Relaxation Impedance –

One Reason for Inductive and Capacitive Behavior in Low Frequency Impedance Spectra of Corroding Electrodes, Batteries and Fuel Cells

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Overview

- Electrochemical systems may exhibit significant inductive contributions to the overall frequency response appearing in particular at low frequencies, when an Ohmic course is expected.

- Also the complementary behavior may occur: Expected is a monotonous Ohmic course of the low frequency impedance, but instead an additional capacitive loop can be observed.

- Many different mechanisms are discussed in the literature explaining special situations, which are leading to inductive or capacitive behavior of electrochemical systems in the low frequency range.

- A simple mechanism may give a common explanation for a lot of such appearances. It traces back such unexpected reactance contributions to the time dependency of some mediating physical magnitude, affecting the impedance.

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Example* EIS at Polymer Fuel Cells (PEFC):
Contributions to the overall U-i characteristic can be determined by EIS
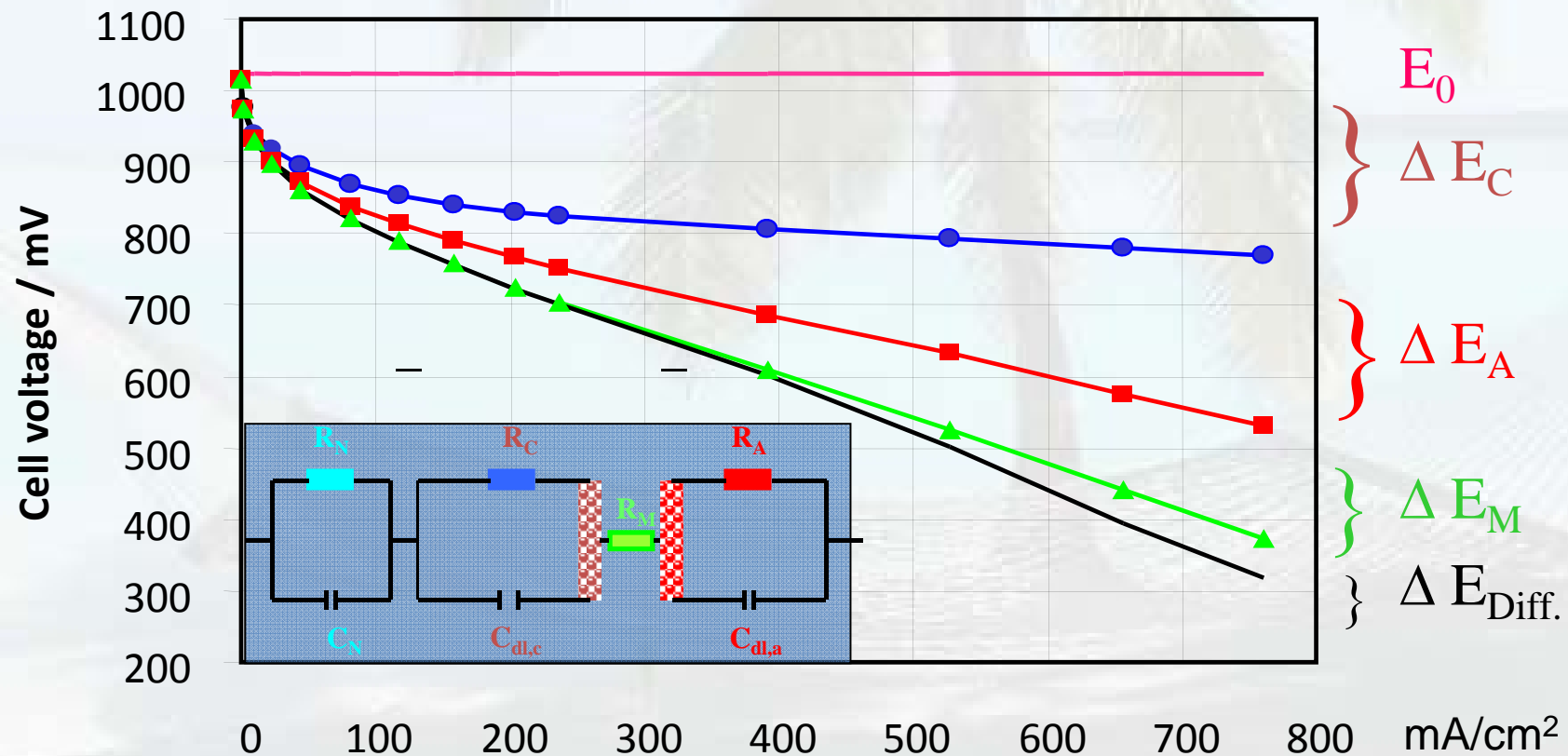
*N. Wagner, Electrochemical Power Sources – Fuel Cells, Impedance Spectroscopy: Theory, Experiment, and Applications, 2nd Edition, Edited by Evgenij Barsoukov and J. Ross Macdonald, John Wiley & Sons, Inc. (2005) 497-537, ISBN: 0-471-64749-7

How Do We Model the Faraday Impedance?

Dynamic transfer function Z_F between AC current $\tilde{I}_F$ and AC voltage $\tilde{U}$

$$Z_F = \tilde{U} / \tilde{I}_F, \quad \tilde{I}_F = f(\tilde{A}, \tilde{B}, \tilde{C}, ...; \quad a, b, c, ...)$$

Modulated magnitudes: $\tilde{U}, \tilde{A}, \tilde{B}, \tilde{C}, ...$ Time independent magnitudes: $a, b, c, ...$

"state variables"   "kinetic parameters"

$$\tilde{I}_F = (\partial \bar{I}_F / \partial \bar{U}) \cdot \tilde{U} + (\partial \bar{I}_F / \partial \bar{A}) \cdot \tilde{A} + (\partial \bar{I}_F / \partial \bar{B}) \cdot \tilde{B} + (\partial \bar{I}_F / \partial \bar{C}) \cdot \tilde{C} + ...$$

where $\bar{U}, \bar{I}_F, \bar{A}, \bar{B}, \bar{C}, ...$ denote the non-periodic shares of the magnitudes.

The Charge Transfer Resistance $R_\eta = \partial \bar{U} / \partial \bar{I}_F$: One important contribution to the total Faraday Impedance.

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Butler-Volmer Equation:

$$i = i_0 \cdot \left[\exp(\alpha \cdot z \cdot F \cdot \eta) - \exp(-(1-\alpha) \cdot z \cdot F \cdot \eta)\right]$$

Deduction[*]

$$i = i^+ + i^-$$

$$i^+ = z \cdot F \cdot k^+ \cdot c_A^a \cdot \exp\left(-\frac{W^+}{RT}\right), \quad z > 0, \qquad k^+, k^- : scaling \ factors \ (reaction \ rate$$
$$constants)$$

$$i^- = z \cdot F \cdot k^- \cdot c_B^b \cdot \exp\left(-\frac{W^-}{RT}\right), \quad z < 0, \qquad W^+, W^+ : activation \ energy \ (anod., cathod.)$$

Remarkable simplification: only W^+, W^- depend on the potential!

$$W^+ = W_0^+ - \alpha \cdot z \cdot F \cdot \left(\varepsilon_r - \varepsilon^0 + \eta\right)$$
$$W^- = W_0^- + (1-\alpha) \cdot z \cdot F \cdot \left(\varepsilon_r - \varepsilon^0 + \eta\right)$$

ε_r : reversible reference potential

ε^0 : reversible standard reference potential

η : charge transfer over-potential

Result from the Butler-Volmer Equation

Charge-transfer resistance R_η under the assumption that only the effective activation energies (W^+, W^-) depend on the potential:

$$\frac{1}{R_\eta} = \frac{\partial i}{\partial \eta} = \frac{|z| \cdot F}{RT}\left(\alpha \cdot i^+ + (1-\alpha) \cdot |i^-|\right)$$

$$\frac{1}{R_\eta} = \frac{|z| \cdot F \cdot i_0}{RT} \qquad \textit{at equilibrum}$$

What happens if, for instance, the rate constants k^+, k^- or the symmetry coefficient α would depend on the potential ?

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- Relaxation is assumed as a simple process, resetting a small perturbation (Δ) of a physical quantity (X) with influence on the impedance after a potential or current change according to a first order rate equation involving just one time constant (τ).

$$-\frac{dX_t}{dt} = \frac{1}{\tau} \cdot \left(X_t - \bar{X} \right) \qquad with \quad \bar{X} = stationary\ value$$

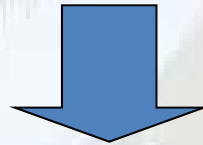- **Consequently X must be considered as a modulated state variable instead as of a steady state kinetic parameter.**

$$\widetilde{X} = \hat{X} \cdot e^{j\omega t} \rightarrow j\omega\widetilde{X} = -\frac{1}{\tau} \cdot \left(\widetilde{X} - \frac{\mathrm{d}X}{\mathrm{d}U} \cdot \widetilde{U} \right)$$

$$for \quad X \equiv k(U) \quad \Rightarrow \quad -\frac{dk_t}{dt} = \frac{1}{\tau_k} \cdot \left(\Delta k - \frac{d\bar{k}}{dU} \Delta U \right) \quad with \quad k = reactionrate\ const.$$

Finding from 1986[*]

R_η — charge transfer resistance

Z_c — concentration impedance

Z_θ — adsorption impedance

$$Z_F = R_\eta + Z_c + Z_\theta$$

$$-\frac{dk_t}{dt} = \frac{1}{\tau} \cdot (k_t - k)$$

$$Z_F = \frac{R_\eta + Z_c + Z_\vartheta}{1 + R_\eta / Z_k} \qquad Z_k = \frac{1 + j\omega\tau}{I_F \cdot d\ln k / d\varepsilon}$$
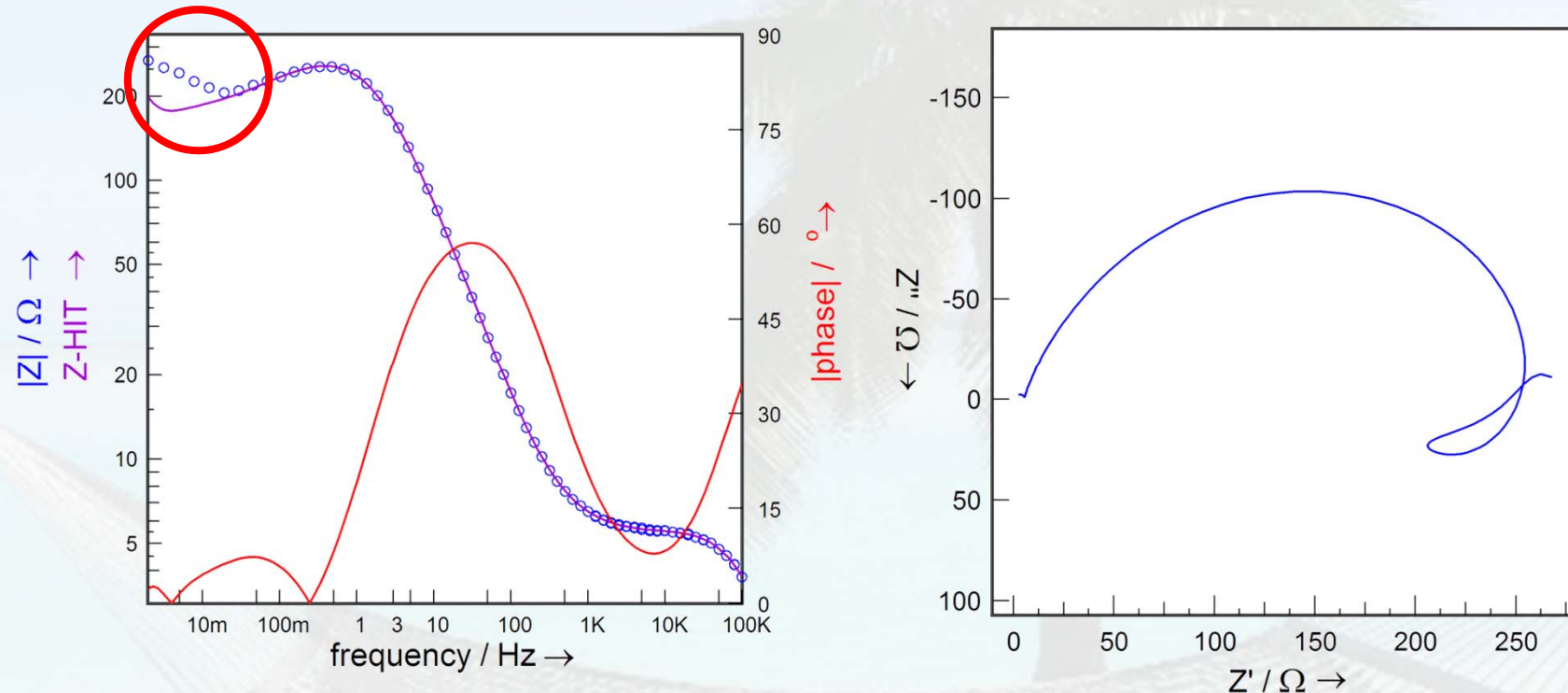
*H. Göhr, C. A. Schiller, *Faraday-Impedanz als Verknüpfung von Impedanzelementen*, ("Faradays Impedance as a Conjunction of Impedance Elements") Z. Phys. Chem. Neue Folge 93 (1986) 105-124

Some Experimental Results for $k=k(U)$ (1992)[*]

Mild steel $Fe_{38}Mn_6$ in aqueous chloride containing electrolyte in presence of CO_2. Potential was around -0.5V vs. SHE. The pink curve in the left diagram is the ZHIT transform of the experimental phase angle data (red curve).

[*]U. Ruhrberg, *Untersuchungen zum Phasengrenzverhalten von grenzflächenaktiven Wirkstoffen bei der Bekämpfung der Stahlkorrosion in Erdgasfördersonden*, Diss. Univ. Bochum (1992).

Some Experimental Results for $k=k$ (U) (2001)[*]
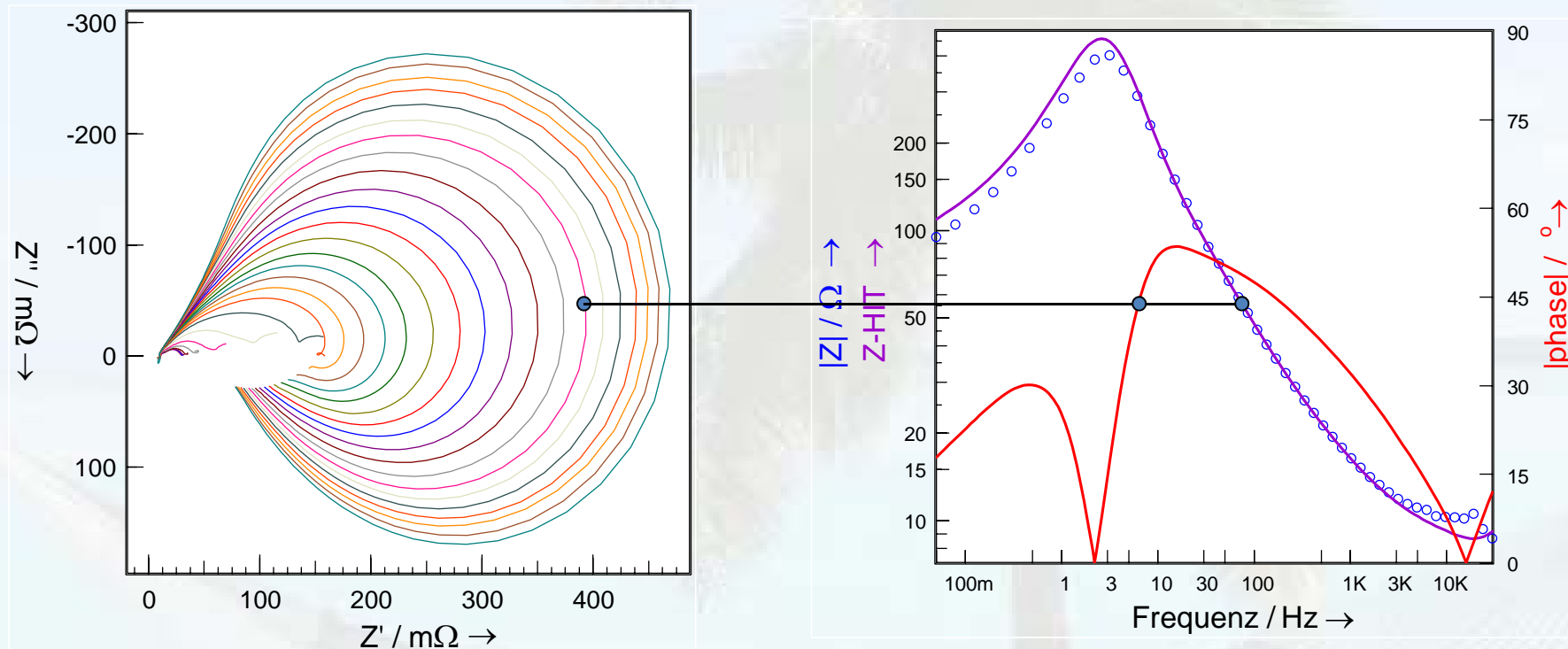
23cm²-PECF-single cell at a current density of 217mA/cm². Left: Spectra series (complex plane representation) after starting an aimed poisoning of the anode by adding 100ppm CO to the fuel. Right: One spectrum (Bode representation) after 4h.

[*]C. A. Schiller, F. Richter, E. Gülzow, N. Wagner, *Relaxation Impedance as a Model for the Deactivation Mechanism of Fuel Cells Due to Carbon Monoxide Poisoning*, J. Phys. Chem. Chem. Phys. 3 (2001) 2113.
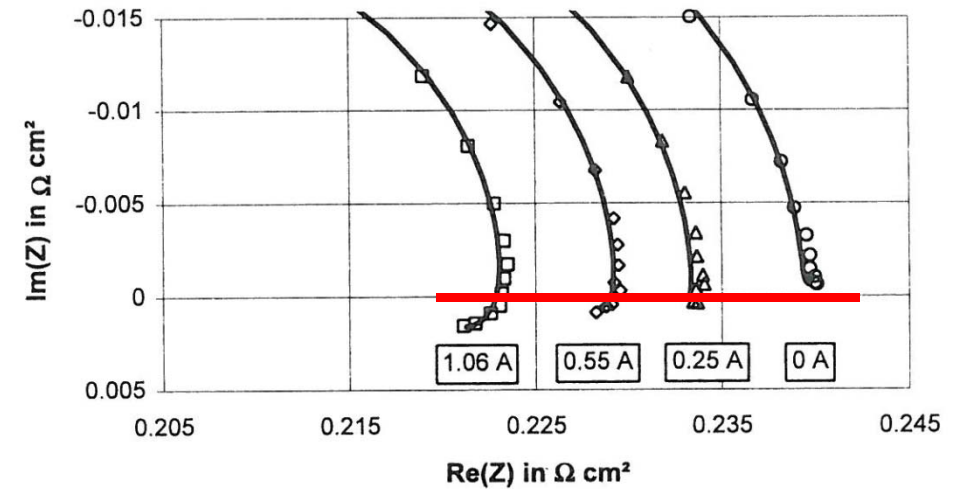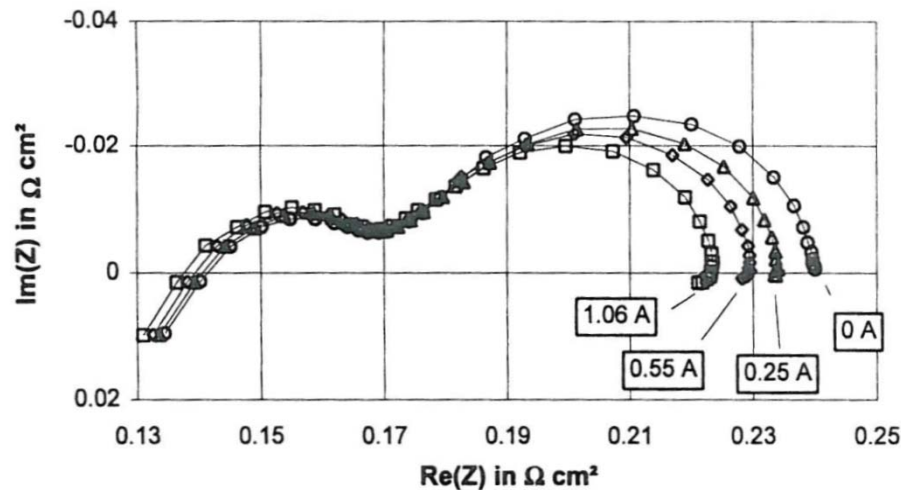
Some Recent Result[*]
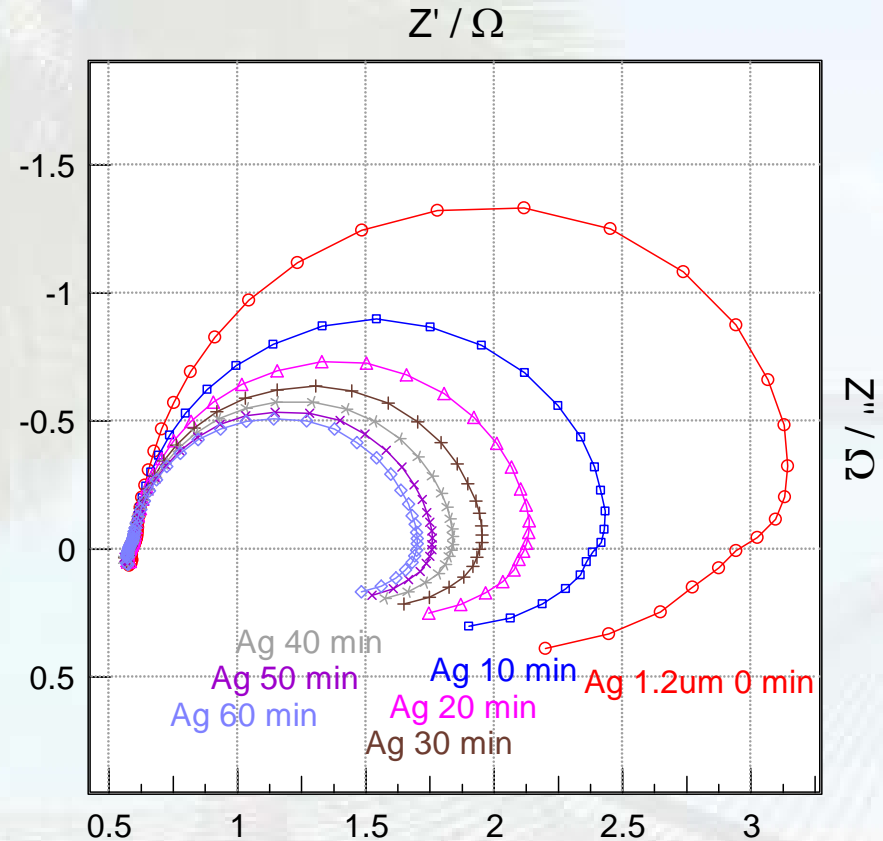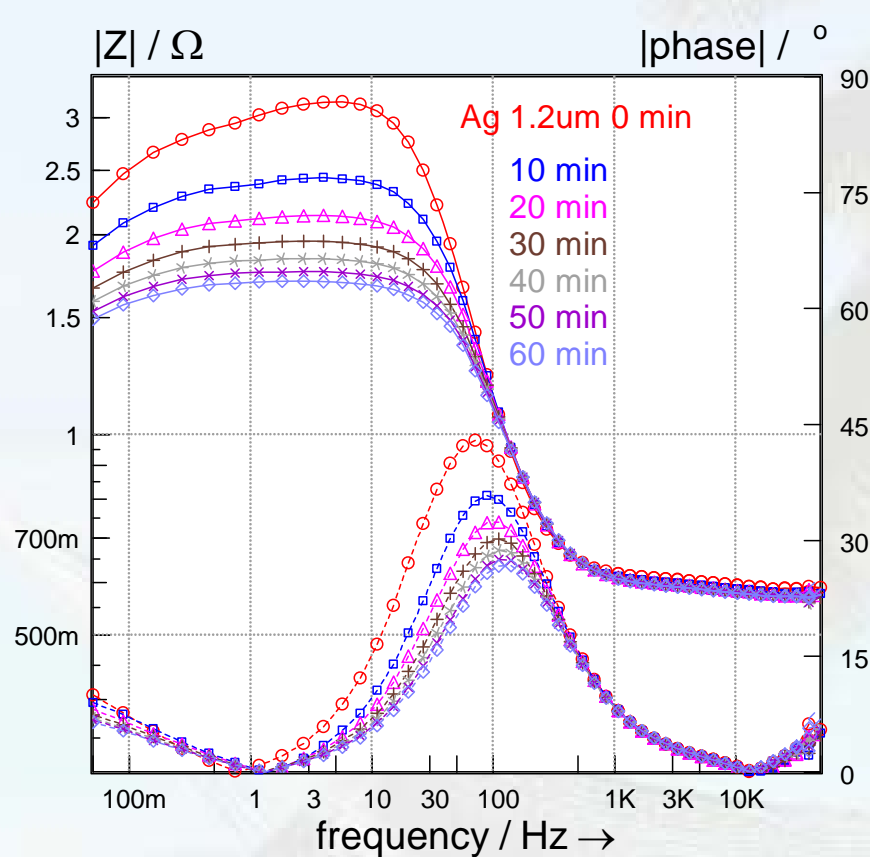
Time dependency of impedance spectra measured at -700 mV vs. Hg/HgO, silver membrane with 1.2 μm pore diameter

[*]N. Wagner, *Electrochemical Characterization of Silver Gas Diffusion Electrodes during Oxygen Reduction in Alkaline Solution*, Lecture at the 9th International EIS Meeting 2013 Okinawa.

$X = X(U, I)$?

- Up till now only the influence of the voltage on kinetic parameters is considered in the examples eg. $k = k(U)$.

- What will happen, if contributions to the impedance on long time scales are influenced in addition by the current?

- Inspiration from literature (H. Landes and A. Hahn 1998): investigations of temperature effects within a high temperature fuel cell (SOFC)

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Some Experimental Results for $X=X(U, I)$, X ≡ T (1998)

Impedance spectra series recorded at an SOFC-MEA at 950°C under different DC load (H. Landes & A. Hahn, thesis of A. Hahn (1998))

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Approach of H. Landes & A. Hahn (1998)[*]

$$Z_{real} = \frac{Z_{ideal} - v \cdot U}{1 + v \cdot I}$$

$$v = \frac{\tanh\left(d \cdot \sqrt{\dfrac{c \cdot \rho}{\lambda} j\omega}\right)}{2 \cdot \lambda \cdot \sqrt{\dfrac{c \cdot \rho}{\lambda} j\omega}} \cdot \frac{dU}{dT}$$

Modeling the thermal flow in a fuel cell in order to estimate the temperature relaxation of the electrolyte resistance

- d: heat penetration depth
- λ: thermal conductivity
- c: specific heat capacity
- ρ: density of heat conducting medium

[*]A. Hahn, Analyse und Optimierung von Zirkoniumoxid-Lanthan-Manganit-Mischgefügen als Kathode in Hochtemperatur-Brennstoffzellen (SOFC), Dissertation Techn. Fak. der Univ. Erlangen-Nürnberg (1998)

$$Z_{R,X} = \frac{R + \left(\dfrac{\partial P}{\partial I}\right)_U \cdot \left(\dfrac{\partial U}{\partial X}\right)_I \cdot \dfrac{dX}{dP} \cdot v}{1 - \left(\dfrac{\partial P}{\partial U}\right)_I \cdot \left(\dfrac{\partial U}{\partial X}\right)_I \cdot \dfrac{dX}{dP} \cdot v}$$

$$R = \left(\frac{\partial U}{\partial I}\right)_X$$

$$v = (1 + j \cdot \omega \cdot \tau)^{-1}$$

$$P = P(U, I)$$

If X represents the temperature T and P the electrical power N ...

$$R = \left(\frac{\partial U}{\partial I}\right)_T = \frac{U_T}{I_T} \quad , \quad R = R_{HF} \quad and \quad V_C = \left(\frac{\partial N}{\partial U}\right)_I \cdot \left(\frac{\partial U}{\partial T}\right)_I \cdot \frac{dT}{dN}$$

…one obtains the expression for $Z_{R,T}$ which has to be verified

$$Z_{R,T} = \frac{R + R \cdot V_C \cdot v}{1 - V_C \cdot v}$$

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Special Impedance Expression for the Relaxation of $T(U, I)$

$$Z_{R,T} = \frac{R + R \cdot V_C \cdot v}{1 - V_C \cdot v}$$

$$v = (1 + j\omega\tau)^{-1}$$

- V_C: dimensionless variation coefficient
- The expression influences the shape of the impedance in **all 4** quadrants of the complex plane

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The Influence of V_C on the Impedance

Parameter V_C	Low frequency limit $Z_0 = Z_R \ (\omega \to 0)$	Low frequency impedance course
$V_C = 0$	$Z_0 = Z_\infty = R_{HF}$	no reactance contribution
$1 > V_C > 0$	$Z_0 > Z_\infty$	capacitive around $\omega \approx 1/\tau$
$-1 < V_C < 0$	$Z_0 < Z_\infty$	inductive around $\omega \approx 1/\tau$
$V_C > 1$	$Z_0 > Z_\infty$, $Z'_0 < 0$!	capacitive around $\omega \approx 1/\tau$
$V_C < -1$	$Z_0 < Z_\infty$, $Z'_0 < 0$!	inductive around $\omega \approx 1/\tau$
$V_C = 1$	$Z_0 \to \infty$	pure capacitive for $\omega << 1/\tau$
$V_C = -1$	$Z_0 \to 0$	pure inductive for $\omega << 1/\tau$

What is a Suitable Reference System for Testing?

- Electrochemical systems like corroding electrodes, batteries, fuel cells exhibit partial aspects i.e. dependence $X(U)$ or $X(I)$ and strong effects appear only in strongly non-stationary systems.

- Temperature dependent resistors can act as suitable reference systems for verifying the theory experimentally in the full parameter range of V_C.

- Reference low frequency EIS measurements on NTC, PTC and light bulbs were performed. They exhibited all expected variations of the relaxation impedance appearance.

- The spectra could successfully modeled by means of the Relaxation Impedance Model.

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Fitting of the experimental results using the General Relaxation Model applied on Temperature Relaxation
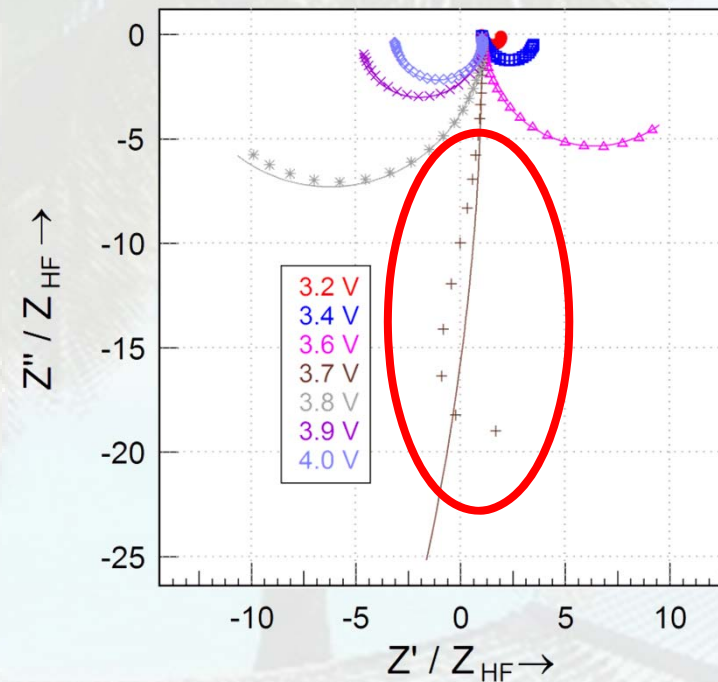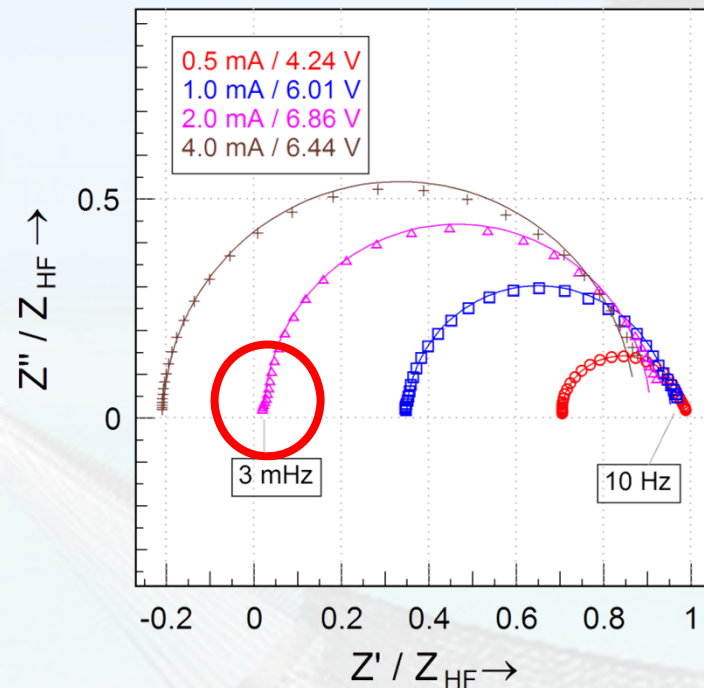
Impedance spectra series of an NTC (left) and a PTC (right) at different dc bias values. Experimental samples are depicted as symbols, fitting results as solid lines.
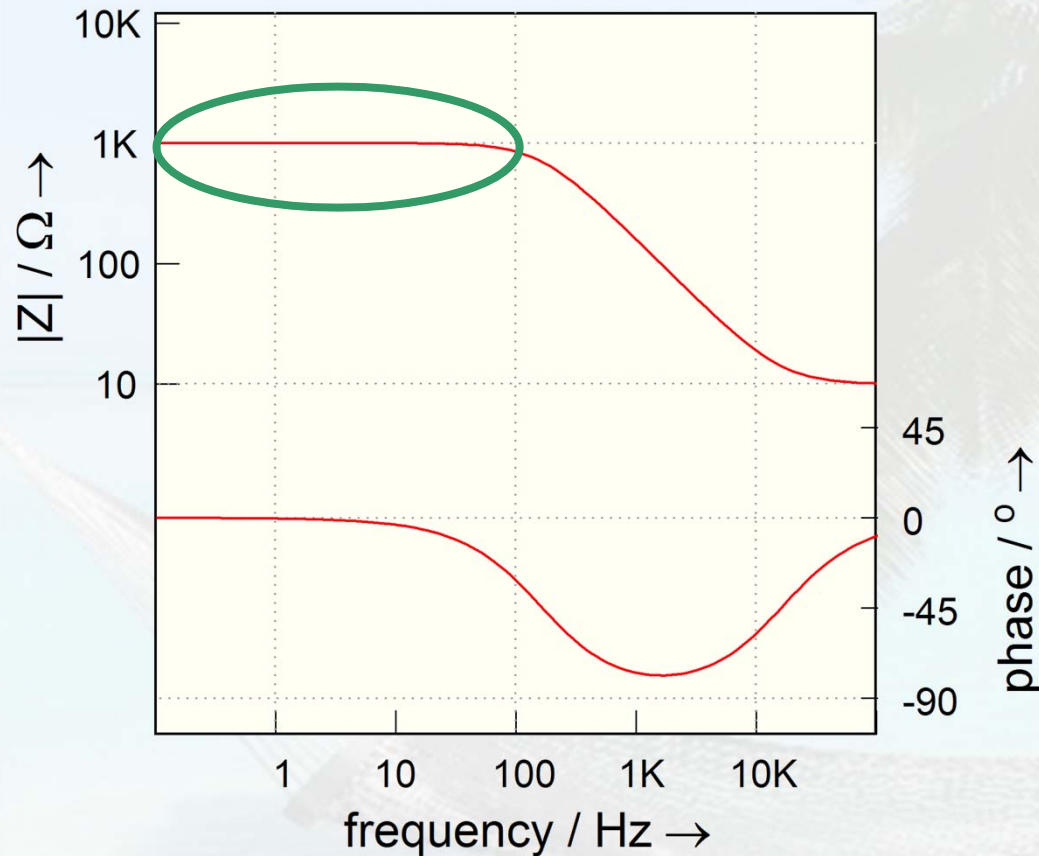
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Summary

- A transfer-function for the comprehensive relaxation impedance was established and verified quantitatively using some reference systems.

- It includes previously found results as special cases.

Conclusions

- Care must be taken in EIS modeling regarding the assignment of impedance relevant magnitudes as modulated "state variables" or as stationary "kinetic parameters" – relaxation processes may be present.

- Neglecting relaxation effects may result in erroneous conclusions, deducing DC-data from AC-experiments

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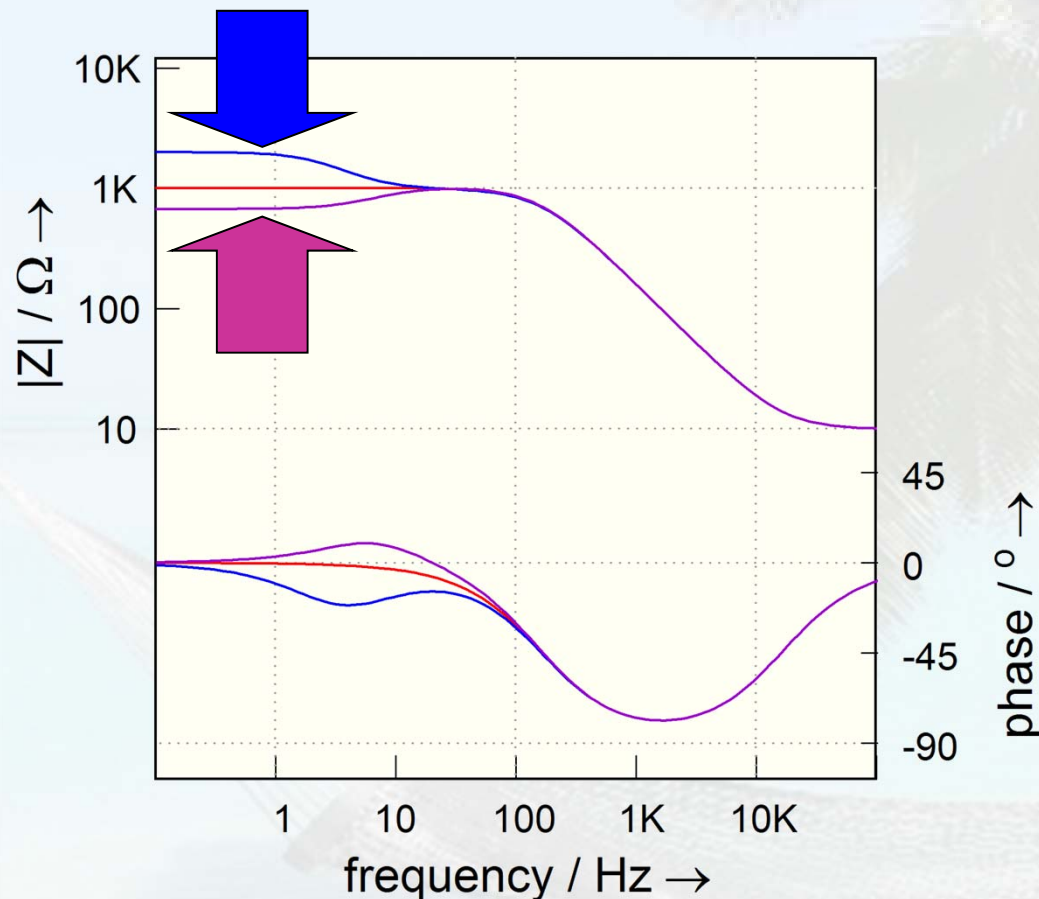
Conclusion

Relevant frequency range for the detection of for instance

- Polarization resistance in fields of corrosion

- Charge transfer resistance of battery and fuel cell electrodes

- Gas diffusion limit resistance of a fuel cell anode

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Relaxation contribution in the case of a passivation process

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Conclusion

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Relaxation contribution in the case of a passivation process

Relaxation contribution in the case of an activation process

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Thank you for your attention !
Consider relaxation...

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$$\tilde{X} = \hat{X} \cdot e^{j\omega t} \rightarrow j\omega \tilde{X} = -\frac{1}{\tau} \cdot \left(\tilde{X} - \frac{\mathrm{d}X}{\mathrm{d}U} \cdot \tilde{U} \right)$$

$$for \quad X \equiv k(U) \quad \Rightarrow \quad -\frac{dk_t}{dt} = \frac{1}{\tau_k} \cdot \left(\Delta k - \frac{d\bar{k}}{dU} \Delta U \right) \quad with \quad k = reaction \, rate \, const.$$

Cartoon showing the deposition of PTFE on the porous silver membrane

Silver membrane,
Electrolyte,
Inner PTFE layer (1st deposition),
Outer PTFE layer (2nd deposition),

Catalytically active area
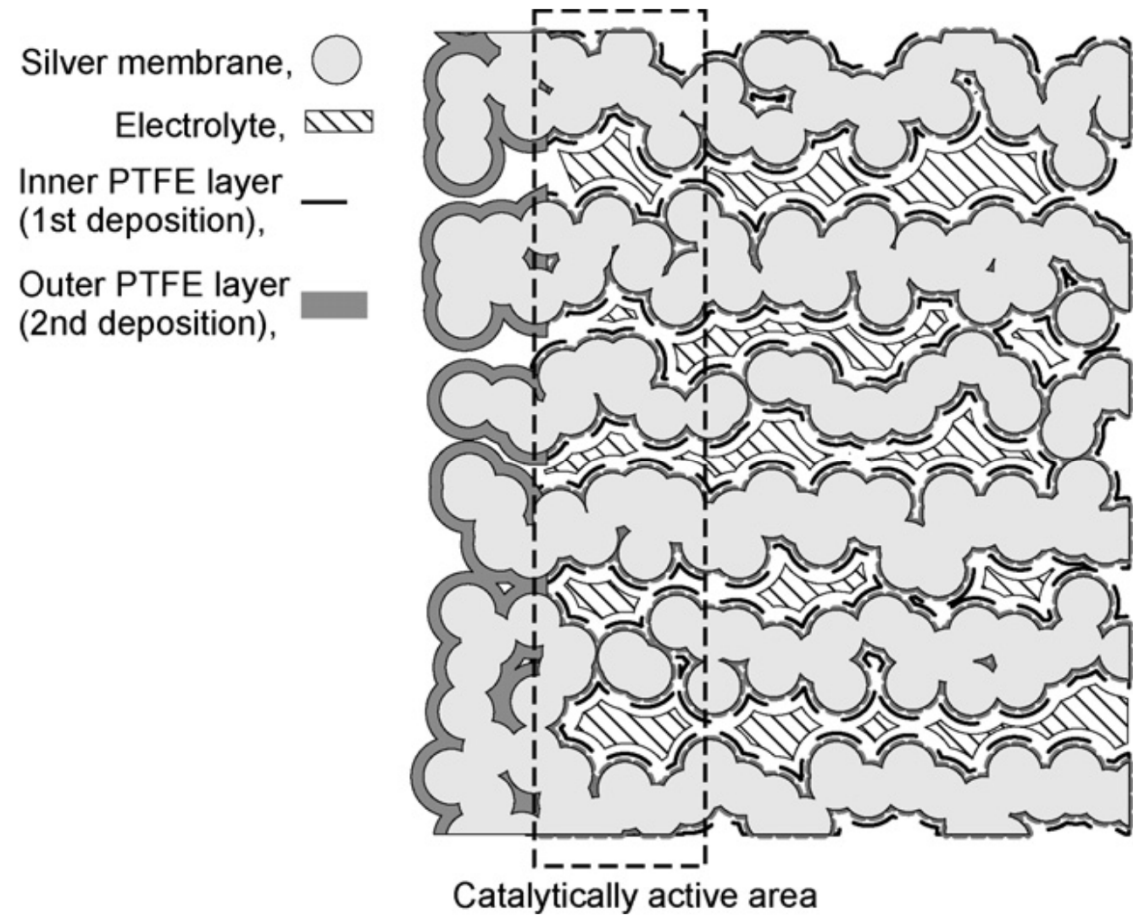
Cartoon showing the deposition of PTFE on the porous silver membrane and GDL from SGL (Sigracet 35 DC)
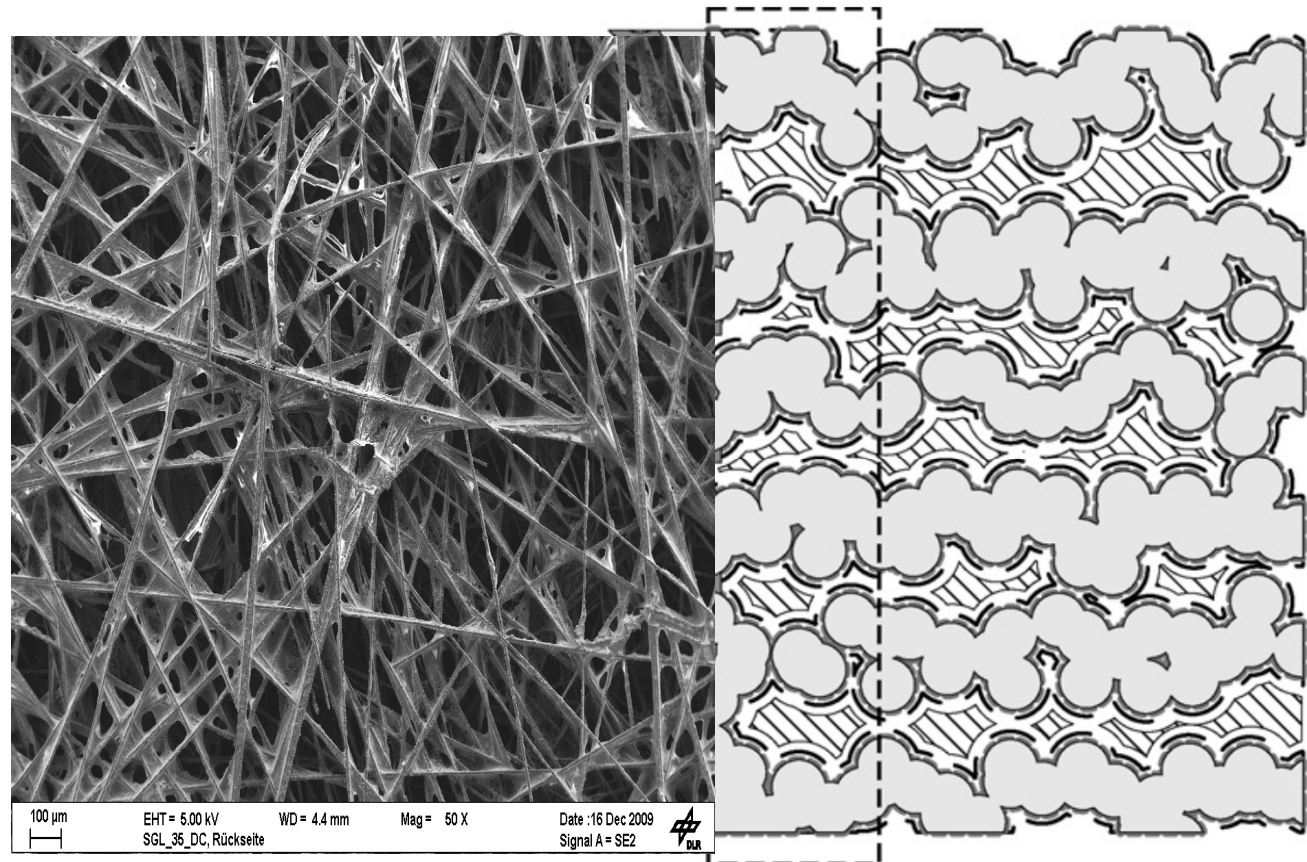
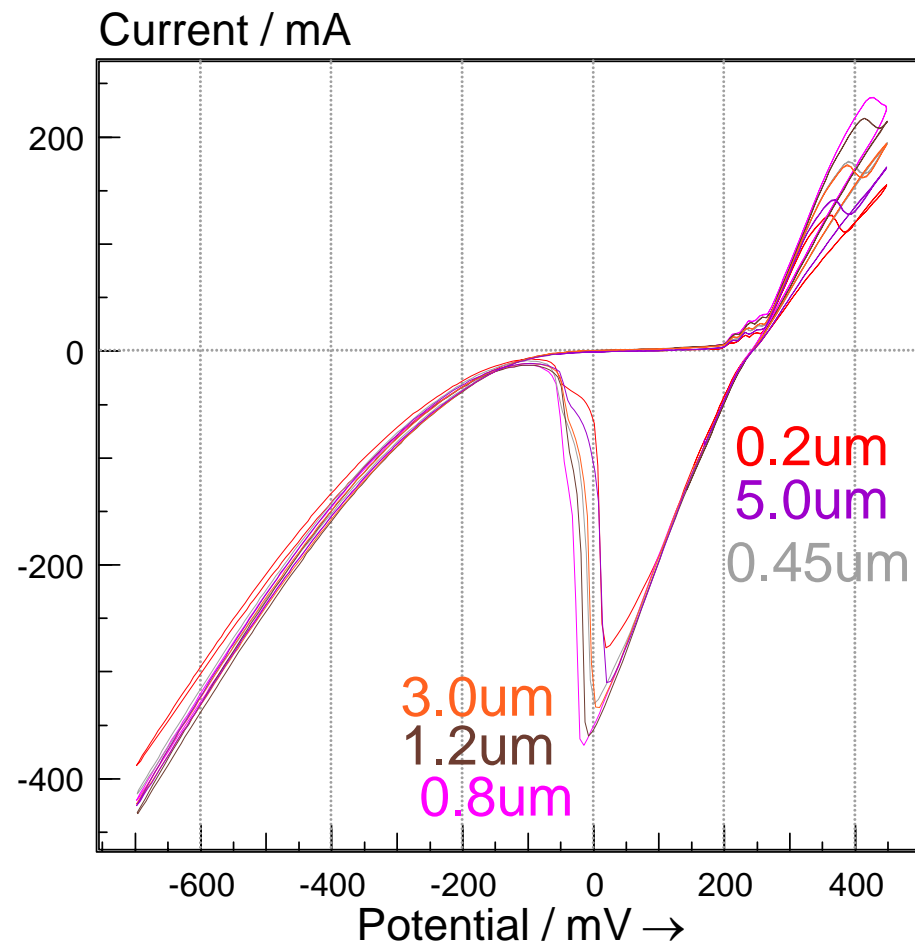**GDL from SGL (Sigracet 35 DC)**   Catalytically active area

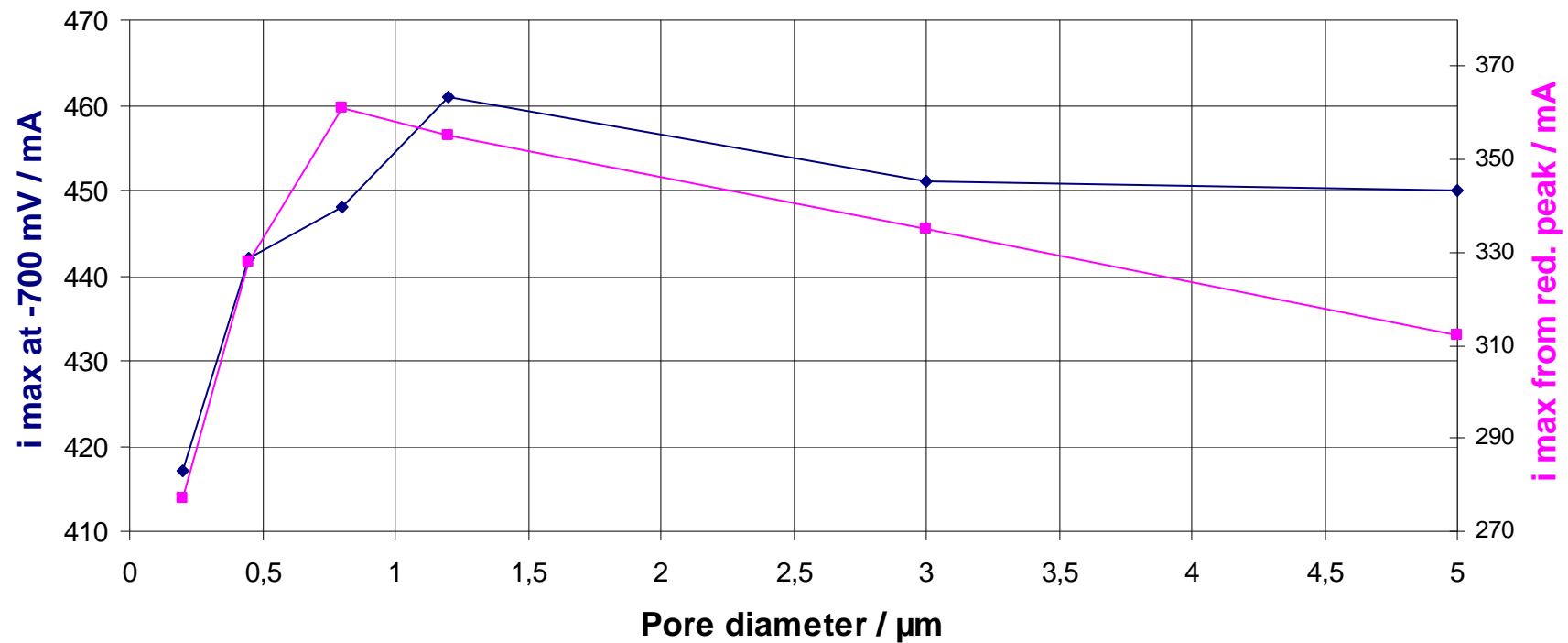# SEM picture of the silver membrane with 0.2µm pore diameter from Sterlitech Inc. (USA)
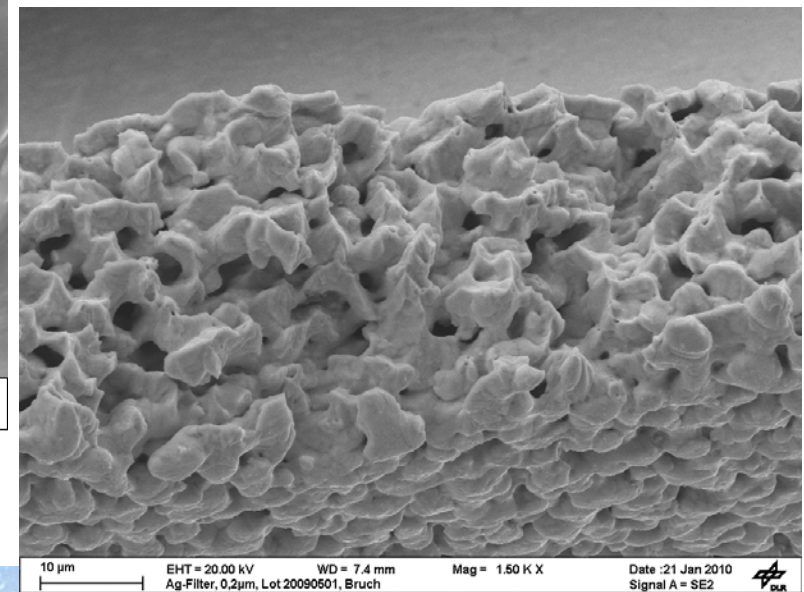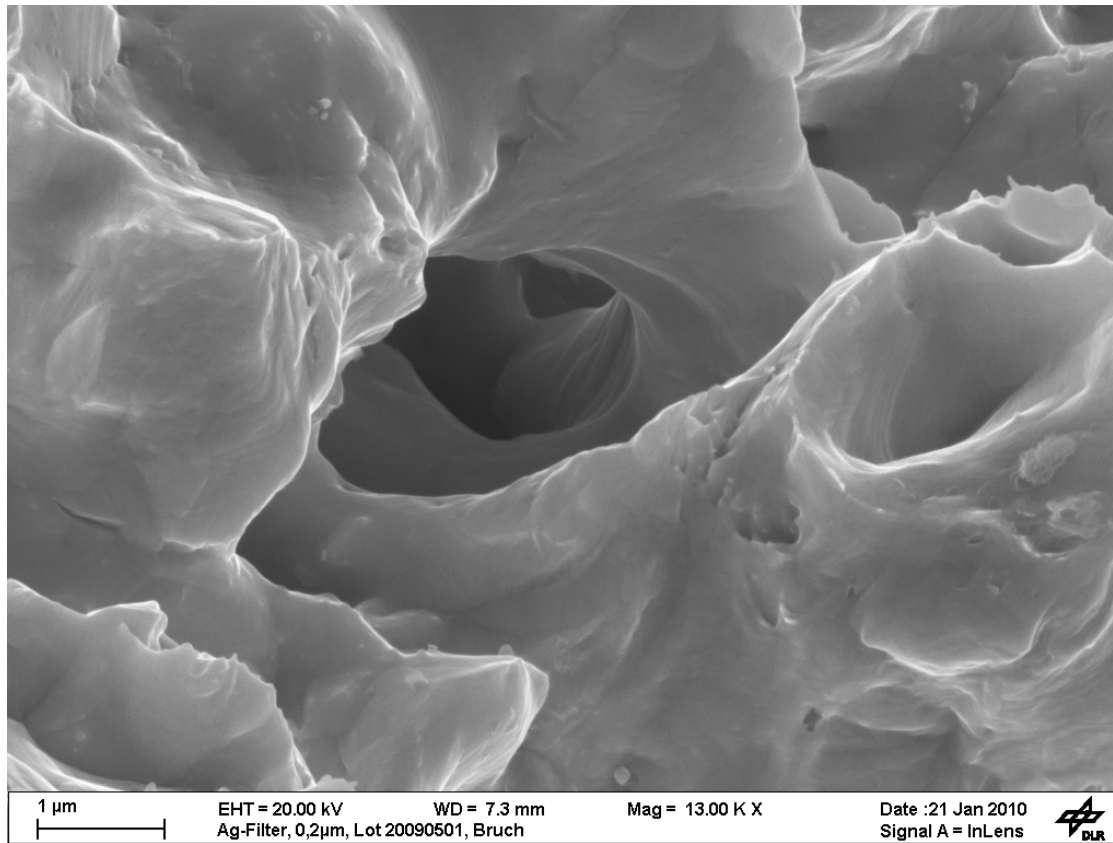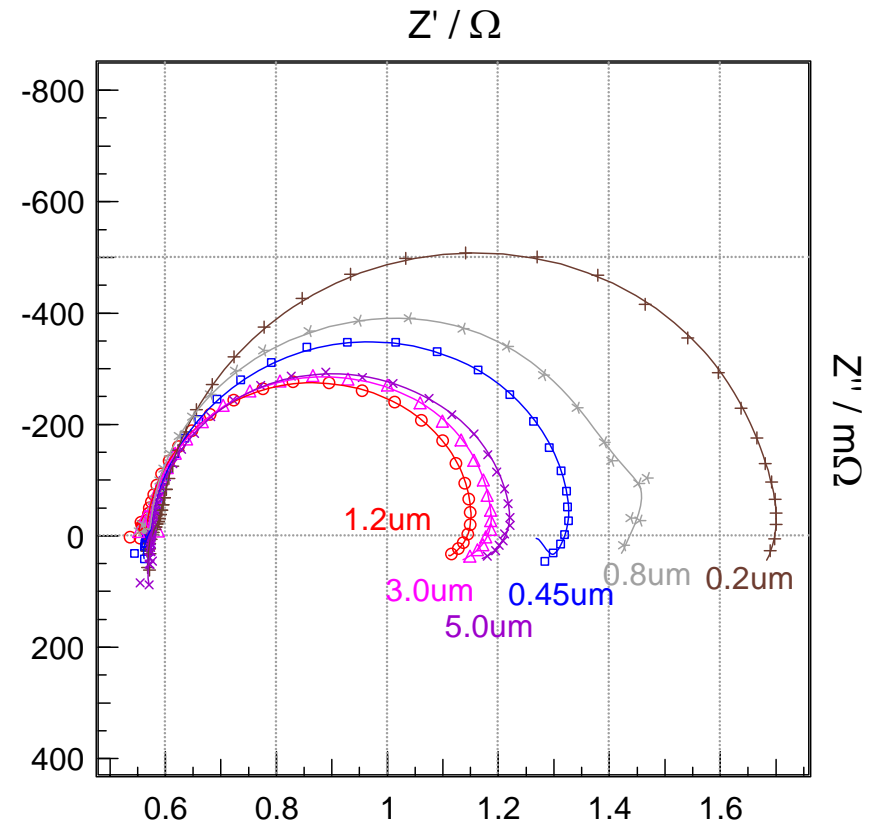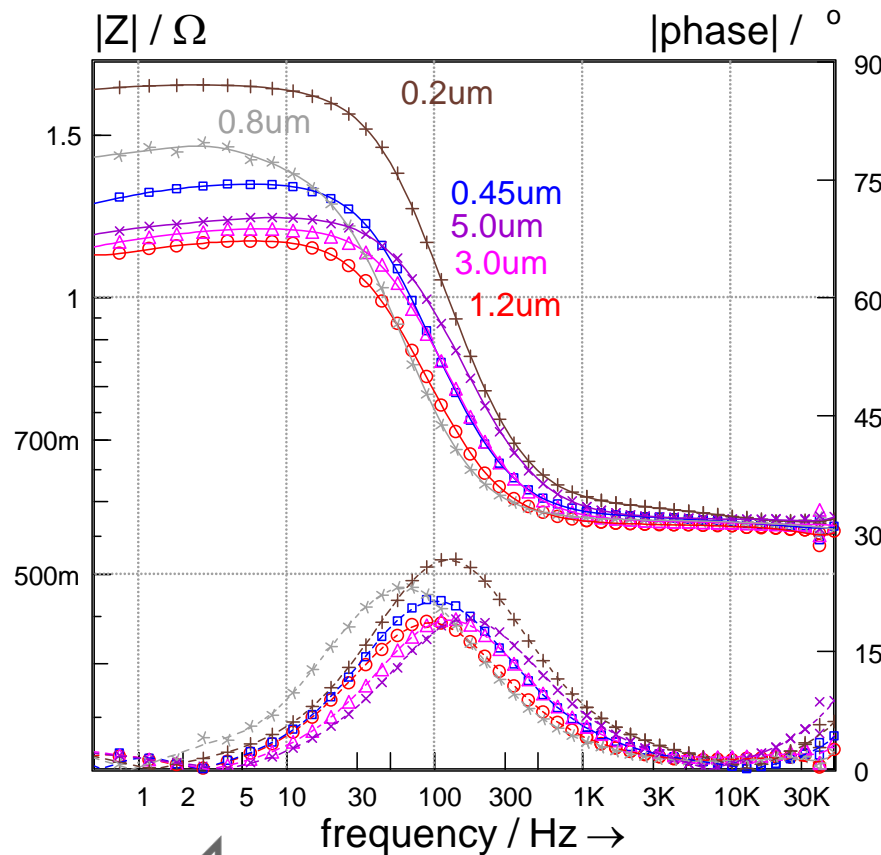
CV with 1 mV/s at 80°C in 10 M NaOH, O$_2$
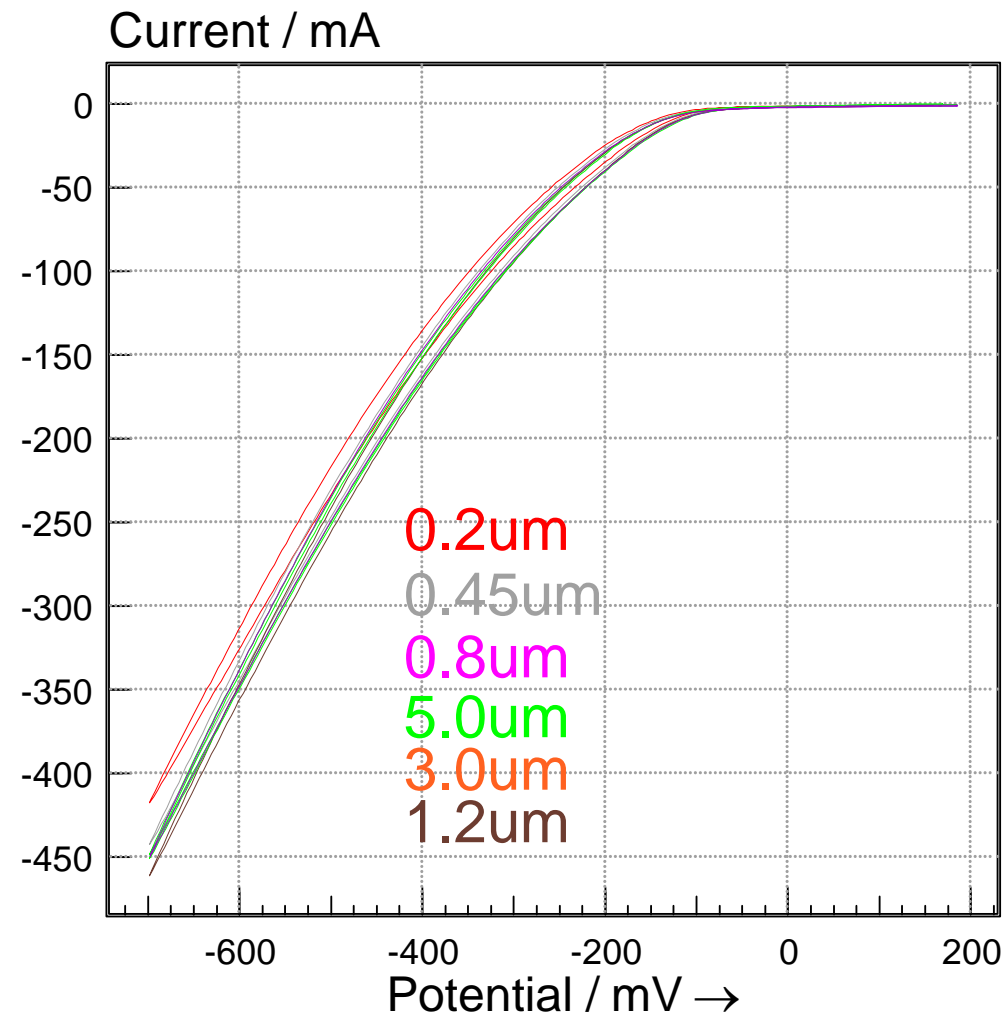
CV's (1 mV/s) from -700 mV to 450 mV vs. Hg/HgO at 80°C in 10 M NaOH, O$_2$

Current density at -700 mV vs. Hg/HgO and i_{max} in the reduction peak in function of the pore diameter

Comparison of measured impedance spectra, measured in 10 M NaOH at 80°C, -700 mV vs. Hg/HgO after 60 minutes

Time dependency of impedance spectra measured at -700 mV vs. Hg/HgO, silver membrane with 1.2 µm pore diameter