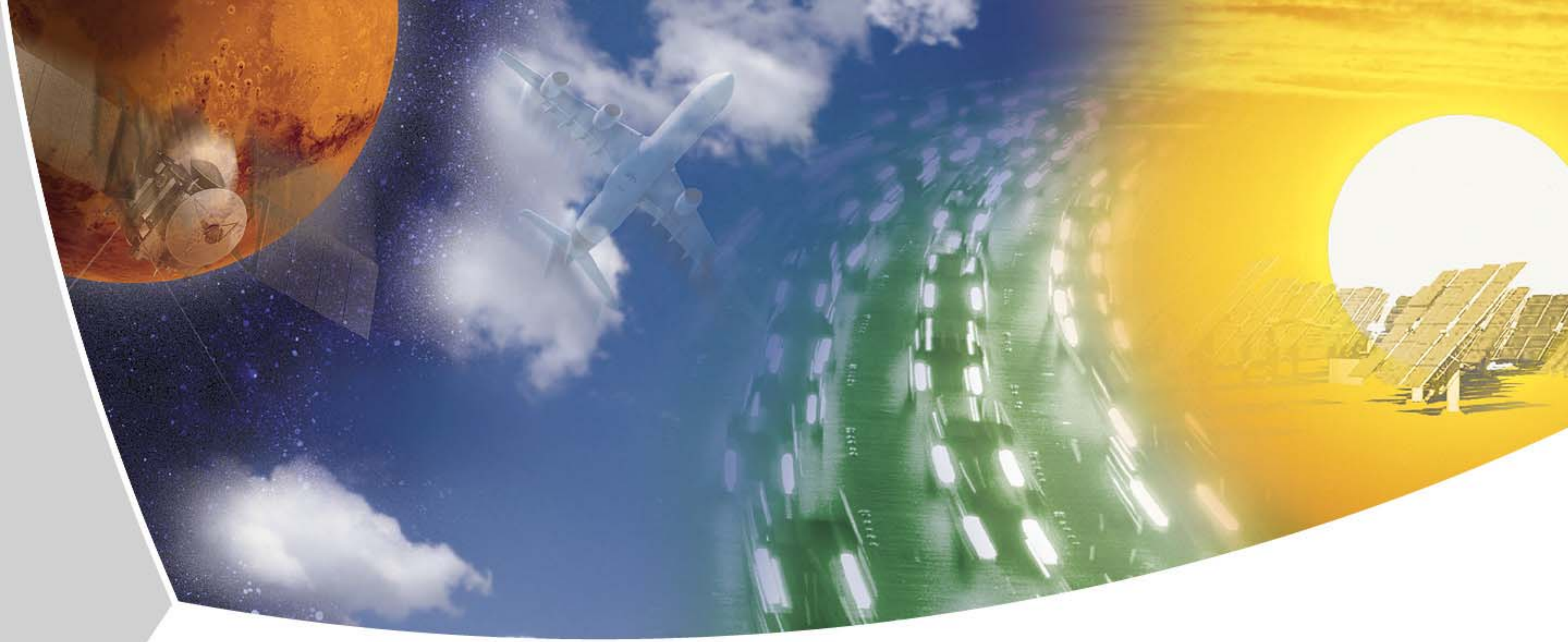

Theory and Application of Electrochemical Impedance Spectroscopy for Fuel Cell Characterization

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

Presentation outline

- Introduction
  - Motivation
  - Types of Fuel Cells
  - Experimental set-up for different types of FCs

- Modeling of fuel cells with equivalent circuits and microstructure of fuel cells electrodes
- Impedance models of porous electrodes
- Different applications of EIS in FC research
  - Contributions to performance loss of PEFC
  - EIS on segmented SOFC
  - EIS measured on Ag-gas diffusion electrodes

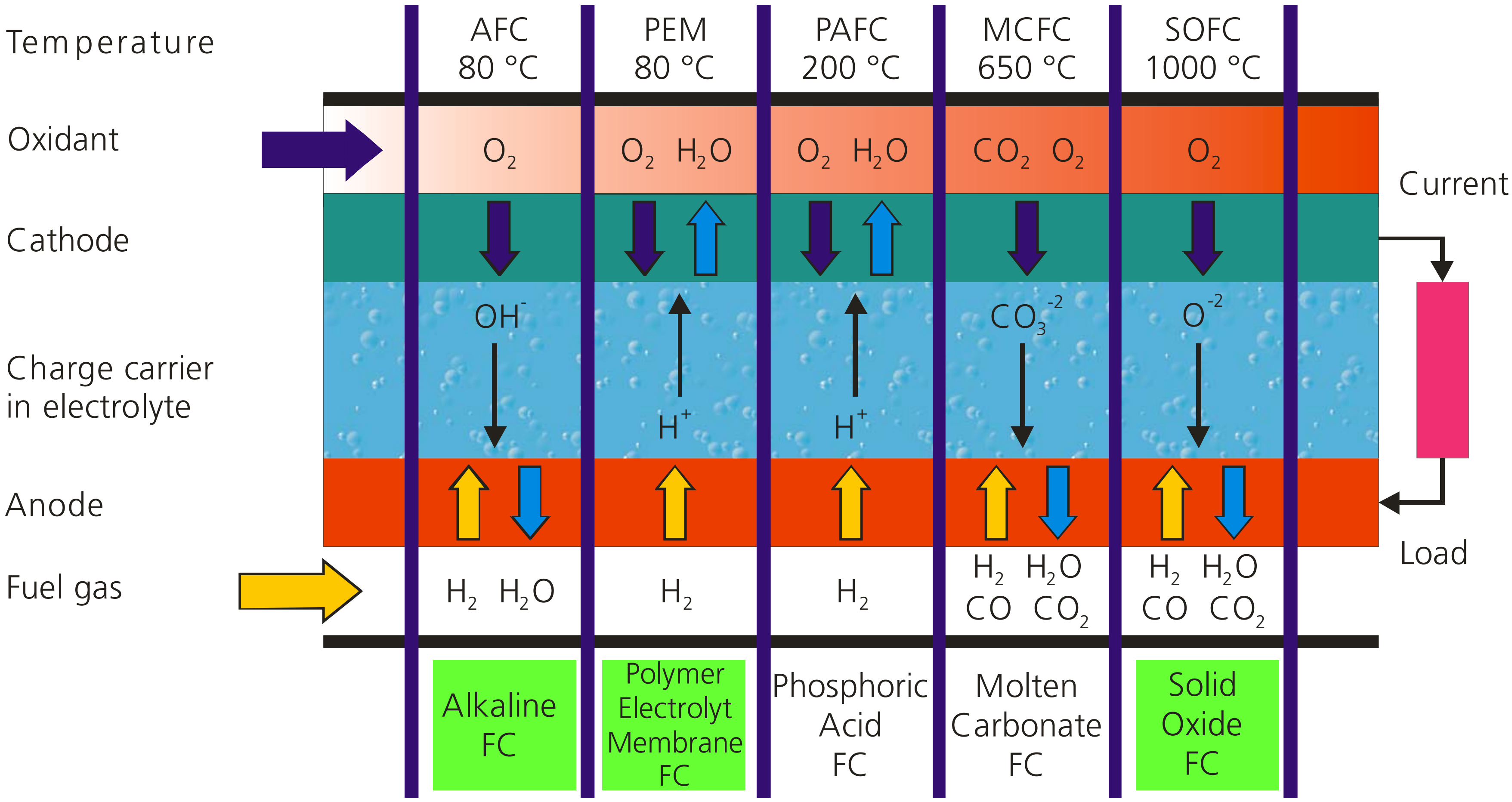
- Conclusion and Outlook

Motivation

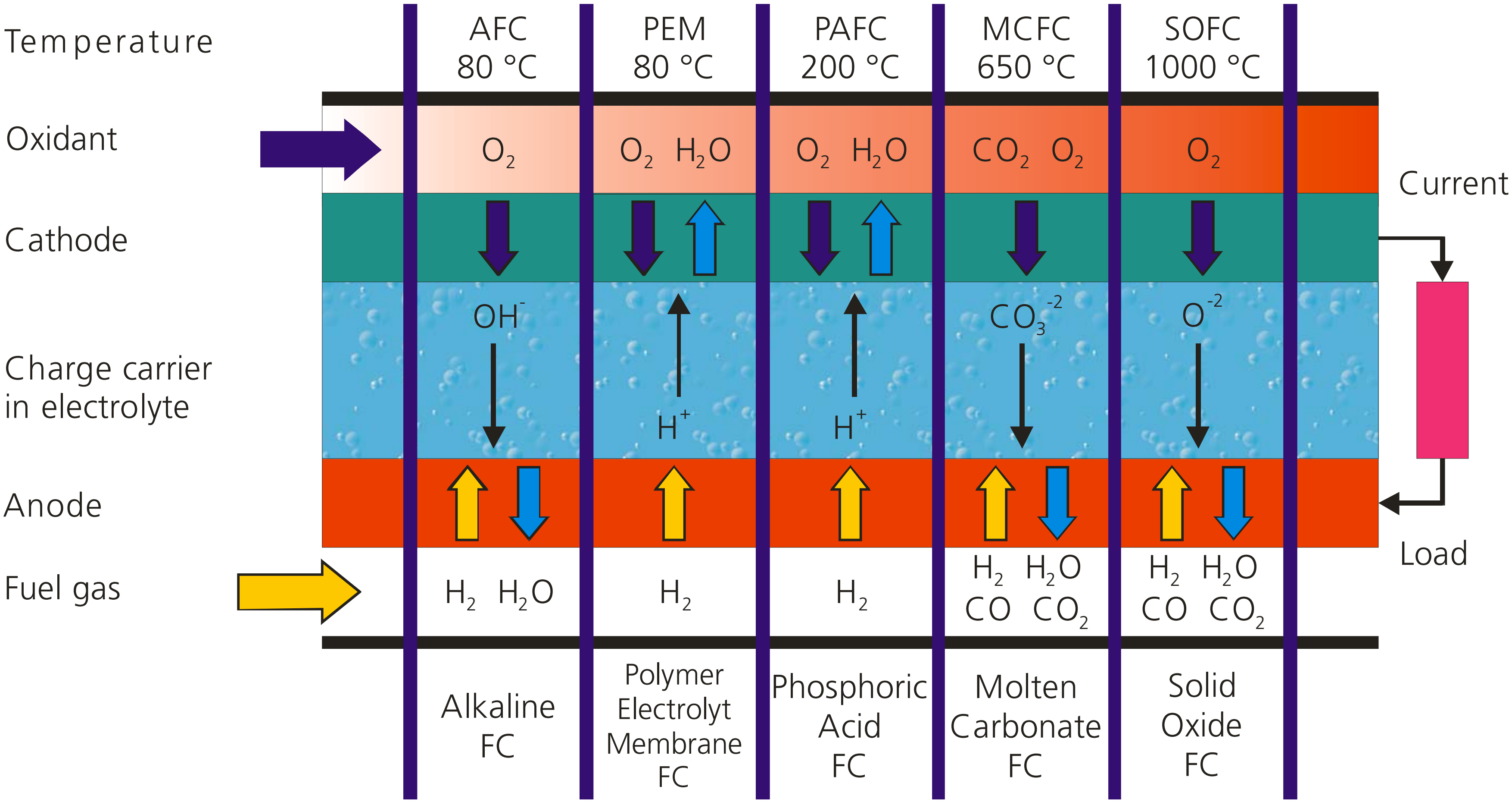
Characterization of Fuel Cells by Electrochemical Impedance Spectroscopy:

- Determination of electrode structure and reactivity, separation of electrode structure from electrocatalytical activity
- Determination of electrochemical active surface (locally resolved)
- Determination of reaction mechanism 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

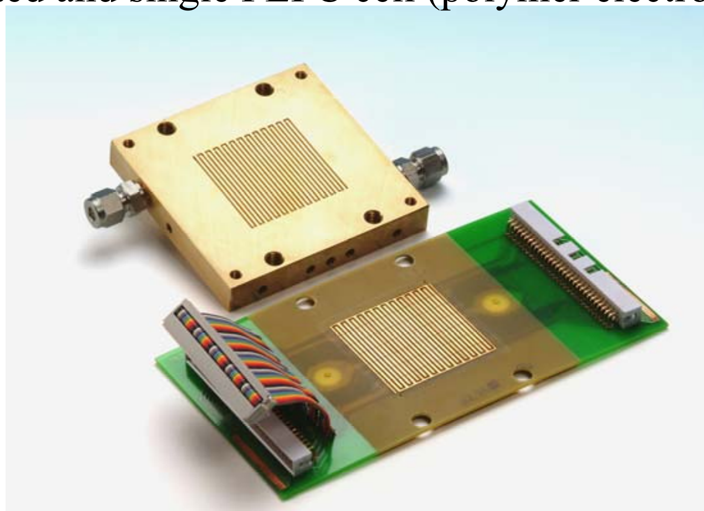


Schematic representation of main types of fuel cells

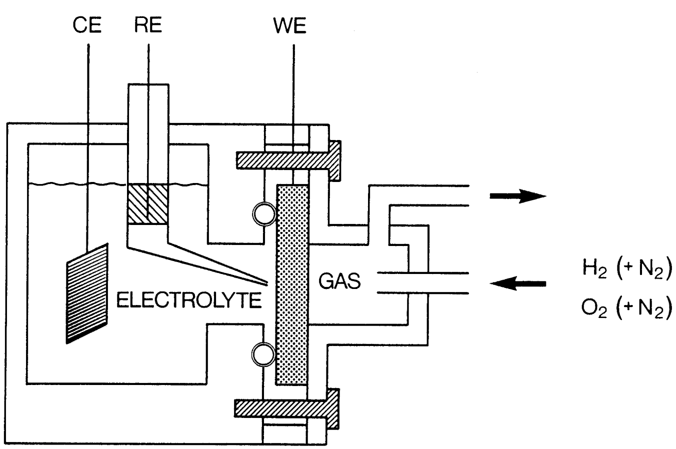


Experimental set up and cells used for EIS

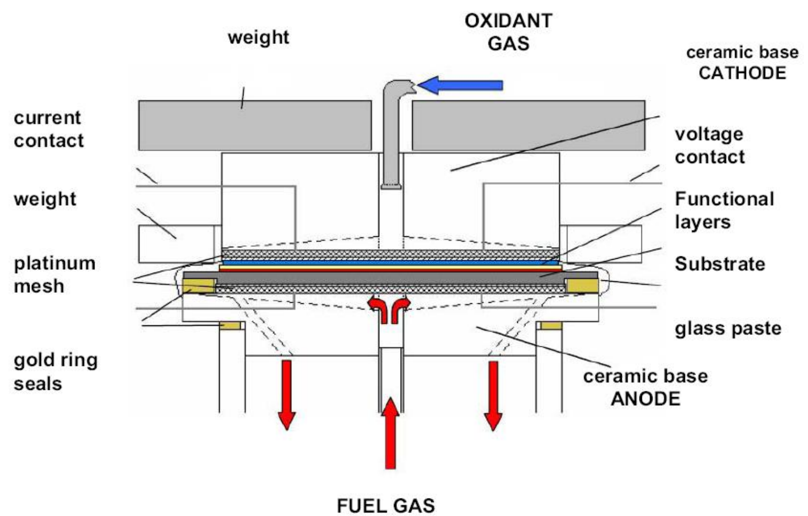
Segmented and single PEFC cell (polymer electrolyte)



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

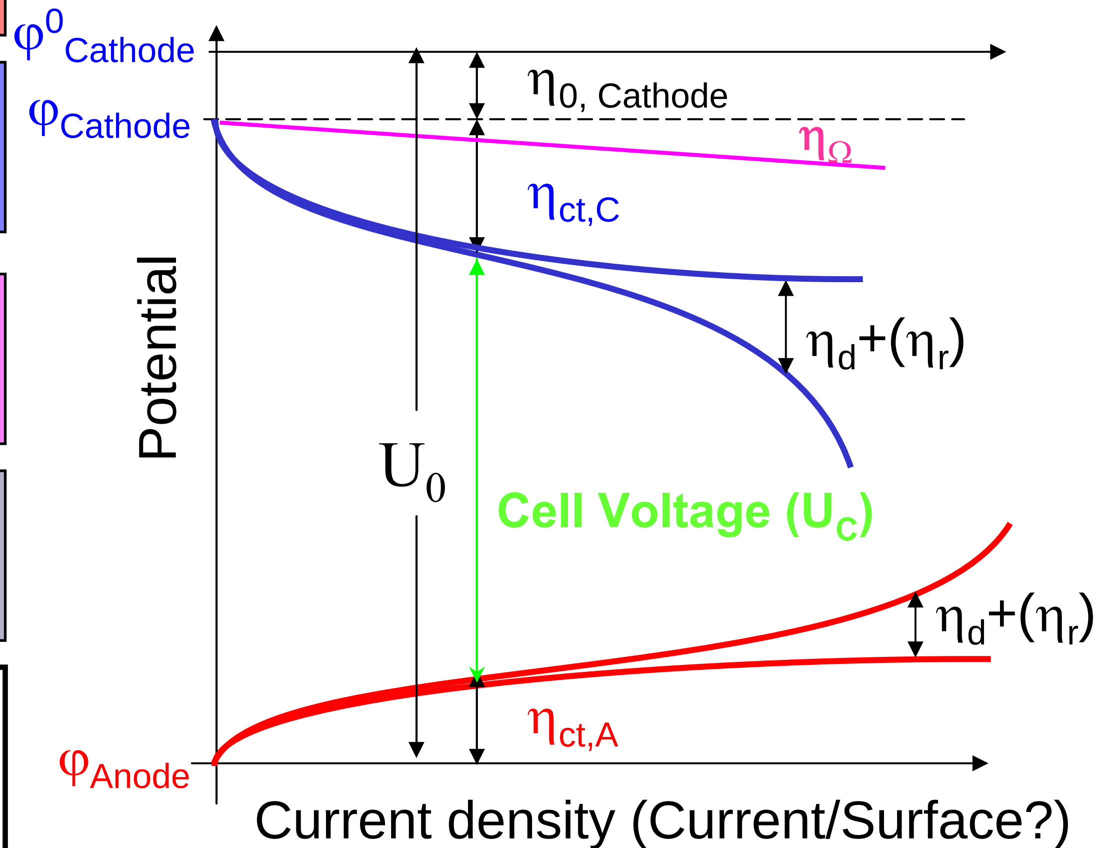
$\eta_\Omega = iR$

Transport limitation (diffusion)

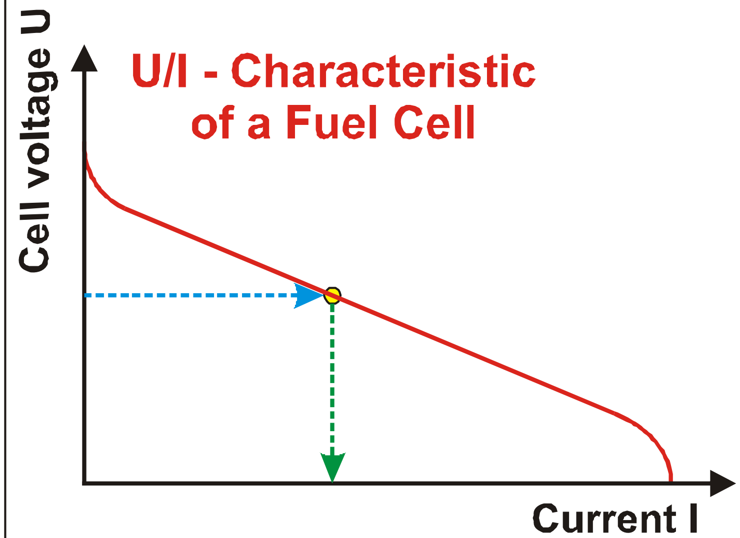
$\eta_d = -RT/2F \ln(1 - i/i_{lim})$

Fuel cell voltage

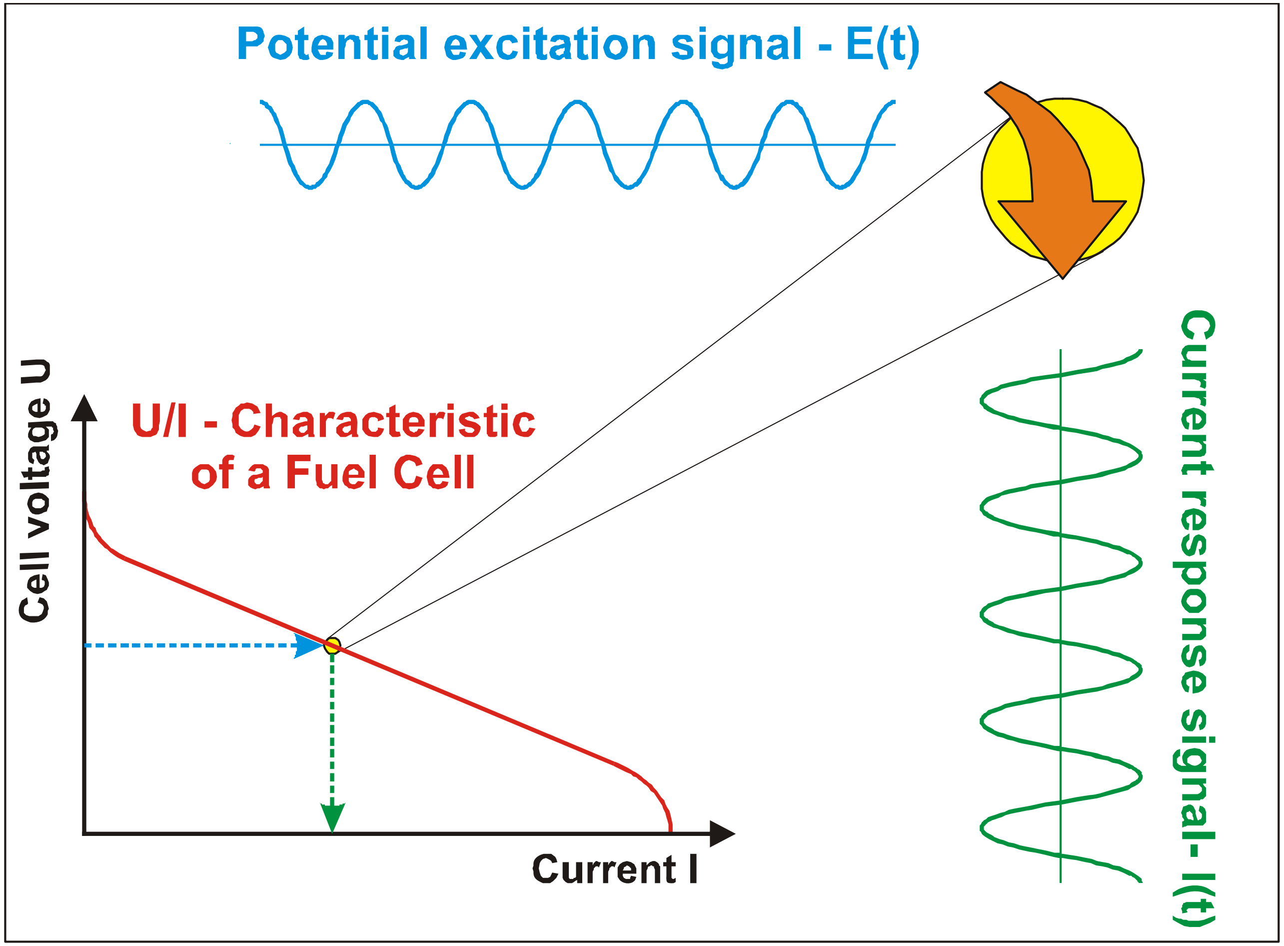
$U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_\Omega$



Electrochemical Impedance Spectroscopy: Application to Fuel Cells

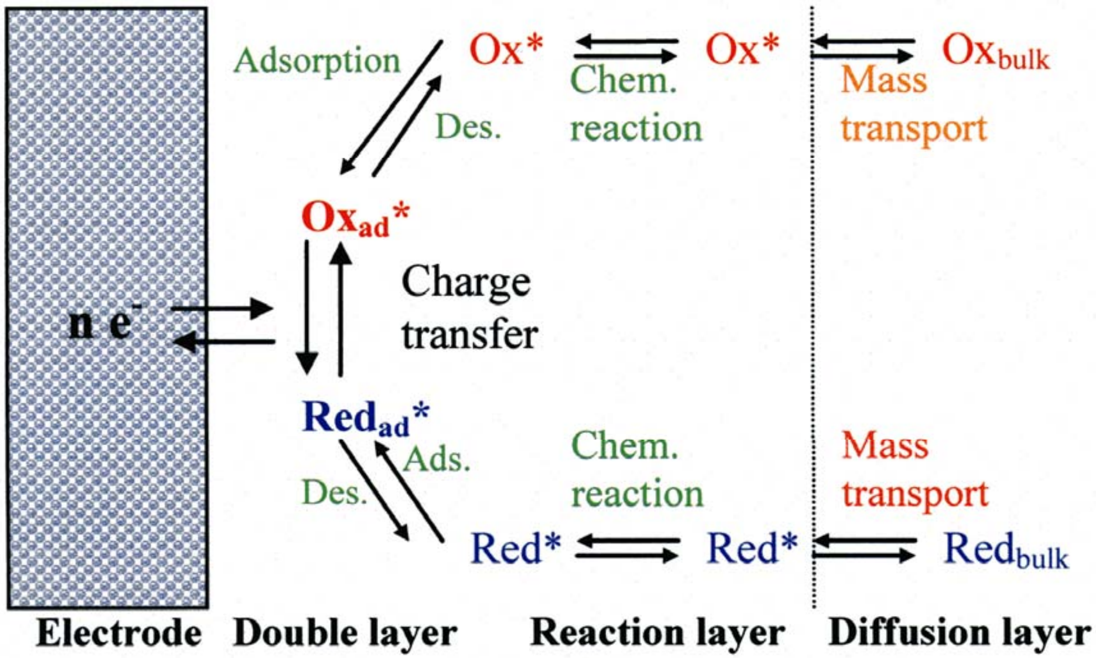


Electrochemical Impedance Spectroscopy: Application to Fuel Cells



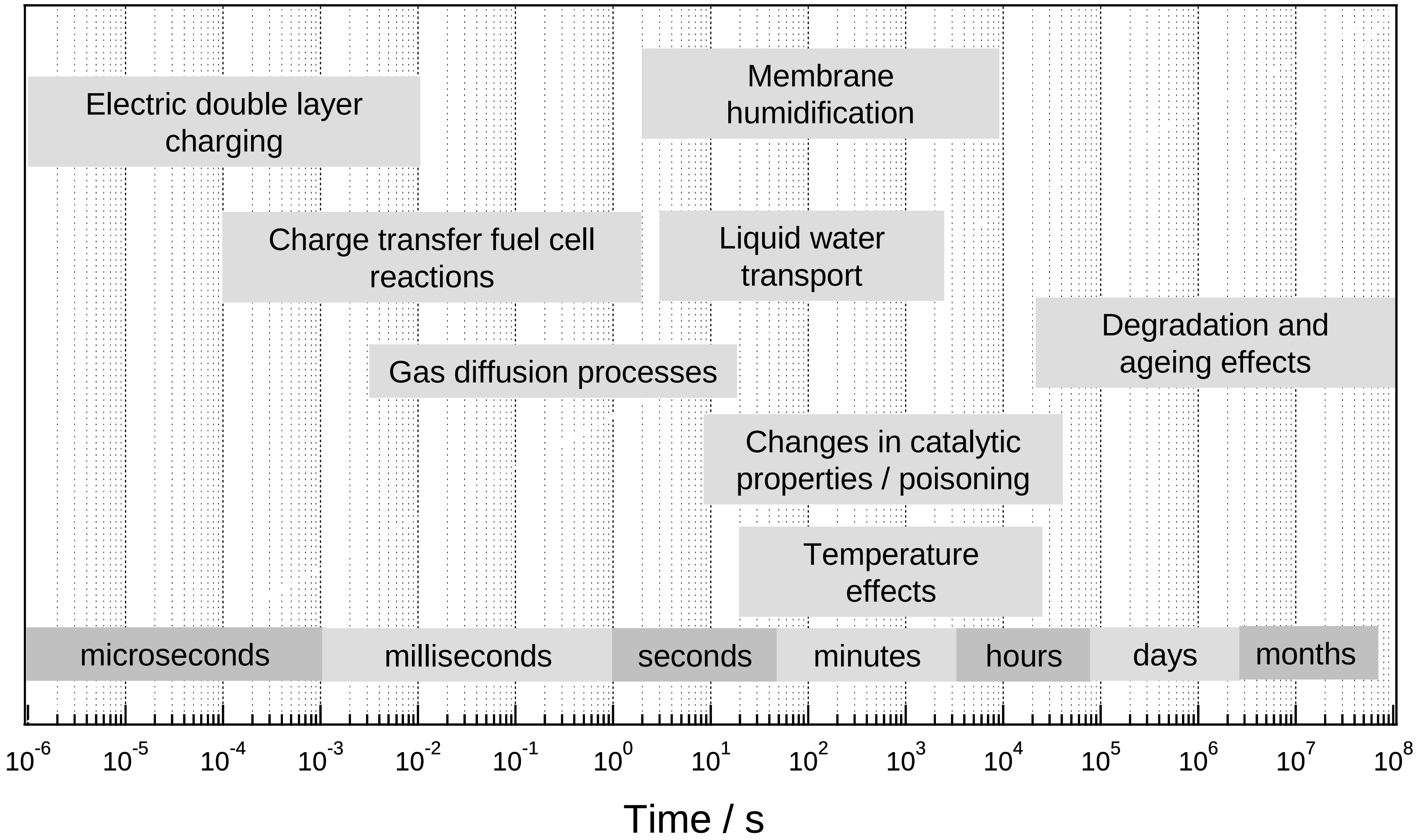
Schematic representation of the different steps and their location during the electrochemical reactions as a function of distance from the electrode surface

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

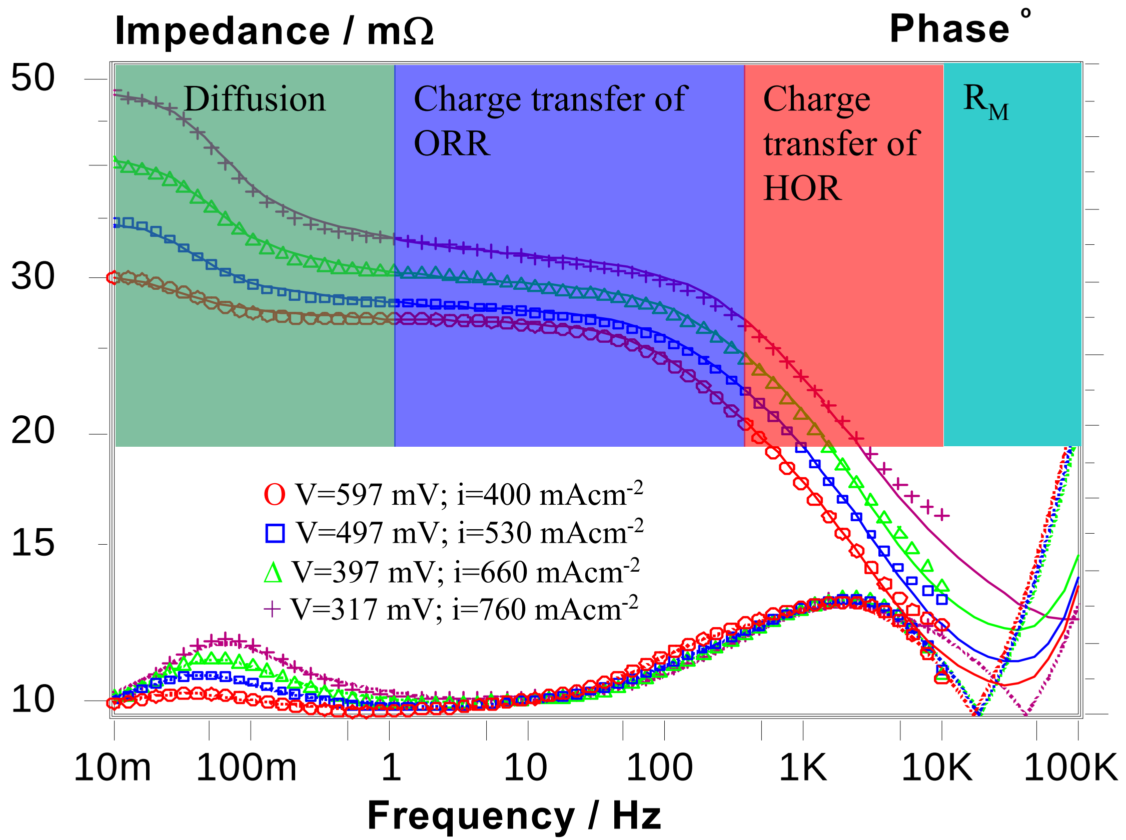


N. Wagner, K.A. Friedrich, *Dynamic Response of Polymer Electrolyte Fuel Cells* in „Encyclopedia of Electrochemical Power Sources“ (Ed. J. Garche et al.), ISBN-978-0-444-52093-7, Elsevier Amsterdam, Vol.2, pp. 912-930, 2009

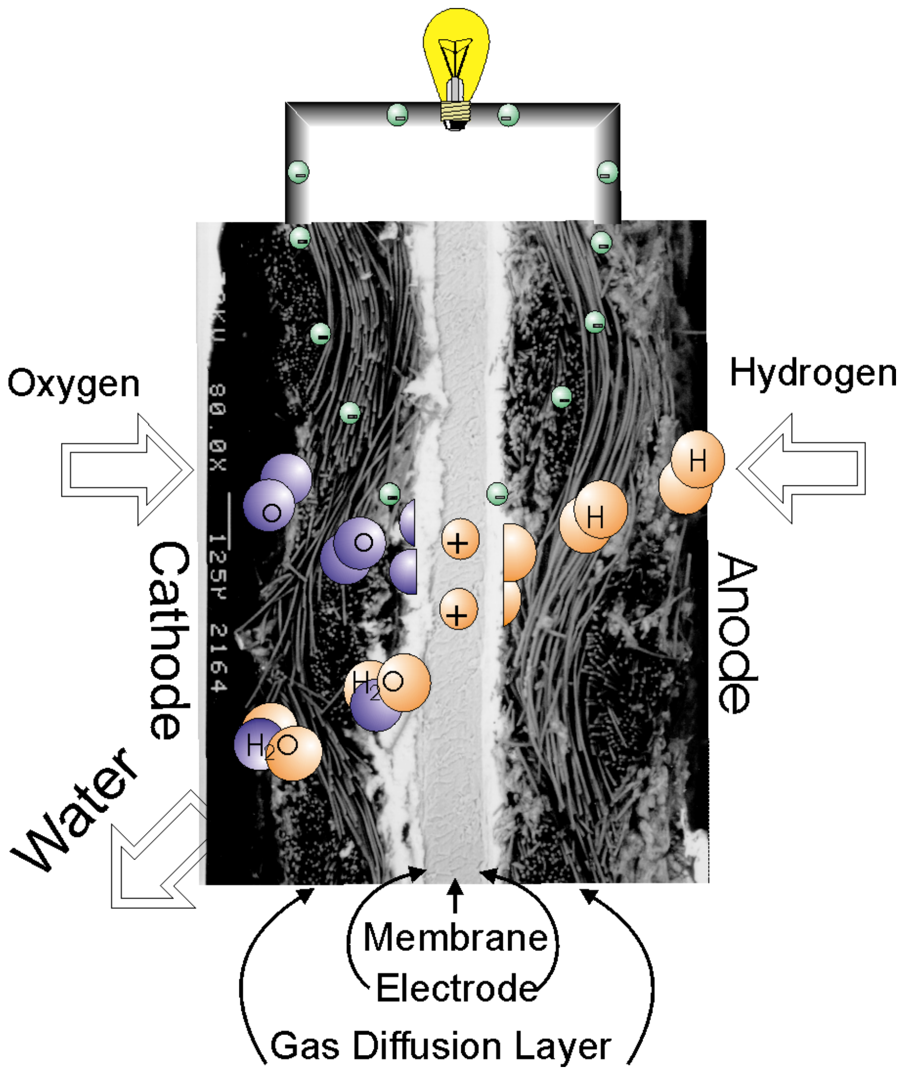
Overview of the wide range of dynamic processes in FC



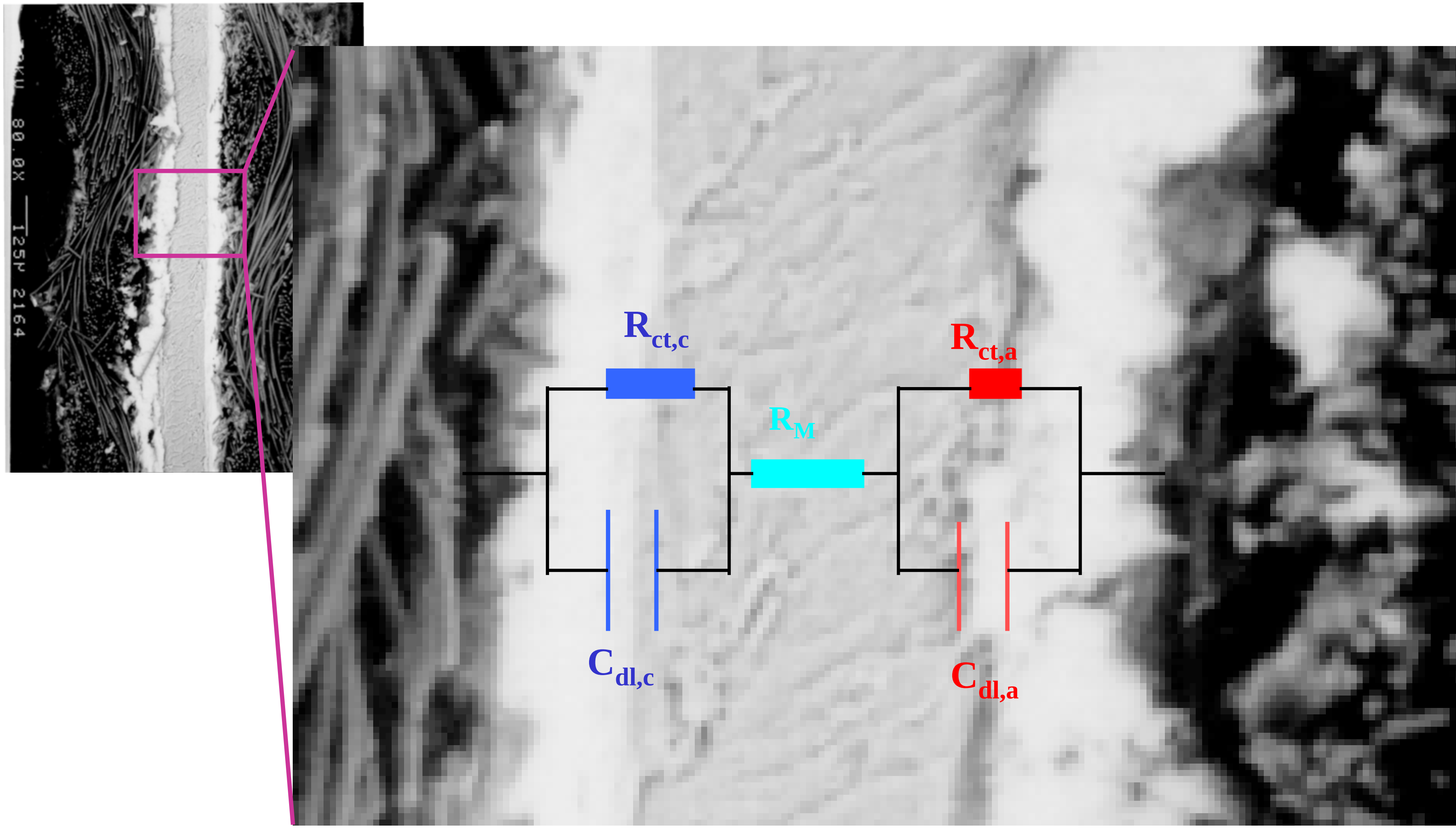
Bode representation of EIS measured at different current densities, PEFC operated at 80°C with H_2 and O_2 at 2 bar



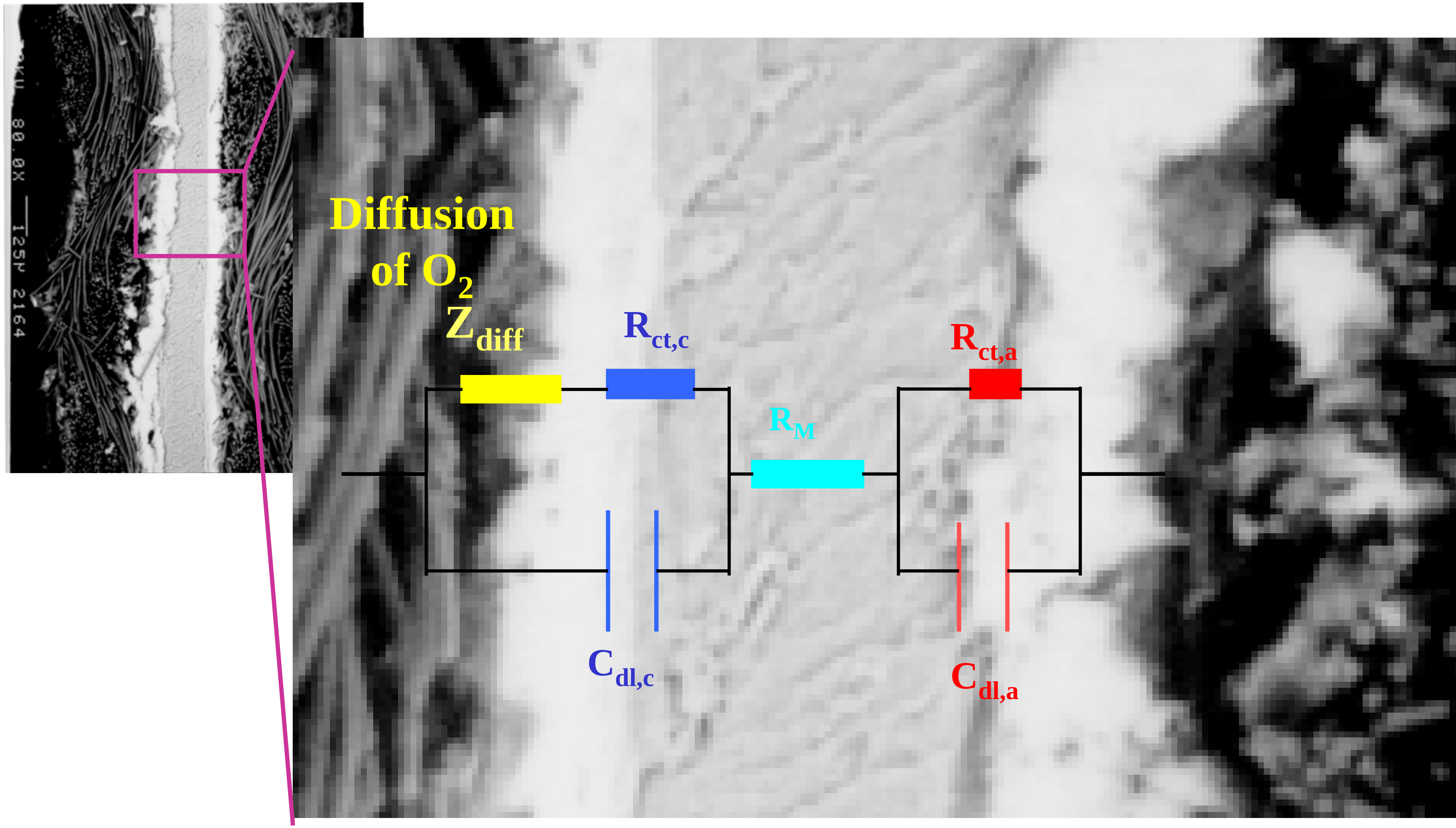
PEFC: Schematic Diagram (cross section)



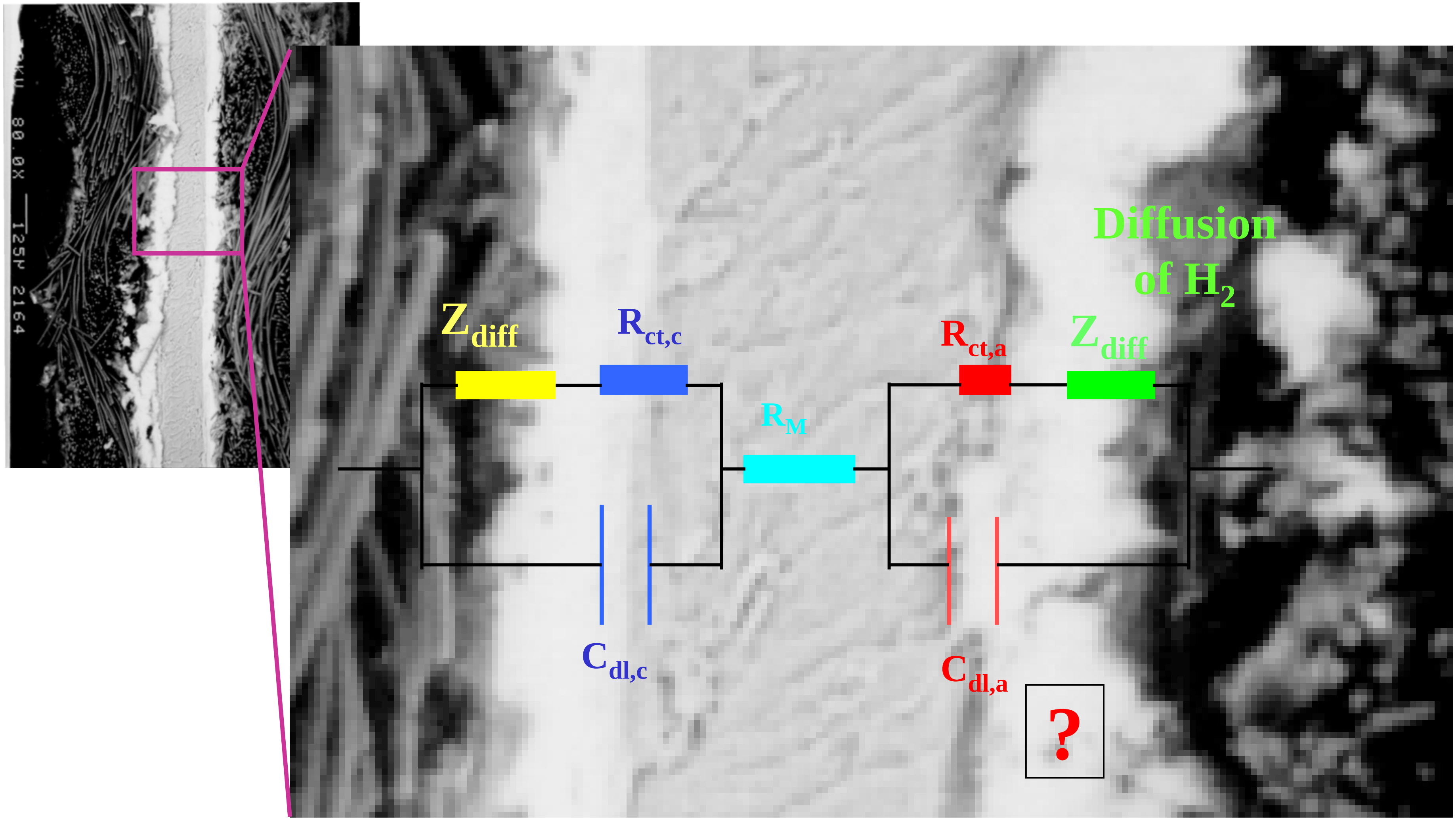
Common Equivalent Circuit for Fuel Cells



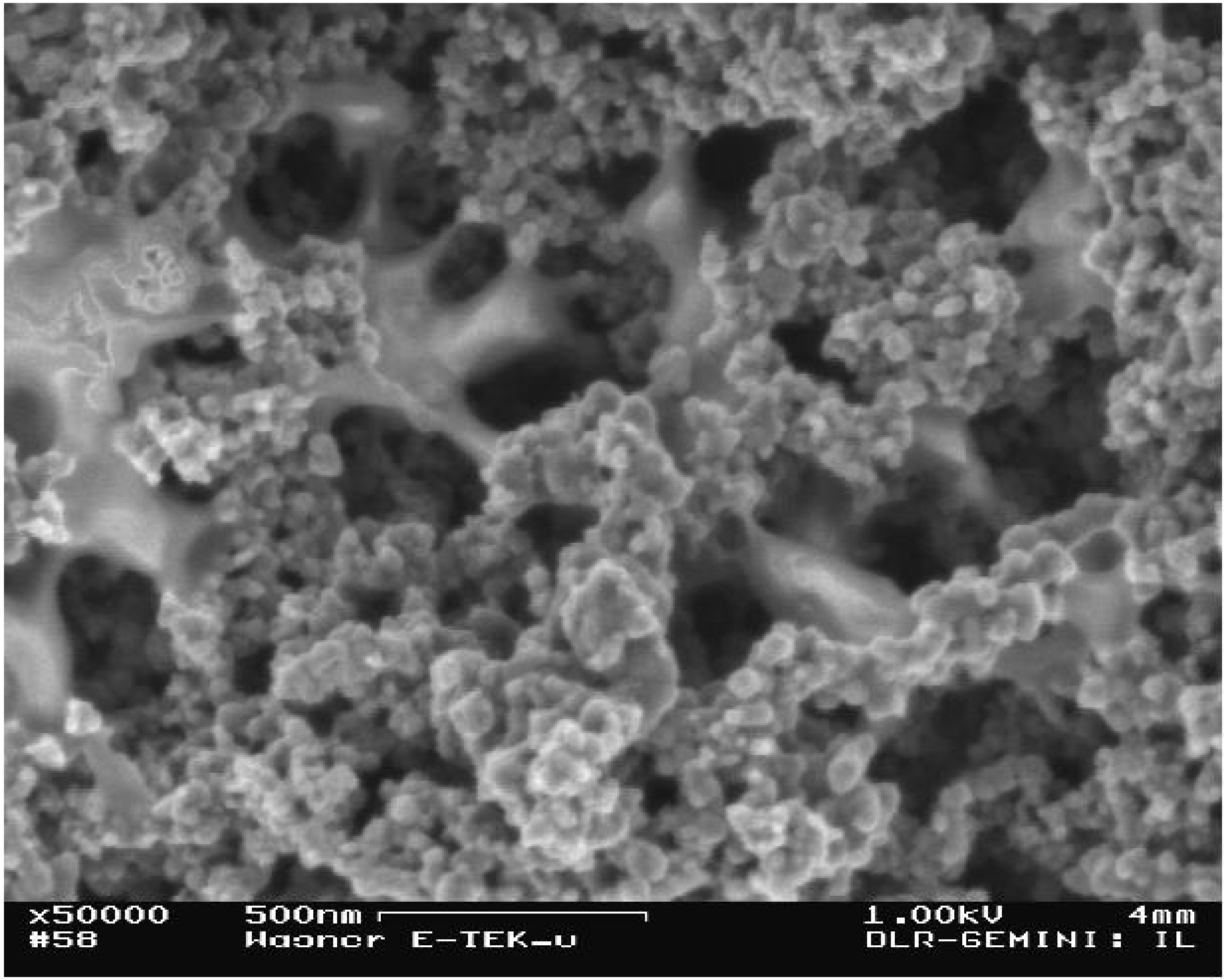
Common Equivalent Circuit for Fuel Cells



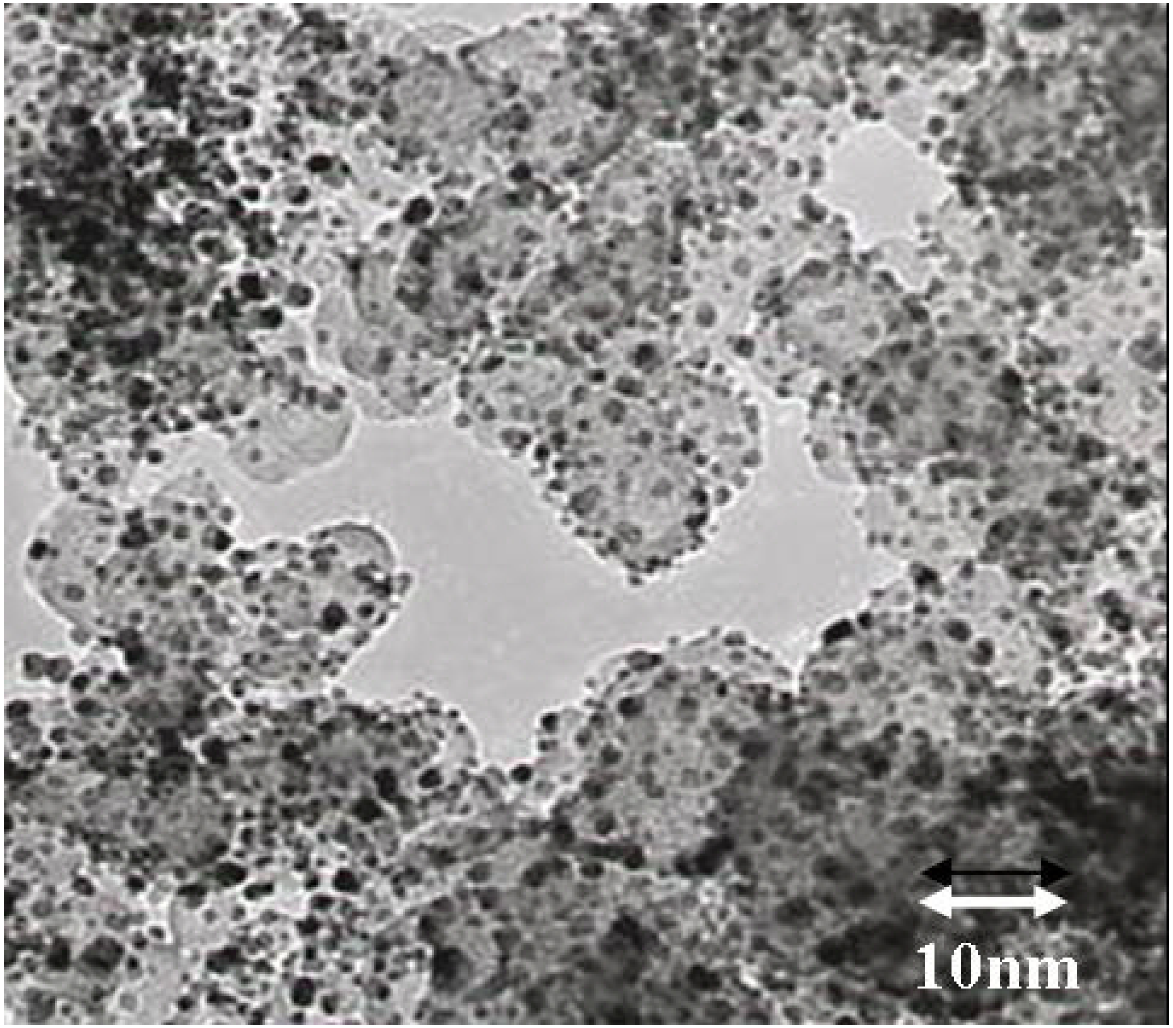
Common Equivalent Circuit for Fuel Cells



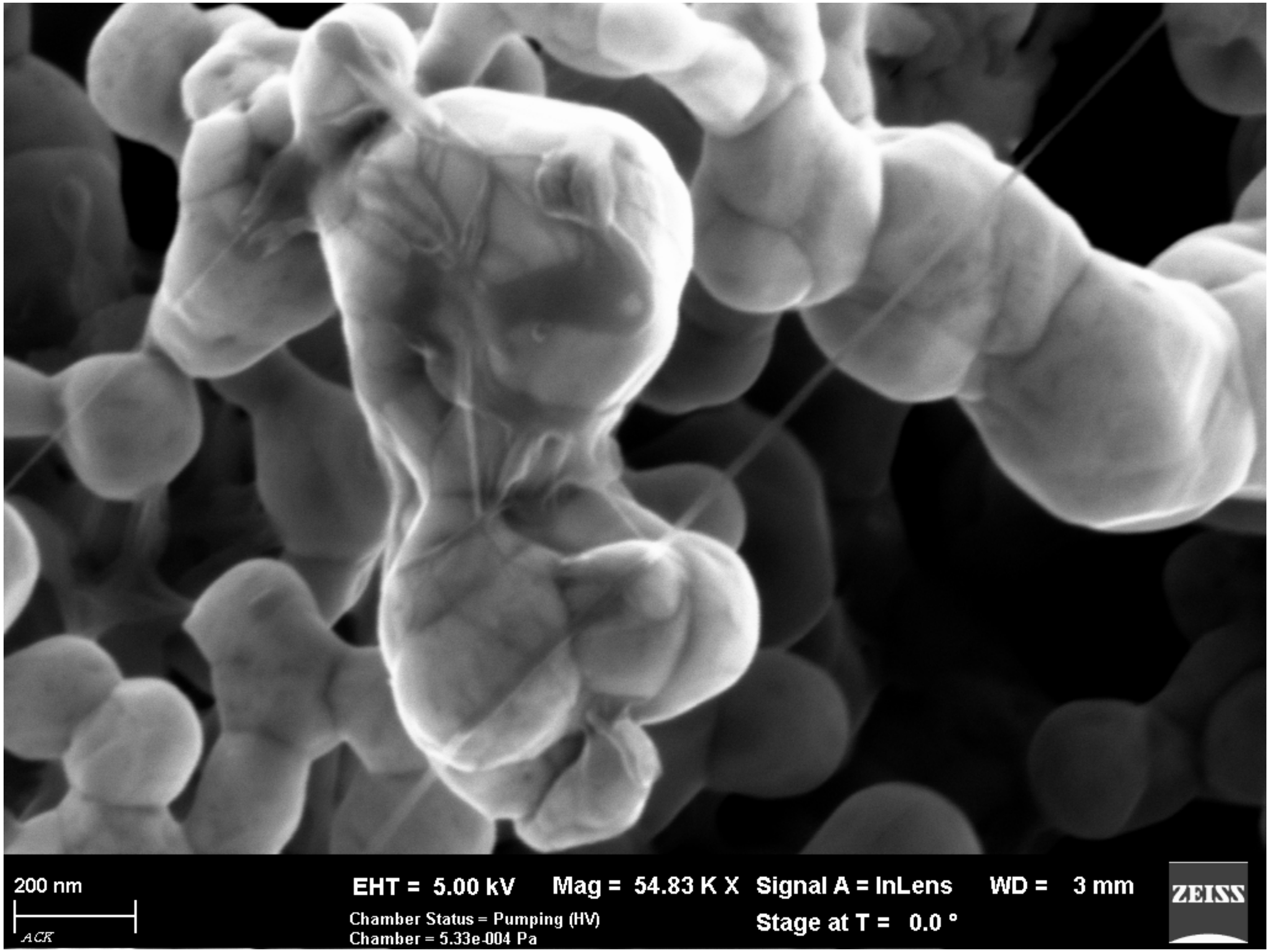
SEM micrograph of PEFC elctrode (Pt/C+PTFE)



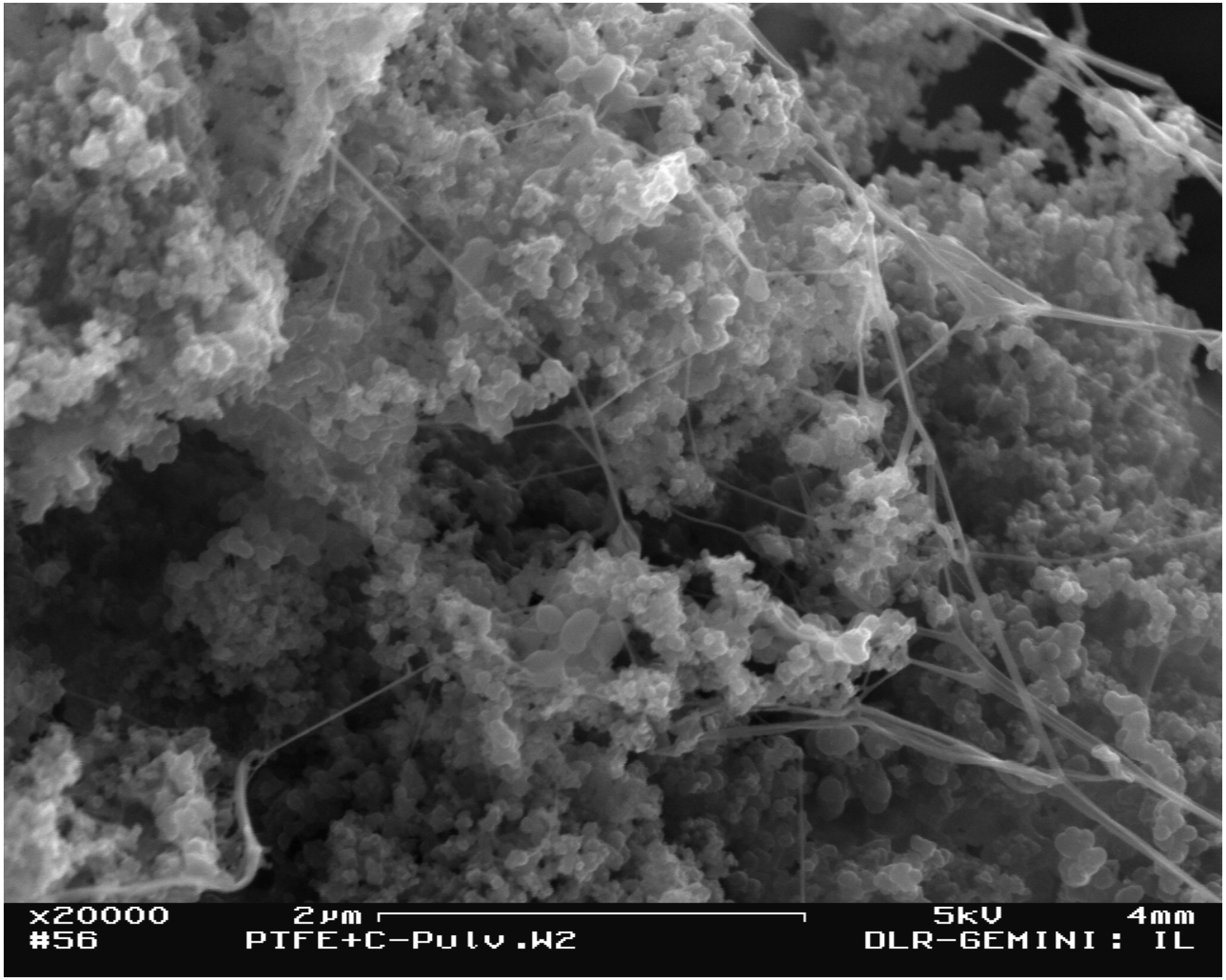
TEM micrograph of Carbon Supported Platinum Catalyst



SEM-picture of Silver-Gas Diffusion Cathode

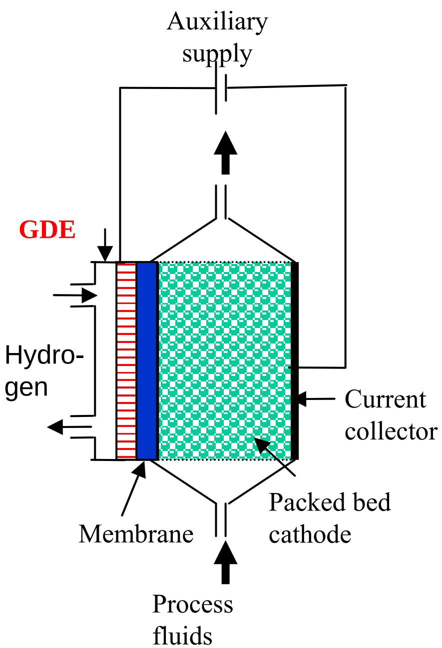


SEM picture of PTFE/C powder



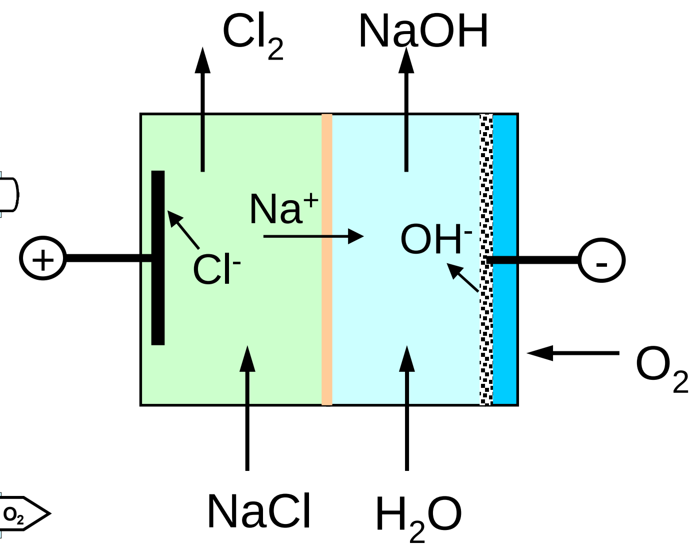
Field of application of porous electrodes

Water purification and treatment
(Bio)-Organic synthesis

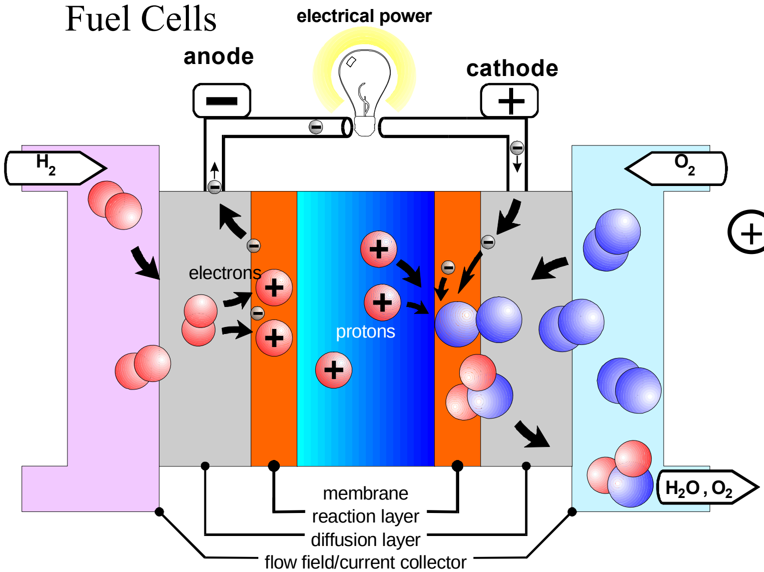


Batteries and supercaps

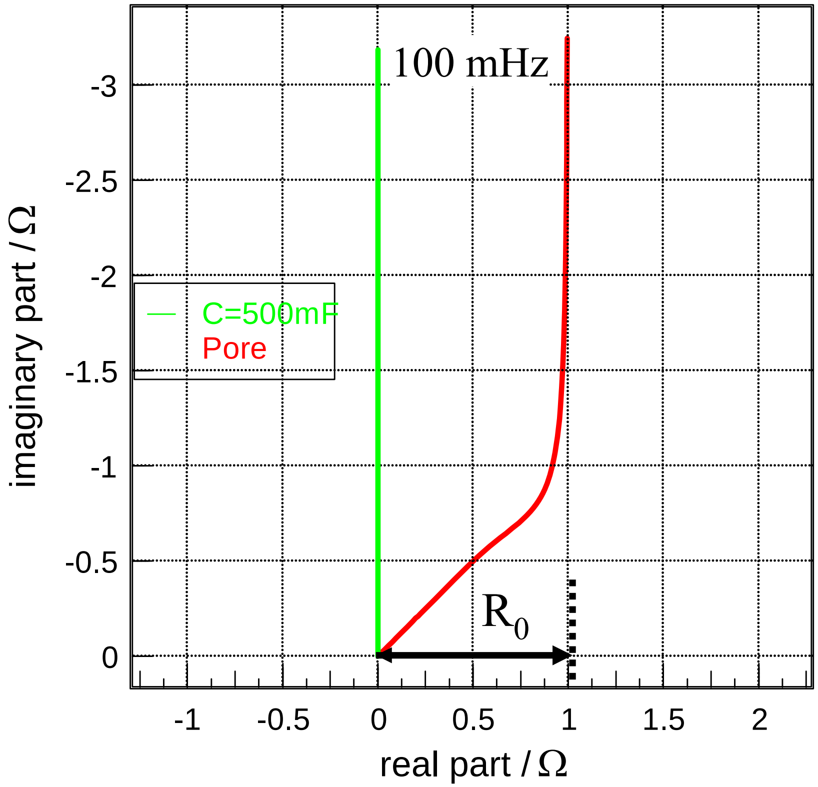
Electrolysis (Water, **NaCl**, HCl, etc.)

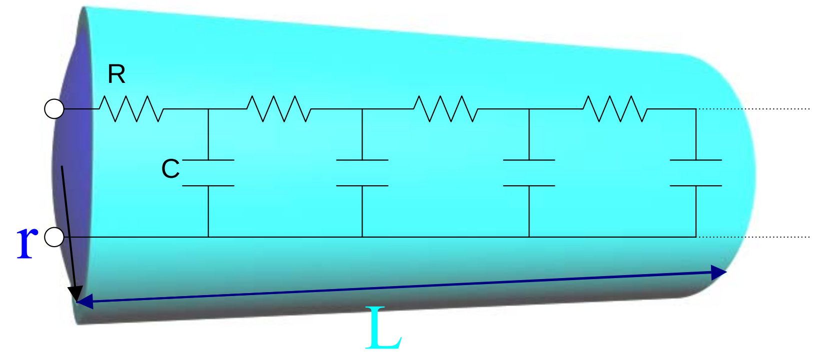


Fuel Cells



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





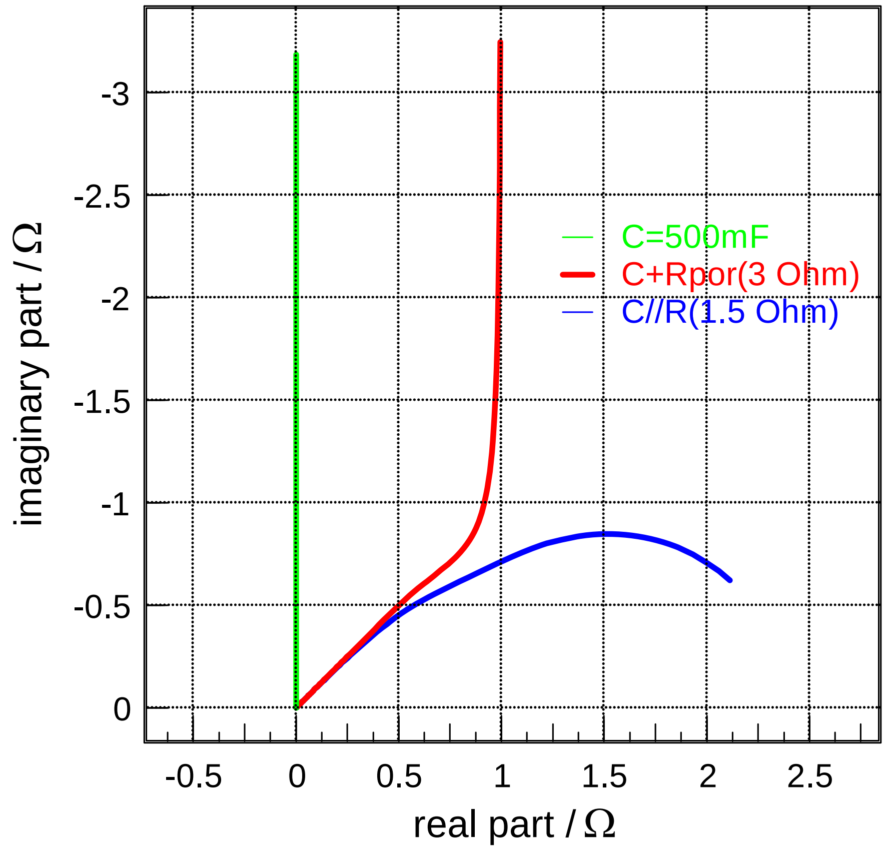
R = 3 Ω
C = 0.5 F

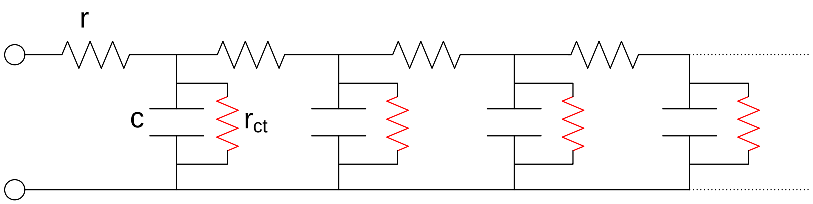
$$Z(i\omega) = \sqrt{\frac{R}{i\omega C}} \coth \sqrt{i\omega RC}$$

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

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

Nyquist representation of porous electrode impedance with faradaic impedance element





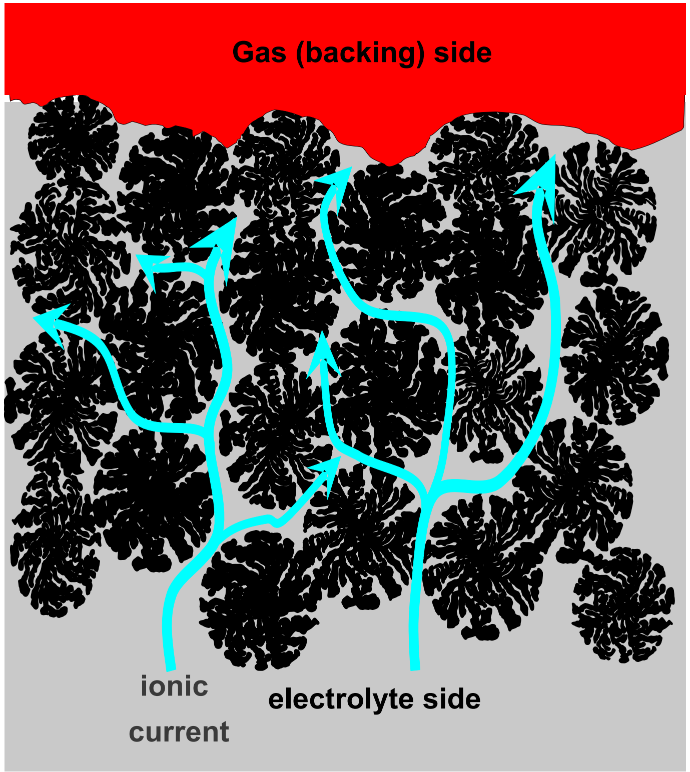
$r = 3\ \Omega$

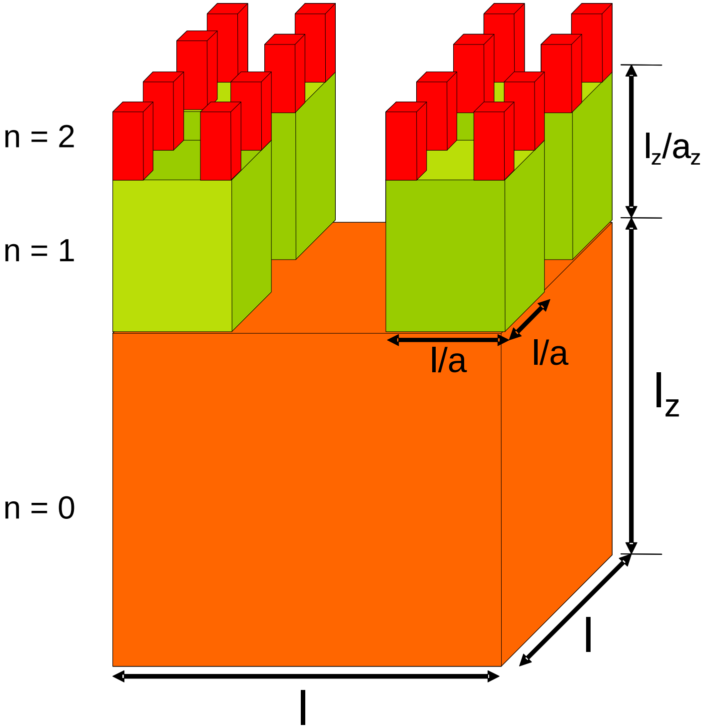
$c = 500\ \mathrm{mF}$

$r_{ct} = 1.5\ \Omega$

Agglomerated Electrodes

Hierarchical model (Cantor-block model)





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

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

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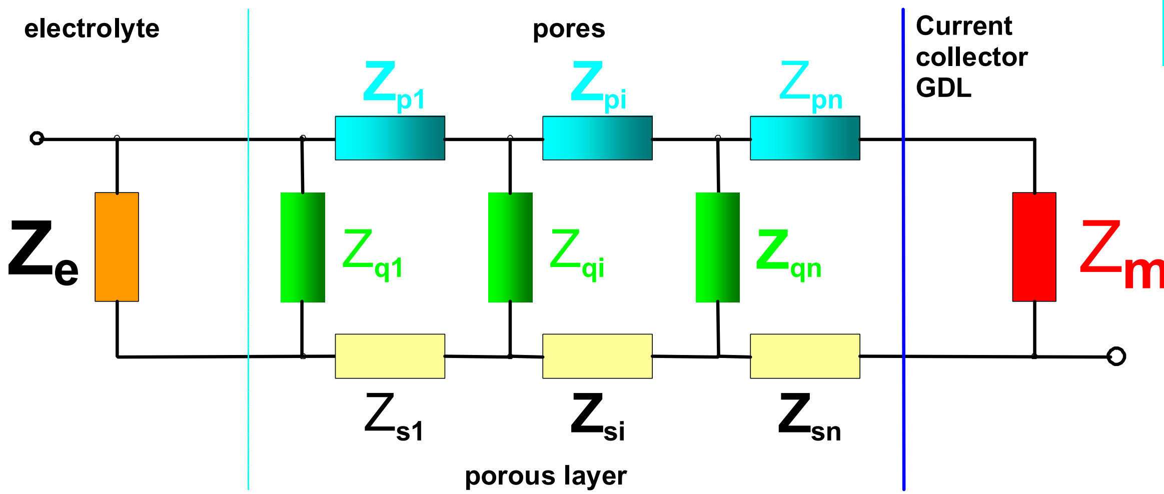
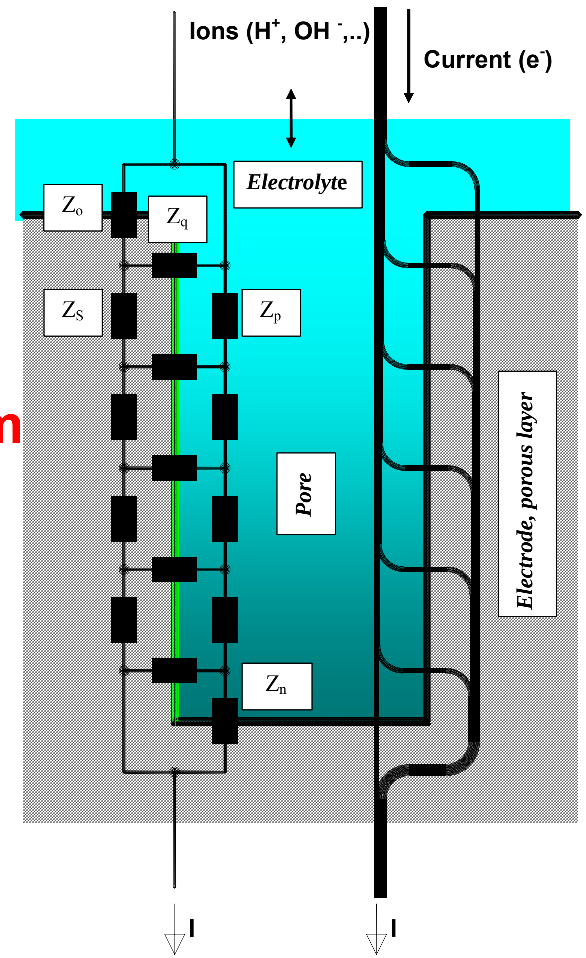
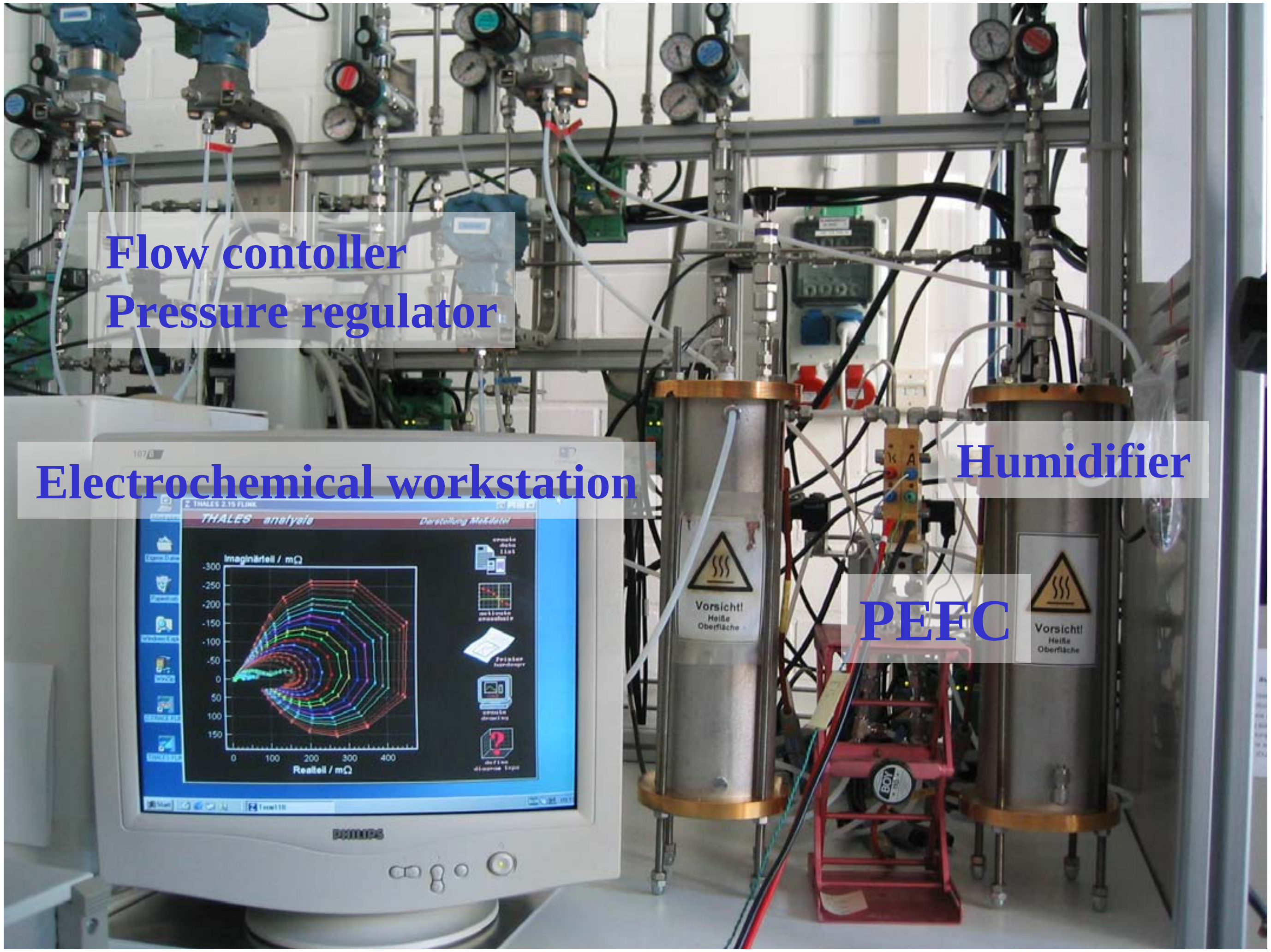
Cylindrical homogeneous porous electrode model (H. Göhr)



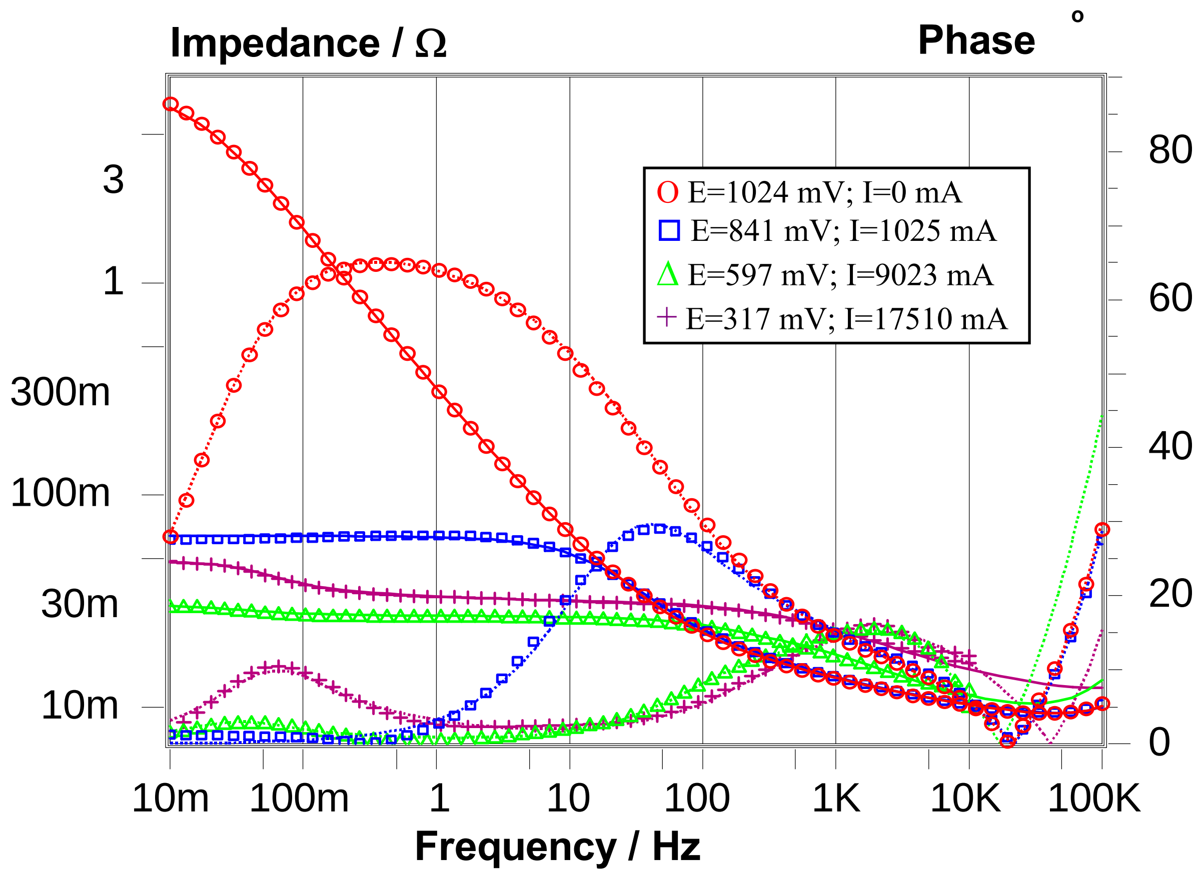


H. Göhr in *Electrochemical Applications/97*, www.zahner.de

Electrochemical Impedance Spectroscopy: Experimental Set-up

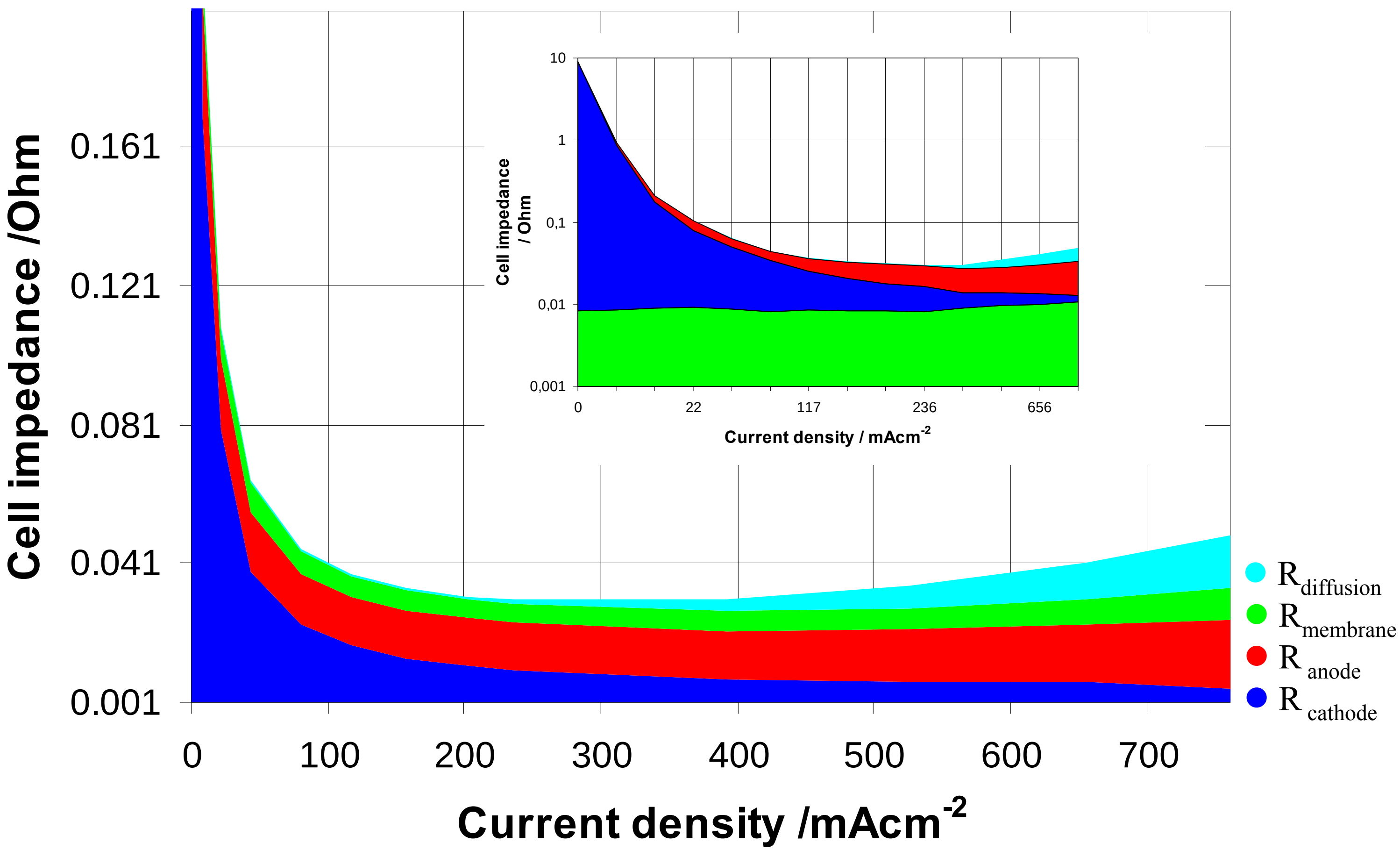


Bode diagram of measured EIS at different cell voltages



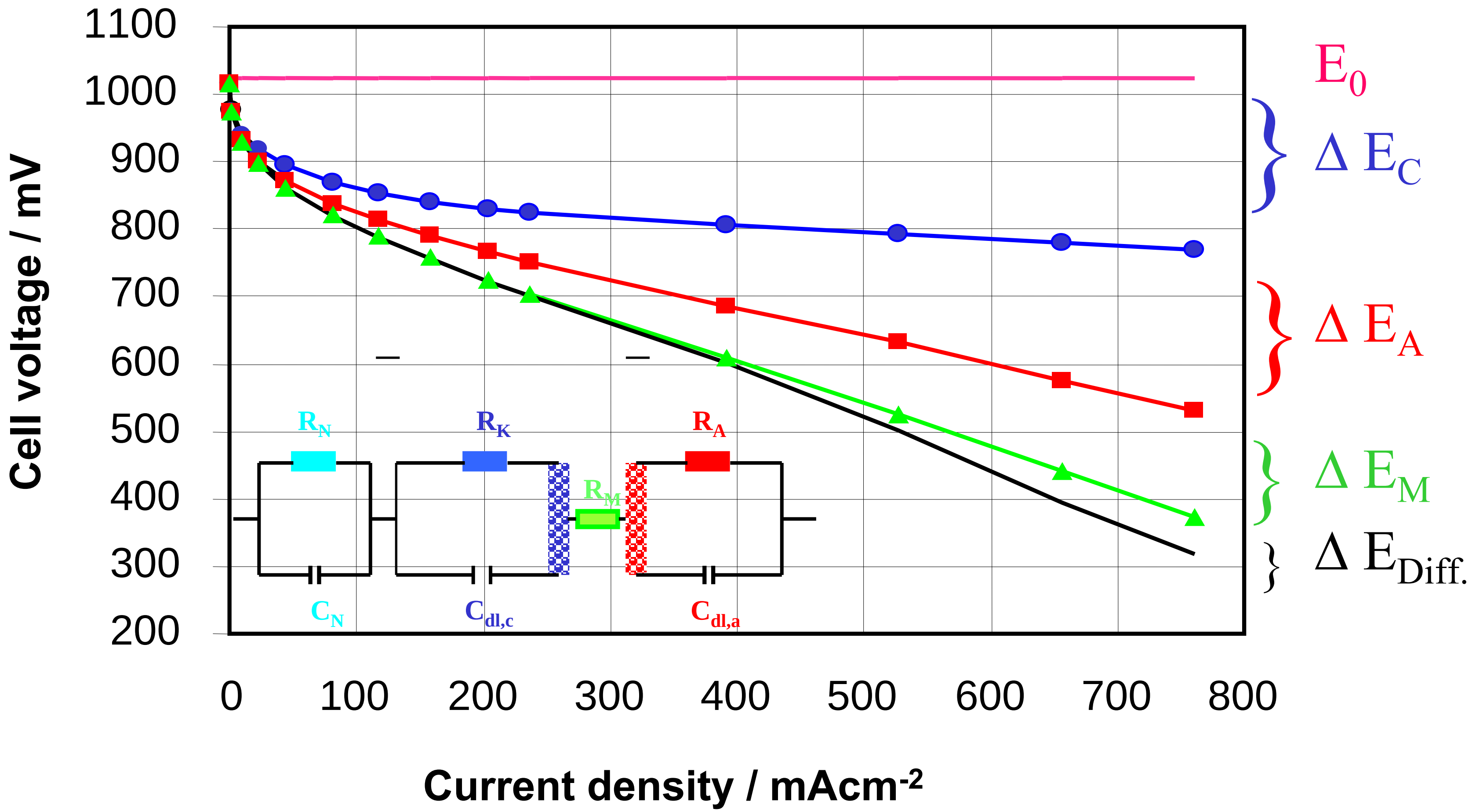
EIS at Polymer Fuel Cells (PEFC):

Contributions to the cell impedance at different current densities



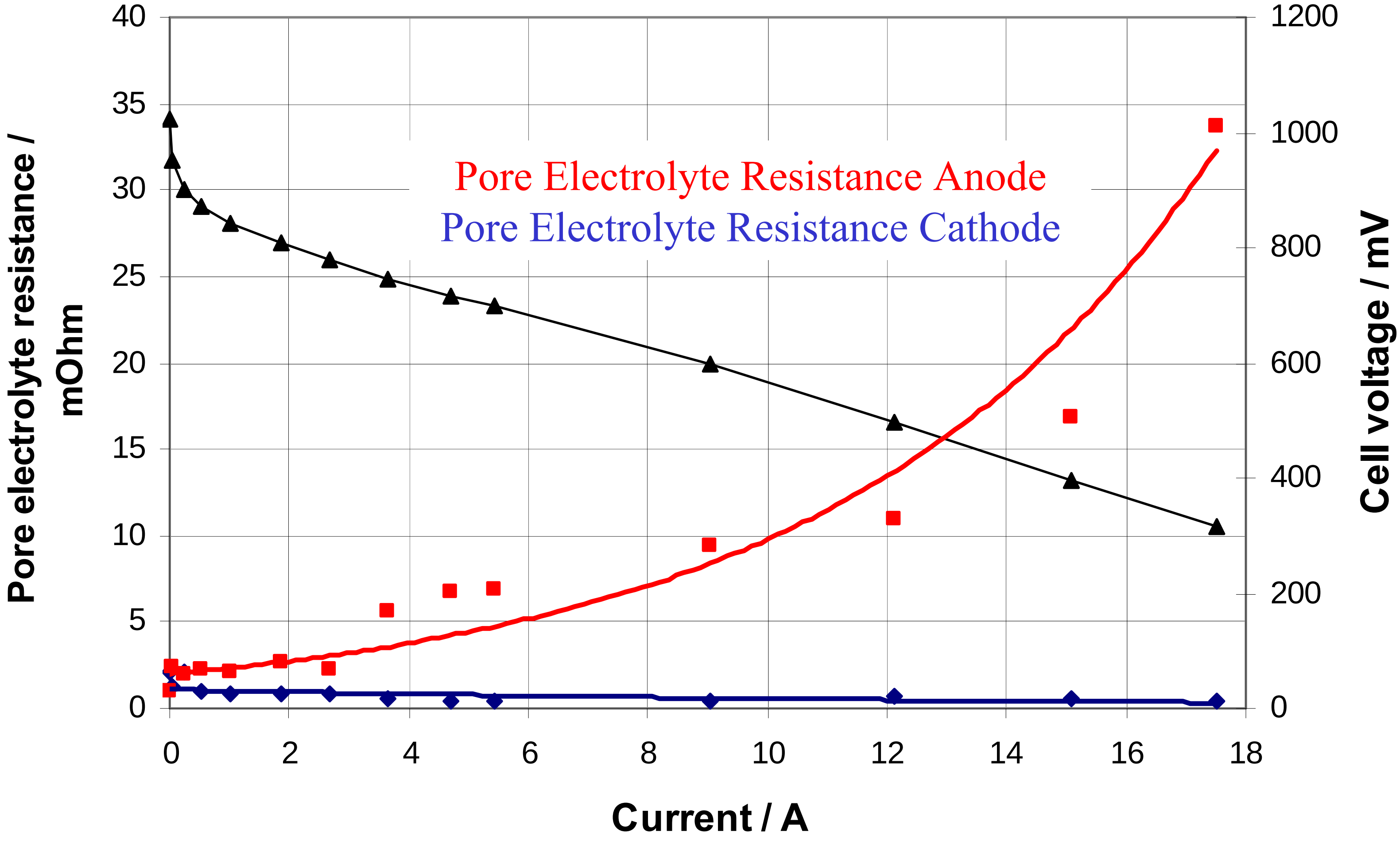
EIS at Polymer Fuel Cells (PEFC):

Contributions to the overal U-i characteristic determined by EIS

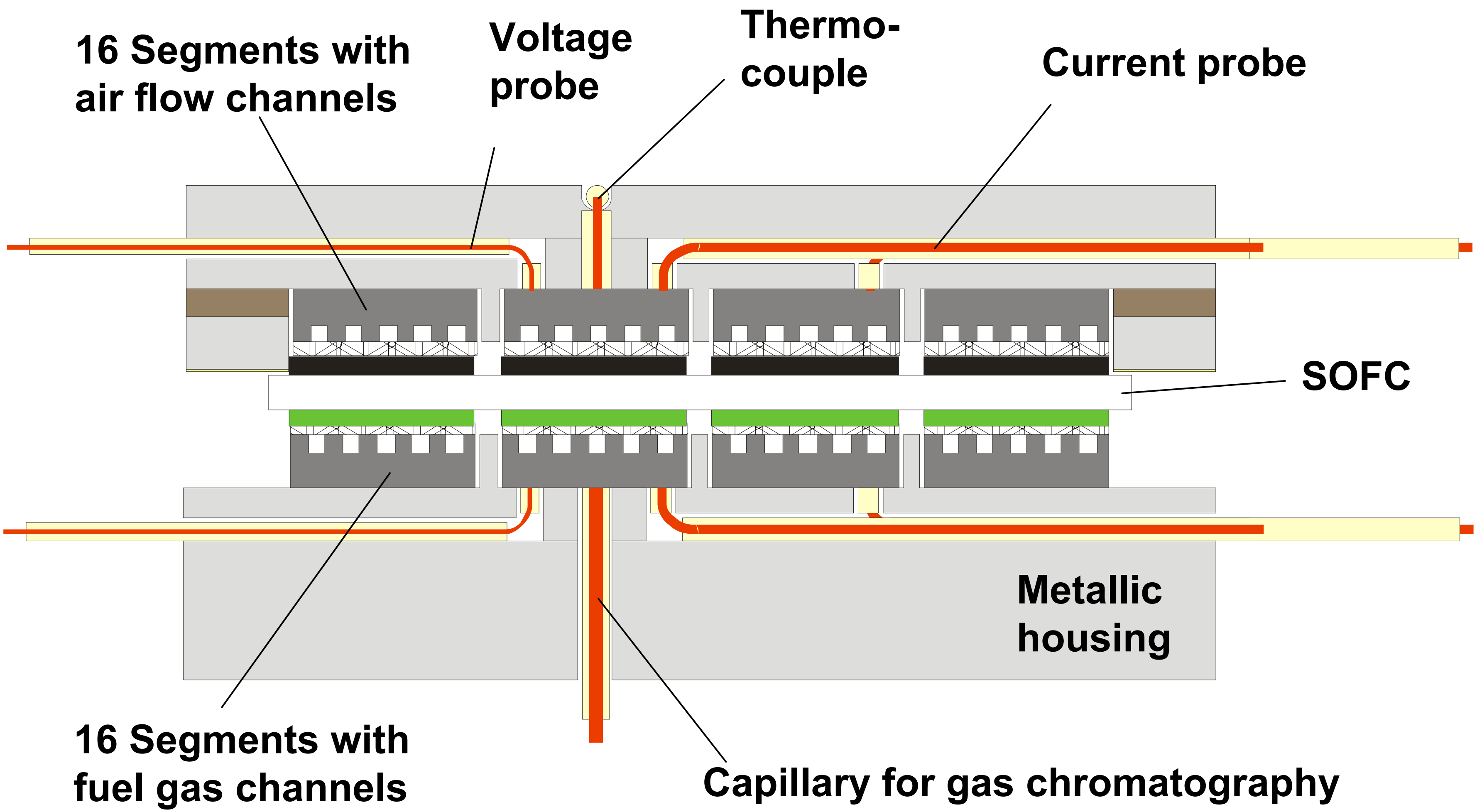


Evaluation of EIS with the porous electrode model

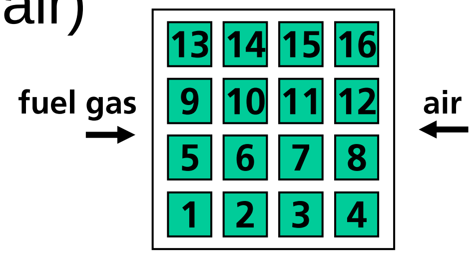
Summary of current density dependency of pore resistance elements



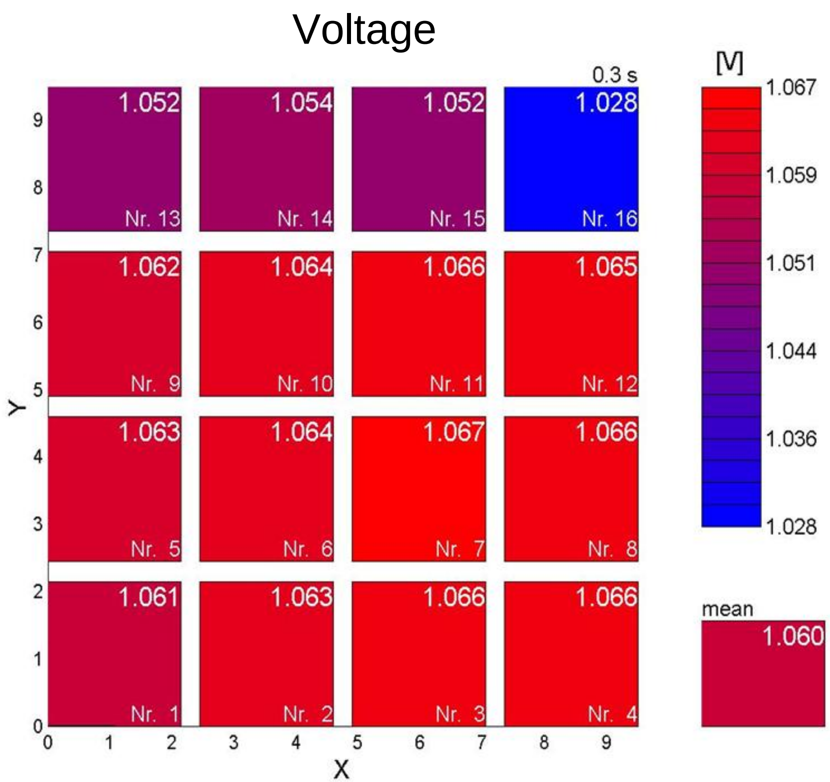
Segmented SOFC cell design with segmented bipolar plates



OCV distribution of ASC at 800°C and simulated reformate ($50\%\ H_2 + 50\%\ N_2 + 3\%\ H_2O$, 0.08 SlpM/cm² air)



Fuel gas



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%,

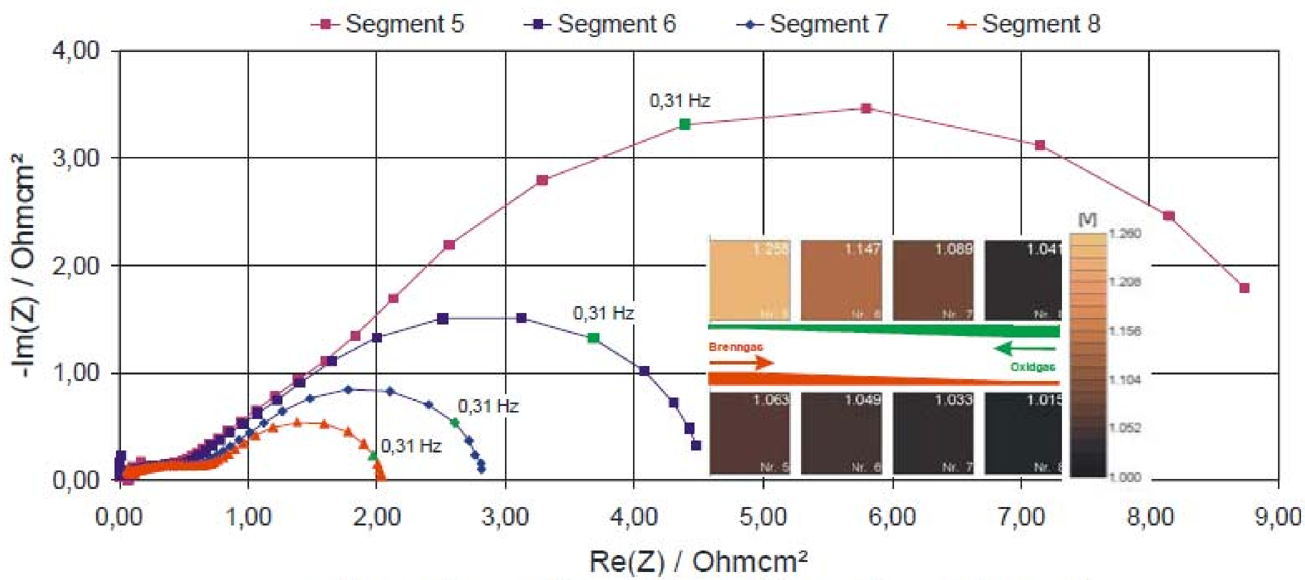
S12: 0.78%,

S16: 3.30%

EIS at OCV, ASC with segmented cathode, 77.44 cm²

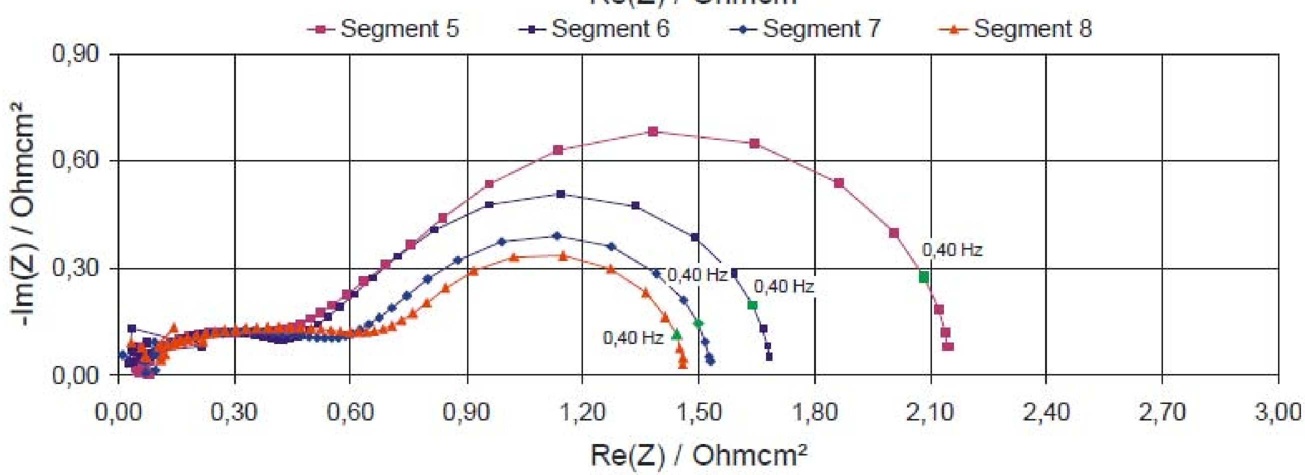
a)

Dry hydrogen



b)

Hydrogen+ 3% H_2O



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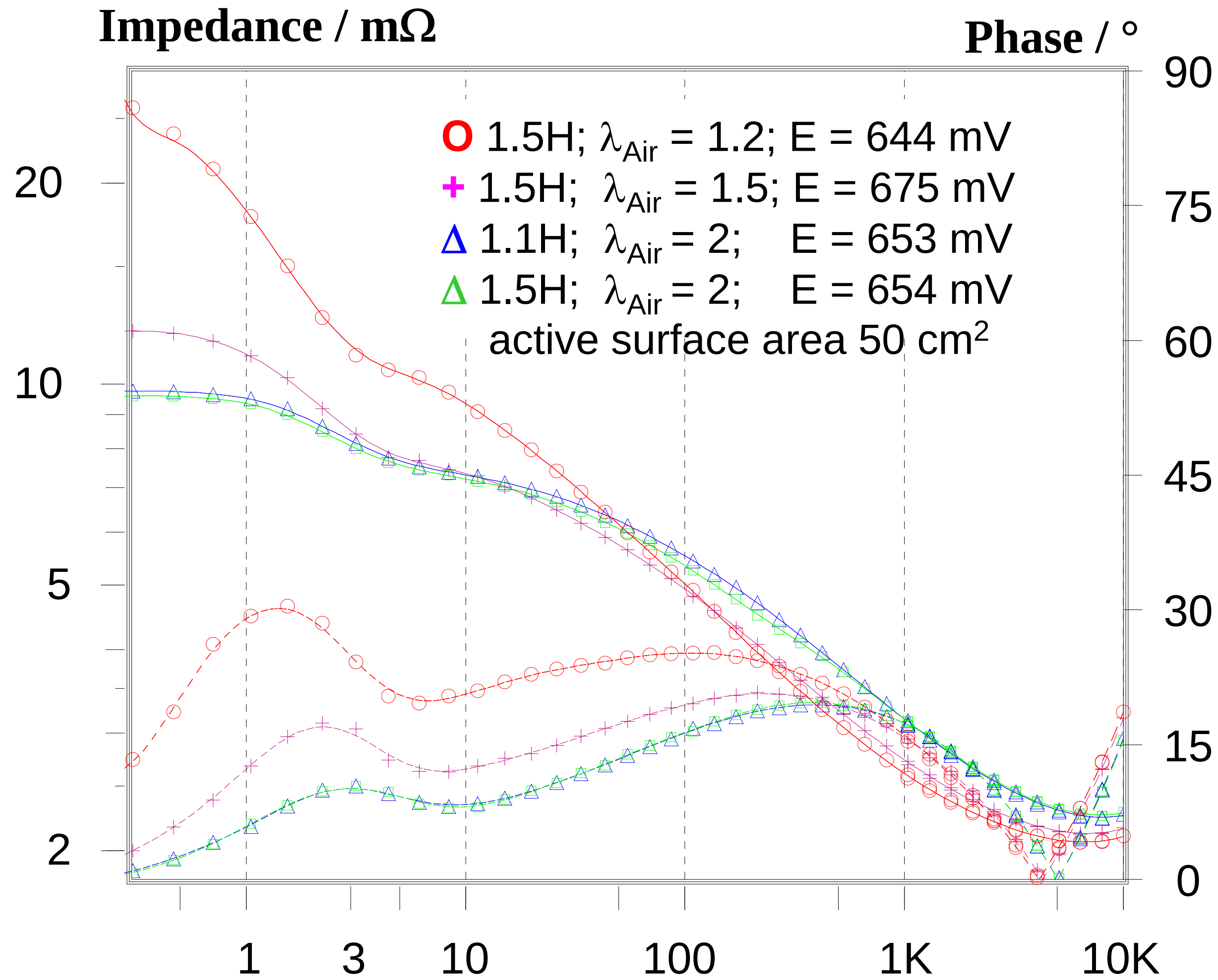
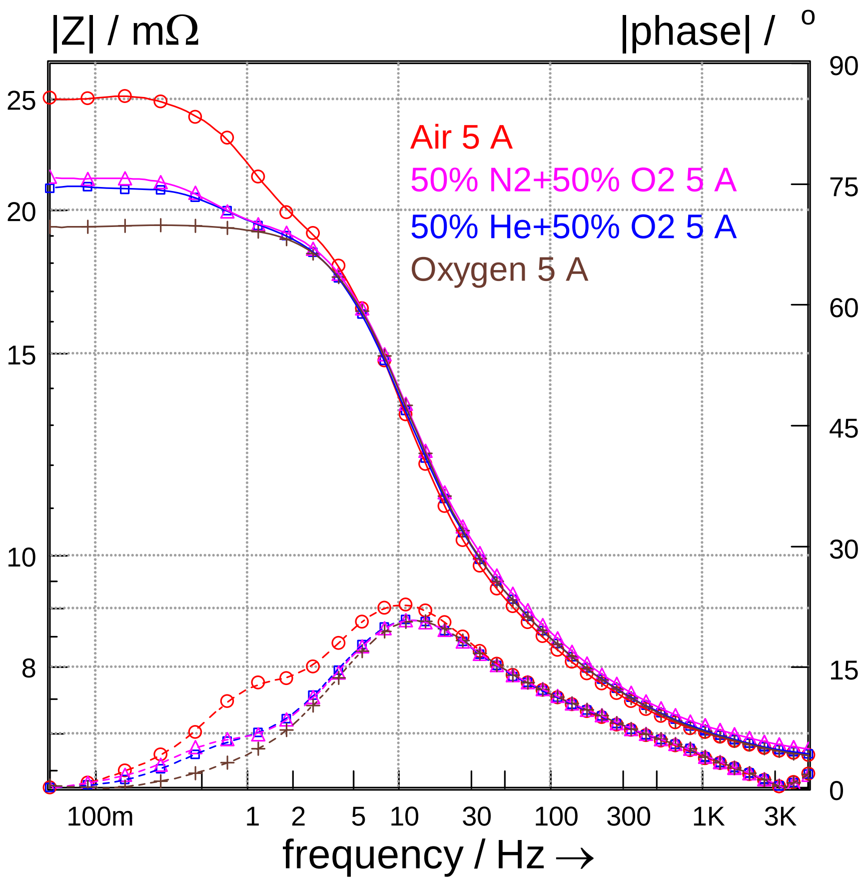
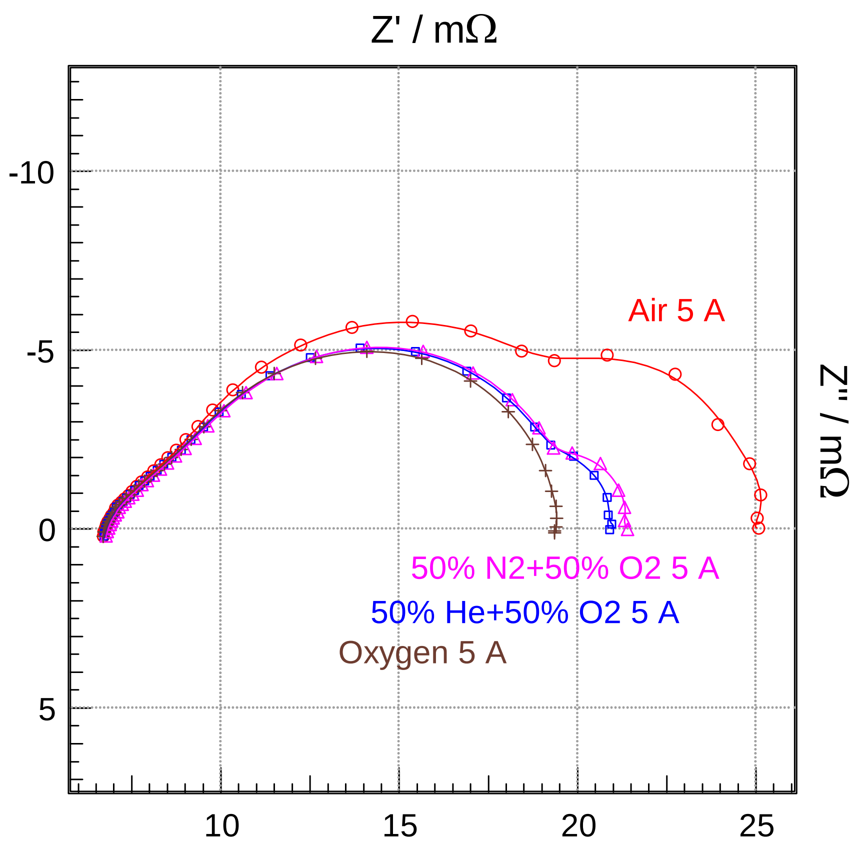
Bode Diagram of EIS, measured at PEFC, 75°C, 0.5 Acm^{-2}
Variation of gas flow rates



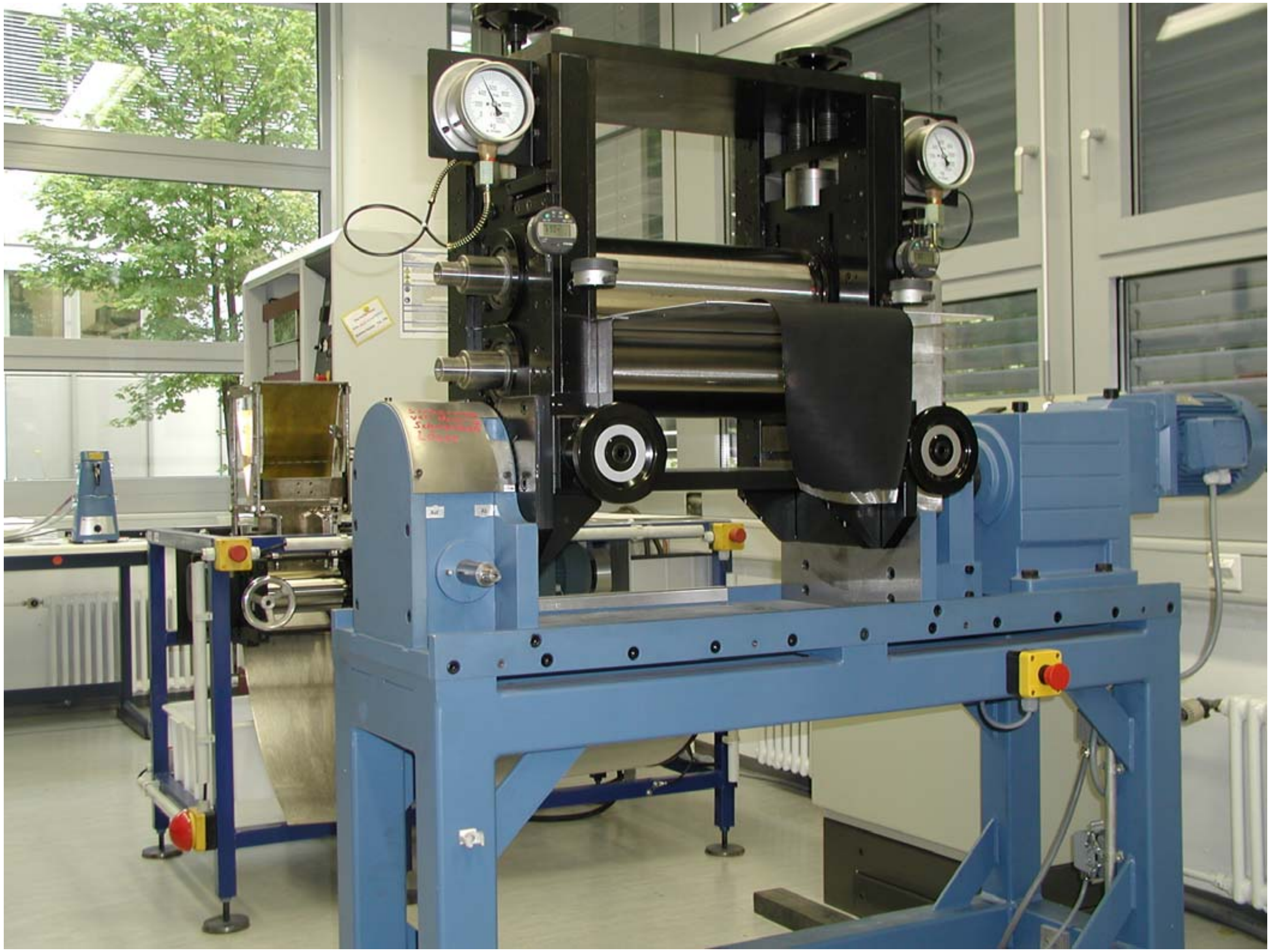
EIS on PEFC, 80°C, 5 A, cathode fed with different gas composition, λ=1.5, N111 IP CCM (Ion Power Inc.)





Reactive Mixing and Rolling (RMR)

GDE Production Technique for AFC Electrodes



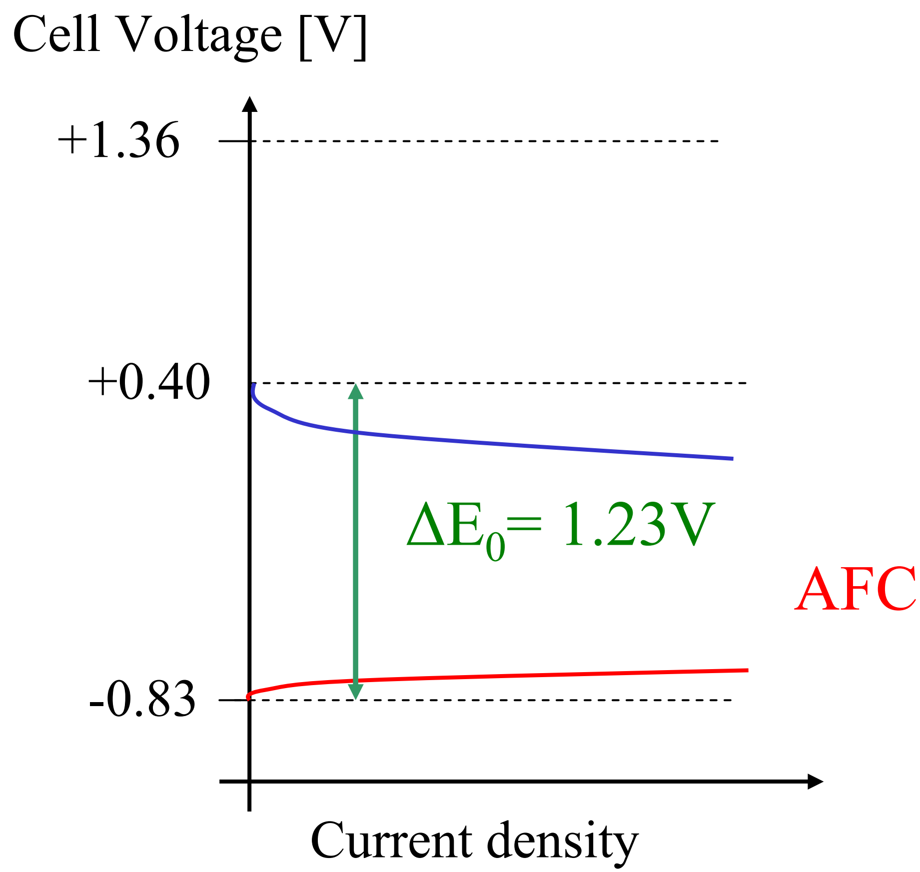
Schematically representation of cell voltage and potentials in an alkaline fuel cell

Cathode with ORR

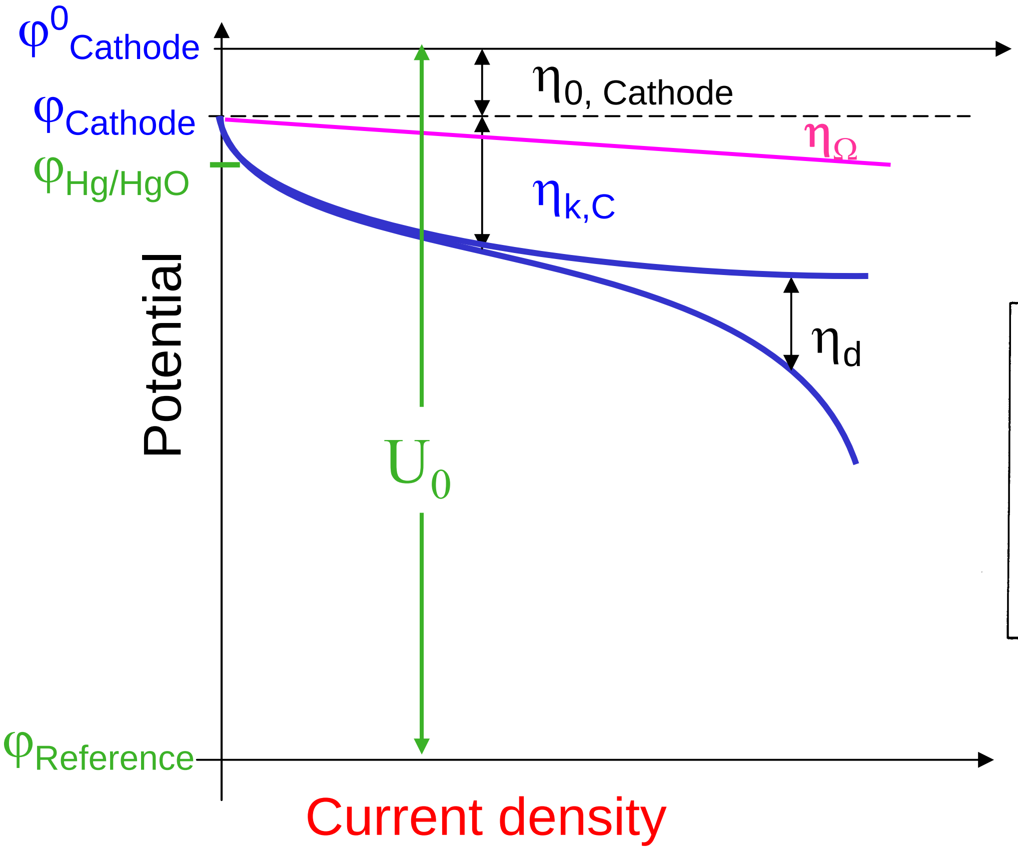
$O_2 + 2\ H_2O + 4\ e^- \rightarrow 4\ OH^-$

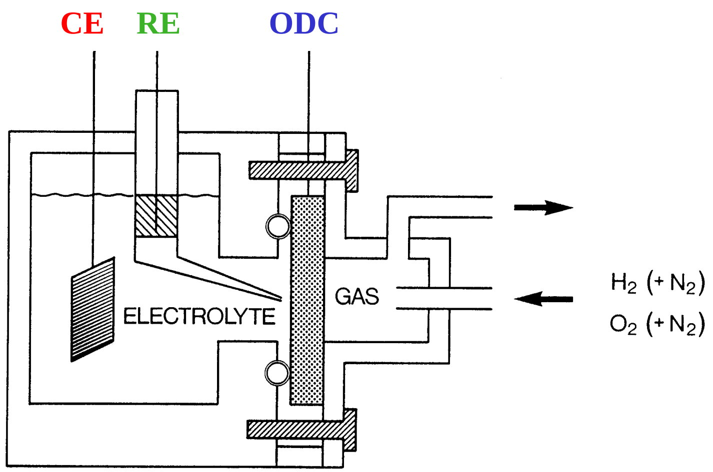
Anode

$2\ H_2 + 4\ OH^- \rightarrow 4\ H_2O + 4\ e^-$

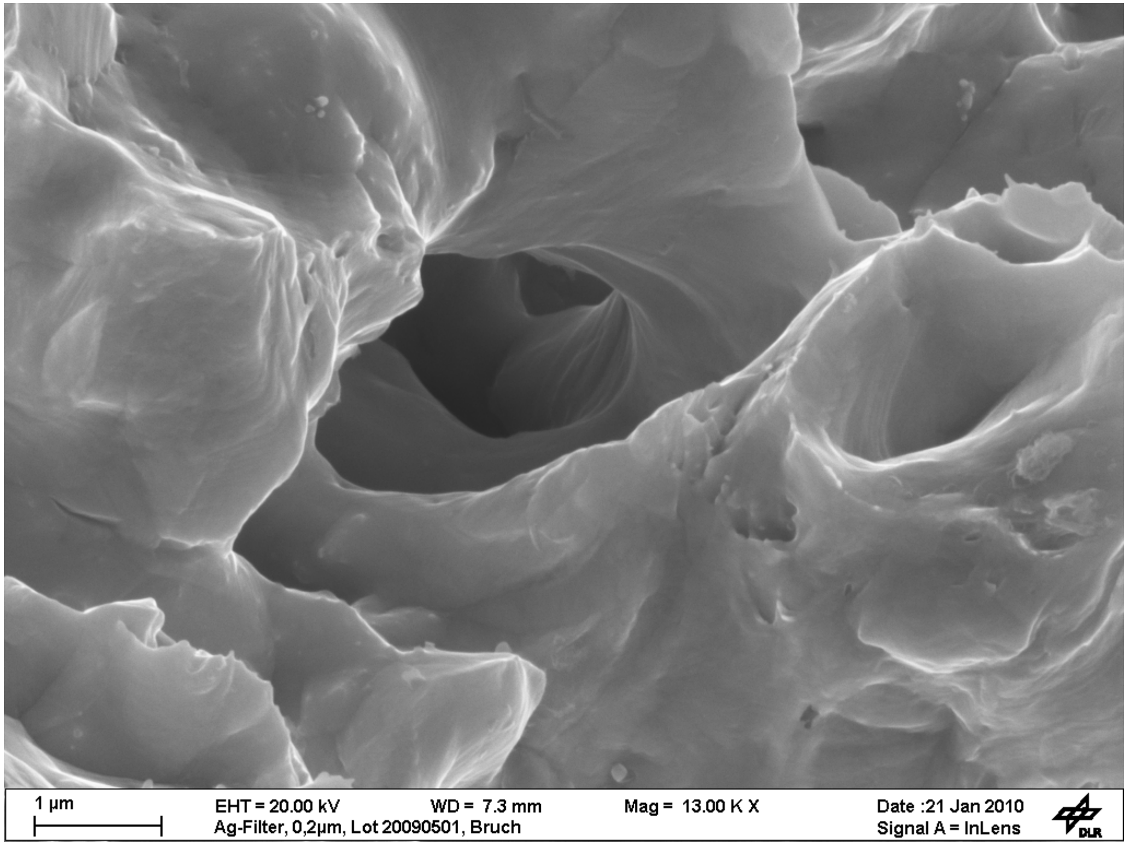


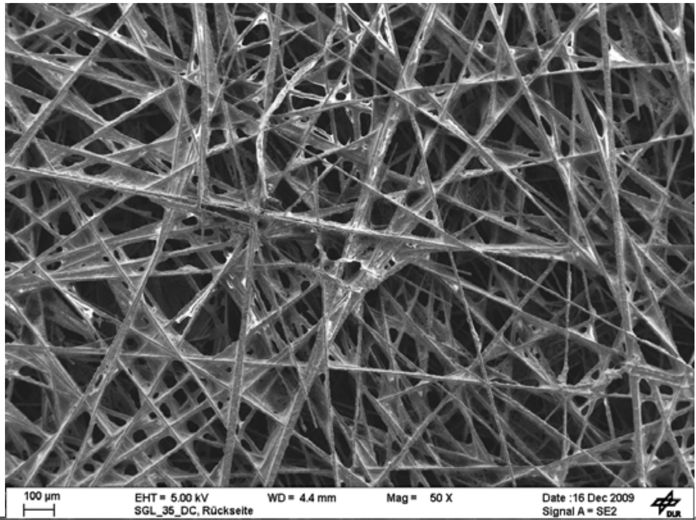
Current density / potential characteristic

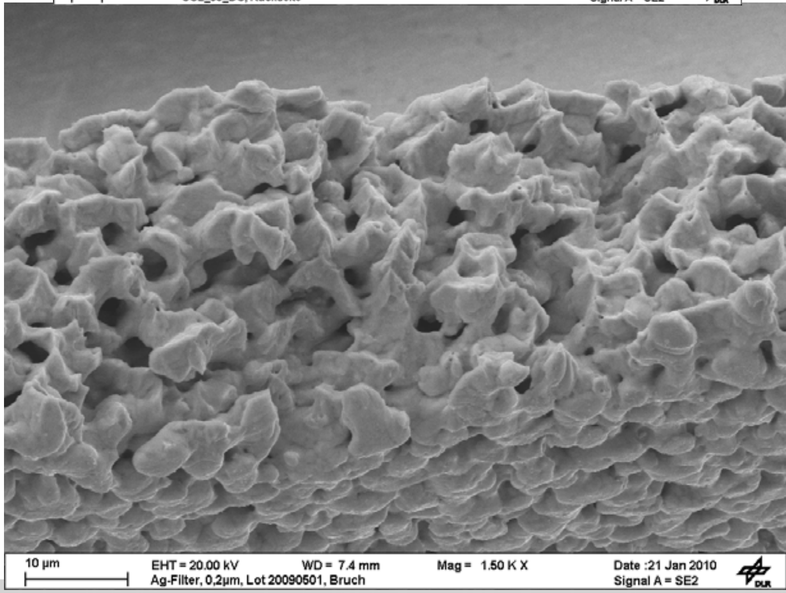




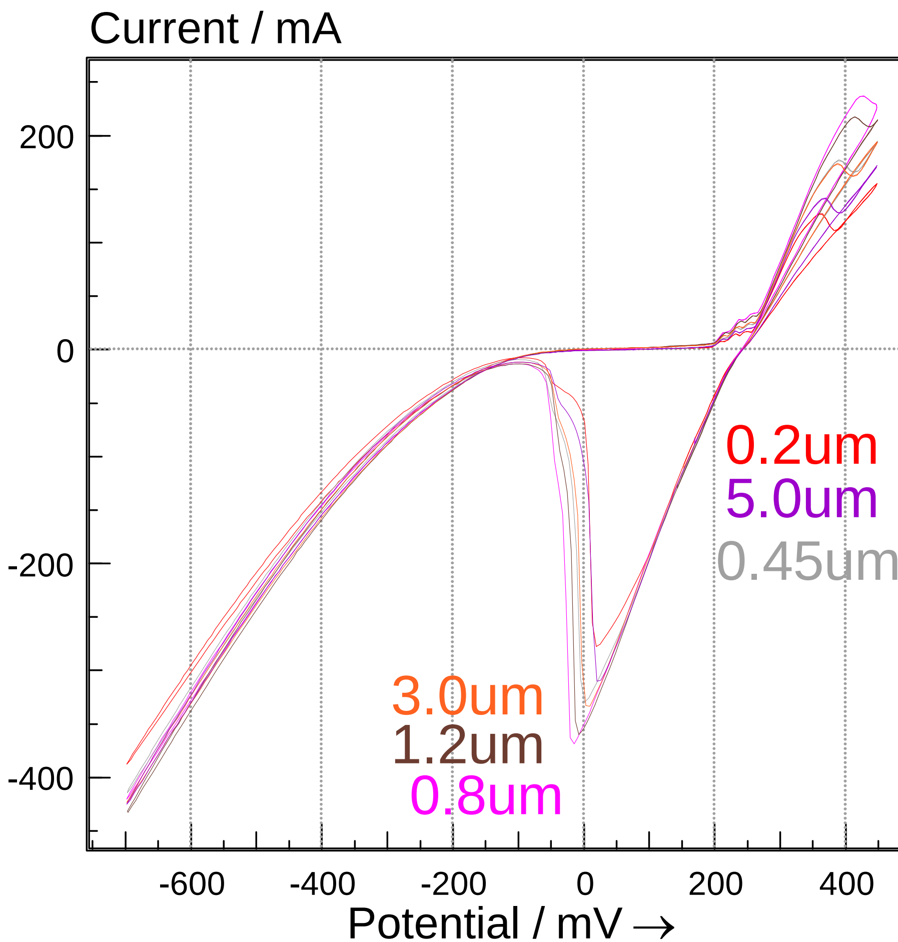
SEM picture of cross section of silver membrane with 0.2µm pores diameter



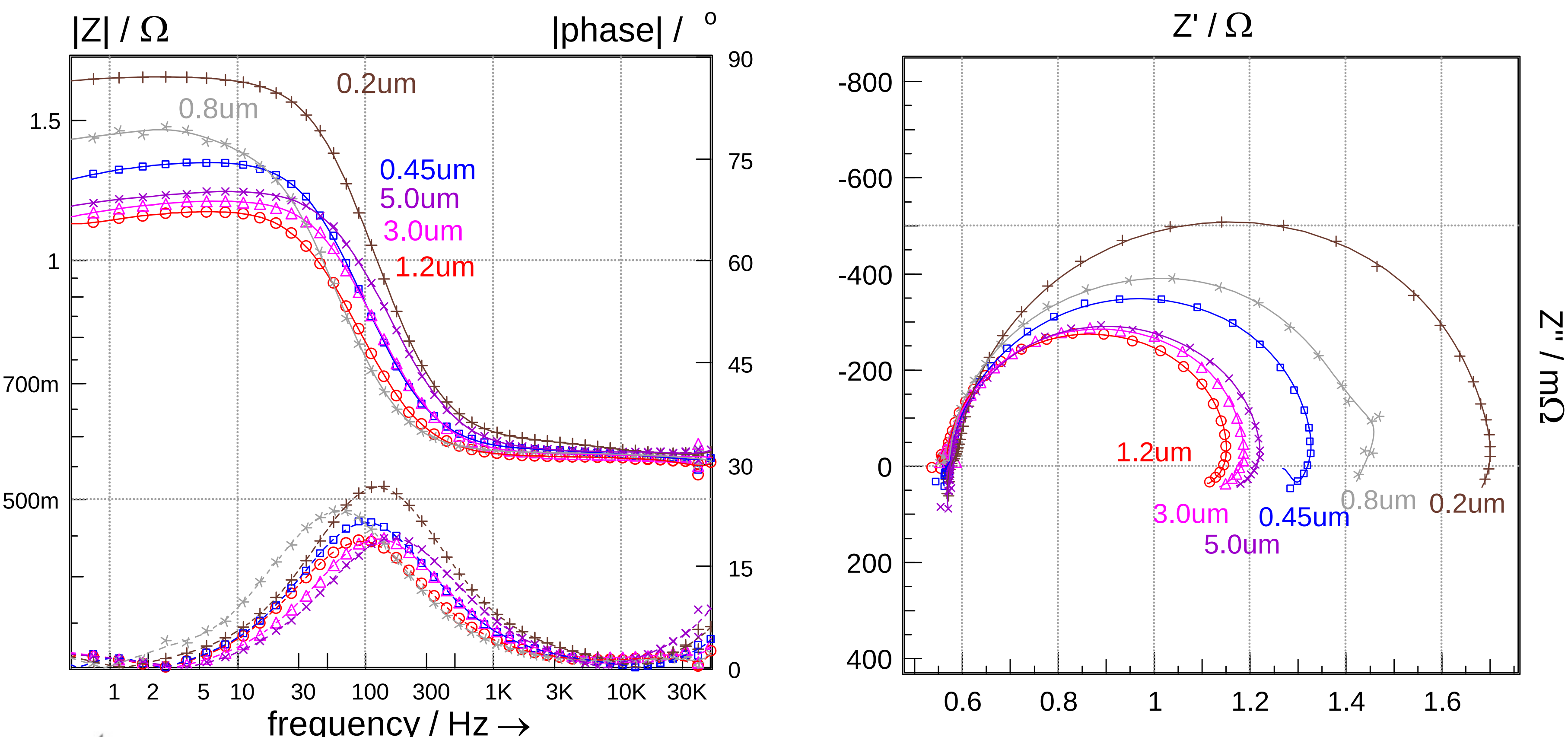




CV's (1 mV/s) from -700 mV to 450 mV vs. Hg/HgO bei 80°C in 10 M NaOH, O_2



Vergleich Impedanzspektren, aufgenommen in 10 M NaOH bei 80°C, -700 mV vs. Hg/HgO nach 60 Minuten



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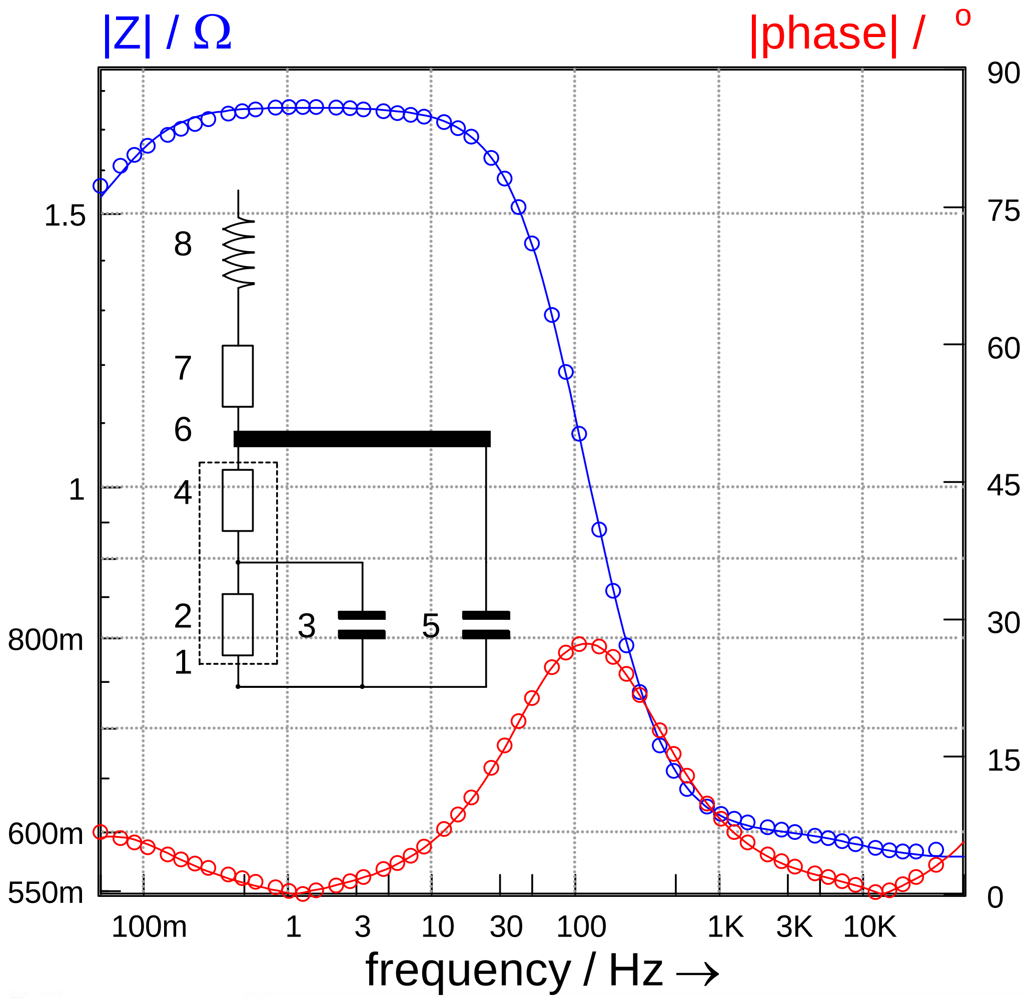
Equivalent circuit with relaxation impedance and measurement at -700 mV, 1.2 µm membrane



1	2	
	20.17	s
	50.84	mΩ
2	394	mΩ
3	2.167	mF$^{\alpha}$
	868.3	m
4	763.4	mΩ
5	1.779	mF$^{\alpha}$
	1.007	
6	1	
	102.6	mΩ
	0	Ω
7	566.7	mΩ
8	213.2	nH

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

Thank you for the attention!