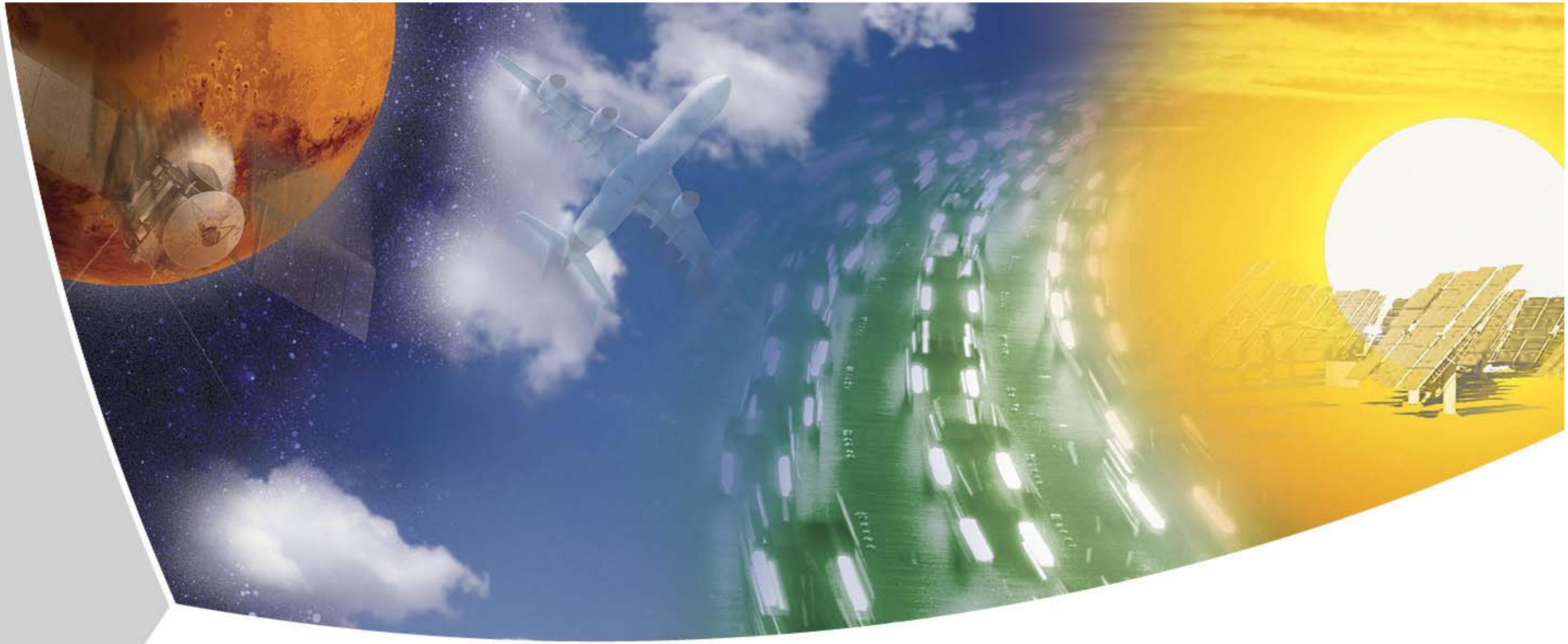


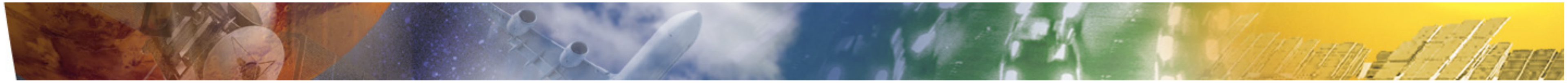
Development of Metal Supported SOFC at DLR

G. Schiller

German Aerospace Center (DLR)
Institute of Technical Thermodynamics

Indo-German Workshop on Fuel Cells and Hydrogen Energy,
Kolkata, January 29-31, 2007

DLR Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft



The DLR
German Aerospace Research Center
Space Agency of the Federal Republic of Germany

DLR Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft

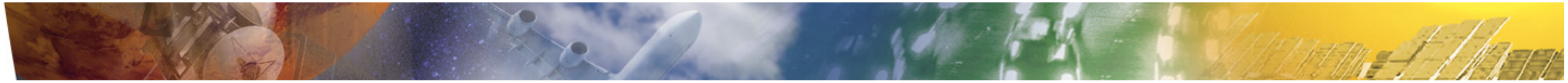
Sites and employees

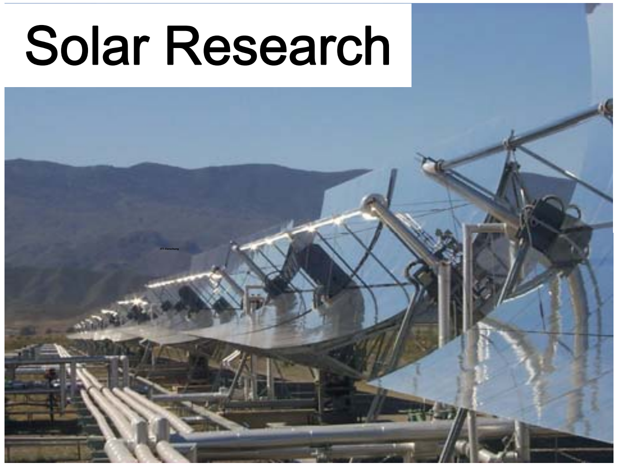
5.100 employees working in 27 research institutes and facilities

- ■ at 8 sites
- ● in 7 field offices.

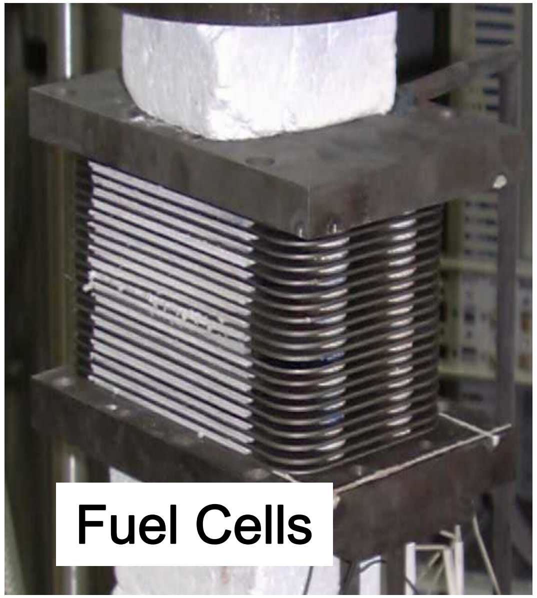
Offices in Brussels, Paris and Washington.

DLR Stuttgart





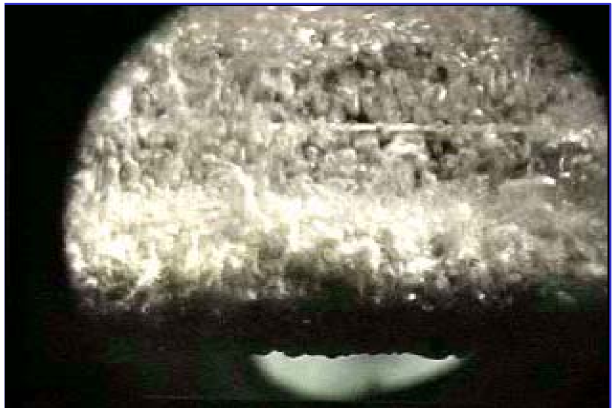
Solar Research



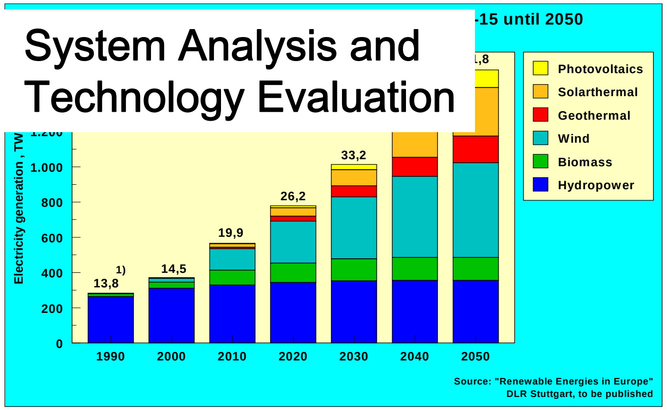
Fuel Cells

DLR-ITT

145 employees
Stuttgart,
Köln-Porz,
Almeria



Thermal Process Engineering

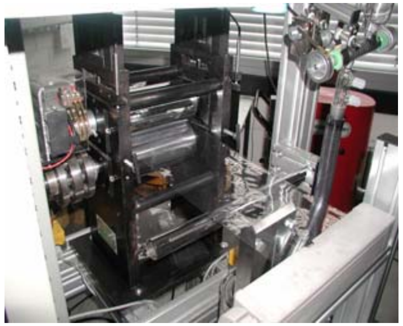


System Analysis and Technology Evaluation

DLR Institute of Technical Thermodynamics

Low Temperature Fuel Cells
AFC, PEFC, DMFC

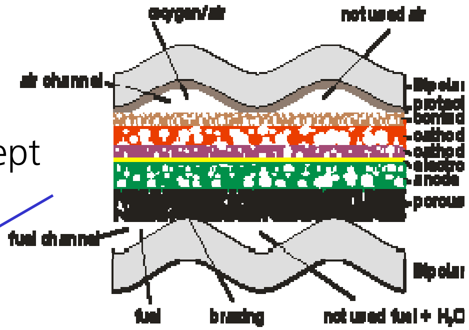
High Temperature Fue
SOFC

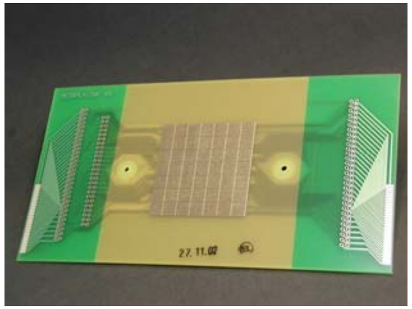


MEA production

Fuel Reforming

Spray Concept

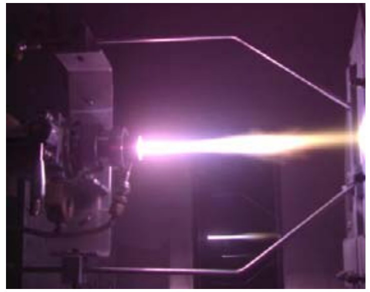


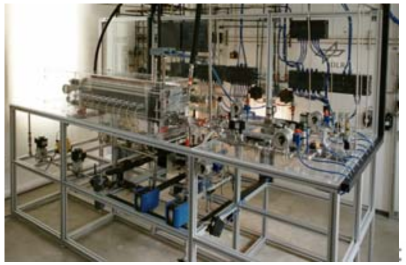


Segmented Cells for analysis and control

Competence and Activities

Plasma deposition process

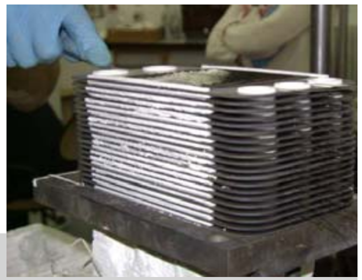




PEMA Test equipment

System Technology and Analysis

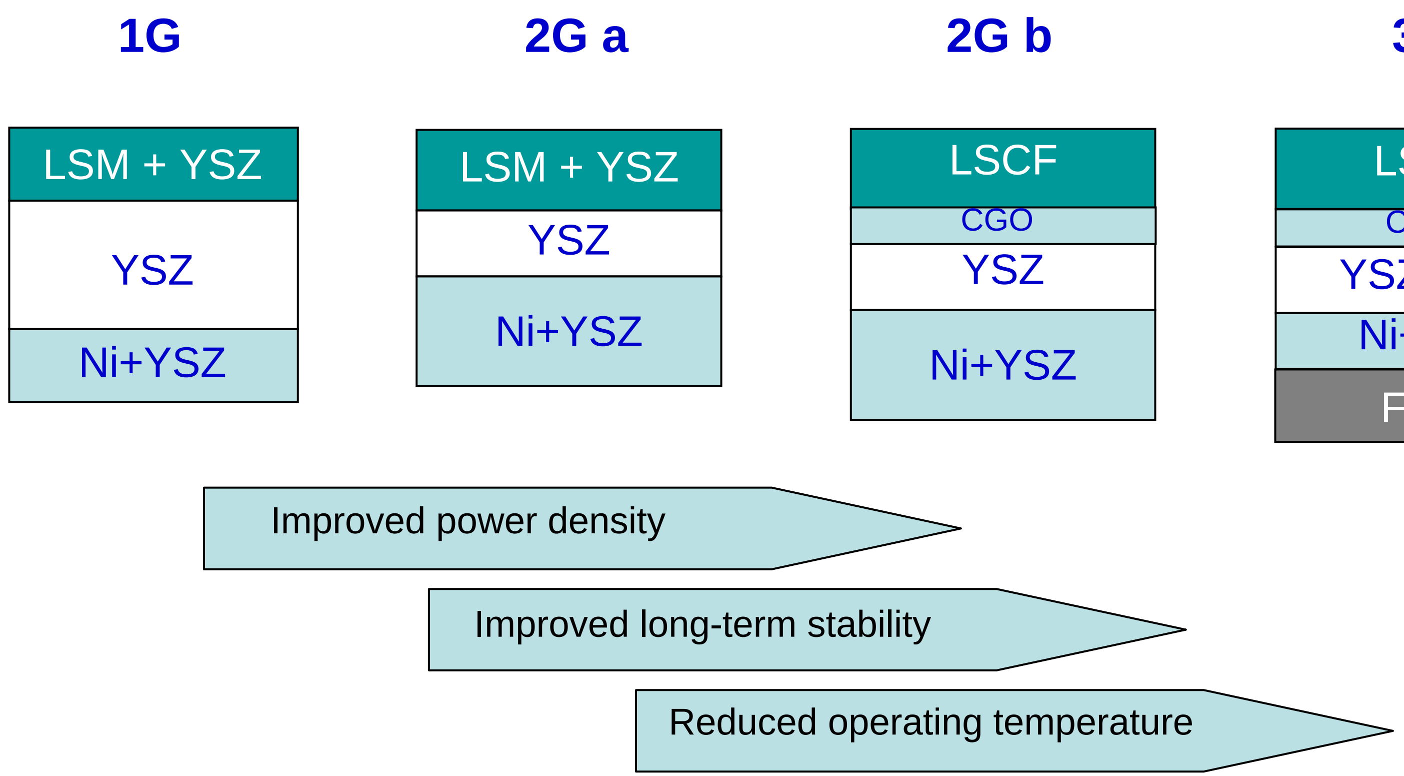
SOFCs for APUs



Outline

1. Introduction
2. SOFC Spray Concept of DLR
3. Plasma Deposition Technologies
4. Development of Cells and Functional Layers
5. Metallic Substrate Support
6. Electrochemical Performance of Cells and Stacks
7. Spatially-Resolved Cell Characterisation
8. Conclusion

SOFC Development from 1st (1G) to 3rd Generation (3G)



Advantages of Metal Supported Cells (MSC)

- High electrical conductivity of the metal support
- High thermal conductivity of the metal support
- High stability of the cell during temperature changes
- High and homogeneous mechanical stability of the cell
- Application of conventional joining and sealing techniques
- Cost reduction for materials and fabrication technologies

Requirements for Metal Substrate Supports

- High electrical conductivity
- Adapted thermal expansion coefficient ($10\text{-}12 \cdot 10^{-6}\ K^{-1}$)
- High corrosion stability in oxidising und reducing, moist atmosphere
- Sufficient mechanical stability
- High gas permeability (porosity > 40 Vol. %)
- Flat surface area for plasma sprayed functional layers

SOFC Spray Concept of DLR

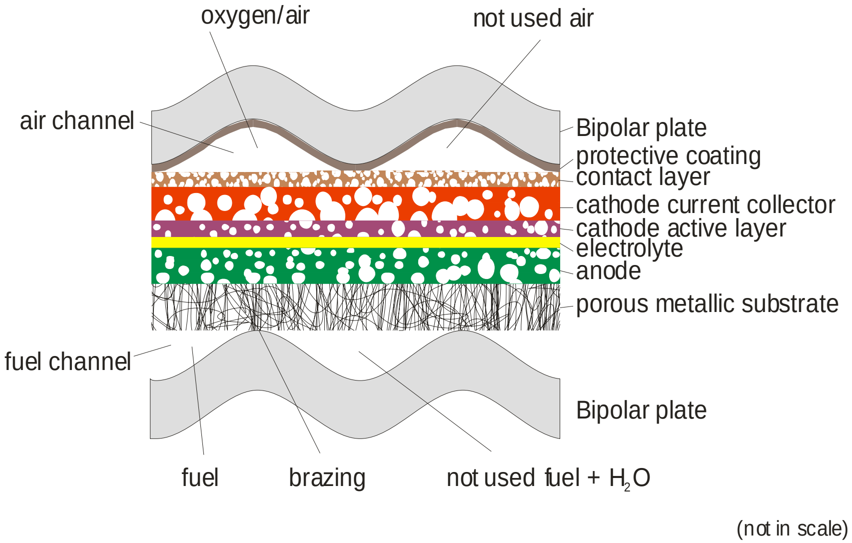
Plasma Deposition Technology

Thin-Film Cells

Ferritic Substrates and Interconnects

Compact Design with Thin Metal Sheet Substrates

Brazing, Welding and Glass Seal as Joining and Sealing Technology

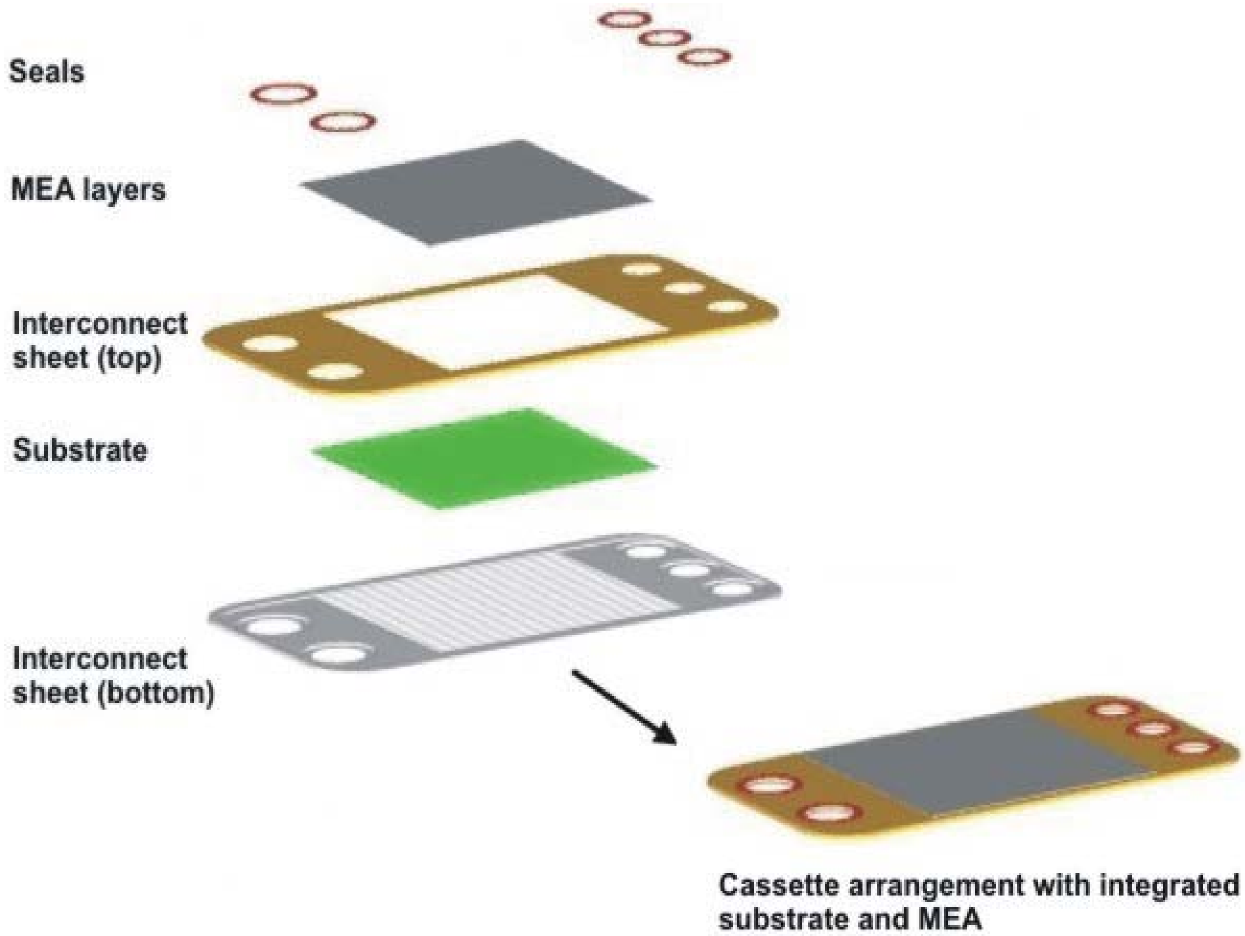


Schematic of DLR-SOFC Design with Metallic Substrate

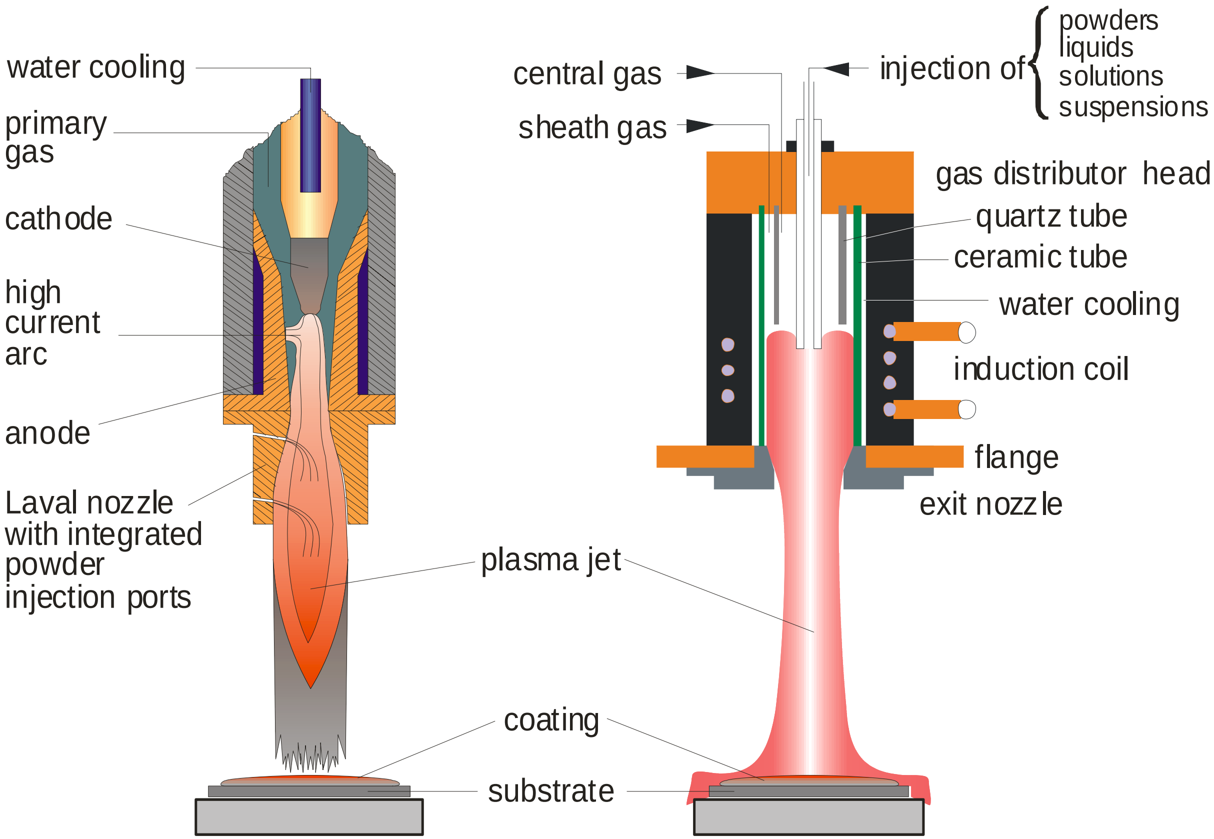
Objective of DLR Development:

Light-weight stack of 5 kW power with high performance, rapid heat-up and good thermal cycling properties

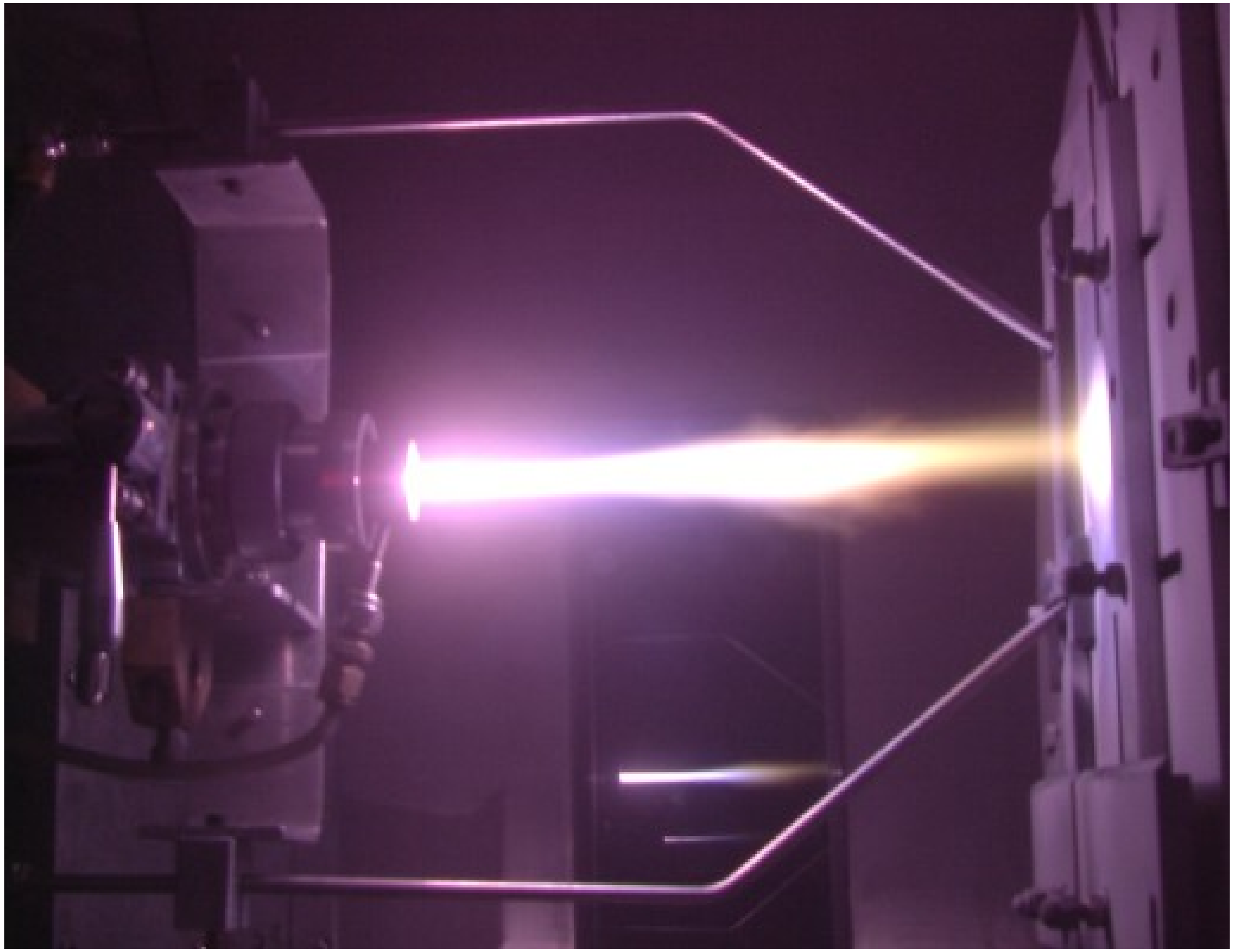
Cell Design for APU Application



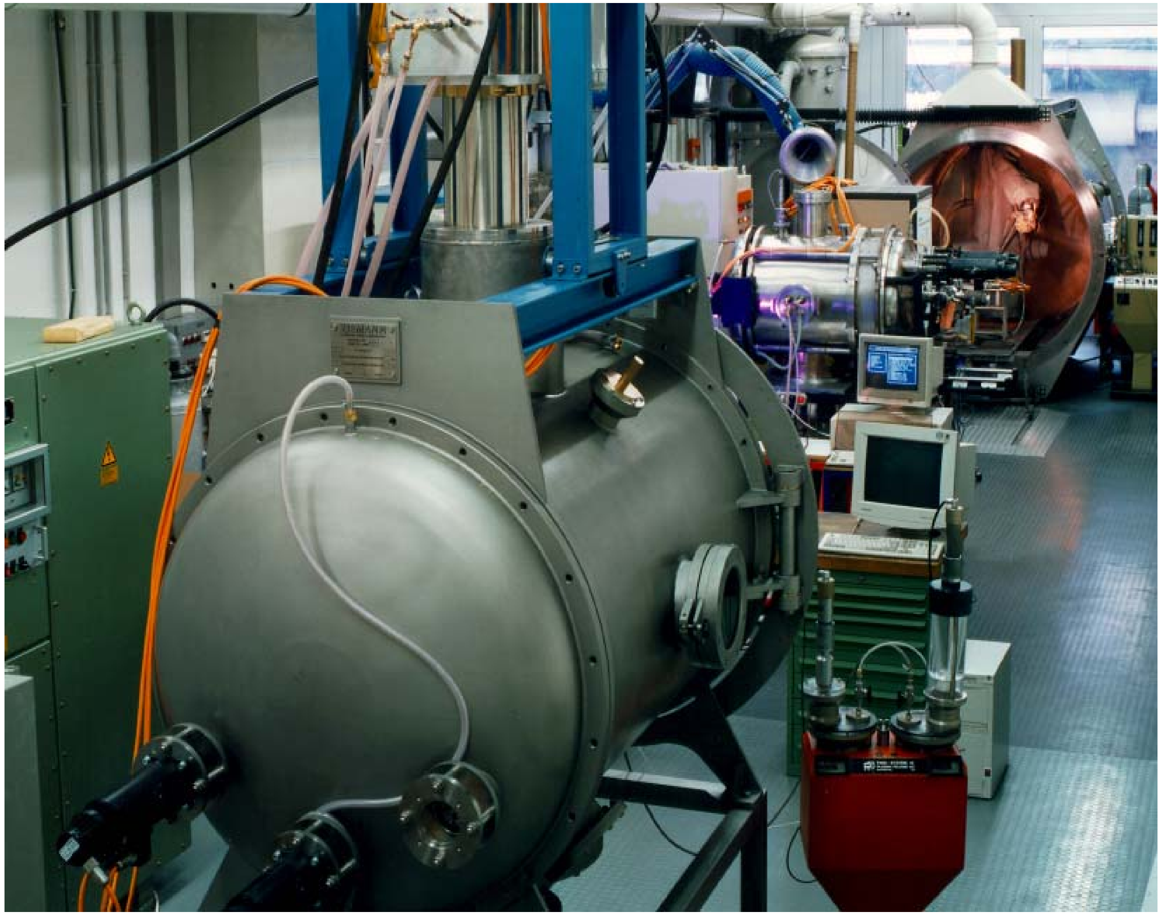
Principles of DC and RF Plasma Spraying



Vacuum Plasma Spraying of SOFC Cells



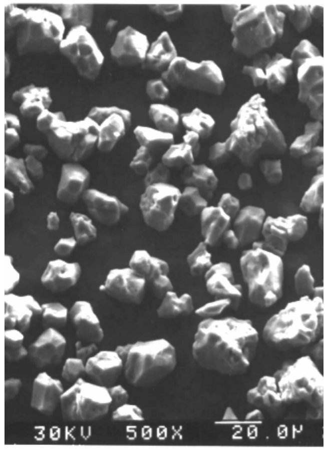
Plasma Spray Laboratory at DLR Stuttgart

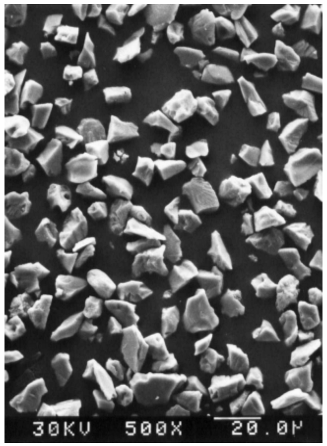


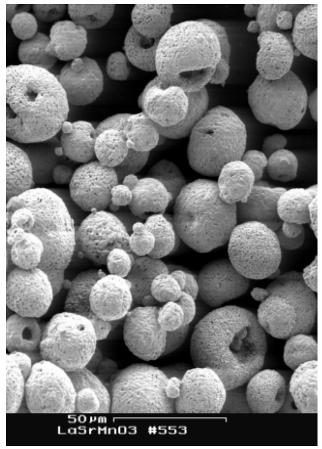
VPS Pilot Facility at DLR Stuttgart

Powders Used for the Spraying of the Cells

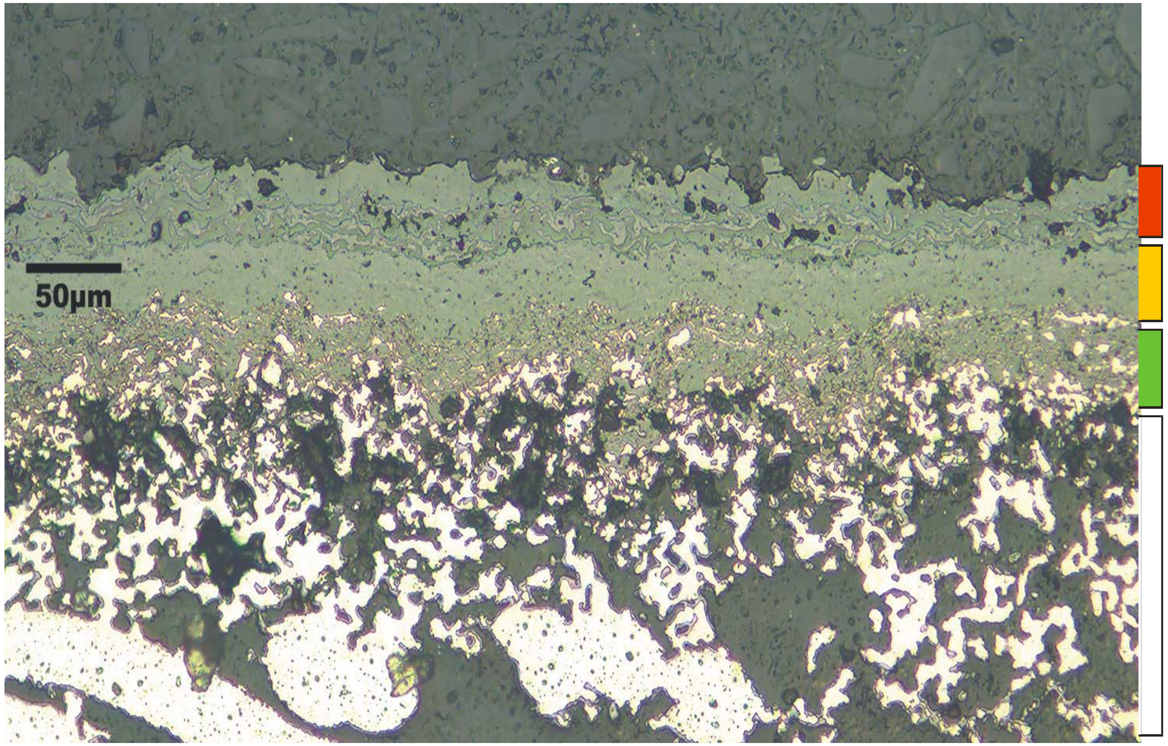
Powder	NiO	ZrO_2- 7 mol %Y_2O_3	ZrO_2- 10 mol%Sc_2O_3	$(La_{0.8}Sr_{0.2})_{0.98}$ MnO_3
Short name	NiO	YSZ	ScSZ	LSM
Morphology	sintered, crushed	sintered, crushed	sintered, crushed	sintered, spherical
Size distribution	10-25 µm	5-25 µm	2-35 µm	20-40 µm
Supplier	Cerac, USA	Medicoat, Switzerland	Kerafol, Germany	EMPA, Switzerland



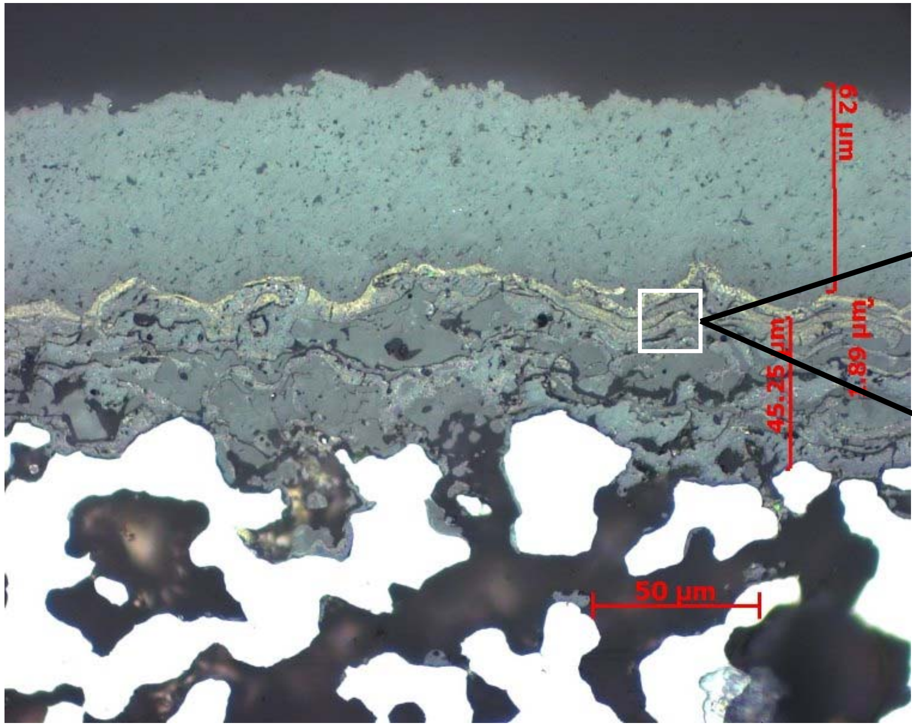


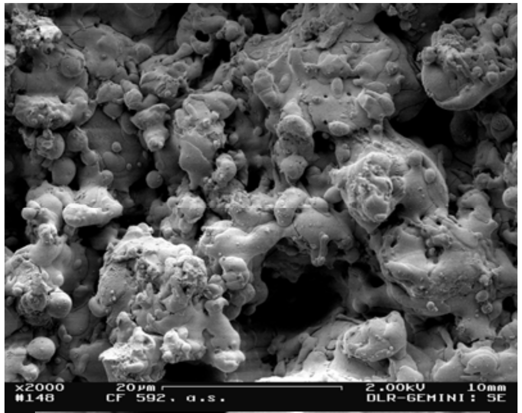


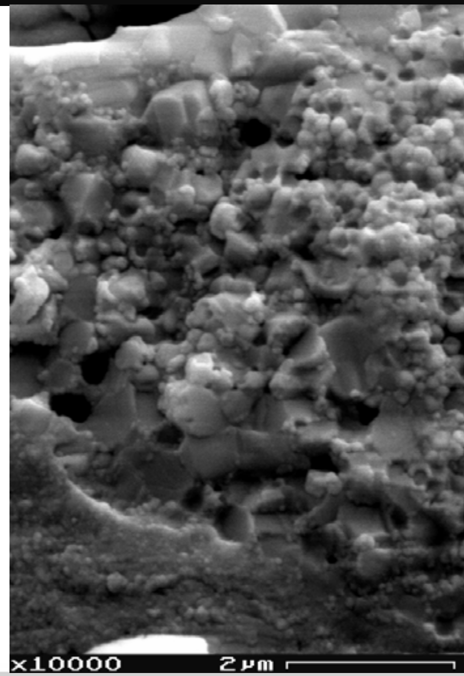
Cross Section of Entirely Vacuum Plasma Sprayed Thin-Film MEA on a Porous Ni Felt



Development of Nanostructured Anode Layer







Permeability coefficient (10^{-15} m^2)

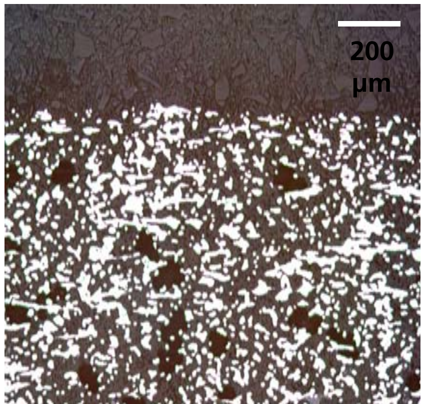
VPS ref	APS conv.	Ni-C	Double Layer
2	12	30	54

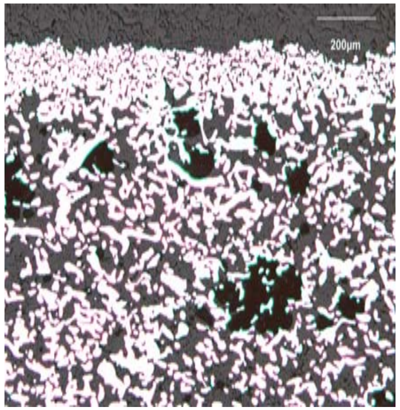
Ferritic Alloys Studied for Porous Metallic Substrates

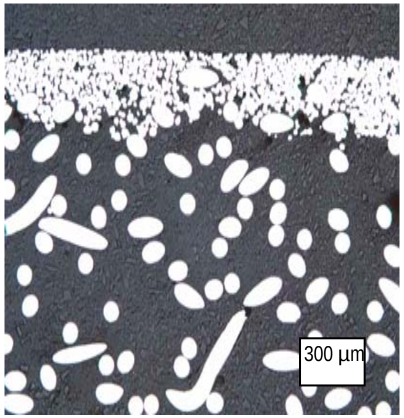
Alloy	Supplier	Composition
Ferrochrom (1.4742)	ThyssenKrupp	18% Cr, 0.9% Al, 0.9% Si, 0.69% Mn, 0.06% C
CrAl20 5 (1.4767)	ThyssenKrupp	19% Cr, 5.5% Al, 0.5% Si, 0.5% Mn, 0.05% C
FeCrAlY	Technetics	22% Cr, 5% Al, 0.1% Y
ZMG 232	Hitachi Metals	21% Cr, 0.08% Al, 0.43% Si, 0.47% Mn, 0.02% C
SUS 430 HA	Nippon Steel	16% Cr, 0.13% Al, 0.29% Si, 0.13% Mn, 0.05% C
SUS 430 Na	Nippon Steel	16% Cr, 0.01% Al, 0.29% Si, 0.56% Mn, 0.05% C
CroFer22 APU	ThyssenKrupp	22% Cr, 0.12% Al, 0.1% Si, 0.41% Mn, 0.16% Ni, 0.05% Ti, 0.08% La
IT 14	Plansee	26% Cr, < 0.03% Al, < 0.03% Si, Mo, Ti, Mn, Y_2O_3

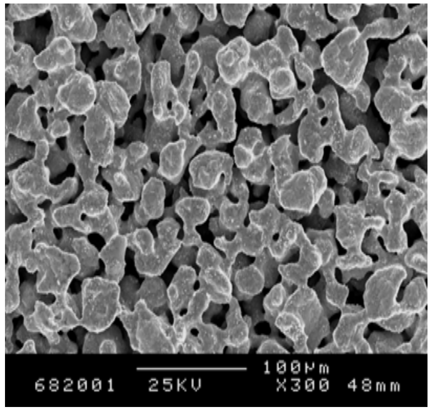
Porous Metallic Substrates Used for the Plasma Spray SOFC Concept

Substrate	Felt	Foam	Knit fabric	Sintered plate
Material	Ni	Fe-22Cr-5Al-0,1Y	Fe-22Cr-0,5Mn	Fe-26Cr (Y_2O_3)
Thickness	~ 1,0	~ 1,8	~ 1,0	~ 1,0
Porosity	~ 85	~ 80	~ 90	~ 50
Supplier	Bekaert, Belgium	Technetics, USA	Rhodius, Germany	Plansee AG, Austria

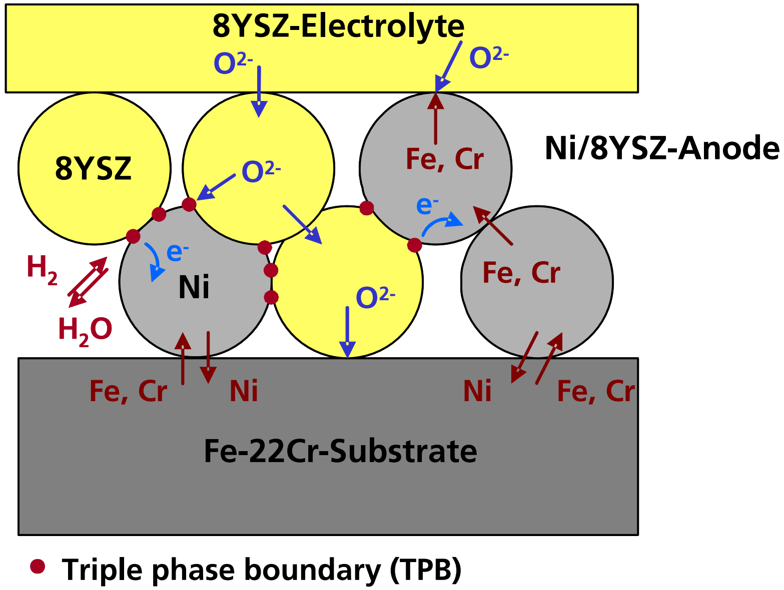


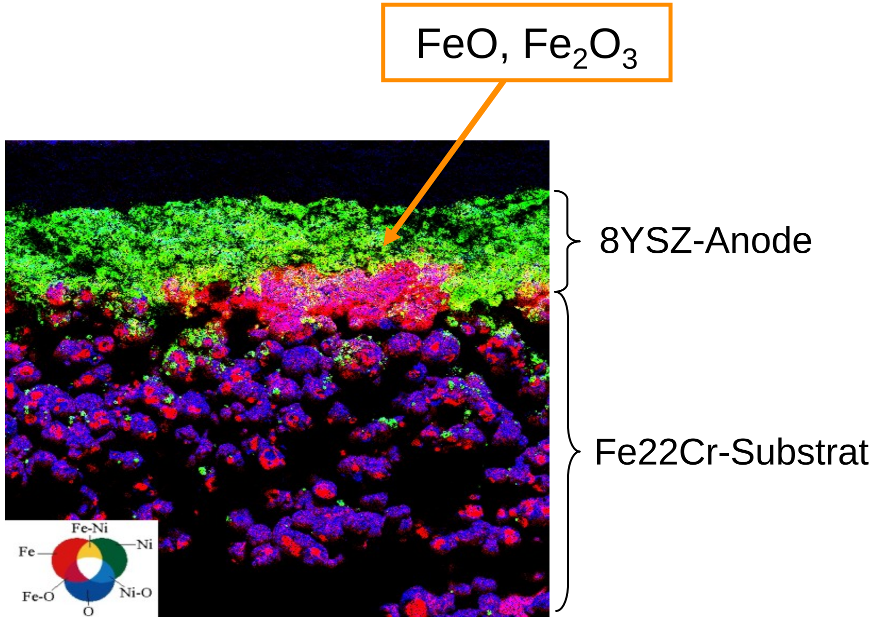


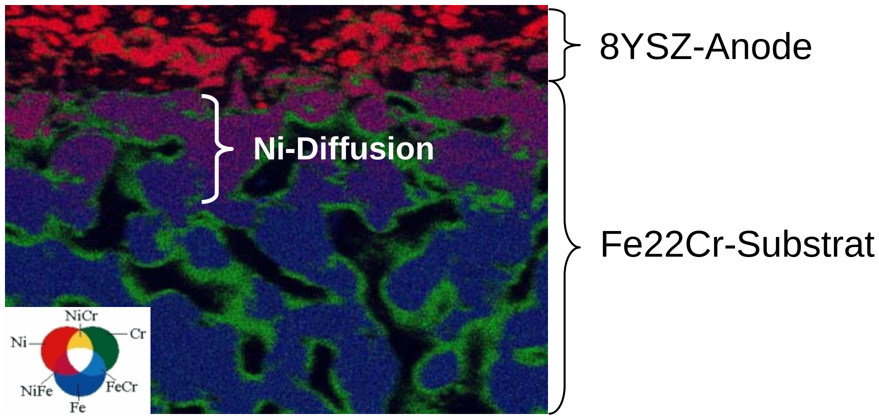




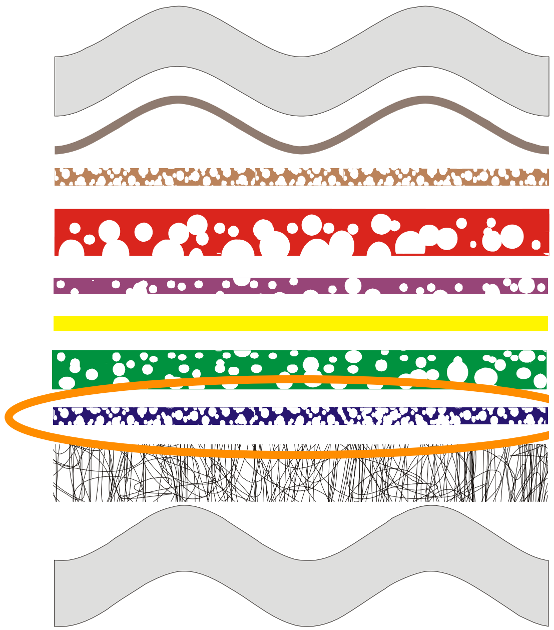
Interdiffusion of Fe, Cr and Ni Between Substrate and Anode







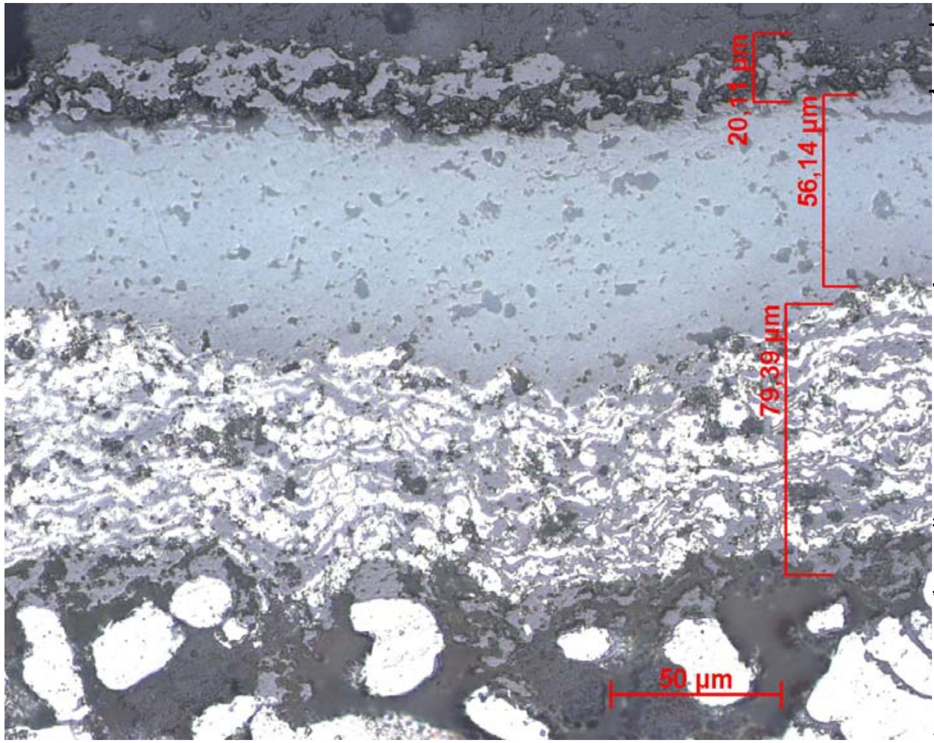
Experimental Approach For a Diffusion Barrier Layer at the Anode Side



Requirements

- Porous structure
- Adapted thermal expansion coefficient ($\alpha_{tech.}$= 10-11 x 10^{-6} K^{-1})
- High electronic conductivity in reducing anode atmosphere [σ = 1-3 S/cm, $p(O_2)$ = 10^{-16} bar]
- Chemical stability in reducing humid anode gas atmosphere
- Barrier effect for Fe, Cr und Ni species
- Elektrochemical compatibility at cell operation (chemical inert behavioer)

Plasma Sprayed Diffusion Barrier Interlayer



$LaSrMnO_3$-cathode

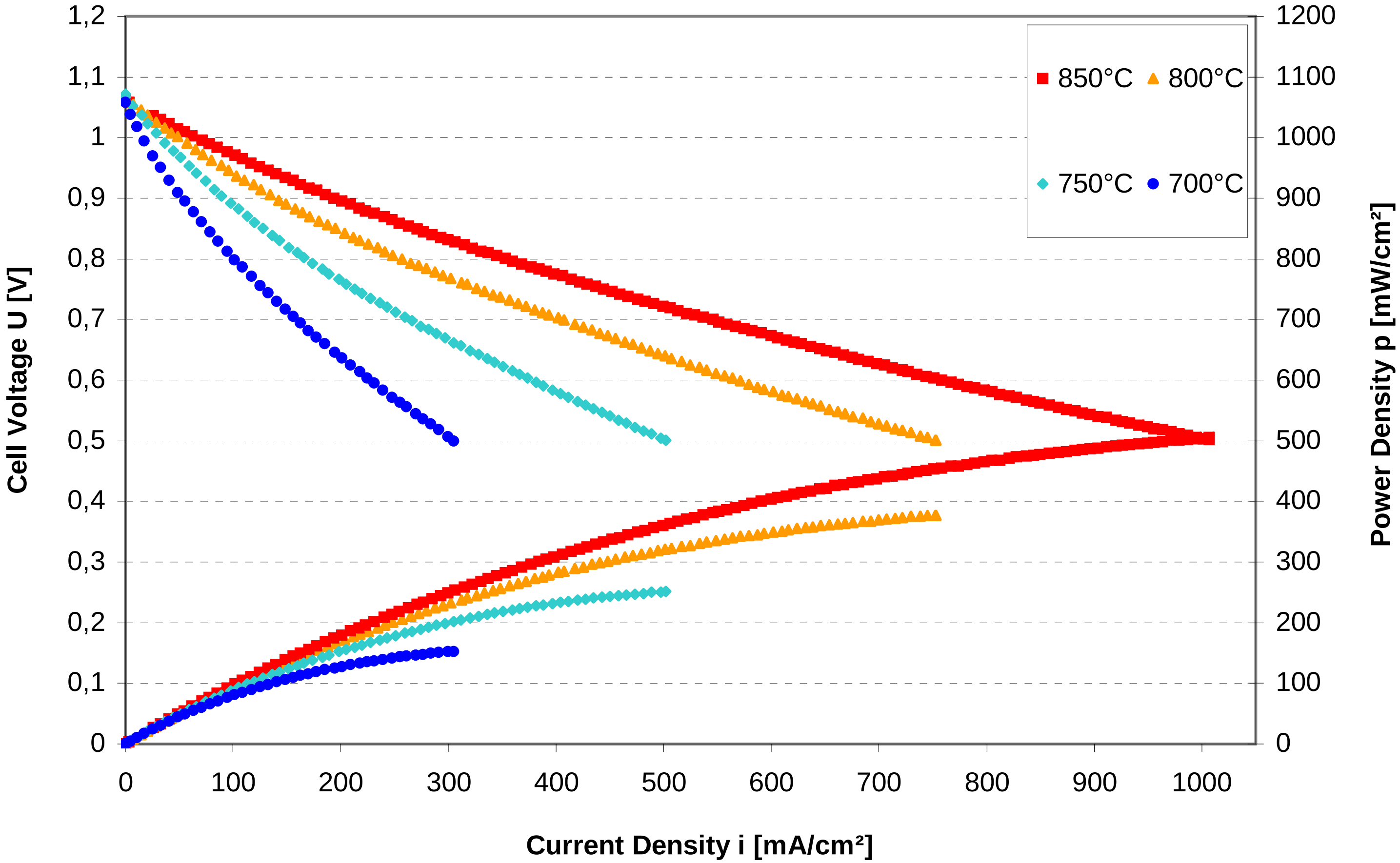
8YSZ-electrolyte

Ni/8YSZ-anode

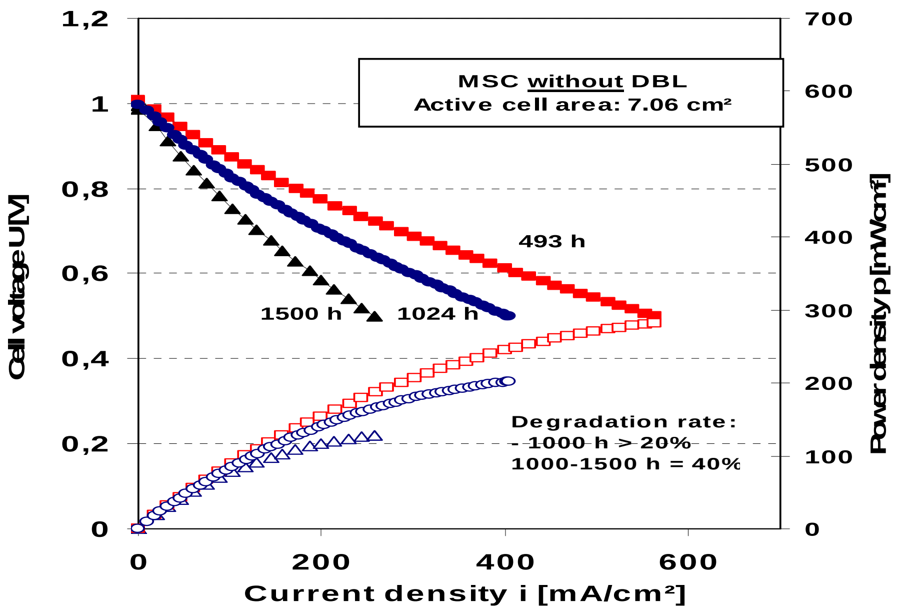
Perovskite-type barrier layer

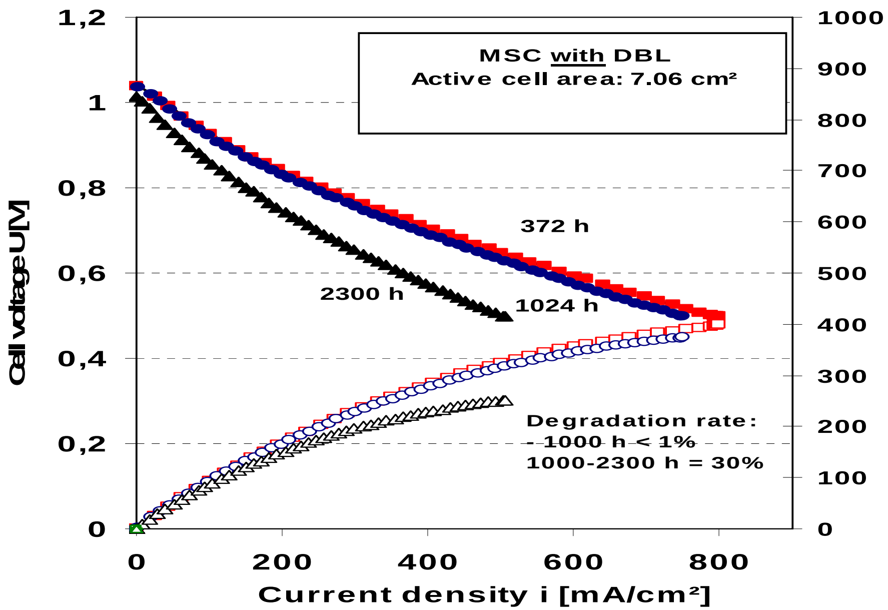
Porously sintered ferrite plate

I-V Characteristics of a VPS Cell with Improved Anode and Cathode Layers (LSM) as a Function of Different Operating Temperatures (0.5 H_2+0.5 N_2 / 2 Air)

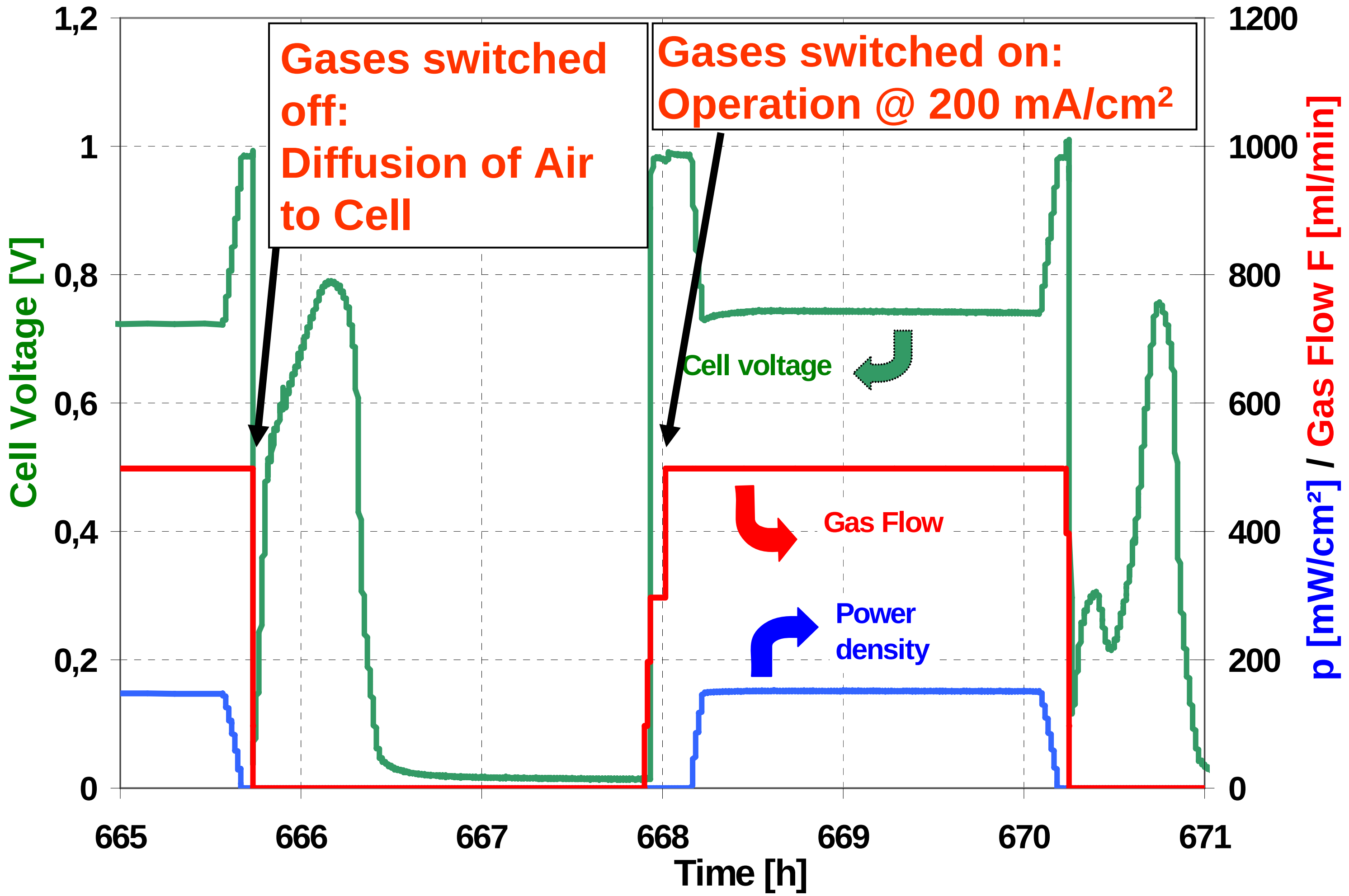


Electrochemical Performance of VPS Cells With and Without Diffusion Barrier Layer in Operation with Simulated Reformate H2/N2 and Air

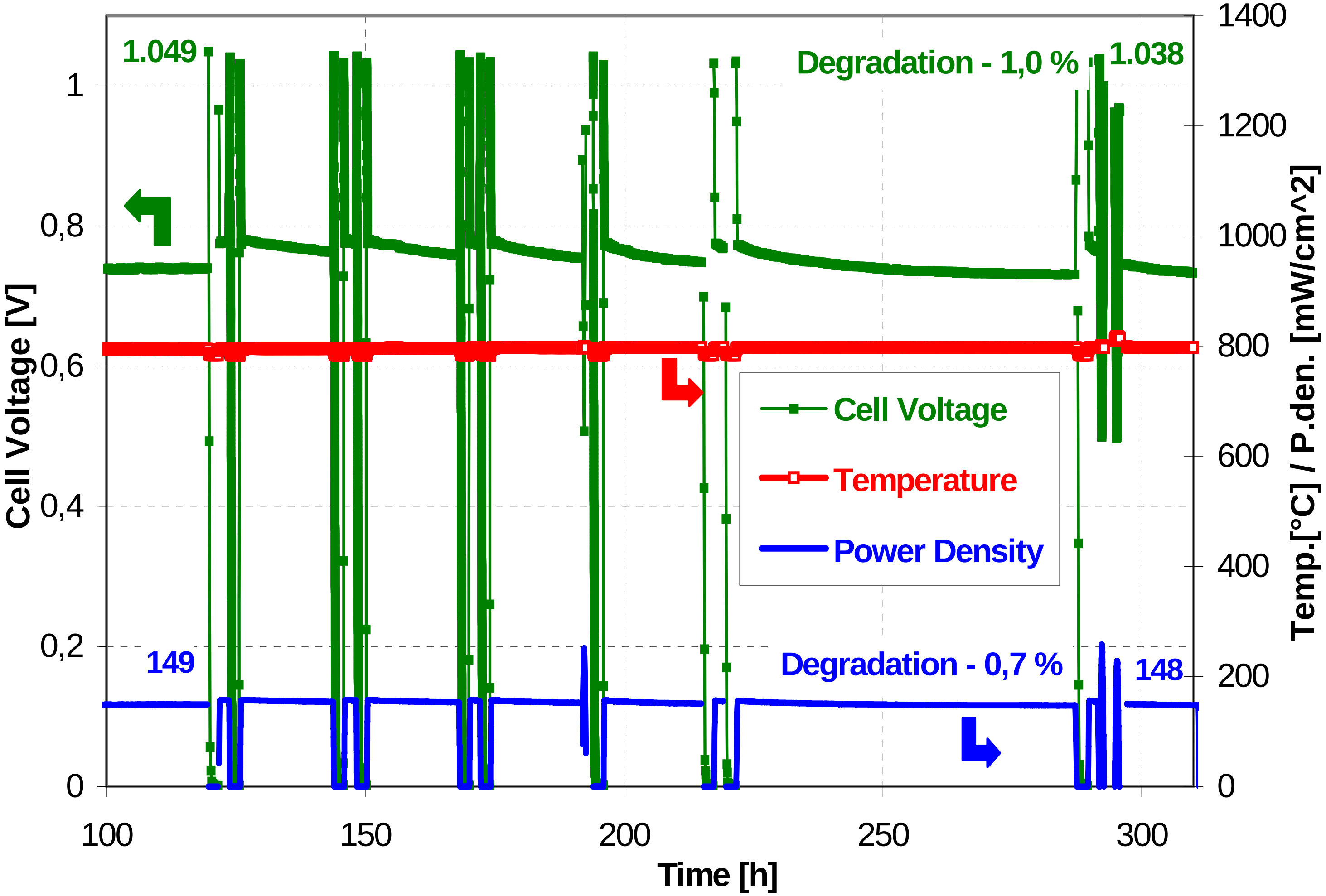




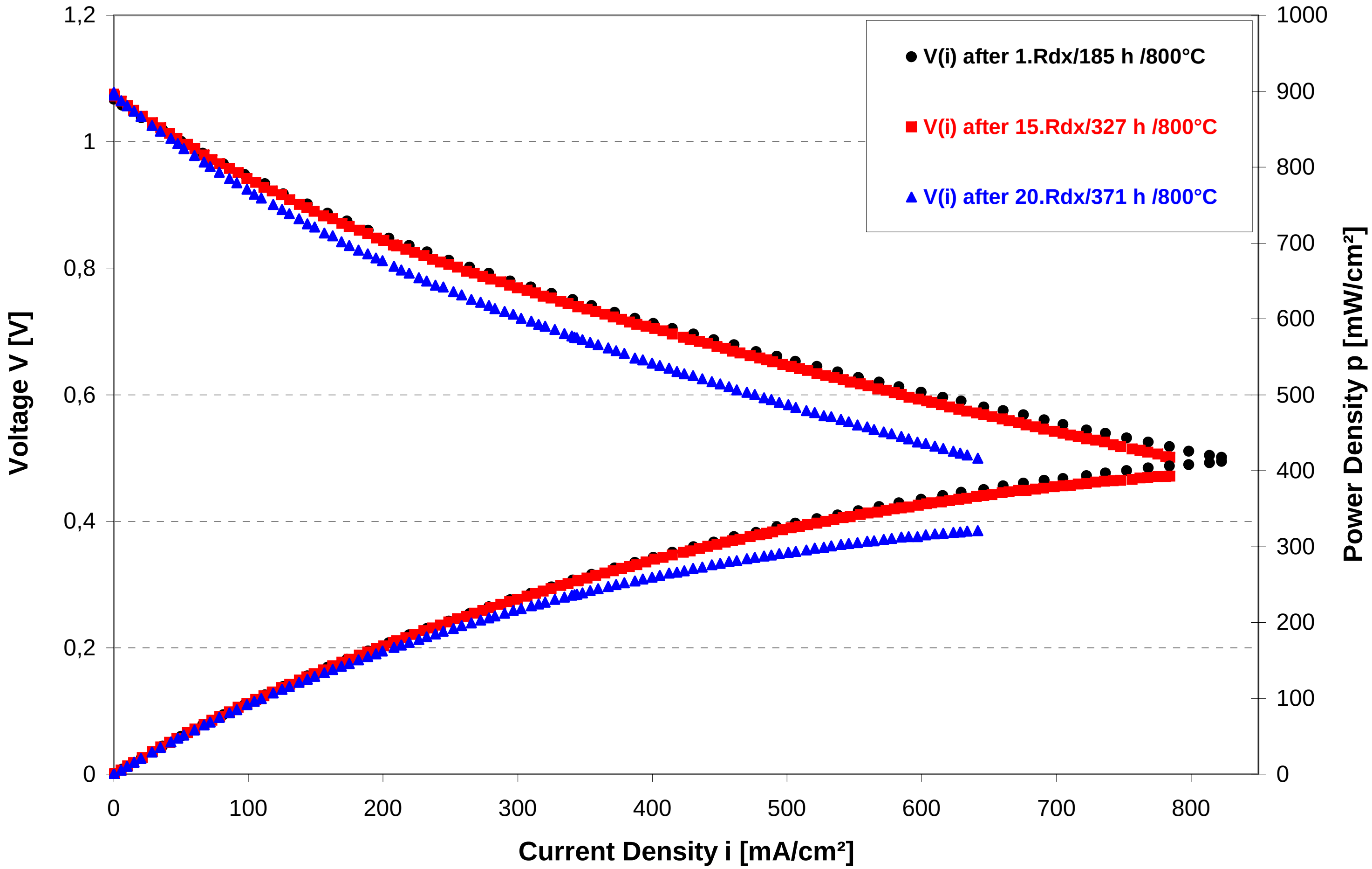
Redox Cycling Conditions



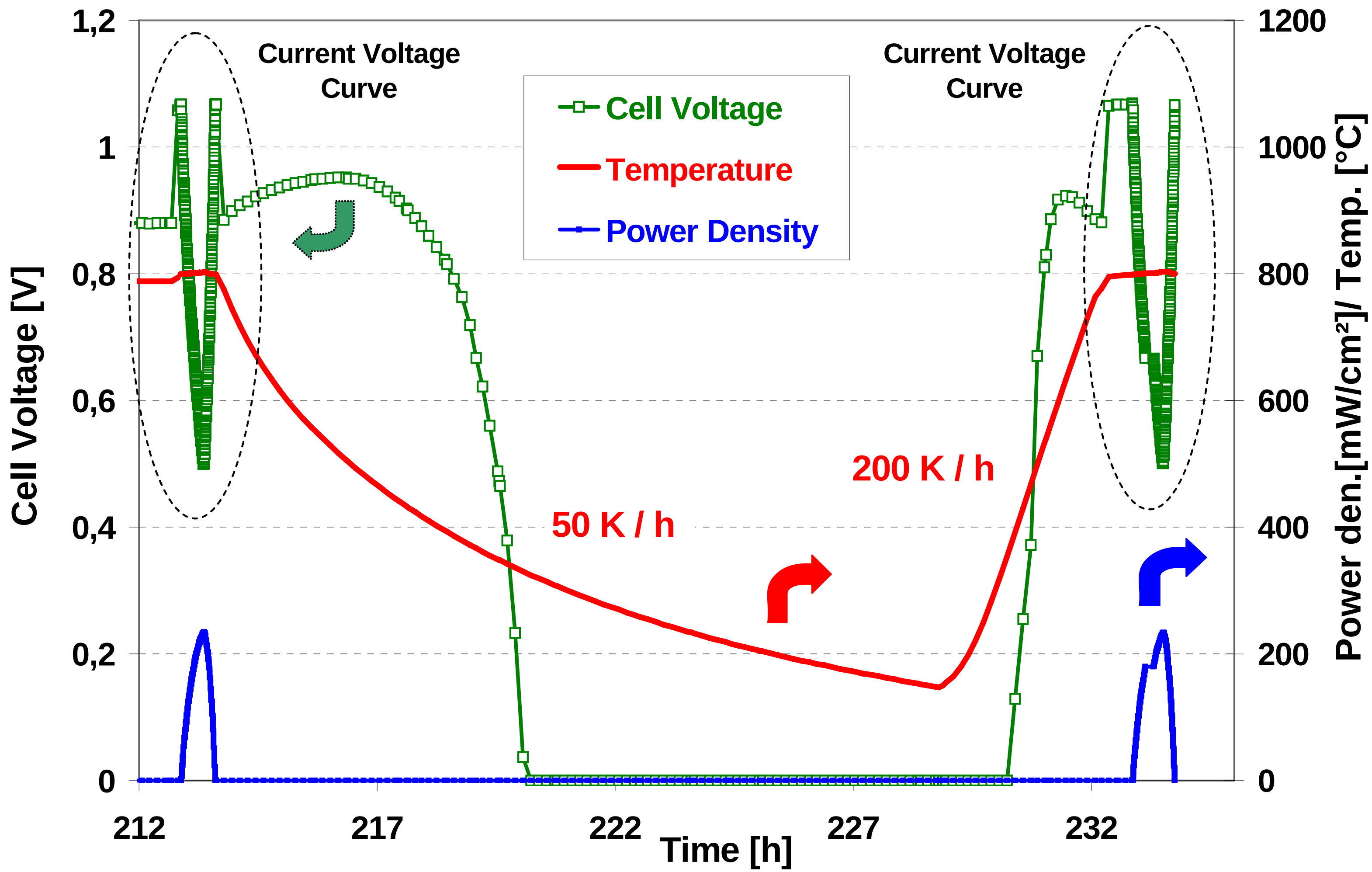
Electrochemical Behaviour of a SOFC ($12cm^2$) during 10 Redox Cycles (800°C, $0.5N_2$+$0.5H_2$ / 2.0 Air, 200 mA/cm^2)



I-V Characteristics of a VPS Cell with Improved Anode and Electrolyte Layers / LSM Cathode after Redox Cycling

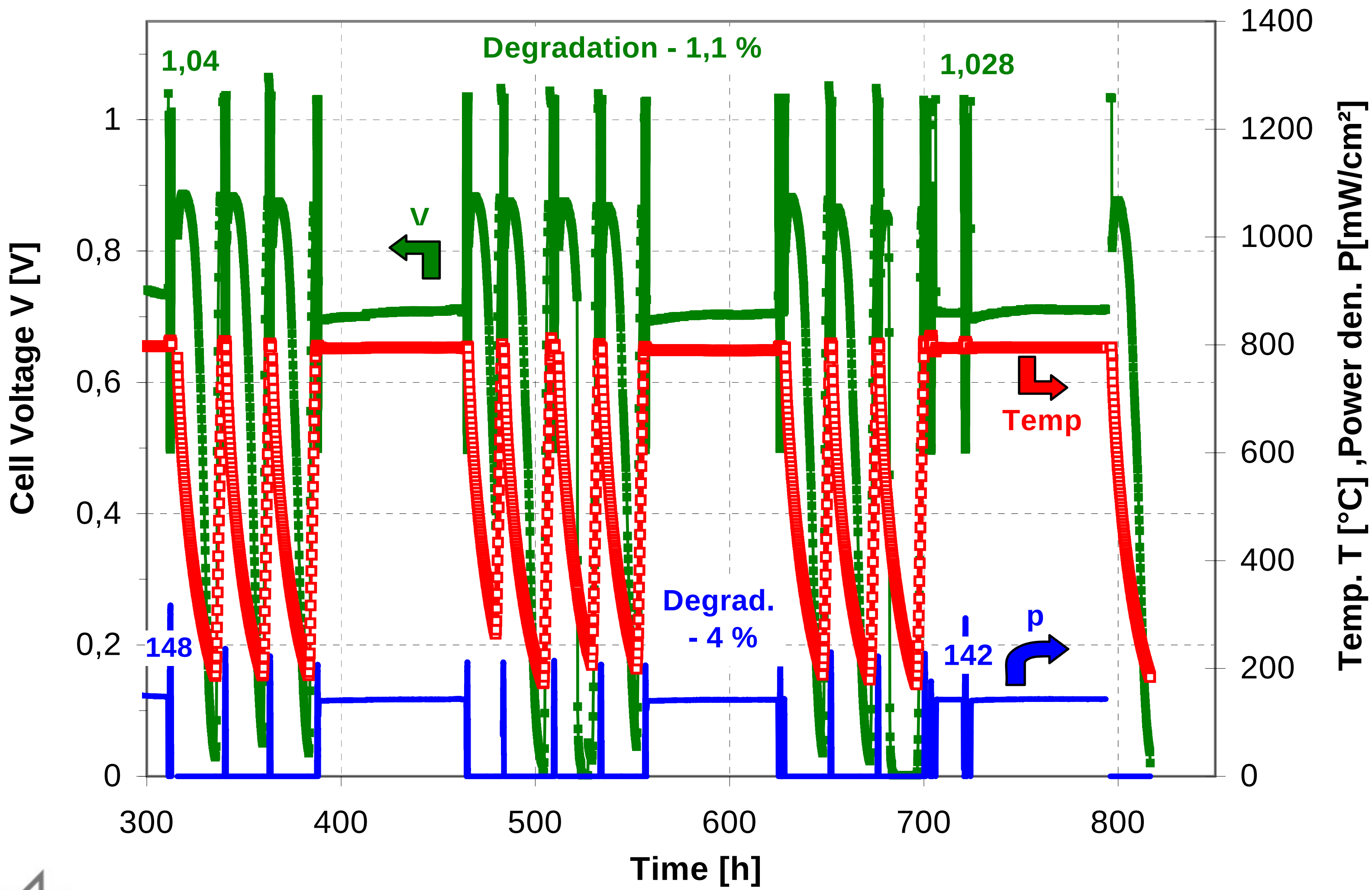


Thermal Cycling Conditions

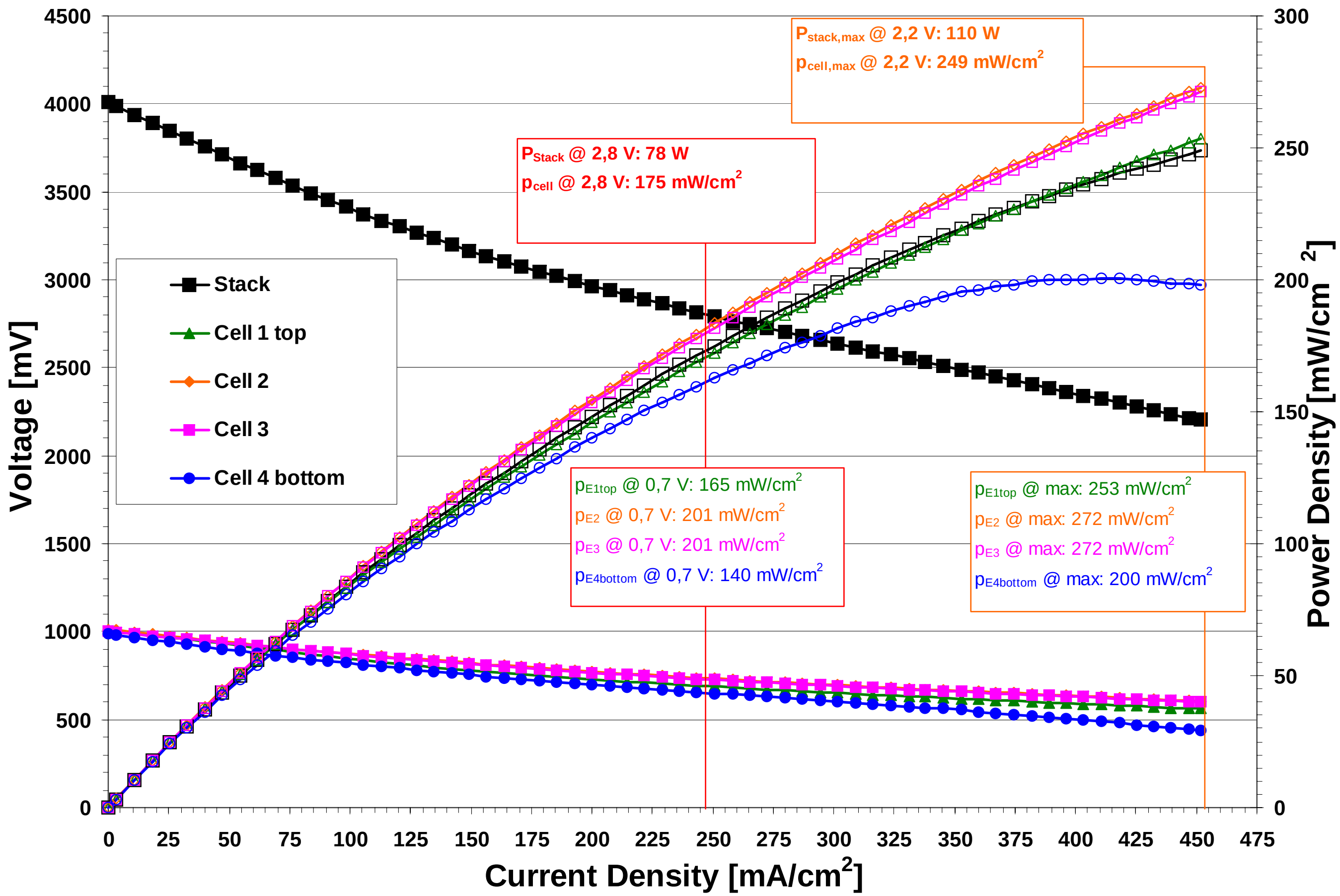


Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft

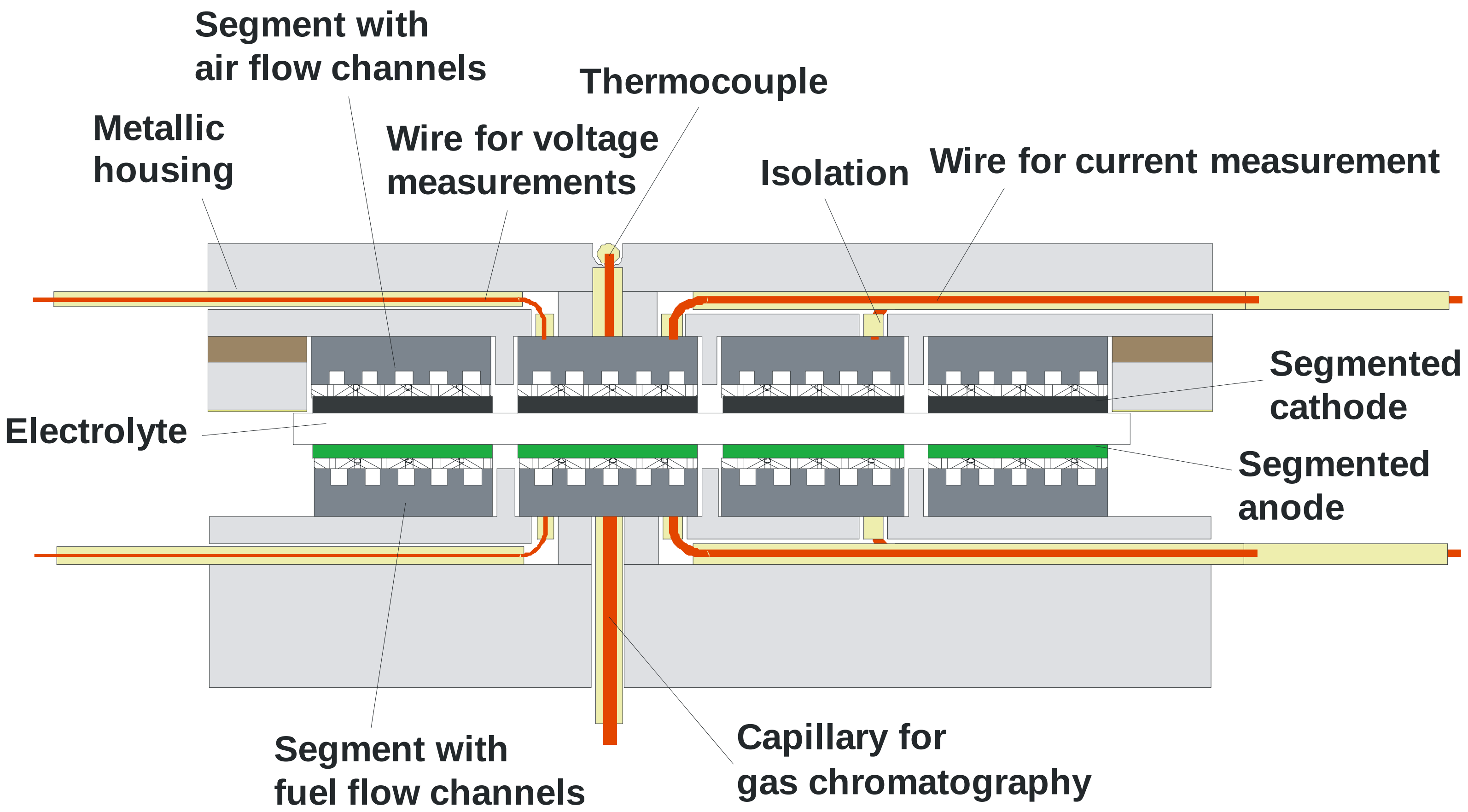
Electrochemical Behaviour of a SOFC (12 cm²) during 10 Thermo Cycles (800°C, $0.5N_2+0.5H_2$ / 2.0 Air, 200 mA/cm²)



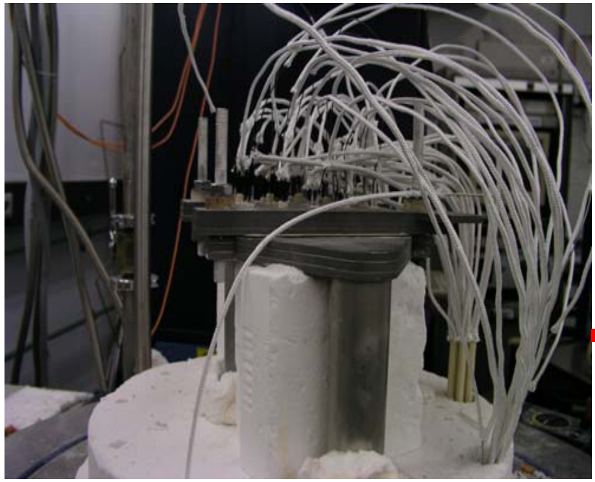
I-V Characteristics of a 4-Cell Stack in Cassette Configu-ration Operated at 800 °C with H_2/N_2-Air (12.5/12.5/80 smlpm/cm²)



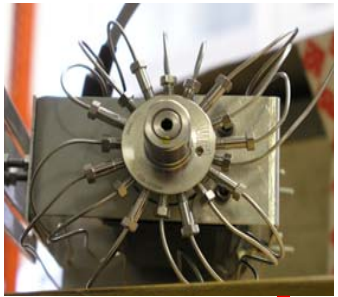
The segmented approach of DLR
Schematic of the metallic housing



Cell Design and Test Rig

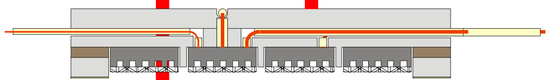


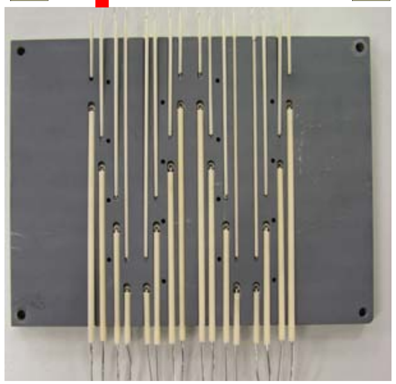
„Simple“measuring device for cassettes



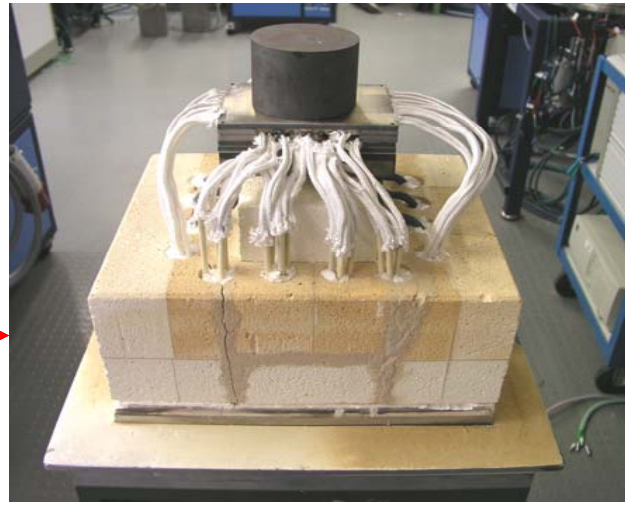
GC measurement

Sealing and contacting





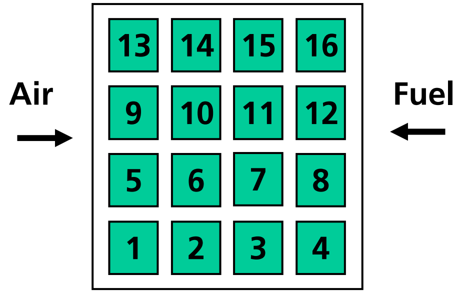
More flexible housing, less disturbed impedance signals

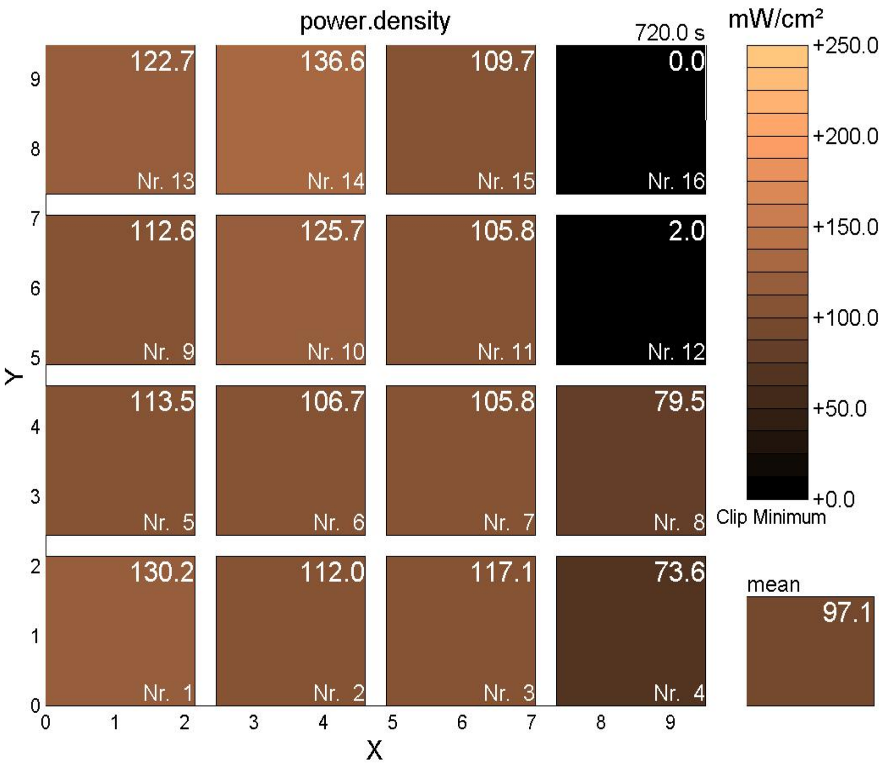


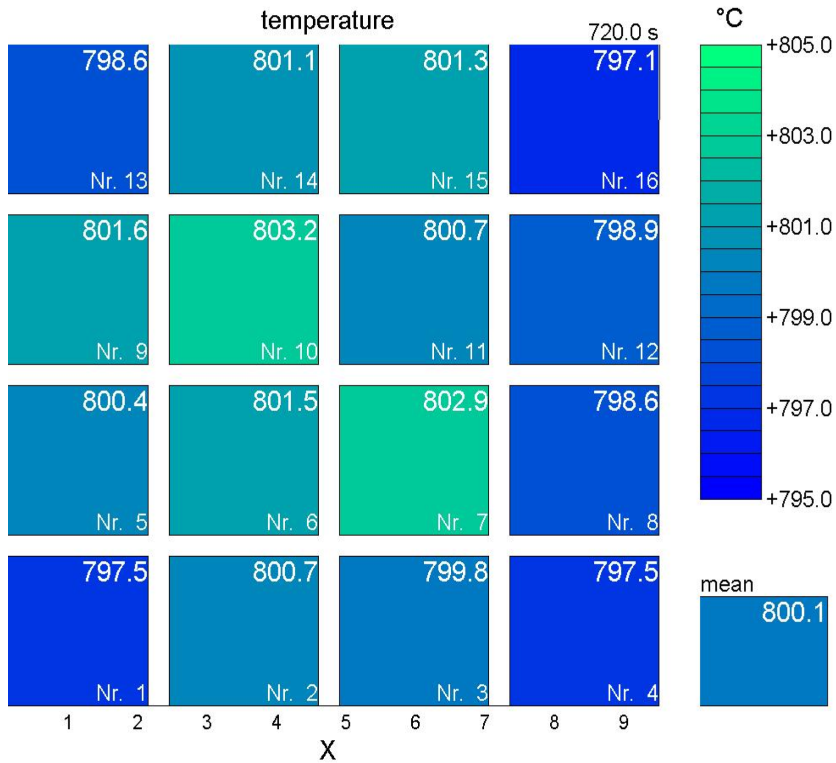
- All cell types applicable
- Improved contacting
- More reliable sealing
- Impedance measurements
- Reliable temperature measurement

Results – flow design
Plasma sprayed cell with LSCF (NT107B02)

- P und T distribution at standard gas flow rates: 12,5/12,5//80 smlpm/cm² H_2/N_2//Air, 800°C, 0,6V, **after 189h, counter flow**

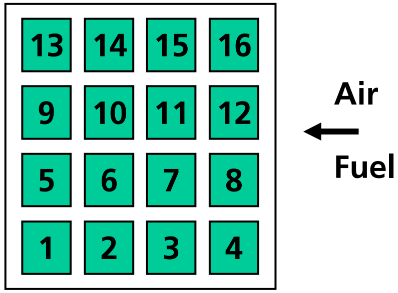




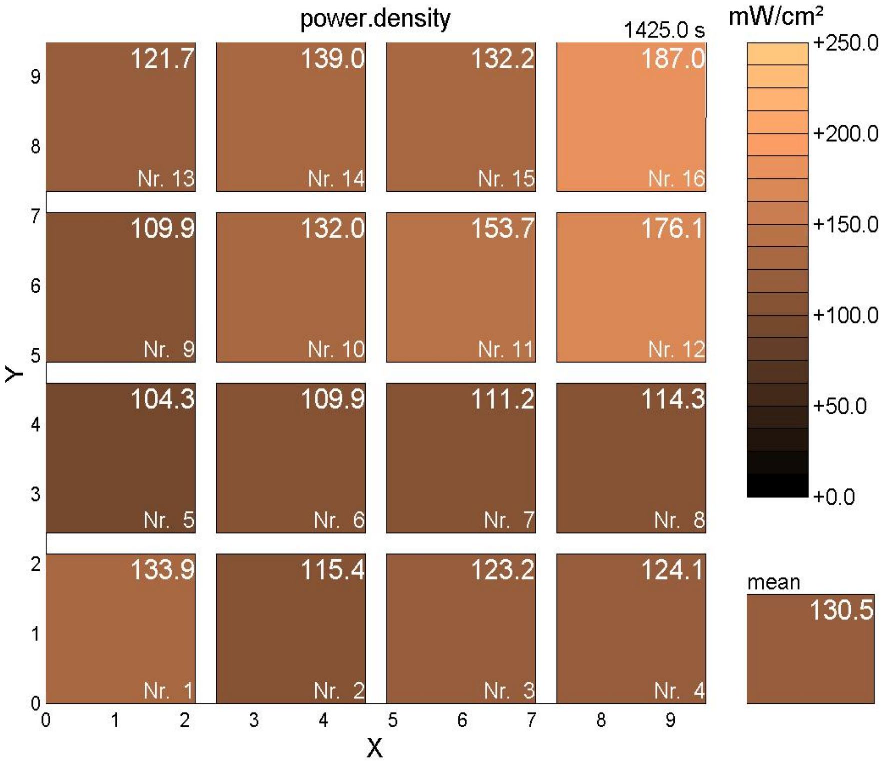


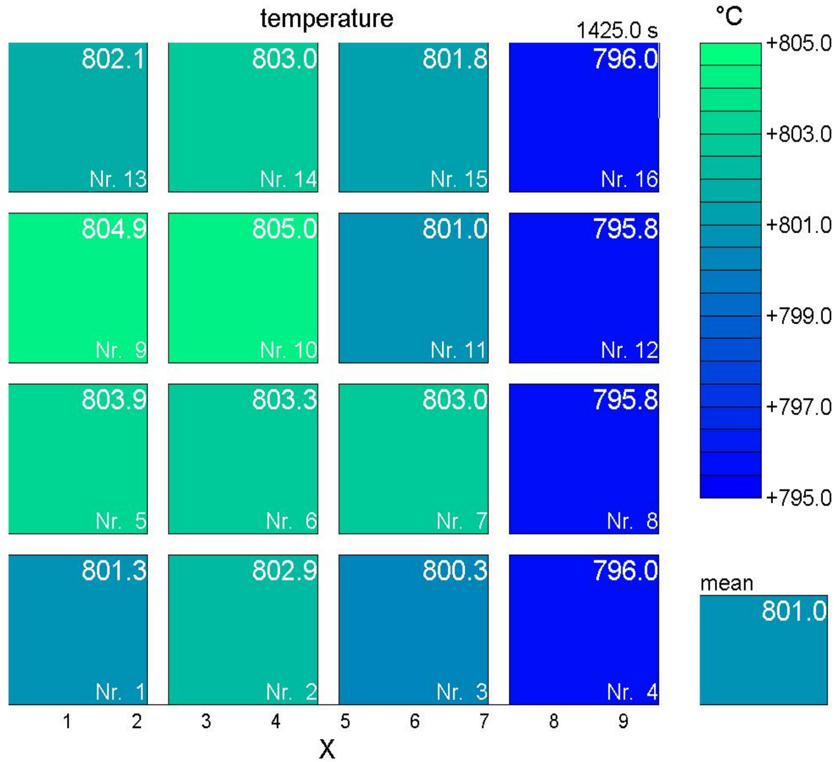
Results – flow design

Plasma sprayed cell with LSCF (NT107B02)

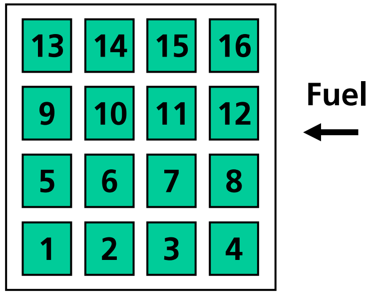


- P und T distribution at standard gas flow rates: 12,5/12,5//80 smlpm/cm² H_2/N_2//Air, 800°C, 0,6V, **after 193h, co flow**

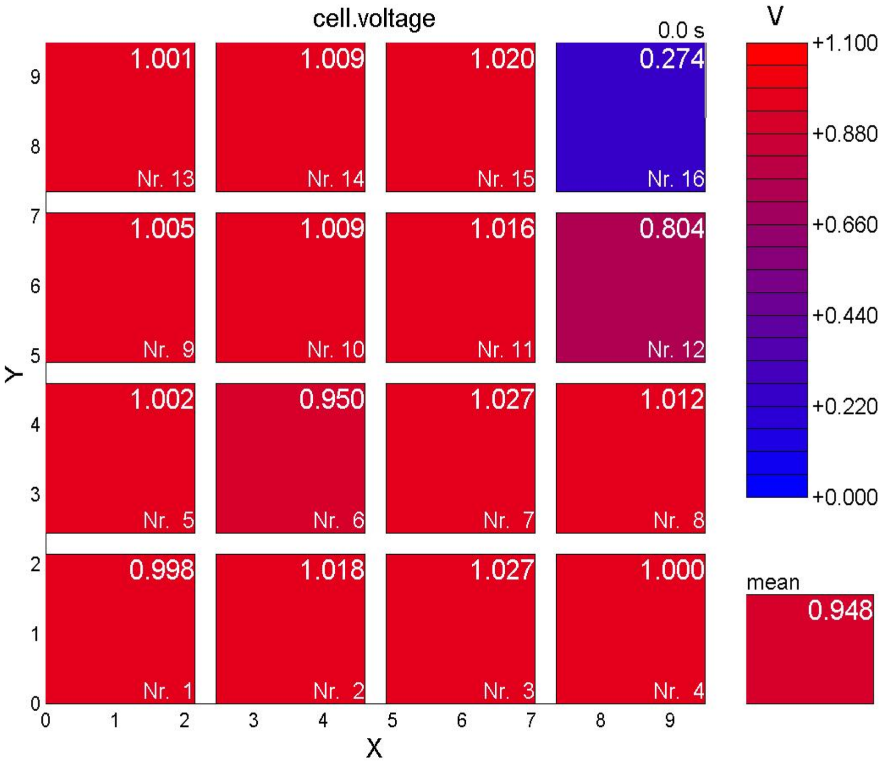


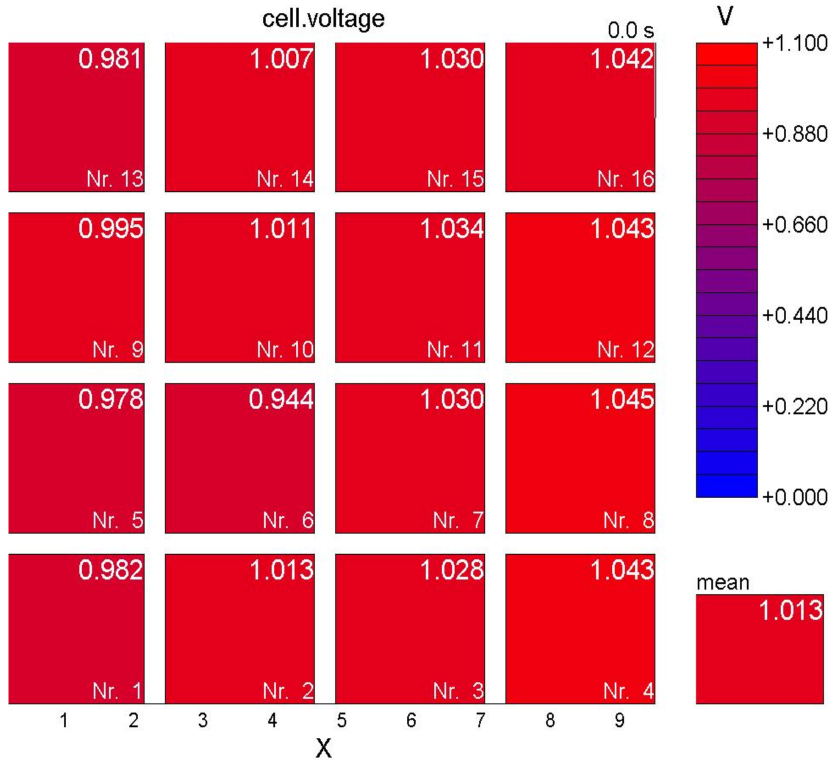


Results – effect of leakage on voltage
Plasma sprayed cell with LSCF (NT107B02)



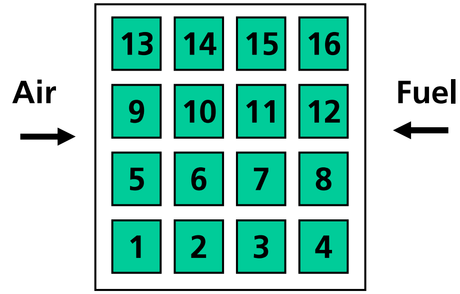
- V distribution at **OCV** with co and counter gas flow:
  L: 12,5/12,5//80 smlpm/cm² H_2/N_2//Air, 800°C, **counter**
  R: 12,5/12,5//80 smlpm/cm² H_2/N_2//Air, 800°C, **co**



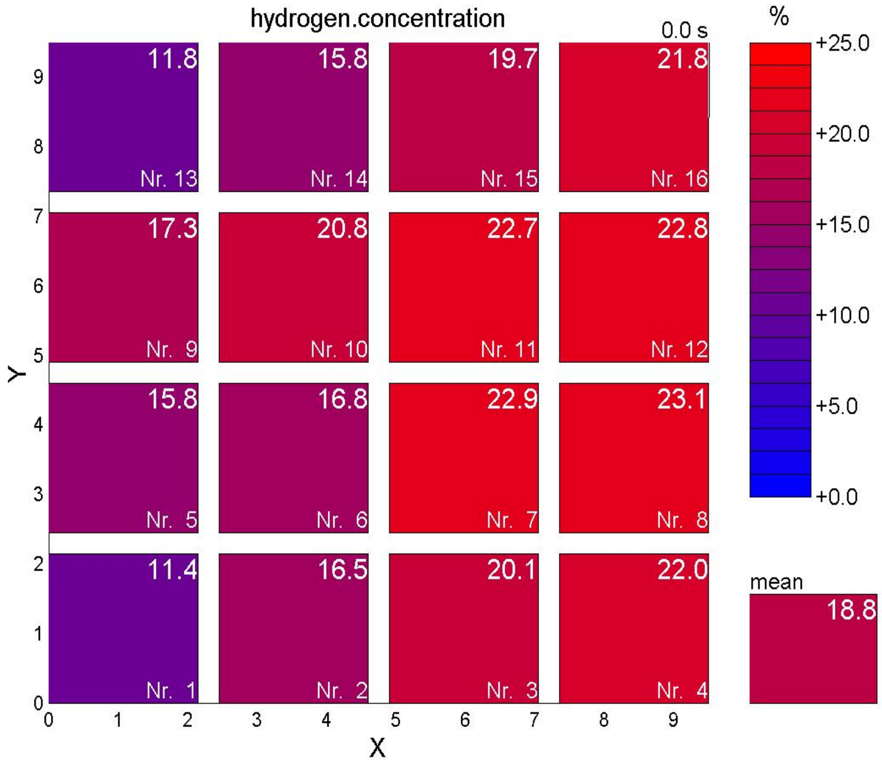


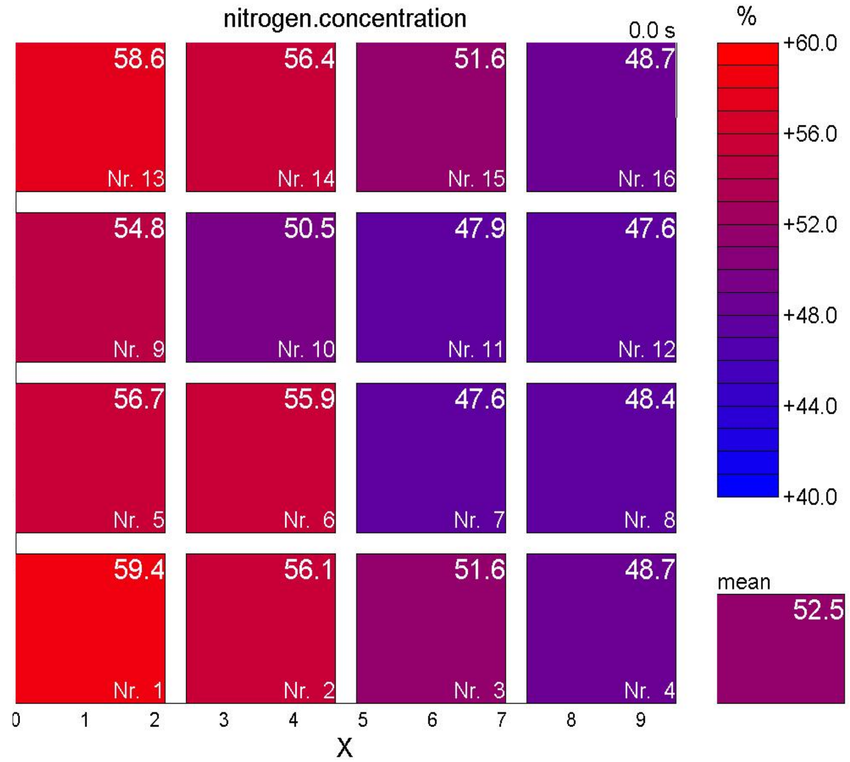
Results – effect of leakage on the concentrations

Leaky pre-test cell (Te142)



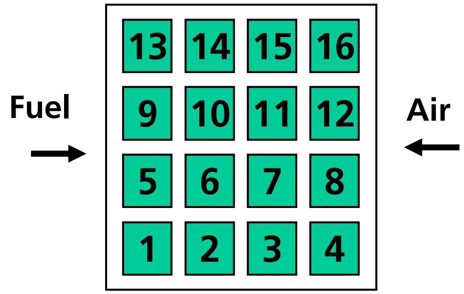
- Gas concentration distribution at 800°C:
  Gas flow rates: 25%H_2, 25%CO, 50%N_2
  6,8/6,8/13,5//68 smlpm/cm² H_2/CO/N_2//Air

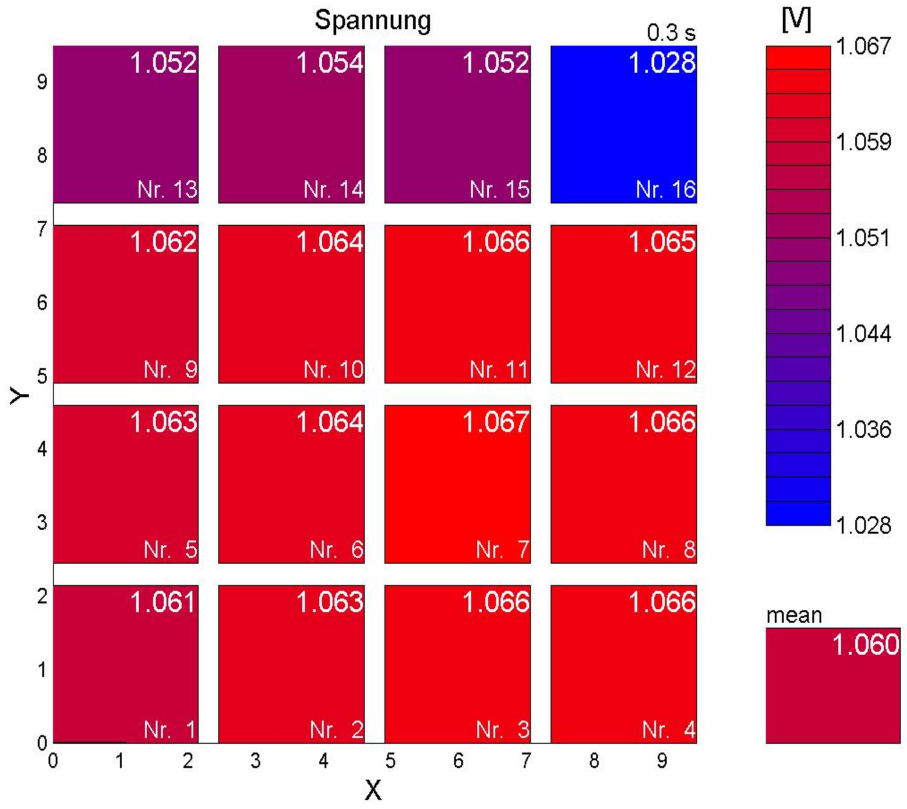




Determination of Steam Content at Operation with Reformate

- Voltage distribution at **standard flow rate:**
- 1.79 A/cm² current density equivalent, 50% H_2, 50% N_2 + 3% H_2O, 0,08 SlpM/cm² air





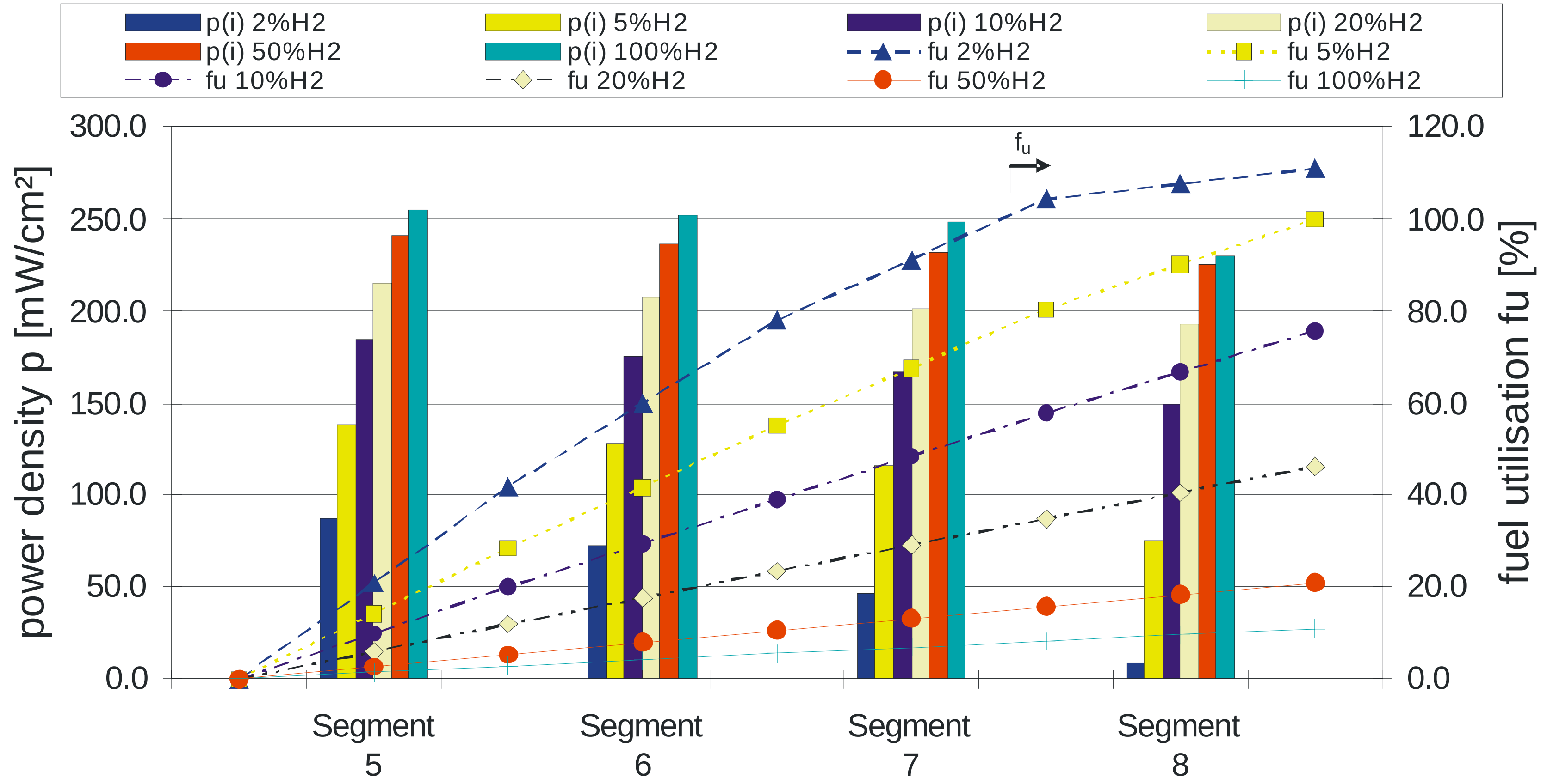
Nernst equation:

$$U_{rev} = U_{rev}^{0} - \frac{RT}{zF} \ln\left(\frac{p_{H2O}}{\sqrt{p_{O2}}\, p_{H2}} \right)$$

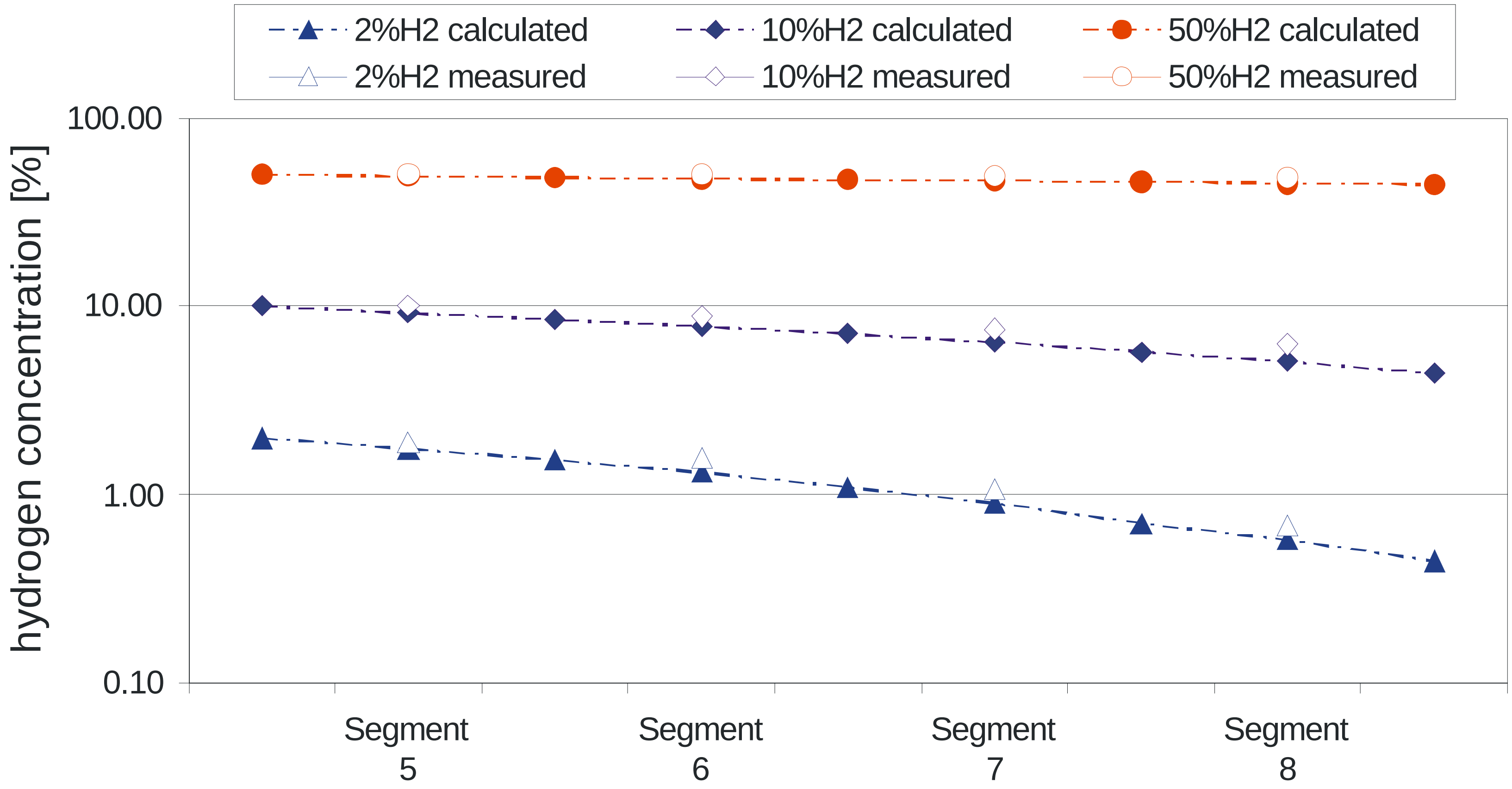
Chemically produced water:

S4: 0,61%, S8: 0,72%,
S12: 0,78%, S16: 3,30%

Locally Resolved Power Density Distribution and Fuel Utilisation in Dependence of H_2 Concentrations



Comparison of Calculated and Measured H_2 Concentration by Gas Chromatography For a Segment Row



Conclusion

- World wide increasing interest on metal supported SOFC cells, particularly for mobile application
- Long-term stability of the metallic support is an important requirement for metal supported cell technology
- Improvement of long-term cell operation by applying plasma sprayed diffusion barrier layer
- An adequate cell and stack design for plasma sprayed cells in cassette configuration has been developed
- The development of the metal supported SOFC concept has a high potential for SOFC application in dynamic operation with multiple thermal and redox cycles
- Spatially-resolved measuring techniques are important analytical tools to optimise cell operation