Ceramic Interconnects / Coatings

SECA Core Technology Program
SOFC Interconnection (IC) Technology Meeting
Argonne National Laboratory, Chicago IL
July 28-29, 2004

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

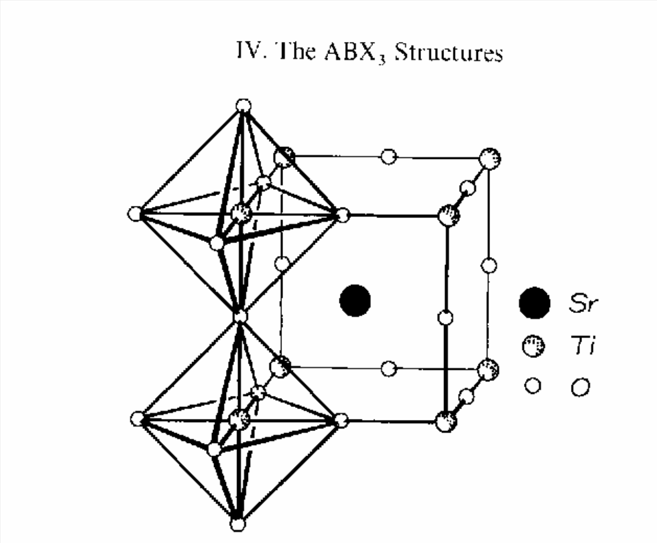
Interconnect Requirements

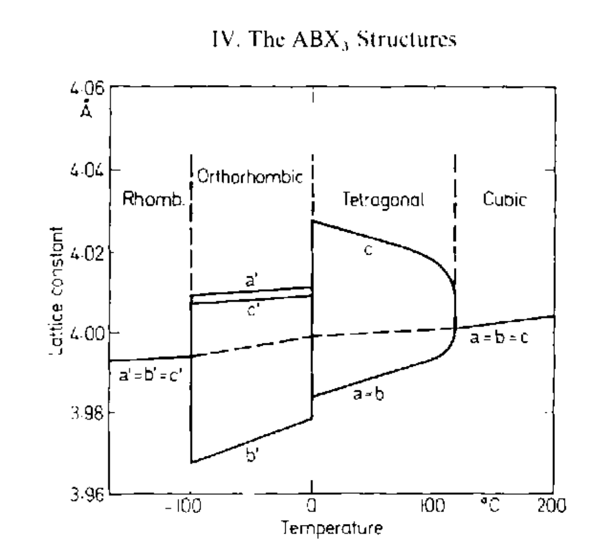
- Thermal expansion match with SOFC components
- Stability over operating pO_2 range (0.2 to 10^{-18} atm)
- High electronic conductivity in air and fuel
- Gas impermeability
- Process compatibility
- Mechanical integrity
- Low material and fabrication costs
- Negligible non-electronic migration

Interconnect Materials

- Two classes of interconnect materials
  - Ceramic
    - suitable for high temp. operation (900 - 1000 C)
    - Electronic conductivity a strong function of temp.
  - Metallic
    - suitable for 650 - 800 C operation
    - Oxidation is a major problem at higher temp.

Introduction and Background





Typical Compositions of interest

- La(Sr)MnO_3 - Cathode
- La(Sr)CoO_3 - Cathode
- La(Sr)CrO_3 - Interconnect
- La(Sr)GaO_3- Electrolyte

- Good Conductivity (ionic, electronic)
- OXYGEN NONSTOICHIOMETRY)

- Good Catalytic Properties for Oxygen Exchange

- CTE flexibility (8.5 - 18.0 ppm / °C)

- Chemical Stability to Severe Conditions (LSCr)

Interconnect Requirements

- Thermal Expansion Match with SOFC components
- Stability over operating pO_2 range
- High electronic conductivity in air and fuel

$LaCrO_3$ meets the necessary electrochemical properties

- Gas Impermeability
- Process Compatibility
- Mechanical Integrity

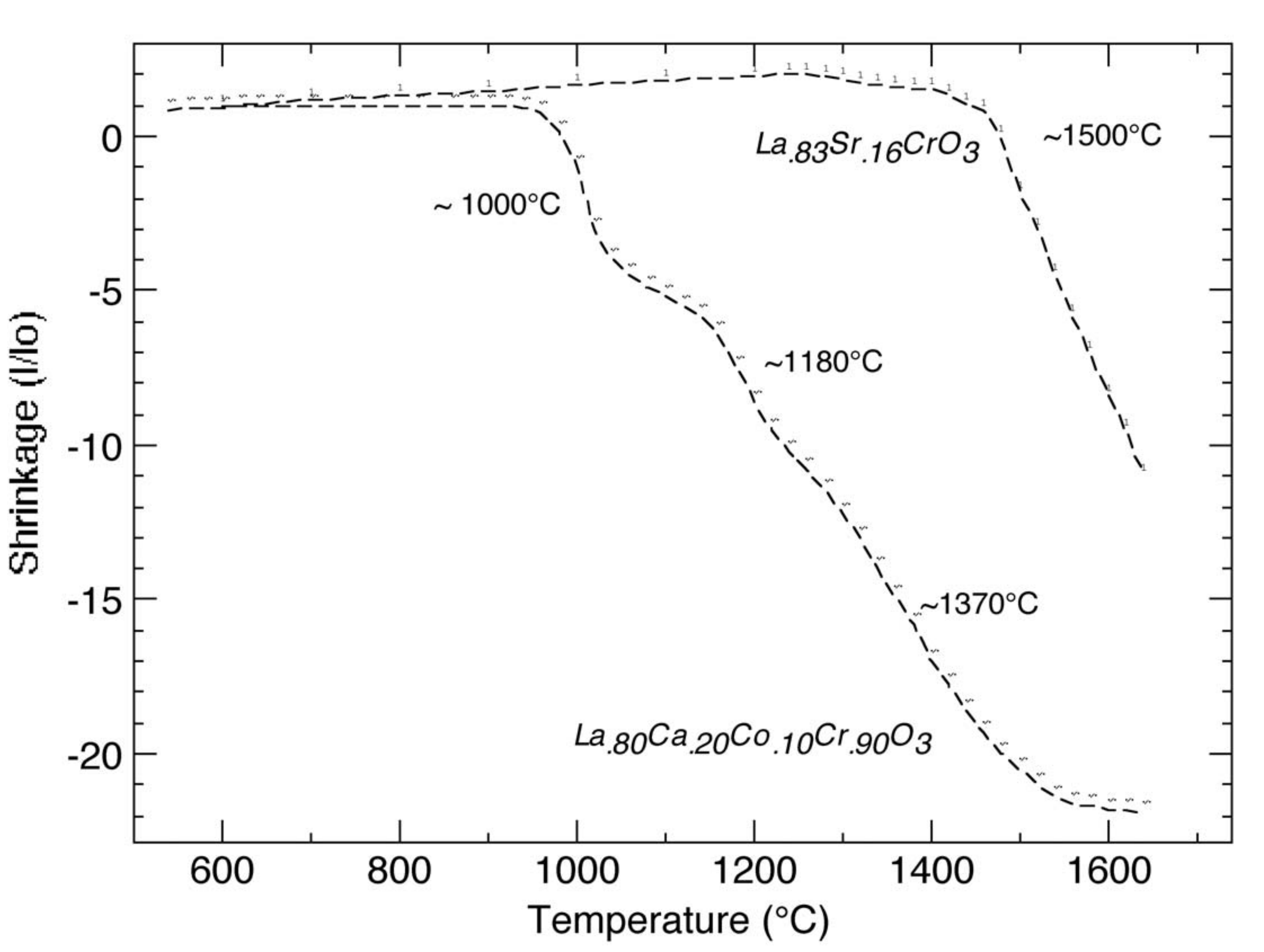
Challenges & Options in Fabrication

- Difficult to sinter due to
  - High Temperature requirements - typically ~ 1700 C
  - control of CrO_3 volatilization - Air Sintering is the preferred option
  - capital and operational cost
- Options
  - Liquid Phase Sintering through addition of low melting eutectic
  - Transient liquid phase sintering in the chromite system

Lower Temperature Air Sintering

- Addition of Ca and Co promotes liquid phase sintering
- Lower Sintering Temperature ~ 1450°C
- High Conductivity > 30 S/cm compared 10 S/cm for Sr doped LCr

Sintering Characteristics of $LaCrO_3$

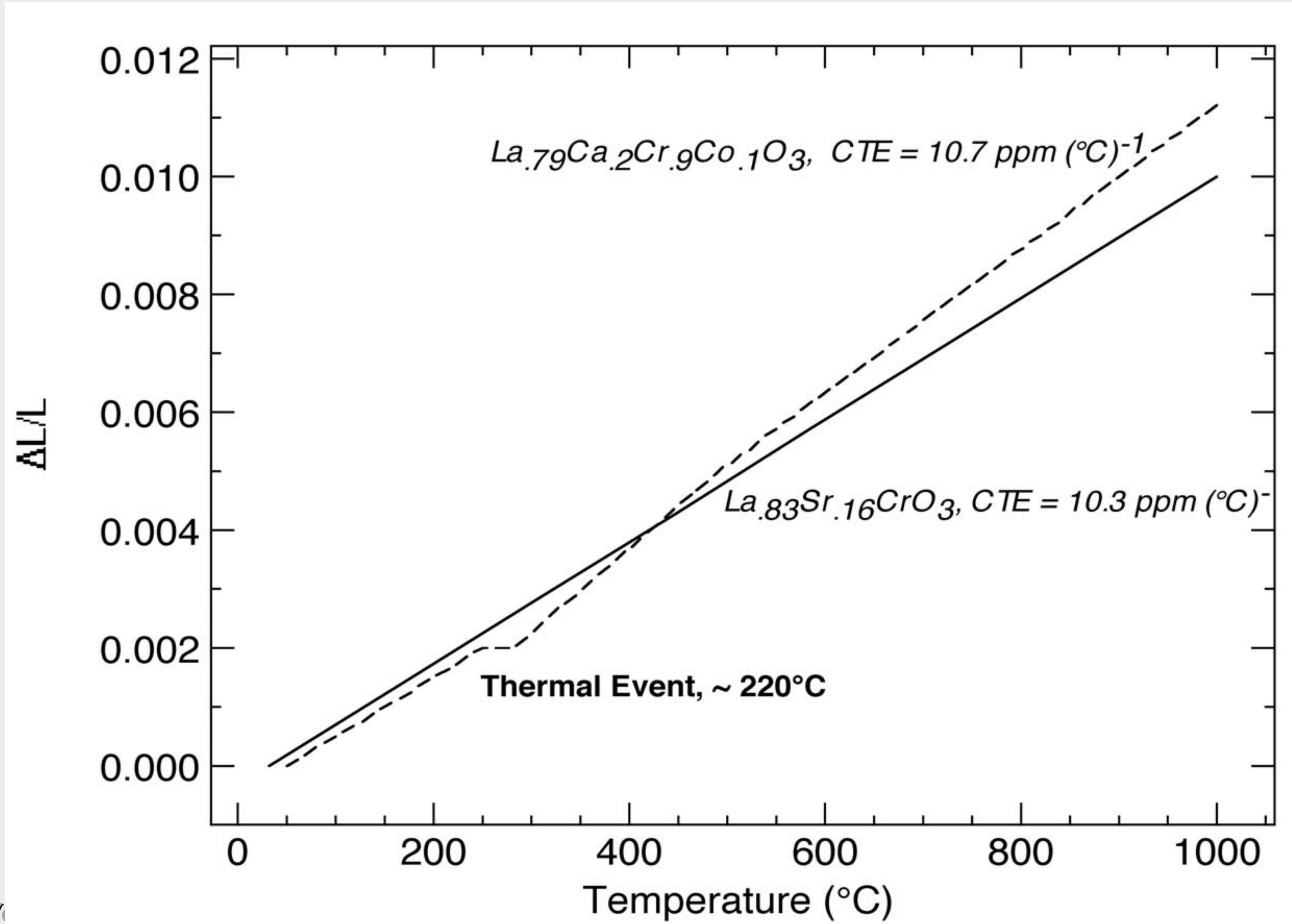


ceramatec®
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Evaluation of Interconnect Compositions

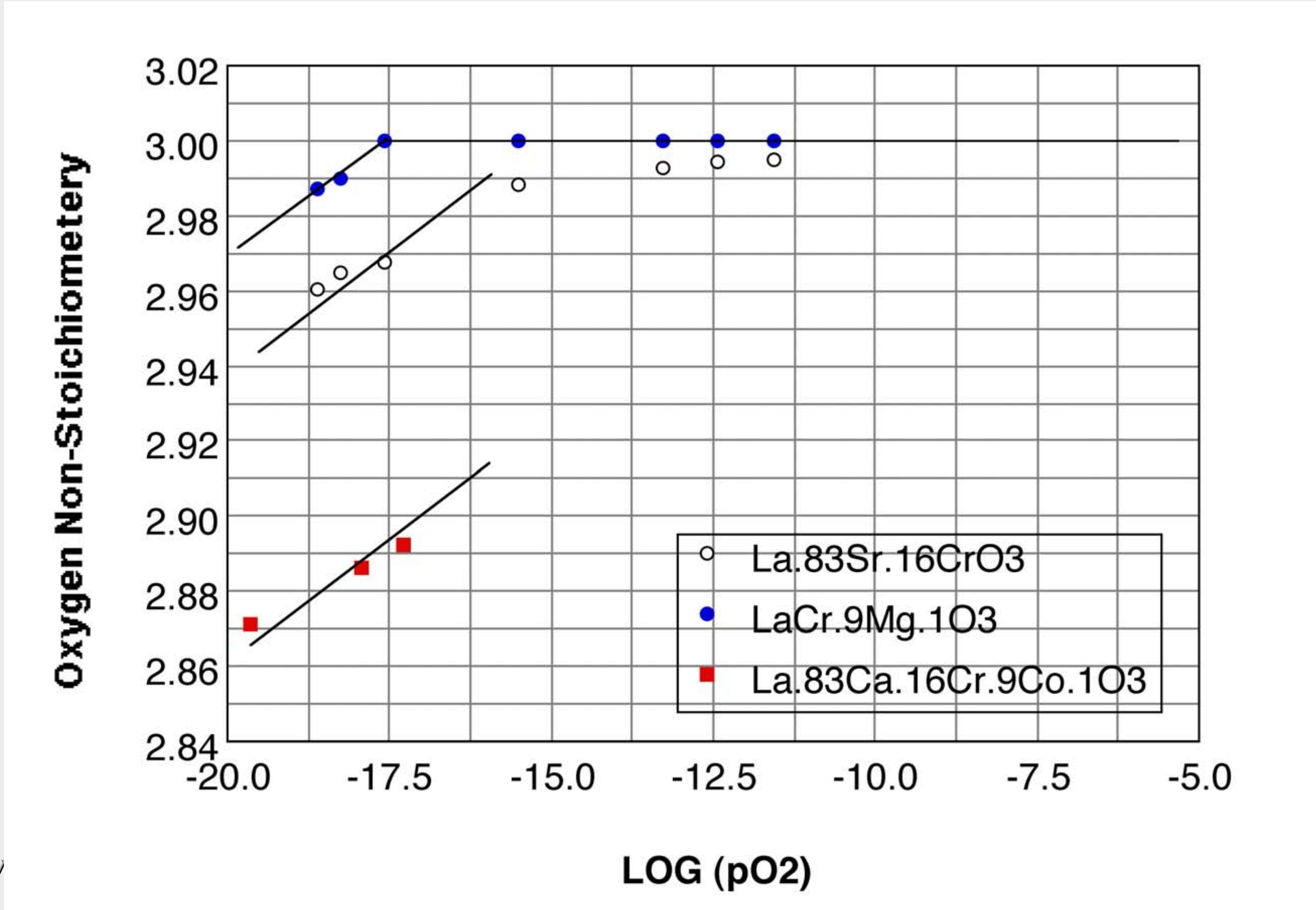
- Thermal Expansion Behavior
- Stability in Fuel Atmosphere
- Mechanical Properties

Thermal Expansion Behavior

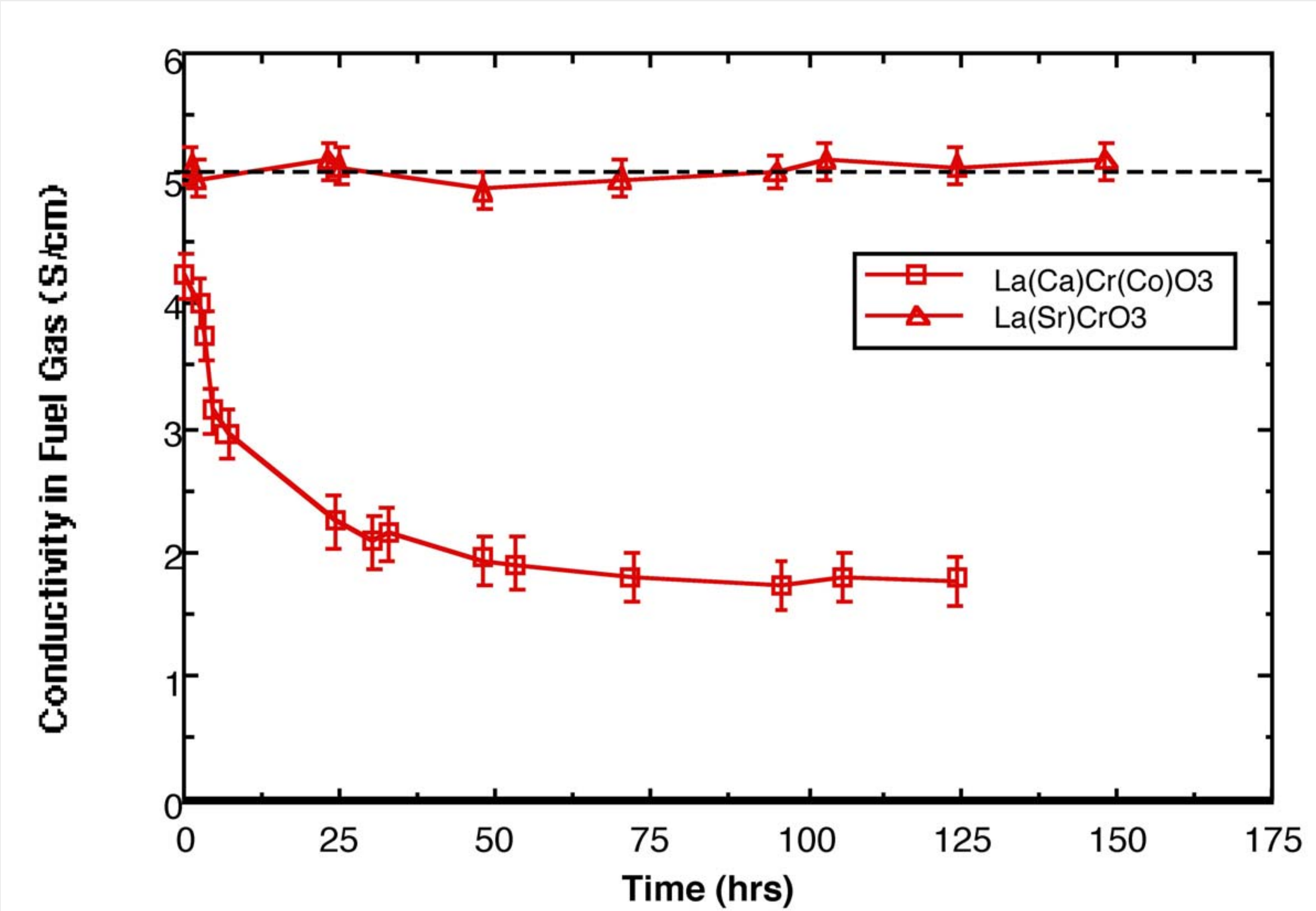


ceramatec

Stability in Fuel Atmosphere
Oxygen Non-stoichiometry

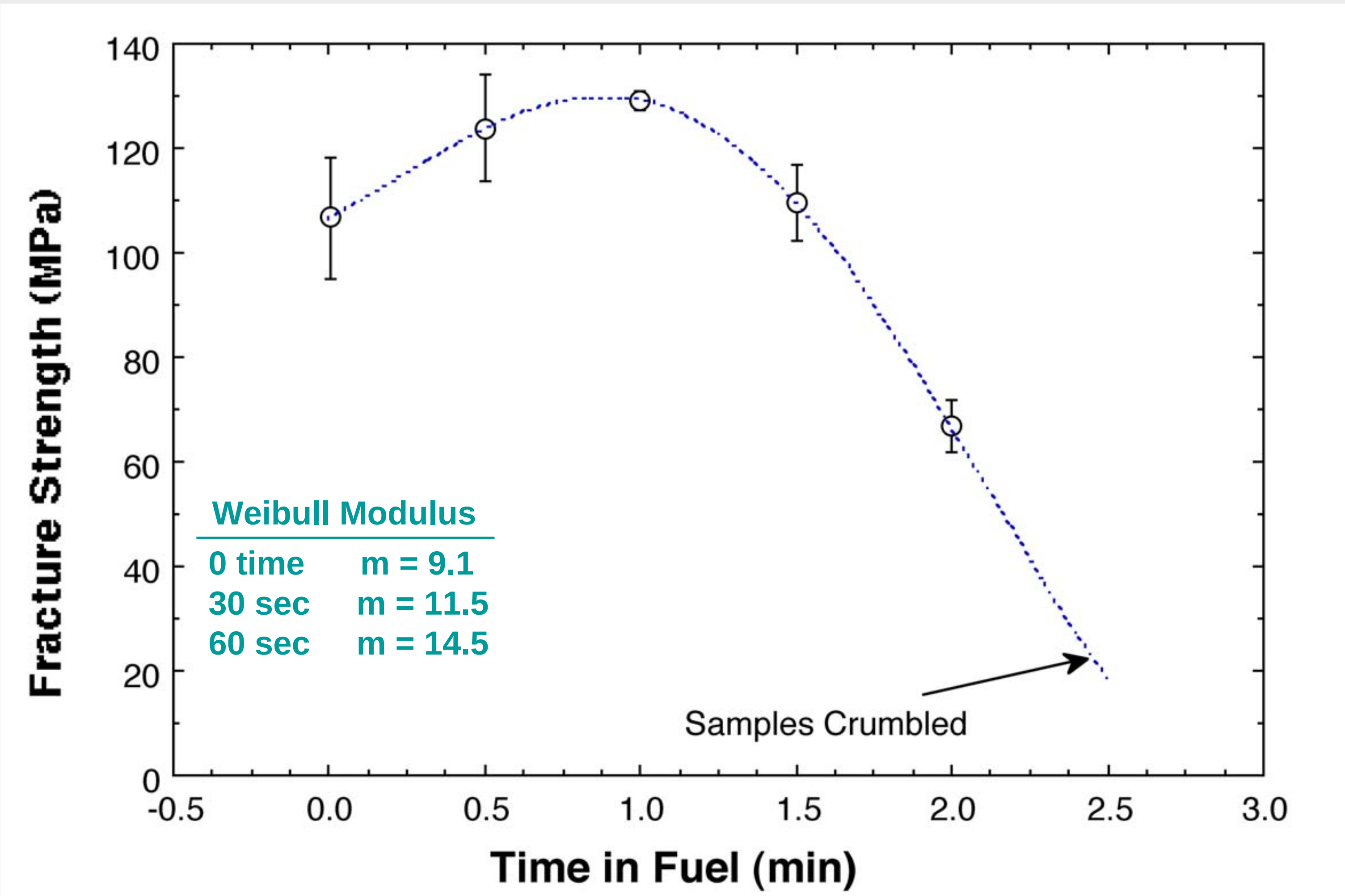


Stability in Fuel Atmosphere
Conductivity



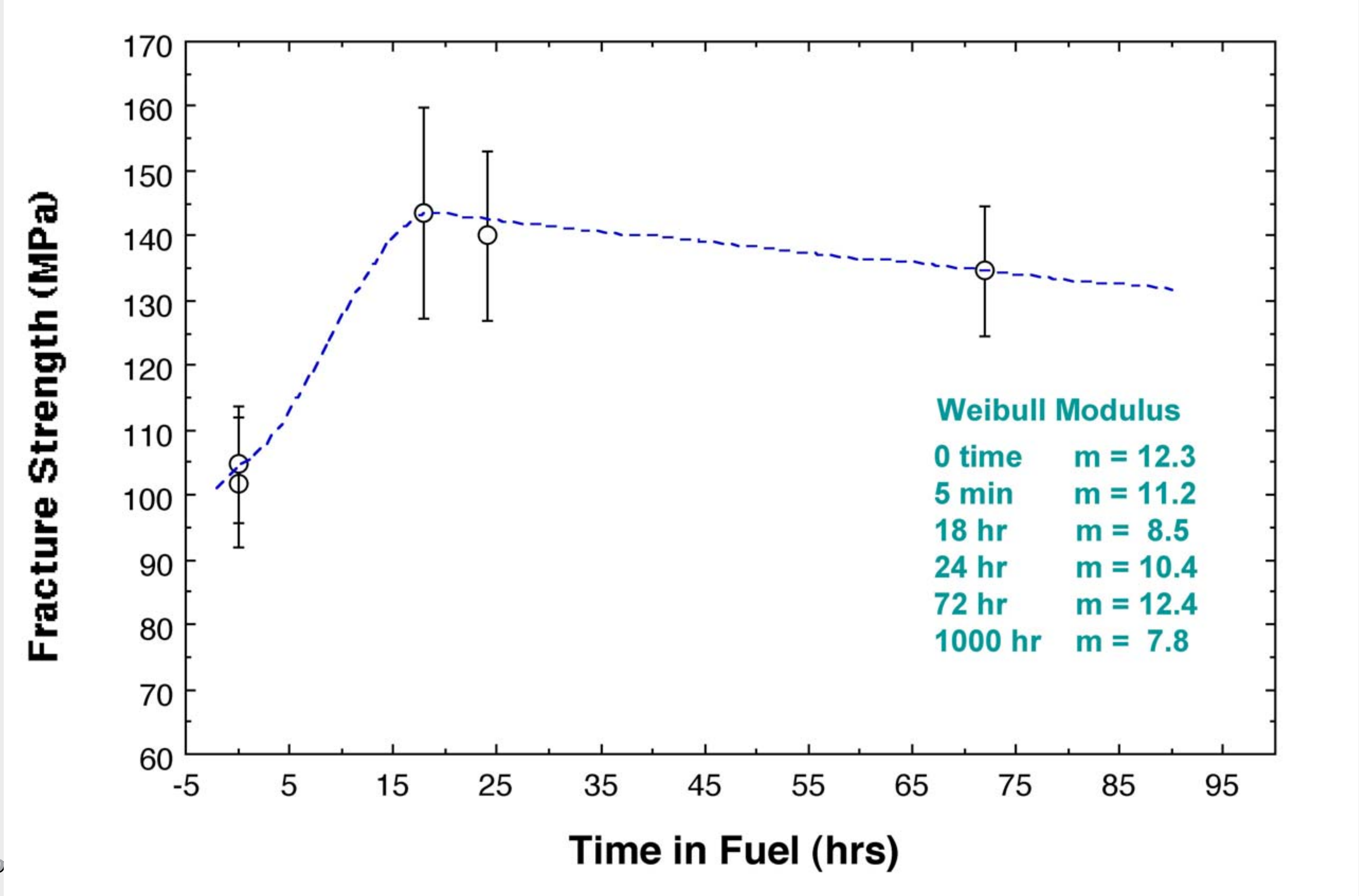
Mechanical Properties

Fracture Strength of $La_{.89}Ca_{.1}Cr_{.9}Co_{.1}O_3$ in Fuel



Mechanical Properties
Fracture Strength of $La_{.83}Sr_{.16}CrO_3$ in Fuel

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES



Comparison of compositions

- LCCr
  - Low sintering temp
  - High conductivity in air
  - Poor stability in fuel
  - Low mech. Properties
- LSCr
  - Better stability in fuel
- LMgCr
  - Best stability
  - Low conductivity

Need to compare ionic transport

Symptoms of Ionic Leakage

- Low OCV
- Low Fuel Utilization

Prior Measurements:

• WE:	Differential pO_2 gas Analysis	Mg doped	<10 μA/cm^2
• Tokyo Gas:	Conductivity Relaxation	Sr, Ca doped	10-300 mA/ cm^2
• NIMCR:	Limiting Current	Ca doped	1 mA/ cm^2
• Ceramatec:	In-line Sensor	Sr doped	50 mA/ cm^2

Ionic Leakage Modeling*

- 3D stack model - thermal, electrochemical, electrical
- Input data: Tokyo Gas (Yasuda et al.)

a) $La_{1-y}Ca_yCrO_3$

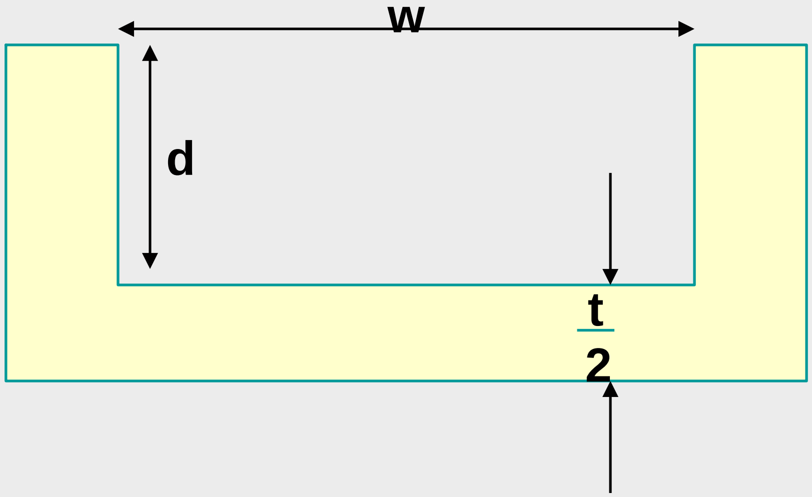
$$j = \frac{1152\,(-\log Po_2 - 12)}{L} \exp(18.72\, Y_{Ca} - 16000/T)$$

b) $La_{1-y}Sr_yCrO_3$

$$j = \frac{2240\,(-\log Po_2 - 12)}{L} \exp(16.1\, Y_{Sr} - 21000/T)$$

*work done at Institutt for energiteknikk, Norway

Geometry Consideration



Geometry 1

Thickness(t): 0.36 mm

Channel Depth(d): 0.71 mm

Channel Width(w): 1.7 mm

Geometry 2

Thickness(t): 0.86 mm

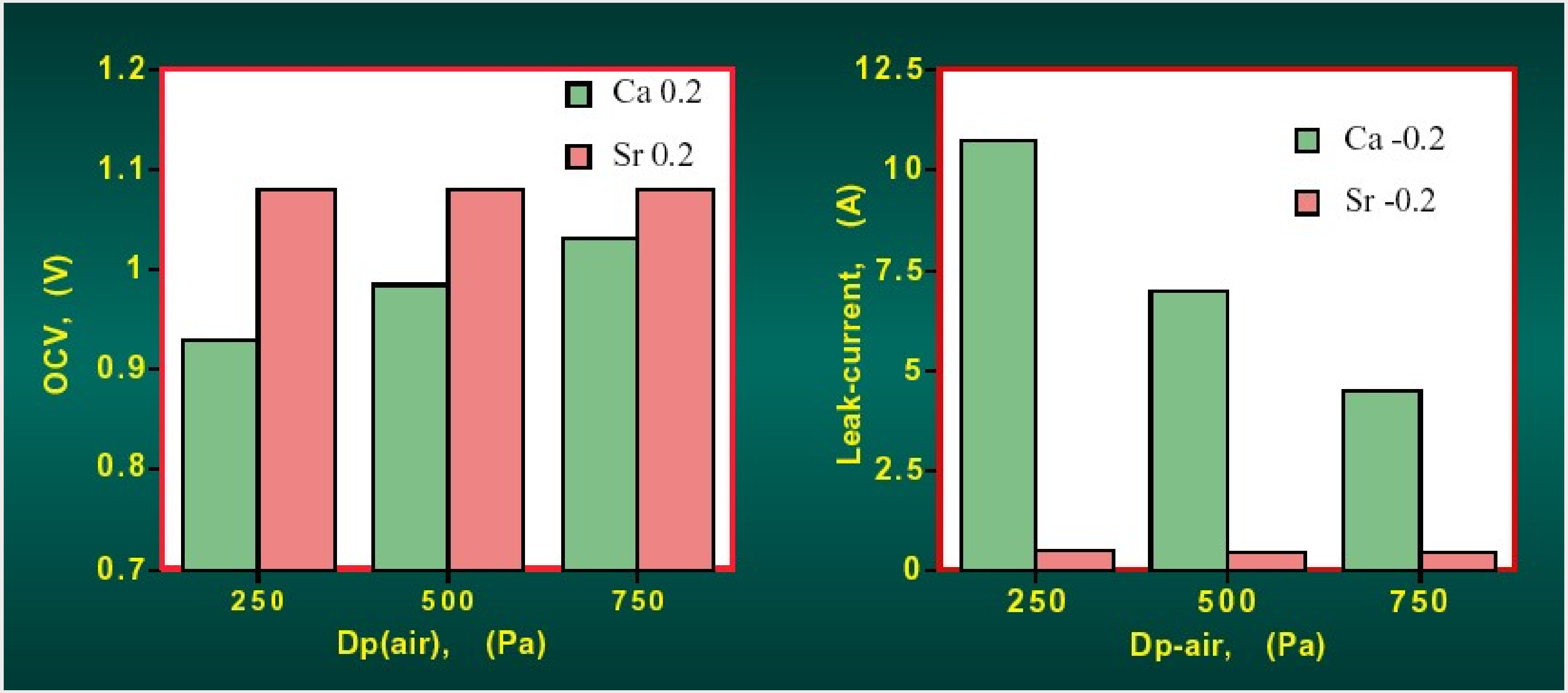
Channel Depth(d): 0.84 mm

Channel Width(w): 1.7 mm

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Effects of Composition on Ionic Leak Current

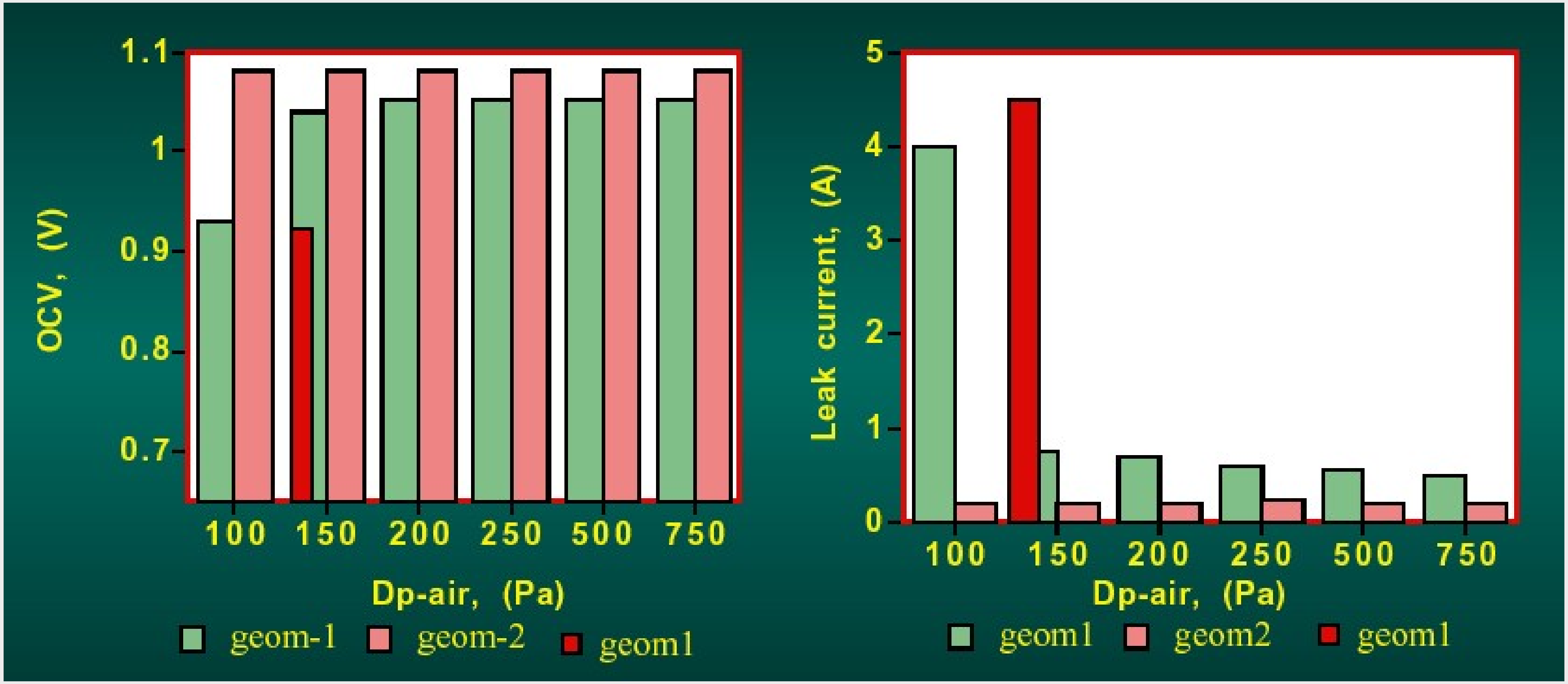
Geometry 1 Inlet Temp. 1125K



Ca doping shows high leakage current

Effects of Geometry: OCV and Leakage Current

$La_{0.8}Sr_{0.2}CrO_3$ Inlet Temp: 1125K



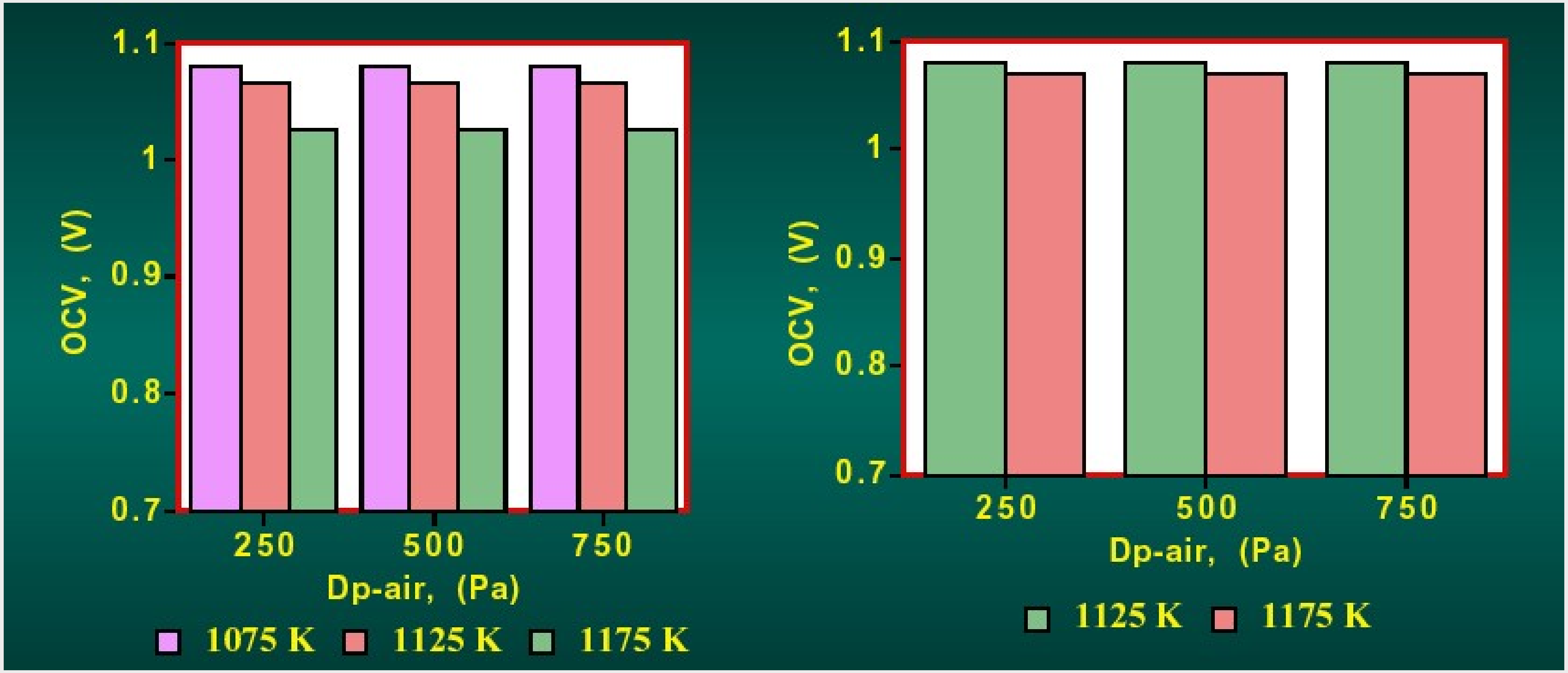
Geometry 2 exhibits lower leakage

Geometry 1: Two solutions

ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Effects of Inlet Temperature: OCV

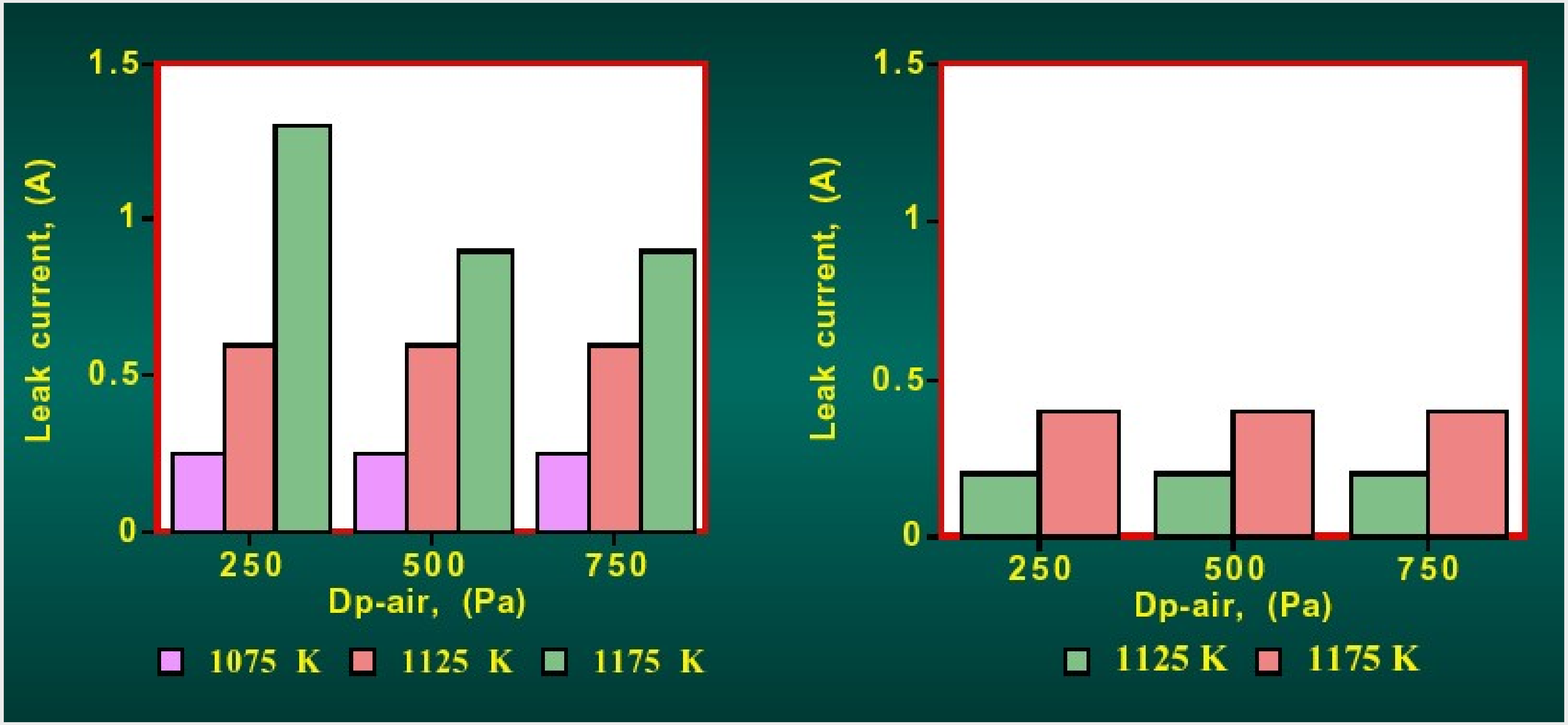
Geometry 1 $La_{0.8}Sr_{0.2}CrO_3$ Geometry 2



- OCV decreases with increasing temp
- OCV of geometry 2 is independent of Dp(air)

Effects of Inlet Temperature: Leakage Current

Geometry 1 $La_{0.8}Sr_{0.2}CrO_3$ Geometry 2

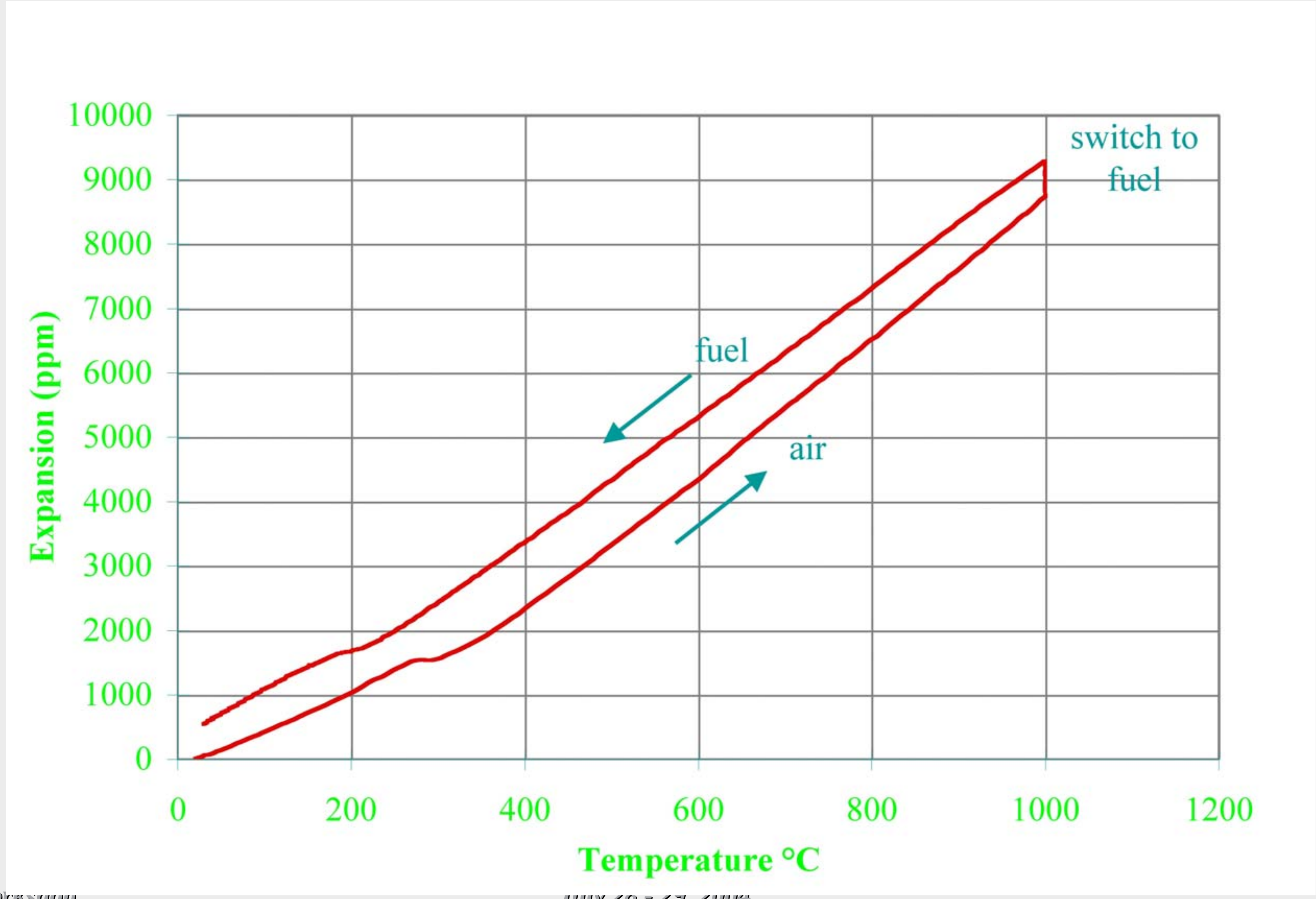


- Leakage current increases with increasing temp.
- Geometry 2 is insensitive to air pressure

Measurement Technique

- Direct measurement of ionic current is cumbersome
- Need an indirect measurement technique
  - Oxygen loss from the lattice causes lattice expansion

Lattice Expansion in Fuel



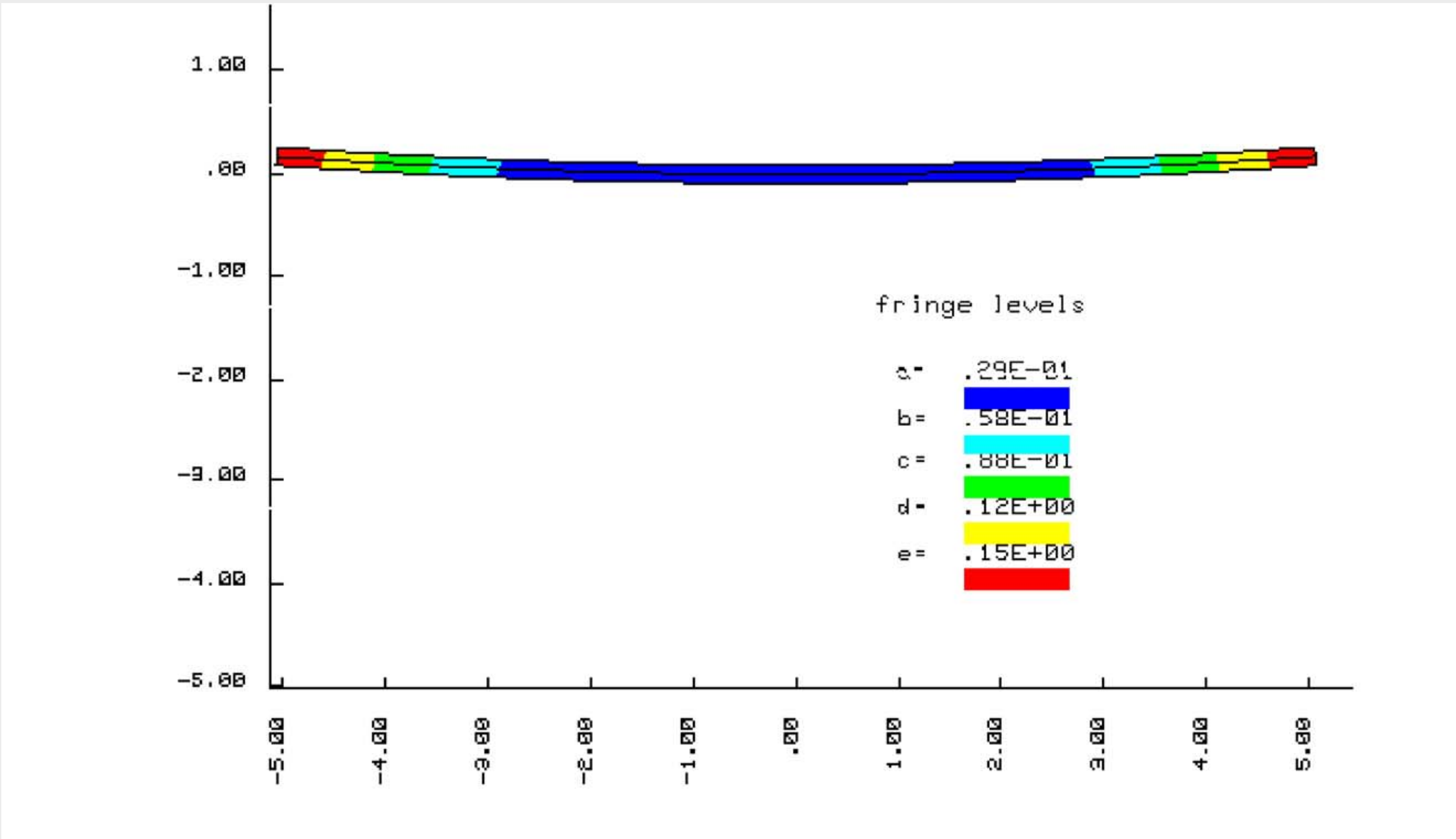
ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Characterization of Lanthanum Chromite

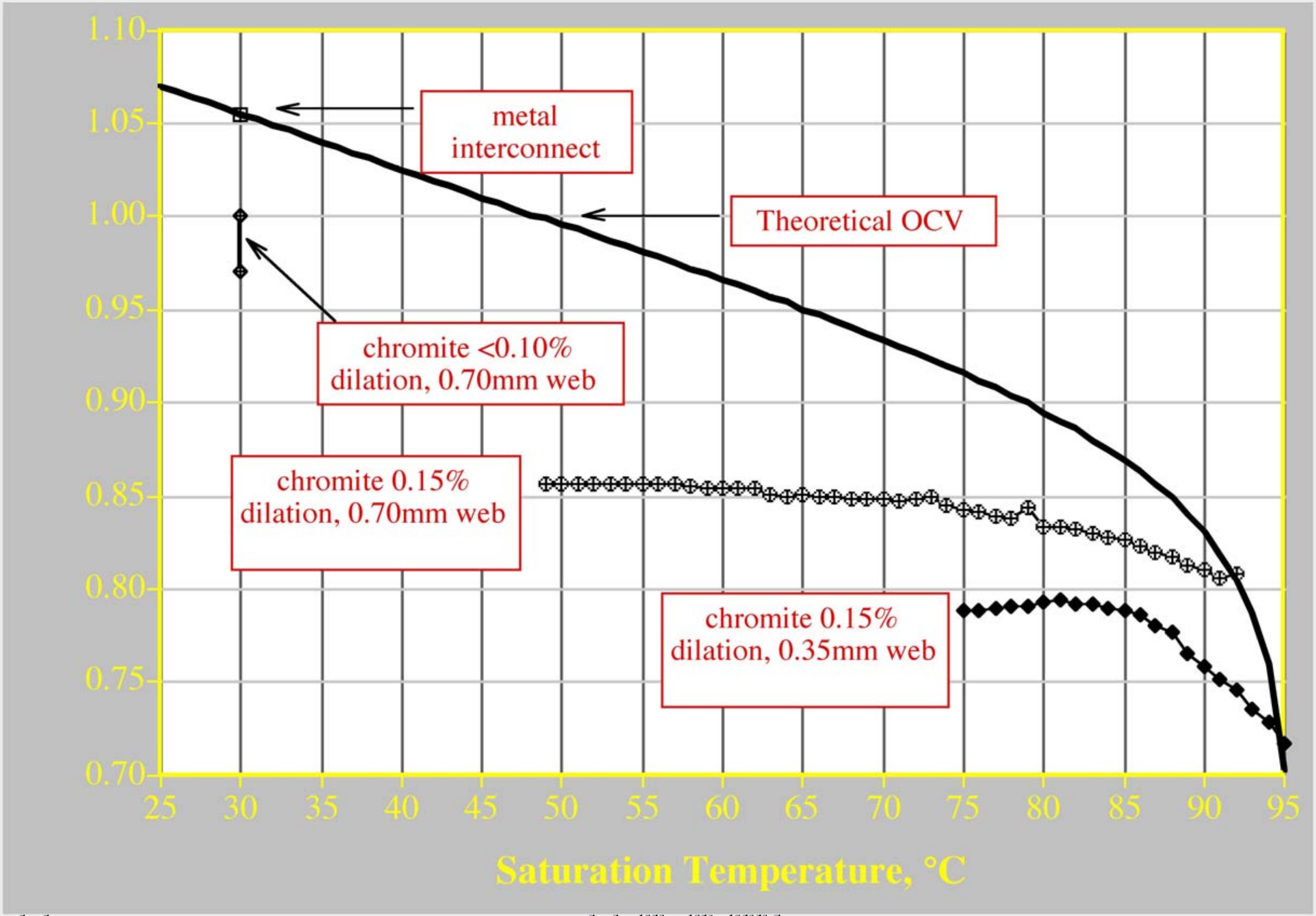
Composition	Conductivity in Air S/cm	Conductivity in Fuel S/cm	Thermal Expansion to 1000°C ppm/°	CCE at 1000°C in 3% H_2 - Argon
$La_{.83}Sr_{.13}Ca_{.03}CrO_3$	15 - 25	2 - 6	10.1	0.135%
$La_{.83}Sr_{.16}Cr_{.98}Fe_{.02}O_3$	~ 15	<1	10.4	0.088%
$La_{.99}Mg_{.1}Cr_{.9}O_3$	8 - 10	1 - 2	8.9	0.05%
$La_{.99}Mg_{.2}Cr_{.8}O_3$	4.44	0.45	9.5	0.077%
$La_{.99}Mg_{.1}Cr_{.85}Fe_{.05}O_3$	5.86	1.01	9.23	0.035%
$La_{.99}Mg_{.1}Cr_{.8}Fe_{.1}O_3$	4.02	0.61	9.32	0.044%
$La_{.99}Mg_{.1}Cr_{.80}Ti_{.10}O_3$	0.62	0.56	9.02	0.025%
$La_{.99}Mg_{.1}Cr_{.85}Al_{.05}O_3$	5.33	0.73	9.40	0.050%
$La_{.99}Mg_{.1}Cr_{.8}Al_{.10}O_3$	8.33	0.86	9.90	0.065%
$La_{.99}Mg_{.1}Cr_{.6}Al_{.3}O_3$	3.85	0.101	10.4	0.07%
$La_{.63}Gd_{.2}Sr_{.16}CrO_3$	22.4	3.99	9.37	0.14%

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

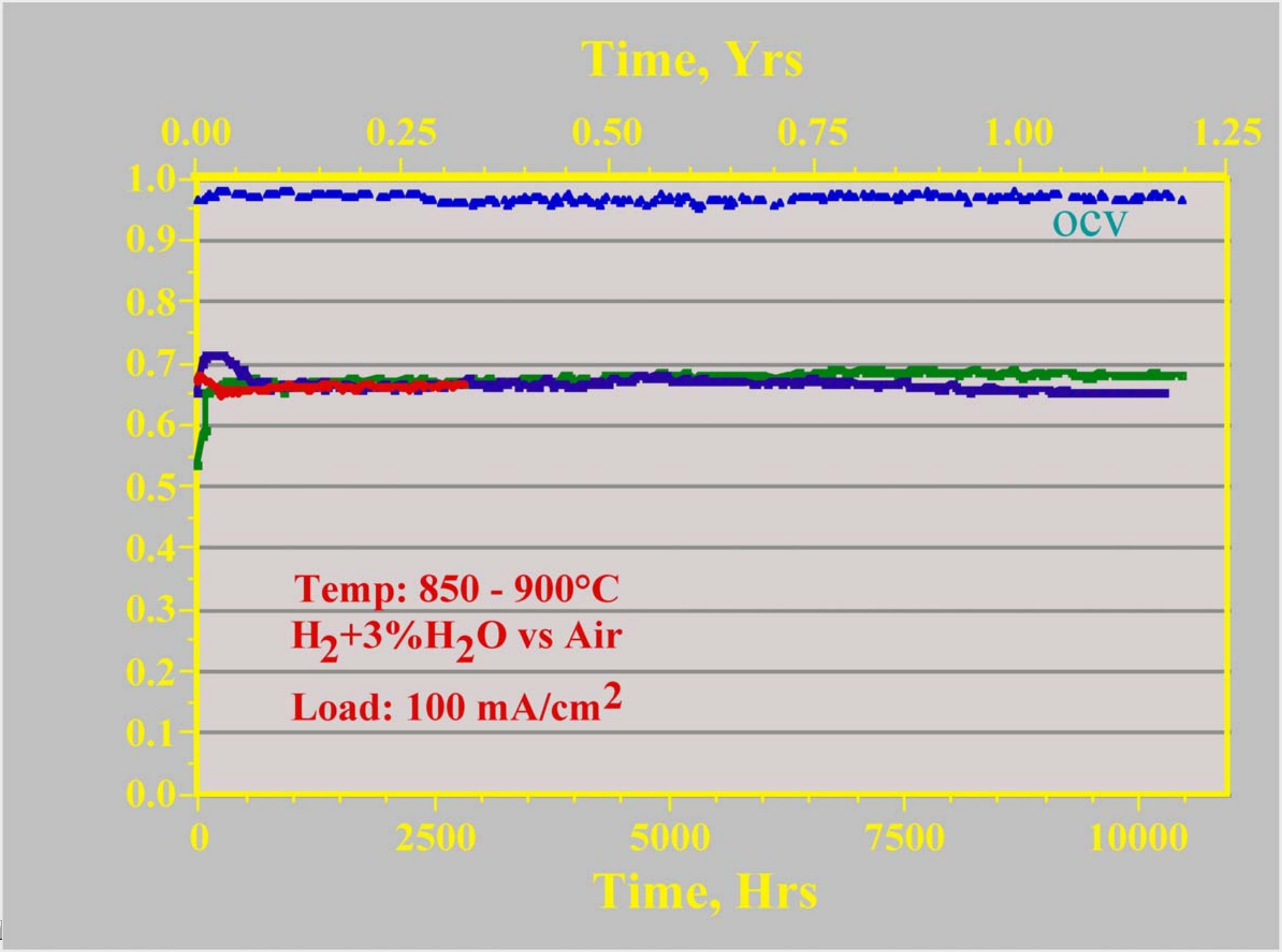
Fuel Induced Warpage



Effect of fuel pO_2 on OCV



Ceramic Interconnect Stack Test



Summary - Ceramic ICs

- Ionic leakage of chromite interconnects must be considered in the selection of material composition
- Global optimization of properties necessary
- Stack endurance demonstrated using this approach
- Materials and fabrication costs need to be addressed

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Metal Interconnects

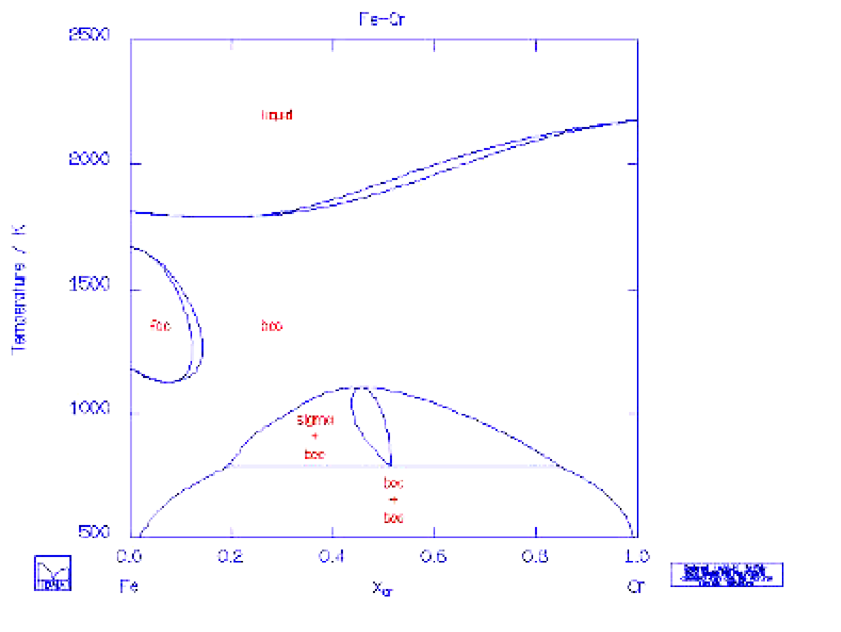
- Additional Requirements
  - High temperature corrosion resistance
  - Scale conductivity
  - Scale adhesion
  - Stability against electrode/bond layer (poisoning effect)
  - Thermal cycle capability

Approach

- Controlled growth of conductive scale to achieve
  - Electronic conductivity in scale
  - Low cation (metal) and anion (oxygen) diffusivity
  - Good adhesion (‘native’ scale)

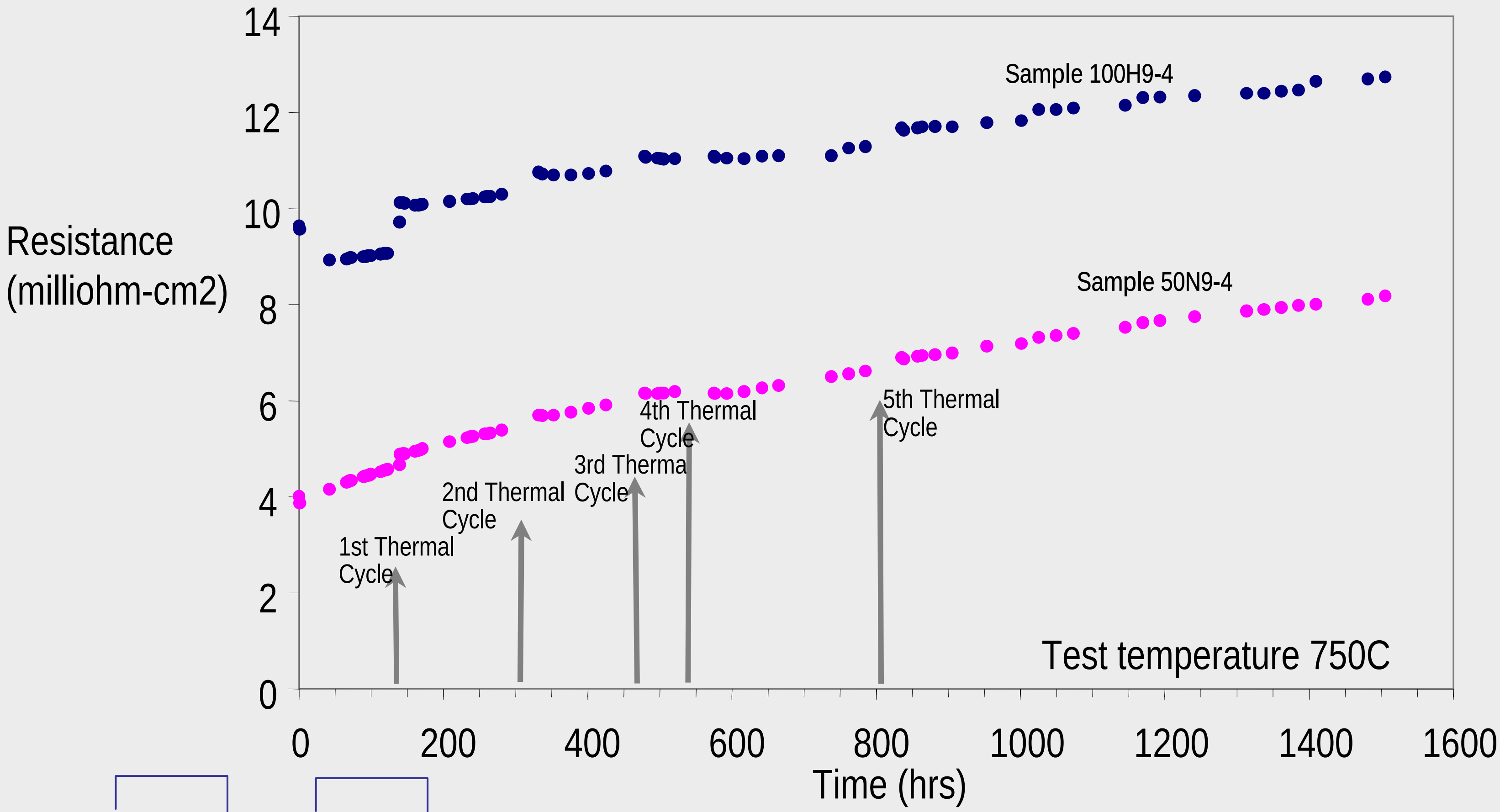
Approach

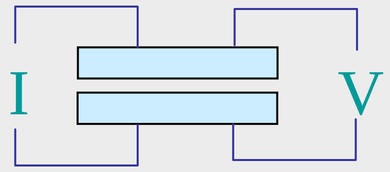
- Alloy Selection (Fe-Cr based ferritic SS)
  - CTE Match, Conductive scale (chromia former)
  - Choice of minor alloying elements
  - < 30% Cr to avoid brittle sigma phase formation
    - Slow cooling to be avoided below 650 C
    - > 12% for Cr_2O_3 formation



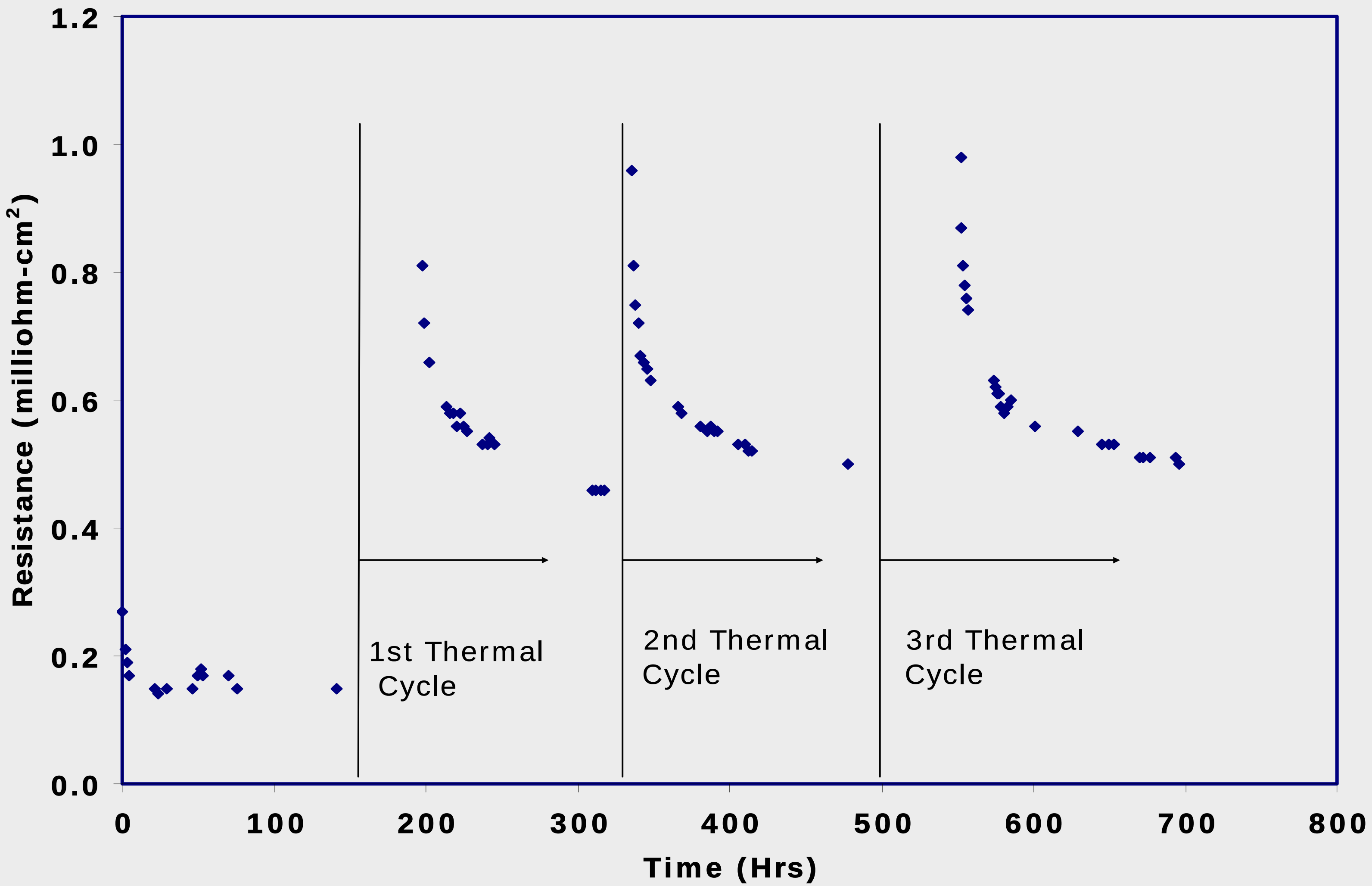
- Surface Treatment & Oxidation
  - Growth of selective oxide scale
    - Control P, T, Xi and t
  - Scale characterization

Scale Resistance in Air (coupon couples)

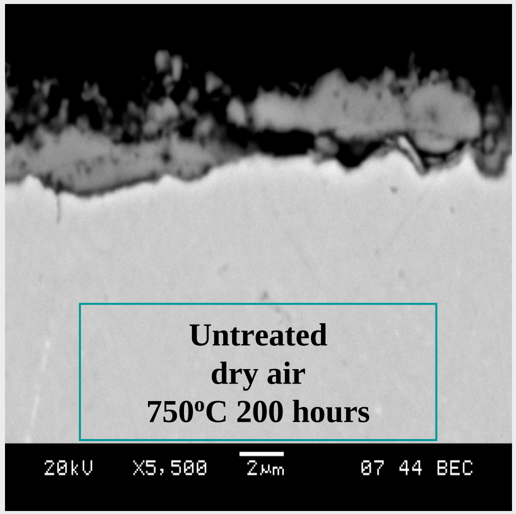


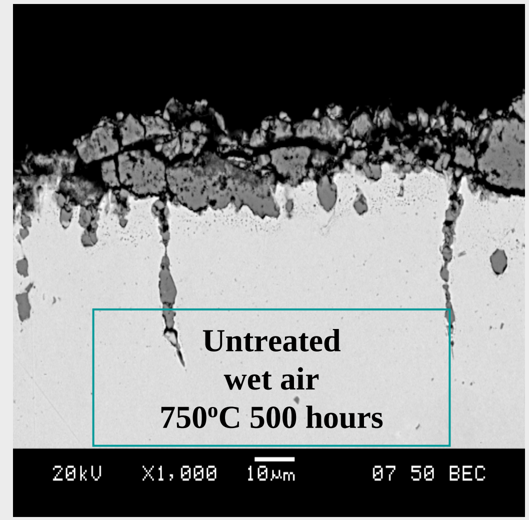


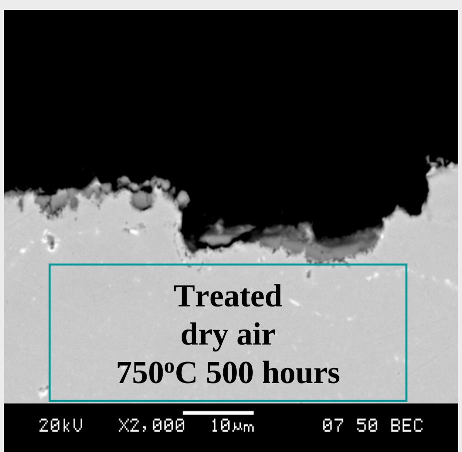
Scale Resistance in H_2/H_2O

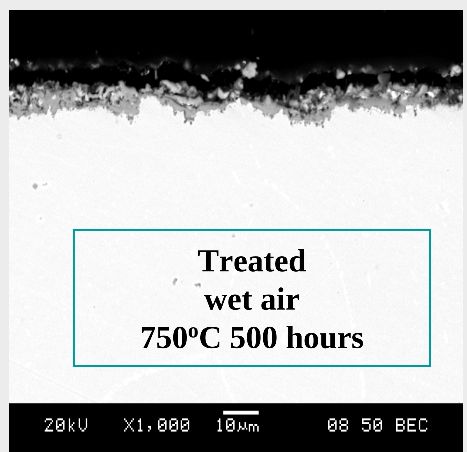


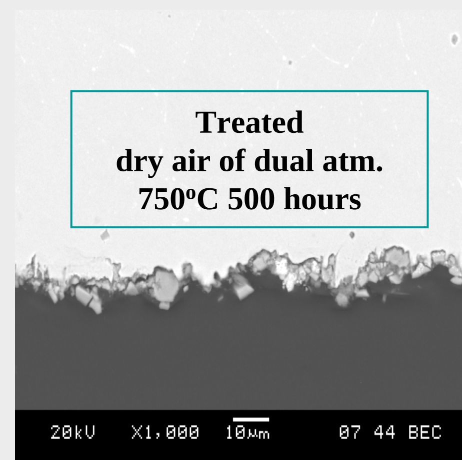
Scale Morphology



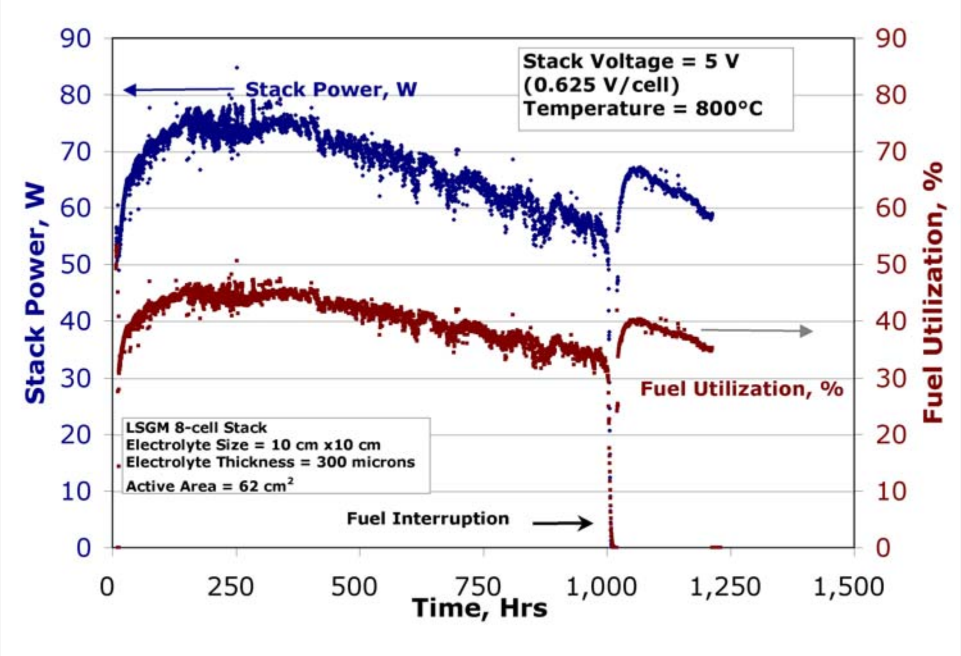


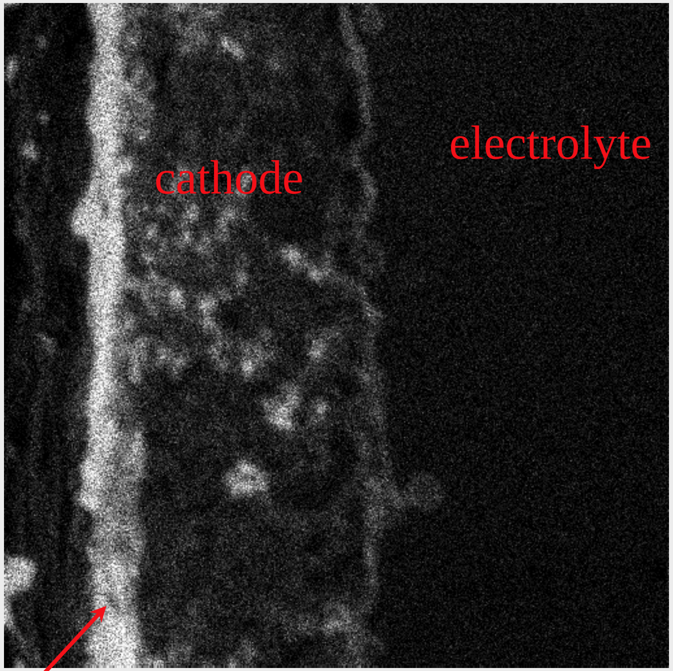






Stack Evaluation (SBIR Project)





Sr,Cr rich

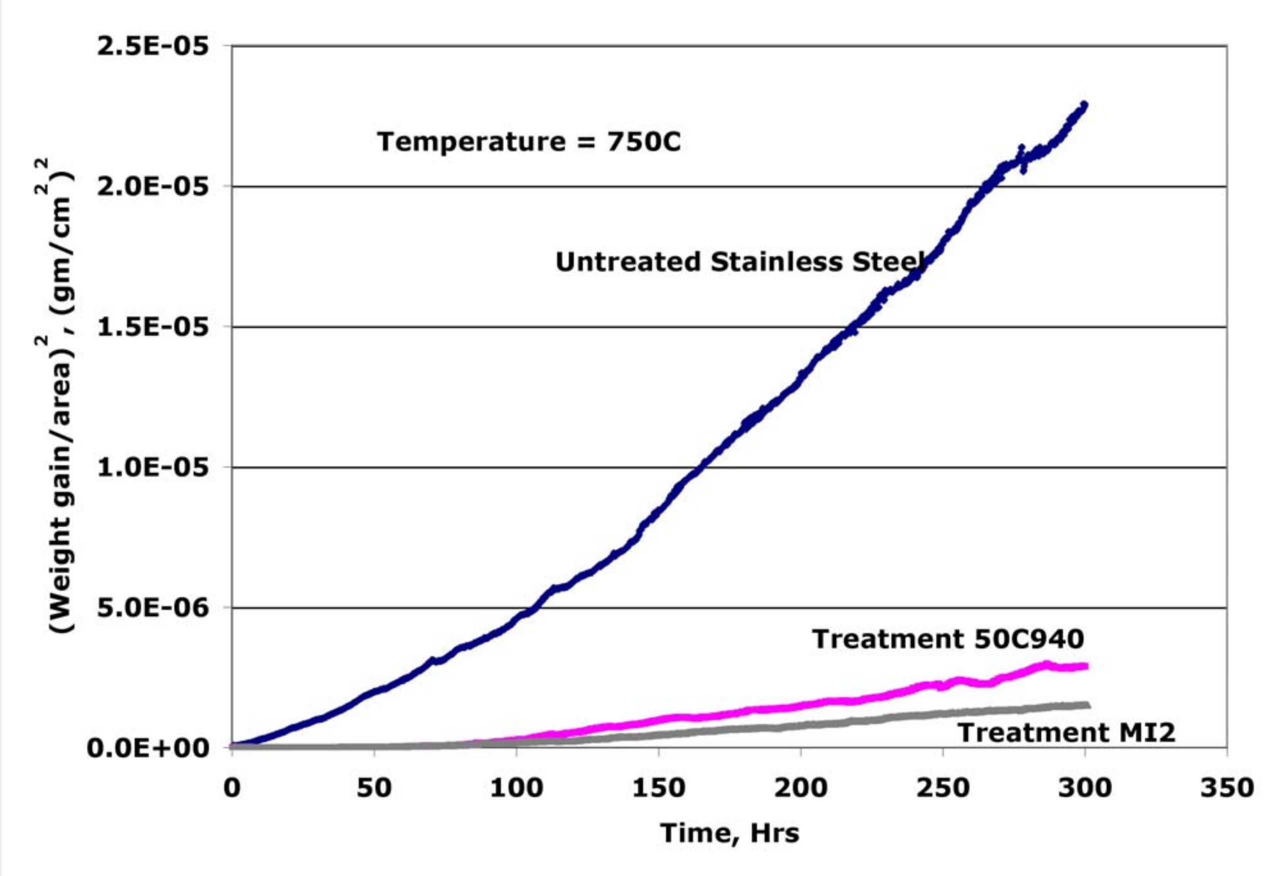
- A treatment process with low resistance in coupon tests evaluated (screen printed contact layer)
- Post-test: Sr-Cr rich phase on La(Sr)CoO_3 cathode

ceramatec
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Phase II Evaluations

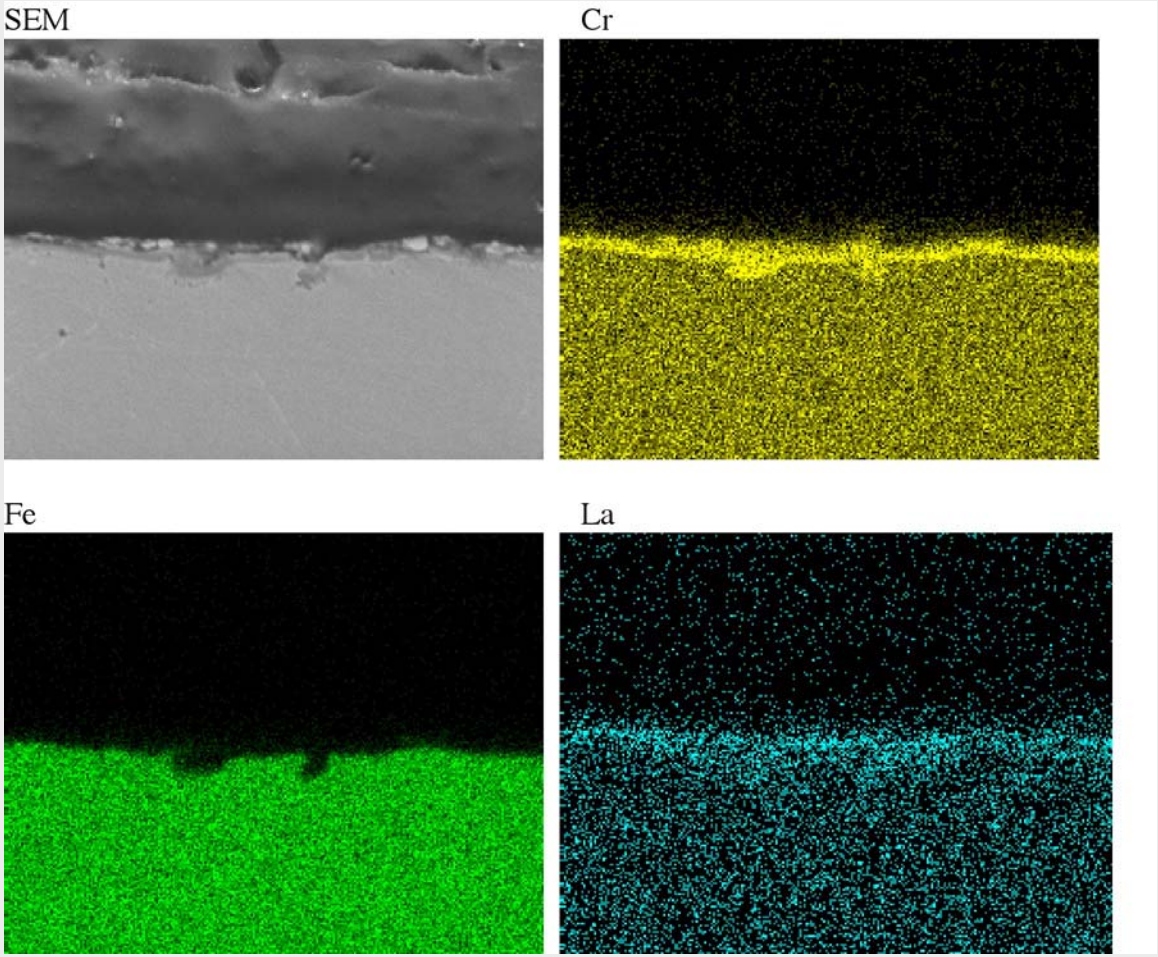
- Approaches to surface treatment optimization
  - Modify intrinsic scale
    - surface treatment and thermal process
    - Objective: Limit scale growth
  - Apply extrinsic layer
    - low Cr activity composition (~$LaCrO_3$)
    - Objective: Limit Cr evaporation
  - Combine the two layers
    - graded composition

TGA



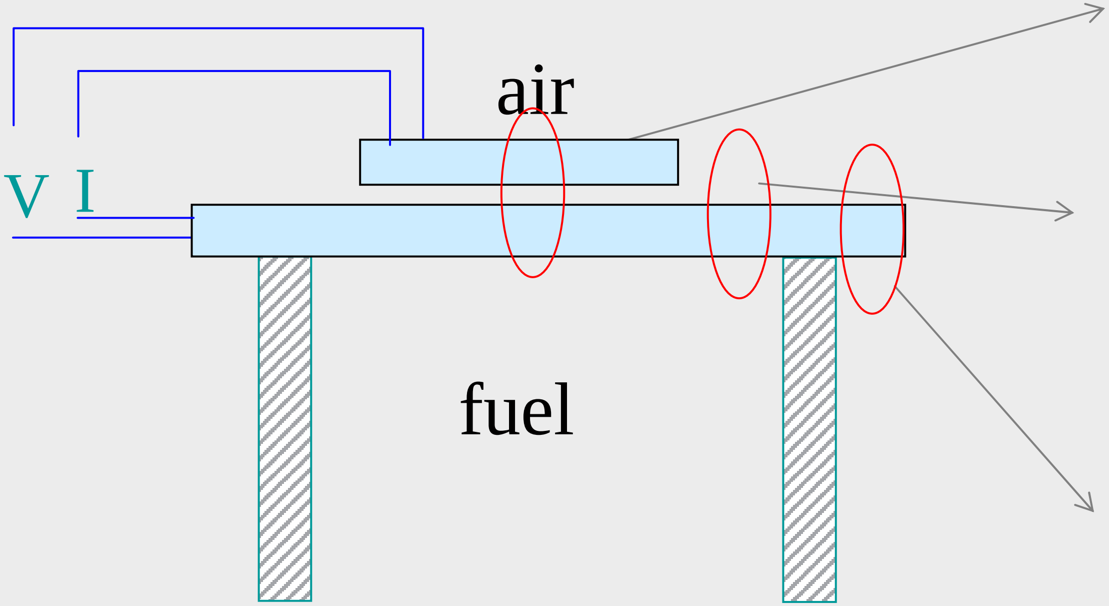
- 50C940: oxide scale modification
- MI2: Graded coating

Elemental Map: Graded coating Post-TGA



Dual atmosphere couples

- Dual atmosphere
- Contact layer
- Continuous load (constant current)

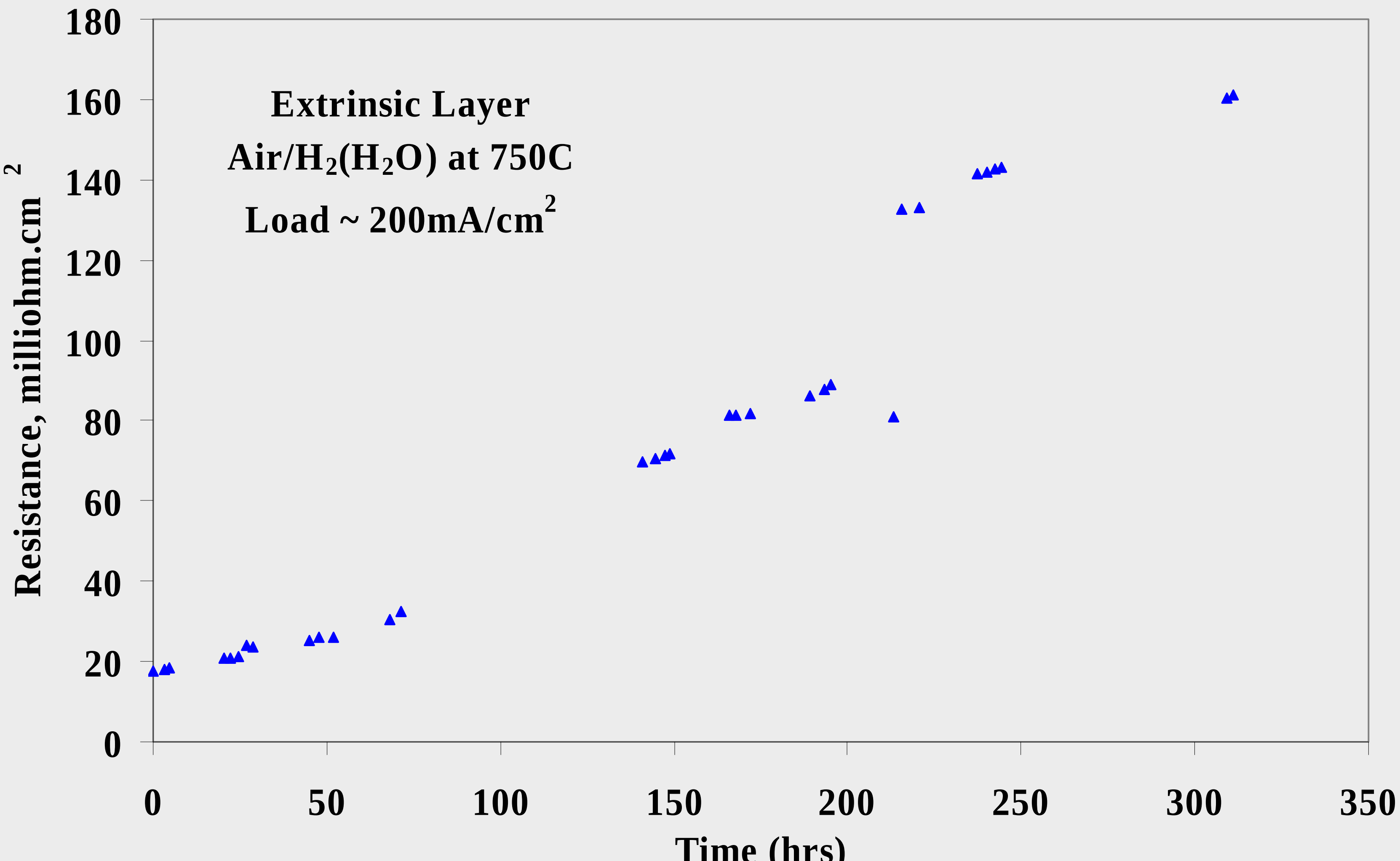


Dual atmosphere
No contact layer
No current

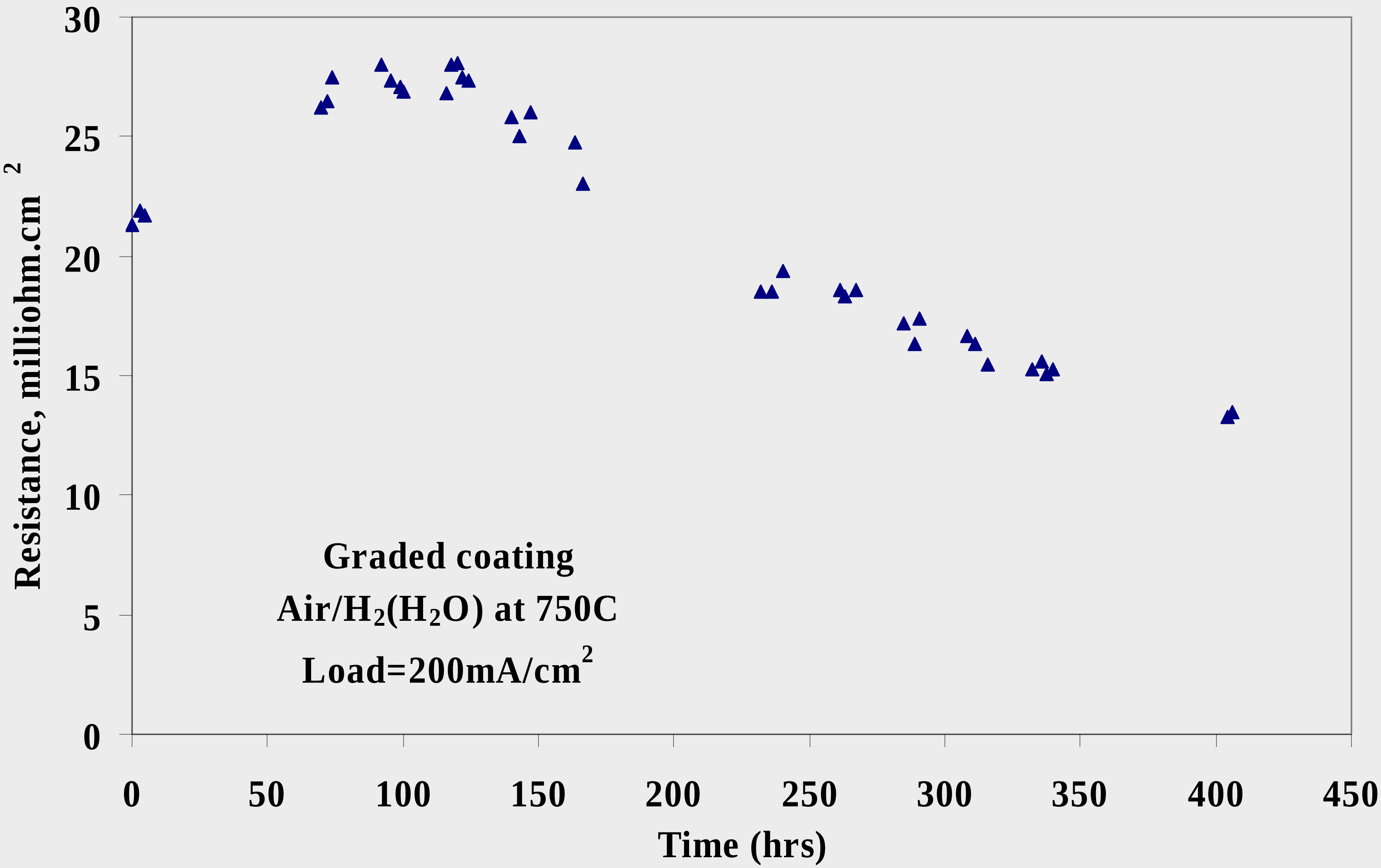
Air atmosphere
No contact layer
No current

1x1 cm coupon on a larger (3.5x3.5 cm) blank
Identical treatment on mating surfaces
Contact layer: cobaltite

$LaCrO_3$ - Dual atmosphere

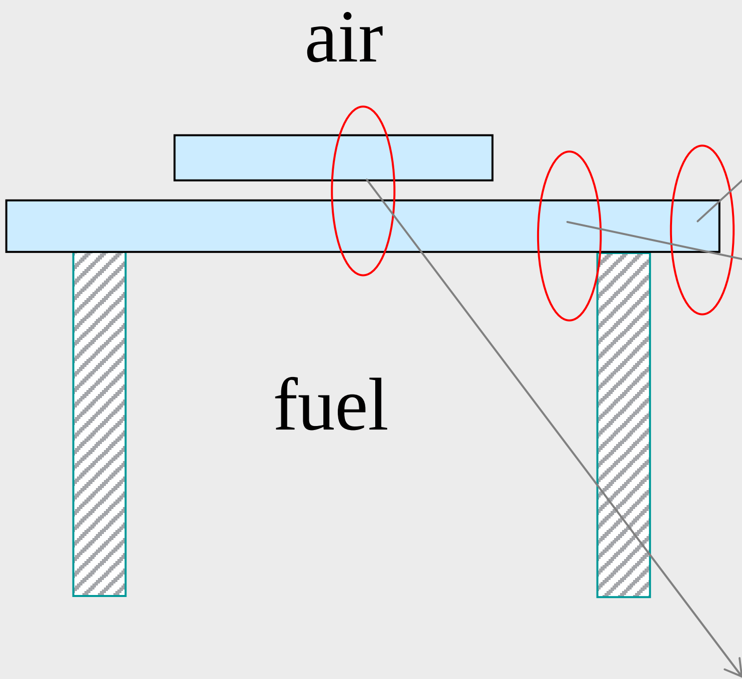


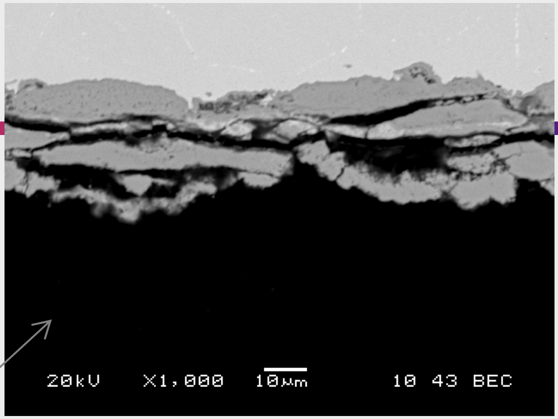
Graded Coating: Dual atmosphere



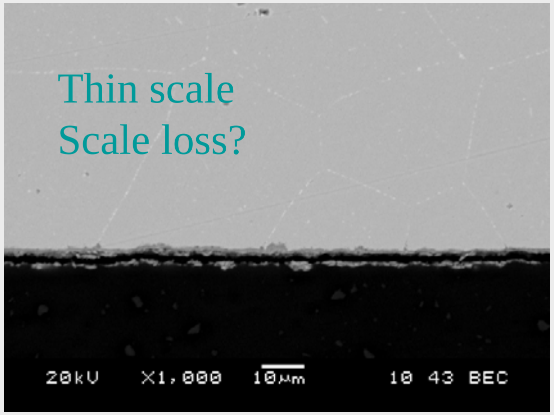
$LaCrO_3$ layer

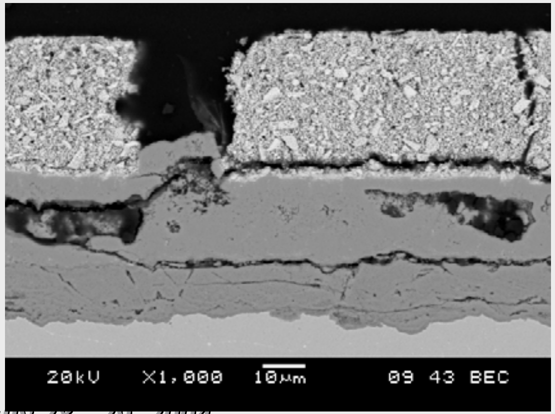
200 mA/cm^2, ~350 hrs
140 milliohm.cm^2





- Thick scale
- Poor adhesion

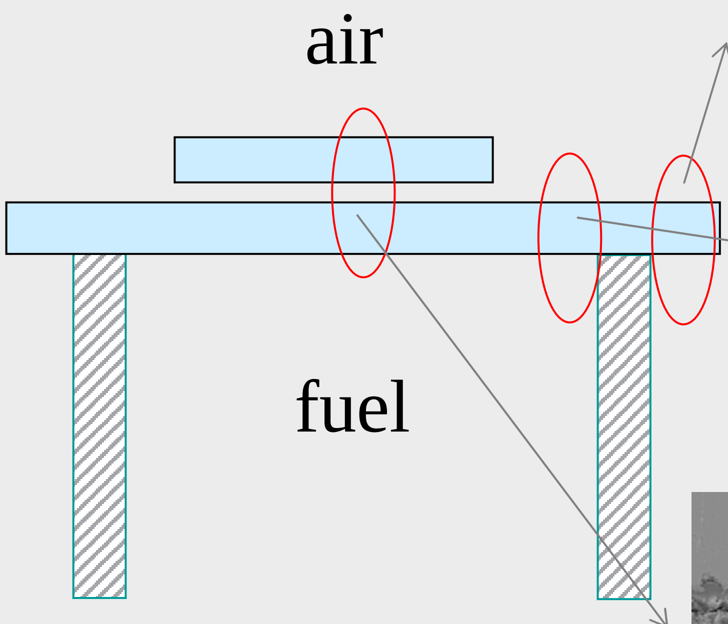


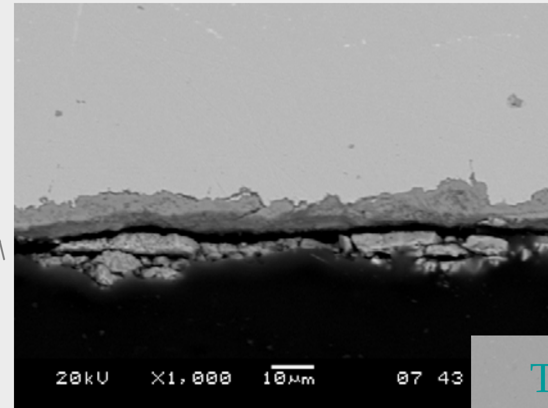


Thick scale under contact layer
Sr-Cr rich interface

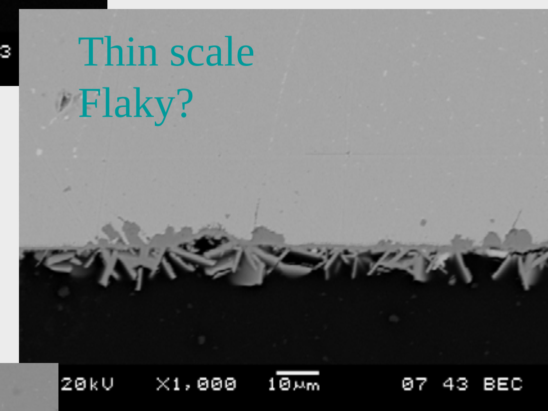
Graded coating - dual atm.

200 mA/cm^2, ~400 hrs
15 milliohm.cm^2

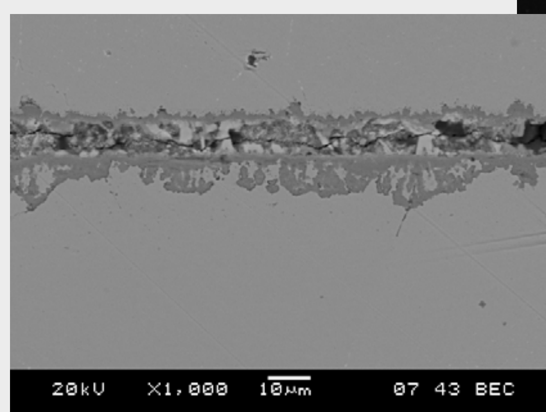




6 µm scale
Influence of dual atm. away from the region?



Thin scale
Flaky?



Thin scale under contact layer

No Sr-Cr phase at the scale

Summary - Metal IC

- New test arrangement
  - Allows resistance measurement in dual atm. exposure
  - Allows continuous load
- Graded coating provides low resistance <u>and</u> thinner oxide scale in initial tests
- Additional work planned
  - Effect of coating variations
  - Effect of current density
- Stack test validation in parallel programs

ceramatec®
ADVANCED MATERIALS & ELECTROCHEMICAL TECHNOLOGIES

Acknowledgement

- GRI
- Ceramatec
- Norcell
- SOFCo
- DOE SECA CTP