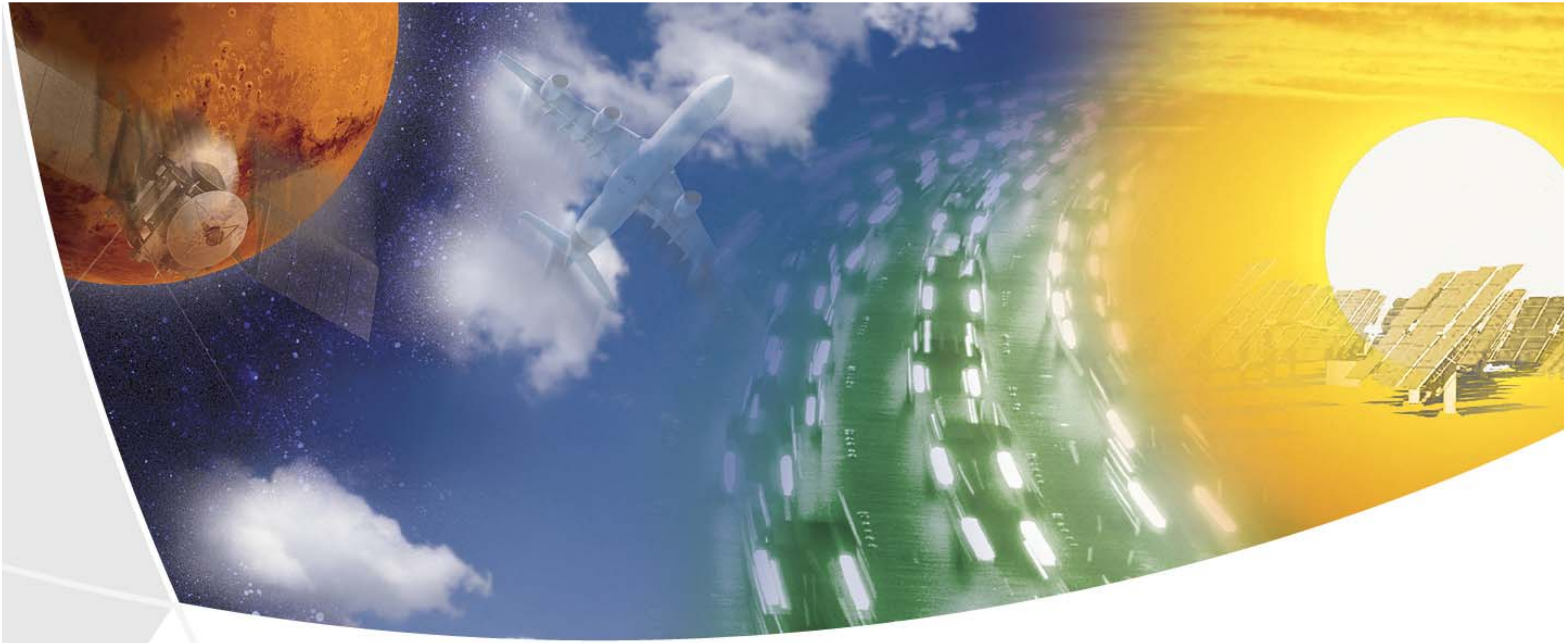

Analytical Investigation of Fuel Cells by Using In-situ and Ex-situ Diagnostic Methods

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in der Helmholtz-Gemeinschaft

Outline

- Introduction
- Spatially Resolved Measuring Technique for PEFC/DMFC
- Investigation of PEM Fuel Cells With Combined In-situ and Ex-situ Methods
- Spatially Resolved Measuring Technique for SOFC
- Conclusion

Motivation for Using Diagnostic Tools

- To understand the processes in fuel cells in great detail
  - Influence of the operating conditions on the conditions inside the fuel cell
  - Understanding of degradation processes
  - Inhibition of degradation processes

- To support the development and improvement of fuel cells
  - Detection of problems of components
  - Targeted development

- To control fuel cell systems
  - Optimization of operating conditions
  - Increase of lifetime
  - Early error detection, increased reliability

Investigation of Degradation Processes

Physical methods (ex-situ diagnostics)

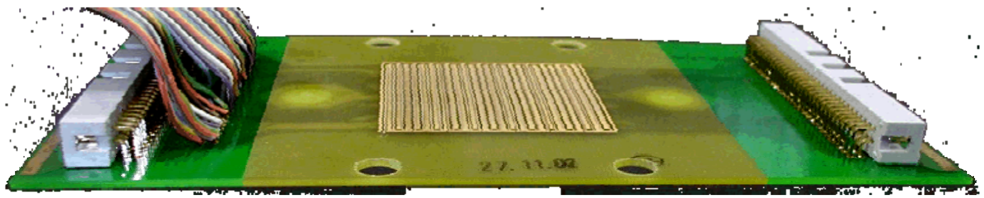
- Scanning Electron Microscopy (SEM/EDX)
- X-Ray Photoelectron Spectroscopy (XPS)
- X-Ray Diffraction (XRD)
- Porosimetry with mercury intrusion & nitrogen adsorption
- Temperature Programmed Desorption / Reduction / Oxidation (TPD / TPR / TPO)

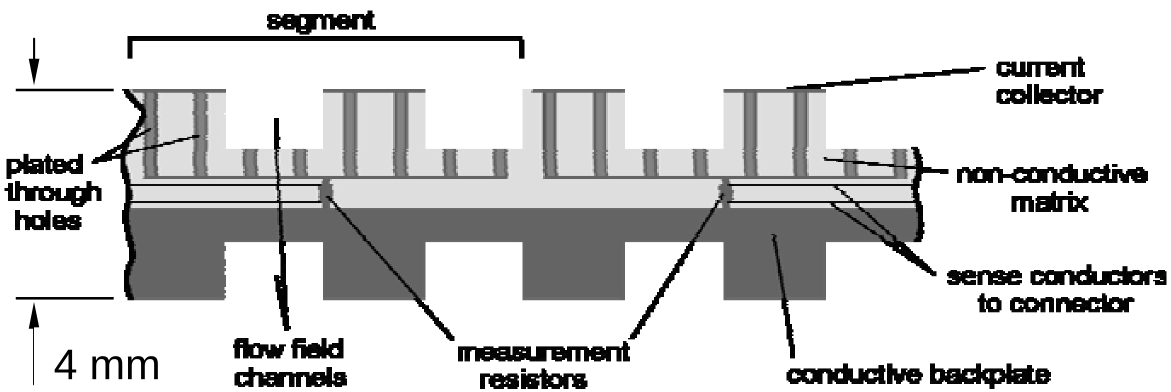
Electrochemical methods (in-situ diagnostics)

- I-V characteristics
- Electrochemical Impedance Spectroscopy (EIS)
- Locally-resolved measurements (e.g. current density distribution)

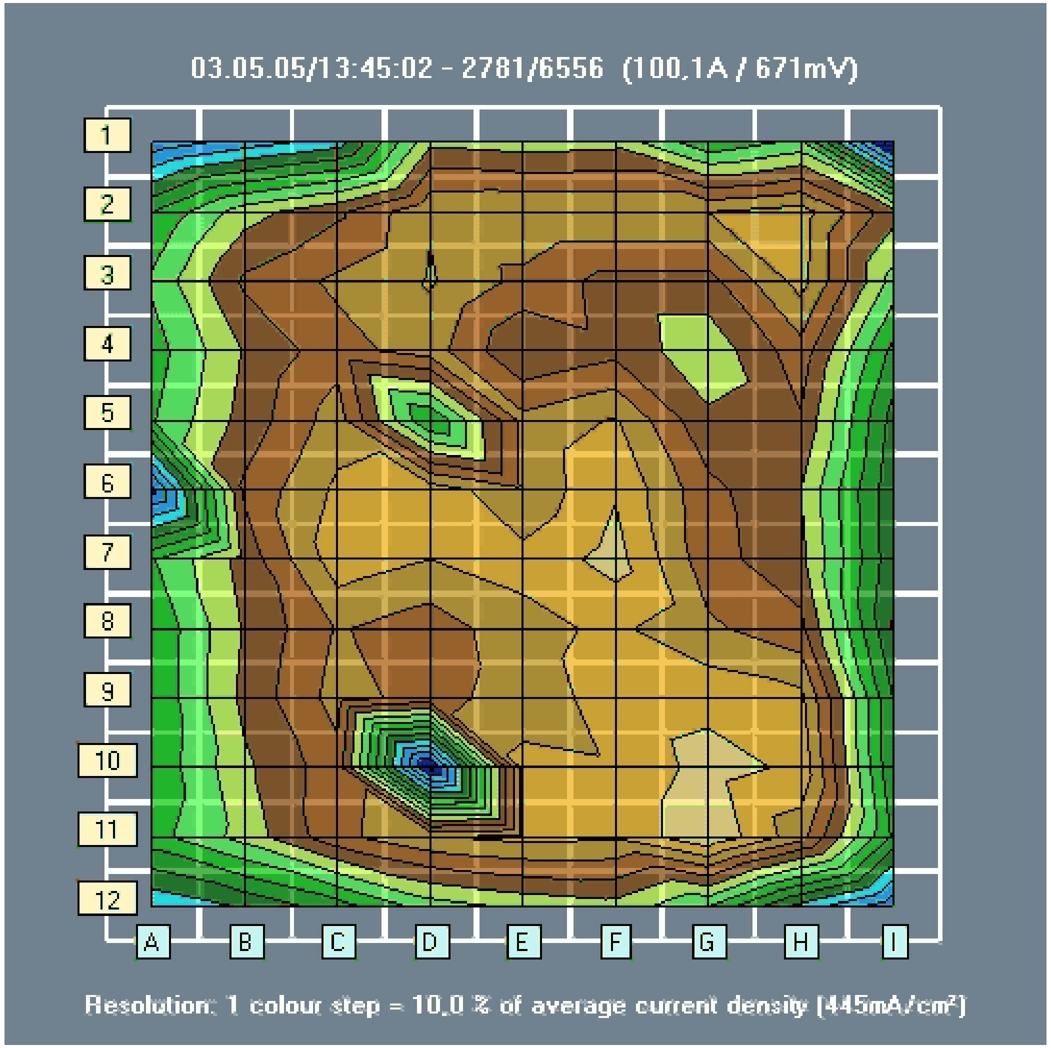
Segmented Cells for Locally Resolved Diagnostics

Current density, Temperature, Impedance Spectroscopy

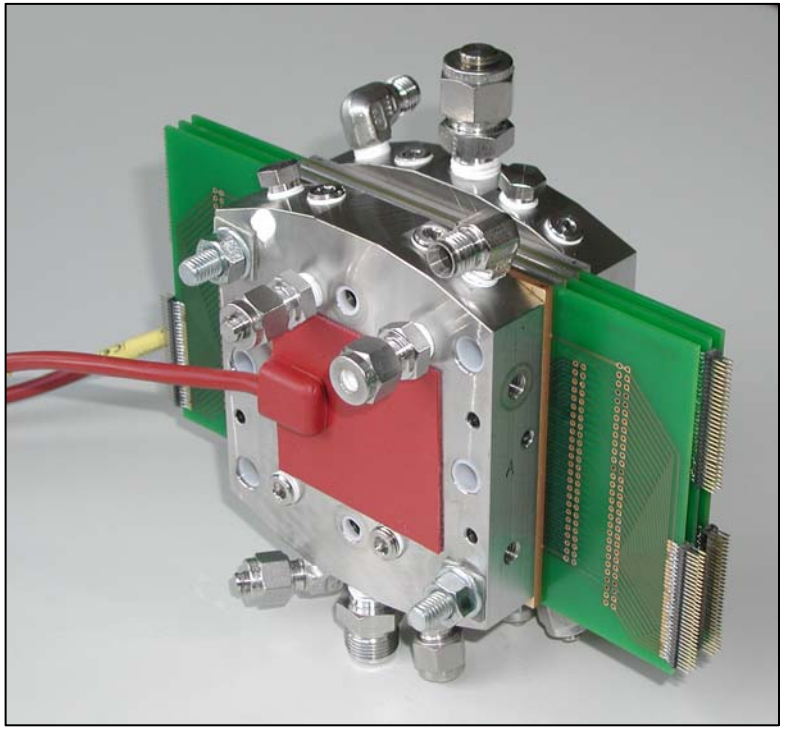


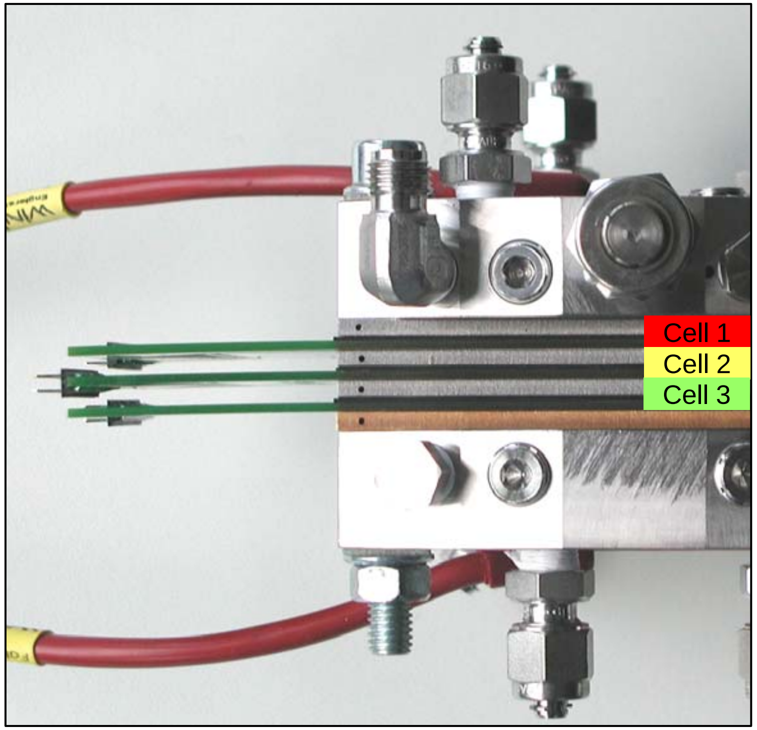


Current Density Distribution at Reduced Humidification

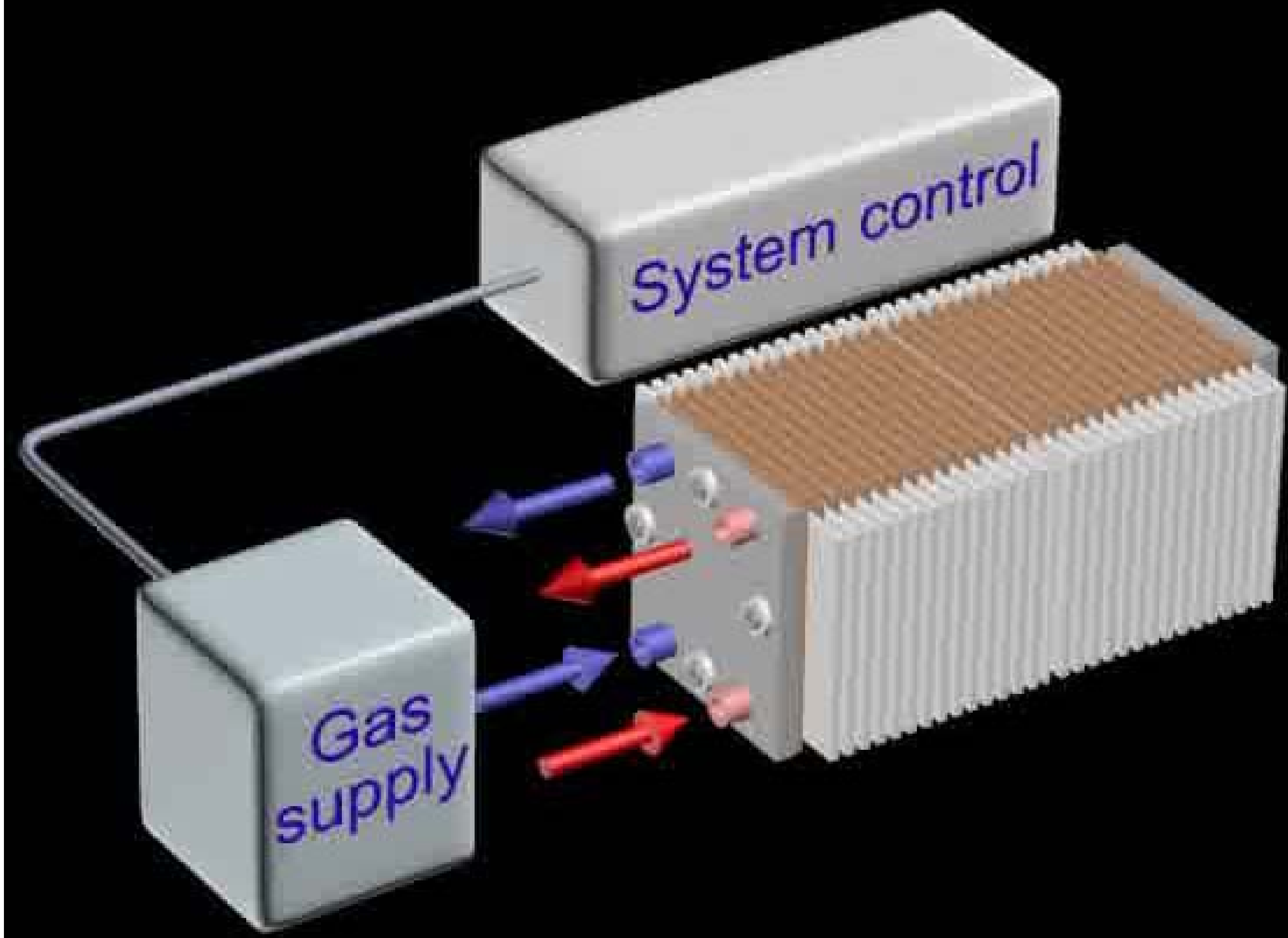


Integration of Segmented Bipolar Plates in a Shortstack

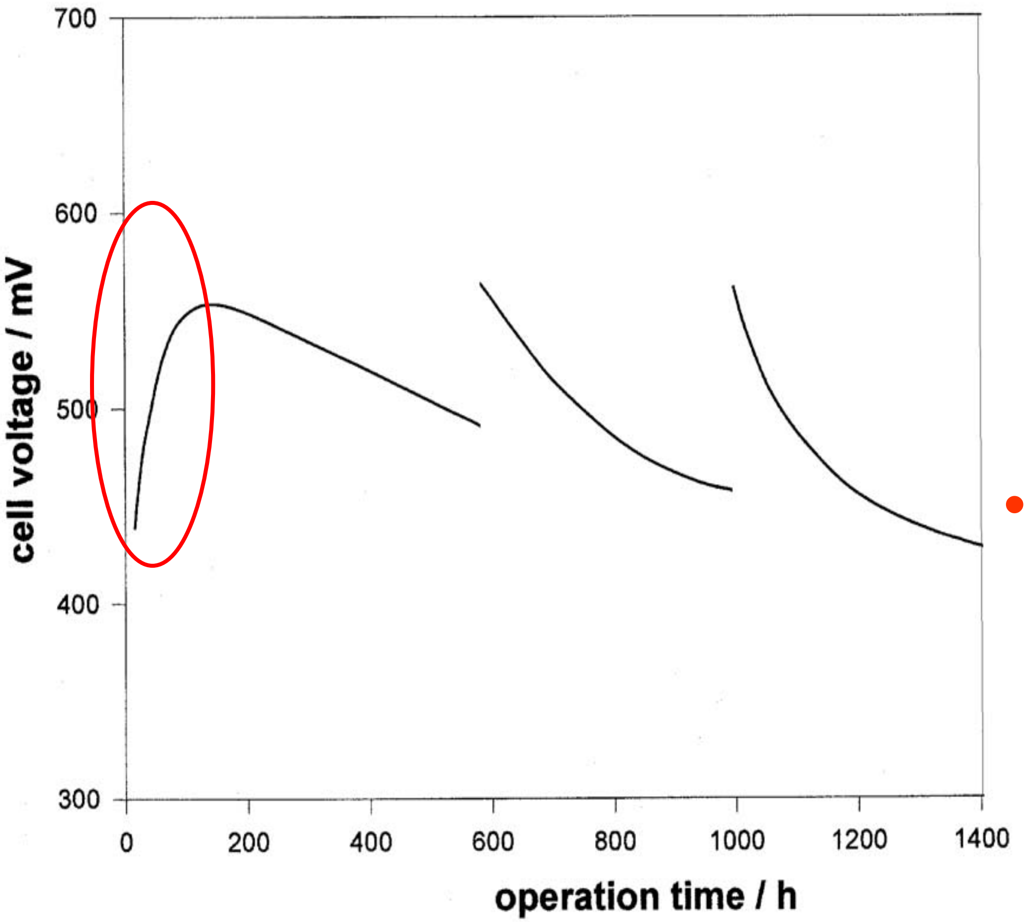




Sensor - Control System



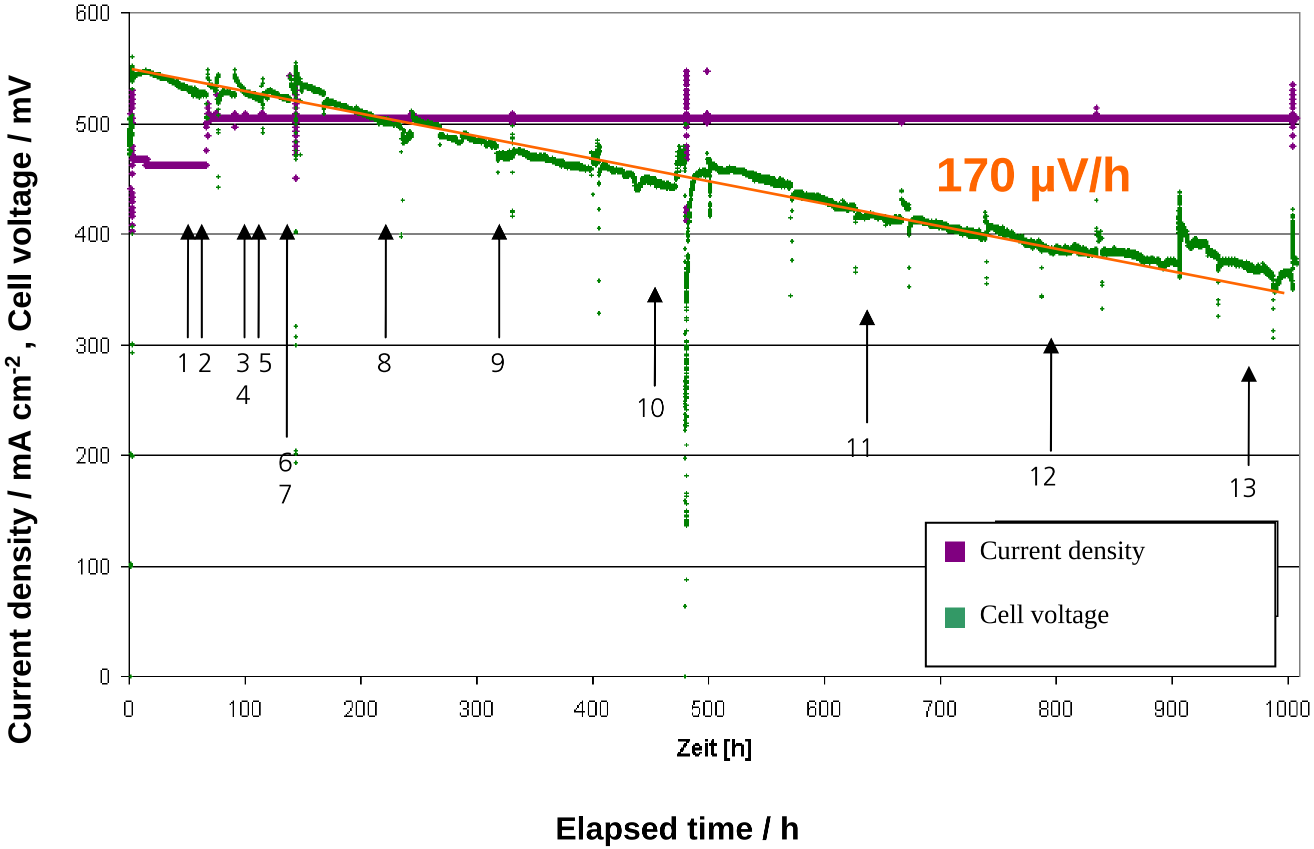
PEFC Long-Term Experiment



Nafion 1135
Pt 0.2 mg/cm^2 each electrode
T = 70 °C
p_{H2} = 2 bar, dead end
p_{air} = 2 bar, λ_{air} = 2
i = 300 mA/cm^2

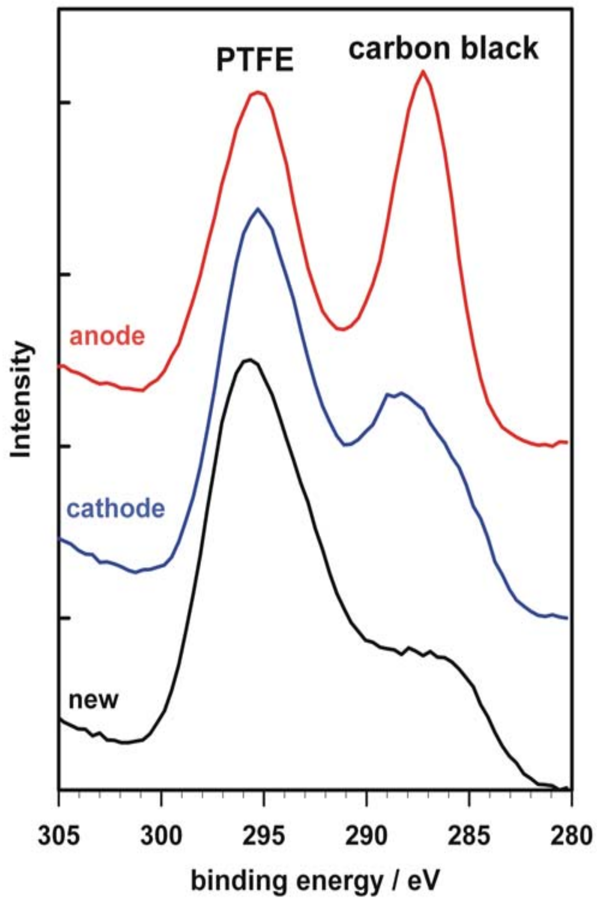
- **The electrochemical performance in-creases during start-up**

Change of Cell Voltage During Constant Load at 500 mA cm^{-2}



Degradation in PEFC

X-ray photoelectron spectroscopy



- Partial decomposition of PTFE identified by X-ray photoelectron spectroscopy
- PTFE decomposition mainly on the anode

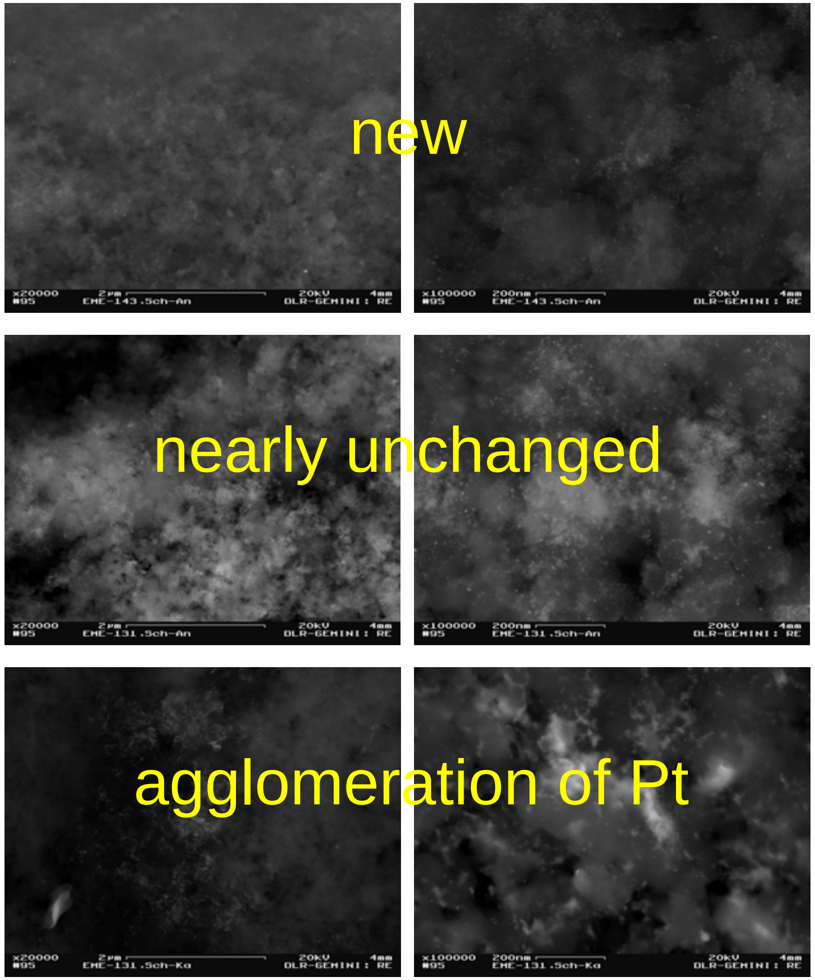
→ Decrease of hydrophobicity

→ Changed water balance

→ Reversible loss of electro-chemical performance

Investigation of Degradation Processes

Platinum catalyst



Reaction layers in MEAs, prepared by the DLR dry spraying technique

Top: **new** electrode

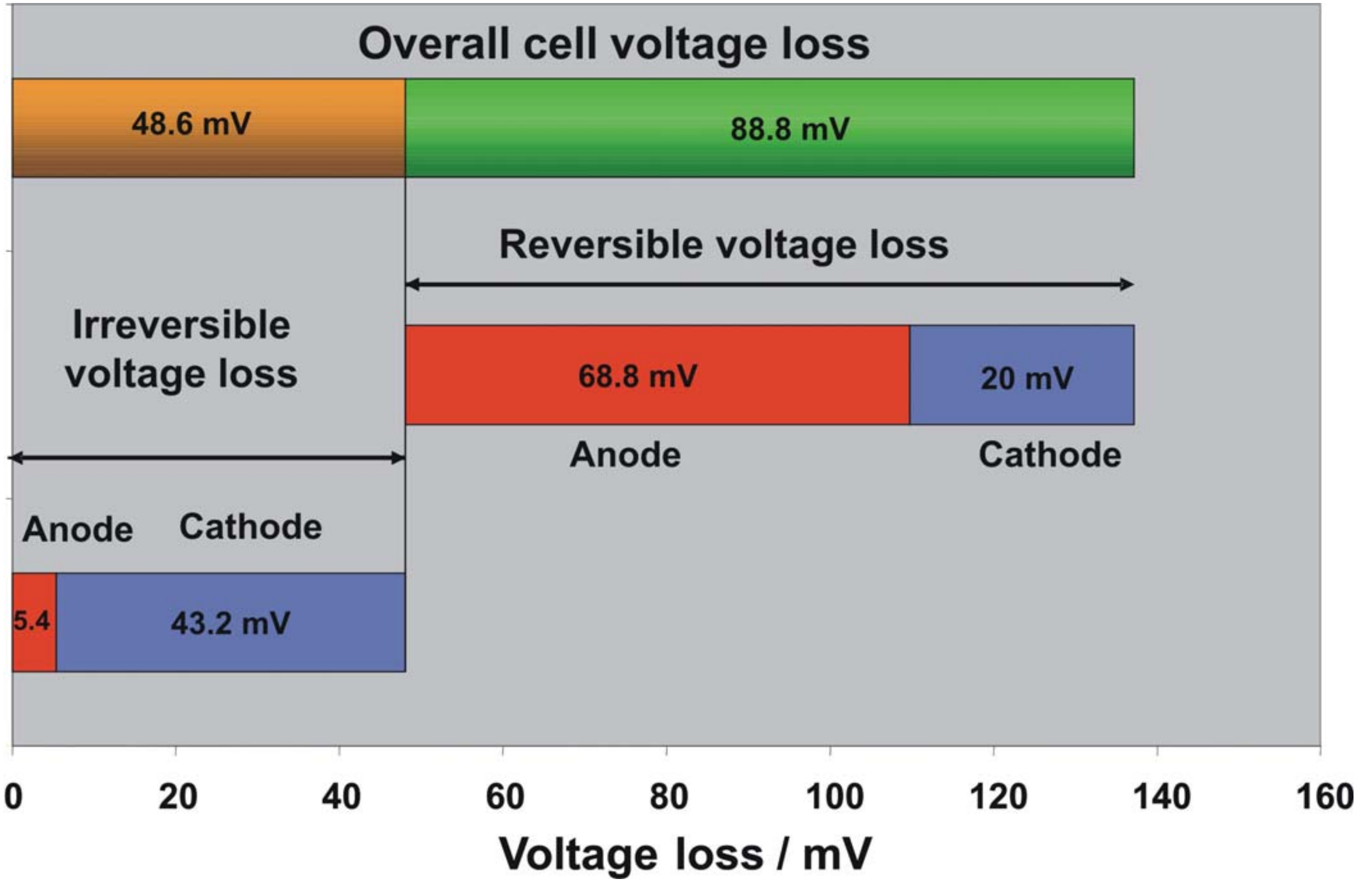
Middle: **anode** reaction layer of an used MEA, normal operation

Bottom: **cathode** reaction layer of an used MEA, normal operation

Left side:
20.000 fold magnification
Right side:
100.000 fold magnification

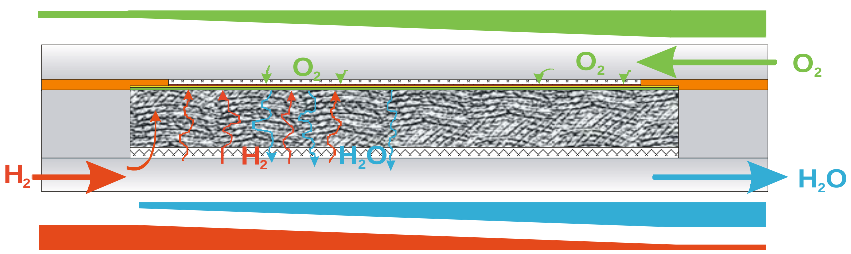
Degradation in PEFC

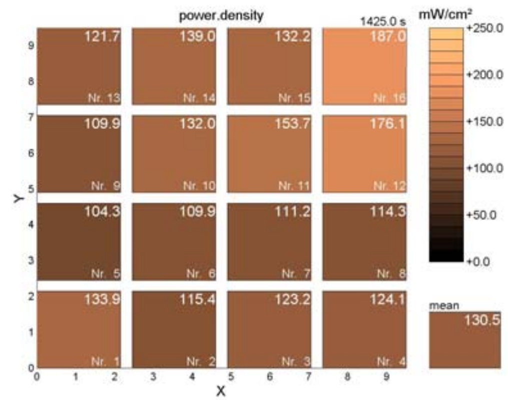
Quantification of voltage losses during degradation by EIS



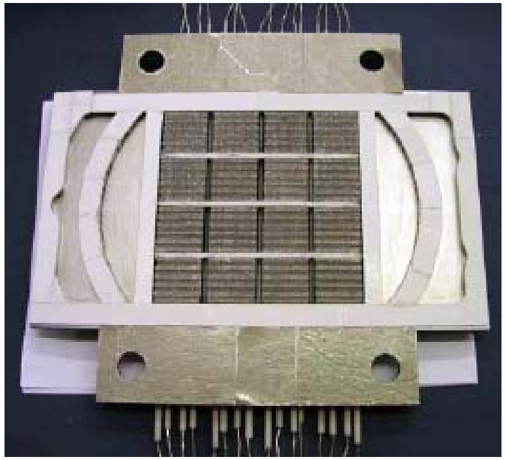
Motivation

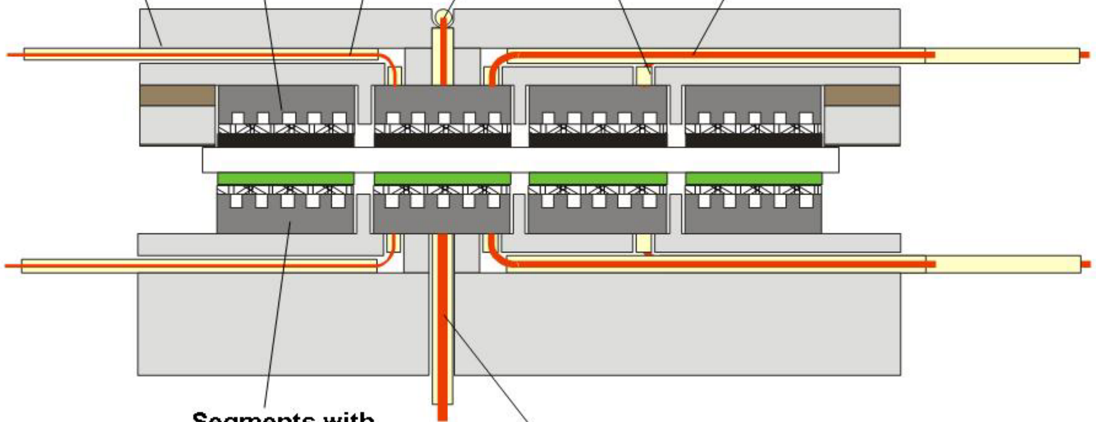
- Strong local variation of gas composition, temperature, current density
- Distribution of electrical and chemical potential dependent on local concentrations of reactants and products
  - Reduced efficiency
  - Temperature gradients
  - Thermo mechanical stress
  - Degradation of electrodes





Measurement Setup for Segmented Cells



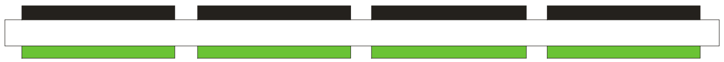


- 16 galvanically isolated segments
- Local and global i-V characteristics
- Local and global impedance measurements
- Local temperature measurements
- Local fuel concentrations
- Flexible design: substrate-, anode-, and electrolyte-supported cells
- Co- and counter-flow

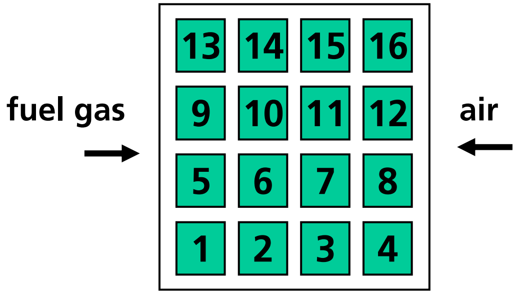
Segmented Cells

➢Anode supported cells with segmented cathode (H.C.Starck/InDEC)

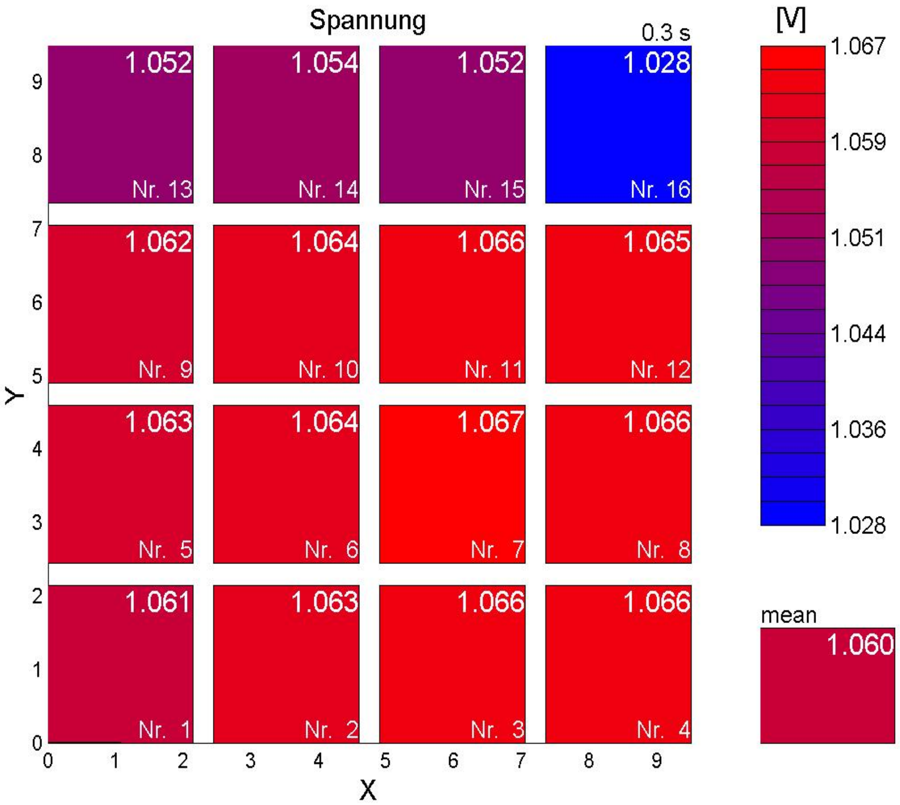
➢Electrolyte supported cells: segmented cathode and anode



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:

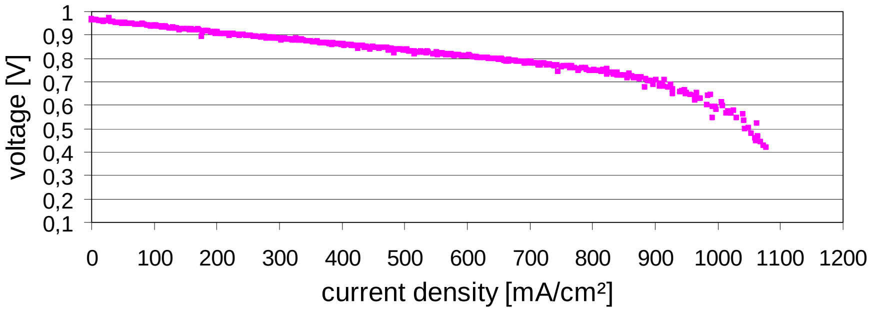
$$U_{rev} = U_{rev}^{0} - \frac{RT}{zF} \ln\left(\frac{p_{H2O}}{\sqrt{p_{O2}}\, p_{H2}} \right)$$

Produced water:

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

Locally Resolved I-V Characteristics at High Fuel Utilisation

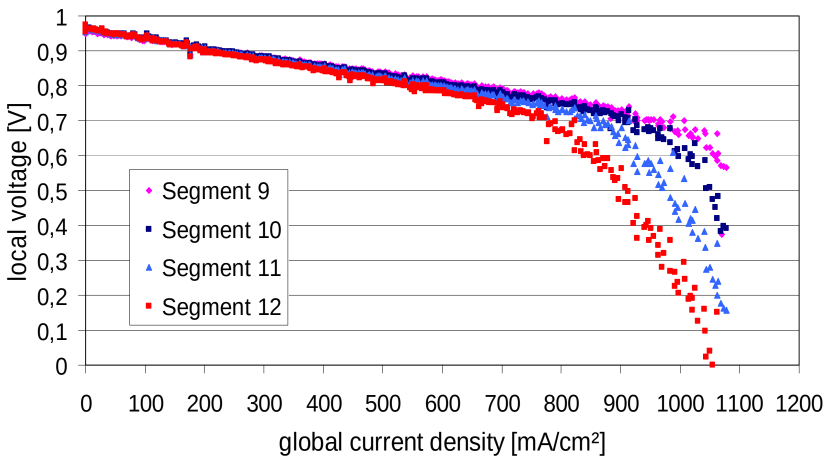
Global I-V characteristics:

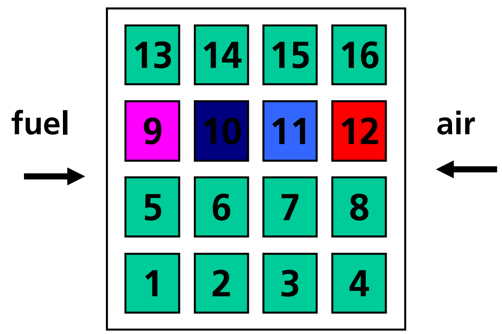


50% H_2, 50% H_2O; fu_{max}= 60%

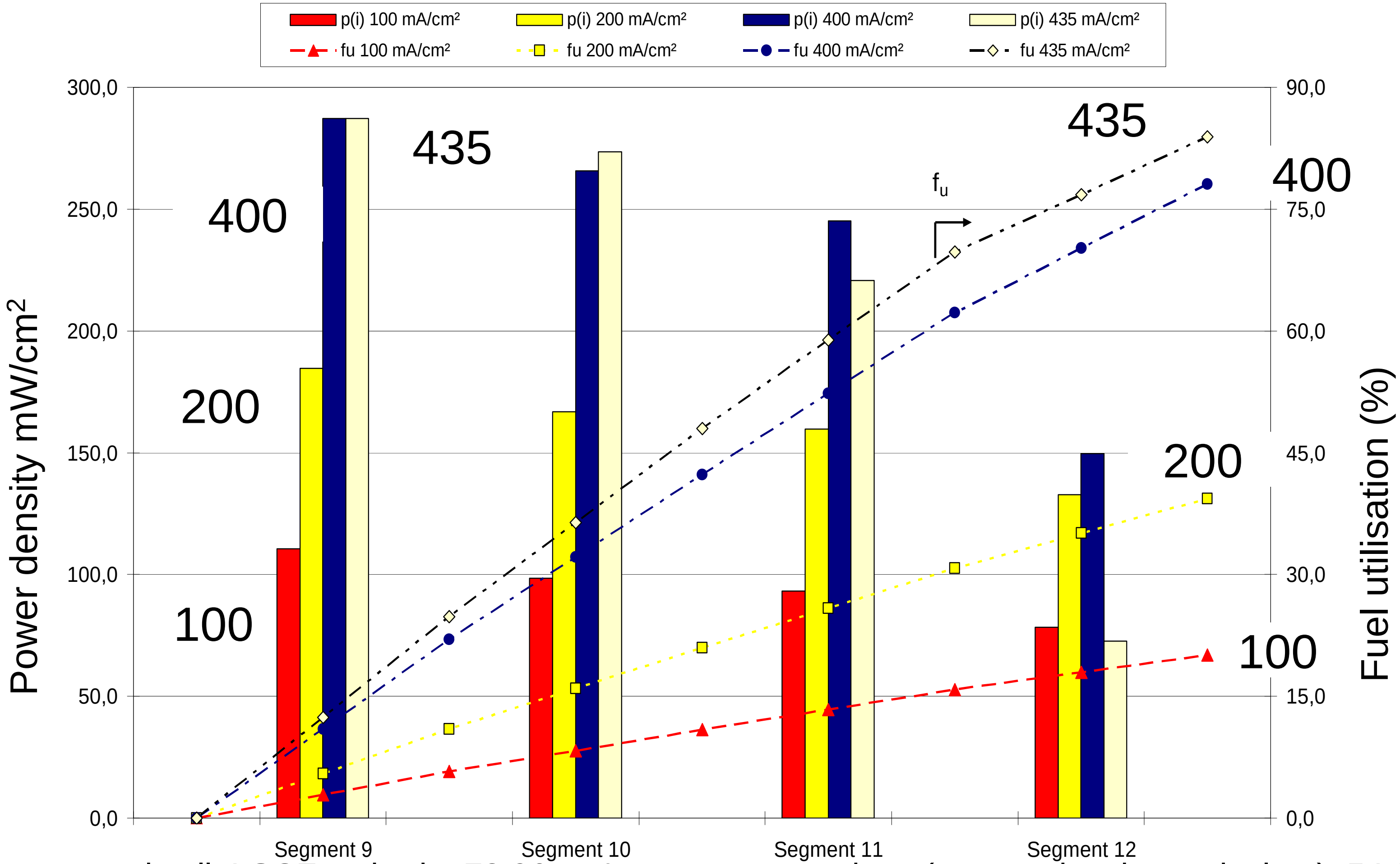
50% O_2, 50% N_2

Local I-V characteristics:



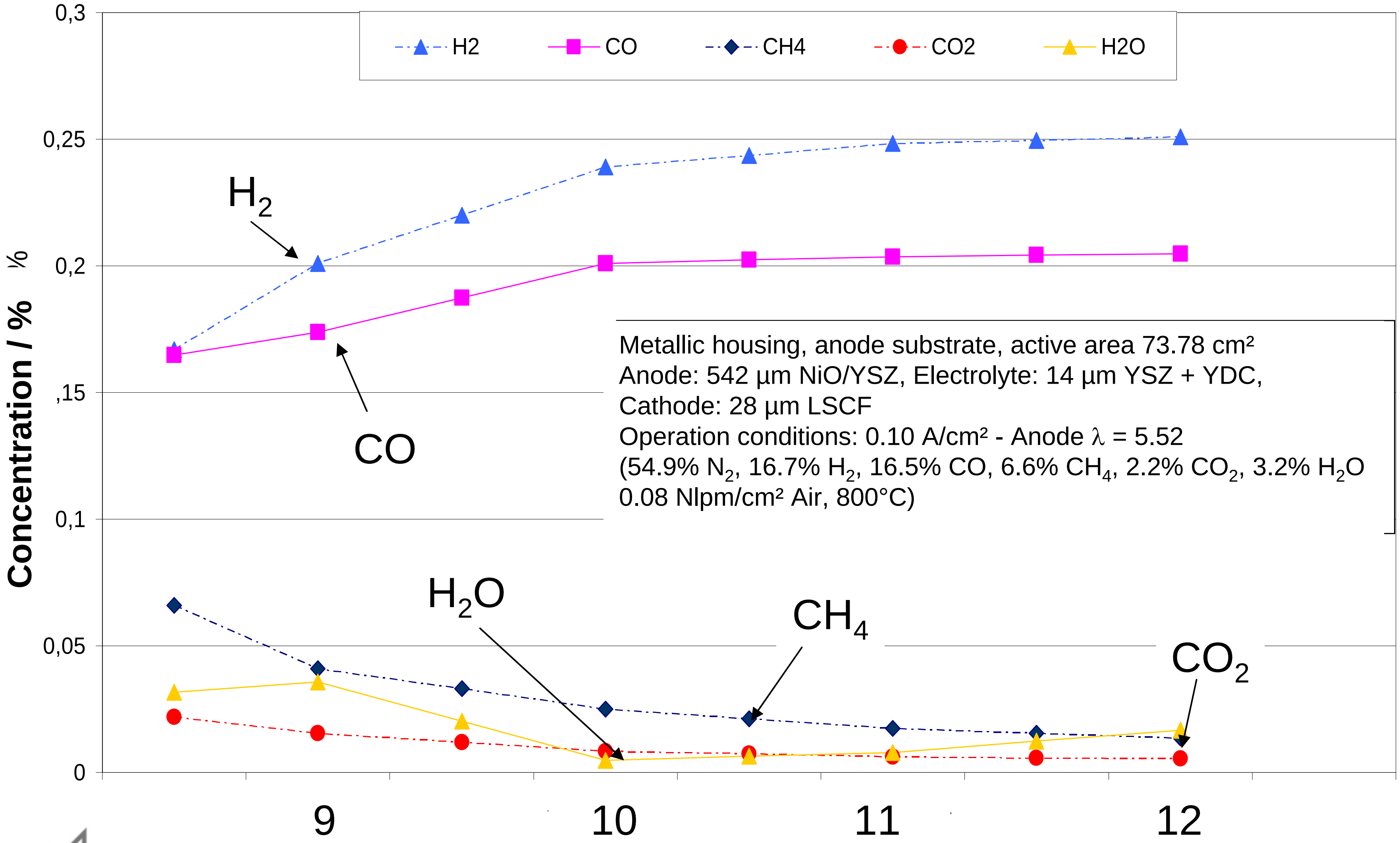


Variation of Load - Reformate

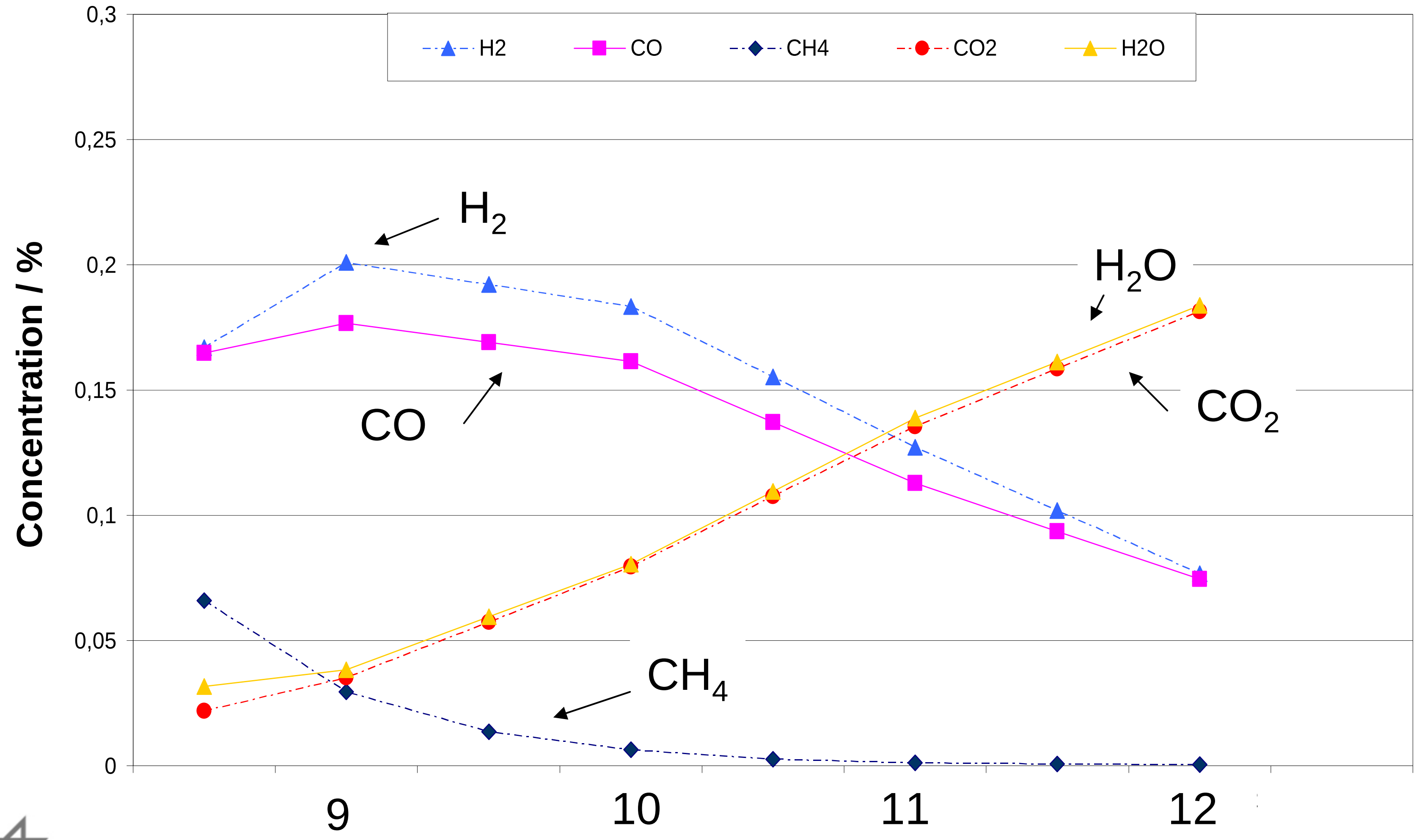


Anode supported cell, LSCF cathode, 73,96 cm², gas concentrations (current density equivalent): 54.9% N_2, 16.7% H_2, 16.5% CO, 6,6% CH_4, 2.2% CO_2, 3.2% H_2O (0.552 A/cm²), 0.02 SlpM/cm² air

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



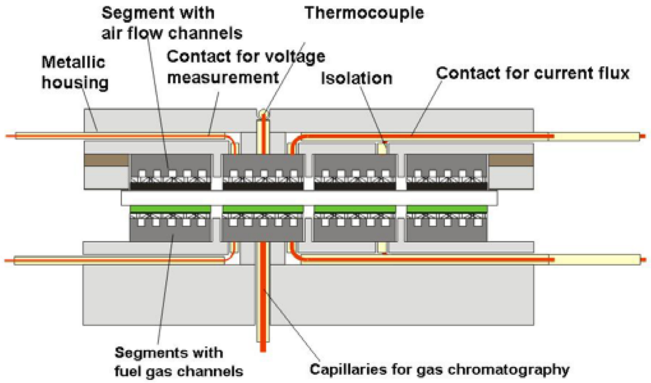
Alteration of the gas composition at 435 mA/cm²



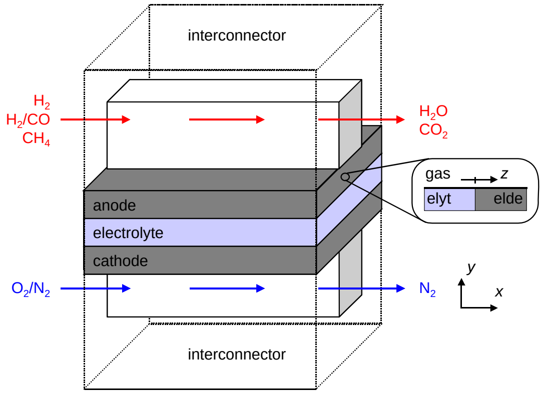
Combined Experimental and Modeling Approach

Objectives of the study:

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

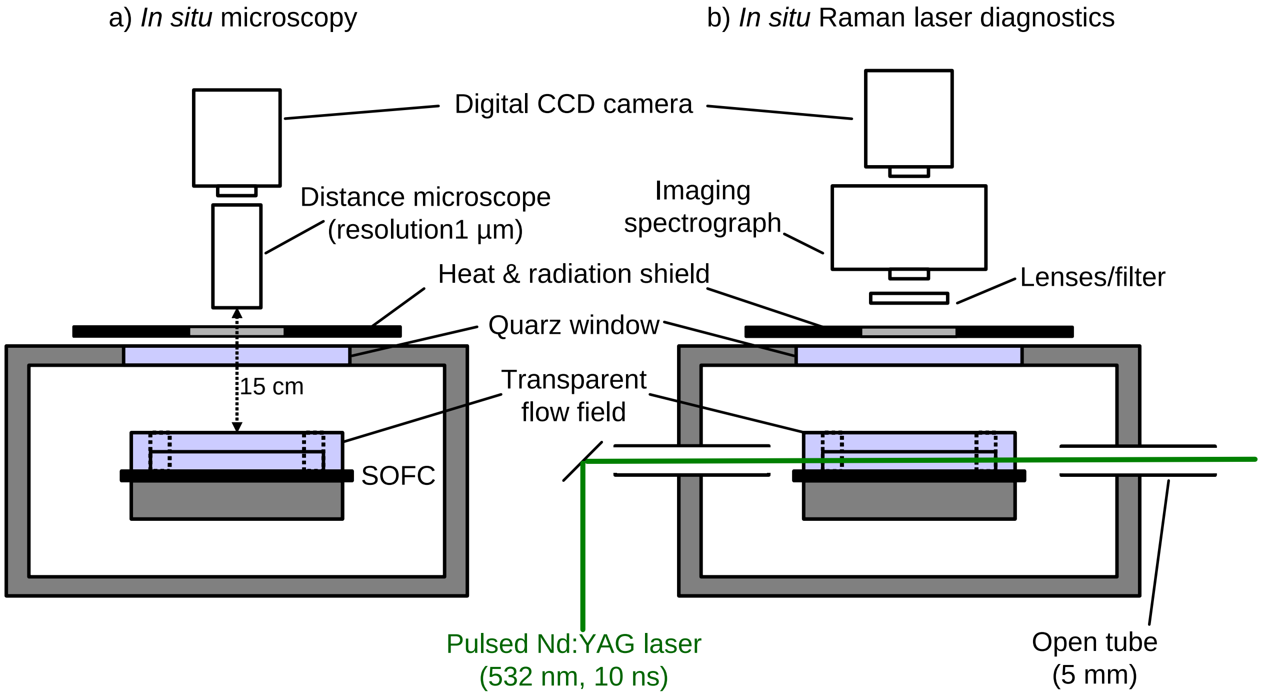


Experiments on single segmented SOFC



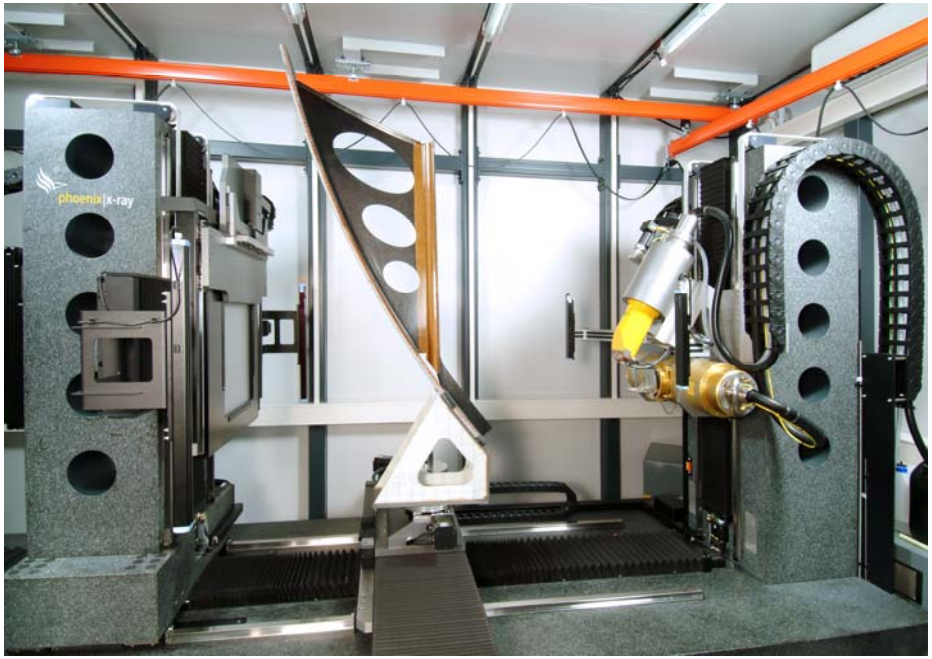
Electrochemical model of local distributions

Potential for Optical Spectroscopies



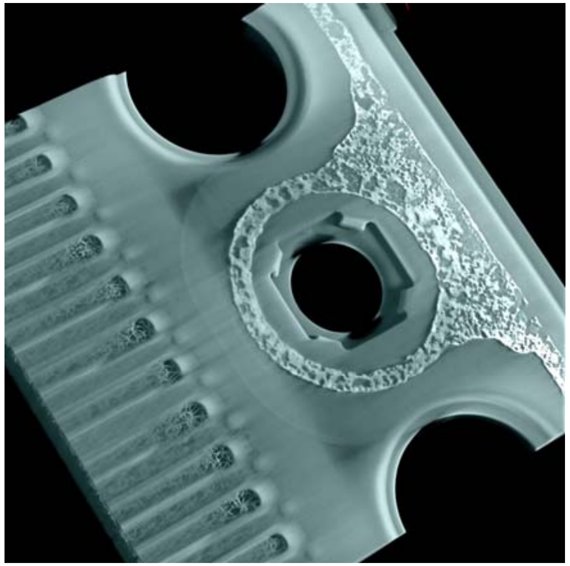
- Raman spectroscopy
- Laser Doppler Anemometry (LDA)
- Particle Image Velocimetry (PIV)
- Fast-Fourier Infrared (FTIR)
- Coherent Anti-Stokes Raman Spectroscopy (CARS)
- Electronic Speckle Pattern Interferometry (ESPI)

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 measuring techniques and exemplary results proved the possibility of
  - identifying different degradation mechanisms in fuel cells
  - optimizing operating conditions in fuel cells
  - establishing control strategies for reliable operation of fuel cells

- Combined in-situ and ex-situ diagnostic methods can provide additional important information:
  - Spatially resolved measurements to obtain local distribution of cell properties (current, voltage, impedance, gas composition, temperature)
  - Application of combined in-situ and ex-situ analytical methods
  - Combined analytical and modeling approach

- In order to overcome the remaining challenges in fuel cell development, i.e. performance, durability, reliability and costs, it is of paramount importance to improve the understanding of fuel cell operating mechanisms by applying sophisticated analytical methodology