Development & Validation of Low-Cost, Highly-Durable, Spinel-Based Materials for SOFC Cathode-Side Contact

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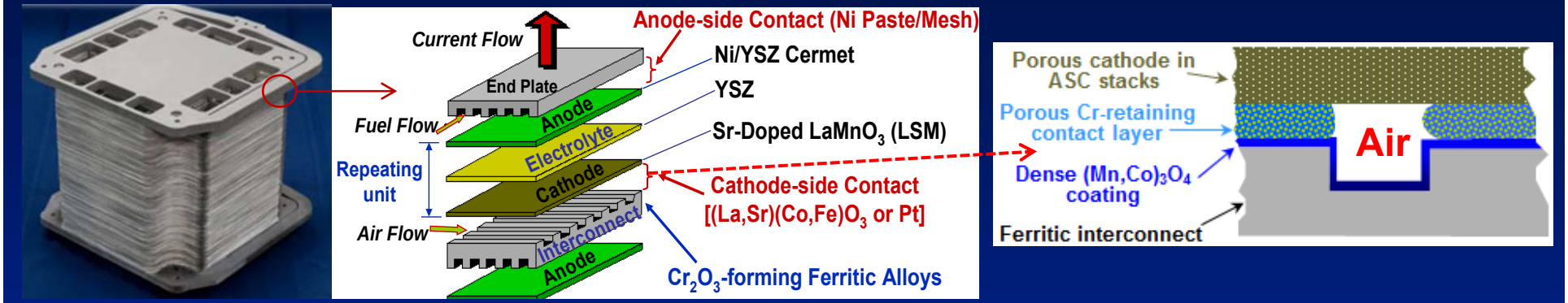
Outline

- Introduction and Project Objectives
- Effect of Spinel Compositions on the Electrical Conductivity and CTE
- Performance Evaluation of the Sintered Spinel Contact Thermally Converted from Metallic Precursors
  - Area Specific Resistance (ASR), Chemical Compatibility, etc.
- Reactive Sintering of Dense $(Mn,Co)_3O_4$ Coatings
- Co-sintering of Spinel-Based Coating/Contact Dual-Layer Structure
- Concluding Remarks
- Acknowledgments

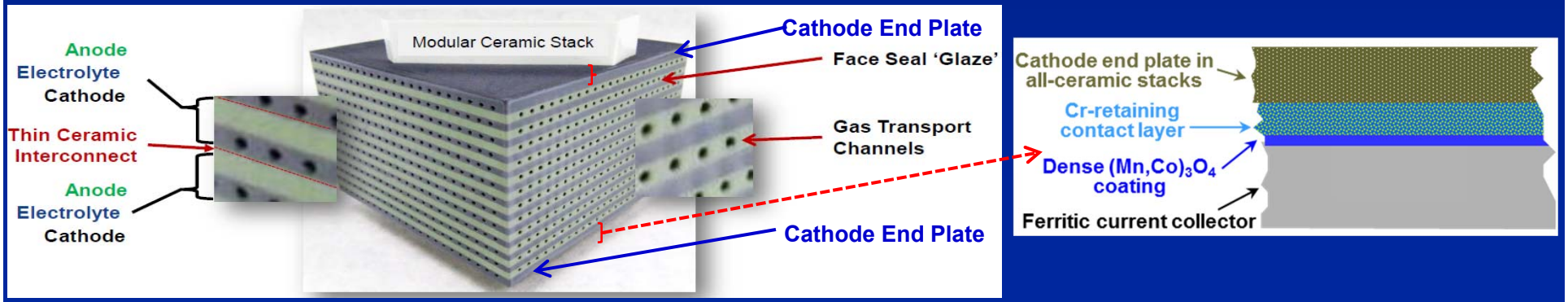
Need of Contacting for Different SOFC Stacks

- In stacks with anode-supported cells (ASC-SOFC), the contact is required to minimize the cathode-interconnect interfacial resistance.



Cathode-Interconnect Interface in ASC SOFC Stacks

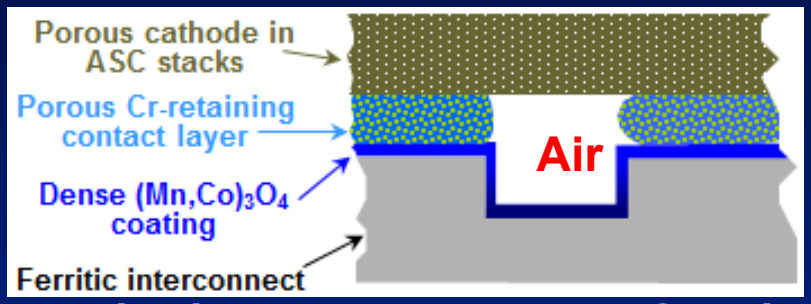
- In all-ceramic stacks, the contact is required to minimize the interfacial resistance between the current collector plate and cathode end plate.



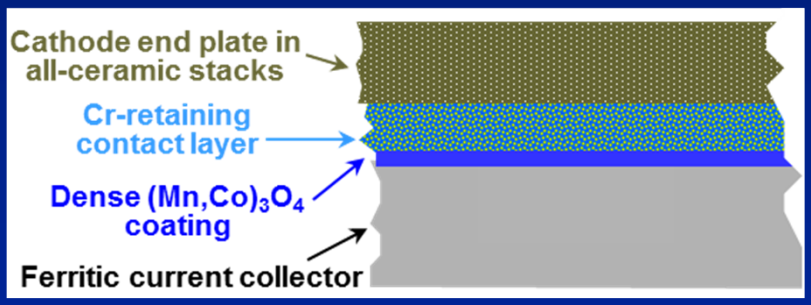
Cathode-Current Collector Interface in All-Ceramic SOFC Stacks

Contact Material Requirements

- Requirements for contact materials in ASC-SOFC and all-ceramic SOFC stacks are generally similar, including:
  - Low material/processing cost
  - High electrical conductivity
  - Match in coefficient of thermal expansion (CTE)
  - Adequate stability and compatibility
  - Appropriate sinterability
  - Good bonding strength with adjacent stack components
  - Absence of volatile species



Cathode-Interconnect Interface in ASC-SOFC Stacks



Cathode-Current Collector Interface in All-Ceramic SOFC Stacks

- Additionally, a reasonable porosity level in the cathode-side contact is needed in ASC stacks for maximizing the triple phase boundaries for cathodic reaction.

Different Contact Materials

- While various materials for ferritic alloy-cathode contacting have been studied, most developments have focused on (La,Sr)(Mn,Co,Fe,Ni,Cu)O_3:
  - Difficulty in balancing the electrical conductivity, CTE, sinterability and chemical compatibility of the perovskites.

Material Type	Example	CTE ($\times 10^{-6}$/K) (20–800°C)	Conductivity (S·cm^{-1}, 800°C)	Main Concern
Noble Metal	Pt	10.0	Metallic	High Cost
	Pd	12.3	Metallic	High Cost
	Au	16.6	Metallic	High Cost
	Ag	22.0	Metallic	Volatility
Perovskite	$(La_{0.8}Sr_{0.2})\ CoO_{3-\delta}$	19.2 (20-1000°C)	1400	CTE Mismatch
	$(La_{0.8}Sr_{0.2})(Co_{0.5}Fe_{0.5})O_{3-\delta}$	18.3 (20-1000°C)	340	CTE Mismatch
	$(La_{0.8}Sr_{0.2})(Co_{0.5}Mn_{0.5})O_{3-\delta}$	15.0 (20-1000°C)	190	CTE Mismatch
	$(La_{0.8}Sr_{0.2})MnO_3$	11.7 (20-1000°C)	170	Sinterability
	$LaMn_{0.45}Co_{0.35}Cu_{0.2}O_3$	13.9	80	Mn/Cu Migration
Spinel	$MnCo_2O_4$	9.7-14.4	24- 89	Sinterability
	$Mn_{1.5}Co_{1.5}O_4$	10.6-11.6	55-68	Sinterability
	$NiCo_2O_4$	12.1	0.93	Sinterability
	$NiFe_2O_4$	11.8	0.3, 6.8, 17.1	Sinterability
	$Ni_{0.85}Fe_{2.15}O_4$	12.1	15.4	Sinterability

Why $(Ni,Fe)_3O_4$- and $(Mn,Co)_3O_4$-Based Spinels as Contact Material?

- Conductive spinels based on $(Ni,Fe)_3O_4$ and $(Mn,Co)_3O_4$, which have been extensively evaluated as interconnect coating, are also promising for contact application, based on electrical conductivity, CTE, chemical compatibility, etc.

Material Type	Example	CTE ($\times 10^{-6}$/K) (20–800°C)	Conductivity ($S \cdot cm^{-1}$, 800°C)	Main Concern
Spinel	$MnCo_2O_4$	9.7-14.4	24- 89	Sinterability
	$Mn_{1.5}Co_{1.5}O_4$	10.6-11.6	55-68	Sinterability
	$NiCo_2O_4$	12.1	0.93	Sinterability
	$NiFe_2O_4$	11.8	0.3, 6.8, 17.1	Sinterability
	$Ni_{0.85}Fe_{2.15}O_4$	12.1	15.4	Sinterability

- Unfortunately, the sinterability of spinels is very poor (typically ≥1000°C), if metal oxides are used as the starting powders.
- Employment of metallic powders (instead of oxide powders) as the starting precursor will lower the sintering temperature via a reactive sintering mechanism called environmentally-assisted reactive sintering (EARS).

Utilization of EARS for Reduced-Temperature Sintering of Spinel-Based Contact

- In EARS, with the participation of oxygen from air, the metallic powder precursor will be oxidized and reacted to form a well-sintered spinel at a reduced temperature (e.g., 900°C):

$$\text{(b): } AO_x + 2BO_y + (2-\tfrac{1}{2}x-y)O_2(g) = AB_2O_4 + \Delta H_1$$

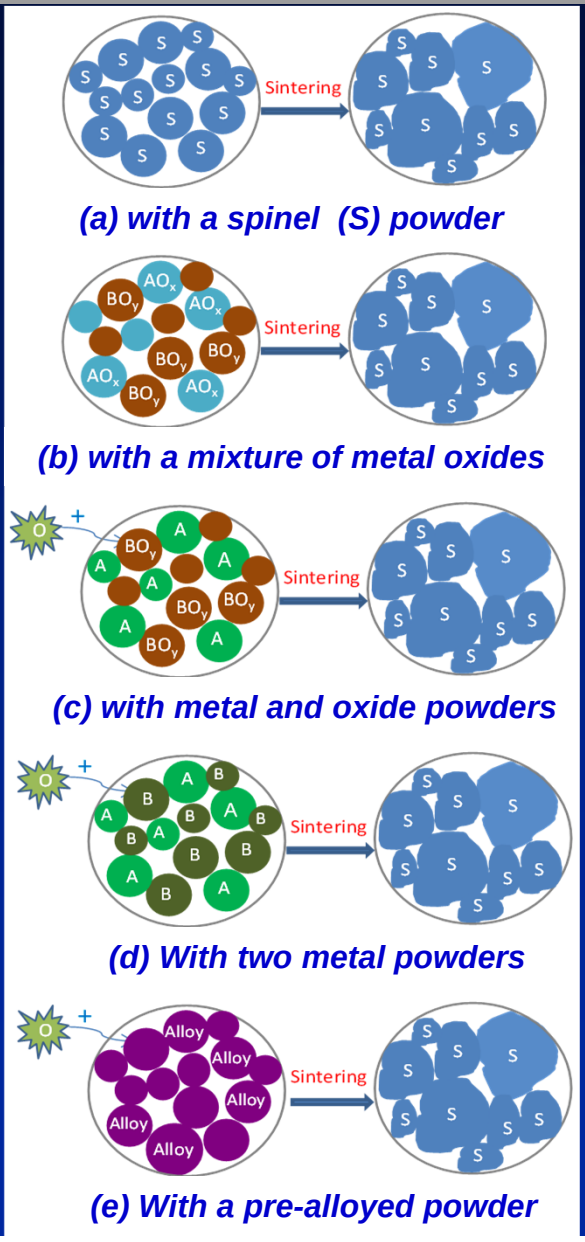
$$\text{(c): } A + 2BO_y + (2-y)O_2(g) = AB_2O_4 + \Delta H_2$$

$$\text{(d) \& (e): } A + 2B + 2O_2(g) = AB_2O_4 + \Delta H_3$$

$$\Delta H_3 > \Delta H_2 >> \Delta H_1$$

- Enhanced sintering via EARS is likely due to:
  - Heat released during the reaction;
  - Volume expansion upon conversion of metal to metal oxide;
  - Formation of highly-active surface nano-oxides;
  - Shorter diffusion distance when a pre-alloyed powder is employed.

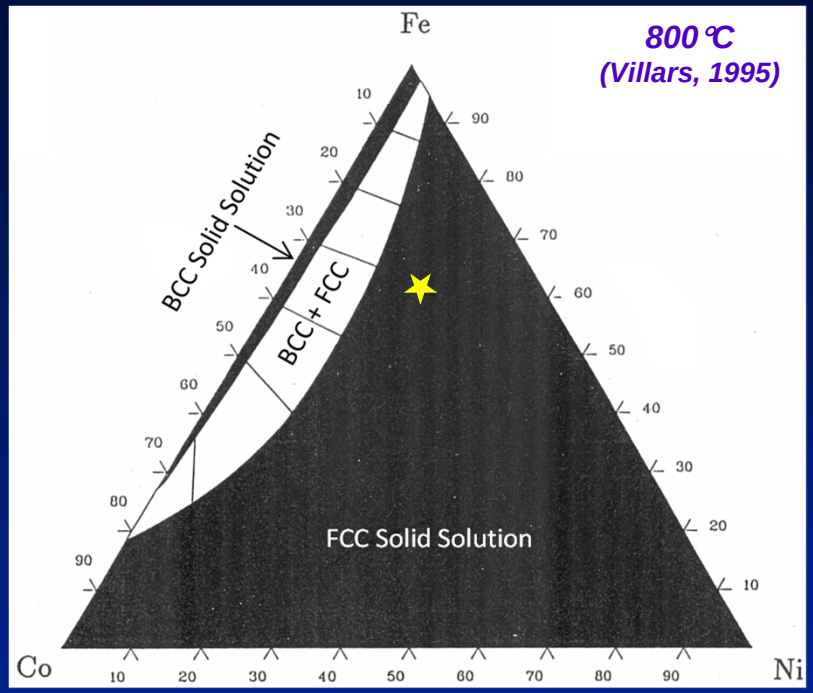
Zhu et al., IJHE, 2018

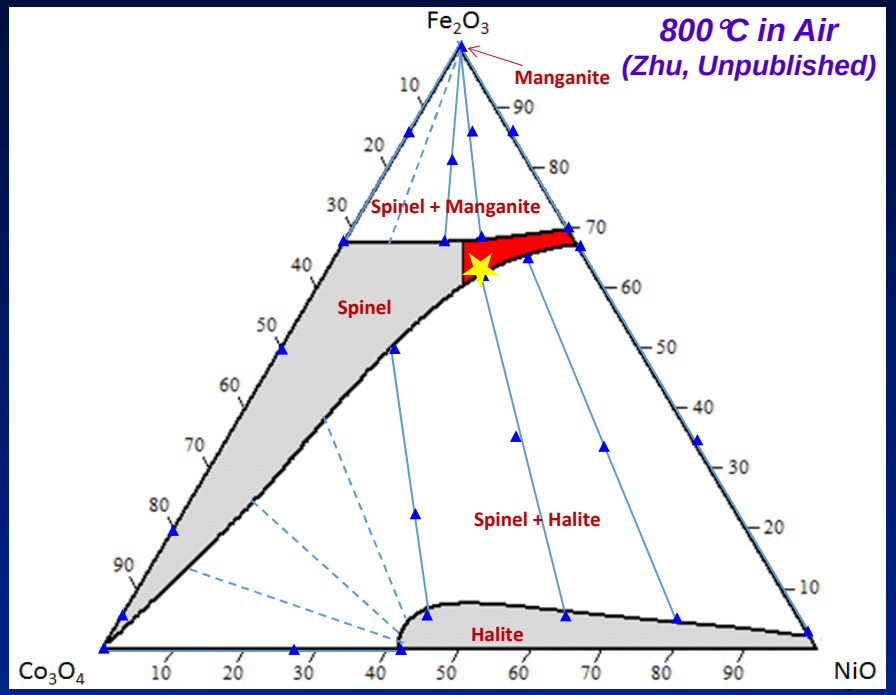


Project Objectives

- **Optimization of the multi-component alloy precursor composition as contact material.** The alloy compositions will be optimized via composition screening in the $(Ni,Fe,Co,X)_3O_4$ and $(Mn,Co,X)_3O_4$ system, alloy design using physical metallurgy principles, and cost considerations. The desired alloy powders will be manufactured & characterized in detail.
- **Demonstration/validation of the contact layer performance in relevant SOFC stack environments.** Long-term ASR behavior and in-stack performance of the contact layer in relevant stack operating environments, its microstructure, chemical compatibility & Cr-retaining capability will be evaluated.
- **Further cost reduction and commercialization assessment.** Approaches to further reducing the stack cost will be explored, such as co-sintering of the interconnect coating and contact layer. Cost analysis and scale-up assessment will be conducted for potential commercialization.

Phase Equilibria in Co_3O_4-Fe_2O_3-NiO System





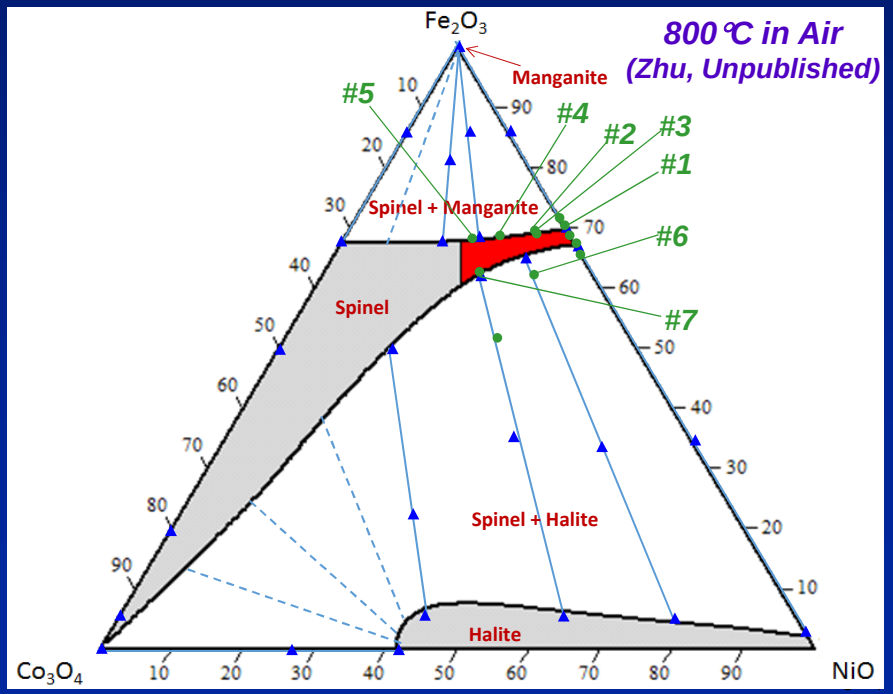
- While the phase equilibria in ternary Fe-Ni-Co system have been well documented, this is not the case for the Fe-Ni-Co-O system.
- By combining the binary system data, thermodynamic assessment, & experimental investigation, we have determined the Fe_2O_3-NiO-Co_3O_4 phase diagram at 800°C in air.
- Of particular interest to our contact material development are the low-Co spinel compositions near the spinel phase boundaries.

Spinel Compositional Optimization in $(Ni,Fe,Co,X)_3O_4$

- The pellets of various $(Ni,Fe,Co,X)_3O_4$ spinel compositions were prepared for electrical conductivity and CTE measurements.
- The Fe/Ni/Co ratio in $(Ni,Fe,Co)_3O_4$ was varied, while keeping the overall composition close to the phase boundaries.
- Additional microalloying elements (X = X', X", etc. – transitional metal and/or a reactive element) were doped into $(Ni,Fe,Co)_3O_4$ to further improve its properties.

Selected Compositions Evaluated in Our Study

Sample #	Composition
1	$Ni_{.84}Fe_{2.16}O_4$
2	$Ni_{.69}Co_{.15}Fe_{2.16}O_4$
3	$Ni_{.72}Co_{.15}Fe_{2.13}O_4$
4	$Ni_{.60}Co_{.30}Fe_{2.10}O_4$
5	$Ni_{.48}Co_{.45}Fe_{2.07}O_4$
6	$Ni_{.84}Co_{.27}Fe_{1.89}O_4$
7	$Ni_{.675}Co_{.48}Fe_{1.845}O_4$
8	$Ni_{.81}X'_{.03}Fe_{2.16}O_4$
9	$Ni_{.66}X'_{.03}Co_{.15}Fe_{2.16}O_4$
10	$Ni_{.81}X''_{.03}Fe_{2.16}O_4$

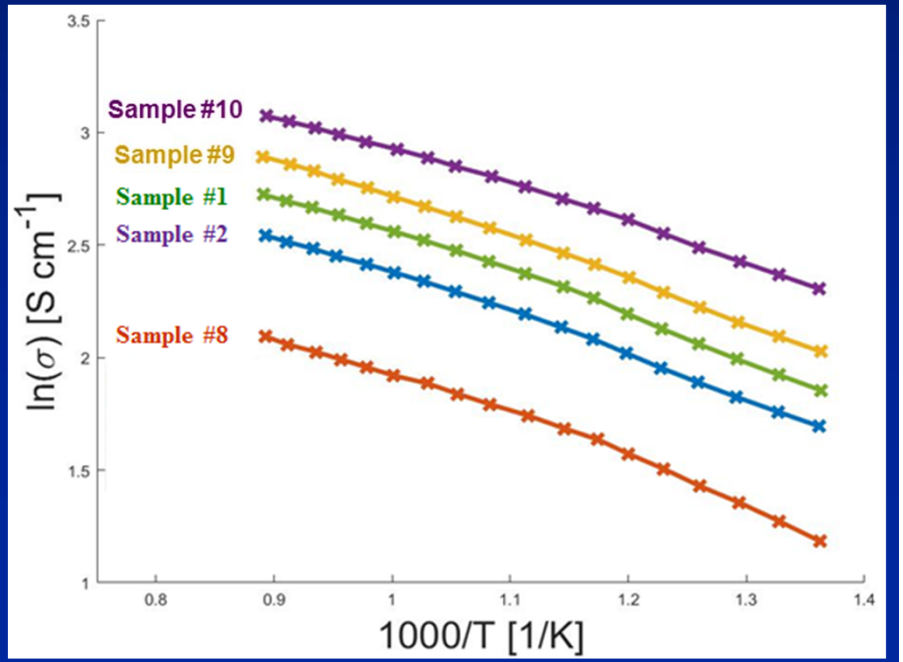


Some Compositions Highlighted on Phase Diagram

Spinel Compositionin in $(Ni,Fe,Co,X)_3O_4$: Electrical Conductivity and CTE

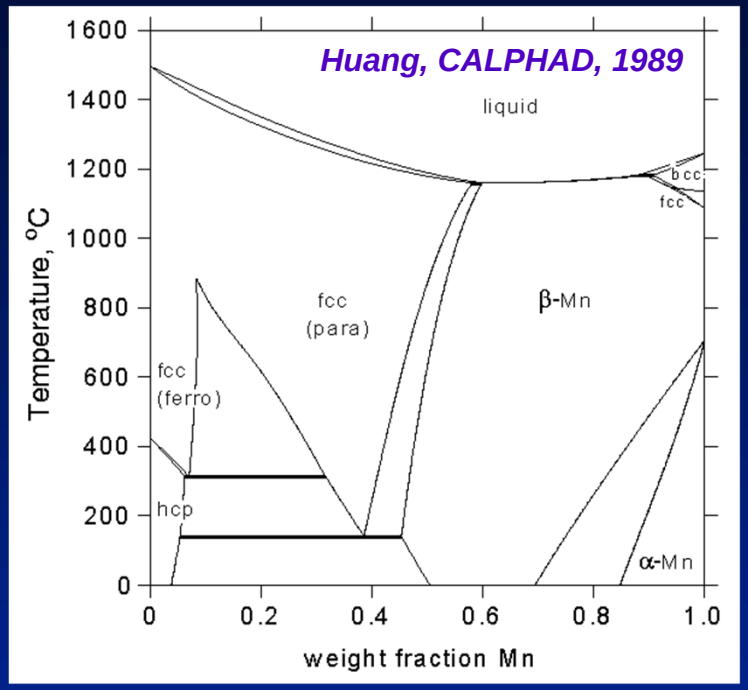
- Regardless of the Co level in the spinel, its Fe level dictated the electrical conductivity, which increased as it became more Fe-excess.
- A combination of Co and X′ doping was beneficial in further increasing the spinel conductivity.
- An even higher electrical conductivity was observed in the X″-doped spinel $Ni_{0.81}X''_{0.03}Fe_{2.16}O_4$.
- Fe/Ni/Co ratio and alloying addition had little effect on CTE (~$12x10^{-6}$/°C).

Sample #	Composition	Conductivity at 800°C (S/cm)
1	$Ni_{.84}Fe_{2.16}O_4$	14.4
2	$Ni_{.69}Co_{.15}Fe_{2.16}O_4$	12.0
3	$Ni_{.72}Co_{.15}Fe_{2.13}O_4$	10.9
4	$Ni_{.60}Co_{.30}Fe_{2.10}O_4$	7.0
5	$Ni_{.48}Co_{.45}Fe_{2.07}O_4$	5.1
6	$Ni_{.84}Co_{.27}Fe_{1.89}O_4$	1.4
7	$Ni_{.675}Co_{.48}Fe_{1.845}O_4$	2.5
8	$Ni_{.81}X'_{.03}Fe_{2.16}O_4$	7.6
9	$Ni_{.66}X'_{.03}Co_{.15}Fe_{2.16}O_4$	16.9
10	$Ni_{.81}X''_{.03}Fe_{2.16}O_4$	21.1



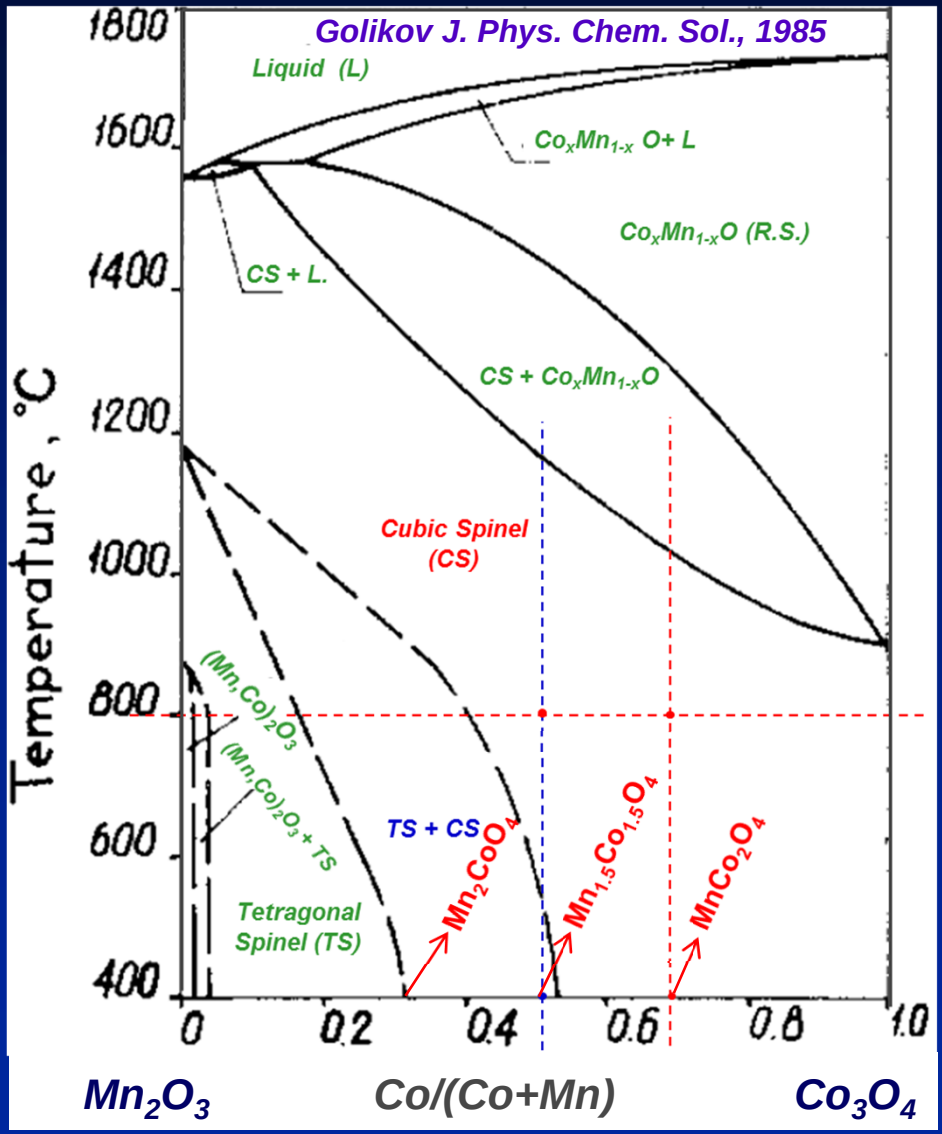
Conductivity as a Function of Temperature

Phase Equilibria in Mn_2O_3-Co_3O_4 System



Phase Diagram of the Co-Mn System

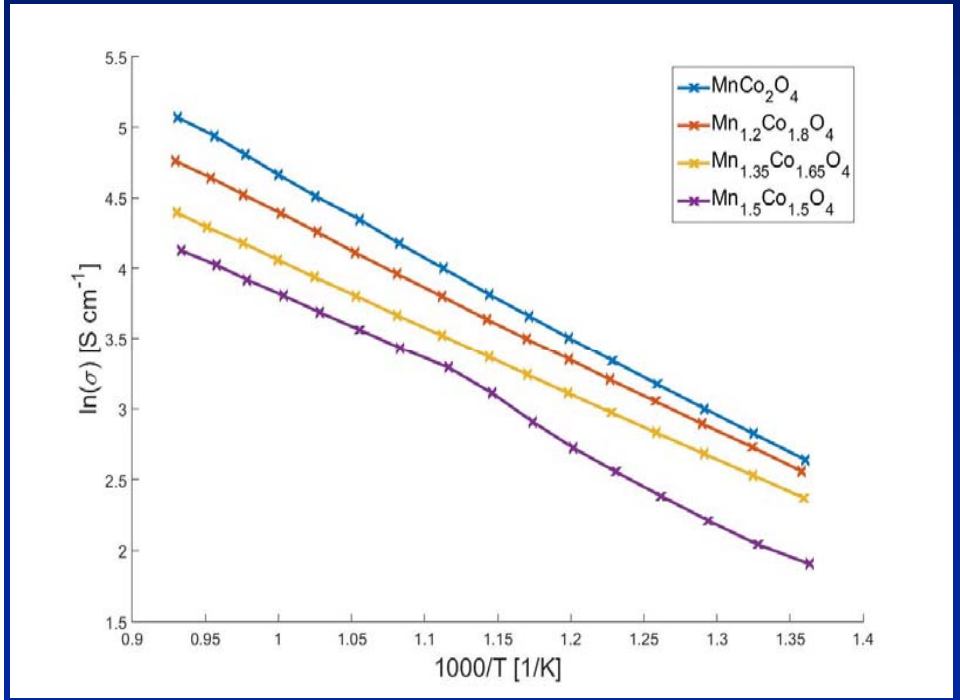
- Some controversies exist for the Mn_2O_3-Co_3O_4 system.
- Two most important compositions in the $(Mn,Co)_3O_4$ spinel system are:
  - ✓ $MnCo_2O_4$: CS at both 800 and 20°C;
  - ✓ $Mn_{1.5}Co_{1.5}O_4$: CS at 800°C and TS + CS at 20°C.



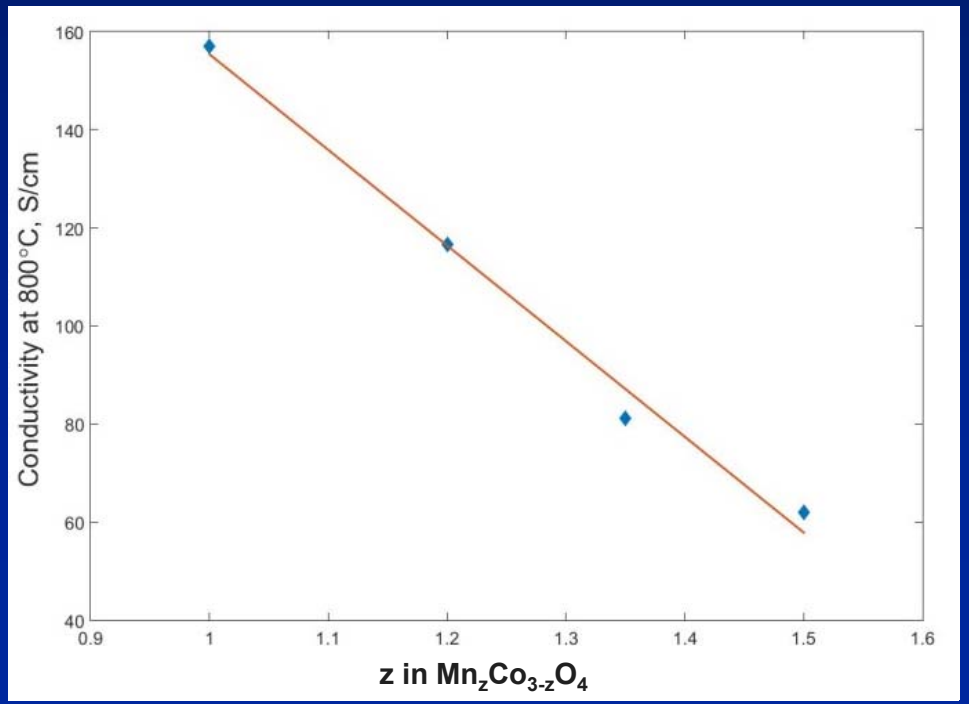
Phase Diagram of the Co-Mn-O System in Air

Spinel Compositional Optimization in $(Mn,Co,X)_3O_4$: Electrical Conductivity of $Mn_zCo_{3-z}O_4$

- A range of electrical conductivity and CTE has been reported for both $MnCo_2O_4$ and $Mn_{1.5}Co_{1.5}O_4$. Some data are contradictory to each other.
- As Mn in $Mn_zCo_{3-z}O_4$ increased from z = 1.0 (i.e., $MnCo_2O_4$) to z = 1.5 (i.e., $Mn_{1.5}Co_{1.5}O_4$), the electrical conductivity of the spinel decreased.
- A change in activation energy for electrical conduction was observed for $Mn_{1.5}Co_{1.5}O_4$, likely due to the phase transition in this spinel.



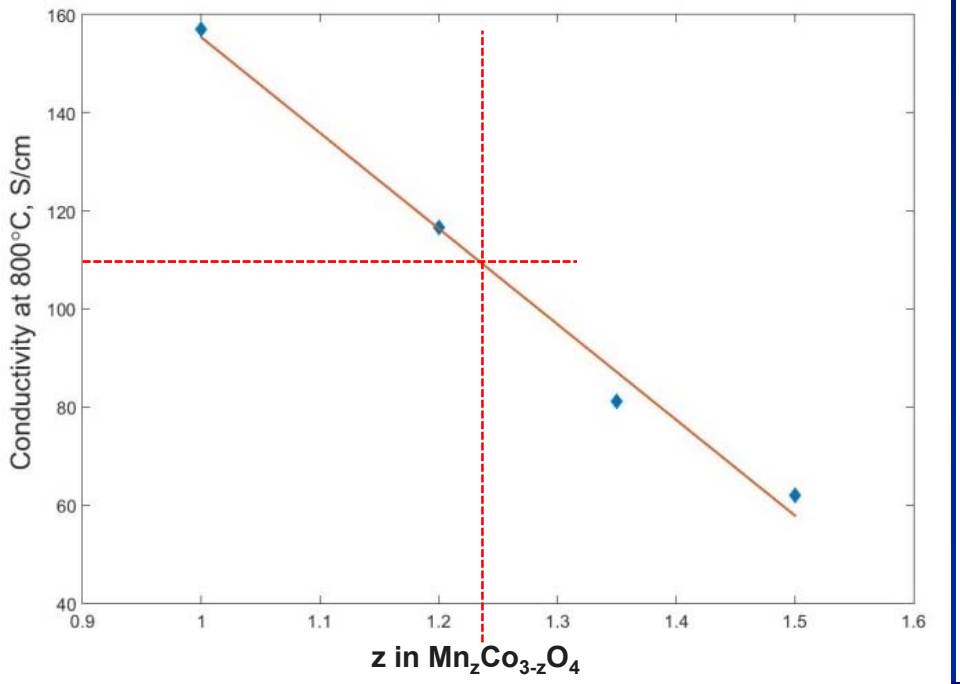
Electrical conductivity vs. Temperature



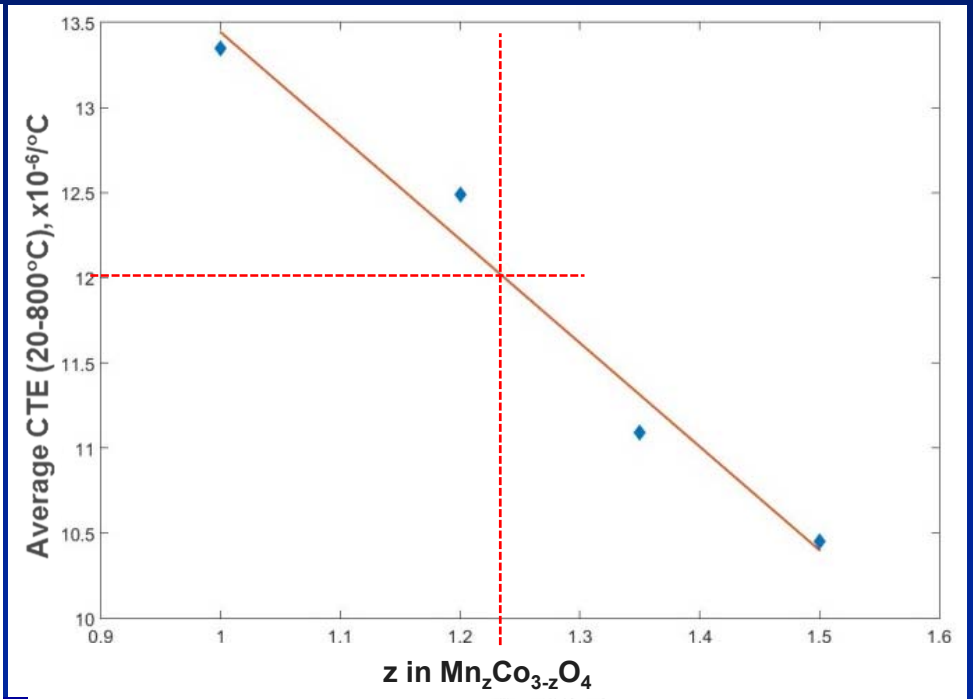
Electrical conductivity at 800°C in Air

Spinel Compositional Optimization in $(Mn,Co,X)_3O_4$: Average CTE of $Mn_zCo_{3-z}O_4$

- As Mn in $Mn_zCo_{3-z}O_4$ increased from z = 1.0 (i.e., $MnCo_2O_4$) to z = 1.5 (i.e., $Mn_{1.5}Co_{1.5}O_4$), the CTE of the spinel decreased.
- A change in the slope of thermal expansion curve for $Mn_{1.5}Co_{1.5}O_4$ is related to the phase transition in this spinel.
- The spinel $Mn_{1.23}Co_{1.77}O_4$ will have a CTE of 12.0×10^{-6}/°C and a conductivity of 110 S/cm at 800°C – likely a better coating choice.



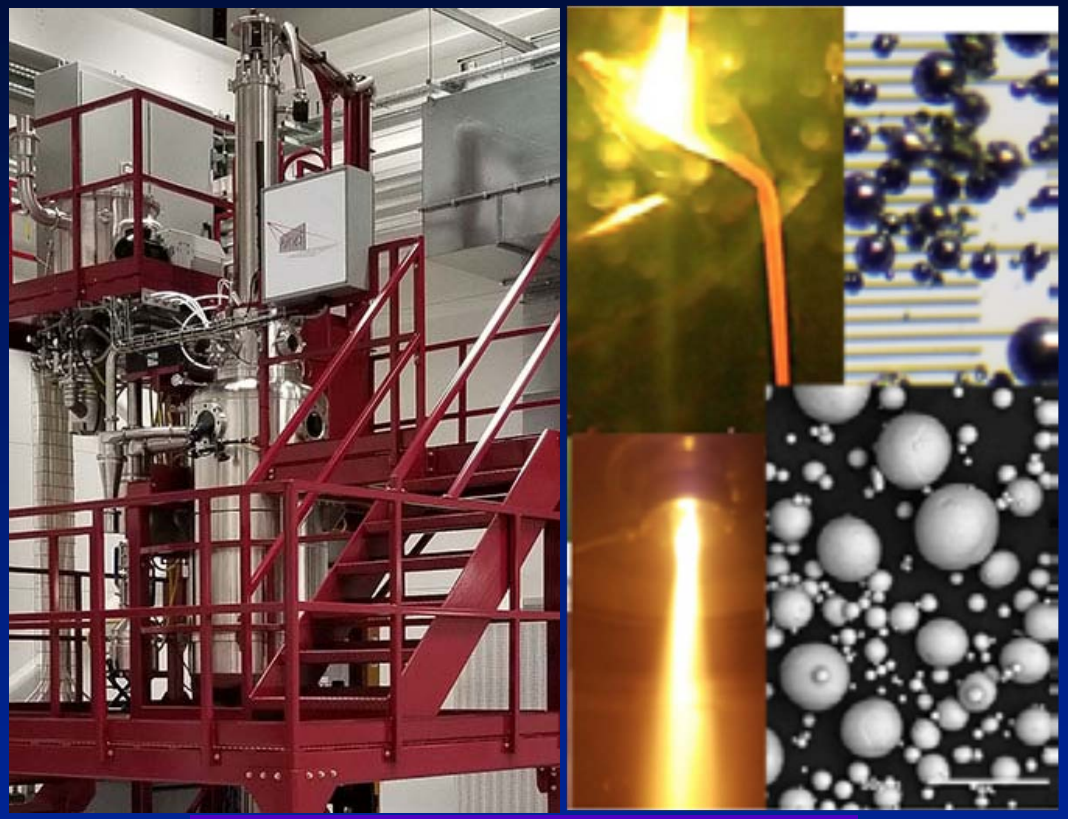
Electrical conductivity at 800°C in Air



Average CTE vs. Spinel Composition

Gas Atomization of the Optimization Alloys

- Based on the phase constitution, electrical conductivity, and CTE, a number of Fe-Ni-Co-X and Mn-Co-X precursor alloy compositions were selected for the powder preparation.
- The powders with the desired composition and particle size were manufactured using a semi-industrial gas atomizer.



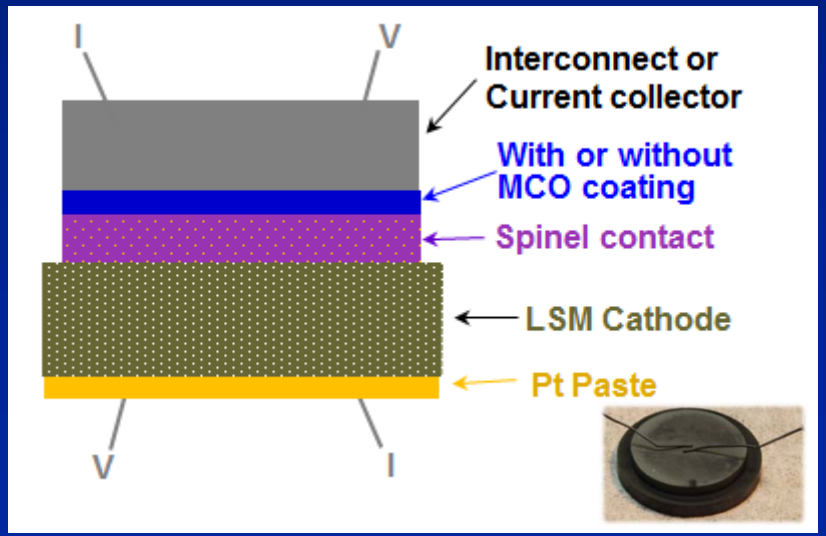
Gas Atomization System

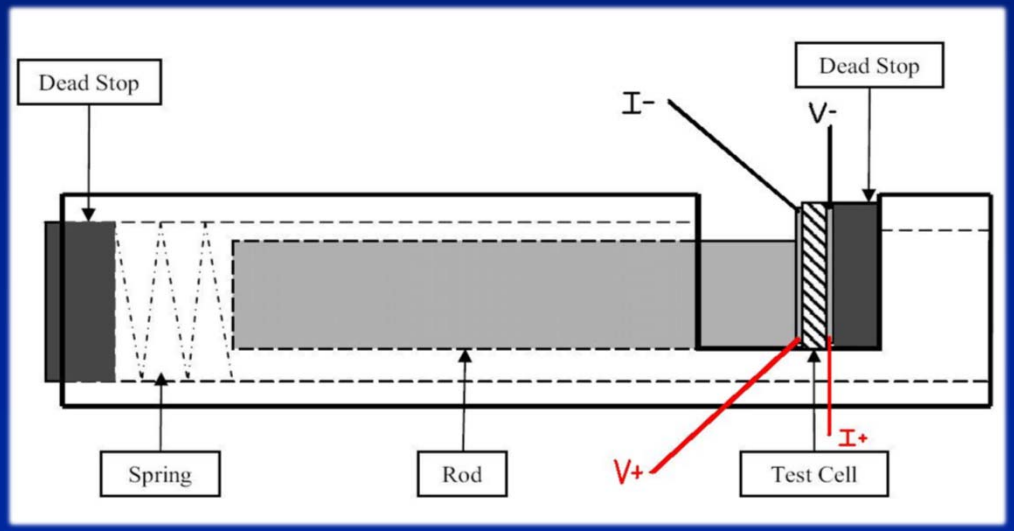
- Chemical analysis of the collected powders was conducted at Dirats Lab – a close match with the targeted compositions was achieved.

TTU is currently in process of acquiring a lab-scale gas atomizer for alloy powder making under a DoD DURIP project.

Area-Specific Resistance (ASR) Measurement

- A number of test cells were constructed, with the spinel-forming contact precursor layer sandwiched between the ferritic alloy [AISI 441, Crofer 22 APU, or $(Mn,Co)_3O_4$ (MCO)-coated ZMG230G10] and the LSM cathode.
- The test cells were spring-loaded and the ASR change during either isothermal or cyclic exposure at 800°C in air was monitored using a special 6-cell test rig.

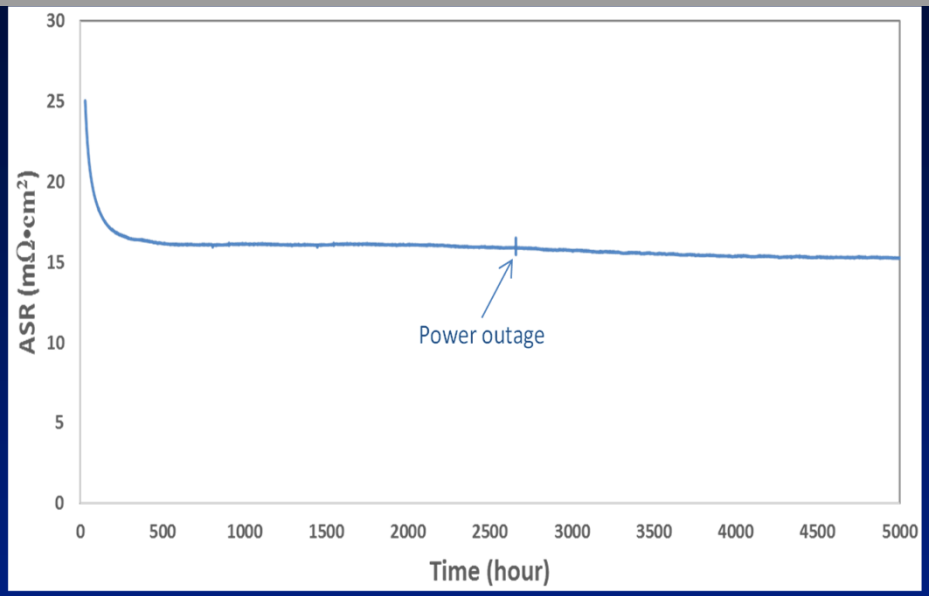




Schematic of the ASR Test Cell and Test Configuration

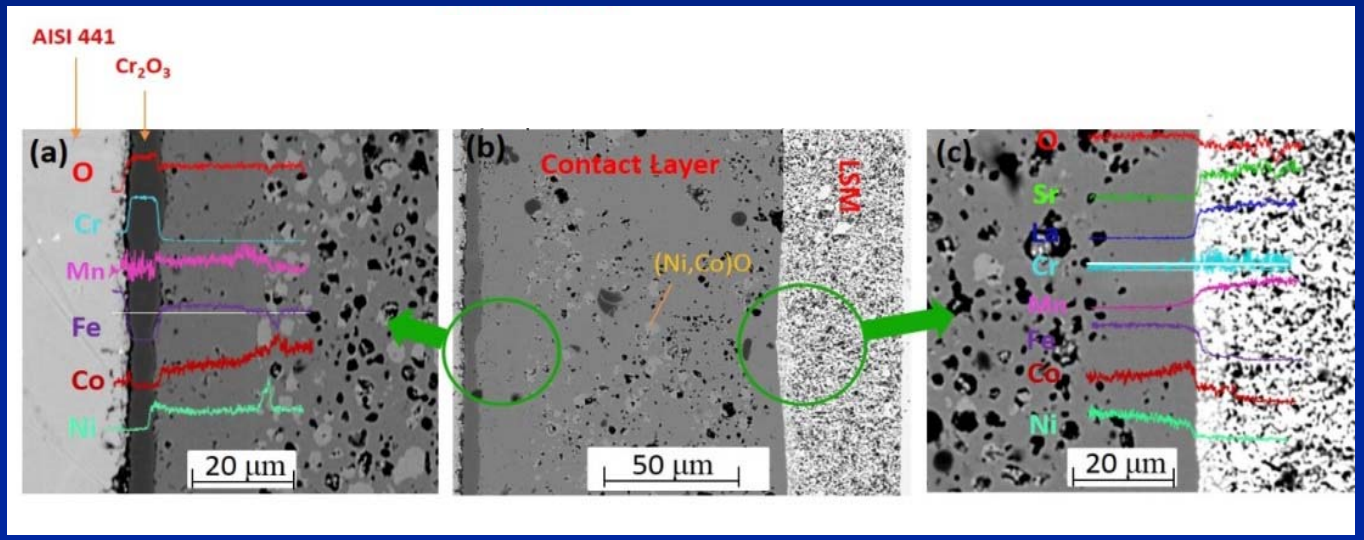
Cell ASR with an Fe-Ni-Co Based Alloy Contact Precursor

- After initial sintering at 900°C for 2 h, the ASR for AISI 441/contact /LSM cell with the Fe-Ni-Co-X alloy precursor was very stable, with an ASR of about 15-17 $m\Omega \cdot cm^2$ during 5000-h isothermal exposure at 800°C in air.
- The contact layer effectively blocked outward diffusion of Cr from the un-coated AISI 441.



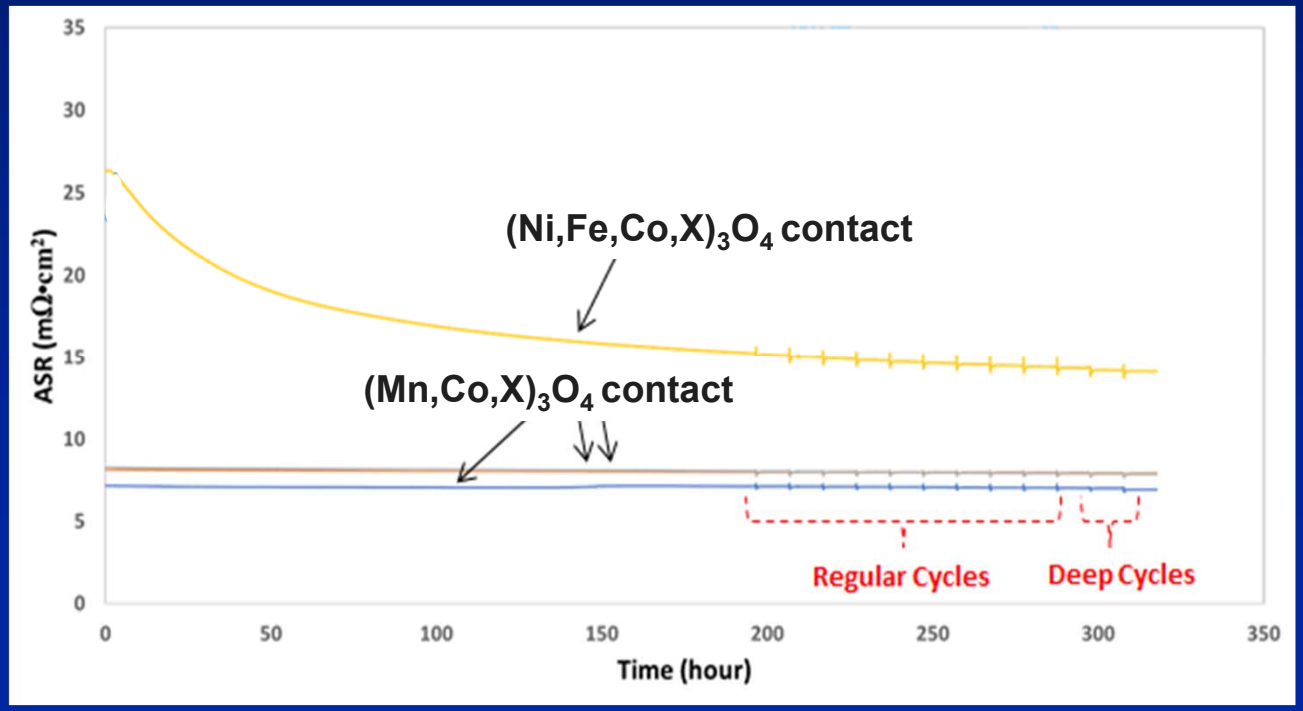
Cell ASR at 800°C during Isothermal Exposure

Cross-sectional View of the Test Cell with EDS Line-scan Results



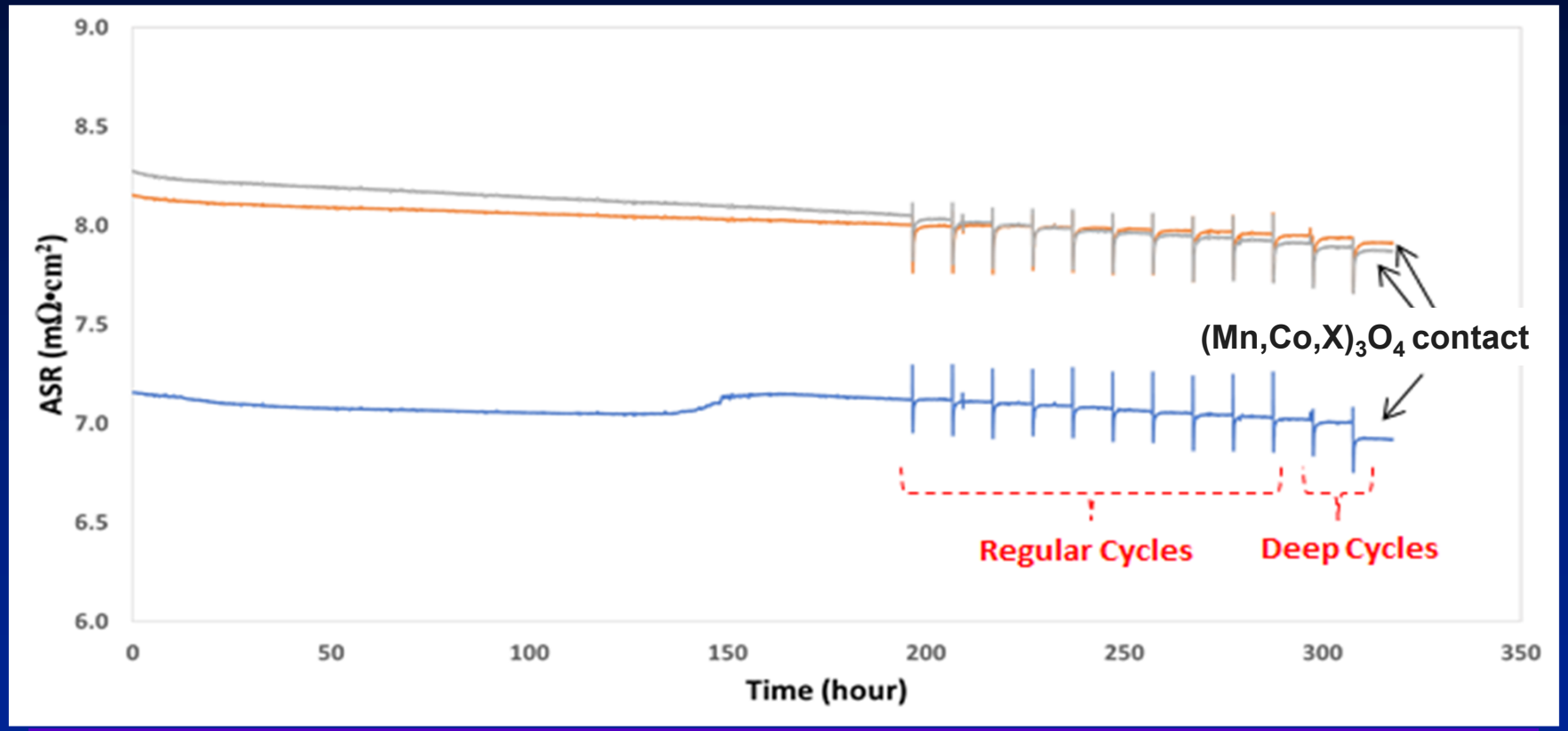
Cell ASR with an $(Mn,Co,X)_3O_4$-Forming Precursor

- After initial sintering at 900°C for 2 h, the MCO-precoated ZMG230G10 /contact/LSM cells with the $(Ni,Fe,Co,X)_3O_4$/$(Mn,Co,X)_3O_4$-forming precursors were isothermally exposed at 800°C for 200 h, followed by 10 regular cycles (cooling to 250°C) and 2 deep cycles (cooling to 20°C).
- Compared to the $(Ni,Fe,Co,X)_3O_4$-forming precursor, the $(Mn,Co,X)O_4$-forming precursor led to lower, more stable ASR values (about 7-9 $m\Omega \cdot cm^2$ at 800°C) for the test cells.



Cell ASR vs. Time for Two Different Contact Materials. (Each regular cycle consisting of cooling from 800 to 250°C, re-heating to 800°C, and then holding at 800° C for 10 h, while during each deep cycle, the cell was cooled to room temperature.)

Stable, low ASR was obtained for the MCO-precoated ZMG230G10/contact/LSM cells with the $(Mn,Co,X)_3O_4$ contact

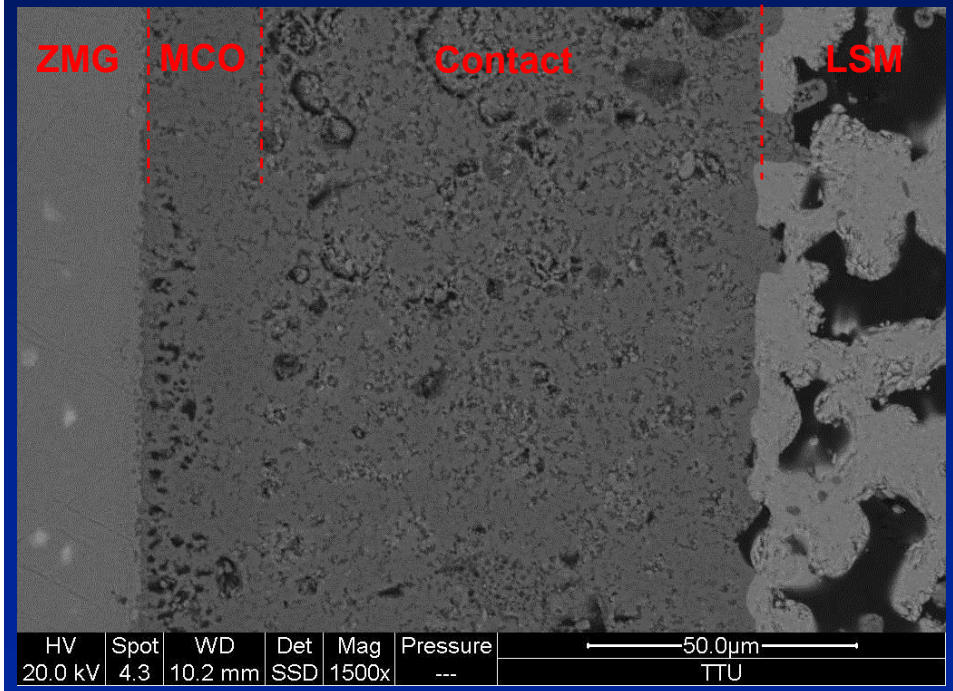


Expanded View of Cell ASR vs. Time for $(Mn,Co,X)_3O_4$-Contacted Cells

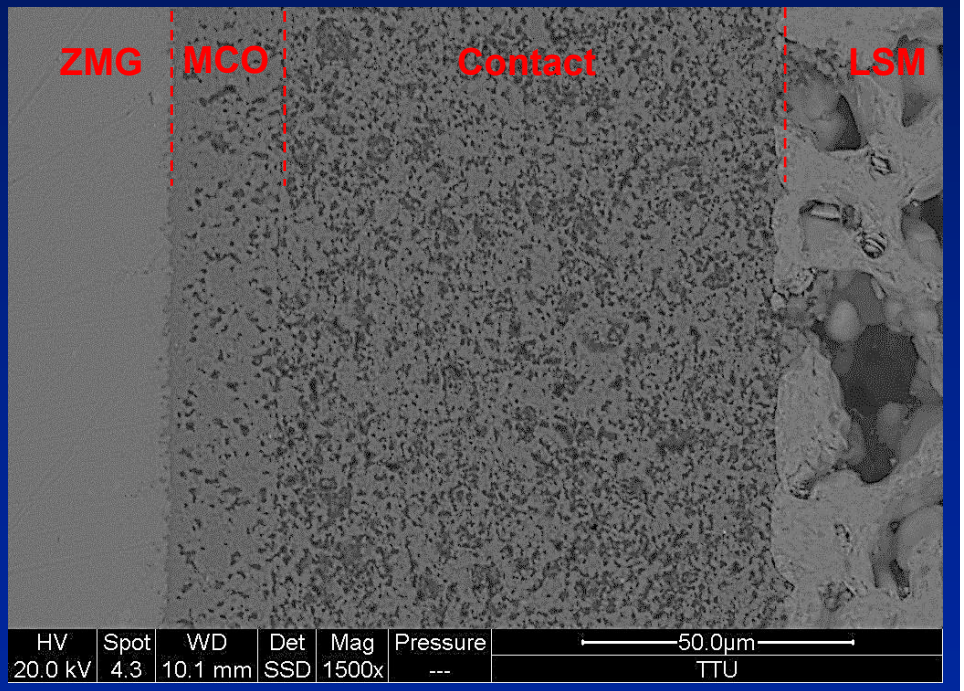
- Very stable, repeatable ASR data was obtained, due to the excellent chemical compatibility between the different components;
- The negligible effect of thermal cycling on the ASR behavior is a result of good matching in CTE between these components.

Cross-sectional View of Tested Cells

- For both cases, a porous contact layer was formed between the coated alloy and the porous cathode. No cracking or delamination near the contact zone was observed.
- Negligible interactions between the contact layer with the MCO coating or the LSM cathode were noticed.



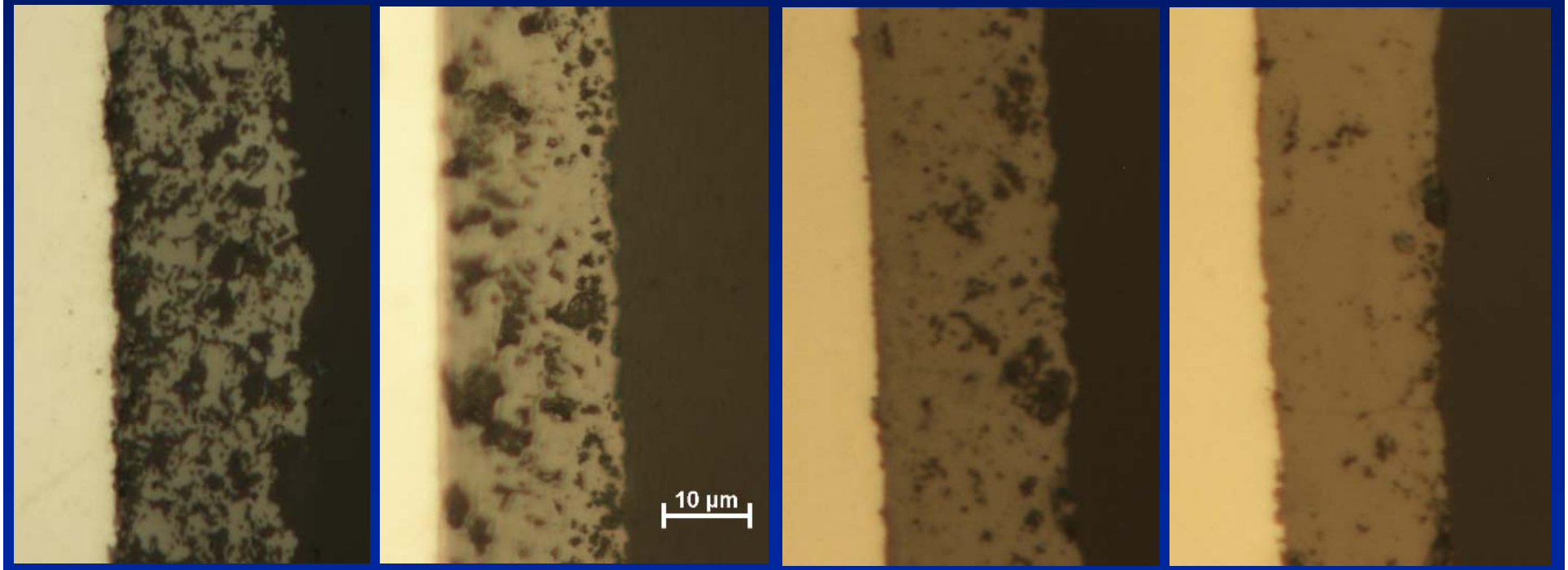
Cross-sectional View of Tested Cell with the $(Ni,Fe,Co,X)_3O_4$ Contact



Cross-sectional View of Tested Cell with the $(Mn,Co,X)_3O_4$ Contact

EARS Processing of Dense MCO Coatings

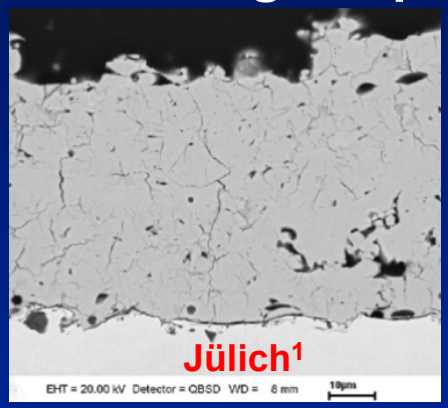
- Reactive sintering of a dense MCO coating via EARS has been explored and initial results are very encouraging:
  - By controlling the composition/shape/size/size distribution/initial packing density of the metallic precursor powders, a dense spinel layer was obtained after thermal conversion at 900°C for 2 h in air.

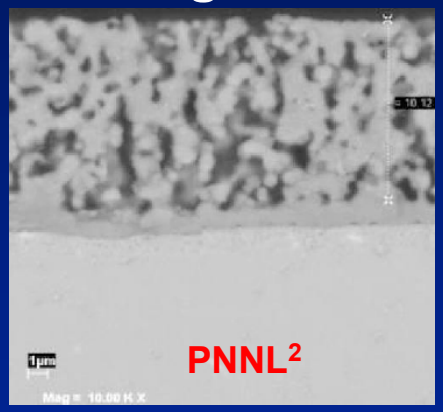


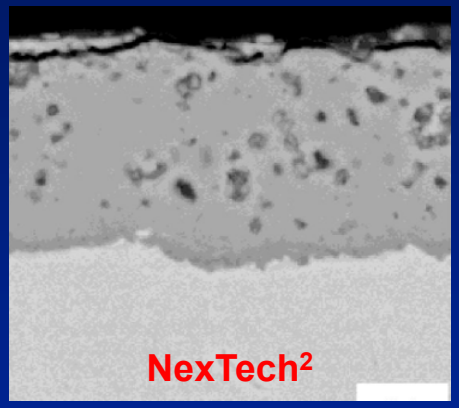
Improvement in Quality of TTU's Reactive Sintered MCO Coatings on Crofer 22 APU

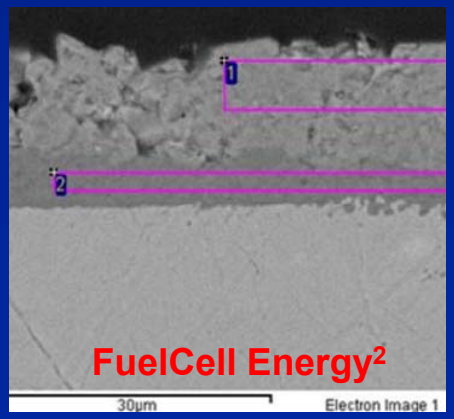
Comparison of Our Coating with the State-of-the-Art

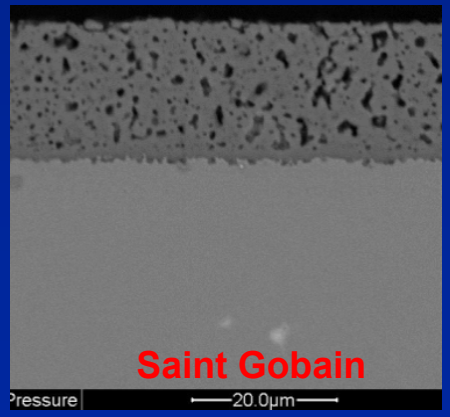
- Current MCO coating processes typically involve costly equipment, high processing temperatures (> 900°C) and/or a reduction treatment.
- Our EARS process offers a potentially better MCO coating quality.
- The EARS-derived coating does not require a reduction treatment or a sintering temperature higher than 900°C.

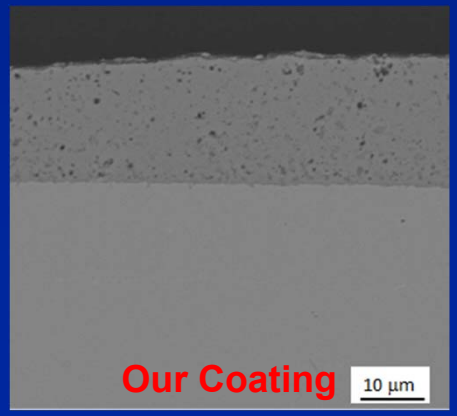










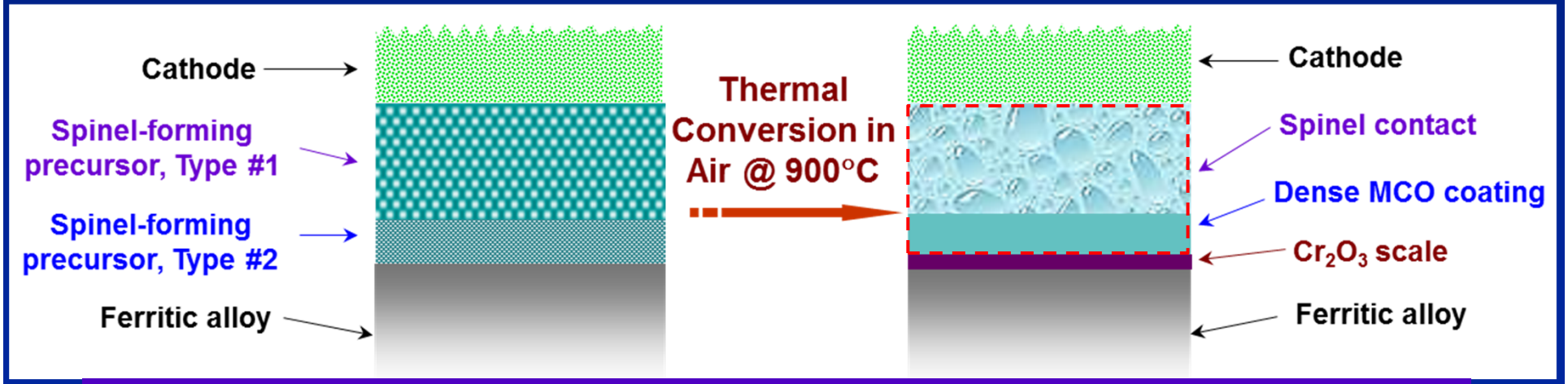


[1]R. Vaßen et al., Surf. & Coat. Tech., 2016;

[2]Ghezel-Ayagh, SECA Coal-Based Systems – Final Report, 2014

Co-sintering of Coating/Contact Dual-Layer Structure: Proposed Approach

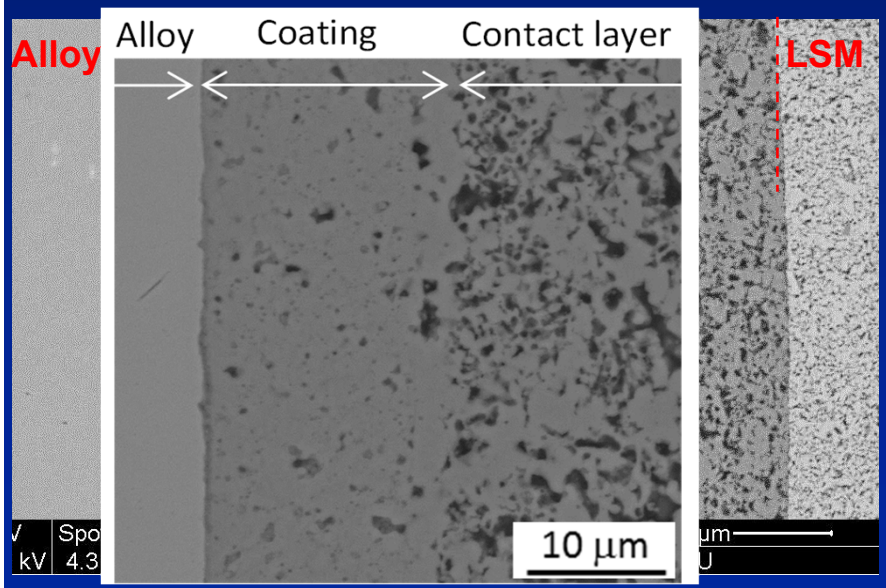
- To lower the interfacial ASR at the alloy/contact interface, improve the contact quality, and reduce the coating and contact processing cost, co-sintering of the coating and the contact layer during initial stack firing/operation is also explored, utilizing two different metallic precursors:
  - Two spinel-forming precursors (Type #1 – for the contact layer and Type #2 – for the dense MCO coating) will be employed;
  - Reactive co-sintering in air at a sintering temperature of 900°C will be utilized for simultaneous formation of the dual-layer structure.



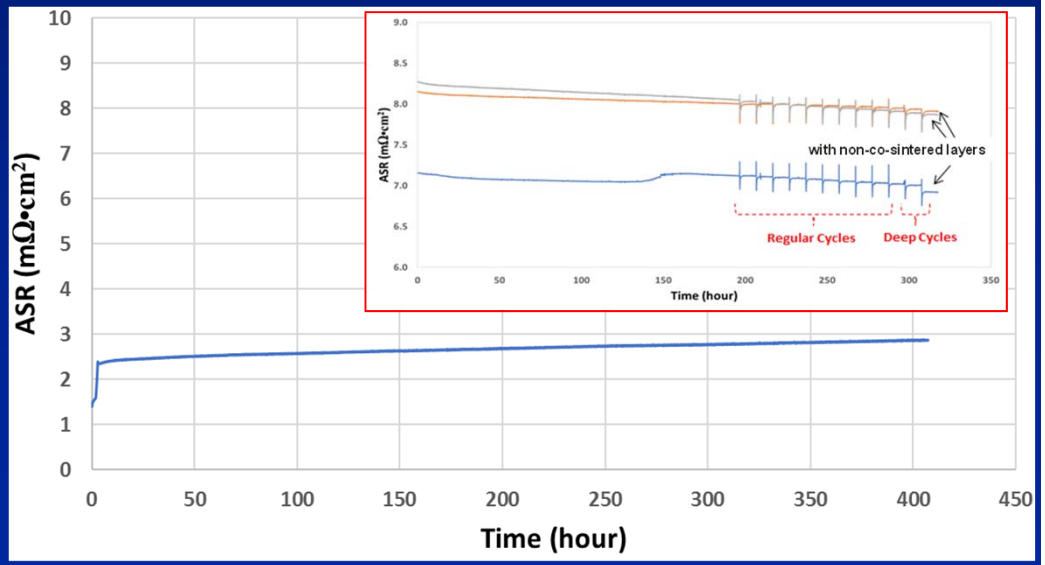
Proposed Co-sintering of Spinel-Based Coating/Contact Dual-Layer Structure

Initial Results on Co-sintering of Coating/Contact Layers

- After screen printing the spinel-forming coating/contact precursor layers on Crofer 22 APU, the alloy/coating/contact /LSM cell was co-sintering in air at 900°C for 2 h.
- A highly dense MCO coating layer and a porous contact layer were obtained, both of which were well sintered.
- Our co-sintered dual-layer structure led to better ASR performance than the non-co-sintered ones.

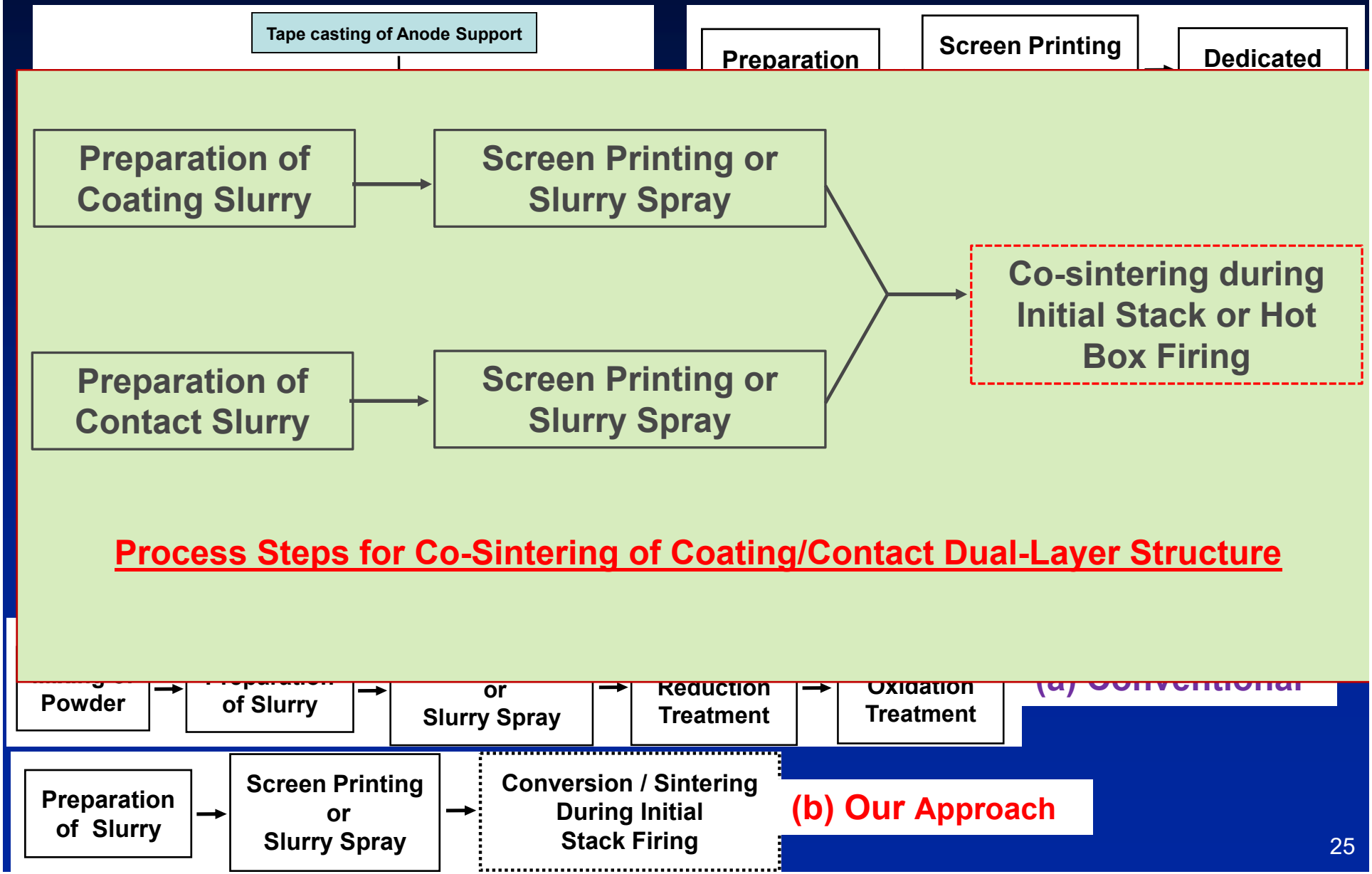


Cross-sectional View of Co-sintered Dual-layer Structure



Cell ASR vs. Time with the Co-sintered Dual-layer Structure between Crofer 22 APU & LSM

Cost Analysis – Simplified Synthesis of Contact Layer and Interconnect Coating for ASC-SOFC Stacks



Concluding Remarks

- Several compositions in the $(Ni,Fe,Co,X)_3O_4$ and $(Mn,Co,X)_3O_4$ systems have been identified for SOFC contacting applications, based on considerations of phase constitution, electrical conductivity, CTE, etc.
- A number of Ni-Fe-Co and Mn-Co based precursor alloy powders have been prepared via gas atomization.
- Low-cost, EARS-processed $(Ni,Fe,Co)_3O_4$- and $(Mn,Co)_3O_4$-based contact layers with promising ASR performance have been successfully demonstrated.
- By controlling the metallic precursor powder composition, size, size distribution, and initial powder packing density, a dense MCO coating have been synthesized for protecting the interconnect or current collector alloys.
- Co-sintering of a dual-layer structure with a dense spinel layer as coating and a porous layer as contact can be achieved by utilizing two tailored metallic precursors.

Acknowledgments

- U. S. Department of Energy - National Energy Technology Laboratory, Solid Oxide Fuel Cell Prototype System Testing and Core Technology Development Program, Award No. DE-FE0031187; Project Manager: Dr. Patcharin Burke

- Allen Yu, Joseph Simpson, David Chesson, and Brian Bates, TTU

- Dr. Hossein Ghezel-Ayagh, FuelCell Energy, Inc.

- Dr. John Pietras and his team at Saint Gobain

Project Milestones

Milestone Title/Description	Planned Start Date	Planned Completion Date	Actual Completion Date	Verification Method	Status
Revised PMP	10/10/2017	10/30/2017	10/23/2017	PMP file	Completed
Kickoff Meeting	10/30/2017	12/29/2017	11/29/2017	Presentation file	Completed
Compositional optimization of Precursor alloy	11/01/2017	06/30/2018	06/28/2018	Optimal Fe/Ni/Co and other alloy additions are identified.	Completed
Preparation of the optimized alloy powder	11/15/2017	09/31/2018	09/20/2018	Atomization of one alloy powder is completed.	Completed
Demonstration of long-term cell ASR stability with the new contact	01/01/2018	06/30/2019	02/20/2019	The ASR stability is demonstrated successfully for about 5,000 h.	Completed
Demonstration of stack performance stability with 1-cell stack testing	04/02/2018	07/31/2019		Stack performance stability testing for ≥ 1,000 h is completed at industrial site.	In progress
Cost analysis and commercialization feasibility	07/01/2019	09/31/2019		Cost analysis and scale-up assessment are completed.	Just started