Insights into Oxygen Electroreduction on $(La,Sr)MnO_3$

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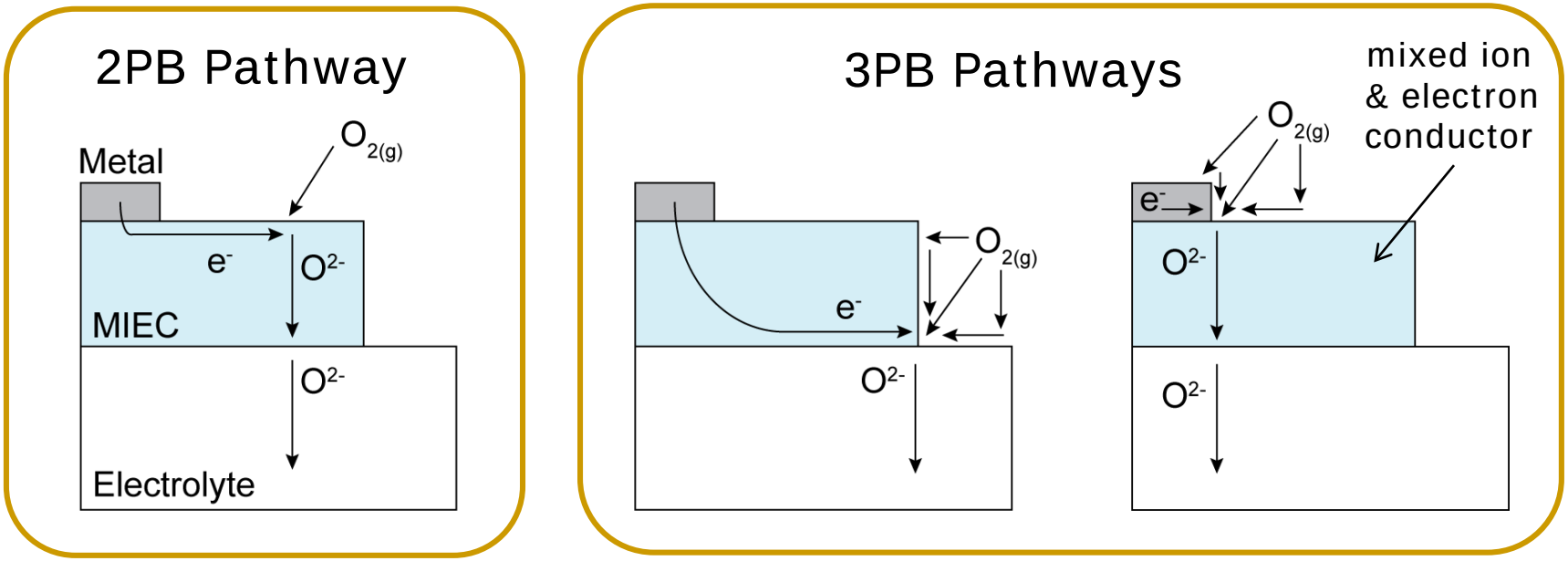
Reaction Pathways: Simplified

W. C. Chueh and S. M. Haile, *Annu. Rev. Chem. Biomol. Eng.* **3**, 313-41 (2012).

$$\frac{1}{2} O_2 + 2e^- \rightarrow O^=$$



activity scales with MIEC area, inversely w/thickness

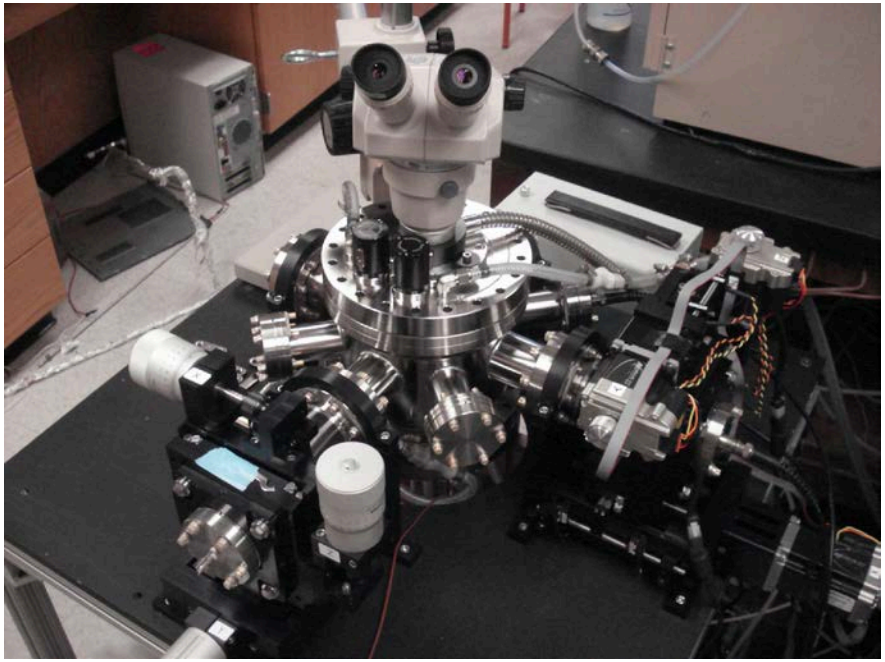
activity scales with perimeter (MIEC or metal), independent of thickness

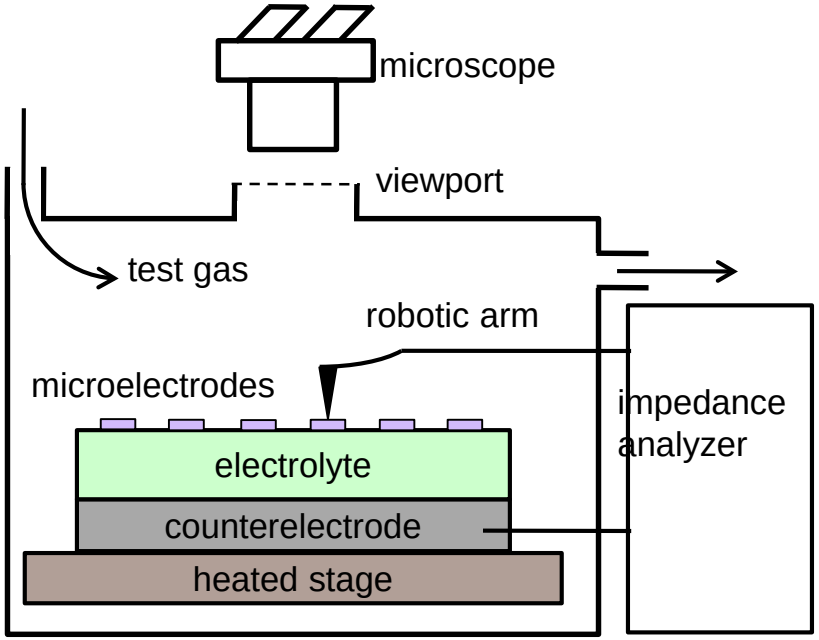
Vary geometric features ⇒ elucidate pathway

Experimental Approach

- $(La_{0.8}Sr_{0.2})_{0.95}MnO_{3-\delta}$
  - Predominantly electronic conductor
  - Small but detectable ionic conductivity
- Create microdot electrode array: PLD
  - Vary dot diameter
  - Thickness library
  - Growth temperature library
- Measure electrochemical impedance
  - Vary pO_2; limited variations in T

Scanning Impedance Probe



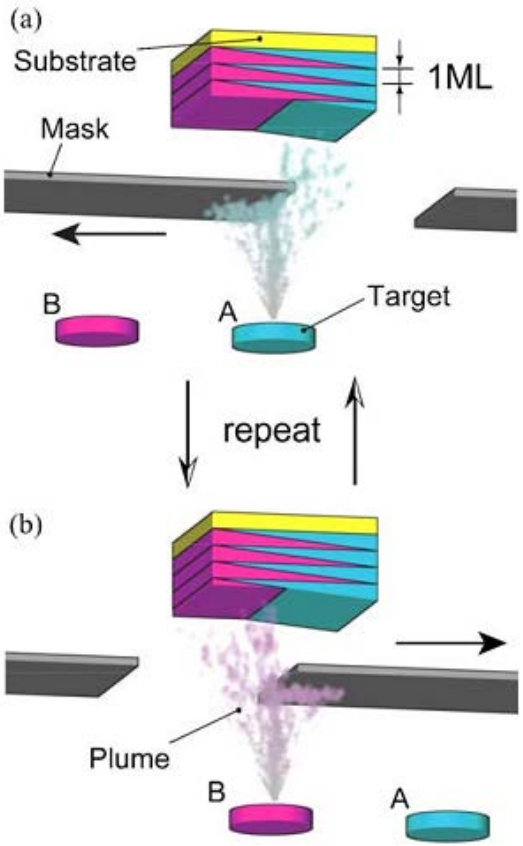


High throughput approach to compositions, geometry, deposition temperature, etc.

Library Fabrication

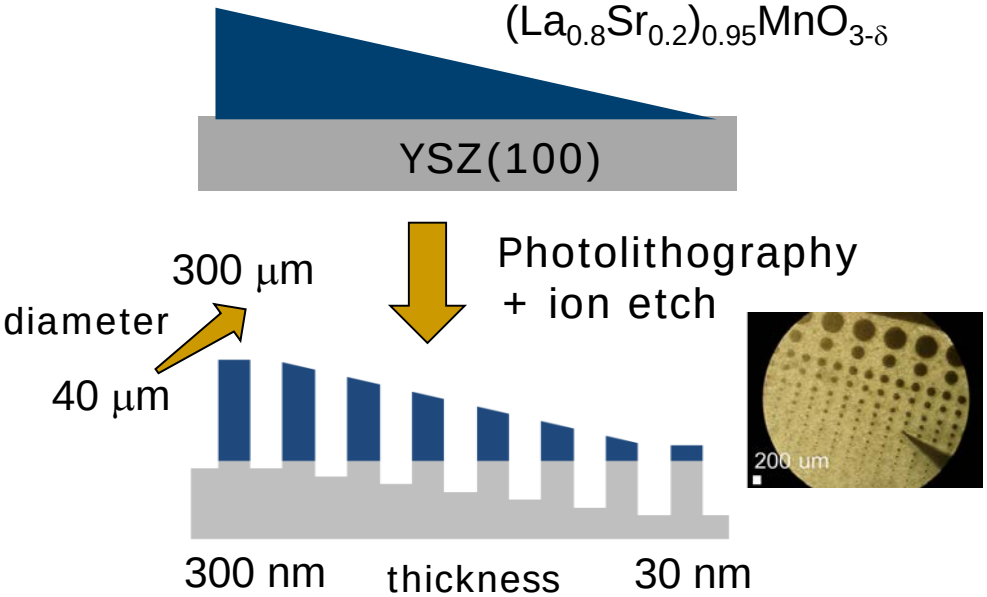
H. Koinuma and I. Takeuchi, *Nature Materials* **2004**, *3*, 429-438

Pulsed laser deposition

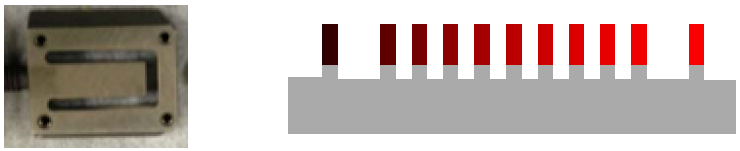


Thickness gradient

Single target, single mask



asymmetric PLD hot-stage

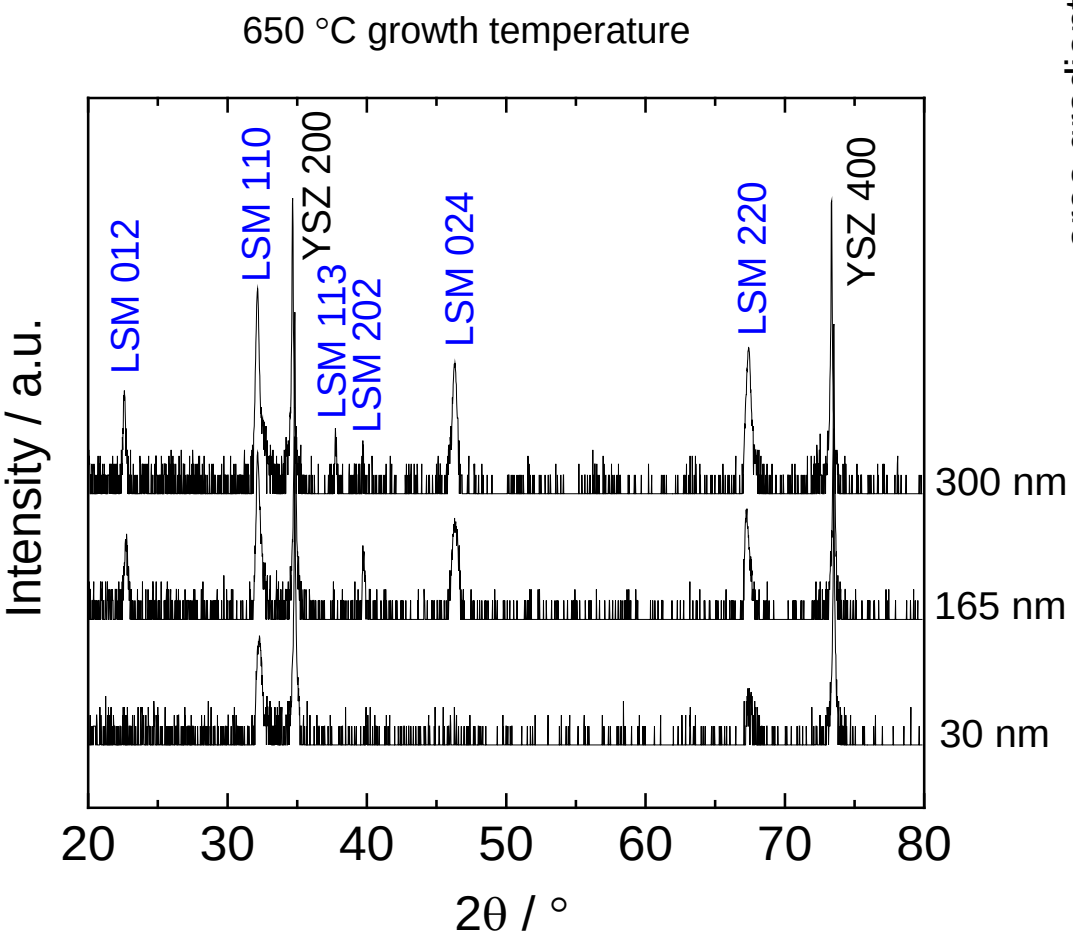


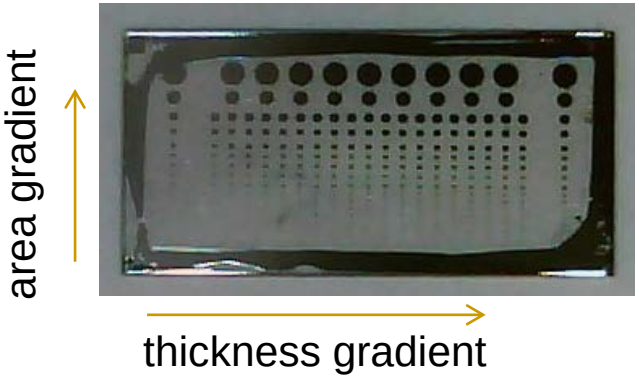
Growth temperature gradient

Library Growth Conditions

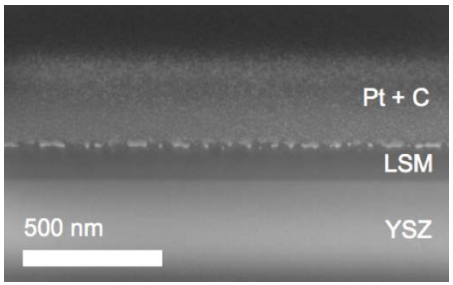
Characteristic	Library 1 Thickness Library	Library 2 Growth T Library	Supplemental Library (thickness)
# of diameters	6	6	6
Range	100 – 500 μm	100 – 500 μm	100 – 500 μm
# of thicknesses	18	1	18
Range	44 – 287 nm	135 nm	44 – 287 nm
# of growth temperatures	1	19	1
Range	650 °C	556 – 692 °C	650 °C
Growth pressure	10 mTorr O_2	30 mTorr O_2	30 mTorr O_2
Laser pulse rate	1 Hz	5 Hz	1 Hz
Growth rate	0.7 nm/min	2.7 nm/min	0.7 nm/min
Cooling rate	100 °C/min	20 °C/min	100 °C/min

Thickness Library

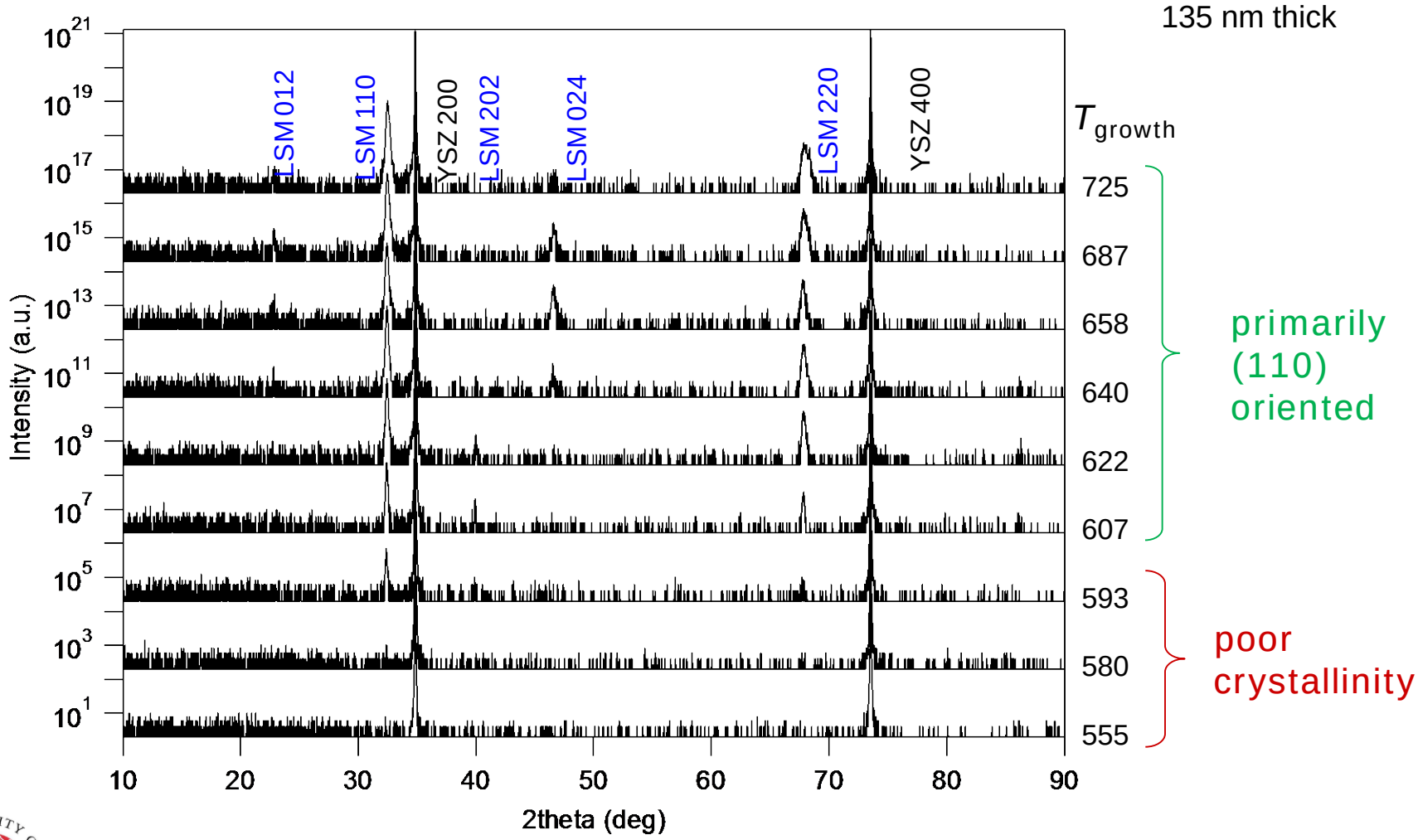




- Slight variation in orientation with thickness
- Crack and pore-free (FIB-SEM)
- Uniform depth-resolved composition (SIMS)

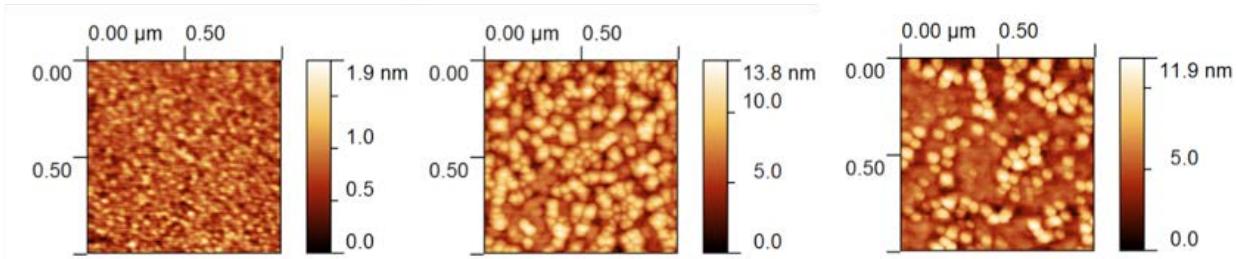


Growth Temperature Library

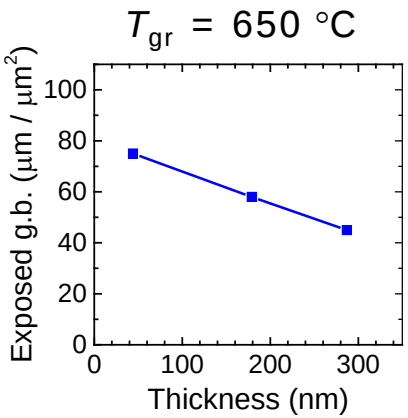


Surface Morphology Variations

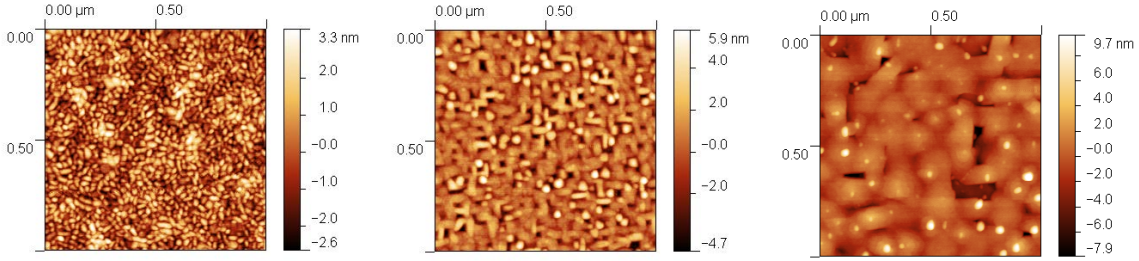
- Thickness gradient



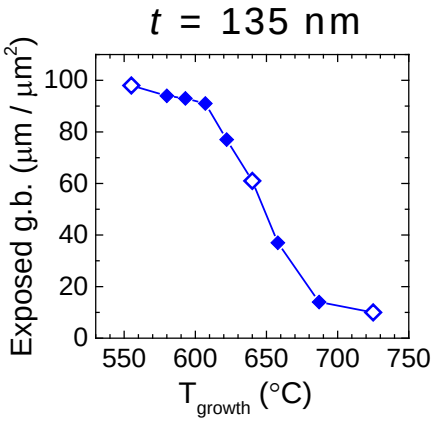
Thickness:	30 nm	165 nm	300 nm
Roughness:	0.2 nm RMS	2.1 nm RMS	1.9 nm RMS



- Growth temperature gradient



Temperature:	555˚C	640˚C	725˚C
Roughness:	RMS=1.1nm	RMS=1.5nm	RMS=1.7nm

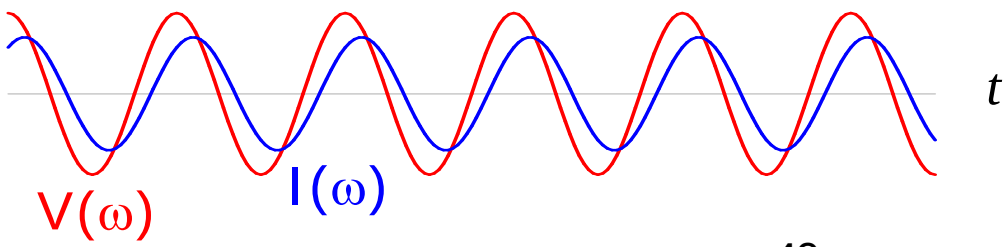


Grain size

A.C. Impedance Spectroscopy

- Apply A.C. voltage, measure A.C. current

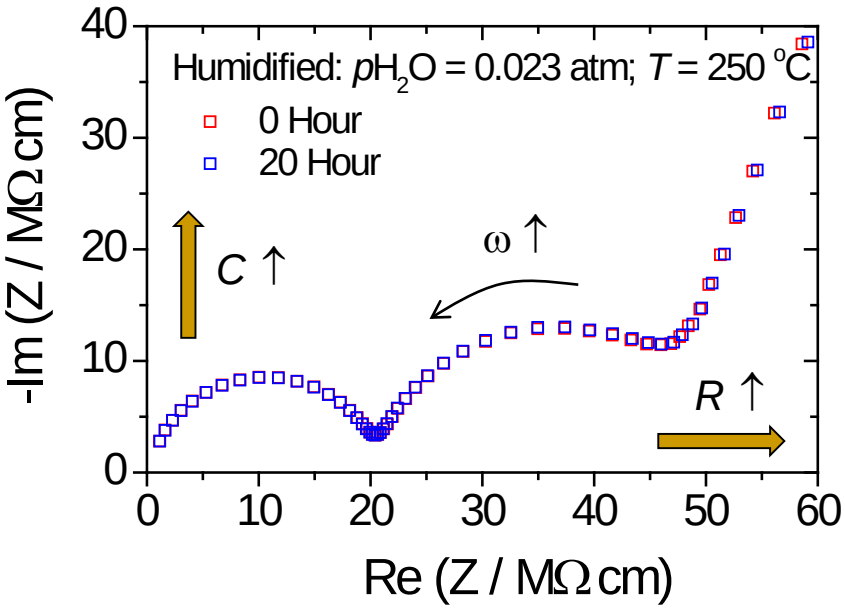
  ⇒ Complex impedance



$$Z(\omega) = \frac{V(\omega)}{I(\omega)}$$

$$Z(\omega) = |Z| e^{-i\phi\omega t}$$
$$= Z_r(\omega) + iZ_i(\omega)$$

$\omega = 10^{-3}$ to 10^{6} Hz
$V_0 = 20 - 40$ mV



Transport in a Mixed Conductor

Multiple species (i)

- Mass transport
  - Fick's law + Ohm's law

flux conductivity electrochemical potential

$$J_i^{mass}(x,t) = -\frac{\sigma_i(x,t)}{(z_i e)^2}\frac{\partial \tilde{\mu}_i(x,t)}{\partial x}$$

position, time charge

- Continuity

concentration

$$\frac{\partial c_i(x,t)}{\partial t} + \frac{\partial J_i^{mass}(x,t)}{\partial x} = 0$$

- Poisson's Equation

electric field

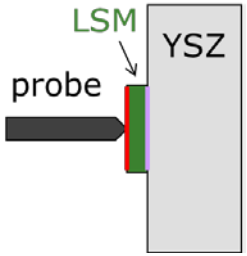
$$-\varepsilon_r \varepsilon_0 \frac{\partial^2 \phi(x,t)}{\partial x^2} = \sum_i z_i e c_i(x,t)$$

permittivity

  - Solve for steady state
  - Consider small perturbation
  - Assume electroneutrality

ion = ionic species
eon = electronic species

Fit Parameters



- LSM Bulk

$$R_{ion} = \rho \frac{t}{A}$$

$$C_{chem} = -\frac{8e^2 V}{k_B T V_m} \frac{\partial \delta}{\partial \ln(pO_2)}$$

- LSM/gas interface

R_{ion}^{S} reaction resistance

C_{ion}^{S} surface ionic capacitance

- YSZ bulk

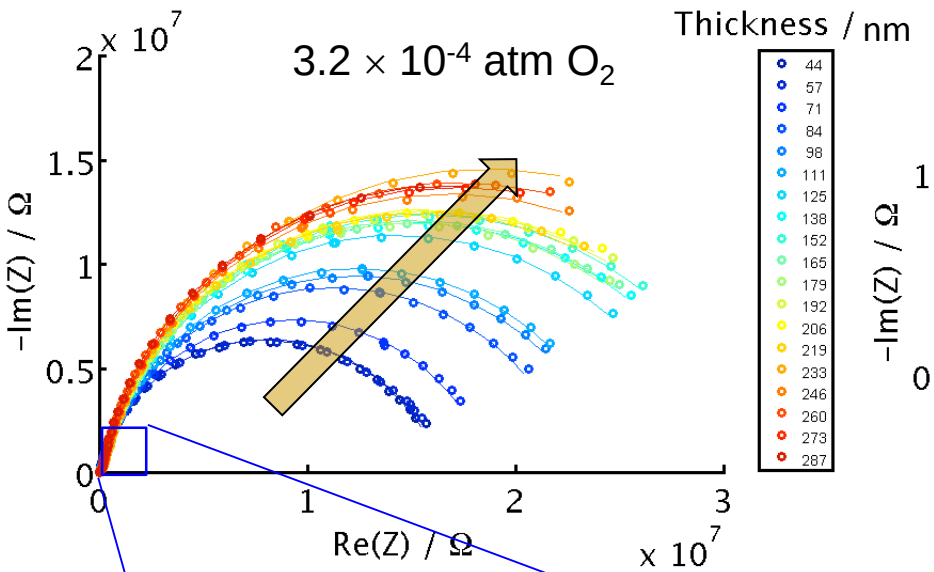
R_0 point contact resistance

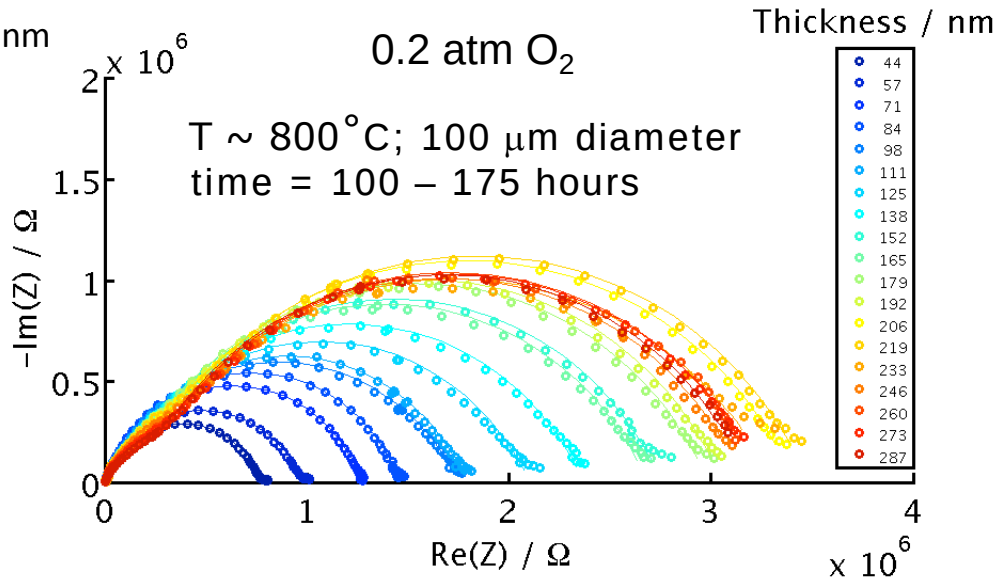
- LSM/YSZ interface

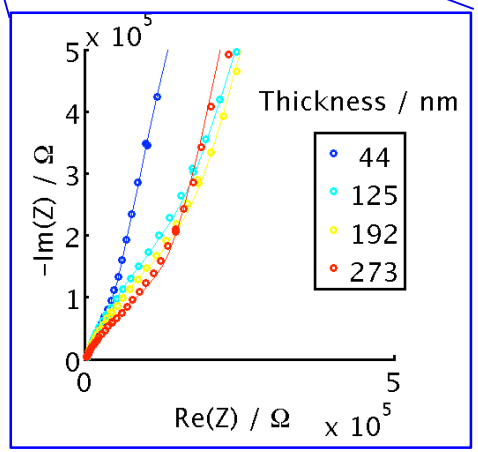
C_{ion}^{S} interfacial electronic capacitance

~ to indicate area normalized quantity

Representative Impedance Spectra

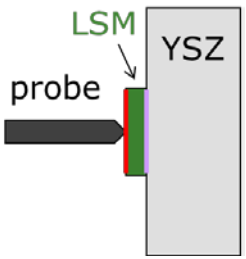




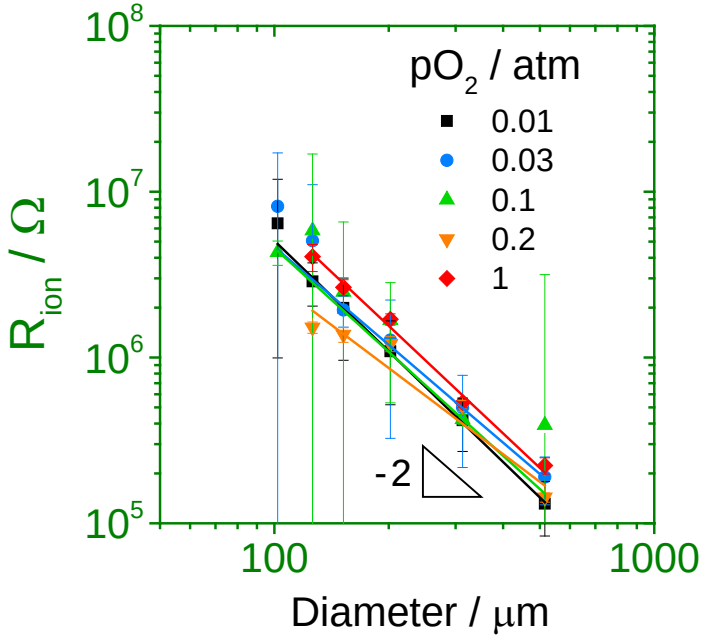


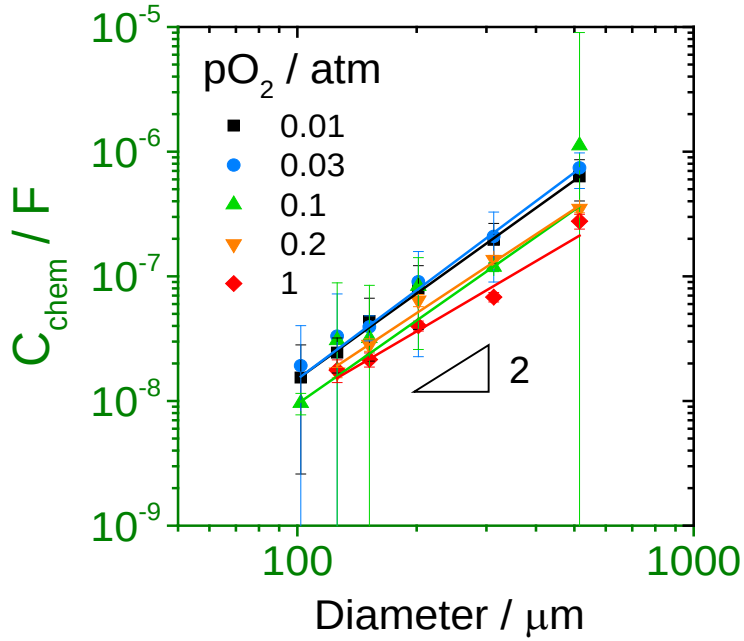
- Solid lines are fits to analytical expression for derived equivalent circuit
- Resolution depends on T, pO_2
- Poorer but acceptable fits with *ad hoc* analysis
- Fleig reports similar results
- Clear thickness trend ⇒ 2PB pathway (?)

Diameter Trends



Thickness: 246 nm (T ~ 710 °C)

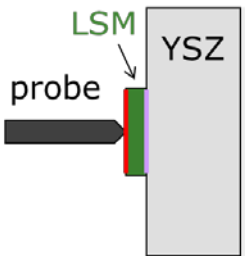




$$R_{ion} = \rho \frac{t}{A} \Rightarrow slope = -2$$

$$C_{chem} = -\frac{8e^2 V}{k_B T V_m} \frac{\partial \delta}{\partial \ln(pO_2)} \Rightarrow slope = 2$$

Diameter Trends



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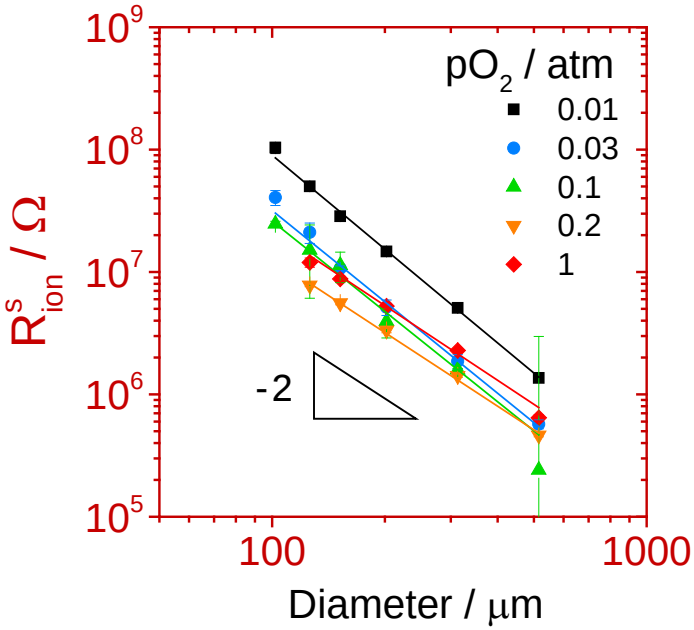
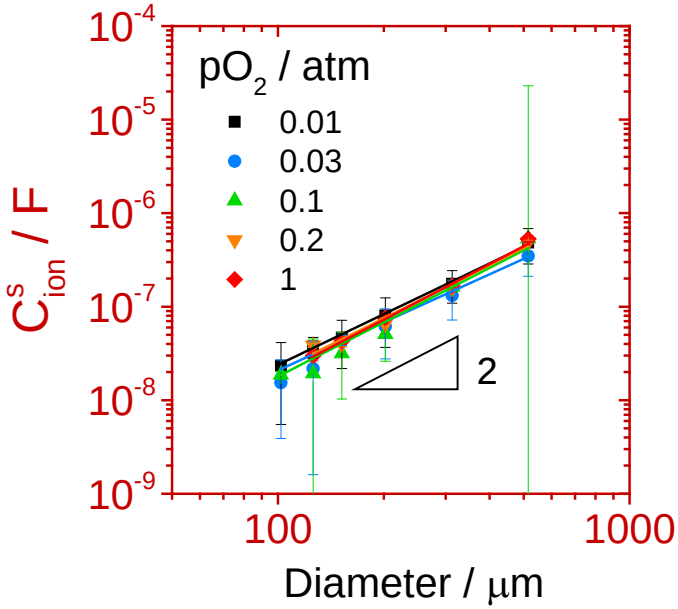




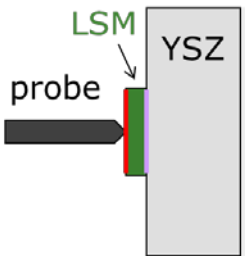
2PB pathway ⇒ slope = -2

Interfacial capacitance ⇒ slope = 2

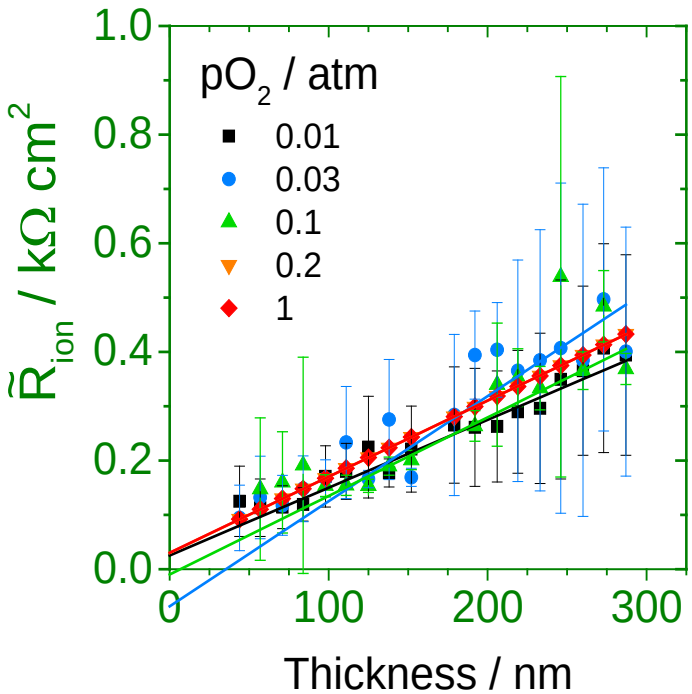
Intermission

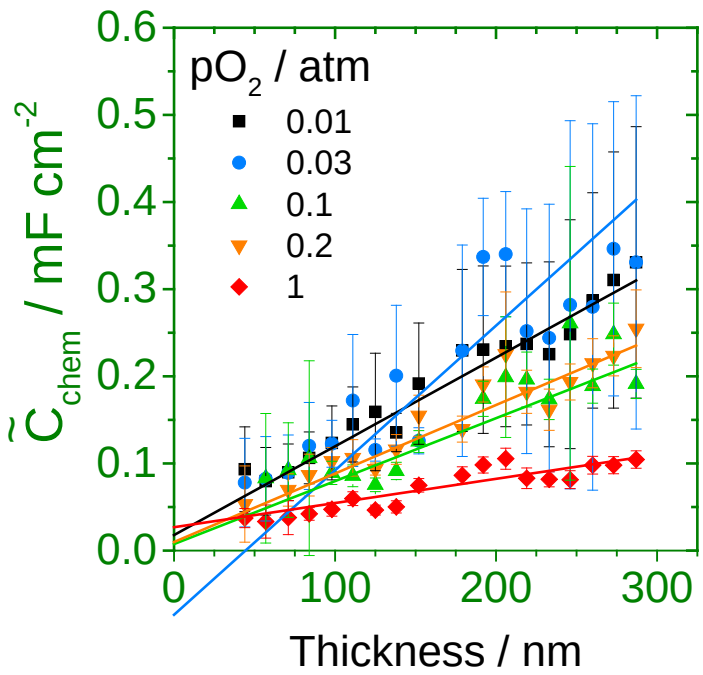
- Impedance model fits data well
  - Under most conditions, good resolution of all variable parameters
- Diameter trends extracted from the model are self-consistent
- Double-phase boundary pathway appears dominant
  - At measurement length-scales
  - For environmental conditions probed

Library 1: Thickness Trends



Diameter: 200 μm (T ~ 710 °C)

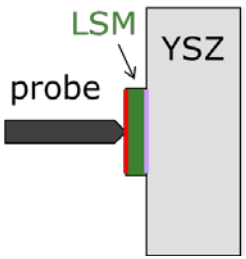




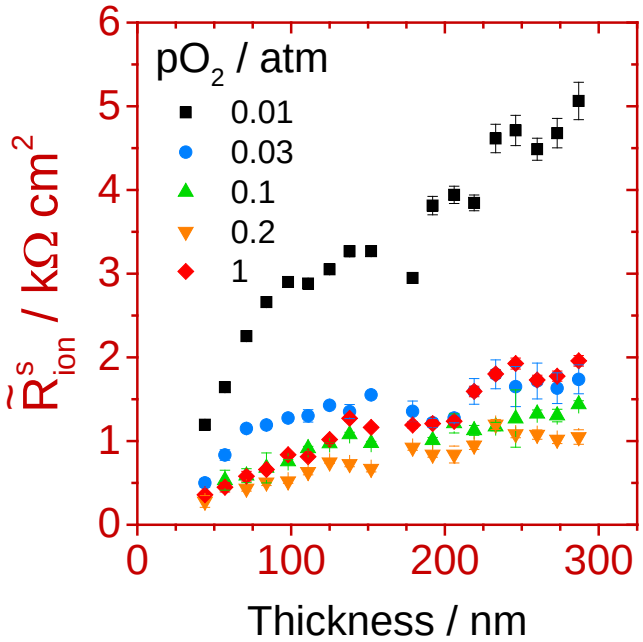
$$R = \rho \frac{t}{A} \Rightarrow linear$$

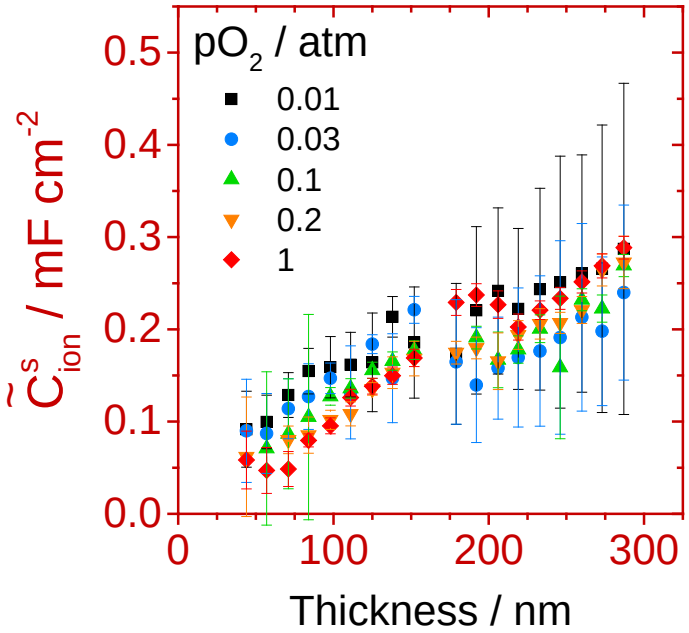
$$C_{chem} = -\frac{8e^2 V}{k_B T V_m} \frac{\partial \delta}{\partial \ln(pO_2)} \Rightarrow linear$$

Library 1: Thickness Trends



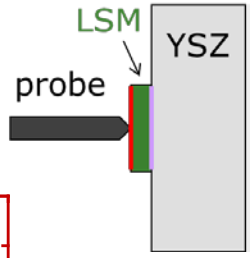
Diameter: 200 μm (T ~ 710 °C)

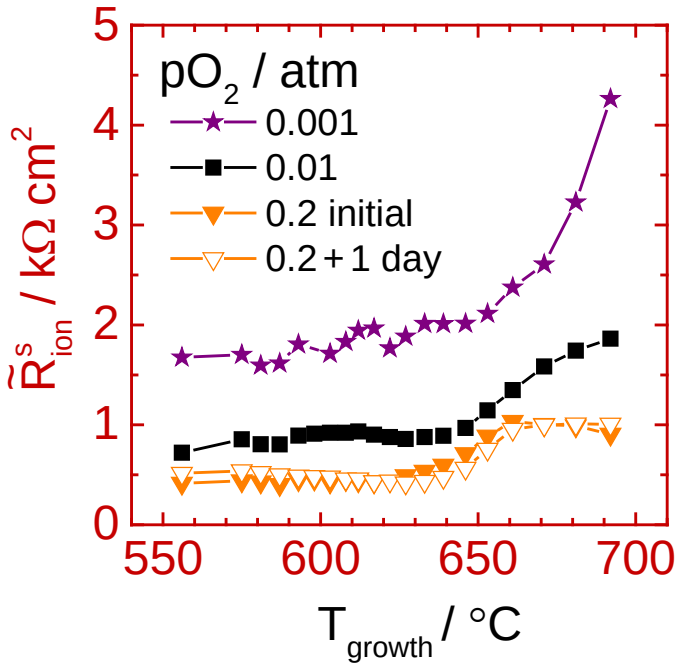


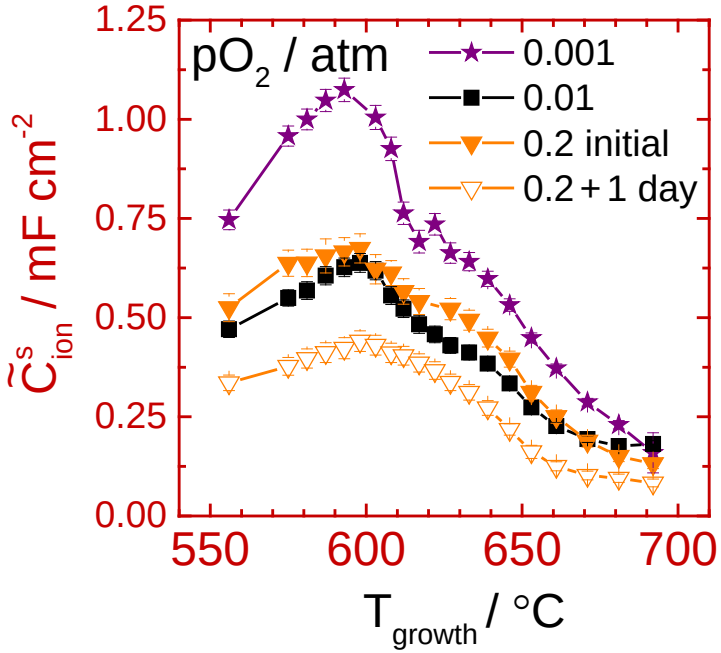


Model implies that the nature of the LSM|gas interface must be changing with film thickness

Library 2: Growth Temp. Trend



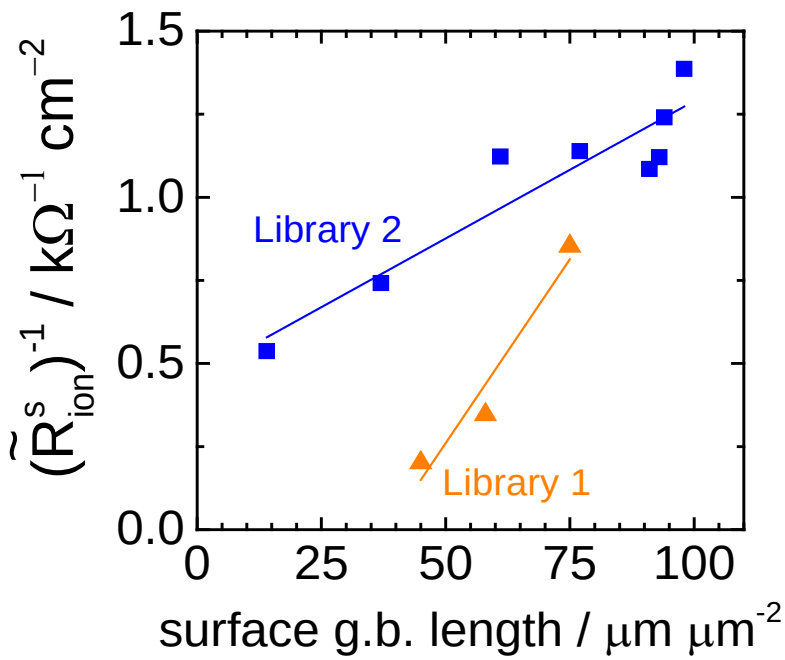


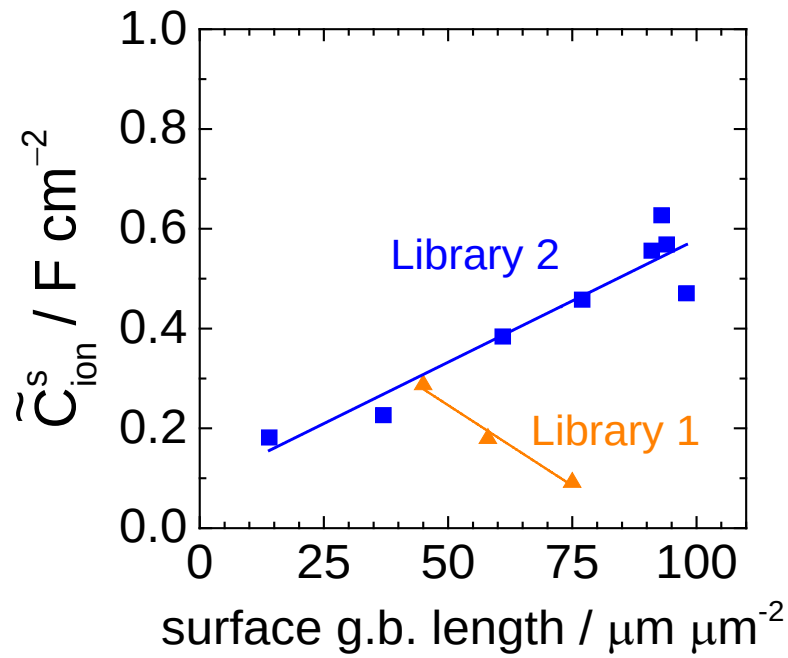


Interface must also be changing with film growth *T*

Hypothesis: Grain Boundary Role

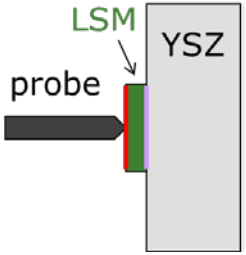
LSM surface properties



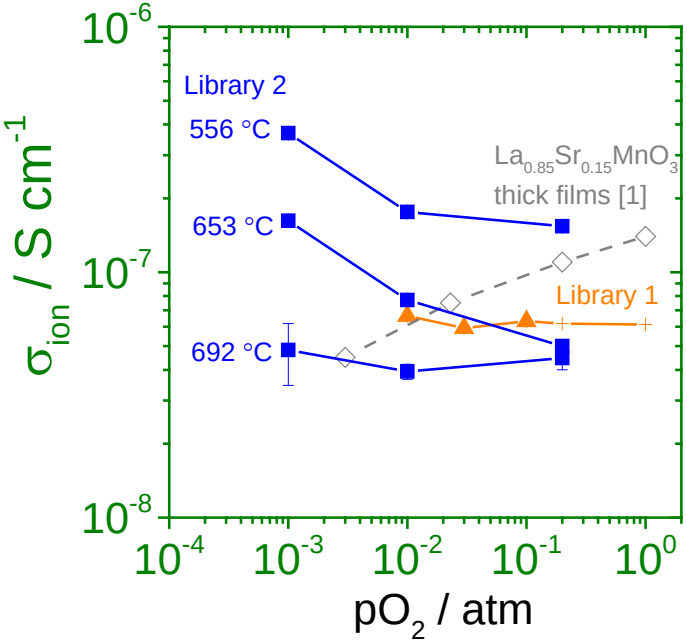


Clear correlations with grain boundary length
Different laser repetition rates of libraries: 1 vs 5 Hz

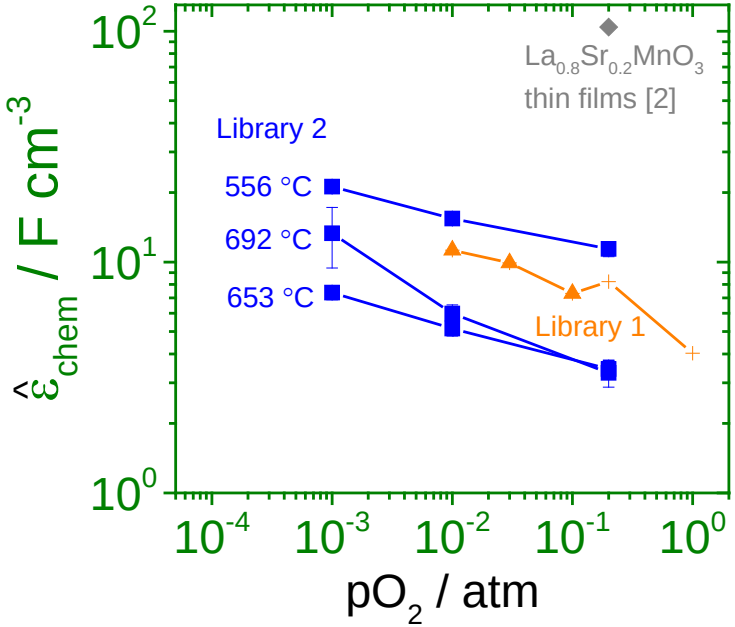
LSM Bulk Properties



Ionic conductivity



Volume specific chemical capacitance



Also: $D_{chem} = t^2 / (\tilde{R}_{ion} \cdot \tilde{C}_{chem}) = \sigma_{\text{ion}} / \hat{\varepsilon}_{\text{chem}}$

"Bulk" properties depend on fabrication conditions – grain boundary mediated? Trends not systematic

[1] Pal, J. Pwr Srcs (2007); [2] Yildiz & Shao-Horn J. Electrochem. Soc. (2007)

Summary and Conclusions

- 1-D impedance model describes data well
  - Minor ‘violation’ due to varied grain size with thickness
- LSM bulk properties are comparable to literature
- Oxygen electroreduction on LSM occurs via 2PB pathway
- Exposed grain boundaries are likely active sites
- Scaling with thickness
  - Increase in total impedance dominated by behavior of surface reaction step, **not** increase in diffusion resistance
  - Care required when comparing thin film samples
- Many questions answers, others have emerged…

in press, *J. Mater. Chem. A*, Usiskin *et al.*

Acknowledgments

- Caltech Students
  - Robert Usiskin, Chris Kucharczyk

- University of Maryland
  - Prof. Ichiro Takeuchi; Dr. Shingo Maruyama; Xiaohang Zhang
- Funding
  - Taiwan National Science Council (Caltech Resnick Institute); National Science Foundation, EFRI
  - Keck Foundation