Oxidation of Interconnect Alloys in an Electric Field

Gordon R. Holcomb
David E. Alman
Thomas A. Adler
Paul D. Jablonski

National Energy Technology Laboratory
1450 Queen Ave. SW, Albany OR 97321

Materials Science & Technology

Cincinnati OH, October 16-19, 2006

NETL

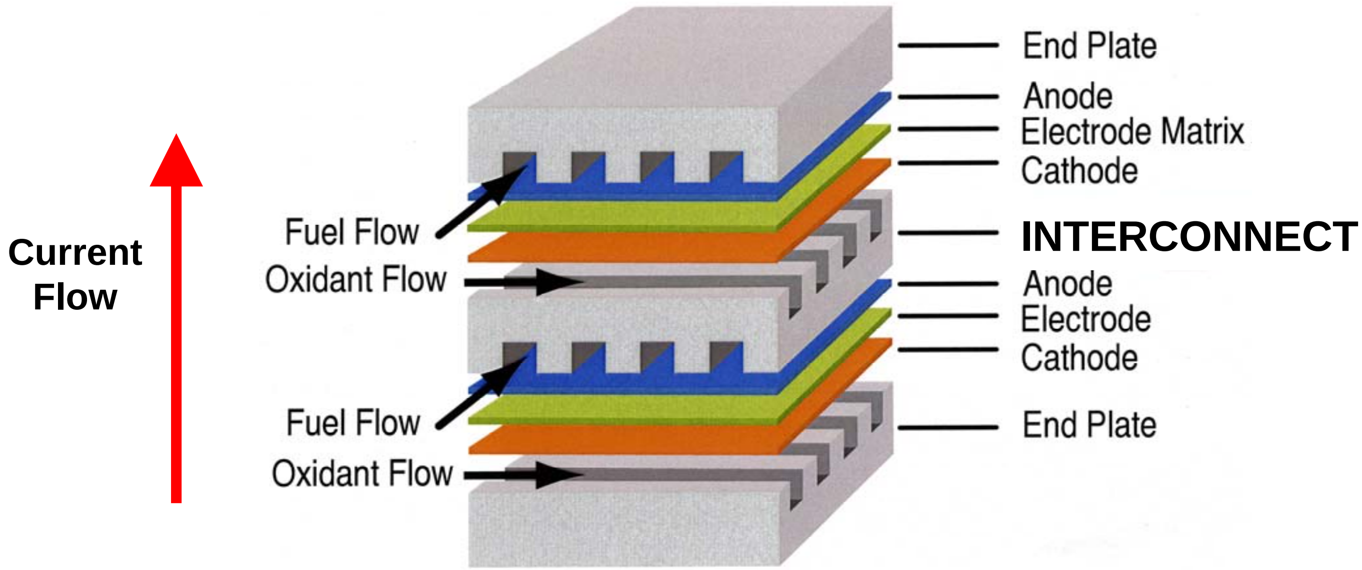
Office of Fossil Energy

Outline

- Introduction
- Research Goals
- Procedures
- Results
- Conclusions

Improving Oxidation Resistance of Alloys for SOFC Applicants

- **Ferritic stainless steel interconnect**
  - Driver for use is to lower cost of stack
  - Questions on performance over a 40,000 hr projected life SOFC span (USDOE-SECA program target)
    - particularly for temperature >700^{o}C



Research Goals

- **Determine the effect, if any, of electric fields on the oxidation of interconnect alloys**
- **Compare the effects between:**
  - EBrite, a Fe-Cr ferritic chromia former
  - Crofer 22 APU, a Fe-Cr ferritic chromia former with Mn and oxygen active additions (La)

Introduction

Current passing from the metal/oxide interface to the oxide/gas interface is + interface

Lattice Transport

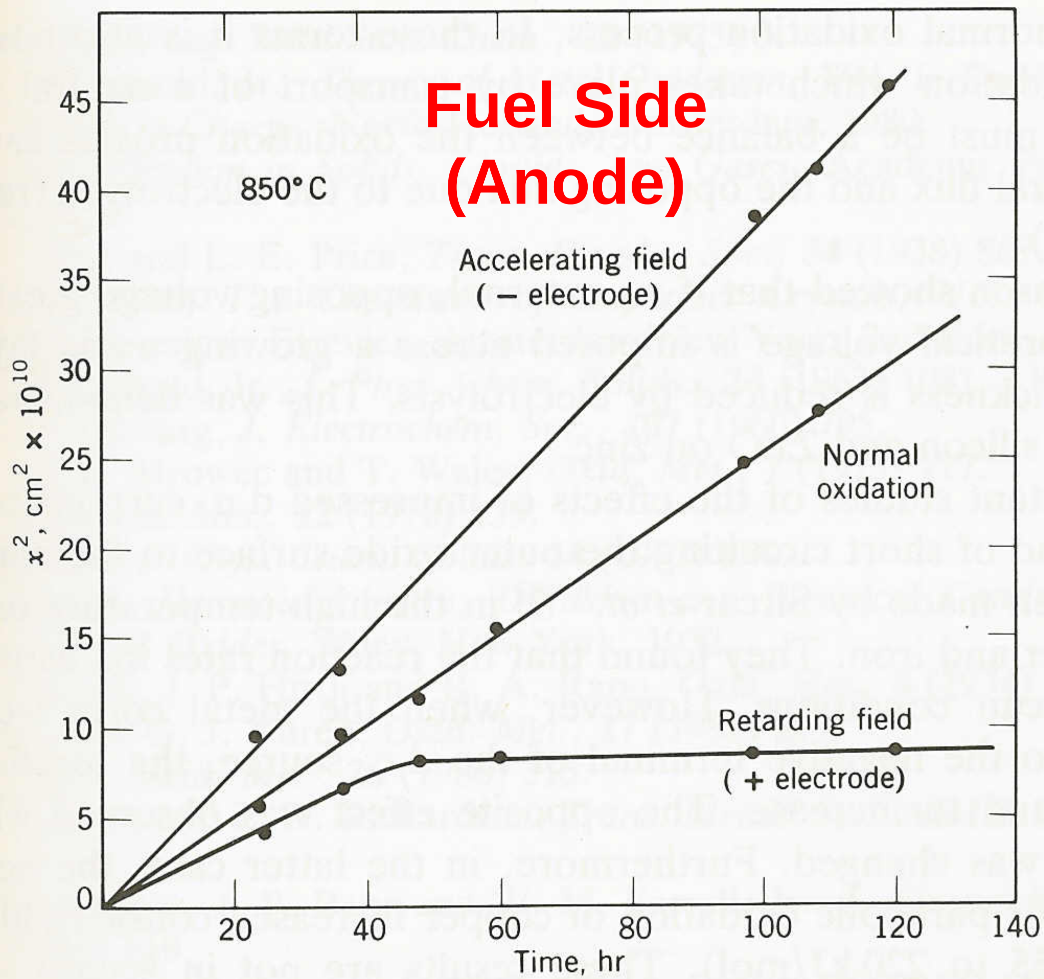


Fig. 6.14. Effect of electric fields on the oxidation of silicon at 850 °C. (After Jorgensen.[73–75])

Strong effect for oxides that are ionic conductors such as SiO_2

Chromia scales should have a much smaller effect

Air Side (Cathode)

Ionic Flux (rate of oxidation)

$$\frac{dn}{dt} = \left(\frac{dn}{dt}\right)_0 + \frac{t_{ion} I_{ext}}{|z_a| e b}$$

Subscript 0 = without an external current

t_{ion} = transport number for ionic conductivity

I_{ext} = Externally applied current

$z_a e$ = charge of the anion

b = the b in M_aX_b

Cr_2O_3 is an electrical semiconductor (t_{ion} is close to 0), so little to no direct effect from an electric field

Electric Field Effects

- Contrasting E-Brite with Crofer 22 APU
- E-Brite forms an essentially pure Cr_2O_3 scale
  - No effect expected
- Crofer 22 APU is more complex, with
  - $MnCr_2O_4$ outer scale
  - $(Al,Ti)_xO_y$ internal oxidation
  - Benefits from reactive element (La)
  - Could possibly see a change in scale or internal oxide morphologies due to electric field effects

{ *Stevenson, Yang, Singh and Meier, 2004* }

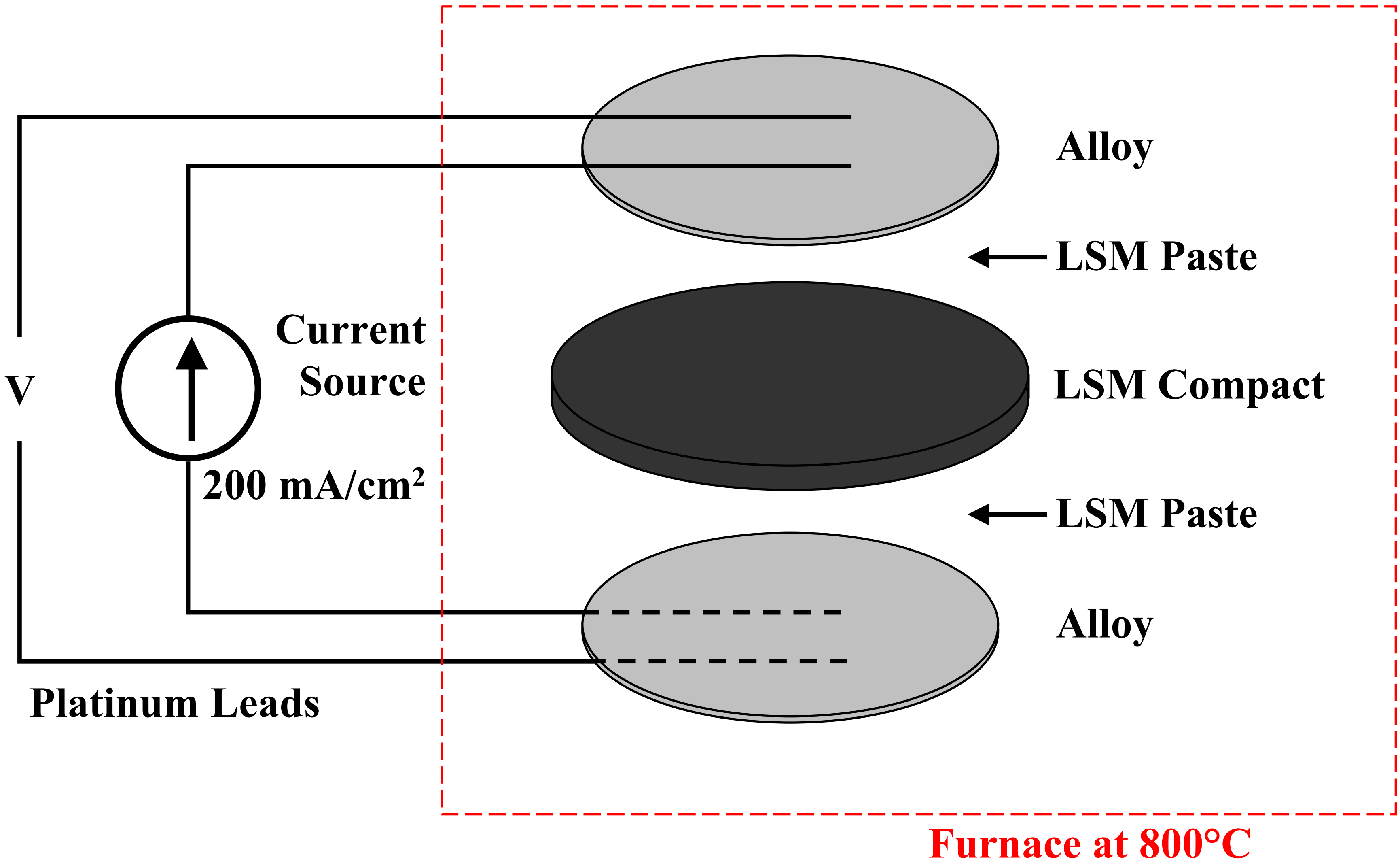
Alloy Composition (wt%) via XRF

	Fe	Cr	Mo	Mn	Si	Ti	Al	Ni
EBrite	72.28	26.13	1.00	0.036	0.13	<0.001	0.04	0.19
Crofer	75.99	22.79	0.003	0.45	0.12	0.098	0.11	0.34

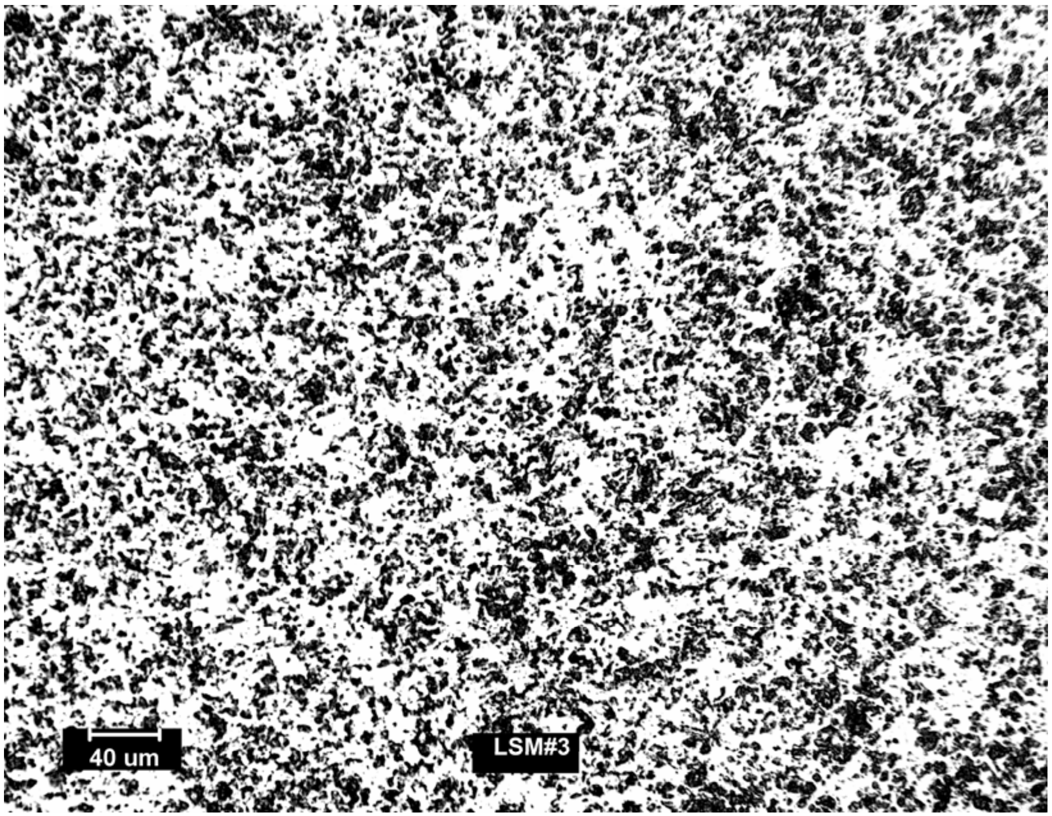
	Co	W	Nb	Cu	Ta	V	P	La*
EBrite	0.025	<0.01	0.12	0.004	<0.01	0.036	<0.01	---
Crofer	0.018	<0.01	<0.01	0.058	<0.01	0.026	<0.01	0.10

La analysis via GDMS

Schematic of Experimental Setup



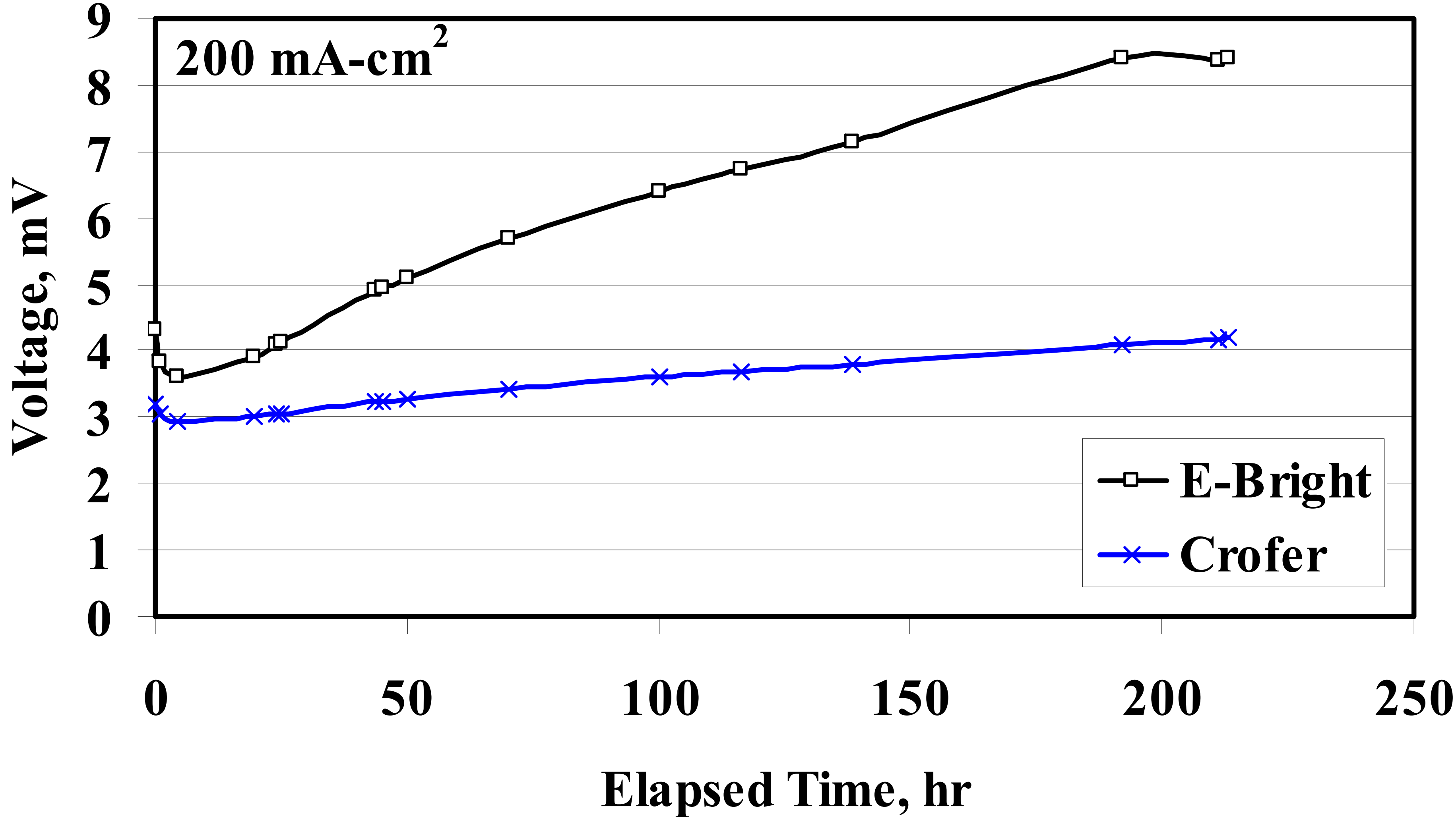
LSM Compact Porosity



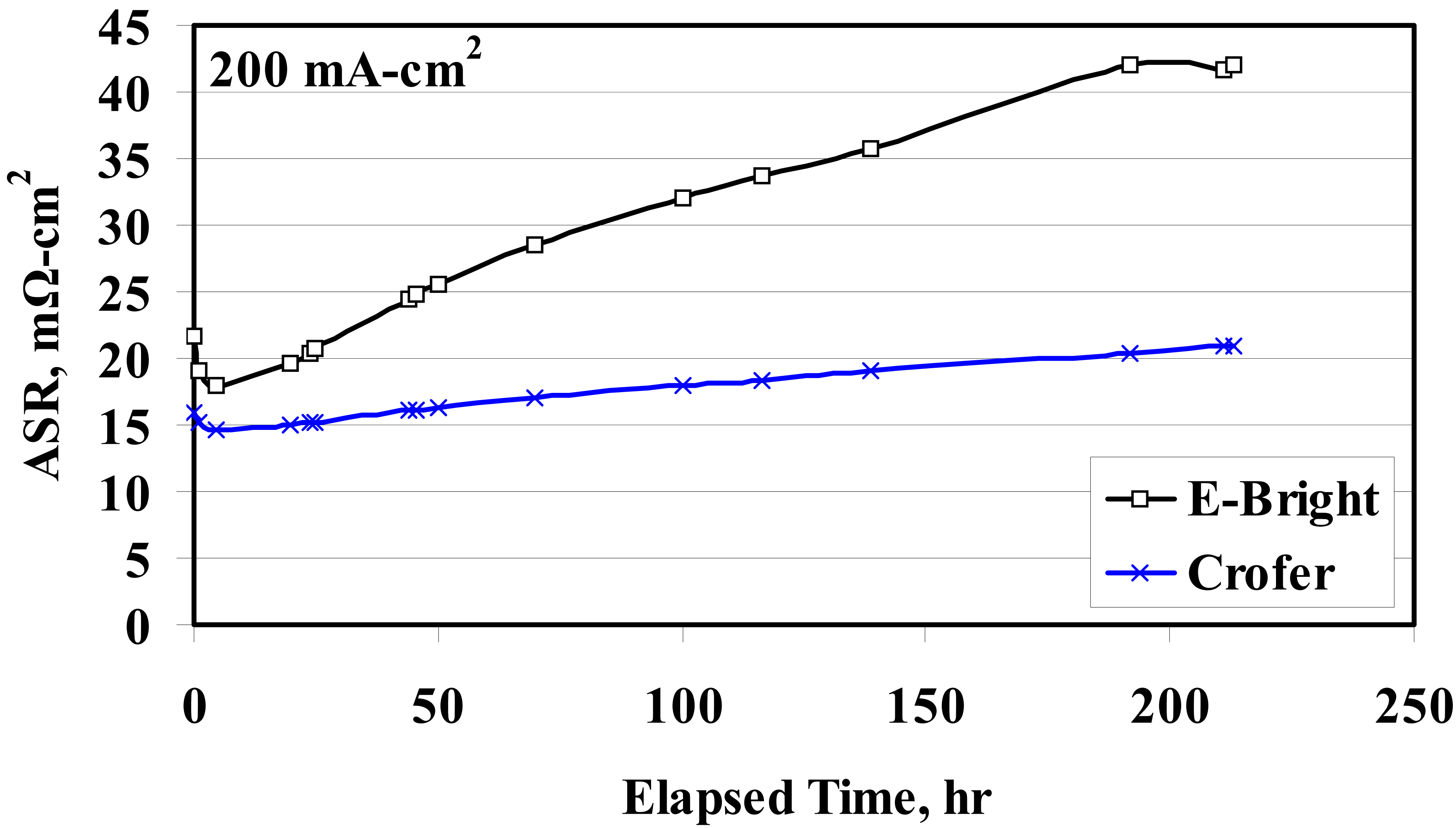
Black areas are pores

- $(La_{0.85}Sr_{0.15})_{0.98}MnO_3$
- 40µm average size
- LSM powder pressed at 260 kg/cm^2
- Fired at 1200°C for 24 hours in air
- Dry Polish to 1000 grit
- 55% Dense

Voltage vs Time

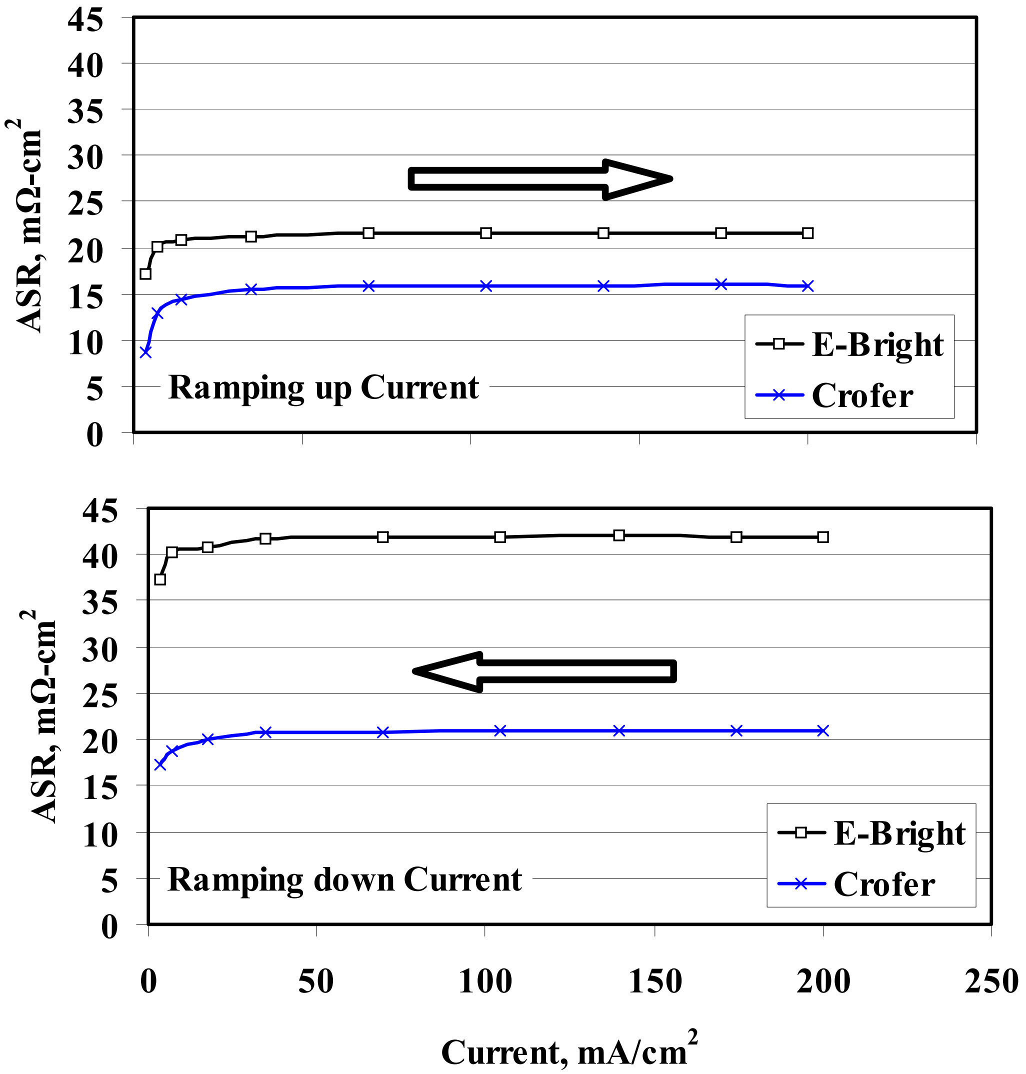


ASR vs Time

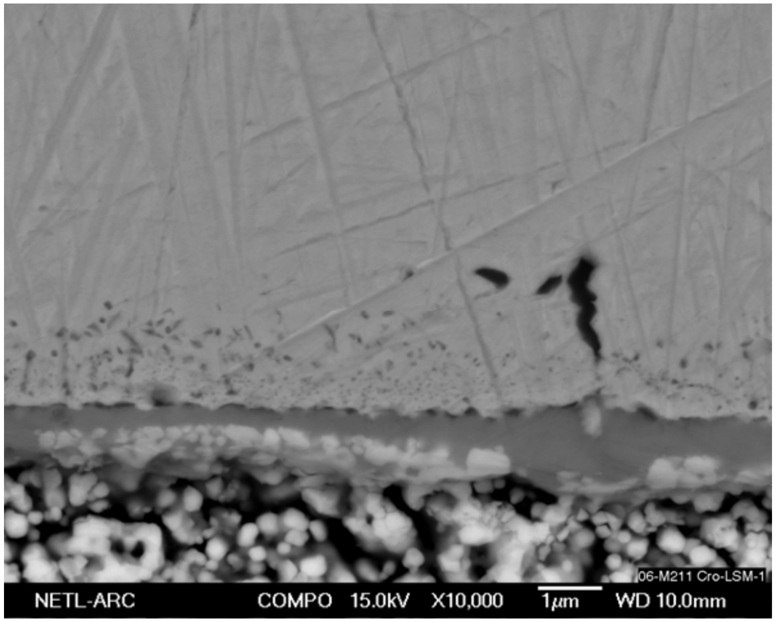


200 mA-cm2
ASR, mΩ-cm2
45
40
35
30
25
20
15
10
5
0
0
50
100
150
200
250
Elapsed Time, hr
E-Bright
Crofer

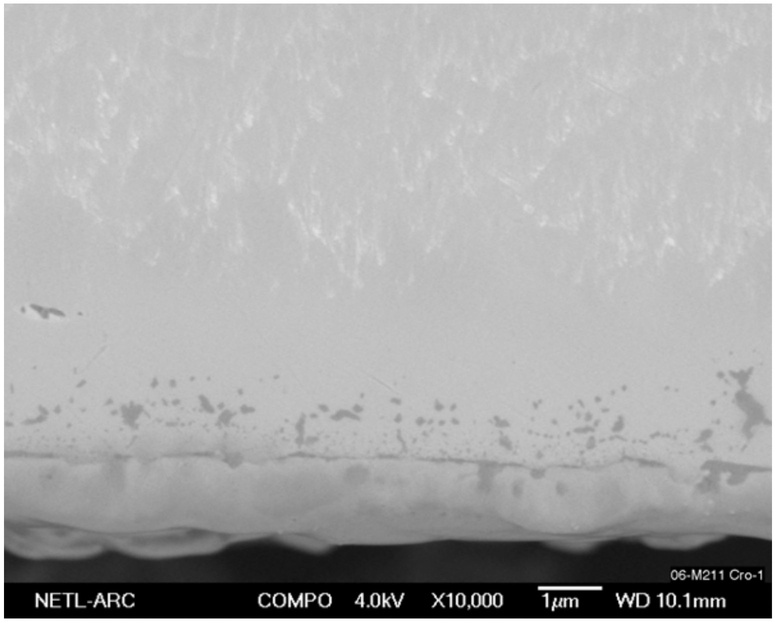
ASR vs Current (before and after)



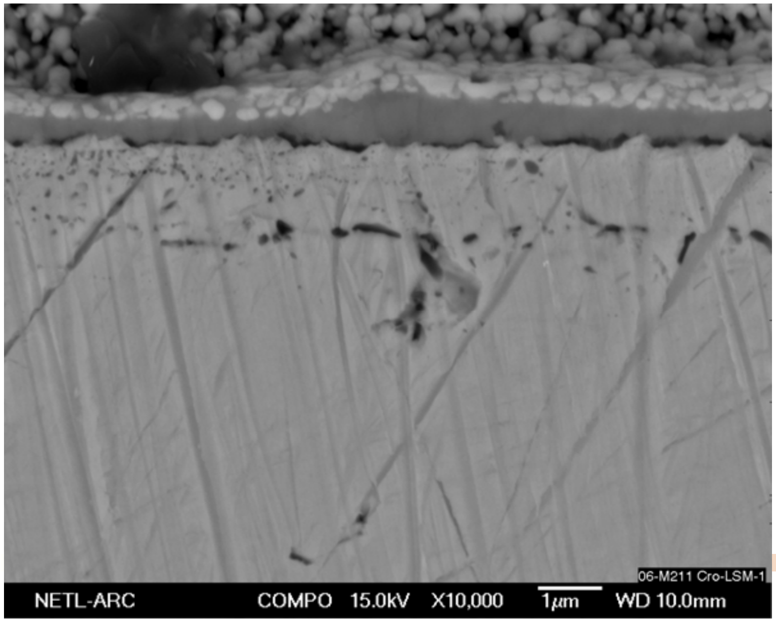
Crofer



200 mA/cm²

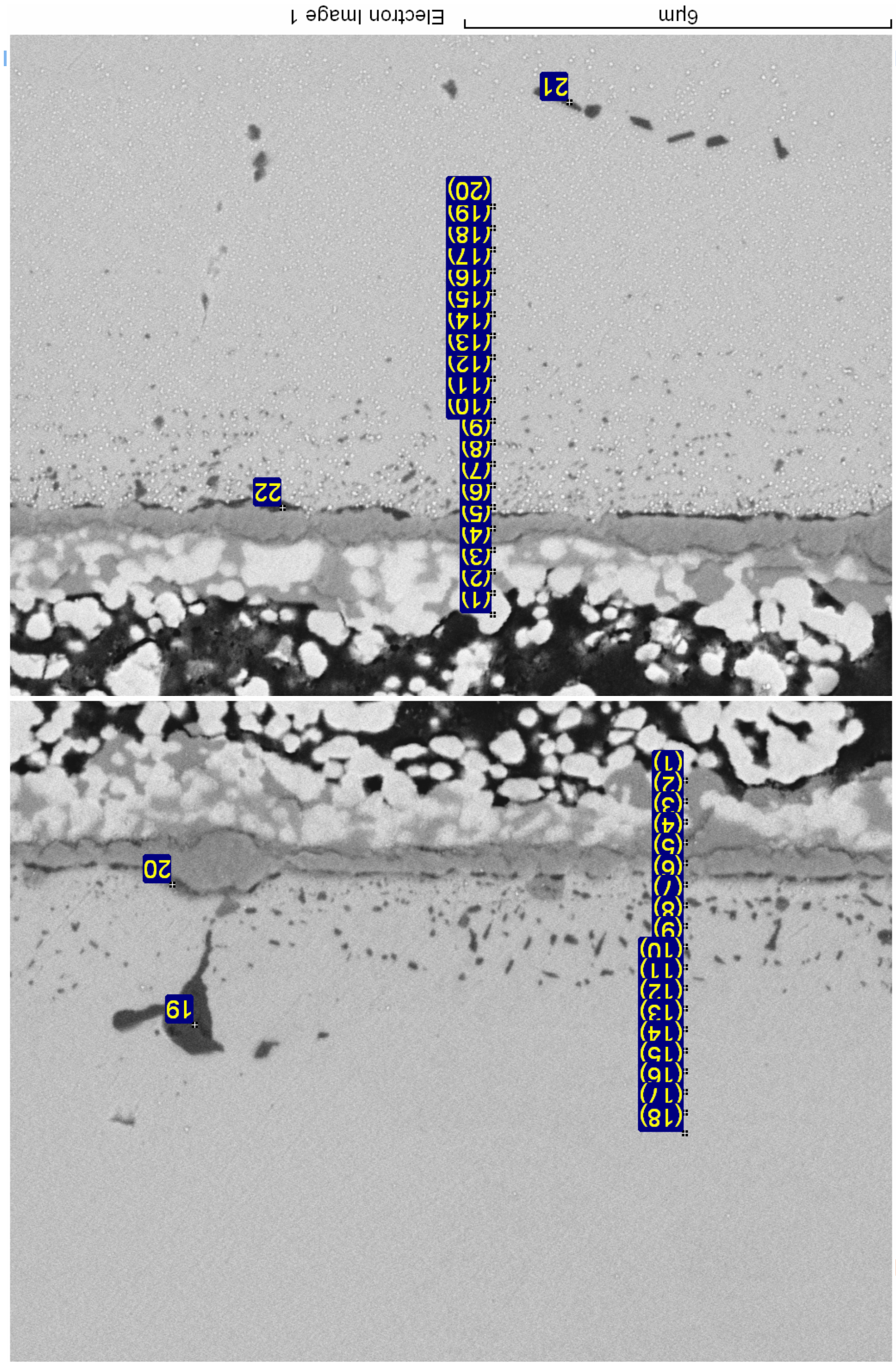


No Current or LSM

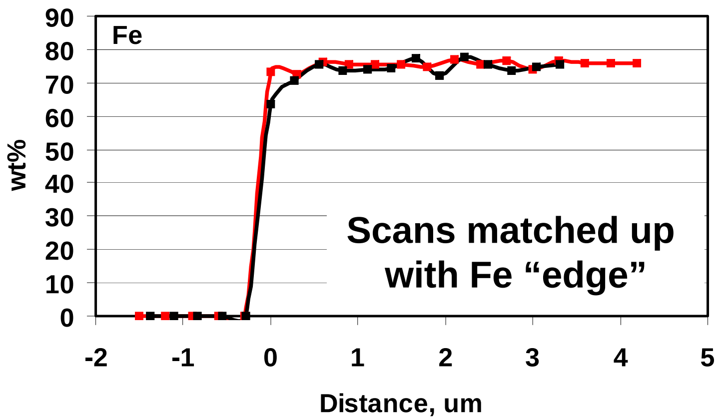


- **Incorporation of LSM paste into scale**
- **Similar morphologies**
  - More dark phase (SiO_2) right next to metal on lower left compared to upper left

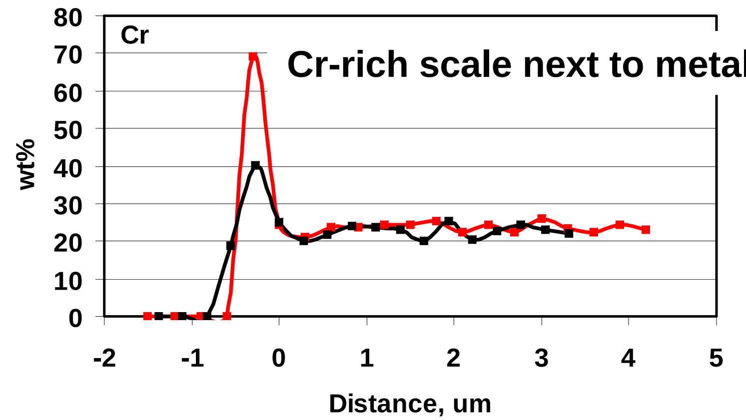
Crofer


6µm
Electron Image 1
(1)
(2)
(3)
(4)
(5)
(6)
(7)
(8)
(9)
(10)
(11)
(12)
(13)
(14)
(15)
(16)
(17)
(18)
(19)
(20)
19
20
21
22

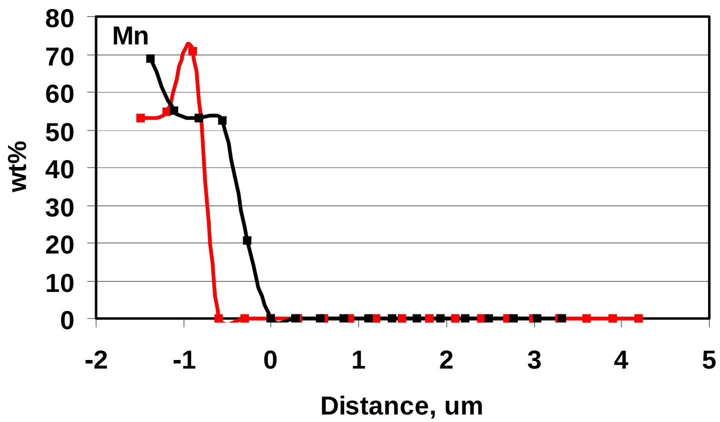
Crofer



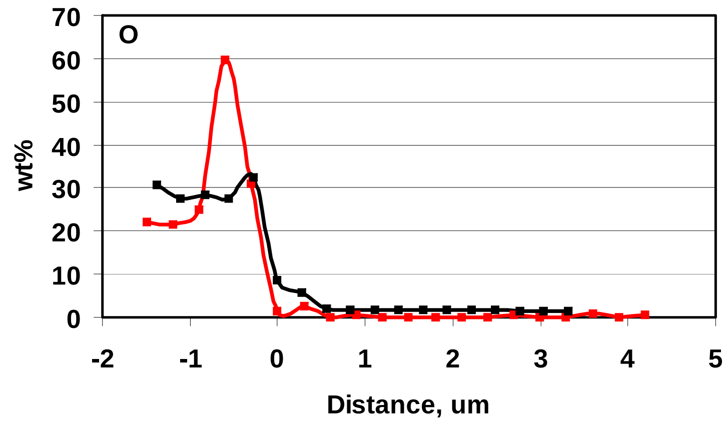
Fe
Scans matched up with Fe "edge"
wt%
Distance, um



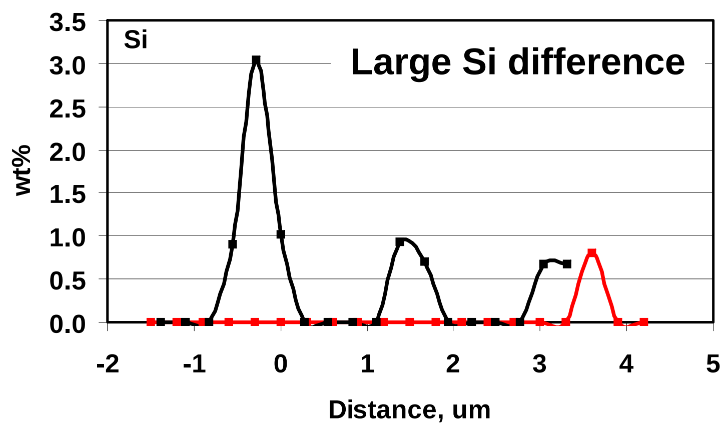
Cr
Cr-rich scale next to metal
wt%
Distance, um



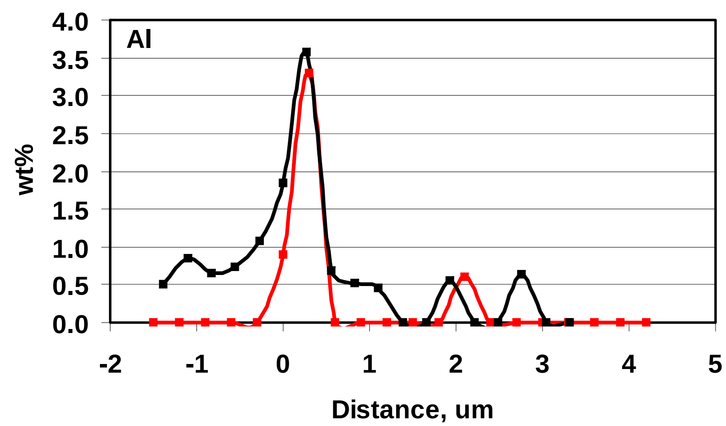
Mn
wt%
Distance, um



O
wt%
Distance, um

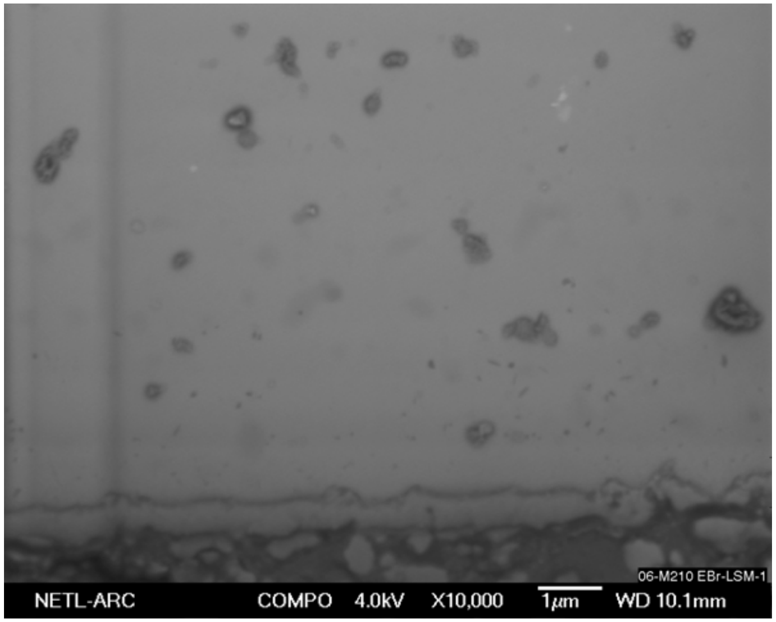


Si
Large Si difference
wt%
Distance, um



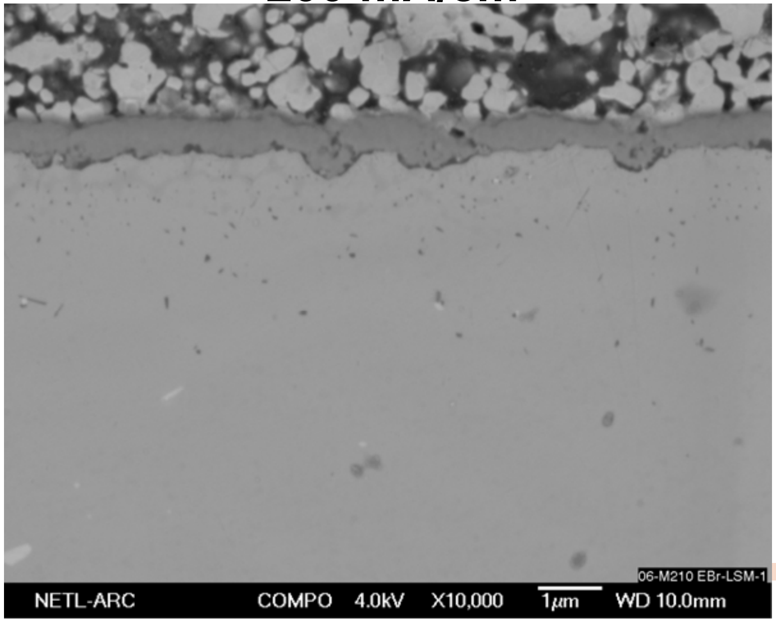
Al
wt%
Distance, um

EBrite

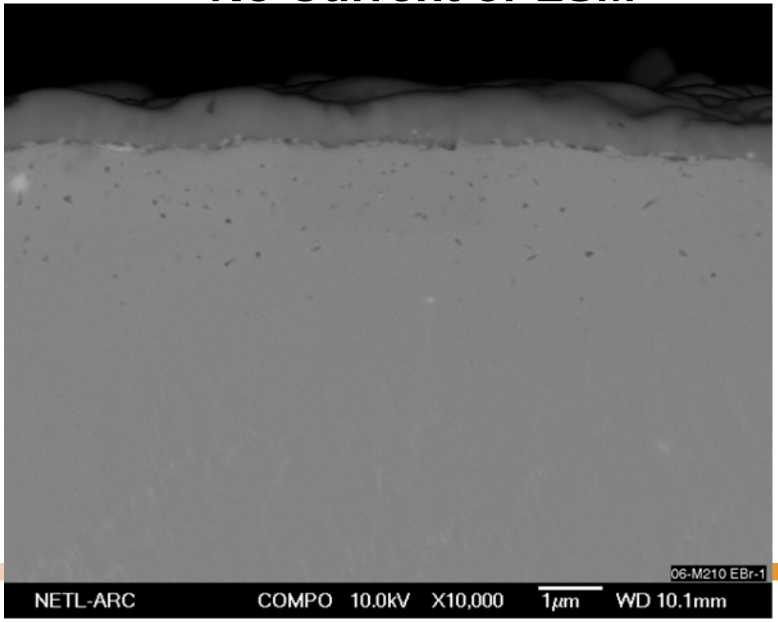


- **Much less incorporation of LSM paste into scale than with Crofer**

200 mA/cm²



No Current or LSM



Future Work

- **Investigate the effect of barrier coatings on the growth of oxides and ASR of SOFC interconnect materials.**
- **Coatings applied by screen-printing.**
- **Perovskite coatings such as**
  - $La_{0.8}Sr_{0.2}CoO_3$
  - $La_{0.8}Sr_{0.2}Co_{0.5}Mn_{0.5}O_3$
  - $La_{0.8}Sr_{0.2}MnO_3$
- **Spinel coatings such as**
  - $(Mn,Co)_3O_4$
- **Applied to interconnect materials such as Crofer 22 APU and J5. With and without Ce surface treatments**

Summary

- **Applied electric field can change the amount of SiO_2 that forms at the base of the scale**
  - Would change ASR behavior
  - Highlights the need for reduced Si in these alloys
- **With Crofer the LSM paste is incorporated into the oxide.**
  - Could be indicative of an outward growing scale
  - Increased Mn levels in the scale lowers Cr activity and so should reduce Cr vaporization