Development of Cathode-Interconnect Contact Materials for SOFC

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Richland, WA 99352

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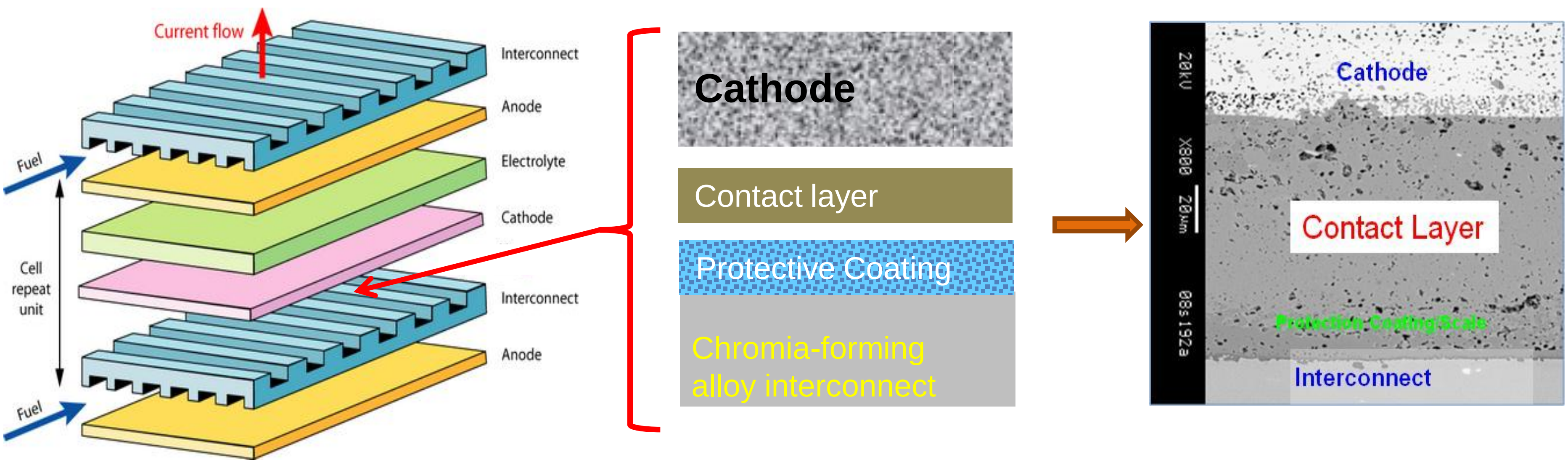
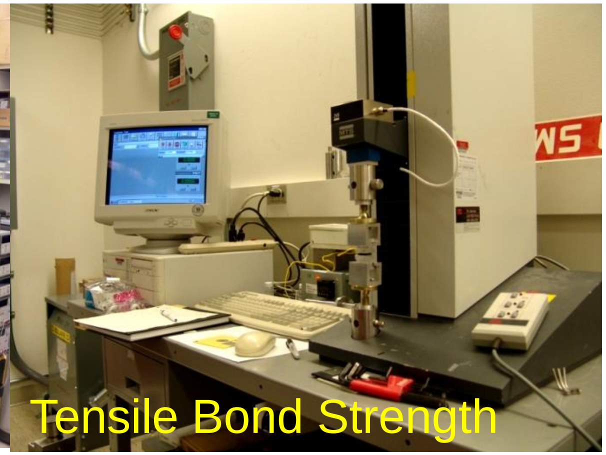
Cathode-Interconnect Contact Materials

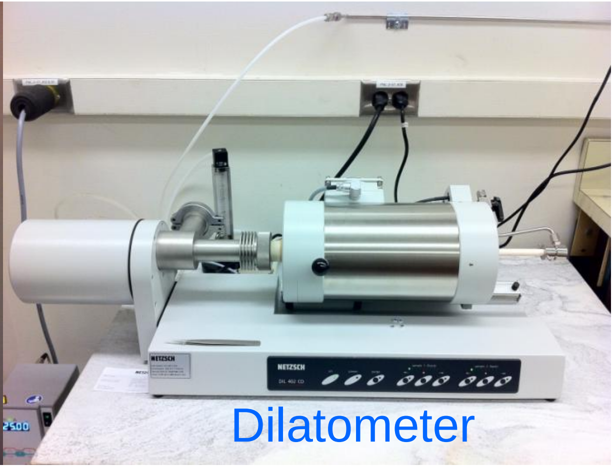


Cathode/Interconnect Contact Materials

- **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 <u>low electrical resistivity</u> and <u>increased mechanical strength</u>**
    - **Modeling results suggest strengthening of contacts can relieve stresses on seals**

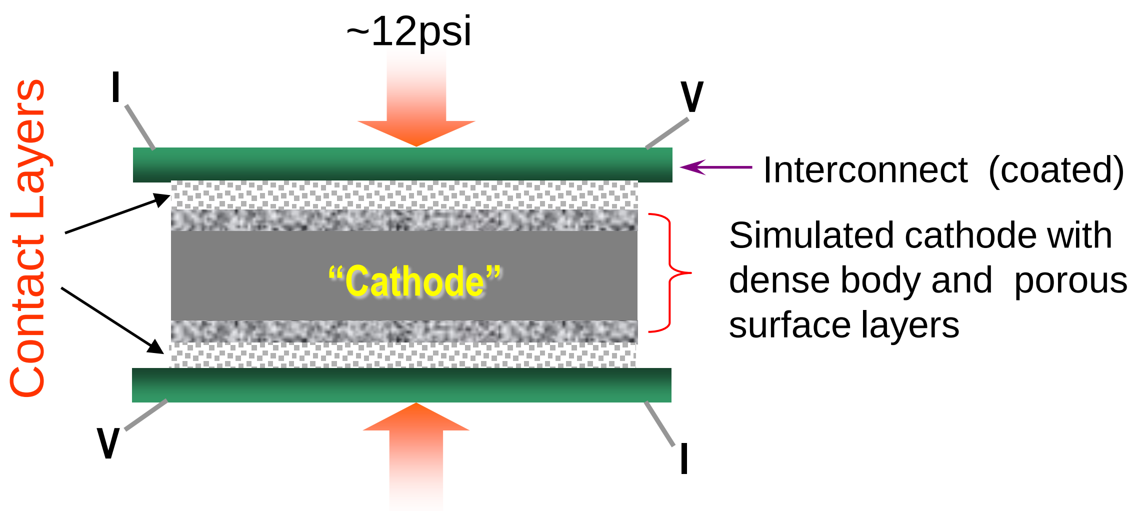
Key Characterization Methods



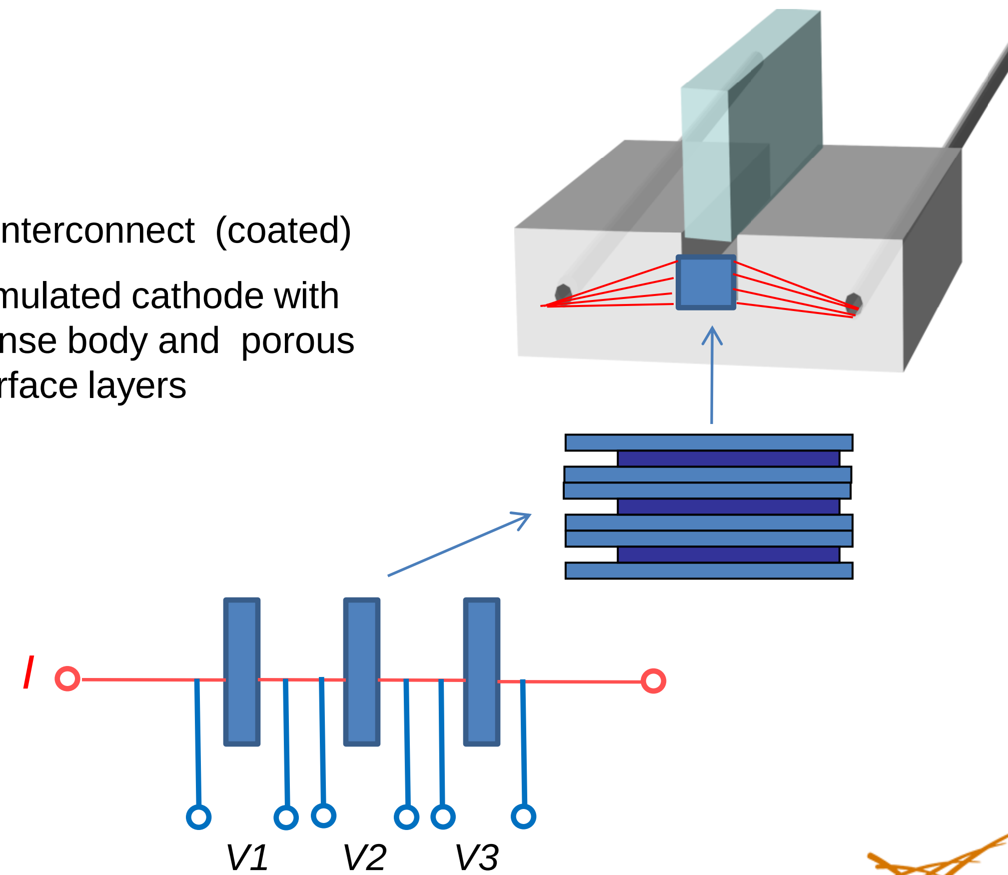


Area Specific Resistance (ASR) Measurements

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



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



ASR Stack (3 sets)

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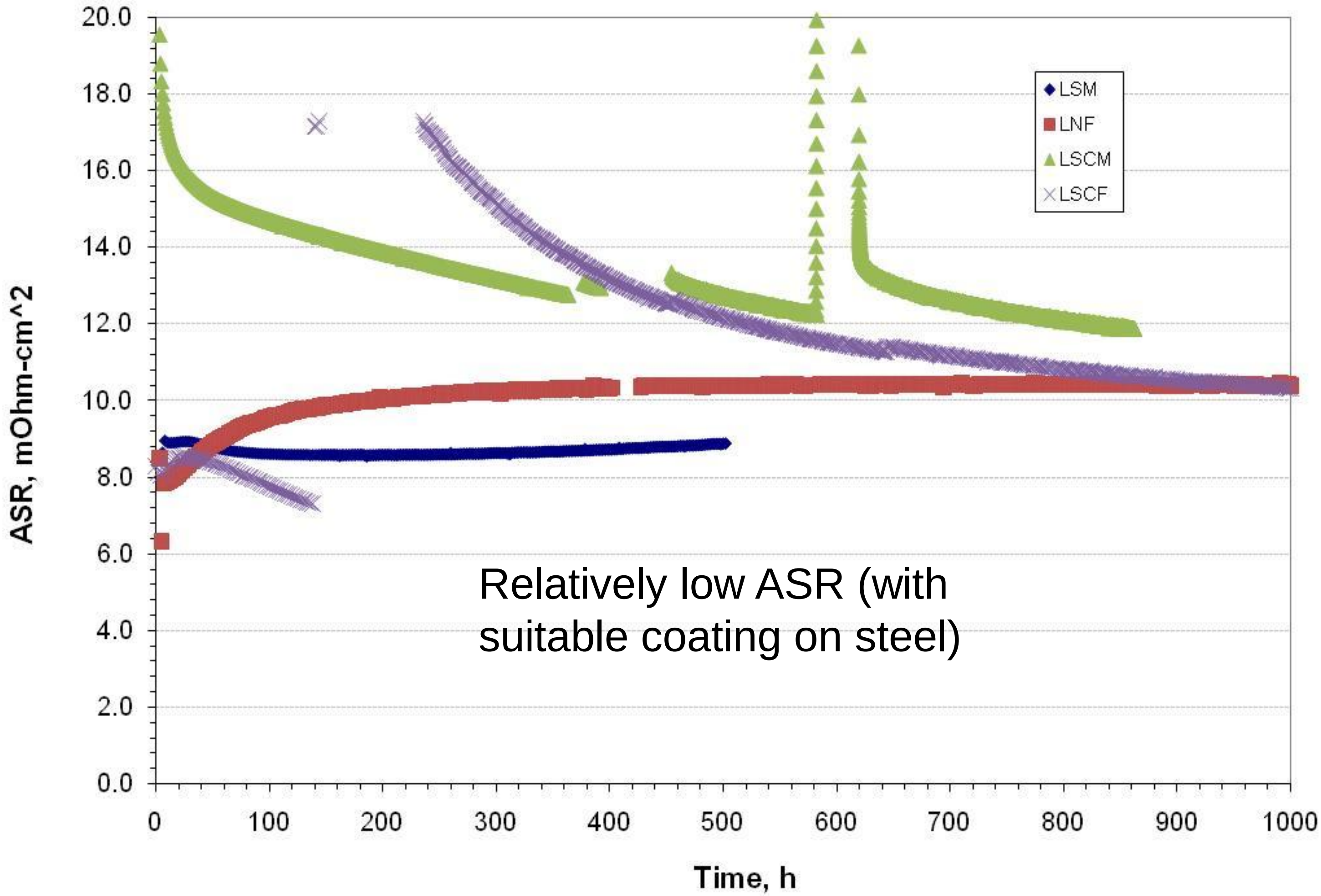
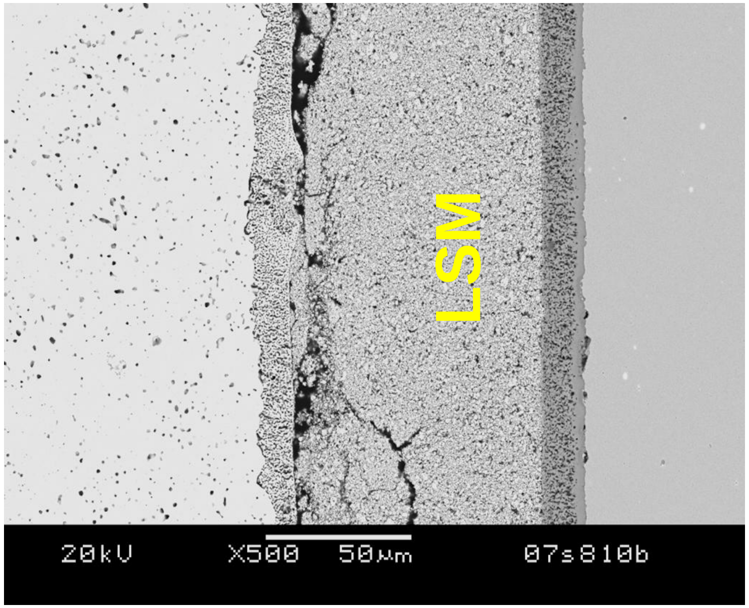
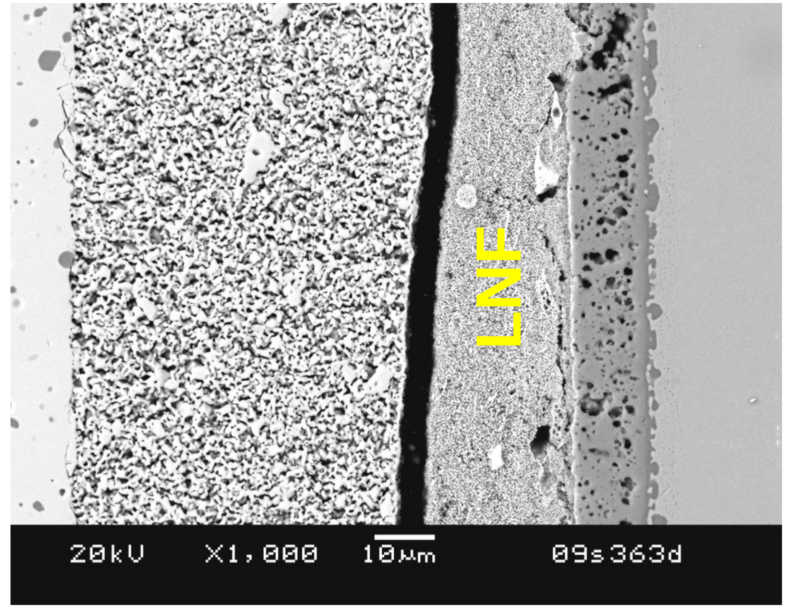
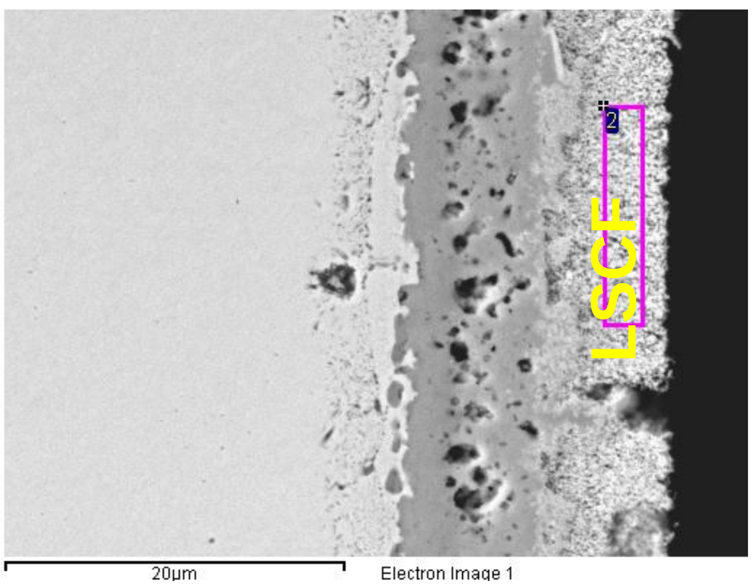
Conventional Contact Pastes: LSM, LSCM, LNF and LSCF



Conventional Contact Materials







Conventional contact layers exhibit low ASR but also low intrinsic strength and bond strength

Approaches to Improve Contact Strength

Sintering Aids

- Goal: Reduce the sintering temperature of contact materials (LSM, LNF, LSCF) 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

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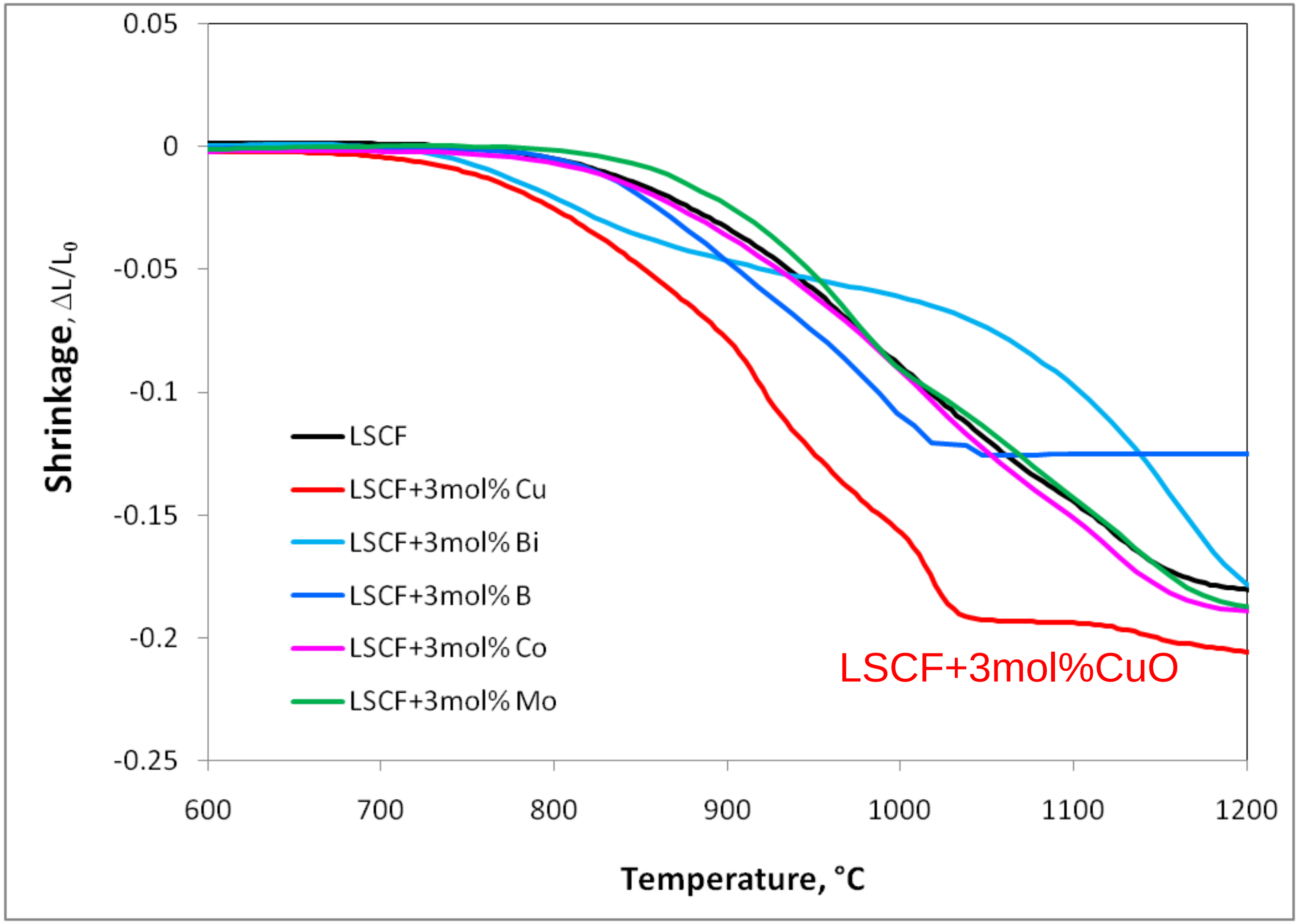
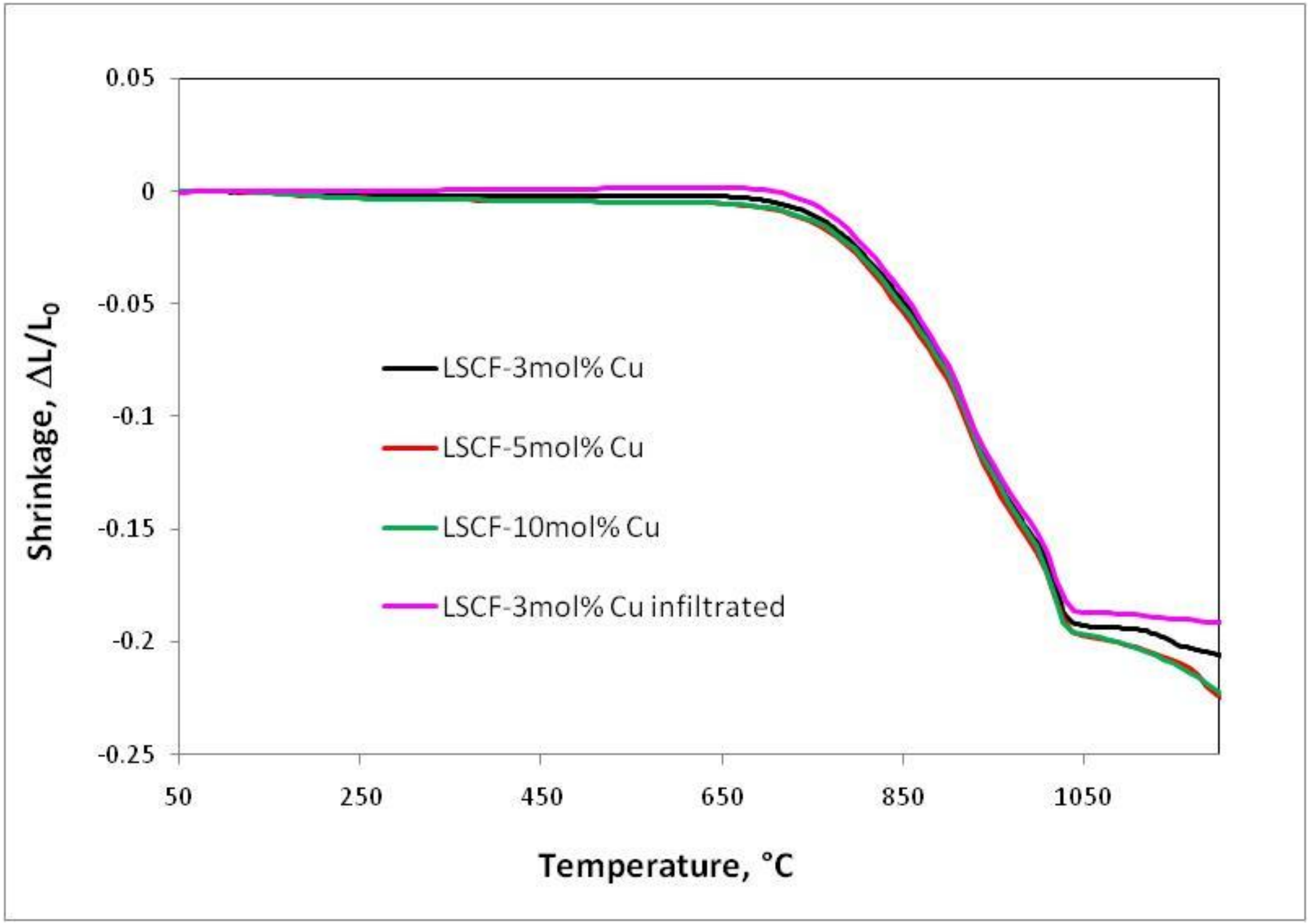
Sintering Curves of LSCF with Various Additives



LSCF with CuO exhibited the highest sintering activity.

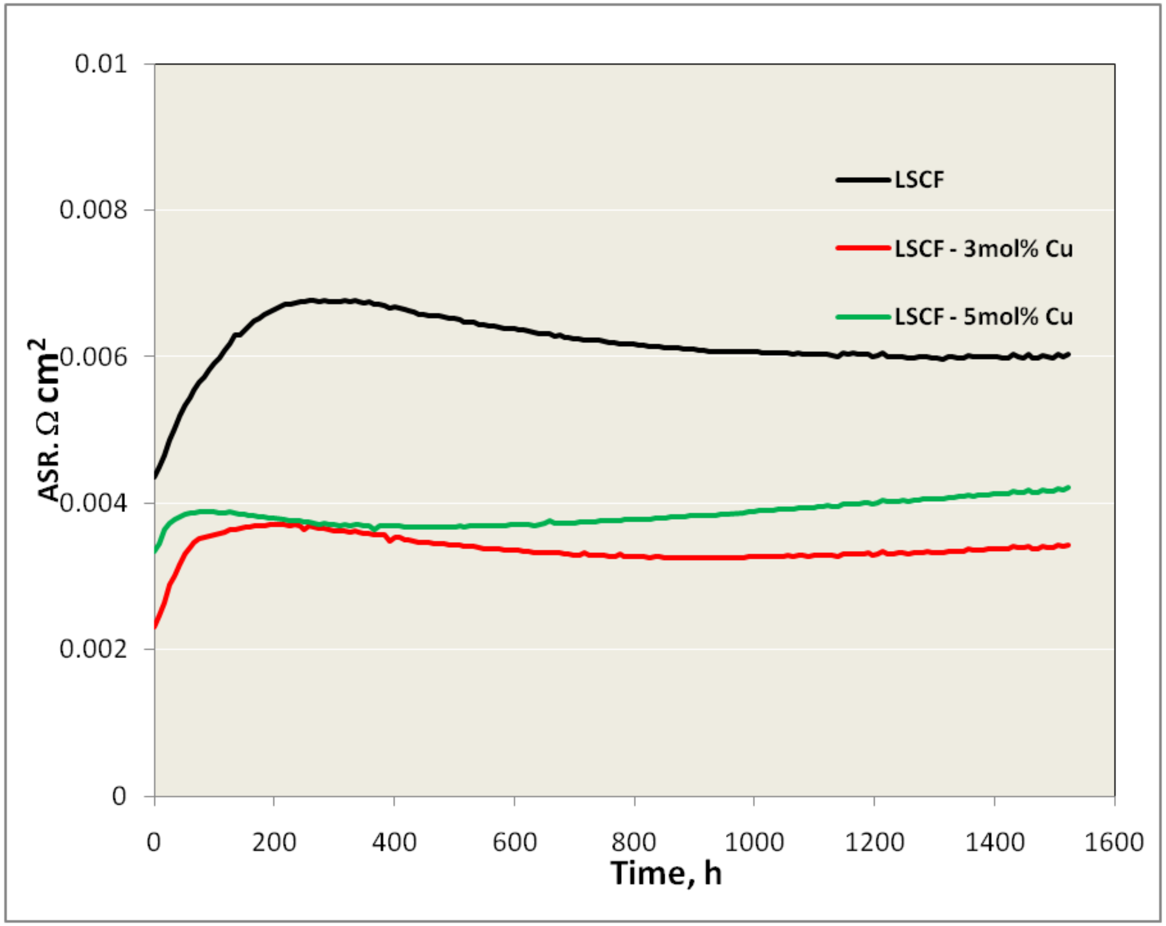
Sintering Curves of LSCF with Various Amounts of CuO Additions



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

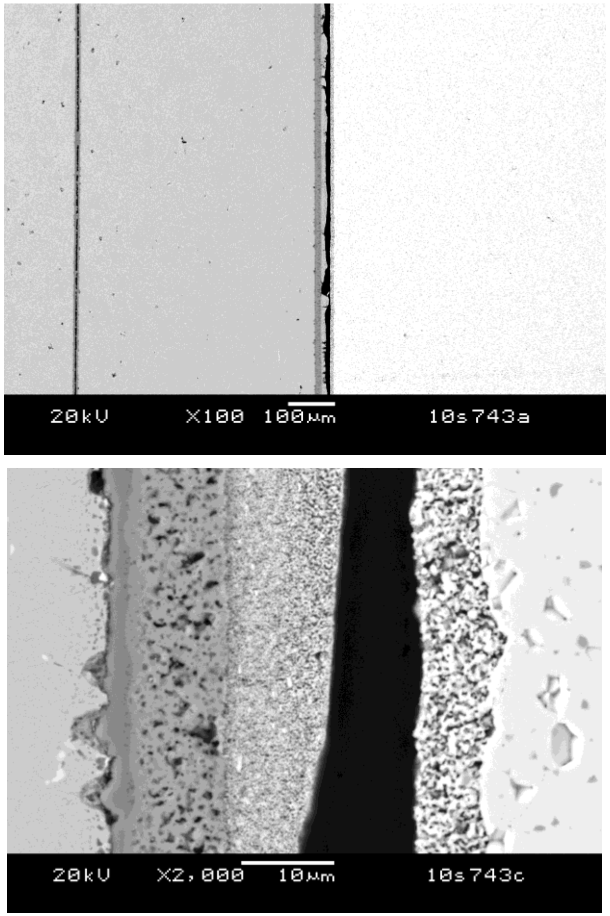
Contact ASR of LSCF with CuO Sintering Aid

(441-$Ce_{0.02}$MC|LSCF-CuO|LSCF)

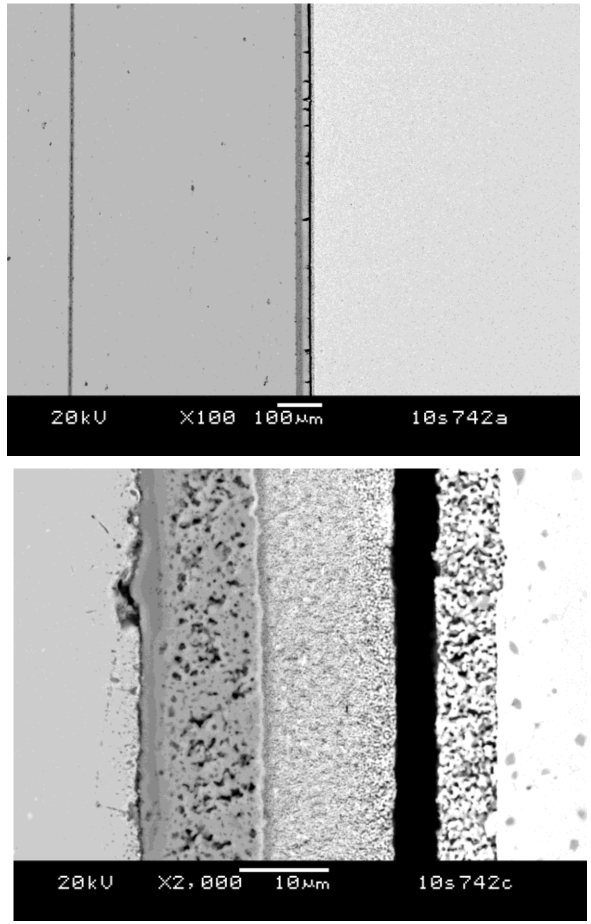


Low ASR, but tensile stress measurements showed very weak bonding strength between contact layer and cathode or interconnect coating

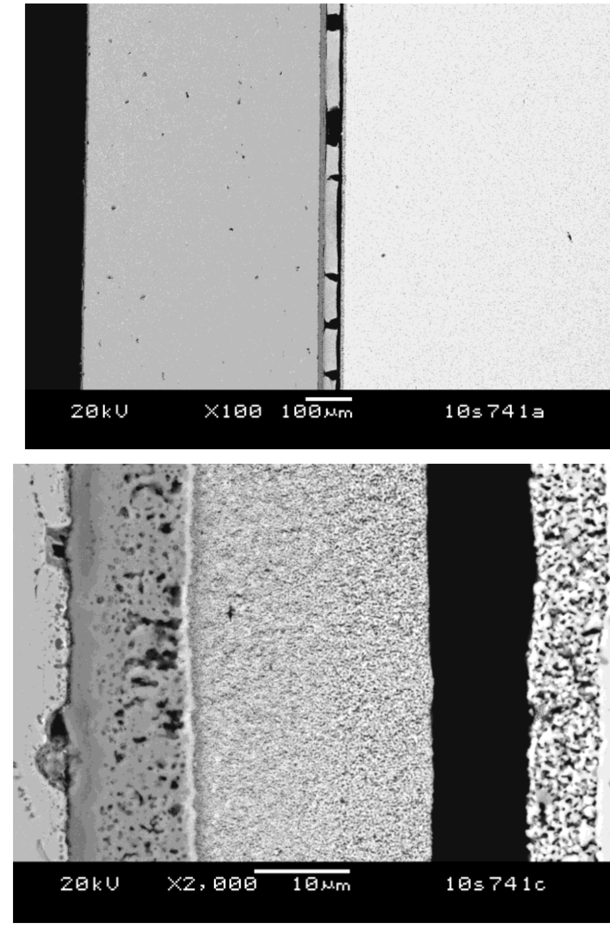
SEM Images of LSCF-x%CuO Contact Materials after ASR Measurements



LSCF only



LSCF+3mol% CuO



LSCF+5mol% CuO

Approaches to Improve Contact Strength

- Sintering Aids
  - Goal: Reduce the sintering temperature of contact materials (LSM, LNF, LSCF) 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

Reaction Sintering of Contact Materials

- Contact material precursor powder contains multiple phases, which react during stack assembly to form a conductive single phase
- Similar to process used in fabricating MnCo spinel coatings

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

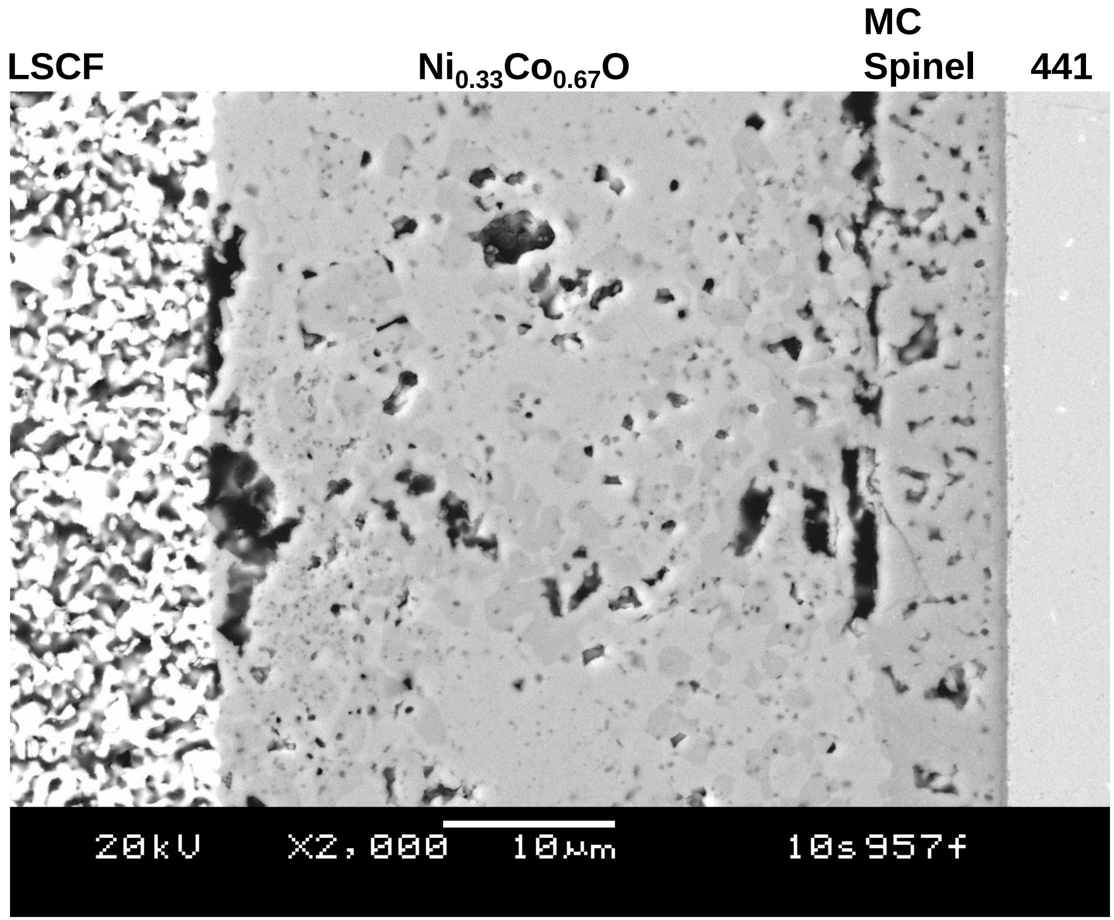
- Driving forces for densification:
  - Reduction of surface energy (~75 J/mol)
  - Enthalpy of formation (~500 kJ/mol)
- Systems of primary interest
  - **$(Ni,Co)O_x$**
  - **$(Mn,Co,Cu)_3O_4$**
  - Numerous compositions evaluated (CTE, conductivity, microstructure, strength); down-selected to **$Ni_{0.33}Co_{0.67}O_x$** and **$Mn_{2.7-x}Co_xCu_{0.3}O_4$**
  - Potential to include fillers and fugitive phases(tailor CTE and porosity, reduce cost)

$Ni_{0.33}Co_{0.67}O$ as cathode-interconnect contact material

- Prepared from mixture of Ni and Co powder
- Paste prepared using binder vehicle and 3 roll mill

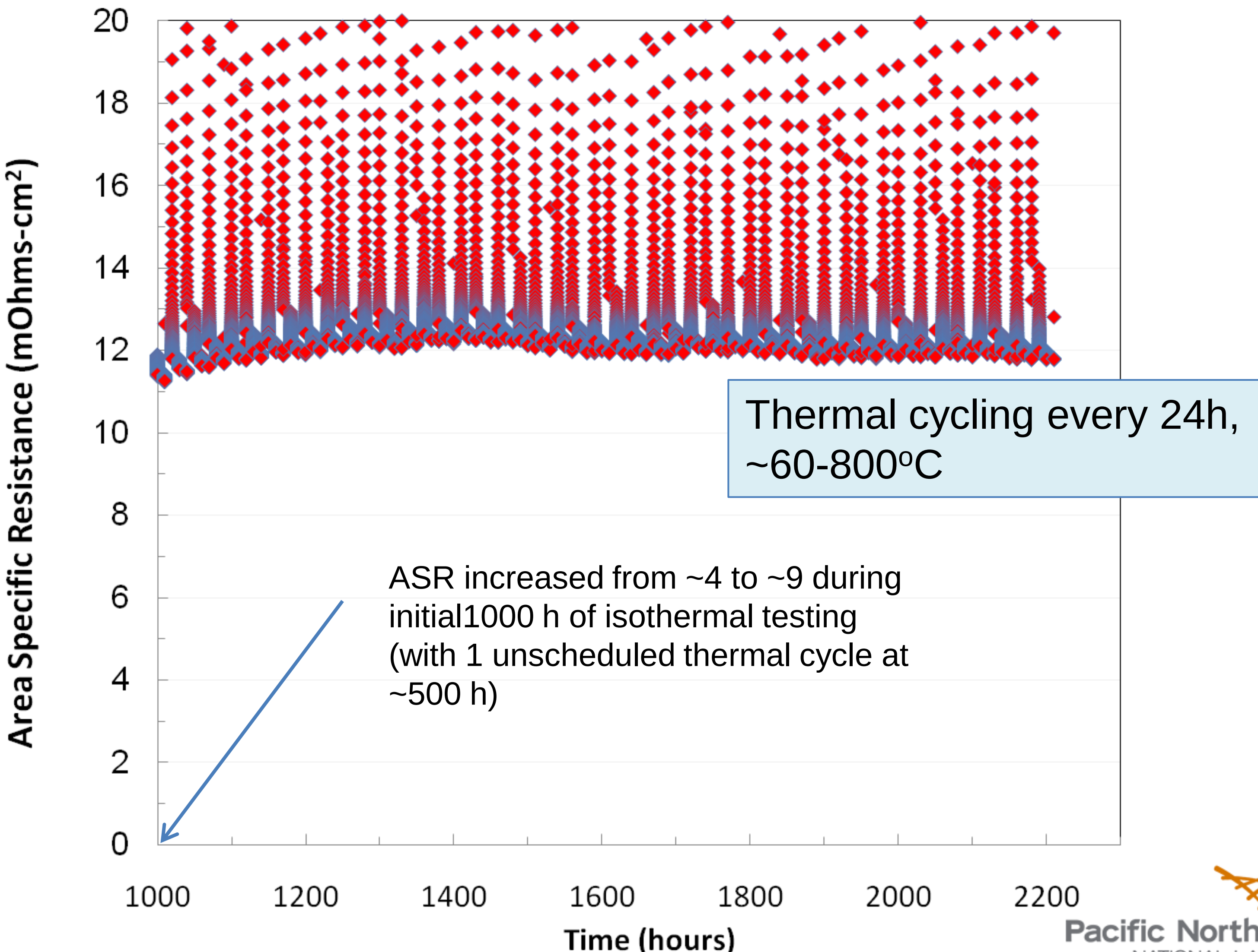
- Primary phase is (Ni,Co)O; secondary phase is $NiCo_2O_4$

- CTE ~14.6 ppm/K
    - Possible inclusion of filler to reduce cost and CTE



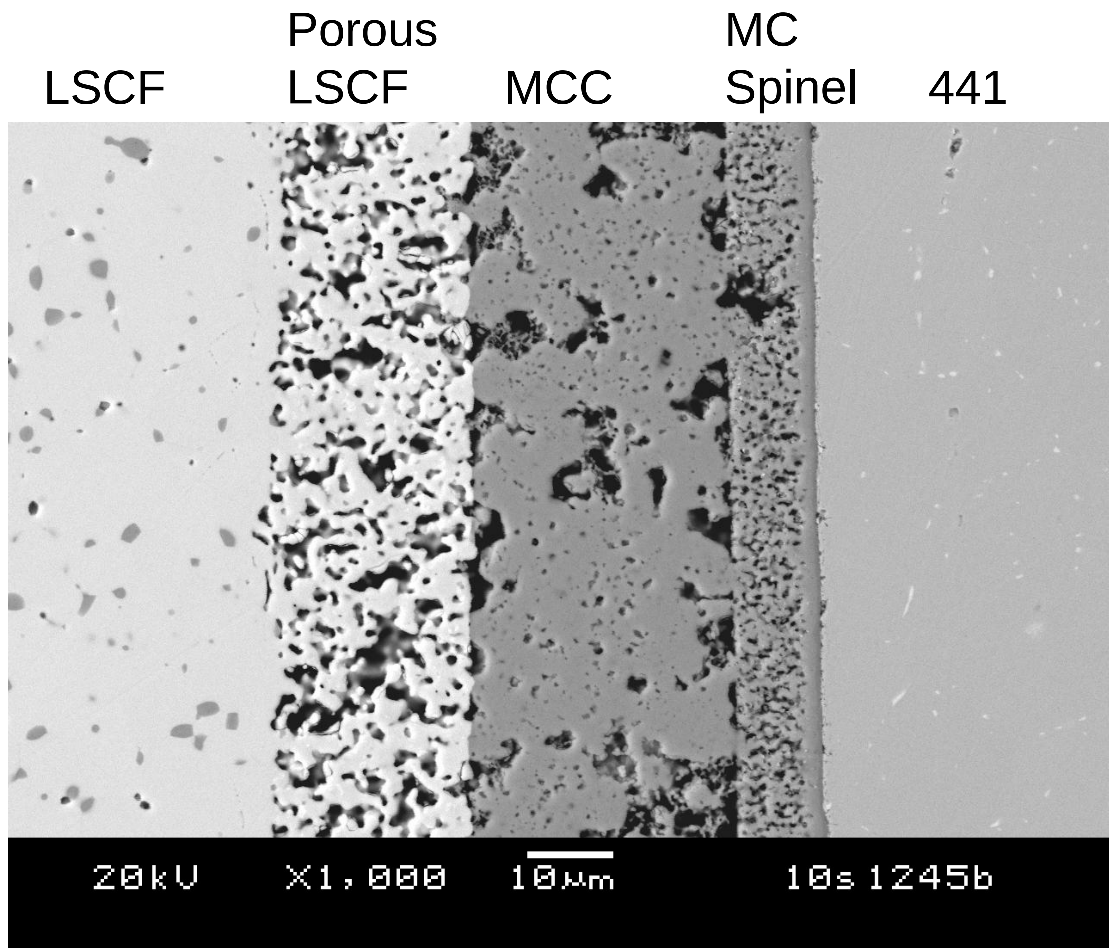
Cross-section SEM image of $(Ni_{0.33}Co_{0.67})O_x$ contact heat treated at 950°C for 30 min in air

ASR test results for $Ni_{0.33}Co_{0.67}O$ as cathode-interconnect contact material: 800ºC



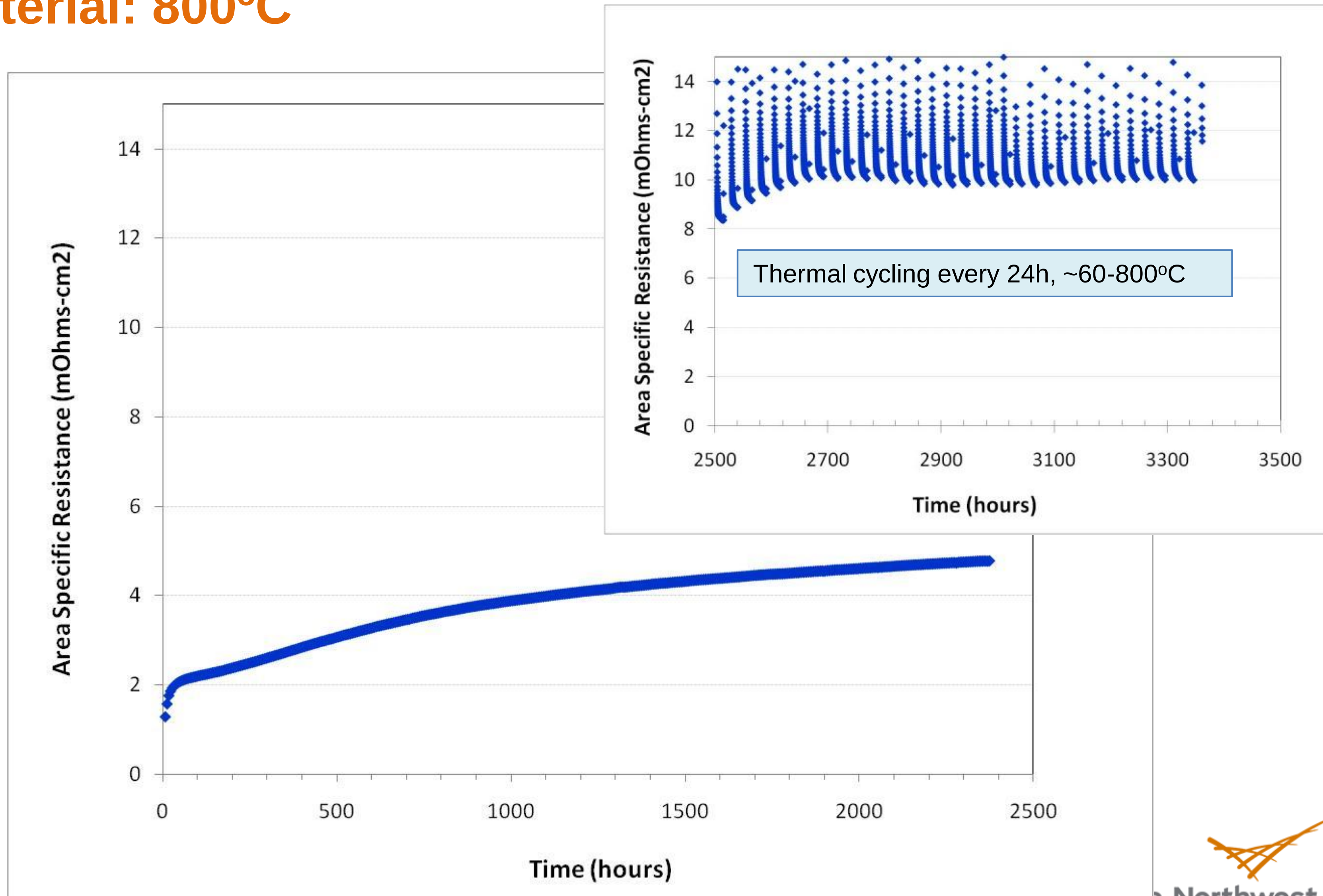
$Mn_{1.5}Co_{1.2}Cu_{0.3}O_4$ as cathode-interconnect contact material

- Prepared from mixture of Mn, Co, and Cu powder
- Paste prepared using binder vehicle and 3 roll mill
- Single phase MCC spinel
- CTE ~12.8 ppm/K



Cross-section SEM image of $Mn_{1.5}Co_{1.2}Cu_{0.3}O_4$ heat treated at 950ºC for 30 min in air, 800ºC for 100 h

Isothermal and cyclic ASR test results for $Mn_{1.5}Co_{1.2}Cu_{0.3}$ as cathode-interconnect contact material: 800ºC



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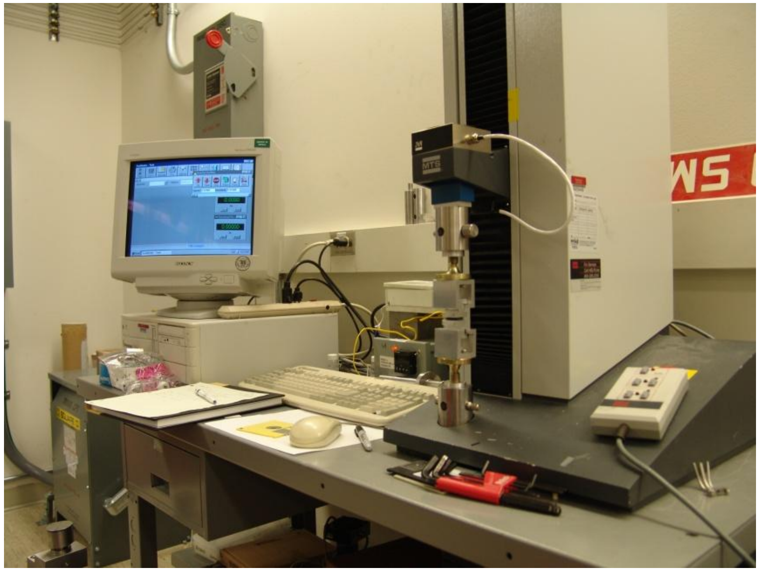
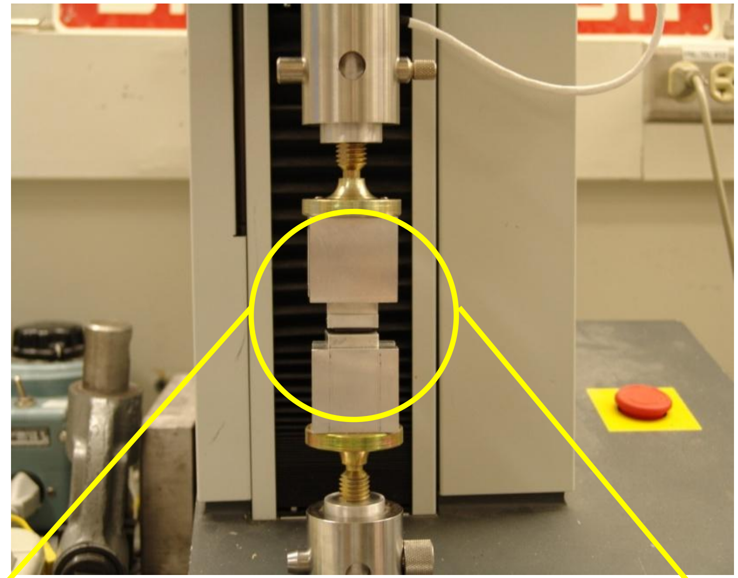
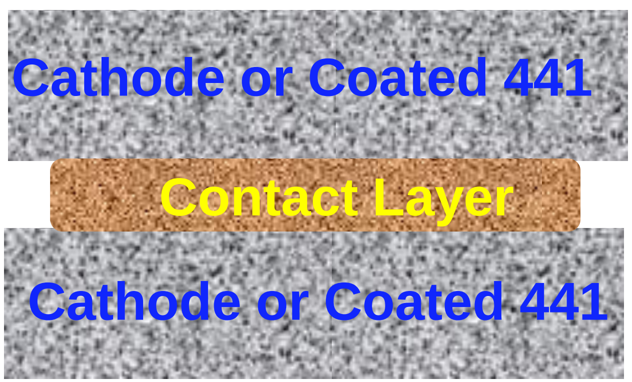
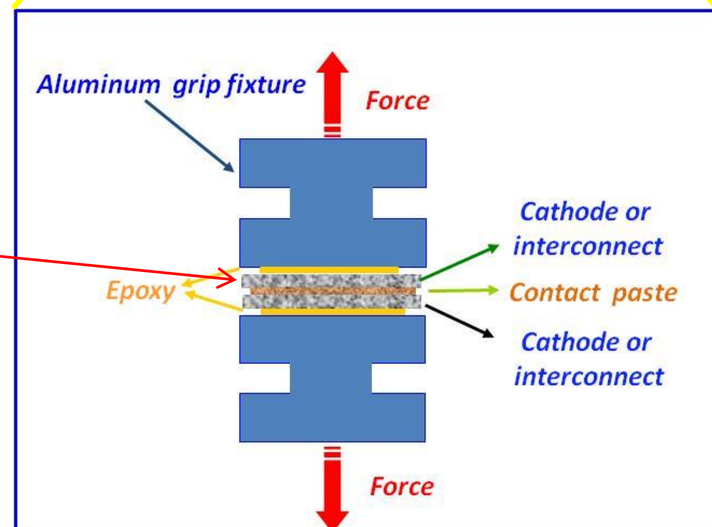
Mechanical Bond Strength Measurement

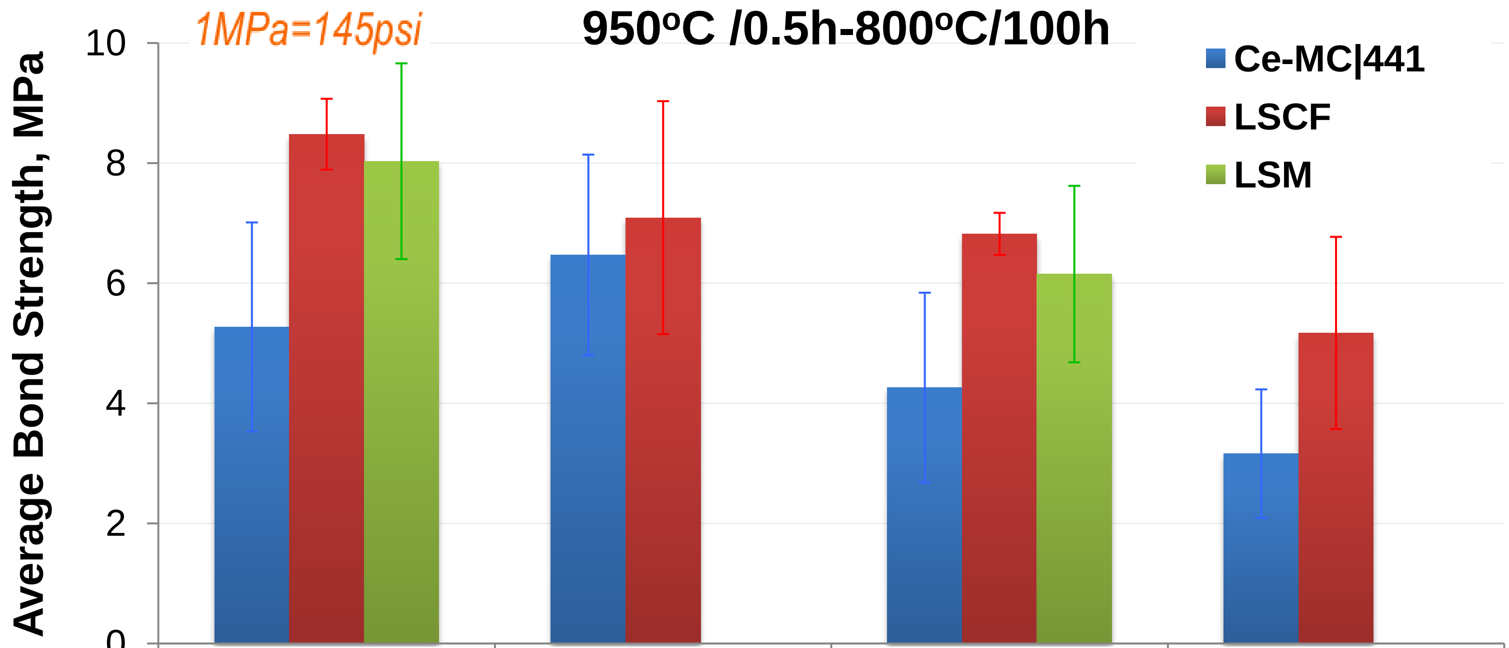








Contact Bonding Strength (950ºC Treated)

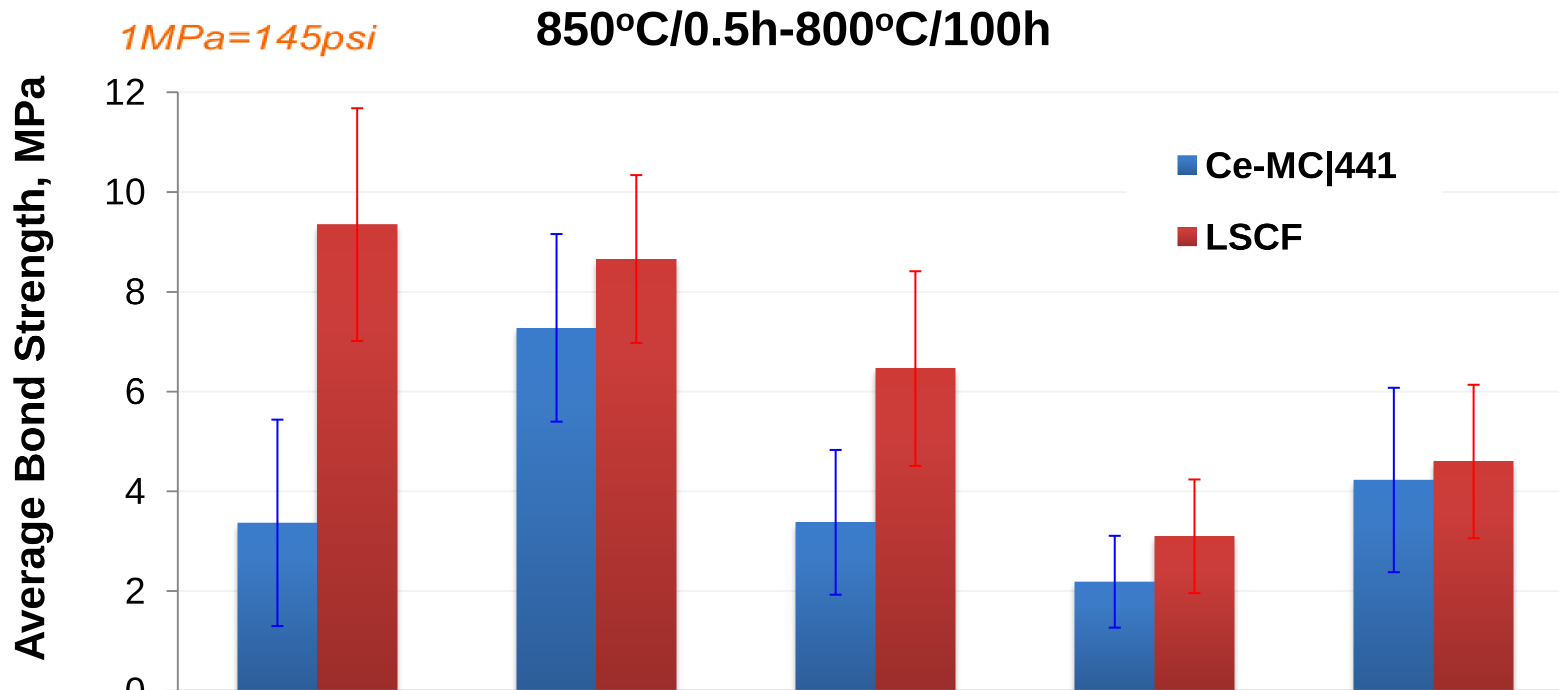


	MnCoCu0.3	MnCoCu0.3+10%YSZ	NiCo2	NiCo2+10%YSZ
Ce-MC|441	5.27	6.47	4.26	3.16
LSCF	8.48	7.09	6.82	5.17
LSM	8.03		6.15	

Contact Materials

◆ Strong bonds can be obtained for both coated 441 and cathode using $Mn_{1.5}Co_{1.2}Cu_{0.3}$ and $NiCo_2$ as contact pastes; bonds on cathode are stronger

Contact Bonding Strengths (850°C Treated)



	MnCoCu0.3	MnCoCu0.3+10 %YSZ	NiCo2	NiCo2+10%YSZ	Red-MnCoCu0.3
Ce-MC|441	3.37	7.28	3.38	2.19	4.23
LSCF	9.35	8.66	6.46	3.1	4.6

Contact Materials

◆ Stronger bonds can be obtained for both coated 441 and cathodes using $Mn_{1.5}Co_{1.2}Cu_{0.3}$ and $NiCo_2$ as contact paste; bonds on cathode are stronger

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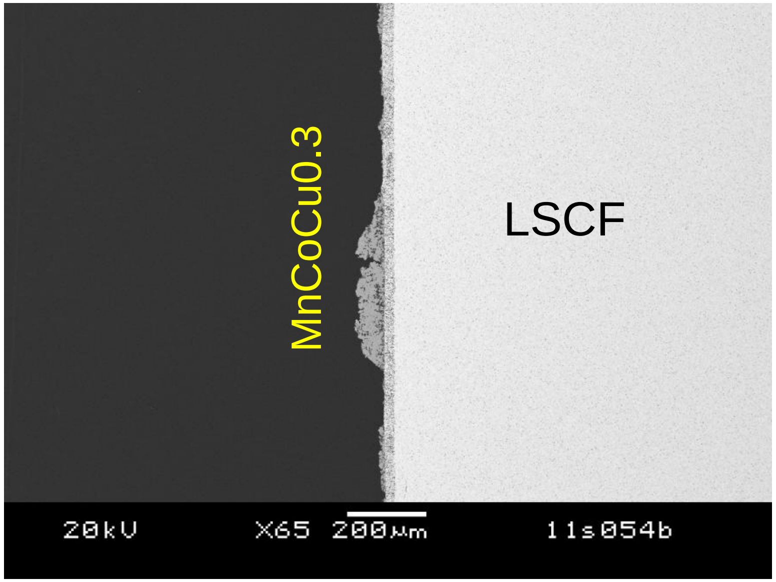
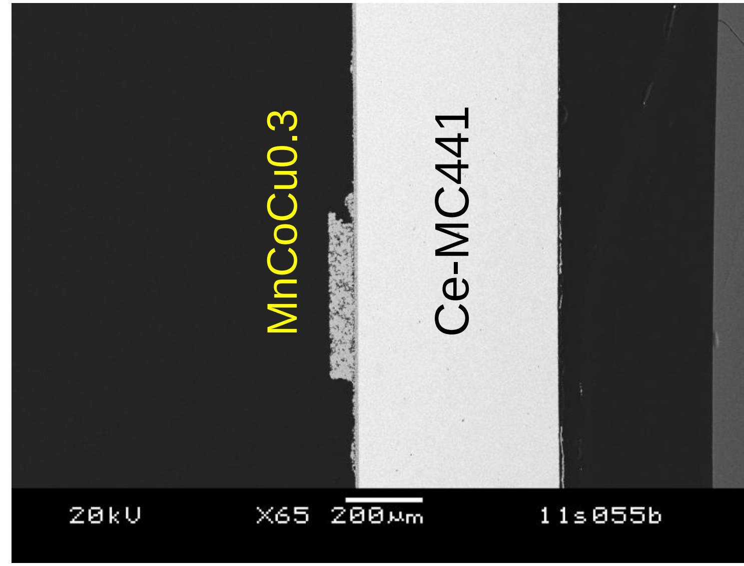
SEM Images of Specimens after Mechanical Bond Strength Measurement (950ºC treated)





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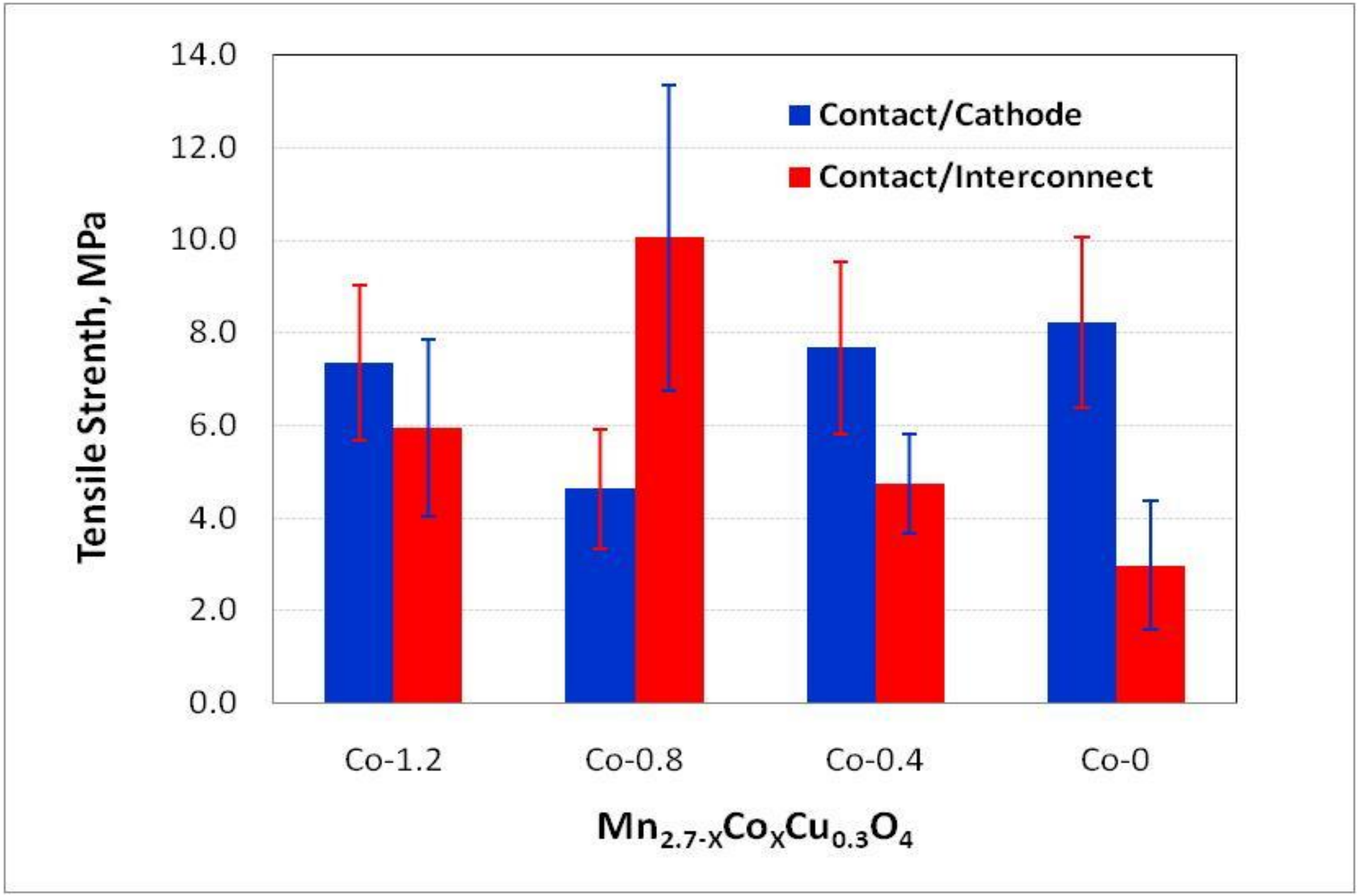
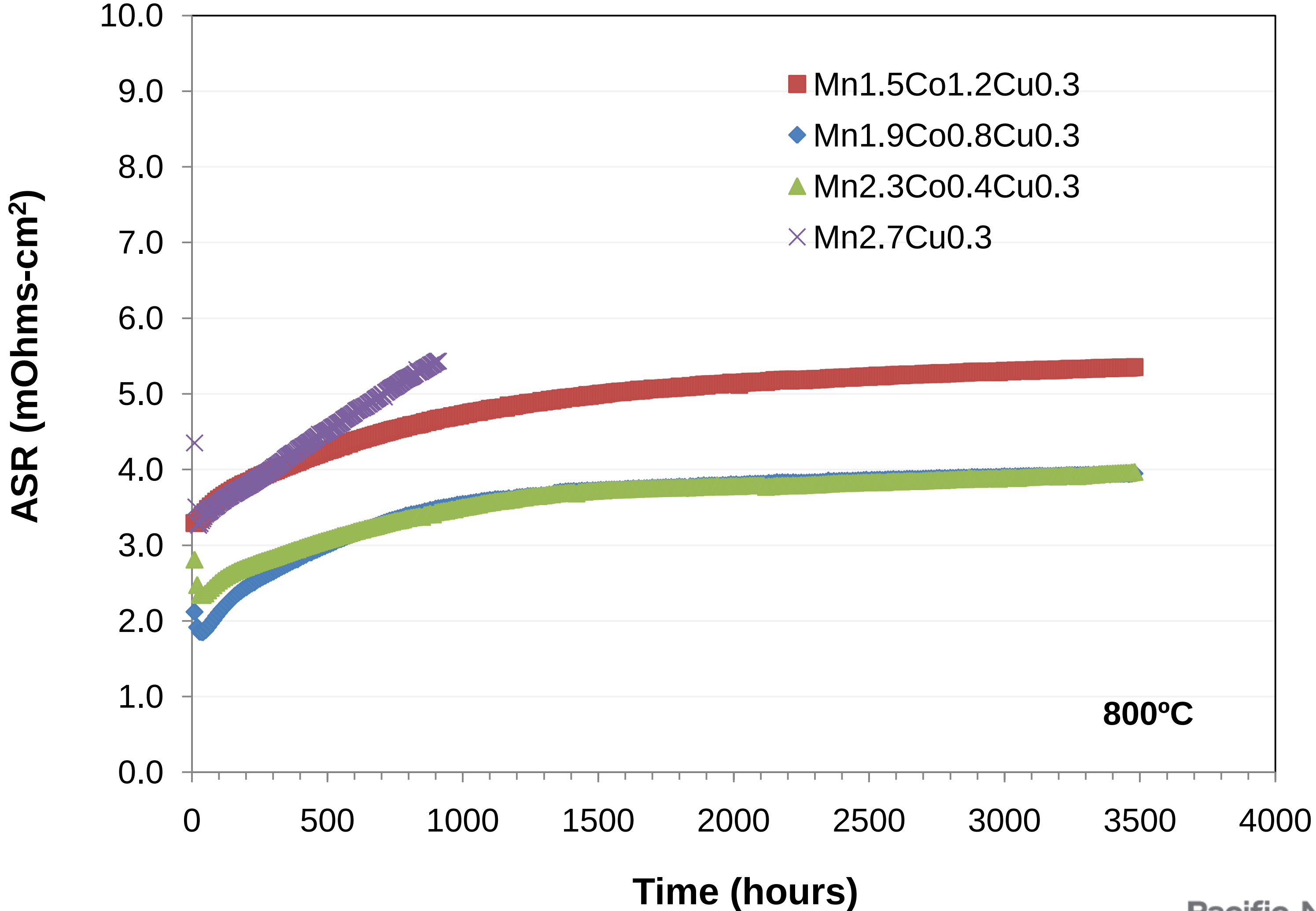
Tensile strength results for Mn-Co-Cu contact materials with varying Co content

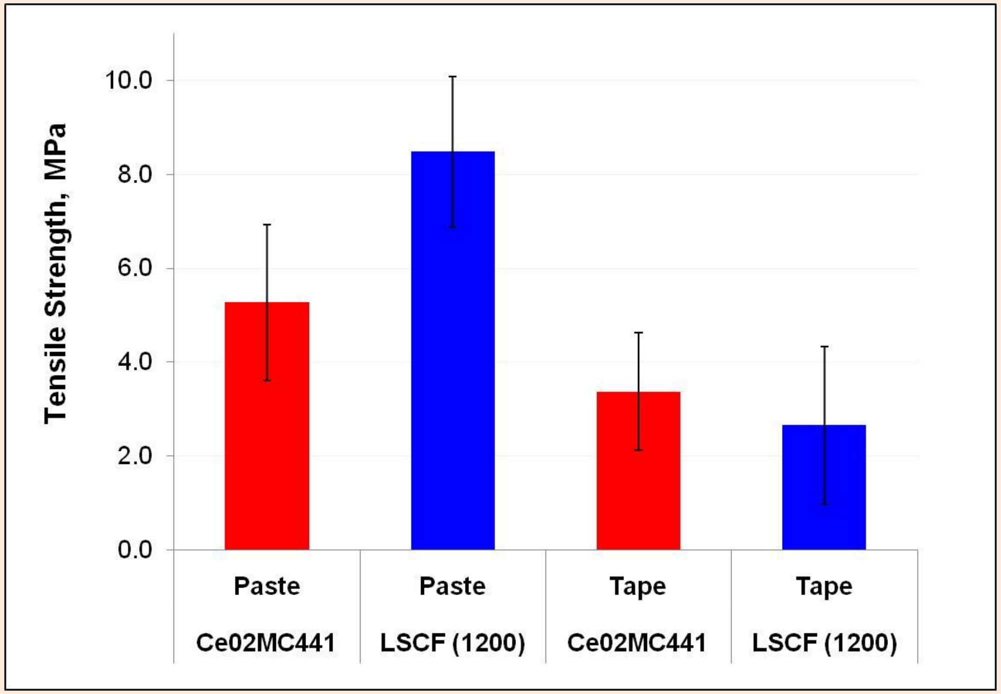


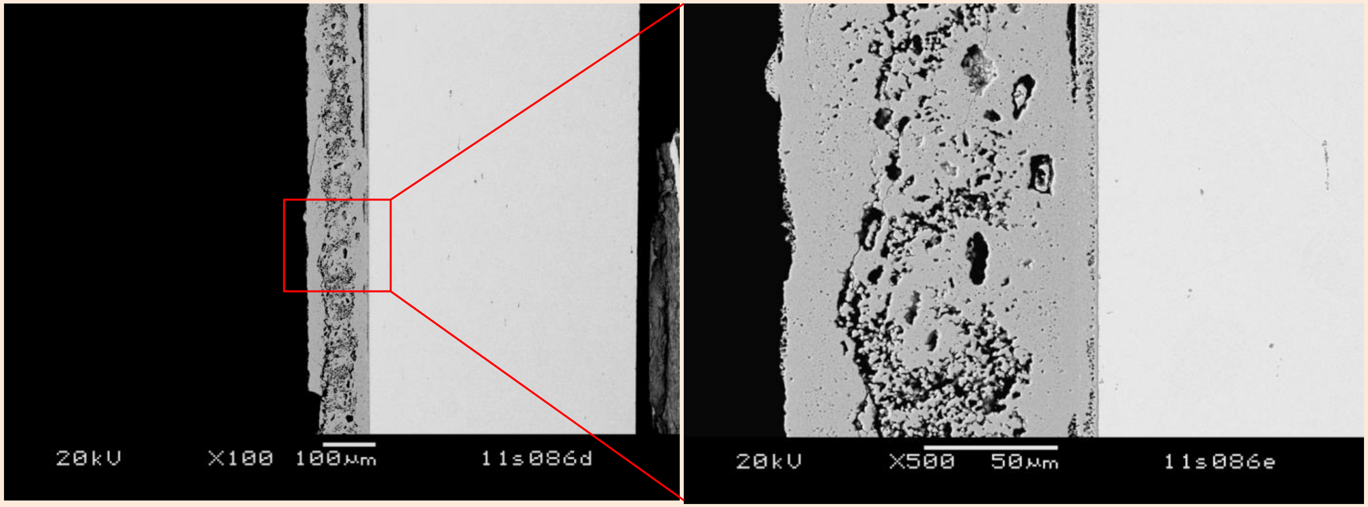
ASR of $Mn_{2.7-x}Co_xCu_{0.3}O_4$ Contact Materials



Alternative Fabrication Approach: Tape-casting

Application of cathode - interconnect contact material in tape form instead of paste form





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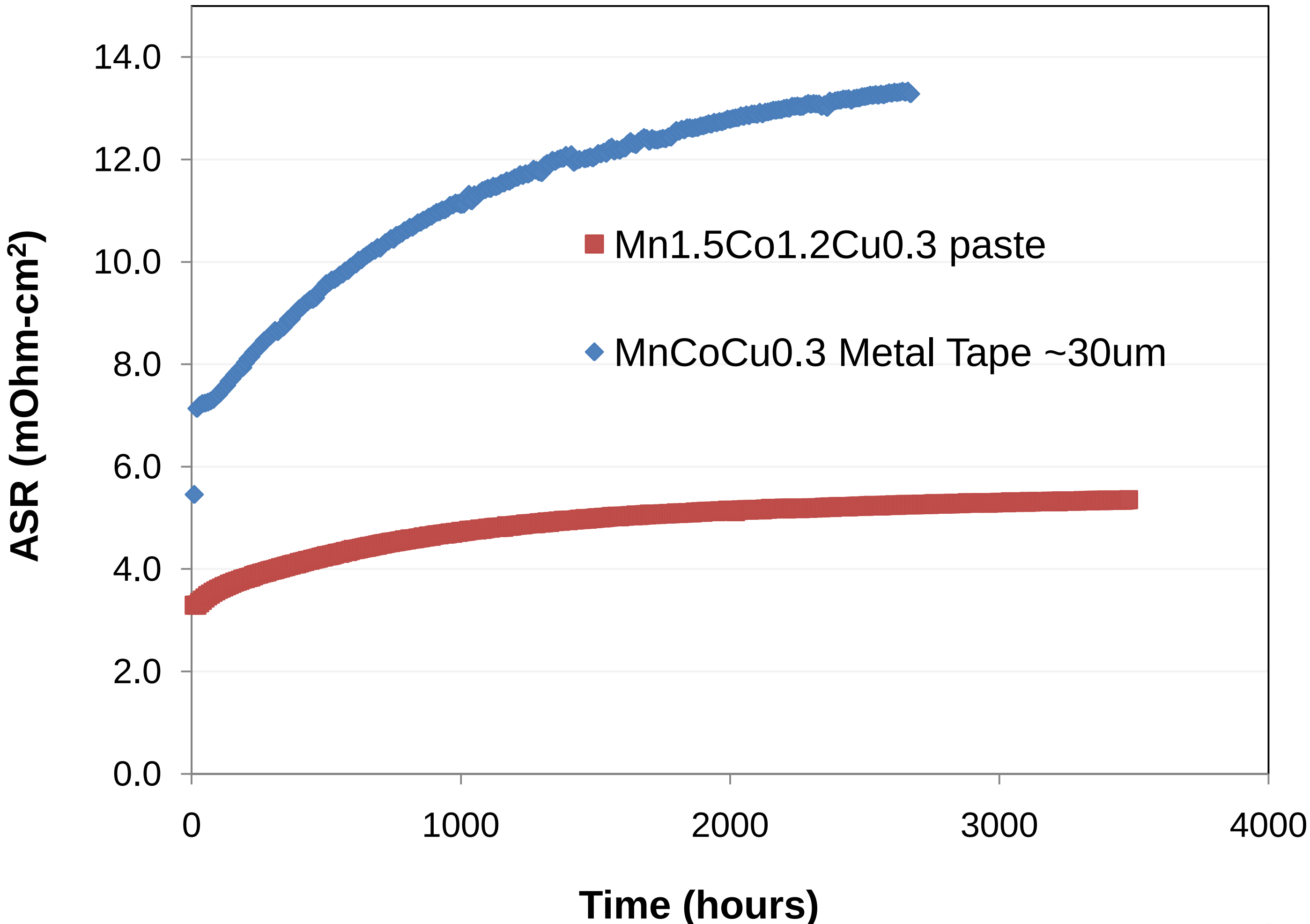

Summary and Future Work

- Reactive sintering has been demonstrated as a means of preparing cathode/interconnect Ni-Co oxide and Mn-Co-Cu oxide contact materials from precursor mixtures of metallic powders.
- The reactive sintering approach resulted in very low cathode-to-interconnect ASR, and high bond strength (compared to conventional contact materials).
- Clearly, the high density of reaction-sintered contacts will restrict gas phase transport through the contact material.
  - Possible solutions:
    - Application of contact material to selected regions only (e.g., lands of ribs of interconnects)
    - Inclusion of controlled porosity through use of fugitive phases
      - Reactive sintering may result in stronger bulk and interfacial bonding compared to conventional contacts prepared from complex oxides with minimal sintering activity at stack fabrication temperatures

- More information: Z. Lu, G. Xia, J.D. Templeton, X. Li, Z. Nie, Z. Yang, J.W. Stevenson, "Development of $Ni_{1-x}Co_xO$ as the cathode/interconnect contact for solid oxide fuel cells," *Electrochemistry Communications*, 13, 642 (2011).

Acknowledgements

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