International Symposium on
Diagnostics Tools for Fuel Cell Technologies

Impedance Spectroscopy as a Diagnosis Tool for SOFC Stacks and Systems

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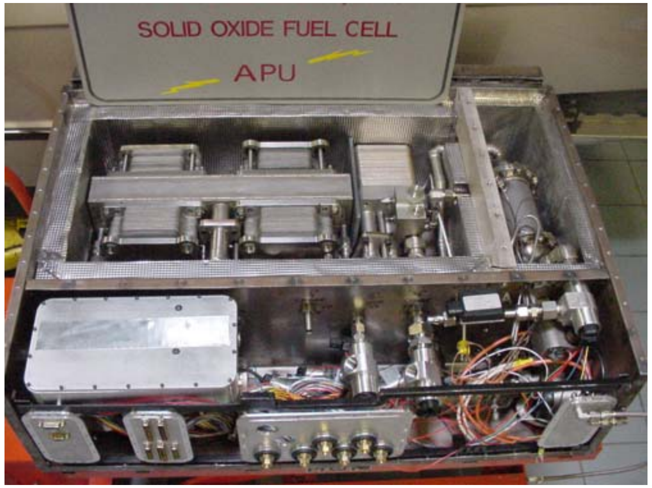
Control an Diagnosis of SOFC-Stacks and Systems
Stack Monitoring by Impedance Spectroscopy



Control of parameters critical for a failure free operation of stack and system

- **stack performance and efficiency**
- **stack temperature(s)**
- **reformer temperature(s)**
- **actual steam to carbon ratio / λ_{POx}-value**
- **fuel (reformate) composition**
- **oxidant and fuel flow rates**
- **oxidant and fuel temperatures at gas inlet**
- **oxidant and fuel pressure inlet**
- **exhaust gas composition** (remaining CO, HC´s)
- **...**

Monitoring of the internal resistance of the stack by electrochemical impedance spectroscopy

Electrochemical Impedance Spectroscopy

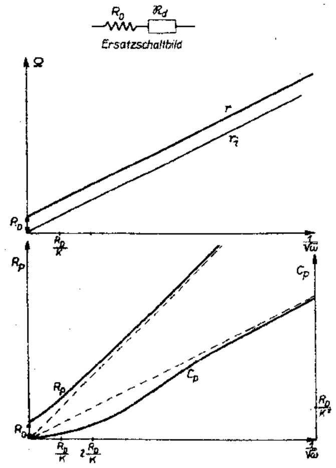


Abb. 8. Entladung + Diffusion.

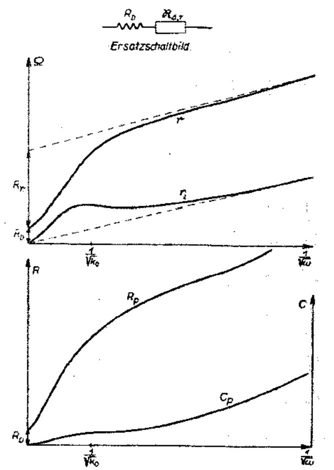
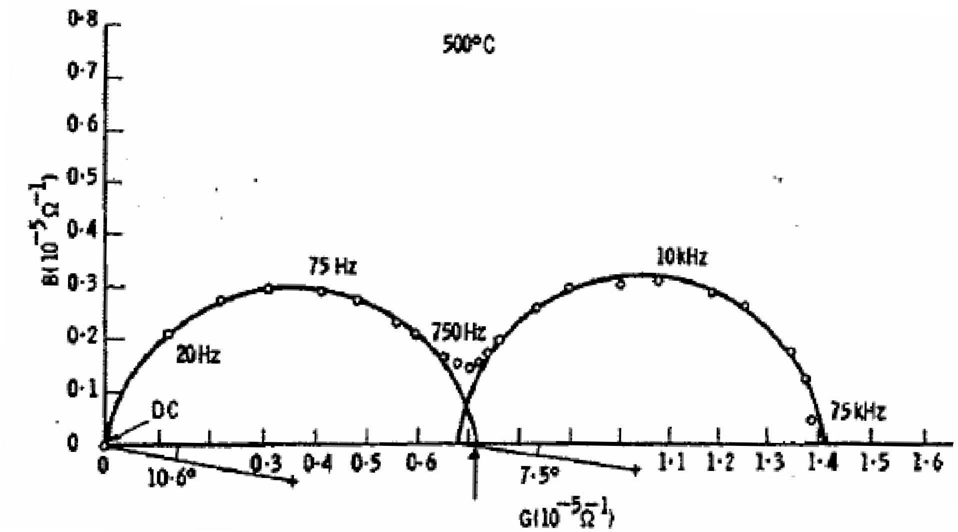


Abb. 9. Entladung + Diffusion mit gleichzeitiger homogener Reaktion.

H. Gerischer, *Elektrodenpolarisation bei Überlagerung von Wechselstrom und Gleichstrom.*
Z. Elektrochem., **58**, 9, 278, 1954

Electrochemical Impedance Spectroscopy

Analysis of Solid Electrolytes by Impedance Spectroscopy



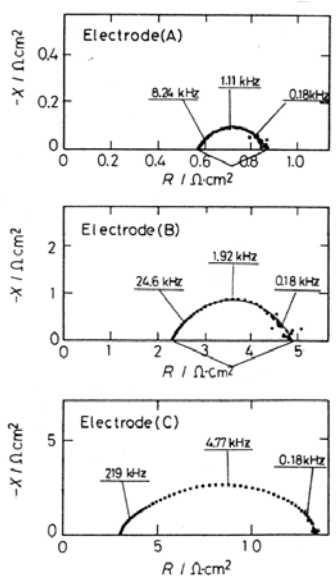
J. E. Bauerle, *Study of solid electrolyte polarization by a complex admittance method,* J. Phys. Chem. Solids **30**, 2657, 1969

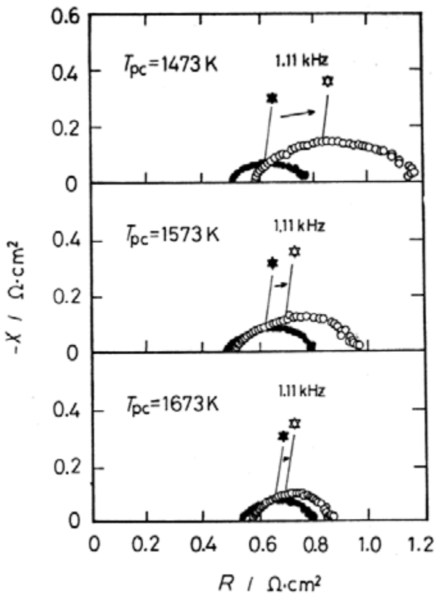
Impedance Spectroscopy
Materials, (Model-) Electrodes and Single Cells

Electrochemical Impedance Spectroscopy

Analysis of Solid Electrolytes by Impedance Spectroscopy

Analysis of Electrode Microstructure and Degradation Behaviour

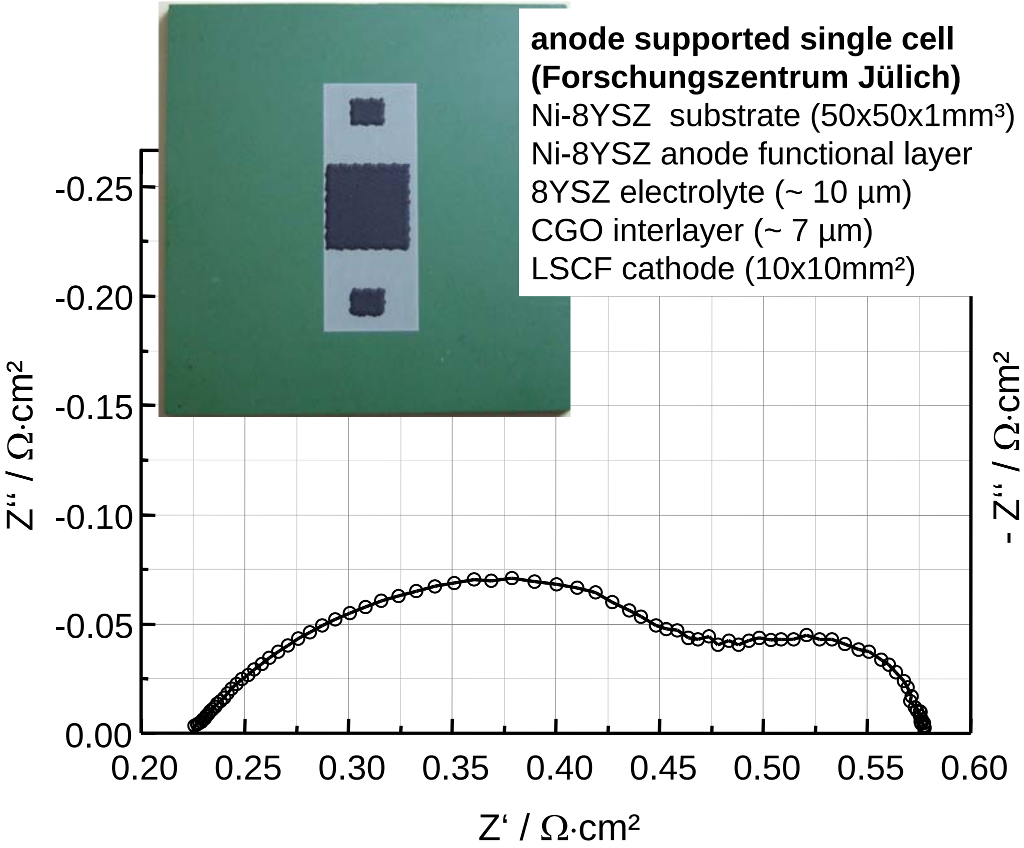


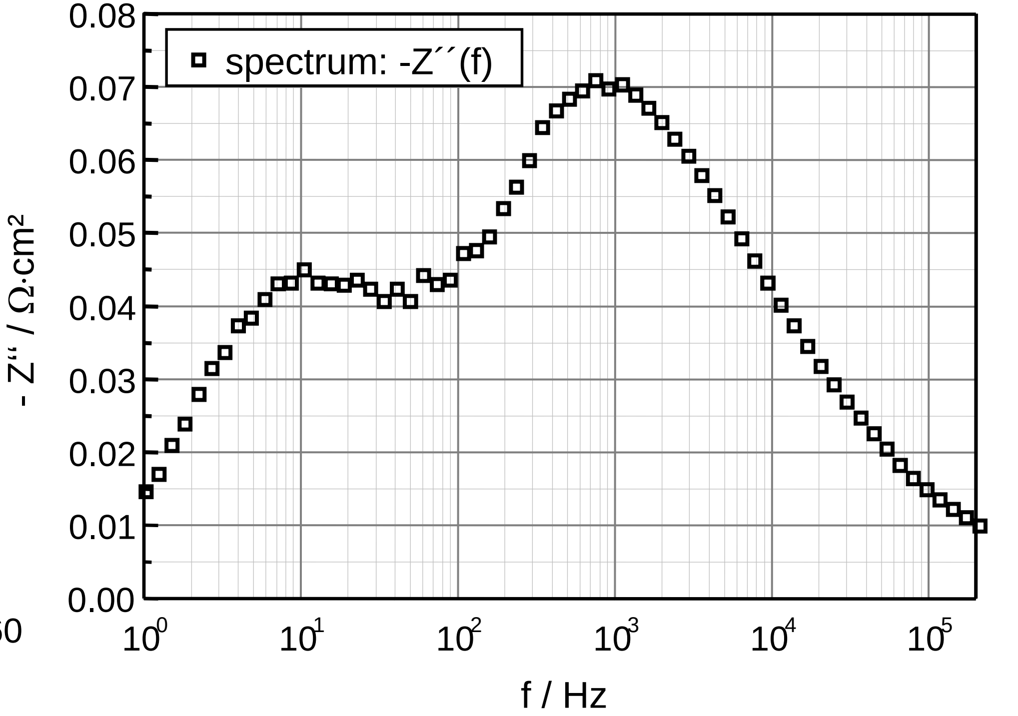


T. Kawada, N. Sakai, H. Yokokawa, M. Dokiya, M. Mori, T. Iwata, *Characteristics of Slurry-Coated Nickel Zirconia Cermet Anodes for Solid Oxide Fuel Cells*, J. Electrochem. Soc., **137**, 3042, 1990

Impedance Spectrum of an Anode Supported Single Cell

anode supported single cell
(Forschungszentrum Jülich)
Ni-8YSZ substrate (50x50x1mm³)
Ni-8YSZ anode functional layer
8YSZ electrolyte (~ 10 µm)
CGO interlayer (~ 7 µm)
LSCF cathode (10x10mm²)



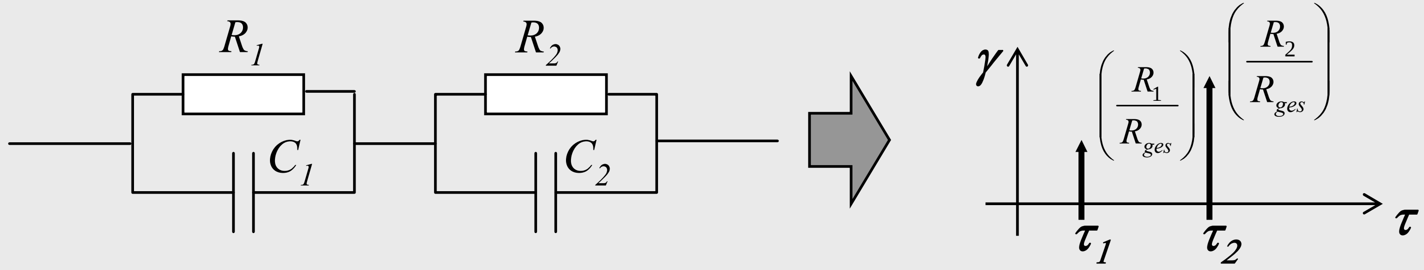


- 2 or more electrochemical processes ???
- **high resolution impedance data analysis required !!!**

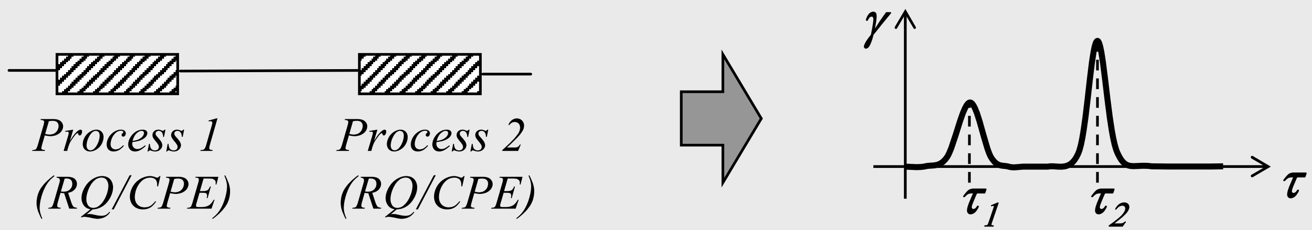
cell type: ASC
el. area: 1 cm²
fuel: H_2 (9.4% H_2O), 250 sccm
oxidant: air, 250 sccm

Impedance Data Analysis
Distribution of Relaxation Times (DRT)

ideal:



real:

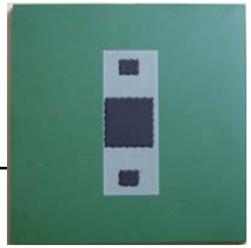


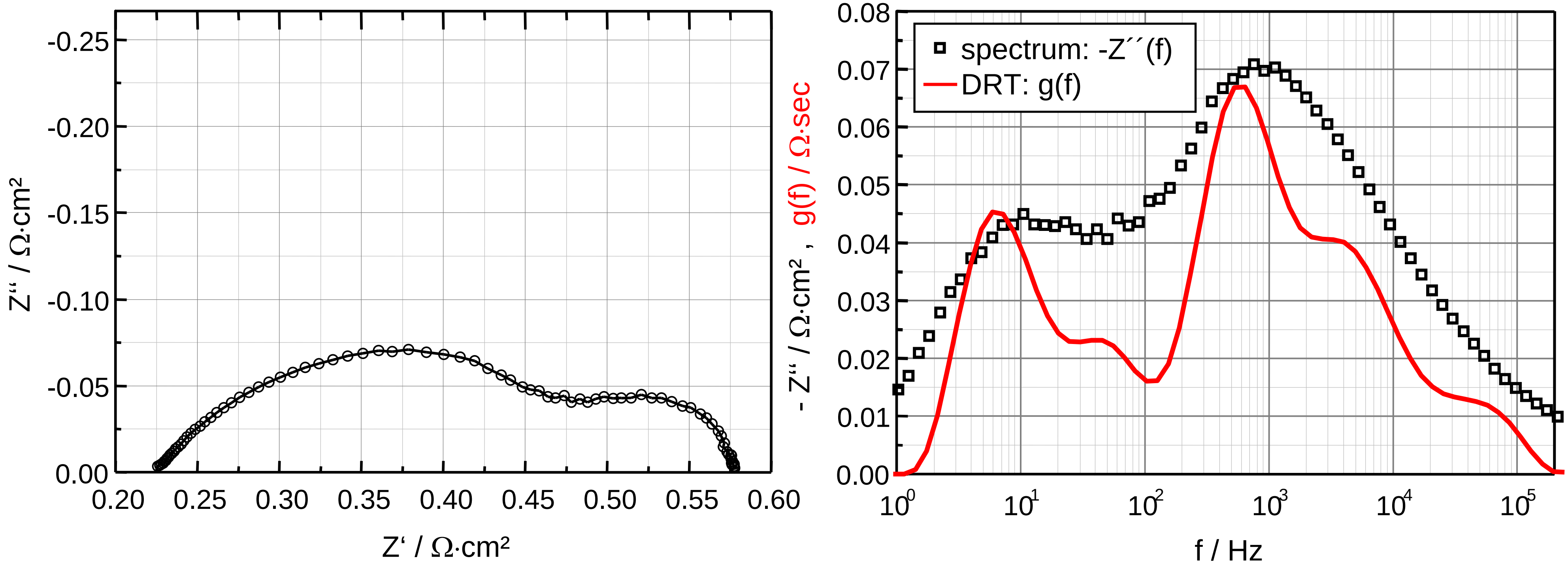
$$\underline{Z}_{pol}(\omega) = R_{pol} \int_0^{\infty} \frac{\gamma(\tau)}{1 + j\omega\tau} d\tau$$

$\gamma(\tau)$: **„Distribution function of relaxation times"**

H. Schichlein et al., Deconvolution of Electrochemical Impedance Spectra for the Identification of Electrode Reaction Mechanisms in Solid Oxide Fuel Cells, J. Appl. Electrochemistry, 32, 8, 875, (2002)

Impedance Spectrum of an Anode Supported Single Cell
Distribution of Relaxation Times





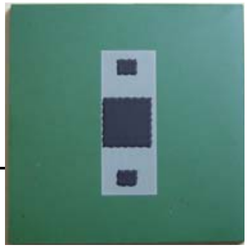
- high resolution data analysis by the DRT
- 5 processes resovable

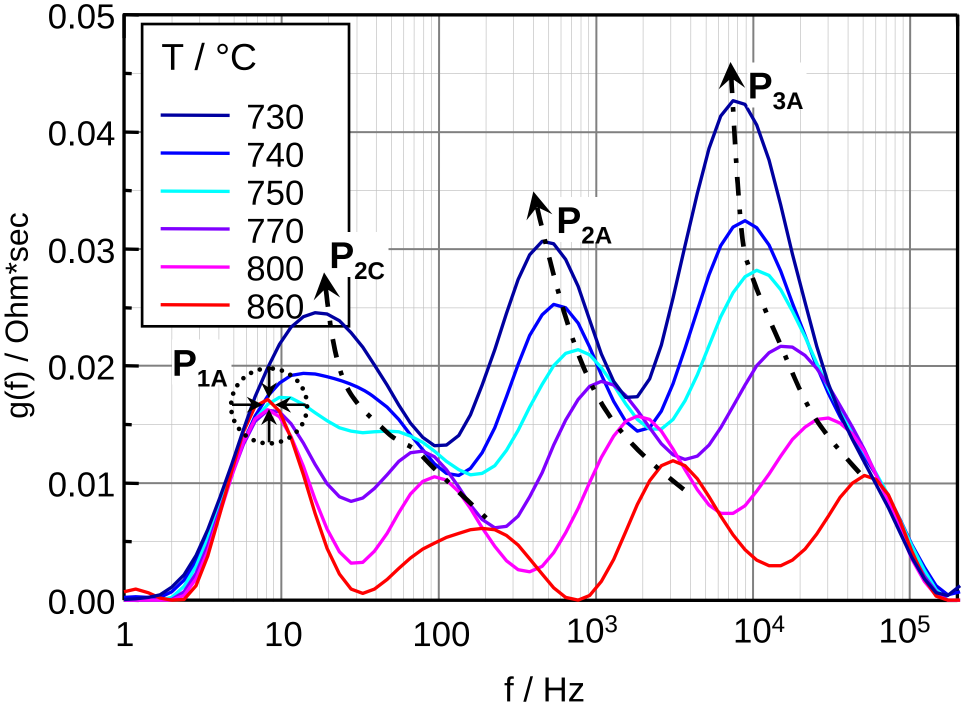
  → **perform impedance measurements at varying operating conditions !**

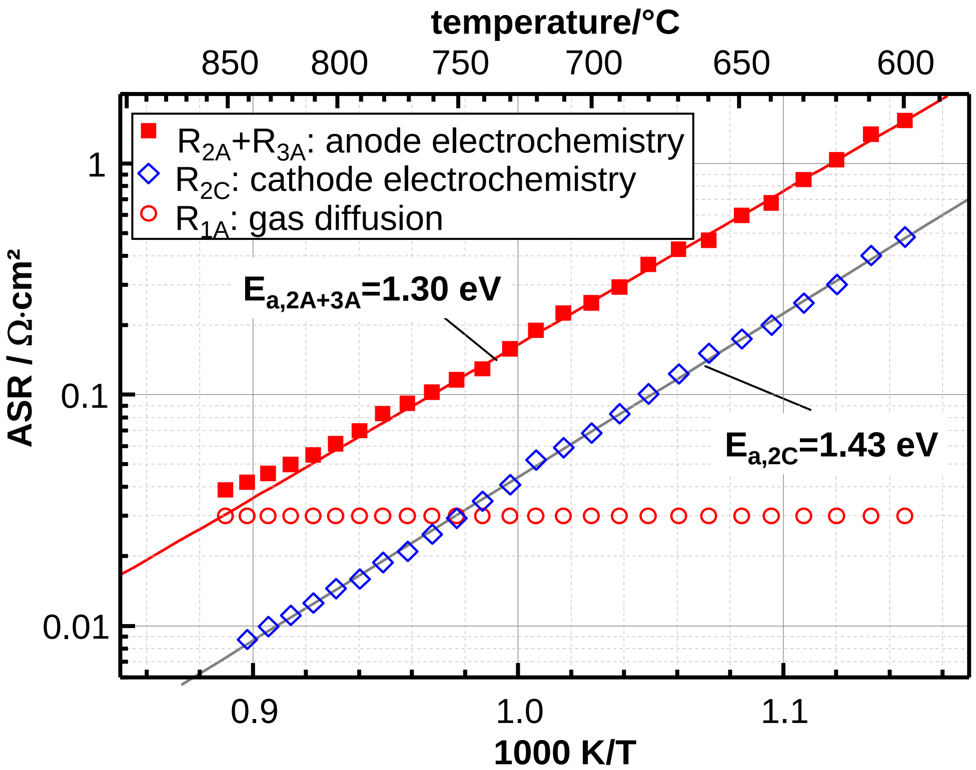
cell type: ASC
el. area: 1 cm²
fuel: H_2 (9.4% H_2O), 250 sccm
oxidant: air, 250 sccm

A. Leonide et al., *J. Electrochem. Soc*, **155** (1), pp. B36-B41, (2008).

Analysis of Electrochemical Processes in an ASC
Variation of Operating Temperature





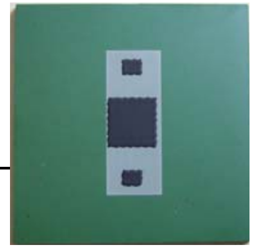


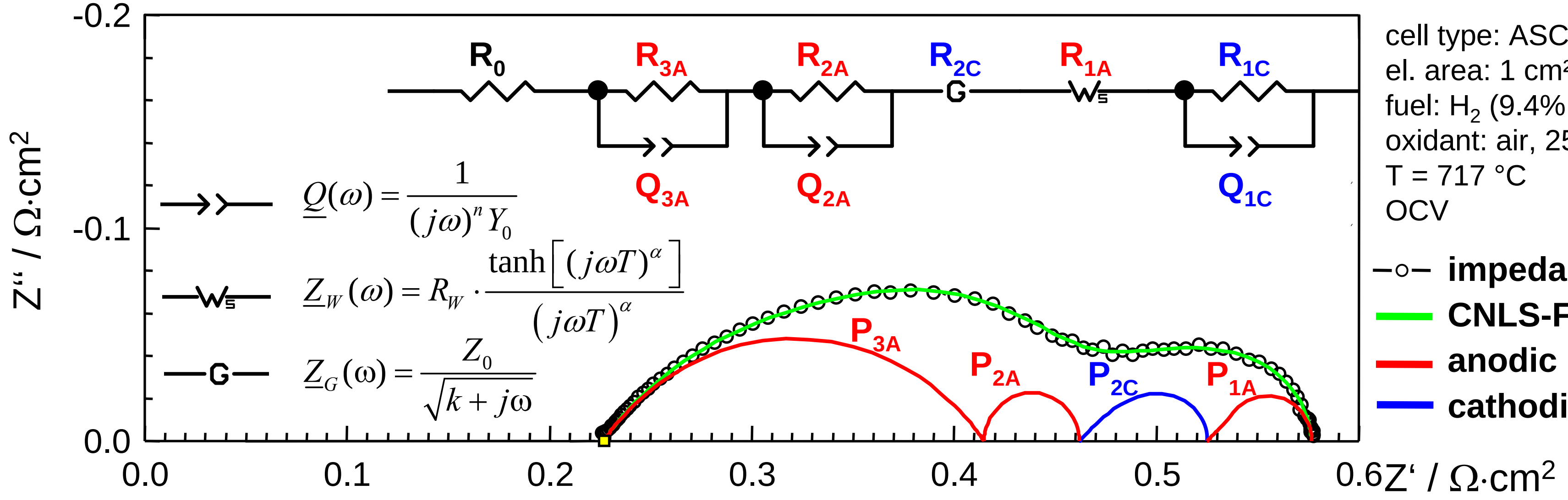
- up to 5 different electrochemical processes resolvable
- impedance values in between 10 and 1000 mΩ·cm²

T = 600 ... 850 °C
fuel: H_2, 250 sccm
$p(H_2O)$ = 0.635 bar
ox.: air, 250 sccm

A. Leonide et al., *J. Electrochem. Soc*, **155** (1), pp. B36-B41, (2008).

Analysis of Electrochemical Processes in an ASC
Impedance Model of a Single Cell





$Q(\omega) = \frac{1}{(j\omega)^n Y_0}$

$Z_W(\omega) = R_W \cdot \frac{\tanh\left[(j\omega T)^\alpha\right]}{(j\omega T)^\alpha}$

$Z_G(\omega) = \frac{Z_0}{\sqrt{k + j\omega}}$

cell type: ASC
el. area: 1 cm²
fuel: H_2 (9.4% H_2O), 250 sccm
oxidant: air, 250 sccm
T = 717 °C
OCV

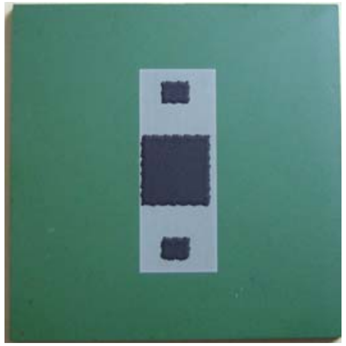
- impedance spectrum
- CNLS-Fit
- anodic
- cathodic

Abbreviation	f_r , ASR	dependence	electrode process / physical origin
P_{1C}	0.3...10 Hz, 2...100 mΩcm²	$p(O_2)$	gas diffusion (<< 10 mΩ·cm² in air)
P_{2C}	10...500 Hz, 8...50 mΩcm²	$p(O_2)$, T	oxygen surface exchange kinetics and O^{2-}-diffusivity
P_{1A}	4...20 Hz, 30...150 mΩcm²	$p(H_2)$, $p(H_2O)$	gas diffusion (anode substrate)
P_{2A}	2...8 kHz, 10...50 mΩcm²	$p(H_2)$, $p(H_2O)$,T	gas diffusion coupled with charge transfer reaction and ionic transport (AFL: anode functional layer)
P_{3A}	12...25 kHz,10...130 mΩcm²	$p(H_2)$, $p(H_2O)$, T	

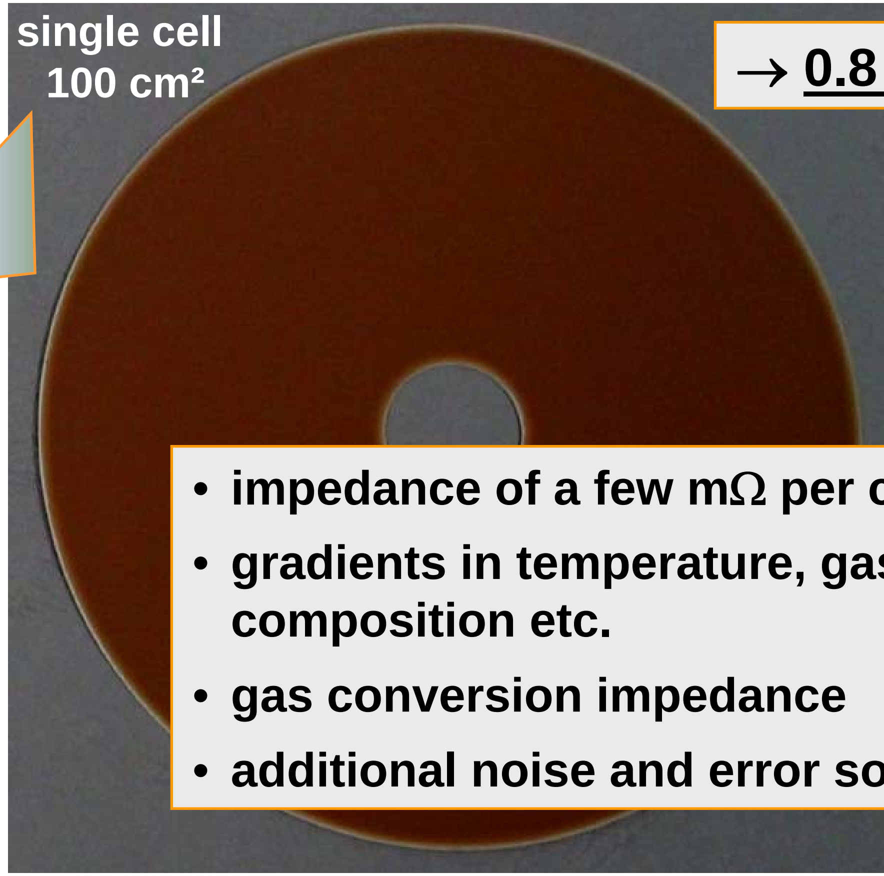
A. Leonide et al., *J. Electrochem. Soc*, **155** (1), pp. B36-B41, (2008).

Electrochemical Impedance Spectroscopy for Stacks
Impact of Cell and Stack Size

anode supported single cell
1 cm² active electrode area



ASR: 0.08 ... 2 Ω·cm²
→ 80 mΩ ... 2 Ω



→ 0.8 ... 20 mΩ

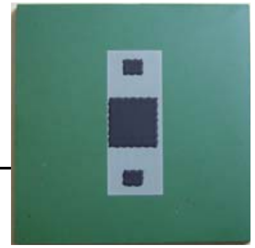
- **impedance of a few mΩ per cell**
- **gradients in temperature, gas composition etc.**
- **gas conversion impedance**
- **additional noise and error sources**

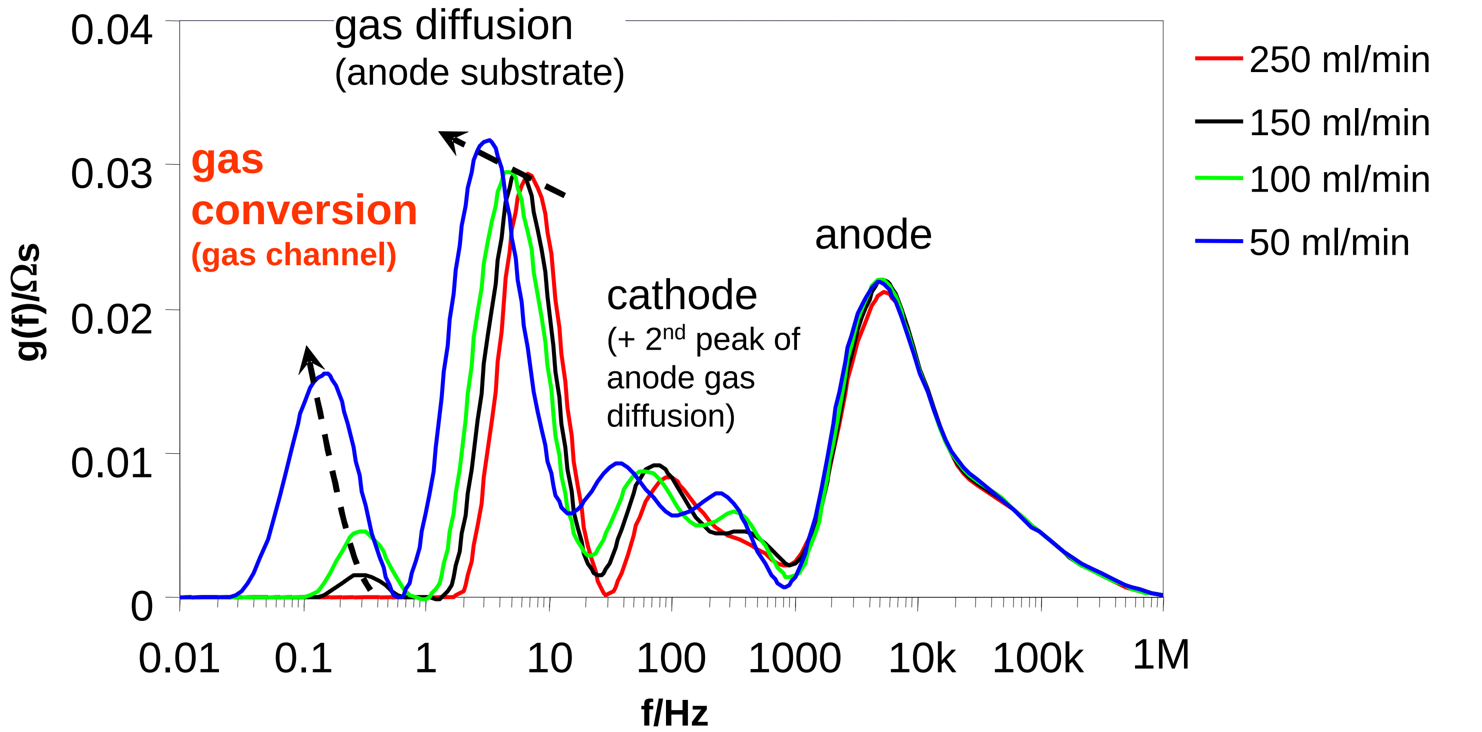
Electrochemical Impedance Spectroscopy for Stacks
Testing Equipment

3 kW$_{el}$ SOFC stack 60 cells a 100 cm² U_{stack} = 42 V I_{stack} = 71.4 A	target values	solartron analytical 1260/1287 + Power Booster	ZAHNER Messsysteme IM6 + PP 2xx	Princeton Applied Research VersaSTAT4 + Power Booster	BioLogic Science Instruments CLB 500	FuelCon TrueData-EIS
frequency range	1 mHz ... 1 MHz	10 µHz ... 100 kHz	10 µHz ... 200 kHz	(10 µHz ... 1 MHz)	10 µHz ... 10 kHz	200 µHz ... 100 kHz
impedance range	0.1 ... 100 mΩ	10 µΩ ... 1 kΩ	1 µΩ ... 1 kΩ	n.s.	n.s.	0.1 mΩ ... 15 Ω
accuracy (error at 1 mΩ / 100 kHz)	1 %	30 % / 30° (@ 10 mΩ)	0.25 % (f, |Z| not specified)	n.s.	2 % / 2°	1 % / 1°
max. bias voltage [V]	100	50	± 5 / 10 / 20	20	10	300
max. bias current [A]	100	25	± 40 / 20 / 10	20	50	1000
max. power diss. [kW]	3	0.125	0.25	n.s.	0.5	150

→ limitations due to the testing equipment

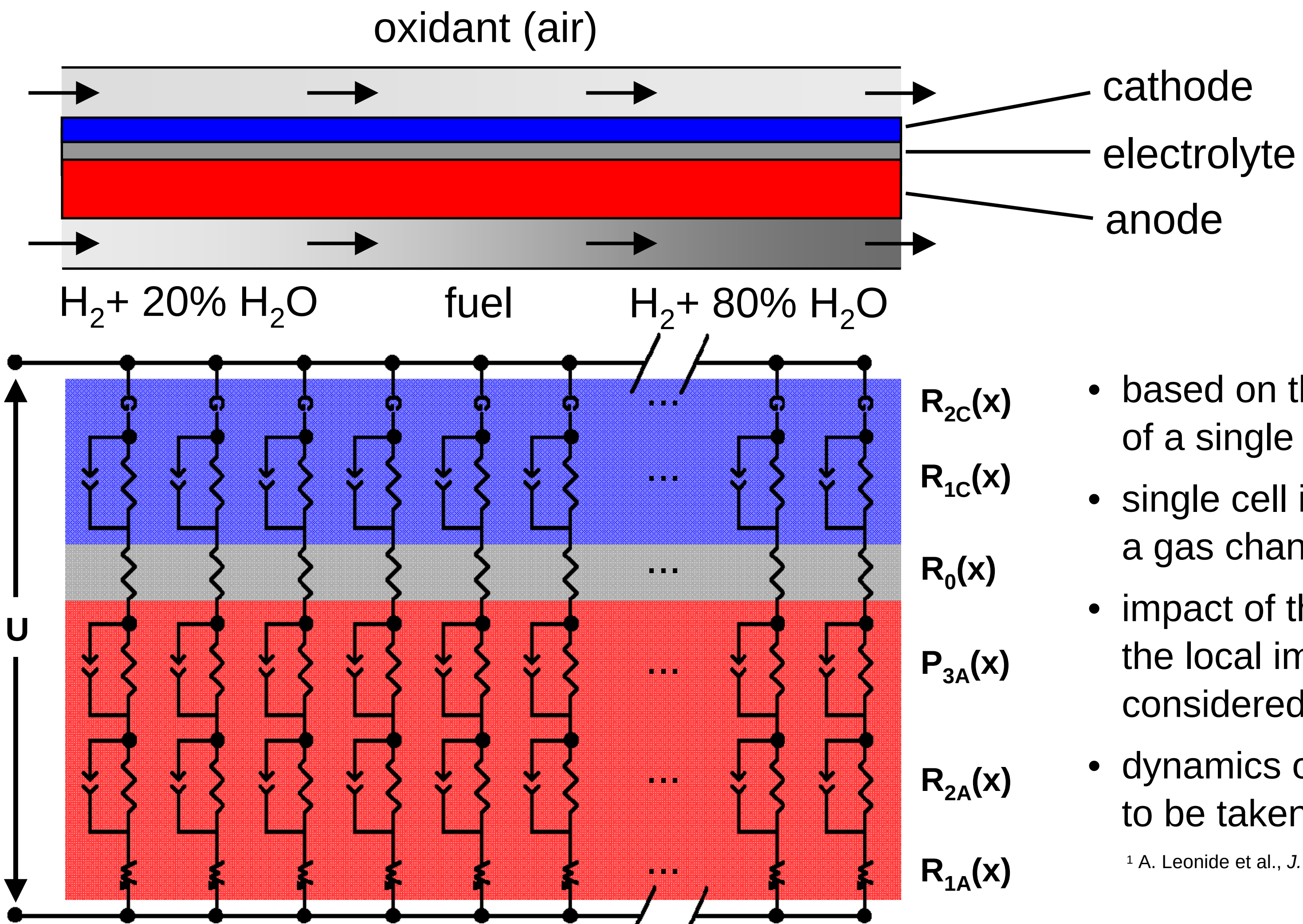
Analysis of Electrochemical Processes in an ASC
Gas Conversion Impedance (at decreased fuel flow rate)





→ the gas conversion impedance will be included in the stack impedance

Electrochemical Impedance Spectroscopy for Stacks
2-dimensional Impedance Model

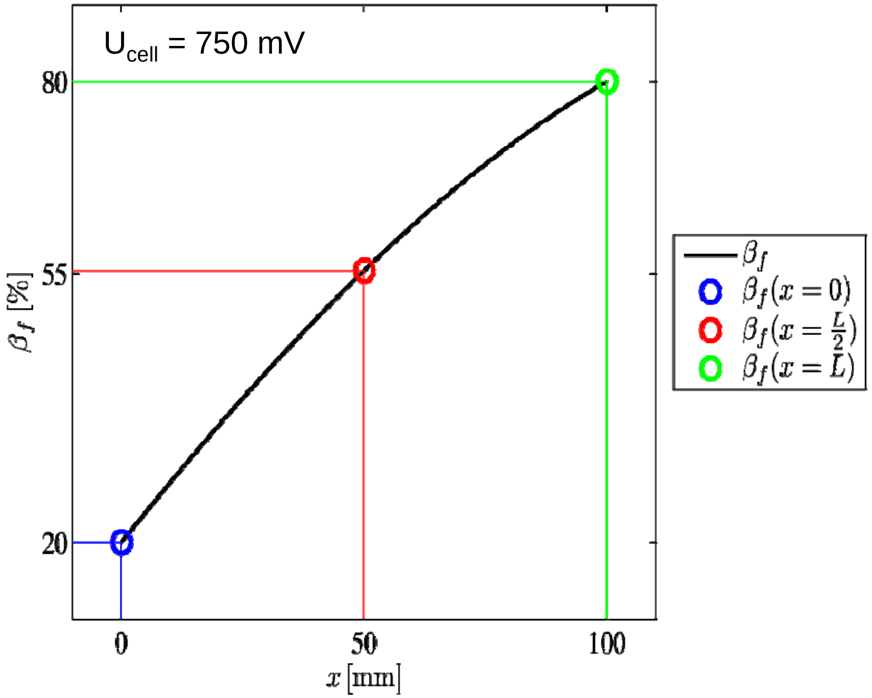


- based on the impedance model of a single cell[1]
- single cell impedance units along a gas channel
- impact of the gas utilization on the local impedance is considered
- dynamics of gas conversion have to be taken into account

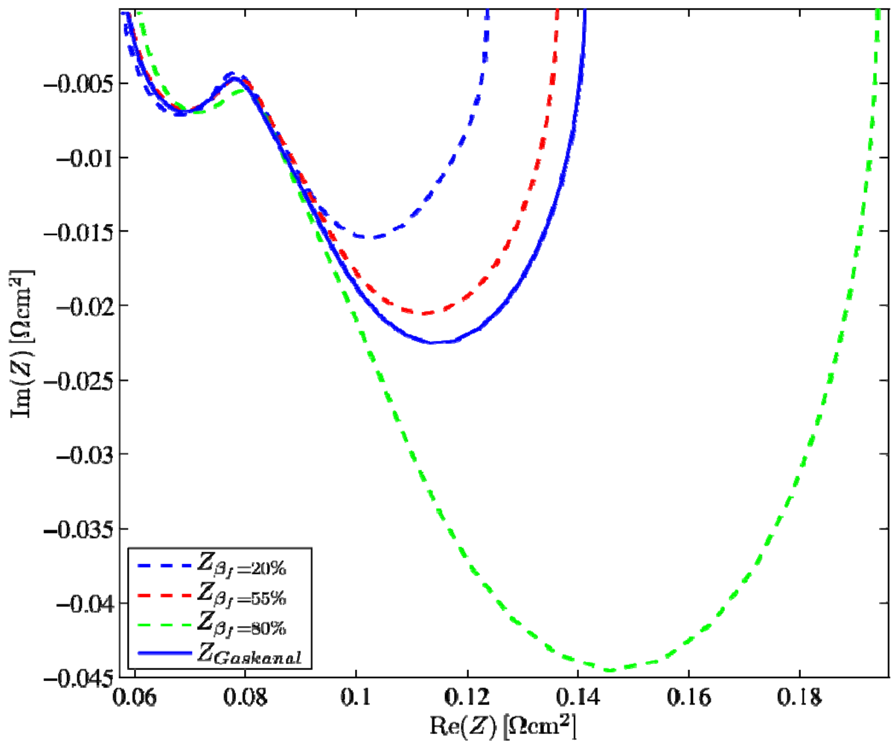
[1] A. Leonide et al., *J. Electrochem. Soc*, **155** (1), pp. B36-B41, (2008).

D. Klotz et al., *accepted for publication in ECS Transactions (2009)*

2-dimensional Impedance Model
Local Impedance Spectra and Stack Impedance



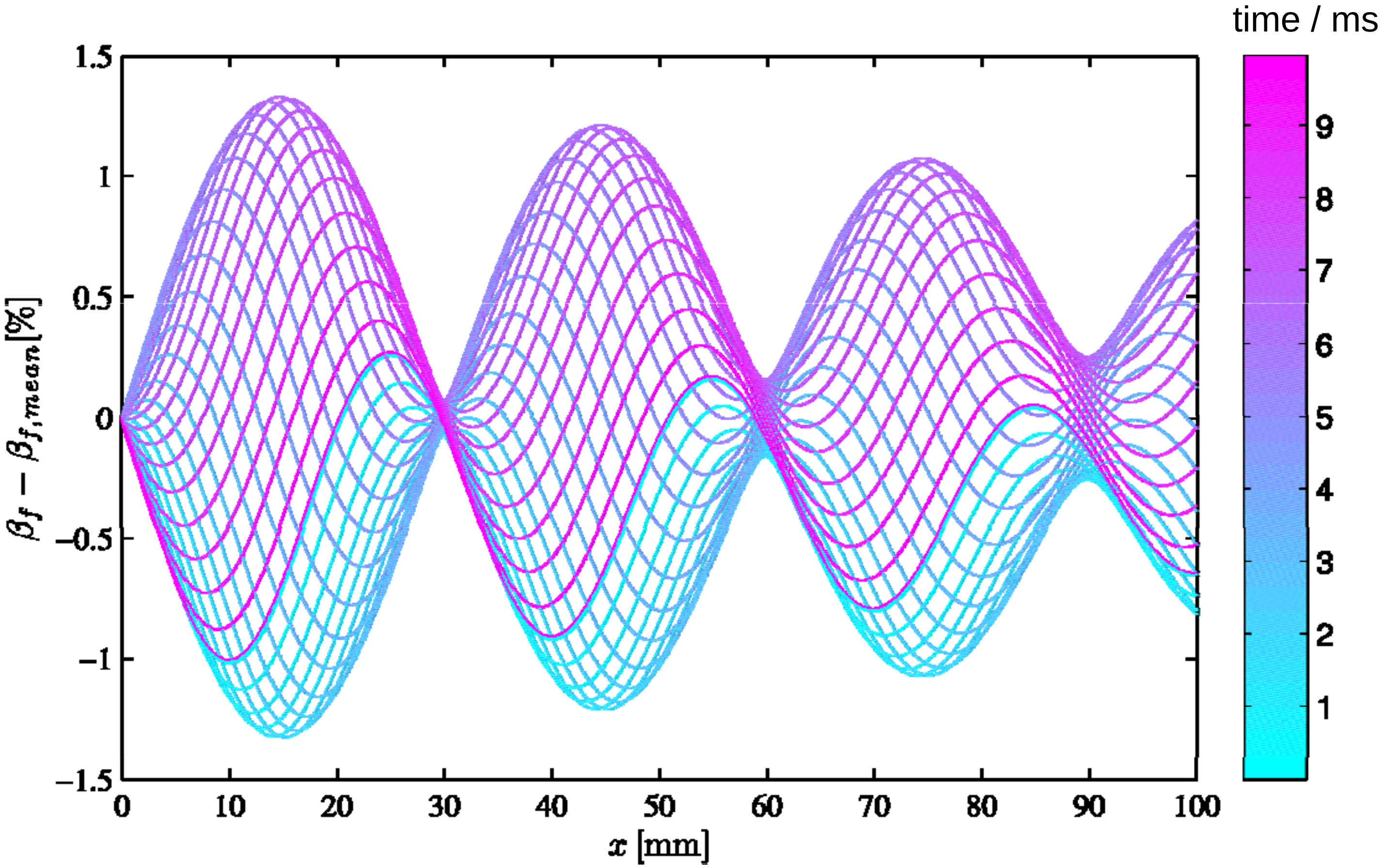
simulated fuel utilization
along the gas channel



simulated local impedance spectra and
impedance spectrum of the stack

D. Klotz et al., *accepted for publication in ECS Transactions (2009)*

2-dimensional Impedance Model for Stacks
Space and Time Dependence of the Fuel Utilization β_f



operating parameters

U_{cell}	0,725 V
$U_{ampl.}$	70 mV
f_{AC}	50 Hz
L	10 cm
v_{gas}	3 m/s
$\beta_{f,in}$	20%
$\beta_{f,out}$	80%

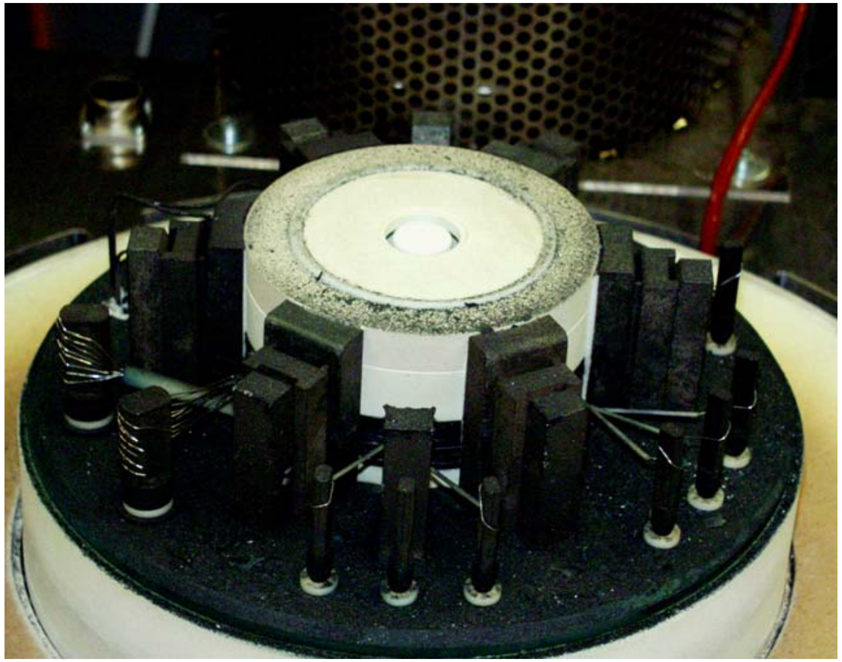
Experimental
Sulzer Hexis Stack Test Bench

Sulzer Hexis stack test bench

- **5 cell stack**
- **100 cm² electrode area**
- **operating on pipeline gas**
- **desulfurization (disengageable)**
- **catalytic partial oxidation**
- **controlled gas flows**
- **controlled stack temperature (not thermal self-sustaining)**
- **variable interconnect / flow field geometry**
- **testing of different MEAs and MICs possible**

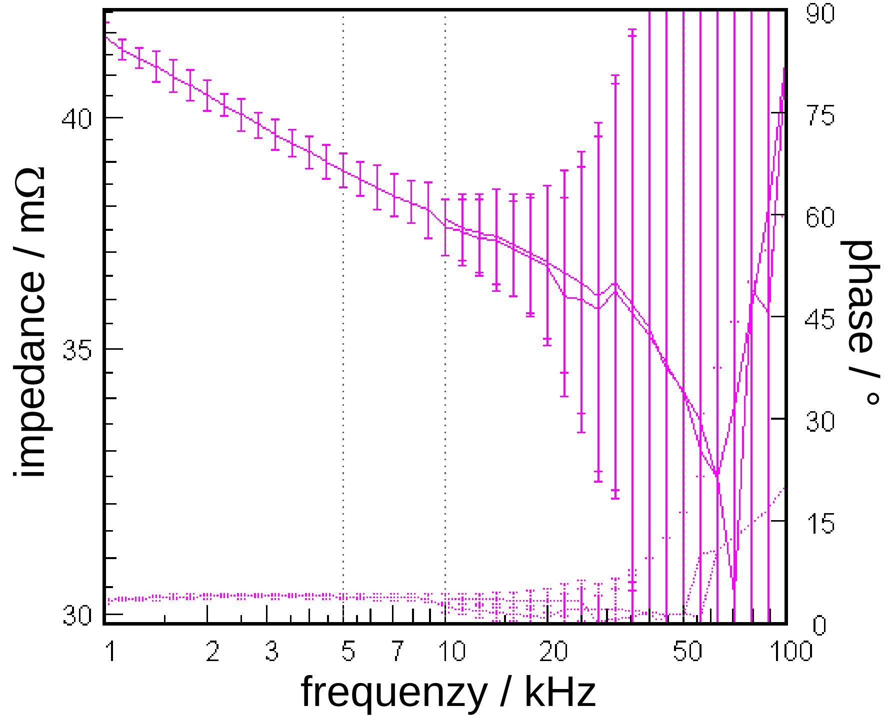
Impedance spectroscopy ?

Sulzer Hexis Stack Test Bench
Modifications for Impedance Spectroscopy



EIS-Equipment
- Zahner IM6 & PP200 potentiostat
- impedance range: 1 µΩ ... 1 kΩ
- frequency range: 10 µHz ... 100 kHz
- dc current: 20 A

initial state

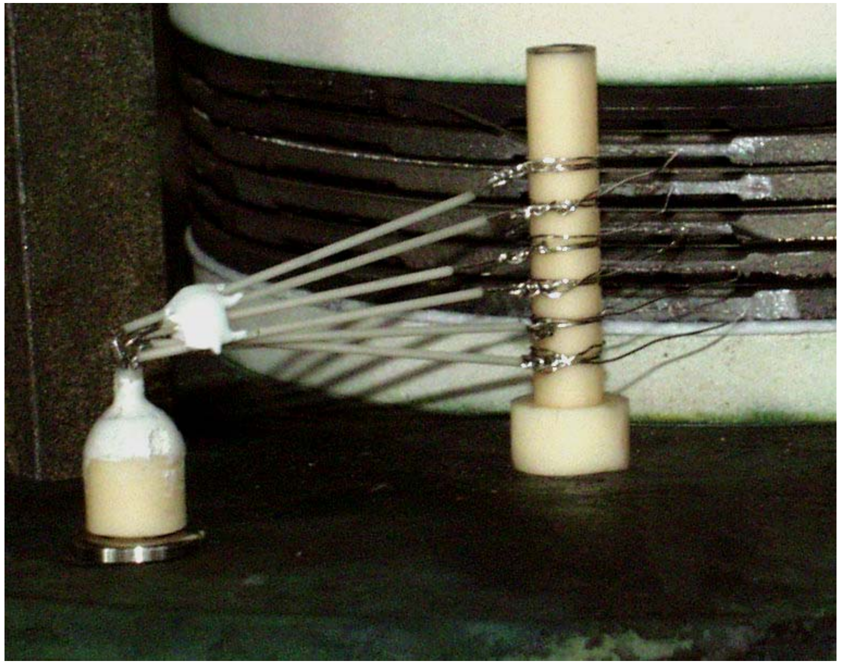


Significant interferences at frequencies above 10 kHz

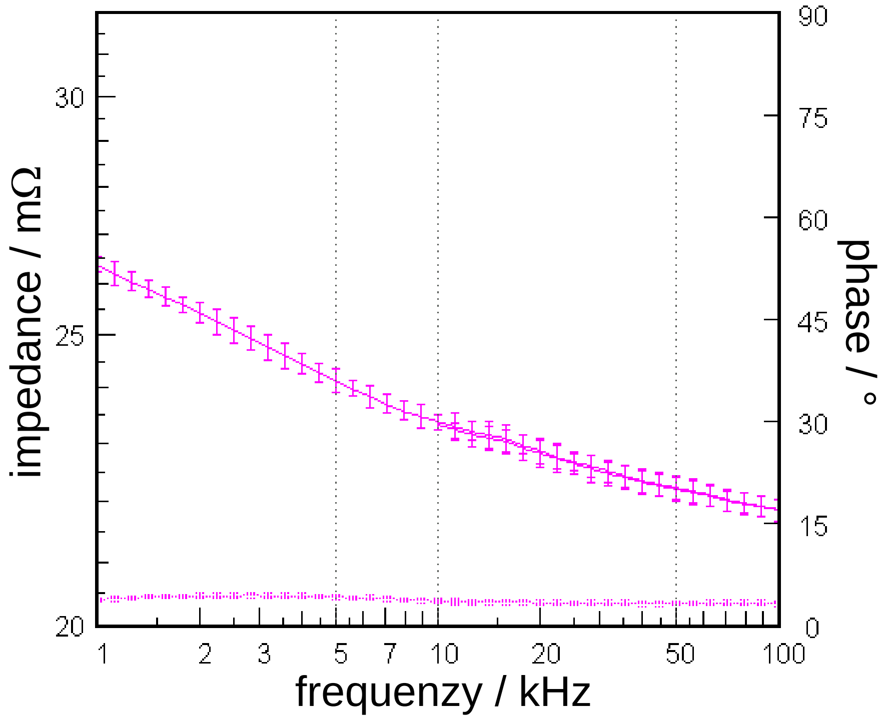
Sulzer Hexis Stack Test Bench
Modifications for Impedance Spectroscopy

Modifications

- adaptation of voltage probes & current lines to decrease mutual inductances
- impedance converters for dc voltage metering
- multiplexer for single cell / stack impedance measurement



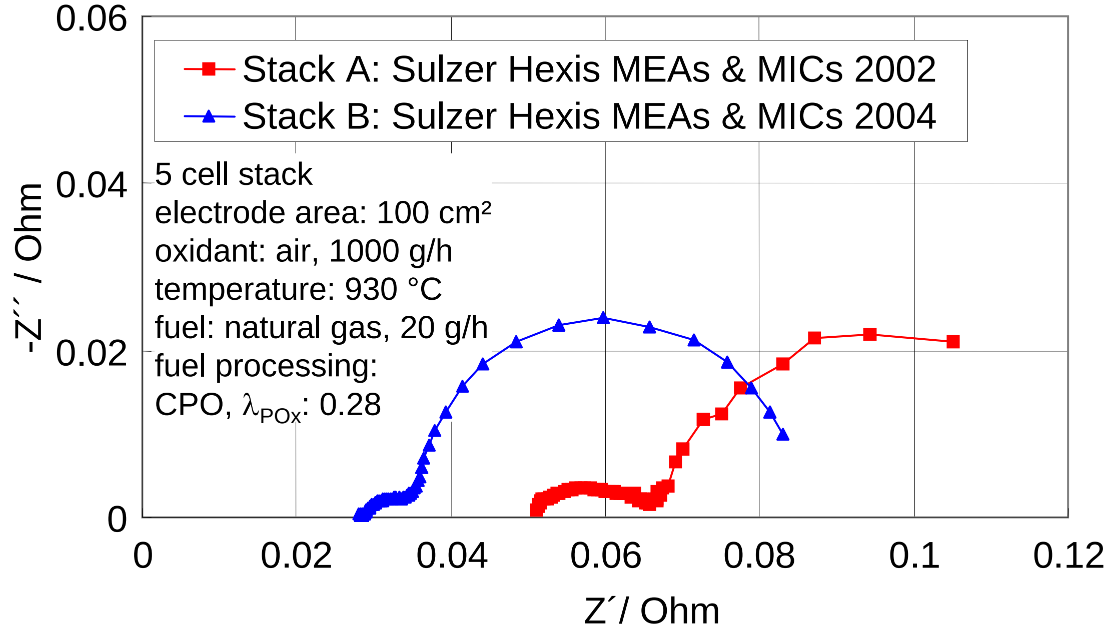
modified



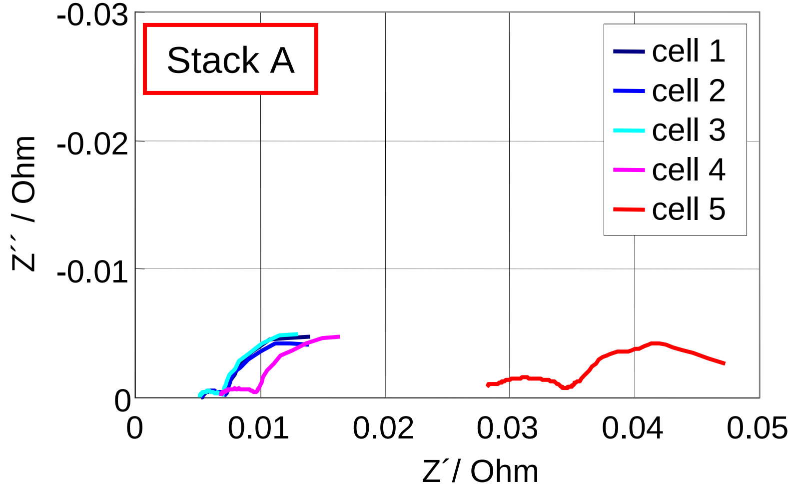
Low interferences over the whole frequency range

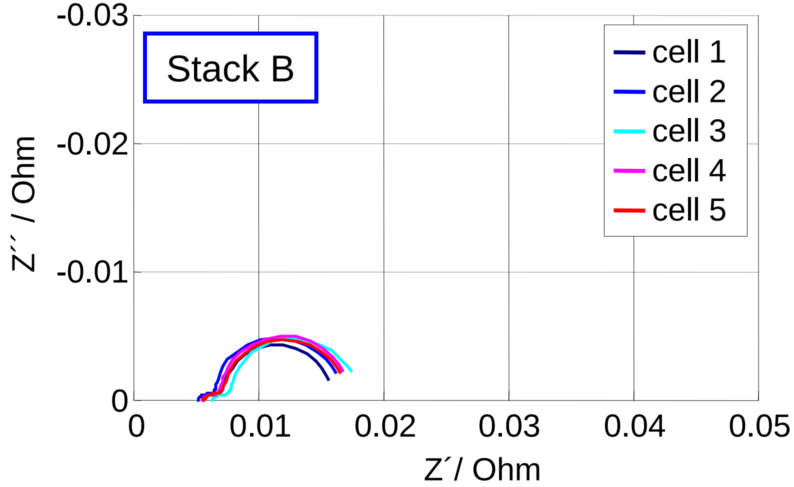
Stack Diagnosis
Impedance Spectra of Stacks and Cell Units

Stack



Single Cell Units 1 to 5

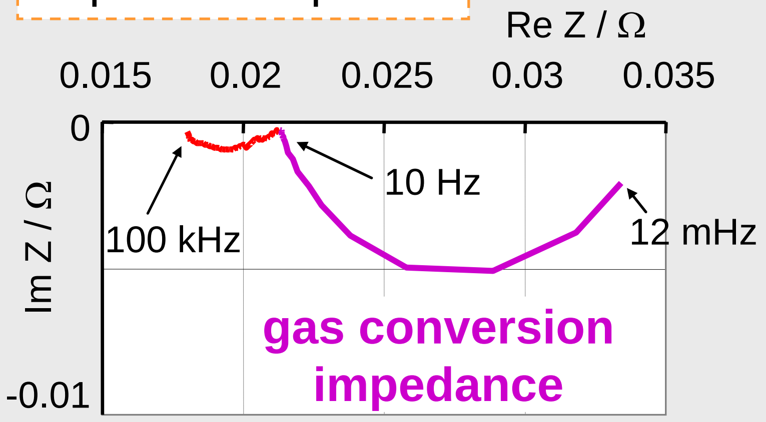




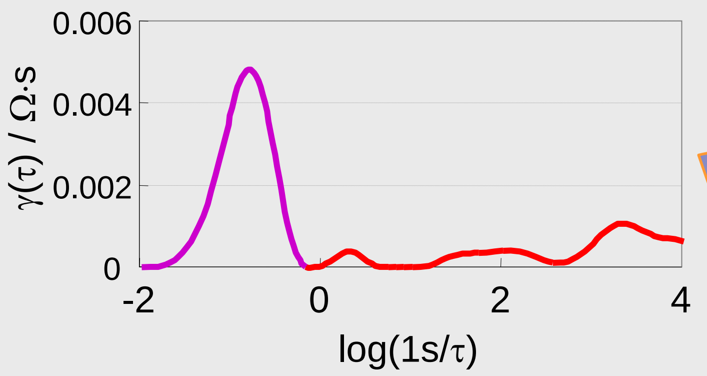
Impedance spectra of the stack provide an averaged ohmic and polarisation resistance
Impedance spectra of the individual cell units provide more detailed information

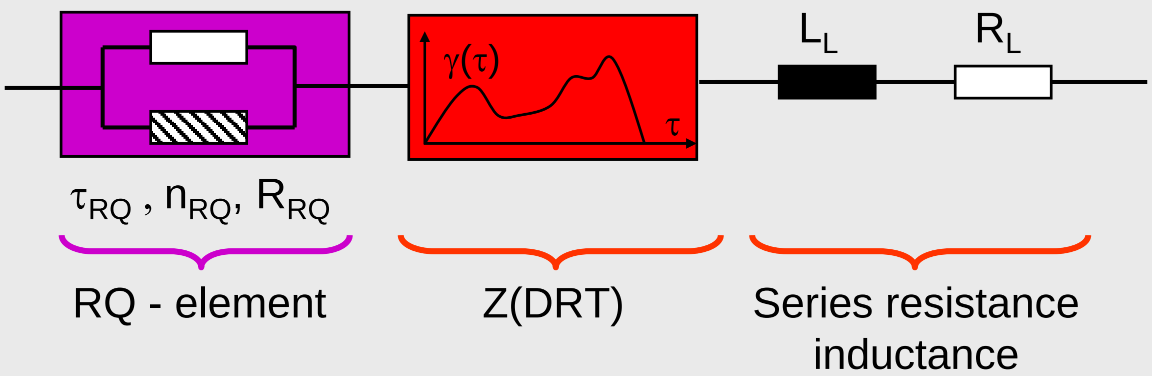
System Diagnosis
Impedance Data Analysis by parametric extended DRT

impedance spectra

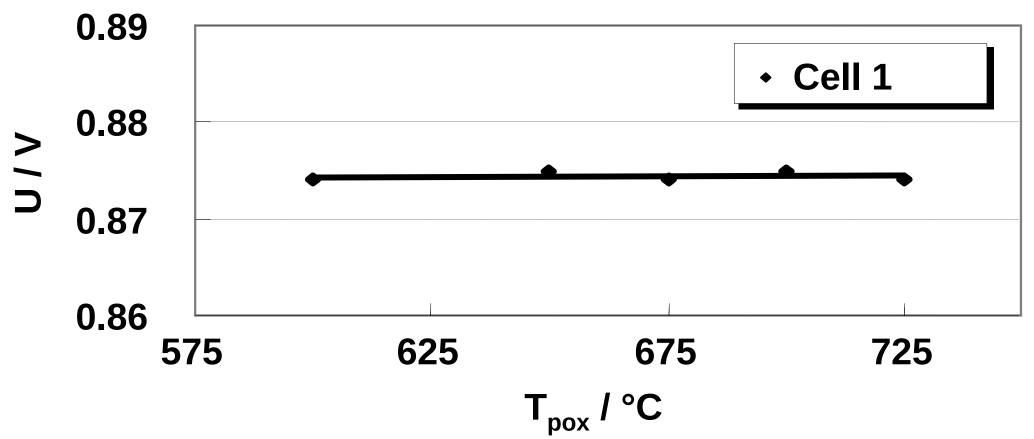


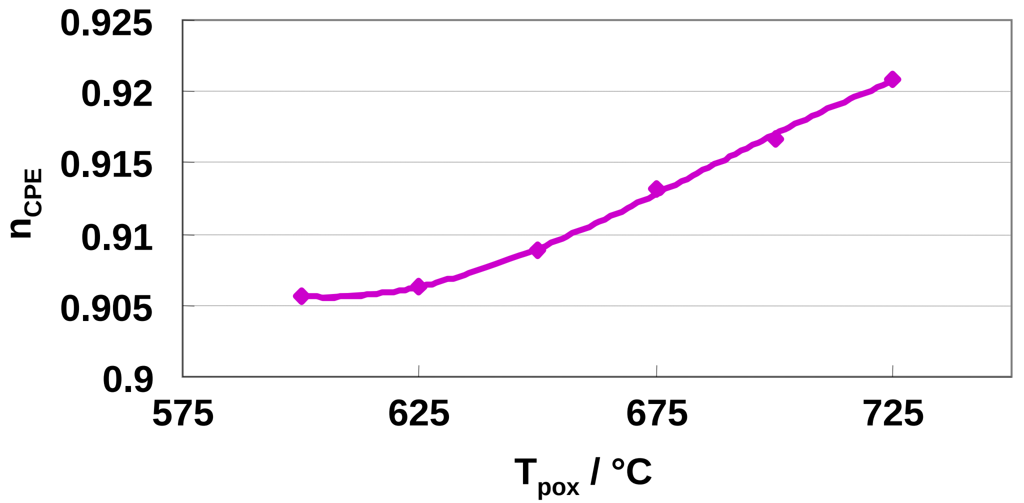
DRT





System Diagnosis
Impact of CPOx Reformer Temperature on cell voltage and $\mathbf{n_{RQ}}$





voltage cell 1

no dependency in cell voltage

RQ exponent n_{RQ}

Variation in fuel composition is detected

theory: n → 1 for pure H_2

Conclusions and Outlook
Future Research Activities - Diagnostic Tools for FC-Technologies

- Impedance spectroscopy is a powerful tool to analyze SOFC stacks but
  - The available testing equipment hardly fulfills the requirements
  - The stack testing facilities have to be designed for impedance spectroscopy
  - Complex impedance models are required to understand the stack impedance
- To do´s:
  - Development of impedance analyzers for (SOFC-) stacks
  - Development of tools for stack impedance modeling and data analysis
  - Standardized testing procedures for stack impedance measurement and data analysis

Impedance Spectroscopy and Impedance Data Analysis
IWE-References

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- A. Leonide, V. Sonn, A. Weber and E. Ivers-Tiffée, "Evaluation and Modelling of the Cell Resistance in Anode Supported Solid Oxide Fuel Cells", *ECS Transactions* **7**, pp. 521-531 (2007).
- A. Leonide, V. Sonn, A. Weber and E. Ivers-Tiffée, "Evaluation and modeling of the cell resistance in anode-supported solid oxide fuel cells", *J. Electrochem. Soc.* **155**, p. B36-B41 (2008).

Acknowledgements
Many Thanks to our Partners and Funding Organizations

ISC Fraunhofer Institut für Silicatforschung

EIfER European Institute for Energy Research

BMW

Eberspächer

SOFC NET

IPHE

ECN

TOPSOE FUEL CELL clean, efficient and reliable

CeramTec THE CERAMIC EXPERTS

FCTESTNET

Forschungszentrum Jülich

Risø DTU National Laboratory for Sustainable Energy

DTU

DLR

ThyssenKrupp

FCTESQA

Institute for Energy

ZSW

ISE

HEXIS

elringklinger

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