EVALUATION OF CATHODE MATERIALS FOR SOFC PERFORMANCE RELIABILITY

BRIAN J INGRAM
LE (GAVIN) GE
ALBERT L. LIPSON
J. DAVID CARTER
VICTOR A. MARONI

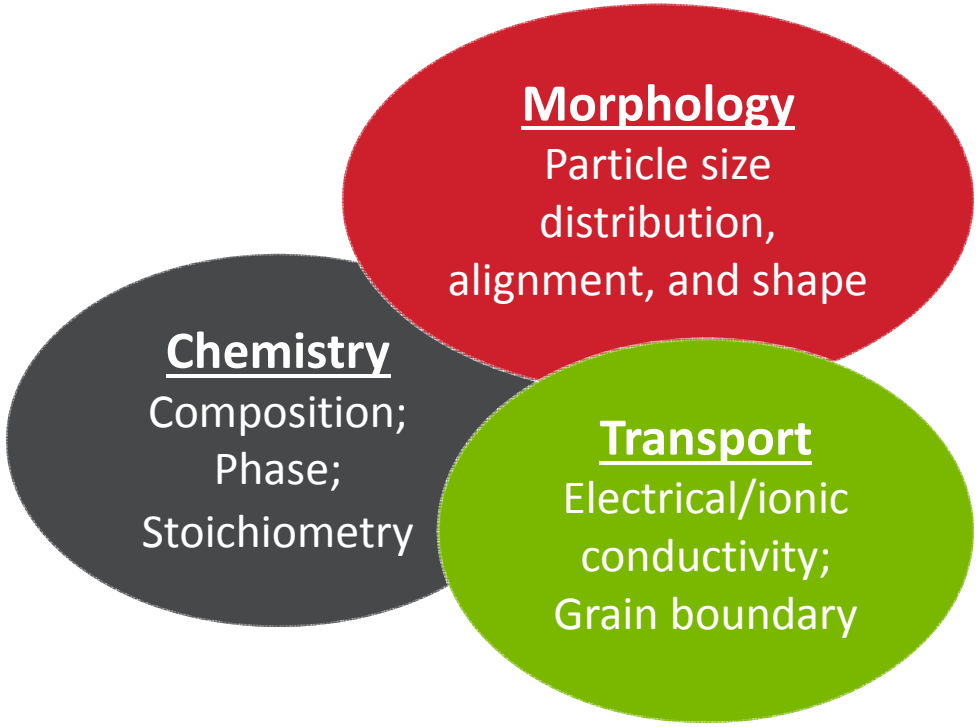
17th Annual Solid Oxide Fuel Cell (SOFC) Project Review Meeting
July 19-21, 2016

CONCLUSIONS/OUTLINE

- An electrochemical test protocol was established and used
  - Short term performance
  - Thermal dependance
- A baseline button cell performance was established allowing for direct statistical comparison from sample to sample
- Variability in feed stock materials is analyzed and shown to affect reliability of electrochemical performance
  - Morphology and chemical/phase composition

OVERVIEW OF EFFORTS: THREE PRONGED APPROACH

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



Feedstock cathode powder properties

↕

Cell Performance Reliability

FUNDAMENTAL STUDIES — RAPID DIAGNOSTIC ANALYSES

Effort will focus on short term electrochemical performance reliability

SOFC RESEARCH AT ARGONNE

Closely aligned with the Electrochemical Energy Storage Department

Applied Research
EERE, OE, DoD
Argonne Battery Dept (80)

Research Facilities
Materials Engineering Research Facility (MERF), Battery Post-Test Facility, Cell Fabrication Facility

JCESR
Joint Center for Energy Storage Research (120)

Basic Research
OS, BES
EFRC – CEES (60)
Universities
LDRD Funding

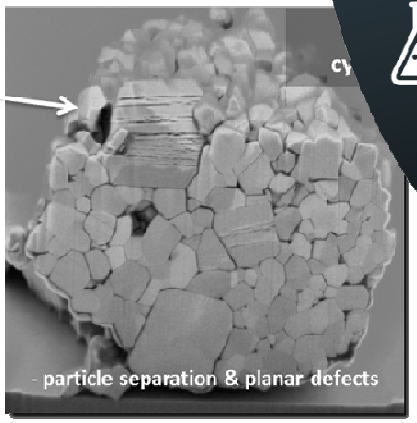
Contract Research
Industry

Argonne Transportation Center

Technology Transfer
IP Generation, Scale up

Materials & Manufacturing • Basic Science • Battery Architecture • Charge/Recharg

Argonne NATIONAL LABORATORY



Industry

TODA AMERICA
SUPERIOR GRAPHITE
Silatronix
BASF
MITEC
XG sciences
ARKEMA
SOLVAY
BoulderIonics
DUPONT
Wildcat Discovery Technologies
nHMs
IMRA
EM
Honeywell
SolRayo
ZEON
JSR Micro
INVENTEK
Argonne NATIONAL LABORATORY

EIGHT DISTINCT LSCF FEED STOCK POWDERS

Various synthetic approaches, materials providers, and lots

Sample#	Nominal Composition	Comment
LSCF-01	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	Standard (nominally identical)
LSCF-02		
LSCF-03		
LSCF-04		high surface area
LSCF-05		high surface area
LSCF-06		precursor
LSCF-07		Standard
LSCF-08		Standard

BASELINE AND ELECTROCHEMICAL PROTOCOL

Current Status:

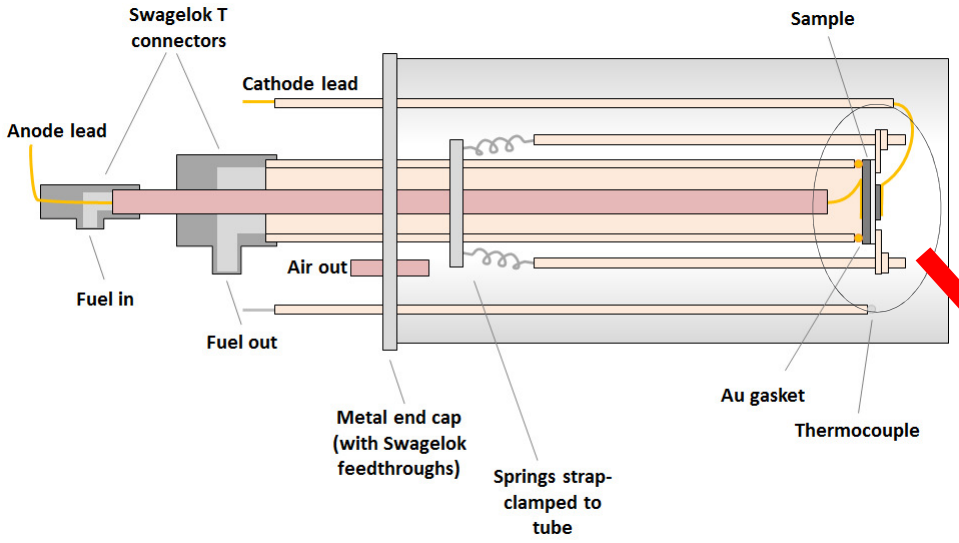
- Reliability tolerances are strict (< 1% performance variability threshold)
- Typical evaluation requires complex full cell fabrication and testing (direct performance comparison, but inefficient for materials verification)
- Long term degradation is a significant concern

Path Forward:

- Single phase porous electrodes (allows for efficient electrochemical testing)
- Measurement reliability must be maximized (understand limitations and baseline statistics in bench-scale analysis)
- Focus on short-term electrochemical performance and eventually map to long-term degradation in partnership with SOFC community

BASELINE AND ELECTROCHEMICAL PROTOCOL: HALF CELL DESIGN

Reduced variation and complexity based on single gas environment

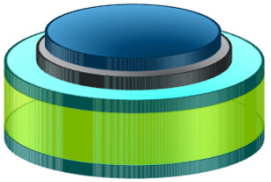


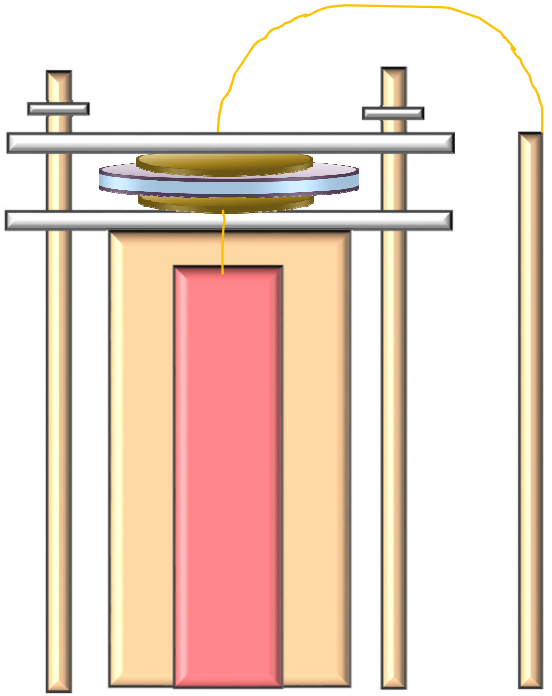
Print 5mm layers on 250µm YSZ

SDC, 1300°C

LSCF, 1100°C

Gold , 800°C



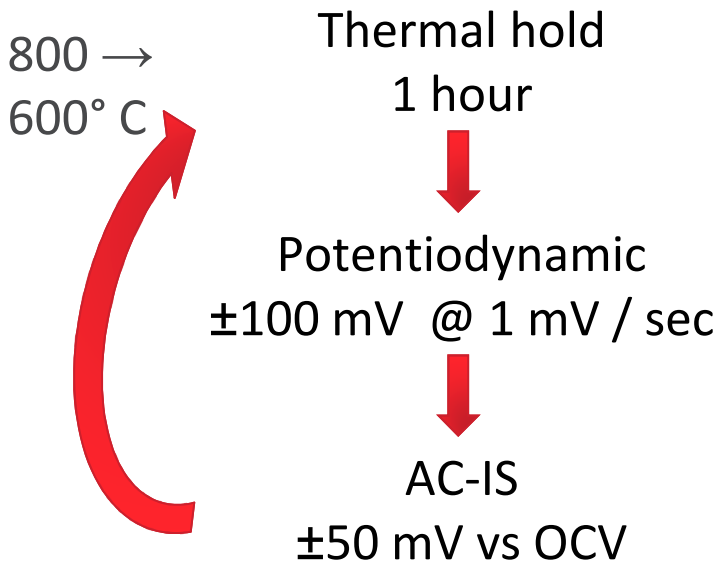


'Sandwich' structure to ensure confirm contact

Argonne NATIONAL LABORATORY

TESTING PROTOCOL

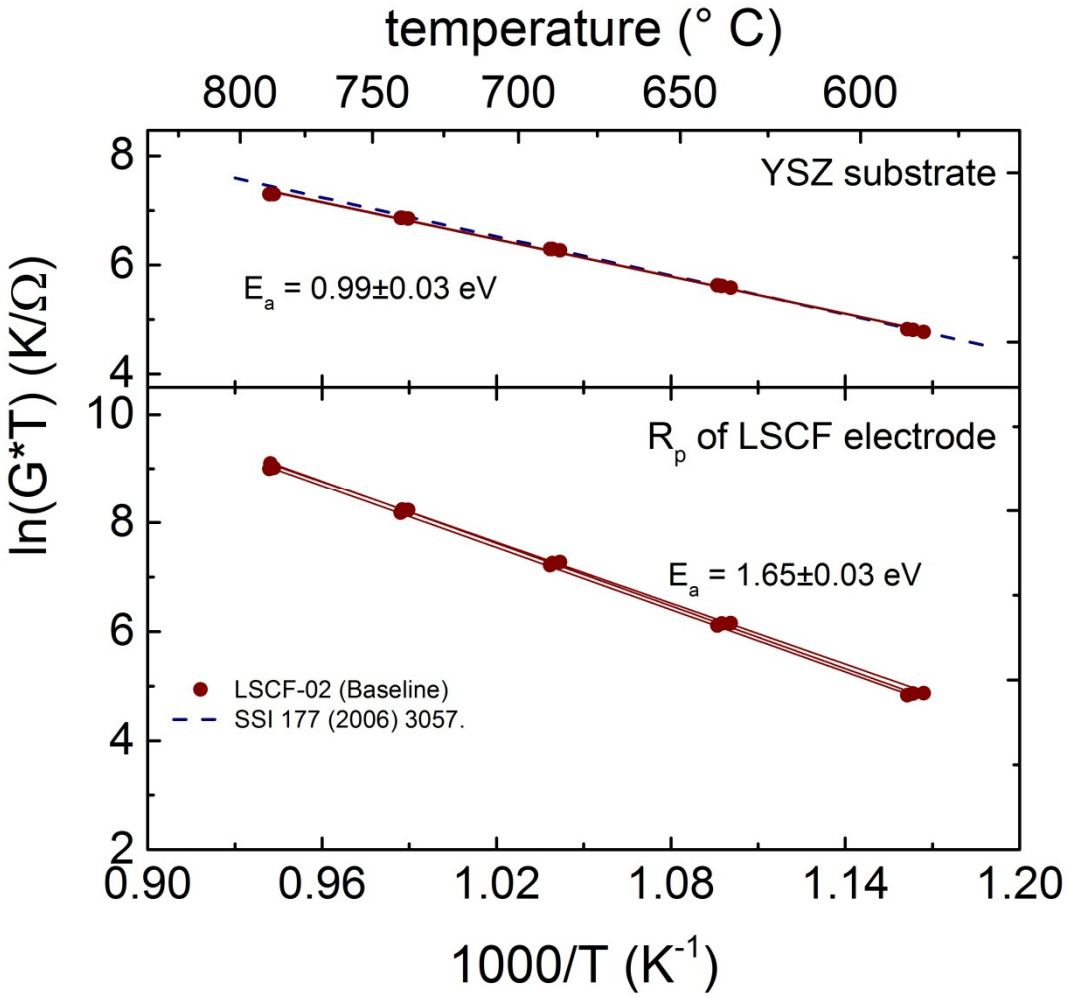
Focus on short term electrochemical performance



Thermal OCV hold for equilibration followed by dc and ac-is measurements

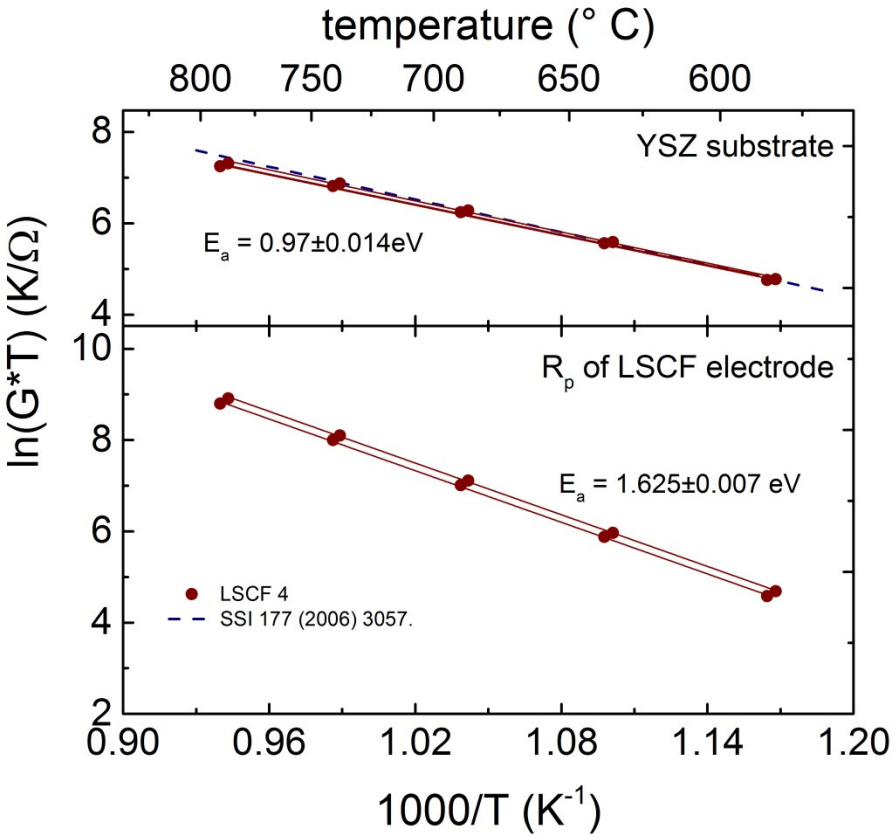
BASELINE PERFORMANCE: LSCF-02

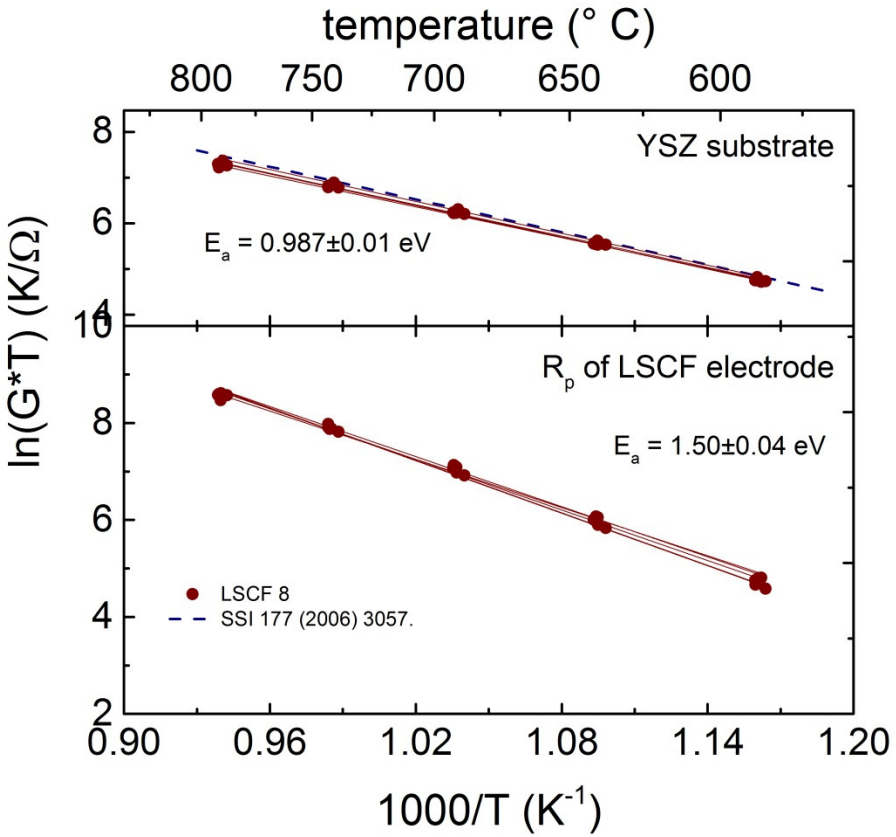
Statistical analysis based on repetitions provides baseline performance



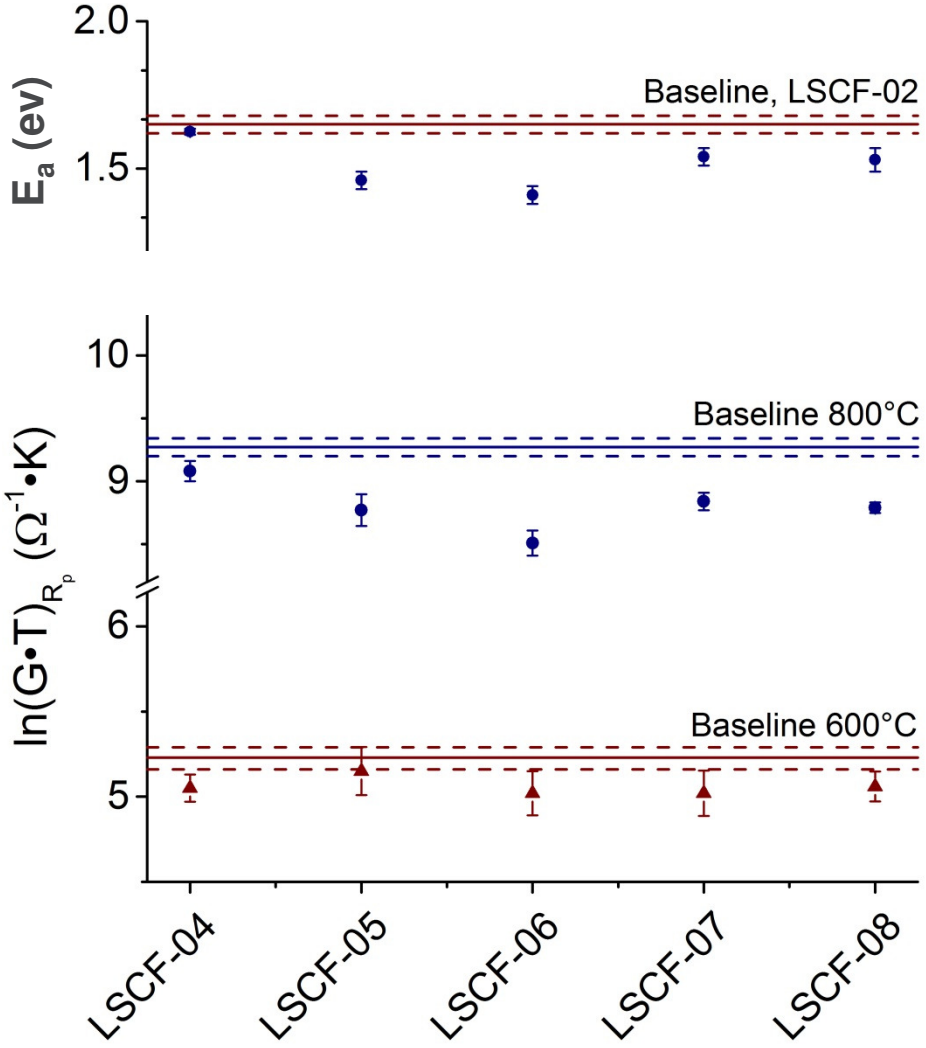
- Representative values derived from impedance measurements
- Sensitivity to electrode thickness and alignment can be resolved
- Typically < 2-3% variation observed in polarization conductance
- Very small variation in thermal activation energy

ANALYSIS OF LSCF SPECIMENS





SIGNIFICANT VARIATION FROM BASELINE



FEEDSTOCK POWDER CHARACTERIZATION: MORPHOLOGY

Current Status:

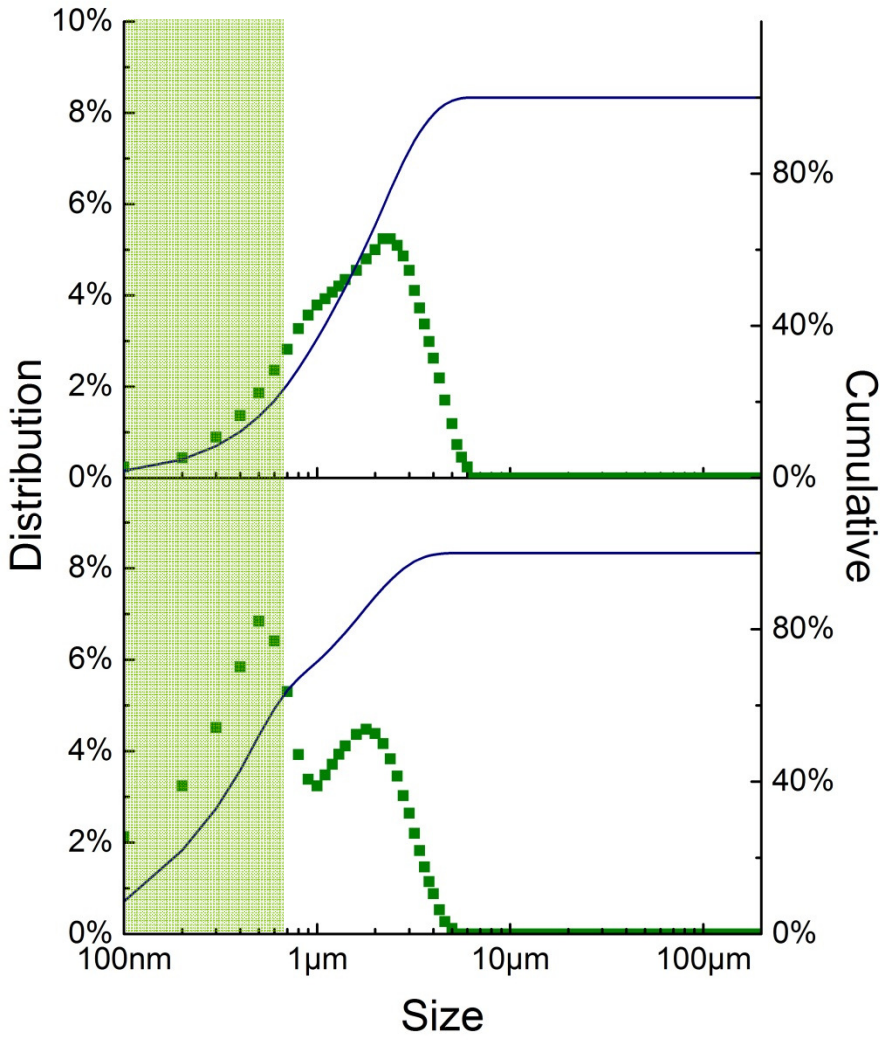
- SOFC materials vendors taking various routes for cathode powder synthesis (e.g., solid state vs wet chemical)
- Cathode powders have fairly wide distributions of particle sizes (ranging from 10 nm to 10 μm)
- No precise control of particle size as compared to Lithium battery materials (technology gap to fill in)

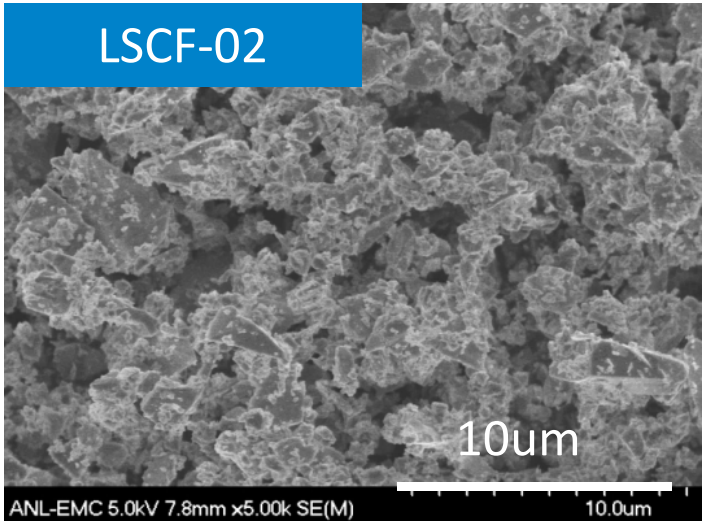
Path Forward:

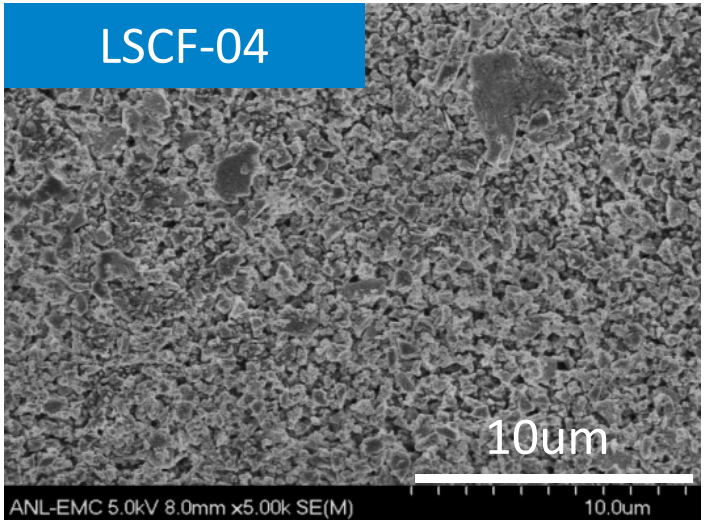
- Choosing appropriate technique is critical for measuring particles size (laser diffraction vs dynamic light scattering)
- Understand morphology evolution with sintering. Final morphology of electrode (focused ion beam SEM, ultra-small angle x-ray scattering)
- Correlating cell electrochemical performance with PSA (better particle size control may be needed)

MORPHOLOGY: PARTICLE SIZE & DISTRIBUTION

Light scattering probes agglomerated particles



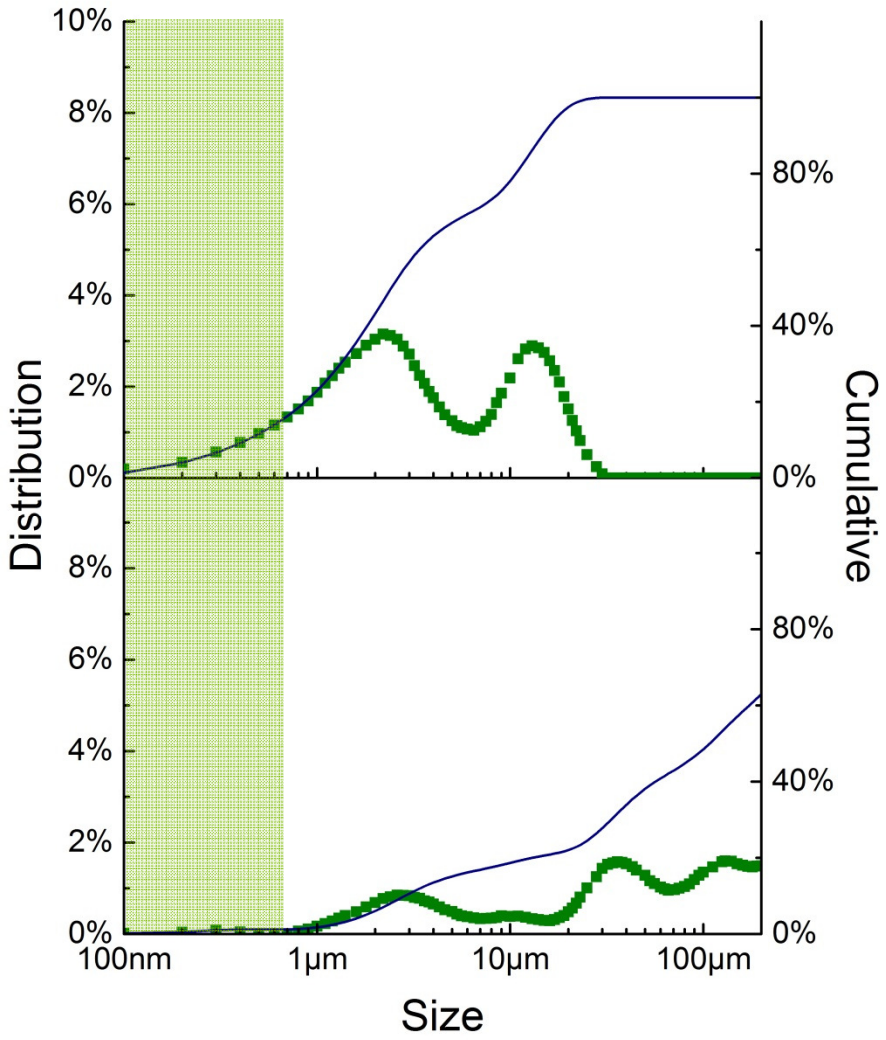


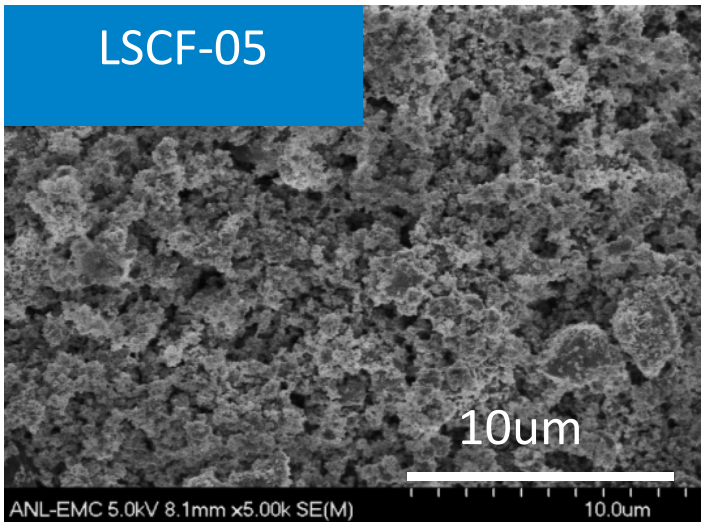


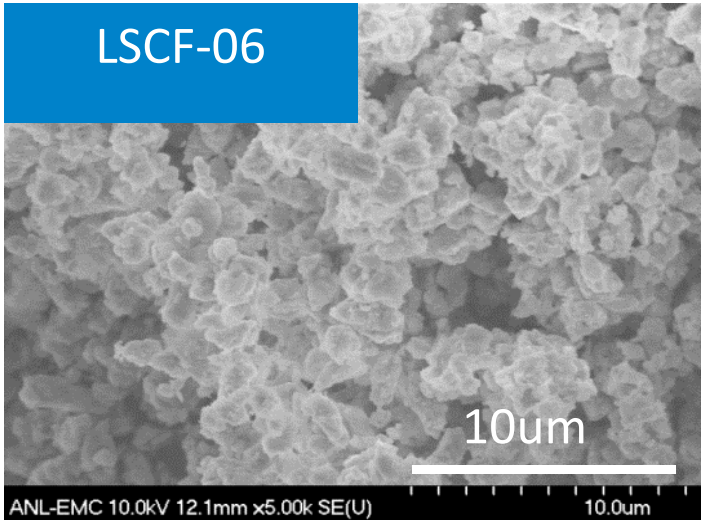
Argonne NATIONAL LABORATORY

MORPHOLOGY: PARTICLE SIZE & DISTRIBUTION

Light scattering probes agglomerated particles



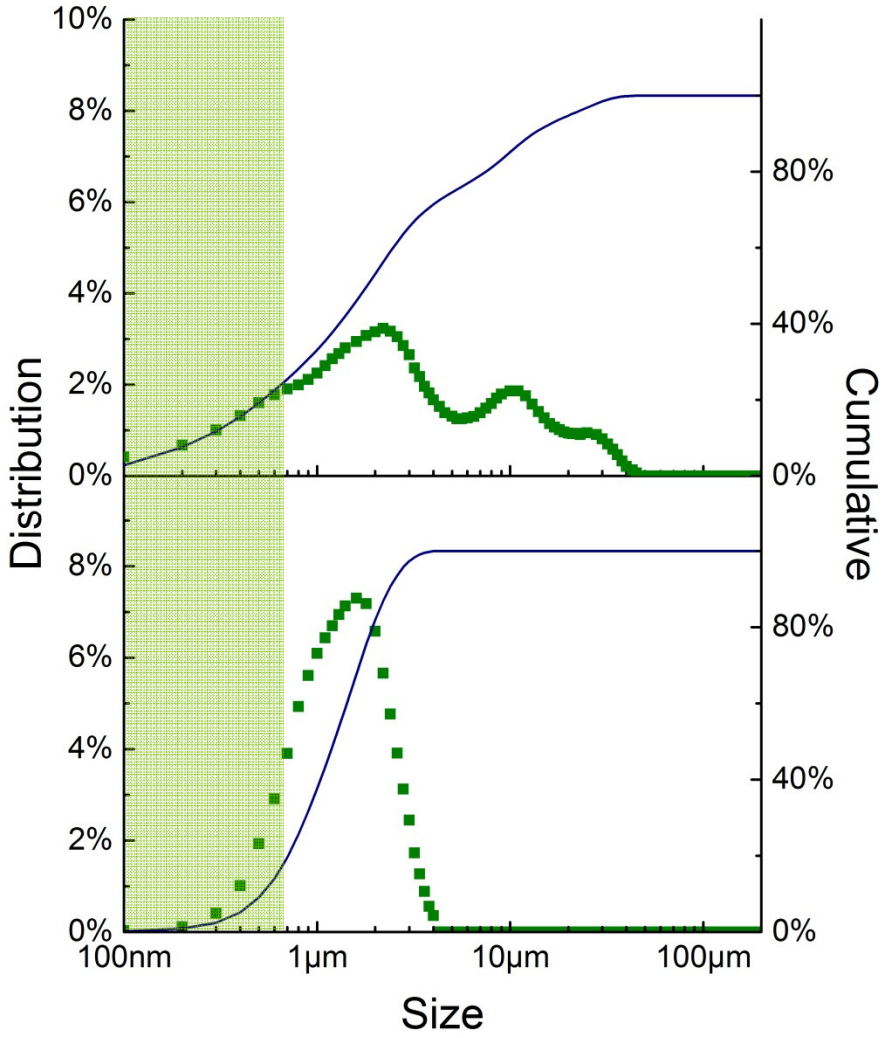


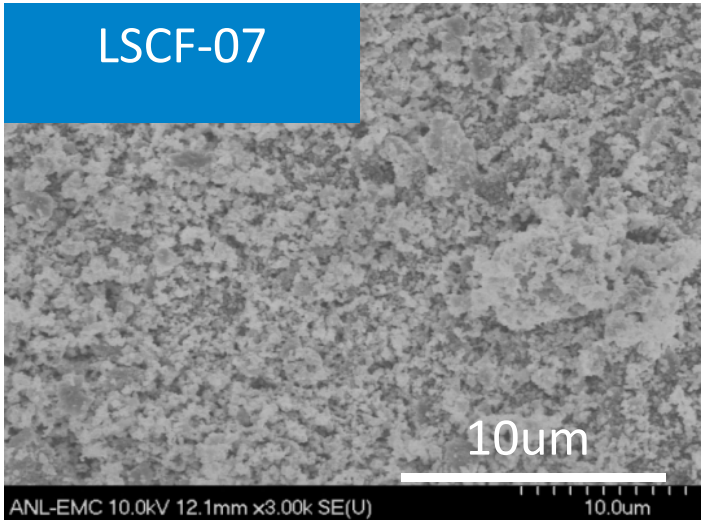


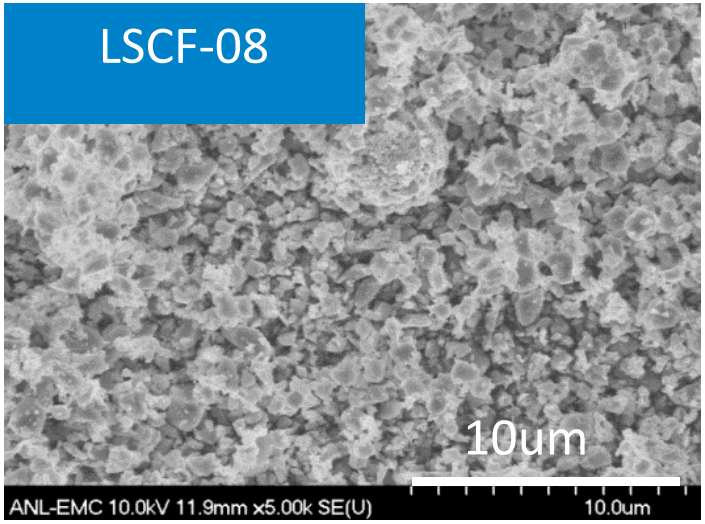
Argonne NATIONAL LABORATORY

MORPHOLOGY: PARTICLE SIZE & DISTRIBUTION

Light scattering probes agglomerated particles

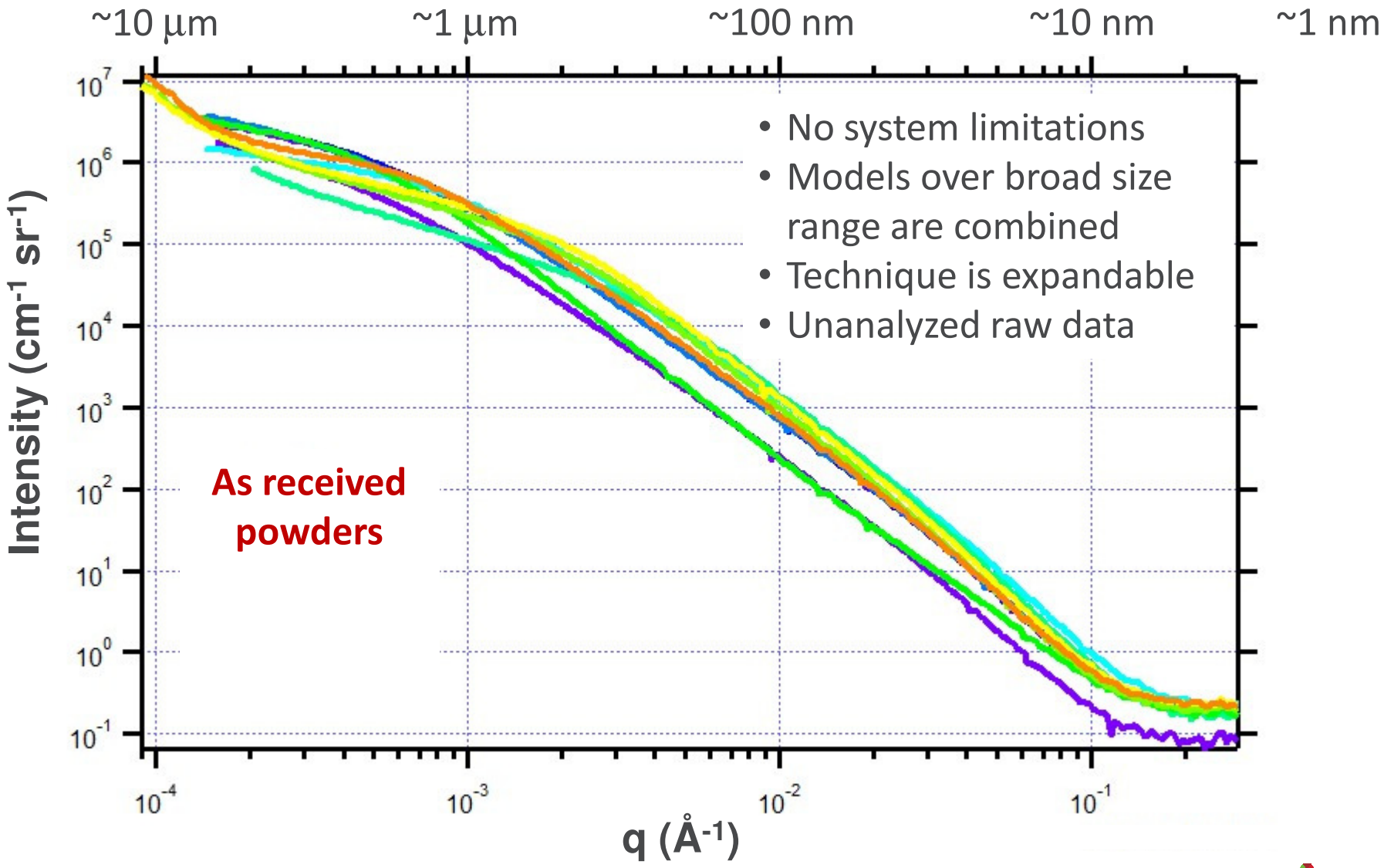






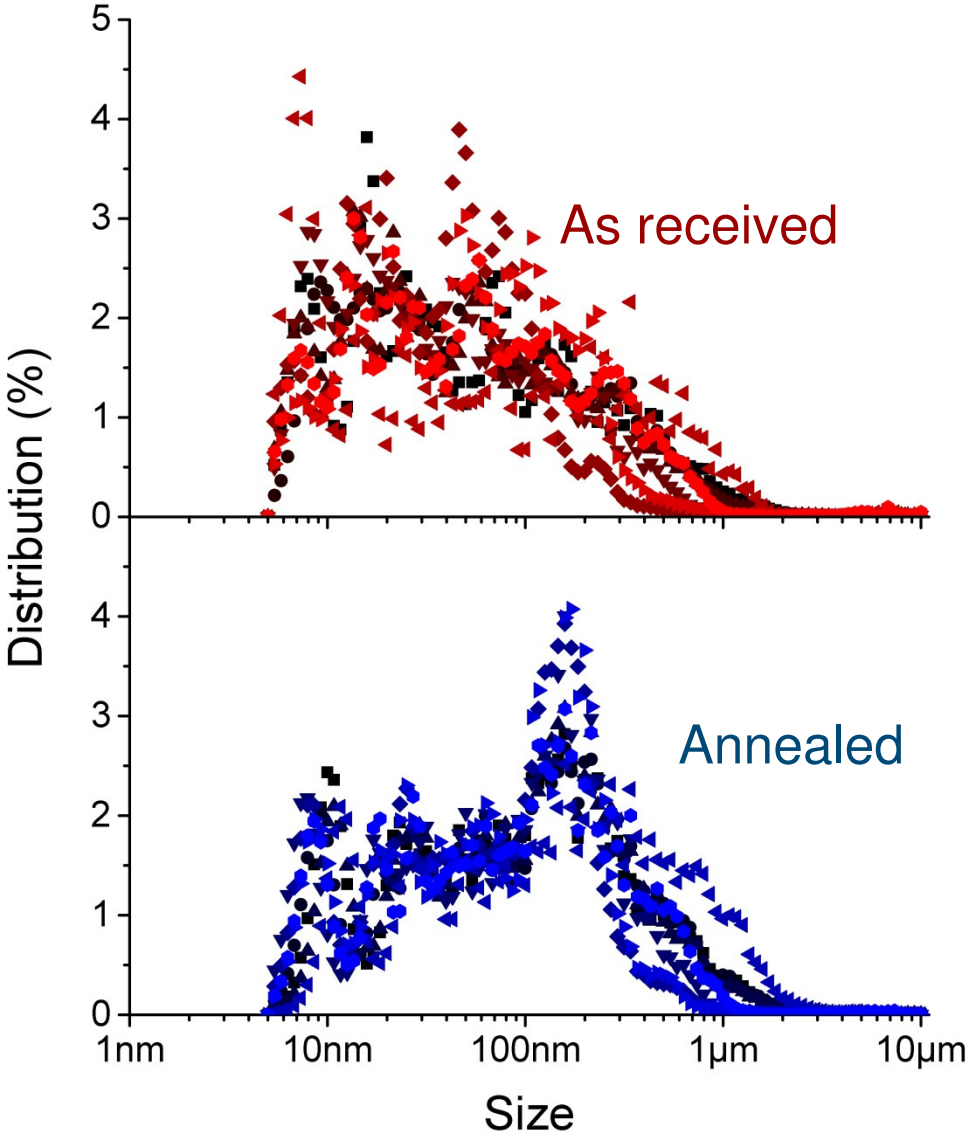
Argonne NATIONAL LABORATORY

MORPHOLOGY: (ULTRA-)SMALL ANGLE X-RAY SCATTERING (U)SAXS



Argonne NATIONAL LABORATORY

USAXS PROBES PRIMARY PARTICLE SIZES

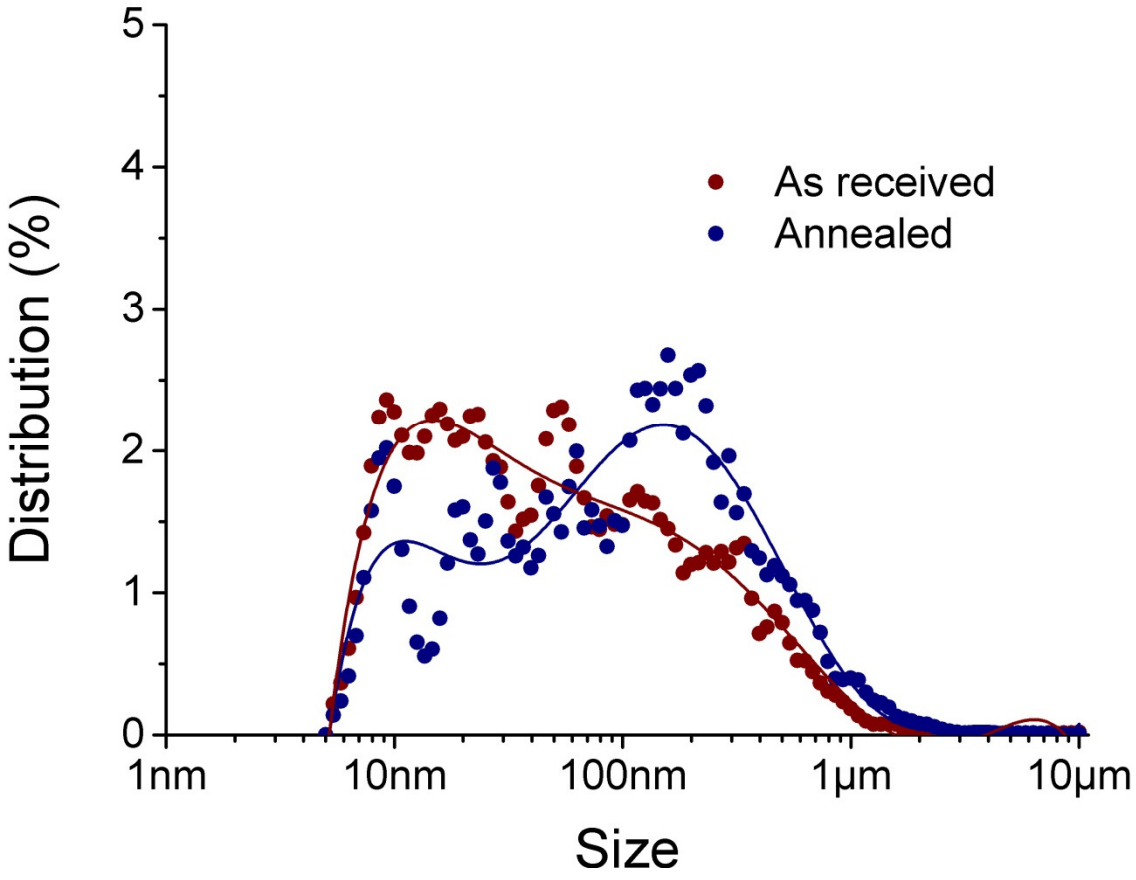


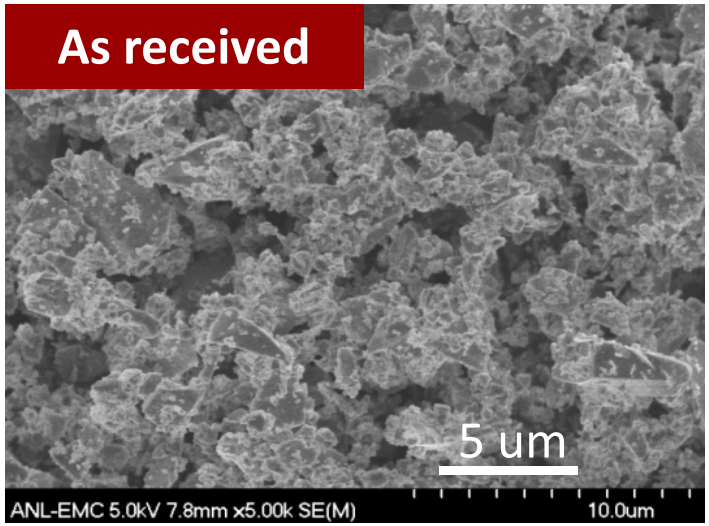
- Comparison of 8 LSCF feed stock powders
- Electrodes annealed to 1000℃ on MgO substrate
- Significant variation are observed even after sintering in size of particles

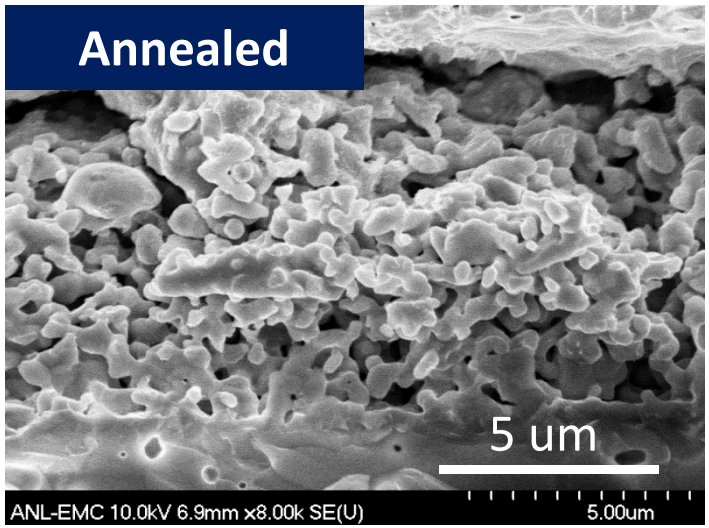
Argonne NATIONAL LABORATORY

USAXS PROBES PRIMARY PARTICLE SIZES

Monitoring in situ sintering



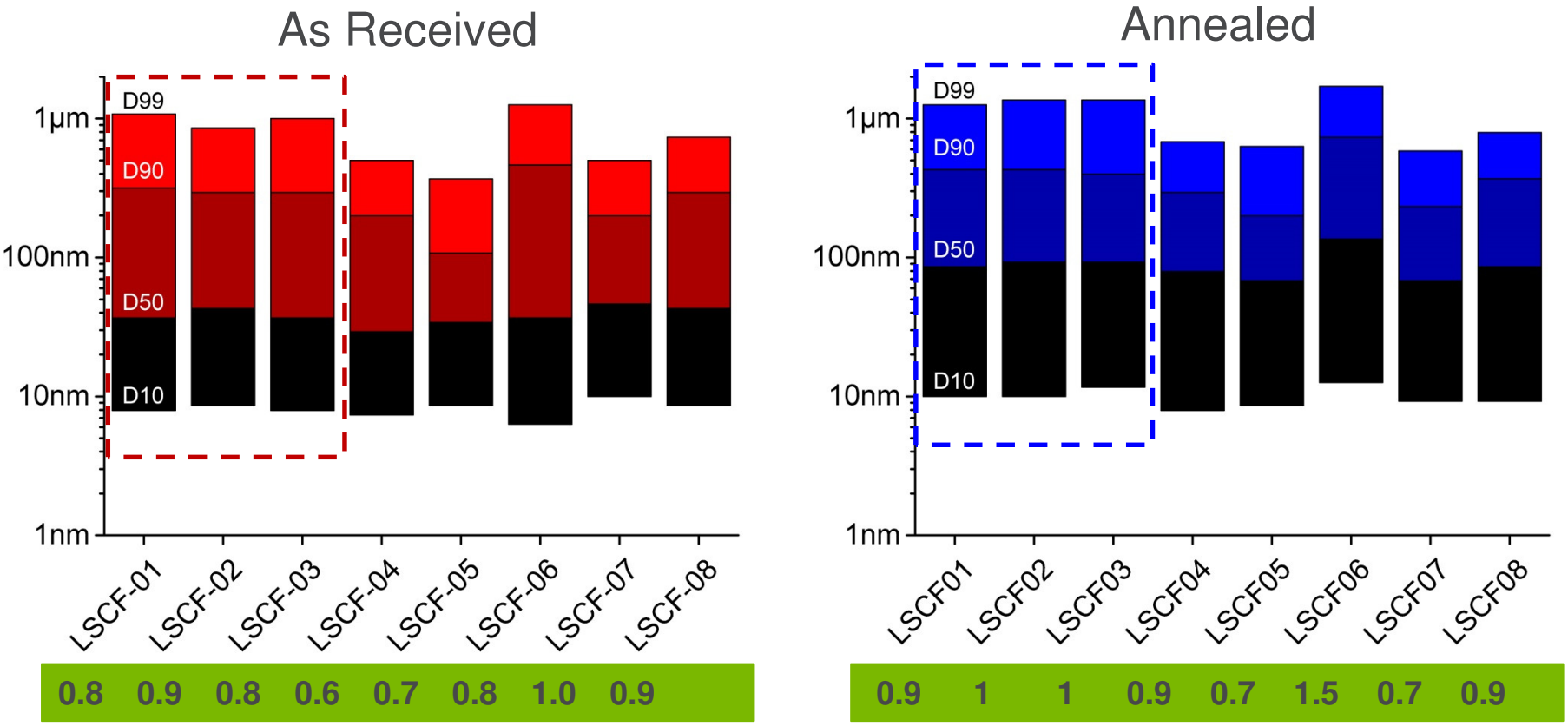




Argonne NATIONAL LABORATORY

PRIMARY PARTICLE SIZE COMPARISON

Growth is evident and variation with synthetic approach



MORPHOLOGY: PARTICLE SIZE & DISTRIBUTION

- Significant variations observed – even in nominally identical powders
- Light scattering techniques are system and technique limited for small particles
  - Inconsistent results are obtained
  - Probes agglomerated particle sizes
- SEM does verify variations in particle morphology
- USAXS allows for an accurate analysis of “primary particles” and in situ annealing

FEEDSTOCK POWDER CHARACTERIZATION: CHEMISTRY

Current Status:

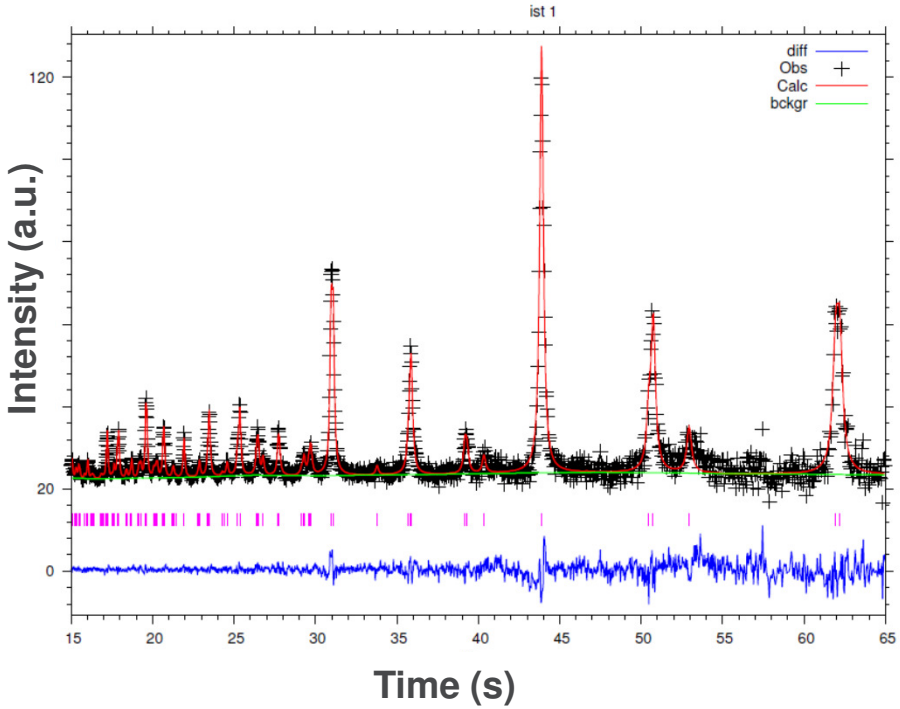
- Perovskite oxygen stoichiometry is highly varying (extremely difficult to measure and control oxygen content)
- Nominal phase pure stoichiometric compositions identical (5% A-site deficient 6428LSCF)
- Limited precision of phase analysis with bench top XRD (< 2-3% second phase detection)

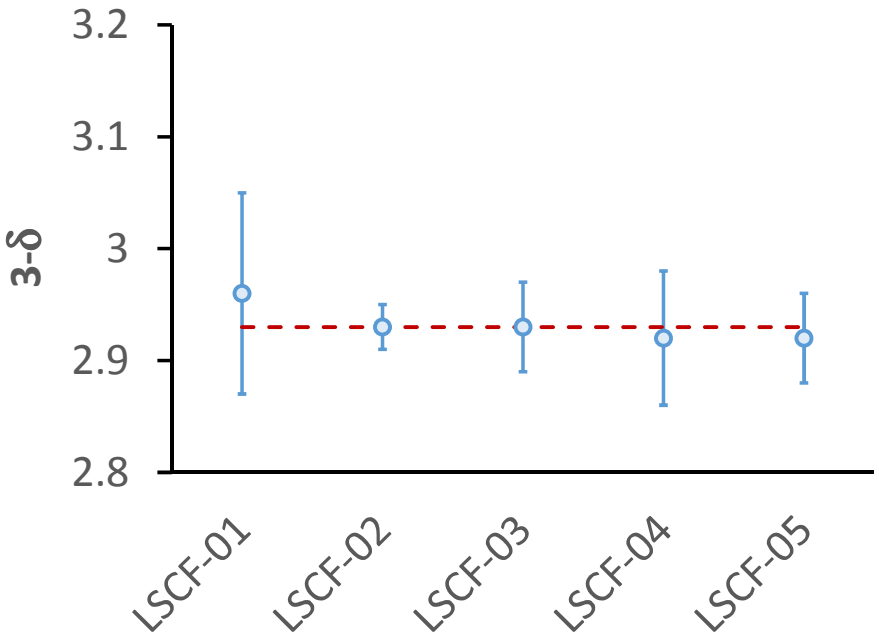
Path Forward:

- Oxygen stoichiometry can be verified by neutron diffraction (non-routine approach)
- Verify phase purity by Raman as routine approach (high resolution XRD key to verification)
- Phase composition evolution is critical to cathode reliability

CHEMISTRY: OXYGEN STOICHIOMETRY BY NEUTRON DIFFRACTION

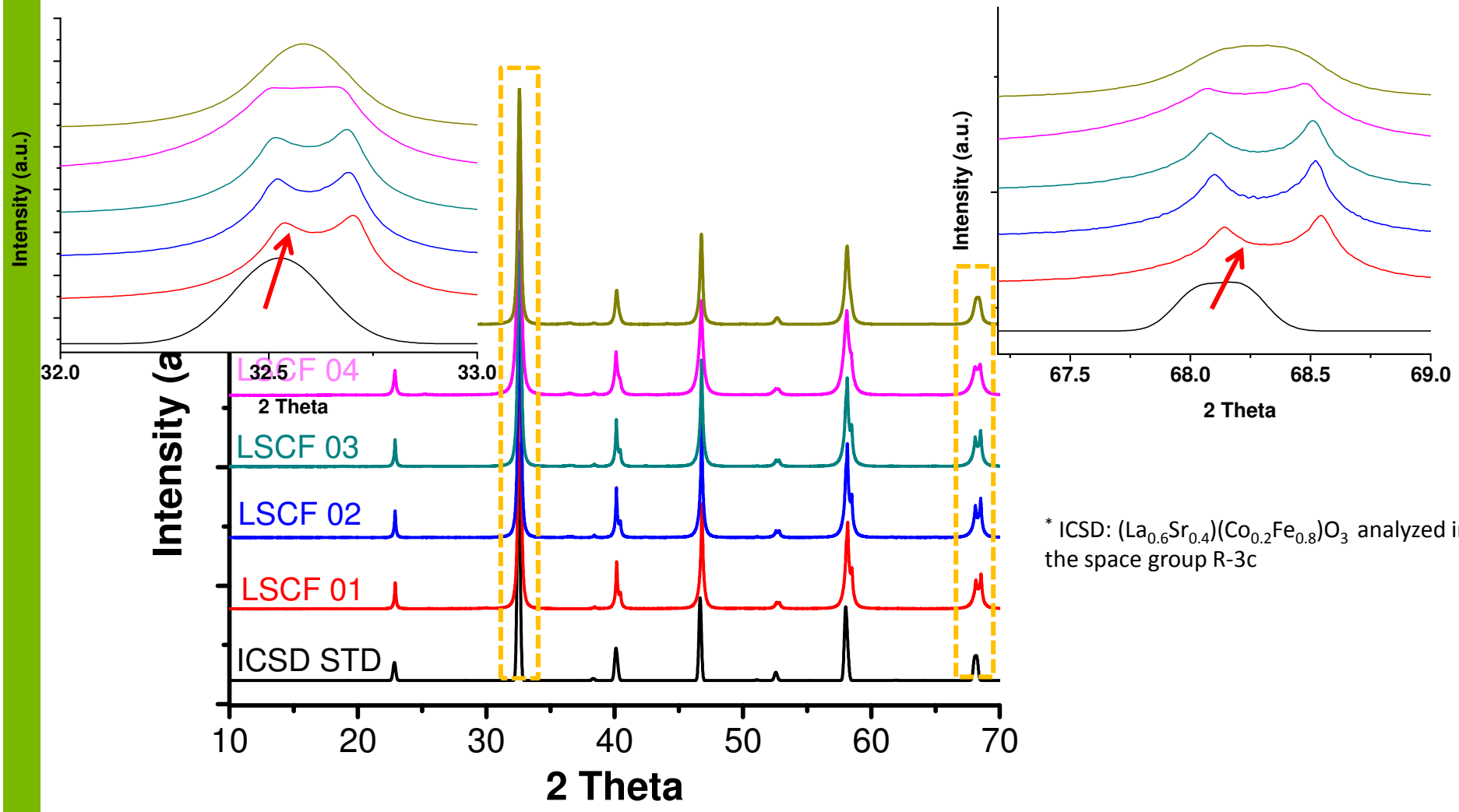
No statistical variation in oxygen stoichiometry is observed





CHEMISTRY: STRUCTURAL CHARACTERIZATION

HR-PXRD indicates strong tetragonal distortion in some powders



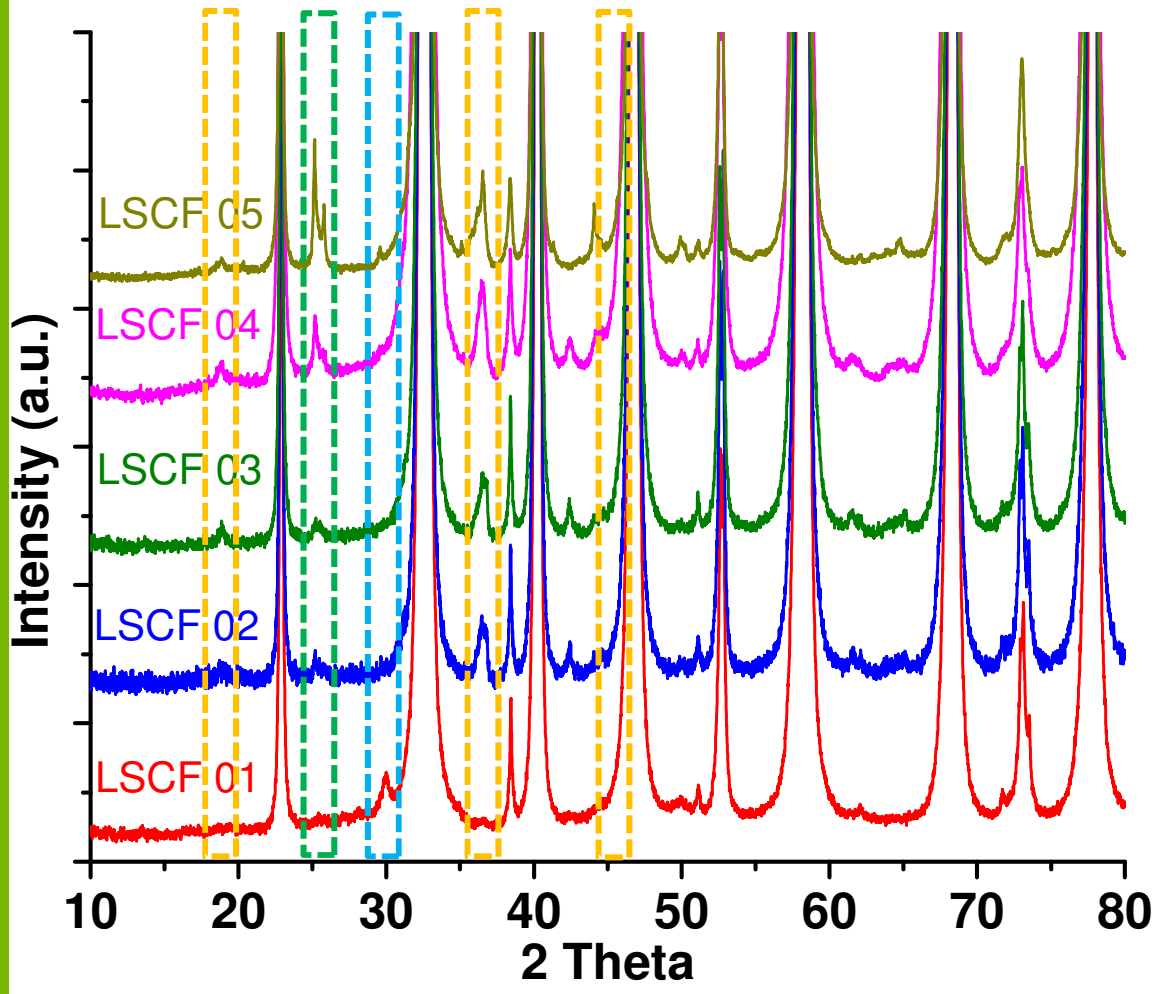
Evidence of tetragonal distortion

* ICSD: $(La_{0.6}Sr_{0.4})(Co_{0.2}Fe_{0.8})O_3$ analyzed in the space group R-3c

Argonne NATIONAL LABORATORY

CHEMISTRY: PHASE PURITY BY HR-PXRD

HR-PXRD indicates evidence small second phase impurities



Second phase found

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

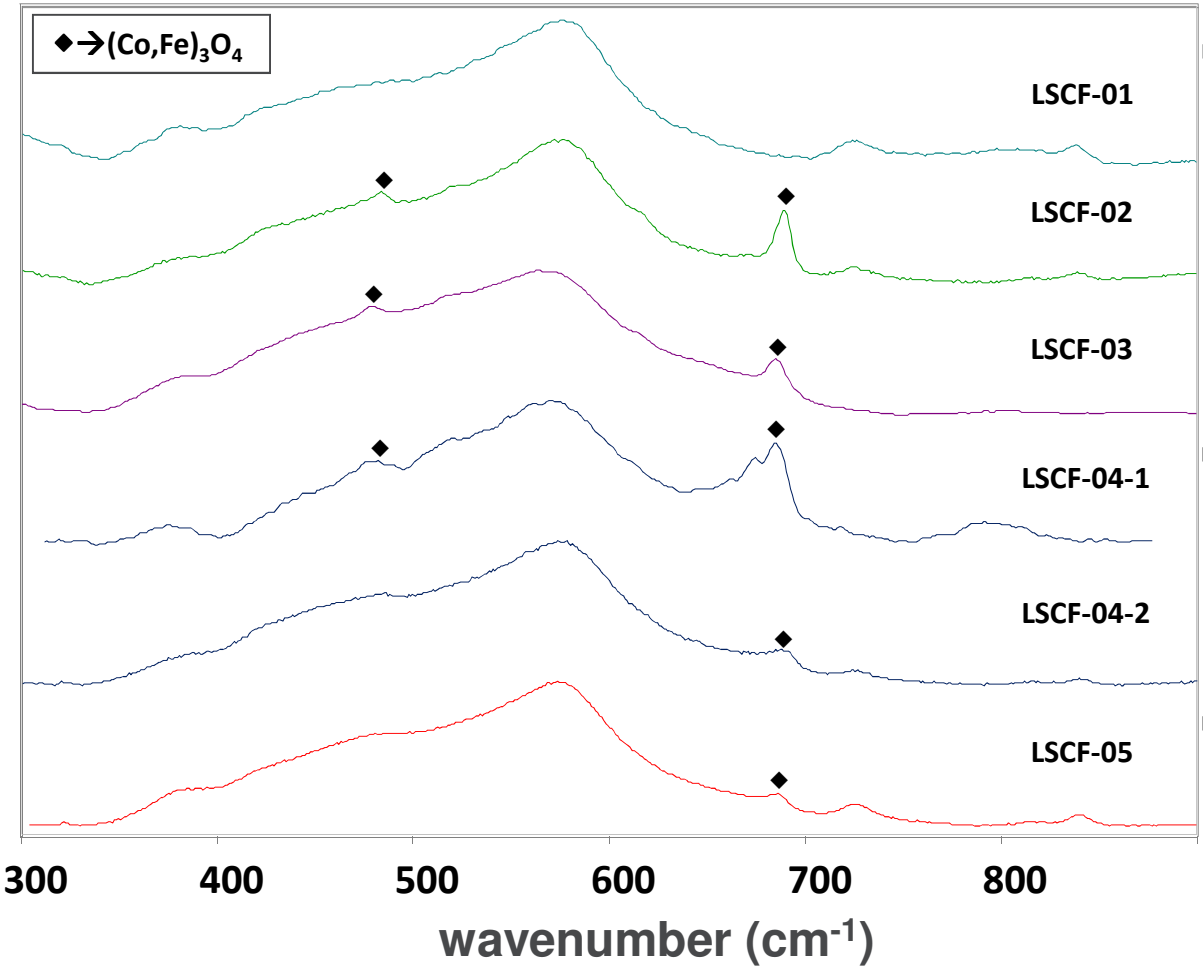
Relatively small amount of second phases are present

Requires high resolution powder x-ray diffraction from synchrotron source to quantify

Argonne NATIONAL LABORATORY

CHEMISTRY: PHASE PURITY BY RAMAN SPECTROSCOPY

A low cost analysis tool verifying evidence of Co,Fe-O spinel

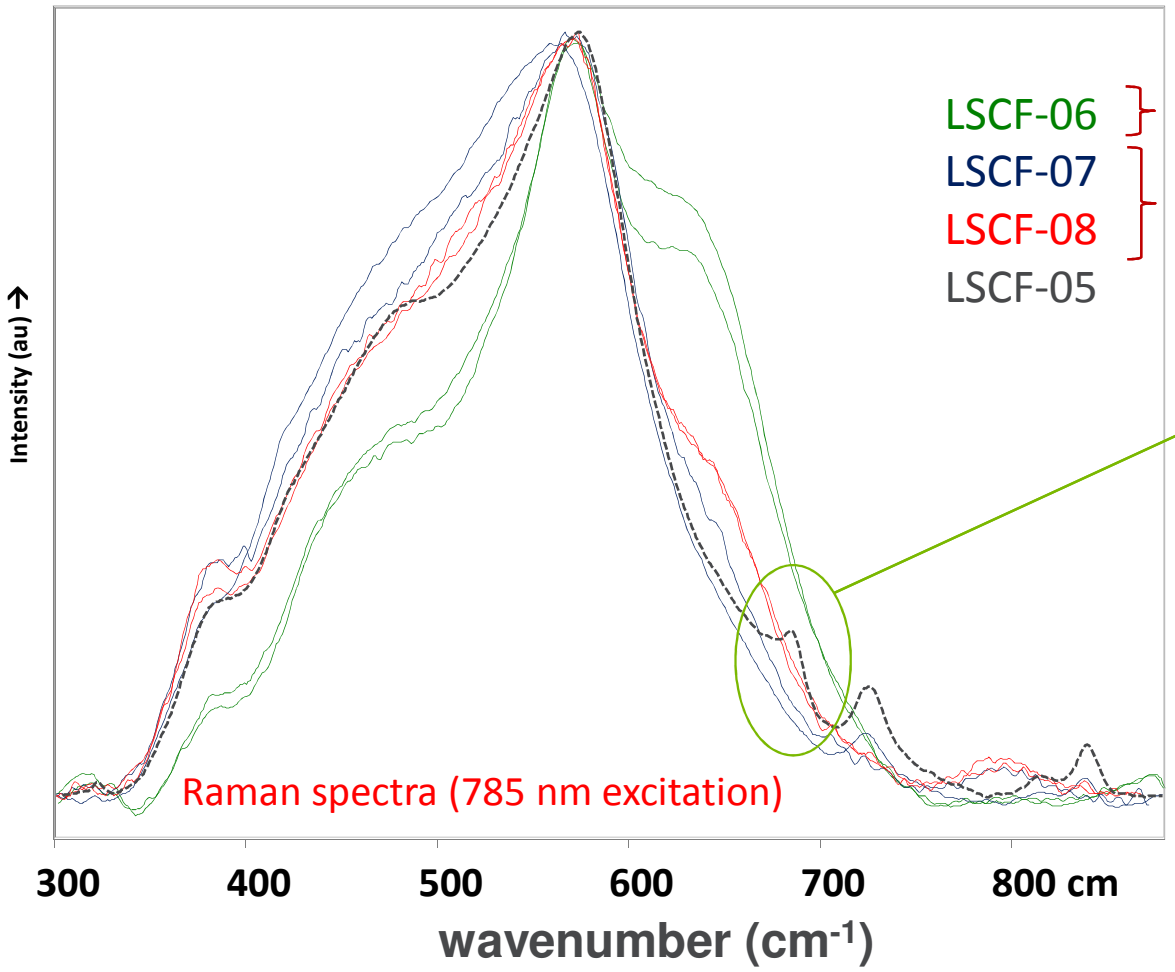


- The broad signal 300-700 cm^{-1} from metal-oxygen vibrations of nearly cubic ABO_3…Symmetry reduction caused by the $AA'BB'O_3$ character
- Small amount of $(Co,Fe)_3O_4$ observed due to symmetry change and high polarization scattering
- Heterogeneous distribution of $(Co,Fe)_3O_4$ second phase

Raman could be used as rapid diagnostic tool for second phase analysis

Argonne NATIONAL LABORATORY

CHEMISTRY: RAMAN SPECTROSCOPY

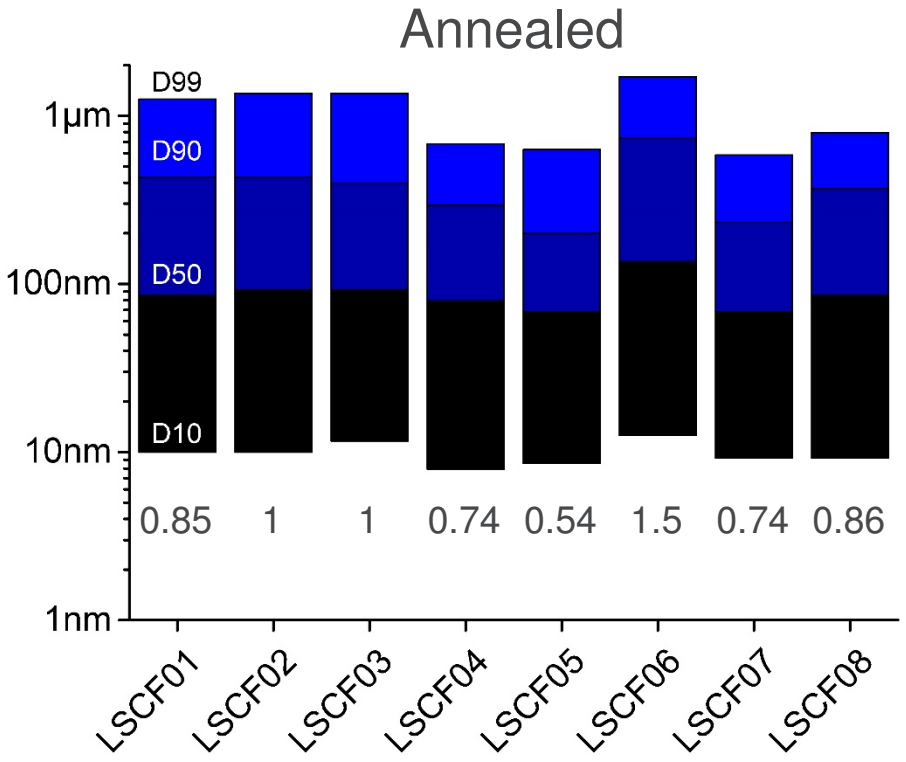


Raman scattering signal from precursor

No second phase apparent

$(Co,Fe)_3O_4$

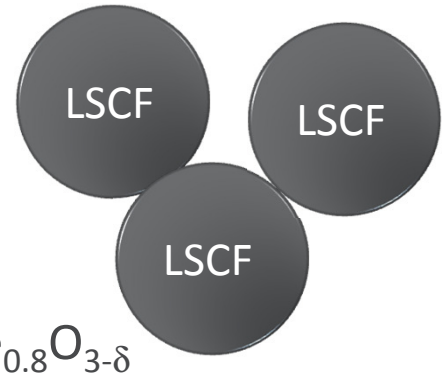
CONCLUSION AND OVERVIEW
CHARACTERIZATION REVIEW



Morphology variation is still unclear, especially post-sintering. More studies are required…

Observed variation in second phase formation

LSCF-06
LSCF-07
LSCF-08



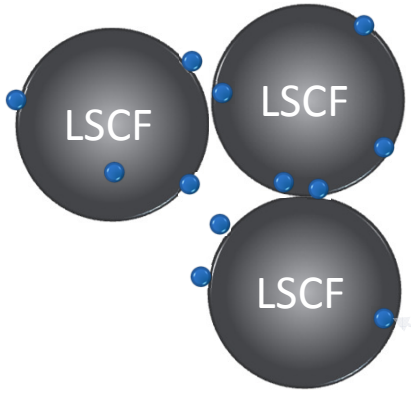
X → 0.95

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

VS.

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

X → 1.0



LSCF-02

$(Co,Fe)_3O_4$

THANK YOU…

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