附錄(四)

High-Temperature Electrical and Microstructural Properties of $La_{0.67}Sr_{0.33}MnO_3$ Coated Ferritic Stainless Steels Using Pulsed DC Magnetron Sputtering

Chien–Kuo Liu (劉建國)
E-mail: ckliu2@iner.gov.tw

Physics Division,
Institute of Nuclear Energy Research

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Institute of Nuclear Energy Research

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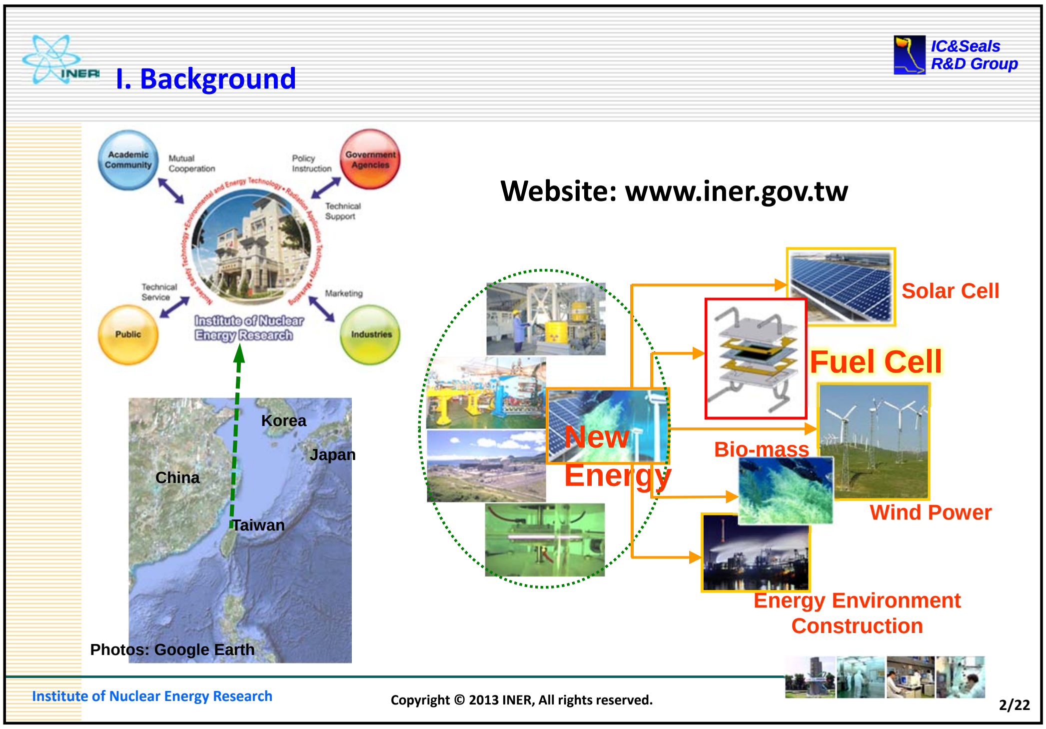
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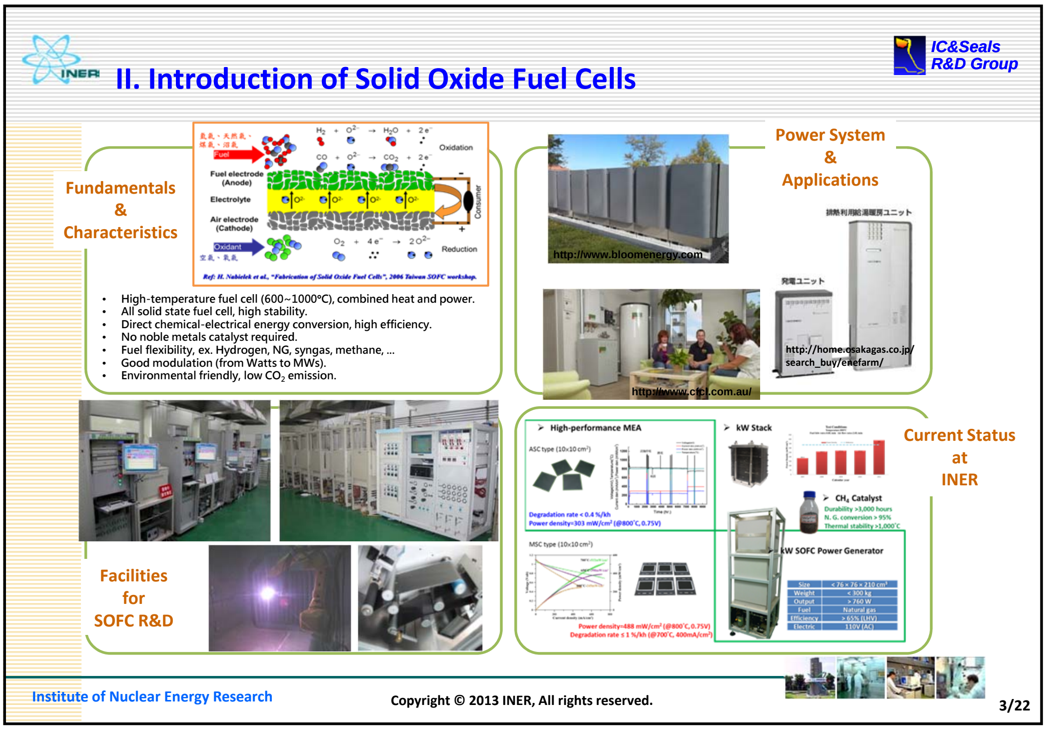
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Fuel electrode (Anode)
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Oxidation
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High-temperature fuel cell (600~1000°C), combined heat and power.
All solid state fuel cell, high stability.
Direct chemical-electrical energy conversion, high efficiency.
No noble metals catalyst required.
Fuel flexibility, ex. Hydrogen, NG, syngas, methane, ...
Good modulation (from Watts to MWs).
Environmental friendly, low CO2 emission.
Power System & Applications
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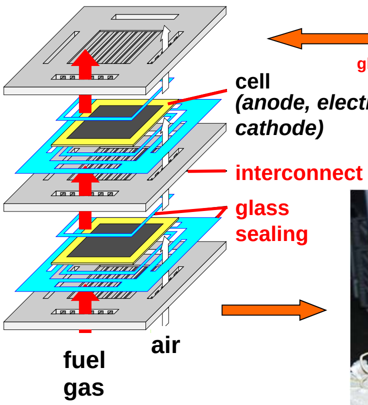
III. Protective Layer Coating on Interconnects for SOFCs

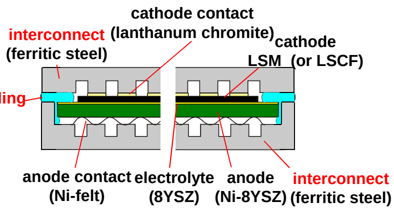
Outline:

- Introduction
- Interconnect Selection
- Protective Layer (LSM) Coating
- SEM/EDS Microstructure Observation
- Area Specific Resistance Measurement
- Summaries

III. Protective Layer Coating on Interconnects for SOFCs

- Introduction





Ref: H. Nabielek et al., "Fabrication of Solid Oxide Fuel Cells", 2006 Taiwan SOFC workshop.

III. Protective Layer Coating on Interconnects for SOFCs

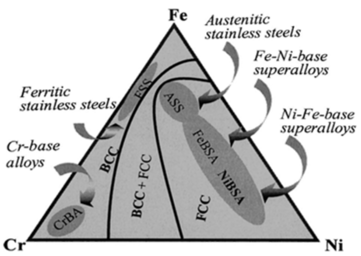
- Introduction

- Physical properties stable at high temperature
- Chemical properties stable at high temperature
- High Electrical Conductivity
- Compatible CTE
- Easy Manufacture
- Low cost

INER's 1 kW SOFC Stack

III. Protective Layer Coating on Interconnects for SOFCs

- Interconnect Selection



Fe-Cr base：Crofer22APU (ThyssenKrupp)
Cr base　：Ducrolloy (Plansee)
Ni-Cr base：HAYNES 230 (PNNL)

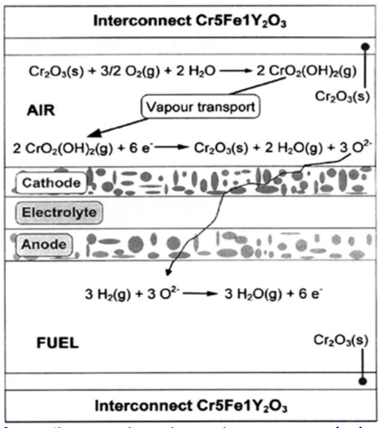
Alloys	Matrix structure	TEC $\times 10^{-6}$ K^{-1}	Oxidation resistance	Mechanical strengths	Manufacturability	Cost
CrBA	bcc	11.0-12.5 (RT-800°C)	Good	High	Difficult	Very expensive
✓ FSS	bcc	11.5-14.0 (RT-800°C)	Good	Low	Fairly readily	Inexpensive
ASS	fcc	18.0-20.0 (RT-800°C)	Good	Fairly high	Readily	Inexpensive
FeBSA	fcc	15.0-20.0 (RT-800°C)	Good	High	Readily	Fairly expensive
NiBSA	fcc	14.0-19.0 (RT-800°C)	Good	High	Readily	Expensive

Ref.: Z. Yang et al., J. Electrochem. Soc., 150(9), A1188-A1201 (2003)

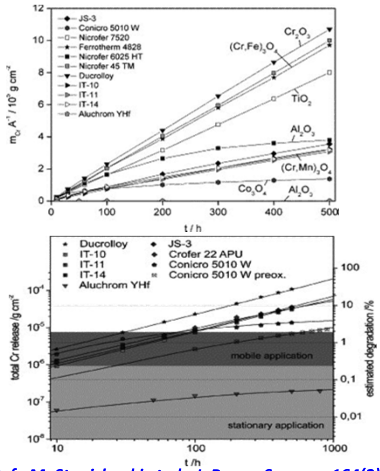
III. Protective Layer Coating on Interconnects for SOFCs

- Interconnect Selection

Cr Poisoning



Ref.: K. Hilpert et al., J. Electrochem. Soc., 143(11), 3642-3647 (1996)

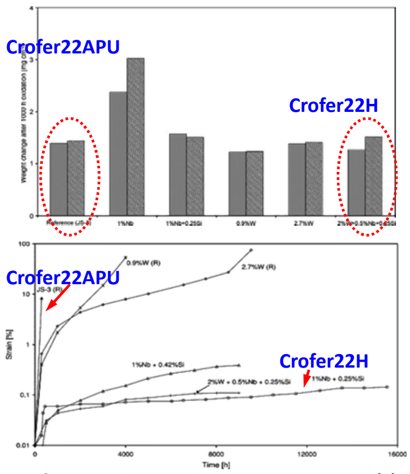


Ref.: M. Stanislowski et al., J. Power Sources, 164(2), 578-589 (2007)

III. Protective Layer Coating on Interconnects for SOFCs

- Interconnect Selection

Additions	Functions
Cr	Improve oxidation resistance, Low CTE
Mn	Low Cr evaporation, Improve conductivity (oxide scale)
La	Improve adherence (oxide scale), Improve oxidation resistance
Ce	Improve adherence (oxide scale)
Al	High oxidation rate, Low conductivity (oxide scale)
Si	High oxidation rate, Low conductivity (oxide scale)
W	Improve mechanical strength (high Temp.)
Nb, Si	Improve mechanical strength (high Temp.)



Ref.: J. Froitzheim et al., J. Power Sources, 178(1), 163-173 (2008)

III. Protective Layer Coating on Interconnects for SOFCs

- Protective Layer Coating

Protection layer: Perovskite – LSM, LSC, LSF, LCC…
Spinel – MnCo, MnCr, NiCr, CoCr…

Name	$\alpha/10^{-6}\ K^{-1}(\Delta T, °C)$	$\sigma(S\ cm^{-1})\ T\ (°C)$	Function
8YSZ	10.8(20–800) [47]	(5.3–4.5) × 10^{-2}(800) [48]	Electrolyte
Crofer22 APU	12.0(20–800) [49]	8.70 × 10^{3}(800) [49]	Interconnect
Cr_2O_3	9.6(20–1400) [50]	1.28(750) [50] 2.50(1000) [50]	Oxide scale
$MnCr_2O_4$	7.2(25–900) [43]	0.22(750) [43] 0.05(800) [43]	Oxide scale
Mn_2CrO_4	–	12.8–30.3(750) [43]	Oxide scale
Co	14.0(20–400) [51]	1.71 × 10^{4}(800) [51]	Coating
Co_3O_4	–	35.5(800) [52]	Coating
$CoCr_2O_4$	7.4(25–900) [43]	1.92(750) [43]	Coating
Ni	16.3(20–900) [51]	2.20 × 10^{4}(900) [51]	Coating
NiO	12.6(100–800) [50]	14.9(590 [50] 71.4(1000) [50]	Coating
$NiCr_2O_4$	7.6(25–900) [43]	62.5(750) [43]	Coating
Cu	20.3(20–1000) [51]	1.23 × 10^{5}(977) [51]	Coating
CuO	–	2 × 10^{3}(700) [50] 10^{5}(1000) [50]	Coating
LSC-80	9.8–11.2(20–1000) [53]	10–40(1000) [53]	Coating/interconnect
LMAC-DLR	–	–	Coating/interconnect
LSM-80	11.4(50–1000) [54]	175(1000) [55]	Coating/cathode
LSM-65	12.3(25–800) [47]	3.39(800) [56]	Coating/cathode

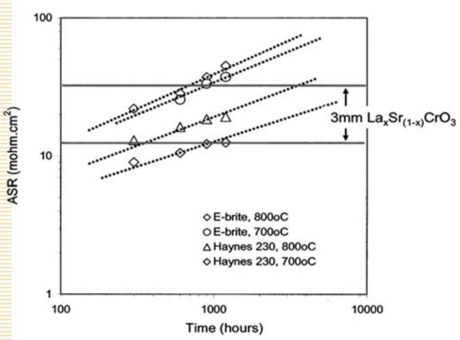
Ref.: M. Stanislowki et al., J. Power Sources, 164(2),578-589 (2007)

III. Protective Layer Coating on Interconnects for SOFCs

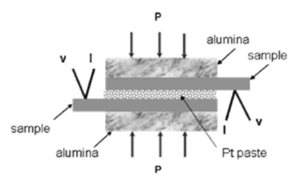
- Protective Layer Coating

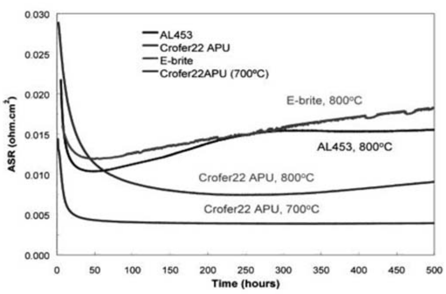
Area Specific Resistance (ASR)

For SOFC: ASR < 0.1 Ω·cm²



Ref.: Z. Yang et al., J. Electrochem. Soc., 150(9), A1188 -A1201 (2003)





Ref.: Z. Yang et al., Int. Mater. Rev., 53(1), 39-54 (2008)

III. Protective Layer Coating on Interconnects for SOFCs

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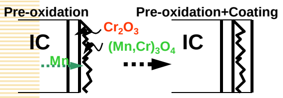
- **Protective Layer (LSM) Coating – Materials & Procedures**

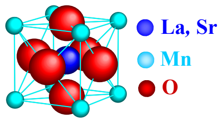
Compositions of Crofer22APU, Crofer22H, ss441, and ZMG232L (in wt.%).

Alloys	Fe	Cr	Mn	Si	Cu	Al	S	P	Ti	La	Nb	Ni	Zr	C
Crofer22APU	Bal.	20–24	0.3–0.8	≦0.50	≦0.50	≦0.50	≦0.02	≦0.05	0.03–0.20	0.04–0.20	–	–	–	≦0.03
Crofer22H	Bal.	20–24	0.3–0.8	0.1–0.60	≦0.50	≦0.10	≦0.03	≦0.03	0.02–0.20	0.04–0.20	0.20–0.10	–	–	≦0.03
ss441	Bal.	18	0.35	≦0.34	–	≦0.05	≦0.02	≦0.023	0.22	–	0.5	0.3	–	≦0.01
ZMG232L	Bal.	21–23	≦0.10	≦0.10	–	≦0.50	≦0.03	≦0.03	–	0.03–0.10	–	≦0.70	0.10–0.40	≦0.10

size: 1×1 cm²
surface polished

w/o Pre-oxidation & w/ Pre-oxidation (850°C/25, 50 hrs)





$La_{0.67}Sr_{0.33}MnO_3$

Sputtering Parameters	
Distance (cm)	5
Power (kW)	1.5
Atmosphere	Ar
Flow Rate (sccm)	150
Vaccum (torr)	7.5~8.0×10⁻³
Rotation (rpm)	20
Time (min)	90
Thickness (μm)	4

III. Protective Layer Coating on Interconnects for SOFCs

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- **SEM/EDS Microstructure Observation (Pre-oxidation Effect)**

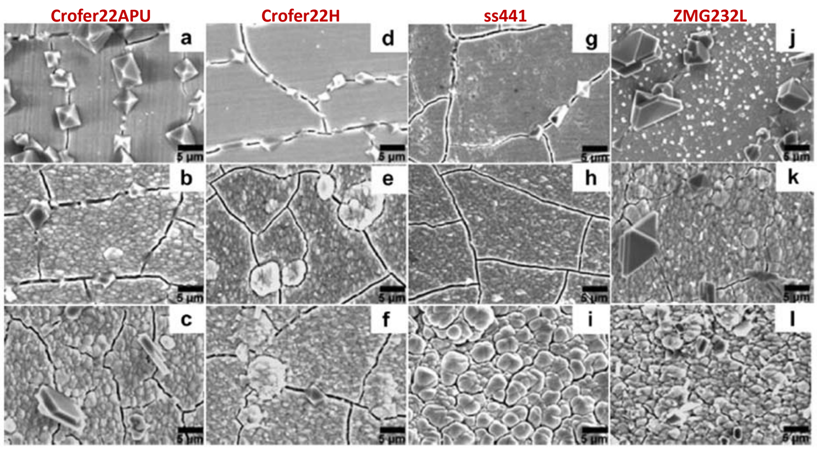

Fig. 4. SEM micrographs (surface morphologies) of LSM-coated (a)–(c) Crofer22APU; (d)–(f) Crofer22H, (g)–(i) ss441 and (j)–(l) ZMG232L after aging at 800 °C for 500 h in air. The substrate's condition was (a) without pre-oxidation; (b) pre-oxidised at 850 °C for 25 h in air; and (c) pre-oxidised at 850 °C for 50 h in air, respectively. (Note: substrate's conditions of (d)–(f), (g)–(i) and (j)–(l) are the same as (a)–(c) in sequence.)

III. Protective Layer Coating on Interconnects for SOFCs

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- SEM/EDS Microstructure Observation (Pre-oxidation Effect)

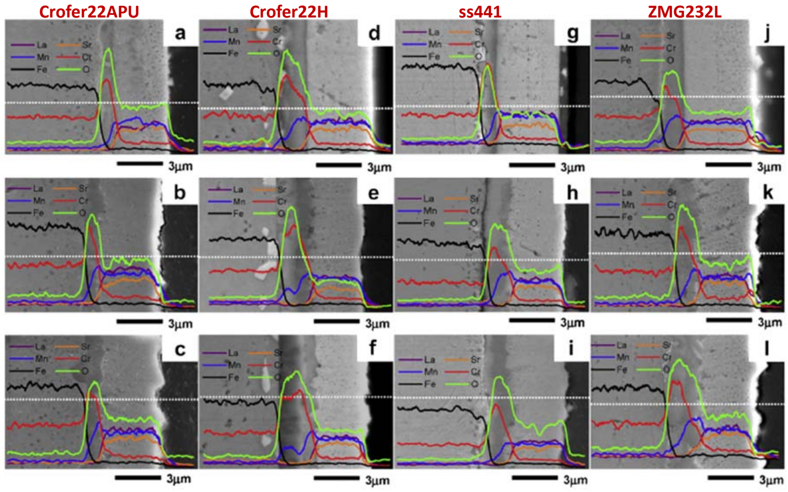

Fig. 3. Cross-section SEM micrographs of LSM-coated (a)–(c) Crofer22APU; (d)–(f) Crofer22H, (g)–(i) ss441 and (j)–(l) ZMG232L after aging at 800 °C for 500 h in air. The substrate's condition was (a) without pre-oxidation; (b) pre-oxidised at 850 °C for 25 h in air; and (c) pre-oxidised at 850 °C for 50 h in air, respectively. (Note: substrate's conditions of (d)–(f), (g)–(i) and (j)–(l) are the same as (a)–(c) in sequence.)

III. Protective Layer Coating on Interconnects for SOFCs

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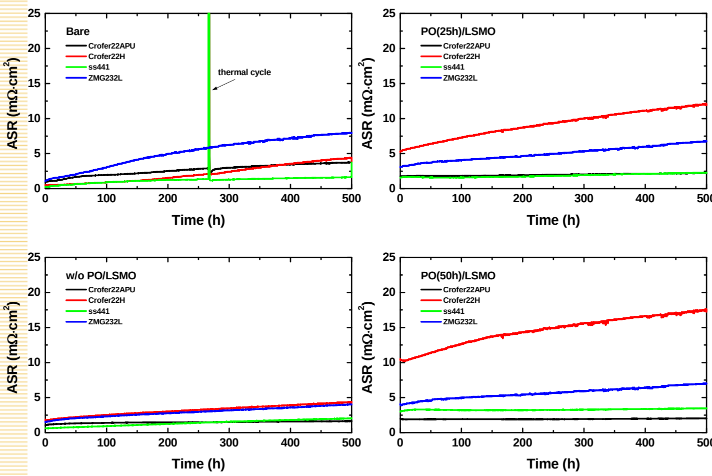
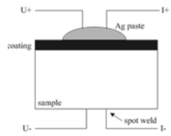
- ASR Measurement (Pre-oxidation Effect)



After 800°C, 500 h

1	Bare
2	w/o PO/LSM
3	PO(25h)/LSM
4	PO(50h)/LSM

Patent:US7,663,384B2



III. Protective Layer Coating on Interconnects for SOFCs

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- ASR Measurement (Pre-oxidation Effect)

ASR (mΩ·cm^2)

Sample	Crofer22APU		Crofer22H		ss441		ZMG232L	
@800°C	0 h	500 h	0 h	500 h	0 h	500 h	0 h	500 h
Bare	0.94	3.76	0.50	4.41	0.28	1.64	1.07	7.96
W/O PO/LSM	1.05	1.63	1.89	4.31	0.62	2.01	1.59	4.03
PO(25h)/LSM	1.77	2.20	5.31	11.89	1.56	2.25	3.17	6.77
PO(50h)/LSM	1.97	2.02	10.54	17.24	2.97	3.44	4.14	7.00

See also: *Yang et al., J. Power Sources, 213, 63-68 (2012).*

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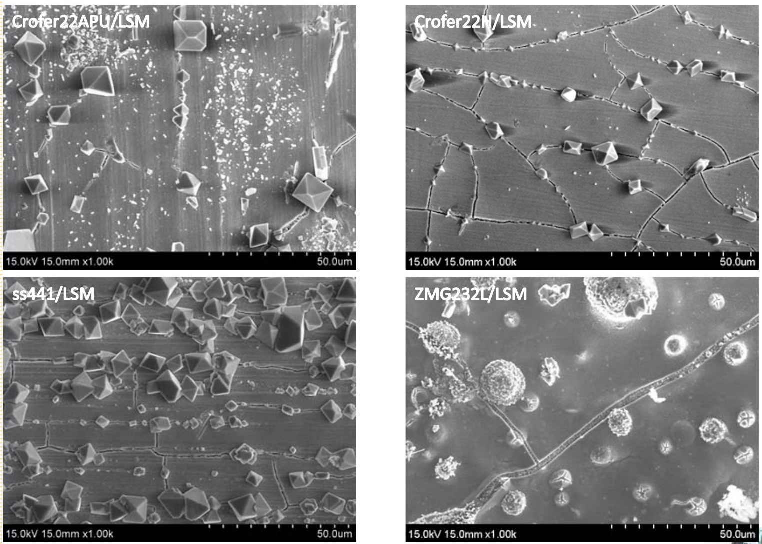
- SEM/EDS Microstructure Observation (Long-term Test)

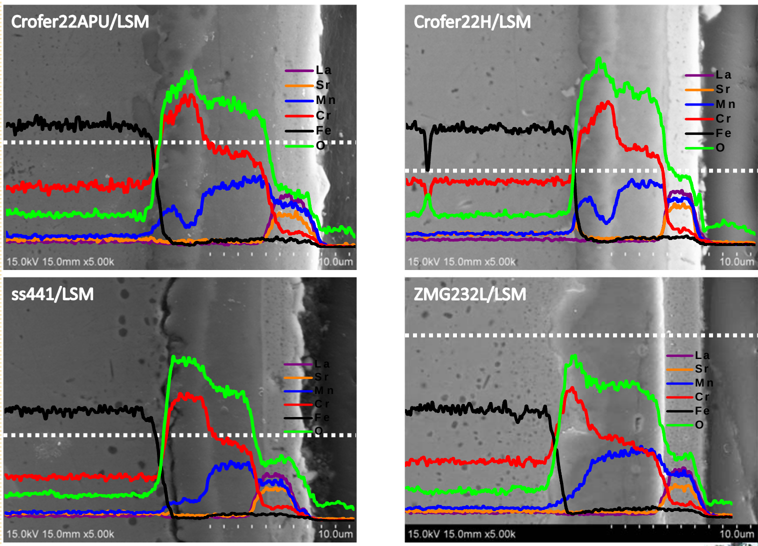


After Aging at 800°C for 10,000 hrs

$(Mn,Cr)_3O_4$ spinels generated along the cracks due to the Cr evaporating from the substrate.

III. Protective Layer Coating on Interconnects for SOFCs

- **SEM/EDS Microstructure Observation (Long-term Test)**



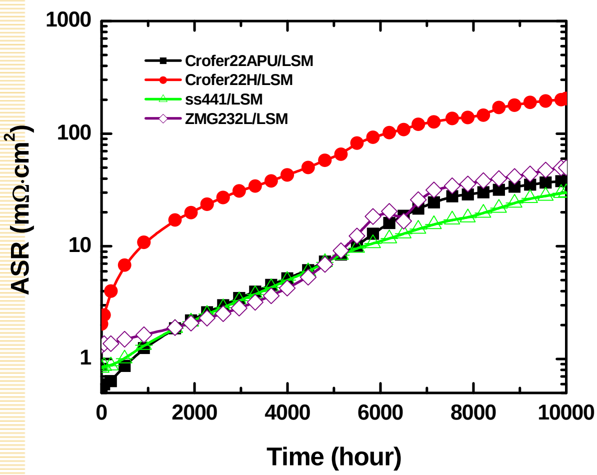
After Aging at 800°C for 10,000 hrs

LSM-coated specimen had a strong effect on the resistance of Cr diffusion. However, the thickness of LSM film reduced from 3~4 μm to 2~3 μm after long-term aging.

See also: Shong et al., *Mater. Chem. Phys.*, *127*, 45–50 (2011).

III. Protective Layer Coating on Interconnects for SOFCs

- **ASR Measurement (Long-term Test)**



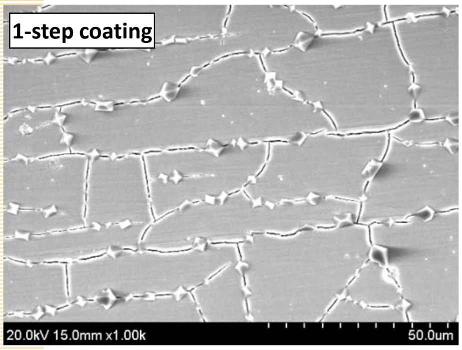
After Aging at 800°C for 10,000 hrs

Sample/Coatings	ASR (mΩ·cm²)
Crofer22APU/LSM	38.49
Crofer22H/LSM	205.39
Ss441/LSM	30.00
ZMG232L/LSM	49.92

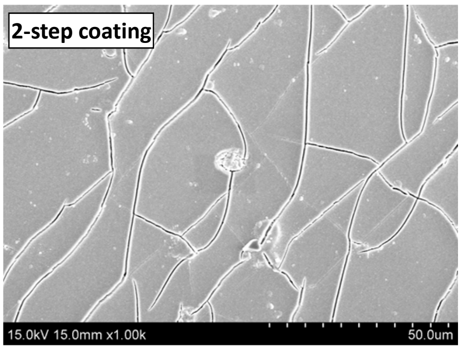
III. Protective Layer Coating on Interconnects for SOFCs

- SEM/EDS Microstructure Observation (2-step Coating)

Comparison of the Surface Morphology of Crofer22H/LSM coated by 1- & 2-step Process After Aging at 800˚C for 500 hours



Thickness of LSM film: 4 μm



Thickness of LSM film: 4 μm

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III. Protective Layer Coating on Interconnects for SOFCs

- Summaries

✓ Pre-oxidation treatment on ferritic stainless steel is a simple and effective way to inhibit the diffusion of Cr element from the oxide scale to the surface, and it lowers the increasing rate of ASR during aging at high temperatures.

✓ The corresponding increments of the ASR values for the specimens with LSM coated on pre-oxidized substrates are lower than for the specimens of LSM/non-pre-oxidized substrates after aging at 800°C for 500h.

✓ The thickness of LSM protective film reduced from 3~4 μm to 2~3 μm after long-term aging. It was attributed to the Mn content of LSM film interacting with the neighboring $(Mn, Cr)_3O_4$ spinel oxide layer at elevated temperatures.

✓ The volume shrinkage at elevated temperatures usually causes the LSM coatings to crack, resulting in chromium diffusion. However, it can be effectively mitigated by introducing a two-step coating process.

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Thank You for Your Attention!