Carnegie Mellon

Electrode Optimization Studies and Cathode Surface Chemistry:

Determination of Key Correlations between Surface Features and Electrochemical Performance

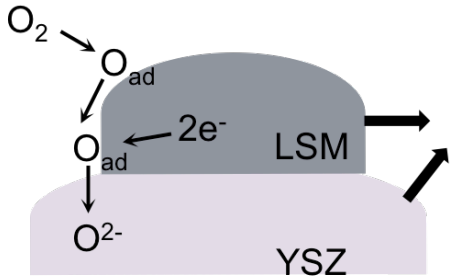
Paul Salvador
Department of Materials Science and Engineering,
Carnegie Mellon University, Pittsburgh, PA, 15213

SECA Review August 6, 2008

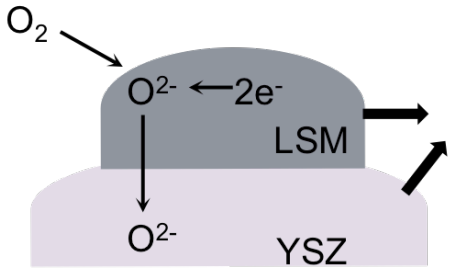
RDS-NETL-SECA: Briggs White and Wayne Surdoval

Thin Film Approach to Investigating Cathode Surface Chemistry

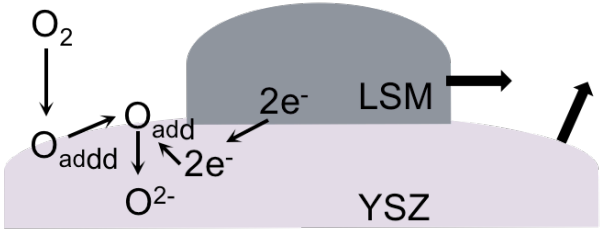
1/2 O_2(g)	**+ $2e^-$**	→	**O^{2-}**
pore	*conductor*		*ion conductor*



LSM Surface Path



LSM Bulk Path



YSZ Surface Path

There is reason to believe that
the surface structure of known backbones is dynamic under load.

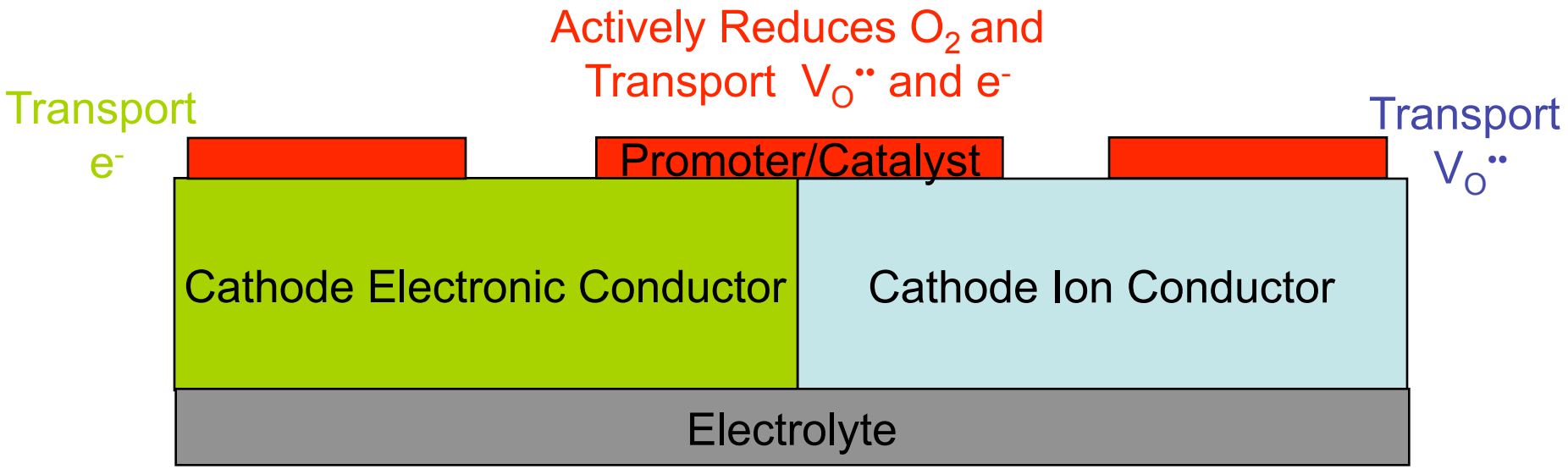
There is no reason to believe that
the ideal backbone will have the ideal surface kinetics.

Can we understand / engineer highly-active and stable surfaces?

Thin Film Approach to Investigating Cathode Surface Chemistry

$1/2\ O_2(g) + 2e^- \rightarrow O^{2-}$

pore *conductor* *ion conductor*



There is no reason to believe that
the ideal backbone will have the ideal surface kinetics.

There is reason to believe that
the surface structure of known backbones is dynamic under load.

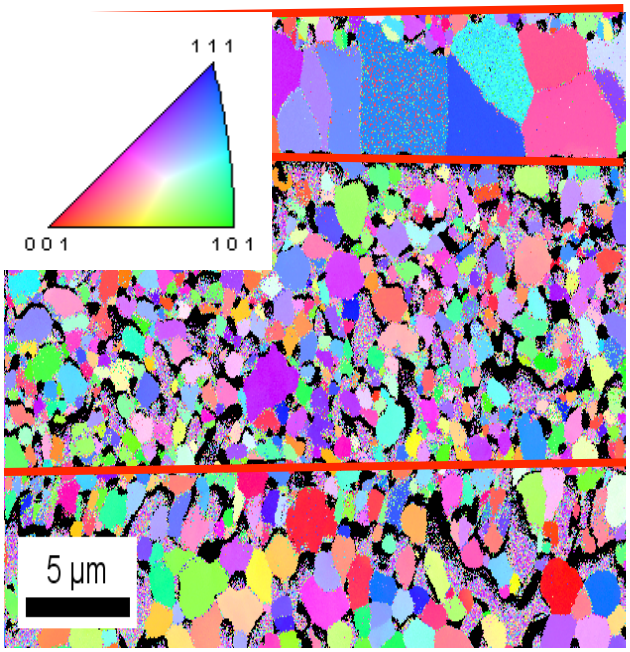
Can we understand / engineer highly-active and stable surfaces?

Orientation Mapping Of Internal Interfaces:

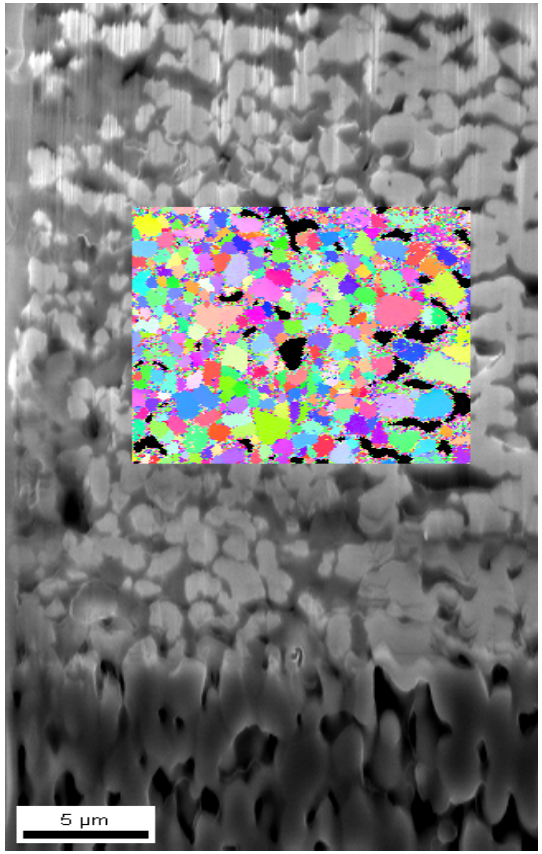
NETL – Carnegie Mellon – NSF MRSEC

Statistical Information on Interfacial Crystallography

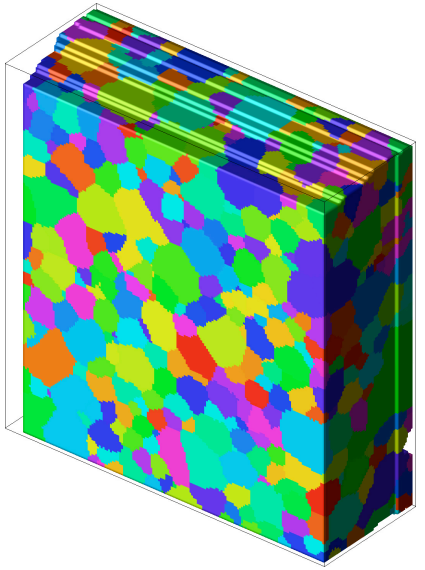
2D Traditional OIM



2D FIB Based OIM

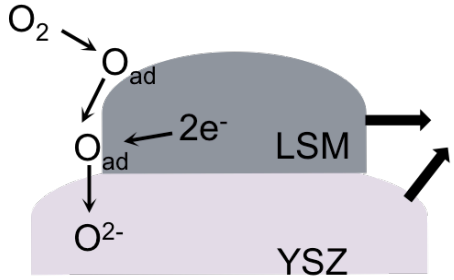


3D FIB Based OIM

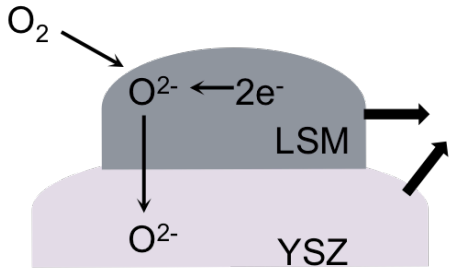


Have 3D Crystallography of Interfaces in all Cell Components
Can Determine Relative Surface / Interface Energies

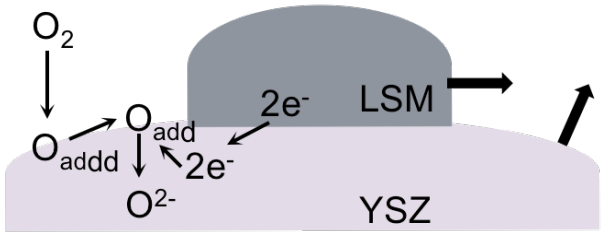
What happens during oxygen uptake?



LSM Surface Path



LSM Bulk Path



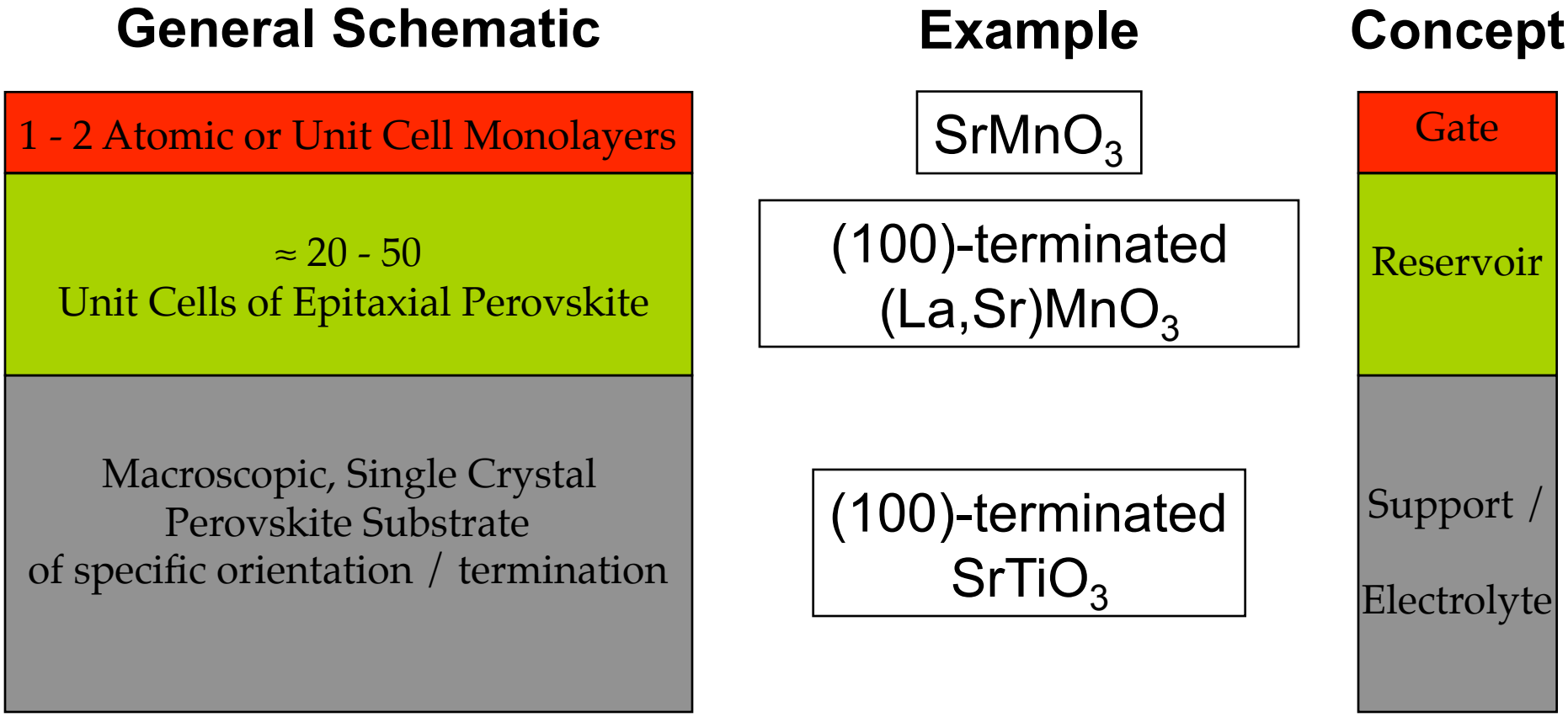
YSZ Surface Path

- *Adsorption*
  - *Mass of Material* *(Gravimetry)*
  - *Surface Chemistry* *(Spectroscopy)*
  - *Surface Electronic Structure* *(Kelvin Probe, STS, Normal Conductivity)*

- *Electronic transfer*
  - *Consumption of holes* *(Parallel Conductivity / Thermopower)*
  - *Fermi Level Changes* *(Kelvin Probe / STS)*
  - *Surface chemistry* *(Spectroscopy)*

- *Oxygen Vacancy Filling*
  - *Mass Change* *(Gravimetry)*
  - *Total charge density* *(Conductivity / Thermopower)*
  - *Surface Chemistry* *(Spectroscopy)*

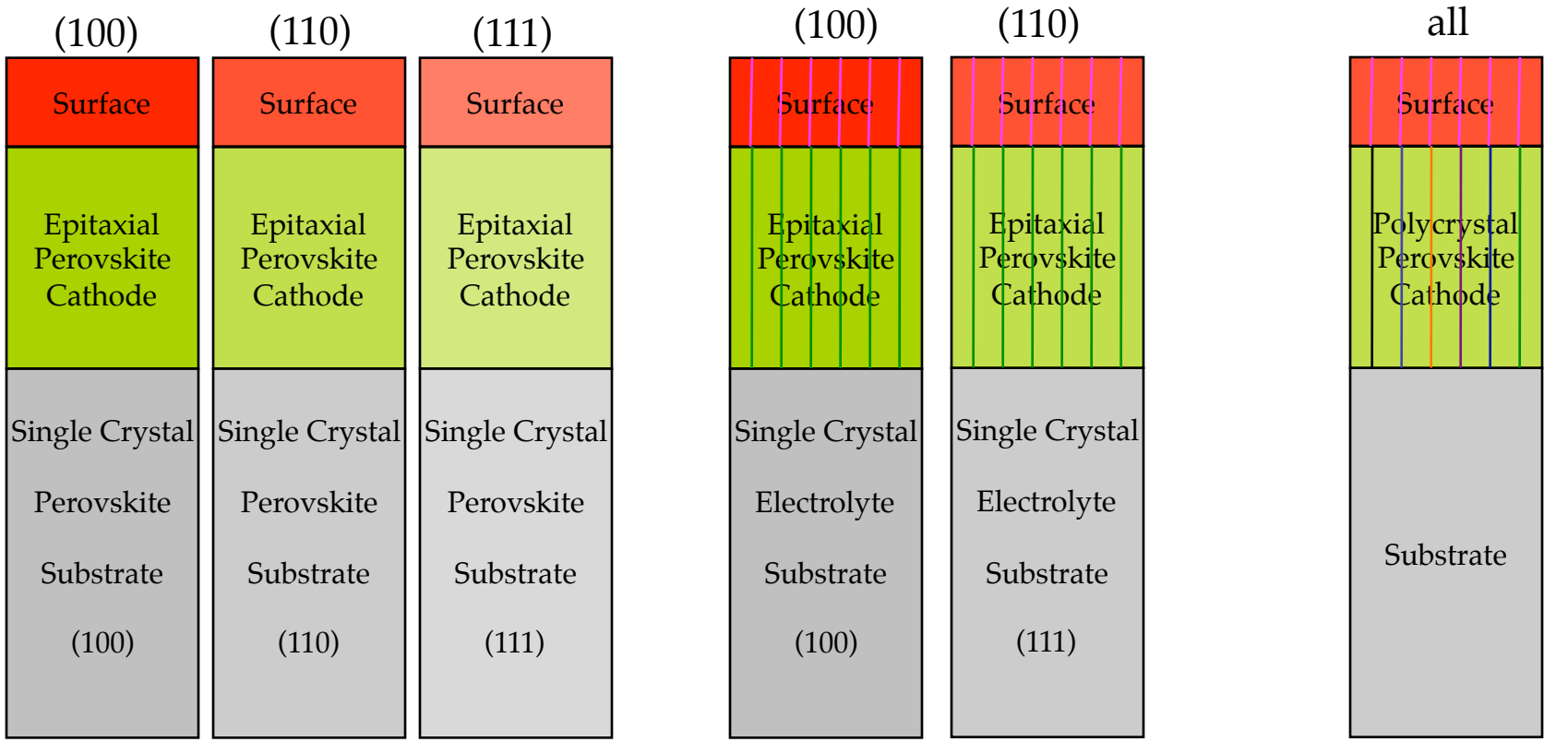
"Ideal" Surface Science Sample



Control Microstructural Complexity and Surface Crystallography

Thin Film Samples Driving Surface Science

Films Allow for Surface / Microstructural Control



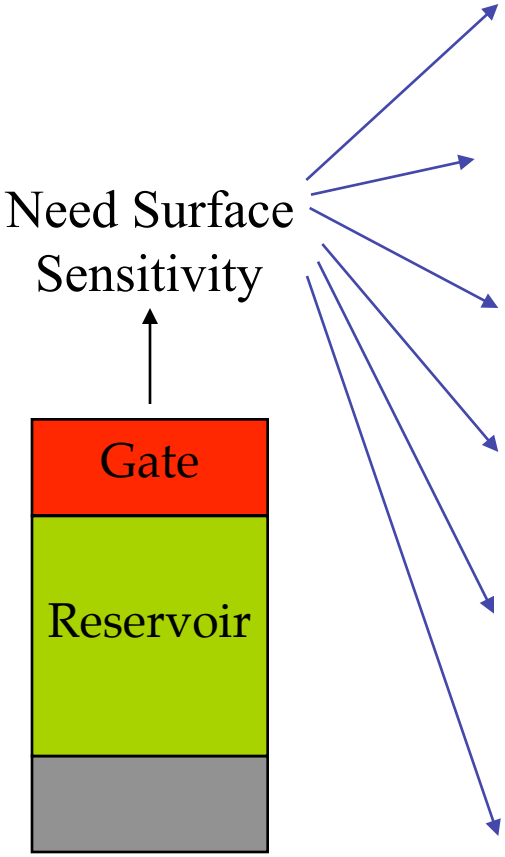
Single Crystal
Specific surface
BULK SURFACES

Multi-variant
Specific surface / boundaries
INFILTRATES

Poly-Xtal
Ensemble

Important to synthesize each version of these.

Experimental Values of Interest that are in Dynamic Equilibrium



1. Oxygen uptake thermodynamics / kinetics
   (CMU / ANL)
2. Surface Structure / cation segregation / dopant distribution
   (CMU / ANL / UNLV / MIT / Stanford)
3. Surface band structure / electronic species
   (MIT / UNLV / CMU / ANL / Stanford)
4. Surface reduction state / surface vacancy concentration
   (CMU / ANL / UNLV / MIT)
5. Performance Characteristics
   (CMU / MIT / ANL)
6. Adsorbed oxygen species
   (…)

Collaborators

Surface Engineering / Characterization / TEM

B. Kavaipatti, L. Yan, S. Wang, R. Petrova
Carnegie Mellon

Surface Stability / Interface Stability

L. Helmick, S. Seetharaman
Carnegie Mellon

R. Gemman, K. Gerdes
NETL

Surface Chemistry

J. Kitchin, Carnegie Mellon

C. Matranga, NETL

Detailed Structure and Surface Segregation vs Oxygen Activity

J. Eastman, D. Fong, P. Fuoss
APS - ANL

Detailed Structure and Surface Segregation vs Electrochemical Activity

K.-C. Chang, D. J. Myers, J. D. Carter, H. You
APS-ANL

B. Yildiz, MIT

Electrochemical Activity and Surface Chemistry

B. Ingram, T. Cruse, M. Krumpelt
ANL

Electronic Structure

Salvador, Carnegie Mellon
W. Harrison, Stanford
C. Heske, UNLV and B. Yildiz, MIT
Y. Mantz, NETL

CMU Work for Cathode Surface Science Project

- ***Growth of High-Quality Thin Film Samples***
  - ***Perovskite / Perovskite Epitaxy and Surface Control***
  - ***Perovskite / Fluorite Epitaxy and Surface Control***
  - *Generation of Surface-Modified Samples*

- ***Surface Kinetics for Oxygen Uptake***
  - ***Electrical Conductivity Relaxation***
  - ***Piezoelectric Crystal Microbalance Gravimetry***
  - *Kelvin Probe Spectroscopy*

- *Surface Thermodynamics of Oxygen Uptake*
  - *Piezoelectric Crystal Microbalance Gravimetry*
  - *Kelvin Probe Spectroscopy*

- *Electronic Structure*
  - *Kelvin Probe Spectroscopy*
  - *STM (MIT)*

- *Ex-situ Surface Characterization for Correlations*
  - *Scanning Auger / XPS*

Pulsed Laser Deposition
Laser MBE / MBE

Advantages of PLD

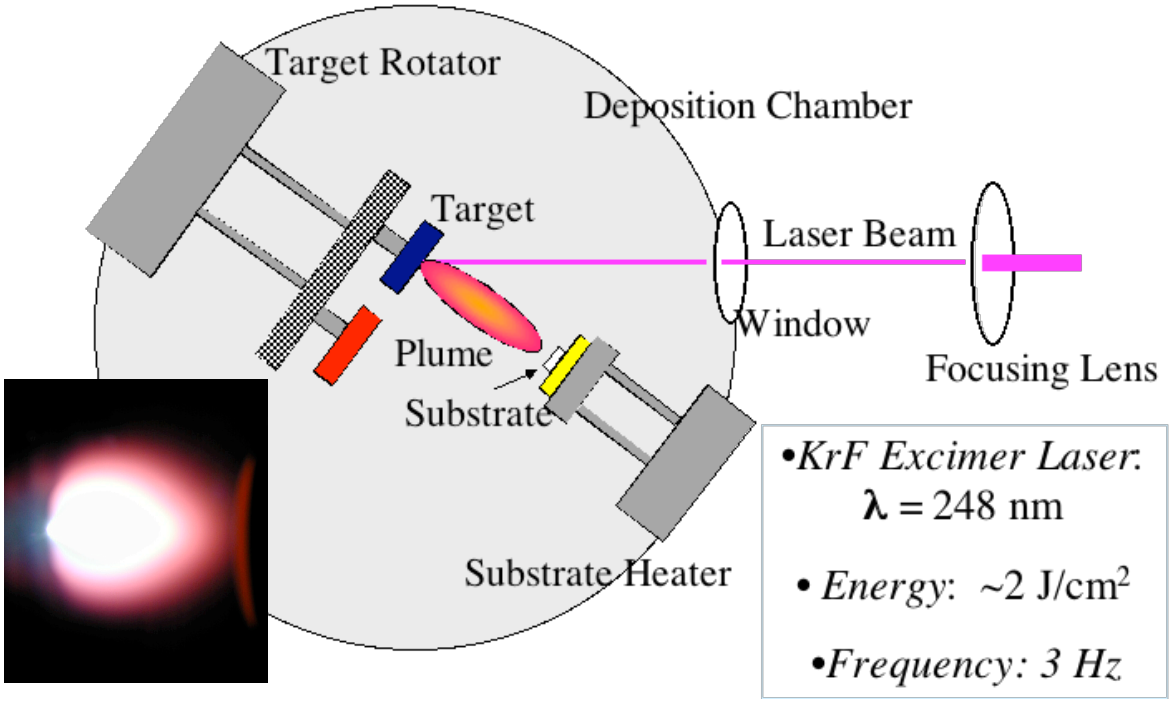
- Targets made via standard methods.
- Stoichiometric transfer from target to film
- High-quality epitaxial films for complex oxides
- High-Quality Metal Films
- Simple, versatile, and relatively inexpensive
- House 6 targets at once

Deposition Parameters

PRESSURE : 0.00001 - 0.2 Torr
TEMPERATURE: RT - 950 °C
FLUENCE : 1-8 J/cm^2
FREQUENCY : 1-10 Hz
COOLING: 0.00001- 300 Torr

Depositions : 1- 4 hrs Max
3 - 4 deps / day
3 - 4 samples / dep

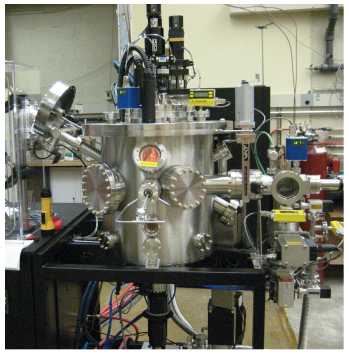
Pulsed Laser Deposition

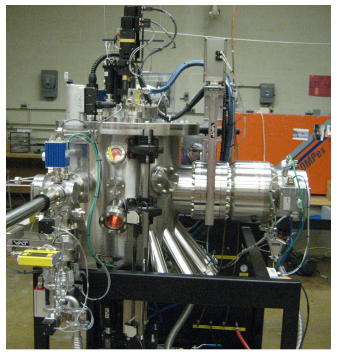


•*KrF Excimer Laser*:
$\lambda = 248$ nm

• *Energy*: ~2 J/cm^2

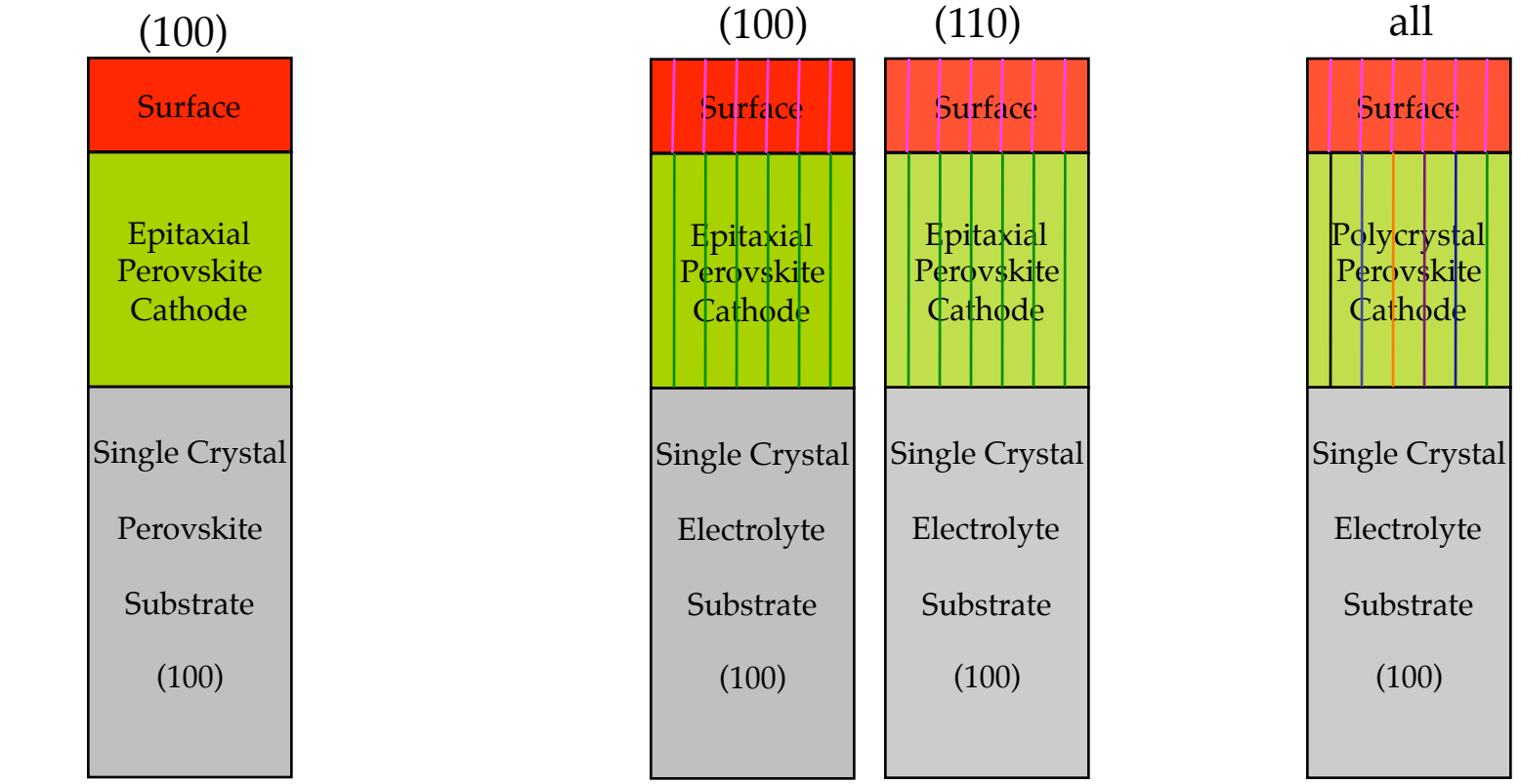
•*Frequency: 3 Hz*





The Natural Starting Point Seems to be YSZ (100)

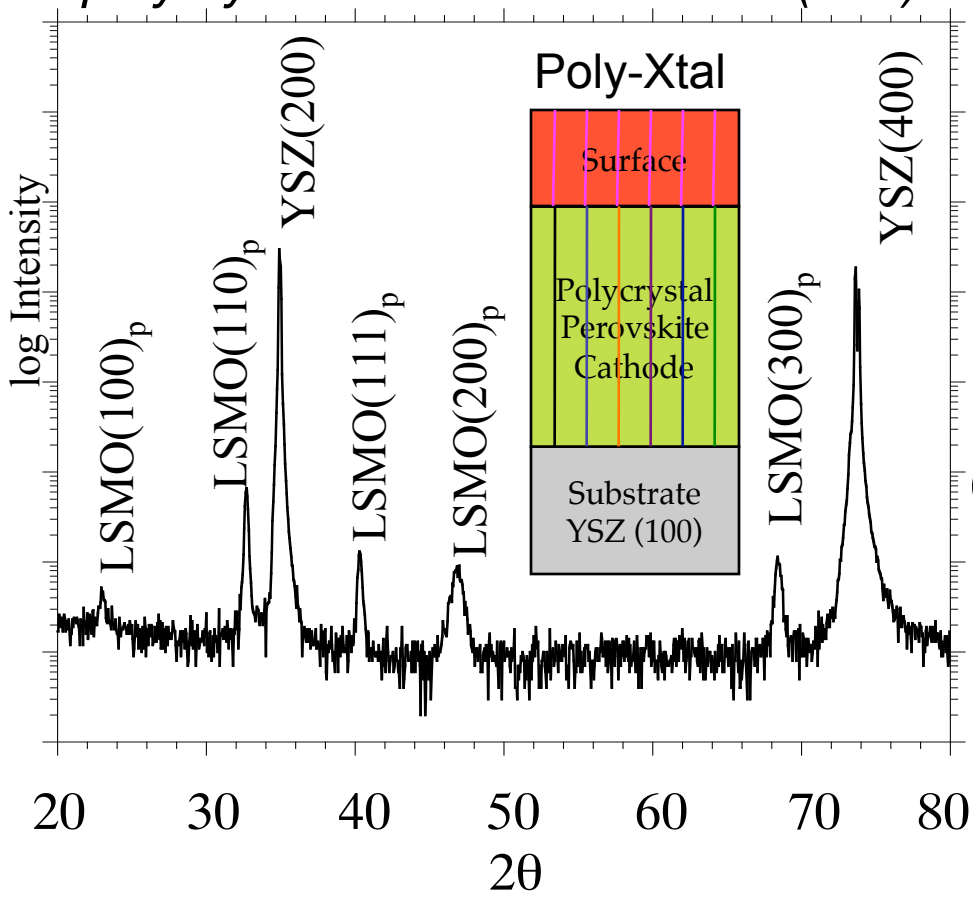
Ideal substrate to do electrochemistry
Ideal Substrate to correlate to real SOFC cathodes
Can we get surface engineered samples routinely?



Single Crystal Multi-variant Poly-Xtal

$(La,Sr)MnO_3$ thin films on YSZ(100)

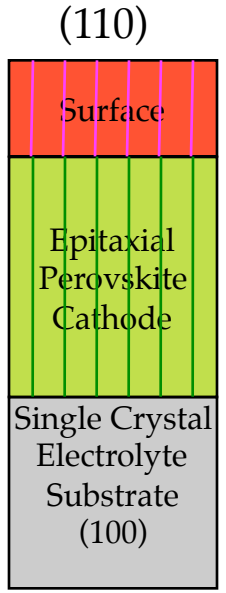
Film prefers to grows in a polycrystalline fashion on YSZ(100)



Good for comparison to real SOFC

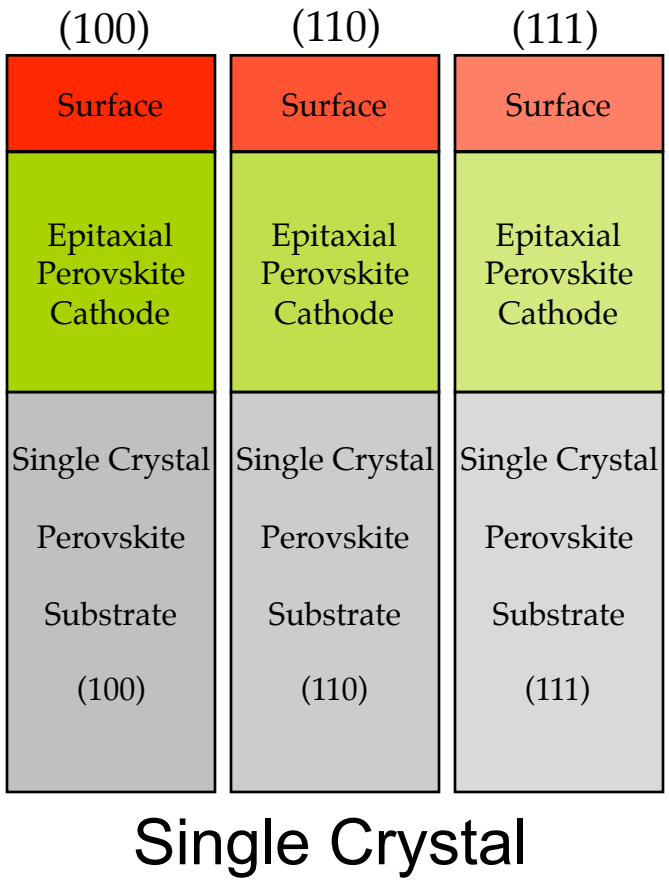
Poor for Surface Science

(110) Textured films are strong function of conditions not fully textured



Perovskite / Fluorite Interface in ESSENTIAL in final ION TRANSFER
But we need better growth

Focus on Epitaxial Films with Controlled Surfaces



- *Many Available Commercial Substrates*
  - *$SrTiO_3$ (100), (111), (110)*
  - *Nb-doped $SrTiO_3$ (100), (110), (111)*
  - *$LaAlO_3$ (100)*
  - *$NdGaO_3$ (100), (110)*
  - *$DyScO_3$ (100)*
  - *LSAT (100)*

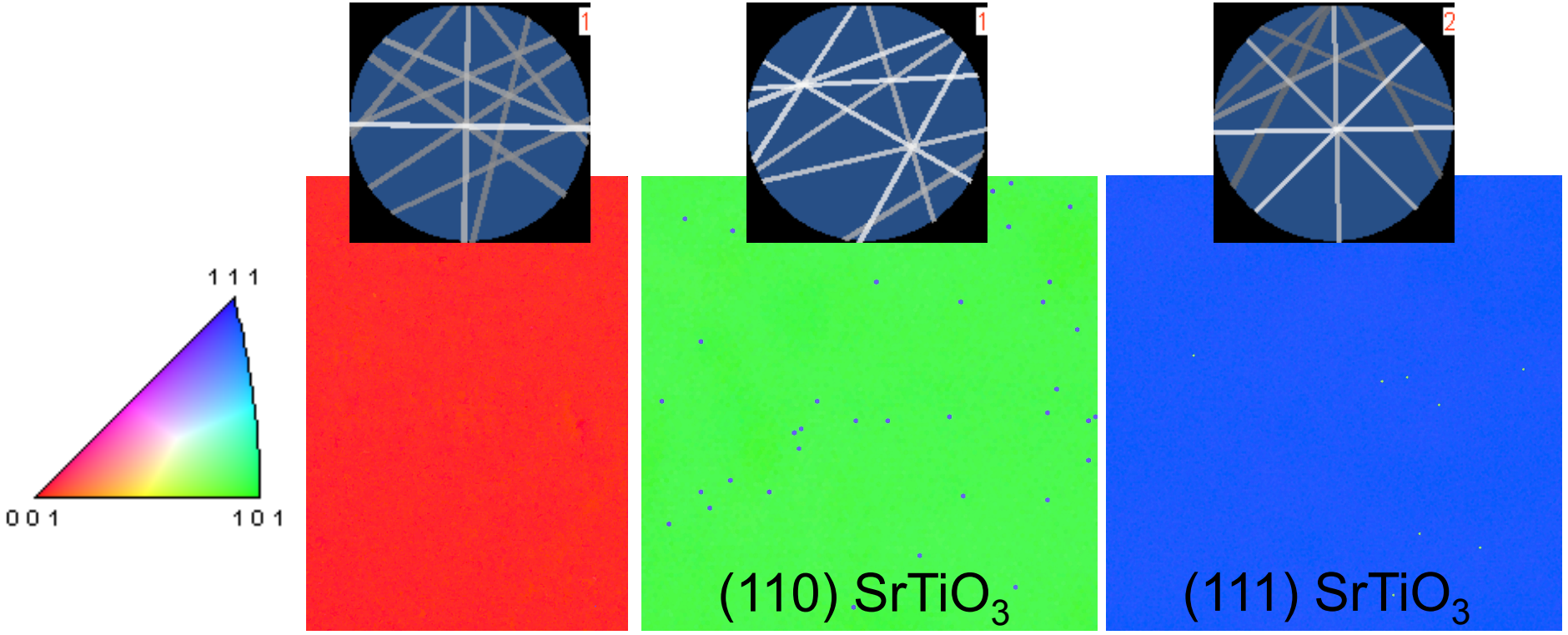
- *Can vary widely*
  - *Chemical elements in substrate*
  - *Strain state*
  - *Crystal Symmetry*
  - *Surface Morphology*
  - *Conductivity (e- / ion)*
  - *Dislocation content*

- *Generates IDEAL surfaces for investigation*

- *How do film properties depend on substrate?*

Epitaxy along various Orientations
Orientation Mapping / Surface Sensitivity

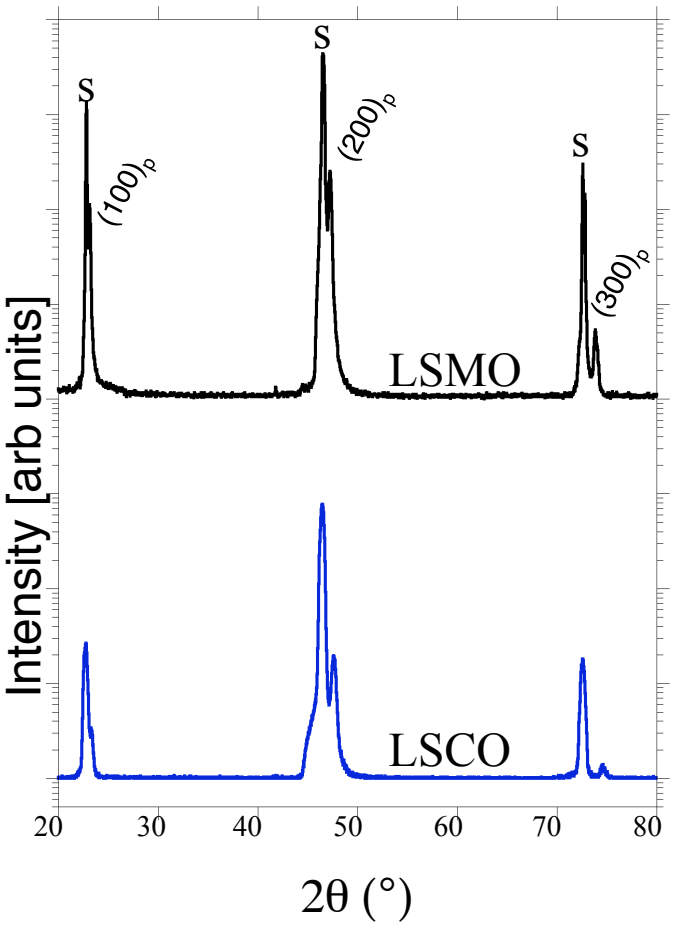
Electron Back-Scattered Diffraction used to Identify Local Orientations
$La_{0.7}Sr_{0.3}MnO_3$ (50 nm) deposited on $SrTiO_3$
All scan areas > 20 x 20 micron^2

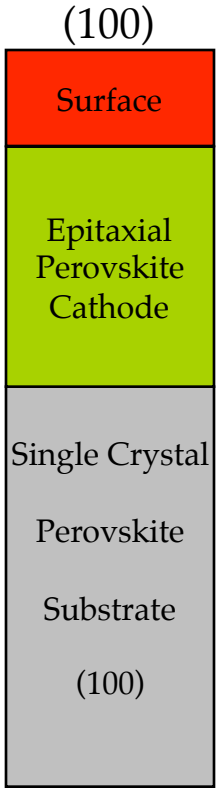


All three low-index surfaces are obtained as epitaxial films

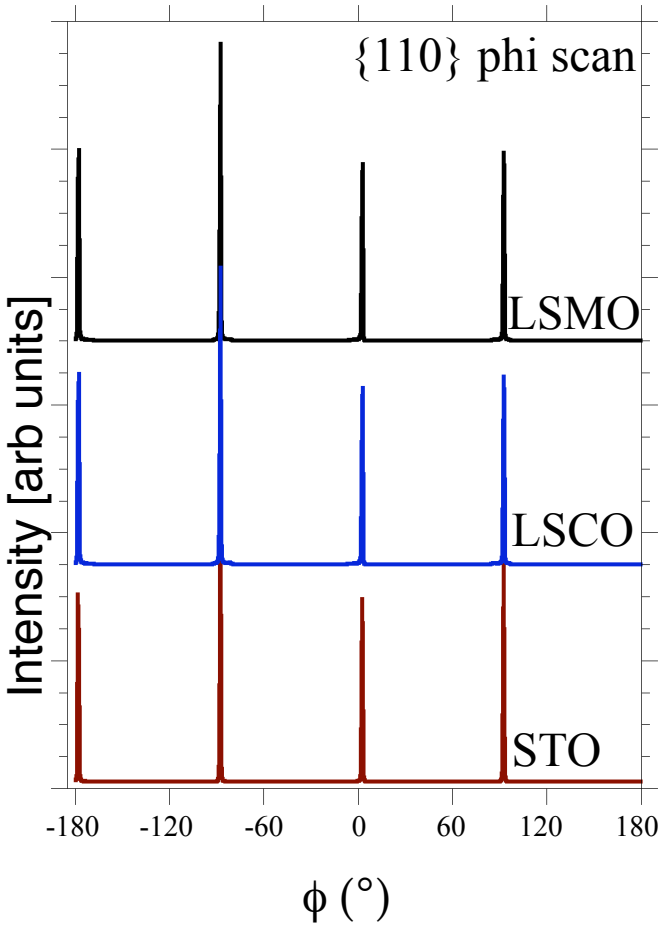
XRD: 60 nm LSMO and LSCO on STO(100) Perovskite – Perovskite Epitaxy

LSM and LSC
Out-of-plane Texture (100)





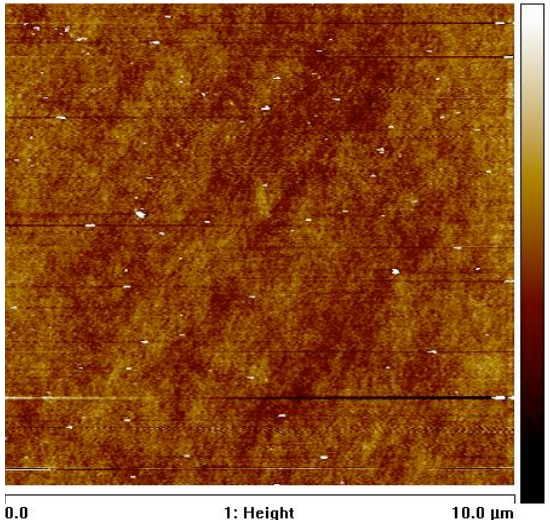
LSM and LSC
In-plane Texture $[100]_{film}||[100]_{subs}$



- *Perovskite - Perovskite Epitaxy is excellent for both film compositions*
- *Similar results are found for other orientations*

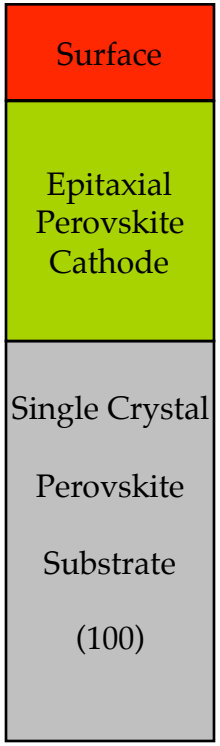
AFM: 60 nm LSMO and LSCO on STO(100)
Surface Features are Unit-Cell Smooth

LSMO

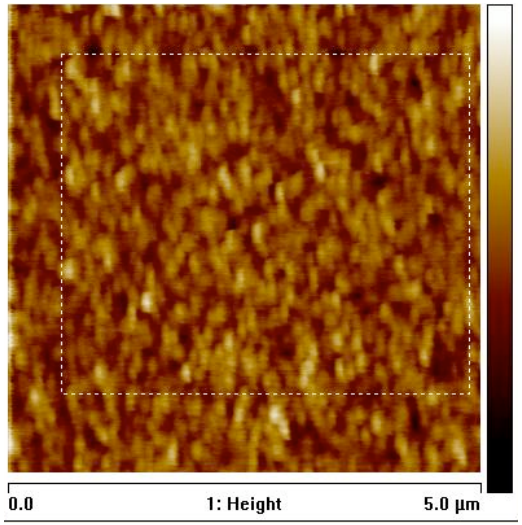


rms roughness = 4.41 A

(100)



LSCO



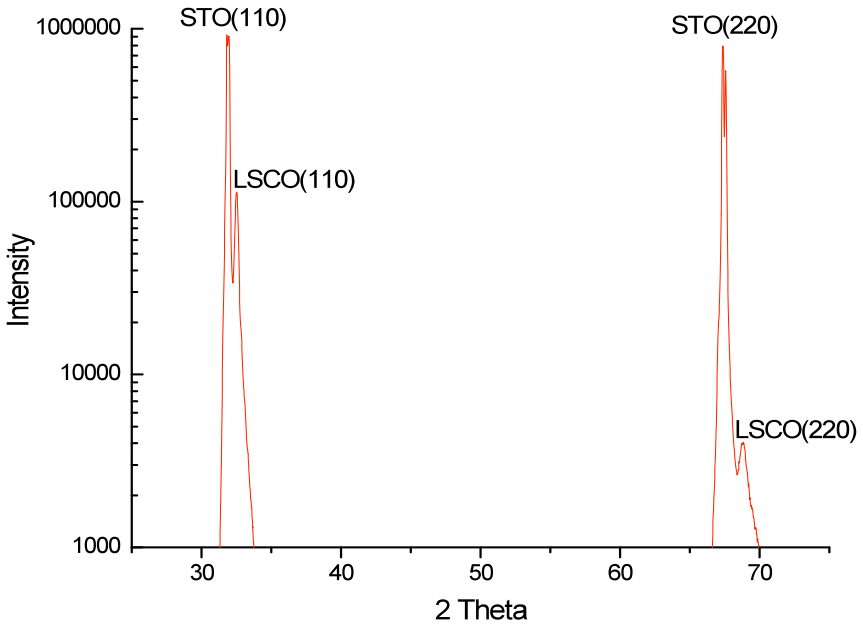
rms roughness = 4.53 A

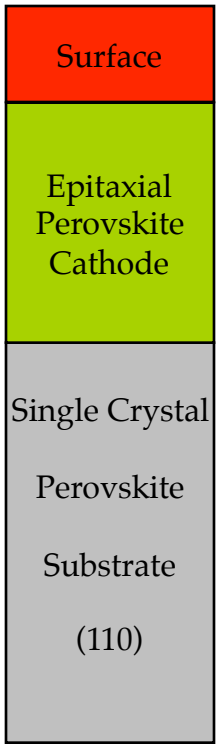
- *Surface Features are well defined*
  - *Films are atomically smooth*
  - *Required for surface sensitive X-ray / STS*
  - *Required for understanding overall surface response*

- *Similar results are found for other orientations*

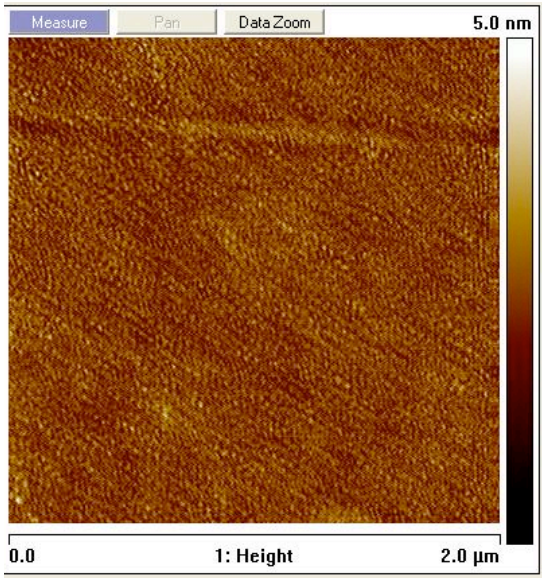
60 nm LSCO on STO(110)
XRD and AFM

LSC
Out-of-plane Texture (110)





LSC
Unit-cell smooth films

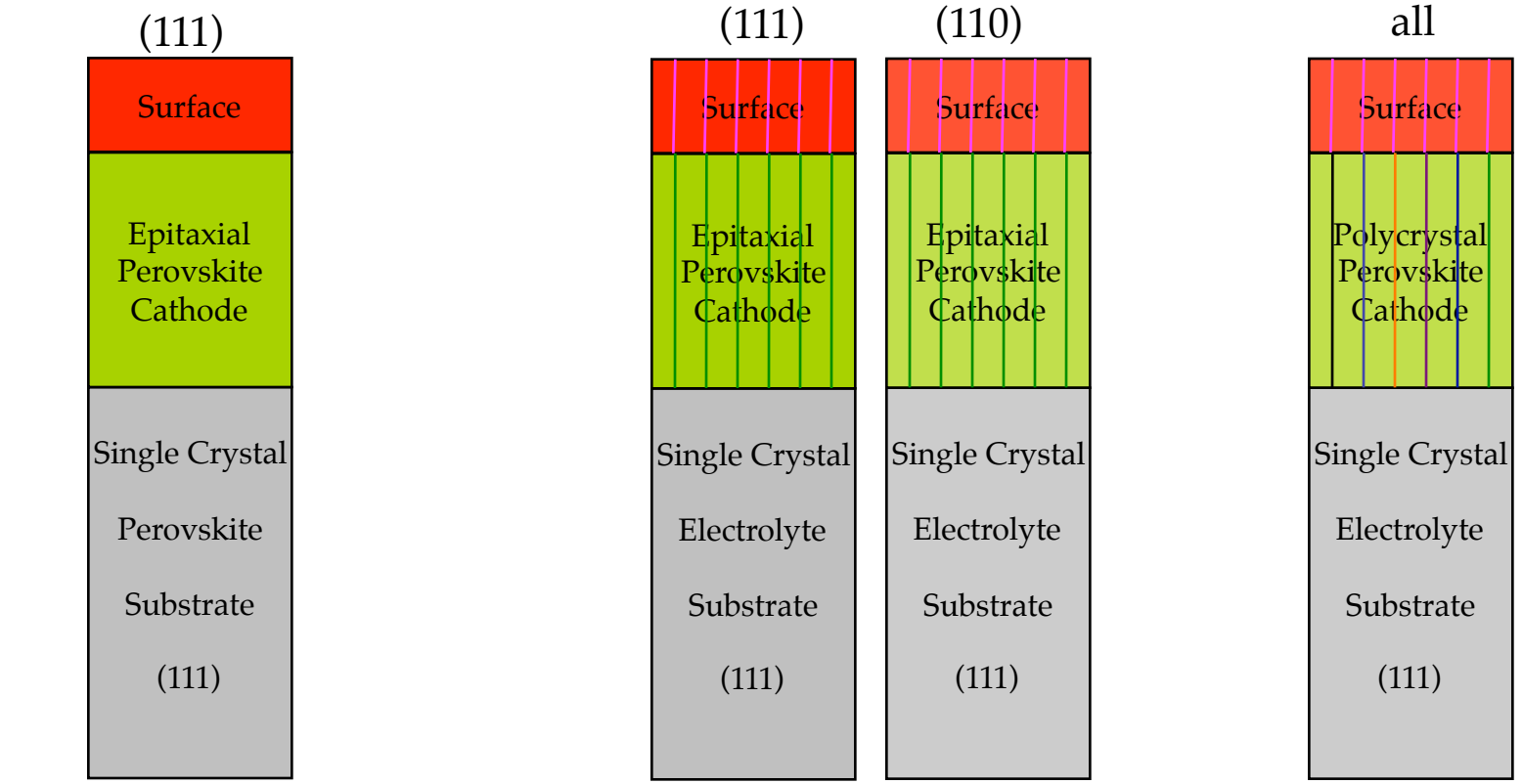


rms roughness = 2.91 A

- *Perovskite - Perovskite Epitaxy is excellent for LSC in this orientation*
- *Similar results are found for other chemistries*

Returning to Electrolyte Substrates: What Happens on YSZ (111)?

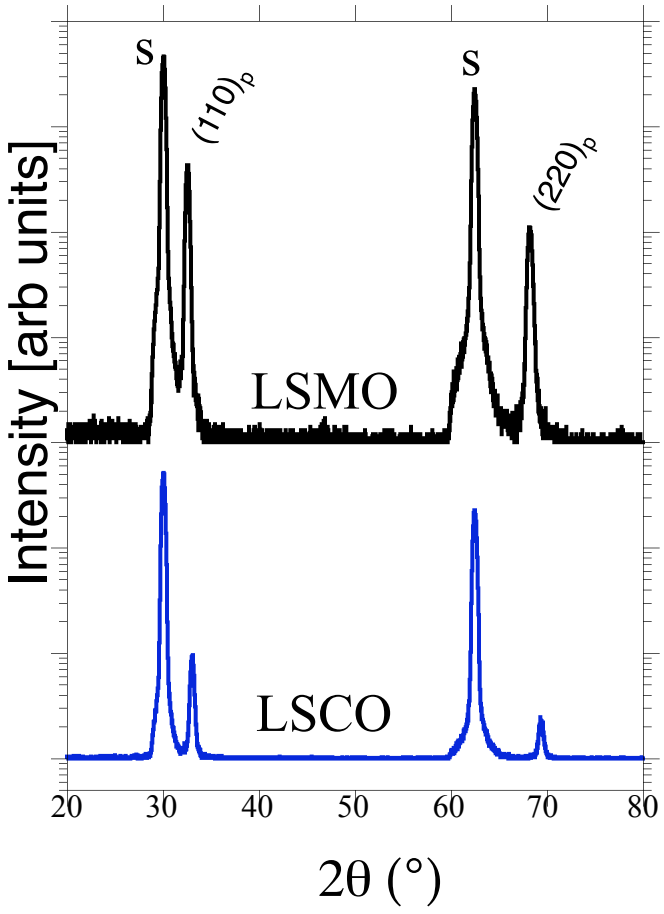
Ideal substrate to do electrochemistry
Ideal Substrate to correlate to real SOFC cathodes
Can we get surface engineered samples routinely?

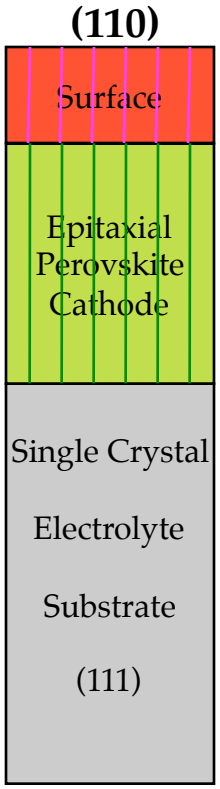


Single Crystal Multi-variant Poly-Xtal

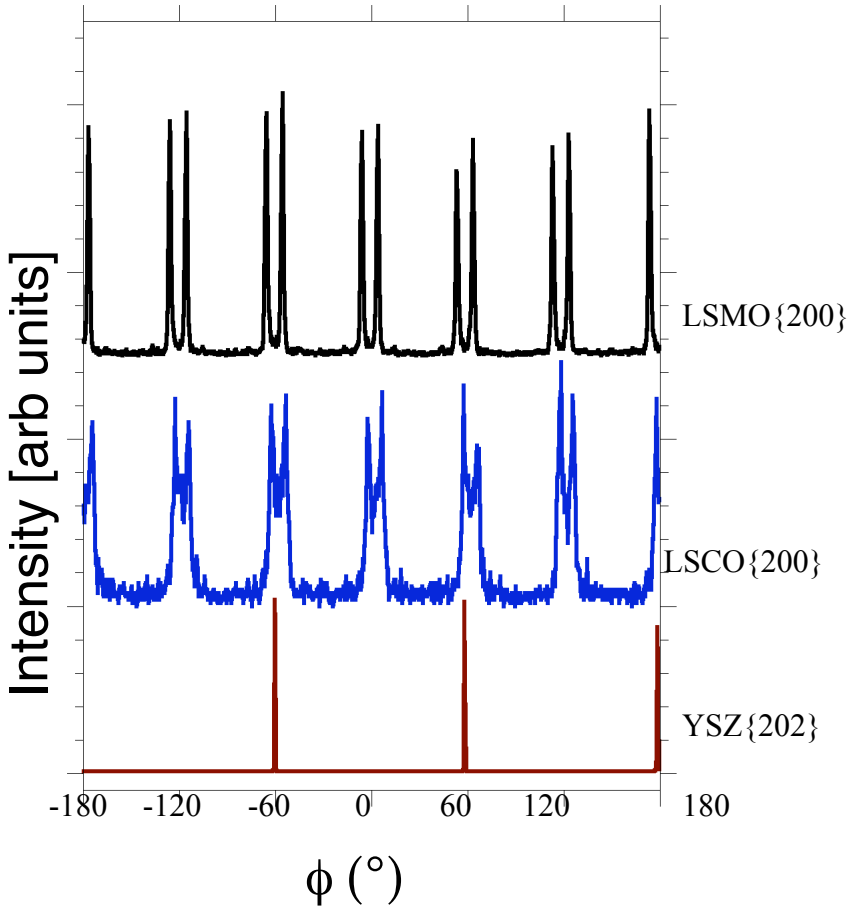
XRD: 60 nm LSMO and LSCO on YSZ(111) Perovskite – Fluorite (electrolyte) Epitaxy

LSM and LSC
Out-of-plane Texture (110) on YSZ (111)





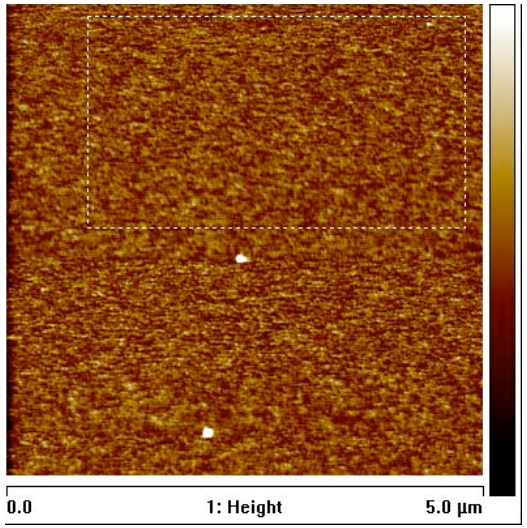
LSM and LSC
In-plane Texture $[111]_{film}||[11\text{-}2]_{subs}$



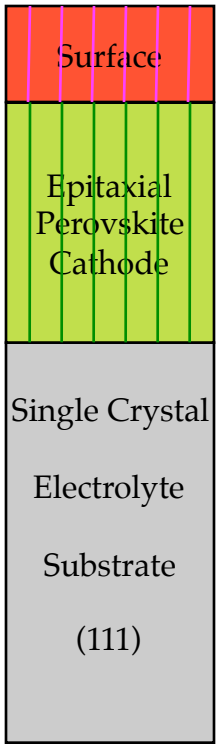
- *Perovskite - Fluorite (YSZ) Epitaxy is same for both film compositions*
- *In-plane epitaxy leads to six degenerate variants: variant boundaries*

AFM: 60 nm LSMO and LSCO on YSZ(111)
Surface Features are Unit-Cell Smooth

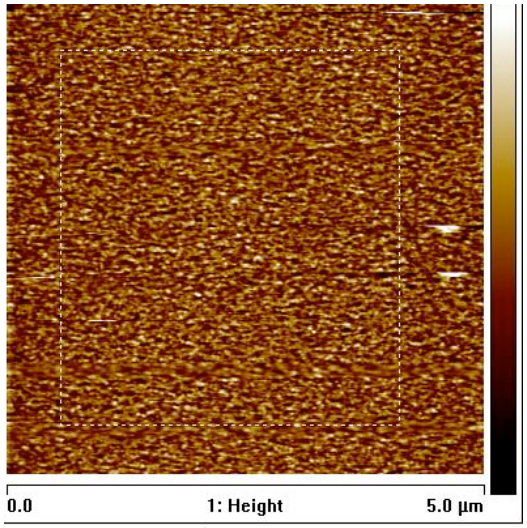
LSMO



rms roughness = 3.21 A



LSCO

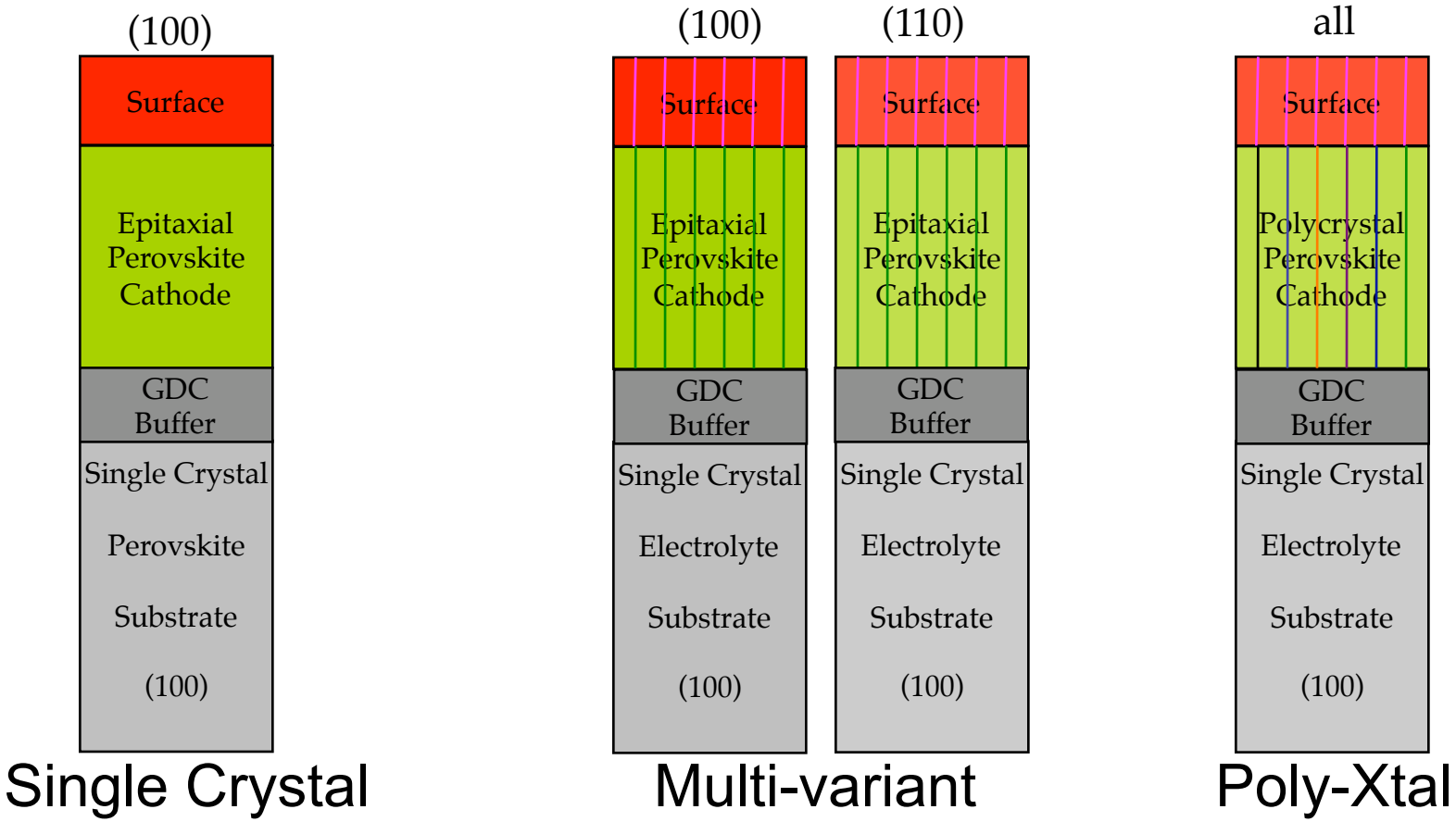


rms roughness = 5.10 A

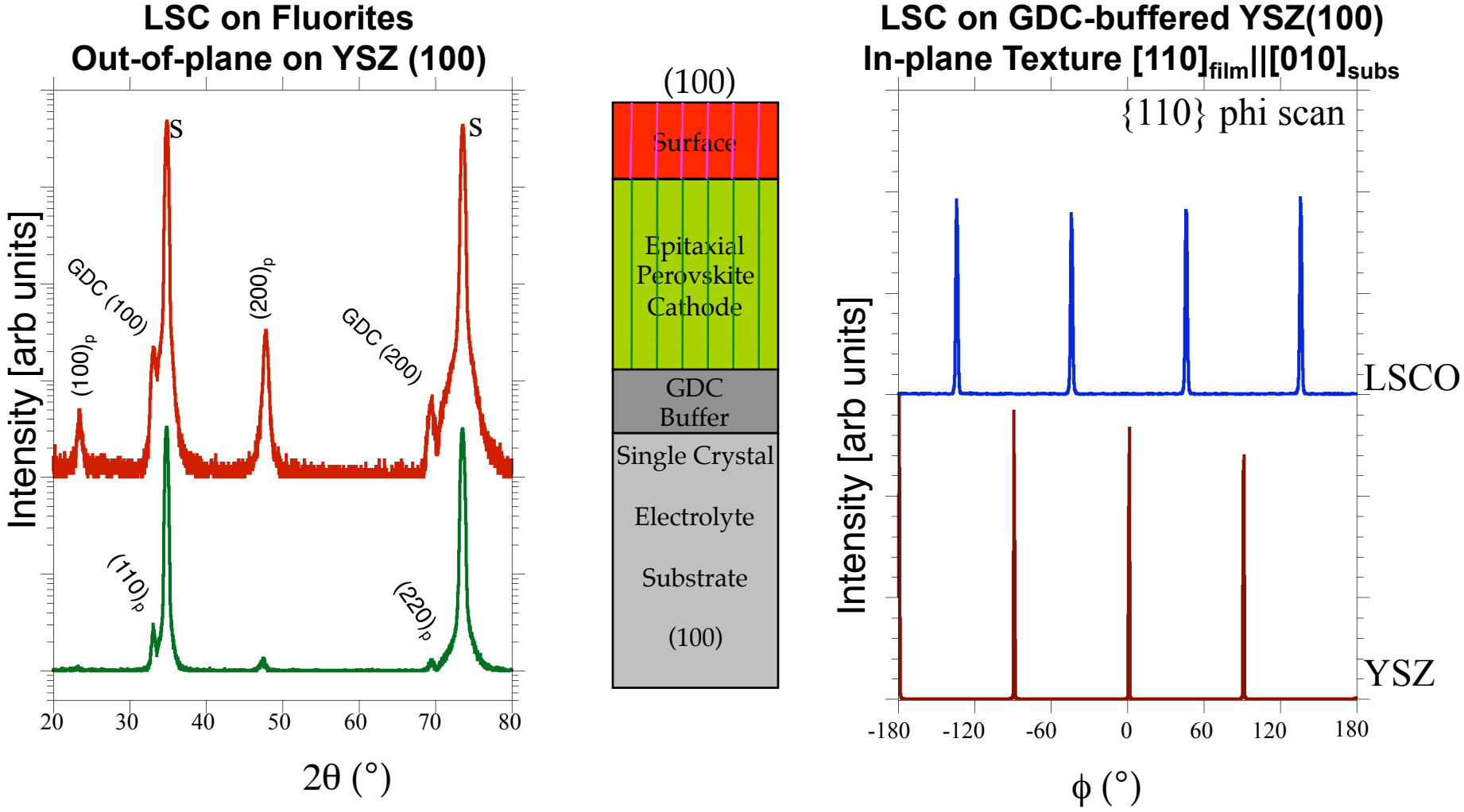
- *Surface Features are well defined*
  - *Films are unit-cell smooth*
  - *slight increase for LSCO roughness, but still unit-cell smooth*

Can we attain Surface Engineered Samples on YSZ (100)?

Insert a Buffer Layer of GDC to Change Mismatch and Chemistry
Useful Heterostructure for LSCF Measurements



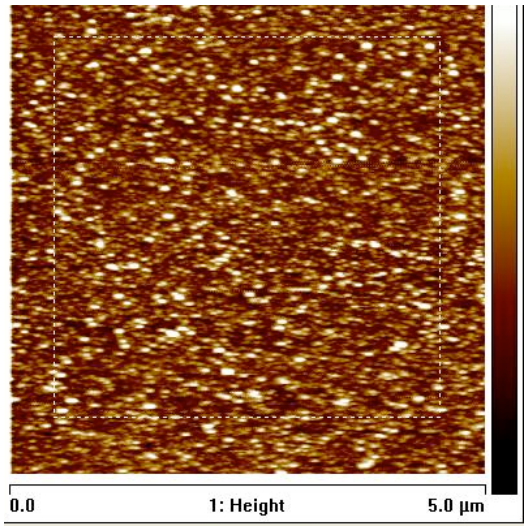
XRD: 100 nm LSCO on YSZ(100) and GDC(50 nm)-YSZ(100)
Epitaxy on 100-oriented electrolyte obtained



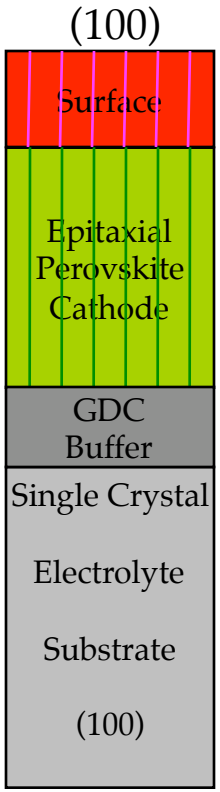
- *Perovskite - Fluorite (YSZ) (100) Epitaxy is found on GDC(100)*
- *In-plane epitaxy leads to four degenerate variants: variant boundaries*

AFM: LSCO on YSZ(100) and GDC-Buffered YSZ(100)
Epitaxial Surface Features are Unit-Cell Smooth

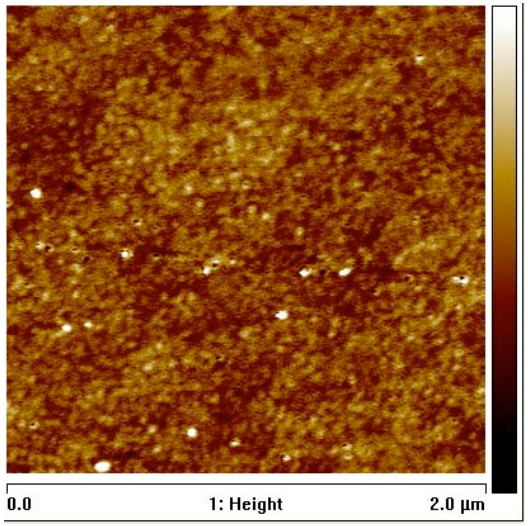
LSC on YSZ(100)



polycrystalline
rms roughness = 6.0 A



LSC on GDC-buffered YSZ(100)



Multivariant epitaxy
rms roughness = 2.67 A

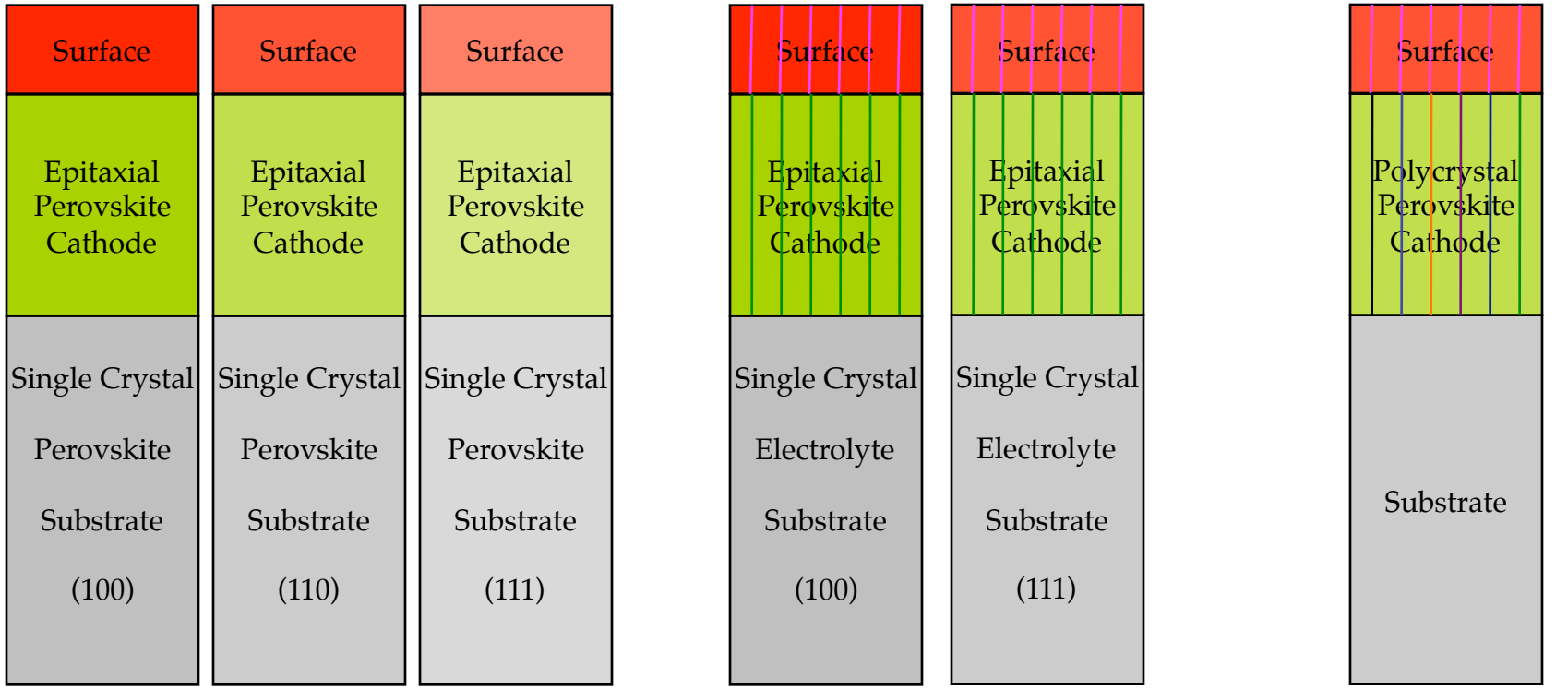
- *Surface Features are well defined*
  - *Films are unit-cell smooth*
  - *Good decrease for epitaxial LSCO films*

Thin Film Samples Driving Surface Science

Reaction Occurs at Surface:

1/2 O_2(g)	**+ 2e^-**	**→**	**O^{2-}**
pore	*conductor*		*ion conductor*

Films Allow for Surface / Microstructural Control



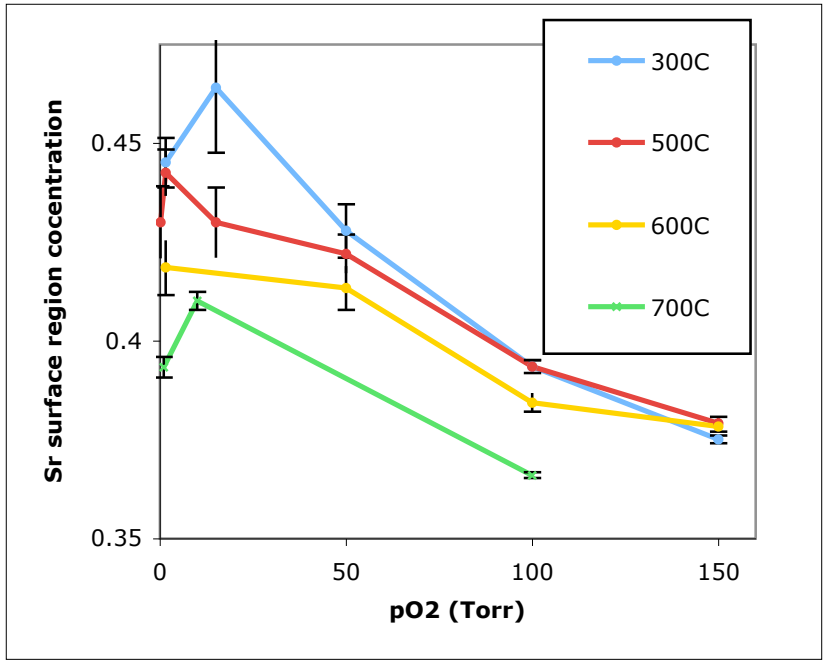
Single Crystal Multi-variant Poly-Xtal

Summary of Sample Preparation

- *Growth of High-Quality Thin Films*
  - *Perovskite / Perovskite Epitaxy and Surface Control Achieved*
    - *LSM and LSC (and LNO) deposited on many Perovskites*
    - *Cube-on-cube epitaxy on various orientations*
    - *Unit-cell roughness obtained*
  - *Perovskite / Fluorite Epitaxy and Surface Control Achieved*
    - *LSM and LSC (110)[111] epitaxy on YSZ (111)[[11-2]*
    - *LSM and LSC (100)[011]epitaxy on GDC-YSZ (100)[010]*
    - *Unit-cell roughness obtained*
    - *6 and 4 variants observed on (111) and (100) fluorites*
  - *Samples Provided to Collaborators*
    - *Measured Surface Chemistry at APS*
    - *Measured Electronic Properties at MIT*

Chemistry of (100) LSMO Surfaces

20 nm thickness $La_{0.7}Sr_{0.3}MnO_3$



TXRF Spectra Show Sr-Enhancement

Not a function of Strain / Substrate

Is a function of T and Pressure
Reversible

How does THIS effect properties?

Detailed Structure and Surface Segregation vs Oxygen Activity

J. Eastman, D. Fong, P. Fuoss
APS - ANL

Detailed Structure and Surface Segregation vs Electrochemical Activity

K.-C. Chang, D. J. Myers, J. D. Carter, H. You
APS-ANL

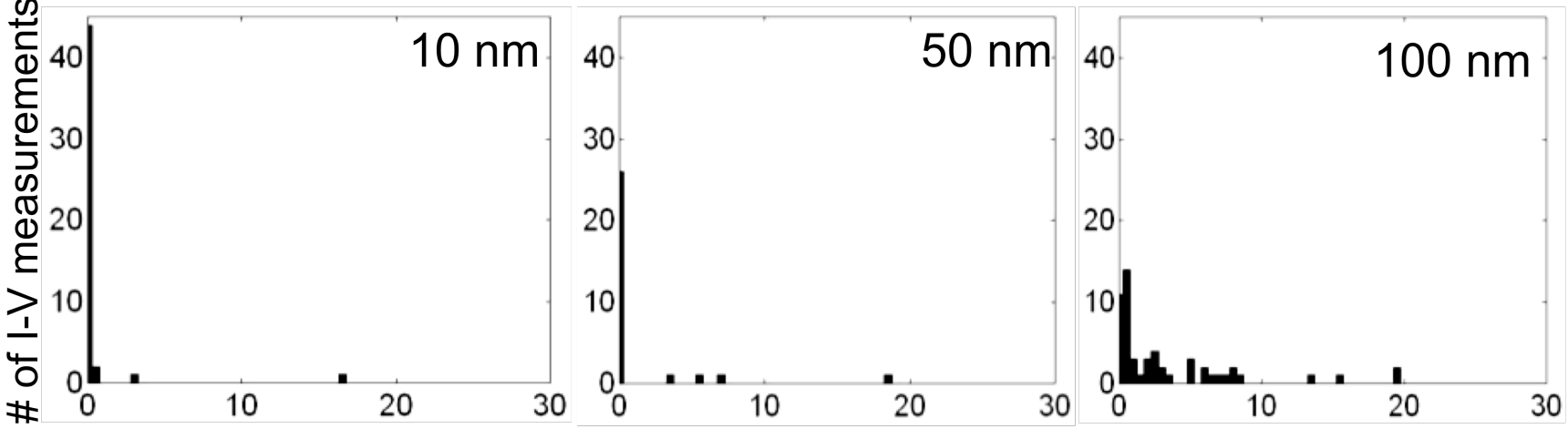
B. Yildiz, MIT

Thickness Dependent Properties
LSMO on Nb-Doped STO(100)

Thin Layers are fully strained (XRD)
Thin layers can relax by point defect formation
Films relax with thickness by dislocation formation
Interface with substrate can affect fermi level location

Scanning Tunneling Spectroscopy

B. Yildiz et al., MIT

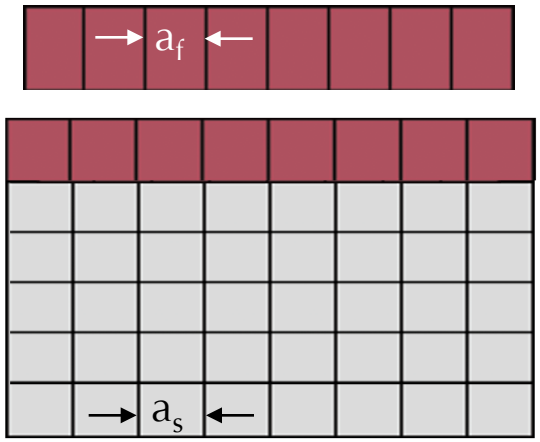


Thinner LSM films have insulating surfaces
with large band gap (1.5 – 2.2 V) at ambient conditions.

Cathode thin film growth – Substrate choice and orientation

Mismatch Strain

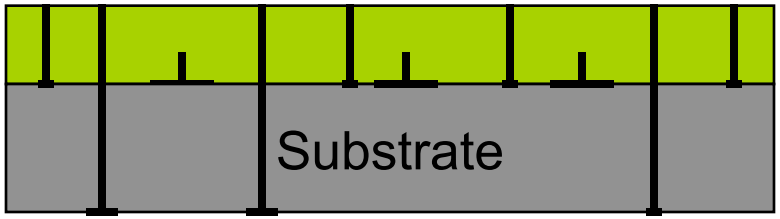
$$f = \frac{(a_s - a_f)}{a_f}$$



$$w_{strain}^{\max} = \frac{2\mu(1+\nu)f^2}{(1-\nu)}$$

Dislocations

Misfit
Threading (relaxation)
Threading (inherited)



Substrates have different lattice mismatches and Different dislocation densities

ECR part: $La_{0.6}Sr_{0.4}CoO_3$ (50nm film) on YSZ (111)

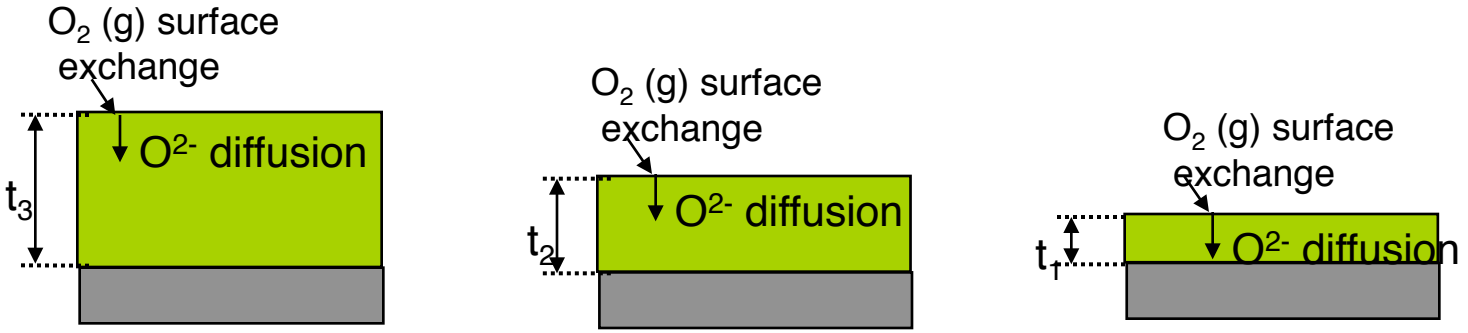
Background:

An abrupt change in oxygen pressure → ΔC_{O2} in MIEC.
Measuring $\Delta\sigma_e$ can → monitor ΔC_{O2} in MIEC.
Analyzing the ECR data → get $\tilde{D}$ and/or k

Characteristic length of the sample: $l_d = \tilde{D}/k$

$\tilde{D}$:chemical diffusion coefficient

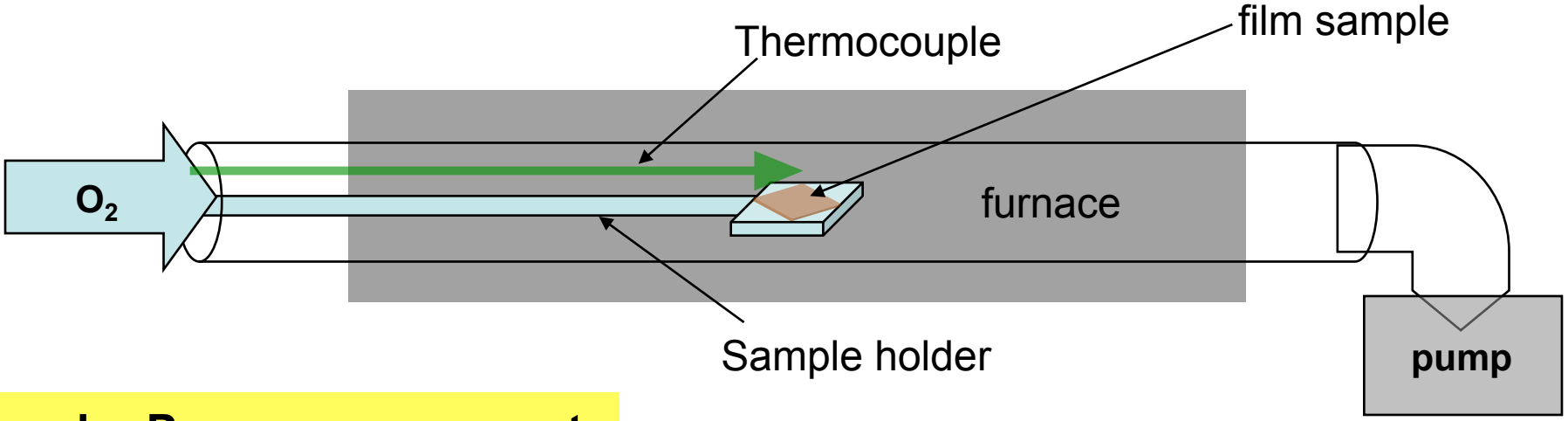
k :surface exchange coefficient



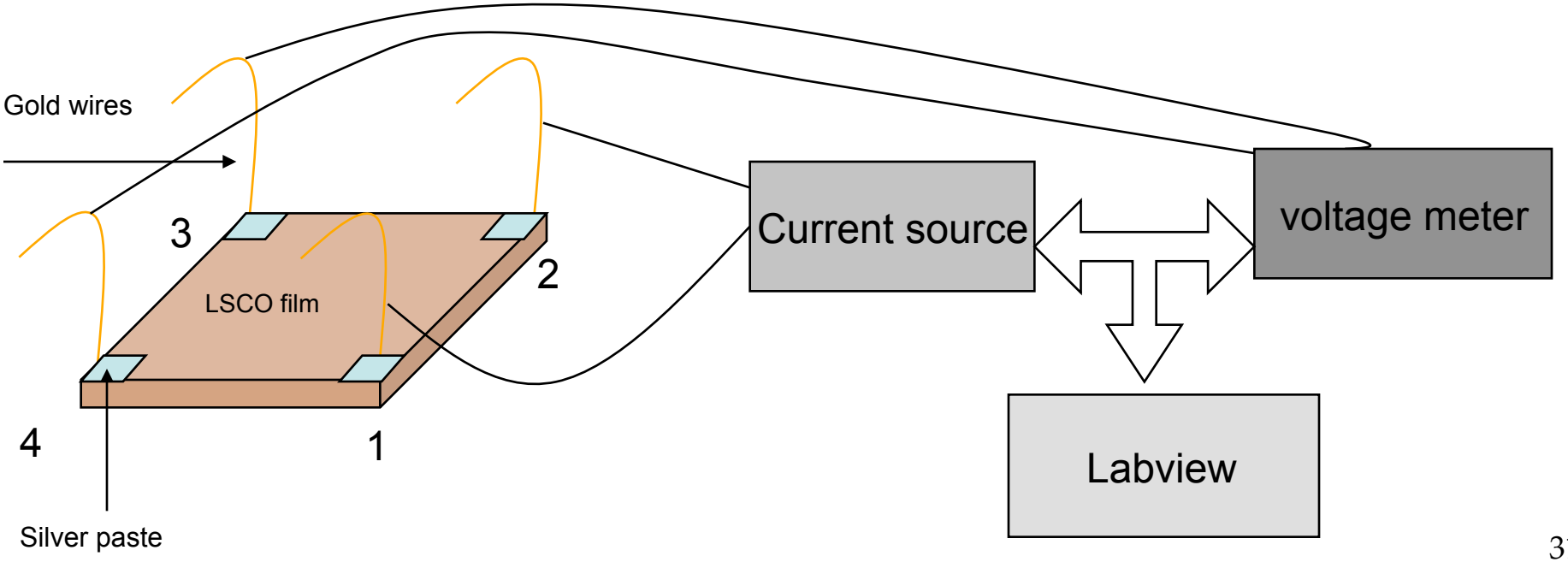
$t_3 \gg l_d$ $\quad$ $t_2 \approx l_d$ $\quad$ $t_1 \ll l_d$

$\tilde{D}$ $\quad$ $\tilde{D}, k$ $\quad$ k

Experimental Approach for ECR: Determine surface exchange constant k_{chem}



Van der Pauw measurement:

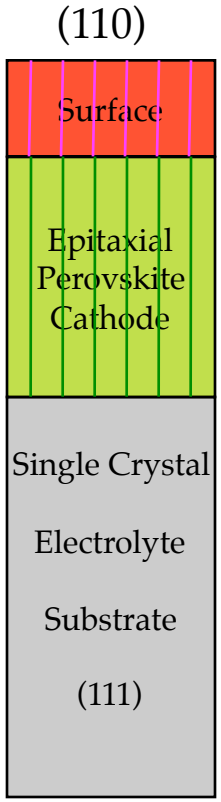


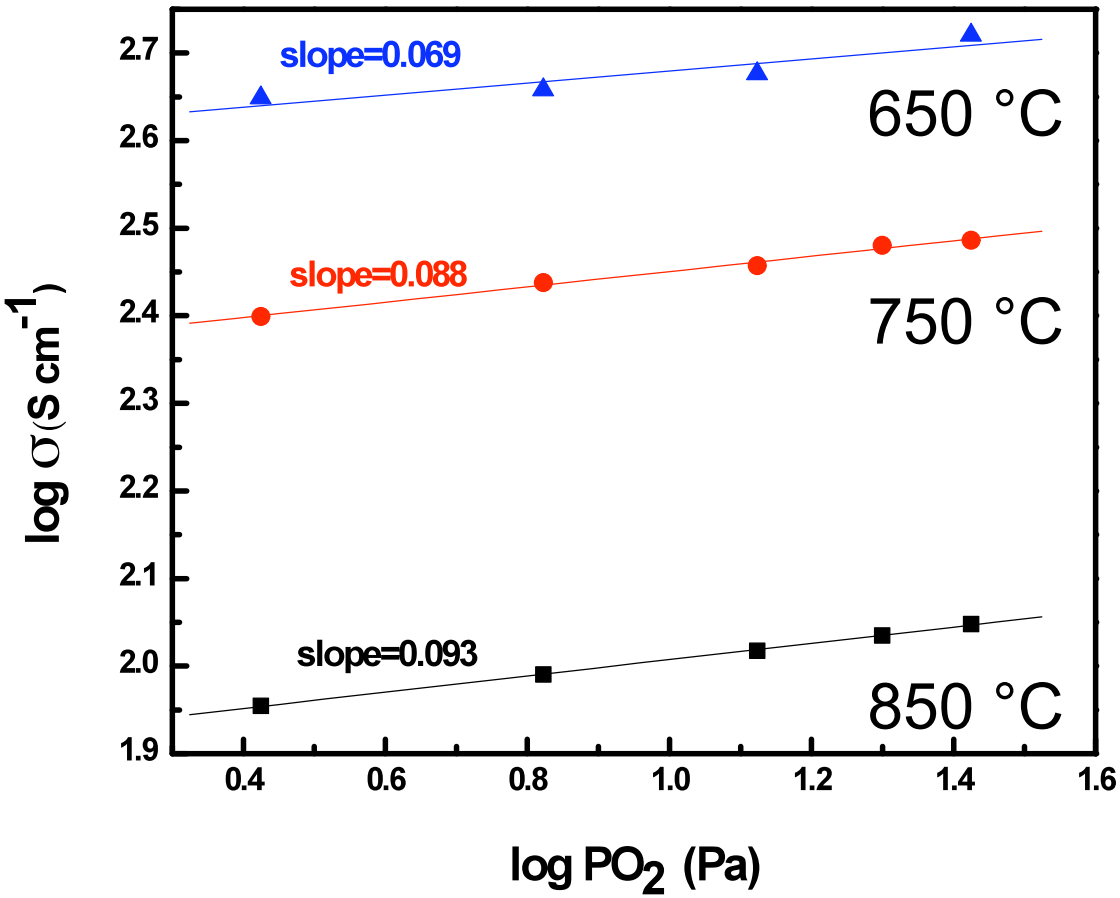
50 nm thick LSCO(110) on YSZ(111) Nanoparticle Infiltration Thickess

Pressure Range Corresponds

reducing regions for cathodes (10^{-8} - 10^{-4} atm)

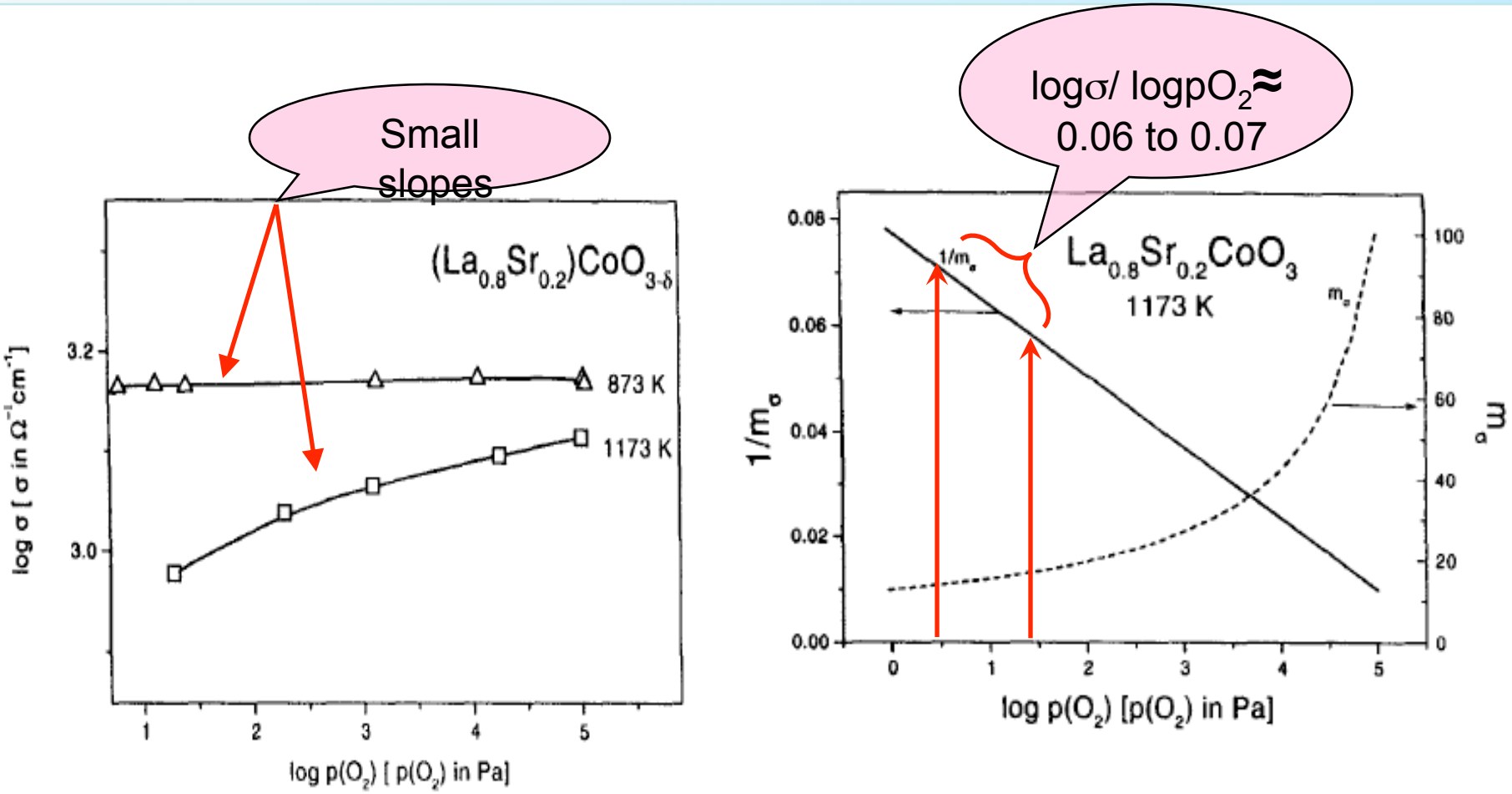
film growth pressure ranges (.01 – 100 mTorr)





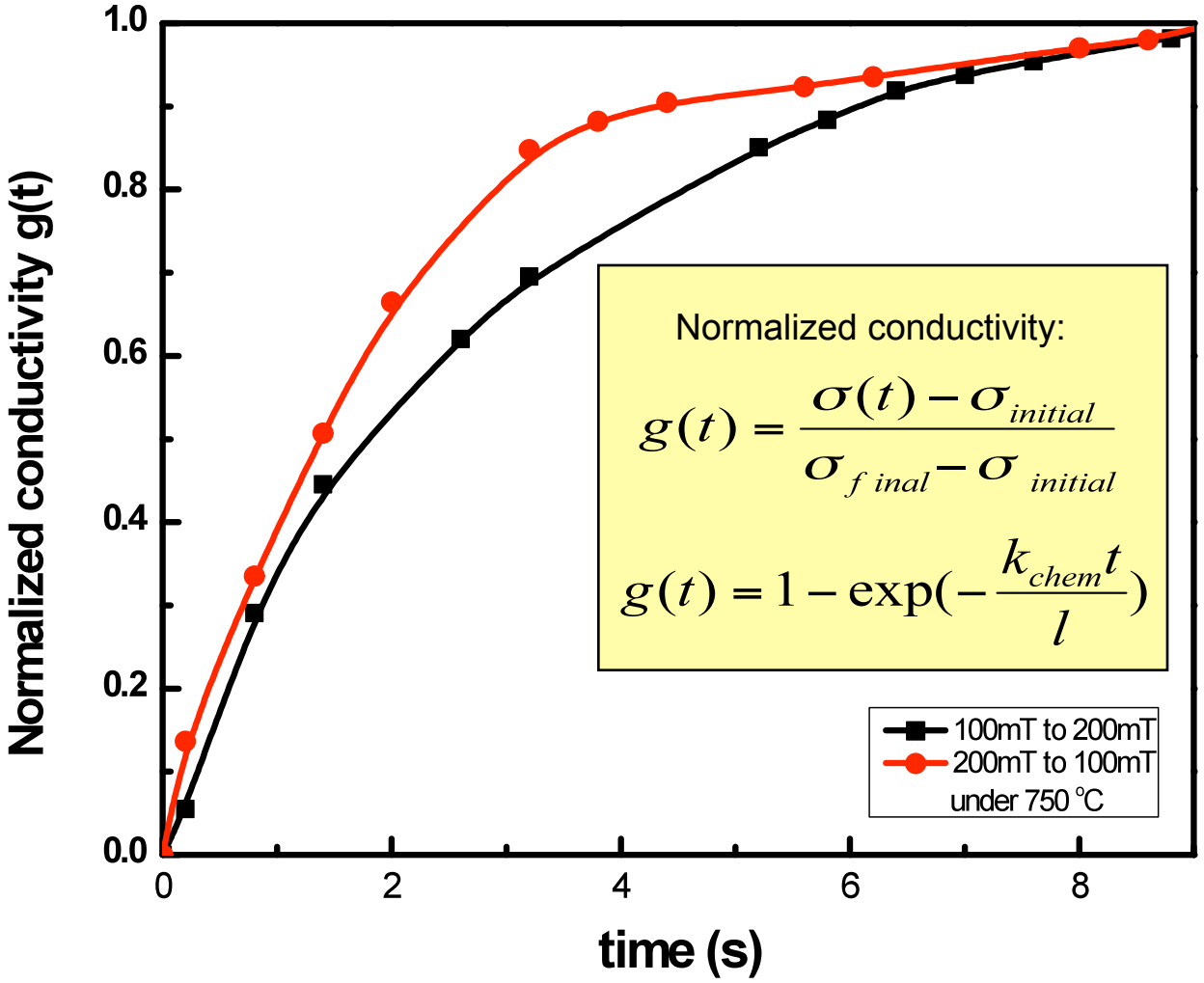
Steady State Values Provide a Reality Check and Allow us to Explore Bulk Changes

LSCO electrical properties Agree with Literature Observations



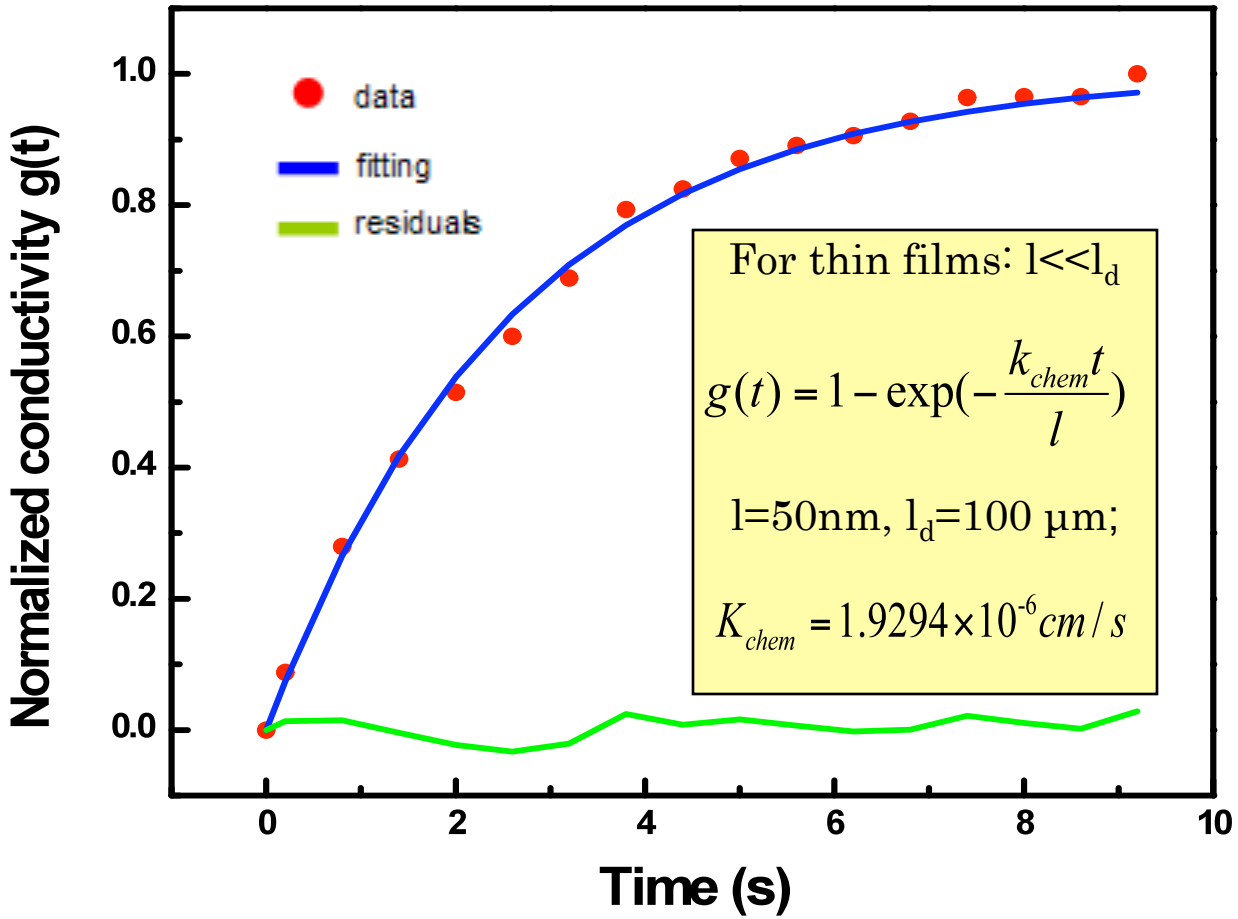
Bak et al., Ionics 7 (2001) 388;
Mizusaki et al., J. Electrochem. Soc., 136 (1989) 2082.

ECR Measurement
(50nm) $La_{0.6}Sr_{0.4}CoO_3$ (110) / YSZ (111)



- *ECR can be measured using the vacuum arrangement*
- *Resistivity values are similar to those reported in literature*

ECR Fitting / k_{chem} determination
(50nm) $La_{0.6}Sr_{0.4}CoO_3$ (110) / YSZ (111)



- *Data fits reasonably well to a single exponent*
- *Values are similar to those observed in literature (on different type samples)*
- *High-throughput / basic surface science experiments can be designed*

Comparison to Literature

	This study	Chen *et al.**
Film composition	Epitaxial Perovskite Cathode $La_{0.6}Sr_{0.4}CoO_3$	Epitaxial Perovskite Cathode $La_{0.5}Sr_{0.5}CoO_3$
Substrate	YSZ(111) (LSC 110)	$LaAlO_3$(100) (LSC 100)
Pressure range	Low 100 to 200mTorr	High 380 to760Torr
K_{chem} at 650℃	1- 4 × 10^{-6} cm/s	≈ 1×10^{-6} cm/s

* X.Chen *et al.*/Solid State Ionics 146(2002)405-413

How are microstructural / surface differences reflected in ECR?

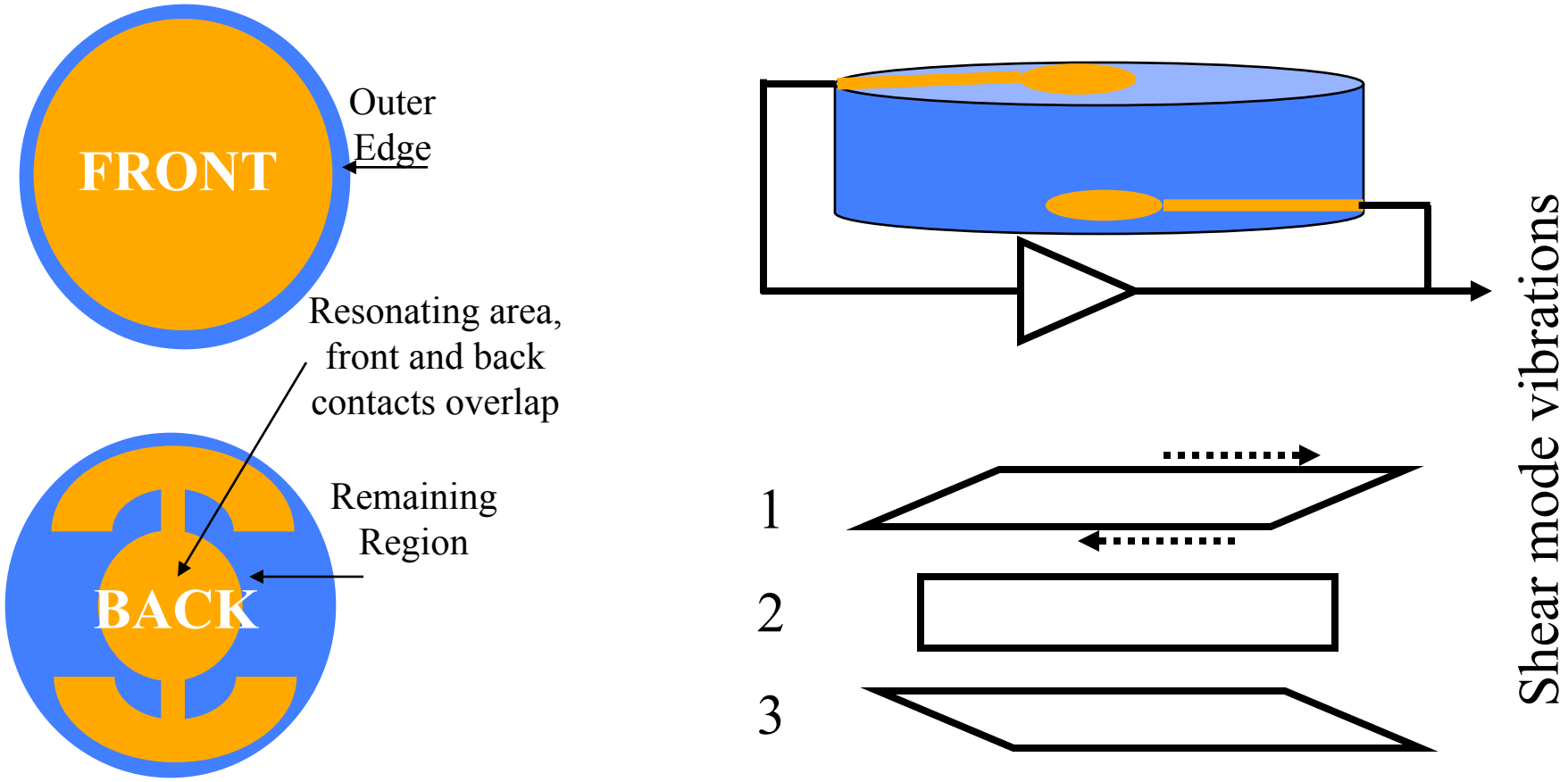
Summary of ECR Measurements

- *High vacuum compatible experimental set-up completed*
  - *Pressure can be changed from 0.01 mTorr to 100 mTorr for ECR*
  - *Van der Pauw or linear 4-probe possible*

- *Measurements at 650°C agree with order of magnitude in literature*
  - *(110)LSC films on (111)YSZ*
  - *k_{chem} = 2-8 x 10^{-6} cm/s*
  - *some differences with respect to trends for values at final P*

- *Future*
  - *Measure different temperature / pressure ranges*
  - *Measure LSC on perovskites / GDC-YSZ(100)*
  - *Measure surface modified samples*
  - *Combine with other work to generate understanding of surface*

High-T Piezoelectric Crystal Microbalances



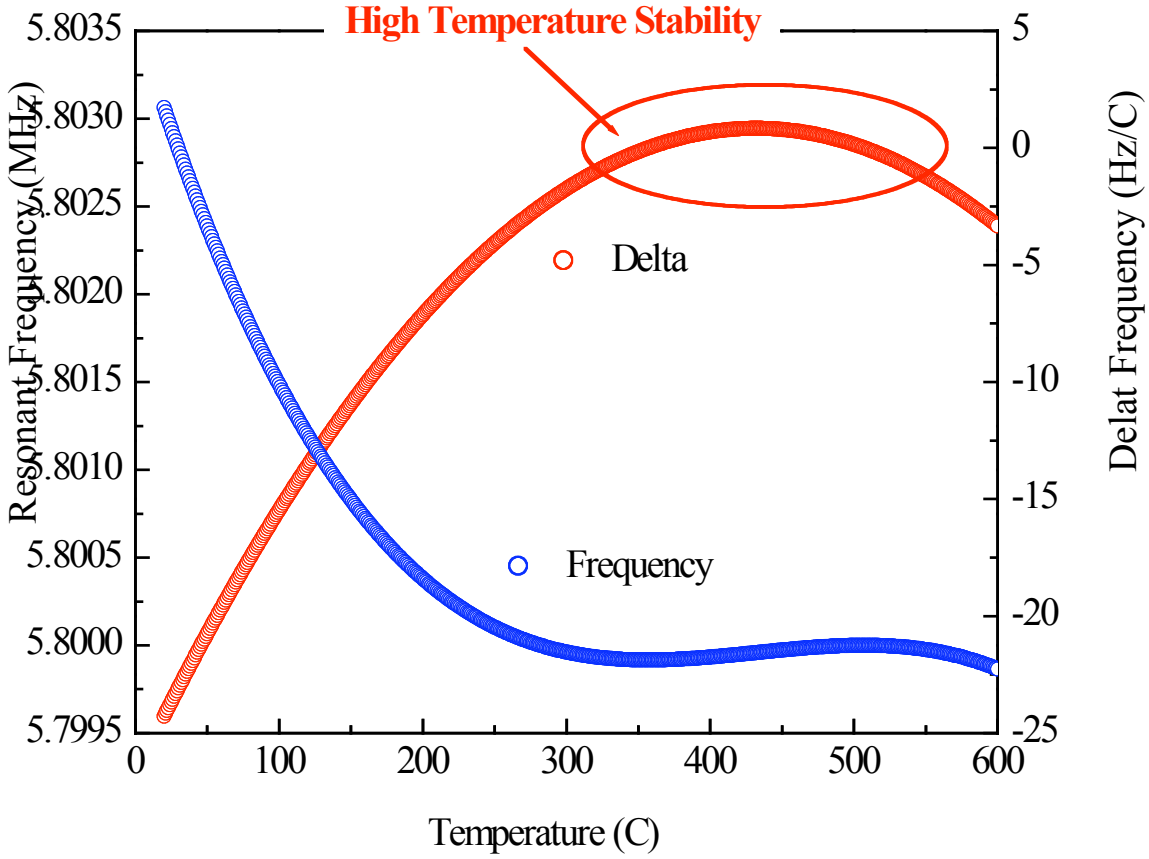
$GaPO_4$

Diameter =0.55 inch; Thickness = 0.2 mm;

F_0 = 5.8 MHz, Sensitivity +/- 3 Hz

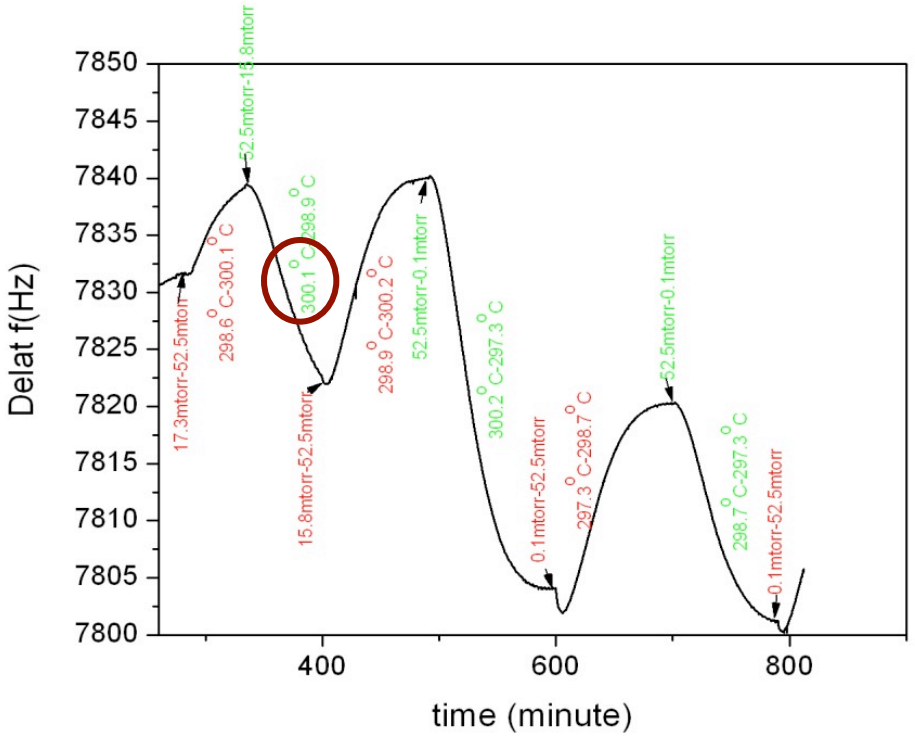
$GaPO_4$ Piezoelectric Crystal Microbalances

$GaPO_4$ is Piezoelectric until > 900°C
Has good temperature stability of Frequency

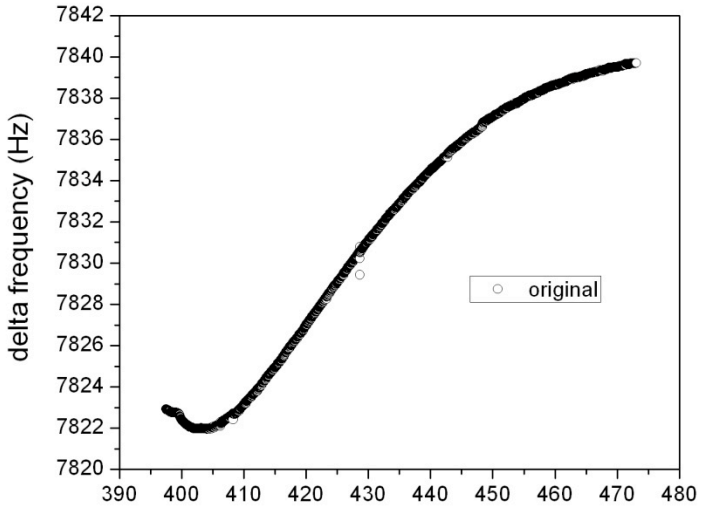


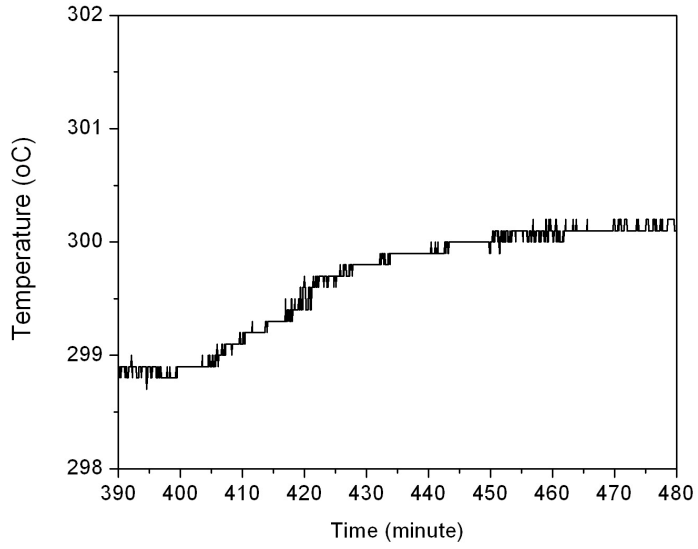
Analyzing PCM Data at 300 °C

$LaNiO_3$/PCM-300°C



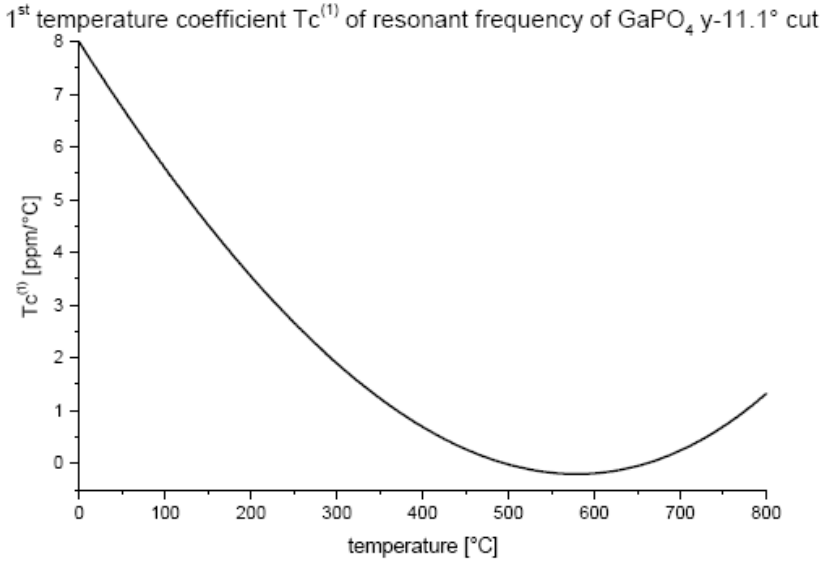
15 to 50 mTorr

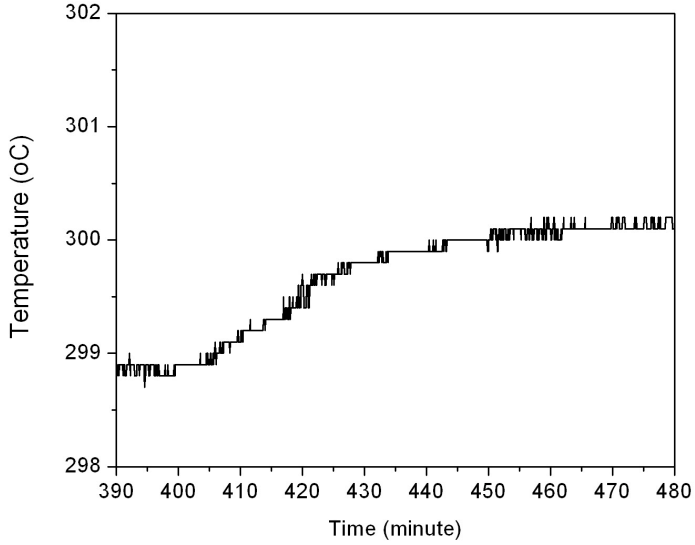


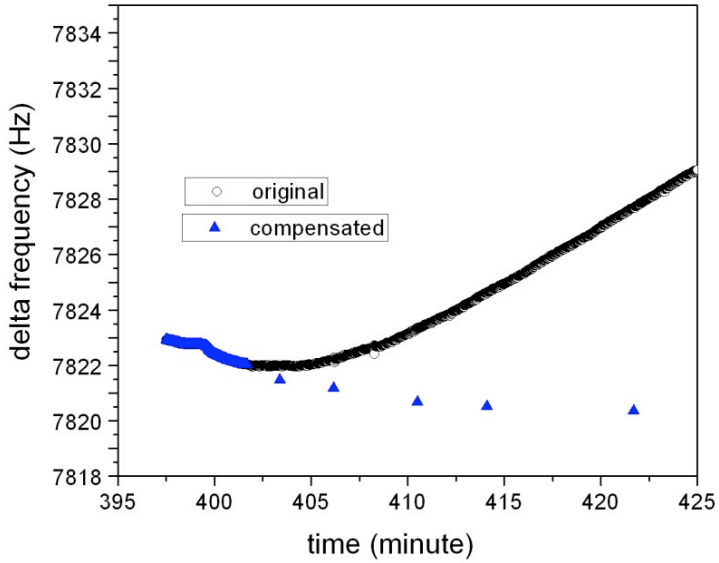


- *Part of the frequency change is caused by temperature change*

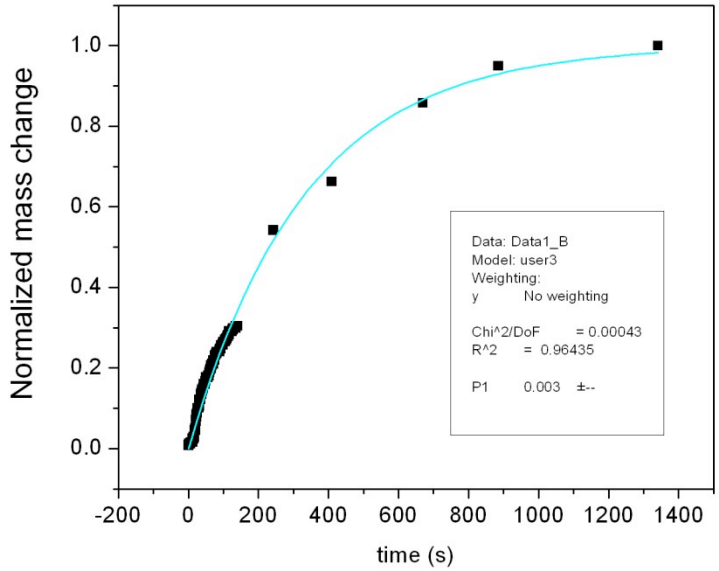
Deconvoluting Temperature and Mass Change at 300 °C for LNO Films







Transient Measurements to Determine Surface Properties

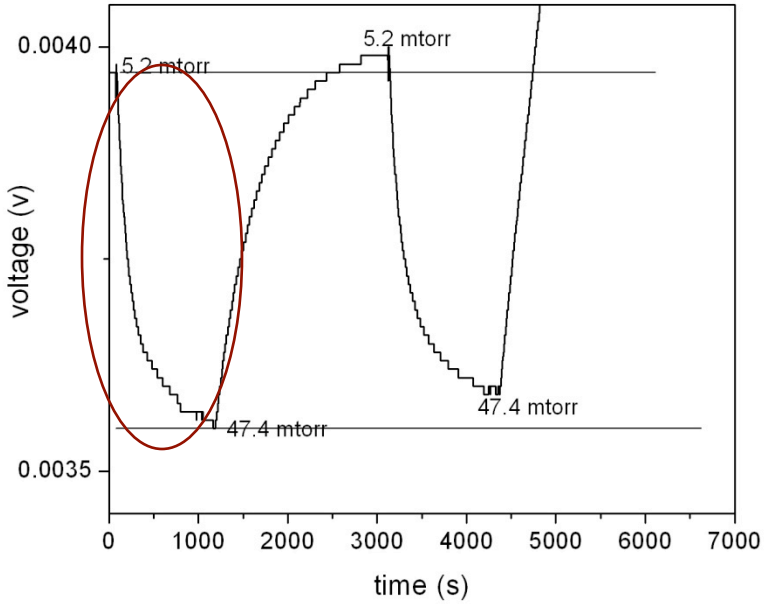


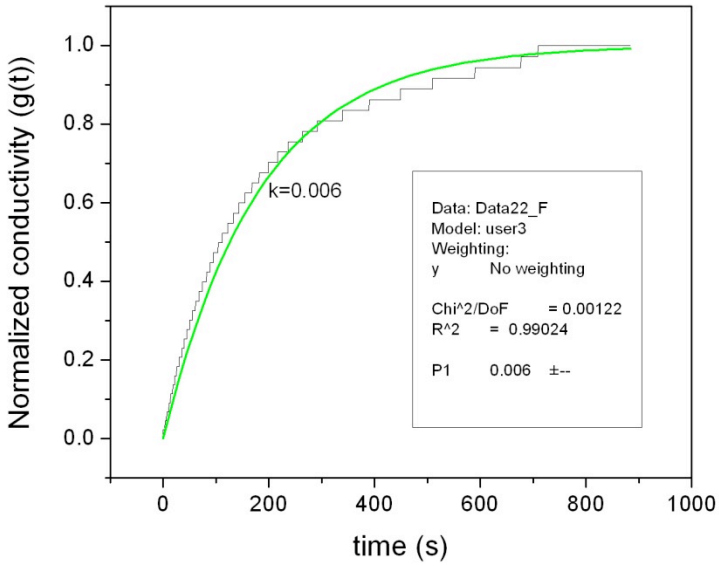
Fitting equation
y = 1- exp(-A*t)
A=0.003

- *for thin film where $k_{chem} = A^{*}l_{film} = 0.003 \times 130nm = 3.9x10^{-8}$ cm/s*

- *Need to focus on extracting*
  adsorption step from dissociation step

ECR-$LaNiO_3$/YSZ(100)-350°C





- *for thin film where $k_{chem} = A^*l_{film}$ = 0.006 x 130nm = $7.8x10^{-8}$ cm/s*
- *This k_{chem} is in the same range as measured with PCM*

➢ *k_{chem} for La_2NiO_{4+x} ceramics at this temperature is $7x10^{-7}$cm/s*
(G .Kim et al Solid State Ionics 177(2006))

PCM Measurements

- *Piezoelectric Crystal Microbalances*
  - *Good intermediate temperature stability*
  - *$LaNiO_3$ films on $GaPO_4$ measured at 350°C*
  - *k_{chem} is reasonable but no good literature comparison*
  - *$LaNiO_3$ films on ultrathin $SrTiO_3$ crystals measured on $GaPO_4$ PCMs*

- *Future*
  - *$LaNiO_3$ films on ultrathin $SrTiO_3$ crystals measured on$GaPO_4$ PCMs*
  - *Temperature dependent measurements*
  - *High-temperature holder (collaboration with company)*
  - *Measure LSM-LSC-LSF surface properties*

Summary

- ***Providing Samples to Large-Scale Effort to Understand / Engineer Cathodes Surfaces for Improved Performance***

- ***Effort focused on Thin Film / Engineered Surfaces***

  Generate three classes of films with engineered microstructure / surface

  Epitaxial Single Crystal (100), (110), (111)

  Epitaxial Multi-variant (100), (110)

  Polycrystalline

- ***Initial Measurements to combine conductivity / mass / electronic structure***

  ECR *(110) LSCO has k_{chem} on in the range of 2-8 x 10^{-6} cm at 650°C*

  k_{chem} affected by final pressure and oxidation/reduction

  STS *thin (strained) epitaxial LSM on STO layers are insulating*

  thick (relaxed) epitaxial LSM on STO layers are conducting

  PCM *Can use polycrystalline films or Epitaxial film/substrate*

  Temperature compensation is essential

  LNO has k_{chem} on the order of of 4-8 x 10^{-8} cm between 300 -350

Future Directions

- ***Growth of High-Quality Thin Film Samples***
  - ***Perovskite / Perovskite Epitaxy and Surface Control***
  - ***Perovskite / Fluorite Epitaxy and Surface Control***
  - *Generation of Surface-Modified Samples*

- ***Surface Kinetics for Oxygen Uptake***
  - ***Electrical Conductivity Relaxation***
  - ***Piezoelectric Crystal Microbalance Gravimetry***
  - *Kelvin Probe Spectroscopy*

- *Surface Thermodynamics of Oxygen Uptake*
  - *Piezoelectric Crystal Microbalance Gravimetry*
  - *Kelvin Probe Spectroscopy*

- *Electronic Structure*
  - *Kelvin Probe Spectroscopy*
  - *STM (MIT)*

- *Ex-situ Surface Characterization for Correlations*
  - *Scanning Auger / XPS*

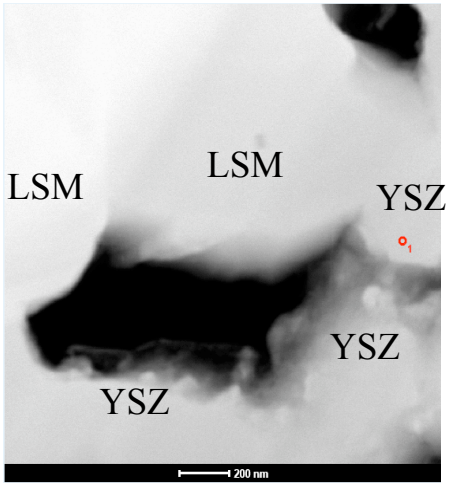
Acknowledgements

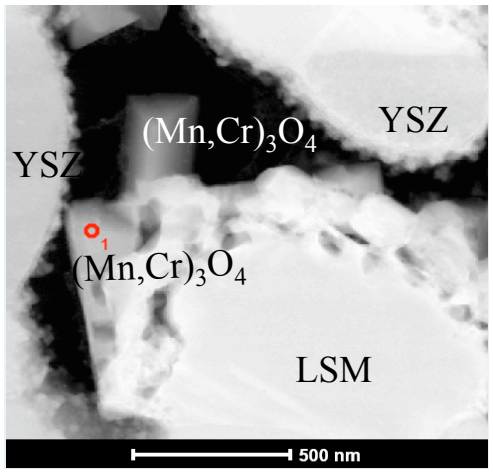
- SECA Program
  - Briggs White and Wayne Surdoval
- RDS – NETL

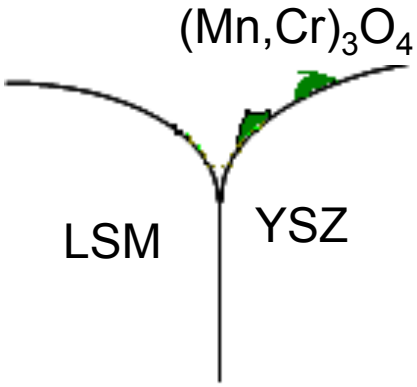
Transmission Electron Microscopy

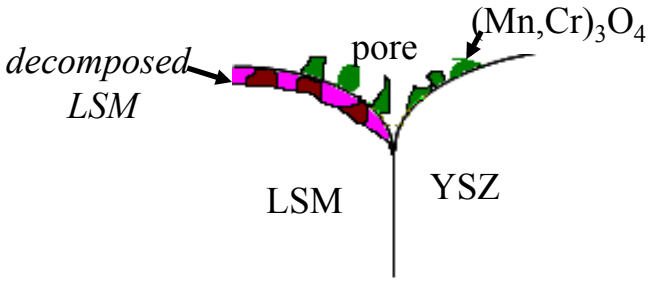
Argonne National Lab – Carnegie Mellon – SECA
Delphi – Carnegie Mellon – SECA

Local Microstructural / Chemical / Phase Information









T. A. Cruse, B. J. Ingram, M. Krumpelt, S. Wang, and P. A. Salvador, in "TMS 2008 Annual Meeting Supplemental Proceedings Volume 1: Materials Processing and Properties," pp. 571-580 (2008).

Investigate Degradation of Cells

Overarching Goals

Put together a team of researchers to carry out
Surface Science on SOFC Cathode Materials
Generate in-situ / ex-situ correlations
Generate a complete description of surfaces / oxygen interaction

Identify the surface sensitive parameter that dictates overall cathode performance:
surface stoichiometry and orientation,
electronic character,
work function,
cation-gas bonding,
vacancy population, etc…

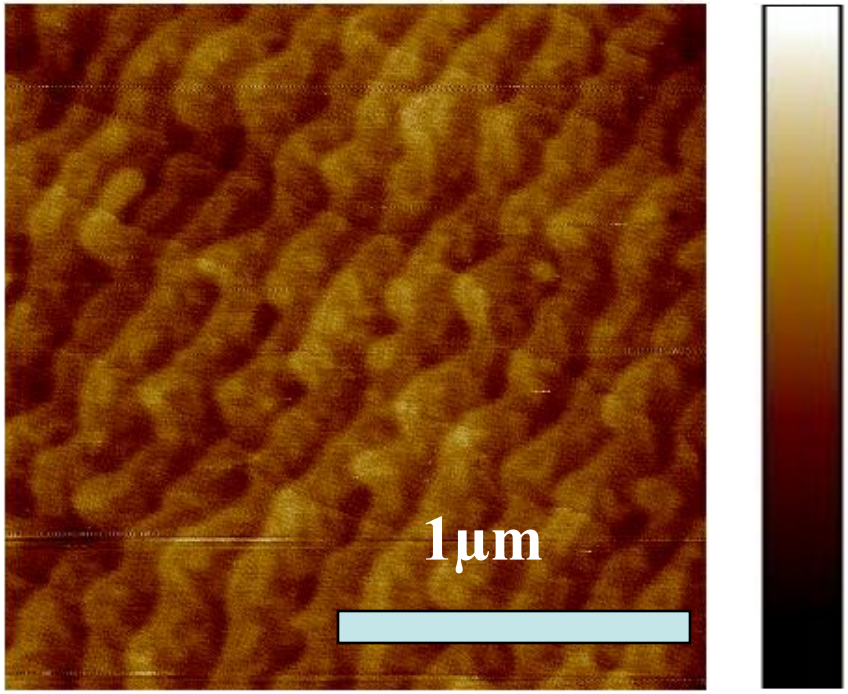
Objectives

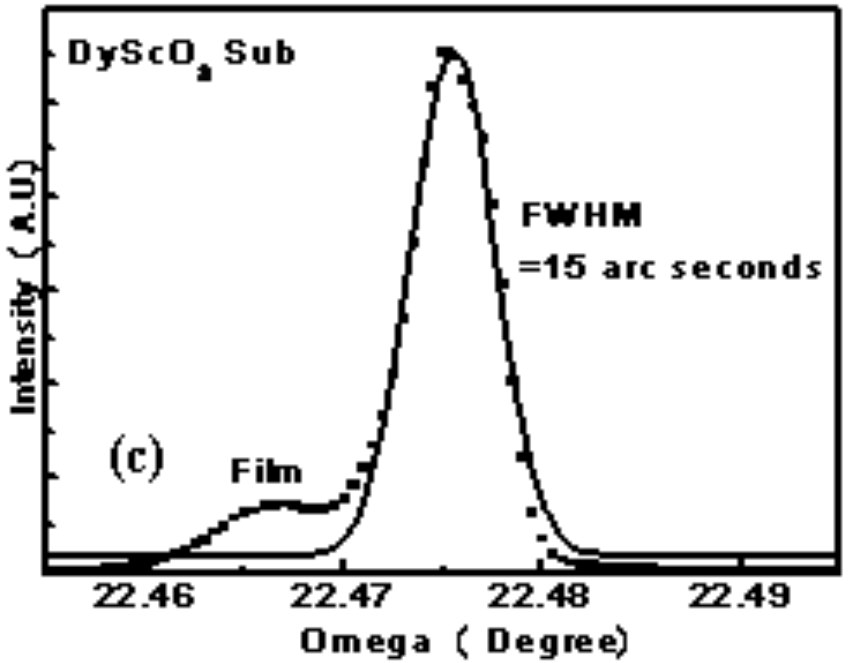
(1) generate well-defined epitaxial, textured, and polycrystalline films having controlled surface chemistries

(2) generate experimental data on surface properties that indicate how the electrocatalytic activity of SOFC cathodes can be optimized to yield improved cathodes.

$DyScO_3$ Crystals

Ultra-high Quality Perovskite Crystals
Ultra high Quality Surfaces
No Overlapping Elements with Films
Highly Insulating (Good for ECR / PCM)



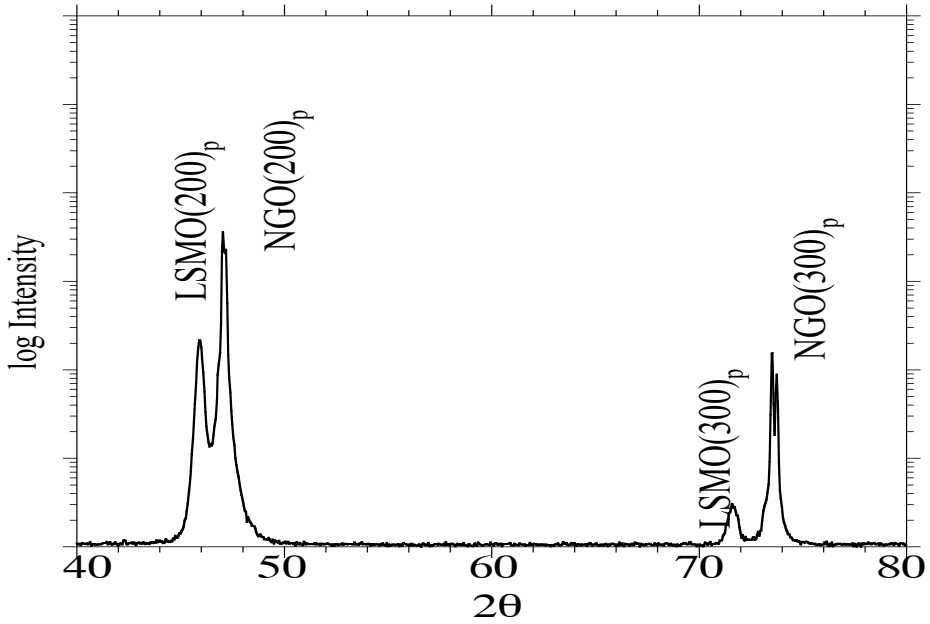


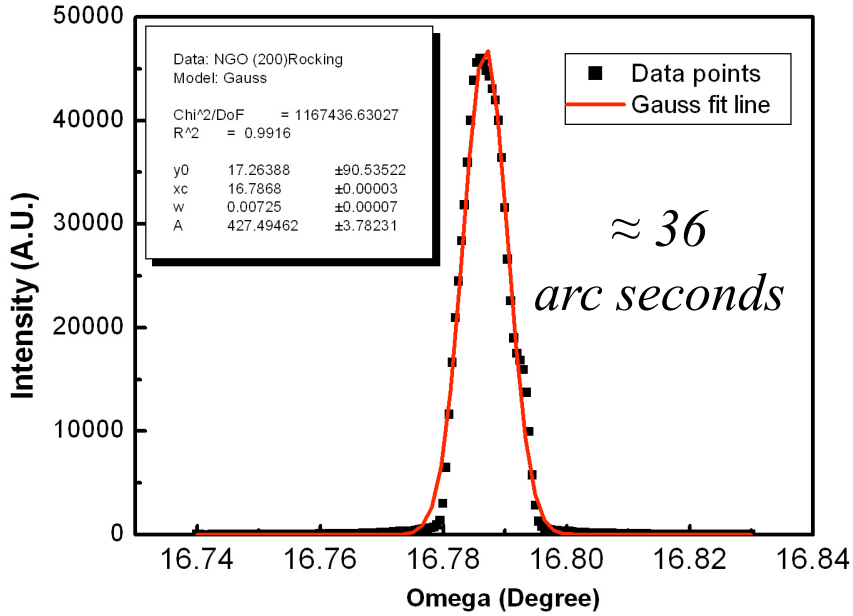
Investigated Surface Chemistry at ANL using these Substrates

$(La,Sr)MnO_3$ thin films on $NdGaO_3$

Very-high Quality Perovskite Crystals
No Overlapping Elements with Films
Highly Insulating (Good for ECR / PCM)

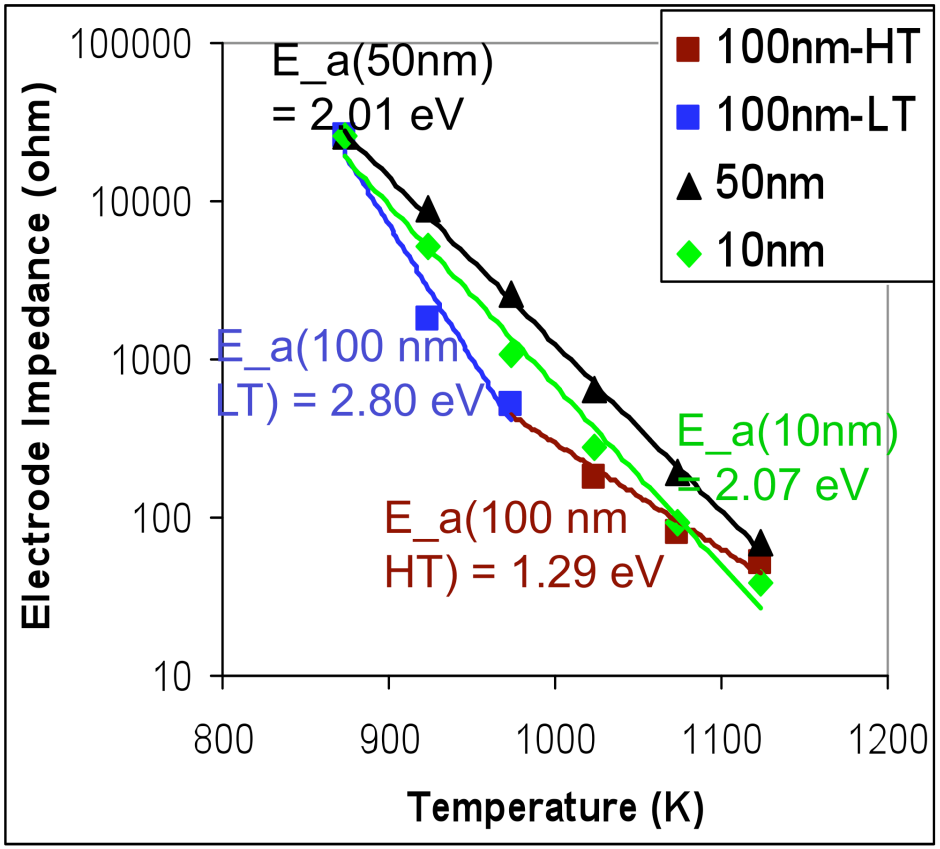
$La_{0.7}Sr_{0.3}MnO_3$ (54 nm) deposited on $NdGaO_3(100)_P$





Need Reasonable Perovskite Electrolyte(s) for Electrochemistry

Impedance vs Thickness and Temperature



2eV of effective activation energy indicates surface-limited oxygen reduction [1,2]

HT region for 100nm thick film indicates a change in the mechanism

Surface Limited Mechanism is Consistent with Fermi Level Conduction Mechanism

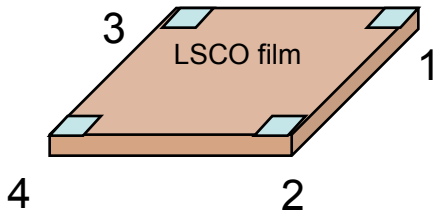
*[1] E. P. Murray, T. Tsai, S. A. Barnett, Solid State Ionics **110**, 235 (1998).*
*[2] S. P. Jiang, J. G. Love, Y. Ramprakash, J. Power Sources **110**, 201 (2002).*

Electronic Structure and Impedance are Correlated

Van der Pauw measurements
Verifying that the Set-up works / Verifying the FILM uniformity

Let current =1μA, then test on the film sample, we get:

V34	I12	0.272592 mv
V34	- I12	-0.272245 mv
V34	I21	-0.272351 mv
V34	-I21	0.272439 mv
V12	I34	0.271918 mv
V12	-I34	-0.272635 mv
V12	I43	-0.272340 mv
V12	-I43	0.272138 mv
V13	I42	-0.276759 mv
V13	-I42	0.271322 mv
V13	I24	0.270765 mv
V13	-I24	-0.274452 mv
V31	I42	0.272788 mv
V31	-I42	-0.27231 mv
V31	I24	-0.274130 mv
V31	-I24	0.272271 mv
V14	I32	0.00mv
V32	I41	0.00mv



Measure on edges :

1,2: current; 3,4: voltage
Or
2,3: current; 1,4: voltage
Or
3,4: current; 2,1: voltage
Or
4,1: current; 3,2: voltage

Gives almost the same resistance value: R=V/I with errors <1%

Measure on diagonals:

1,3: current; 2,4: voltage

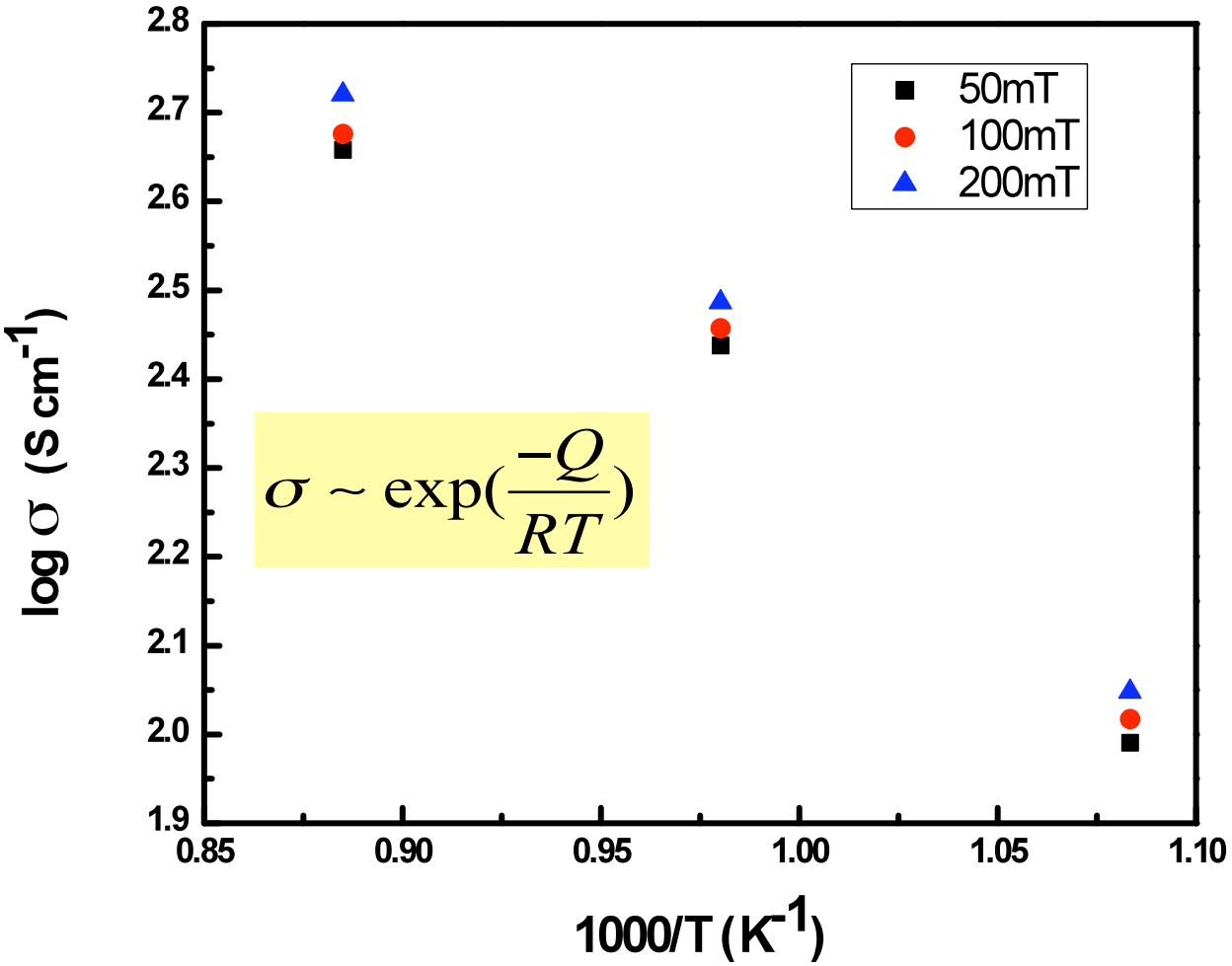
Or

2,4: current; 1,3: voltage

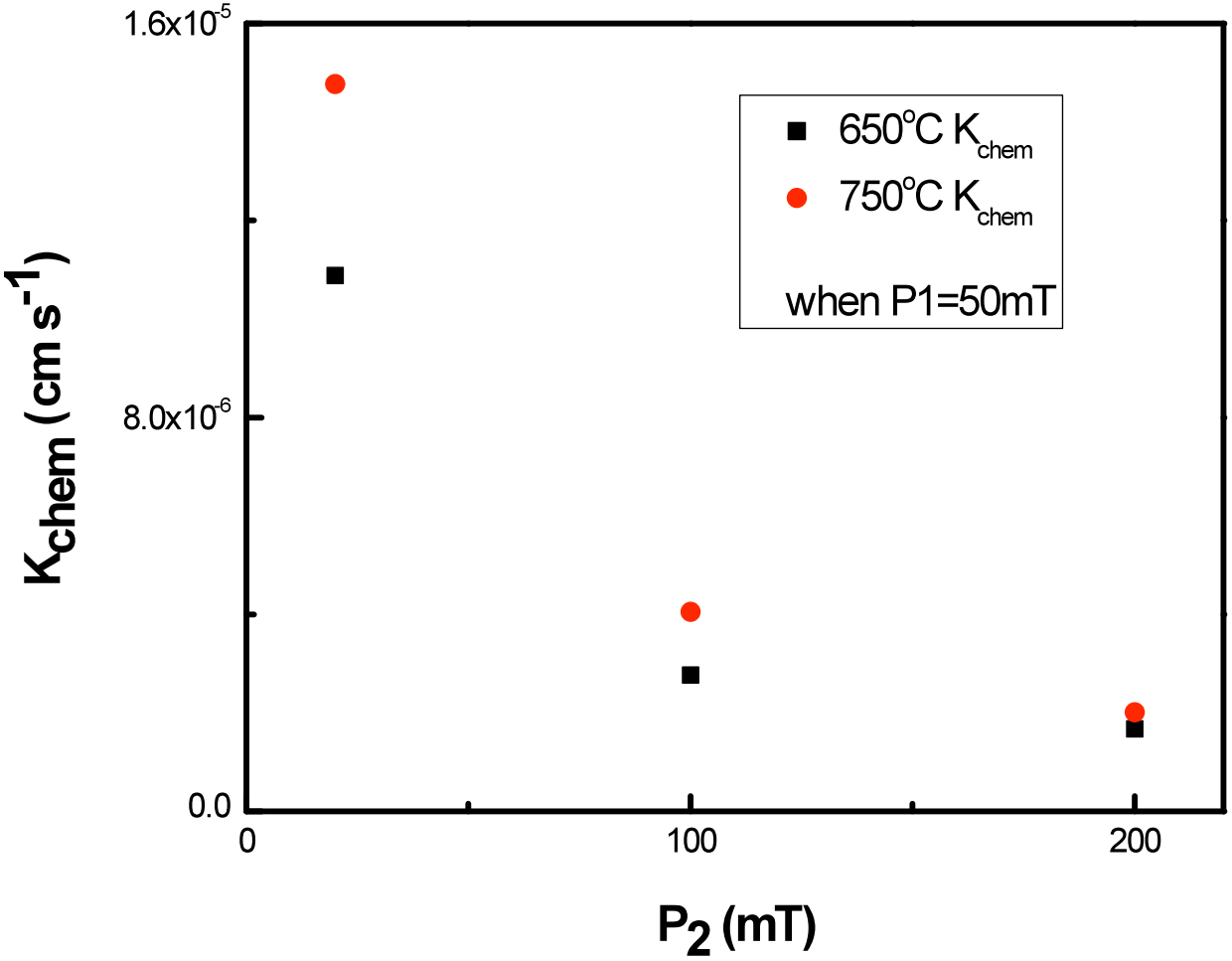
gives R=0

Thus, it is reasonable to do VDP measurement without switching.

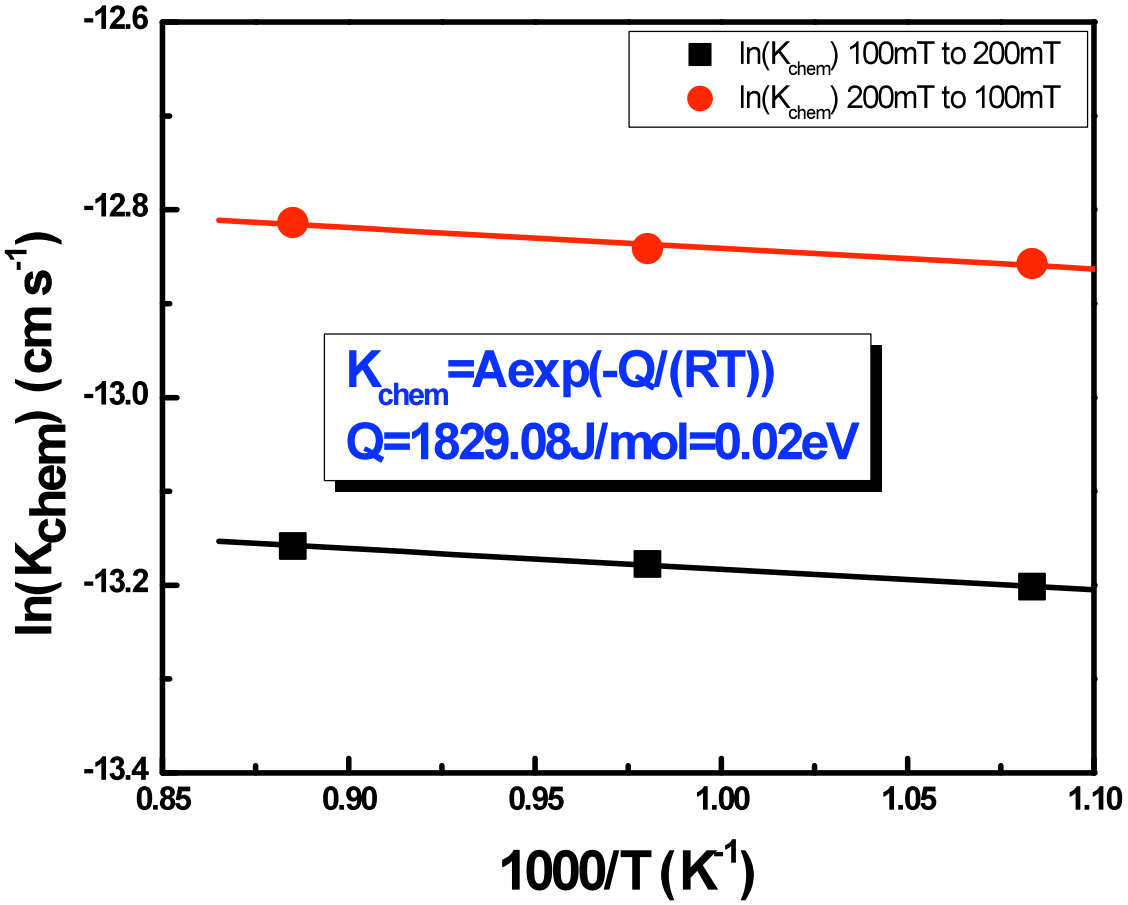
LSCO conductivity change with temperature



K_{chem} dependency on final oxygen pressure



Activation energy (Q) determination



650℃ K_{chem}=1.85E-6 (100->200mTorr)
K_{chem}=2.61E-6 (200->100mTorr)

50nm LSCO(110) on YSZ(111)

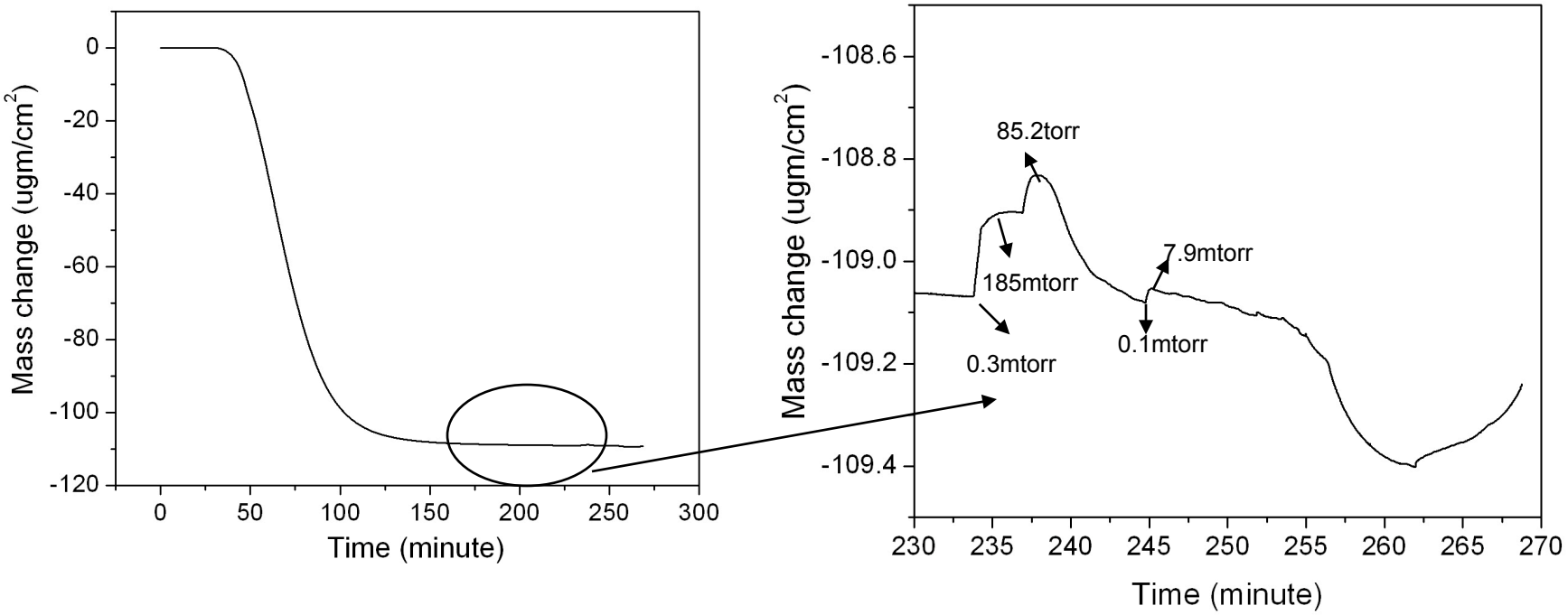
in this study

650℃ K_{chem}=0.92E-6 (380Torr>760Torr)
K_{chem}=0.84E-6 (760Torr>380Torr)

500nm LSCO (100) on LAO(100)

* X.Chen *et al.*/Solid State Ionics 146(2002)405-413

Mass Changes on Pressure Changes
QCM is Sensitive to Mass Changes

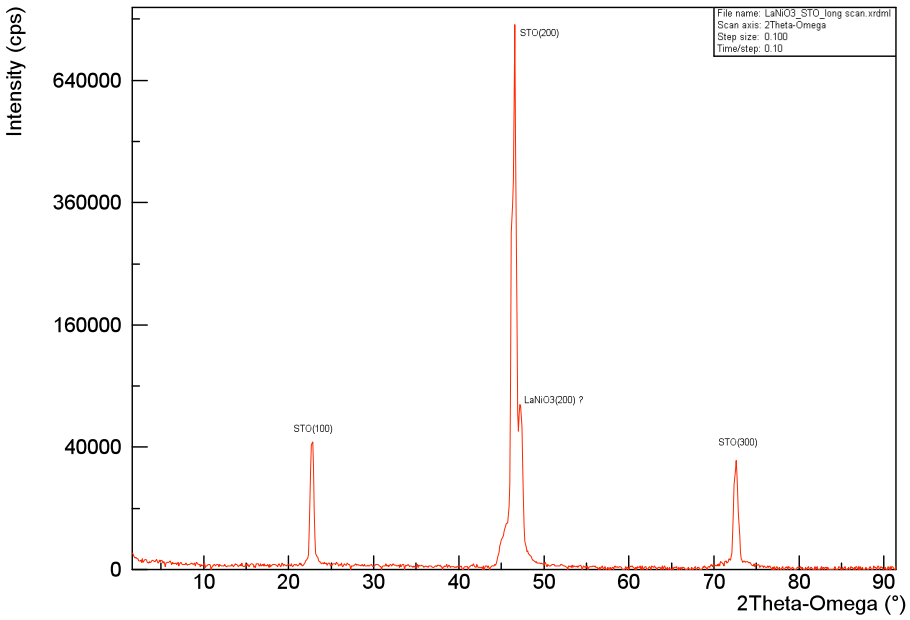


- *Changes in Pressure lead to reasonable changes in mass*
- *Initial variations have reasonable transients*
- *Can measure surface and bulk properties*

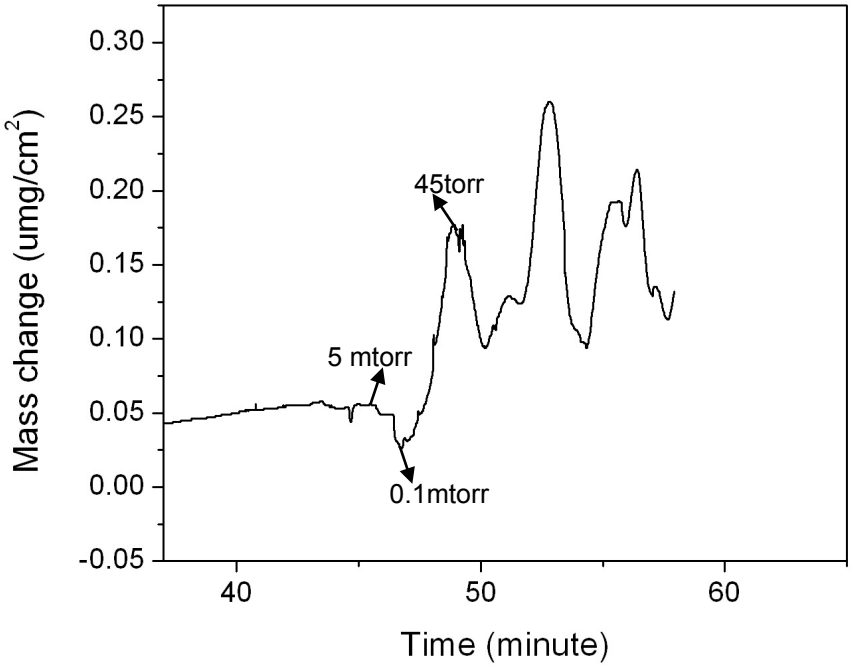
Frequency Shifts occur on pressure changes: temperature or mass?

Initial Measurements on Single Crystal Sample

XRD of LNO on STO



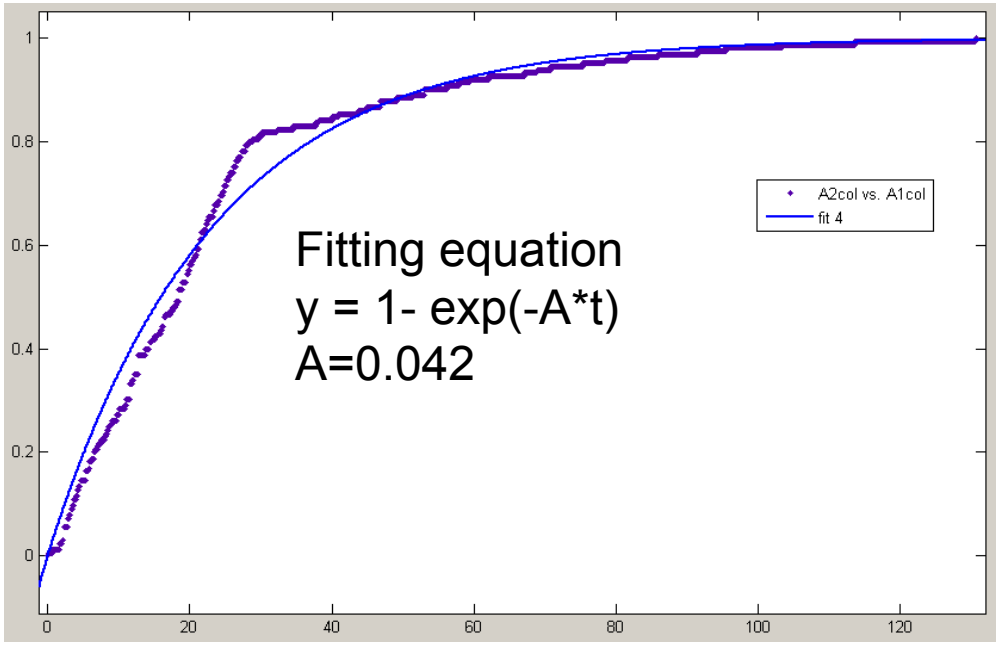
PCM with LNO deposited on STO(100)



- *Changes in Pressure lead to reasonable changes in mass*
- *Noise is a little higher with single crystal*
- *Procedure is promising for direct comparisons to APS work*

Transient Measurements to Determine Surface Properties

Mass change vs. time when PO_2 change from 0.3 mtorr to 185 mtorr at 350°C



- transient measurement is not quite exponential, need more work
- for thin film where $k_{chem} = A*l_{film}$ = 0.042 x 130nm = $5.88x10^{-7}$ cm/s
- k_{chem} for La_2NiO_{4+x} ceramics at this temperature is $7x10^{-7}$cm/s
  (G .Kim et al Solid State Ionics 177(2006))

PCM measurements can yield surface properties of Thin Films!

Determining Appropriateness of Measurements

- Oxygen vacancy in deposited LNO thin film
  - Thin film weight from G-PCM measurement: 16×10^{-6}g
  - Thin film thickness 140nm
  - Total oxygen vacancy in this thin film if assuming it is $LaNiO_{2.5}$:

    1.9×10^{16}

- Measurement oxygen vacancy when PO_2 change from 0.3 mtorr to 185 mtorr
  - Weight change from G-PCM measurement: 0.056×10^{-6}g
  - Corresponding oxygen vacancy loss:

    2.1×10^{15}

- Summary
  - At 350^{o}C, 1/10 possible oxygen vacancy change was observed in LNO film

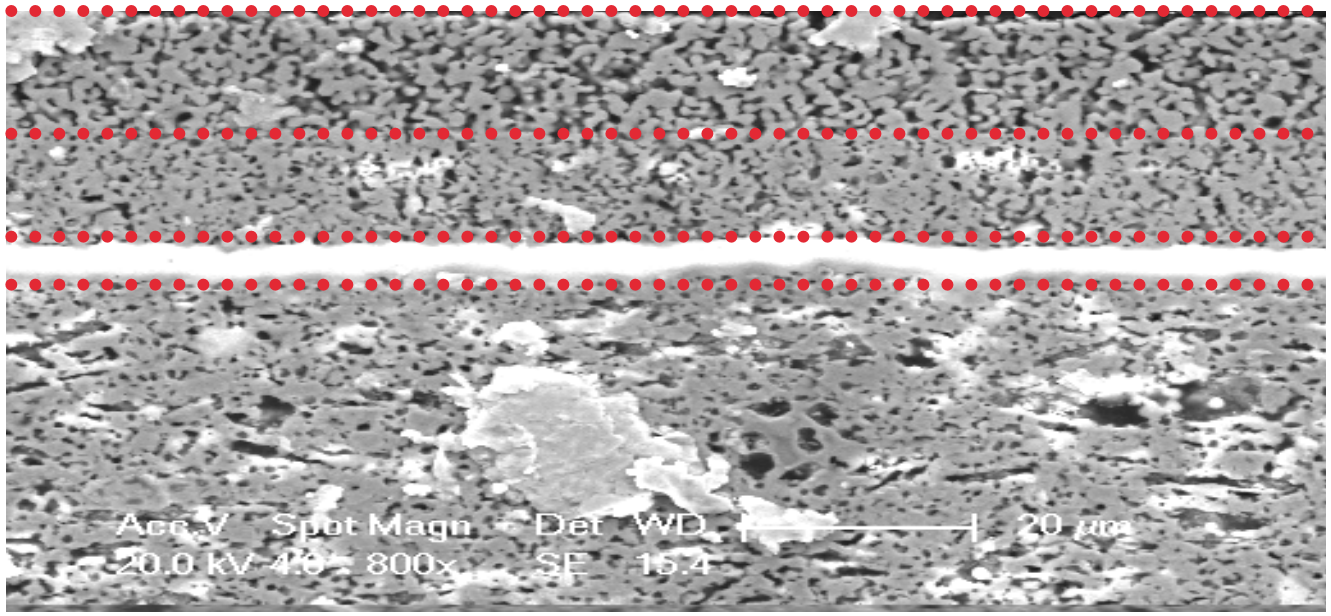
Why Study Cathode Surfaces?

Current Collector
Pores + $(La,Sr)MnO_3$

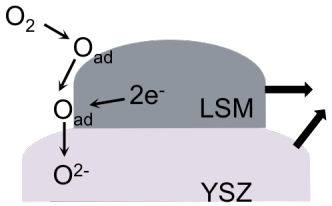
Active Cathode
P + LSM + YSZ

Electrolyte (YSZ)

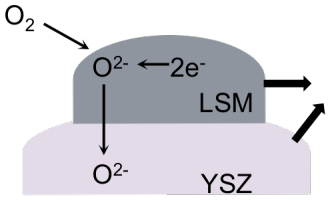
Anode
P + YSZ + NI



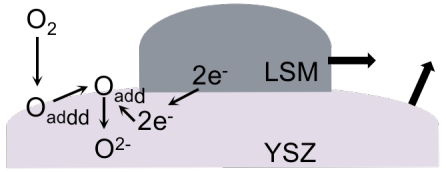
The oxygen reduction reaction is surface specific and is related to two and three phase boundaries in SOFCs.



LSM Surface Path



LSM Bulk Path



YSZ Surface Path

We don't understand Surfaces OR Internal Interfaces!