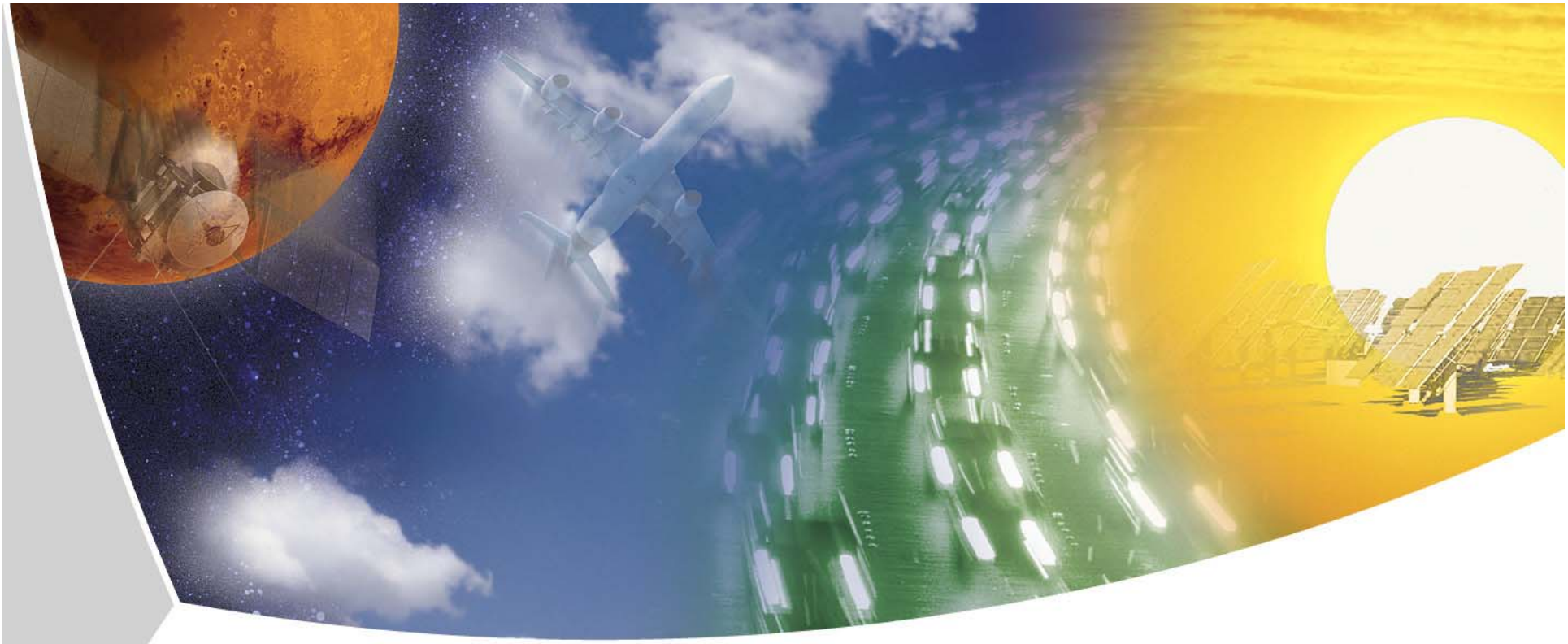

Study of SOFC Operational Behavior by In-Situ Laser Raman Spectroscopy

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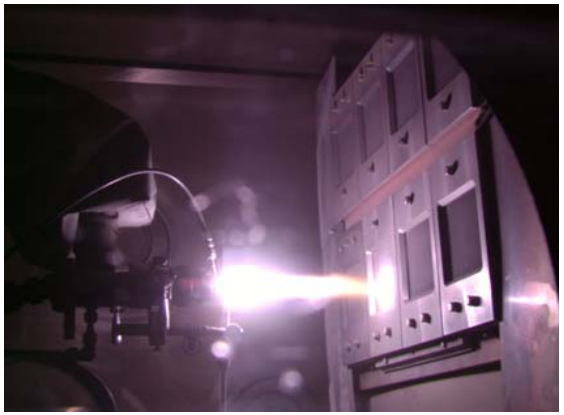
220th ECS Meeting, Electrochemical Processes for Fuels, Boston, MA, October 9-14, 2011

Outline

- Introduction
- Experimental setup for Raman spectroscopy
- Exemplary results
- Outlook: Optical microscopy
- Conclusion

Development of Metal Supported Cells (MSC)

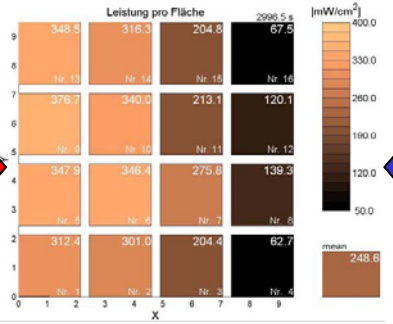


Characterization of Short Stacks and Stacks (ASC, MSC)

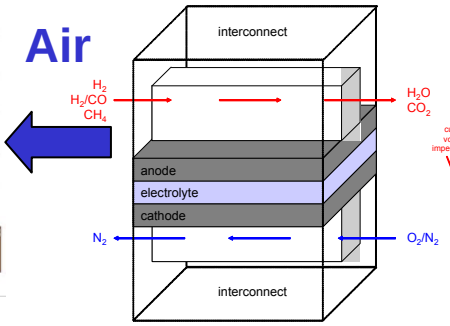
SOFC Activities at DLR

SOFC Diagnostics

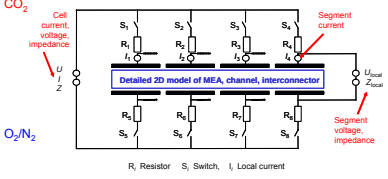
Fuel gas



Air



SOFC Modeling



System Technology

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

Investigation of Degradation and Cell Failures

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

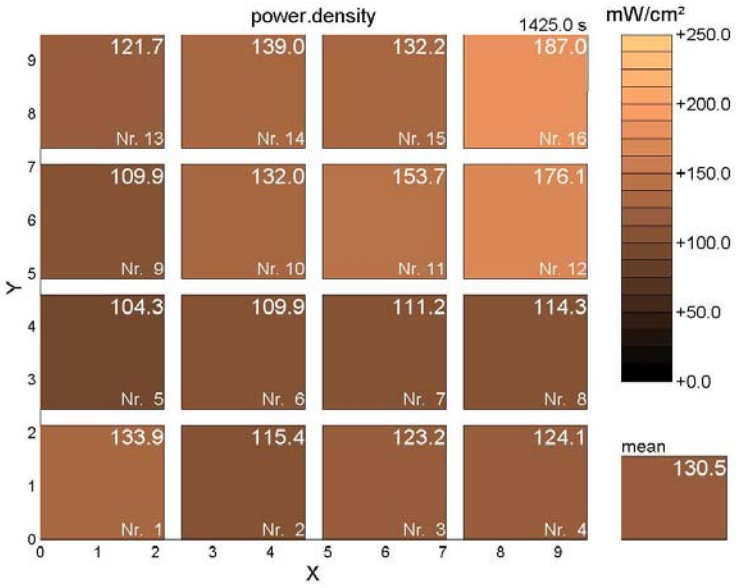
„Sophisticated“ (non-traditional) In-Situ Diagnostics

- Electrochemical impedance spectroscopy on stacks
- Spatially resolved measuring techniques for current, voltage, temperature and gas composition (Poster A3-0445O)
- Laser Raman spectroscopy
- Optical imaging
- Acoustic emission detection
- X-ray tomography

Motivation

Problems in planar cell technology:

- Strong local variation of gas composition, temperature, and current density
- Distribution of electrical and chemical potential dependent on local concentrations

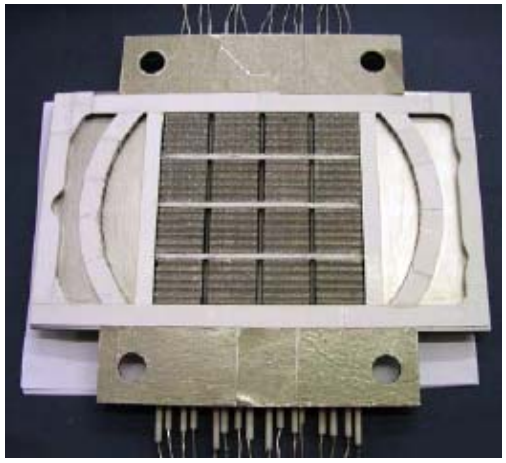


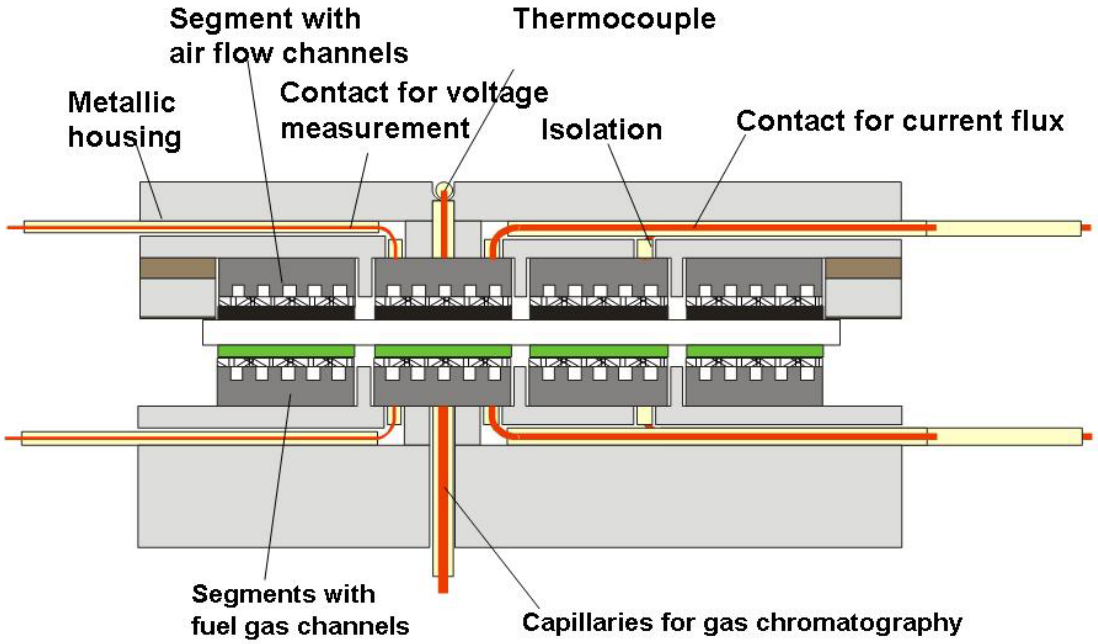
This may lead to:

- Reduced efficiency
- Thermo mechanical stress
- Degradation of electrodes

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

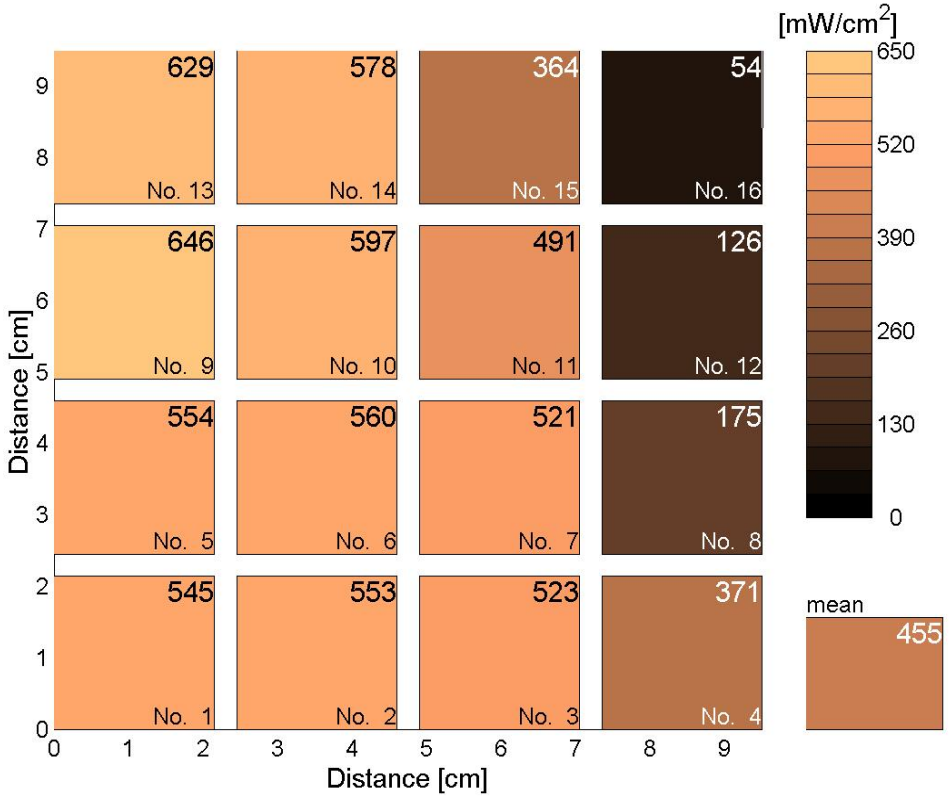
Measurement Setup for Segmented Cells





- 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

Power Density Distributution under Conditions of High Fuel Utilization



Counter-flow

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

Cathode: air

T = 800 °C

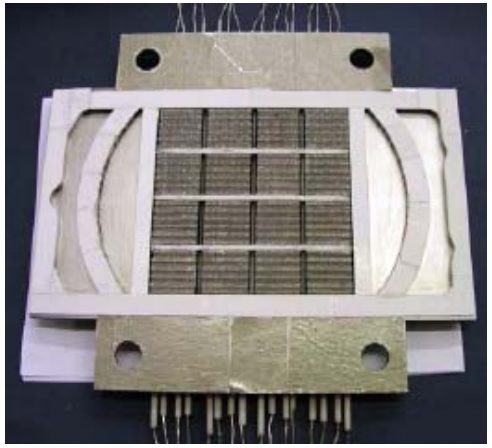
Cell voltage: 0.59 V

F_u = 80%

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

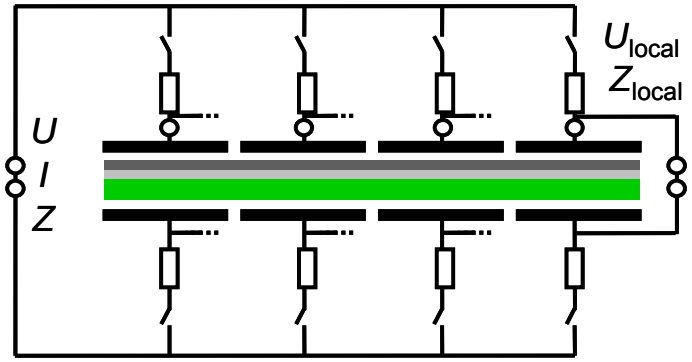
Assessment of Local Performance with Segmented SOFCs

Experiment

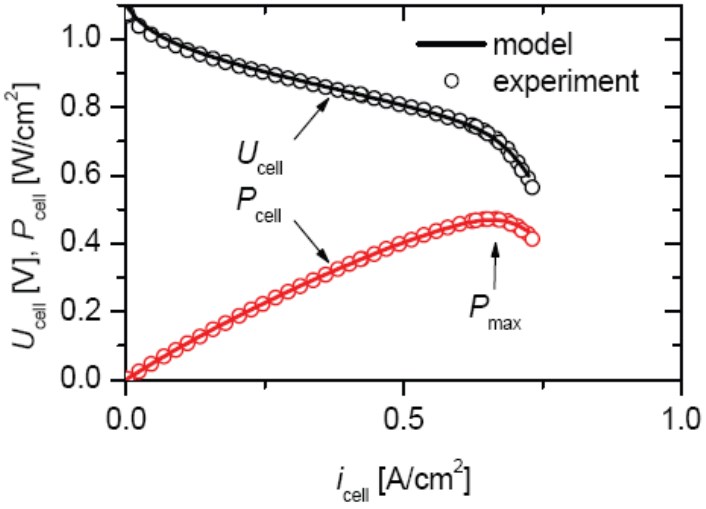


16 segments

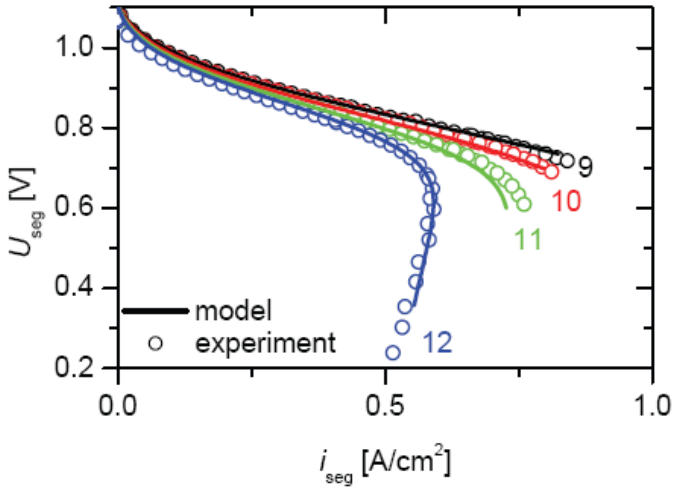
Model



Global behavior

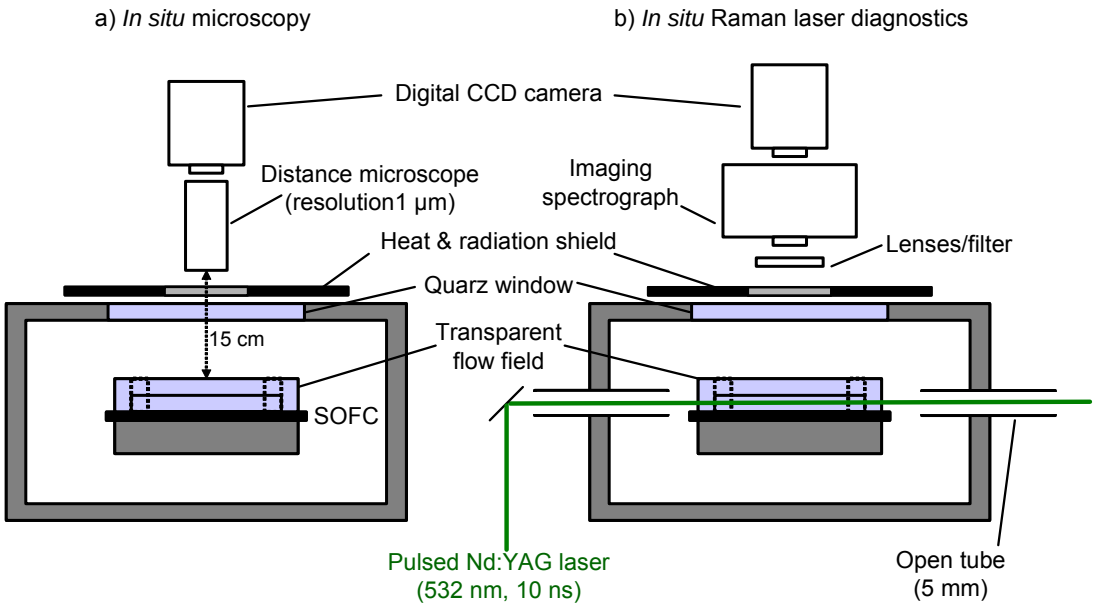


Local behavior



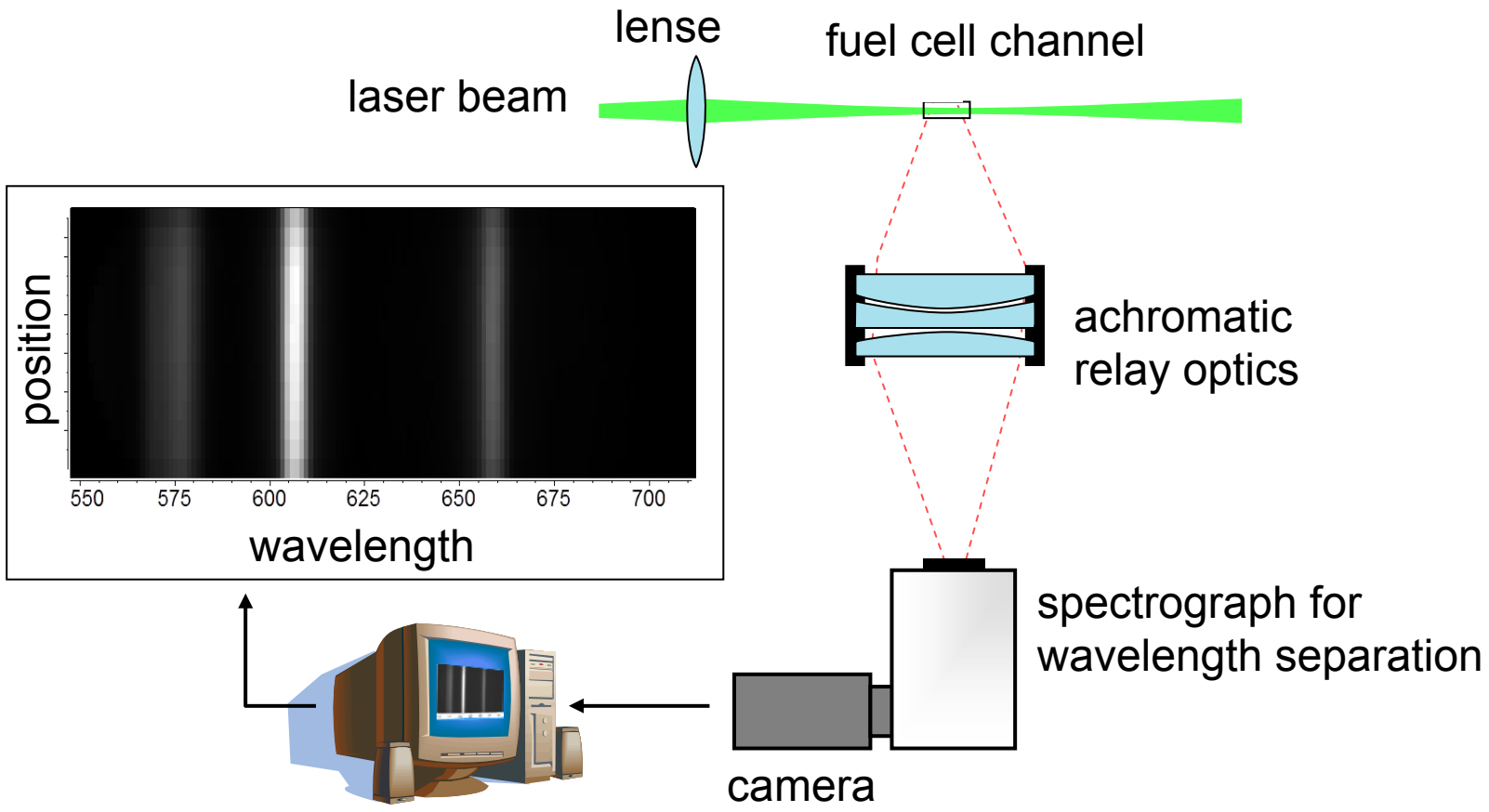
Cell can be locally in critical conditions!

Potential for Optical Spectroscopies



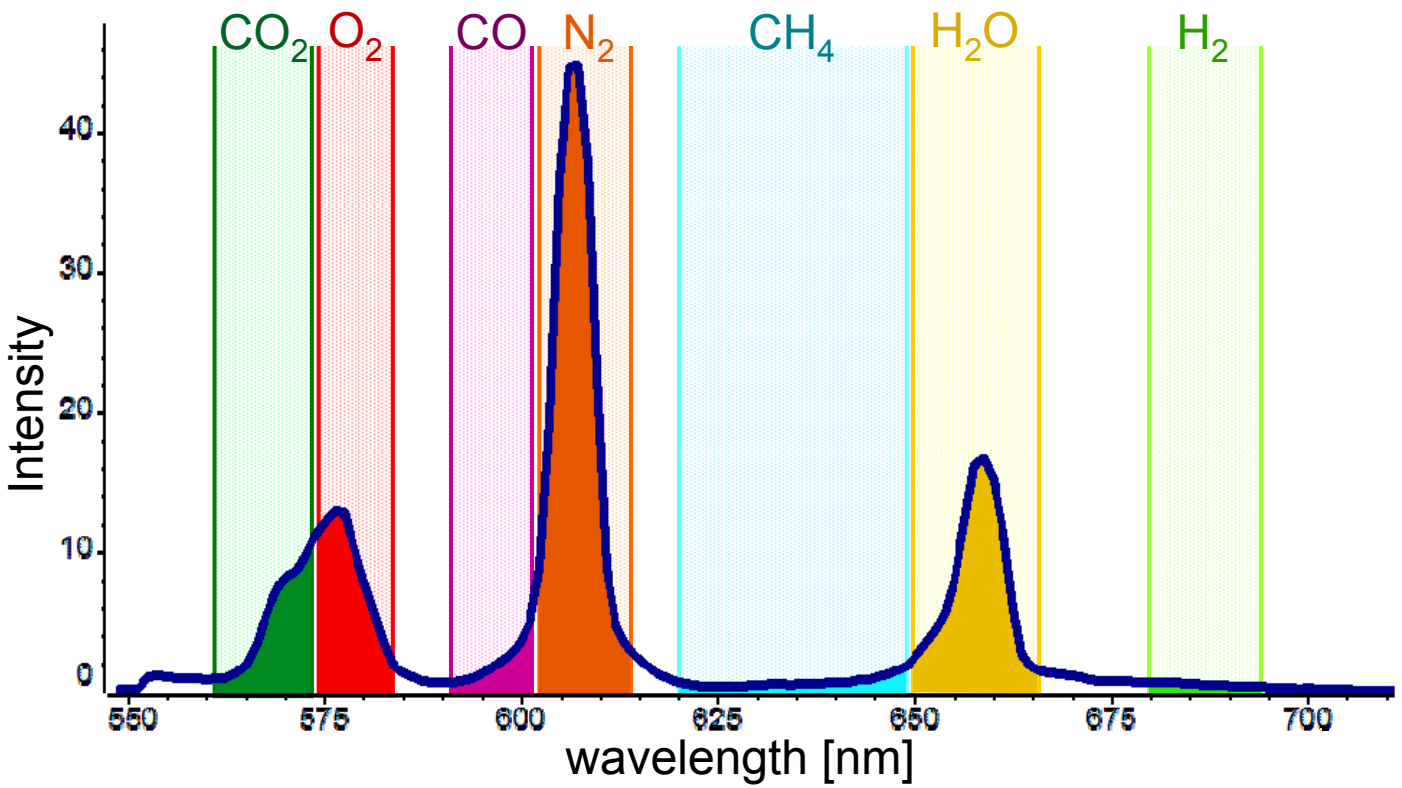
Raman spectroscopy
Laser Doppler Anemometry (LDA)
Particle Image Velocimetry (PIV)
Fast-Fourier Infrared (FTIR)
Coherent Anti-Stokes Raman Spectroscopy (CARS)
Electronic Speckle Pattern Interferometry (ESPI)

1D Laser Raman Scattering: Experimental Arrangement



Simultaneous detection of CH_4, O_2, N_2, CO, H_2, CO_2, H_2O

Raman Spectrum from Flame



Raman bands are partly overlapped (cross talk)

Challenges when Applying Laser Raman Spectroskopy with SOFC Cells

- Coupling of highest possible laser pulse energy into the gas channel without damaging the flow field; beam has to be focused to a diameter of 1 mm

- Exact adjustment of laser beam through the channel at high operating temperature in a closed furnace

- Suppression of scattering light through laser induced luminescence

Setup for 1D-Raman Spectroscopy

3 double pulse Nd:YAG PIV 400 laser systems

λ = 532 nm

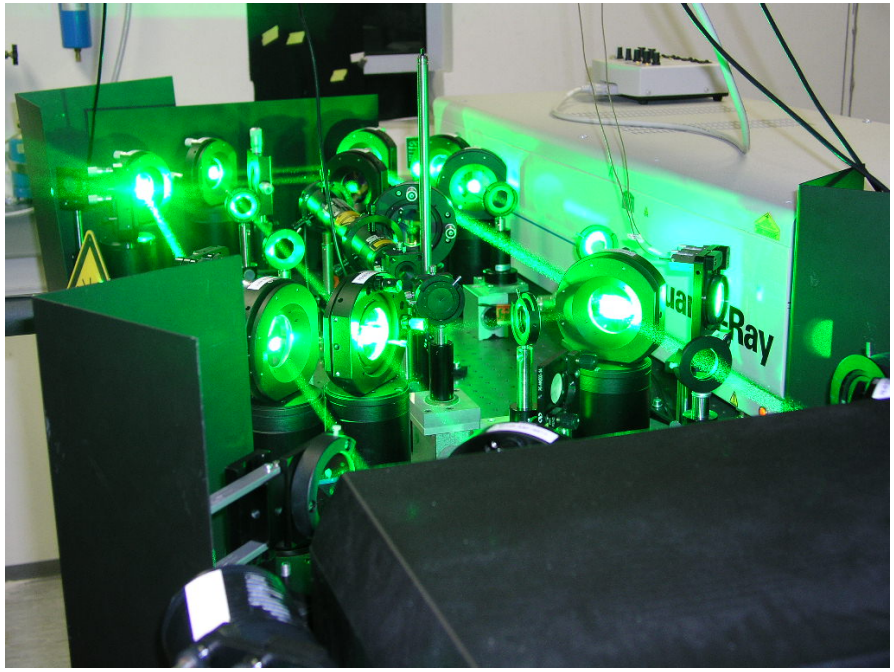
Repetition rate: 10 Hz

Single pulse: E ≤ 350 mJ / ~7 ns

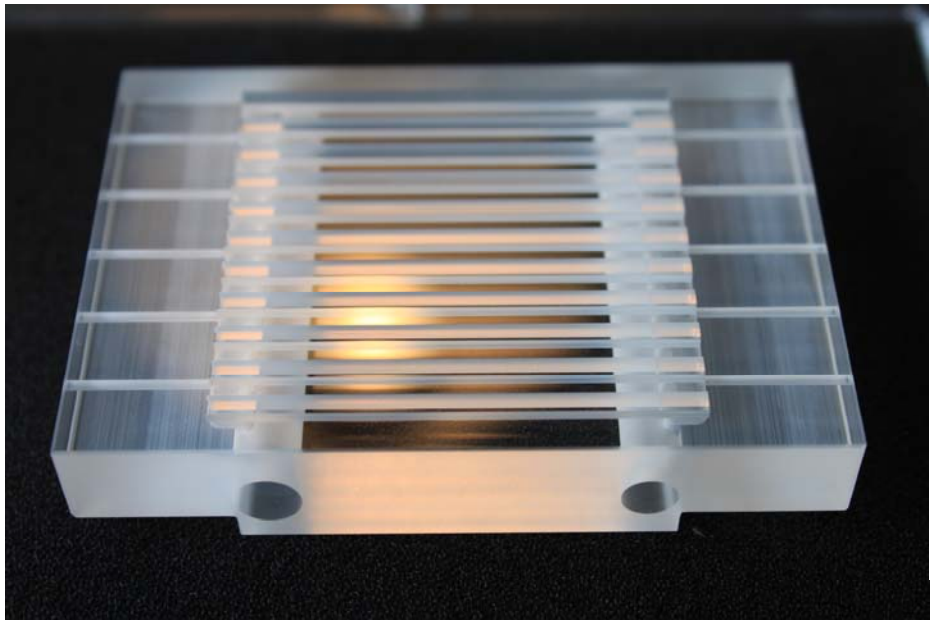
Pulse energy: 6 x 300 mJ

Pulse length: ~380 ns

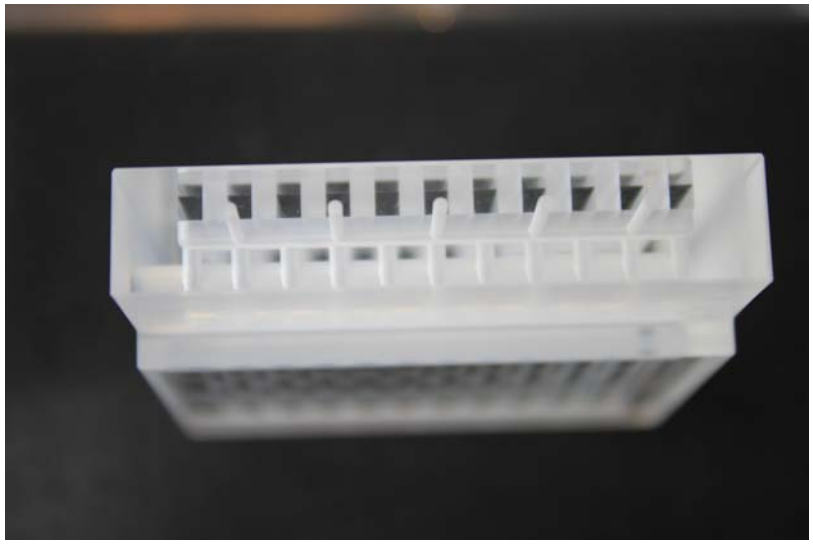
(temporal resolution)



Transparent Flowfield for SOFC



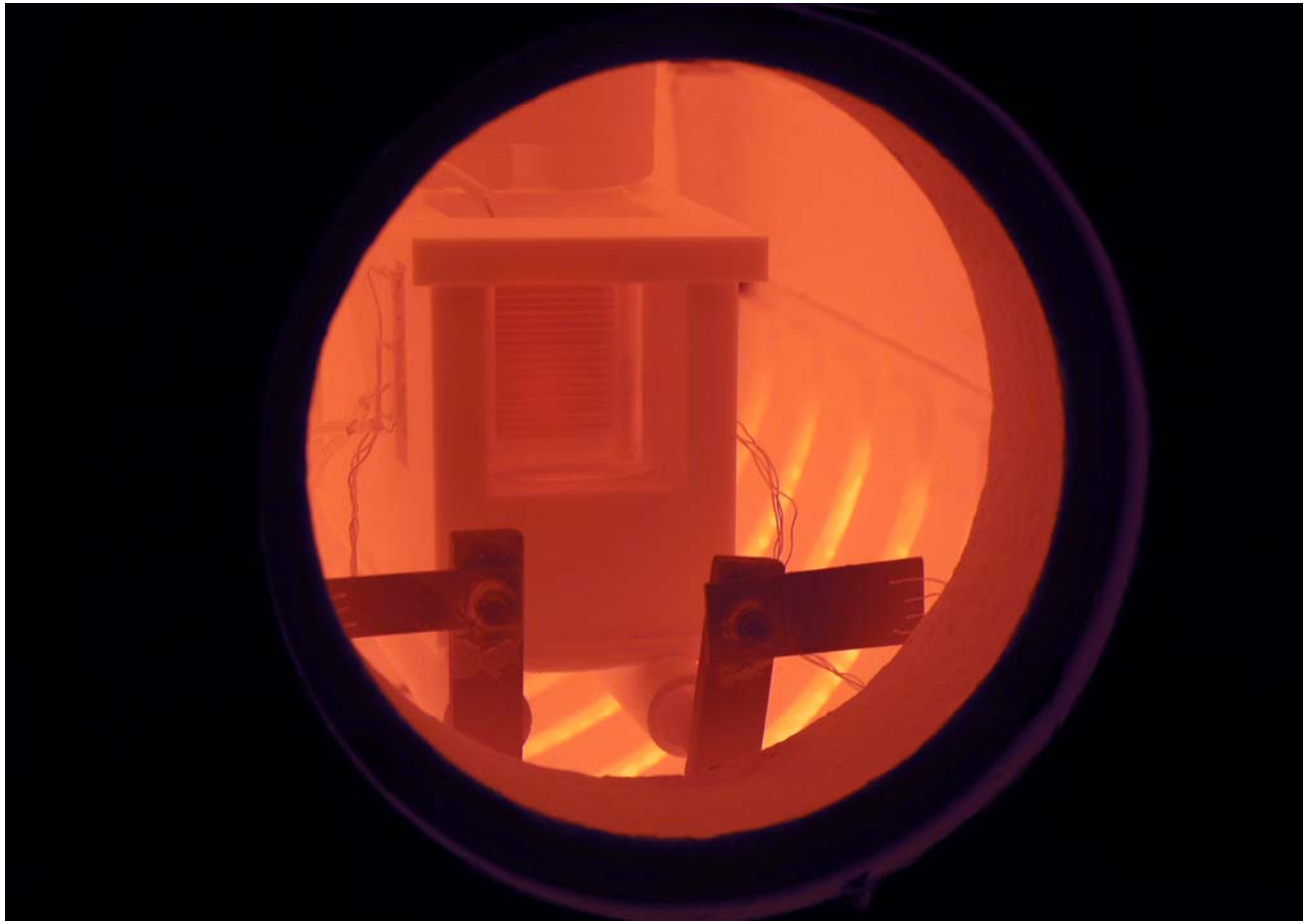
Top view



Side view

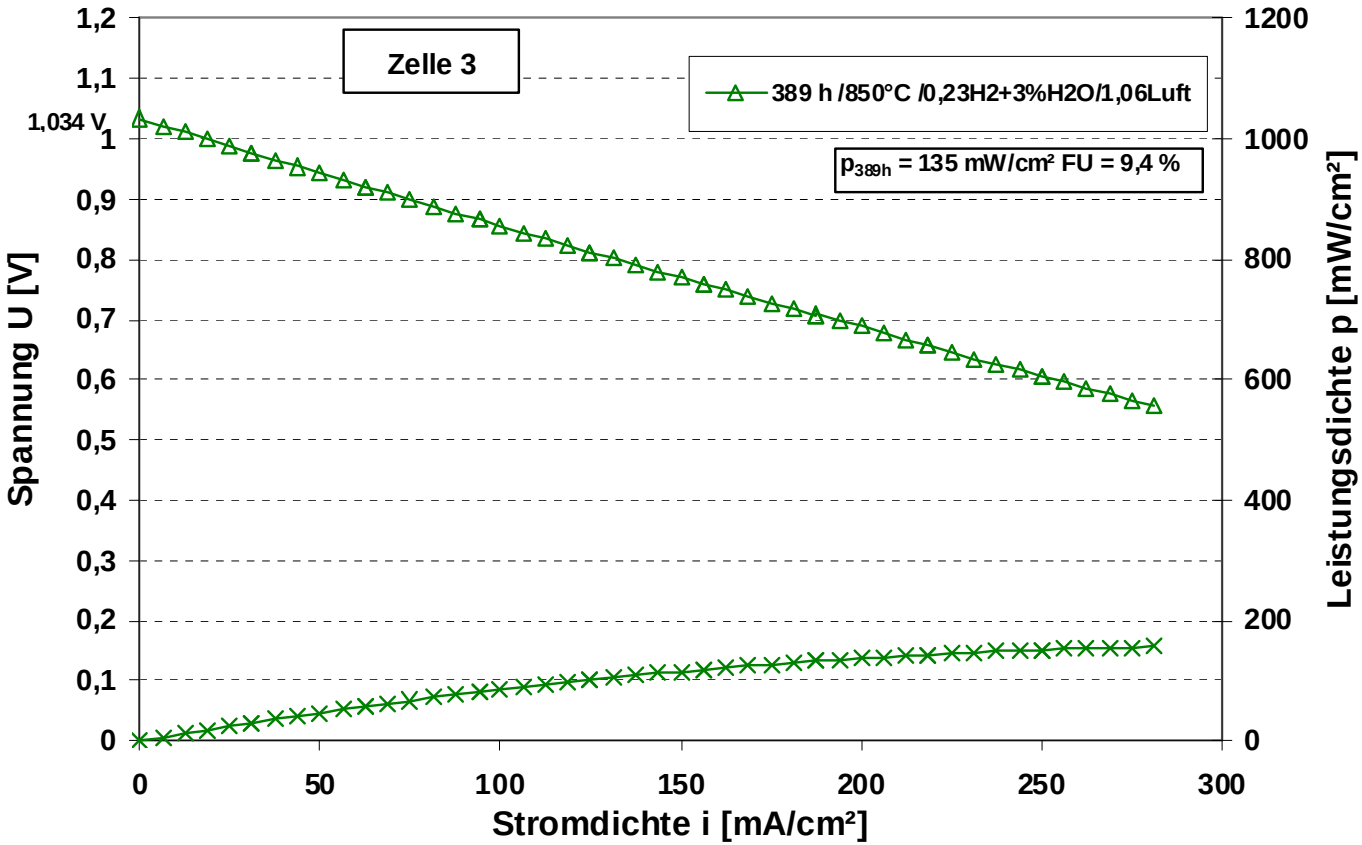
Experimental Setup for Raman Spectroscopy Measurements

Cell Housing with Transparent Flowfield in Hot Furnace

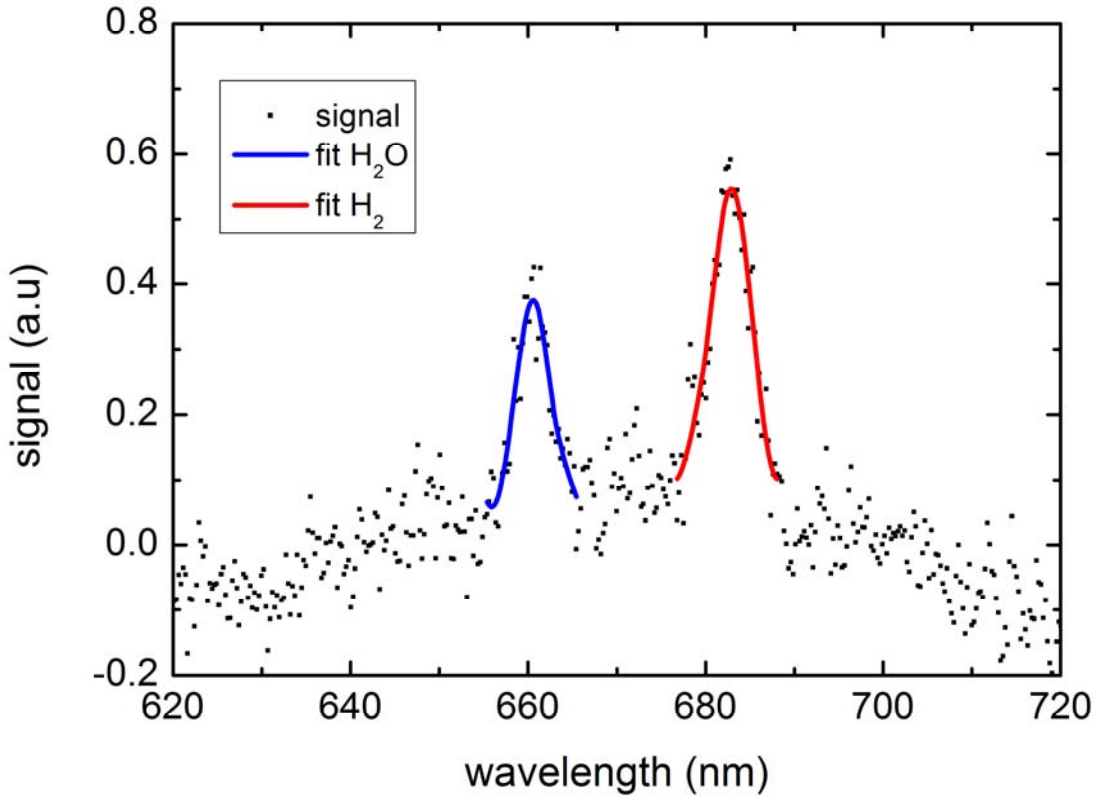


IV Characteristics of ESC Cell

0,23 NL/min H_2 + 3 % H_2O / 1,06 NL/min air, 850 °C



First Results of Raman Spectra

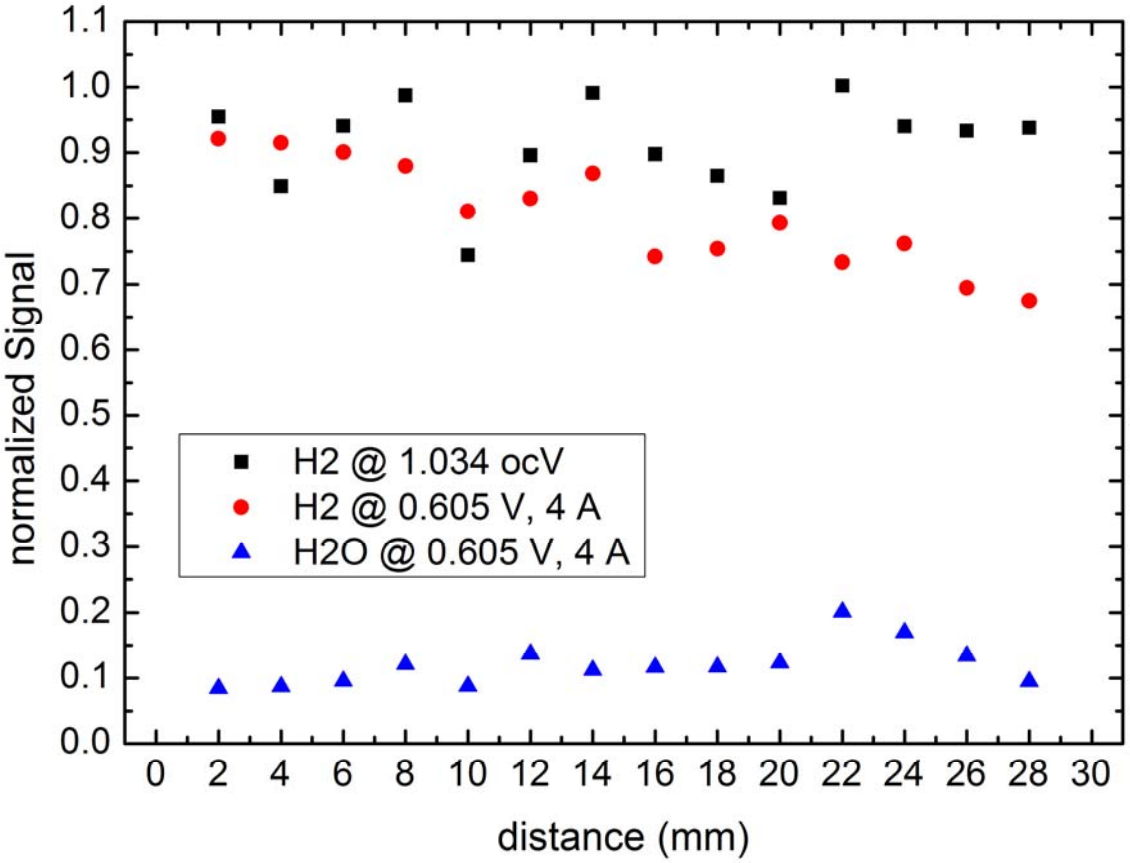


H_2+3%H_2O
850°C

Large scatter in detected signal

Improvement of S/N ratio needed

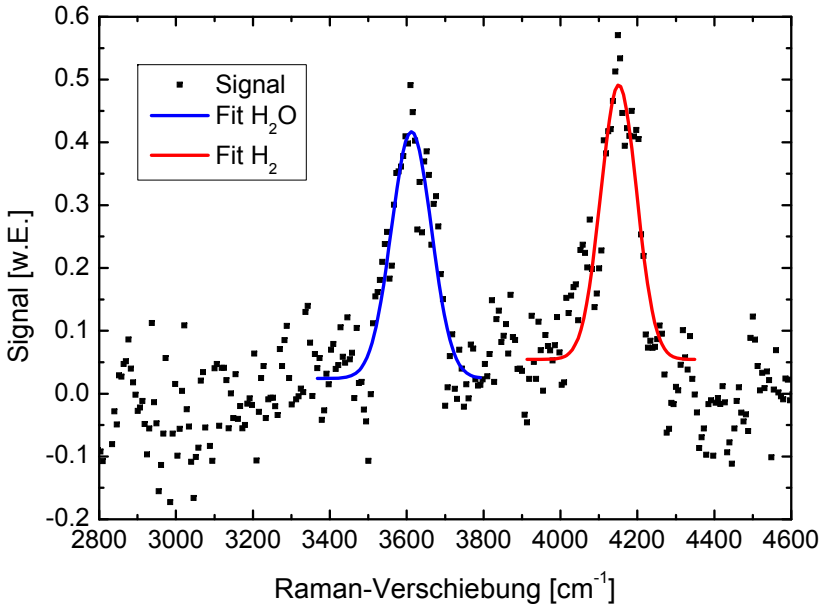
Raman Signals as a Function of Distance Along Channel

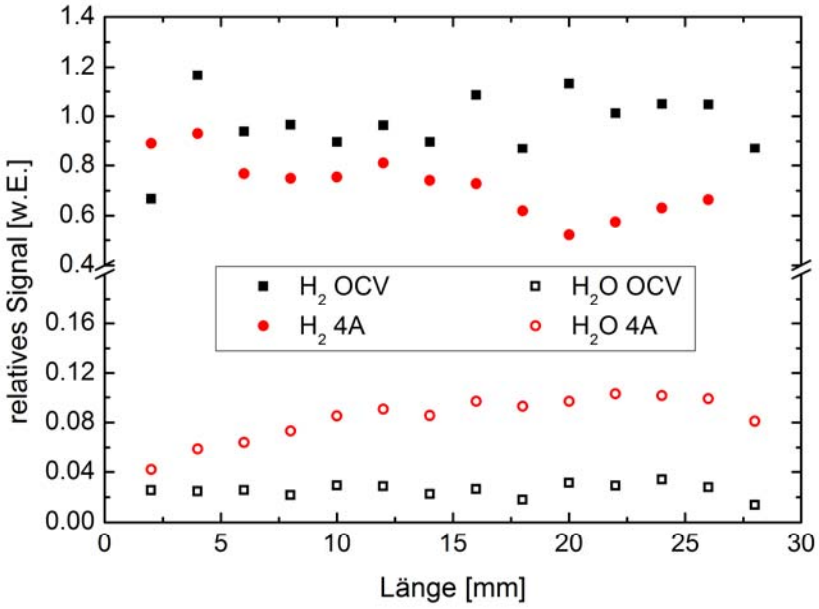


H_2+3%H_2O
850°C

Tendencies of the species concentration profiles can be seen

Raman Spectra of H_2 and H_2O Concentrations Along the Flow Channel





H_2 + 3% H_2O; 0,112 NL/min H2, 1,06 NL/min air, 850 °C

Improvements Needed for a Following Measuring Campaign

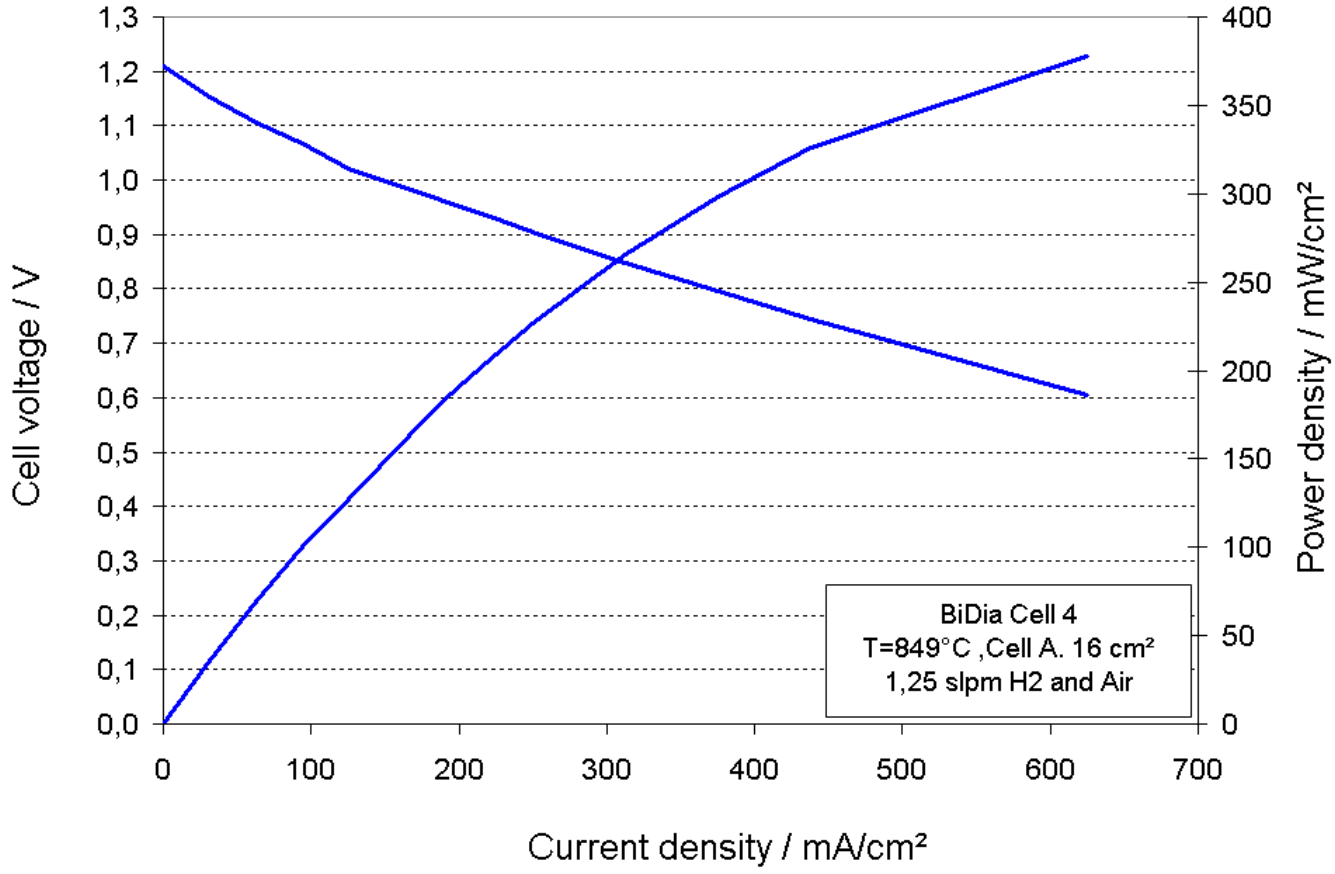
- Improved flowfield with broader and higher gas channels (3 x 4 mm instead of 2 x 2 mm)

- Adaptation of cell housing to changed geometries

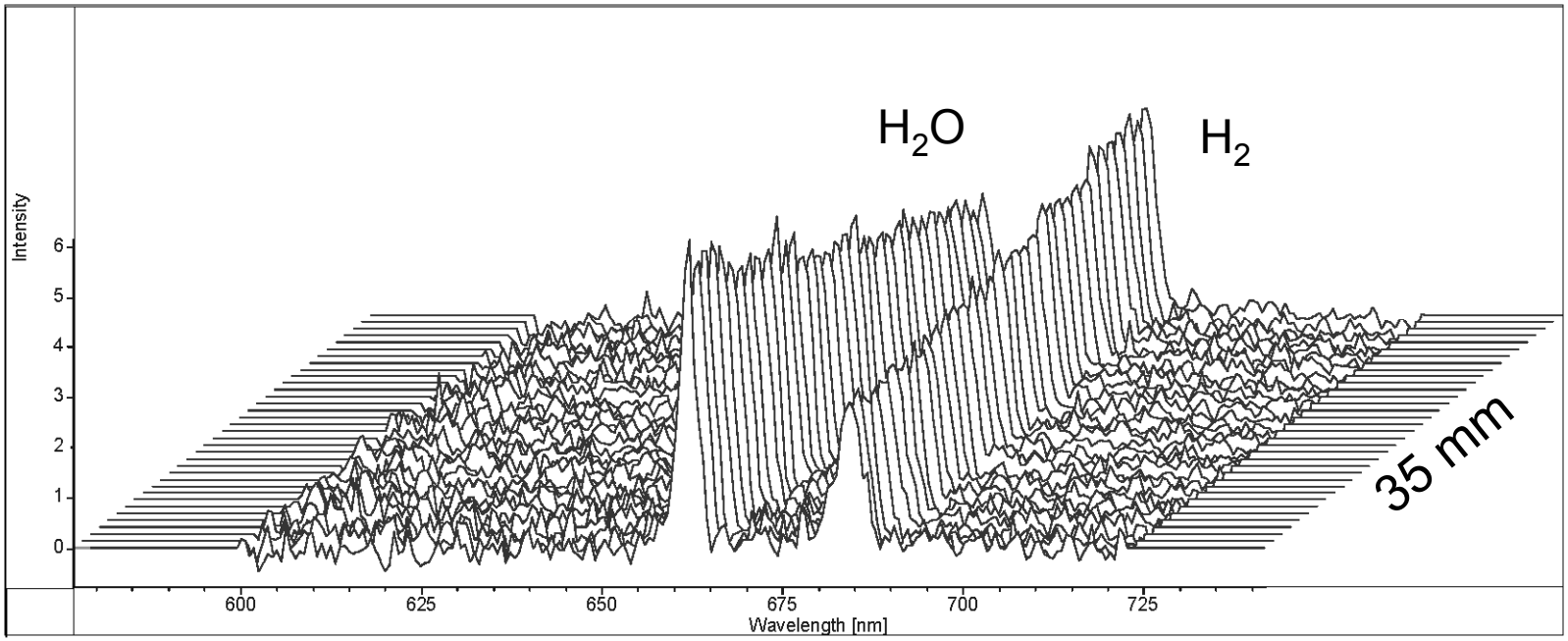
- Laser detection with a CCD camera with higher sensitivity

⇒ Measurements at different temperatures, with different gas compositions and different water contents

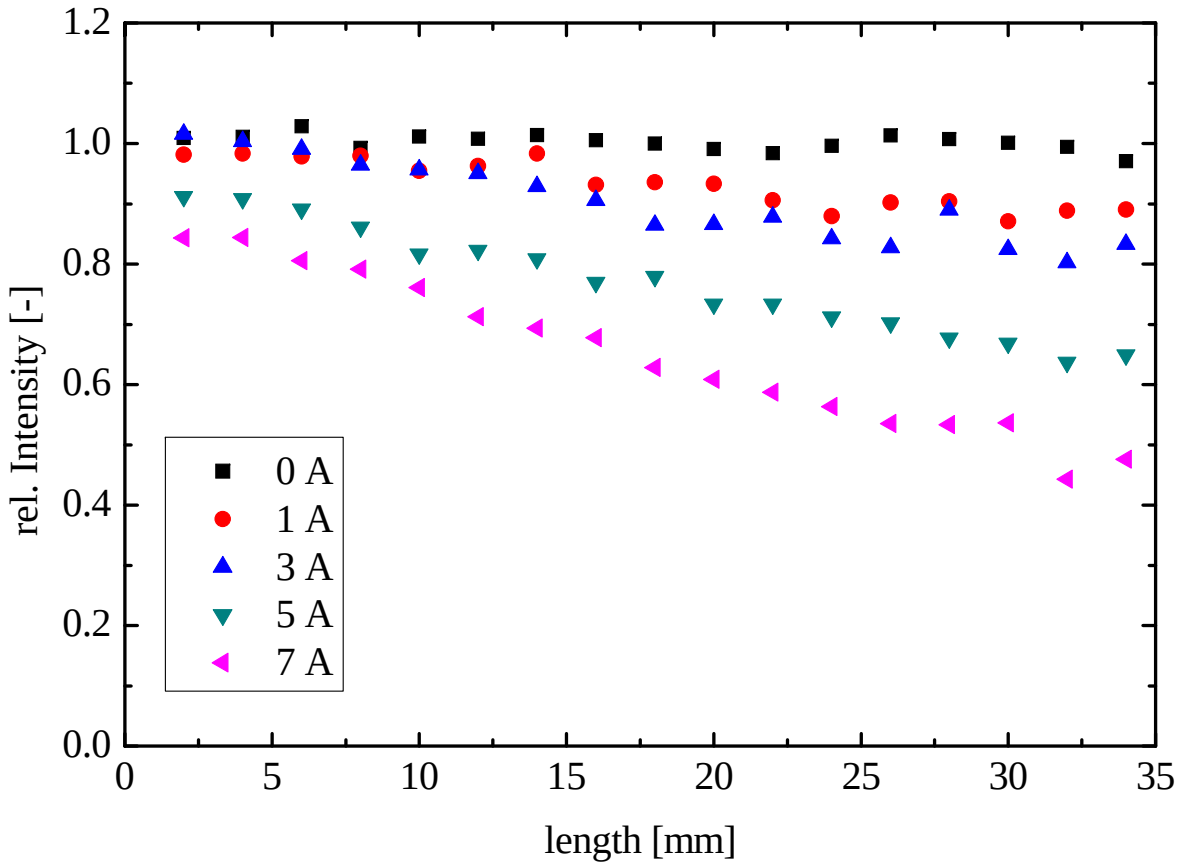
IV Characteristics of ESC Cell



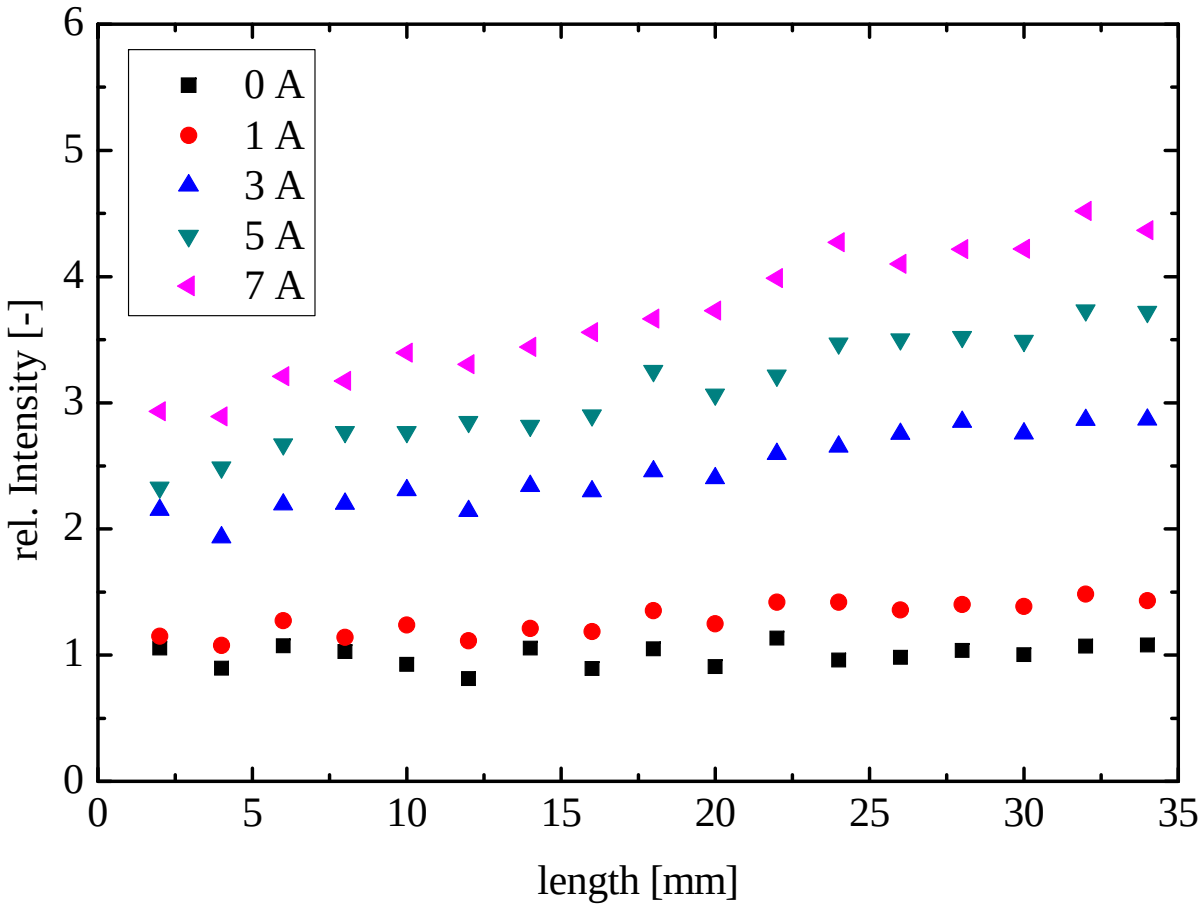
Raman Spectra of an ESC Cell Operated at 5 A



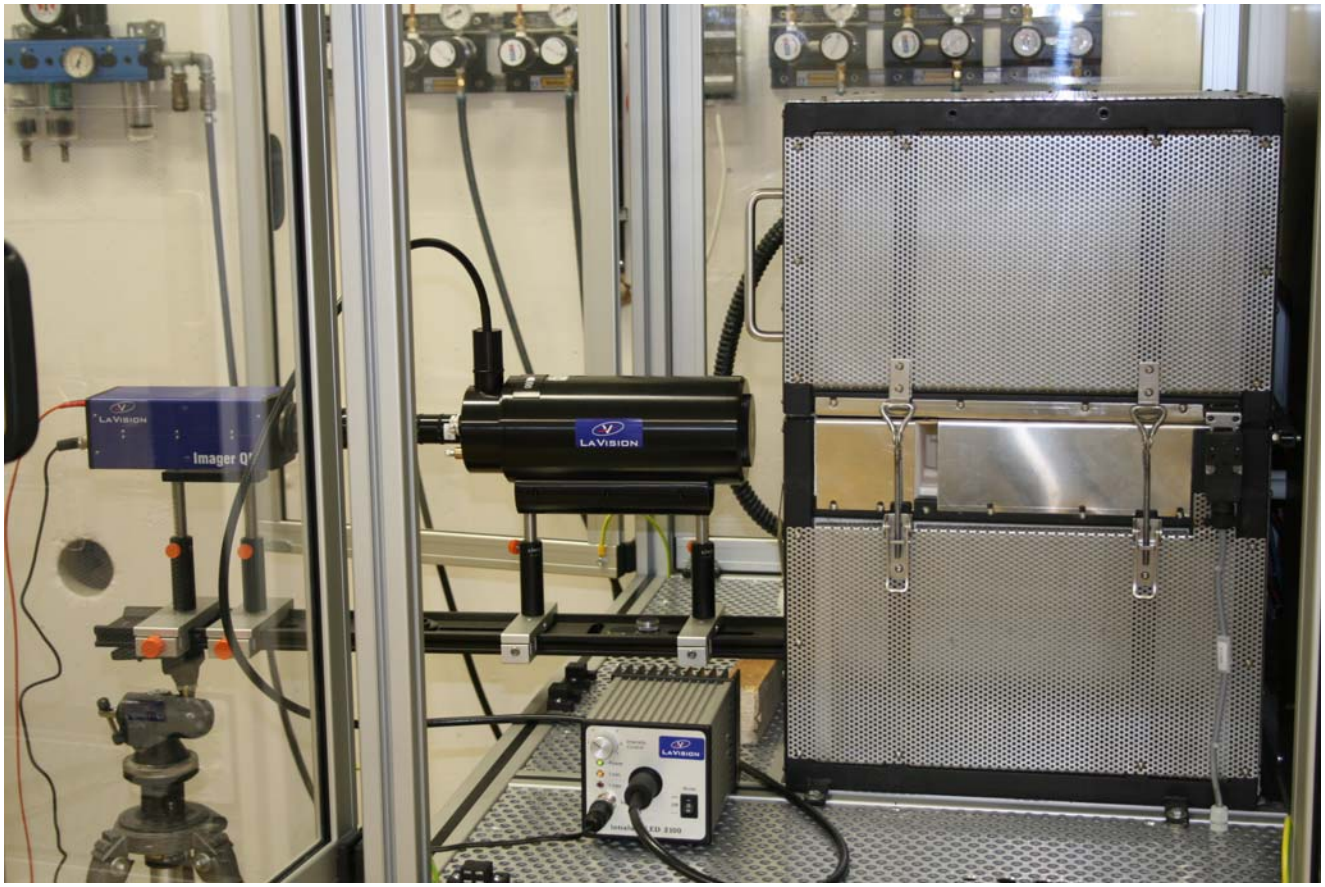
Raman Signals of H_2 as a Function of Distance Along the Flow Channel



Raman Signals of H_2O as a Function of Distance Along the Flow Channel



Setup for In-Situ Optical Microscopy



Conclusion

- In-situ diagnostic techniques allow for a largely extended insight into fuel cell processes (fundamental understanding, optimization of flow field)
- The potential of spatially resolved diagnostics was demonstrated with some exemplary results
- The obtained data can be used for modeling and simulation for identification of critical operating conditions
- Strong gradients of gas concentrations and current density particularly at operation with high fuel utilization may result in locally critical operating behavior
- Qualitative results of Laser Raman Spectroscopy measurements have been shown, quantitative measurements are in progress.