Electrochemical Impedance Spectroscopy

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My 'where abouts'

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Electrochemical techniques

Time domain (*incomplete!*):

- Polarisation, (V - I) — steady state
- Potential Step, (ΔV - $I(t)$) — relaxation
- Cyclic Voltammetry, ($V_{f(t)}$ - $I(V)$) — dynamic
- Coulometric Titration, (ΔV - $\int I\,dt$) — relaxation
- Galvanostatic Intermittent Titration (ΔQ - $V(t)$) — transient

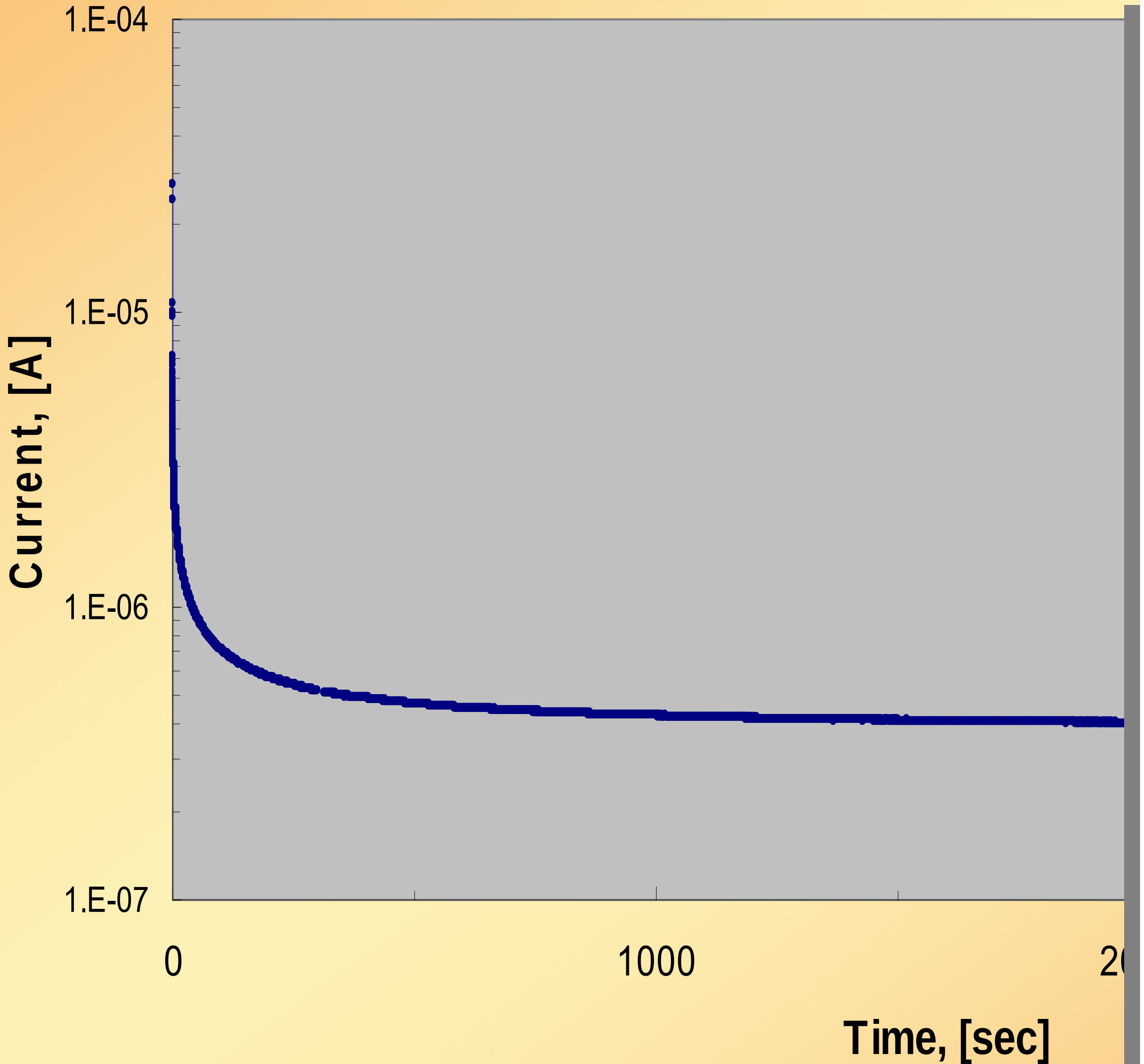
Next slide

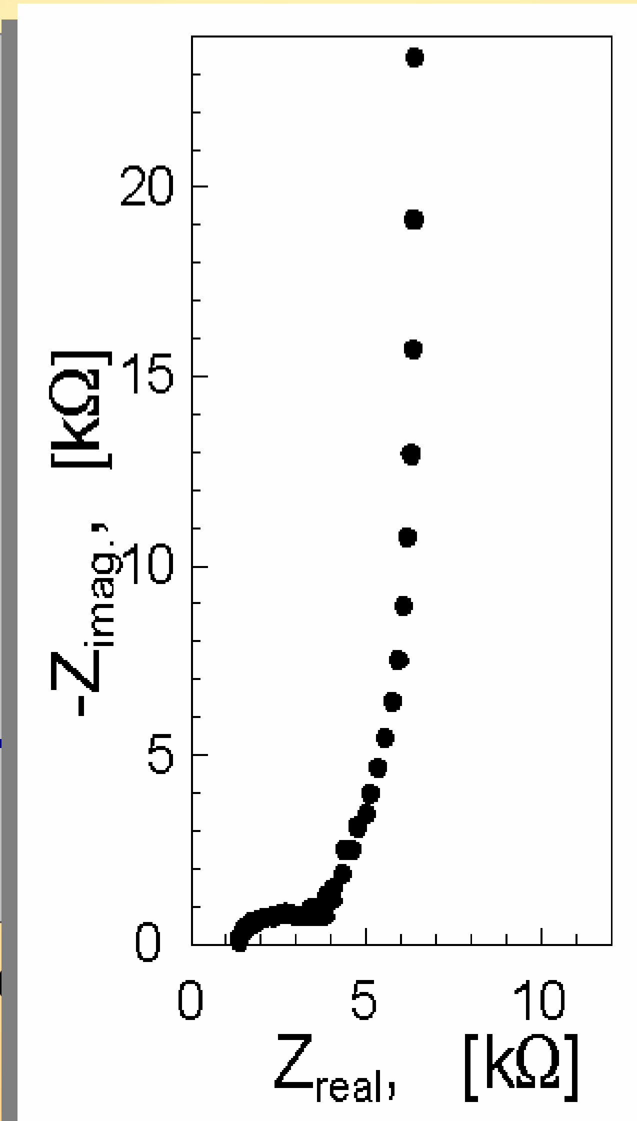
Frequency domain:

- Electrochemical Impedance Spectroscopy (EIS) — perturbation of equilibrium state

EIS &
Nano-El-Cat
Nov. '08.

Time or frequency domain?





Advantages of EIS:

System in thermodynamic equilibrium

Measurement is small perturbation (approximately linear)

Different processes have different time constants

Large frequency range, μHz to GHz (and up)

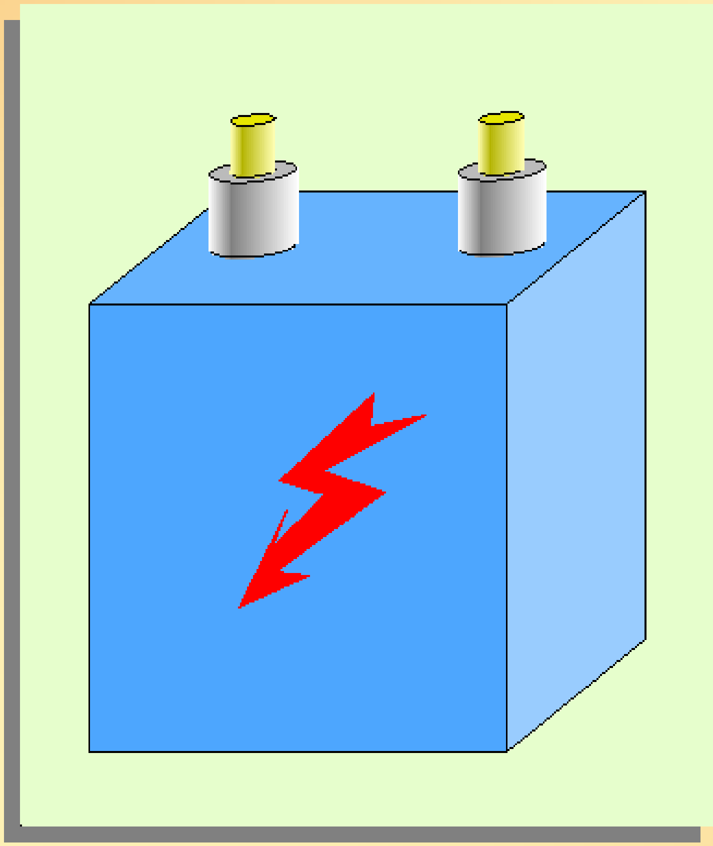
- Generally analytical models available
- Evaluation of model with 'Complex Nonlinear Least Squares' (CNLS) analysis procedures (later).
- Pre-analysis (subtraction procedure) leads to plausible model and starting values (also later)

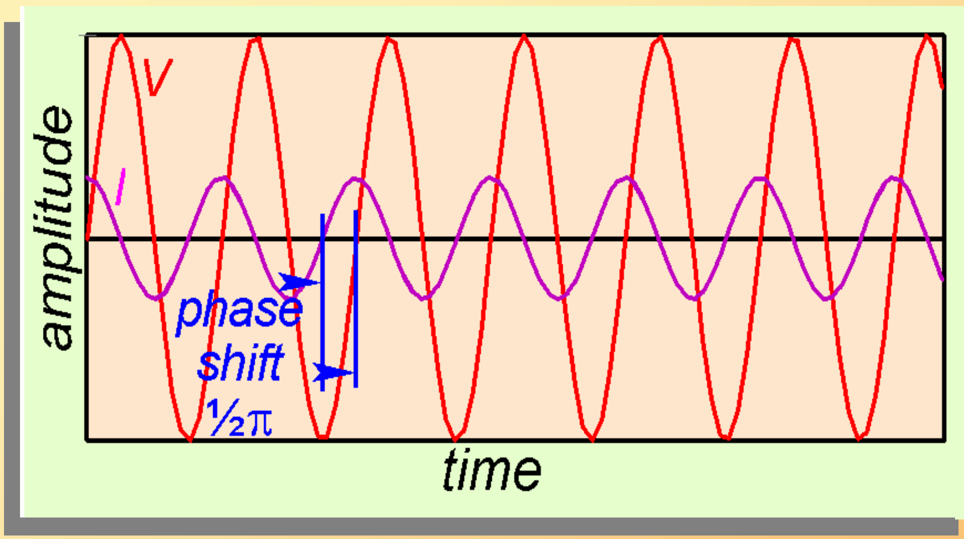
Disadvantage: rather expensive equipment,
low frequencies difficult to measure

Black box approach

Assume a black box with two terminals (electric connections).

One applies a voltage and measures the current response (or visa versa). Signal can be dc or periodic with frequency f, or angular frequency $\omega=2\pi f$, with: $0 \leq \omega < \infty$





Phase shift and amplitude changes with ω!

So, what is EIS?

Probing an electrochemical system with a small ac-perturbation, $V_0 \cdot e^{j\omega t}$, over a range of frequencies.

The **impedance** (resistance) is given by:

$\omega = 2\pi f$
$j = \sqrt{-1}$

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_0 \quad e^{j\omega t}}{I_0 \quad e^{j(\omega t + \varphi)}} = \frac{V_0}{I_0}\left[\cos\varphi - j\sin\varphi\right]$$

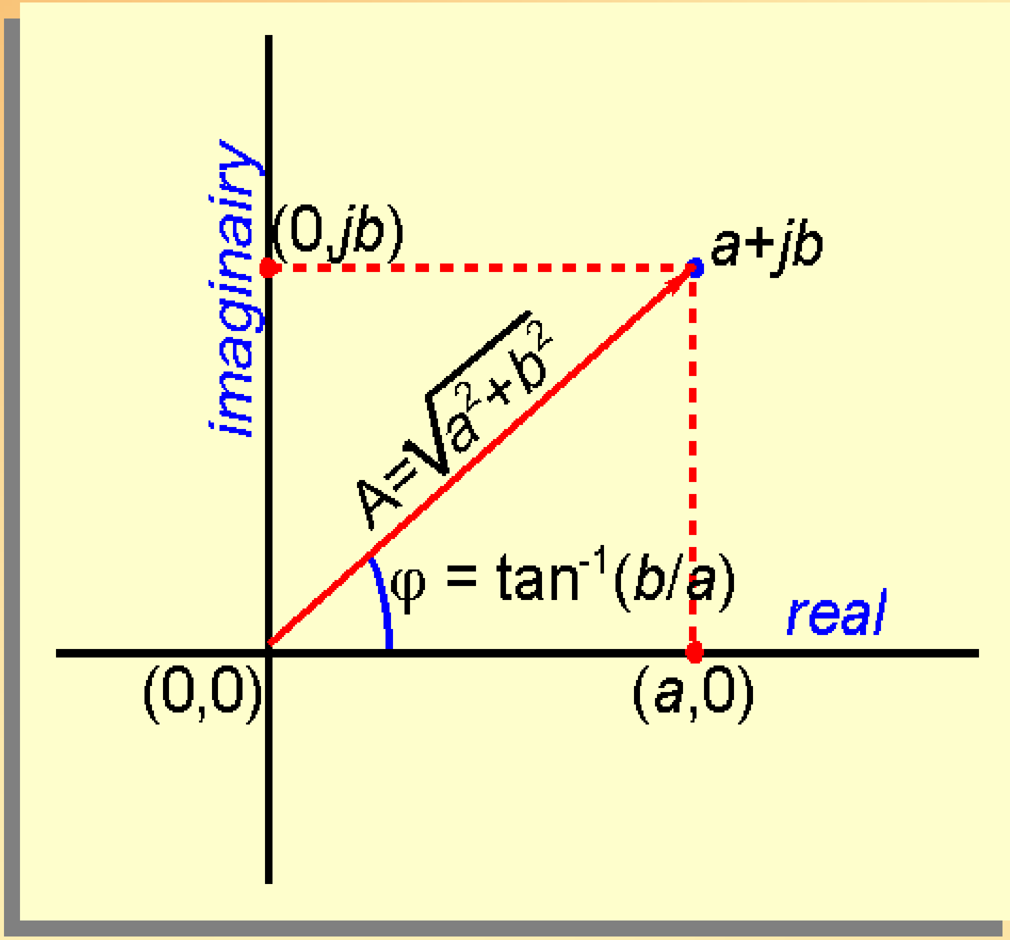
The magnitude and phase shift depend on frequency.

Also: **admittance** (conductance), inverse of impedance:

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{I_0\, e^{j(\omega t + \varphi)}}{V_0\, e^{j\omega t}} = \frac{I_0}{V_0}\left[\cos\varphi + j\sin\varphi\right]$$

"real +j imaginary"

Complex plane



Representation of impedance value,
$Z = a + jb$, in the complex plane

Impedance ≡ 'resistance'

Admittance ≡ 'conductance':

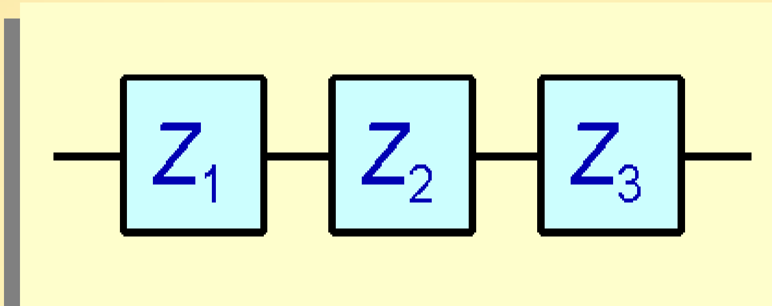
$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{Z_{re} - jZ_{im}}{Z_{re}^2 + Z_{im}^2}$$

hence:

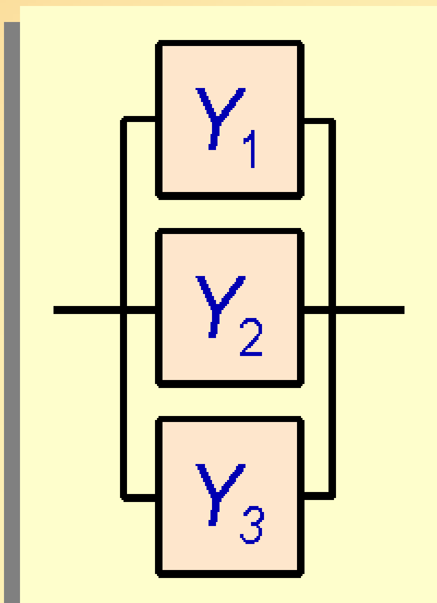
$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{Y_{re} - jY_{im}}{Y_{re}^2 + Y_{im}^2}$$

Adding impedances and admittances

A linear arrangement of impedances can be added in the impedance representation:



$$Z_{total} = Z_1 + Z_2 + Z_3 + \ldots = \sum_n Z_n$$



A 'ladder' arrangement of admittances (inverse impedances) can be added in the admittance representation :

$$Y_{total} = Y_1 + Y_2 + Y_3 + \ldots = \sum_n Y_n$$

Simple elements

The most simple element
is the resistance:

$$Z_R = R \ ; \quad Y_R = \frac{1}{R}$$

(e.g.: electronic- /ionic conductivity,
charge transfer resistance)

Other simple elements:

- Capacitance: dielectric capacitance, double layer C, adsorption C, 'chemical C' (redox)

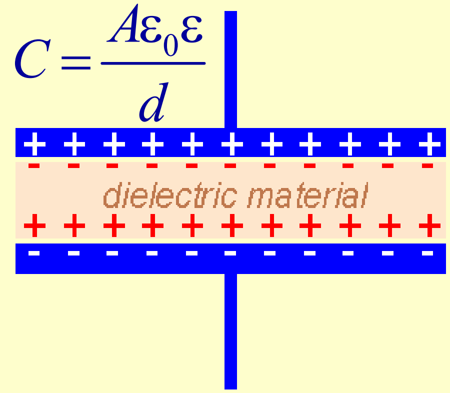
See next page

- Inductance: instrument problems, leads, 'negative differential capacitance' !

Capacitance?

Take a look at the properties of a capacitor:

$$C = \frac{A\varepsilon_0\varepsilon}{d}$$



Charge stored (Coulombs): $Q = C \cdot V$

Change of voltage results in current, *I*: $$I = \frac{\mathrm{d}Q}{\mathrm{d}t} = C\frac{\mathrm{d}V}{\mathrm{d}t}$$

Alternating voltage (ac): $$I(\omega t) = C\frac{\mathrm{d}V_0 \cdot e^{j\omega t}}{\mathrm{d}t} = j\omega C \cdot V_0 \cdot e^{j\omega t}$$

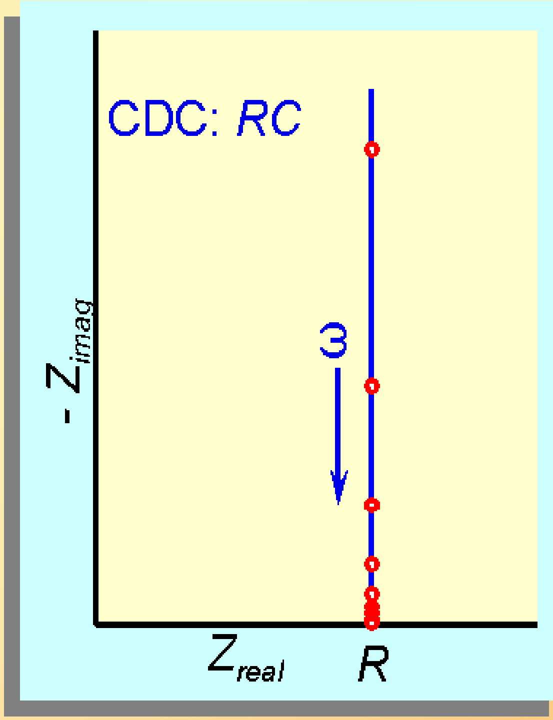
Impedance: $$Z_C(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{1}{j\omega C}$$

Admittance: $$Y_C(\omega) = Z(\omega)^{-1} = j\omega C$$

Combination of elements

What is the impedance of an -R-C- circuit?

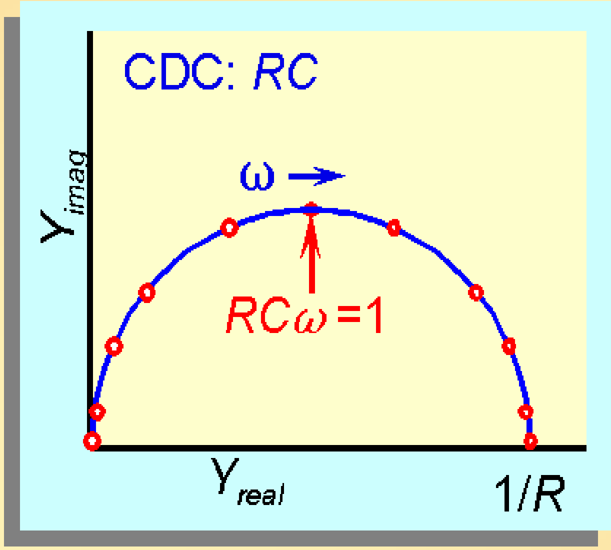
$$Z(\omega) = R + \frac{1}{j\omega C} = R - j/\omega C$$



Admittance?

$$Y(\omega) = \frac{1}{R - j/\omega C} =$$

$$\frac{\omega^2 C^2 R}{1+\omega^2 C^2 R^2} + j\frac{\omega C}{1+\omega^2 C^2 R^2}$$



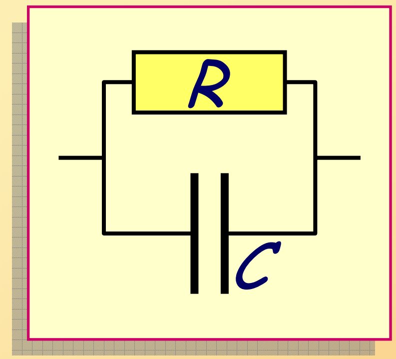
Semi-circle

'time constant':
$\tau = RC$

A parallel R-C combination

The parallel combination of a resistance and a capacitance, start in the admittance representation:

$$Y(\omega) = \frac{1}{R} + j\omega C$$



Transform to impedance representation:

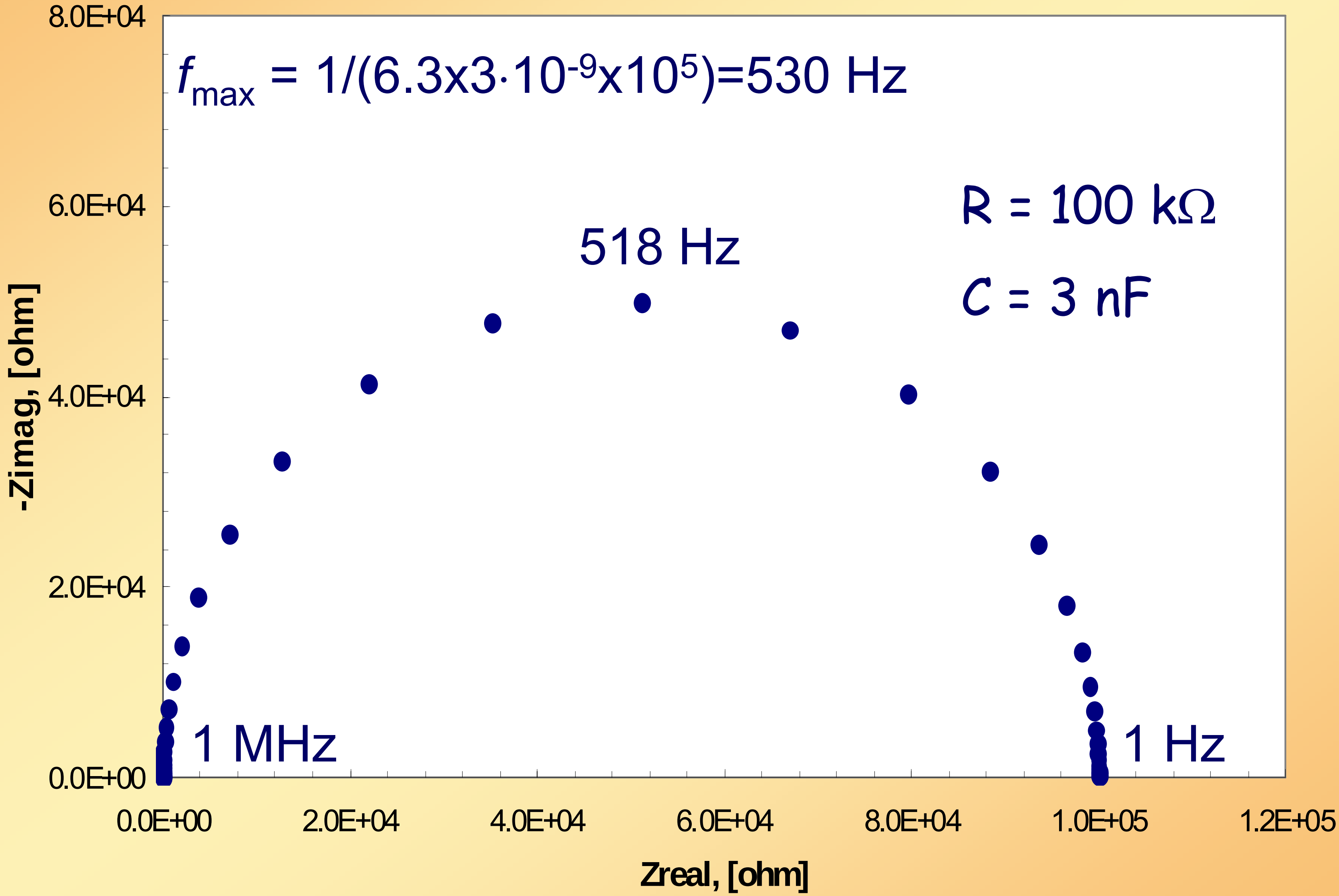
$$Z(\omega) = \frac{1}{Y(\omega)} = \frac{1}{1/R + j\omega C} \cdot \frac{1/R - j\omega C}{1/R - j\omega C} =$$

$$\frac{R - j\omega R^2 C}{1 + \omega^2 R^2 C^2} = R\frac{1 - j\omega\tau}{1 + \omega^2\tau^2}$$

A semicircle in the impedance plane!

Plot next slide

Impedance plot (RC)



Limiting cases

What happens for $\omega \ll \tau$ and for $\omega \gg \tau$?

$\omega \ll \tau$:
$$Z(\omega) = R\frac{1 - j\omega\tau}{1 + \omega^2\tau^2} \approx R - j\omega R\tau \approx R - j\omega R^2 C$$

$\omega \gg \tau$:
$$Z(\omega) = R\frac{1 - j\omega\tau}{1 + \omega^2\tau^2} \approx \frac{R}{\omega^2\tau^2} - j\frac{R}{\omega\tau} \approx \frac{1}{\omega^2 R C^2} - j\frac{1}{\omega C}$$

This is best observed in a so-called Bode plot

$\log(Z_{re})$, $\log(Z_{im})$ vs. $\log(f)$, or

$\log|Z|$ and phase vs. $\log(f)$

Next slides

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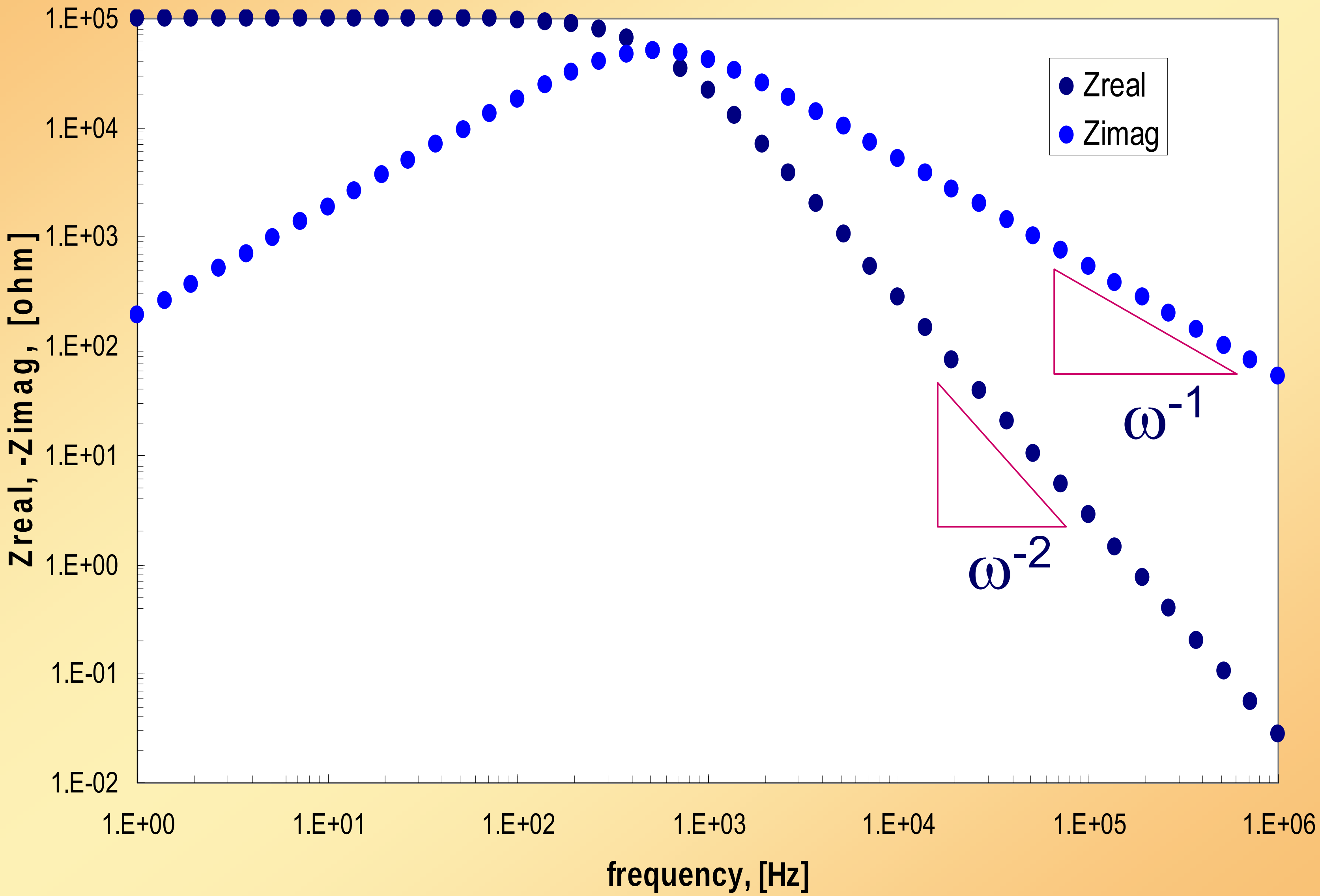
Bode plot (Z_{re}, Z_{im})



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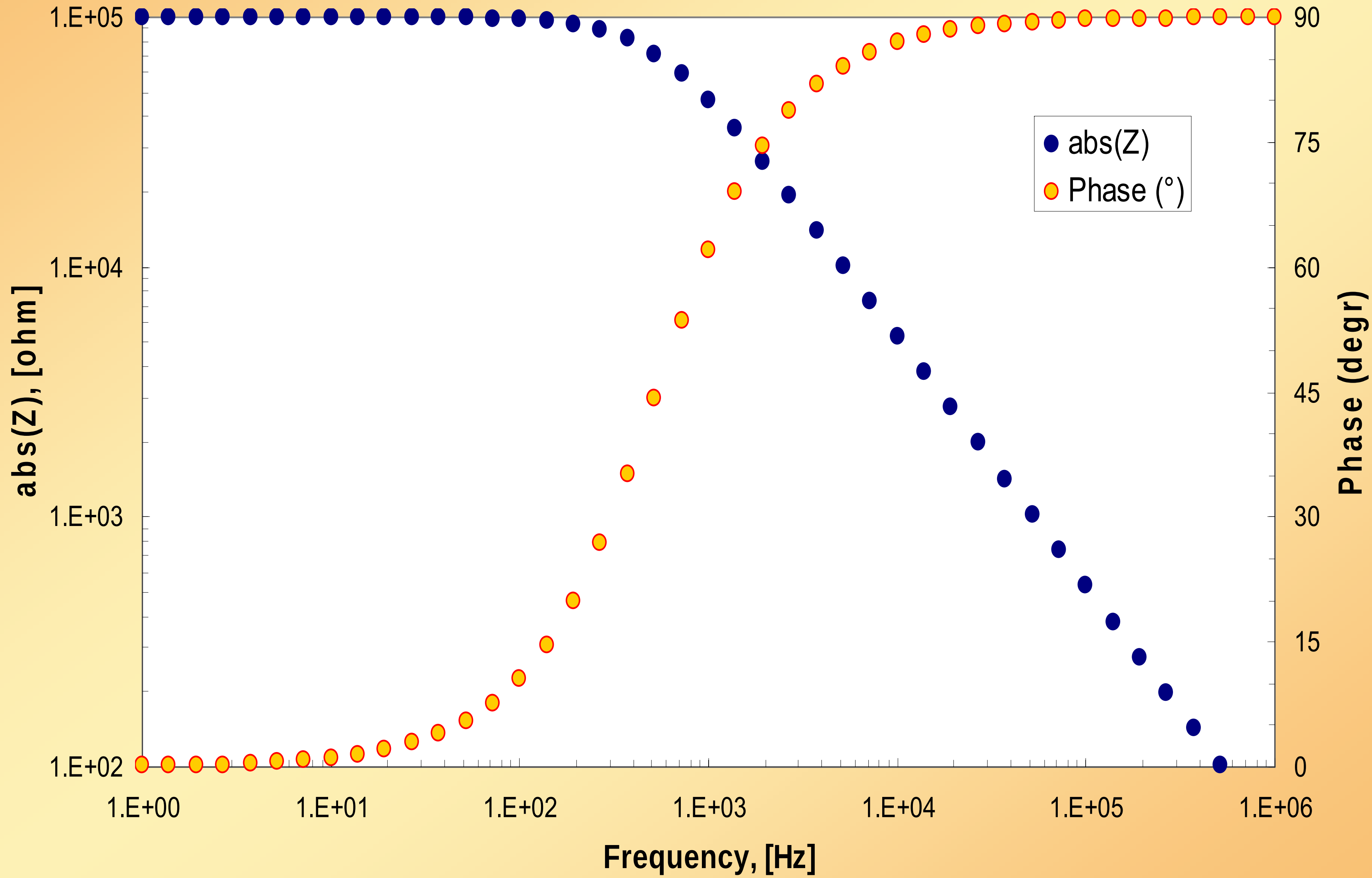
Bode, abs(Z), phase



Other representations

Capacitance: $C(\omega) = Y(\omega) / j\omega$ for an (RC) circuit:

$$C(\omega) = Y(\omega) / j\omega = \left[\frac{1}{R} + j\omega C\right] / j\omega = C - j\frac{1}{\omega R}$$

Dielectric: $\varepsilon(\omega) = Y(\omega) / j\omega C_0$ $C_0 = A\varepsilon_0/d$

$$\varepsilon(\omega) = Y(\omega) \cdot \frac{d}{A\varepsilon_0} = \varepsilon' - j\frac{\sigma_{ion}}{\omega\varepsilon_0}$$

d: thickness

A: surf. area

Modulus: $M(\omega) = Z(\omega) \cdot j\omega$

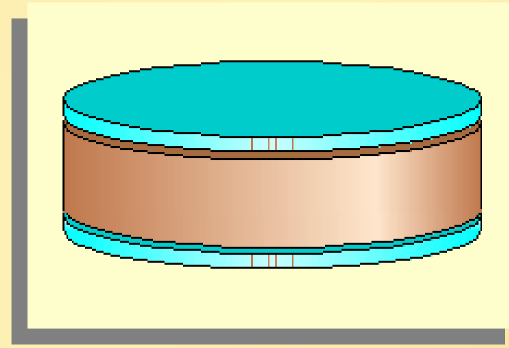
$$M(\omega) = Z(\omega) \cdot j\omega = \frac{\omega^2 CR^2 + j\omega R}{1 + \omega^2 C^2 R^2}$$

Simple model

Example: an ionically conducting solid,
e.g. yttrium stabilized zirconia,

$$Zr_{1-x}Y_xO_{2-\frac{1}{2}x}.$$

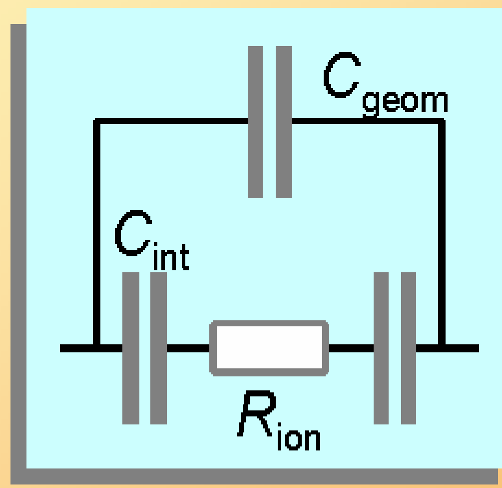
Apply two ionically blocking electrodes, in this case thick gold.



Schematic arrangement of sample and electrodes.

Measure the 'resistance' (impedance) as function of frequency:

$$Z(\omega) = \frac{1}{j\omega C_g + \frac{1}{R_{ion} + \frac{1}{\frac{1}{2} j\omega C_{int}}}}$$



Equivalent circuit: (C[RC])

Low & high f - response

Low frequency regime,
series combination R_{ion}-C_{int}: $Z(\omega) = R_{ion} - j/\tfrac{1}{2}\omega C_{int}$

Straight vertical line in impedance plane.

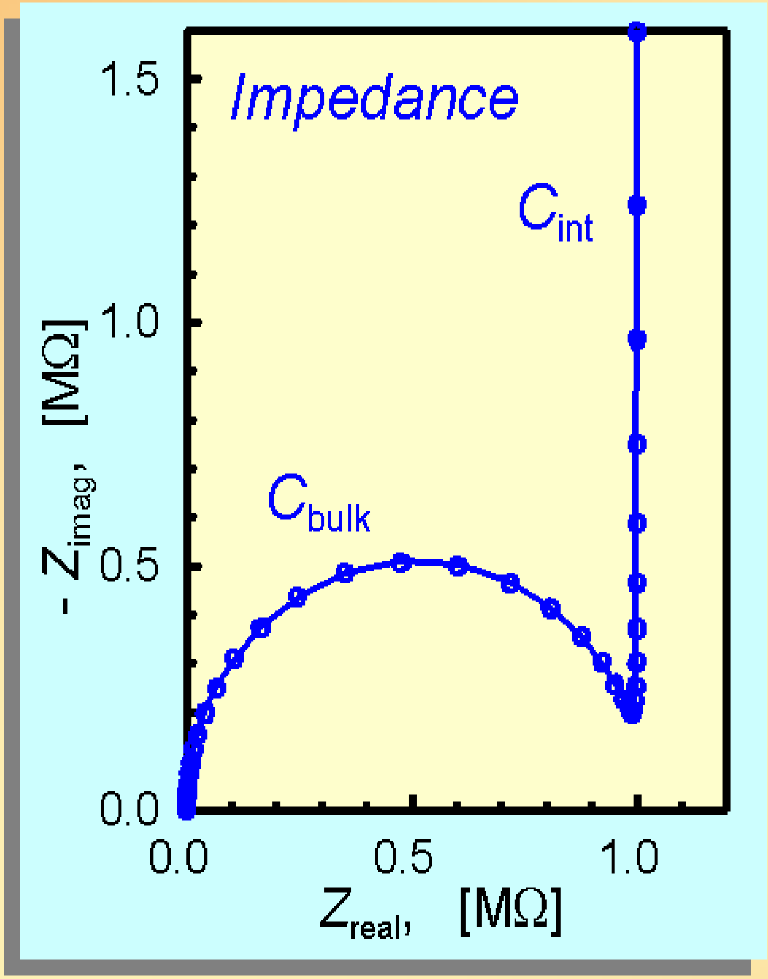
High frequency regime,
parallel combination of $R_{ion}//C_{geom}$:

$$Z(\omega) = \frac{R_{ion}}{1+\omega^2 R_{ion}^2 C_{geom}^2} - j\frac{\omega R_{ion}^2 C_{geom}}{1+\omega^2 R_{ion}^2 C_{geom}^2}$$

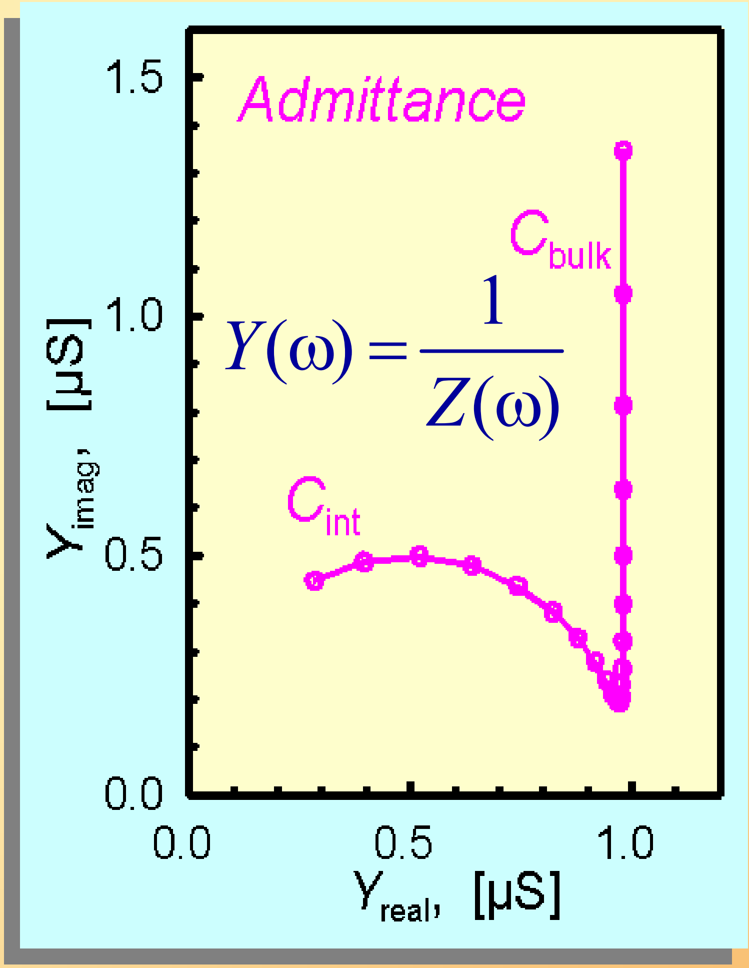
Semicircle through the origin.

'Debije' model:

An ionic conductor between two blocking electrodes:

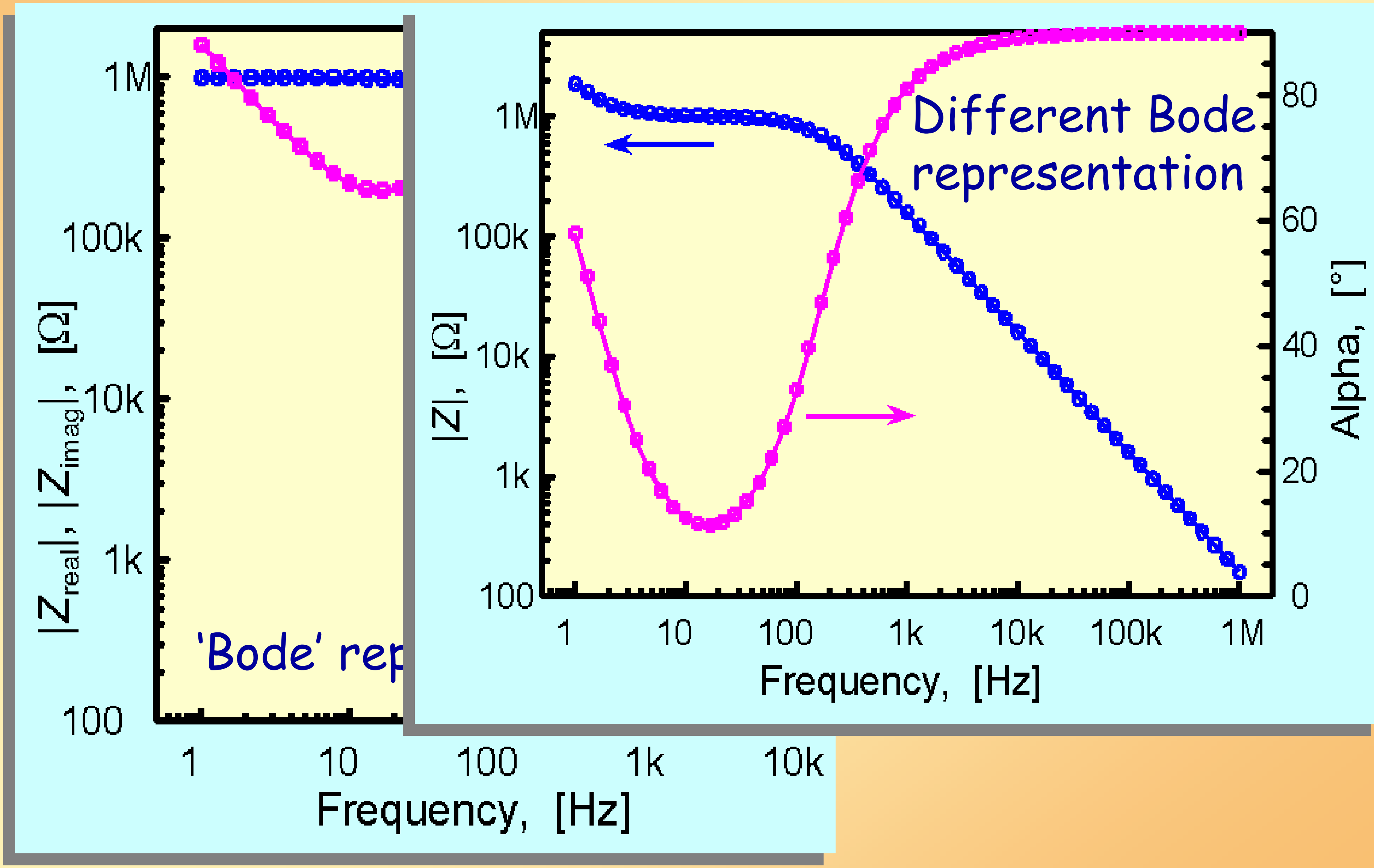


Impedance representation



Admittance representation

Other representations



Diffusion, Warburg element

Semi-infinite diffusion,

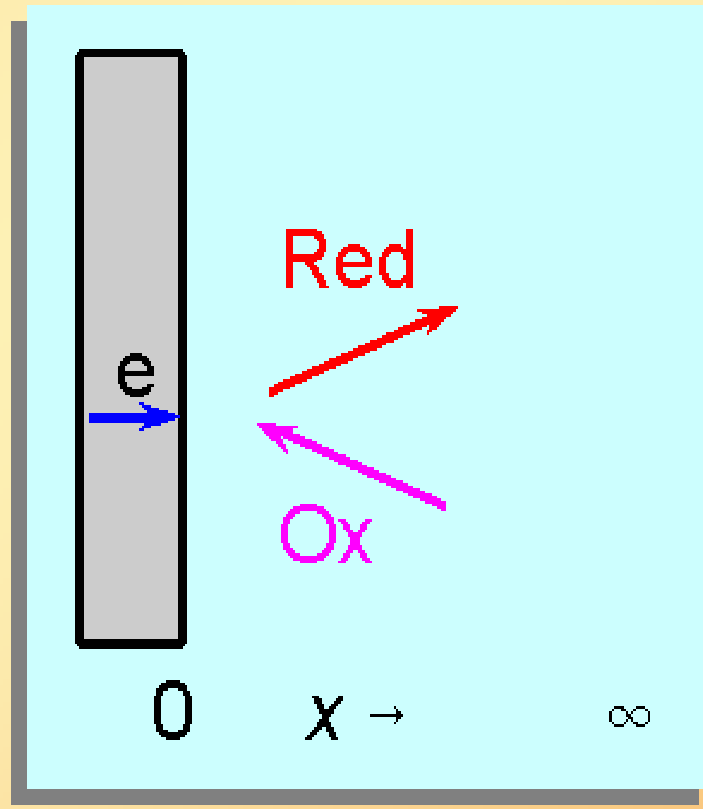
Flux (current) (Fick-1) : $$J = -D \left. \frac{\partial C}{\partial x} \right|_{x=0}$$

Potential : $$E = E^{o} + \frac{RT}{nF} \ln C$$

ac-perturbation: $$C(t) = C^{o} + c(t)$$

Fick-2 : $$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2}$$

Boundary condition : $$\left. C(x,t) \right|_{x \to \infty} = C^{o}$$



Redox on inert electrode.

Solution through Laplace transform: next page

Warburg element, cont.

Laplace transform: $c(x,t) \Rightarrow C(x,p)$

Transform of Fick-2: $p \cdot C(x,p) = D\dfrac{\partial^2 C(x,p)}{\partial x^2}$

General solution: $C(x,p) = A \cdot \cosh x\sqrt{p/D} + B \cdot \sinh x\sqrt{p/D}$

Transform of $V(t)$: $E(p) = \dfrac{RT}{nFC^{\circ}} C(x,p)$

Transform of $I(t)$: $I(p) = -nFD\left.\dfrac{\partial C(x,p)}{\partial x}\right|_{x=0}$
(Fick-1)

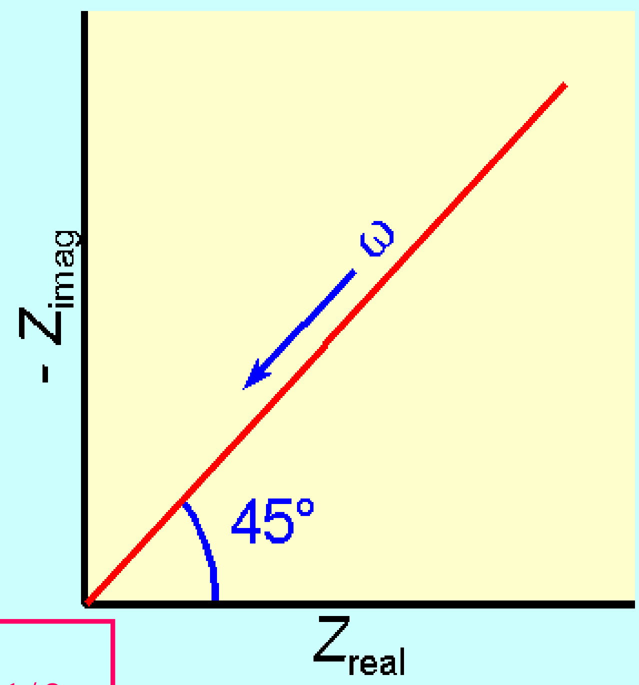
Boundary condition:
$C(x,p)\big|_{x\to\infty} = 0$

Warburg impedance

Define impedance in Laplace space!

$$Z(p) = \frac{E(p)}{I(p)} = \frac{RT}{(nF)^2 C^{o} \sqrt{D \cdot p}}$$

Take the Laplace variable, *p*, complex:
p = *s* + *j* ω. Steady state: *s* $\Rightarrow$ 0,
which yields the impedance:



$$Z(\omega) = \frac{RT}{(nF)^2 C^{o} \sqrt{j\omega D}} = Z_0(\omega^{-1/2} - j\omega^{-1/2})$$

with:

$$Z_0 = \frac{RT}{(nF)^2 C^{o} \sqrt{2D}}$$

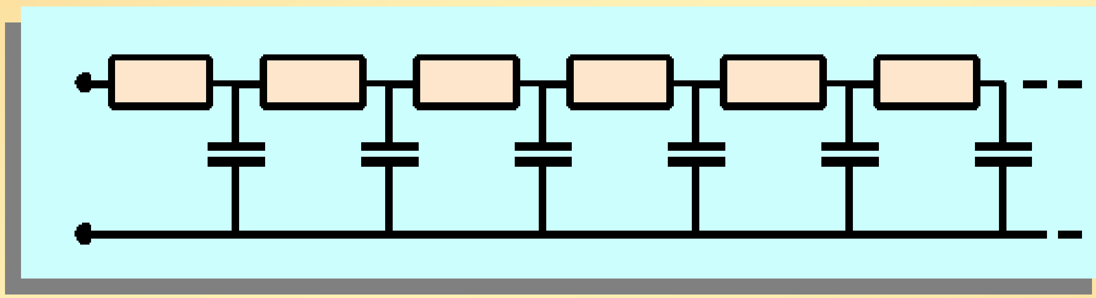
In solution:

$$Z_0 = (\sigma =) \frac{RT}{n^2 F^2 A \sqrt{2}} \left(\frac{1}{C_O^* \sqrt{D_O}} + \frac{1}{C_R^* \sqrt{D_R}} \right)$$

Transmission line

Real life Warburg,
semi-infinite coax cable
with $r\,\Omega$/m and c F/m:

$$Z_W(\omega) = \sqrt{\frac{r}{j\omega c}}$$



Combination:

- Electrolyte resistance, $R_{e'lyte}$
- Double layer capacitance, C_{dl}
- Charge transfer resistance, R_{ct}
- Warburg (diffusion) impedance, W_{diff}

Equivalent circuit

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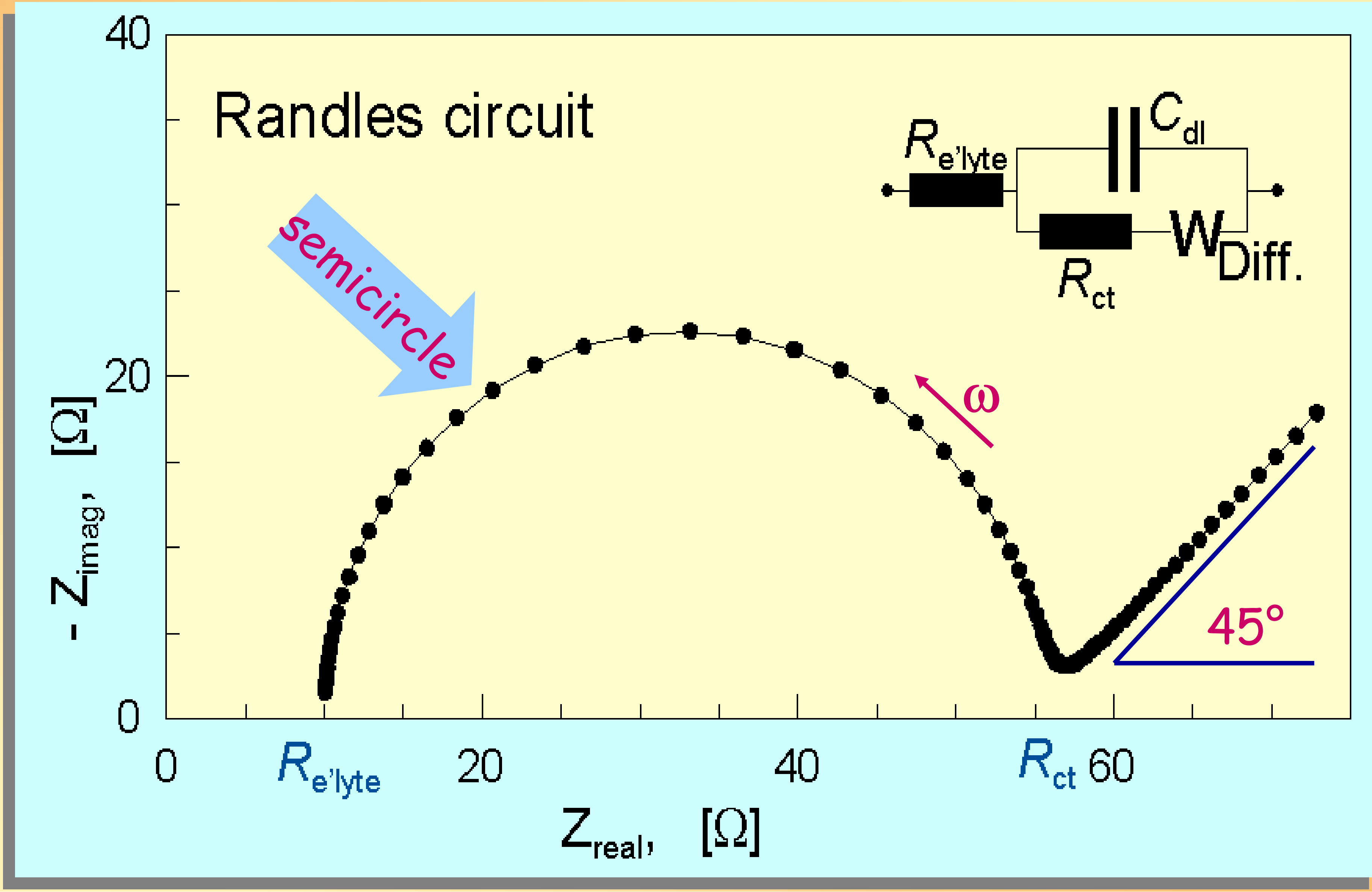
Equivalent Circuit Concept



Measurement methods

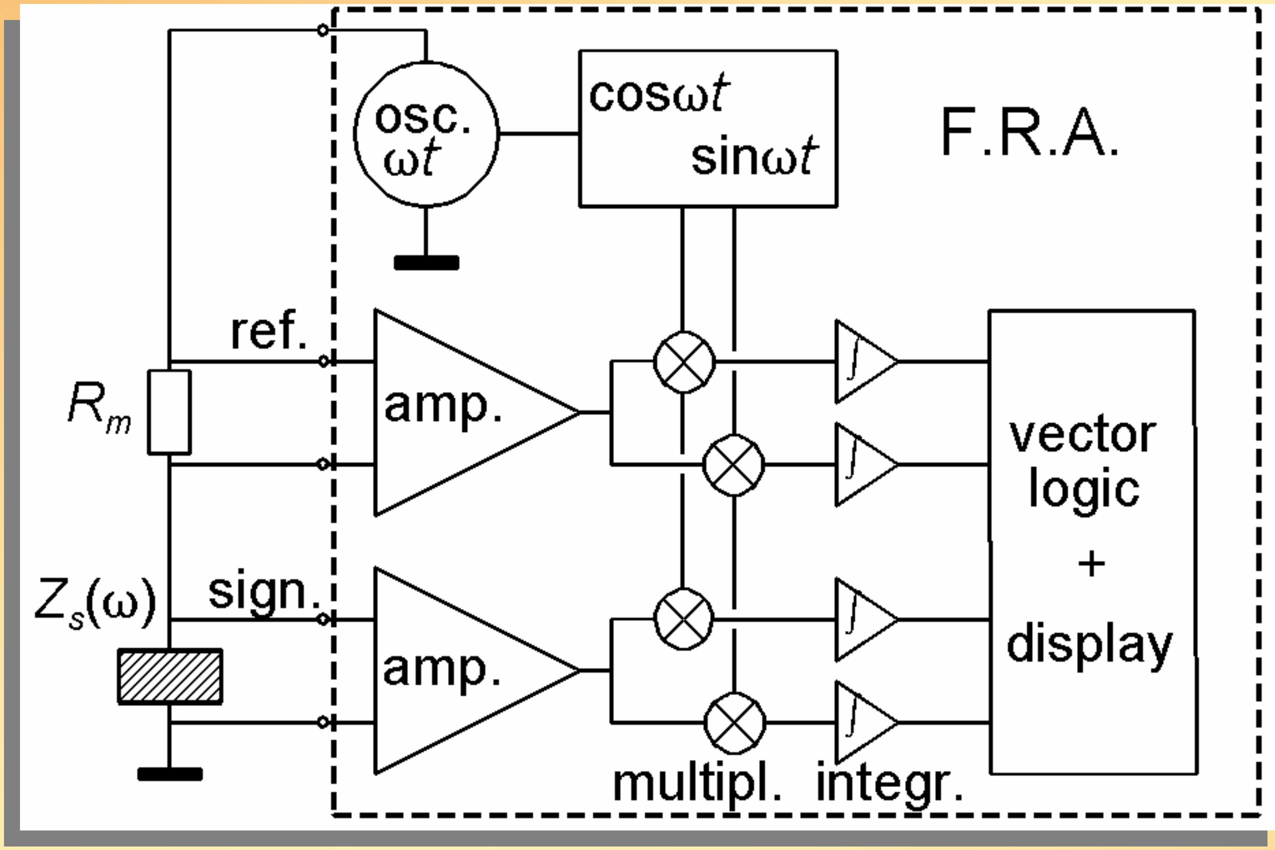
Bulk, conductivity:

- two electrodes
- pseudo-four electrodes
- true four electrodes

Electrode properties:

- three electrodes

Frequency Response Analyser



Multiplier:

$V_x(\omega t) \times \sin(\omega t)$ &

$V_x(\omega t) \times \cos(\omega t)$

Integrator: integrates multiplied signals

Display result:

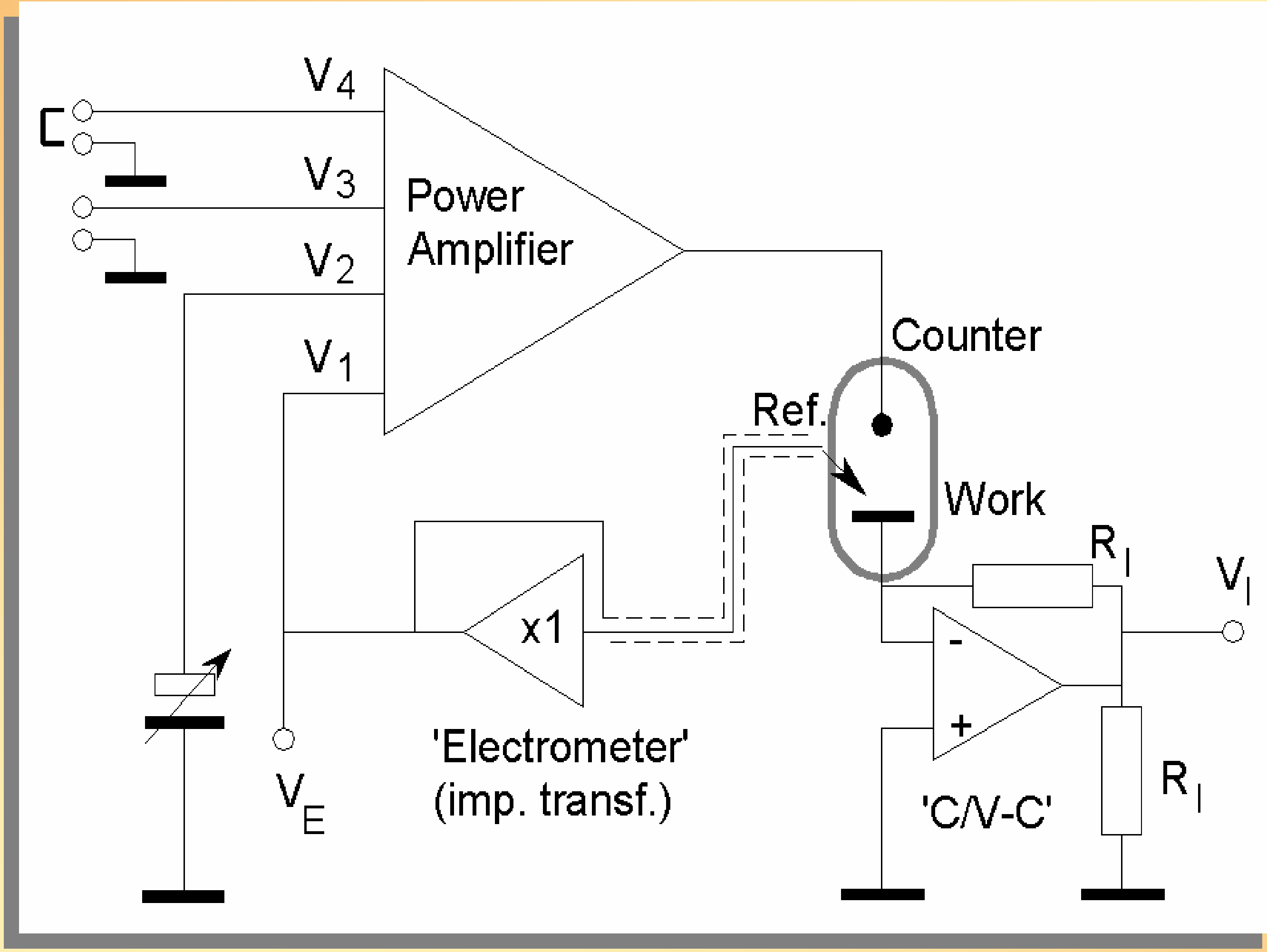
$a + jb = V_{sign}/V_{ref}$

Impedance:

$Z_{sample} = R_m\,(a + jb)$

But be aware of the input impedance of the FRA!

Potentiostat, electrodes



General schematic

$V_{pwr.amp} = A \Sigma_k V_k$

A= amplification

$V_{work} - V_{ref} =$
$V_{pol.} + V_3 + V_4$

Current-voltage converter provides virtual ground for Work-electrode.

Source of inductive effects

Data validation

Kramers-Kronig relations (old!)

Real and imaginary parts are linked through the *K-K* transforms:

Kramers-Kronig conditions:

- causality
- linearity
- stability
- (finiteness)

Response only

Response

State of system may not change during measurement

Putting 'K-K' in practice

Relations,

Real → imaginary: $$Z_{im}(\omega) = \frac{2\omega}{\pi}\int_0^\infty \frac{Z_{re}(x) - Z_{re}(\omega)}{\boxed{x^2 - \omega^2}}\,dx$$

not a singularity!

Imaginary → real: $$Z_{re}(\omega) = R_\infty + \frac{2}{\pi}\int_0^\infty \frac{xZ_{im}(x) - \omega Z_{im}(\omega)}{x^2 - \omega^2}\,dx$$

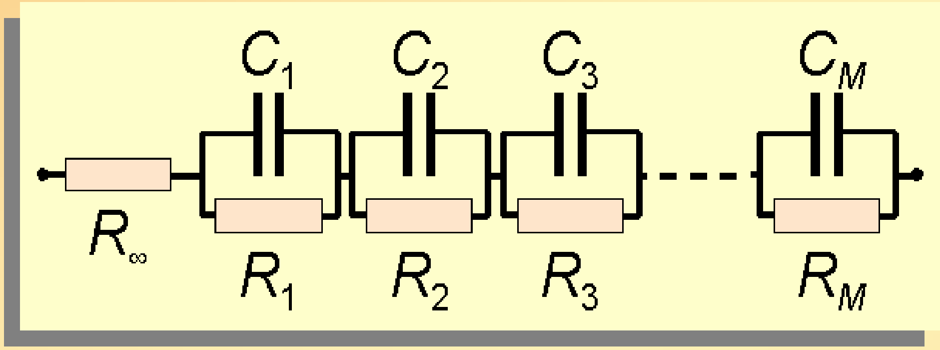
Problem:

Finite frequency range: extrapolation of dispersion ☞ assumption of a model.

[1] M. Urquidi-Macdonald, S.Real & D.D. Macdonald, *Electrochim.Acta*, **35** (1990) 1559.
[2] B.A. Boukamp, *Solid State Ionics*, **62** (1993) 131.

Linear KK transform

Linear set of parallel *RC* circuits:



$\tau_k = R_k \cdot C_k$

Create a set of τ values: $\tau_1 = \omega_{max}^{-1}$; $\tau_M = \omega_{min}^{-1}$
with ~7 τ-values per decade (logarithmically spaced).

If this circuit fits the data, the data must be K-K transformable!

[3] B.A.Boukamp, *J.Electrochem.Soc*, **142** (1995) 1885

Actual test

Fit function simultaneously to real and imaginary part:

$$Z_{KK}(\omega_i) = R_\infty + \sum_{k=1}^{M} R_k \frac{1 - j\omega_i \cdot \tau_k}{1 + \omega_i^2 \cdot \tau_k^2}$$

Shortcut to KKtest.lnk

Set of linear equations in R_k, only one matrix inversion!

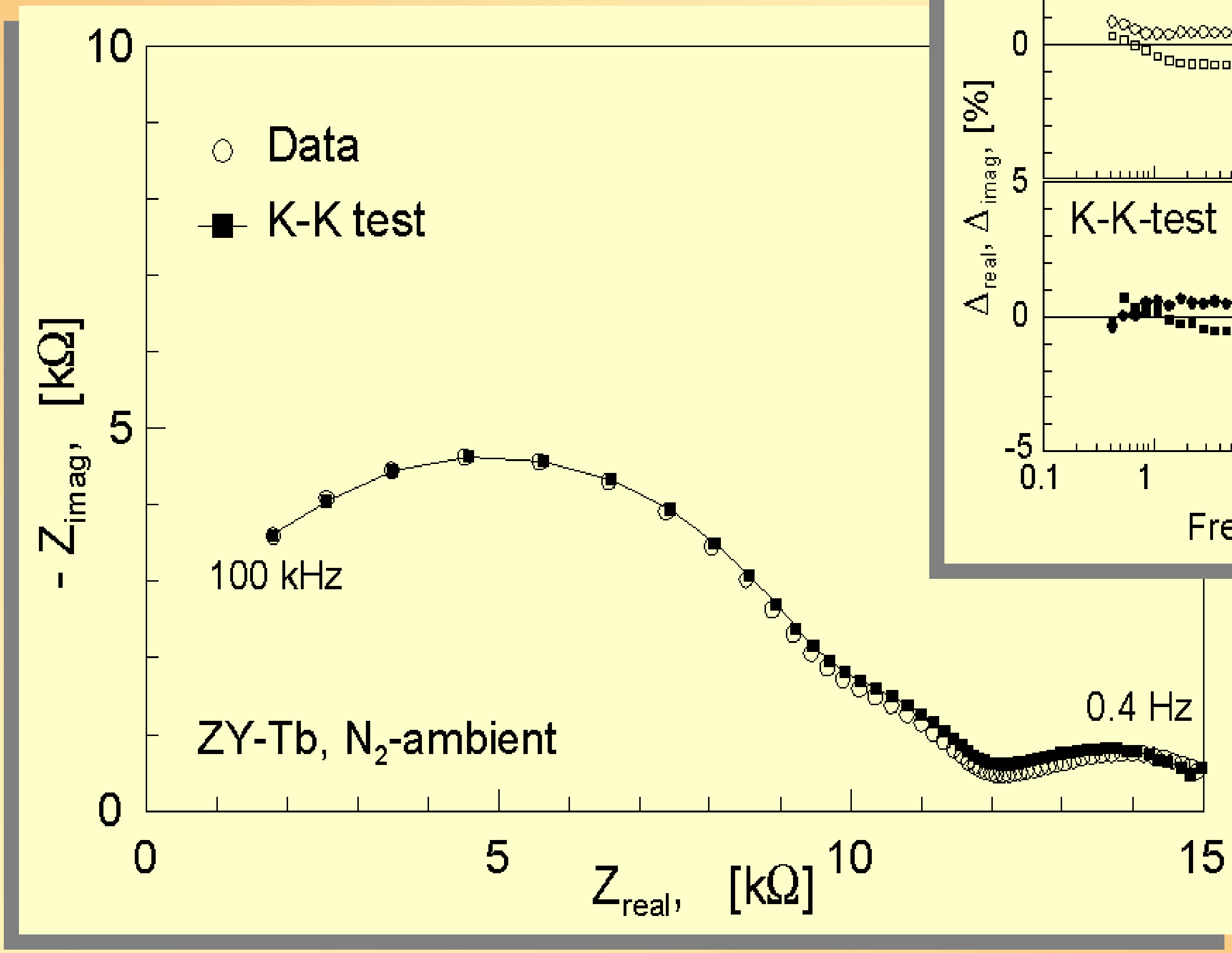
It works like a 'K-K compliant' flexible curve

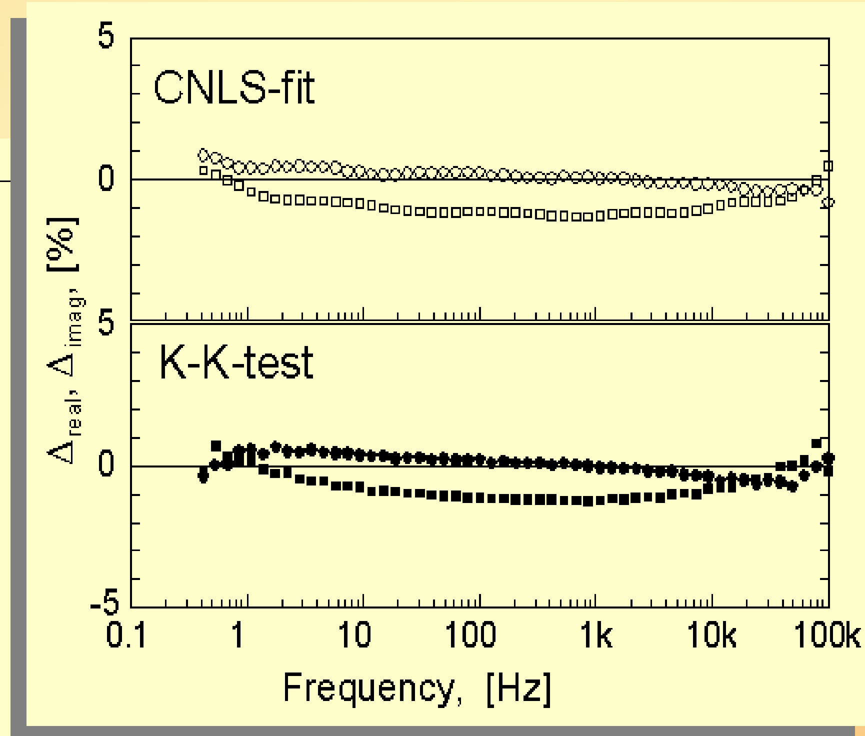
Display relative residuals:

$$\boxed{\Delta_{real} = \frac{Z_{re,i} - Z_{KK,re}(\omega_i)}{|Z_i|}, \quad \Delta_{imag} = \frac{Z_{im,i} - Z_{KK,im}(\omega_i)}{|Z_i|}}$$

Example 'K-K check'

Impedance of a sample, not in equilibrium with the ambient.





$\chi^2_{KK} = 0.9 \cdot 10^{-4}$

$\chi^2_{CNLS} = 1.4 \cdot 10^{-4}$

Finite length diffusion

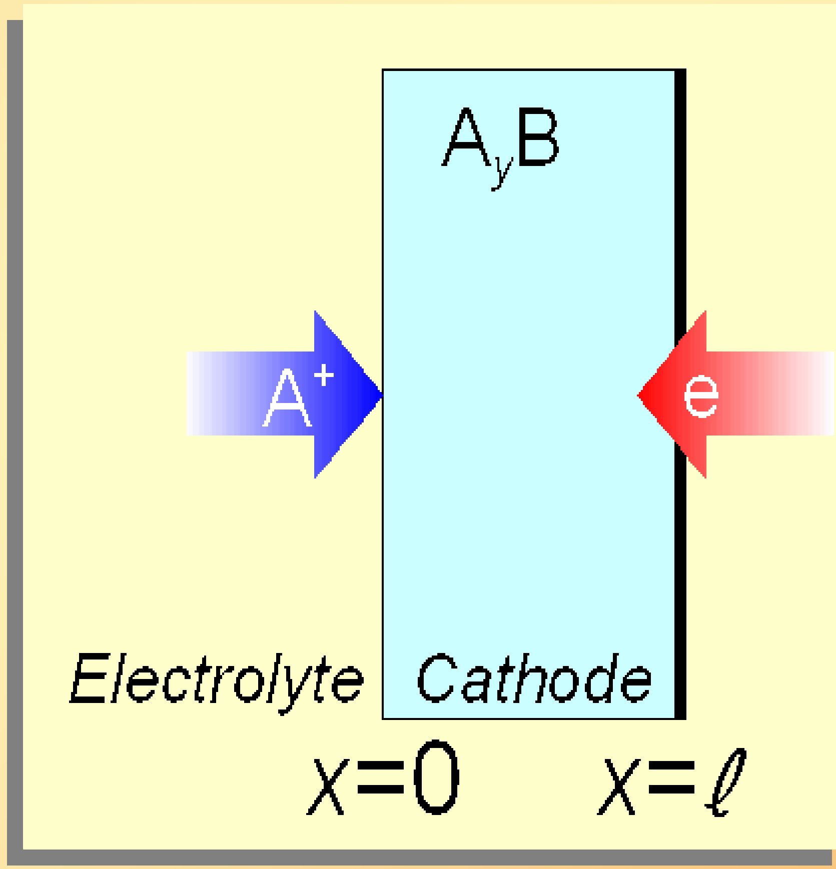
Particle flux at x=0:

$$J(t) = -\widetilde{D}\left.\frac{\mathrm{d}C(x,t)}{\mathrm{d}t}\right|_{x=0}$$

Fick's 2nd law:

$$\frac{\mathrm{d}C(x,t)}{\mathrm{d}t} = \widetilde{D}\frac{\mathrm{d}^2C(x,t)}{\mathrm{d}x^2}$$

But now a boundary condition at x = L.



Activity of A is measured at the interface at x=0. with respect to a reference, e.g. A_{met}

Finite length diffusion

Replace concentration by its perturbation:

$$c(x,t) = C(x,t) - C^0$$

Impermeable boundary at $x = L$:

$$\left.\frac{\mathrm{d}C(x,t)}{\mathrm{d}x}\right|_{x=l} = 0$$

FSW

Ideal source/sink with $C = C_L$ ($=C^0$):

$$C(x,t)\big|_{x=l} = C_l \left(= C^0\right)$$

FLW

General expression for permeable boundary:

$$\left.\frac{\mathrm{d}C(x,t)}{\mathrm{d}x}\right|_{x=l} = -k\left[C(x,t)\big|_{x=l} - C_l\right]$$

General!

FLD, continued

Voltage with respect to reference C^0 (a^0):

$$E(t)=\frac{RT}{nF}\ln\frac{a_{x=0}}{a^0}=\frac{RT}{nFC^0}\left[\frac{\mathrm{d}\ln a}{\mathrm{d}\ln C}\right]c(x,t)\Big|_{x=0}$$

Current through interface at $x = 0$:

$$I(t)=nF\cdot S\cdot J(t)=-nF\cdot S\cdot\widetilde{D}\left.\frac{\mathrm{d}c(x,t)}{\mathrm{d}x}\right|_{x=0}$$

Assumption: $\Delta a \ll a^0$:

$$\ln\frac{a}{a^0}=\ln\frac{a^0+\Delta a}{a^0}=\ln\left(1+\frac{\Delta a}{a^0}\right)\approx\frac{\Delta a}{a^0}$$

Relation $a \Leftrightarrow C$ from 'titration curve':

$$\frac{\mathrm{d}a}{\mathrm{d}C}=\frac{a^0}{C^0}\frac{\mathrm{d}\ln a}{\mathrm{d}\ln C}\approx\frac{\Delta a}{\Delta C}=\frac{\Delta a}{\Delta c(x,t)\big|_{x=0}}$$

Up to the Frequency Domain!

Laplace transformation of $E(t)$ and $I(t)$ gives the complex impedance (with $p=j\omega$):

FSW
$$Z(\omega)=\frac{E(\omega)}{I(\omega)}=\frac{Z_0}{\sqrt{j\omega\tilde{D}}}\coth l\sqrt{\frac{j\omega}{\tilde{D}}}$$

FLW
$$Z(\omega)=\frac{E(\omega)}{I(\omega)}=\frac{Z_0}{\sqrt{j\omega\tilde{D}}}\tanh l\sqrt{\frac{j\omega}{\tilde{D}}}$$

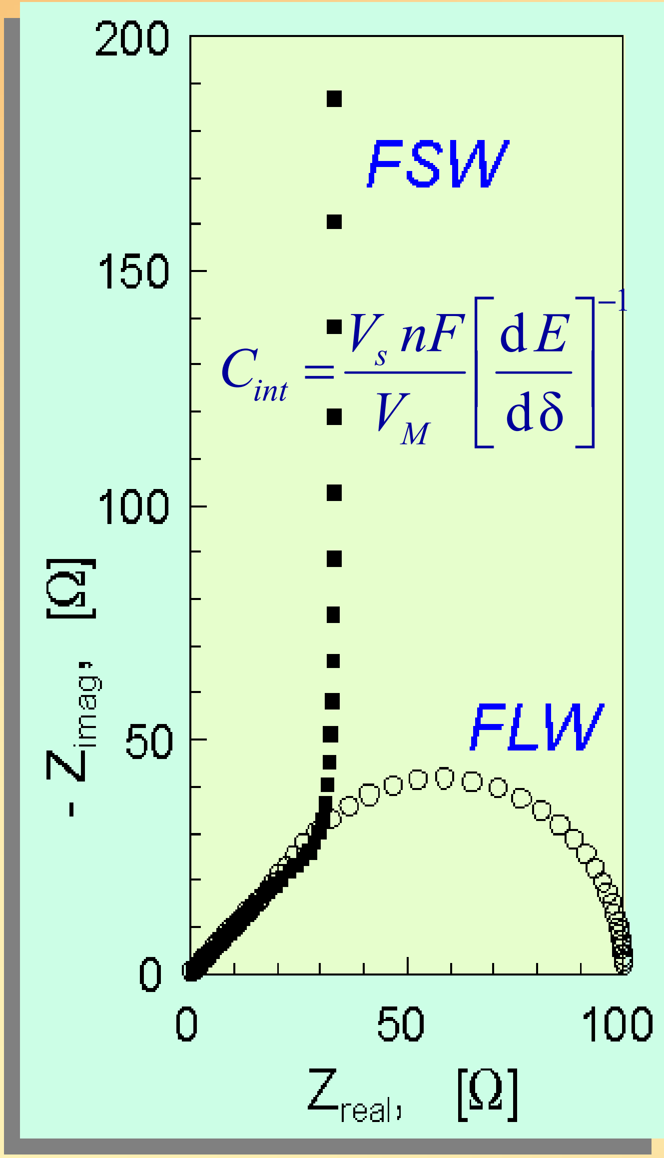
with:

$$Z_0=\frac{RTV_m}{n^2F^2S}\left[\frac{\mathrm{d}\ln a}{\mathrm{d}\ln c}\right]=$$
$$=\frac{V_m}{nFS}\left[\frac{\mathrm{d}E}{\mathrm{d}\delta}\right]$$

Laplace space solution of Fick-2:

$$C(p)=A\cosh x\sqrt{\frac{p}{\tilde{D}}}+B\sinh x\sqrt{\frac{p}{\tilde{D}}}$$

Dispersions



High frequencies:

$$Z(\omega) = Z_0\, (j\,\omega)^{-1/2}$$

= Warburg diffusion

Low frequency limit:

FSW = capacitive

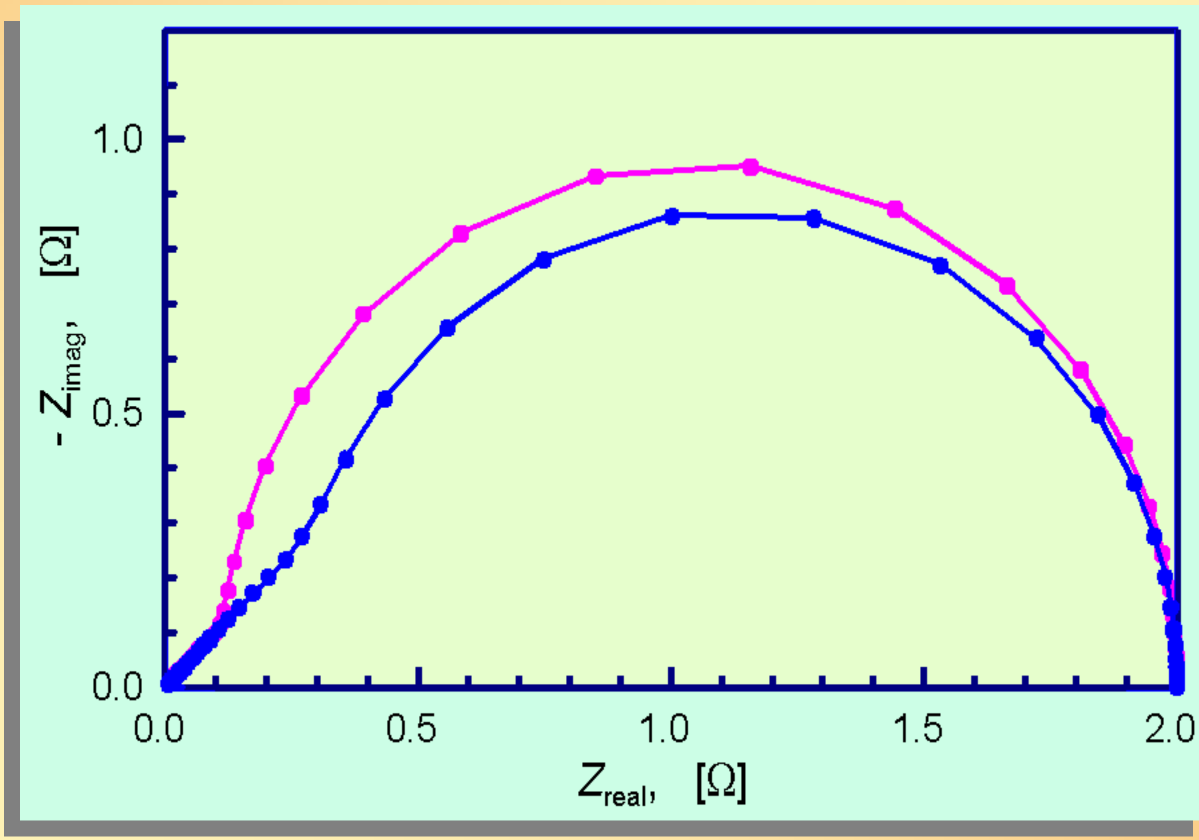
FLW = dc-resistance

Impedance representation of FSW and FLW.

General finite length diffusion

Generic finite length diffusion:

$$Z(\omega) = \frac{Z_0}{\sqrt{j\omega D_0}} \frac{\sqrt{j\omega D_0}\coth l\sqrt{\frac{j\omega}{D_0}} + k}{k\coth l\sqrt{\frac{j\omega}{D_0}} + \sqrt{j\omega D_0}}$$

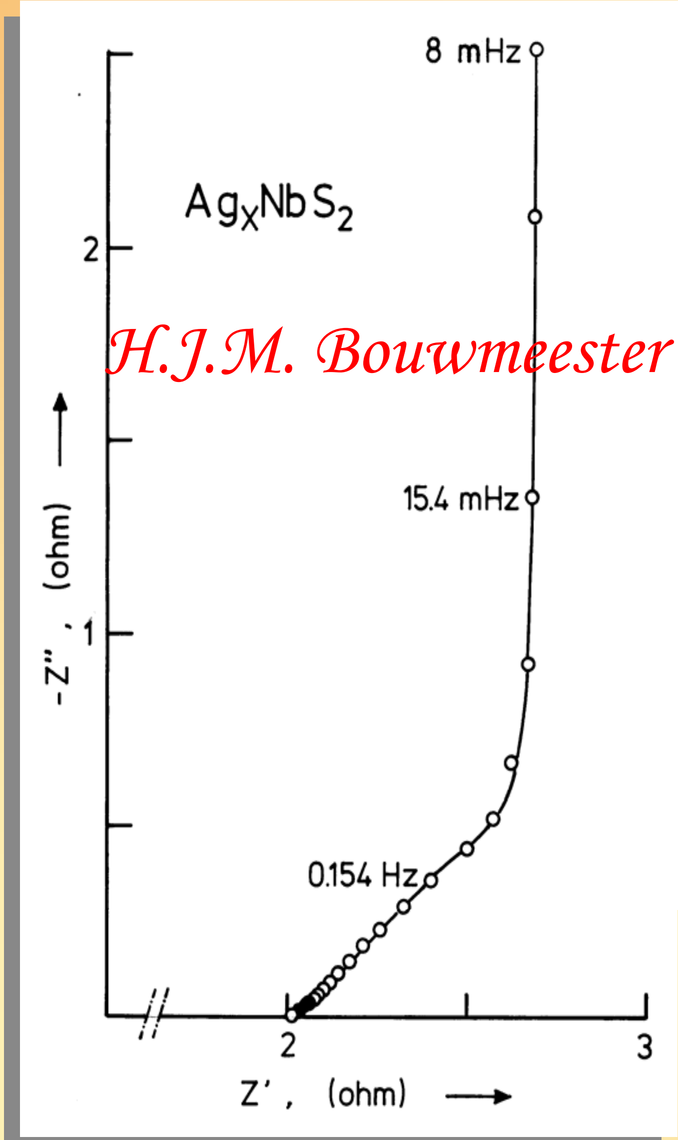


If k =0 then blocking interface ⇒ FSW

If k = ∞ then ideal passing interface ⇒ FLW

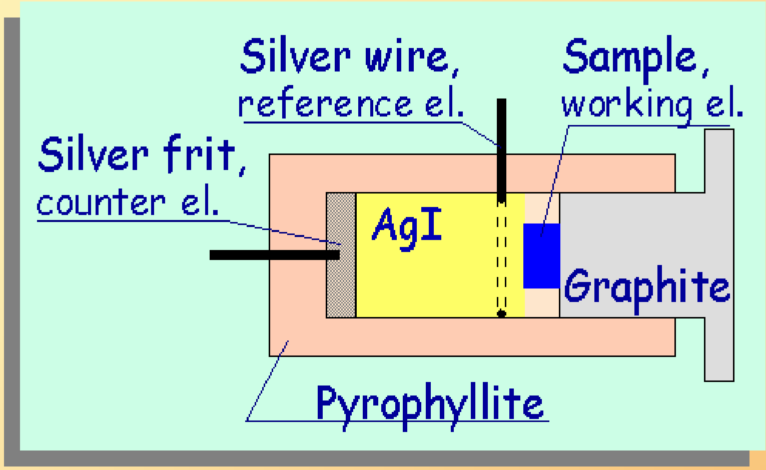
← Plot for different values of k.

A Simple Example



Ag_xNbS_2 is a layered structure, consisting of two-dimensional NbS_2 layers. Insertion and extraction of Ag^+ ions goes in an ideal manner (see graph).

Isostatically pressed and sintered sample. Some preferential orientation (in the proper direction!) will occur.



Simple cell design for EIS measurements.

Circuit Description Code

The Circuit Description Code presents an unique way to define an equivalent circuit in terms suitable for computer processing.

Elements: R, C, L, W

Finite length diffusion:

T = FSW = Tanhyp (Adm.) Cothyp (Imp.)

O = FLW = Cothyp (Adm.) Tanhyp (Imp.)

Constant Phase Element:

Q = CPE = $Y_0(j\,\omega)^n$ (Adm.) $Z_0(j\,\omega)^{-n}$ (Imp.)

The CPE

Constant Phase Element:

$$Y_{CPE} = Y_0\, \omega^n \{\cos(n\,\pi/2) + j\ \sin(n\,\pi/2)\}$$

- $n = 1$ ➔ Capacitance: $C = Y_0$
- $n = \frac{1}{2}$ ➔ Warburg: $\sigma = Y_0$
- $n = 0$ ➔ Resistance: $R = 1/Y_0$
- $n = -1$ ➔ Inductance: $L = 1/Y_0$

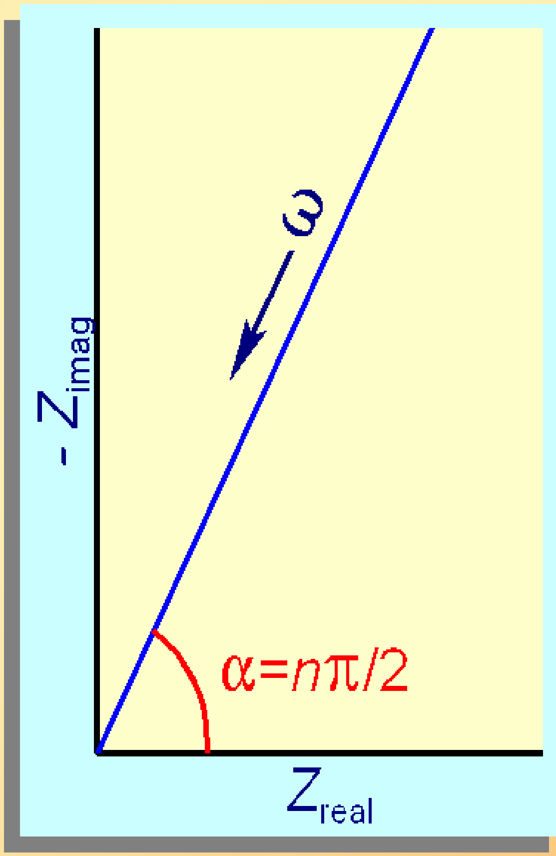
All other values, 'fractal?'

'Non-ideal capacitance', $n < 1$ (between 0.8 and 1?)

Non-ideal behaviour

General observations:

- Semicircle (*RC*) ⇒ depressed
- vertical spur (*C*) ⇒ inclined
- Warburg ⇒ less than 45°



Deviation from 'ideal' dispersion:

Constant Phase Element (CPE),

(symbol: Q)

$$Y_{CPE} = Y_0 (j\omega)^n = Y_0 \omega^n \left[\cos\frac{n\pi}{2} + j\sin\frac{n\pi}{2} \right]$$

$n = 1, \frac{1}{2},$
0, -1, ?

The Fractal Concept

How to explain this non-ideal behaviour?

1980's: 'Fractal behaviour' (Le Mehaut)

= fractal dimensionality

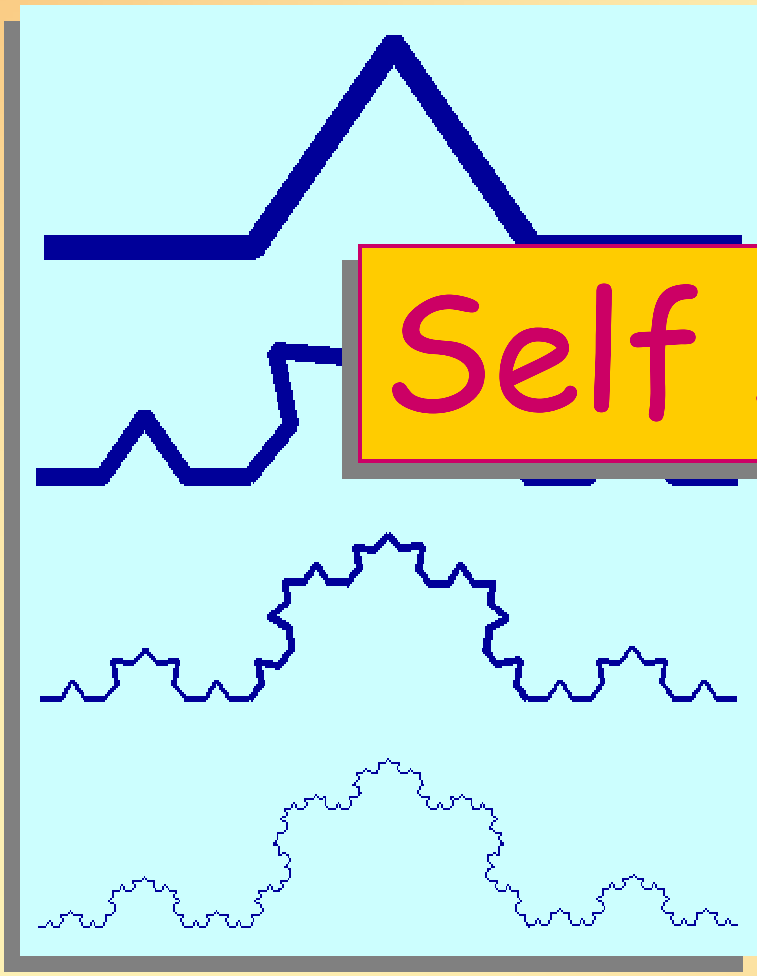
i.e.: 'What is the length of the coast line of England?'

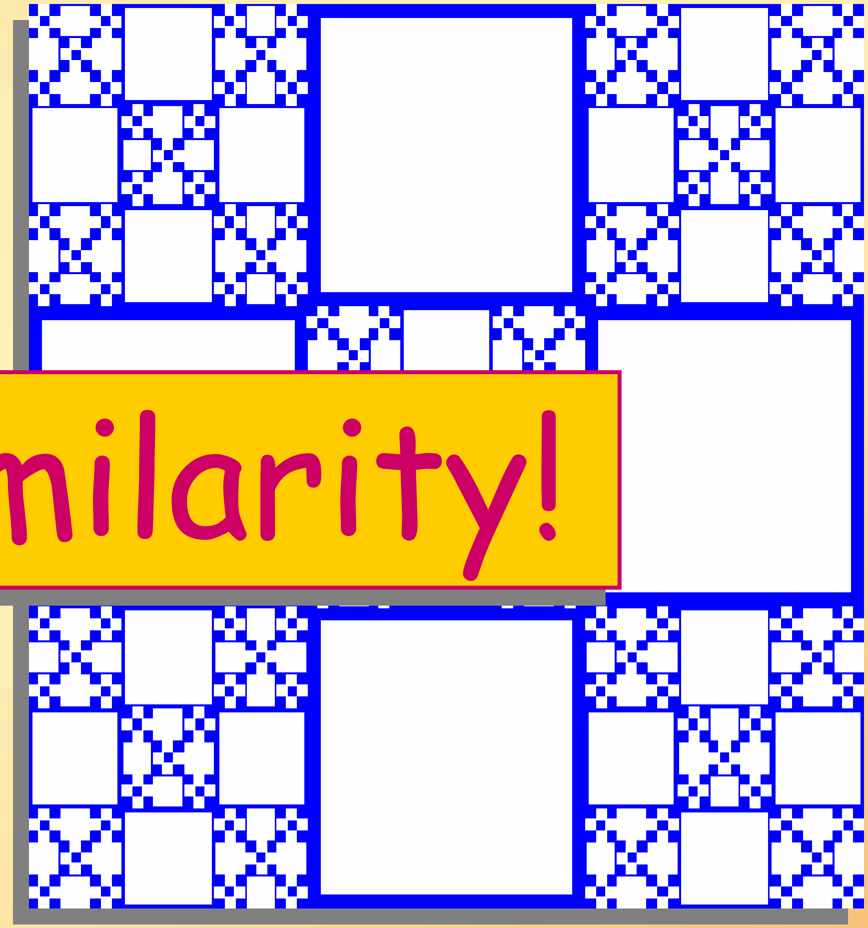
☞ Depends on the size of the measuring stick!

☞ **Self similarity** ☜

Fractals

Fractal line

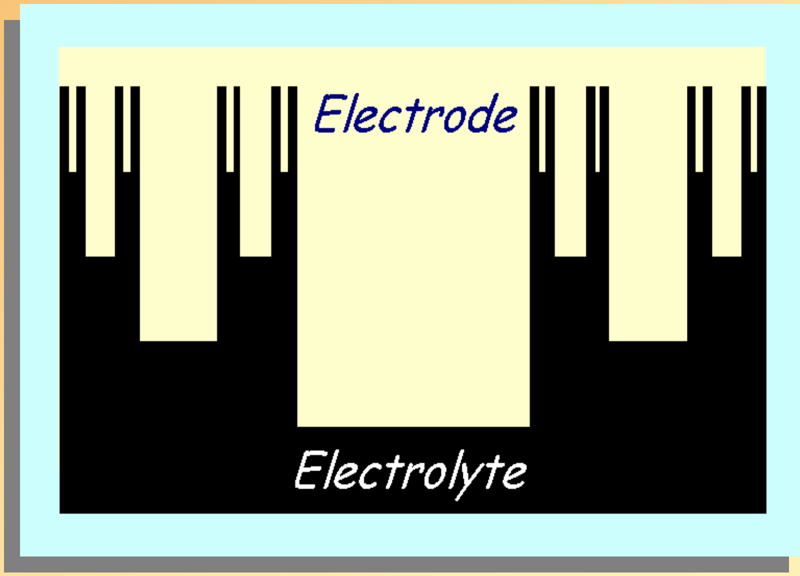




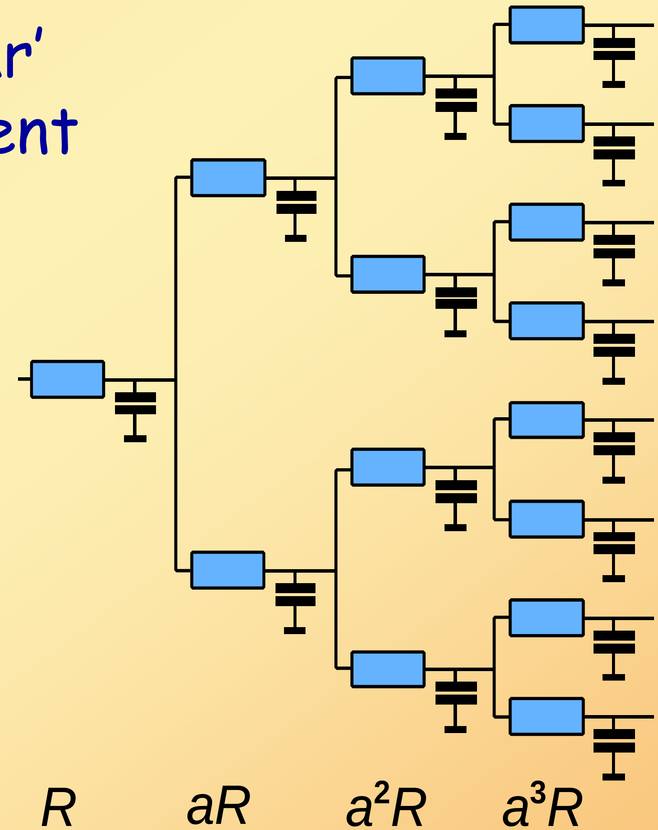
Self similarity!

'Sierpinski carpet'

'Fractal electrode'



'Cantor bar' arrangement



Impedance of the network:

$$Z\left(\frac{\omega}{a}\right) = R + \frac{a\,Z(\omega)}{j\omega C\,Z(\omega) + 2}$$

Arriving at the 'CPE'

Frequency scaling relation: $$Z\left(\frac{\omega}{a}\right) = R + \frac{aZ(\omega)}{j\omega C Z(\omega) + 2}$$

In the low frequency limit this reduces to: $$Z\left(\frac{\omega}{a}\right) = \frac{a}{2}Z(\omega)$$

Which is satisfied by the formula: $$Z(\omega) = A(j\omega)^{-n}$$

with $n = 1 - \ln 2/\ln a$
Fractal dimension of Cantor bar, $d = \ln 2/\ln a$
Hence: $n = 1 - d$

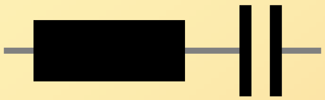
S.H. Liu and T. Kaplan, Solid State Ionics **18 & 19** (1986) 65-71.

CDC

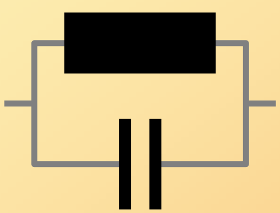
CDC = 'instruction string' for response calculation

Uses brackets:

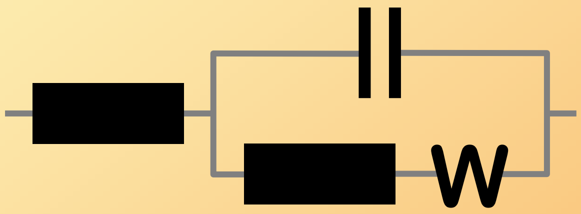
- […] series combination, e.g.: [RC]



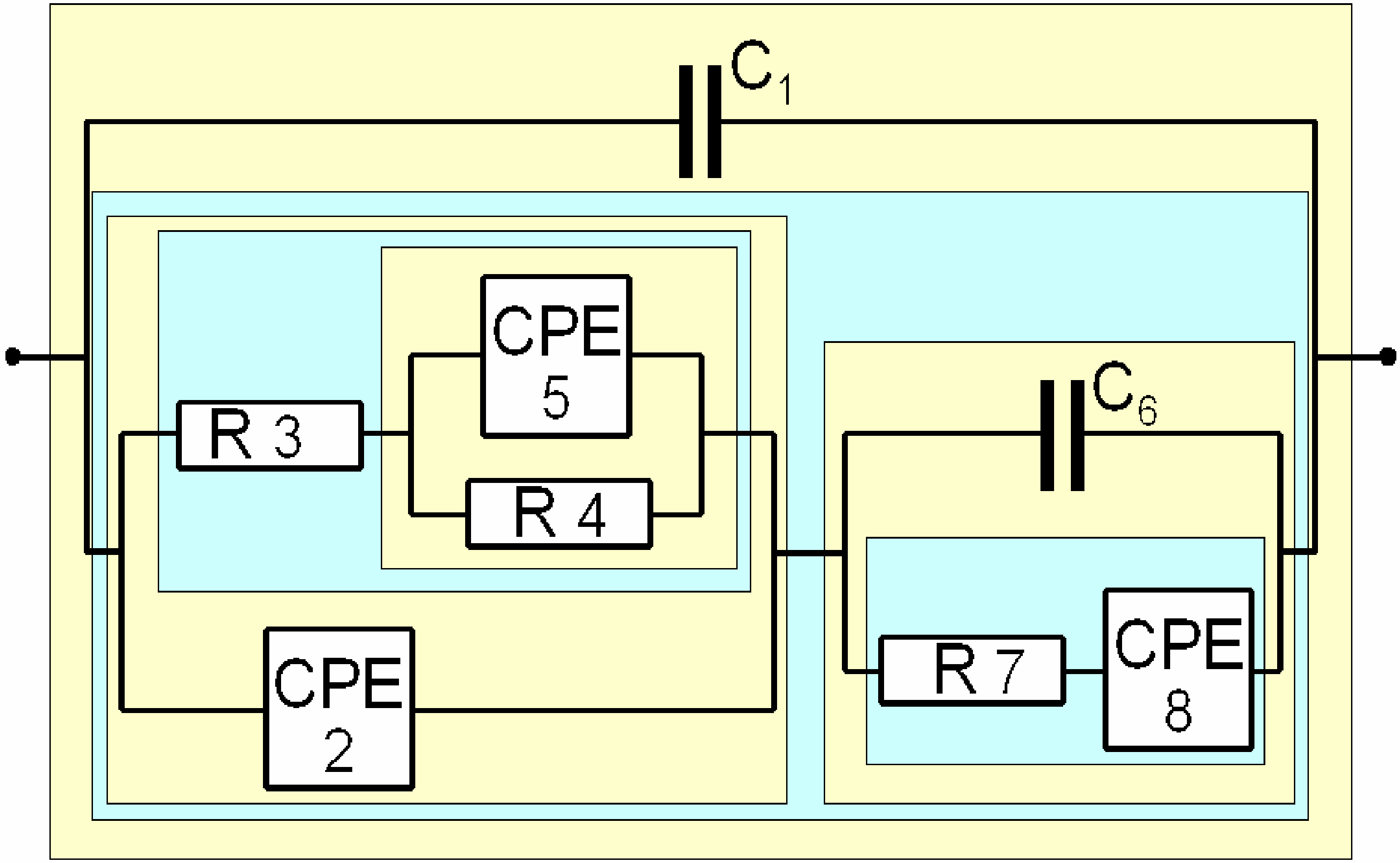
- (…) parallel combination, e.g. (RC)



Randles circuit: R(C[RW])



Determining the CDC



(C [(Q [R (R Q)]) (C [R Q])])

CNLS data analysis

Model function, $Z(\omega,a_k)$, or equivalent circuit.

Adjust circuit parameters, a_k, to match data,

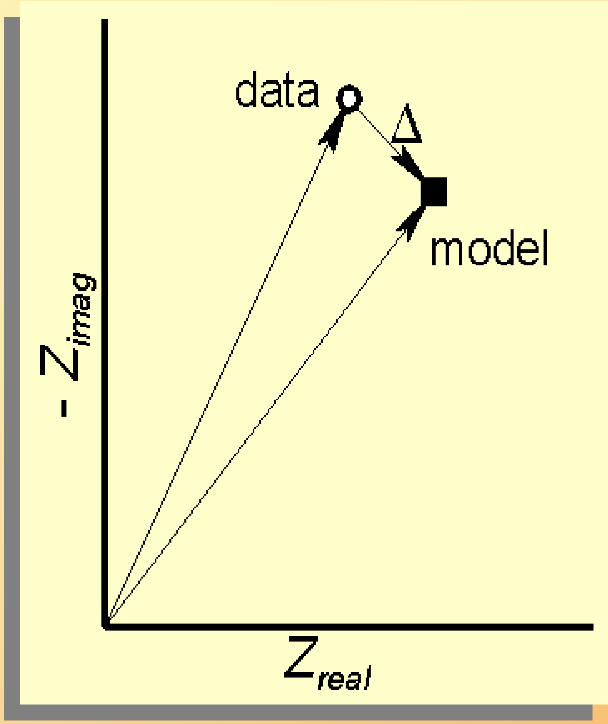
Minimise error function:

$$\boxed{S=\sum_{i=1}^{n} w_i\left\{\left[Z_{re,i}-Z_{re}(\omega_i)\right]^2+\left[Z_{im,i}-Z_{im}(\omega_i)\right]^2\right\}}$$

with: $w_i=\left[Z_i\right]^2 \approx \left[Z(\omega_i,a_k)\right]^2$ (weight factor)

for $k = 1 .. M$ $\quad \dfrac{\mathrm{d}}{\mathrm{d}a_k}S=0$

Non-linear, complex model function!



Effect of minimisation

Non-linear systems

Function $Y(a_1..a_M)$ is not linear in its parameters, e.g.:

$$Z(\omega) = Z_0 \cdot \left[k + \left(j\omega\right)^{\beta}\right]^{-\alpha} = Z(\omega, Z_0, k, \alpha, \beta)$$

('Gerischer')

Linearisation: Taylor development around 'guess values', a_j^o:

$$Y(x, a_1..a_M) = Y(x, a_1^{o}..a_M^{o}) + \sum_j \left.\frac{\partial Y(x, a_1..a_M)}{\partial a_j}\right|_{a_1^{o}..a_M^{o}} \cdot \delta a_j + \ldots$$

Derivative of error sum with respect to δa_j:

$$\frac{\partial S}{\partial a_j} = 0 = 2\sum_i w_i \left[y_i - Y(x_i, a_{1..M}^{o}) + \sum_k \frac{\partial Y(x_i, a_{1..M})}{\partial a_k} \delta a_k \right] \frac{\partial Y(x_i, a_{1..M})}{\partial a_j}$$

NLLS-fit

A set of *M* simultaneous equations, in matrix form:

$$\alpha \cdot \delta \mathbf{a} = \beta \ , \qquad \text{solution: } \delta \mathbf{a} = \alpha^{-1} \cdot \beta = \varepsilon \cdot \beta$$

With: $$\alpha_{j,k} = \sum_i w_i \frac{\partial Y(x_i, a_{1..M})}{\partial a_j} \cdot \frac{\partial Y(x_i, a_{1..M})}{\partial a_k}$$

and: $$\beta_k = \sum_i w_i \left[y_i - Y(x_i, a_{1..M}) \right] \frac{\partial Y(x_i, a_{1..M})}{\partial a_k}$$

Derivatives are taken in point $a^o_{1..M}$.

Iteration process yields new, improved values: $a'_j = a^o_j + \delta a_j$.

Marquardt-Levenberg

Analytical search: fast and accurate near true minimum
slow far from minimum
(and often erroneous)

Gradient search or steepest descent (diagonal terms only):
fast far from minimum
slow near minimum

Hence, combination!

Multiply diagonal terms with $(1+\lambda)$.

- $\lambda \ll 1$, analytical search
- $\lambda \gg 1$, gradient search

Successful iteration:
$S_{new} < S_{old}$
➔ decrease λ (= $\lambda/10$).
Otherwise increase
λ (= $\lambda \times 10$)

Bottom line: good starting parameter estimates are **essential**!

Error estimates

For proper statistical analysis the weight factors, w_i, should be established from experiment.

Other (dangerous) method:

Step 1: set weight factors, $w_i = g \cdot \sigma_i^{-2}$

Step 2: assume variances can be replaced by parent distribution, hence $\chi_\nu^2 \approx 1$ (with $\nu = N - M - 1$)

Step 3:

$$\chi_\nu^2 = \frac{\chi^2}{\nu} = \frac{1}{\nu}\sum_i \frac{\left[y_i - Y(x_i, a_{1..M})\right]^2}{\sigma_i^2} = \frac{1}{\nu} S \sum_i \frac{1}{w_i \cdot \sigma_i^2} = \frac{S}{g \cdot \nu} \cong 1$$

Hence proportionality factor, $g = S/\nu$.

Error analysis NLLS-fit

Based on this assumption we can derive
the variances of the parameters: $\sigma_{a_k}^2 = g \cdot [\alpha_{k,k}]^{-1} = g \cdot \varepsilon_{k,k}$

Error matrix, ε, also contains the covariance of the parameters:

$$\sigma_{a_j} \cdot \sigma_{a_k} = g \cdot \varepsilon_{j,k}$$

$g \cdot \varepsilon_{j,k} \cong 0$, no correlation between a_j and a_k.

$g \cdot \varepsilon_{j,k} \cong 1$, strong correlation between a_j and a_k.

Only acceptable for many data points AND random distribution of the 'residuals'

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Nov. '08.

Weight factors and error estimates

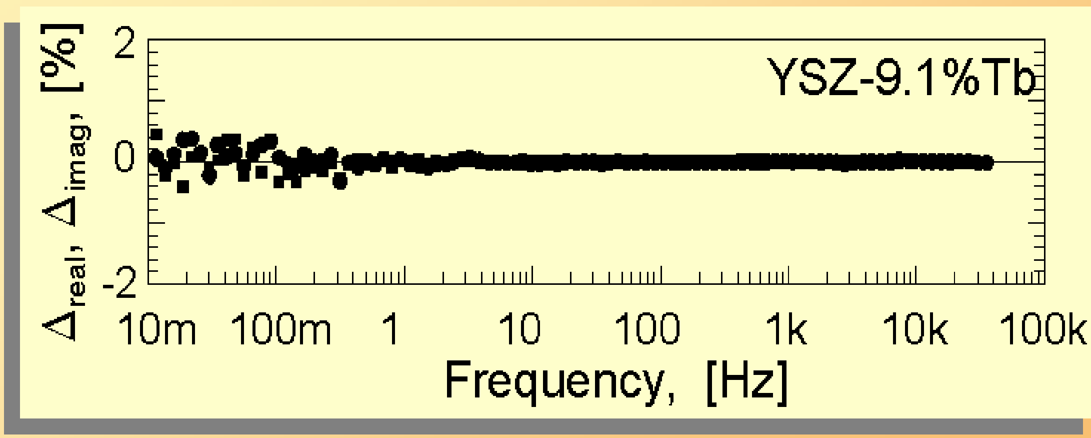
Errors in parameters:

- estimates from CNLS-fit procedure
- assumption: error distribution equal to 'parent distribution'
- *only valid* for random errors,
- no systematic errors allowed!

→ Residuals graph:

$$\Delta_{re} = \frac{Z_{re,i} - Z_{re}(\omega_i)}{|Z(\omega_i)|}, \quad \Delta_{im} = \frac{Z_{im,i} - Z_{im}(\omega_i)}{|Z(\omega_i)|}$$

Large error estimates: strongly correlated parameters (+ noise).
Option: modification of weight factors.



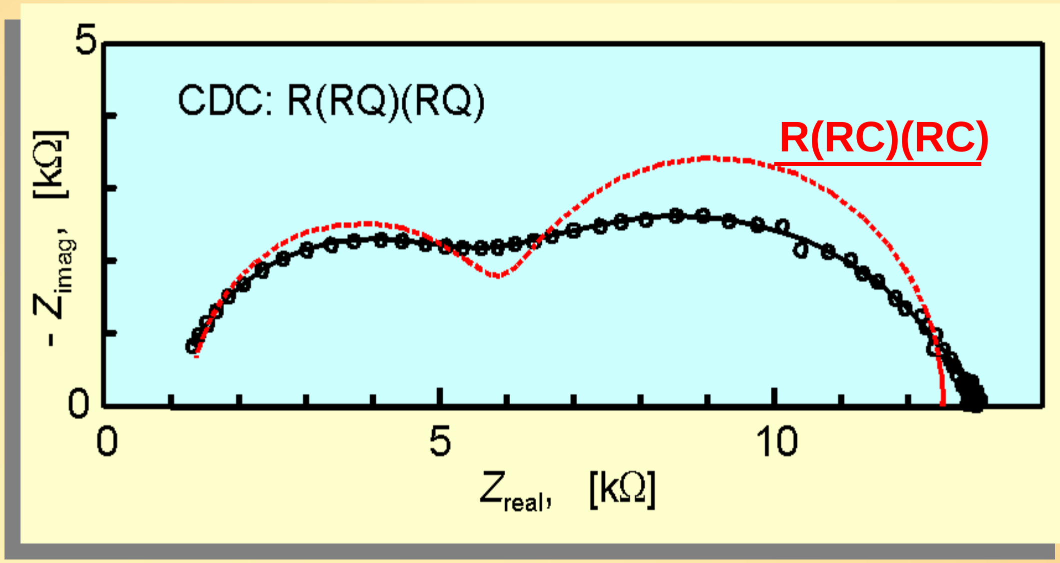
Two different CNLS-fits

Example of correct error estimates:

CDC: R(RQ)(RQ)

χ^2 $2.4 \cdot 10^{-5}$

R_1	999	0.8%
R_2	4000	1.7%
Q_3	$1.03 \cdot 10^{-9}$	7%
$-n_3$	0.898	0.6%
R_4	8020	0.9%
Q_5	$1.03 \cdot 10^{-7}$	3.6%
$-n_5$	0.697	0.7%



And of incorrect error estimates:

CDC: R(RC)(RC)
Values seem O.K. but look at the residuals!

χ^2 $3.8 \cdot 10^{-3}$

R_1	1290	4%
R_2	4650	2.7%
C_3	$2.38 \cdot 10^{-10}$	3.8%
R_4	6580	2.6%
C_5	$6.07 \cdot 10^{-9}$	7.3%

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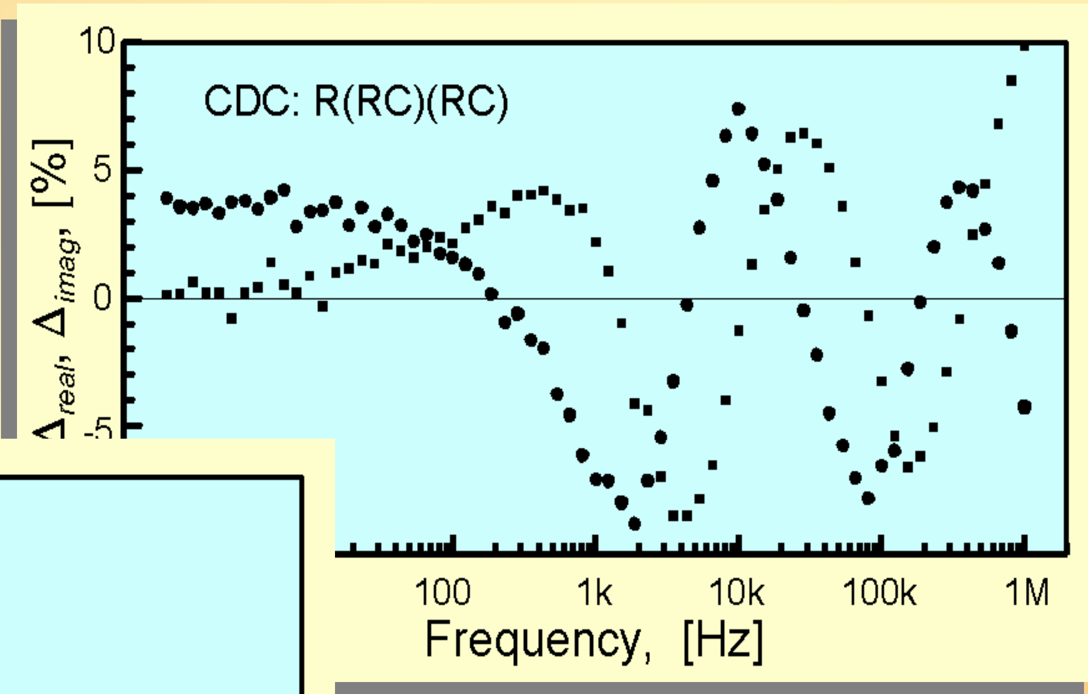
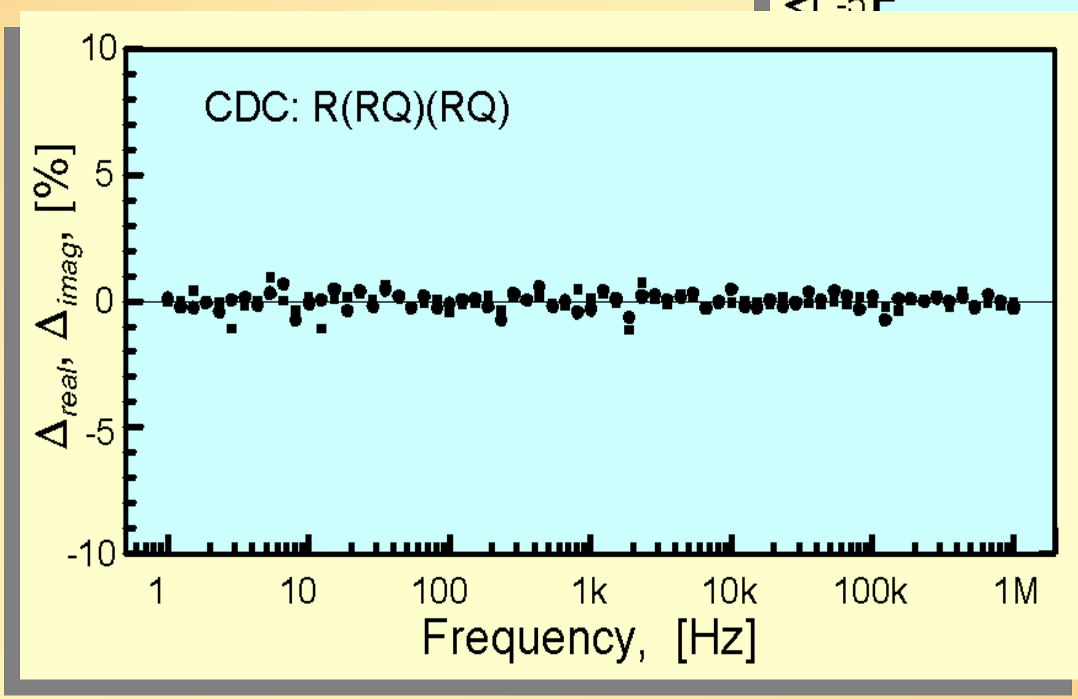
Residuals plot!

Systematic deviation,

'Trace', bad fit





Good fit (not bad for a straight simulation!)

'Fingerprinting'

Classification of capacitance

source	approximate value
geometric	2-20 pF (cm^{-1})
grain boundaries	1-10 nF (cm^{-1})
double layer / space charge	0.1-10 $\mu F/cm^2$
surface charge /"adsorbed species"	0.2 mF/cm^2
(closed) pores	1-100 F/cm^3
"pseudo capacitances"	
"stoichiometry" changes	large !!!!

Modified after: Peter Holtappels, TMR symposium 'Alternative anodes...', Jülich, March 2000.

Gas phase capacitance

Capacitance of gas volume (*e.g.* O_2):

PV=nRT

Capacitance: $i = C\dfrac{\mathrm{d}E}{\mathrm{d}t}$ or: $C = \dfrac{i\,\mathrm{d}t}{\mathrm{d}E}$

O_2 produced: $i\,\mathrm{d}t = 4F\,\mathrm{d}n$

Nernst: $\mathrm{d}E = \dfrac{RT}{4F}\ln\dfrac{P+\mathrm{d}P}{P} \approx \dfrac{RT}{4F}\dfrac{\mathrm{d}P}{P} = \dfrac{(RT)^2}{4F}\dfrac{\mathrm{d}n}{V}$

Combination: $\boxed{C_{ox} = \left(\dfrac{4F}{RT}\right)^2 V\cdot P}$

Example:

air, 700°C, Vol. = 10 mm^3

C_{ox} = 0.456 F !

Conclusions on 'fitting'

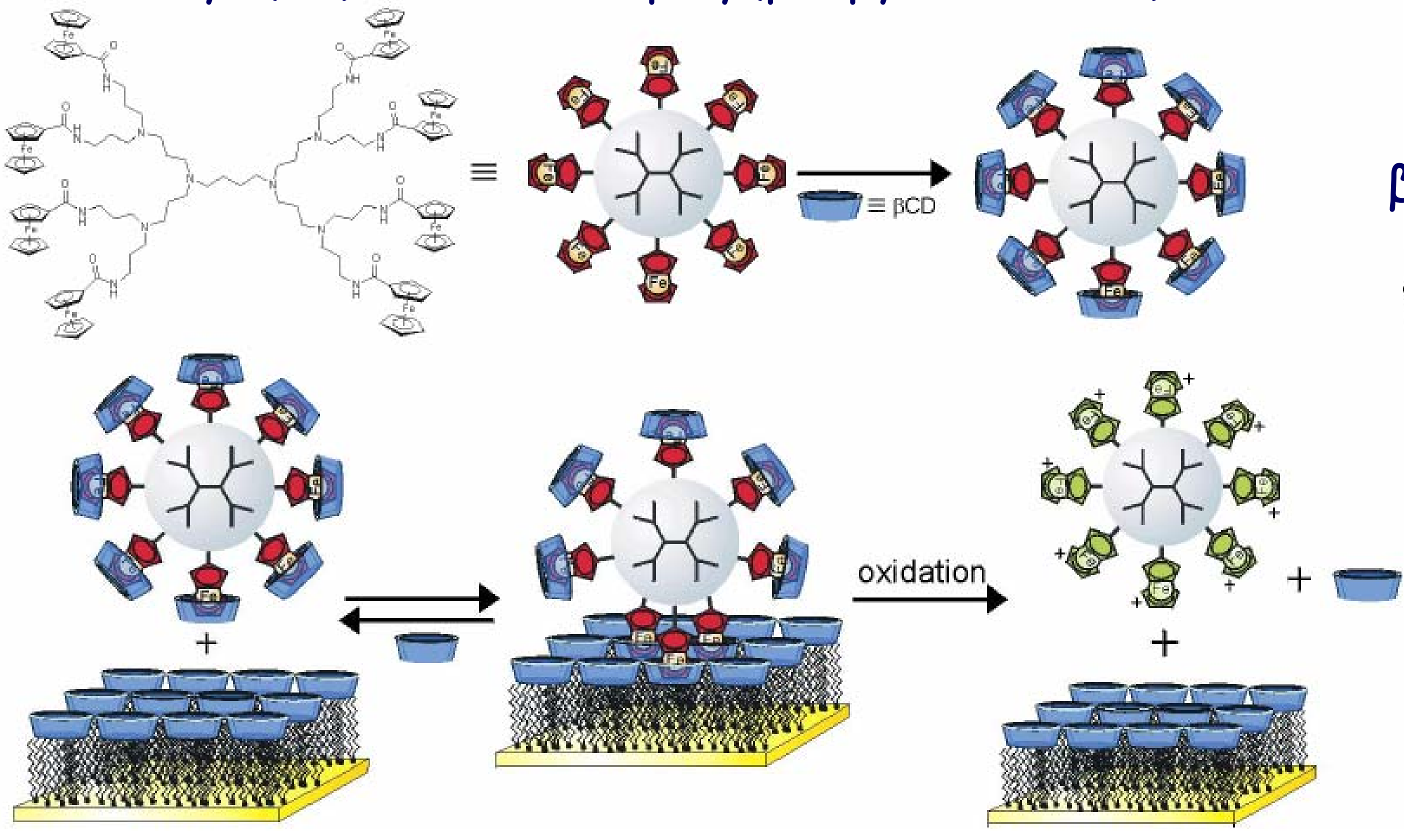
Many parameter, complex systems modelling:

- Use Marquardt-Levenberg when quality starting values are available
- Simplex (or Genetic Algorithm) for optimisation of 'rough guess' starting values, as input for M-L NLSF
- Check residuals when calculating Error Estimates
- Look for systematic error contributions, remove if feasible.
- Provide error estimates in publications!

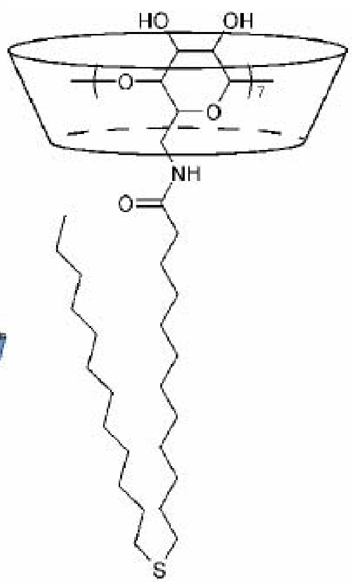
It's human to err, its dumb not to include an error estimate with a number result

'Molecular Printboard'

ferrocenyl (Fc) decorated poly(propylene imine) dendrimer



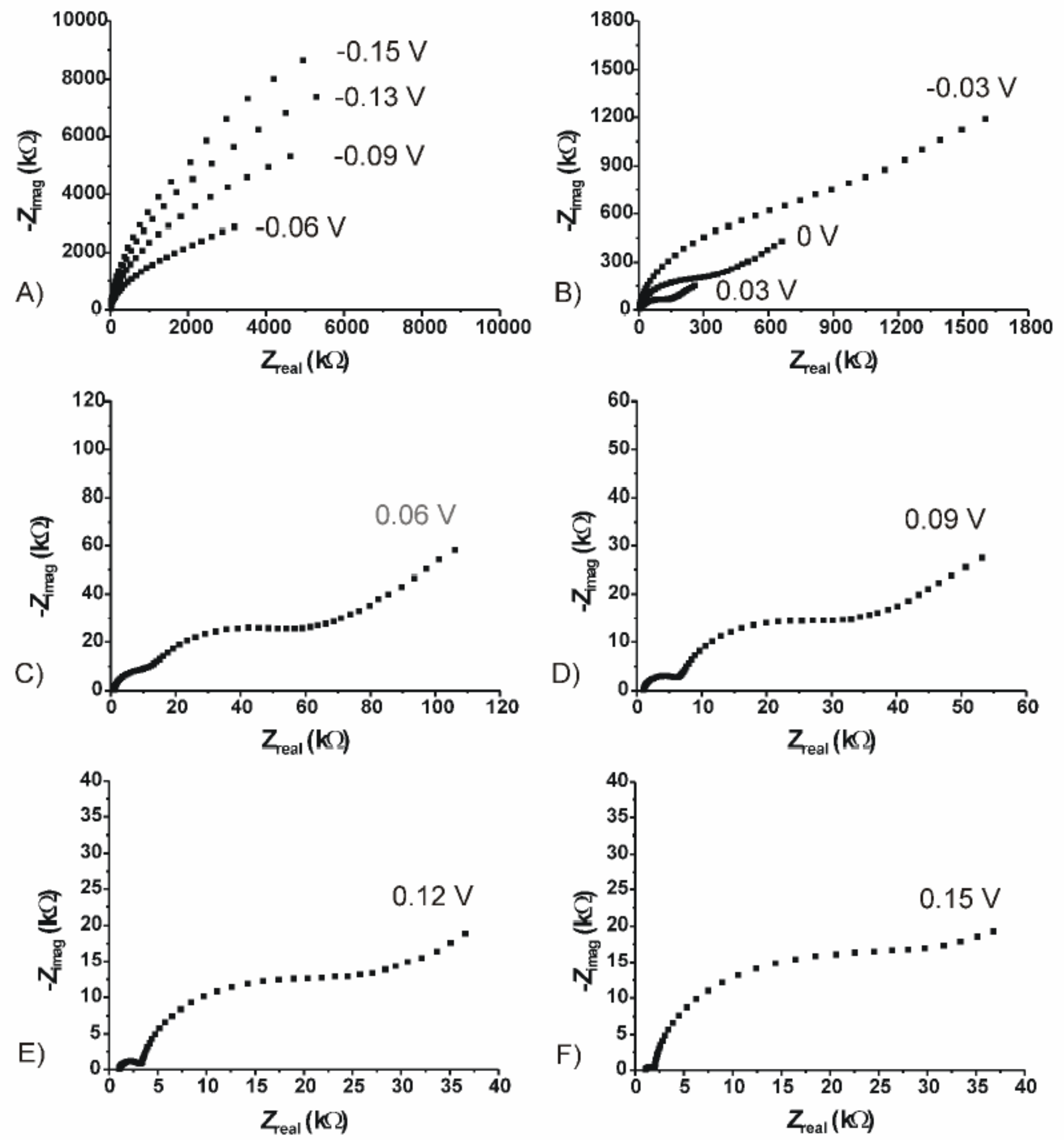
β-cyclodextrin



<u>Christian A. Nijhuis</u>, B.A. Boukamp, B-J. Ravoo, J. Huskens and D.N. Reinhoudt

J. Phys. Chem. C 111 (2007) 9799

Electrochemical response



Impedance graphs of an aqueous solution of 1 mM (in Fc functionality) of G4-PPI-(Fc)32-(β-CD)32 at a β-CD SAM.

(10 mM β-CD at pH = 2)

Potential: -0.15 V to 0.15 V
Frequency: 10 kHz to 10 mHz
KK-test: $< 10 \times 10^{-6}$

Subtraction procedure

- Partial CNLS-fit of recognizable structure
  - Semicircle
  - Straight line (CPE, Cap., Ind.)
- Subtract dispersion as series- or parallel component
- Repeat steps until 'garbage' is left
- Be aware of 'errors' due to consecutive subtractions
- Sometimes restart and do a partial fit of a larger group of parameters

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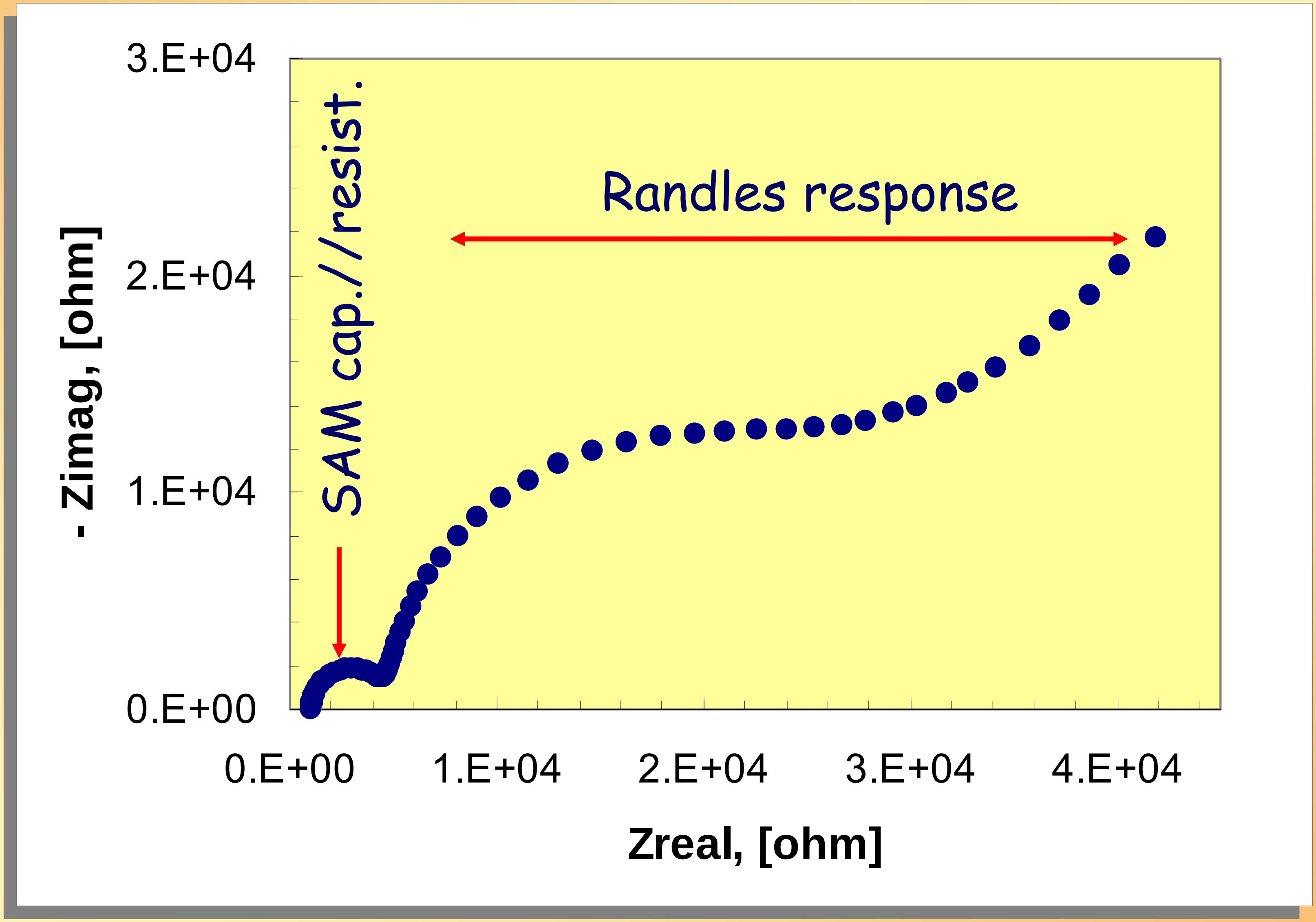
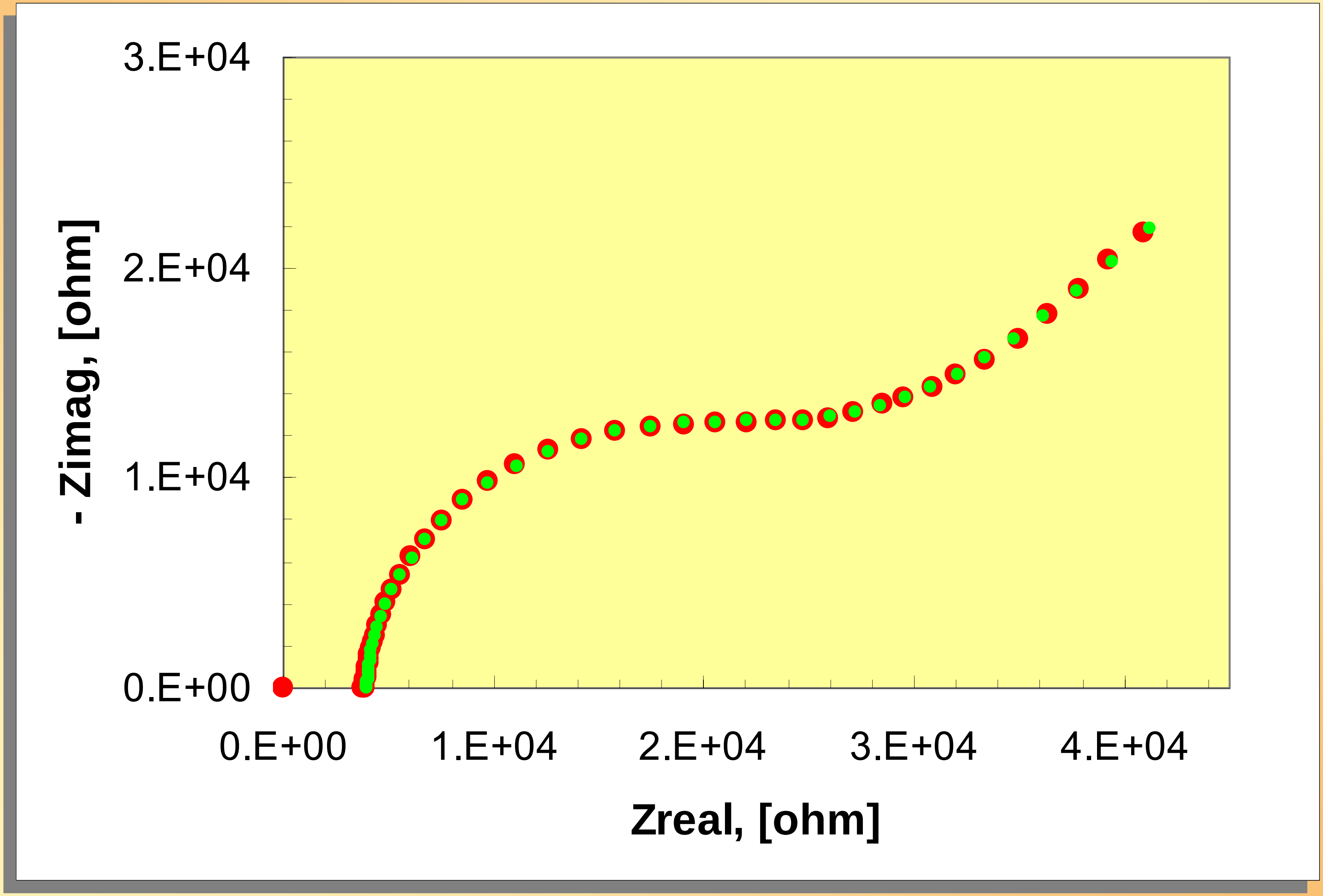
Impedance G-4 at 0.105 V



Subtract $R_{el'lyte}$, C_{SAM}



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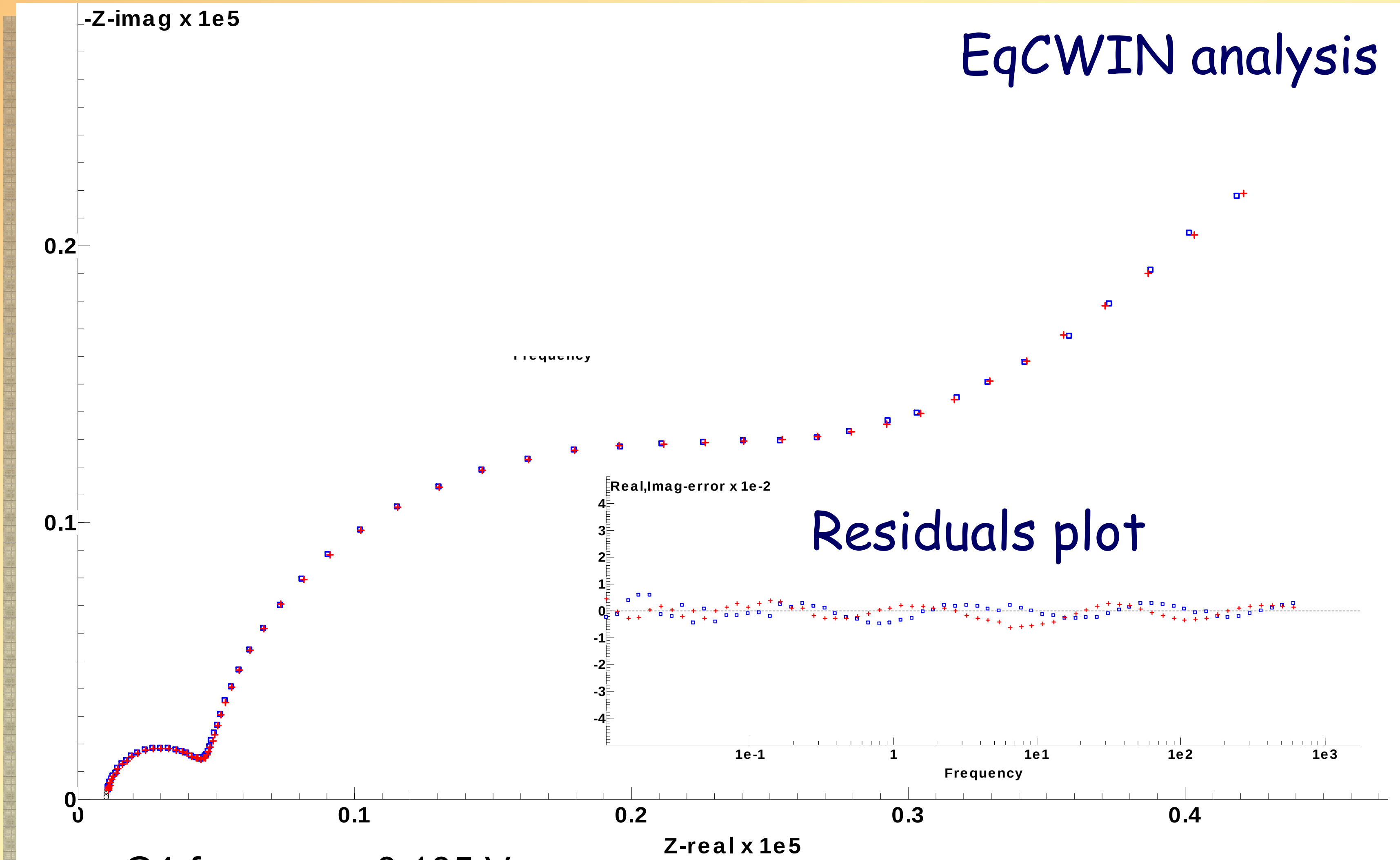
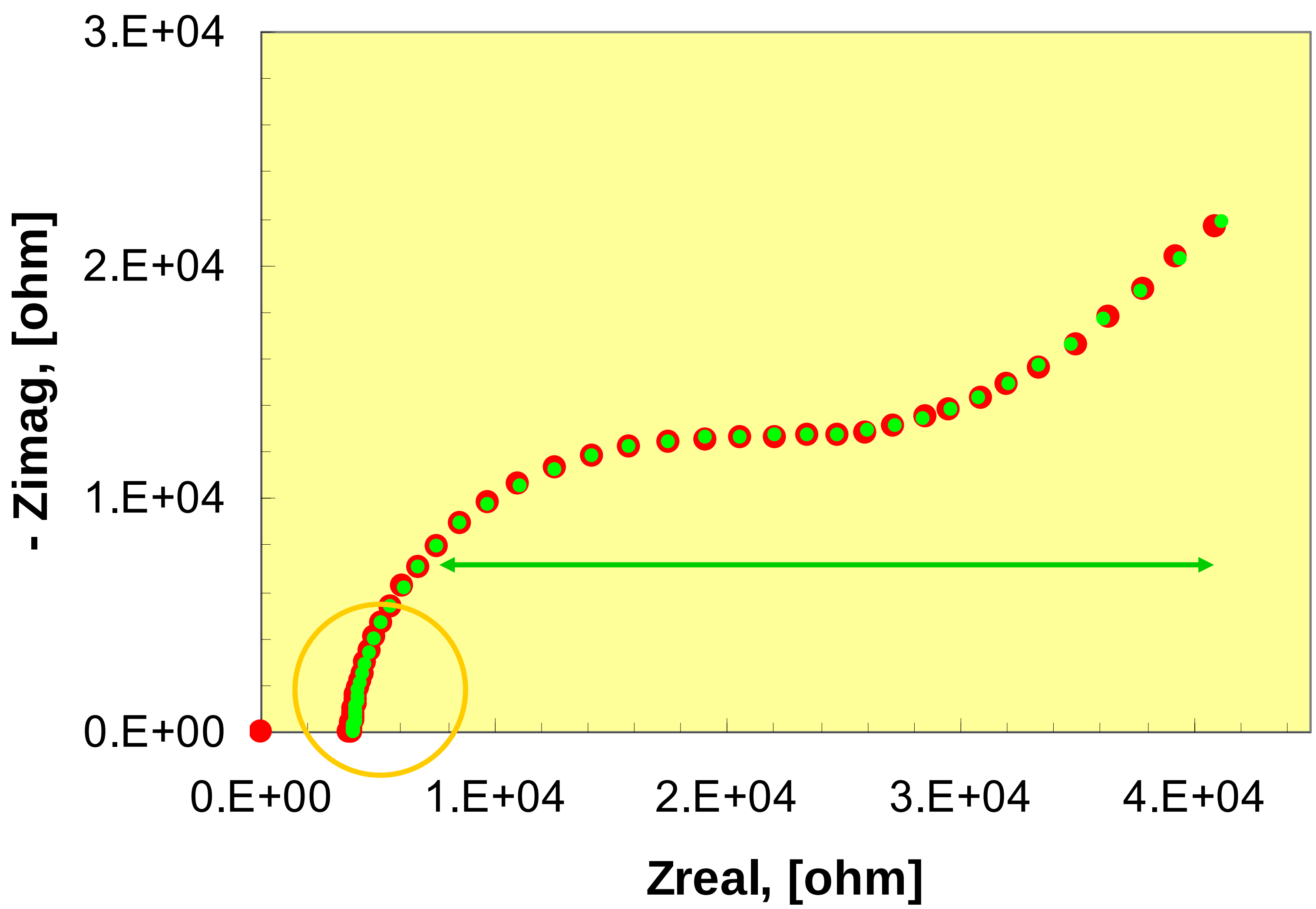
First CNLS-result

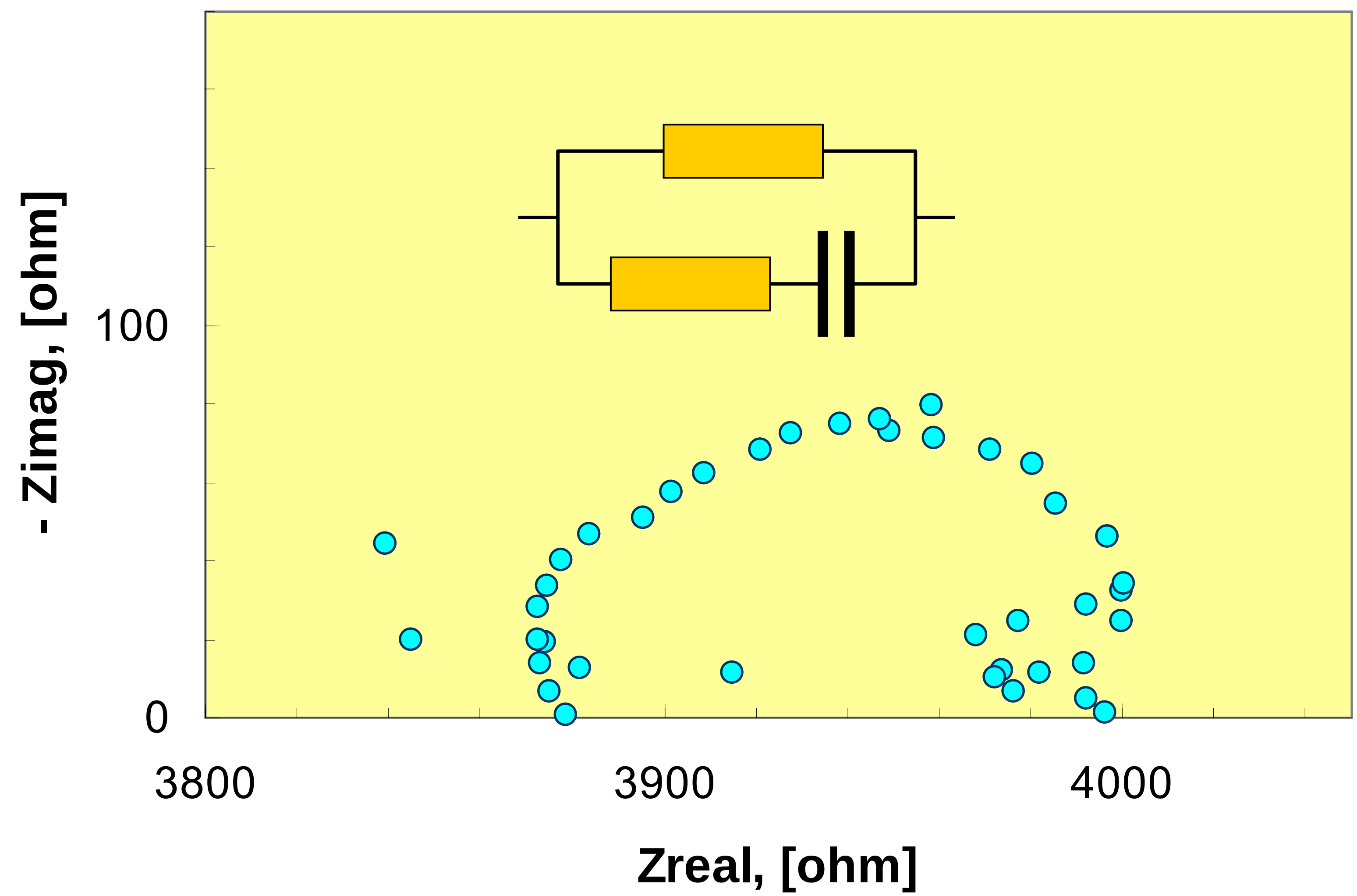


G4-ferrocene, 0.105 V

Subtract $R_{el'lyte}$, C_{SAM}



Subtract Randles



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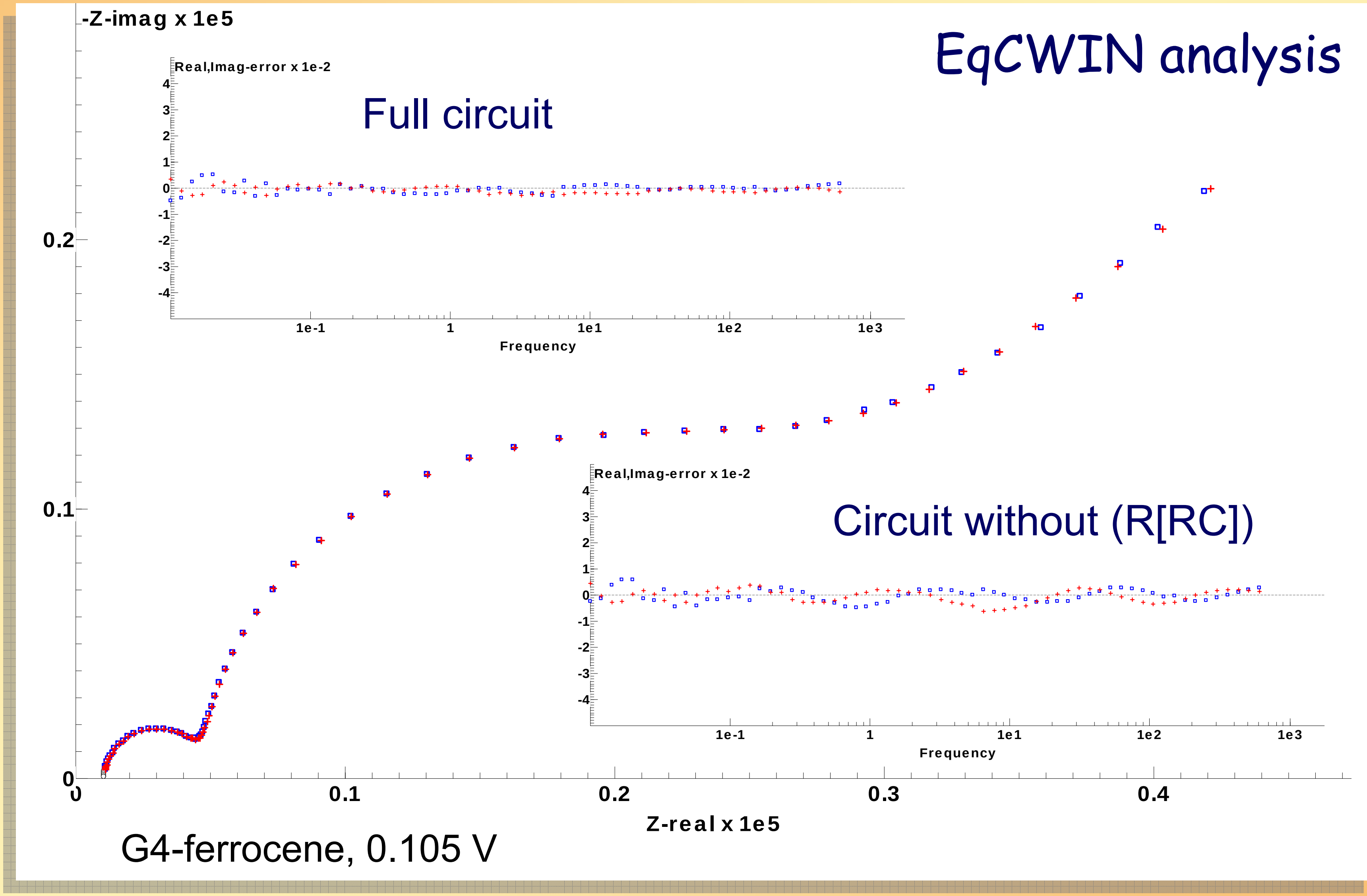
Small difference, but …



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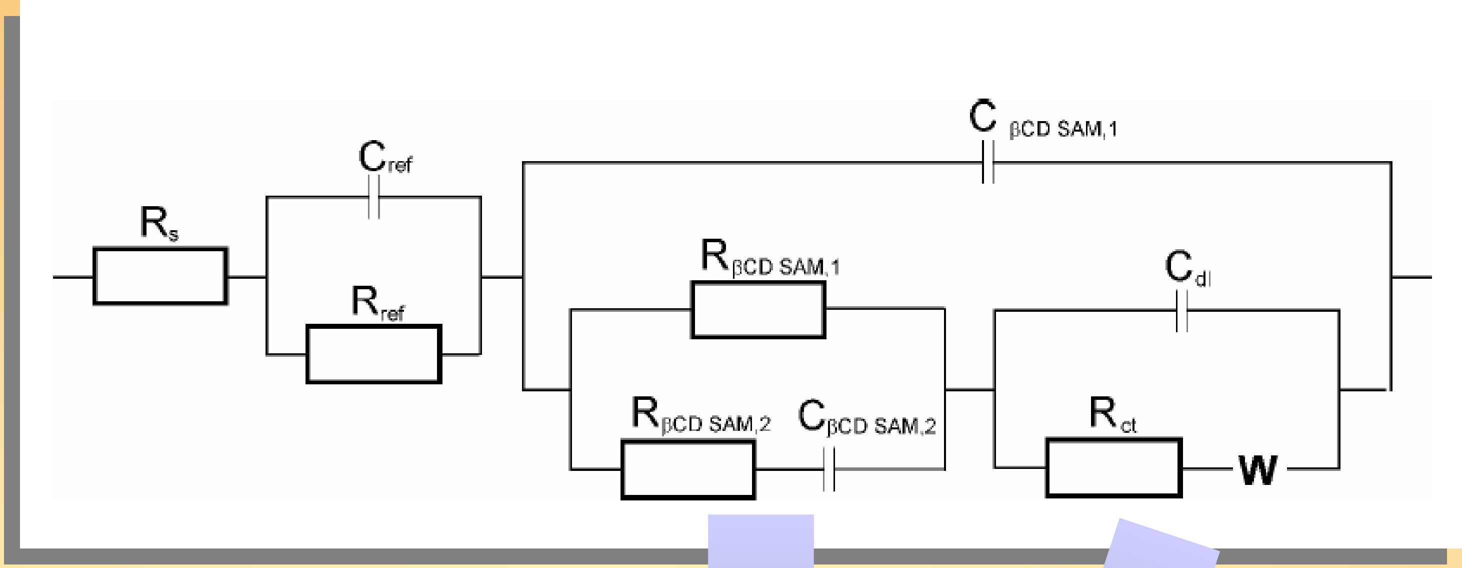
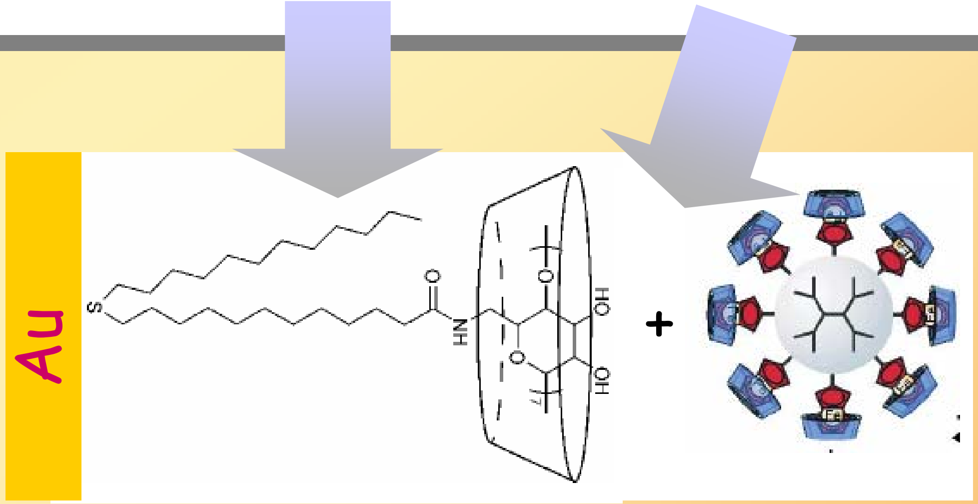
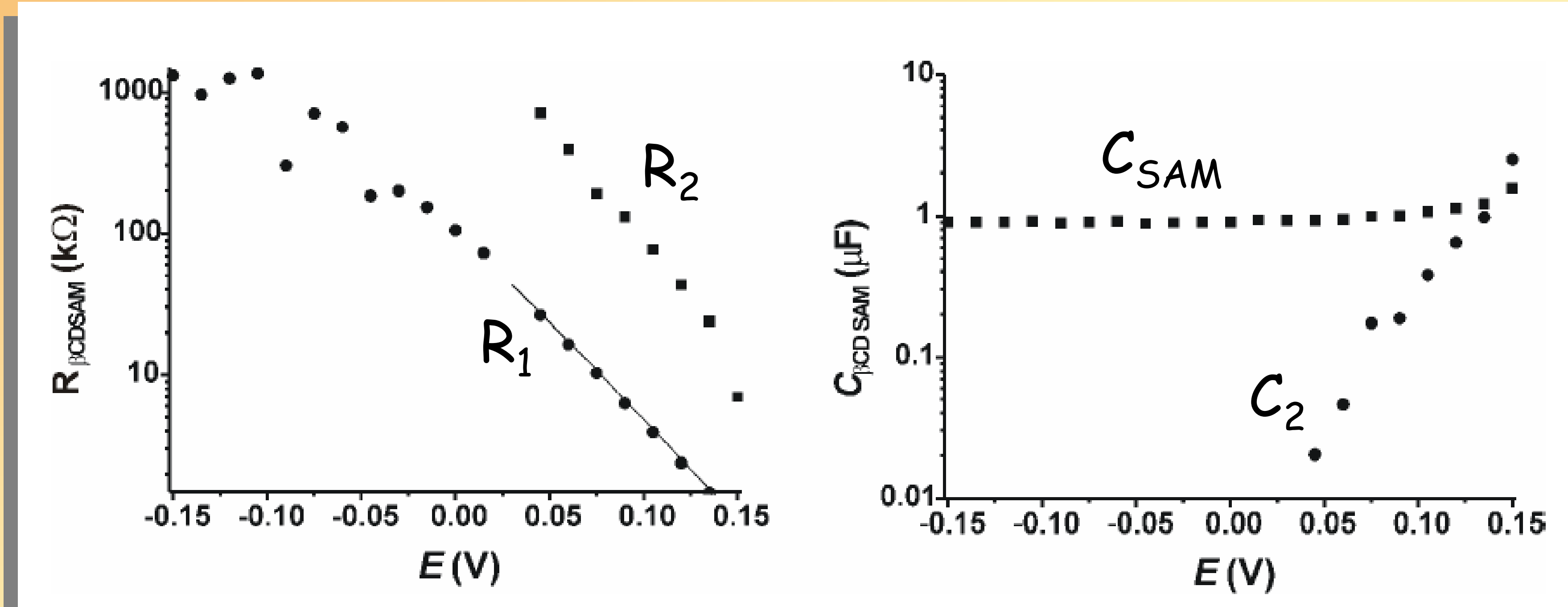
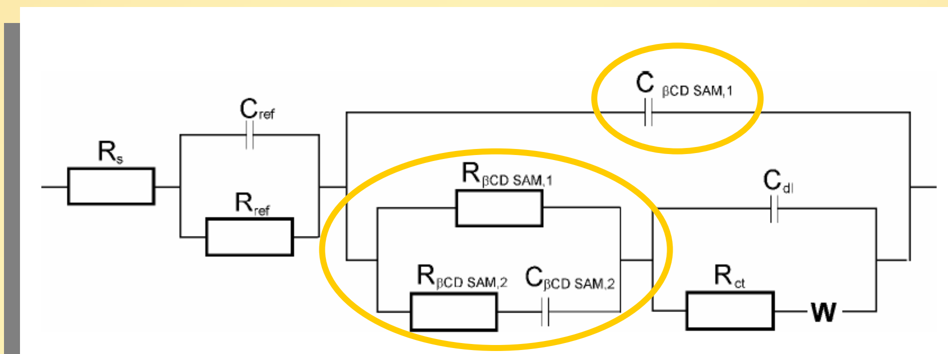
Equivalent Circuit





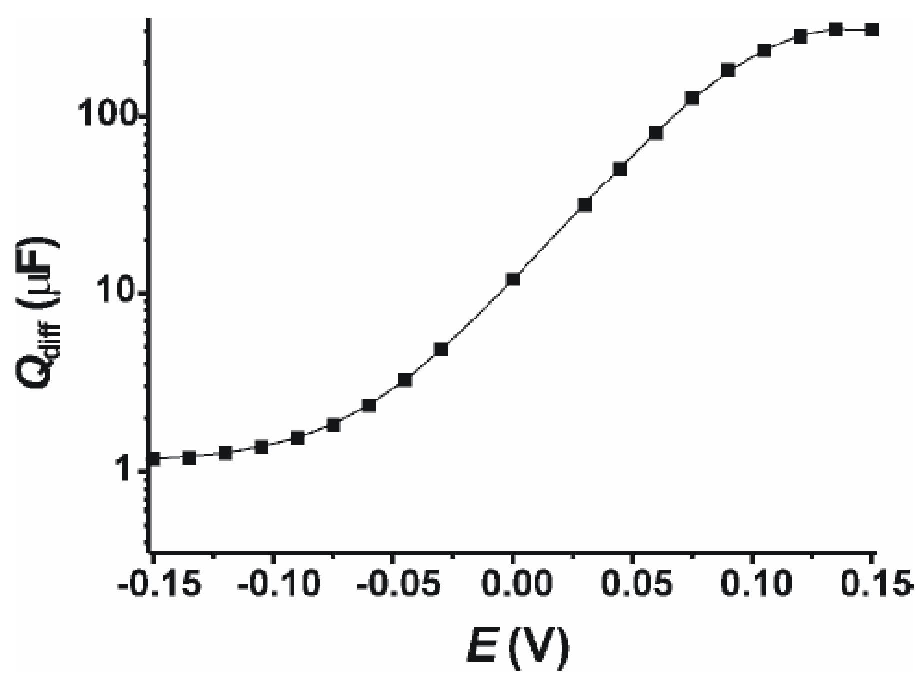
Consistency of Circuit!





Tentative model

Modelling of diffusion



Modelling diffusion:

$$Q_{diff} = Q_0 \frac{1}{\left(1+\frac{1}{K_\theta}\right)+\left(1+K_\theta\sqrt{\frac{D_O}{D_R}}\right)}$$

with: $Q_0 = \frac{n^2F^2A\sqrt{2}}{RT} C^0_{Fc,tot}\sqrt{D_O}$

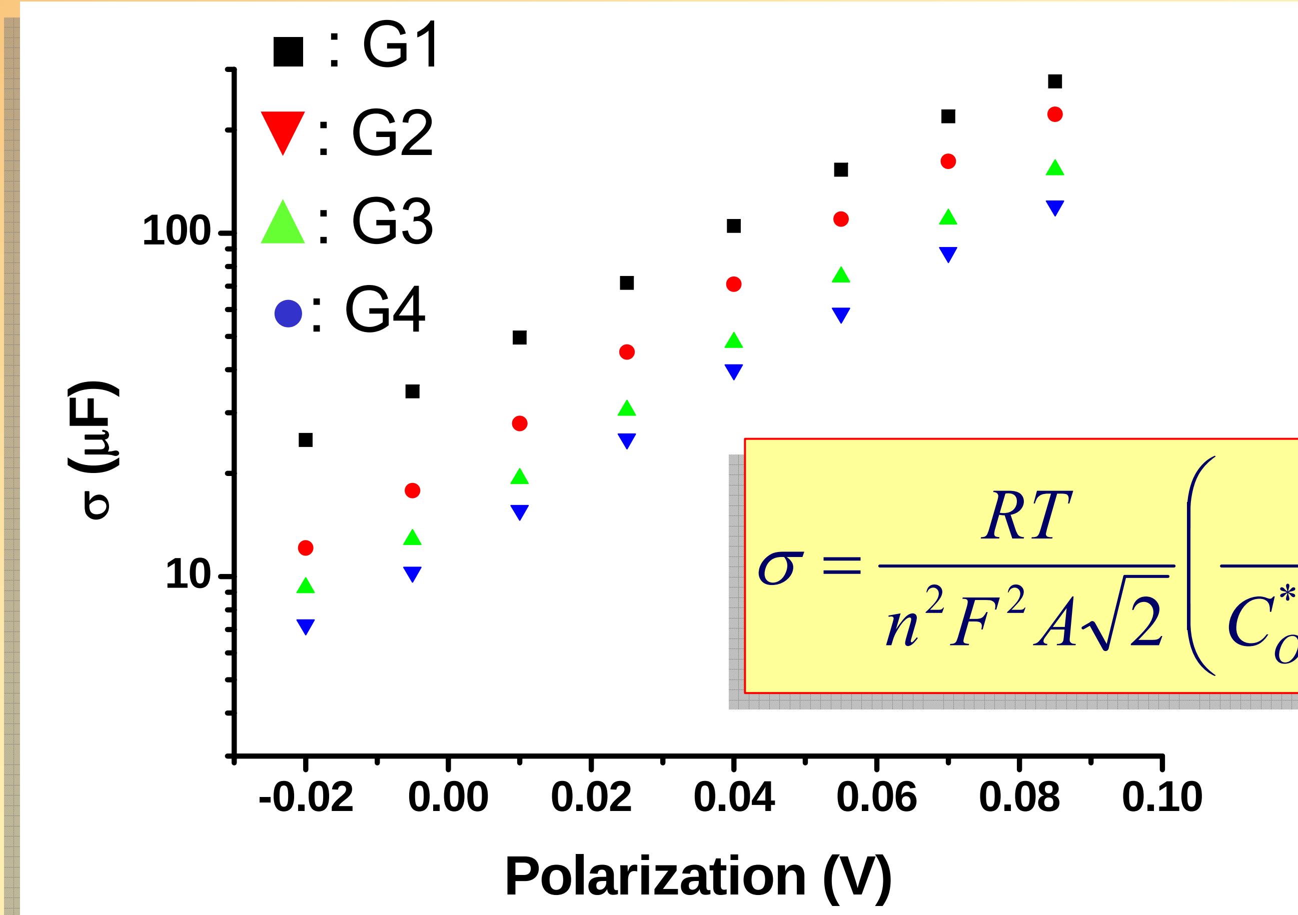
for right hand side only.

Actually: $Q_{diff} = Q_{const} + Q_{diff}(V)$

Modelling of double-layer capacitance: $C_{dl} = C_{dl,1}\theta + C_{dl,2}(1-\theta)$, with: $\theta = \frac{e^{\frac{nF}{RT}(\eta-\eta_0)}}{1+e^{\frac{nF}{RT}(\eta-\eta_0)}}$

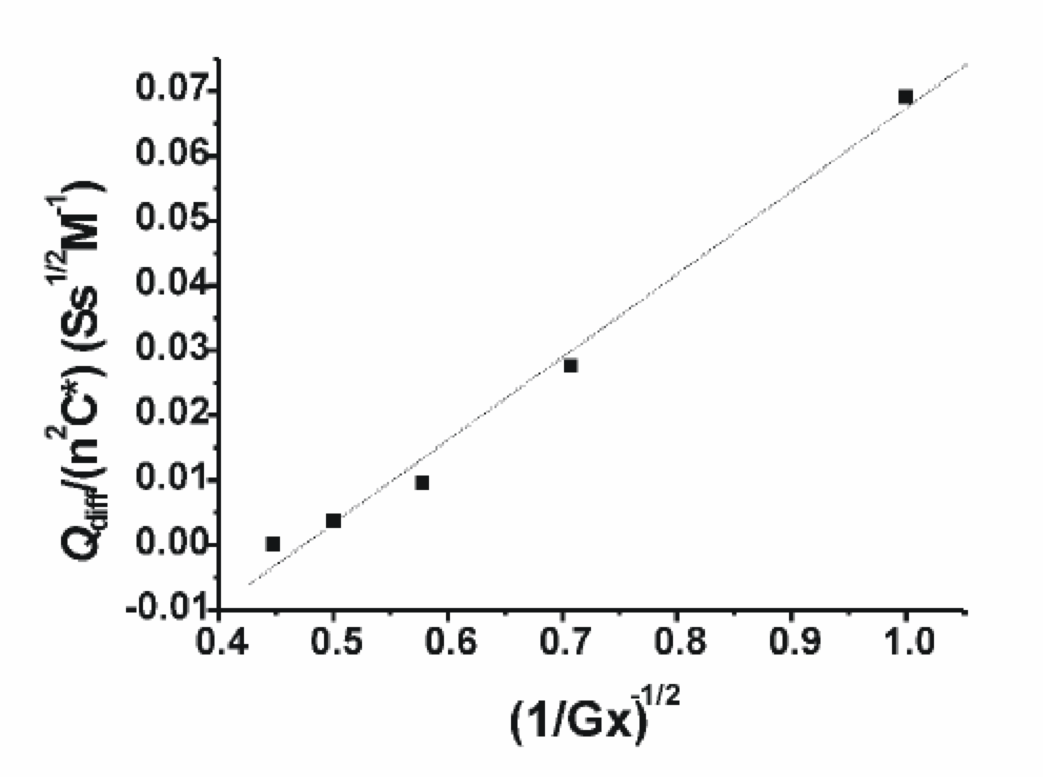
Diffusion & generation

Generation 1 to 4 measured at the same βCD SAM:



$$\sigma = \frac{RT}{n^2F^2A\sqrt{2}}\left(\frac{1}{C_O^*\sqrt{D_O}} + \frac{1}{C_R^*\sqrt{D_R}}\right)$$

Stokes-Einstein



Stokes-Einstein relation:

$$D = \frac{kT}{6\eta\pi r}$$

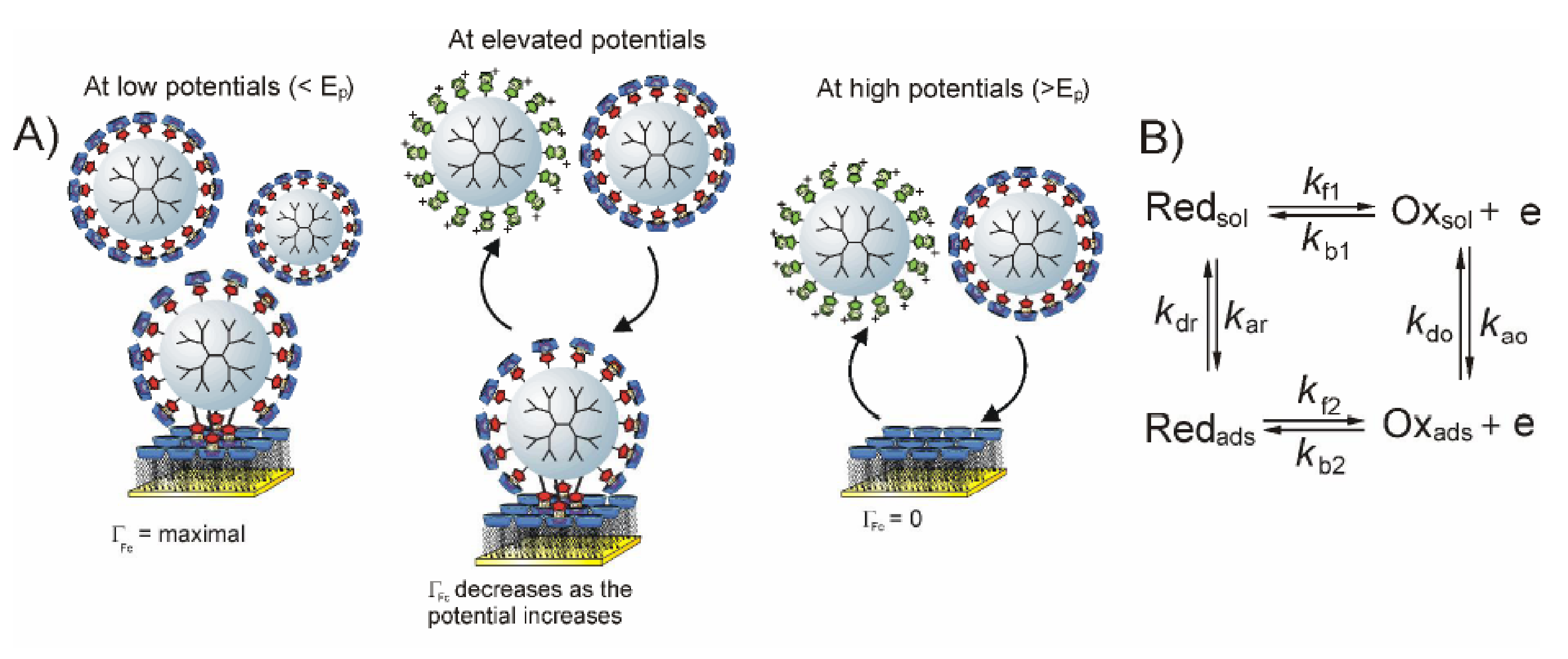
$Q_{diff} \div \sqrt{D}$

and $r \div$ Generation nr.

Hence: $Q_{diff} \div (G_x)^{-1/2}$

The *Warburg* admittance corrected for the concentration of dendrimers and the number of electrons involved per molecules plotted vs the (square root of generation)$^{-1}$.

Reaction Pathways



Schematic of the potential-dependent surface coverage of the dendrimers (left), and a scheme of adsorption and desorption kinetics (right), Red_{sol} = reduced dendrimers in solution, Red_{ads} = dendrimers adsorbed at the βCD SAM, Ox_{sol} = oxidized dendrimers in solution, Ox_{ads} = oxidized dendrimers at the surface; k_{dr}, k_{ar}, k_{do} and k_{ao} are adsorption (a) and desorption (d) rates of oxidized (o) and reduced (r) dendrimers; k_b and k_f are electrochemical rate constants.

Praise of the time domain ...

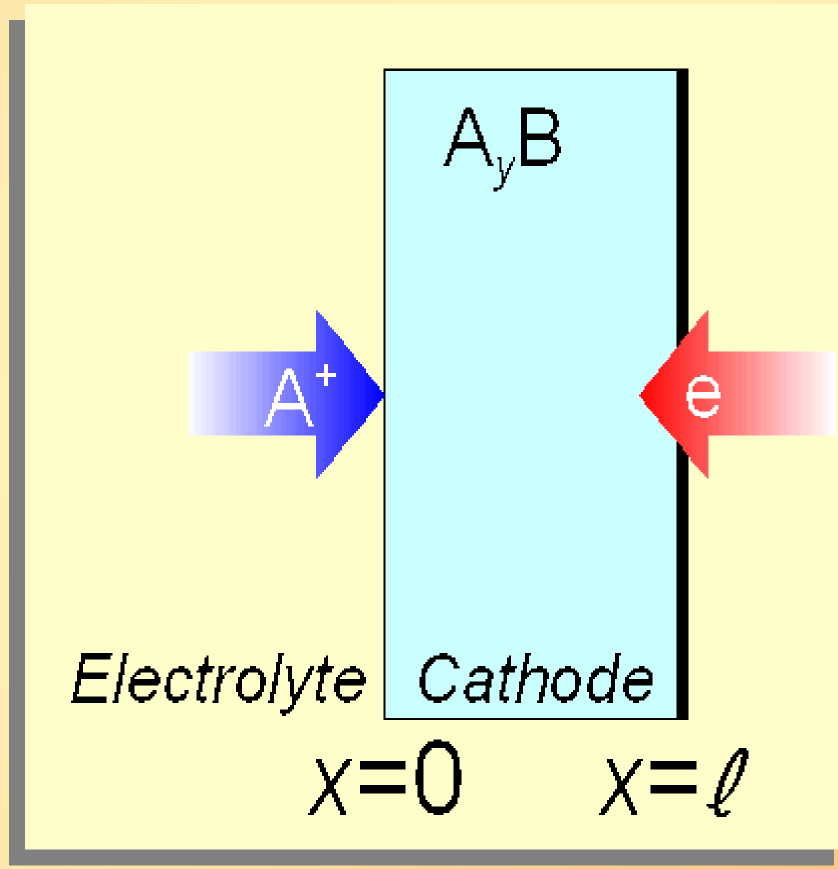
Intercalation cathode.

Change of potential = change of a_A at the interface, hence A-diffusion:

$$J(t) = -\tilde{D}_A^0 \left.\frac{\mathrm{d}C_A(x,t)}{\mathrm{d}x}\right|_{x=0}$$

Voltage-activity relation:

$$E(t) = \frac{RT}{nF} \ln \frac{a_{A,x=0}}{a_A^0}$$



Fick 1 & 2, boundary conditions + Laplace transform:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{Z_0}{\sqrt{j\omega\tilde{D}^0}} \coth l \sqrt{\frac{j\omega}{\tilde{D}^0}}$$

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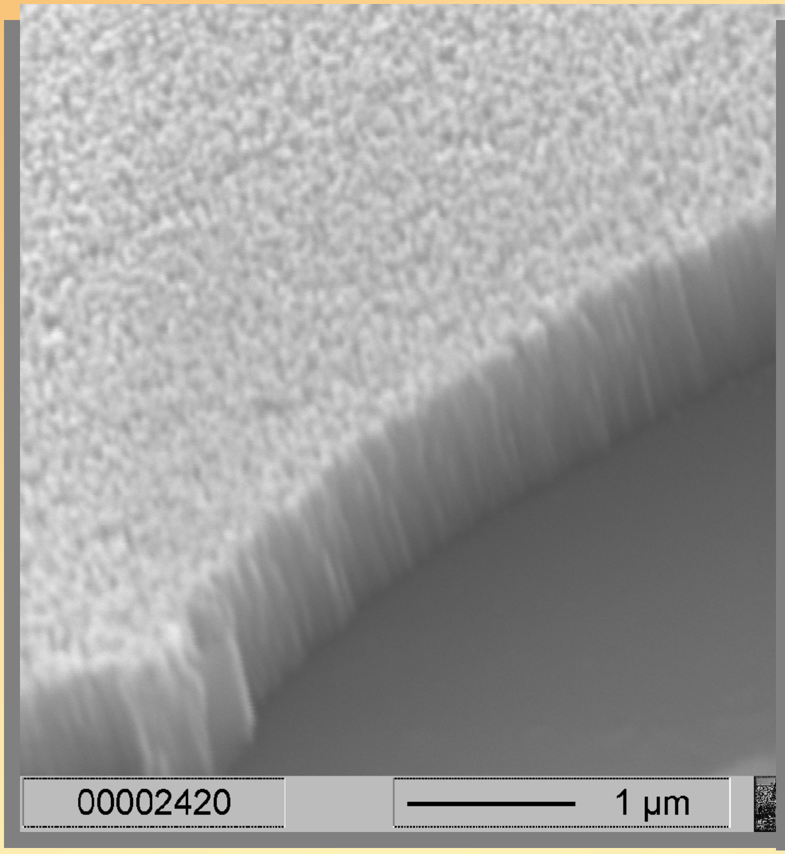
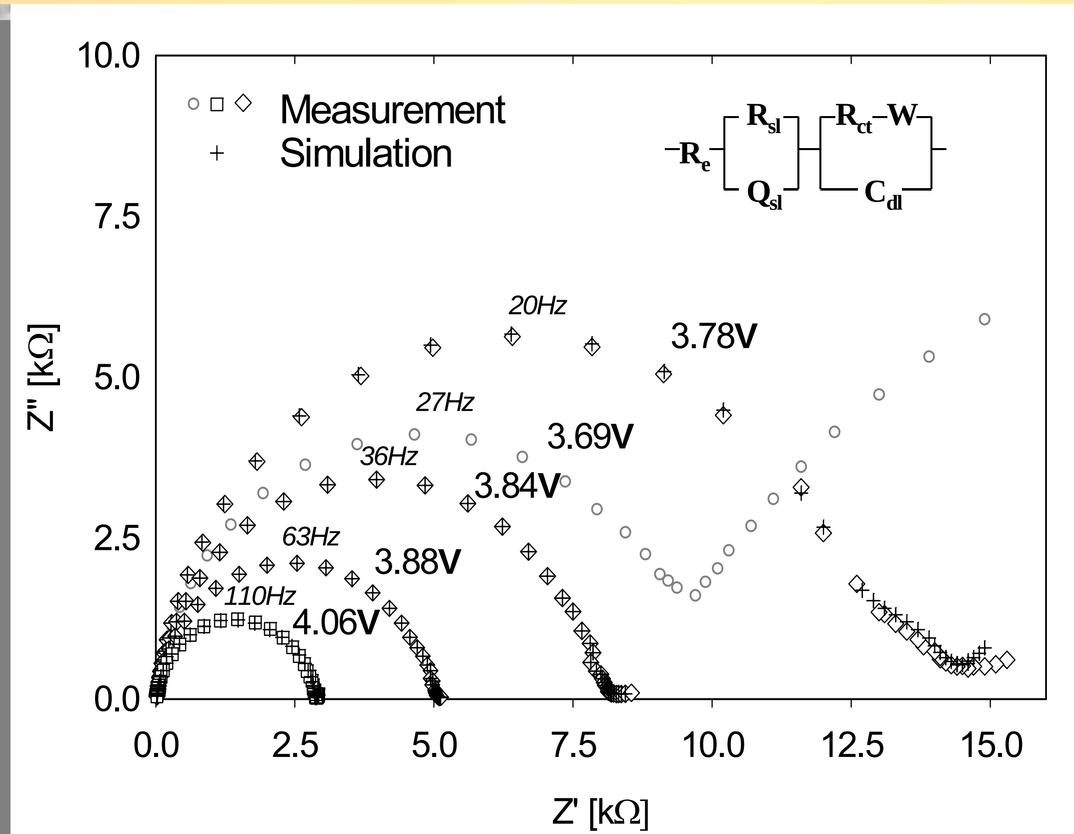
Real cathode: Li_xCoO_2



$LiCoO_2$, RF film on silicon.

Peter J. Bouwman, *Thesis*, U.Twente 2002.



IS of a RF-film electrode: (○) 'fresh'; (□) charged; (◇) intermediate SoC's. (+) CNLS-fit. Range: 0.01 Hz – 100 kHz.

Diffusive part?

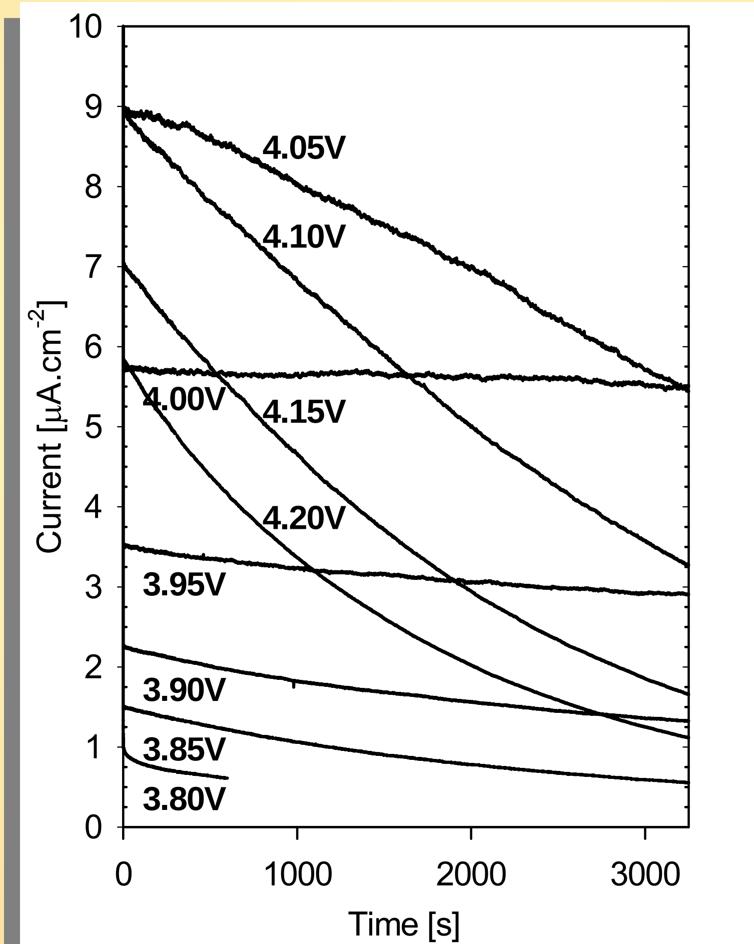
The lithium diffusion process is found at lower frequencies!

Compare the potential-step response time with lowest frequency of EIS experiment:

$t_{eq.} \gg 3000$ s (~ 0.3 mHz)

f_{min} ~ 10 mHz

MEASURE RESPONSE IN THE TIME DOMAIN!



Current response of a 0.75μm RF-film to sequential 50mV potential steps from 3.80V to 4.20V.

Fourier transform

Fourier transform of a temporal function $X(t)$:

$$\overline{X(\omega)} = \int_0^\infty X(t) \cdot e^{-j\omega t}\, dt$$

Impedance: $$Z(\omega) = \frac{\overline{V(\omega)}}{\overline{I(\omega)}}$$

E.g. with a voltage step, V_0: $$V(\omega) = \frac{V_0}{j\omega}$$

Model function: Laplace transform of transport equations and boundary conditions, with $p = s + j\omega$. Set $s = 0$: $\Rightarrow$ impedance

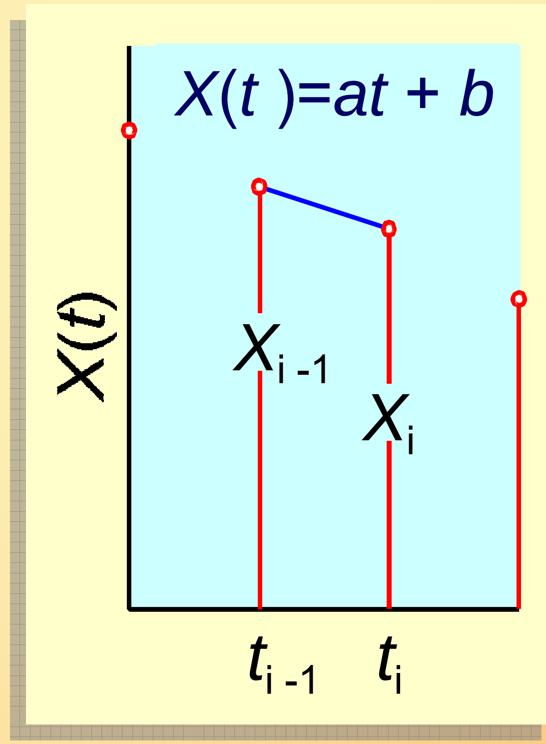
Fourier Transform

Two problems with F-T:

- Data is discrete:

  approximate by summation ($X = at + b$)

- Data set is finite (next slide)



Very Simple Summation Solution (VS³):

$$\bar{X}(\omega)=\sum_{i=1}^{N}\left[X_i\sin\omega t_i - X_{i-1}\sin\omega t_{i-1} + \frac{a}{\omega}\left(\cos\omega t_i-\cos\omega t_{i-1}\right)\right]\omega^{-1}+$$

$$-j\sum_{i=1}^{N}\left[X_i\cos\omega t_i - X_{i-1}\cos\omega t_{i-1} - \frac{a}{\omega}\left(\sin\omega t_i-\sin\omega t_{i-1}\right)\right]\omega^{-1}$$

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Simple exponential extension

Assume finite value, Q_0, for $t \Rightarrow \infty$,
this value can be subtracted before total *FT.*

Fit exponential function to
selected data set in end range: $Q(t) = Q_0 + Q_1\, e^{-t/\tau}$

Full Fourier Transform:

$$\bar{X}(\omega) = \int_0^{t_N} [X(t) - Q_0]\, \mathrm{e}^{-j\omega t}\, \mathrm{d}t - j\frac{Q_0}{\omega} + Q_1 \int_{t_N}^{\infty} e^{-t/\tau}\, e^{-j\omega t}\, \mathrm{d}t$$

Analytical transform of exponential extension:

$$Q_1 \int_{t_N}^{\infty} e^{-t/\tau}\, e^{-j\omega t}\, \mathrm{d}t = Q_1 \cdot e^{-t_N/\tau} \cdot \left\{ \frac{\tau^{-1} \cos\omega t_N - \omega \sin\omega t_N}{\omega^2 + \tau^{-2}} + j\frac{\omega \cos\omega t_N + \tau^{-1} \sin\omega t_N}{\omega^2 + \tau^{-2}} \right\}$$

Fourier transformed data

Simple discrete Fourier transform:

$$\overline{X}(\omega) = \int_0^{t_N} X(t)\, e^{-j\omega t}\, \mathrm{d}t \approx$$

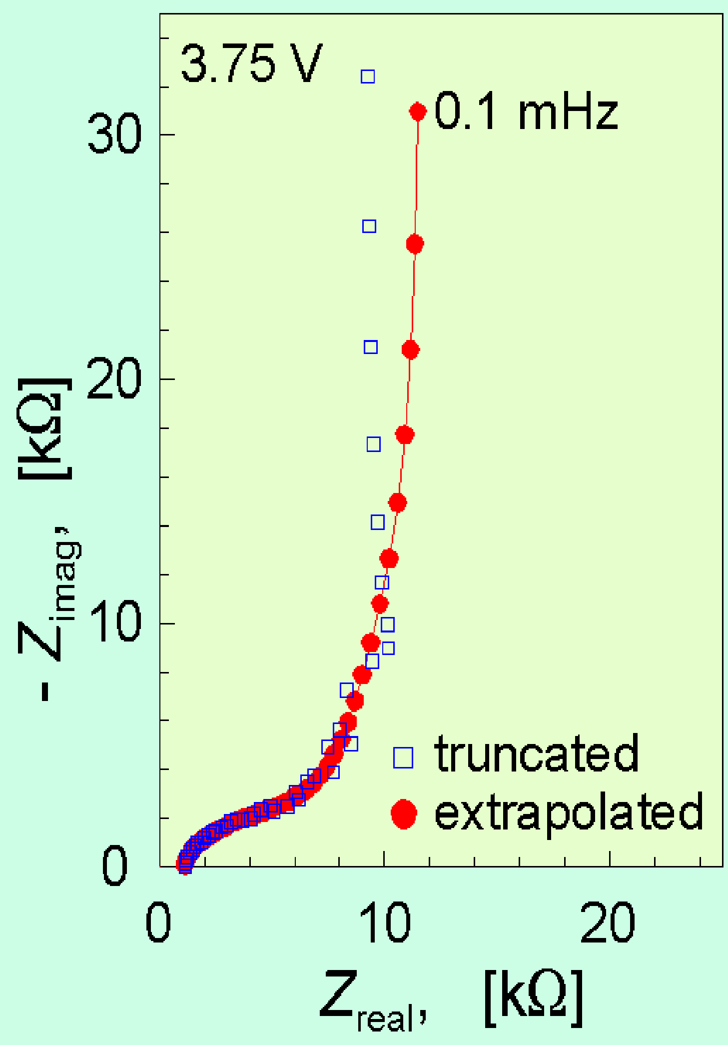
$$\sum_{k=1}^{N} \frac{X(t_k) - X(t_{k-1})}{t_k - t_{k-1}} \left(\cos\omega t - j\sin\omega t\right)$$

Correction / simulation for $t \to \infty$:

$$X(t) = X_0 + X_1 e^{-t/\tau}$$

X_0 = leakage current.

Impedance: $\boxed{Z(\omega) = \dfrac{\overline{V(t)}}{\overline{I(t)}}}$



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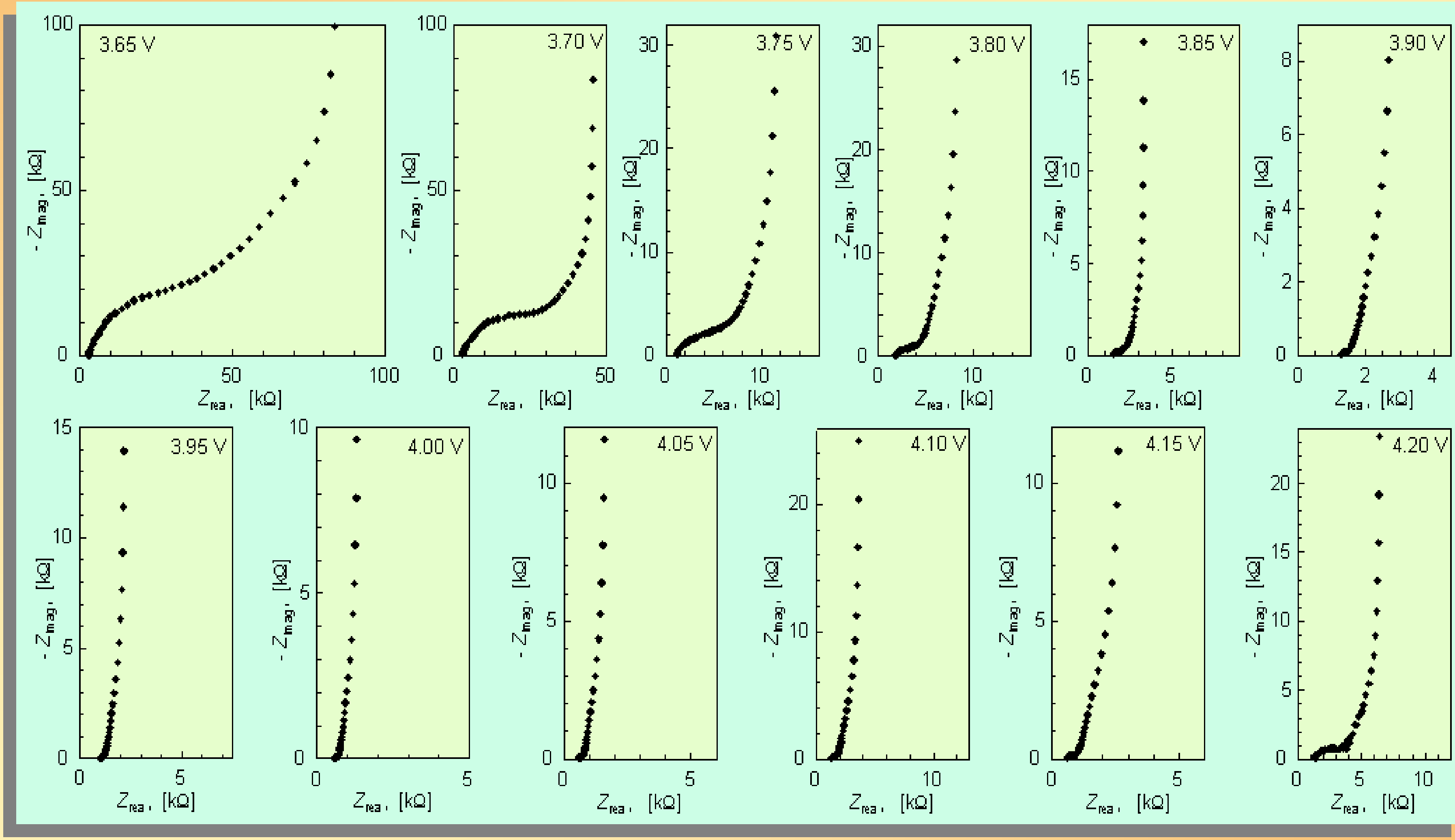
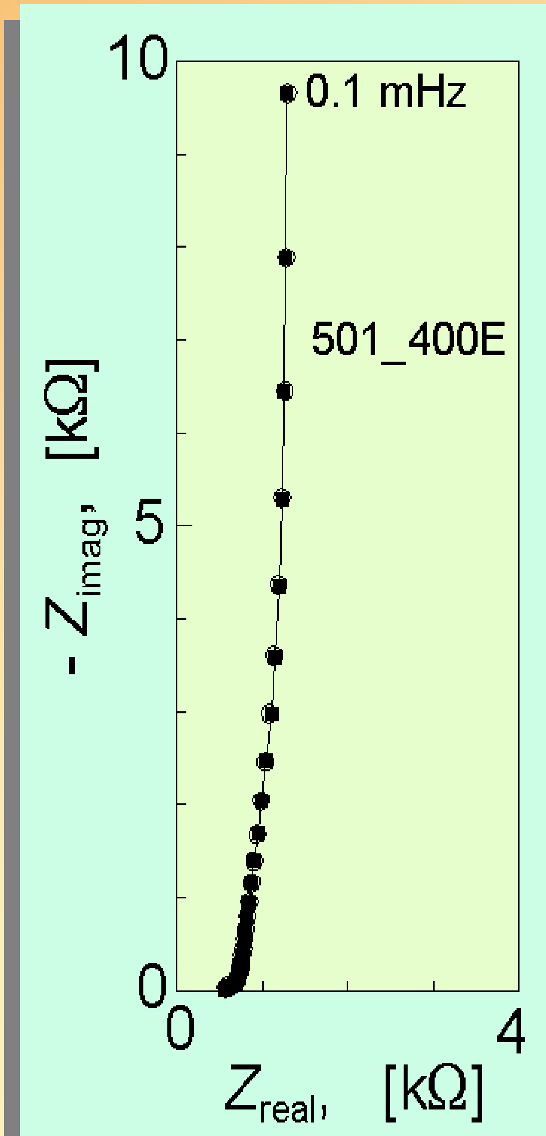
V-step experiment



Sequence of 10 mV step Fourier transformed impedance spectra, from 3.65 V to 4.20 V at 50 mV intervals. F_{min} = 0.1 mHz

CNLS-fit of FT-data



Circuit Description Code:

R(RQ)OT *)

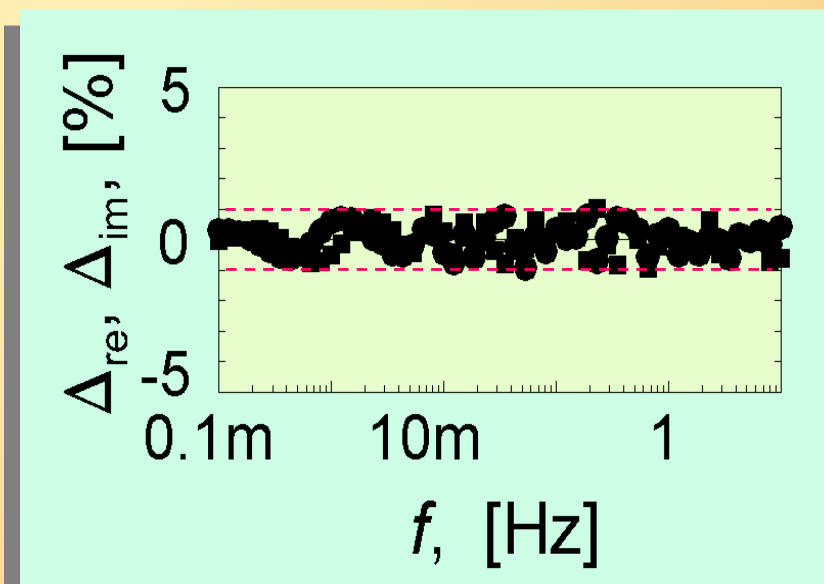
Fit result:

$\chi^2_{CNLS} = 3.7{\cdot}10^{-5}$

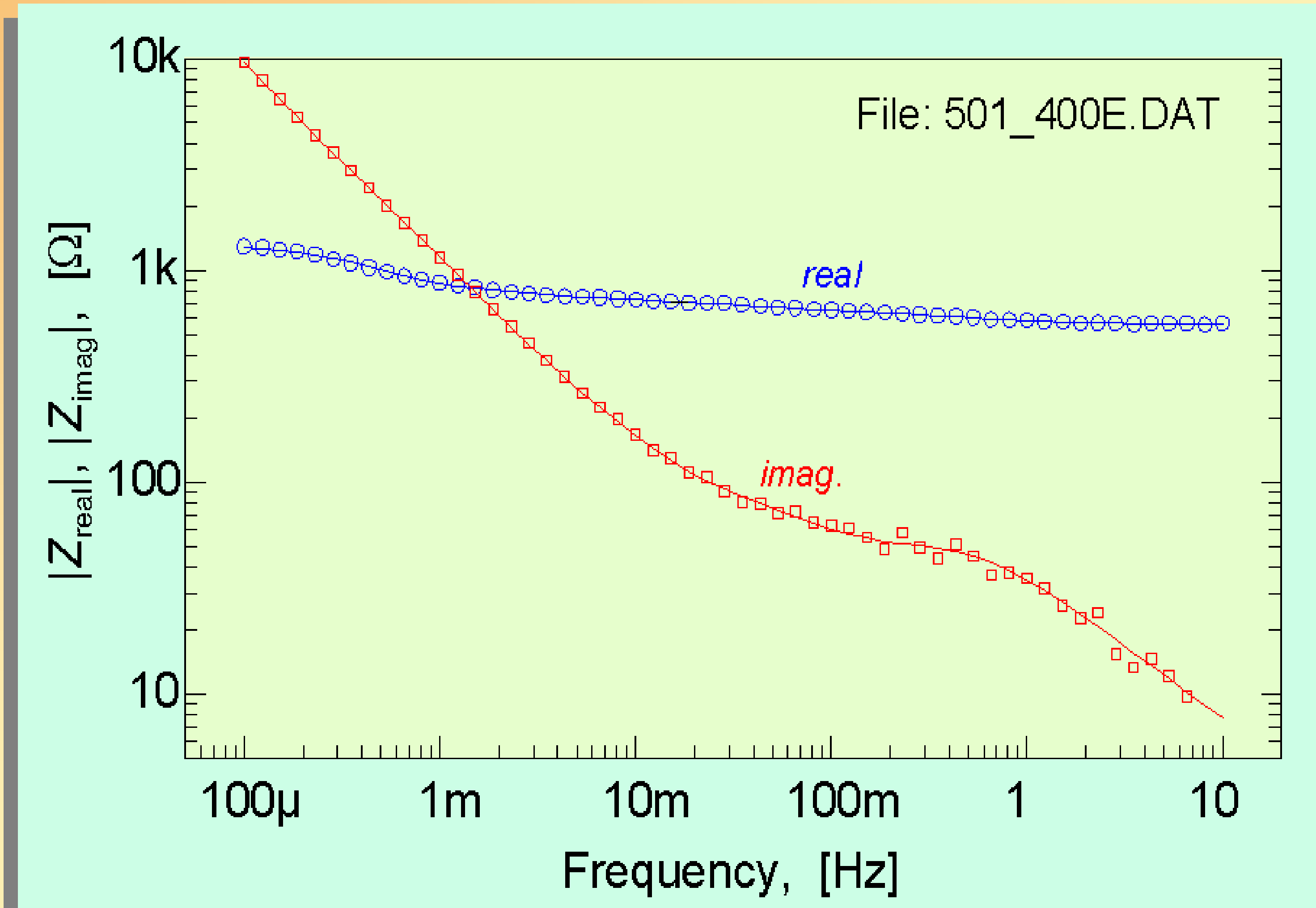
R_1	:	550	0.5 %
R_2	:	49	10 %
Q_3, Y_0	:	$6.8{\cdot}10^{-3}$	12 %
,, n	:	0.96	8 %
O_4, Y_0	:	0.047	1.5 %
,, B	:	30	2.4 %
T_5, Y_0	:	0.028	2.9 %
,, B	:	5.9	2.9 %

*) O = 'FLW'

T = 'FSW'



Bode Graph



Double logarithmic display almost always gives excellent result !

'Bode plot', Z_{real} and Z_{imag} versus frequency in double log plot

Conclusions

Electrochemical Impedance Spectroscopy:

- Powerful analysis tool
- Subtraction procedure reveals small contributions
- Presents more 'visual' information than time domain
- Almost always analytical expressions available
- Equivalent Circuit approach often useful
- Data validation instrument available (KK transform)
- Also applicable to time domain data
  (FT: ultra low frequencies possible)
- Able to analyse complex systems

Unfortunately, analysis requires experience!

Not just electrochemistry!

Data analysis strategy is applicable to any system where:

- a **driving force**
- a **flux**

can be defined/measured.

Examples:

- mechanical properties, e.g. polymers: $G(\omega)$ or $J(\omega)$ & γ
- catalysis, pressure & flux, e.g. adsorption
- rheology
- heat transfer, etc.

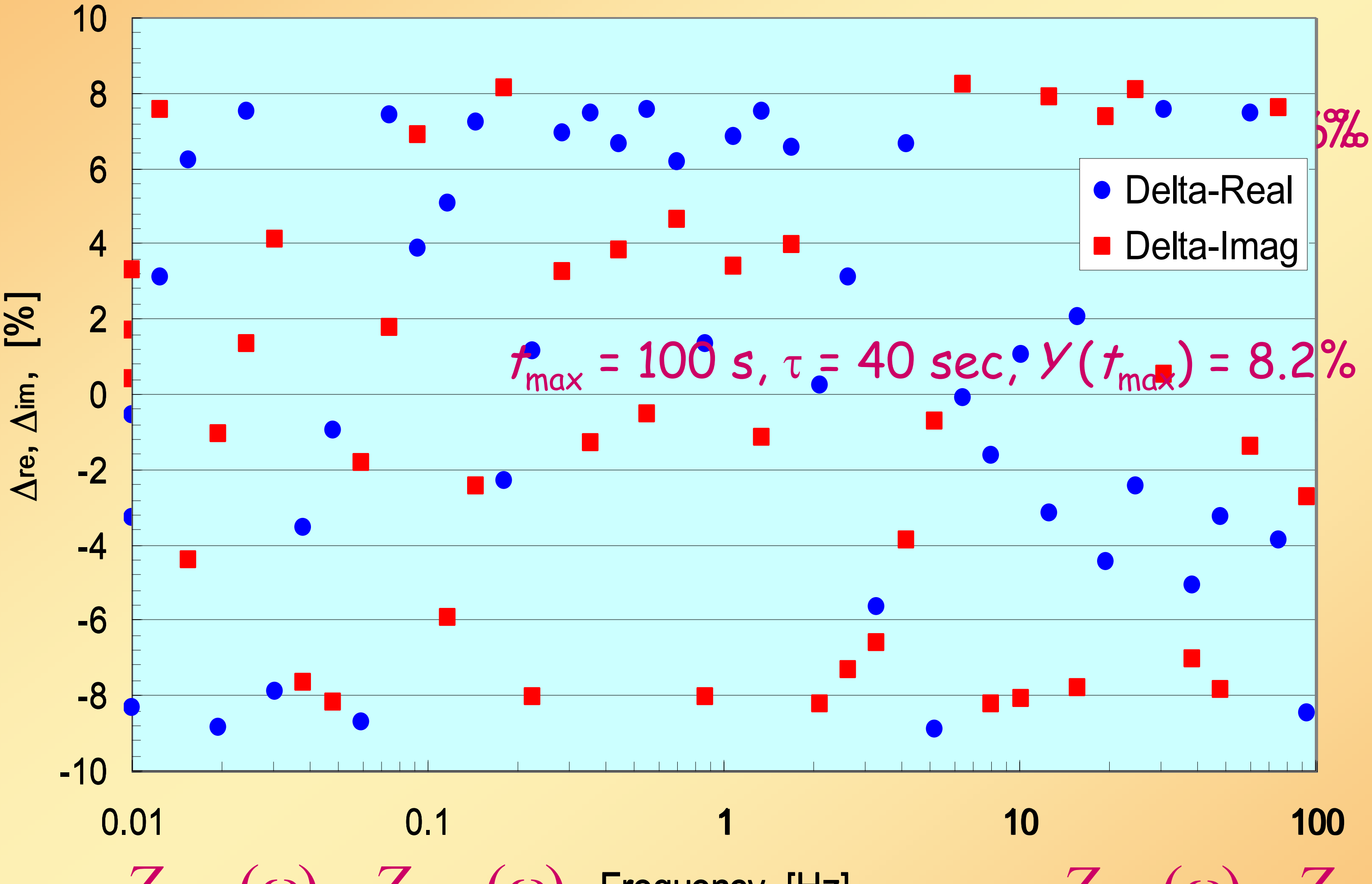
No need to measure in the frequency domain!

Last slide

Questions?

[redacted]

Effect of truncation



$$\Delta_{im} = \frac{Z_{imag}(\omega) - Z_{im,tr}(\omega)}{|Z(\omega)|}$$

$$\Delta_{re} = \frac{Z_{real}(\omega) - Z_{re,tr}(\omega)}{|Z(\omega)|}$$

More Fourier transform

piece wise integration

Method Martijn Lankhorst:

- fit polynomials to small sets of data points (sections): $P_m(t)\Big|_{t_q}^{t_r} = \sum_{k=0}^{m} A_k t^k$
- analytical transformation to frequency domain:

$$\bar{P}(\omega)\Big|_{t_q}^{t_r} = \sum_{i=0}^{m}\sum_{k=1}^{i+1} A_i \frac{(i-1)!}{(i-1-k)!}\cdot\frac{t_q^{i-1-k}\cdot e^{-j\omega t_q} - t_r^{i-1-k}\cdot e^{-j\omega t_r}}{(j\omega)^{k+1}}$$

More general extrapolation function (stretched exponential):

$$Q(t) = Q_0 + Q_1\cdot e^{-(t/\tau)^{\alpha}},\ 0\le\alpha\le 1$$

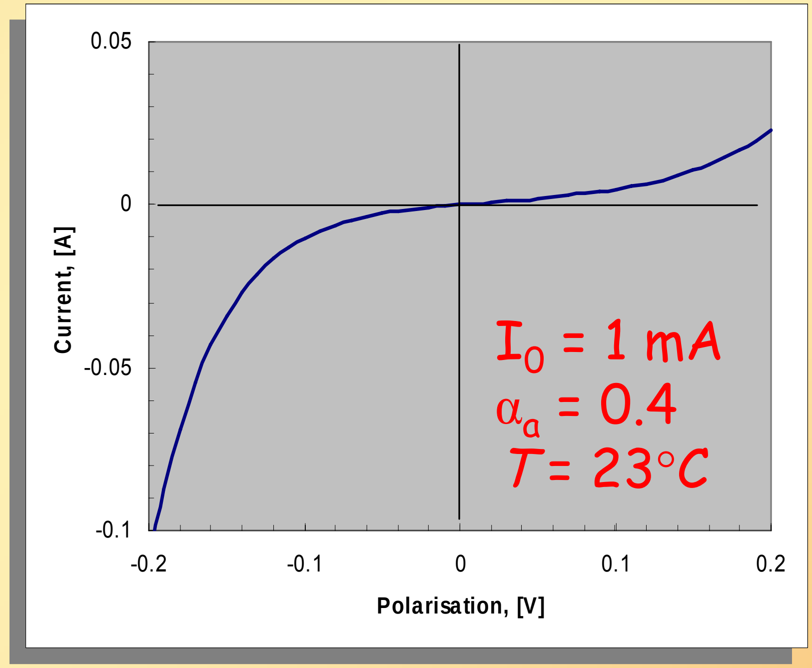
(Fourier transform complicated, can be done numerically)

Non linear effects

Electrode response based on Butler-Vollmer:

$$I = I_0 \left[e^{\frac{\alpha_a F}{RT}\eta} - e^{-\frac{(1-\alpha_a)F}{RT}\eta} \right]$$

When the voltage amplitude is too large, the current response will contain higher harmonics (i.e. is not linear with V).



Substituting
$a = \alpha_a F/RT$,
$b = (1-\alpha_c)F/RT$
and a serial expression for exp(), we obtain:

$$I = I_0 \left[1 + a\eta + \frac{a^2\eta^2}{2!} + \frac{a^3\eta^3}{3!} + \ldots - 1 + b\eta - \frac{b^2\eta^2}{2!} + \frac{b^3\eta^3}{3!} + \ldots \right]$$

$$= I_0 \left[(a+b)\eta + \frac{(a^2 - b^2)\eta^2}{2!} + \frac{(a^3 + b^3)\eta^3}{3!} + \ldots \right]$$

Higher-order terms

At zero bias, with the perturbation voltage, $\Delta \cdot e^{j\omega t}$, this equation yields:

$$I(t) \quad = I_0 \left[(a+b)\Delta e^{j\omega t} + \frac{(a^2-b^2)}{2!}\Delta e^{j2\omega t} + \frac{(a^3+b^3)}{3!}\Delta e^{j3\omega t} + \ldots \right]$$

This clearly shows the occurrence of higher-order terms. When the polarization current is 'symmetric' the even terms will drop out as $a = b$. At a dc-polarization the response is more complex:

$$I(t) = I_0 \left\{ \left[(a+b) + (a^2-b^2)\eta + \frac{(a^3+b^3)\eta^2}{2!} + \ldots \right] \Delta e^{j\omega t} + \right.$$

$$\left. + \left[\frac{a^2-b^2}{2!} + \frac{(a^3+b^3)\eta}{2!} + \ldots \right] \Delta e^{j2\omega t} + \left[\frac{a^3+b^3}{3!} + \ldots \right] \Delta e^{j3\omega t} + \ldots \right\}$$

The derivatives!

Having the derivatives is essential!

- best method, calculate the derivatives on basis of the function: accuracy and speed.
- Second best: numerical evaluation* (for *proper* derivatives we have to calculate $F(x_i, a_{1..M})$ $2M+1$ times!!

$$\frac{\partial}{\partial a_j} F(x_i, a_{1..M}) = \frac{F(x_i, a_1.., a_j + \Delta a_j, ..a_M) - F(x_i, a_1.., a_j - \Delta a_j, ..a_M)}{2\Delta a_j}$$

* This is actually an approximation