Effect of Ce Doping in $(Mn,Co)_3O_4$-Based Spinel Coatings on the Performance of SOFC Interconnect Alloys

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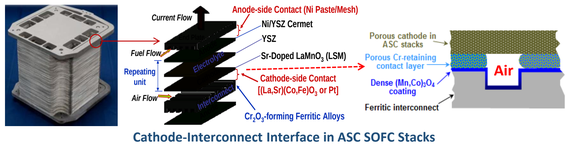
Introduction

- Environmentally-assisted reactive sintering (EARS) has been used to produce high-quality spinel coatings/contact layers using Mn-Co Alloy precursor powders.
- Further improvements are possible via Ce doping in the coating to reduce the chromia scale growth and increase the scale adhesion.
- Research performed to verify the effectiveness of the Ce-doped $(Mn,Co)_3O_4$ spinel coatings is divided into two major aspects:
  - Ce-doping in a spinel layer that acts as a contact (as well as a coating) simultaneously;
  - Ce-doping in a spinel layer that acts as a protective coating.

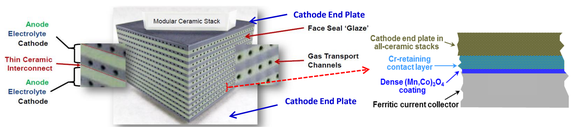
Need of Contact/Coating for SOFC Stacks

- In stacks with anode-supported cells (ASC-SOFC), Contact is required to minimize the cathode-interconnect interfacial resistance.



Cathode-Interconnect Interface in ASC SOFC Stacks

- In all-ceramic stacks, the contact is required to minimize the interfacial resistance between the current collector plate and cathode end plate.



Cathode-Current Collector Interface in All-Ceramic SOFC Stacks

- In both, the coating is used to reduce chromia scale growth and Cr evaporation.

How EARS Reduces Sintering Temperature for Spinels

- EARS is a method of producing a protective spinel layer from a metallic precursor powder by oxidizing it at a reduced temperature. (e.g. 900°C)

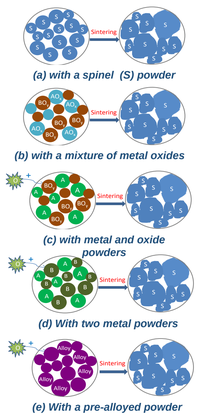
(b): $AO_x + 2BO_y + (2-\frac{1}{2}x-y)O_2(g) = AB_2O_4 + \Delta H_1$

(c): $A + 2BO_y + (2-y)O_2(g) = AB_2O_4 + \Delta H_2$

(d) & (e): $A + 2B + 2O_2(g) = AB_2O_4 + \Delta H_3$

$\Delta H_3 > \Delta H_2 >> \Delta H_1$

- Enhanced Sintering in EARS is due to:
  - Heat released during the oxidization reaction.
  - Volume expansion upon conversion from metal-to-metal oxide.
  - Formation of highly-active surface nano-oxides.
  - Shorter diffusion distance when a pre-alloyed powder is used. *Zhu et al., IJHE, 2018*



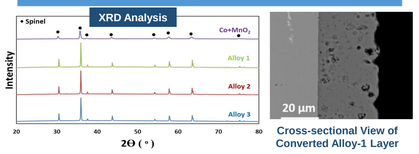
Gas Atomization and Ce Doping of Co-Mn Based Alloys

- The $(Mn,Co)_3O_4$ (MCO) spinel has been shown to have a good balance between cost-effectiveness and performance.
- The atomized Mn-Co powder precursor layers were successfully converted to a single-phase MCO spinel structure after 900°C for 2 h in air.

Gas Atomizer at TTU

Chemical Compositions of Some Co-Mn Alloy Powders (wt.%) & Corresponding Spinel Compositions

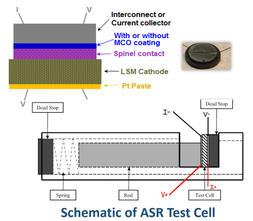
Alloy	Co	Mn	Fe	Ce	Spinel Composition
Alloy 1	68.21	31.79	—	—	$MnCo_2O_4$
Alloy 2	64.72	31.80	3.23	—	$MnCo_{1.9}Fe_{0.1}O_4$
Alloy 3	64.72	31.77	3.23	0.41	$MnCo_{1.895}Fe_{0.1}Ce_{0.005}O_4$



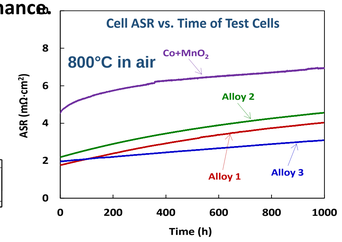
Cross-sectional View of Converted Alloy-1 Layer

Cell Area Specific Resistance (ASR) With Different Contact Layers

- Several test cells were constructed, with the contact precursor layer sandwiched between bare Crofer 22 APU and the LSM cathode.
- The cell ASRs with all the alloy-derived contacts were significantly lower than that with the mixed $Co+MnO_2$ derived contact.
- The cell with the Ce-doped alloy (Alloy-3) contact had the best overall ASR performance.



Schematic of ASR Test Cell

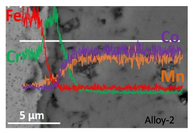


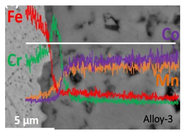
Cell ASR and Cross-Sectional View of Tested Cells

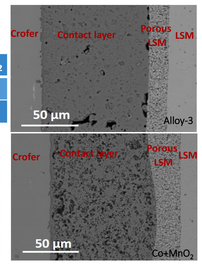
- The cell ASR with $Co+MnO_2$ derived contact had the highest final ASR (R_f) as well as the highest final ASR degradation rate (DR_f), likely due to the more porous nature of the contact layer.
- The cell ASR with Alloy-3 derived contact had the lowest R_f, DR_i & DR_f, likely as a result of the Ce dopant modifying the Cr_2O_3 scale growth.

Cell ASR at 800°C during Isothermal Exposure

	Alloy 1	Alloy 2	Alloy 3	Co+MnO_2
R_f (mΩ·cm²)	4.0	4.6	3.1	7.0
DR_f (μΩ·cm²/h)	1.4	1.3	1.0	1.4





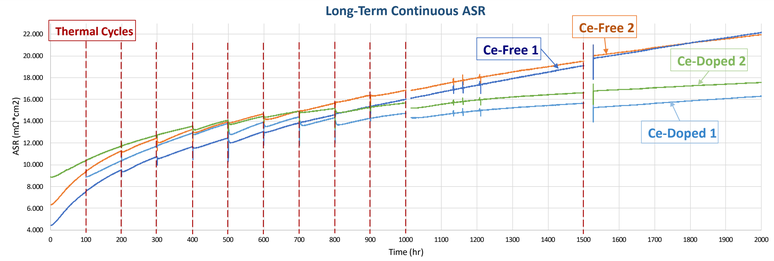


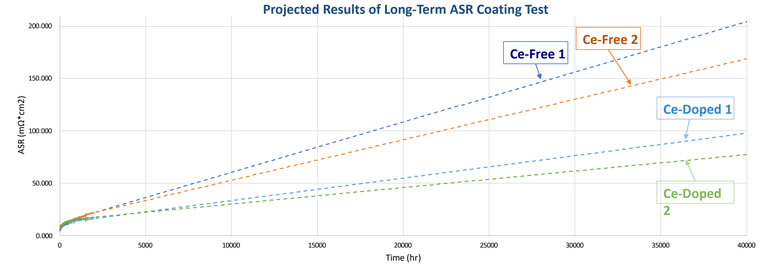
Long-Term ASR Testing of Ce-Doped Coatings

- The coating samples were exposed at 850°C to accelerate the oxidation testing.
- Ce-doped MCO coated samples had much lower ASR degradation rates than Ce-free coating samples despite starting with a higher ASR
- The ASRs were projected assuming a linear oxidation beyond 2000 hours.
- The projected ASR of Ce-doped coating samples after 40,000-h was below the target value of 100 mΩ*cm² despite the accelerated oxidation temperature of 850°C being employed.

The ASR and Degradation Rate of the samples after 2000-h

	Ce-Free 1	Ce-Free 2	Ce-Doped 1	Ce-Doped 2
R_f (mΩ·cm²)	22.15	21.95	16.29	17.56
DR_f (μΩ·cm²/h)	4.71	3.75	2.14	1.58



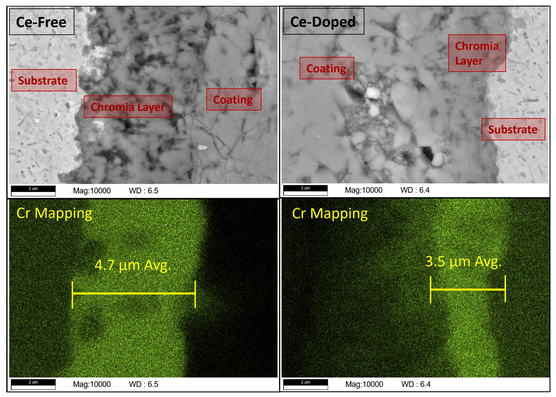


Cross-Sectional View of the Coatings after Long-Term Testing

- A thicker and more discrete chromia layer was observed on all Ce-free coating samples.
- Ce-doped coating samples exhibited a reduced chromia scale thickness and a more developed $(Mn,Co,Cr)_3O_4$ reaction layer.
- The Ce doping also improved interfacial bonding.

Comparison Between Ce-Doped and Ce-Free samples at the end of 2000-h and after a projected 40,000-h

Averaged	Non-Doped	Ce-Doped	%Reduction
Cr Scale Size (μm)	4.73	21.95	26.9%
R_f (mΩ·cm²)	22.05	16.93	23.2%
DR_f (μΩ·cm²/h)	4.33	1.86	57.0%
$R_{f\_projected}$ (mΩ·cm²)	186.6	87.6	52.8%

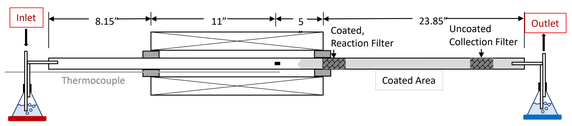


Cr Blocking Ability of Ce-Doped MCO Coatings

- Cr volatilization testing was performed at 800°C over 500-h using the denuder method.
- The Ce-doped coatings were proved to be very effective at blocking Cr evaporation compared to bare Crofer 22.

Comparison of Coated and Uncoated Cr Evaporation of Crofer 22

Bare Crofer – Cr Evaporation Rate (kg/m²·s)	9.05e-10
Coated Crofer – Cr Evaporation Rate(kg/m²·s)	6.51e-11
% Reduction in Cr Evaporation Rate with the Coating	92.8 %



Schematic of the Cr Collection Setup

Concluding Remarks

- Ce doping in the MCO spinel layer improved all aspects of the performance of the spinel coating/contact layer formed via the EARS.
- The cell with the Ce-doped alloy (Alloy-3) derived contact had the best overall ASR performance, likely as a result of the Ce dopant modifying the Cr_2O_3 scale growth on the interconnect alloy.
- The presence of Ce in the MCO coating increased the initial ASR, which was more than compensated for by the significant reduction in ASR degradation rate.
- The Ce-doped MCO coating was very effective in reducing the Cr evaporation from the ferritic interconnect alloys.
- Our industrial partner is currently performing in-stack testing to verify the performance of the new coating/contact.
- Further cost reductions and process optimizations are being explored.

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