Unraveling Oxygen Reduction Kinetics on SOFC Cathodes Using Patterned Electrodes and X-Ray Techniques

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Phase I accomplishments (mainly focused on LSM):

- Determined that “surface path” is ~4 fold less resistive than “bulk path”.
- Modified the SSM model developed by Mitterdorfer *et al.* to account for surface potential ($\Delta\chi$) and implemented in Matlab.
- Estimated temperature and pO_2 dependence of: D_s, k_{ad}, k_{des}, k_f^{eq}, k_b^{eq} , and surface coverage (θ).
- At temperatures below 700 °C was co-limited by diffusion and adsorption. At high temperatures charge transfer contributes significantly to rate.
- Low scatter between samples suggests that samples were successfully fabricated, and model correctly accounts for the geometry changes.
- Used TXRF to measure surface compositions of LSM thin film cathodes

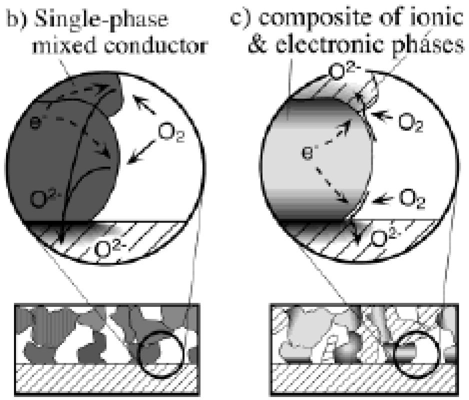
- L.Miara, J.N.Davis, S.Basu, U.B.Pal, and S.Gopalan, "Application of a State-Space Model to Patterned Cathodes of (La0.87Ca0.13)0.95MnO3”, *J.Electrochem.Soc, 158 B1523 (2011)*

Work covered in this year's SECA workshop

- Measurement of Electrode Kinetics on LSCF electrodes using micropatterning
- Surface spectroscopy of LSCF thin films using HAXPES

Have examined “Bulk Path”:

Now include “Surface Path”:

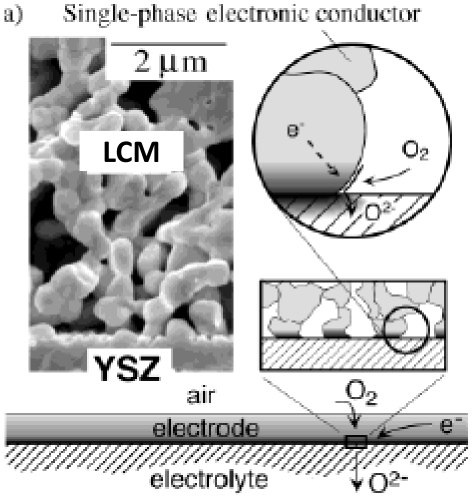


The “Bulk Path”

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

Necessary first steps:

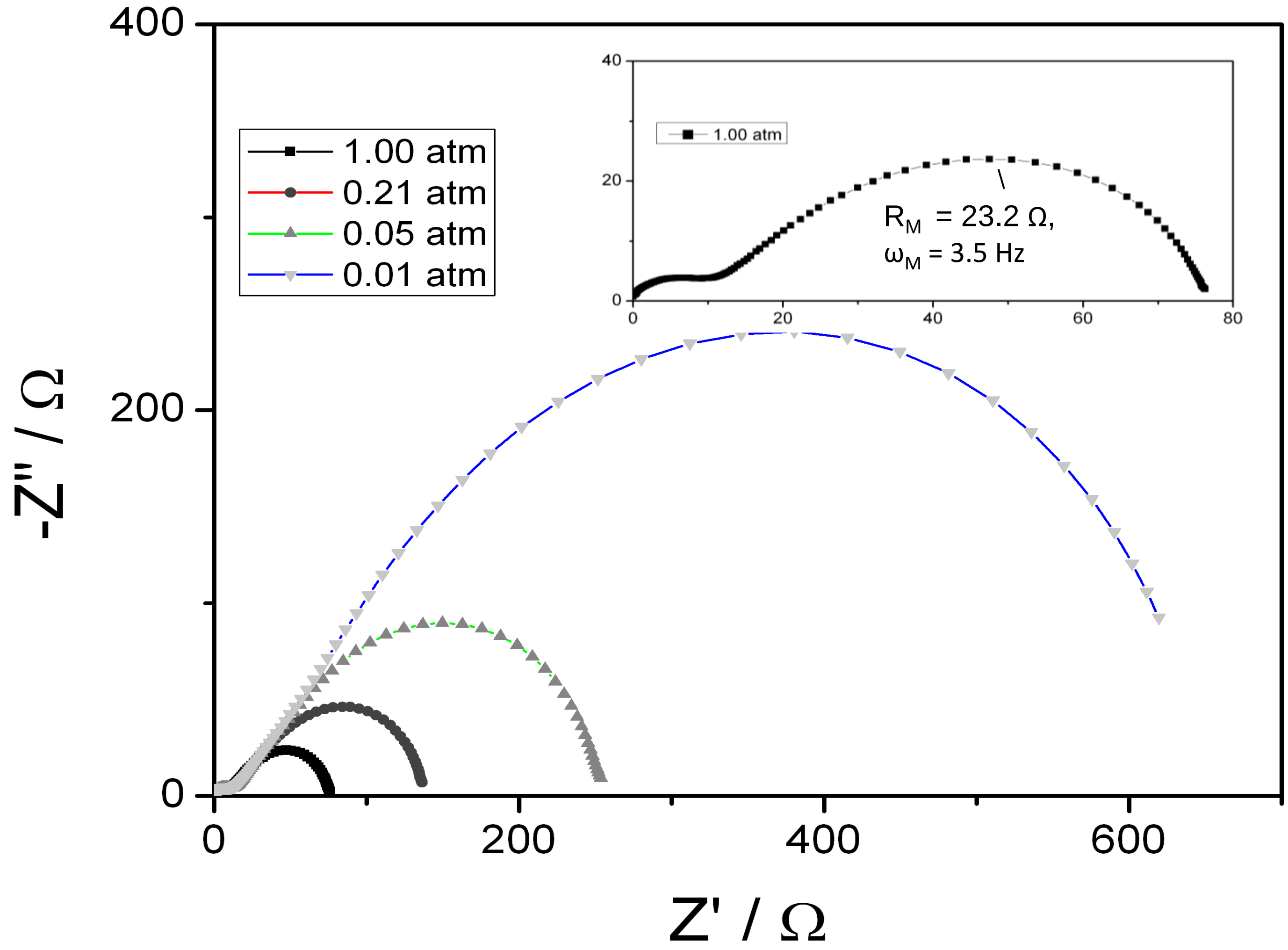
- Gas Phase Diffusion
- Surface Adsorption
- Dissociation
  - Electronation and Incorporation to cathode
    - Bulk Diffusion to Electrolyte
    - Incorporation into Electrolyte
  - Surface Diffusion to Triple Phase Boundary (TPB)
    - Electronation and Incorporation to electrolyte at TPB

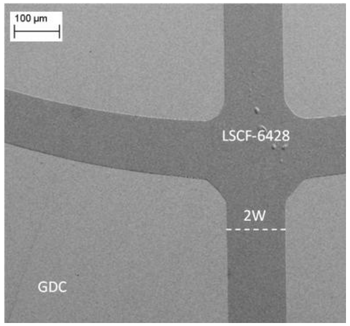


The “Surface Path”

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

LSCF-6428: EIS results l_{TPB} =50 cm^{-1}, 800°C





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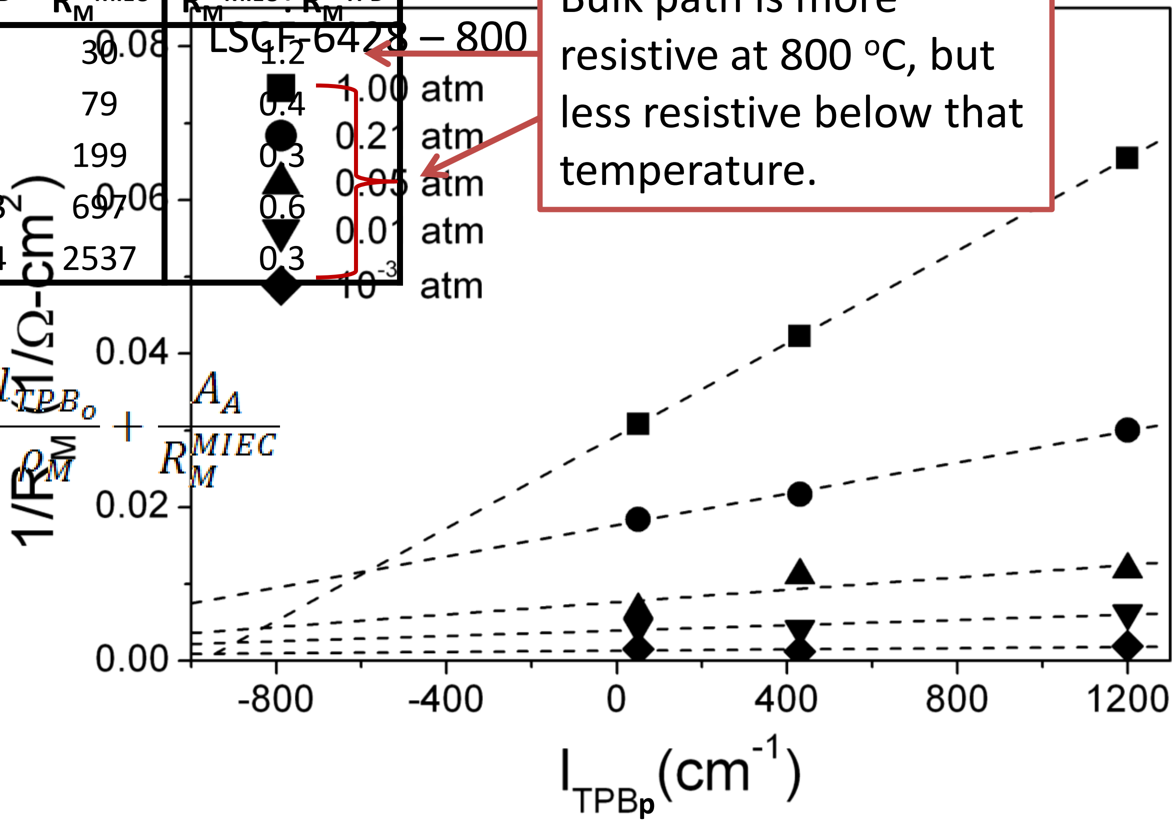
Primary Evidence of Mixed Conduction LSCF-6428: $1/R_c$ vs. TPB length

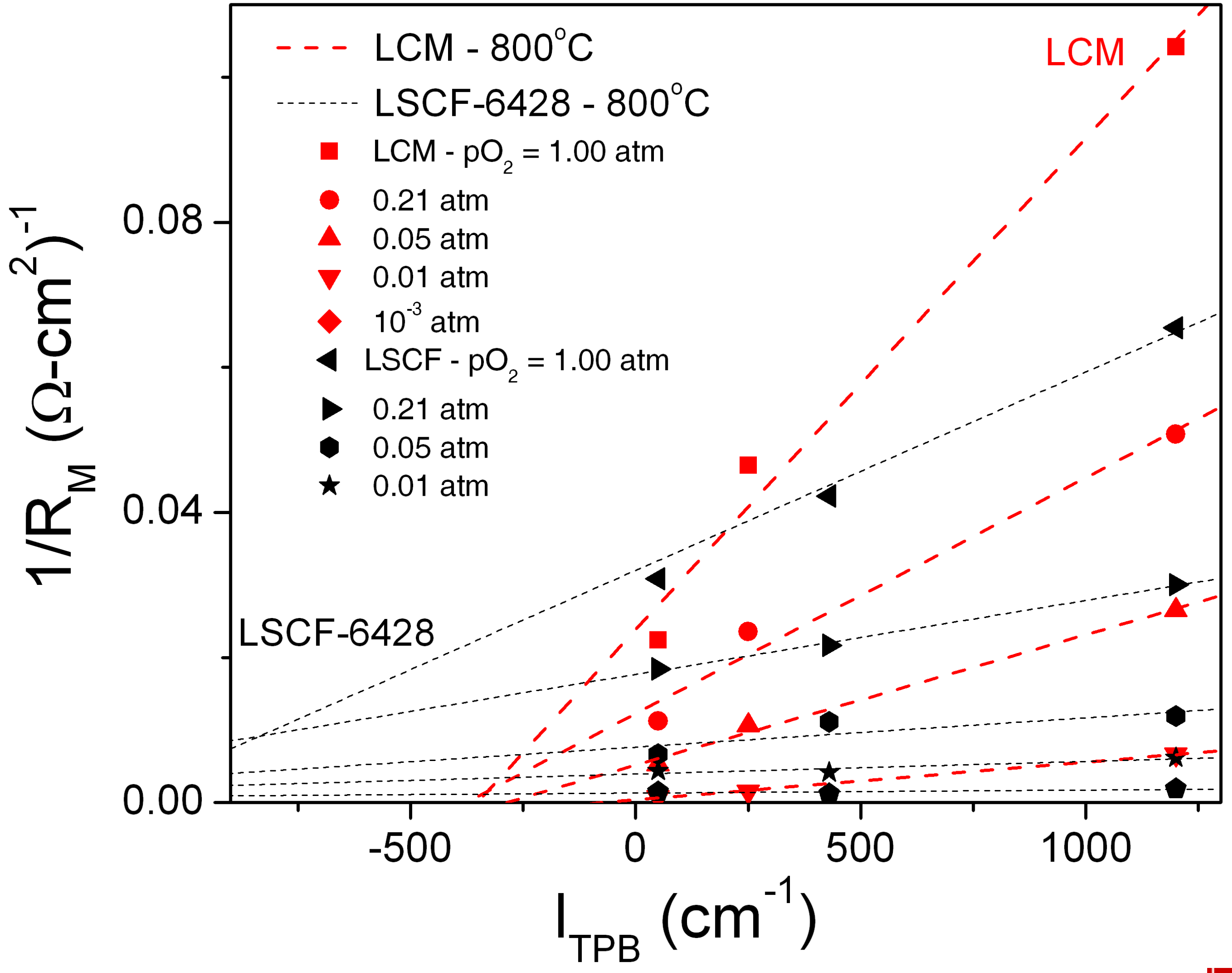
T°C	R_M	R_M^{TPB}	R_M^{MIEC}	$R_M^{MIEC} : R_M^{TPB}$
800	15	26	30	1.2
750	66	195	79	0.4
700	189	779	199	0.3
650	488	1113	697	0.6
600	2321	8654	2537	0.3

$$\frac{1}{R_M} = \frac{l_{TPB_p}}{\rho_M} + \frac{l_{TPB_o}}{\rho_M} + \frac{A_A}{R_M^{MIEC}}$$



Bulk path is more resistive at 800 °C, but less resistive below that temperature.

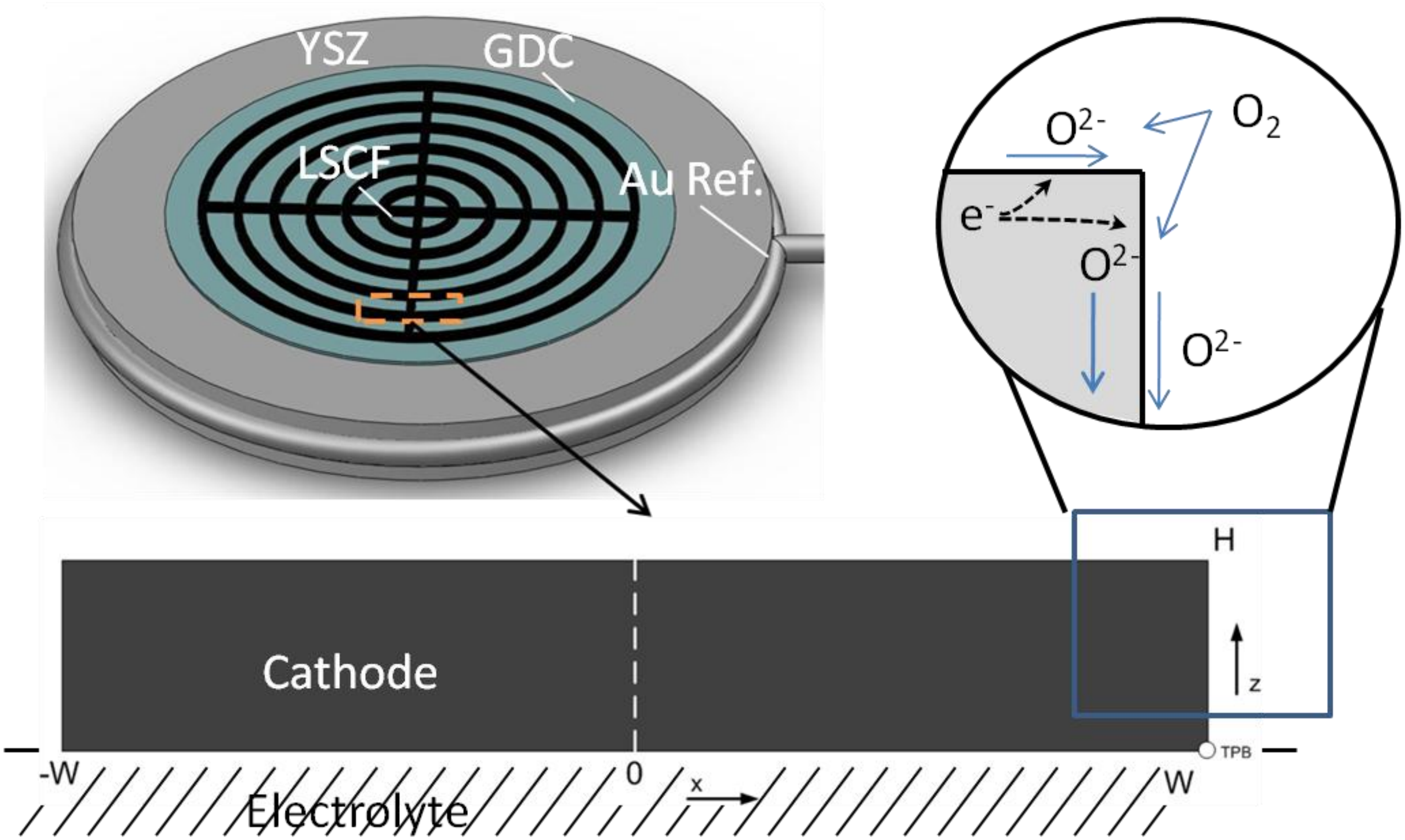
LSCF vs. LCM – far weaker TPB dependence



Goals:

1. Develop model to account for:
    - surface transport
    - bulk transport
    - surface exchange
2. Combine with experimental data to Identify influence of each on overall rate.

Use 2-D Model: Geometry



Model Assumptions

- LSCF-6428 has high electron mobility: uniform electron electrochemical potential.
- Overpotential at interface given by Nernst Equation:

$$4F\eta = RT\ln f_{O_2}^{\mathrm{solid}}\big|_{y=0} - RT\ln p_{O_2}$$

  - Where $f(T,x_v)$ is the fugacity in the solid and $x_v = \delta/3$
- No gas phase limitation
- Oxygen exchange is driven by bulk vacancy concentration changes away from equilibrium with gas phase, but ion exchange across cathode interface considered equilibrated
- Electrolyte resistance and lead wire inductance is subtracted directly from experimental data.

Parameters in model:

$$R_D = \frac{RT}{8F^2}\frac{(W+H)}{c_o x_v^o D_v} \qquad t_D = \frac{W^2}{A^o D_v} \longrightarrow$$

Both functions of D_V:
(intrinsic vacancy diffusivity)

$$\sigma_M = \omega_M t_D$$

$$\kappa = \frac{4R_o W}{c_o x_v^o D_v} \equiv \frac{\text{surface oxygen exchange}}{\text{bulk oxygen diffusion}} \qquad \nu = \frac{\Gamma_o \theta_{O_s}^{\,o} D_{O_s}}{W c_o x_v^o D_v} \equiv \frac{\text{surface oxygen diffusion}}{\text{bulk oxygen diffusion}}$$

$$\phi = \frac{A^o}{A^o_{O_s}}\frac{\Gamma_o \theta_{O_s}^{\,o}}{W c_o x_v^o} \equiv \frac{\text{surface oxygen storage}}{\text{bulk oxygen storage}} \longrightarrow$$

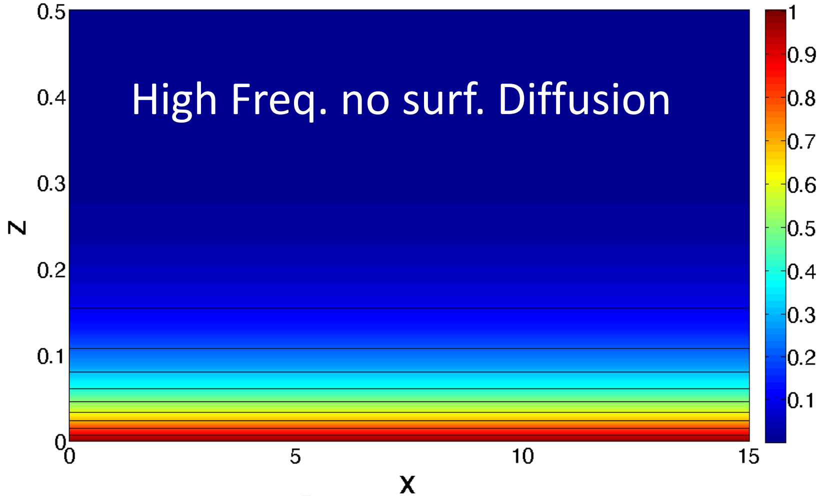
Set equal to zero

Numerical Model:

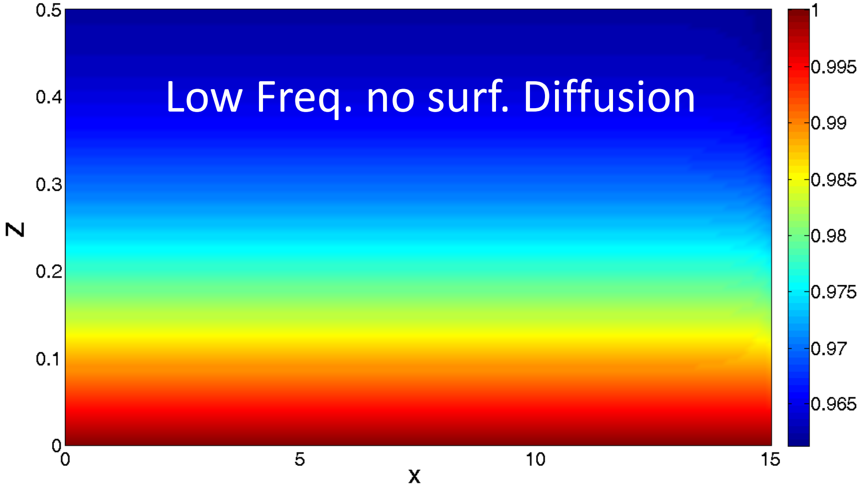
- Solved using Gauss-Siedel Method, with a tolerance of 10^{-5}
- Implemented in Matlab, usually converges in about 30 s (per σ), with mesh size of 200 (width) by 100 (height).
- Boundary conditions: flux/reaction boundary on top and right wall
- Fixed (potential) at cathode/electrolyte interface
- No flux at symmetrical (left wall) boundary.

Model Predictions – Oxygen Vacancy pertubation:

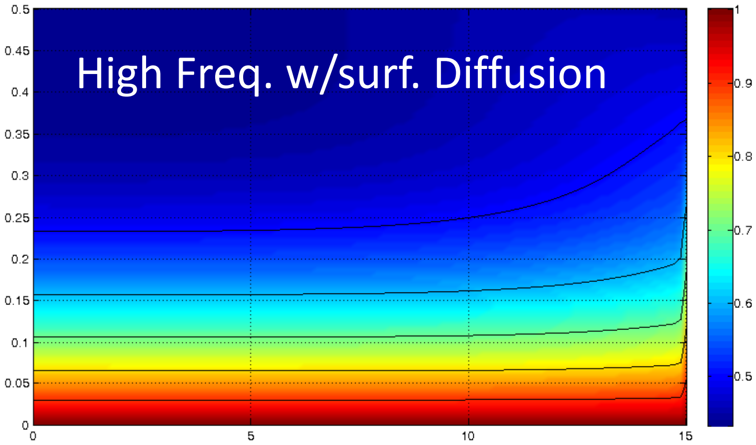
l_{TPB} = 1200 cm^{-1}



σ = 10^5 , κ = 0.1, ν = 0



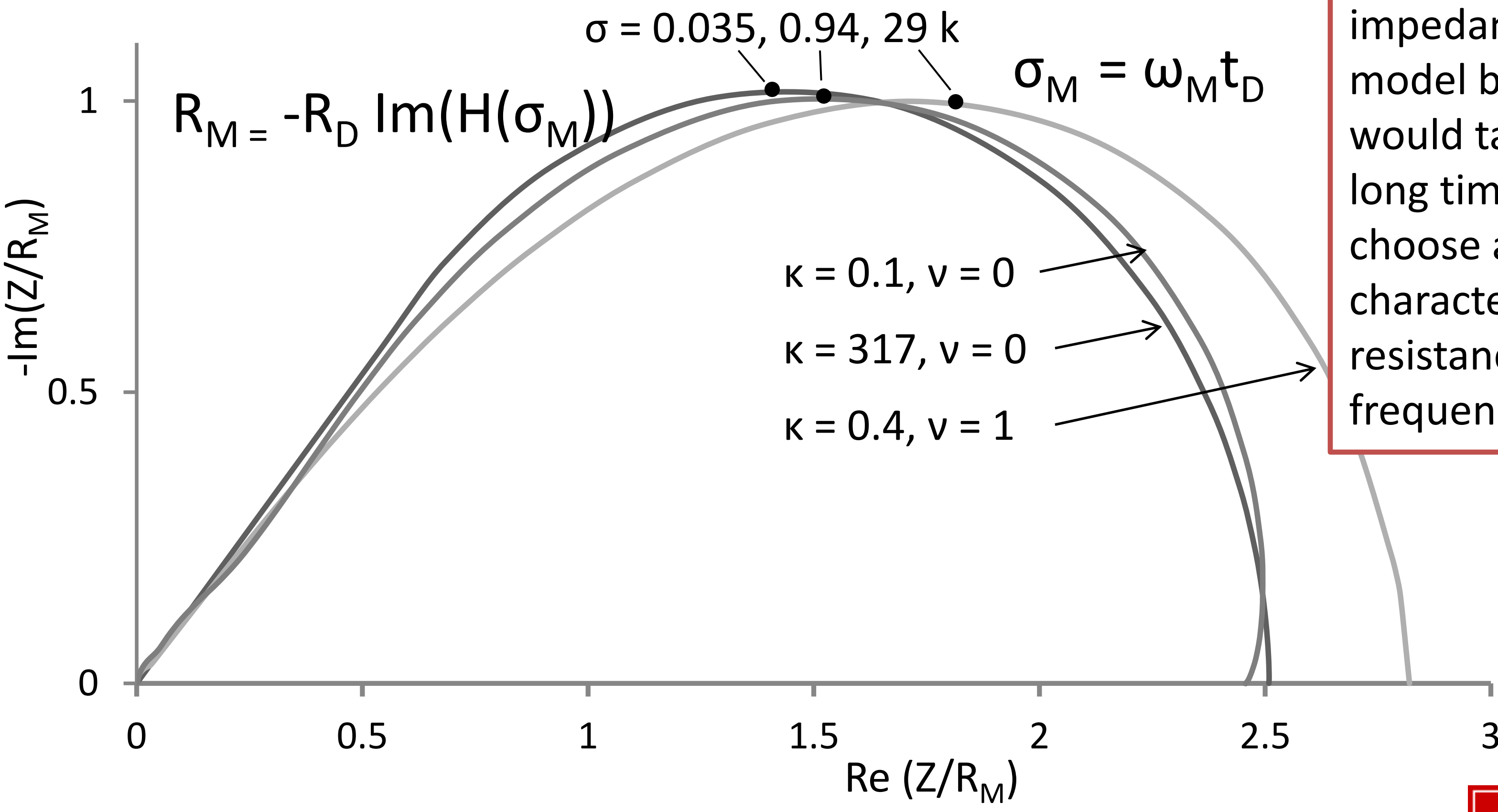
σ = 100, κ = 0.1, ν = 0



σ = 10^5 , κ = 2, ν = 10

- At high frequency, disturbance limited to interface.
- At low frequency extends through entire cathode.
- With surface diffusion, extends up wall faster

Generate Nyquist Plots from Model:



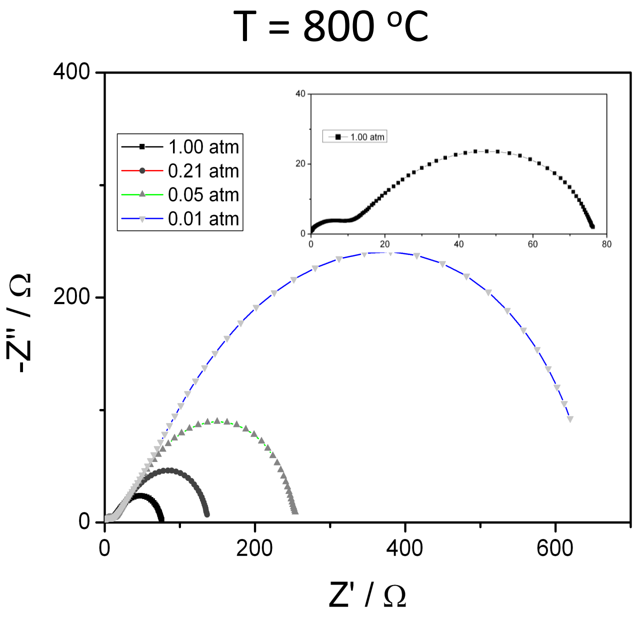
$$R_M = -R_D \, \mathrm{Im}(H(\sigma_M))$$

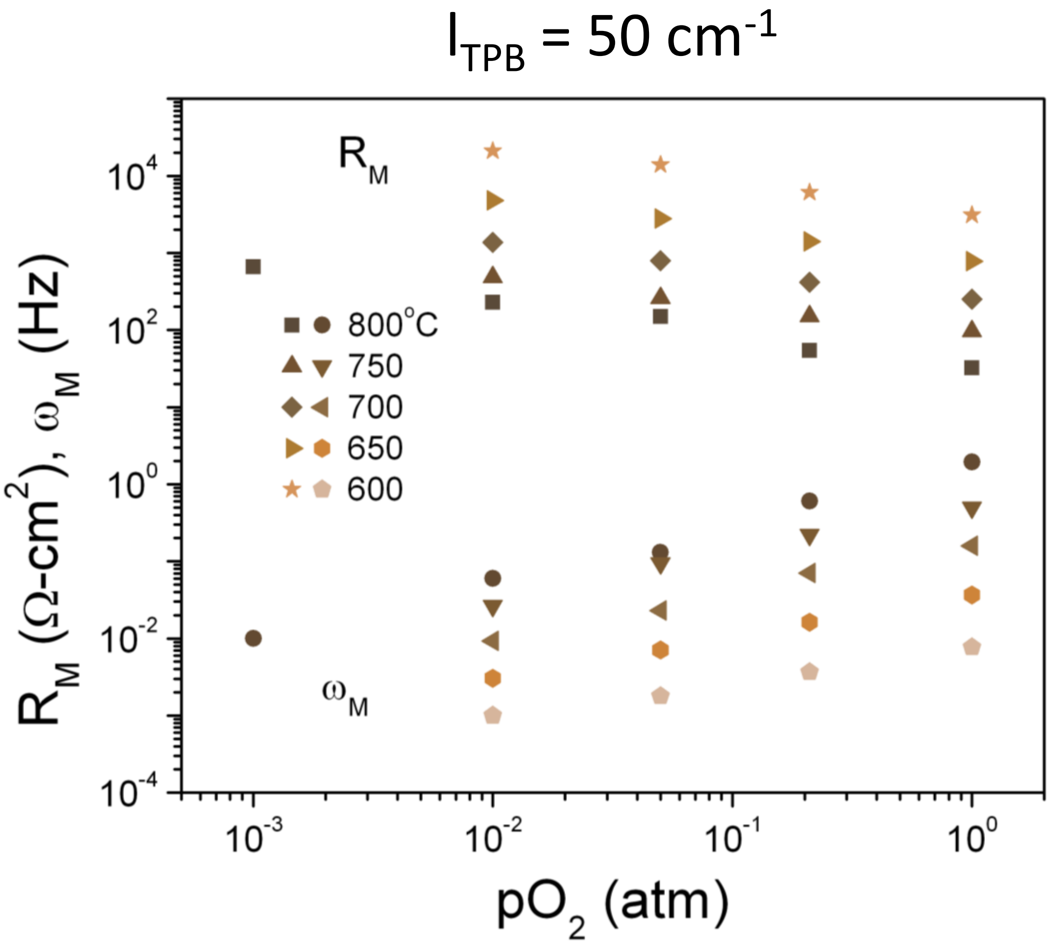
$$\sigma_M = \omega_M t_D$$

NOTE:

It is *NOT* practical to fit the ***entire*** impedance vs. the model because it would take a *very* long time, instead choose a characteristic resistance, R_M , and frequency, ω_M.

EIS results – l_{TPB} = 50 cm^{-1}


T = 800 °C


l_{TPB} = 50 cm^{-1}

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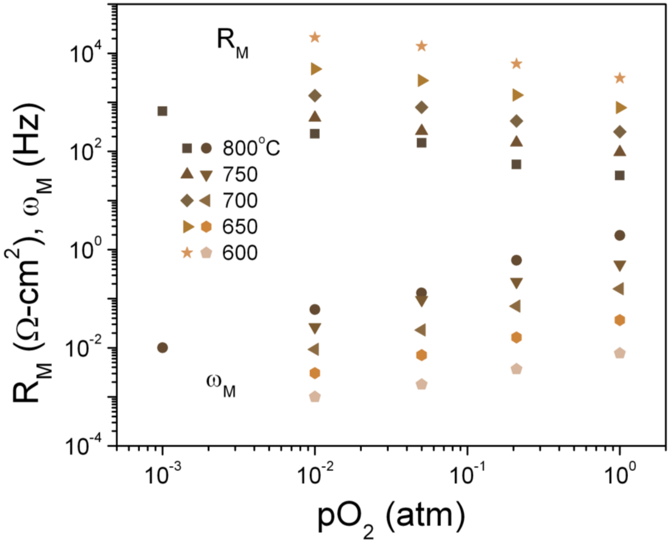
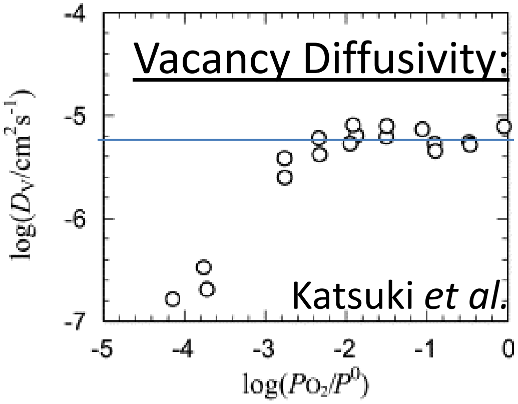
Fitting Routine:

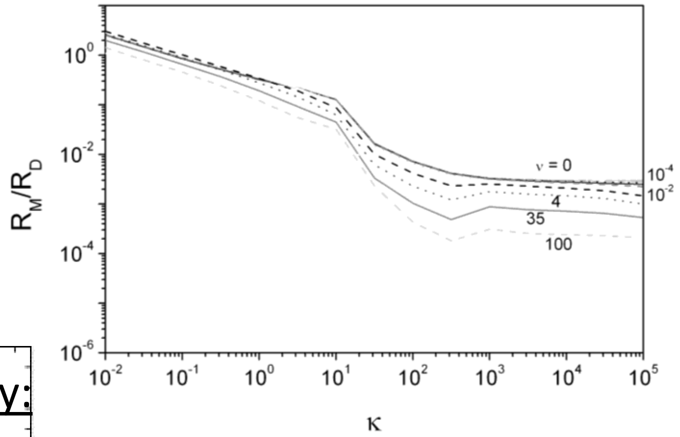
Have two known (R_M and ω_M) and 3 fitting parameters (D_V, κ, and ν):

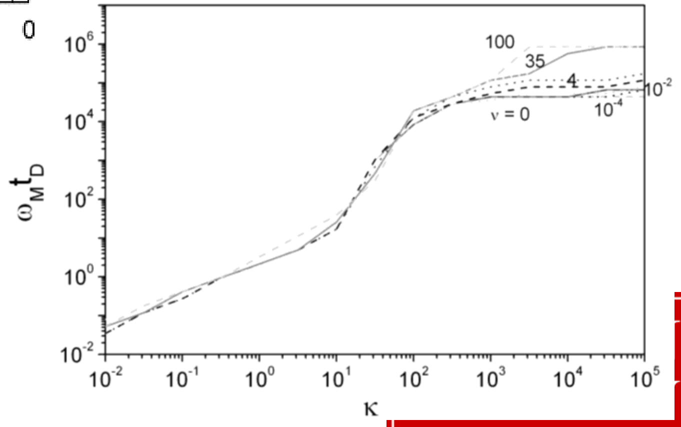
D_v is relatively constant in experimental pO_2 range, so fix it, and fit the other two.



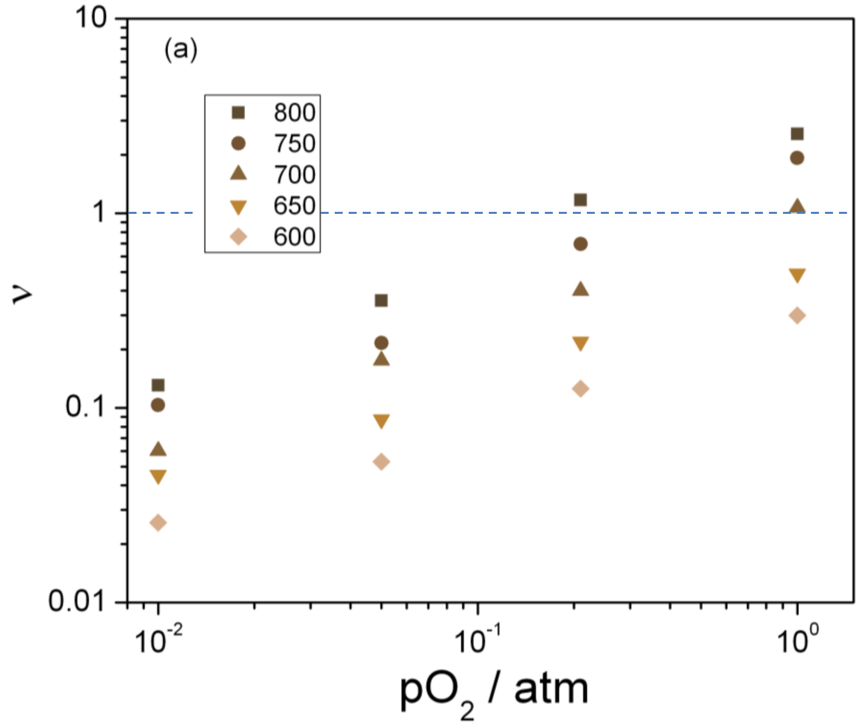

Vacancy Diffusivity:

Katsuki *et al.*



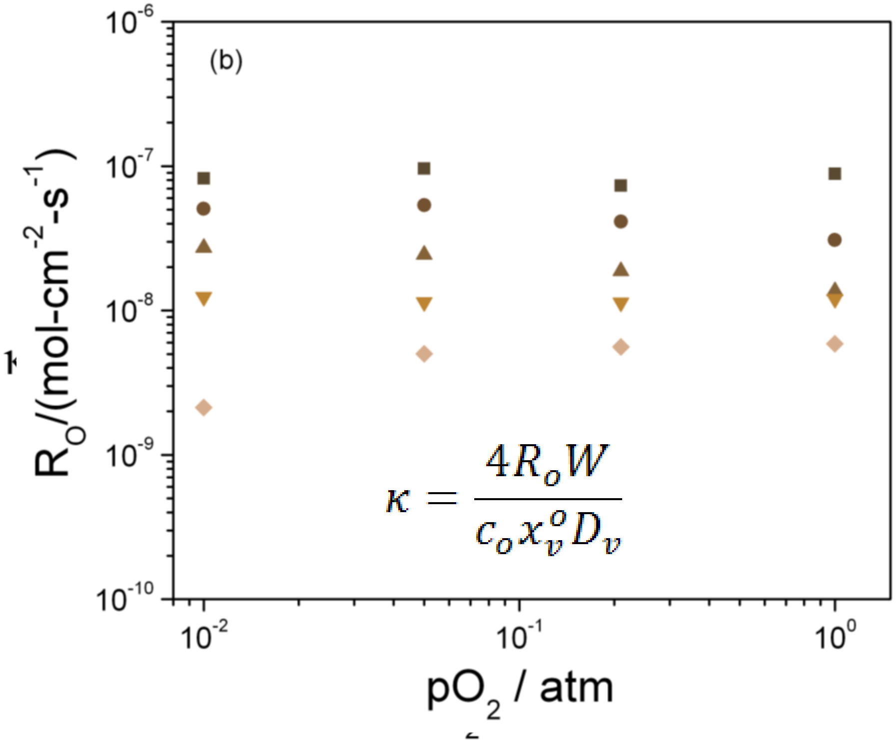


Fitting Results (l_{TPB} = 430 cm^{-1})



Surface Diffusion Contribution

increases with pO_2 and T –



$$\kappa = \frac{4R_oW}{c_o x_v^o D_v}$$

Surface Exchange Contribution

increases with pO_2 and T –

dominates rate at all pO_2

R_O is roughly constant with pO_2 – activation energy is 115 kJ/mol

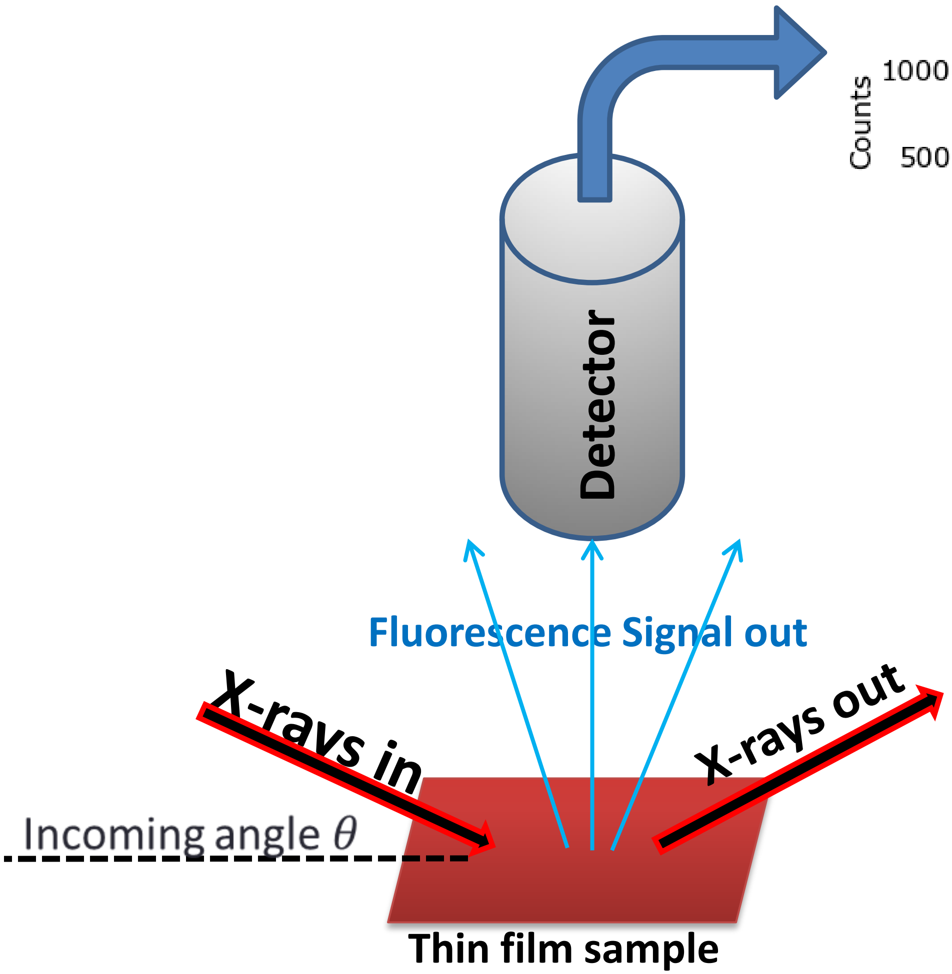
Conclusions from LSCF-6428:

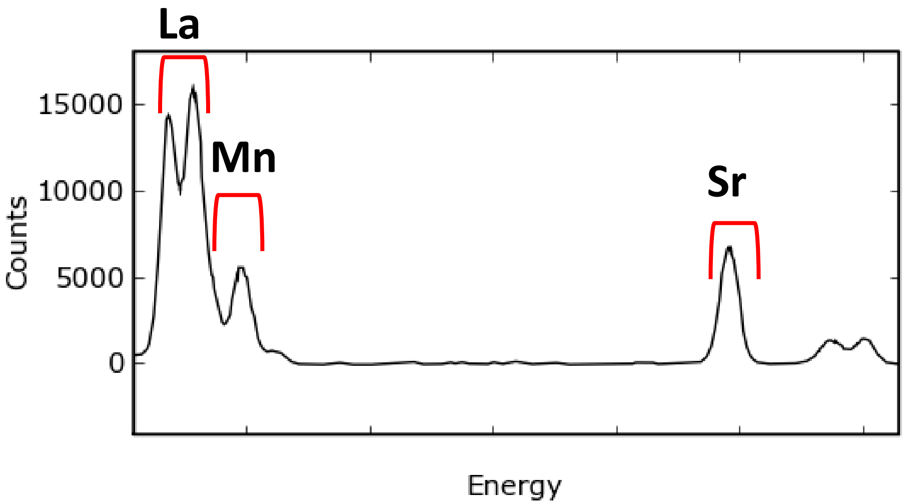
- ☐ Numerical model based on work by Adler’s group but modified to account for entire surface activation, and different geometry.
- ☐ First time applied to well-defined patterns: increases confidence in fitting results.
- ☐ Surface diffusion is equally (to bulk diffusion) *transport* path at highest temperatures and pO_2: evidence from TPB dependence of $1/R_M$ and from fitting model results ($\nu > 1$).
- ☐ Surface exchange high at all measured T and pO_2.

- L.Miara, S.Basu, U.Pal, and S.Gopalan, “2D Numerical Model for Identification ofOxygen Reduction Reaction Mechanisms in Patterned Cathodes of La0.6Sr0.4Co0.2Fe0.8O3-δ”, *J.Electrochem.Soc. (In Print)*

X-ray spectroscopy techniques

Energy Resolving Fluorescence



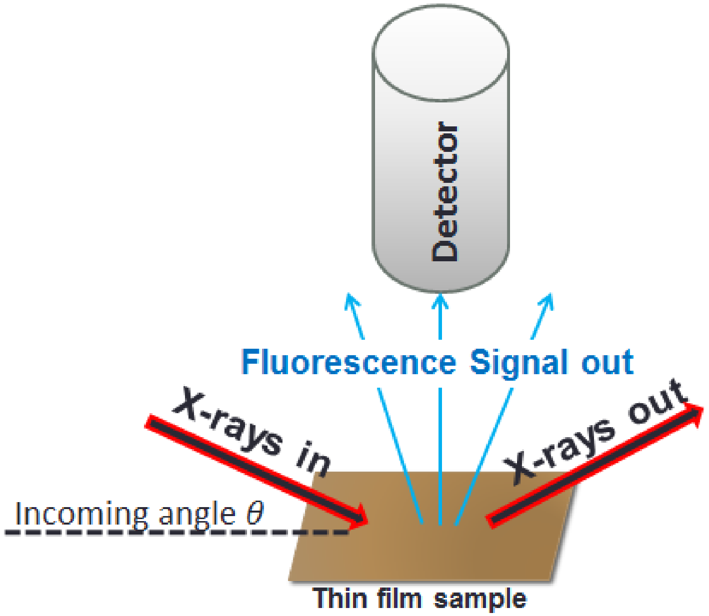


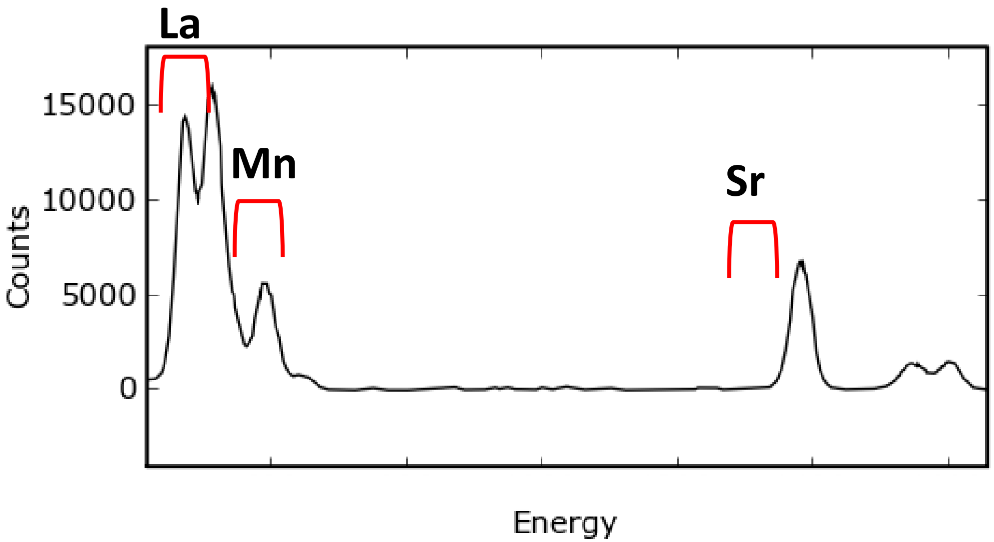
- Small energy range corresponds to emission line of specific atomic species

- Window energy range for fluorescence signal.

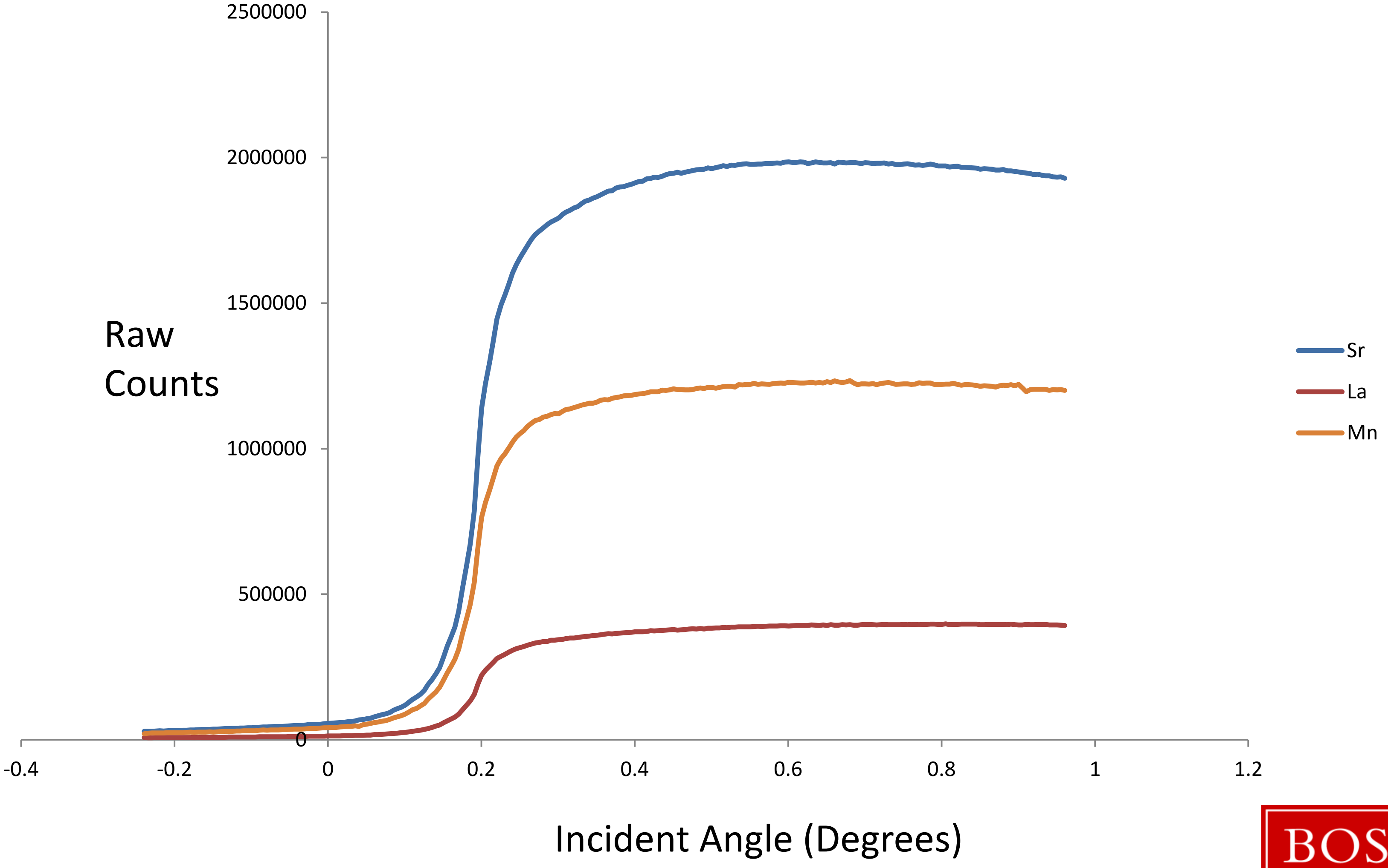
Total Reflection X-ray Fluorescence (TXRF)

- Total Reflection X-ray Fluorescence (TXRF) data was taken as a function of angle. Probing with an incident angle larger than the critical angle α_c, x-rays penetrate the entire sample and bulk properties are measured.
- $\alpha_c = \lambda\sqrt{\frac{\rho r_o}{\pi}}$
- At low angle the beam is totally reflected, and only the topmost nanometers of the film fluoresce.





LSM on NGO as-deposited



$$N(\theta) \propto I(\theta)$$

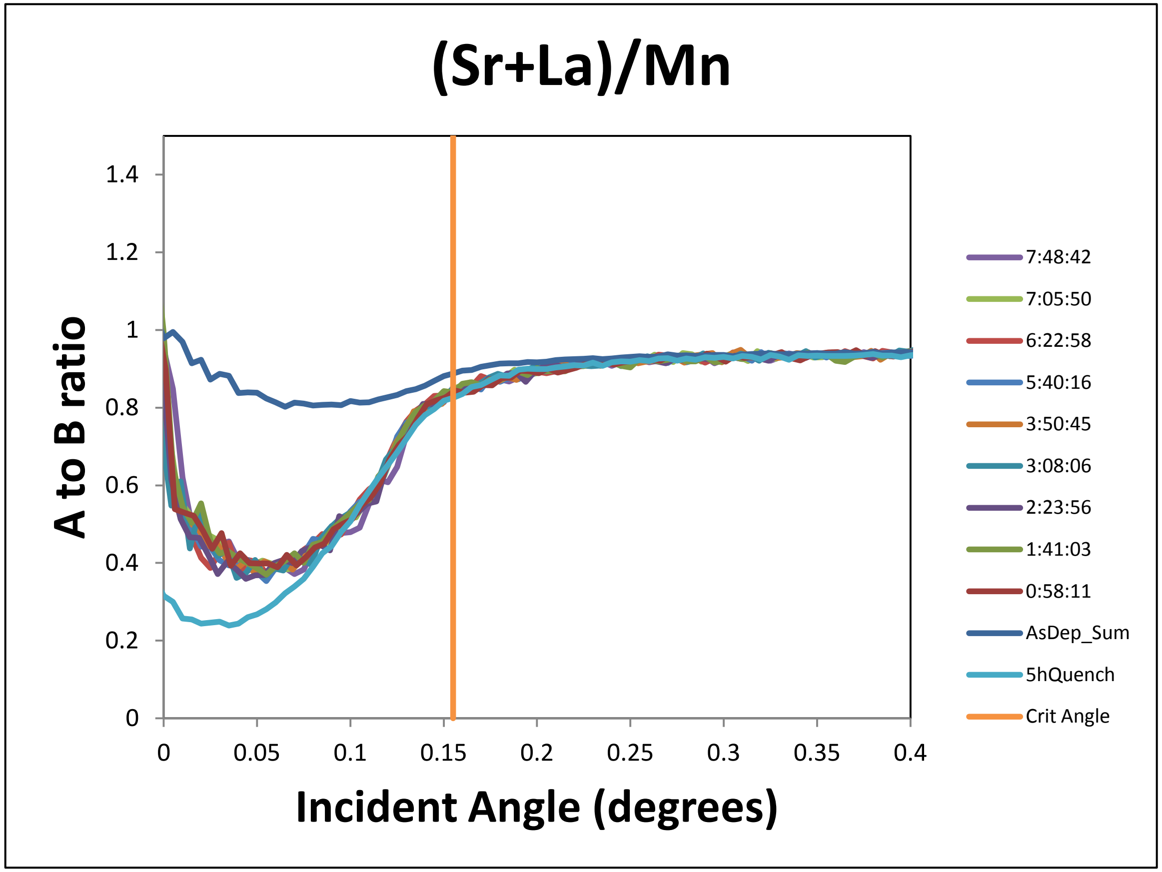
- $N_{Sr} = \alpha I_{Sr}$, $N_{La} = \beta I_{La}$, $N_{Mn} = \gamma I_{Mn}$

- Want $\frac{N_{Sr}}{N_{Sr}+N_{La}}$, $\frac{N_{Sr}+N_{La}}{N_{Mn}}$

$R_1 = \frac{N_{Sr}}{N_{Sr}+N_{La}} = \frac{I_{Sr}}{I_{Sr}+\frac{\beta}{\alpha}I_{La}}$ Define $C_1 = \frac{\beta}{\alpha}$

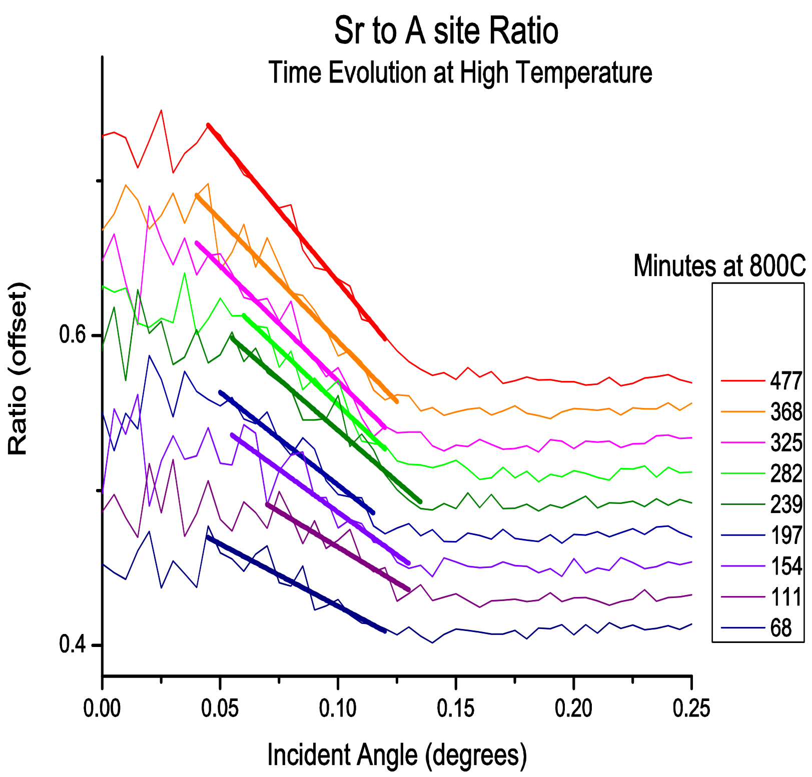
$C_1 = \frac{I_{Sr}(1-R_1)}{R_1 I_{La}}$ For $\theta > \alpha_c$, R_1=0.21

Can now plot R_1 for all angles.



LSM – TXRF *in-situ* measurements

A-site to B-site for LSM. Change upon anneal. Quenched agrees with high T.



LSCF – TXRF *in-situ* measurements

Above the critical angle the bulk value is unchanging. Below the critical angle an increase in the ratio value indicates a higher strontium content. At 800°C the surface is still evolving over eight hours.

Understanding TXRF compositional changes

- We assume that the near-surface behaves in a bulk-like way that allows for a bulk defect model explanation.

- Using the Defect model to relate surface concentration changes to defect concentration.

LSM-20 Defect Chemistry Model for an Electronic Conductor

Electroneutrality:

$$2[V_{O}^{\cdot\cdot}] + [Mn_{B}^{\cdot}] = [Mn_{B}^{'}] + [Sr_{A}^{'}] + 3[V_{A}^{'''}] + 3[V_{B}^{'''}]$$

A-site balance:

$$[La_{A}^{x}] + [Sr_{A}^{'}] + [V_{A}^{'''}] = 1$$

B-site balance:

$$[Mn_{B}^{'}] + [Mn_{B}^{x}] + [Mn_{B}^{\cdot}] + [V_{B}^{'''}] = 1$$

O-site balance:

$$[O_{O}^{x}] + [V_{O}^{\cdot\cdot}] = 3$$

Metal contents:

$$\frac{[La_{A}^{x}]}{[Sr_{A}^{'}]} = \frac{1-x}{x}$$

$$\frac{\{[La_{A}^{x}] + [Sr_{A}^{'}]\}}{\{[Mn_{B}^{'}] + [Mn_{B}^{x}] + [Mn_{B}^{\cdot}]\}} = y$$

Shottky-reaction:

$$K_S = [V_{O}^{\cdot\cdot}]^3 \cdot [V_{A}^{'''}] \cdot [V_{B}^{'''}]$$

Redox reaction:

$$K_r = \frac{[Mn_{B}^{x}] \cdot [V_{O}^{\cdot\cdot}] \cdot PO_2^{1/2}}{[Mn_{B}^{\cdot}] \cdot [O_{O}^{x}]}$$

Charge disproportionation:

$$K_i = \frac{[Mn_{B}^{'}] \cdot [Mn_{B}^{\cdot}]}{[Mn_{B}^{x}]^2}$$

Direct measurement from TXRF

Direct measurement from HAXPES

F.W. Poulsen, Solid State Ionics, vol 129, 145-162, 2000

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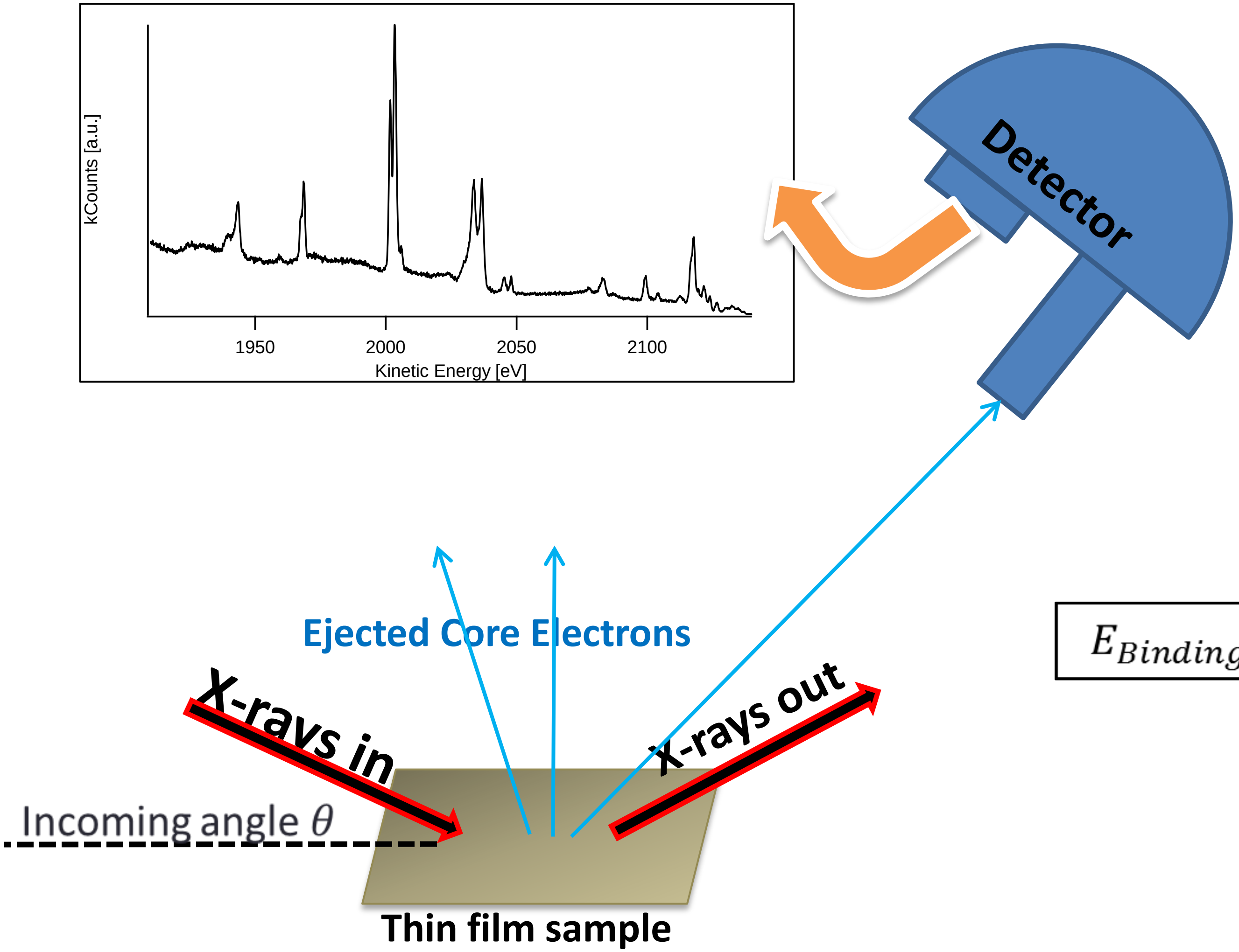
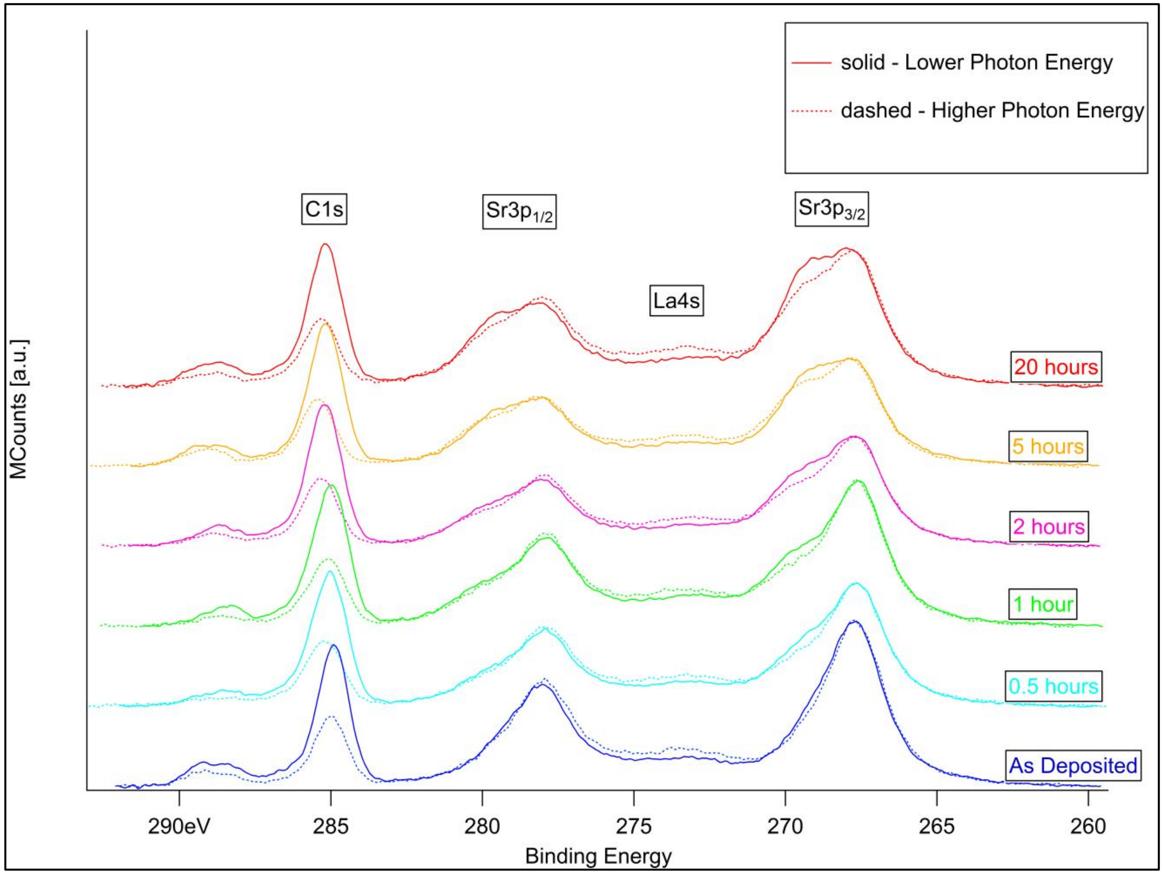
X-Ray Photoelectron Spectroscopy



$$E_{Binding} = h\nu - \phi - E_{Kinetic}$$

Hard X-ray Photoelectron Spectroscopy HAXPES

- Overcomes surface contamination problems of soft x-ray spectroscopies.
- Tunable penetration depth.
- Identify Cation states as a function of probing depth.
- Apply defect model to Cation states.

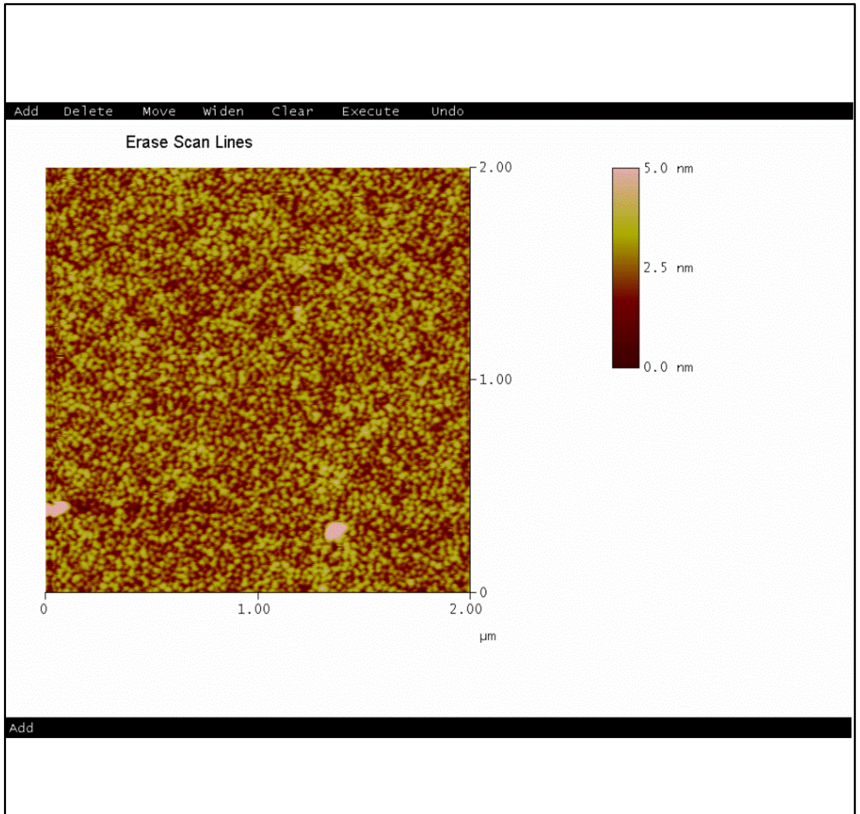


LSCF Sr3p

Incident photon energy of 3000eV compared to 2140eV.

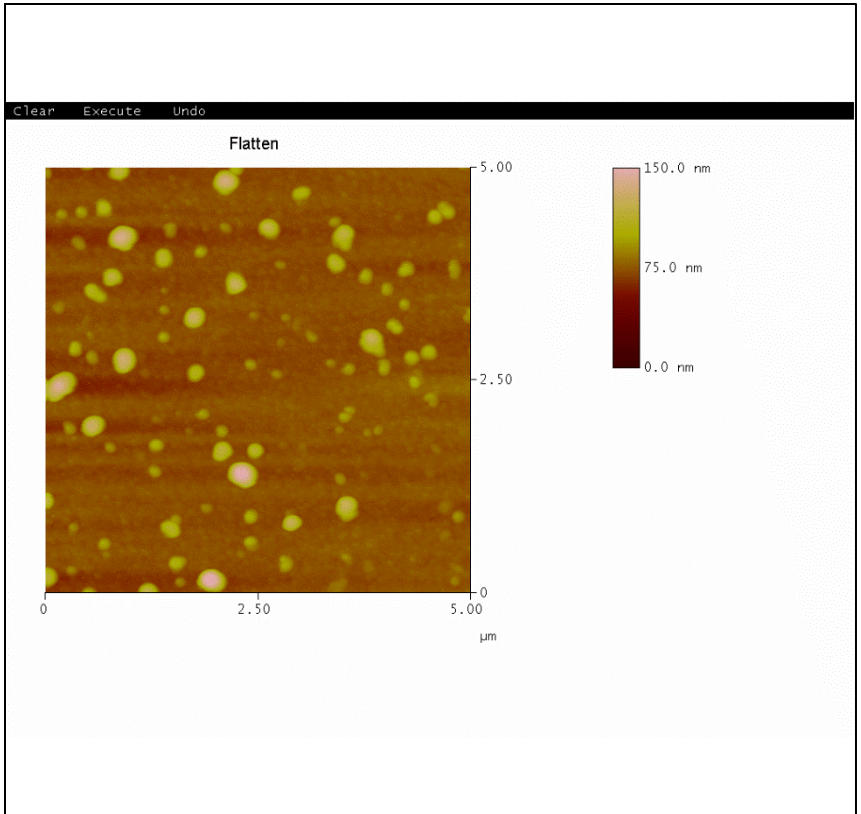
AFM Surface Evolution

As Deposited



RMS Surface Roughness **0.68nm**

800°C 5 hours Quench



RMS Surface Roughness **9.4nm**

Summary

- Using TXRF to do composition analysis of surfaces versus bulk
- Using HAXPES to probe electronic structure of surfaces versus bulk
- Goal – converge on a complete picture of the defect chemistry of the structure versus the bulk
- Correlate results with the kinetics of oxygen reduction measured on patterned thin films

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- NSLS facilities at Brookhaven National Lab.

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