Current Activities on Solid Oxide Cells at DLR

Asif Ansar, Rémi Costa, Michael Hörlein, and <u>Günter Schiller</u>

German Aerospace Center
Institute of Engineering Thermodynamics
Stuttgart, Germany

Outline

- Brief Introduction of DLR-ITT

- Metal Supported Cell Concepts for SOC
    - Plasma spray concept
    - EVOLVE concept

- SOEC activities
    - Hi2H2 project
    - Degradation study
    - Solar fuels

- Conclusion

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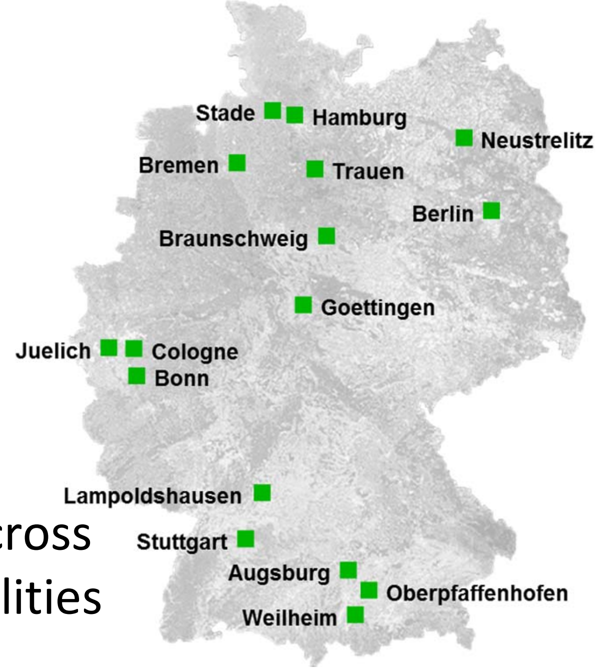
Aeronautics
Space
Transport
Energy

Research Institution



Space Agency
Project Management Agency

> 7500 employees across
32 institutes and facilities

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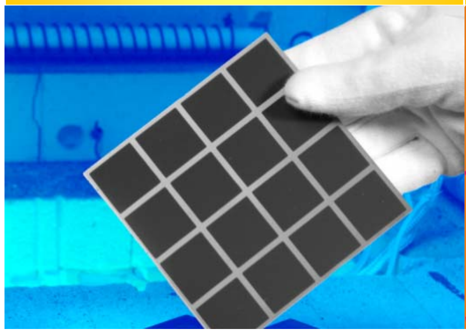
Institute of Engineering Thermodynamics

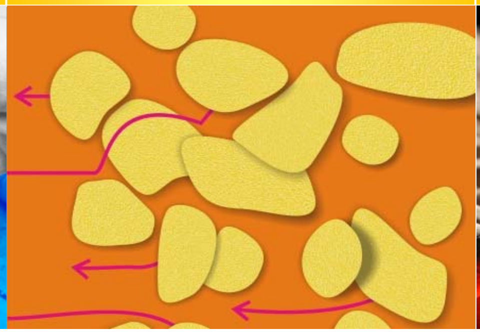
Prof. Dr. André Thess

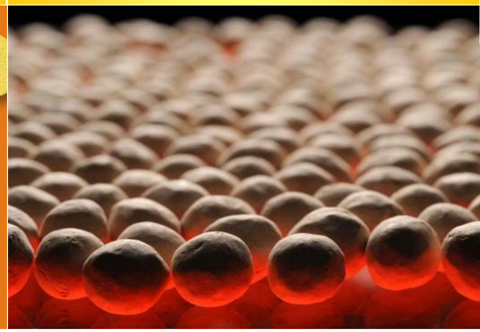
Administration

Jörg Piskurek

Electrochemical Energy Technology	**Computational Electrochemistry**	**Thermal Process Technology**	**System Analysis and Techn. Assessment**
Prof. A. Friedrich	*Prof. A. Latz*	*Dr. A. Wörner*	*Dr. C. Schillings / C. Hoyer-Klick (komm.)*







Staff: About 190 in Stuttgart, Köln, Hamburg and Ulm
Yearly budget: About 18 Mio. EUR including 50% third party funding

„... innovative solutions for sustainable and environmentally friendly energy storage and conversion processes ...“

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Electrochemical Energy Technology

R&D of efficient electrochemical energy storage and conversion

5 Fields of Research

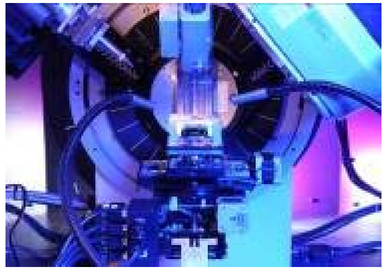
Solid Oxide Cells
Realization of durable, powerful and cost effective SOFC-stacks

Polymer Electrolyte Fuel Cells
Improvement of longevity and reliability with regard to electric mobility and residential power supply

Lithium Metal and Lithium Ion Batteries
Development of mobile energy storages

Modeling & Simulation
Improvement of the efficiency factor, longevity and costs of fuel cells and batteries

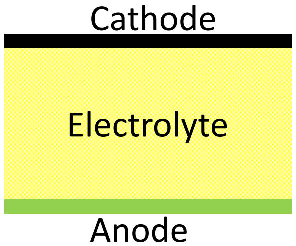
Electrochemical Systems
Development of efficient and effective, multifunctional fuel cells systems for stationary and mobile applications



Generations of planar SOFCs

1st gen. → **2nd gen.** → **3rd gen.**

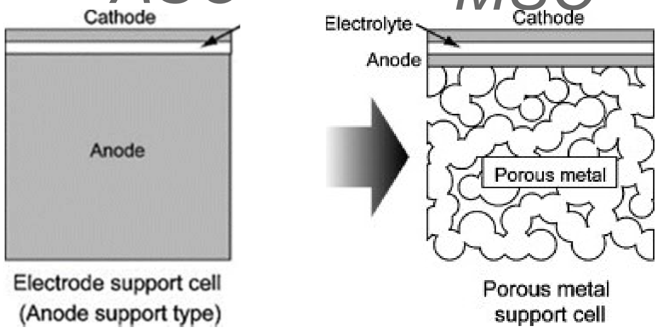
ESC



Limited power density
Fuel flexibility
Robustness

Stationary
Transportation

ASC / MSC



ASC (2nd gen.)

High power density
Fuel flexibility
Sulfur poisoning
Thermal cycling
Redox Cycling

Stationary
Transportation

MSC (3rd gen.)

High power density
Fuel flexibility
Sulfur poisoning
Thermal cycling
Redox Cycling

Stationary
Transportation

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Metal Supported SOFC

Plasma Spray for Functional Layers

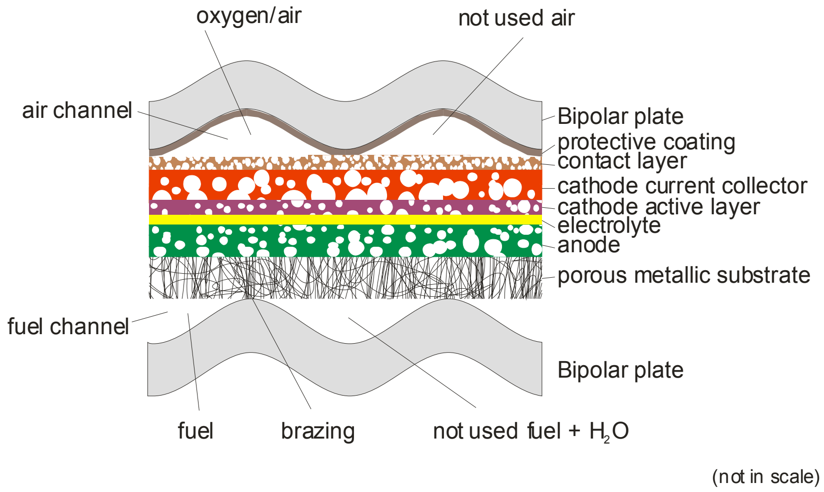
Compact design with thin sheet
ferritic substrates and interconnects

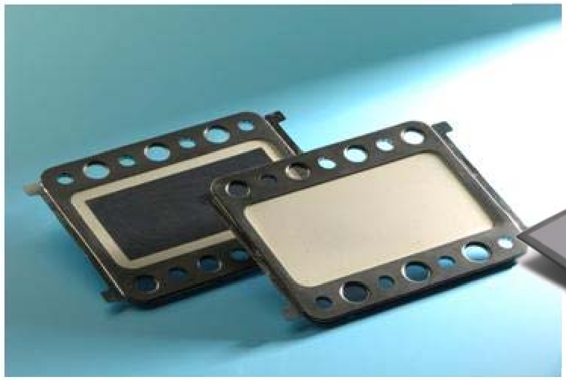
100 cm² foot print

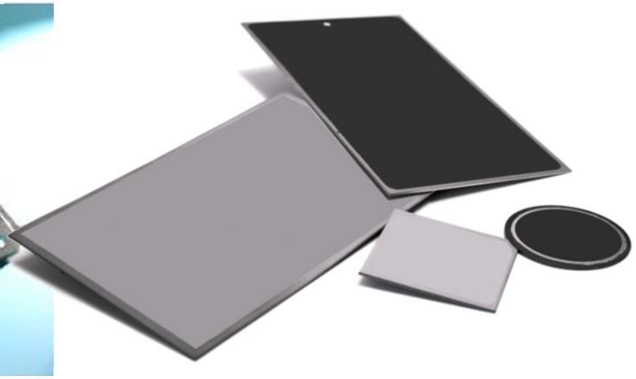
Counter flow stamped gas manifold

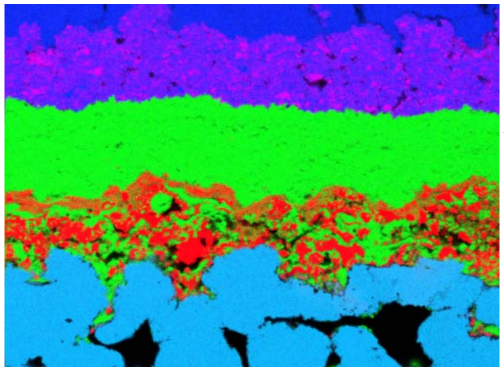
Welded substrate with the interconnect

Brazing or Glass Seal as joining of repeat units









Cathode 20 µm
Electrolyte 35 µm
Anode 35 µm
Substrate

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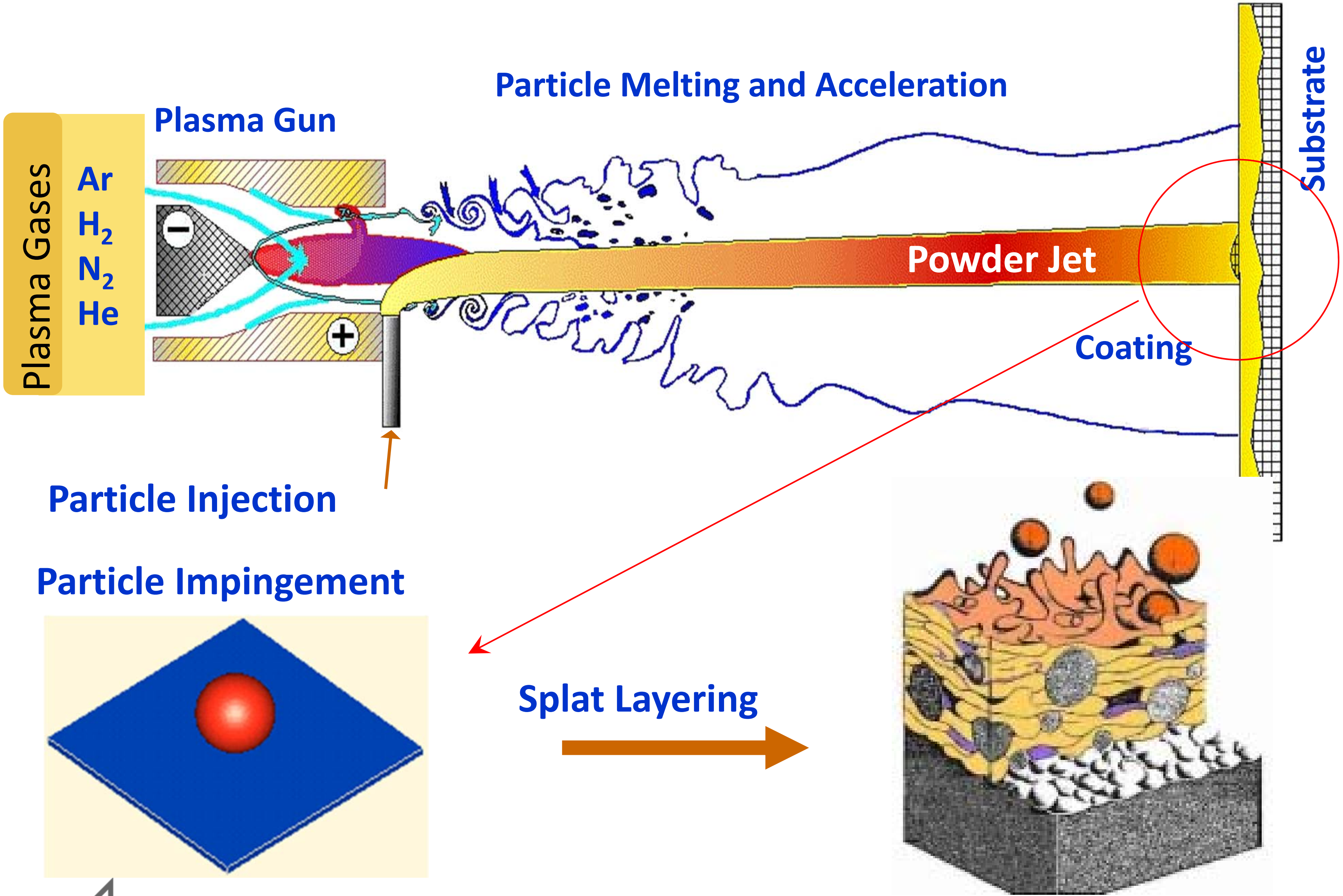
Functional Principle of DC Plasma



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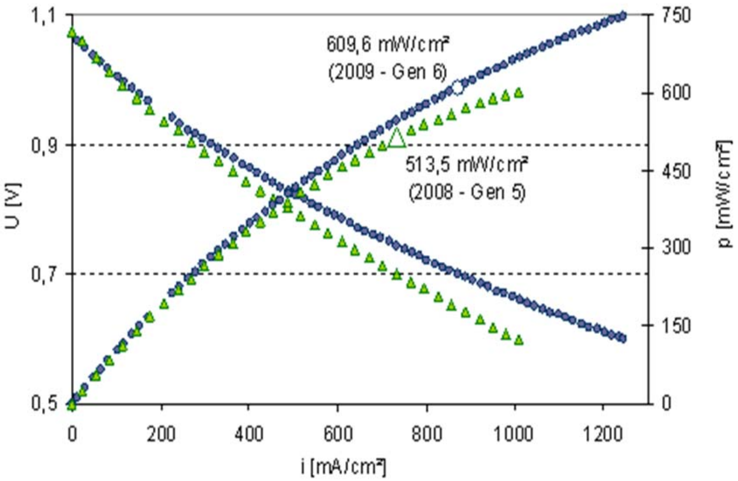
Metal Supported SOFC - Performance

MSC Cell

12.5 cm² cell at 800°C; H_2/N_2 and air

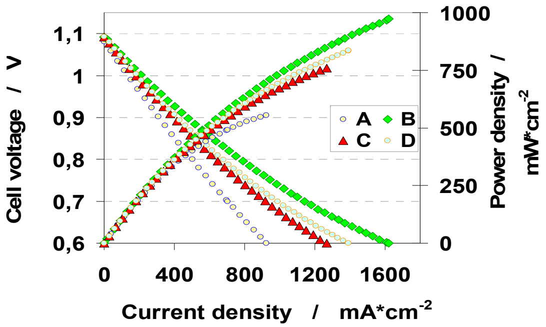


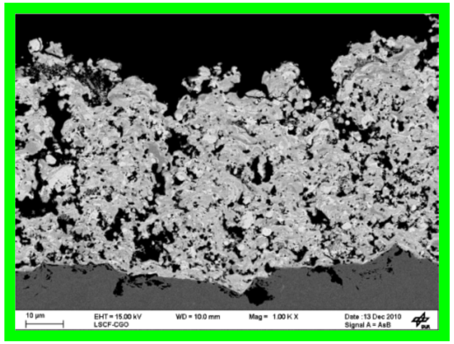
610 mW/cm² @ 0.7V (2009- G6)

MSC Cell with Suspension Plasma Spray Electrodes

Power density above 800 mW/cm² at 0.7 V

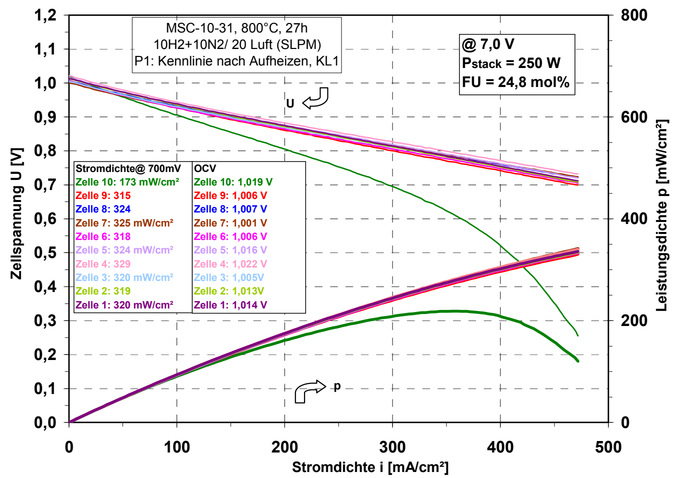
12.5 cm² cell at 800°C; H_2/N_2 and air



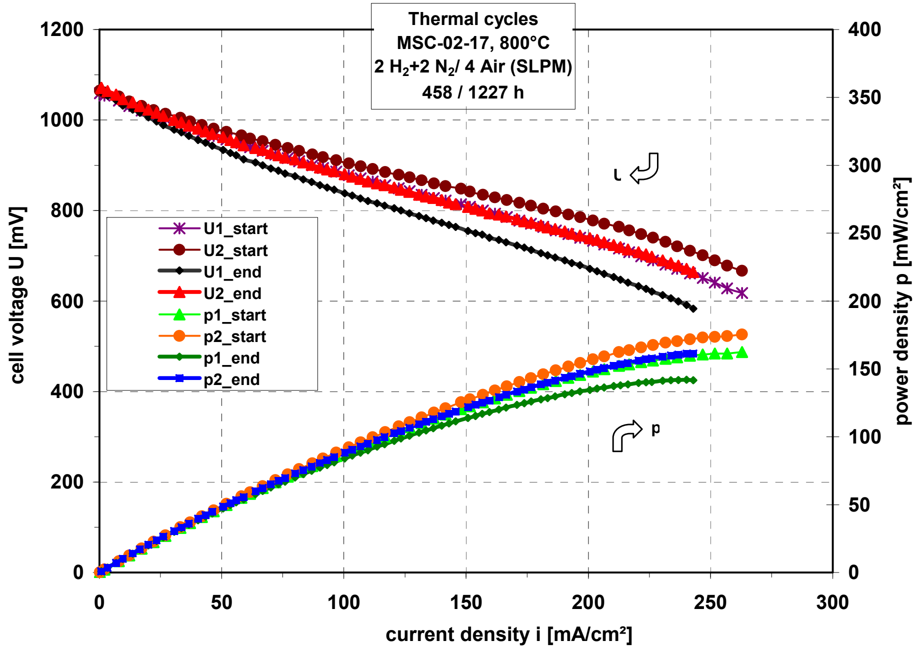


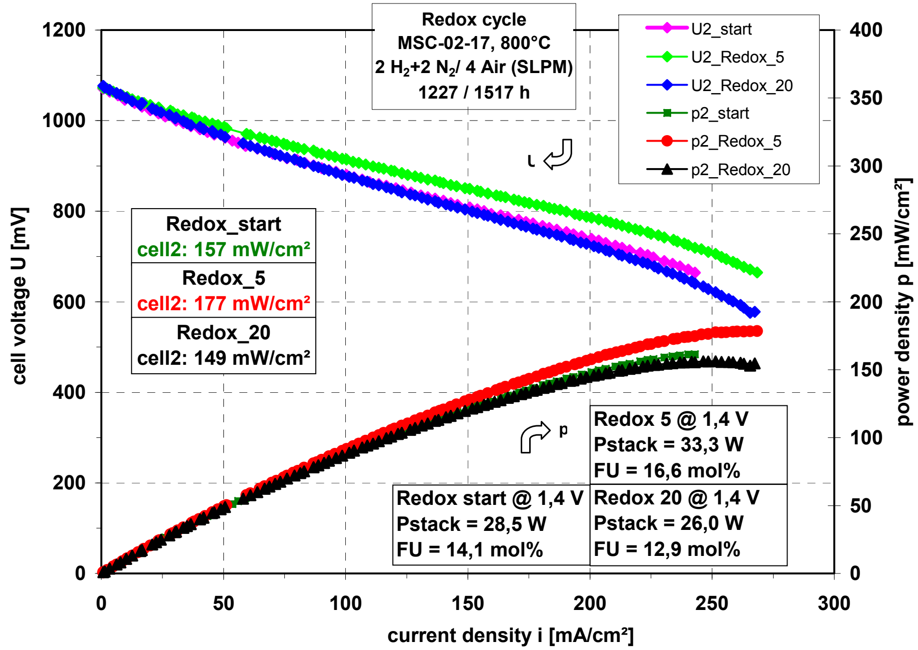
10-Cell Stack

100 cm² cells at 800°C; H_2/N_2; air



Cyclability of Metal Supported Cells





15 thermal cycles performed, 12 down to 350 °C and 3 to ambient temperature

Degradation after thermal cycles was 10.3 %

20 forced redox cycles performed with 50 ml/min O_2 on the anode side per layer

Increase of power density after 5 cycles (Improving contact Ni-YSZ?)

Degradation of the stack was 9.1 % after 20 redox cycles

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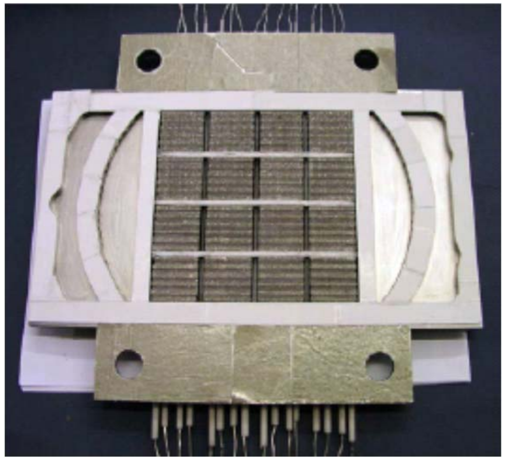
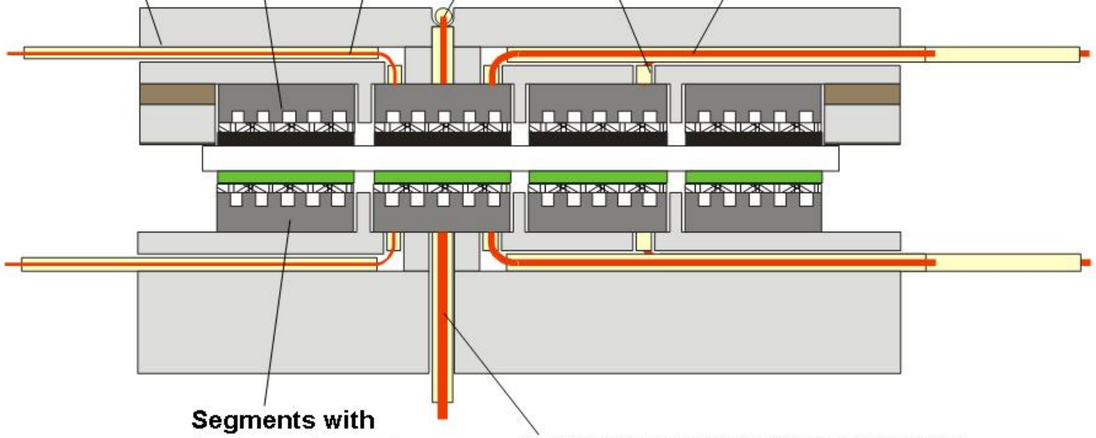
Measurement Setup for Segmented Cells





- 16 galvanically isolated segments
- Local and global i-V characteristics
- Local and global impedance measurements

Local temperature measurements

Local fuel concentrations

Flexible design: substrate-, anode-, and electrolyte-supported cells

Co- and counter-flow

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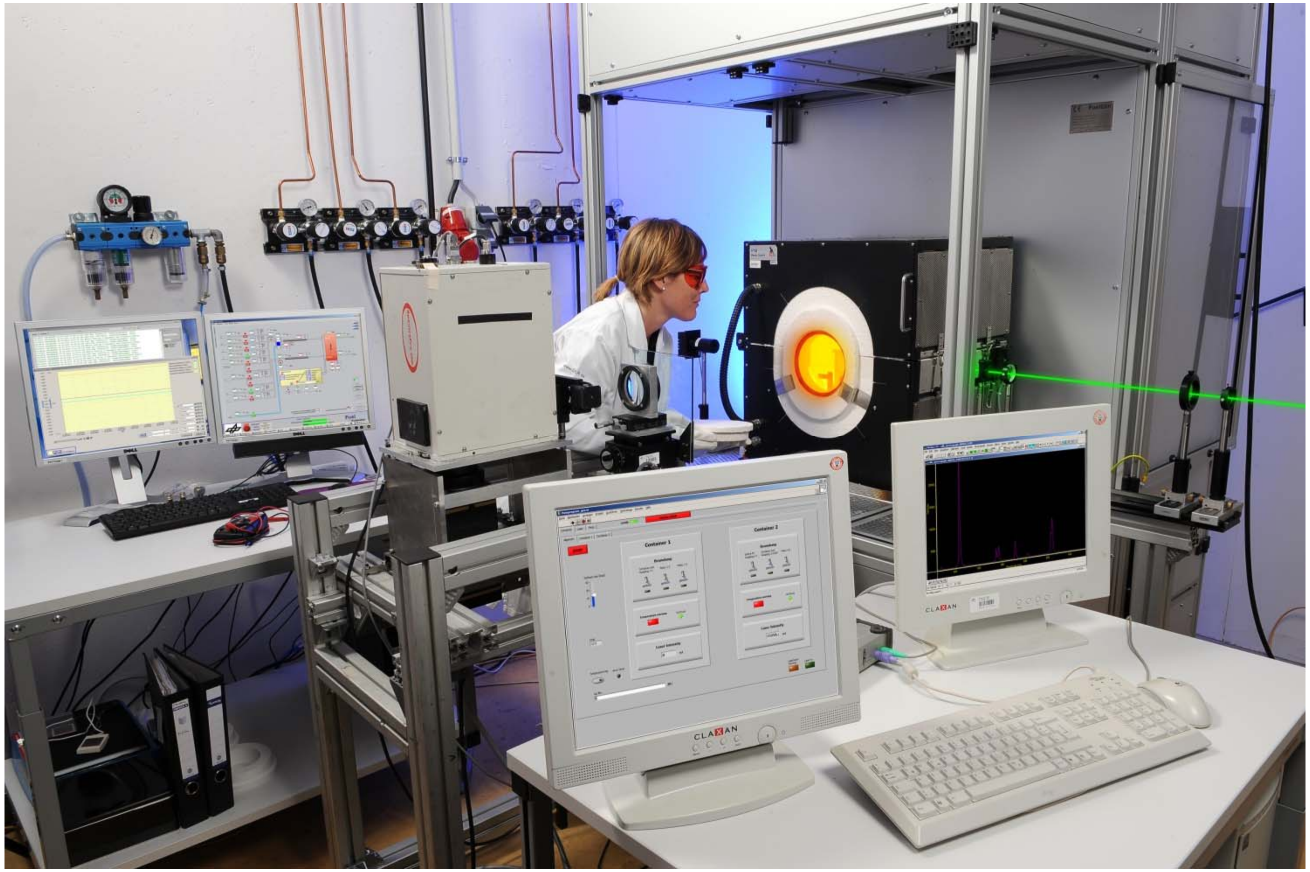
Experimental Setup for Raman Spectroscopy Measurements



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Beyond the 3rd Gen. SOFC:

Issues to be addressed for improving MSCs

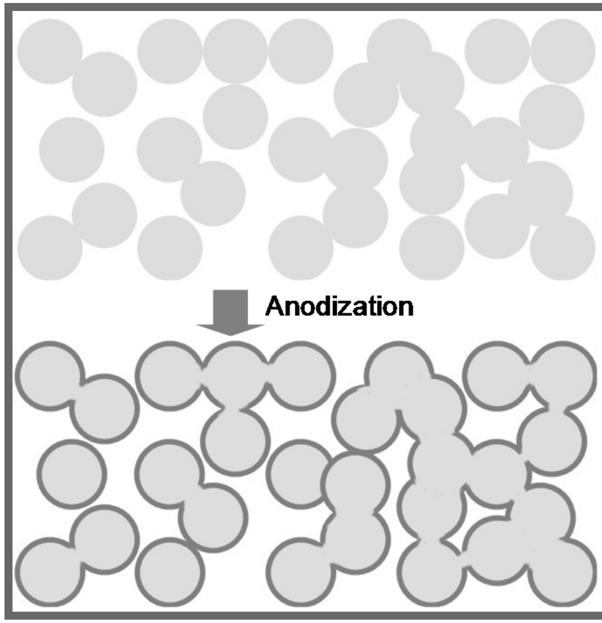
- Cr-poisoning at the cathode side > Protective coating required

- Improve tolerance toward sulfur poisoning
- Lifetime of metal substrate if stationary applications are considered
- Hermetic electrolyte

→ Which materials and architecture for the next generation SO(F)C?

Beyond the 3rd Generation SOFC

Metal substrate resistant toward oxidation



Metallic alloy foam (such as FeCrAlY), capable of forming alumina protective scale
Excellent mechanical properties, but high sensitivity to chemical reactions (high degradation)

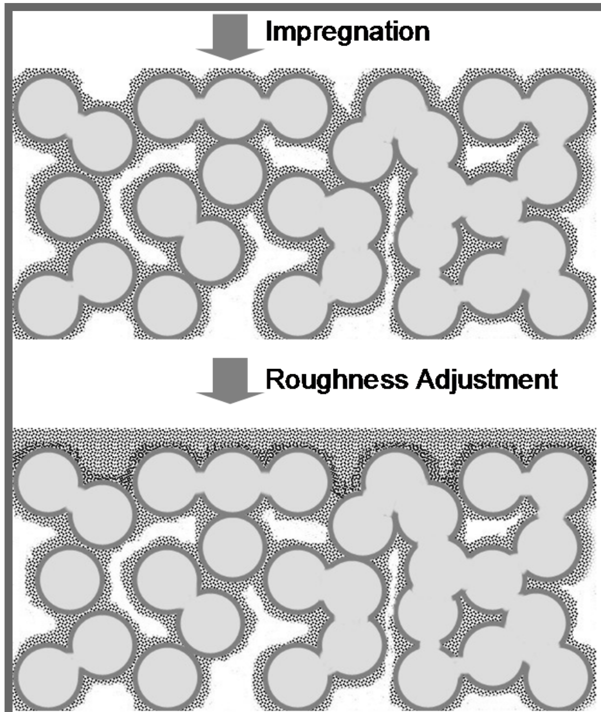
Oxidized metal alloy foam, with stable aluminum oxide scale
Excellent mechanical properties and stable oxide scale to protect against chemical reactions (low degradation), but poor or no electronic conductivity

***Formation of an Al_2O_3* layer as a durable protective coating**

Al rich alloys, on the basis of MCrAl(Y) with M being Fe, Ni, Co or a mixture

EVOLVE FUEL CELL

Nickel-free Hybrid Metal-Ceramic Supported SOFC



<u>Anode current collector - Oxidized alloy foam with impregnated conductive ceramic (LSCM or LST).</u>
Excellent mechanical properties and stable oxide scale to protect against chemical reactions (low degradation), high electronic (and ionic) conductivity

<u>Smooth current collector</u>
Low roughness surface ready for coating of functional layers of cell

Infiltration with an electronic conductor (ideally a ceramic)

Dense $La_{0.1}Sr_{0.9}TiO_3$ (800°C): sintering in H_2: $\sigma_{tot} \approx$ 150 S/cm

O. Marina et al. Solid State Ionics, 149 (2002) 21-28.
S. Hashimoto et al. Journal of Alloys and Compounds, 397 (2005) 245-249.
Y. Tsvetkova et al. Materials and Design, 30 (2009) 206-209.

Hybrid current collector mechanically and chemically stable in both oxidant and reducing atmosphere

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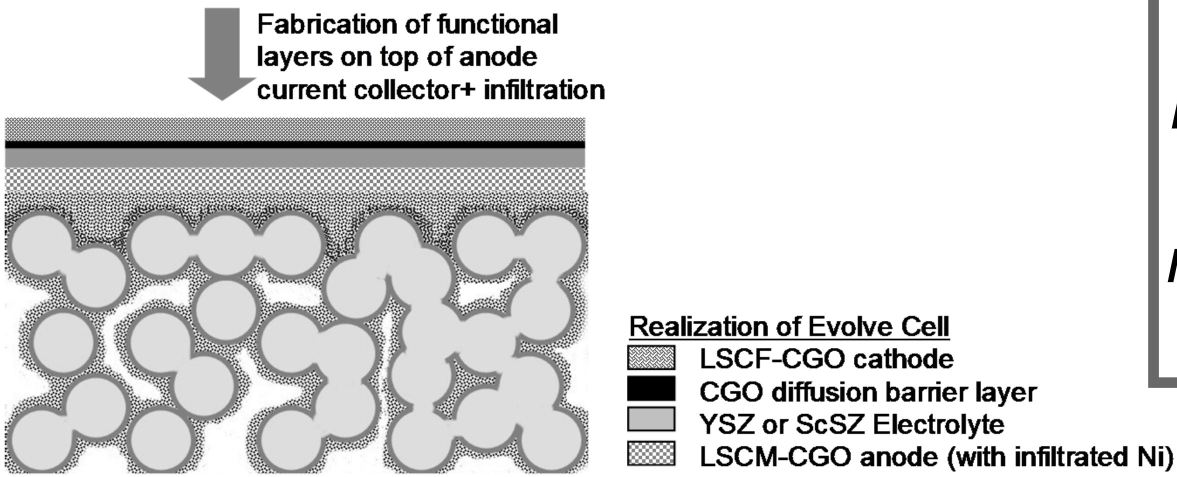
EVOLVE FUEL CELL

Beyond the 3rd Generation SOFC



Use of perovskite materials at the anode and cathode, being modified by addition of suitable catalysts

High power density, sulfur resistant, fuel flexibility, thermal cycling, redox cycling

Stationary applications …

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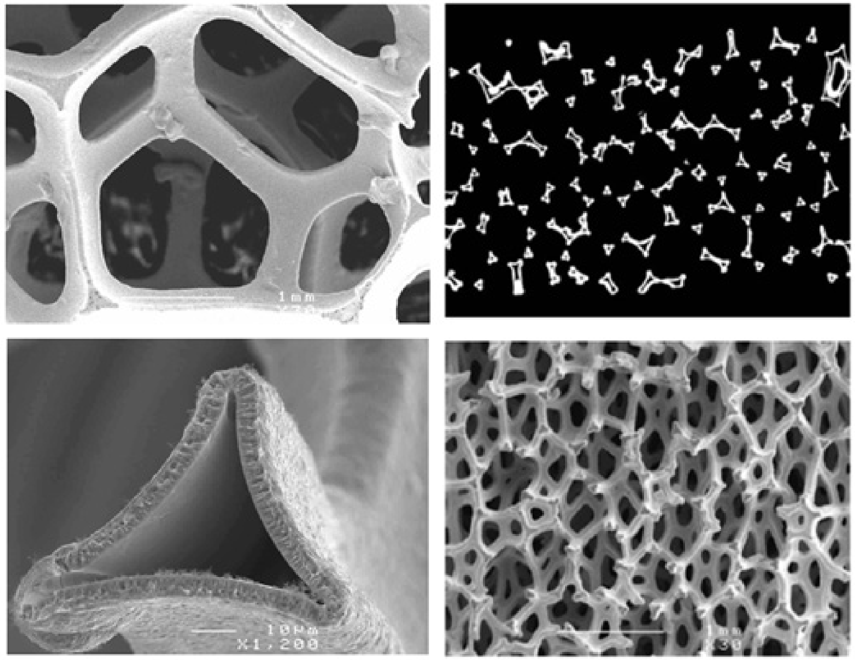
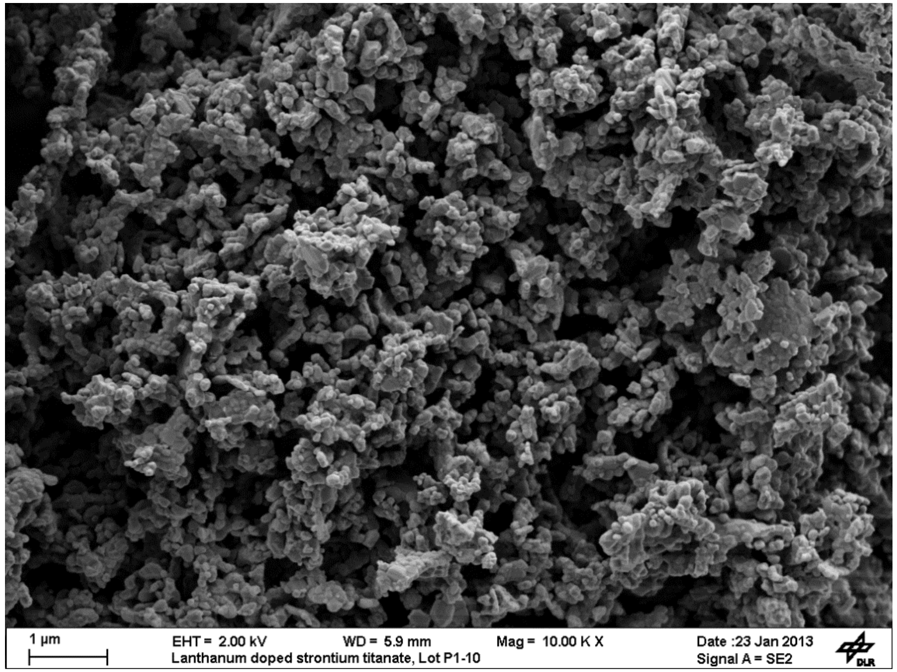
Beyond the 3rd Generation SOFC





Source: Alantum Europe GmbH

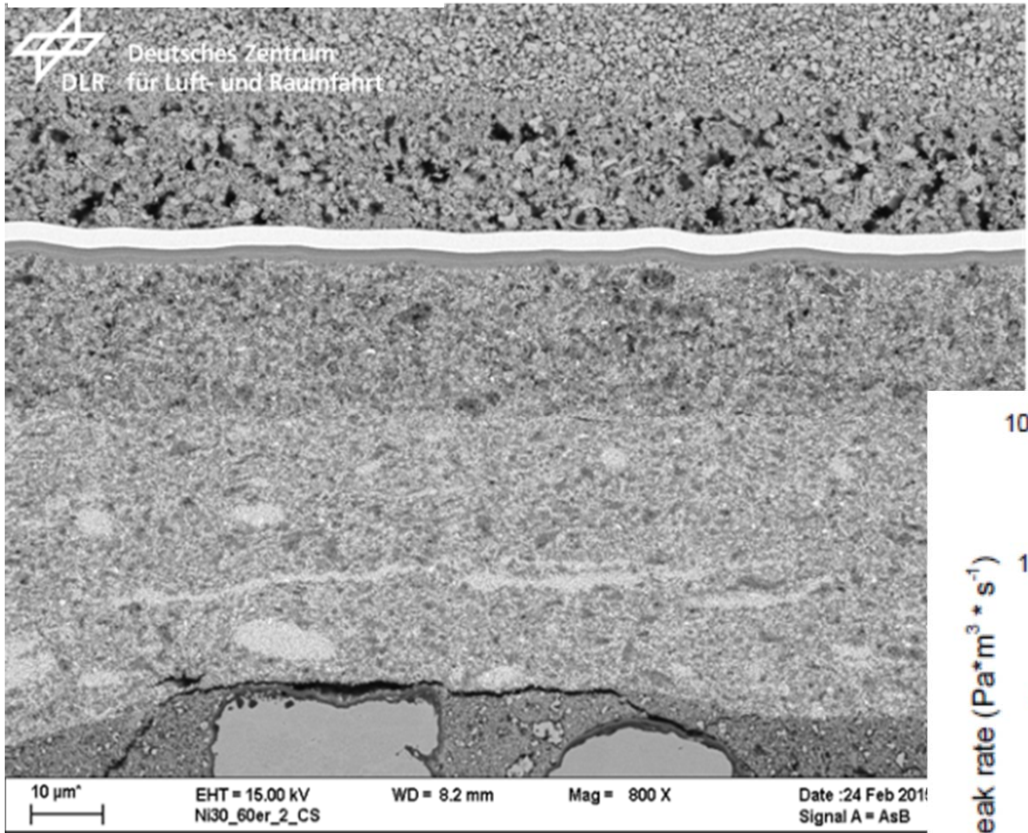
Metal Foam: NiCrAl

Composition of the anode: $Ce_{1-x}Gd_xO_{2-\alpha}$ / $La_{0,1}Sr_{0,9}TiO_{3-\alpha}$

Electrolyte: 8-YSZ / 10-GDC

Cathode : $La_{0,4}Sr_{0,6}Co_{0,2}Fe_{0,8}O_{3-\alpha}$

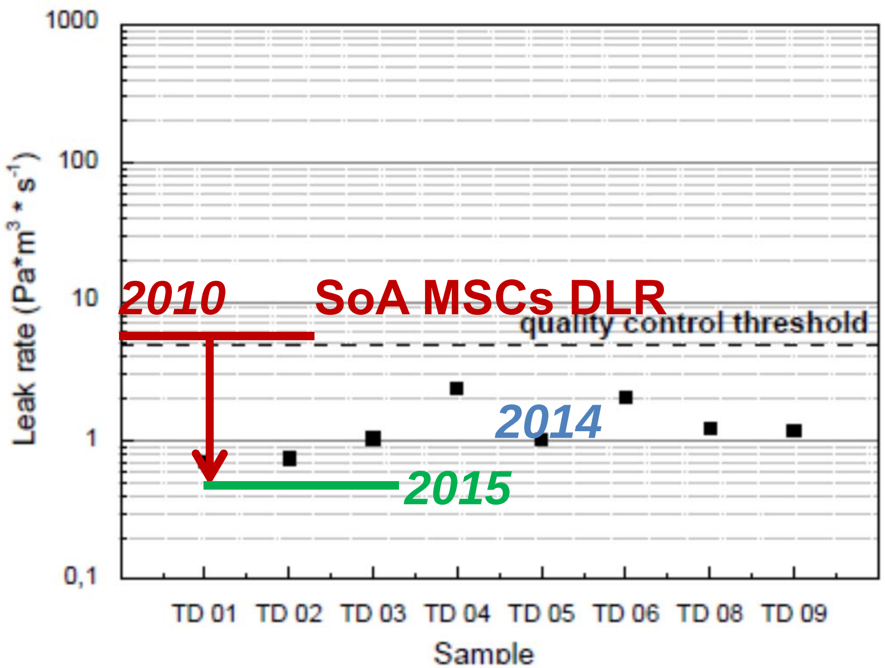
Beyond the 3rd Generation SOFC



Manufactured in air (except PVD layer)

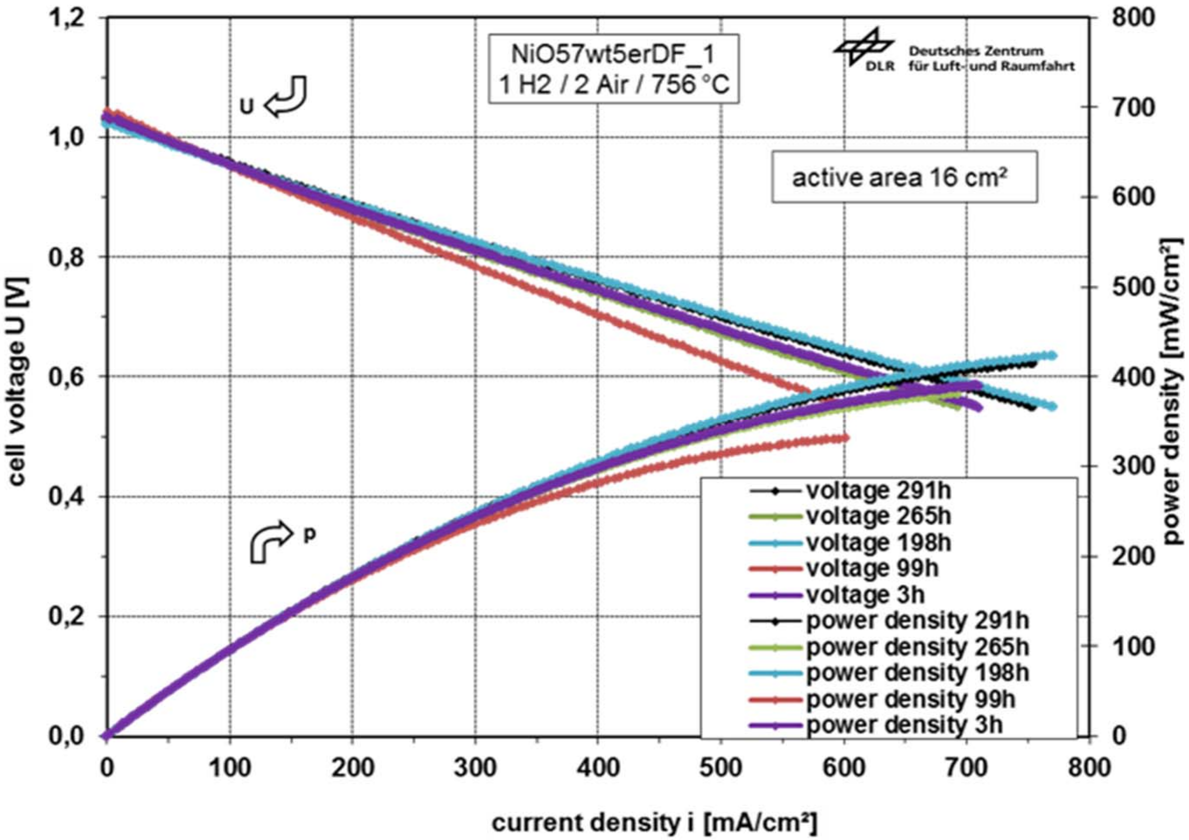
Perovskite based anode

Thin film electrolyte (1 µm YSZ+ 2 µm CGO) with improved hermiticity (in collaboration with Ceraco GmbH)



EVOLVE FUEL CELL

Beyond the 3rd Generation SOFC



50 mm x 50 mm with active surface 16 cm²

P @ 0.7V and 750°C

- ***340 mW /cm²***
- ***Redox cycles tested: 10***

- ***But… with addition of Nickel!!!***
  AFL: LST-CGO 50:50 modified with 5 wt% Nickel
  Current collector: NiCrAl + LST 50vol% - Ni 50vol%

- ***Issue with sulfur poisoning still expected***

Replacement of Nickel still remains challenging!

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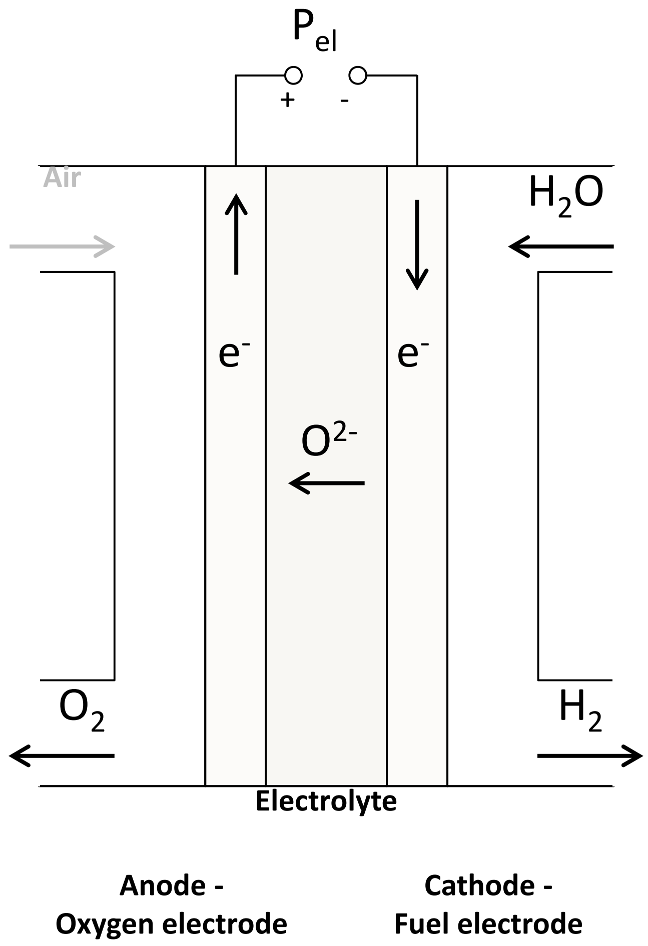
Solid Oxide Electrolysis

Advantages:

- High temperature (600 - 900°C)
  - Fast reaction kinetics
  - Low overvoltage
  - High efficiency & high current densities
- No noble metals as catalysts
- Fuel versatility: CO_2 electrolysis
  - → Co-electrolysis of H_2O/CO_2 possible
  - → Syn-gas production
  - → External (or internal) hydrocarbon formation



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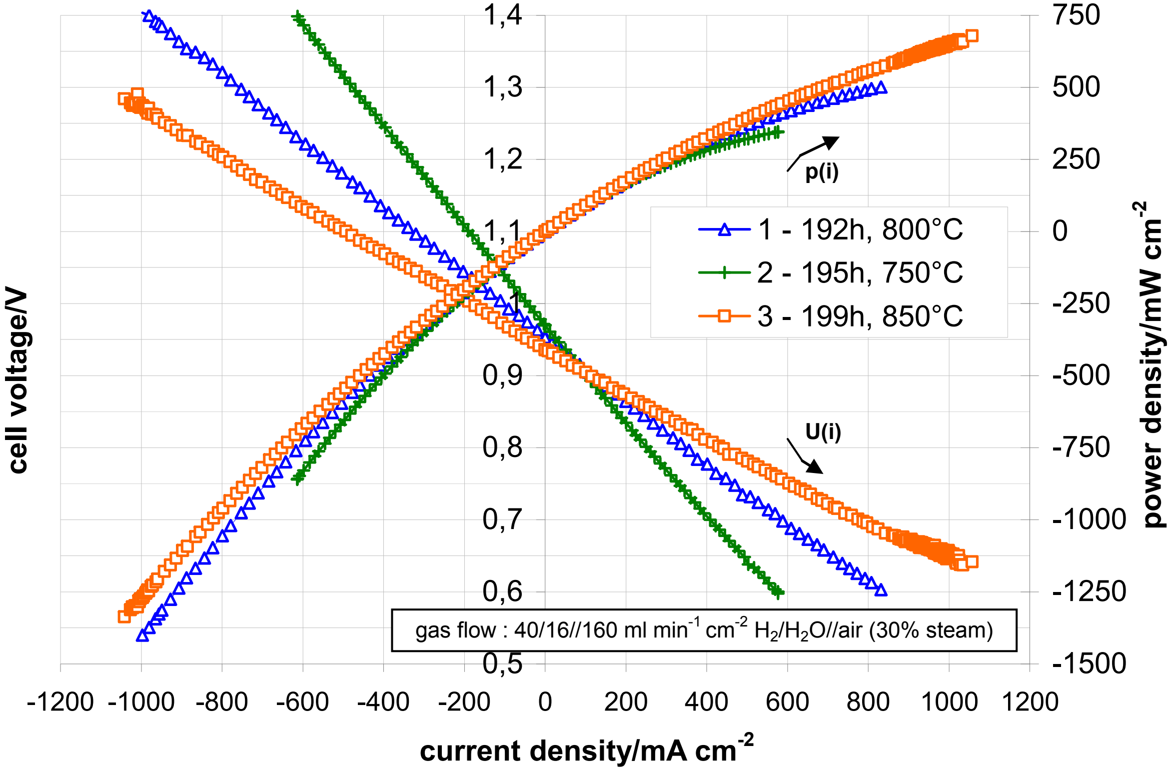
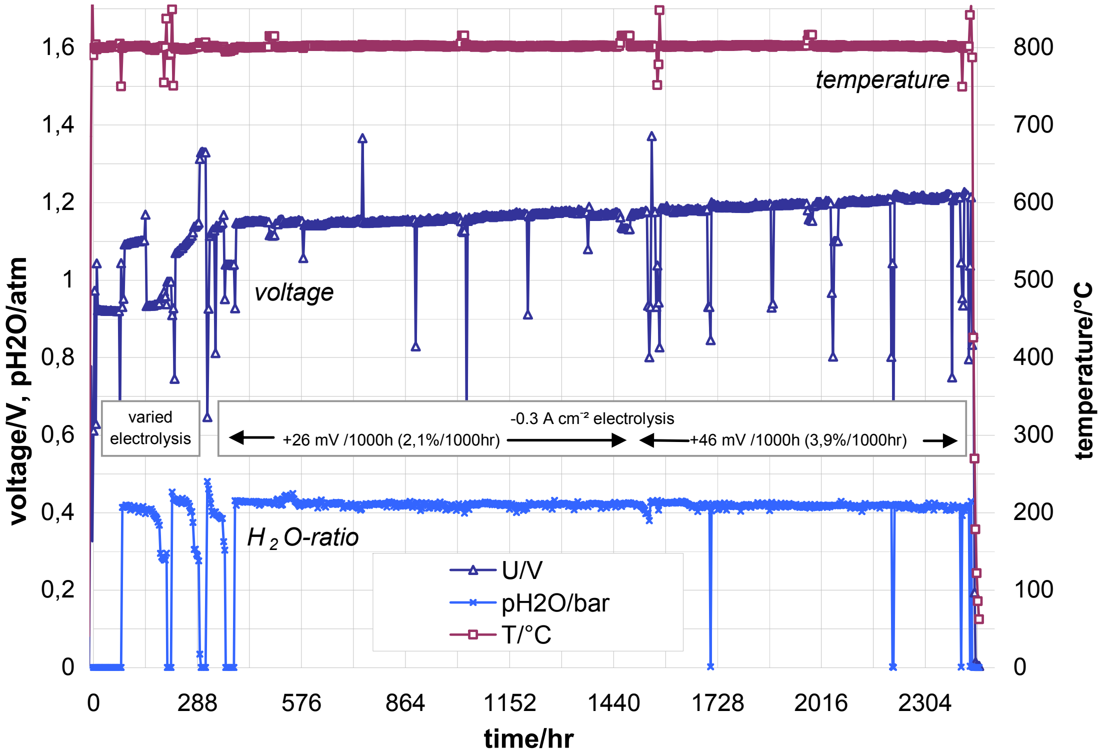
Hi2H2: I-V Curves of a VPS Cell in SOFC and SOEC Mode as a Function of Temperature



Hi2H2: Complete Test Run of a VPS Cell in Electrolysis Mode



Lit: G.Schiller et al., J. Appl. Electrochem., 39, 293-301, 2009

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Challenges in SOEC technology

- Improvement of performance and particularly durability (reduced degradation) by
  - Development of improved materials (cathodes and anodes) for steam electrolysis
  - Study of degradation behaviour and elaboration of mitigation strategies
- Integration of high-temperature heat (solar heat, waste heat from industrial processes)
- Development of operation strategies with use of integrated heat (heat management)
- Development of co-electrolysis process (steam + CO_2) for production of synthetic fuels
  - Development of cells for co-electrolysis operation
  - Development of electrocatalysts for synthesis of liquid and gaseous fuels
  - Operation at elevated pressure conditions > 10 bar
  - Development of system concepts and demonstration of functionality
- Efficient operation in bi-functional mode

Development work at DLR in the frame of internal project („Future Fuels“) and in POF III phase of Helmholtz Association (HGF) with a transportable research platform („e-Xplore“)

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Motivation and Objective of Systematic Degradation Study

<u>Problem: low longevity – degradation</u>

A variety of long-term degradation data

→ about 3-5% / 1000h at 800°C and 80% absolute humidity (AH)

→ about 35% / a

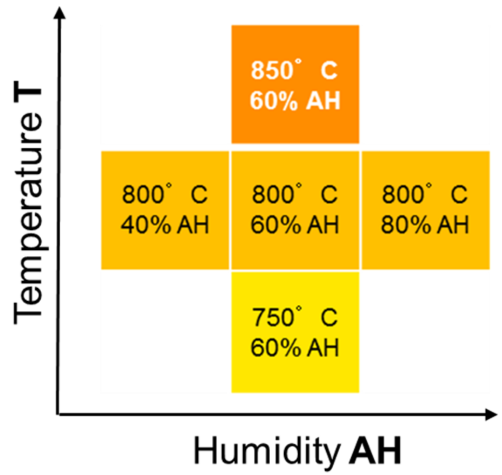
Different studies hard to compare!

Systematic parameter study of:

→ Temperature T

→ Humidity AH

→ Current density i



Test setup – quadruple cell measurement

→ Four different current densities simultaneously

→ Identical temperature, gas supply (and also incidents)

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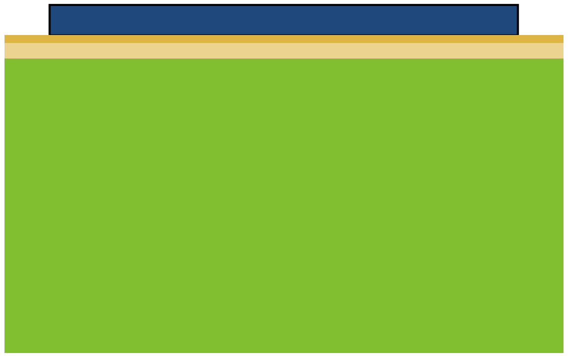
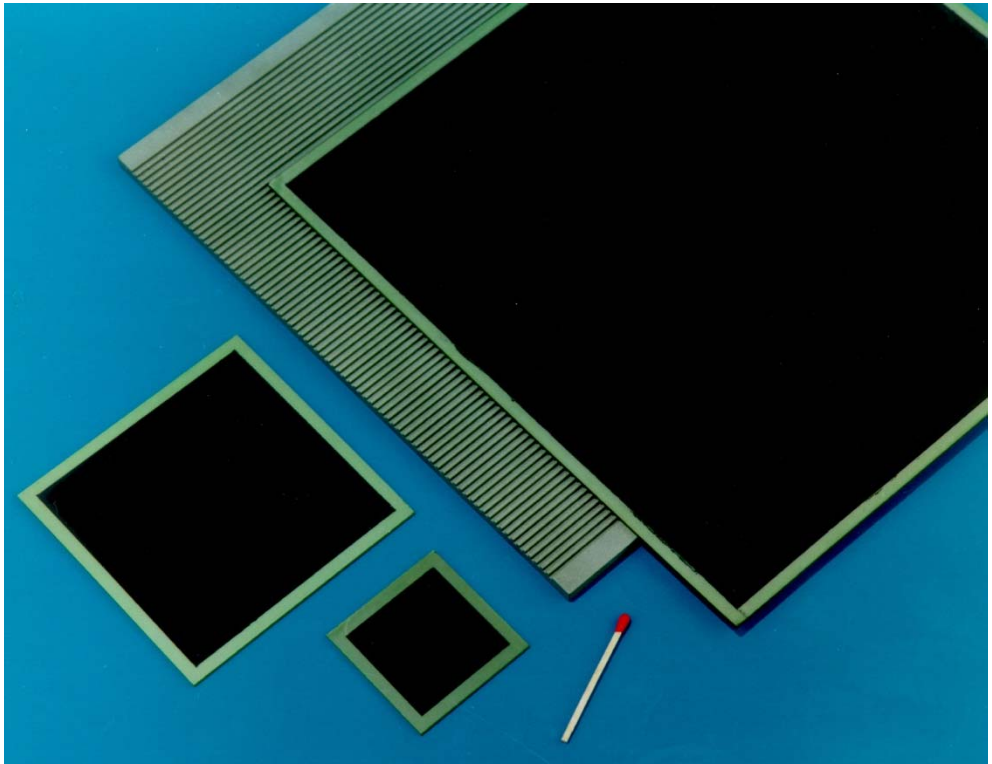
Solid Oxide Fuel Cells: Planar Design

	Materials
Cathode:	$(La,Sr)(Fe,Co)O_3$
Diffusion barrier:	CGO – 1-5 µm
Electrolyte:	8YSZ – 5-10 µm
Anode:	Ni/YSZ
Anode Substrate:	Ni/YSZ
Interconnect:	ferritic steel





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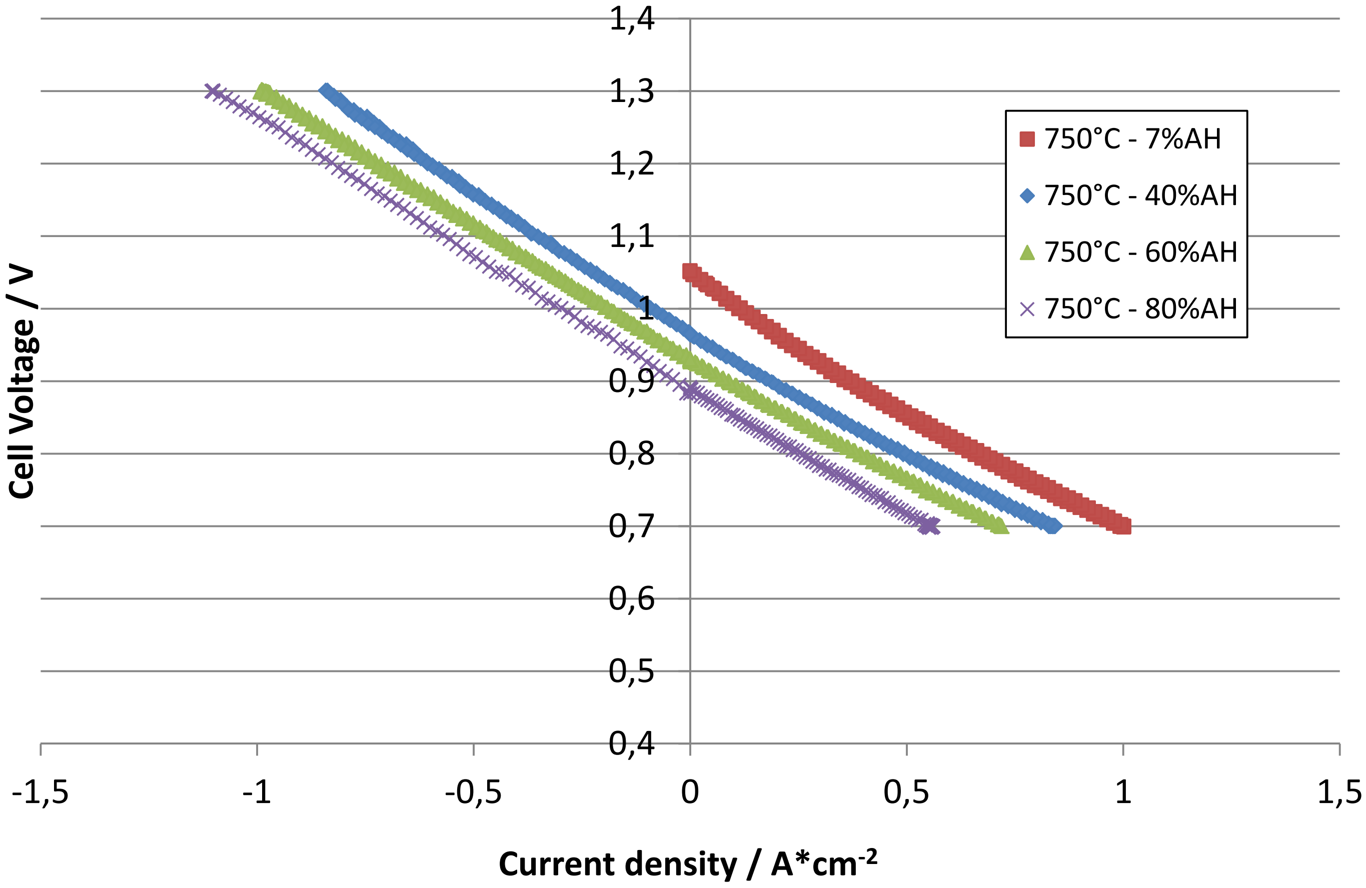
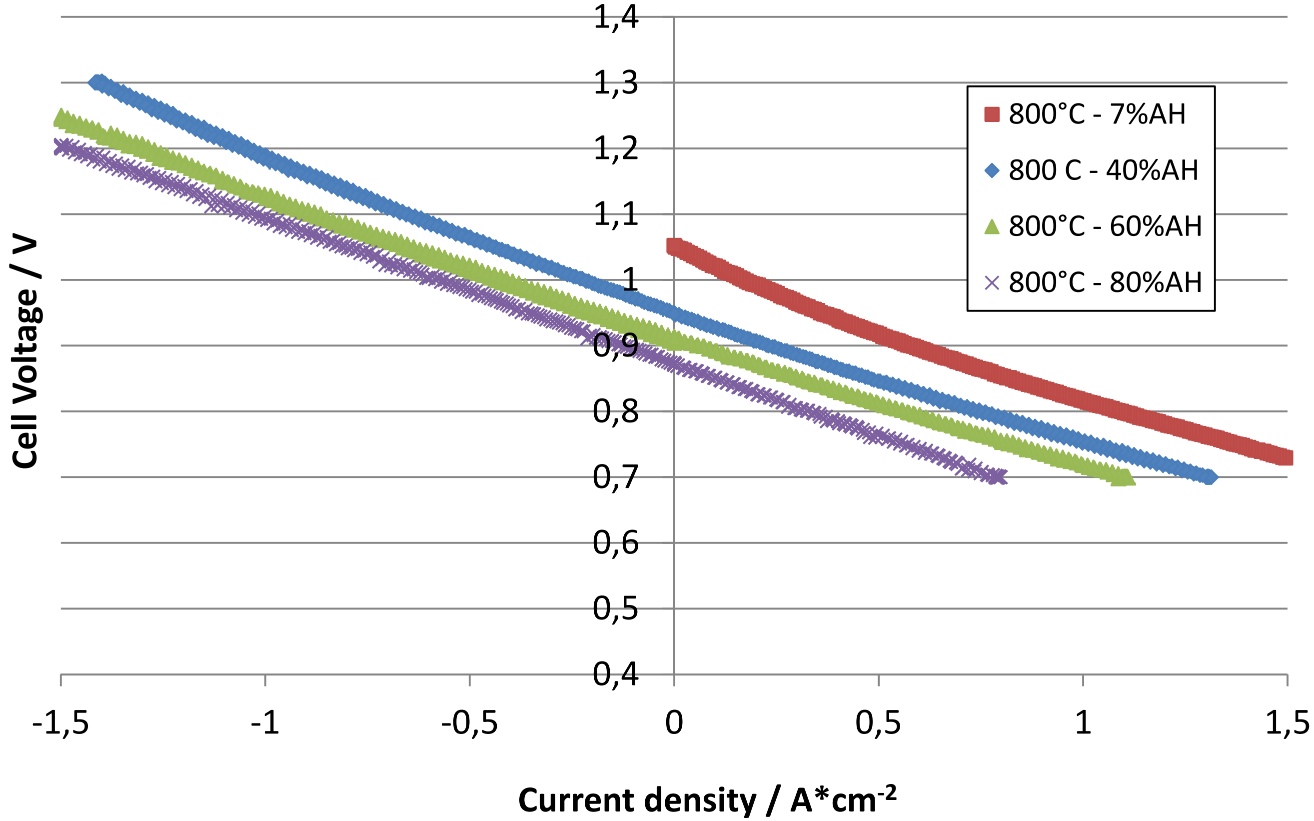
I-V Curves at 750 °C as a Function of Steam Content

(Flow rates: 2 l/min H_2/H_2O, 3 l/min air)

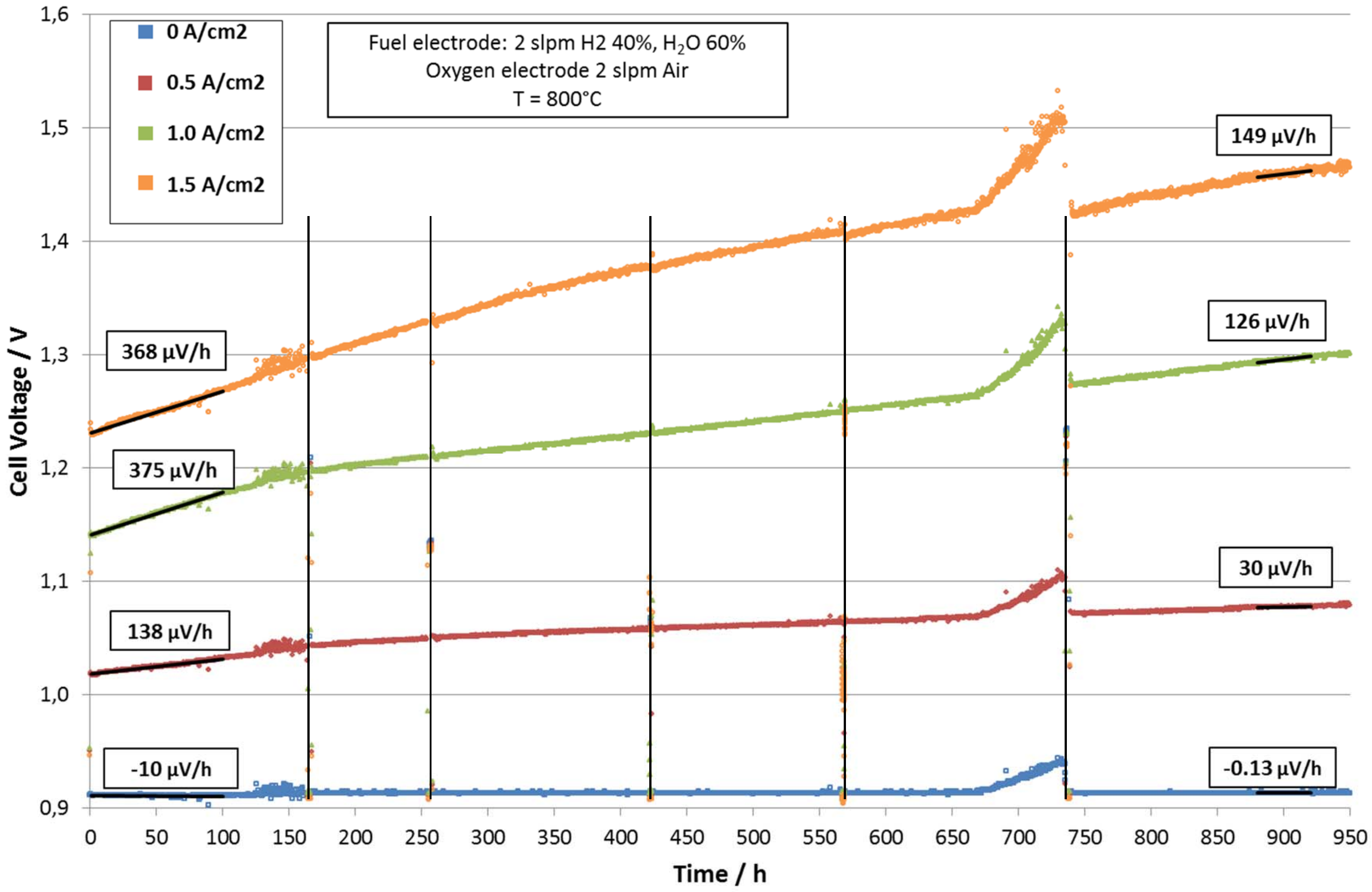


I-V Curves at 800 °C as a Function of Steam Content

(Flow rates: 2 l/min H_2/H_2O, 3 l/min air)



Degradation Measurements



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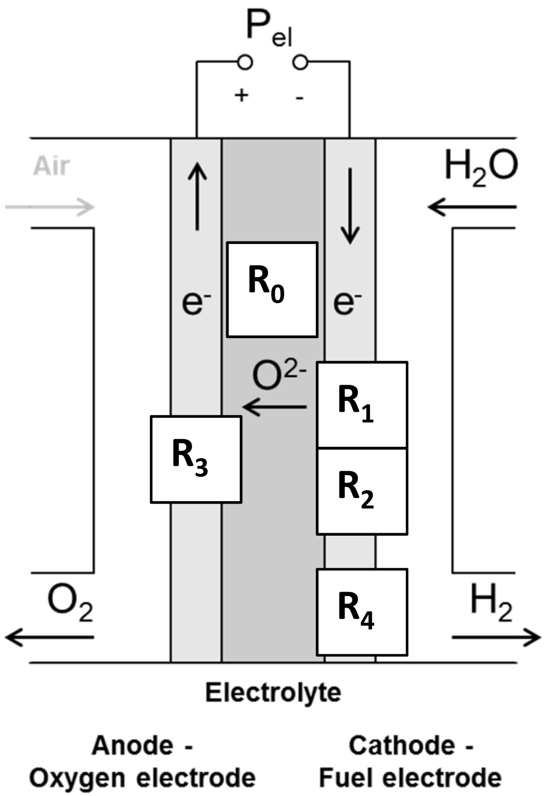
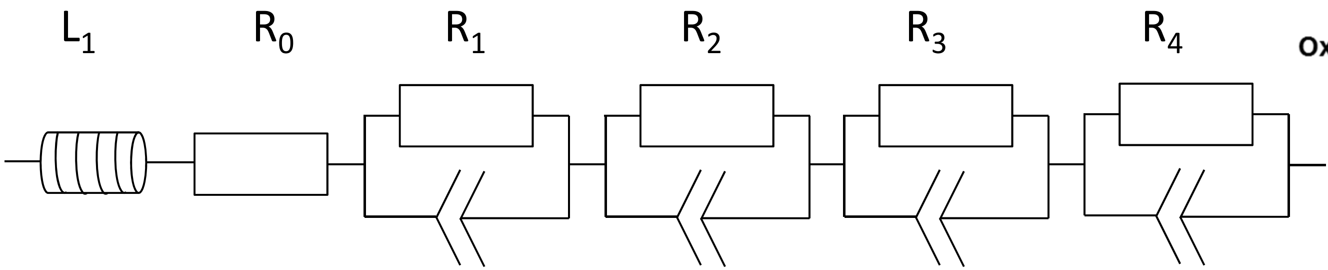
Degradation Measurements

Impedance analysis – equivalent circuit

High freq. (10^5 Hz) ⟶ Low freq. (0.5 Hz)

- L_1: High frequency interference (~ 10^5 Hz)
- R_0: Ohmic resistance (~ 10^5 Hz)
- R_1: Fuel electrode process A (~ 10^4 Hz)
- R_2: Fuel electrode process B (~ 10^3 - 10^4 Hz)
- R_3: Oxygen electrode process (~ 10^2 Hz)
- R_4: Fuel electrode mass transport (~ 10^1 Hz)





A. Leonide, V. Sonn, A. Weber, and E. Ivers-Tiffée
Journal of The Electrochemical Society, 155 (1) B36-B41 (2008)

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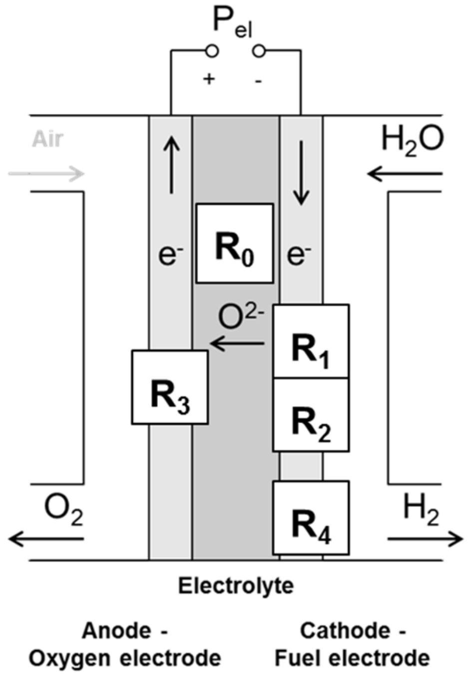
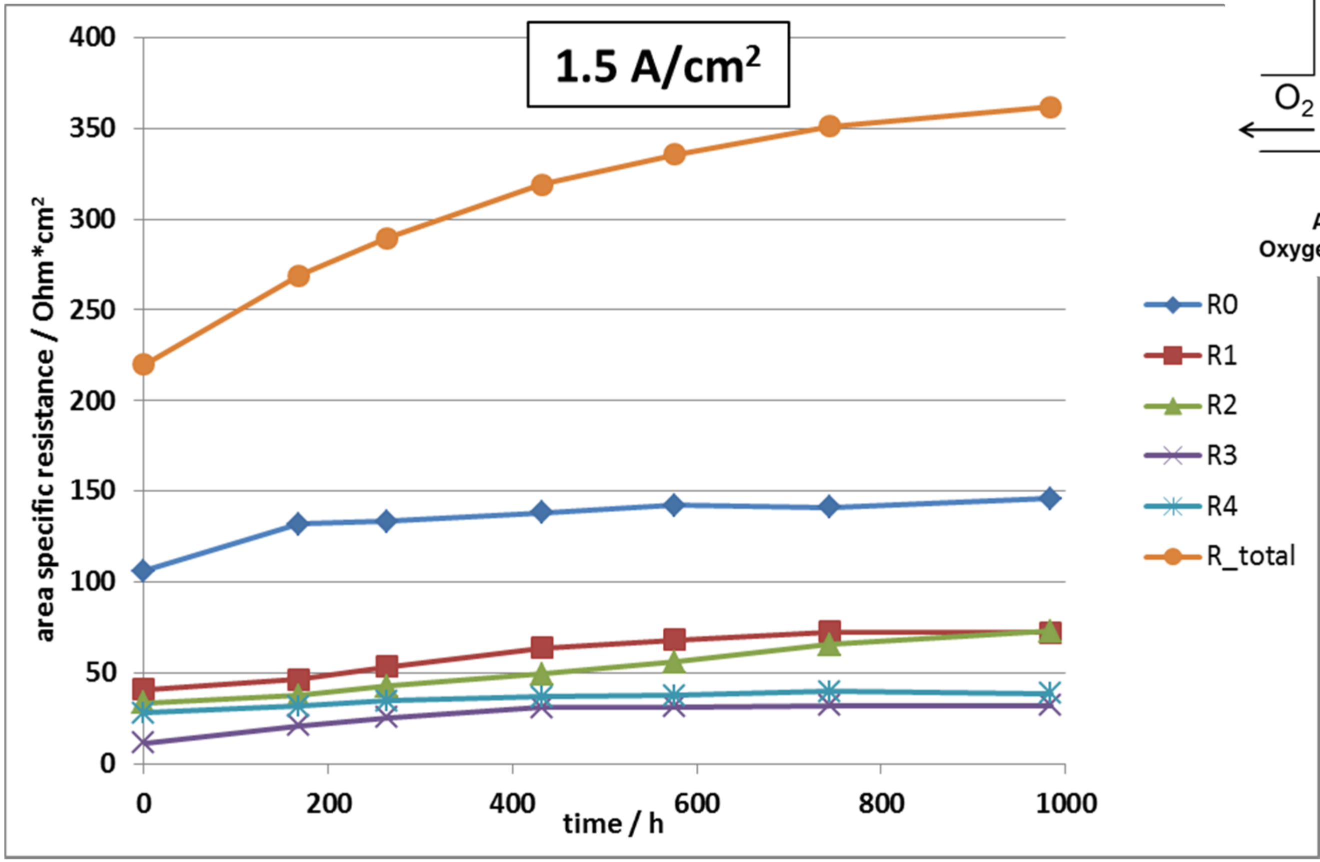
Degradation Measurements

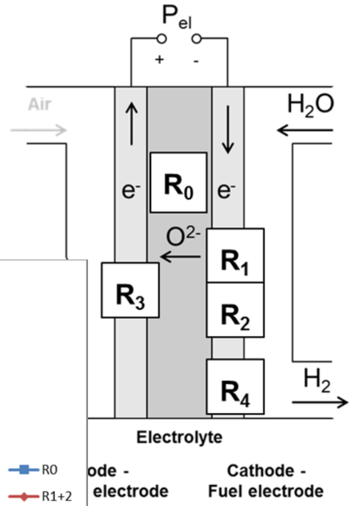


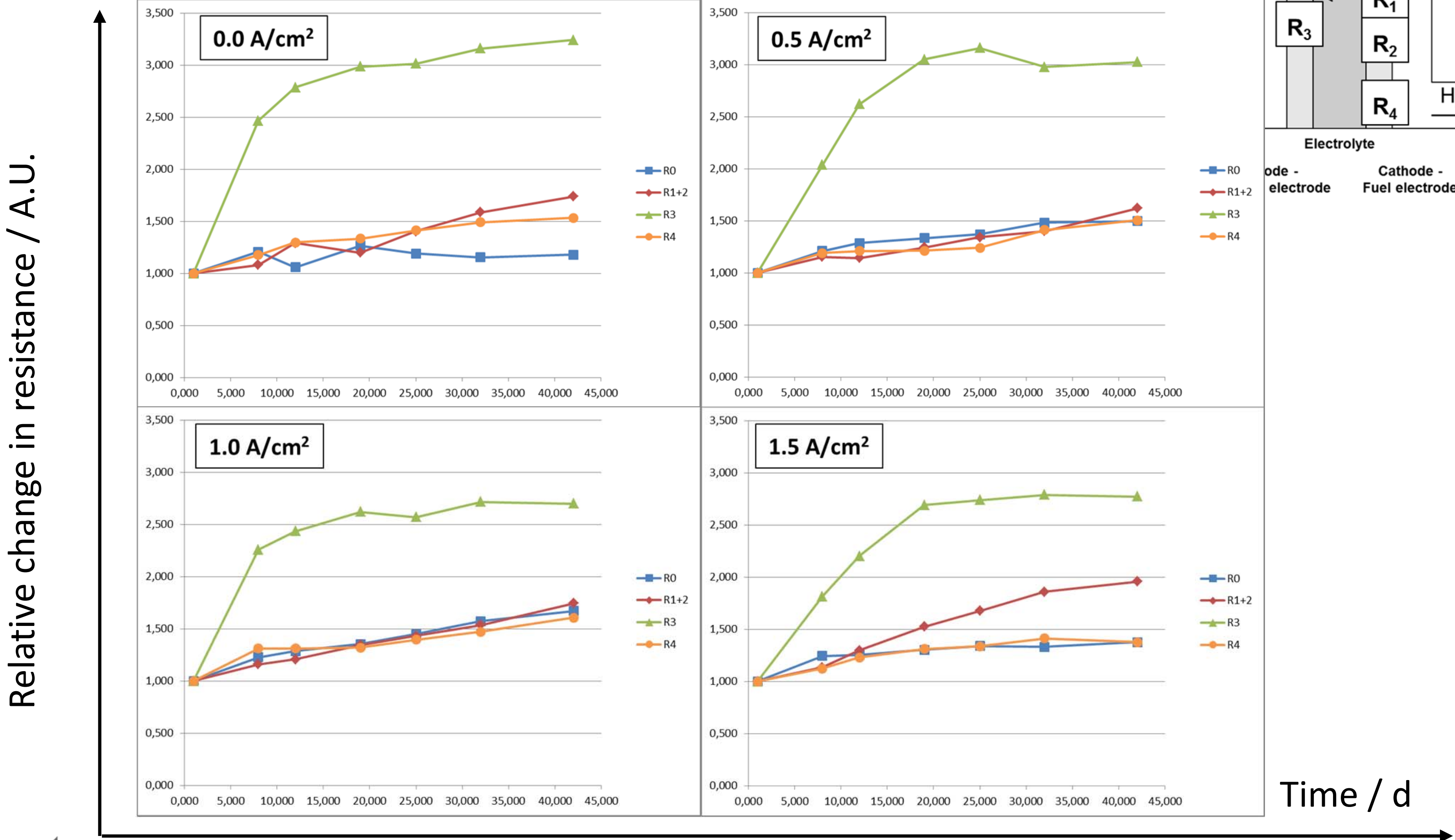
Change of each resistive process with time



Bias: 0.5 A/cm^2

Degradation Measurements





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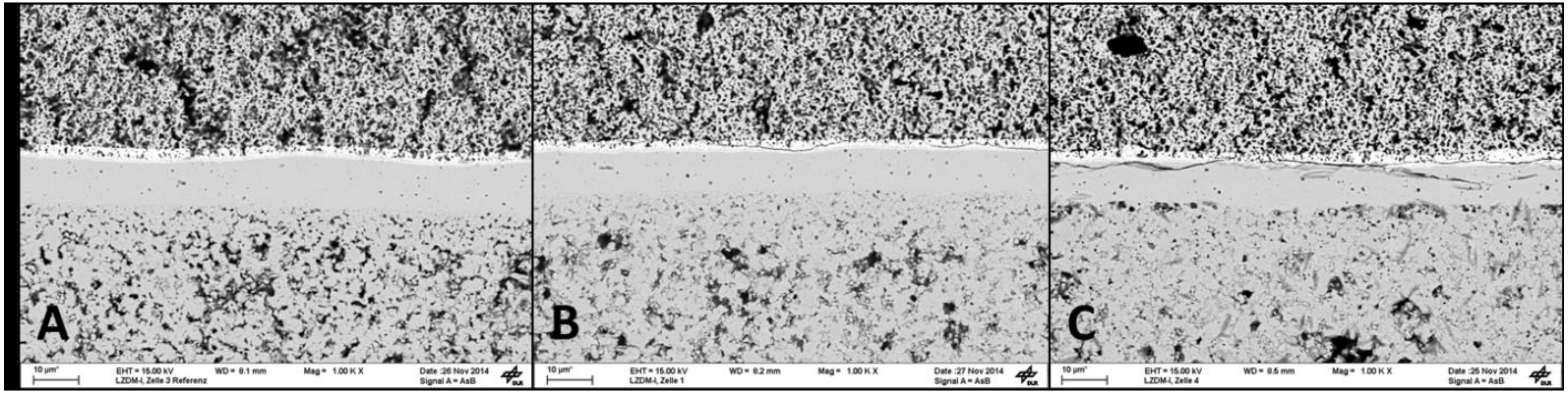
Post mortem Analysis (SEM)

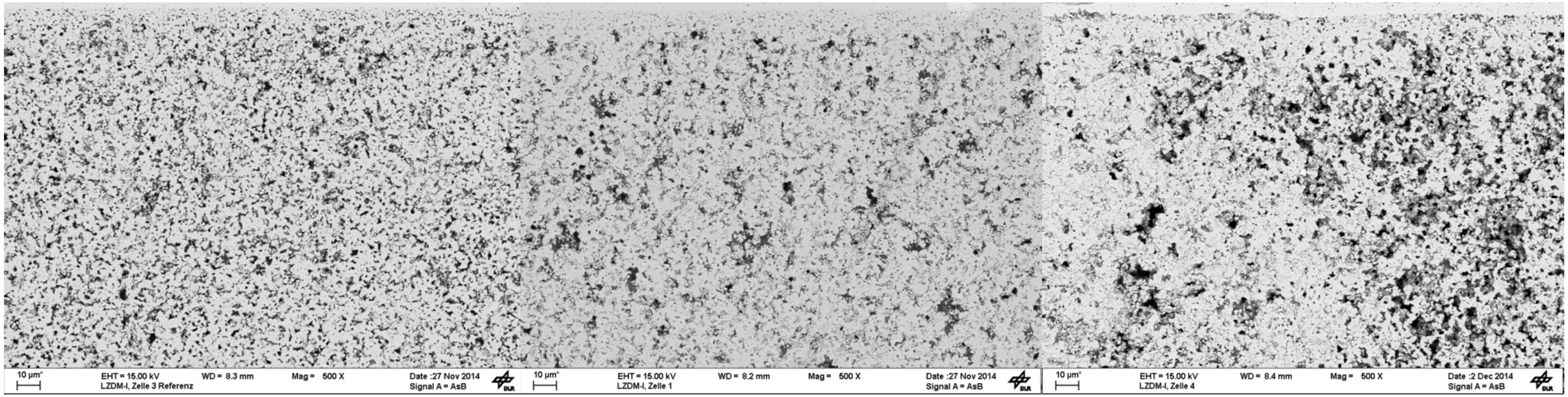


Solely reduced | 1000 h @ OCV | 1000 h @ 1.5 A/cm^2

Ohmic resistance:

- Weakening of YSZ|CGO|LSCF interface
- Visible cracks probably formed during sample preparation along weakened microstructure

Post mortem Analysis (SEM)

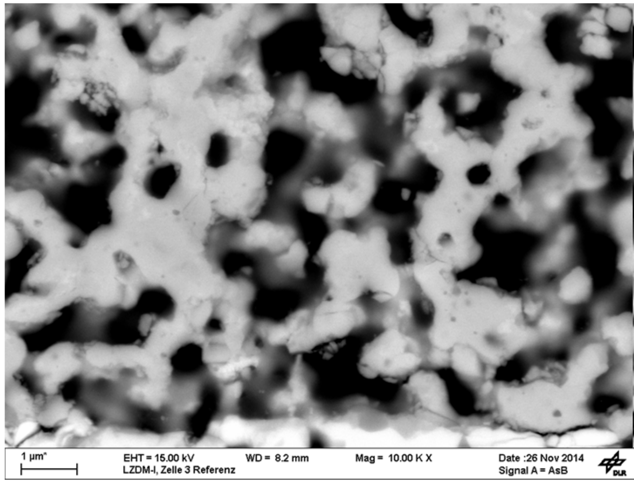


Solely reduced | 1000 h @ OCV | 1000 h @ 1.5 A/cm^2

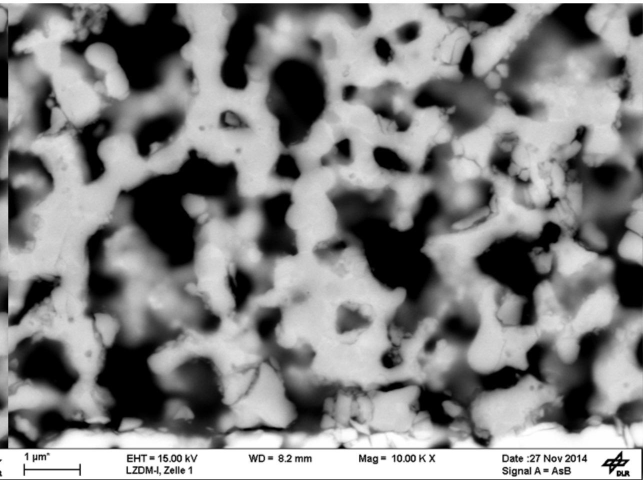
Fuel electrode:

- Change in microstructure
- Likely due to Ni-coarsening
- → decrease TPB
- Decreased percolation ?

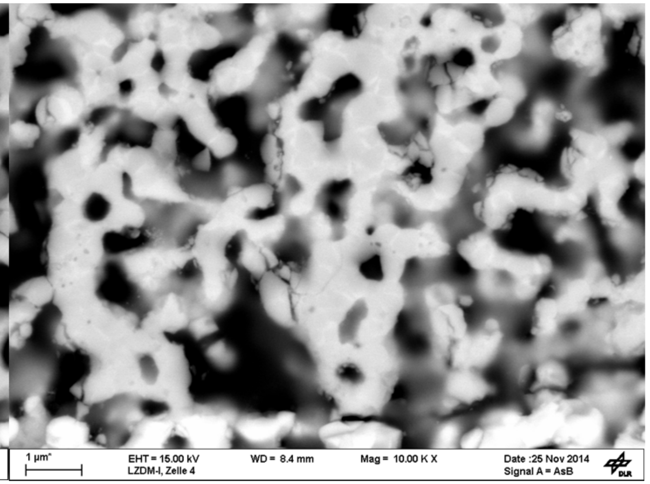
Post mortem Analysis (SEM)



Solely reduced



1000 h @ OCV



1000 h @ 1.5 A/cm^2

Oxygen electrode:

- No obvious change in microstructure
- Appearance of brittleness
- Degradation due to change in perovskite stoichiometry close to surface
  → Sr-rich surface layer?
- Difficult to measure surface sensitively with high focus XPS

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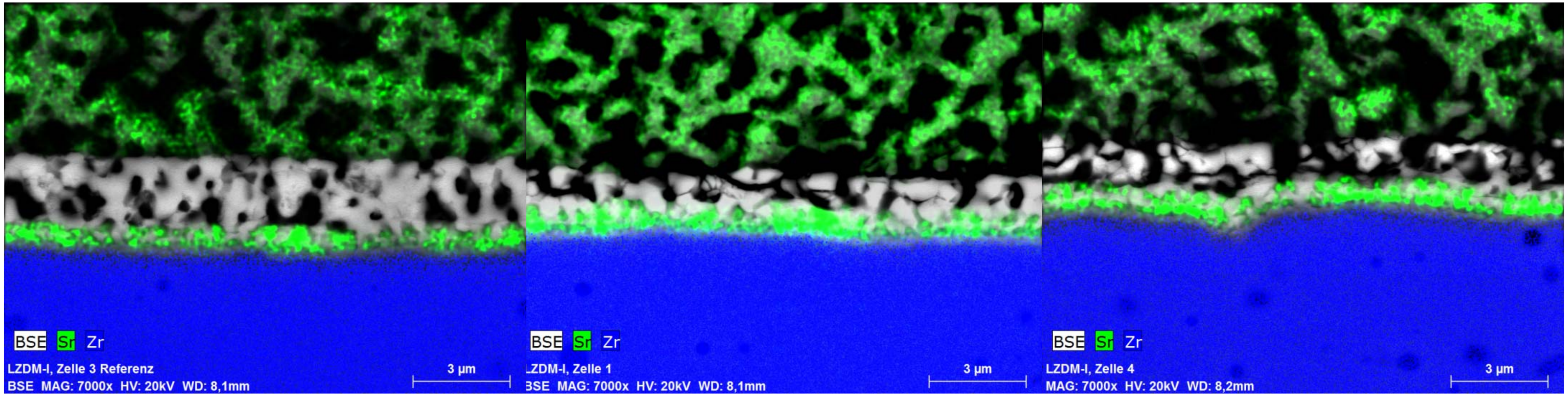
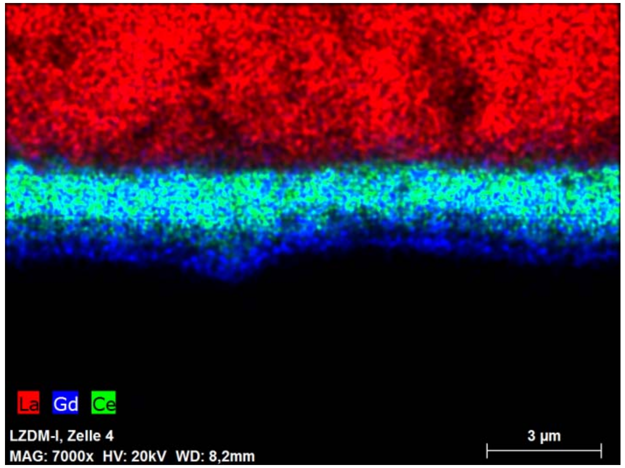
Post mortem Analysis (SEM)



Solely reduced | 1000 h @ OCV | 1000 h @ 1.5 A/cm^2

Diffusion barrier layer:

- No reaction between Sr and Zr (or generally LSFC with YSZ)
- General Sr-enrichment at CGO|YSZ interface
- Ce depletion at CGO|YSZ interface



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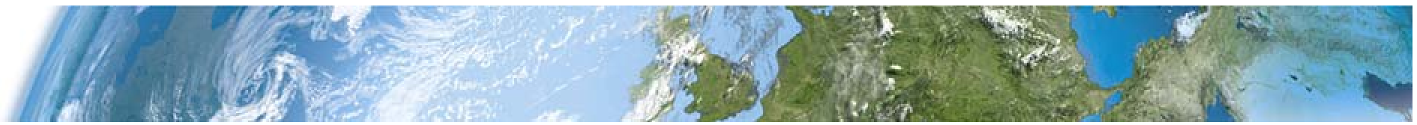
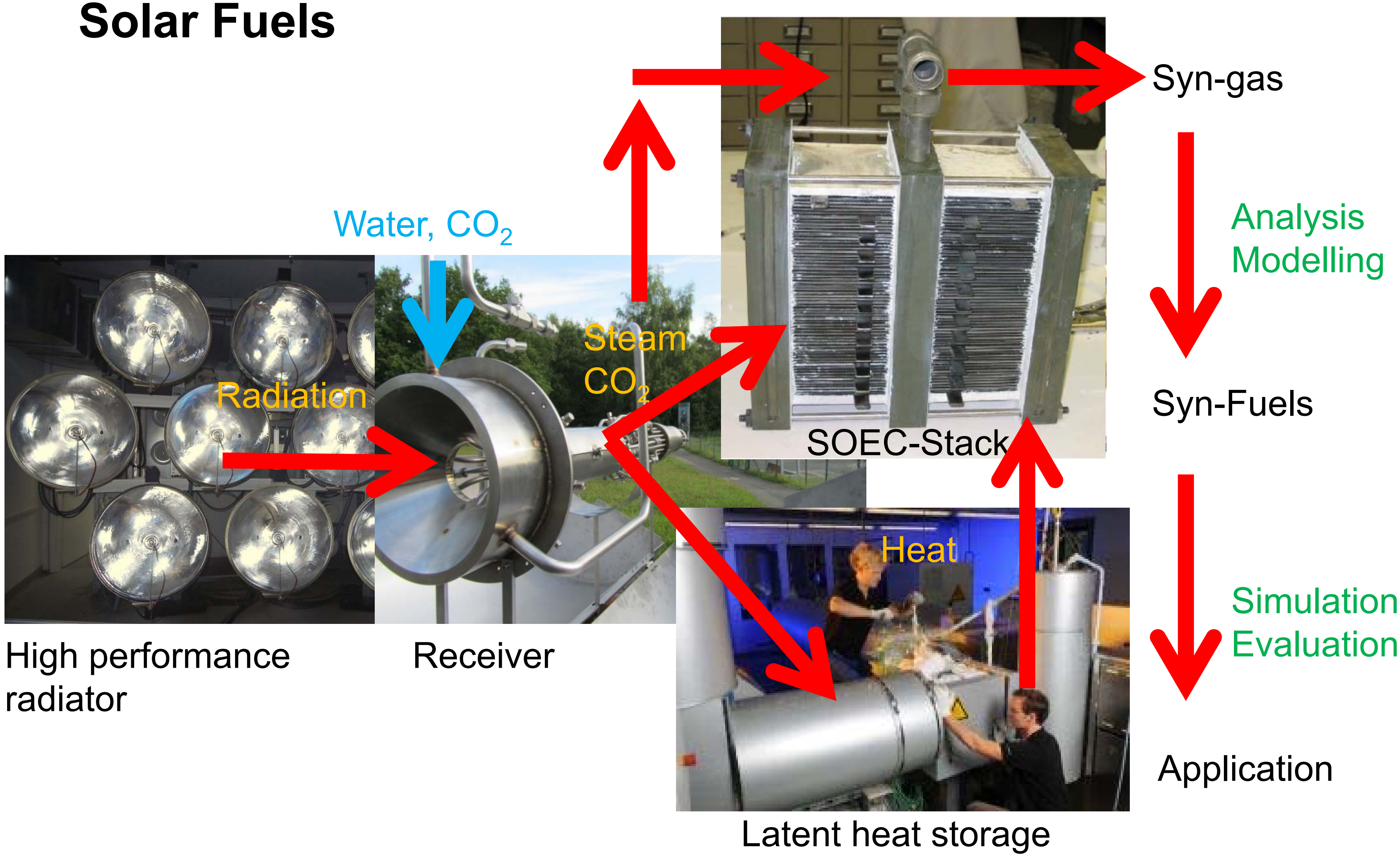
Future Fuels: TP 3 Solar Fuels

DLR Internal Project: SF, TT, VT, AT

- **Objective:**
  - Production of synthetic liquid hydrocarbons through solarthermal and solarelectrical processes
- **Duration: 2015-2017**



Solar Fuels


Water, CO_2
Radiation
Steam
CO_2
SOEC-Stack
Syn-gas
Analysis
Modelling
Syn-Fuels
Heat
Simulation
Evaluation
Application
High performance radiator
Receiver
Latent heat storage

Conclusion

- Plasma sprayed metal supported cell technology has been developed
- Stability of ferritic stainless steel against corrosion remains an issue for long-term operation.
- Use of perovskite as current collector and anodic electro-catalysts are still challenging because of the reduced electronic conductivity and the stringent manufacturing parameters required for high performance
- Current and future SOEC activities in cell degradation, co-electrolysis and synthetic fuel production

Acknowledgment

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