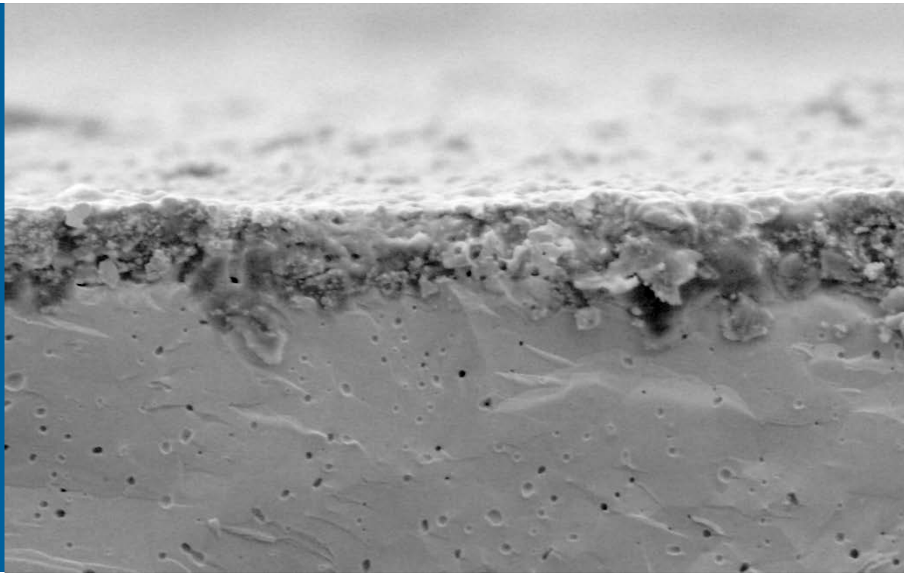
Evaluation of Cathode Materials for SOFC Performance Reliability



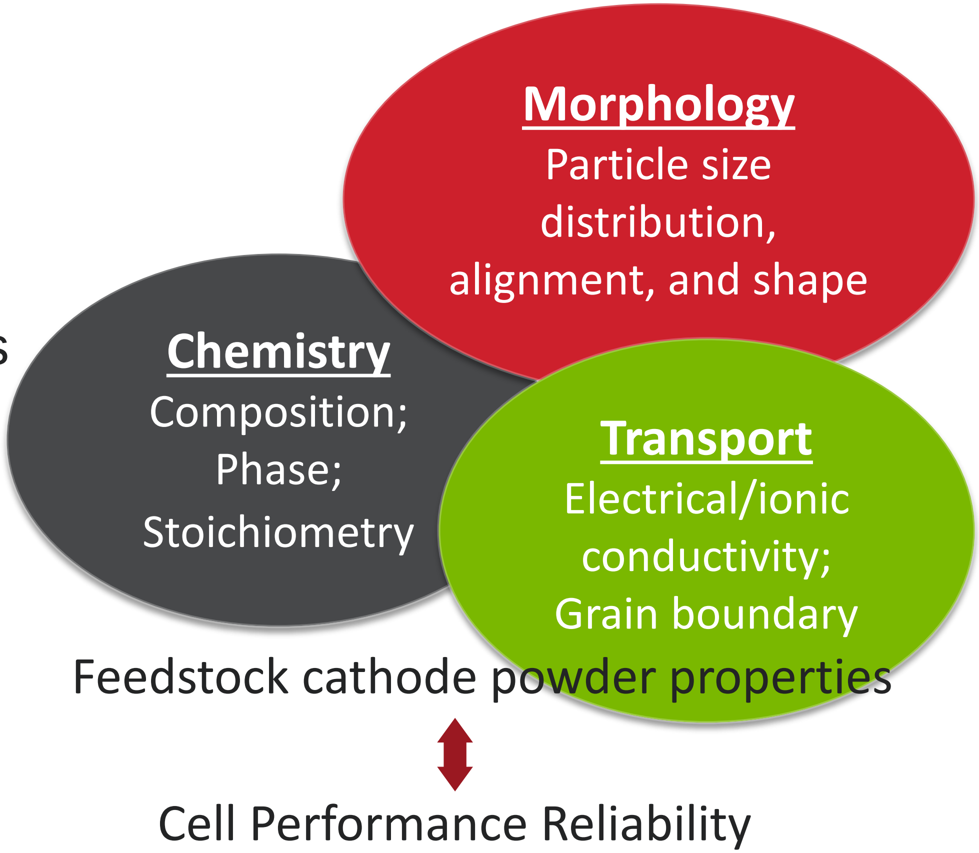
BRIAN J INGRAM
Le (Gavin) Ge
J. David Carter
Donald C. Cronauer
Victor A. Maroni

18th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting
June 12-14, 2017

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

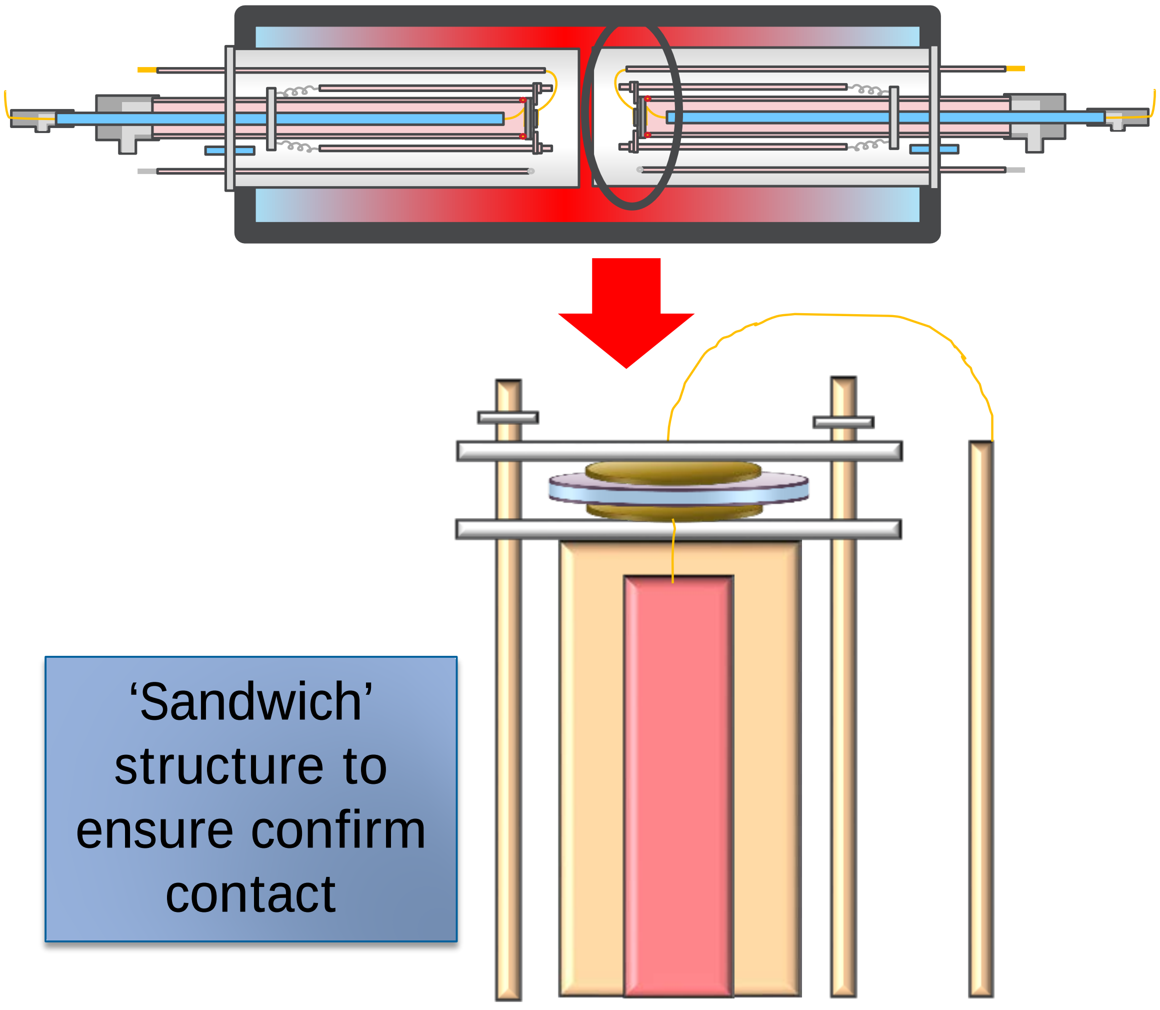
- Electrochemical test protocol was refined to improve comparative performance diagnostics
- Continued to understand relationship between feedstock powder and short term electrochemical performance
  - Morphology of as-received powders direct relationship to sintered electrodes
  - Performance trends with as-received surface area with complex particle size distributions observed
  - Effort to decouple morphology effects from macro-surface chemistry/structure effects
- Developing predictive understanding to mitigate cell-to-cell variability based on feedstock variations

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

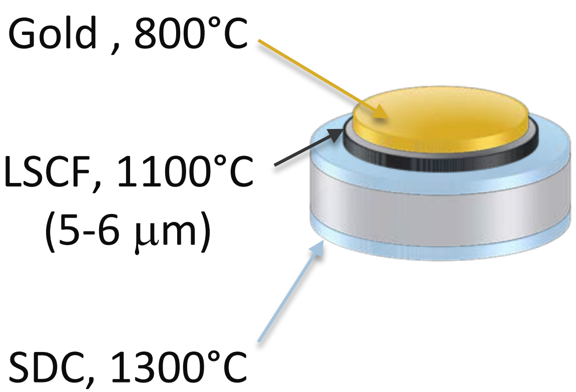
- Understand and reduce variation contribution from
  - Temperature
  - Electrical contact
  - Temporal variations in performance response
  - Electrode design

Half cell design

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



‘Sandwich’ structure to ensure confirm contact



Modified test protocol

Minimize temporal performance variation, identify initial performance and projected degradation

800 → 600° C

OCV, 8 min

↓

Potentiodynamic
±100 mV @ 1 mV / sec

↓

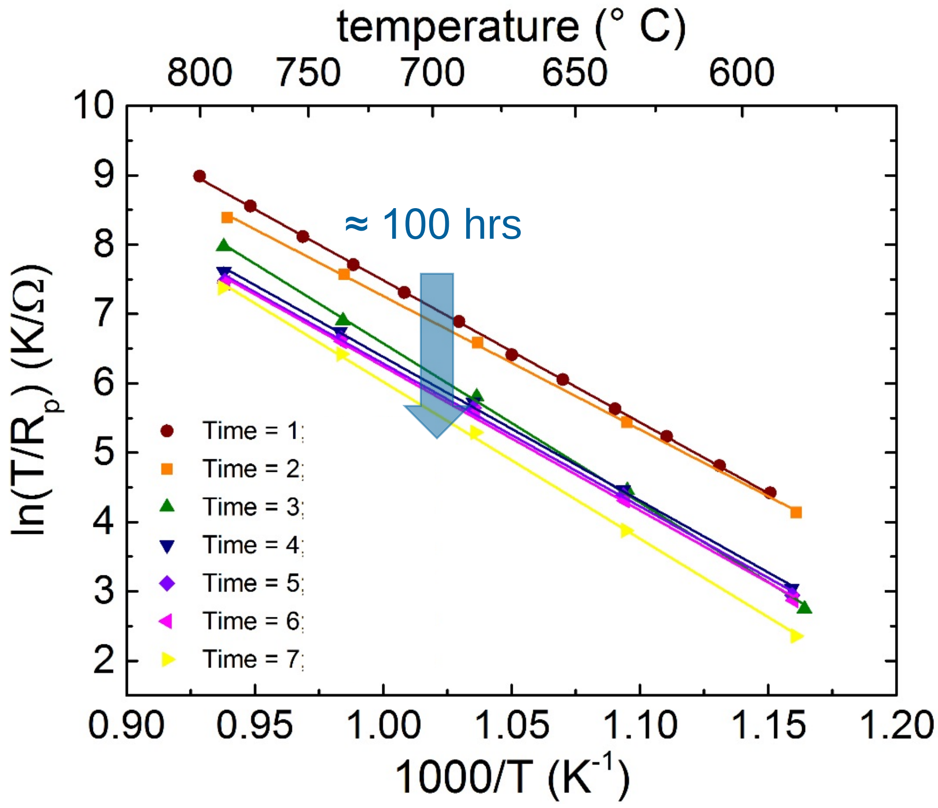
AC-IS
±50 mV vs OCV

Short thermal OCV hold for temperature equilibration

Immediately followed by DC and AC-IS measurements

Protocol identifies initial performance at t=0

Decouple feedstock variation contributions from long term degradation mechanisms



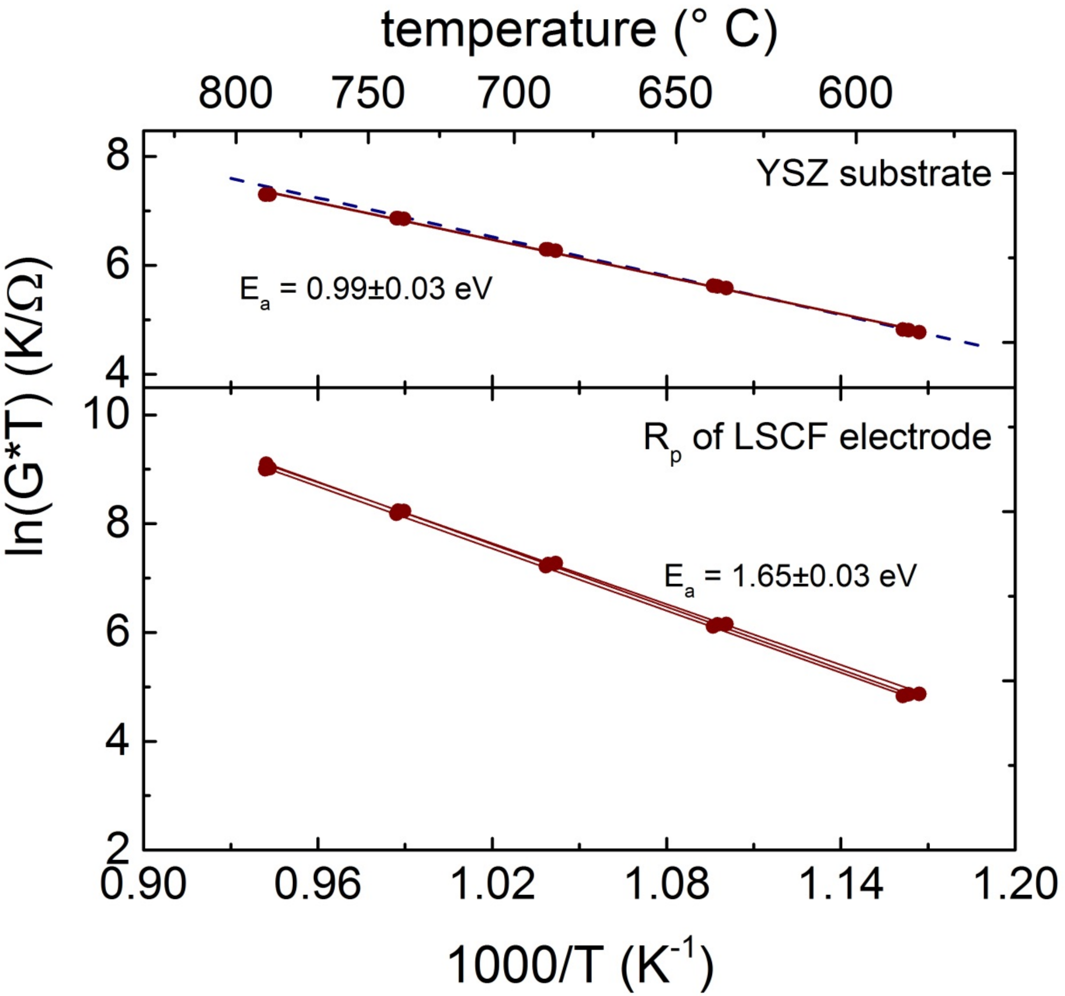
Typical LSCF electrode on YSZ/GDC impedance analysis
Time intervals are not equivalent

- Typical time-dependent changes evolve from initial performance
  - Polarization resistance increases observed over days
  - Transport mechanisms (E_a) does not appear to change
- Building collaboration with NETL program to identify pathway to model long term variations
  - Predictively link long term to initial performance

Argonne NATIONAL LABORATORY

Established performance baseline

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

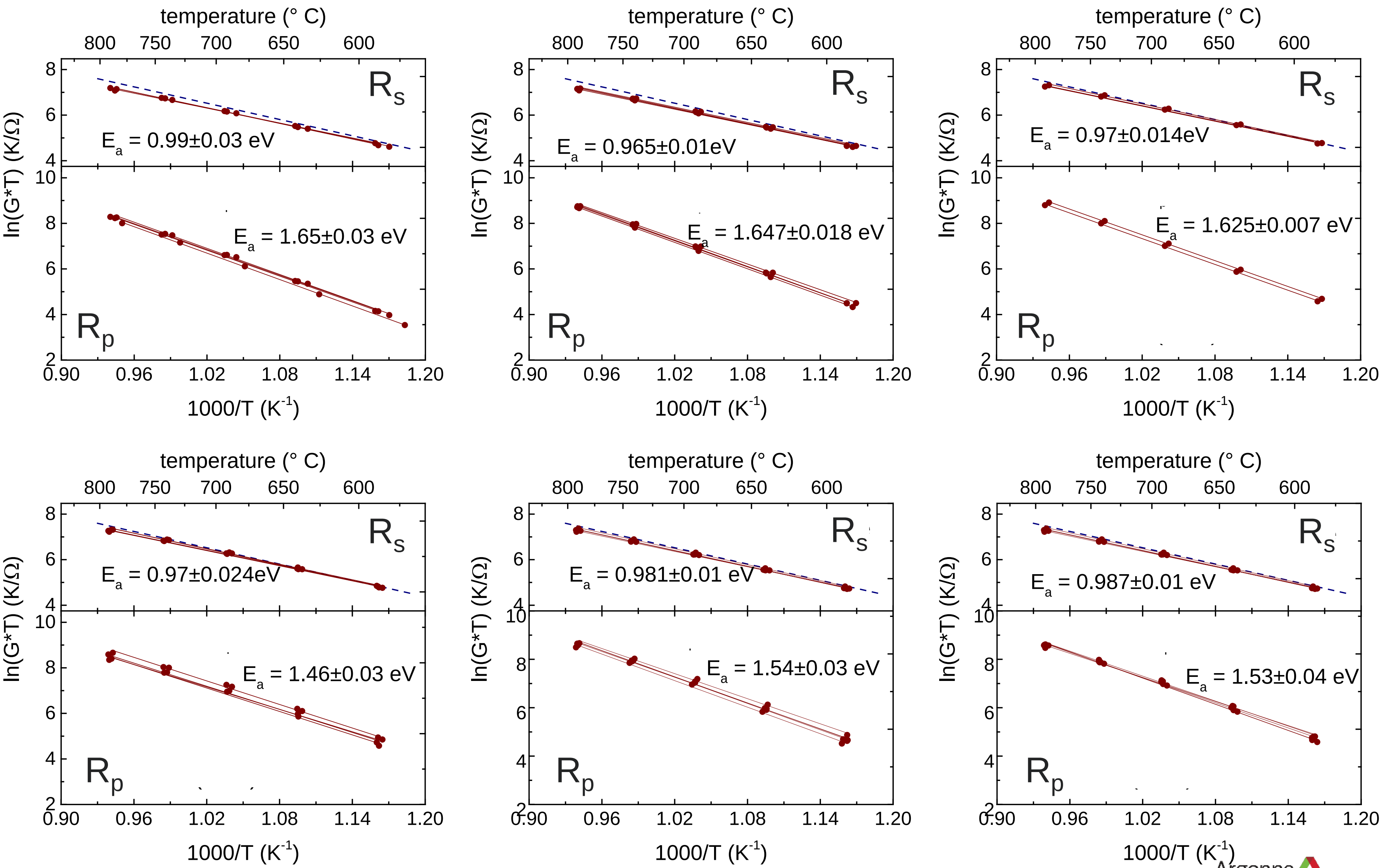


- Representative values derived from impedance measurements
- Sensitivity to electrode thickness and alignment can be resolved
- This baseline shows ~1% variation
- Typically < 2-3% variation observed in polarization conductance from other LSCF materials
- Very small variation in thermal activation energy

Argonne NATIONAL LABORATORY

Performance baseline determination

Reproducibility of < 5% for each LSCF material investigated

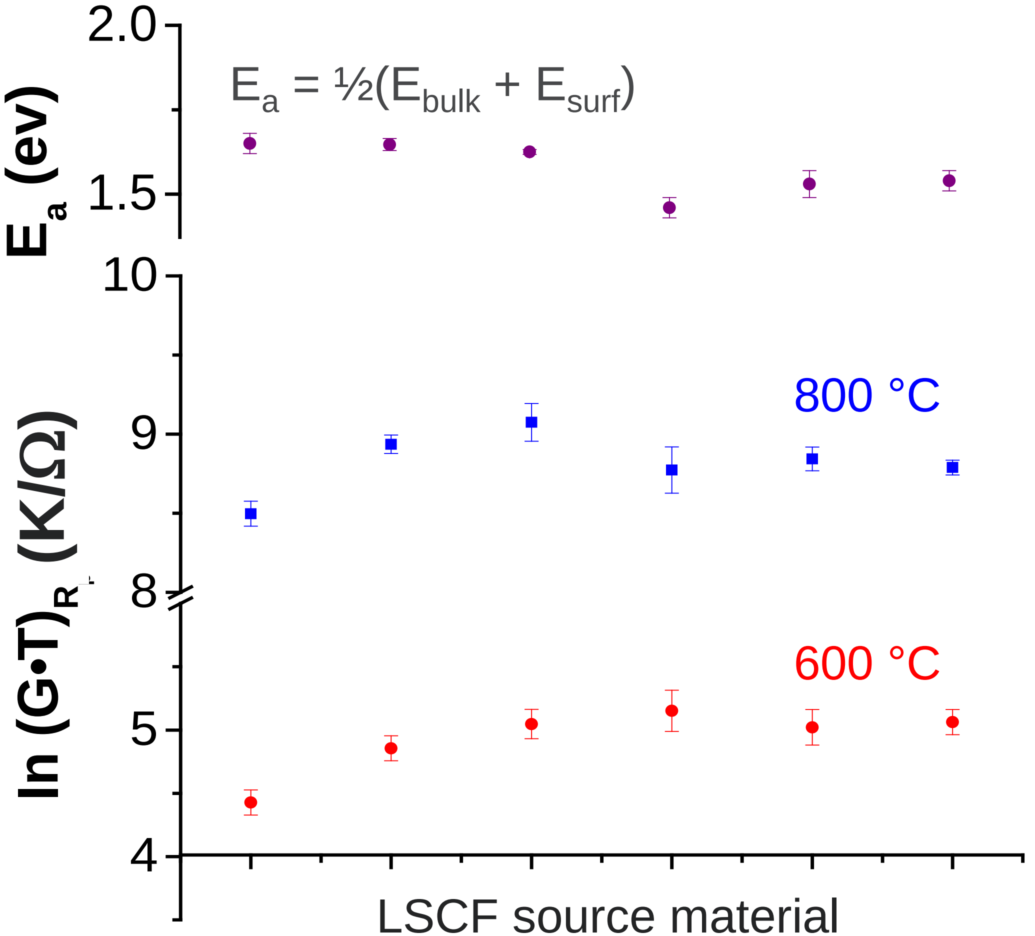


YSZ conduction: SSI 177, 3057 (2006)

Argonne NATIONAL LABORATORY

LSCF powder performance comparison complete

Observed statistical cell-to-cell variation within LSCF source material as well as differences in R_p and E_a between LSCF source material



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

- Significant net differences in R_p and E_a are observed between LSCF feedstock powders
  - Overall ORR mechanistic variations suggested
  - Specific mechanism changes are not identified
- Standard deviation varies between systems as depicted by error bars
  - Variation in electrode fabrication affected by feedstock powder

LINK MORPHOLOGY TO PERFORMANCE RELIABILITY

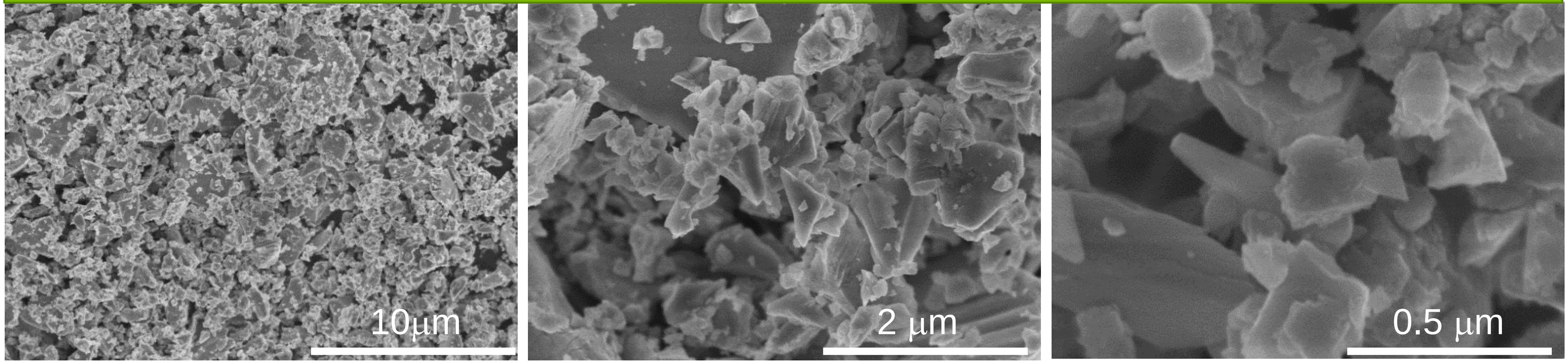
- Various synthetic routes for cathode powder synthesis, e.g., solid state vs. wet chemical
- Wide distributions of particle sizes, 10 nm to 10 μm
- Variable aspect ratio / surface structure: primary & secondary particles

- 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)

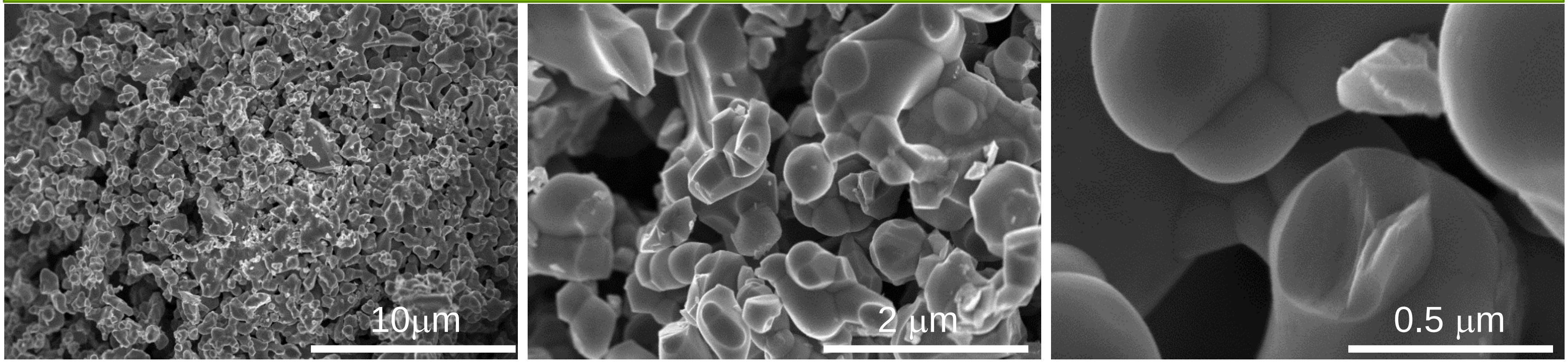
Microscopy of LSCF powders, one example

Complex morphology changes observed beyond size distribution

As Received



Sintered

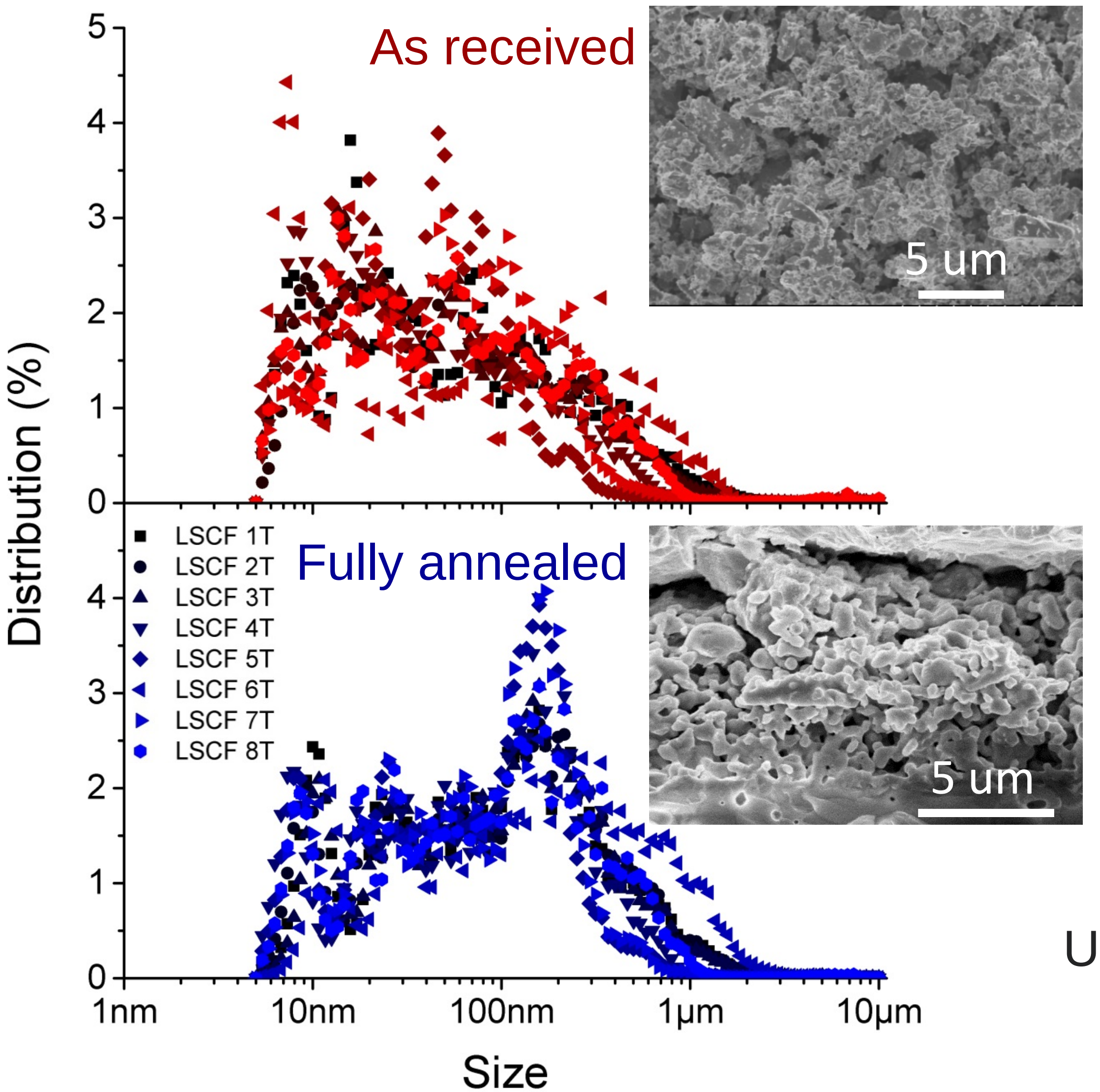


Need to quantify initial state and evolution to sintered electrode state

Argonne NATIONAL LABORATORY

USAXS to monitor in situ morphology evolution

Quantitative analysis of primary particles during electrode sintering



- Comparison of separate LSCF feedstock powders as received
- Electrodes annealed and monitored to 1000°C on single crystal MgO substrates
- Significant variation are observed even after sintering in size of particles comparing LSCF feedstock sources

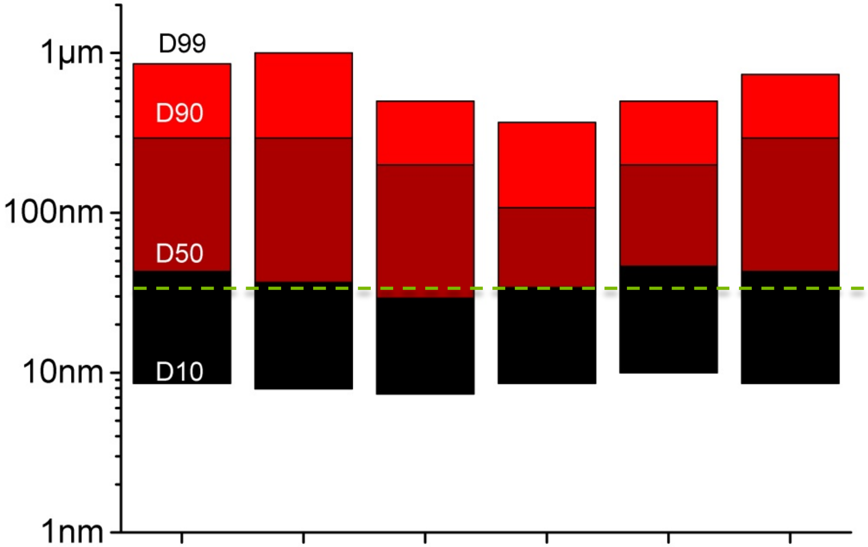
Ultra-small angle x-ray scatterin

Argonne NATIONAL LABORATORY

Primary particle size comparison with annealing

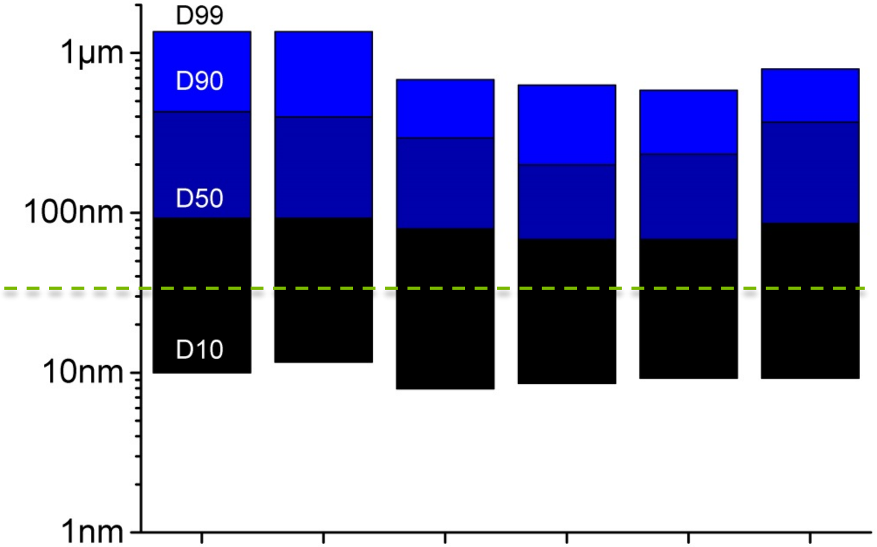
Broad variation between LSCF source material is observed; growth is evident with sintering while qualitatively maintaining initial distribution variations

As Received



LSCF source material

Annealed (1000°C, 1 hr)

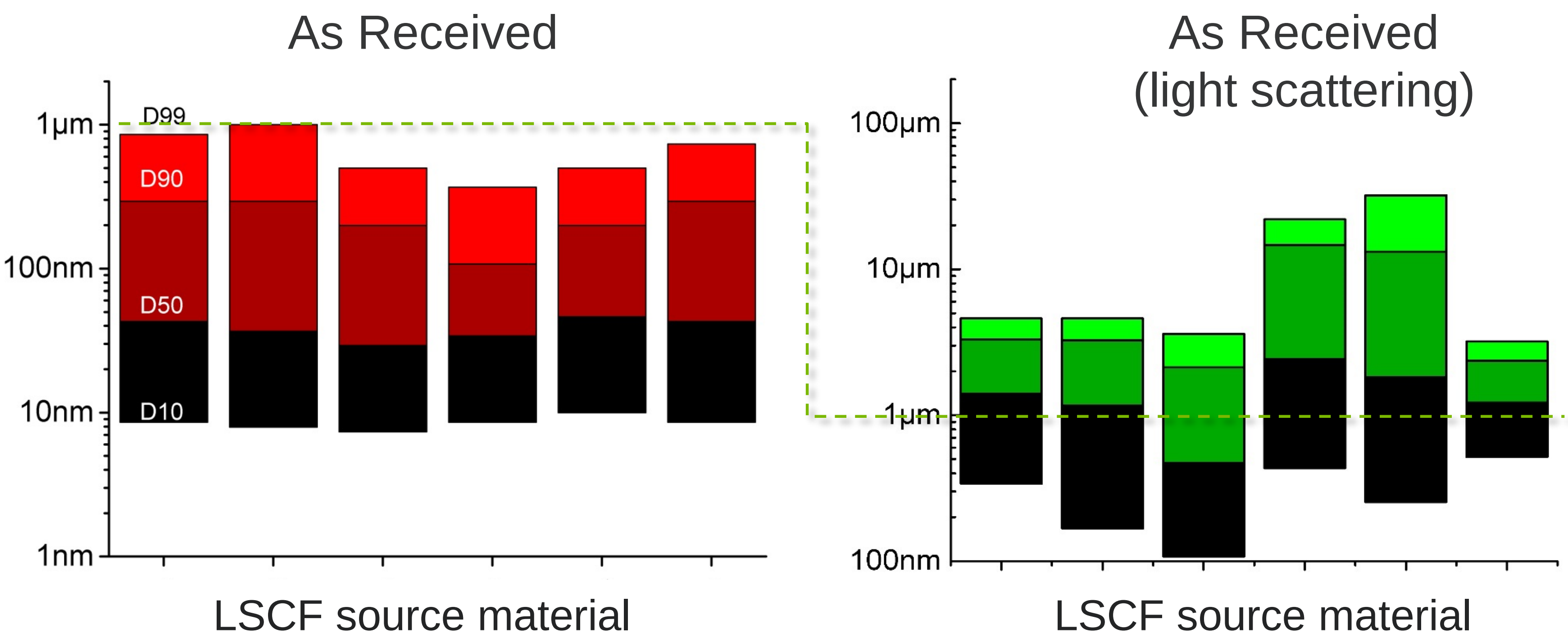


LSCF source material

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

Primary particle size comparison with secondary

Light scattering probes secondary (agglomerated) particles



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

Linking morphology and performance

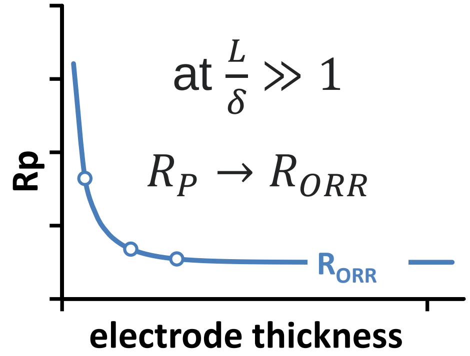
characteristic thickness

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

morphology

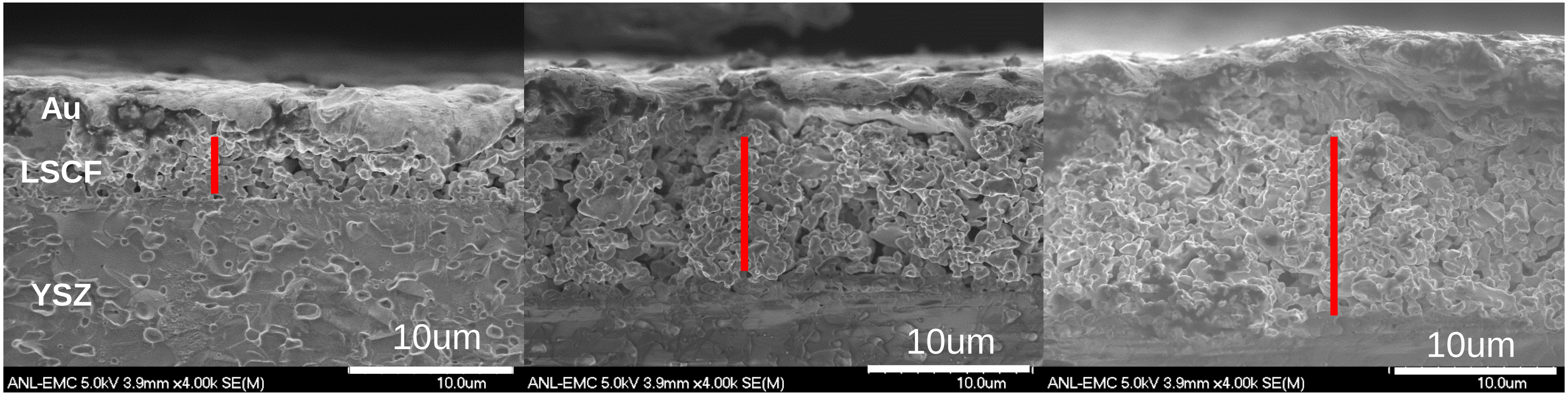
chemistry

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



Sample	R_{ORR} (Ω)	δ (μm)
A	0.08	10
B	0.12	7
C	0.03	25
D	0.07	12

Sample "C" behaves significantly different



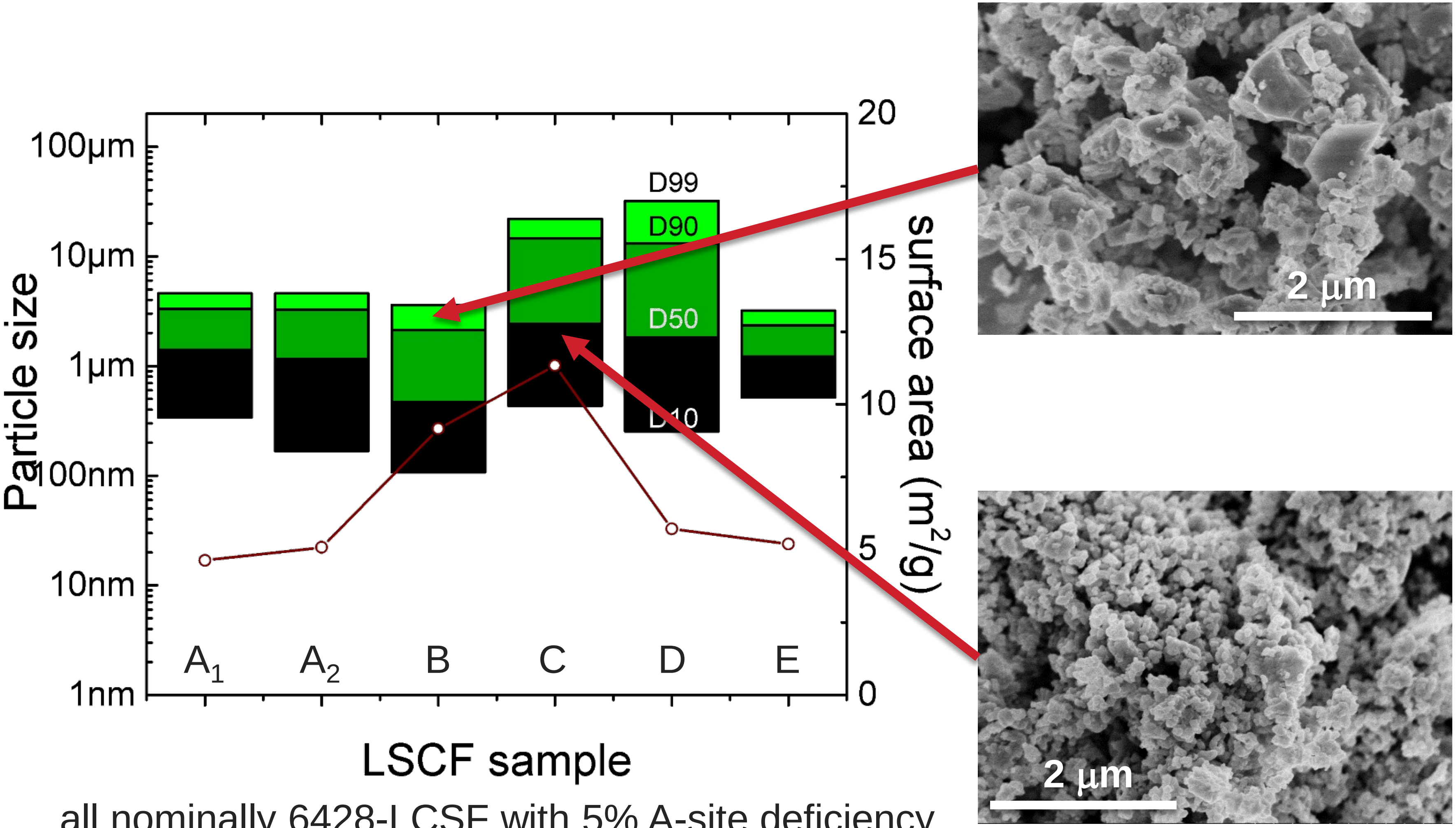
δ is the characteristic length, L is the electrode thickness, τ is tortuosity, ε is porosity, a is the surface area, D^* oxygen chemical diffusivity, and k is the oxygen surface exchange rate

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).

Argonne NATIONAL LABORATORY

BET / PSA as-received materials

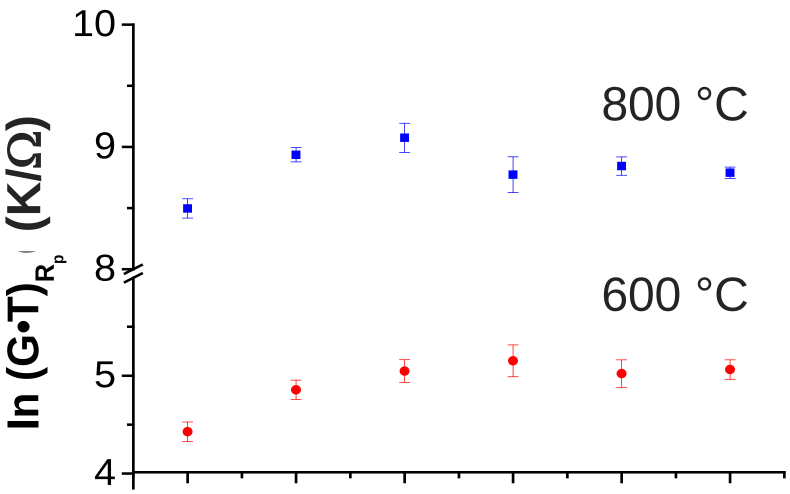
Surface area and PSA are not universally proportional



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

Variations trend with as-received surface area

Error bars can be explained by large characteristic length and electrode thickness control. Cell-to-cell variation trends with as-received surface area



LSCF source material

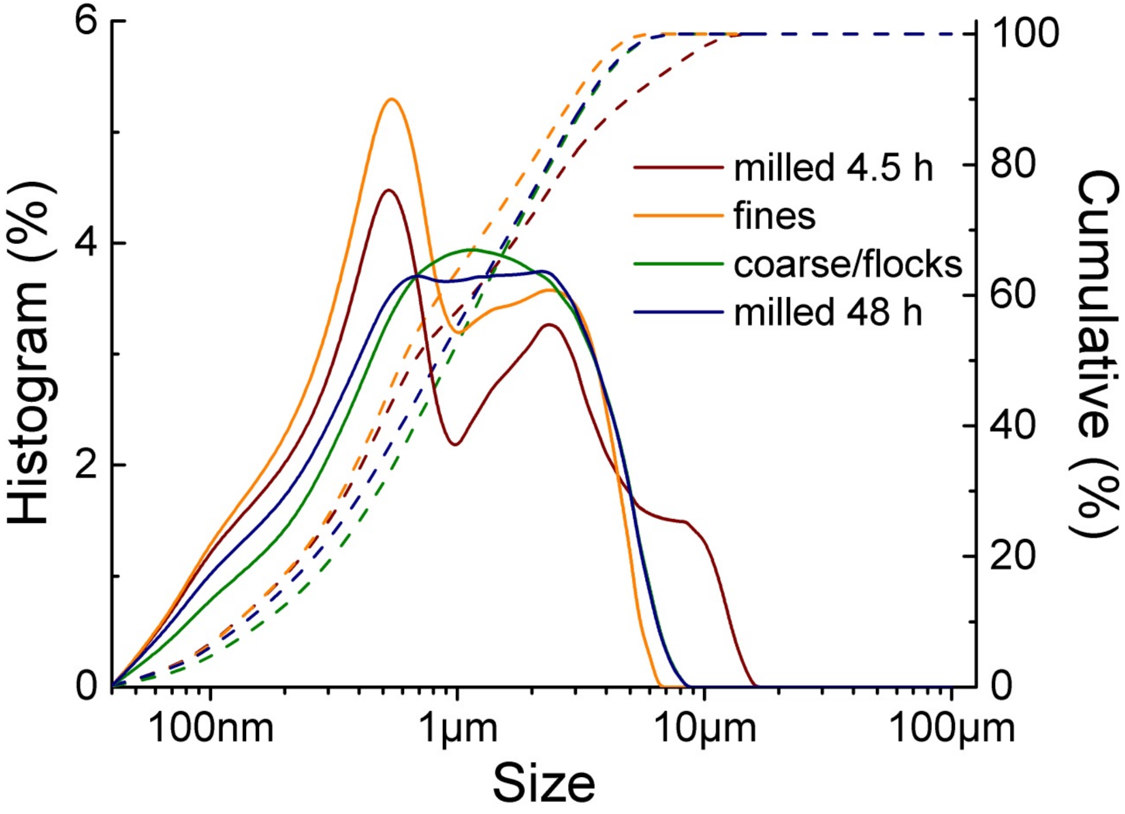
all nominally 6428-LCSF with 5% A-site deficiency
various synthetic techniques and morphologies

- Significant variations observed – even in nominally identical powders
- Light scattering techniques are system and technique limited for small particles
- USAXS allows for an accurate analysis of "primary particles" and in situ annealing
- SEM qualitatively verify variations in particle morphology
- Surface area is correlated parameter to performance

Controlling size distribution through separation

Vary morphology parameters of given LSCF source material using Stoke’s Law for sphere in viscous fluid used to segregate particles

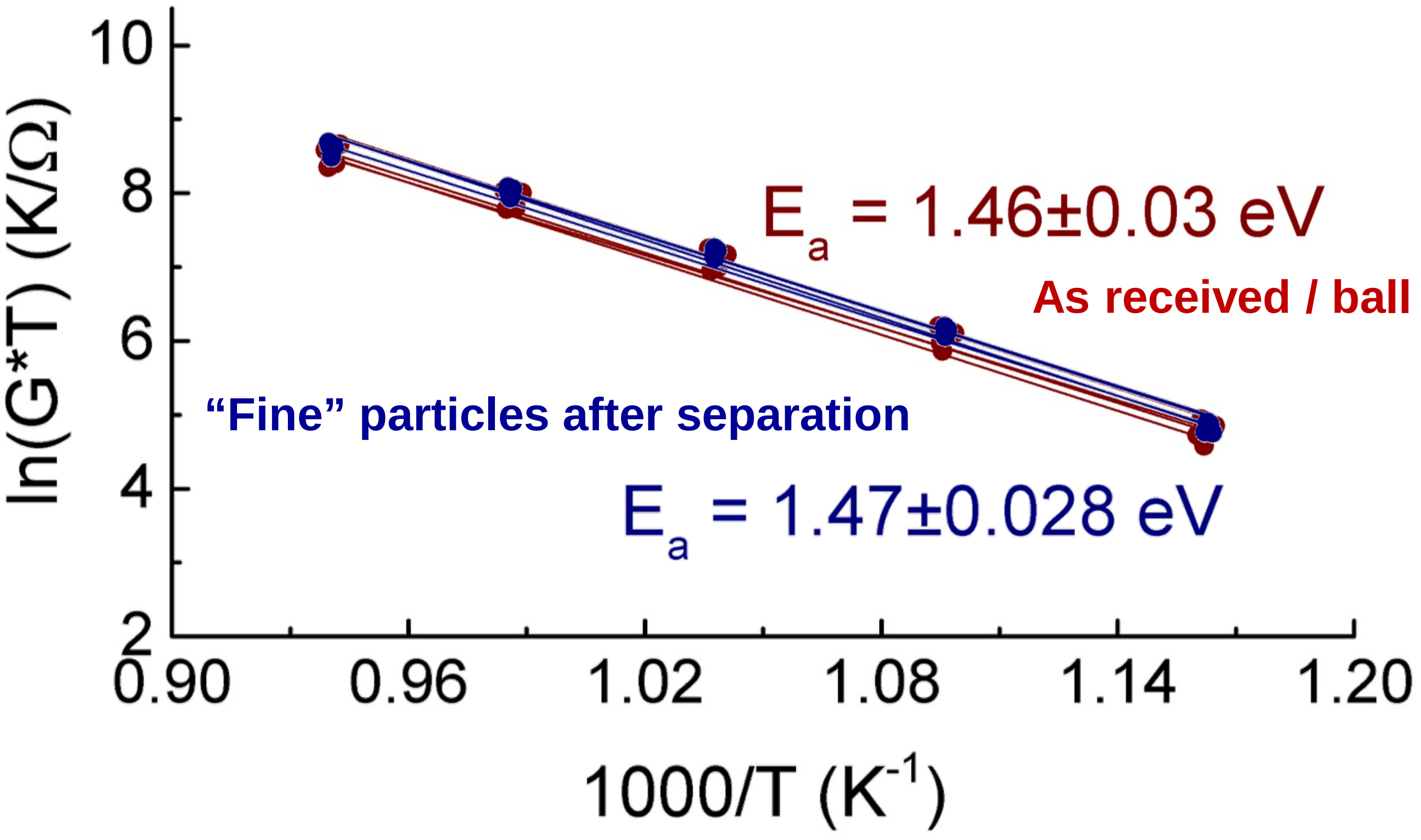
$$t = \frac{9 \cdot h \cdot \mu}{2 \cdot \Delta\rho \cdot r^2}$$



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

Results of separation study…

Observed polarization resistance variation after segregating particle size consistent with increase in surface area



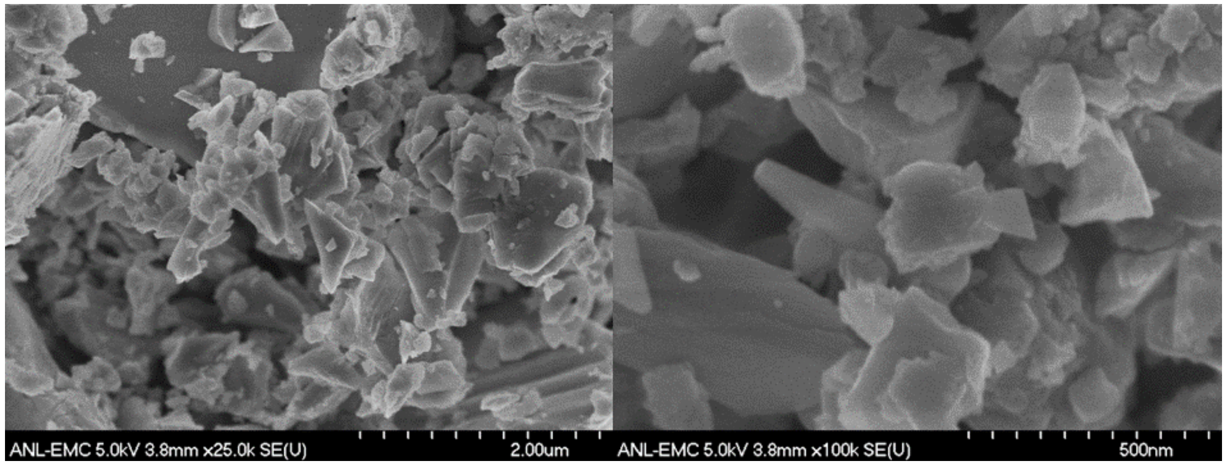
LINK CHEMISTRY TO PERFORMANCE RELIABILITY

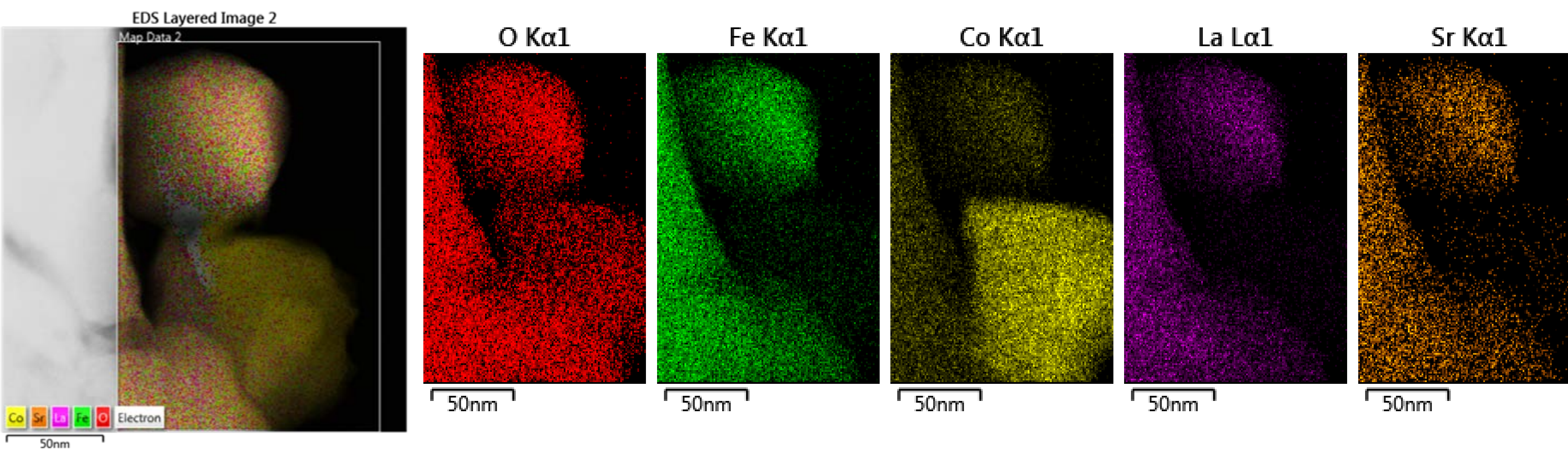
- Observed variations in stoichiometric distributions
- Secondary phase formation is consistent

- Final stoichiometric ratios are unknown

Distribution of Co-rich second phase

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

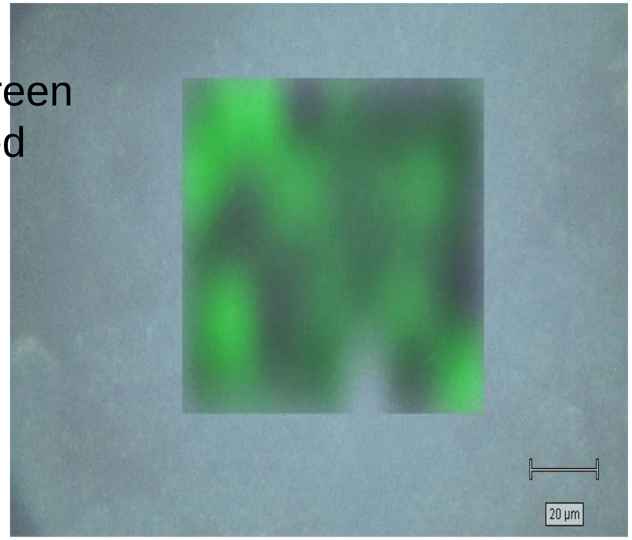


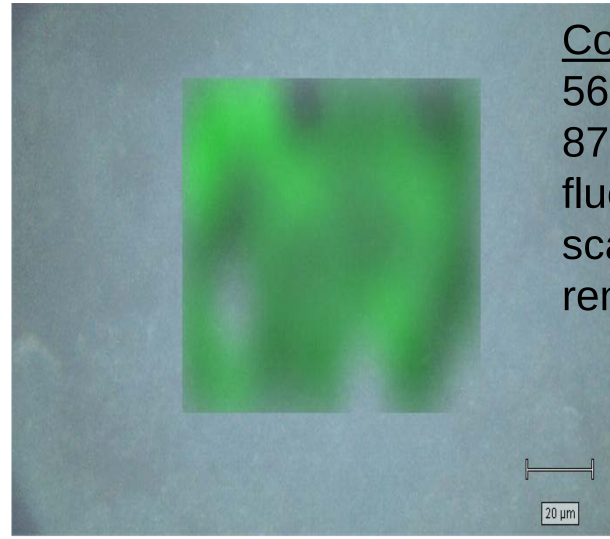


Raman spectra of separated coarse LSCF

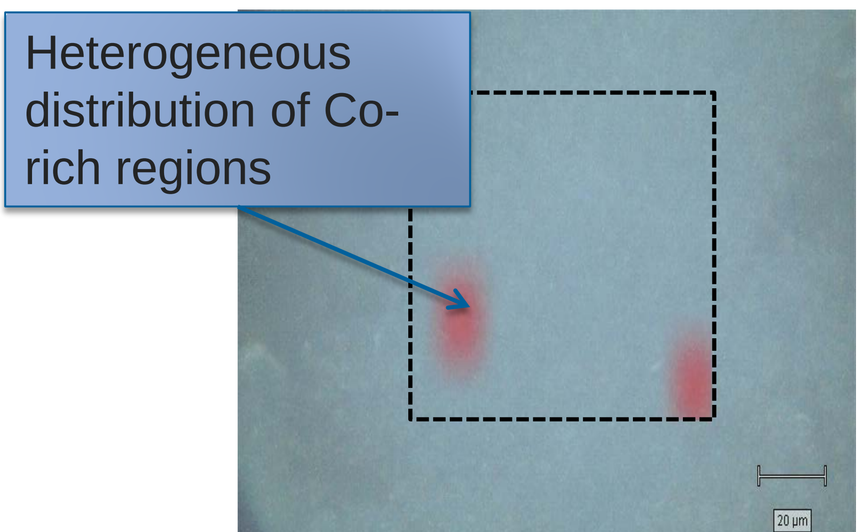
Strong fluorescence (878 cm^{-1}) isolated locations indicate localization of Co provides low cost diagnostic approach

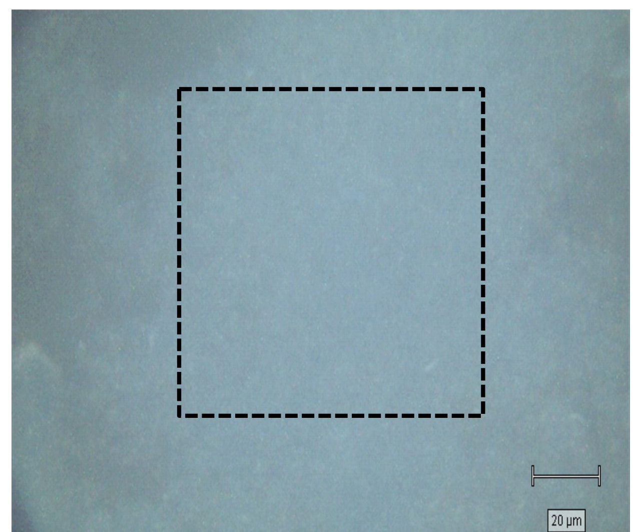
<u>Raw signal</u>
565 cm^{-1} green
878 cm^{-1} red





<u>Corrected data</u>
565 cm^{-1} green
878 cm^{-1} red (all fluorescent scattering removed)

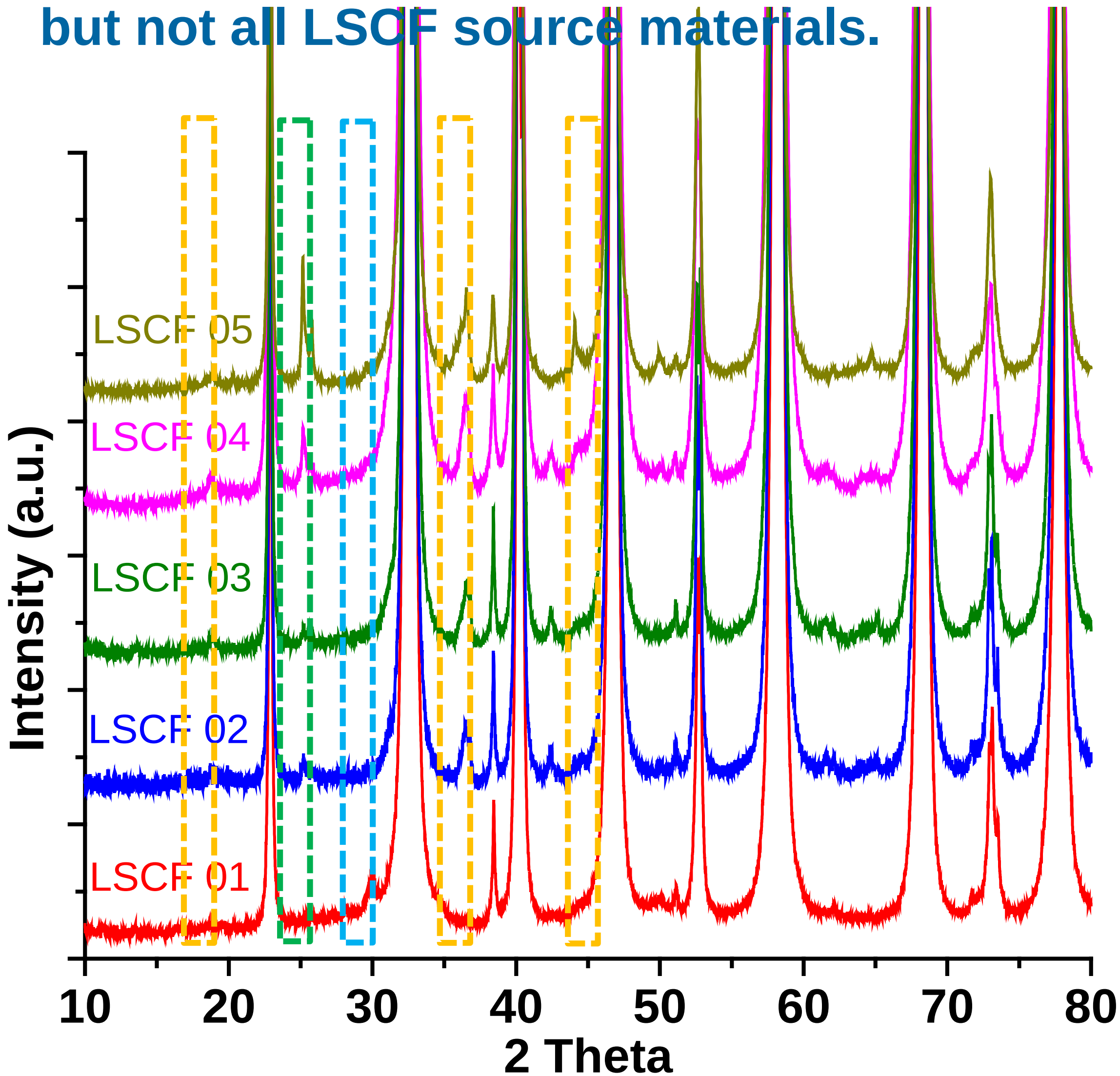




Argonne NATIONAL LABORATORY

Chemistry: Phase purity by HR-PXRD

HR-PXRD indicates evidence small second phase impurities in some, but not all LSCF source materials.



Second phase found

- $(Co,Fe)_3O_4$
- La_2O_3
- Sr_2CO_3

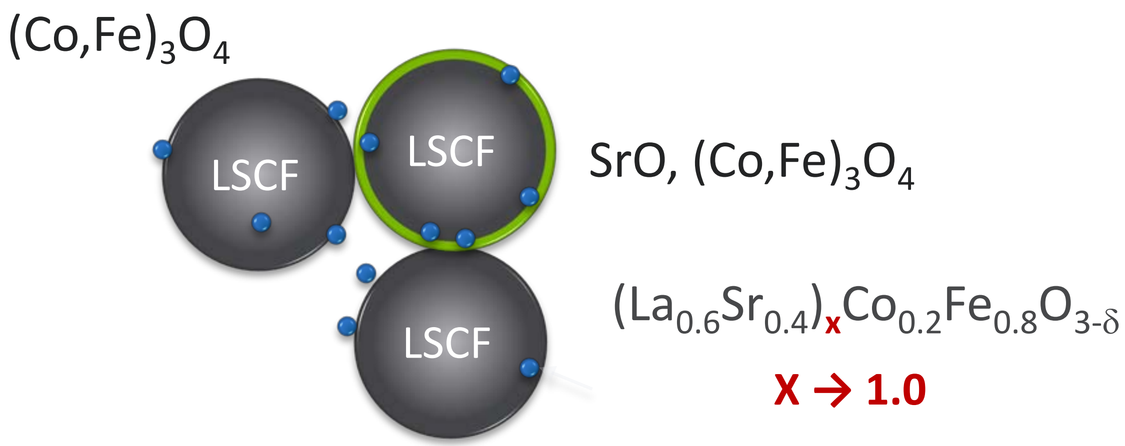
Relatively small amount of second phases are present

Dependent on LSCF source material

Argonne NATIONAL LABORATORY

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:

- BRIDGE KNOWLEDGE TO LONGER TIME SCALE VARIABILITY WITH MODELING
- USE 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

Thank you…

- We would like to thank the U.S. Department of Energy, Office of Fossil Energy, Solid Oxide Fuel Cell Program
- Joseph Stoffa, SOFC project manager

- Use of the Advanced Photon Source was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DEAC02-06CH11357
- Use of the Center for Nanoscale Materials, an Office of Science user facility, was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357

Argonne NATIONAL LABORATORY