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High Temperature performances of coated and non-coated ferritic stainless steel interconnects for Solid Oxide Electrolyzer Cell application

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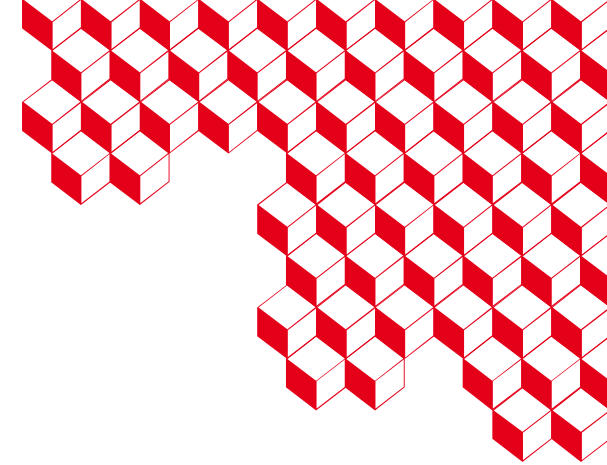
HAL Id: hal-04579119

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Submitted on 23 May 2024

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High Temperature performances of coated and non-coated ferritic stainless steel interconnects for Solid Oxide Electrolyzer Cell application

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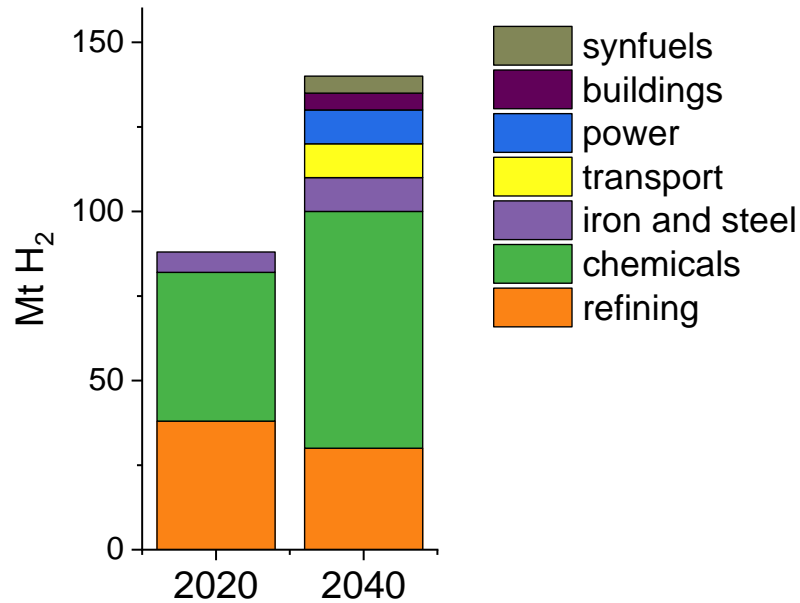
(2) Université Paris-Saclay, CEA, Service de Recherche en Métallurgie Appliquée, 91191, Gif-sur-Yvette, France

(3) Université Grenoble Alpes, CEA LITEN, 38054 Grenoble, France

(4) GENVIA, 34535 Béziers France

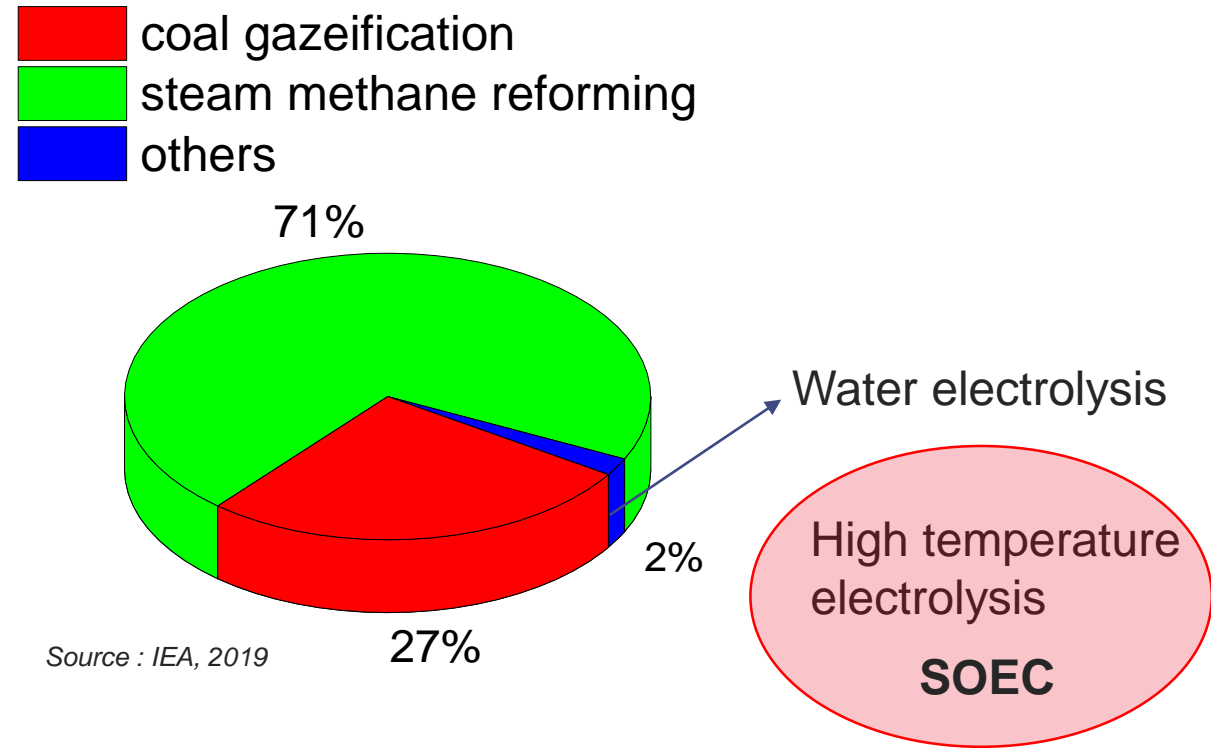
Context : H₂ consumption and production

Current (2020) and expected (2040) worldwide hydrogen consumption



Source: Global Hydrogen Review 2021, IEA

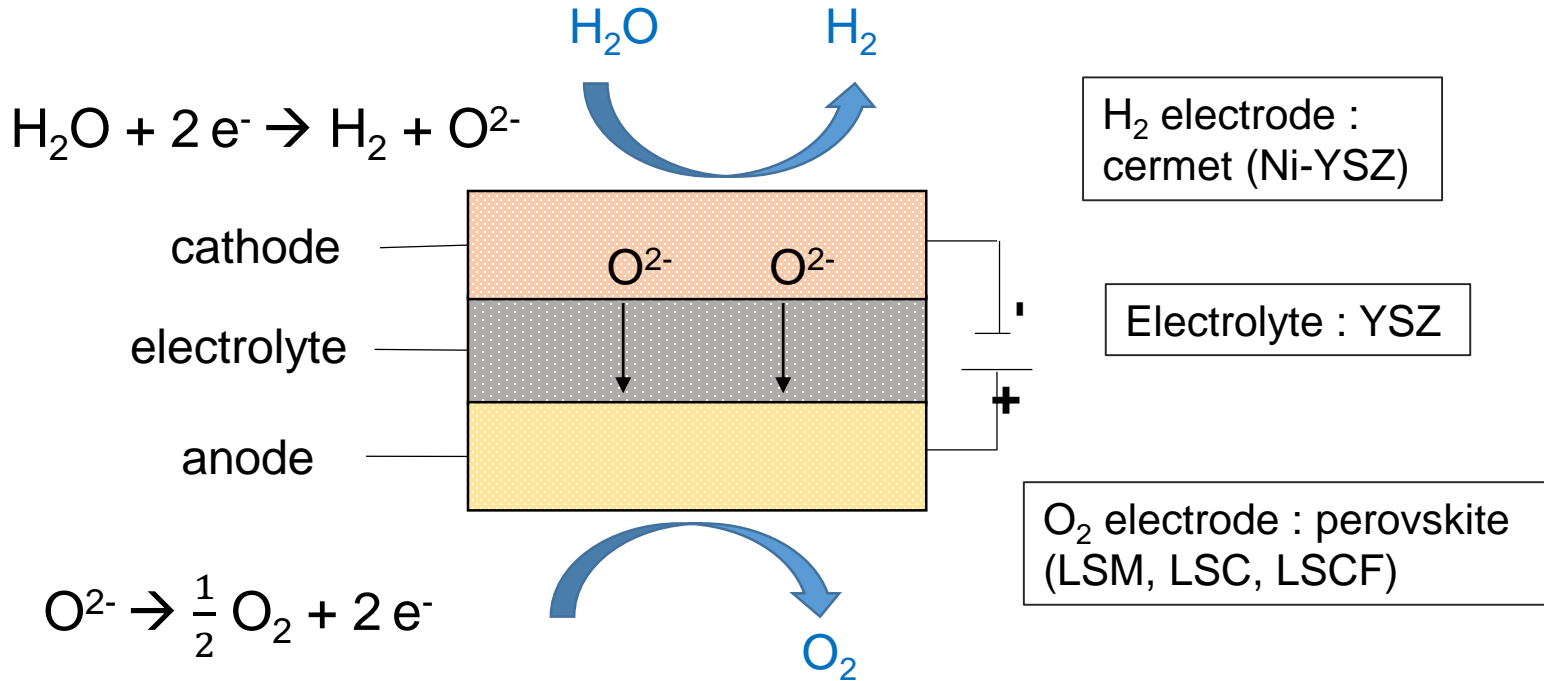
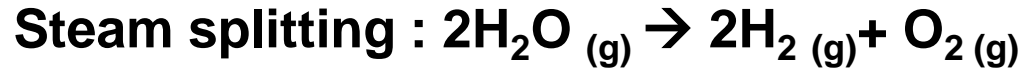
Worldwide Hydrogen production (2018)



Source : IEA, 2019

Development of H₂ production by H₂O electrolysis powered by sustainable electricity

High temperature Solid Oxide Electrolyzer Cell



- Working temperature : 700-800°C

- Reversible process :
 $\text{H}_2\text{O} + \text{electricity} \rightarrow \text{H}_2 + \text{O}_2$ (SOEC)
 $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O} + \text{electricity}$ (SOFC)

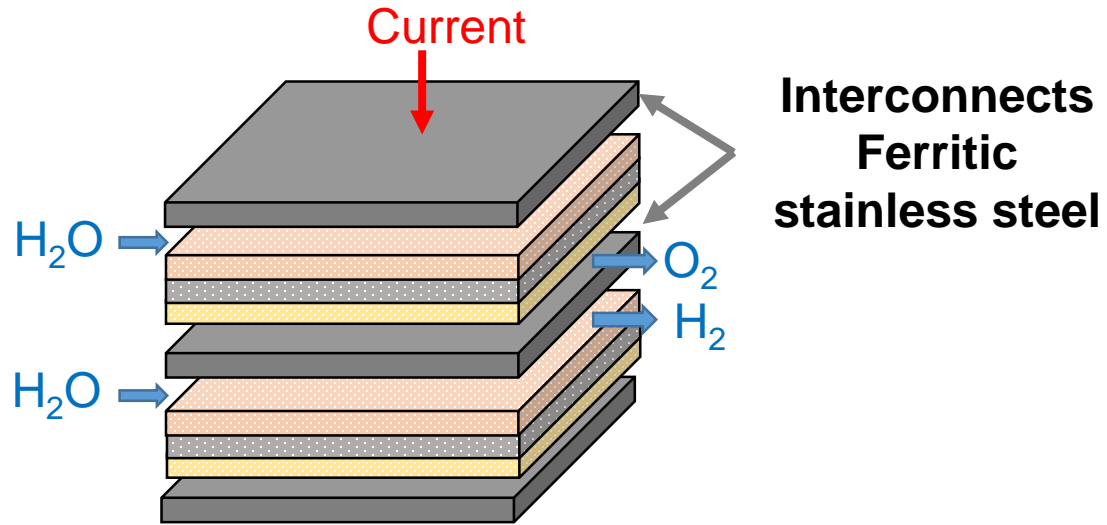
YSZ = Y₂O₃ stabilized ZrO₂
 LSM = La_xSr_{1-x}MnO_{3-δ}
 LSC = La_xSr_{1-x}CoO_{3-δ}
 LSCF = La_xSr_{1-x}Co_yFe_{1-y}O_{3-δ}

Electrochemical cell working both in electrolyzer and fuel cell modes

Interconnects for SOEC/SOFC



Electrolyzer = stack of cells separated by interconnects



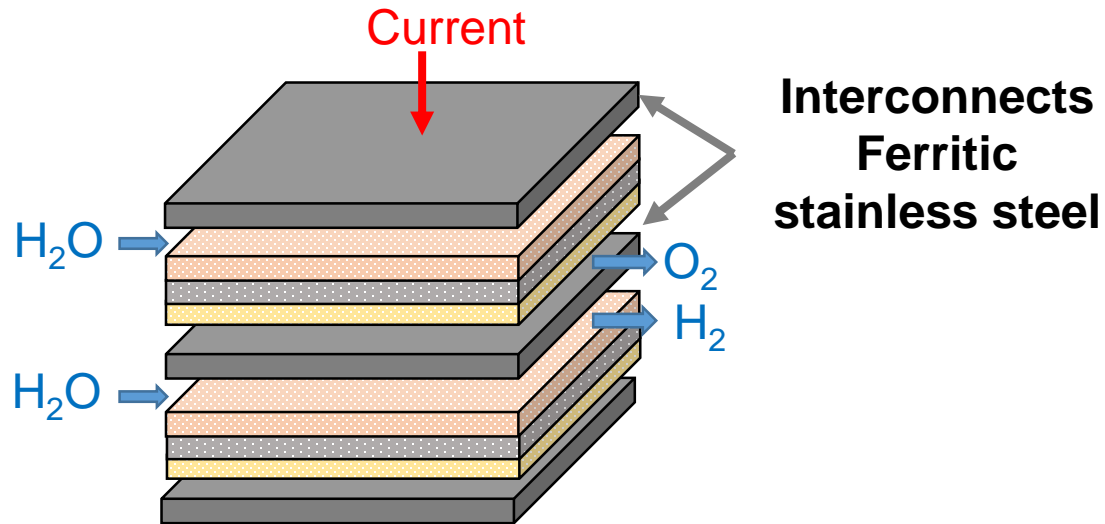
Interconnects properties:

- High electrical conductivity
- Chemical stability at HT in O₂ and H₂
- CTE compatible with cell materials

Interconnects for SOEC/SOFC

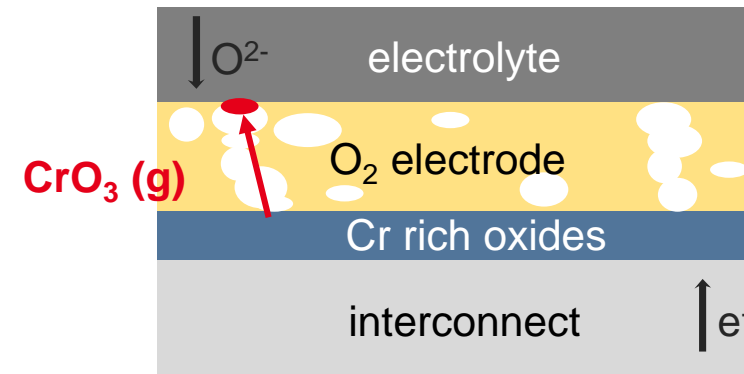
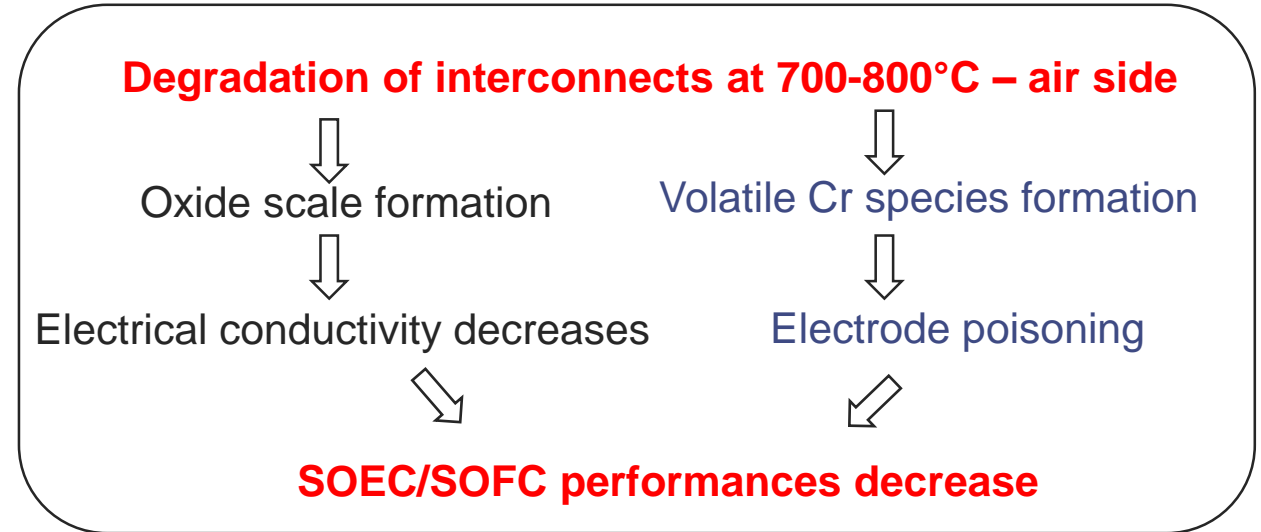


Electrolyzer = stack of cells separated by interconnects



Interconnects properties:

- High electrical conductivity
- Chemical stability at HT in O_2 and H_2
- CTE compatible with cell materials



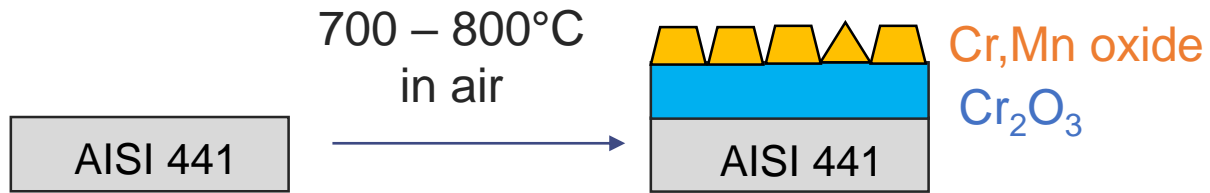
Degradation of air-side interconnects in SOFC/SOEC working conditions

AISI441 interconnect

Low cost ferritic steel alloy **AISI 441** used as interconnect

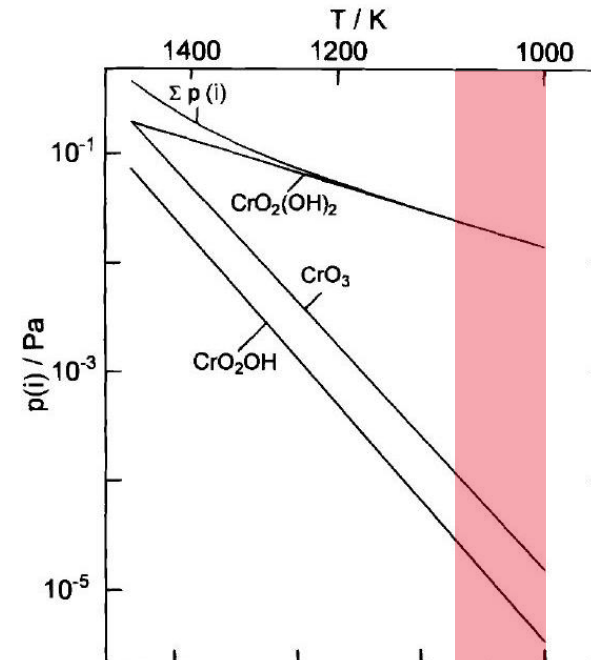
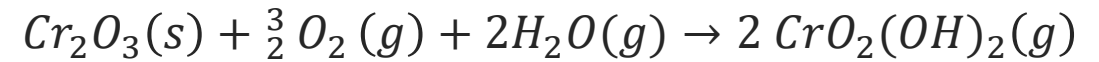
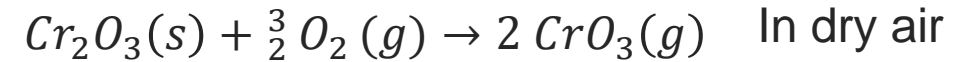
Elements	Cr	Mn	Si	Ti+Nb	C	N	Fe
%wt.	17.80	0.30	0.60	0.65	0.015	0.015	Bal.

- Highly resistive Cr_2O_3 layer formation



Need for protective coatings to prevent degradation of AISI441 interconnects.

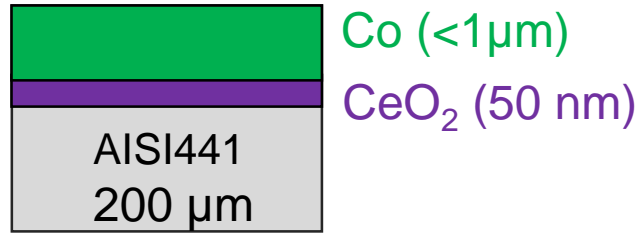
- Cr volatilization in air



K. Hilpert et al 1996 J. Electrochem. Soc. 143 3642

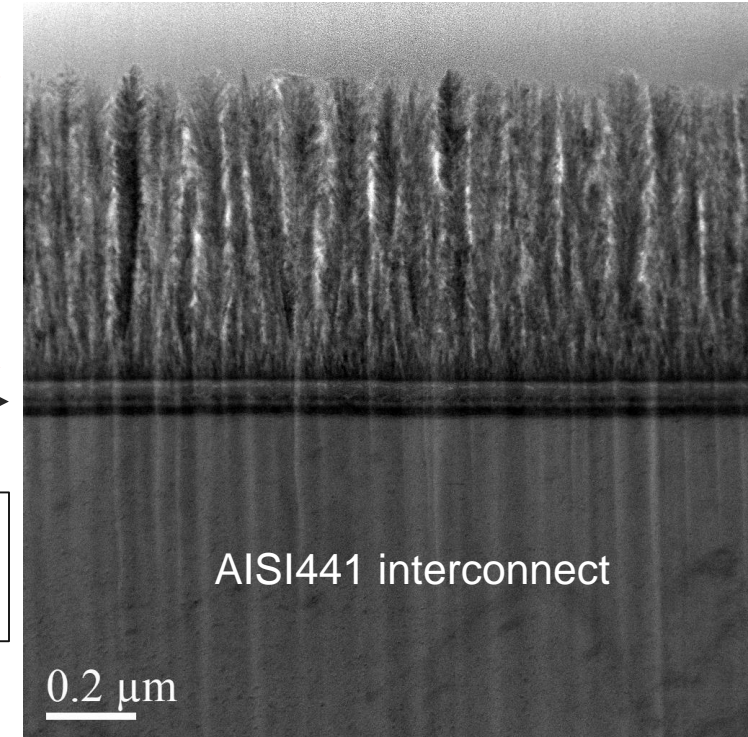
Objectives

Use of CeO_2 + Co protective coating made by PVD HiPIMS



Metallic cobalt
(600 nm)

CeO₂ (50 nm) →



- CeO_2 : accelerates the nucleation of Cr_2O_3 and slows down its growth
- Co : limits Cr volatilization and forms conductive Co oxides

Canovic, S. et al. 2013. Surface and Coatings Technology, 215

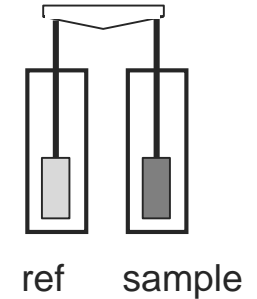
Objectives :

- to characterize interconnects performances (electrical properties, oxidation, Cr retention) in the working environment (O_2 electrode) on **long term exposure (> 1 year)**
- to evaluate the impact of protective coatings on interconnect performances

Criteria to assess interconnects performances

1. Short term oxidation (200 – 500 h)

1. Oxidation kinetics : Thermogravimetric analysis in dry synthetic air
2. Oxide scales observations and characterization



2. Long term oxidation (> 10 000h)

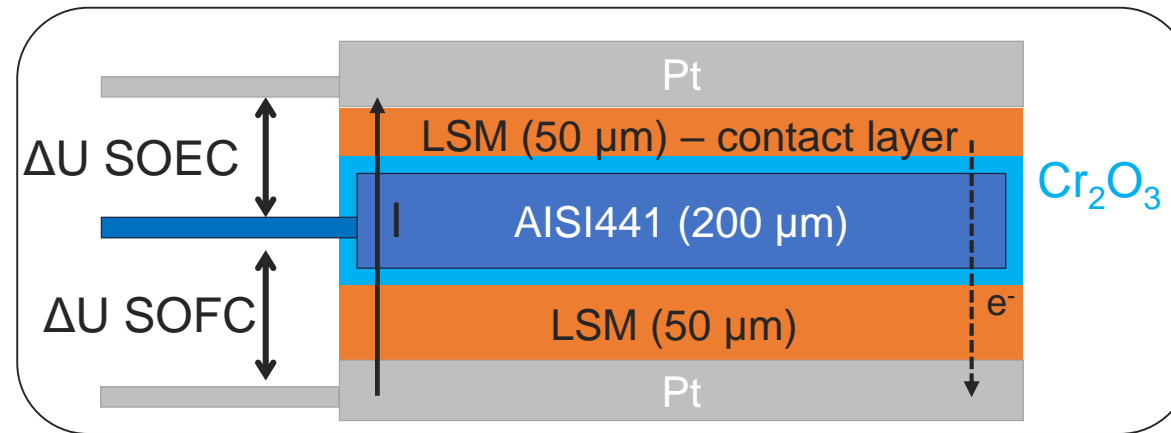
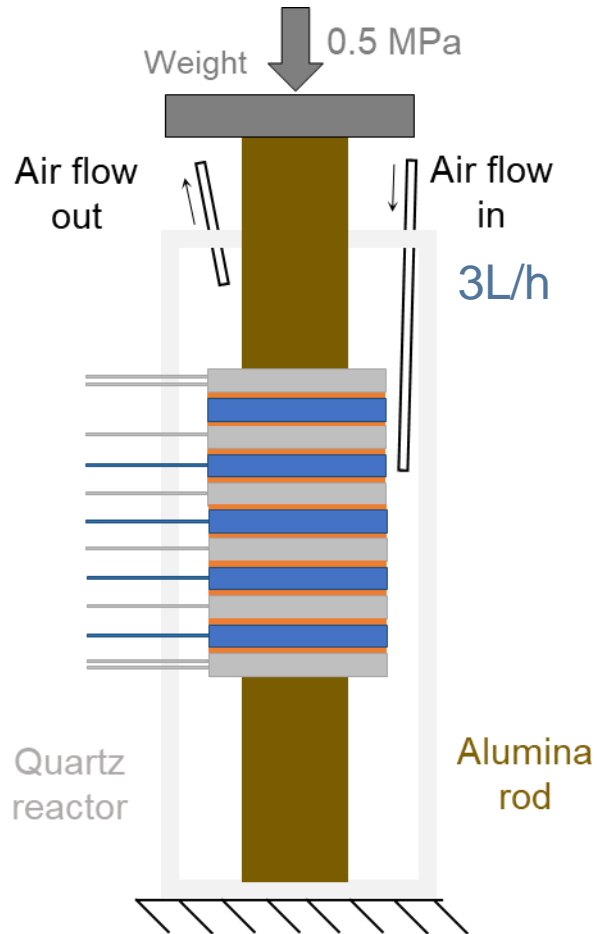
Electrical resistance : Area Specific Resistance (ASR)

ASR measurements

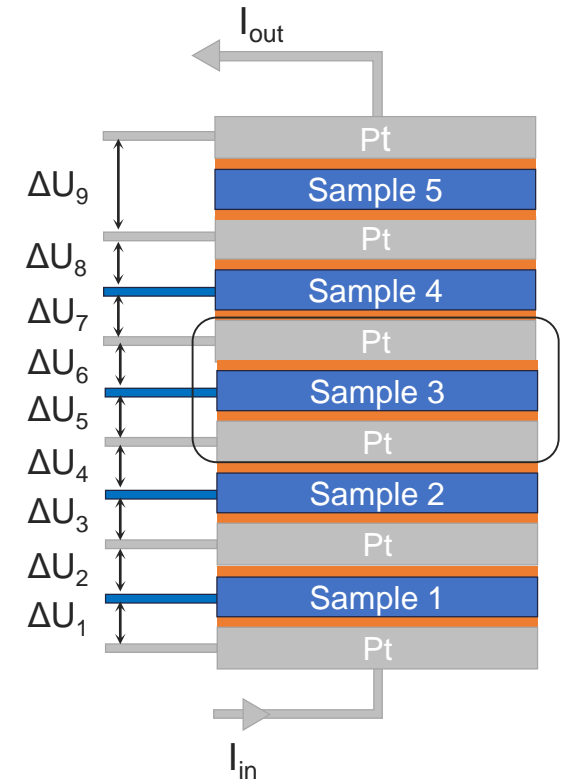
Experiments in air : O₂ electrode

SOEC mode = oxidation

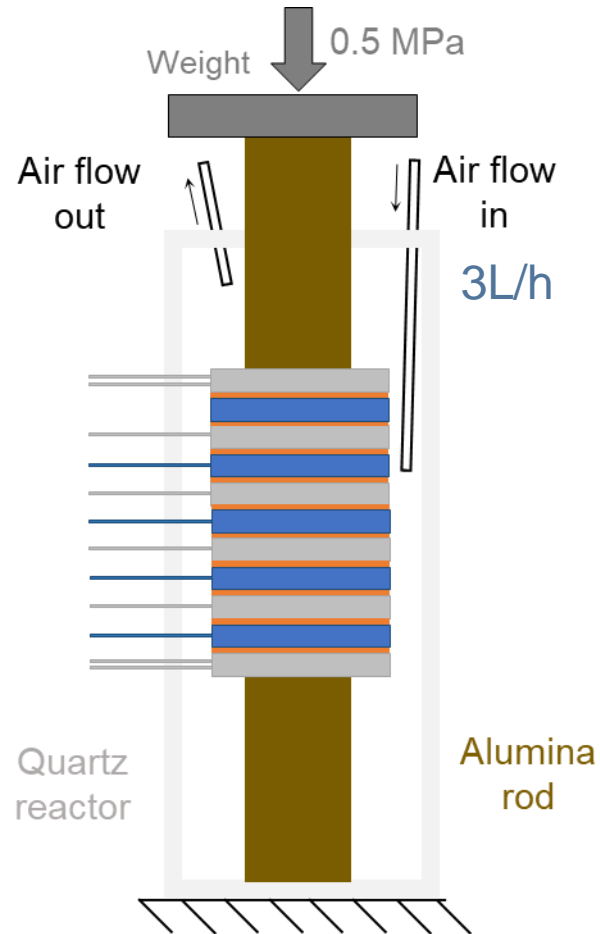
SOFC mode = reduction



0.4 A/cm²



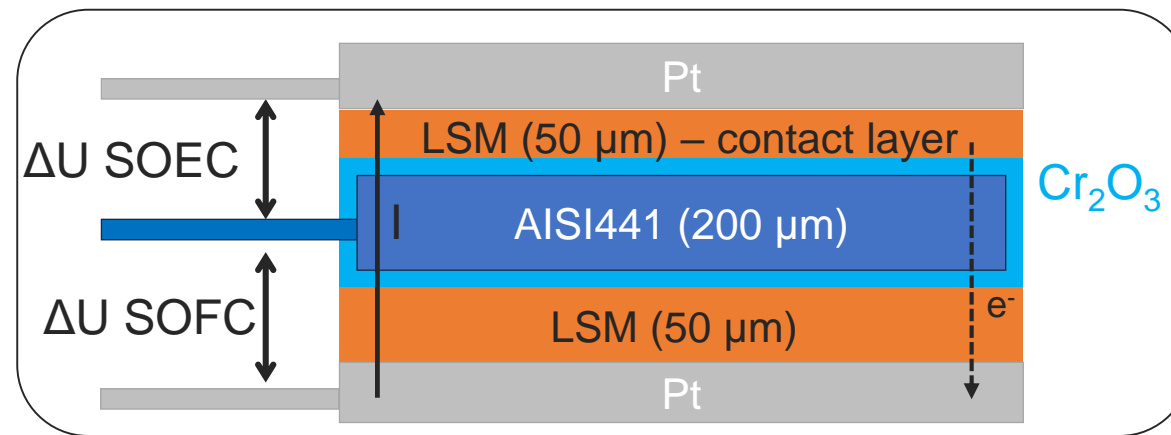
ASR measurements



Experiments in air : O₂ electrode

SOEC mode = oxidation

SOFC mode = reduction



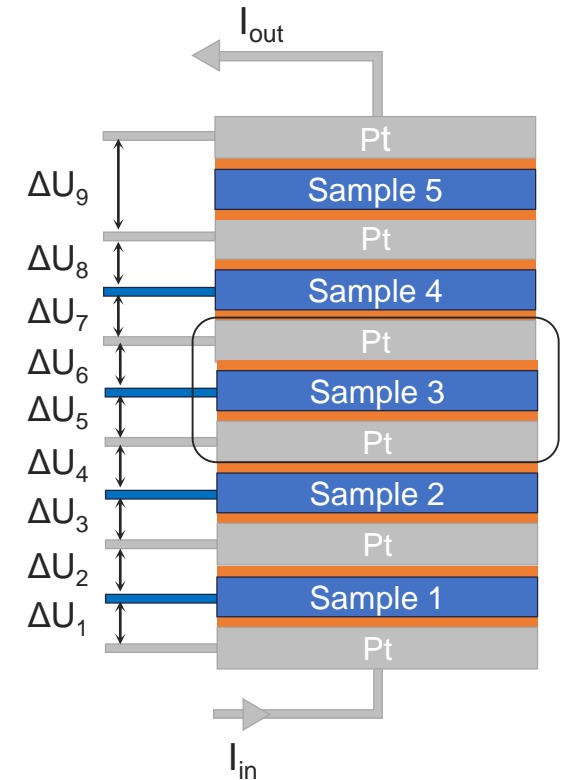
$$ASR(t) = R(t) \times A$$

$$\frac{\Delta U(t)}{I} = R(t) = \frac{1}{\sigma(t)} \times \frac{e_{ox}(t)}{A}$$

Oxide layer(s) thickness

Electrical conductivity ← Sample area

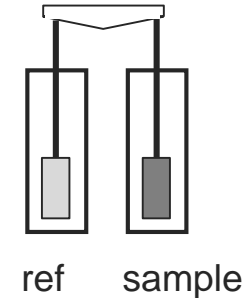
0.4 A/cm²



Criteria to assess interconnects performances

1. Short term oxidation (200 – 500 h) : coated vs uncoated samples

1. Oxidation kinetics : Thermogravimetric analysis in synthetic air
2. Oxide scales observations and characterization



2. Long term oxidation (> 10 000h) : coated vs uncoated samples

Electrical resistance : Area Specific Resistance (ASR)

Home-made specific facility developed at CEA which enables:

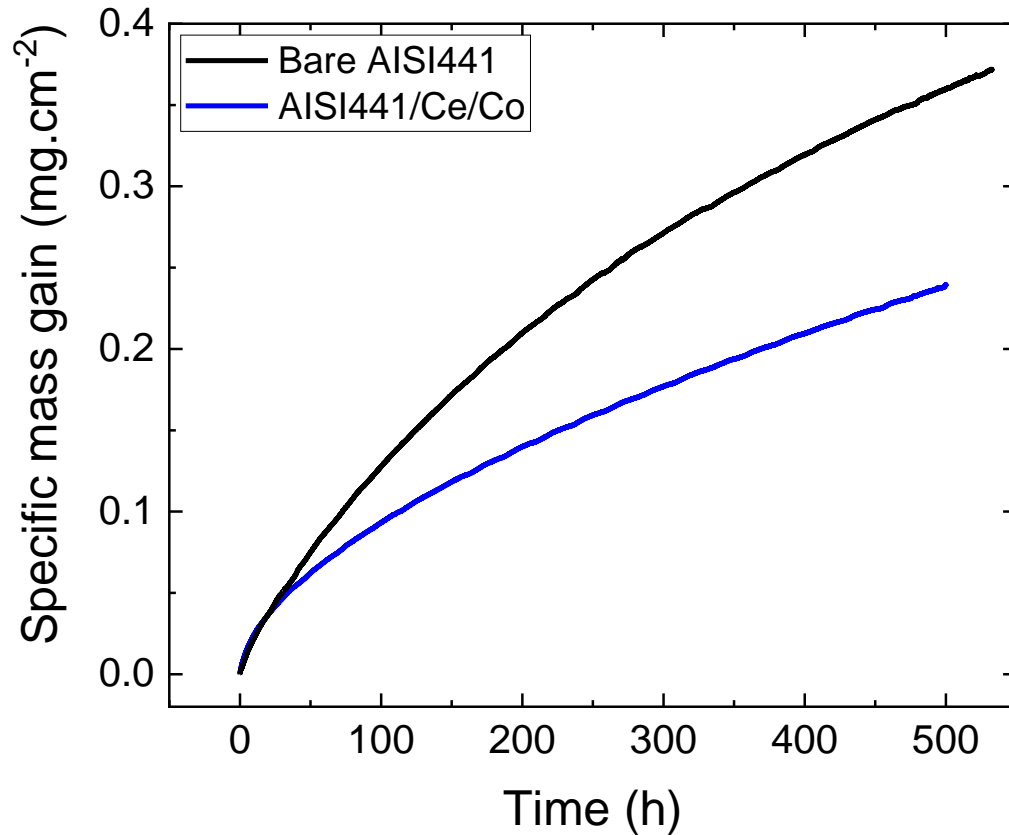
- To have reliable and repeatable ASR measurements
- To measure long-term ASR ($t \gg 1$ year) – expected SOEC lifetime 4-5 years
- To get ASR values as close as possible as what is expected in the commercial SOEC configuration
- To measure ASR both in SOEC and SOFC mode



1 ■ Short term oxidation

Oxidation kinetics : AISI441 and AISI441/CeO₂/Co

Oxidation in synthetic dry air at 800°C - thermogravimetric analysis



$$t = A + B\Delta m + C\Delta m^2 \rightarrow C = \frac{1}{k_p}$$

Monceau, D. & Pieraggi, B.; 1998. Oxidation of metals, Vol 50, Nos 516

	k_p (g ² .cm ⁻⁴ .s ⁻¹)
AISI 441	$1.1 \pm 0.6 \times 10^{-13}$
AISI441/CeO ₂ /Co	$3.7 \pm 0.2 \times 10^{-14}$

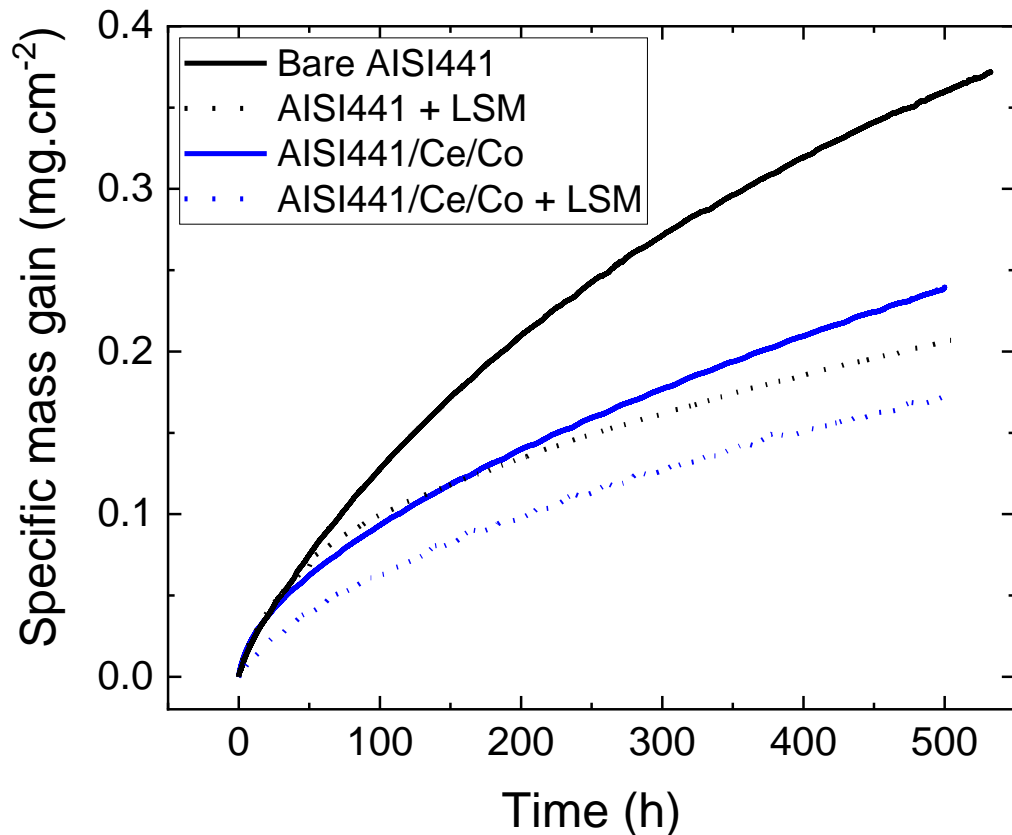
÷ 1.5 - 3

CeO₂/Co coating reduces the oxidation kinetics of AISI441 by a factor **1.5 to 3**

CeO₂/Co coating efficiently lowers the mass gain of AISI441.

Oxidation kinetics : LSM coating

Oxidation in synthetic air at 800°C - thermogravimetric analysis



	k_p (g ² .cm ⁻⁴ .s ⁻¹)
AISI 441	$1.1 \pm 0.6 \times 10^{-13}$
AISI 441 + LSM	$2.6 \pm 0.5 \times 10^{-14}$
AISI441/CeO₂/Co	$3.7 \pm 0.2 \times 10^{-14}$
AISI 441/CeO₂/Co + LSM	$1.7 \pm 0.6 \times 10^{-14}$

÷ 1.6 - 5

÷ 1.5 - 3.5

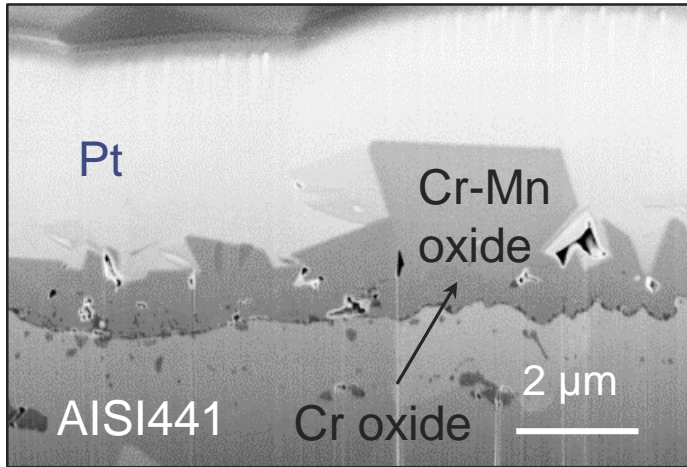
The LSM layer lowers the oxidation kinetics of both AISI441 and AISI441/CeO₂/Co.

Both CeO₂/Co and LSM coatings reduce the oxidation kinetics of AISI441.

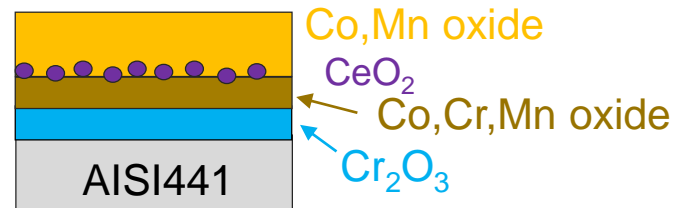
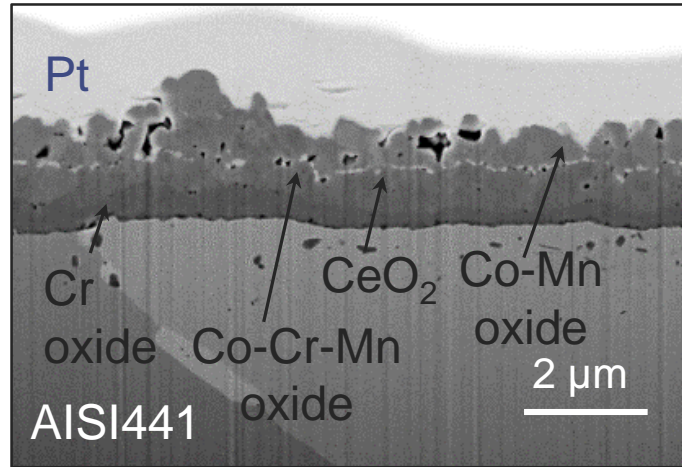
Oxide scales : AISI441 and AISI441/CeO₂/Co

Oxidation in synthetic air at 800°C for 200h

AISI441

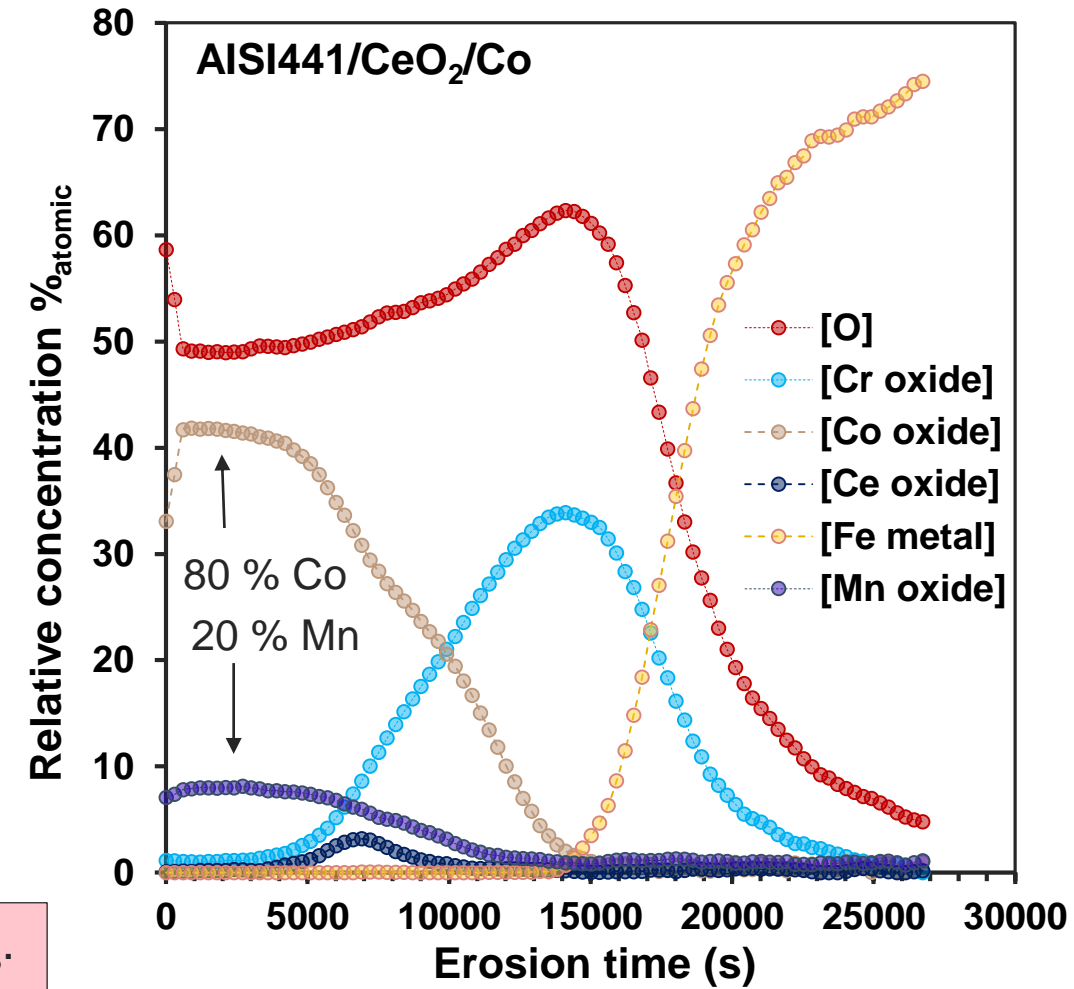


AISI441/CeO₂/Co



Formation of a (conductive) Co – Mn rich oxide on top of Cr₂O₃.
No Cr in the outer part of the scale.

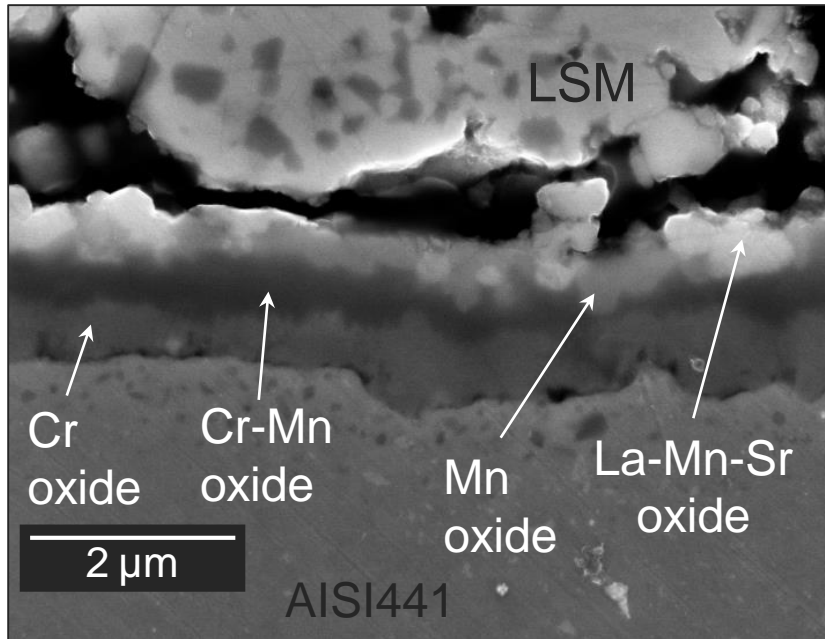
Sputtering XPS analysis



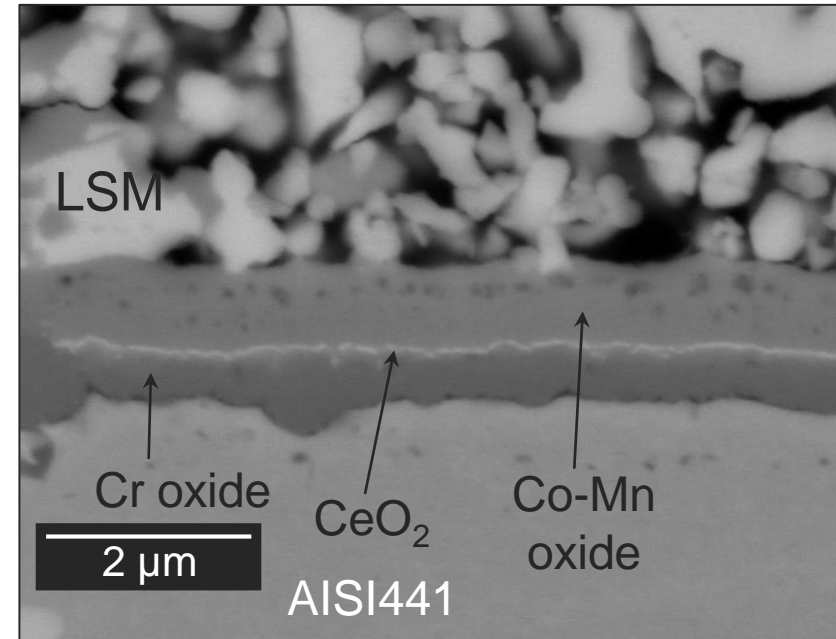
Oxide scales : LSM coating

Oxidation in synthetic dry air at 800°C for 500h

AISI441 + LSM



AISI441/CeO₂/Co + LSM



- LSM precipitates mixed in Mn rich top layer
- Thinner oxide scale compared to AISI441

- Same oxide scale arrangement as without LSM
- Thinner oxide scale compared to AISI441/Ce/Co

LSM coating modifies the top surface of AISI441 scale and decreases the oxide scale thicknesses.

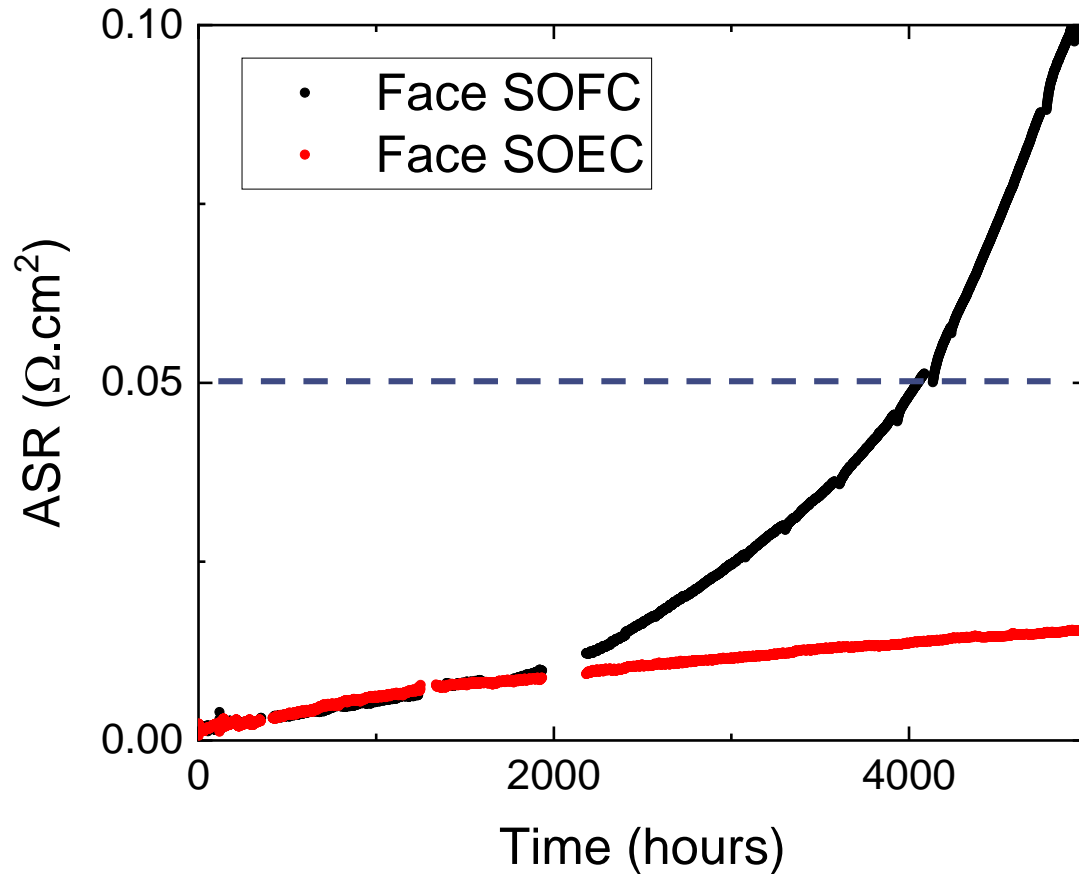


2 ■ Long term oxidation performances

ASR : AISI441

Oxidation in synthetic air at 800°C

AISI441 + LSM

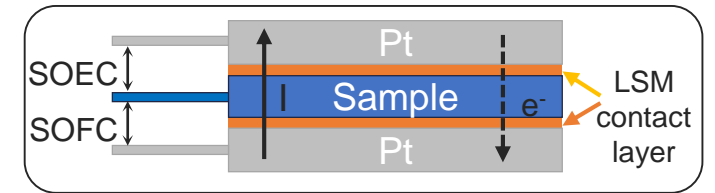


ASR limit = 50 mΩ.cm²
for 40 000h operation

Zhu, W. Z., & Deevi, S. C, 2003,
Materials Research Bulletin, 38(6)

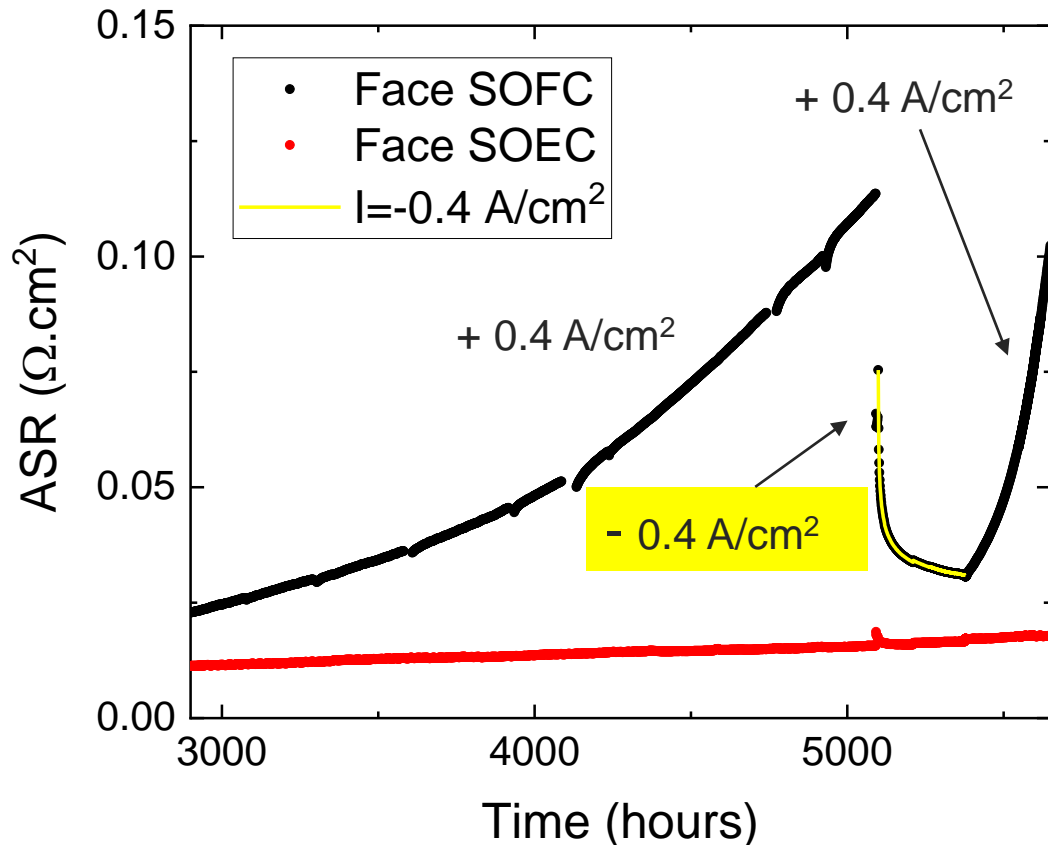
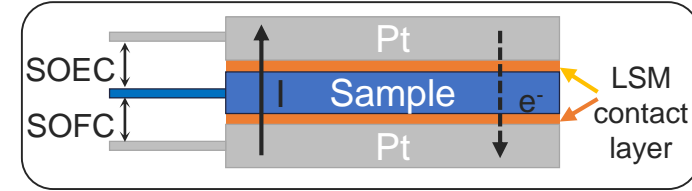
Same behaviour for SOEC and SOFC faces for the first 2000h of oxidation.

After 2000h, drastic ASR increase of SOFC face.



ASR increase of AISI441 SOFC face

Switch from $+0.4 \text{ A/cm}^2$ (SOFC mode) to -0.4 A/cm^2 (SOEC mode).



SOFC mode :
 ASR decreases when SOFC \rightarrow SOEC
 ASR increases when SOEC \rightarrow SOFC

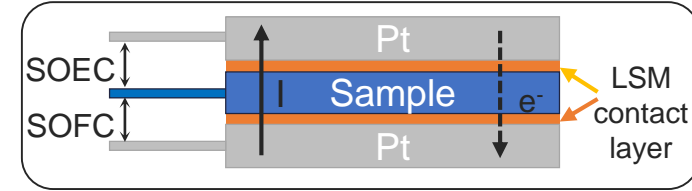
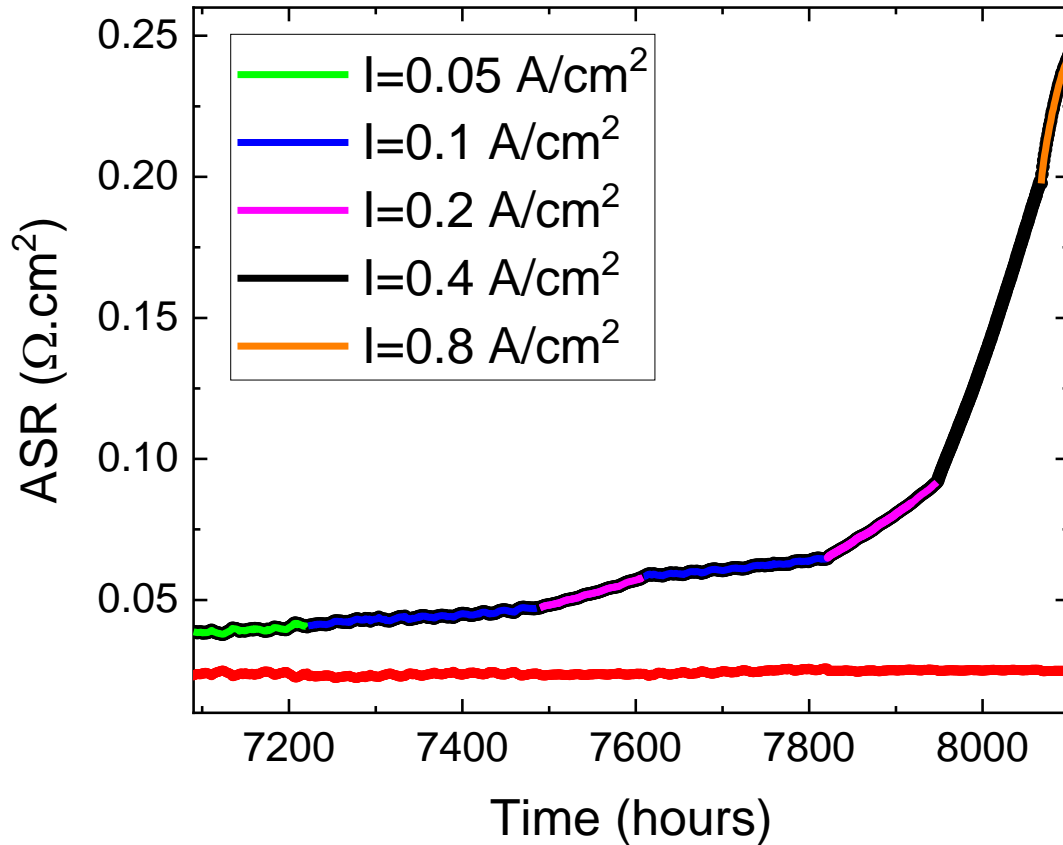
Current driven phenomenon

Assumption : The drastic ASR increase may be due to the deposition of Cr oxides on the Pt electrode through the electrochemical reduction of Cr volatile species.



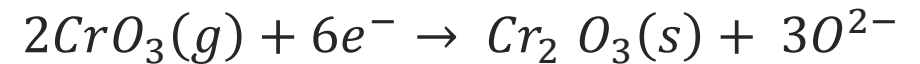
ASR increase of AISI441 SOFC face

Check influence of applied current on ASR of SOFC face.



SOFC mode :

The ASR increasing rate increases with the applied current, as expected if the formation of Cr_2O_3 from $\text{CrO}_3(\text{g})$ on Pt is rate limited by the electron transfer.

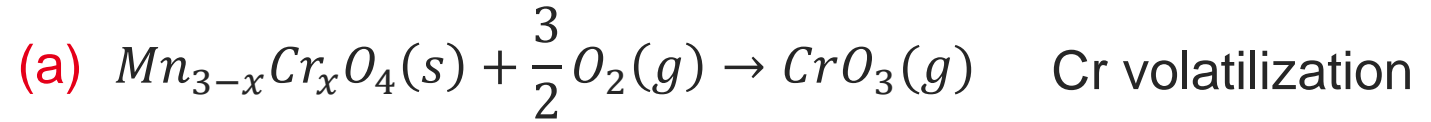
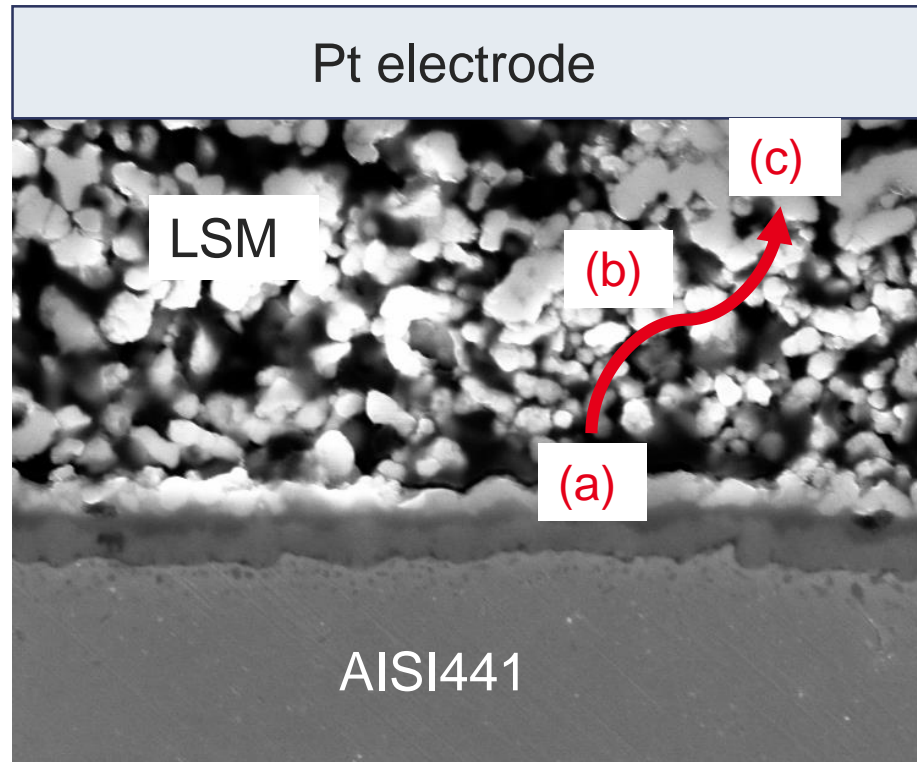


SOEC mode :

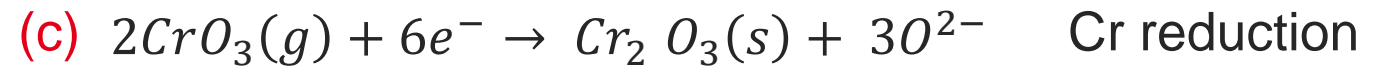
No impact of current : the ASR increasing rate is independent of applied current.

ASR increase of AISI441 SOFC face

Scenario : Cr volatile species formation and reduction on the Pt electrode.



(b) $CrO_3(g)$ diffusion through LSM contact layer

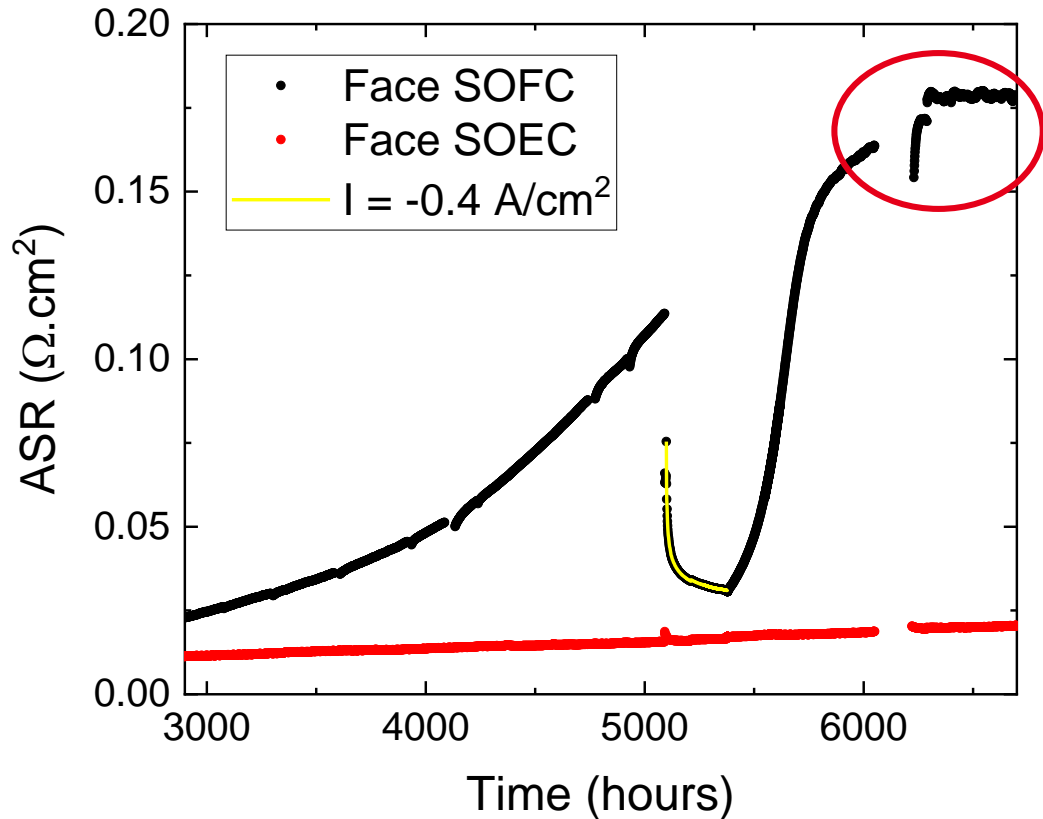


ASR increases with available Pt surface decrease induced by Cr_2O_3 deposition then growth

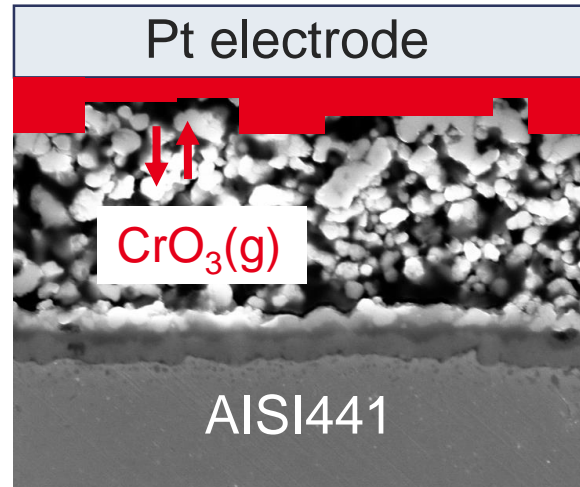
- When the current is reversed, Cr volatilization is favoured

ASR increase of AISI441 SOFC face

Oxidation in synthetic dry air at 800°C

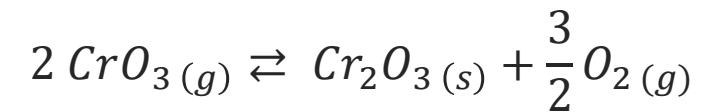


ASR reaches a plateau after 6000h of oxidation



Cr₂O₃

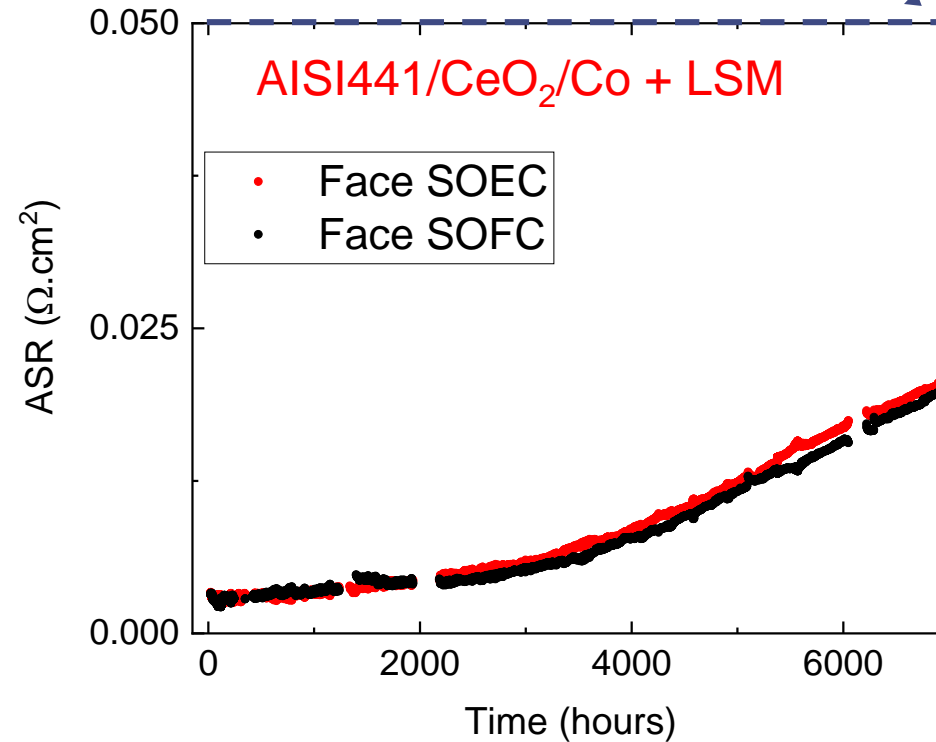
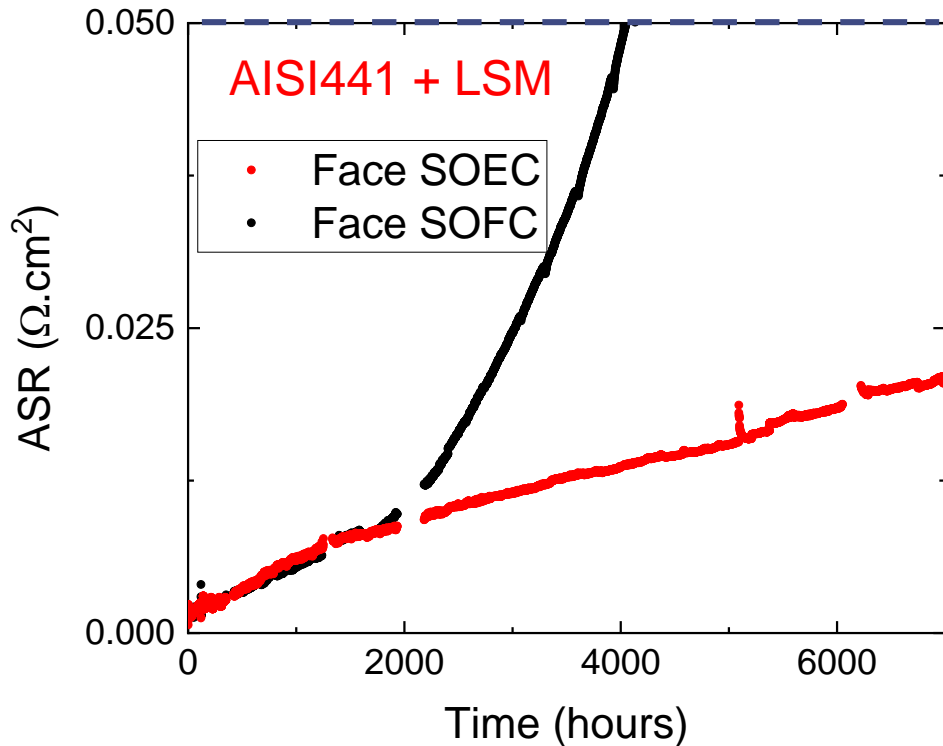
- Fully covered Pt surface with low conductive Cr₂O₃
- Steady state



ASR drastic increase stops once all Pt surface is covered by Cr₂O₃.

ASR : AISI441 vs AISI441/CeO₂/Co

Oxidation in synthetic dry air at 800°C

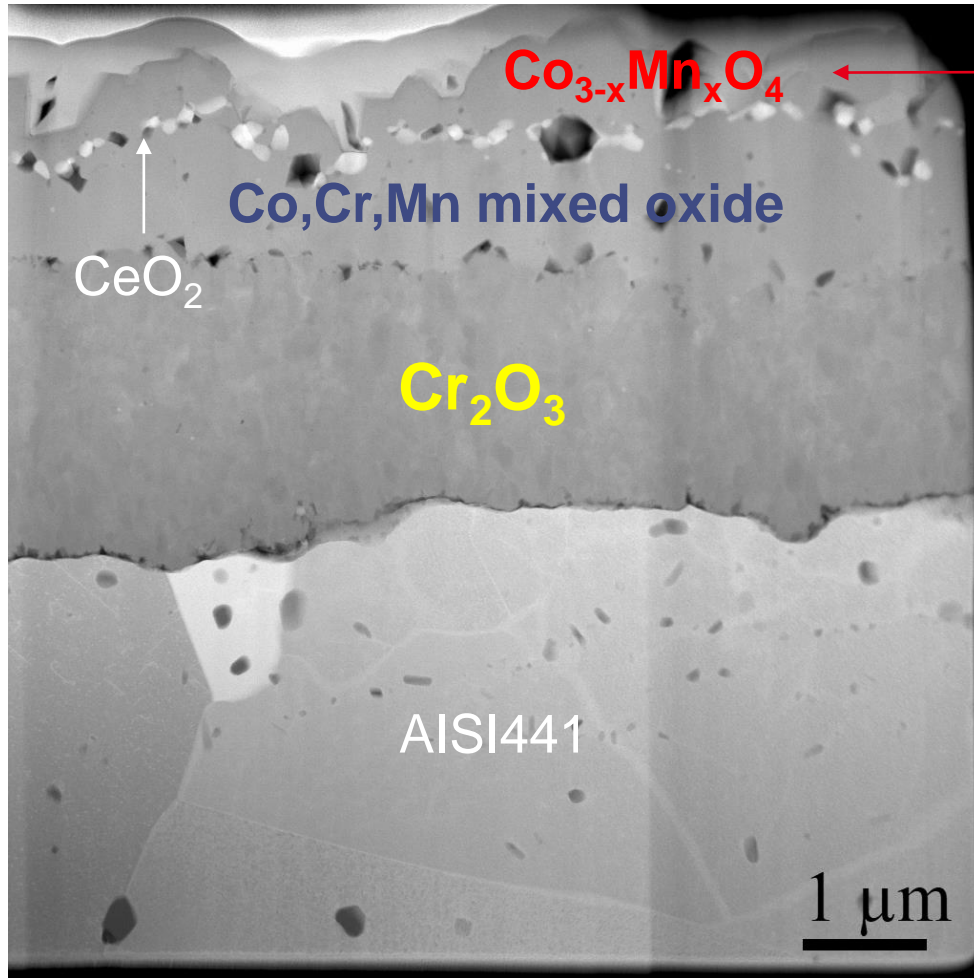


ASR limit = 50 m $\Omega \cdot \text{cm}^2$
for 40 000h operation

Similar ASR degradation of coated and uncoated AISI441 in SOEC mode.
With CeO₂/Co coating : no difference between SOEC and SOFC behaviour, no drastic ASR increase.

ASR : AISI441 vs AISI441/CeO₂/Co

AISI441/CeO₂/Co oxidized in air at 800°C for 5000h



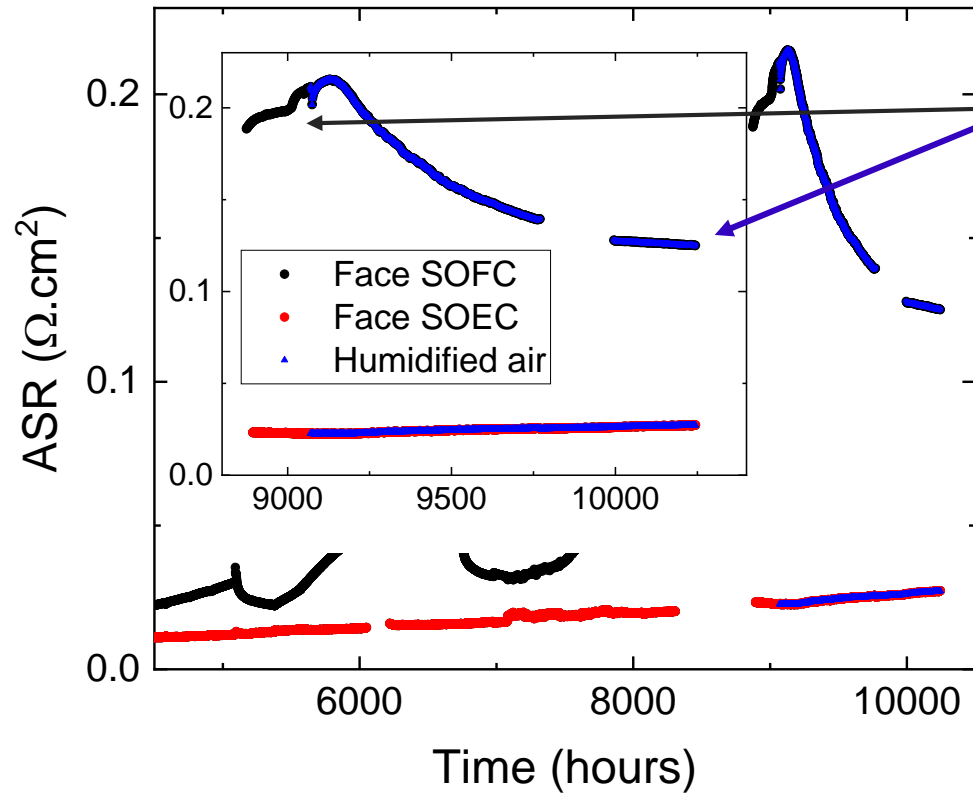
Cr cations (< 3 at%)

The coating is an efficient diffusion barrier for Cr and offers a good protection against Cr vaporization.

ASR : Effect of humidified air

Add H₂O bubbling in air inlet to humidify air (3%_{vol} H₂O) —

AISI441 + LSM

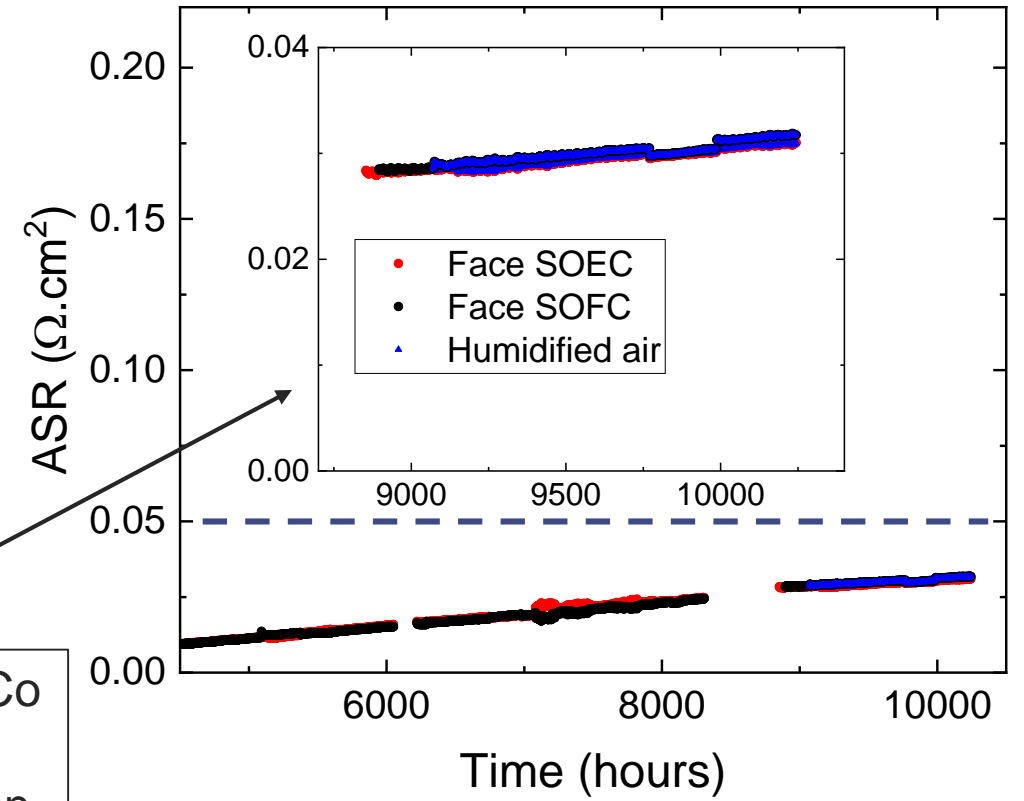


New « steady state » plateau

Cr vaporization favoured → diminution of Cr₂O₃

No impact on CeO₂/Co coated AISI441 → no/low Cr volatilization

AISI441/CeO₂/Co + LSM



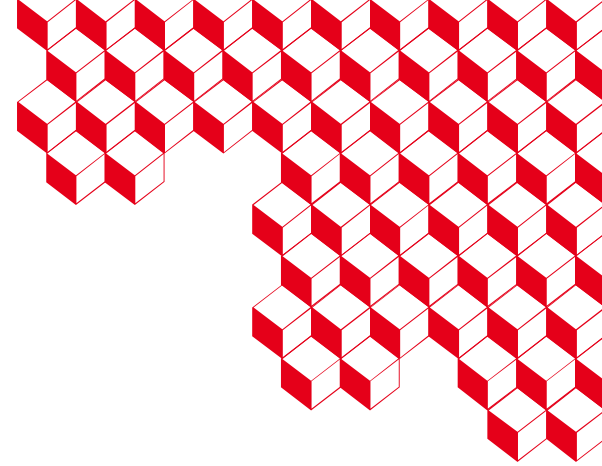
For now, no considerable effect of humidified air on ASR of interconnects



3 ■ Conclusion

Conclusions

- Evaluation of the performances of coated and uncoated air side SOEC/SOFC interconnects
 - Short term : **oxidation kinetics** and **oxide scales characterizations**
 - Long term : **Area Specific Resistance (ASR)**
- Both **CeO₂/Co** and **LSM** coatings are efficient to **reduce the oxidation kinetics** of AISI441 at 800°C in dry air
- ASR of LSM coated interconnect is **influenced by the current direction**.
 - SOFC mode shows drastic ASR increase contrary to SOEC mode
 - ↳ Reduction of Cr volatile species
- **SOFC ASR data interpretation have to be confirmed by ex-situ analysis of the sample**
- The use of CeO₂/Co coatings (PVD) is positive
 - CeO₂/Co coating prevents Cr volatilization even in humidified air



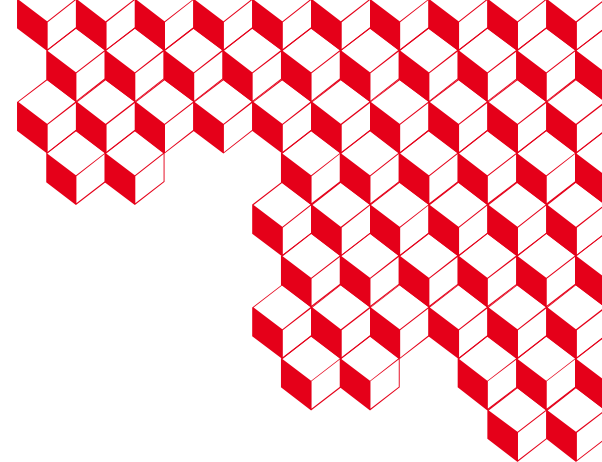
Thank you for your attention

CEA SACLAY

91191 Gif-sur-Yvette Cedex

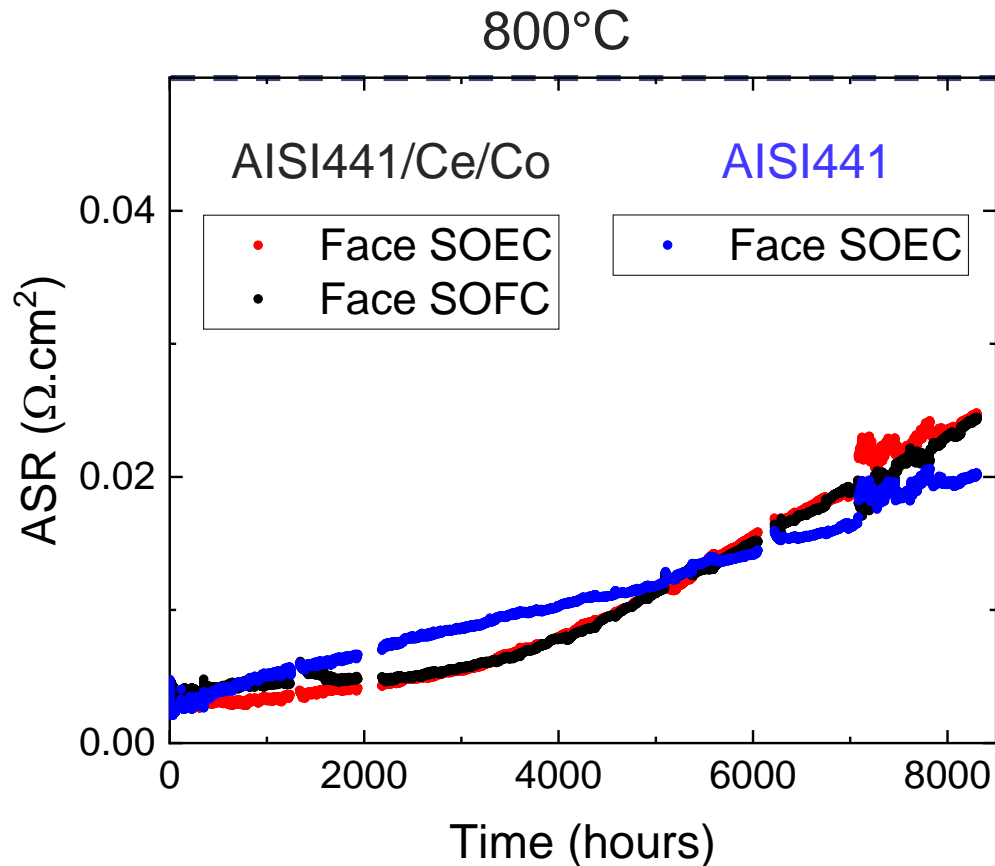
France

mathilde.bouvier@cea.fr

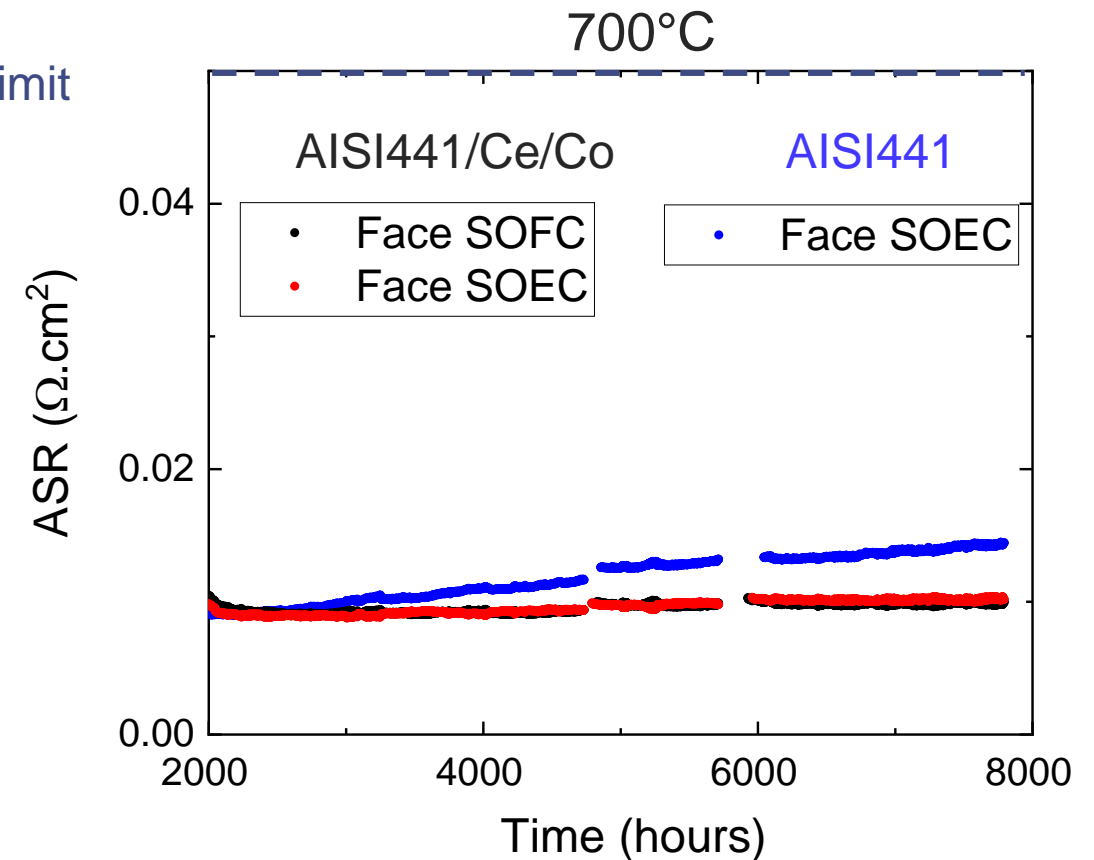


ASR : SOEC face of AISI441 vs AISI441/Ce/Co

Oxidation in synthetic dry air

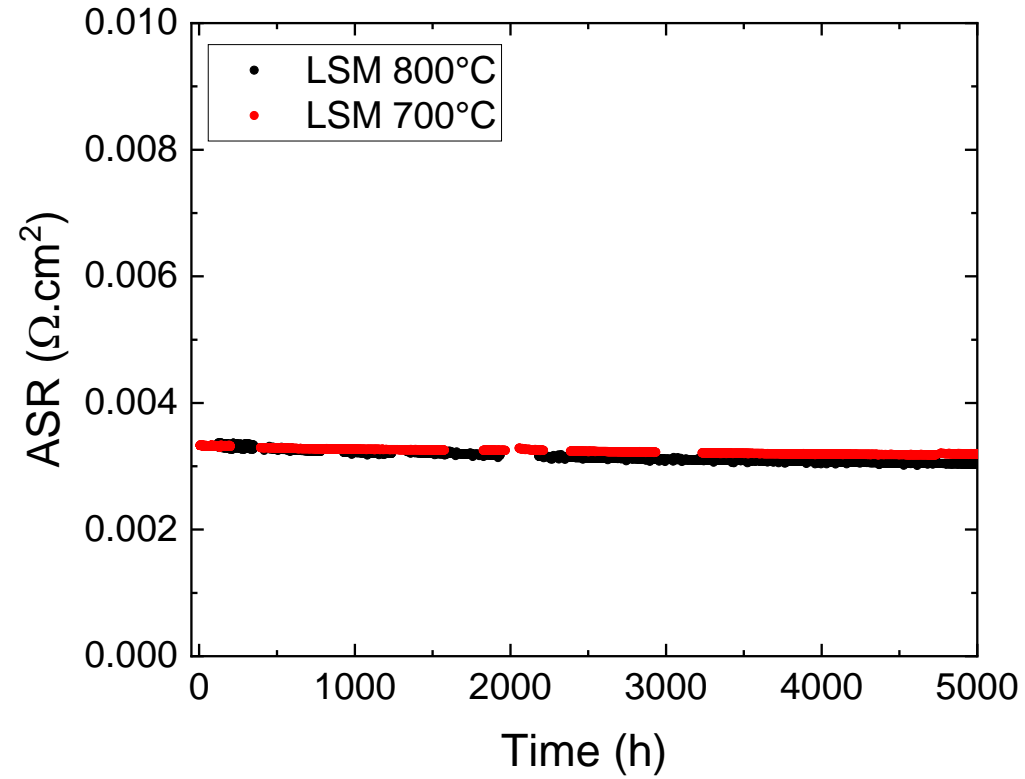


ASR limit

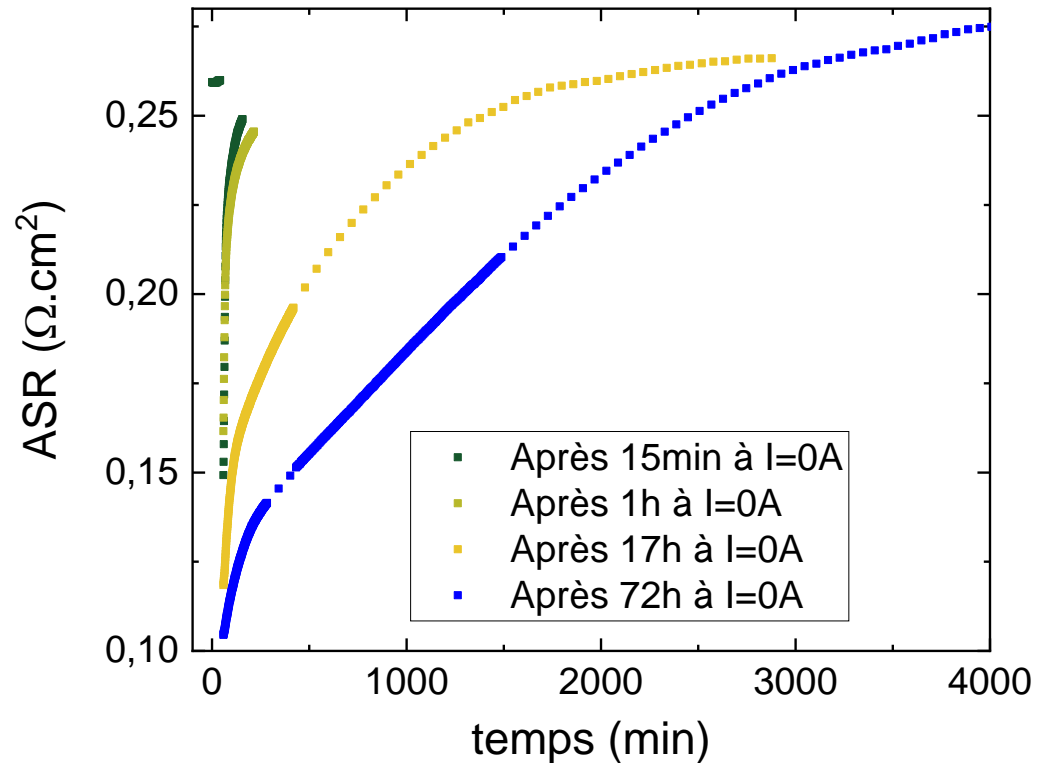


800°C : Very similar ASR degradation of coated and uncoated AISI441 in SOEC mode.
700°C : Positive effect of Ce/Co coating.

ASR of LSM alone



ASR increase of SOFC face : additional tests

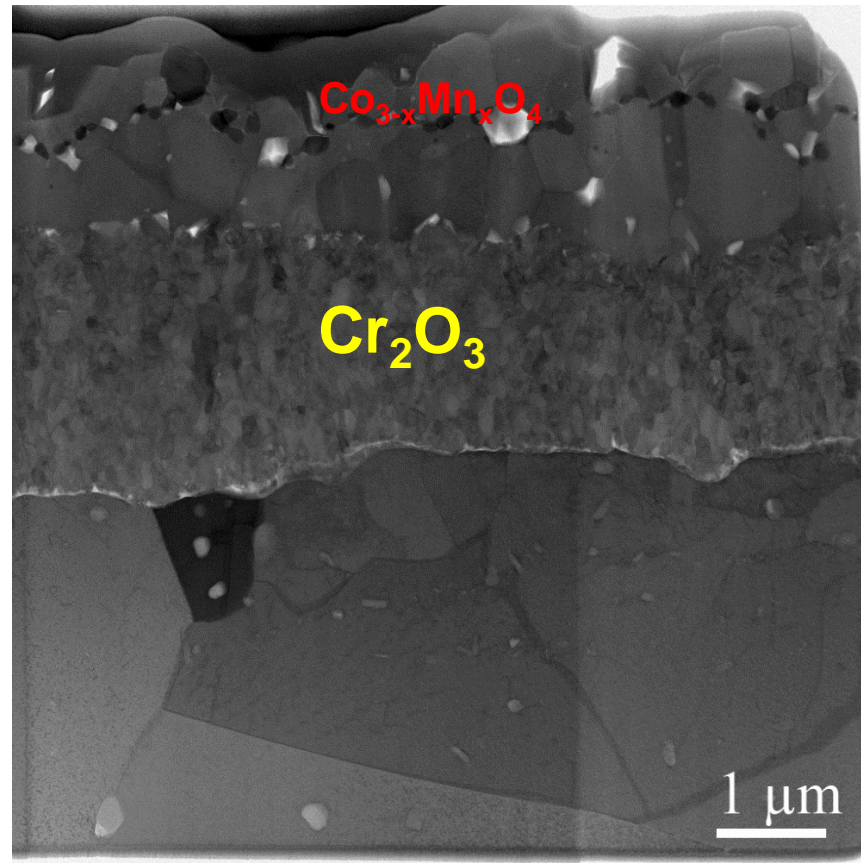


Switch off the current : ASR drops and increases back again after current is switched on.

ASR : AISI441 vs AISI441/Ce/Co

Oxidation in synthetic air at 800°C

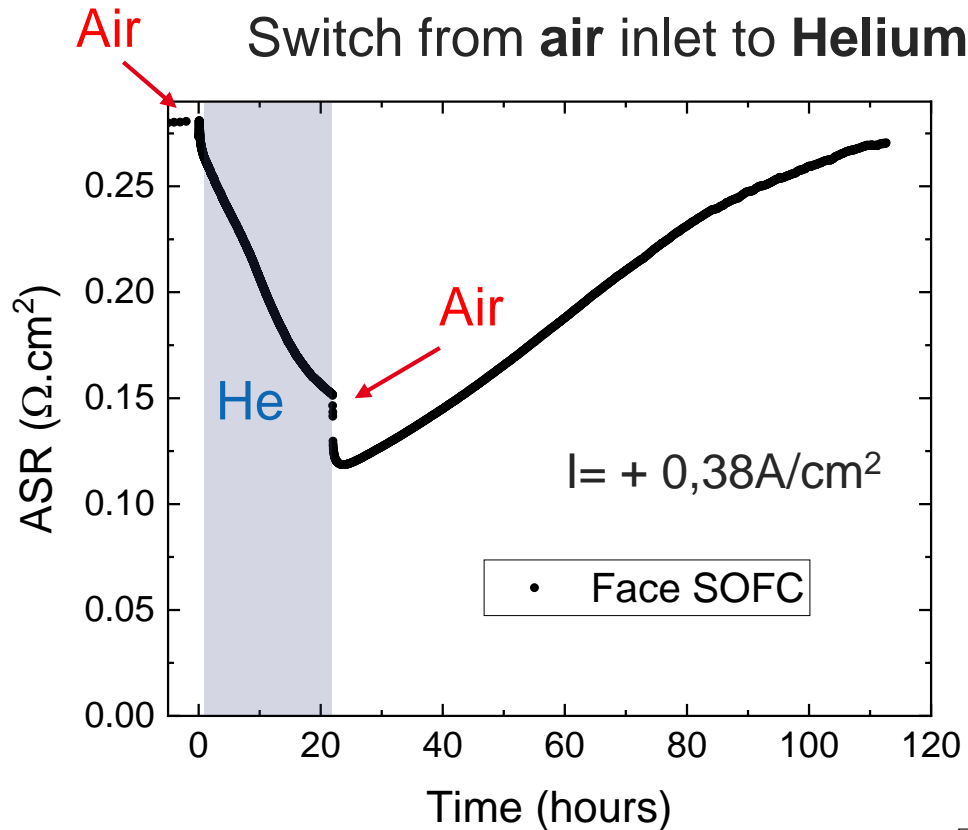
Cr cations (< 3 at%)



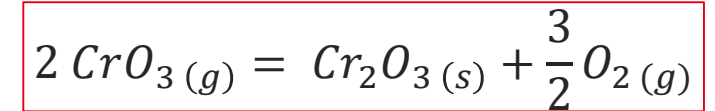
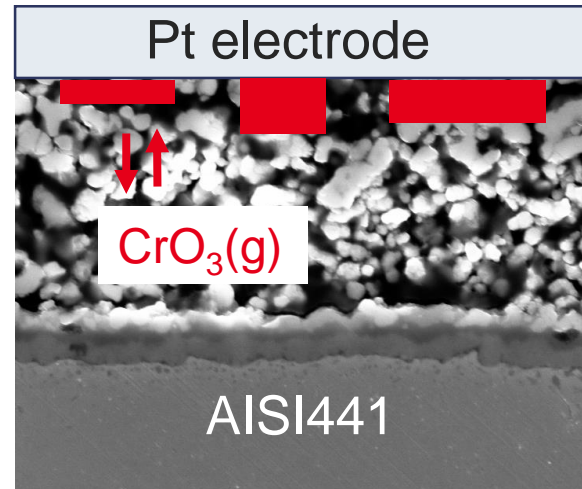
5000h oxidation in air

ASR increase of AISI441 SOFC face

SOFC mode : ASR reaches a plateau after 6000h of oxidation



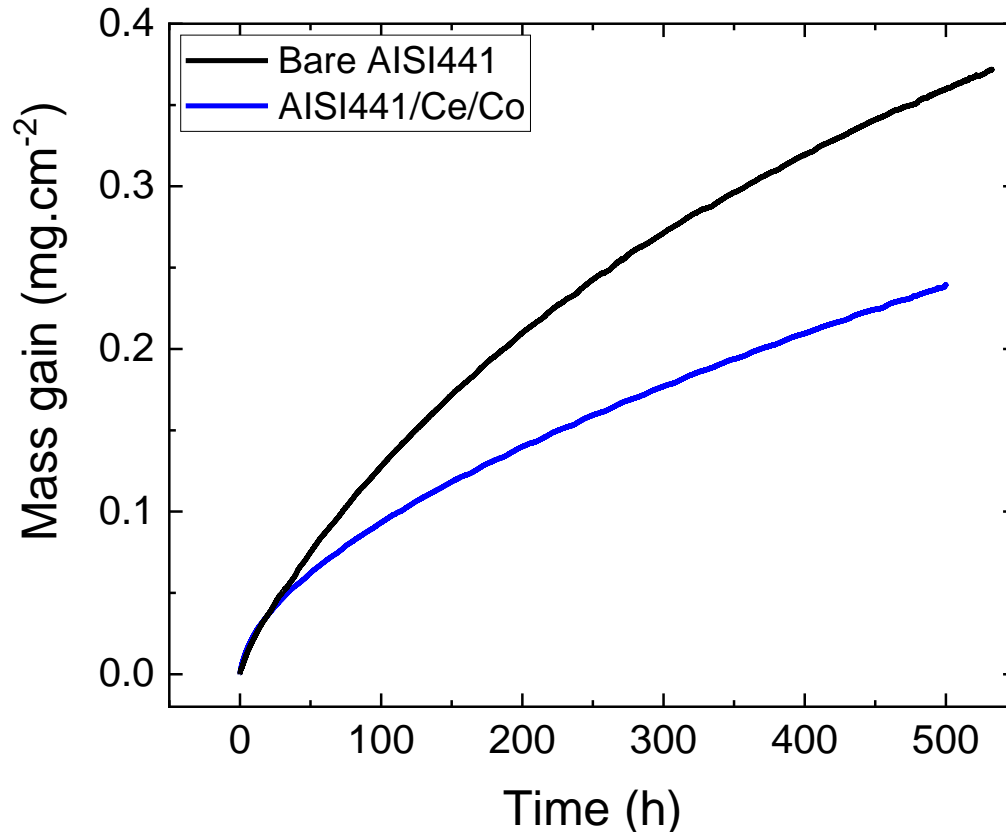
ASR decreases under He flow \rightarrow Cr volatilisation from Pt electrode
ASR increases when back in air flow \rightarrow Cr oxide redeposition on Pt



An equilibrium between Cr oxide solid and Cr volatile species is reached after some time.

Oxidation kinetics : AISI441 and AISI441/Ce/Co

Oxidation in synthetic dry air at 800°C - thermogravimetric analysis



	k_p (g ² .cm ⁻⁴ .s ⁻¹)
AISI 441	$9.0 \pm 2.8 \times 10^{-14}$
AISI441/Ce/Co	$3.5 \pm 0.5 \times 10^{-14}$

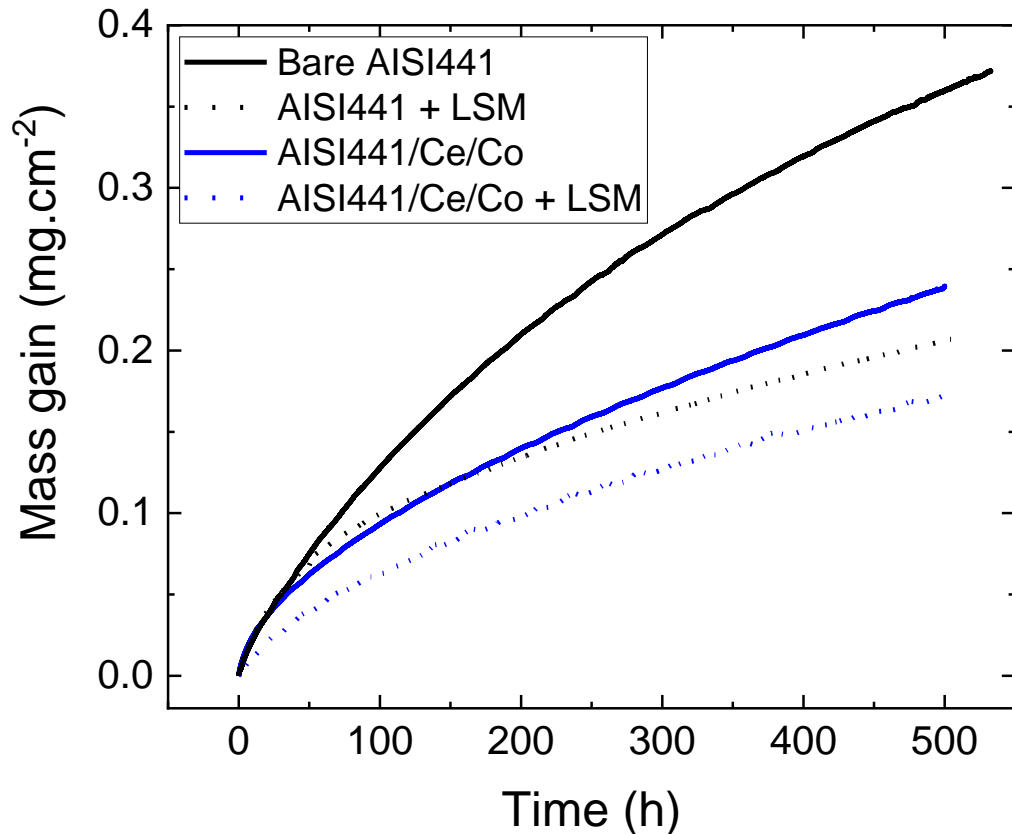
÷ 2.5

Ce/Co coating reduces the oxidation kinetics of AISI441 by a factor **2.5**

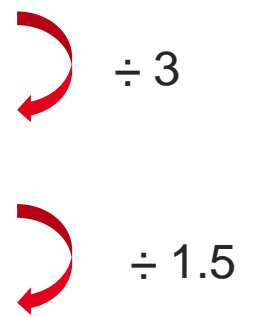
Ce/Co coating efficiently lowers the mass gain of AISI441.

Oxidation kinetics : LSM coating

Oxidation in synthetic air at 800°C - thermogravimetric analysis



	k_p (g ² .cm ⁻⁴ .s ⁻¹)
AISI 441	$9.0 \pm 2.8 \times 10^{-14}$
AISI 441 + LSM	$2.4 \pm 0.4 \times 10^{-14}$
AISI441/Ce/Co	$3.5 \pm 0.5 \times 10^{-14}$
AISI 441/Ce/Co + LSM	$2.0 \pm 0.5 \times 10^{-14}$



LSM layer lowers the oxidation kinetics of both AISI441 and AISI441/Ce/Co.

Both Ce/Co and LSM coatings reduce the oxidation kinetics of AISI441.