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European Institute
for Energy Research
by EDF and KIT

Degradation assessment in solid oxide cell operated in electrolysis mode.

Energy Transition

by EDF and KIT

Transition from a high-performing carbon-based energy system:

to low carbon energy system and to *net-zero* energy system.

Transition enabler: early deployment of hydrogen produced from renewable electricity and water electrolysis

- Total planned electrolyzer capacity by 2030: 40 GW in Europe
  - » By expanding the actual renewable energy and water electrolyzer capacity (move to GW scale system)
  - » By industrializing the manufacturing process
  - » By reducing the (voltage) degradation rate over long-term operation of the cell, stack and system

Target EU	2027	2030
	0.7%/kh @1.0 $A \cdot cm^{-2}$	0.5%/kh @1.5 $A \cdot cm^{-2}$

HTEL – Scaling up

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From cell to system

Initial conditions

- Initial performance

Cell
W

Stack
kW

Module
KW…MW

System
100 MW

Move to
GW
scale

Final conditions

- Final performance
- Lifetime
- Degradation rate

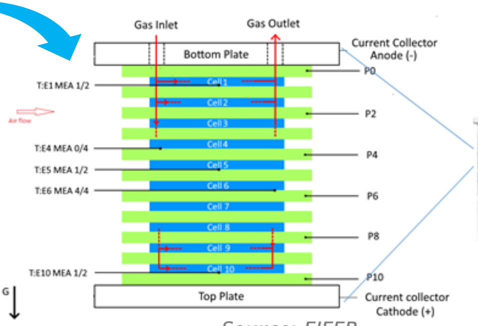
Operation parameters

- Temperature, T = 750 – 850 °C
- Current density, j = 0.5 – 1.2 – 1.x Acm^{-2}
- Feed humidity (FH) > 50 vol.%
- Steam conversion (SC)= 50 % – 80%

Cell

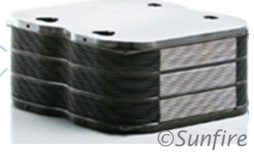
Cell

Single cell



Source: EIFER

10 cell stack



3x10 cell stack

3x30 cell stack module

System

Module

Module

Module

Module

4x 90 cell module

HTEL - operation

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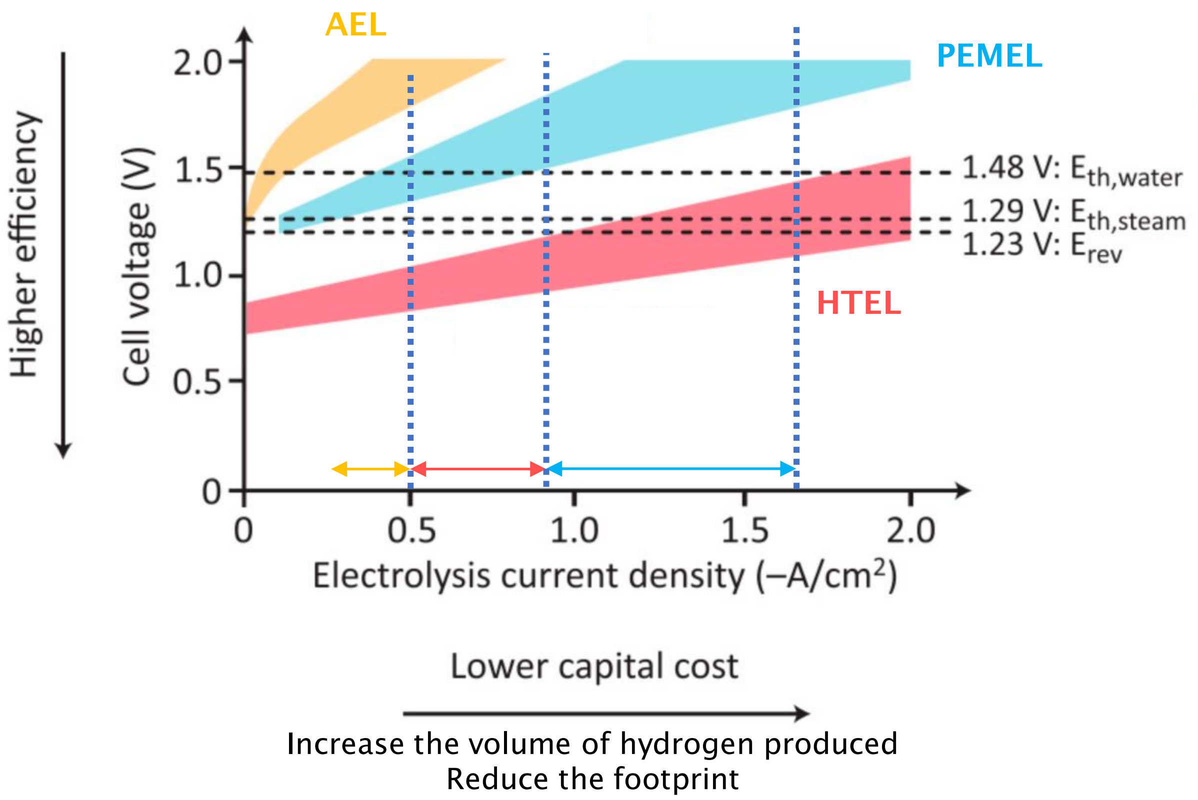
What are the parameters to follow?

- Current density
  - » amount of hydrogen produced per cell area (kgH_2/cm^2)
- Cell voltage
  - » the specific electric needs in kWh/Kg, so the efficiency
  - » *Performance V = f(I), durability V = f(t)*
- Degradation rate
  - » Origin of the degradation
  - » *Impedance spectroscopy*
  - » *Post-test analysis using imaging, scattering and spectroscopy techniques*



Source: L. Barelli, G. Bidini and G. Cinti, ChemEngineering 1 (2017) 13

HTEL - Degradation rate

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Definitions

- Deterioration of the cell performance over time according to a specific performance indicator
  - Voltage degradation (test performed at constant current); mV/kh
  - Area specific resistance degradation; mΩ cm^2/kh
  - %/kh referring to the thermoneutral voltage

- $DR = \left|\frac{(U(i,t) - U(i,t=0))}{U(i,t=0)}\right| \cdot \frac{1000}{t} \cdot 100\%$
  - Linear approach limited: changes in temperature, reactant/product composition not taken into account
  - Additional degradation to be added on the raw voltage degradation to estimate the real voltage degradation

HTEL – cell architecture

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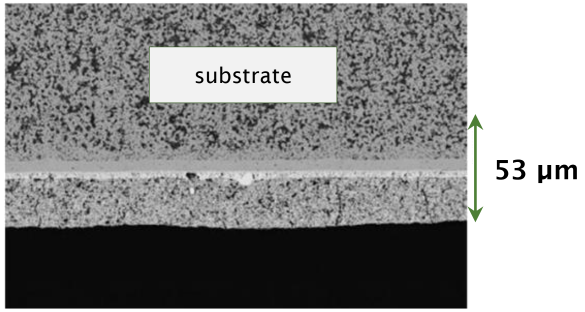
Cathode (Electrode) Supported cell

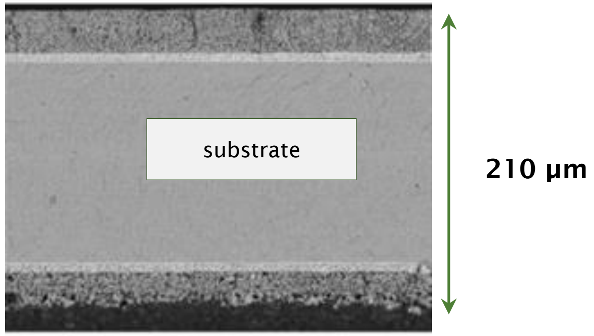
Ni/YSZ – Substrate $Ni/(Y_2O_3)ZrO_2$ (1.5 mm)
Ni/YSZ – hydrogen electrode $Ni/(Y_2O_3)ZrO_2$ (8 µm)
8YSZ – electrolyte $(8Y_2O_3)ZrO_2$ (10 µm)
CGO – gas diffusion barrier $Ce_{0.8}Gd_{0.2}O_{1.9}$ (5 µm)
LSCF – oxygen electrode $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (30 µm)



Source: Elfer

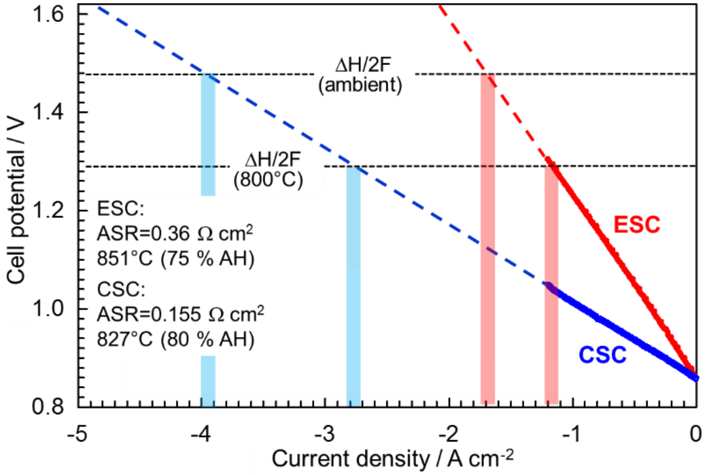
Electrolyte Supported cell (ESC)

Ni/CGO – hydrogen electrode $Ni/Ce_{0.8}Gd_{0.2}O_{1.9}$ (30 µm)
CGO – contact layer $Ce_{0.8}Gd_{0.2}O_{1.9}$ (7 µm)
6Sc1CeSZ – electrolyte $(6Sc_2O_3 \cdot 1CeO_2)ZrO_2$ (130 µm)
CGO – diffusion barrier $Ce_{0.8}Gd_{0.2}O_{1.9}$ (7 µm)
LSCF – oxygen electrode $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ (30 µm)



Source: Elfer

Measured and extrapolated U-j curves for both type of cells



Source: J. Schefold et al., Electrochim. Acta 179 (2015) 161-168

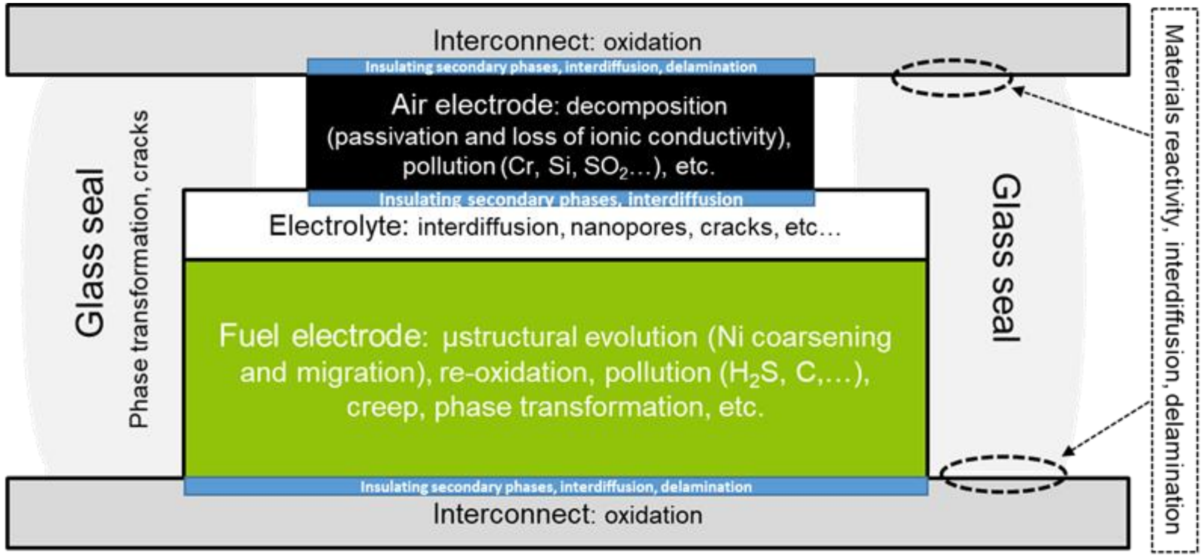
HTEL – Degradation causes

Cell level

- Material properties (phase segregation, cation diffusion)
- Electrochemical processes (polarization resistance of the fuel and air electrode)
- Cell architecture, operating conditions
  - » Electrode supported cell: Ni depletion at high current density
  - » Electrolyte supported cell: ohmic resistance related partly to a ionic conductivity decrease of the electrolyte

Stack level

- Larger scale cell
  - » Current density, gas and steam flow distribution
  - » Temperature gradient
  - » Interconnect coating material, glass seal



Summary of the main degradation phenomena; source: McPhail et al. Electrochem. Sci. Adv.2021, doi.org/10.1002/elsa.202100024

HTEL – Degradation analysis

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Types of Degradation

- Progressive linear degradation rate
- Chemical and /or electrochemical degradation
- Sudden incident or failure/malfunction of components; irreversible or with possible recovery
  - Thermal cycling
  - Current load
  - Mechanical wearing
  - Poisoning

Tools for tracing degradation

- Electrochemical characterization
- In-situ electrochemical impedance spectroscopy
- Ex-situ:
  - Imaging
    - Scanning electron microscopy SEM, STEM
    - High-resolution transmission electron microscopy
    - X-ray nanotomography (3D reconstruction)
  - Scattering
    - μ and nano-X-ray diffraction
  - Spectroscopy
    - μ and nano-X-ray fluorescence spectroscopy and X-ray absorption spectroscopy
    - Ambient pressure X-ray photoelectron spectroscopy
    - Secondary ion-mass spectroscopy
    - Raman Spectroscopy
- Electrochemical model

HTEL – Performance, Durability

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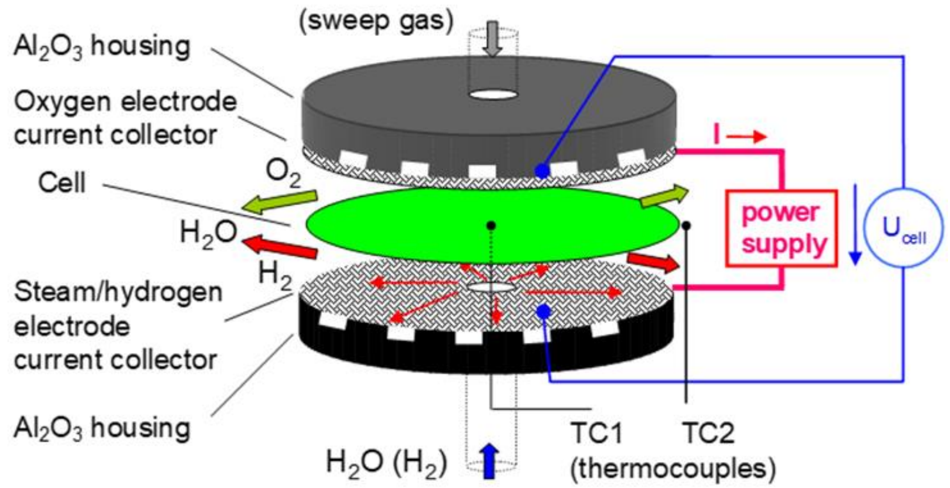
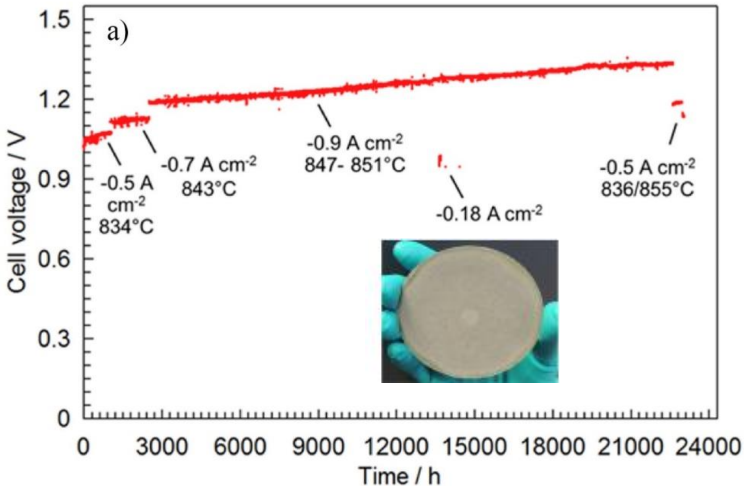
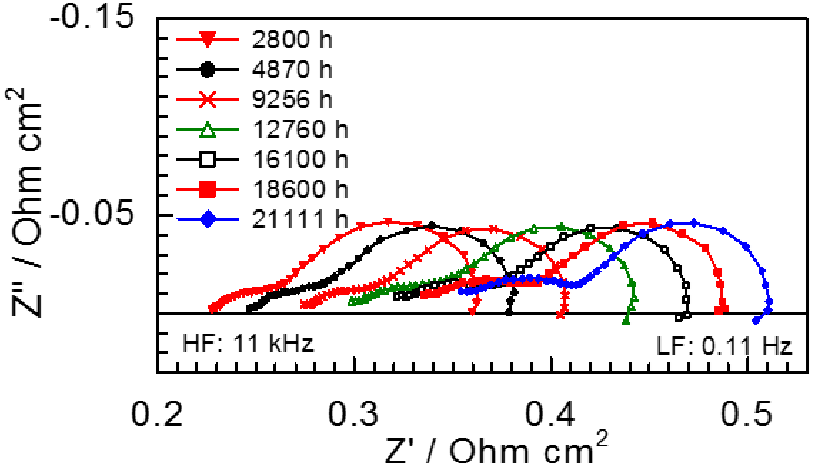
Kerafol GmbH cell

- Cell operation at EIfER facilities
  - ESC: Ni(GDC)/GDC/**6Sc1CeSZ (130 µm)**/GDC/LSCF
    - 847 - 851 ºC, FH = 75 vol.%, SC = 50%
    - Operated for 20,100 hours @ -0.9 Acm^{-2}
    - Kerafol cell tested 23,000 hours in total
  - Degradation rate ~ 7.4 mV/1000h @ - 0.9 Acm^{-2}
  - Degradation is mainly ohmic with 7 mΩcm^2/1000h



Source: EIfER





J. Schefold et al., IJHE 42, (2017), 13415

Degradation – nanoscale analysis

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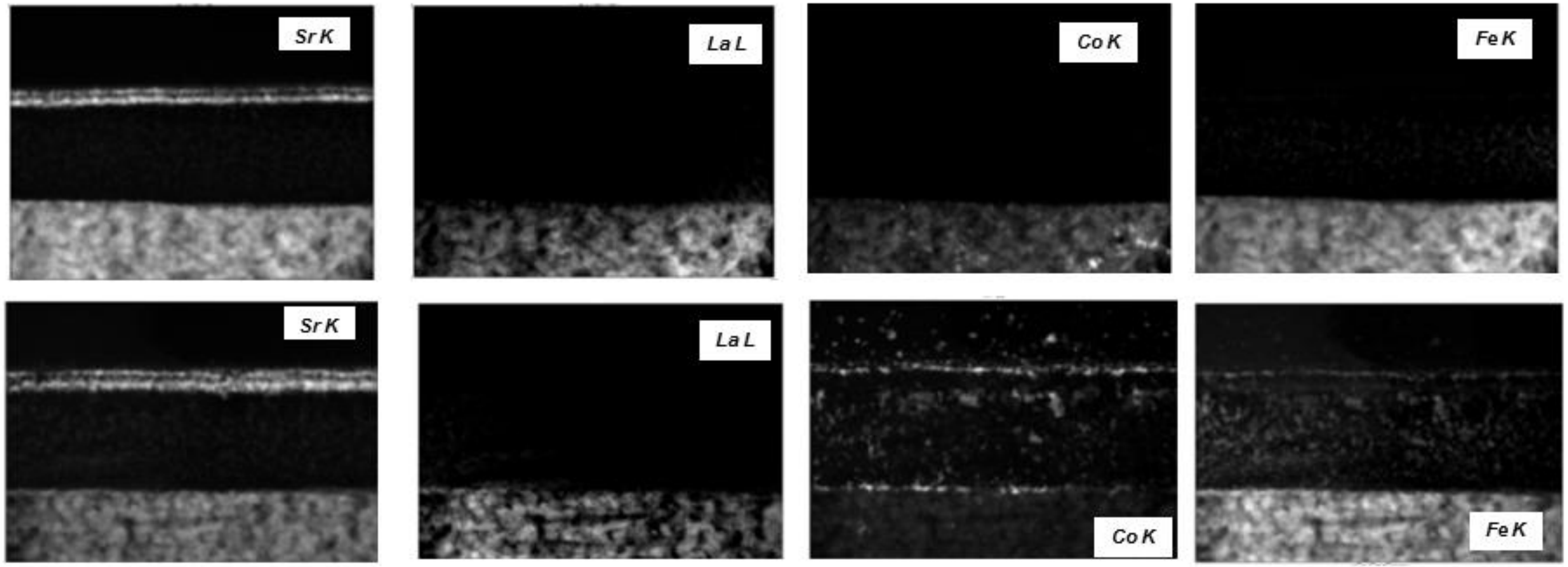
2D Nano-XRF maps- oxygen electrode side

Reference



Operated for 23,000 hours

Source: J. Villanova et al., Journal of Power Sources 421 (2019) 100

- Double layer of Sr
- Layer of Sr, Co, Fe
- Co, Fe in the diffusion barrier
- Layer of Co and Fe

Degradation –nanoscale analysis

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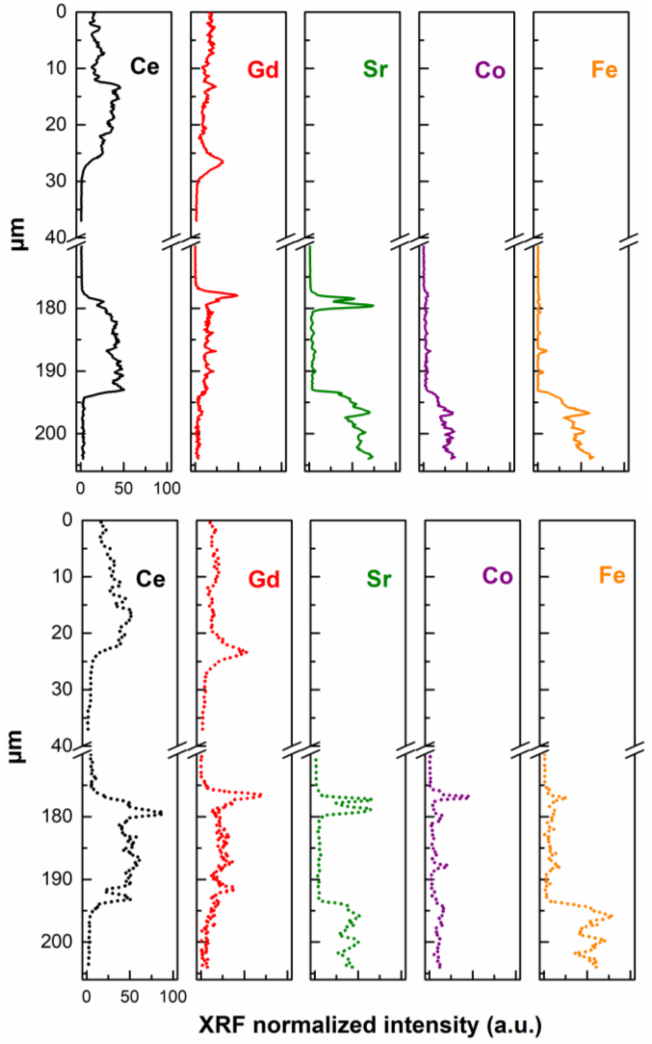
XRF map - Concentration profile



- After sintering
  - » LSCF/CGO/Sr/Ce/Sr/Gd/6Sc1CeSZ/Gd/Ce/CGO/Ni(CGO)
  - » Sr is not the contact layer with the electrolyte but Gd
- After operation
  - » LSCF/CGO/Sr/Ce/Sr/Gd/6Sc1CeSZ/Gd/Ce/CGO/Ni(CGO)
  - » Sr is not the contact layer with the electrolyte but Gd
  - » Co in the diffusion barrier layer, in the electrolyte, layer at the interface of the electrolyte

HTEL – Stack Performance, Durability

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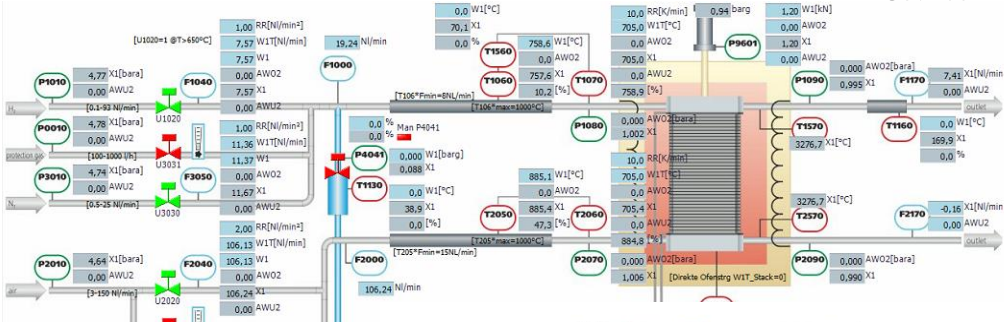
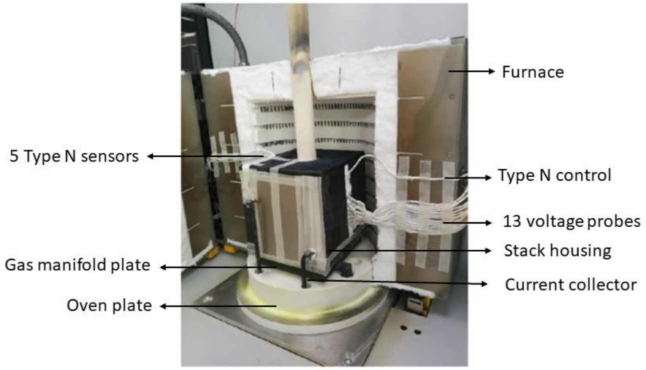
30 cells based stack

- Stack design
  - » Ni-GDC/GDC/3YSZ/GDC/LSCF (Sunfire GmbH)
  - » Rectangular shape single cell
    - > active area is 127.9 cm^2
  - » Co-flow configuration for the gas flow
  - » Compression load of 1200 N

- Stack integration
  - » Commercial test station
    - > Horiba – FuelCon GmbH
  - » Hotbox design for gas supply
  - » Temperature of the stack controlled by the oven
  - » Steam
    - > from high-purity water
    - > direct-injection evaporator unit

Source: EIfER





Source: EIfER

HTEL – Stack degradation

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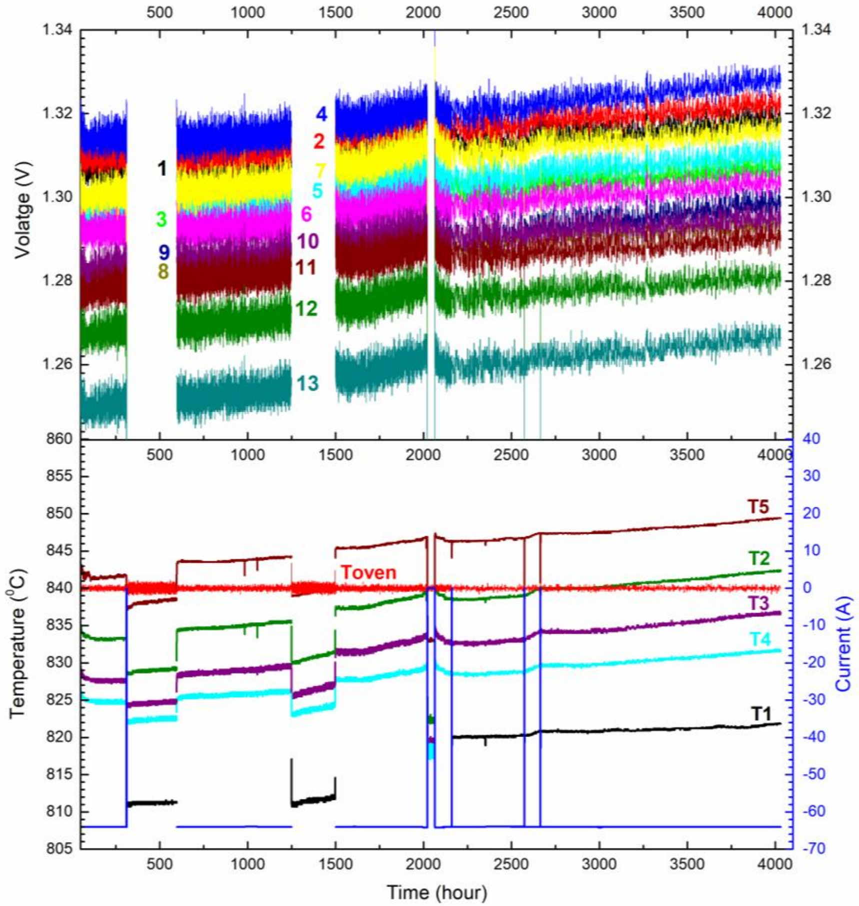
30 cells based stack

- Testing parameters close to real working conditions
  - » 90/10 vol.% H_2O/H_2, steam conversion = 70%
- Degradation rate analysis
  - » Raw voltage degradation
    - > 3.5 mV/kh
  - » Temperature induced degradation
    - > Temperature voltage calibration: - 3.5 mV/°C
    - > Temperature increase of 2°C/kh
  - » Temperature corrected degradation
    - > 10.5 mV/kh per cell
    - > Area specific resistance: 21 mΩ cm²/kh

Cell voltage and temperature evolution during the electrolysis test of a 30 cells based stack



Source: A. Léon et al., Journal of Power sources 510 (1) (2021) 230346

In-situ overpotential

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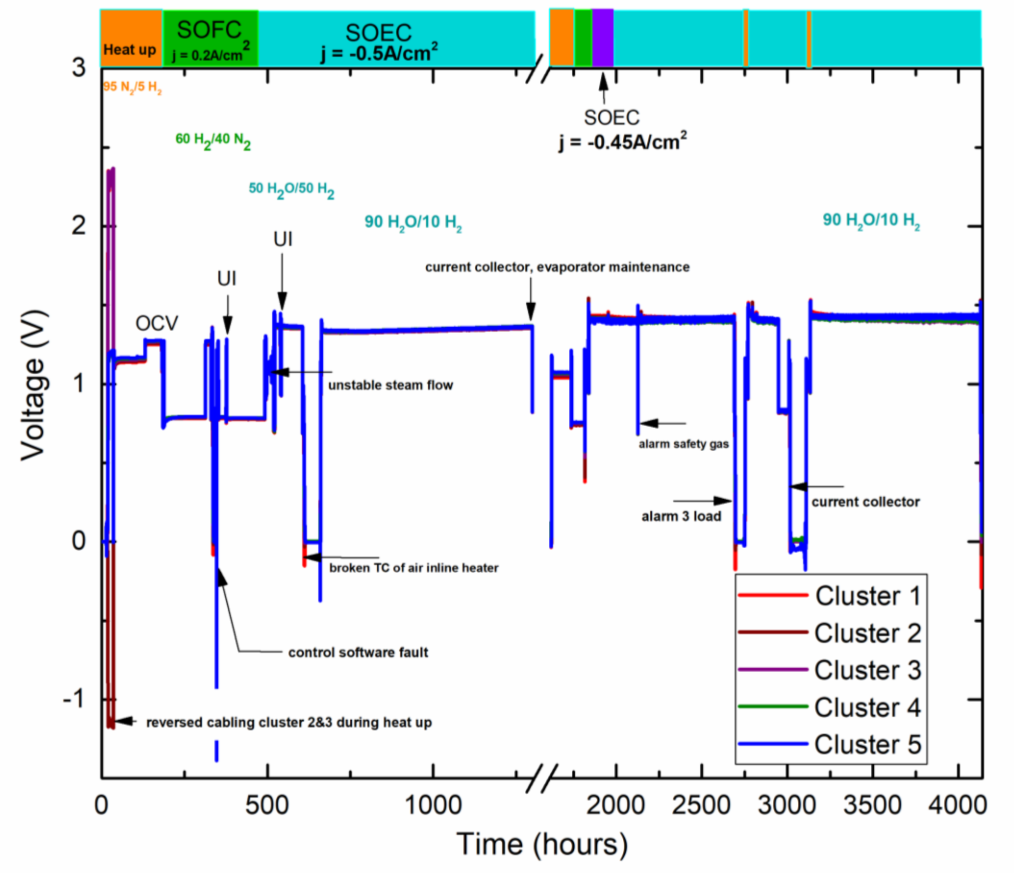
Short-stack at high current density



- SOFC @ j = 0.2 A/cm^2
- 2000 hours of SOEC @ j = -0.5 A/cm^2
- 2000 hours of SOEC @ j = -0.5 A/cm^2

- Incidences during testing are hindering the evaluation of the degradation
  - Current collector surface contact damaged
  - Evaporator maintenance
  - Water pump

In-situ overpotential

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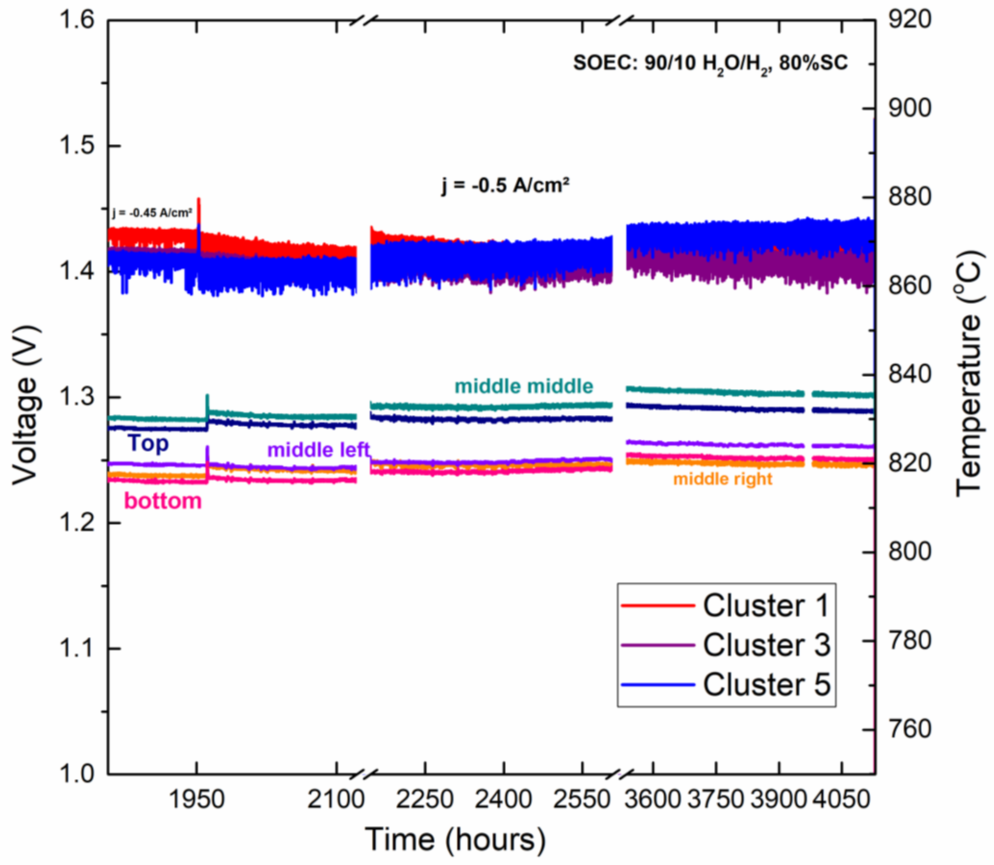
Short-stack at high current density

- ASR correction from temperature rise:
  - > 3.5 mV/°C
- ~2000 hours of SOEC taken into account

	Voltage degradation (corrected), mV/kh/cell
Cluster 1	10.5
Cluster 2	10.8
Cluster 3	21.5
Cluster 4	15.6
Cluster 5	24.8
Average stack	16.6



→ Stack moved to high current density up to – 0.65 Acm^{-2}

Summary and perspectives

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Degradation assessment

- Solid oxide system
  - Complex multiphase layers
  - Multiple degradation processes
  - Increased complexity when scaling up from cell to stack
- Degradation assessment approached with multimodal techniques
  - Electrochemical characterization
  - In-situ electrochemical impedance spectroscopy
  - Ex-situ post-test microstructural analysis
  - Electrochemical models

Ad-Astra project

- Long-term testing combined with characterization
  - Time consuming and costly
  - Not always in relevant real operating conditions
- Introduction of accelerated stress tests (AST)
  - Experimental evaluation of cell & stack at nominal and aggravated conditions
  - Comparison to assess that induced degradation is similar
  - Development of models

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Thank You

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