Solid Oxide Fuel Cell Cathodes: Unraveling the Relationship between Structure, Surface Chemistry and Oxygen Reduction

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Milestones, Metrics, and Decision Points

1. Narrow down process conditions for depositing LSM and LSCF heteroepitaxial layers and polycrystalline thin films. ***Deposition conditions for LSM identified and films with consistent quality are being produced.***

2. Demonstrate use of X-ray as an in-situ technique and TEM as an ex-situ technique to study the surface and near-surface structural rearrangement. ***Both X-ray and TEM are being used regularly to check film quality. In situ x-ray studies still in progress.***

3. Make impedance measurements**.** ***Impedance measurements have been standardized.***

4. Correlate electrochemical measurements with ex-situ x-ray structure, TEM, and electronic structure measurements. ***Initial very promising results have been obtained by combining soft x-ray measurements (XAS and XES) with impedance measurements. Other studies still in progress.***

5. O-18 studies on very limited samples with very different surface and near surface structures. ***First diffusion experiment on LSM thin film complete. SIMS analysis of first experiments complete. More experiments under progress.***

Milestones, Metrics, and Decision Points

6. Build X-ray furnace. ***Done***

7. Demonstrate first in-situ use of high temperature x-ray furnace on polycrystalline films (pristine and electrochemically polarized). ***EXAFS data of LSM thin films obtained. Partial analysis done; more ongoing.***

8. Demonstrate at least one spectroscpic technique as a viable ex-situ technique on bulk and/or polycrystalline thin films. ***XES/XAS has been demonstrated as an ex-situ characterization tool on LSM epitaxial thin films***

Outline

- Introduction
- Sample Fabrication and Characterization
  - PLD, RBS, TEM, AFM, XRD
- Results
  - Wide scan XPS, XAS: OK-edge, MnL-edge, EIS
  - X-ray analysis – EXAFS, truncation rod analysis
- Future Path

Introduction:

Question:

• What changes occur to the surface chemical composition and the oxidation states of cations in a Solid Oxide Fuel Cell (SOFC) cathode as a result of the occurrence of the oxygen reduction reaction (ORR) during operation?

•Similarly what changes to the surface crystal structure occur and how are they related to the ORR?

Techniques:

• Use synchrotron based soft x-ray techniques: XPS and XAS to observe composition changes at the surface under SOFC operating conditions.

•Use synchrotron based hard x-ray techniques : x-ray diffraction, EXAFS etc.

•TEM

Some Challenges:

• Soft x-ray techniques are performed in vacuum,

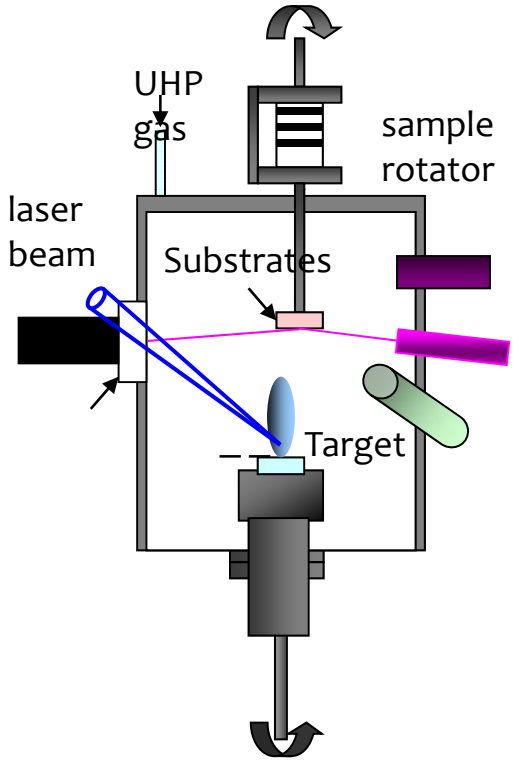
•XPS is highly surface sensitive.

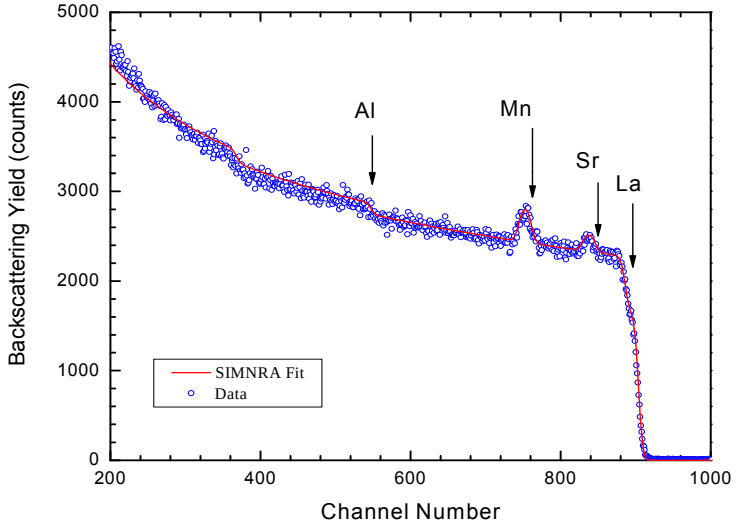
• Must create clean gas-cathode interface

Sample Prep and Characterization

The solution:

Grow heteroepitaxial thin films of LSM on LAO(001) and YSZ(111)



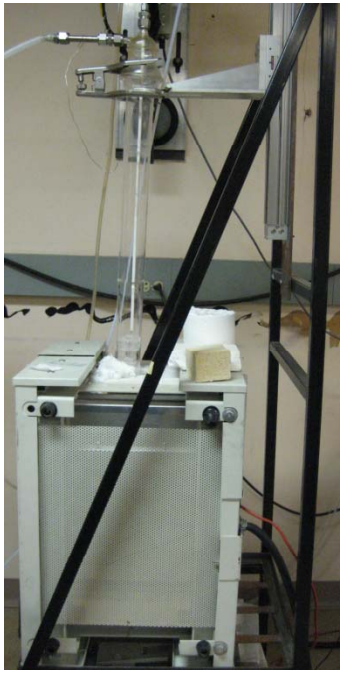


PLD performed at the Pacific Northwest National Laboratory

RBS Results:
Target Composition: $(La_{0.8}Sr_{0.2})_{0.97}MnO_{3\pm\delta}$
Cation Ratios: Sr/(La +Sr) = 0.21 (La + Sr)/Mn = 0.95
Film composition: $(La_{0.79}Sr_{0.21})_{0.95}MnO_{3\pm\delta}$

Sample Annealing…

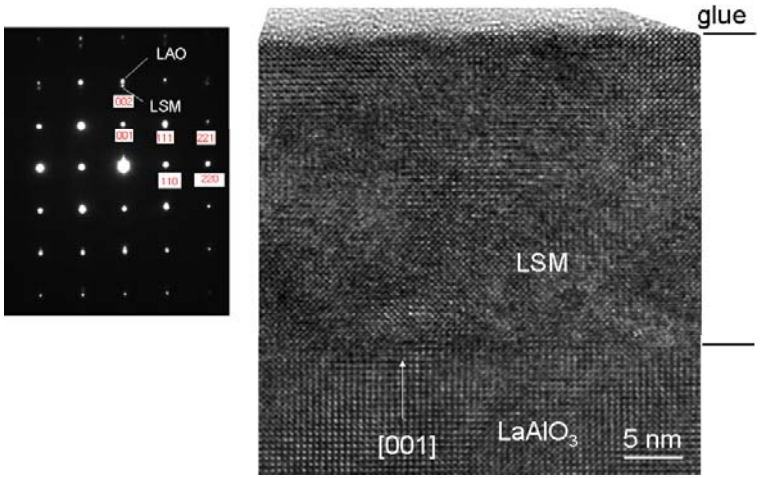
To transport clean samples to the synchrotron, the samples are annealed in a tube furnace, quenched, and then sealed in glass ampoules.



LSM on LAO

TEM

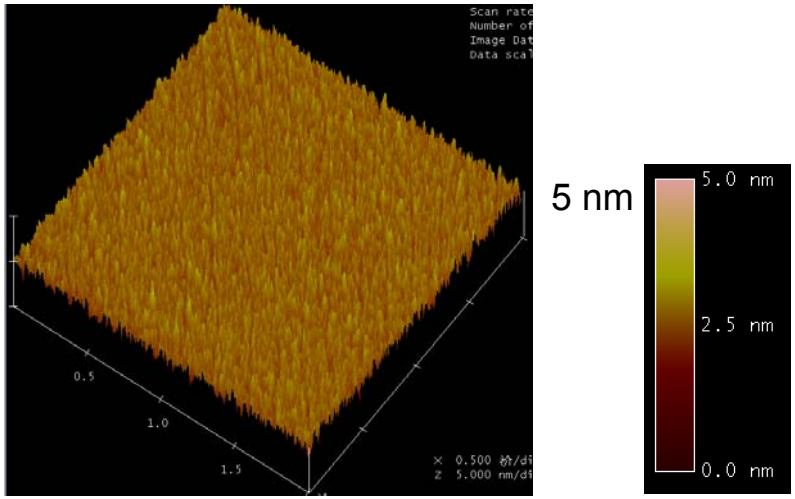
- Heteroepitaxial LSM deposited on LAO[001].



LSM on LAO [001]. Left: electron diffraction patterns. Right: HREM micrograph.

AFM

- 250 nm LSM on (001)LAO
- RMS roughness = 0.522 nm

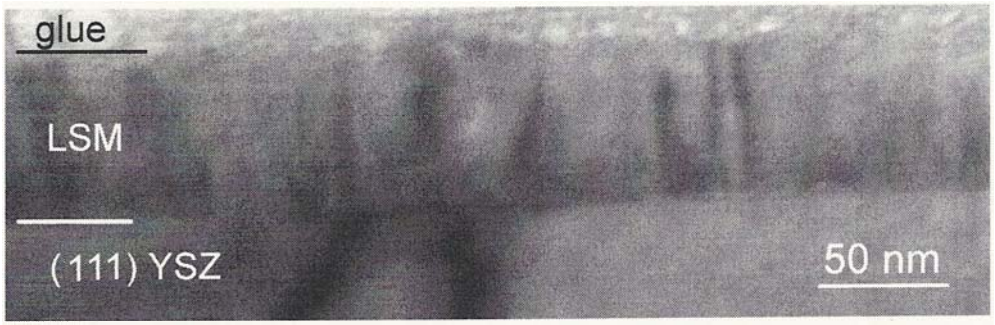


LSM on LAO [001]. AFM image of surface.

- RMS does not change after annealing 12 hours at 800°C

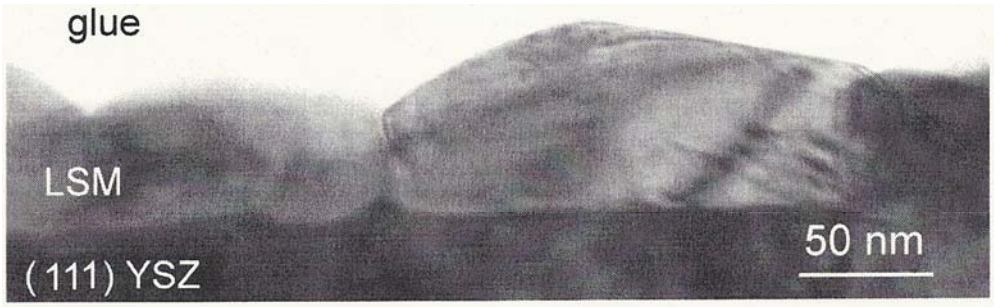
LSM on YSZ
TEM

- As deposited films show ~30nm wide columnar grain growth.



TEM image of as deposited film and substrate.

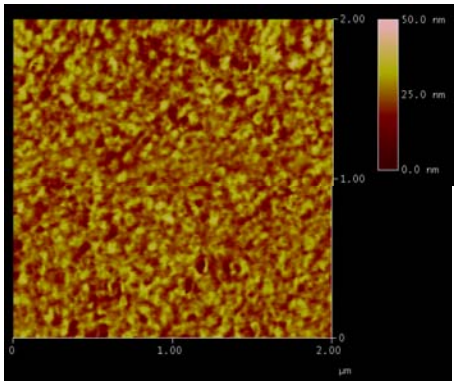
- Annealing at 1100^{o}C for 4 hours introduces large grain growth (~150 nm) and associated surface roughening.



TEM image of annealed film and substrate.

LSM on YSZ
AFM

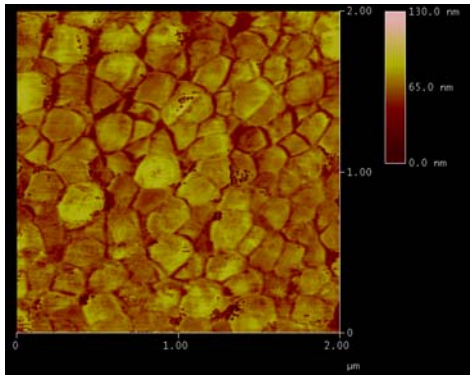
- RMS of as deposited films seems to be dependent on film thickness. 100nm films have an RMS surface roughness of ~0.5 nm. 250nm films are not as smooth (~5nm surface roughness).
- 250nm films have a trend to roughen more as annealing temperatures are increased past 800C.



As deposited

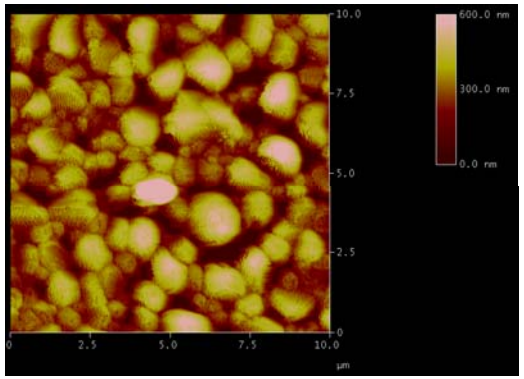
RMS = 4.8nm

RMS unchanged when annealed 40 hours at 800°C.



Annealed 1000 1hr.

RMS = 11.6nm



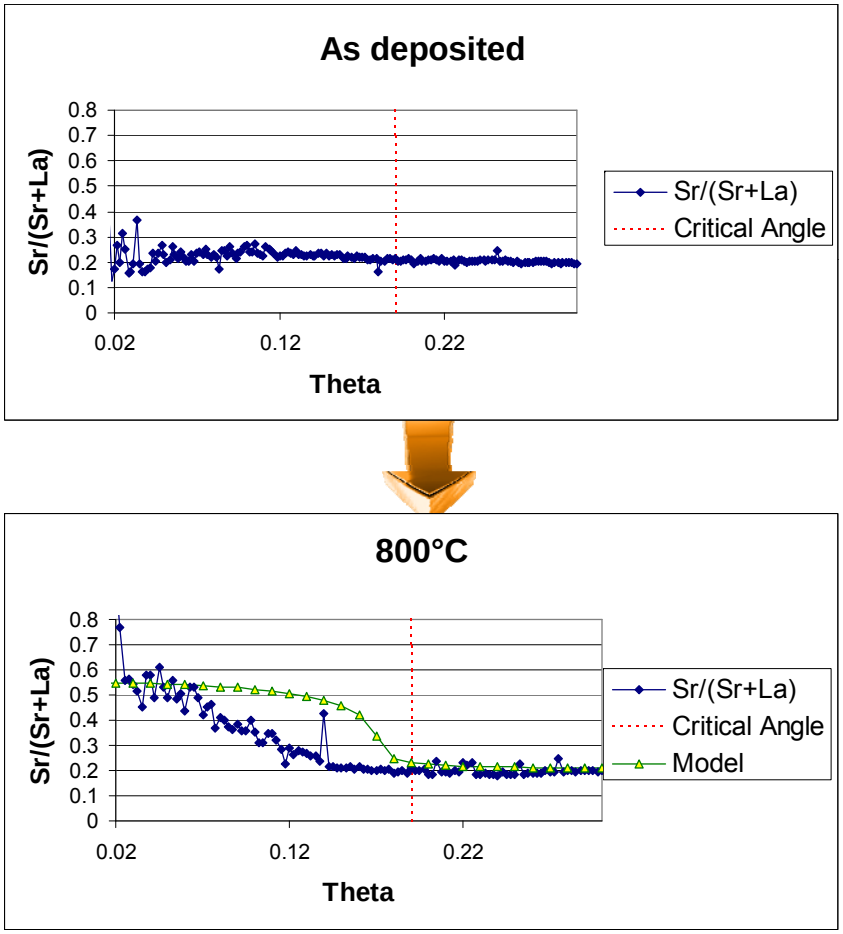
Annealed 1200 1hr.

RMS = 131.3nm

- Need to optimize annealing conditions for grains to crystallize while keeping surface intact.

X-ray Fluorescence

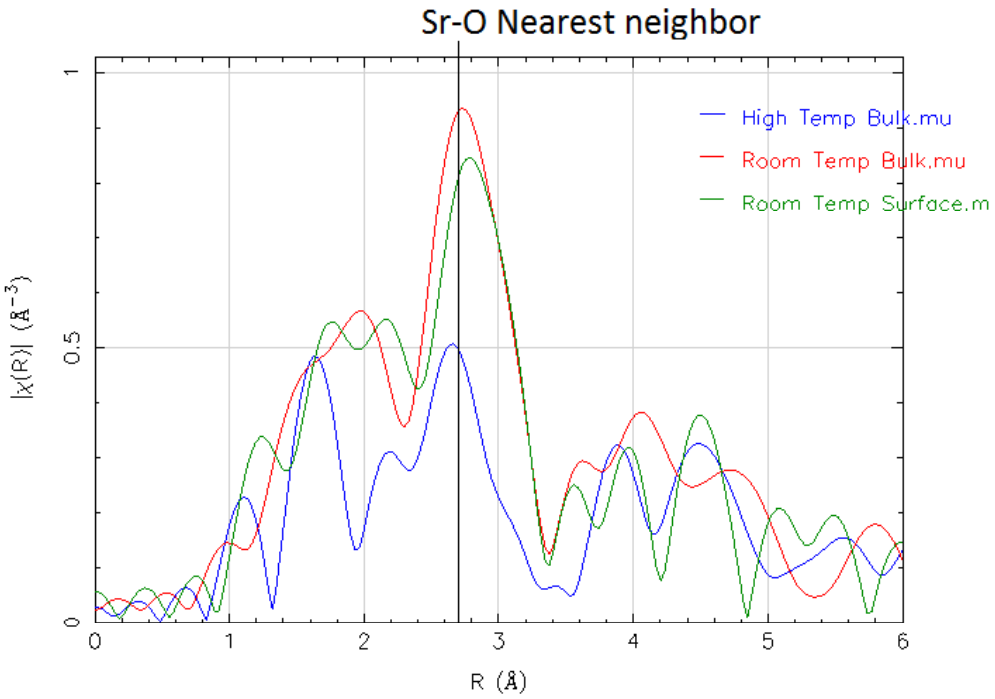
- Monitor fluorescence signals from strontium, lanthanum and manganese simultaneously.
- Total Reflection X-ray Fluorescence (TXRF) data was taken as a function of angle to probe composition ratios as a function of depth.
- Evidence of strontium enrichment on surface upon annealing.
  - Process is not reversible.
- Behavior near the critical angle has been seen by Argonne groups:
  - K. Chang, B. et al., Proc. 2008 MRS Fall Meeting, Symposium S: Solid-State Ionics. 1128S08-10.
  - T.T. Fister et al., Appl. Phys. Lett. 93 (15) (2008) 151904.
- Shape not what we expect for segregation to the surface with simple exponential decay into material.



Ratio of strontium to total A site. LSM on YSZ.

EXAFS

- Extended X-ray Absorption Fine Structure spectrum taken at strontium and manganese edges.
- At current level of accuracy data shows no differences between grazing surface sensitive and more bulk sensitive modes.
- High temperature data shows reduced Sr-O coordination number.
  - Could be actual O loss or due to increased vibrations at high temperature.
- Have collected more recent data with better statistics; under analysis

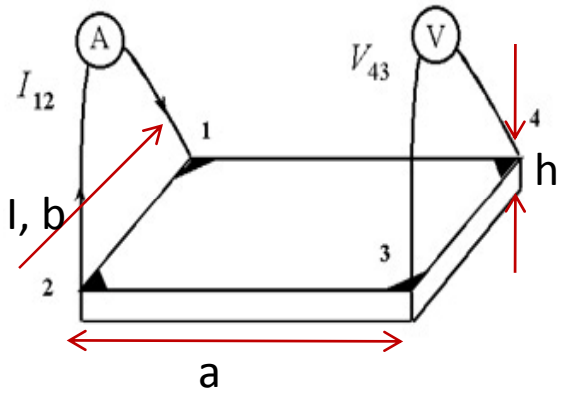


Electrochemical Characterization

Electrical Conductivity Relaxation…

Electrical conductivity relaxation (ECR):

-Step change the P_{O2} and follow the conductivity change as a function of time



$$\exp\left(\frac{-\pi R_A}{R_S}\right) + \exp\left(\frac{-\pi R_B}{R_S}\right) = 1$$

Van der Pauw Equation

Change in PO2 leads to change in conductivity via change in stoichiometry:

$$\frac{1}{2}O_2(g) + 2Mn_{Mn}^{x} + V\ddot{o} = O_O^x + 2Mn_{Mn}^{\cdot}$$

$$2Mn_{Mn}^{x} \leftrightarrow Mn_{Mn}^{\cdot} + Mn_{Mn}^{\prime}$$

Electrical Conductivity Relaxation…

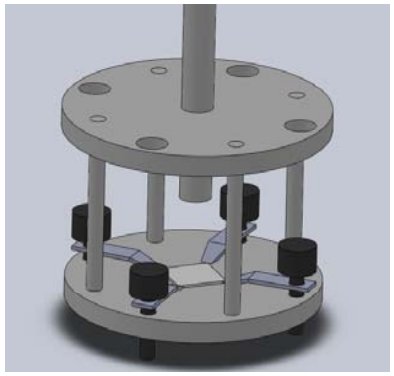
• For very thin samples where h << l_{crit} = (k/D) diffusion equation reduces to:

$$\frac{\sigma(t)-\sigma(0)}{\sigma(\infty)-\sigma(0)} = 1 - e^{-(t/\tau)}$$

Where:

$$k_O = \frac{h}{\tau}$$

• Thus, after verifying that we are in the correct regime, we only have one fitting parameter the surface exchange coefficient.
• This allows straightforward comparison between different materials.

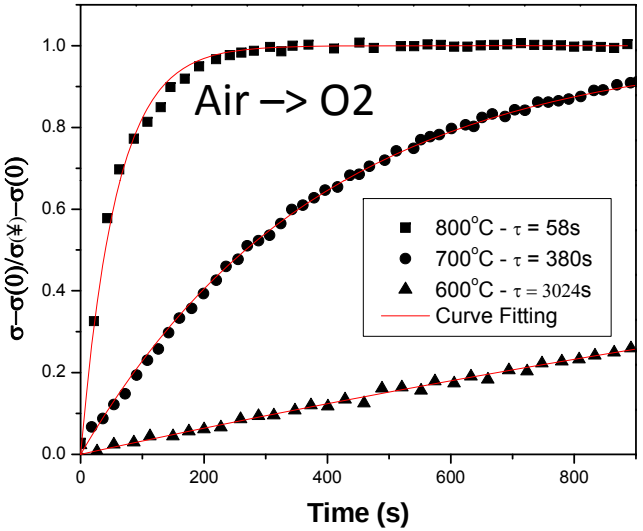


New setup allows measurement of surface exchange coefficient over a wide range of temperature and pO_2

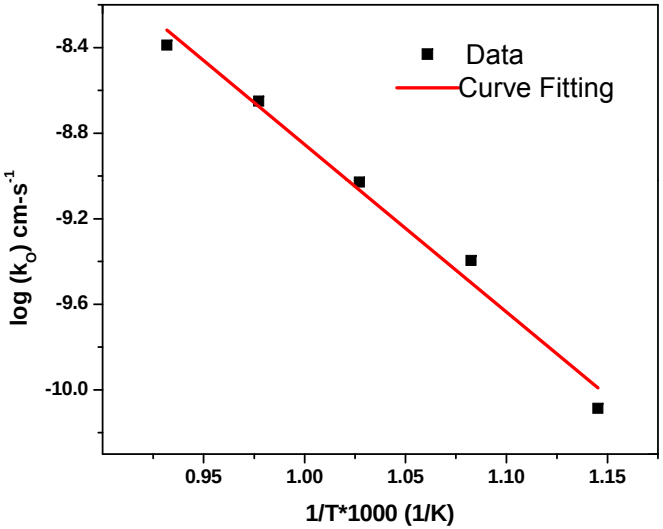
W. Wang and A. V. Virkar, *Sensors and Actuators B: Chemical, vol. 98, pp. 282-290, 2004.*

Electrical Conductivity Relaxation…

Normalized conductivity

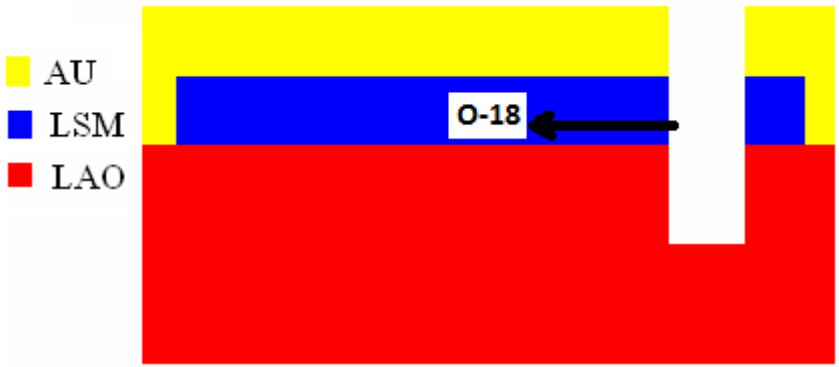


Arrhenius Plot of k_o

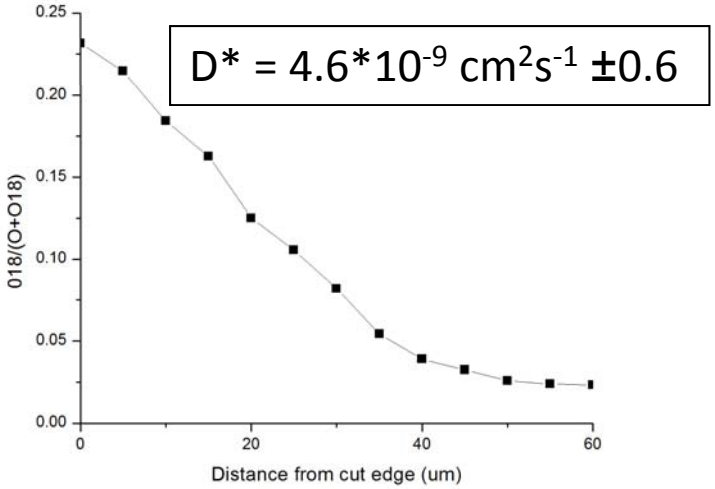


- k_o was in good agreement with literature values at $4x10^{-9}$ at 800°C
- For LSM, Activation energy was found to be 1.4 eV.

Oxygen-18 tracer diffusion



Cross section of samples



- Samples are exposed to O-18 at 800°C and then quenched to room temperature.
- Using TOF-SIMS technique, O-16 and O-18 concentrations are measured at intervals from the exposed edge.

Oxygen-18 tracer diffusion

- Ability to extract tracer diffusion coefficient (D*), if k* is known.

$$c_r^*(x,t) = erfc\left(\frac{x}{2\sqrt{D^*t}}\right) - \exp\left(\frac{k^*x}{D^*} + \frac{k^{*2}t}{D^*}\right) \cdot erfc\left(\frac{x}{2\sqrt{D^*t}} + k^*\sqrt{\frac{t}{D^*}}\right)$$

J. Crank, *The Mathematics of Diffusion, 2 ed. New York: Oxford University Press, 1975.*

Where we insert k_o to have 1 fitting parameter:

- D* is tracer diffusion coef.
- $k^* \approx k_o$ is surface exchange coef.

$D^* = 4.6*10^{-9}\ cm^2s^{-1} \pm 0.6$

•Agreement with literature. T. Bak, J. Nowotny, M. Rekas, C. C. Sorrell, E. R. Vance, Solid State Ionics 2000, 135, 557.

Effect of an applied DC Bias…

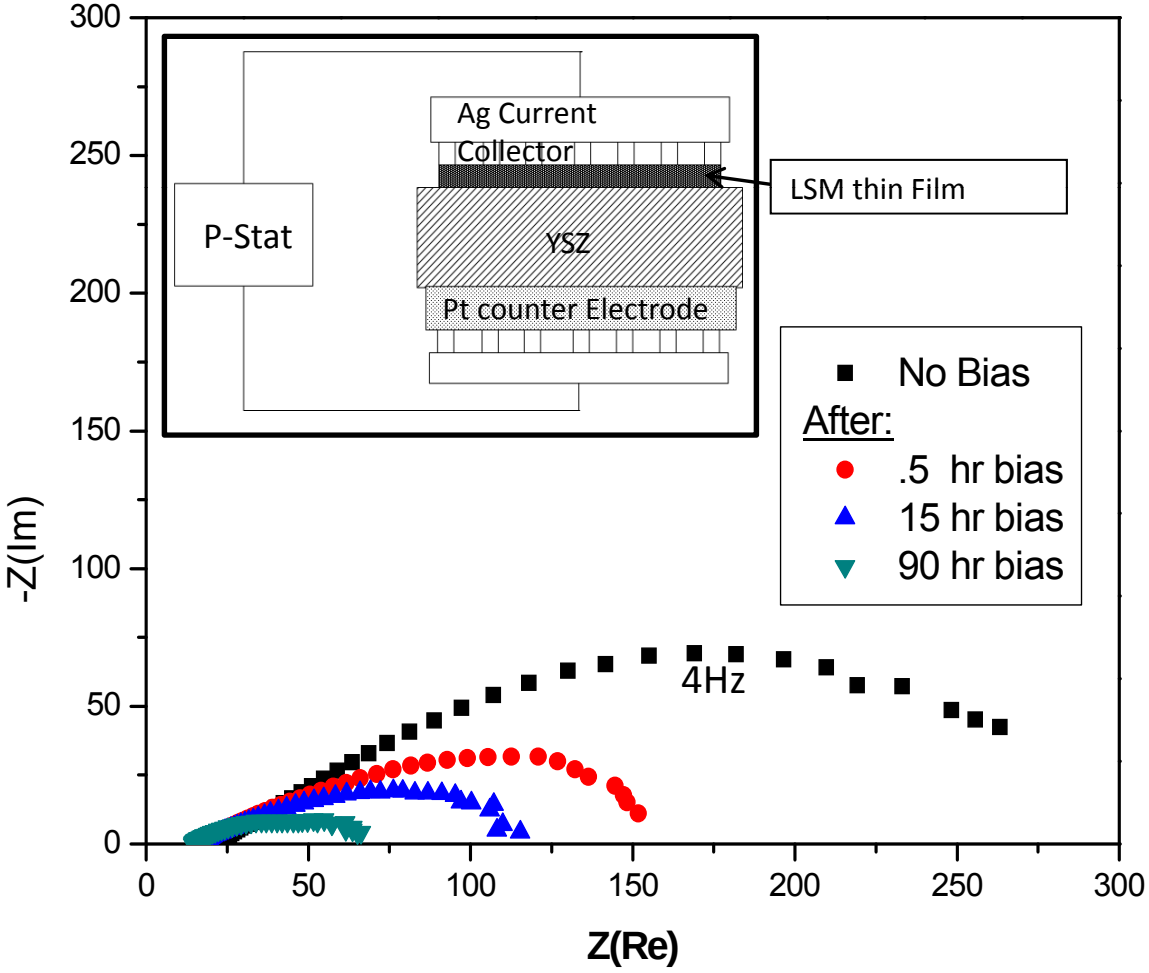
Three Sample sets of LSM/YSZ(111) were compared:

LSM #1: As Deposited	LSM #2: Heated to 800C in air, equilibrated, quenched	LSM #3: Heated to 800C in air, equilibrated, -1V bias, quenched

All samples were sealed in ampoules as described above. The biasing was performed at BU.

LSM#3: Biased Thin Film Experiments…

Impedance Results



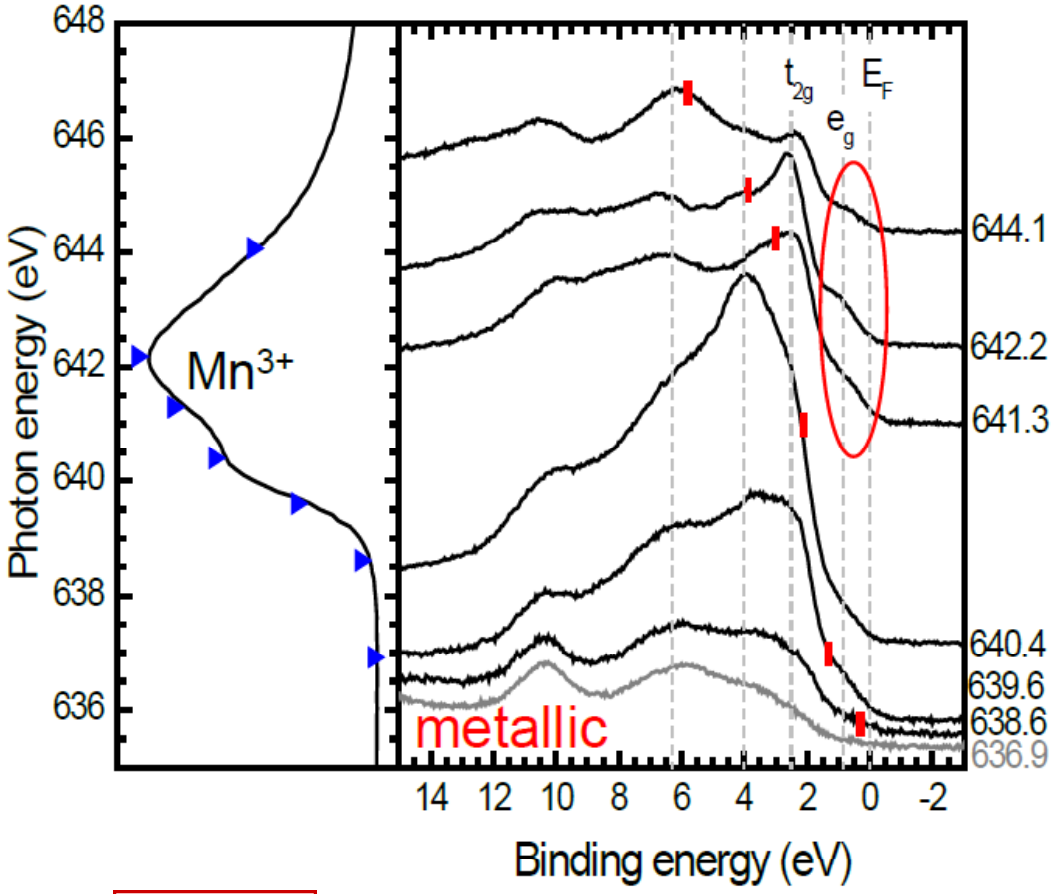
Results:

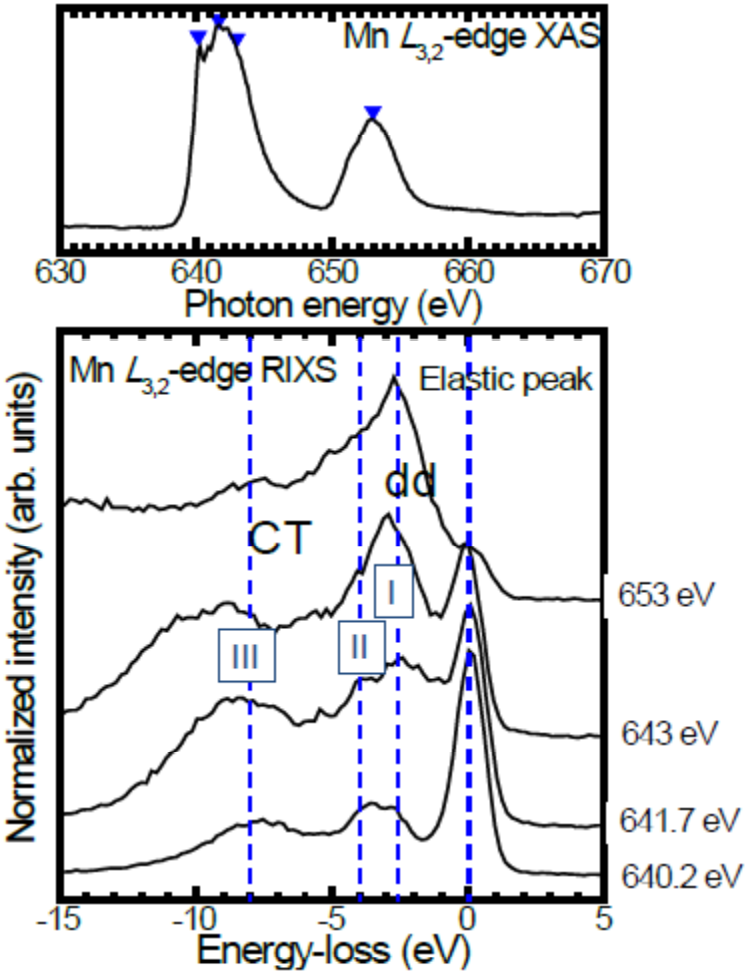
•With the application of a 1V cathodic bias, the real impedance initially drops rapidly, and then continues to decrease over a 5 day treatment.

• By using a mesh we ensure an even current distribution across entire film.

Soft X-ray Spectroscopy of $La_{0.8}Sr_{0.2}MnO_3$ cathodes

Pristine $La_{0.8}Sr_{0.2}MnO_3$ (Recall)





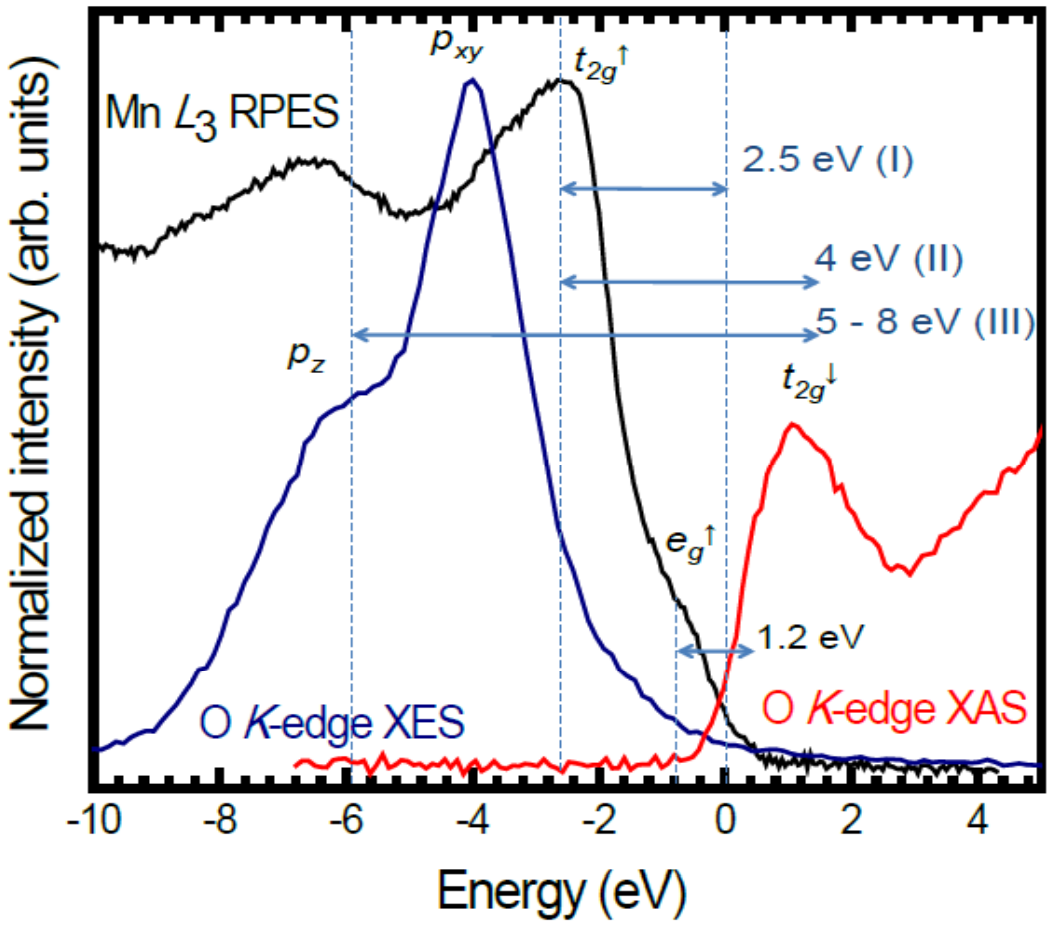
Resonant Photoemission Spectroscopy (RPES)

Resonant Inelastic X-ray Scattering (RIXS)

Pristine $La_{0.8}Sr_{0.2}MnO_3$ cont…

Combining O *K*-edge XES/XAS to obtain a complete description of DOS and possible low energy excitations

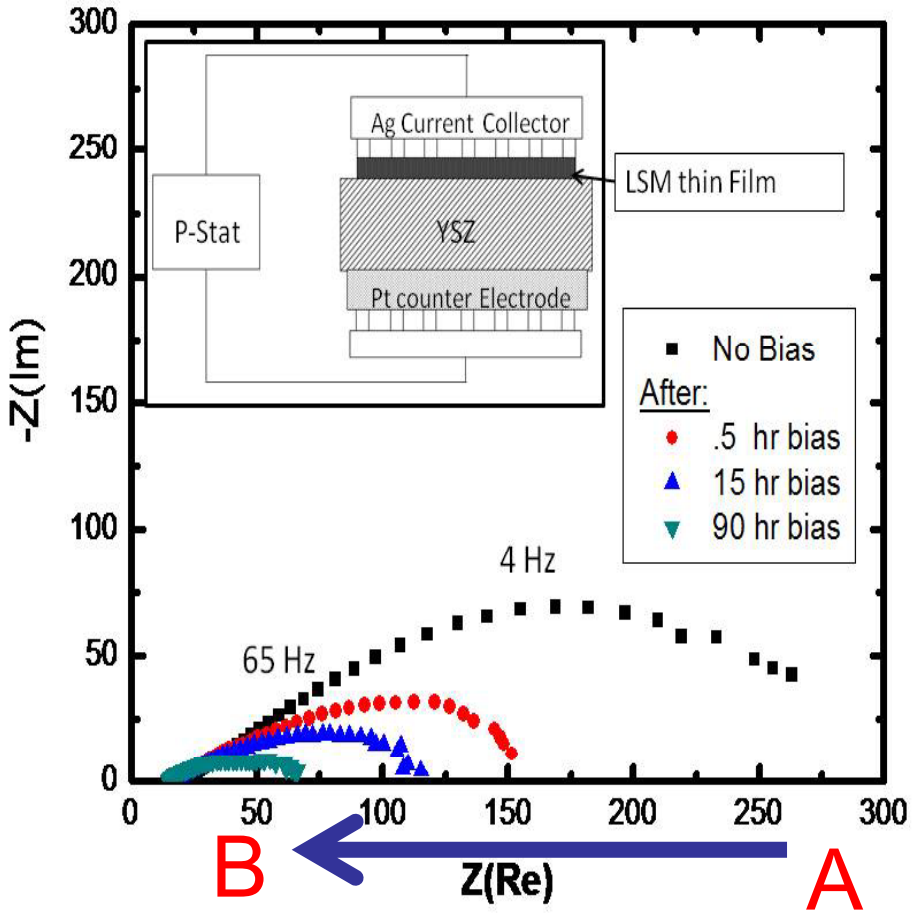
Agreement with our Mn $L_{3,2}$-edge RIXS



Aim: to provide complete descriptions before and after burn-in effect

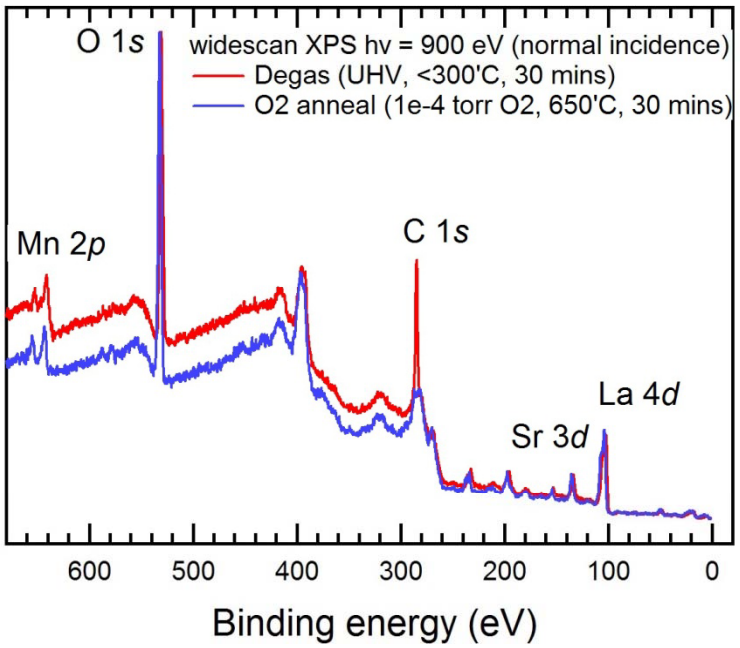
Rapid Quench Method

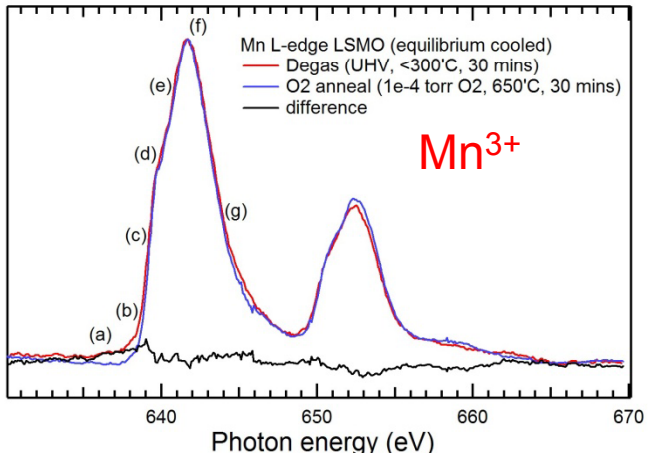
Why? Ability to compare electronic and chemical composition before and after burn-in effects. Cannot perform in-situ measurements with soft X-rays
Seal samples in glass vacuums, transfer in N_2-rich environment.

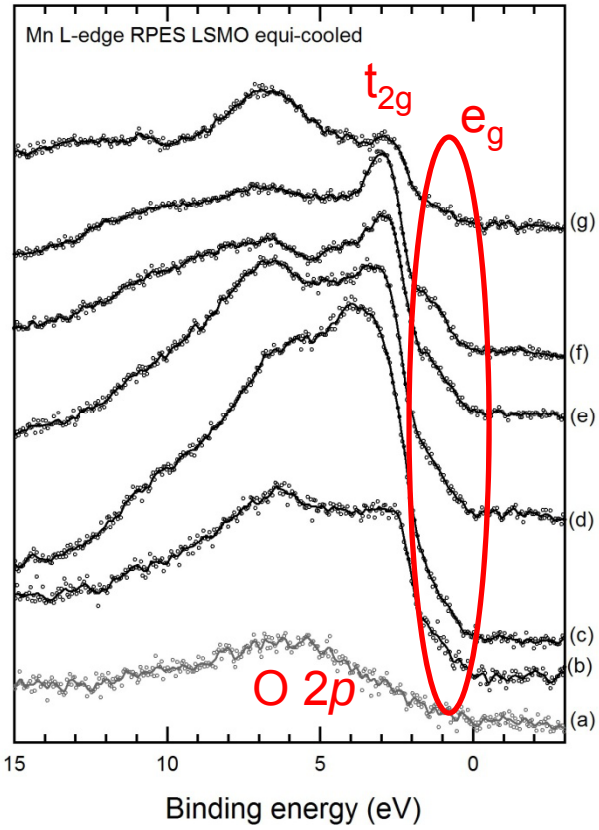


Testing Quenching Method

Compared chemical composition (core-level XPS) and valence band structure (RPES) of equilibrium-cooled samples.







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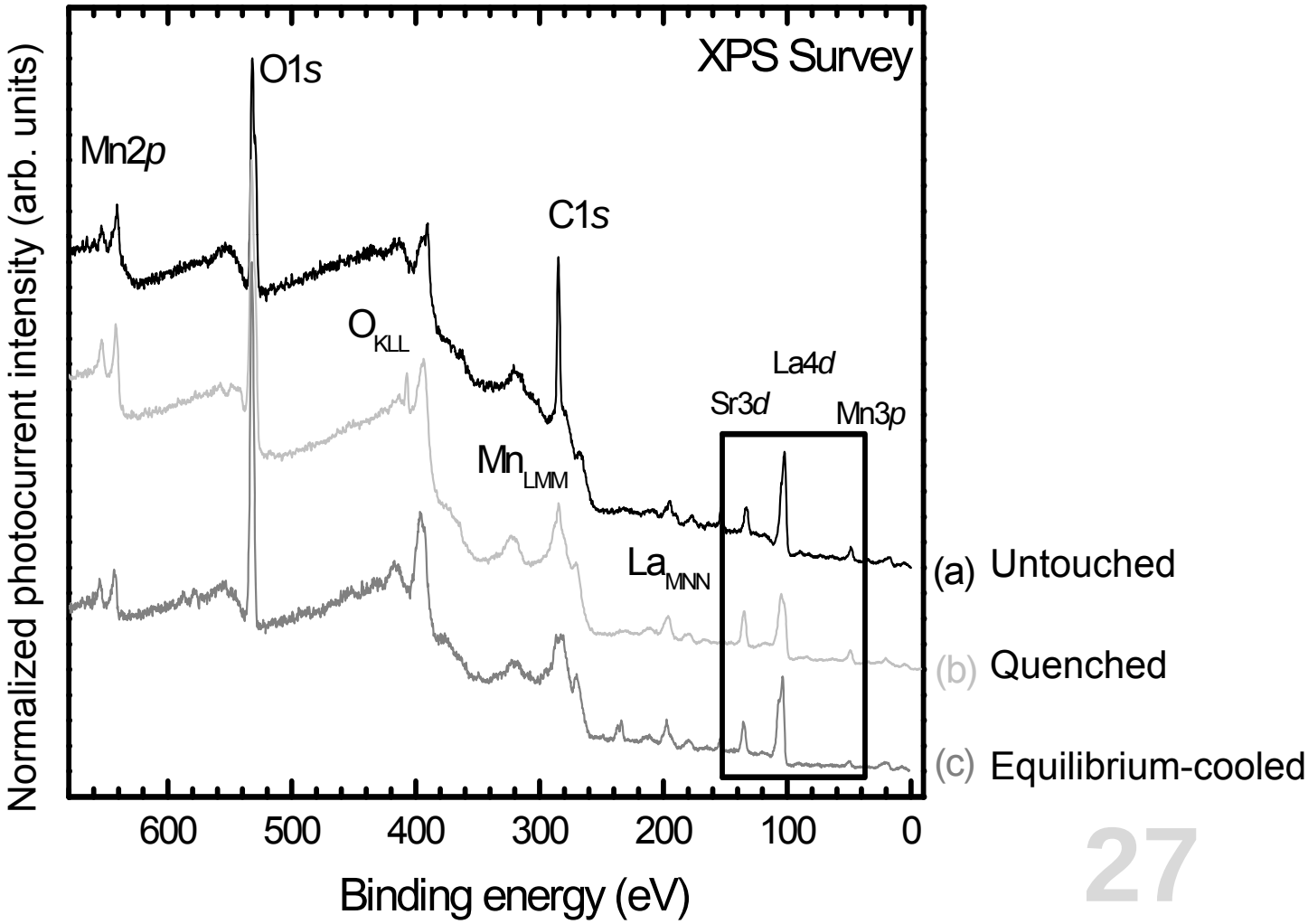
Same La/Sr and valence band structure as for pristine case AS EXPECTED

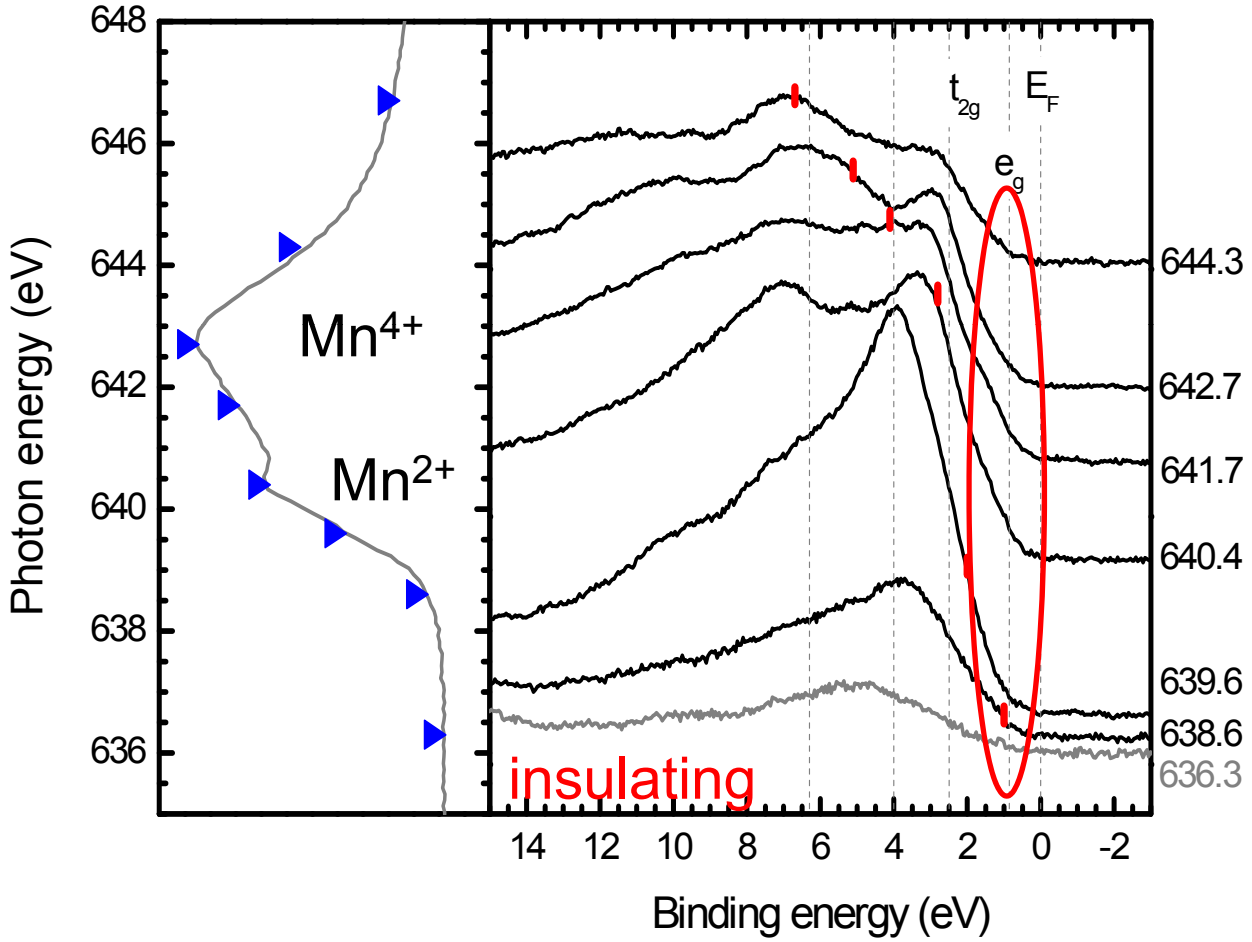
Rapid Thermal Quenching No Bias (A)

Clear change in Sr/La ratio with Rapid Thermal Quenching

Surface-sensitive



Rapid Thermal Quenching No Bias (A)



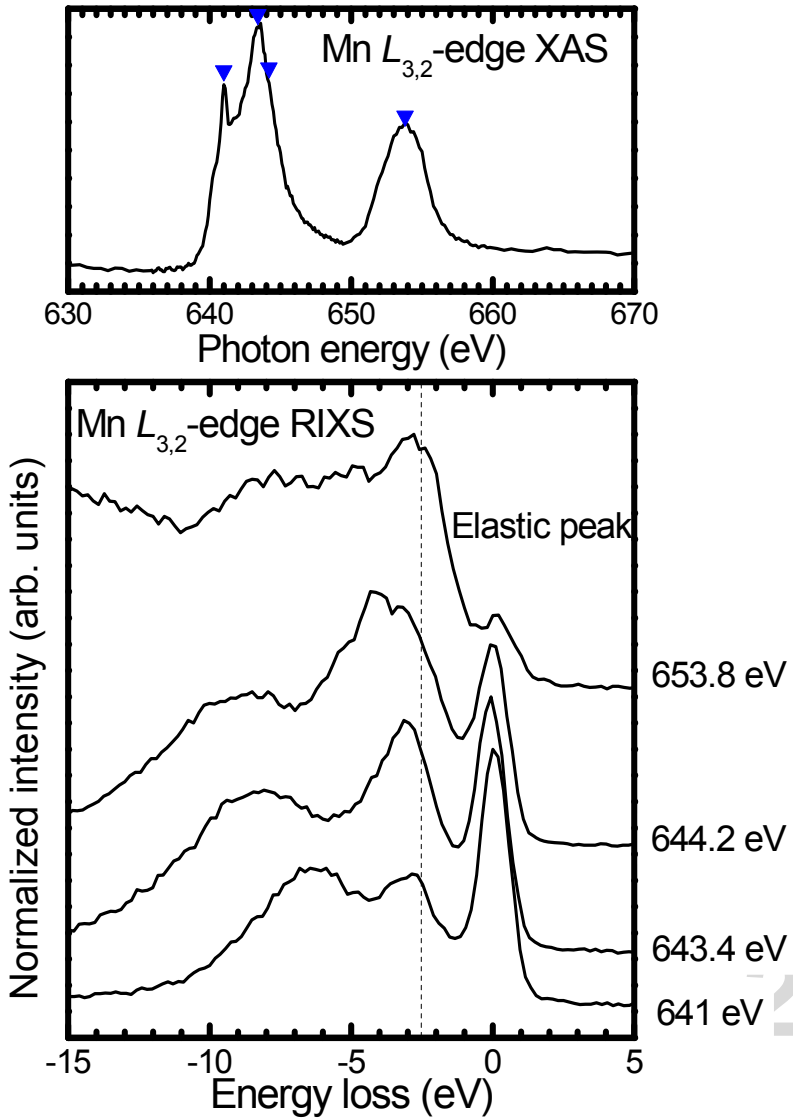
Absence of e_g state → increased hole doping (x > 0.55)
consistent with La/Sr ratio at surface
Mixed Mn valence states

Rapid Thermal Quenching No Bias (A)

Photon-in, photon-out RIXS increased bulk-sensitivity but in glancing geometry

Change in RIXS spectrum in agreement with increased hole-doping of x > 0.5

e.g. K. Kuepper, et al., J Phys Chem B 109, 9354 (2005)



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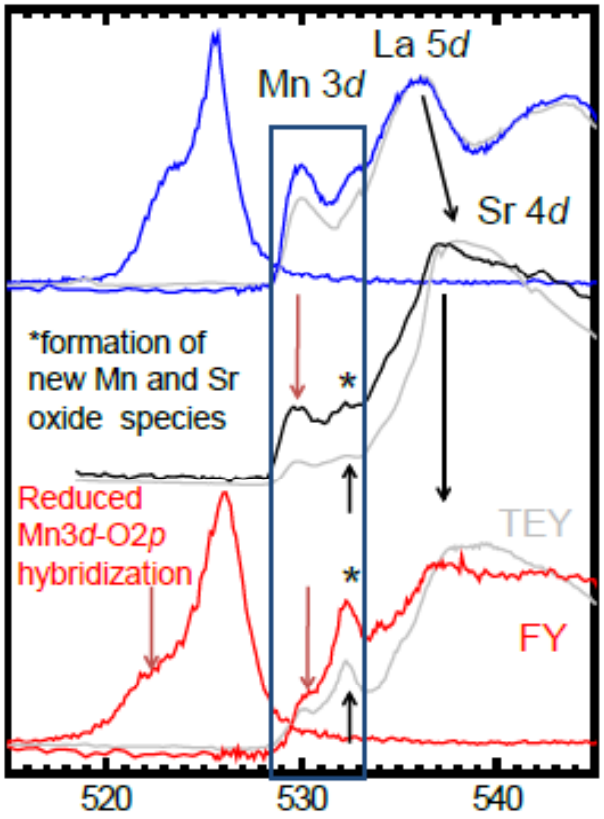
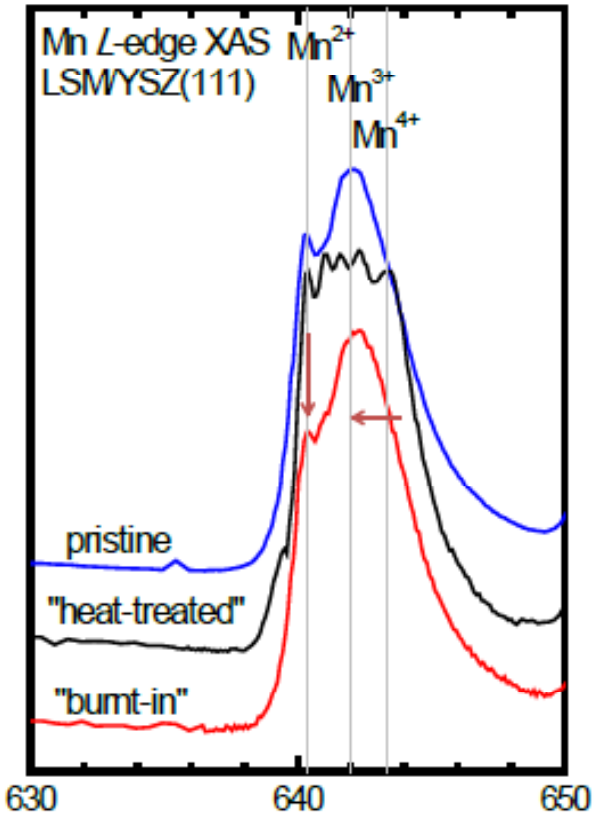
Quenched with bias (B)

Cannot perform Mn *L*-edge RPES yet due to the Pt mesh used to apply bias, but….



Severe change in O environment mainly upon heating alone
MnO_2, Mn_3O_4 and $Sr_xMn_yO_z$ formation at initial stages



Mn charge state changes upon heating AND cathodic bias
Mn^{2+} migration and Mn^{4+} reduction after activation

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Summary

✓ Increased hole-doping (related to La/Sr) and formation of new species at operating temp. and pressure.

✓ Clear changes in O K-edge following application of bias

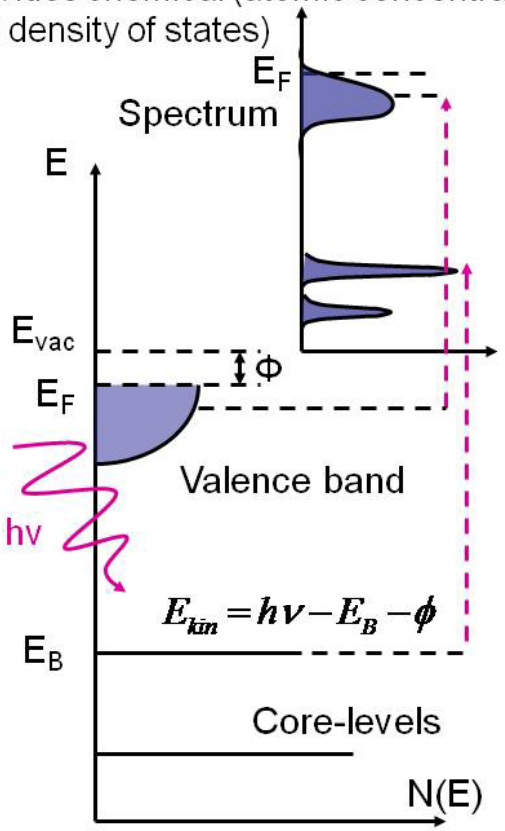
Future Directions

1) Development of a suitable mesh to apply bias and enable RPES measurements of “burnt-in” films to build up a complete DOS picture.

2) Comparison with density functional theory calculations (Xi Lin) to confirm increased hole-doping and formation of $Sr_xMn_yO_z$ species

Spare Slides 1 of 2

Surface sensitive (KE = 900 eV electrons, mean free path length ~ 10-20 Å)
Provides chemical (atomic concentration) and electronic
(VB density of states)



Resonant *L*-edge Photoemission

X-ray absorption process

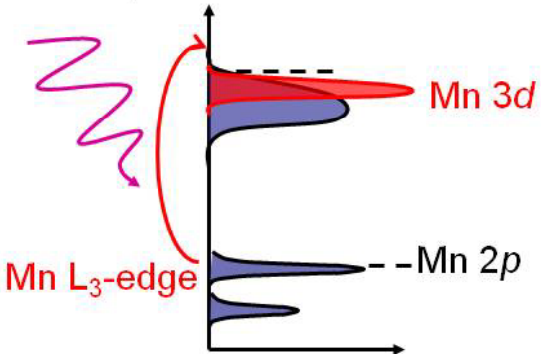
$$2p^6 3d^n \rightarrow \left[2p^6 3d^{n+1}\right]^* \quad \text{Excitation}$$

$$\rightarrow 2p^6 3d^{n-1} + e(\varepsilon) \quad \text{Direct recombination}$$

X-ray Photoemission process

$$2p^6 3d^n + h\nu \rightarrow 2p^6 3d^{n-1} + e(\varepsilon)$$

Emitted 3*d* photoelectrons have same KE



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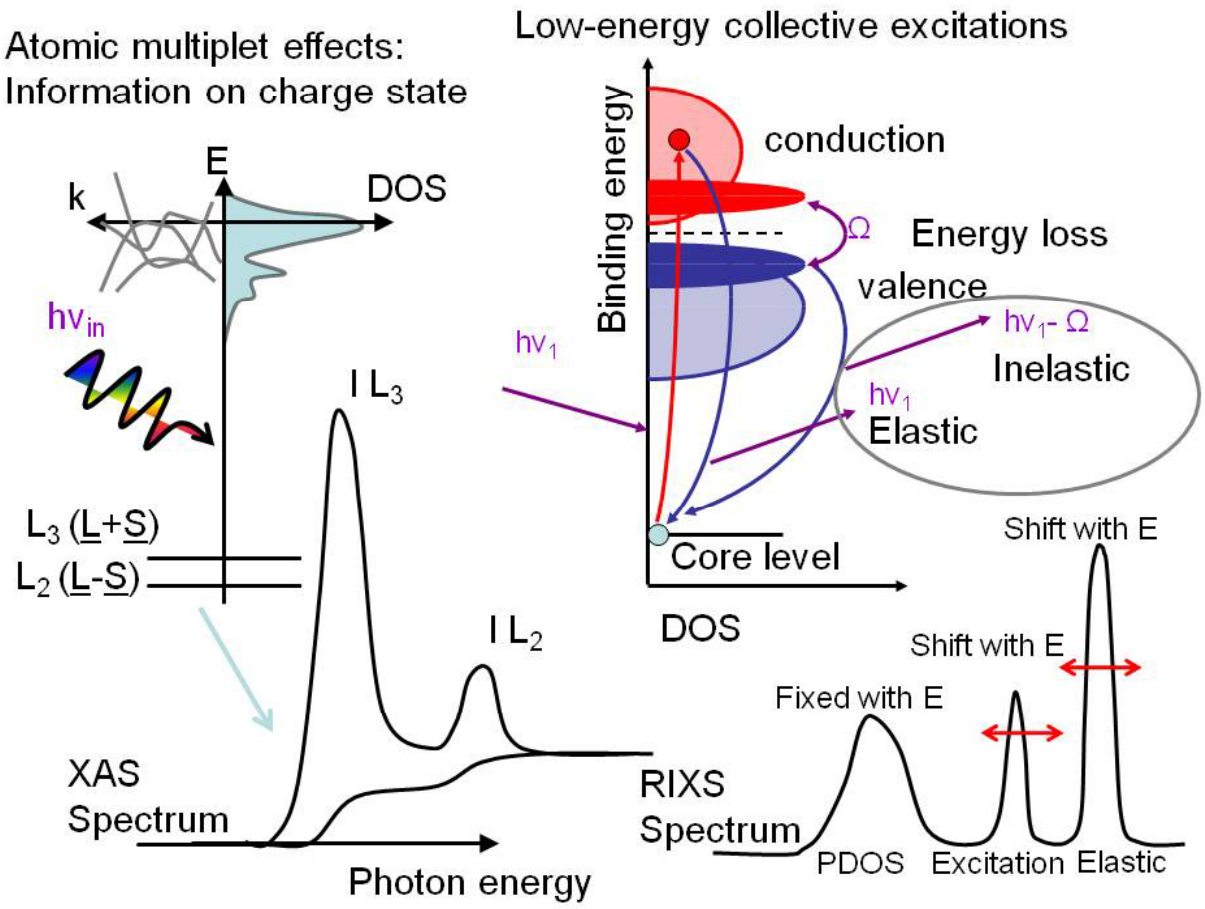
Spare Slides 2 of 2



Path Forward

- Continue to pursue ex-situ XAS as a method to probe cathode surface, especially on “conditioned” cathode films.
- Extend the technique to study samples under a wider operating conditions range and to LSCF.
- Continue to pursue in-situ EXAFS and commence studies on truncation rod analysis
- Extend use of TEM to ex-situ analysis of “conditioned” films
- Continue O-18 SIMS analysis in conjunction with other techniques.

Acknowledgements

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- National Synchrotron Light Source: Brookhaven National Laboratory.

- Advanced Light Source: Lawrence Berkeley National Laboratory.