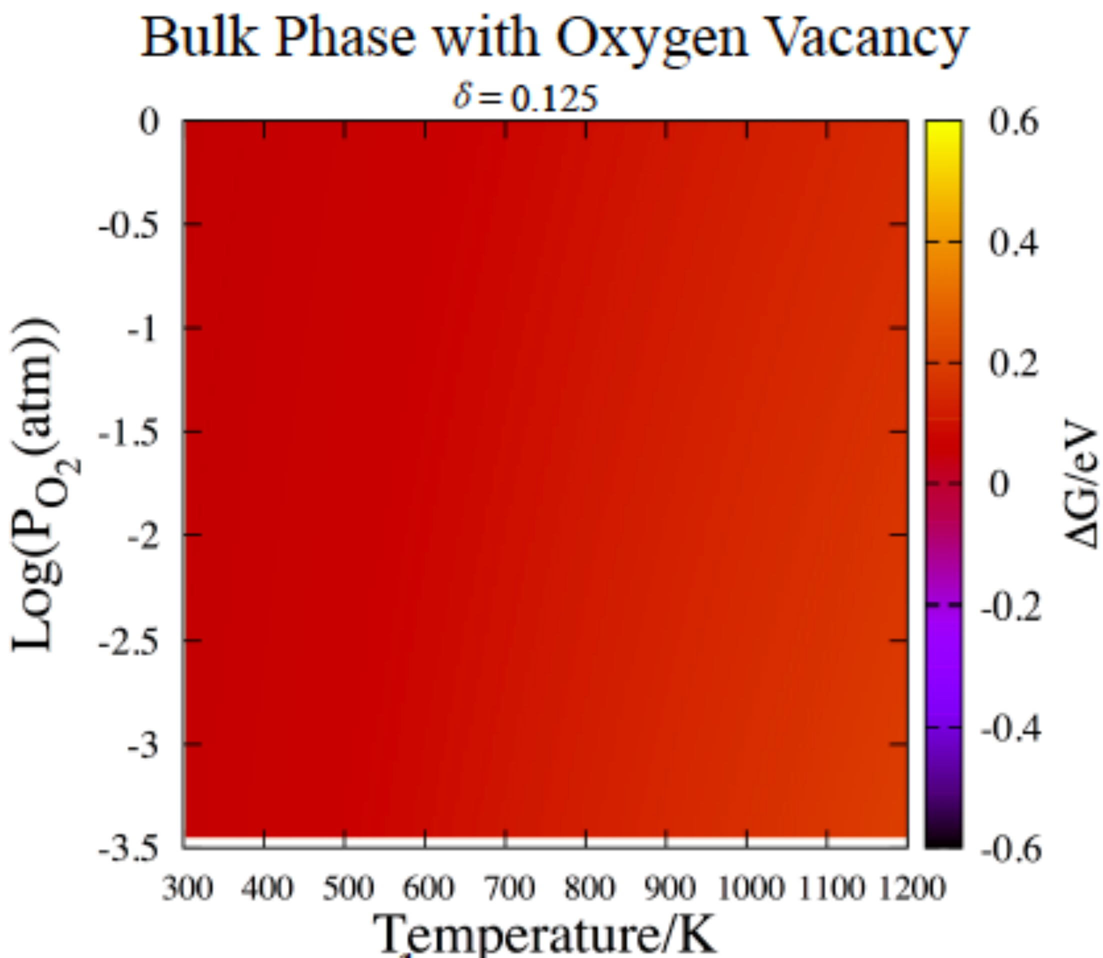


# Surface Phase with Oxygen Vacancy





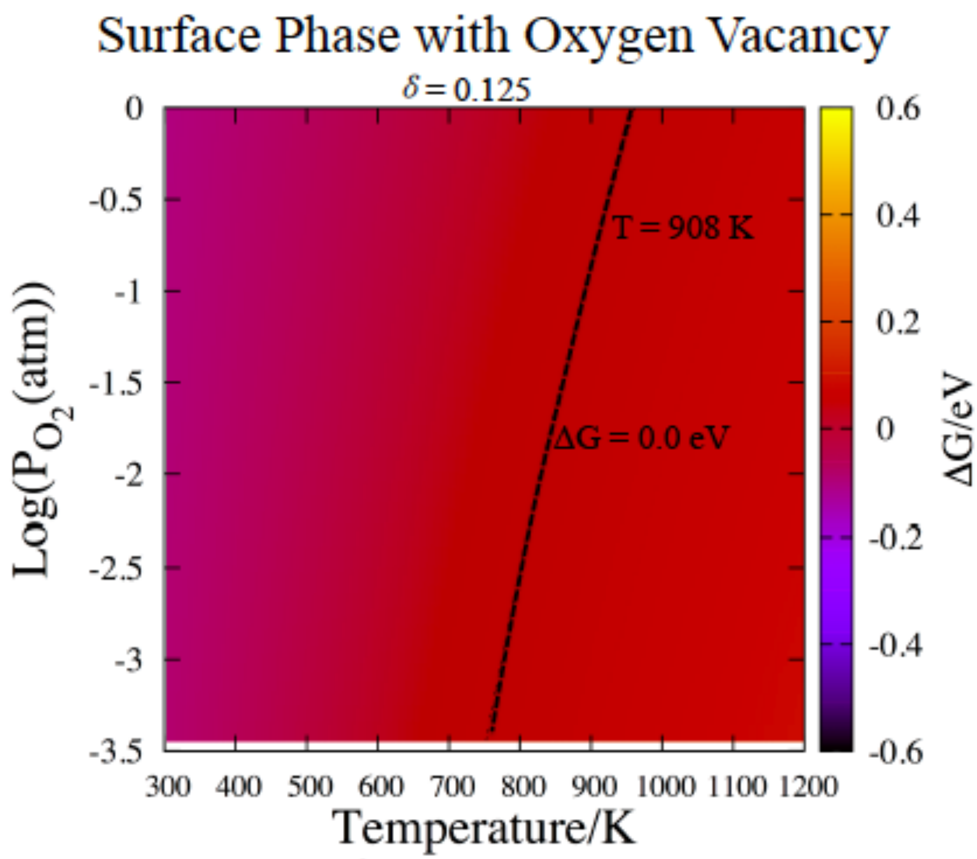

$$\underset{\text{Bulk Phase}}{La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_3} + \frac{1}{16}O_2 \rightarrow La_{0.75}Sr_{0.125}Co_{0.25}Fe_{0.75}O_3 + \frac{1}{8}SrO$$




$$La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_{3-\delta} + \frac{1}{16}O_2 \rightarrow La_{0.75}Sr_{0.125}Co_{0.25}Fe_{0.75}O_{3-\delta} + \frac{1}{8}SrO$$

Bulk Phase

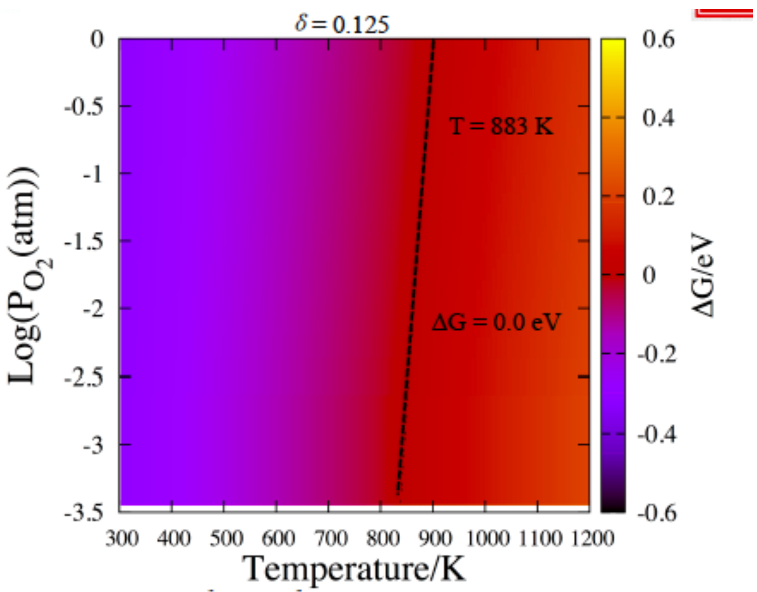
# Surface segregation in the absence of $CO_2$



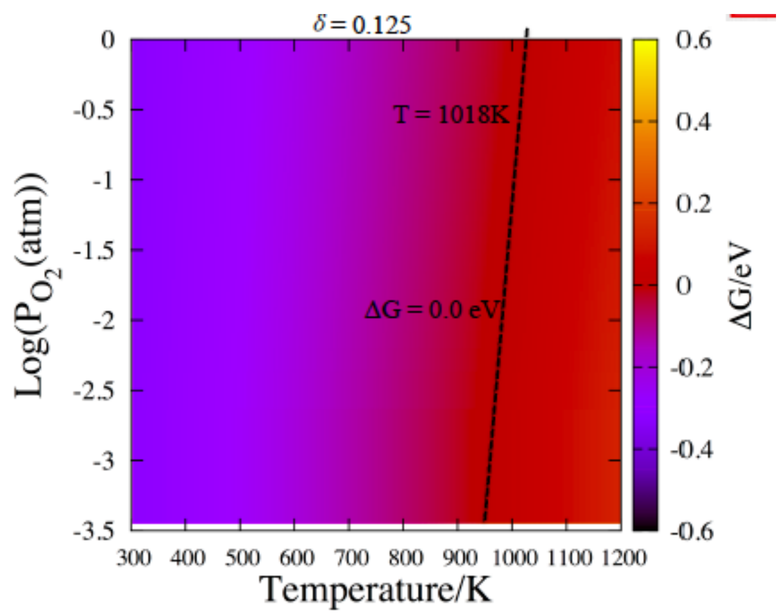

$$La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_{3-\delta}+\frac{1}{16}O_2 \rightarrow La_{0.75}Sr_{0.125}Co_{0.25}Fe_{0.75}O_{3-\delta}+\frac{1}{8}SrO$$

Surface Phase

# Surface carbonate formation



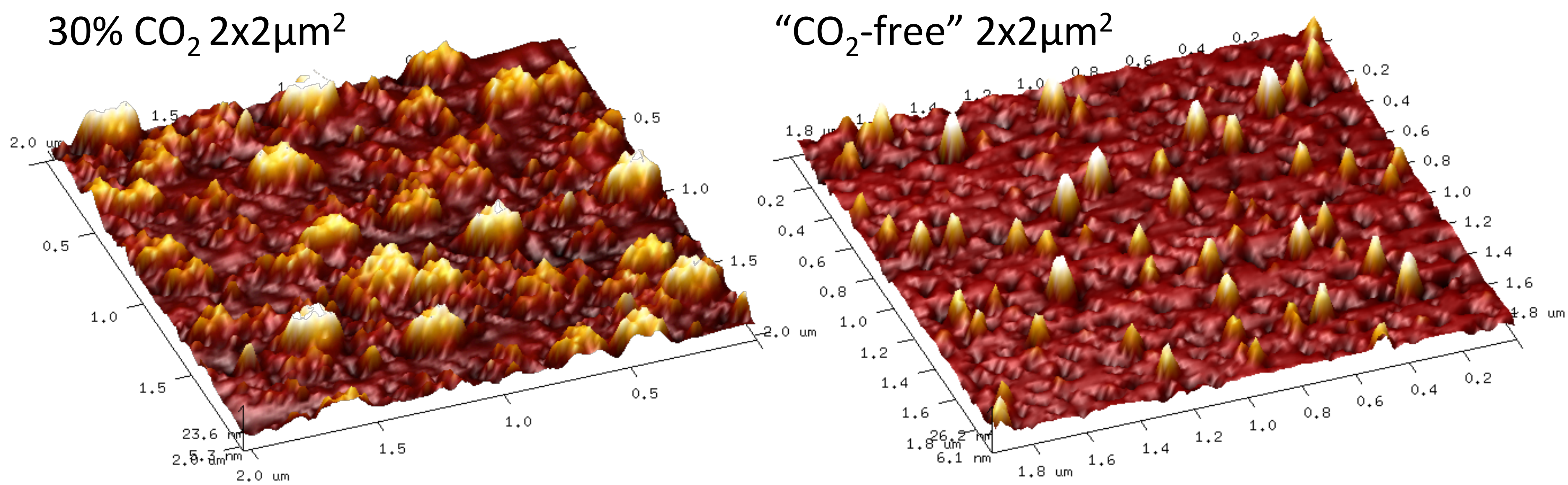

$Pco_2 = 4.0 \times 10^{-4}$ atm




$Pco_2 = 0.5$ atm

$$La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_{3-\delta} + \frac{1}{16}O_2 + \frac{1}{8}CO_2 \rightarrow La_{0.75}Sr_{0.125}Co_{0.25}Fe_{0.75}O_{3-\delta} + \frac{1}{8}SrCO_3$$

# Atomic Force Microscope (AFM) Analyses



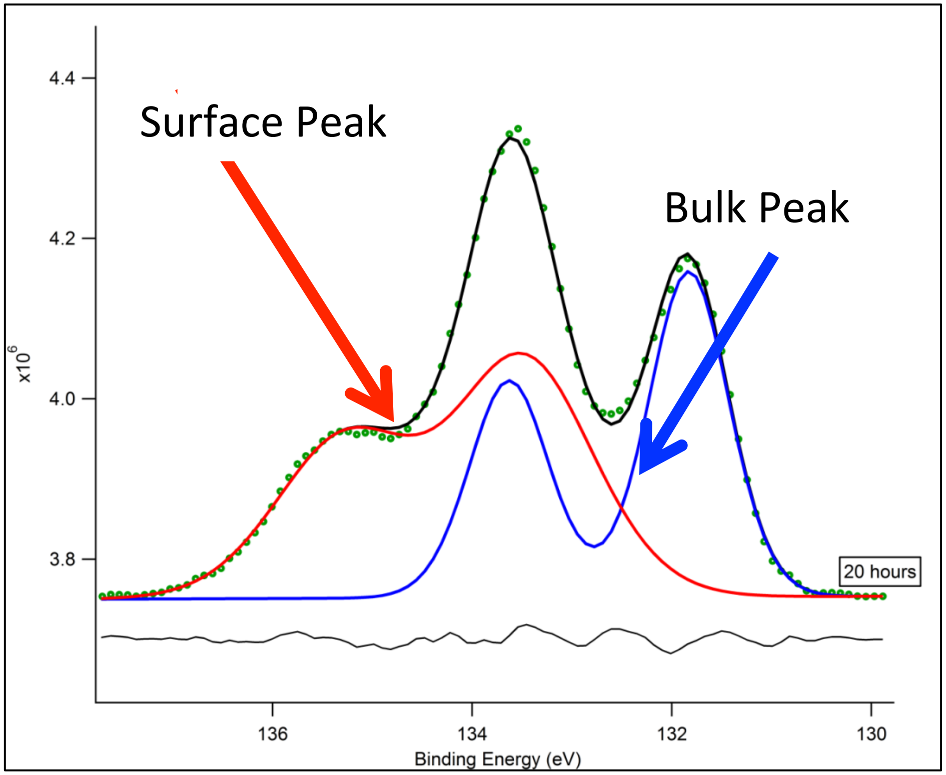

| | Roughness RMS (nm) | Number of Particles per μm$^2$ | Average Base Diameter of Particles (μm) | Surface Area Coverage Ratio (%) |
|---|---|---|---|---|
| 30% $CO_2$ | 5.59 | 10.25 | 0.276 | 61.3% |
| “$CO_2$-free” | 4.18 | 12.63 | 0.111 | 12.2% |

# HAXPES analysis of Sr3$d_{3/2}$ & Sr3$d_{5/2}$ orbitals

- hν=2140eV.
- Doublet from spin orbit splitting
- Surface Sr 3d signal consistent with:

Sr-O 133.0eV

Sr-$CO_3$ 134.0eV*




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

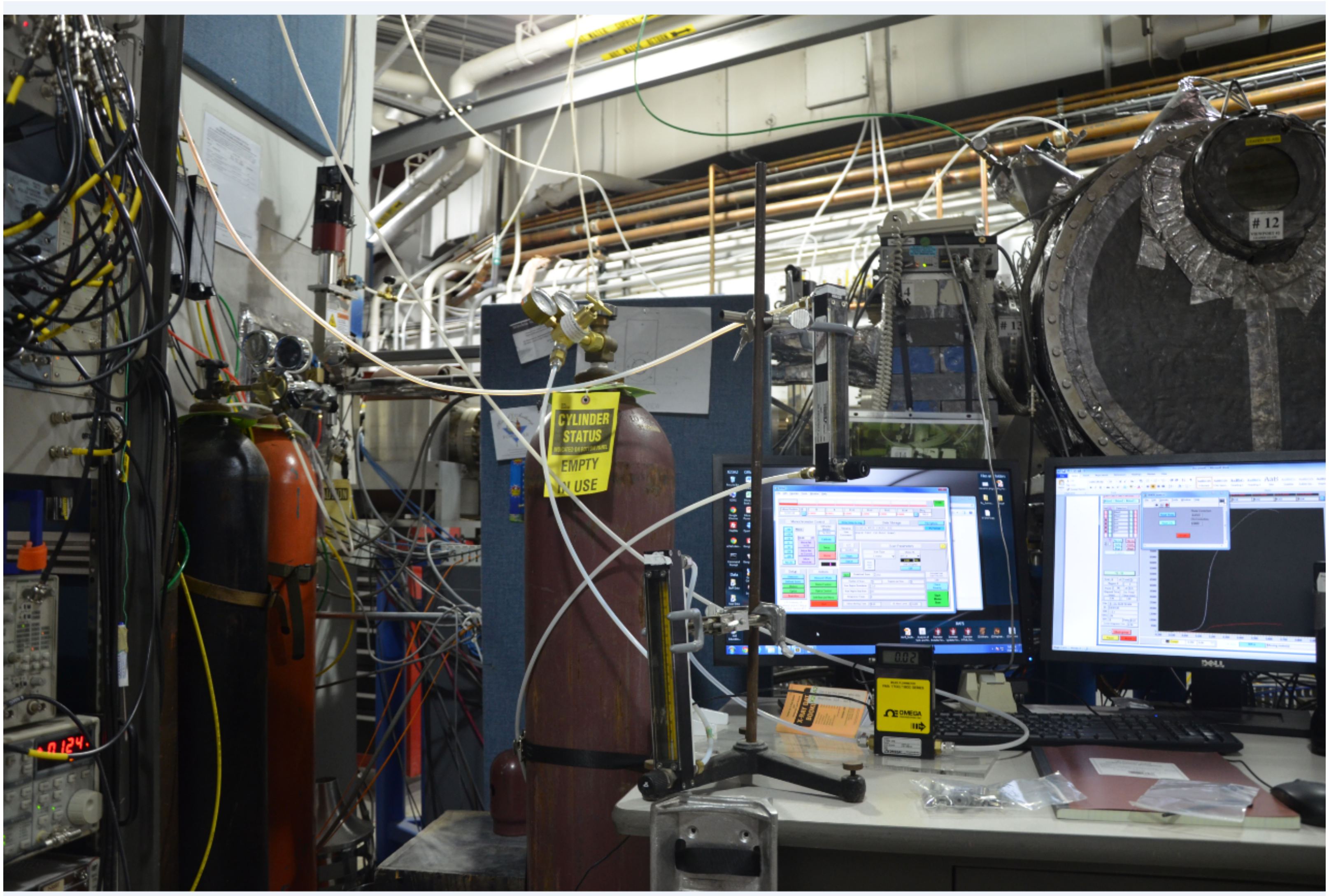
# Consensus on Sr segregation

- Sr segregation occurs in the case of LSCF
- Need to distinguish between enrichment/depletion due to the usual space-charge effect present at grain boundaries and surfaces of all ionic materials, and actual precipitation and formation of second phases.
- SrO formation indeed occurs in the case of LSCF.

# More Pic (if needed)


Feedback System

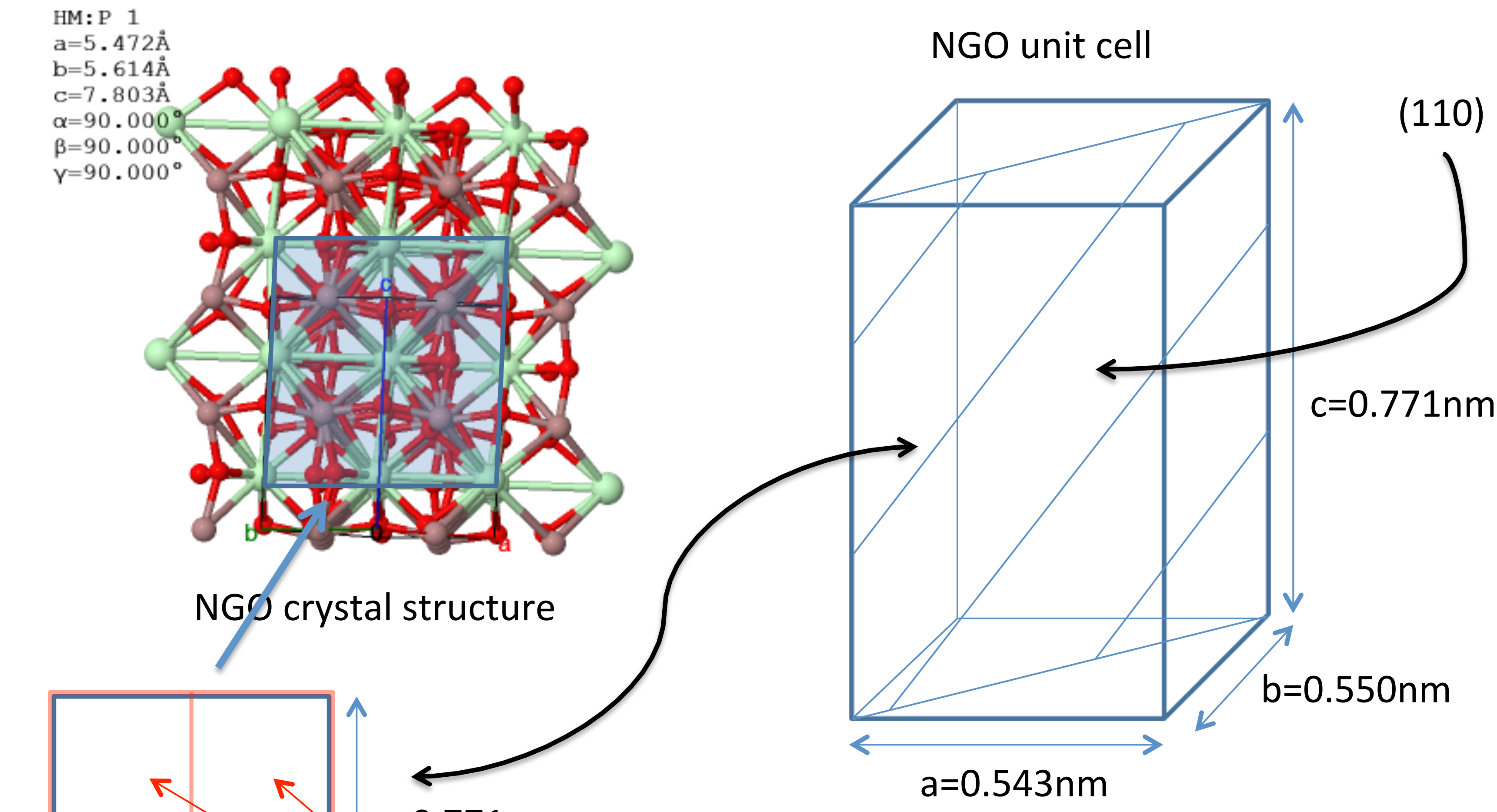
View inside the hutch




View outside the hutch

Monitoring the Temp

# Additional slides (for questions)



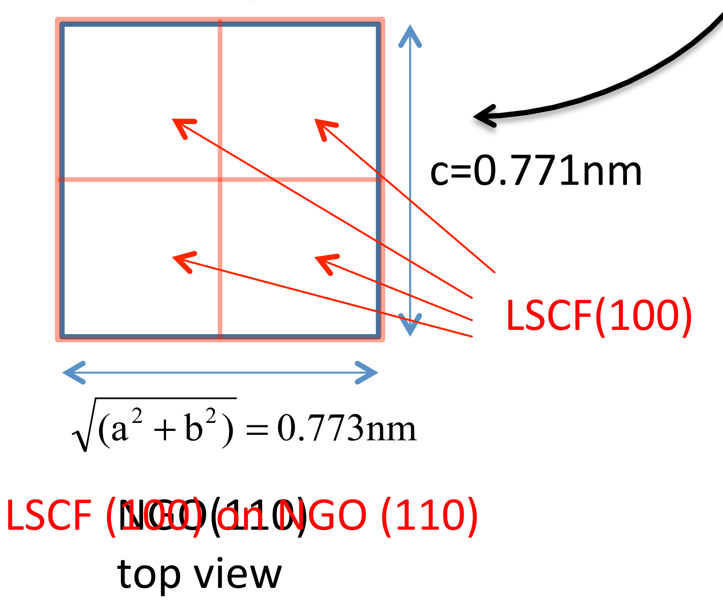
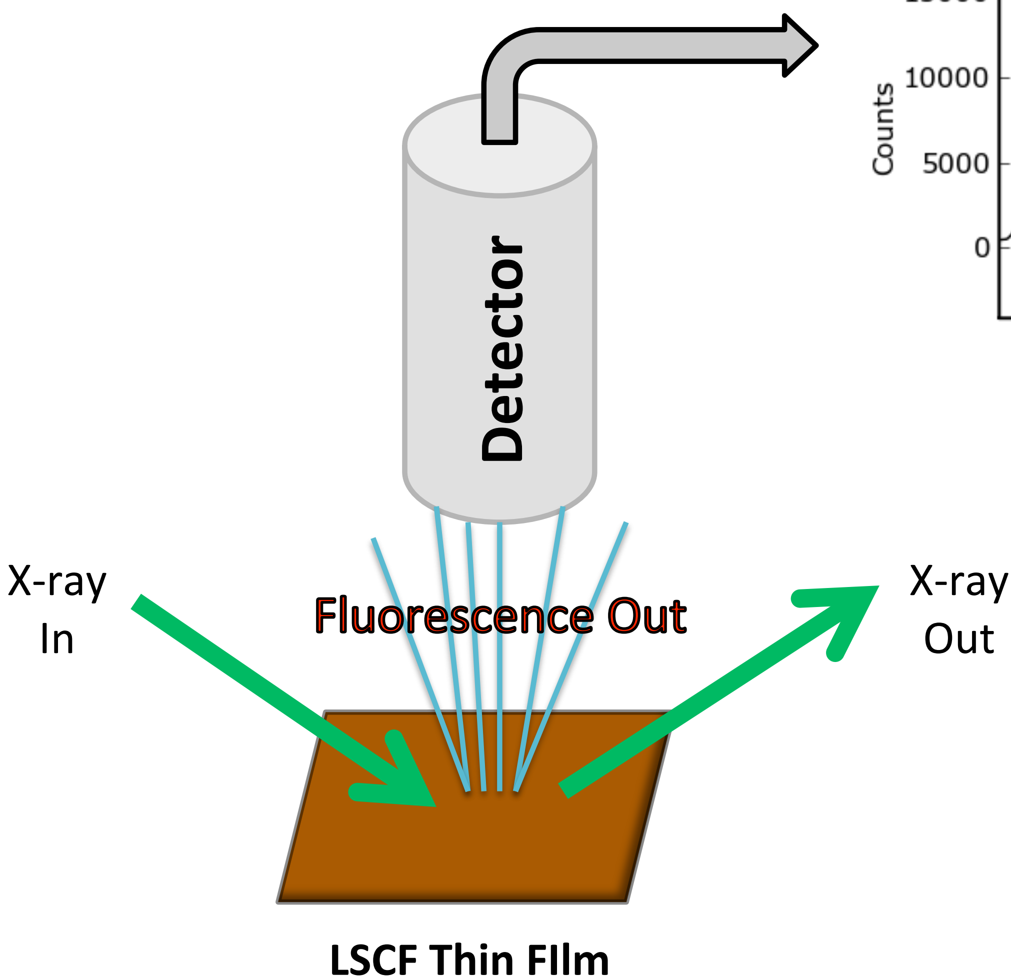
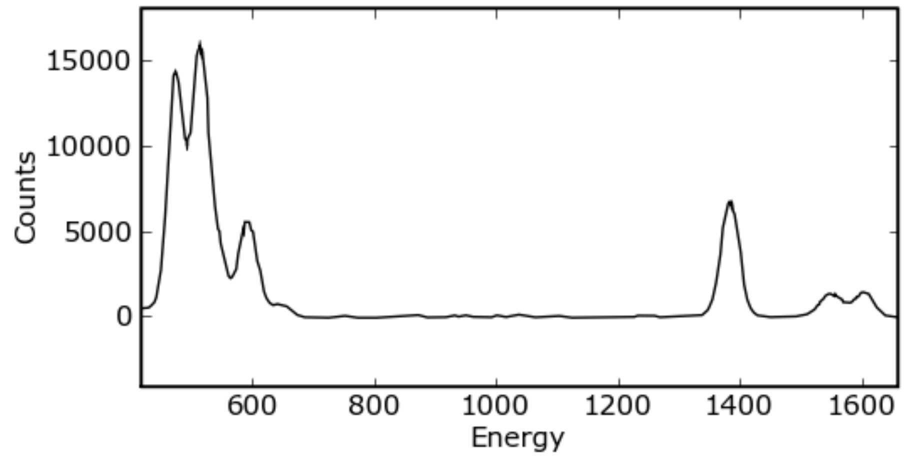




Table: LSCF lattice parameters (cubic structure)

| Composition | 6428 | 7328 | 8228 |
|---|---|---|---|
| Lattice C(nm) | 0.3893 | 0.3886 | N/A |
| X2 (nm) | 0.7786 | 0.7772 | N/A |

# Energy Resolving Fluorescence




- Small energy range corresponds to emission line of specific atomic species
- Window energy range for fluorescence signal.

# Method of TXRF Analysis

$$N(\theta) \propto I(\theta) \qquad N_{Sr} = \alpha \cdot I_{Sr} \quad N_{La} = \beta \cdot I_{La}$$

$$Want \quad R_{Sr/(Sr+La)} = \frac{N_{Sr}}{N_{Sr} + N_{La}}$$

$$R_{Sr/(Sr+La)} = \frac{N_{Sr}}{N_{Sr} + N_{La}} = \frac{I_{Sr}}{I_{Sr} + \frac{\beta}{\alpha} I_{La}} \qquad \text{Define C} = \frac{\beta}{\alpha}$$

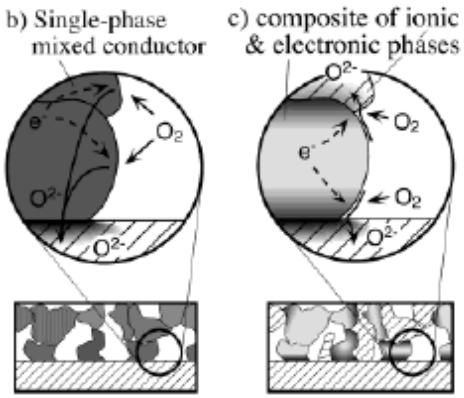
$$C = \frac{I_{Sr}(1 - R_{Sr/(Sr+La)})}{R_{Sr/(Sr+La)} I_{La}} \quad \text{For } \theta > \theta_c, \; R_{Sr/(Sr+La)} = 0.4$$

Can now plot $R_{Sr/(Sr+La)}$ for all angles.

# Reason for SSS

- The different vacancy-formation energies of the components.
- The elastic strain energy due to lattice distortion around a defect.
- The effect of the ambient atmosphere.
- The macroscopic electrostatic potential, which appears as a consequence of the locally non-stoichiometric charged species.
- The effect of surface energy.
- The energies due to the interactions between the defects

# 2 Pathways for Oxygen Reduction Reaction…




The "Bulk Path"

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF-6428)

Necessary first steps:

Gas Phase Diffusion

↓

Surface Adsorption

↓

Dissociation

**Bulk path:**

Electronation and Incorporation to cathode

↓

Bulk Diffusion to Electrolyte

↓

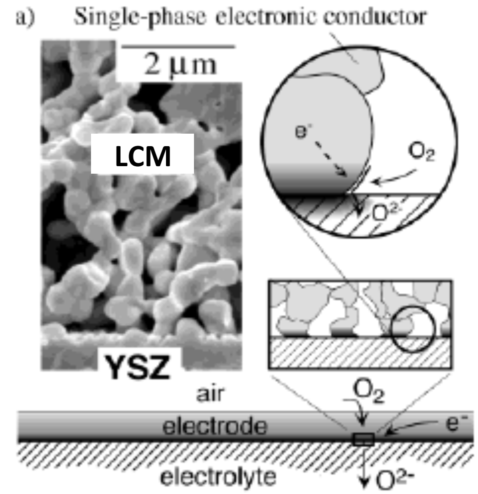
Incorporation into Electrolyte

**Surface path:**

Surface Diffusion to Triple Phase Boundary (TPB)

↓

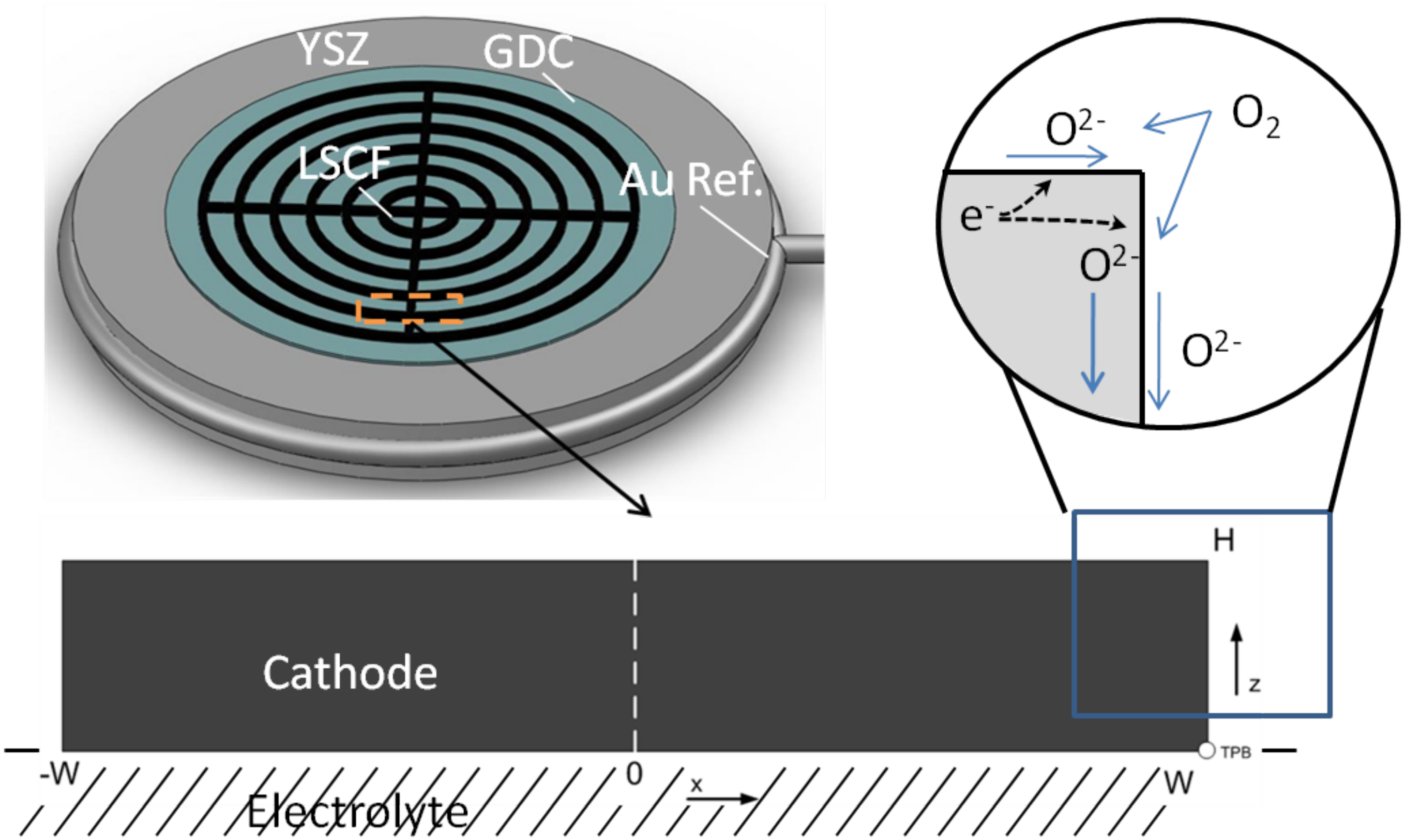
Electronation and Incorporation to electrolyte at TPB




The "Surface Path"

$(La_{0.87}Ca_{0.13})_{0.95}MnO_{3\pm\delta,}$ (LCM)

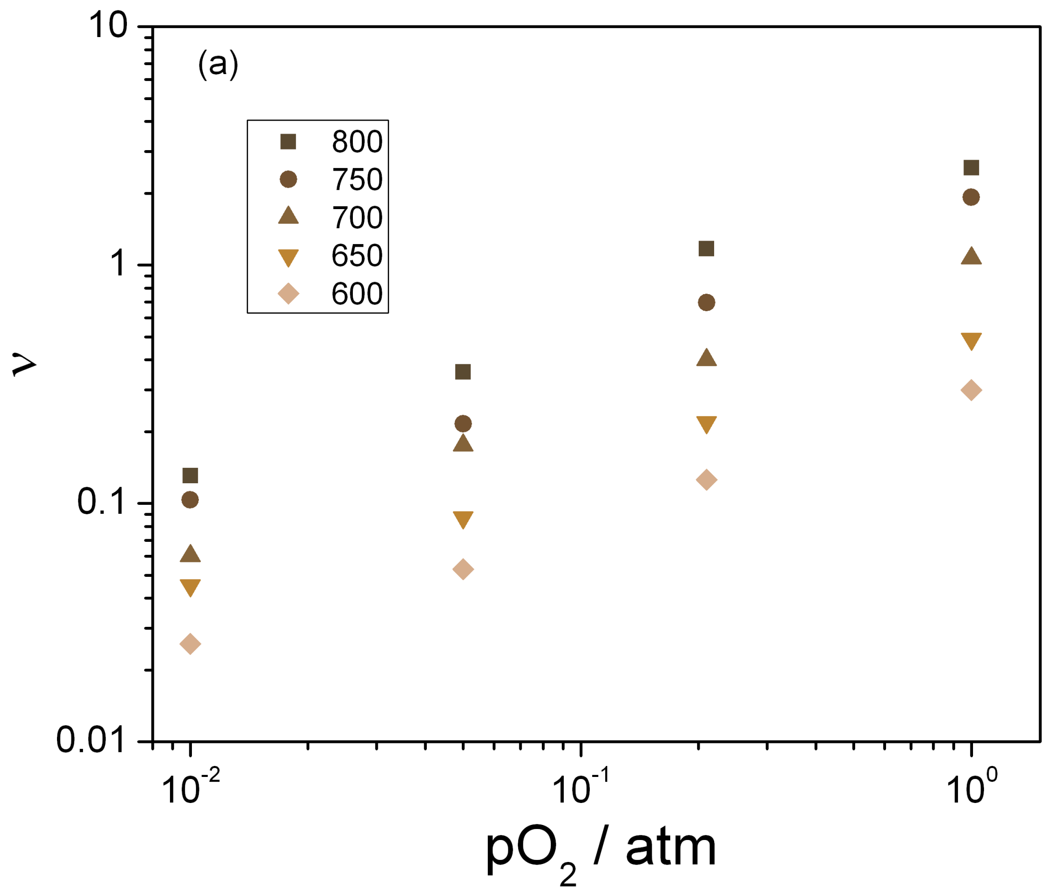
# Patterned electrode experiments (LSCF- 6428)




"2D Numerical Model for Identification of Oxygen Reduction Reaction Mechanisms in Patterned Cathodes of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$", L.J.Miara, S.N. Basu, U.B.Pal, and S.Gopalan, *J.Electrochem.Soc.,* 159 (8) F419-F425 (2012)

# Surface diffusion versus bulk diffusion

$$\nu = \frac{\Gamma_o \theta_{O_s}^{o} D_{O_s}}{W c_o x_v^o D_v} = \frac{\text{surface oxygen diffusion}}{\text{bulk oxygen diffusion}}$$




"2D Numerical Model for Identification of Oxygen Reduction Reaction Mechanisms in Patterned Cathodes of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$", L.J.Miara, S.N. Basu, U.B.Pal, and S.Gopalan, *J.Electrochem.Soc.,* 159 (8) F419-F425 (2012)

# Implications for SOFCs

- Prior work shows that bulk diffusion is more important at lower oxygen partial pressures, presumably due to higher oxygen vacancy concentrations.
- Prior work also shows that at lower temperatures, bulk diffusion is more dominant, in contradiction with expectations.
- The present work on the surface chemistry of Sr segregation and the attendant SrO and $SrCO_3$ provides a plausible explanation.
- Does the formation of these second phases inhibit surface diffusion thereby forcing the oxygen transport through the bulk pathway even at lower temperatures?
- Experimental work underway to answer these questions.

# Ongoing work

- Cathodes with lower Sr dopant levels and alternate cathode materials (e.g. BSCF)
- Impedance measurements in air passed through $CO_2$ getter and comparison to $CO_2$ containing atmospheres
- Time studies to understand longer term effects

# Acknowledgments

- This work was funded through DOE's SECA program.

- Helpful discussions with Dr.Patcharin Burke, Dr.Briggs White, Dr. Harry Abernathy, and Dr. Kirk Gerdes are acknowledged.

- EMSL personnel Dr. Tiffany Kaspar and Dr. Lax Saraf are acknowledged for fabrication of thin films.