CHALMERS

CORROSION CHALLENGES IN SOFC APPLICATIONS

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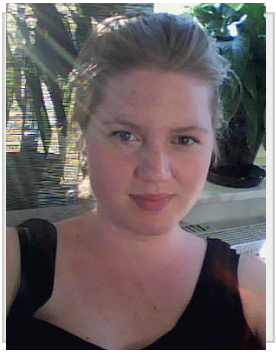

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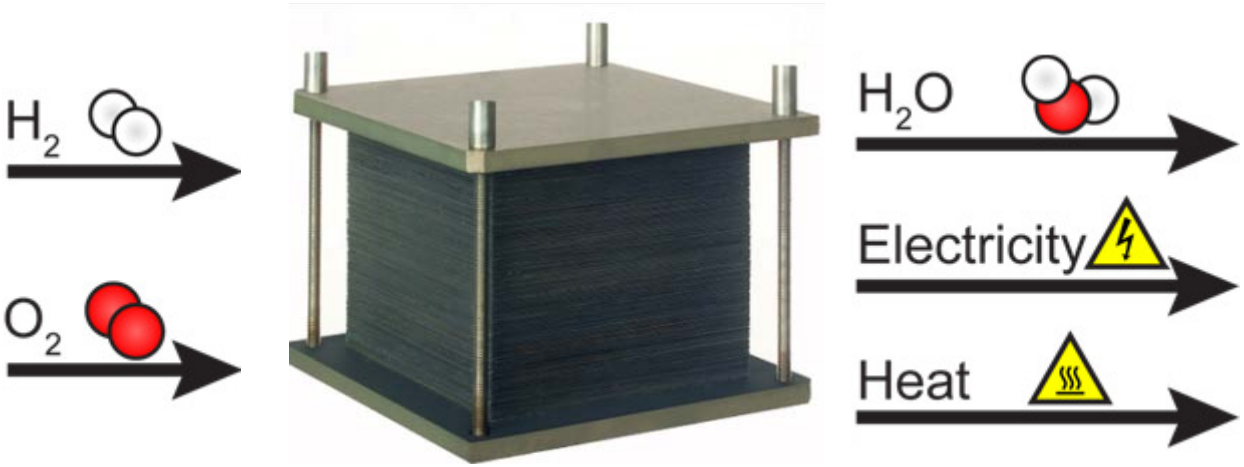
Introduction

What is a Fuel Cell?



Chemical Energy → Electrical Energy

Advantages and Usage of Solid Oxide Fuel Cell

- Efficient power generation (60 el%)
- Fuel flexible
- Low emissions
- Scalable

Truck or RV Auxilliary Power Units (APUs)

Combined Heat & Power (CHP)

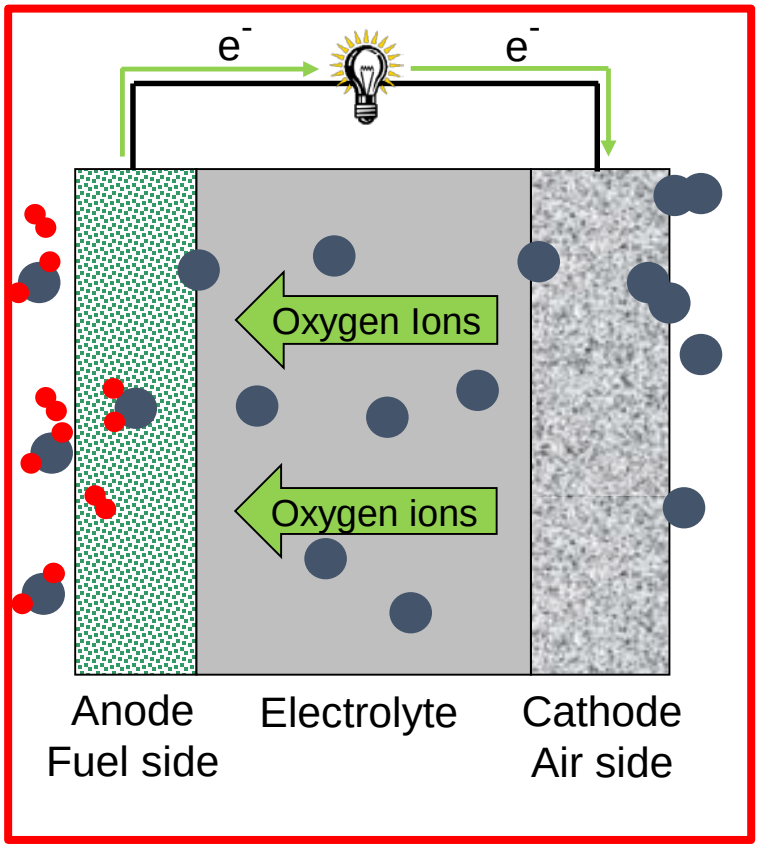
Off-grid power generation

Solid Oxide Fuel Cell (SOFC)

Cathode: $O_2 + 4\ e^- \rightarrow 2\ O^{2-}$

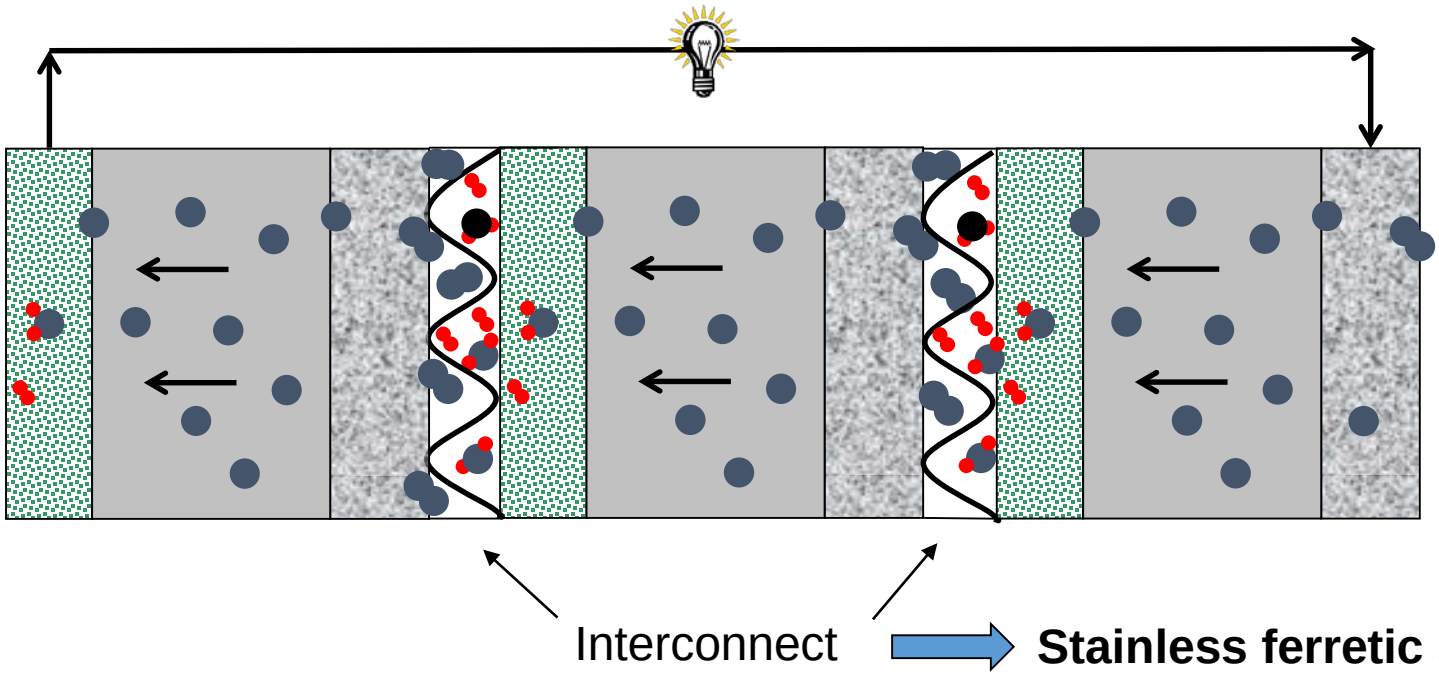
Anode: $2\ O^{2-} + 2\ H_2 \rightarrow 2\ H_2O + 4\ e^-$

Total reaction: $O_2 + 2\ H_2 \rightarrow 2\ H_2O$

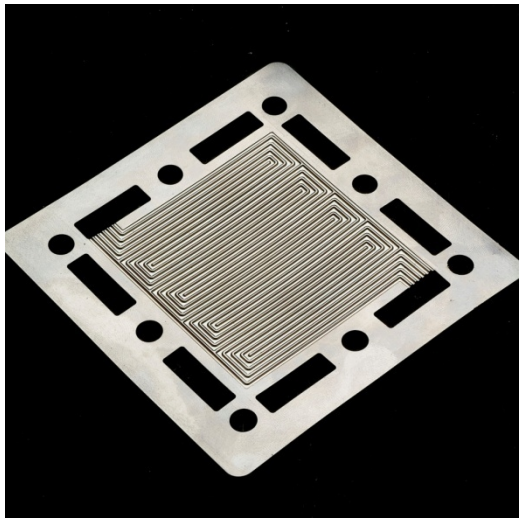


U < 1 V

Solid Oxide Fuel Cell Stack

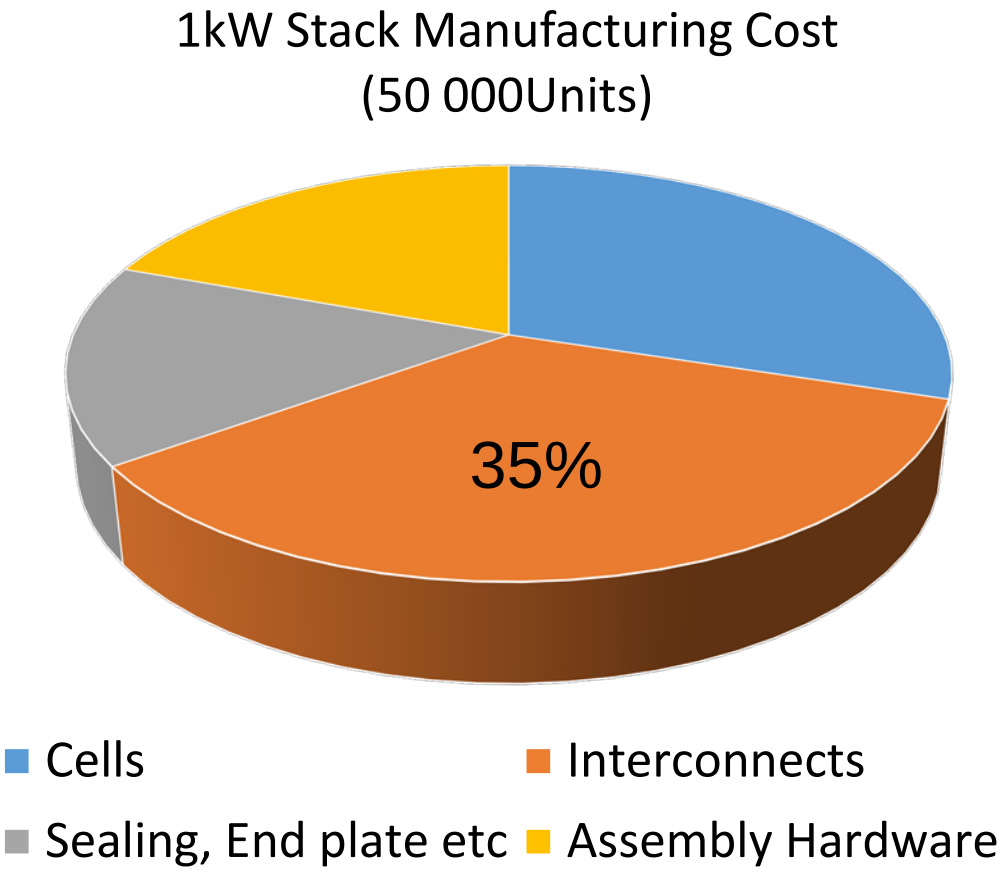


Requirement for Interconnects



- Similar thermal expansion as the ceramics used in SOFC
- Good electrical and thermal conductivity
- Form conductive oxide scales (Cr_2O_3)
- Formability
- Cheap to produce

Importance of reducing Costs for Interconnects



Source: Battelle study prepared for US DOE (2014)

Problems at Interconnect level

Corrosion

- Chromium evaporation leads to poisoning of cathode
- Growing Cr_2O_3 layer

  → In combination of Chromium evaporation leads to increased Chromium consumption

  → Increase in electrical resistance
- Dual atmosphere effect leads to increased corrosion

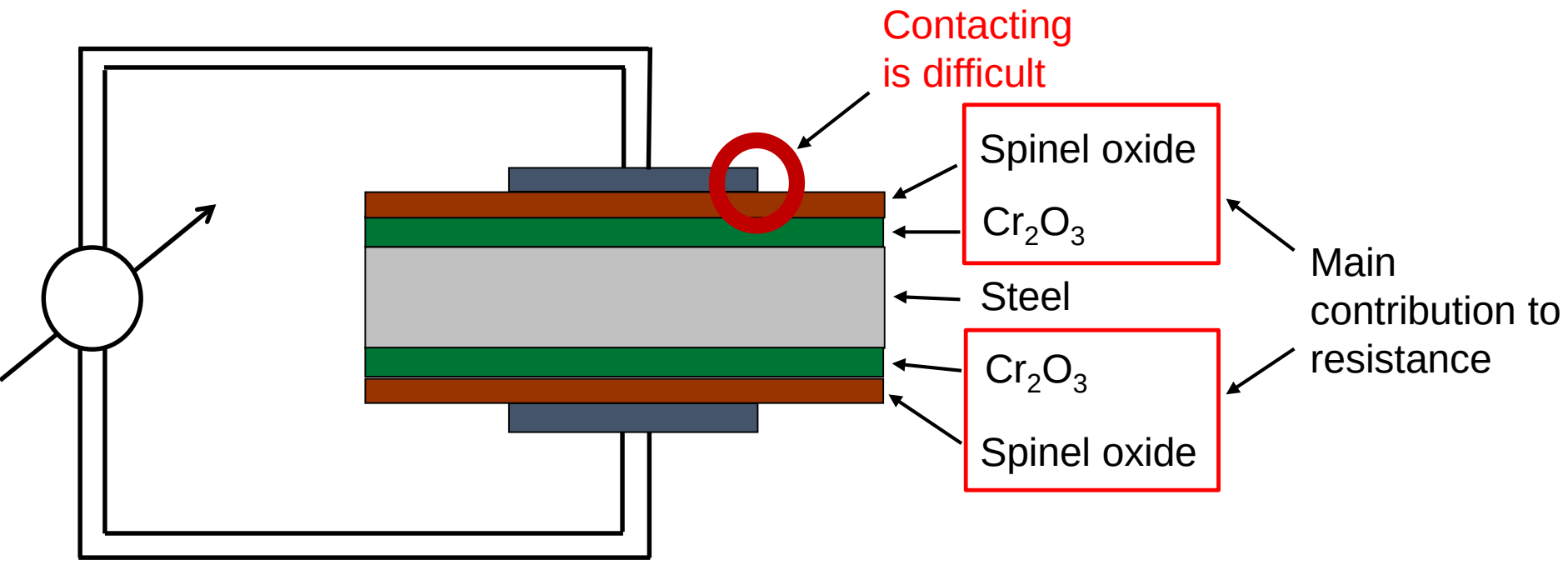
Electrical Resistance Measurements

The influence of the thickness of Co-spinel layers in relation to the Cr_2O_3 layer

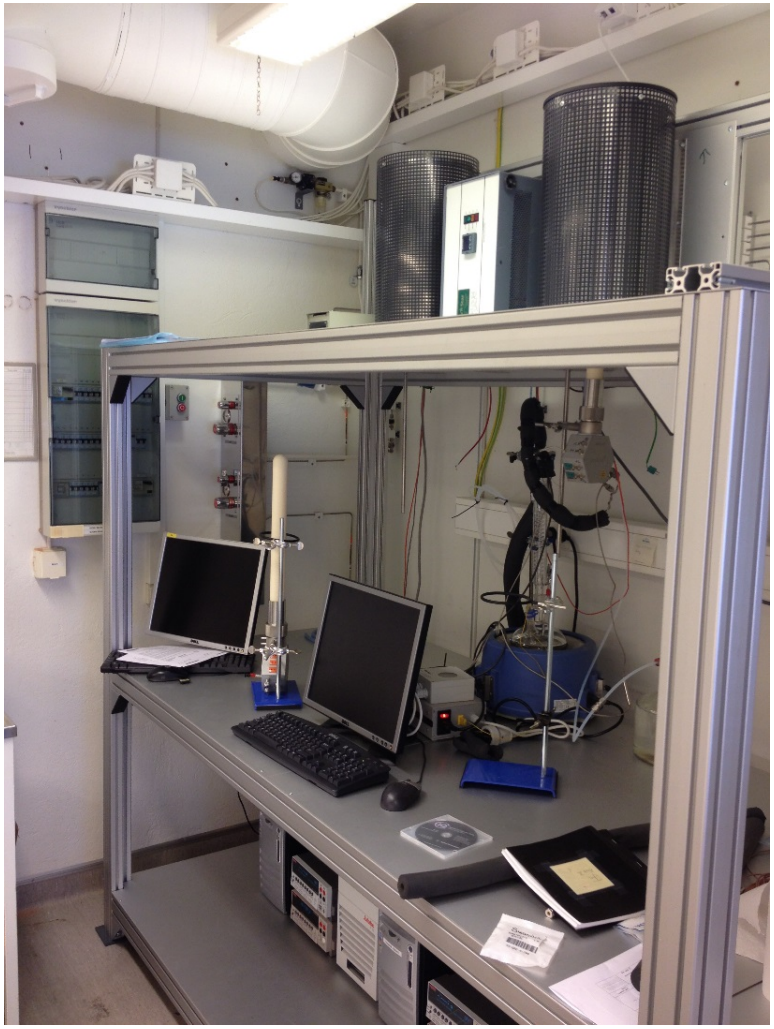
Area Specific Resistance

MEASUREMENT PROCEDURE

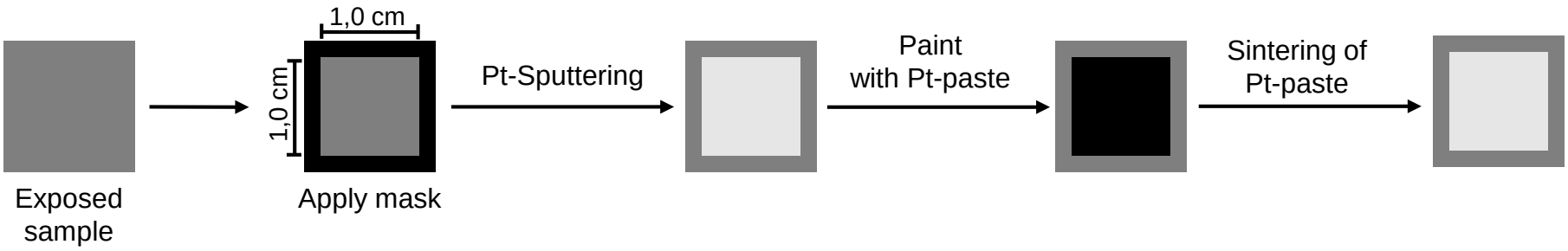
Basic Idea

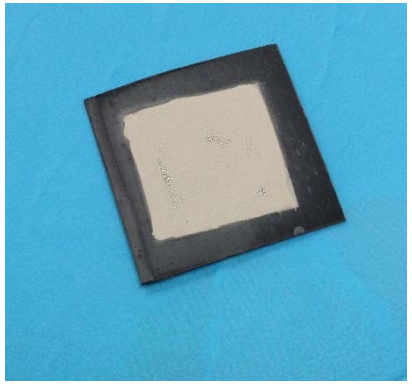

Contacting
is difficult
Spinel oxide
Cr_2O_3
Steel
Cr_2O_3
Spinel oxide
Main
contribution to
resistance

Experimental setup



Electrode Preparation

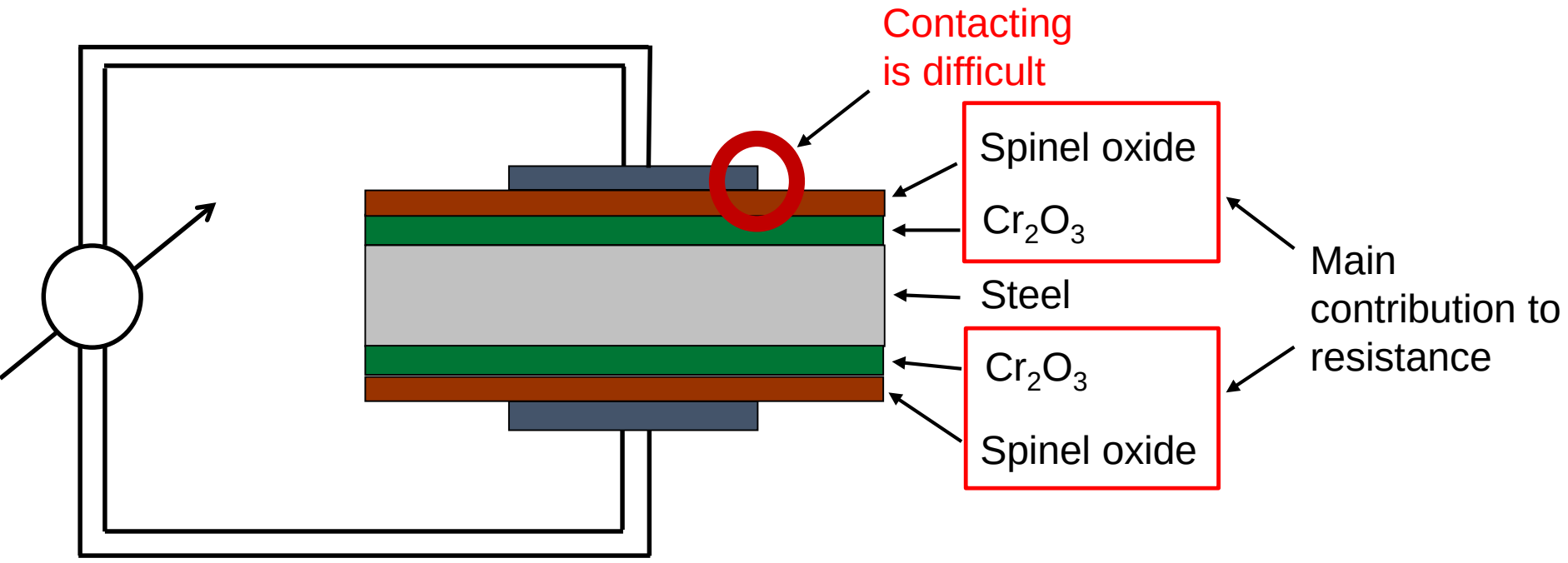


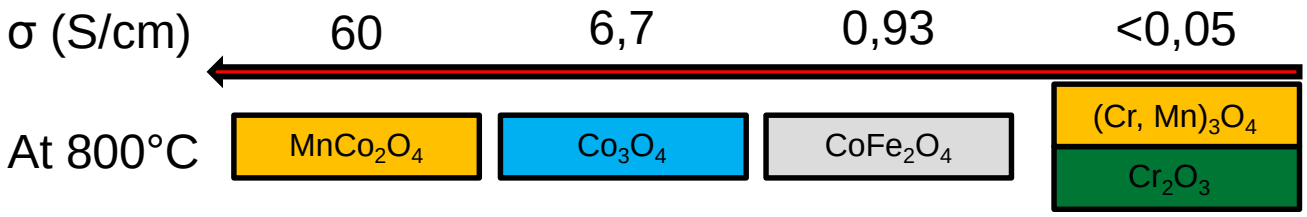


Prepared sample

Sample mounted on Probostat, inclusive Pt-electrode

Basic Idea

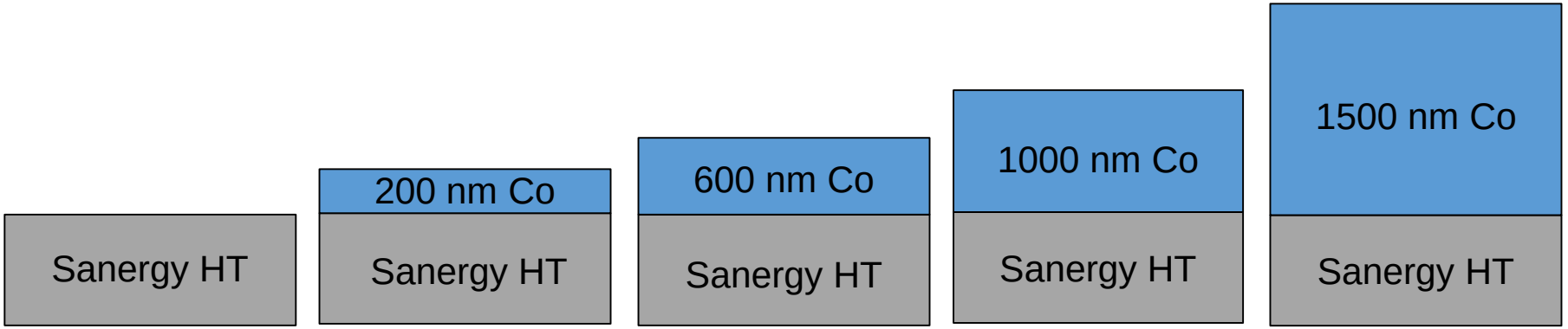




From "A. Petric, H. Ling, J. Am. Ceram. Soc. 90 (2007) 1515-1520"
and "A. Holt, P. Kofstad, Solid State Ionics 69 (1994) 137-143"

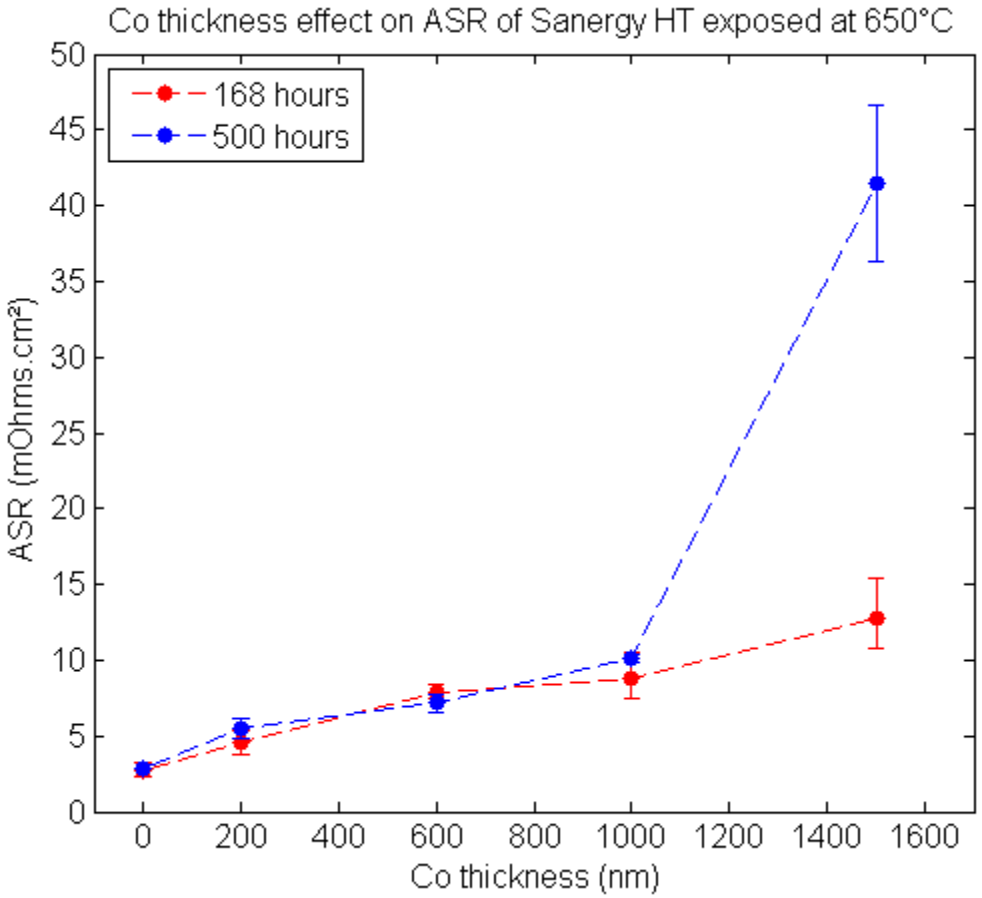
INFLUENCE OF Co- SPINEL AND Cr_2O_3 LAYER ON AREA SPECIFIC RESISTANCE

Idea

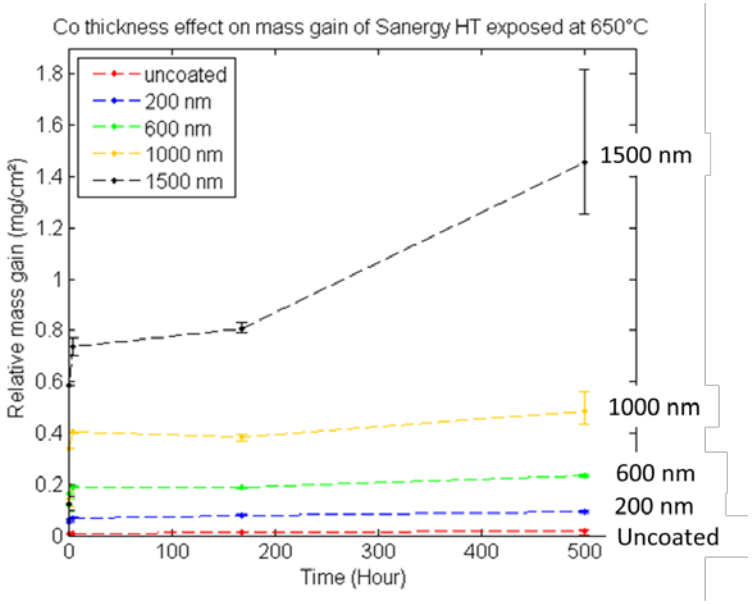


168 h or 500 h @ 650 °C, no flow, laboratory air

ASR

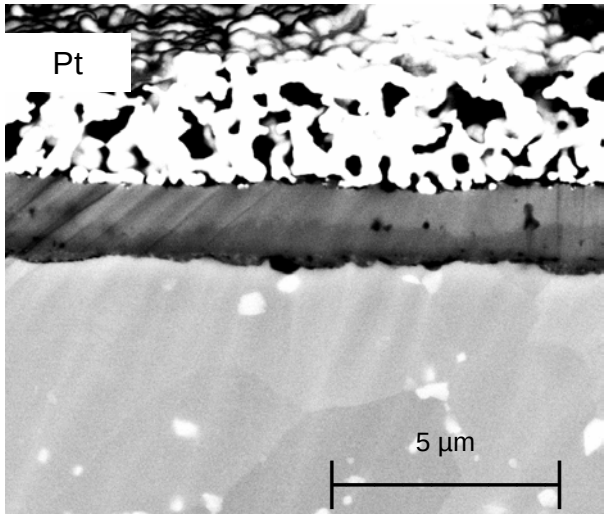


Mass gain

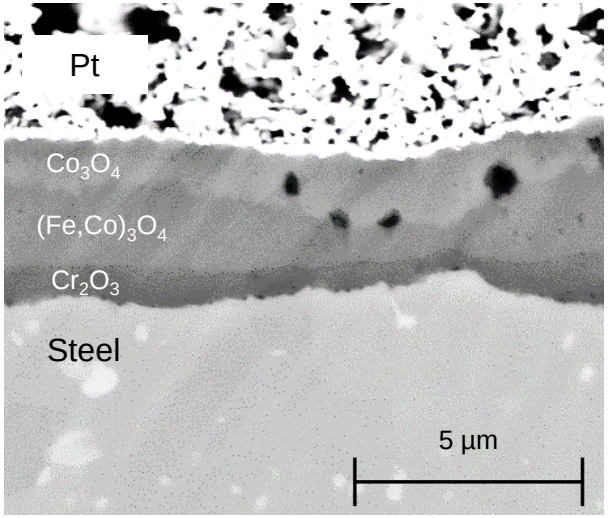


168 h or 500 h @ 650 °C, no flow, laboratory air

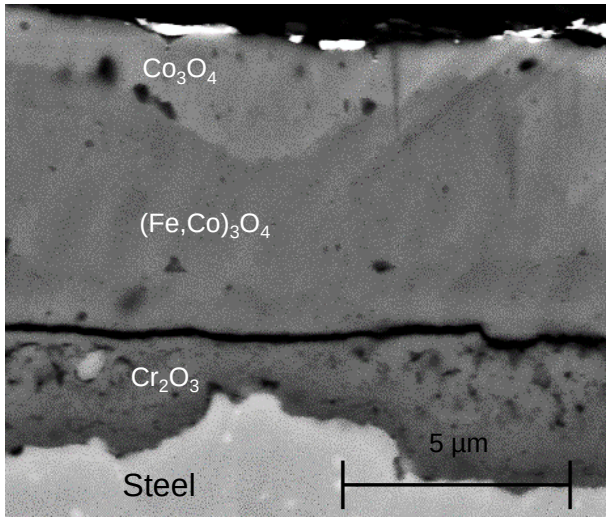
600 nm Co, 500 h



1000 nm Co, 500 h



1500 nm Co, 500 h



Thickness of the Co_3O_4 top layer is not really influenced by the Co coating thickness

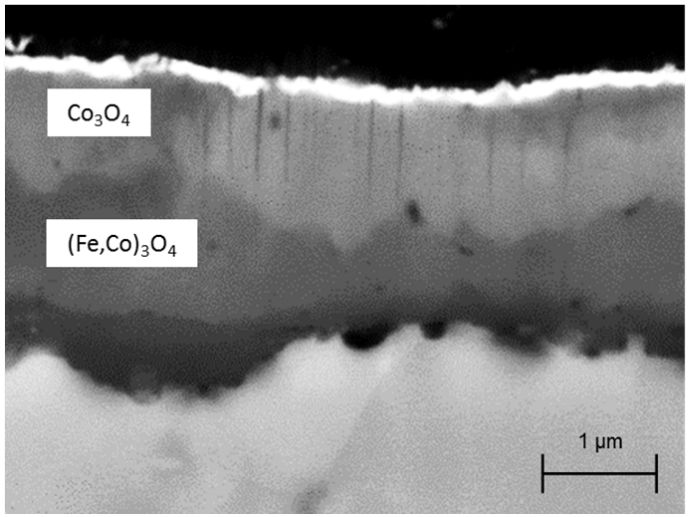
Thicker Co coating => Thicker $(Co,Fe)_3O_4$ layer and thicker Cr_2O_3 scale

Areas where the $(Co,Fe)_3O_4$ layer is thick, the underlying Cr_2O_3 scale is also thicker!

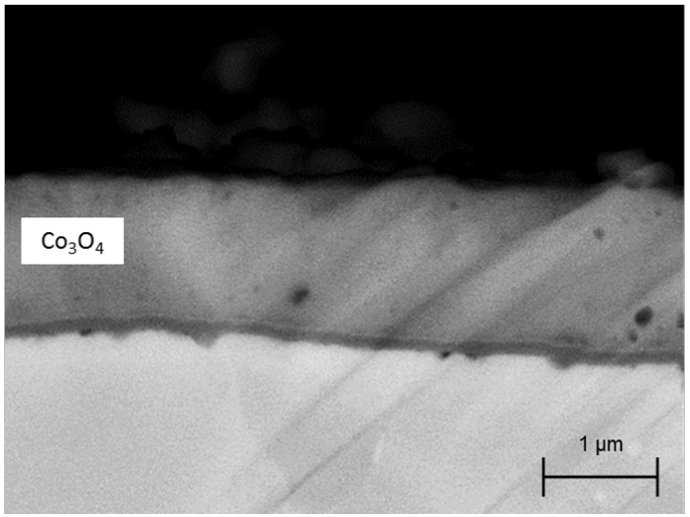
500 h @ 650 °C, no flow, laboratory air

Ce- effect

640 nm Co

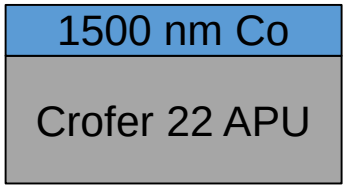


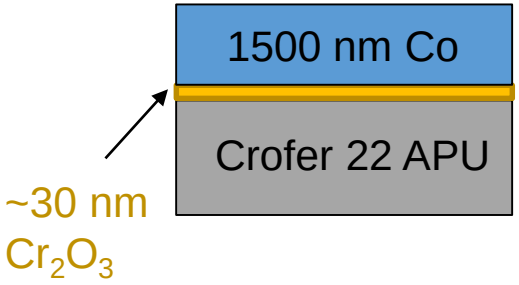
640 nm Co + 10 nm Ce



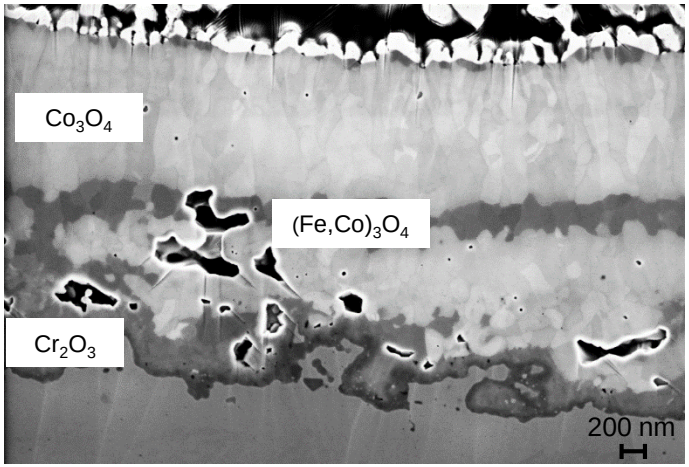
500 h @ 650 °C, no flow, laboratory air

Can we duplicate the Ce effect, by first pre-oxidizing the steel and then Co-coating?



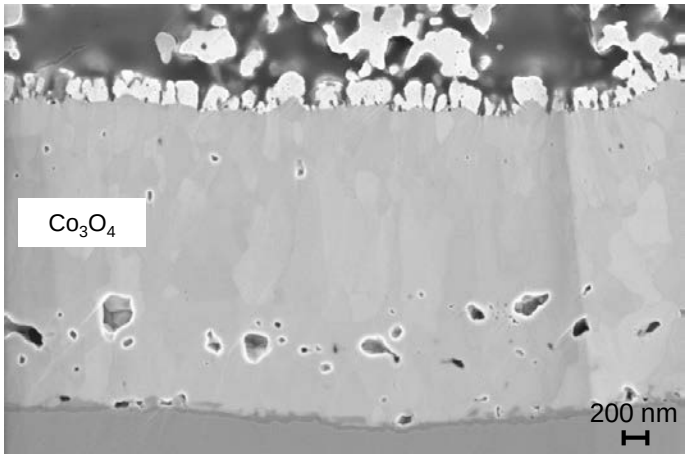


non-preox



2,9 µm

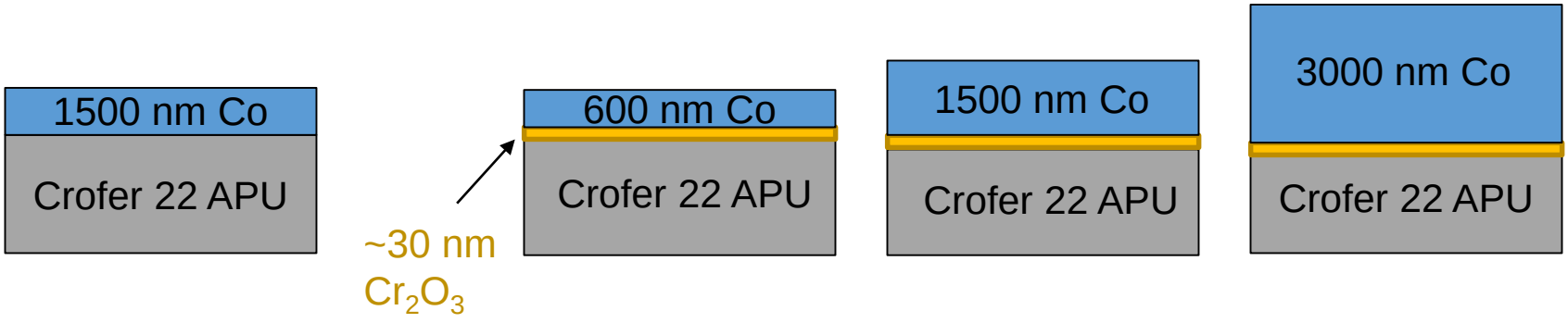
preox

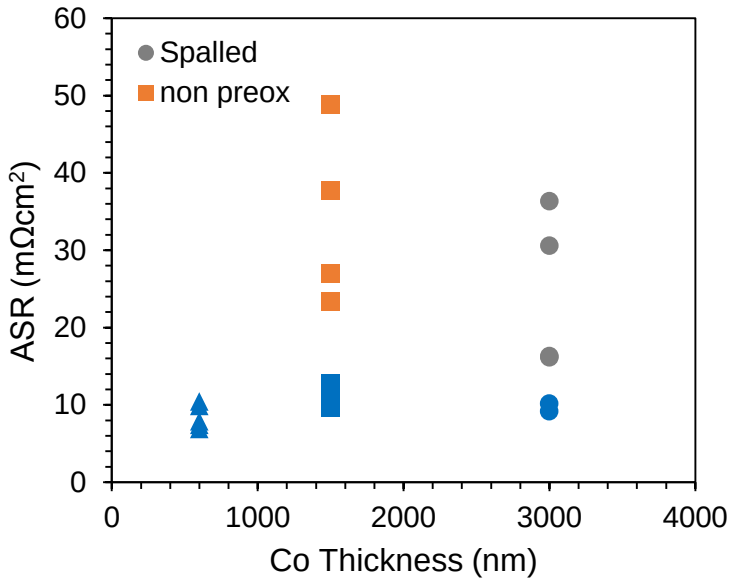


2,8 µm

500 h @ 600 °C, no flow, laboratory air

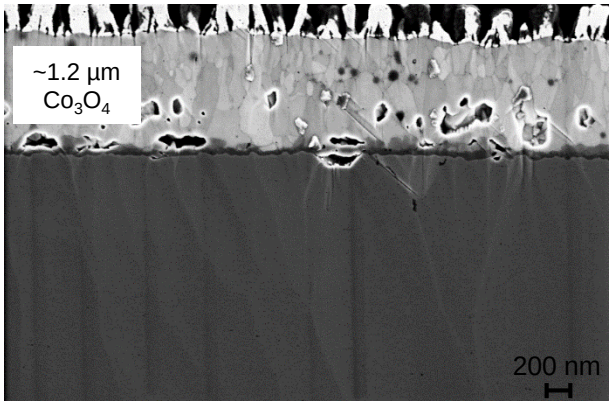
Can we duplicate the Ce effect, by adding a thin Cr_2O_3 layer between steel and Co?



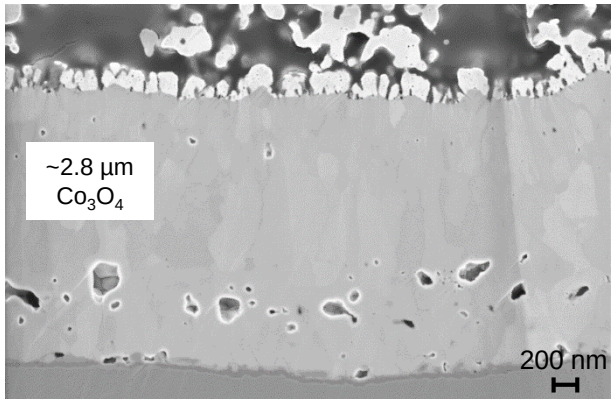


500 h @ 600 °C, no flow, laboratory air

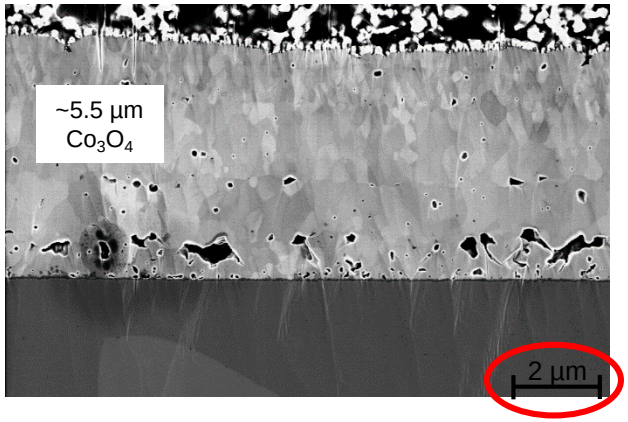
600 nm Co

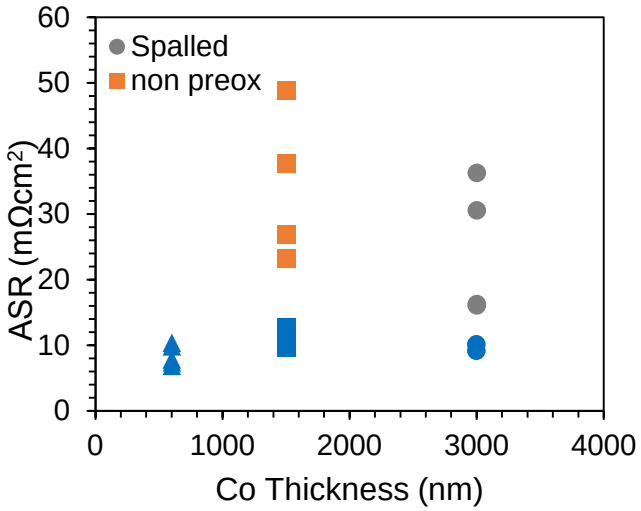


1500 nm Co



3000 nm Co





- Co-Spinel thickness does not influence the ASR
- Cr2O3 main contribution to ASR

500 h @ 600 °C, no flow, laboratory air

Summary – Electrical Resistance

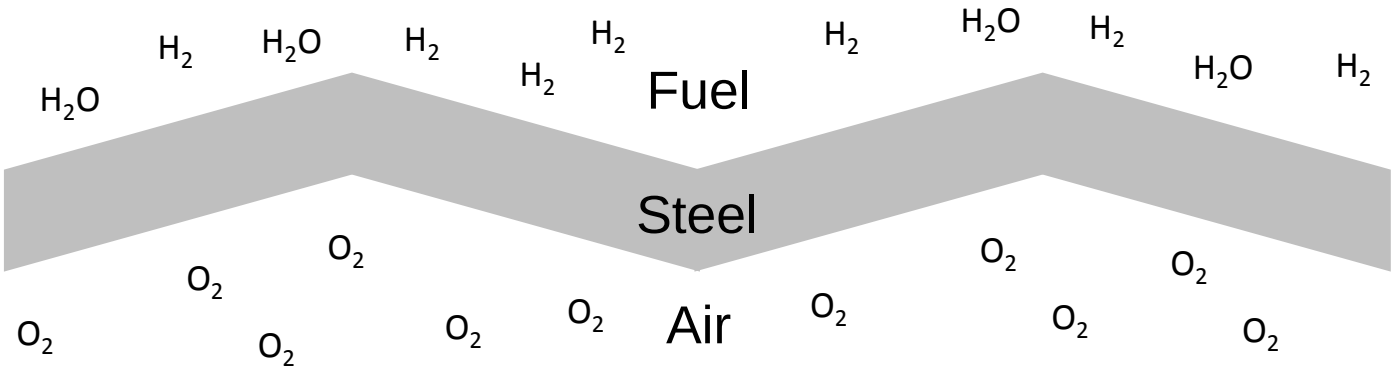
- Thicker Co coating => porous and thicker Cr_2O_3 scale => higher ASR
- Pre-oxidation or Ce suppress this effect
- Spinel (Co_3O_4) thickness does not affect ASR

Dual atmosphere effect

Inverse Temperature effect

Question

Does the dual atmosphere influence the corrosion behavior?



Motivation

Closer to reality

Reexamine this effect in regard to reduced SOFC operating temperatures

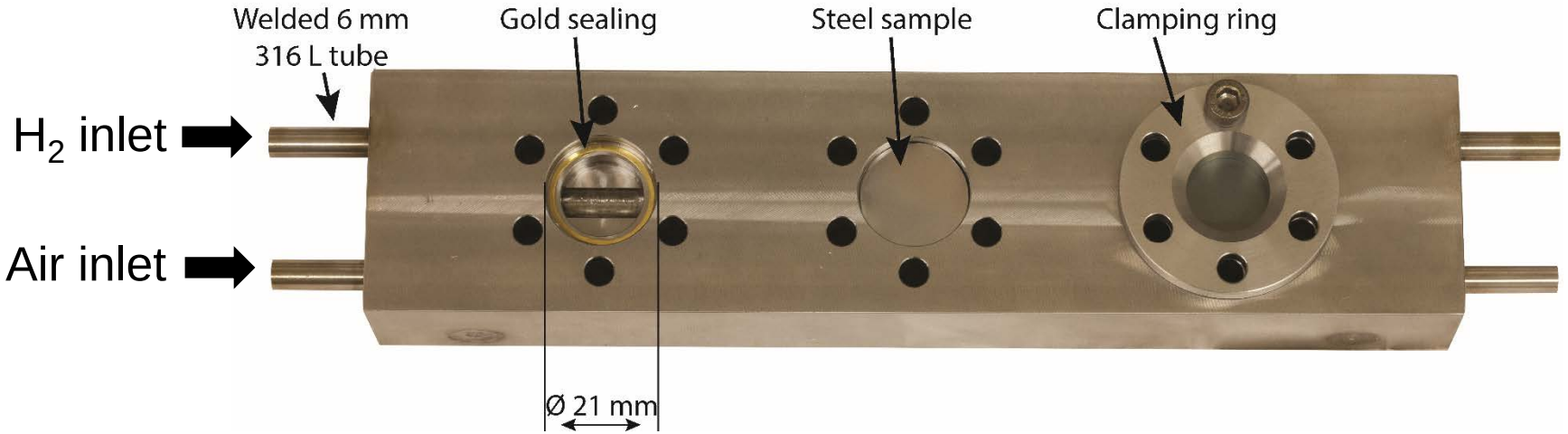
Exposure conditions

Material:

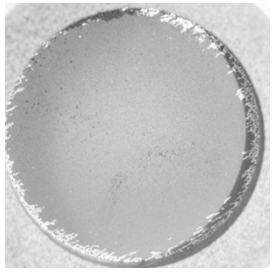
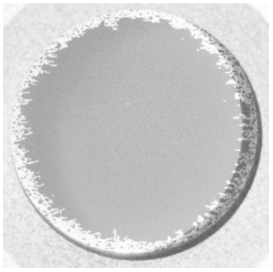
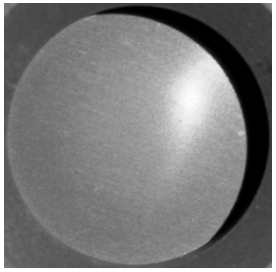
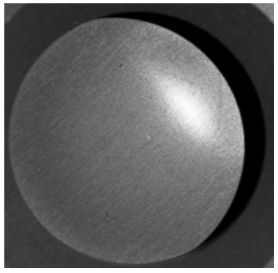
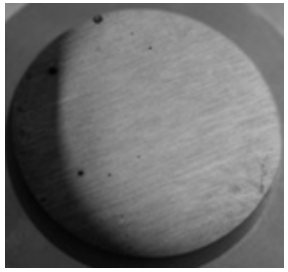
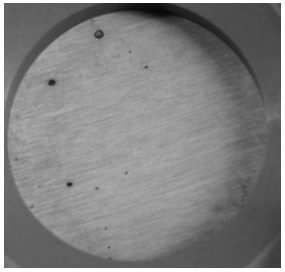
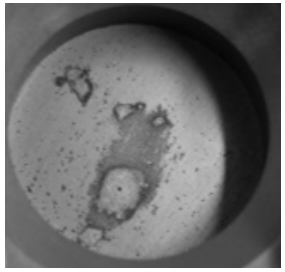
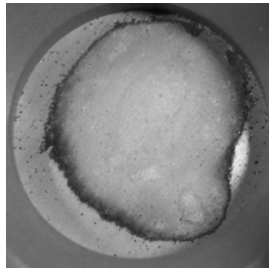
AISI 441 pre-oxidized for 180 min @ 800 °C, low flow (~250 sml/min), dry air

Exposure conditions:

Temperatures: 600 °C, 700 °C & 800 °C

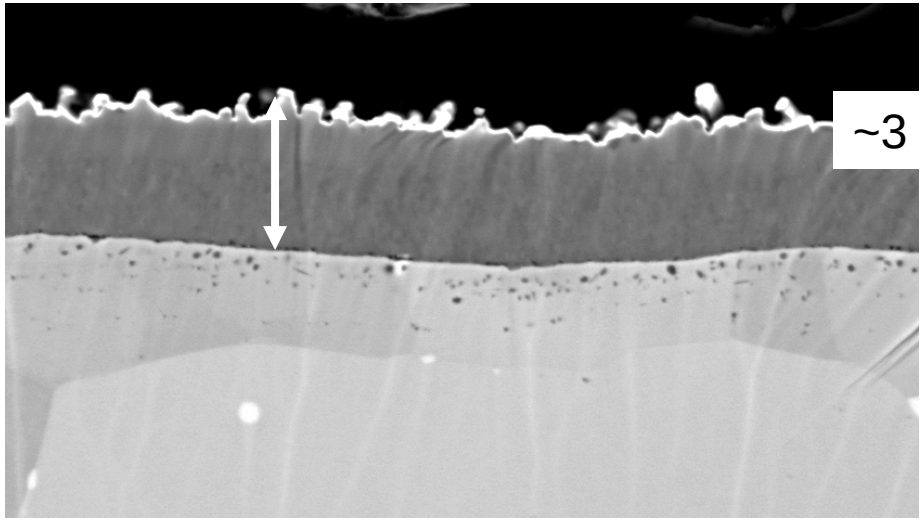


Visual inspection of air sides

	Single atmosphere		Dual atmosphere		
800 °C					No obvious effect
700 °C					No obvious effect
600 °C					Strong dual atm effect
	1000 h	3000 h	1000 h	3000 h	

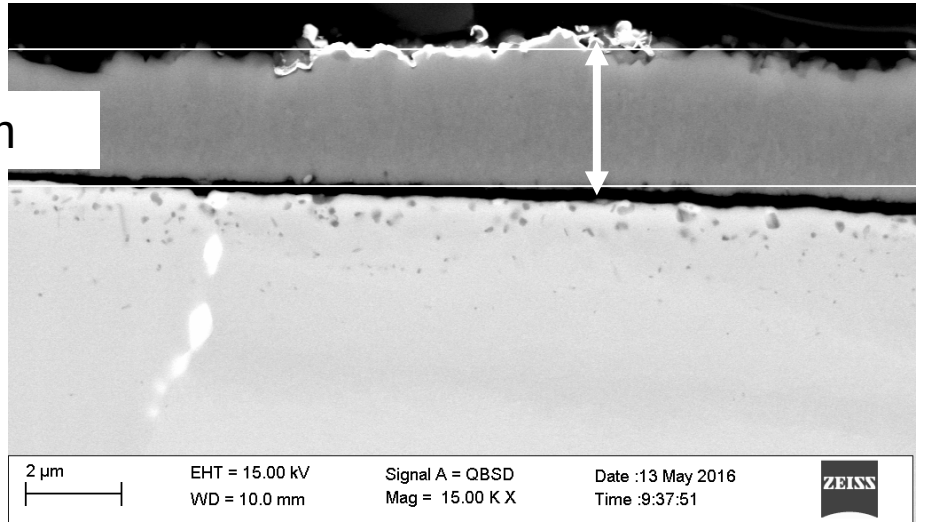
800 °C

Single atmosphere



~3 µm

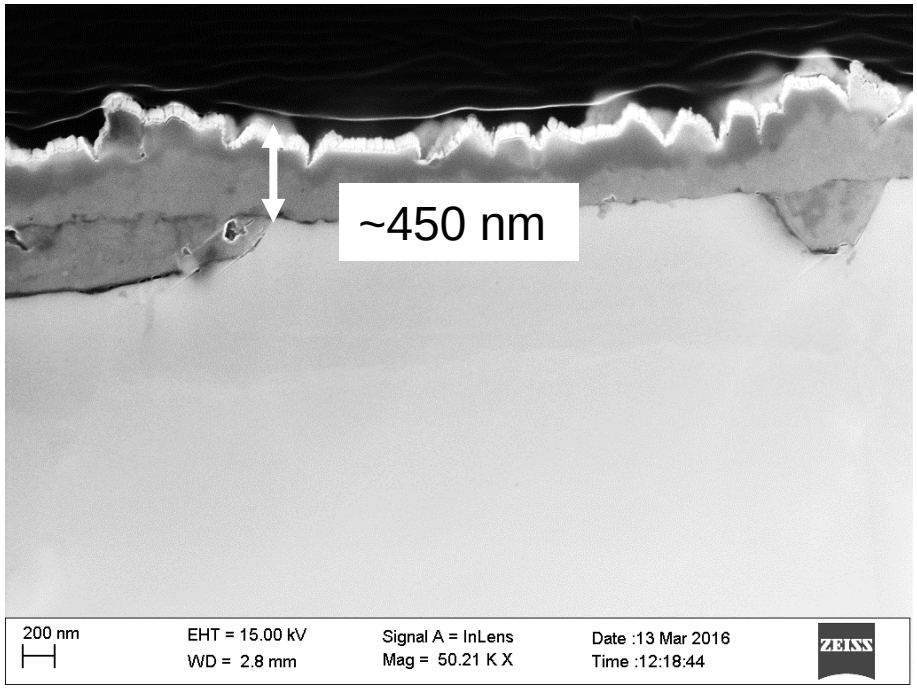
Dual atmosphere (air side)



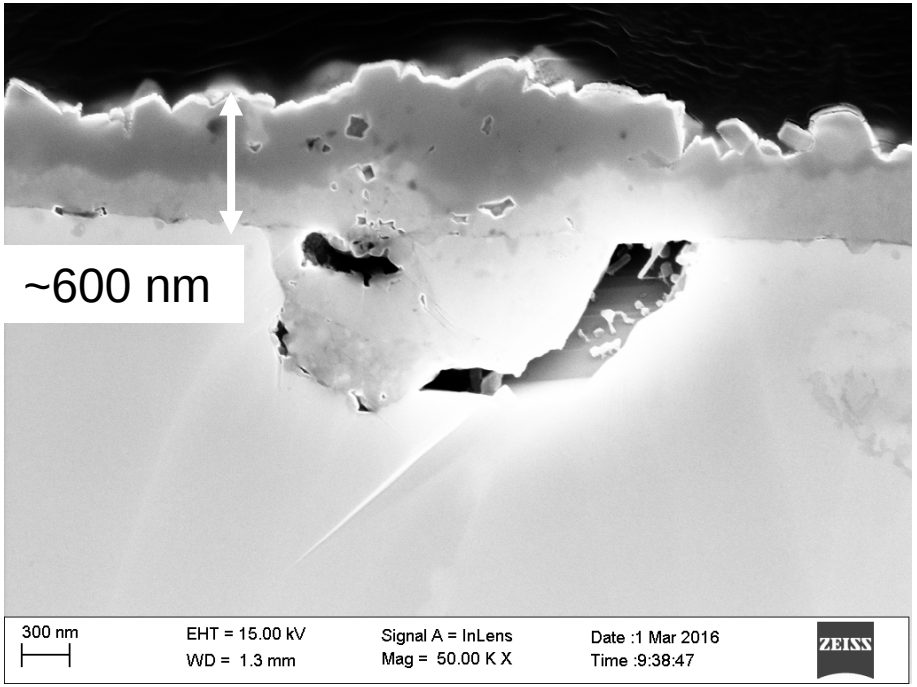
- Oxide thickness similar
- Oxide composition similar

700 °C

Single atmosphere



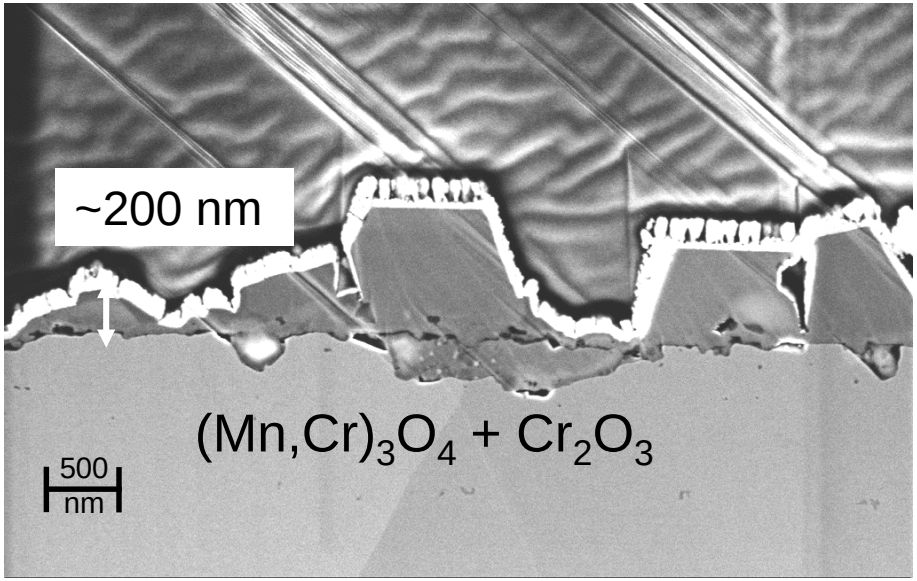
Dual atmosphere (air side)



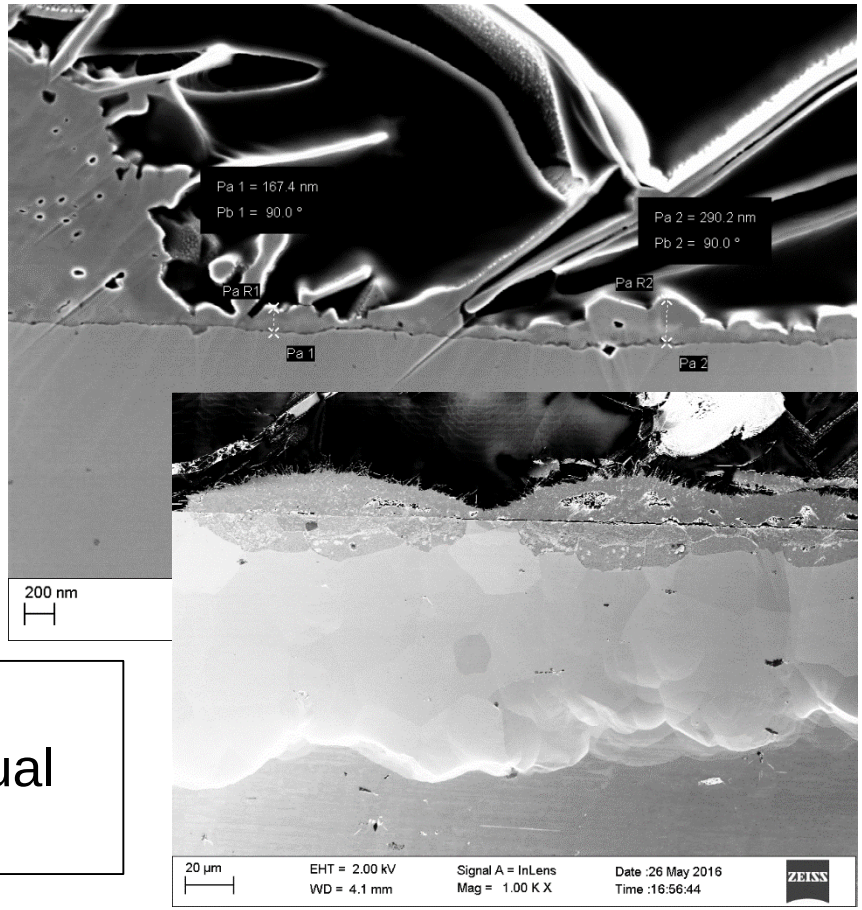
- Slightly thicker oxide in dual atmosphere
- Oxides too thin for SEM/EDX

600 °C

Single atmosphere



Dual atmosphere (air side)



- Protective oxide similar in thickness
- Breakaway corrosion visible under dual atmosphere conditions

Summary - Temperature effect

- 700 and 800 °C do not exhibit a significant dual atmosphere effect

- Severe dual atmosphere effect at 600 °C

Inverse Temperature effect

Dual atmosphere effect

Pre-oxidation Correlation

Questions

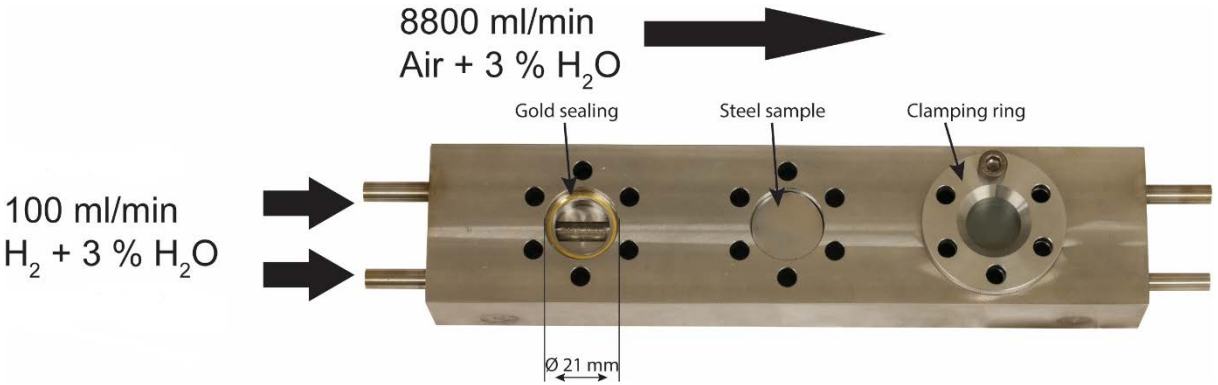
- Can we correlate pre-oxidation time to the onset of breakaway oxidation?
- Short preoxidation = Accelerated testing?

Preoxidation

- Material: 5 x AISI 441
- 800 °C, low flow (~250 sml/min), air + 3 % H_2O
- Different pre-oxidation times chosen:
  - 0 min
  - 11 min
  - 45 min
  - 180 min
  - 280 min

Exposure conditions

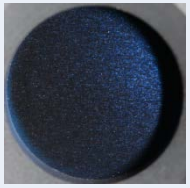
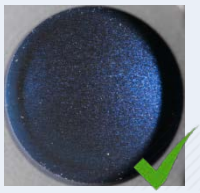
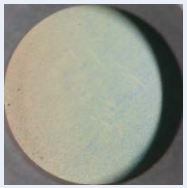
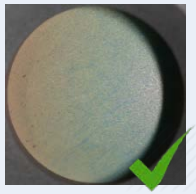
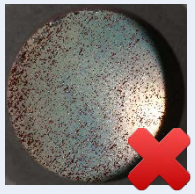
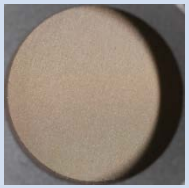
- Temperature: 600 °C



- Intervals in which photos were taken:
  - 0 h
  - 24 h
  - 168 h
  - 500 h
  - 730 h
  - 1000 h

1000 hours

VISUAL INSPECTION

Pre-oxidation times \ Exposure times	0 h	24 h	168 h	500 h	730 h	1000 h
0 min						
11 min						
45 min						
180 min						
280 min						

Summary – Pre-oxidation Correlation

- Good correlation between pre-oxidation and onset of breakaway corrosion

Conclusions

Conclusions

- Electrical Resistance study:
  - Thicker Co coating => porous and thicker Cr_2O_3 scale => higher ASR
  - Pre-oxidation or Ce suppress this effect
  - Spinel (Co_3O_4) thickness does not affect ASR
- Dual Atmosphere effect:
  - Inverse Temperature effect -> severe effect visible at lower temperatures (600 °C), no visible effect at higher temperatures (800 °C)
  - Good correlation between pre-oxidation and onset of breakaway oxidation

Thank you for your attention!