# EIS in Fuel Cell Science

**Dr. Norbert Wagner**
**German Aerospace Center (DLR)**
**Institute for Engineering Thermodynamics**
**Pfaffenwaldring 38-49, 70569 Stuttgart, Germany**

**Electrochemical Impedance Spectroscopy**
**Fundamentals and Applications**
**5.-6. November 2015**
**Frankfurt am Main**




## Presentation outline

- Introduction
  - Motivation
  - Types of Fuel Cells
  - Experimental set-up for different types of FCs
- Microstructure of fuel cells and modeling of fuel cells with equivalent circuits
- Impedance models of porous electrodes
- Different applications of EIS in FC research
  - Contributions to performance loss of PEFC
  - Degradation mechanism of PEFC
  - Time dependent EIS
    - CO poisoning of PEFC-anodes
    - Flooding of PEFC cathodes
  - EIS measured on Ag-Gas Diffusion Electrodes (GDE) during Oxygen Reduction in alkaline electrolyte (AFC)
  - EIS measured at fuel cell stack (SOFC)
- Conclusion

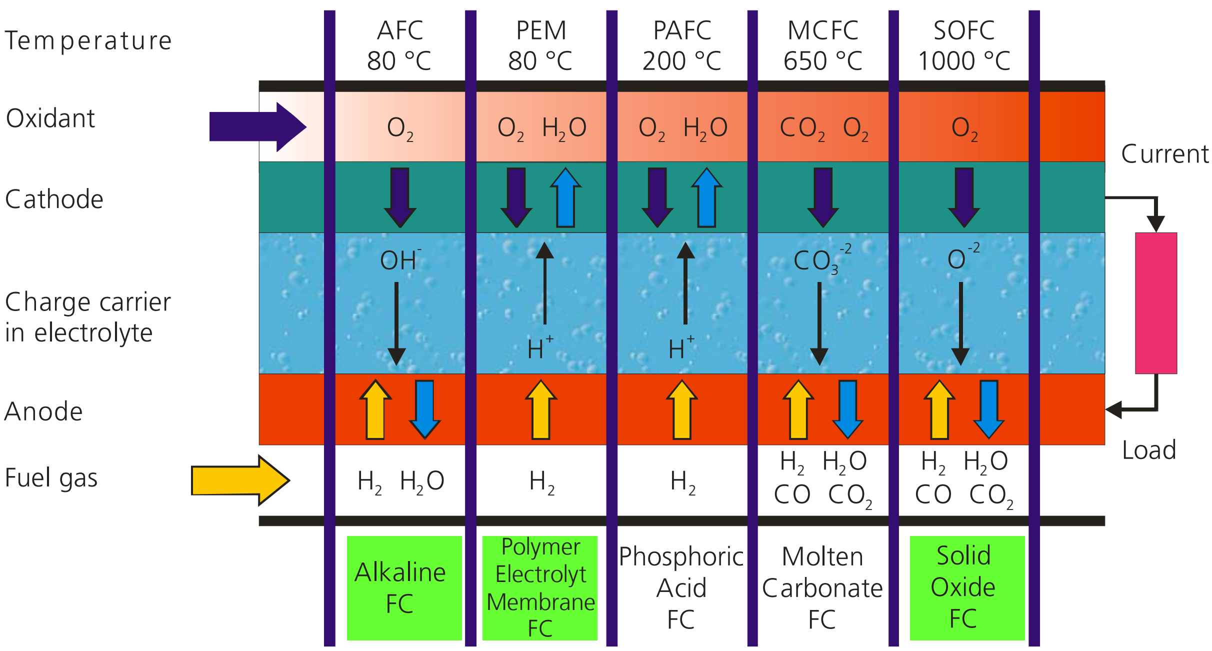
# Motivation

## Characterization of Fuel Cells by Electrochemical Impedance Spectroscopy:

- Determination of electrode **structure** and reactivity, separation of electrode structure from electrocatalytically activity
- Determination of reaction mechanism (**kinetic**) and separation of different overvoltage contributions to the fuel cell performance loss
- Determination of **degradation** mechanism of electrodes, electrolyte and other fuel cell components (bipolar plates, end plates, sealings, etc.)
- Determination of optimum **operation condition** (e.g. gas composition, temperature, partial pressure), cell design (flow field) and stack design

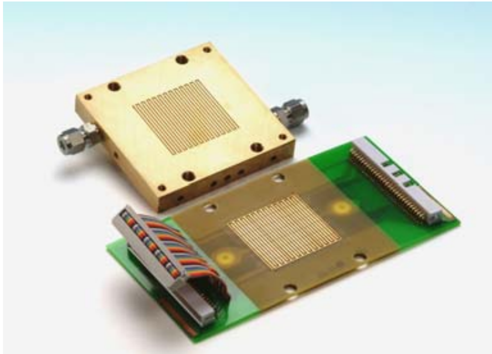


# Schematic representation of main types of fuel cells

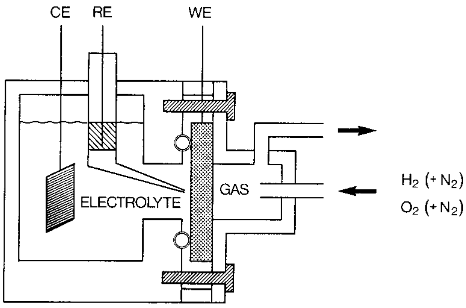


# Experimental set up and cells used for EIS

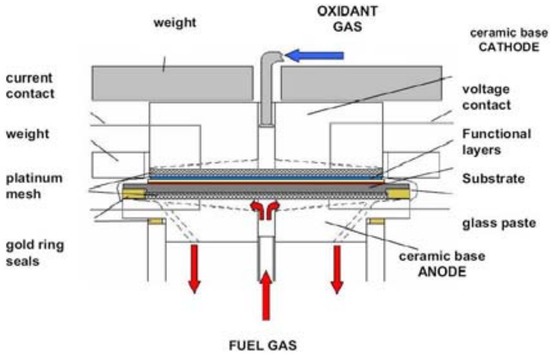
Segmented and single PEFC cell (polymer electrolyte)



Fuel „half“ cell with liquid electrolyte




Test cell for SOFC (short stack)
(Solid Oxide Electrolyte)






# Fuel cell overvoltage and current density / voltage characteristic

Hydrogen Oxidation Reaction (HOR):

$\eta_{H_2} = RT/2F\ i/i^*$

Oxygen Reduction Reaction (ORR):

$\eta_{O_2/air} = RT/[(1-\alpha)2F]\ [\ln i - \ln i^*]$

Ohmic loss

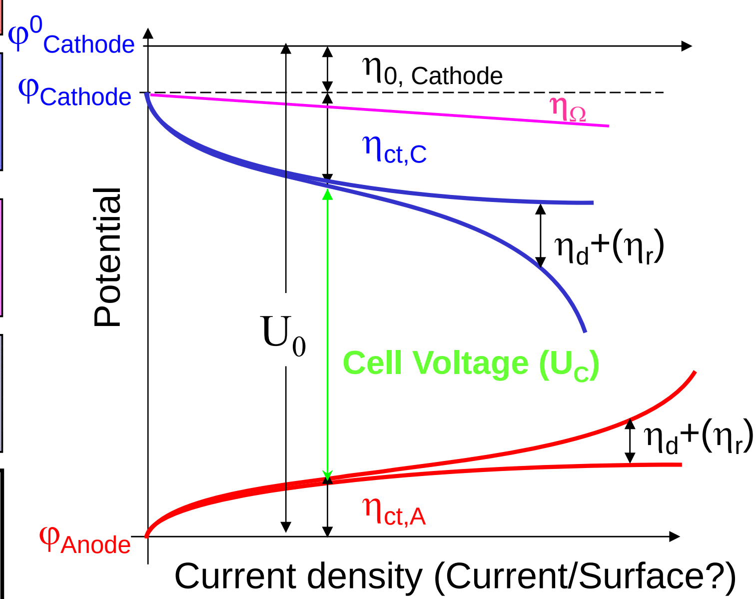
$\eta_\Omega = iR$

Transport limitation (diffusion)

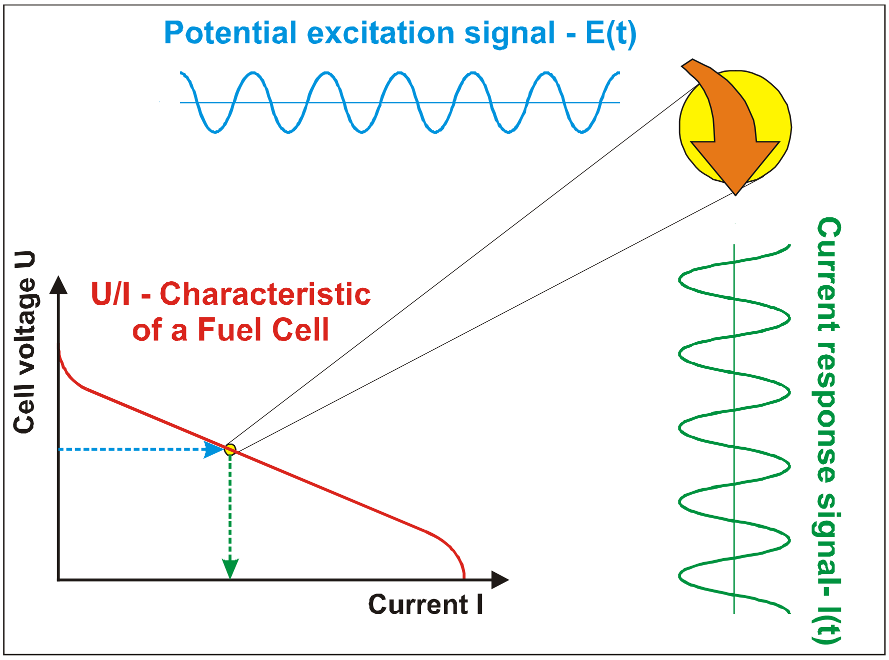
$\eta_d = -RT/2F \ln (1 - i/i_{lim})$

**Fuel cell voltage**

$U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_\Omega$



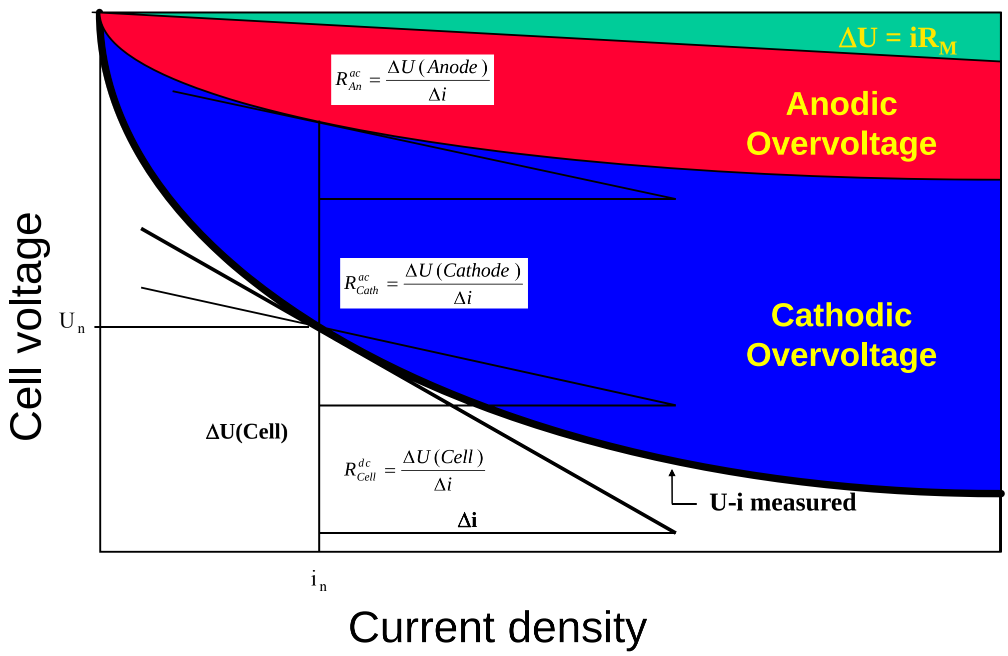
# Electrochemical Impedance Spectroscopy: Application to Fuel Cells





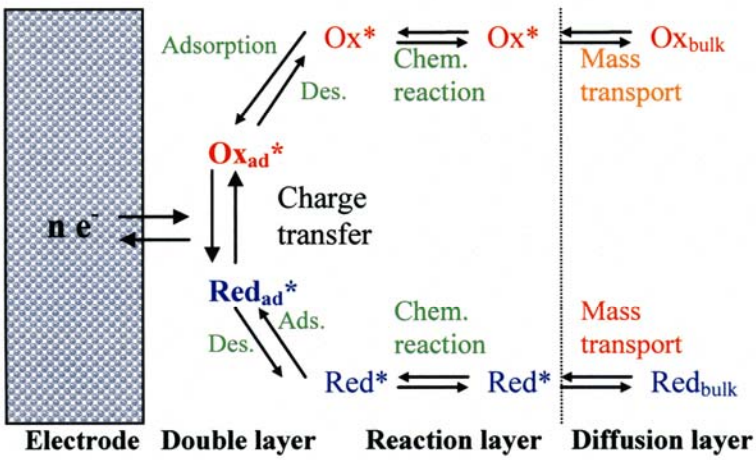



# Schematic diagram of the U-i characteristic of PEFC and Electrochemical Impedance



# Schematic representation of the different steps and their location during the electrochemical reactions as a function of distance from the electrode surface

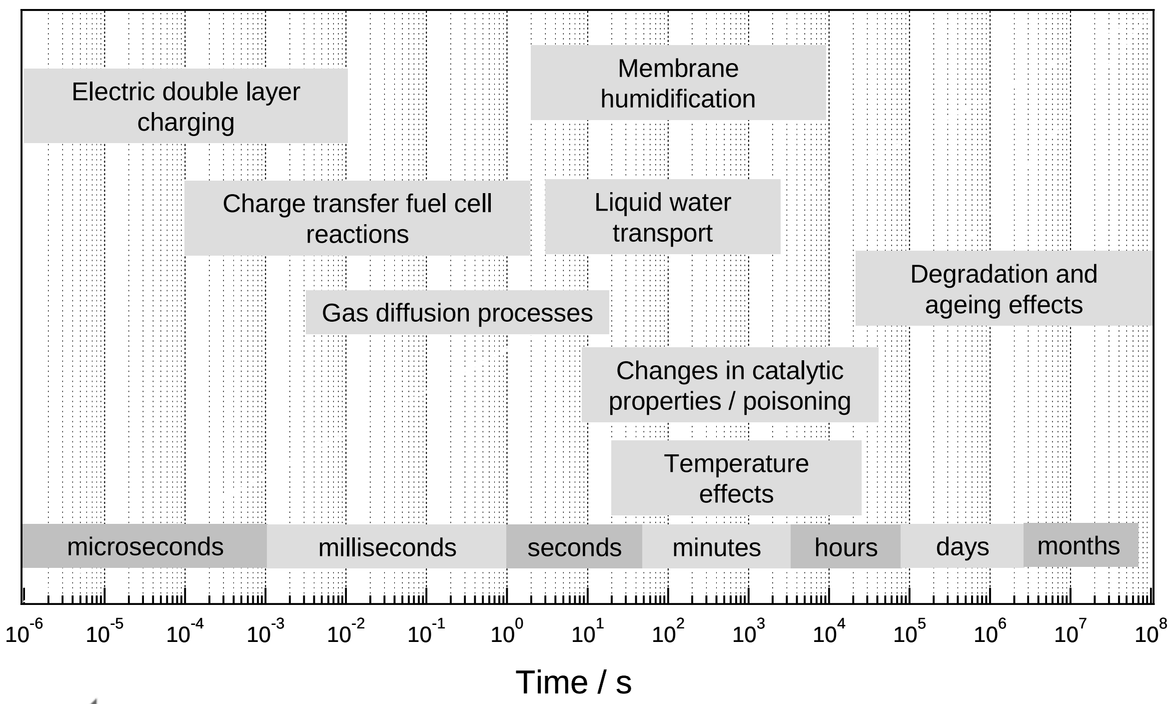
$$Ox + ne^- \leftrightarrow Red$$



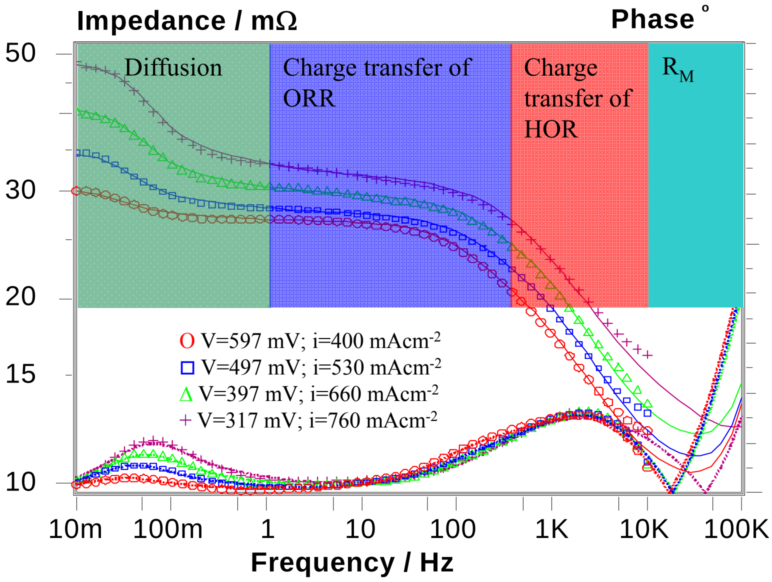

N. Wagner, K.A. Friedrich, *Dynamic Response of Polymer Electrolyte Fuel Cells* in „Encyclopedia of Electrochemical Power Sources“ (Ed. J. Garche et al.), ISBN-978-0-444-52093-7, Elsevier Amsterdam, Vol.2, pp. 912-930, 2009

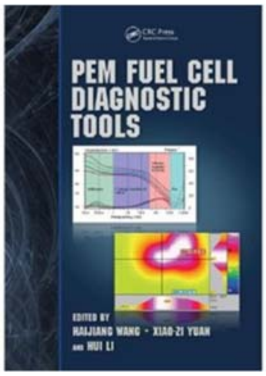


# Overview of the wide range of dynamic processes in FC



# Bode representation of EIS measured at different current densities, PEFC operated at 80°C with $H_2$ and $O_2$ at 2 bar



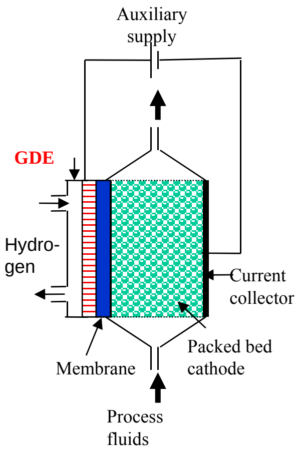

N. Wagner in „Pem Fuel Cell Diagnostic Tools“ , Haijaing Wang, Xiao-Zi Yuan, Hui Li (Eds.), 2011



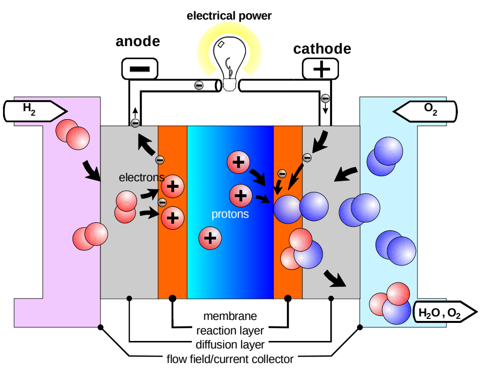
# Field of application of porous electrodes

Batteries and supercaps

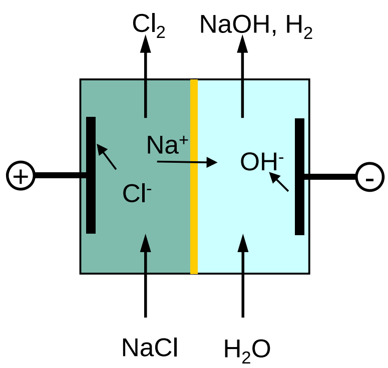
Water purification and treatment
(Bio)-Organic synthesis



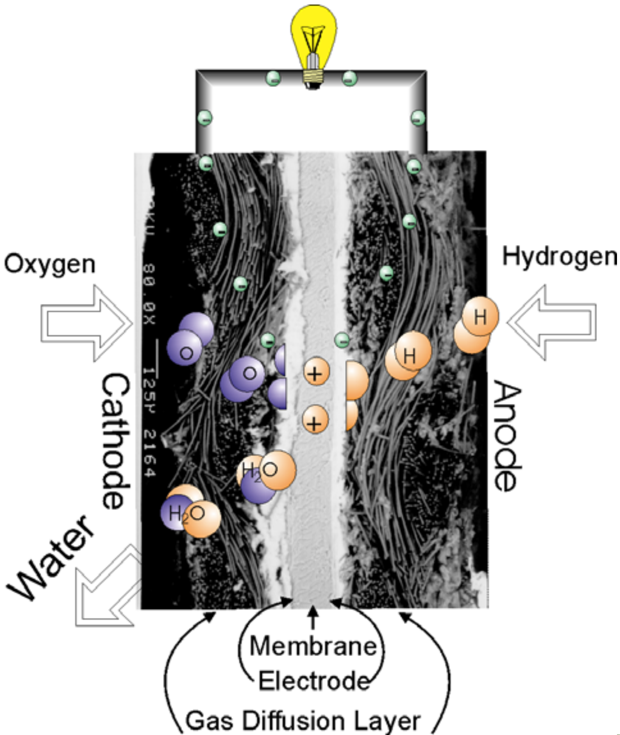

Fuel Cells




Electrolysis (Water, NaCl, etc.)



# PEFC: Schematic Diagram (cross section)

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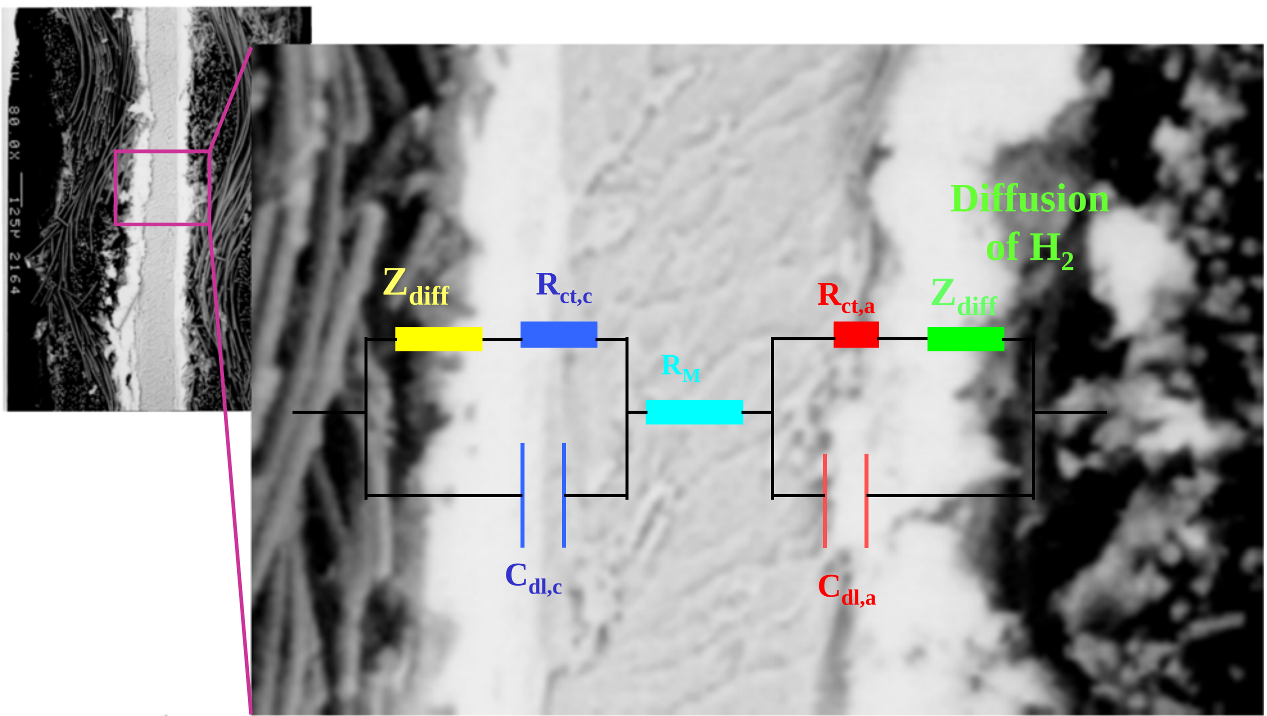
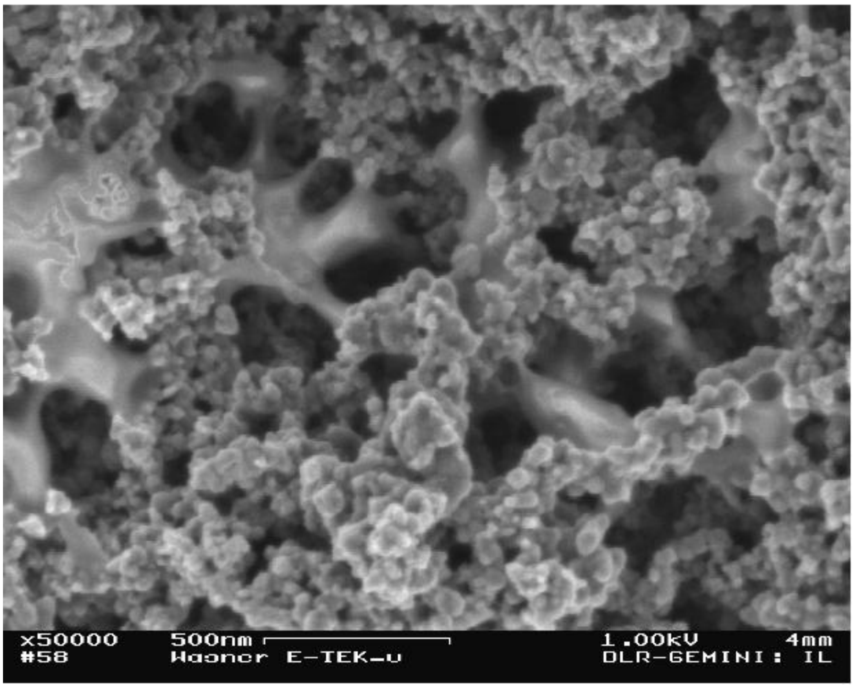
# Common Equivalent Circuit for Fuel Cells

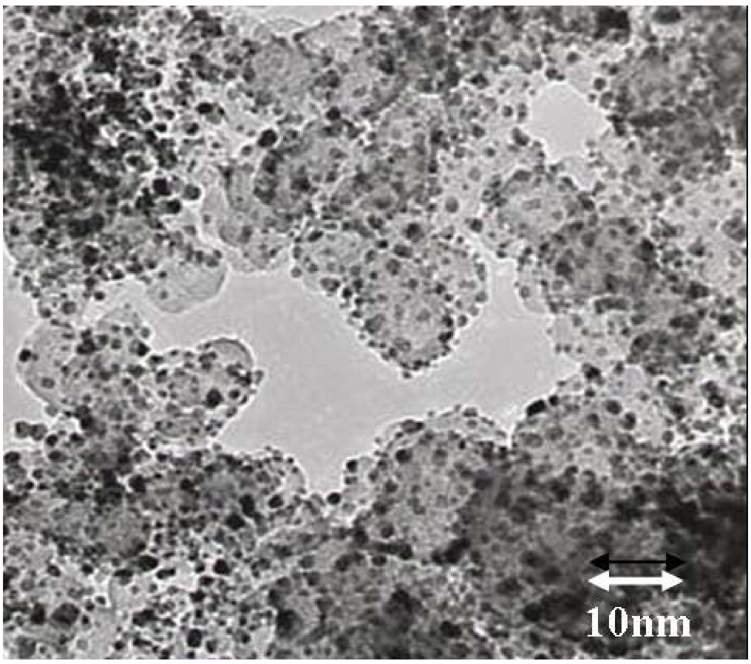


# SEM micrograph of PEFC elctrode (Pt/C+PTFE)

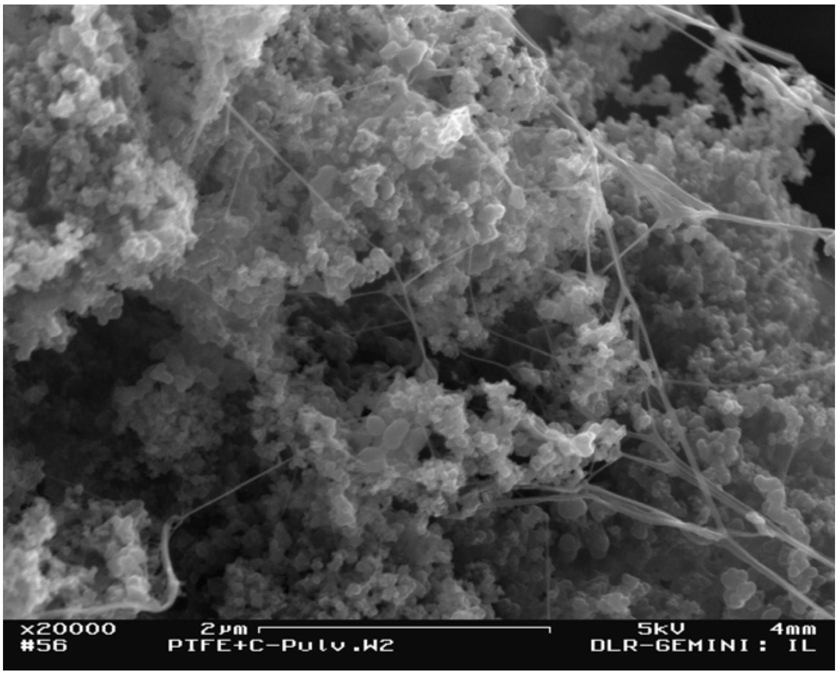





# TEM micrograph of Carbon Supported Platinum Catalyst



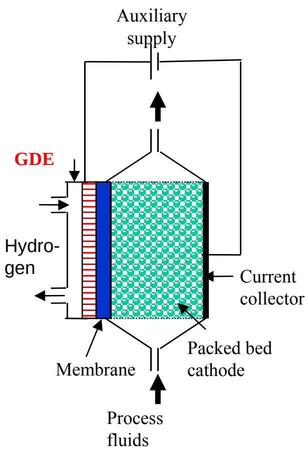
# SEM picture of PTFE/C powder





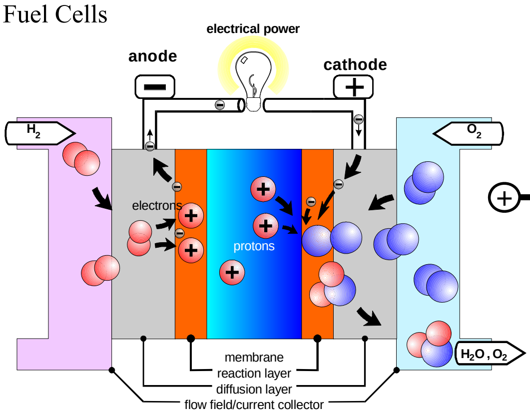

# Field of application of porous electrodes

Water purification and treatment
(Bio)-Organic synthesis

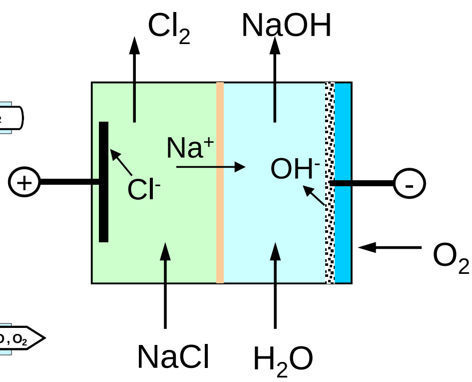



Batteries and supercaps

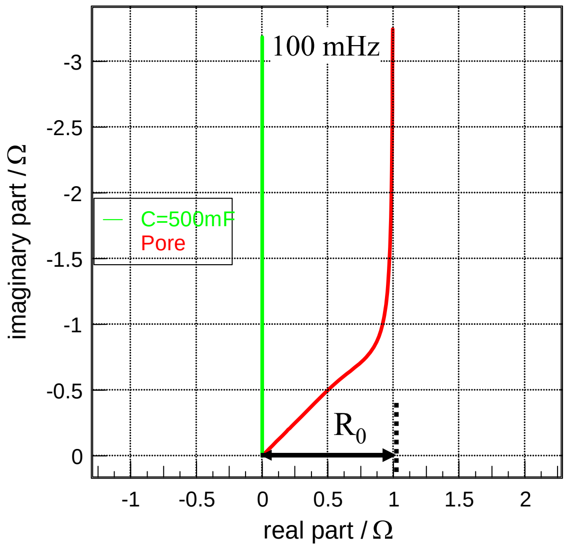
Fuel Cells

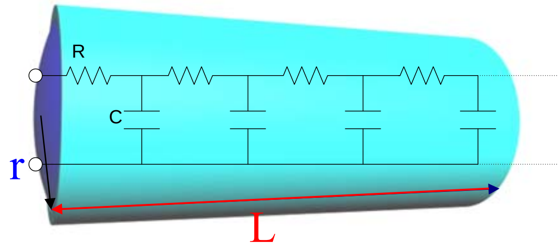



Electrolysis (Water, **NaCl**, HCl, etc.)



# Nyquist representation of Impedance of RC-transmission line, model of a flooded pore




R = 3 Ω
C = 0.5 F

$$Z(i\omega) = \sqrt{\frac{R}{i\omega C}} \coth \sqrt{i\omega RC}$$

$$R_0 = R/3 = \delta L/3\pi r^2$$

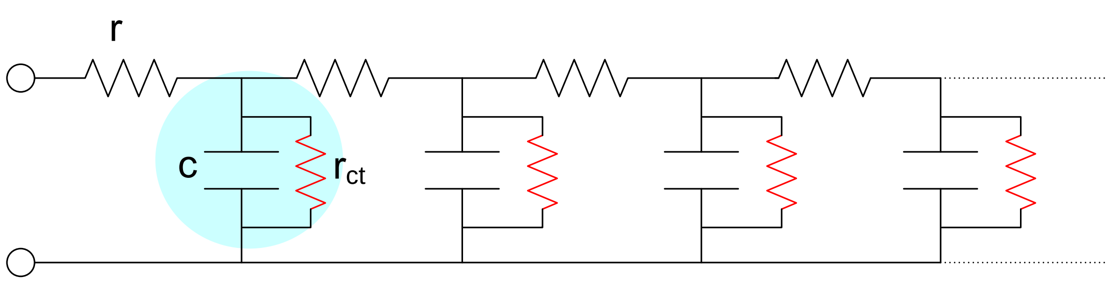
δ = specific electrolyte resistance
r = pore radius
L = pore lenght



# Simple pore model with faradaic processes in pores

## RC-transmission line of a flooded pore

R. De Levie, Electrochim. Acta, **8**(1963) 751

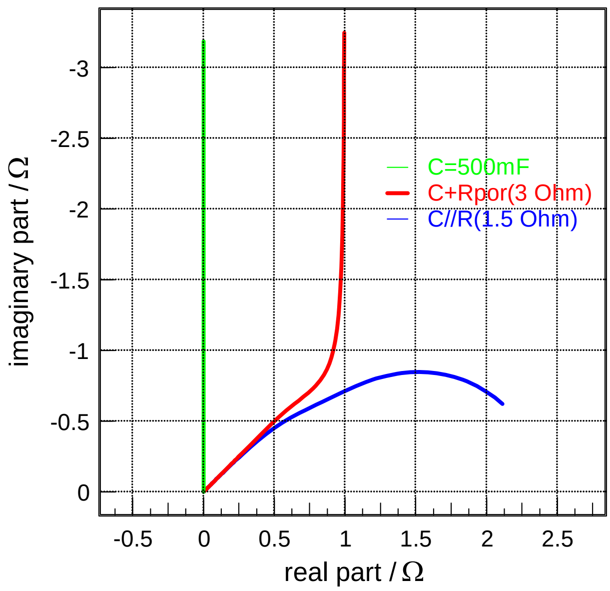


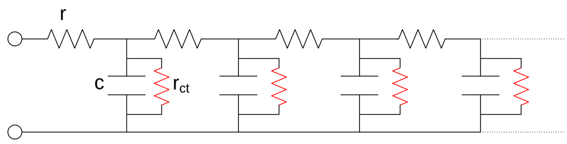

r = electrolyte resistance inside the pore per unit length

c = interface capacitance per unit length

$r_{ct}$ = interface charge transfer resistance per unit lenght

# Nyquist representation of porous electrode impedance with faradaic impedance element



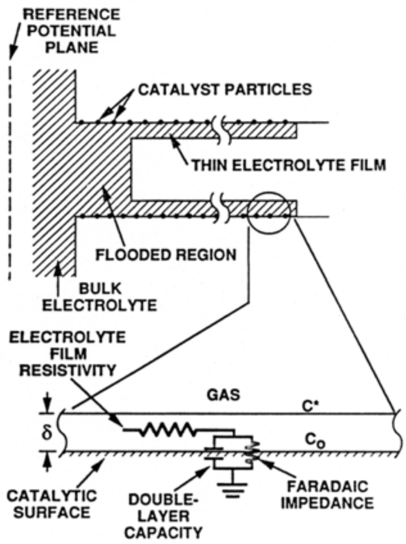

$r = 3\ \Omega$

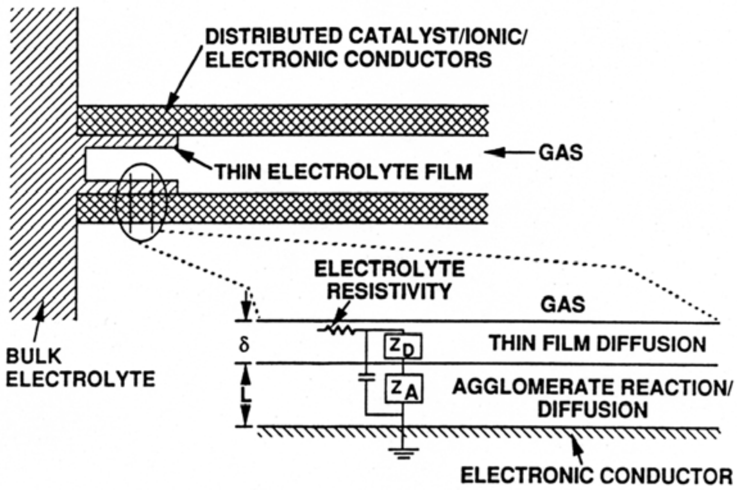
$c = 500\ mF$

$r_{ct} = 1.5\ \Omega$



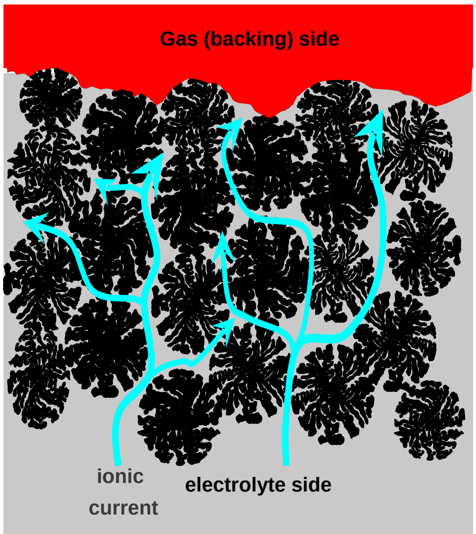
# Thin-film model and agglomerate plus thin-film model of a porous electrode



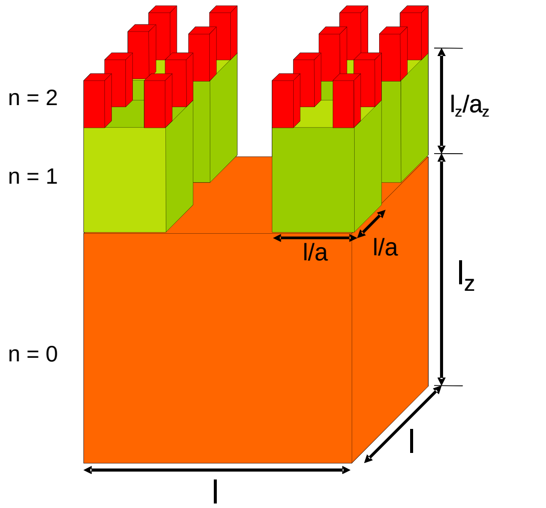

I.D. Raistrick, *Electrochim. Acta*, **35**(1990) 1579

## Agglomerated Electrodes



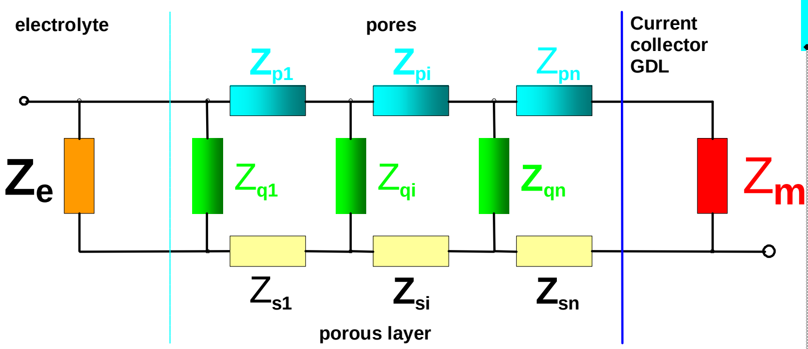

M. Eikerling, A.A. Kornyshev, E. Lust
*J. Electrochem. Soc.,* **152** (2005) E24

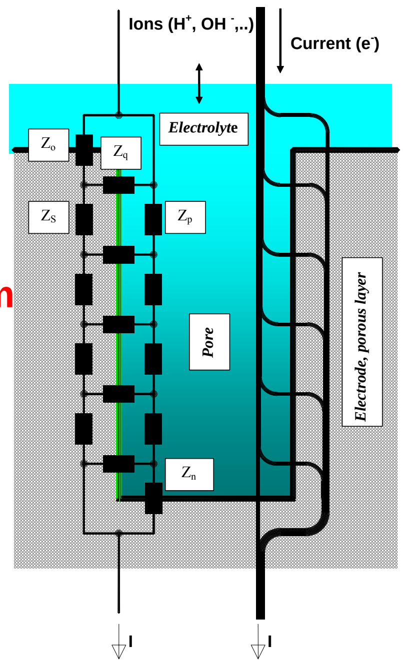
## Hierarchical model (Cantor-block model)




S.H. Liu, *Phys. Rev. Letters*, **55**(1985) 5289
T.Kaplan, L.J.Gray, and S.H.Liu, *Phys. Rev.* **B 35** (1987) 5379

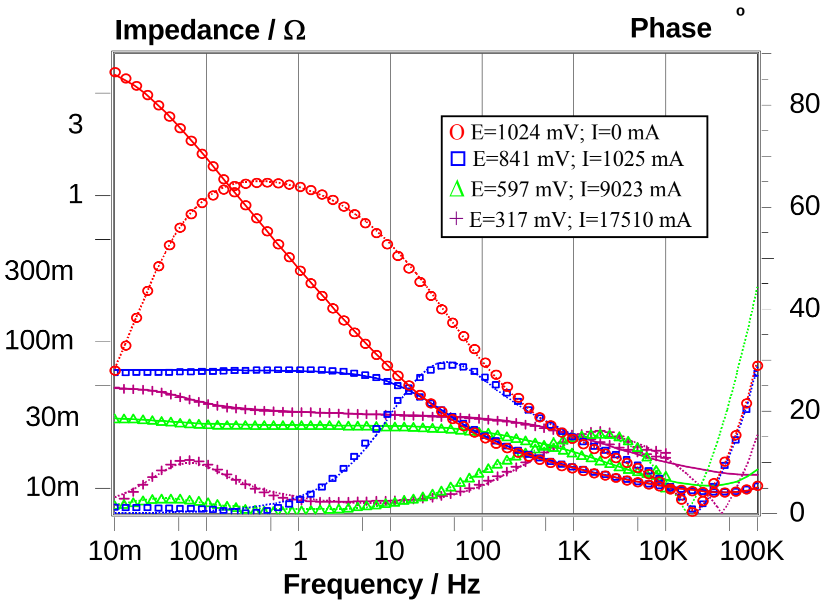
## Cylindrical homogeneous porous electrode model (H. Göhr)




H. Göhr in *Electrochemical Applications/97*, www.zahner.de

# Bode diagram of EIS at different cell voltages measured at PEFC ($H_2/O_2$) at 80°C,

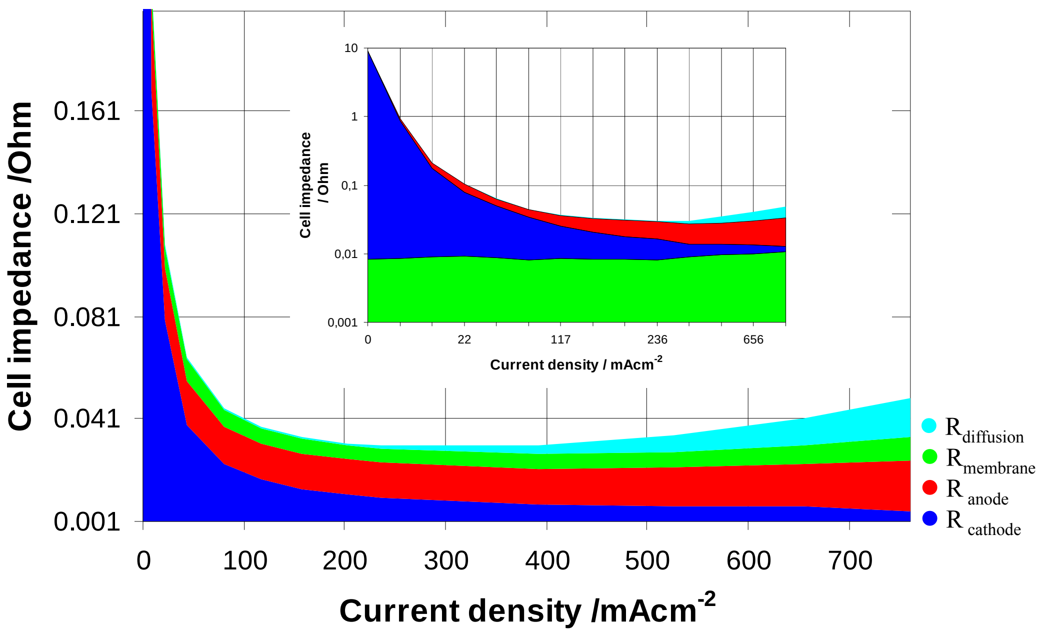



DLR



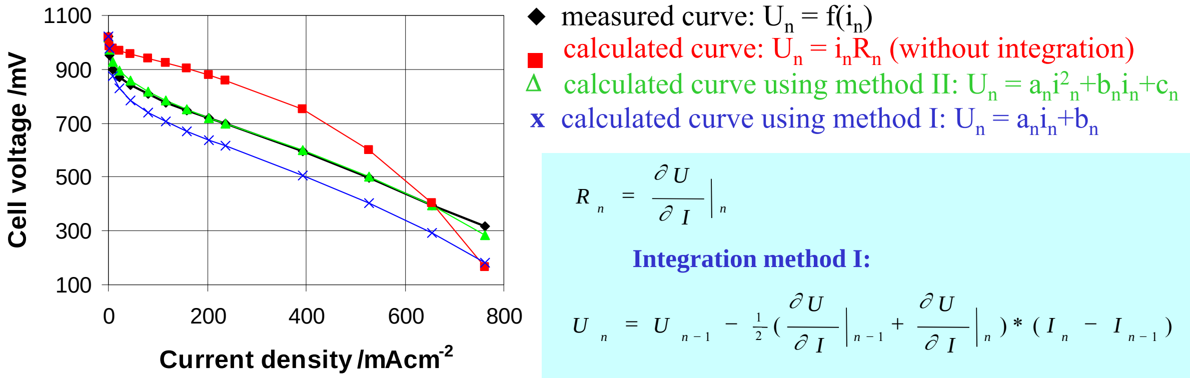
# EIS at Polymer Fuel Cells (PEFC):

Contributions to the cell impedance at different current densities




DLR

# Evaluation of the U-i characteristics from EIS




$$R_n = \frac{\partial U}{\partial I}\Big|_n$$

**Integration method I:**

$$U_n = U_{n-1} - \tfrac{1}{2}\left(\frac{\partial U}{\partial I}\Big|_{n-1} + \frac{\partial U}{\partial I}\Big|_n\right) * (I_n - I_{n-1})$$

**Integration method** II:

$$U_n = a_n I_n^2 + b_n I_n + c_n \quad \text{with:}$$

$$a_n = \frac{R_{n+1} - R_n}{2(I_{n+1} - I_n)}$$

$$b_n = R_{n+1} - 2 a_n I_{n+1}$$

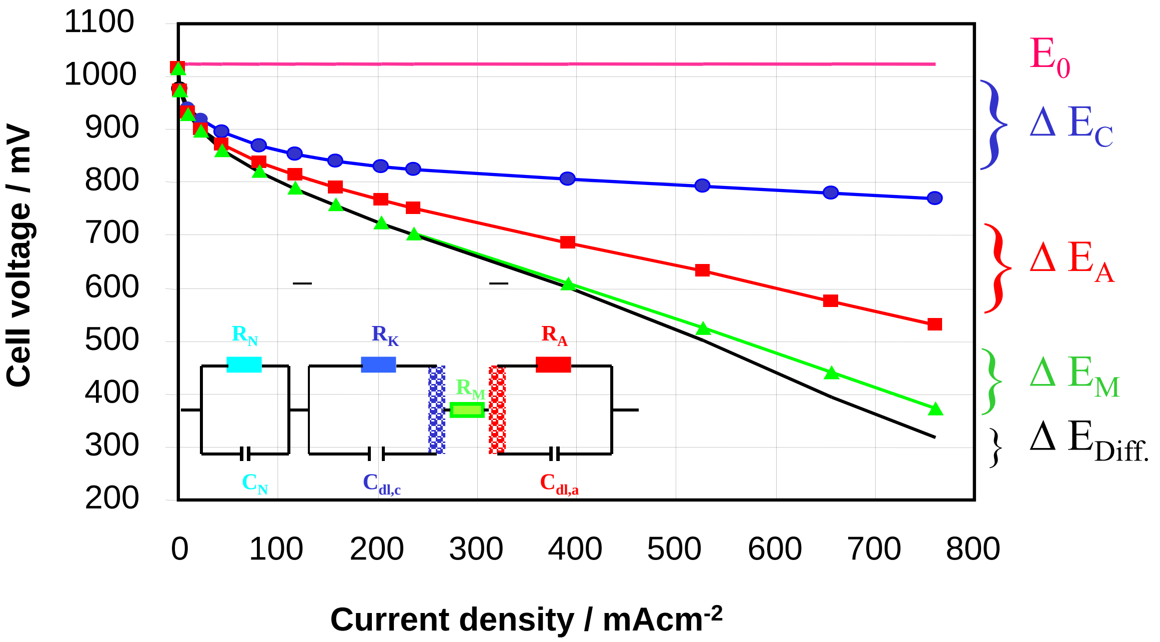
$$c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1}$$

DLR



# EIS at Polymer Fuel Cells (PEFC):

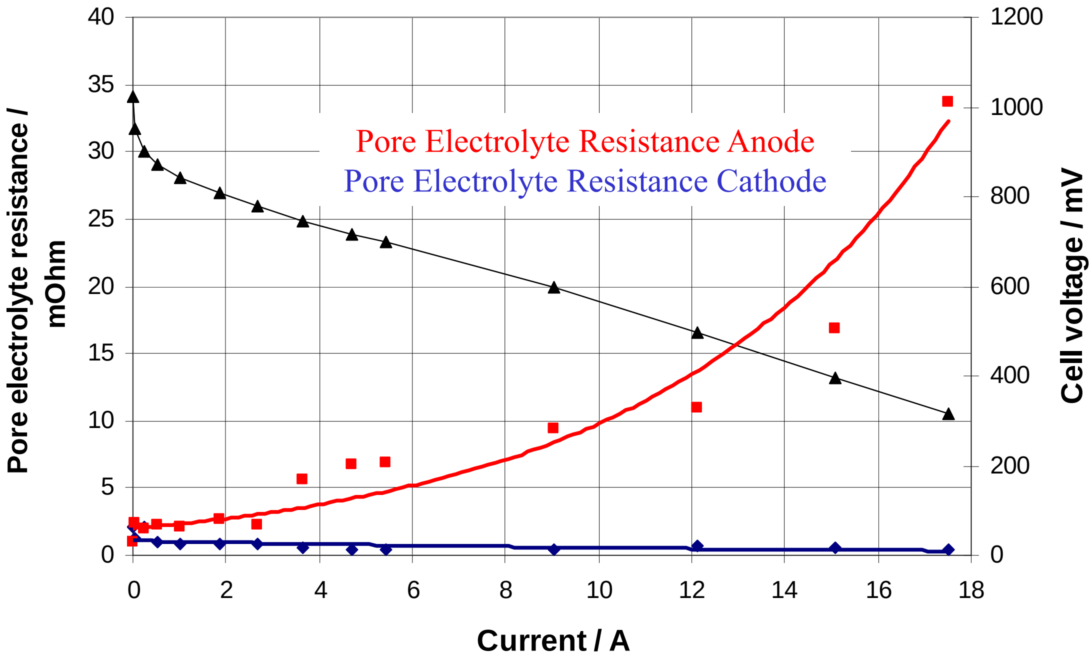
## Contributions to the overal U-i characteristic determined by EIS




DLR

# Evaluation of EIS with the porous electrode model

## Summary of current density dependency of pore resistance elements

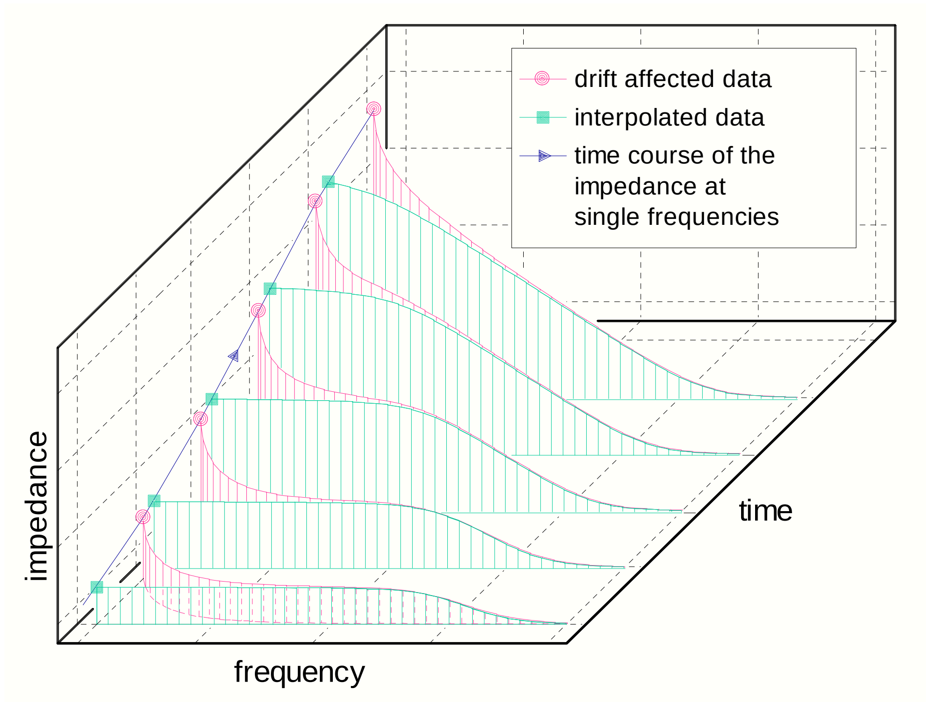





# Improved Evaluation Techniques for Time Resolved Electrochemical Impedance Spectroscopy (TREIS)

- Real time drift compensation
- **Time course interpolation**
- Z-HIT compensation

# Improved evaluation technique: Time course interpolation



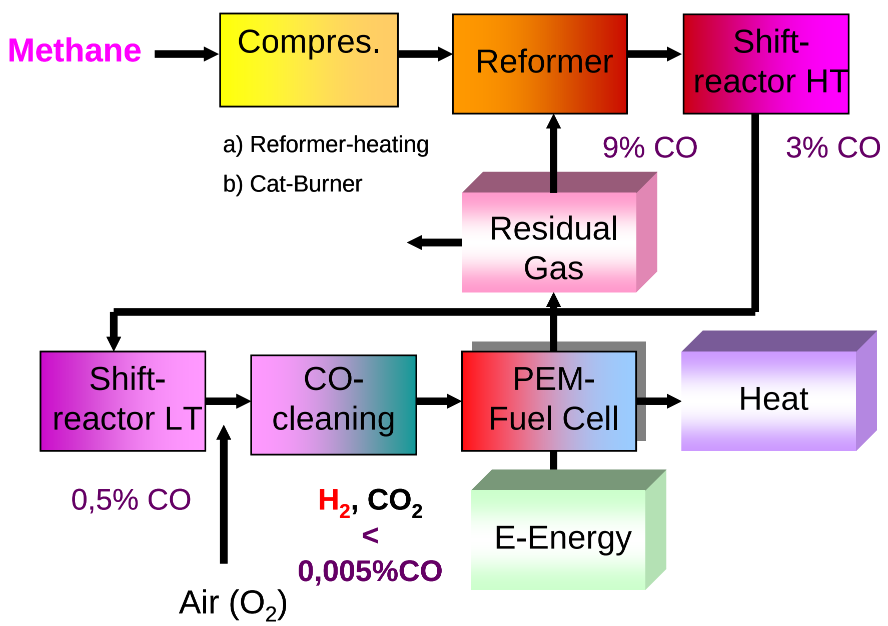

**Requirements**

- Series measurement
- Time for each
- measured frequency AND for each spectrum

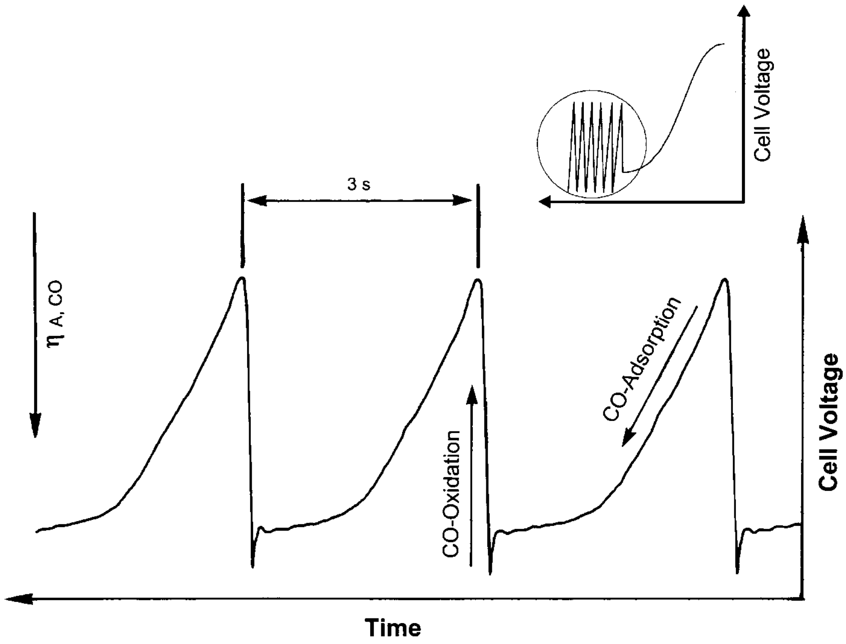


# Reforming of Methane

$CH_4 + 2H_2O \Rightarrow 4H_2 + CO_2\ (CO)$

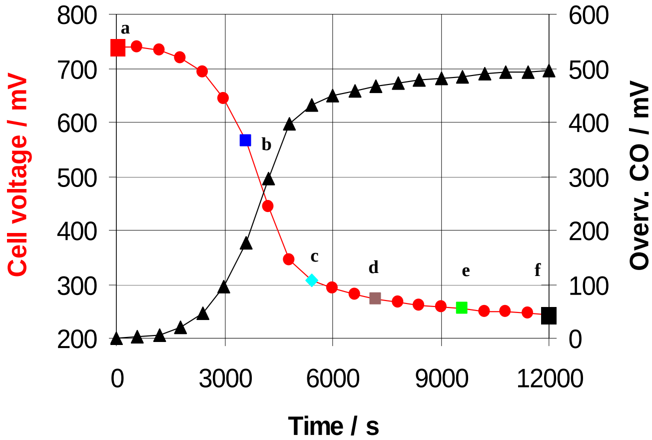


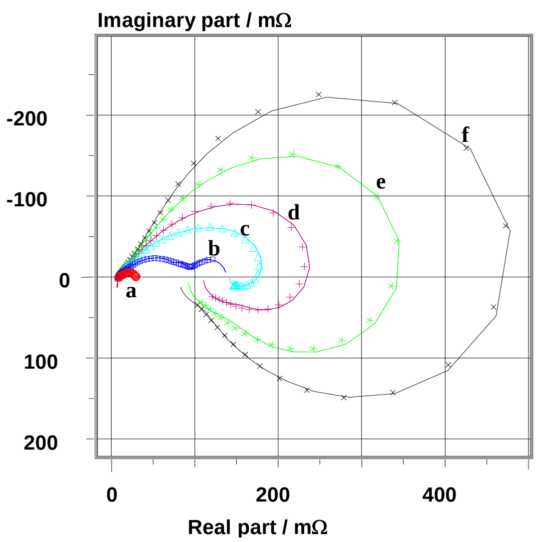
# Appearance of voltage oscillations during galvanostatic operation of PEFC with $H_2$+ 100ppm CO






# Time resolved EIS - CO poisoning of Pt-anode

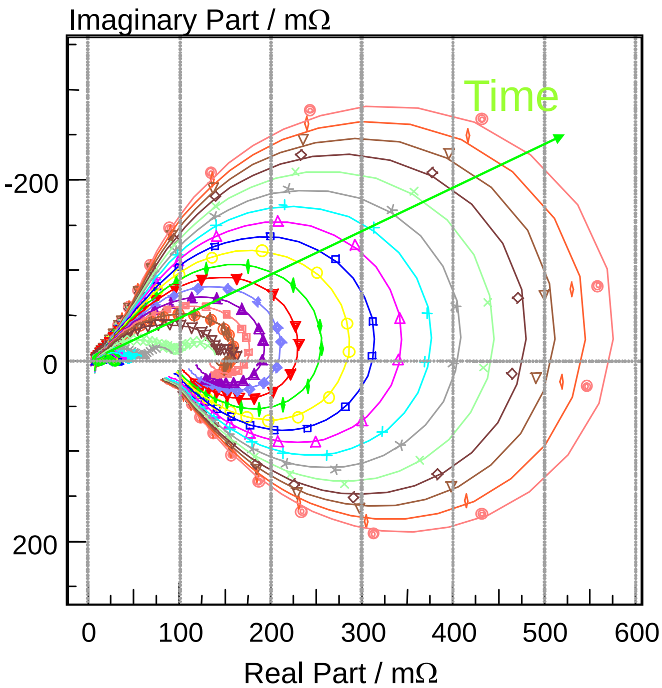



Time progression of **cell voltage** and overvoltage in galvanostatic mode of PEFC operation (217 mAcm$^{-2}$) Pt-anode , $H_2$ + 100 ppm CO at 80°C

Nyquist plot of **EIS** measured at different times during poisoning of the Pt-anode with CO

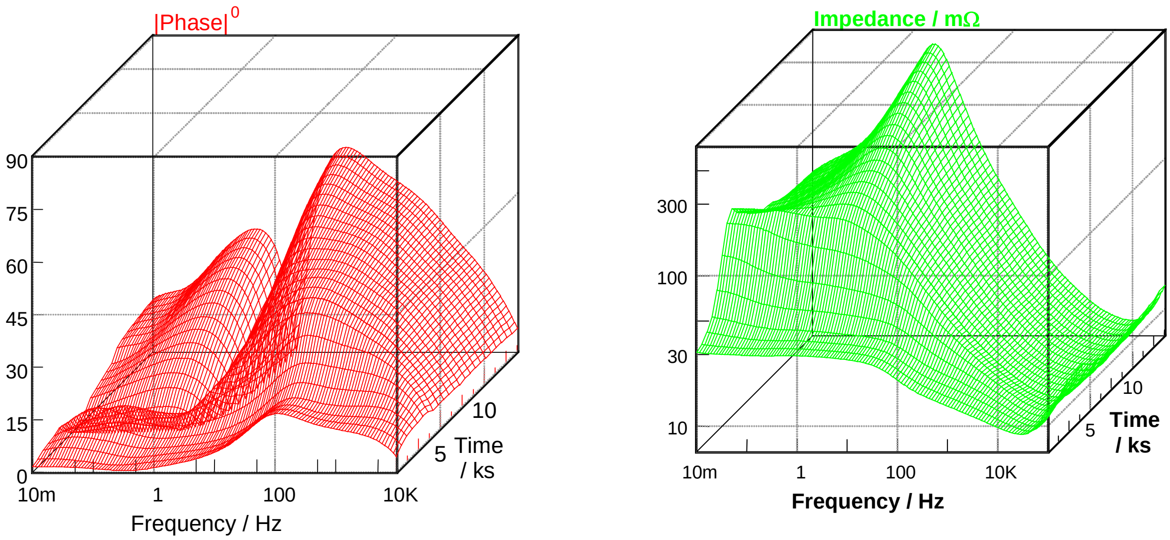
# Measured and simulated time resolved EIS - CO poisoning




Nyquist plot of EIS during CO poisoning of the Pt-anode at 217 mAcm$^2$, $H_2$+100 ppm CO

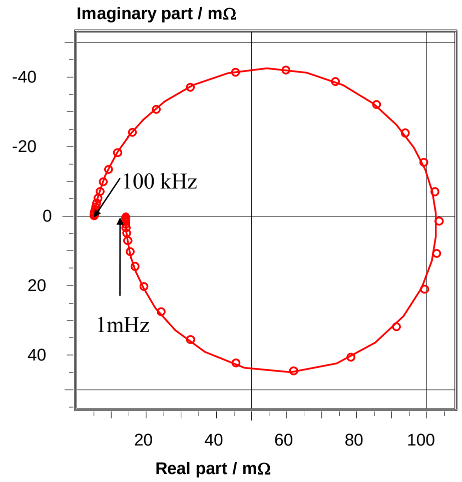


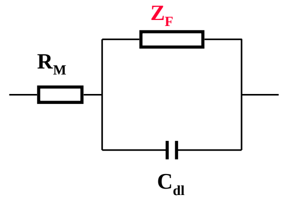
# Time resolved EIS - CO poisoning

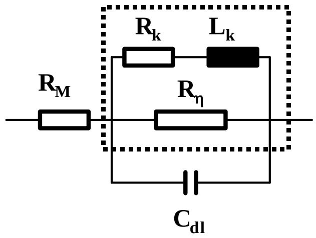



**Bode plot of EIS during CO poisoning of the Pt-anode at 217 mAcm$^2$, $H_2$+100 ppm CO**

# Simulated EIS with Relaxation Impedance: Theory



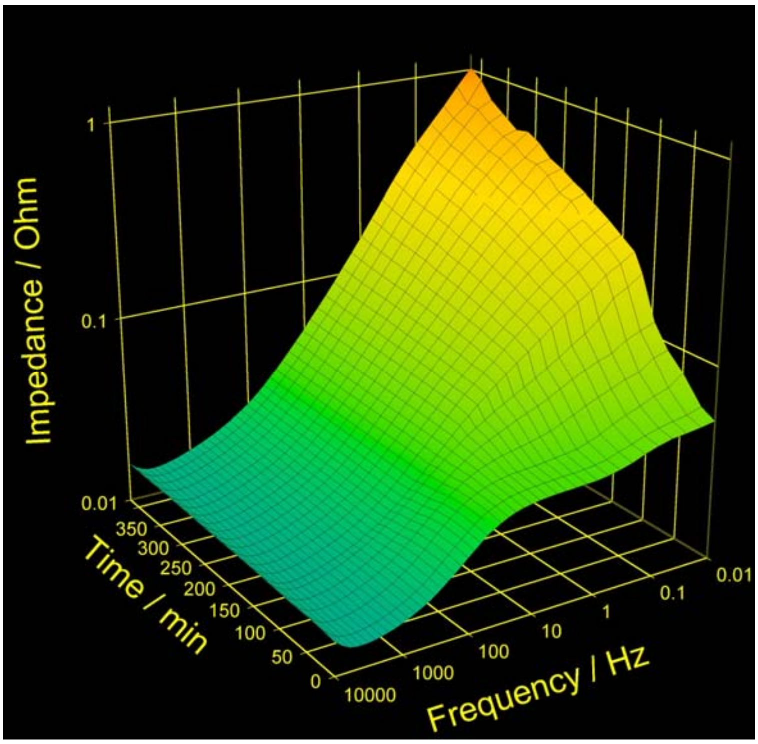

$\tau$ = 1 s; $R_k$ = 10 mΩ; $R_\eta$ = 100 mΩ
$R_M$ = 5 mΩ; $C_{dl}$ = 10 mF
$Z_{F\,(\omega\to 0)} = R_F$ = 9,1 mΩ

**Faraday-impedance: $Z_F$** = $R\eta/(1+ R\eta/Z_k)$
Relaxation imp.: $Z_k = (1+ i\omega\tau) / I_F$ dlnk/dE
Time constant: $\tau = R_k L_k$
Relaxation resistance: $R_k = 1 / I_F$ dlnk/dE
Relaxation inductivity: $L_k = \tau R_k$

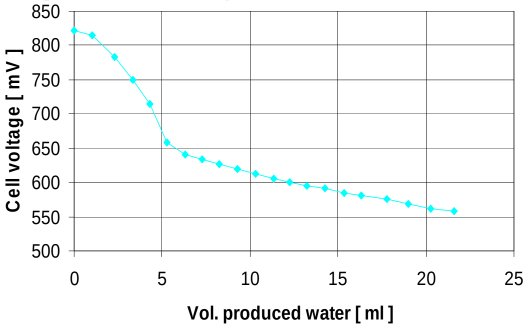


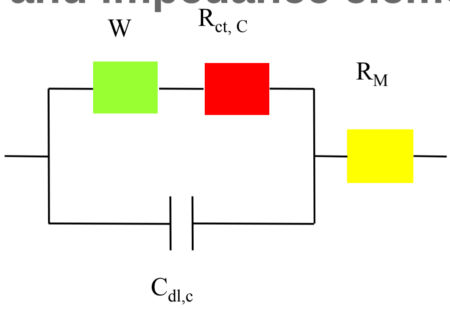


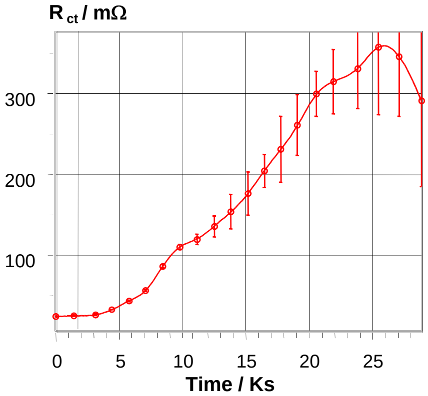
# Time resolved EIS
# Flooding the cathode at 2 A, dead end

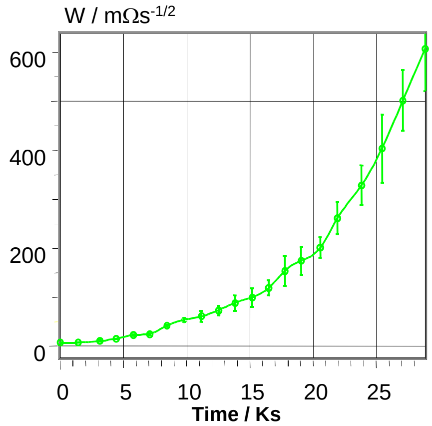


# Time resolved EIS, flooding the cathode at 2 A, 80°C; time dependency of the cell voltage and impedance elements



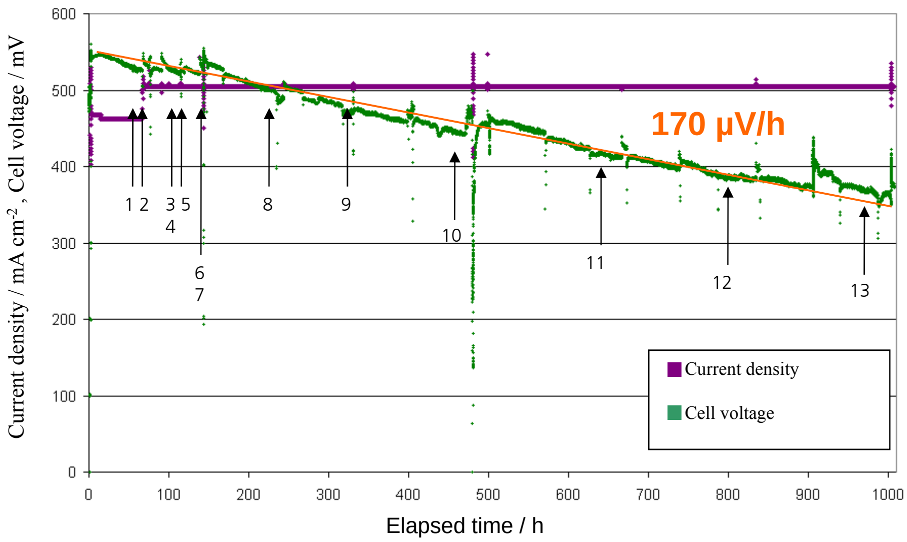



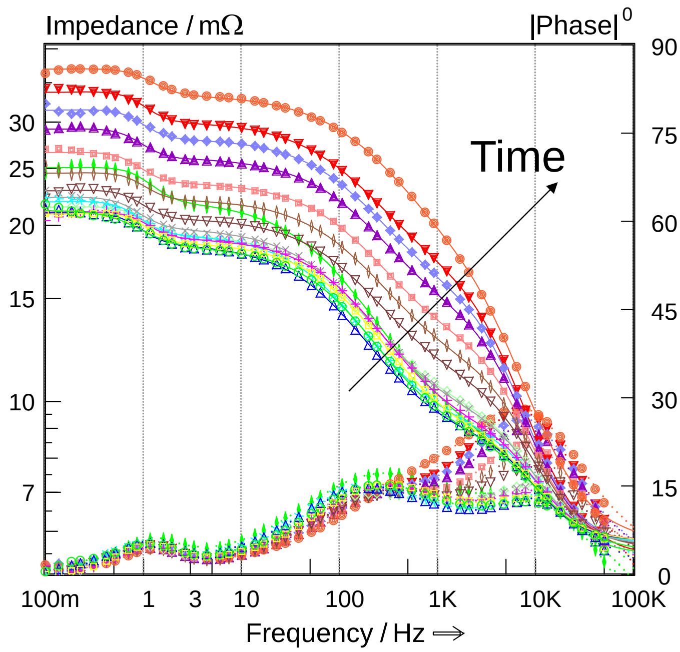






# Change of cell voltage during constant load at 500 mA cm$^{-2}$



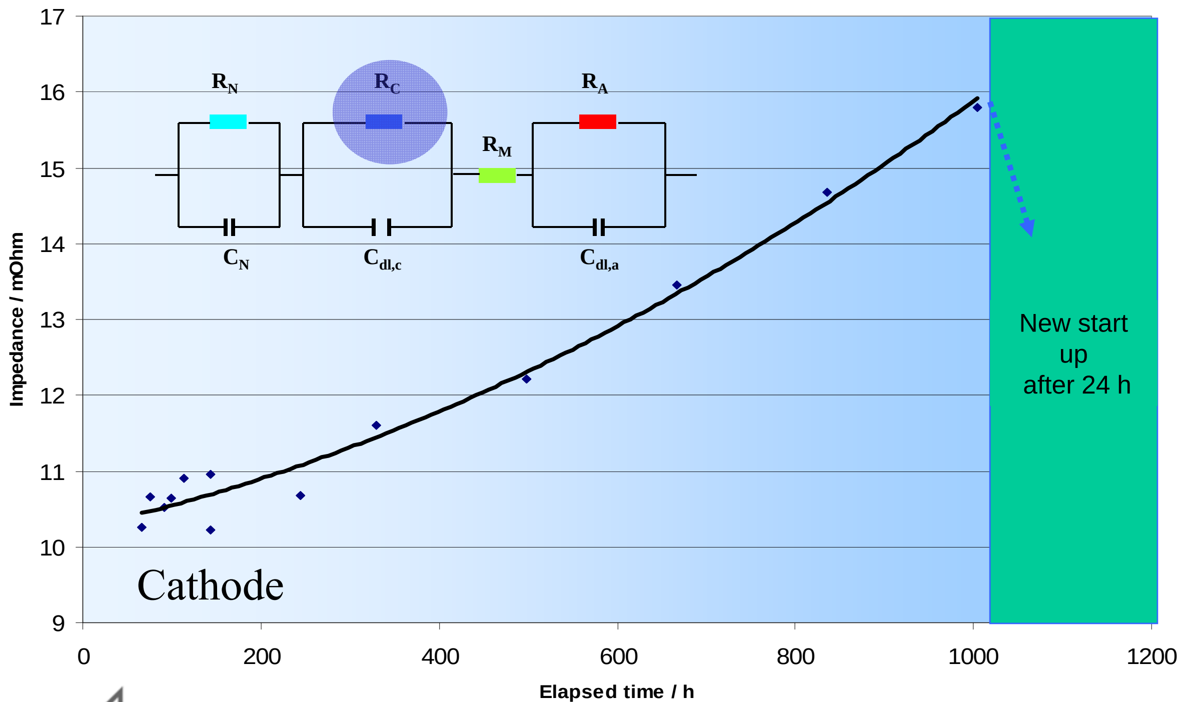
# Bode Plot of EIS measured during PEFC operation over 1000 h at 500 mA $cm^{-2}$



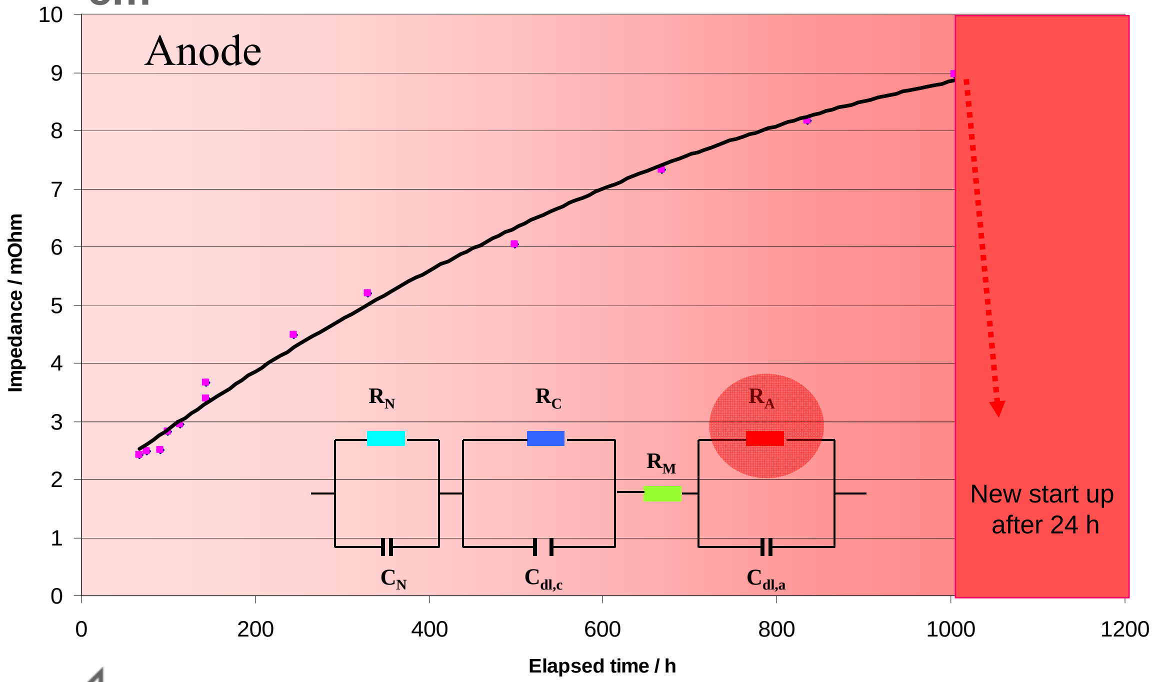




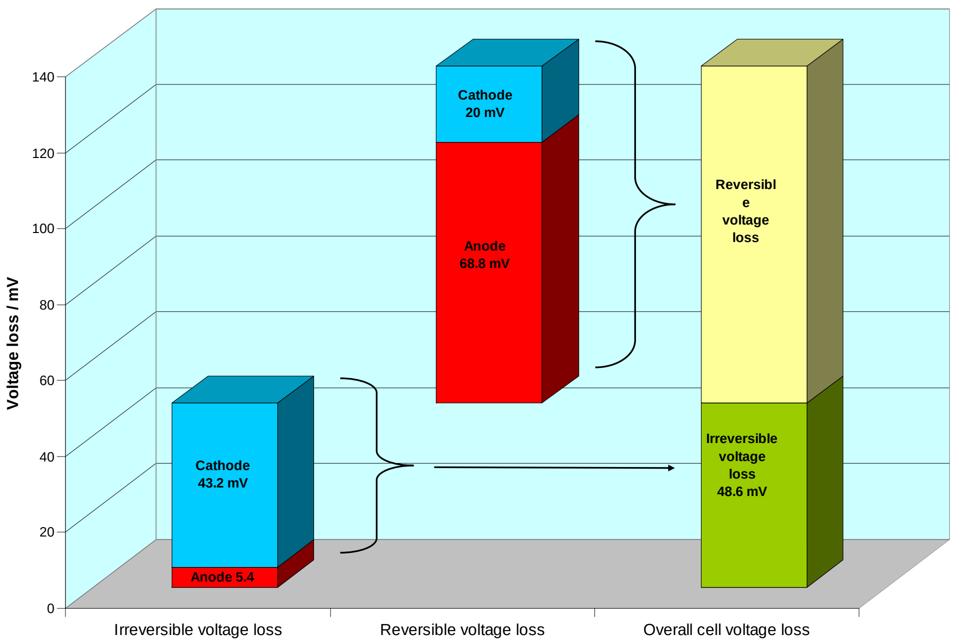

# Variation of RC during PEFC operation at 500 mA $cm^{-2}$



# Variation of $R_A$ during PEFC operation at 500 mA cm$^{-2}$

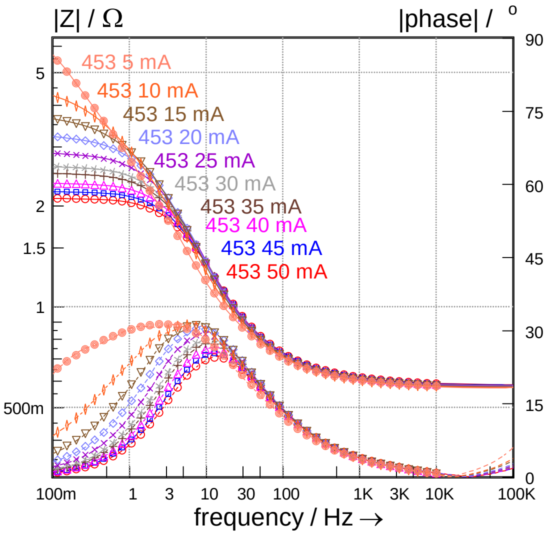


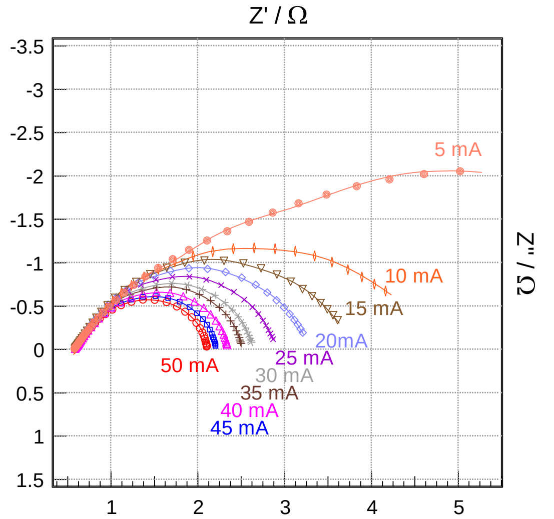

# Evaluation and Analyse of Voltage Loss by EIS




M. Schulze, N. Wagner, T. Kaz, K.A. Friedrich, *Electrochim. Acta* **52** (2007) 2328–2336

# AFC: Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, i< -50 mAcm$^{-2}$



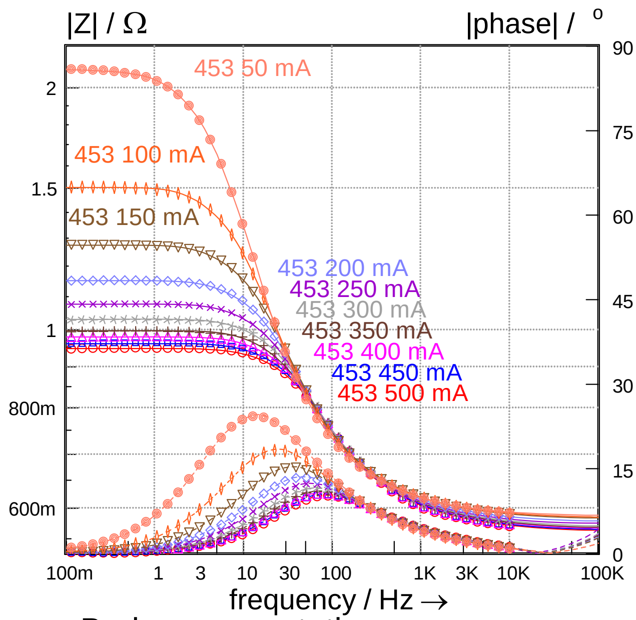




Bode representation

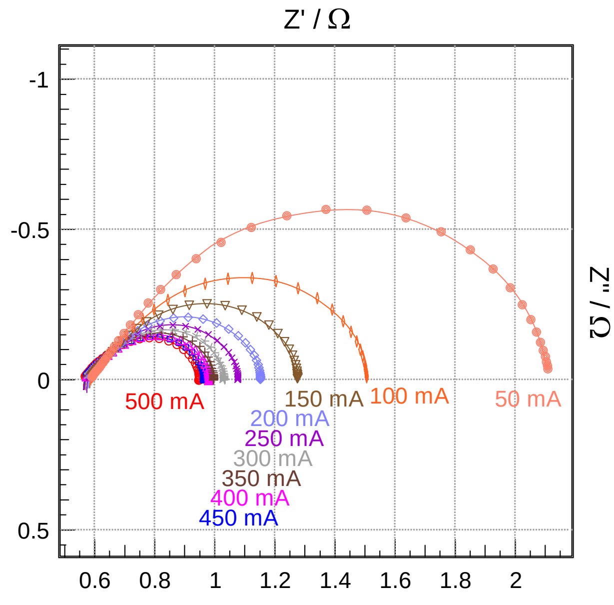
Nyquist representation



# Impedance Measurements during ORR in 10 N NaOH, on Silver Electrodes at Different Current Densities, i> -50 mAcm$^{-2}$




Bode representation




Nyquist representation

# Adsorptions- and heterogeous reaction impedance

Definition of $Z_{ad/het}$ :

$Z_{ad/het} = RT(k-\omega i)/n^2F^2c_sA(k^2+\omega^2)$

With A=electrode surface, k= first order reactions rate, F=Faraday constant, $c_s$=surface concentration and angular frequency $\omega=2\pi f$.

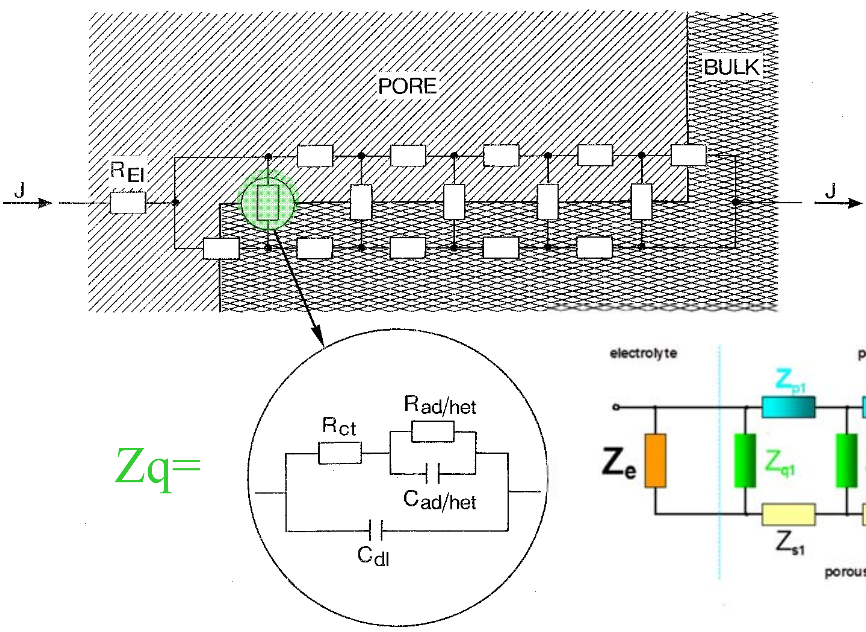
The heterogenous reaction impedance can be converted into a parallel combination of $R_{ad/het}$ and $C_{ad/het}$ :

$R_{ad/het} = RT/(n^2F^2c_sAk)$

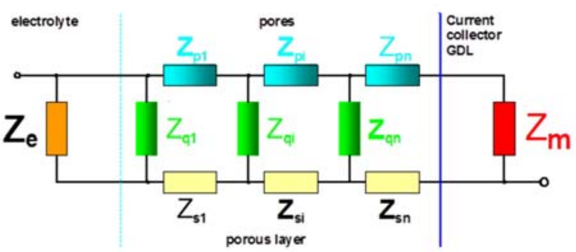
$C_{ad/het} = n^2F^2c_sA/(RT)$



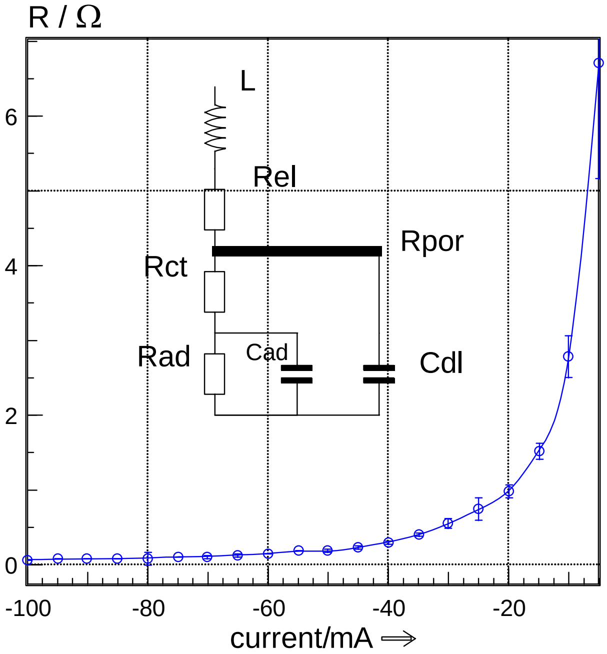
# Electrode Model with cylindrical , homogeneous pores and complex Faraday-impedance




Zq=



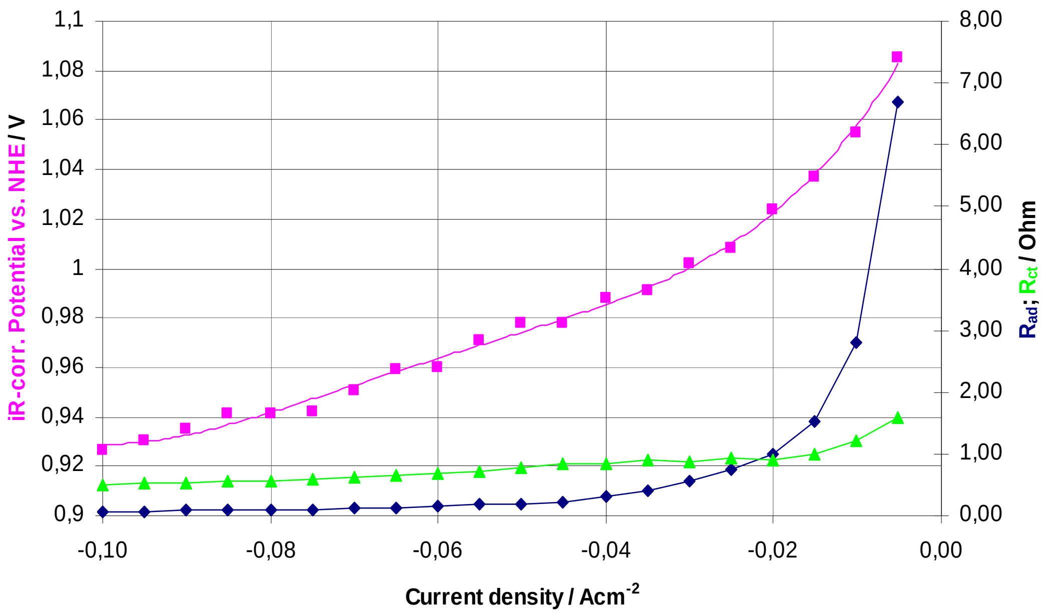
# Evaluation of EIS measured during ORR Equivalent circuit and $R_{ad}$ = f(i)



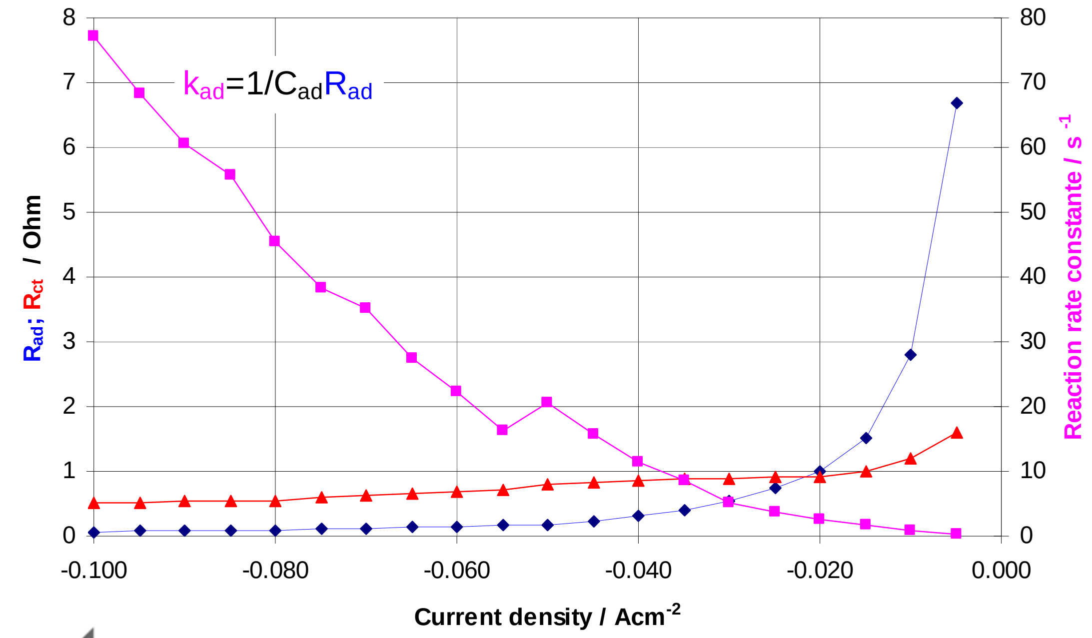




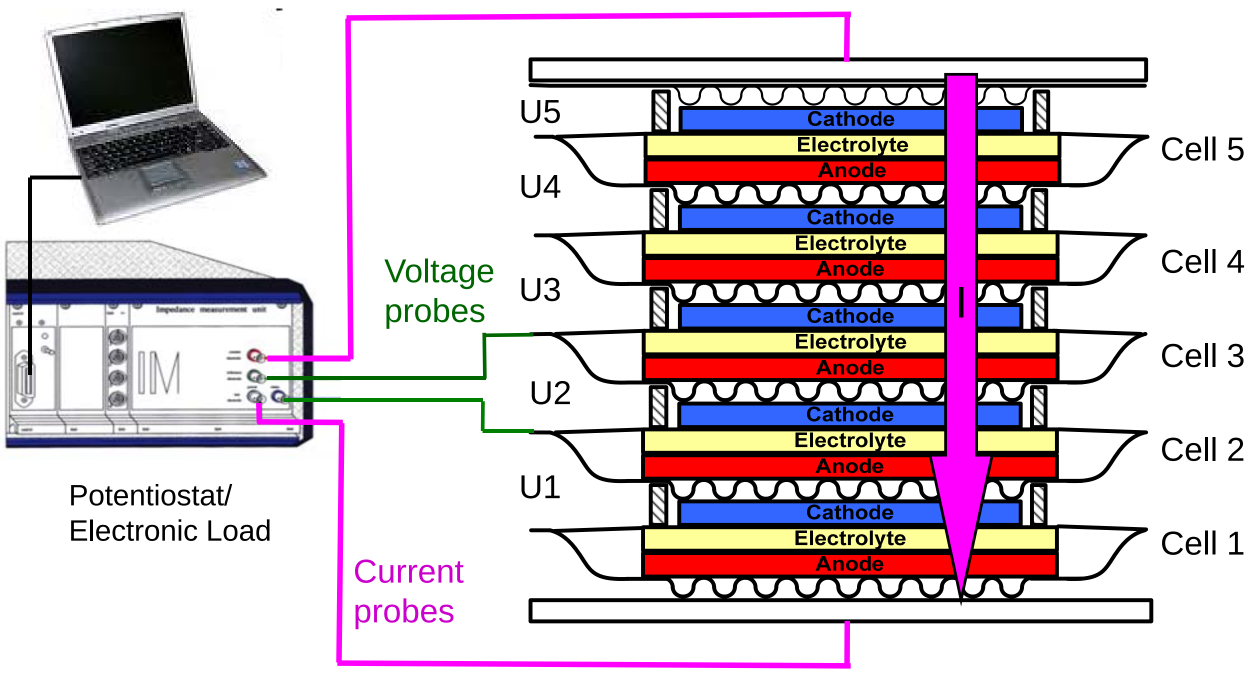

# U-i characteristic and current density dependency of impedance elements $R_{ad}$ and $R_{ct}$



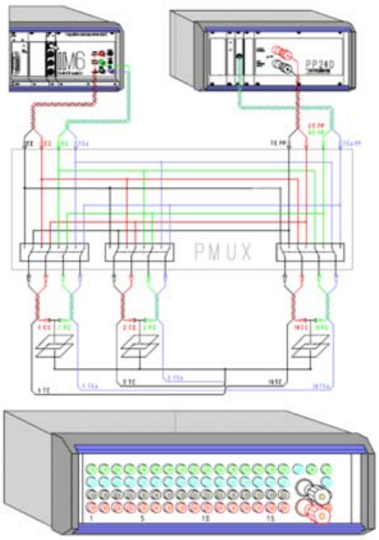
# Current density dependency of $k_{ad}$, $R_{ad}$ and $R_{ct}$, determined from EIS evaluation

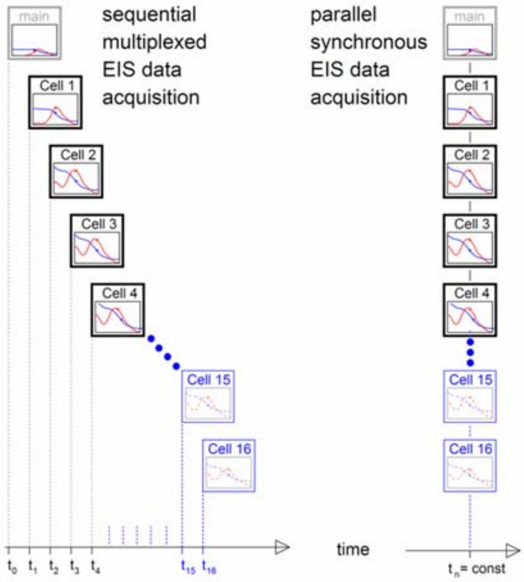



# Impedance Spectroscopy at SOFC short stack



# Comparison of the sequential measurement principle for impedance spectra data acquisition with the synchronous parallel approach



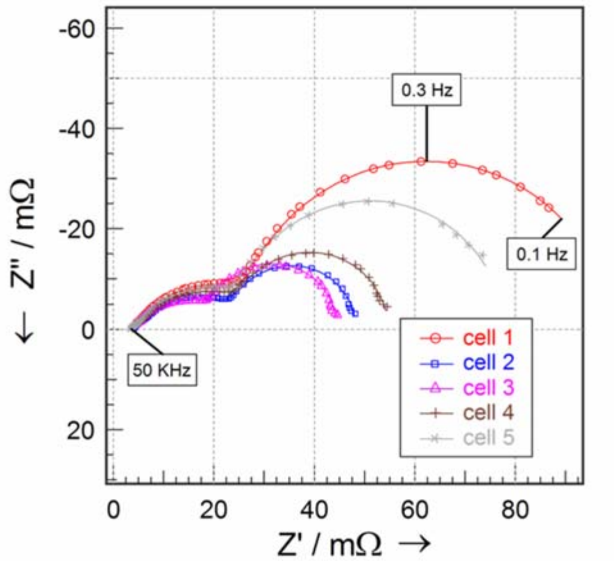




http://www.zahner.de/products/addon-cards/pad4.html





# Nyquist impedance diagram of the five individual cells within the SOFC short stack at OCP (1.19 V), measured synchronously




Operation under dry fuel gas (50 % $H_2$ + 50 % $N_2$ and air at 750 Cº. Symbols: measurement data, solid lines: model fit

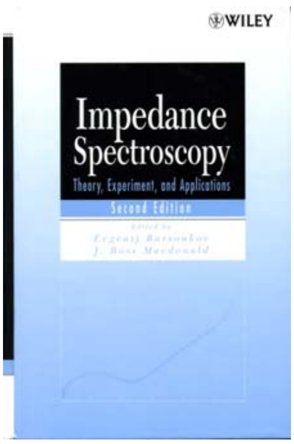
# Conclusion

- **Determination of the individual potential losses during fuel cell operation**
- **Determination of degradation mechanism and performance loss**
- **Improvement of fuel cell performance and stability by understanding instead of trial and error**
- **Determination of critical operation conditions of fuel cells**

DLR



# Thank you for the attention!




Norbert Wagner, “Electrochemical power sources – Fuel cells”, in Impedance Spectroscopy: Theory, Experiment, and Applications, 2nd Edition, Edited by Evgenij Barsoukov and J. Ross Macdonald, John Wiley&Sons, Inc., 2005, pp. 497-537, ISBN: 0-471-64749-7

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