Oxidation Behavior and In-Cell Performance of Developmental SOFC Interconnect Alloys

M.P. Brady, B.A. Pint, T.R. Armstrong,
Oak Ridge National Laboratory, Oak Ridge, TN

C.E. Milliken and E. D. Kreidler
Technology Management, Inc., Cleveland, OH

Z.G. Lu and J.H. Zhu
Tennessee Tech University, Cookeville, TN

Materials Issues for Distributed Energy Resources
2002 ASM Fall Meeting, Columbus, OH Oct. 7-10, 2002

Exploratory Effort

•Background- Key issues for metallic interconnects

•First Screening: Microalloyed Ni and ferritic alloy
- Oxidation
- Electrical Resistivity
- In-Cell Performance

•Results on oxidation (volatility) and electrical resistivity studies for 2nd series of ferritic alloys

•Concluding remarks

Metallic Interconnects in SOFC Fuel Cells

Key Interconnect Functions are to Electrically Connect Series of Cells into Stacks and to Separate Fuel/Oxidant

- Environment: 700-850°C, Oxidizing/Reducing, Thermal expansion compatibility with ceramic cell components is important in some designs

- Benchmark: Coated Cr-5Fe-1Y_2O_3 or Doped Perovskite Ceramic ($, Brittle)

Advantages of Planar Metallic Interconnects

•Potentially Significantly Lower Cost Than Ceramics

-Raw Materials and Processing/Machining

•Mechanical Integrity-Thinner Plates than Ceramics

•Dense (Important for Fuel/Oxidant Separation)

•Potential for Better Performance Due to High Electrical Conductivity

Major Issue for Metallic Interconnects is Maintenance of Electrical Conductivity

- Metals Oxidize in Fuel Cell Environments

- Oxidation Products Usually Electrically Resistive, Can Contaminate/Degrade Other Cell Components

- Manage Surface Chemistry via Alloy Design and Processing to Maintain Sufficient Electrical Conductivity

No Clear Choice for Metallic Interconnects

Oxide	Max Theoretical Scaling Limit	*Bulk Resistivity (ohm-cm)	*Source
SiO_2	1750℃	$7 X 10^6$ 600℃	44^{th} CRC
Al_2O_3	1450℃	$5 X 10^8$ 700℃	MSE CRC
Cr_2O_3	1100℃	$1 X 10^2$ 800℃	Holt+Kofstad
NiO	850℃	$5\text{-}7 X 10^0$ 900℃	Nowotny + Sorrell
CoO	700℃	$1 X 10^0$ 950℃	Nowotny +

- SiO_2, Al_2O_3 too insulating
- Cr_2O_3: high volatility-contaminates cell, borderline resistivity
- NiO,CoO: high CTE, sulfur, borderline scaling

Options are Limited

•No Uncoated, Non-Precious Metal Viable Above 850°C

•Ni/NiO has a Chance in Range of 700 to 850°C if Successfully Doped to Lower Scale Growth Rate

-No volatility issues
-Noble (won't oxidize) in fuel-side environment
-Fuel Sulfur Impurities May Lead to Low Melting Ni-S Compounds
-CTE mismatch requires use as coating (substrate interdiffusion)

•Literature Data Suggests Conventional Cr_2O_3-Formers Not Viable Above ~700-800°C (possibly lower). Will need to:

-Microalloy to reduce scale growth rate/increase scale conductivity
-Reduce volatility

No One Alloy May be Able to Meet Conductivity and CTE Requirements

•Optimize for Scale Growth Rate and Conductivity

-May require different alloy for anode/cathode environments

-May not be possible to co-optimize for CTE compatibility

•Eventual Implementation as Cladding or Coating on CTE Optimized Alloy Substrate

•Investigate **Microalloyed Ni** and **Microalloyed Ferritic**

Candidate Alloys

•Microalloyed Ni
- Hot-Pressed Ni-0.3Y_2O_3 Wt.%, Cast/Rolled Ni-0.15Y Wt.%
- Hot-Pressed Li-Doped Ni-0.3Y_2O_3 (0.07 wt.%, 0.6 at.% Li)
- Rationale:
  Y or Y_2O_3 to reduce NiO growth rate
  Li to reduce NiO growth rate, increase conductivity

•Microalloyed Ferritic (Based on Quadakkers et al.)
-Cast and Rolled Fe-25Cr-1Mn-0.5Ti-0.4La wt.%
-Rationale: reduced volatility, scale growth rate, and contact resistance reported with Mn, Ti, La additions

Screening Evaluation

- Air oxidation screening: 3, 1 week cycles at 850°C (500 h Total)

- Area specific resistance (ASR) measurements

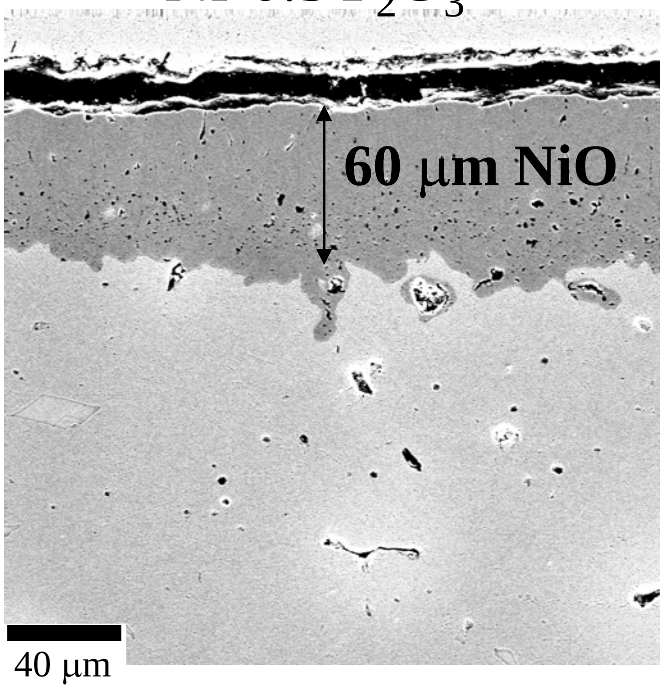
- In-cell stack test: 400-800 h at 850°C (isothermal)

Adherent NiO Formed at 850°C in Air

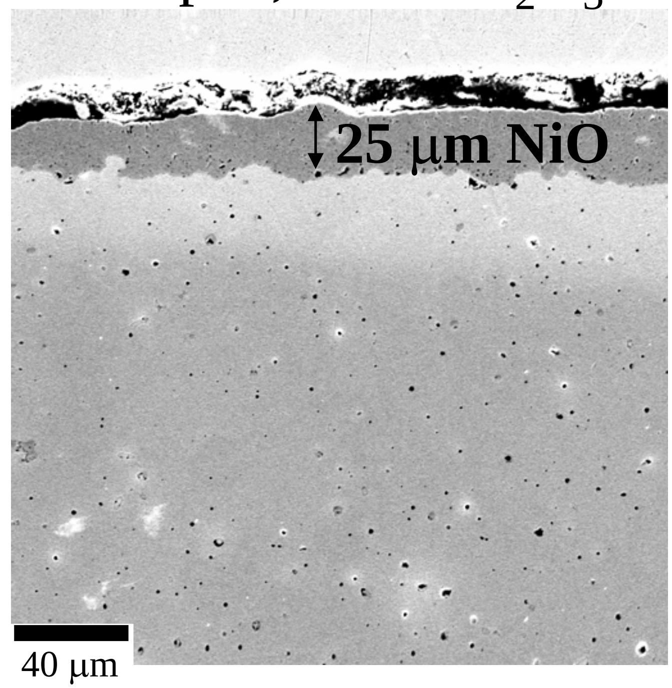
(similar behavior for 0.15Y and 0.3Y_2O_3 doping)

SEM Cross-sections after 3, 1 week cycles (500 h), 850°C, Air

Ni-0.3Y_2O_3



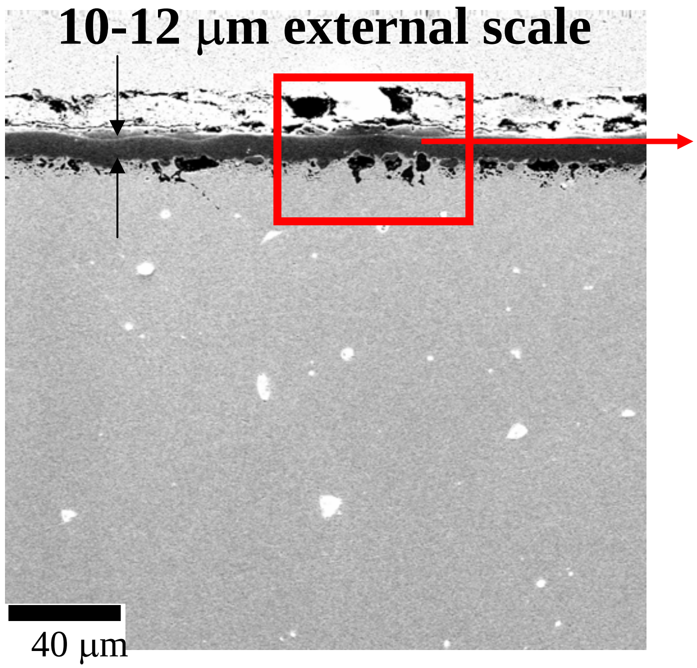
Li Doped, Ni-0.3Y_2O_3

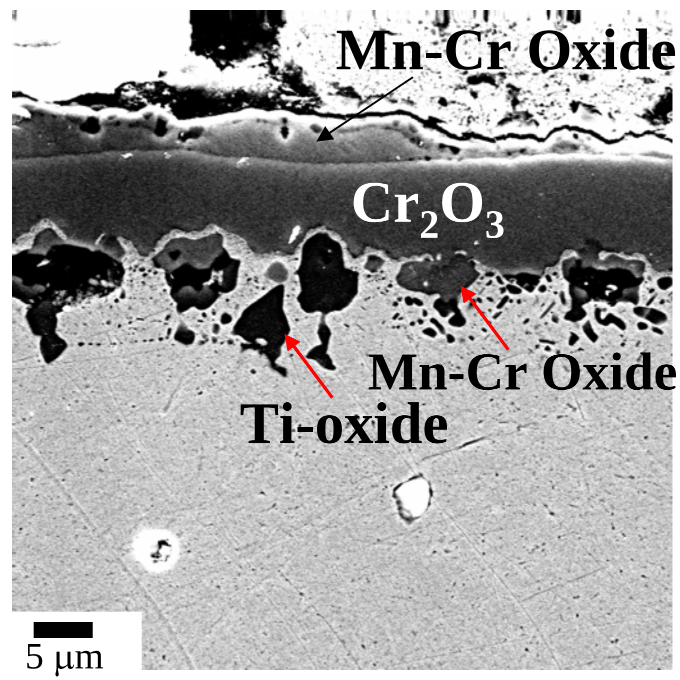


- Li slowed NiO growth beyond that achieved with Y_2O_3
- NiO growth at 850°C in range of estimated growth rate for potentially acceptable resistivity (based on bulk NiO)

Duplex Scale Formed on Fe-25Cr-1Mn-0.5Ti-0.4La at 850°C in Air

SEM Cross-section after 3, 1 week cycles (500 h), 850°C, Air

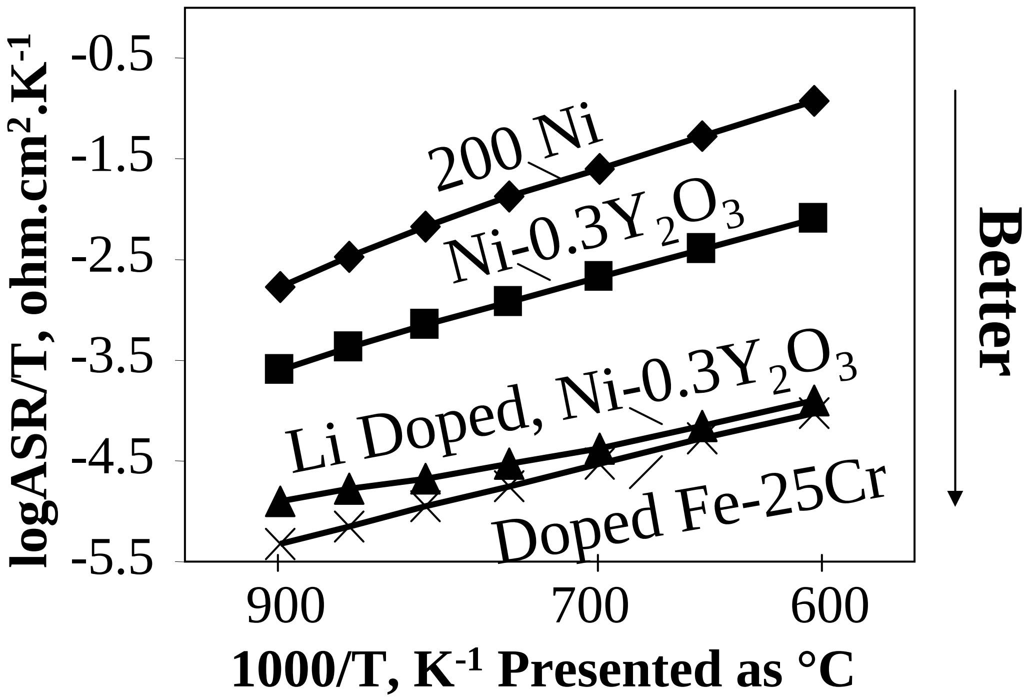




- Mn, Cr-based oxide (likely spinel) above continuous Cr_2O_3
- Internal oxidation suggests overdoping of Ti, possibly La (levels not optimized)

Li-Doped Ni-0.3Y_2O_3 Exhibits Similar ASR to Fe-25Cr-1Mn-0.5Ti-0.4La wt.%

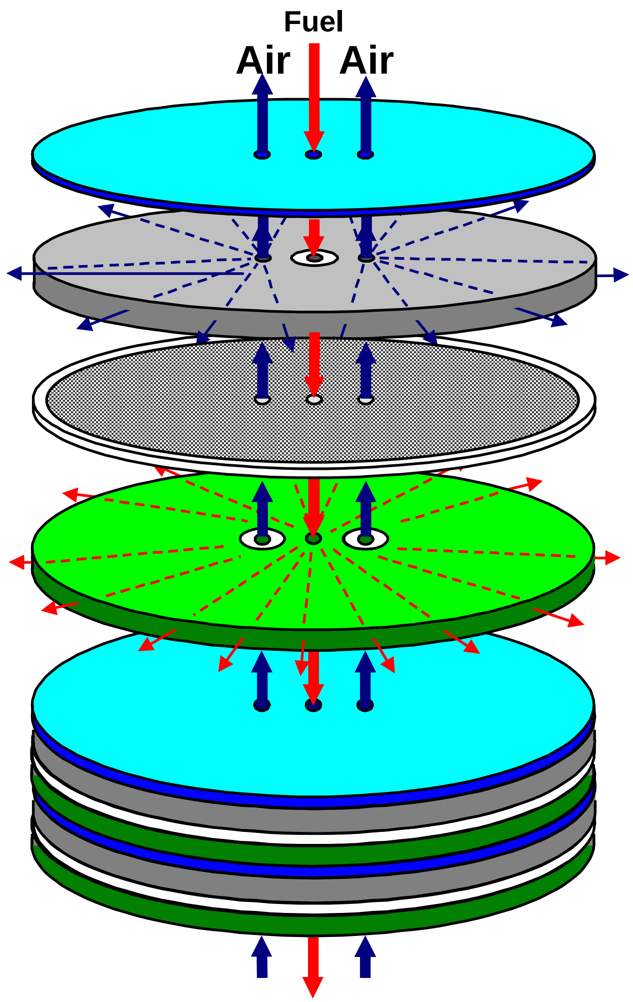
Arrhenius Plot of Area Specific Resistance vs. 1/T
3, 1 week cycles (500 h), 850°C, Air
(Pt Electrode, DC 4 point method)



•Cross-section analysis of scale thickness not yet performed

(ASR trends for Ni-alloys consistent w/oxidation mass change data)

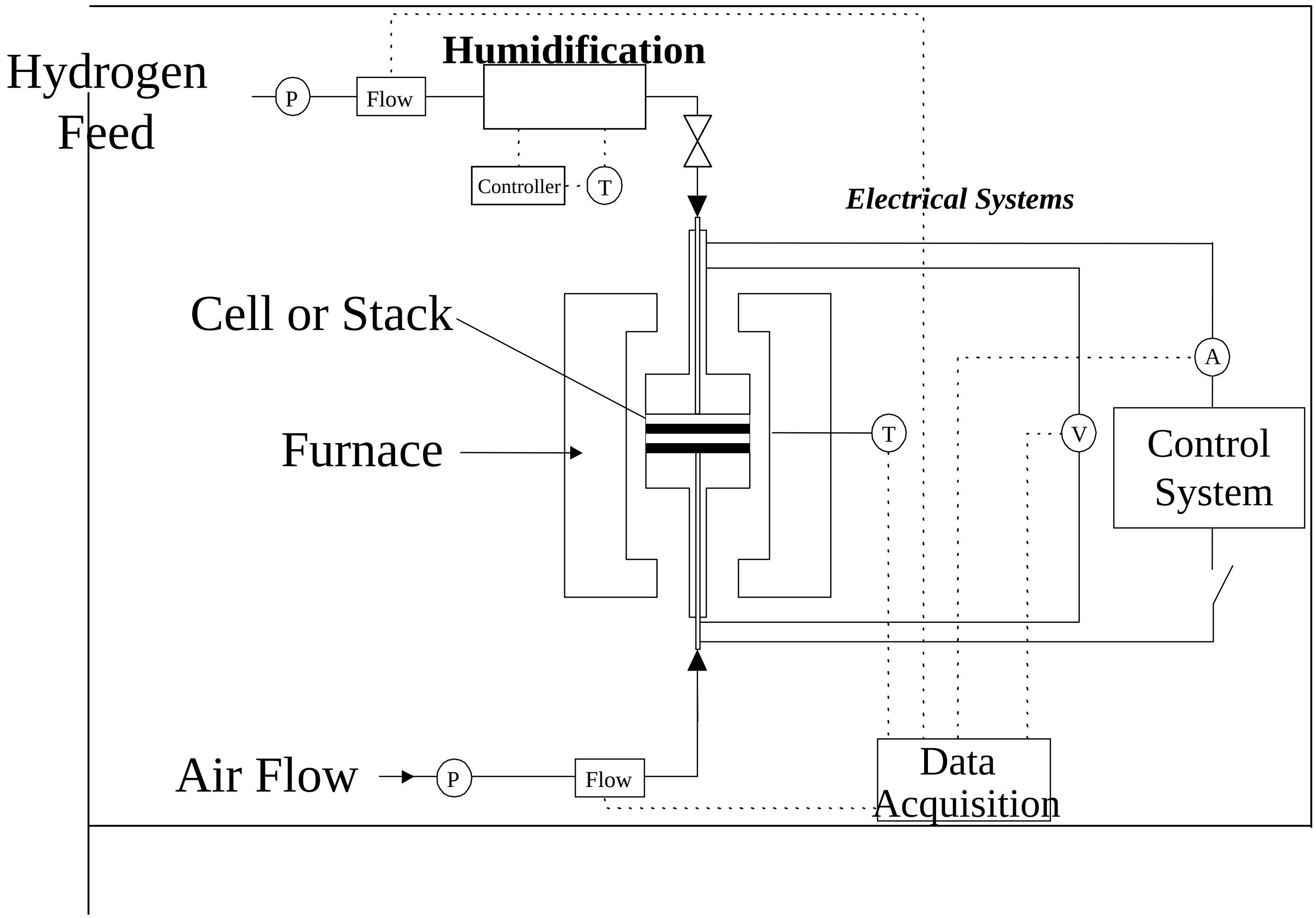
TMI's Radial Flow Cell



Component	Functional Requirement
Interconnect	**Metal Alloy** <subject of tests>
Cathode with Seal	$LaMnO_3$-type Perovskite
Electrolyte (w / Primary Electrodes)	Yttria-Stabilized Zirconia
Anode with Seals	Metal/Ceramic Composite
Repeating Stack	

- Cell Design Tolerates Some Metal CTE Mismatch-Ideal Test Bed for Candidate Interconnect Alloys

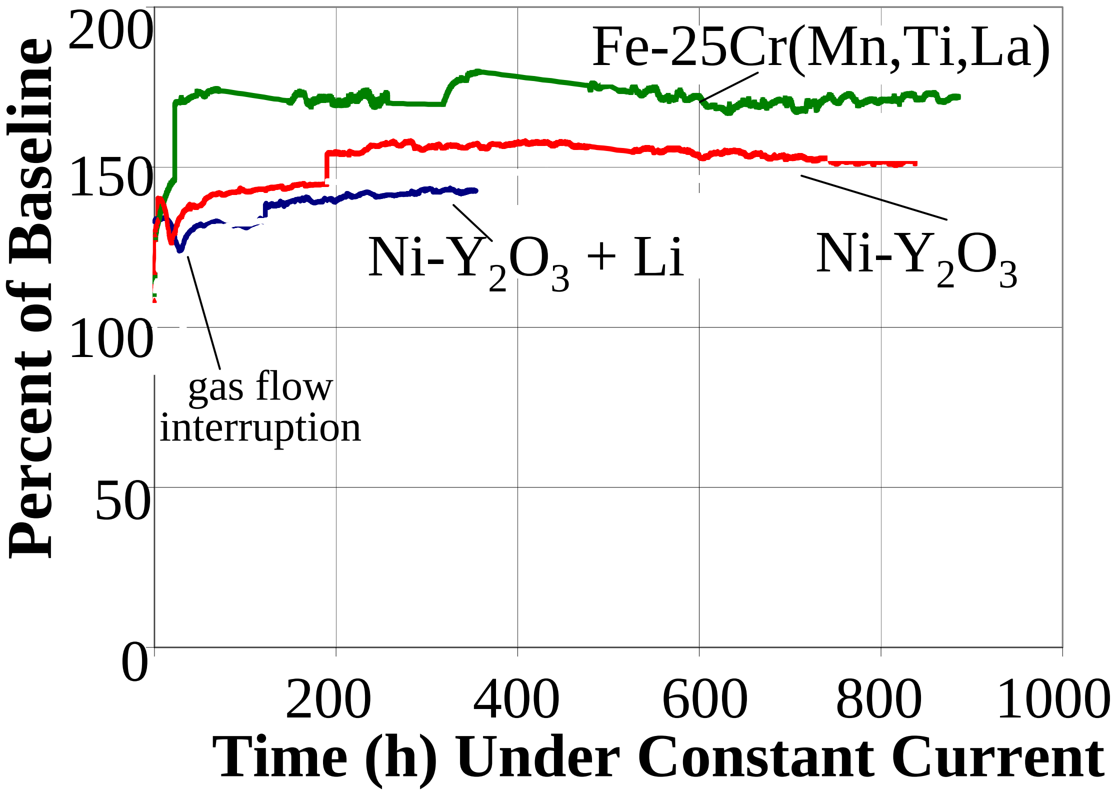
Cell Test Configuration



•2-5 Cell Stacks Tested at ~ 850°C Run with Humidified H_2

Moderate Performance Improvement Over Conventional Cr_2O_3-Forming Alloys

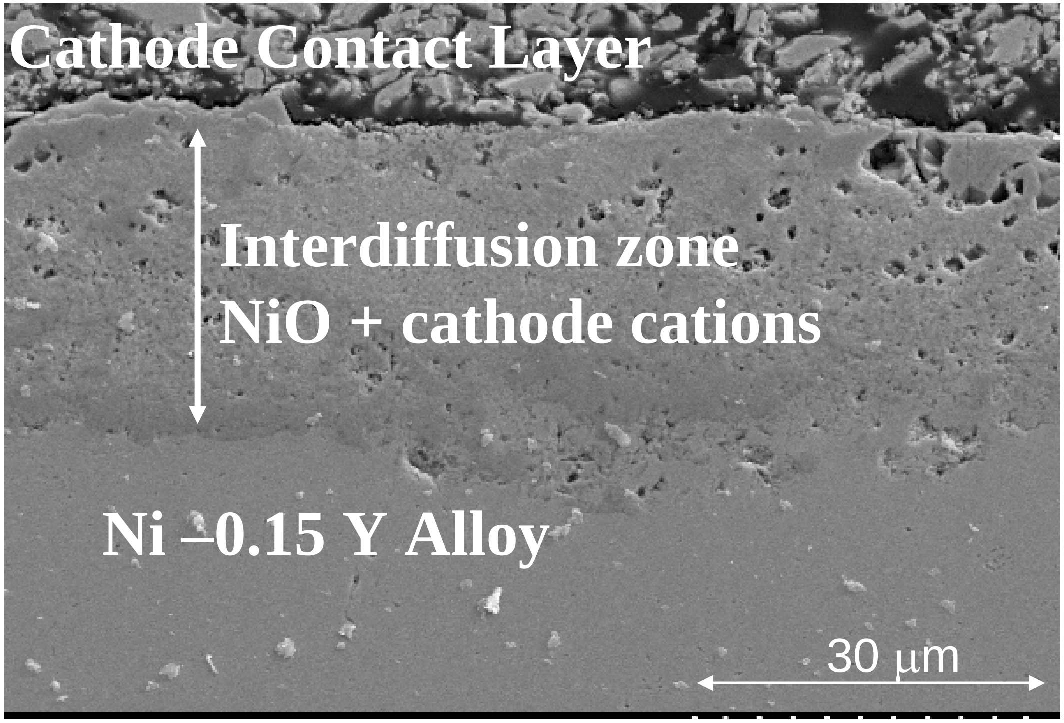
850°C In-Cell Performance Relative to 100% Baseline for Commercial Cr_2O_3-Forming Alloys



- •Ferritic 1.7X better than baseline, Ni 1.6X baseline
- •Li doping effect in Ni did not translate to better performance
- •Stack degradation rates 2-3X greater than long term target rates

Ni-0.15Y Alloy Reacted with Cathode
(similar behavior for Ni-0.3Y_2O_3)

SEM Cross-Section of Ni Interconnect/Cathode Interface
after ~ 600 h in-cell at 850°C



•No Ni alloy oxidation or reaction at anode contact layer

•Preliminary analysis of Fe25Cr(Mn,Ti,La) alloy revealed thin dense scale at anode and cathode-not yet analyzed

Alloy Optimization Will Require Detailed Oxidation and Electrical Resistivity Studies

Ferritic Baseline Composition of Fe-18Cr-9W wt.% Selected for Study

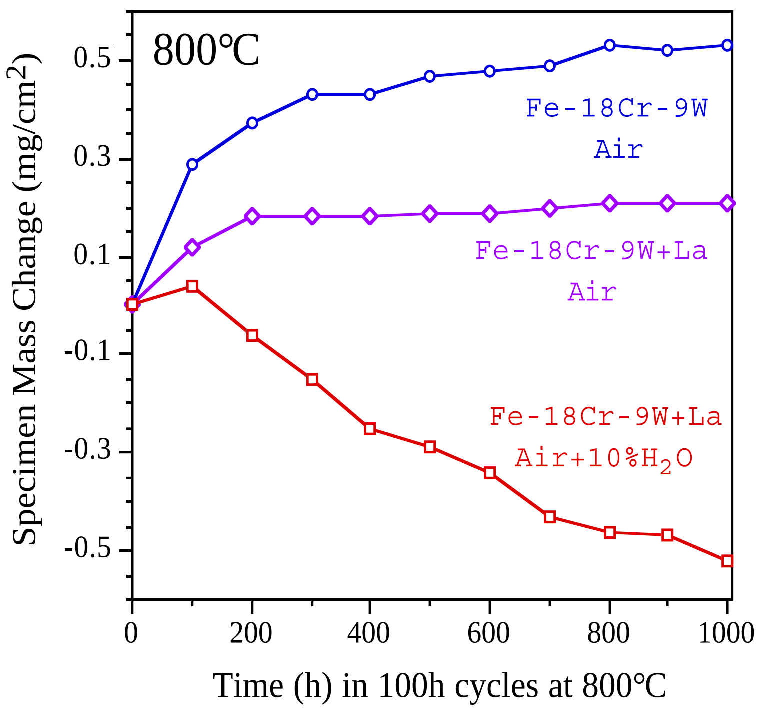
- Ueda and Taimatsu, 2000 baseline composition for lower CTE (improved thermal compatibility with zirconia)

- Controlled levels of La, Mn, Ti (Quadakkers et al, 2000)

- Oxidation/Volatility Assessment in 10% H_2O, 800-900°C, 1h or 100h cycles, 500-1000+ total h

- Post-Oxidation Area Specific Resistance (ASR) Measurements

Performance of microalloyed Fe-18Cr-9W
Laboratory oxidation testing at 800°C (1472°F)



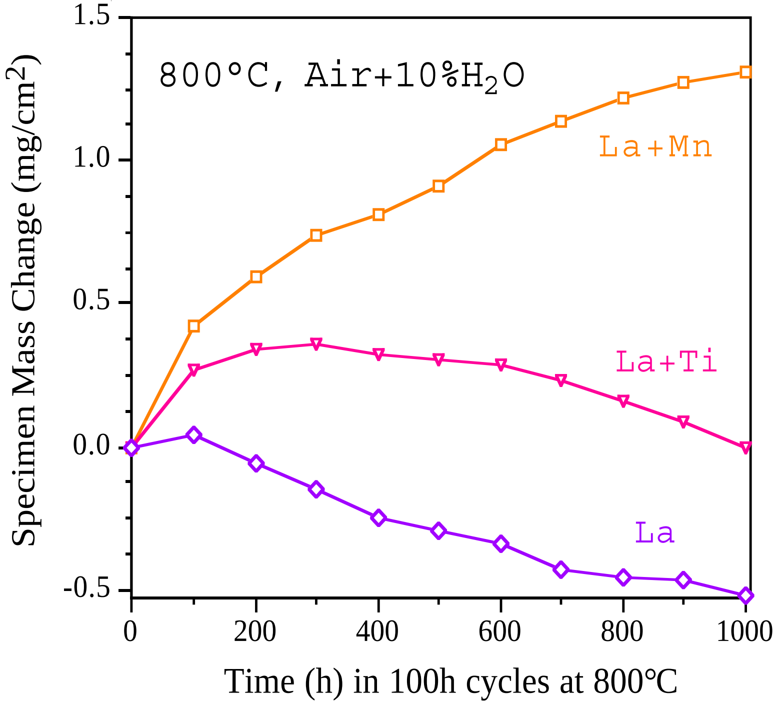
Base alloy - protective scale in air

La - reduces scale growth rate (lower mass gain)

Add H_2O - mass loss due to volatilization of $CrO_2(OH)_2$

This volatilization causes a contamination problem in fuel cells!

Performance of microalloyed Fe-18Cr-9W
Laboratory oxidation testing at 800°C (1472°F)

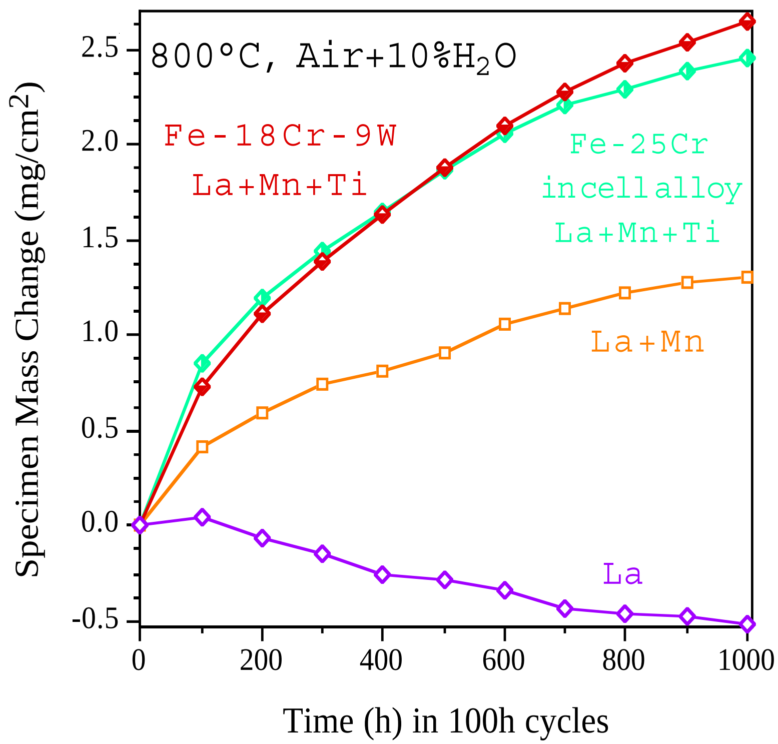


Try to minimize evaporation:

La+Ti - higher initial mass gain, but mass loss at later times

La+Mn - no mass loss detected, suggests reduction in volatility

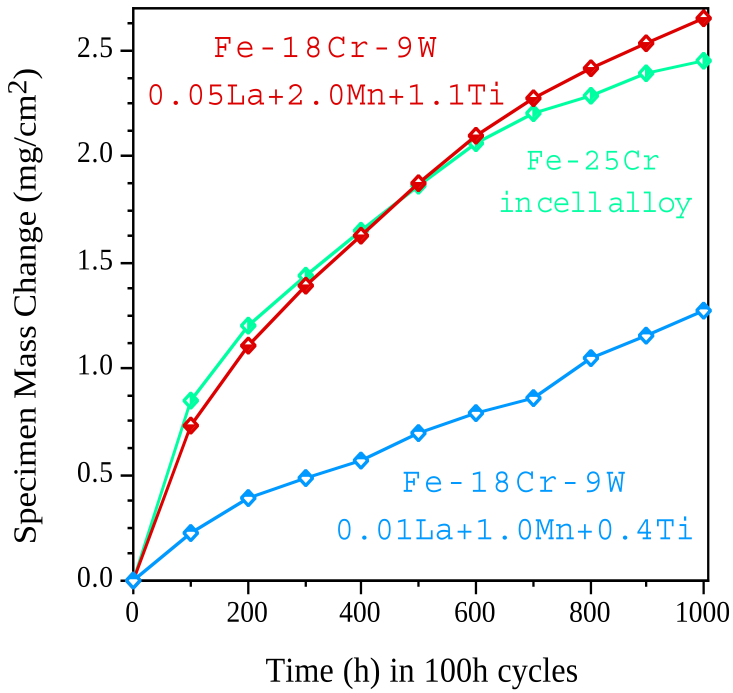
Optimization of microalloyed Fe-18Cr-9W
Laboratory oxidation testing at 800°C (1472°F)



Combination of La+Mn+Ti reported to have best performance

Adding more elements to alloy leads to higher mass gains due to internal oxidation of La, Mn and Ti

Optimization of microalloyed Fe-18Cr-9W
Laboratory oxidation testing at 800°C (1472°F)



First attempt at optimization:

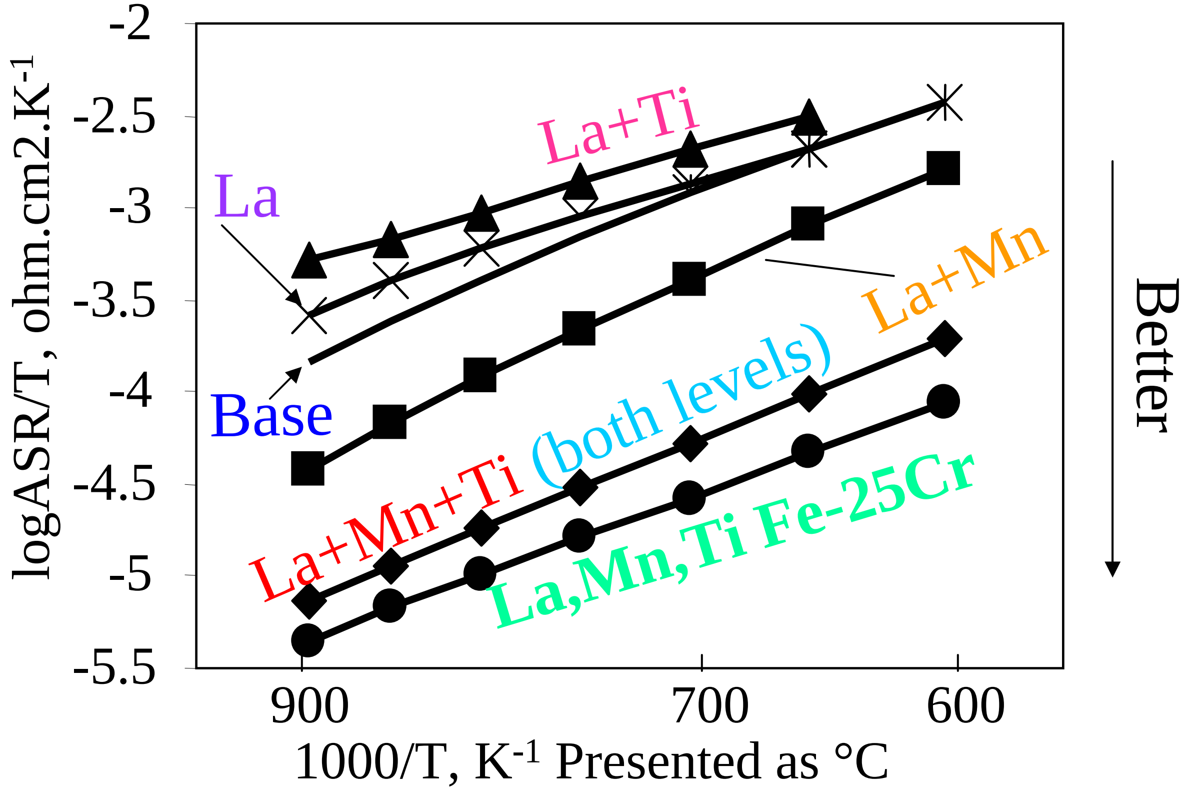
By dropping La, Mn and Ti (at.%):

- cut mass gain by 50% (in cell test: attack 2-3X high)
- further optimization possible!

However, can't rely only on mass change data alone...

Results Suggest Co-Doping of Mn and Ti Significantly Reduces Scale ASR

Arrhenius Plot of Area Specific Resistance vs. 1/T
Fe-18Cr-9W Base, 550 1h Cycles, 10% H_2O



- La,Mn,Ti synergistic trends consistent with Quadakkers et al.
- Need oxide thickness & chemistry to better assess results

Summary

Using commercial Cr_2O_3-forming interconnects as baseline :

•Microalloyed Ferritic Cr_2O_3 Former up to 80% Performance Improvement Over Baseline Alloy

- In-cell degradation rate too high (2-3X long term target)
- Series of Fe-Cr-W alloys indicated:
  - La: reduce Cr_2O_3 growth rate
  - La +Mn: reduce Cr_2O_3 evaporation (less cell contamination?)
  - La+Mn+Ti: synergistic decrease in ASR (Pt electrode)
- Further optimization of composition may be possible

•Microalloyed Ni/NiO up to 60% Performance Improvement Over Baseline Alloy

- Comparable ASR to doped ferritic (Pt electrode)
- Reactivity with cathode may limit performance
- Degradation rate also too high (2-3X long term target)
- Merits further investigation (possibility as cladding)