Development of Cathode Contact Materials for SOFC

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Richland, WA 99352

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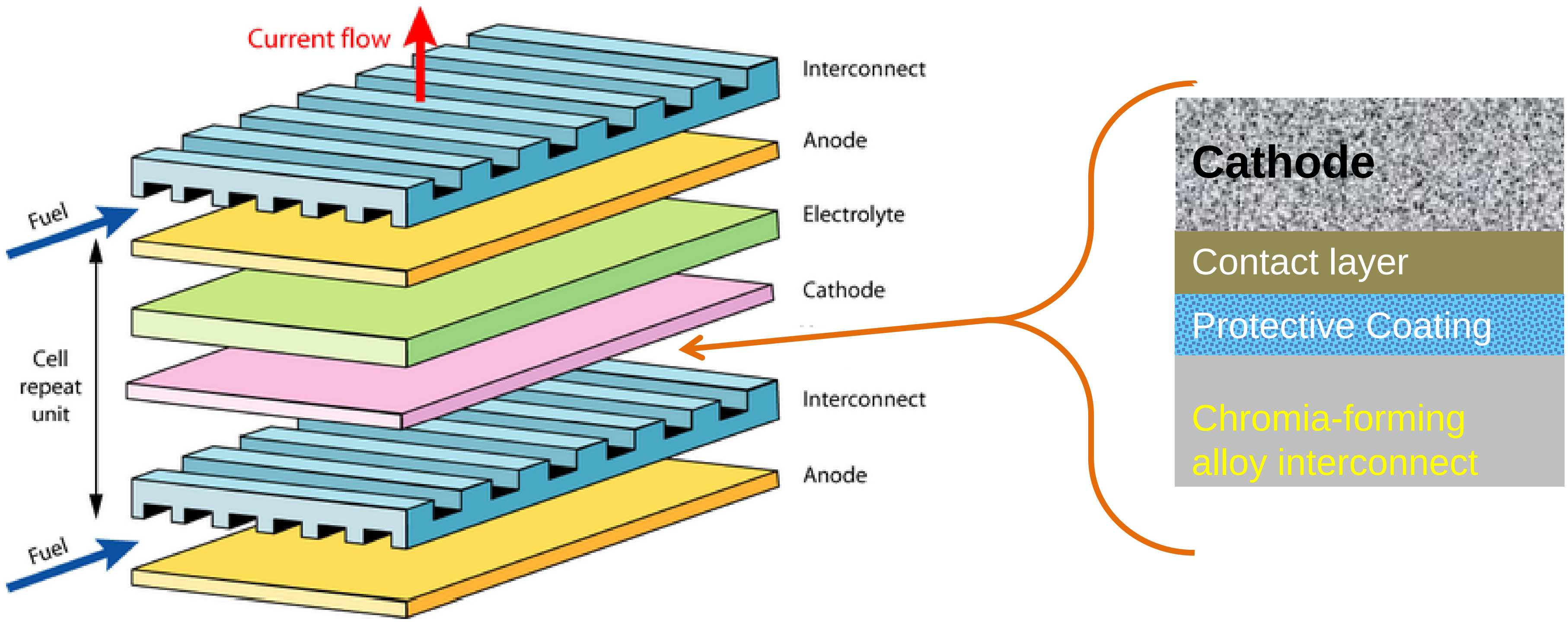
Cathode/Interconnect Contact Materials

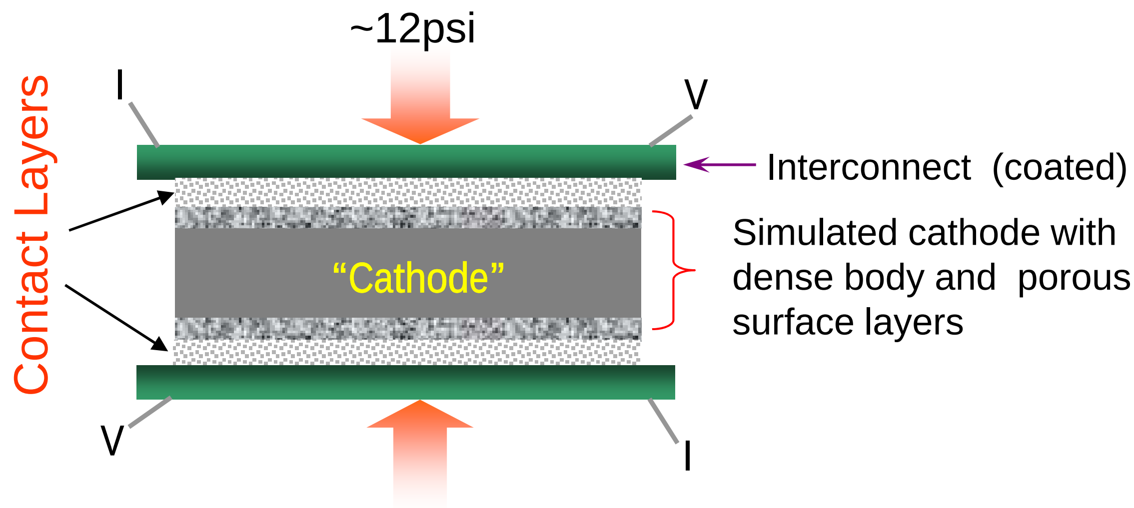


Cathode/Interconnect Contact Materials

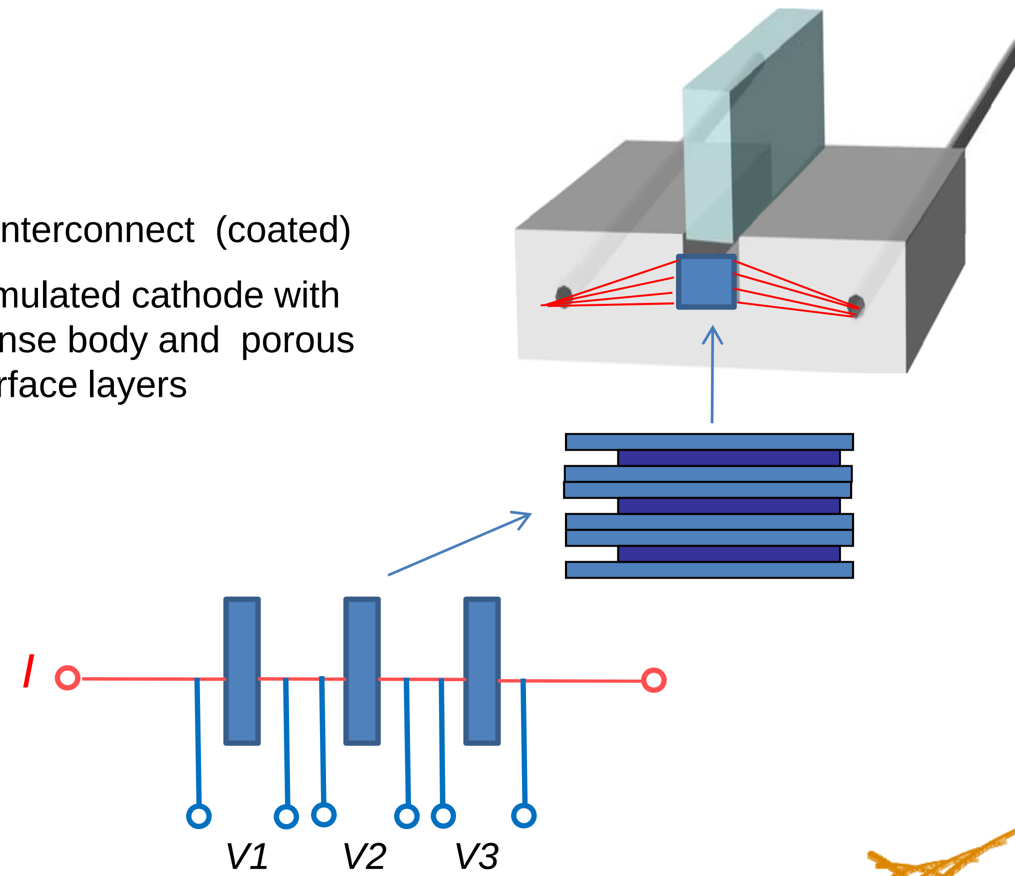
- Requirements:
  - High electrical conductivity to reduce interfacial electrical resistance between cathode and interconnect
  - Chemical and structural stability in air at SOFC operating temperature
  - Chemical compatibility with adjacent materials (perovskite cathode, interconnect coating)
  - Adequate mechanical strength and bonding to adjacent components
  - Low cost materials and fabrication
- Challenges:
  - Low processing temperature during stack fabrication (800-1000ºC)
    - Low density results in low intrinsic strength and bond strength, reduced conductance
  - Brittle nature of ceramics; Cost/volatility of noble metals
- Goal:
  - Develop cathode/interconnect contacts with low electrical resistivity and increased mechanical strength
    - Modeling results suggest strengthening of contacts can relieve stresses on seals

Area Specific Resistance (ASR) Measurements

$$ASR_{cathode-interconnect} = \Phi(scale, contact material, coatings)$$

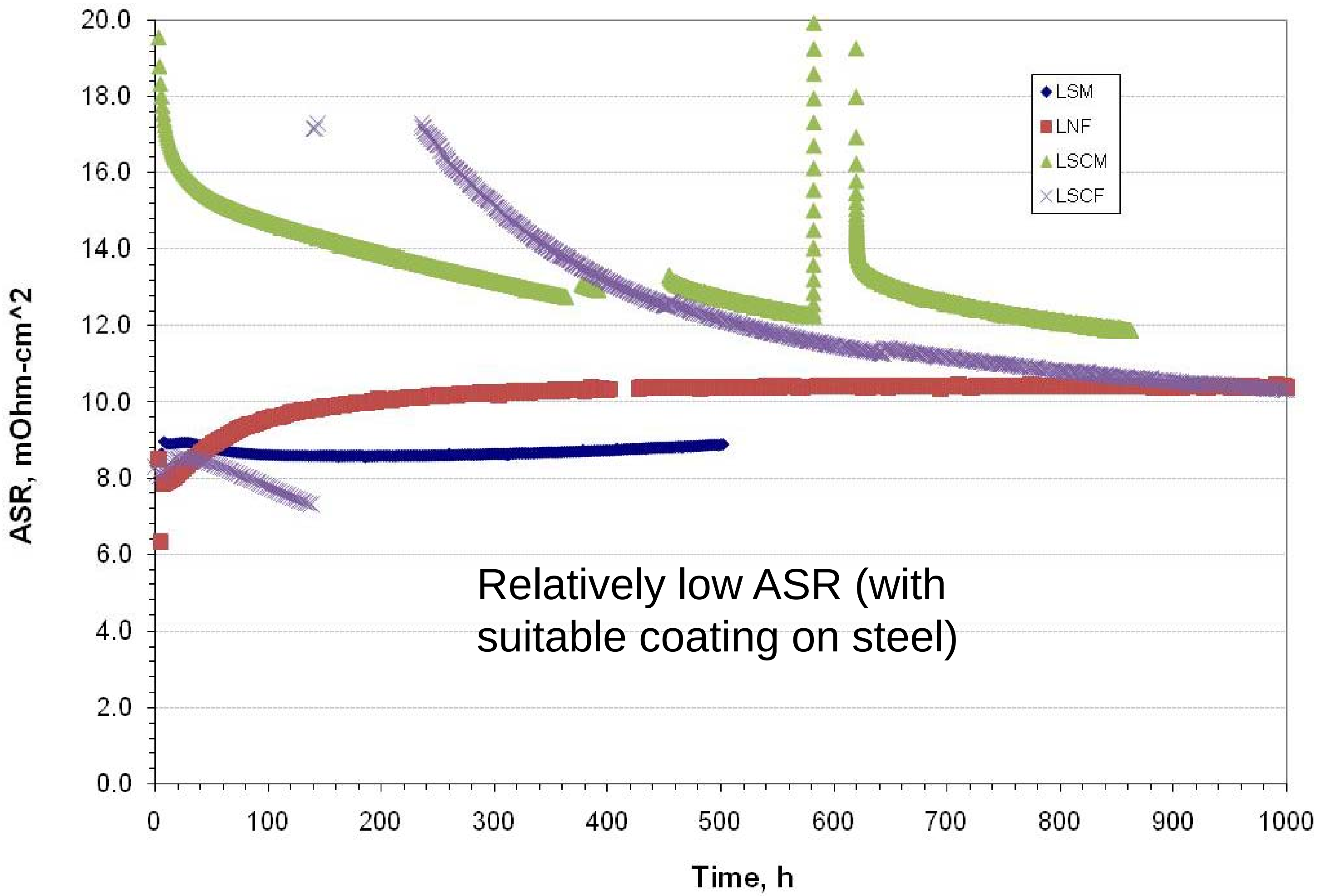


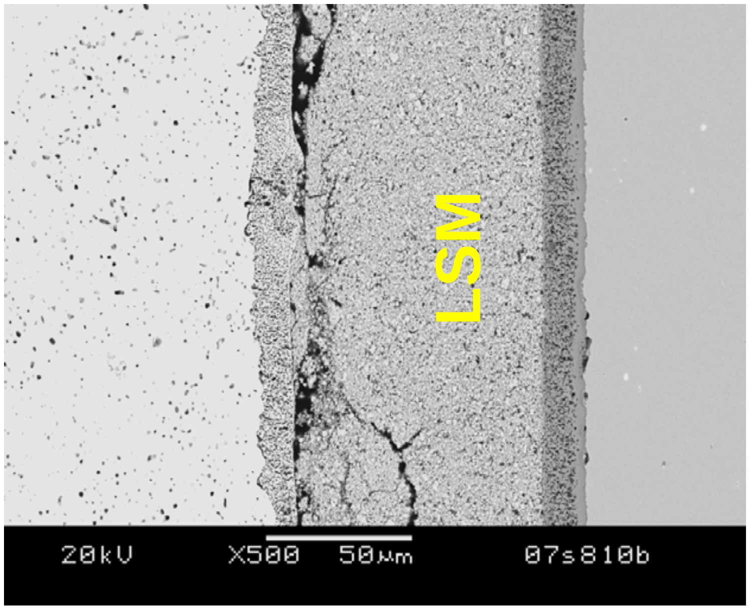
Current Density: 0.5A.cm^{-2}

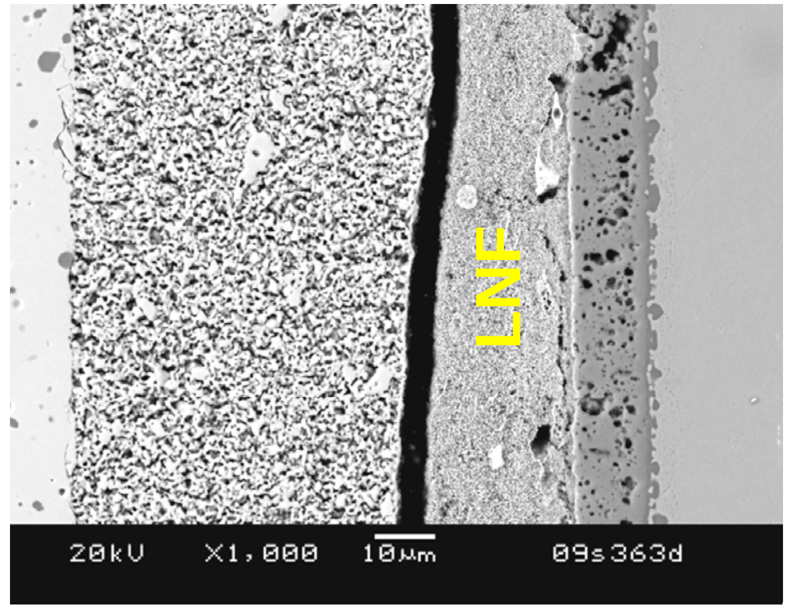


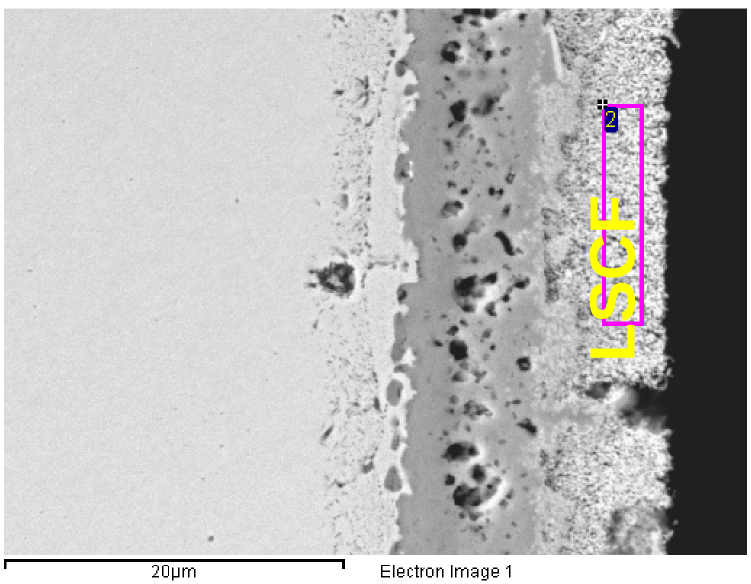
ASR Stack (3 sets)

Conventional Contact Pastes: LSM, LSCM, LNF and LSCF









Conventional contact layers exhibit low intrinsic strength and/or bonding strength

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Approaches

- Sintering Aids
  - Reduce the sintering temperature of contact materials to obtain increased density/conductance/strength
- Reaction-Sintering
  - Similar to process used to prepare MnCo spinel coatings for steel interconnects
  - Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
  - Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification
- Transition Layers
  - Apply to cathode and/or interconnect coating to enhance bond strength of contact material
  - Used in conjunction with either of above approaches

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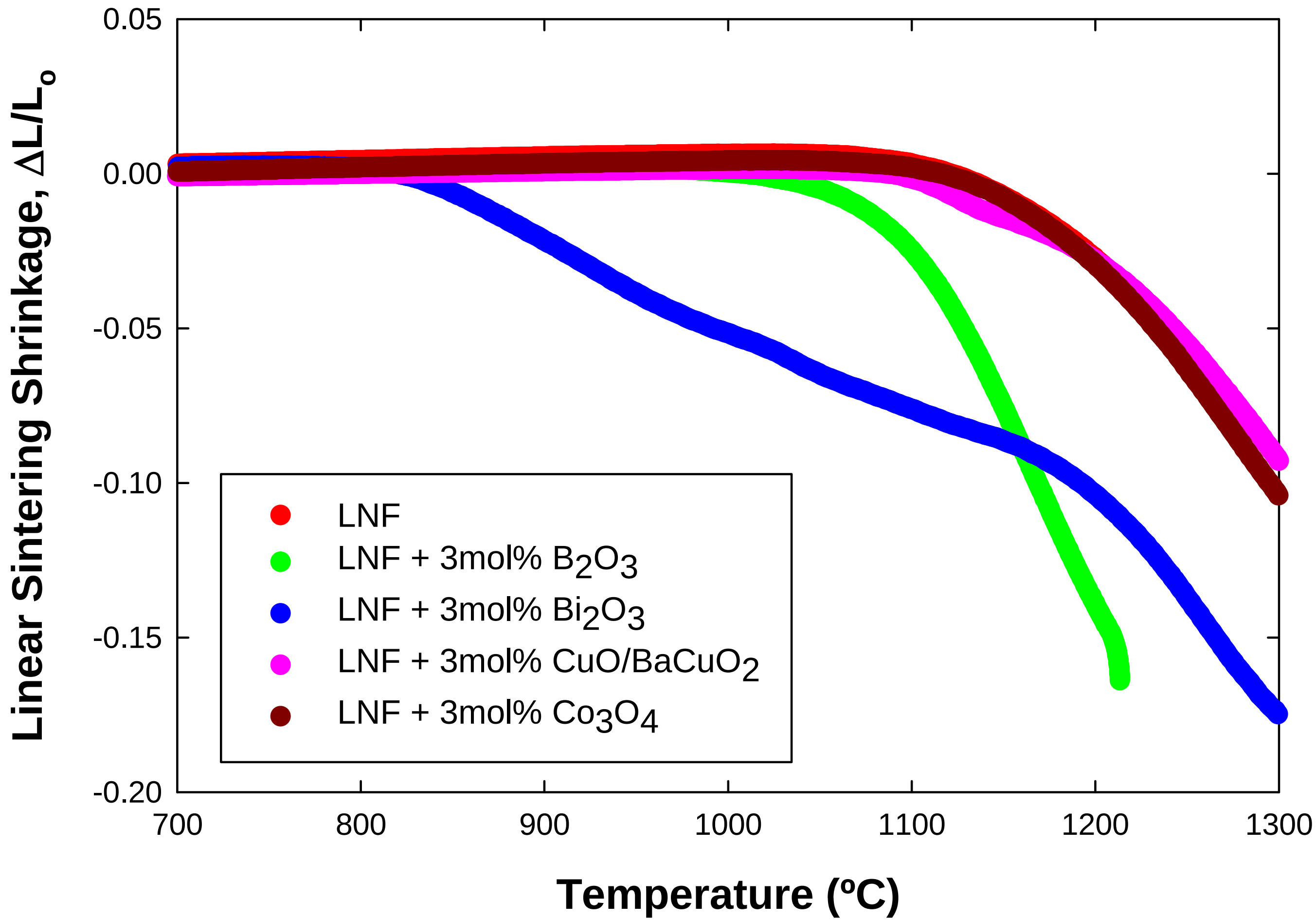
Effect of Sintering Aids on LNF-60/40: Sintering Activity



Dilatometric measurements: Constant heating rate of 3ºC/min

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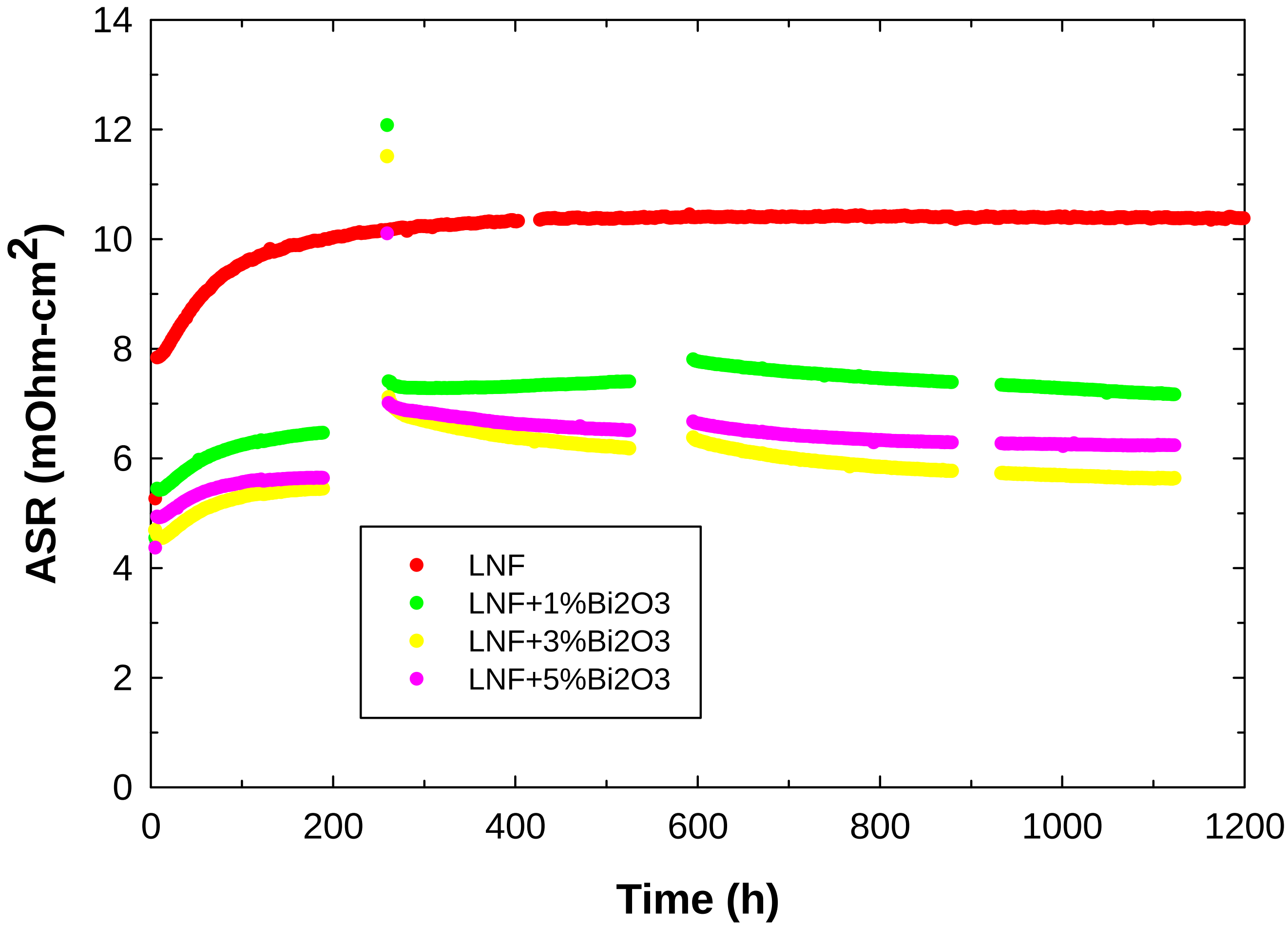
Effect of Sintering Aids on LNF-60/40: Electrical Resistance



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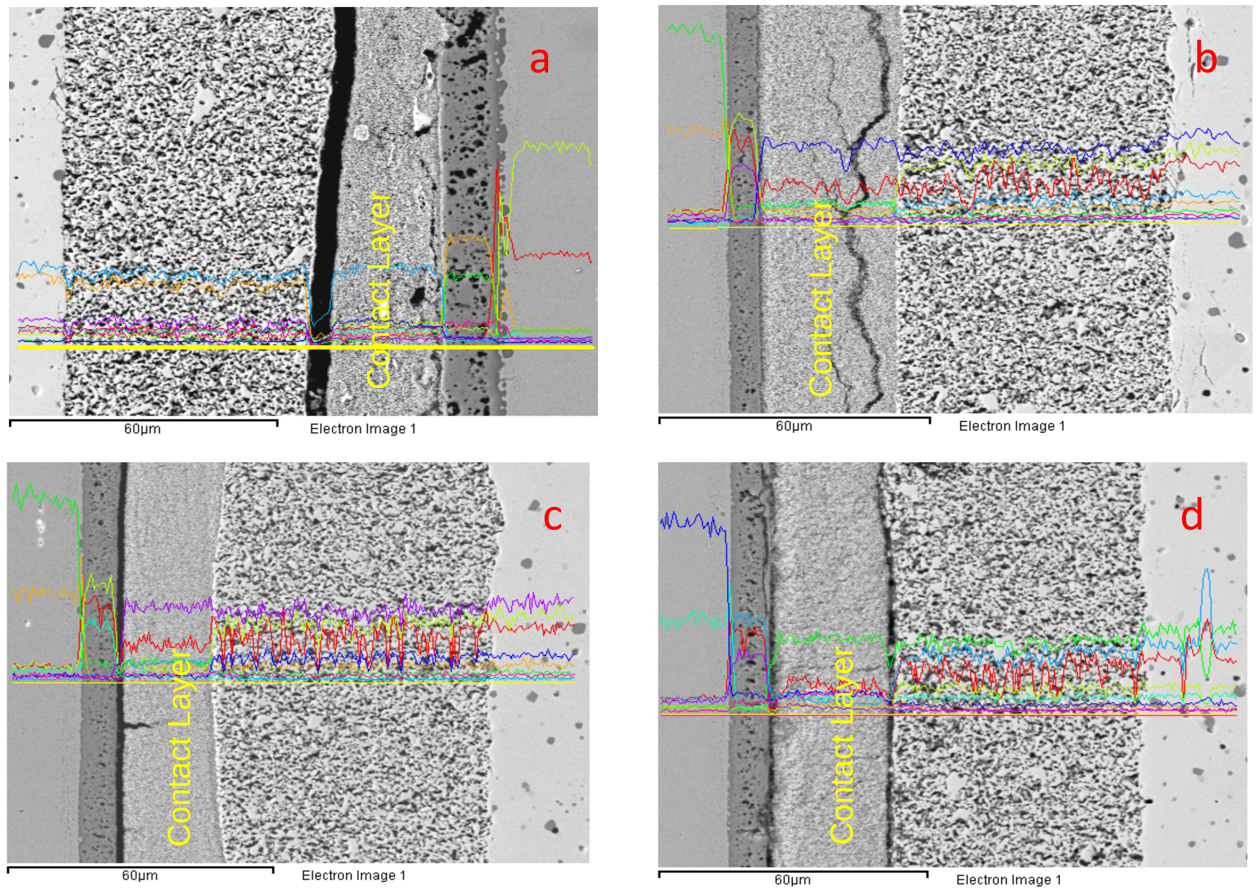
Minimal improvement in density, bond strength



Cross-section SEM images of the samples after the contact ASR measurements:
(a) LNF only, (b) LNF+1mol% Bi_2O_3, (c) LNF+3mol% Bi_2O_3, and (d) LNF+5mol% Bi_2O_3.

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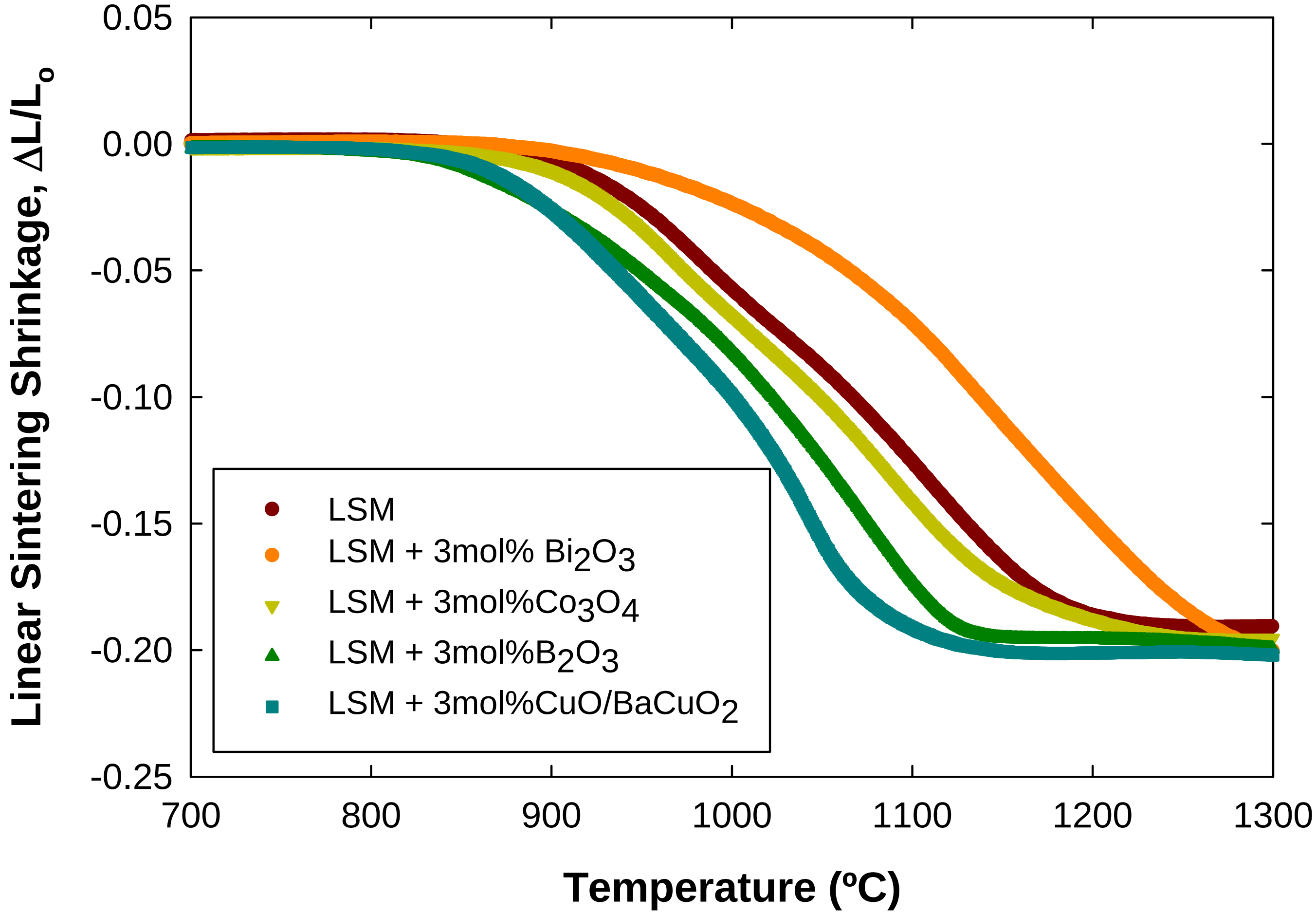
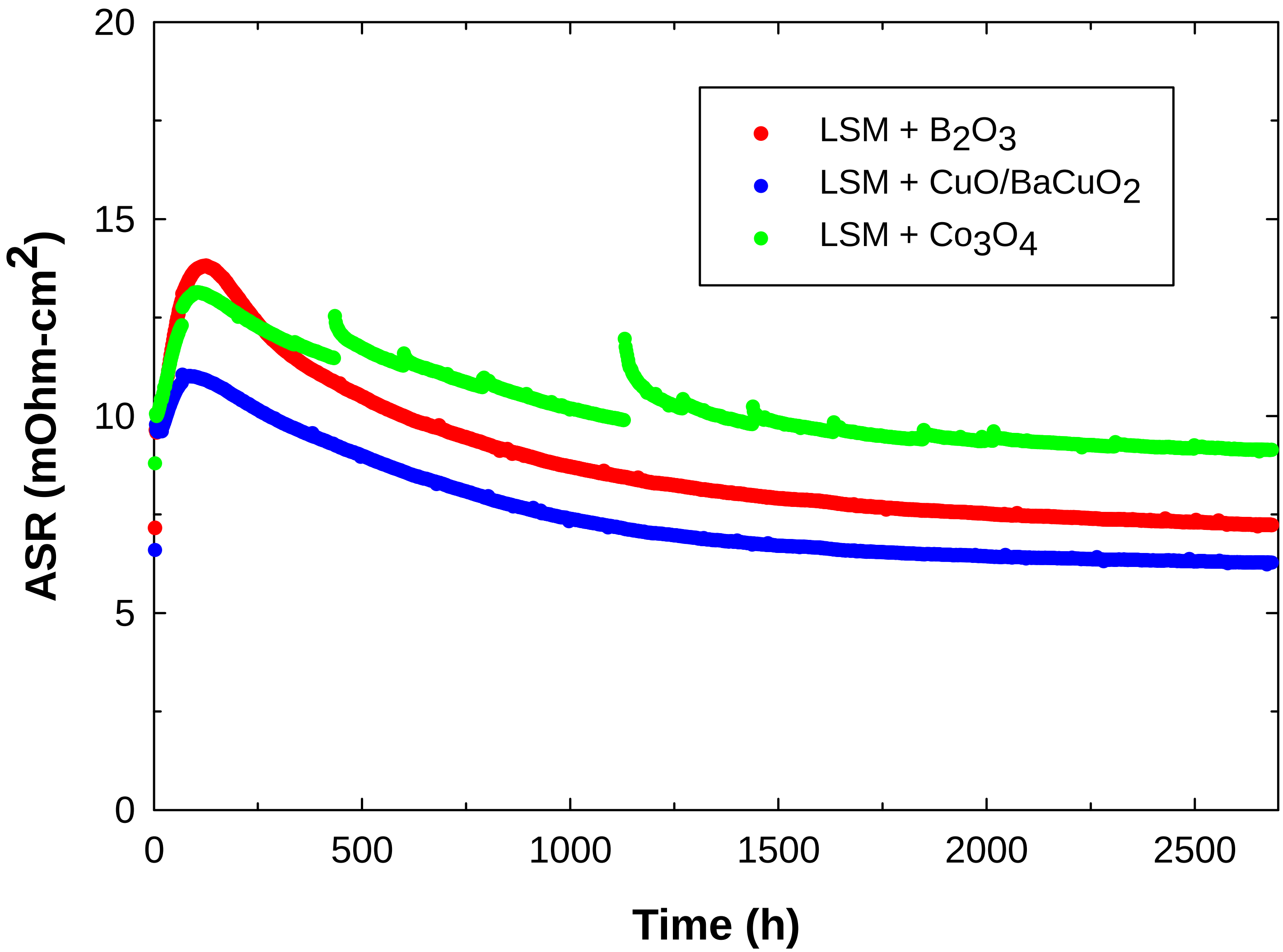
Effect of Sintering Aids on LSM-20: Sintering Activity



Dilatometric measurements: Constant heating rate of 3ºC/min

Effect of Sintering Aids on LSM-20: Electrical Resistance



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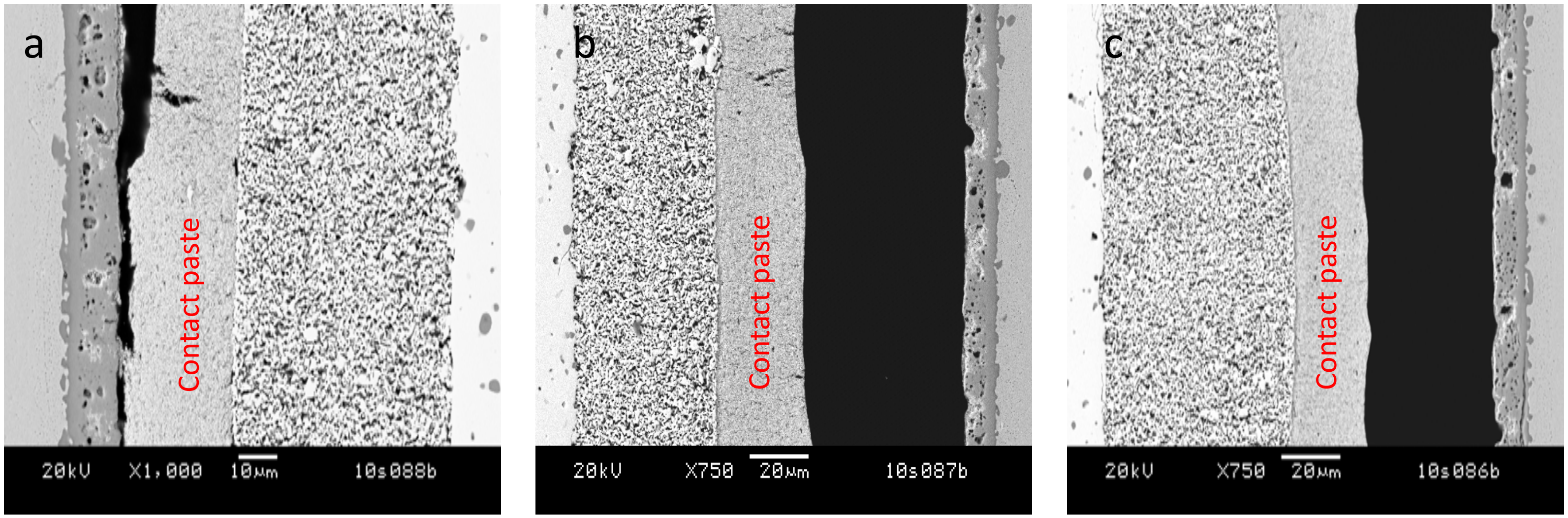
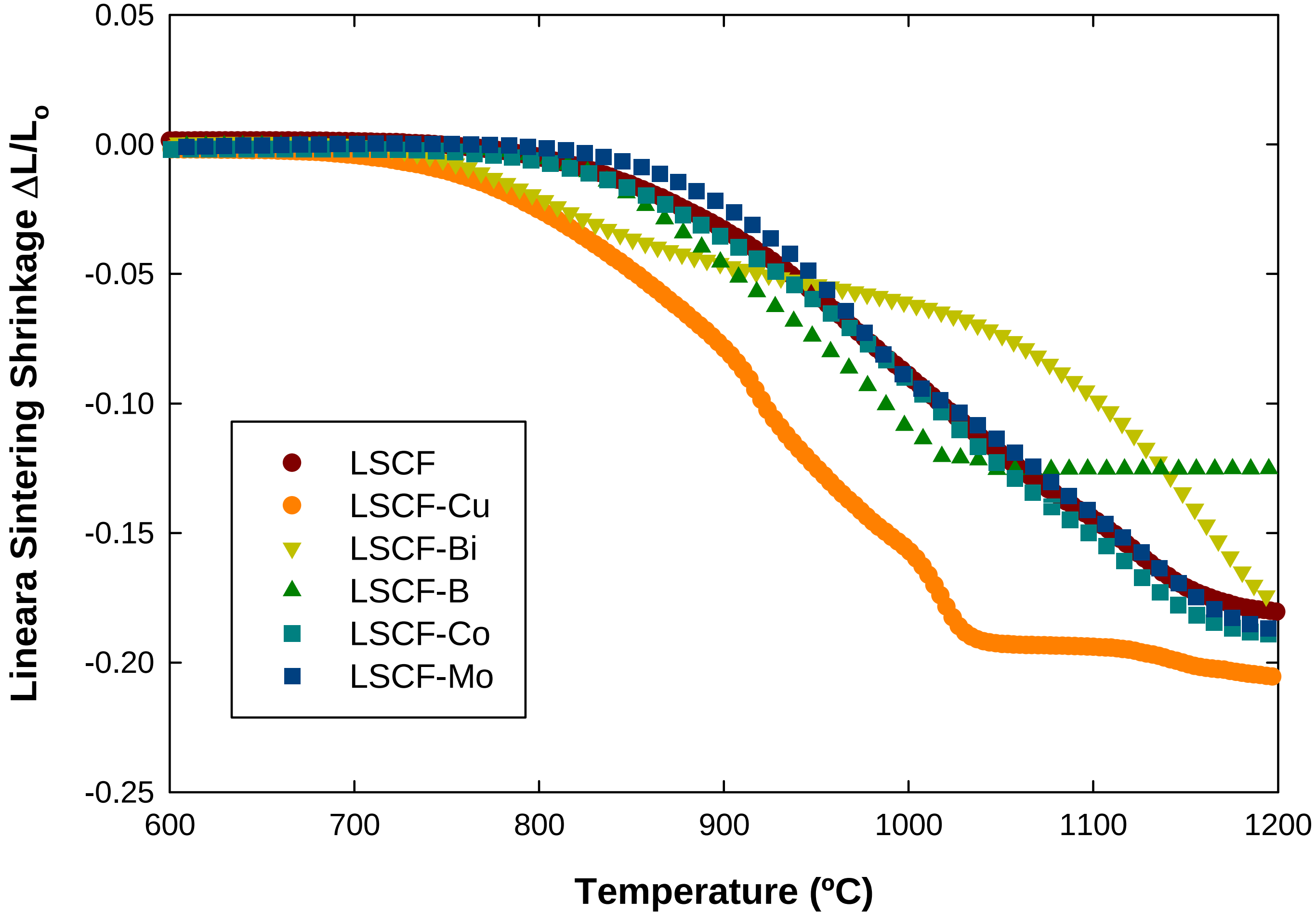


LSM+B_2O_3 LSM+$BaCuO_2$ LSM+Co3O4

Sintering Curves of LSCF-6428 with Various Additives



3 mol% additions

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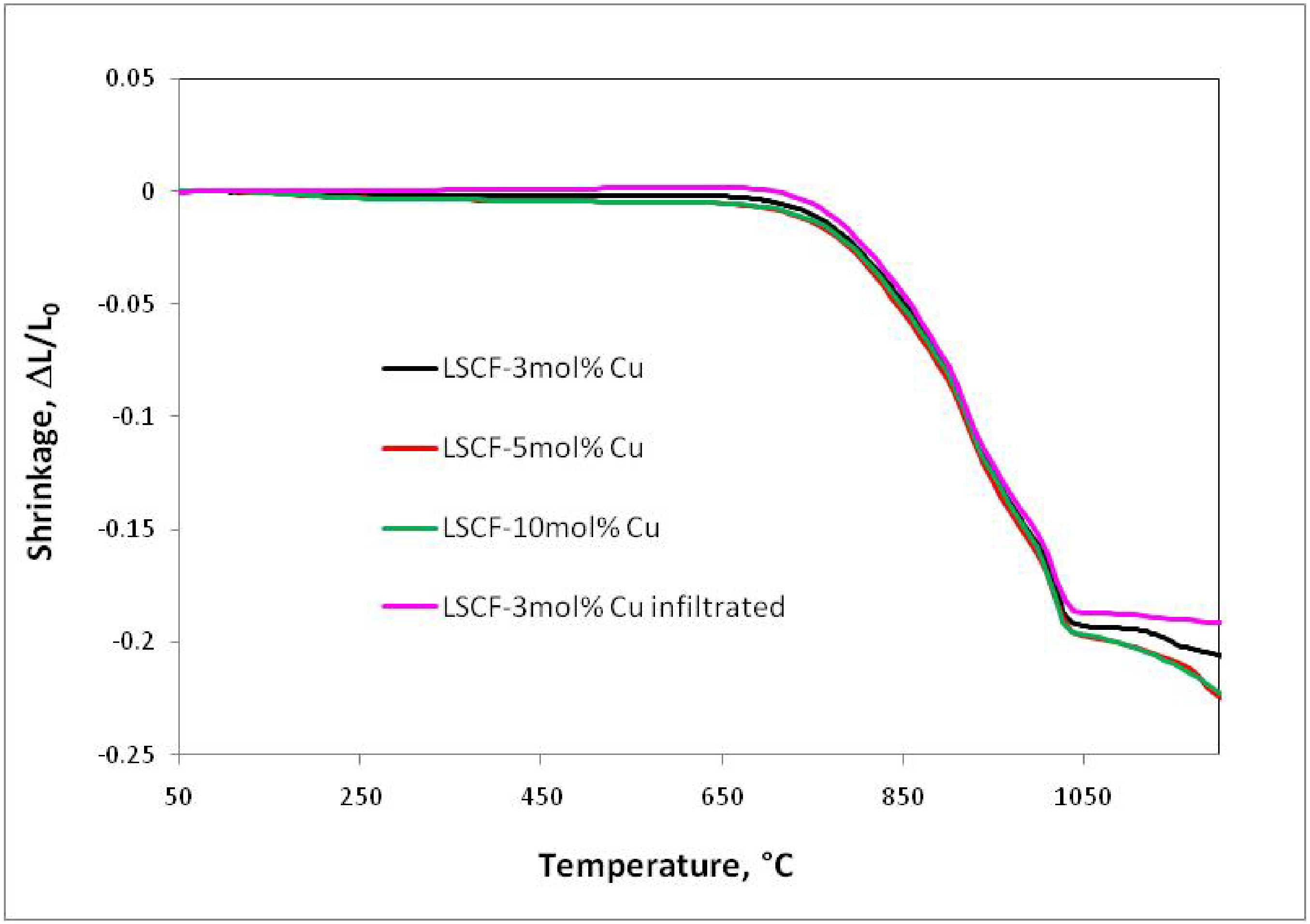
Sintering Curves of LSCF with Various Amounts of CuO Additions



LSCF with infiltrated CuO did not show significant difference of sintering activity with powders prepared by mixing LSCF with CuO

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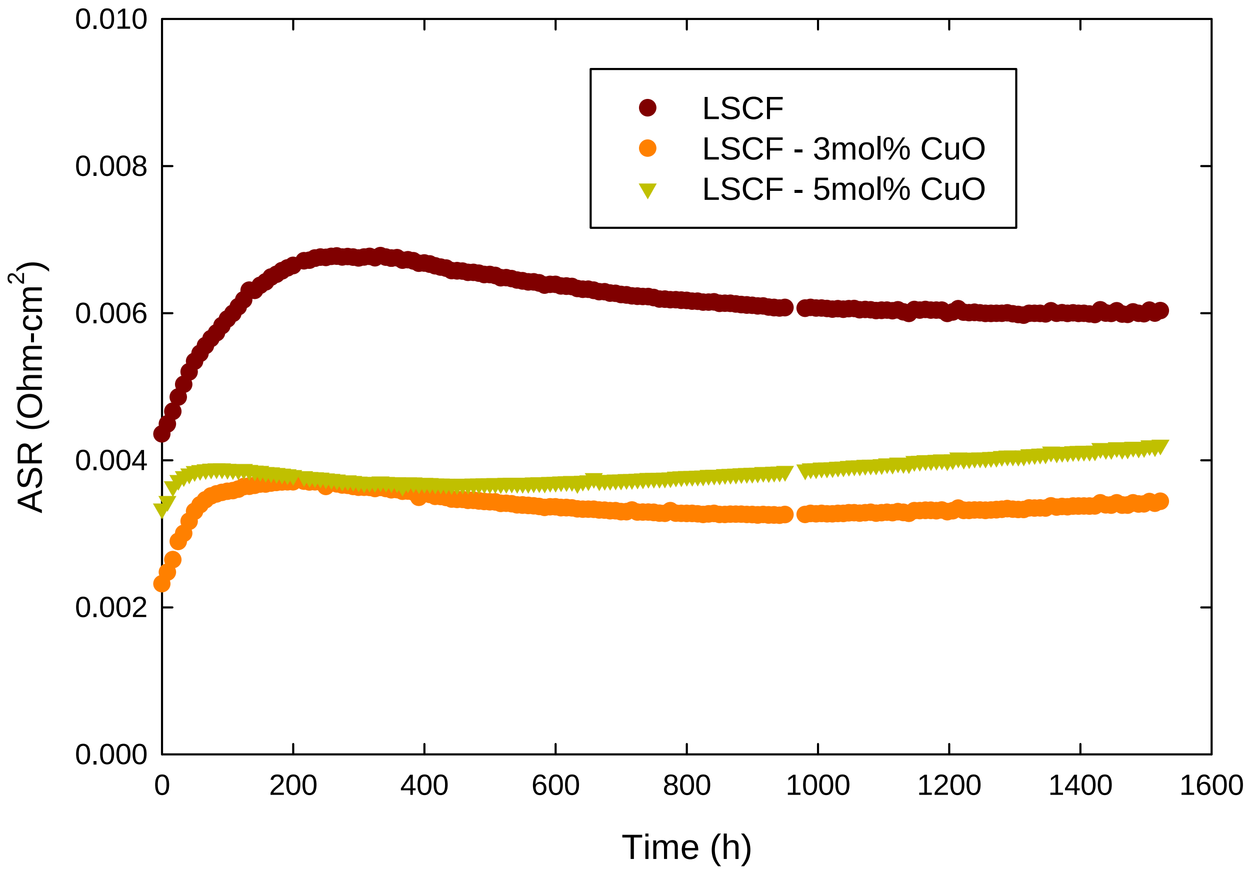
Contact ASR Results of LSCF with Sintering Aid CuO

(441-0.02MC|LSCF-CuO|LSCF)



Will perform SEM to evaluate densification, bonding

Approaches

- Sintering Aids
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- Reaction-Sintering
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  - Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
  - Enthalpy of reaction provides additional driving force (besides surface energy reduction) for densification
- Transition Layers
  - Apply to cathode and/or interconnect coating to enhance bond strength of contact material
  - Used in conjunction with either of above approaches

Reaction Sintering

- Successfully used in fabricating MnCo spinel coatings

$$MnO + Co + 3.5O_2 \rightarrow 2(Mn_{0.5}Co_{0.5})O_4$$

- Driving force for densification:
  - Reduction of surface energy (~75 J/mol)
  - Enthalpy of formation (~500 kJ/mol)
- 2 methods:
  - Oxidation/Reduction
    - Reduction of complex oxide to binary oxides, metals
    - Re-oxidation to simultaneously densify coating and form complex oxide
  - Direct fabrication from precursor oxides and/or metals
    - Single oxidation heat treatment

Primary systems of interest

- Reaction sintered $(Ni,Co)O_x$ with fillers (tailor CTE, reduce cost)

- Reaction sintered $Mn_{1.5}Co_{1.5-x}Cu_xO_4$

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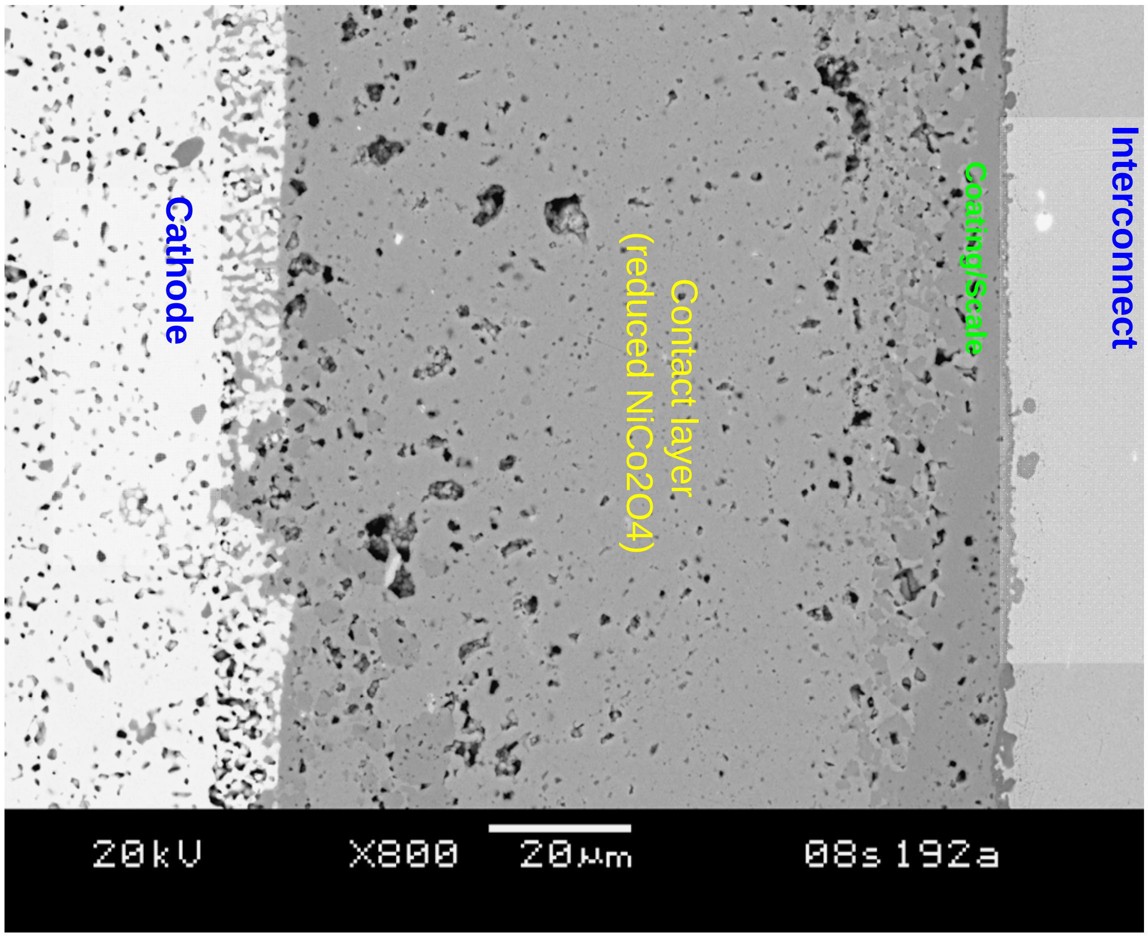
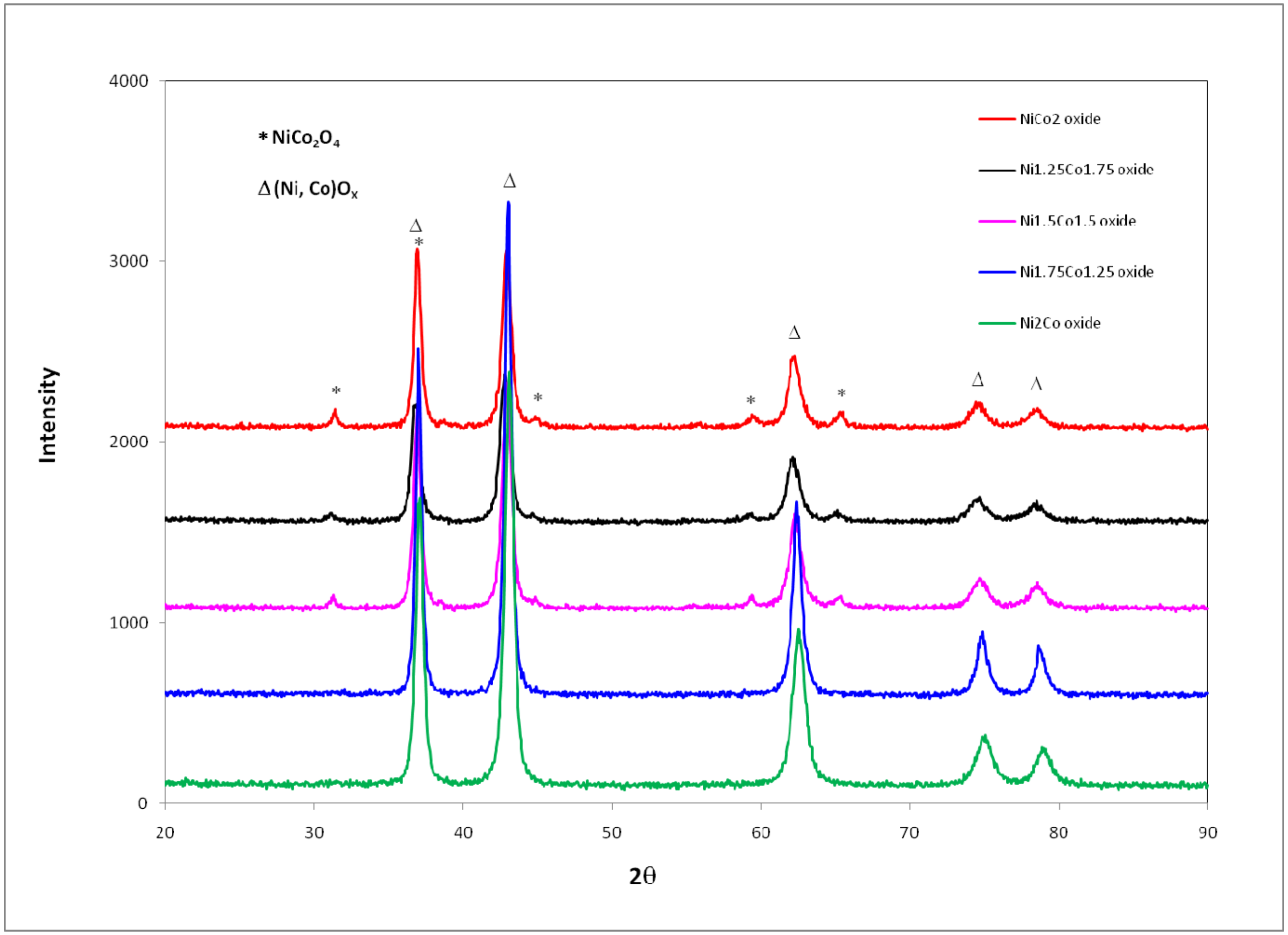
Reaction-Sintered Ni-Co Oxide (Ni:Co=1:2)



Reaction Sintered (Ni,Co)O_x

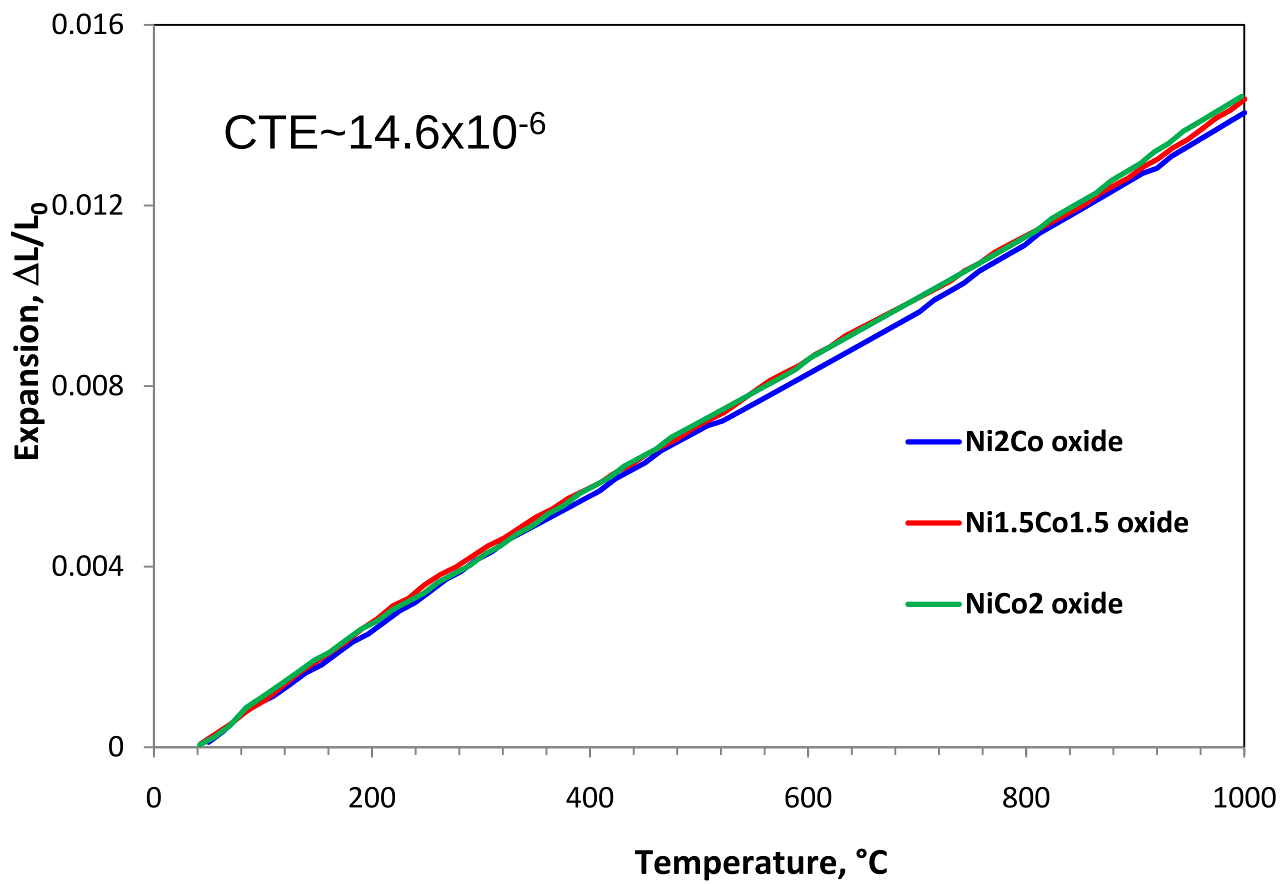
- Reduced (Ni, Co) O_x
  - 5 compositions with Ni: Co=1:2, 1.25:1.75, 1.5:1.5, 1.75:1.25 and 2:1
- Characterization
  - Phase analysis (XRD)
  - CTE (Dilatometry)
  - Electrical Conductivity
  - ASR
  - Microstructure
  - Mechanical Strength
- Approach:
  - Select optimum (Ni,Co)O_x composition
  - Add alloying elements if needed for higher conductivity
  - Add fillers to reduce cost; also can adjust CTE (if needed)

XRD of Ni-Co oxides



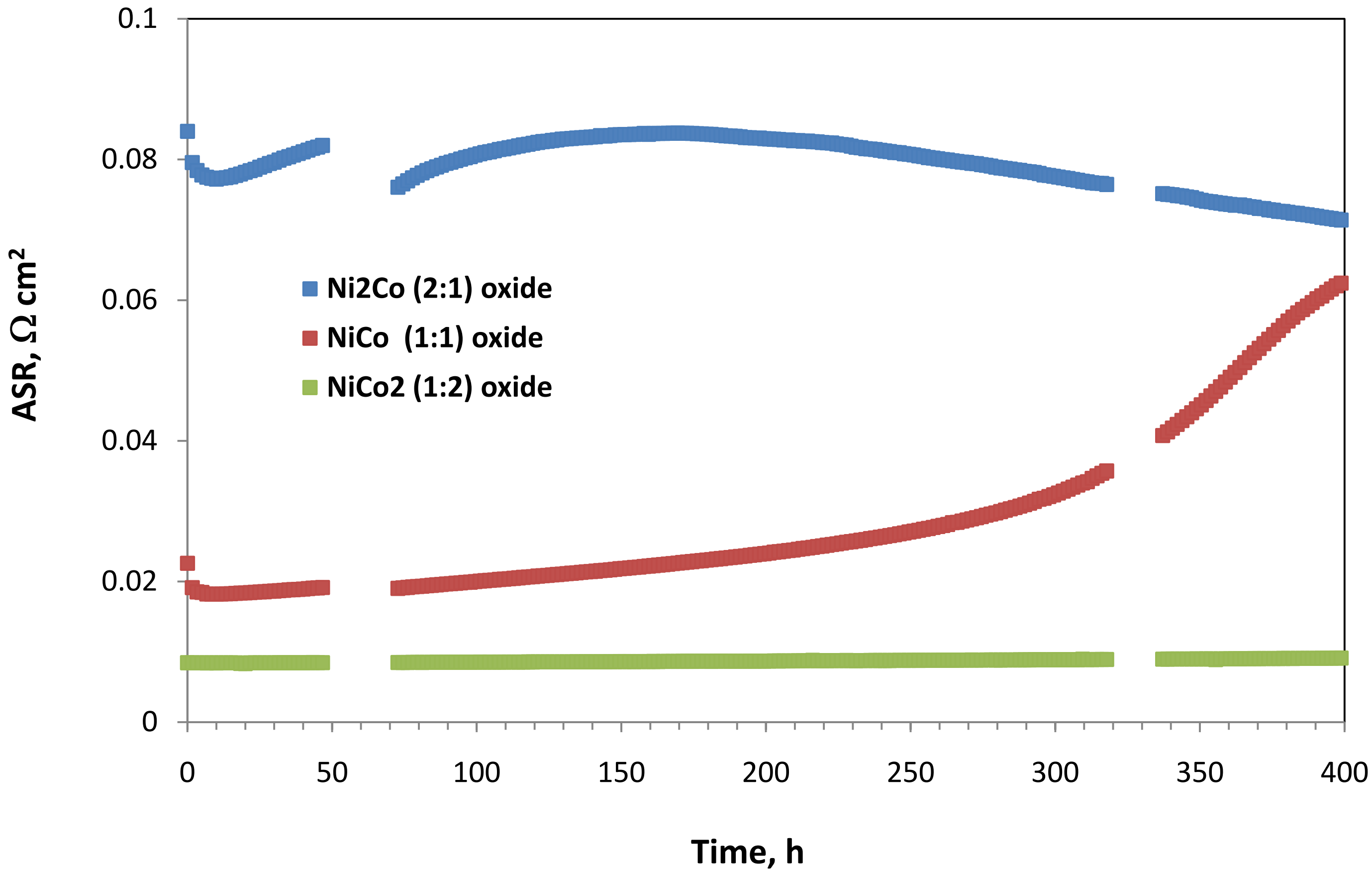
- Powders with various Ni:Co ratios were synthesized by GNP process
- Powders were calcined at 850C for 5h, then attrition-milled for 7h
- The majority of the powder is (Ni,Co)O

CTE of Ni-Co Oxides



Will investigate addition of fillers to reduce CTE and cost

ASR results of NiCo oxides contact layer with various Ni:Co ratios



Abnormal behaviors for Ni2Co and NiCo oxides were observed, with current density over $0.1 A/cm^2$ resulting in oscillating ASRs.

New Compositions in Mn-Co-Cu System

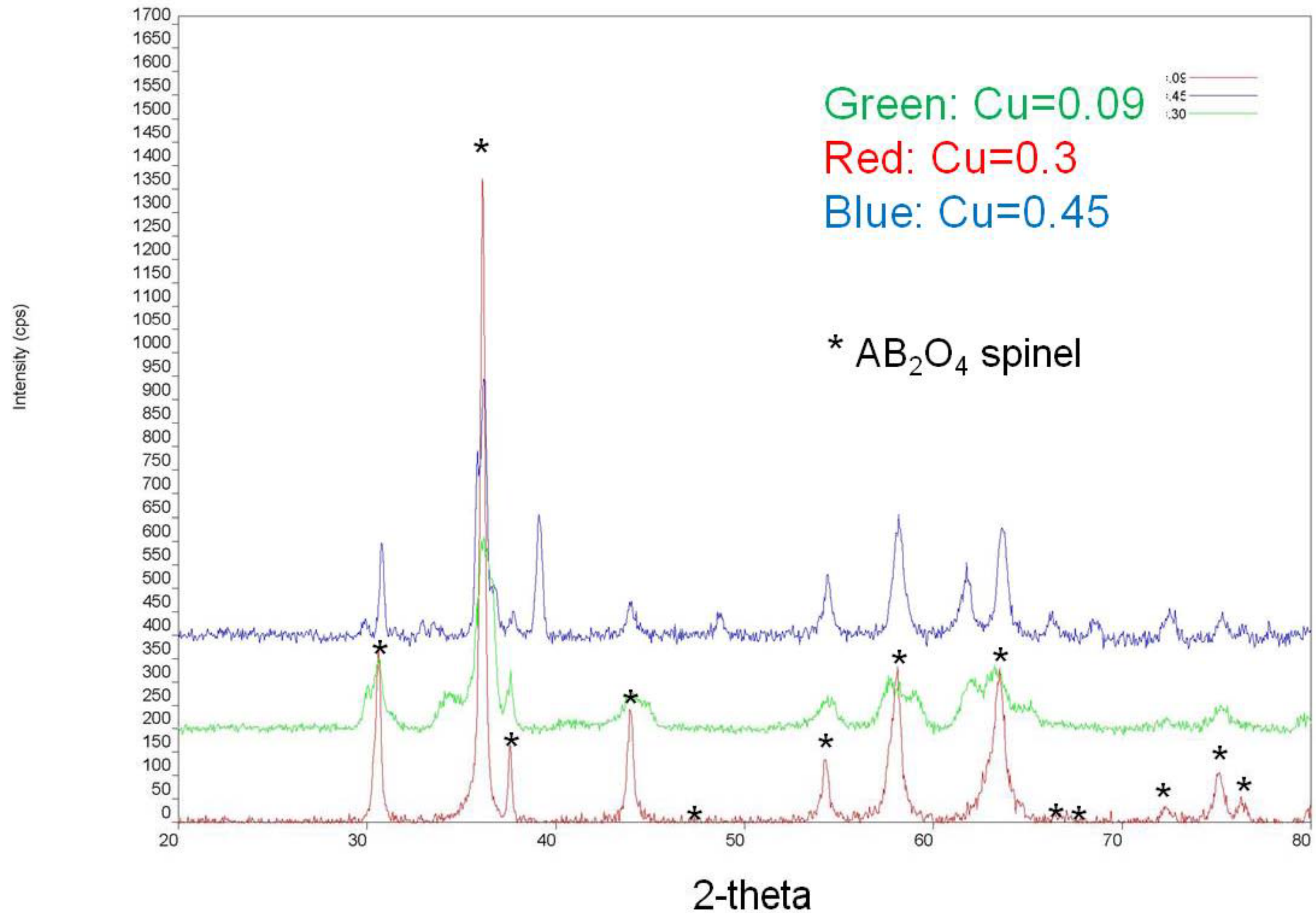
Precursor	Compositions Mn:Co:Cu	Current Status
Oxide Powders	1.5:1.41:0.09 (3mol% Cu) 1.5:1.35:0.15 (5mol%Cu) 1.5:1.2:0.3 (10mol%Cu) 1.5:1.05:0.45 (15mol%Cu)	Powder synthesis and reduction
Metal Mixtures	Same as oxide powders	Ball milling

Characterization:

- Phase analysis (XRD)
- CTE (Dilatometry)
- Electrical Conductivity
- ASR
- Microstructure
- Mechanical Strength

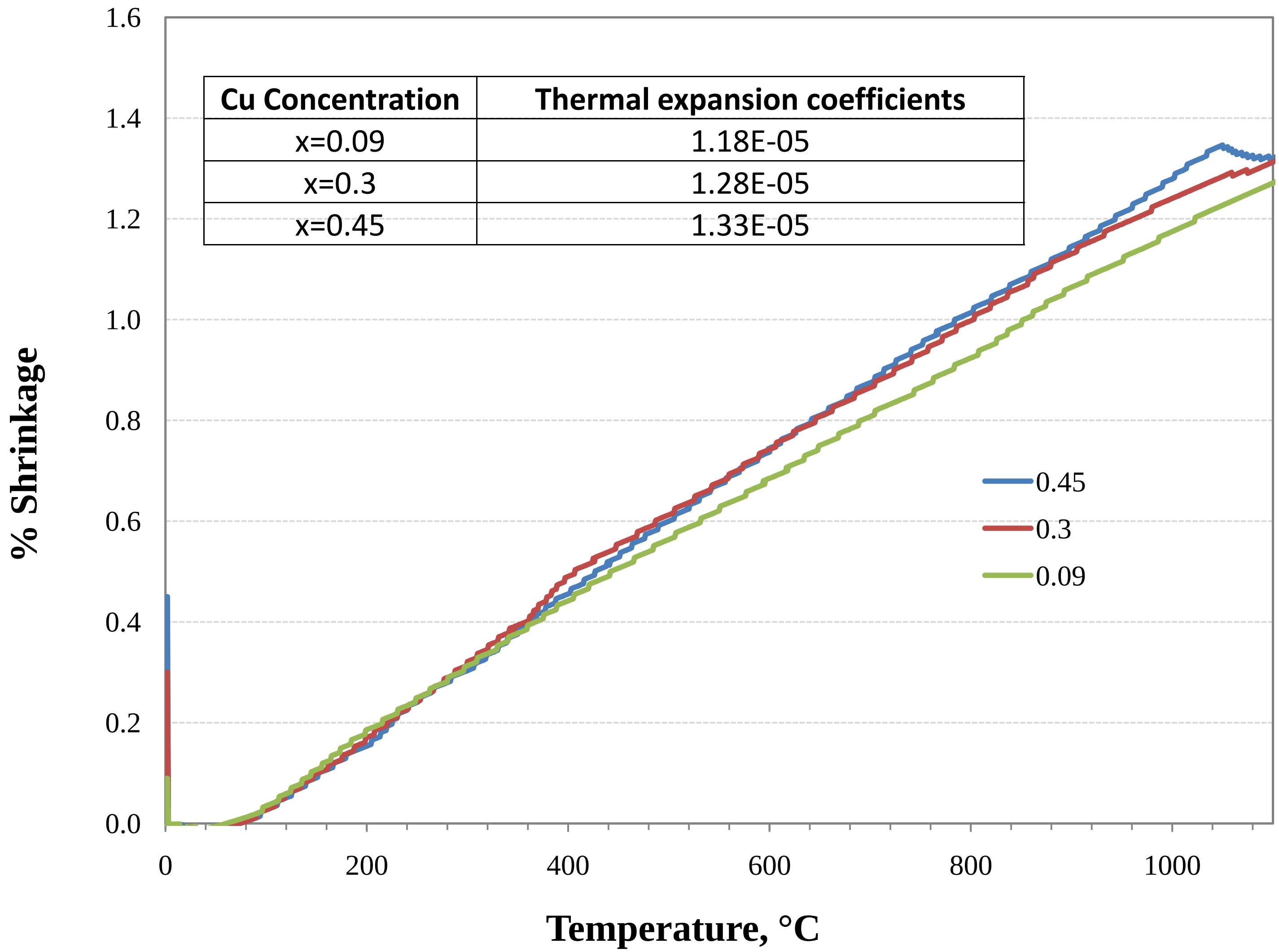
Approach: Select optimum composition, investigate fillers to reduce cost and adjust CTE (if needed)

XRD of dense bars of $Mn_{1.5}Co_{1.5-x}Cu_xO_4$ Oxides after sintering shrinkage tests



Non-spinel peaks (CuO_x) appear when x=0.45

CTE Curves of $Mn_{1.5}Co_{1.5-x}Cu_xO_4$ Oxides



Cu Concentration	Thermal expansion coefficients
x=0.09	1.18E-05
x=0.3	1.28E-05
x=0.45	1.33E-05

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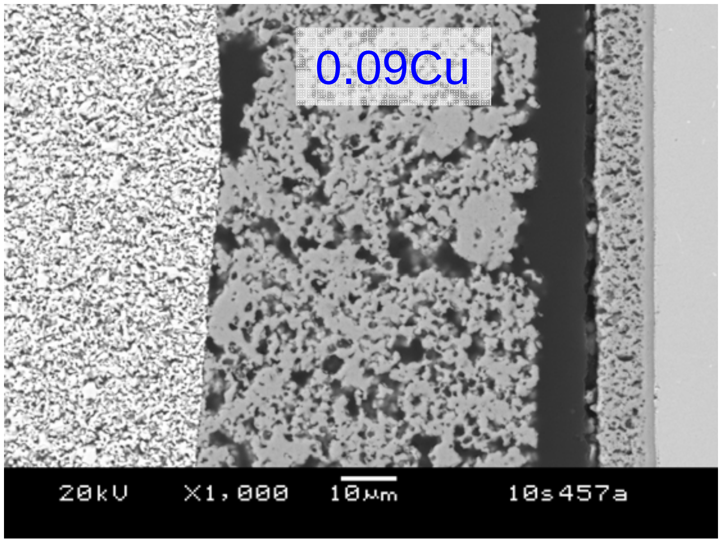
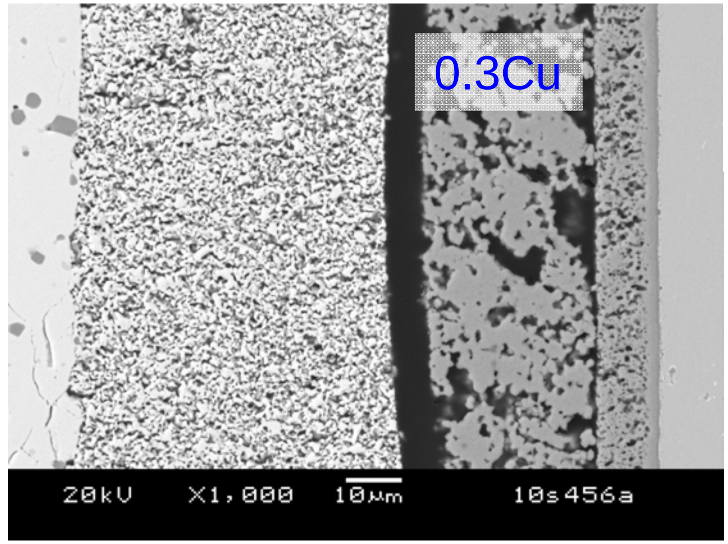
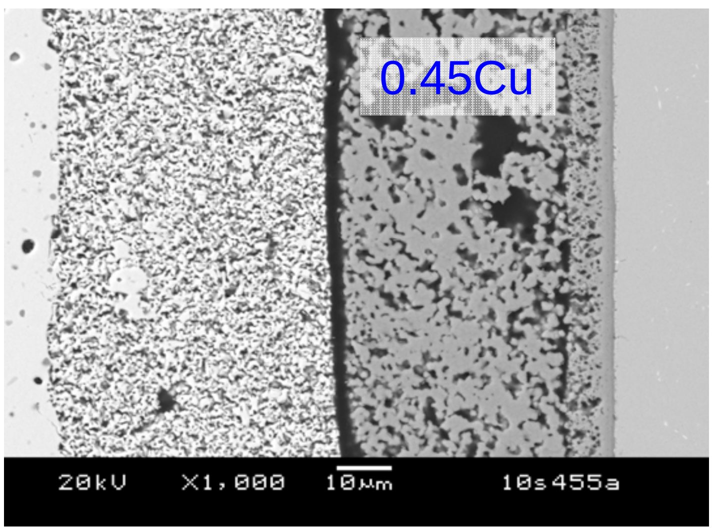
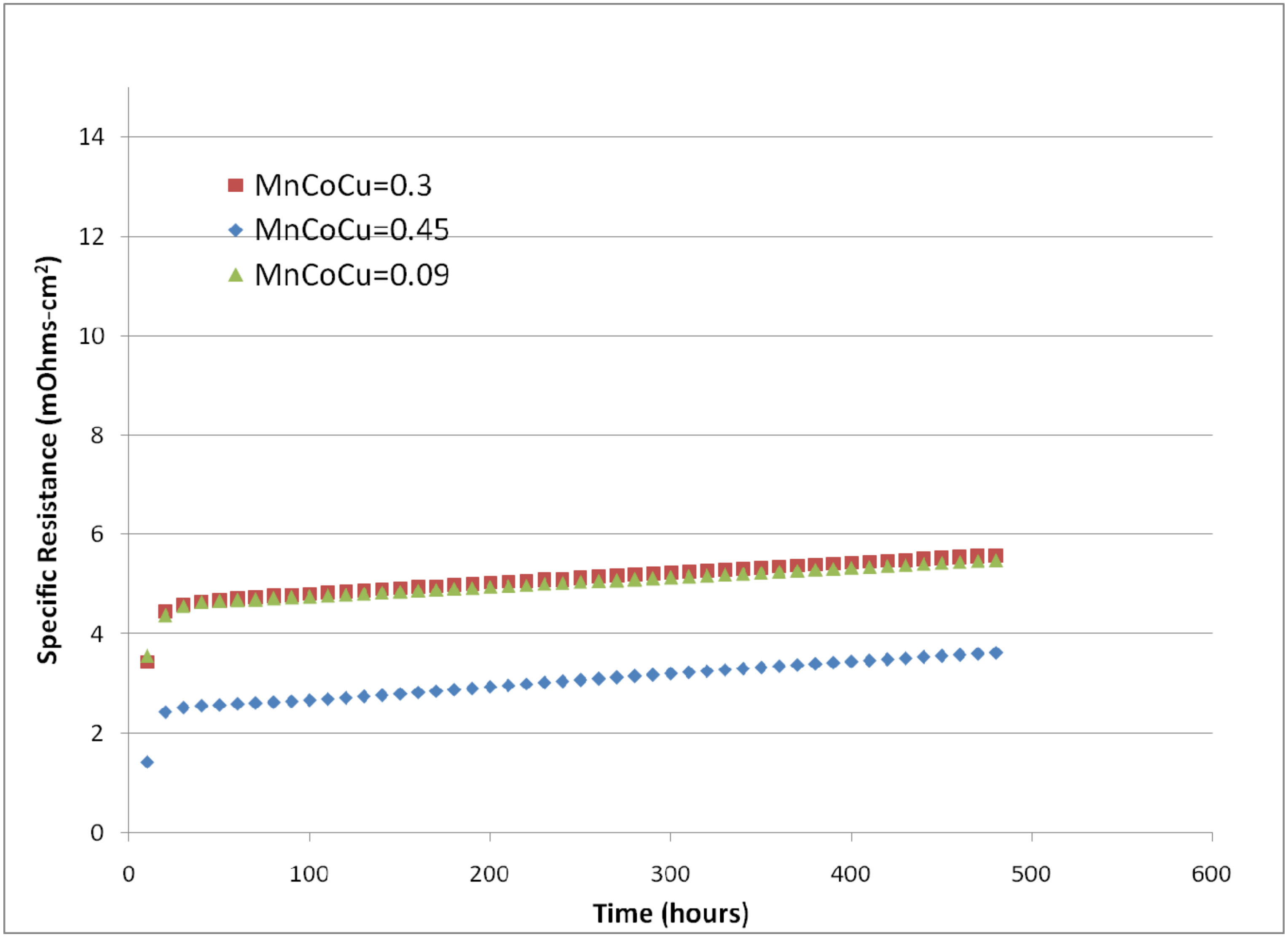
SEM Images of Reduced $Mn_{1.5}Co_{1.5-x}Cu_xO_4$ Powders as Contact Pastes (800ºC for 100hrs)







ASR Test Results for Mn-Co-Cu Contacts



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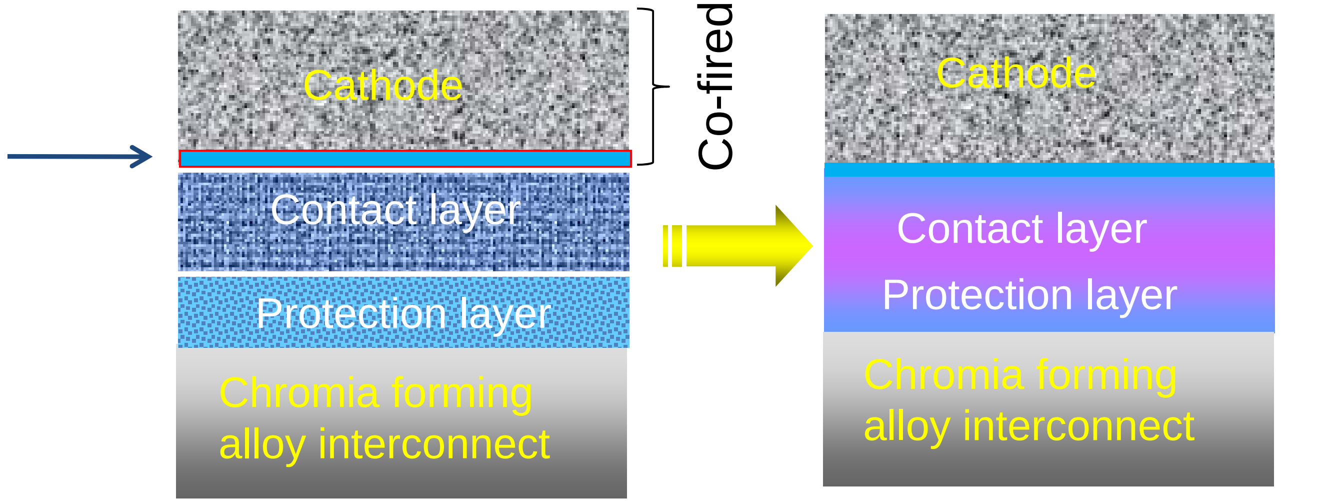
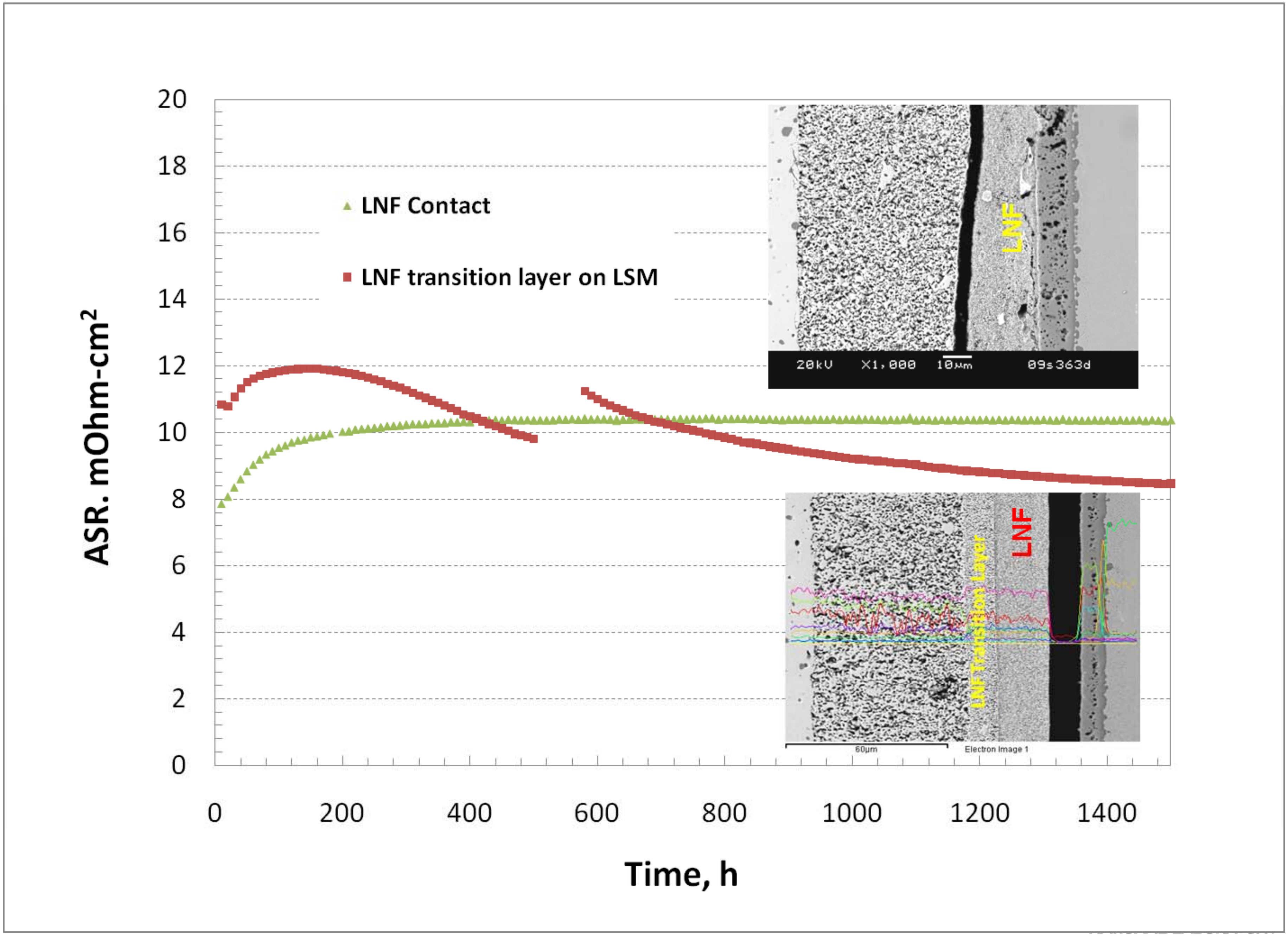
Transition Layer to Enhanced Bonding Strength between Cathode and Contact Layer



Before assembly

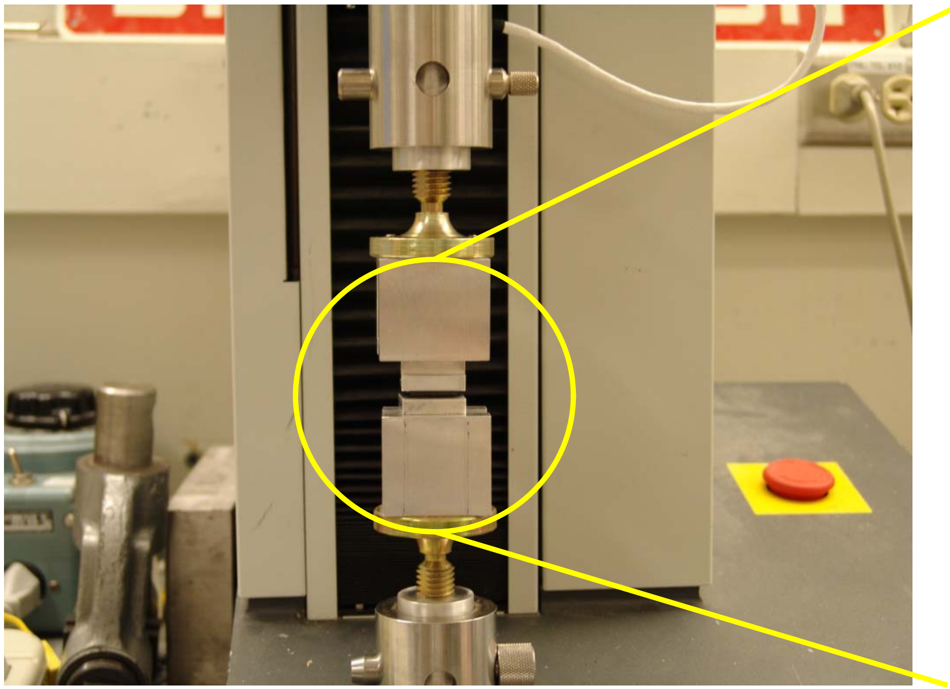
During stack fabrication

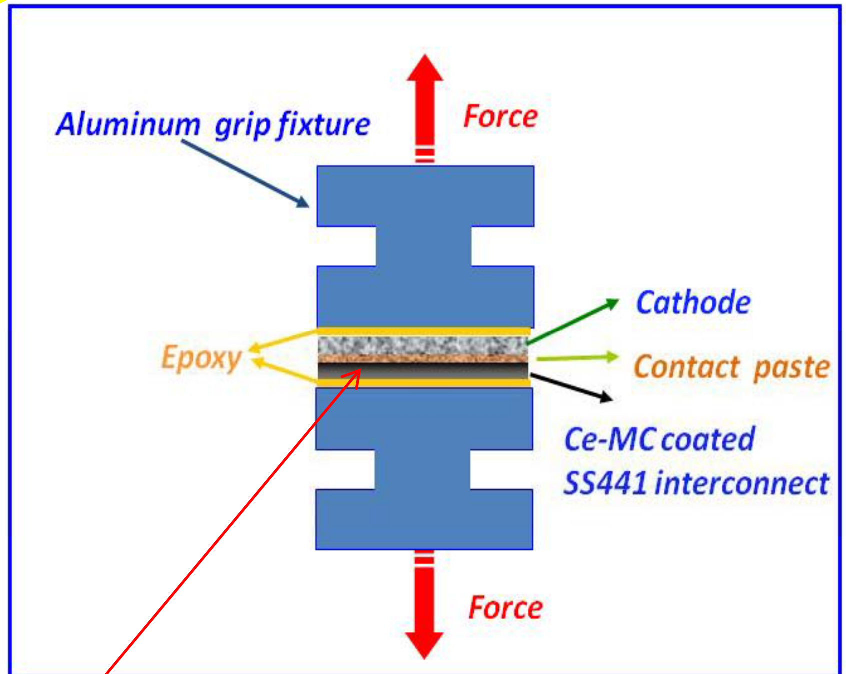
- Approach: Co-sintered transition layers may help to increase bonding strength between interconnect
- Example: Co-sinter thin layer of contact material on cathode during cathode sintering heat treatment
- Enhanced chemical bonding of like materials may strengthen cathode/contact interface

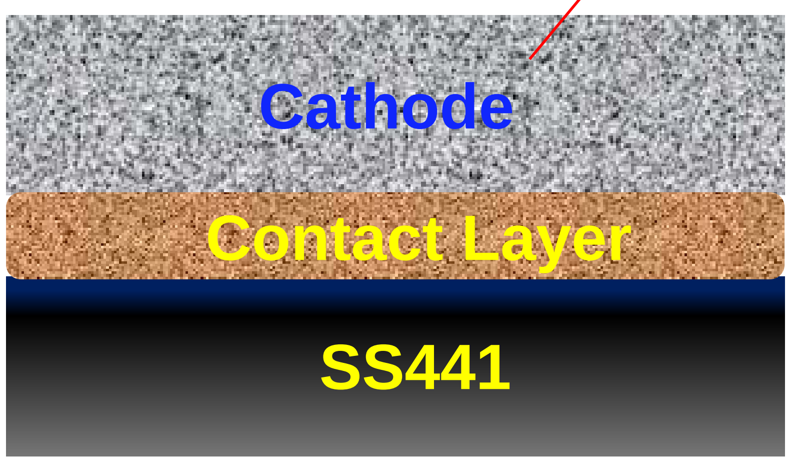


LNF Contact
LNF transition layer on LSM
ASR. mOhm-cm2
Time, h
LNF
20kV X1,000 10µm 09s363d
LNF Transition Layer
LNF
60µm
Electron Image 1

Measurement of Mechanical Properties of Interconnect/Contact/Cathode Structure



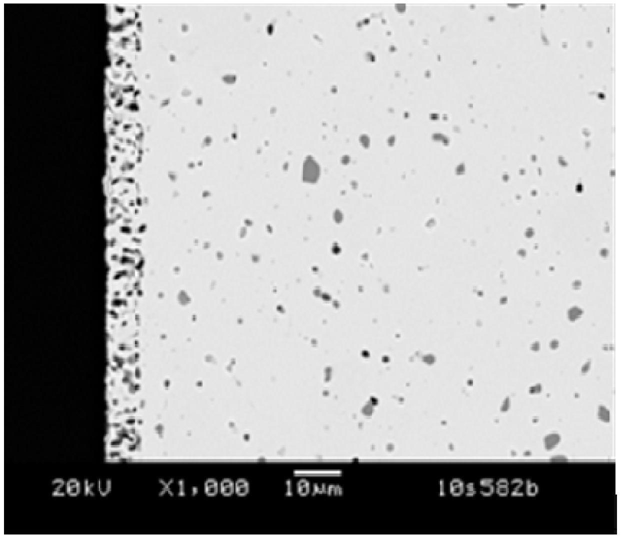




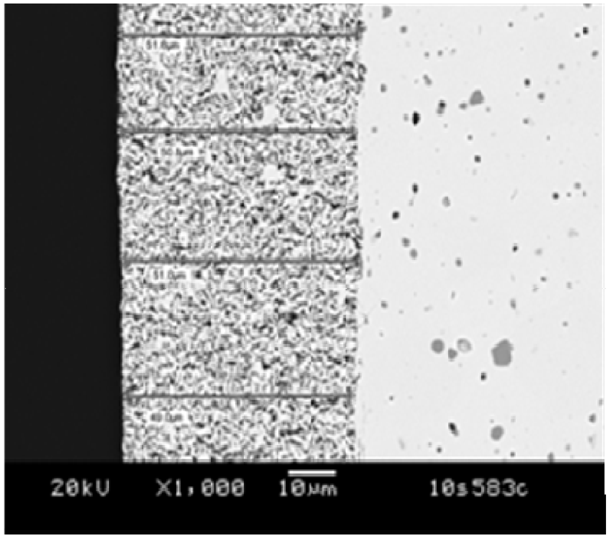
Effect of Cathode Surface Morphology on Cathode/Interconnect Bond Strength

Tensile Strength (lbs)

LSM #1	LSM #2
5.6	23.0
0.0	13.0
0.7	40.6
0.0	25.0
1.1	71.1
10.6	6.8



(a)



(b)

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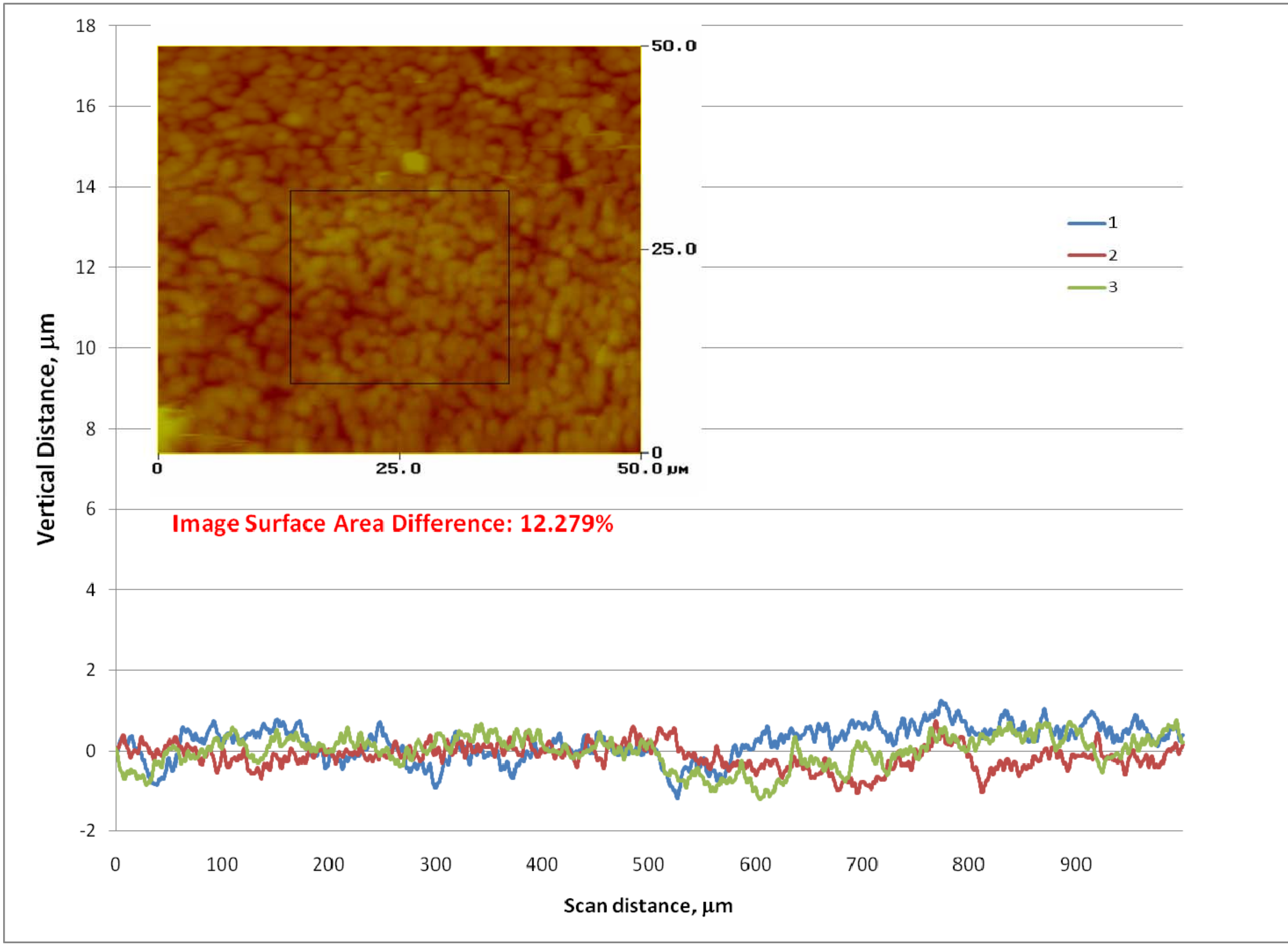
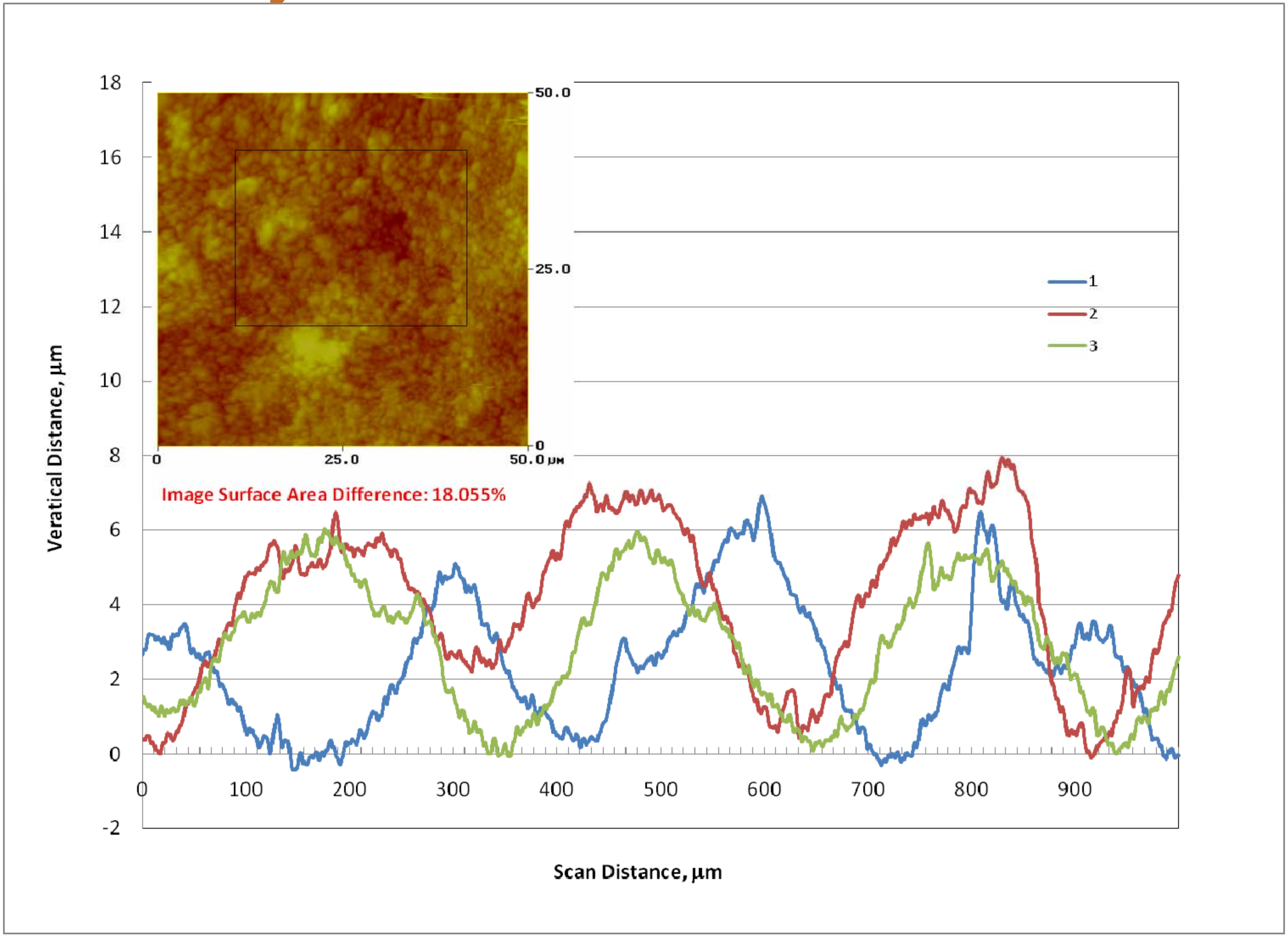
LSM-20 layer #1



LSM-20 layer #2



Summary and Future Work

- Sintering aids can provide some improvement to sintering activity of candidate contact materials at stack fabrication temperatures
- Reactive sintering approaches are being applied to Ni-Co oxide and Mn-Co-Cu oxide systems.
- Above approaches result in very low cathode-to-interconnect ASRs
- Transition layers may reduce contact resistance and reinforce bonding strength between cathode and interconnect.
- Tensile testing of cathode/contact/interconnect structures has been initiated.
  - Determine “weak link”: bulk or interfacial bonding
  - Effects of cathode/coating surface morphology
  - Effects of contact materials composition/processing

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- NETL: Briggs White, Travis Shultz, and Wayne Surdoval
- PNNL: Jim Coleman, Shelley Carlson, Nat Saenz, Rick Williford