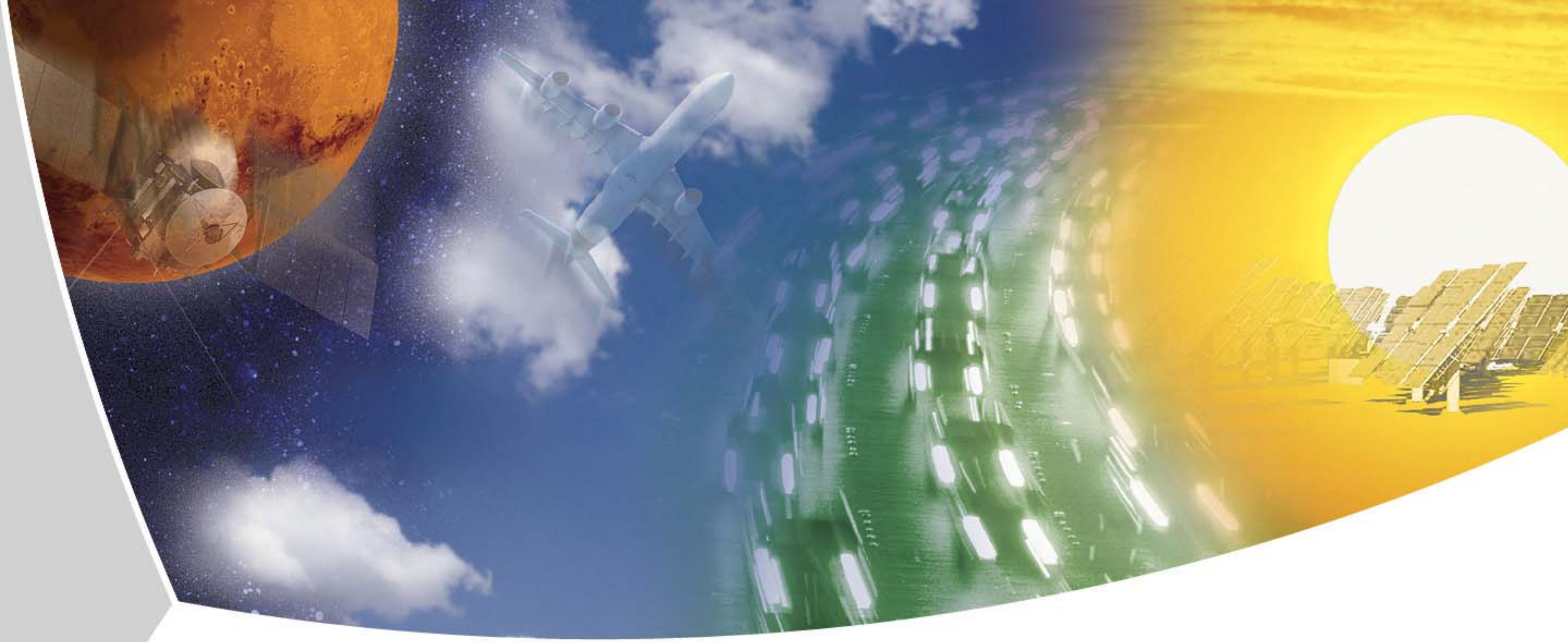

Theory and Application of Porous Electrodes in Fuel Cell Characterization

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DLR, Institut für Technische Thermodynamik, Stuttgart

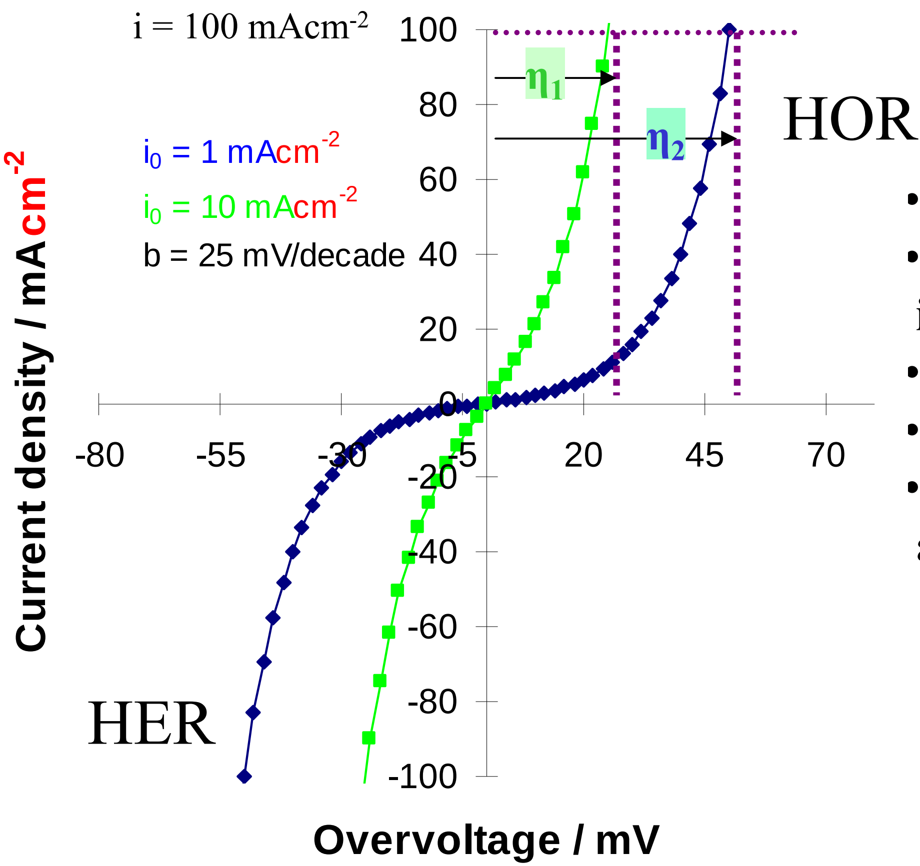
Kronach Impedance Days 2009 "Hermann Göhr"
Kloster Banz, May, 27th – 29th , 2009

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

Presentation outline

- Introduction
  - Examples of porous (technical) electrodes
- Theory and models of porous electrodes
  - Impedance models
- Application of Göhr‘s porous electrode model
  - EIS measured at PEFC
  - EIS measured during oxygen reduction on silver in alkaline solution
- Outlook
  - Experimental set up for EIS applied for stack measurements

Why porous electrodes?



Butler-Volmer equation for hydrogen oxydation (HOR) and hydrogen evolution reaction (HER)

- **Enlargement of active electrode surface**
- **Lowering of overvoltage at same current input (electrolyzer) or output (fuel cell)**
- **Increasing of power density (galvanic cells)**
- **Increasing of storage capacity (supercaps)**
- **Lowering catalyst loading by increasing active surface**

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

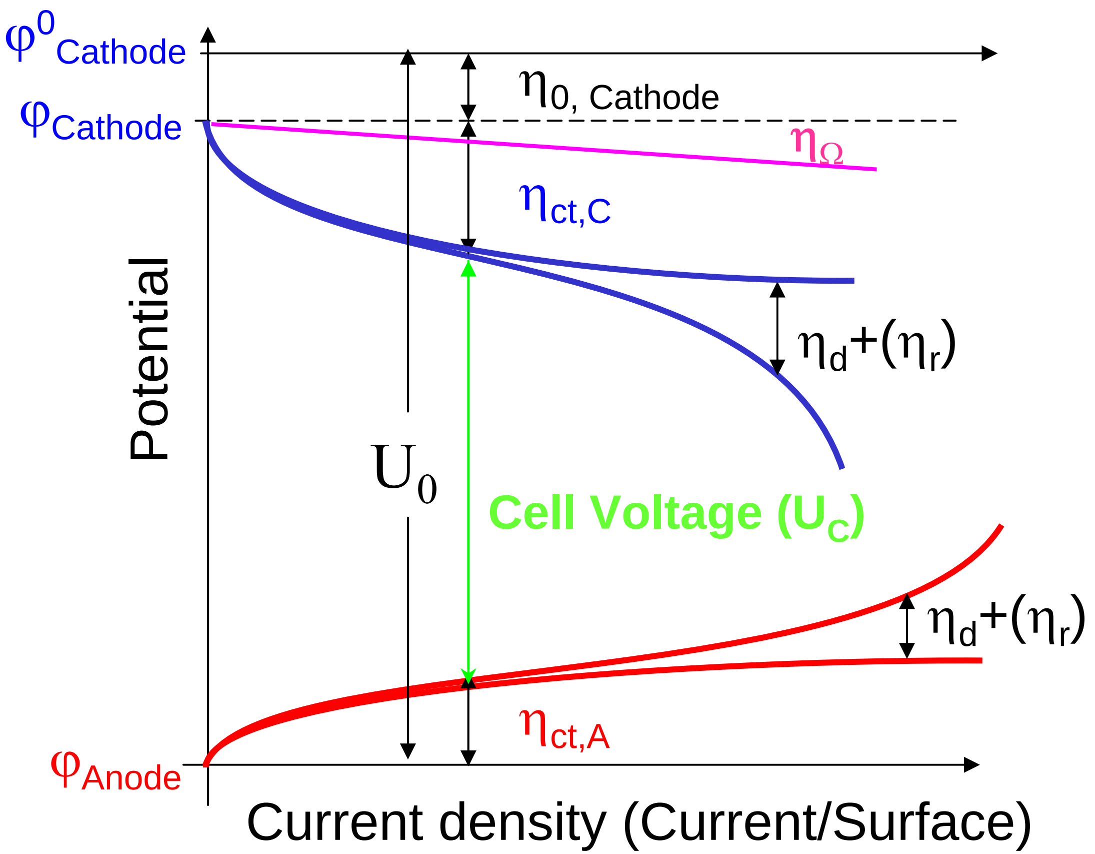
$\eta_\Omega = iR$

Transport limitation (diffusion)

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

Fuel cell voltage

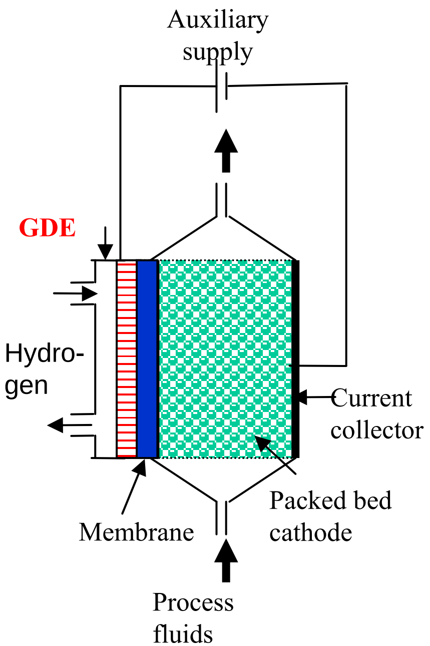
$U_C = U_0 - \eta_{ct,H_2} - \eta_{ct,O_2/air} - \eta_d - \eta_\Omega$



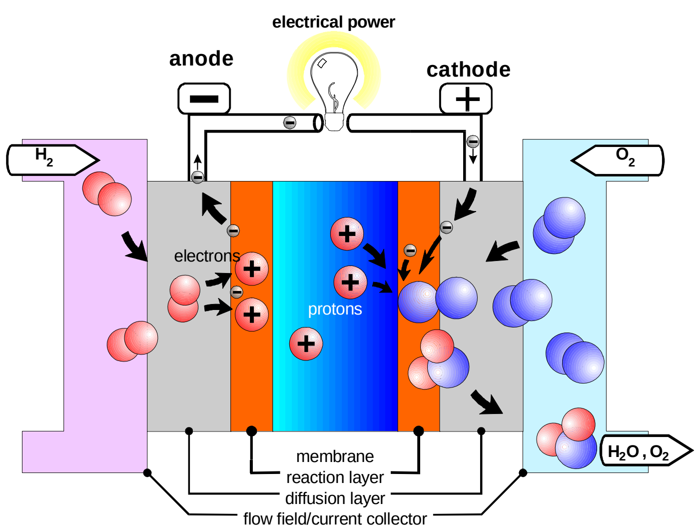
Field of application of porous electrodes

Batteries and supercaps

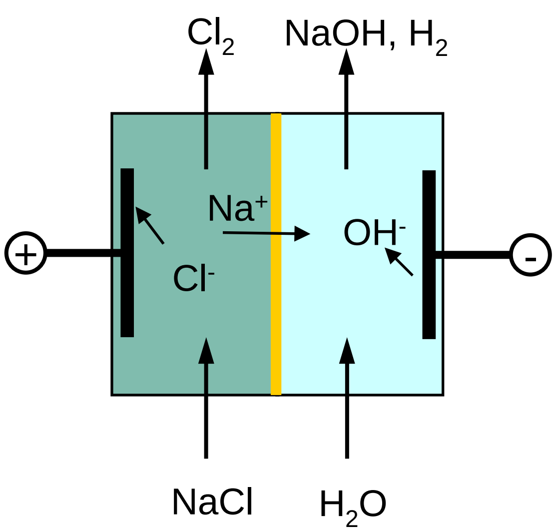
Water purification and treatment
(Bio)-Organic synthesis



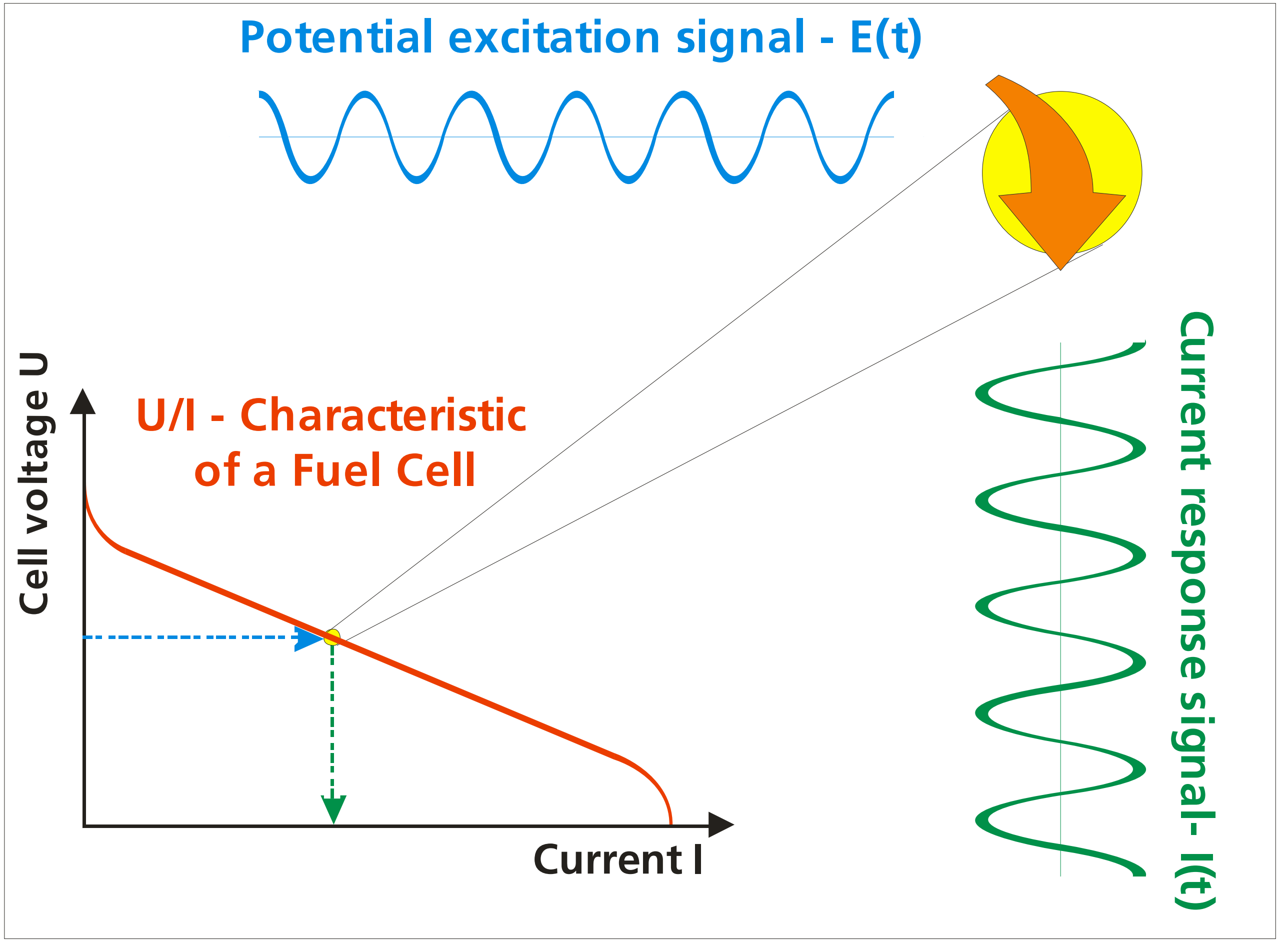
Fuel Cells



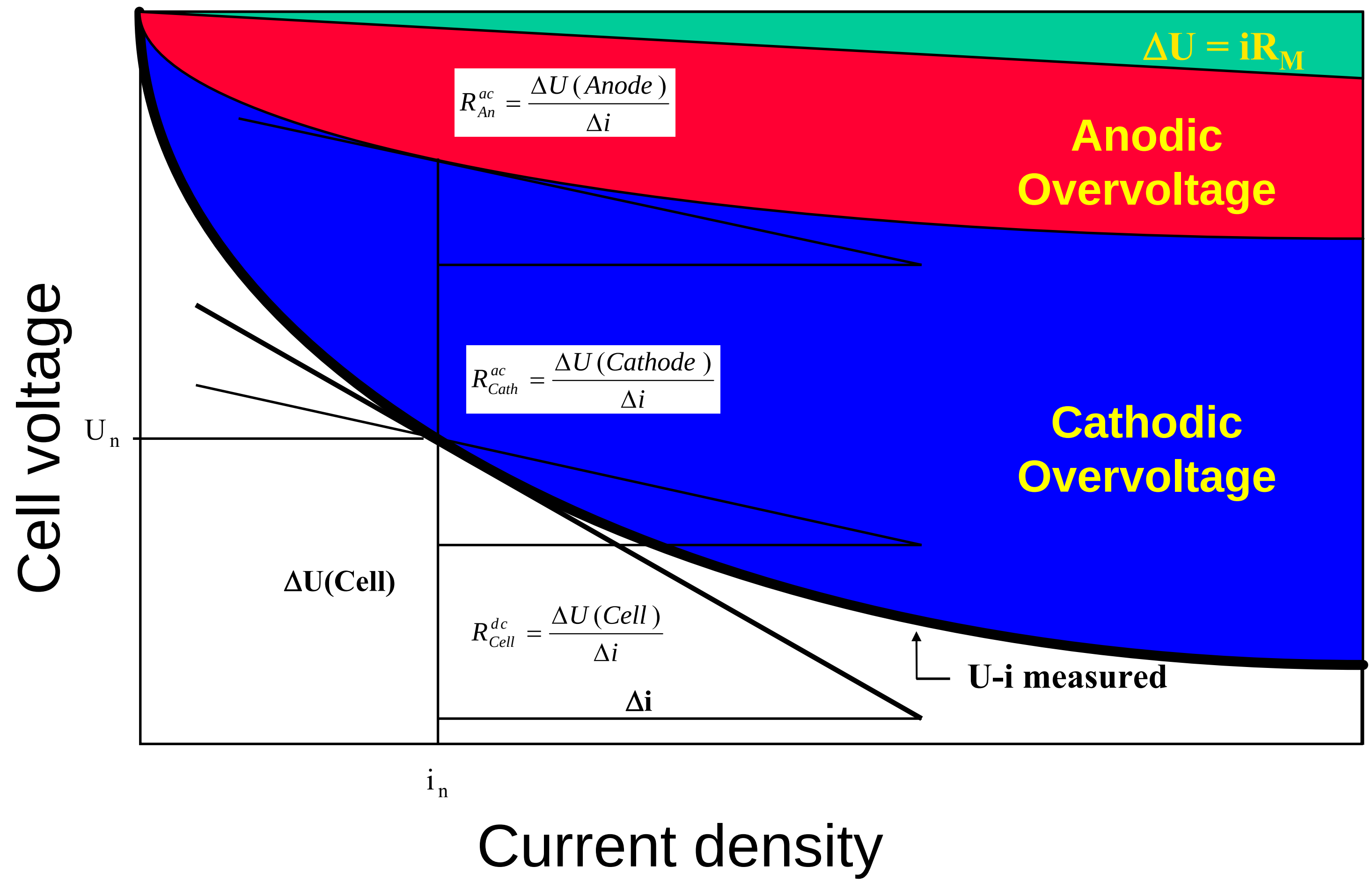
Electrolysis (Water, NaCl, etc.)



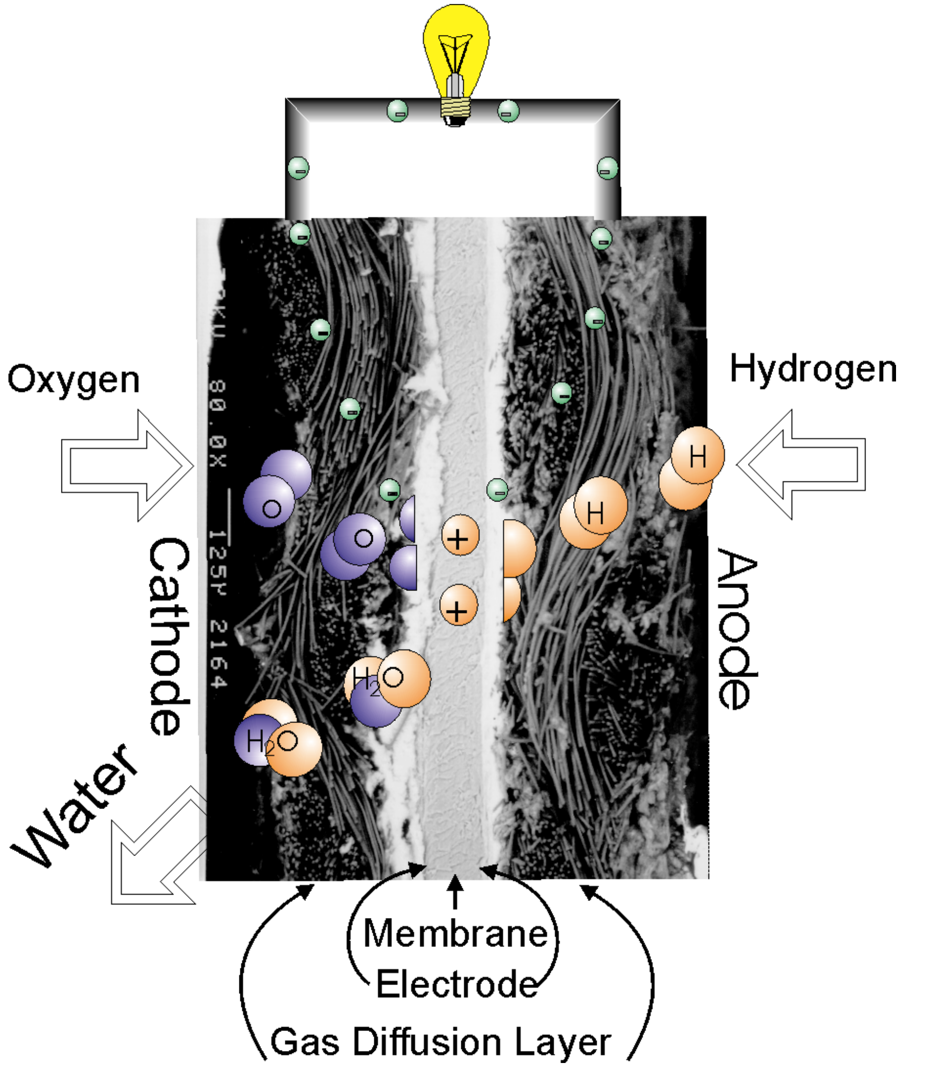
Electrochemical Impedance Spectroscopy: Application to Fuel Cells



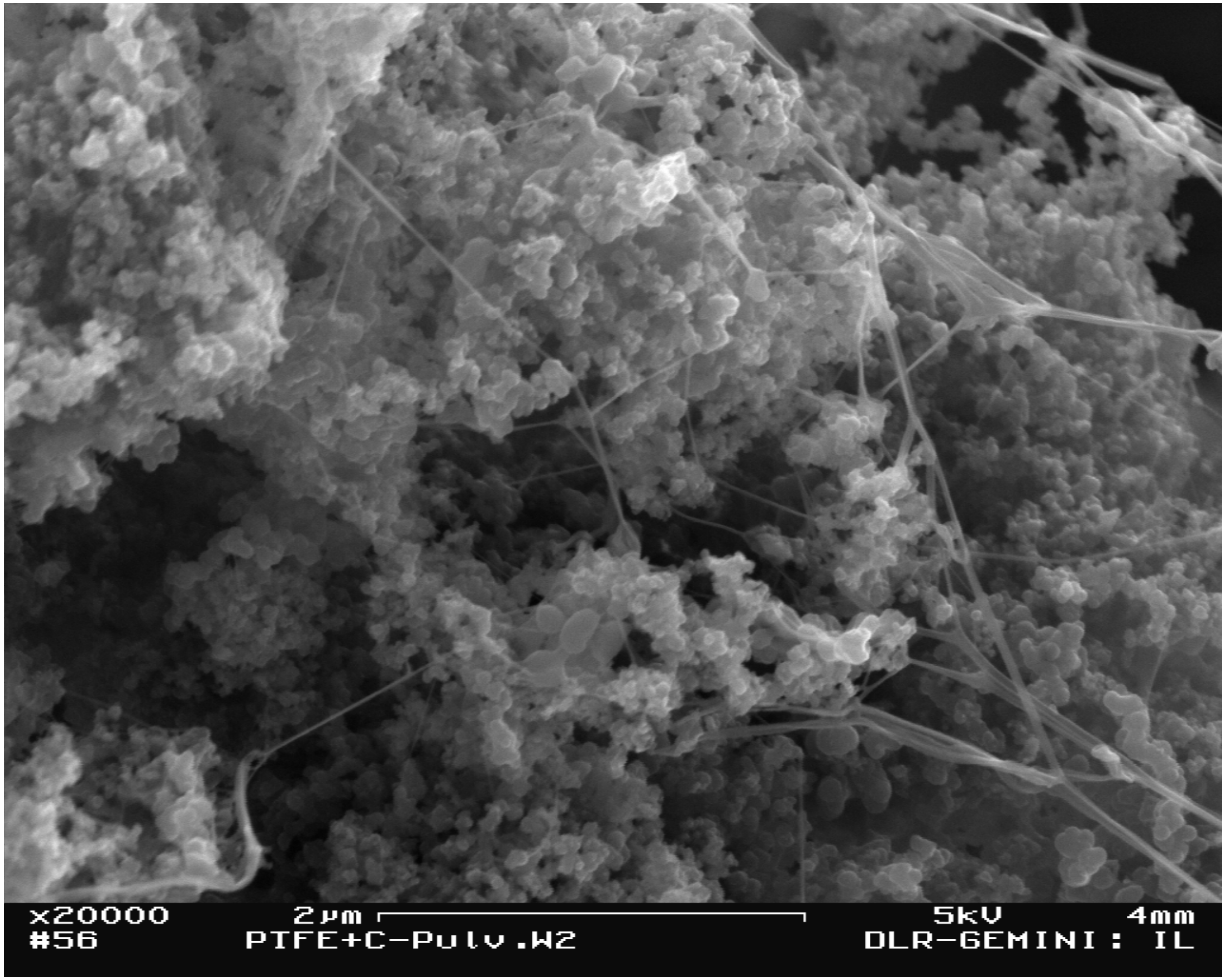
Schematic diagram of the U-i characteristic of PEFC and Electrochemical Impedance Measurements



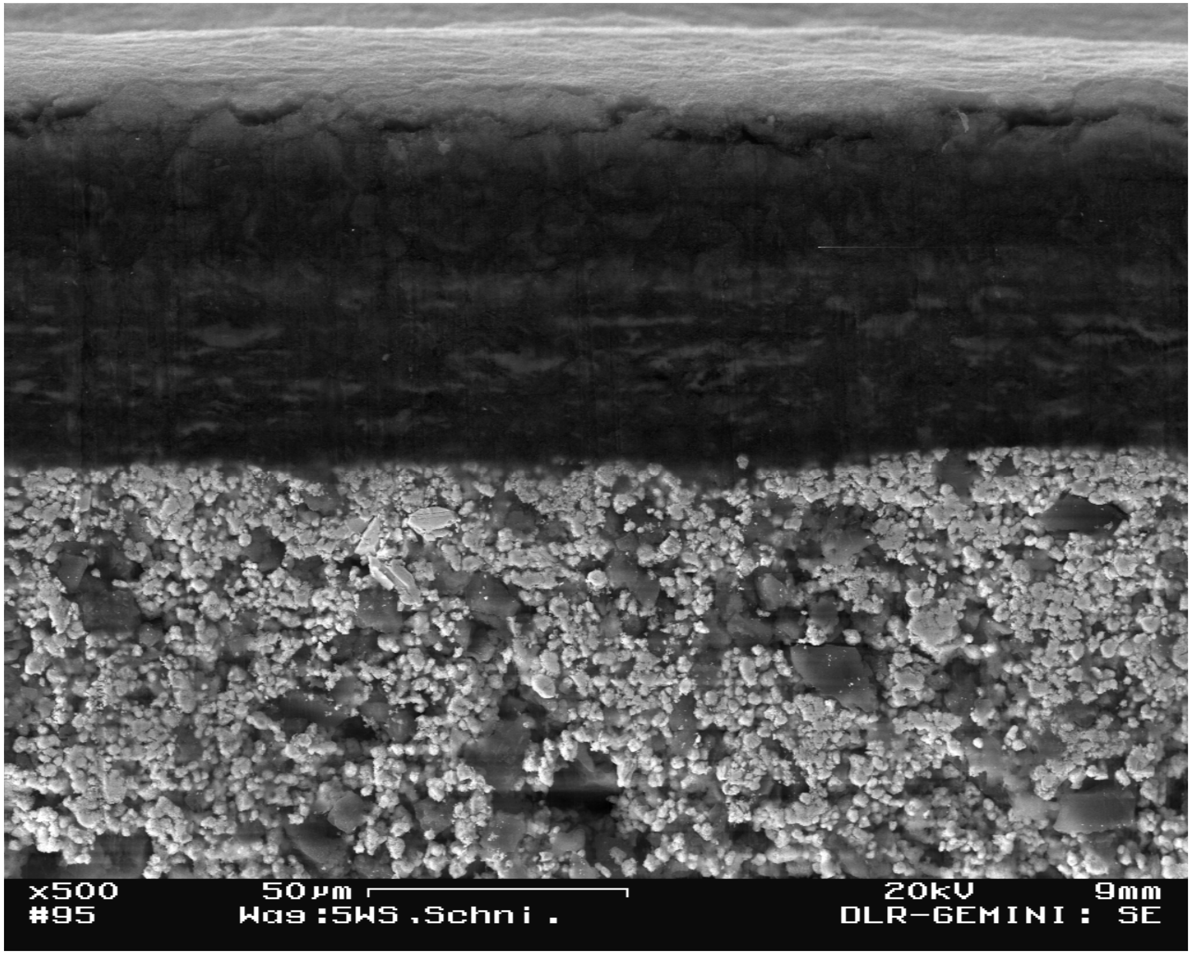
PEFC: Schematic Diagram (cross section)



SEM picture of PTFE/C powder



Multi-layer Gas Diffusion Electrodes with different porous layers



Carbon-PTFE Layer
(Dry sprayed)

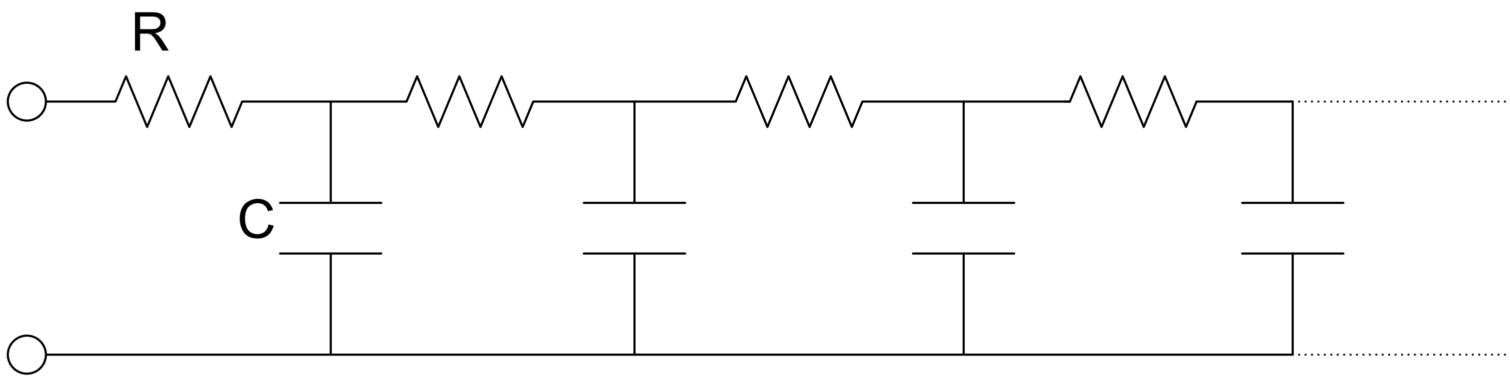
Ag-PTFE Layer
(Rolled Layer)

Brief Overview of Porous electrode models and Applications

Authors	Reference	Model and system
J. -P Candy, P Fouilloux, M. Keddam, H. Takenouti	Electrochim. Acta, 26(1981) 1029	Ni in alkaline solution
R. De Levie	Electrochim. Acta, 8(1963) 751	Transmission line model,
J.S. Newman and C.W. Tobias	J. Electrochem. Soc., 109(1962) 1183	Steady-state
J. Giner, C. Hunter	J. Electrochem. Soc., 116(1969) 1124	Flooded-agglomerate model, Pt-GDE, OCR in alkaline solution
K. Mund, F.v. Sturm	Electrochim. Acta, 20(1975) 463	HOR on Ni in alkaline solution
S. Sunde,	Electrochim. Acta, 42(1997) 2637	Composites, SOFC
P. Björnbom	Electrochim. Acta, 32(1987) 115	Steady state model
R. Holze, W. Vielstich	J. Electrochem. Soc., 131(1984) 2298	OCR in alkaline solution
T.E. Springer, I.D. Raistrick	J. Electrochem. Soc., 136(1989) 1594	Flooded-agglomerate and thin film model, differential element of a pore wall
H. Göhr	Poster ISE Erlangen, 1983	Homogeneous porous model, Pb in sulfphuric acid
G. Paasch, K. Micka, P. Gersdorf	Electrochim. Acta, 38(1993) 2653	Macrohomogeneous porous electrode model
W. Scheider	J. Phys. Chem., 79(1975) 127	Model with pore branching
S. Srinivasan, H. D. Hurwitz, J. O'M Bockris	J. Chem. Phys., 46(1967) 3108	Thin film model
M. Kramer, M. Tomkiewicz	J. Electrochem. Soc. 131(1984)	Stochastic approach with interpenetrating network
A. Winsel, E. Bashtavelova	J. Power Sources, 73(1998) 242	Agglomerate-of-spheres model
M. Tomkiewicz, B. Aurian-Blajeni	J. Electrochem. Soc. 135(1988) 2743	True effective medium approach
H. Keiser, K.D. Beccu, M.A. Gutjahr	Electrochim. Acta, 21(1976) 539	Various geometries of single pore, Ni-GDE

Simple pore model of interface charging

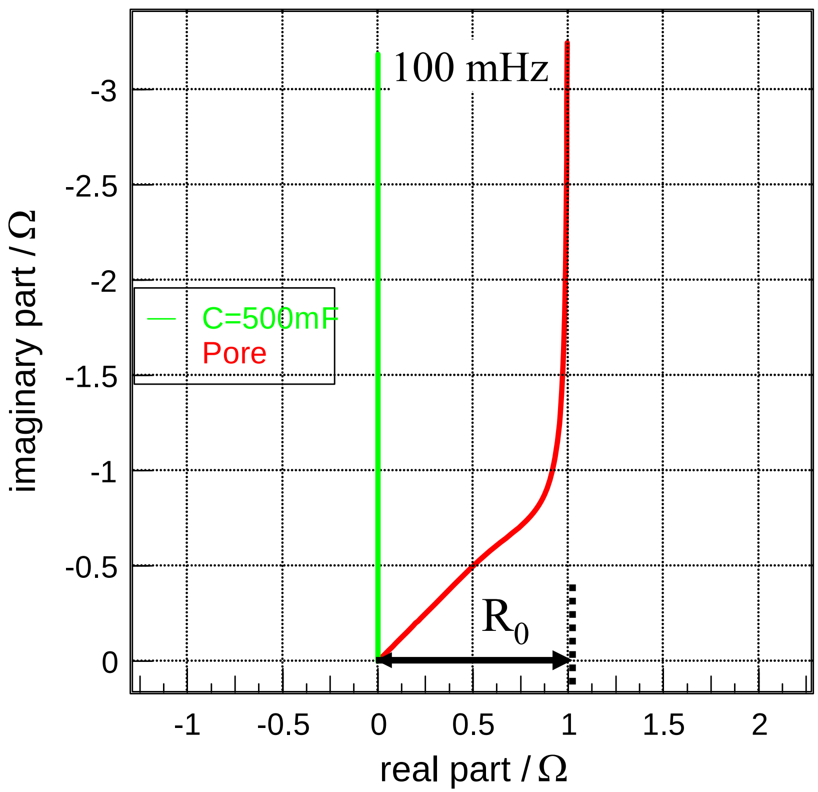
RC-transmission line of a flooded pore

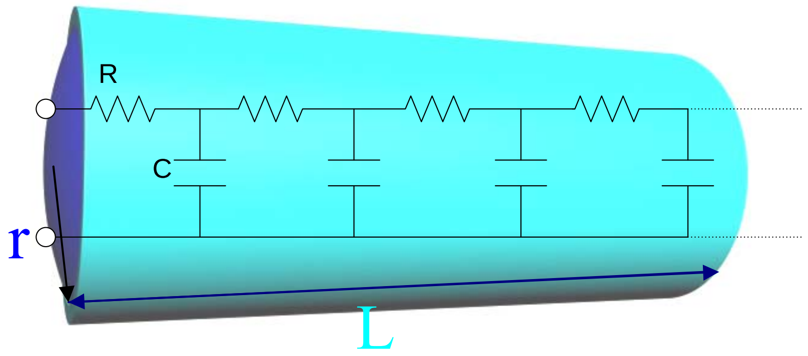


R = electrolyte resistance inside the pore per unit length
C = interface capacitance per unit length

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

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





R = 3 Ω

C = 0.5 F

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

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

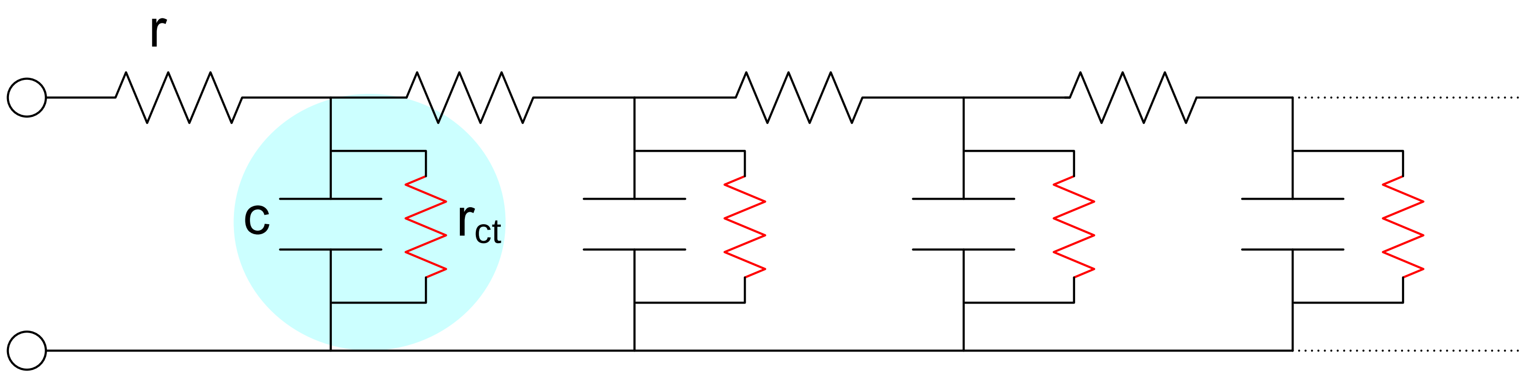
δ = specific electrolyte resistance

r = pore radius

L = pore lenght

Simple pore model with faradaic processes in pores

RC-transmission line of a flooded pore

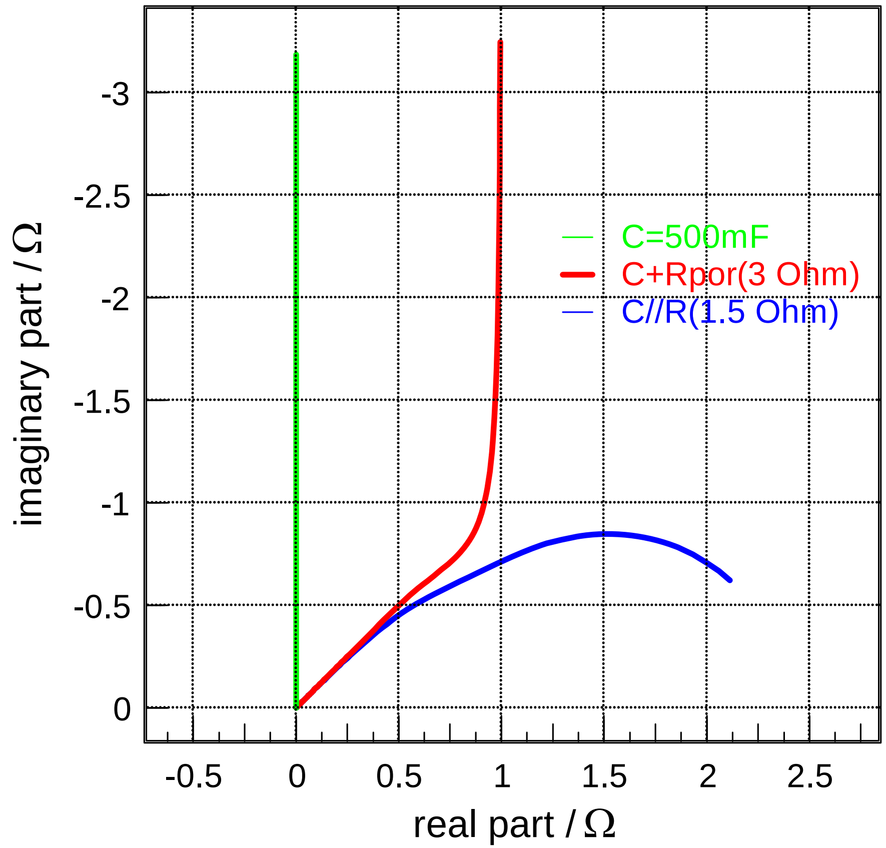


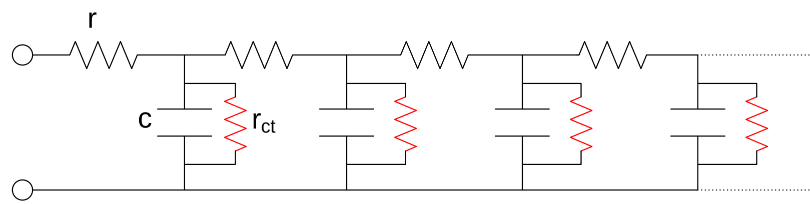
r = electrolyte resistance inside the pore per unit length

c = interface capacitance per unit length

r_{ct} = interface charge transfer resistance per unit lenght (Faraday impedance y_2)

Nyqusit representation of porous electrode impedance with faradaic impedance element



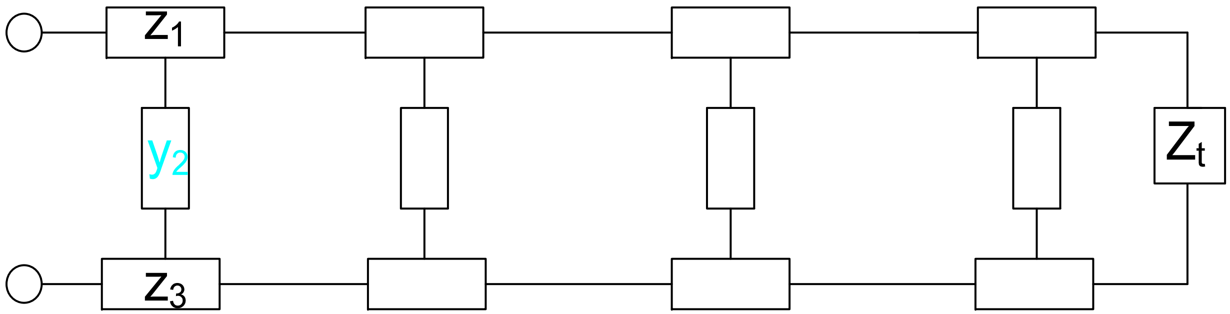


$r = 3\ \Omega$

$c = 500\ \text{mF}$

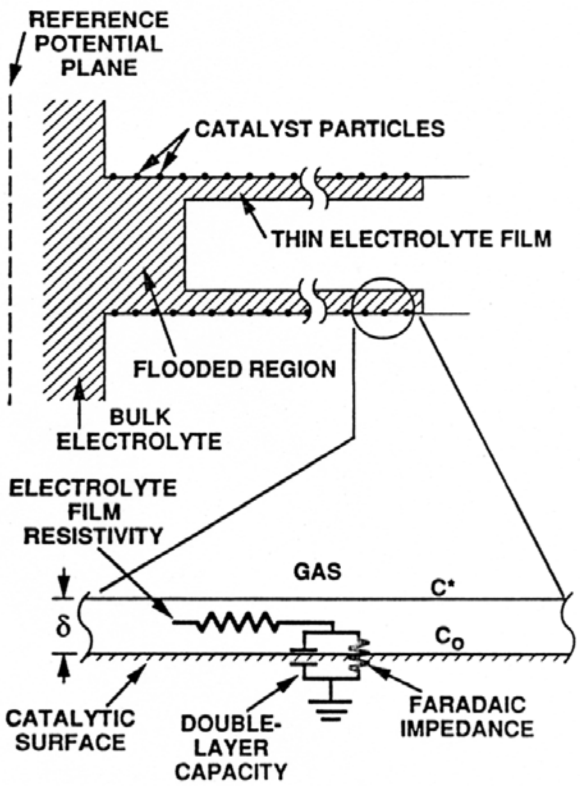
$r_{ct} = 1.5\ \Omega$

Generalization of RC-transmission line of a flooded pore

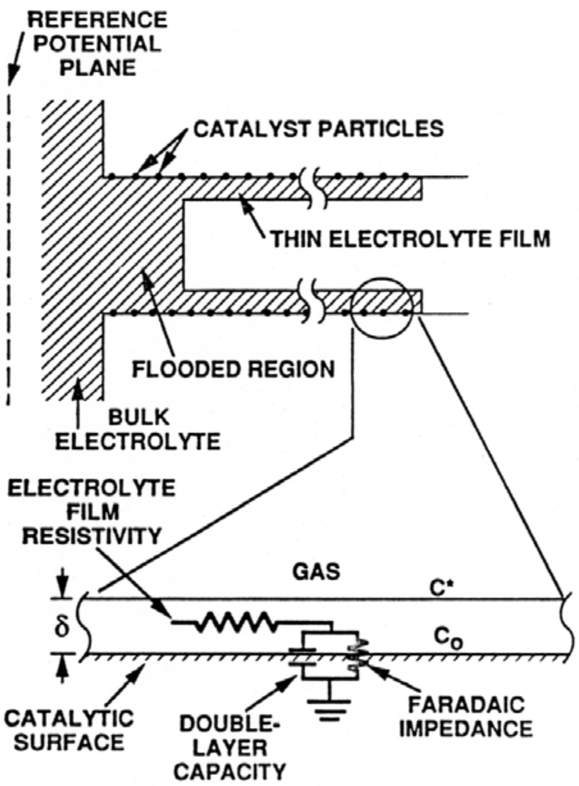


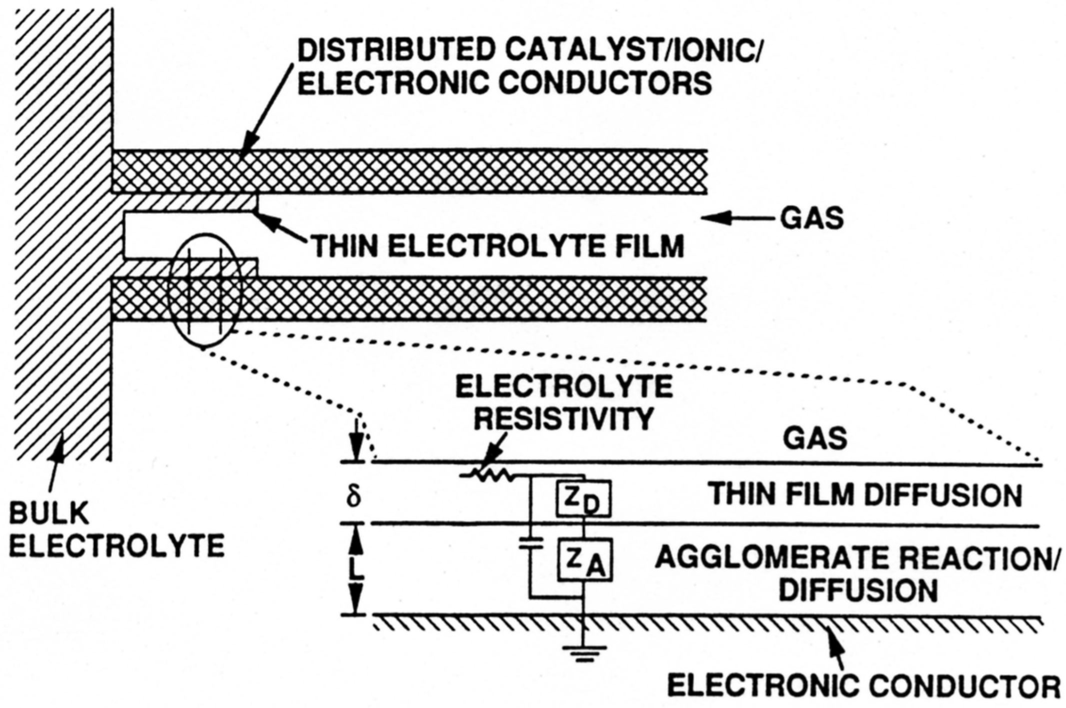
$$Z = \frac{\frac{(z_1 L)}{(y_2 L)}\frac{1}{Z_t} + \sqrt{\frac{(z_1 L)}{(y_2 L)}}\coth\sqrt{(z_1 L)\cdot(y_2 L)}}{1 + \sqrt{\frac{(z_1 L)}{(y_2 L)}}\frac{1}{Z_t}\coth\sqrt{(z_1 L)\cdot(y_2 L)}}$$

Thin-film model of a porous electrode



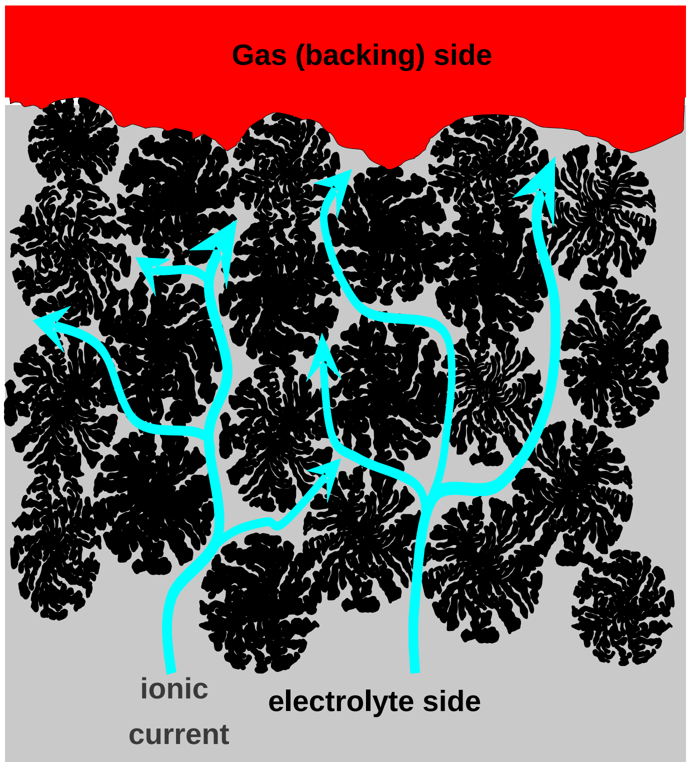
Thin-film model and agglomerate plus thin-film model of a porous electrode





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

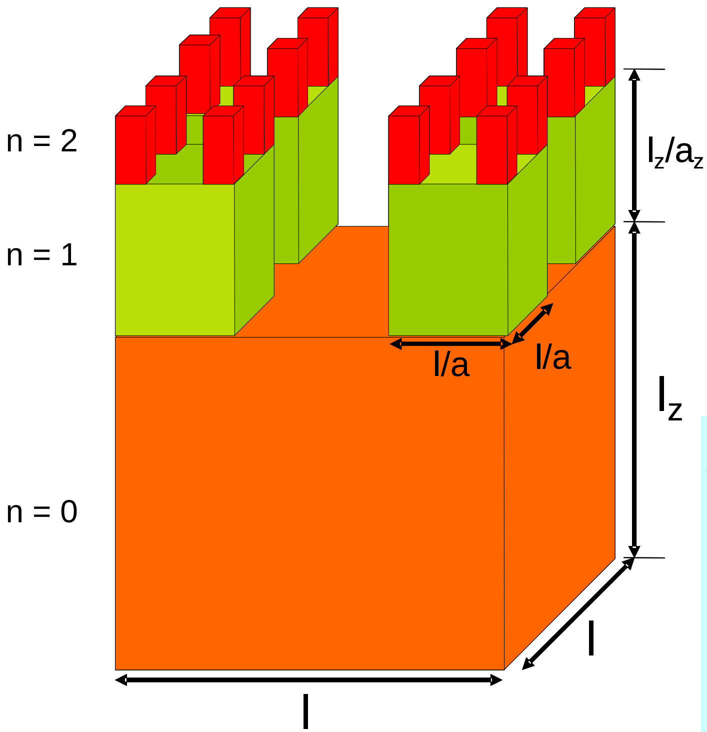
Theory of Agglomerated Electrodes

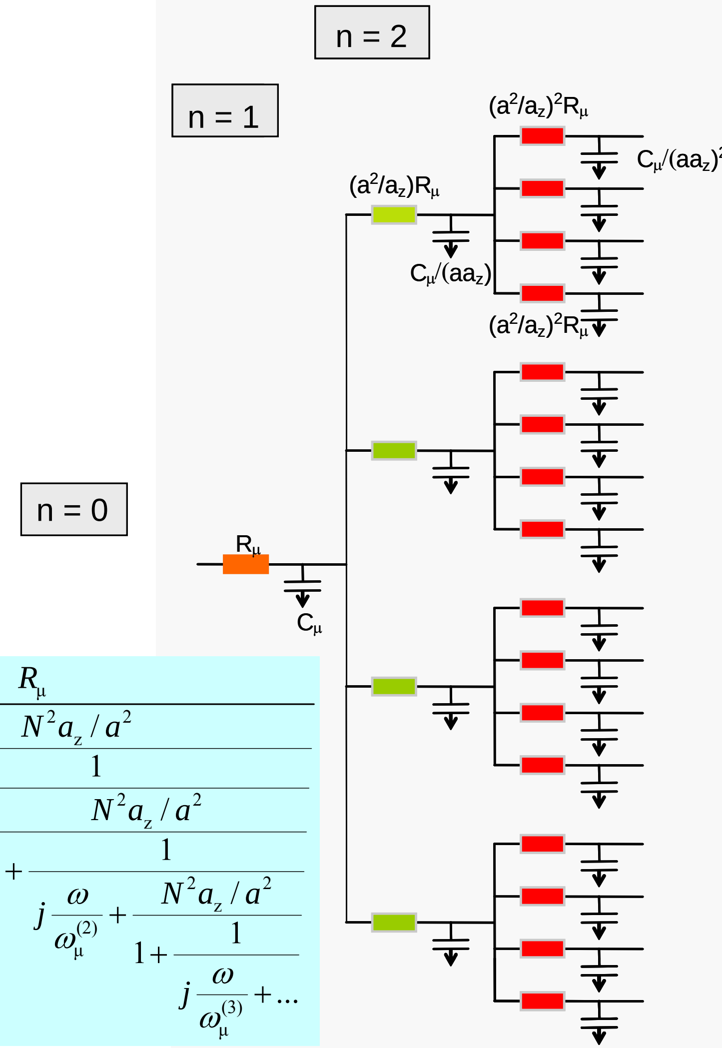


M. Eikerling, A.A. Kornyshev, E. Lust, *J. Electrochem. Soc.*, **152** (2005) E24

Hierarchical model

(Cantor-block model)

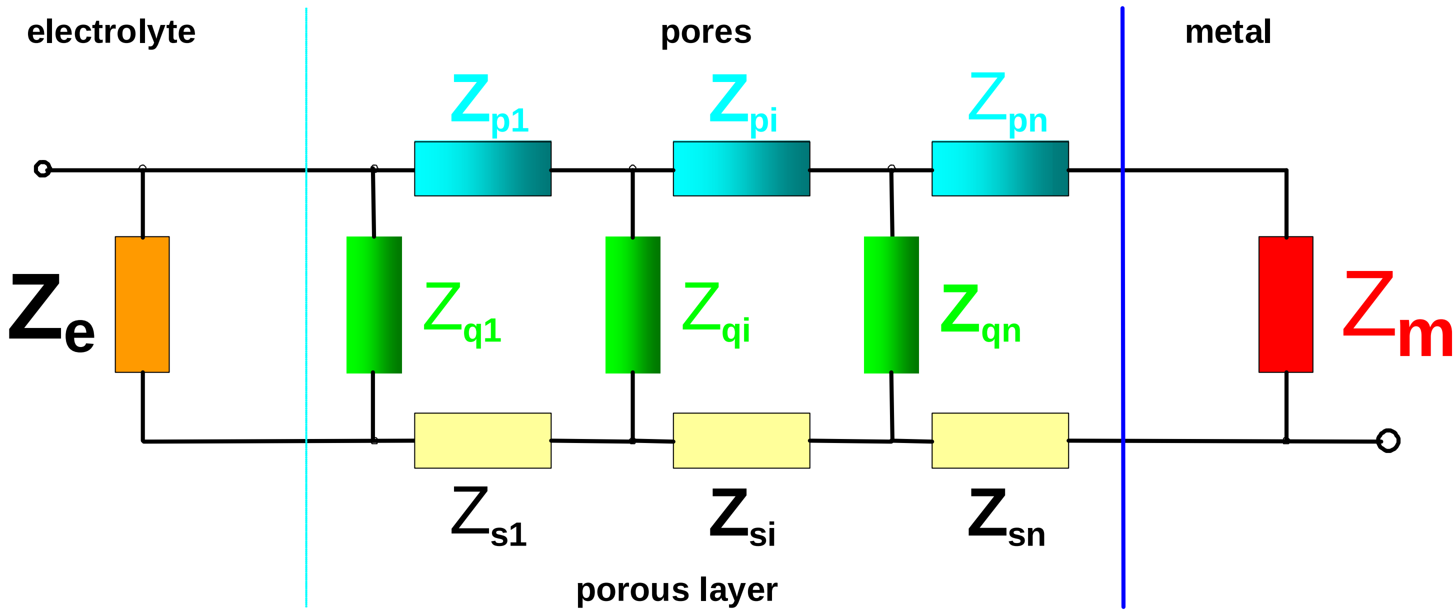




$$Z_L^s(\omega) = R_\mu + \cfrac{R_\mu}{j\frac{\omega}{\omega_\mu} + \cfrac{N^2 a_z/a^2}{1+\cfrac{1}{j\frac{\omega}{\omega_\mu^{(1)}} + \cfrac{N^2 a_z/a^2}{1+\cfrac{1}{j\frac{\omega}{\omega_\mu^{(2)}} + \cfrac{N^2 a_z/a^2}{1+\cfrac{1}{j\frac{\omega}{\omega_\mu^{(3)}} + \dots}}}}}}}$$

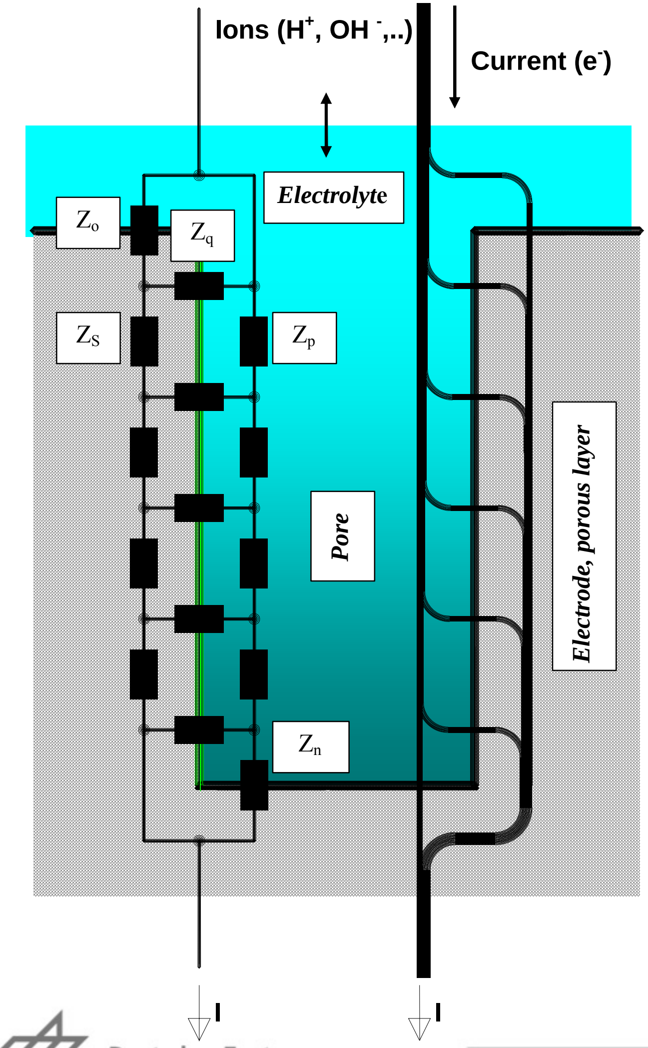
S.H. Liu, *Phys. Rev. Letters*, **55**(1985) 5289
T.Kaplan, L.J.Gray, and S.H.Liu, *Phys. Rev.* **B 35** (1987) 5379

Cylindrical homogeneous porous electrode model (H. Göhr) I



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

Cylindrical homogeneous porous electrode model (H. Göhr) II



$$Z^* = \sqrt{(Z_p + Z_s) \cdot Z_q}$$

$$Z^\# = \frac{Z_p \cdot Z_s}{(Z_p + Z_s)}$$

$$C = \cosh\left(\frac{Z_p + Z_s}{Z^*}\right)$$

$$S = \sinh\left(\frac{Z_p + Z_s}{Z^*}\right)$$

$$P = \frac{Z_p}{Z_p + Z_s}$$

$$q_0 = \frac{Z^*}{Z_o}$$

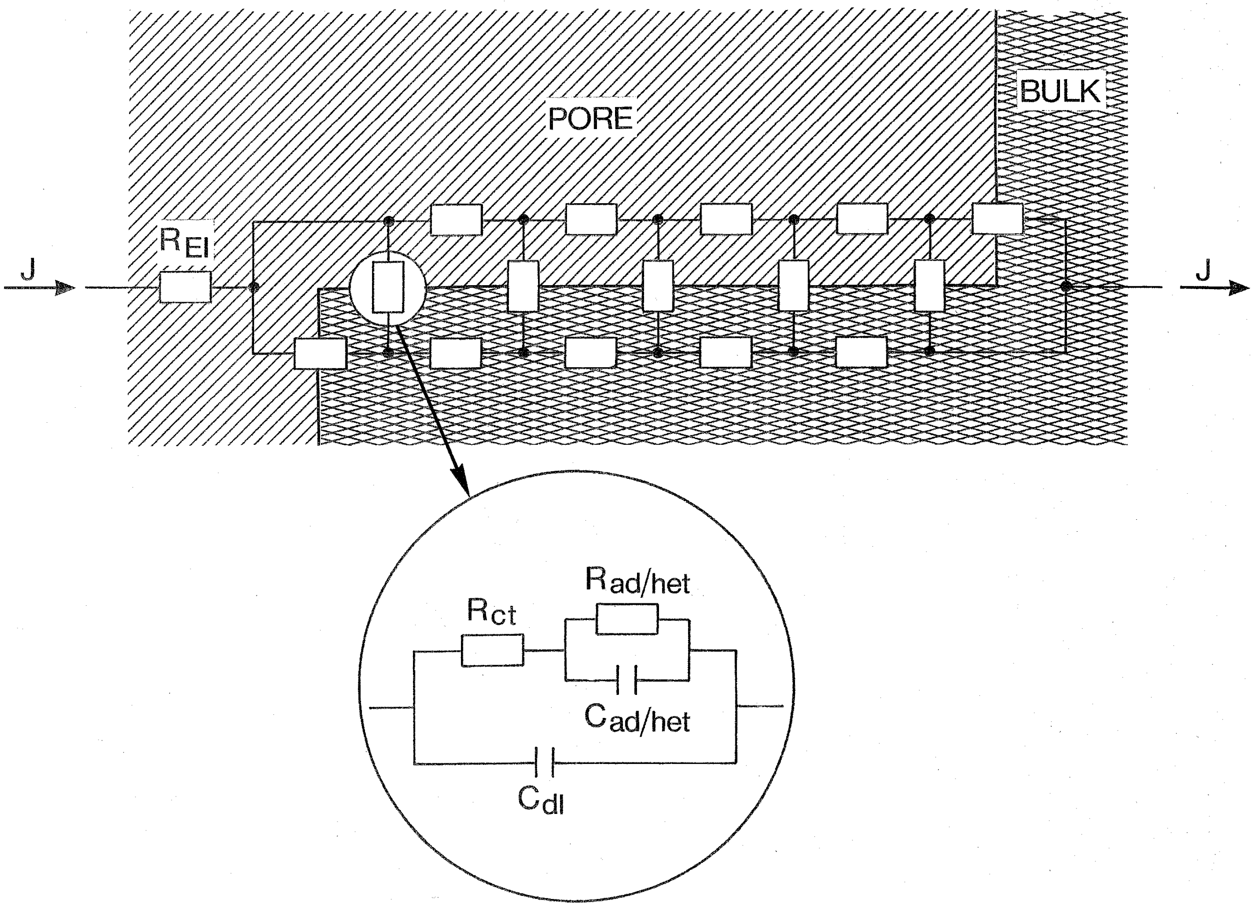
$$v = \frac{Z_p + Z_s}{Z^*}$$

$$q_n = \frac{Z^*}{Z_n}$$

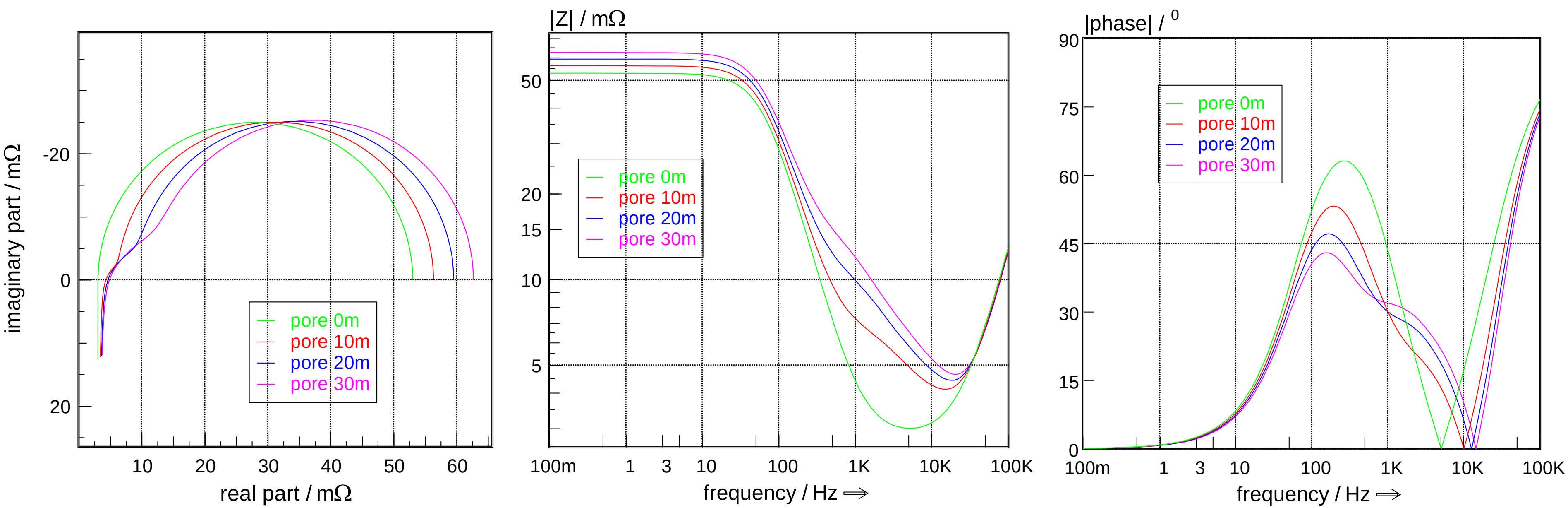
$$s = \frac{Z_s}{Z_p + Z_s} = 1\text{-}p$$

$$Z = Z^\# + Z^* \cdot \frac{C + (1 - C) \cdot 2 \cdot p \cdot s + S \cdot (p^2 \cdot q_n + s^2 \cdot q_o)}{S \cdot (1 + q_n \cdot q_o) + C \cdot (q_n + q_o)}$$

Porous electrode model with faradaic impedance



Simulation of Impedance Spectra using Porous Electrode Model



$(R_{ct}||C_{dl}$ "+" $R_{el,por})+R_M+L$

$R_{ct} = 50\ m\Omega$

$C_{dl} = 50\ mF$

$R_M = 3 m\Omega$

$L = 20\ nH$

Rel,por = 0 m Ω

10mΩ

20 mΩ

30mΩ

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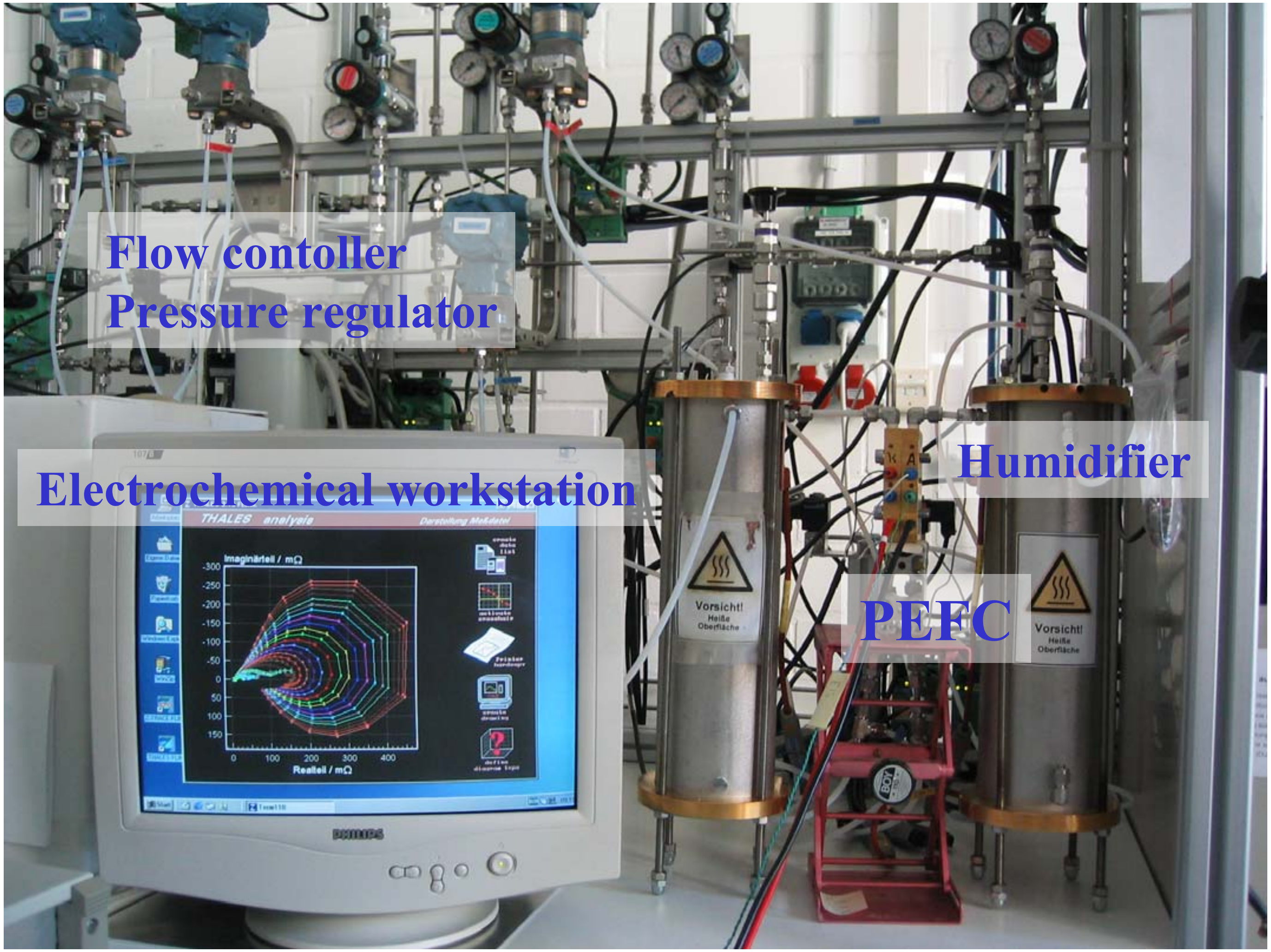
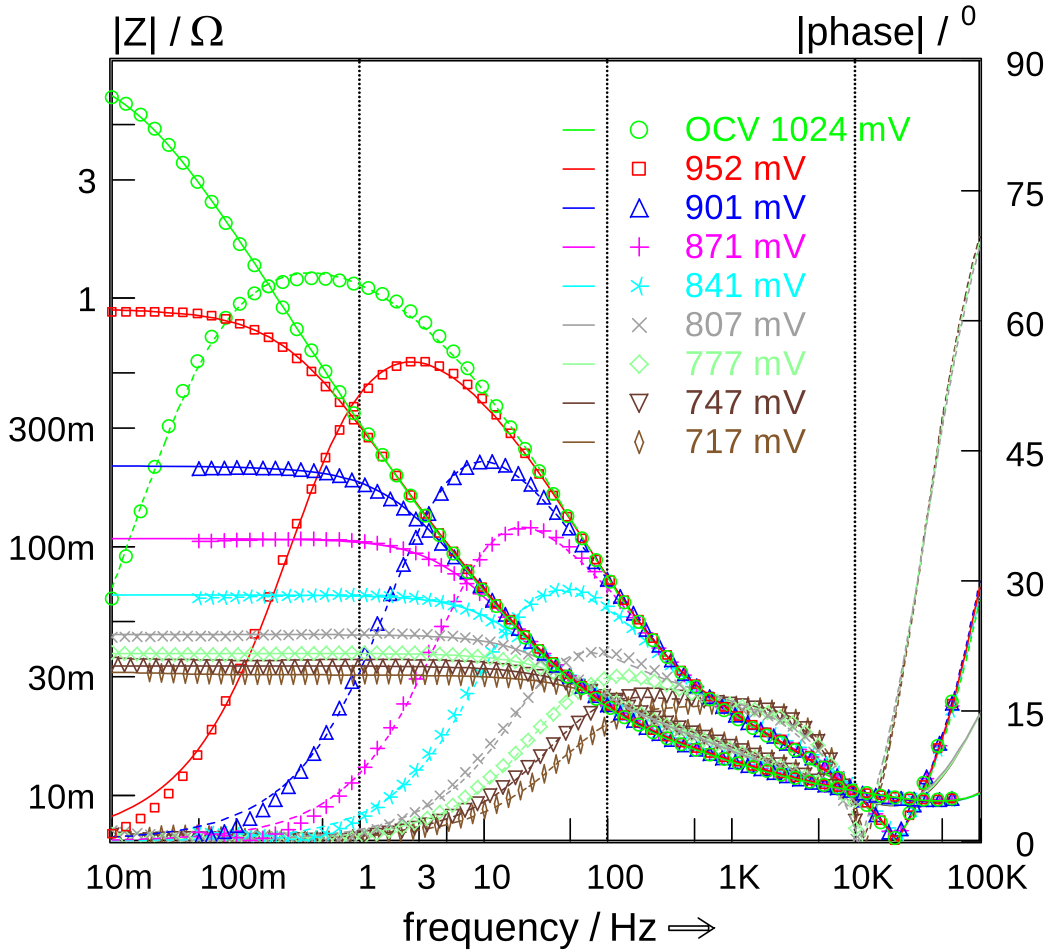
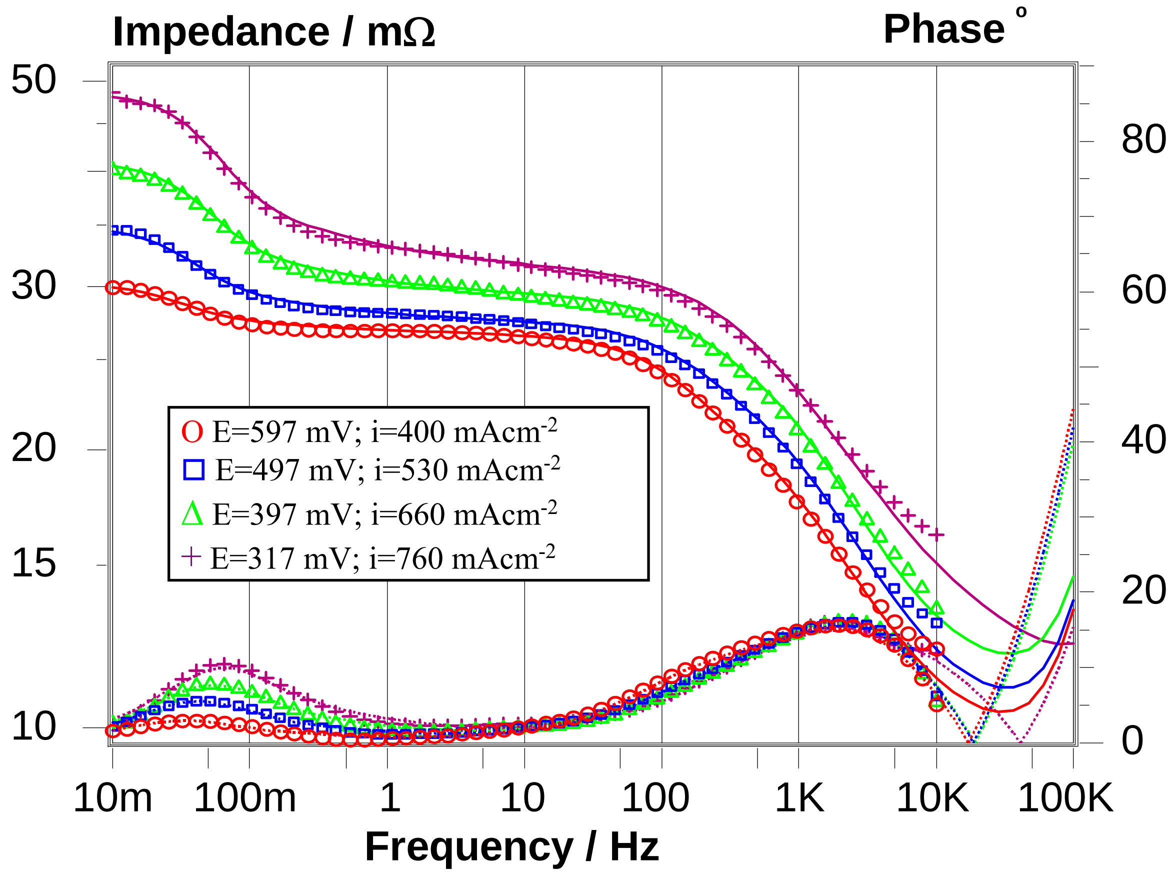
Electrochemical Impedance Spectroscopy: Experimental Set-up



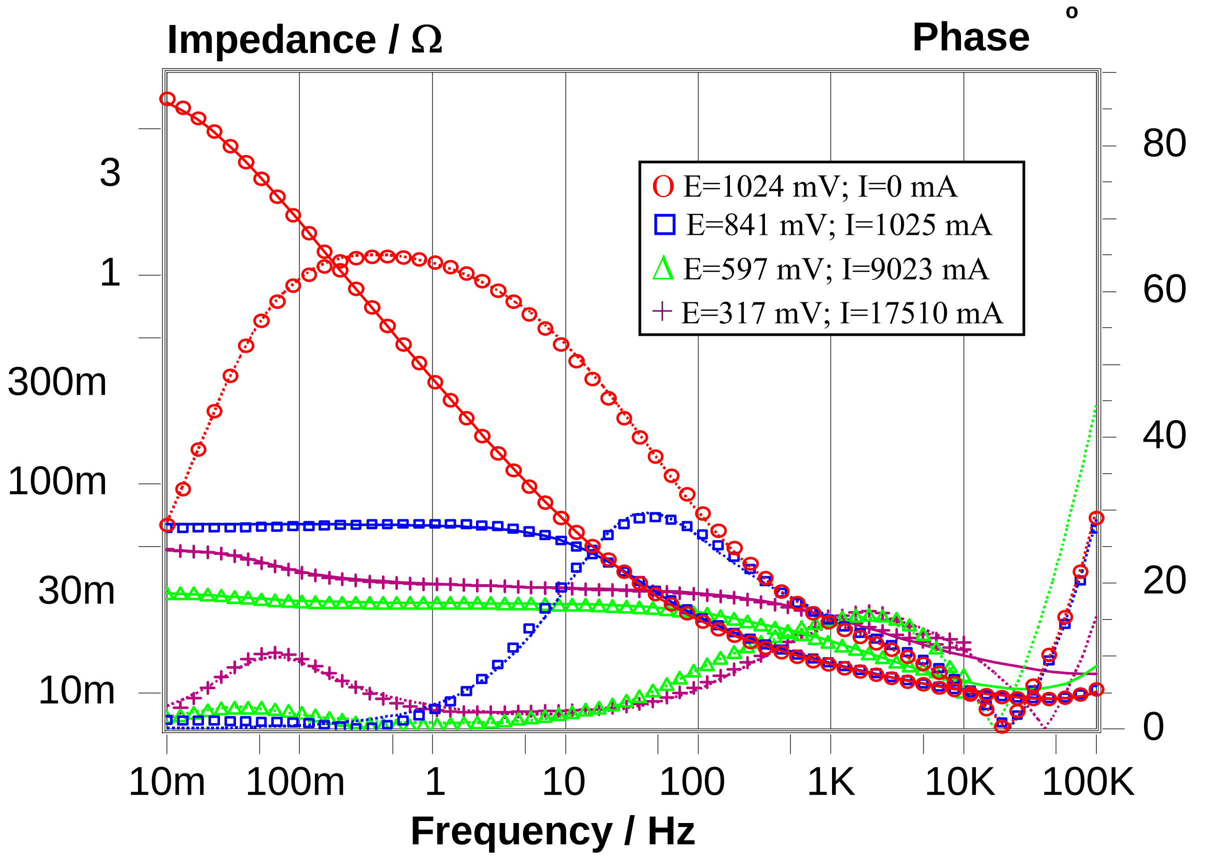
Bode diagram of measured EIS at different cell voltages (current densities) I



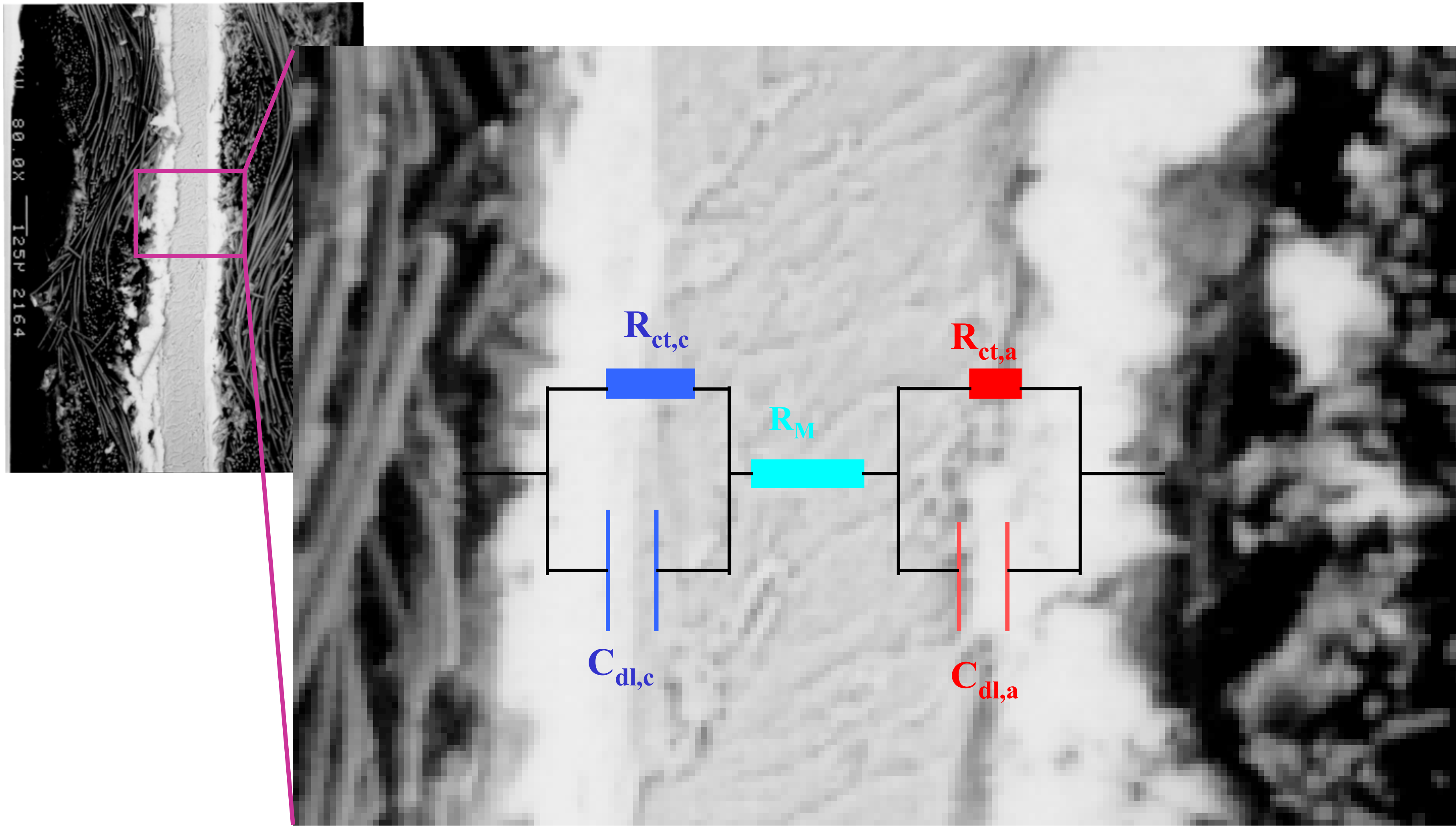
Bode diagram of measured EIS at different cell voltages (current densities) II



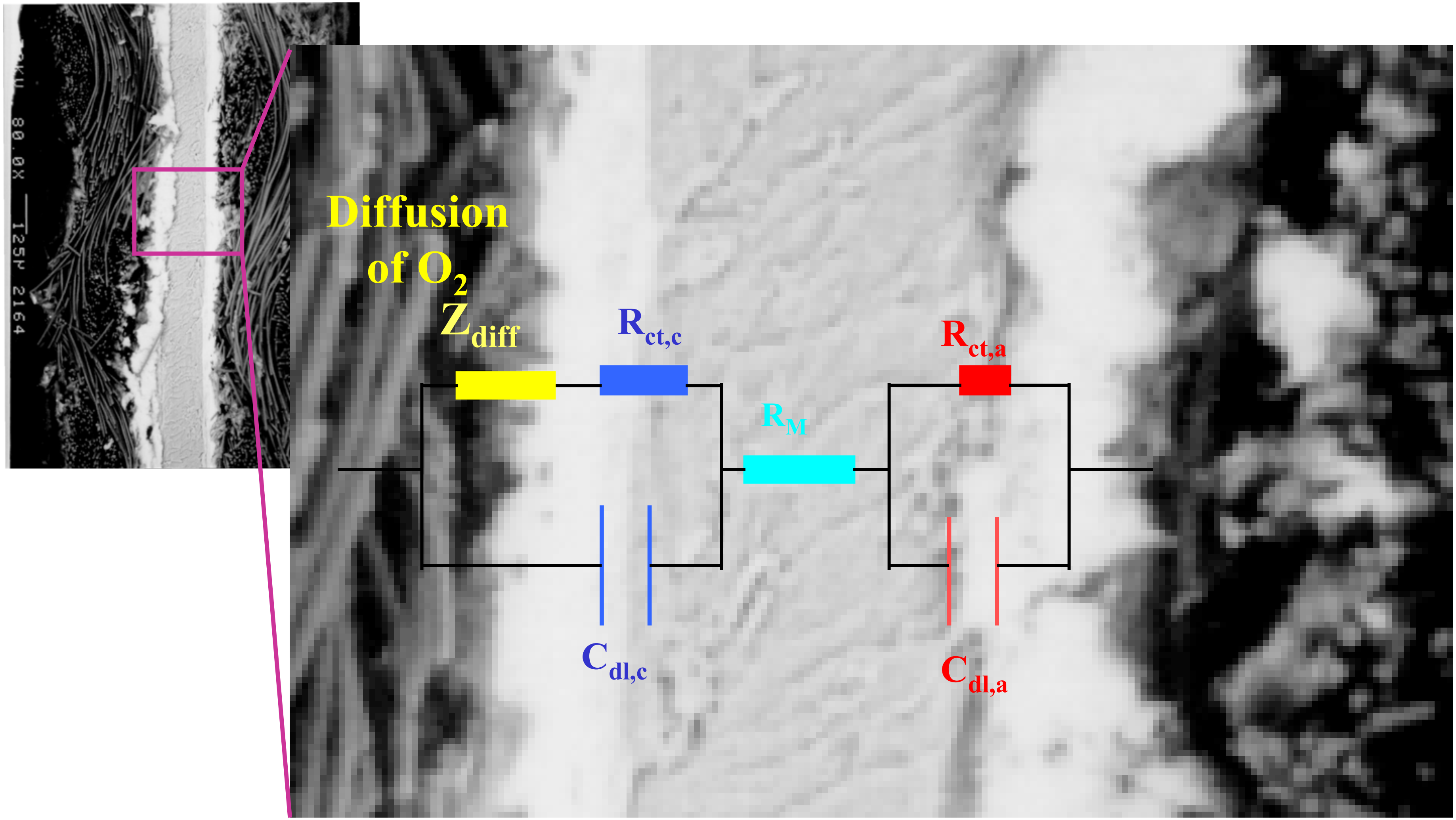
Bode diagram of measured EIS at different cell voltages (current densities) III



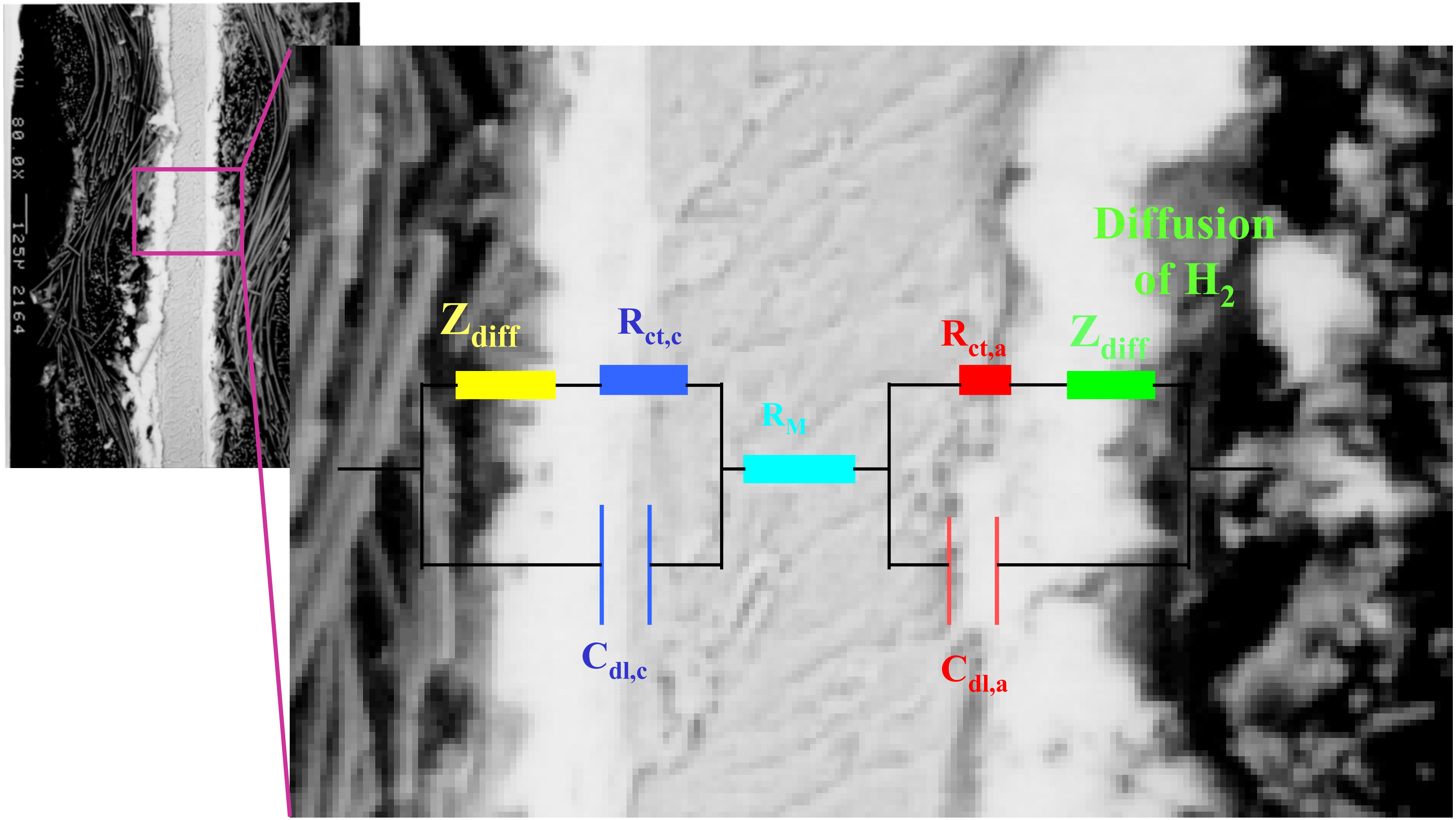
Common Equivalent Circuit for Fuel Cells



Common Equivalent Circuit for Fuel Cells

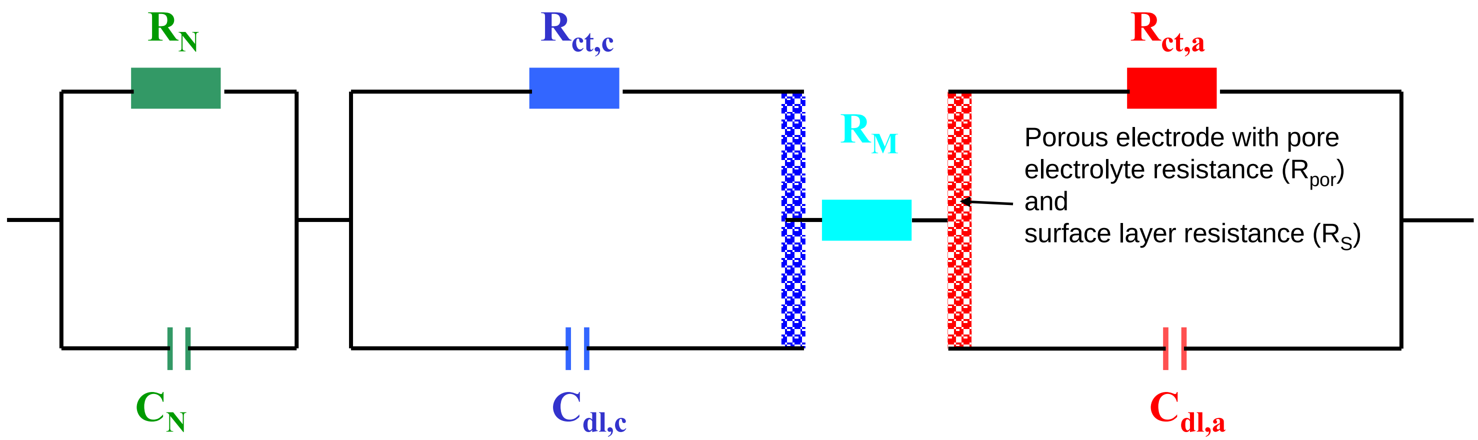


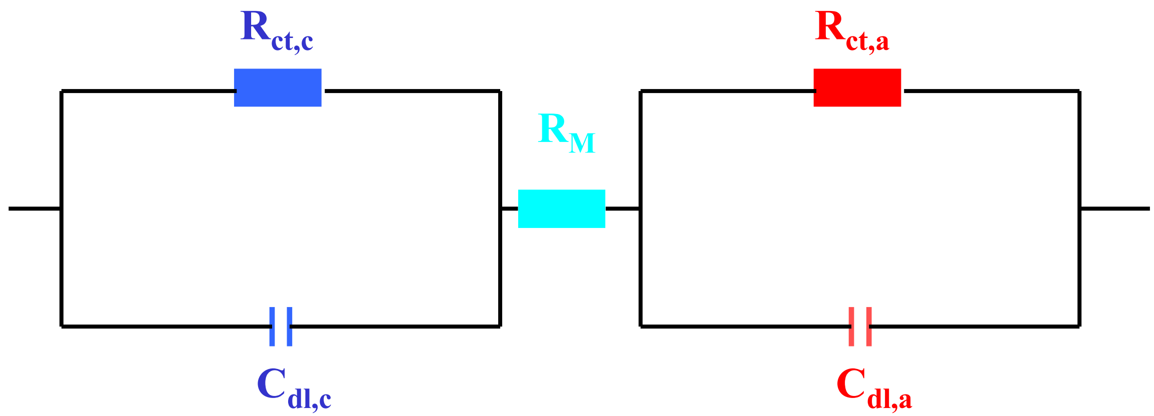
Common Equivalent Circuit for Fuel Cells



EIS at Polymer Fuel Cells (PEFC):

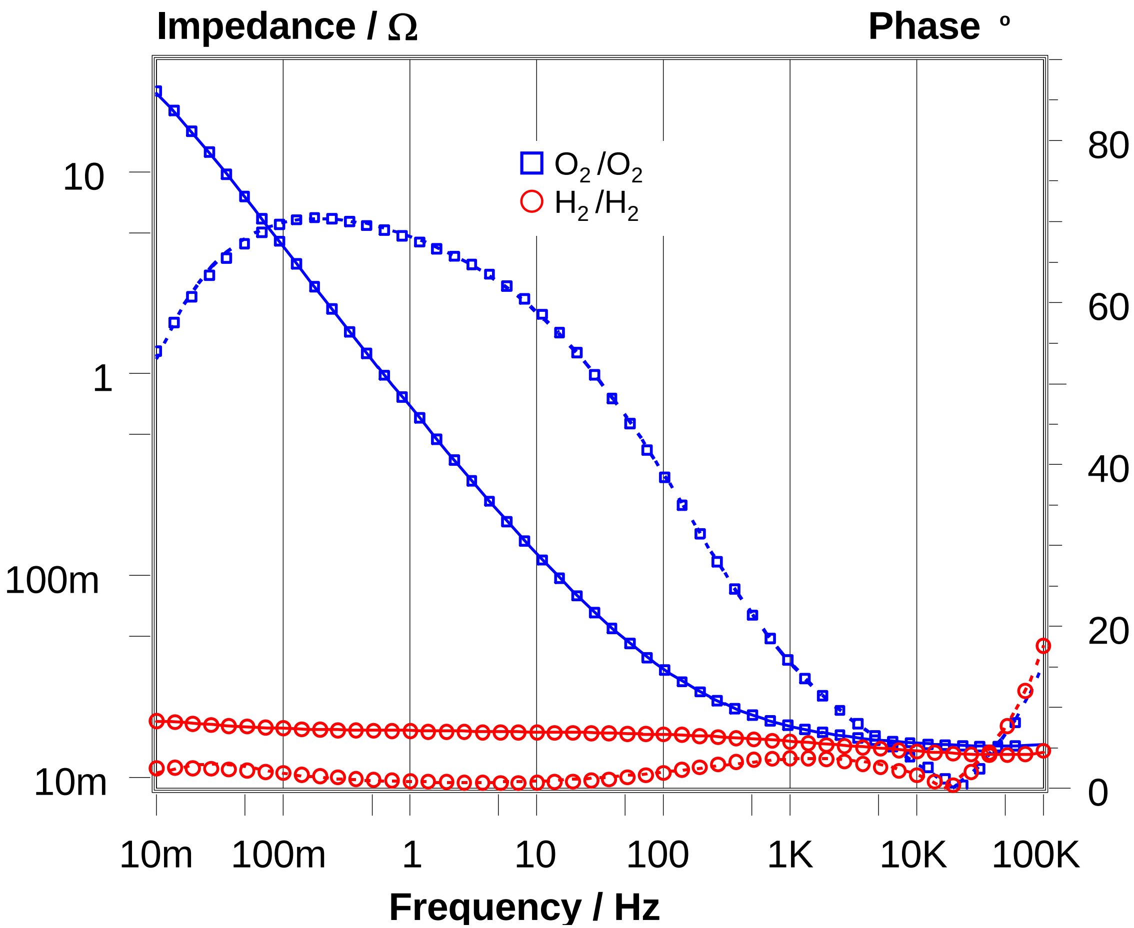
Common equivalent circuit and boundary case





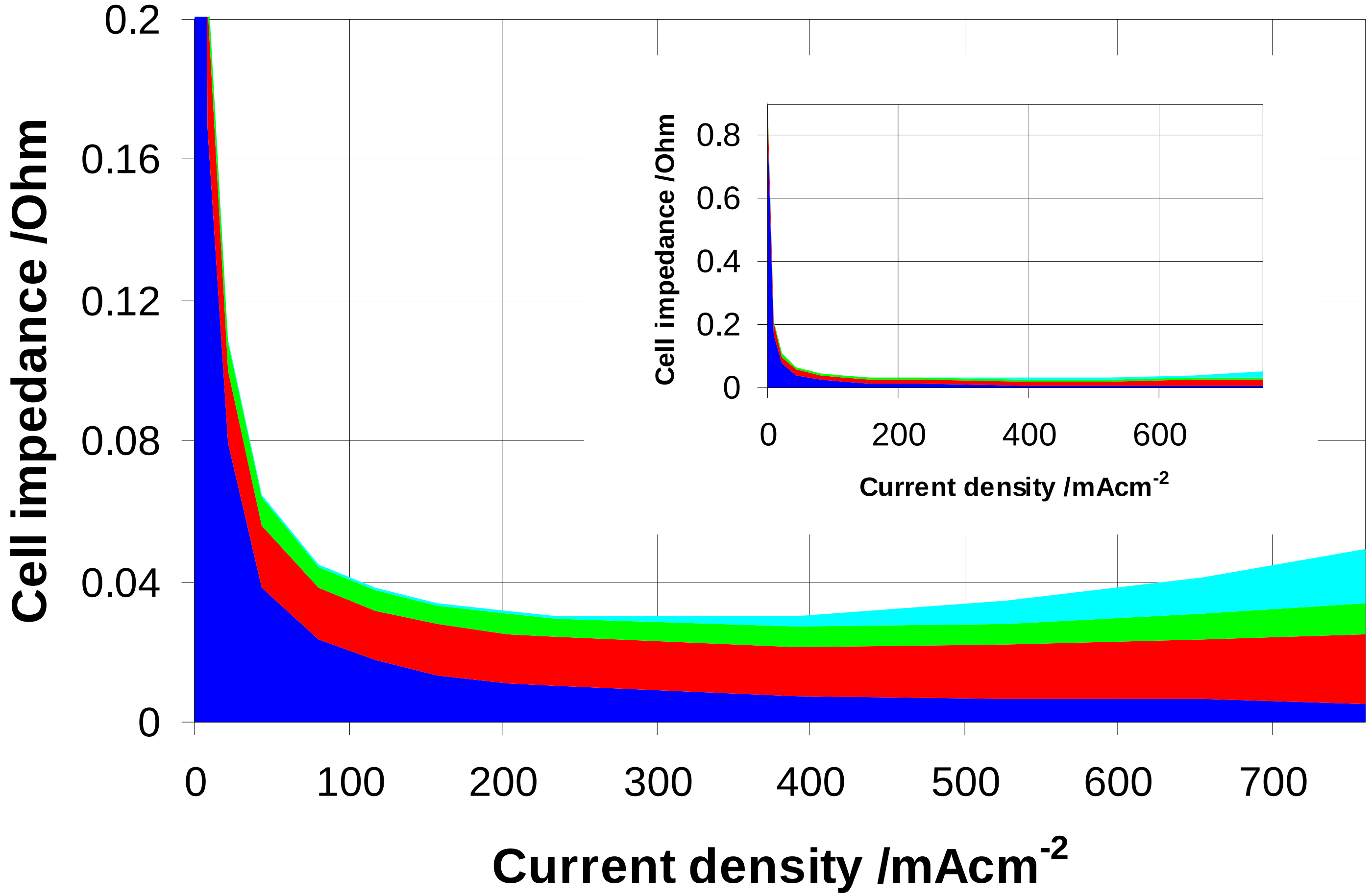
Equivalent circuit of the PEFC: anode and cathode simulated without pores, without diffusion (valid for example at lower current densities)

Bode diagramm of the EIS, measured at the PEFC at 80°C, symmetrical gas supply of the cell

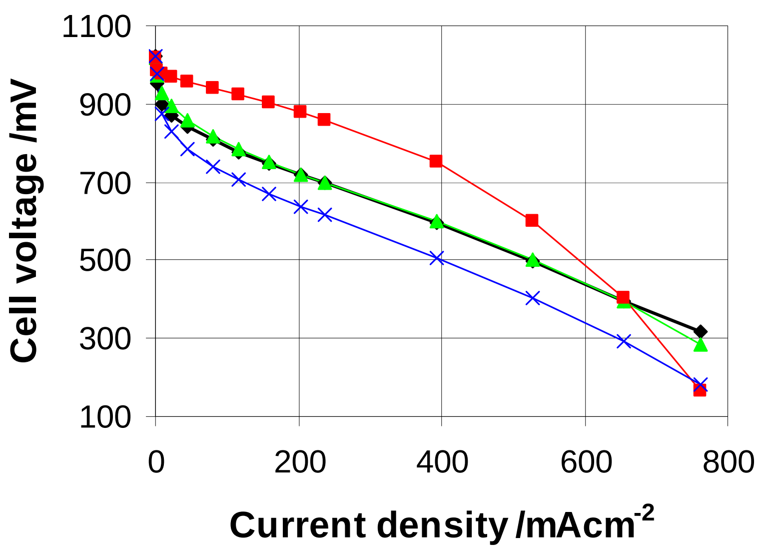


EIS at Polymer Fuel Cells (PEFC):

Contributions to the cell impedance at different current densities



Evaluation of the U-i characteristics from EIS



◆ measured curve: $U_n = f(i_n)$

■ calculated curve: $U_n = i_n R_n$ (without integration)

Δ calculated curve using method II: $U_n = a_n i^2_n + b_n i_n + c_n$

x calculated curve using method I: $U_n = a_n i_n + b_n$

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

Integration method I:

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

Integration method II:

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

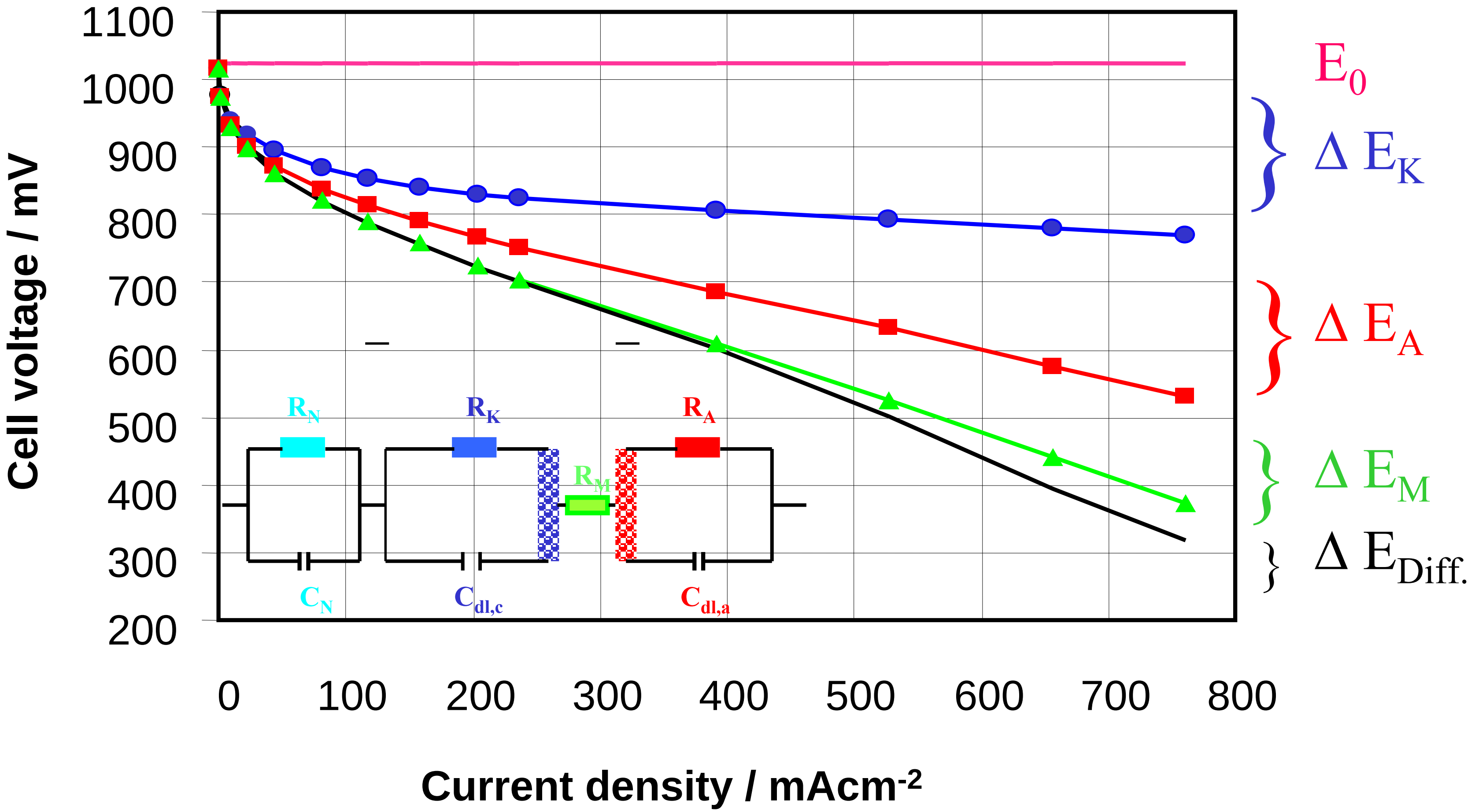
$$a_n = \frac{R_{n+1} - R_n}{2(I_{n+1} - I_n)}$$

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

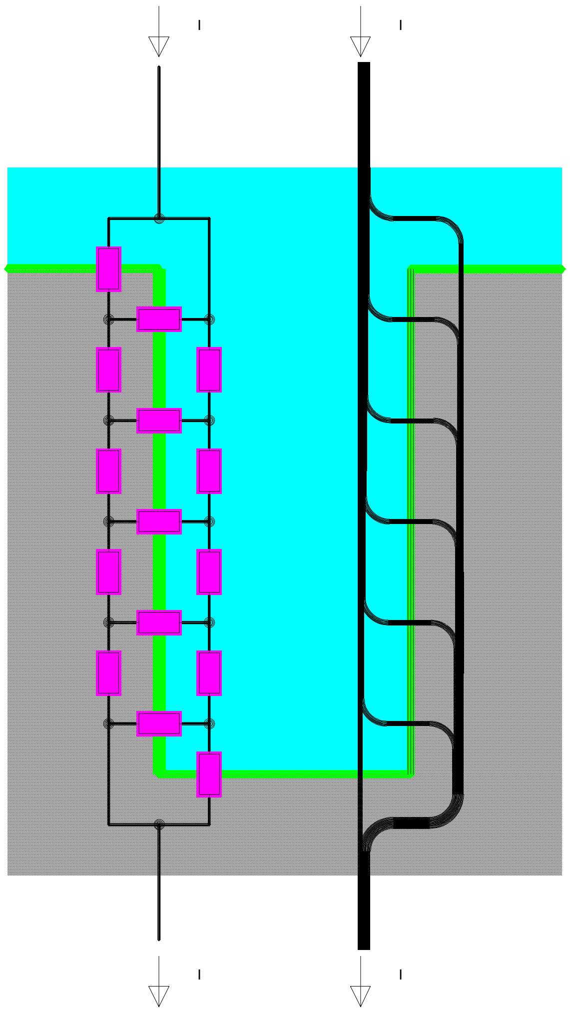
$$c_n = U_{n-1} - a_n I_{n-1}^2 - b_n I_{n-1}$$

EIS at Polymer Fuel Cells (PEFC):

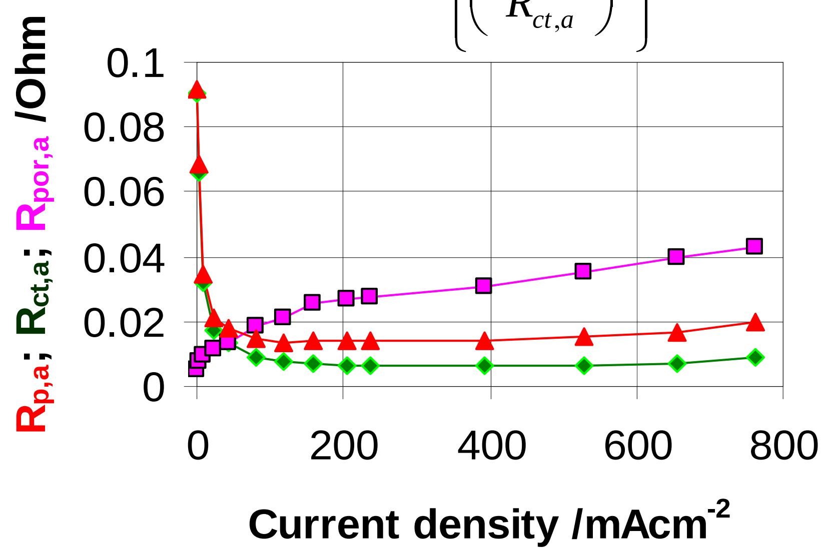
Contributions to the overal U-i characteristic determined by EIS



Evaluation of EIS with the porous electrode model



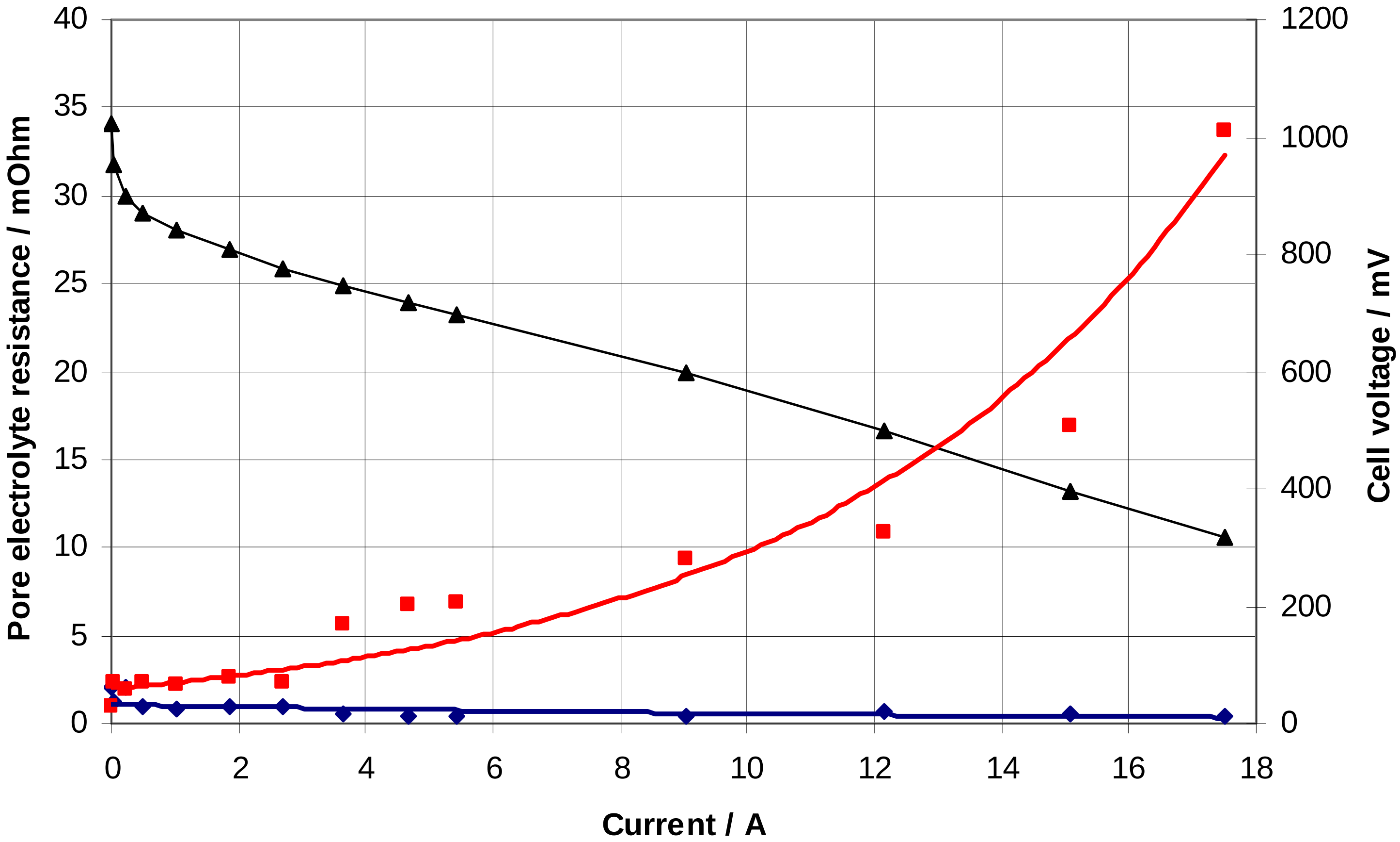
$$R_{p,a} = \frac{(R_{por,a} \cdot R_{ct,a})^{\frac{1}{2}}}{\tanh\left\{\left(\frac{R_{por,a}}{R_{ct,a}}\right)^{\frac{1}{2}}\right\}}$$



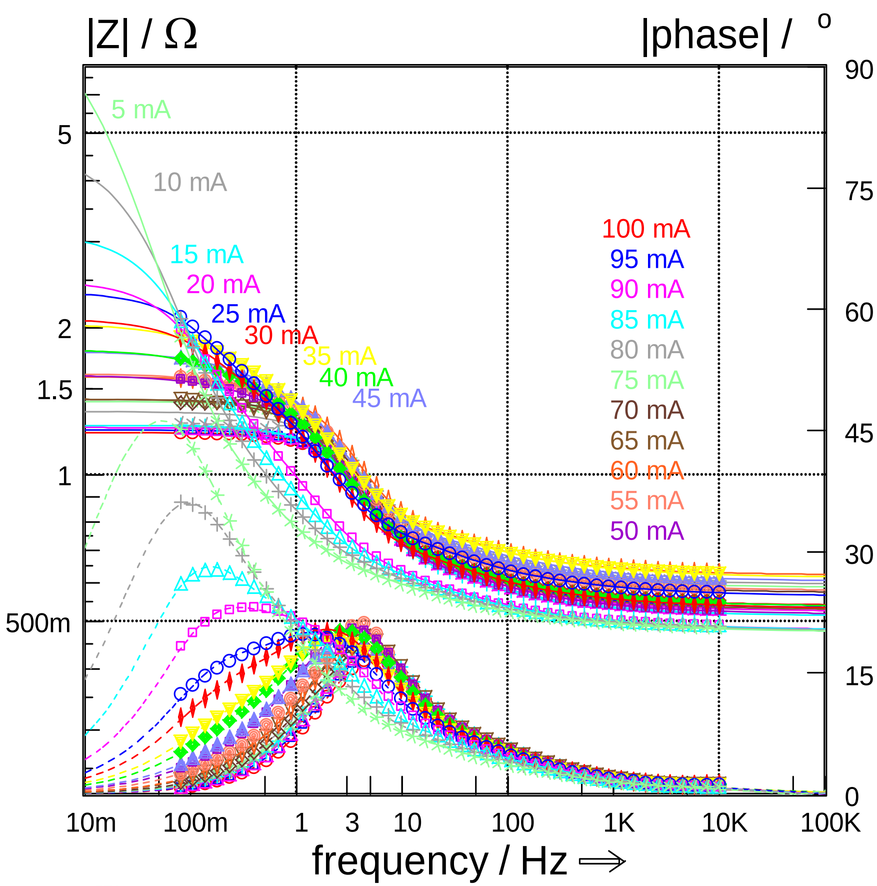
Porous electrode resistance ($R_{p, a}$), charge transfer resistance ($R_{ct, a}$) and electrolyte resistance ($R_{por, a}$) in the pore of the anode at different current densities

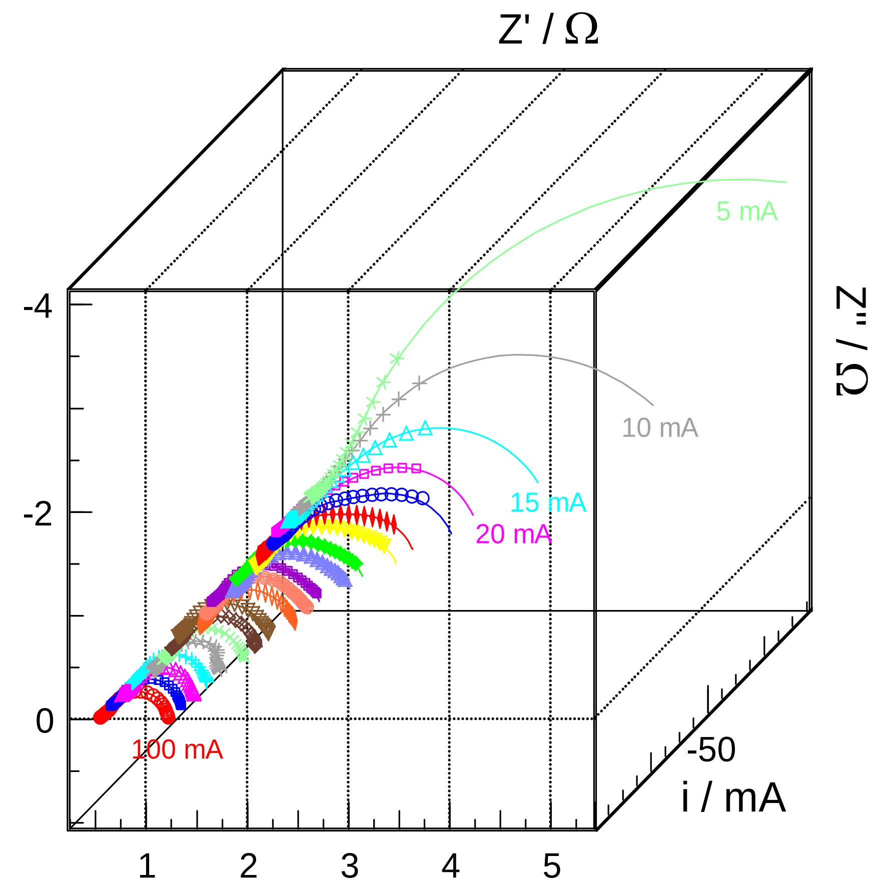
Evaluation of EIS with the porous electrode model

i-V characteristic and current dependency of pore electrolyte resistance of the anode and cathode



Impedance Measurements during Oxygen Reduction Reaction (ORR) in 10 N NaOH, on Silver Electrodes at Different Current Densities





Outlook

- Further improvement of porous electrode models
- Combination and extension of existent and new models
- Application of EiS to segmented cells
- Experimental validation of models using
  - PEFC and DMFC electrodes with different porous structure
  - Gas Diffusion Electrodes (GDE) for Oxygen Consumption Reaction (OCR) in alkaline solution using different gas compositions