National Energy Technology Laboratory

Evaluation of a Surface Treatment on the Performance of Stainless Steels for SOFC Interconnect Applications

D.E. Alman, G.R. Holcomb, T.A. Adler,
R.W. Wilson, and P.D. Jablonski
NETL, Albany, OR
www.netl.doe.gov

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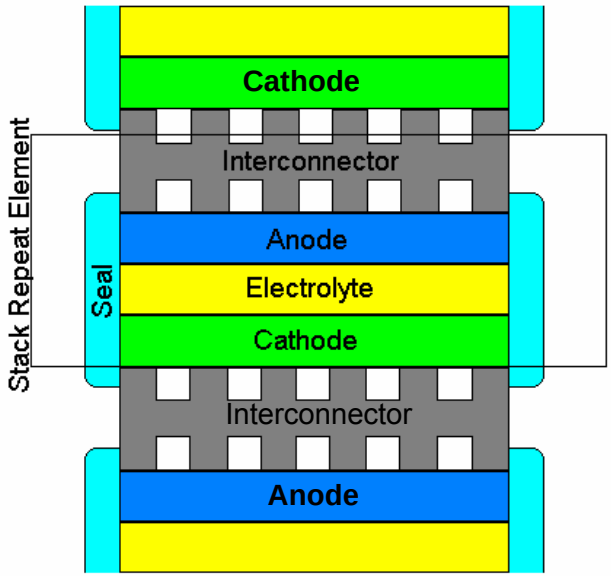
OUTLINE

- WHY RARE EARTH SURFACE TREATMENTS
- OXIDATION BEHAVIOR OF SURFACE TREATED CROFER 22APU
- WHY SURFACE TREATMENT WORKS IN IMPROVING OXIDATION RESISTANCE
- SOFC BUTTON CELL WITH TREATED ANNODE CURRENT COLLECTORS
- IMPROVING ELECTRICAL PERFORMANCE
  - "Half-cell" ASR-measurements
- SUMMARY AND CONCLUSION

CHROMIA FORMING FERRITIC STEELS AS METALLIC INTERCONNECTS



- ✓ ***Low Cost***
- ✓ ***Physical Compatibility***
- ? ***SOFC Degradation***
  - i. Cr poisoning due to evaporation from alloy
  - ii. Formation of non-conductive internal oxides at alloy/oxide scale interface
  - iii. Excessive oxide scale growth

REACTIVE ELEMENT EFFECT

- **Characteristics**
  - Reduction in the oxidation rate
    - Change in scale growth mechanisms
      - cation transport → anion transport
    - Modification of scale microstructure
      - Large columnar grains → small grains
  - Stabilize Cr_2O_3 scales at lower Cr levels
    - Lower Cr levels
  - Improvement in scale adhesion
    - resistance to spallation

Alloy	*Fe*	*Cr*	*Mn*	*Si*	*Ti*	*Al*	*La*
Crofer 22APU	Bal	22.0	0.5	--	0.08	--	0.06 La
ZMG232	Bal	22.0	minor: Mn, Ni, Zr, La				

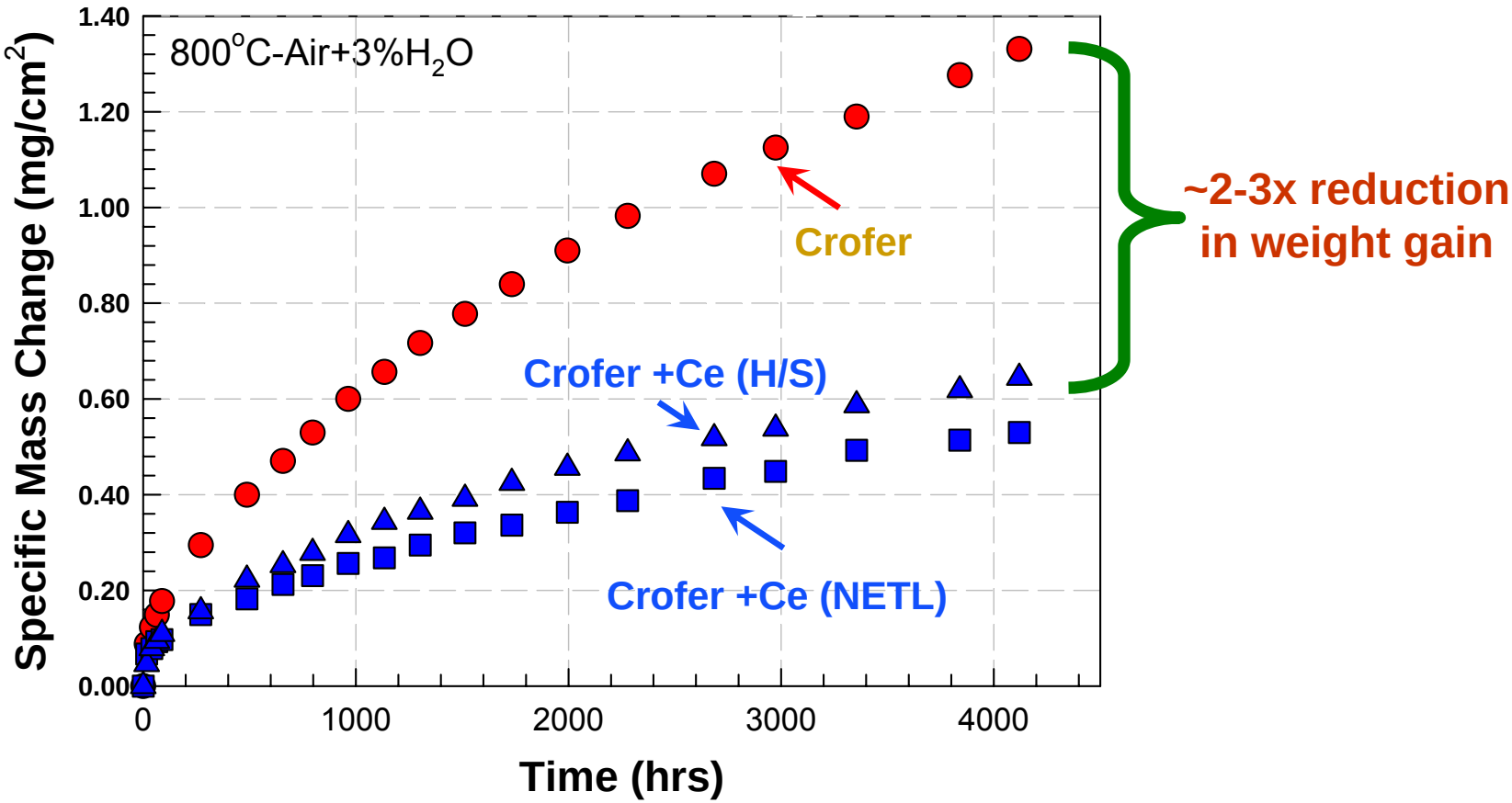
IMPROVING OXIDATION RESISTANCE WITH RARE EARTHS

- **Melt addition**
  - + Elements added during ingot production (single manufacturing step)
  - – Difficulty in melting (react with crucibles)
  - – Surface concentration limited by solubility and diffusivity
- **Surface treatments**
  - + Rare Earth concentrated where needed (at surface and have most benefit)
  - – $ "Extra" manufacturing step.
  - ? ***Long term effectiveness (as with any coating or surface treatment)***

NETL DEVELOPED SURFACE TREATMENT

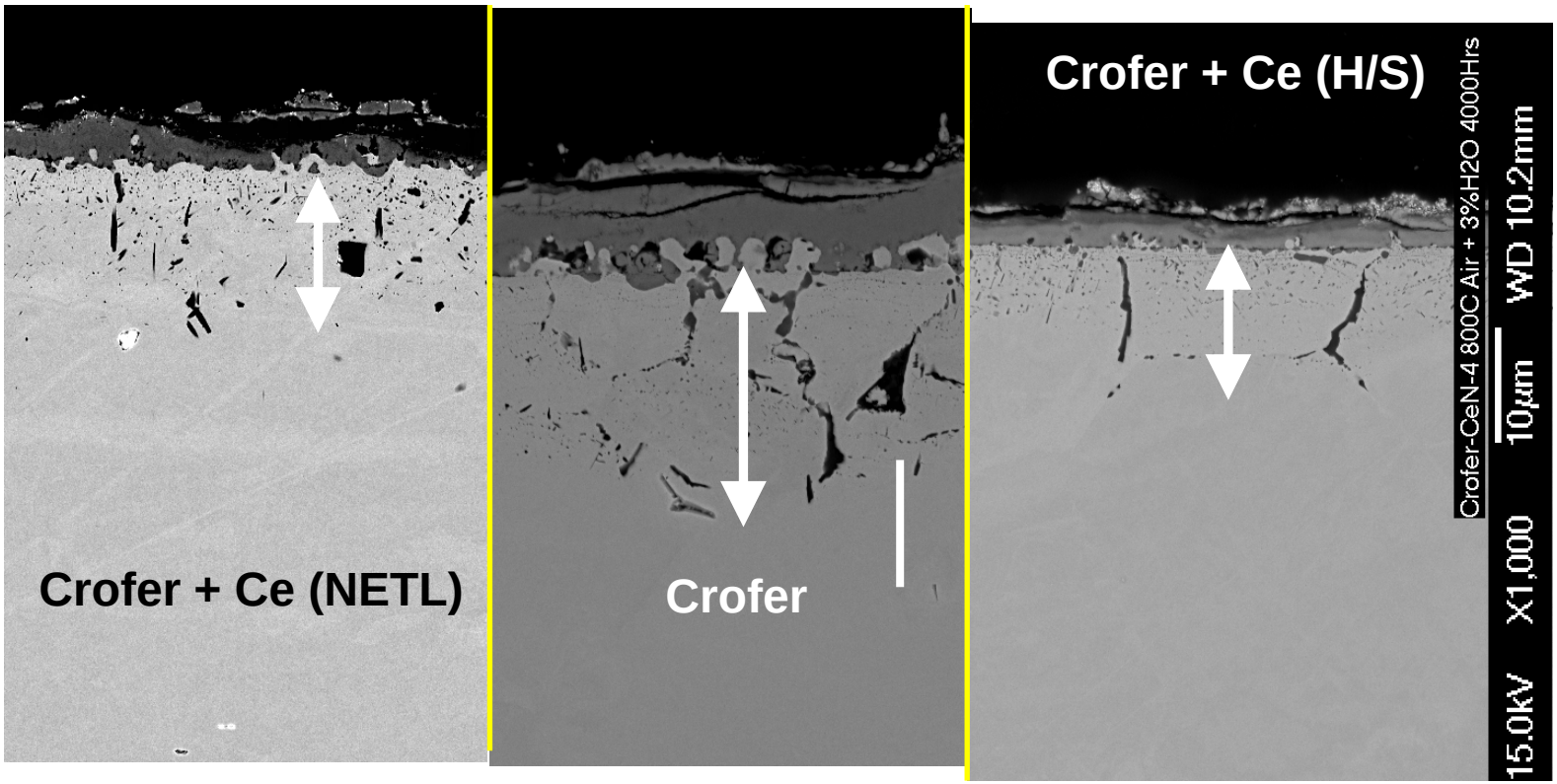
- **Investigate rare earth surface treatment for improving oxidation resistance of ferritic steels for SOFC interconnect applications.**
- **Two different surface treatments investigated**
  - Developed at NETL
    - Similar to pack cementation: coated with a powder mixture containing CeO_2 and halide activator followed by heating in a controlled atmosphere (900^{o}C-12 hrs), after which residual “pack” coating is washed off the surface.
    - Patent application filed with USPTO in September, 2005.
    - Applied to over 50 alloys.
  - Described in a paper by P.Y. Hou and J. Stringer (H/S)
    - J. Electrochem Soc., Vol 134, No. 7, July 1987, pp. 1836-1849
    - Coupons heated to 200^{o}C were coated with a cerium-nitrate slurry (10w/o nitrate adjusted with HNO_3 to pH=2), followed heating in air at 400^{o}C to decompose to CeO_2

CROFER 22APU+Ce SURFACE TREATMENT



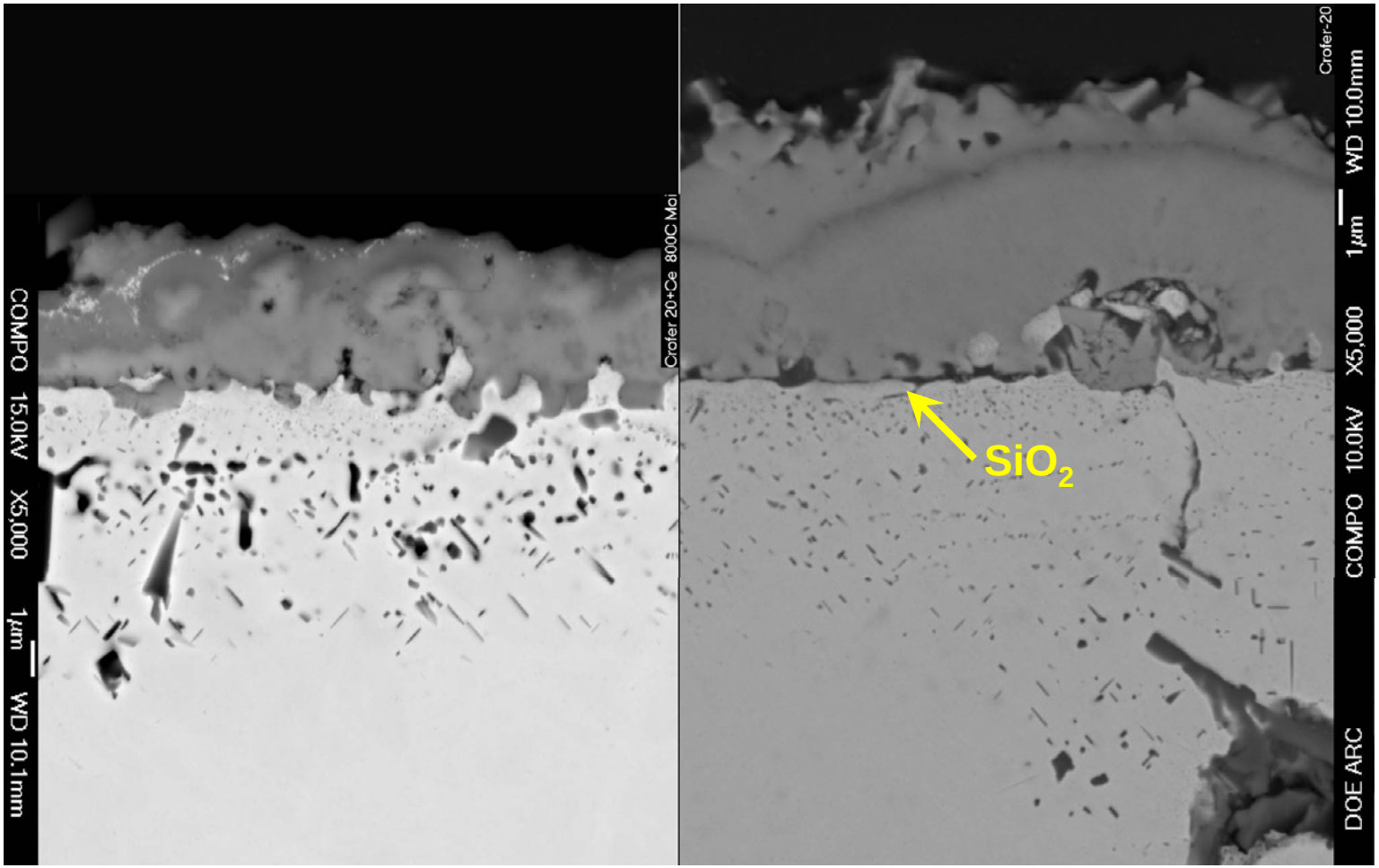
CROFER 22APU+Ce SURFACE TREATMENT

800°C-4000hrs-Air+3%H_2O



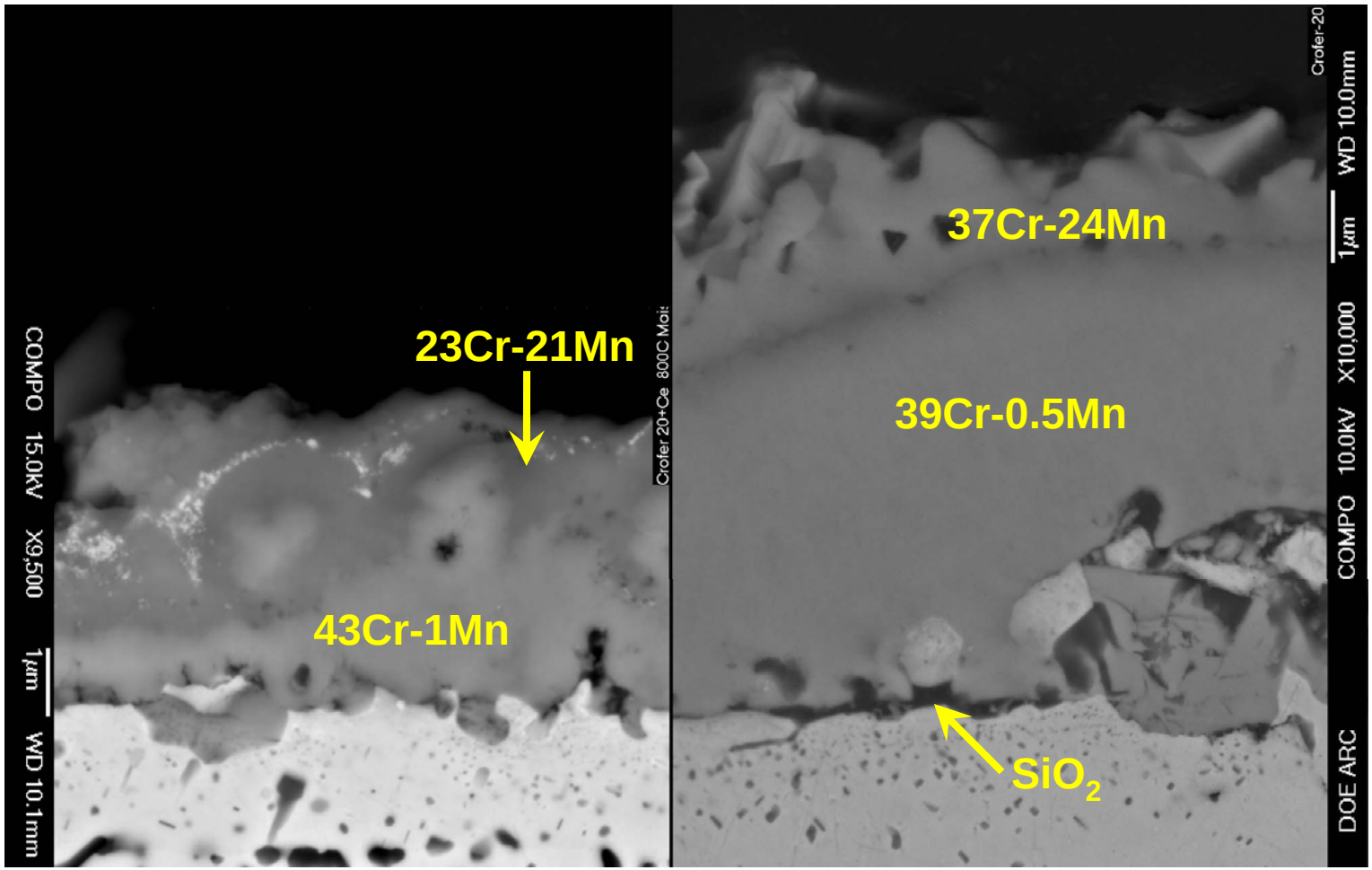
"smaller" internal oxidation zone

CROFER 22APU+Ce SURFACE TREATMENT



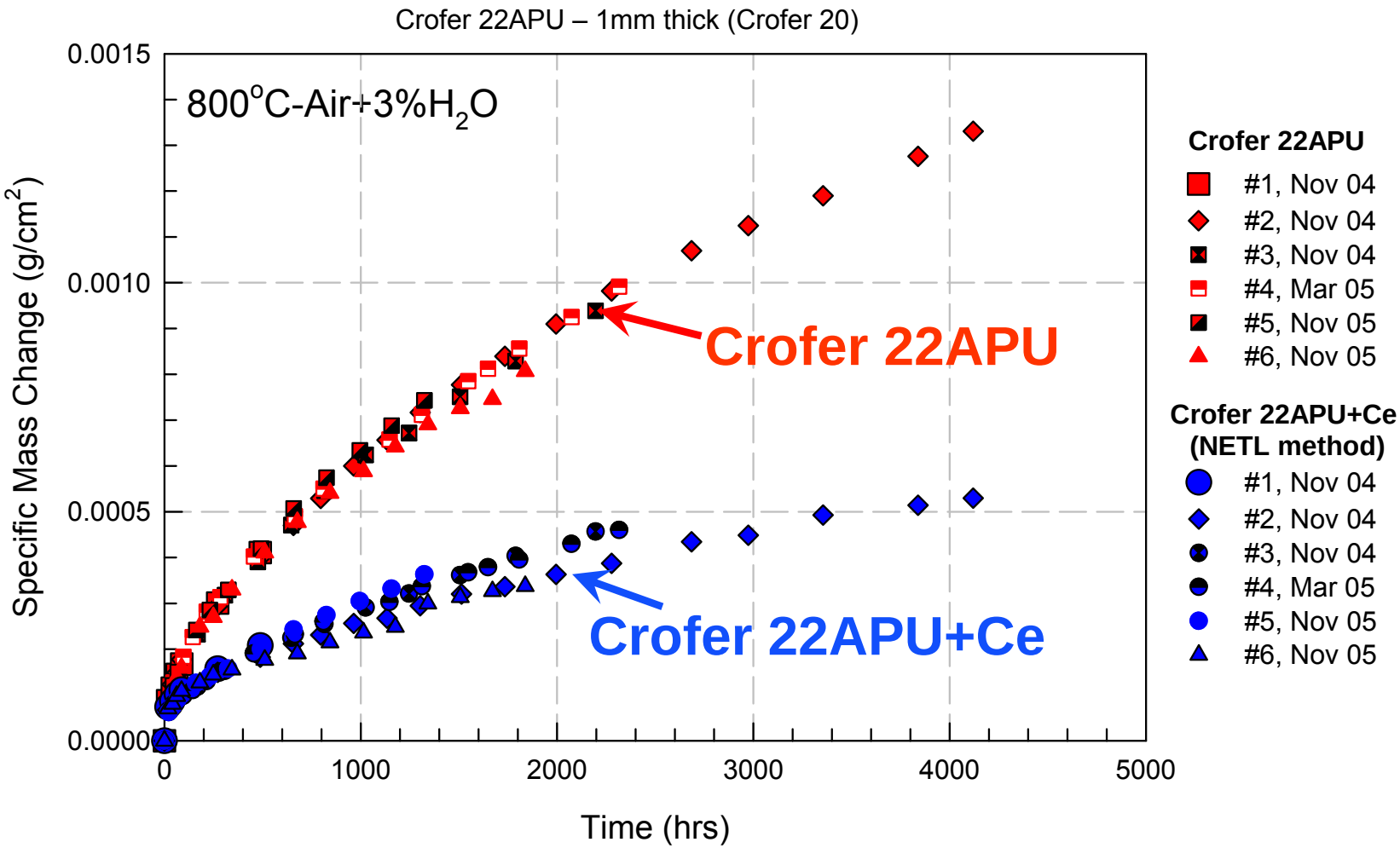
Early batch of Crofer w/ high Al and Si contents (610 ppm Al, 530 ppm Si by GDMS)

CROFER 22APU+Ce SURFACE TREATMENT



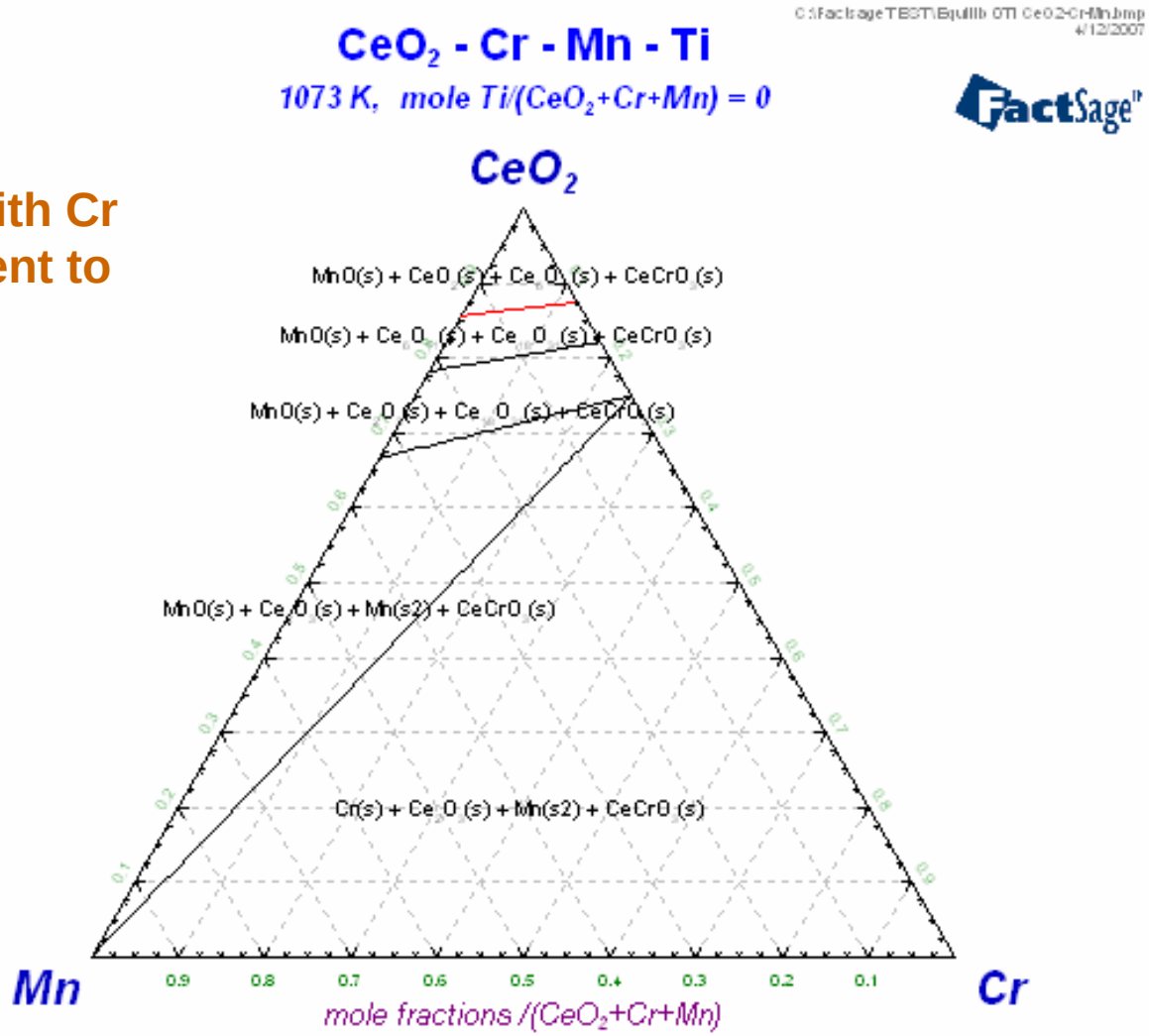
Early batch of Crofer w/ high Al and Si contents (610 ppm Al, 530 ppm Si by GDMS)

REPEATABLE RESULTS

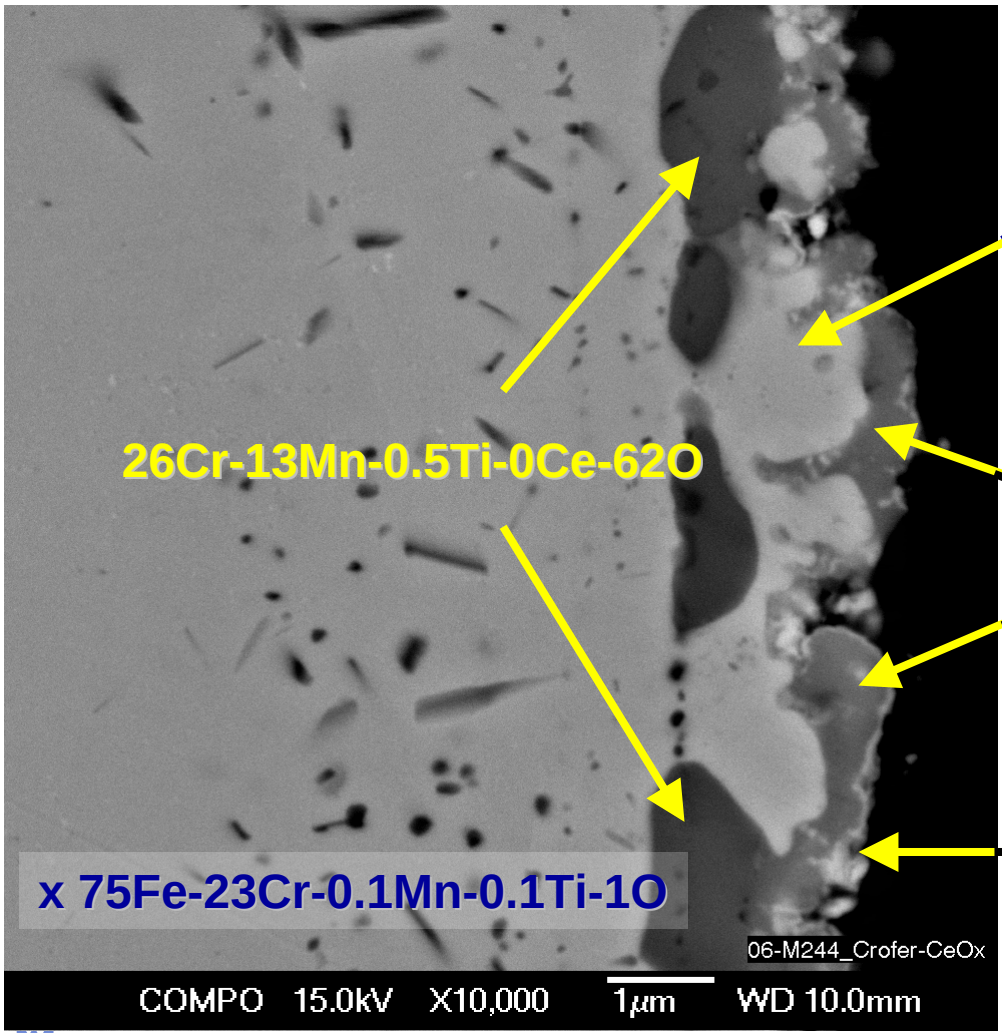


THERMODYNAMIC PREDICTION

CeO_2 reacts with Cr during treatment to form $CeCrO_3$



AS-TREATED SURFACE: PRIOR TO TESTING



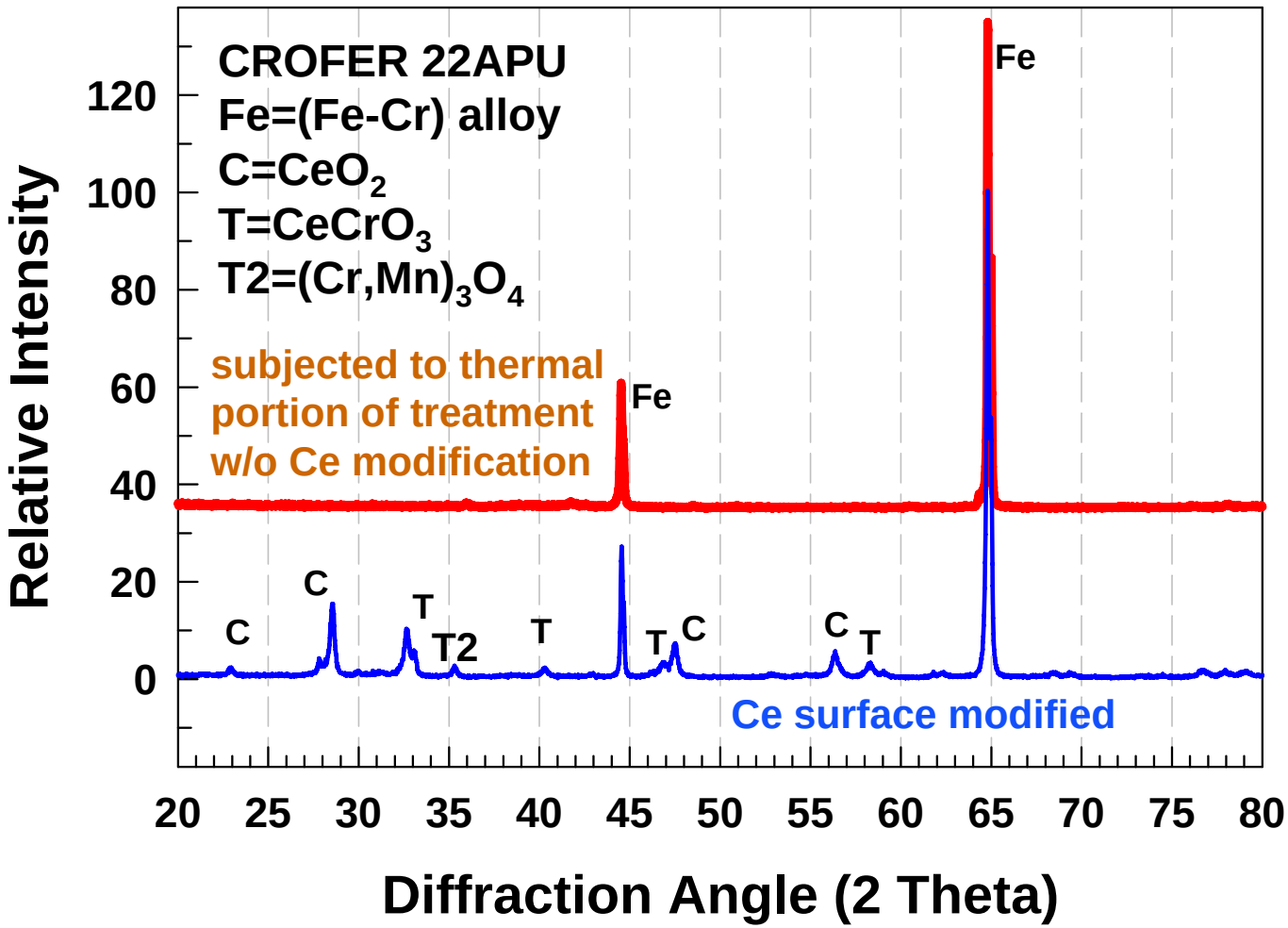
72Fe-23Cr-0.3Mn-0.1Ti-4.3O

24Cr-11Mn-1.1Ti-2.2Ce-64O

18Cr-5.4Mn-8.8Ce-61O

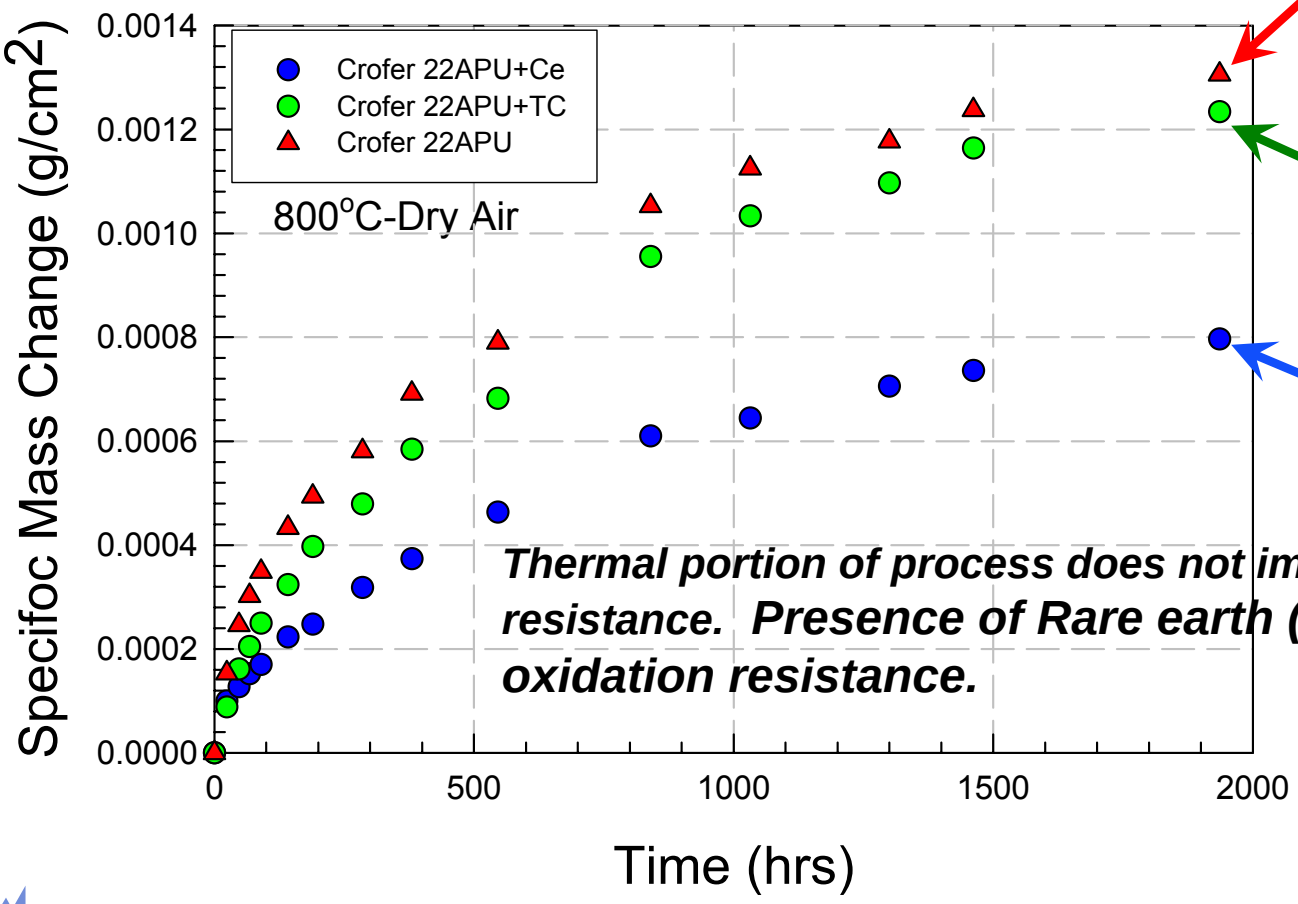
composition in at%
determined through WDX analysis

SURFACE PRIOR TO OXIDATION



THERMAL PORTION OF SUFACE TREATMENT

Surface modification process includes a thermal treatment in a controlled atmosphere. Does this influence oxidation behavior by “pre-oxidizing” surface?



as received

subjected to thermal portion of treatment w/o Ce modification

Ce surface modified

Thermal portion of process does not improve oxidation resistance. Presence of Rare earth (Ce) improves oxidation resistance.

OXIDATION RESITANCE

- **Nucleation**
  - CeO_2 → $CeCrO_3$ during treatment → nominally continuous surface oxide
  - ? Finer Cr_2O_3 grain size.
- **Ce in scale changes mechanism of subsequent Cr_2O_3 (or $(Cr,Mn)_xO_y$) scale growth**
  - oxygen controlled mechanism → slower scale growth, less internal oxidation.
- **Future work: TEM examination of scales.**

LABORATORY SCALE SOFC

- **SOFC button cell**
  - Nextech Materials (Nextcell-2.5D).
  - 2.5 cm diameter Zirconia-based electrolyte supported cell.
  - 1.27 cm diameter, 50 μm thick LSM cathode
  - Gd-doped CeO_2 layer at the electrolyte-cathode interface.
  - 1.27 cm diameter, 50 μm thick Ni-GDC anode.
- **Fe-22Cr-0.5Mn steel current collector**
  - Crofer, NETL-Alloy F5
- **Results of experiments in press:**
  - D.E. Alman, Johnson, Collins, Jablonski, J. Power Sources, available on line at www.sciencedirect.com

STAINLESS STEEL CATHODE CURRENT COLLECTOR

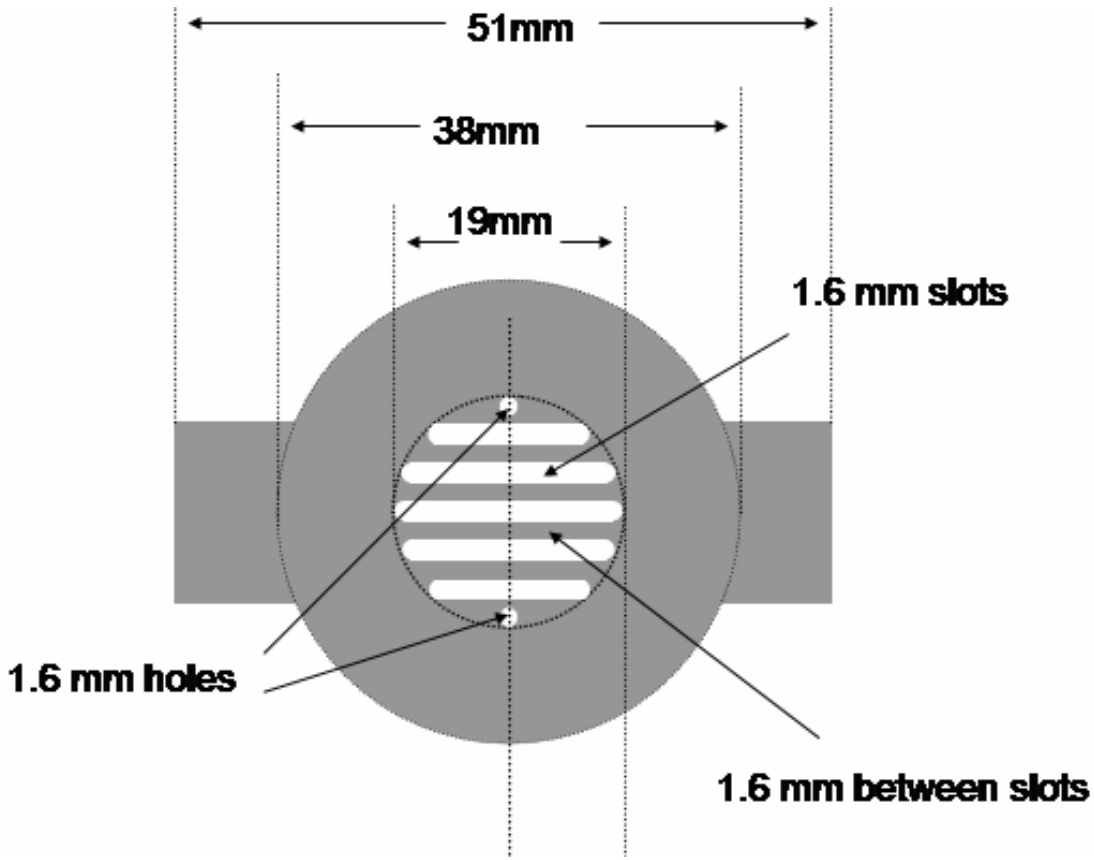
- **Alloy Composition (wt%)**

Alloy	*Fe*	*Cr*	*Mn*	*Ti*	*Al*	*Si*
F5	73.3	22.0	0.44	0.007	0.03	0.02
Crofer 22APU	75.9	22.7	0.45	0.095	0.11	0.27

F5: Produced in house at NETL-Albany (VIM, forging and rolling).
Crofer 22APU: procured from ThyessenKrupp.
1 mm thick

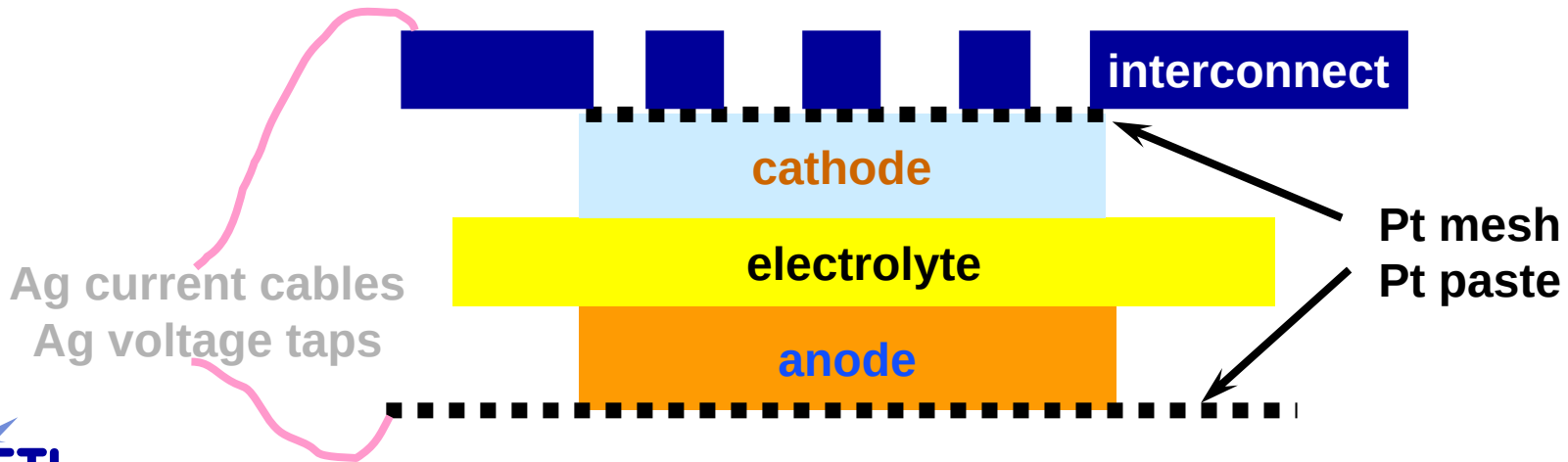
CATHODE CURRENT COLLECTOR

Machined Current Collectors were Ce Surface Treated

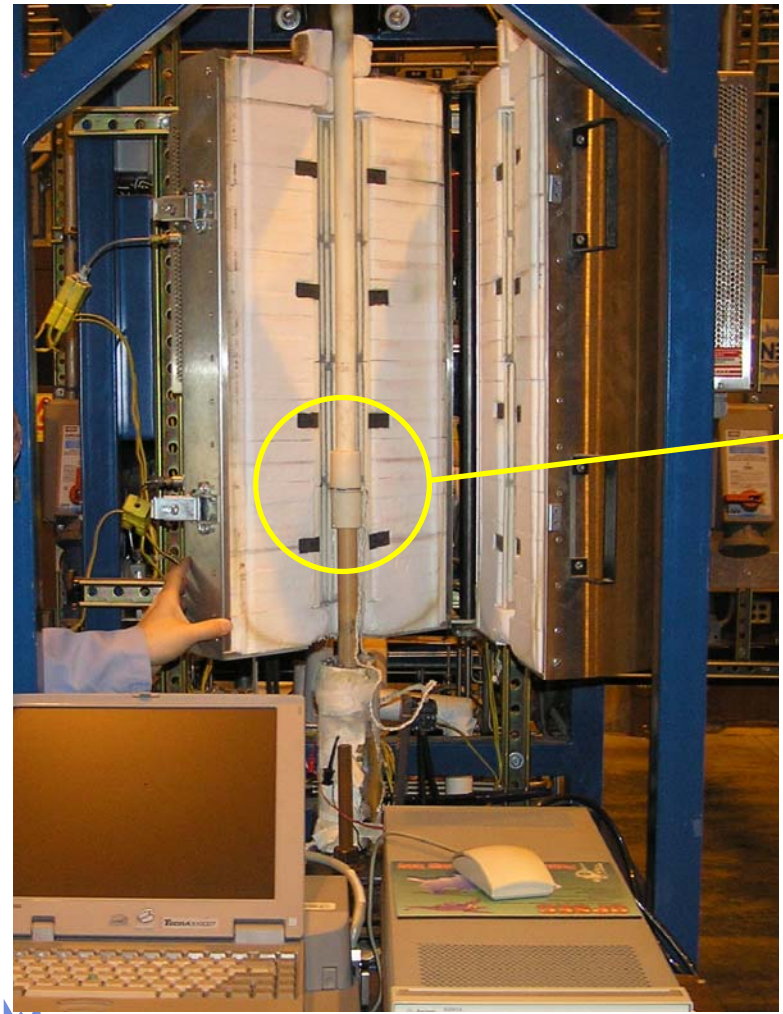


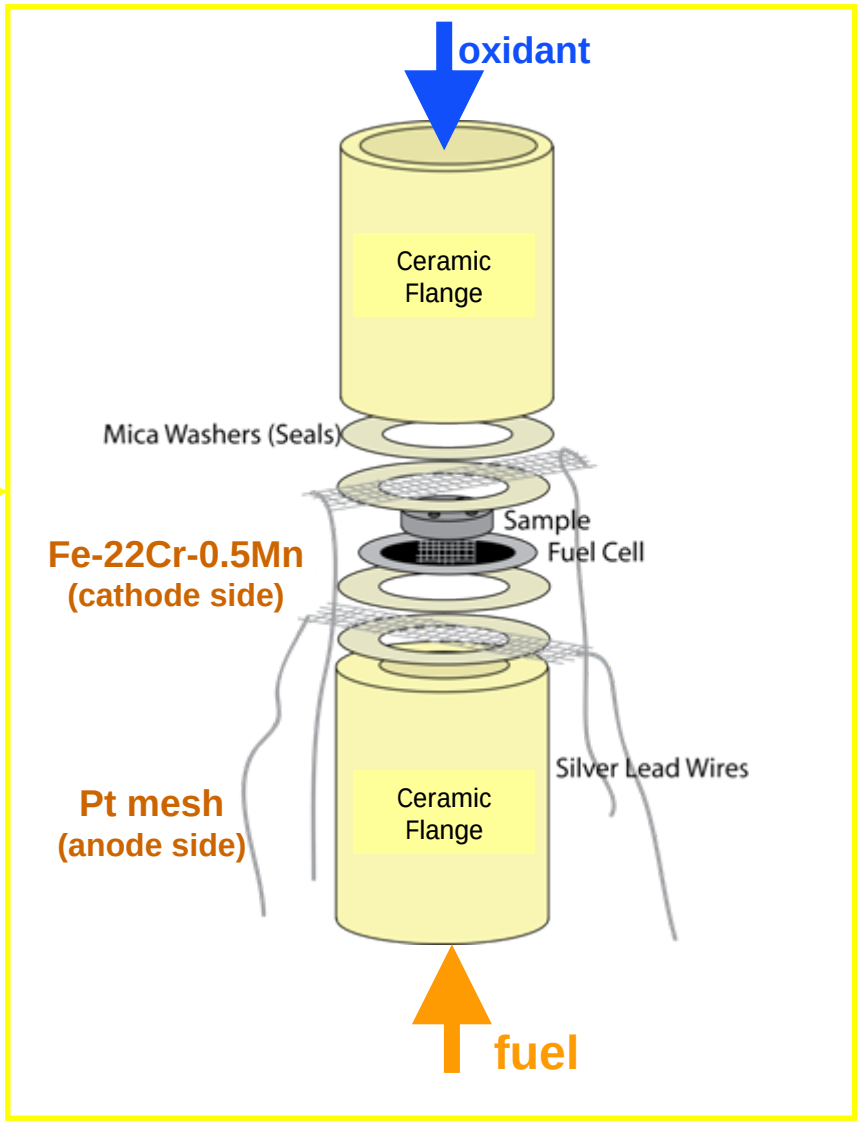
SOFC ASSEMBLY

- Fe-22Cr-0.5Mn steel current collector was attached to the cathode with Pt paste (a Pt mesh placed between interconnect and cathode).
- Pt mesh attached to anode.
- Ag current cables and voltage taps spot welded to current collectors



SOFC TEST APPARATUS





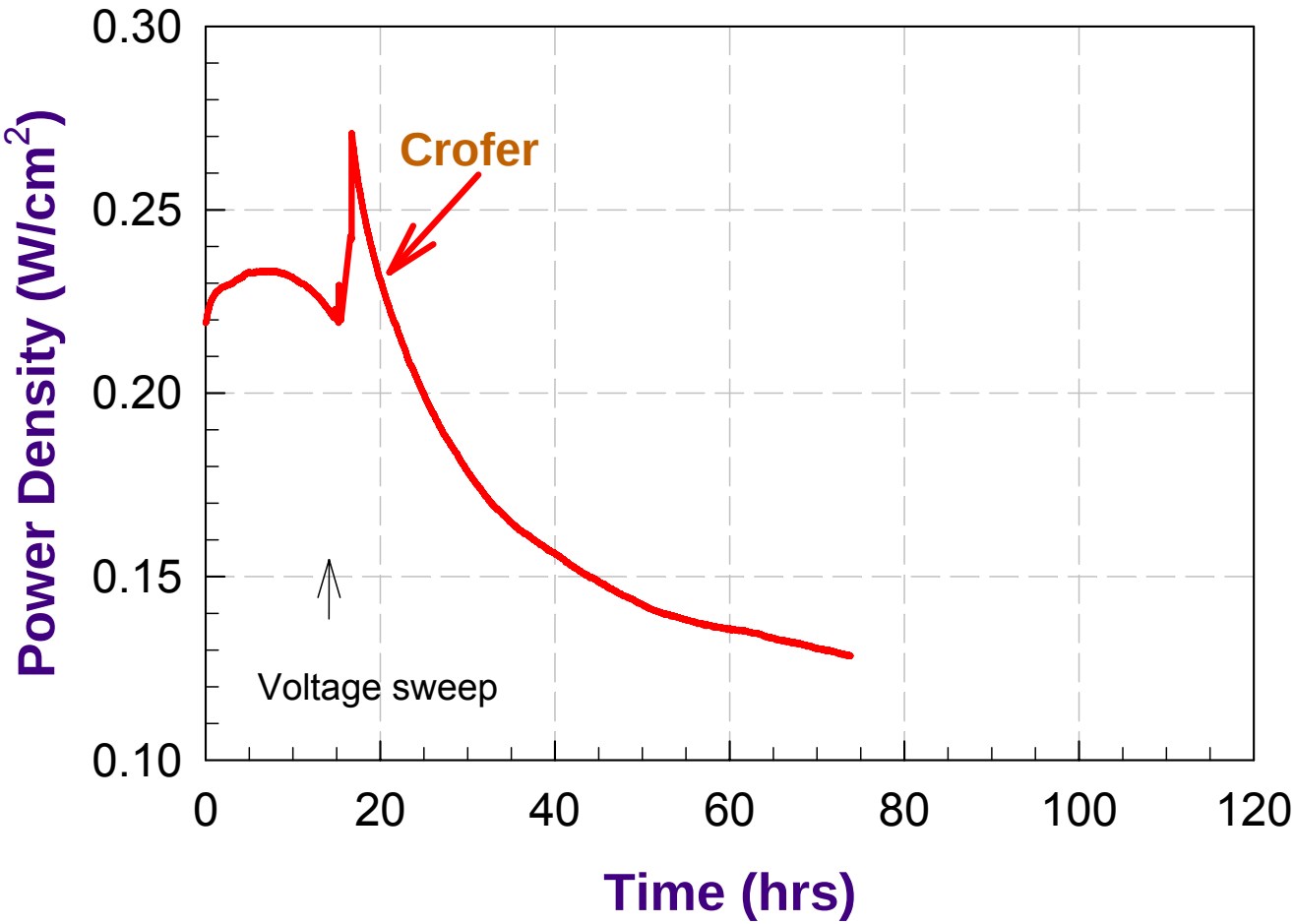
LABORATORY SCALE SOFC TESTING: OPERATING CONDITIONS

- **Heated to 800ºC (2hrs)**
  - ➢ N_2 on anode side: air+3%H_2O on cathode side
- **800ºC (2hrs)**
  - ➢ 10%H_2/90%N_2 mixture on anode side
- **Cell Operation**
  - ➢ Fuel: 97% H_2/3%H_2O at 400 cm^3/min
  - ➢ Oxidant: air+3%H_2O at 1000 cm^3/min
  - ➢ Constant voltage: 0.7V
  - ➢ Periodic voltage sweeps: 1.1V to 0.V
- **Cathode Current Collector Surface Condition**
  - ➢ Untreated condition: polished (1 μm diamond)
  - ➢ Ce-treated condition: cleaned with scotch-brite® pad in water

CELL PERFORMANCE

0.7V/800°C; Fuel: H_2+3%H_2O; Oxidant: Air +3% H_2O

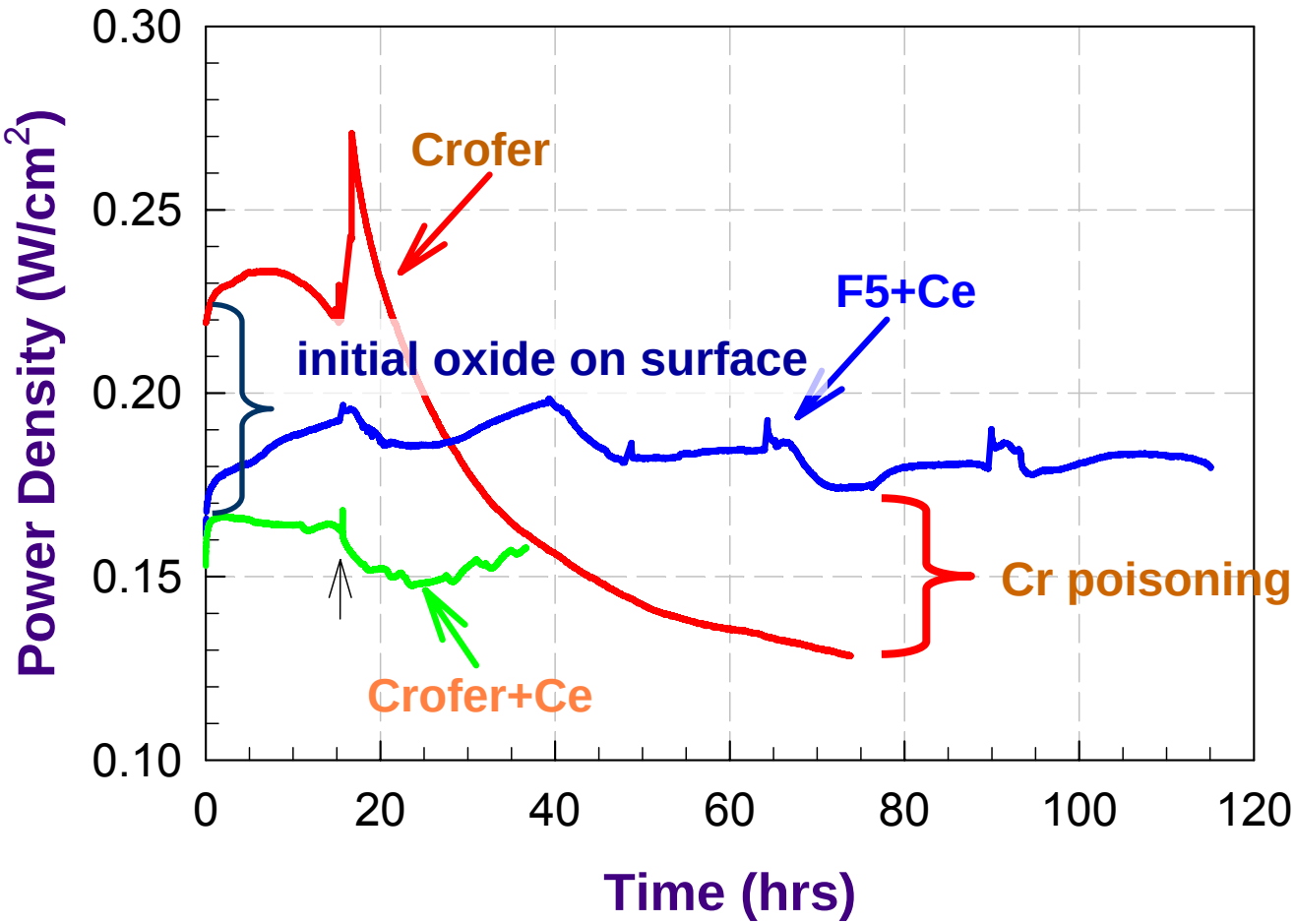
LSM Cathode/Fe-22Cr-0.5Mn Interconnect



CELL PERFORMANCE

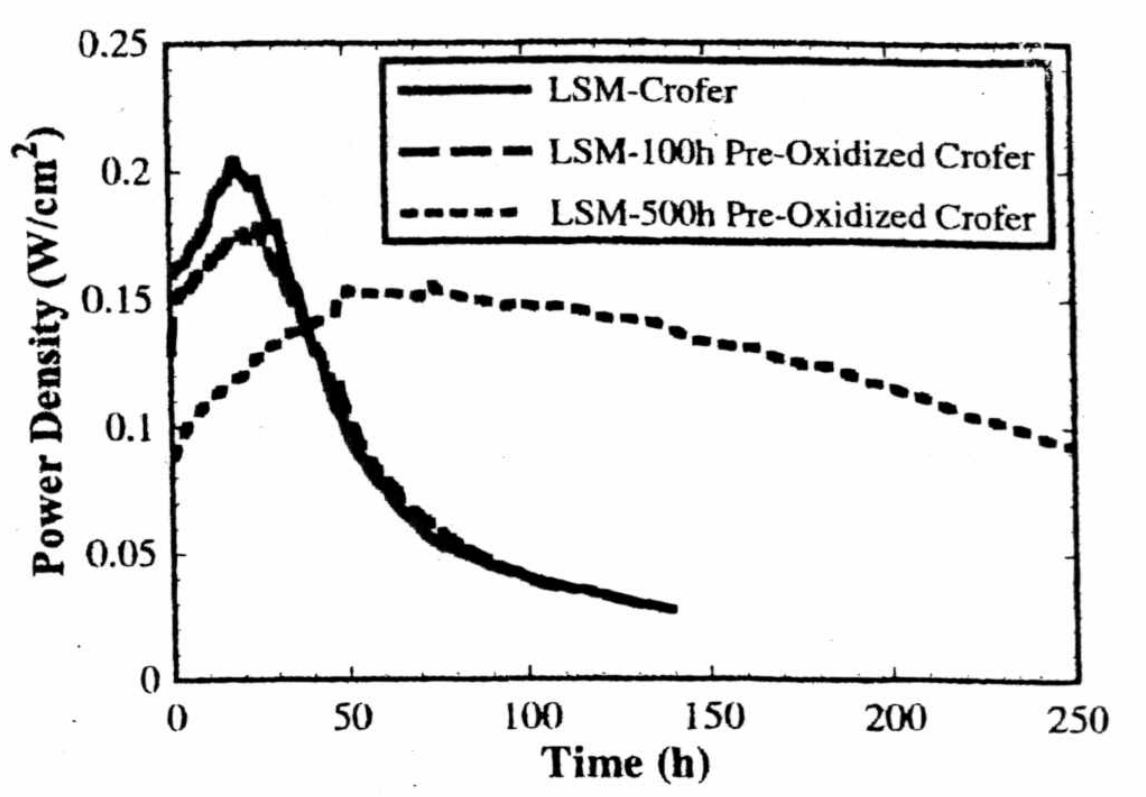
0.7V/800°C; Fuel: H_2+3%H_2O; Oxidant: Air +3% H_2O

LSM Cathode/Fe-22Cr-0.5Mn Interconnect



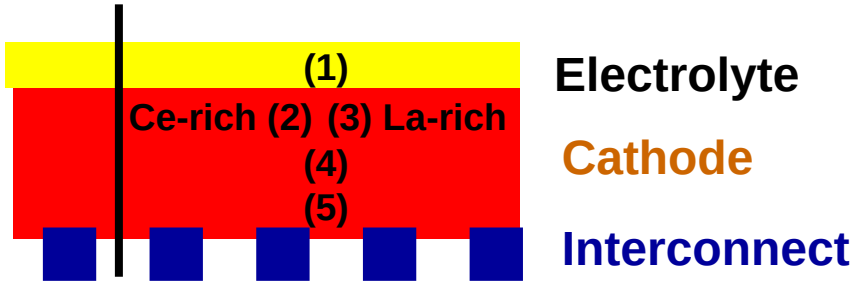
PRE-OXIDIZED CROFER 22APU CURRENT COLLECTORS: PNNL

- *S.P. Simner, Anderson, Xia, Yang, Pederson, Stevenson, J. Electrochemical Soc., vol 154 (4), pp. A740-A745, 2005*



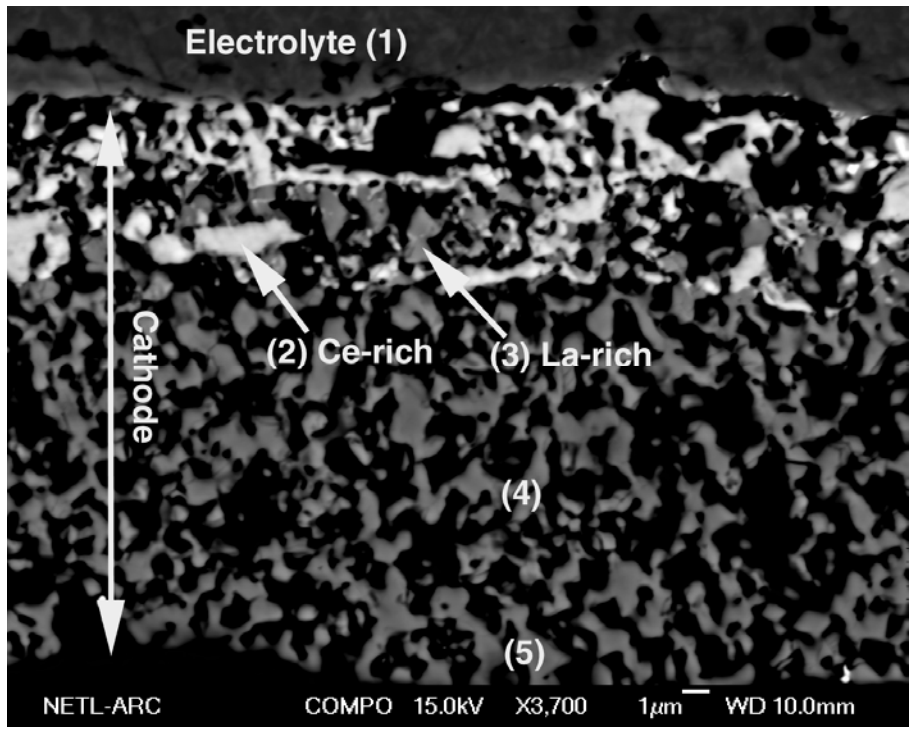
ANALYSIS OF Cr IN CATHODE

Under Channel



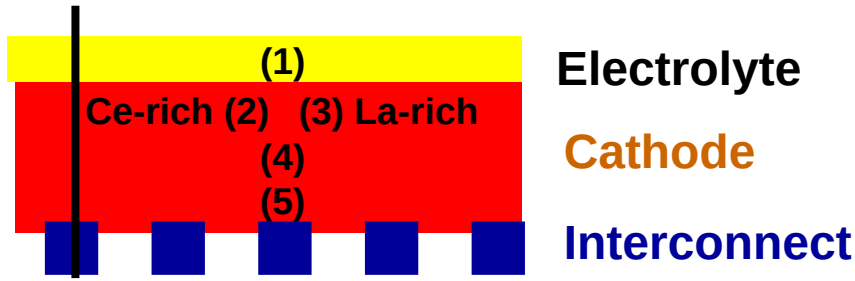
Cr composition by WDX (weight percent)

	Crofer (78 h)	F5+Ce (117 h)	Crofer+Ce (38 h)
(1)	0.00	0.00	0.00
(2)	*0.02*	*0.02*	*0.06*
(3)	*0.48*	*0.15*	*0.08*
(4)	0.08	0.08	0.11
(5)	0.09	0.09	0.08



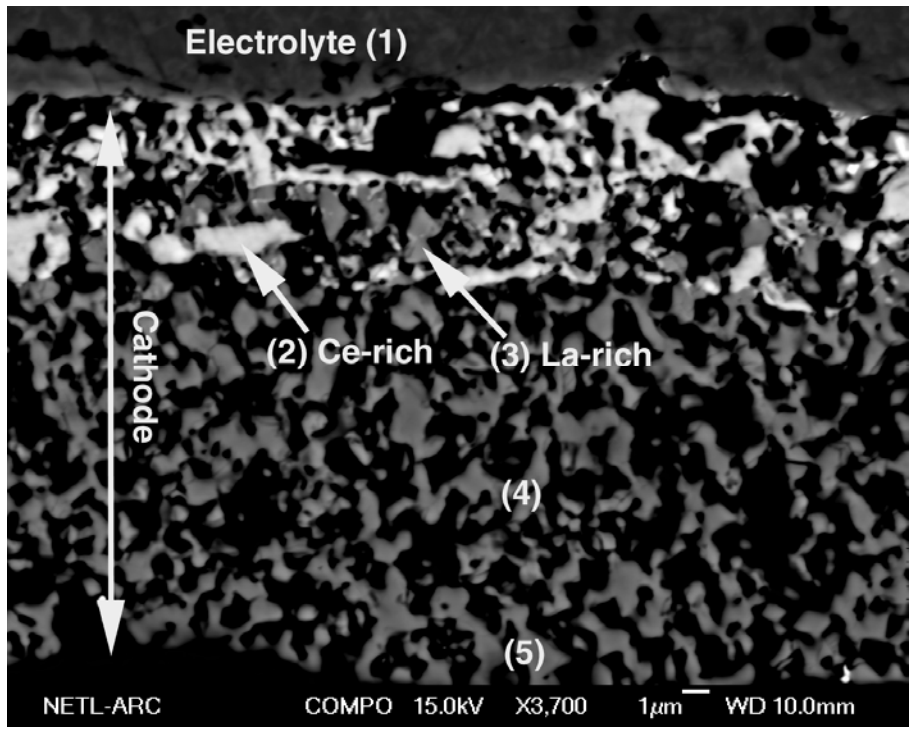
ANALYSIS OF Cr IN CATHODE

Adjacent Metal

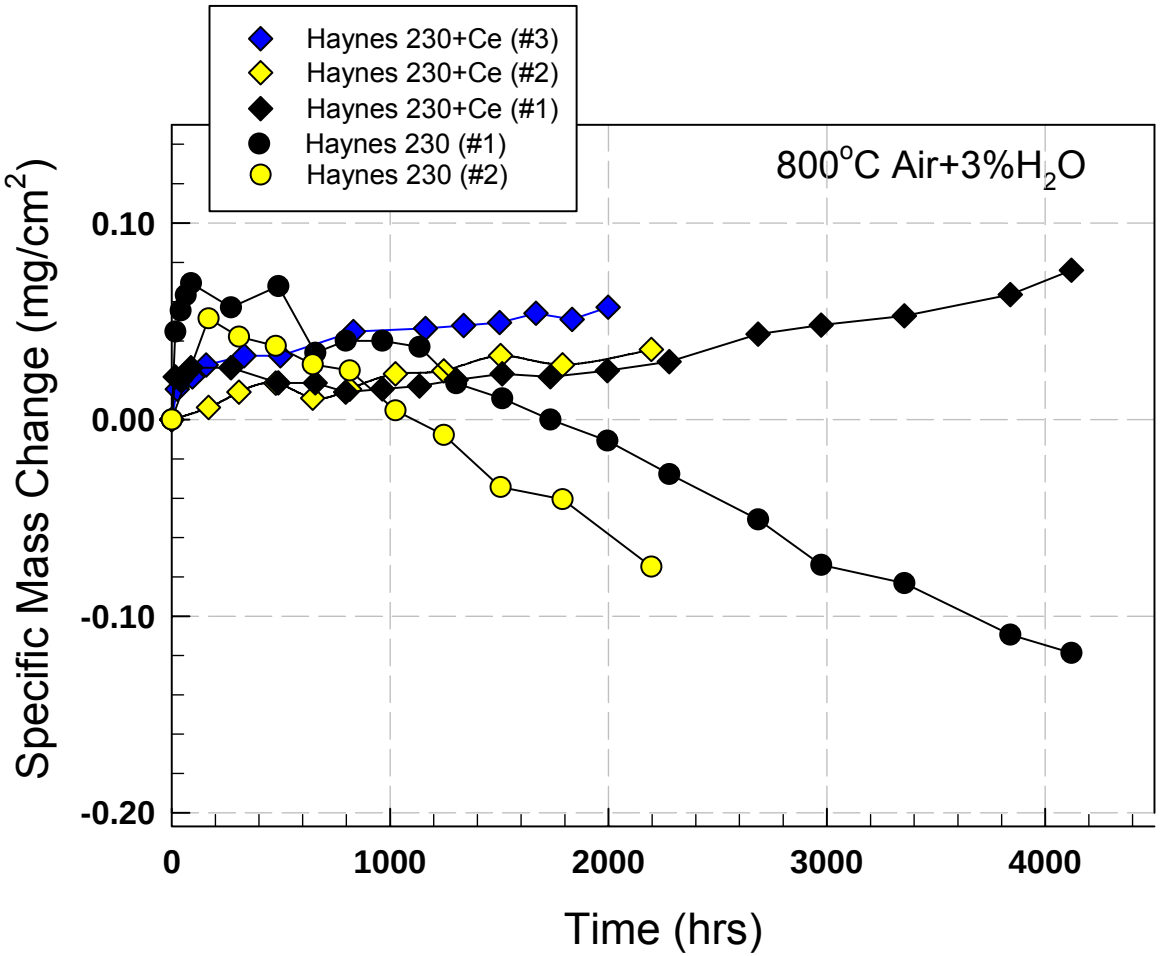


Cr composition by WDX (weight percent)

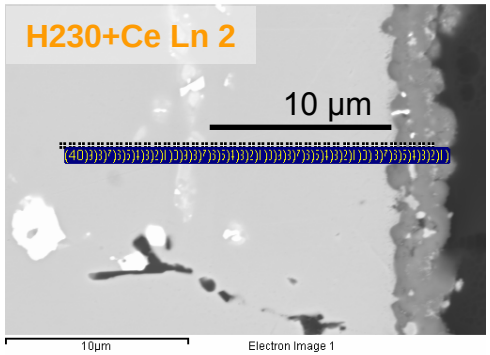
	Crofer (78 h)	F5+Ce (117 h)	Crofer+Ce (38 h)
(1)	0.00	0.00	0.00
(2)	*0.12*	*0.09*	*0.00*
(3)	*0.56*	*0.24*	*0.08*
(4)	0.09	0.14	0.09
(5)	0.13	0.17	0.10

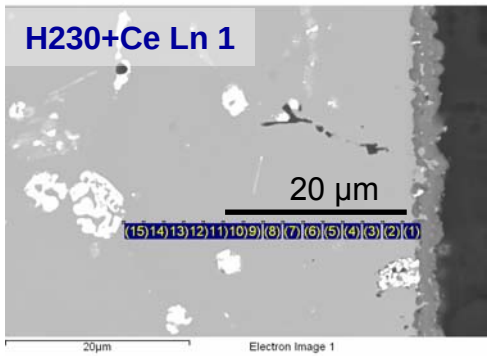


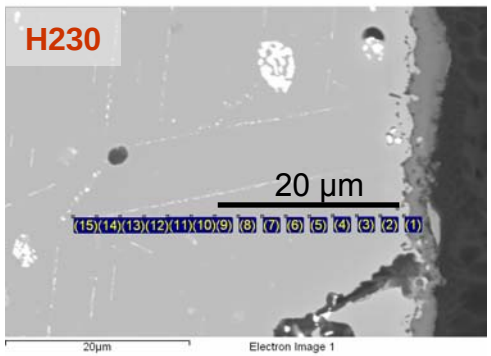
Haynes 230

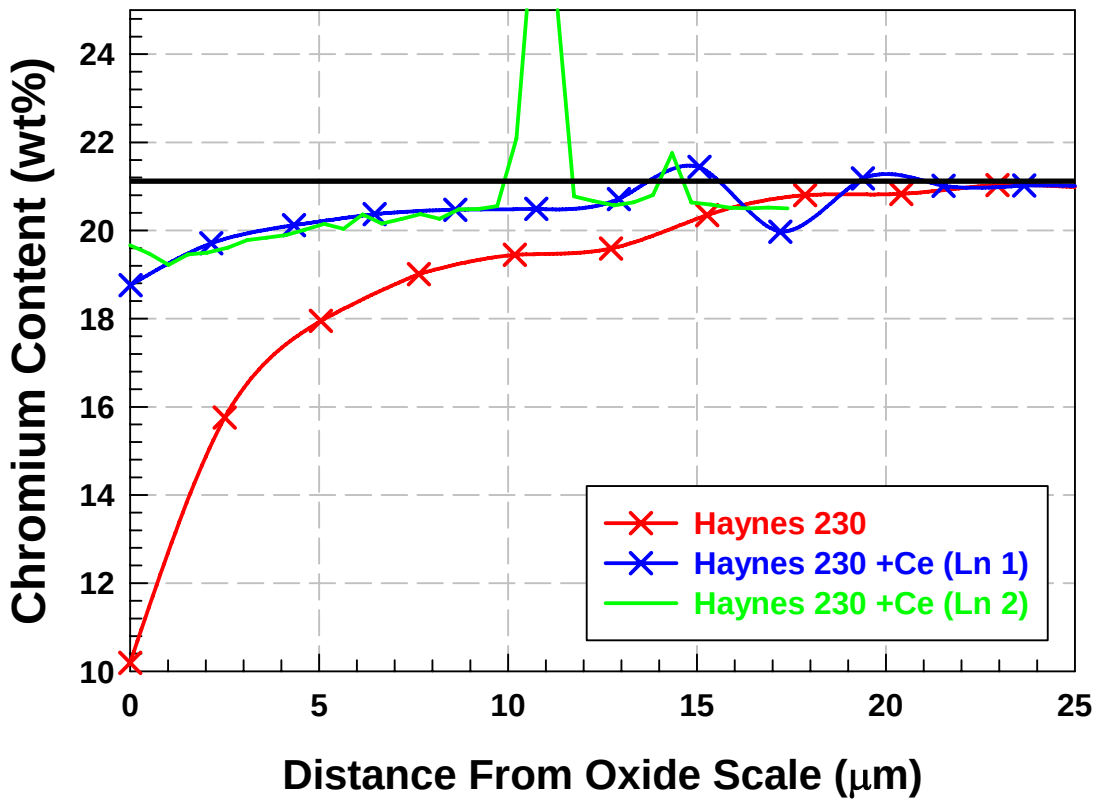

Haynes 230+Ce (#3)
Haynes 230+Ce (#2)
Haynes 230+Ce (#1)
Haynes 230 (#1)
Haynes 230 (#2)
800°C Air+3%H2O
Specific Mass Change (mg/cm2)
0.10
0.00
-0.10
-0.20
0
1000
2000
3000
4000
Time (hrs)

Cr-Depletion



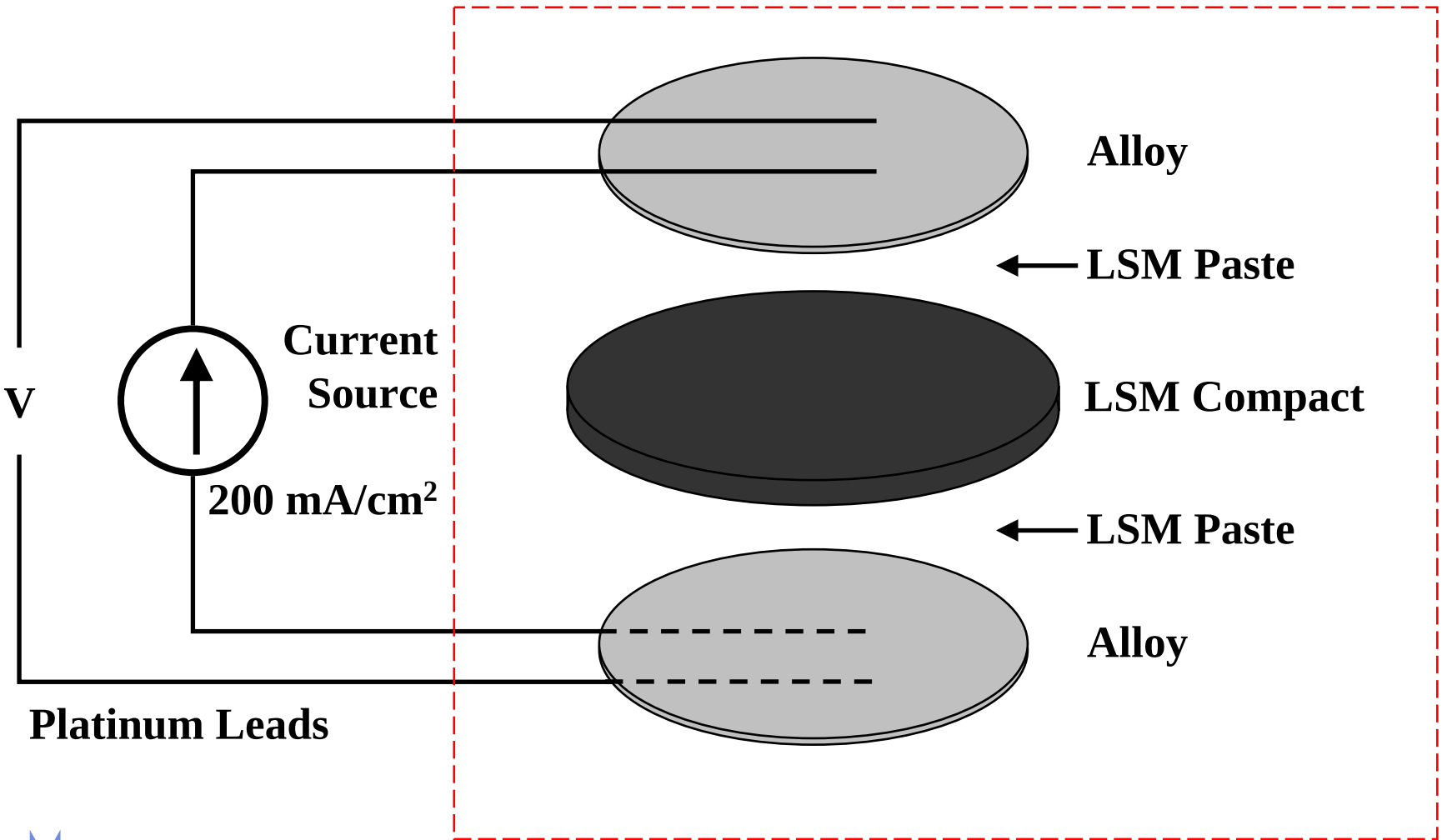




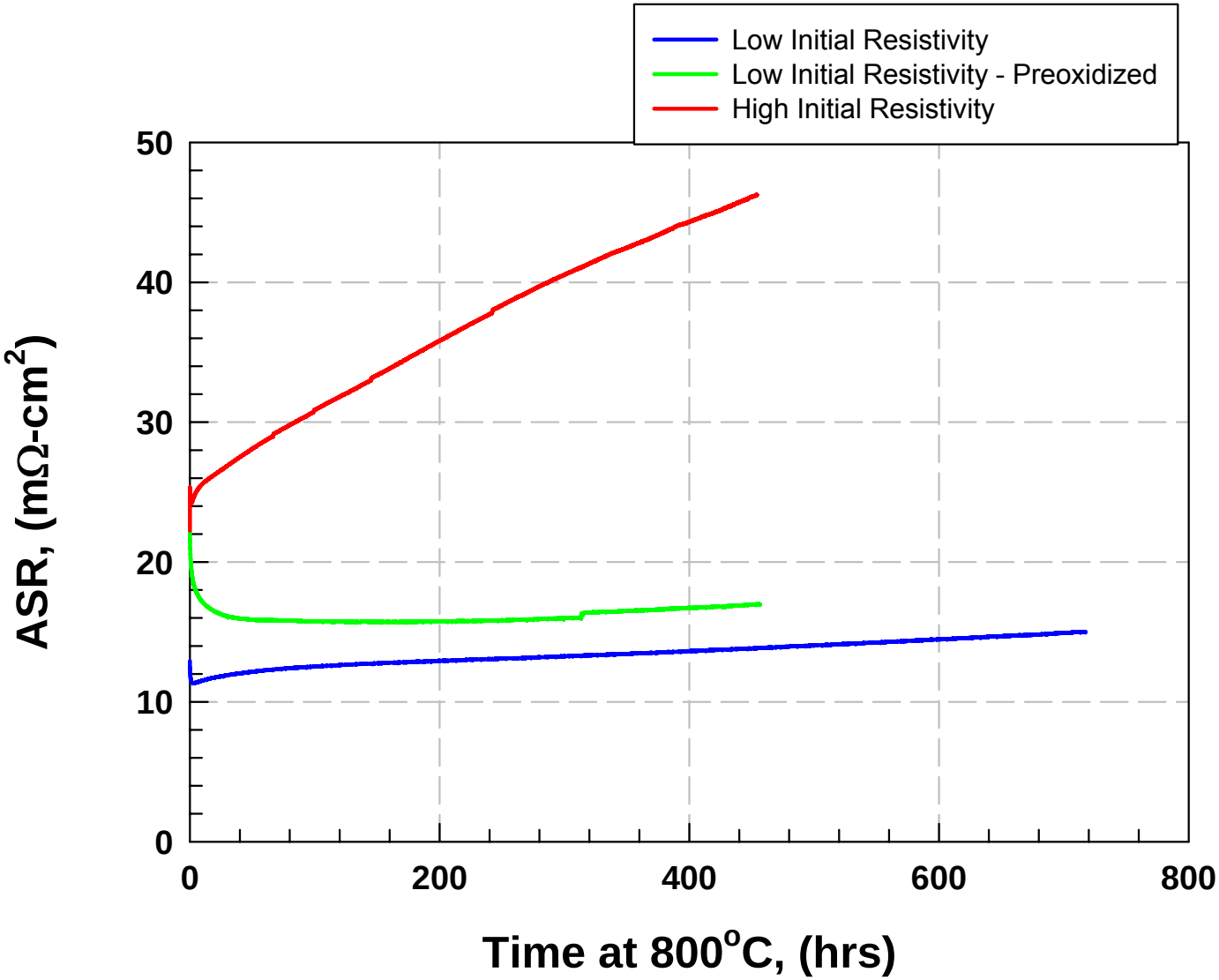


Chromium content determined by WDX analysis

Initial Conductivity: ASR Experimental Setup



ASR


Low Initial Resistivity
Low Initial Resistivity - Preoxidized
High Initial Resistivity
ASR, (mΩ-cm²)
50
40
30
20
10
0
0
200
400
600
800
Time at 800°C, (hrs)

SUMMARY

- **Ce-surface treatment Fe-22Cr-0.5Mn steels**
  - Improves oxidation resistance → thinner scales, less internal oxidation
  - Pre-oxidizes surface
  - Modifies scales w/ RE to get RE benefit upon subsequent oxidation.
- **Ce-surface treated interconnects in SOFC**
  - Act in a similar manner as pre-oxidized steels
  - Delays Cr poisoning
  - Longer duration testing required
- **Working on improving process to improve initial contact resistance.**