How cells and metal interconnects respond to operating parameters up to 40.000 hours

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Why?

- To increase awareness on the evolution of materials in stacks under operation
- To offer data for modelling
- To guide accelerated and stressed tests

Operating parameters

Operation type	SOFC (µCHP)
Total runtime/h	a) 5000h reformed hydrogen b) 9000 and 20000 h lab conditions c) 40000 h initial 30000 h in reformed hydrogen followed by 10000 h in lab conditions
Fuel gas (Co-flow)	Reformed hydrogen: 44% N_2 34% H_2 16% CO 4% H_2O 2% CO_2 Lab conditions: $H_2/N_2/CO_2$ 2%/H_2O 3% humidified
Nominal temperature/K	1123
Current density/mA•cm^{-2}	90-200

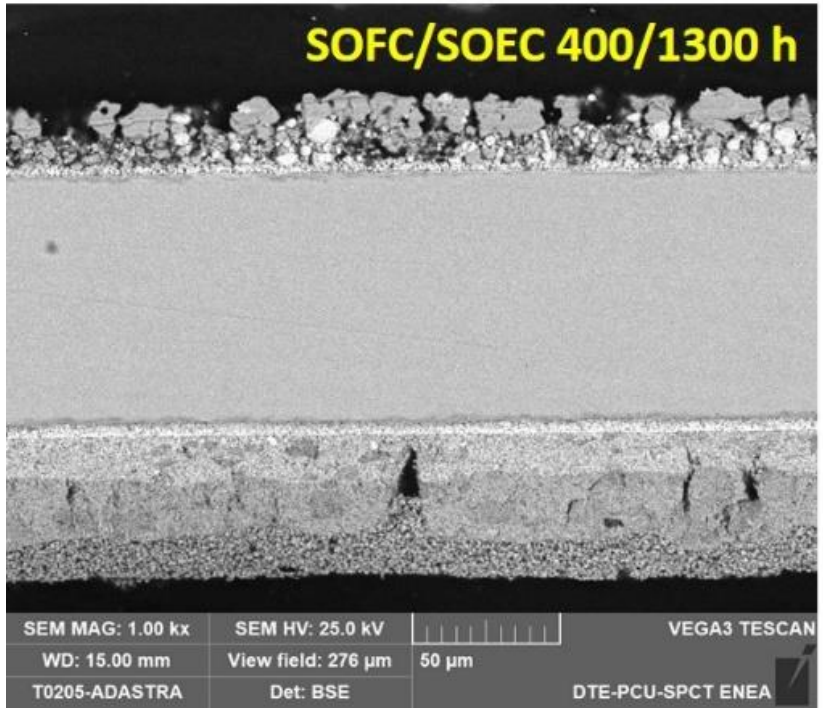
Investigations of on-field operated SOC

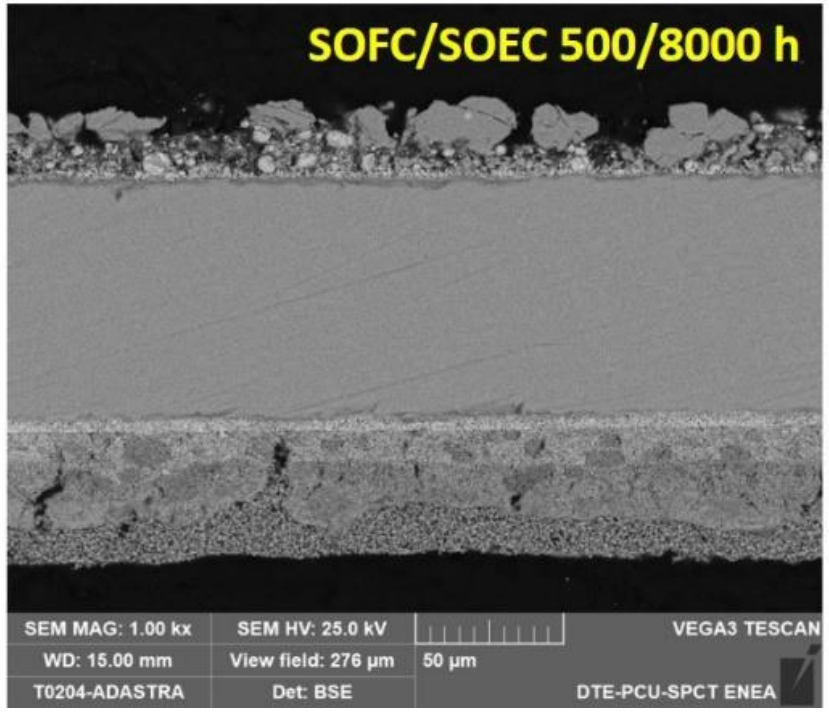
- Cell samples were extracted from cells that have operated in both SOFC and SOFC/SOEC mixed mode for various times ranging from 2000h hours up to 20000 hours.
- The cells used by SUNFIRE are electrolyte-supported (ESC) with a selection of cathode and anode differing in agreement with the main operating mode:
- SOFC have LSM as cathode with a GDC diffusion barrier within the dense electrolyte and the anode
- SOEC uses LSCF as cathode and the diffusion barrier is placed at the air side
- In both configurations the electrode interacting with oxygen or air resulted stable and having minor issues regardless to the operating time
- In SOFC configuration the anode has shown severe modifications during operation
- In SOEC the electrolyte as well suffered some alterations related to the operating parameters.
- No information can be disclosed about the electrochemical behaviour of the stacks

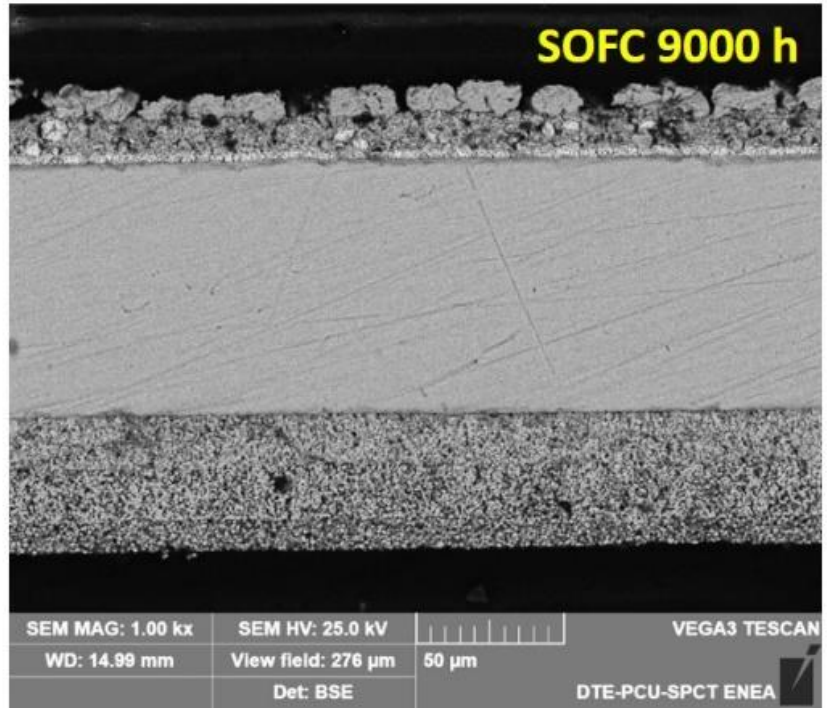
Issues on air / oxygen electrodes

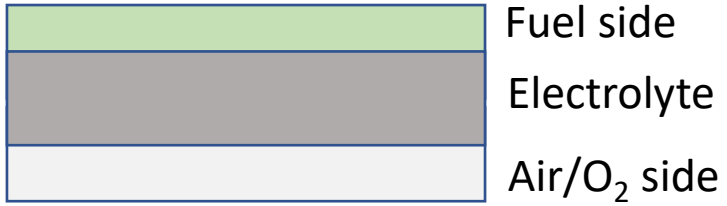
- Delamination of layers (depending on temperature, rare)
- Pollution from the stram (SOFC mode, rare)
- Chromium poisoning (depending on the strategy adopted for the interconnect, rare)
- Elements diffusion among layers (depending on the temperature, rare)
- Formation of cracks orthogonal to the layers (depending on thermal gradients, temperature and formation of interphases, possible, mainly observed in SOEC mode)

Representative cross sections of complete cell





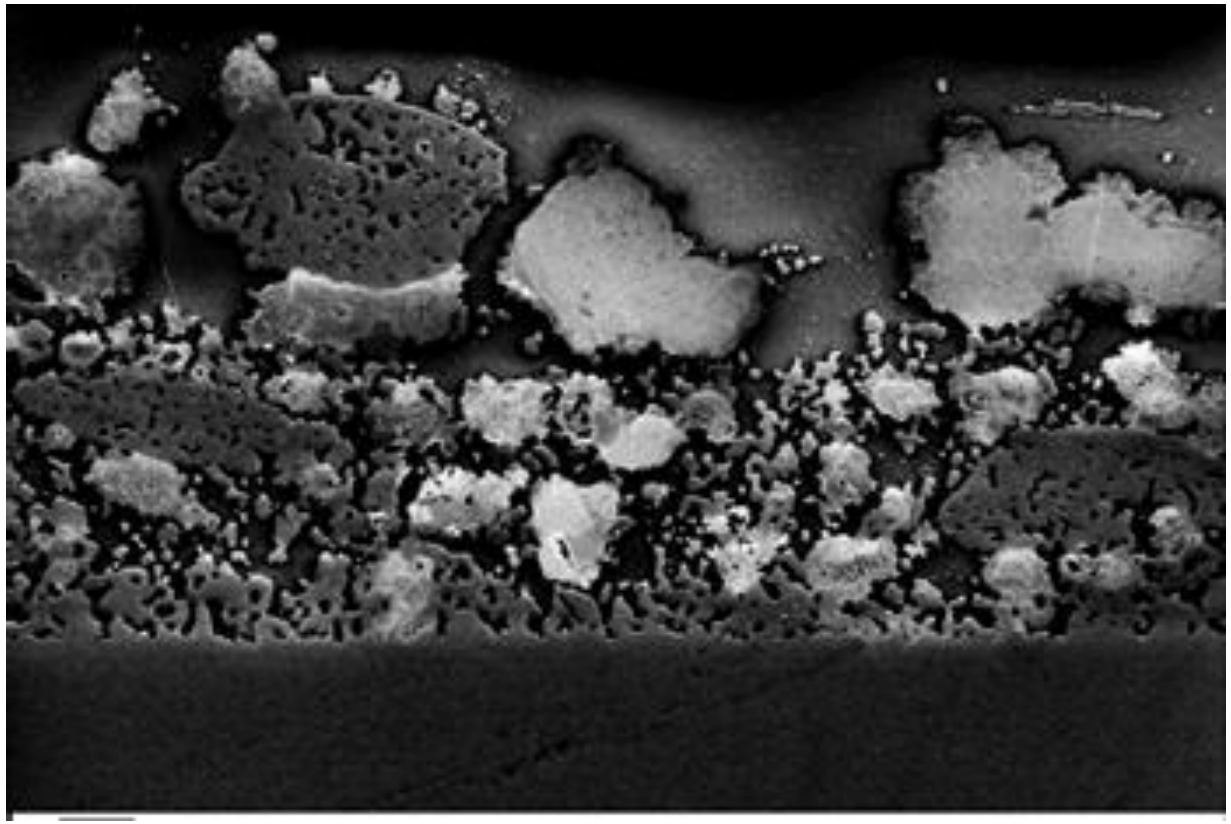


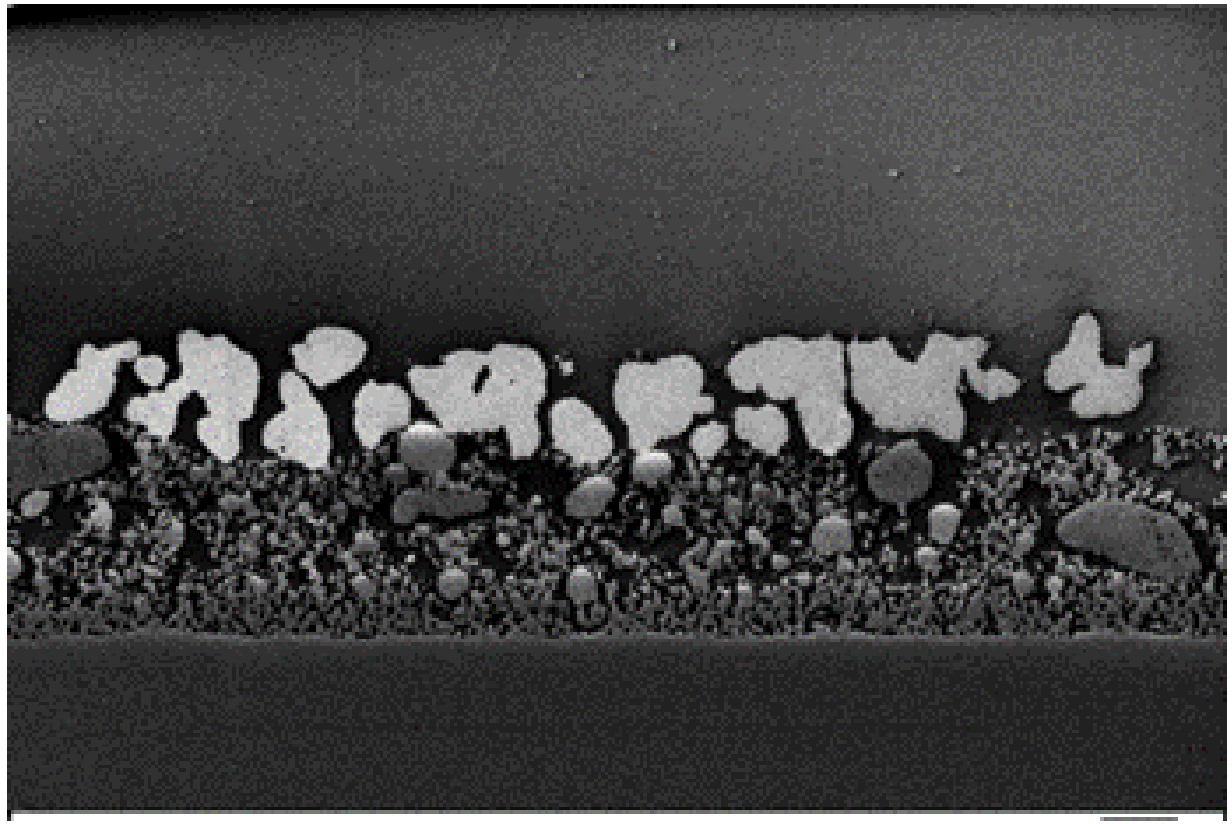


Issues on fuel electrode

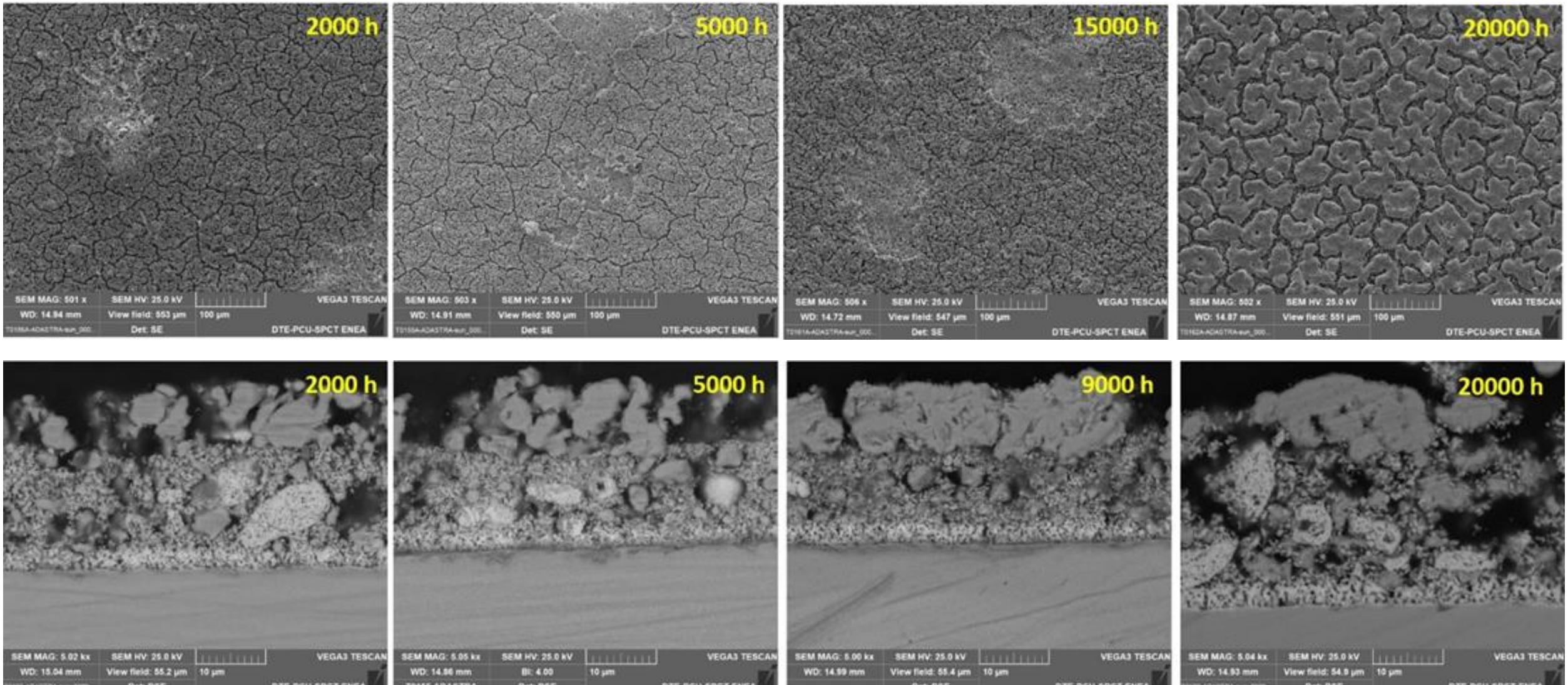
- Nickel coarsening: reduced surface of catalysis (frequent)
- Reduction of the percolating network based on Nickel (frequent)
- Nickel depletion (rare and limited to specific zones)
- Nickel redistribution (moderate and limited by grainsize)
- Redistribution of phases between GDC grains and Ni (moderate)
- Pollution from the fuel stream (depending on the quality of the fuel)
- Pollution from the sealing materials (moderate, formation of silicates)

Percolation imaging of the fuel electrode of the ESC from the field tests. Images were captured at 1keV using an in-lens detector



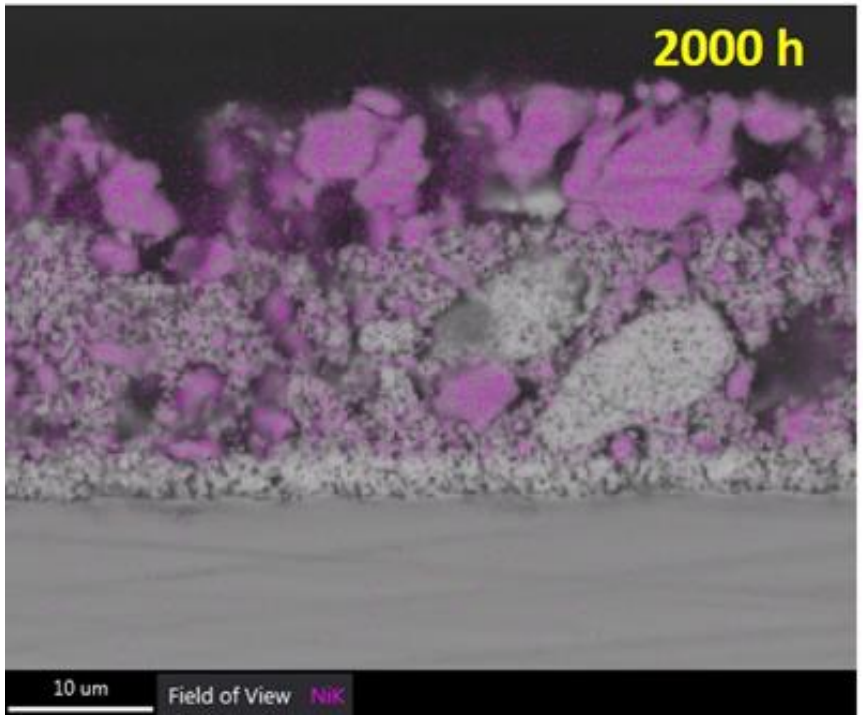


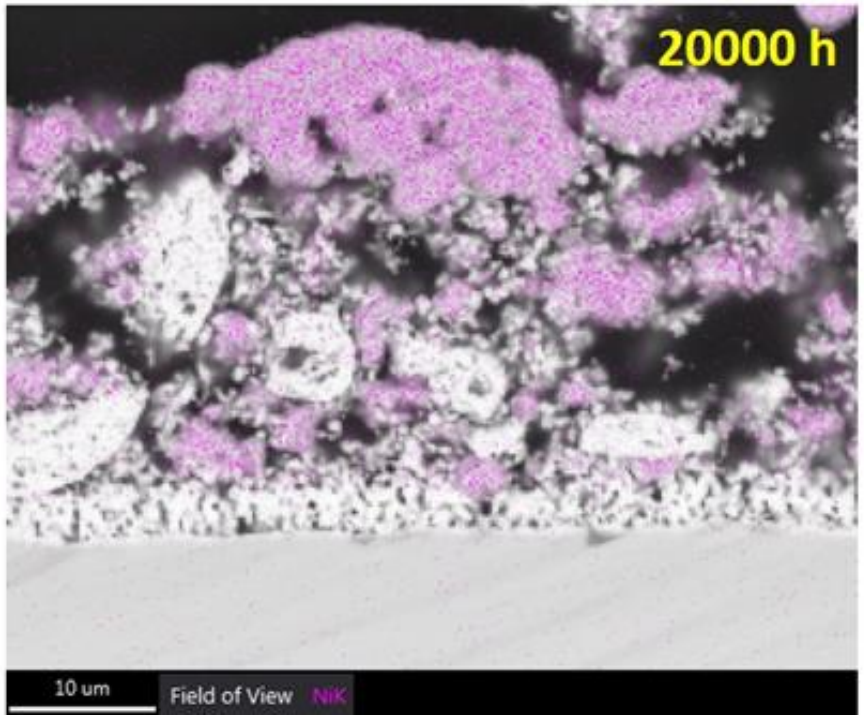
anode surfaces and cross sections of SOFC operated samples (outlet)



Ni mapping applied to SEM images of the cross-sections

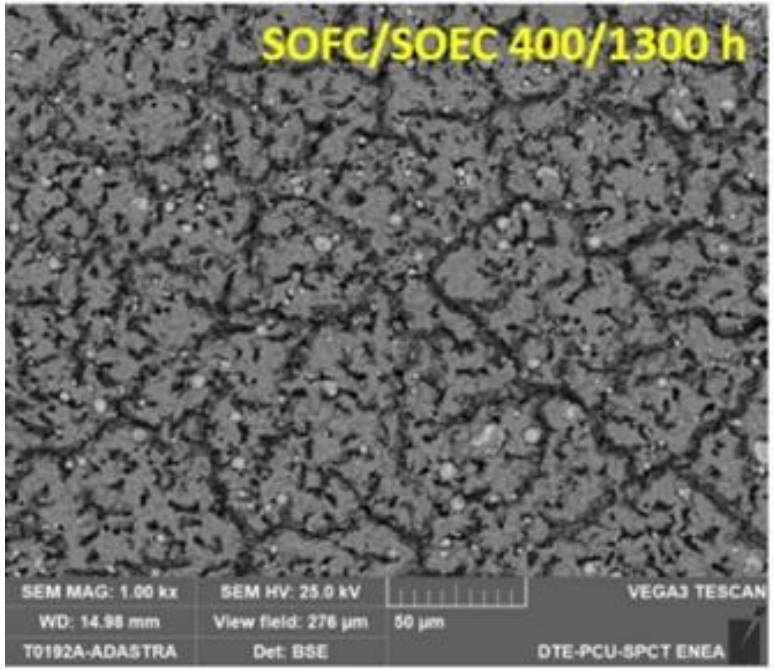
The cross-section images also reveal the depletion of Ni from layers below the outer one, where void spaces appear in zones where Ni was probably located

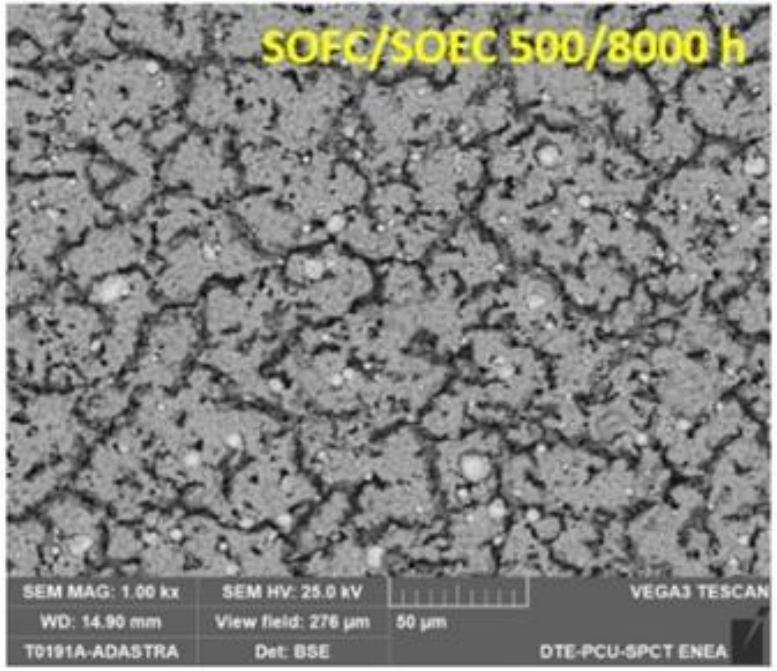


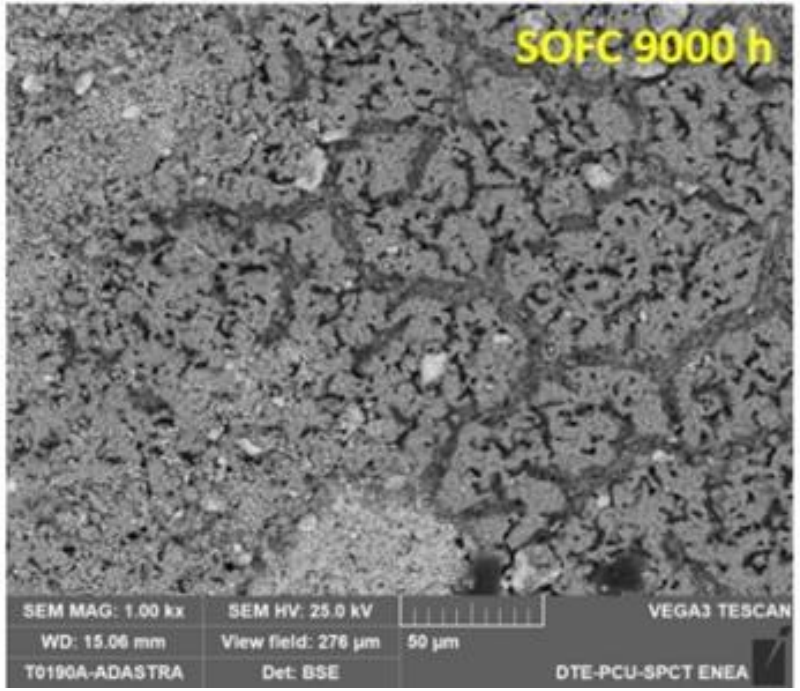


On-field operated samples in SOFC/SOEC mode

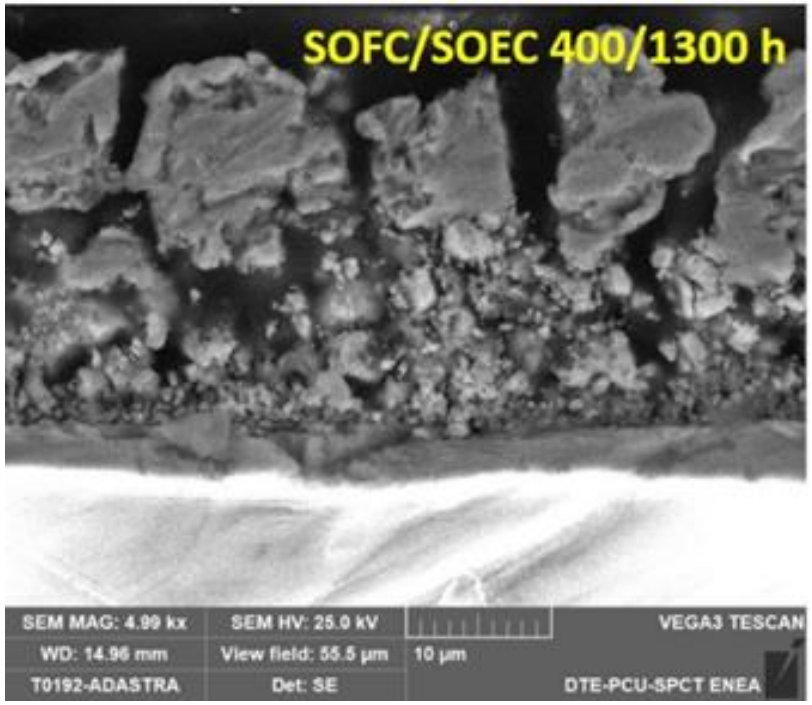
SUNFIRE cells were operated in stacks under SOFC/SOEC mode for 400/1300, 1100/2900, and 500/8000 hours respectively

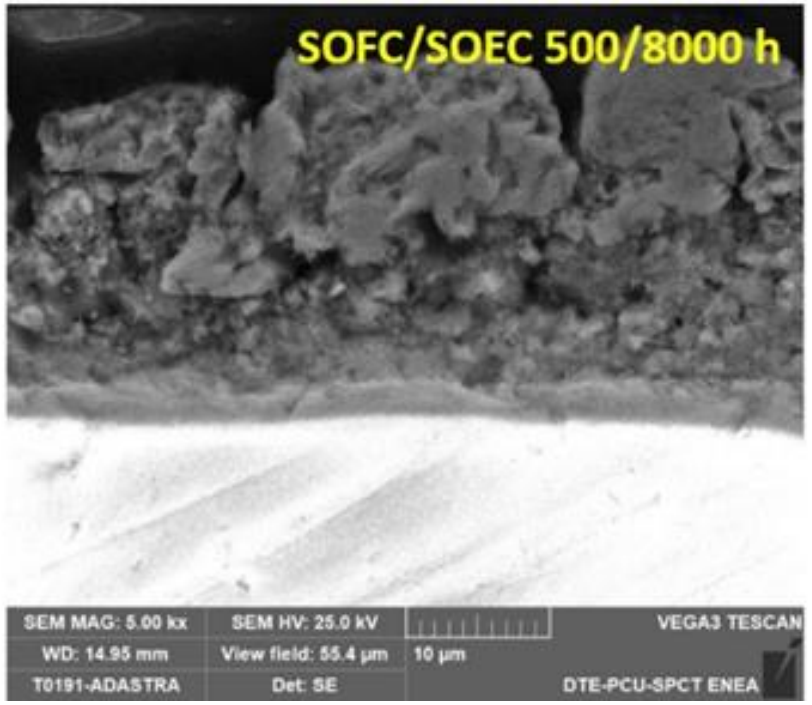


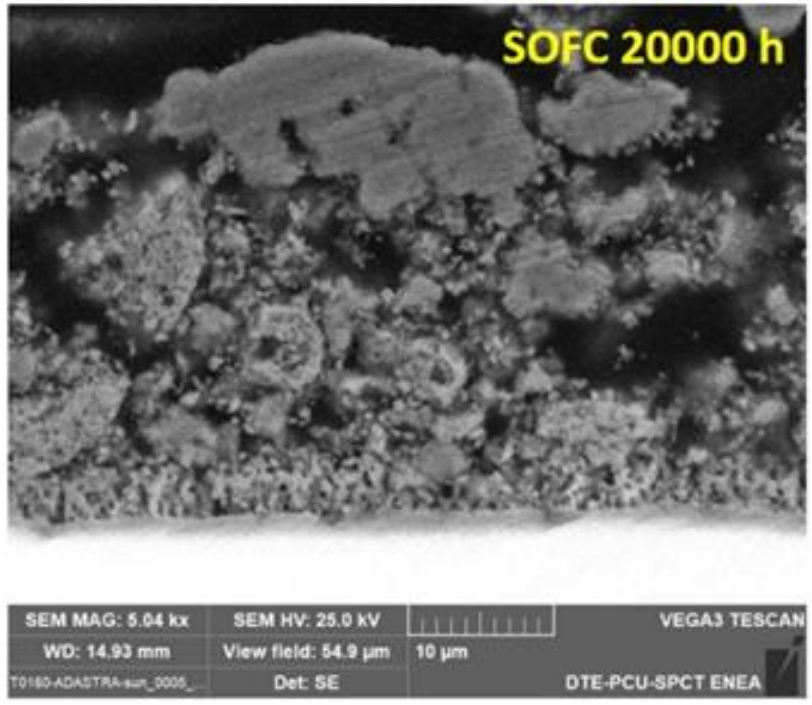




Cross-sections of fuel electrodes





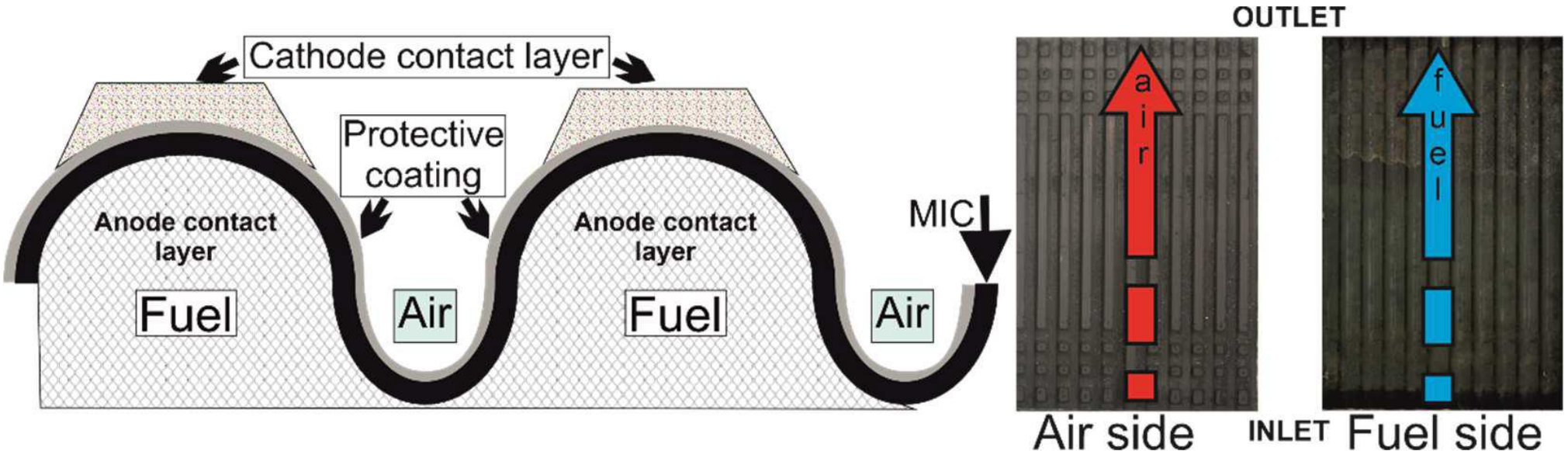


Comments and conclusions on cells and anodes

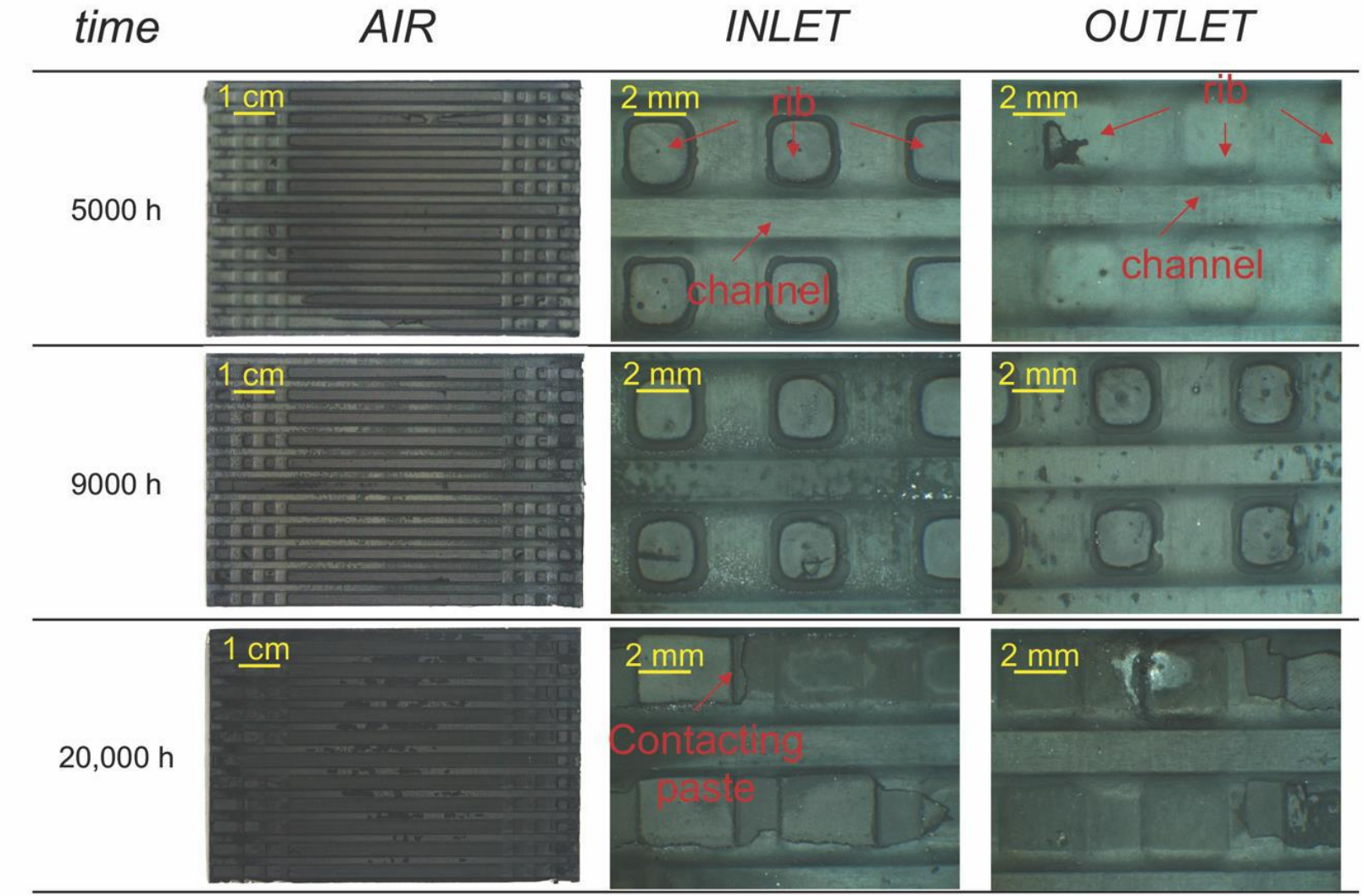
- It is worth noting that phenomena occurring in SOFC operation in 10000-20000 hours, occurs in SOFC/SOEC mode to a similar extent in a time scale that is about 4 - 10 times shorter. This suggests that not only the high steam content, but also the electrolysis polarization may result in an acceleration of the degradation phenomena at the fuel electrode for SOFC operation. Thus said, high steam partial pressure and cathodic polarization can represent accelerating factors for the degradation of SOC fuel electrodes.
- Nickel coarsening on the surface and nickel depletion from the bulk of the fuel electrode has been observed on both SOFC and SOFC/SOEC samples.

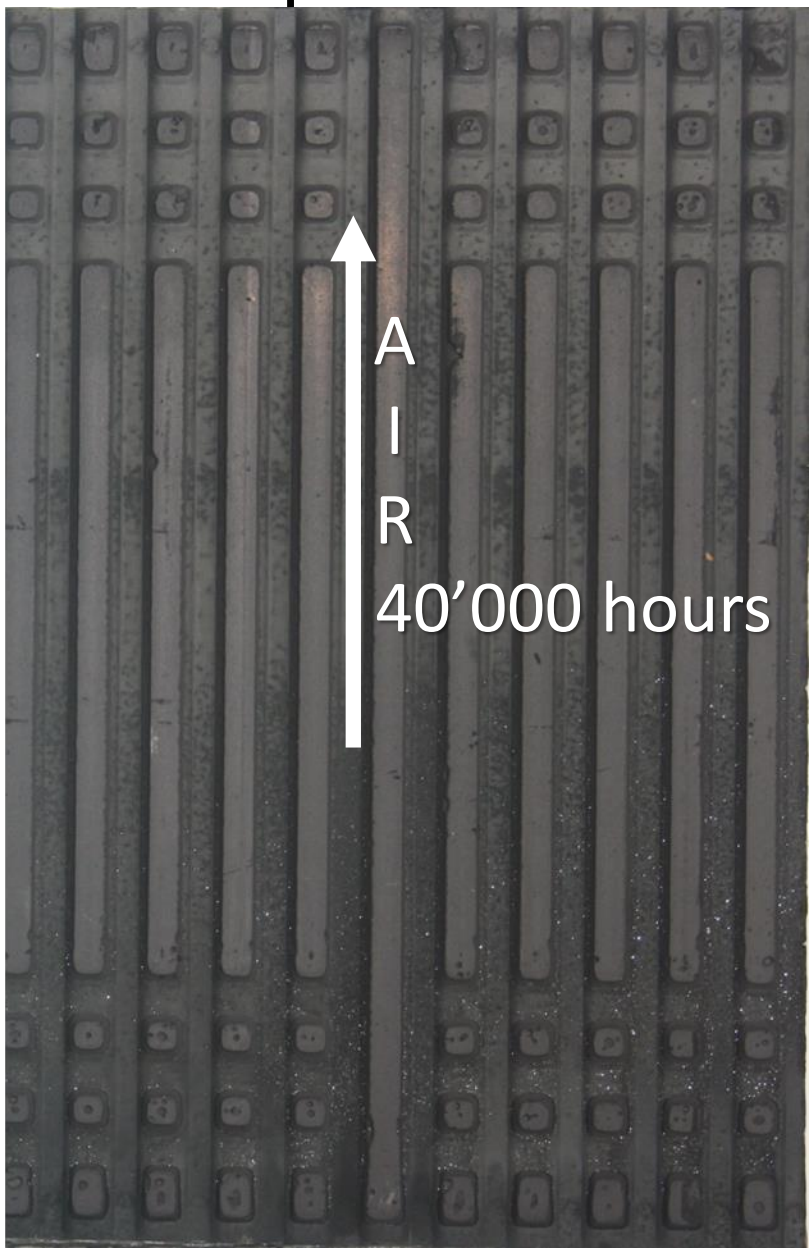
Interconnects

- The metal interconnects are the state of the art for stacking in the following configuration
  - Ferritic stainless steel without elements forming insulating oxides thus able to form a thermally grown oxide stable, conductive and protective
  - Coating on the air / oxygen side suitable to hinder the formation of volatile compounds rich in Cr^{VI}
  - No coating on the fuel side
  - Usage of sealing materials suitable to grant mechanical stability, gas tigthness and electrical insulation, extremely low diffusion
  - Suitable CTE



CROFER 22 APU ® coated with Co-Mn spinel and contacting layer: air side

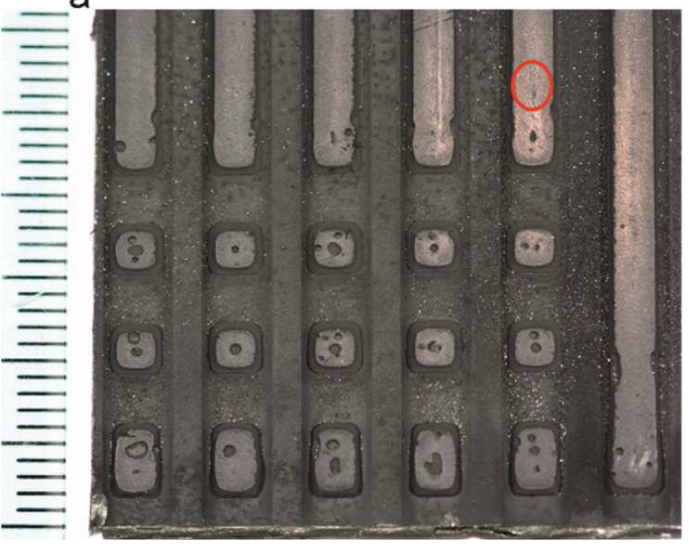




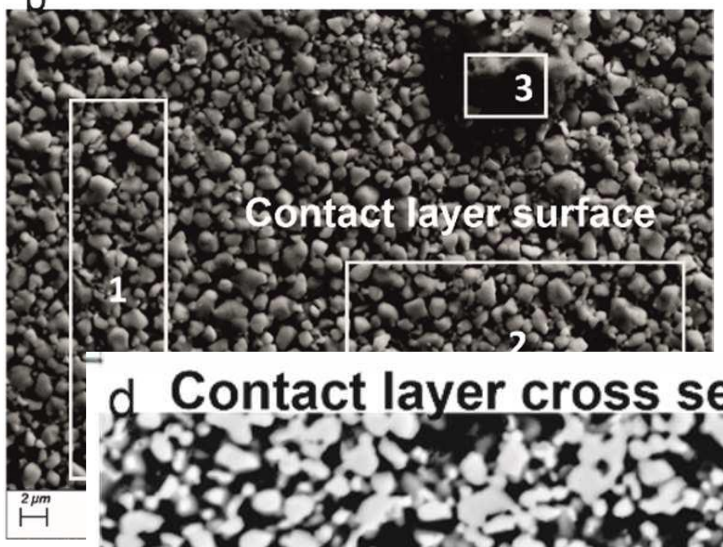
Details after 40’000 hours: air side

- The top of the rib still shows the double layer (coating + contacting) in excellent conditions even after 40khours of activity

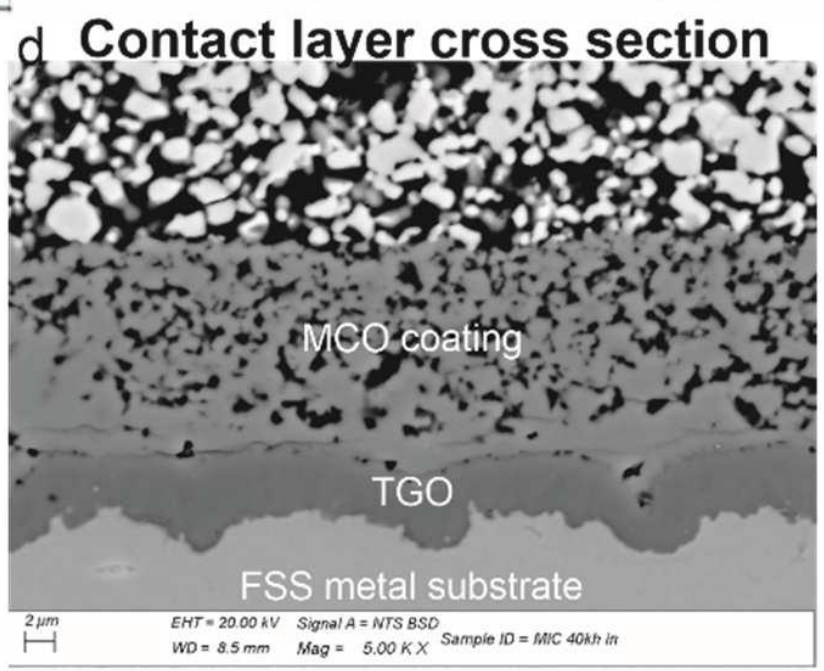
a



b



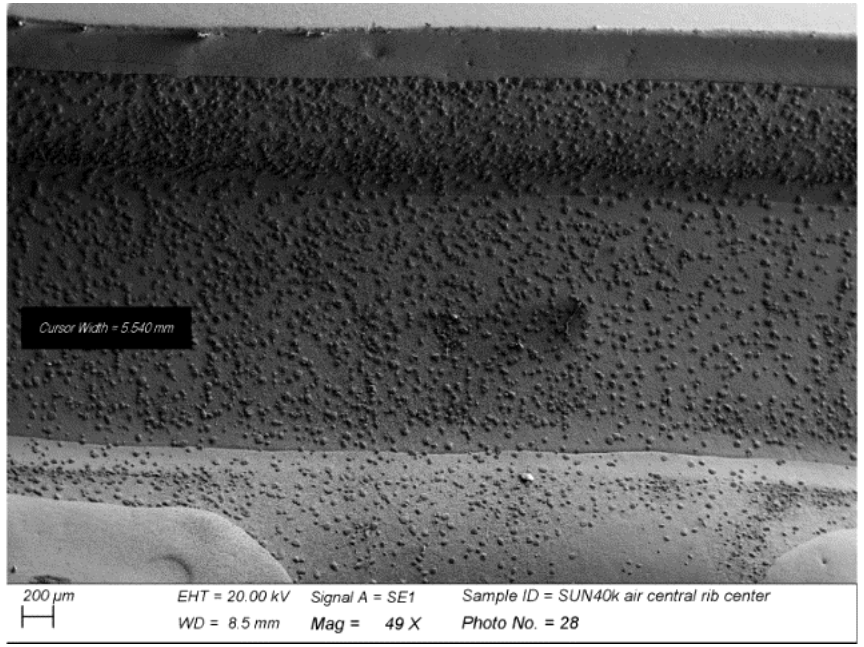
d Contact layer cross section

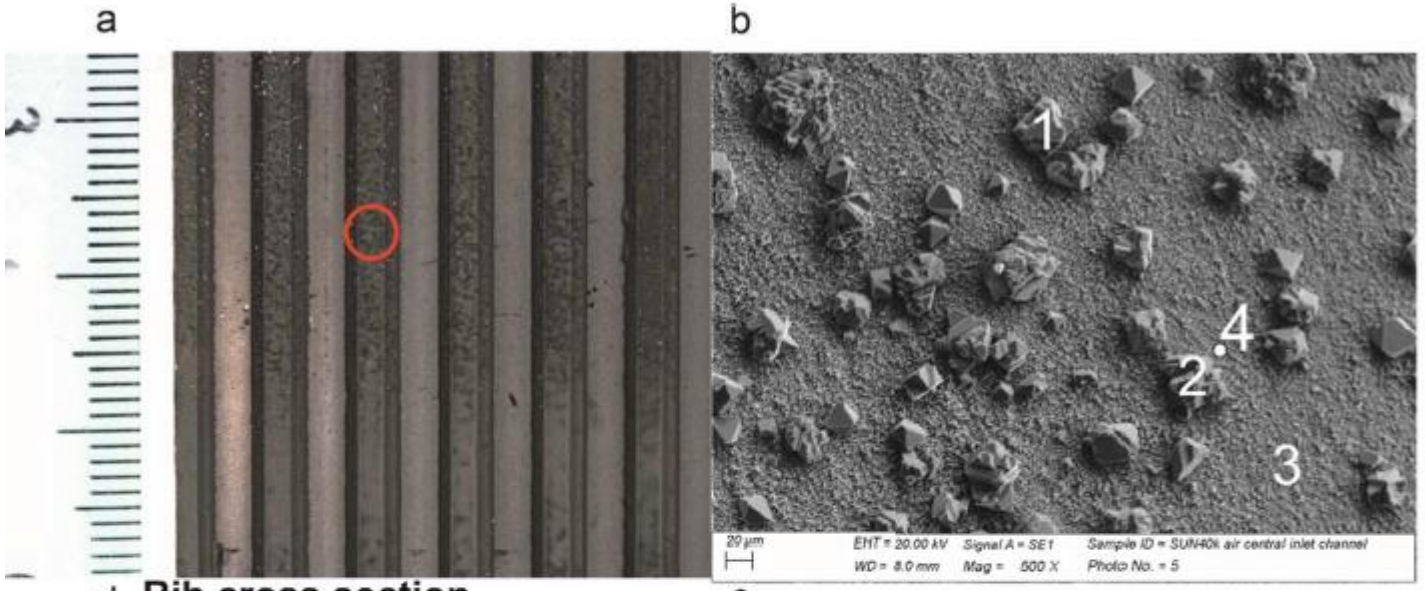


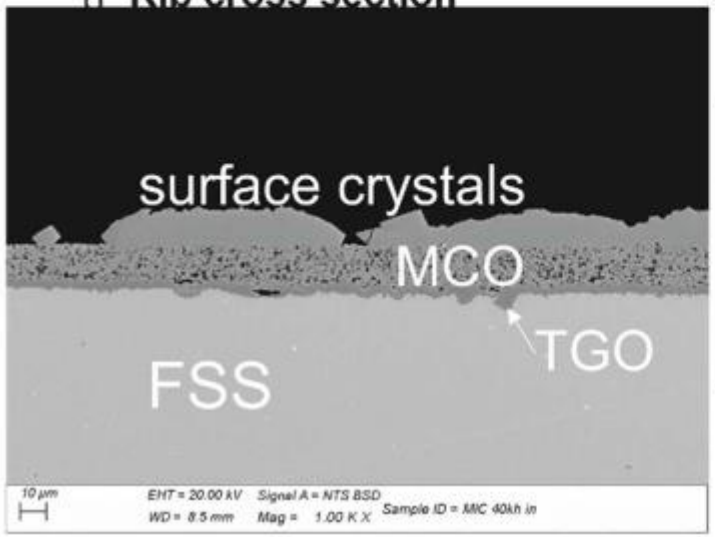
c

At. % Element	Area 1	Area 2	Area 3
O	63.0 ± 0.5	63.9 ± 0.6	71.5 ± 0.5
Mn	16.4 ± 0.4	15.8 ± 0.4	14.3 ± 0.3
Co	1.5 ± 0.2	1.5 ± 0.2	11.9 ± 0.4
Sr	3.3 ± 0.3	3.3 ± 0.3	
La	15.8 ± 0.6	15.5 ± 0.6	1.8 ± 0.3
Cr			0.6 ± 0.1

- The channels show the formation of crystals of spinel containing all elements of the coating + Cr
- The absence of Cr in the air electrode signifies the stability of the superficial spinels



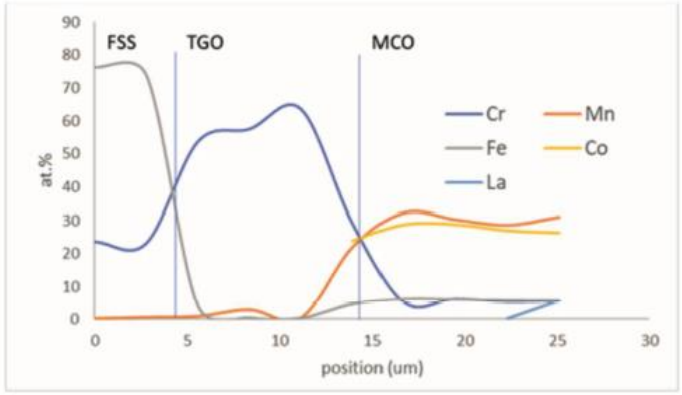




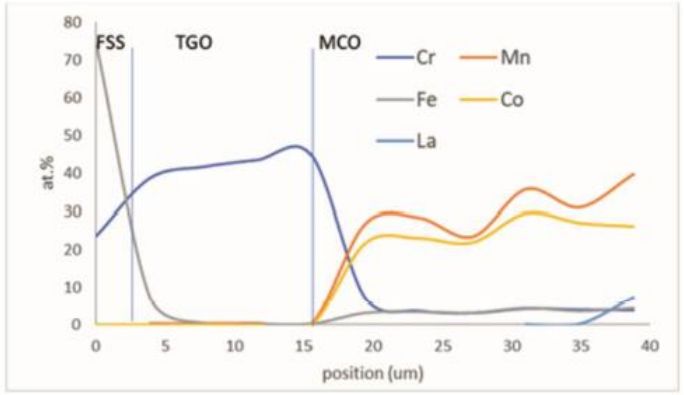
c

At. % Element	Area 1	Area 2	Area 3	Area 4
O	65.5 ± 0.6	59.9 ± 0.6	60.0 ± 0.6	88.9 ± 0.04
Cr	13.1 ± 0.4	16.1 ± 0.4	7.2 ± 0.3	11.1 ± 0.02
Mn	8.6 ± 0.4	9.2 ± 0.3	15.4 ± 0.4	
Fe	1.4 ± 0.2	1.7 ± 0.2	3.0 ± 0.3	
Co	11.4 ± 0.2	13.1 ± 0.5	14.4 ± 0.3	

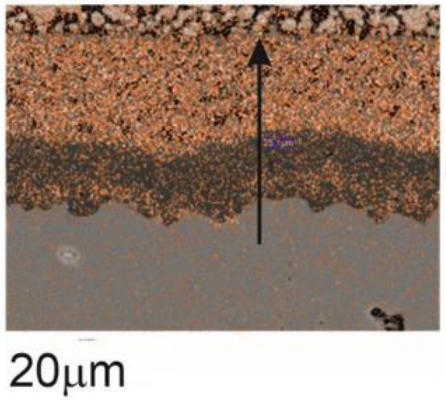
Impact of polarization ?

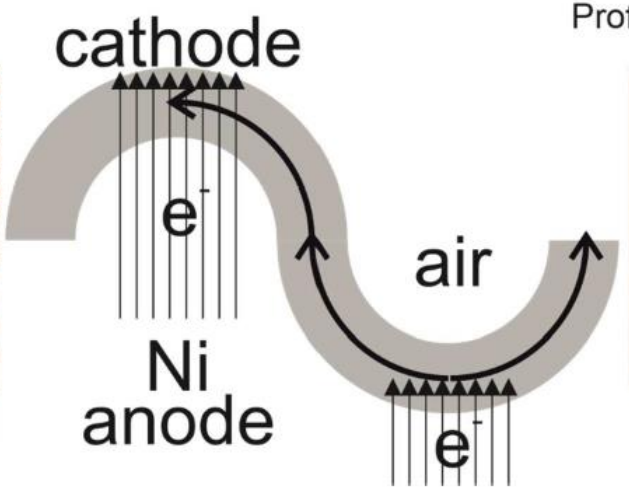


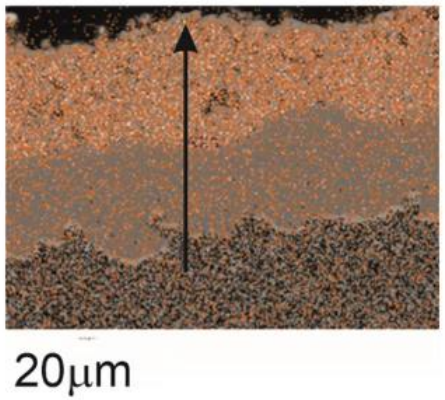
Profile acquired on RIB



Profile acquired on CHANNELS

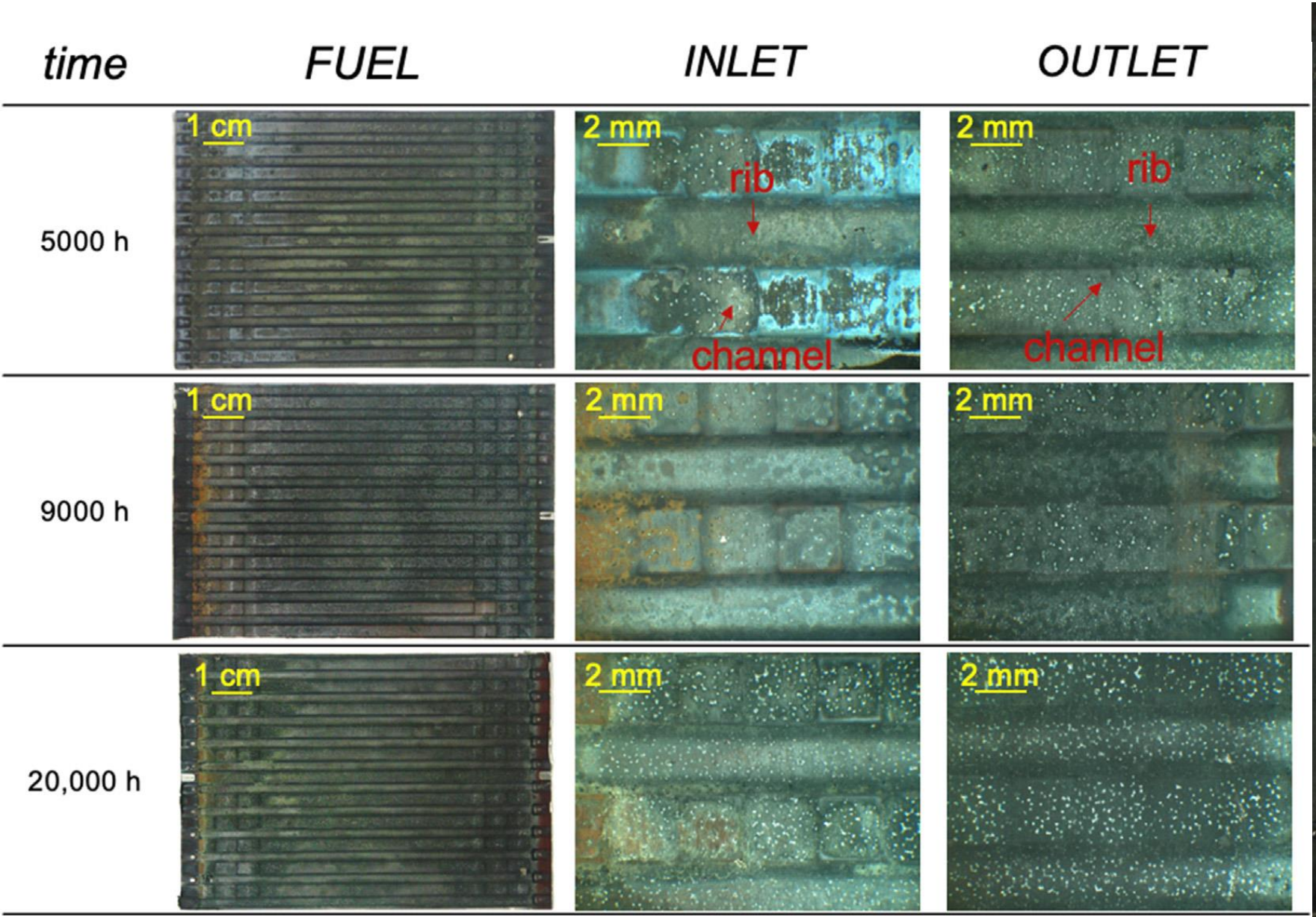




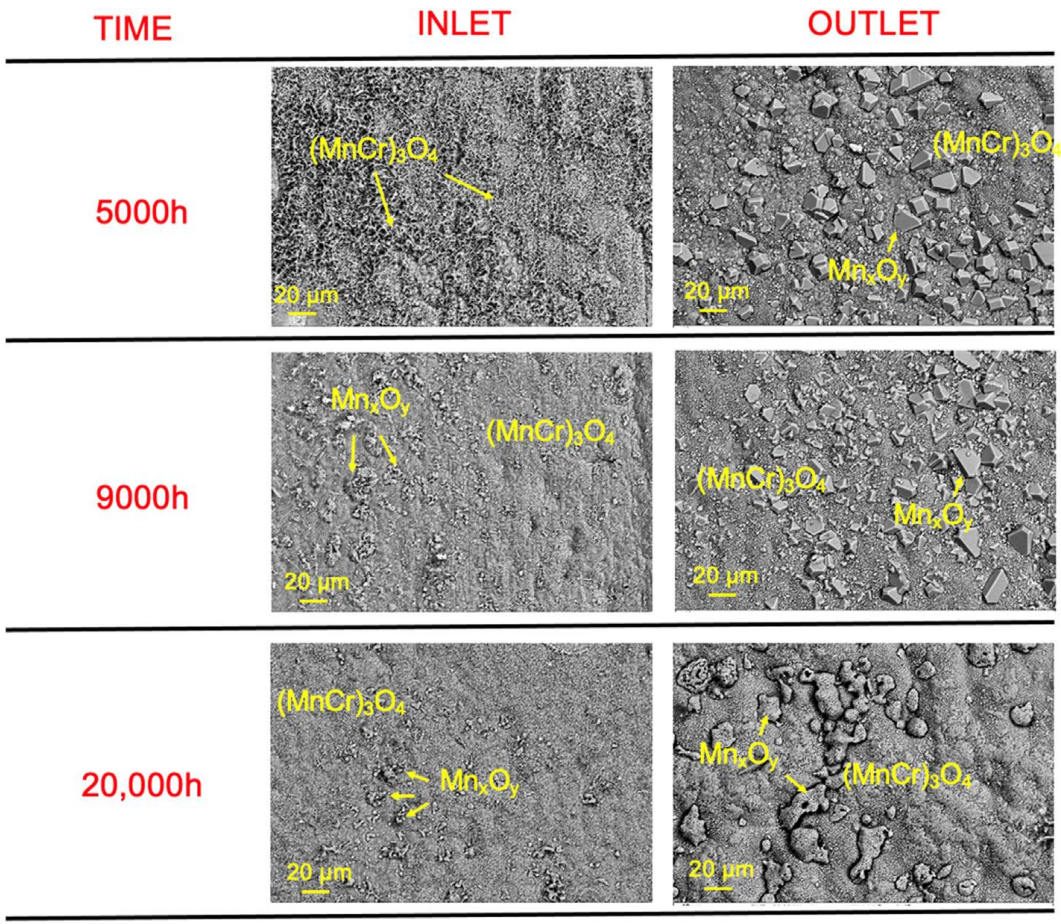


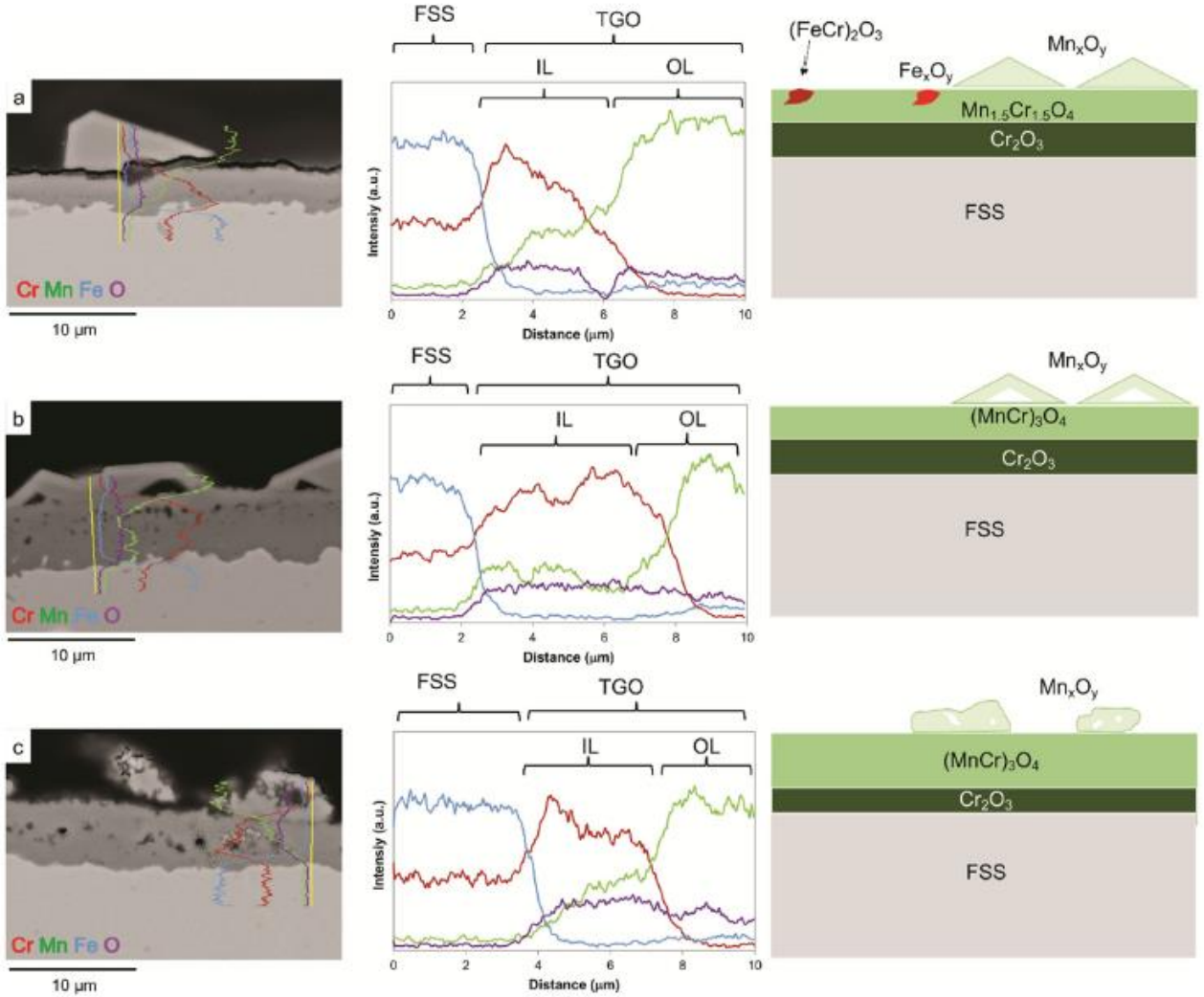
The figure presents on the left the distribution of the main elements in both the TGO and MCO differentiating the rib (on the left of the drawing) and the channel (on the right of the drawing.
The sketch helps to understand the path followed by the electrons while the cell stack operates (i.e., the electrons generated at the anode of one cells moves through the interconnect to the cathode of the neighbouring cell). The X-ray maps represent the distribution of Mn only

CROFER 22 APU ® uncoated: fuel side

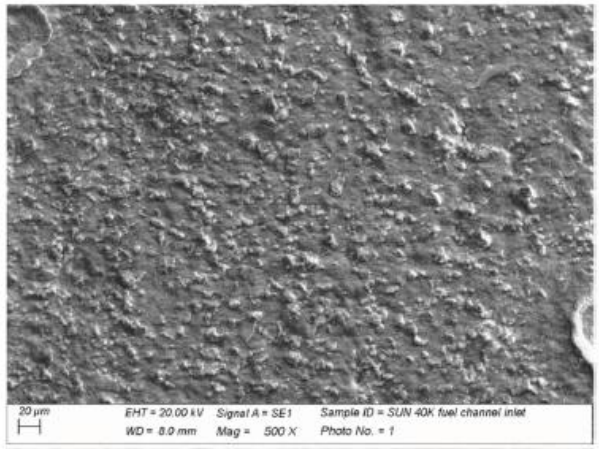


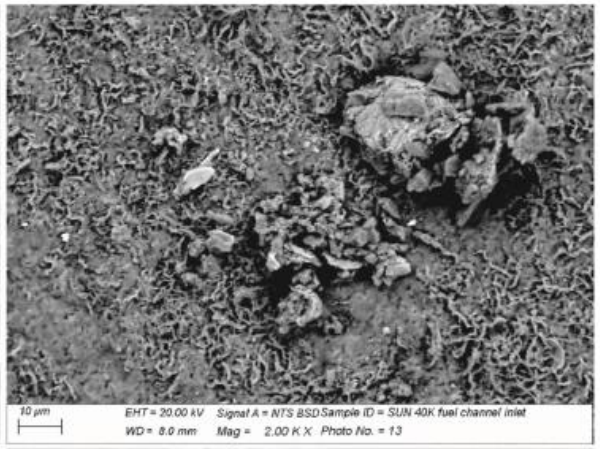
Details up to 40’000 hours: fuel side

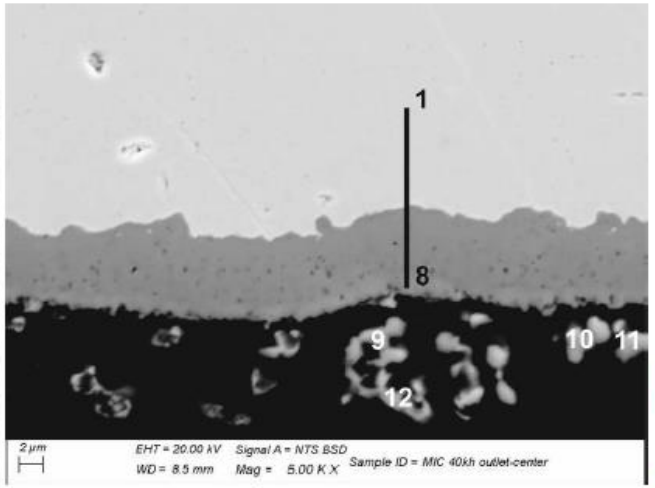


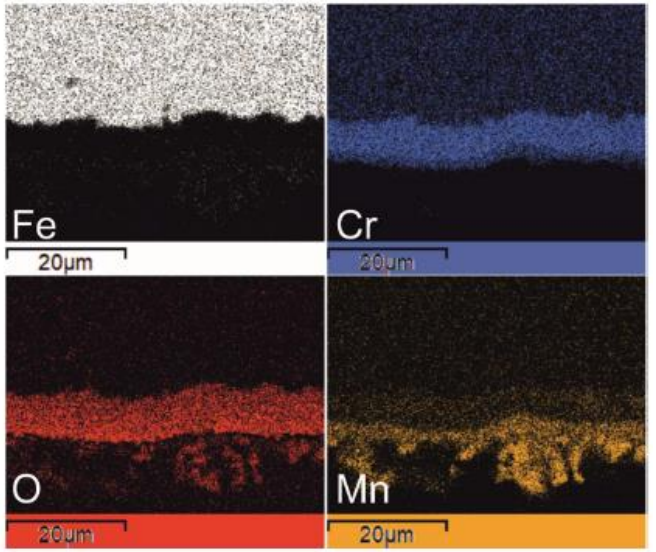


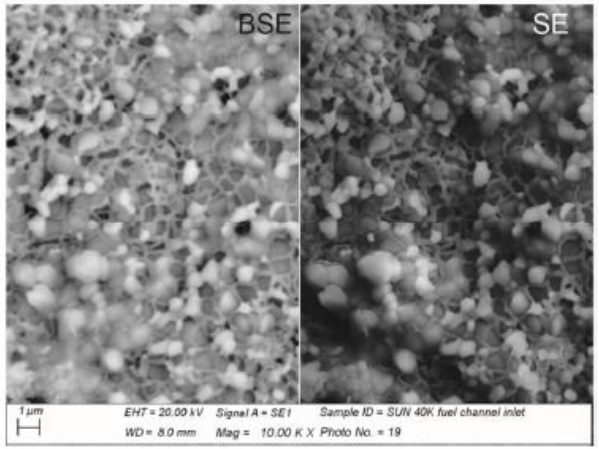
Details up to **40’000 hours**: fuel side

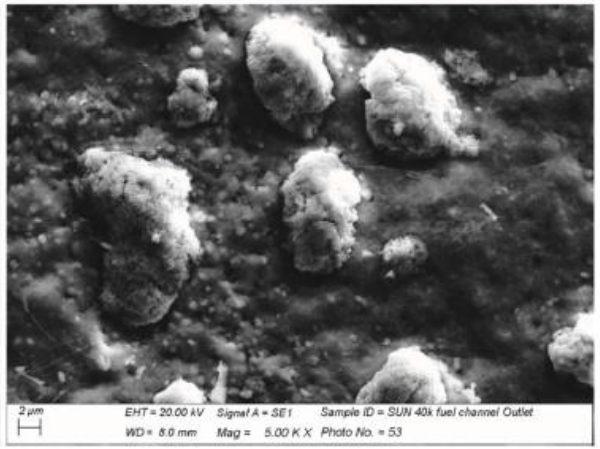


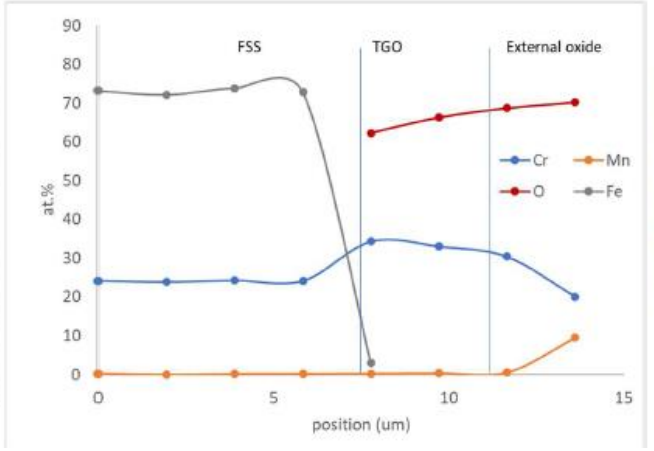






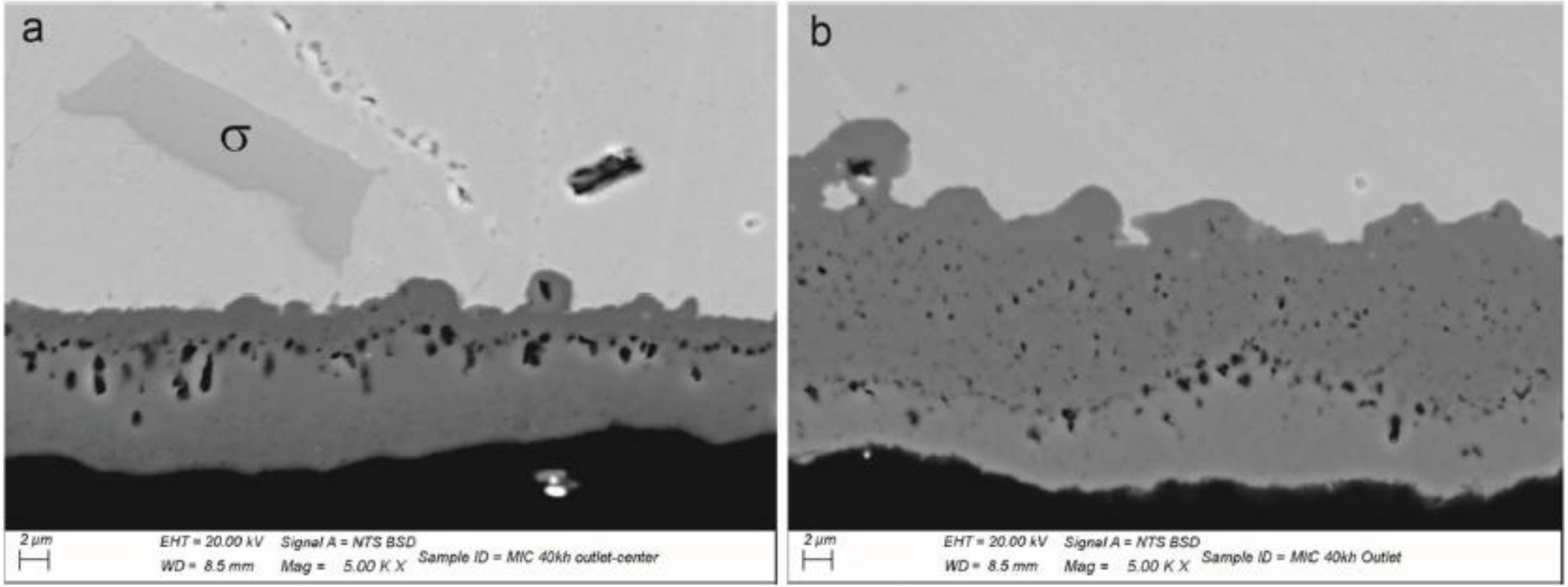






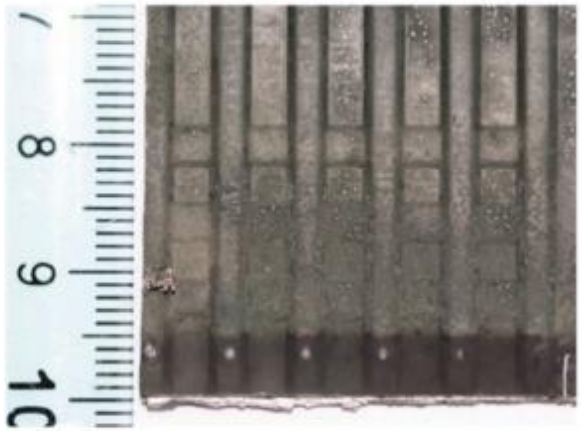
Spectrum	distance	O	Cr	Mn	Fe
Line Spectrum(1)	0	0	24.2	0.3	73.2
Line Spectrum(2)	1.9	0	23.9	0	72.2
Line Spectrum(3)	3.9	0	24.3	0.2	73.9
Line Spectrum(4)	5.8	0	24.2	0.2	72.8
Line Spectrum(5)	7.8	62.3	34.4	0.3	3
Line Spectrum(6)	9.7	66.3	33.1	0.4	0.3
Line Spectrum(7)	11.7	68.7	30.4	0.6	0.3
Line Spectrum(8)	13.6	70.2	20.1	9.5	0.3
Spectrum 9		70.4	0.8	28.3	0.4
Spectrum 10		69.7	3.7	26.1	0.3
Spectrum 11		70	1.8	27.7	0.3
Spectrum 12		65.4	0.7	33.3	0.5

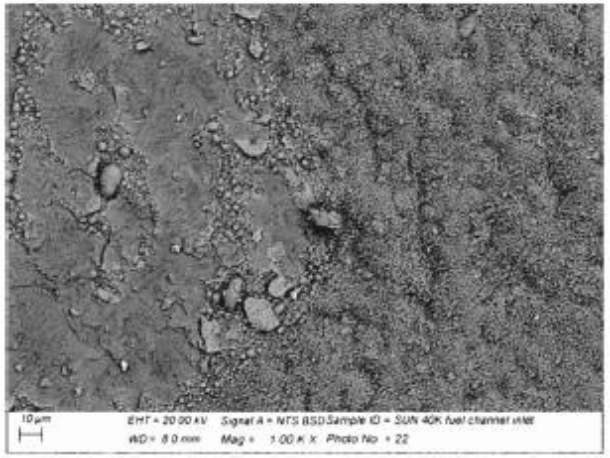
Kirkendall effect on the scale due to Mn diffusion

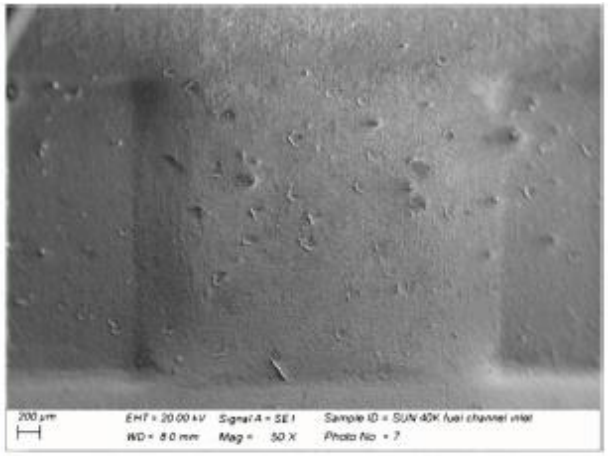


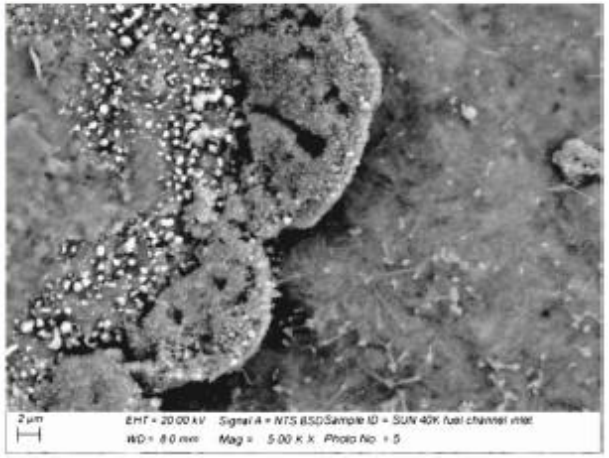
Fuel side, a) center of the stream (850°C, average P_{H2O}), b) outlet of the stream (ca. 890°C, high P_{H2O})

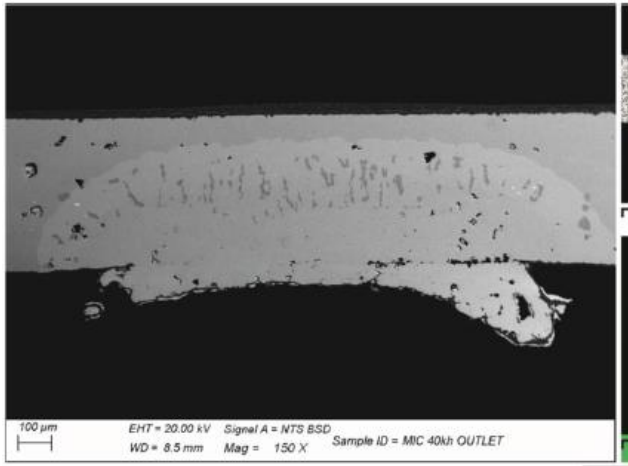
Fuel side, 40k hours, Ni contacting layer / MIC

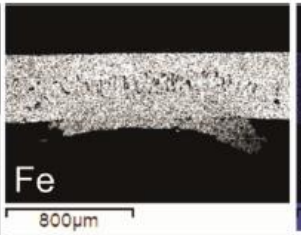


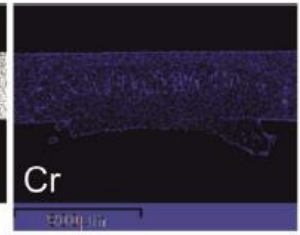


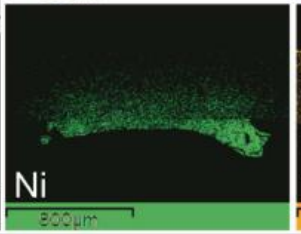


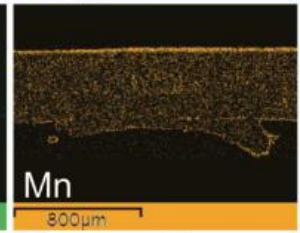




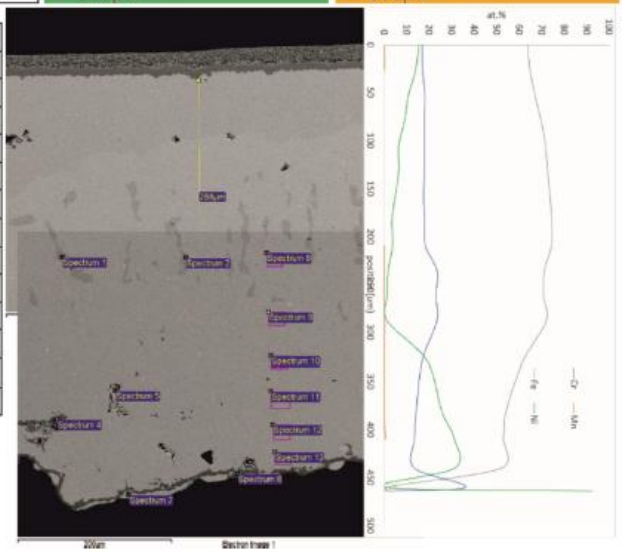




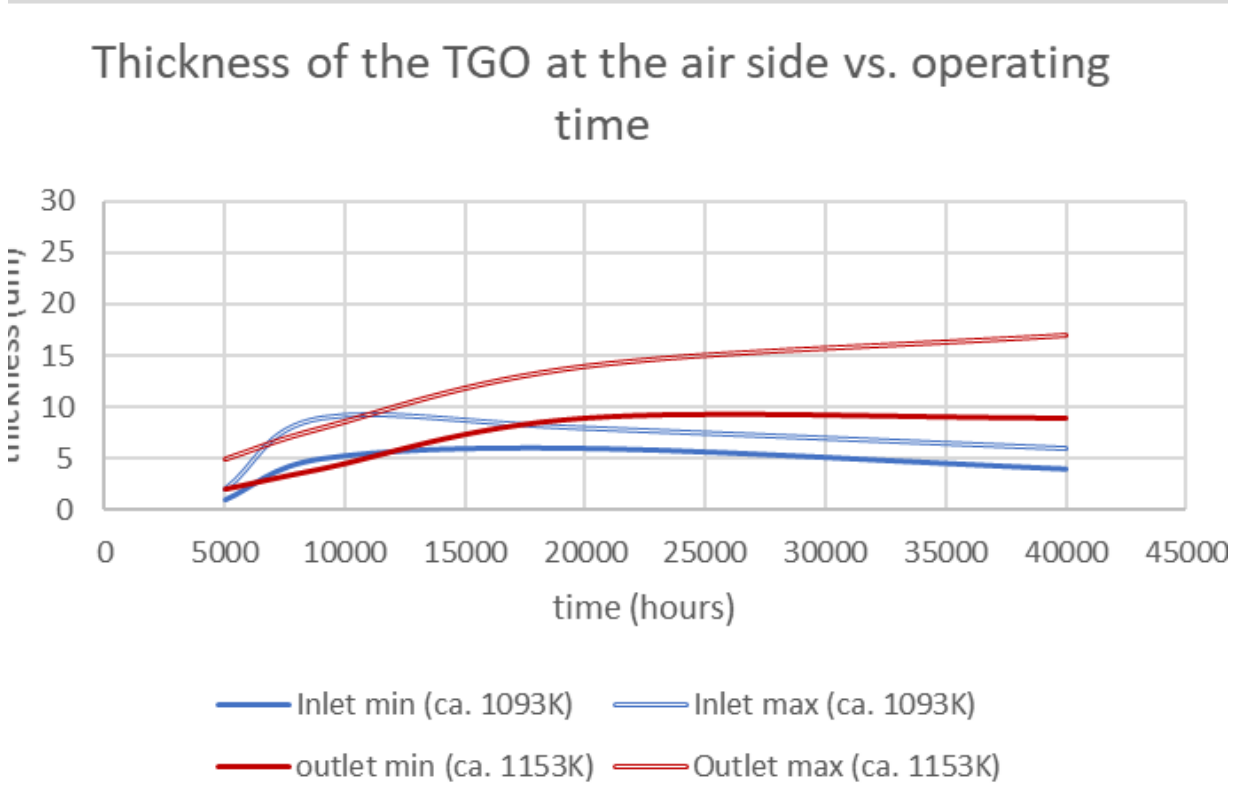


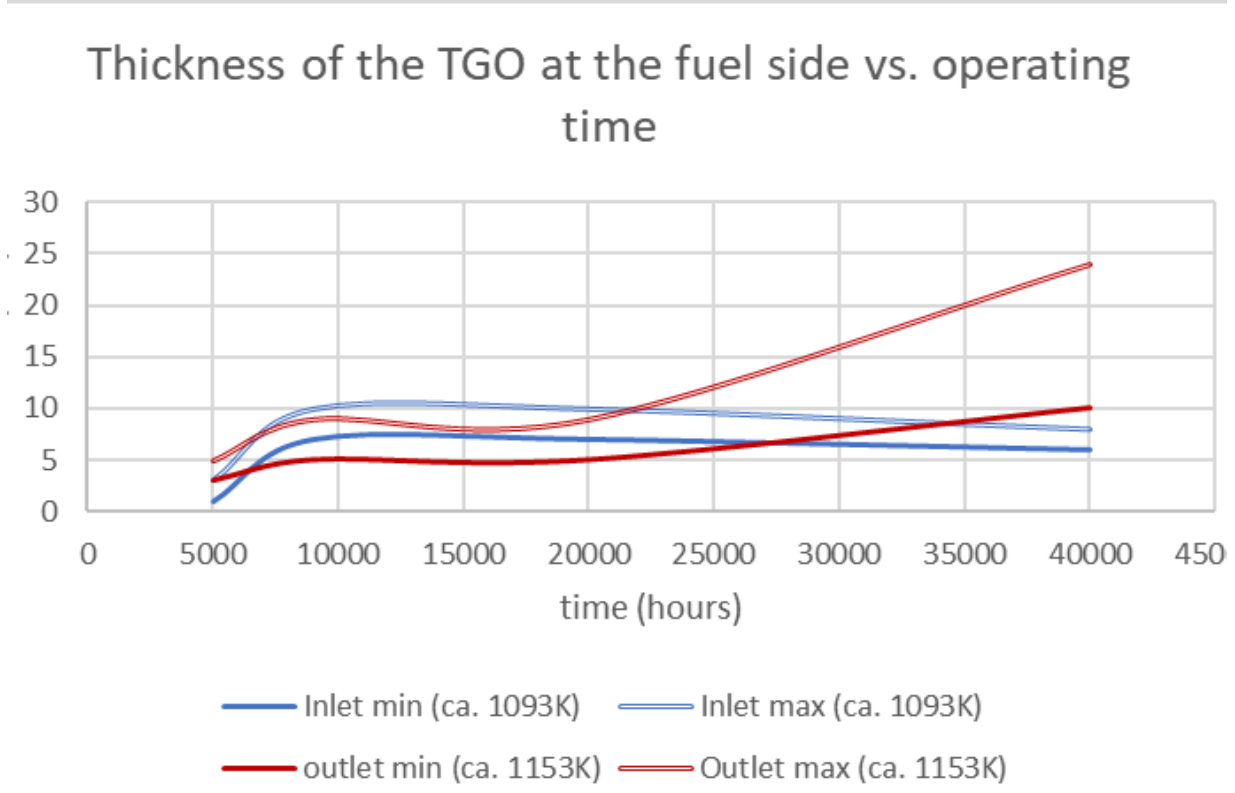


Spectrum	O	Cr	Mn	Fe	Ni
Spectrum 1	0.9	79.5	0.8	17.4	1.4
Spectrum 2	0.5	79.1	0.6	18.3	1.5
Spectrum 3	2.8	78.1	0.5	17.1	1.4
Spectrum 4	58.7	29.2	10.3	1.3	0.4
Spectrum 5	9.9	14.7	0	56.2	19.3
Spectrum 6	61.4	36.2	1	0.7	0.8
Spectrum 7	3.8	1.1	0.3	2	92.7
Spectrum 8	2.4	17.8	0.2	71.9	7.6
Spectrum 9	1.8	17.4	0.2	64.6	16
Spectrum 10	2.1	16.9	0.1	61.7	19.3
Spectrum 11	5.7	14.4	0.1	54.3	25.5
Spectrum 12	1.7	13.5	0.5	53.1	31.3
Spectrum 13	2.6	13.5	0	52.3	31.5



Scale evolution over time





Degradation of long-term aged SOFC interconnects (ICs)

Samaneh Daviran[1], Stéphane Poitel[1], Emmanuelle Boehm Courjault[1], Hassan Javed[2], Christian Walter[2], Jan Van herle[1]

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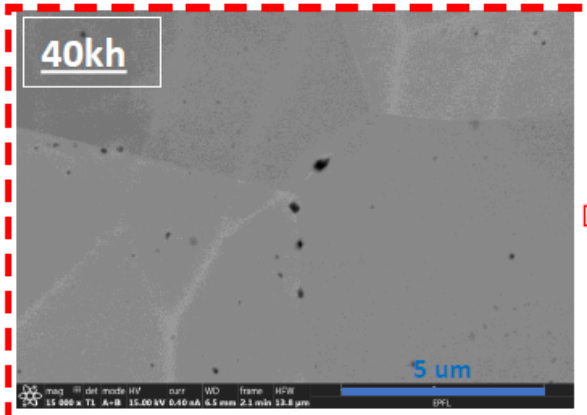
The MIC

Steel Bulk

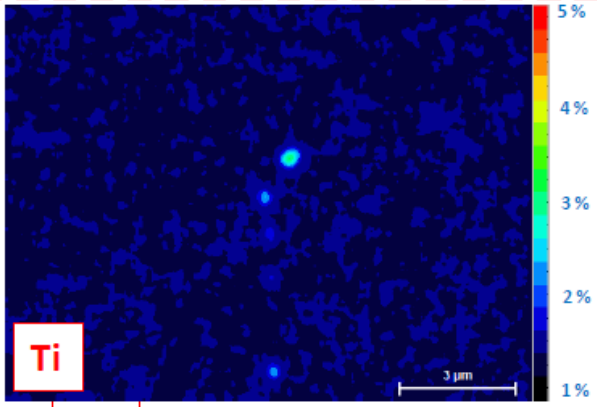
Internal oxidation: precipitation of **Ti oxide** and **Al oxide** in the bulk and mostly close to the Cr thermally grown scale interface

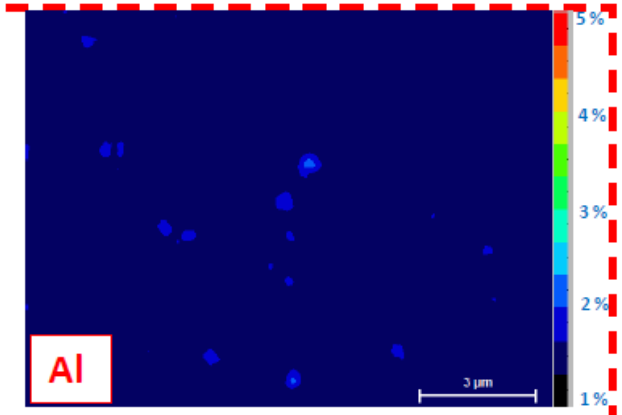
bulk

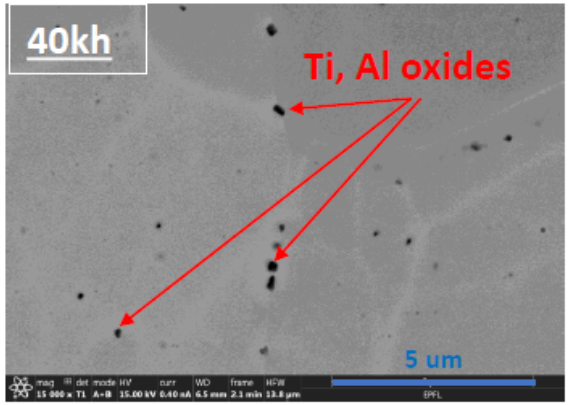


Quantified map

(at %)







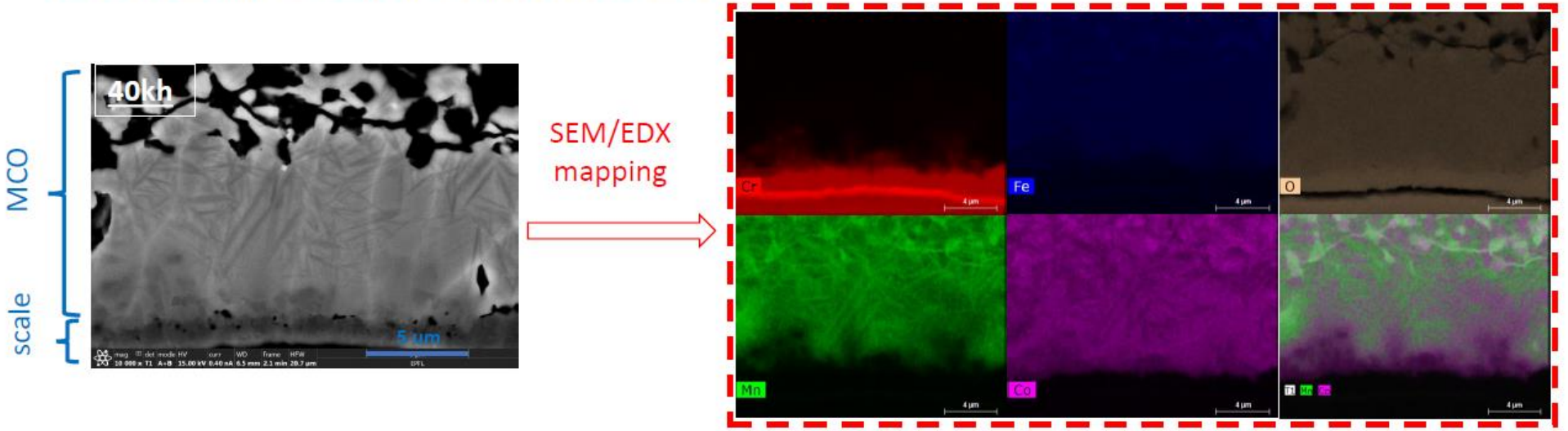
oxides precipitation: Ti: 3,52% Al: 2,81% O: 12,8%

bulk: Ti: 0,62% Al: 0,87% O: 2,66%

Insights : the coating

Coating: Fe doped $MnCO_2O_4$ (MCO)

- decomposition of MCO: Mn-rich needles in Co-rich matrix
- observed only in outlet, rib (reported also in [3])



Possible reasons of MCO decomposition:

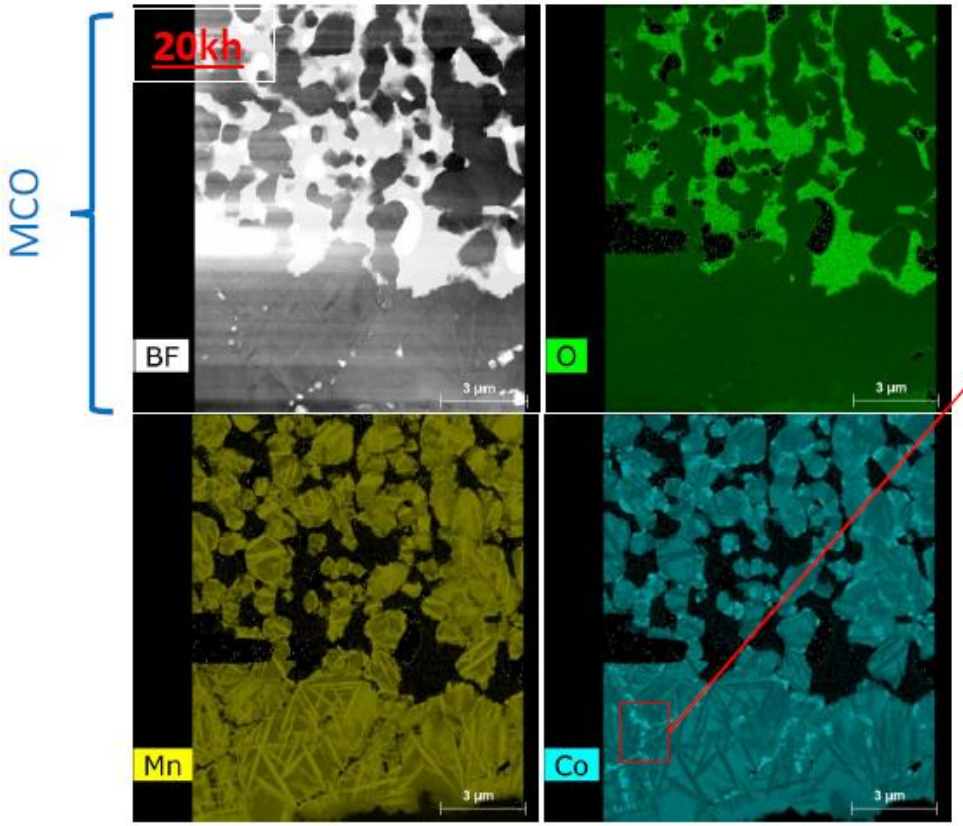
- local heating up in rib location
- local decrease in ox partial pressure
- current effect

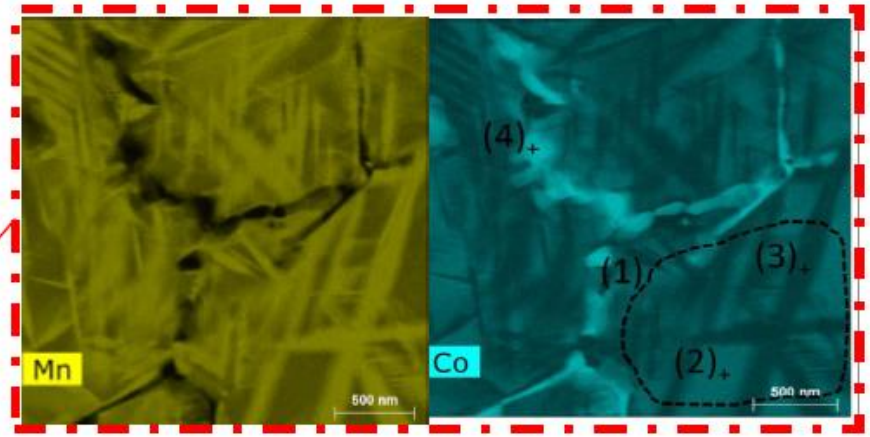
[3] Grünwald, et al., "Microstructure and Phase Evolution of Atmospheric Plasma Sprayed Mn-Co-Fe Oxide Protection Layers for Solid Oxide Fuel Cells" *J. Eur. Ceram. Soc.* (*2019*), *39* (2), 449–460. https://doi.org/10.1016/j.jeurceramsoc.2018.08.027

Insights : the coating

Coating: Fe doped $MnCO_2O_4$ (MCO)

- MCO phase separation also observed in **20kh** ICs (TEM/EDX)





➔ Co-rich zone *at grain boundaries*

% in at	O	Mn	Co
(1) Average of whole grain	48	25	21
(2) Co-rich matrix	45	18	28
(3) Mn-rich needle	45	32	16
(4) Co area at grain boundaries	46	2	49

Conclusions on MIC

- The interconnect survived the 40,000 hours of field operation in a stack with the presence of a limited number of changes at the air side and some more issues at the fuel side
- The air side ribs have shown the formation of a TGO at the interface between the protective layer and the metal substrate. The contacting layer results untouched by the presence of Cr or any other issues worth of notice
- The air side channels present on top large crystals of spinel oxide containing Cr, Mn, Co, and Fe
- Some decomposition of the coating was observed after 20k hours and precipitates formed in the steel
- The fuel side is more affected by the oxidation The combination of T and water vapour is deleterious for steel
  - The TGO formed at the outlet is thicker than the one observed at air side
  - There are several indications for the formation of volatile Cr-rich compounds carried away by the fuel stream
  - The Ni contact layer left numerous traces on the metal surface
- The T confirms to be a strong accelerating parameter of the oxidation process
  - At T> 850°C where after 40,000 hours the TGO thickness is still increasing
  - At T<1123 K a shrinkage process starts after 9,000 hours
- The water vapour is another important accelerating factor even in presence of hydrogen.
  - It forms a TGO and affects its composition (e.g., formation of Mn rich oxides on top of the scale
  - Once combined with T the TGO growth rate is increased
  - The synergy between T and PH2O is mainly visible at T>850°C.
- These results support the usage of T and water vapour in AST tests to simulate long lasting operating period and open the route for further studies on protective coating to apply on the fuel side.

Thank you

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