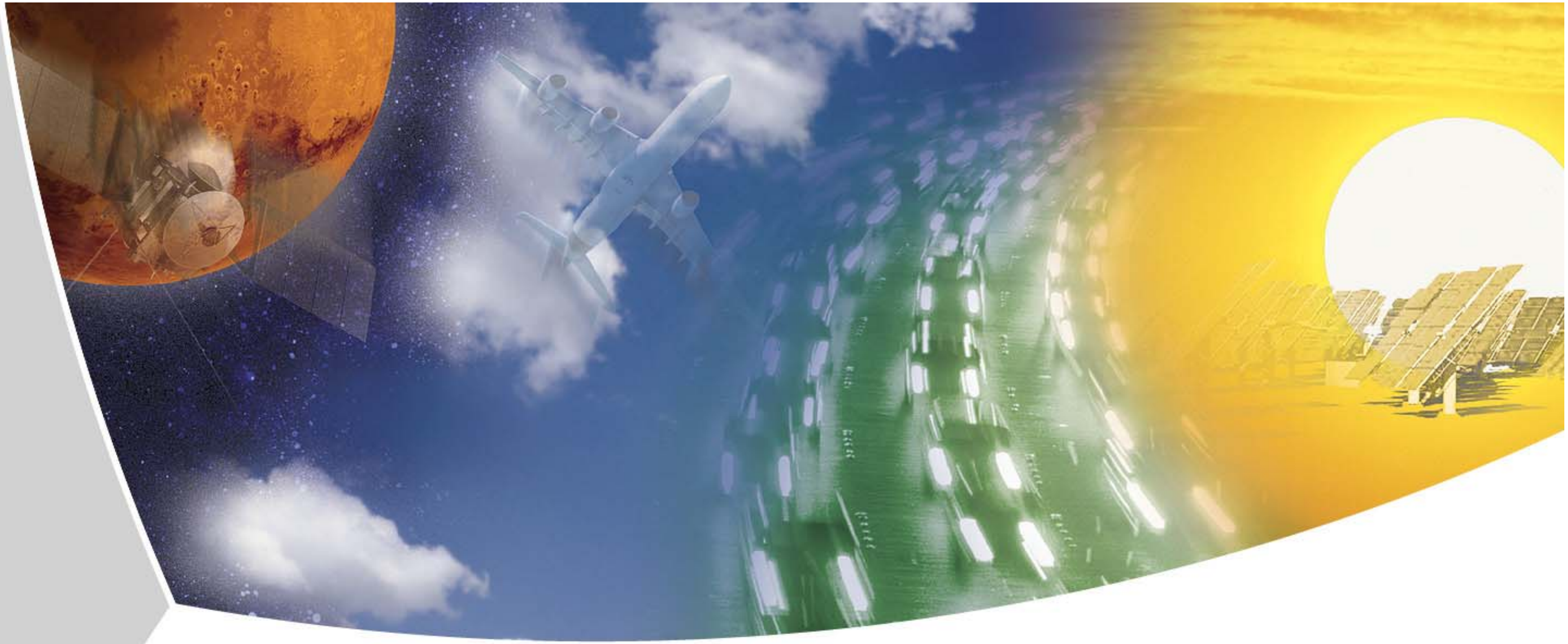


Development and Characterisation of Metal-Supported Solid Oxide Fuel Cells

G. Schiller

German Aerospace Center (DLR)
Institute of Technical Thermodynamics

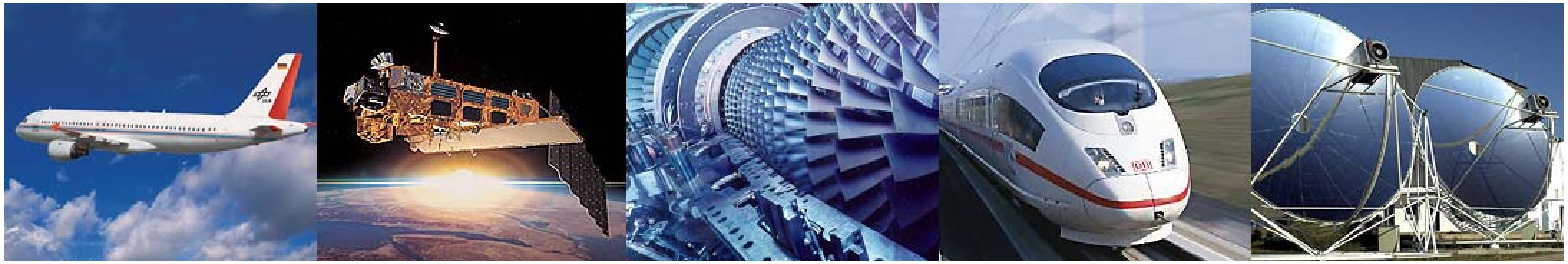
9th International Symposium on Advances in Electrochemical Science and Technology (ISAEST-9), December 2-4, 2010, Hotel Green Park, Chennai, India

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

Outline

- Introduction
  - German Aerospace Center (DLR)
  - SOFC Activities at DLR
- Development of Metal Supported SOFC Concept of DLR
  - Development of Functional Layers and Cells
  - Electrochemical Cell Performance
- Advanced Characterisation Techniques
  - Spatially Resolved Cell Characterisation
  - New Imaging Methods for SOFC Characterisation
- Conclusions

DLR
German Aerospace Center



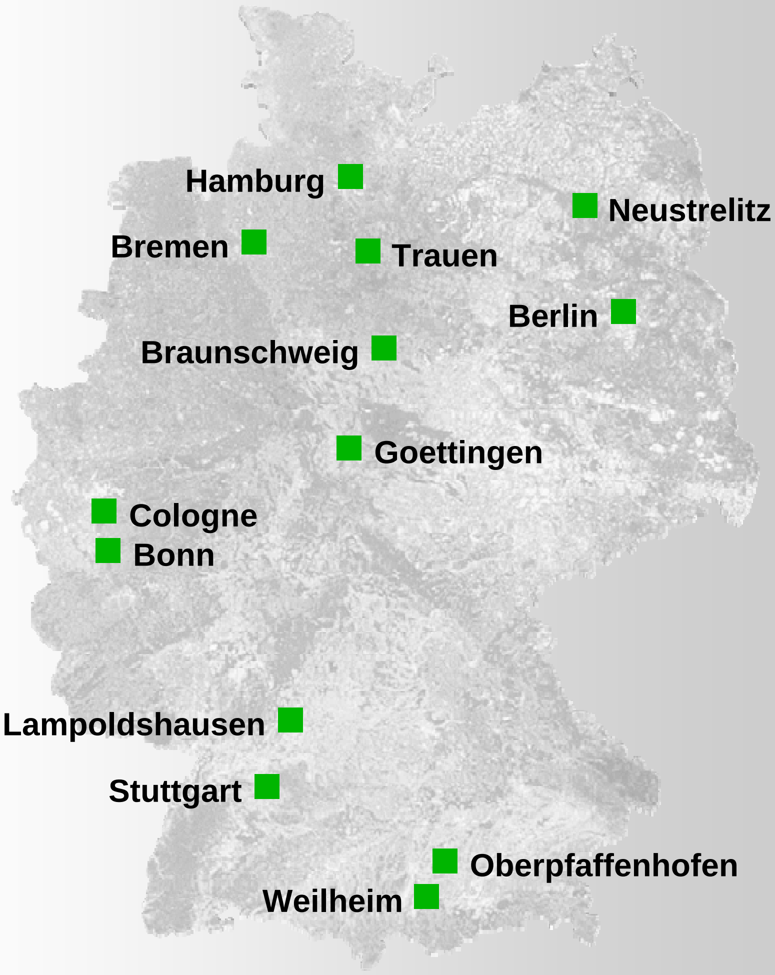
- Research Institution
- Space Agency
- Project Management Agency

Locations and Employees

6700 employees across
33 institutes and facilities at

- 13 sites.

Offices in Brussels,
Paris and Washington.



Research Areas

- Aeronautics
- Space
- Transport
- Energy
- Space Agency
- Project Management Agency

DLR Site Stuttgart

Employees: 560

Size of site: 25 860 m²

Research institutes:

- Institute of Structures and Design
- Institute of Vehicle Concepts
- Institute of Technical Physics
- Institute of Technical Thermodynamics
- Institute of Combustion Technology

Institute of Technical Thermodynamics

Prof. Dr. Dr.-Ing. *habil* H.Müller-Steinhagen

Solar Research
Prof. Dr.-Ing. R. Pitz-Paal

Electro-Chemical Energy Technology
Prof. Dr.rer.nat. A. Friedrich

Thermal Process Technology
Dr.rer.nat. R.Tamme

Systems Analysis and Technology Assessment
Dr.-Ing. W. Krewitt

Administration and Infrastructure
Dipl.-Wirt.Ing. J. Piskurek

Logistics & Purchasing

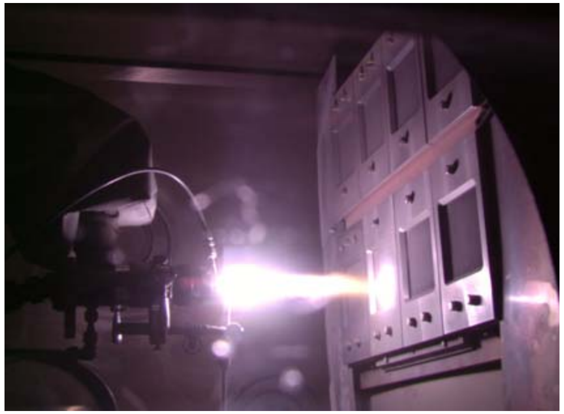
Project Administration

Computing Support

Workshops


Deutsches Zentrum für Luft- und Raumfahrt e.V.
DLR
Noordoostpolder
Hamburg
Neustrelitz
Trauen
Berlin
Braunschweig
Adlershof
Charlottenburg
Köln-Porz
Göttingen
Brüssel
Bonn
Bad Godesberg
Lampoldshausen
Paris
Stuttgart
Weilheim
Almería
Standorte
Außenstellen
Verbindungsbüros im Ausland
Deutsch-Niederländischer Windkanal
Standorte Institut TT

Development of Metal Supported Cells (MSC)

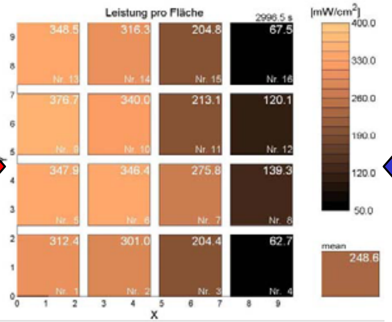


SOFC Activities at DLR

Characterization of Short Stacks and Stacks (ASC, MSC)

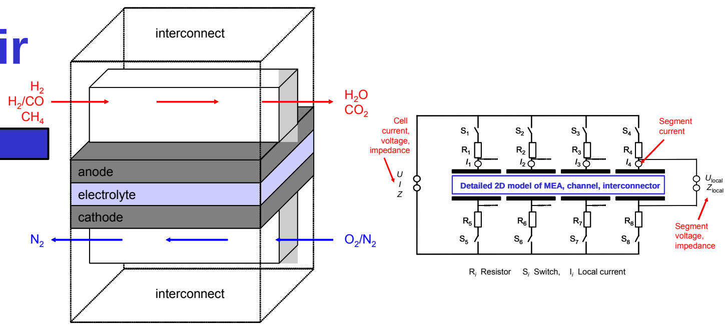
SOFC Diagnostics

Fuel gas



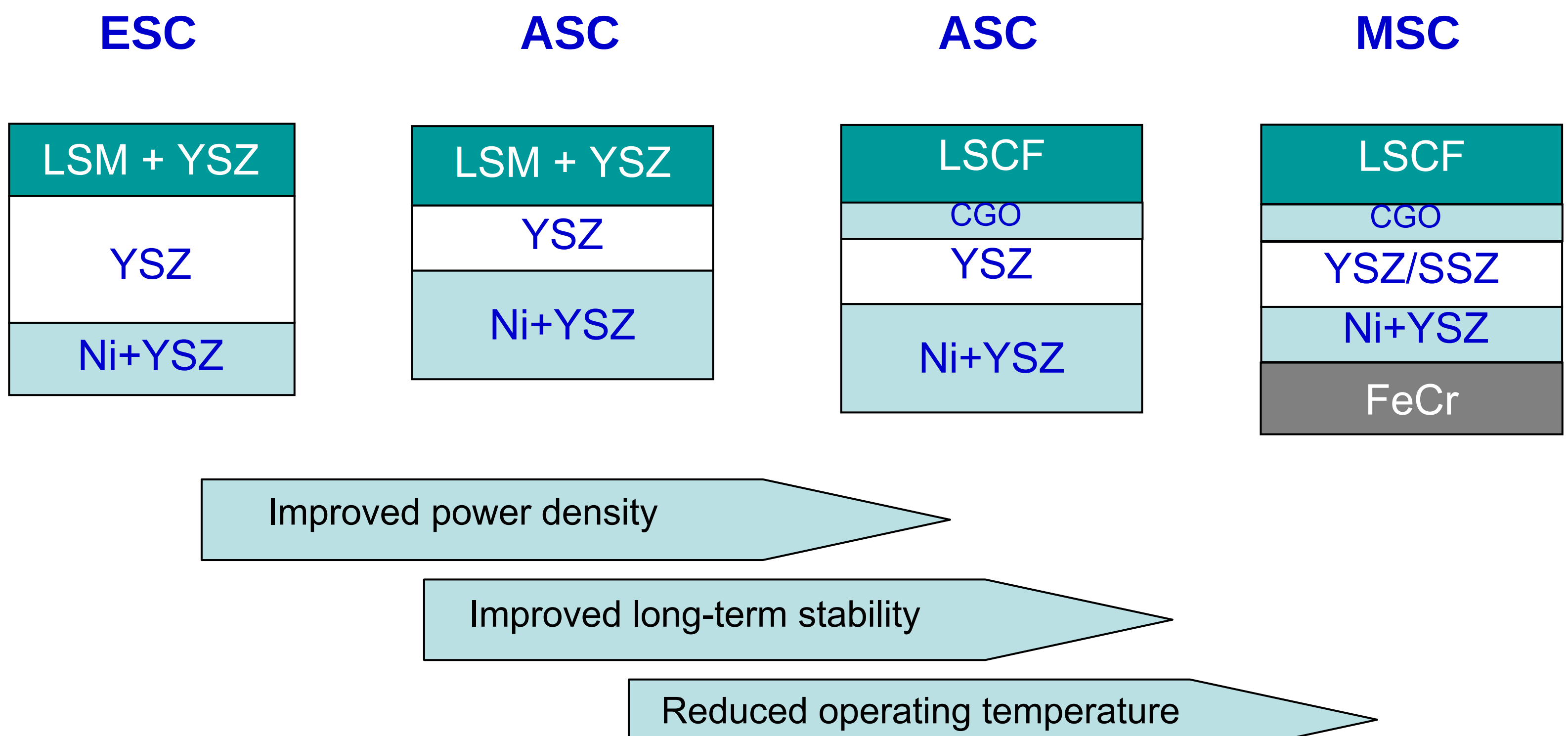
Air

SOFC Modeling



System Technology

Development of Metal Supported Cells



Advantages of MSC:

- **High robustness**
- **High resistance against thermal and redox cycling**
- **Good integration into interconnects (bipolar plates)**
- **Low cost of metal support and cell materials (thin layers)**

SOFC Metal Supported Cell

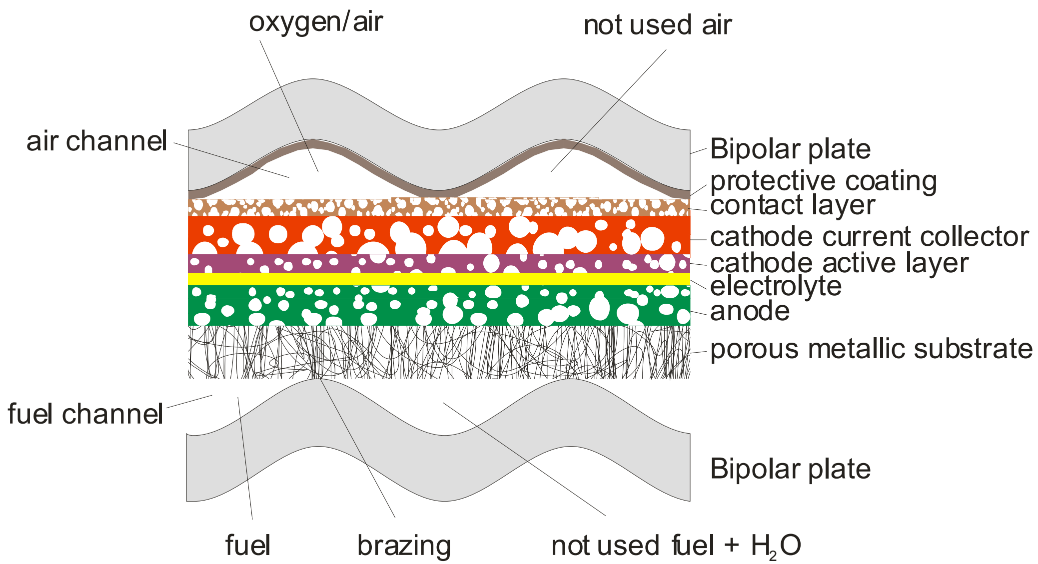
Plasma Deposition Technology

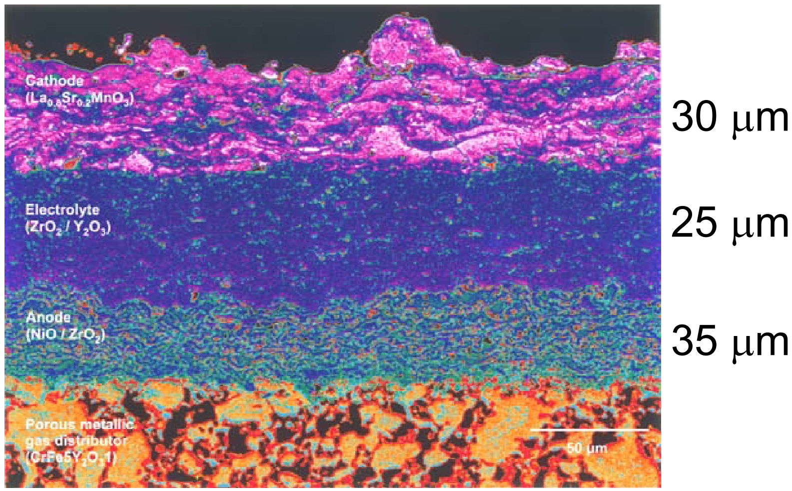
Thin-Film Cells

Ferritic Substrates and Interconnects

Compact Design with Thin Metal Sheet Substrates

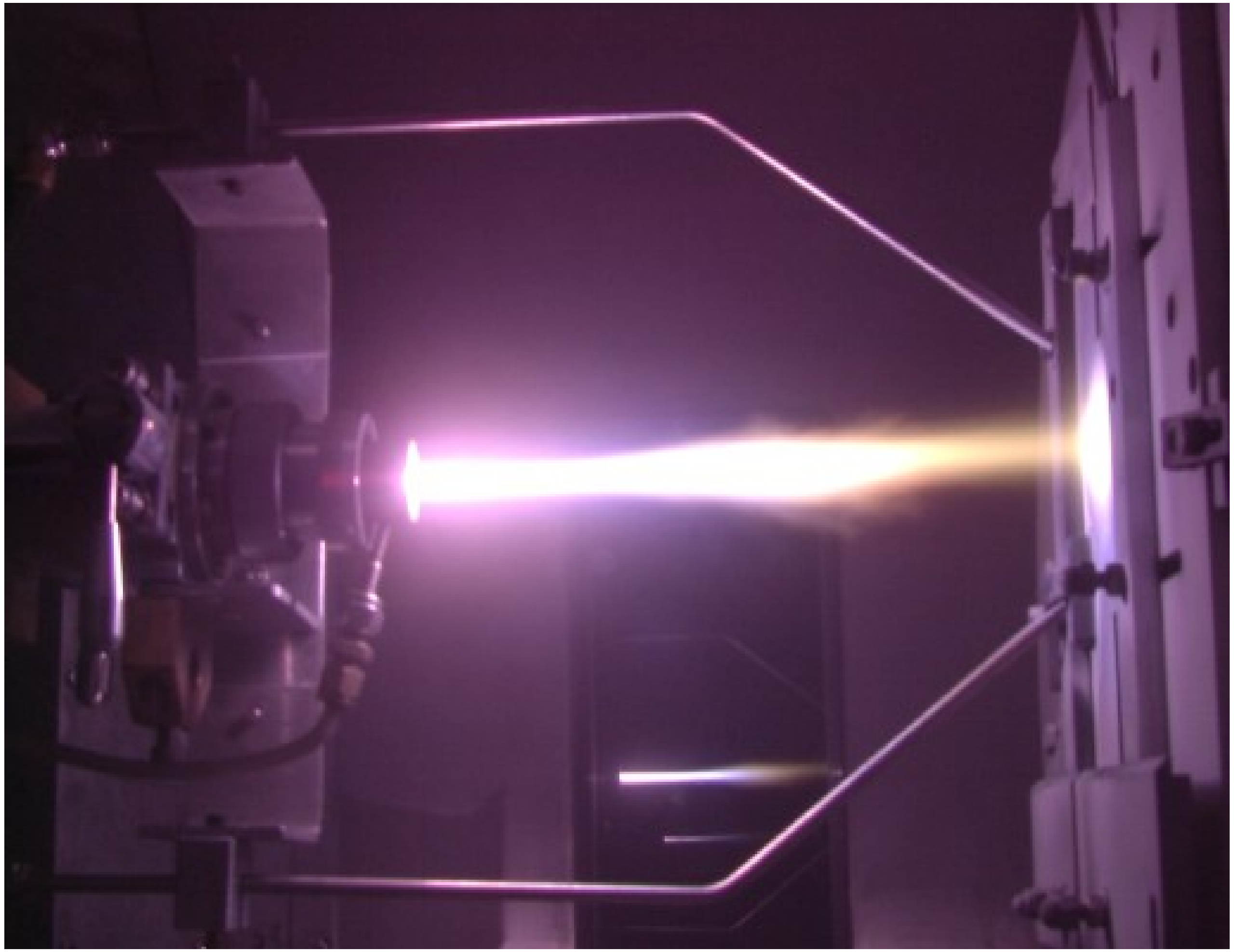
Brazing, Welding and Glass Seal as Joining and Sealing Technology



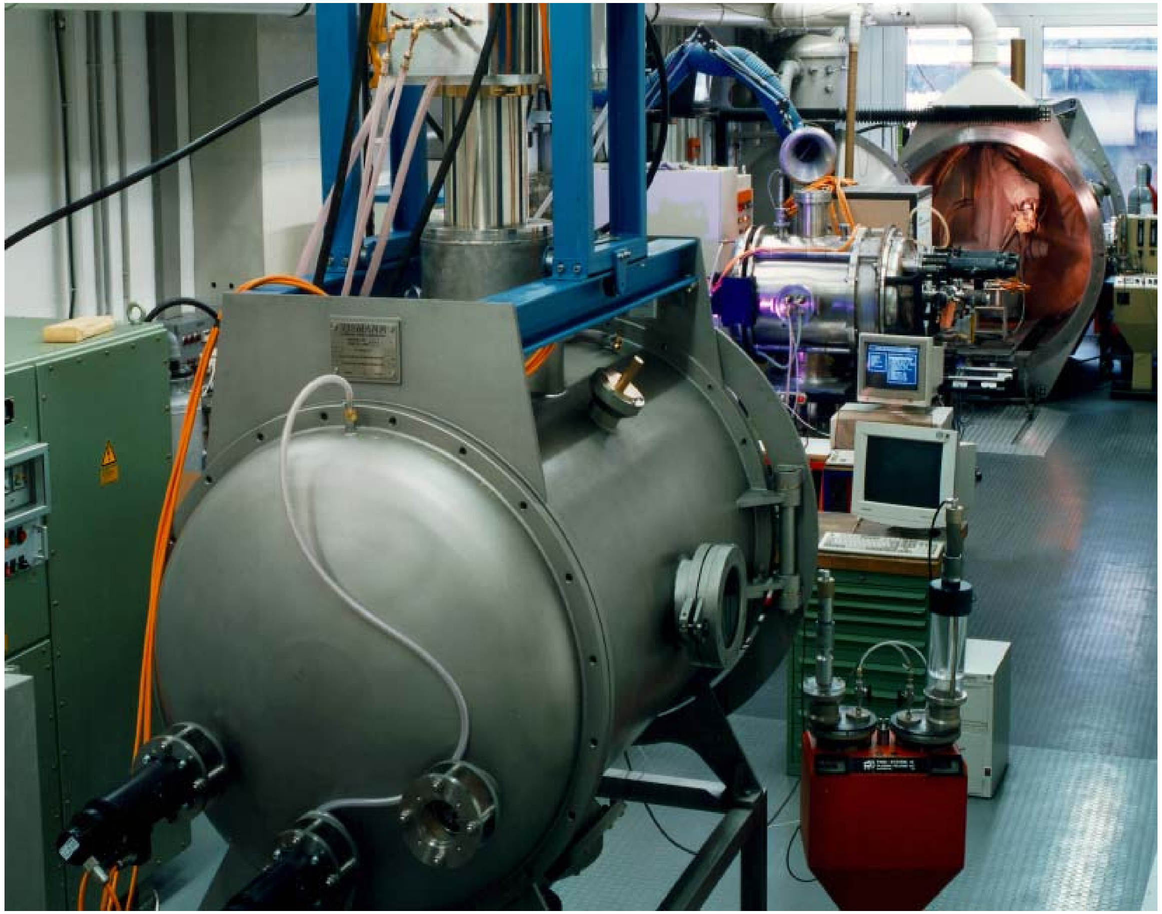


(not in scale)

Vacuum Plasma Spraying of SOFC Cells

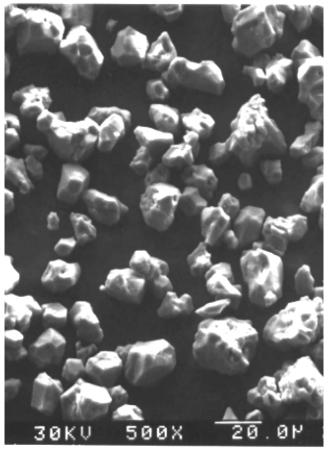


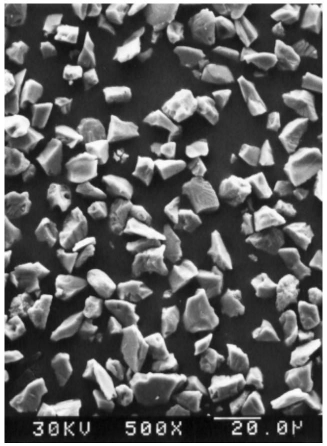
Plasma Spray Laboratory at DLR Stuttgart

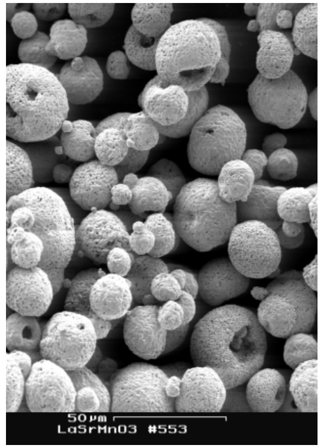


Powders Used for the Spraying of the Cells

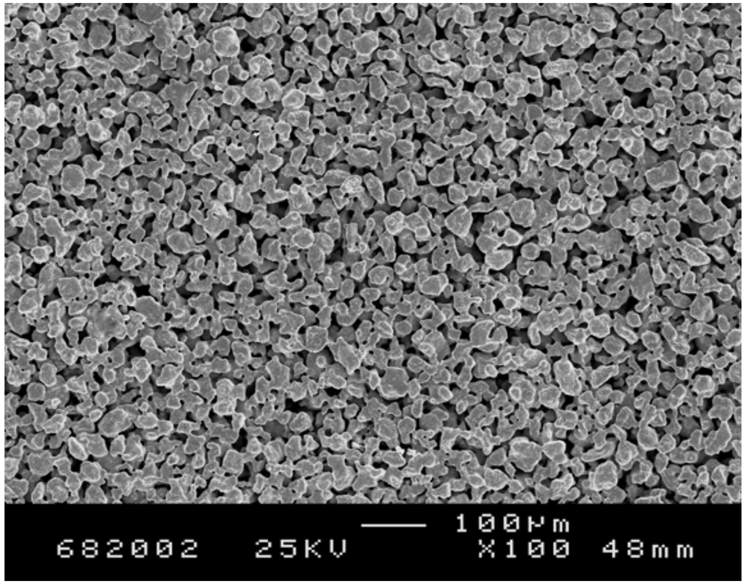
Powder	NiO	ZrO_2- 7 mol %Y_2O_3	ZrO_2- 10 mol%Sc_2O_3	$(La_{0.8}Sr_{0.2})_{0.98}$ MnO_3
Short name	NiO	YSZ	ScSZ	LSM
Morphology	sintered, crushed	sintered, crushed	sintered, crushed	sintered, spherical
Size distribution	10-25 µm	5-25 µm	2-35 µm	20-40 µm
Supplier	Cerac, USA	Medicoat, Switzerland	Kerafol,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

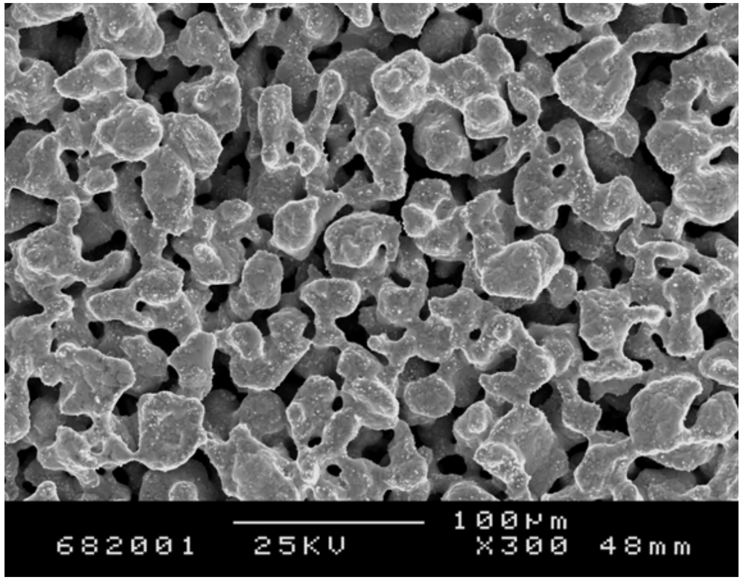




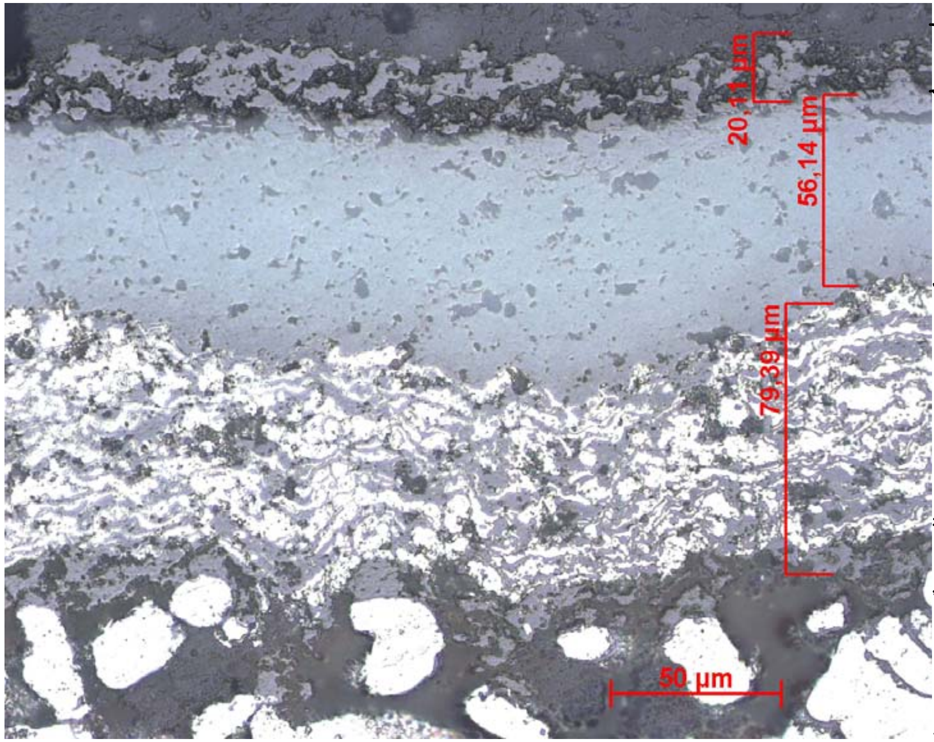


Morphology of Porous Metal Substrate PM Fe-26Cr-(Mo,Ti,Mn,Y_2O_3) of Plansee SE





Metallographic Cross Section of MSC Cell



$LaSrMnO_3$-cathode

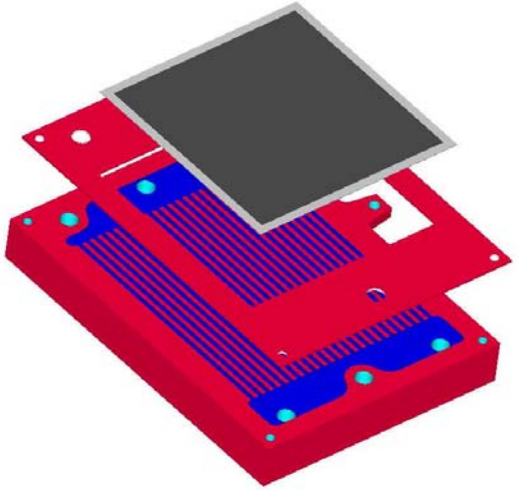
8YSZ-electrolyte

Ni/8YSZ-anode

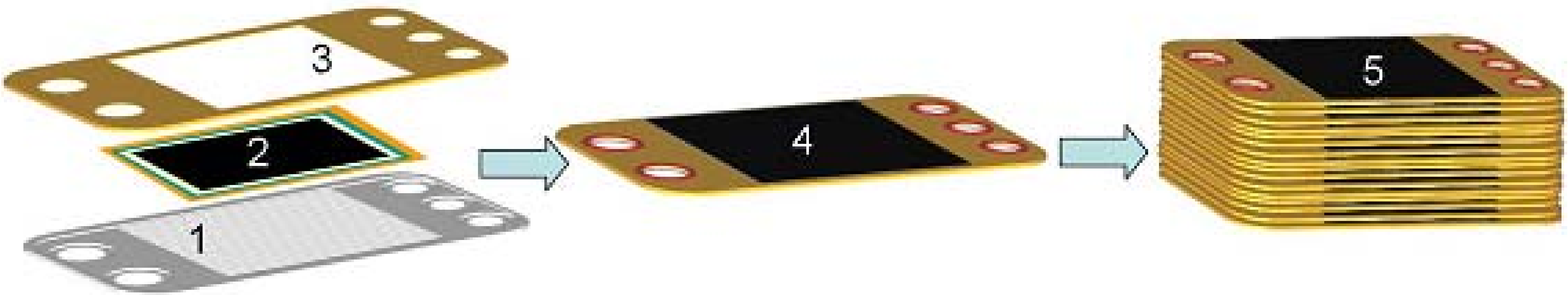
Perovskite-type barrier layer

Porously sintered ferrite plate

Stack Assembly Based on Metal Supported Cell



Plasma-spayed cell with sealing by laser welding



1 = Metallic lower plate
2 = Active cell on substrat
3 = Metallic frame

4 = Cassette

5 = Stack

Stack Assembly Based on Metal Supported Cell

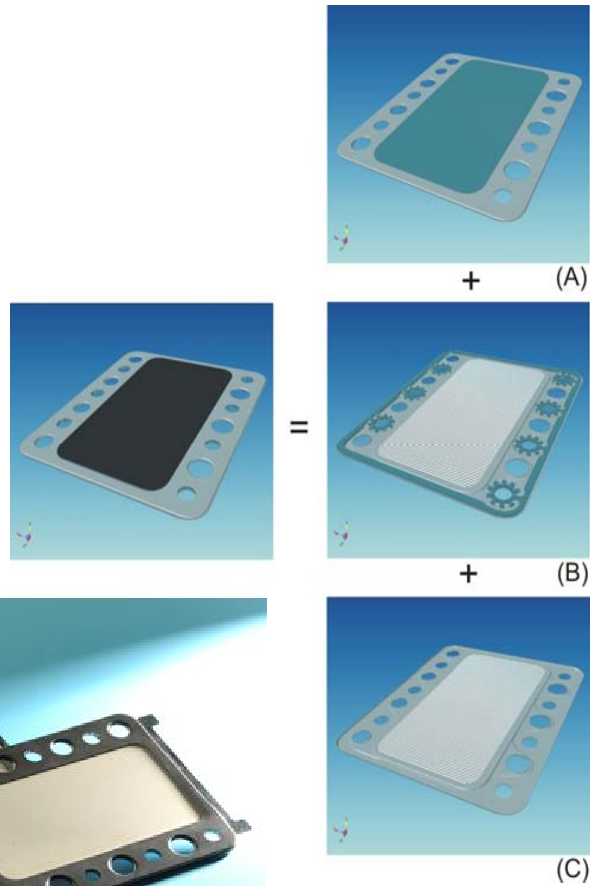
Current MS-SOFC Repeat Unit

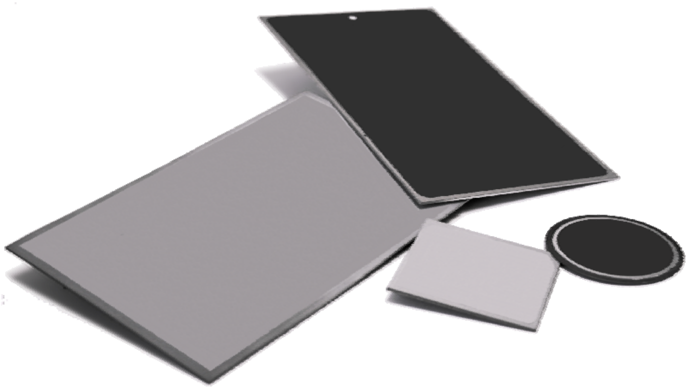
90x120 mm² footprint – ca 100 cm² cell area

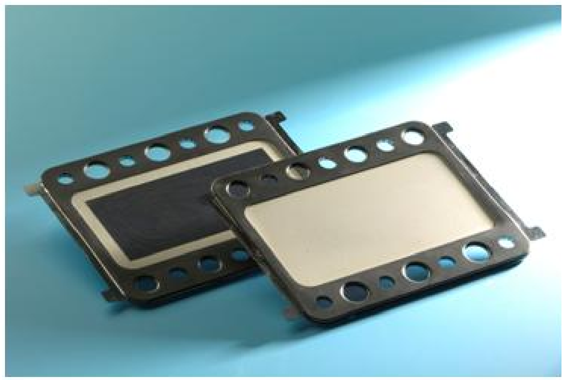
Counter flow design

Stamped sheet ferritic steel bipolar plate

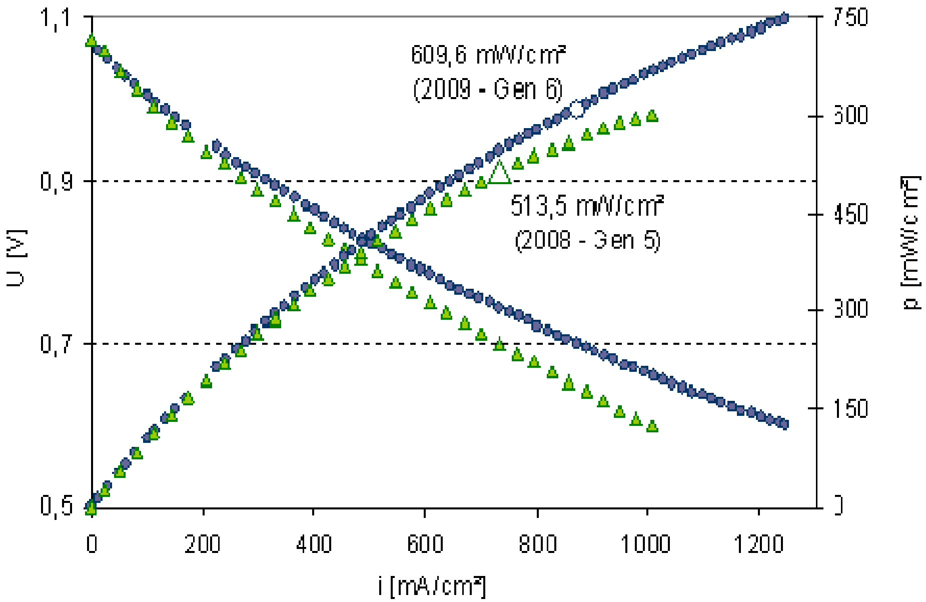
Welded Fe-Cr substrate

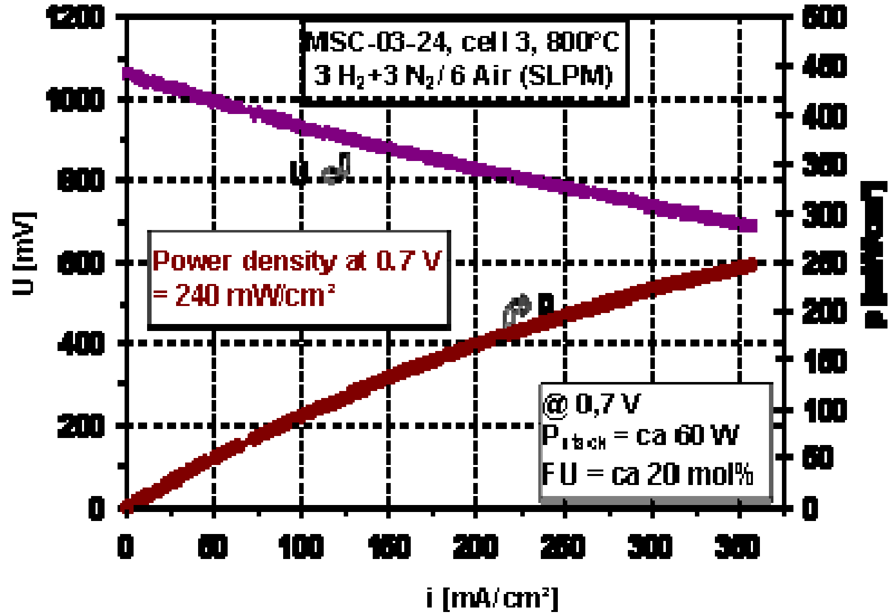






Performance of Plasma Sprayed Metal Supported Cell





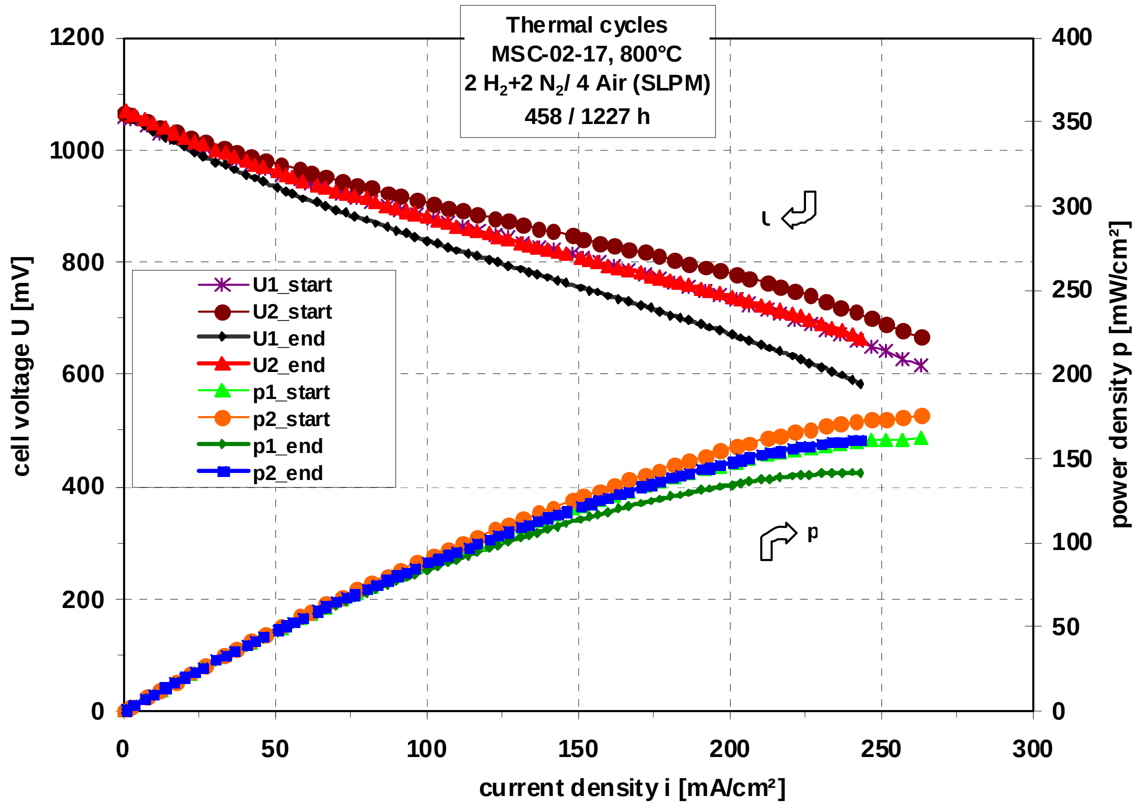
MSC Cell

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

3-Cell Stack

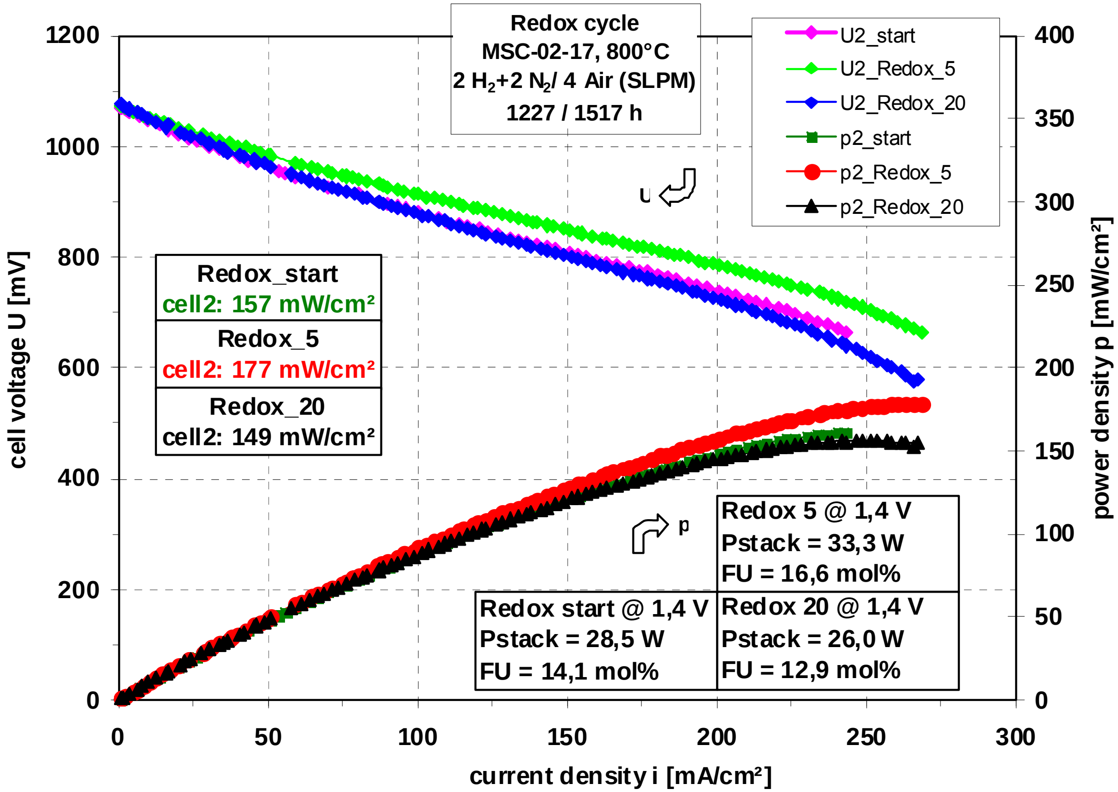
100 cm² single cells at 800°C; H_2/N_2; Air

Thermal Cycling



- 15 thermal cycles performed, 12 down to 350 °C and 3 to ambient temperature
- Degradation after thermal cycles was 10.3 %

Redox Cycling



- 20 forced redox cycles performed with 50 ml/min O_2 on the anode side per layer
- Increase of power density after 5 cycles
- Degradation of the stack was 9.1 % after 20 redox cycles

Investigation of Degradation and Cell Failures

- Insufficient understanding of cell degradation and cell failures in SOFC
- Extensive experimental experience is not generally available which would allow accurate analysis and improvements
- Long term experiments are demanding and expensive
- Only few tools and diagnostic methods available for developers due to the restrictions of the elevated temperatures

„Sophisticated“ (non-traditional) In-situ Diagnostics

- Electrochemical impedance spectroscopy on stacks
- Spatially resolved measuring techniques for current, voltage, temperature
- and gas composition
- Optical imaging
- Optical spectroscopy
- Acoustic emission detection
- X-ray tomography

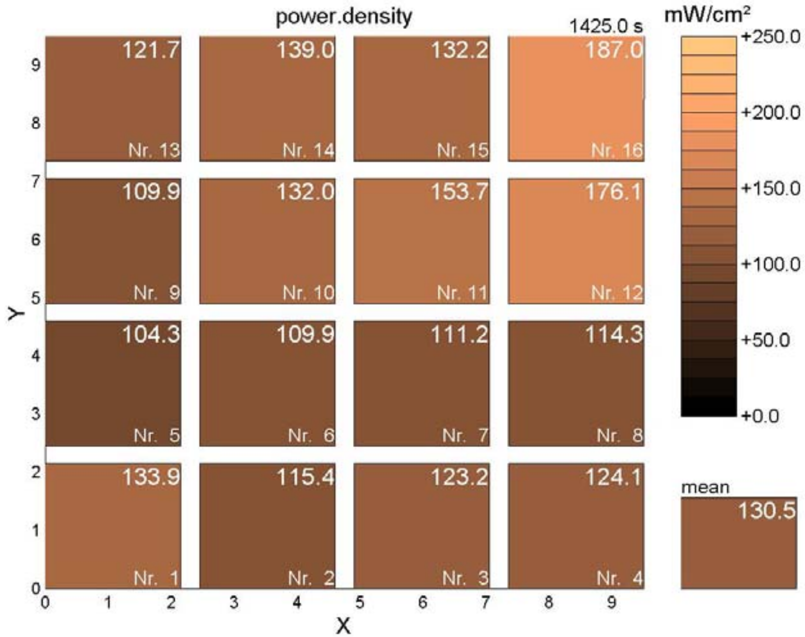
Motivation for Spatially Resolved Cell Characterisation

Problems:

- Strong local variation of gas composition, temperature, and current density

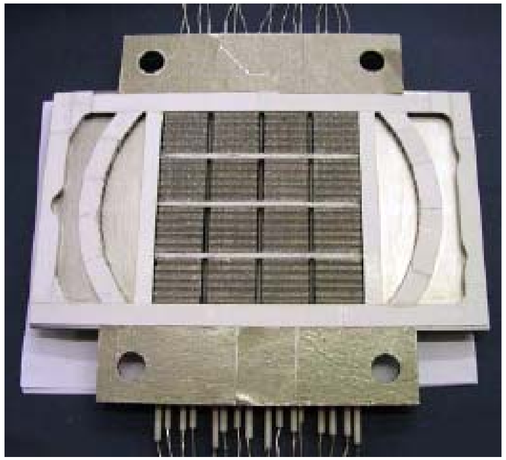
This may lead to:

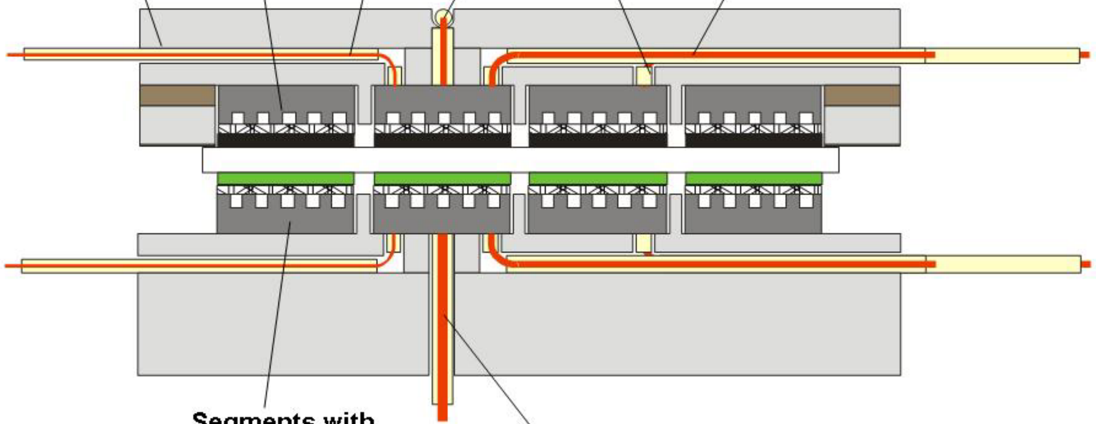
- Reduced efficiency
- Thermomechanical stress
- Degradation of electrodes



Effects are difficult to understand due to the strong interdependence of gas composition, electrochemical performance and temperature

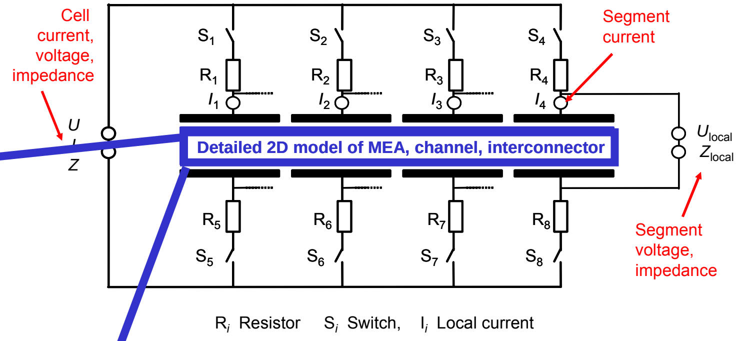
Measurement Setup for Segmented Cells

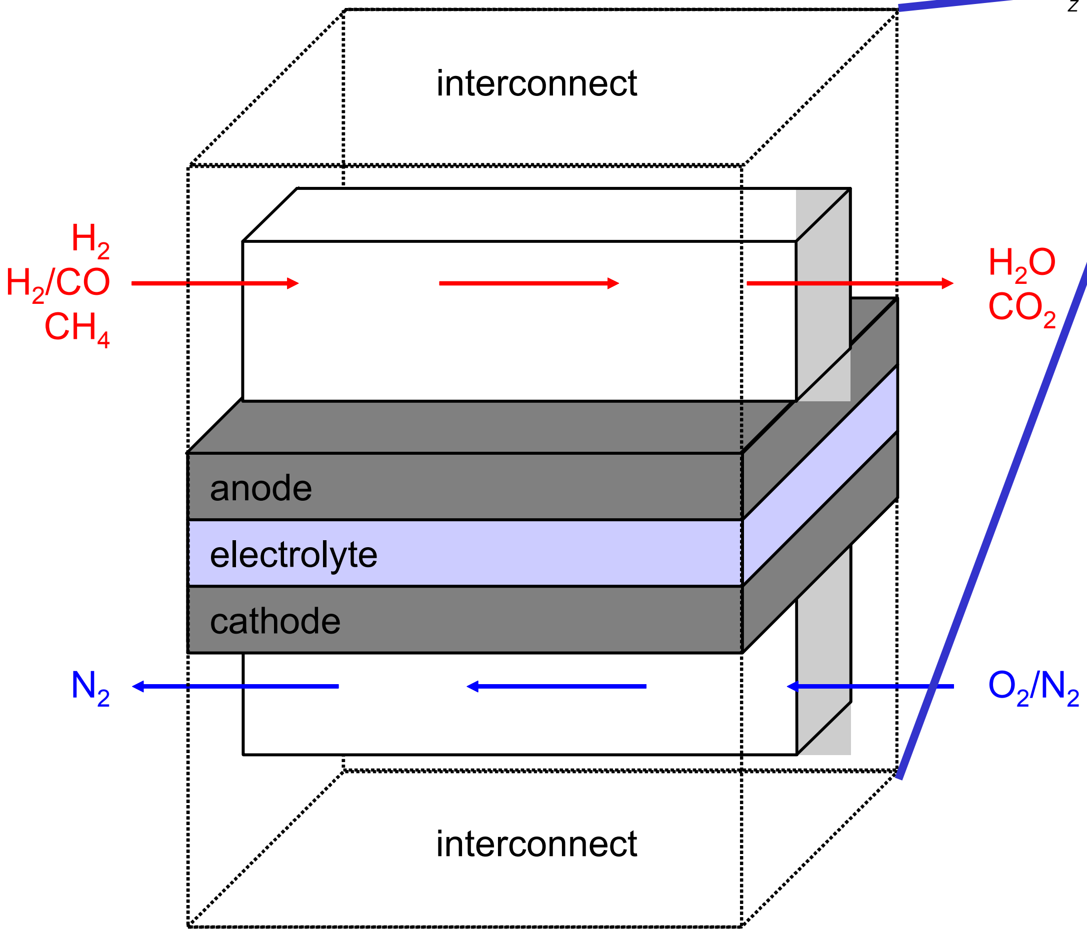




- 16 galvanically isolated segments
- Local and global i-V characteristics
- Local and global impedance measurements
- Local temperature measurements
- Local fuel concentrations
- Flexible design: substrate-, anode-, and electrolyte-supported cells
- Co- and counter-flow

Modelling and Simulation





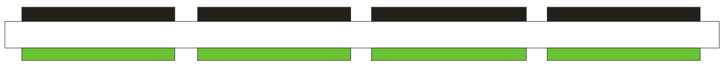
- Electrochemistry: Elementary kinetics
- Porous electrodes: Mass and charge transport
- Channels: Transient Navier-Stokes conservation equations (Mass, momentum, particles, energy)
- Interconnects: energy conservation

W. G. Bessler, S. Gewies, and M. Vogler, Electrochimica Acta 53, 1782-1800 (2007)

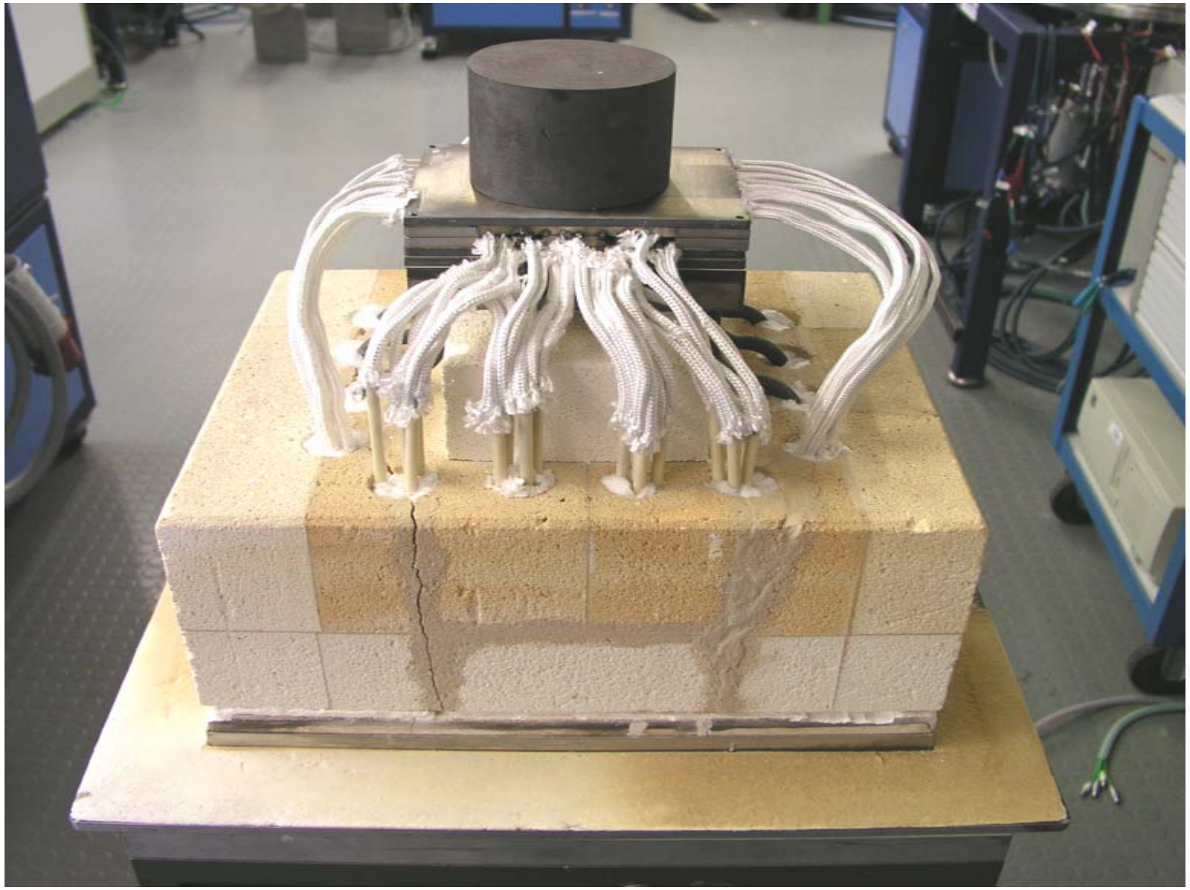
Segmented Cells

- Anode supported cells:
  Segmented cathode
  (H.C.Starck/InDEC)

- Electrolyte supported cells:
  Segmented cathode and anode

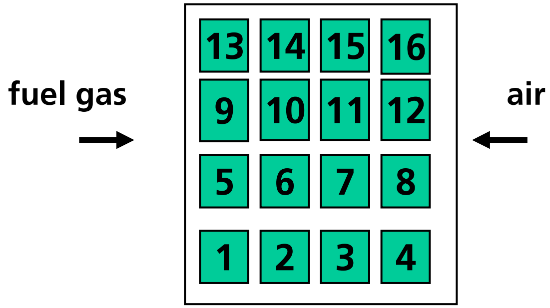


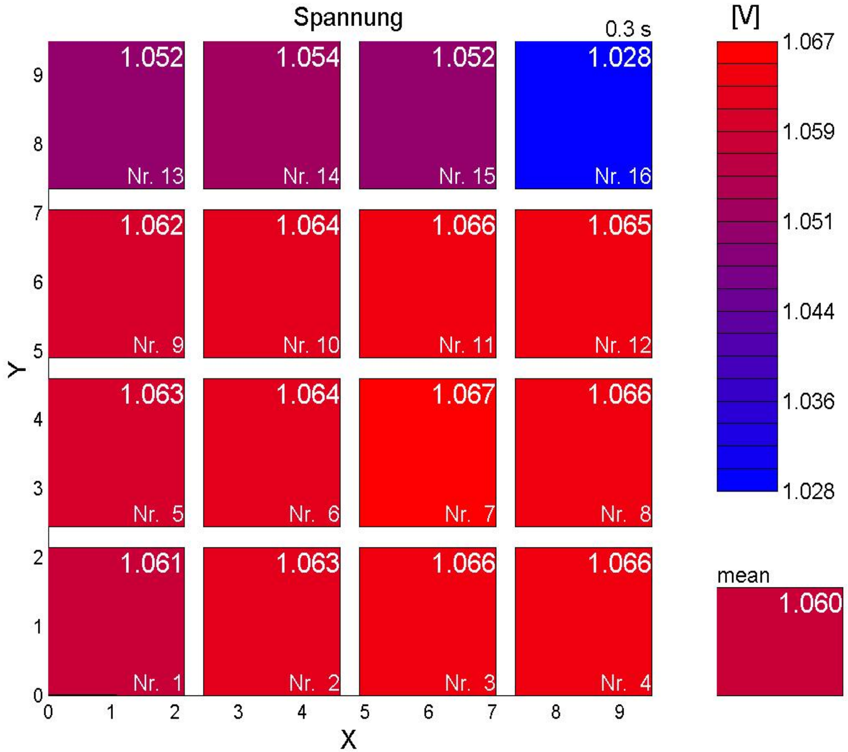
Test Rig



OCV Voltage Measurement for Determination of Humidity

- Voltage distribution at standard flow rates:
- 50% H_2, 50% N_2 + 3% H_2O, 0.08 SlpM/cm² air





Nernst equation:

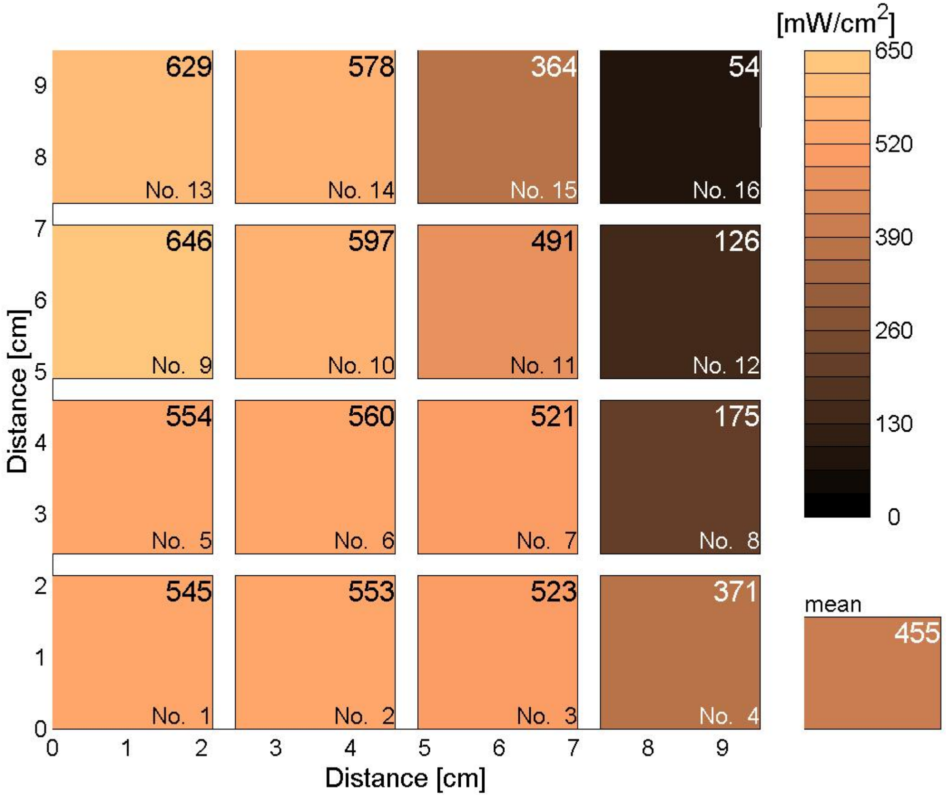
$$U_{rev} = U_{rev}^{0} - \frac{RT}{zF} \ln\left(\frac{p_{H2O}}{\sqrt{p_{O2}}\, p_{H2}} \right)$$

Produced water:

S4: 0.61%, S8: 0.72%,

S12: 0.78%, S16: 3.30%

Power Density Distributution under Conditions of High Fuel Utilisation



Counter-flow

Anode: 33% H_2, 1% H_2O, 66% N_2

Cathode: air

T = 800 °C

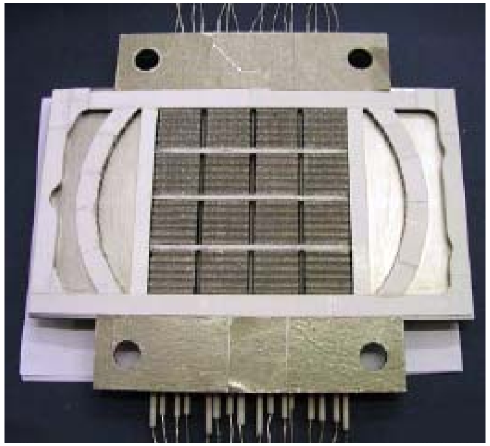
Cell voltage: 0.59 V

F_u = 80%

Lit.: Fuel Cells, 10 (3), 411-418 (2010)

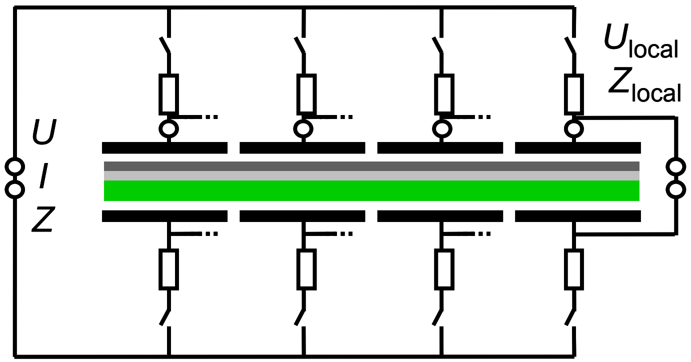
Assessment of Local Performance with Segmented SOFCs

- **Experiment**

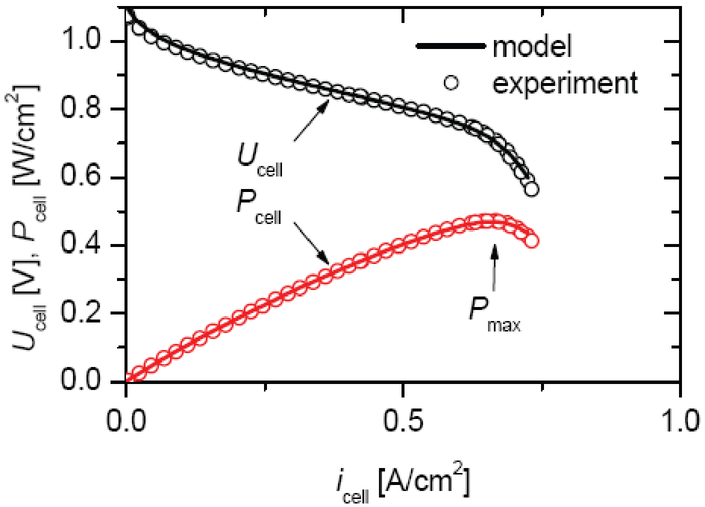


16 segments

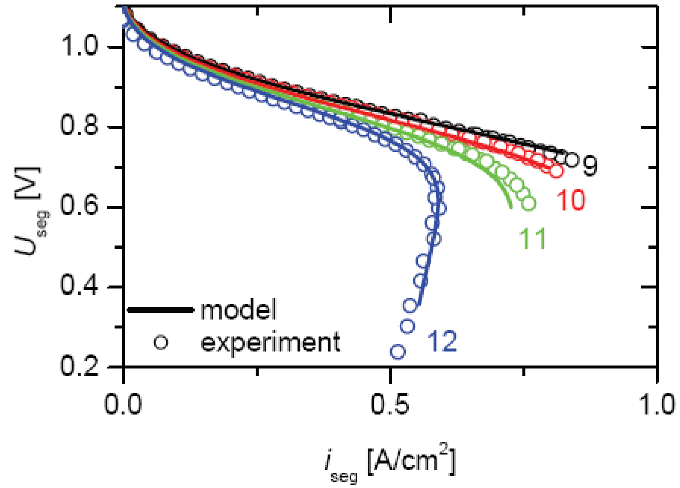
- **Model**



Global behavior

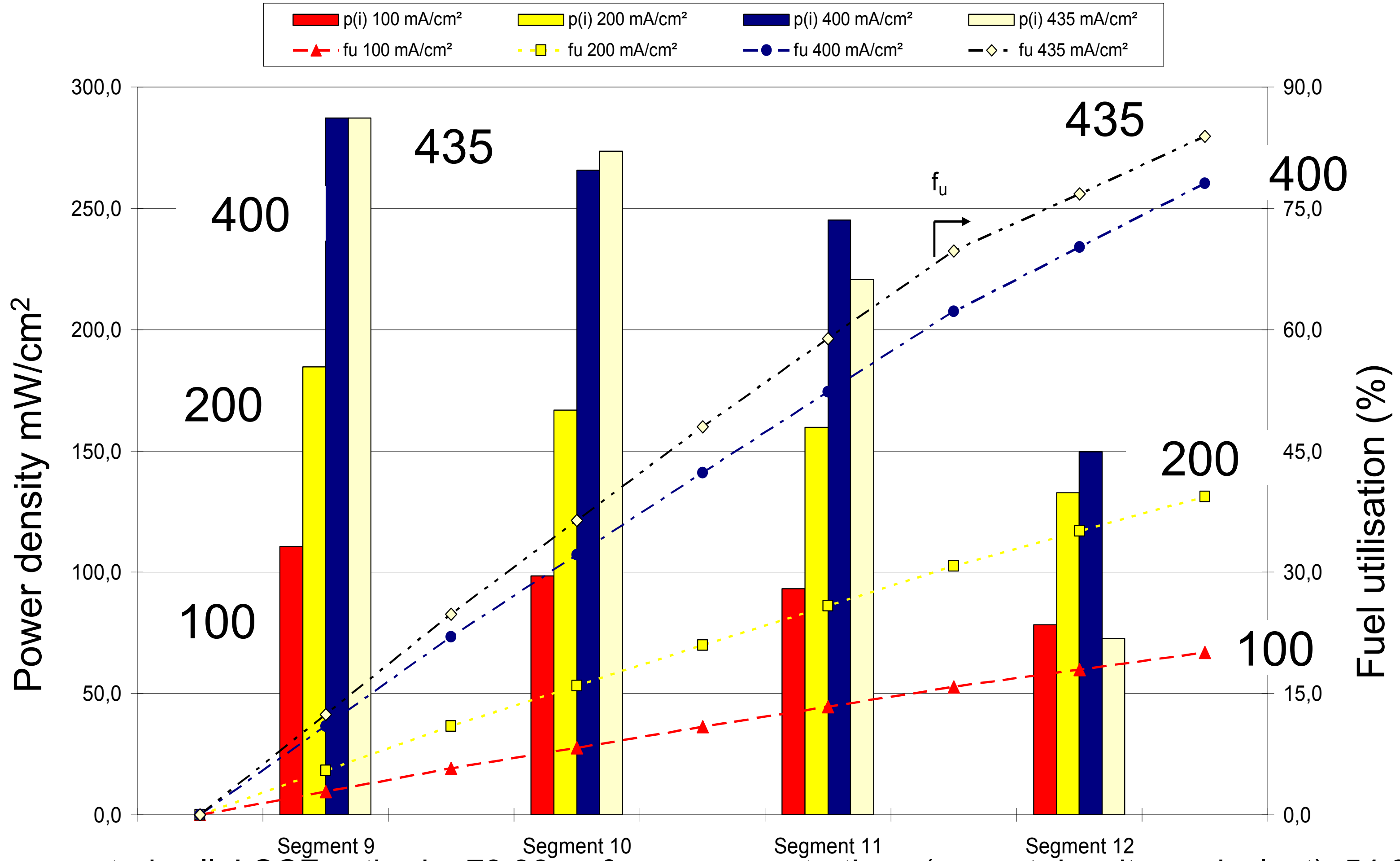


Local behavior



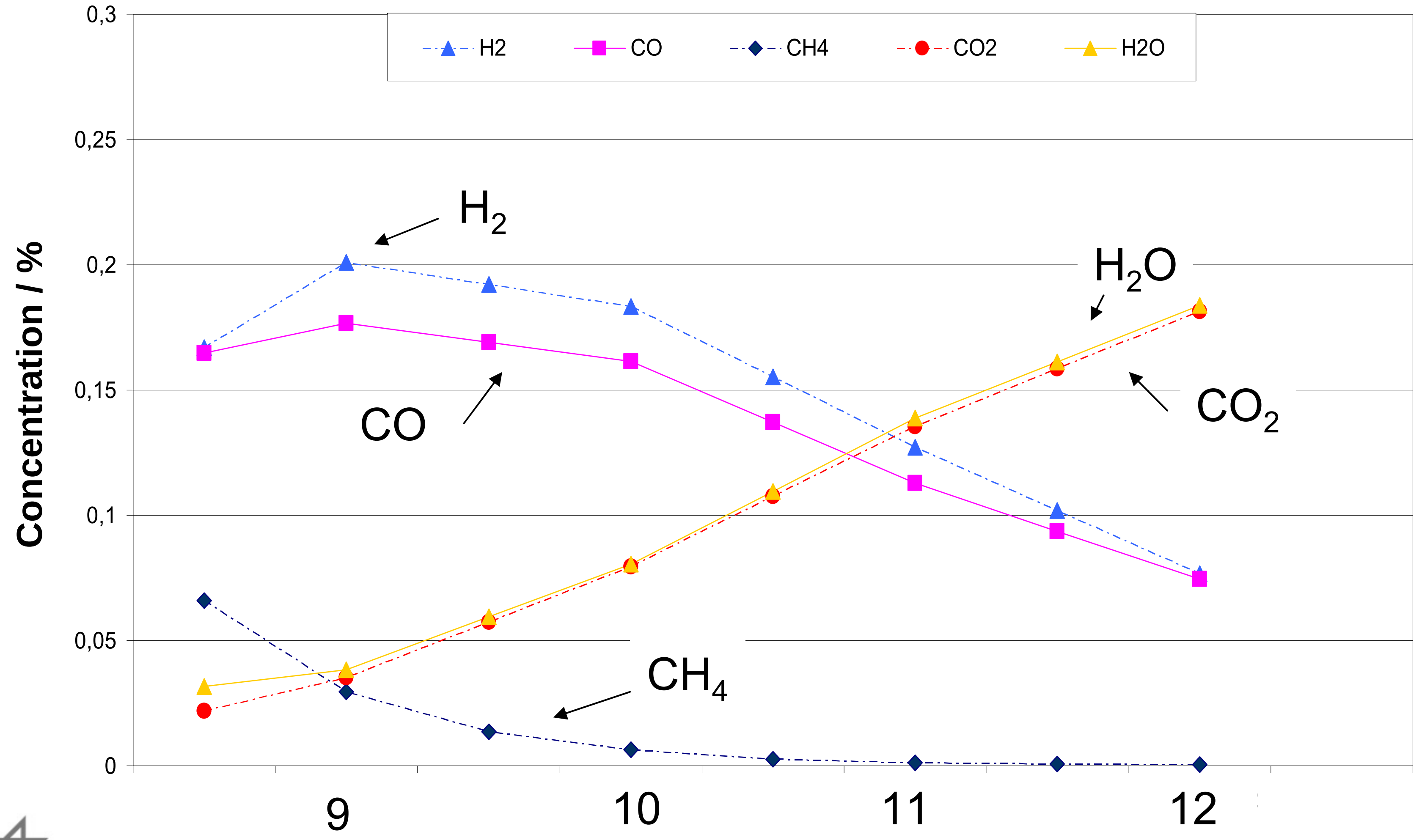
Cell can be locally in critical conditions!

Variation of Load - Reformate

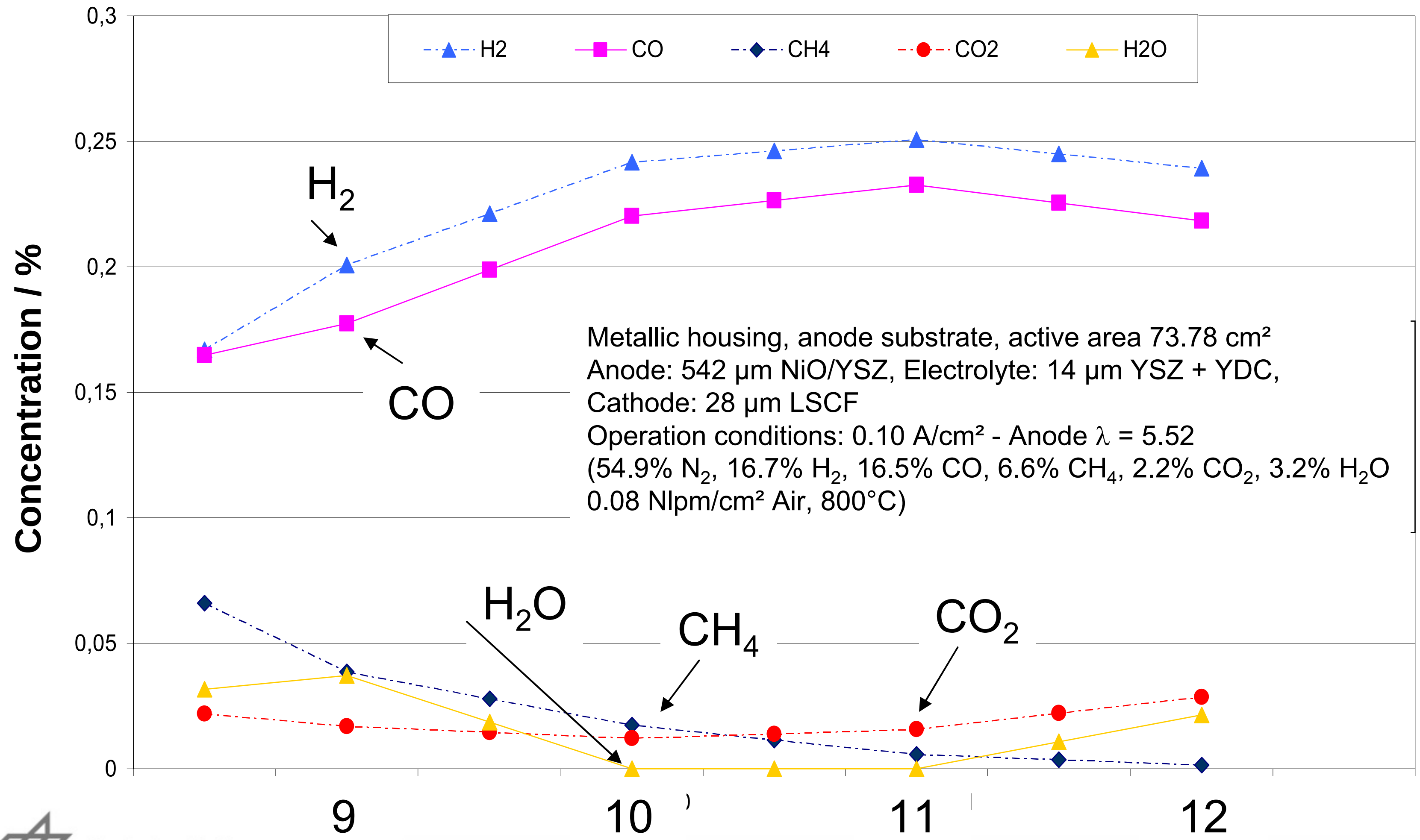


Anode supported cell, LSCF cathode, 73,96 cm², gas concentrations (current density equivalent): 54.9% N_2, 16.7% H_2, 16.5% CO, 6,6% CH_4, 2.2% CO_2, 3.2% H_2O (0.552 A/cm²), 0.02 SlpM/cm² air

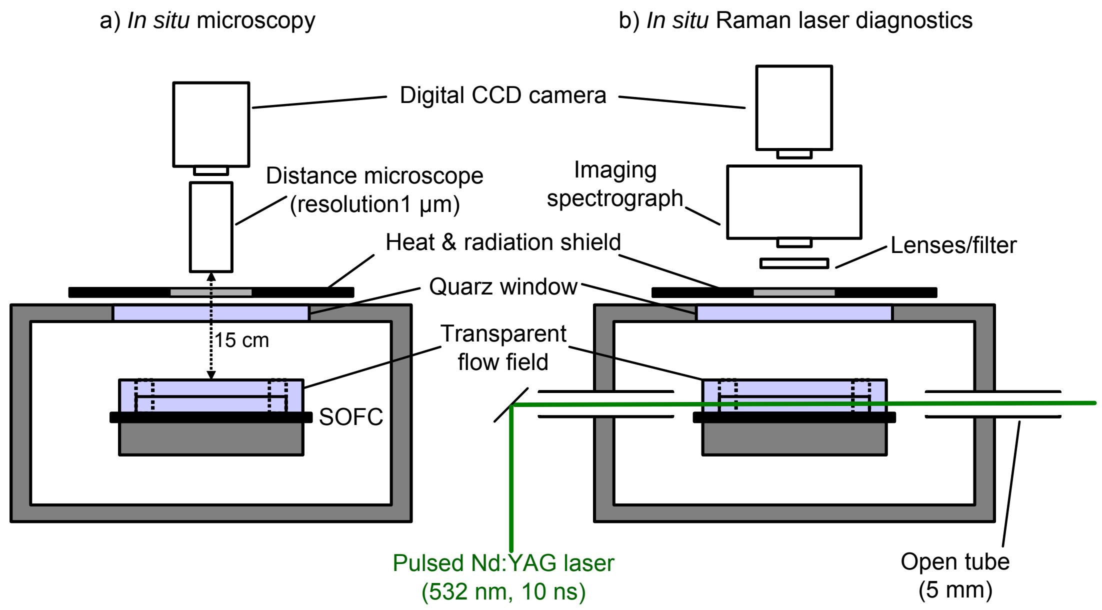
Alteration of the Gas Composition at 435 mA/cm²



Alteration of the Gas Composition at 100 mA/cm²



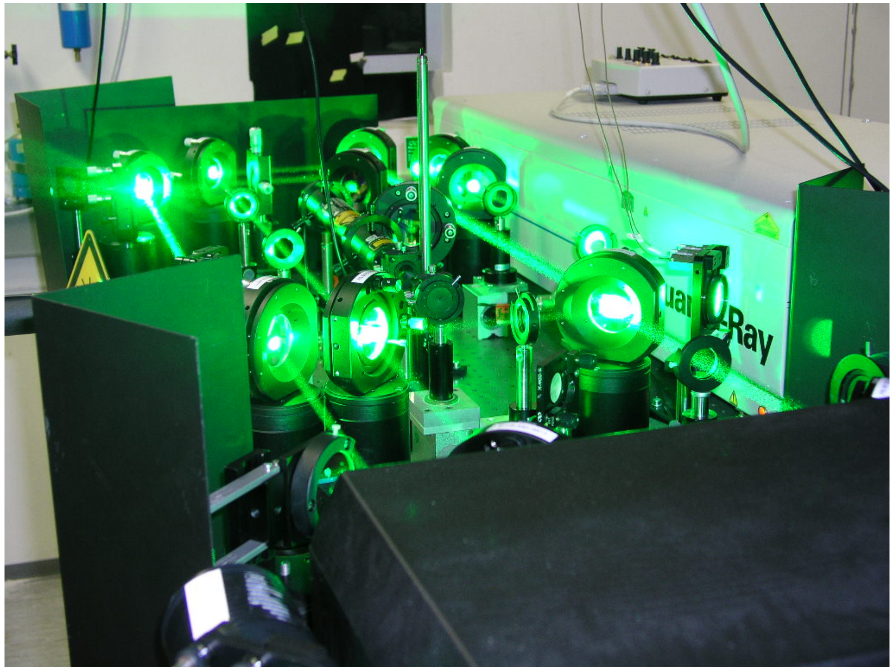
Potential for Optical Spectroscopies



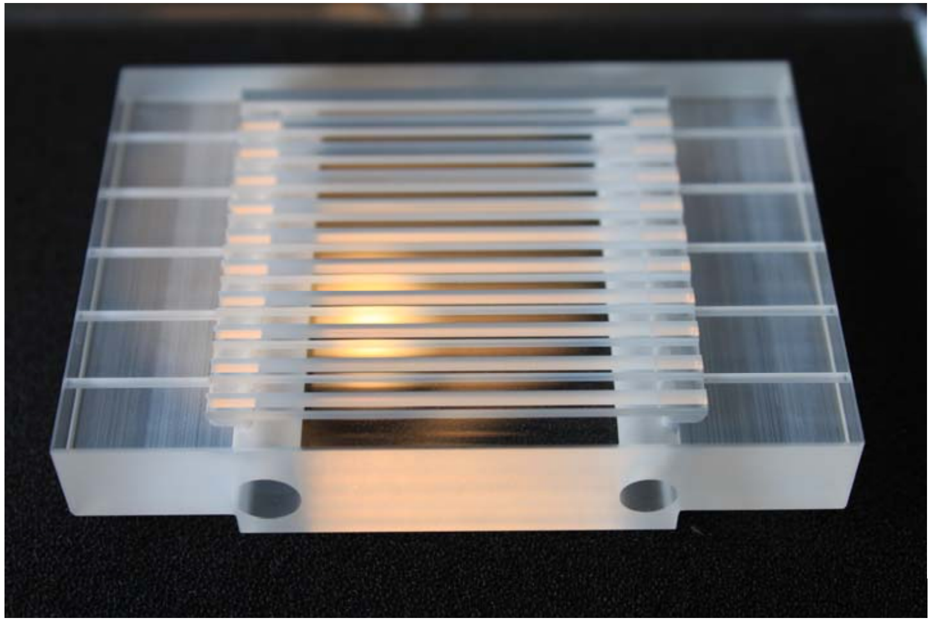
- Raman spectroscopy
- Laser Doppler Anemometry (LDA)
- Particle Image Velocimetry (PIV)
- Fast-Fourier Infrared (FTIR)
- Coherent Anti-Stokes Raman Spectroscopy (CARS)
- Electronic Speckle Pattern Interferometry (ESPI)

Setup for 1D-Raman Spectroscopy

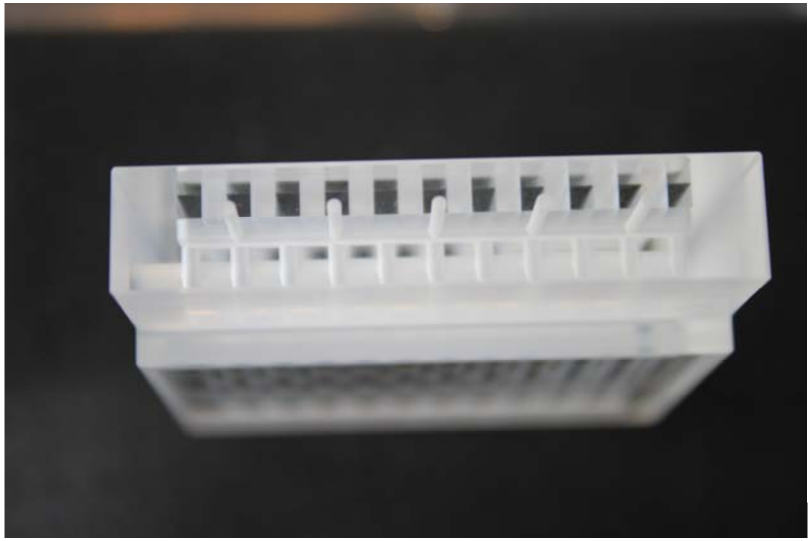
- 3 double pulse Nd:YAG PIV 400 laser systems
- λ = 532 nm
- Repetition rate: 10 Hz
- Single pulse: E ≤ 350 mJ / ~7 ns
- Pulse energy: 6 x 300 mJ
- Pulse length: ~380 ns
- (temporal resolution)



Transparent Flowfield for SOFC

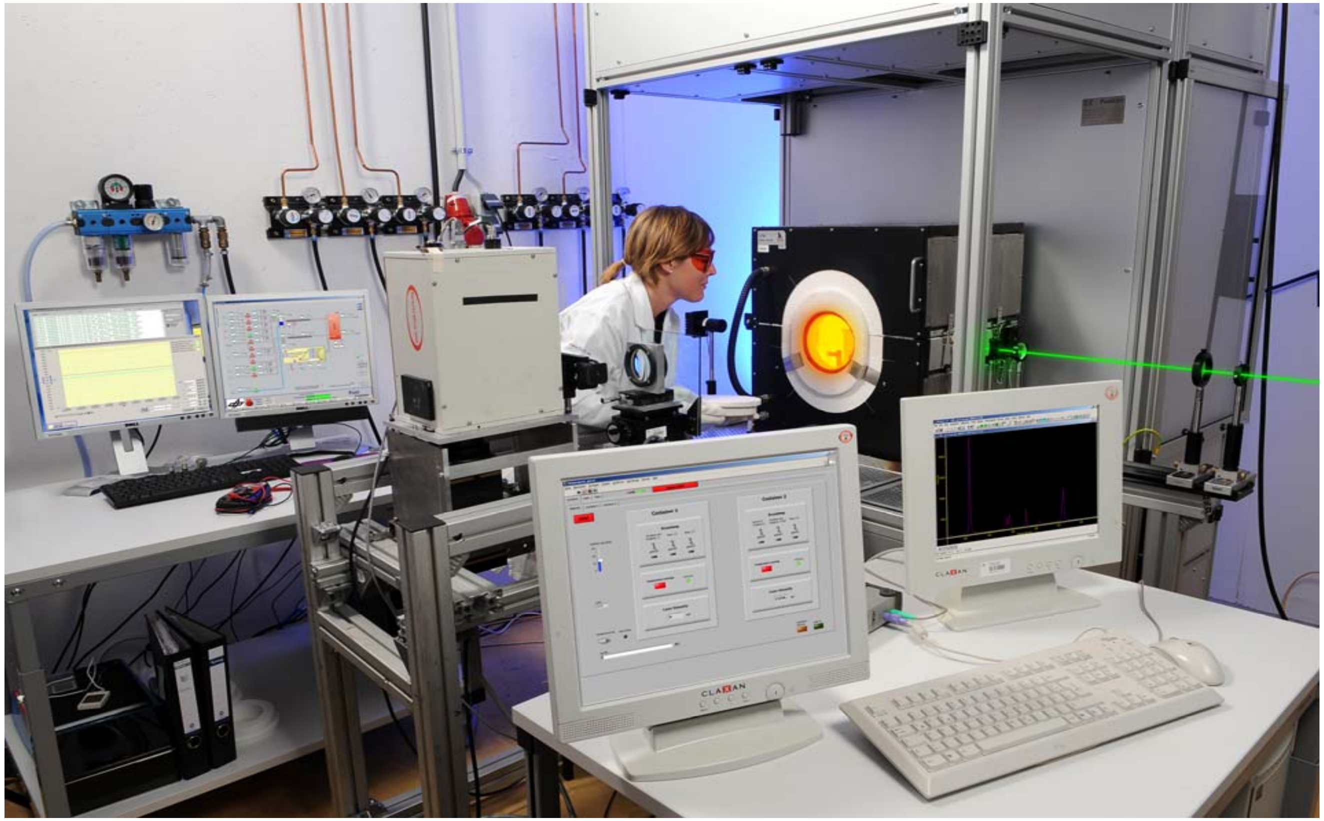


Top view

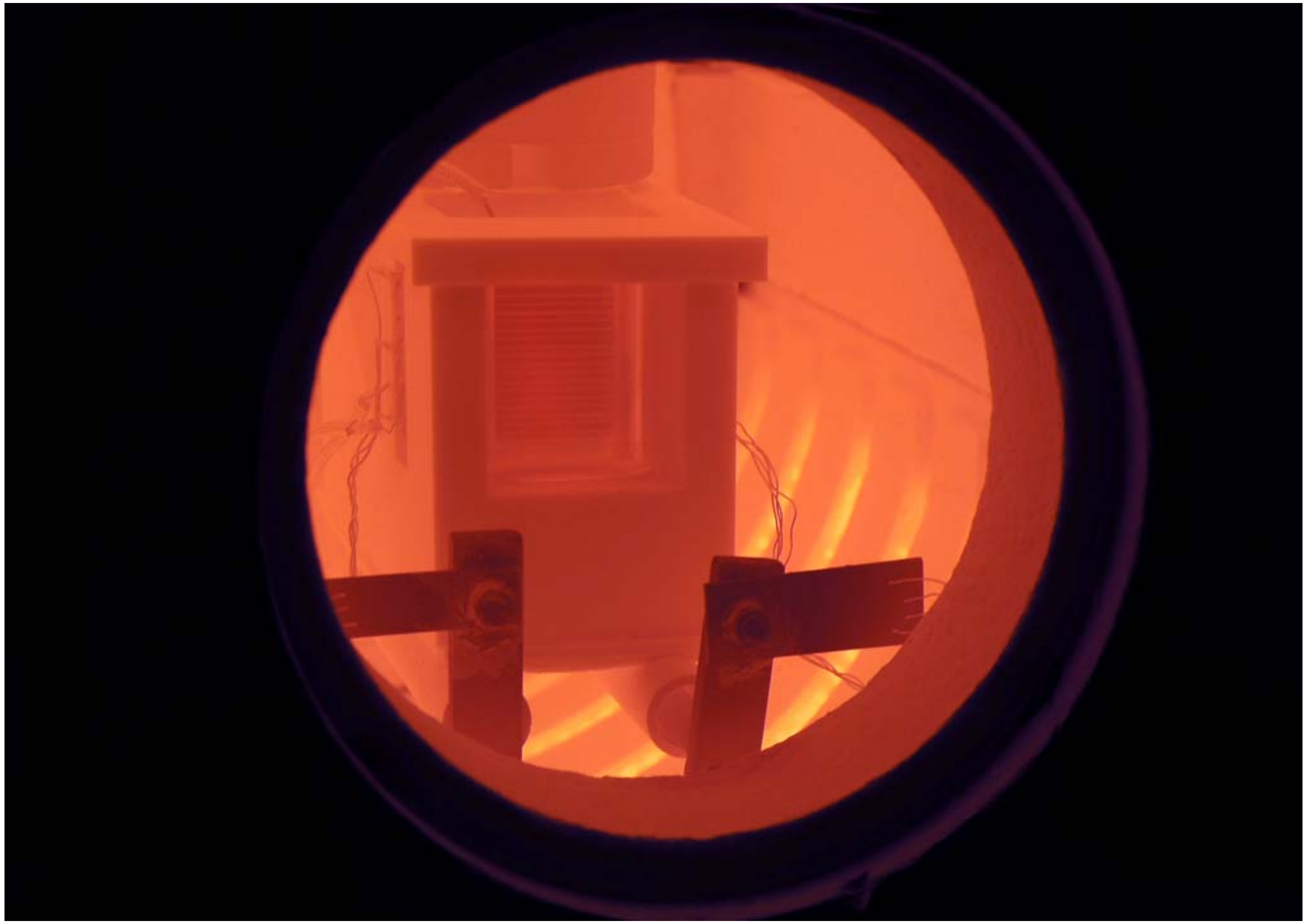


Side view

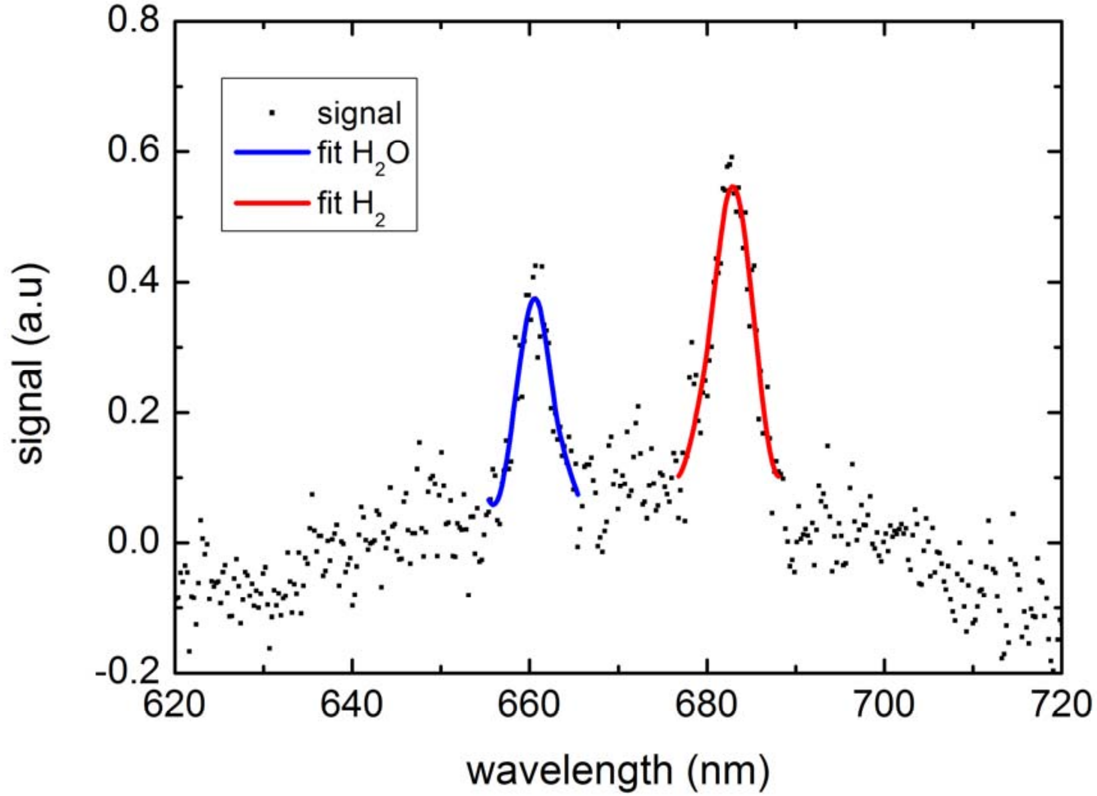
Experimental Setup for Raman Spectroscopy Measurements



Cell Housing with Transparent Flowfield in Hot Furnace



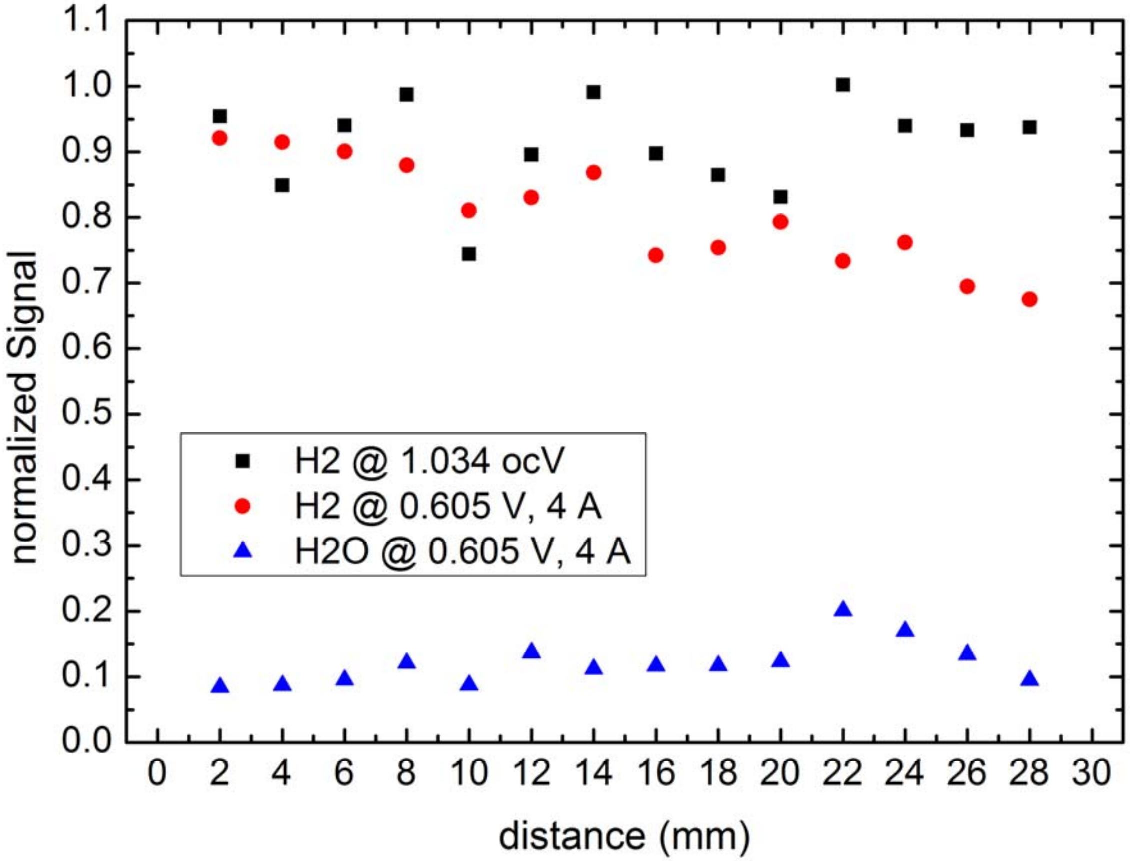
Preliminary Results



- H_2 + 3% H_2O
- 850 °C

- Large scatter in detected signal
- Improvement of S/N ratio needed

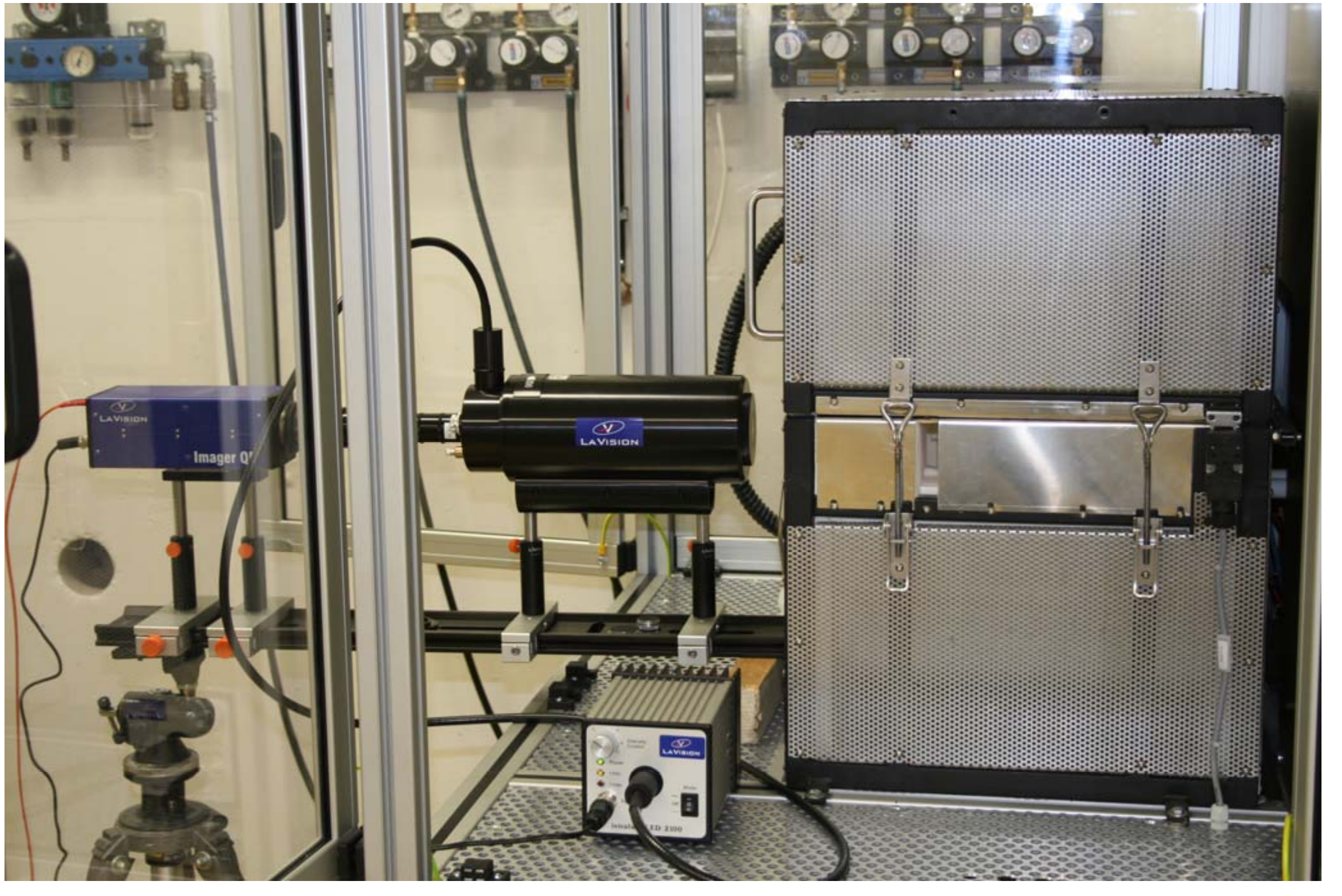
Preliminary Results



- H_2 + 3% H_2O
- 850 °C

- Measurements and evaluation still in progress
- Tendencies of the species concentration profiles can be seen

Setup for In-Situ Optical Microscopy



Conclusions

- The development of the metal supported SOFC concept has a high potential for SOFC application in dynamic operation with multiple thermal and redox cycles
- Scale-up to a full size cassette with adequate cell performance is under way
- In-situ diagnostic techniques allow for a largely extended insight into fuel cell processes
- The obtained experimental data using a segmented cell setup that allows for the measurement of local i-V characteristics, gas composition and temperature can be used for modeling and simulation
- Strong gradients of gas concentrations and current density particularly at operation with high fuel utilisation may result in locally critical operating conditions
- Additional in-situ diagnostic methods such as optical microscopy and gas-phase Raman Spectroscopy can provide further information for the understanding of cell reactions and processes

Acknowledgment

- I‘d like to thank my colleagues who contributed to this presentation:

  Asif Ansar

  Corinna Auer

  Holger Ax

  Wolfgang Bessler

  Claudia Christenn

  Patric Szabo

  Caroline Willich

  and all co-workers in our Department „Electrochemical Energy Technology“

- Financial support from German Federal Ministry of Economics and from State Ministry of Baden-Württemberg is gratefully acknowledged.

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