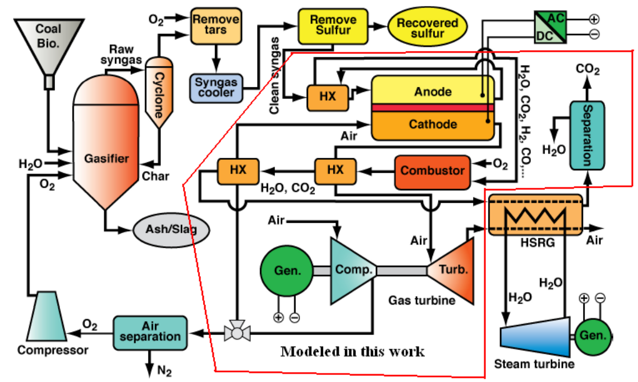
# Kinetics of Oxygen Reduction in LSM and LSCF

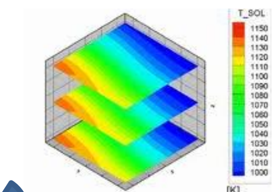
Linc Miara, Jacob Davis,, U.B.Pal, S.N.Basu, K.Ludwig, and S.Gopalan

Division of Materials Science and Engineering, Boston University

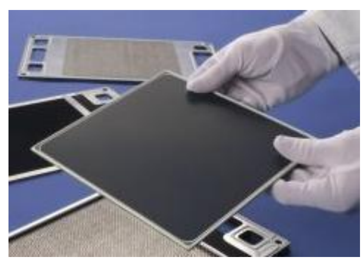
# Motivation:

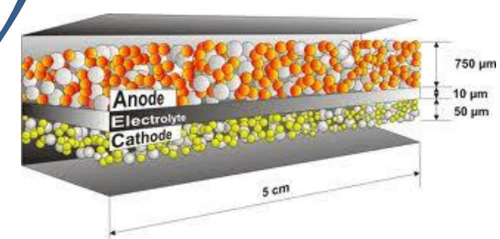



Power plant design: IGFC Concept

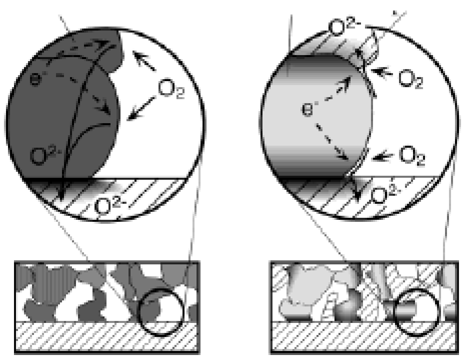



SOFC Stack: current collection, thermal management, interconnects.






Single Cell: degradation, mass and thermal transport




Electrodes: Reaction Kinetics, Oxygen Transport, Material and Geometry effects

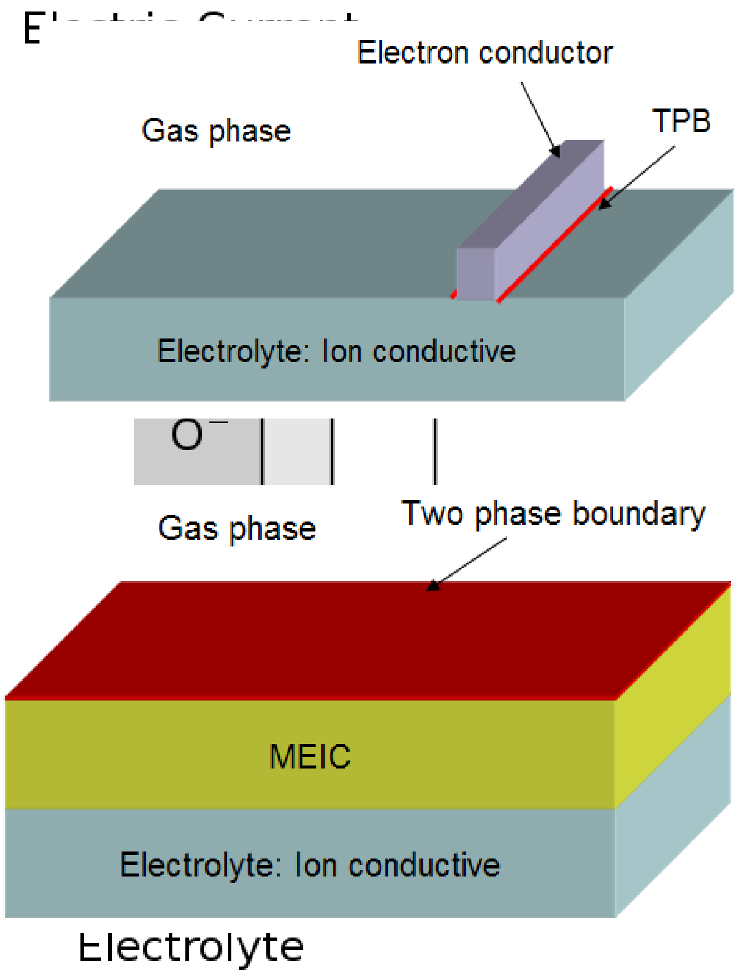
# The Oxygen Reduction Reaction:

## Where does this take place:

- On the surface?
- In the bulk?
- On the electrolyte?
- At the three phase boundary?
- At the cathode/electrolyte interface?
- Does it depend on the material?

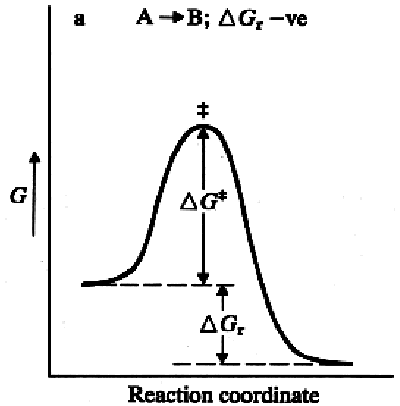
$$O_2(g) + 4e' = 2O^{2-}$$

## What processes are important?

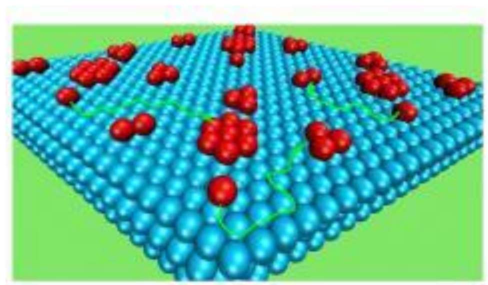


# What processes are important for oxygen reduction?

<u>Kinetics and Rate Laws:</u>
Is one rate determining?

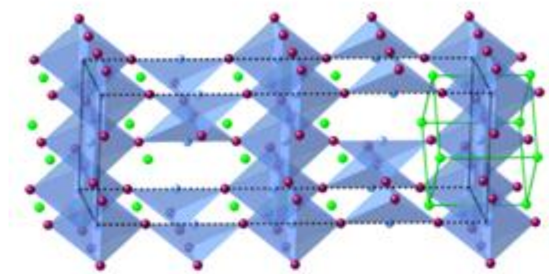



<u>Surface Diffusion:</u>
What are the mechanisms?

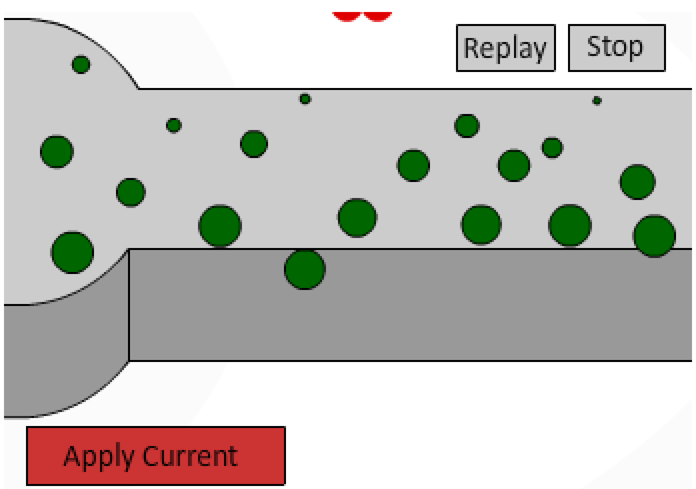


M.C. Marinica *et al.*,
*Phys. Rev. B 72, 115402 (2005).*

<u>Bulk Diffusion:</u>
When is it important?



J.D. Ferguson *et al. Advanced Materials*
*V. 23, Issue 10, p 1226–1230*



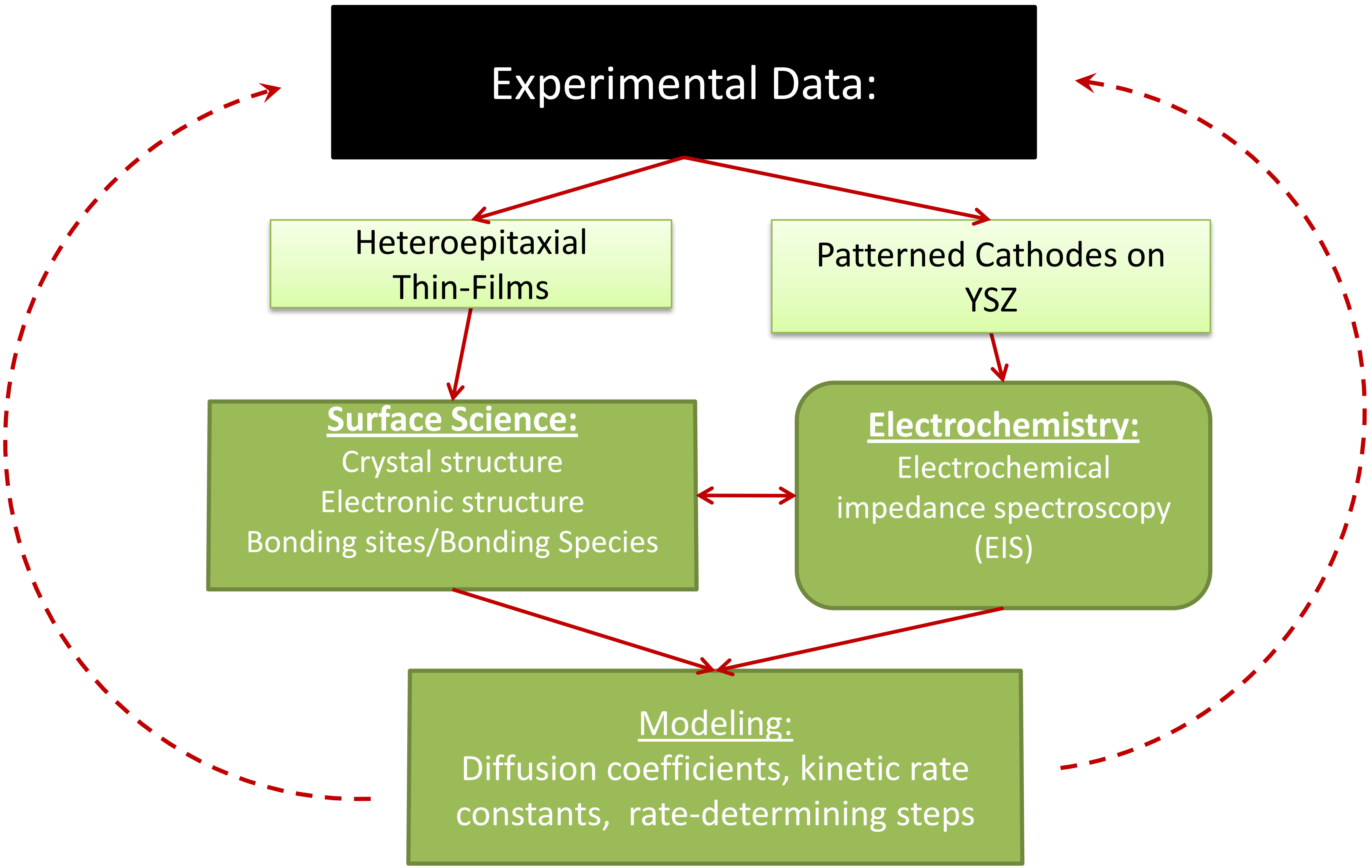

$$O_2 + 2s \rightleftharpoons 2O^{ad}$$ surface

$$j_{Oad} = -D_s(\partial[O^{ad}]/\partial z)$$

TPB

$$2O^{ad} + 2V_{\ddot{o}}^{YSZ} \rightleftharpoons 2O_o^{x\text{-}YSZ} + 2h + 2s$$

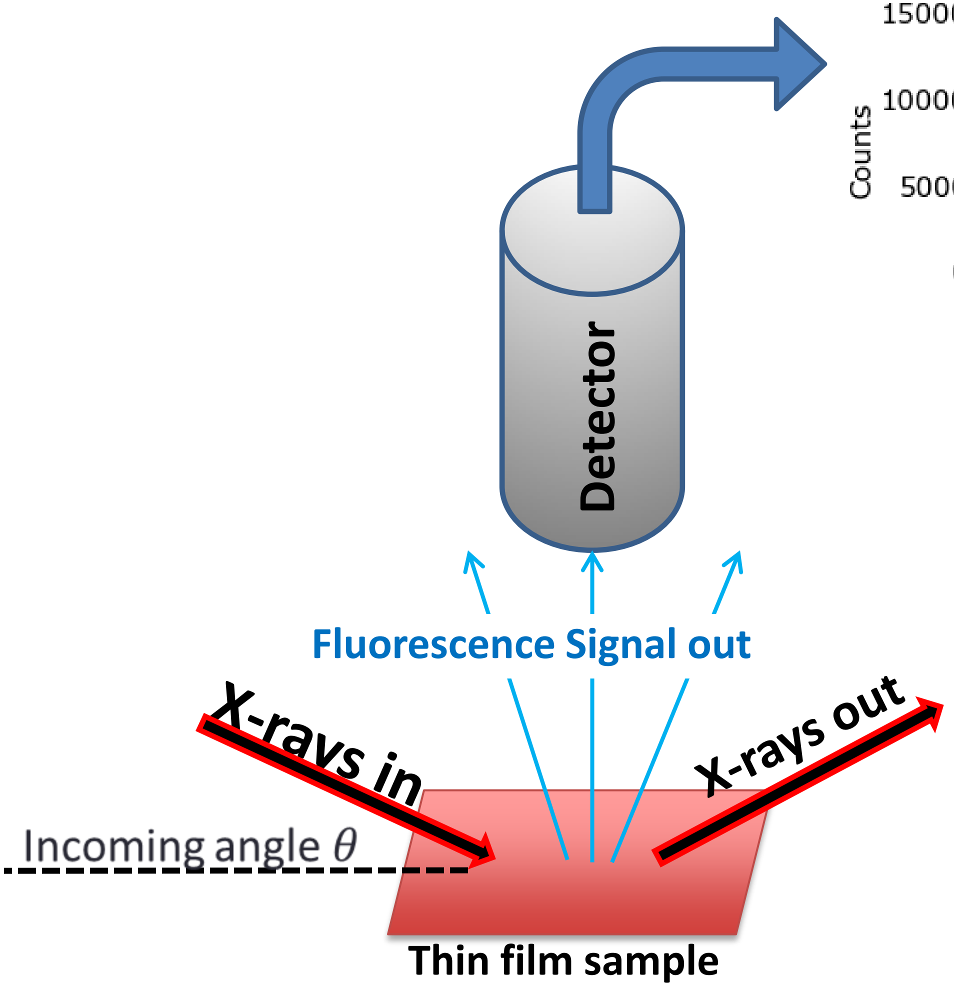
# BU Cathode Project…

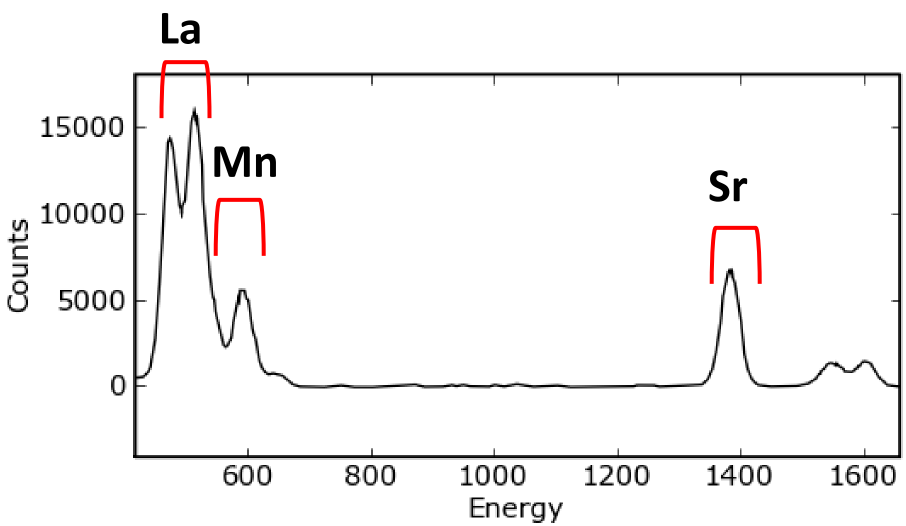


# X-ray Techniques

- Surface Composition [TXRF]
- Local Electronic Structure [EXAFS], [XANES]

# Energy Resolving Fluorescence



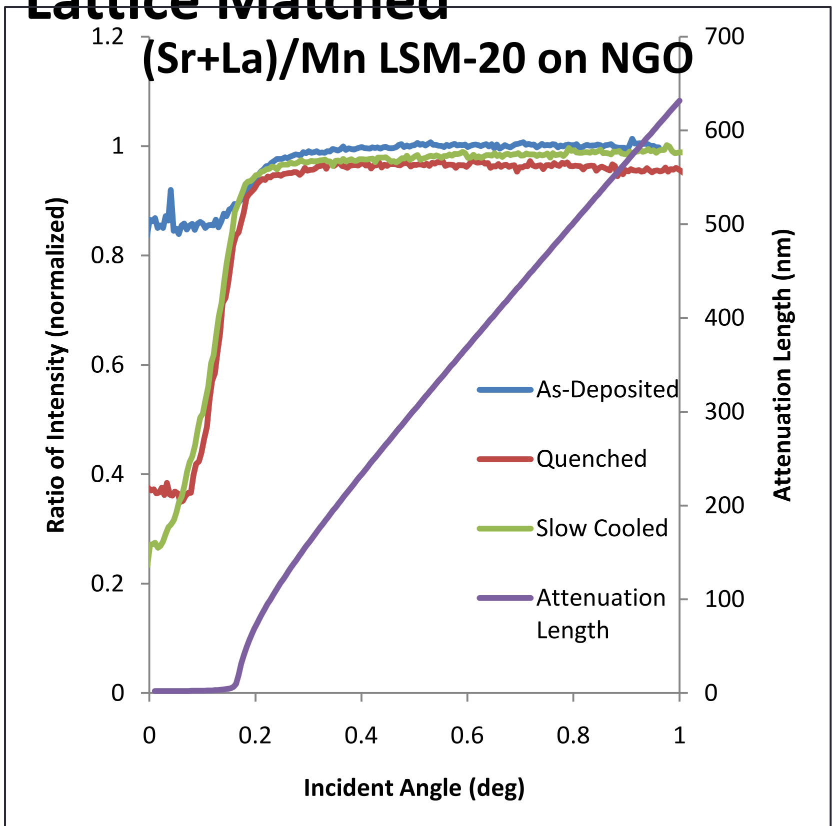




- Small energy range corresponds to emission line of specific atomic species
- Window energy range for fluorescence signal.

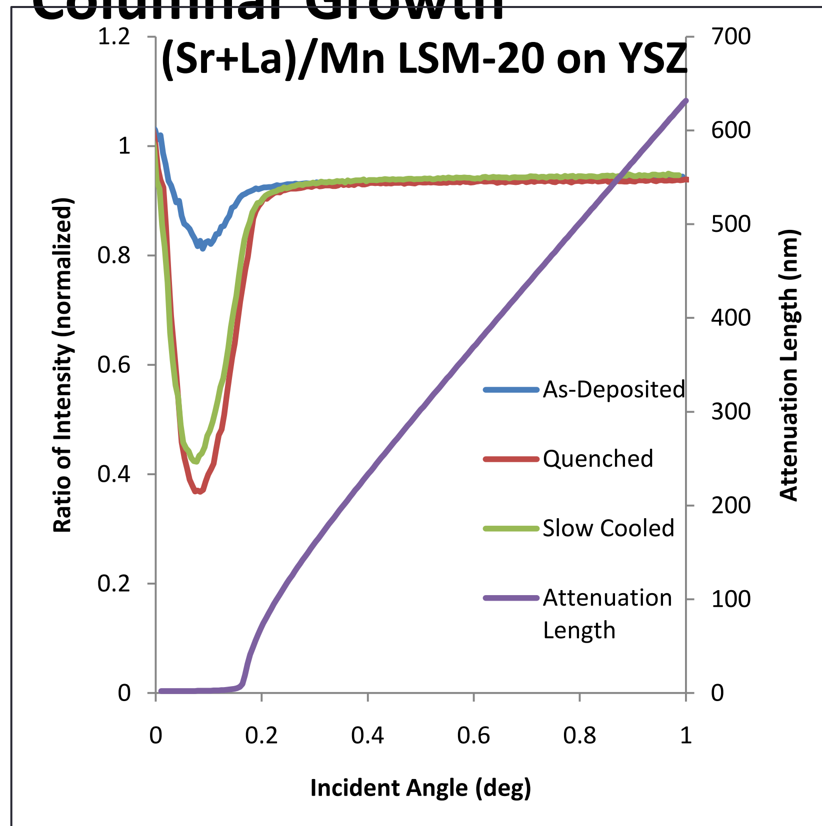
# Ratio of the A-site to B-site, $\frac{Sr+La}{Mn}$

Annealed at 800°C for 1 hour

## Lattice Matched




## Columnar Growth




- **There is manganese enrichment at the surface during annealing.**
- **Quenched and cooled sample are similar.**
- **Suggests surface composition developed at high temperature is preserved.**
- **Experiments at high temperature are not done yet.**

# 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:

$$K_S = [V_O^{\cdot\cdot}]^3 \cdot [V_A^{'''}] \cdot [V_B^{'''}]$$

Redux 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:

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

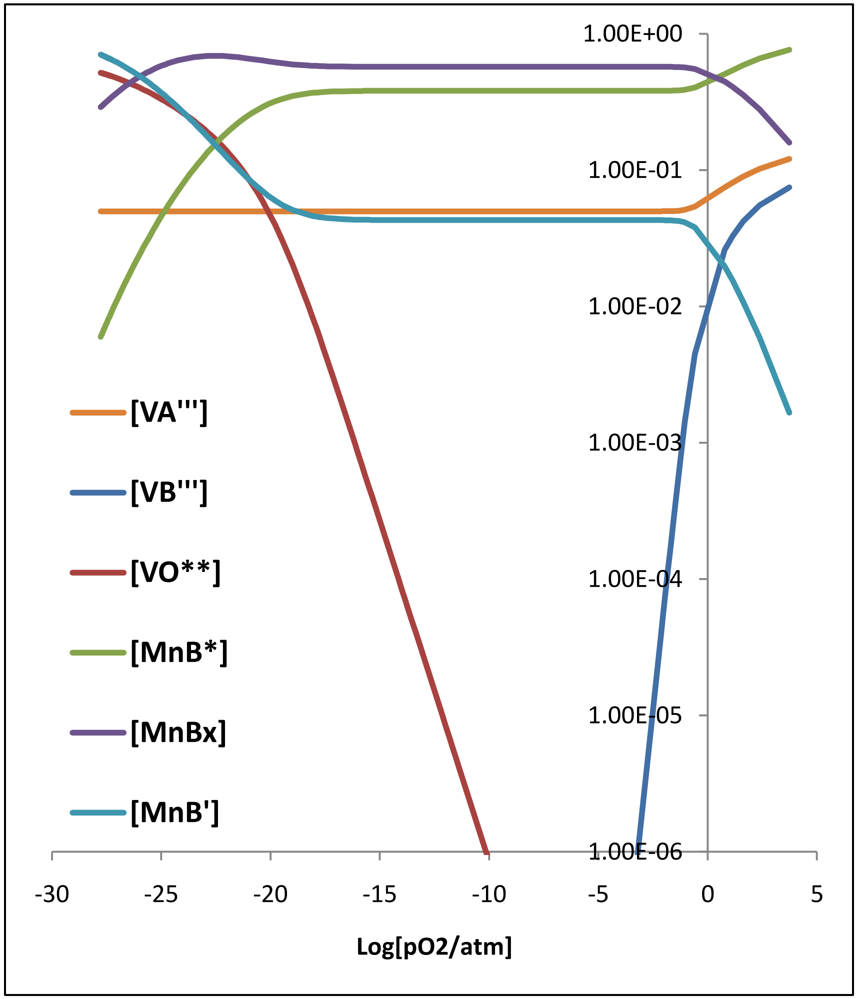


F.W. Poulsen, Solid State Ionics, vol 129, 145-162, 2000

# Solved Concentrations

For a given x, y $K_s$, $K_r$, $K_i$ can generate relevant concentrations versus T and $P_{O2}$.

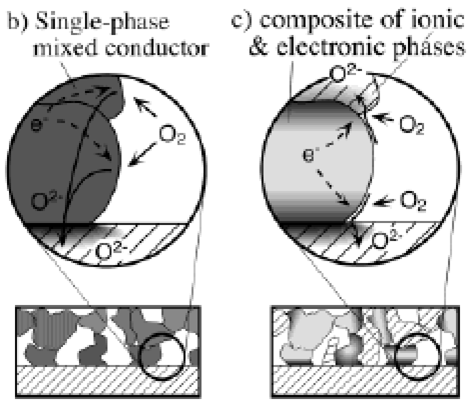
TXRF provides specific information about x and y on the surface. Next step is to calculate the Brouwer diagram of LSM surface.



# Kinetic Measurements Using Polycrystalline Thin Film Electrodes

# 2 Pathways for Oxygen Reduction…

# First, I'll focus on the "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

↓

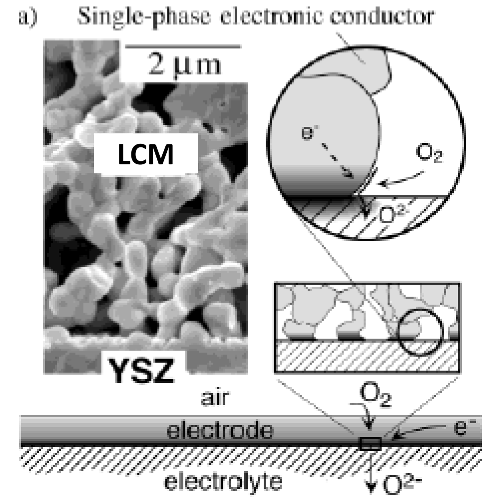
Surface Adsorption

↓

Dissociation

↙ ↘

| | |
| --- | --- |
| Electronation and Incorporation to cathode | Surface Diffusion to Triple Phase Boundary (TPB) |
| ↓ | ↓ |
| Bulk Diffusion to Electrolyte | Electronation and Incorporation to electrolyte at TPB |
| ↓ | |
| Incorporation into Electrolyte | |

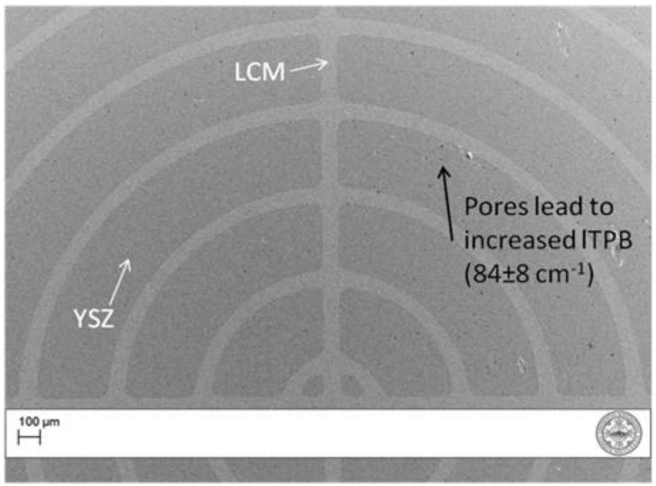


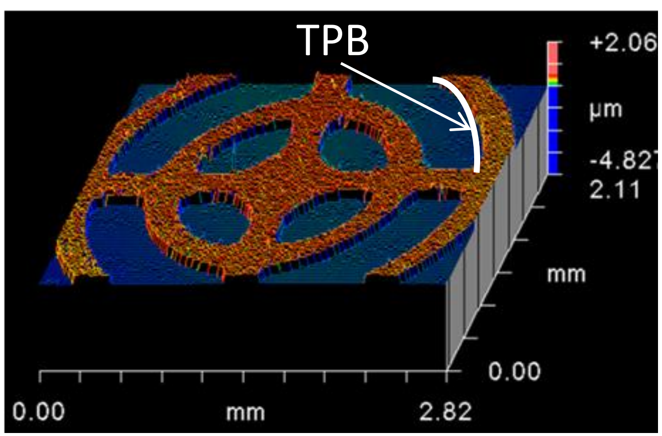

The "Surface Path"

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

# Experimental – LCM Patterned Cathodes:

Known to have low ionic conductivity, can we find evidence of "Surface Path?"

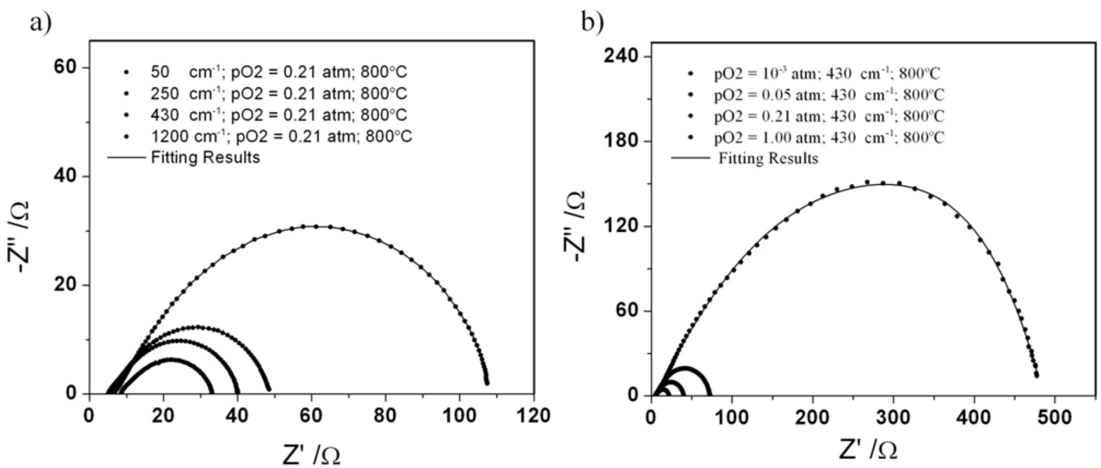



## Generate Patterns:

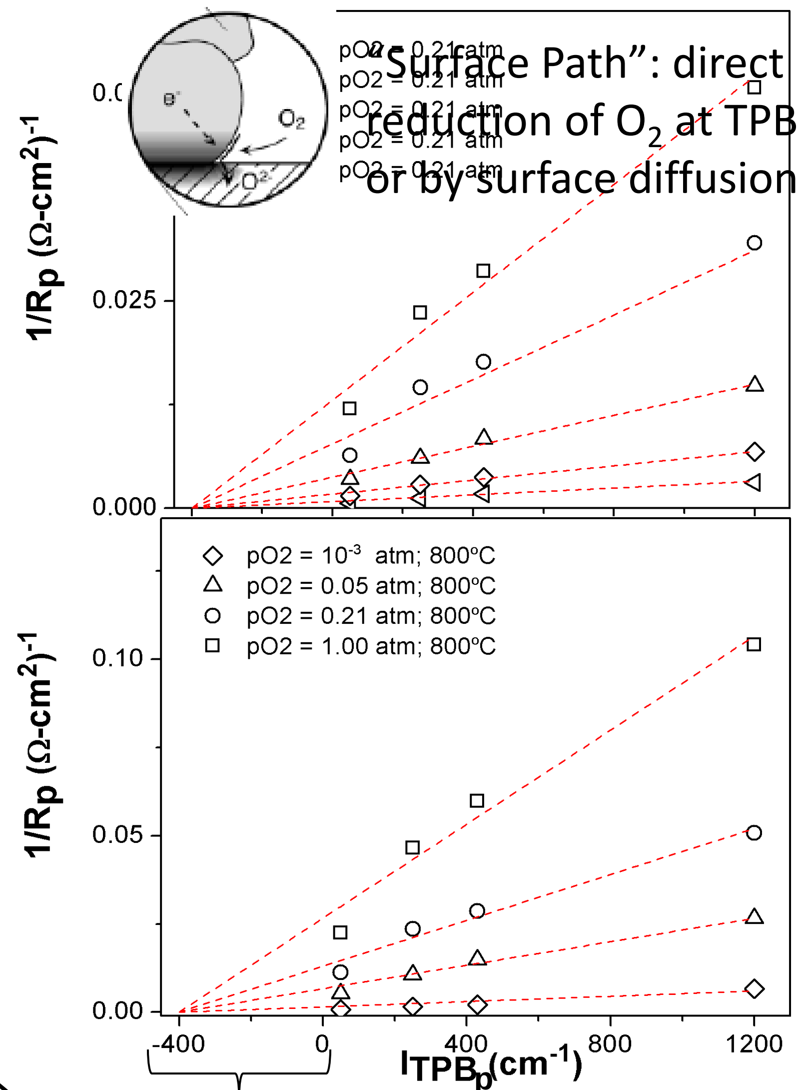
- TPB length = 450 – 1600 cm $cm^{-2}$
- Cathode/electrolyte area = constant

$R_p$ ($\Omega$-$cm^2$) = Nyquist ($Lf_{intercept}$ – $Hf_{intercept}$)*Area



# LCM – Evidence of Surface Path:

Total Polarization scales inversely with TPB



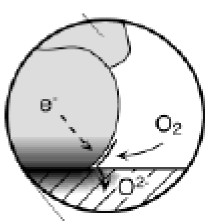

## Two parallel paths:

$$\frac{1}{R_p} = \frac{1}{R_p^{TPB}} + \frac{A_A}{R_p^{MIEC}}$$

## Where:

$$R_P^{TPB} = \frac{\rho_P}{l_{TPB}}, \qquad l_{TPB} = \underbrace{l_{TPB_p}}_{\text{Pattern TPB}} + \overbrace{l_{TPB_o}}^{\text{TPB due to pores}}$$

$$\frac{1}{R_p} = \frac{l_{TPB_p}}{\rho_p} + \boxed{\frac{l_{TPB_o}}{\rho_p} + \frac{A_A}{R_p^{MIEC}}}$$




“Surface Path”: direct reduction of $O_2$ at TPB or by surface diffusion

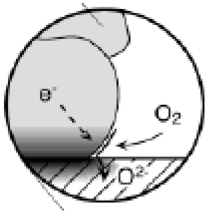
R. Radhakrishnan, A. V. Virkar, and S. C. Singhal, *JECS*, vol. 152, pp. A210-A218, 2005.

# LCM – Evidence of Surface Path:

$$\frac{1}{R_p} = \frac{l_{TPB_p}}{\rho_p} + \frac{l_{TPB_o}}{\rho_p} + \frac{A_A}{R_p^{MIEC}}$$

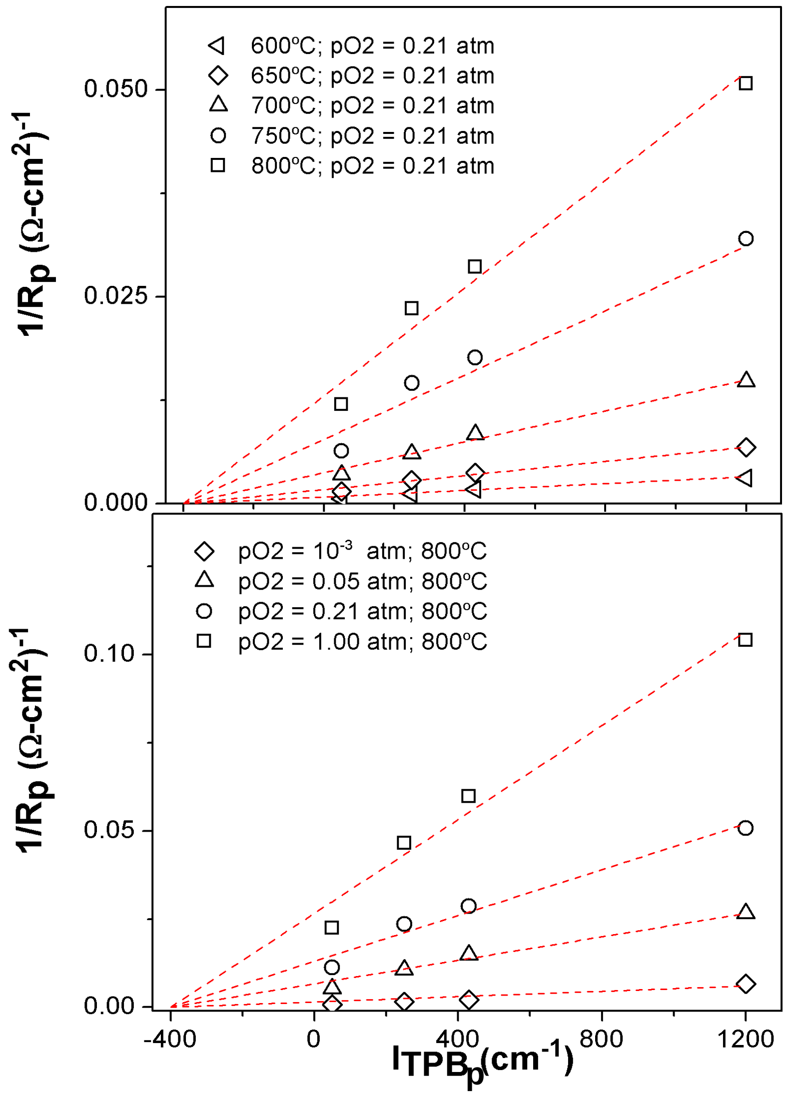
| T °C | $R_p$ | $R_p^{(TPB)}$ | $R_p^{(miec)}$ |
|---|---|---|---|
| 800 | 15 | 19 | 74 |
| 750 | 25 | 30 | 121 |
| 700 | 53 | 62 | 285 |
| 650 | 116 | 134 | 662 |
| 600 | 253 | 290 | 1,597 |

On average **TPB path** is ~4 fold **less resistive**, and thus the most likely path




"Surface Path": direct reduction of $O_2$ at TPB or by surface diffusion

Total Polarization scales inversely with TPB



# Goals:

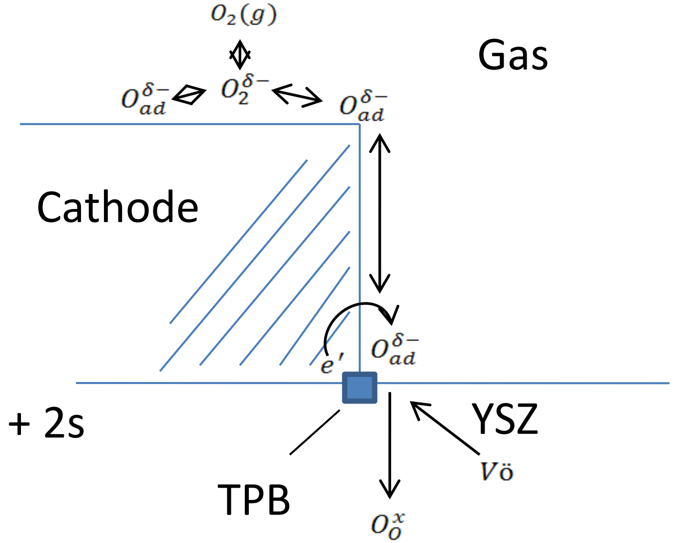
1. Derive a model incorporating dominant processes.
2. Simulate impedance data to extract relevant kinetic parameters.
3. Determine rate limiting steps.

# Model: Reaction Scheme

Dissociative Adsorption: $O_2 + 2s \underset{k_{des}}{\overset{k_{ad}}{\rightleftharpoons}} 2O^{ad}$

Surface Diffusion: $\frac{d[O_{ad}]}{dt} = D_s \frac{d^2[O_{ad}]}{dz^2}$

Reduction/
Incorporation Reaction: $2O^{ad} + 2V_{ö}^{YSZ} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} 2O_o^{x\text{-}YSZ} + 2h + 2s$

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Define: θ = $[O^{ad}]/\Gamma$ and s = $\Gamma \cdot (1 - \theta)$
Γ = Total # of oxygen adsorption sites

Mass balance at TPB:

$$\frac{d\theta}{dt} = 2k_{ad}P_{O2}\Gamma(1-\theta)^2 - 2k_{des}\Gamma\theta^2 - k_1[V_{ö}]\theta + k_{-1}[O_O^x](1-\theta)$$

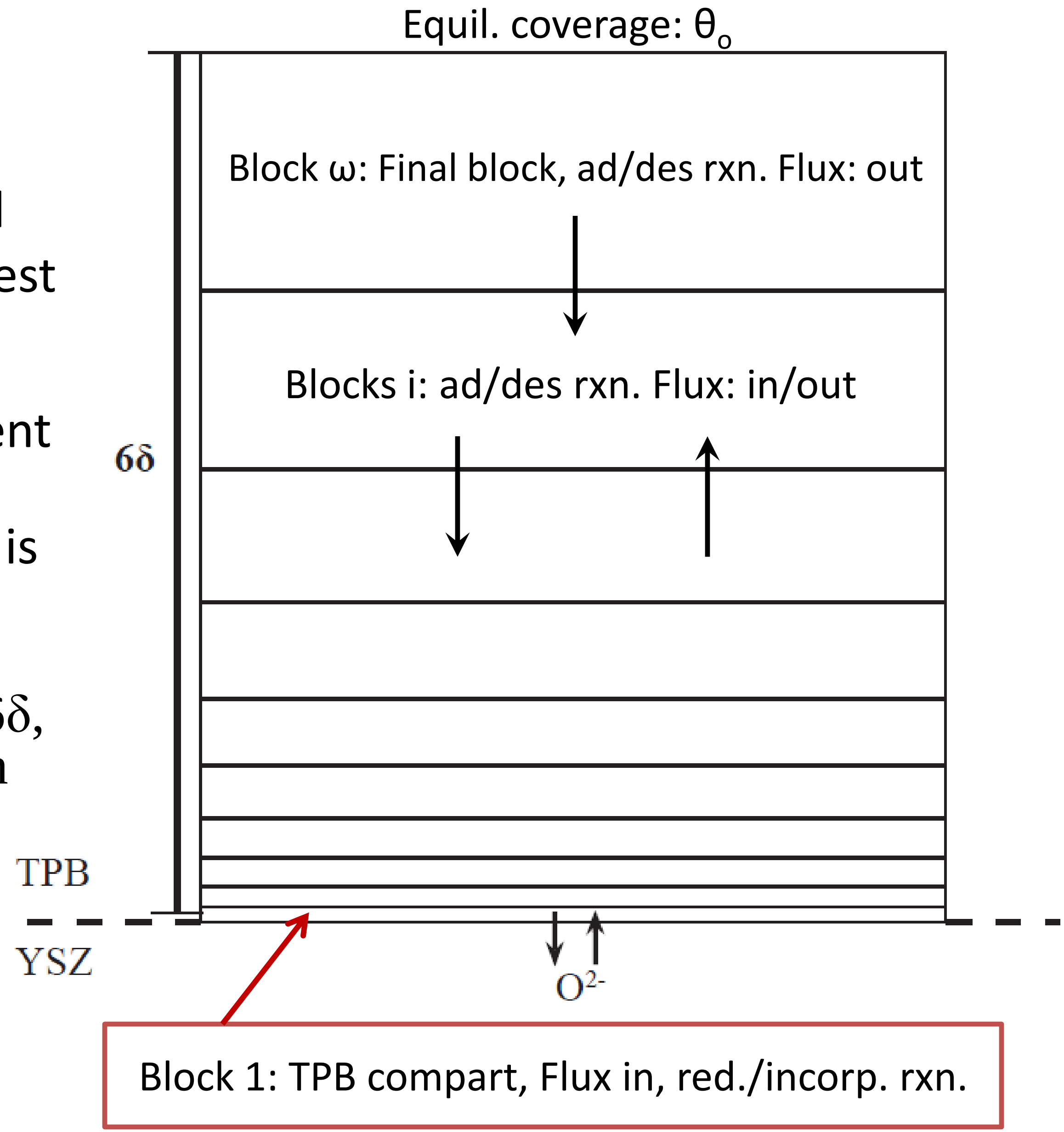
Charge Balance: $I_F = 2\Gamma F A_a[k_{-1}[O_O^x](1-\theta) - k_1[V_{ö}]\theta]$

Based on model by Mitterdorfer *et al.: Solid State Ionics,* 117, 187 (1999).

# Surface Mass Transport:

- Incorporated using 1D Finite-Difference Method
- Compartments are smallest closest to TPB (expand geometrically away) to capture the higher gradient at the interface.
- The concentration of $O^{ad}$ is considered uniform in a given compartment
- Surface is discretized to $6\delta$, where $\delta$ is the penetration depth determined by:

$$2\pi^{-1/2} = \delta\sqrt{\omega_{max} / 2D_S}$$



# Initial and Boundary Conditions:

- Initial Condition: $\theta(z,0) = \theta_O$
  - Where: $\frac{\theta_O}{1-\theta_O} = K\sqrt{pO_2};\ with\ K = \sqrt{\frac{k_{ad}}{k_{des}}}$
- Boundary conditions:
  - Infinitely far away (i.e. $6\delta$): $\theta(\infty,t) = \theta_O$
  - At the TPB interface:
    - The current equals the charge balance
    - The electron transfer reaction only takes place in this compartment

# Dependence of kinetic Parameters on:

Temperature:

$$k_{ad} = \mathrm{k}_{\mathrm{ad}}^{\mathrm{o}} \exp\left(\frac{-E_{ad}}{RT}\right) \qquad \mathrm{k}_1^{\mathrm{eq}} = k_1^o \exp\left(\frac{-E_{fc}}{RT}\right)$$

$$k_{des} = \mathrm{k}_{\mathrm{des}}^{\mathrm{o}} \exp\left(\frac{-E_{des}}{RT}\right) \qquad \mathrm{k}_{-1}^{\mathrm{eq}} = k_{-1}^o \exp\left(\frac{-E_{bc}}{RT}\right)$$

Electrode Potential:

$$k_1 = \mathrm{k}_1^{\mathrm{eq}} \exp\left(-\frac{\beta F}{RT}(\Delta\chi)\right) \qquad k_{-1} = \mathrm{k}_{-1}^{\mathrm{eq}} \exp\left(\frac{(1-\beta)F}{RT}(\Delta\chi)\right)$$

Where:

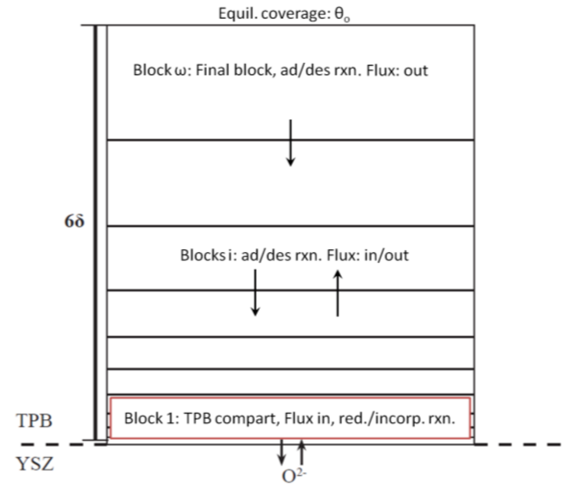
$$\Delta\chi = 2\eta - \frac{RT}{F}\ln\left(\frac{\theta}{1-\theta}\,\frac{1-\theta_o}{\theta_o}\right)$$

η = applied overpotential at cathode/electrolyte interface

And:

$$\frac{\theta_O}{1-\theta_O} = K\sqrt{pO_2};\ with\ K = \sqrt{\frac{k_{ad}}{k_{des}}}$$

# Final form for Simulink:




Adsorption/Desorption

Final Block (ω): $$\frac{d\theta_\omega}{dt} = 2k_{ad}p_{O_2}\Gamma(1-\theta_\omega)^2 - 2k_{des}\Gamma{\theta_\omega}^2 + \frac{1}{T_\omega}\left(\frac{q*\theta_{\omega-1}}{1+q} - \frac{(2q+1)\theta_\omega}{1+q} + \theta_O\right)$$

Diffusion

Block i: $$\frac{d\theta_i}{dt} = 2k_{ad}p_{O_2}\Gamma(1-\theta_i)^2 - 2k_{des}\Gamma{\theta_i}^2 + \frac{1}{T_i}\left(\frac{\theta_{i-1}}{1+q} - \theta_i + \frac{\theta_{i+1}}{1+q}\right)$$

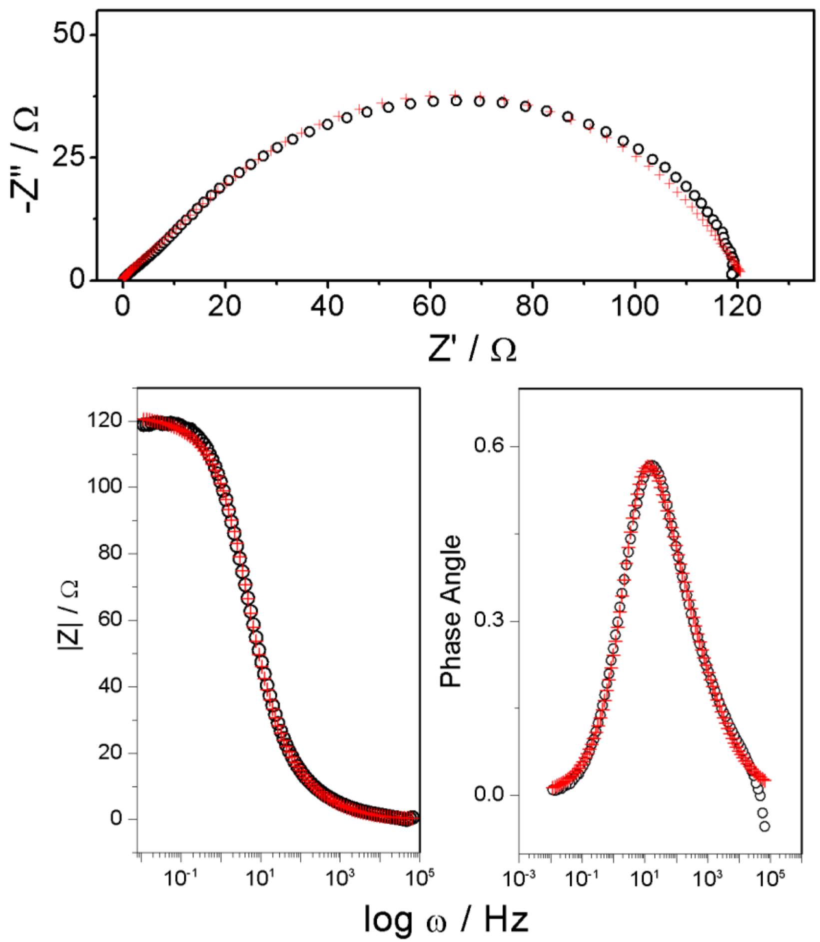
Charge Transfer/Incorporation

TPB Block (1): $$\frac{d\theta_1}{dt} = 2k_{ad}p_{O_2}\Gamma(1-\theta_1)^2 - 2k_{des}\Gamma{\theta_1}^2 - k_f^{eq}\exp\left(-\frac{\beta F}{RT}\Delta\chi\right)\theta_1 + k_b^{eq}\exp\left(\frac{(1-\beta)F}{RT}\Delta\chi\right)(1-\theta_1) + \frac{1}{T_1}\left(-\frac{\theta_1}{1+q} + \frac{\theta_2}{1+q}\right)$$

* $T_i = \Delta {z_i}^2/2D$; q = geometric factor expanding block size

# Typical Simulation Results:

T = 700$^o$C, $P_{O2}$ = 0.21, TPB Length = 7.0 m




minimization to

$\cdot \left|Z_{sim}(i) - Z_{exp}(i)\right|^2$

$)^5$ $m^2 \cdot (s\ mol\ atm)^{-1}$

$10^6$ $m^2 \cdot (s\ mol)^{-1}$

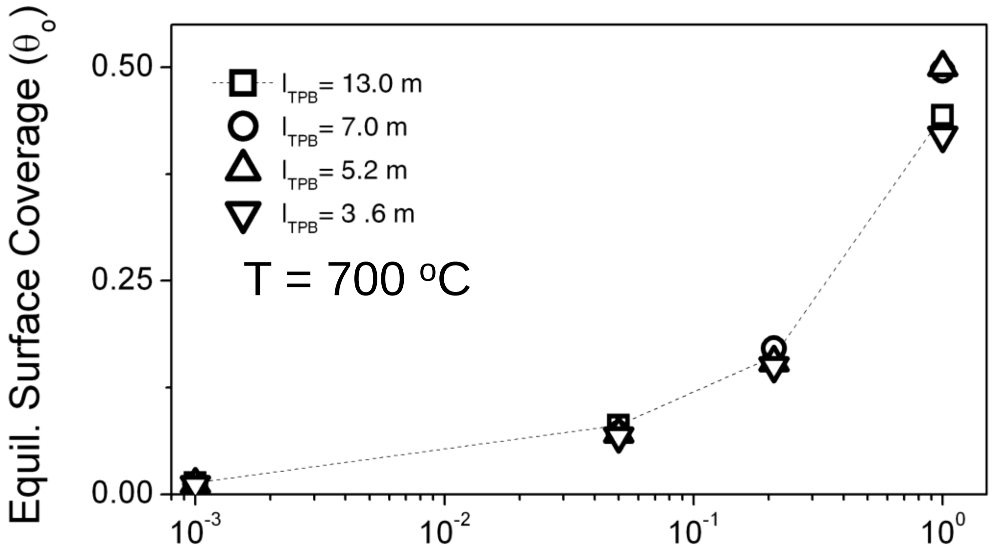
$^{-9}$ $m^2\ s^{-1}$,

$m^3\ (mol\ s)^{-1}$ ,

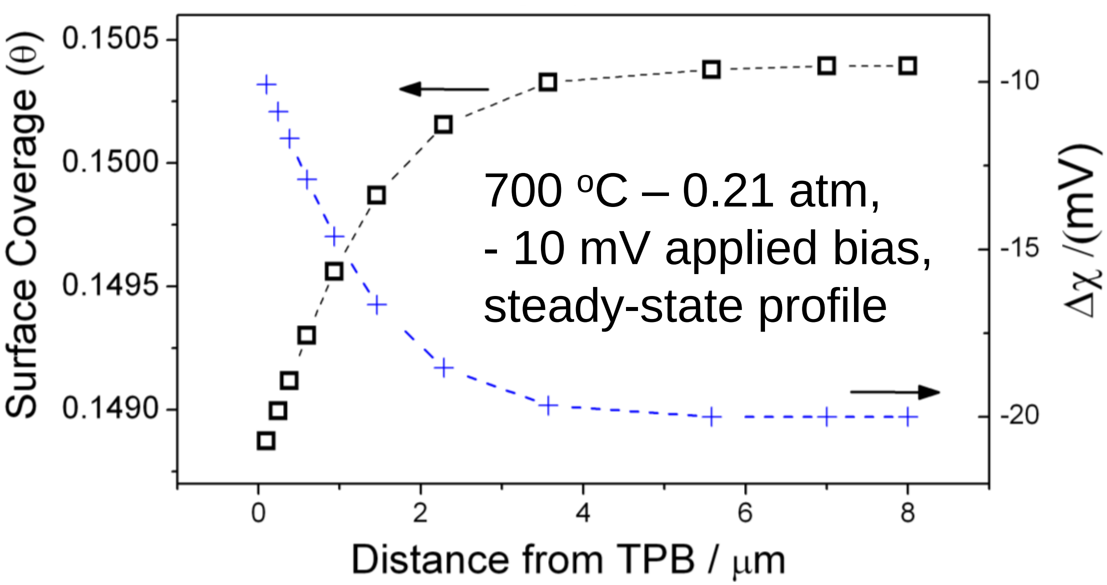
$(mol\ s)^{-1}$ ,

$.0^{-4}$ F

# Surface Coverage:




**Equilibrium surface coverage** increases with $pO_{2.}$ Little scatter between samples shows experimental reliability

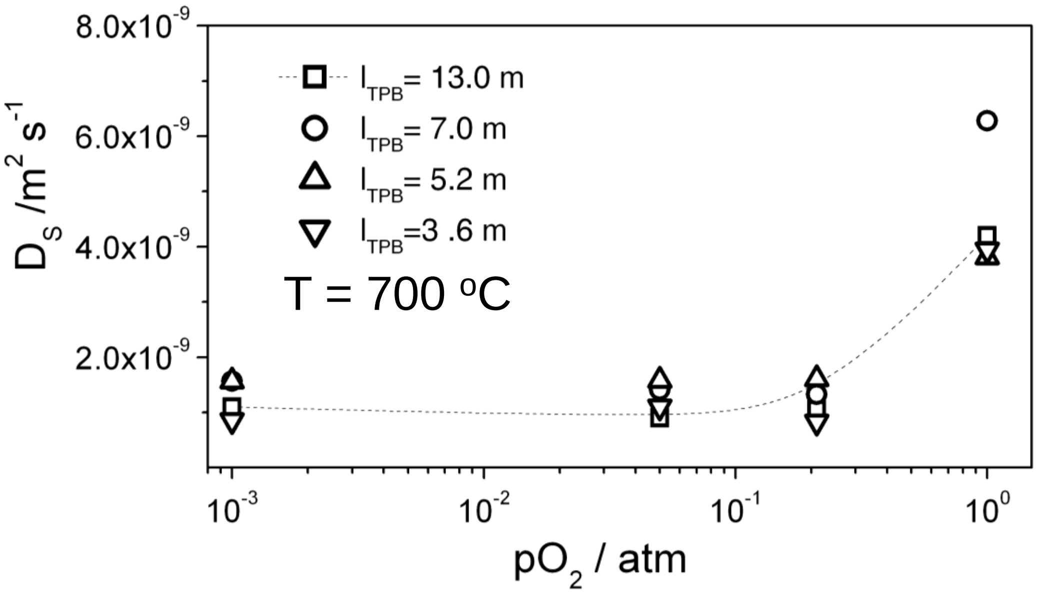



The surface coverage increases away from TPB, and then plateaus (Dirichelet condition).

$$\Delta\chi = 2\eta - \frac{RT}{F}\ln\left(\frac{\theta}{1-\theta}\,\frac{1-\theta_o}{\theta_o}\right)$$

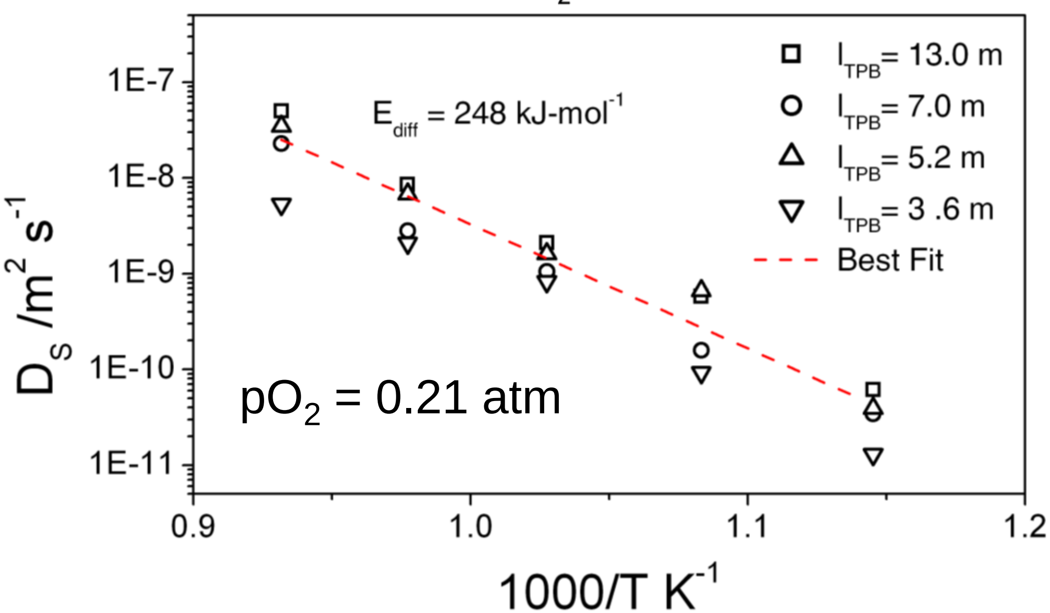
Δχ decreases to a max of 2η as $\theta \rightarrow \theta_o$

# Surface Diffusivity:



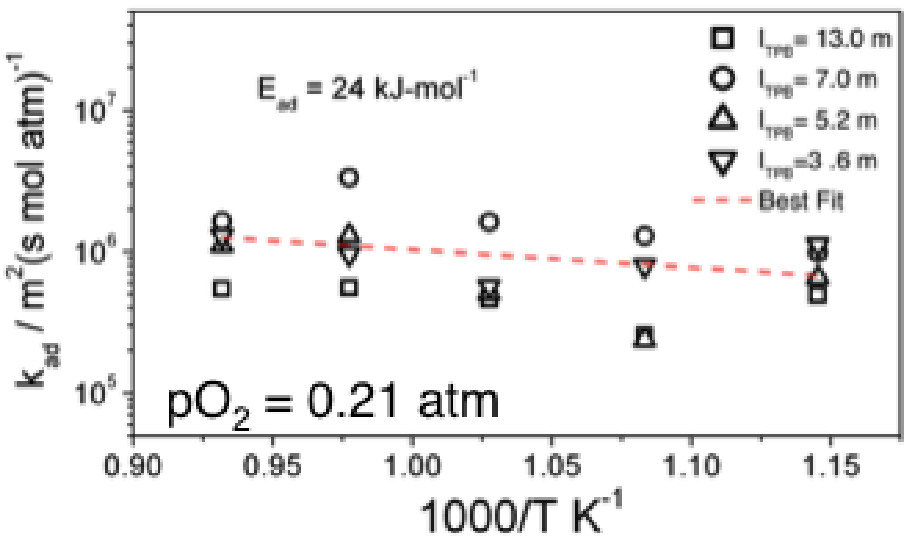

Surface diffusivity is flat at low coverage: $D_s \approx D_s^o$ (intrinsic diffusivity).

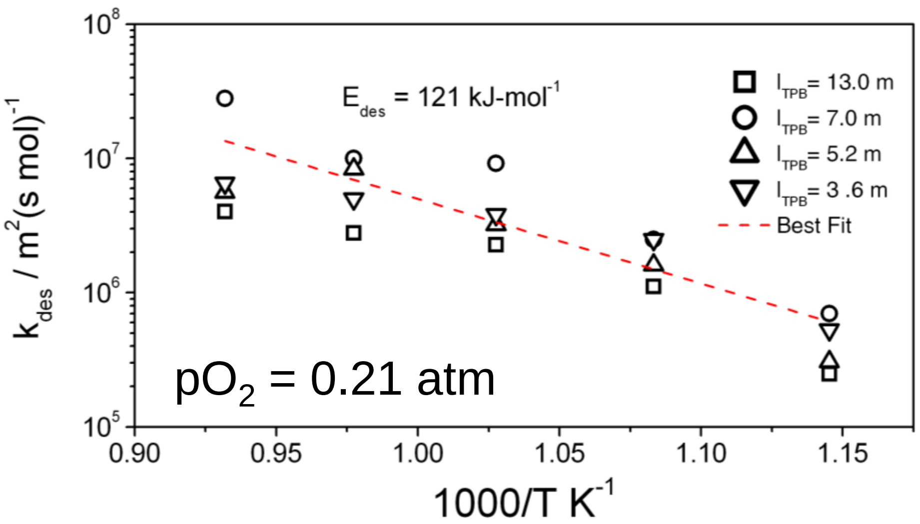
At high coverage need thermodynamic factor, A(θ): $D_S = A(\theta)D_s^o$ , to account for repulsive interactions between adatoms.




Activation energy is very high. Surface migration was estimated to have activation energy of ~194 kJ/mol from DFT calculations (Kotomin et al. *Phys. Chem. Chem. Phys.*, 2008, **10**, 4644-4649).

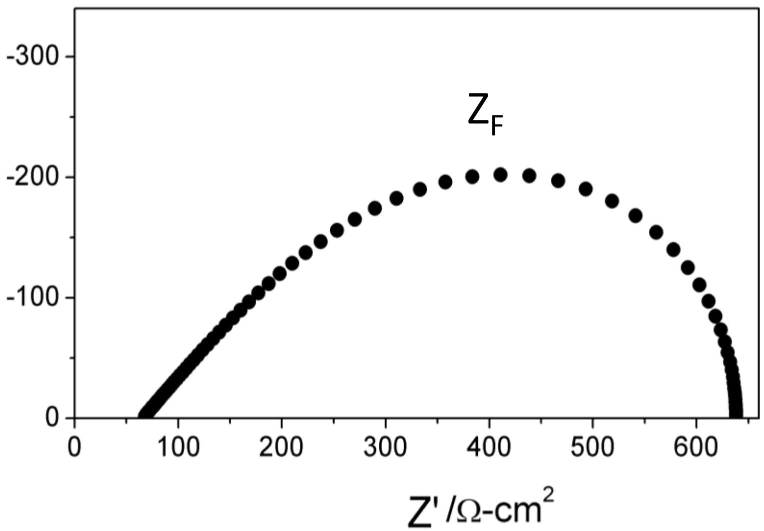
# Adsorption and Desorption Coefficients



# Surface processes:

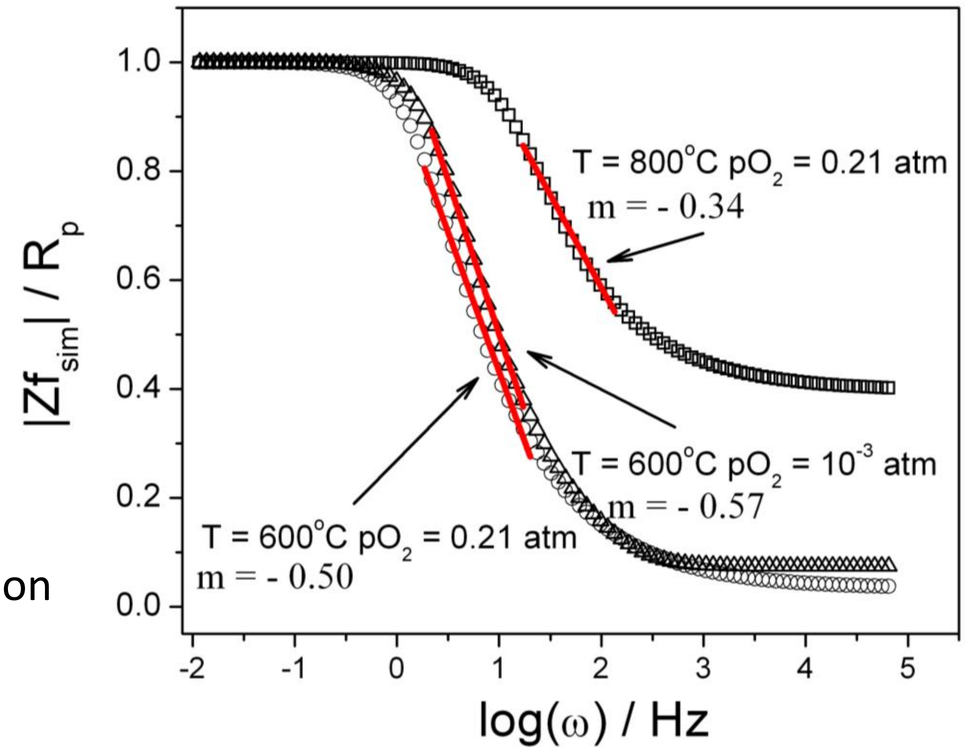
700C – $P_{O2}$ = 0.21 atm



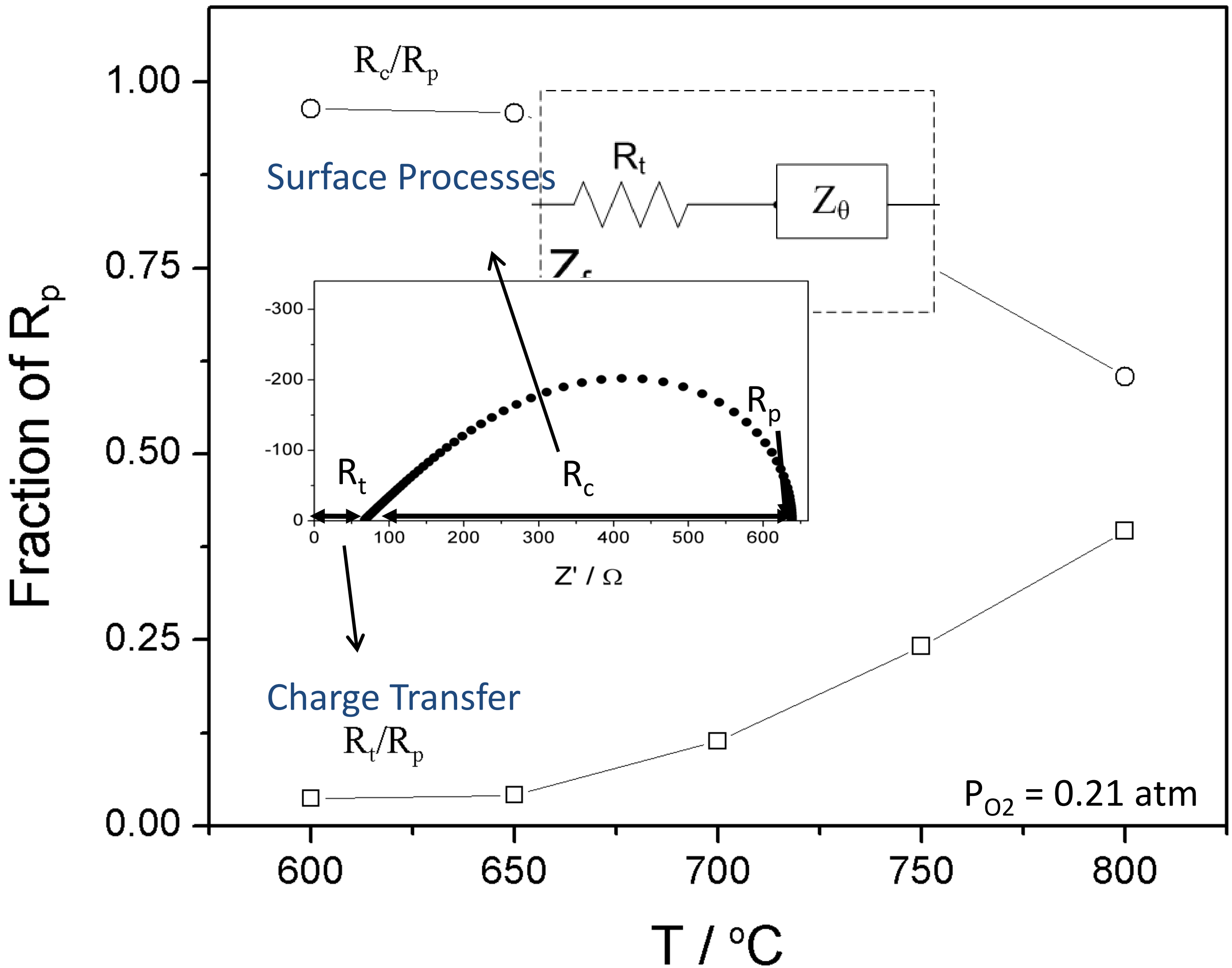

"Gerischer" shaped indicates – co-limitation

$$Z_G = R_{chem}\sqrt{\frac{1}{1 - j\omega t_{chem}}}$$

Bode Plot Analysis:



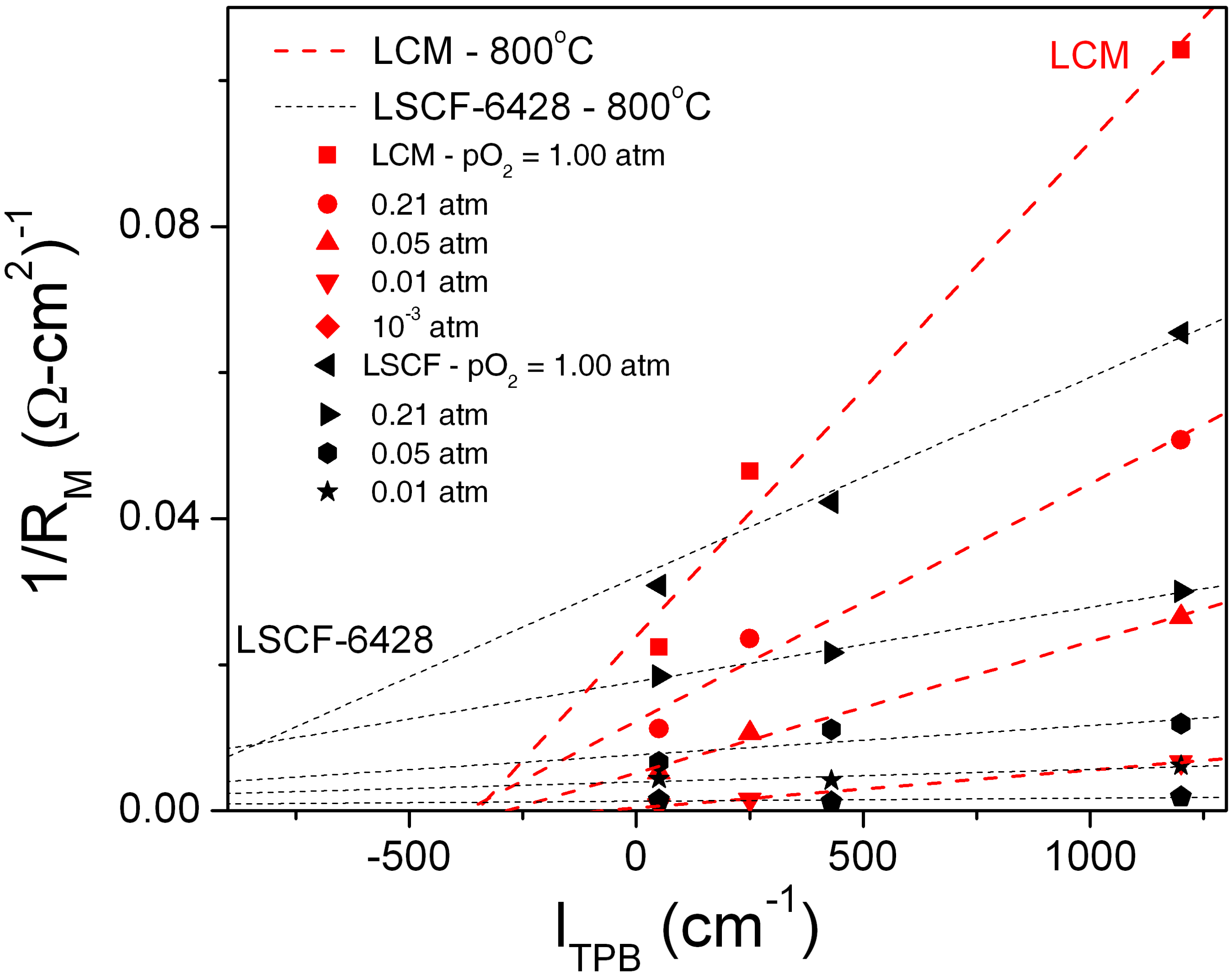
# Rate Determining Steps:



# Conclusions from LCM patterned Cathodes:

- 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 ($\theta$).
- At temperatures below 700 $^oC$ was co-limited by diffusion and adsorption. At high temperatures incorporation reaction contributions to total polarization increase significantly.
- Low scatter between samples suggests that the model correctly accounts for the geometry changes.

# LSCF vs. LCM – far weaker TPB dependence



# Acknowledgments

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- Lax Saraf and Tiffany Kaspar at the EMSL @ PNNL for experimental support.