Advanced Interconnect and Interconnect/Electrode Interfaces Development at PNNL

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Objectives and Approach

- Objectives
  - Develop cost-effective, optimized materials and fabrication approaches for SOFC interconnect and interconnect/electrode interface (i.e. contacts) applications
  - Identify and understand degradation processes in interconnects and interconnect/electrode interfaces
- Approach
  - Materials and process development
    - Cost-effective oxidation resistant alloys
    - Surface modification via coatings
    - Interconnect/electrode contact materials
  - Materials evaluation and degradation study
    - Screening study of alloys and ceramics for interconnect and interface applications, respectively
    - Investigation and understanding of oxidation/corrosion and interfacial reactions and stability under SOFC operating conditions.

Accomplishments in FY07

- Investigation and development of cost-effective ferritic stainless steels (In collaboration with Allegheny Ludlum Corp.)
  - Systematically investigated 430
  - Identified and evaluated 439 and 441, two modified versions of 430
  - Applied protection layers onto candidate alloys and evaluated their performance
- Development of protection layers and fabrication approaches
  - Completed long-term thermal stability and electrical performance evaluation
  - Initiated optimization of materials and fabrication for further cost-reduction
- Investigation and development of contact layers between metallic interconnects and electrodes
  - Screening-studied more than a dozen materials systems via different fabrication approaches
  - Identified two promising material groups and three approaches
  - Evaluated electrical performance of selected candidates

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Investigation and Development of Novel Interconnect Alloys

- **Goal**: Identify/develop a novel ferritic stainless steel (FSS) with an optimized alloy chemistry that offers comparable or improved performance relative to the state-of-the-art compositions such as Crofer 22 APU, while being more cost-effective.

- **Approach**: To achieve the desired alloy chemistry or control residual alloy elements of Si, C, N, etc., via alloying, instead of extra refining that adds cost.

- Accomplishments
  - Investigated properties of 430 relevant to interconnect applications
  - Identified potential candidates 441 and 439, two modified versions of 430
  - Evaluated their properties relative to interconnect requirements
  - Surface-modified the potential candidates with spinel protection layers and investigated their stability and electrical performance

Slide 4

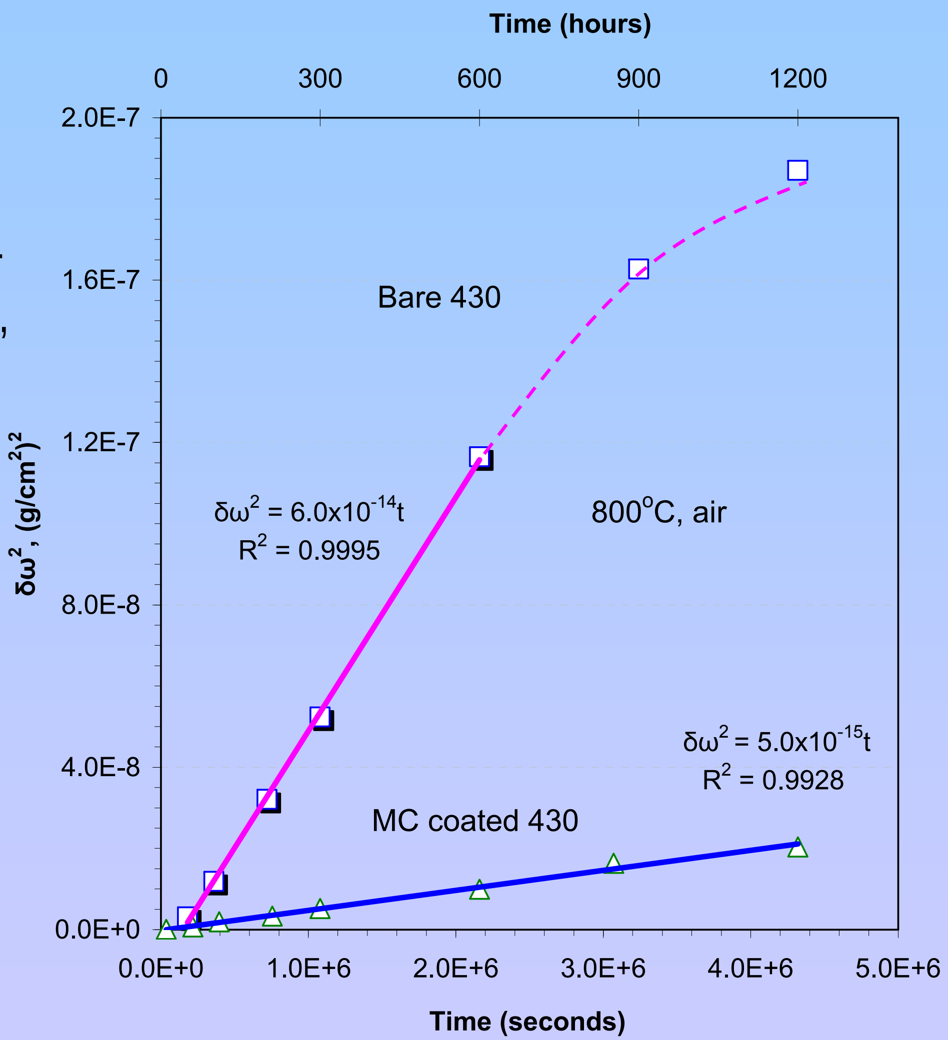
S3 Staff, 7/30/2007

Oxidation Kinetics of Bare and Coated 430

Why 430: cost reduction

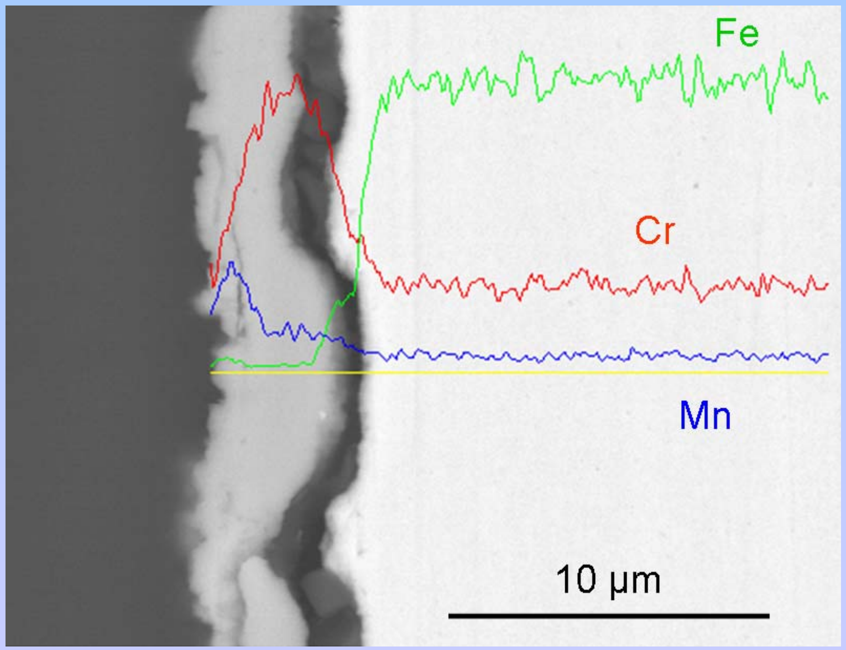
- 430: 17% Cr, via conventional melting – more cost-effective
- Crofer 22 APU: 23%Cr, extra refining (e.g. vacuum refining) for cleaning residual elements, Si, C, N, etc.

- Bare 430 demonstrated a fairly low scale growth rate at early stages
- Leveling off of the weight gain indicated likely spallation
- $Mn_{1.5}Co_{1.5}O_4$ (MC) spinel protection layers drastically mitigated the scale growth beneath the coating

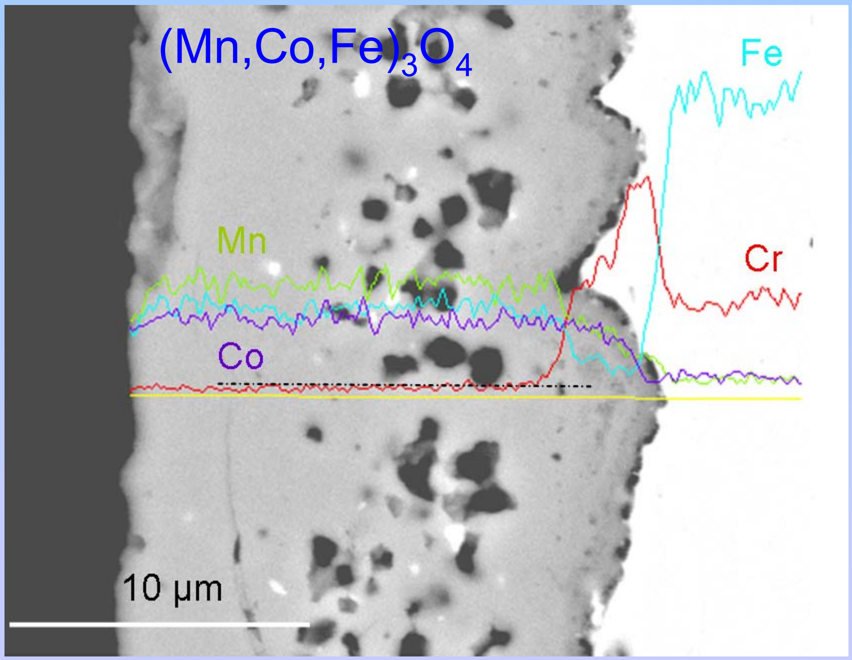


Surface Stability of 430

- Unlike bare 430, no spallation observed on MC 430
- Fe transported through the coating, BUT not Cr
- No solubility of SiO_2 in Cr_2O_3
- Formation of continuous, insulating SiO_2 layer b/w scale and Fe-Cr substrate



Bare 430

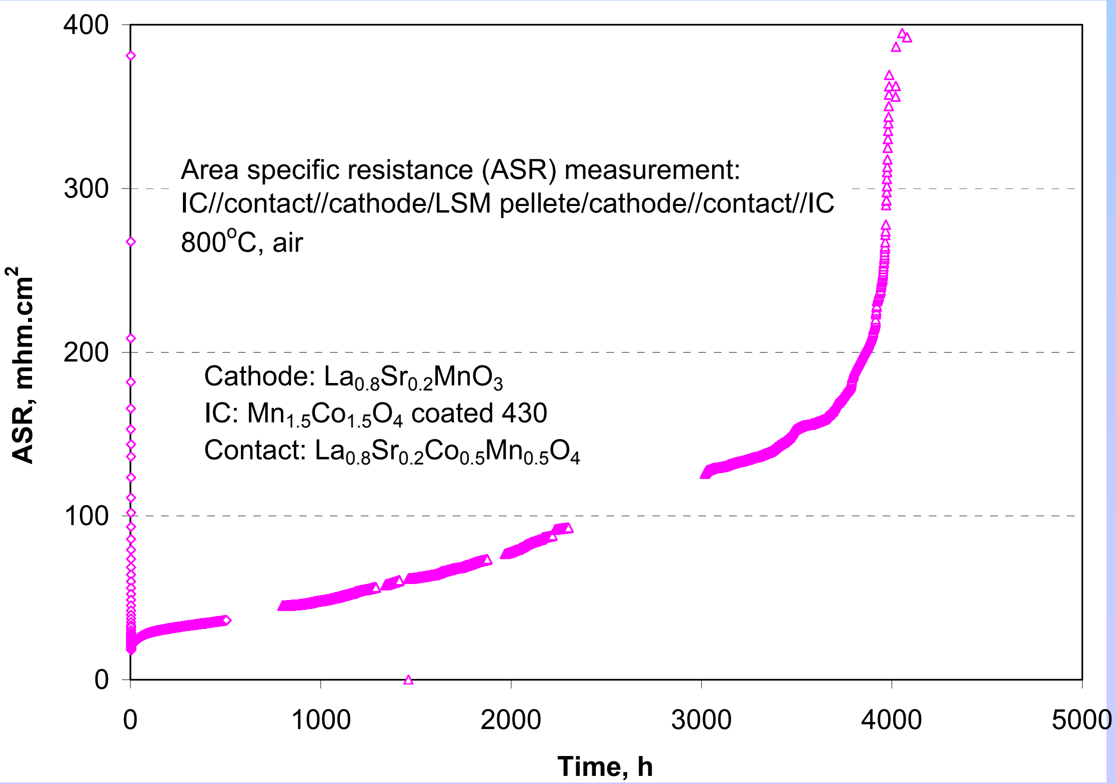


MC coated 430

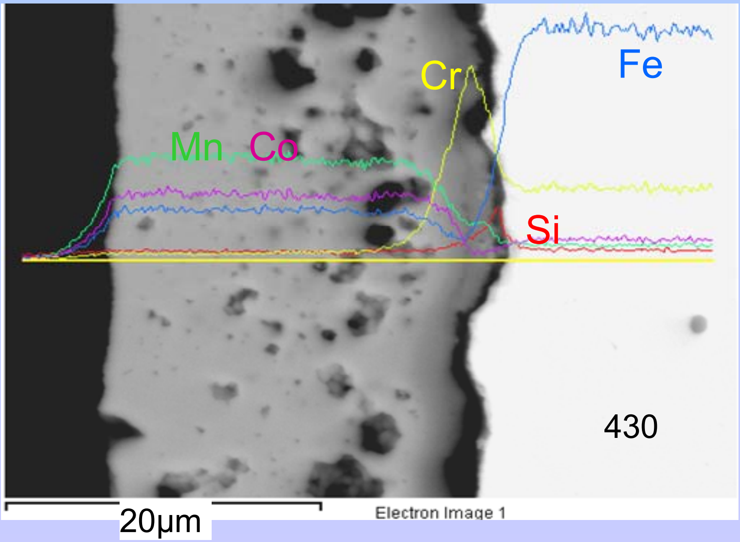
1,200 hrs, air, 800°C

Long-Term Performance of MC Coated430

- The formation of a continuous insulating SiO_2 layer at the scale/metal interface led to a high ASR.
- The ASR became unstable after about 4,000 hours, likely due to detachment of scale from the metal substrate.



MC protection layer||scale||Fe-Cr



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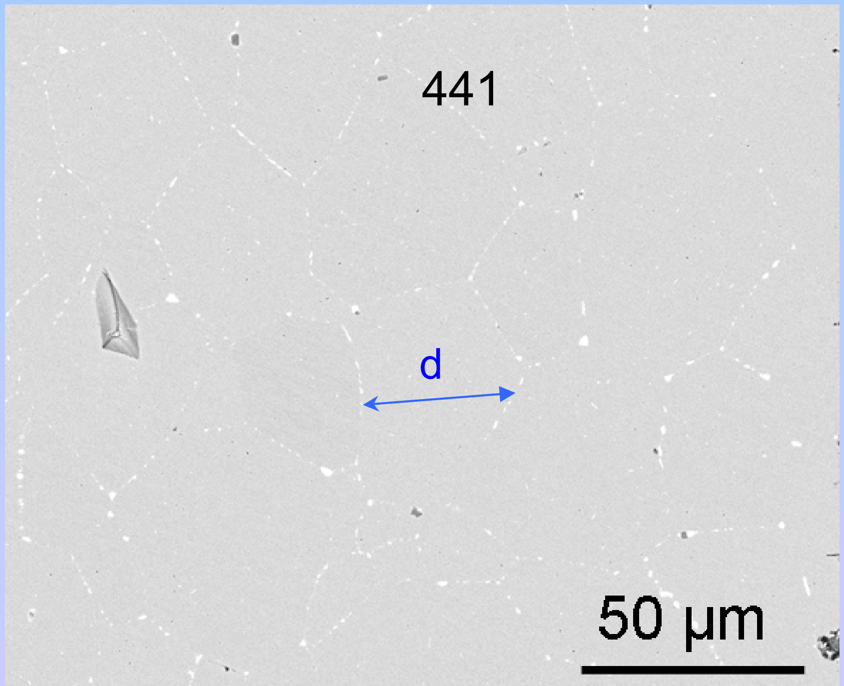
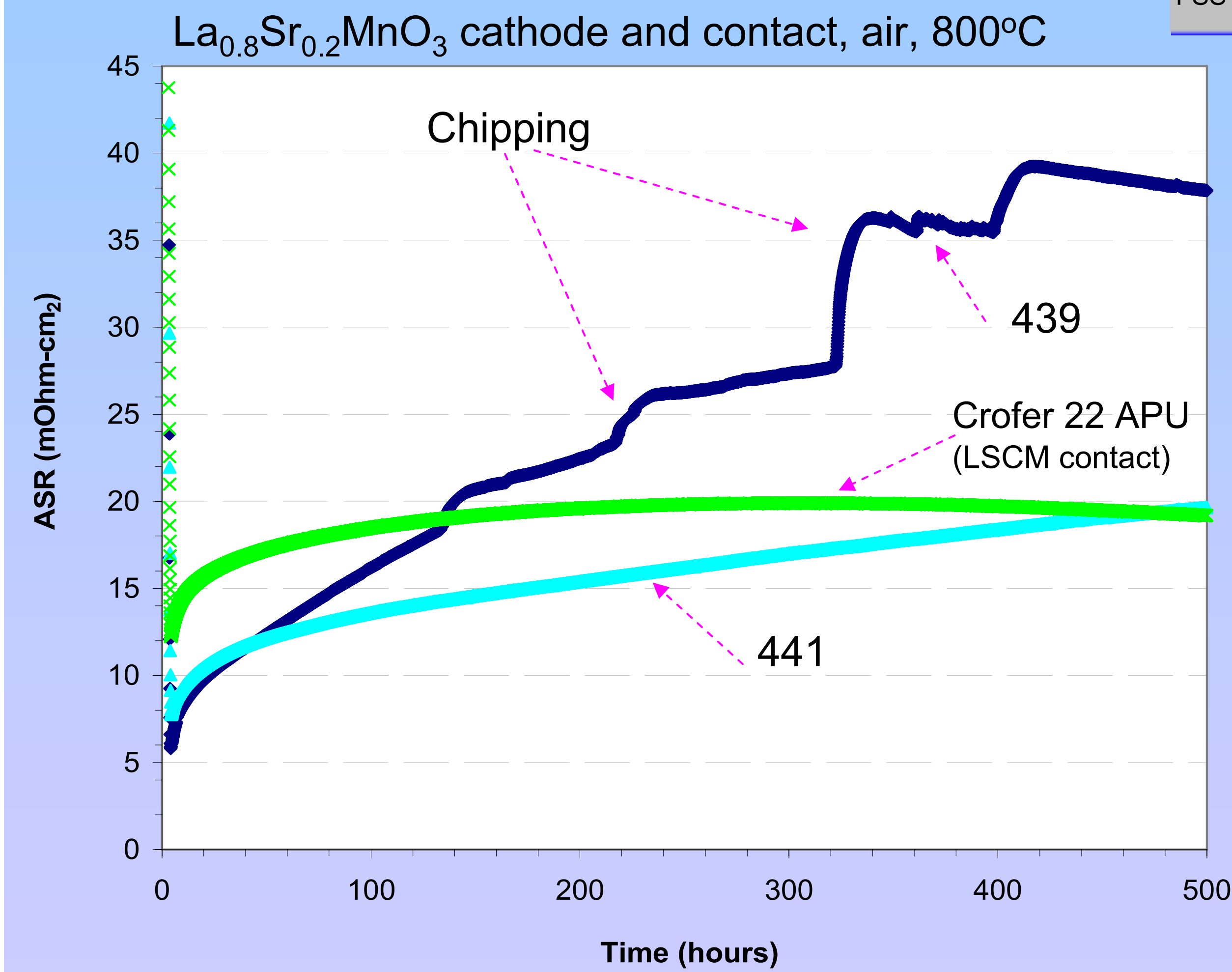
Metallurgy of 441 and 439

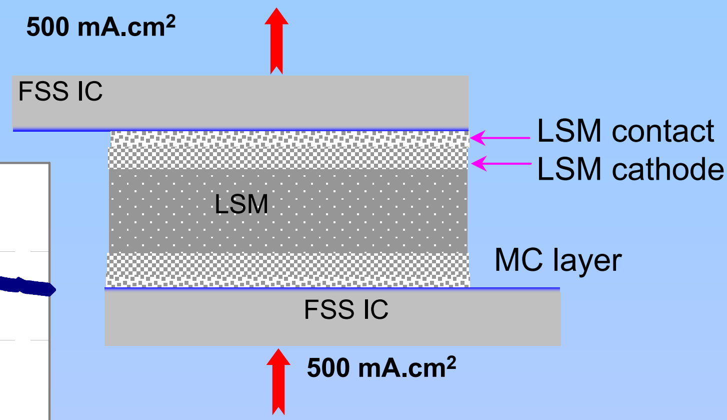
Designation	Cr	Mn	Ni	C	Al	Si	P	S	Ti	Nb	Re
T-441	17.8	0.33	0.20	0.010	0.045	0.47	0.024	0.001	0.18	0.46	
439 HP	17.5	0.44	0.20	0.012	0.040	0.73	0.016	0.0004	0.41		
AL 430	17.0	≤1.0	≤0.75	≤0.12		≤1.0					
Crofer 22 APU	23.0	0.4-0.8		0.030	≤0.50	≤.50	0.020	0.050	≤0.2		0.04-0.20

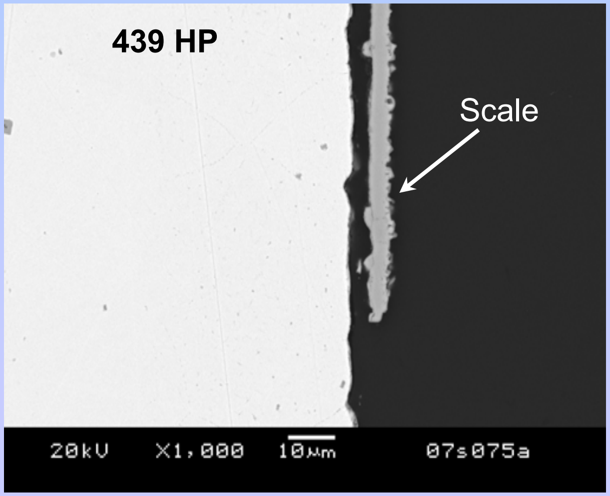
- Fractional % of Ti and Ti/Nb were added into Fe-17%Cr substrate for 439 and 441, respectively
- Nb leads to laves phase (Fe_2Nb) precipitation along grain boundaries that significantly improves high temperature strength and creep resistance of the Fe-Cr substrate (double yield strength at 800ºC)
- As strong carbide/nitride formation elements, Ti and Nd lower interstitial elements C and N in the substrate
- Can Nb (or Ti) tie up Si to prevent SiO_2 layer?



Electrical Evaluation of 441 and 439

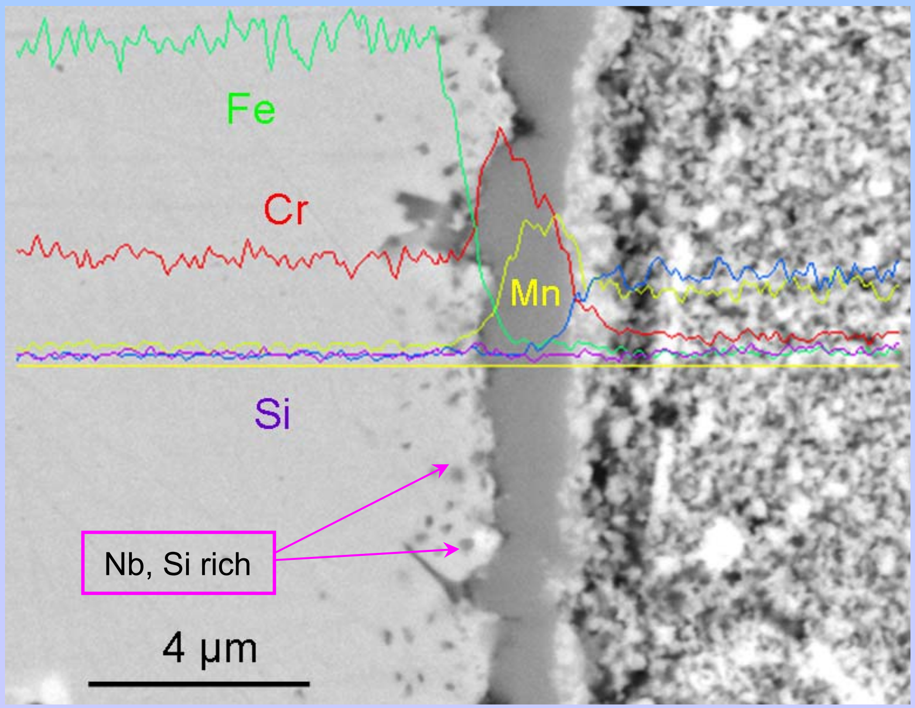


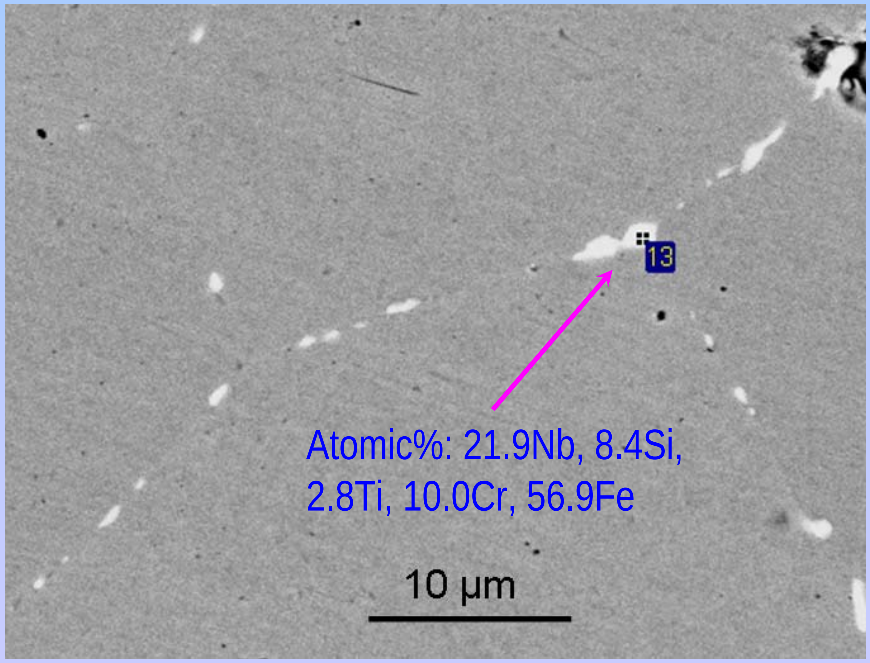




Effects of Minor Alloying Elements in 441

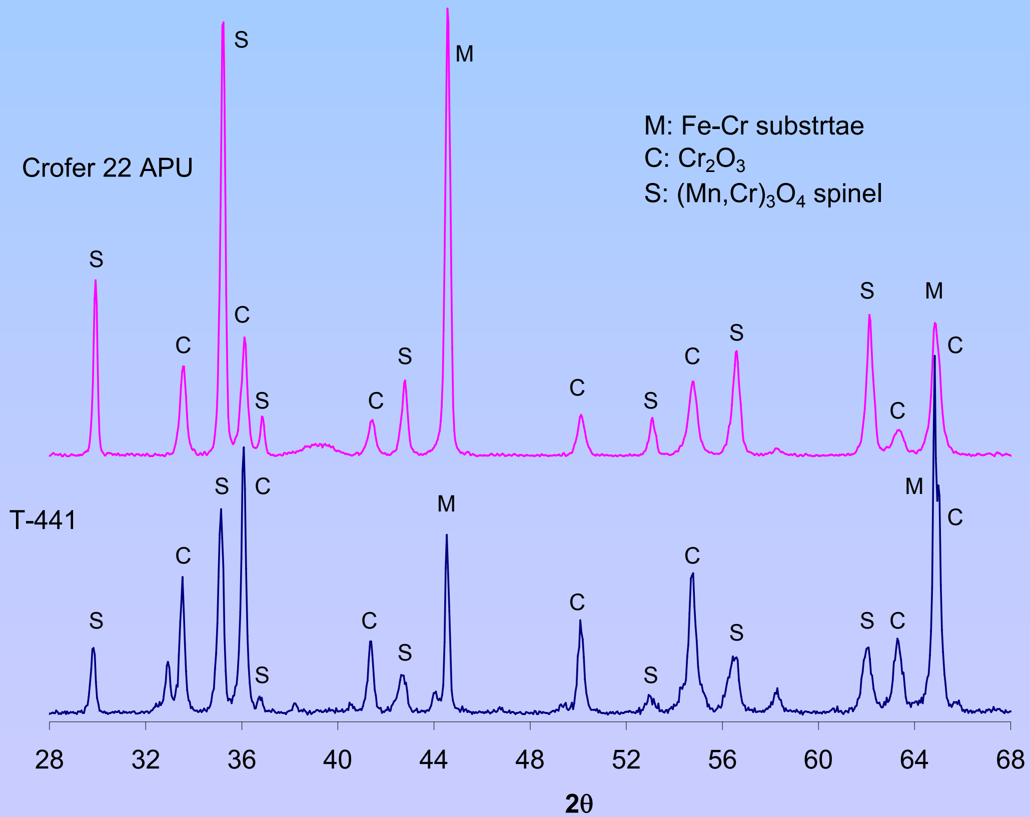
- There was Si buildup or silica layer formation between scale/metal interface, in spite of about 0.5% residual Si in the metal substrate
- Nb tied up Si, preventing formation SiO_2 layer at the scale/metal interface



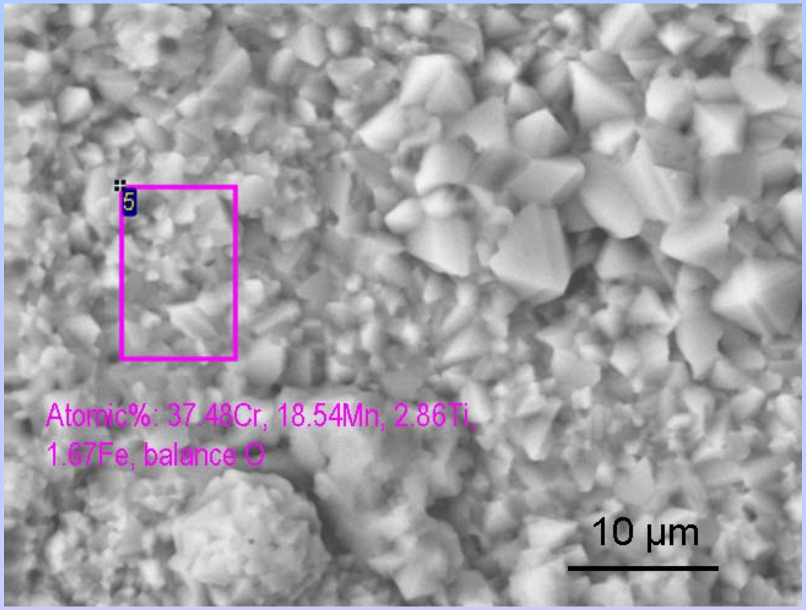


Scale Structure and Compositions of 441

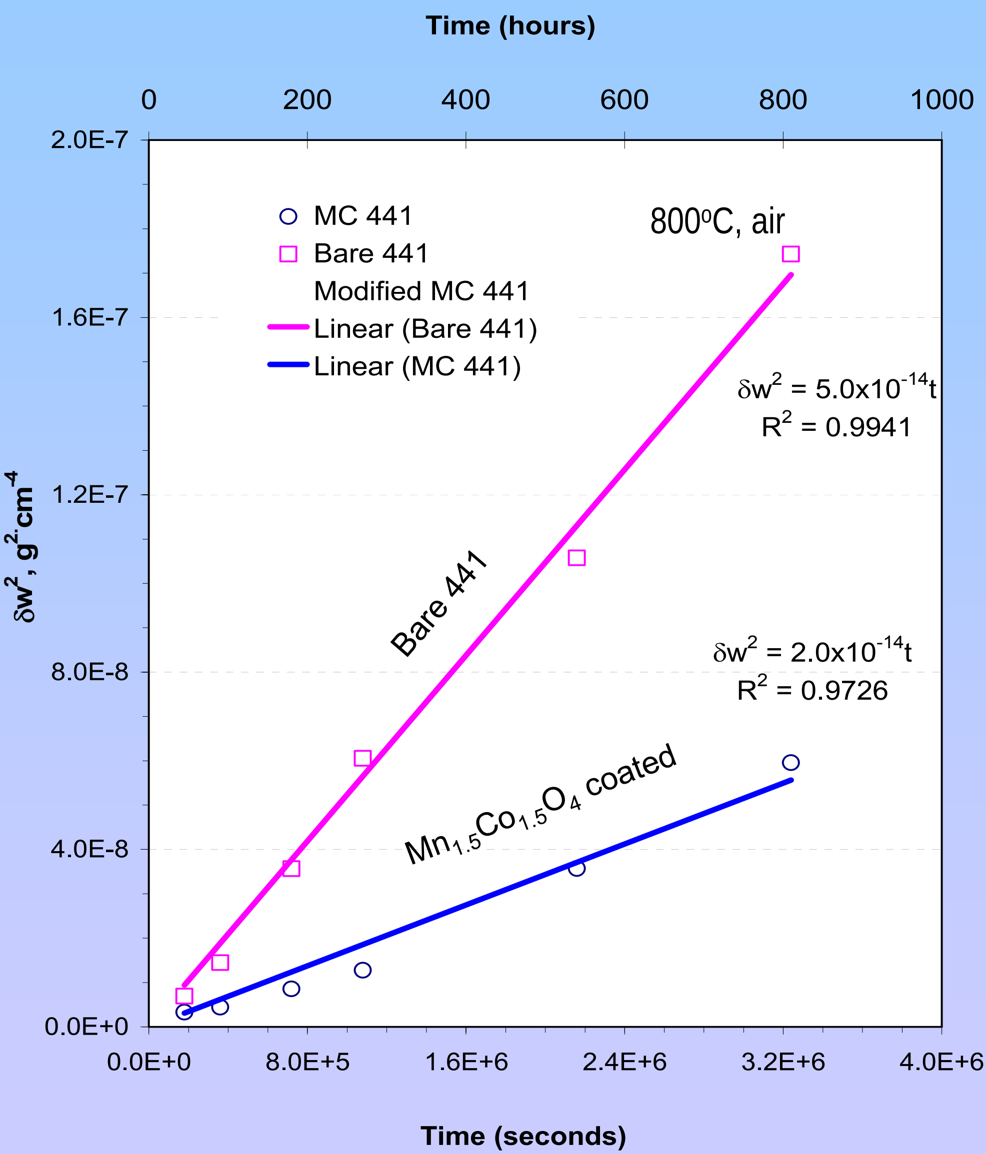
- Scale grown on 441 is mainly comprised of $(Mn,Cr)_3O_4$ and Cr_2O_3, similar to that of Crofer 22 APU
- Negligible Fe or iron oxides in the scale, different from that of 430



300 hours, 800°C, air



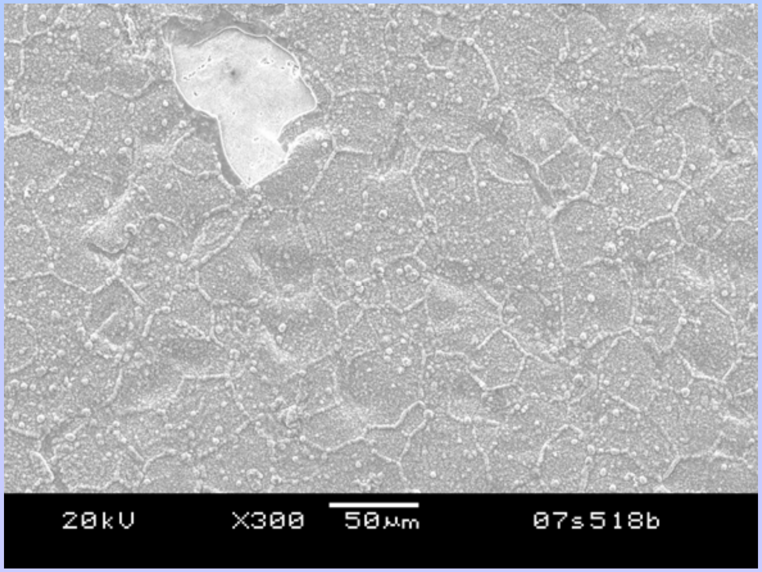
Kinetics of Scale Growth on 441



- Scale growth rate comparable to Crofer 22 APU, but with inferior scale adherence

  (Local spallation found occasionally after extensive oxidation)

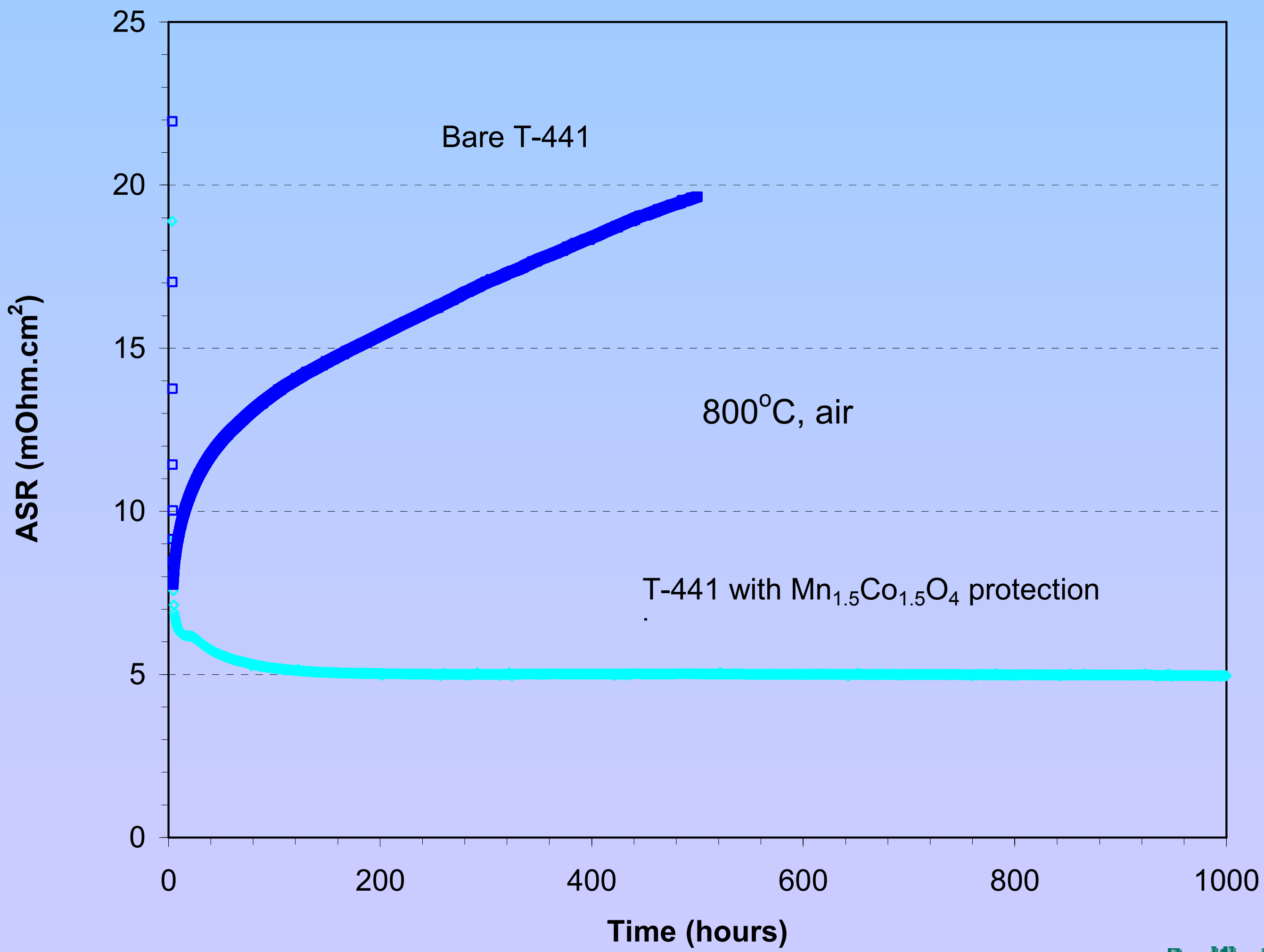
- 2~3 times lower for MC coated specimens; no spallation



After 900 hours

Electrical Performance of Surface-Modified 441

- $Mn_{1.5}Co_{1.5}O_4$ spinel protection layers minimized area specific electrical resistance (ASR)
- ASR of coated sample increased little, if any, over the course of the test



Cathode: LSM

Contact: LSM

IC: bare 441 or

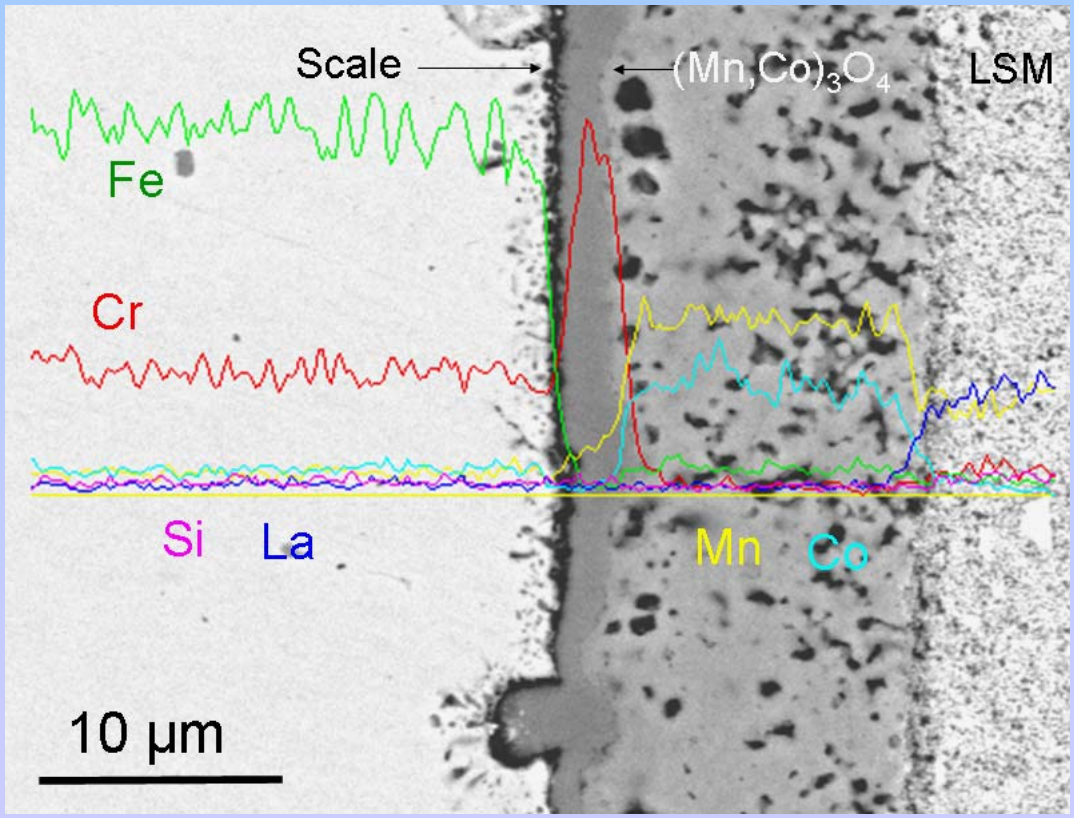
MC coated 441

Current: 500 mA.cm^{-2}

SEM Cross-Sections of ASR Samples

- Improved surface stability: no spallation or detachment observed
- No penetration of Cr through the protection layer, though there appeared Fe migration into the coating (similar to 430).

MC coated 441



BS image

Summary

- 441 exhibited promising alloy chemistry: addition of a small amount of Nb helps avoid formation of a continuous silica layer and promote desirable second phase precipitation, thus leading to a lower scale resistance and higher mechanical strength.
- The alloying approach eliminates the costly refining process that is currently employed for making Crofer 22 APU and other super-grade ferritic stainless steels for IC applications .
- Protection layers are required to further improve alloy surface stability and electrical performance, and seal off Cr.

Future Work

- Evaluate long-term thermal stability and electrical performance of bare and surface modified 441
- Further understand the alloy chemistry via advanced diagnostic study
- Investigate and optimize bulk alloy chemistry and surface modification for satisfactory long-term stability and performance. (In collaboration with Allegheny Ludlum Corp.)

Protection Layer Development and Investigation

- **Goal**: develop cost-effective, optimized protection layers that are effective barriers to both oxygen inward and chromium outward diffusion, while being stable over lifetime of SOFC operation.

Previous work:

- Developed spinel protection layers with a nominal composition $Mn_{1.5}Co_{1.5}O_4$
- Systematically studied $(Mn,Co)_3O_4$ spinel materials
- Developed slurry-based approaches for fabrication of the spinel protection layers
- Evaluated kinetics of scale growth, stability under thermal cycling, electrical and electrochemical performance, chromia volatility, etc., of coated Crofer 22 APU
- Completed one year thermal stability evaluation of coated Crofer 22 APU

Recent Accomplishments:

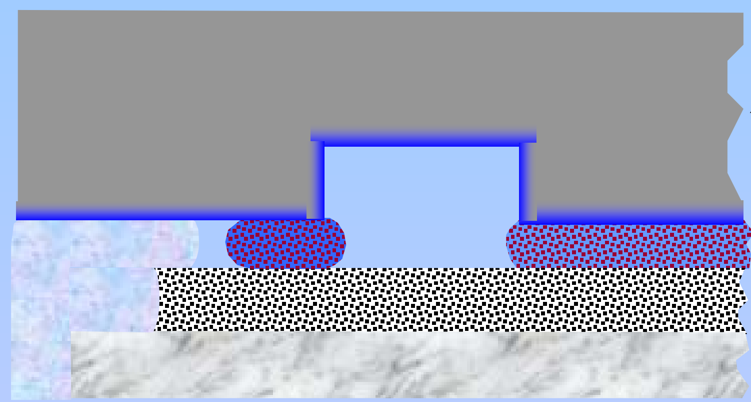
- Completed half year electrical evaluation of MC coated Crofer 22 APU and 430 (with LSM cathode & contact paste)
- Investigated suitability and performance of the spinel protection layers on 430 and 441 (see previous slides)
- Started developing alternative fabrication approaches, e.g. electrochemical deposition

Summary and Future Work

- Spinel protection layers with a nominal composition $Mn_{1.5}Co_{1.5}O_4$ and fabricated with slurry coating approaches are an effective oxygen inward and chromium outward diffusion barrier, mitigating scale growth and sealing off chromium
- Interconnect FSS, e.g. Crofer 22 APU, with the spinel protection layers demonstrated excellent long-term stability and electrical performance
- Developing cost-effective approaches compatible with mass production and practical shapes of interconnect
  - Electroplating, electrophoresis, etc., in addition to spray process.

Contact Layer Investigation and Development

♦ **Goal**: develop cost-effective, optimized contact layers between metallic interconnects and electrodes.



Functions

❍ Promote electrical contact

❍ Facilitate stack assembling

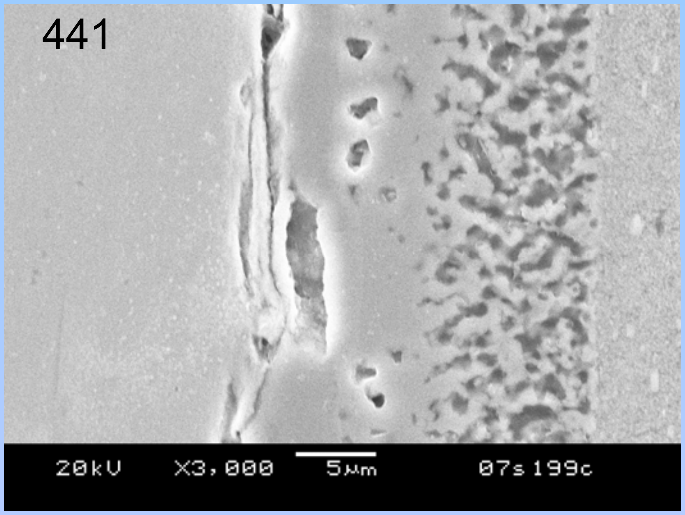
❍ Act as a potential buffer zone to prevent unwanted reactions and transport, such as Cr volatility

Challenges

❍ A metallurgical bond can be built between a metallic interconnect and Ni-YSZ anode, providing a low resistance path for electrons.

❍ Oxide-metal interfaces are present between metallic interconnects and cathodes, increasing electrical resistance and thus causing power loss.

Previous Work and Current Strategy



Previous work and accomplishments:

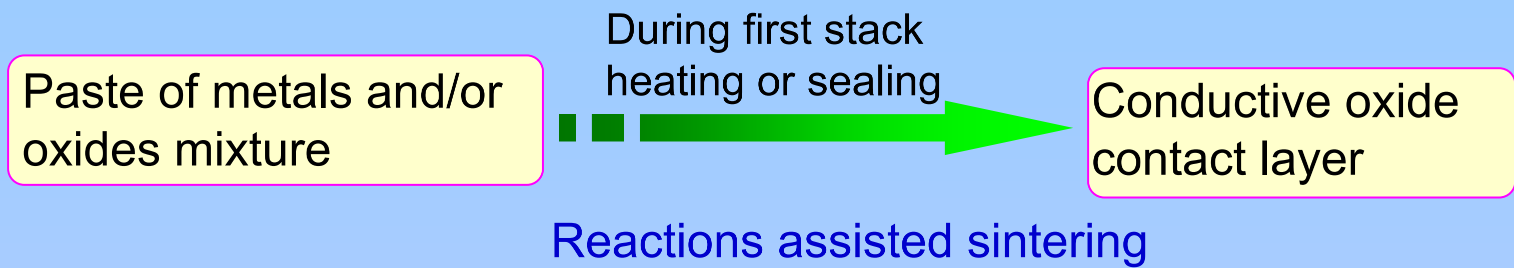
- Evaluated metals and varied conductive oxides, including LSM, LSCo, LSCM, MC, etc.
- Investigated interfacial interactions
- Initiated enhanced sintering approaches for LSM and MC

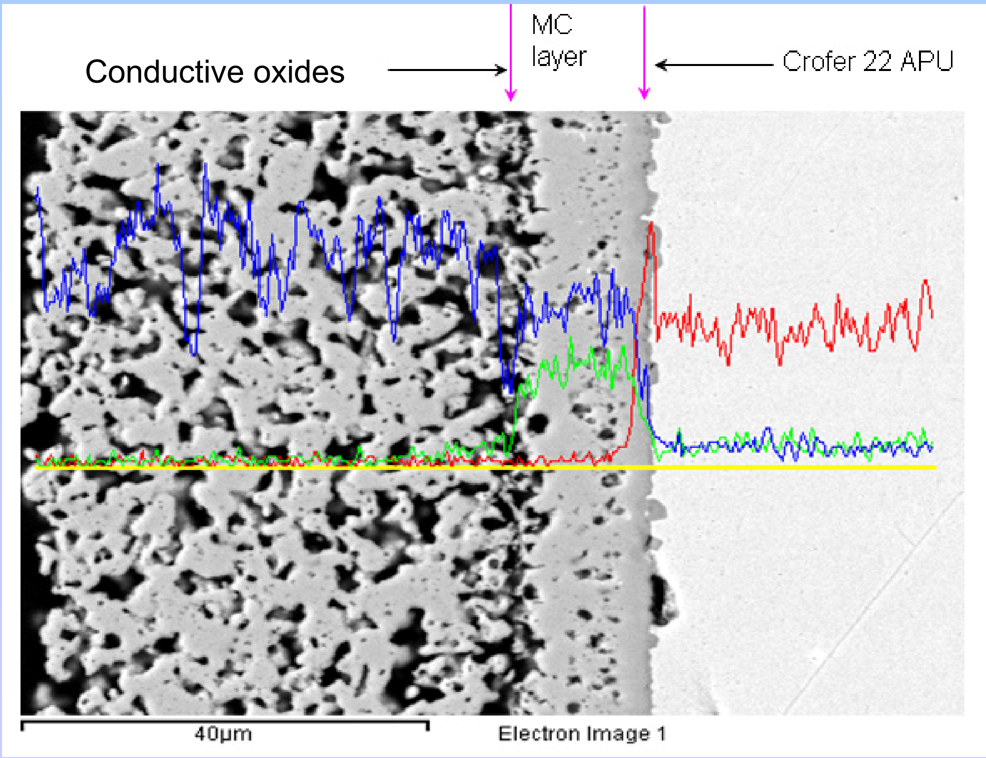
Challenges of current materials

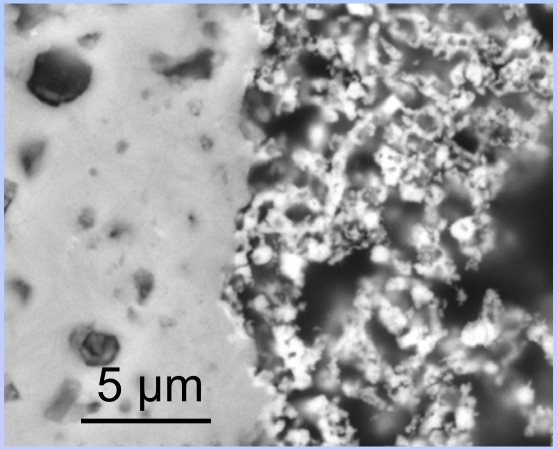
- Precious metals demonstrate suitable properties, but too expensive (Ag, a possible exception).
- Conductive oxides of high sintering activity, e.g. superconductors, usually too reactive, negatively affecting the stack and interface stability
- Conductive oxides, e.g. LSM, that are typically used as cathode compositions demonstrated good compatibility, but need improvement in sintering activity at 800-900^{o}C and thus better electrical contact

Approach: improve sintering activity via reaction sintering, addition of sintering agents or chemical modification

Fabrication of Contact Layers via Reaction Sintering





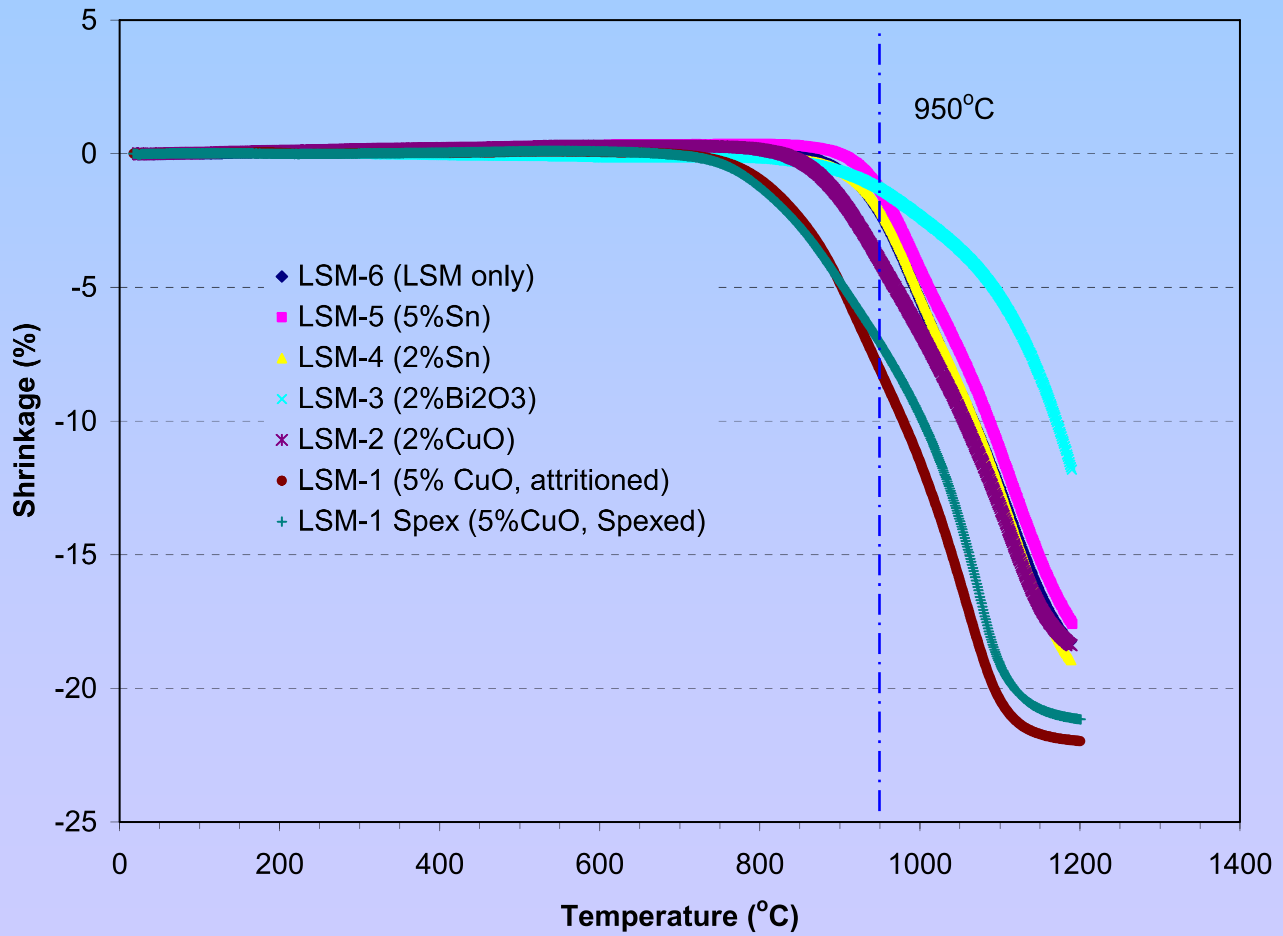


Without sintering

After reaction sintering

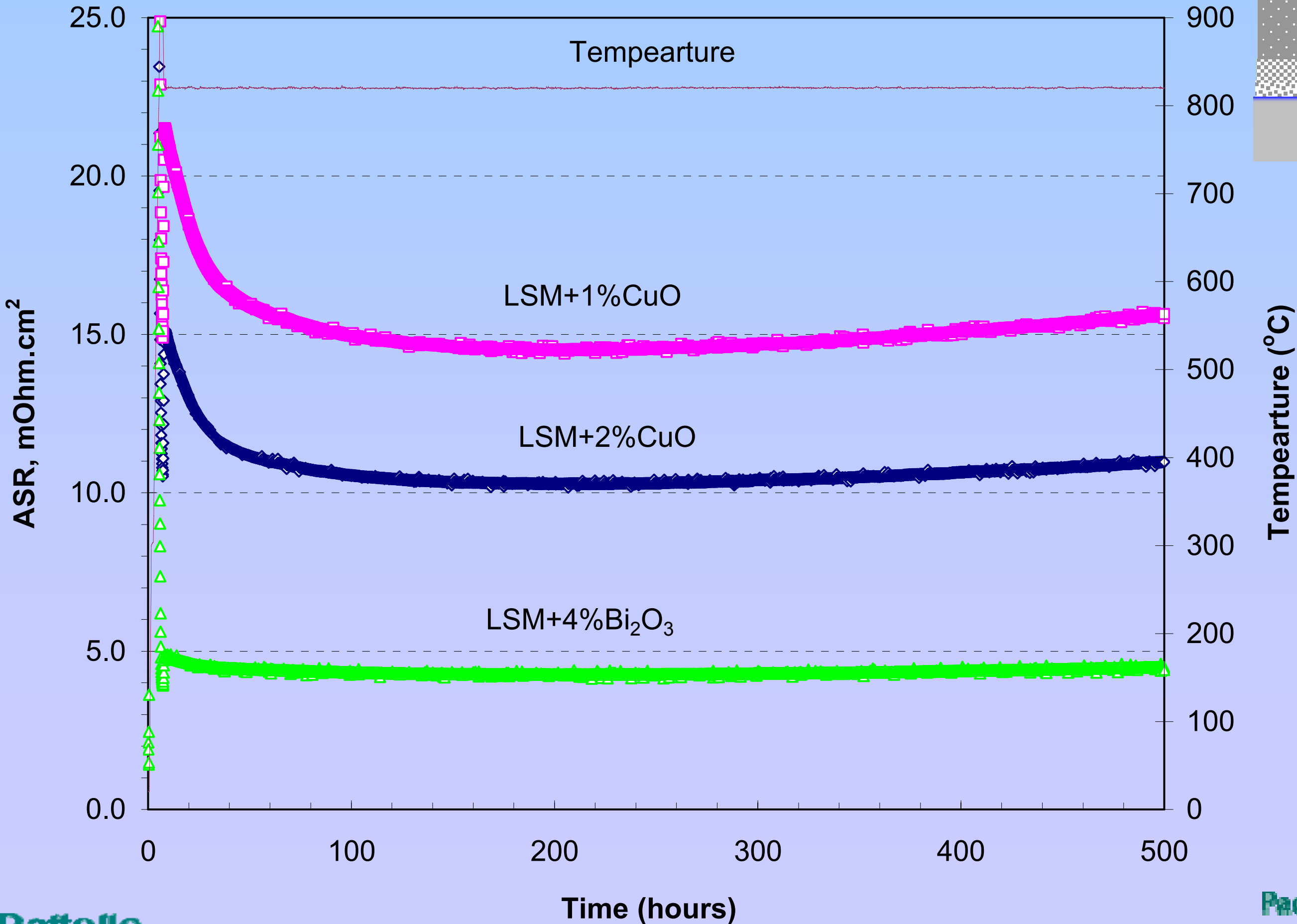
Contac Layers via Adding Sintering Agents

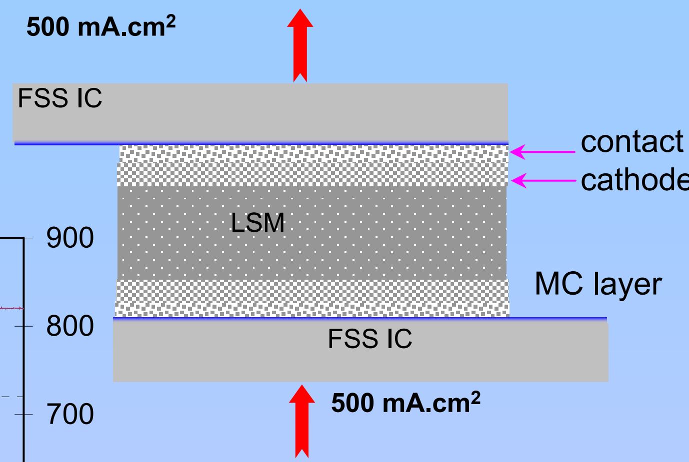
- Among studied, CuO and Bi_2O_3 more effective for LSM
- To be effective needs 4~5%



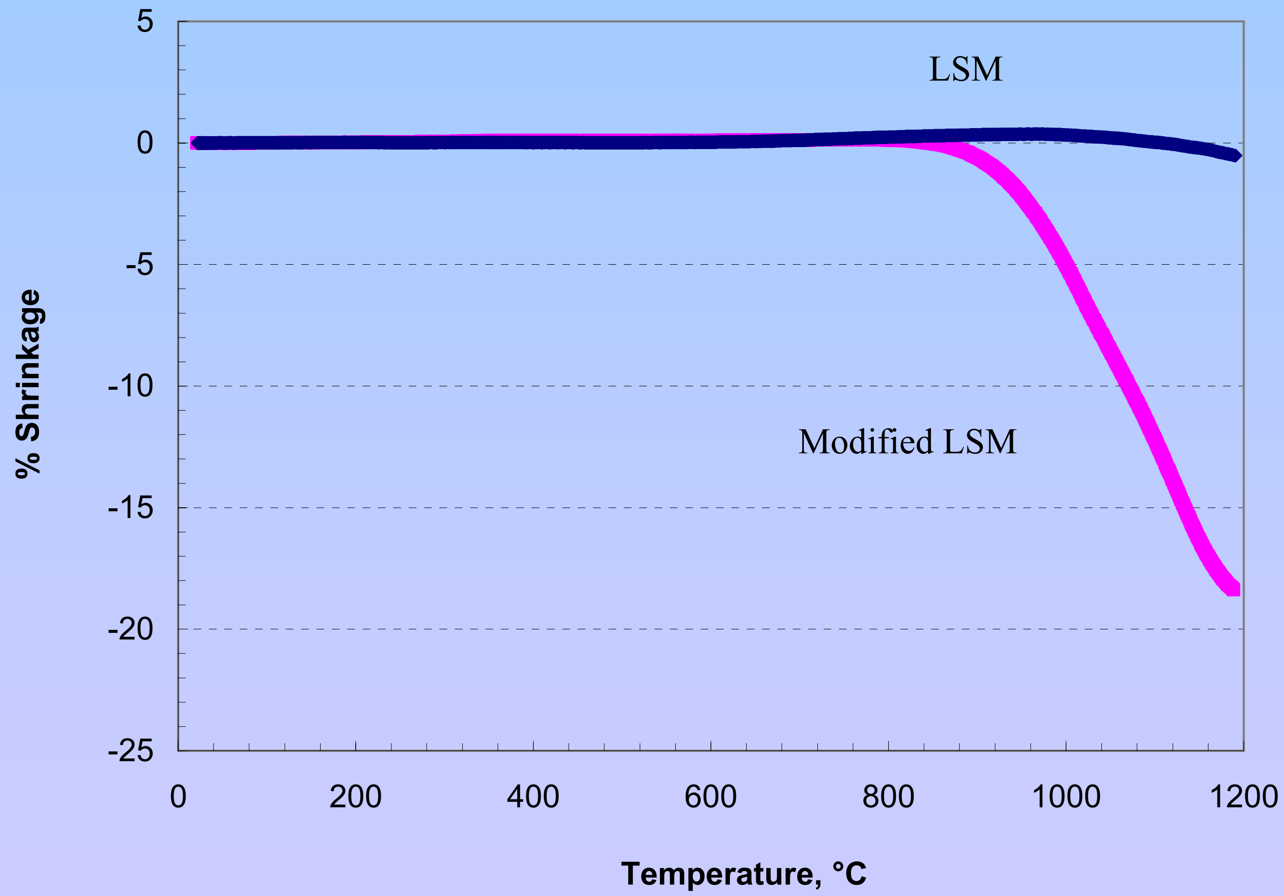
Electrical Performance and Stability Evaluation

Interfacial resistance evaluation unit (IRU)





Enhanced Sintering via Chemical Modifications



Summary

- Reaction sintering appears to be a promising approach to fabricate contact layers between perovskite cathodes and metallic interconnects.
- Addition of sintering aids and chemistry modifications also help improve sintering activity of conductive oxides.

Future work

- Continue to search and optimize contact materials and processing approaches
- Systematically evaluate candidate systems: dilatometry, IRU (ASR), SEM, XRD.
- Evaluate long term electrical performance and interface stability under isothermal and thermal cycling

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