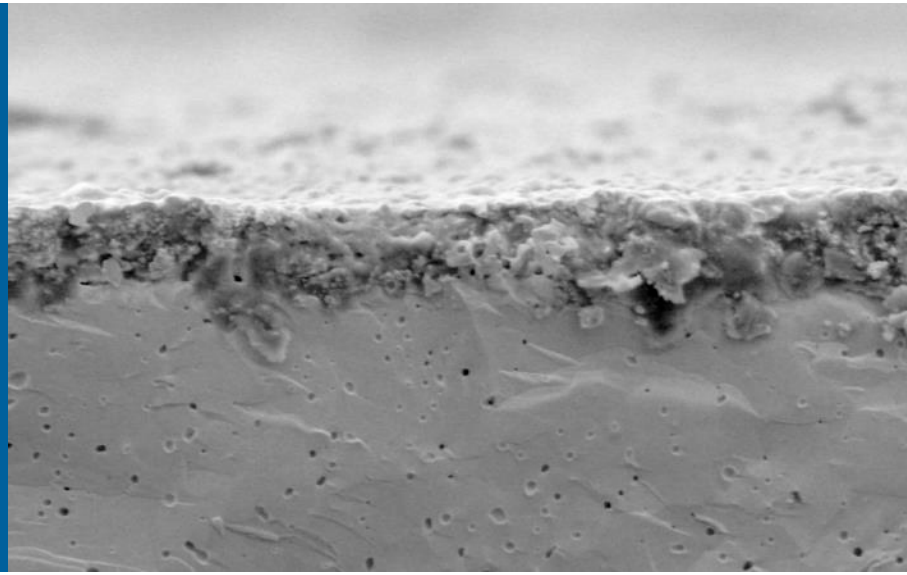
Cathode Evaluation for SOFC Reliable Performance



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U.S. DOE H_2 and Fuel Cells Program
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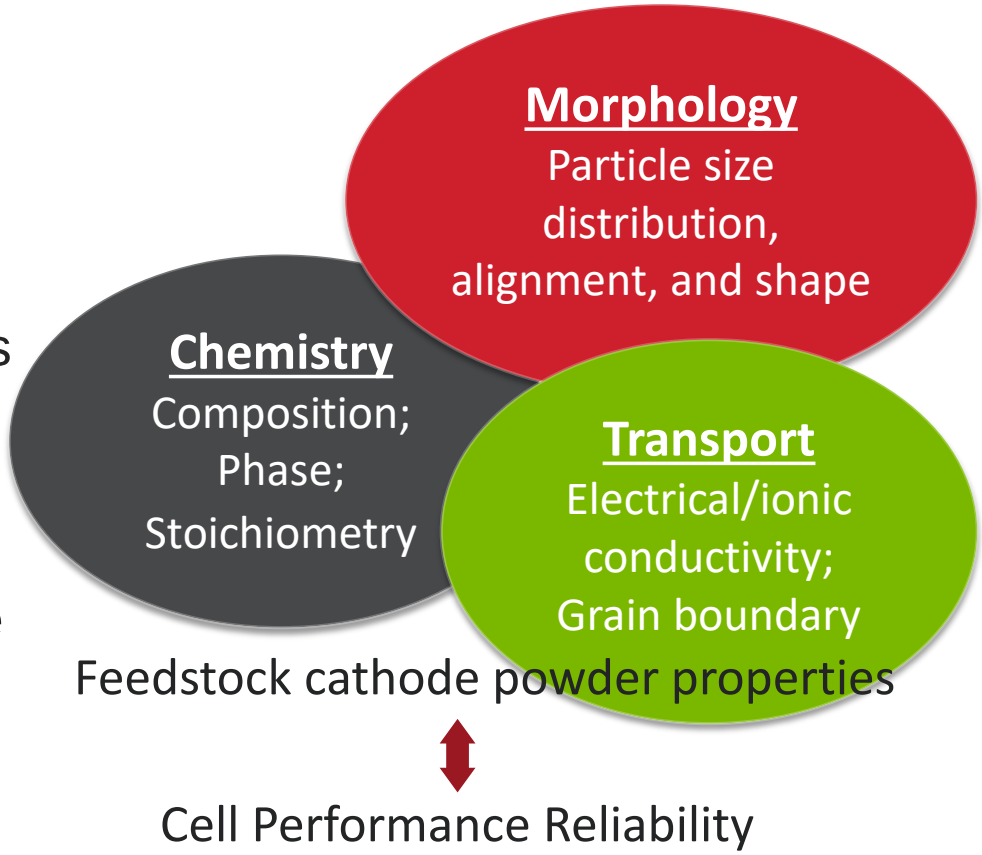
June 13-15, 2018

* Now at Fuel Cell Energy

Scope and research objectives

Enable SOFC performance reliability & low cost materials diagnostics for high cell fabrication yields

- Develop a diagnostic half-cell and full-cell testing protocol and establish a baseline performance for statistical comparison
- Identify key factors and tolerances in feedstock powders mapping to cell electrochemical reliability
- Develop rapid and simple diagnostic approach to predict the performance characteristics of feed stock powders as they are received



FUNDAMENTAL STUDIES → RAPID DIAGNOSTIC ANALYSES

Effort will focus on short term electrochemical performance reliability

Conclusion and outline

- Feedstock powder variations in morphology and phase composition exhibits broad variation
- Rapid and simple diagnostic approaches have been thoroughly investigated including Raman and FTIR to probe chemical and phase composition
  - $SrCO_3$ and M_3O_4 second phase is evident, quantified, and mapped.
  - Performance trends with chemical variation is ongoing
- Effort to decouple morphology effects from macro-surface chemistry/structure effects is inconclusive to date
- Developing predictive understanding to mitigate cell-to-cell variability based on feedstock variations

Specific materials in study

Compositional, synthetic, and morphology variations

- Refining our focus, as you'll see
- Determine the relationship between specific chemical and morphological features of the materials produced by various vendors and the performance of these materials in solid oxide electrochemical devices
- A lot of variation in commercially available / received cathode powders

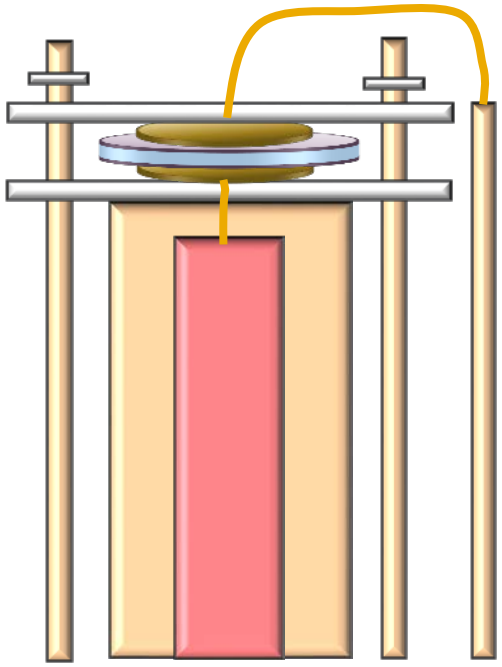
VENDOR	COMPOSITION	SYNTHESIS (?)
V1 a, b coarse/fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	SS + mill
V2 fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	combust
V3 (coarse)	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	Uncertain
V4 a, b, c (bimodal, varying)	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	Coprecip + sint

DIAGNOSTIC HALF-CELL TESTING PROTOCOL AND BASELINE PERFORMANCE FOR STATISTICAL COMPARISON

- Understand and reduce variation contribution from
  - Temperature
  - Electrical contact
  - Temporal variations in performance response
  - Electrode design

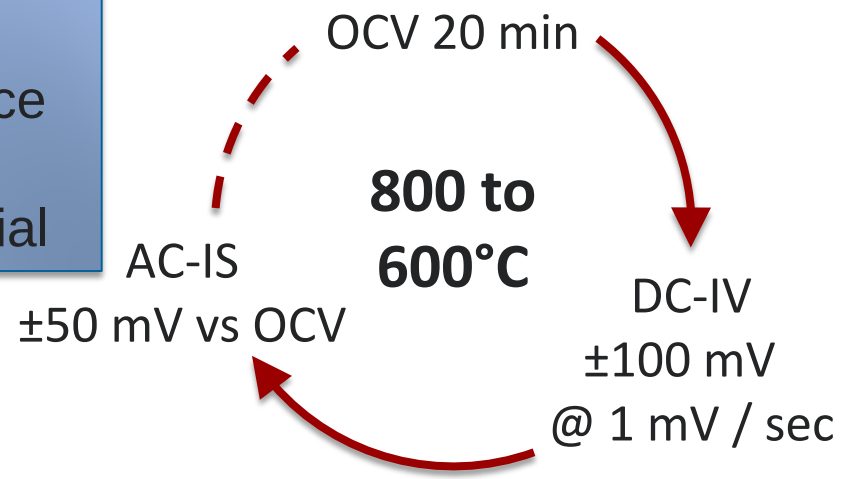
Symmetric half-cell design

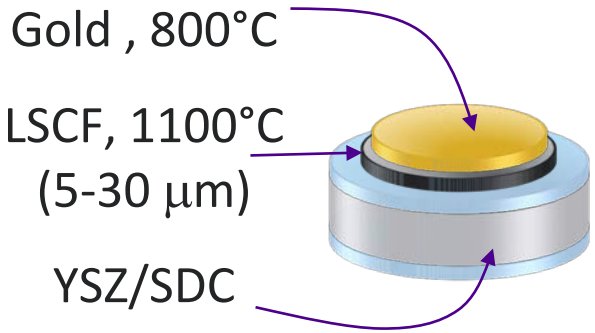
Mitigate contribution from temperature and contact variation; reduce complexity by using single gas environment



'Sandwich' structure to ensure confirm contact

Minimize temporal performance variation, identify initial





Screen printed electrodes and Au contact paste, oversized CE

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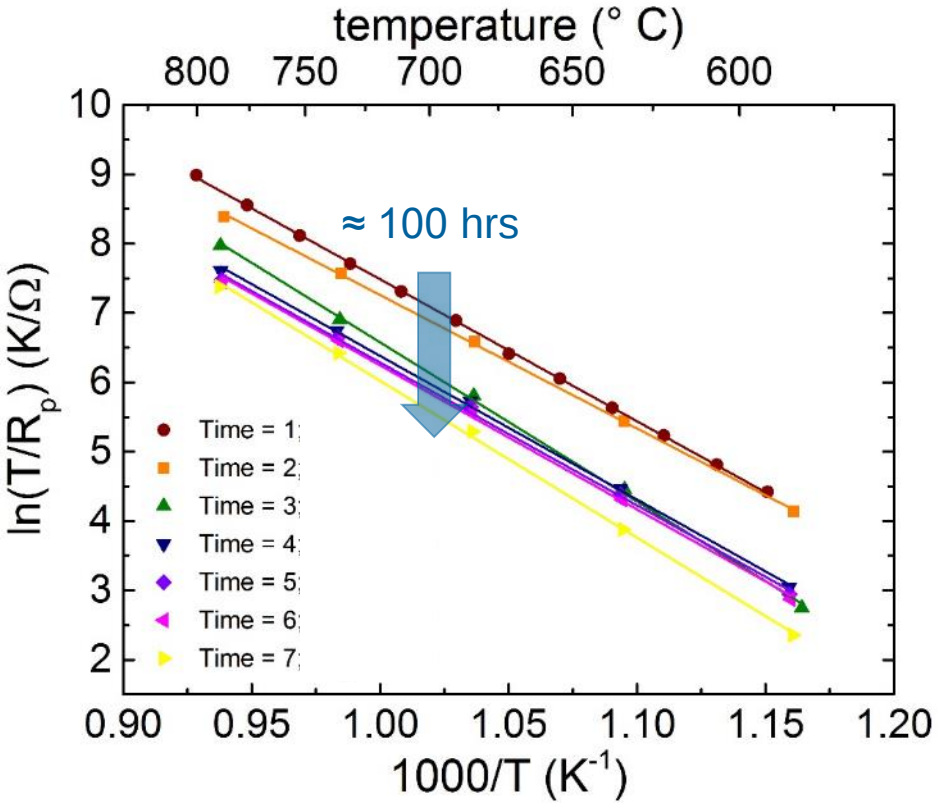
Protocol identifies initial performance at t=0

Decouple feedstock variation contributions from long term degradation mechanisms

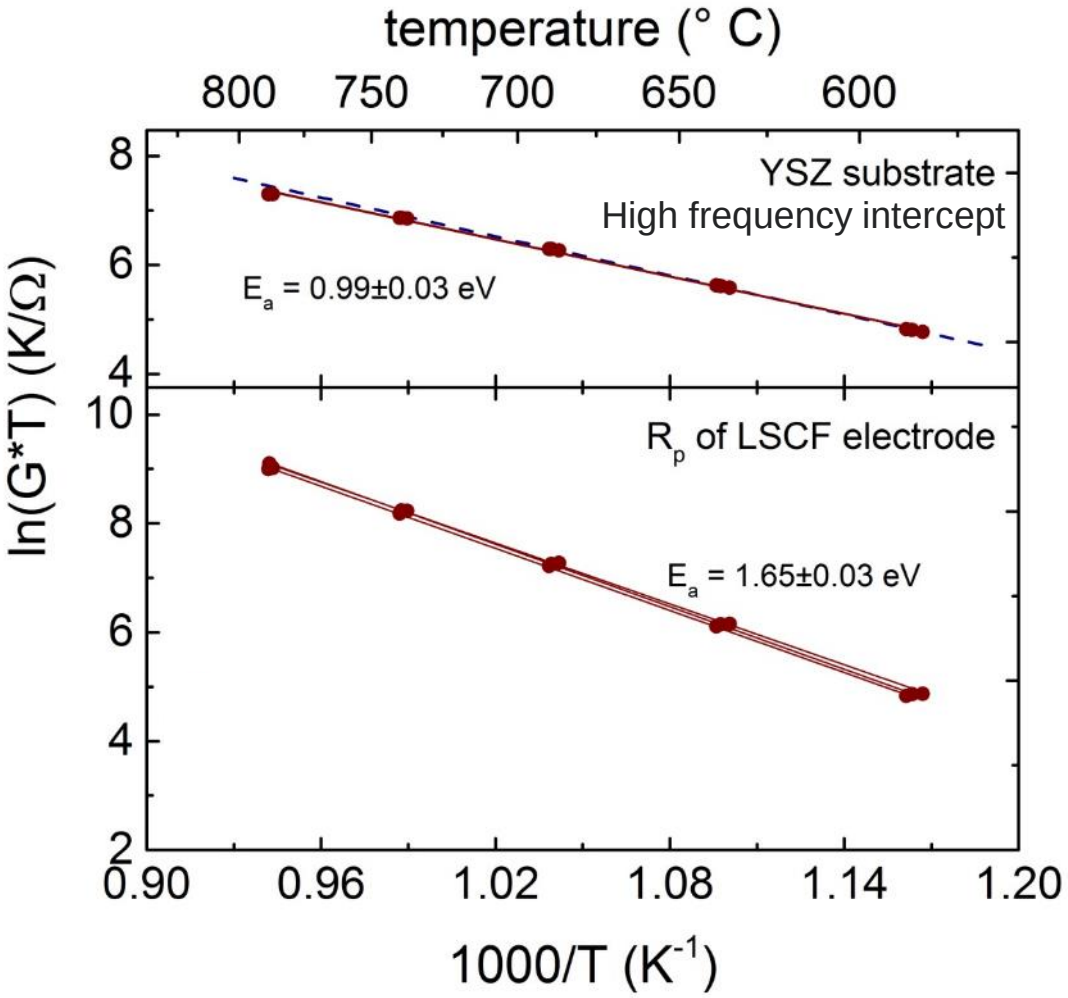


Typical LSCF electrode on YSZ/GDC
impedance analysis
Time intervals are not equivalent

- Typical time-dependent changes evolve from initial performance
  - Polarization resistance increases observed over days
  - Transport mechanisms (E_a) does not appear to change

Established performance baseline

Statistical analysis based on repetitions provides baseline performance controlling for experimental variations



- Representative values derived from impedance measurements
- Sensitivity to electrode thickness and alignment can be resolved
- This baseline shows ~1% variation
- Typically < 2-3% variation observed in polarization conductance from other LSCF materials
- Very small variation in thermal activation energy
- But: User and potentiostat serendipitously observed

LINK MORPHOLOGY TO PERFORMANCE RELIABILITY - REVIEW

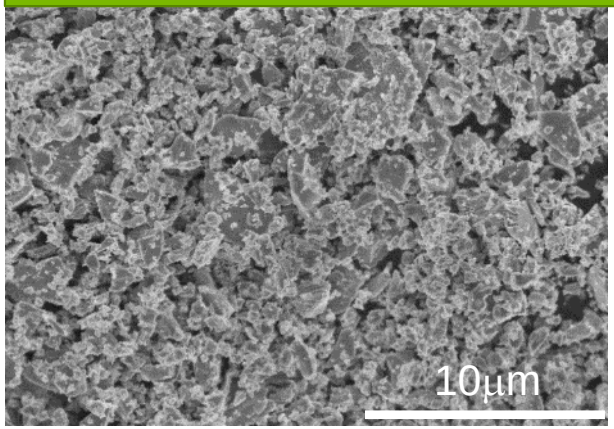
- Various synthetic routes for cathode powder synthesis, e.g., solid state vs. wet chemical
- Wide distributions of particle sizes, 10 nm to 10 μm
- Variable aspect ratio / surface structure: primary & secondary particles

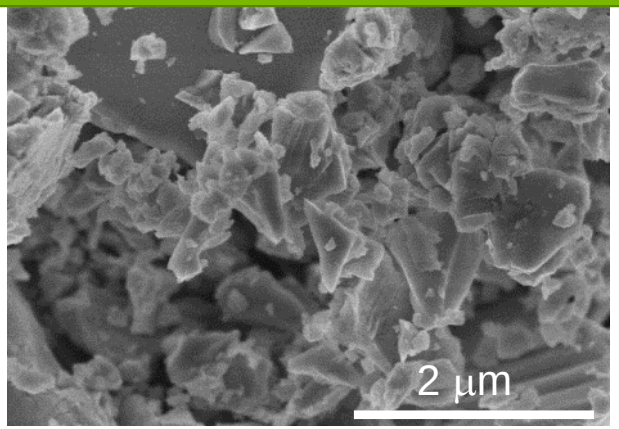
- Techniques for fully describing initial morphology and evolution
  - Scattering or diffraction techniques (ultra-small angle x-ray scattering); BET; Microscopy techniques
- Establish final morphology of electrode: complete description (ε, a, r, τ)

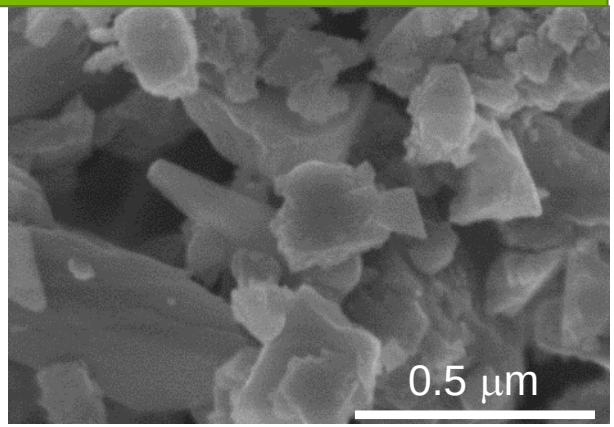
Microscopy of LSCF powders, one example

Complex morphology changes observed beyond size distribution

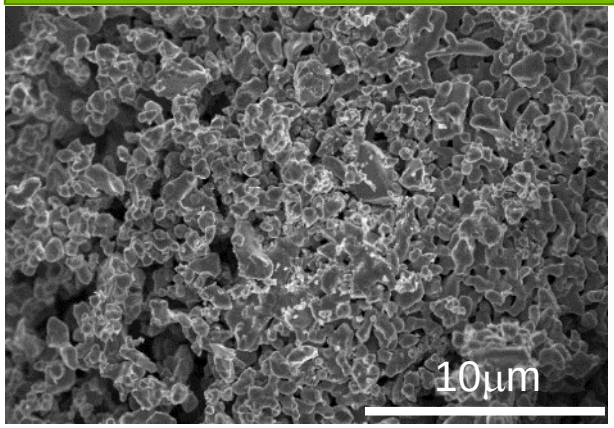
As Received

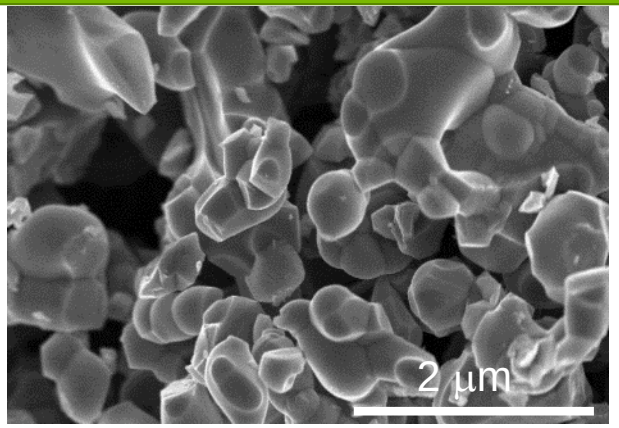


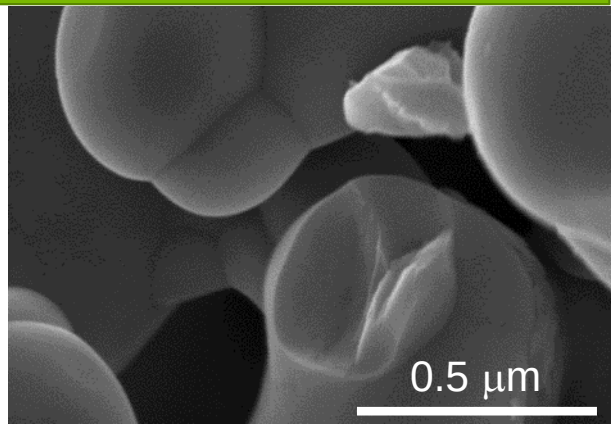




Sintered







Need to quantify initial state and evolution to sintered electrode state

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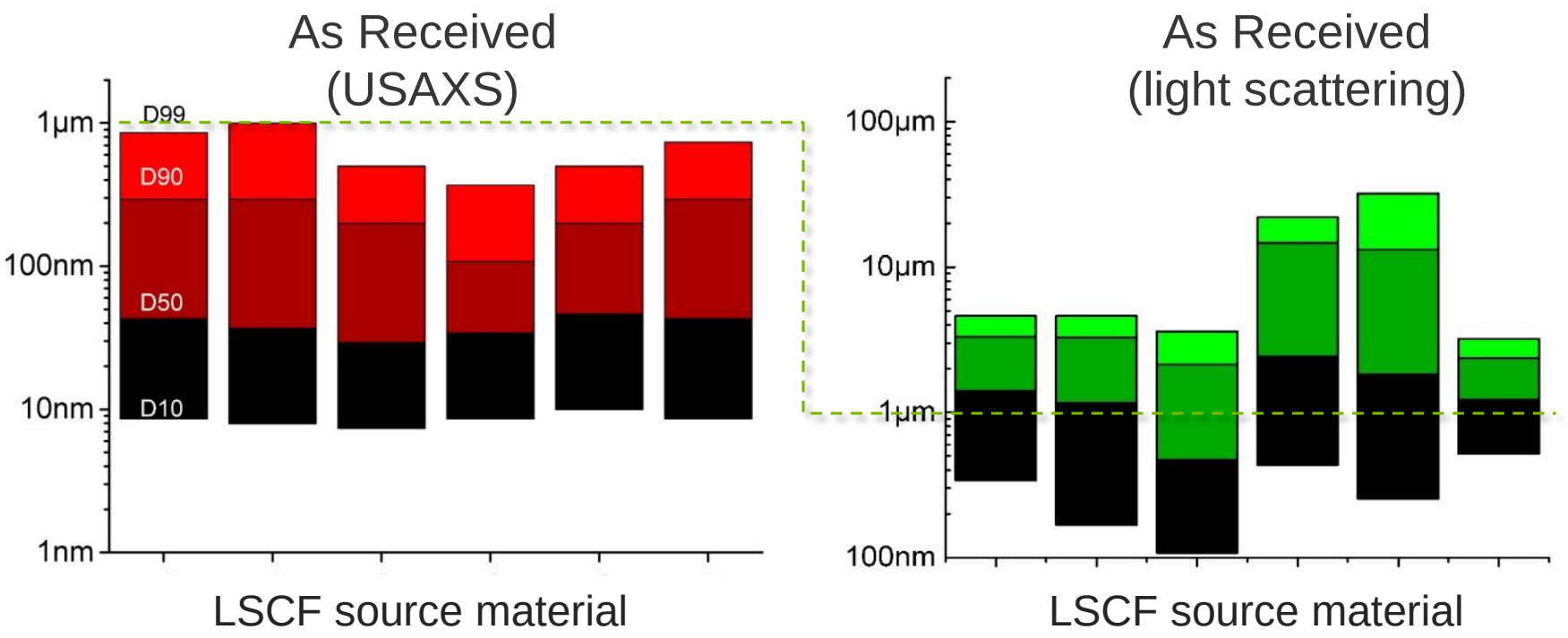
Primary particle size comparison with secondary

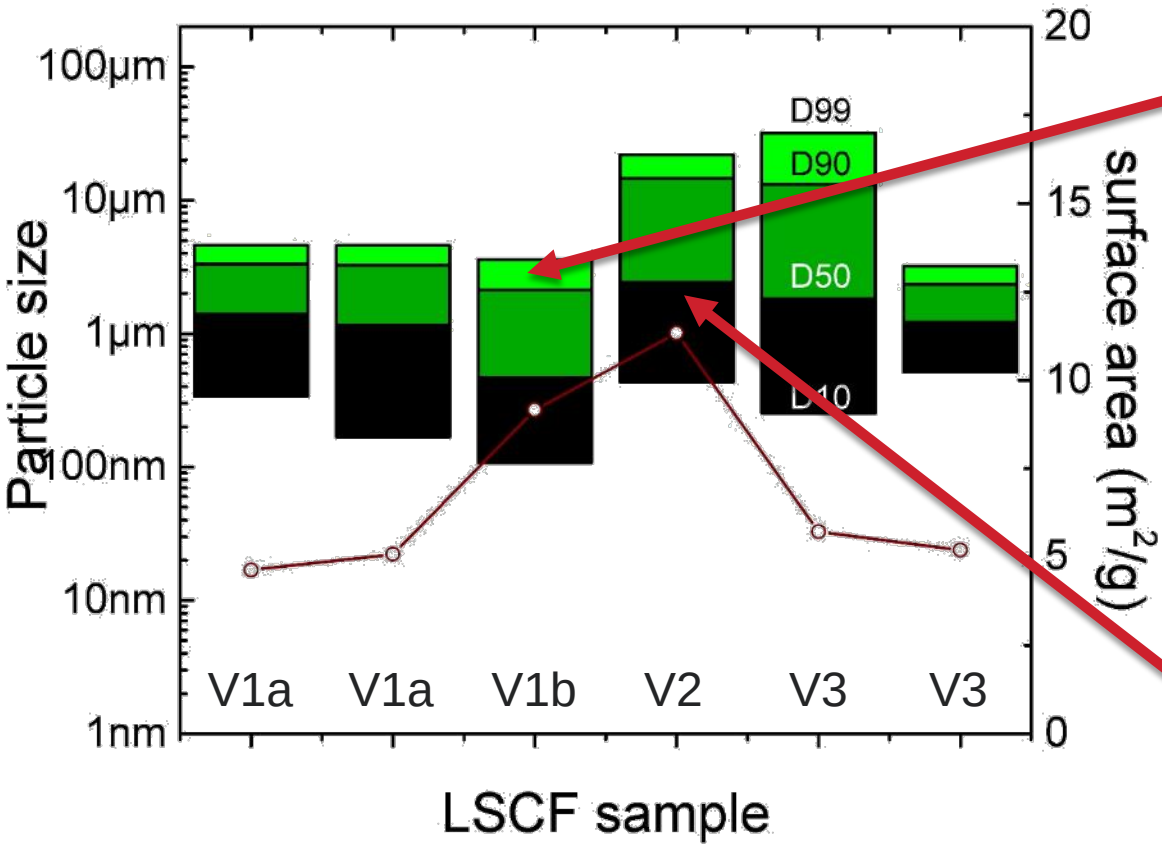
Light scattering probes secondary (agglomerated) particles, whereas USAXS probes primary particles

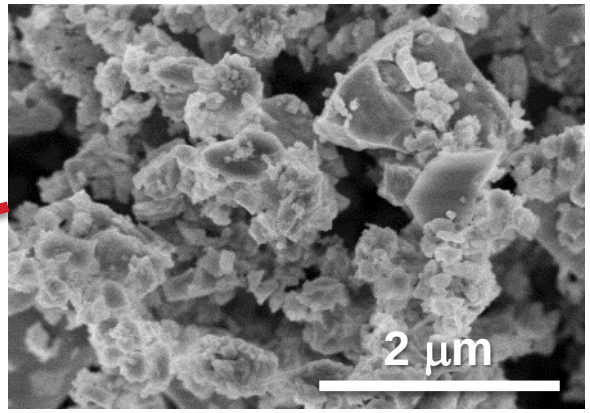


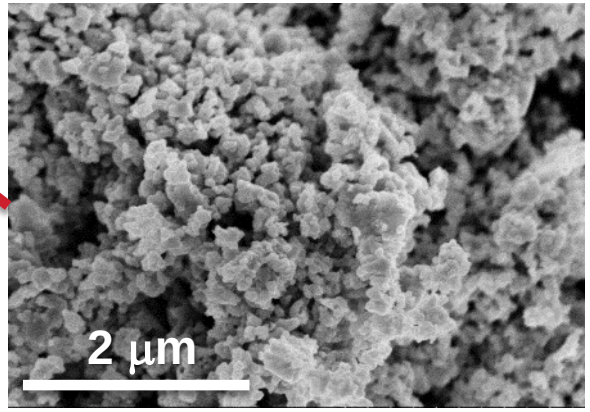
all nominally 6428-LCSF with 5% A-site deficiency
various synthetic techniques and morphologies

BET / PSA as-received materials

Surface area and PSA are not universally proportional







all nominally 6428-LCSF with 5% A-site deficiency
various synthetic techniques and morphologies

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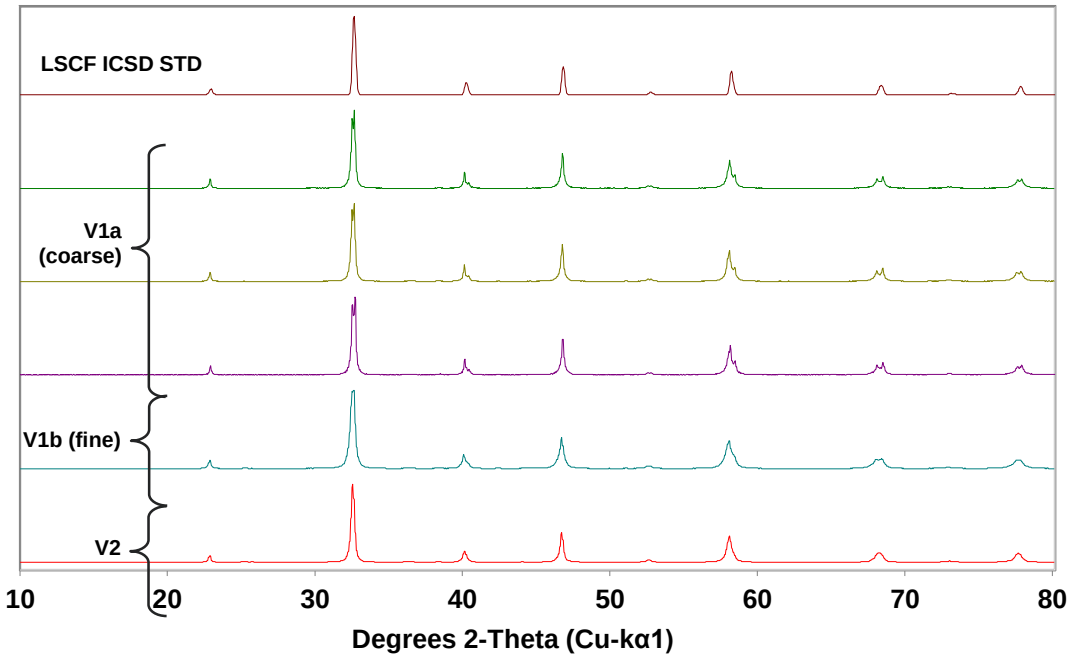
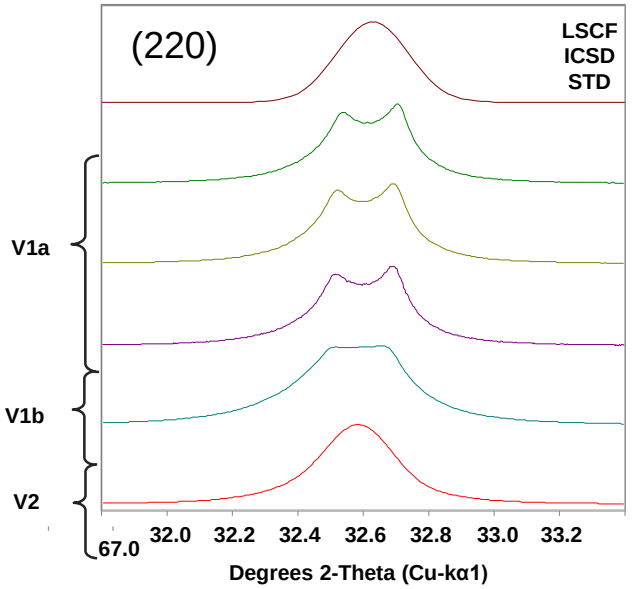
LINK CHEMISTRY TO PERFORMANCE RELIABILITY

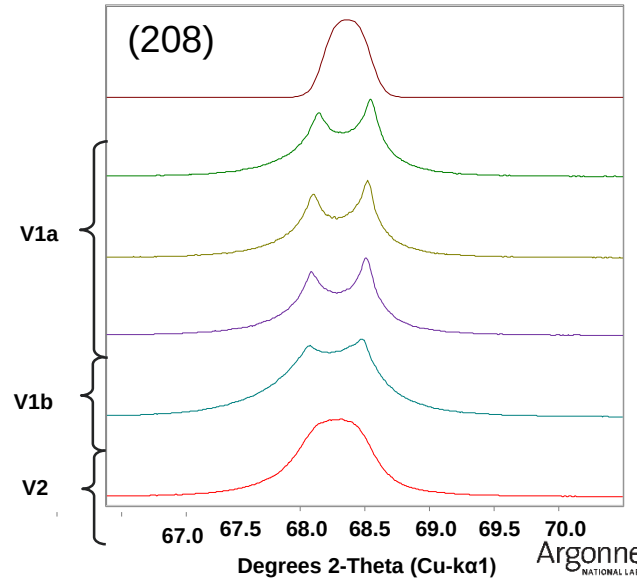
EXAMINE THE LSCF MICROSTRUCTURE (AT THE UNIT CELL LEVEL), INVESTIGATE LSCF LATTICE DYNAMICS, AND DETECT/IDENTIFY/QUANTIFY SECOND PHASES

- high resolution x-ray diffraction (HR-XRD)
- Raman spectroscopy
- mid-infrared spectroscopy
- STEM

Unique lattice variationss in received a-site deficient LSCF samples







- Tetragonal distortion for V1a and b
- No observed distortion in V2

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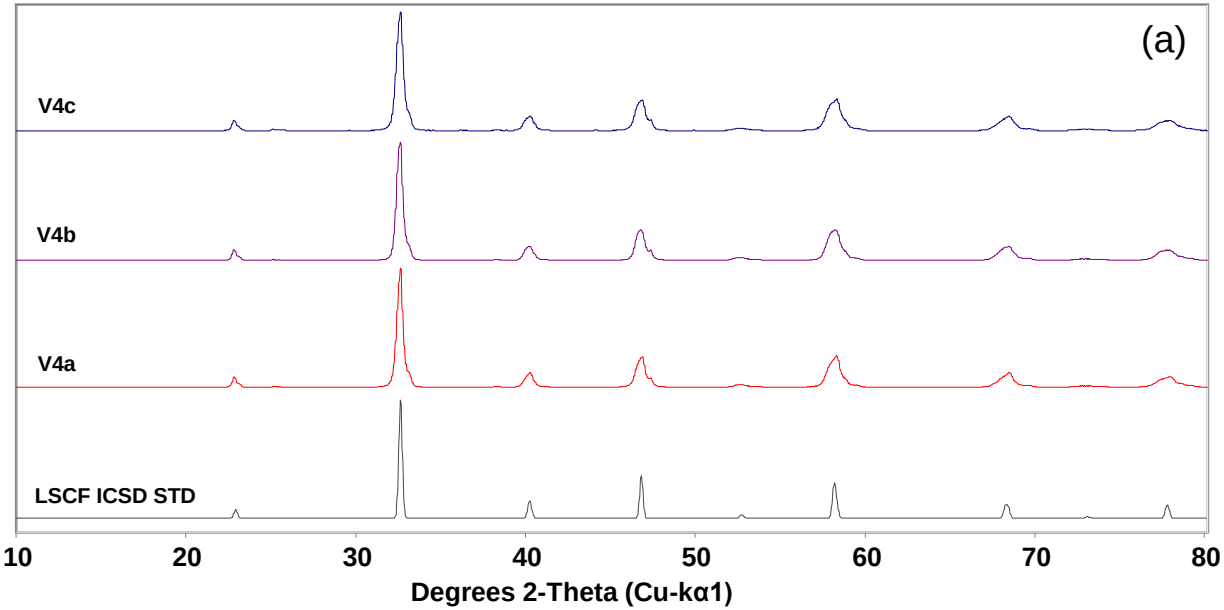
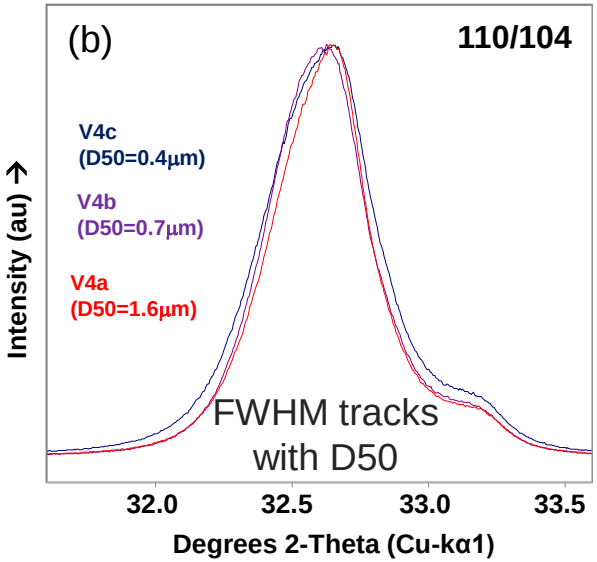
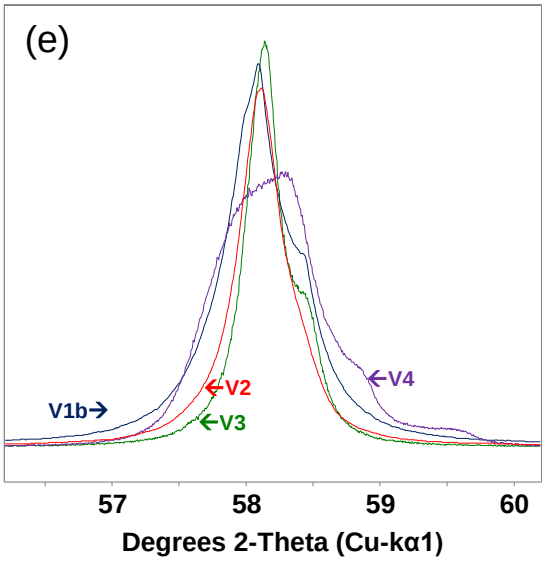
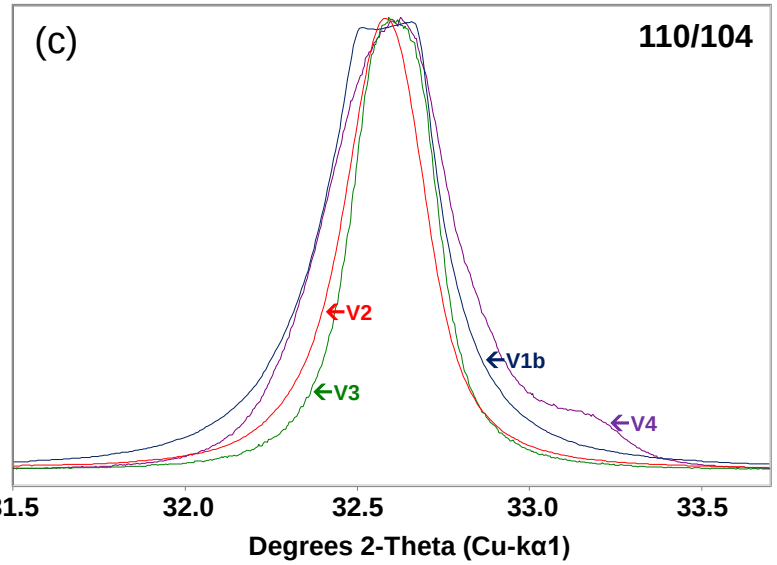
Received stoichiometric LSFC (V4) no distortion









Significant lattice distortion that varies with vendor

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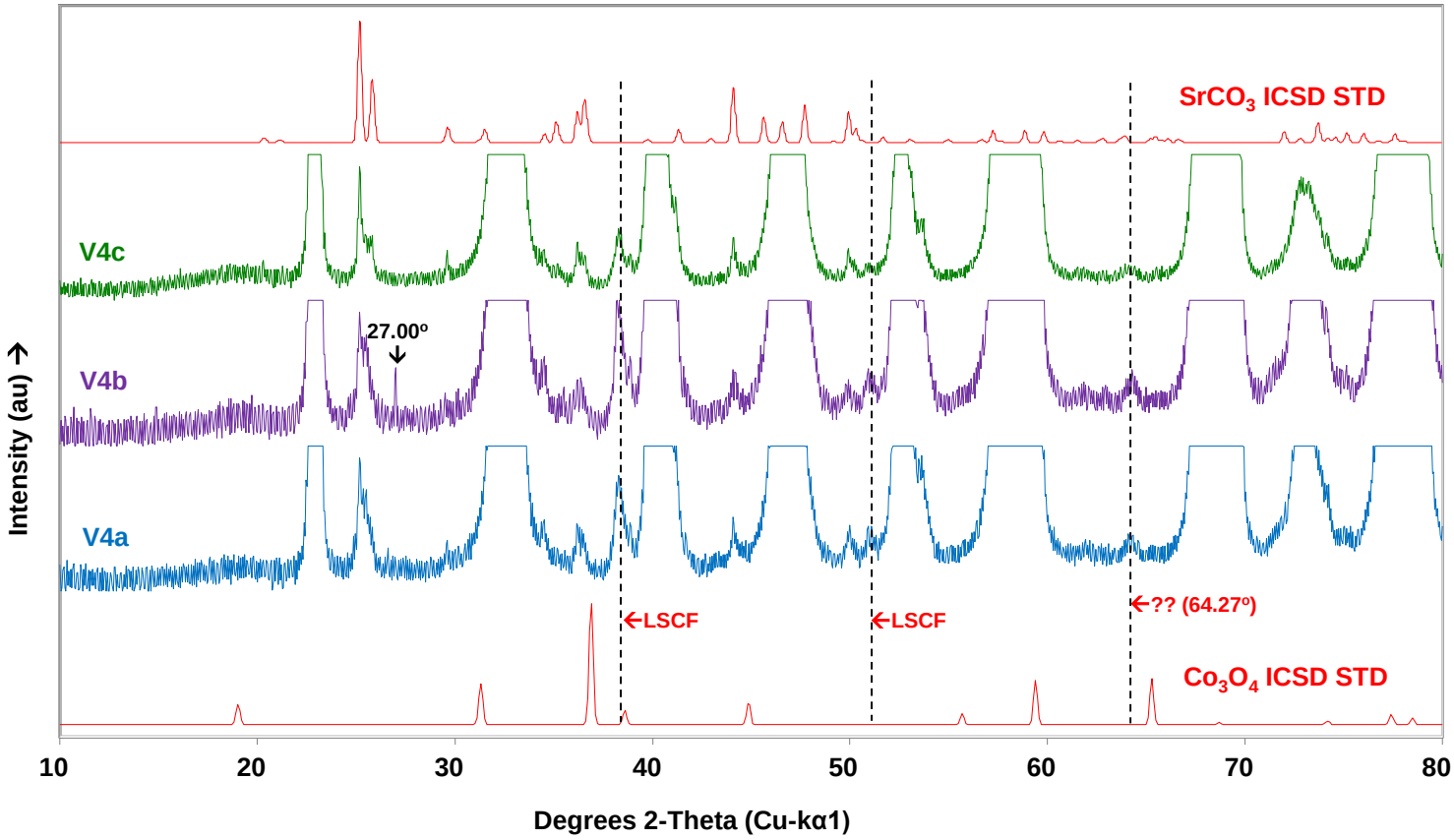
Stoichiometric LSCF exhibits $SrCO_3$: no M_3O_4

Sr segregation clearly shown in a-site deficient LSCF, previously M_3O_4 spinel phase is present in a-site deficient LSCF



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Summary of HR-XRD results

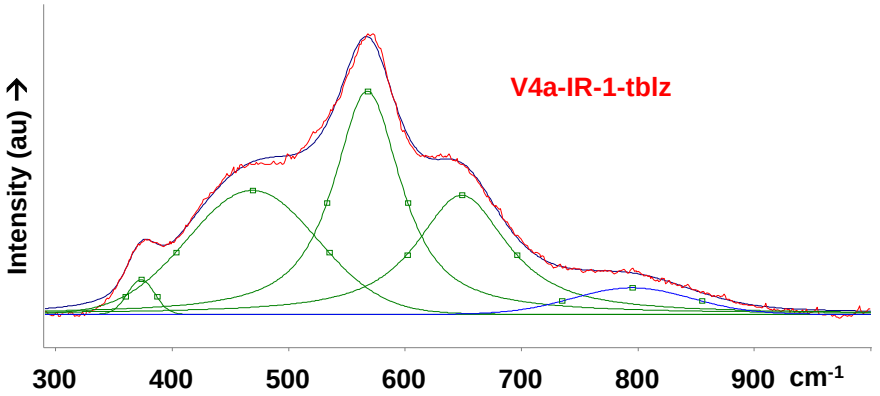
VENDOR	COMPOSITION	PROPOSED SYNTHESIS	LATTICE DISTORTION
V1 a, b coarse/fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	SS + mill	YES rhombohedral
V2 fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	combust	YES tetrahedral
V3 (coarse)	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	Uncertain	NO ?
V4 a, b, c (bimodal, varying)	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	Coprecip + sint	NO

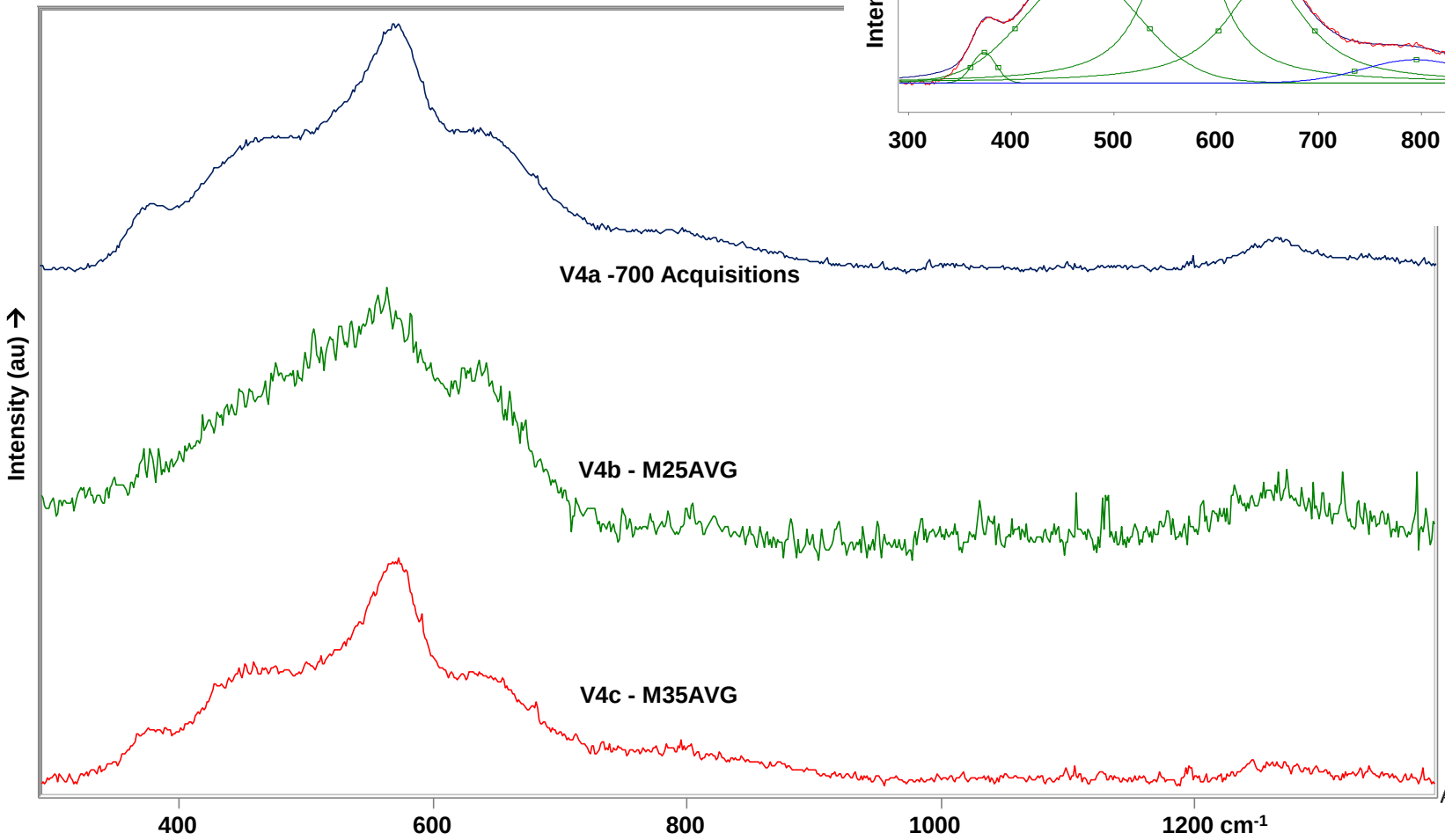
- Designed compositional does not correlate as expected
- Widely varying, with slight distortions
- Need to look closer at existing operando data that we have

Raman spectra stoichiometric LSCF (V4)

Deconvolution for each gives same scattering behavior

Function	cm^{-1}	Height	Width	Area
G+L	373	141	27.4	4115
G+L	469	499	131.6	70078
G+L	568	899	69.4	88660
G+L	649	480	94.2	63470
G+L	795	108	120.5	13867





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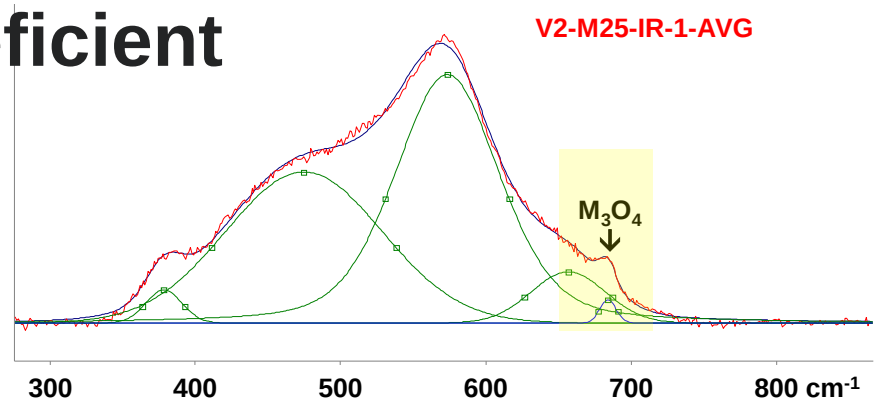
Comparison with a-site deficient

Second phase is present in a-site deficient not in stoichiometric LSCF

Function	cm^{-1}	Height	Width	Area
G+L	378	143.1	29.4	4577
G+L	475	648.9	127.0	88027
G+L	573	1066.9	85.3	108426
G+L	657	220.3	60.6	14357
G+L	684	98.7	13.3	1398



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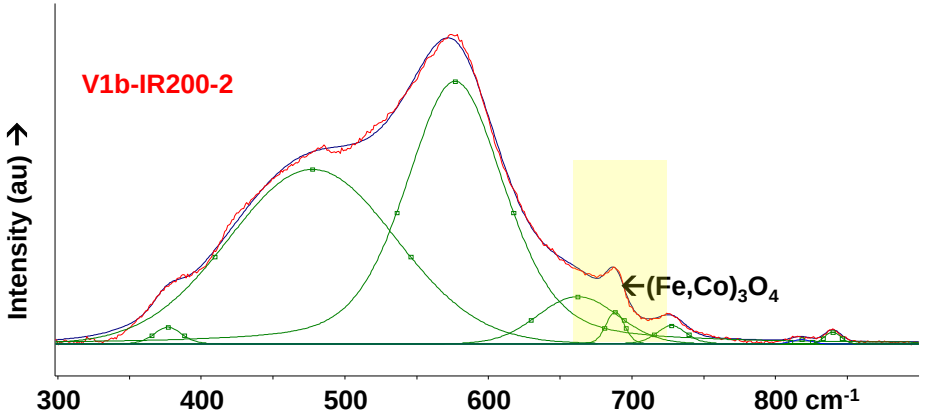
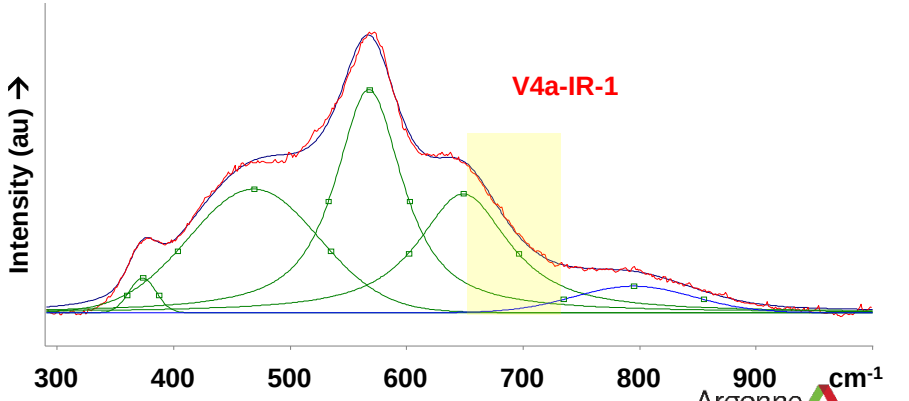


Function	cm^{-1}	Height	Width	Area
G+L	377	53.9	22.6	1385
G+L	477	572.2	136.5	83255
G+L	577	861.2	81.4	85030
G+L	662	154.1	65.0	10669
G+L	688	104.3	15.0	1763
G+L	727	60.2	24.1	1719
G+L	818	13.9	15.4	236
G+L	840	37.4	13.5	536



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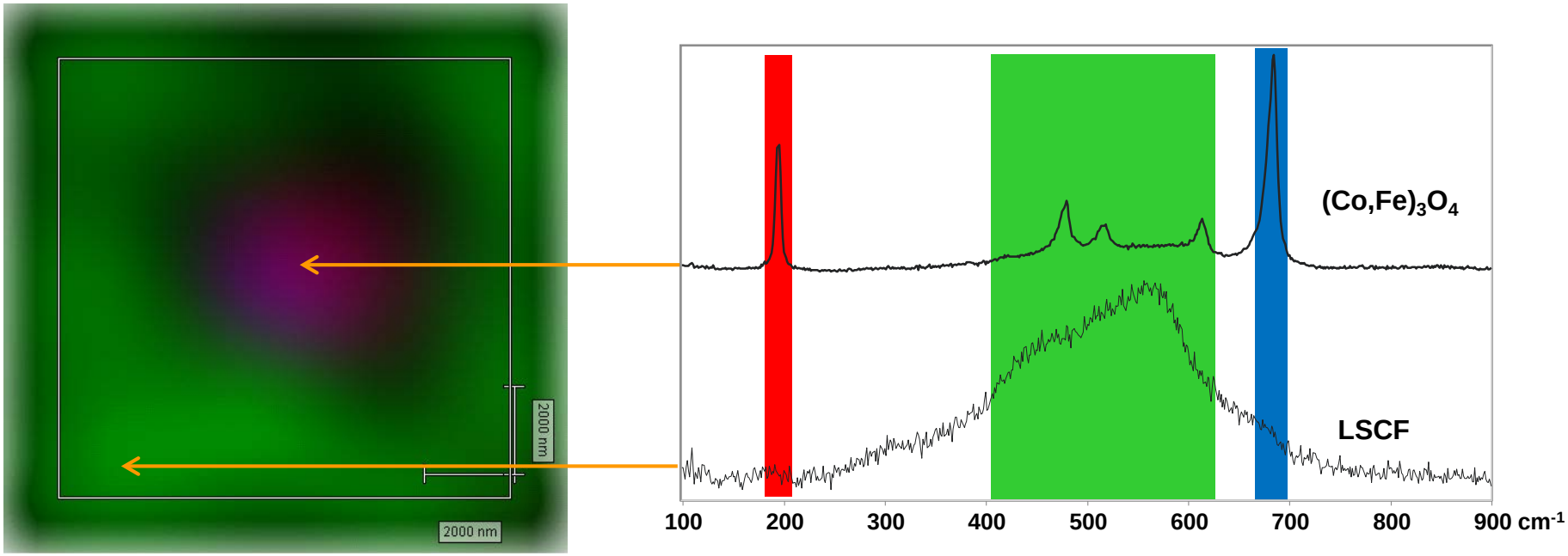
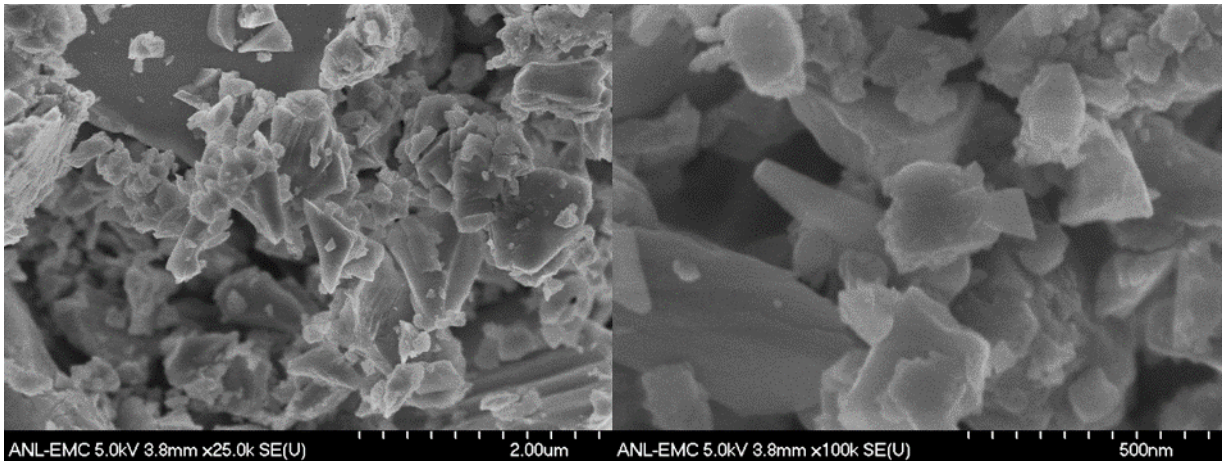
Raman can investigated heterogeneous phase distribution

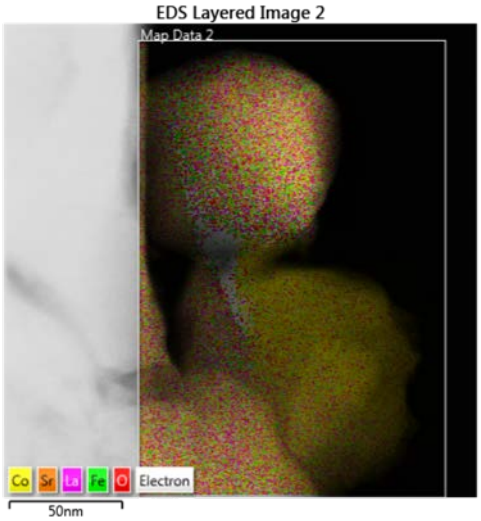
- Raman spectral map of an area on the rim of an V1a Cell cathode
- Observe $(Co,Fe)_3O_4$ crystallite approximately 5 μm in dimension
- The blue and red images for the two M_3O_4 bands lie on top of one another in the center of the map creating a purple-like color.

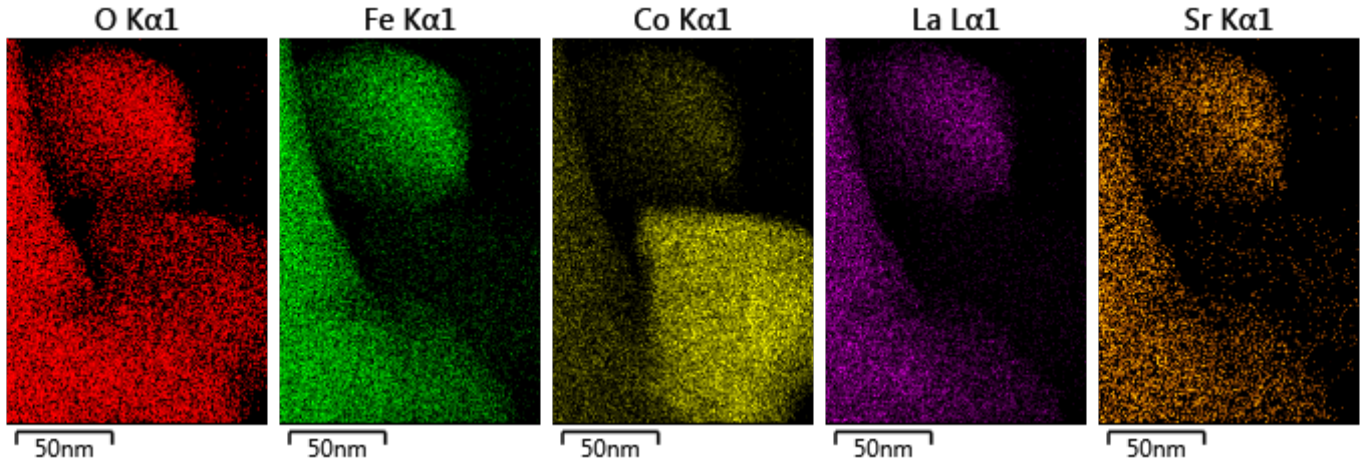


Distribution of Co-rich second phase validated

Clear evidence of "Co_3O_4" second phase identified with STEM for a given LSCF source material

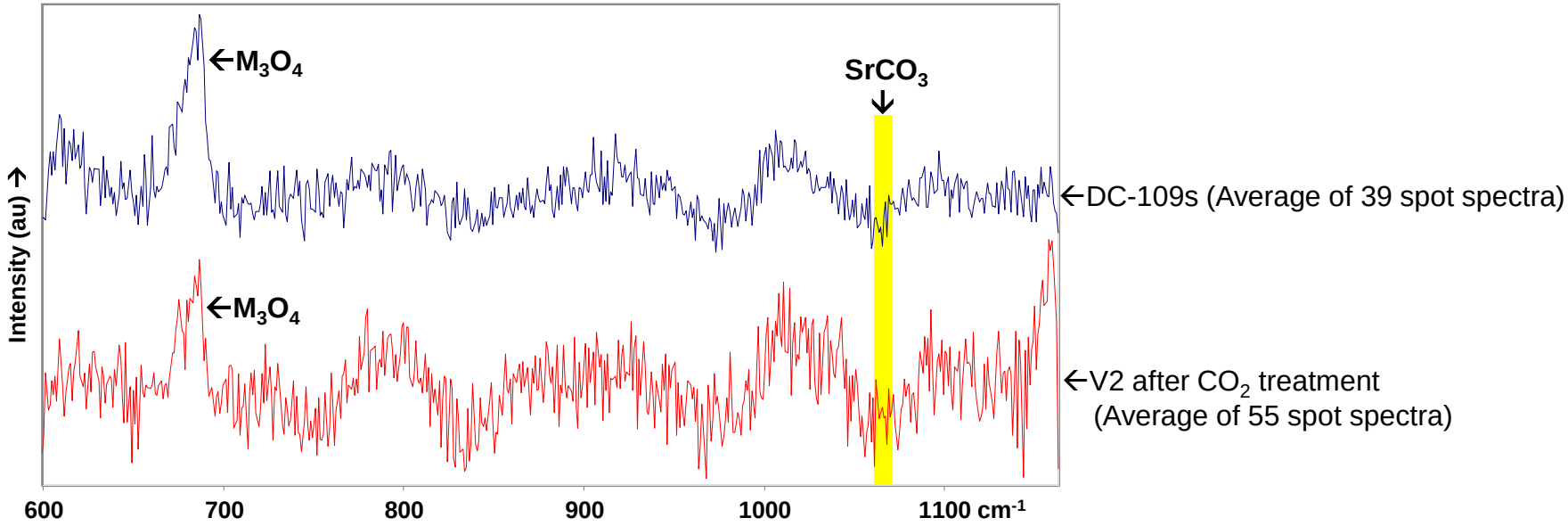






Note that Raman detects M_3O_4 phase, but is poor at detecting Sr-segregation products

This data summarize the quick diagnostic Raman is for the B-site rich spinel second phase. Known Sr-segregation needs another approach



Raman mapping of V2 samples: Searching for M_3O_4 and $SrCO_3$

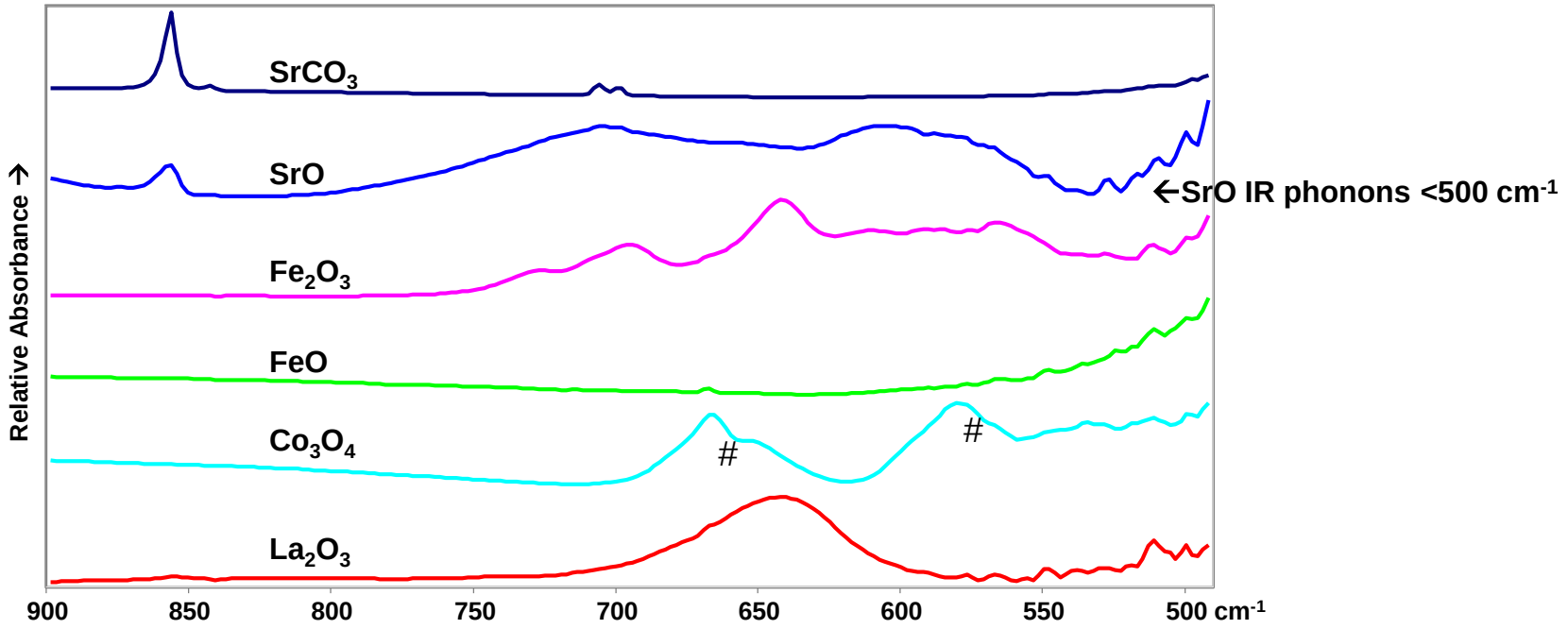
Summary of Raman results

VENDOR	COMPOSITION	PROPOSED SYNTHESIS	$(Co,Fe)_3O_4$
V1 a, b coarse/fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	SS + mill	Yes, but inconsistent
V2 fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	combust	YES
V3 (coarse)	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	Uncertain	YES
V4 a, b, c (bimodal, varying)	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	Coprecip + sint	NO

- Quick and low cost methodology
- Clearly shows distortion – now that we know to look for it
- Identifies B-site second phase species, but not Sr-phases

Consider FTIR absorption spectra from impurity oxides

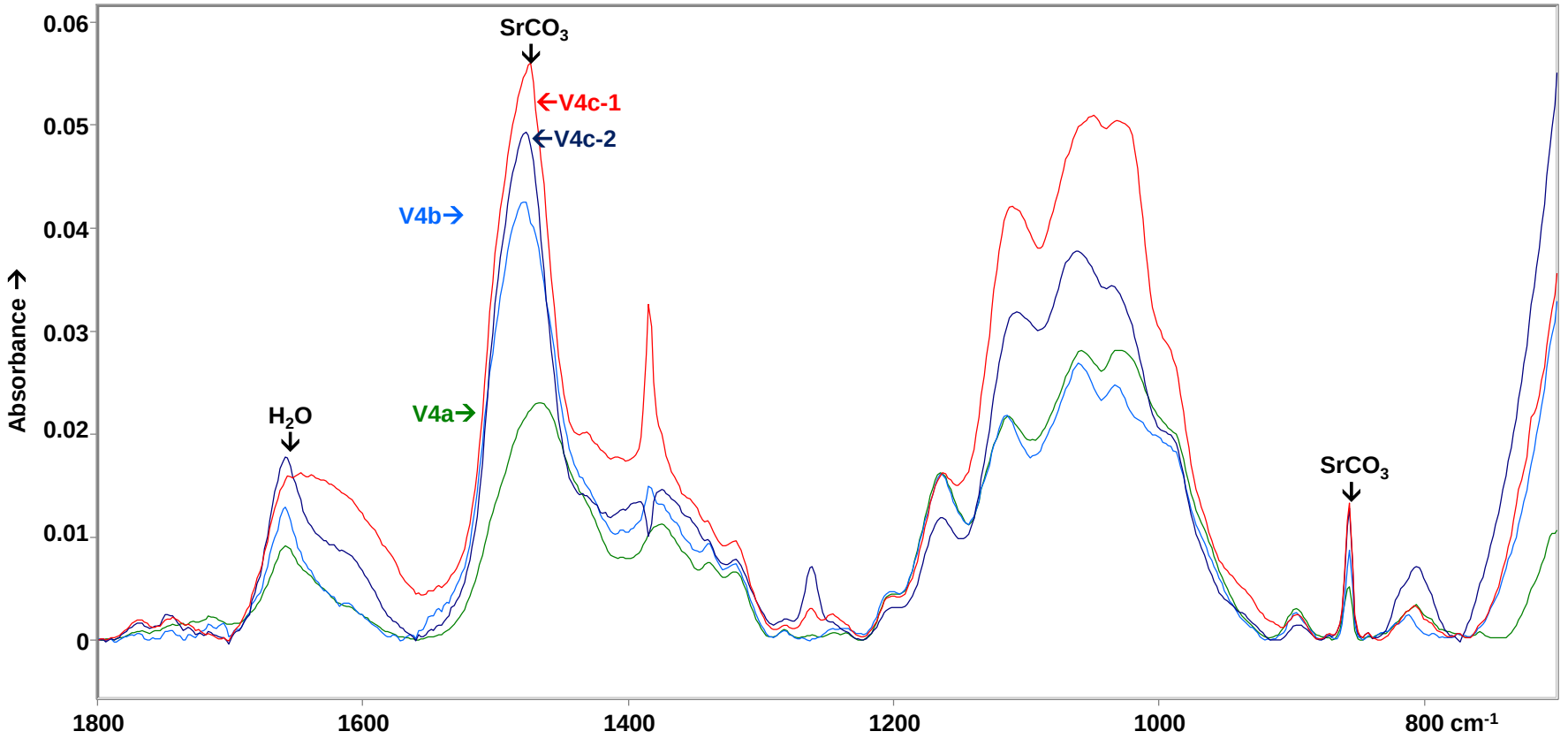
Doubtful to detect trace oxide impurities in LSCF materials using FTIR methods < 600 cm^{-1}



- Most of the IR active phonons of Fe, Sr, and La oxides are below 600 cm^{-1}
- $SrCO_3$ and SrO are positively identified ~ 860 cm^{-1}
- Calibration of for quantitative analysis of Sr phase is possible

FTIR of stoichiometric LSCF (V4), normalized

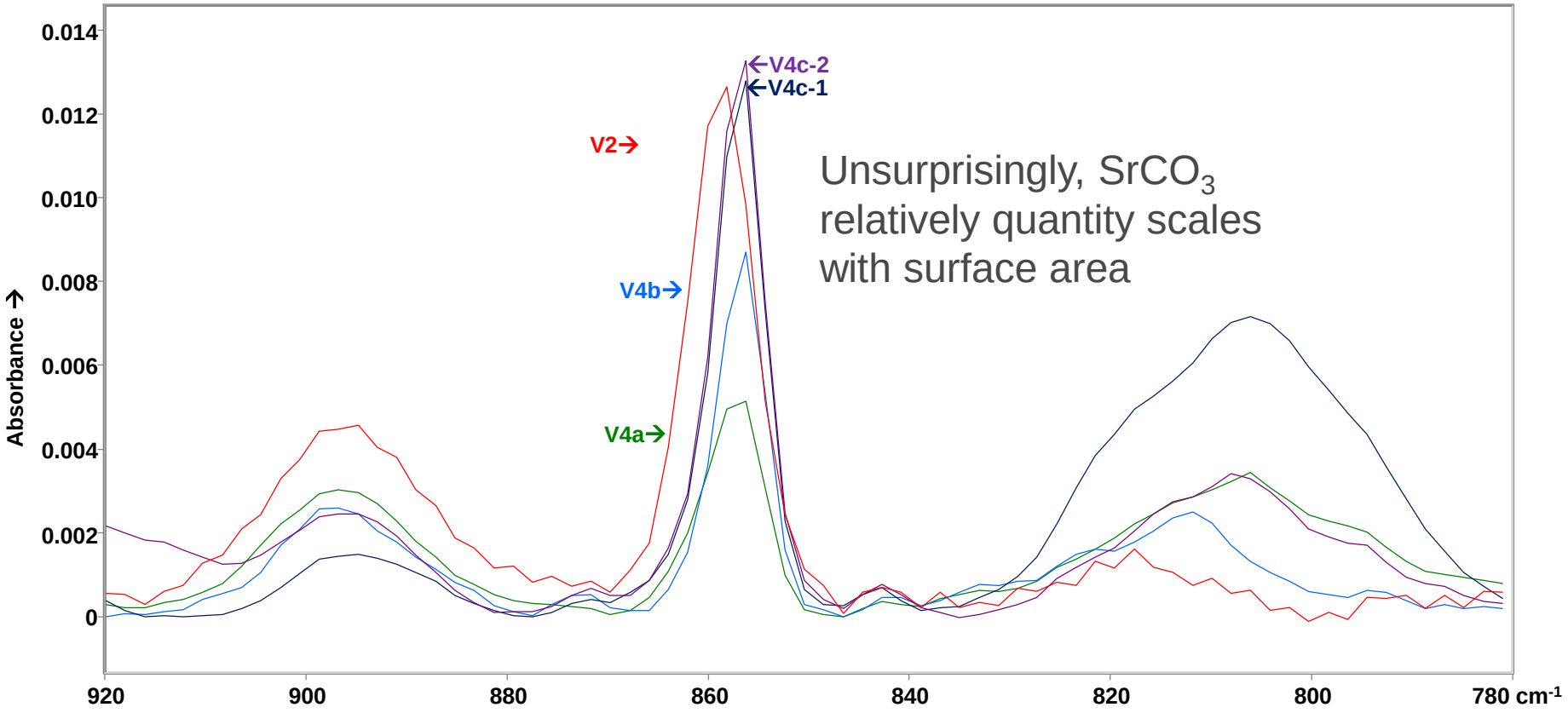
Clear evidence of $SrCO_3$



(for this data set, organic solvents were present in glove box atmosphere where we press the KBr pellet)

FTIR of stoichiometric LSCF (V4), normalized

Compared to a-site received deficient LSCF



	Lot No.	Particle Size D50 (µm)	Specific Surface Area (m^2/g)
LSCF6428-A **V4a**	1	1.6	3.9
LSCF6428-B **V4b**	1	0.7	6.0
LSCF6428-C **V4c**	1	0.4	10.9

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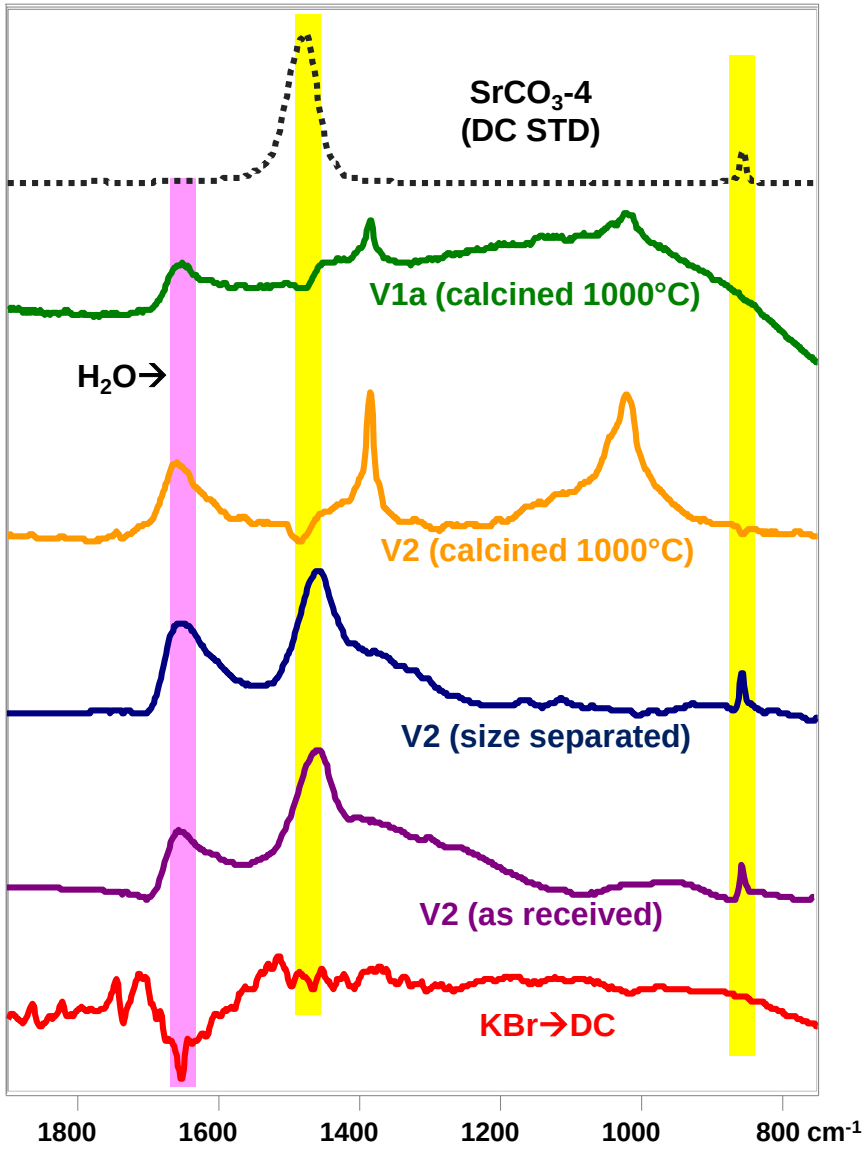
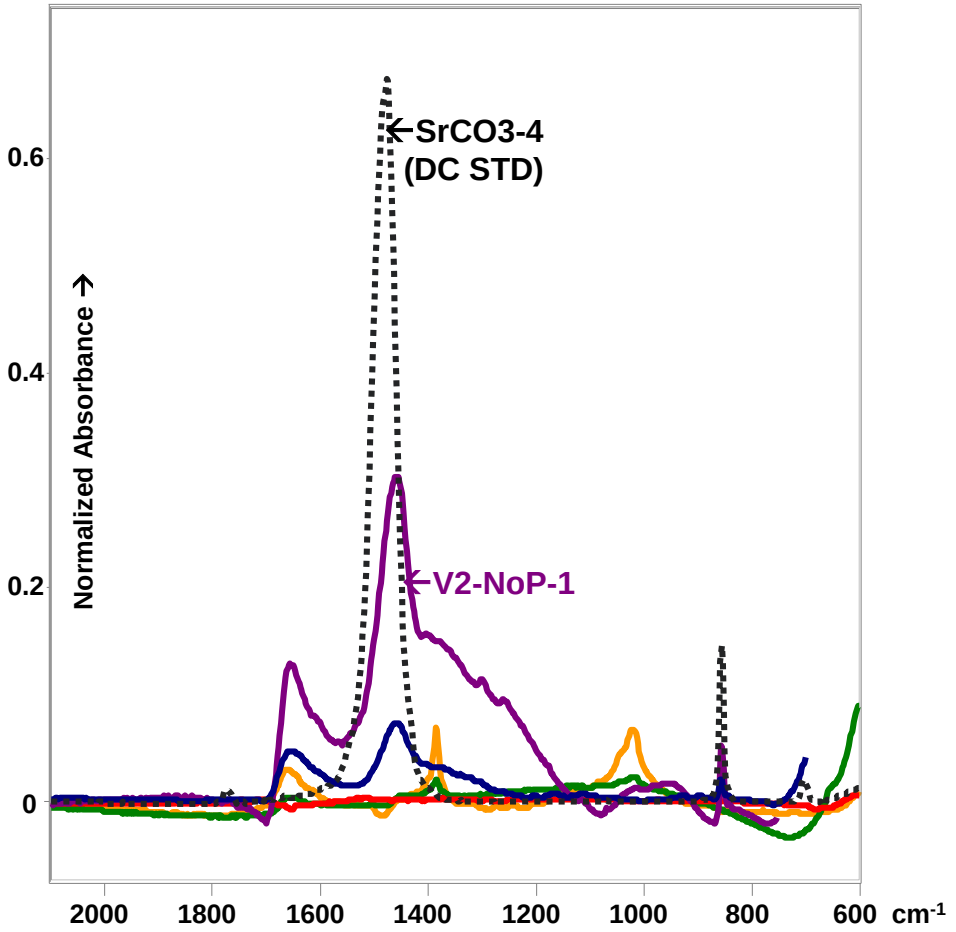
Calcining negates observation of $SrCO_3$



Does Sr reenter the LSCF lattice during sintering or operation?

The separated spectra to the left are plotted on a common absorbance scale below



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Summary of FTIR results

VENDOR	COMPOSITION	PROPOSED SYNTHESIS	$SrCO_3$
V1 a, b coarse/fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	SS + mill	YES
V2 fine	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	combust	YES
V3 (coarse)	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	Uncertain	YES
V4 a, b, c (bimodal, varying)	$La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$	Coprecip + sint	YES

- All as received have ~2-6% of their Sr as $SrCO_3$
- Surface area dependent
- The nature of Sr and persistence at calcination temperature is inconsistent

DECOUPLE CHEMISTRY AND MORPHOLOGY EFFECTS ON PERFORMANCE

Linking morphology and performance

characteristic thickness

$$\delta = \sqrt{\left(\frac{(1-\varepsilon)}{\tau \cdot a}\right)\frac{D^*}{k}}$$

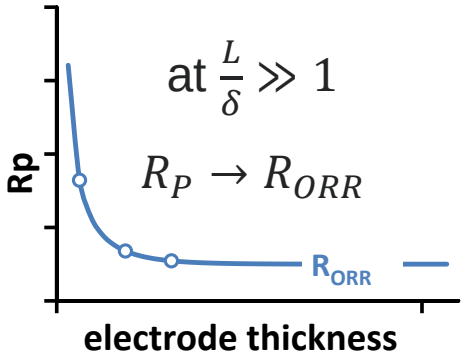
morphology

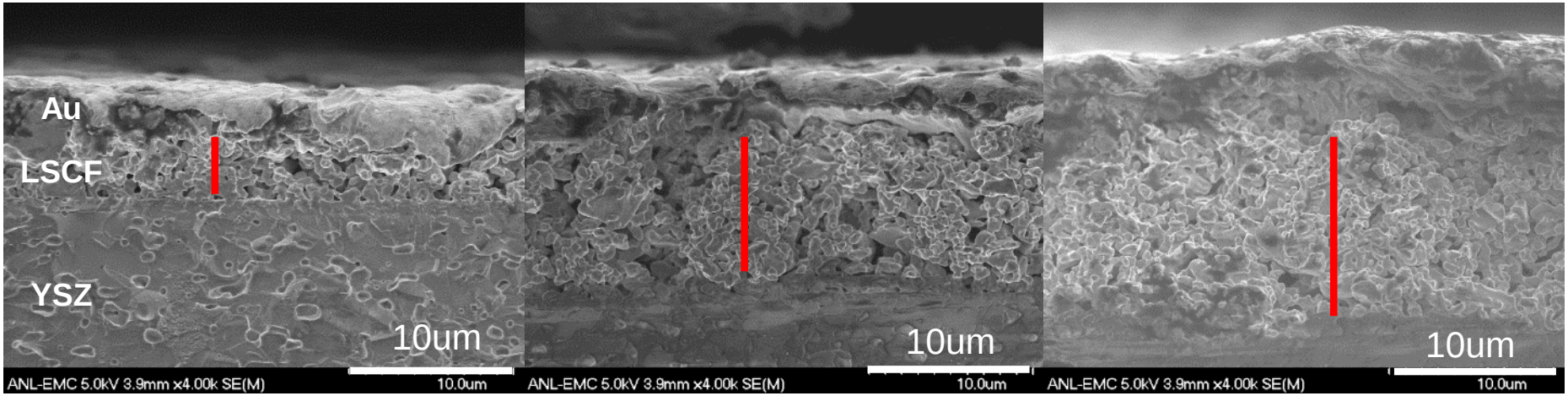
chemistry

$$R_p \sim \frac{R_{ORR}}{tanh\left(\frac{L}{\delta}\right)}$$

at $\frac{L}{\delta} \gg 1$

$R_P \rightarrow R_{ORR}$





δ is the characteristic length, L is the electrode thickness, τ is tortuosity, ε is porosity, a is the surface area, D^* oxygen chemical diffusivity, and k is the oxygen surface exchange rate

SB. Adler, J.A. Lane, B.C.H. Steele. *J. Electrochem. Soc.* 143(11), 3554-3564 (1996).
SB Adler, *Solid State Ionics* 111(1–2), 125–134 (1998).

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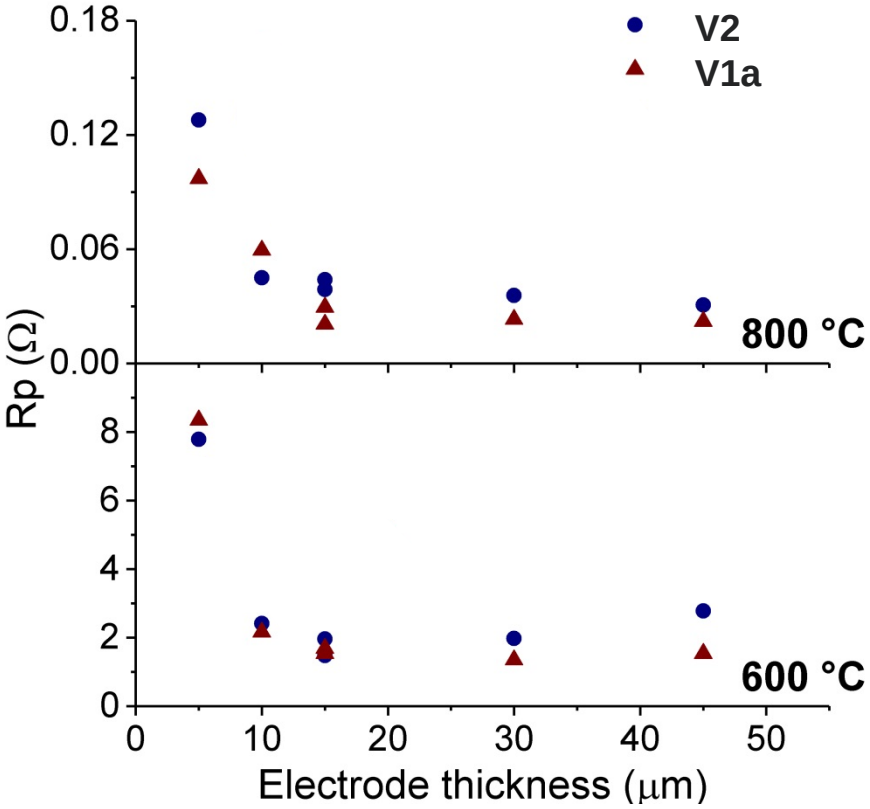
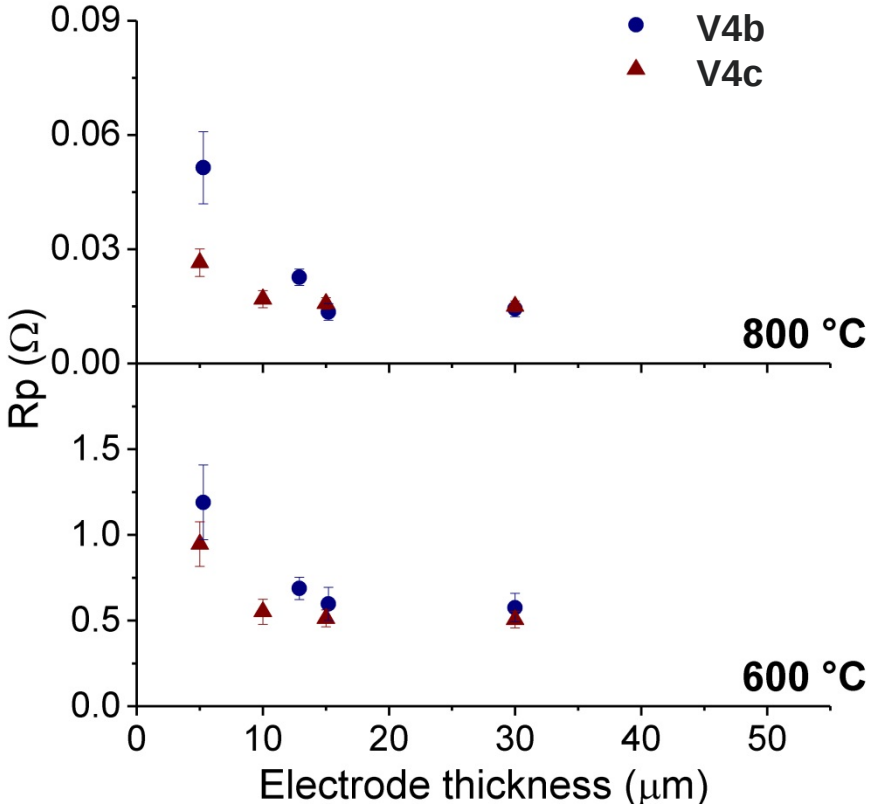
Electrode thickness effects

A-site deficient LSCF



- different synthetic approaches and dramatic particle size distributions
- Nominally similar chemistries, phase distributions, etc.

A-site stoichiometric LSCF



- same synthetic methods followed by processing to decrease particle size
- Nominally similar chemistry, phase distribution, etc.

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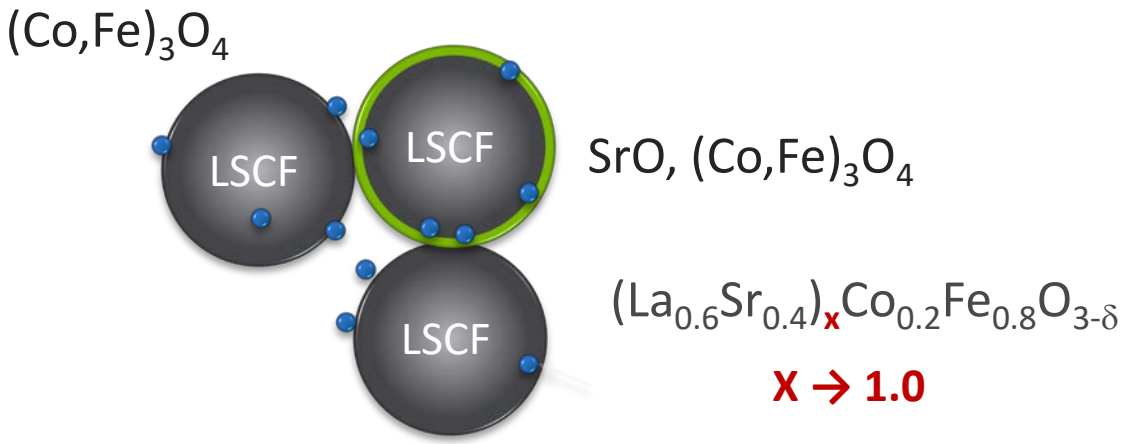
Open questions related to composition

- Understanding the evolution of phase impurities and cation distributions with initial sintering (and long term operation) to link to performance reliability
  - Does this affect the chemistry and catalytic behavior of ORR?
  - Does B-site segregation / 2nd phase result in performance degradation?
- Does as-received feedstock material chemistry or morphology affect this evolution?



LINKS ARE COMING TOGETHER:

- REFINE APPROACH TO SEPARATE CONTRIBUTION OF $^{(1-\varepsilon)}/_{\tau a}$ AND $^{D^*}/_{k}$ TO MACROSCALE ELECTRODE PERFORMANCE
- SYNTHETIC APPROACHES TO TEST HYPOTHESES OF LSCF STRUCTURE AND CHEMISTRY
- VERY LARGE VARIATION IN FEEDSTOCK POWDERS IS OBSERVED
- PERFORMANCE VARIATION IS CHALLENGING TO ASCERTAIN

Thank you…

- **We great appreciate the U.S. Department of Energy, Office of Fossil Energy, Solid Oxide Fuel Cell Program**
- **Joseph Stoffa, SOFC project manager**

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