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

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"Solid Oxide Fuel Cell Prototype System Testing and Core Technology Development Program" Kickoff Meeting

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Outline

- Background
- Technical Approach
- Project Objectives
- Project Structure
- Project Schedule
- Project Budget
- Project Management Plan (Including Risk Management)
- Summary
- Acknowledgments

Contractor Organization Information

- **Tennessee Technological University (TTU, Contractor)**
  - **Most of the proposed research efforts will be conducted in the Center for Manufacturing Research (CMR) at TTU.**
    - **Established in 1985, the CMR is an accomplished *Center of Excellence* focusing on advanced manufacturing.**
    - **In addition to Dr. Zhu's SOFC research lab, CMR houses a variety of materials characterization facilities, including HT-XRD, SEM/EDS, microprobe, etc., some of which are free to use.**
- **FuelCell Energy, Inc. (FCE, Subcontractor)**
  - **FCE has commercialized MW-class molten carbonate fuel cell power plant, and is also working on commercializing coal-based SOFC power plant.**
  - **Over the past years, FCE has successfully developed and tested 50 - 200 kW SOFC system.**
  - **Dr. Ghezel-Ayagh, PI of FCE Subaward, will offer guidance on contact material development and test our developed materials.**

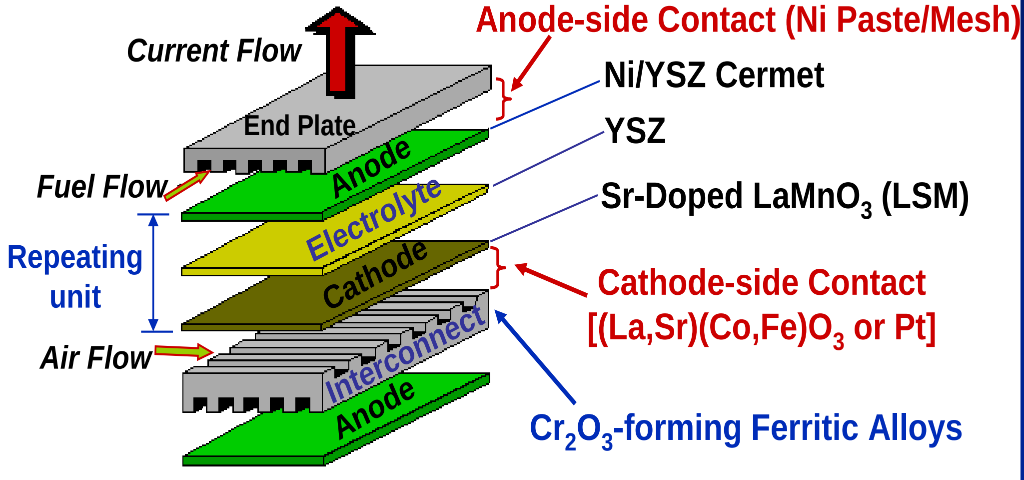
Past and Current SOFC Contact Material Projects by the PI at TTU

- ***"Novel Composite Materials for SOFC Cathode-Interconnect Contact"***, **DOE Support of Advanced Coal Research at U.S. Colleges & Universities, Core Program, DE-FG26-05NT42533, 08/2005 -07/2009**
- ***"Development of Low-Cost, Highly-Sinterable, Co-Free $(Ni,Fe)_3O_4$ Spinel-Based Contact Materials for SOFC Cathode-Side Contact Application"***, **DOE SOFC Innovative Concepts and Core Technology Research Program, Contract # DE-FE0026210, 10/2015 — 07/2017.**
- ***"GOALI: Simple Low Cost Methods for Making Conductive Interfacial Coatings for Solid Oxide Fuel Cells "***, **NSF-GOALI Program, Grant No. CMMI-1362680, 08/2014 – 07/2018**
- ***"Development & Validation of Low-Cost, Highly-Durable, Spinel-Based Materials for Cathode-Side Contact"***, **DOE SOFC Prototype System Testing & Core Technology Development Program, this project.**

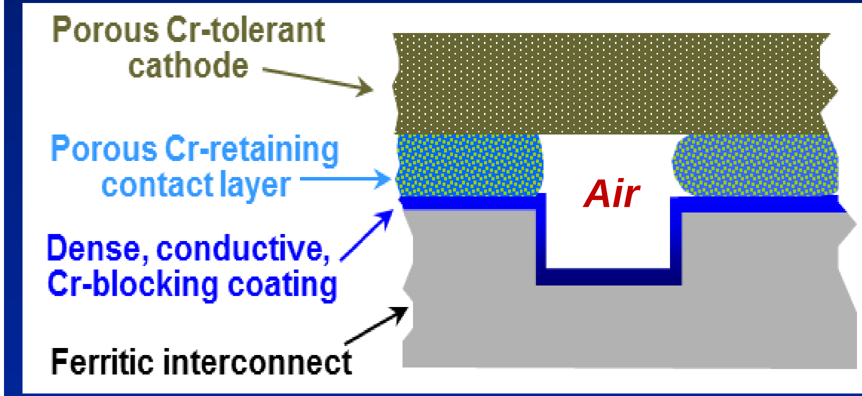
The PI has established an SOFC Materials Synthesis & Testing Laboratory with capabilities of arc melting, electroplating, screen printing, spin coating, powder synthesis, ball milling, area-specific resistance (ASR) and single cell testing facilities.

Main Functions of Contact Layers in SOFC Stack

- To provide and maintain stable electrical conduction paths between the interconnect and electrodes in an SOFC stack assembly and thus minimize the ohmic resistance and stack power loss.
- To provide for the gas channels and mechanical bonding.



Schematic of a Planar SOFC Stack

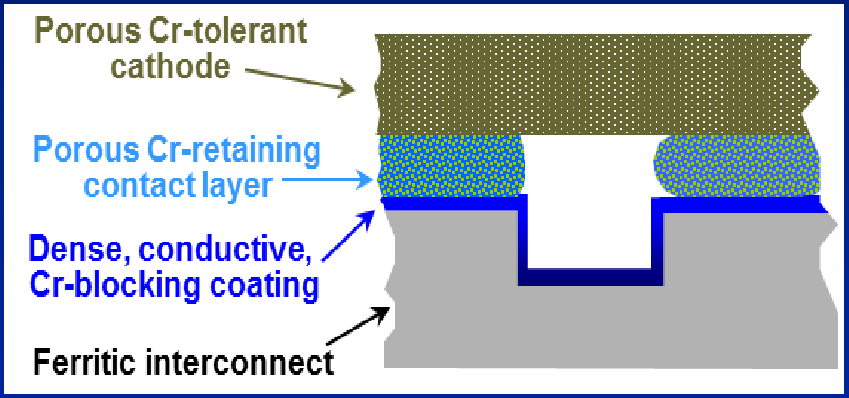


Schematic of the Cathode-Interconnect Interface

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

Material Requirements for Cathodes-Side Contact

- Sufficiently high and stable electrical conductivity over the SOFC lifetime
- Reasonable match in coefficient of thermal expansion (CTE) with other stack components
- Adequate stability/ compatibility with adjacent components
- Appropriate sintering activity, porosity level, and mechanical bonding
- Absence of volatile species (preferably with some Cr-retaining capability)
- Low-cost raw material and manufacturing

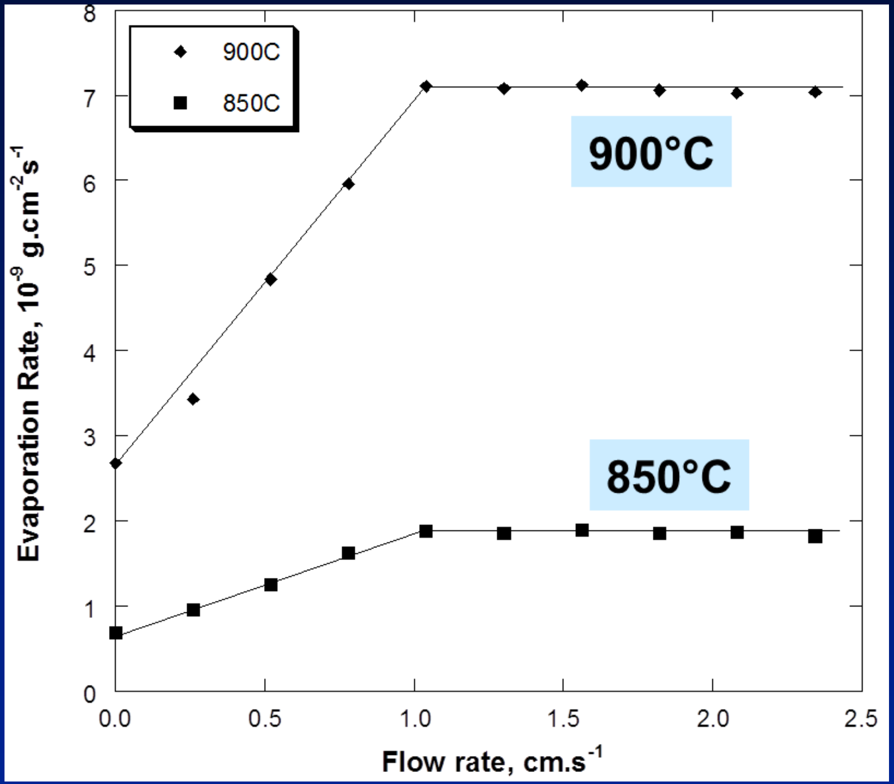


Schematic of the Cathode-Interconnect Interface

(Zhu & Ghezel-Ayagh, Int. J. Hydrogen Energy, 2017)

Cathode-Side Contact Material Choices

- Noble Metals
  - Pt, Pd, and Au (high cost)
  - Ag (relatively low cost)
- Conductive Ceramics
  - Perovskites based on $(La,Sr)(Mn,Ni,Co,Fe)O_3$
  - Spinels such as $(Co,Mn)_3O_4$, $(Ni,Co)_2O_4$, and $(Ni,Fe)_3O_4$

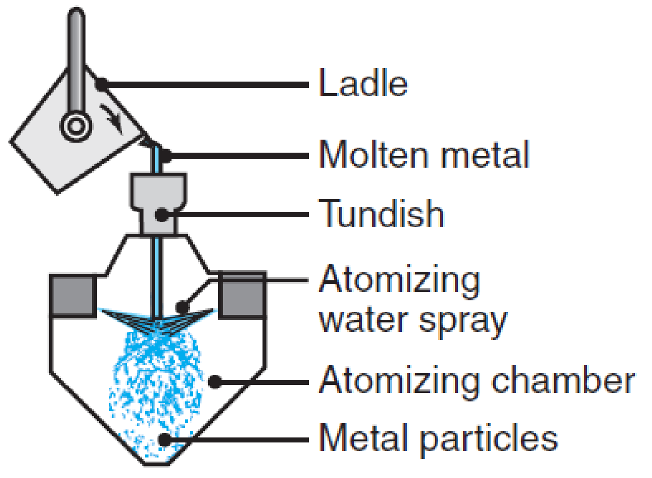


(Lu & Zhu, Electrochem. Solid-State Lett., 2007)

- Composites & Other Structures
  - Nobel Metal-Perovskite, Perovskite-Perovskite, etc.
  - Multilayered Structures, Foams, Felts, etc.

Processes for Contact Layer Fabrication

- **Powder Preparation**
  - Metal powders: atomization, solid state reduction, electrolysis, chemical processes (e.g. solution precipitation, thermal decomposition), etc.
  - Ceramic powders: combustion synthesis, solid state reaction, or chemical processes, mechanical milling
- **Contact Layer Application**
  - The contact layer can be applied on the cathode or the interconnect, via painting, screen printing, wet spray, etc.
- **Sintering**
  - After drying, the contact layer can be sintered in a dedicated sintering step or during stack startup (800-950°C x 1-4 h).

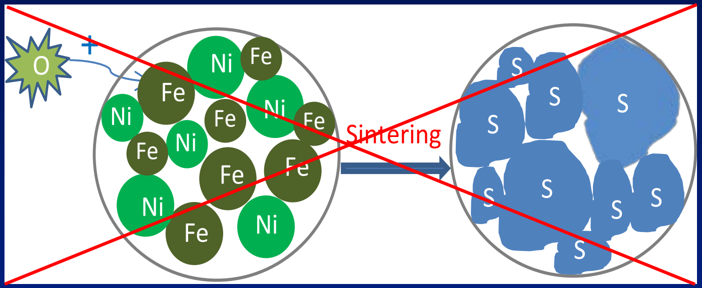


Gas Atomization for Making Metal Powder

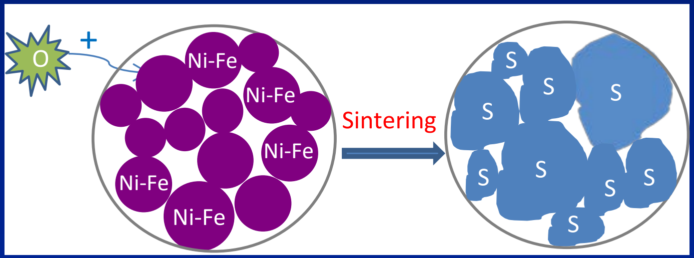
Screen printing for Applying the Contact Layer

Our previous DOE project evaluated the potential of $(Ni,Fe)_3O_4$-based spinel as Contact Materials

- **$(Ni,Fe)_3O_4$-based spinels have reasonable electrical conductivity and CTE.**
- **Due to the absence of Co and relatively low Ni content, these spinels are potential low cost alternatives.**
- **The sinterability of the spinels can be enhanced by utilizing the environmentally-assisted reactive sintering (EARS) process.**



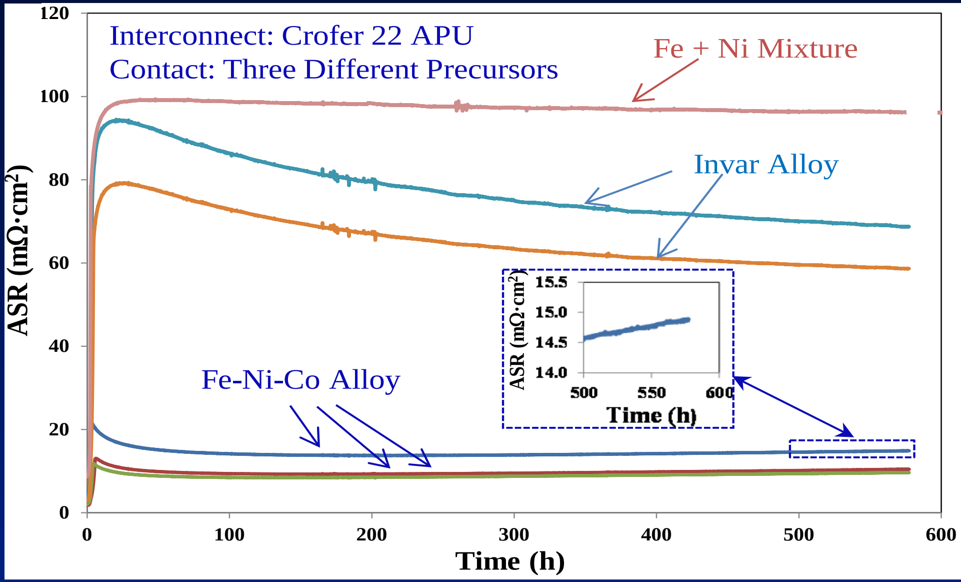
(a)
Using a mixture of metallic Fe and Ni powders as precursor



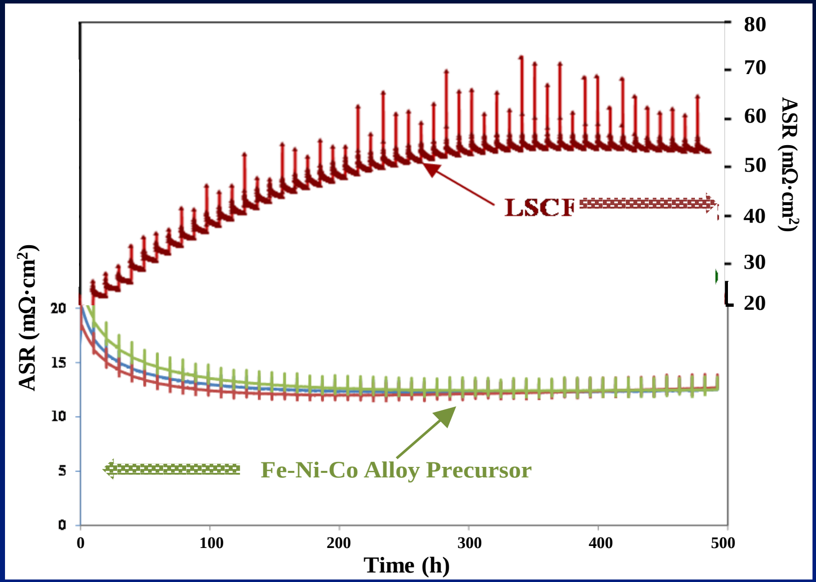
(b)
Using a Ni-Fe alloy powder as precursor.

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

Precursor alloy design & development offers the potential to further improve the spinel-contact performance



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

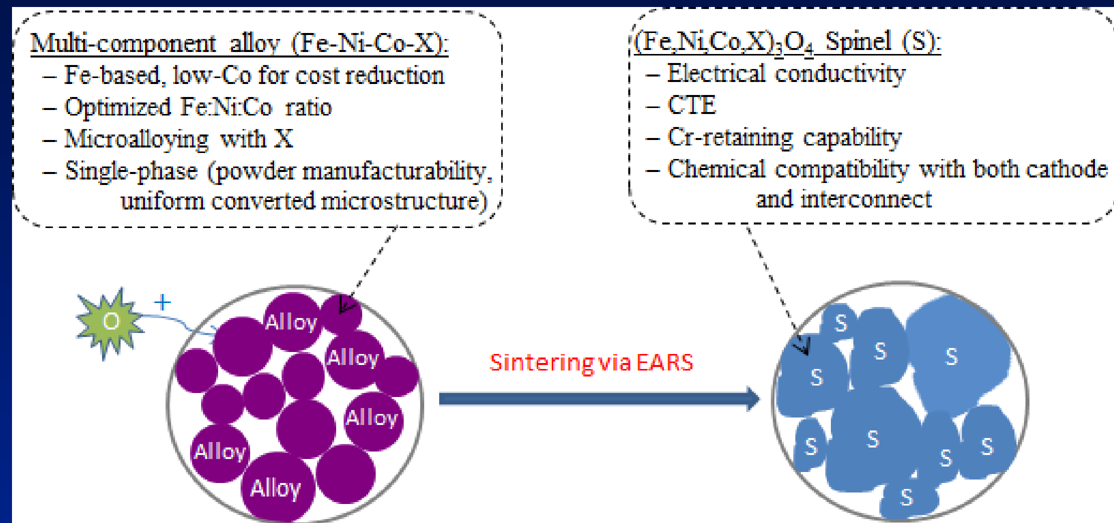


Cell ASR at 800°C during Cyclic Exposure of Test Cells with Ternary Alloy Precursor

- **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.**

Technical Approach

- **While the alloy derived spinel-base contact concept is very promising, there are still some important questions that need to be answered:**
  - **What is the best alloy composition in the ternary Fe-Ni-Co system? Are there additional alloying elements that can be added to the alloy to further improve the spinel contact performance?**
  - **How does the alloy contact layer perform during the longer-term ASR testing as well as in-stack testing?**



Proposed approach for reduced-temperature sintering of the contact layer with the $(Ni,Fe,Co,X)_3O_4$-base spinel ("S") using a multi-component alloy precursor.

We propose to develop a low-cost, multi-component Fe-Ni-Co-X alloy precursor powder that is compositionally optimized and specifically fabricated for synthesis of a spinel contact layer at a reduced sintering temperature via EARS. The developed alloy precursor will be critically evaluated and validated for SOFC cathode-side contact application.

Project Objectives

- **Optimization of the multi-component alloy precursor composition.** The precursor alloy composition will be optimized via composition screening in the $(Ni,Fe,Co)_3O_4$ system, alloy design using physical metallurgy principles, and cost considerations. The desired alloy powder will be manufactured via gas atomization and characterized in detail.
- **Demonstration/validation of the contact layer performance in relevant SOFC stack environments.** Longer-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 contact layer and interconnect coating. Cost analysis and scale-up assessment will be conducted for potential commercialization.

Project Structure

Task 1 Project Management, Planning, and Reporting (TTU)

Task 2

Optimization of Precursor Alloy Composition (TTU)

2.1 Composition Screening in $(Ni,Fe,Co)_3O_4$ Spinel System

2.2 Alloy Design of Fe-Ni-Co-X Alloy Precursor

2.3 Manufacturing and Characterization of New Alloy Powders

Task 3

Demonstration/Validation of Contact Layer Performance in Relevant SOFC Stack Environments

3.1 ASR under Isothermal and Cyclic Exposure Conditions (TTU)

3.2 In-Stack Performance Testing (FCE)

3.3 Cross-Sectional Examination (TTU/FCE)

Task 4

Further Cost Reduction and Commercialization Assessment

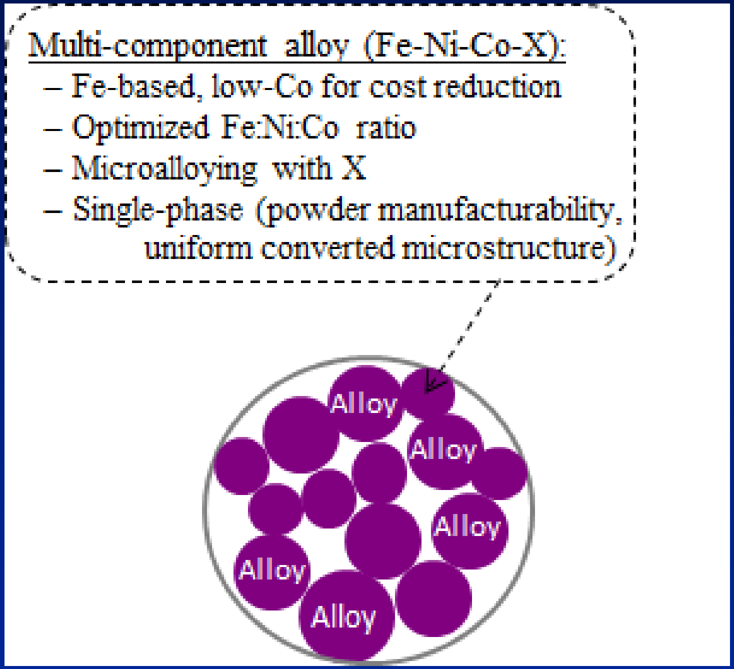
4.1 Interconnect Coating Synthesis with Alloy Precursor (TTU)

4.2 Co-sintering of Interconnect Coating/Contact Layer (TTU)

4.3 Cost Analysis and Commercialization Assessment (FCE/TTU)

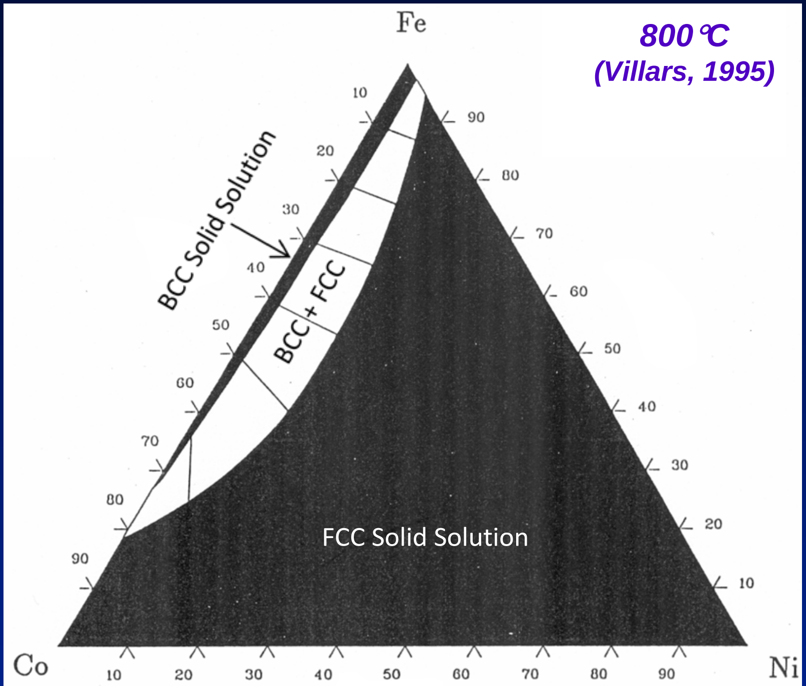
Optimization of Precursor Alloy Composition

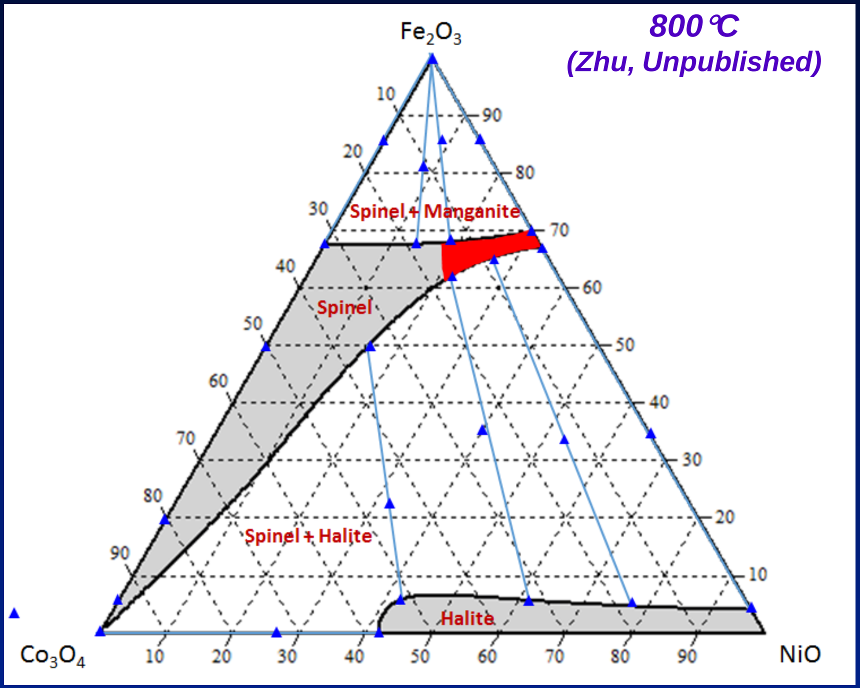
- The optimization of the precursor alloy composition will be achieved via a combination of the following:
  - Composition screening in the $(Ni,Fe,Co)_3O_4$ spinel system
  - Alloy design of the multi-component Fe-Ni-Co-X alloy using physical metallurgy principles
  - Cost considerations



In addition to the Fe/Ni/Co ratio in the alloy, effective micro-alloying elements will identified/optimized.

Compositional Screening in the $(Ni,Fe,Co)_3O_4$ Spinel 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 diagram at 800°C.
- Of particular interest to our contact material development are the low-Co spinel compositions in the region highlighted in red above.

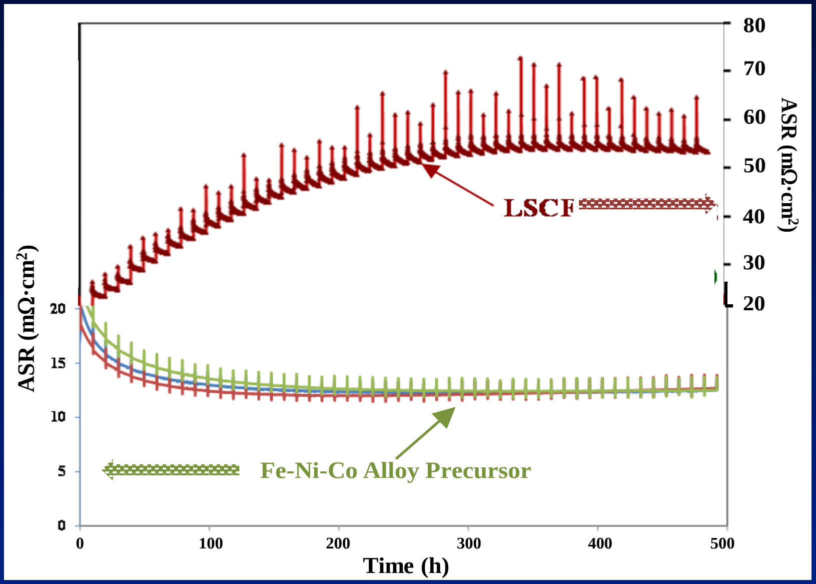
Gas Atomization of the Optimization Alloys

- Once the Fe-Ni-Co-X alloy precursor composition is optimized, the alloy powder with the desired composition and particle size will be manufactured using a semi-industrial gas atomizer.
- Several atomization service providers have been contacted for powder processing. Quotes for processing 1-10 kg of the specified powder have ben obtained.
- The final selection of the vendor for supplying the custom powders will be based on cost, expected delivery date, quality of the powder (size, size distribution, purity, etc.)

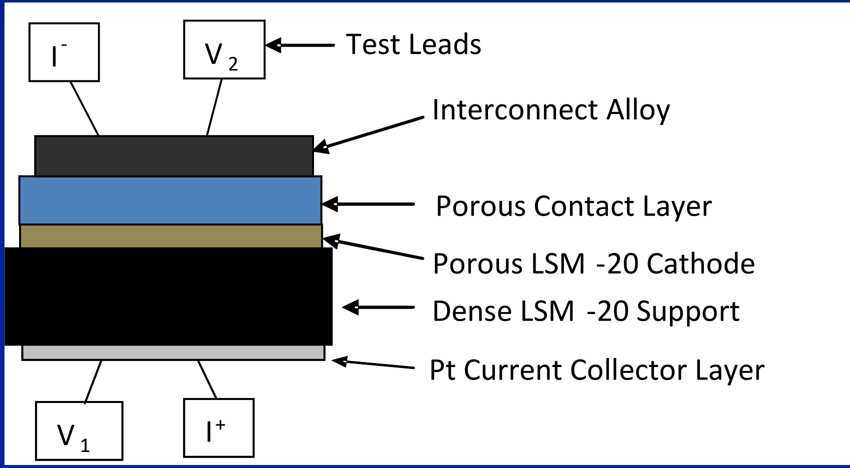
Based on the feedback from the powder producer, we expect that the cost for processing one batch of powder will be around 4,000-8,000 dollars with an expected delivery date of 3-6 months after the order is placed.

ASR and Bonding Strength Testing

- **ASR change during the isothermal and cyclic exposures will be monitored using a specially-constructed 6-cell test rig for up to 5,000 h.**
- **The bonding strength of the developed contact material will be determined using pull testing.**



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



In-Stack Testing of the Developed Contact at FCE

- The contact material will be tested at FCE using the full-size 1-cell stack testing facility. This unique stack contains only one full-size cell, which simplifies the stack construction and performance analysis. Such stack configuration has been extensively used by FCE to validate individual components in a stack prototype with component integration similar to the final application in most respects.
- The performance degradation behaviors of the 1-cell stack with both the new contact layer and FCE's state-of-the-art will be analyzed and compared.
- The microstructural features and compositional profiles of the contact layer in the tested cells/stacks will be studied and the Cr content at each location within the cells/stacks will be quantified.

Further Cost Reduction and Commercialization Assessment

- To further reduce the stack cost, the developed alloy powder and other metallic powders will also be utilized as precursor for potential synthesis of spinel-based interconnect coating. Co-sintering of the interconnect coating and the contact layer both fabricated with the metallic precursors will also be explored.
- To achieve a dense interconnect coating, the powder composition/size, the initial packing density in the precursor layer, and the sintering condition will be modified to minimize the porosity in the coating and improve its performance.

Near the end of the project, cost analysis for the new contact/interconnect coating system and cost comparison with the state-of-the-art will also be conducted. Furthermore, the feasibility for scale-up and potential implementation of the new technology at FCE's stack manufacturing facilities will be assessed for potential technology transfer/licensing.

Project Schedule

Task/ Subtask	Activity Description / Month after Start	Year 1				Year 2			
		3	6	9	12	15	18	21	24
1	Project Management, Planning, & Reporting								
2.1	Composition Screening of $(Ni,Fe,Co)_3O_4$								
2.2	Alloy Design of Fe-Ni-Co Based Precursor								
2.3	Alloy Powder Manufacturing/Characterization								
3.1	ASR Testing								
3.2	In-Stack Performance Testing								
3.3	Cross-Sectional Examination								
4.1	Interconnect Coating Synthesis								
4.2	Co-sintering of Interconnect Coating/Contact								
4.3	Cost Analysis & Commercialization Assess.								

⊕ *indicates a milestone for the task/subtask;* ▲ *indicates a quarterly, progress or final report*

Project Budget

- $376,960 Total
- DOE Share: $300,000; TTU Cost Share: $76,960 (20.4%)

Table 1 Budget Period/Fiscal Year Project Costing Profile

Budget Period	Fiscal Year (year in which the cost will be incurred, not appropriated)	Performing Organization	Planned Costs	
			Federal Share	Non-Federal Share
1	FY18	Recipient (TTU)	$154,861	$37,718
1	FY19	Recipient (TTU)	$145,139	$39,242

Project Management Plan – Risk Management

Description of Risk	Probability (Low, Moderate, High)	Impact (Low, Moderate, High)	Risk Management Mitigation and Response Strategies
Technical/Scope Risks:			
(a) Alloy powder Fabrication	Low	High	(1) Identify multiple suppliers and communicate with them simultaneously and periodically. (2) Place the orders for powder making as soon as possible to avoid delay. (3) Identify a powder supplier that can provide powder sizing service to get the powder of desired size.
(b) Co-sintering of interconnect coating and contact layer	Moderate	low	(1) Start the co-sintering work immediately with commercial alloy powder. (2) Pre-sintering of the interconnect coating with the metallic precursor to ensure the formation of the desired two-layer microstructures.
Resource Risks:			
Microstructural characterization equipment breakdown	Low	Low	(1) Ask the Center for Manufacturing Research (CMR) at TTU to speed up the repair. (2) Utilize the facilities at Oak Ridge National Laboratory on a fee-based agreement.
Management Risks:			
Difficulty in hiring the suitable graduate students initially.	Low	Low	(1) Having current graduate students to work part-time on this project. (2) Hiring hourly undergraduates.
Schedule Risks:			
Delay in addressing the technical risks	Low	Moderate	(1) Pursue multiple approaches simultaneously to address these technical concerns. (2) Have the R&D engineer to devote more time on this project initially to speed up the progress.

Project Management Plan – Project Milestones

MILESTONE LOG							
Budget Period	Milestone Number	Subtask Number	Milestone Title/Description	Planned Start Date	Planned Completion Date	Actual Completion Date[a]	Verification Method
1	A	1	Revised Project Management Plan	10/10/2017	10/30/2017	10/23/2017	PMP file
1	B	1	Kickoff Meeting	10/30/2017	12/29/2017	11/29/2017	Presentation file
1	C	2.2	Compositional optimization of multi-component Fe-Ni-Co based alloy	11/01/2017	06/30/2018	In progress	The optimal Fe/Ni/Co contents as well as other alloy additions are identified.
1	D	2.3	Preparation of the powder of the optimized alloy via atomization	11/15/2017	09/31/2018	In progress	Atomization of one alloy powder is completed, and its composition and particle size are determined.
2	E	3.1	Demonstration of long-term ASR stability of the cell with the new contact	01/01/2018	06/30/2019	Not started	The ASR stability over 5,000-h isothermal exposure or over 500 10-h cycles is demonstrated with an overall low degradation rate.
2	F	3.2	Demonstration of stack performance stability with 1-cell stack testing	04/02/2018	07/31/2019	Not started	Stack power output stability testing for over 1,000 h is completed at FCE, and the results are analyzed.
2	G	4.3	Cost analysis and commercialization feasibility	07/01/2019	09/31/2019	Not started	Cost analysis and scale-up feasibility assessment are completed.

[a] To be reported in the Quarterly Progress Reports.

Project Management Plan – Success Criteria and Decision Points

- The success criteria for this project include:
  - Demonstration of a fully-converted, well-sintered $(Ni,Fe,Co)_3O_4$-based spinel layer via the EARS process using the specially-designed multi-component alloy;
  - Improved ASR and in-stack performance of the new alloy derived contact materials as compared to the state-of-the-art commercial cathode-side contact;
  - Significant reductione in both raw materials and processing cost.
- Decision point
  - Near the end of this project, a decision point will be reached with regard to whether or not to pursue potential follow-up stack/system prototype validation.
    - ✓ If a follow-on study is desired, communication/negotiation with DOE will be initiated and FCE will be invited to further collaboratively assess the performance of the proposed contact materials and to commercialize the developed technology.

Summary

- The proposed research is to develop and validate low-cost, highly-durable, spinel-based materials synthesized with a multi-component alloy precursor for SOFC cathode-side contact application.
  - Determine the optimized composition of the multi-component alloy precursor.
  - Assess and validate the performance of the sintered spinel layer in realistic stack-relevant environments.
  - Explore potential approaches for further reducing the stack cost as well as conduct cost analysis and scale-up assessment.
- Research activities since the project started
  - ~ 10 spinel compositions have been prepared & are being tested.
  - The preferred vendor for gas atomization has been identified.
  - A new ASR test rig is being constructed for more reliable testing.

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
- Center for Manufacturing Research, TTU
- Department of Mechanical Engineering, TTU