

# Extrinsic Factors that Control Oxygen Exchange in (La,Sr)MnO<sub>3</sub>

**Paul Salvador**

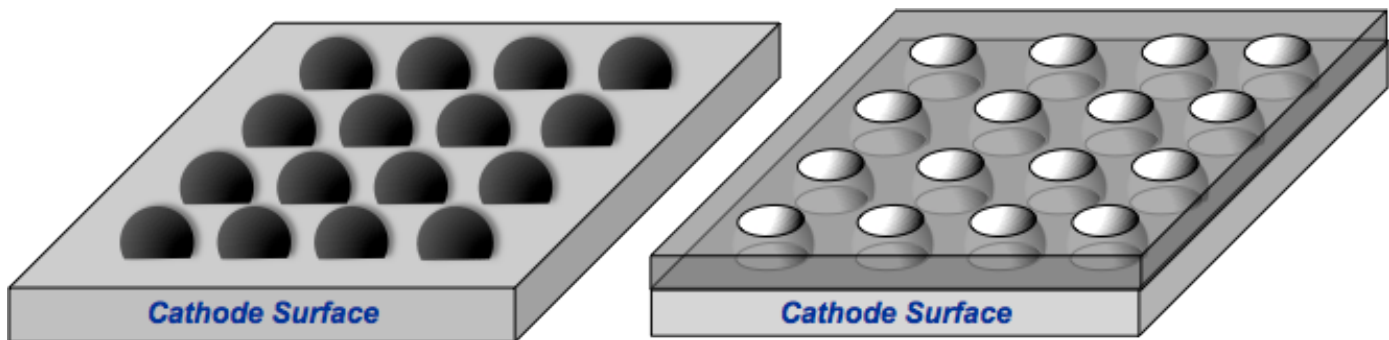
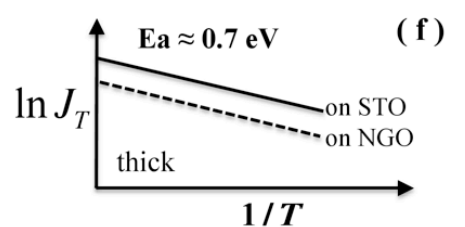
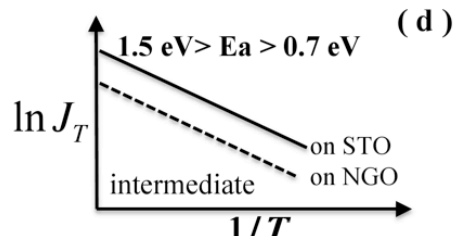
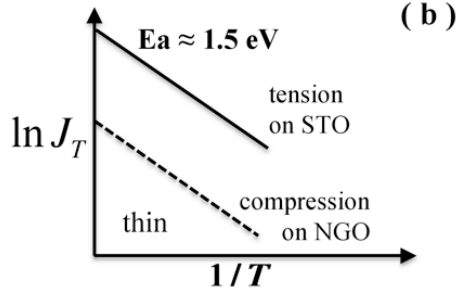
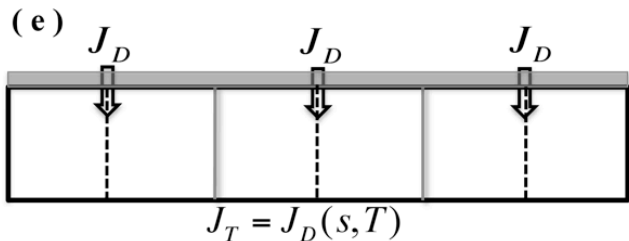
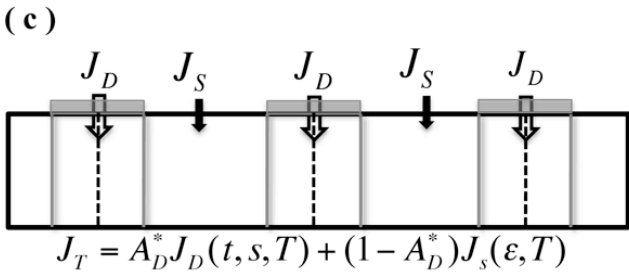
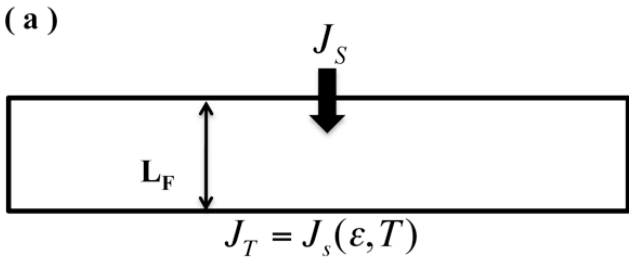
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# Surface Chemistry and Activity of (La,Sr)MnO<sub>3</sub>

## **Surface activity of thin films: Electrical Conductivity Relaxation**

Epitaxial, Thick Films: Orientation of Relaxed Films

Epitaxial, Thin Films: Orientation, Strain, Dislocations

Textured Films: Orientation, Extended Boundaries

## **Mesoporous infiltrates: Performance and Stability**

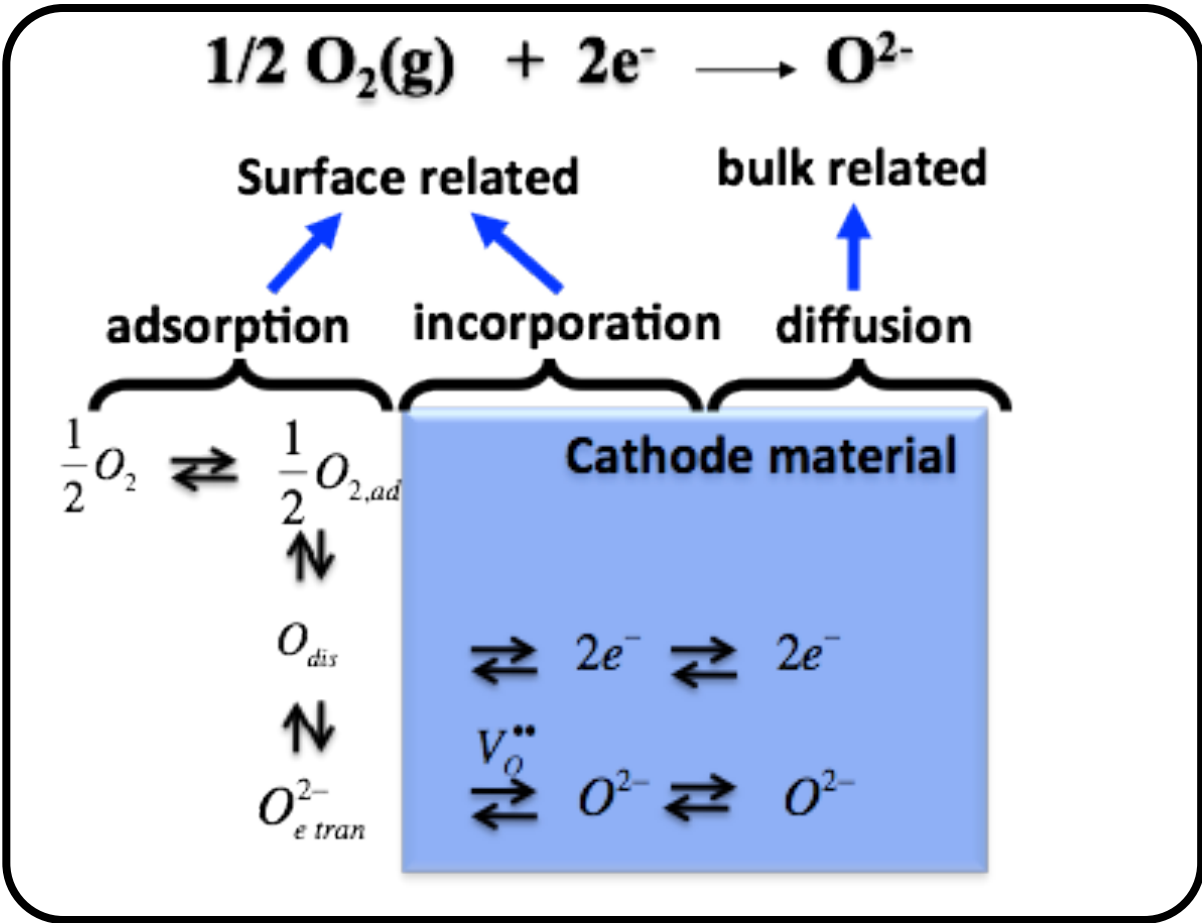
Infiltration

Reduction in Polarization Resistance

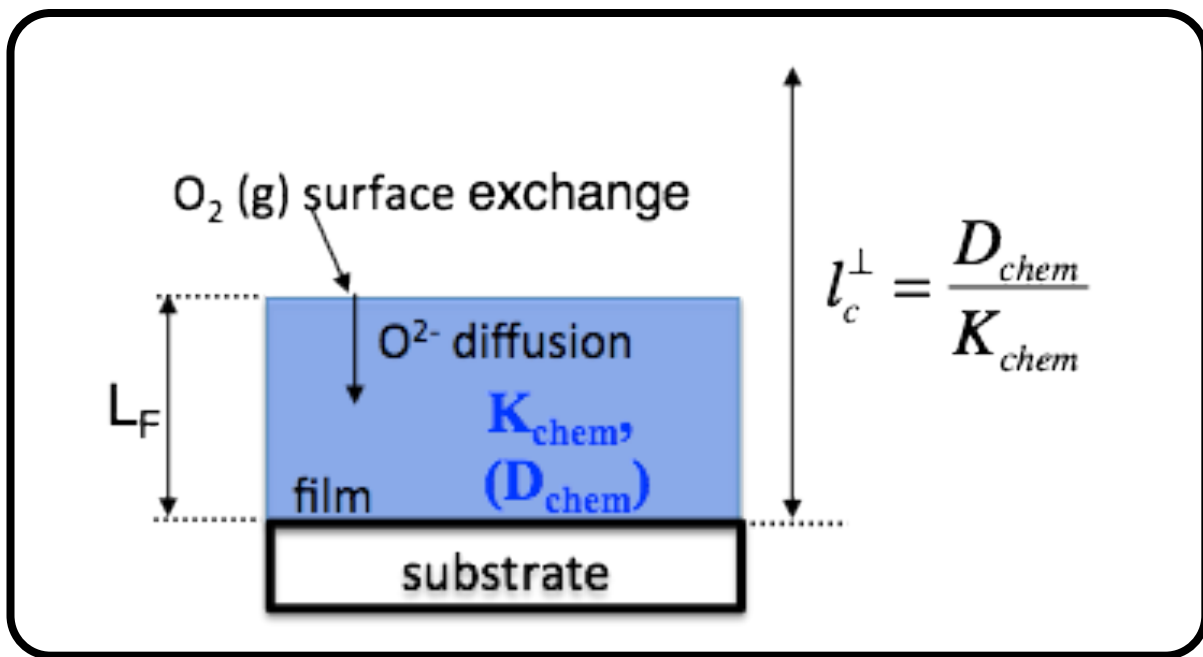
SOFC Performance Improvements

# Thin films to measure surface exchange

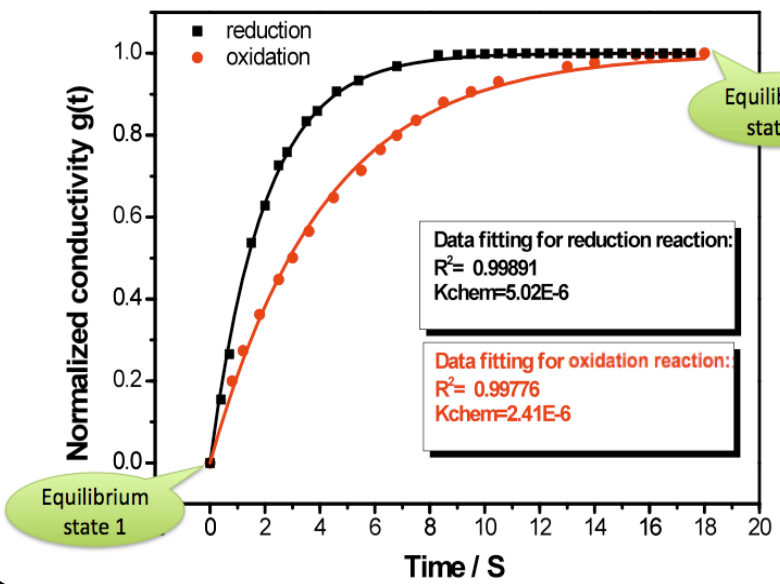
## Schematic Processes in Oxygen Exchange



## Isolation of Surfaces with thin Films

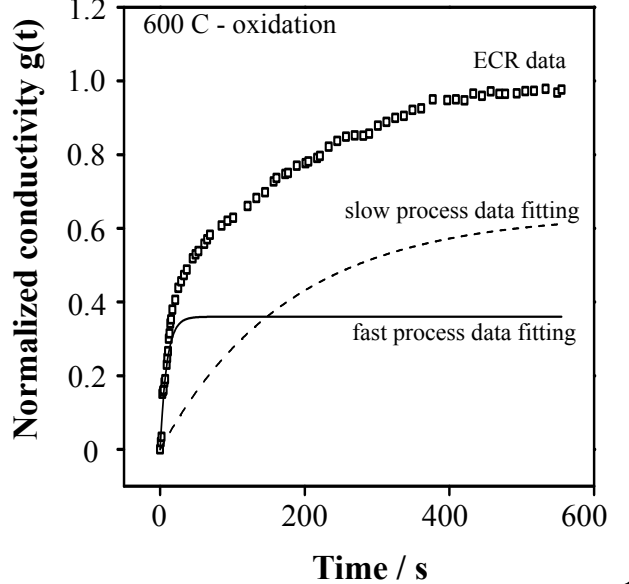


## Electrical Conductivity Relaxation



- Verify Electrical Properties
- Correct for gas flush times
- Average several runs
- Confirm reversibility
- Fit to 1 or 2 time constants
- Verify surface affect not diffusion

$$g(t) = \frac{\sigma_t - \sigma_{final}}{\sigma_{final} - \sigma_{initial}} = 1 - A \exp\left(-\frac{K_{1,chem} t}{L}\right) - (1 - A) \exp\left(-\frac{K_{2,chem} t}{L}\right)$$



# Surface exchange properties of (La, Sr)MnO<sub>3</sub> : Experimental studies

	<i>Yasuda et al.<sup>1</sup></i>	<i>De Souza et al.<sup>2</sup></i>	<i>Kan et al.<sup>3</sup></i>	<i>Fleig et al.<sup>4</sup></i>	<i>la O' et al.<sup>5</sup></i>
<b>Film/bulk composition</b>	La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub> bulk	La <sub>0.8</sub> Sr <sub>0.2</sub> MnO <sub>3</sub> bulk	(La <sub>0.8</sub> Sr <sub>0.2</sub> ) <sub>0.98</sub> MnO <sub>3</sub> powder	(La <sub>0.8</sub> Sr <sub>0.2</sub> ) <sub>0.92</sub> MnO <sub>3</sub> film on YSZ	(La <sub>0.8</sub> Sr <sub>0.2</sub> )MnO <sub>3</sub> film on YSZ
<b>Method</b>	Electrical Conductivity Relaxation	Oxygen tracer	Oxygen tracer	Electrochemical Impedance Spectroscopy	Electrochemical Impedance Spectroscopy
<b>Pressure</b>	10 <sup>-11</sup> to 10 <sup>-8</sup> mTorr	760 Torr	15.4 Torr	2.3 Torr	0.76-760 Torr
<b>k<sub>chem, equivalent</sub> ≈ 800°C / cms<sup>-1</sup></b>	≈ 1.78 × 10 <sup>-5</sup>	≈ 3.6 × 10 <sup>-4</sup>	≈ 3.8 × 10 <sup>-5</sup>	≈ 7 × 10 <sup>-8</sup>	≈ 4 × 10 <sup>-6</sup>
<b>E<sub>a</sub> / eV</b>	<b>0.75</b>	<b>1.33</b>	<b>0.8</b> (600°C) 0.07 (800°C)	N/A	<b>1.7-2.0</b> (surf.ex) <b>1.1-1.6</b> (suf.dif)

•I. Yasuda *et al.* J. Solid State Chem., 123 (1996).

•R. A. De Souza *et al.* Mater. Lett., 43 (2000).

•C.C. Kan *et al.* Solid State Ionics 338 (2010).

•J. Fleig *et al.*, Fuel Cells 330 (2008).

•A. Belzner *et al.*, Solid State Ionics 327 (1992).

•la O' *et al.*, J. Electrochem.Soc. 156 (2009); 154 (2007)

**Critical thickness (*l<sub>c</sub>*) from literatures  
vary from 0.5 cm to couple of um.**



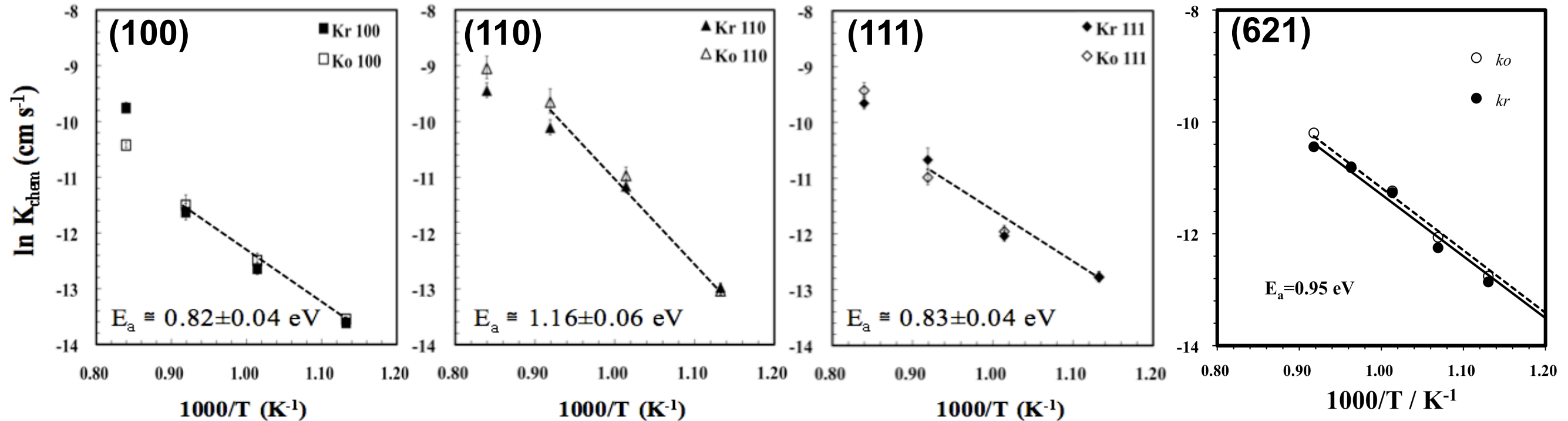
# Surface exchange properties of (La, Sr)MnO<sub>3</sub> : Computational studies

	<i>Evarestov et al.<sup>1</sup></i>	<i>Choi et al.<sup>2</sup></i>	<i>Lee et al.<sup>3</sup></i>	<i>Kitchin et al.<sup>4</sup></i>	<i>Han et al.<sup>5</sup></i>
<b>Surface</b>	LaMnO <sub>3</sub> (110) (100)	La <sub>0.5</sub> Sr <sub>0.5</sub> MnO <sub>3</sub> (110)	LaMnO <sub>3</sub> (001) BO <sub>2</sub> terminated	LaMnO <sub>3</sub> (100) under strain	(La <sub>0.7</sub> Sr <sub>0.3</sub> )MnO <sub>3</sub> (100) film on LaAlO <sub>3</sub> and SrTiO <sub>3</sub>
<b>Method</b>	DFT	DFT+MD	DFT+ thermodynamic correction	DFT	DFT
<b>Pressure or Temperature</b>	N/A	0.2 atm 800 °C	0.2 atm, 800 °C	N/A	N/A
<b>Adsorption</b>	<b>the Mn site</b>	the Mn site	O <sub>2</sub> <sup>2-</sup> -B	the Mn site	<b>Sr-segregation</b>
<b>Mechanisms</b>	surface energy: (100) < (110)	fast surface charge transfer to adsorbents	<b>very low surface coverage of adsorbents</b>	as tensile ↑ ΔH <sub>vac</sub> ≈ 0.2 eV ↑ ΔH <sub>ads</sub> ≈ 0.2 eV ↑	3% compress. E <sub>seg</sub> ≈ -0.15 eV 2% tensile E <sub>seg</sub> ≈ -0.35 eV

1. Evarestov et al, Phys. Rev. B (2005).
2. Choi et al, Angewandte Chemie (2007)
3. Lee et al, Phys, Rev. B (2009).
4. Kitchin et al. in preparation
5. Han et al. Electrochem. Soc. Trans. (2011)

- 1. (100) is expected to be the most stable surface;**
- 2. Mn site is the preferential adsorption site;**
- 3. Strain related effects.**
- 4. Surface is dynamic and complex.**

# Crystallographic Anisotropy in Apparent $E_A$



## Observations

(111) is fastest at low temperatures.

(110) is fastest at high temperatures.

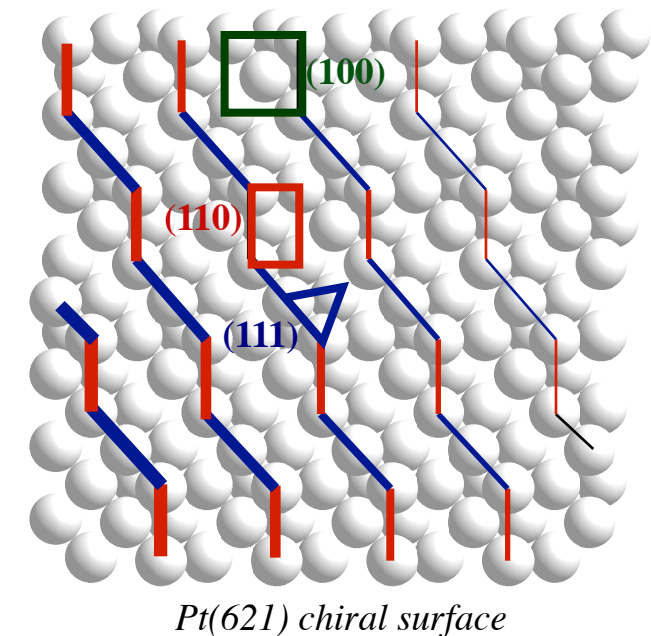
Activation energies vary from  $\approx 0.8$  to  $\approx 1.2$  eV.

General high index surfaces are intermediate with low index surfaces.

## Relaxed Films

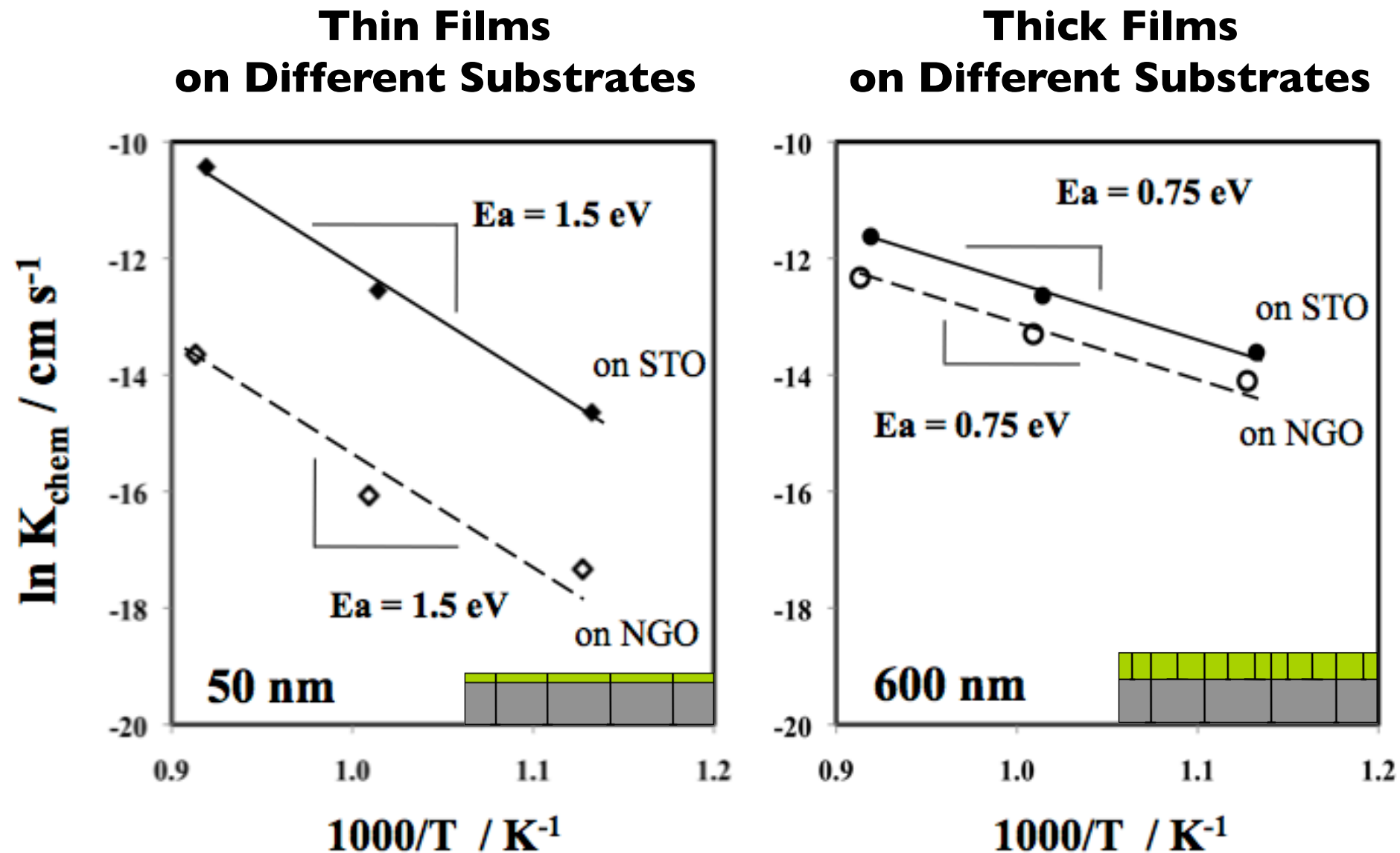


## (621): a generic surface



L. Yan et al., *Solid State Ionics*, **194**, 9-16 (2011).

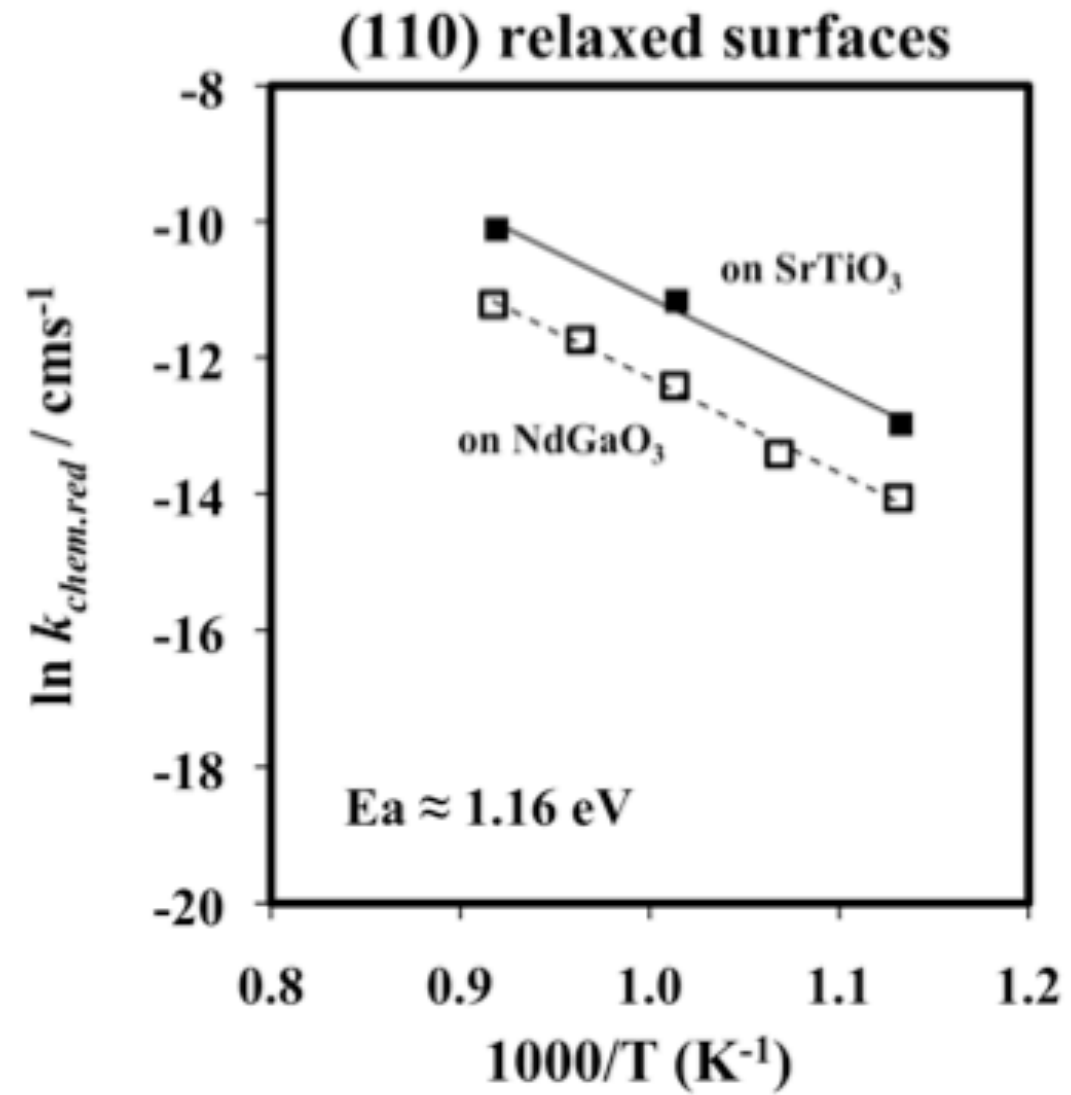
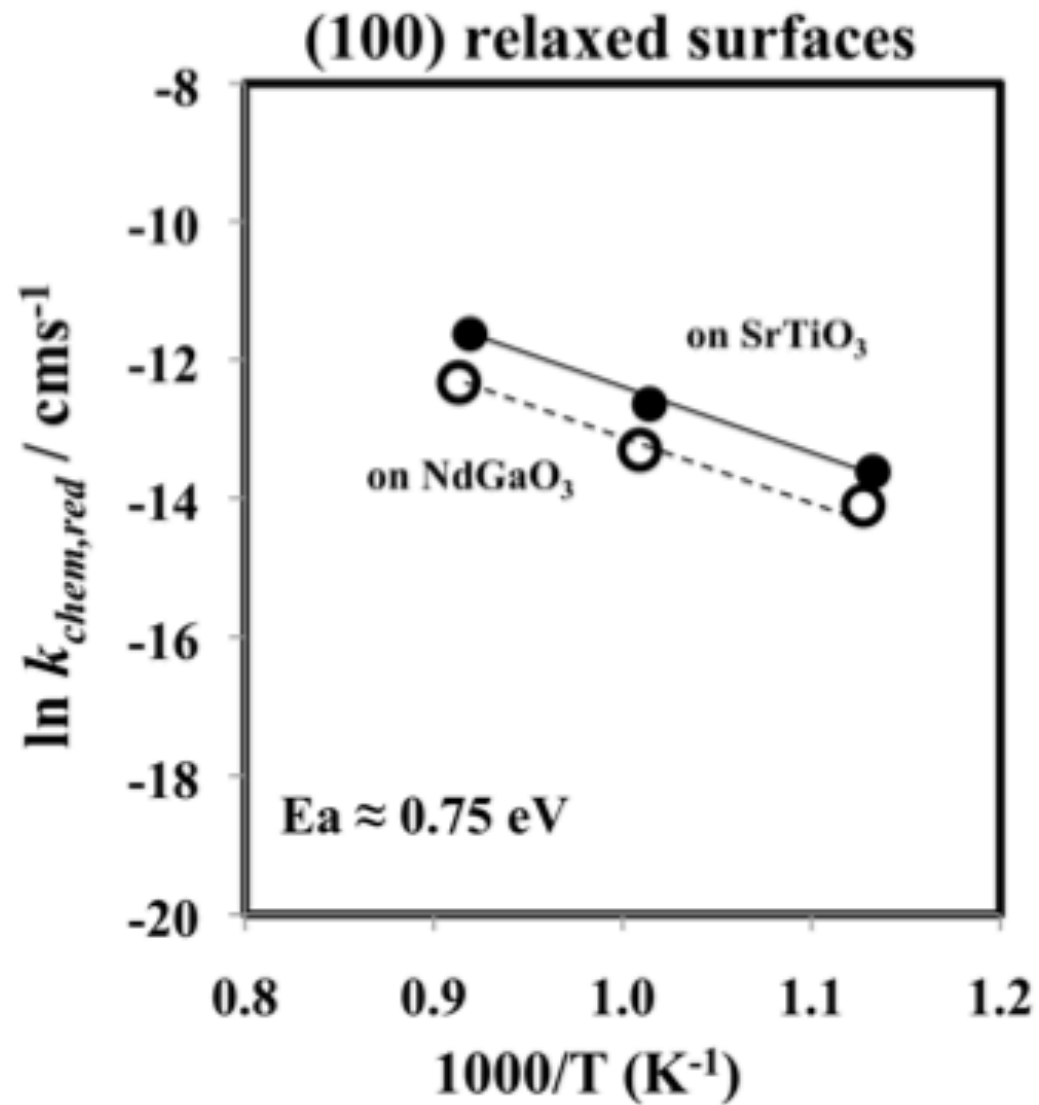
# Activation energy vs thickness and substrate



- Two different activation Energies: two different processes
- Thick Films are more similar to one another and are generally more active
- at higher temperature, thinnest film on STO is most active
- for thin films, values are almost and order of magnitude different

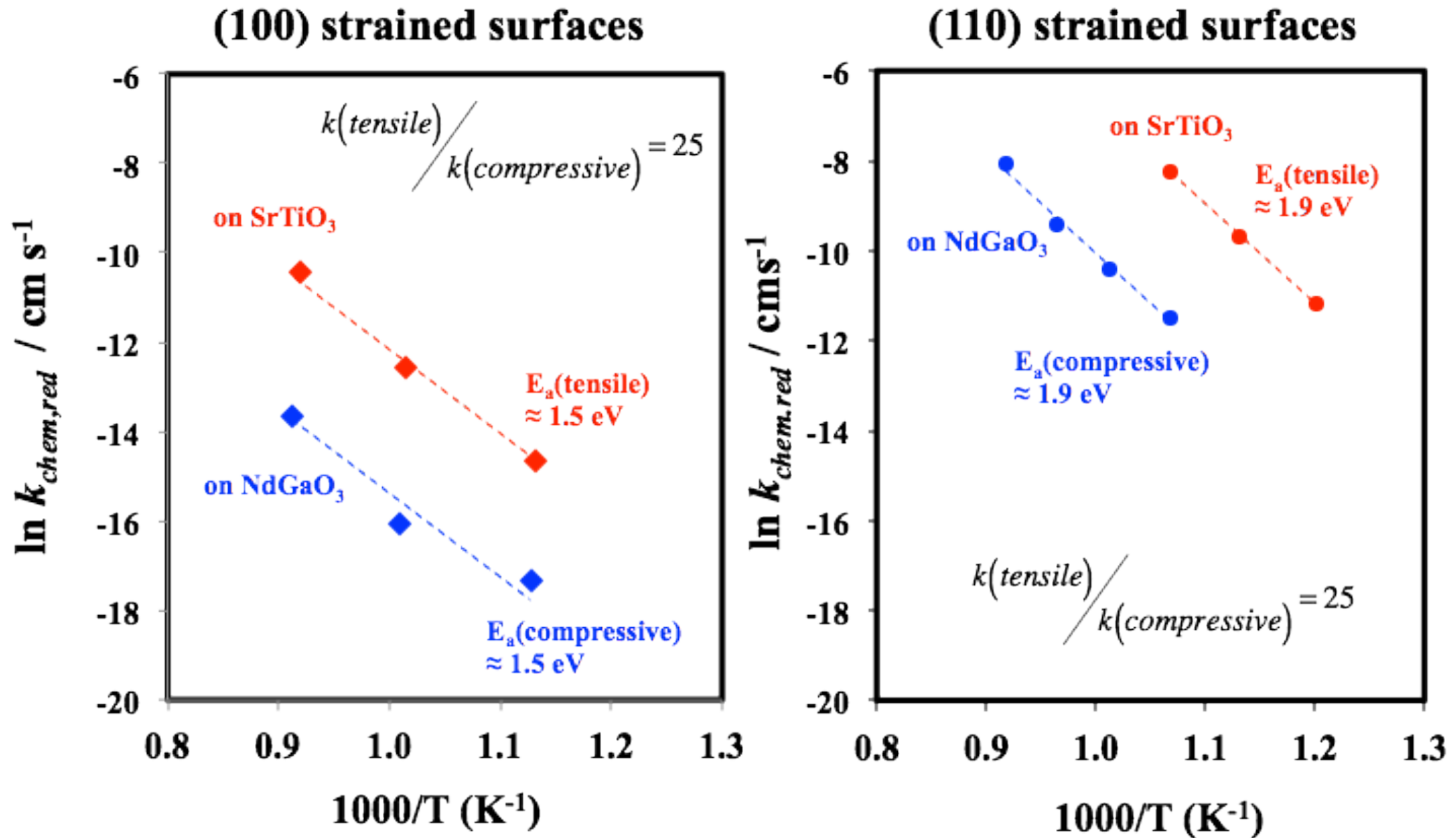
L. Yan and P. A. Salvador, *ACS Applied Materials and Interfaces*, online (2012). doi: 10.1021/am300194n

# Relaxed Surfaces : Substrate and Orientation

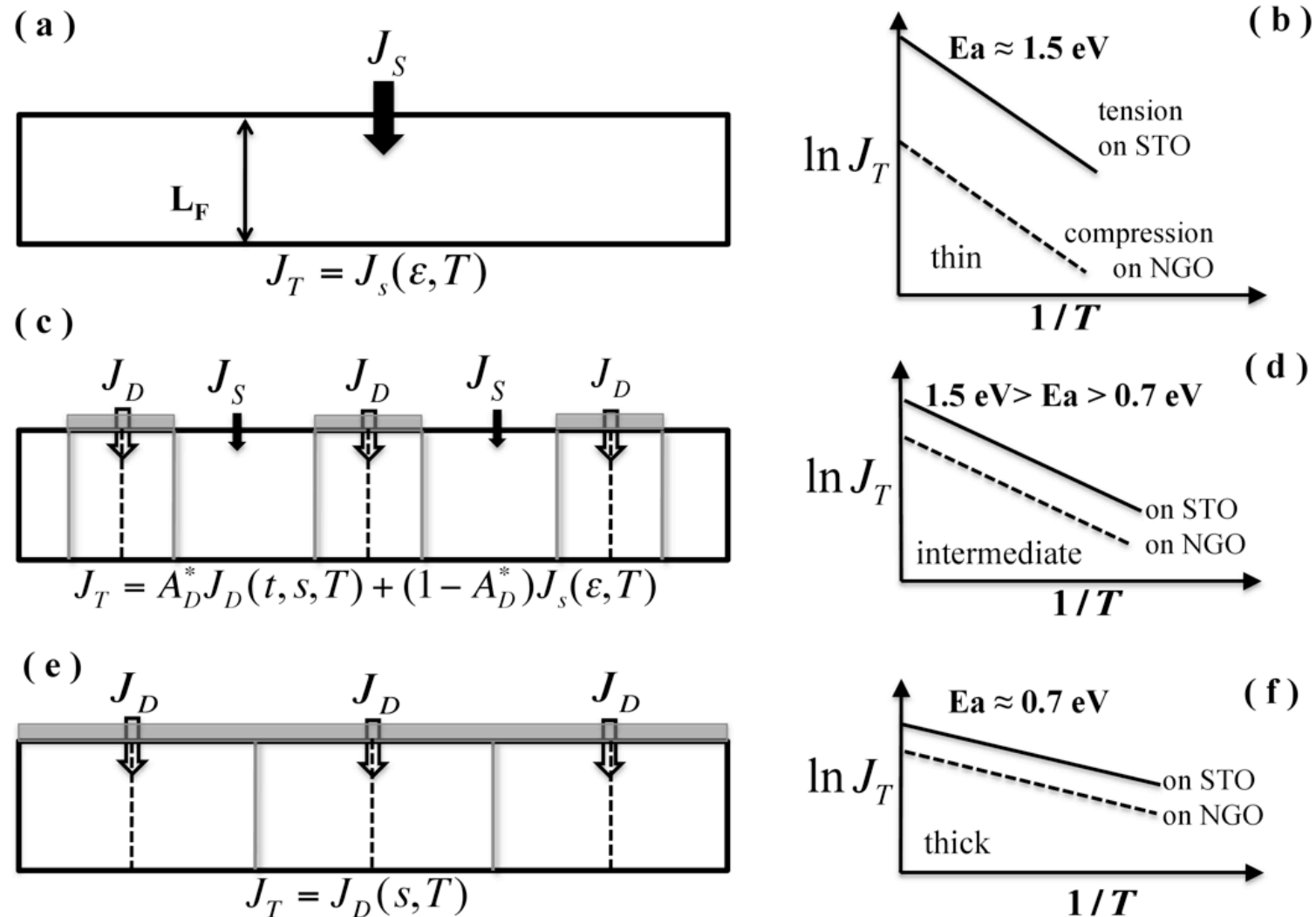




# Strained surfaces : Substrate and Orientation

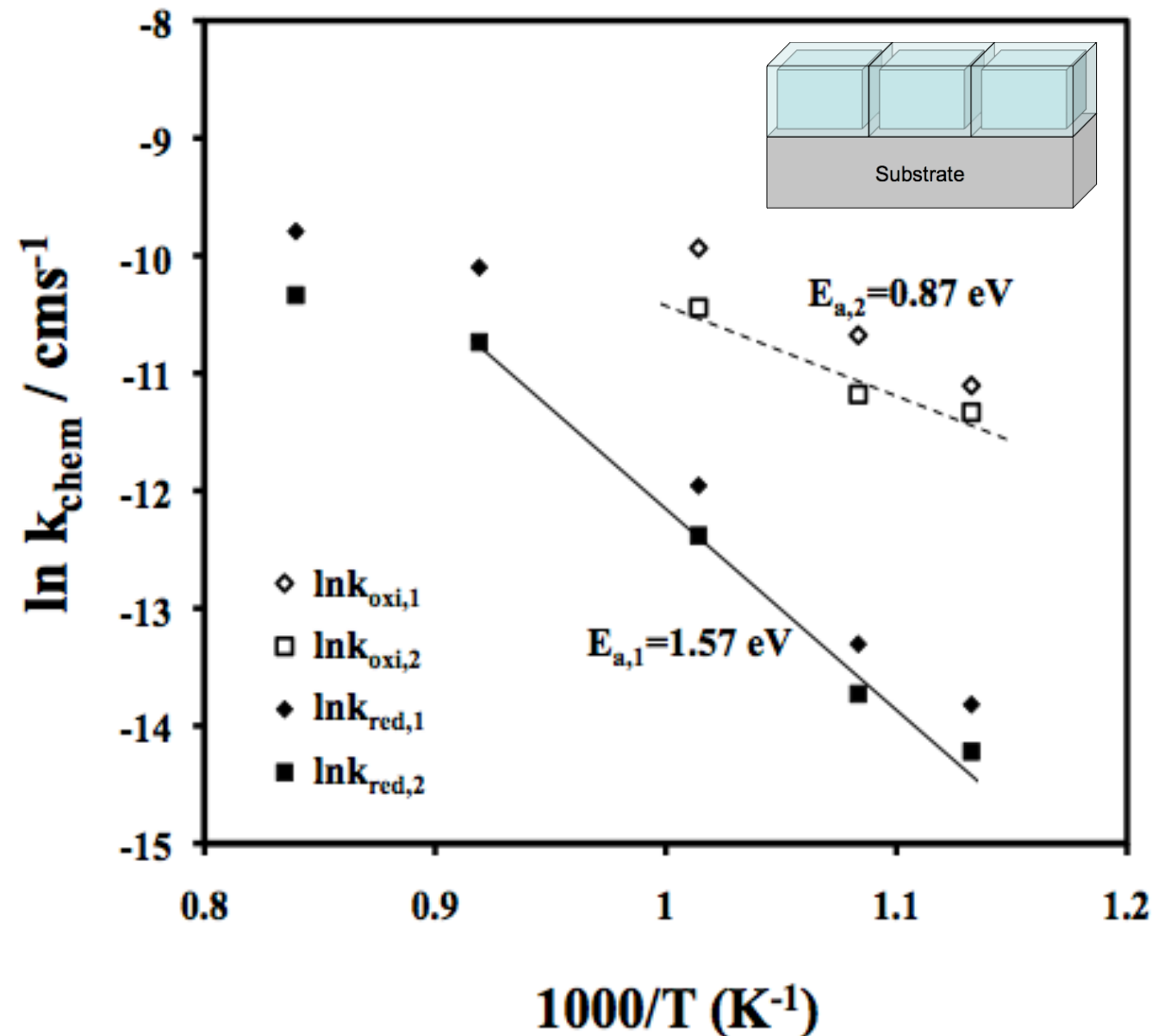


# Crossover behavior also observed



- High T data on STO and Low T data on NGO are more complex
- Crossover between two mechanisms
  - At high-T surface takes over owing the  $E_A$
- At low-T surface takes over because other process freezes out source/sink to/from defects

# Temperature dependence of two mechanisms



Our data agree with literature:

$K_{\text{chem}}$  is on the order of  $10^{-5} \text{ cm/s}$ .<sup>1-5</sup>

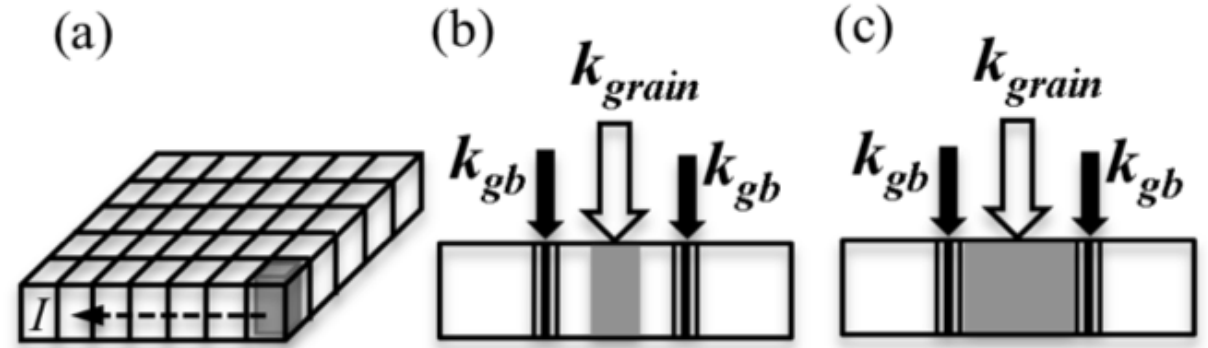
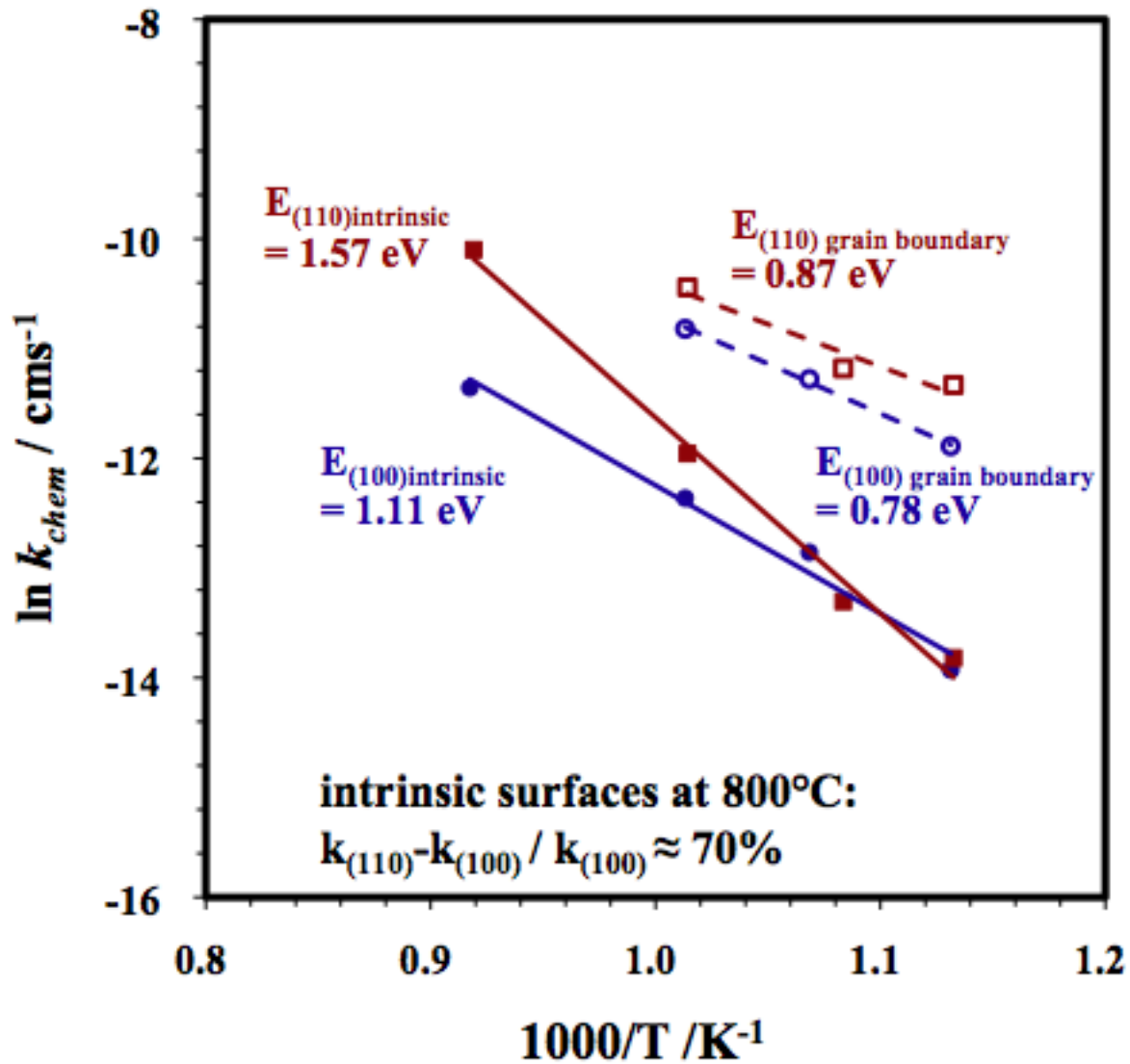
$E_{a1}$ : 1.48 eV for microelectrode<sup>1</sup>,  
1.32 eV dense pellet<sup>2</sup>,

$E_{a2}$ : 0.8 eV (100) and (111) on STO<sup>3</sup>,  
0.07-0.8 eV powder<sup>4</sup>.

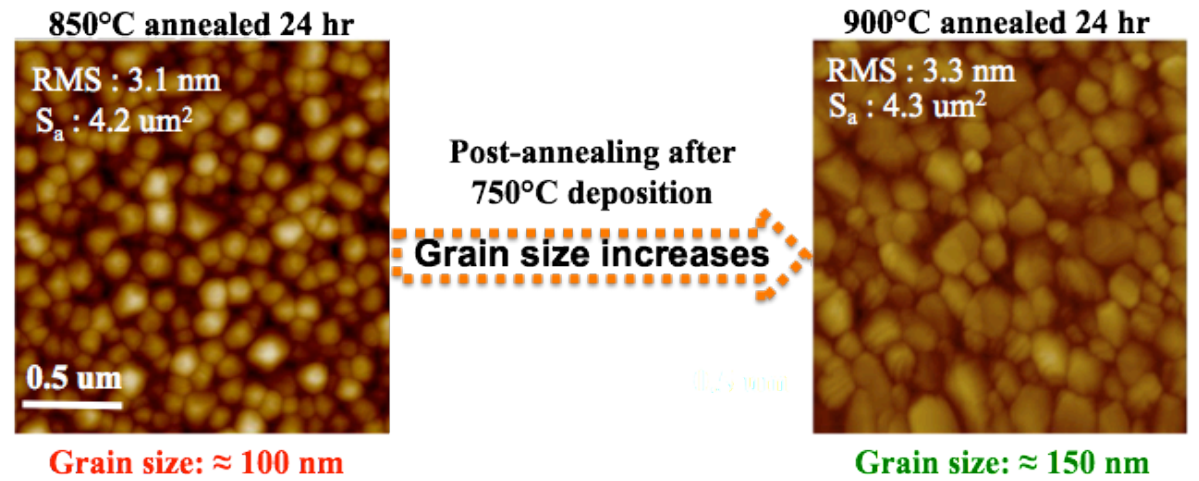
1. la O' et al, J. Electrochem sec. (2009).
2. De Souza et al, Mater. lett. (2000).
3. Yan et al, Solid state ionics. (2011).
4. Kan et al, Solid state ionics. (2010).
5. Yasuda et al, J Solid State Chem. (1996).

# Relative Contribution to Responses

$\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (110) and (100) intrinsic surfaces



## 110 Surfaces

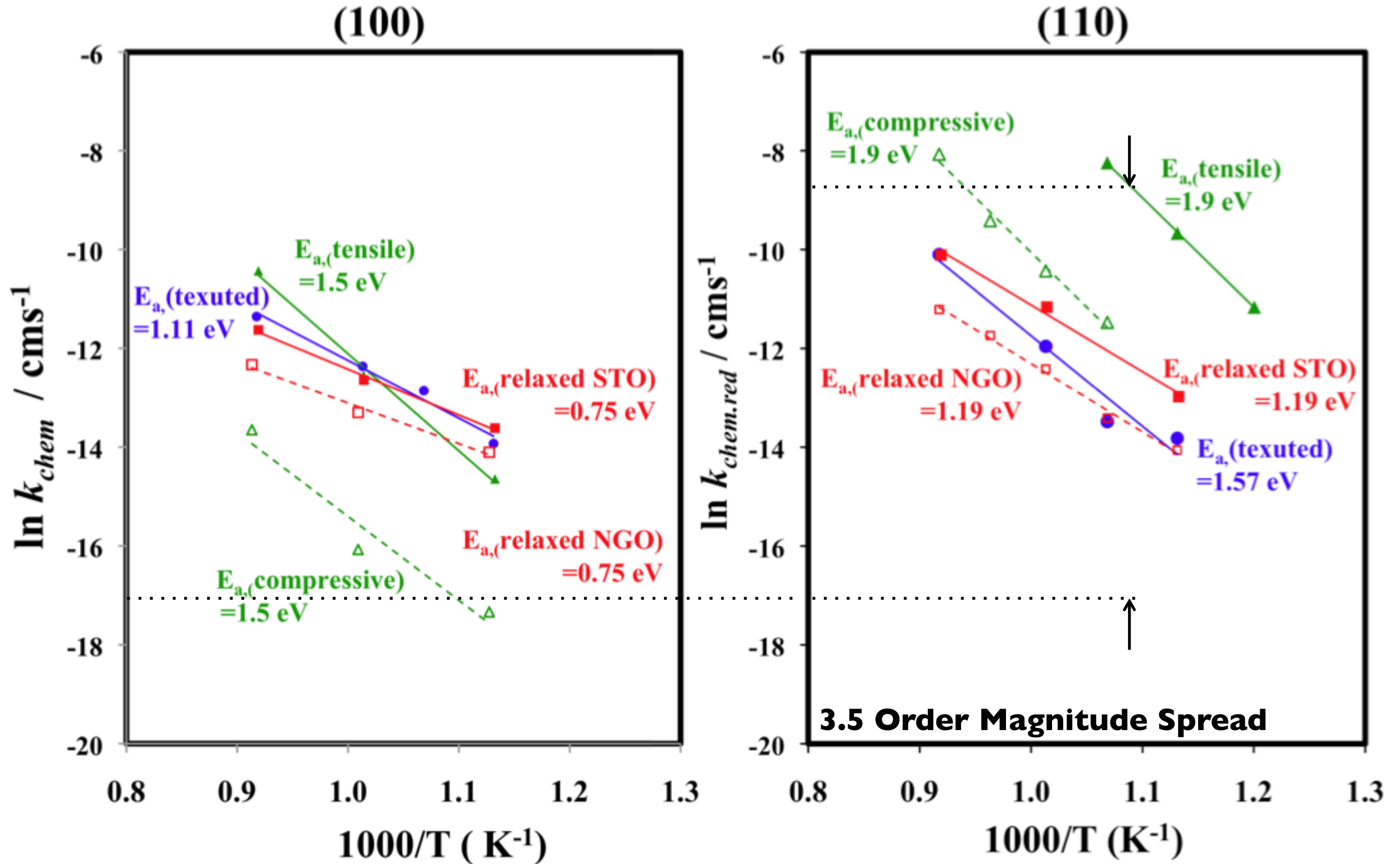


Temp / K	883	923	986	1088	1191
A small grain	0.6	0.7	0.8	1	1
A big grain	0.7	0.75	0.84	1	1

## 100 Surfaces

Temp / K	884	936	987	1090	1141
A	0.23	0.4	0.78	1	1

# Comparison of all Values for $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$





# Summary

Two apparent processes occurring on the surface ( $E_a$ ) for  $K_{\text{chem}}$  for both epitaxial and textured films.

These were interpreted as belonging to:

- (1) the native surface response of individual grains/variants and
- (2) the extended defects (dislocations / grain boundaries) intersecting surface of the films.

Epitaxial Films:           the first (native surface) process :  $E_{A,1} \approx 1.5 \text{ eV}$  and  $1.9 \text{ eV}$   
the second (extended defect) process  $E_{A,2} \approx 0.75 \text{ eV}$  and  $1.2 \text{ eV}$

Textured Films:           the  $K_{\text{chem},2}$  values are almost 2 orders of magnitude higher than the  
 $K_{\text{chem},1}$  values at low temperatures ( $< 700^\circ\text{C}$ )

at high T the native surface dominates all films

All films have orientation dependences to the values / activation energies.

One composition shows 3 ORDERS OF MAGNITUDE differences in exchange coefficients.  
Widely varying surface reactivity possible in the microstructures.

The native surface processes are strong functions of :

Strain

Orientation

Extended Defects

Temperature

*Understanding the utility of this data will come with improved modeling of electrochemical systems*

# Surface Chemistry and Activity of (La,Sr)MnO<sub>3</sub>

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Epitaxial, Thin Films: Orientation, Strain, Dislocations

Textured Films: Orientation, Extended Boundaries

## **Mesoporous infiltrates: Performance and Stability**

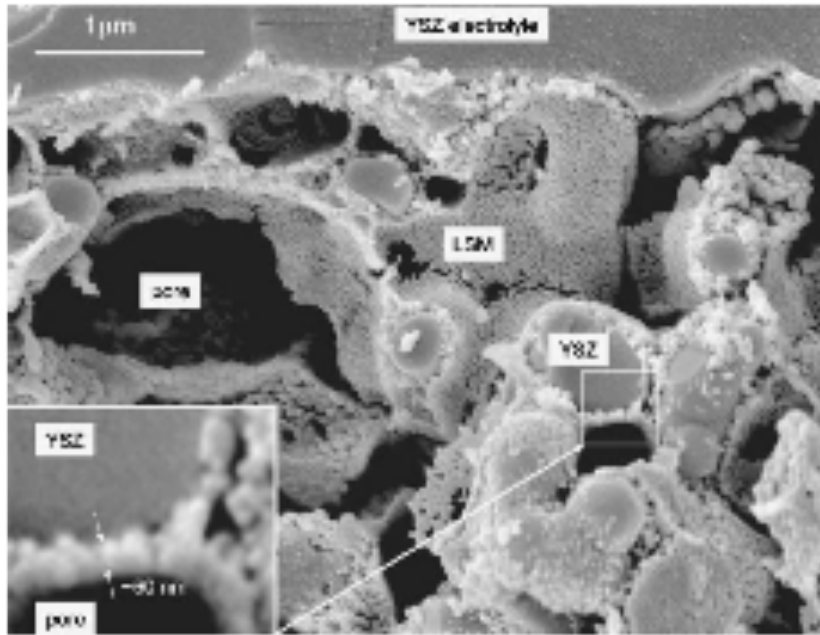
Infiltration

Reduction in Polarization Resistance

SOFC Performance Improvements

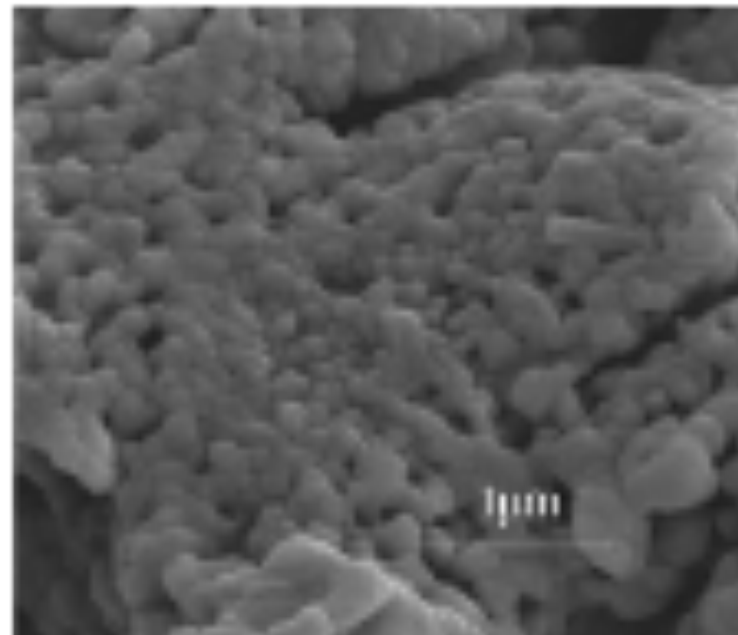
# Infiltration: Surface Active nanoparticles for SOFCs Activation

LSM on YSZ  
LBL



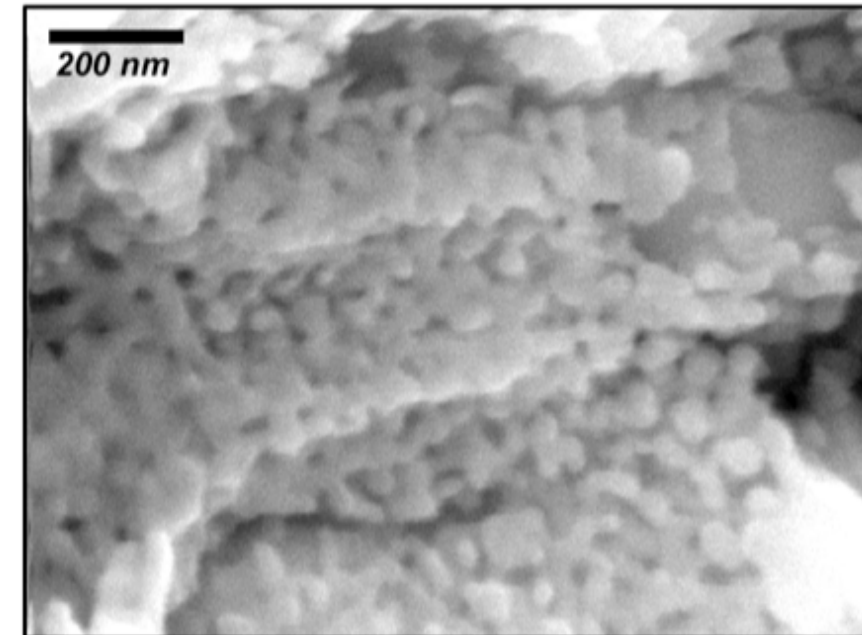
Scholklapper et al. (LBL),  
Electrochem. Solid-State Lett., 9, A376 (2006)

LSCF on YSZ  
Penn



W. Wang et al. (Penn)  
J. Electrochemical Society, 154, B439-B445 (2007).

LSM on LSCF  
CMU



Chao, Gerdes, Kitchin, Salvador (CMU)  
Electrochemical Society Trans, 35, 2387-2399, (2011).

What are the optimal materials to use for infiltration?

What are the surface properties of cathode materials?

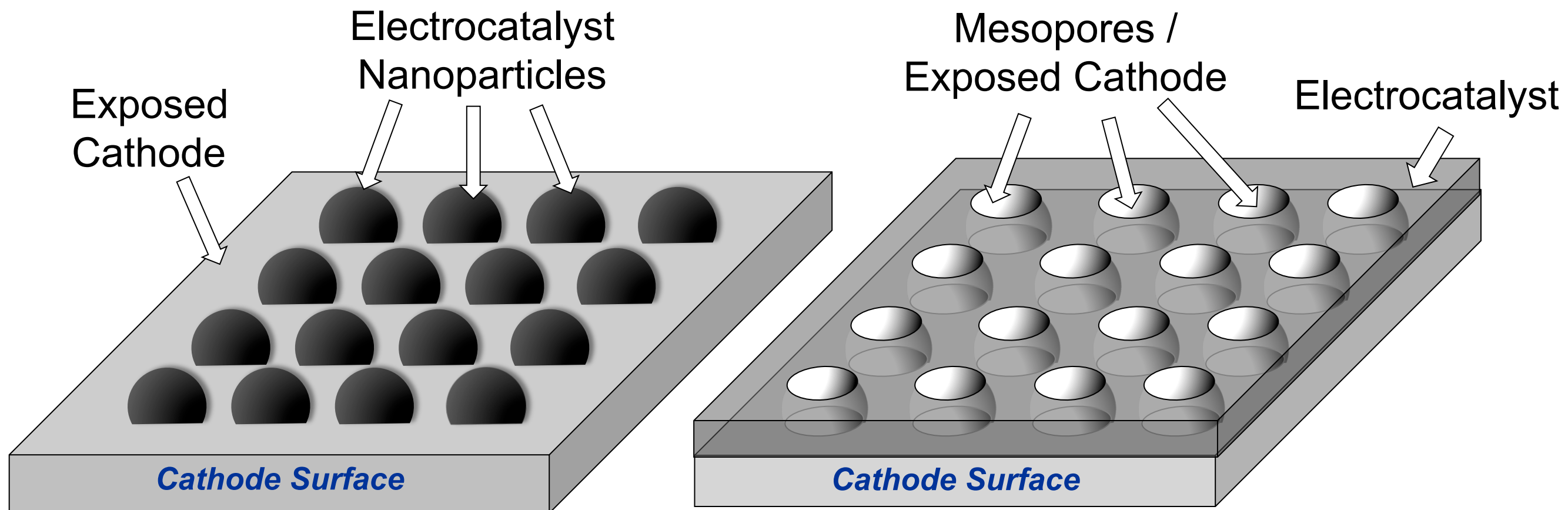
What are the mechanisms of enhanced performance / degradation?

What are the properties of nanosized particles?

What are the effects of the support on the properties of cathodes?

# Project Goal

- ❑ To improve the power density of the SOFC cathodes by coating pore surfaces with mesoporous electrocatalysts

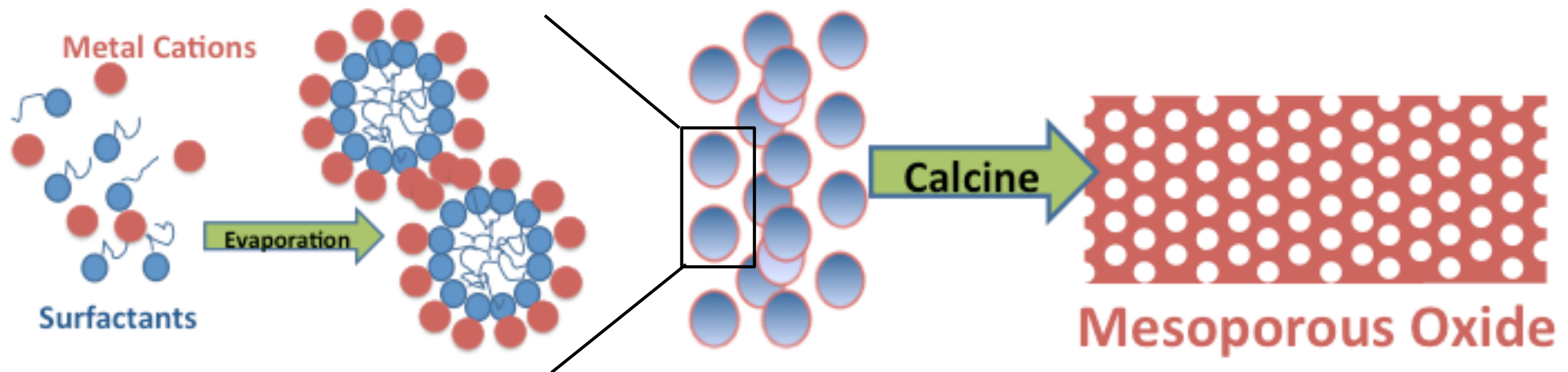


Catalysts:  $\text{La}_{0.8}\text{Sr}_{0.2}\text{MnO}_3$

Depending on mechanism, one may be preferable to other

# Evaporation-induced Self-assembly (EISA)

- Developed by Mobil Researchers in 1991
- Self-assembly of surfactants provides controlled mesopore formation



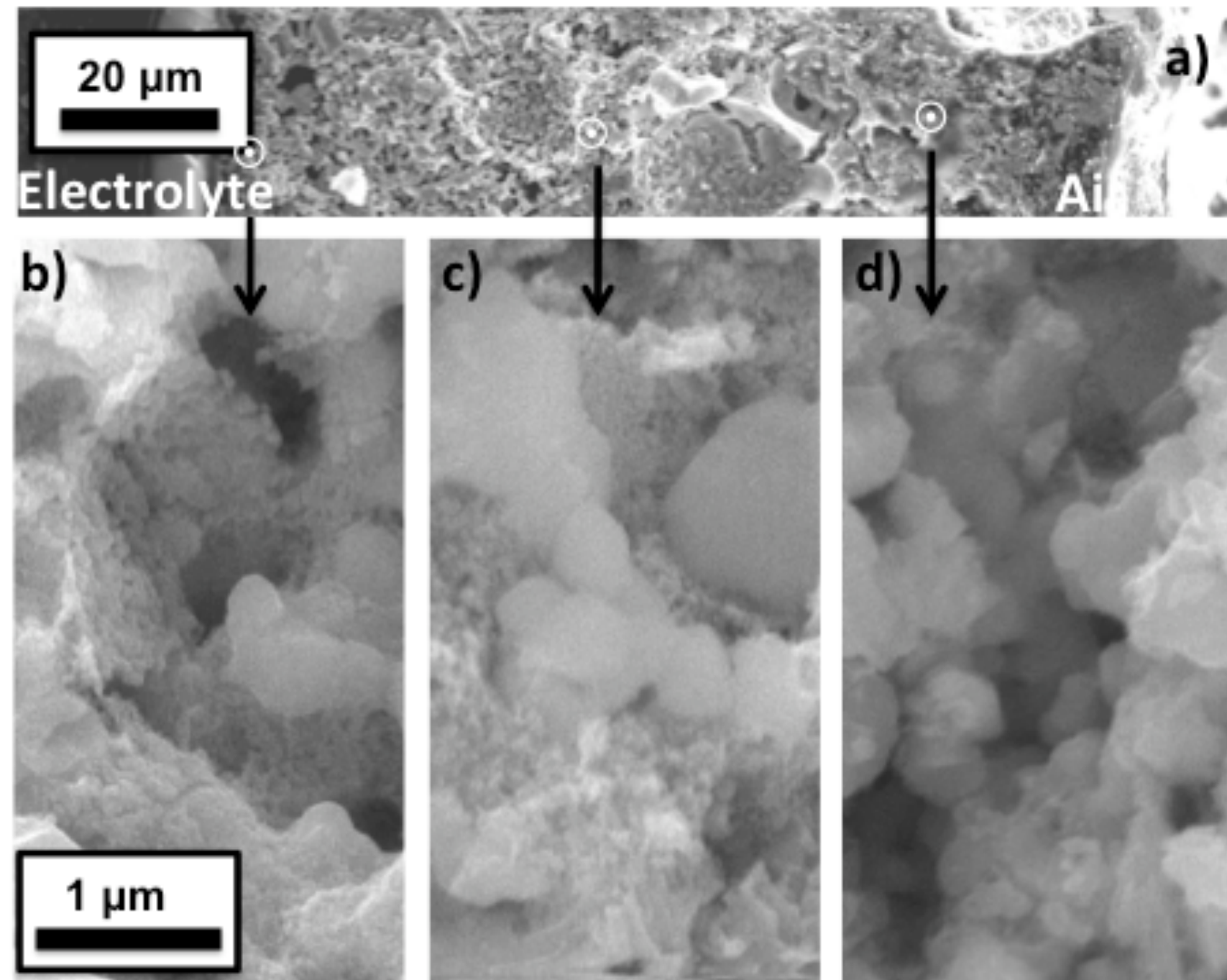
## □ Parameters that control outcome

- Drying rate
- Aging temperature
- Calcination temperature
- Sol composition
- Relative humidity
- Templating agents

[6]



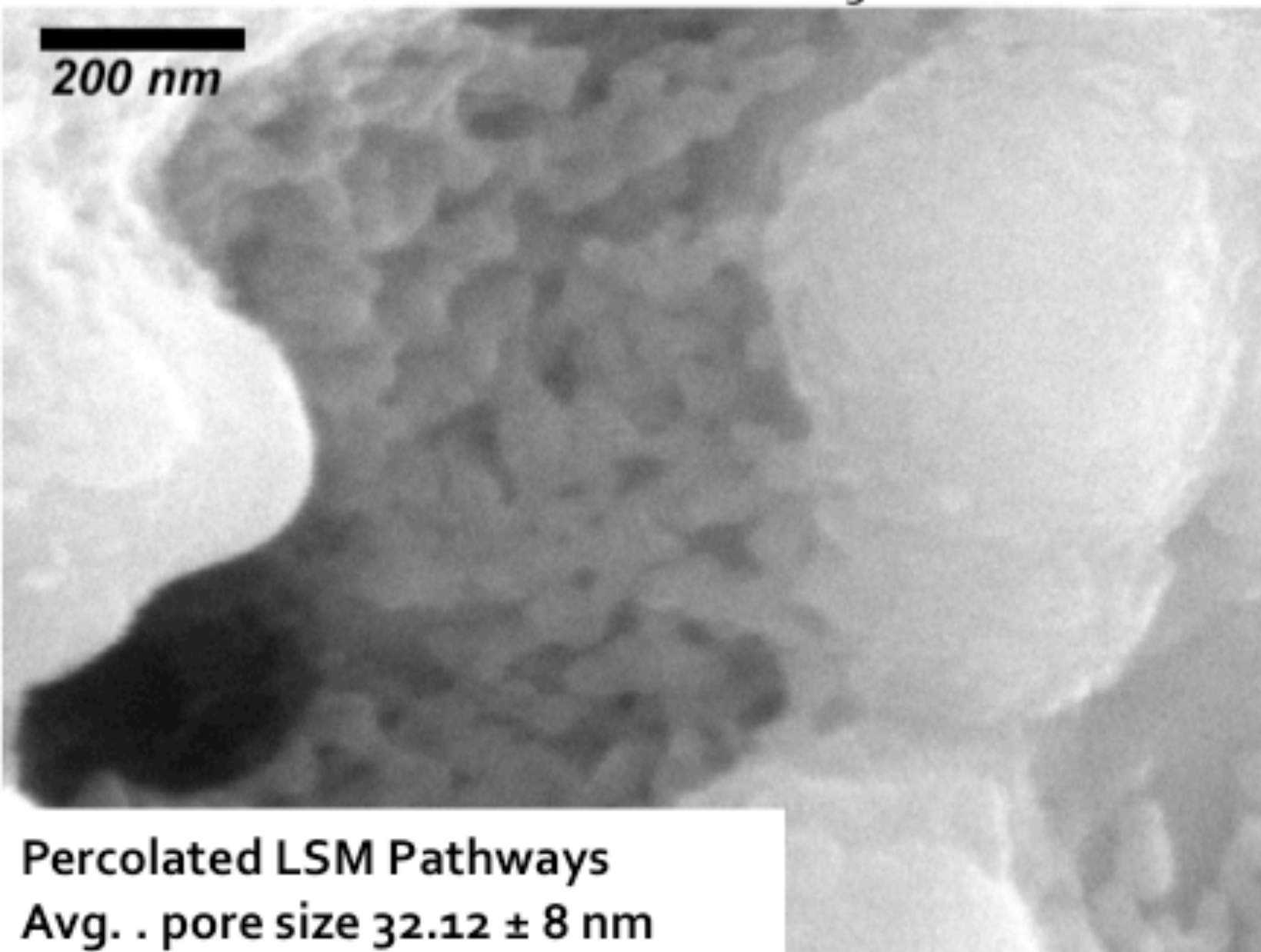
# Infiltration Using 2 M Precursor Solution with 60 °C Preheating Step



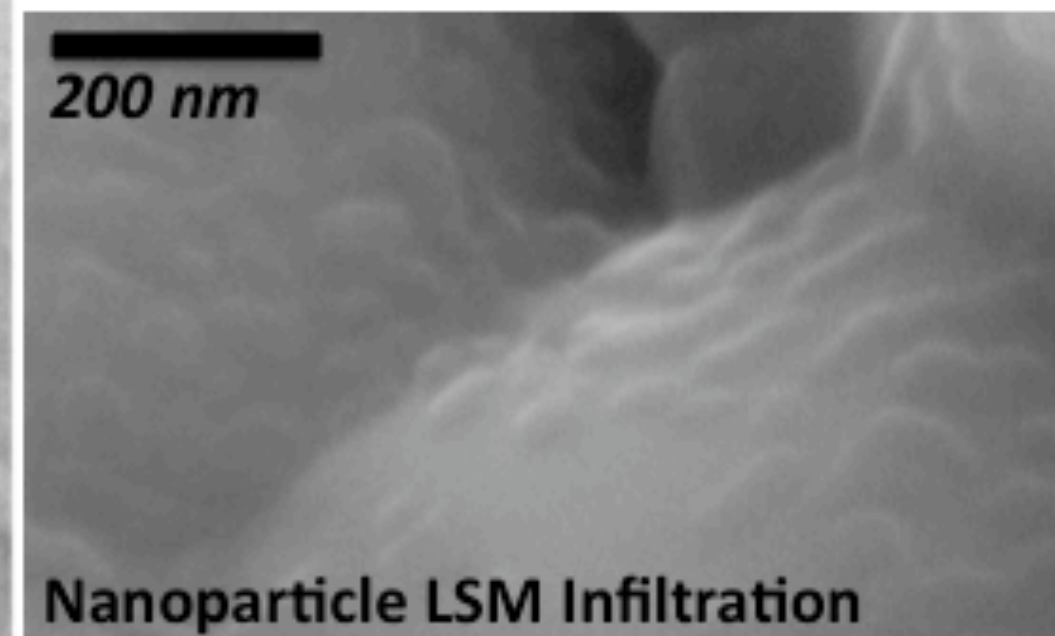
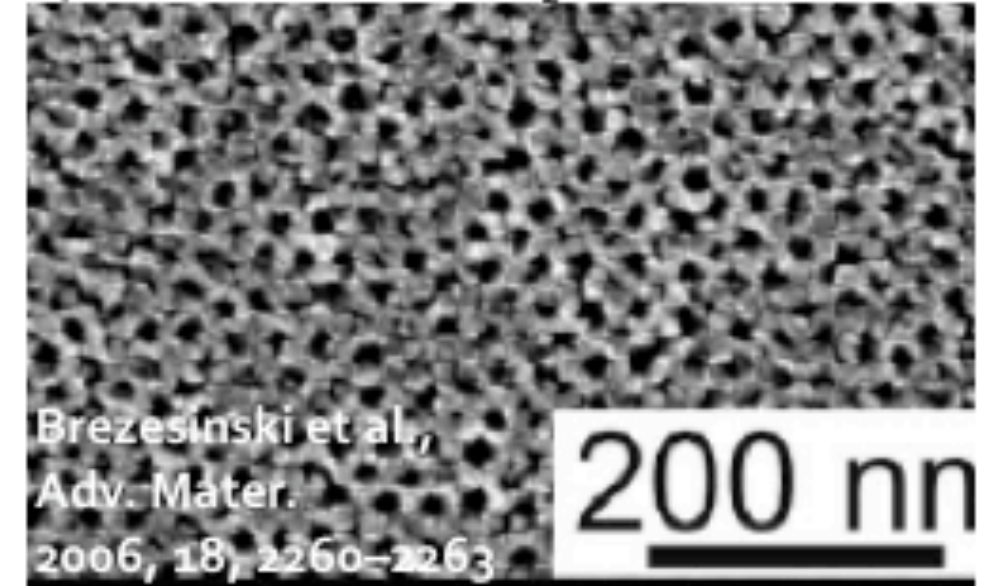
- A preheating stage at 60 C was added prior to infiltration step
- A uniform distribution of LSM particles is observed in functional layer
- The solution viscosity is reduced without dilution

# Mesoporous Coatings in Cathodes

Cathode Pore Wall Coating



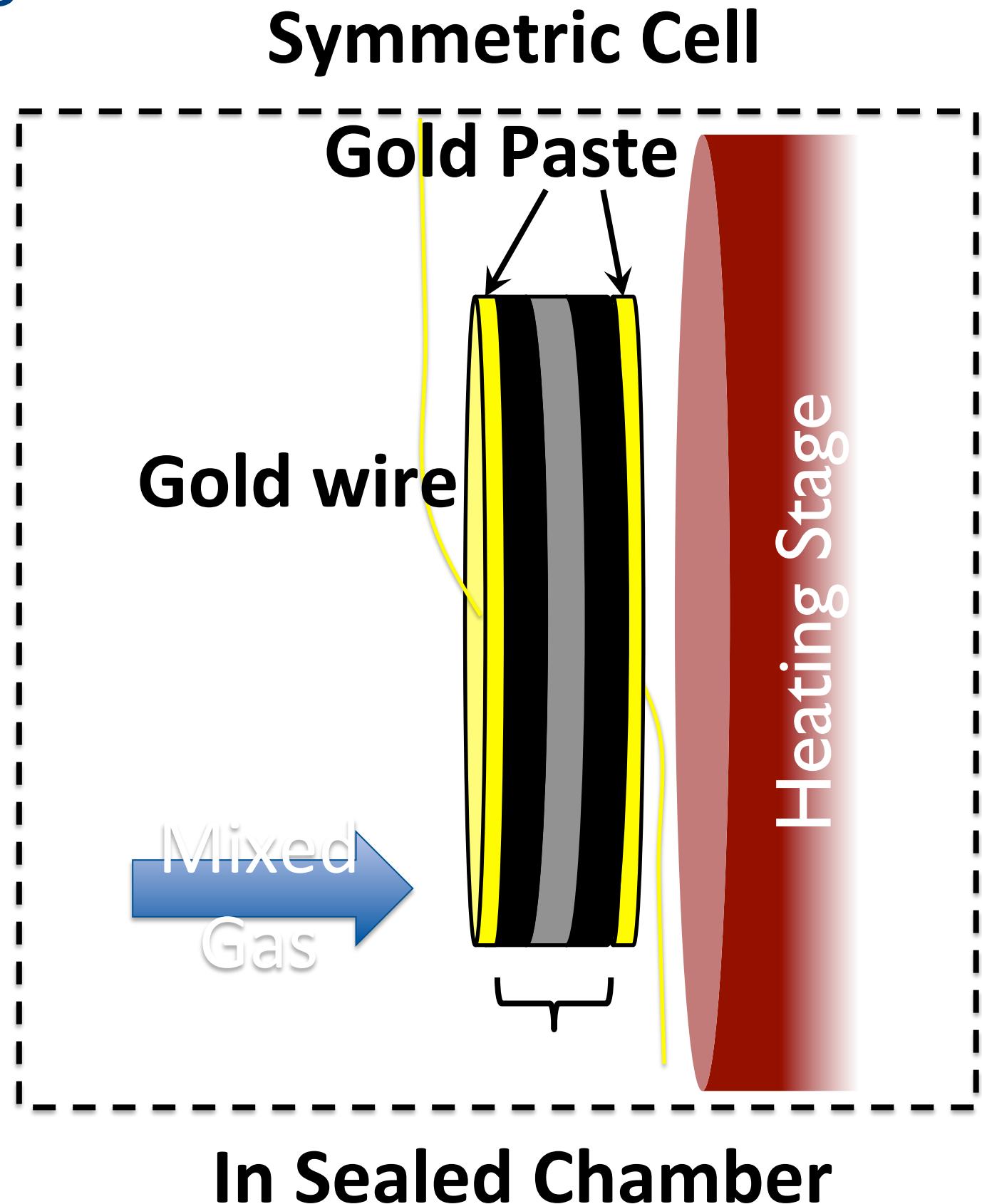
Dip Coated Meso-TiO<sub>2</sub> on Si Wafer



Pore morphologies resembles mesoporous thin film works by Brezesinski

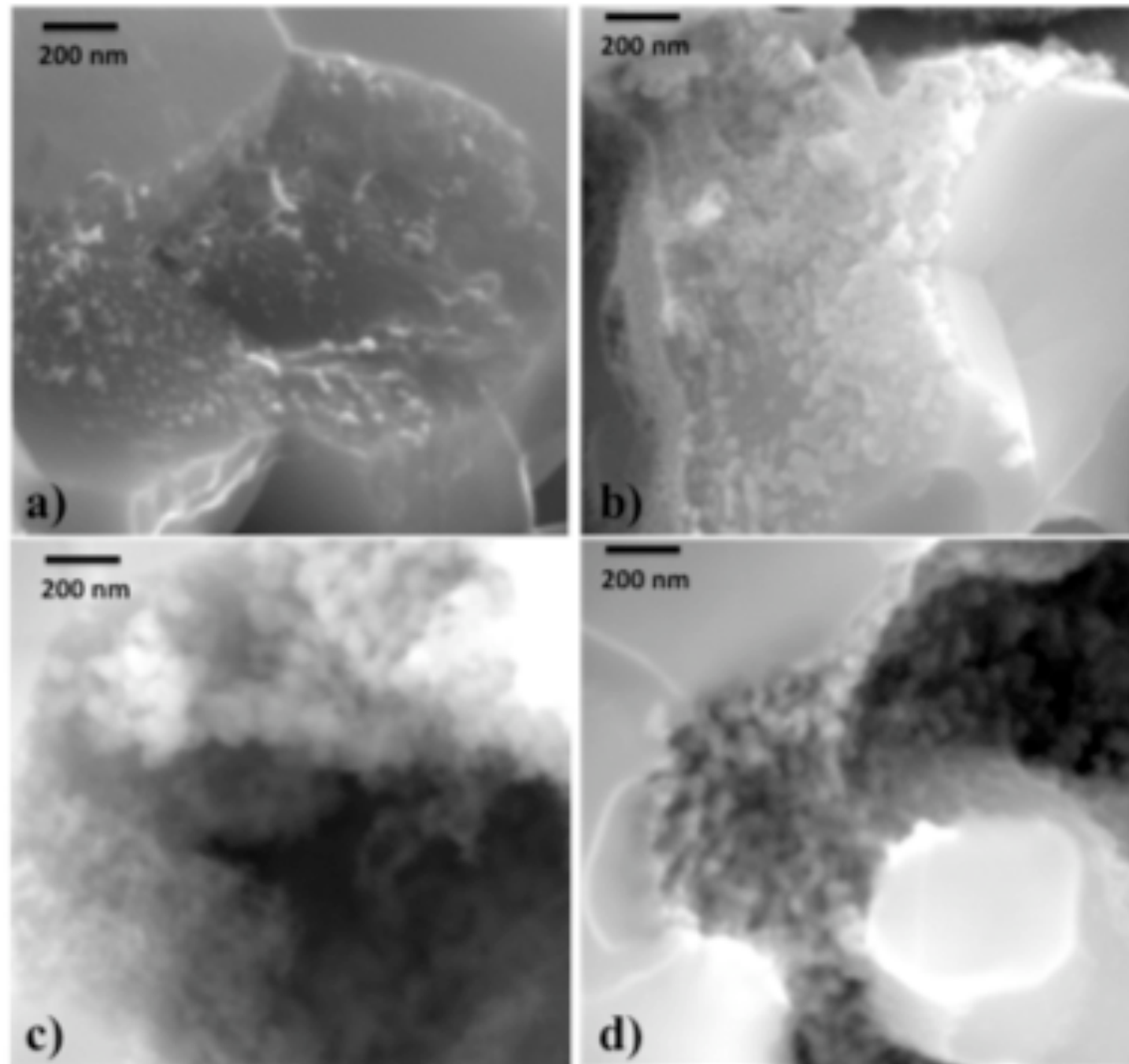
# Homemade Cells Testing

- Test Conditions:
  - Used gold paste and gold wire for current collection
  - The cell is suspended in a sealed chamber
  - 700, 750, and 800 °C
  - Controlled  $pO_2$  at 0.2 atm using 100 sccm  $O_2 + N_2$  mixed flow
  - Impedance data is collected by Gamry REF600 (1MHz-0.5Hz)





# LSM Infiltrate Morphologies Comparison in LSM Cells



□ All cells were infiltrated with 10 wt% LSM

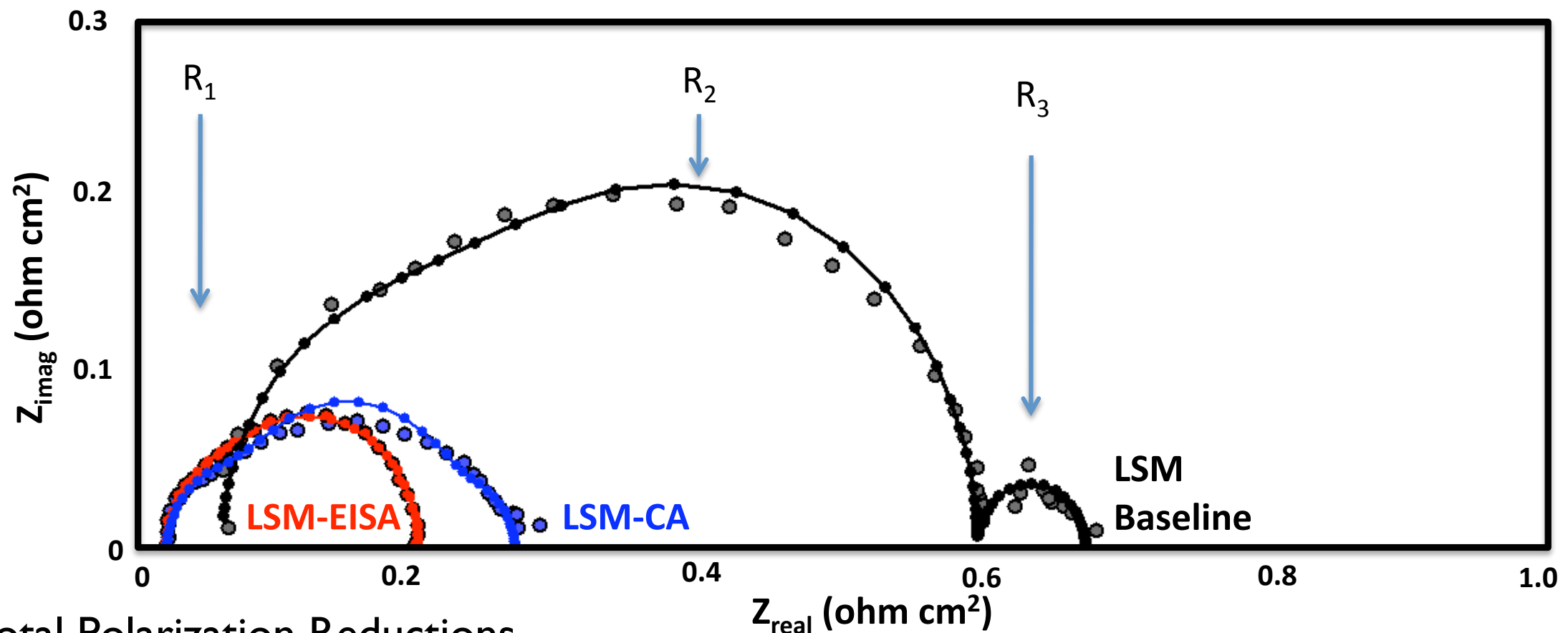
□ **Pechini infiltration (a-b)**

- generates a thin layer of LSM nanoparticles
- isolated or agglomerate

□ **EISA infiltration (c-d)**

- generates thicker LSM coatings
- 3-D mesoporous network

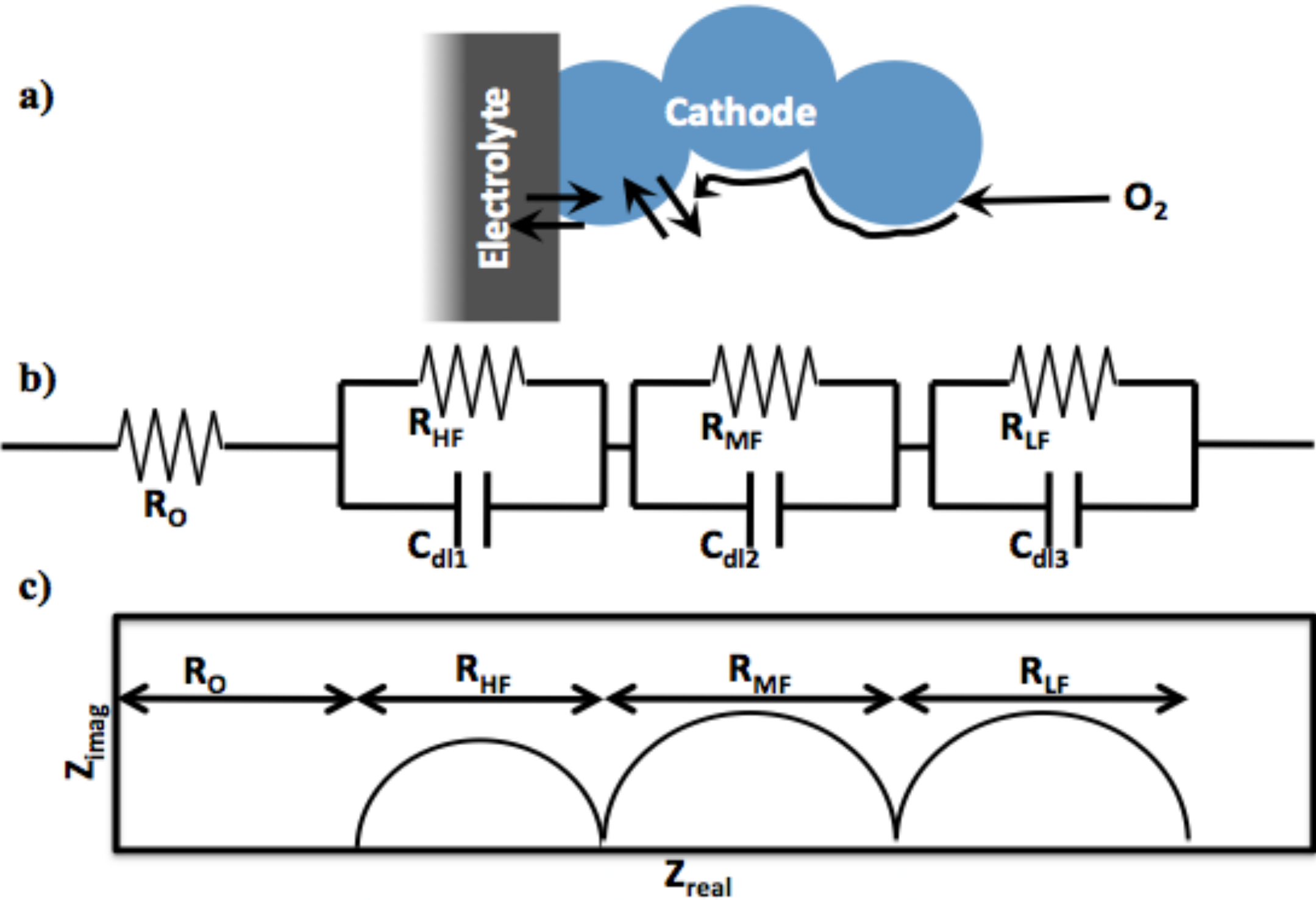
# EIS – Symmetric Cells at 750 °C



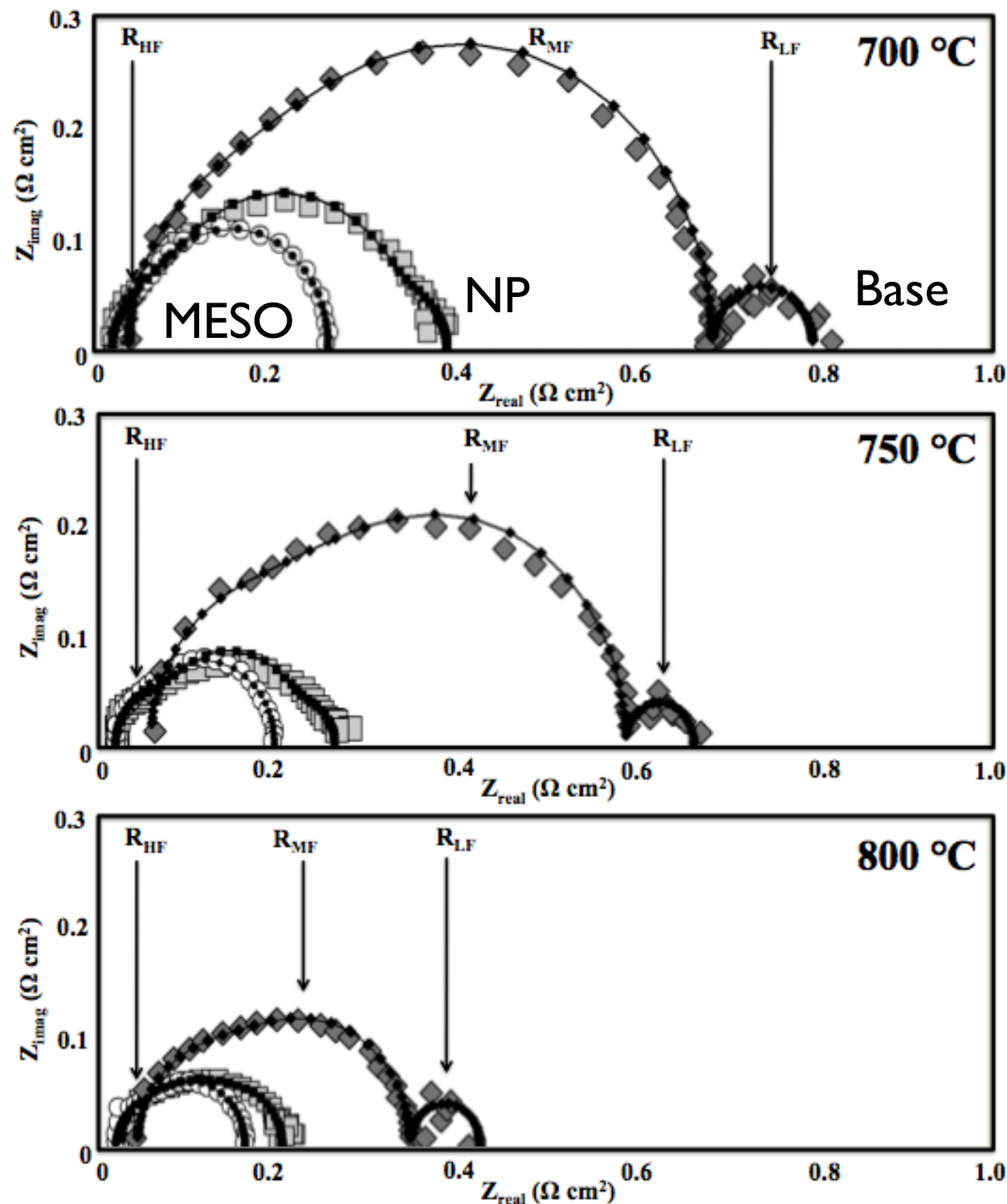
- Total Polarization Reductions  
**Nano-LSM: 57%**                      **Meso-LSM: 68%**
- Comparing Meso-LSM and Nano-LSM infiltration
  - High frequency ( $> 10$  kHz) : both infiltration are similar  $\rightarrow$  Similar interface polarization resistance
  - Mid-frequency (1 kHz – 10 Hz) : Meso-LSM is further reduced  $\rightarrow$  faster charger transfer rate
  - Low frequency ( $< 1$  Hz) : very small RP observed  $\rightarrow$  improved dissociative adsorption/diffusion of oxygen
- Major improvement is seen in surface reaction processes



# Literature Model of Three Arcs



# EIS – Mesoporous vs. Nanoparticle Infiltration

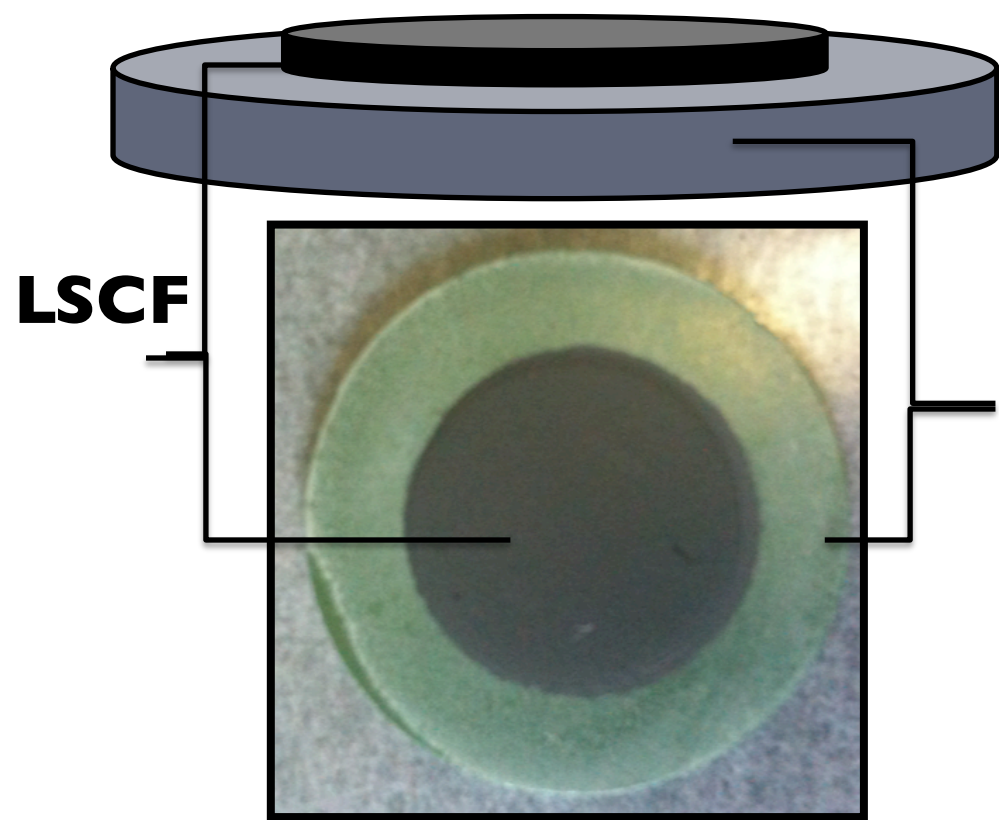


Both infiltrations were at 10 wt%

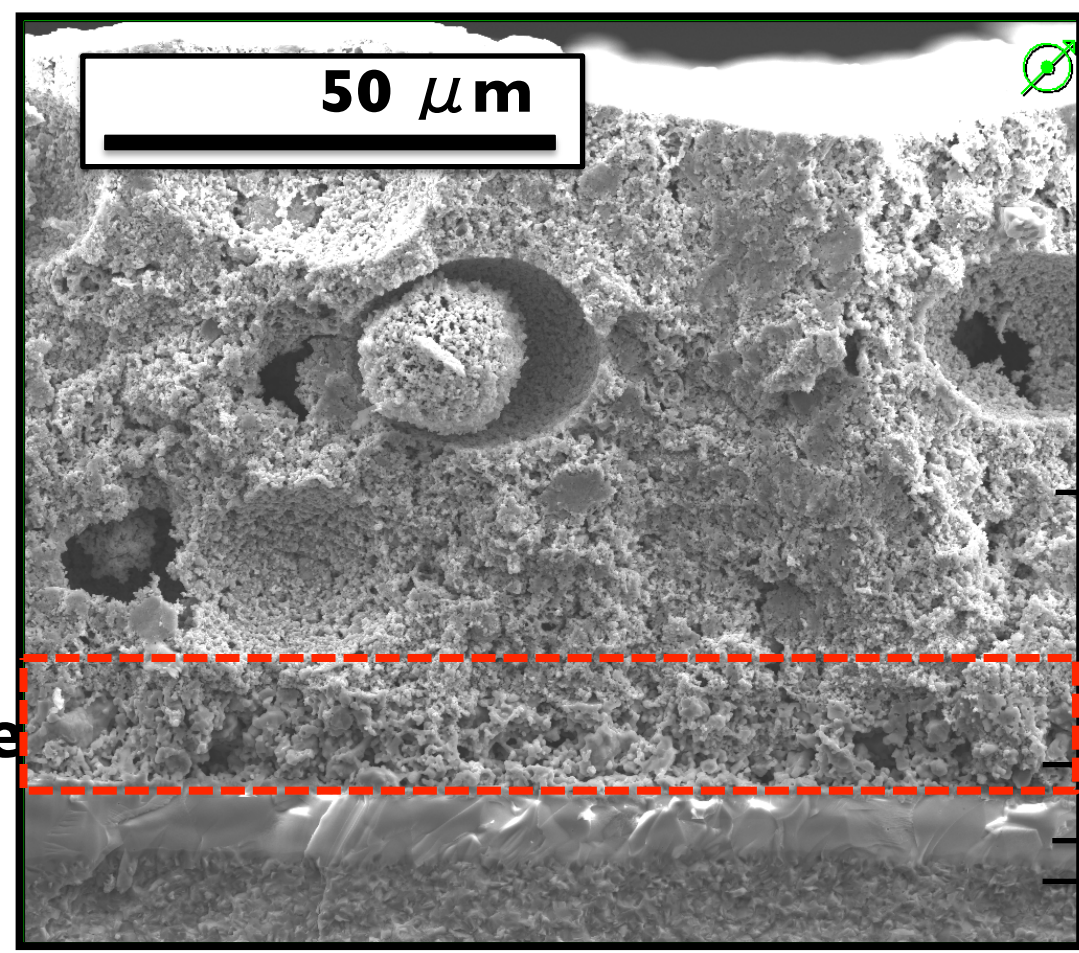
- In LSM infiltration, mesoporous coating infiltration led to **20% further  $R_p$  reduction** than nanoparticle infiltration for all temperatures (700-800 °C)
- The  $R_p$  reduction at each frequency range are consistent at 700-800 °C

# Commercial SOFC Button Cells

MSRI Anode Supported SOFC button cell  
with a  $\text{La}_{0.8}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3$  Cathode



**NiO/  
YSZ  
Anode**



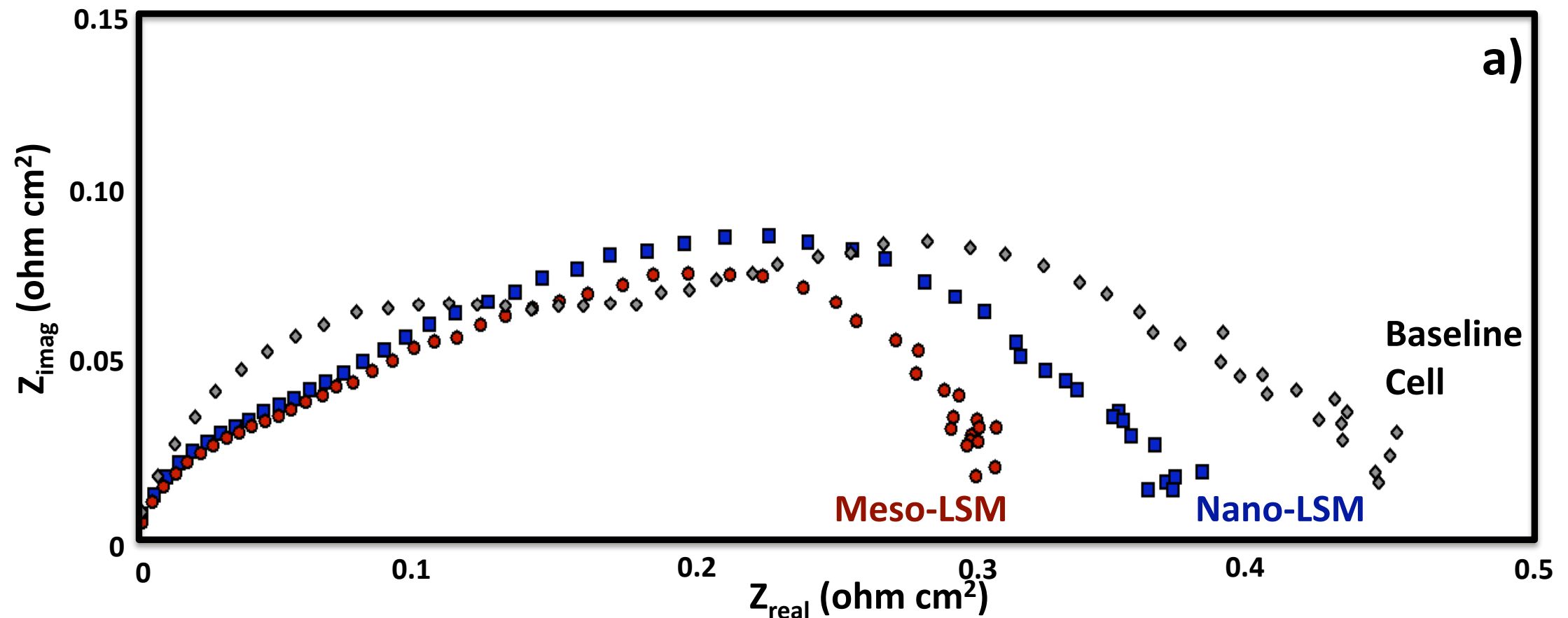
**LSCF  
Current  
Collection  
Layer**

**LSCF/SDC  
Functional  
Layer**

**Dense YSZ  
Electrolyte**

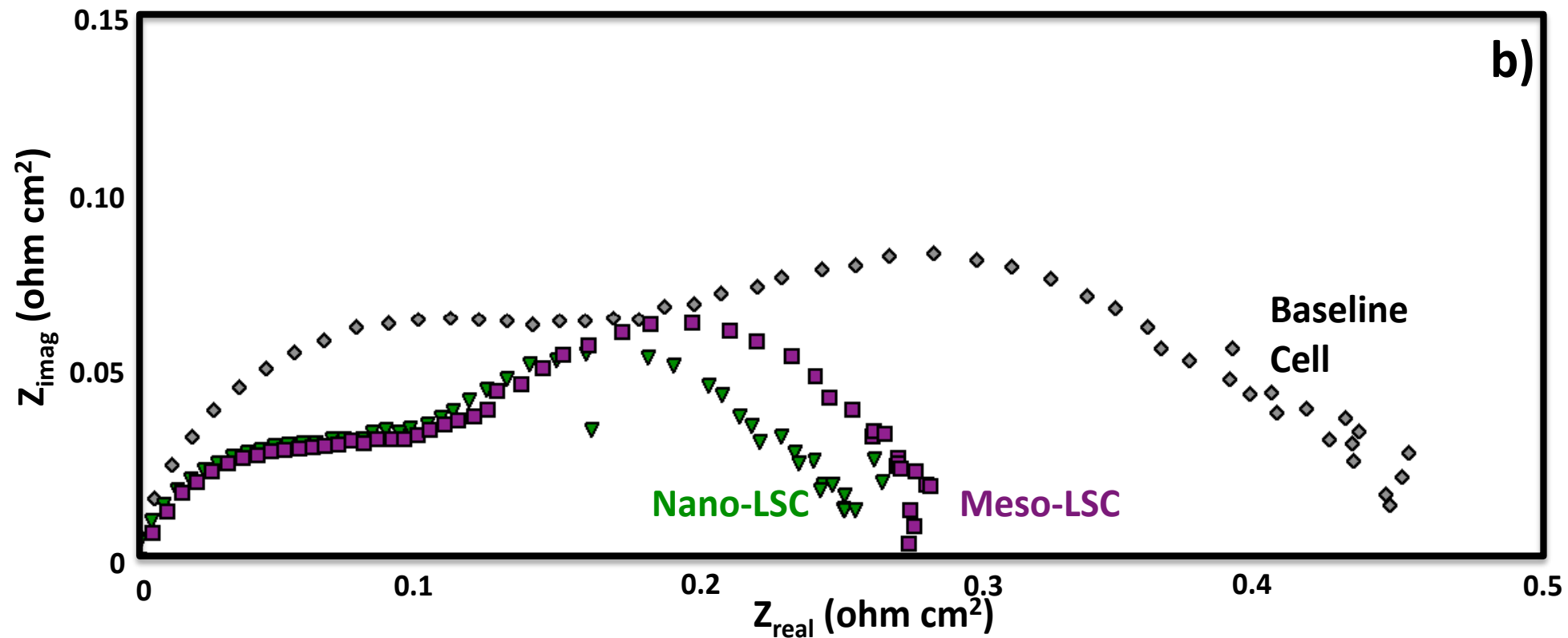
**NiO/YSZ  
Anode**

# EIS – Mesoporous LSM vs. Nanoparticle LSM



- Both infiltrations were at 10 wt%  
**Meso-LSM: 28%**      **Nano-LSM: 15%**
- In LSM infiltration, mesoporous coating infiltration led to **larger electrode polarization reduction** than nanoparticle infiltration

# EIS – Mesoporous LSC vs. Nanoparticle LSC



- LSC ( $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ ) infiltrations showed higher  $R_p$  reduction than LSM

**Meso-LSC: 37%**

**Meso-LSM: 28%**

**Nano-LSC: 38%**

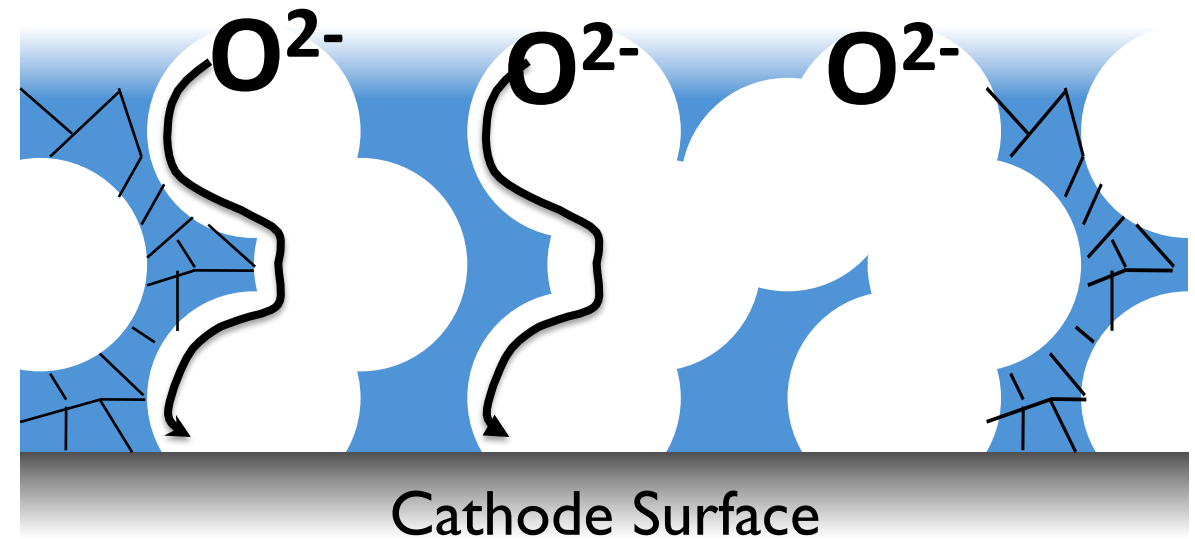
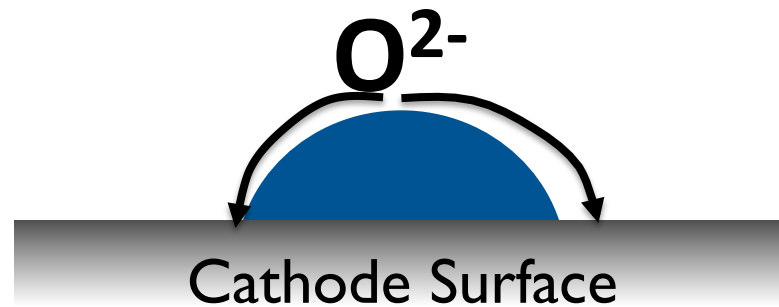
**Nano-LSM: 15%**

- Nanoparticle LSC shows **similar / lower** polarization resistance reduction than mesoporous LSC

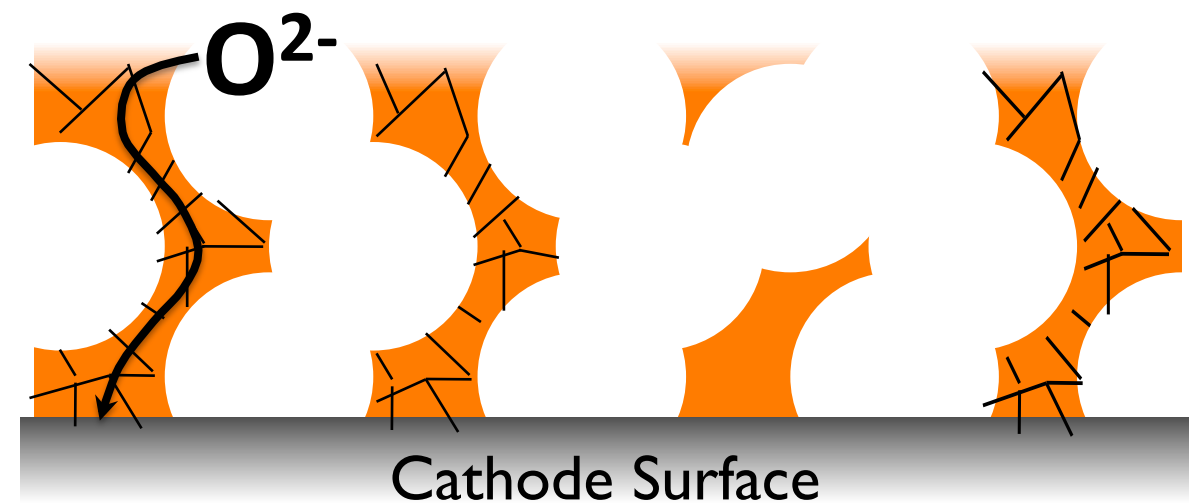
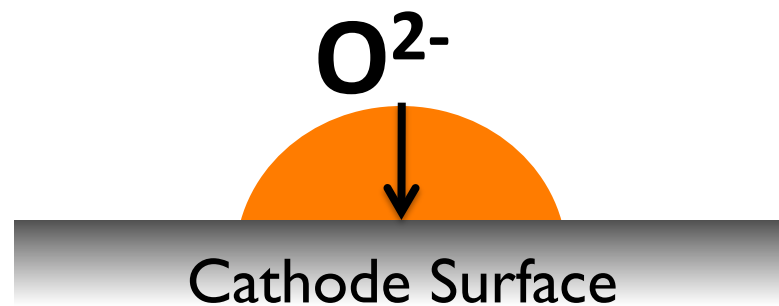


# Different Effects of Mesoporous LSC and LSM: Oxygen Transport

**LSM**



**LSC**



□ **LSM**

- Fast surface diffusion
- Need to pass along interconnected surface
- No effects from grain boundaries
- Transport of oxygen adsorbed away from the phase boundaries is **FAST**

□ **LSC**

- Fast bulk diffusion
- Need to pass through tortuous pore walls
- Need to cross over multiple grain boundaries
- Transport of oxygen species adsorbed away from the phase boundaries is **SLOW**

# Summary

One-step EISA process yields high surface area, well-dispersed mesoporous nanoscale coatings as infiltrates.

Mesoporous infiltrates are comparable to or better than “standard” nanoparticle infiltrates.

LSM mesoporous infiltrates are much improved owing to reduction in all surface polarizations:

*half cells and commercially available MSRI cells*

LSC coatings are less sensitive to microstructure in commercially available MSRI cells.