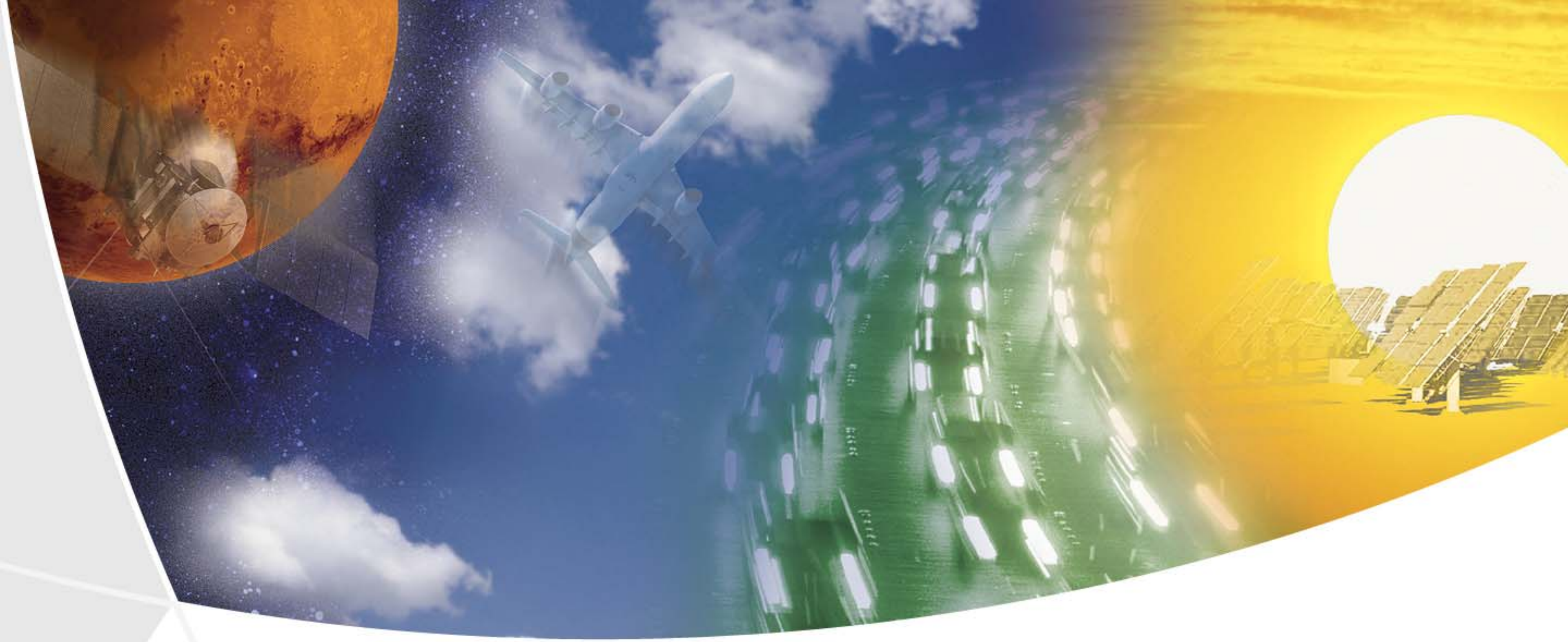


In-Situ Diagnostic Methods for SOFC

G. Schiller, K.A. Friedrich, M. Lang, P. Metzger, N. Wagner

German Aerospace Center (DLR), Institute of Technical Thermodynamics,
Pfaffenwaldring 38-48, D-70569 Stuttgart, Germany

International Symposium on Diagnostic Tools for Fuel Cell Technologies,
Trondheim, Norway, June 23-24, 2009

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

Outline

- Introduction
- Electrochemical Impedance Spectroscopy on Stacks
- Spatially Resolved Measurements: Current density
  Voltage
  Impedance
  Temperature
  Gas Composition
- Optical Spectroscopy
- X-Ray Tomography
- Conclusion

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

Conventional Test Stand Diagnostics

- **Conventional test stand diagnostics:** provide important and essential information about fuel cell performance and behaviour:
  - U(i) characteristics, OCV…
  - EIS on single cells
  - Current interrupt methods
  - Performance degradation with time U(t); i(t) …
  - Cell voltage distribution $U_{stack} = U_1 + U_2 + U_3$….
  - Pressure loss / Gas tighness test
  - Gas utilization measurement
  - Temperature distribution and control

„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

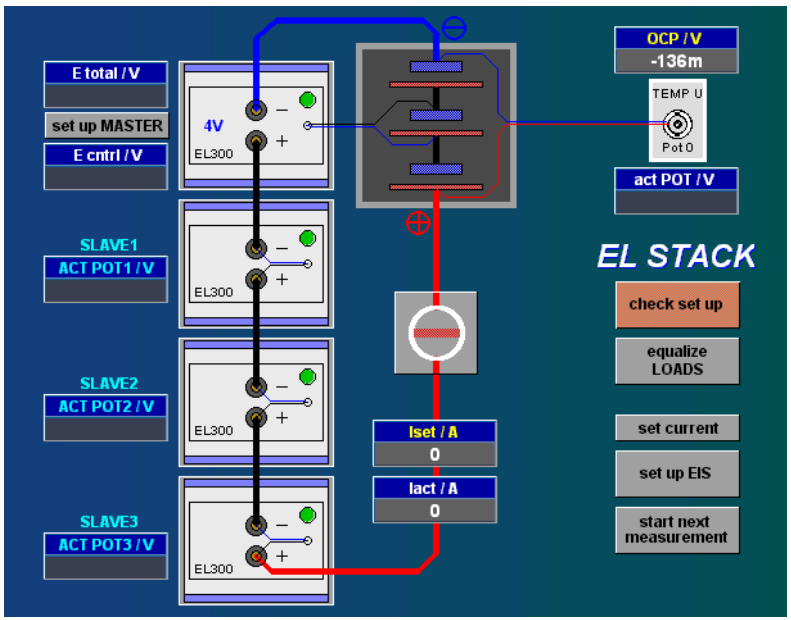
Challenges for EIS for Stack Investigations

- Large areas (e.g. 100 cm^2) lead to high current and low impedances of about 1 mOhm.
- Electrochemical processes appear at high frequencies (up to 100 kHz) due to the high reaction rates at high temperatures.
- Stacks generally contain metallic components leading to high frequency disturbances.
- Contacting of all cells and sensing in specific cells does not account for the voltage distribution in the stack.
- The sensor wires are at high temperatures: an optimization of the measurement system is not possible during operation.
- Strong overlapping of electrode processes; evaluation with equivalent circuits can be inaccurate.
- For system with current > 40 A no commercial equipment available.

Mitigation of EIS Problems

- Reduction of the high frequency disturbances by optimization of the wiring of the electrical sensing of the SOFC stack.
- Variation of the operating conditions (gases, temperature) in order to determine the different impedances of the electrode processes
- Modeling of the spectra by an equivalent circuit.
- Development of advanced EIS equipment for high currents / high frequencies in corporation with instrument manufacturer (Zahner Elektrik GmbH).

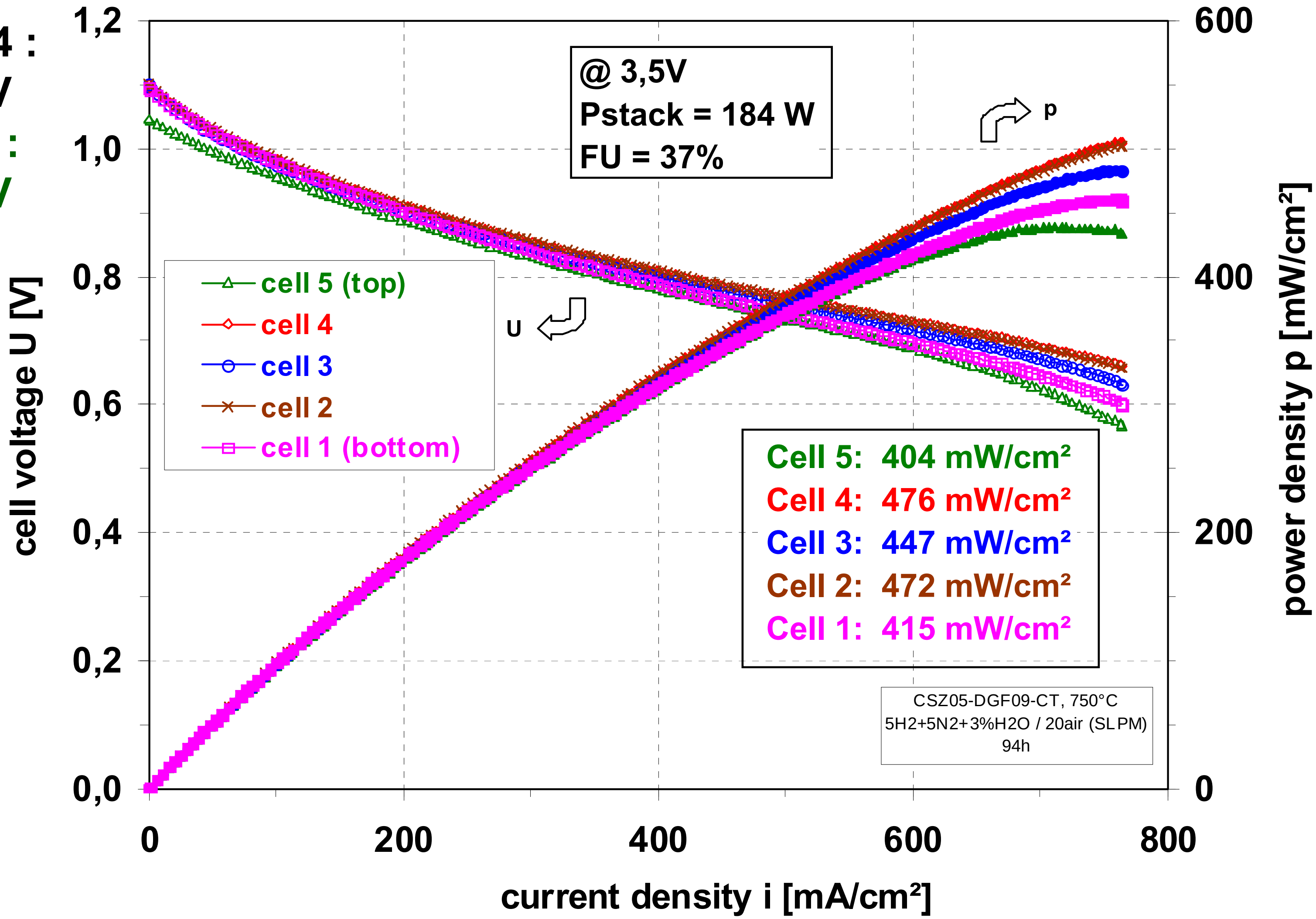
Experimental Set-up for EIS Measurements of Stacks at DLR



Performance of the 5-Cell Short Stack at 750°C

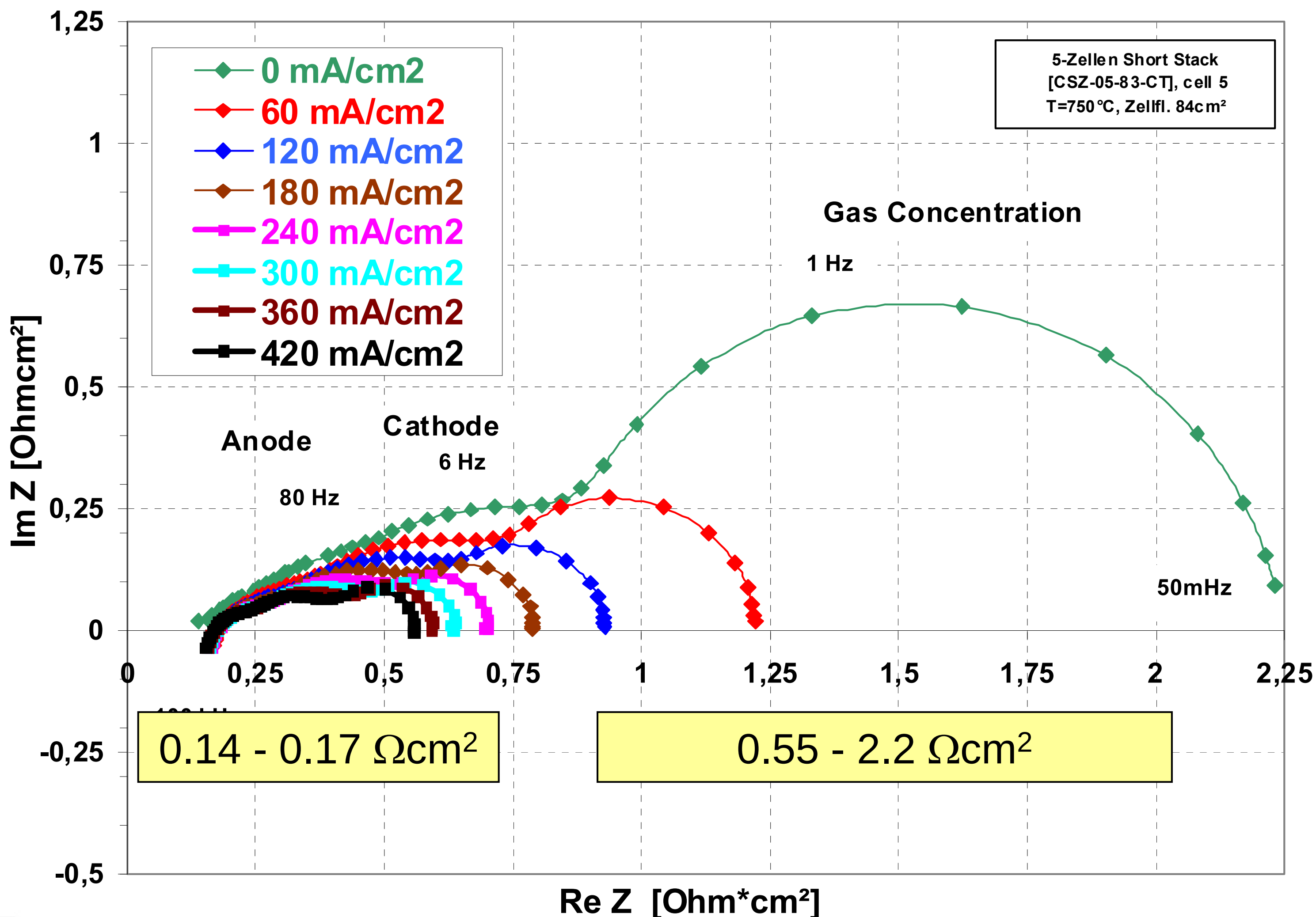
(5 H_2+5 N_2+3%H_2O / 20 air (SLPM), 94 h)

Cell 1-4 :
1.10 V
Cell 5 :
1.05 V

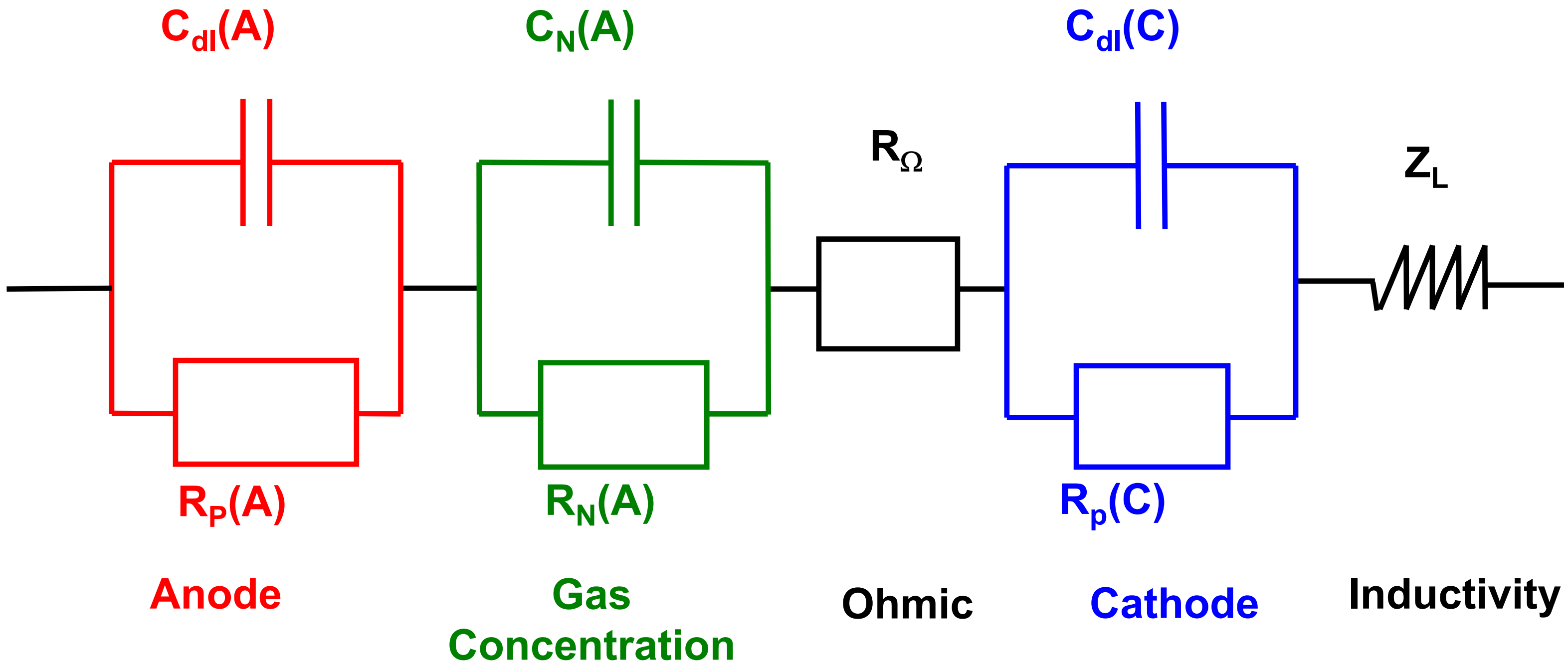


Nyquist Plot of one Cell of a 5-Cell Short Stack at Different Current Densities

(750°C, 2.5 H_2+2.5 N_2 / 20 air (SLPM), 142 h)

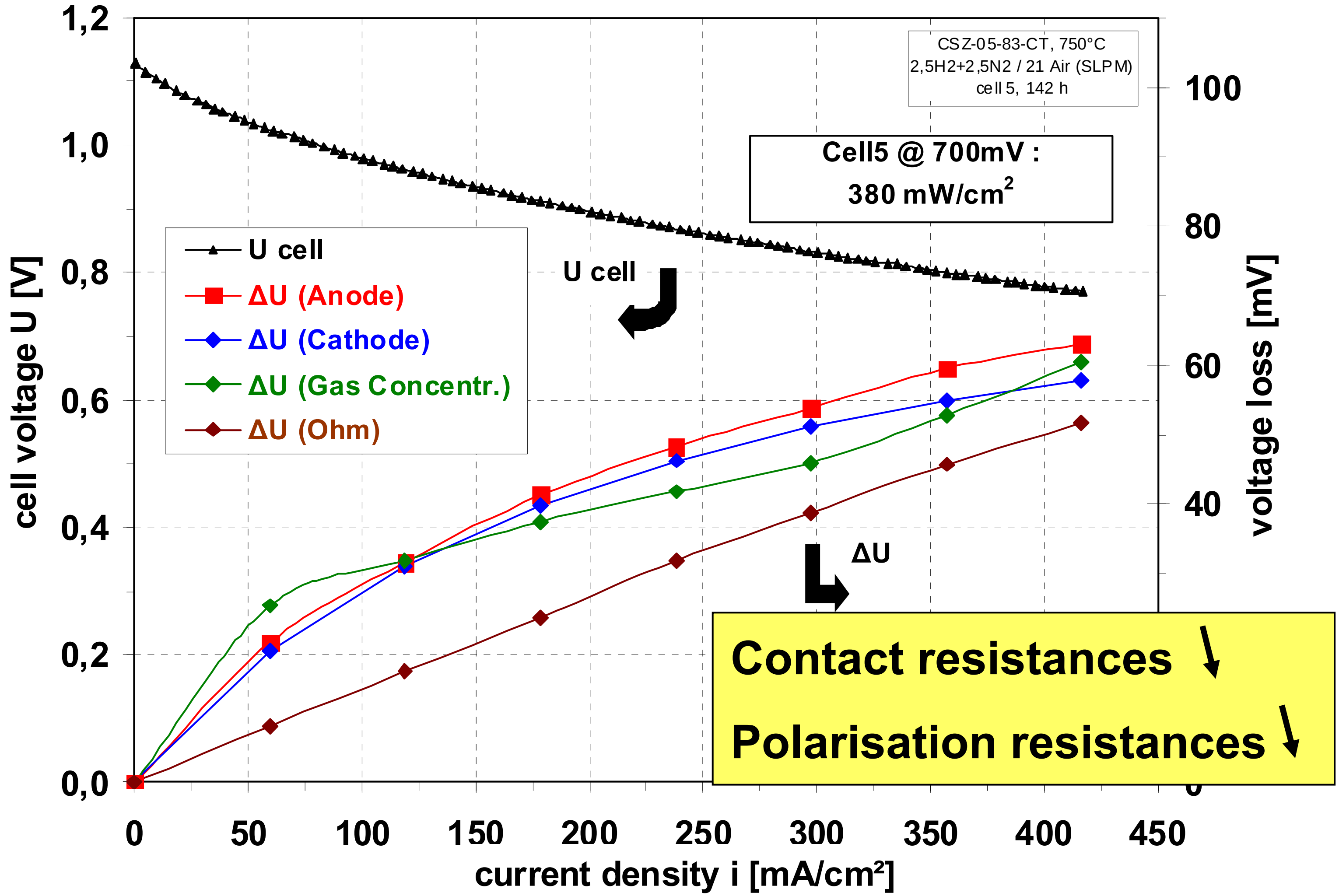


Equivalent Circuit for the Fitting of the Impedance Spectra



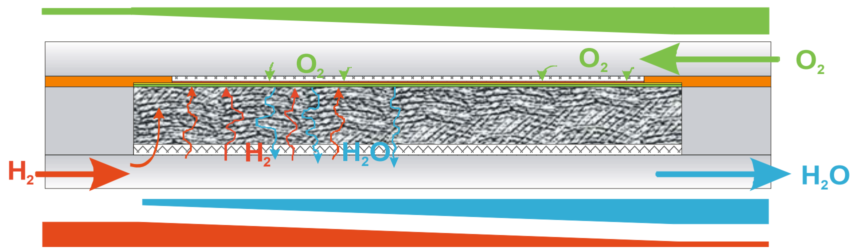
Voltage Losses at one Cell of a 5-cell Short Stack at Different Current Densities

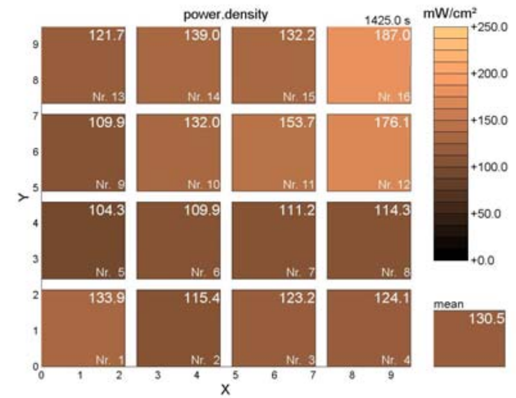
(750°C, 2.5 H_2+2.5 N_2 / 20 air (SLPM), 142 h)



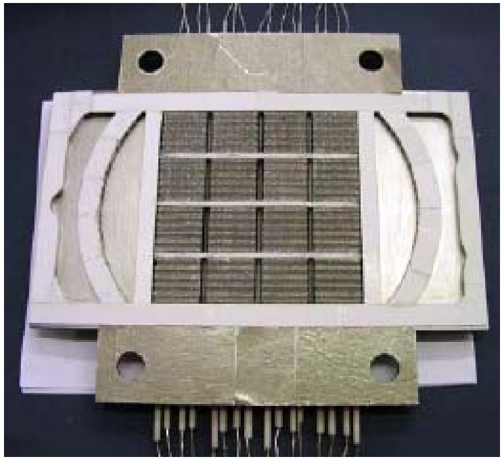
Motivation

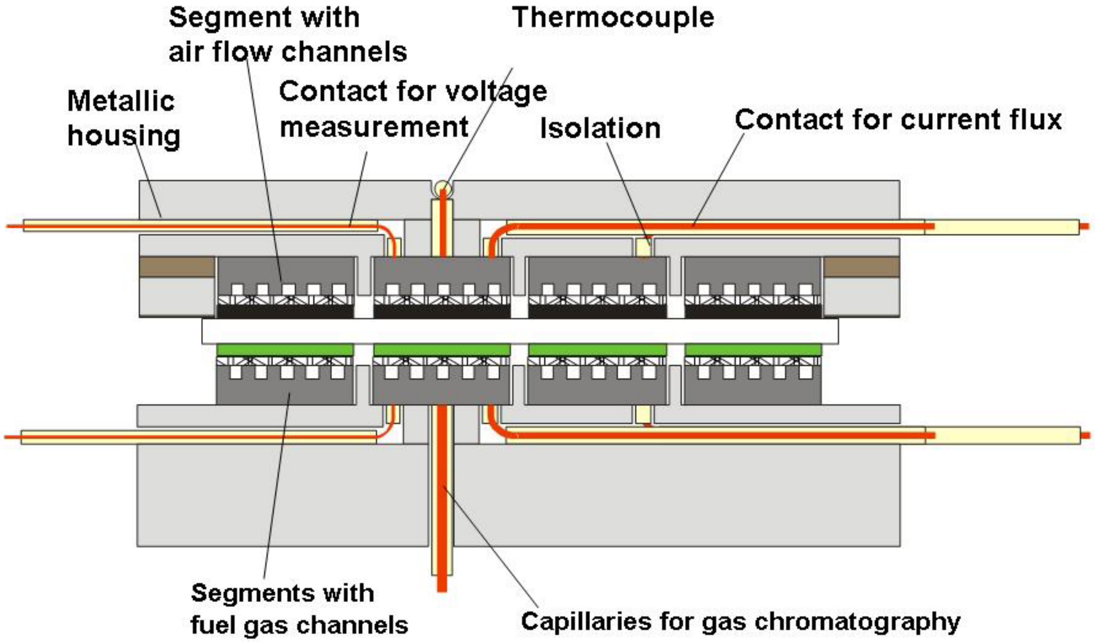
- Strong local variation of gas composition, temperature, current density
- Distribution of electrical and chemical potential dependent on local concentrations of reactants and products
  - Reduced efficiency
  - Temperature gradients
  - Thermo mechanical stress
  - Degradation of electrodes





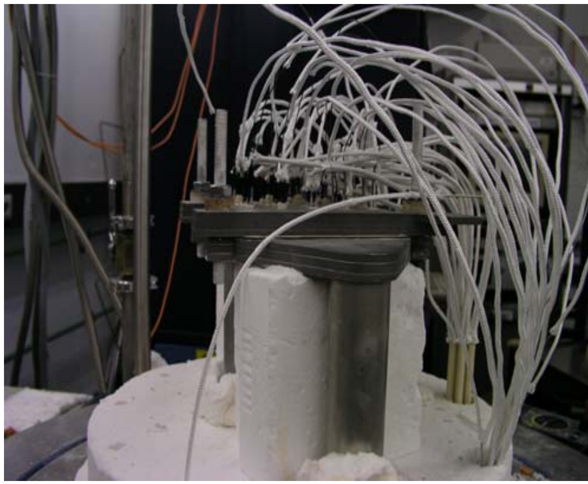
Measurement Setup for Segmented Cells



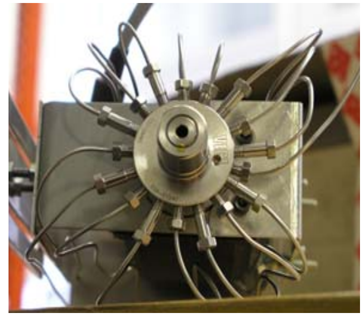


- 16 galvanically isolated segments
- Local and global i-V characteristics
- Local and global impedance measurements
- Local temperature measurements
- Local fuel concentrations
- Flexible design: substrate-, anode-, and electrolyte-supported cells
- Co- and counter-flow

Cell design and Testing Station

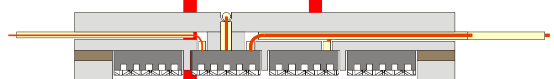


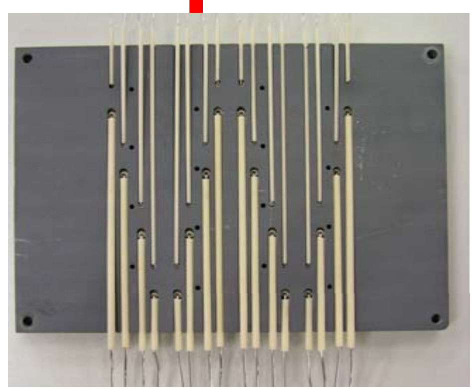
From a „simple“ cell design with manually controlled features

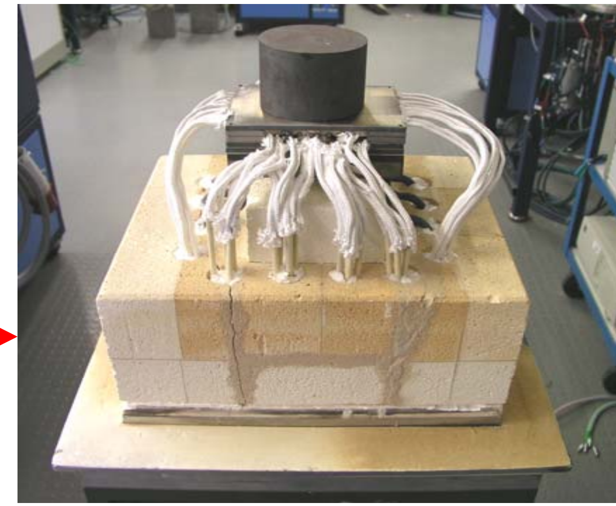


GC measurement

Assembly and contacts



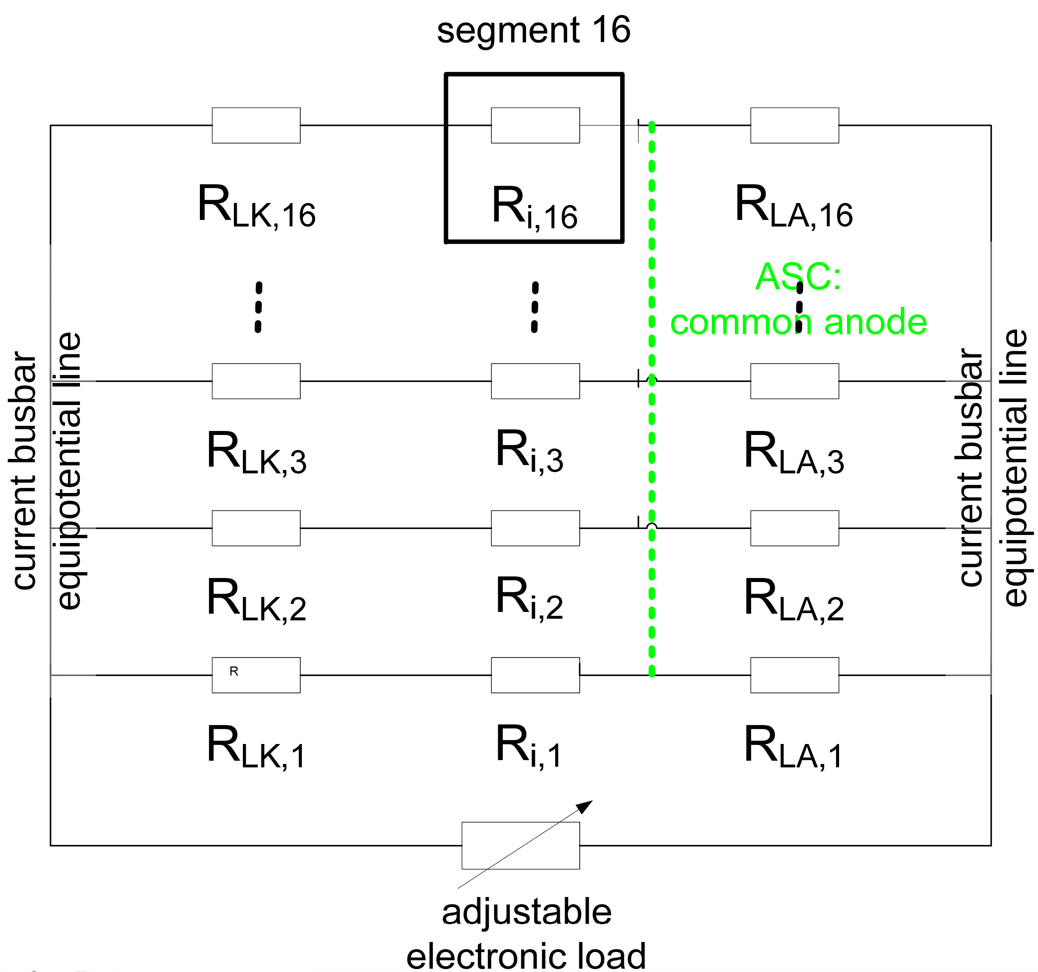




- All cell concepts
- Improved contacting
- Reliable assembly
- Impedance measurement
- Temperature measurement

Flexible housing, impedance spectra with reduced interferences

Schematic Lay-out of the Electrical Circuit of the Segmented Cell Configuration



Internal cell resistances:
Ri,j,

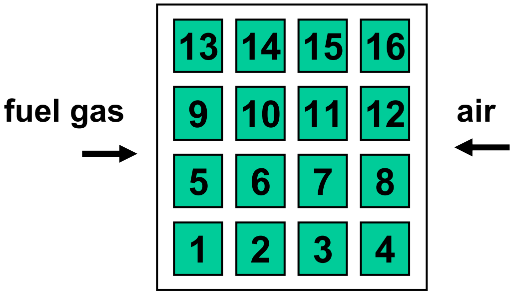
Resistances of the wires contacting the anode:
RLA,j

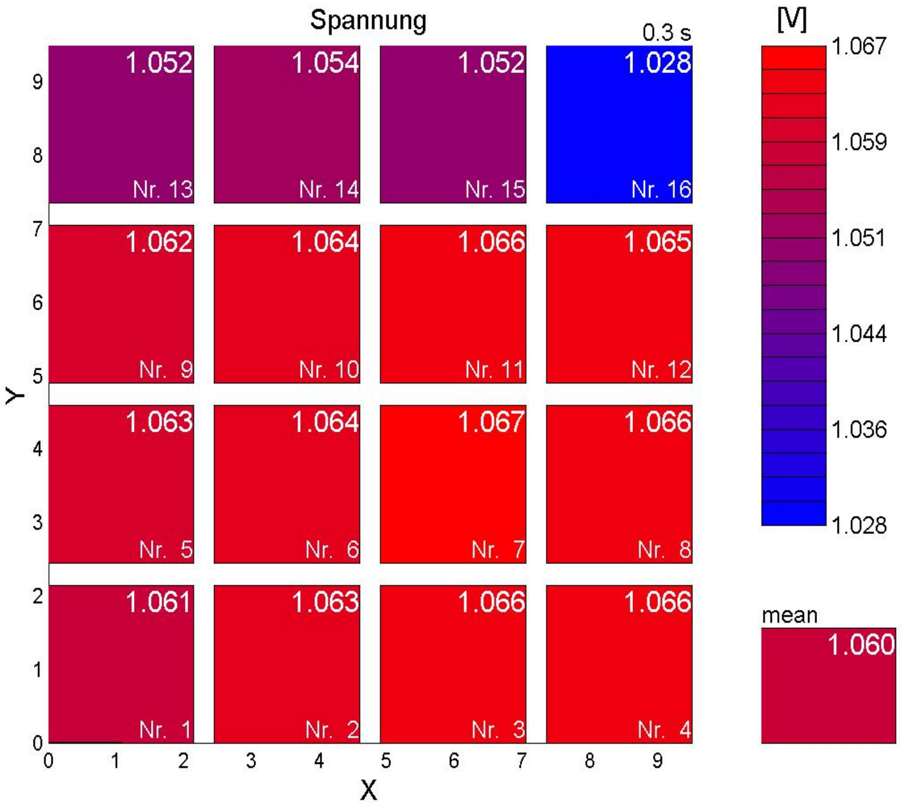
Resistances of the wires contacting the cathode:
RLK,j

Only segments 1, 2, 3, 16 are illustrated

OCV Voltage Measurement for Determination of Humidity

- Voltage distribution at standard flow rates:
- 48.5% H_2, 48.5% N_2 + 3% H_2O, 0.08 SlpM/cm² air





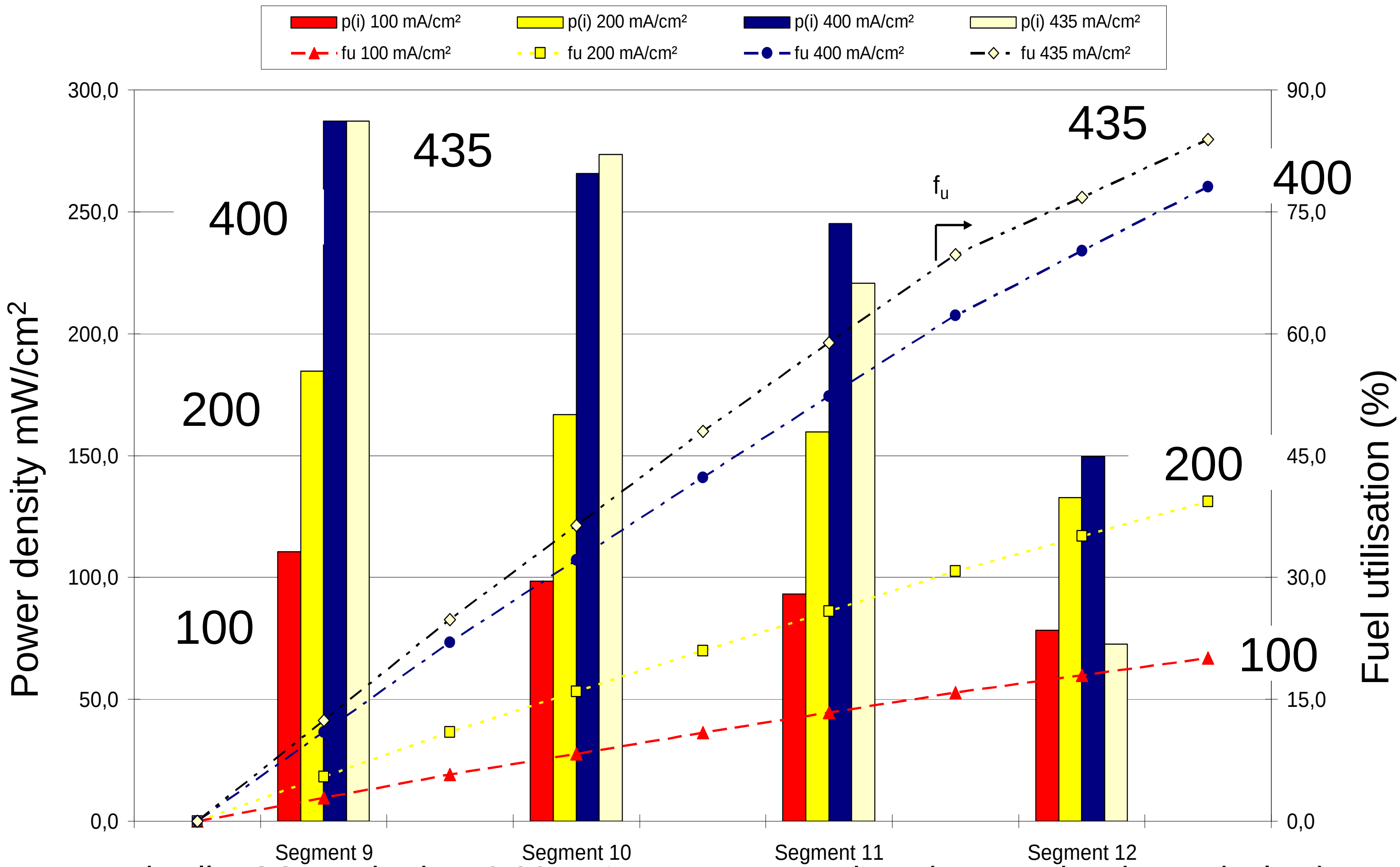
Nernst equation:

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

Produced water:

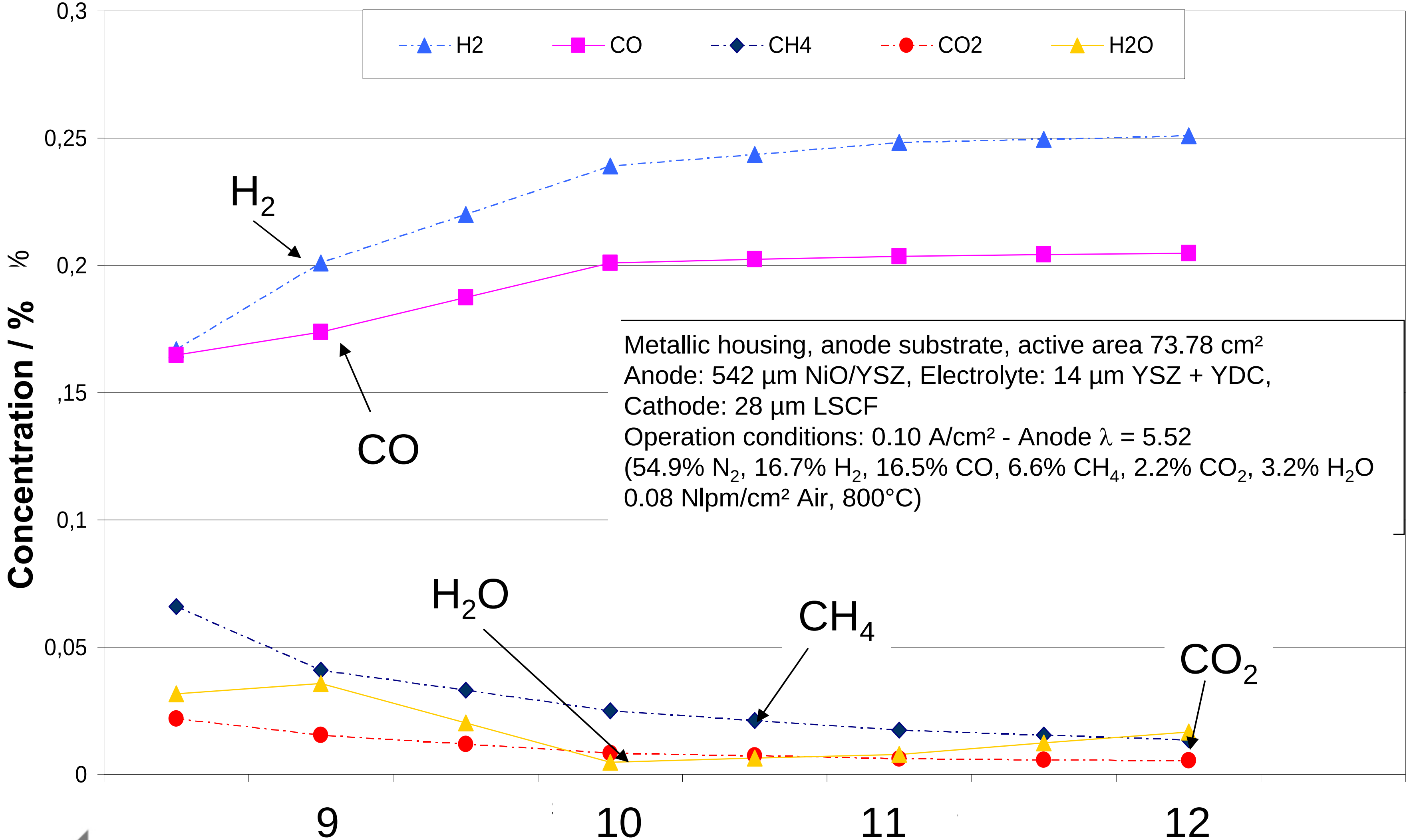
S4: 0.61%, S8: 0.72%,
S12: 0.78%, S16: 3.30%

Variation of Load - Reformate

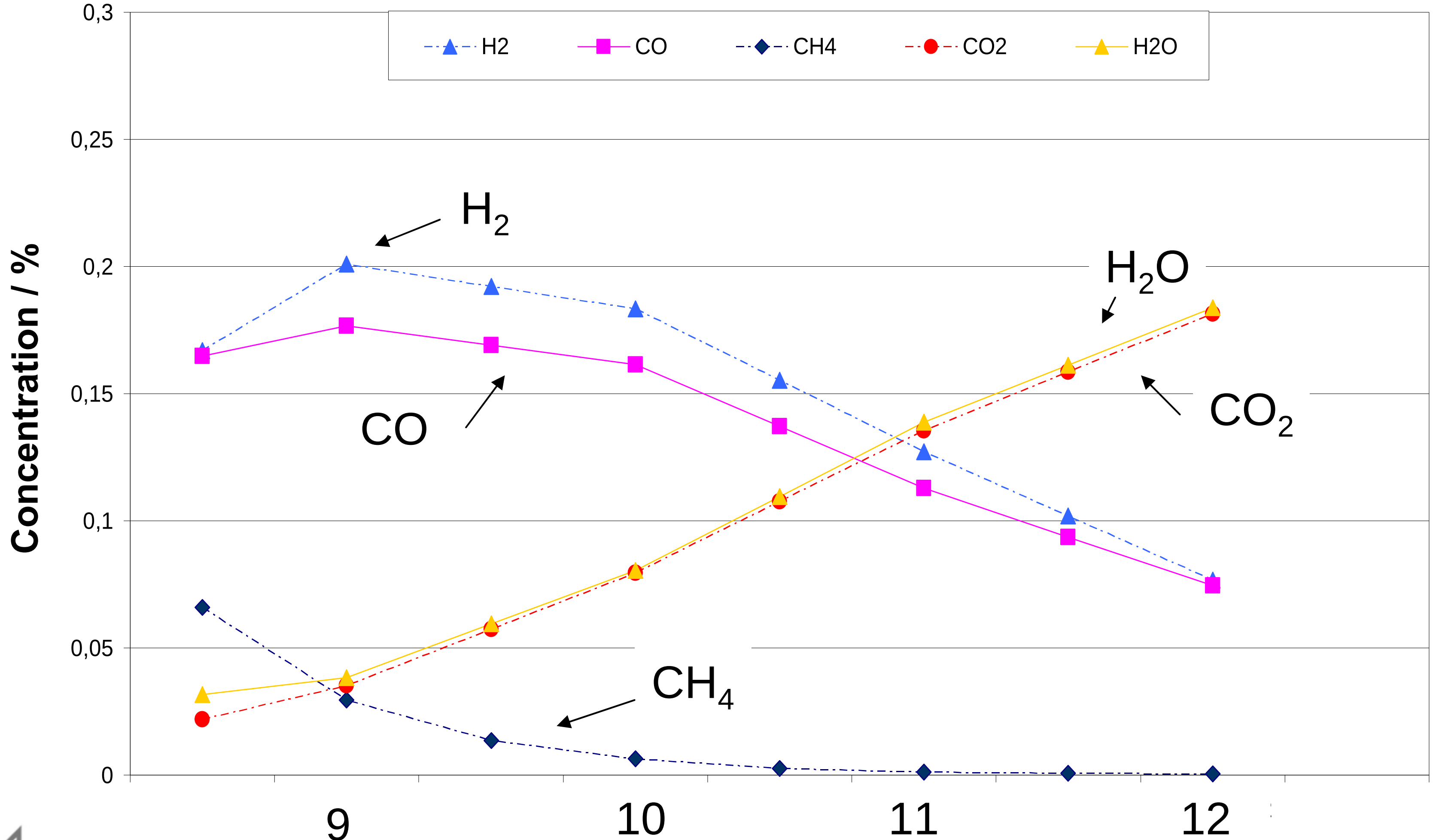


Anode supported cell, LSCF cathode, 73,96 cm², gas concentrations (current density equivalent): 54.9% N_2, 16.7% H_2, 16.5% CO, 6,6% CH_4, 2.2% CO_2, 3.2% H_2O (0.552 A/cm²), 0.02 SlpM/cm² air

Reformate: Changes of the Gas Composition at 0 mA/cm²



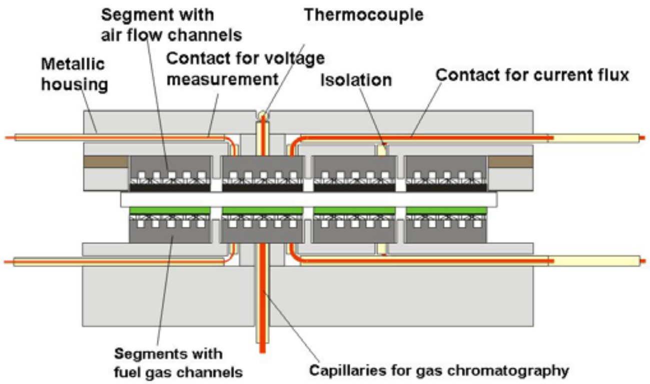
Alteration of the gas composition at 435 mA/cm²



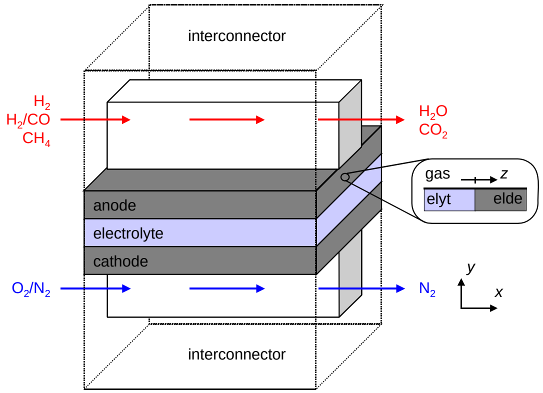
Combined Experimental and Modeling Approach

Objectives of the study:

- Better understanding of the local variations
  - Identification of critical conditions
  - Optimisation of cell components

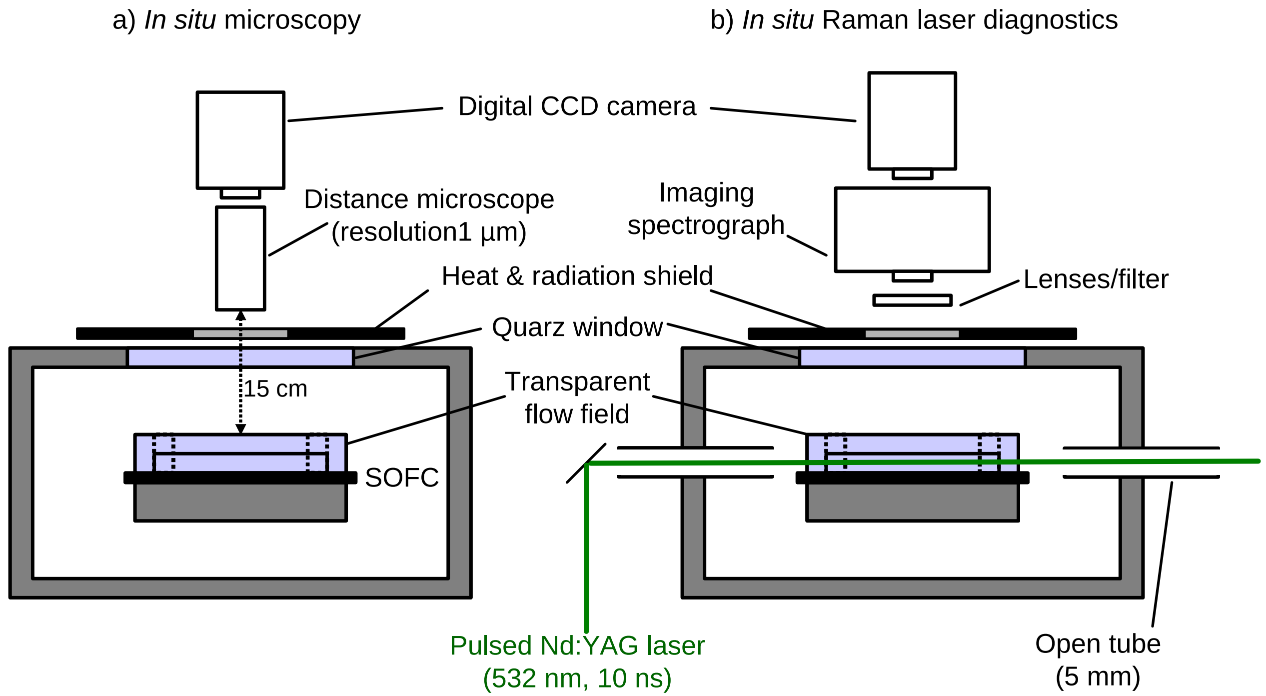


Experiments on single segmented SOFC



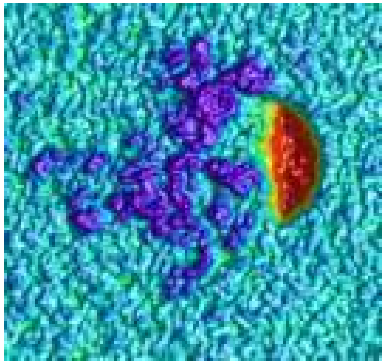
Electrochemical model of local distributions

Potential for Optical Spectroscopies

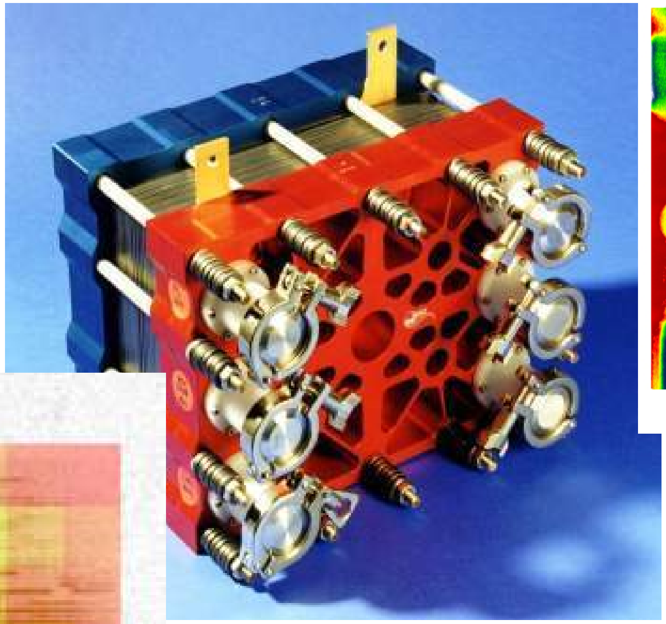


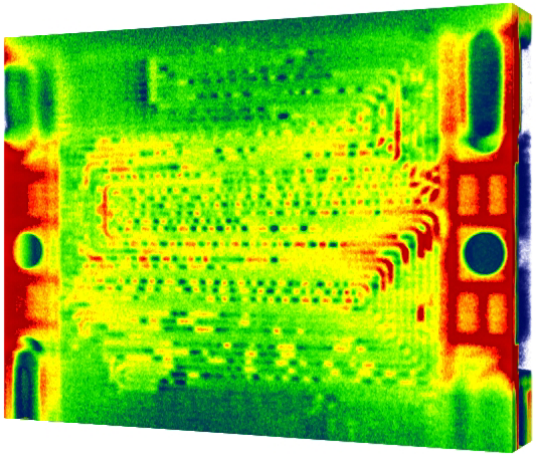
- Raman spectroscopy
- Laser Doppler Anemometry (LDA)
- Particle Image Velocimetry (PIV)
- Fast-Fourier Infrared (FTIR)
- Coherent Anti-Stokes Raman Spectroscopy (CARS)
- Electronic Speckle Pattern Interferometry (ESPI)

Tomography Diagnosis of PEM Fuel Cells

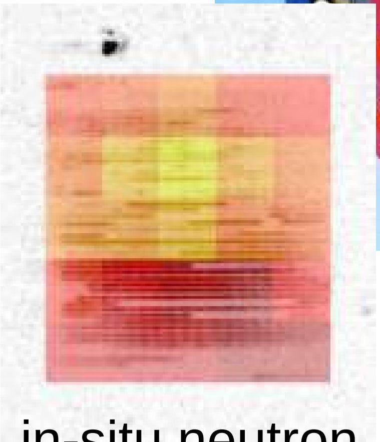


in-situ synchrotron radiography





neutron tomography



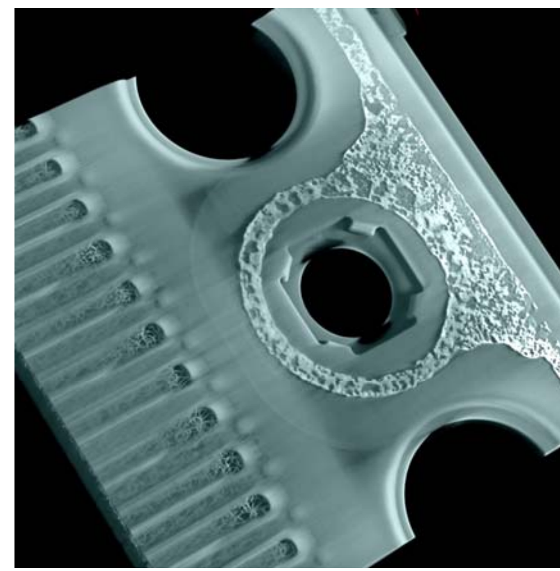
in-situ neutron radiography

Investigation of water management under operating conditions

X-Ray Tomography (CT) Facility at DLR

X-Ray CT Facility v|tome|x L450 at DLR Stuttgart

3 dimensional non intrusive imaging of SOFC cassette



Summary

- The operating conditions (elevated temperature) reduce significantly the possibilities for in-situ SOFC diagnostic methods.
- EIS will remain the main diagnostic probe of the state of SOFC.
- Non-traditional in-situ diagnostics methods can provide additional important information:
  - Spatially resolved measurements to obtain local distribution of cell properties (current, voltage, impedance, gas compo-sition, temperature)
  - Combined analytical and modeling approach
- Large future potential for optical spectroscopies (e.g. Raman spectroscopy) and x-ray tomography.