Effect of Spinel Composition on Electrical Conductivity and Coefficient of Thermal Expansion in the $(Ni,Co,Fe)_3O_4$-Based System

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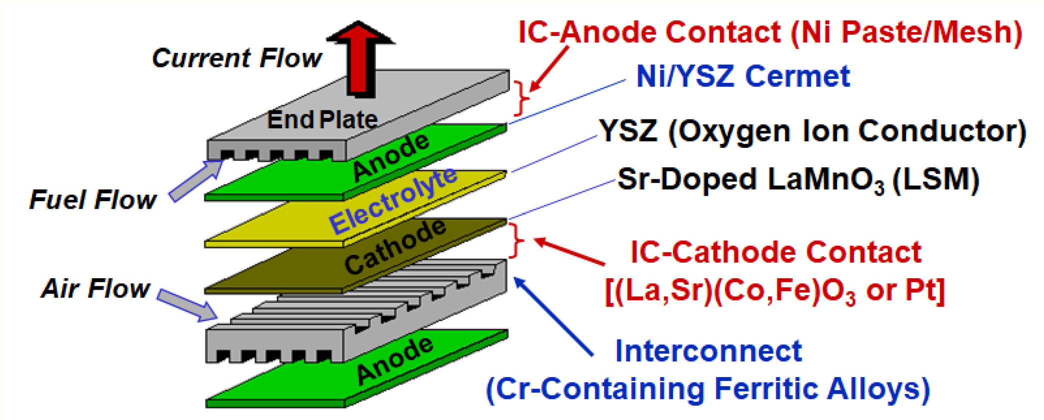
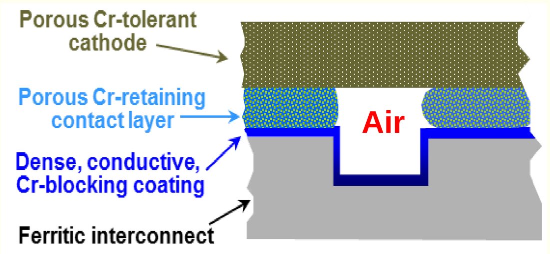
Introduction

- Electrical contact layers are used to reduce the electrode/interconnect interfacial resistance.
- While Ni-paste/mesh is widely used to establish electrical contact on the anode side, finding a suitable material for electrical contact between the cathode and interconnect is challenging.



Issues with Current Contact Materials

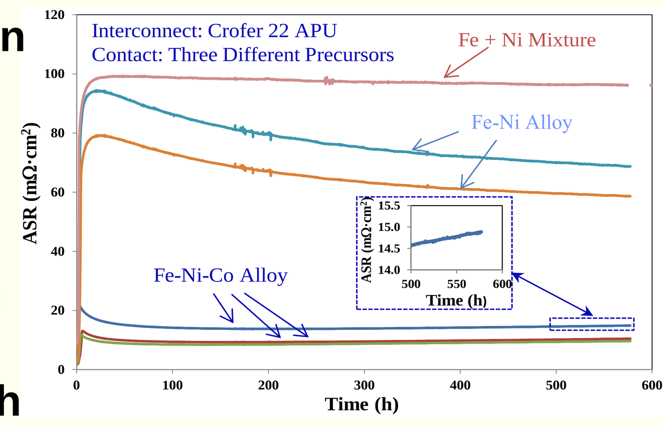
The major issues for different cathode-interconnect contact materials:



- Noble metals
  - Pt & Au: too expensive
  - Ag: highly volatile
- Perovskites
  - Difficult to balance the electrical conductivity, coefficient of thermal expansion (CTE), and sinterability:
    - $(La_{0.6}Sr_{0.4})(Co_{0.8}Fe_{0.2})O_3$ (LSCF) has higher coefficient of thermal expansion (CTE)
    - $(La_{0.8},Sr_{0.2})MnO_3$ (LSM) possesses poor sinterability
- Spinels - $(Co,Mn)_3O_4$, $(Ni,Fe)_3O_4$, $NiCo_2O_4$, etc.
  - Limited studies, poor sinterability

Why $(Ni,Co,Fe)_3O_4$-Based Spinel as Contact?

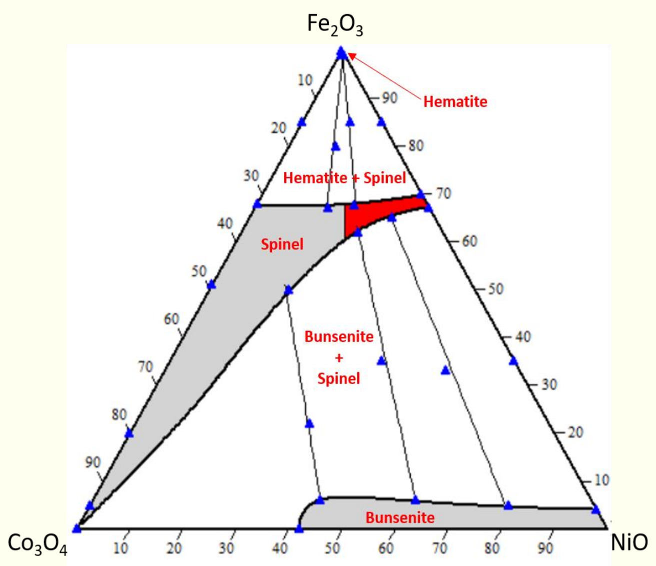
- Our recent studies indicate spinels based on $(Ni,Co,Fe)_3O_4$ thermally converted from the Fe-Ni-Co alloy powders are very promising candidates as cathode-side contact: lower area-specific resistance (ASR), excellent sinterability, and adequate CTE match with other cell components.
- Compositional optimization of $(Ni,Co,Fe)_3O_4$ based spinel is needed to further improve its electrical conductivity, while maintaining its CTE match with stack components & chemical compatibility with both interconnect/cathode.



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

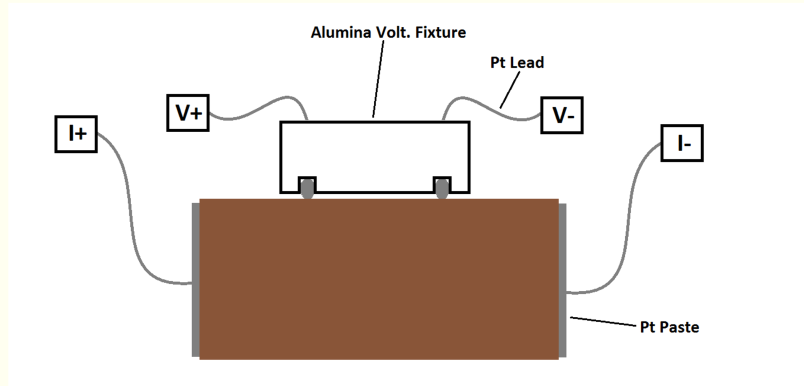
Phase Diagram Determination

- The Fe-Ni-Co phase diagram was determined experimentally.
- Solid state sintering was used to synthesize the samples, which were annealed for 200 h at 800°C in air prior to SEM/EDS examination.
- The spinel compositions located in the red region was identified as being the most promising.



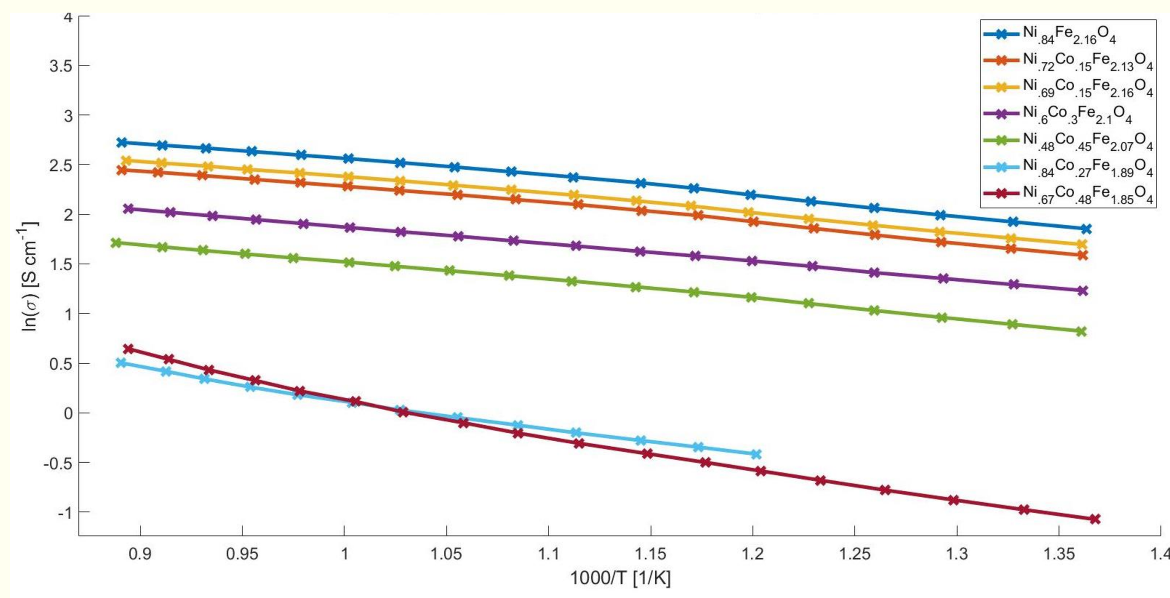
4-Probe Conductivity Measurement

- Test samples were fabricated via solid state sintering of precursor oxides mixed in proportions according to desired spinel composition.



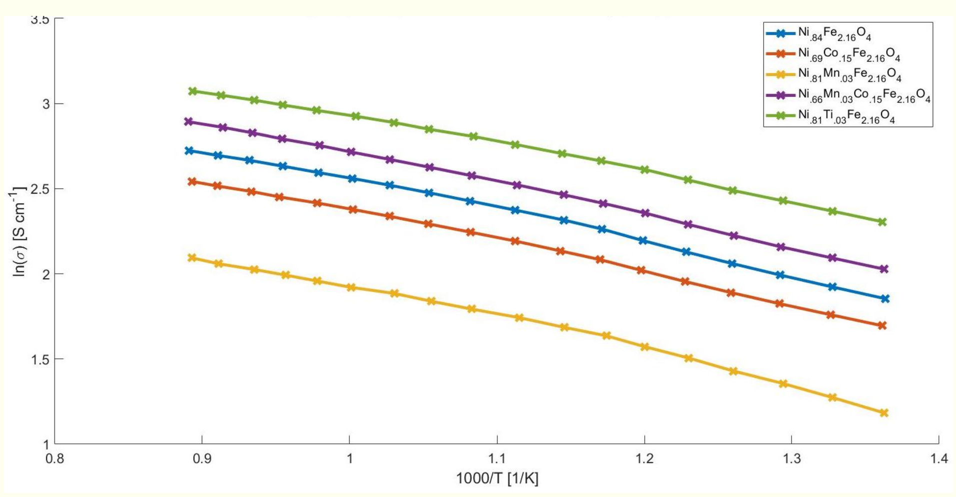
- Electrical conductivity was measured using the standard 4-probe method with a constant current of 100 mA at temperatures from 460 to 850°C.

Comparison of Electrical Conductivity for Different $(Ni,Co,Fe)_3O_4$ Compositions



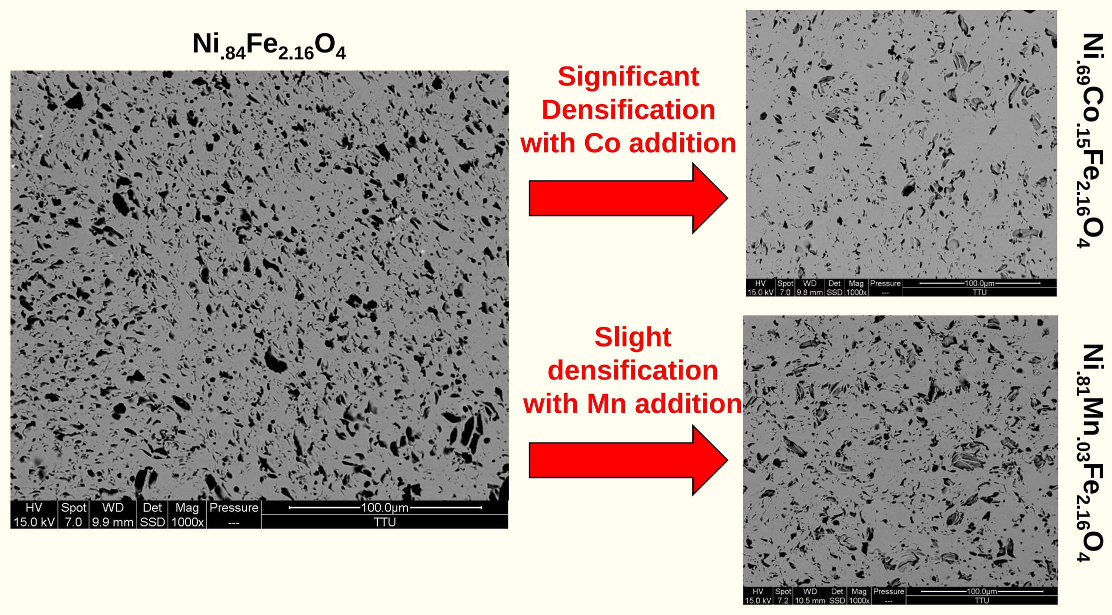
- Conduction was largely dependent on the amount of excess Fe in the spinels.
- Co doping was not effective in increasing the conductivity.

Further Doping in the $(Ni,Co,Fe)_3O_4$ Spinel



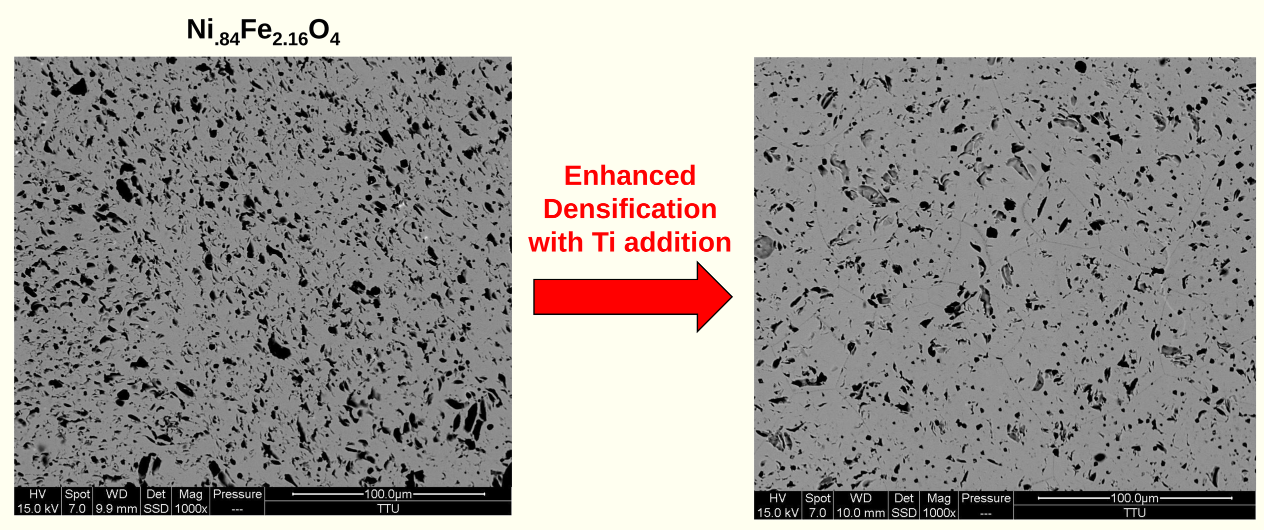
- Binary $Ni_{.84}Fe_{2.16}O_4$ spinel was identified as the promising composition for further doping with minor amounts of Co, Mn, and Ti.
- Ti addition effectively improved the conductivity.
- Co/Mn addition individually performed poorly, while Co and Mn co-doping increased the conductivity.

Effect of Co and Mn on Spinel Microstructure



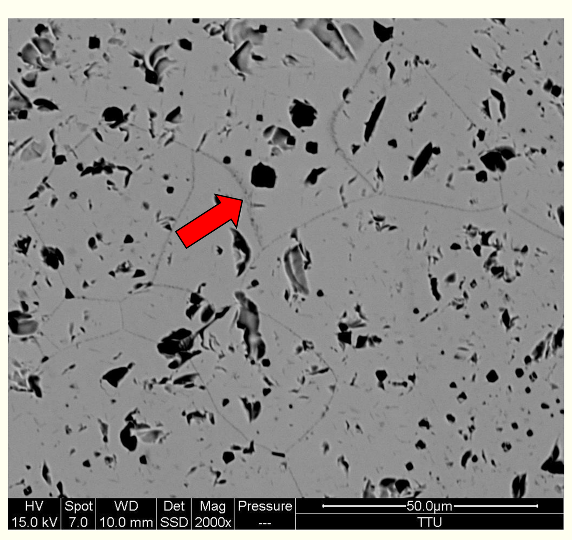
- Co appeared to have a large densifying effect.
- Mn exhibited slightly improved densification.
- No second phase formation was observed.

Effect of Ti on Spinel Microstructure



- Ti appeared to improve the spinel density.
- A grain boundary phase was observed, which was the Fe-rich $(Fe,Ti,Ni)_2O_3$ perovskite.
- The grain boundary phase was responsible for higher conductivity.

Ti-Containing Second Phase Formation



- The grain boundary phase was semi-continuous within the sample.
- Activation energy of electrical conduction revealed that conduction was still controlled by the spinel phase.

CTEs of Doped Fe-Rich Spinels

- Maintaining CTE match of the contact material with adjacent stack components is critical in reducing thermal stresses at various interfaces, which in turn increases thermal-cycling life of the stack.

Composition	Avg. CTE 20-800°C (ppm/°K)
Crofer APU 22	11.9
$Ni_{.84}Fe_{2.16}O_4$	12.08
$Ni_{.81}Ti_{.03}Fe_{2.16}O_4$	12.26
$Ni_{.79}Ti_{.05}Fe_{2.16}O_4$	12.36
$Ni_{.66}Mn_{.03}Co_{.15}Fe_{2.16}O_4$	11.55
$Ni_{.64}Mn_{.03}Ti_{.02}Co_{.15}Fe_{2.16}O_4$	12.11

- The effect of the doping addition on the CTE of the spinel was minimal. All spinels had suitable CTE values for cathode-side contact application.

Summary

- Fe-rich $Ni_{.84}Fe_{2.16}O_4$ exhibited the highest conductivity among the Fe-Ni-Co spinels; Co addition acted as buffer to primary conduction mechanism in ferrites.
- Co-Mn co-doping led to increased conductivity while individual Co- and Mn- doped samples showed decreased conductivity.
- Ti doping resulted in a mark increase in conductivity, which was due to conductive $(Fe,Ti,Ni)_2O_3$ grain boundary phase. This phase was discontinuous, so conduction was still controlled by the ferrite phase in the sample.
- All compositions showed adequate CTE matching with adjacent stack materials.

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