Argonne NATIONAL LABORATORY

Evaluation of Feedstock Materials for SOFC Performance Reliability

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Conclusions/Outline

- Fundamental surface investigations can lead to understanding of real-word SOFC behavior
  - SOFC performance as defined by oxygen exchange rates is affected by both:
    - Gas phase environment
    - Solid-state surface composition affect the oxygen exchange rates

- Variability in feed stock materials is analyzed
  - Very good reproducibility in morphology and chemical composition
  - Phase analysis indicates some phase separation
  - "low cost" Raman analysis shown to be incredibly powerful

- A baseline button cell performance is being established
  - Statistical analysis required to provide meaningful analysis of feedstock materials

Argonne's background in SOFC technology

1980

- Technical support to DOE solid oxide fuel cells
- Cell/stack design planar monolithic SOFC (MSOFC)

1990

- Materials development:
  - Invented glass-ceramic seal (basis of current formulations)
  - Developed ceria-based low temperature SOFC (~500°C)
  - Invented powder metal interconnect 440 SS

2000

- Cell/stack design: TuffCell – metal supported SOFC
- High Temperature Steam Electrolysis (HTSE) anode and cathode materials

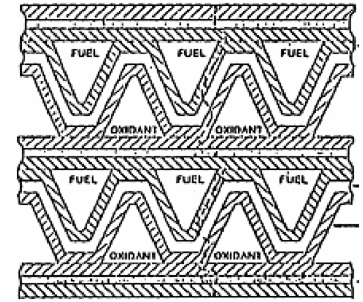
2010

- HTSE stack degradation analysis
- Cr-poisoning mechanism in SOFC cathode
- Investigation of oxygen transport kinetics
  - Developed technique to investigate environmental perturbations on oxygen reduction kinetics

2012-14

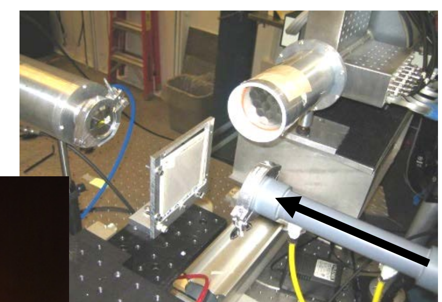
- Performance Reliability

MSOFC



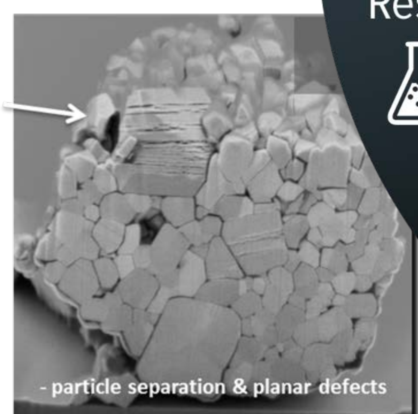
TuffCell

X-ray fluorescence/absorption



In situ APS experiments

Today… SOFC research is closely aligned with Argonne's Electrochemical Energy Storage Department



Industry

TODA AMERICA, SUPERIOR GRAPHITE, Silatronix, BASF, MILTEC, XG sciences, ARKEMA, SOLVAY, Boulderionics, DUPONT, Wildcat Discovery Technologies, NOHMs, IMRA, EM, Honeywell, SolRayo, ZEON, JSR Micro, INVENTEK

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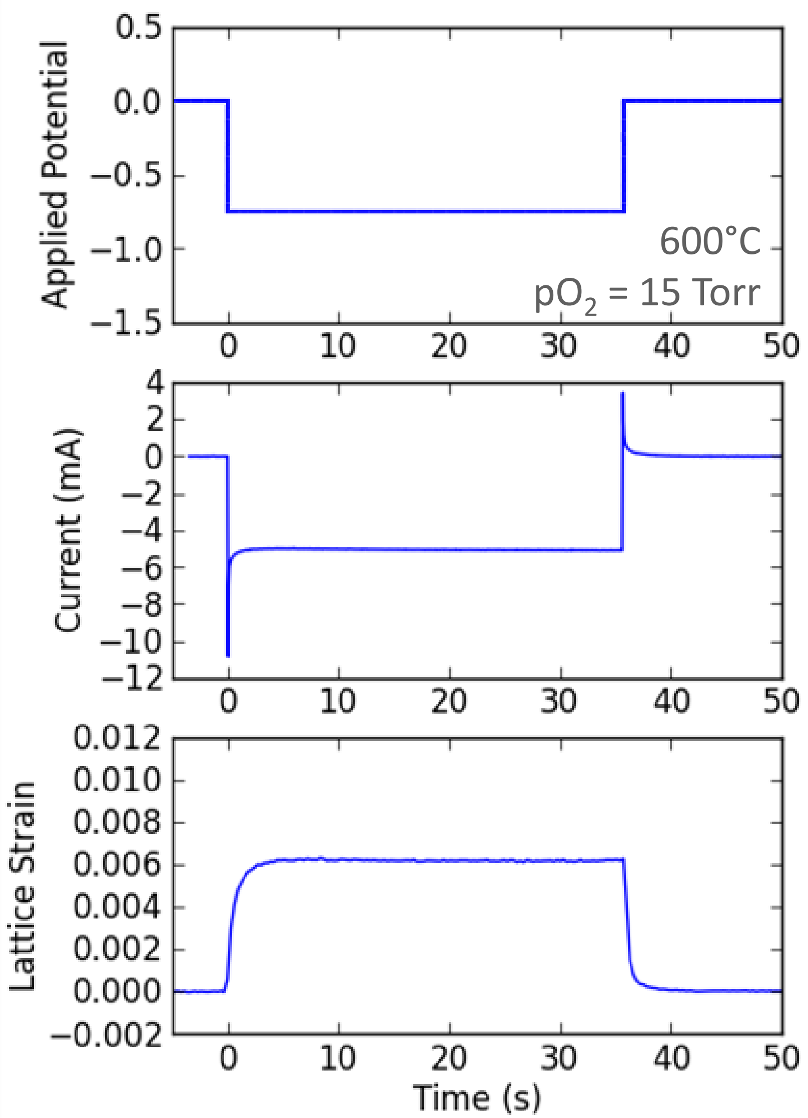
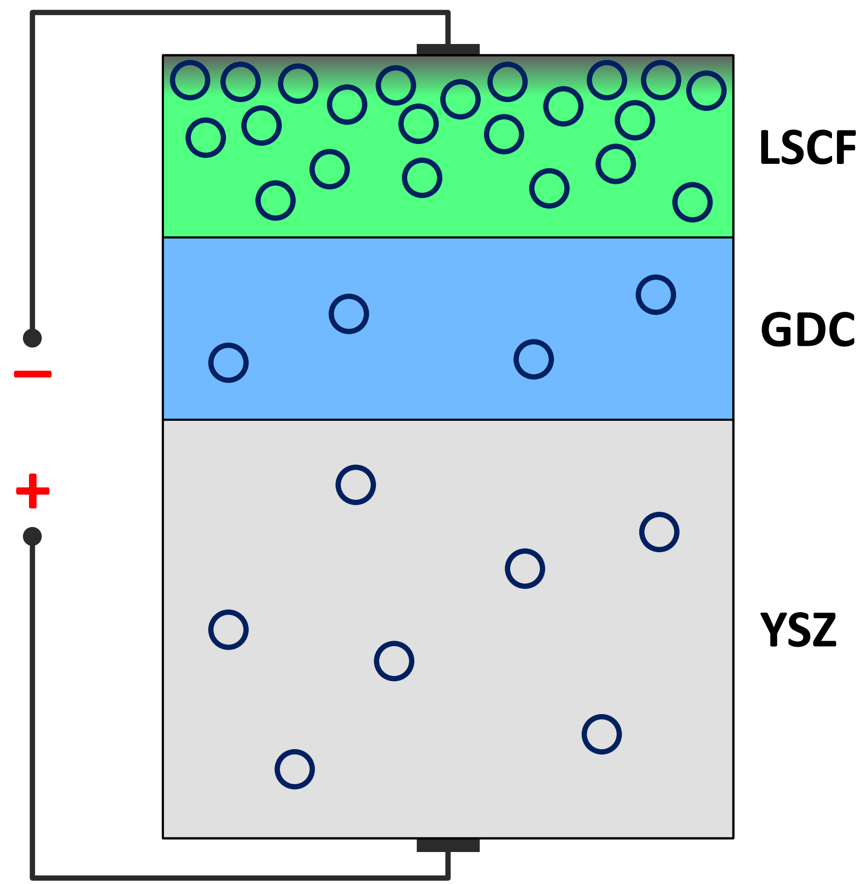
Electrochemical response to applied potential





Positive strain = ↑ O vacancies

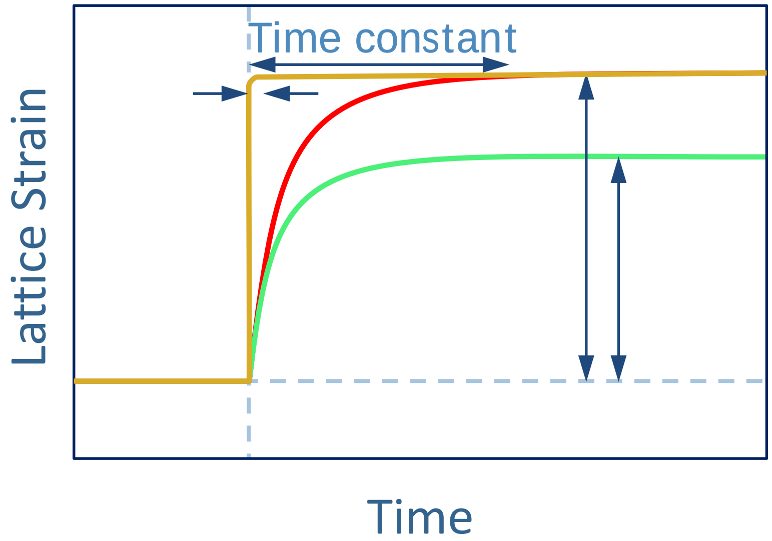
GDC & YSZ lattice parameters do not change

Surface reaction is rate-limiting step in ORR

B.J. Ingram, J.A. Eastman, K.-C. Chang, S.K. Kim, T.T. Fister, E. Perret, H. You, P.M. Baldo, P.H. Fuoss, Appl. Physics Lett. 101 (2012) 051603.

Oxygen exchange coefficients

<u>Relaxation time constant</u> →
linear combination of interface &
surface rate coefficients

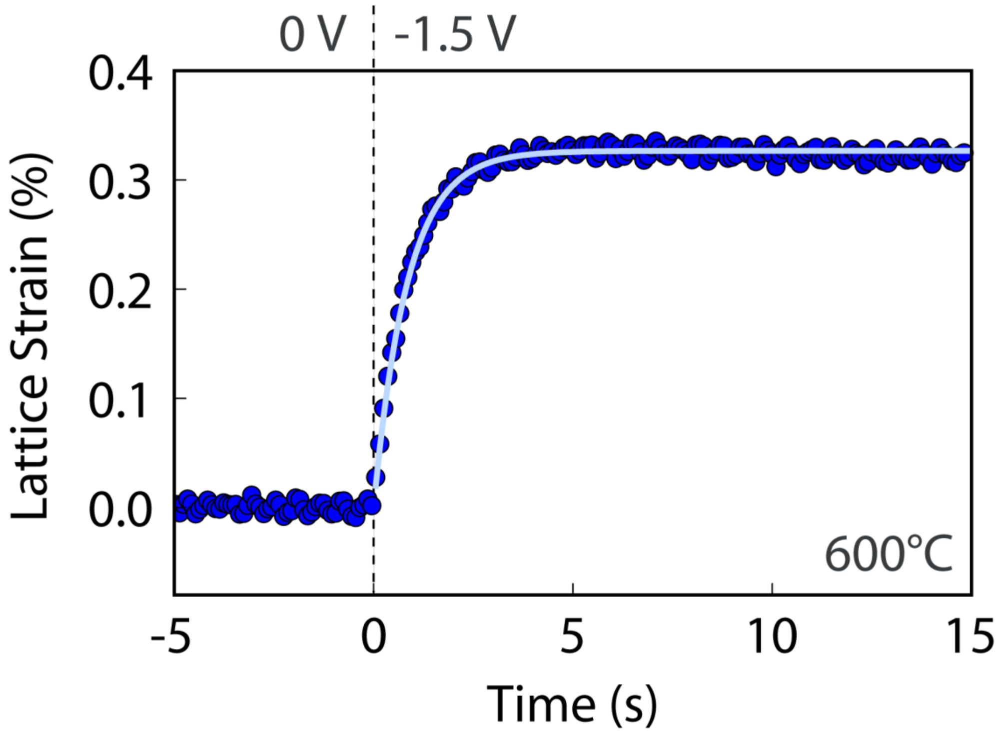


$\varepsilon_{steady\text{-}state}$

<u>Steady state strain</u> →
Ratio of interface to surface
rate coefficients

Decreased $\varepsilon_{steady\text{-}state}$, → decreased time constant → **<u>increased oxygen exchange coefficient</u>**

Modeling the oxygen exchange coefficient



Fraction of vacant O sites

Lattice strain

$$\frac{X_V(t)-X_{V,0}}{X_{V,\infty}-X_{V,0}} = \frac{\varepsilon(t)}{\varepsilon_{\infty}} = 1-exp\left(-\frac{t}{\tau}\right)$$

$$\tau = \frac{f\left(k_{surface}, k_{interface}\right)}{d}$$

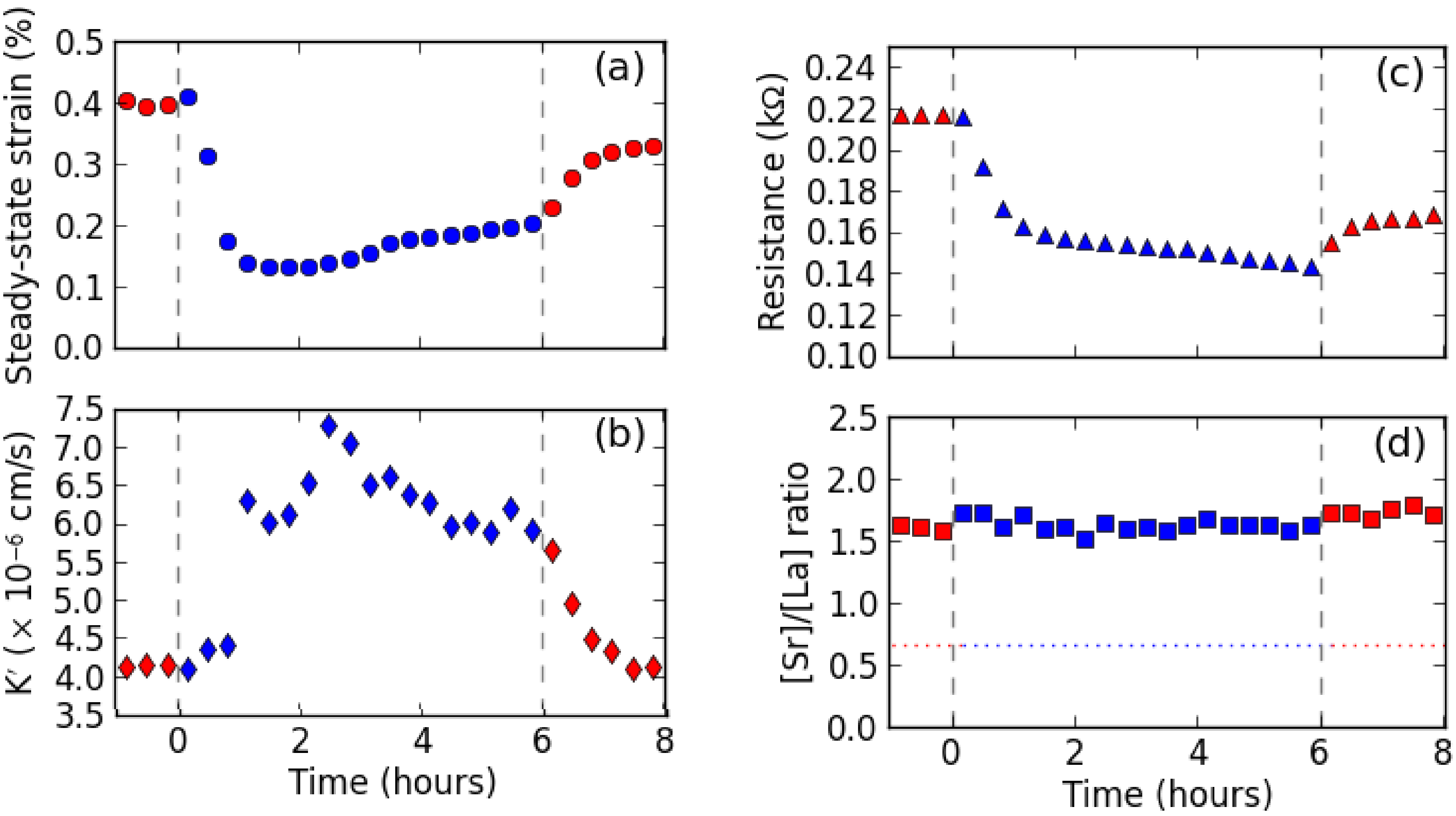
Film thickness (60 nm)

Oxygen exchange coefficients extracted from kinetics of $\Delta[V_O]$

Depends on cathode surface AND cathode/electrolyte interface

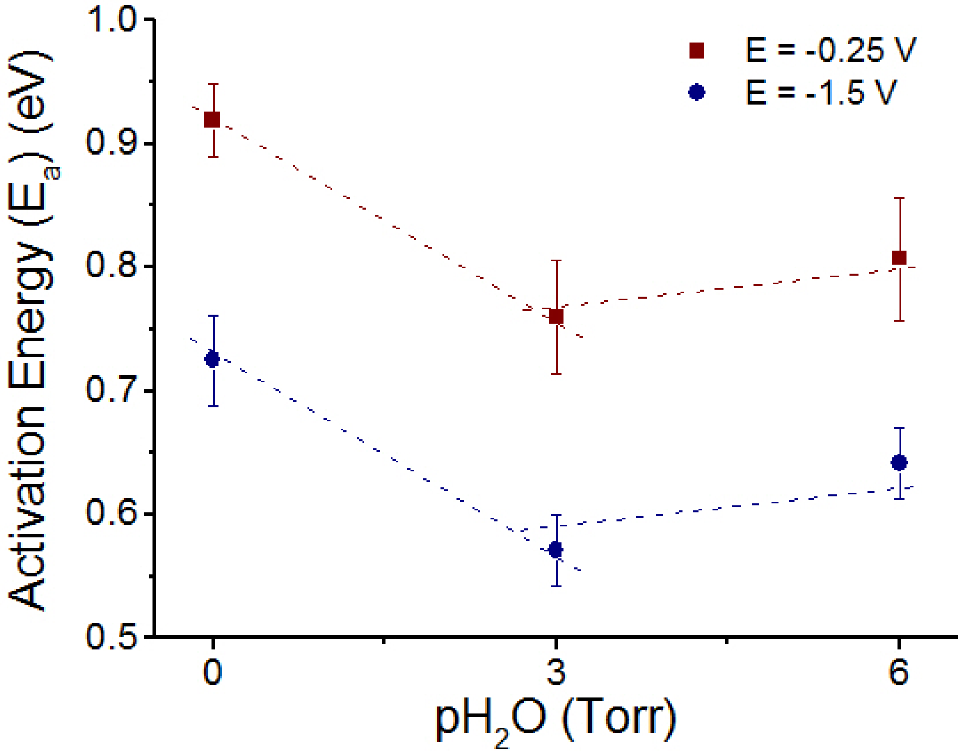
Hopper, E.M.; Perret, E.; Ingram, B.J.; You, H.; Chang, K.-C.; Baldo, P.M.; Fuoss, P.M.; and Eastman, J.A.
Submitted *J. Phys. Chem. C*

Effects of 4% H_2O in oxidant atmosphere on SOFC cathode performance



Hopper, E.M.; Perret, E.; Ingram, B.J.; You, H.; Chang, K.-C.; Baldo, P.M.; Fuoss, P.M.; and Eastman, J.A.

Final words on H_2O and surface exchange rates



- H_2O reduces observed:
  - lattice strain
  - system resistance
  - surface exchange coefficient
- Sr segregation is unaffected by addition/removal of H_2O (on experiment time scale)
- The activation energy for oxygen surface exchange was reduced by approximately 0.1 eV
- Short term observation: does not account for long term degradation processes.

Hopper, E.M.; Perret, E.; Ingram, B.J.; You, H.; Chang, K.-C.; Baldo, P.M.; Fuoss, P.M.; and Eastman, J.A.

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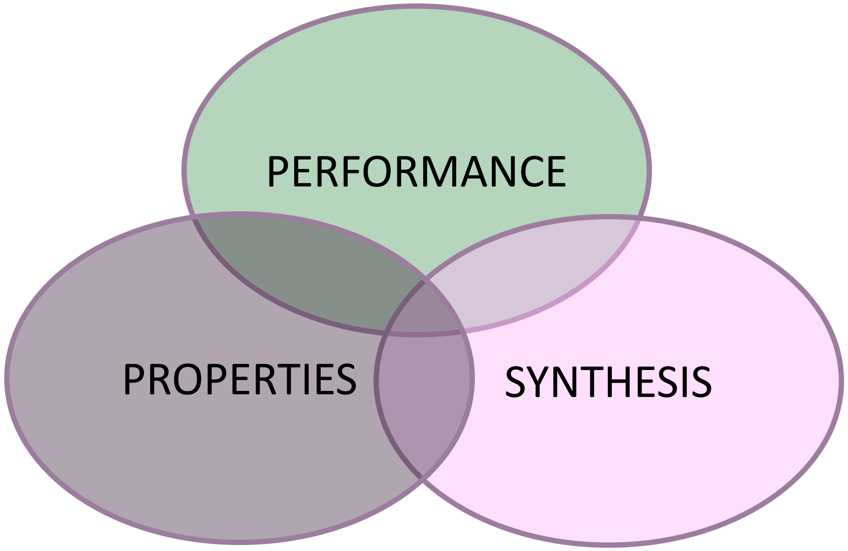
What is needed to advance SOFC technology?

Background:

- SOFC designs and materials have sufficient maturity, activity and efficiency to be put into practice
- Cost, reliability, and lifetime need to continue to be addressed
- Focus on manufacturing practice will address cost and reliability



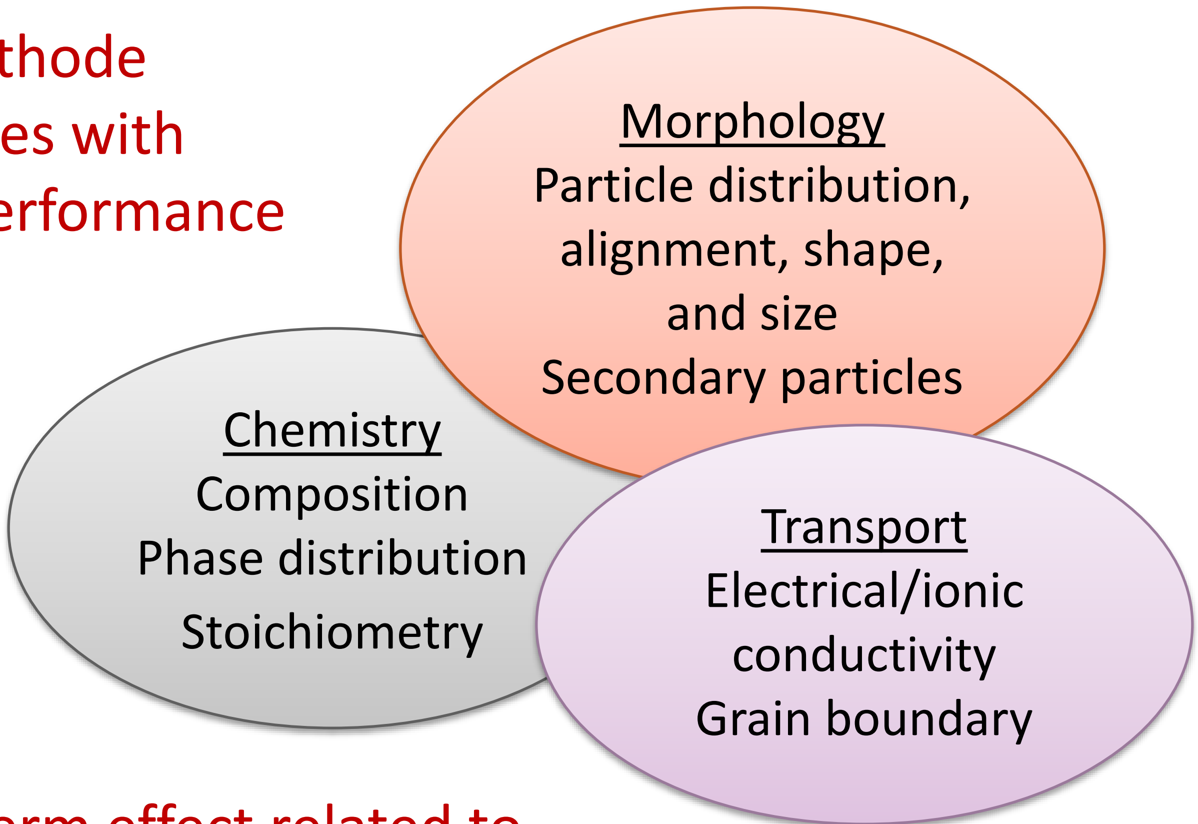
Path forward:

- Development of "low cost" analysis of feedstock materials
- Identify tolerance level of feedstock specifications

Improve reliability in the manufacturing and operation of SOFCs

Performance ↔ Properties relationship of cathode feedstock materials

Vet feedstock cathode powder properties with respect to cell performance reliability



Focus on short term effect related to electrochemical performance in cells and "low cost" characterization techniques

Assess LSCF batches of same composition: Identify and assess non-uniformity

4 lots of LSCF from **fuelcell**materials (FCM)

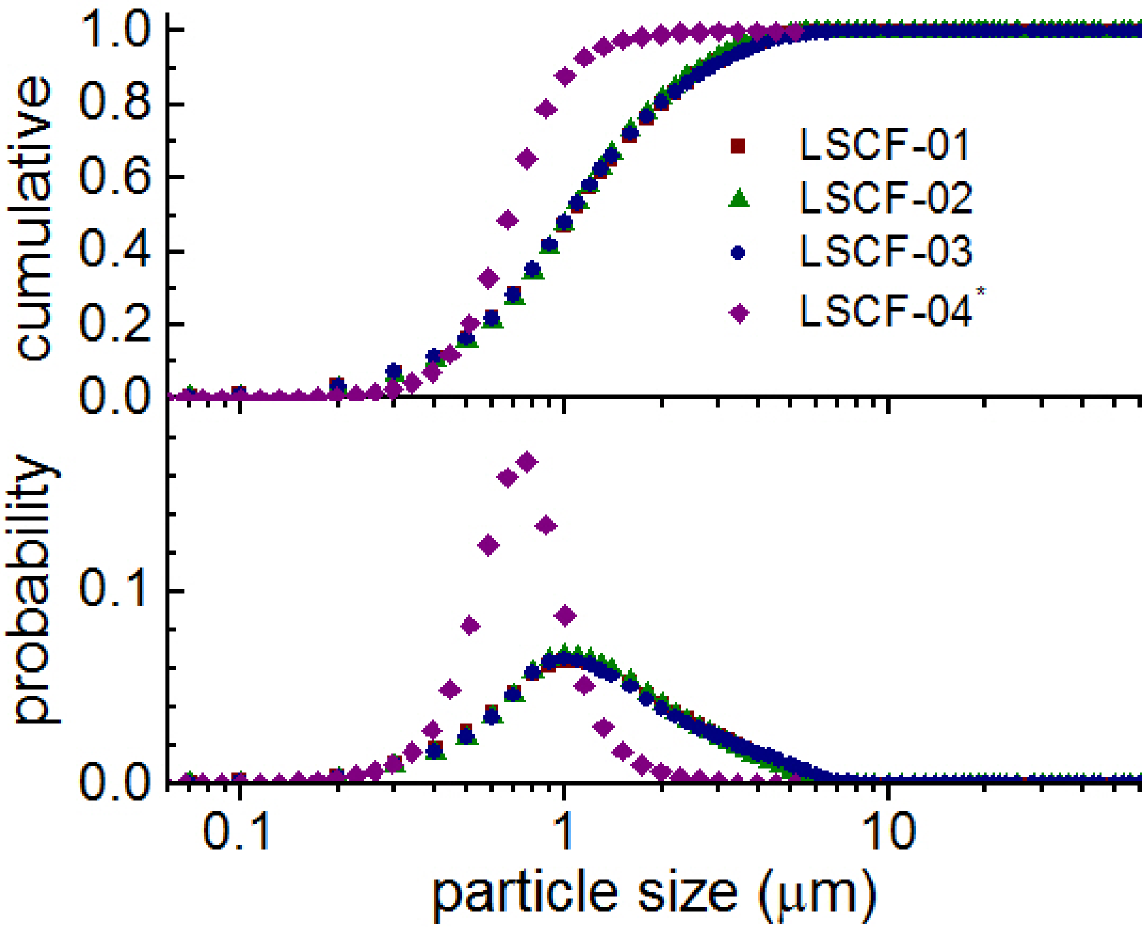
All were designed with 5% A-site deficiency

fuelcellmaterials.com

PERFORMANCE AND QUALITY DELIVERED

Sample#	Nominal Composition	Surf area (m^2/g)	Particle size (μm)
LSCF-04	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	10 - 14	0.4 - 0.8
LSCF-03	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	4 - 8	0.7 - 1.1
LSCF-02	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	4 - 8	0.7 - 1.1
LSCF-01	$(La_{0.6}Sr_{0.4})_{0.95}Co_{0.2}Fe_{0.8}O_{3-\delta}$	4 - 8	0.7 - 1.1

Morphology comparison: Particle size analysis

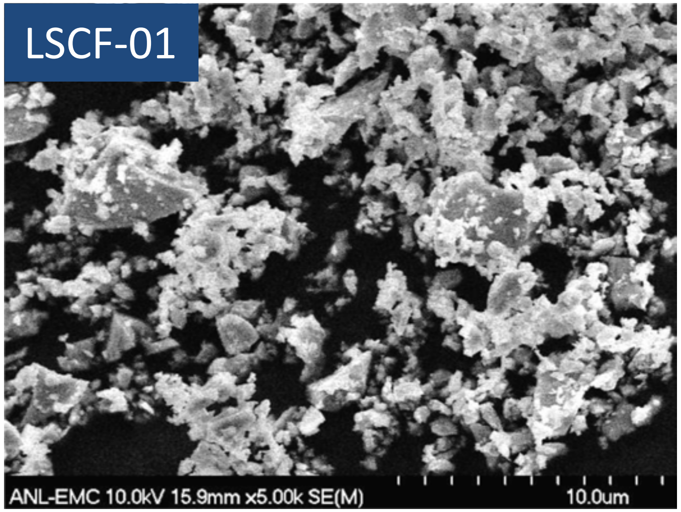


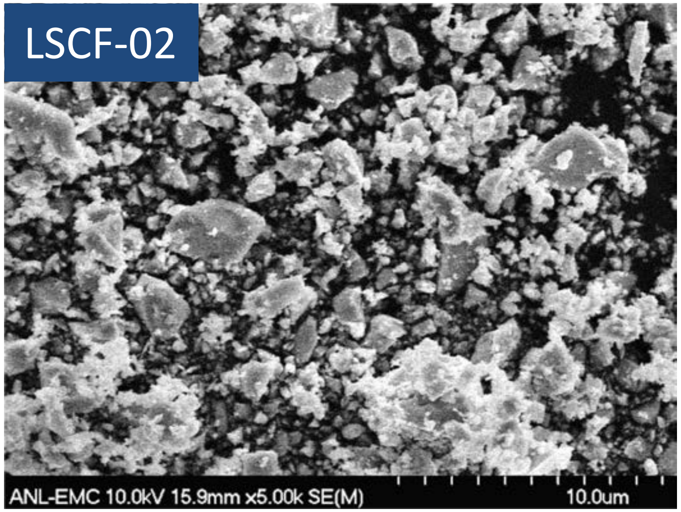
	D10	D50	D90
LSCF-01	0.367	1.053	2.774
LSCF-02	0.379	1.040	2.620
LSCF-03	0.365	1.038	2.836
LSCF-04*	0.419	0.676	1.066

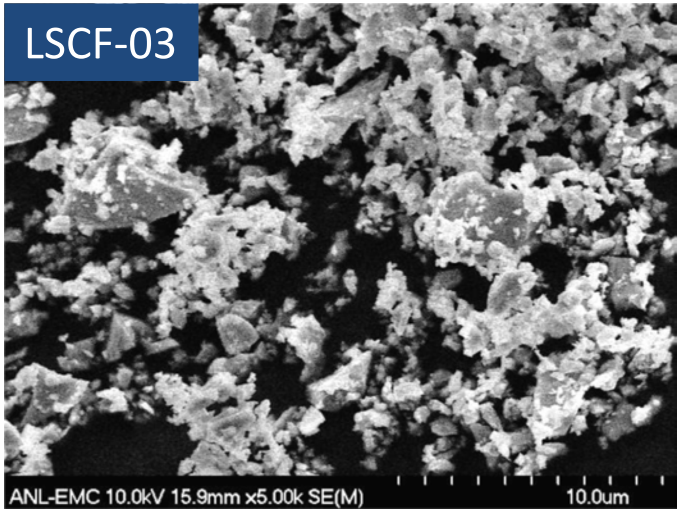
* Data provided by FCM

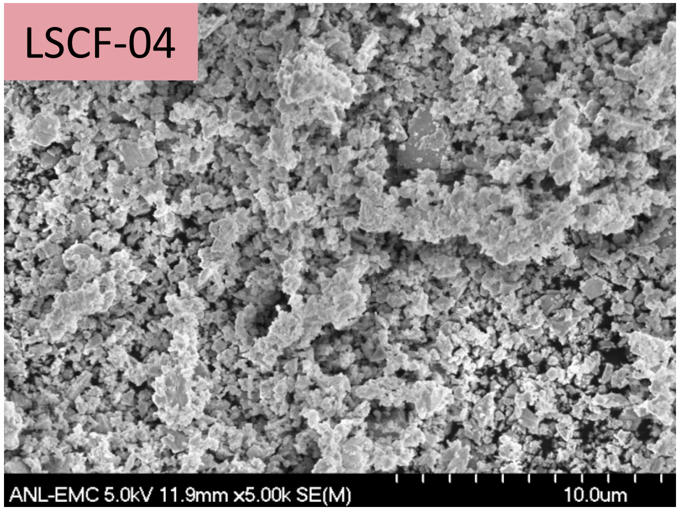
Morphology comparison: Imaging LSCF

Particle morphology has excellent consistency between different lots at different time periods spanning 6 months to 1 year apart



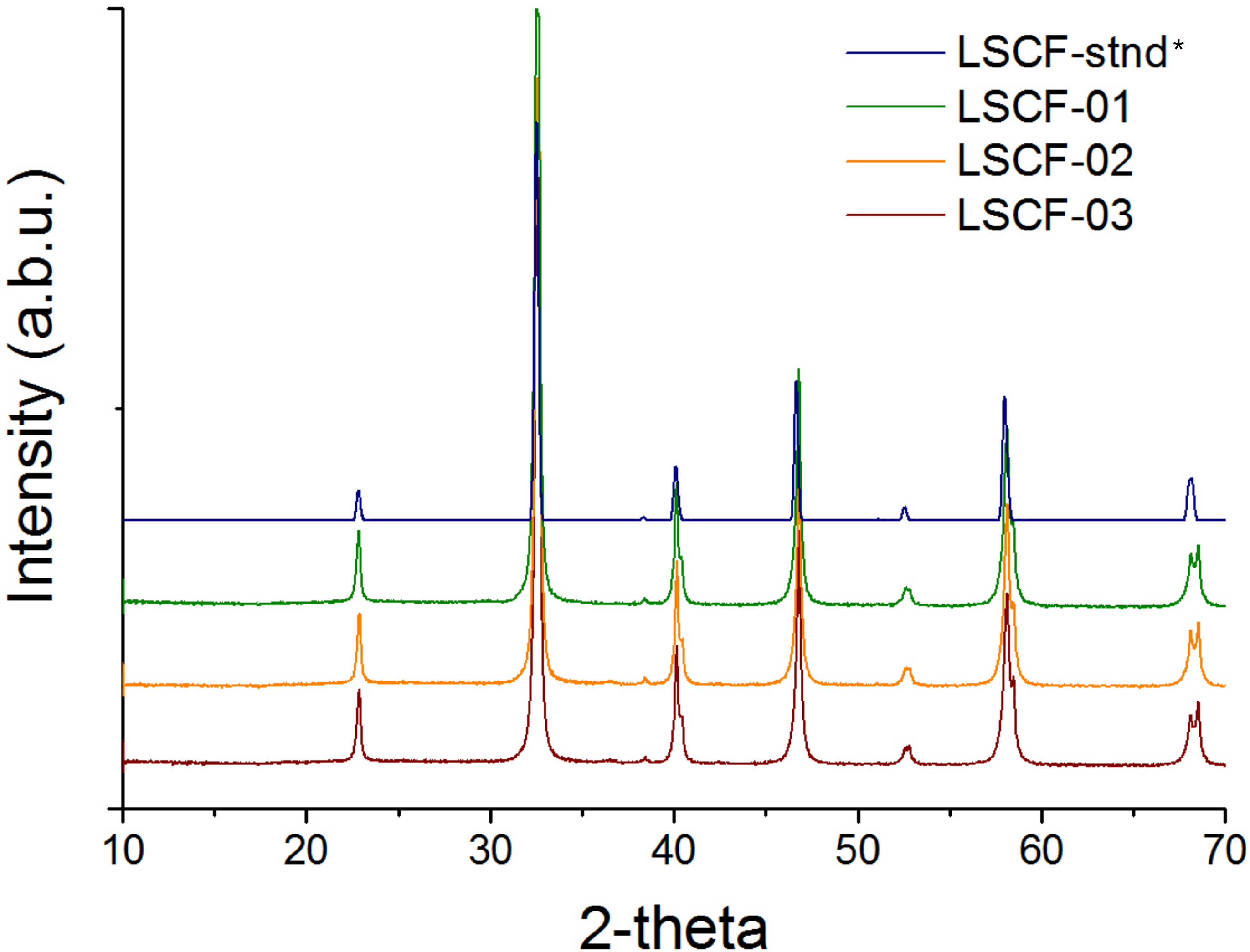






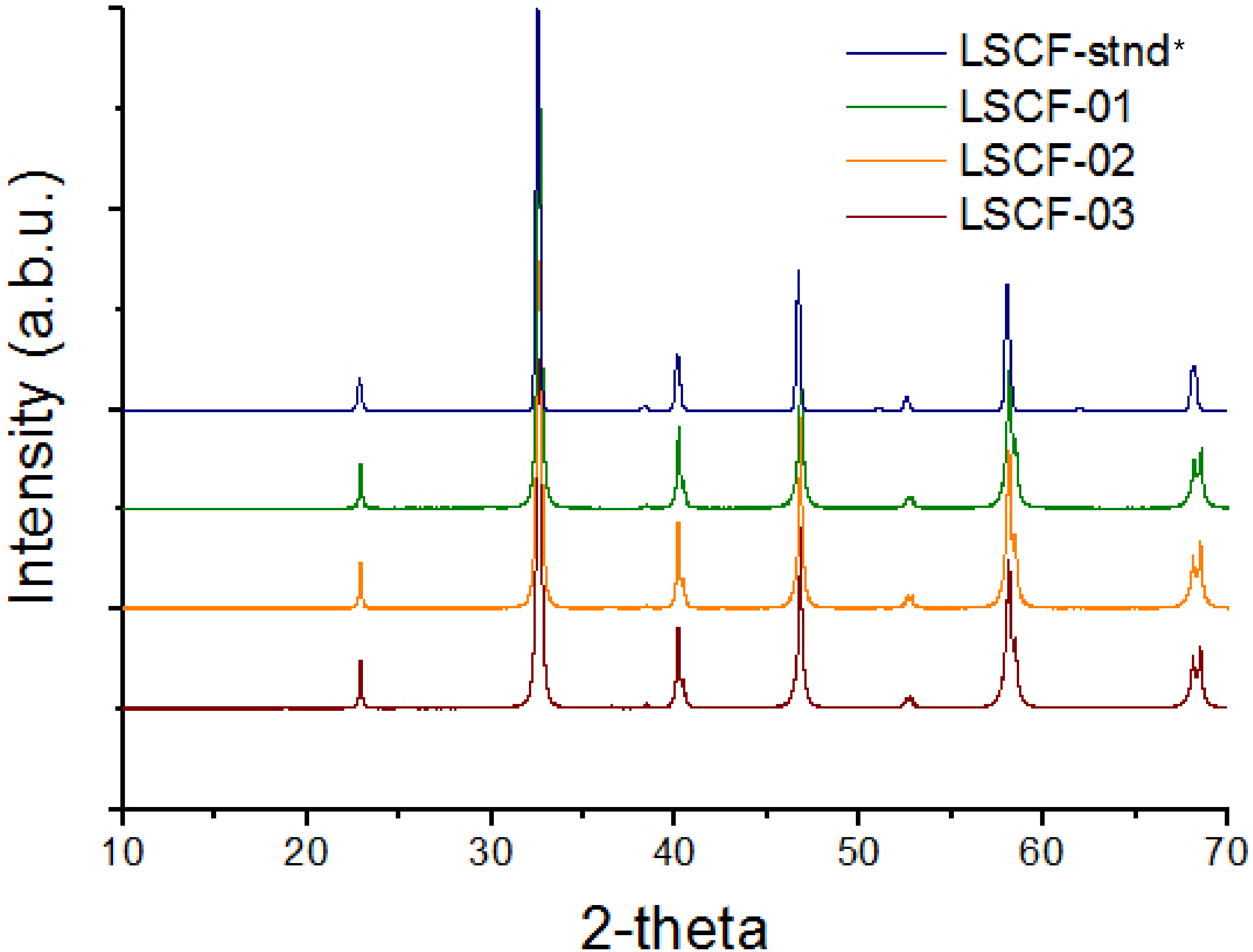
LSCF XRD (lab source)

Phase reproducibility and purity confirmed



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

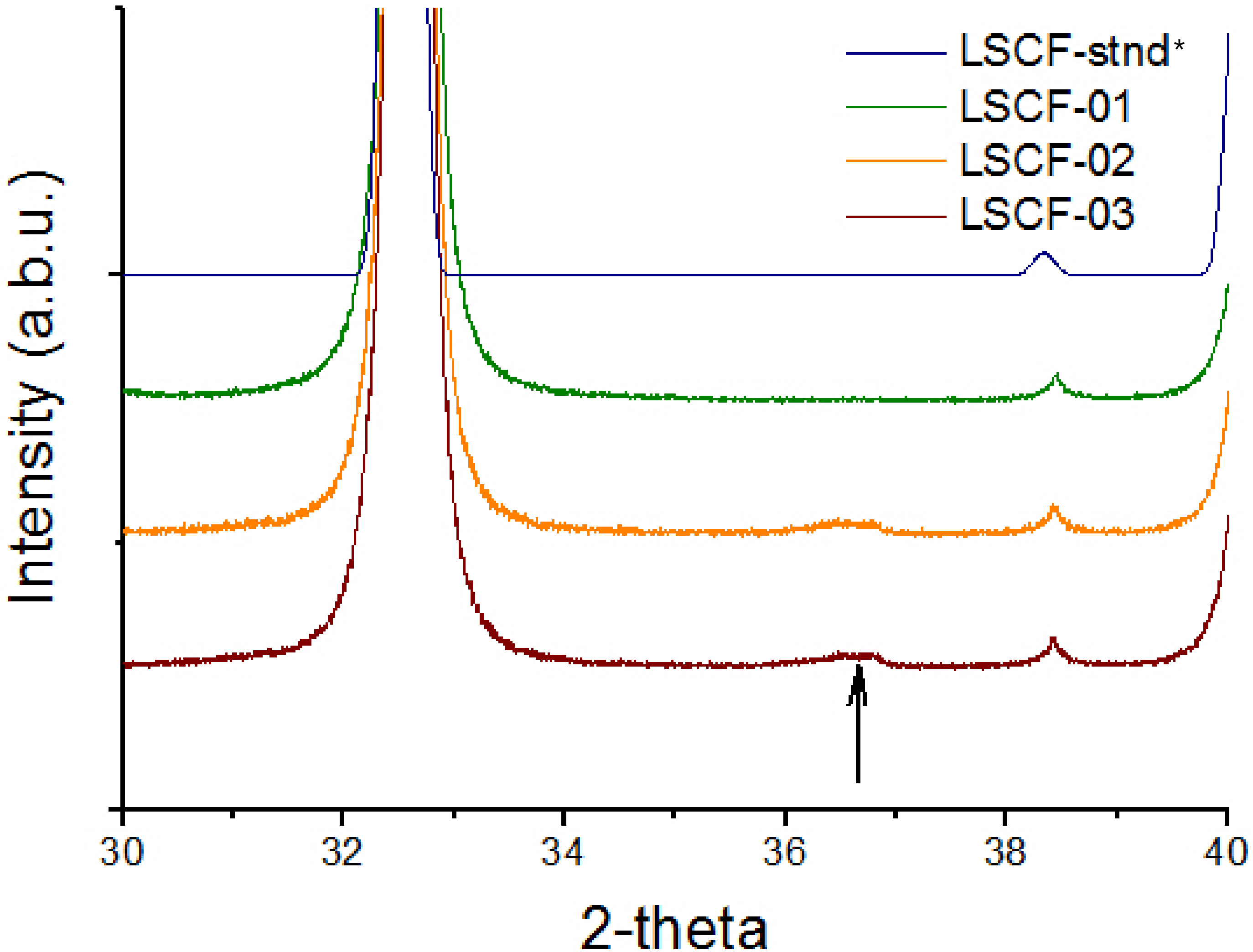
LSCF XRD (synchrotron)



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

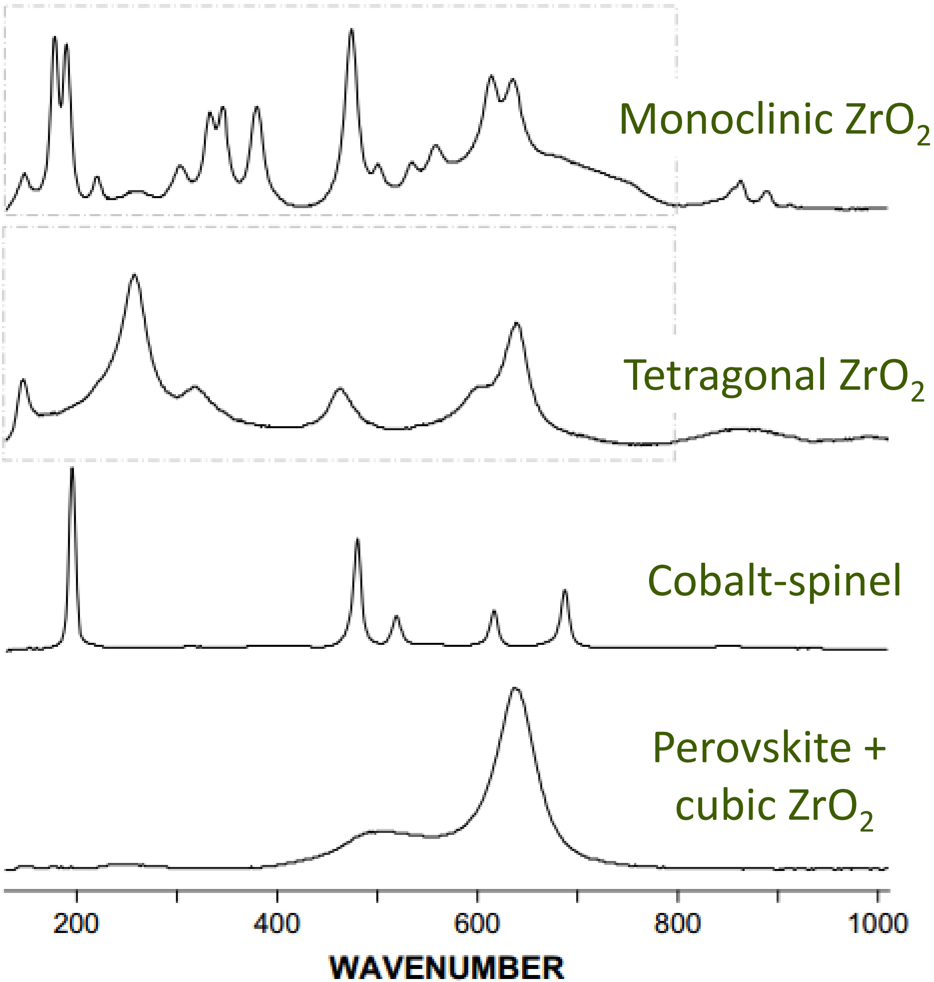
LSCF XRD (synchrotron)

Evidence of second phase, phase impurity



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

Previous work: Raman Spectroscopy



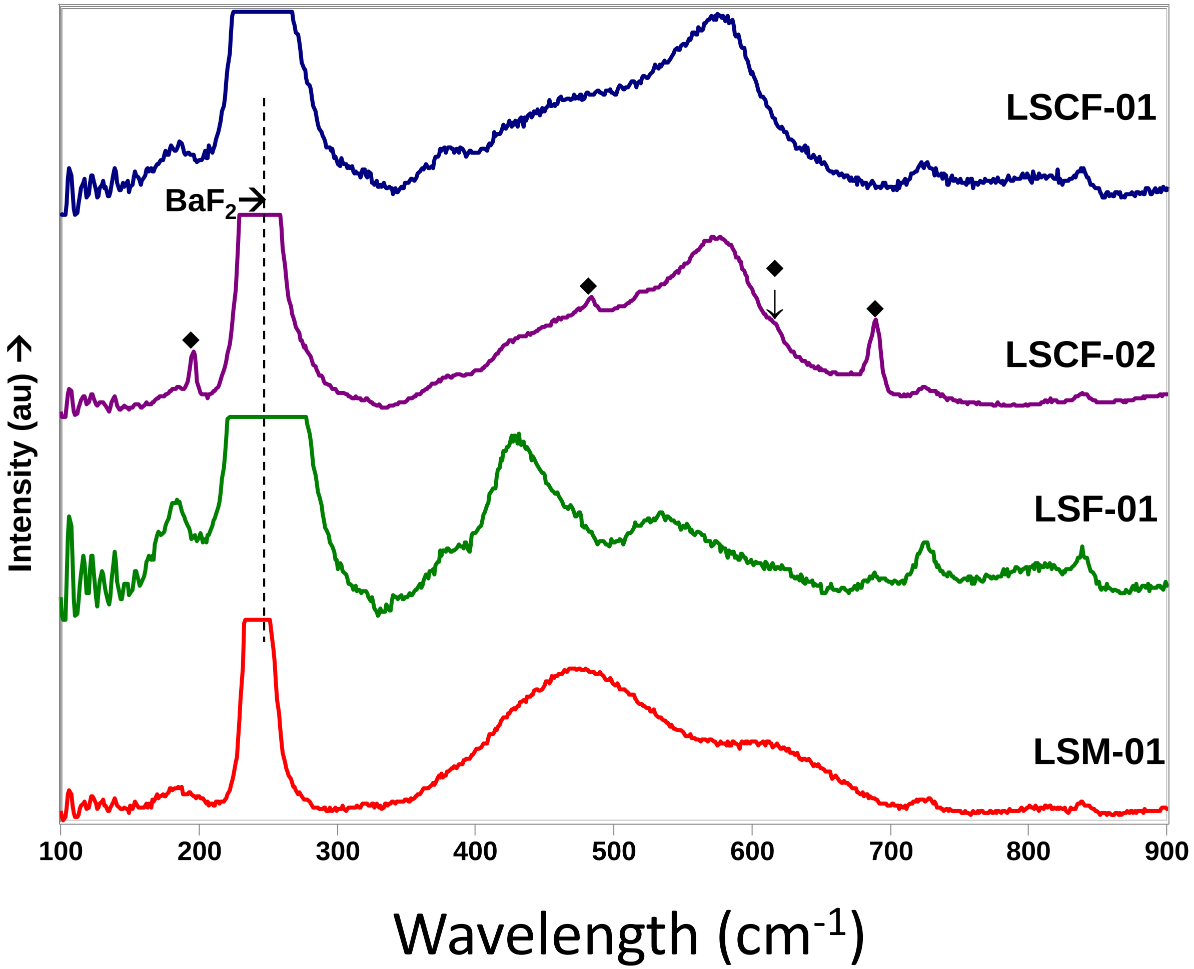
- Experience in using Raman microspectroscopy to identify unexpected phases
- Degradation study on O_2 electrodes for manufacturer supplied SOEC stacks
- Identified Co_3O_4, ZrO_2(mon), and ZrO_2(tet) zirconia under oxygen seal of electrolysis cell

Identify and assess non-uniformity in used SOEC stack components

J.R. Mawdsley, et al. *Int. J. Hydrogen Energy*. **34**(9) 4198 (2009).

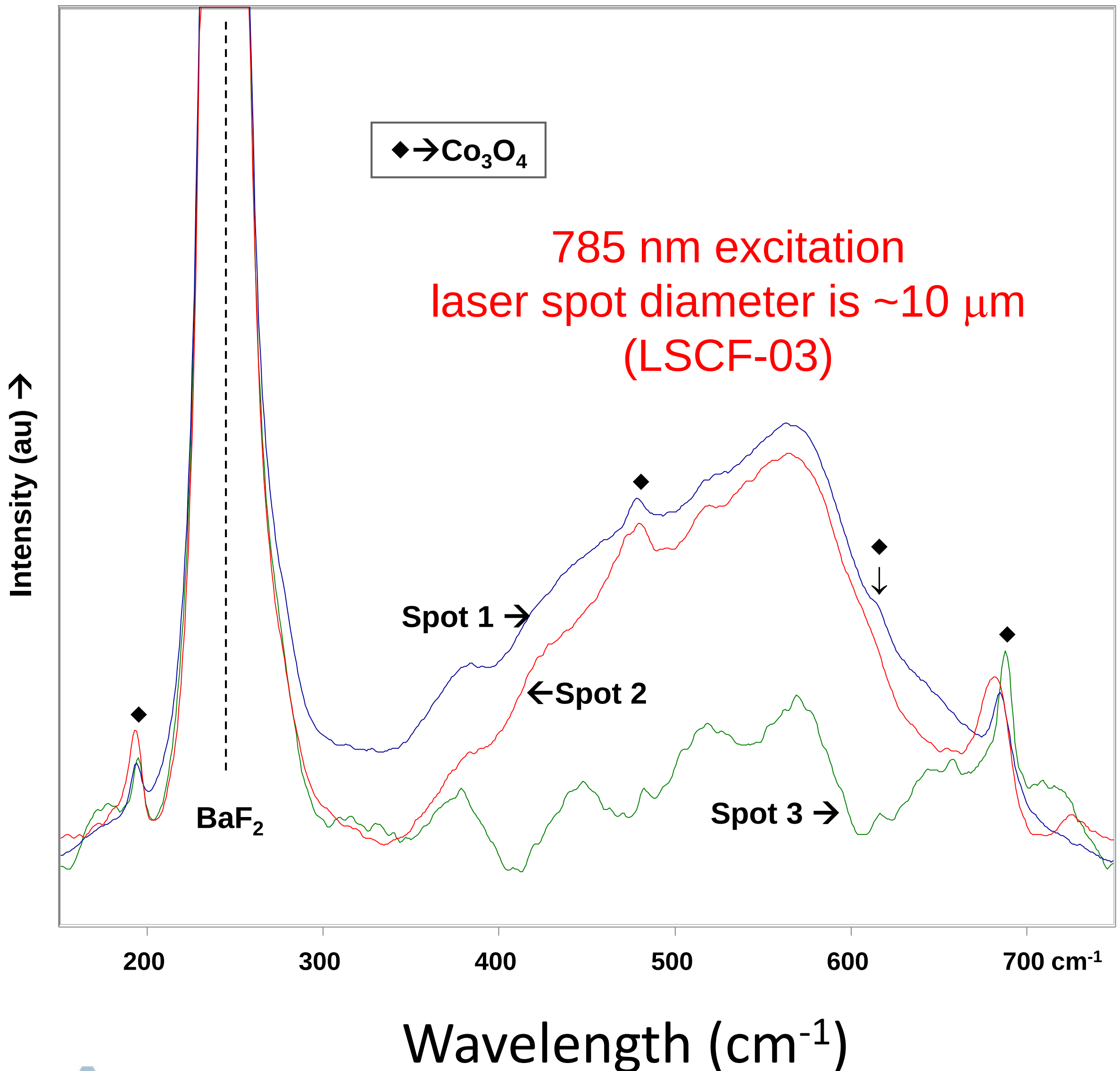
Raman phase analysis: second phase present

785 nm excitation



- Relatively weak reproducible Raman spectra
- Broad underlying features → scattering from the AA'BO3 and AA'BB'O3 phases
- Sharper bands (◆) are known phonons of Co_3O_4
- Relative amount of Co_3O_4 is quite small
- Co_3O_4 is a very strong Raman scatterer

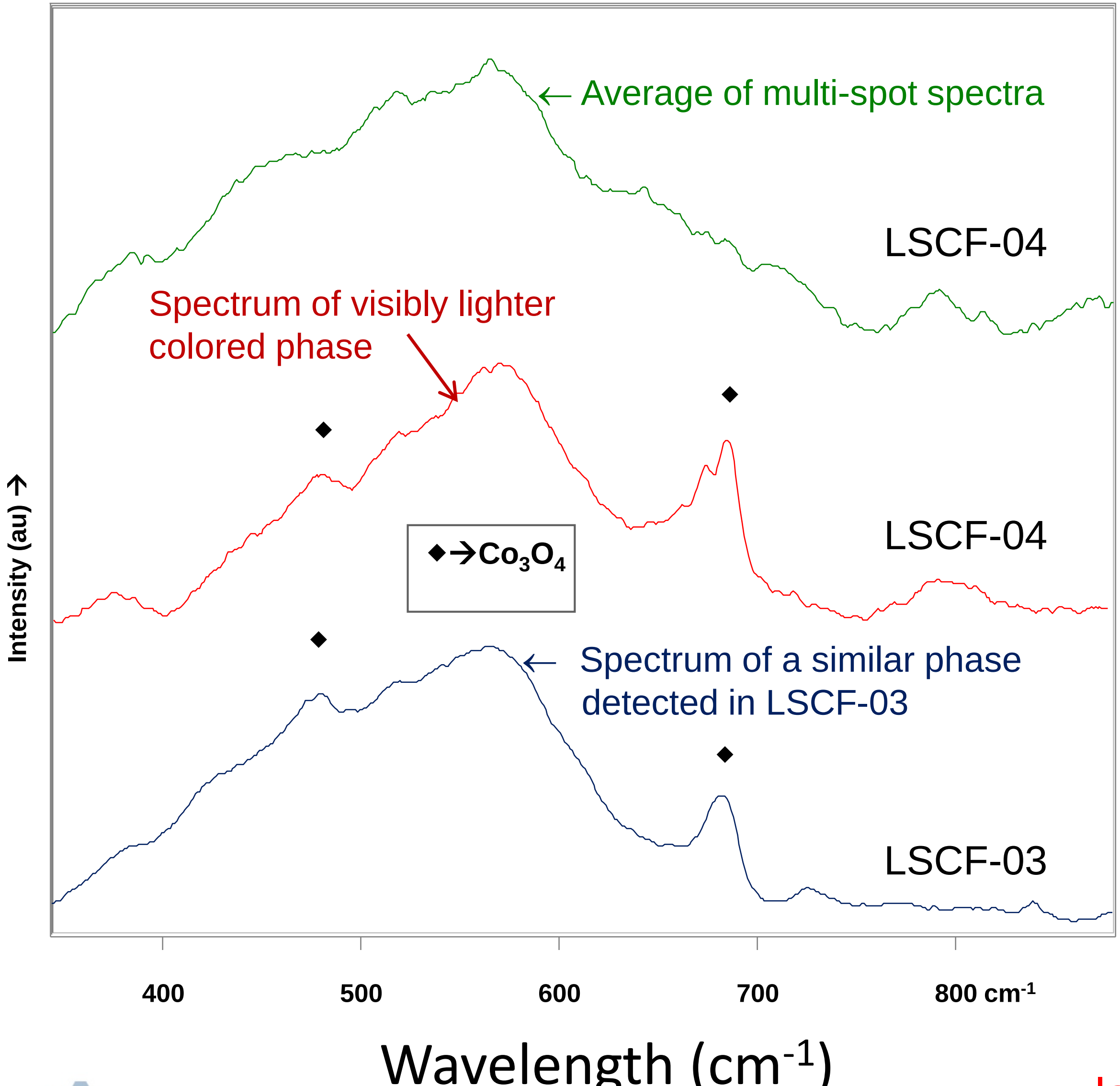
Raman phase analysis: heterogeneous distribution



- Likely that the detected Raman scattering is coming from the outer 200-300 nm
- Spot 3 seems to be a Co_3O_4 rich region
- Spots 1 and 2 replicate spectra taken at most of the random spots probed.
- All intensities are normalized to the BaF_2 phonon intensity

Mapping of LSCF powder sample reveals Co_3O_4 rich regions

Raman phase analysis: heterogeneous distribution



- FCM provided XRD showing phase purity
- Heterogeneous distribution of Co_3O_4 second phase
- Similar to LSCF-03 (shown) and LSCF-02
- All intensities are normalized to the BaF_2 phonon intensity

Mapping of LSCF powder sample reveals Co_3O_4 rich regions, heterogeneously distributed

785 nm excitation
laser spot diameter is ~10 μm

GSAS-II refinement of synchrotron diffraction

Sample	a/b lattice Parameter (Å)	c lattice Parameter (Å)	Unit Cell Volume (Å³)	M20 (Fit quality)
ICSD*	5.508	13.441	353	NA
LSCF-01	5.499(6)	13.367(9)	350	482
LSCF-02	5.503(5) 5.503(1)	13.372(5) 13.373(1)	351	222 171
LSCF-03	5.503(8) 5.504(0)	13.373(1) 13.373(2)	351	171 220

LSCF = *$(La_{0.6}Sr_{0.4})_{0.95}(Co_2Fe_{0.8})O_3$: Space group R-3c

- No clear differences in lattice parameter between LSCF-01, LSCF-02, and LSCF-03
- Could slight compression (ca. 0.07 Å) along c axis for FCM LSCF samples be due to reduced stoichiometry on the A site of the AA’BB’O3 structure?
- Other than obvious impurity phases, it is not clear whether XRD is sensitive to changes in critical materials properties.

Half-cell test protocol

Effect of impurity phase on performance and reliability. What is the tolerance to impurity phases?

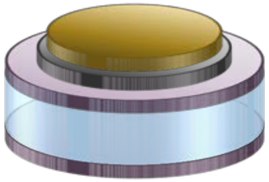
Button cell variability must be considered.

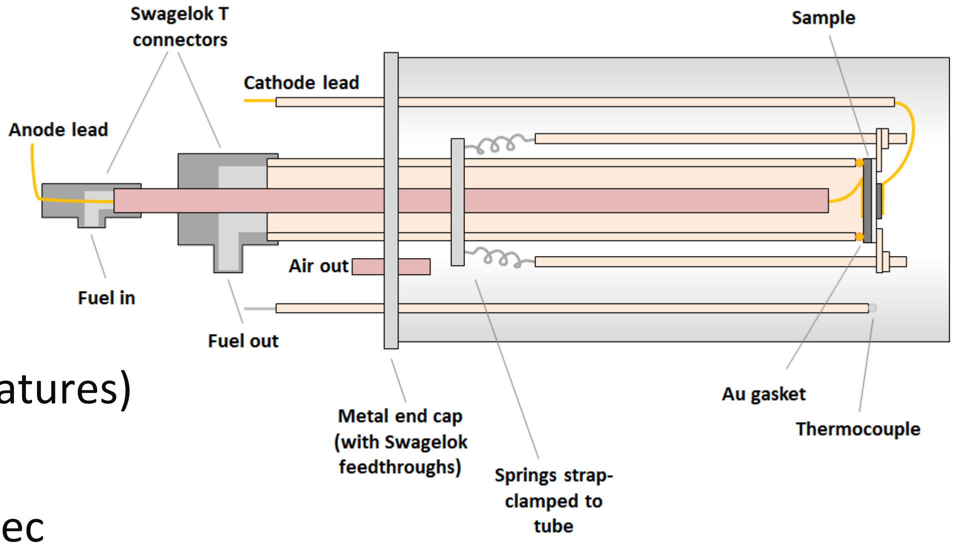
Screen print 5μm layers on 250 μm YSZ

GDC, 1300°C

LSCF, 950°C

Gold , 800°C

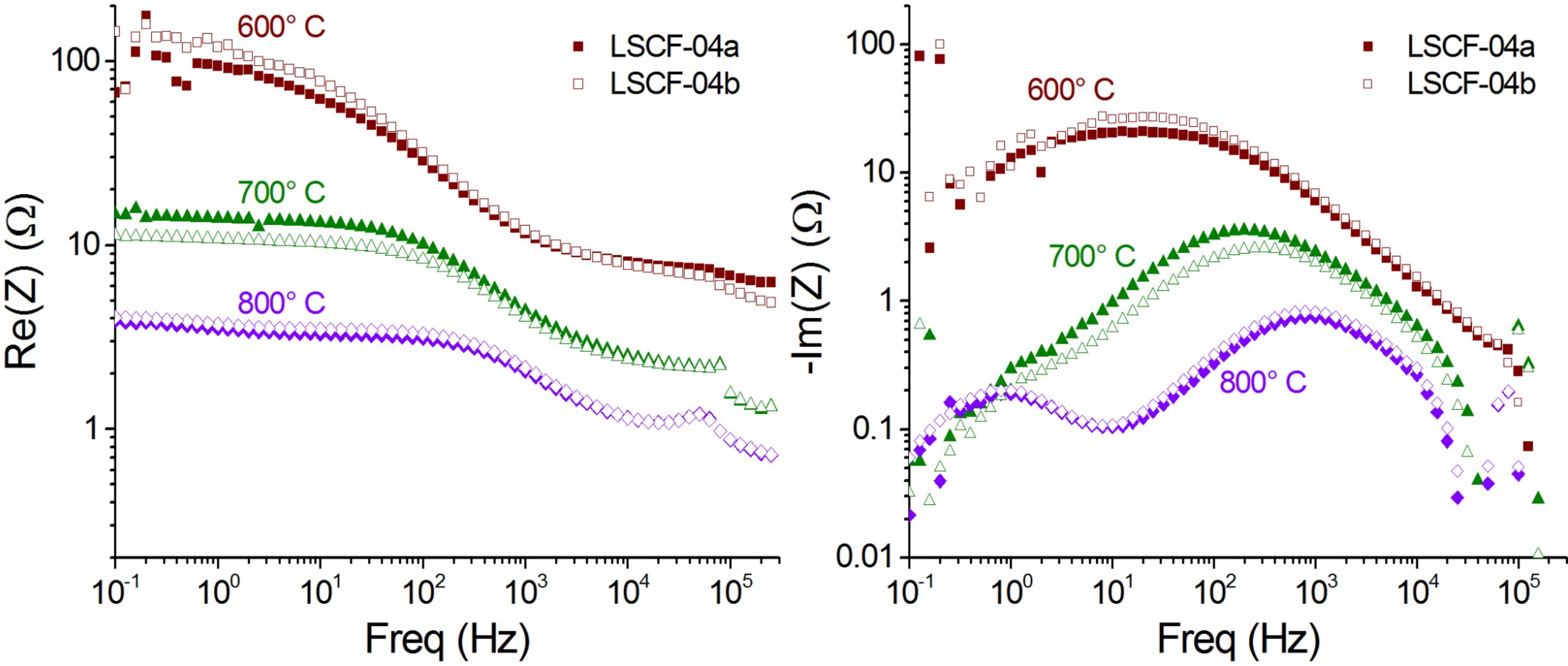




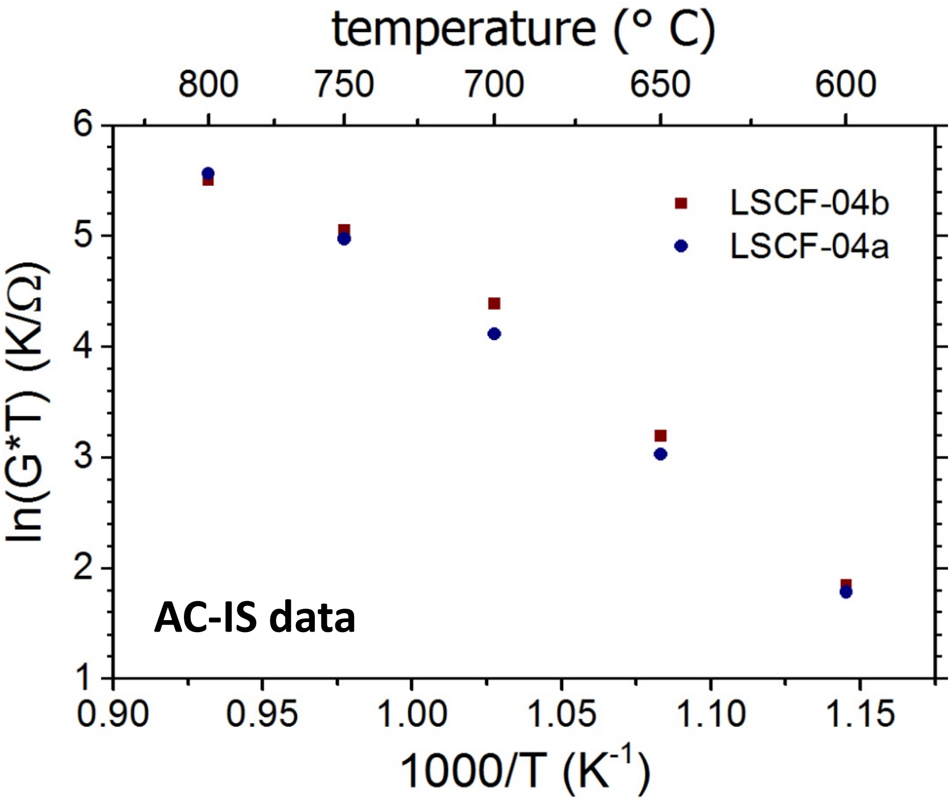
Standardized testing procedure (5 temperatures)

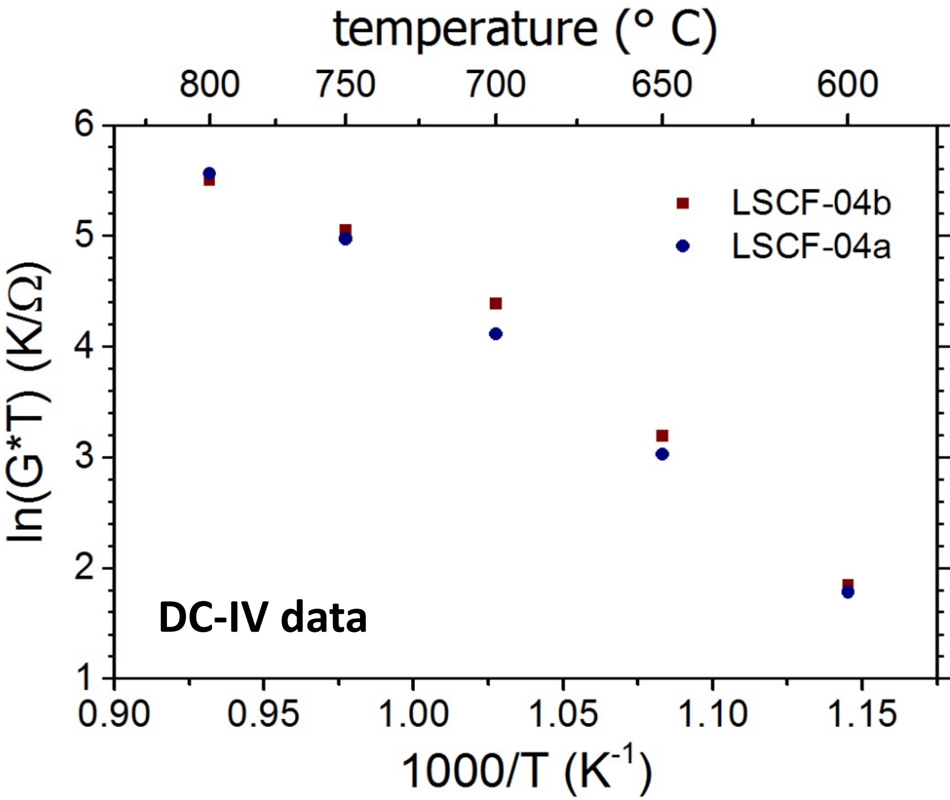
- Galvanostatic 100 mA, 1 hour
- Potentiodynamic ±100 mV @ 1 mV / sec
- AC-IS ±50 mV vs OCV

Electrochemical analyses: AC-IS repeatability



Electrochemical analyses: Temperature dependence repeatability



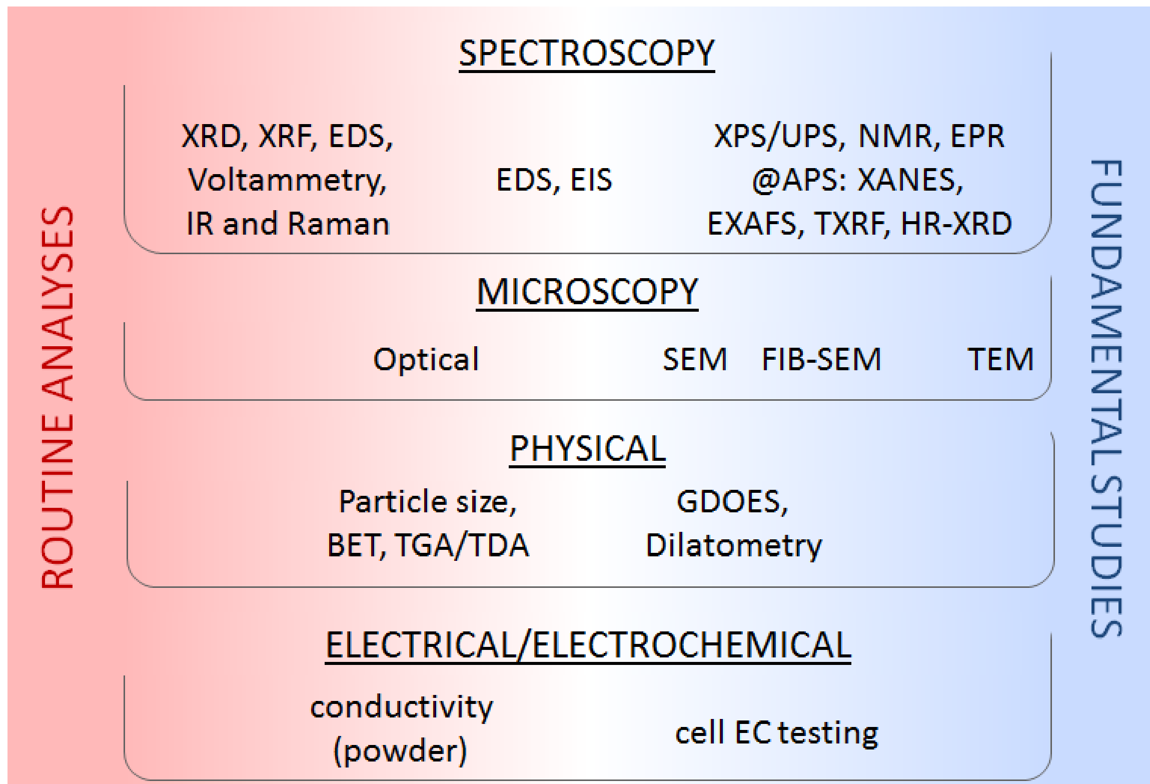


E_a = 1.55±0.07 eV (b)
= 1.44±0.05 eV (a)

E_a = 1.50±0.13 eV (b)
= 1.49±0.13 eV (a)

Future direction - Discussions

- Determine the variability and tolerance of cathode materials composition and phase to maintain predictable performance and reliability.
- Determine key indicators of performance and reliability of the SOFC cathode
- Link simple and rapid characterization methods to high temperature performance and reliability



Tools available at Argonne

AND OTHERS… ?

Thank you

- Jeffery A. Eastman (ANL, MSD)
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- **fuelcell**materials.com
- Fuel Cell Energy
- LG Fuel Cell Systems, Inc

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