



Efficient parameter estimation impedance-based sensors by local, linear transformation

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10th International Symposium on
Electrochemical Impedance Analysis 2014

04.06.2014 Borovetz, Bulgaria

Outline

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- Demonstration for model data
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 - ? Evaluation of results

Motivation

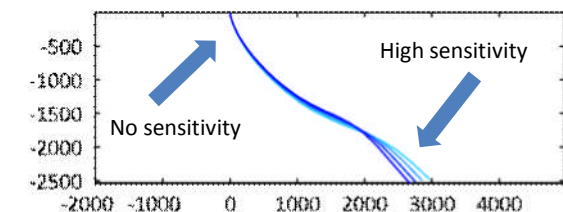
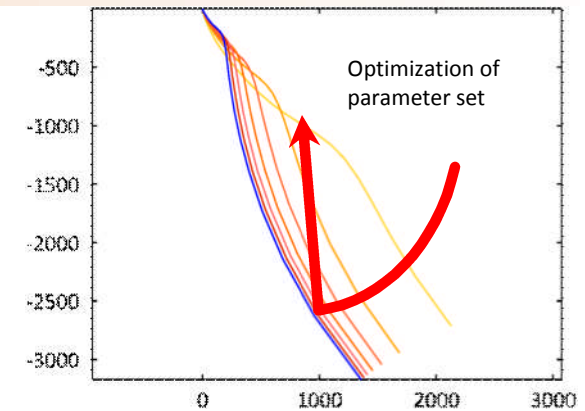
Extraction of spectral information often requires non-linear regression by iterative algorithms

Consequences :

- High computational effort for nonlinear fitting
- Suitable model must be found
- Increased effort by computation-intensive models

Alternative approach:

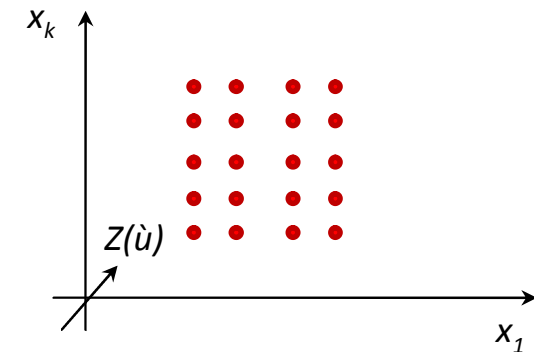
- Parts of the spectra are sensitive to targeted quantity
- Sensitivity means information on this quantity
- Can sensitivity be used to obtain the quantity ?



General Approach

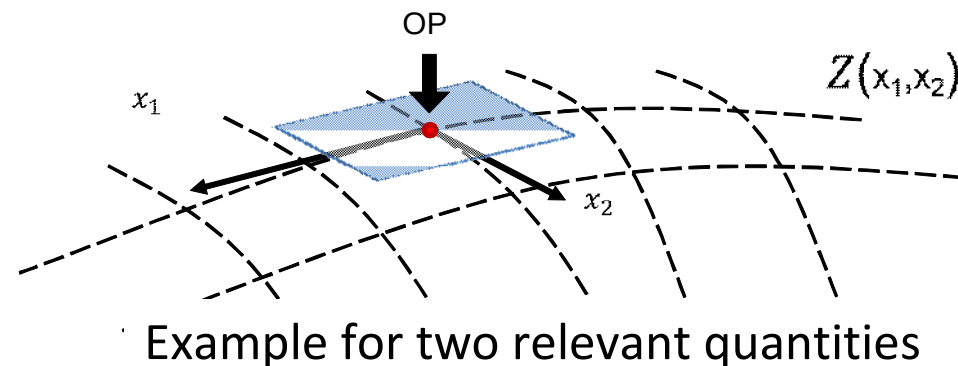
Initial conditions:

- set of impedance spectra for various quantities
- obtained by measurement or calculated by model



Linearization at the operating point for each frequency:

$$\tilde{Z} = \sum_{k=1}^m \frac{\partial Z}{\partial x_k} \Delta x_k + Z_{OP}$$



Selection of frequencies with high sensitivity and high linear independency

Linear transformation in order to separate influence of different relevant quantities

General Approach – linear transformation

Aim: Transformation of data to obtain the targeted quantity

Approach: Weighted sum of impedance

$$x_1 \sim a_1 Z_1 + a_2 Z_2 + \dots + a_p Z_p = \sum_{n=1}^p a_n Z_n$$

Weighted Sum of those linear approximations can be rearranged

$$\sum_{n=1}^p a_n \tilde{Z}_n = \underbrace{\sum_{k=1}^m \left(\left[\sum_{n=1}^p \frac{a_n \partial Z_n}{\partial x_k} \right] \Delta x_k \right)}_{\text{Weighted sum of individual sensitivities}} + \underbrace{\sum_{n=1}^p a_n Z_{OP,n}}_{\text{Weighted sum of constants}}$$

Weighting factors a_n are variable $\rightarrow$ adjustable sensitivity of the sum

General Approach – linear transformation

$$\sum_{n=1}^p a_n \tilde{Z}_n = \sum_{k=1}^m \left(\left[\sum_{n=1}^p \frac{a_n \partial Z_n}{\partial x_k} \right] \Delta x_k \right) + \sum_{n=1}^p a_n Z_{OP,n}$$



Measurand x_1

Cross sensitivities

$$\left. \begin{aligned} \sum_{n=1}^p a_n \frac{\partial Z_n}{\partial x_1} &= S_1 \\ \sum_{n=1}^p a_n \frac{\partial Z_n}{\partial x_2} &= 0 \\ &\vdots \\ \sum_{n=1}^p a_n \frac{\partial Z_n}{\partial x_m} &= 0 \end{aligned} \right\} \begin{array}{l} \text{Sensitivity of the} \\ \text{entire sum can be} \\ \text{defined} \end{array}$$

The individual sensitivities need to be linearly independent
→ Suitable selection of the sampling points required

General Approach – linear transformation

Reduced sensitivity to one parameter

$$\sum_{n=1}^p a_n \frac{\partial Z_n}{\partial x_1} = S_1$$

$$\sum_{n=1}^p a_n \frac{\partial Z_n}{\partial x_2} = 0$$

$\vdots$

$$\sum_{n=1}^p a_n \frac{\partial Z_n}{\partial x_m} = 0$$

- Derived impedance at p frequencies
- S_1 is the constant sensitivity to parameter 1

Single parametric function can be inverted

$$\sum_{n=1}^p a_n Z_n = S_1 (x_1 - x_{OP}) + \sum_{n=1}^p a_n Z_{OP,n}$$

Formula for direct calculation of the target parameter :

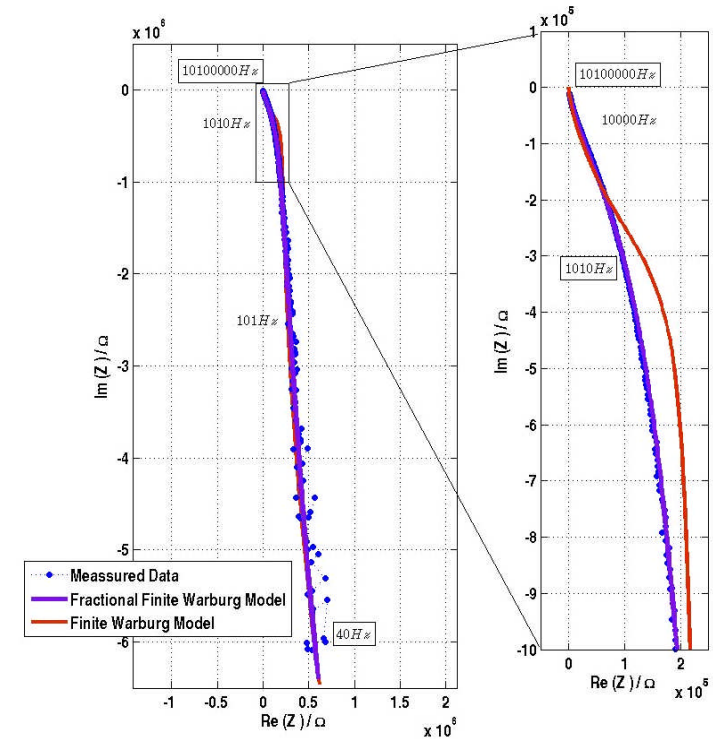
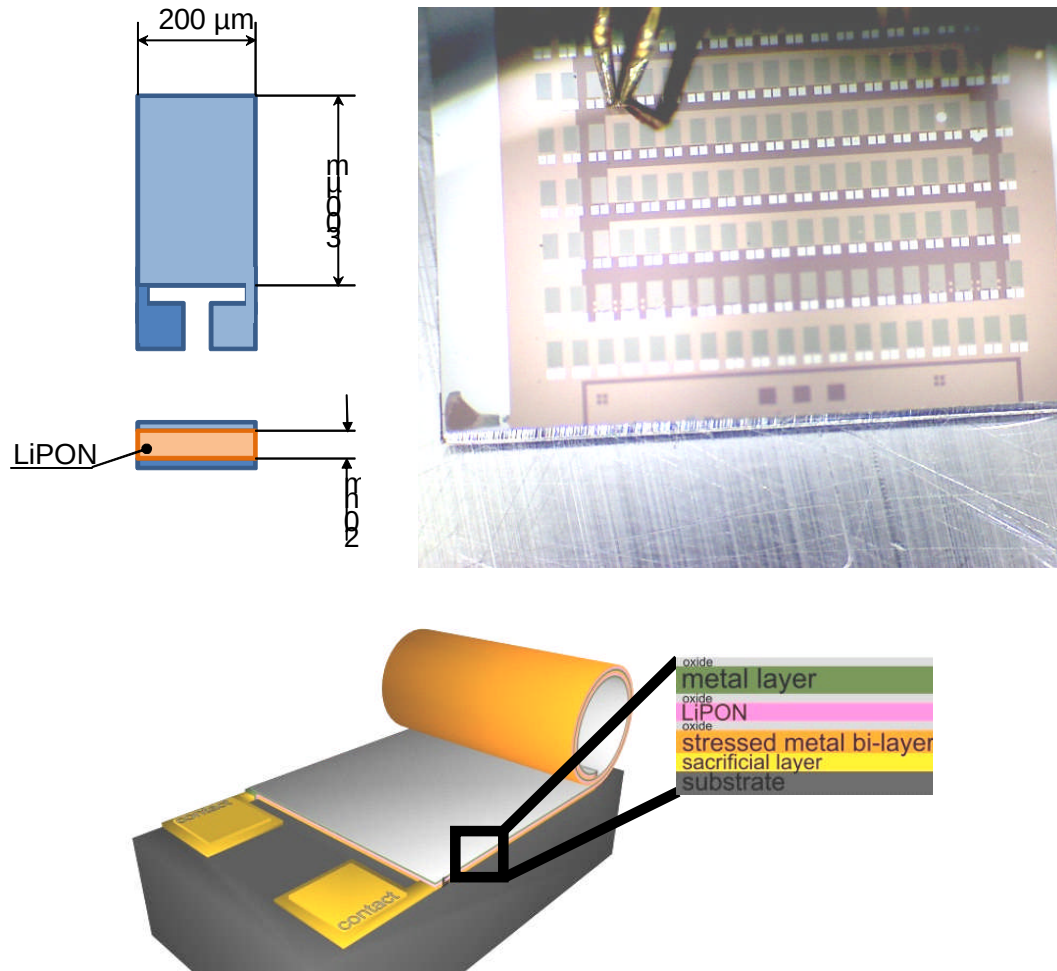
$$x_{1,\text{estimated}} = \sum_{n=1}^p \frac{a_n Z_n}{S_1} + x_{\text{offset}}$$

$$x_{\text{offset}} = x_{OP} - \sum_{n=1}^p \frac{a_n Z_{OP,n}}{S_1}$$

(constant part)

Demonstration for model data

System: on chip solid electrolyte capacitor

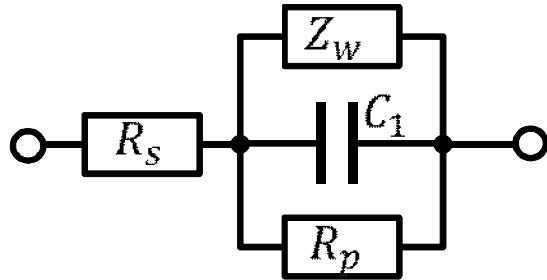


Unknown quantities

- diffusion constant
- ion concentration

Introduction to the model

Electrode properties difficult to model

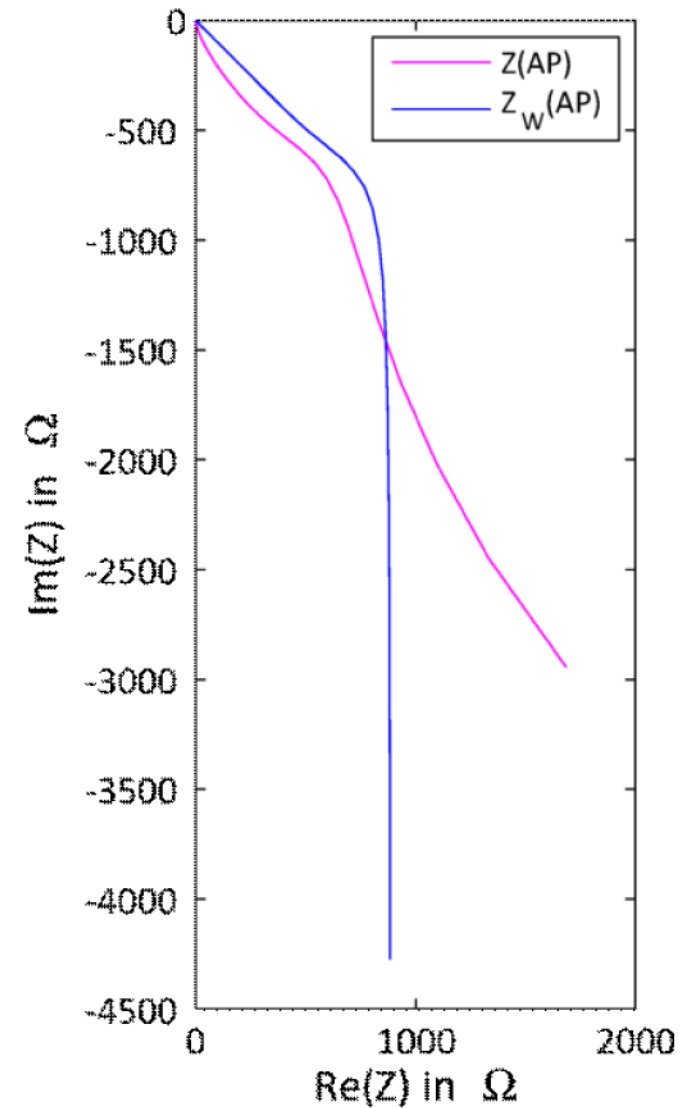


$$Z = R_s + \frac{1}{j\omega C_1 + \frac{1}{R_p} + \frac{1}{Z_w}}$$

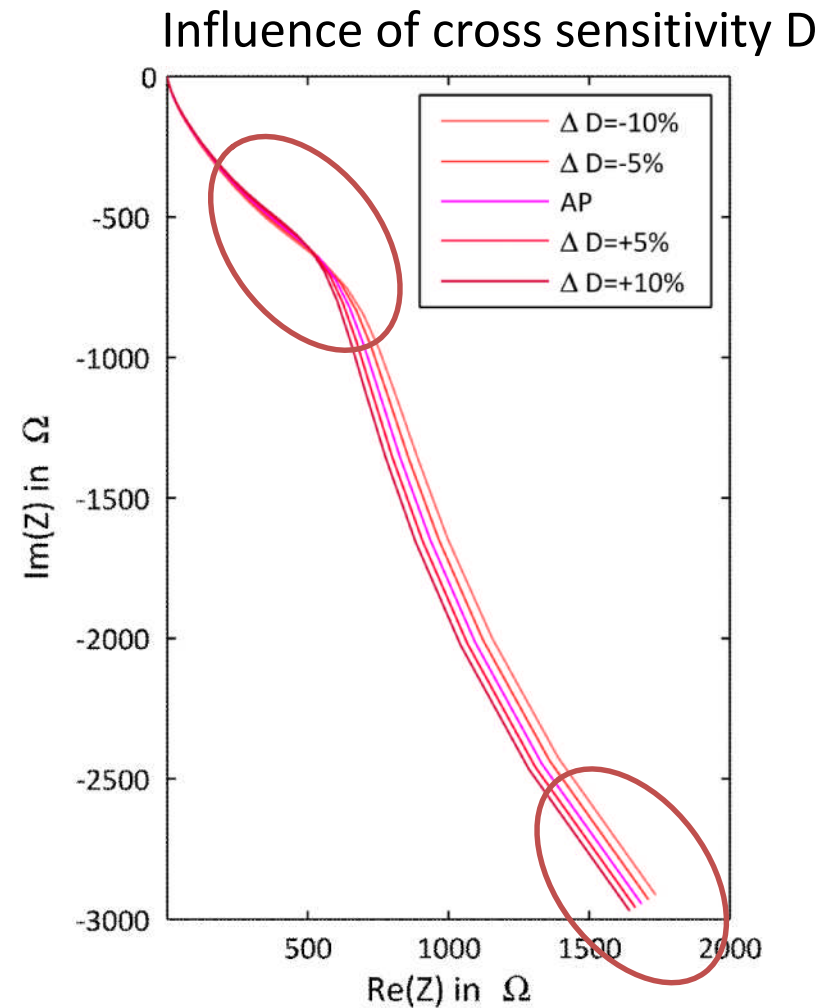
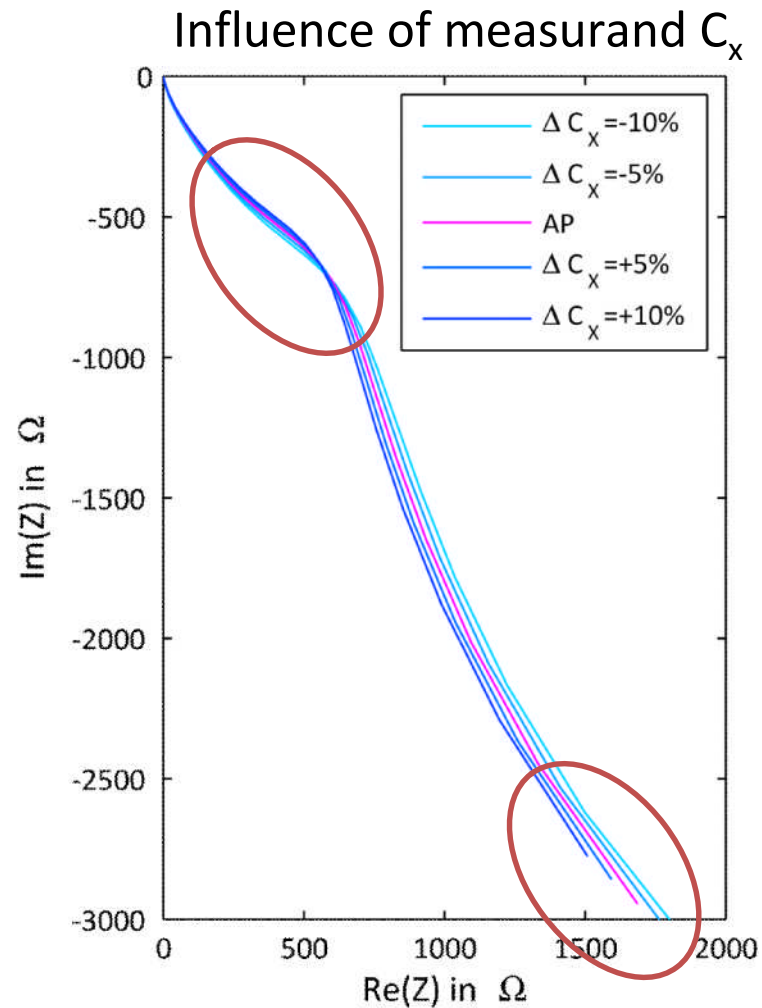
Finite Warburg-Impedance

$$Z_w = \frac{RT}{I^2 F^2 \mathbf{C}_x A \sqrt{2\omega \mathbf{D}}} (1 - j) \coth \left(\delta (1 + j) \sqrt{\frac{\omega}{2\mathbf{D}}} \right)$$

diffusion coefficient ($\mathbf{D}$) $\rightarrow$ undefined parameter
ion concentration ($\mathbf{C}_x$) $\rightarrow$ targeted measurand



Characteristics of the analytical model



Selection of frequencies for two parameters (x_1, x_2)

Criterion I: high sensitivity to target parameter x_1

$$K_1 = \left| \frac{\partial Z_d}{\partial x_1} \right| + \left| \frac{\partial Z_e}{\partial x_1} \right| \quad \text{d, e index of frequency}$$

Criterion II: a high degree of independent information on the other parameters x_2

$$K_2 = \frac{\partial Z_d}{\partial x_2} \frac{\partial x_1}{\partial Z_d} - \frac{\partial Z_e}{\partial x_2} \frac{\partial x_1}{\partial Z_e} \quad K_I \text{ and } K_{II} \text{ should be non zero}$$

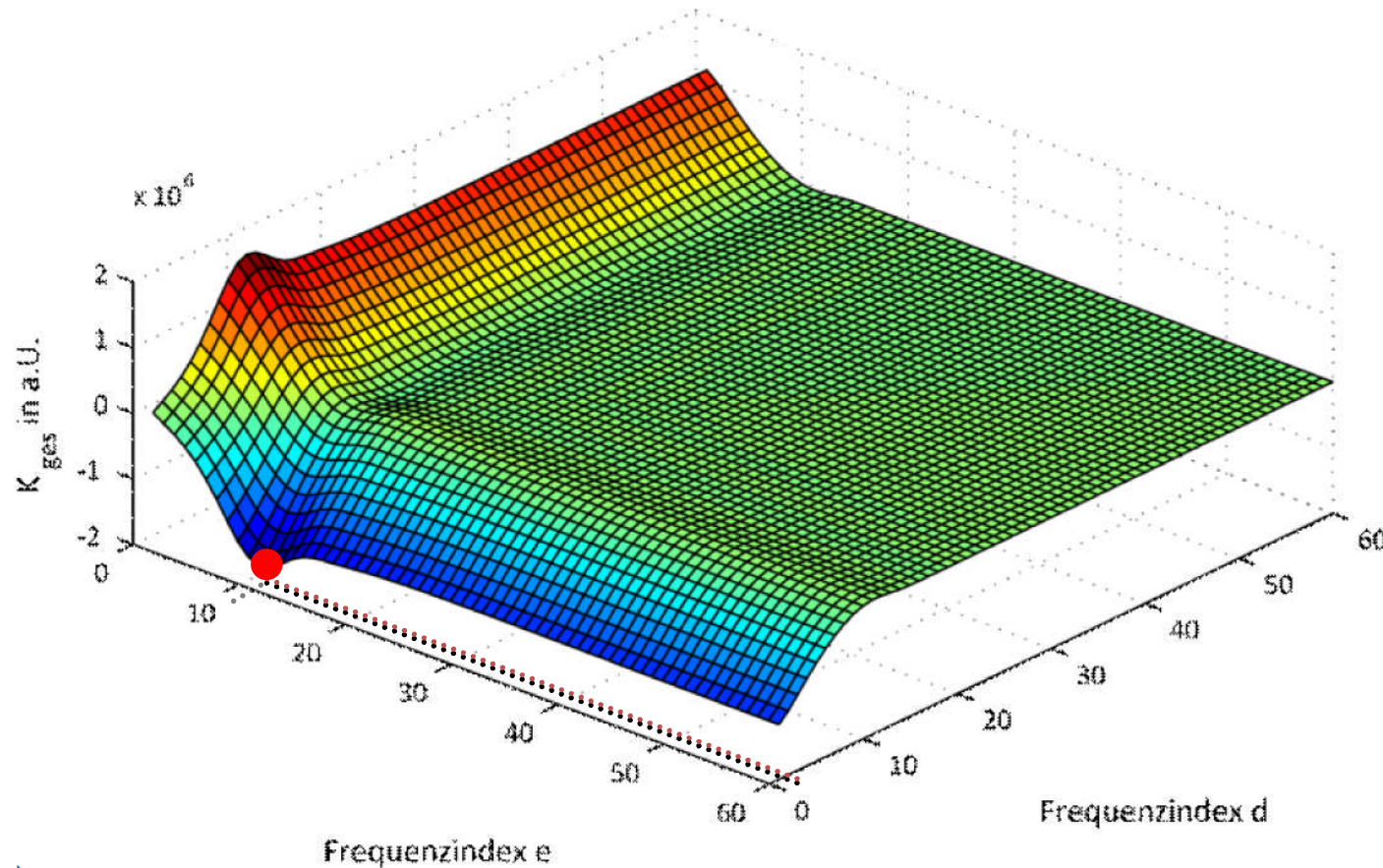
Common criterion by multiplication

$$K_{ges} = K_1 K_2 = \left(\frac{\partial Z_d}{\partial x_2} \frac{\partial x_1}{\partial Z_d} - \frac{\partial Z_e}{\partial x_2} \frac{\partial x_1}{\partial Z_e} \right) \left(\left| \frac{\partial Z_d}{\partial x_1} \right| + \left| \frac{\partial Z_e}{\partial x_1} \right| \right)$$

The analysis is restricted to the imaginary part of the impedance

Selection of frequencies for two parameters (x_1, x_2)

Suitable points have a large distance from zero

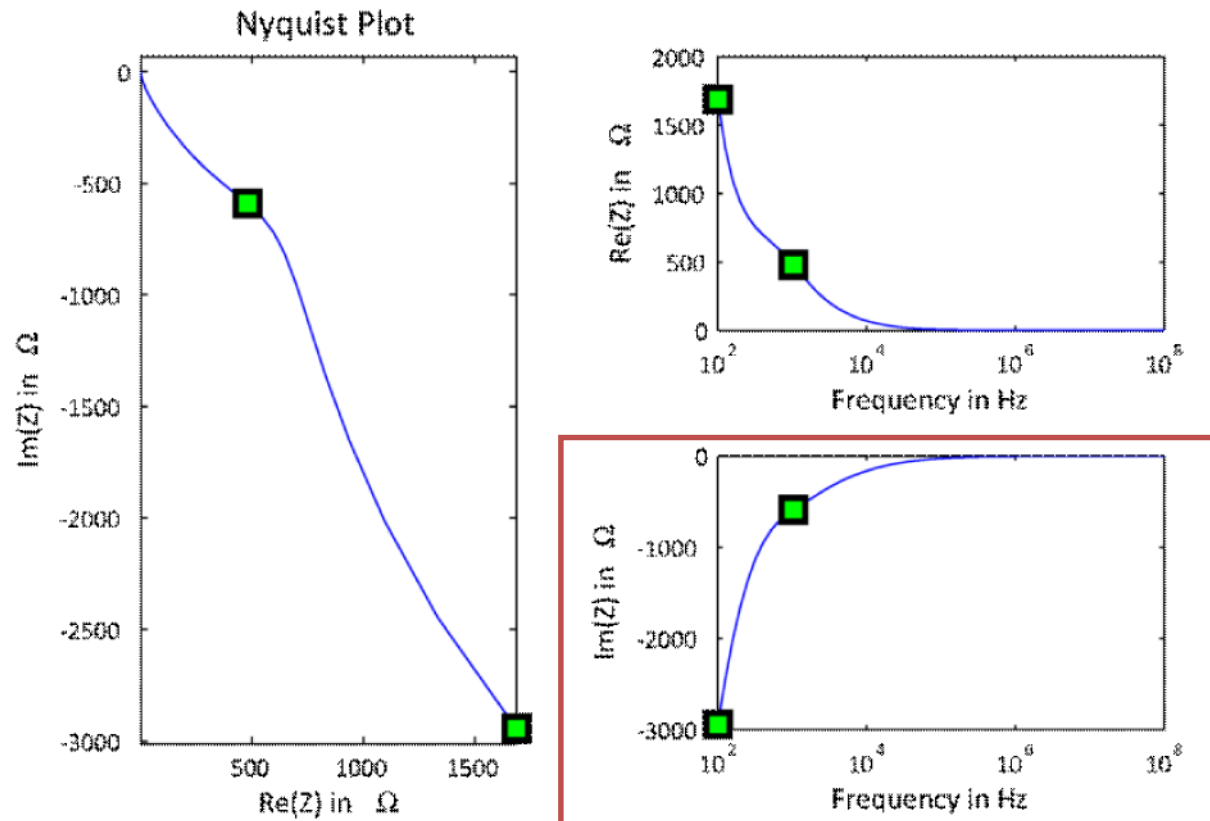


➔ Sampling at frequencies $Z_e |_{e=1}$ und $Z_d |_{d=11}$ is recommended

Selection of frequencies for two parameters (x_1 , x_2)

Only the imaginary part of impedance at selected sampling points is used:

- High degree of independence of the varied parameters with each other
- High sensitivity of the targeted parameter



Calculation of the transformation rule

For solving the system of equations:

Measurand $a_1 \frac{\partial Z_e}{\partial x_1} + a_2 \frac{\partial Z_d}{\partial x_1} = 1 \frac{[\text{Unit of } Z_d]}{[\text{Unit of } x_1]}$

Cross sensitivity $a_1 \frac{\partial Z_e}{\partial x_2} + a_2 \frac{\partial Z_d}{\partial x_2} = 0 \frac{[\text{Unit of } Z_d]}{[\text{Unit of } x_2]}$

All derivatives of the model at the operating point (OP) can be obtained by numerical derivation or experiment.

a_1 and a_2 are to be calculated.
Sensitivity S_1 was defined to 1.

Separation of C_x :

$$\rightarrow x_1 = C_x$$

$$\rightarrow x_2 = D$$

Separation of D:

$$\rightarrow x_1 = D$$

$$\rightarrow x_2 = C_x$$

$$x_{1,\text{estimated}} = \sum_{n=1}^p \frac{a_n Z_n}{S_1} + x_{\text{offset}}$$

$$x_{\text{offset}} = x_{\text{OP}} - \sum_{n=1}^p \frac{a_n Z_{\text{OP},n}}{S_1}$$

Evaluation of Results

$$C_{x,\text{estimated}} = 4,487 * 10^{-7} \frac{\text{mol}}{\text{m}^3\Omega} * Z_d + 4,172 * 10^{-7} \frac{\text{mol}}{\text{m}^3\Omega} * Z_e + 2,567 * 10^{-3} \frac{\text{mol}}{\text{m}^3}$$

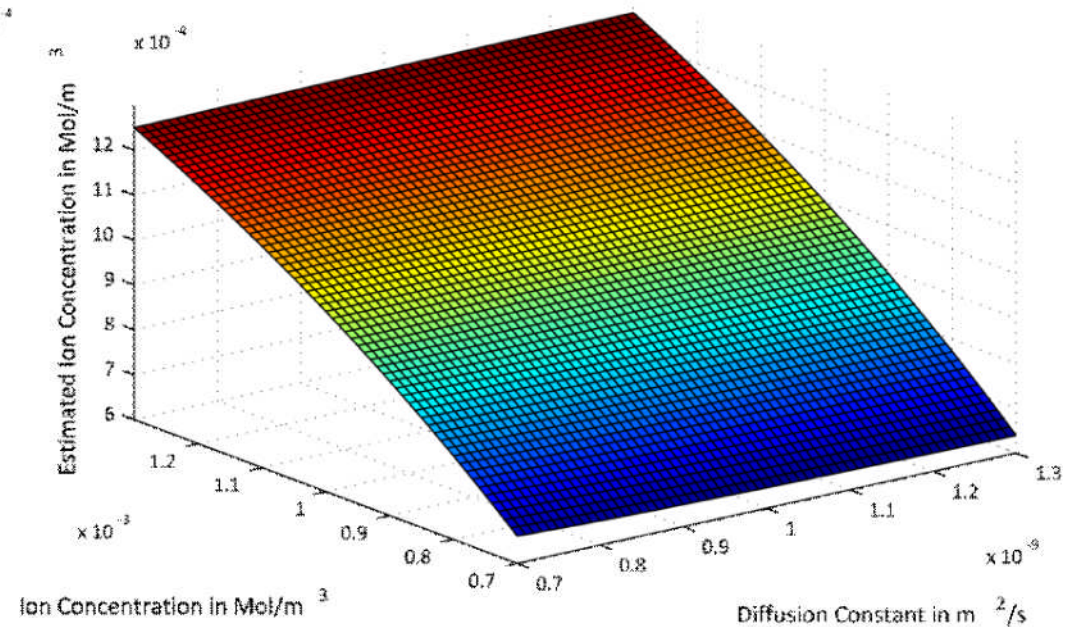
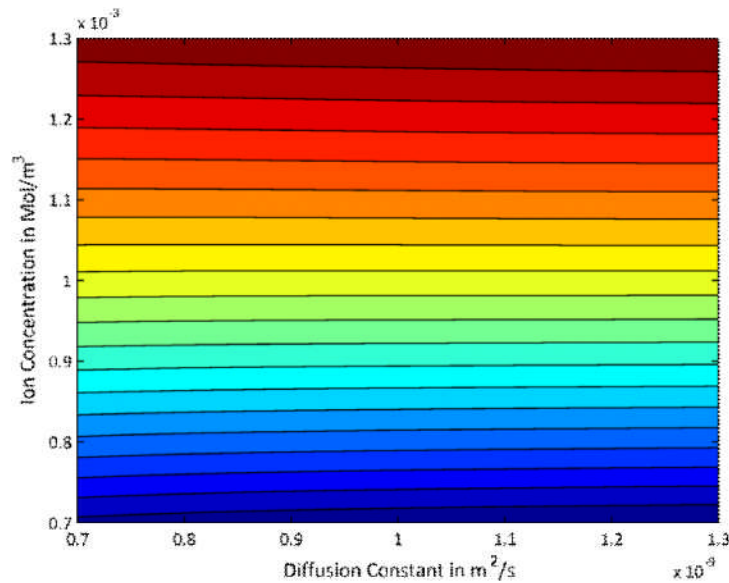


100 Hz



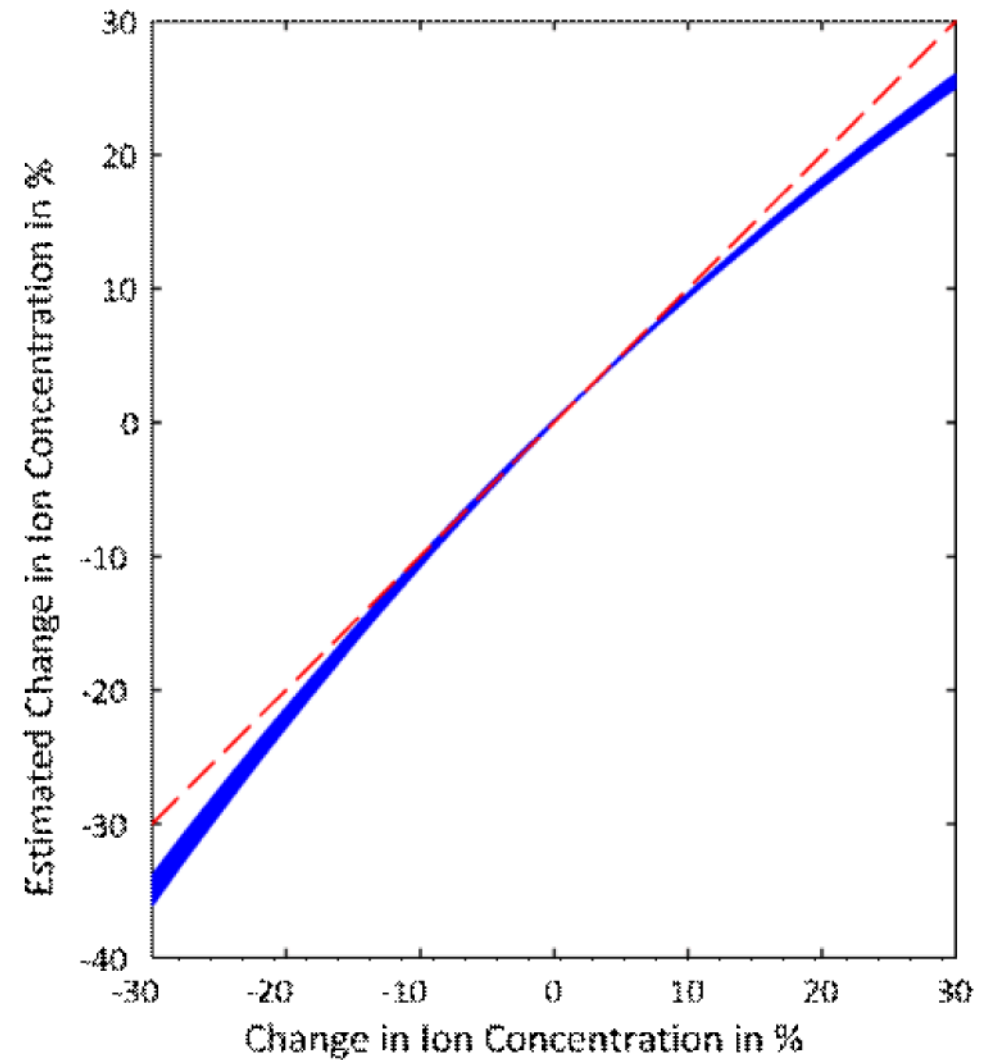
1004 Hz

- Influence of D eliminated
- C_x at defined sensitivity



Evaluation of Results

- Diffusion coefficient has little effect on the characteristic curves
- Deviation from the ideal C_x -characteristic curve with large variations of the ion concentration



Summary

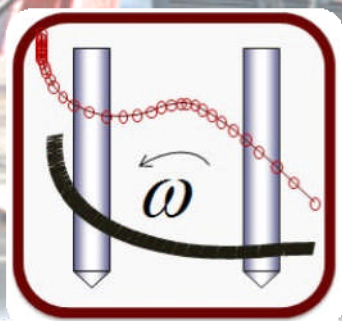
- By linear transformation, the extraction of spectral information without regression calculation can be done
- Advantages of the introduced method
 - ✓ No modelling required
 - ✓ Compensation of cross sensitivities at the operating point
 - ✓ Measurand can be obtained from very few frequency points
 - ✓ Choice of frequency points is done automatically and by objectively defined criteria
 - ✓ Calculation for the analysis is limited to linear equations

Thank you for your attention!



5th Symposium on Environmental Instrumentation and Measurement (IMEKO TC19)

September 23-24 , 2014 Chemnitz/GERMANY



7th International Workshop on Impedance Spectroscopy (IWIS'14)

September 24-26 , 2014 Chemnitz/GERMANY