Synthesizing Core-Shell Heterostructures for SOFCS Using a Solution Precipitation Method

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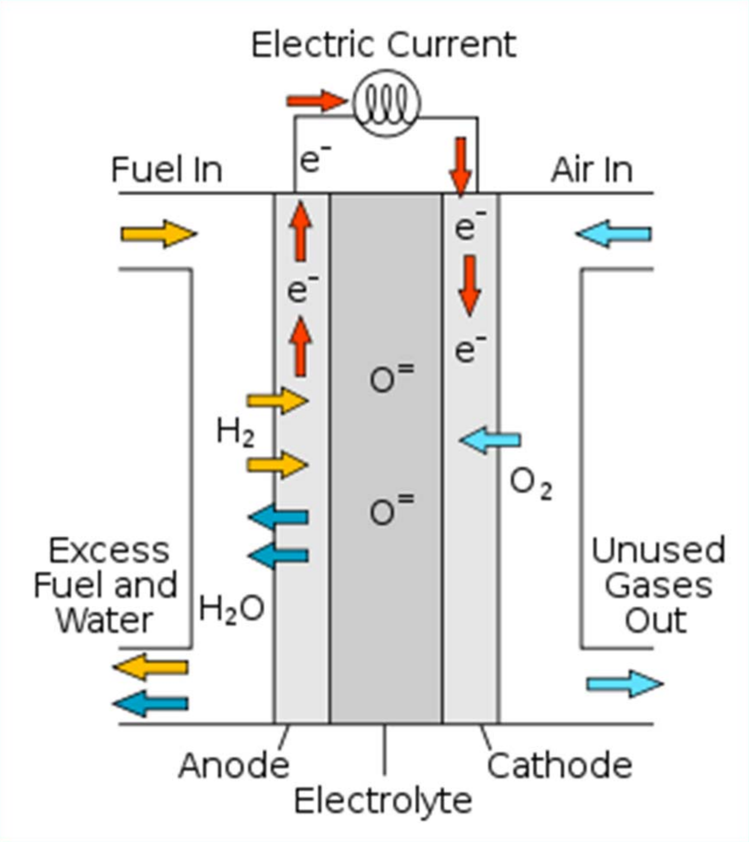
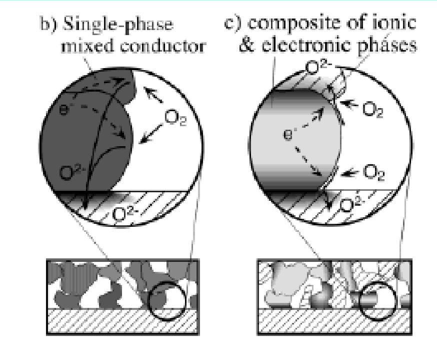
Outline

- Motivation
- Materials Background
- Why Core-Shell Cathodes?
- Molten Salt Method
- STEM Analysis Results
- Future Directions

SOFC Electrode Reactions



Pathways for Cathodic Oxygen Reduction Reaction



The “Bulk Path”

$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF-6428)

Necessary first steps:

Gas Phase Diffusion

↓

Surface Adsorption

↓

Dissociation

Electronation and Incorporation to cathode

↓

Bulk Diffusion to Electrolyte

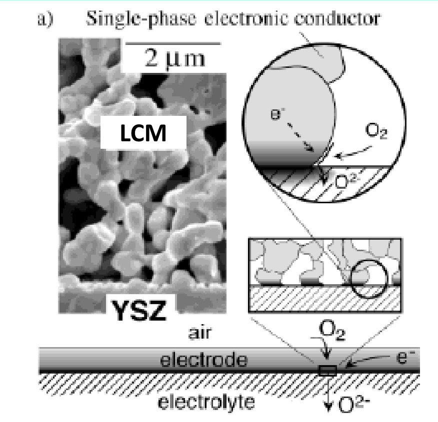
↓

Incorporation into Electrolyte

Surface Diffusion to Triple Phase Boundary (TPB)

↓

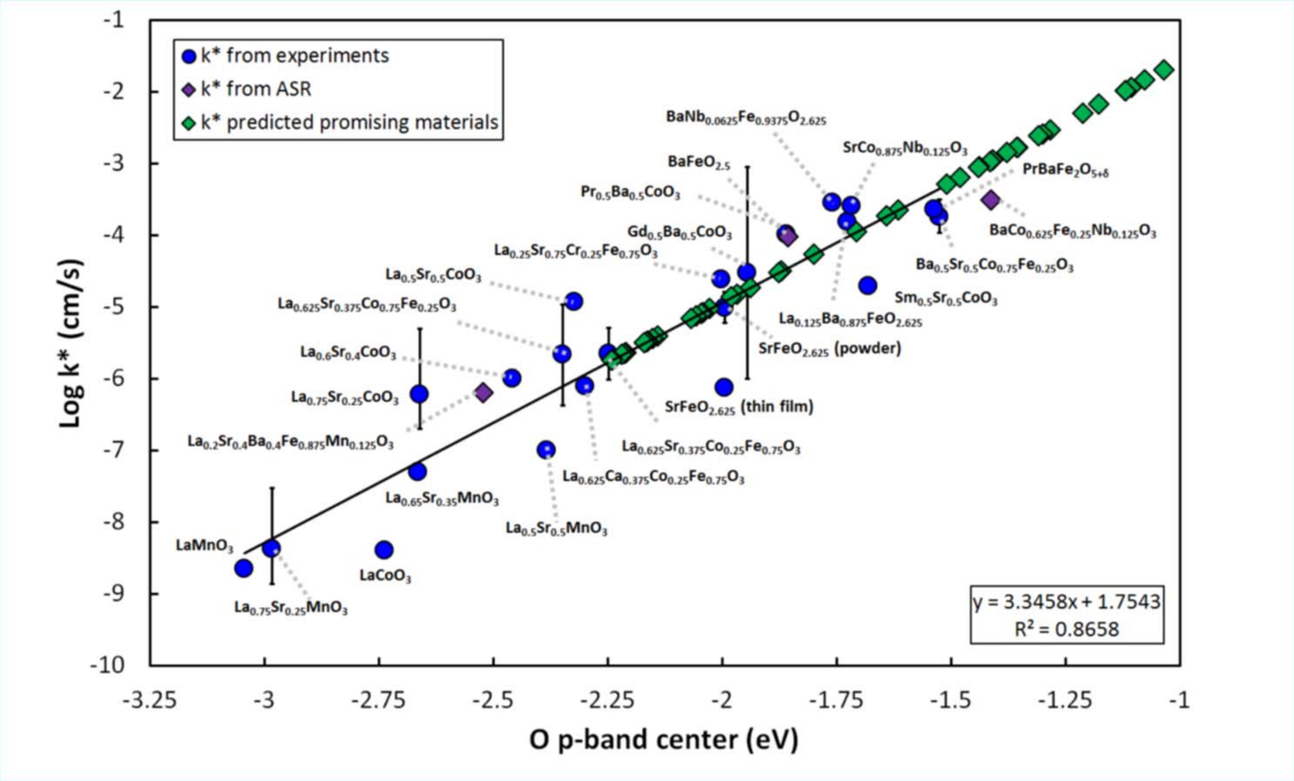
Electronation and Incorporation to electrolyte at TPB



The “Surface Path”

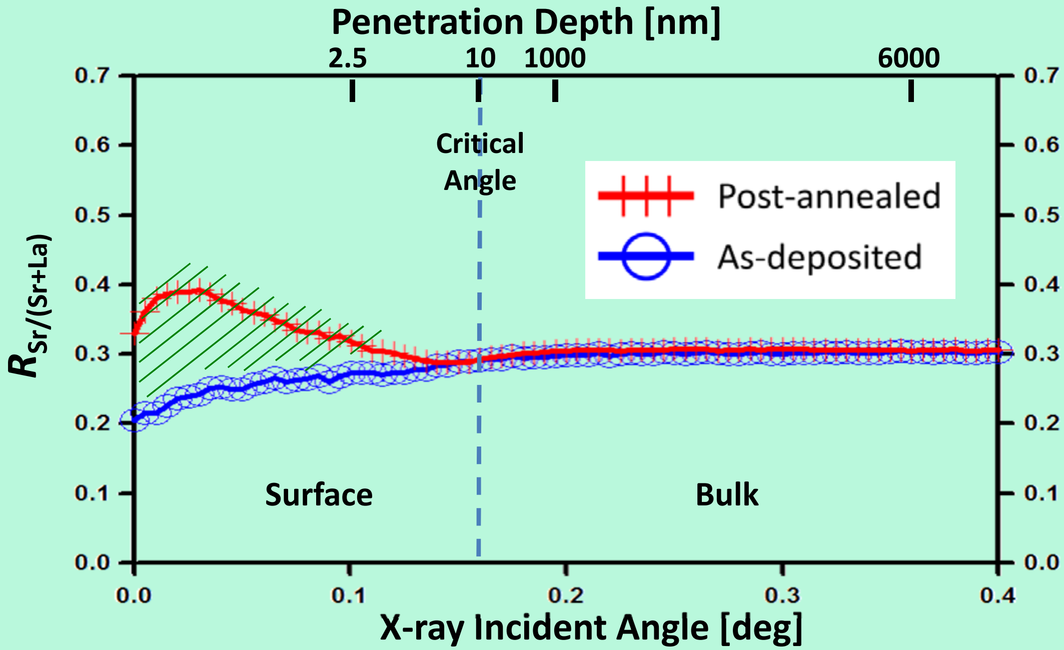
$(La_{0.87}Ca_{0.13})_{0.95}MnO_{3\pm\delta}$, (LCM)

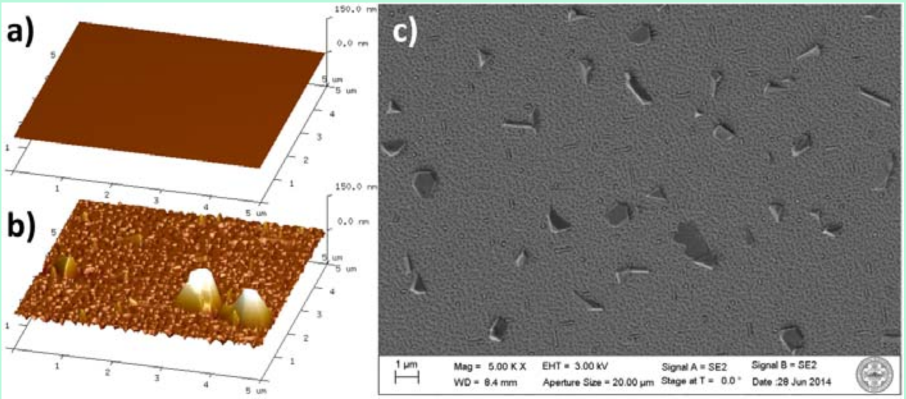
Oxygen Exchange Electrocatalysts



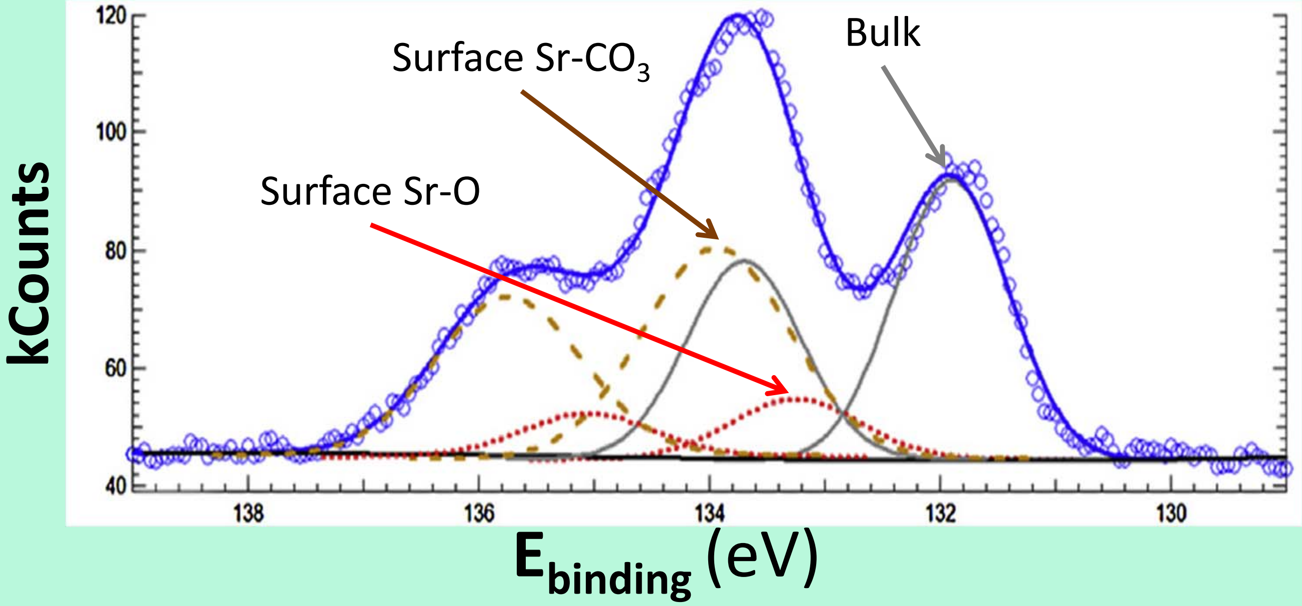
[1] Jacobs et al (https://arxiv.org/ftp/arxiv/papers/1801/1801.06109.pdf)

Cation Surface Segregation of LSCF





HAXPES Analysis of $Sr3d_{3/2}$ & $Sr3d_{5/2}$ Orbitals



$Sr3d_{5/2}$ energies in LSCF

Bulk Sr^{2+}:	131.6eV
Surface Sr-O:	133.1eV
Surface $Sr\text{-}CO_3$:	134.0eV

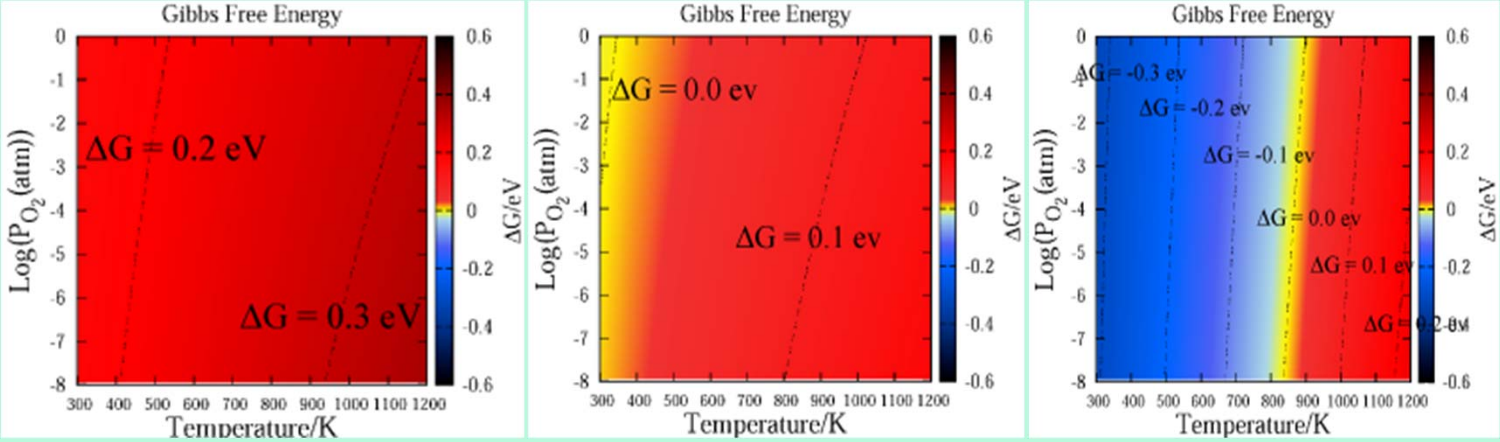
[2] P.A.W van der Heide, *Surf. Interface Anal.* 2002

Sr Surface Segregation Enhancement by CO_2

Step 1. $\mathrm{Sr\ from\ LSCF\ lattice} + \frac{1}{2}\mathrm{O_2} \rightarrow \mathrm{SrO}\quad \mathrm{(by\ Sr\ Surface\ Segregation)}$

Step 2. $\mathrm{SrO} + \mathrm{CO_2} \rightarrow \mathrm{SrCO_3}$

$$La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_3 + O_2 \rightarrow La_{0.75}Sr_{0.125}Co_{0.25}Fe_{0.75}O_3 + SrO$$



Bulk

Surface

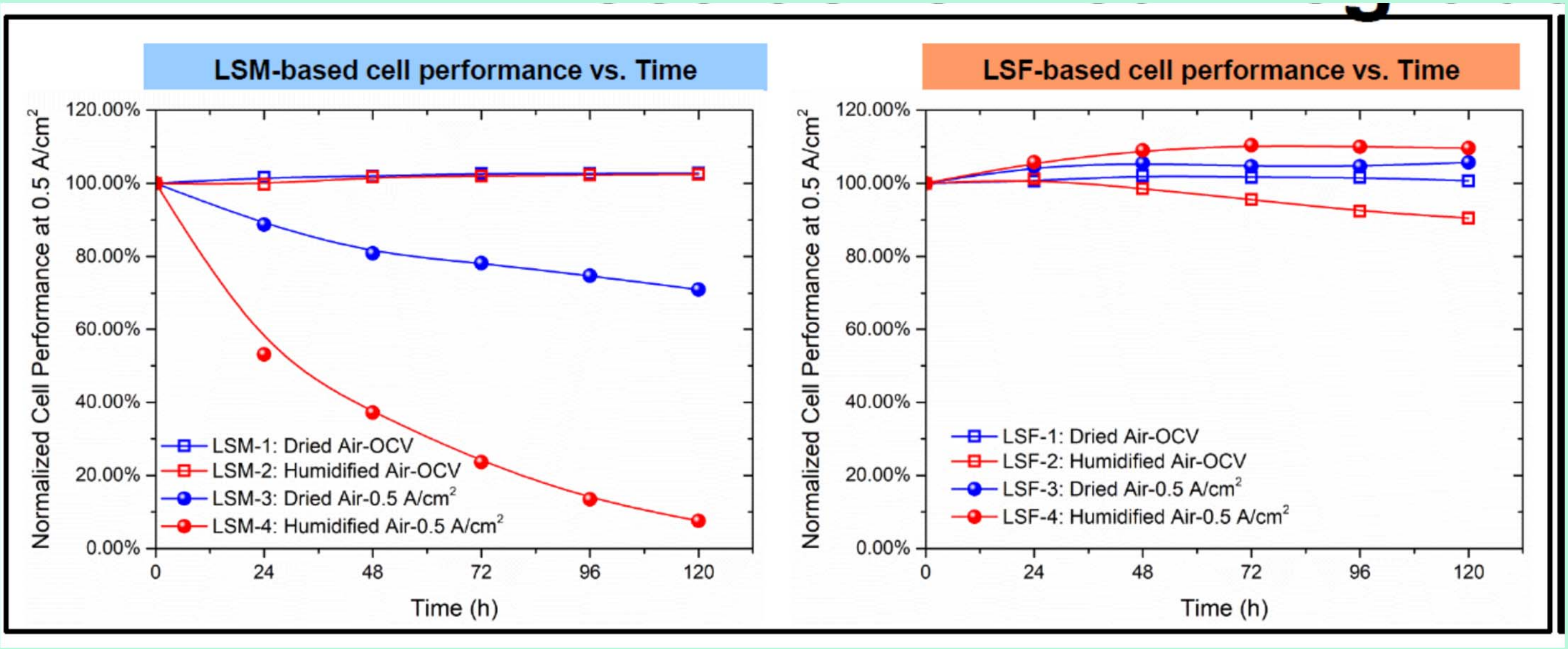
Surface + CO_2

$$La_{0.75}Sr_{0.25}Co_{0.25}Fe_{0.75}O_{3-\delta} + O_2 + CO_2 \rightarrow La_{0.75}Sr_{0.125}Co_{0.25}Fe_{0.75}O_{3-\delta} + SrCO_3$$

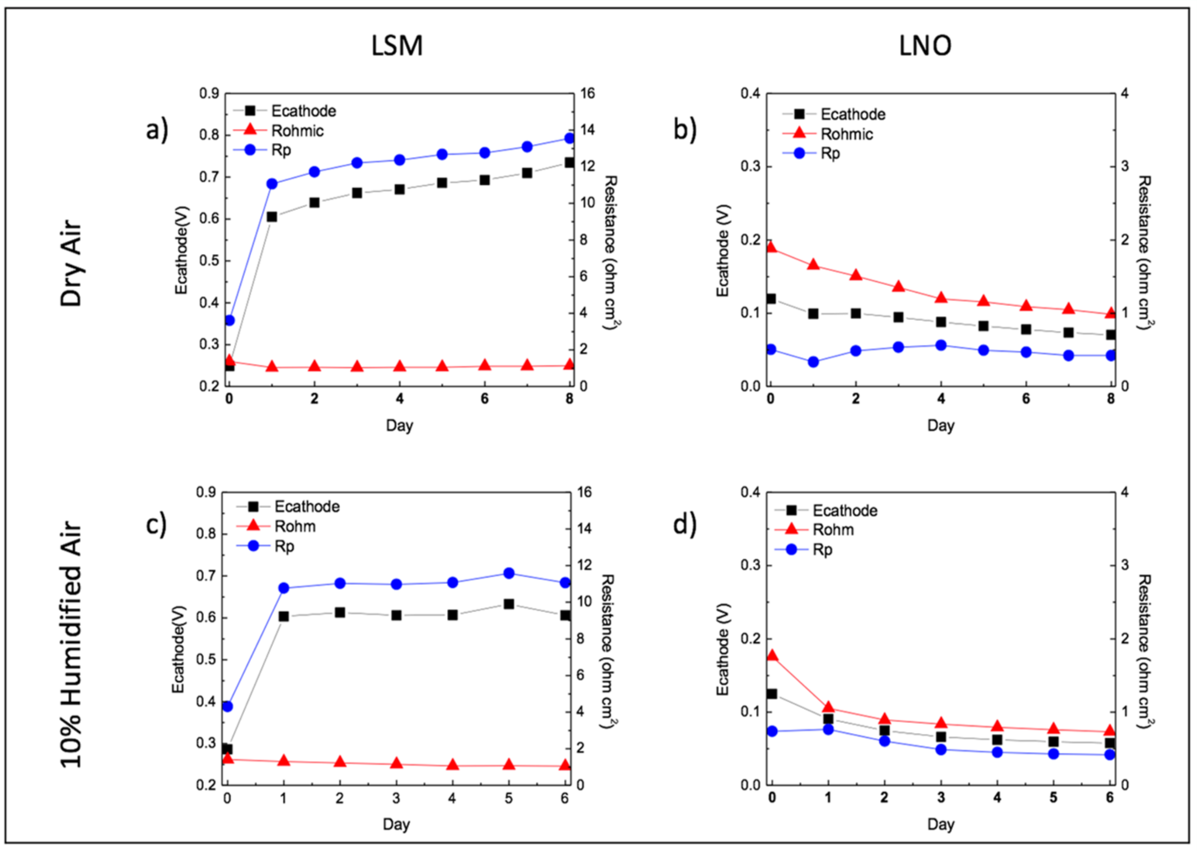
Surface in LSCF is more unstable than the bulk. Presence of atmospheric CO_2 further destabilizes the surface.

[3] Yang, Y., Luo, H., Cetin, D., Lin, X., Ludwig, K., Pal, U., Gopalan, S., Basu, S. Effect of atmospheric CO2 on surface segregation and phase formation in $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\text{-}\delta}$ in thin films. *Applied Surface Science.* 2014

Cr-Induced Degradation: LSM vs LSCF



Cr-Induced Degradation: LSM vs LNO



Summary of Observations

- Good ORR activity appears to be inversely correlated with materials stability
- Many double perovskites show excellent ORR activity, but appear to suffer from instabilities
- Even standard LSCF cathode appears to suffer from surface instabilities in the presence of CO_2
- LSM has very poor tolerance to Cr-impurity poisoning compared to LSCF and LNO

Prior Approaches to High Performance Stable SOFC Cathodes

- Skeleton of perovskite with excellent MIEC transport properties, e.g. LSCF or BSCF
- Infiltrate materials which exhibit good oxygen surface coverage such as LSM
- Requires extra infiltration step and surface coverage by infiltrated material can be non-uniform

[4] J. R. Welty, C. E. Wicks, G. Rorrer, and R E. Wilson. *Fundamentals of momentum, heat, and mass transfer*. John Wiley & Sons, 2009.

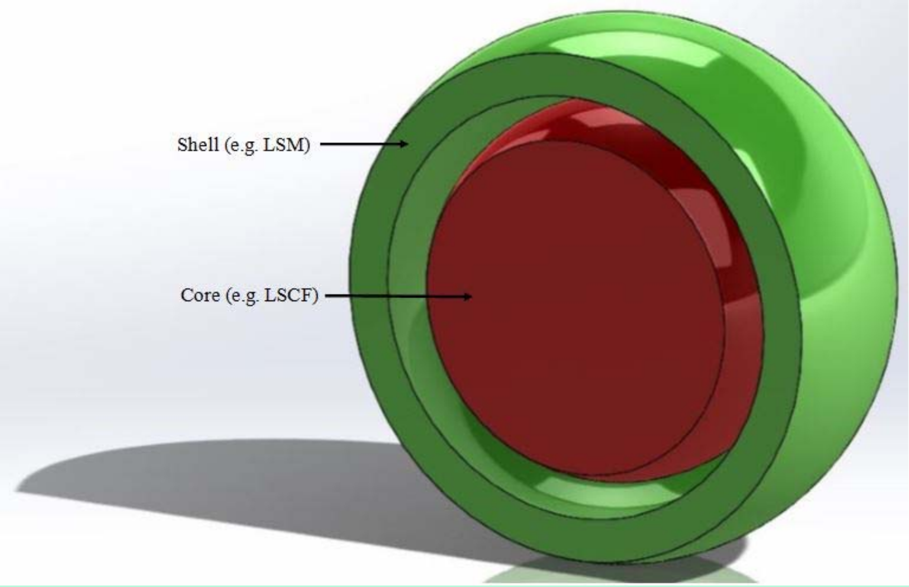
Prior Approaches to Improving Cr-Impurity Tolerance

- Gettering

- Protective interconnection coatings

Core Shell Nanoparticles

- Core Shell heterostructures have use in a variety of technological applications such as catalysis, optics, plasmonics, magnetics, etc



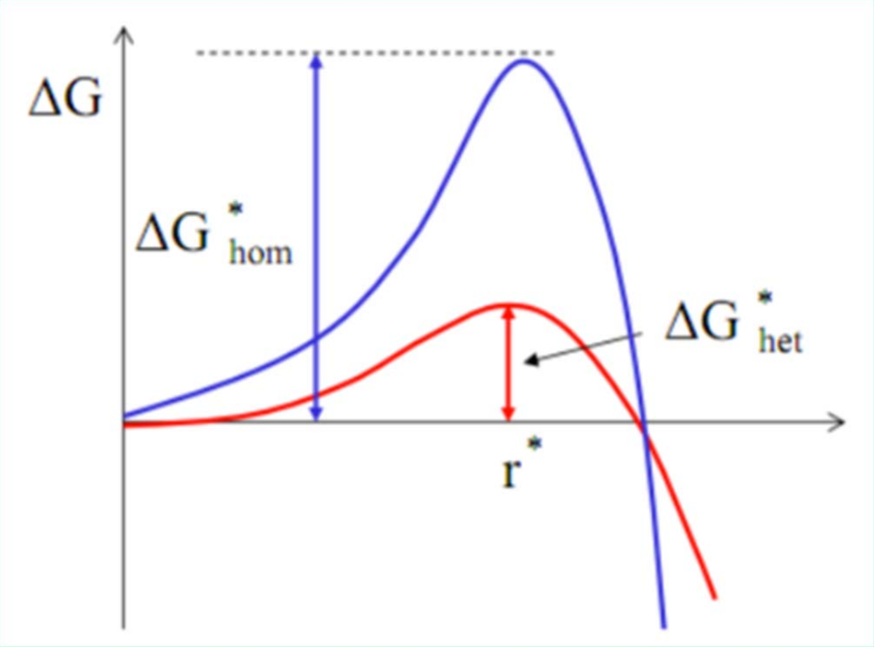
- Idea: Core material comprising MIEC material with high ORR rates but bulk or surface instability (e.g. BSCF/LSCF etc). Thin continuous shell material comprising stable perovskite e.g. LSM

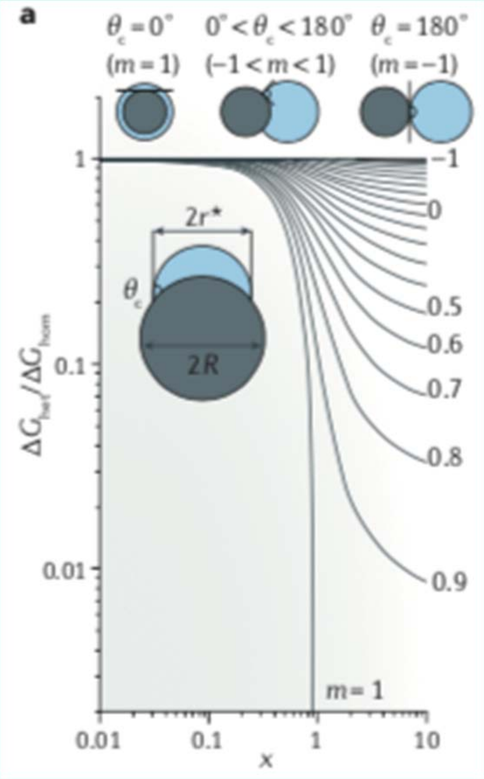
- Idea: Core material LSCF (higher-Cr tolerance) and thin shell LSCr (no reaction to Cr)

Core-Shell Nanoparticles

- Combines benefits of cathode materials such as:
  - LSCF-LSM: LSM exhibits high rates of oxygen adsorption and electronation, while LSCF exhibits high bulk diffusivity.
  - LSCF-La(Sr)CrO_3: A thin LSCrM shell would address the significant problem of Cr-poisoning of the cathode arising from stainless steel interconnects in SOFCS.
  - Key point: Core-shell cathode materials effectively combine the properties of two or more cathode materials for new functionalities.
  - Does not require expensive organic precursor materials unlike ALD

Synthesis of CSNPS: Heterogeneous Nucleation





- Heterogeneous nucleation has a lower free energy barrier than homogeneous nucleation

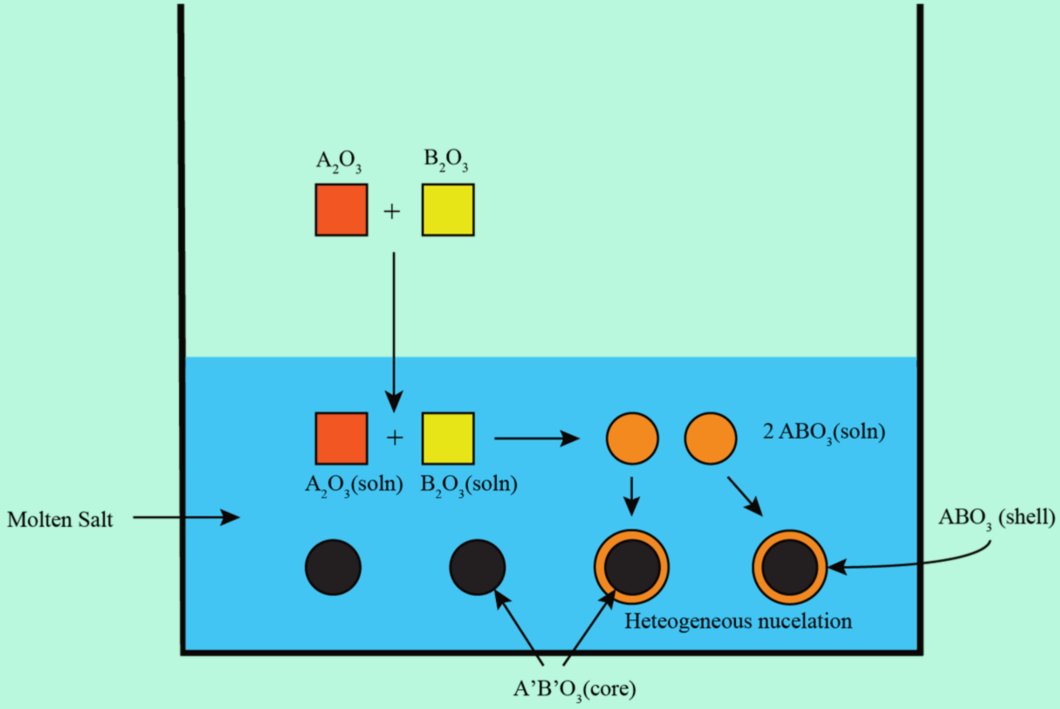
- Heterogeneous nucleation becomes more stable as the contact angle between core and shell decreases

[7] J. Lee, J. Yang, S.G. Kwon, T. Hyeon. Nonclassical Nucleation and Growth of Inorganic Nanoparticles. *Nature Reviews.* **2016.**

Proposed Solution Precipitation Method – Molten Salt

- Diffusion through liquid is orders of magnitude faster than diffusion through solids.

- Important to select salt systems which have low, but non-zero, solubility for both the precursors and the products of interest

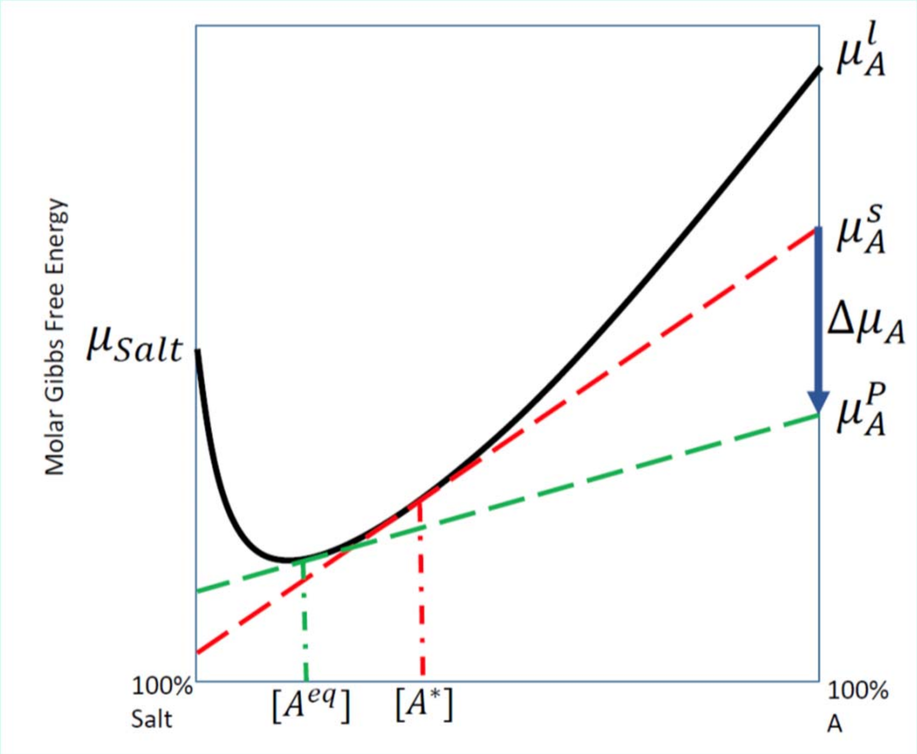


[8] S.Gopalan, K. Mehta, and A.V. Virkar, “Synthesis of Oxide Perovskite Solid Solutions Using the Molten Salt Method,” J.Mater.Res., 1996, 11(8) 1863-1865

Thermodynamics of Molten Salt Solvent

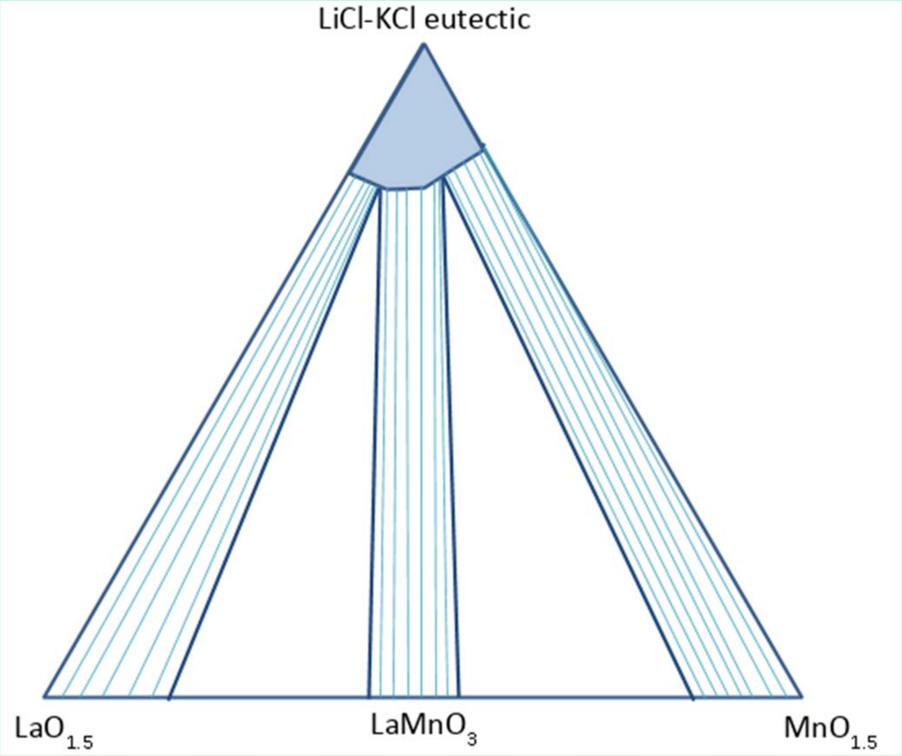
- Due to rapid transport of components in a molten salt system, the chemical reactions that occur in a solid state reaction are now in equilibrium with the liquid phase.
  - Therefore, phase equilibria that are normally not accessible in solid state reactions are accessible at lower temperatures in the liquid phase

- Since products have low solubility in melt, products precipitate out of solution once solubility limits are reached



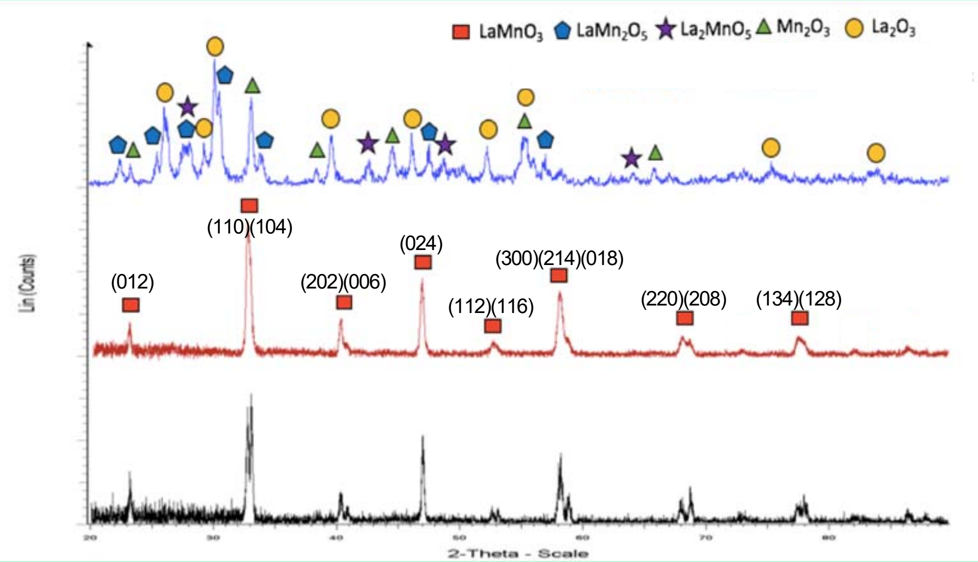
Schematic of Phase Equilibria Involved in the Molten Salt

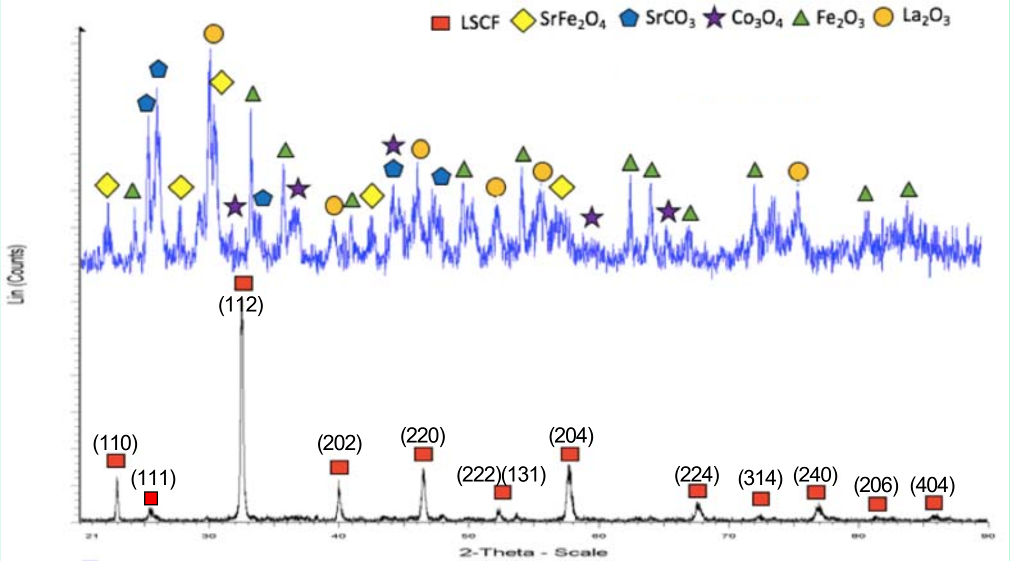
Molten Salt



- Psuedo-ternary system of molten salt /$LaO_{1.5}$/$MnO_{1.5}$
- The solid light blue region at the molten-salt vertex shows the supernatant liquid in equilibrium with the solid phases. The tie lines indicate the two-phase equilibria between the supernatant liquid and the individual solid phases
- The target composition is the singe phase region surrounding the $LaMnO_3$ phase

Accelerating Reaction Kinetics: Molten Salt Method





- Left: $LaMnO_3$ solid state 500 ^{o}C (blue), via molten salt at 500 ^{o}C (red) and via solid state reaction at 1200 ^{o}C (black)

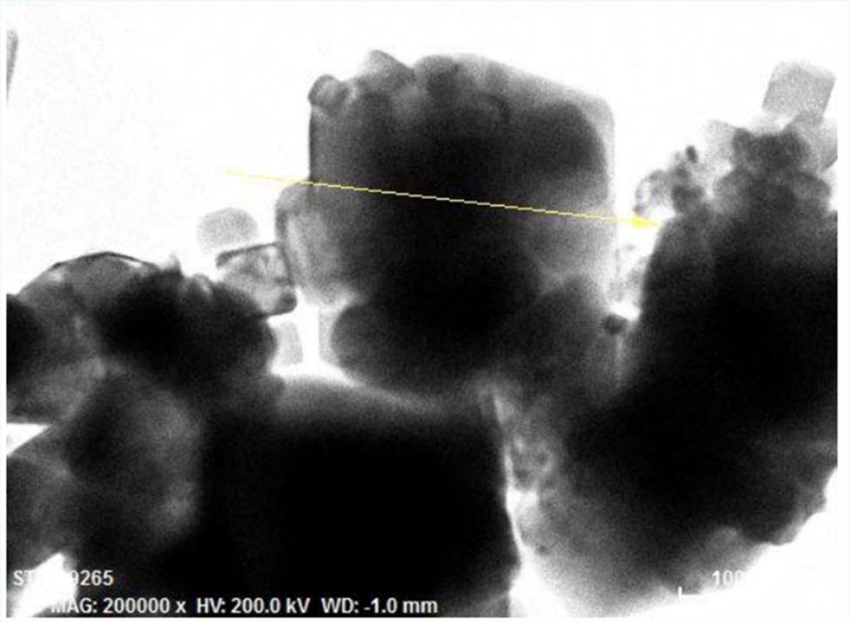
- Right: $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ solid state reaction at 500 ^{o}C (blue) and molten salt at 500 ^{o}C (black)

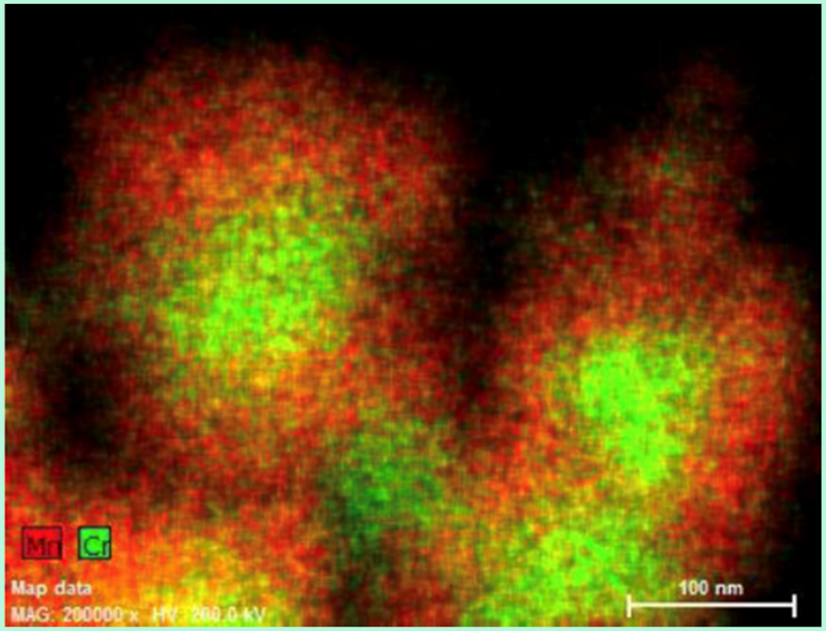
Experimental Procedure

- Synthesize LSCF (or other) cores using molten salt synthesis
  - Mix oxide precursors with LiCl-KCl, heat, cool mixture, wash salt, and filter reaction products

- Start with a molten salt, add cores, add precursors of shell (e.g. LSM), allow reaction and heterogeneous nucleation to occur. Cool mixture, wash salt and filter reaction products.

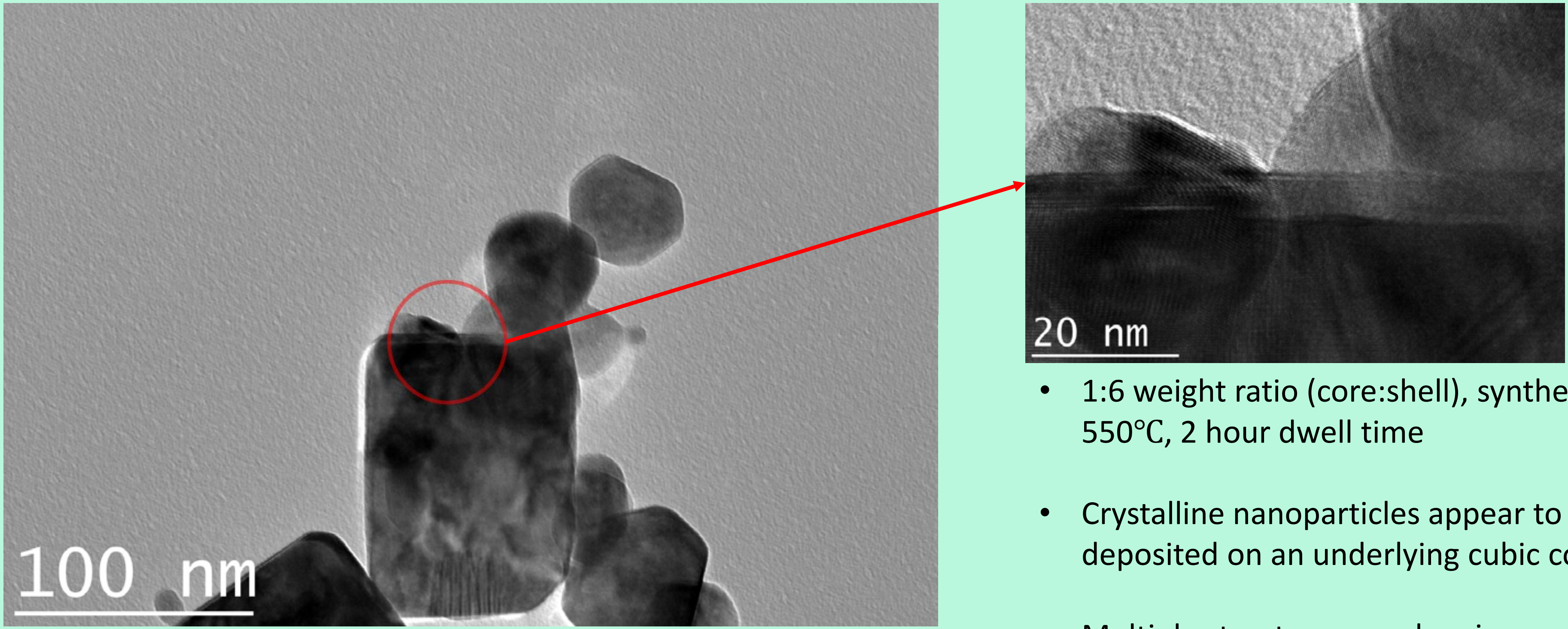
TEM Results for $LaCrO_3$ (core) -$LaMnO_3$ (shell)





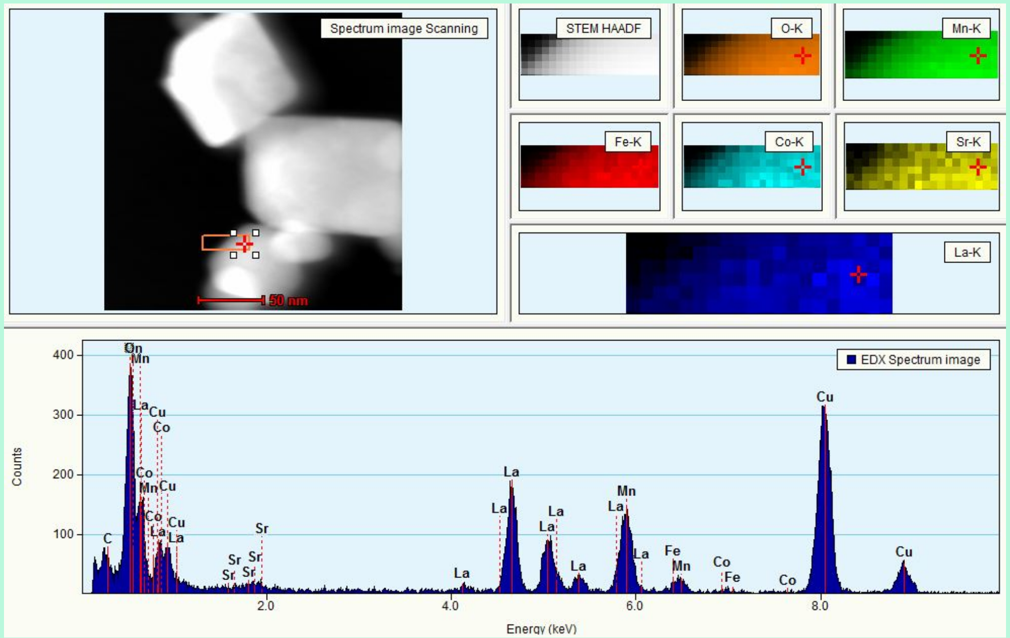
- Sample analyzed: $LaCrO_3$-$LaMnO_3$, 1:6 weight ratio (core:shell), 550℃ synthesis temperature, 8 hour dwell time
- Bright field (BF) and EDS data of $LaCrO_3$ (core)-$LaMnO_3$ (shell). The BF images show numerous small particles deposited on a central structure. The EDS data indicates Mn coverage of the nanoparticles, while Cr is rich in the center.
- This data suggests the formation of a $LaCrO_3$-$LaMnO_3$ core-shell nanoparticle, since Mn is only present on the surfaces

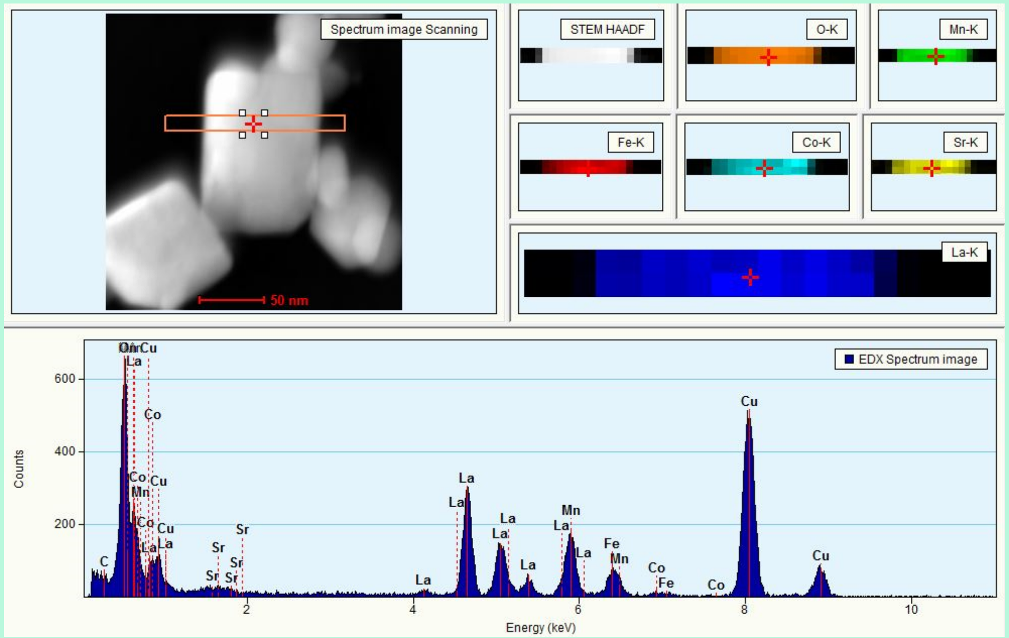
$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$(core)-$La_{0.8}Sr_{0.2}MnO_3$(shell)



- 1:6 weight ratio (core:shell), synthesized at 550°C, 2 hour dwell time
- Crystalline nanoparticles appear to have deposited on an underlying cubic core edge
- Multiple structures overlapping on cubic face
- STEM/EDS necessary to probe elemental composition on satellite nanoparticles

STEM/EDS Results of LSCF (core)/LSM (shell)

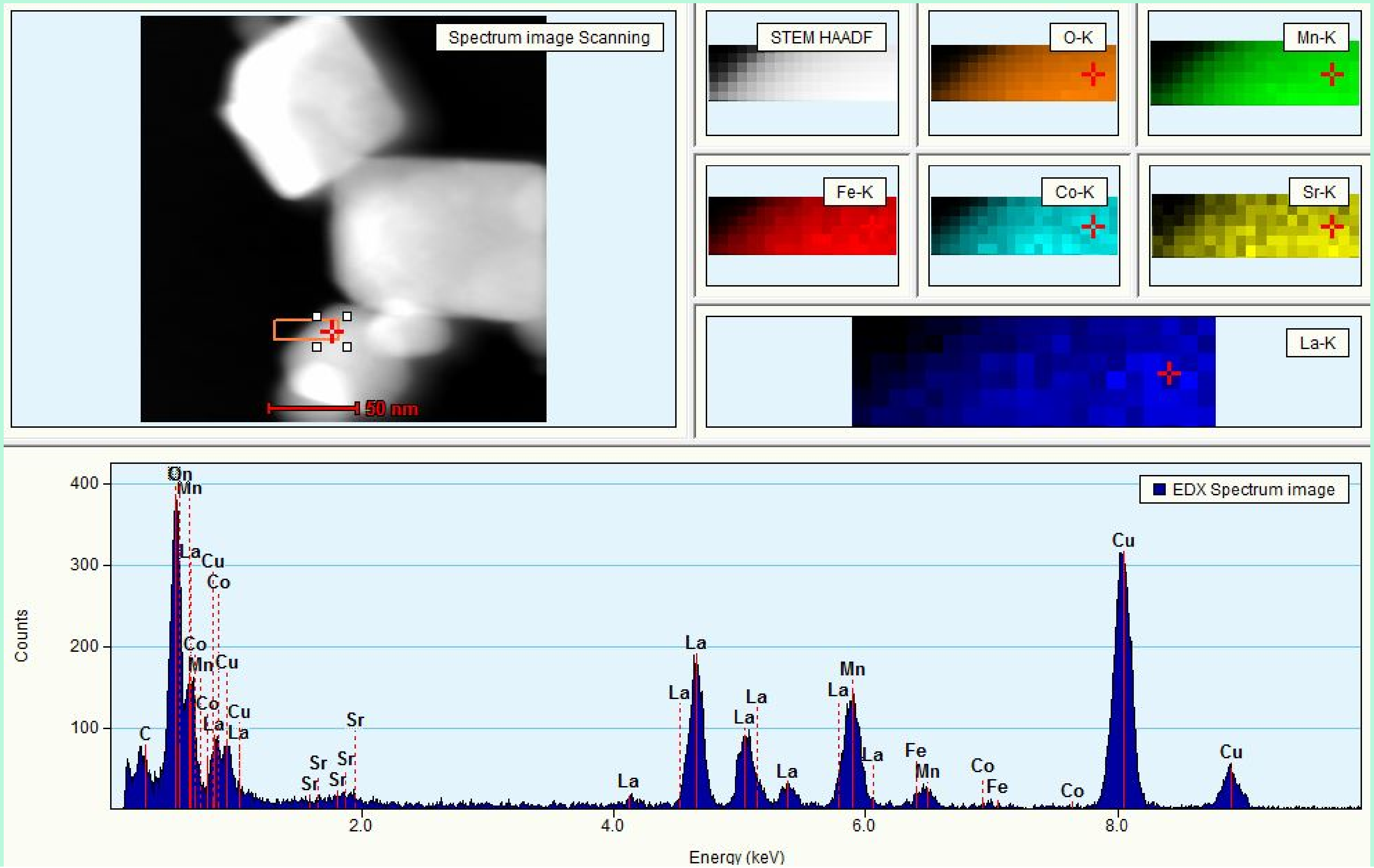




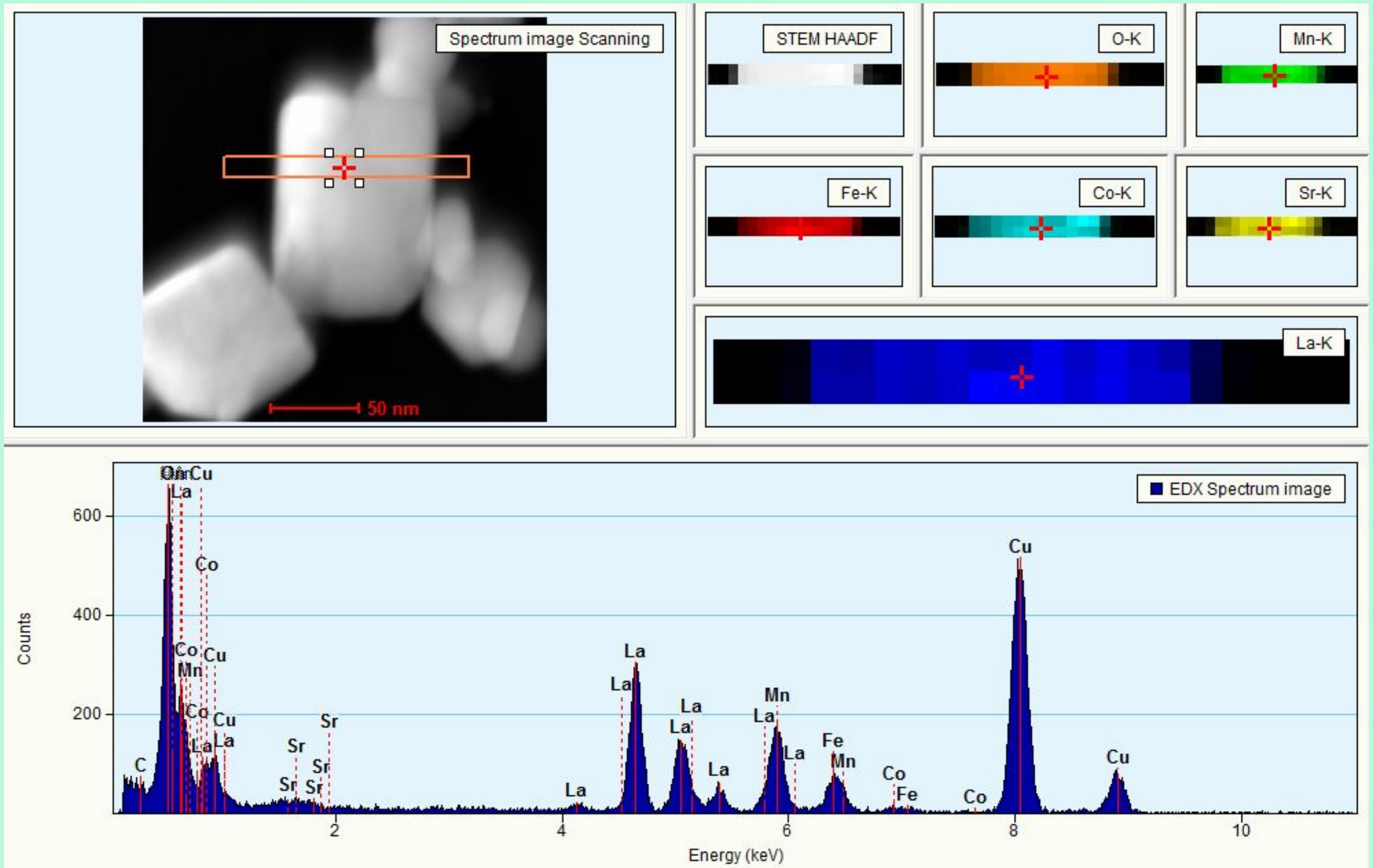
- Left: EDS maps and spectra collected towards center of satellite nanoparticle. The high intensity Mn Kα peak and very low Fe and Co Kα peaks suggest the satellite nanoparticles are LSM

- Right: Maps and spectra collected across cubic structure. At the center of the particle, where Fe and Co intensities should be highest, the Mn Kα peak is still much larger. This suggests that if a LSCF-LSM CSNP has formed, the LSM shell is much thicker than desired.

Analysis of LSCF/LSM Satellite Particles



Analysis of Larger Cubic Particle

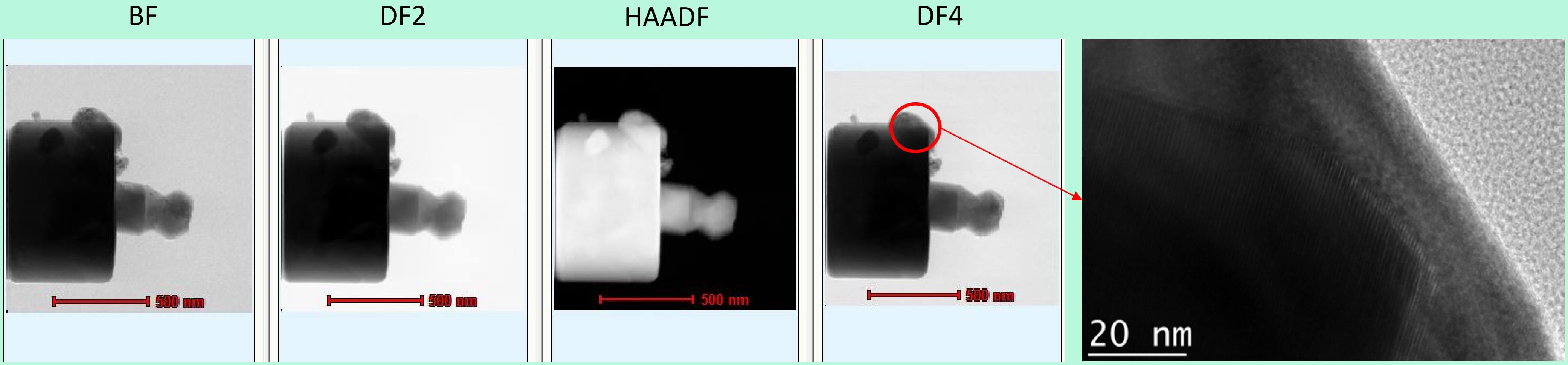


Summary of Observations

- Left: EDS maps and spectra collected towards center of satellite nanoparticle. The high intensity Mn Kα peak and very low Fe and Co Kα peaks suggest the satellite nanoparticles are LSM

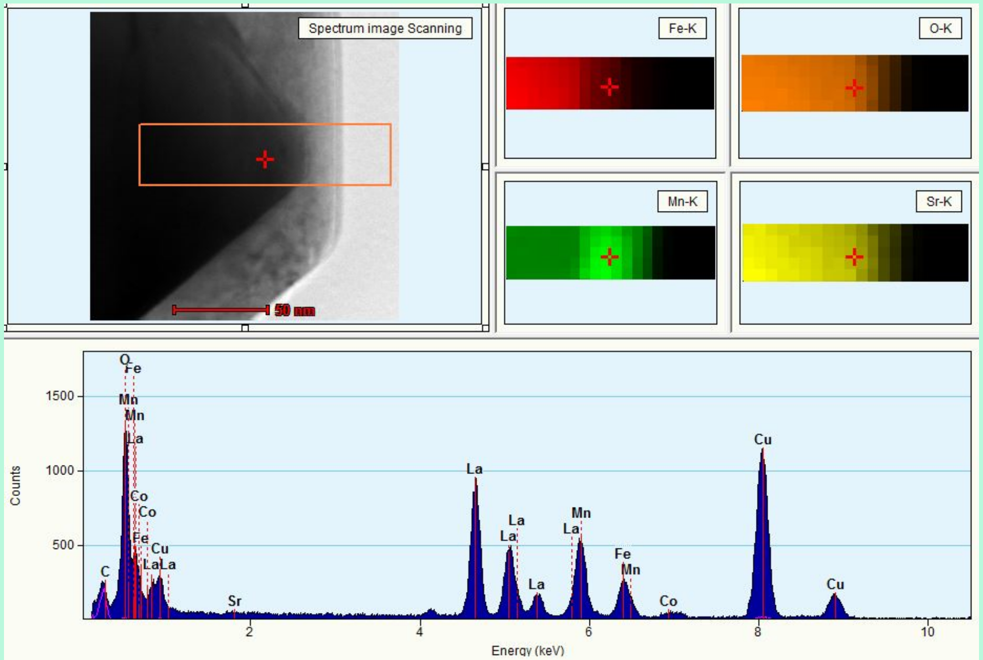
- Right: Maps and spectra collected across cubic structure. At the center of the particle, where Fe and Co intensities should be highest, the Mn Kα peak is still much larger. This suggests that if a LSCF-LSM CSNP has formed, the LSM shell is much thicker than desired.

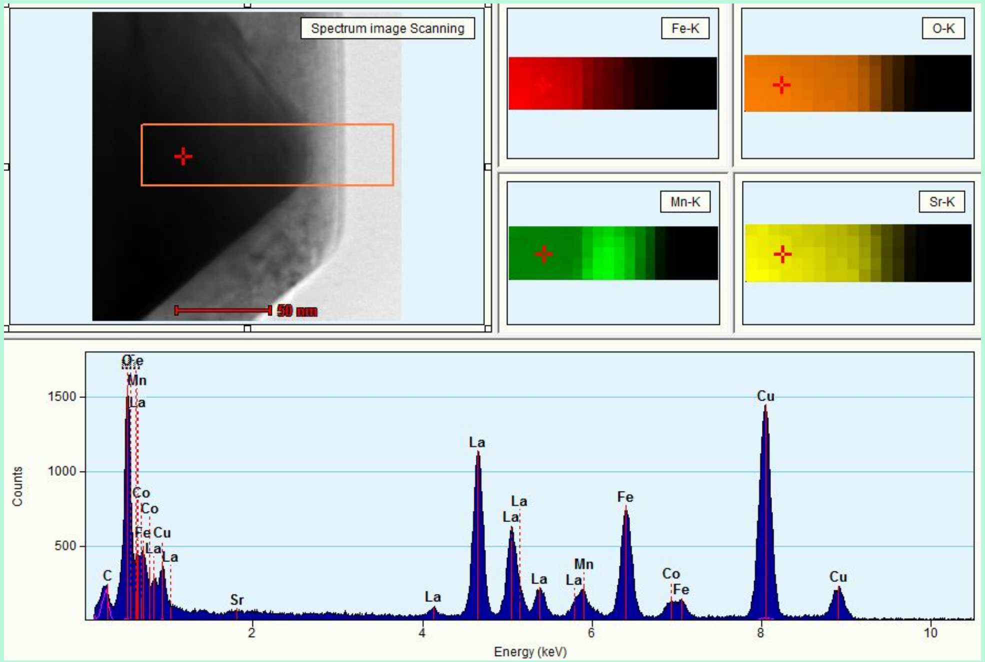
LSCF(core)-LSM(shell) Reversed Weight Ratio



- Bright Field(BF), Dark Field(DF), and High Angle Annular Dark Field (HAADF) images are shown on the left. The region of interest is circled in red and a high resolution image is shown on the right
- Sample analyzed: LSCF-LSM, 3:1 weight ratio (core:shell), 550 °C, 2 hour dwell time

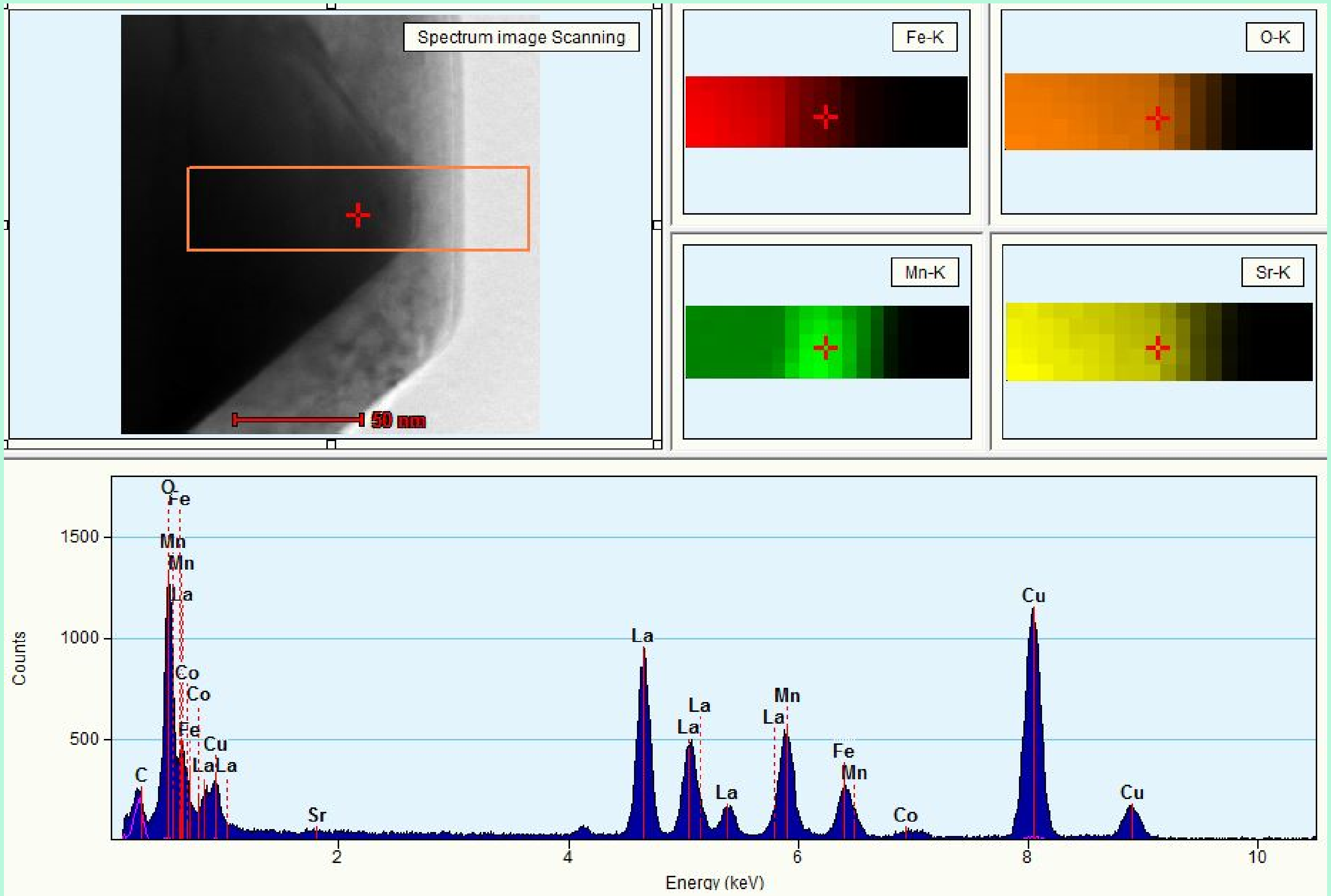
Analysis of LSCF (Core)-LSM (Shell): Reversed Weight Ratio



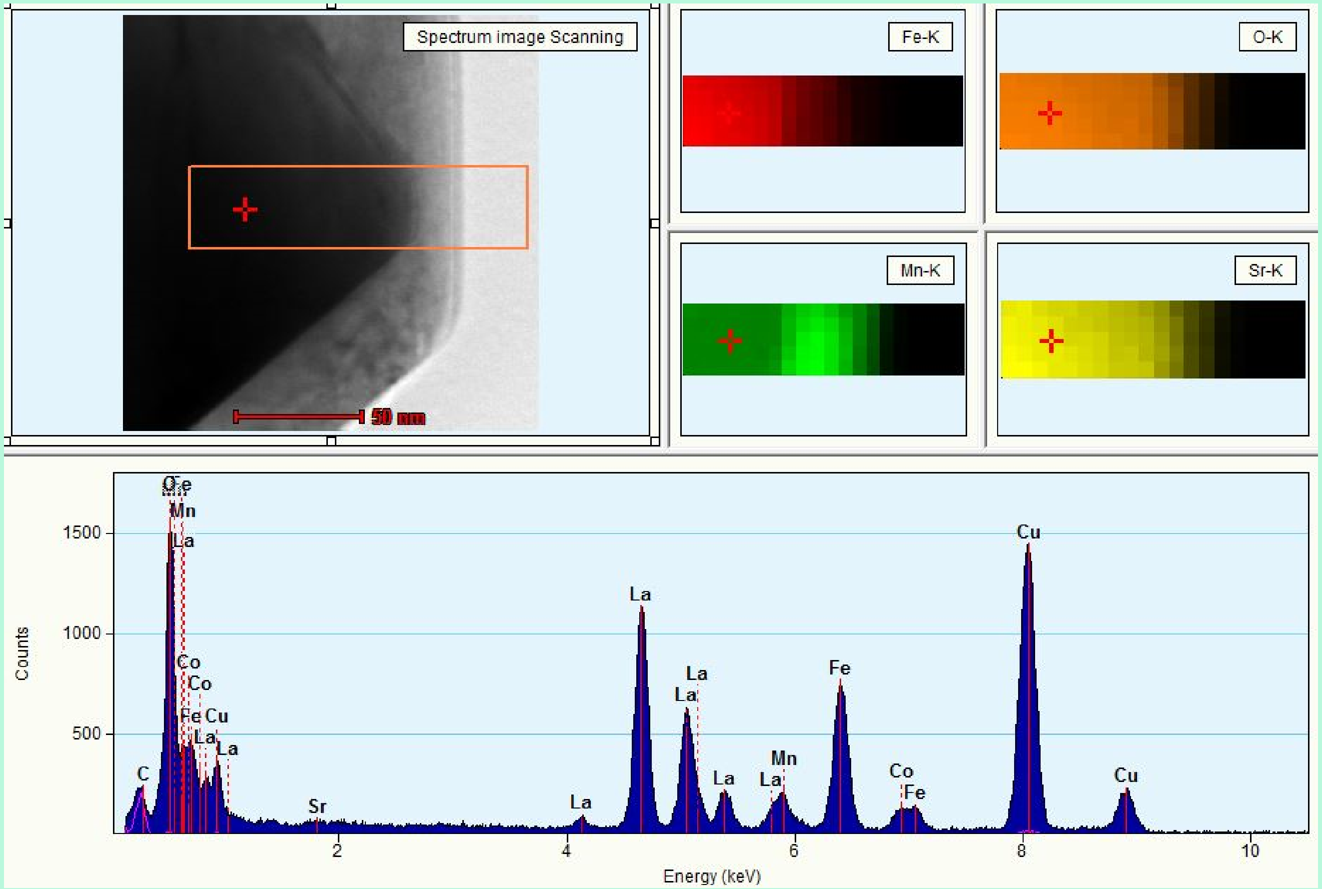


- Left: EDS maps and spectra collected at the edge of the deposited satellite nanoparticle. The maps indicate a high intensity region of Mn, with little Fe present. The corresponding spectrum indicates a more intense Mn Kα peak compared to the Fe Kα peak.
- Right: Maps and spectra collected towards the center of the deposited nanoparticle. The spectrum collected reflects a region with much more Fe present than Mn.
- Data indicates a Mn rich particle deposited on a Fe rich core. This suggests partial deposition of LSM shell on an LSCF core

Analysis of LSCF (Core)-LSM (Shell): Reversed Weight Ratio



Analysis of LSCF (Core)-LSM (Shell): Reversed Weight Ratio



Summary of Observations

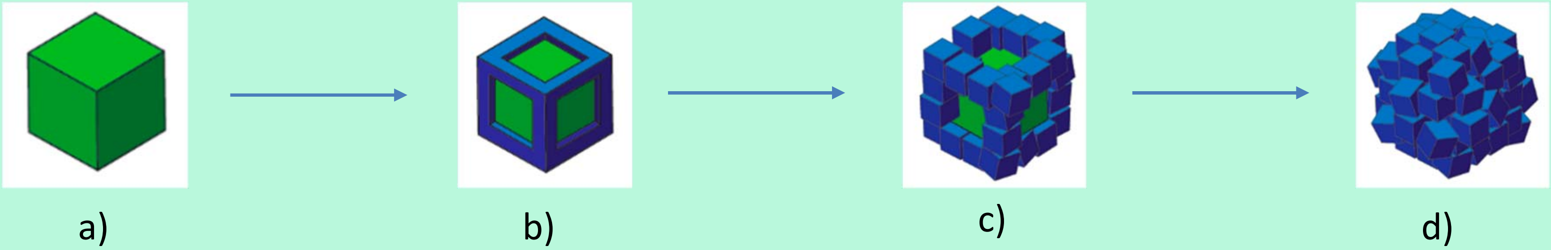
- EDS maps and spectra collected at the edge of the deposited satellite nanoparticle indicate a high intensity region of Mn, with little Fe present. The corresponding spectrum indicates a more intense Mn Kα peak compared to the Fe Kα peak.

- Maps and spectra collected towards the center of the deposited nanoparticle. The spectrum collected reflects a region with much more Fe present than Mn.

- Mn rich particle deposited on a Fe rich core with partial coverage.

Addressing Challenges to Optimize CSNP Formation

- Nanoparticle aggregation
  - Critical to obtain standalone particles for accurate compositional analysis using EDS
  - Combination of diluting, sonicating, and centrifuging samples prior to TEM analysis
- Optimizing molten salt synthesis reaction conditions
  - Synthesis temperature, weight ratio of core to shell precursors, reaction time
  - Need to achieve complete encapsulation yet maintain a thin shell

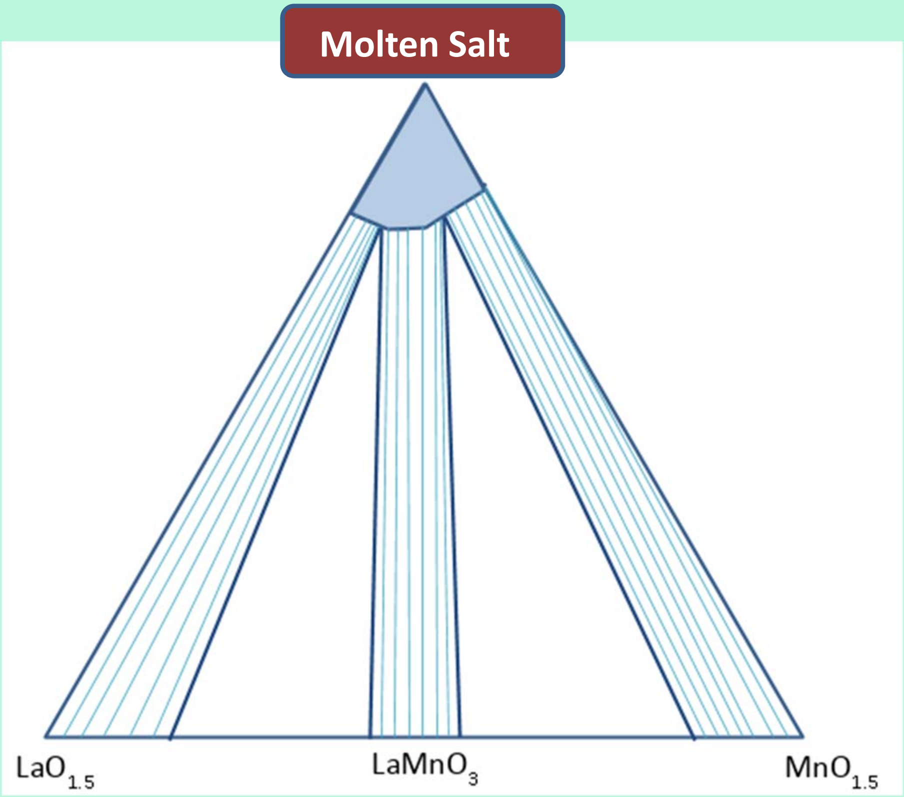


Ongoing Directions/Modifications

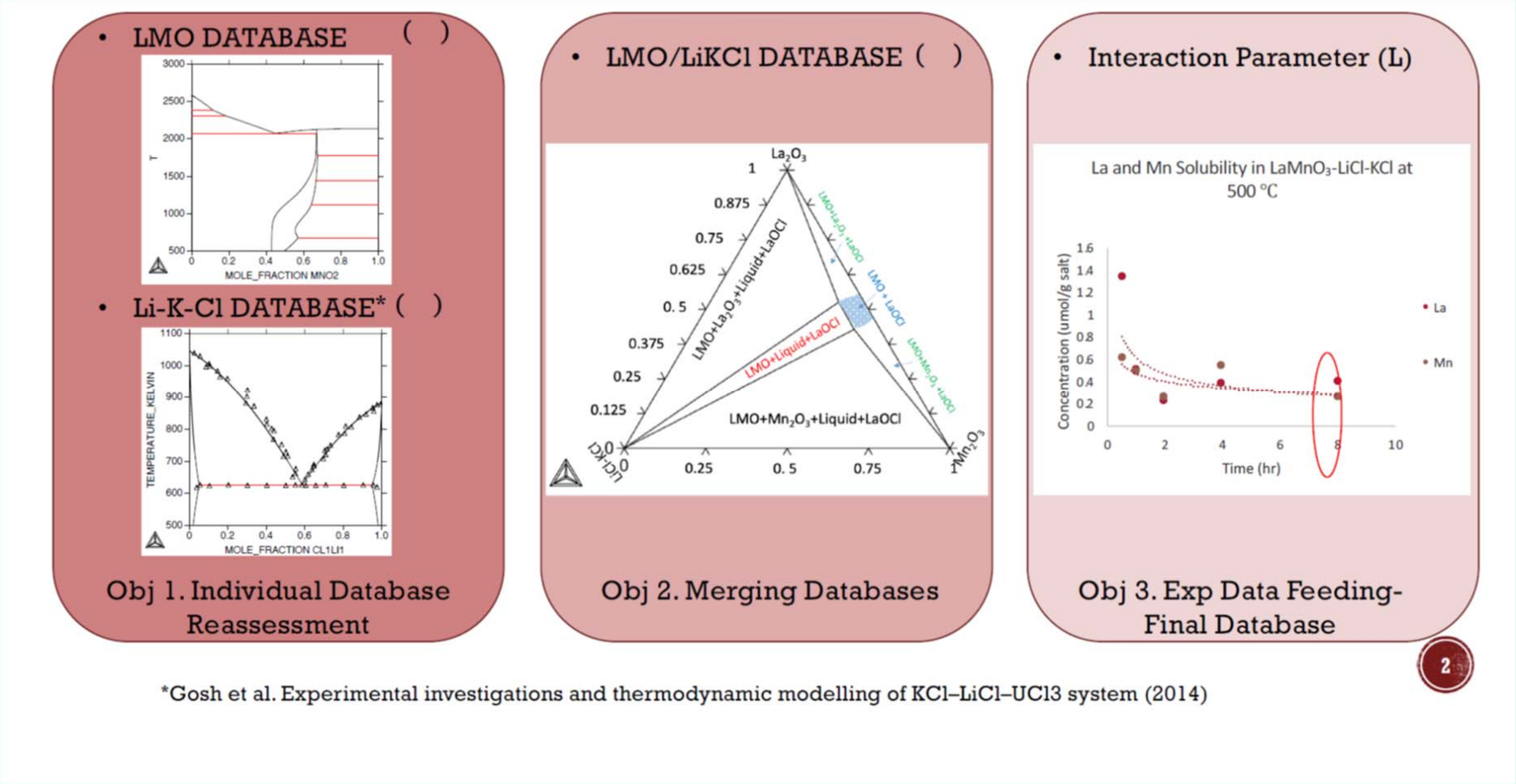
- Adjusting weight ratio of core to shell
  - 1:2, 1:3, 1:4 instead of a 1:6 weight ratio (core:shell)
- Adjust A/B ratio of $(La_xSr_{1-x})_AMn_BO_3$ shell precursors
  - Surface energy landscape important to explore to optimize heterogeneous nucleation and shell deposition onto LSCF cores
- Varying reaction time (Kinetic studies)
  - Extended reaction duration could result in very thick shells. Will explore a shorter reaction times and quenching the solution may provide promising results.
- Half cell fabrication and electrochemical testing
  - Compare polarization resistances of baseline cells containing LSM(MS/HT)-YSZ and LSCF(MS/HT)-YSZ working electrodes, along with potential (LSCF-LSM)-YSZ core shell working electrodes
  - Counter electrode = LSM(HT)-YSZ

Modeling of Phase Equilibria

Schematic of Phase Diagram: Pseudo Ternary



Database Assessment



- LMO DATABASE ( )
- Li-K-Cl DATABASE* ( )

Obj 1. Individual Database Reassessment

- LMO/LiKCl DATABASE ( )

Obj 2. Merging Databases

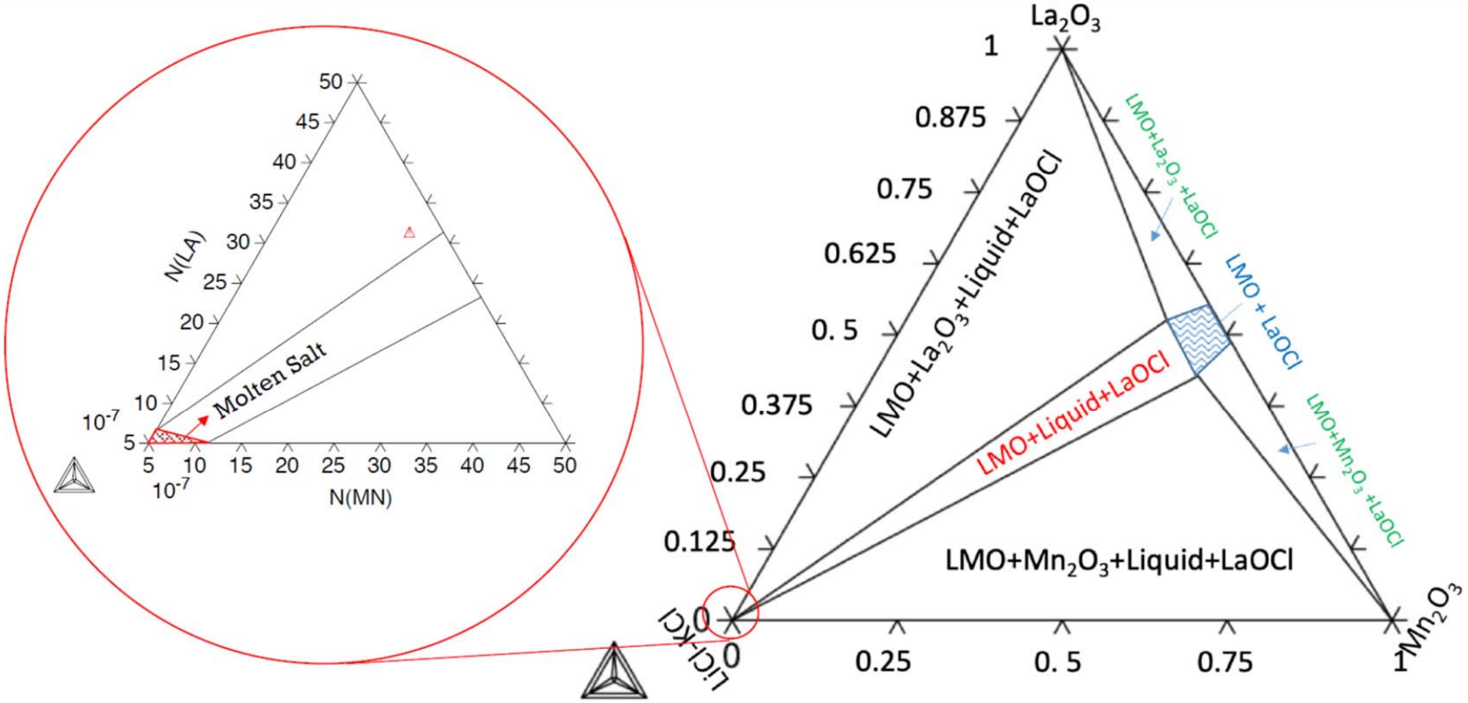
- Interaction Parameter (L)

La and Mn Solubility in $LaMnO_3$-LiCl-KCl at 500 °C

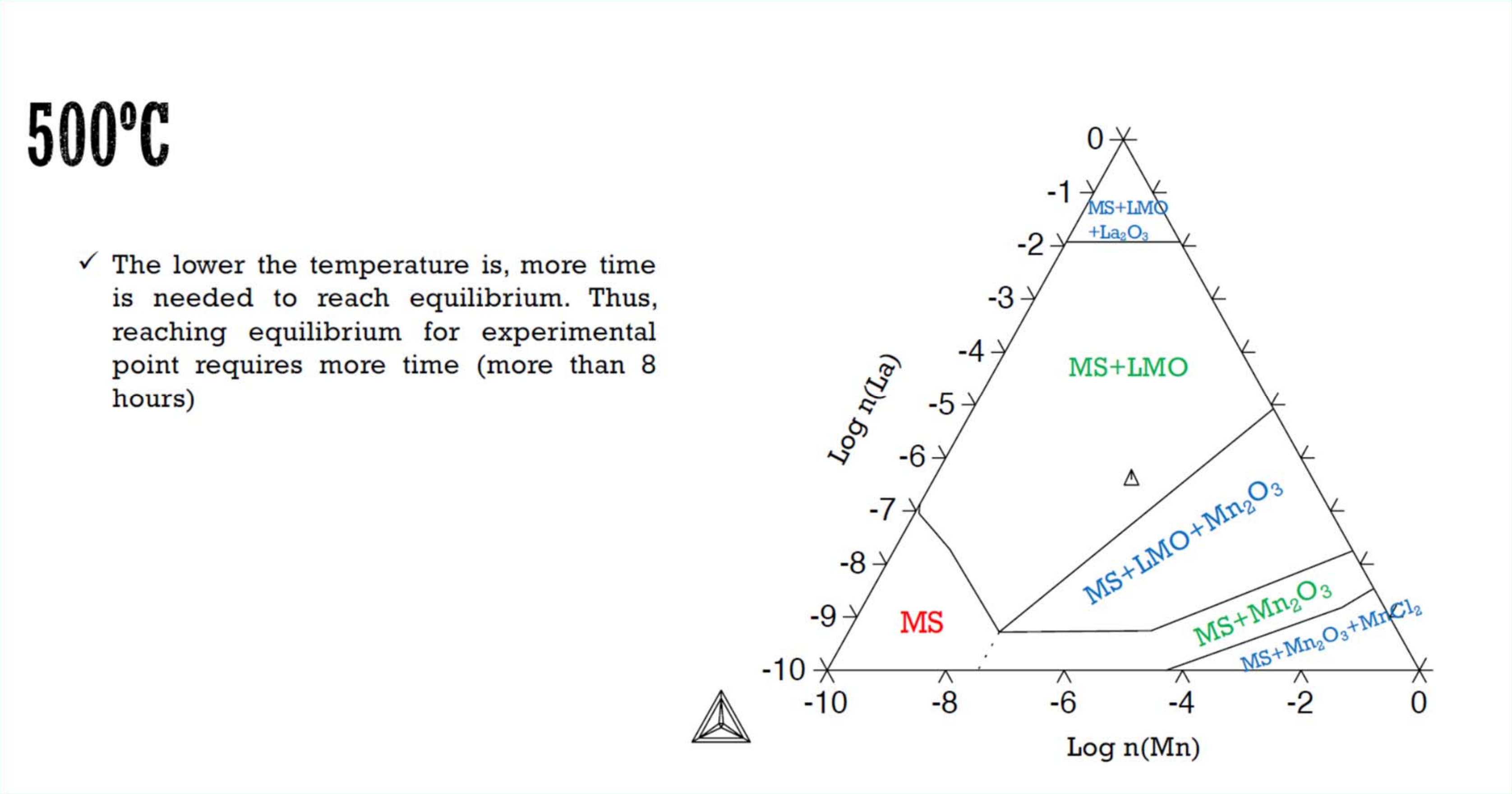
Obj 3. Exp Data Feeding- Final Database

*Gosh et al. Experimental investigations and thermodynamic modelling of KCl–LiCl–UCl3 system (2014)

Psuedoternary Version 1



Psuedoternary Version 2: 500ºC

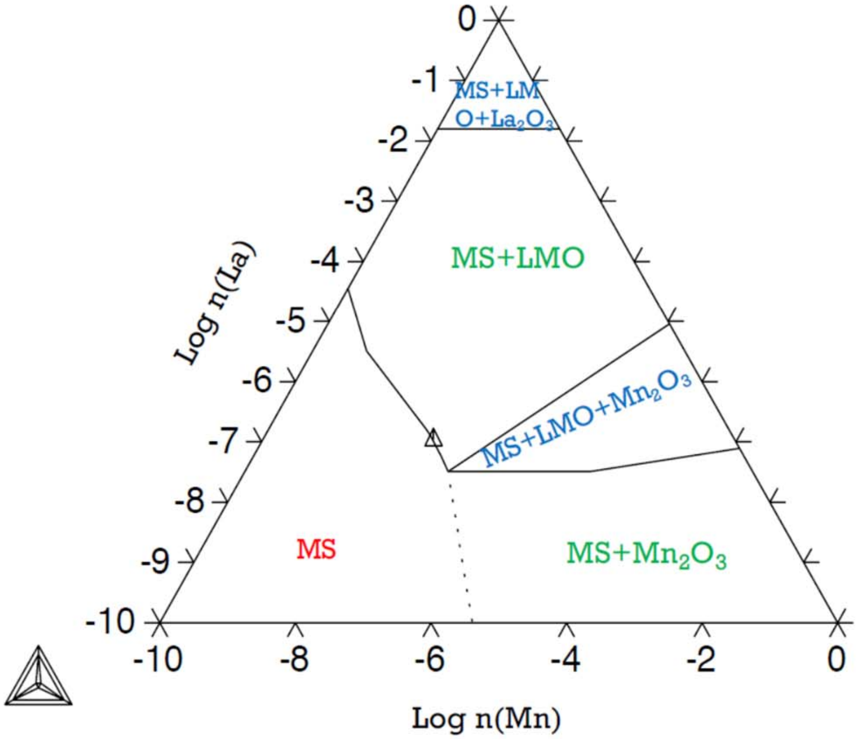


500ºC

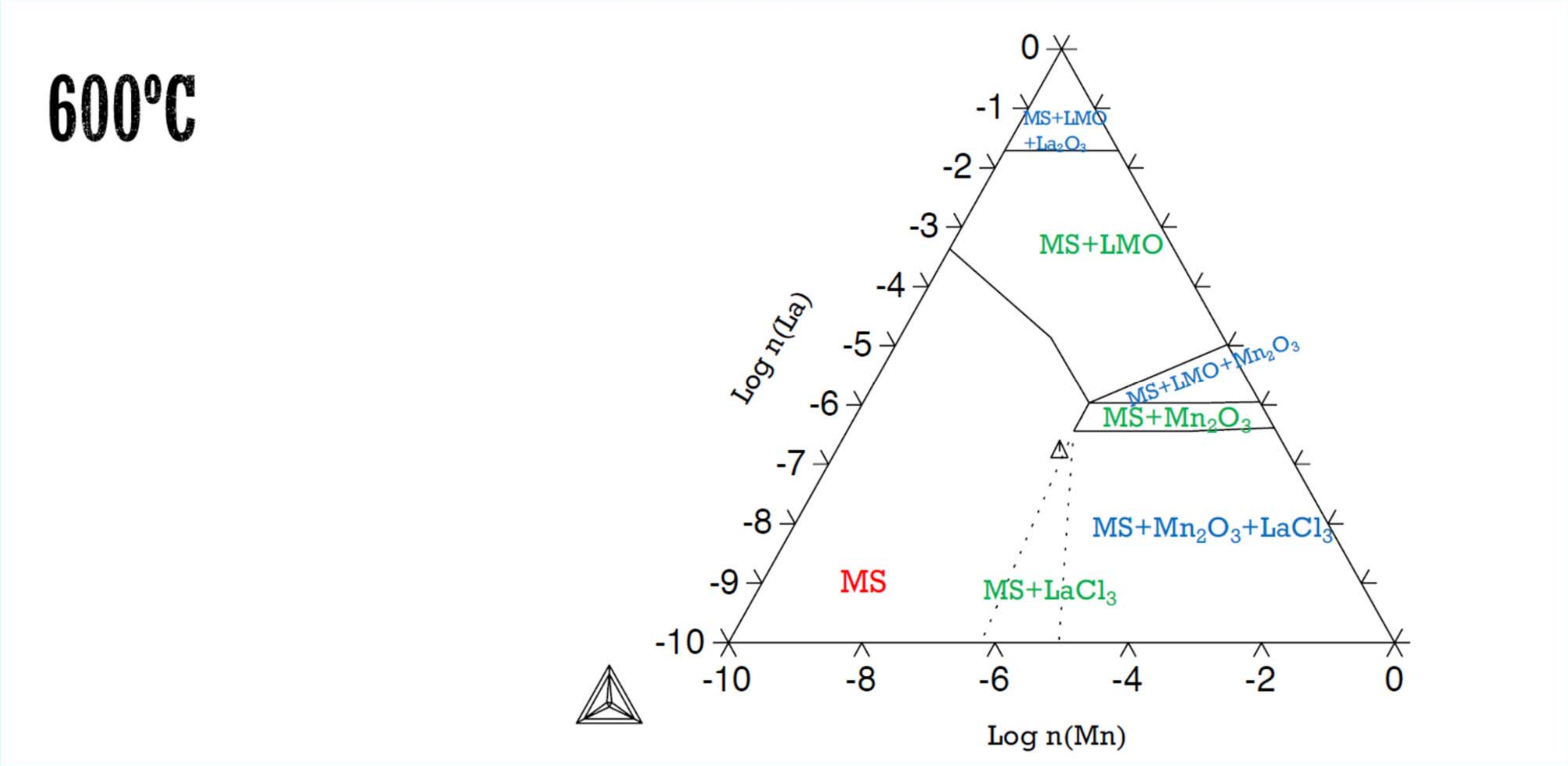
- ✓ The lower the temperature is, more time is needed to reach equilibrium. Thus, reaching equilibrium for experimental point requires more time (more than 8 hours)

Psuedoternary Version 2: 550^{o}C

550°C

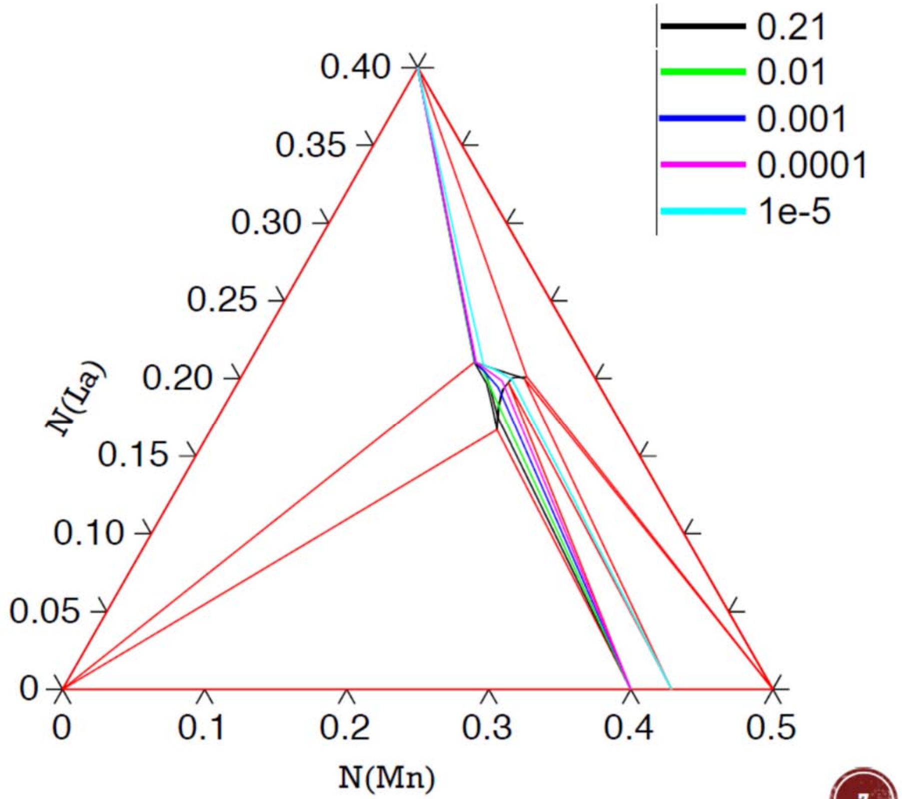


Psuedoternary Version 2: 600ºC

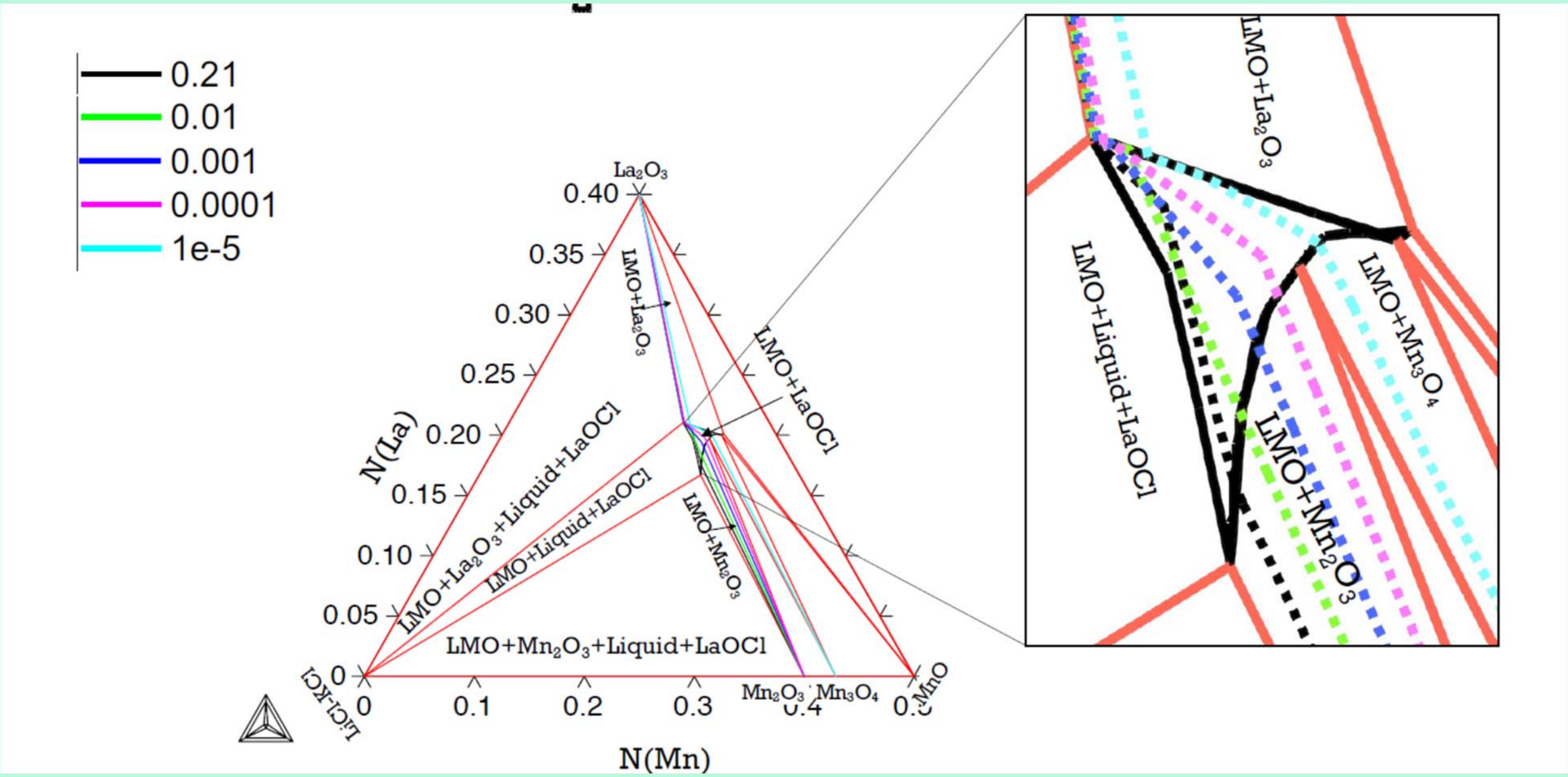


Effect of pO_2 (T = 550^{o}C)

- ✓ As PO_2 decreases, the perovskite stability region gets smaller



Effect of pO_2 (T = 550°C)



Summary

- Molten salt synthesis an excellent method to synthesize phase pure, monodisperse powders at low temperatures
- Partial LSCF (core) and LSM (shell) particles have been obtained; Work to achieve conformal coverage is ongoing
- Methodology to perform analysis of single particles being improved
- Identification of processing conditions leading to high yield with the desired structures is ongoing; will be followed by electrochemical testing on half-cells
- Calculations of phase equilibria to identify thermodynamically favorable regimes and control of compositions of LSM and LSCF is ongoing

Acknowledgments

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And FE0031205

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