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

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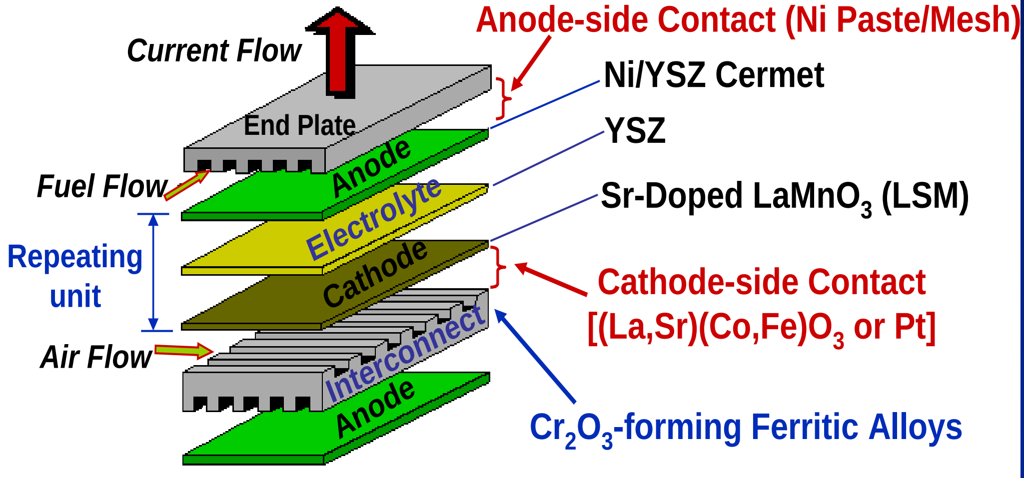
Outline

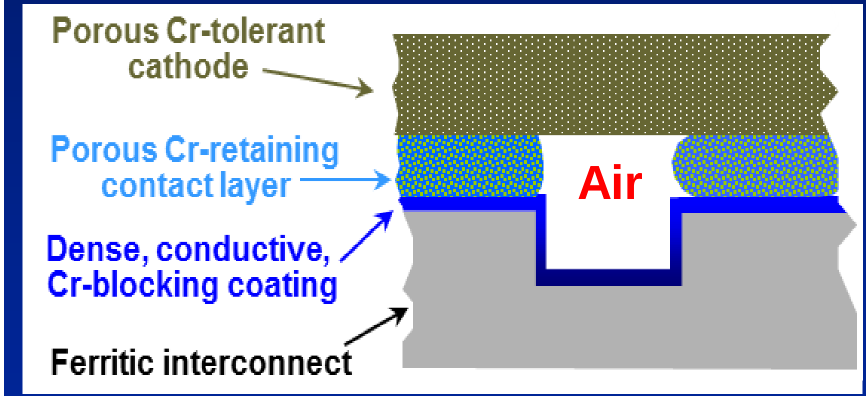
- Introduction and Project Objectives
- Major Progress/Conclusions
- Effect of Starting Powders on the Spinel Layer Formation
- Performance Evaluation of the Spinel Contact Layer
  - Area Specific Resistance (ASR), Chemical Compatibility, etc.
- Ongoing Research Efforts
- Concluding Remarks
- Acknowledgments

Contact Layers in SOFC Stack

- To minimize the ohmic resistance at the interconnect-electrode interfaces.
- To improve mechanical bonding
- To provide for additional gas channels to the electrodes



Schematic of a Planar SOFC Stack

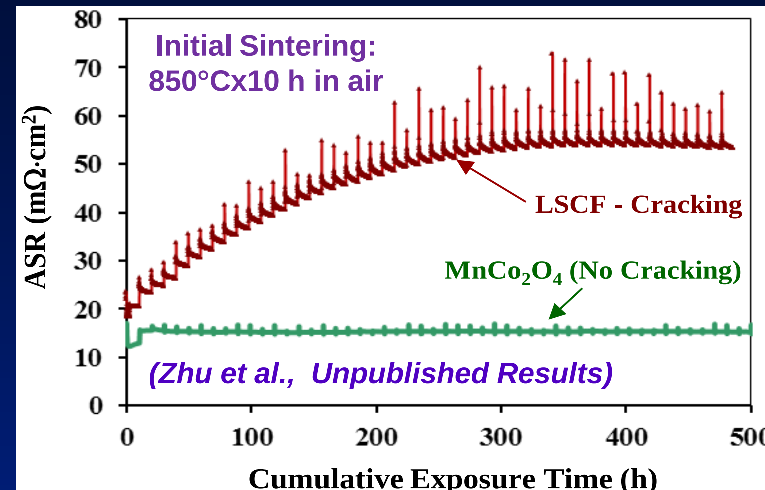


Schematic of the Cathode-Interconnect Interface

Finding a suitable material for electrical contact between the cathode and interconnect is more challenging.

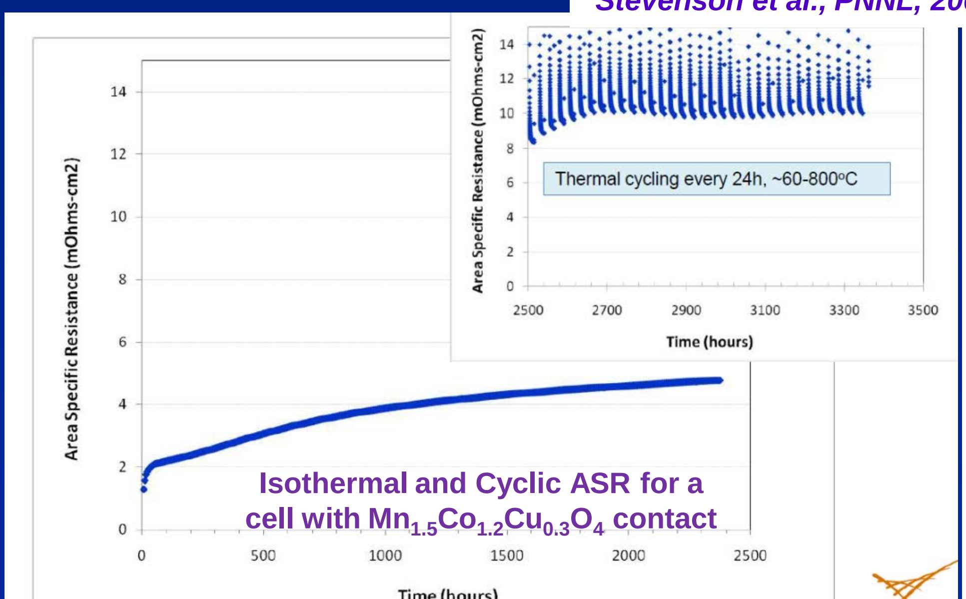
Why $NiFe_2O_4$-Based Spinel as Contact Material?

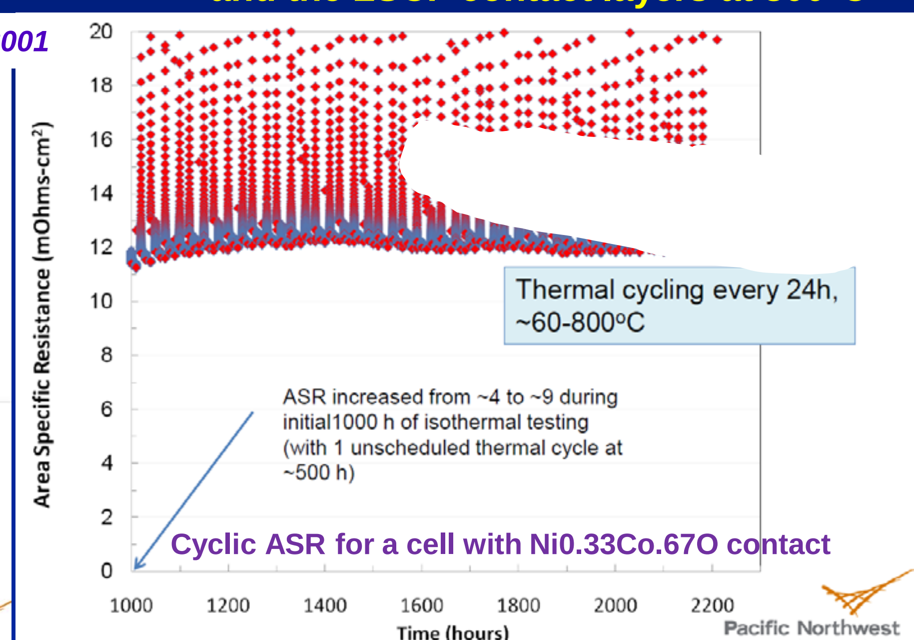
- Most of cathode contact developments have focused on (La,Sr)(Mn,Co,Fe,Ni)O_3 perovskites; however, it is difficult to balance the electrical conductivity, CTE, and sinterability.
- Several spinels such as $(Co,Mn)_3O_4$, $CoFe_2O_4$, $NiCo_2O_4$ and $NiFe_2O_4$ are also promising candidates as cathode-side contact.



Comparison in cell ASR with the $MnCo_2O_4$ and the LSCF contact layers at 800°C

Stevenson et al., PNNL, 2001



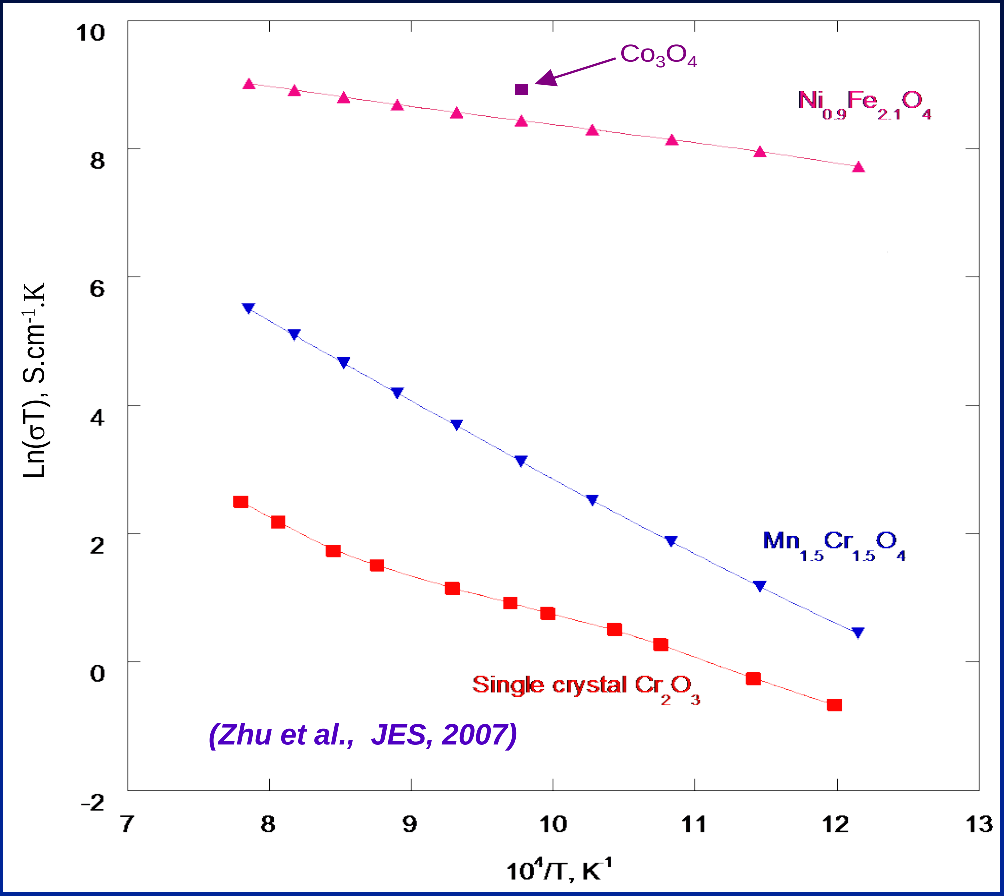


Why $NiFe_2O_4$-Based Spinel as Contact Material?

- $NiFe_2O_4$-based spinels have reasonable CTE ($12x10^{-6}/°C$) and electrical conductivity.
- With the absence of Co and a low Ni content, this spinel system is a low cost alternative.

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

- The sinterability of $NiFe_2O_4$ is poor (≥1200°C).
  - *How to lower the sintering temperature?*



Electrical Conductivity of the $(NI,Fe)_3O_4$ Spinel, as Compared with Several Other Oxides.

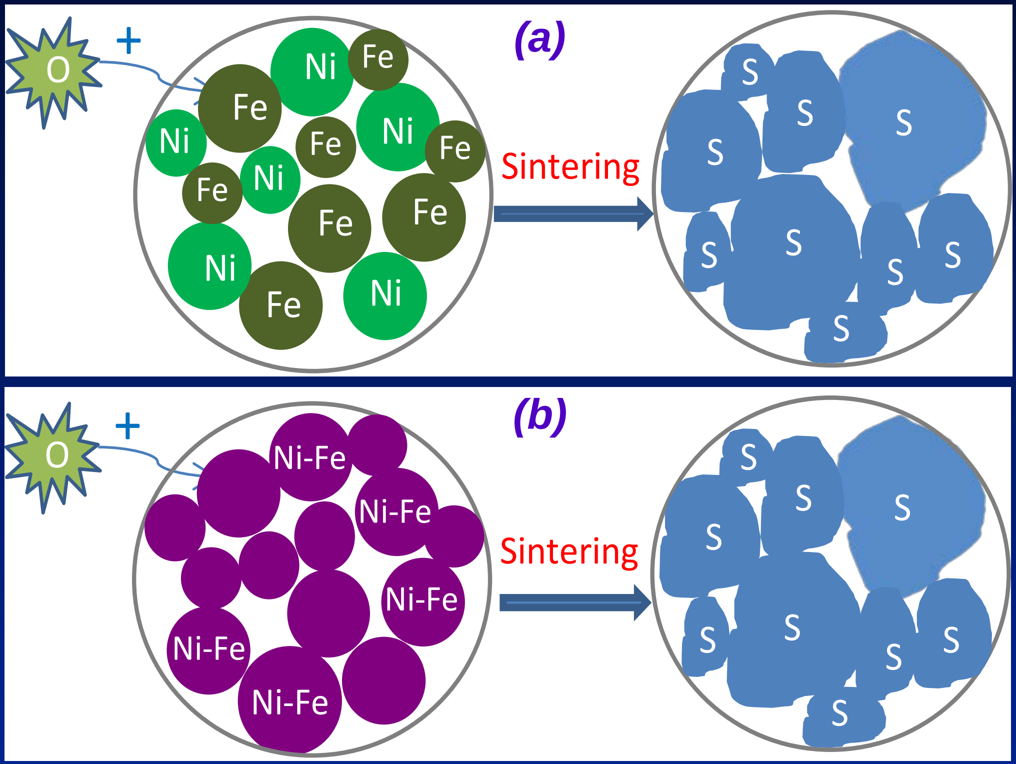
Utilization of EARS for Reduced-Temperature Sintering of Co-free $(Ni,Fe)_3O_4$ spinel Contact

- **Employment of metallic powders instead of oxide powders as the starting precursor to lower the sintering temperature**
  - **Environmentally-Assisted Reactive Sintering (EARS) with the participation of oxygen from environment in the spinel forming reaction:**

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

vs.

$$NiO + 2Fe_2O_3 = NiFe_2O_4$$

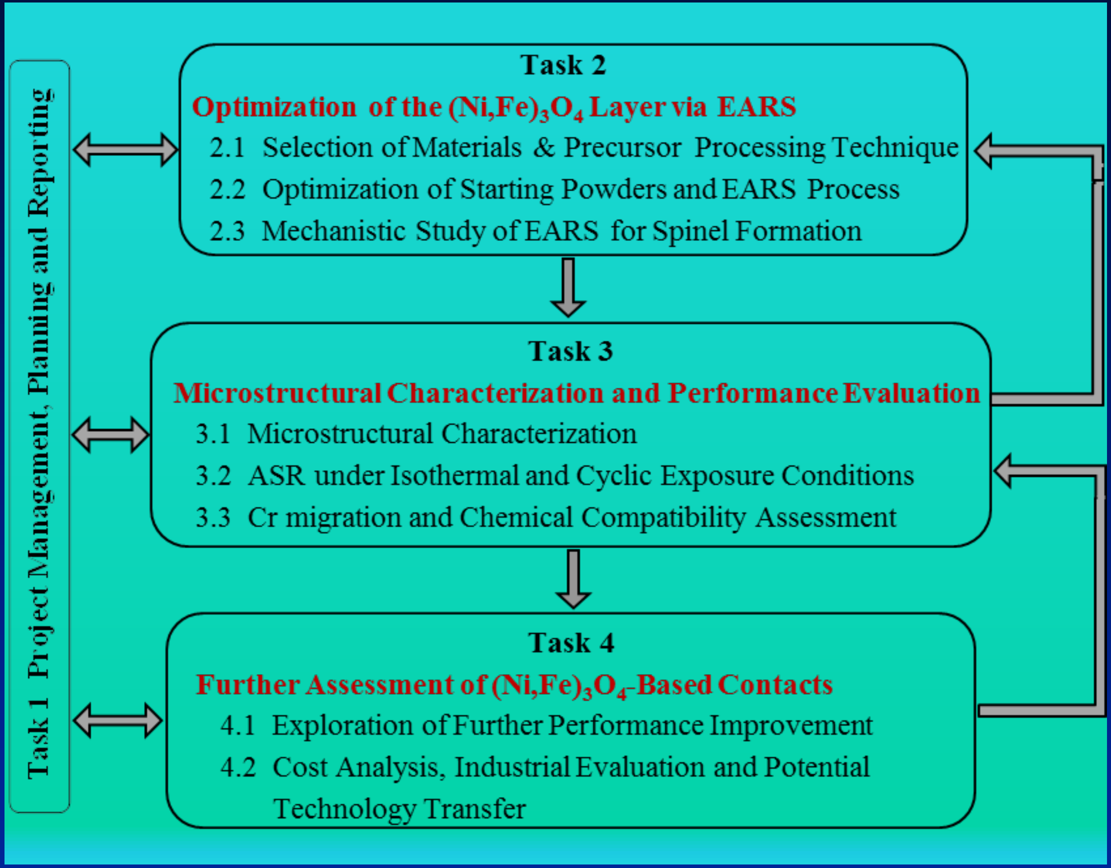


EARS process for synthesis of $(Ni,Fe)_3O_4$ ("S") using different precursors: (a) a mixture of Fe and Ni powders; (b) a Ni-Fe alloy powder.

- **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**

Project Objectives

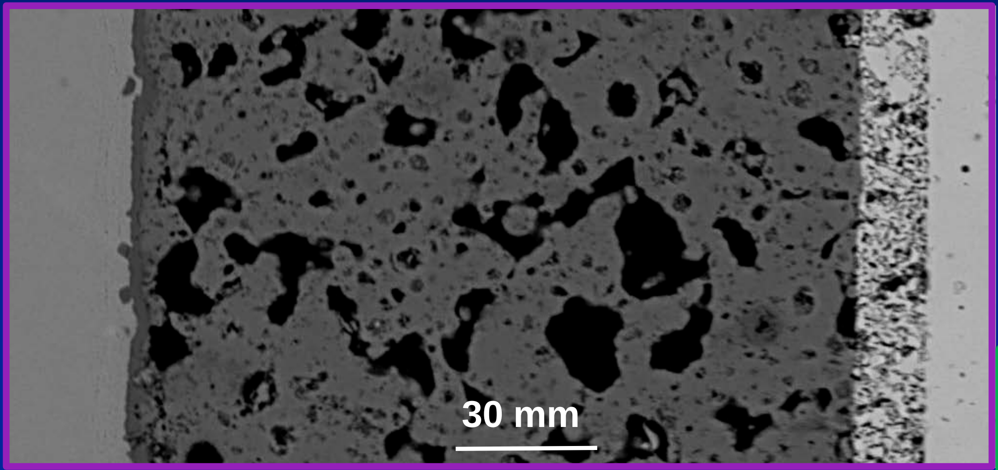
- **Optimization of the $(Ni,Fe)_3O_4$ spinel layer formation via controlling the parameters involved in EARS (especially the metallic precursors).**
- **Critical assessment of the performance of the EARS $(Ni,Fe)_3O_4$ layer**
- **Exploration of further performance improvement of the spinel-based contacts**



Flow Chart of the Research Tasks Involved in this Project

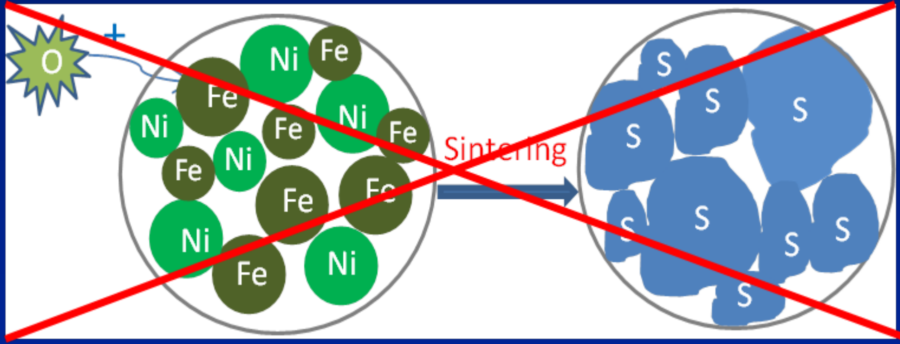
Major Progress/Conclusions

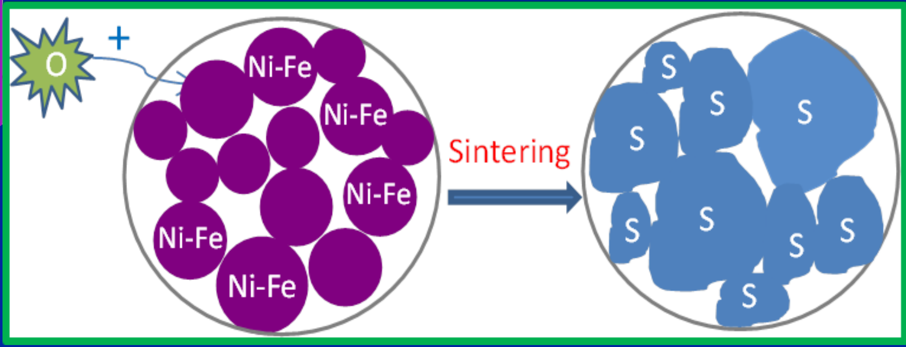
- Both a mixture of Ni and Fe powders and an Ni-Fe alloy powder can be used as the precursor to form a spinel contact layer.
- The alloy powder is preferred, due to more uniform spinel conversion, better microstructure and lower ASR.
- Approaches to further improve the performance of the spinel contact are being pursued.



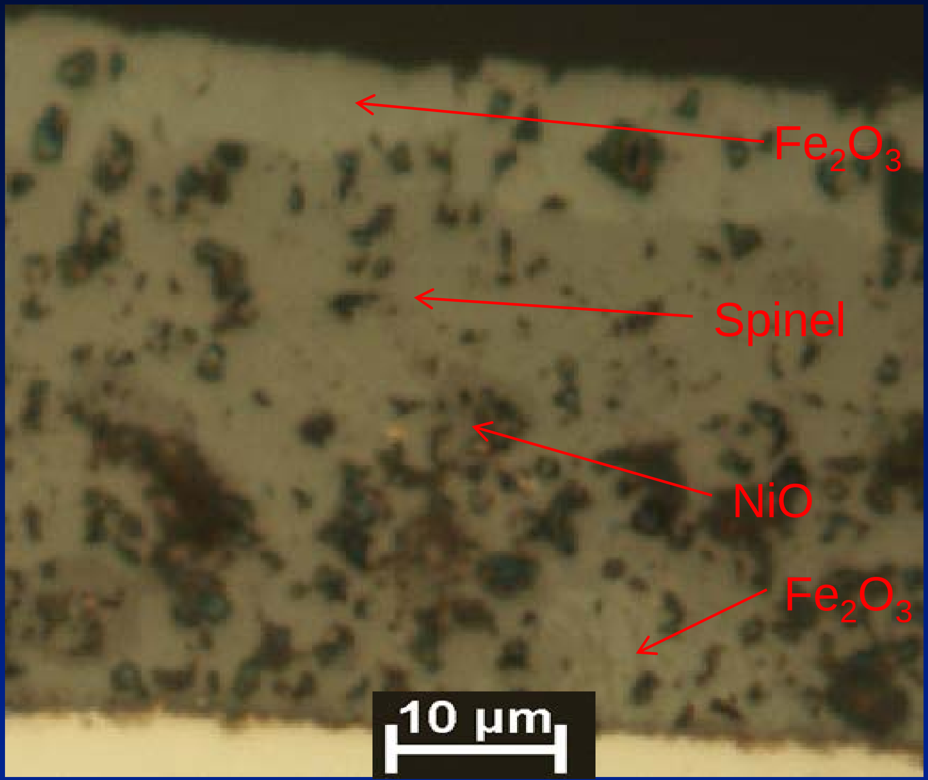
Crofer $NiFe_2O_4$ Contact Layer LSM

Cross-Sectional View of a Crofer//$NiFe_2O_4$//LSM Cell with a Ni-Fe Alloy Precursor Layer after ASR Testing in Air at 800°C for 1000 h

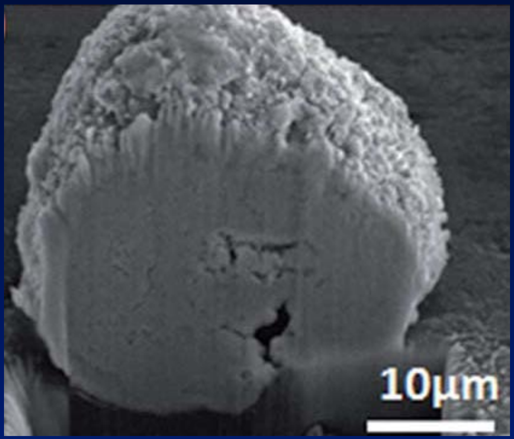




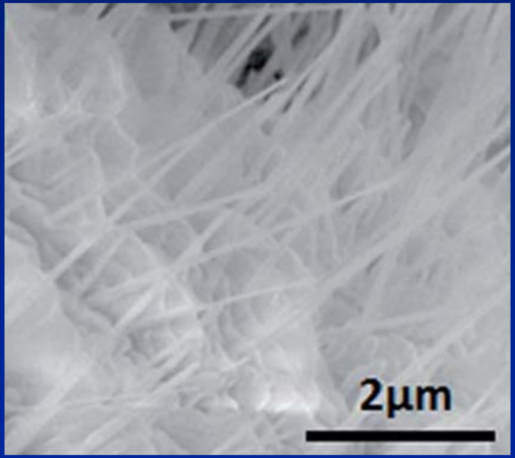
With mixed Ni and Fe powders, the converted layer had a significant amount of Fe_2O_3 near the surface



- With the starting powder mixture of 2 μm Ni and 3 μm Fe, the metallic layer was fully converted after 900°Cx2h in air;
- A surface Fe_2O_3 layer and some areas of internal NiO and Fe_2O_3 were observed, indicating a non-uniform microstructure.



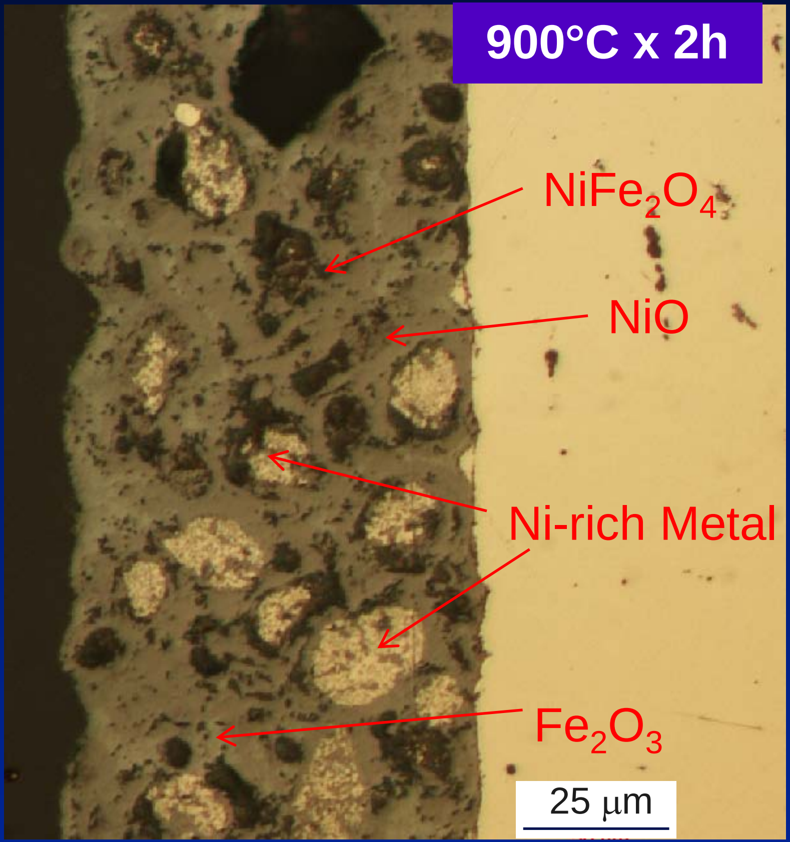
Cross-section of an Fe microparticle after oxidation at 700°C for 30 min

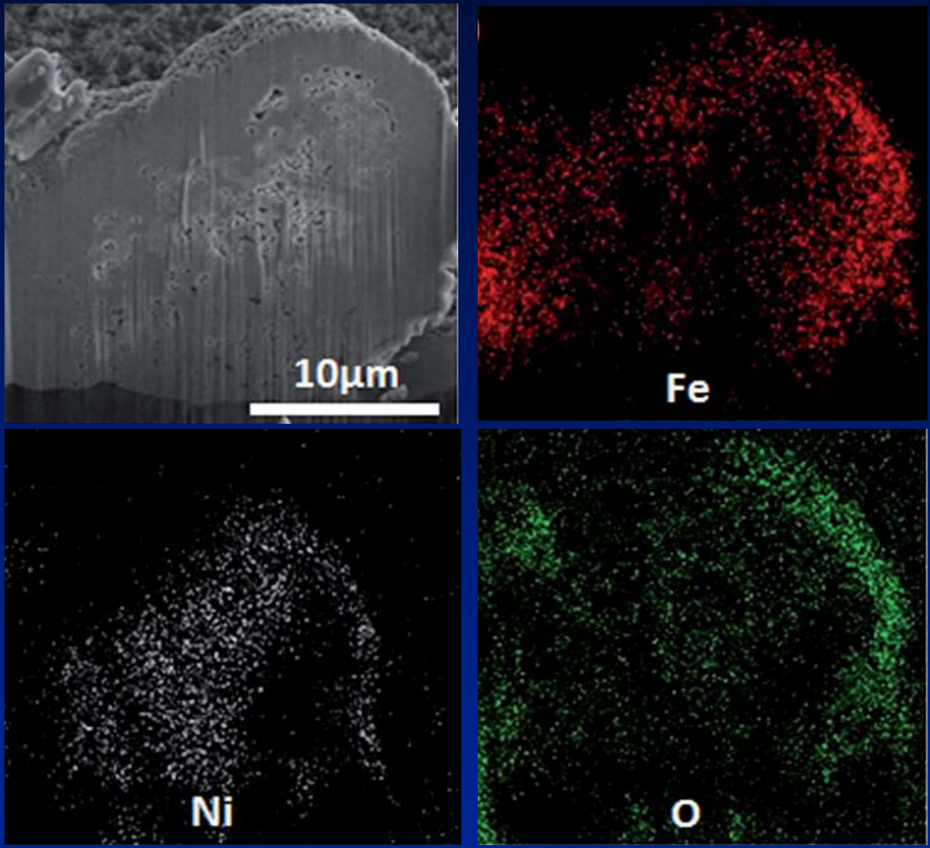


Surface morphology of an Fe microparticle after oxidation

Qin et al., J. Mater. Chem. A, 2 (2014)

With a large-sized Ni-Fe alloy powder, a fully-converted contact layer could not be achieved after 900°C exposure





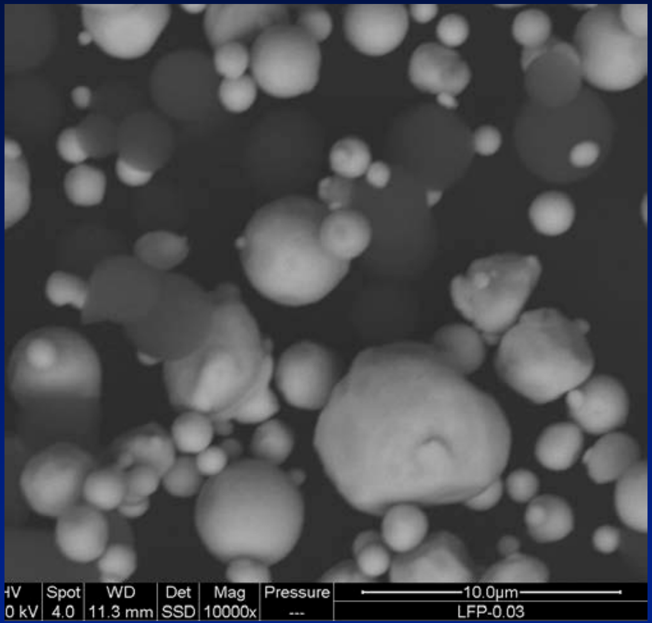
Cross-section and area mapping of an Ni-Fe microparticle after oxidation at 700°C for 30 min

Qin et al., J. Mater. Chem. A, 2 (2014)

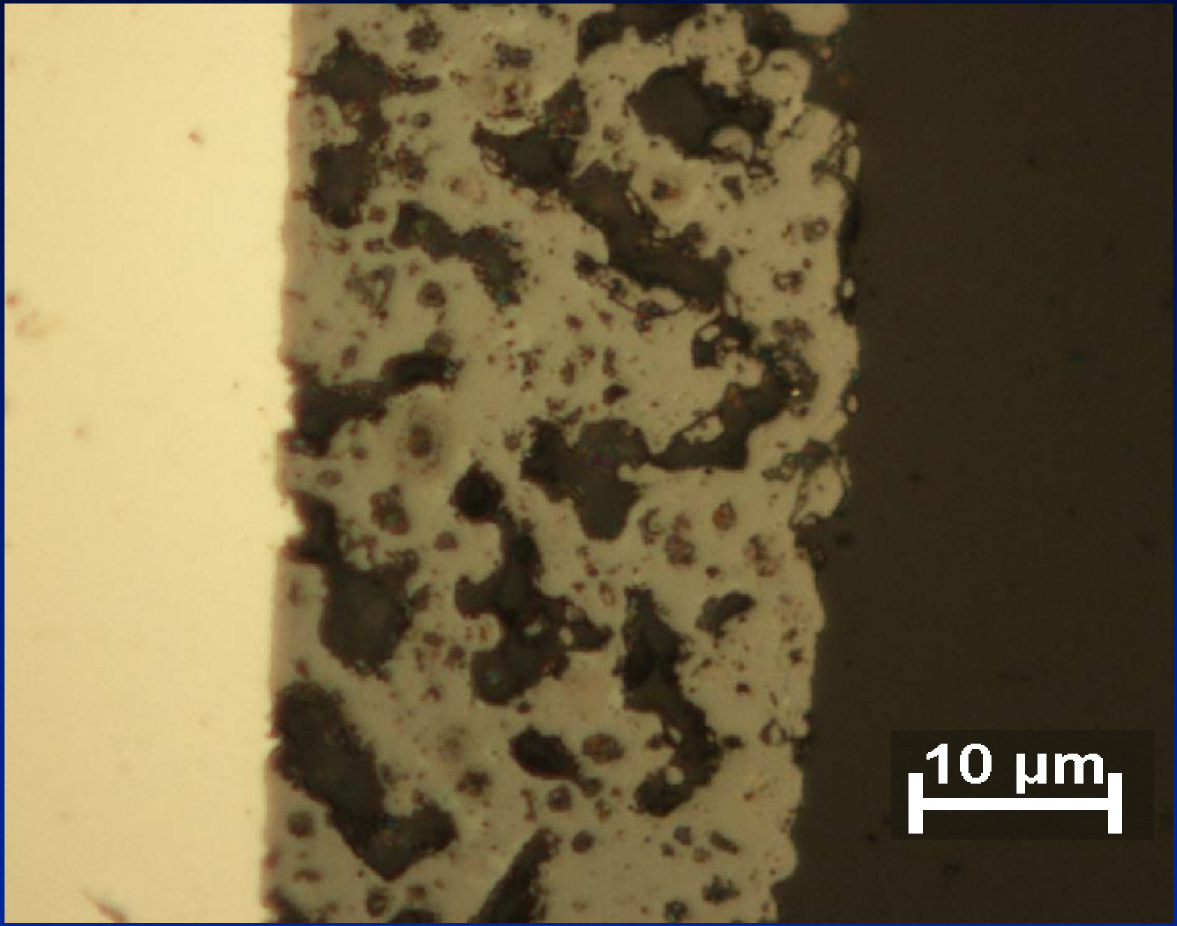
– The Ni-Fe powder was sieved through a 625-mesh screen, and the collected powder was ≤ 20 μm in size.

– After 900°C x 2 h conversion, the metallic particles were not fully oxidized, and a graded composition/structure was obtained.

Further Reduction of the Ni-Fe Powder Size via Sonication + Skimming

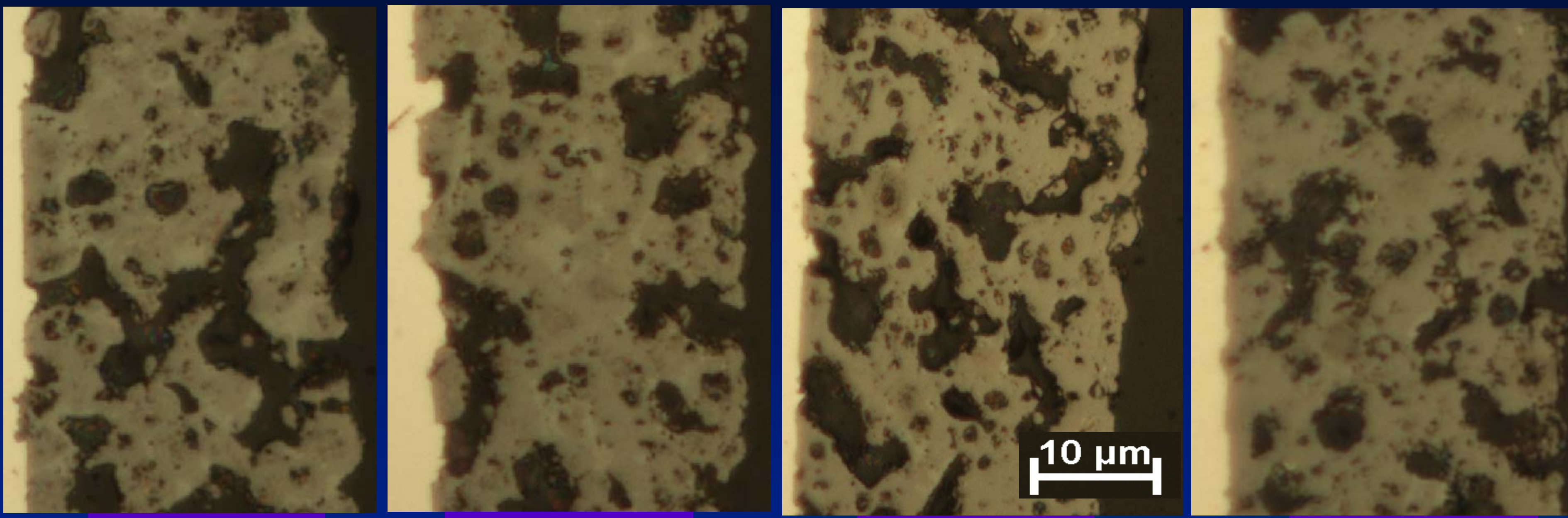


Morphological Features of the Skimmed Particles



- The size of the skimmed particles was reduced to < 7 μm.
- The converted spinel layer with the skimmed powder was relatively uniform microstructurally and compositionally.

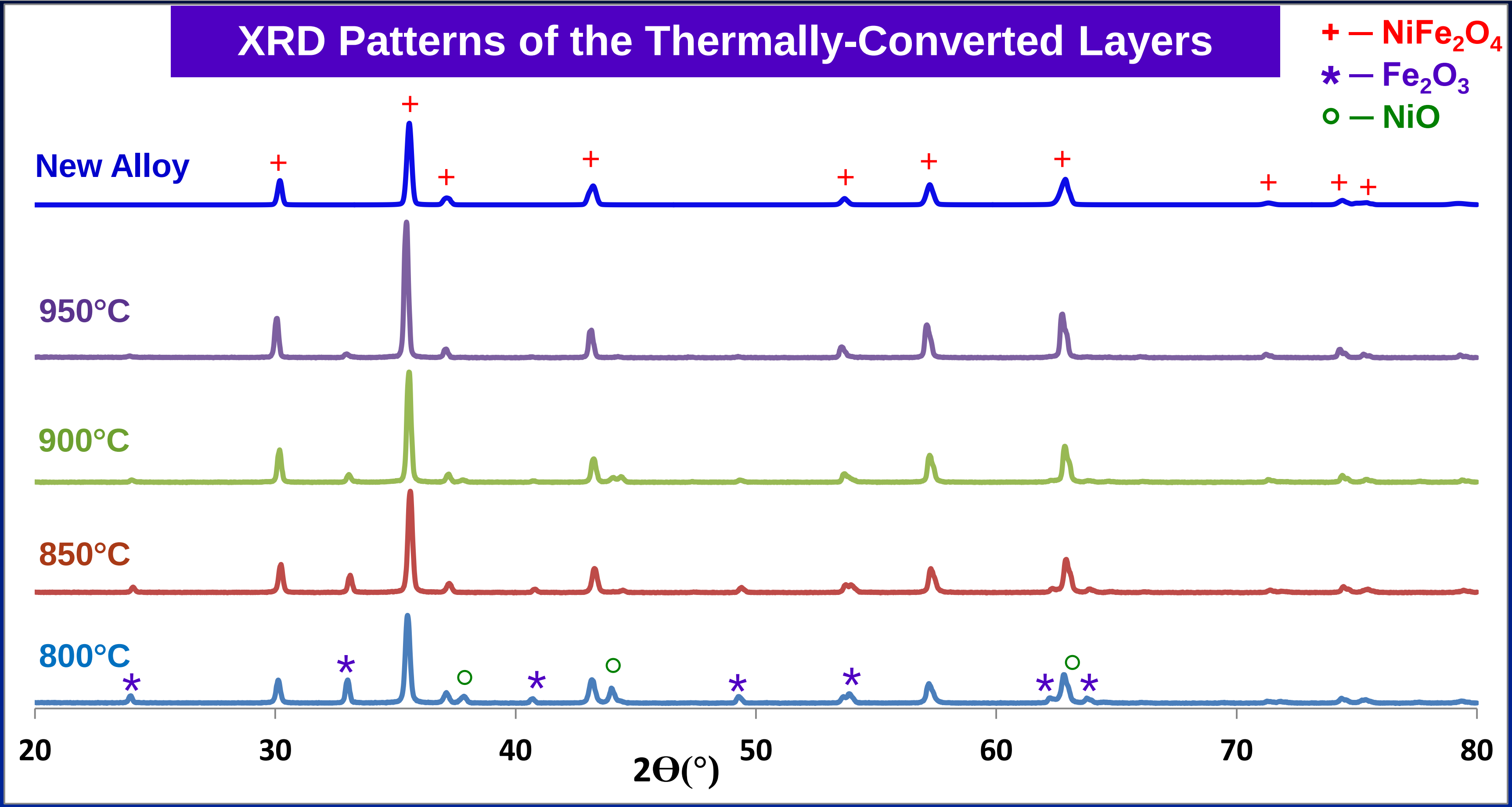
Effect of Sintering Temperature on the Phase Formation in the Contact Layer



800°C x 2h | 850°C x 2 h | 900°C x 2h | 950°C x 2 h

- For the skimmed alloy powder, regardless of the conversion temperature used the Ni-Fe alloy layer was fully converted to an oxide layer.
- As the sintering temperature increased, the microstructure became more uniform and a higher amount of the spinel was detected in the contact layer.

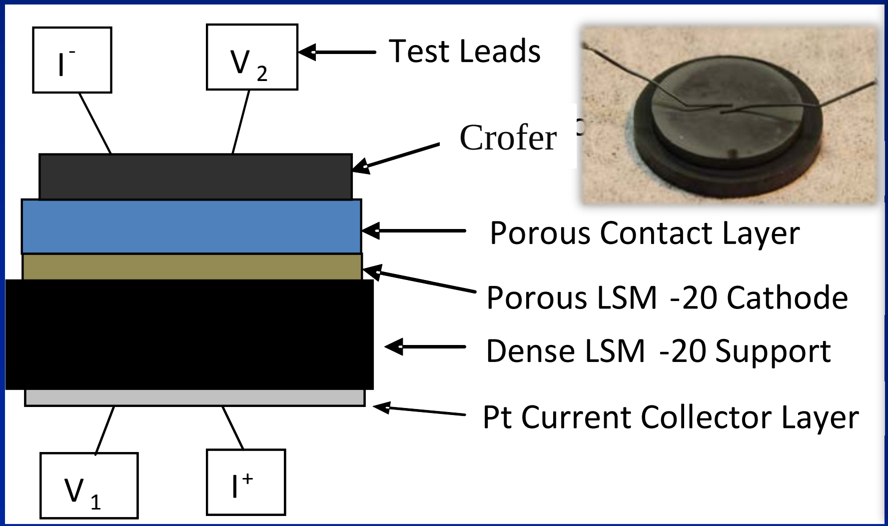
XRD Results of the Phases Present in the Contact Layer Thermally Converted at Different Temperatures

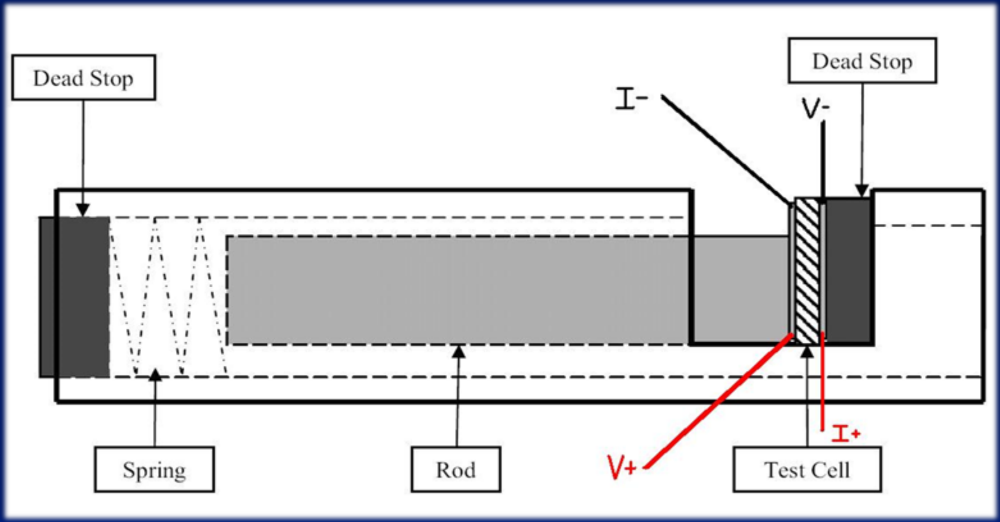


- As the conversion temperature increased, the amount of $NiFe_2O_4$ increased while the amounts of Fe_2O_3 and NiO dropped significantly.
- For a new alloy powder with a modified composition, a single-phase spinel layer was achieved after 900°Cx2h conversion.

Area-Specific Resistance (ASR) Measurement

- A number of test cells were constructed, and significant improvement of the contact layer uniformity with regard to its thickness and microstructure has been made.
- The test cells are spring-loaded and the ASR change during either isothermal or cyclic exposure at 800°C in air is monitored using a special 6-cell test rig.

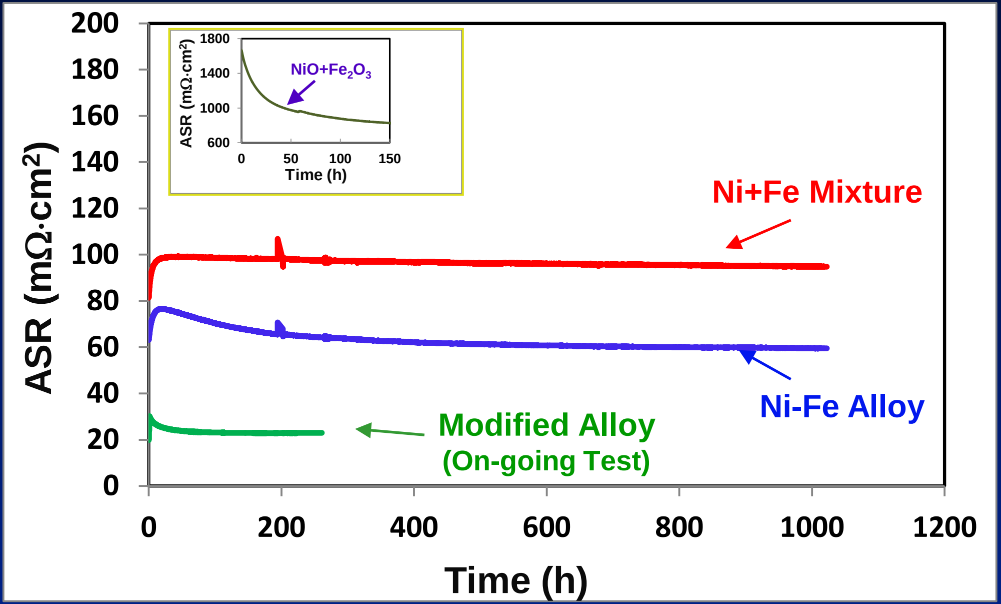




Schematic of the ASR test cell and test configuration

ASR Change as a Function of Time for Test Cells with Different Contact Pastes

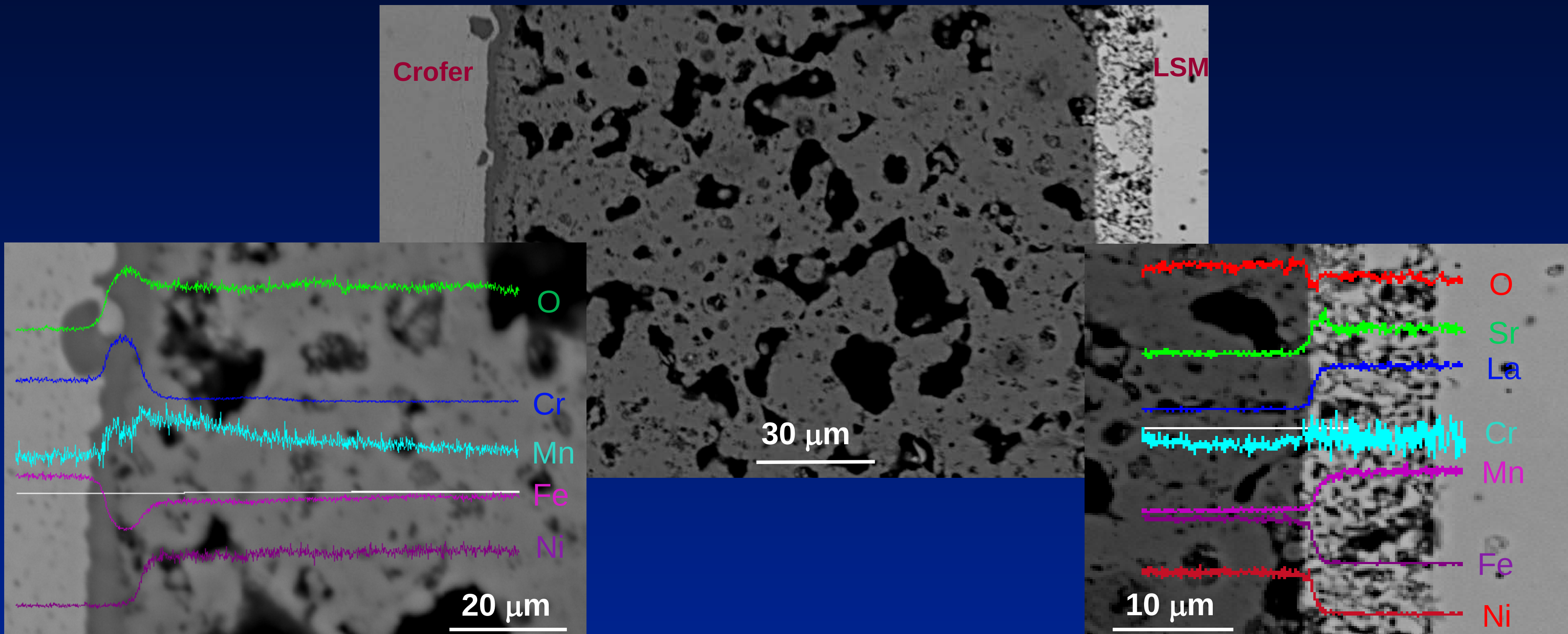
- **The ASR for the test cell with NiO and Fe_2O_3 precursors were the highest, due to poor contact layer sintering.**
- **Low and stable ASR was observed for the cells with metallic precursors in the contact layer.**
- **The lowest ASR was observed in the cell with the alloy precursor.**



Comparison in cell ASR with several contact layers with either oxide or metal precursors at 800°C in air during isothermal exposure (initial sintering: 900°Cx2 h in air)

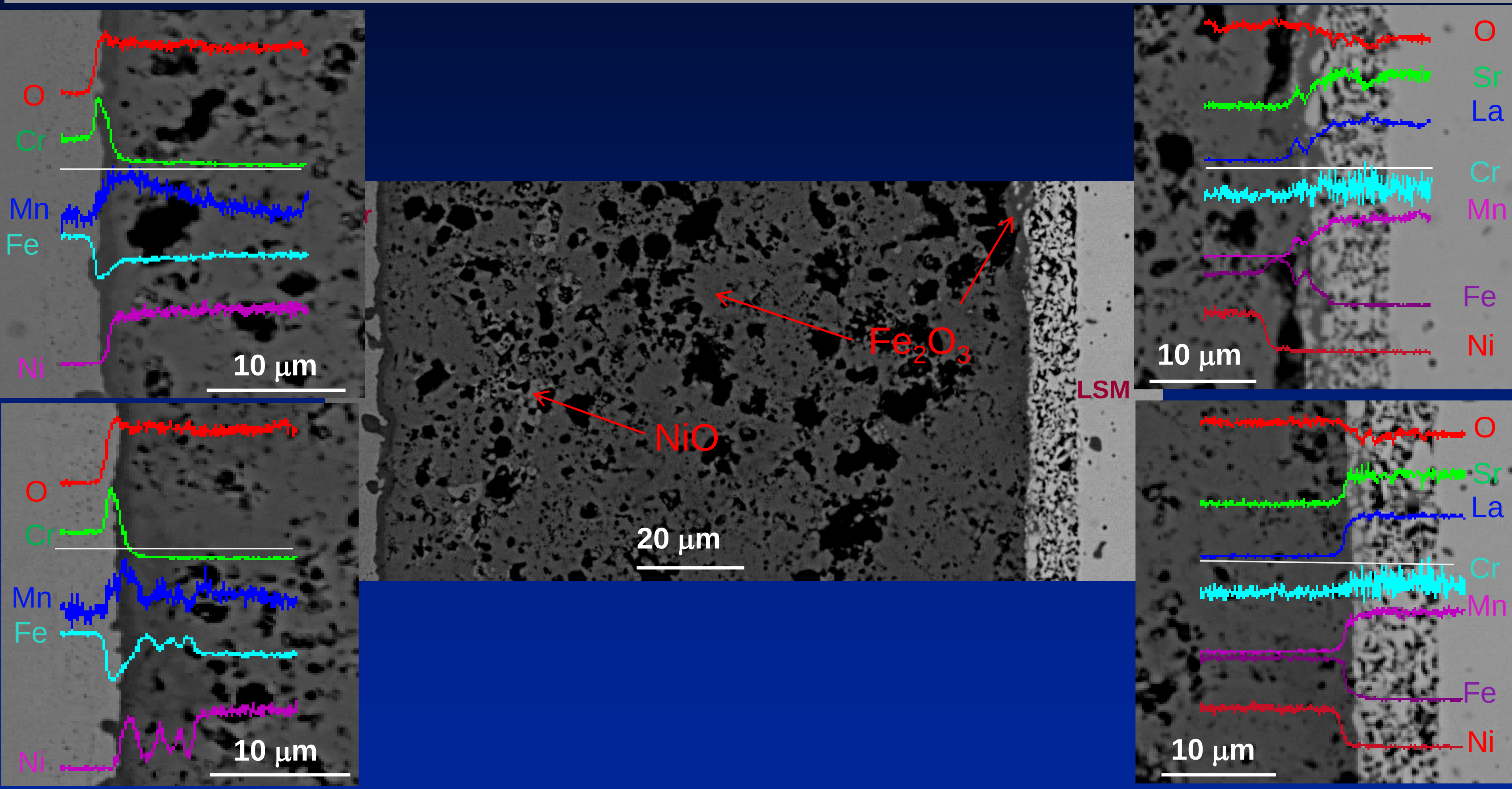
The cell ASR was either stable or dropping for the cells with the metallic precursors, indicative of their exceptional performance.

Cross-Sectional View of Tested Cells with the Ni-Fe 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.**

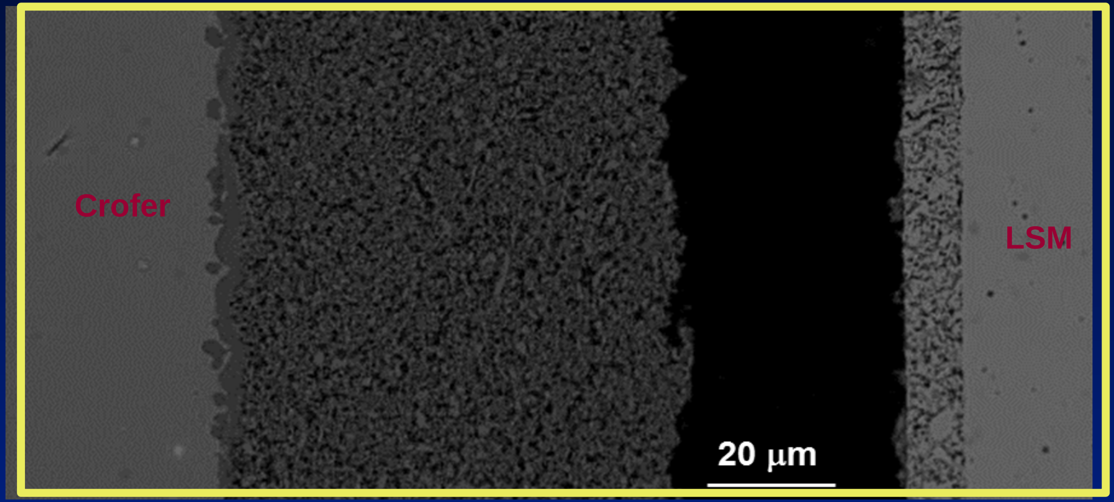
Cross-Sections of Tested Cells with the Contact Paste of a Mixture of Ni+Fe Powders

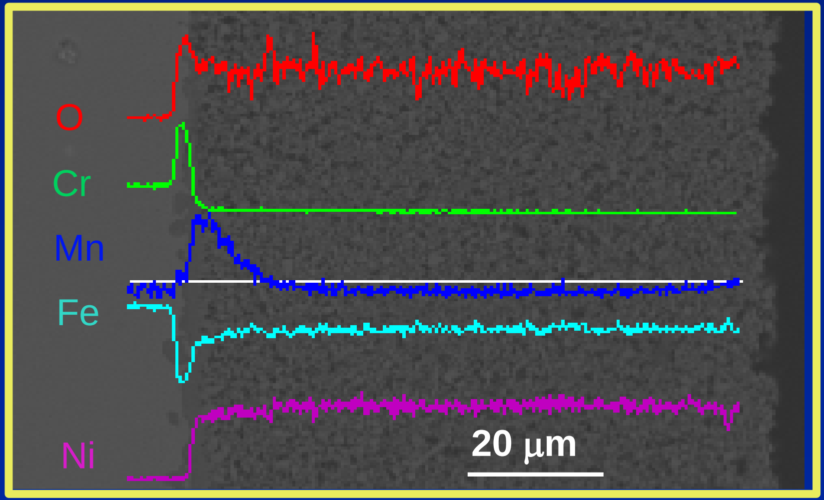


- **The Ni+Fe contact layer was less uniform compositionally and structurally compared to the Ni-Fe alloy contact.**
- **Mn and Cr diffusion into the contact layer was observed.**

Cross-Sections of Tested Cells with the Contact Paste of a Mixture of $NiO+Fe_2O_3$ Powders

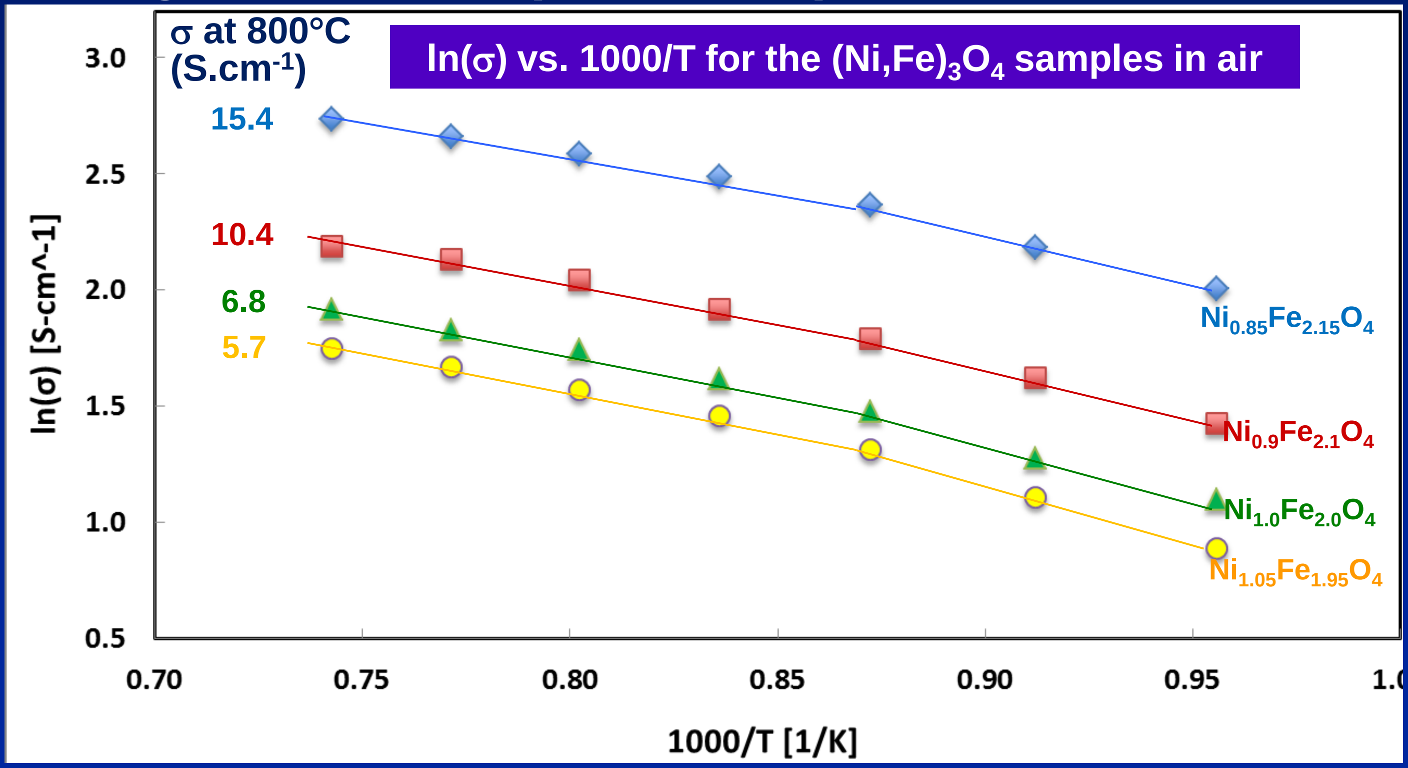
- The $NiO+Fe_2O_3$ contact layer cracked and detached from the cathode after cooling down to room temperature, due to the poor sintering of the contact layer, consistent with its higher ASR.
- More significant diffusion of Mn and Cr into the contact layer.

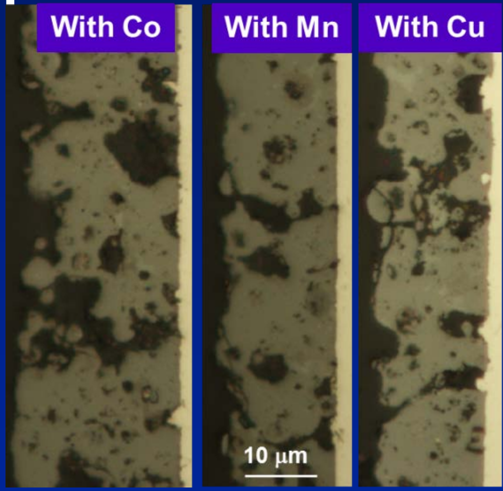




Further Improvement of $NiFe_2O_4$-Based Spinel Contact: Effect of Stoichiometry and Doping

- CTE of $(Ni,Fe)_3O_4$ with different Ni/Fe ratios was measured, which ranged from 11.6 to 12.1 x 10^{-6} /°C.
- As the Fe content in the spinel increases, the electrical conductivity increases accordingly.
- Doping with transition metal cations such as Mn, Co, Cu, etc. might further improve the performance of this spinel.





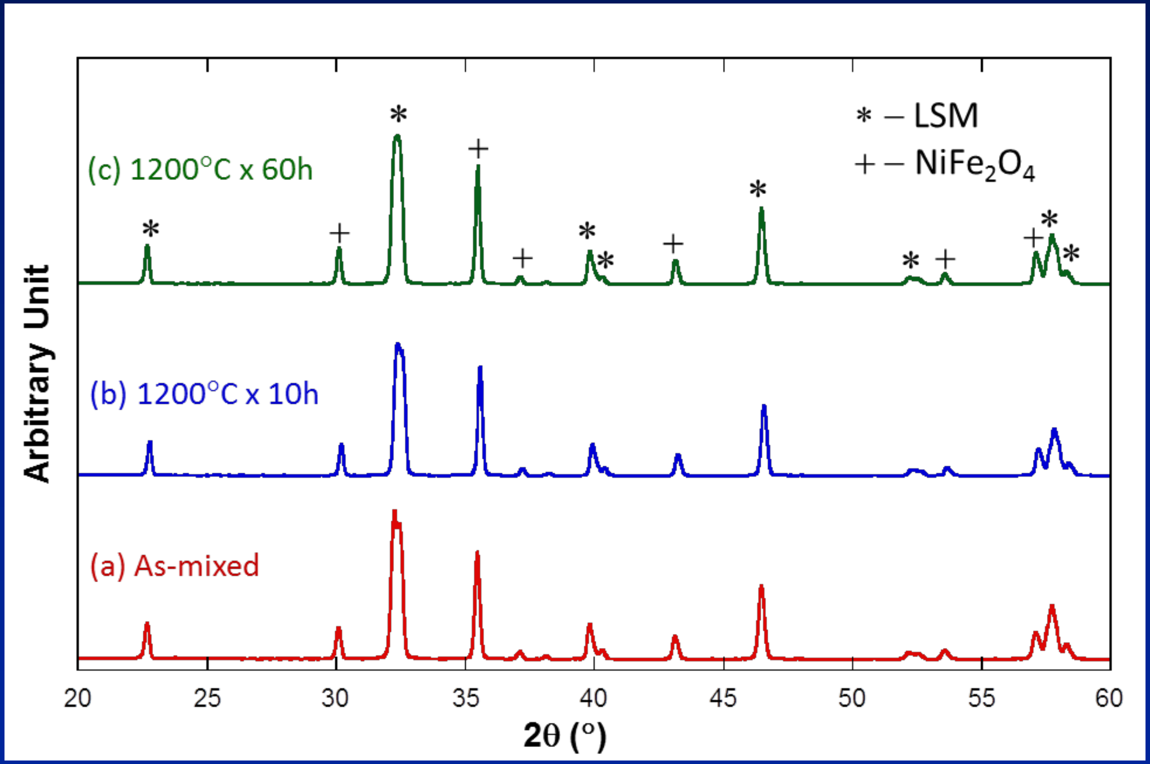
Formation of a Doped Spinel Layer via Mixing a Metal Elemental Powder (5wt.%) with the Ni-Fe Alloy Powder after 900°Cx2h Conversion

Further Improvement of $NiFe_2O_4$-Based Spinel Contact: Formation of a Composite Contact by Second-Phase Addition

– The second phase should be highly electrically conductive, CTE-matched, and chemically compatible with the cathode, interconnect, and the $NiFe_2O_4$ spinel, and preferably Cr-absorbing.

– Potential candidates includes LSM, LSCF, LNF, LCN, LSCM, etc.

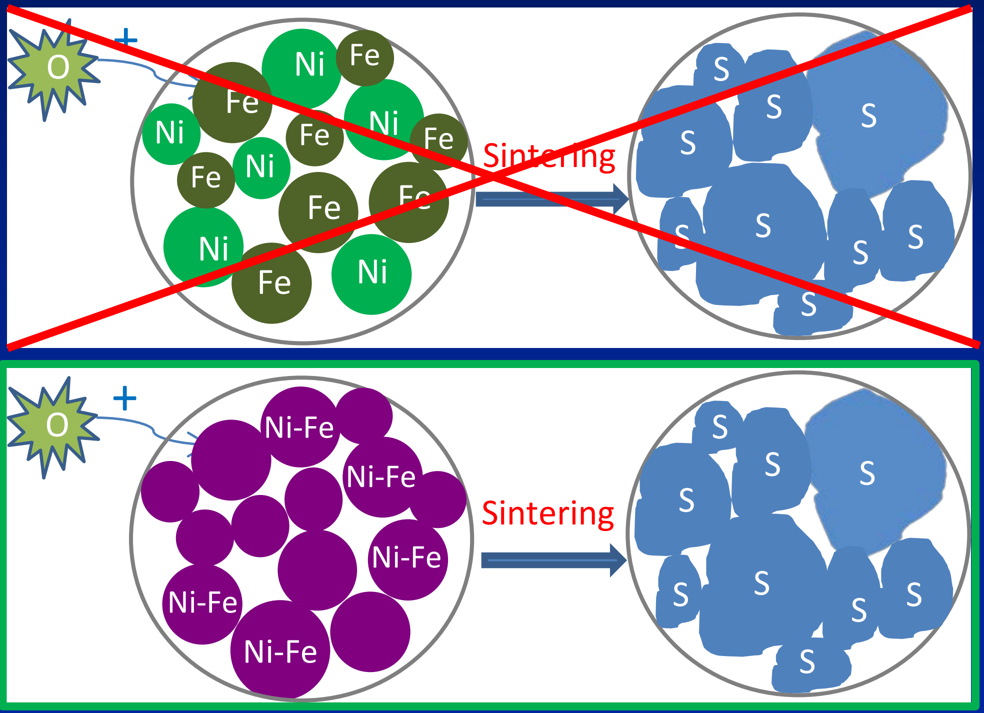
– Initial study indicates minimal interdiffusion between LSM and $NiFe_2O_4$.



XRD Patterns of a 50wt% LSM + 50 wt.% $NiFe_2O_4$ Composite After Firing at 1200°C in Air

Concluding Remarks

- Low-cost, EARS-processed $(Ni,Fe)_3O_4$-based layers with promising performance have been successfully synthesized.
- While both a mixture of Ni & Fe powders and an Ni-Fe alloy powder can be used as the precursor for the spinel-layer synthesis, the alloy powder approach is preferred:
  - Better spinel phase purity
  - Lower 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)



(J.H. Zhu et al., "Reduced-temperature sintering of coatings and layers with metallic alloy powder precursors", US Patent Application #62/349,997, 2016.)

Acknowledgments

- U. S. Department of Energy - National Energy Technology Laboratory, SOFC Innovative Concepts and Core Technology Research Program, Award No. DE-FE0026210; Project Manager: Dr. Patcharin Burke
- Allen Yu, Joseph Simpson, David Chesson, and Brian Bates from TTU
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