# Development of Low-Cost, Highly-Sinterable $(Ni,Fe)_3O_4$-Based Materials for SOFC Cathode-Side Contact Application

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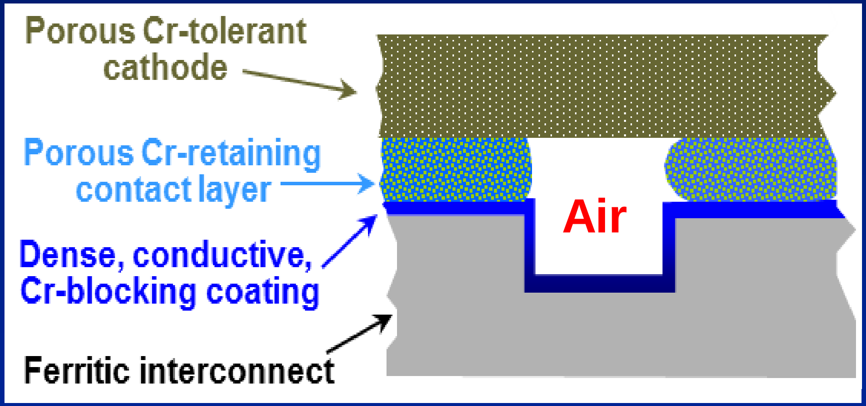
# Outline

- Introduction and Project Objectives
- Major Progress/Conclusions from the Phase I Study
- Effect of Starting Powders on the Spinel Layer Formation
- Performance Evaluation of the Sintered Spinel Contact
  - Area Specific Resistance (ASR), Chemical Compatibility, etc.
- Cost Analysis
- Concluding Remarks
- Acknowledgments

# Cathode-Side Contact in SOFC Stacks

- **Major functions of cathode-side contact:**
  - To minimize the ohmic resistance at the interconnect-electrode interface
  - To improve mechanical bonding
  - To provide for additional gas channels to the electrode

- **Requirements of cathode-side contact materials:**
  - Low material/processing cost
  - High electrical conductivity
  - Match in CTE
  - Adequate stability and compatibility
  - Appropriate sinterability and porosity level
  - Good bonding strength with adjacent stack components

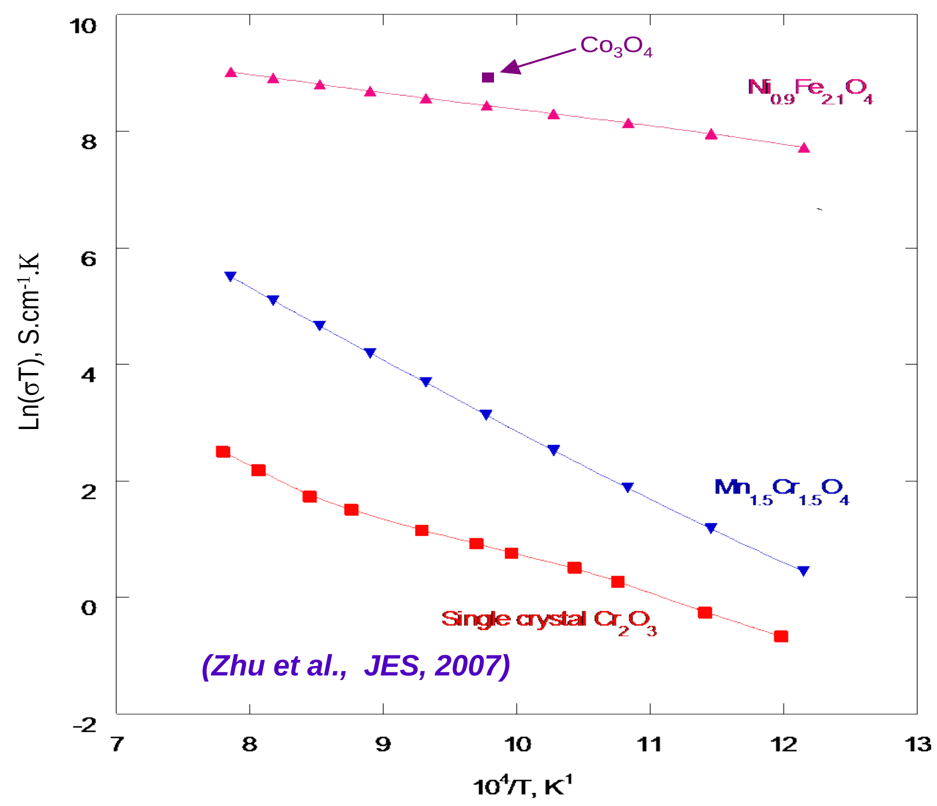



*Schematic of the Cathode-Interconnect Interface*

# Why $NiFe_2O_4$-Based Spinel as Contact Material?

- **Most of cathode contact developments have focused on (<u>L</u>a,<u>S</u>r)(<u>M</u>n,<u>C</u>o,<u>F</u>e,<u>N</u>i)$O_3$:**
  - **Difficulty in balancing the electrical conductivity, CTE & sinterability of perovskites.**
- **Conductive spinels based on $NiFe_2O_4$ are also promising:**
  - **Low cost, decent electrical conductivity and CTE ($12x10^{-6}$/°C).**

| Metal | Cost ($/lb) |
|---|---|
| Cobalt | 13.5 |
| Nickel | 4.5 |
| Iron | 0.2 |




**Electrical Conductivity of $(Ni,Fe)_3O_4$, as Compared with Other Oxides**

- **Unfortunately, the sinterability of $NiFe_2O_4$ is poor (≥1200°C) if metal oxides are used. Novel sintering mechanisms need to be identified and utilized to lower its sintering temperature.**

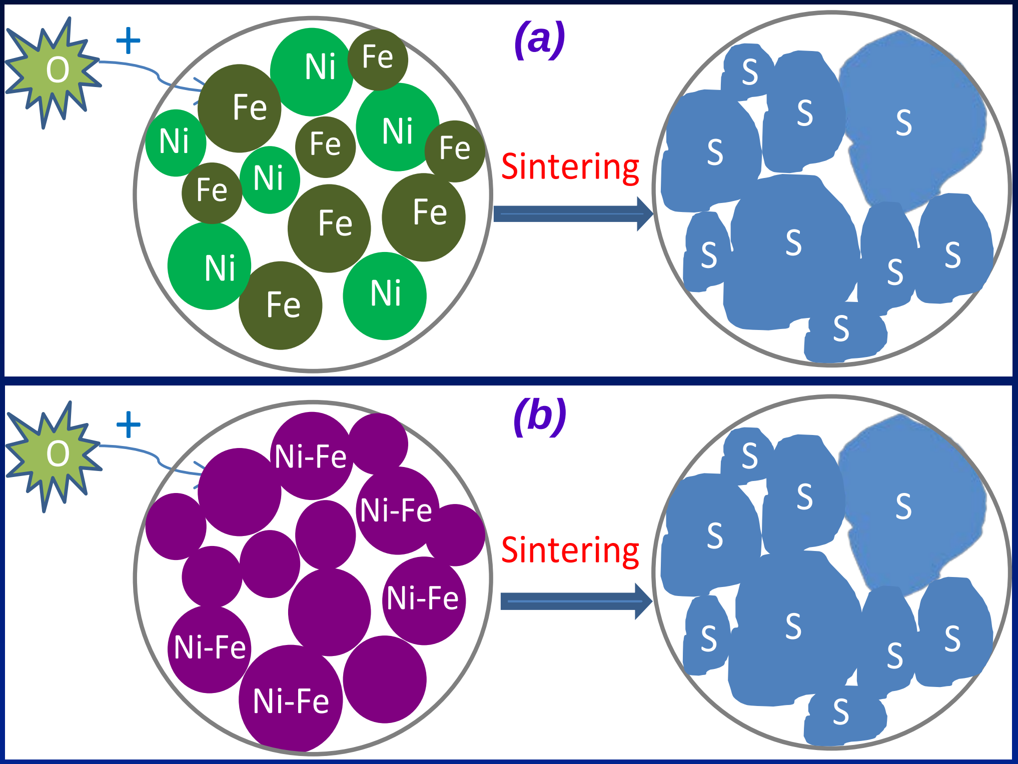
# Utilization of EARS for Reduced-Temperature Sintering of $(Ni,Fe)_3O_4$-Base Spinel Contact

- **Employment of metallic powders instead of oxide powders as the starting precursor to lower the sintering temperature**
  - **Environmentally-Assisted Reactive Sintering (EARS) :**

$$Ni + 2Fe + 2O_2(g) = NiFe_2O_4$$

**vs.**

$$NiO + 2Fe_2O_3 = NiFe_2O_4$$

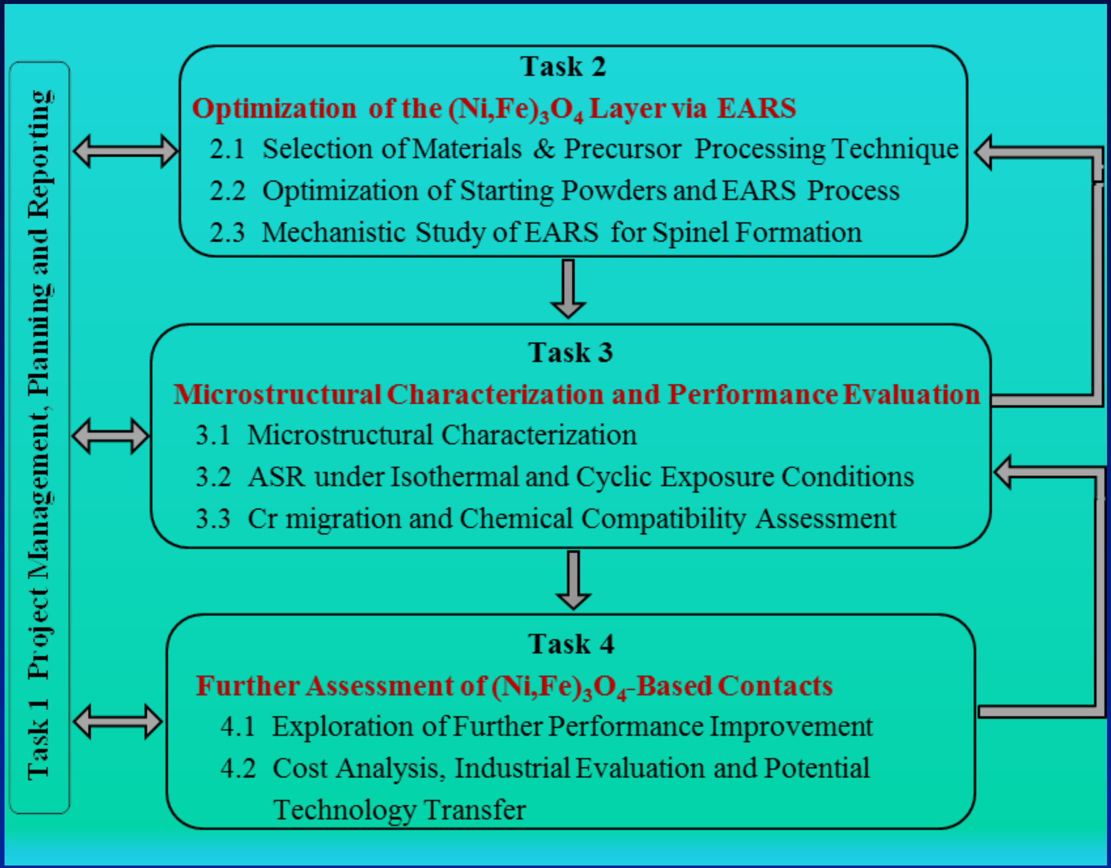



**Synthesis of $(Ni,Fe)_3O_4$ ("S") via EARS using (a) Mixed Fe & Ni Powders; (b) Fe-Ni Alloy Powder**

- **Enhanced sintering via EARS due to the following facts:**
  - **Heat released during the reaction;**
  - **Volume expansion upon conversion of metal to metal oxide;**
  - **Formation of highly active, nanoscale surface oxides**
  - **Shorter diffusion distance when a prealloyed powder is employed.**

# Phase I Project Objectives

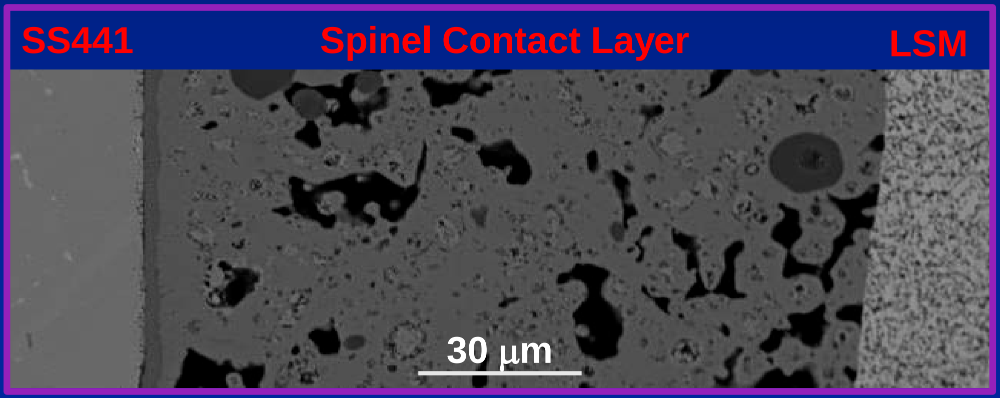
- **Optimization of the $(Ni,Fe)_3O_4$ spinel layer formation via controlling the parameters involved in EARS (especially the type of metallic precursors).**
- **Critical assessment of the performance of the EARS $(Ni,Fe)_3O_4$ layer**
- **Exploration of further performance improvement & cost analysis**



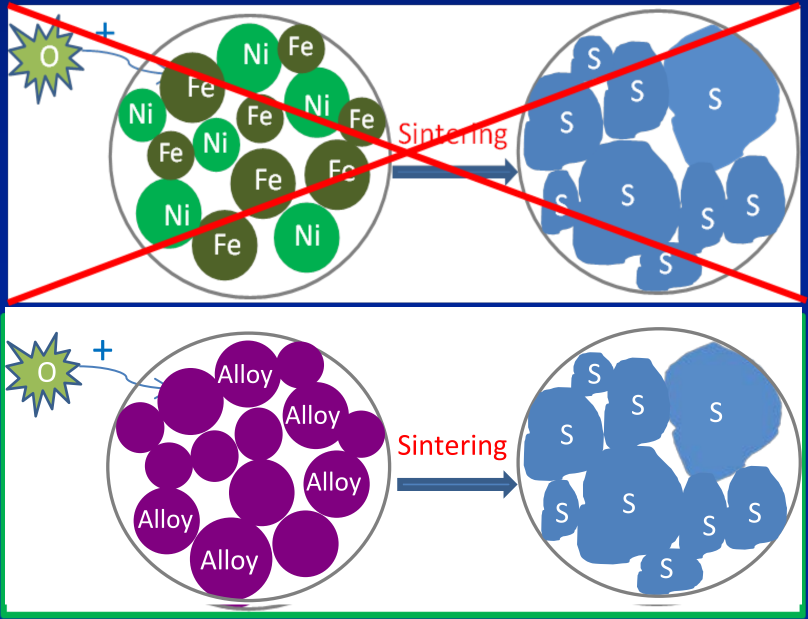

**Flow Chart of the Research Tasks Involved in the Phase I Project**

# Major Progress/Conclusions

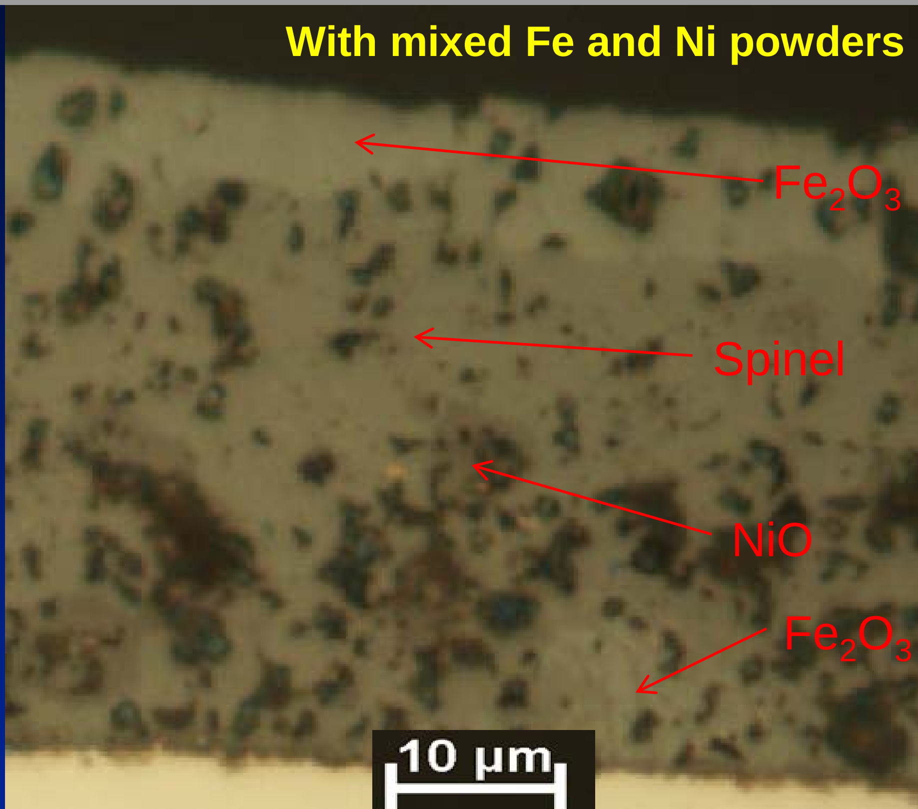
- **A mixture of Fe + Ni powders, binary Fe-Ni or ternary Fe-Ni-Co alloy powder can be used as precursor to form a spinel layer.**
- **The ternary alloy powder is preferred, due to more uniform spinel conversion, better compatibility, and lower ASR.**
- **Approaches for further improving the performance of the spinel contact have been identified.**
- **A total stack cost reduction of around 6.9% can be achieved with the implementation of the new alloy contact precursor.**

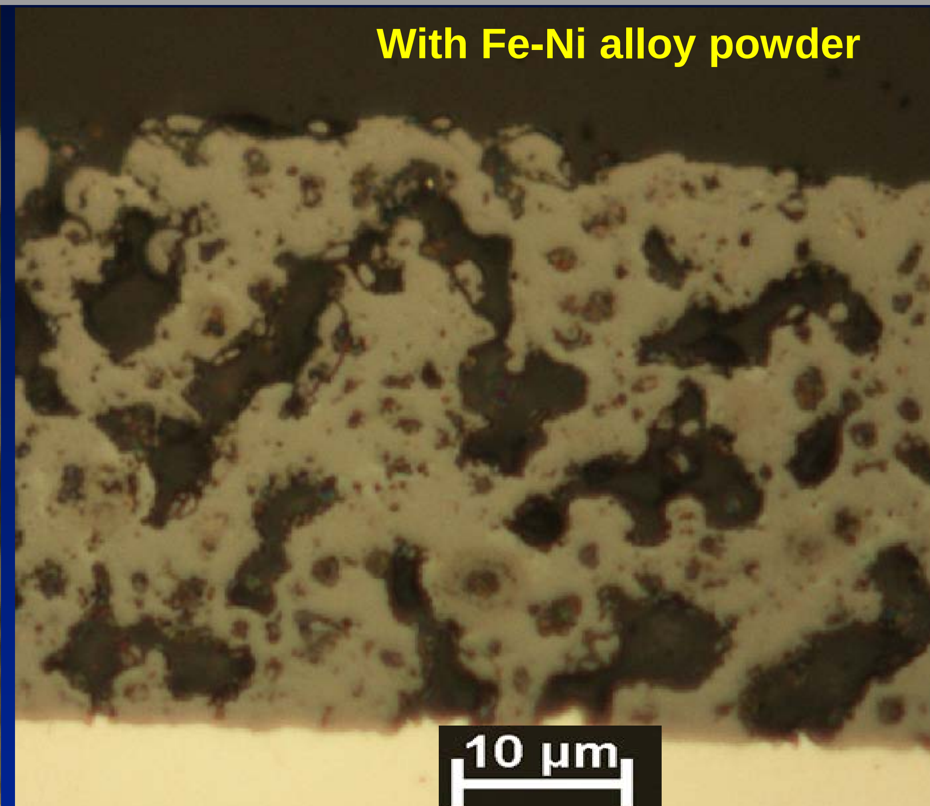



**Microstructure of Test Cell with Fe-Ni-Co Alloy Precursor Contact after Thermal Exposure at 800°C for 1000 h**



# The Fe-Ni alloy powder is preferred over a mixture of Fe and Ni powders as spinel-forming precursor

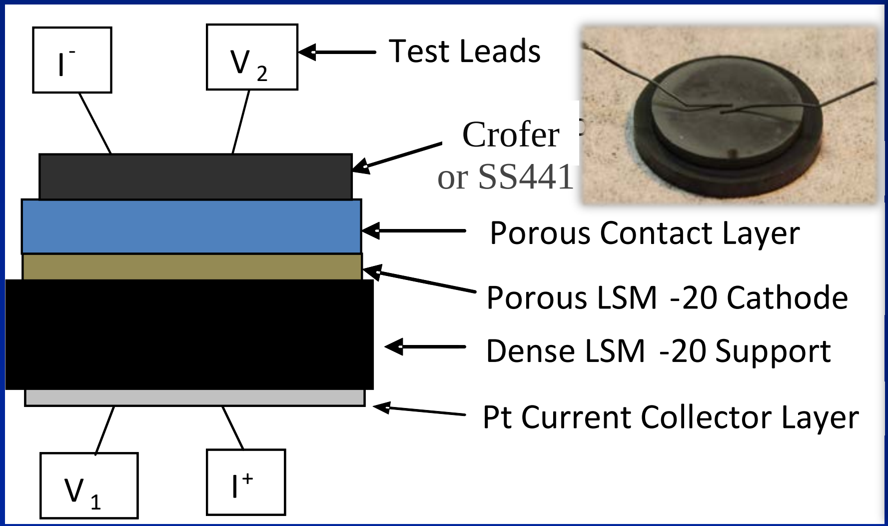


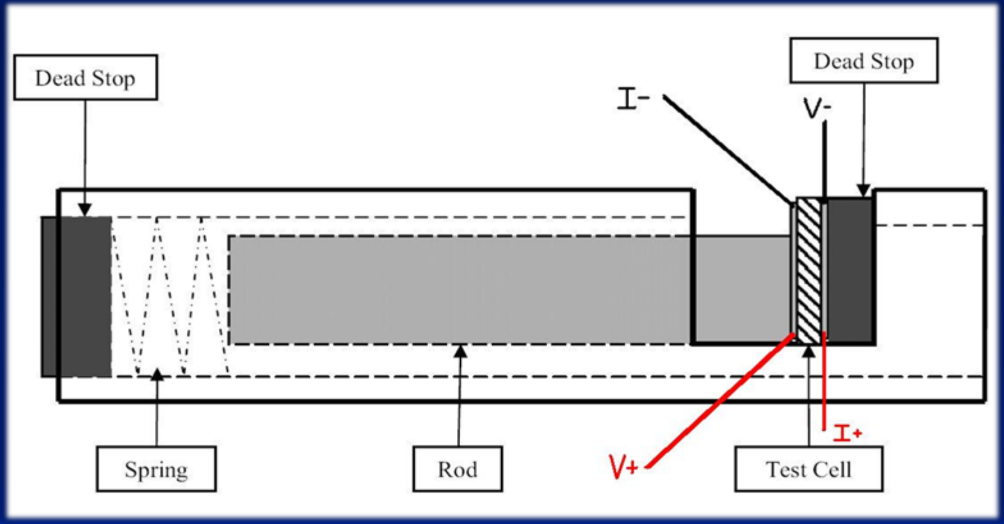




- With the starting powder mixture of 3-µm Fe and 2-µm Ni, the metallic layer was fully converted into an oxide layer after 900°Cx2h in air;
- A surface $Fe_2O_3$ sub-layer and some areas of internal NiO and $Fe_2O_3$ were observed, indicating a non-uniform microstructure.
- The converted spinel layer with the Fe-Ni alloy powder was relatively uniform microstructurally and compositionally.

# Area-Specific Resistance (ASR) Measurement

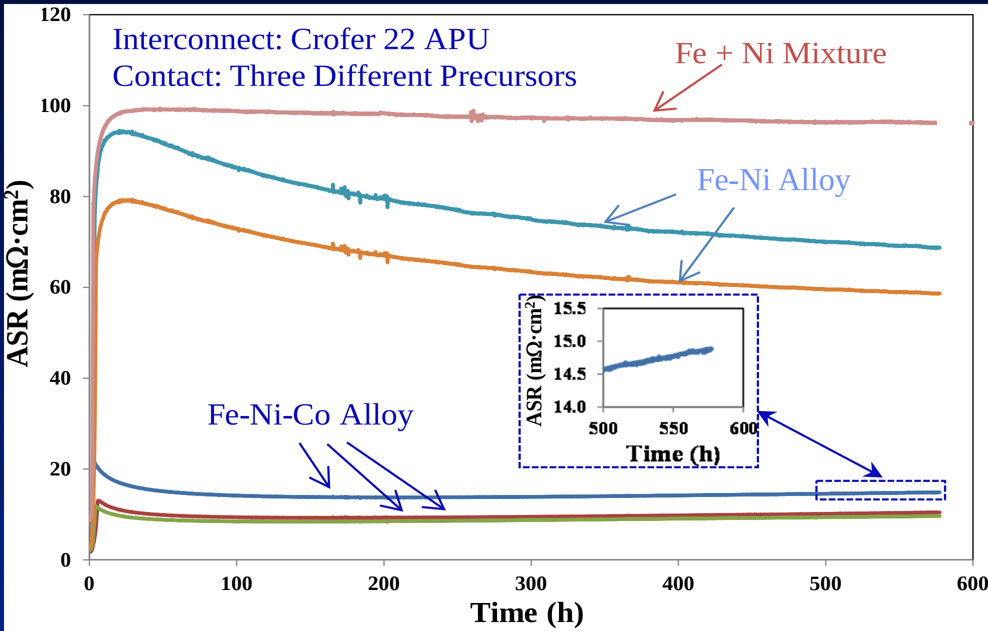
- A number of test cells were constructed, with the spinel-forming contact precursor layer sandwiched between the interconnect (Crofer 22 APU or SS 441) and the LSM cathode.
- The test cells were spring-loaded and the ASR change during either isothermal or cyclic exposure at 800°C in air was monitored using a special 6-cell test rig.



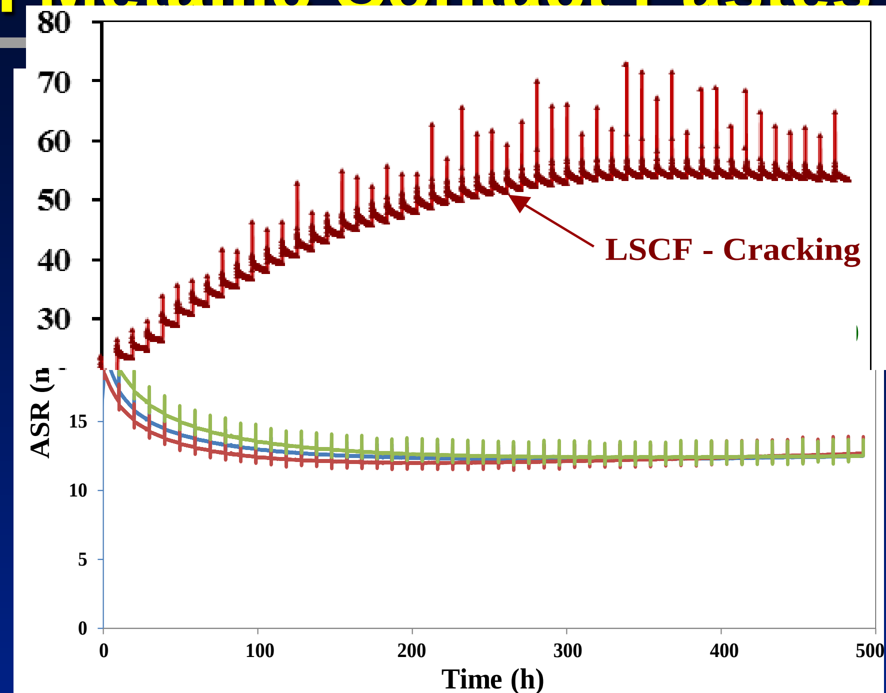




Schematic of the ASR Test Cell and Test Configuration

# ASR Change as a Function of Time for Crofer 22 APU/Contact/LSM Cells with Metallic Contact Pastes



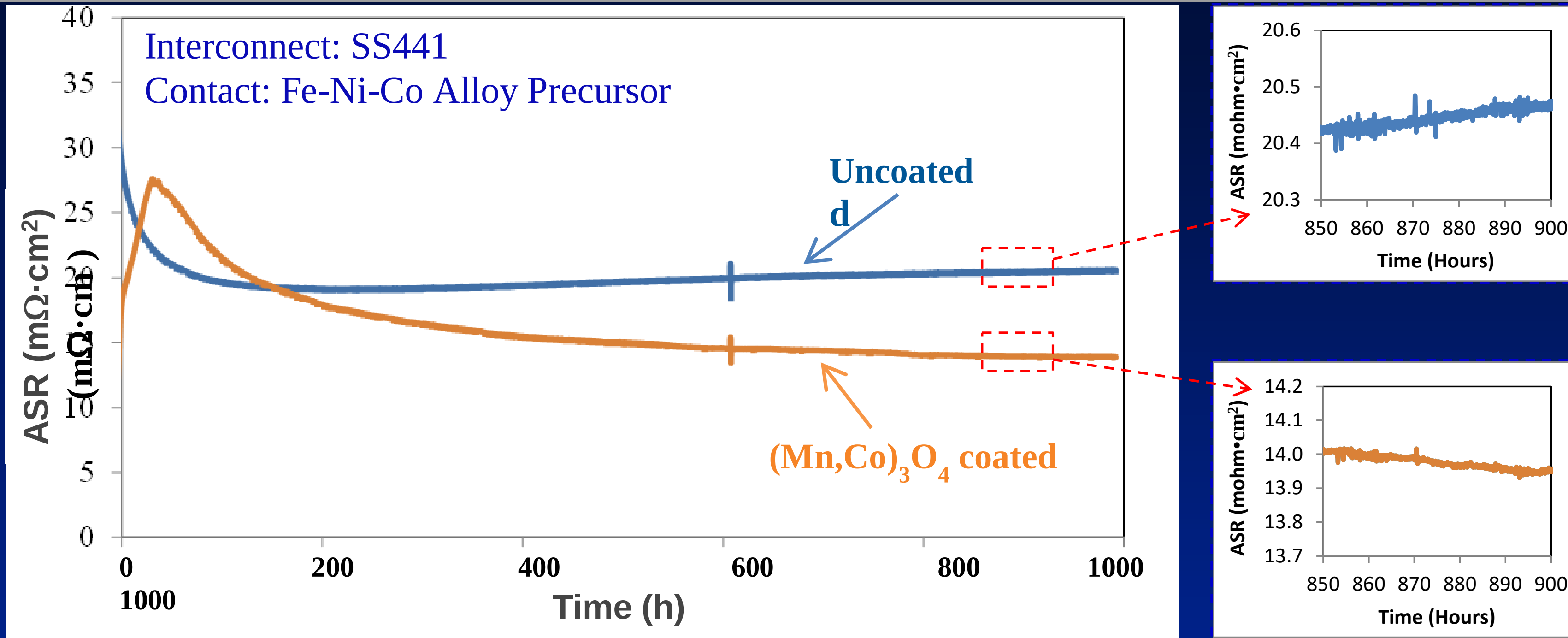

Cell ASR at 800°C during Isothermal Exposure of Test Cells with Various Contact Precursors




Cell ASR at 800°C during Cyclic Exposure of Test Cells with Ternary Alloy Precursor

- During isothermal exposure, the ASR for test cells with the mixed Fe+Ni precursor were higher than those with the alloy precursors, and the cell with the Fe-Ni-Co alloy precursor exhibited the lowest ASR.
- Thermal cycling had minimal effect on the ASR performance for test cells with the Fe-Ni-Co alloy contact precursor, due to the excellent CTE match of the contact layer with adjacent stack components.

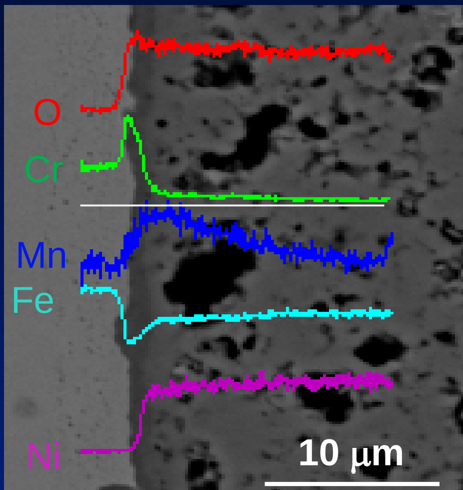
# Effect of Spinel-Based Interconnect Coating on the ASR Performance of SS 441/Fe-Ni-Co Contact/LSM Cells

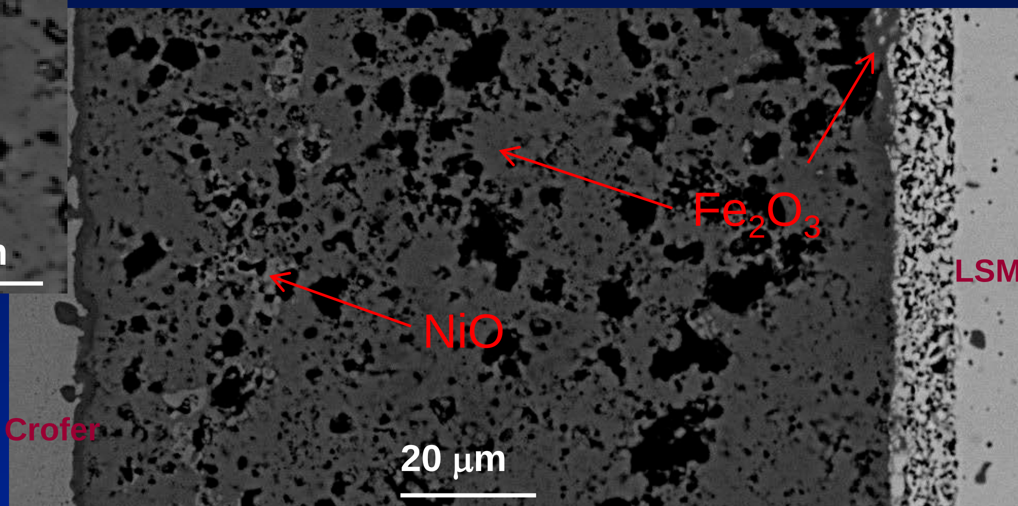


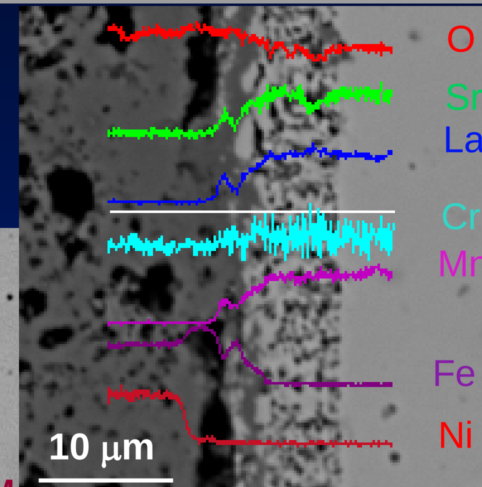

**ASR vs. Time during 1000-h Isothermal Testing at 800°C in Air for Test Cells with Uncoated and $(Mn,Co)_3O_4$-Coated SS 441 Interconnects**

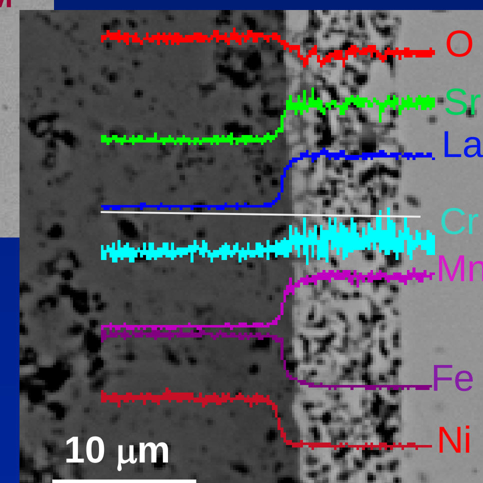
- **With SS 441 as interconnect, the cell ASR was ~20 mΩ·cm² and increased at a low rate, similar to the results with Crofer 22 APU as interconnect.**
- **However, with application of an EARS-processed, Ce-modified $(Mn,Co)_3O_4$ coating on SS 441, the cell ASR continued to drop during the test.**
- **The overall promising ASR performance of interconnect/contact/LSM cells with the ternary alloy as the contact precursor was further confirmed.**

# Cross-Section of Crofer 22 APU/Contact/LSM Cells with a Mixture of Fe+Ni Powders as Contact Precursor



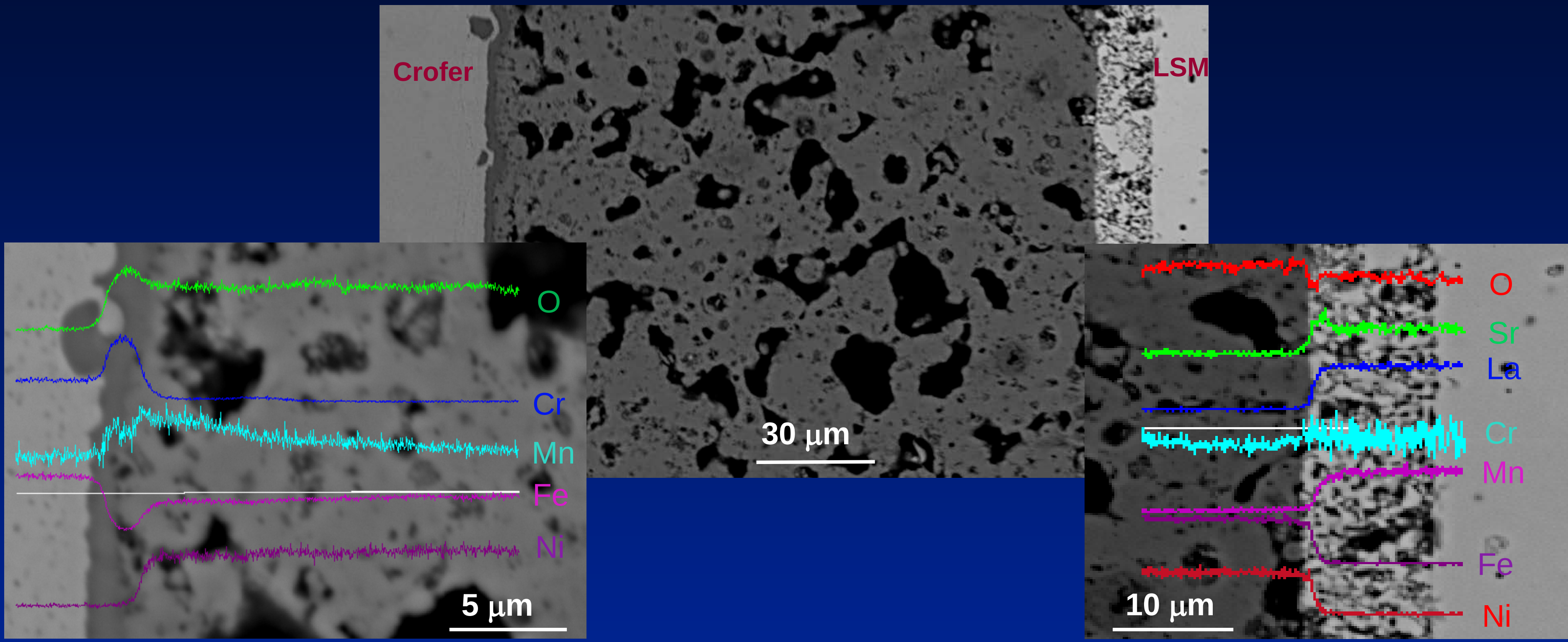



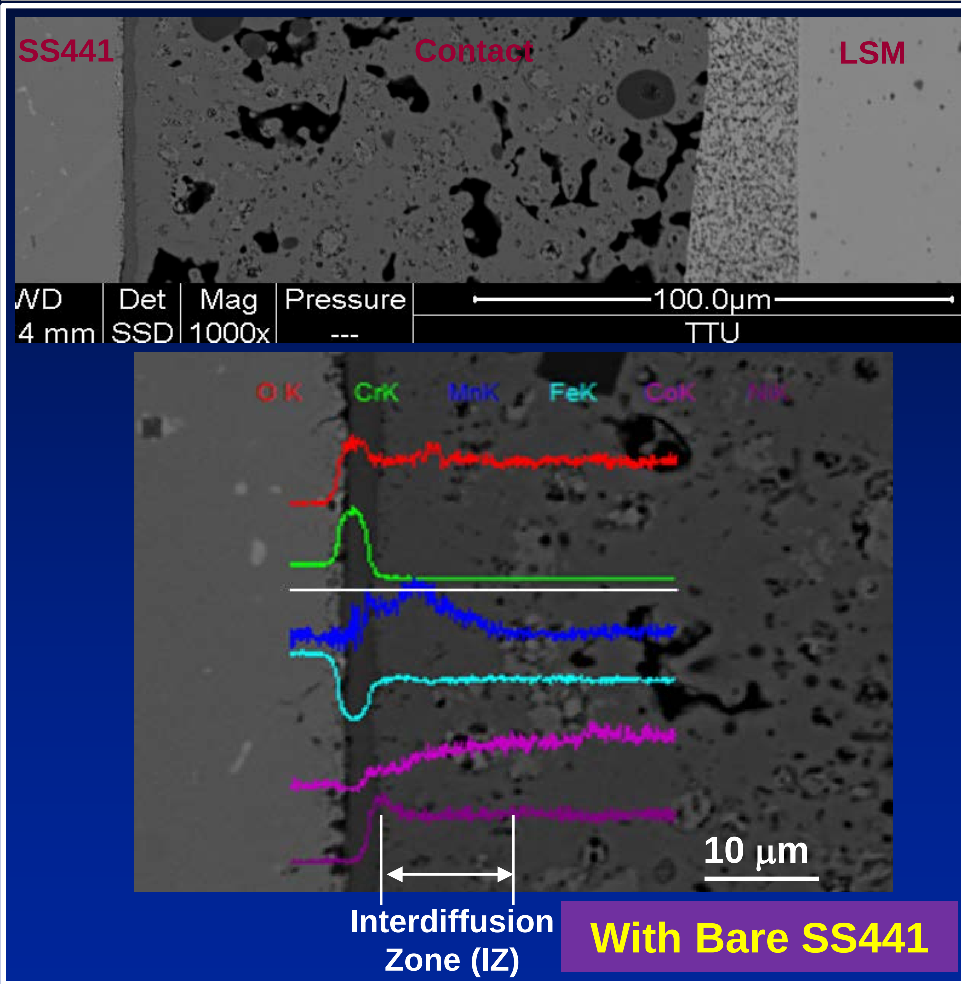

- **On the Crofer 22 APU side, a thin $Cr_2O_3$ scale was formed after 1000-h testing. Both Cr and Mn were detected in the contact layer near the interface.**
- **The Fe+Ni contact layer was less uniform compositionally and structurally near the cathode-contact interface. $Fe_2O_3$ penetration into the cathode observed in some areas.**

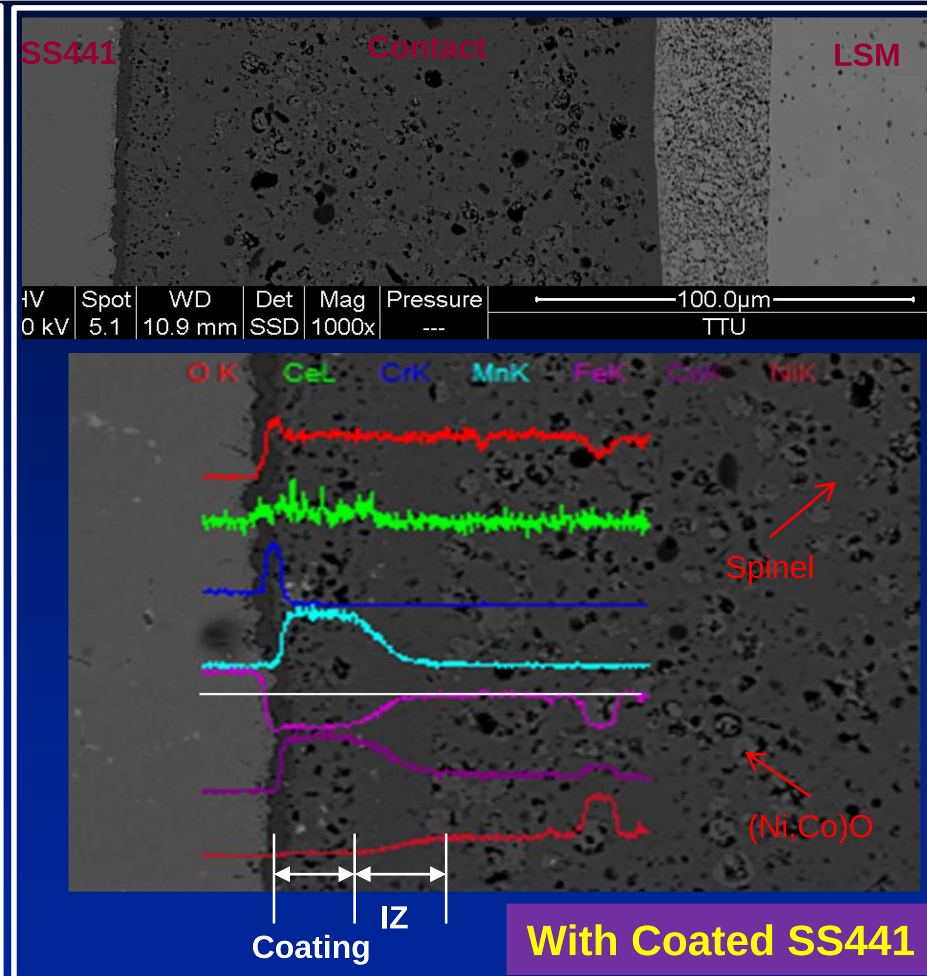
# Cross-Section of Crofer 22 APU/Contact/LSM Cells with the Fe-Ni Alloy Contact Paste




- On the Crofer 22 APU side, a thin $Cr_2O_3$ scale was formed after 1000-h testing and both Cr and Mn were detected in the contact layer near the interface.
- On the cathode side, negligible interdiffusion between the contact layer and LSM was observed. No Cr was detected in LSM.

# Cross-Sectional Views of SS441/Contact/LSM Cells with the Fe-Ni-Co Alloy Contact Precursor

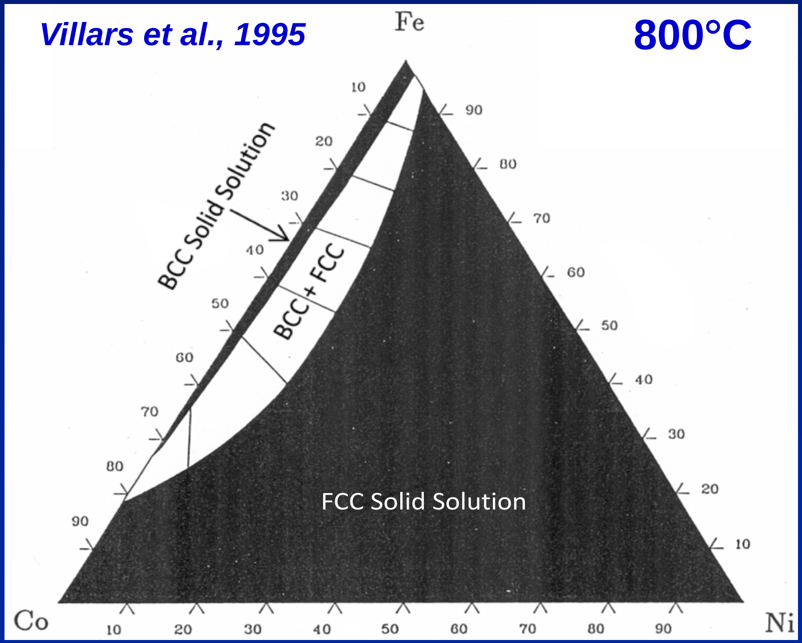



- A thicker $Cr_2O_3$ scale and a larger interdiffusion zone (IZ) were formed between SS441 and the contact layer for the cell with the bare (uncoated) interconnect.
- The application of the spinel coating on the interconnect alloy significantly reduced the interdiffusion between the interconnect and the contact layer.

# Further Improvement of $NiFe_2O_4$-Based Spinel Contact: Alloy Design Approach

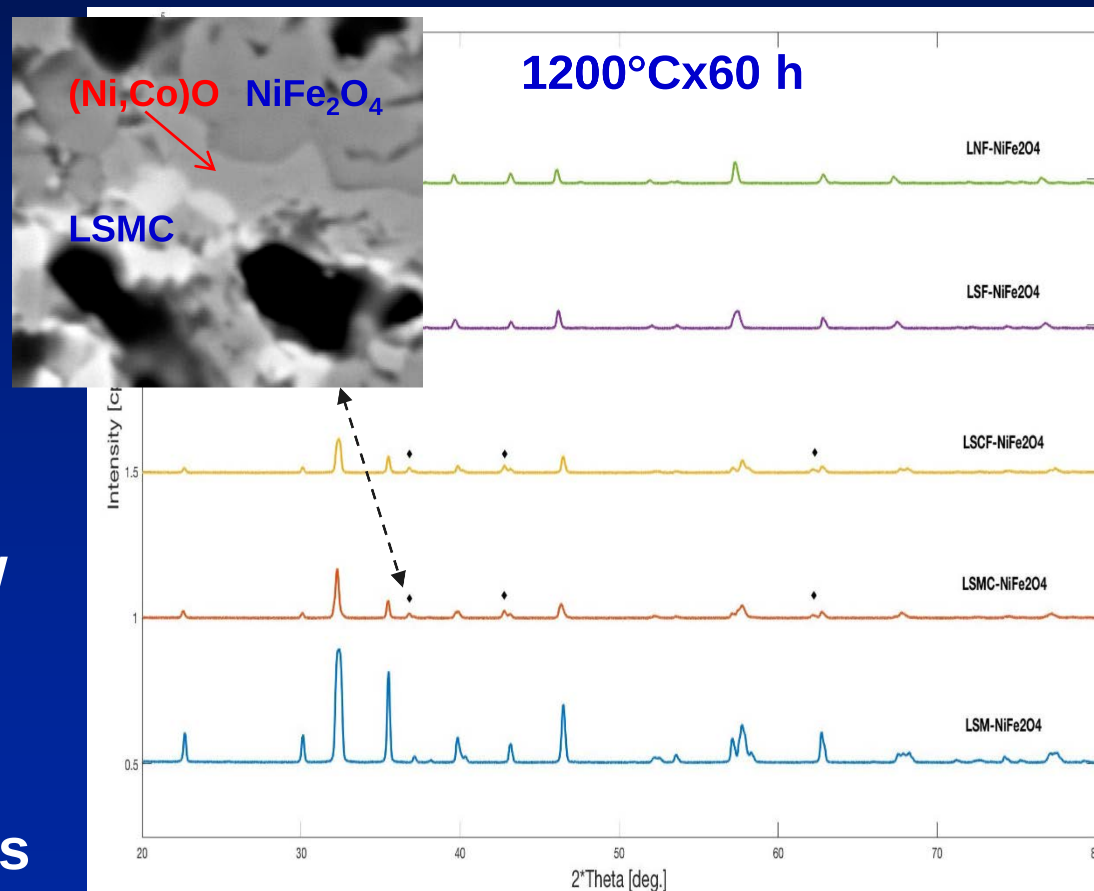
- The alloy composition can be optimized via a combination of fundamental study of phase equilibria & composition screening in the $Fe_2O_3$-NiO-$Co_3O_4$ system, alloy design using physical metallurgy principles, and cost considerations.
  - ✓ Optimization of the Fe/Ni/Co levels
  - ✓ Addition of microalloying elements
  - ✓ Powder fabrication and characterization




Ternary Fe-Ni-Co Phase Diagram

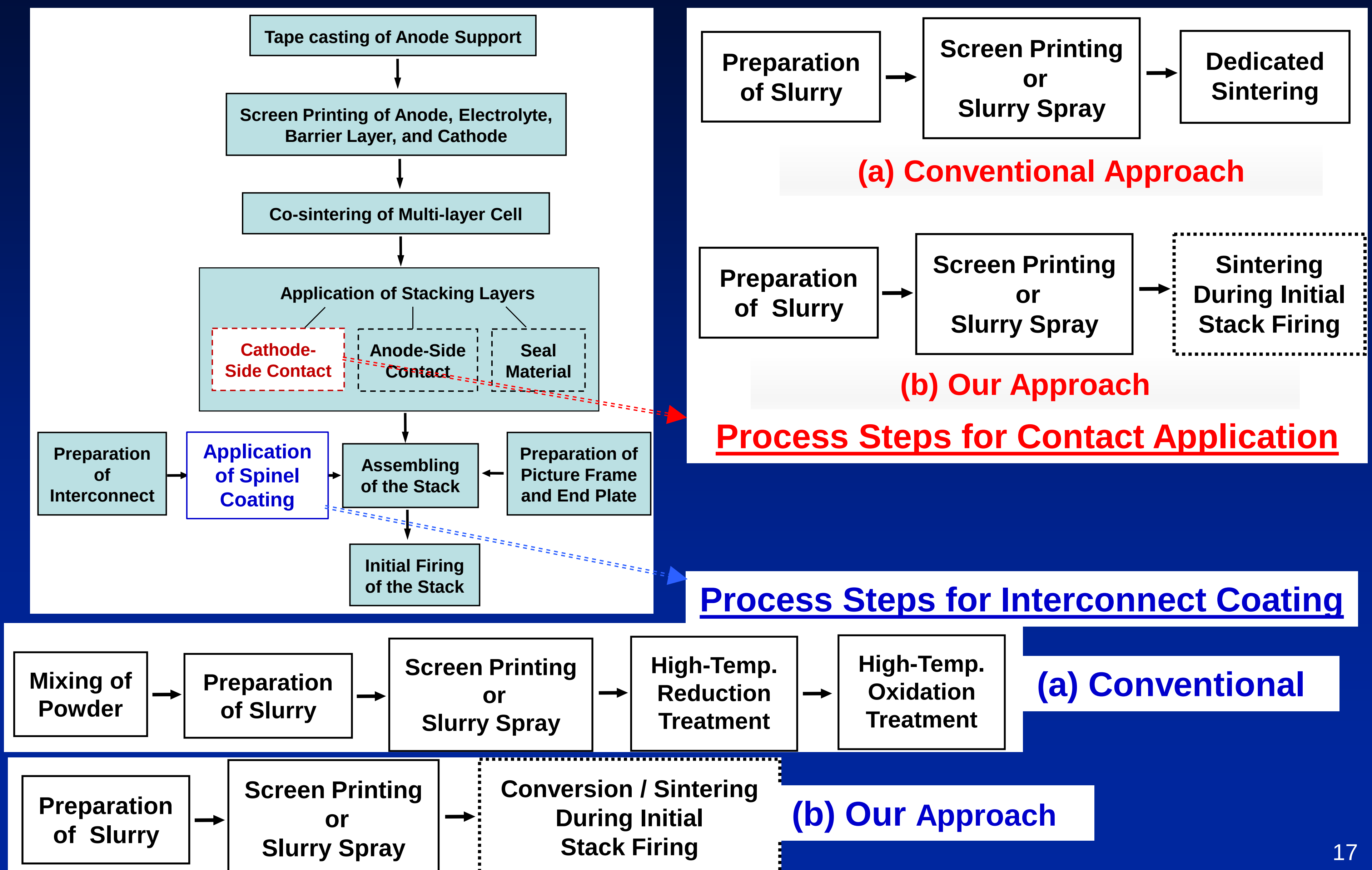
# Further Improvement of $NiFe_2O_4$-Based Spinel Contact: $2^{nd}$-Phase Addition to Form Composite Contact

- **The $2^{nd}$ phase should be electrically conductive, CTE-matched, and chemically compatible with the cathode, interconnect, and $(Ni,Fe)_3O_4$, and preferably Cr-absorbing.**
  - **Potential candidates includes LSM, LSF, LSCF, LSMC, LNF, LCN, etc.**
  - **While $NiFe_2O_4$ is compatible with Co-free perovskites (LSM/LSF/LNF), a new (Ni,Co)O phase is formed between the spinel and Co-containing perovskites (LSCF/LSMC/LCF).**




**XRD Patterns of Two-Phase Mixtures after Firing**

# Cost Analysis – Simplified Synthesis of Both Contact Layer and Interconnect Coating



# Cost Analysis - Production costs of contact layer, interconnect coating, and stack per system

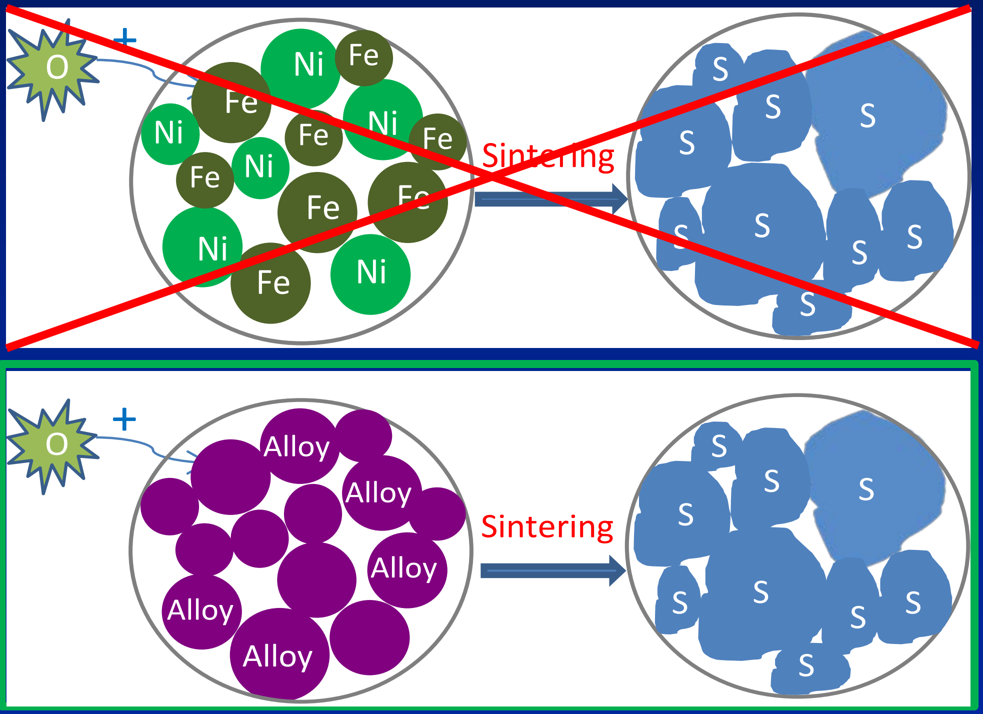
- A stack cost reduction of 6.9% can be achieved, if our new alloy precursor concept is implemented as cathode-side contact.
- An additional 1.1% cost reduction is expected, if interconnect coating can also be synthesized using metallic precursor powder and co-sintering of the interconnect coating/contact layer can be realized during initial stack firing.
- A total stack cost saving of ~8.0% can be achieved, if both of them are considered.

| System \ Cost | | Material Cost ($) | Annualized Capital and O&M ($) | | | | Total ($) | Stack Cost Reduction |
|---|---|---|---|---|---|---|---|---|
| | | | Capital | Electricity | O&M | Labor | | |
| Contact Layer | Conventional | 792 | 769 | 12 | 92 | 225 | 1,890 | 6.9% |
| | New | 109 | 59 | 6 | 16 | 25 | 215 | |
| Interconnect Coating | Conventional | 160 | 125 | 55 | 35 | 49 | 424 | 1.1% |
| | New | 36 | 59 | 6 | 16 | 25 | 142 | |
| Stack | Conventional | 13,285 | 7,401 | 251 | 1,684 | 1,806 | 24,427 | 8.0% |
| | New | 12,478 | 6,625 | 196 | 1,589 | 1,582 | 22,470 | |

*Note: The data for the conventional approach was derived from Weimar et al. (PNNL-22732, 2013); however, instead of Ag, LSM was selected as the contact in the current cost study.*

# Concluding Remarks

- Low-cost, EARS-processed $(Ni,Fe)_3O_4$-based layers with promising performance have been successfully synthesized.
- While a mixture of Fe & Ni powders and an Fe-Ni alloy powder can be used as the precursor for the spinel-layer synthesis, the ternary alloy powder derived contact offers the best performance:
  - Uniform microstructure
  - Low and stable ASR
  - Cost advantages
    - Only one powder is needed (lower powder process cost)
    - No need of powder mixing
    - Doped spinel formation via alloy composition adjustment (multi-component alloys)




- Multi-component alloy development should be further pursued.

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