BULGARIAN ACADEMY OF SCIENCES | ENERGY RESOURCES AND ENERGY EFFICIENCY

ELECTROCHEMICAL IMPEDANCE SPECTROSCOPY

ADVANCEMENTS AND APPLICATIONS

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INSTITUTE OF ELECTROCHEMISTRY AND ENERGY SYSTEMS
ACADEMICIAN EVGENI BUDEVSKI

ABOUT THE INSTITUTE

ИМООД

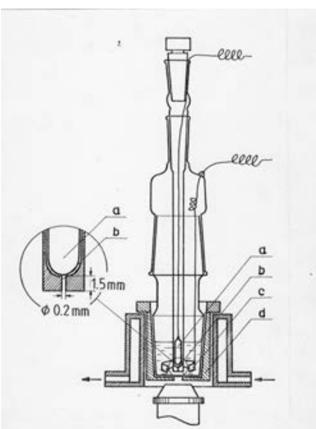
PROFILE

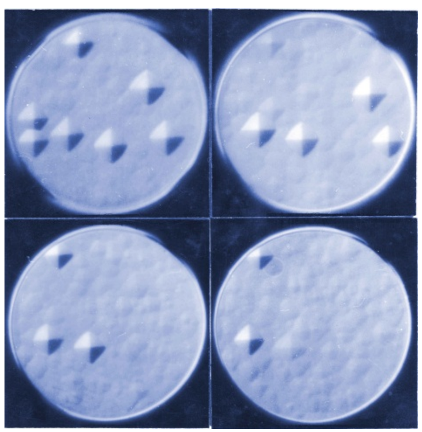
Established in 1967 as an Institute for Fundamental and Applied Research and Development in the Field of Electrochemistry and Electrochemical Power Sources.

- **Scientific & Industrial Background**
  - Electric cars (fork-lift) for industrial applications – 1st place
  - Lead/Acid Batteries – 4th in the world
  - First dislocation free single crystal

SIENTIFIC BACKGROUND

- 1936 - two-dimensional theory of crystal growth of Stranski-Kaischew
- 1965 - the first dislocation free single crystal
- 16 months latter – Texas Instruments (USA) – first dislocation free Si crystal





•Silver single crystal [100] face

INSTITUTE OF ELECTROCHEMISTRY AND ENERGY SYSTEMS
ACADEMICIAN EVGENI BUDEVSKI

PROFILE

2 THEMATIC PLARFORMS:

BATTERIES + FUEL CELLS

STAFF ~ **100 people**

<u>Academic:</u>

2 Academicians

6 Professors

5 Emeritus Professors

4 Honorable Professors

12 Assoc. Professors

24 Research fellows (15 with Ph. D.)

20 <u>Technical research staff</u>
(14 with Masters degree)

12 Ph. D. Students

ИМООД

8 SCIENTIFIC DEPARTMENTS in 2 JOINED THEMATIC PLATFORMS:

BATTERIES & FUEL CELLS AND HYDROGEN

LEAD-ACID BATTERIES	ELECTRO-CATALYSIS and ELECTROCRYSTALLIZATION	SOLID STATE ELECTRO-LYTES	LITHIUM SYSTEMS	ELECTRO-CHEMICAL METHODS	HYDROGEN SYSTEMS with POLYMER ELECTROLYTE	NANOSCALED MATERIALS

TECHNICAL LABORATORIES AND GROUPS

- LABORATORY FOR MATERIALS TESTING
  - SEM/ED
  - Hg-porosimeter
  - X-ray diffractometer
  - BET surface analyzer
  - Thermo/analytical equipment
- MECHANICAL WORKSHOP
- ELECTRIC WORKSHOP

+ access to BAS Equipment (about 200 instruments)

- Administration and Accounting

2015 - 25 Projects and Contracts (National and International)

ИМООД

INSTITUTE OF ACADEMICIAN EVGENI BUDEVSKI ELECTROCHEMISTRY AND ENERGY SYSTEMS

✓ **European Comission :** FP 3 - 7 (14 projects); NATO; IUPAC;

2003 - *Centre of Excellence* **on Portable and Emergency Energy Sources**

FP 7 – 5 projects

✓ **Companies:** ILZRO (TRP – USA); ALABC (USA) & EALABC (Europe), Gould (USA), US Army; ChemTek GmbH (D); Fraunhofer (D); Lucas (UK); Oerlicon (Sw); Bohemia (Cz), ENEL…… ***Segasa (Sp); Varta (D),***

✓ **Academic:** CNRS (Fr); Royal Society (UK); CNR (It); JRC- Petten; Polish, Rumanian Academies of Sciences; Many Universities (Greece, UK, Germany); ERASMUS

Scientific & business partners :

(for the last 5 years)

more than 150 from

~ 30 countries

ИМООД

JOINT THEMATIC PLATFORMS

- **BATTERIES**

- **FUEL CELLS & HYDROGEN**

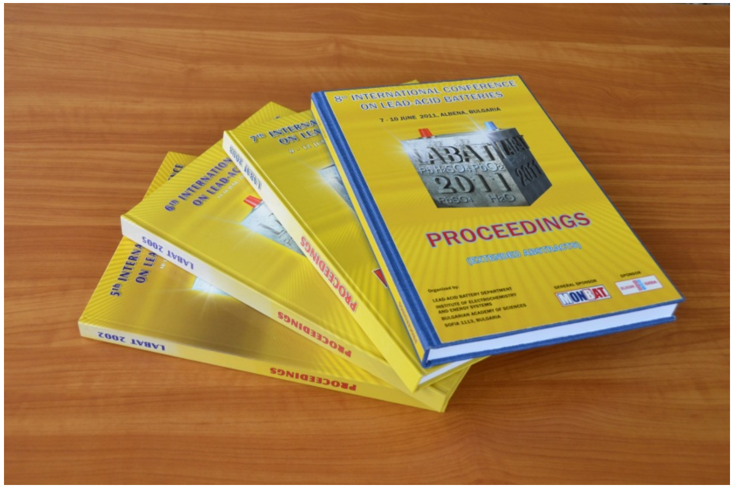
90ths of the 20th century

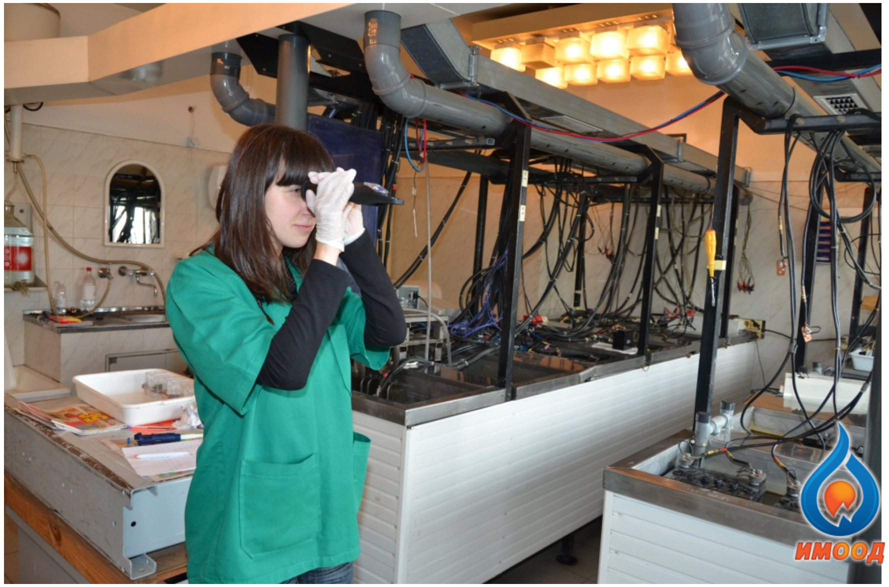
Scientific Strategy: "TRADITION AND INNOVATIONS"

➢ **BATTERIES**

✓lead-acid batteries

- International research support - contracts with the largest international companies
- LABAT
- Optimization for RES and electric cars NEW TRENDS





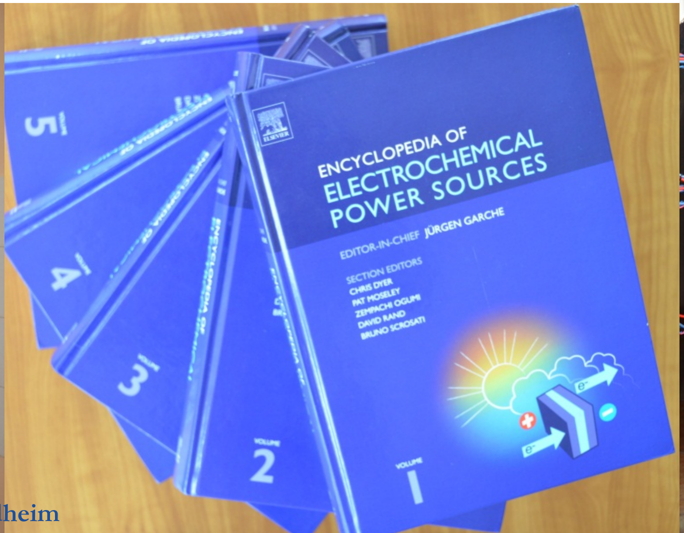
- **BATTERIES**
  - ✓ Metal (Zn, Mg)/air batteries (3 generations)
    - primary
    - mechanically rechargeable
    - Rechargeable – recently

World record

Salt Lake (USA) - 1997

➤ BATTERIES

- ✓ **Li and Li-ion batteries (**4th country in the world in production of primary Li-SO2)
  - new designs (Li/air)
  - nano- nano-scaled composites (metal-carbon, silicon-carbon)
- ✓ **Ni-Zn rechargeable –** project with Bohemia
- ✓ **Electrochemical methods for batteries and fuel cells testing** - diagnostic of batteries r accumulation from RES (> 500 V) – project with ENEL



- Fuel Cells & Hydrogen – 90ths of the 20th century

Renewable Energy Sources (Energy Efficiency) - NOW

- ✓ **fuel cells – PEM, SOFC**
- ✓ **hydrogen production**
- ✓ **hydrogen storage**
- ✓ **electrochemical methods for fuel cells testing (impedance spectroscopy)**

4 FP 7 contracts:

1 in FCH JU

1 in Energy;

2 in Marie Currie

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✓ **Electrochemical methods for batteries and fuel cells testing (impedance spectroscopy)**

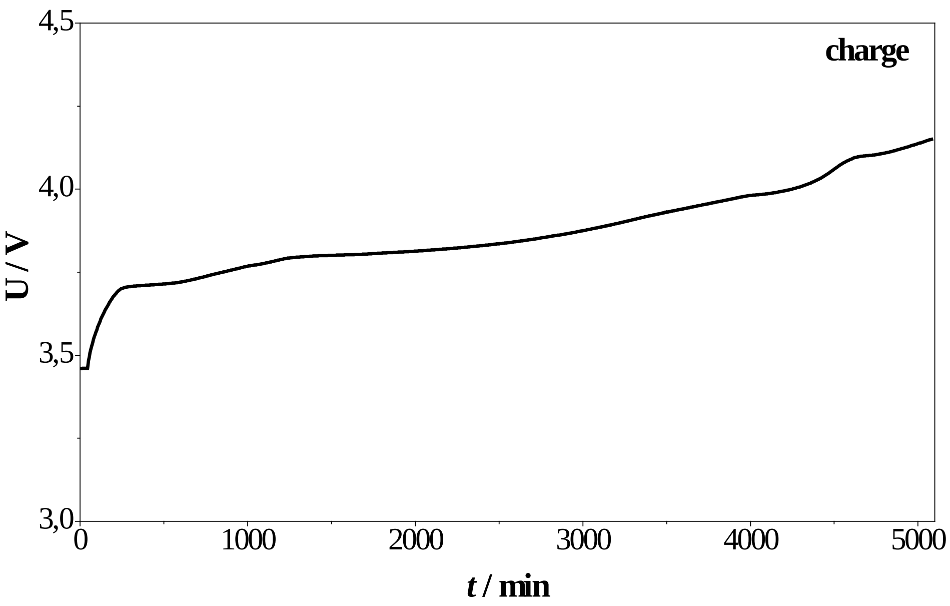
- **Non-standard equipment**
- **Innovative electrochemical methods for characterization and testing of functional materials**
    - o Nonstationary impedance (Mitsubishi (*Li-batteries*),
    - o Differential Impedance Analysis (data analysis without preliminary working hypothesis)

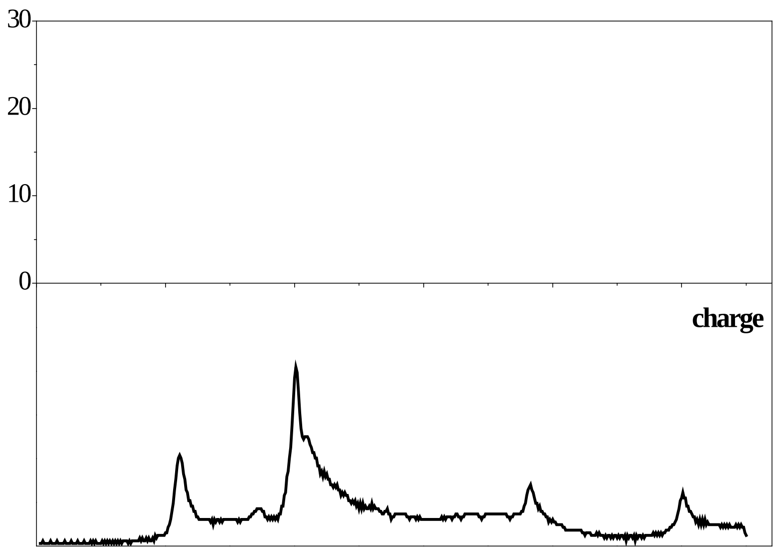
-

ИМООД

✓ **Electrochemical methods for batteries and fuel cells testing (impedance spectroscopy)**

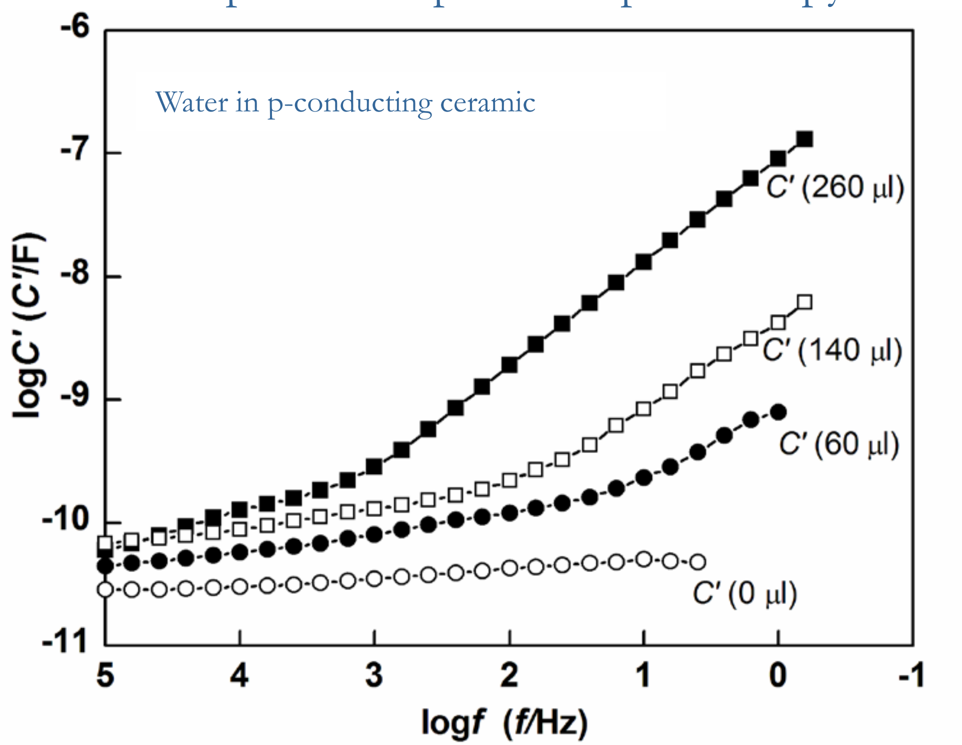
- **Innovative electrochemical methods for characterization and testing of functional materials**
  - Differential Coulometry Spectroscopy – for precise characterization and testing of batteries





✓ **Electrochemical methods for batteries and fuel cells testing (impedance spectroscopy)**

- **Innovative electrochemical methods for characterization and testing of functional materials**
  - Capacitive Impedance Spectroscopy



Last years:

- **Impedance based approaches for characterization and testing of fuel cells**

Testing Units (can be used for impedance)

0.1 A/0.01 A; 5 V

5A ; 2V

200A; 24V

1000A; 12/6V

Star1

0.1 A C/D
16 channels

1

Star2

5 A Dch
16 channels

2

Star3

100/200 A C/D
Single
channel

3

Star6

1000 A
12 V
Single
Channel

6

1. **Why Impedance**
2. **What is impedance**
3. **Impedance measurements**
   - Basic Working Hypotheses
4. **Presentation of the experimental data**
5. **Interpretation of the measured data (data analysis)**
   - Impedance elements
   - Simple models
   - Identification

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Why Impedance - Advantages

➢ From scientific point of view:

- **UNIQUE ADVANTAGE:** to separate the kinetics of the different steps involved in the total process under investigation
- Assessment of processes with different velocity
- Easy performance of experiments with accessible digital instruments
- Maturity in the software exploitation
- Easy performance of virtual impedance data analysis (*e*-data analysis)

➢ From applied point of view:

Covers wide range of objects:

- Batteries
  Semiconductors
- Fuel cells
- Nano-materials
- Biosensors
- Ceramics
- Biological objects
  Materials testing
- Corrosion
  Crystallization

Internat. Symp. on EIS (every 3 years)

Ist - 1989 - FRANCE

IInd - 1992 - USA

IIIrd - 1995 - BELGIUM

IVth - 1998 - BRAZIL

Vth - 2001 - ITALY

VIth - 2004 - USA

VIIth - 2007 - FRANCE

VIIIth – 2010 - PORTUGAL

IXth - 2013 - JAPAN

Internat. Mycrosymp on EIA (every 3 years)

Ist - 1987 - RUSSIA

IInd - 1990 - BULGARIA

IIIrd - 1993 - BULGARIA

IVth - 1996 - POLAND

Vth - 1999 - HUNGARY

VIth - 2002 - CZECHIA

VIIth - 2006- CZECHIA

VIIIth - 2008 - CHECHIA

IXth - 2011 - CROATIA

Xth - 2014 - BULGARIA

Xith - 2017 - ITALY

2001 *Established*

European Internet Centre For Impedance Spectroscopy (EICIS)

base organization

IEES - BAS

Online Journal *Impedance Contributions Online*

Online consultations

ИМООД

OUTLINES

1. Why Impedance
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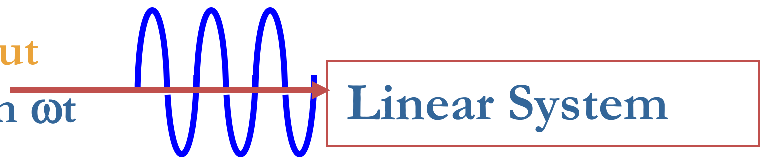
- The Electrochemical Impedance Spectroscopy is based on the classical method of the TRANSFER FUNCTION (TF)

Linear System

➢ The Electrochemical Impedance Spectroscopy is based on the classical method of the TRANSFER FUNCTION (TF)

Sinwave input
$x(i\omega) = A \sin \omega t$



Principle:

➢ If the system under investigation is LINEAR (LS),

sin-wave input $x(i\omega)$ perturbation ⟶ $y(i\omega)$ output measurement

The response $y(i\omega)$ is also sin wave with the same frequency and different amplitude and phase;

➢ The ratio output / input signal determines the complex transfer coefficient for the corresponding frequency:

$k(i\omega) = y(i\omega) / x(i\omega)$

- Complex number (Re; Im)
- Depends on ω and the object's properties

- The Electrochemical Impedance Spectroscopy is based on the classical method of the **TRANSFER FUNCTION (TF)**

Principle:

- If the system under investigation is LINEAR (LS),

  sin-wave input x(iω) perturbation → y(iω) output measurement

  The response y(iω) is also sin wave with the same frequency and different amplitude and phase;

- The ratio output / input signal determines the complex transfer coefficient for the corresponding frequency:

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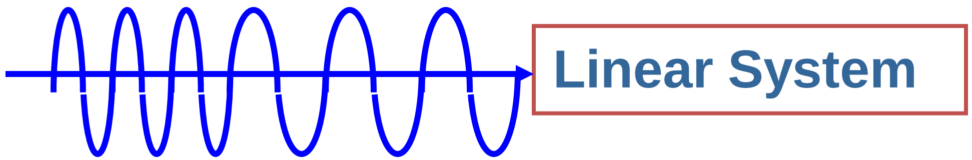
Linear System



$X(i\omega_i)$ = Sinwave input signals
(ω_1- ω_n)

$$H(i\omega_i) = Y(i\omega_i) / X(i\omega_i)$$

is the Transfer Function

TF describes the frequency dependence of the transfer coefficient $k(\omega i)$

- The transfer from the time-domain to the frequency domain is performed by LAPLAS transform. For steady state linear systems it is replaced by FOURIER transform.

$X(i\omega_i)$ = Sinwave input signals (ω_1- ω_n)

$Y(i\omega_i)$ = Sinwave output signals (ω_1 - ω_n)

$$H(i\omega_i) = Y(i\omega_i) / X(i\omega_i)$$

is the Transfer Function

TF describes the frequency dependence of the transfer coefficient $k(\omega i)$

- The transfer from the time-domain to the frequency domain is performed by LAPLAS transform. For steady state linear systems it is replaced by FOURIER transform.

- TF is impedance → $H(i\omega_i) = Z(i\omega_i)$

  input signal - current (I)

  output signal - voltage (U)

- TF is admittance → $H(iw_i) = Y(i\omega_i) = Z^{-1}(i\omega_i)$

  input signal - voltage (U)

  output signal is current (I)

- When the frequency range (ω_1-ϖ_n) is ω large and covers all the properties of the system , the system is observable, otherwise it is partially observable.

Conclusion:

The Transfer Function $H(iw_i)$ describes totally a linear, steady-state and observable system.

1. Why Impedance

2. What is impedance

3. **Impedance measurements**

   - Basic Working Hypotheses

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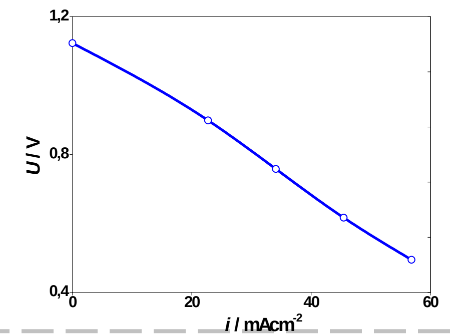
Impedance as a Transfer Function *H*(i*wi*) describes totally a linear, steady-state and observable system.

- **Electrochemical systems:**
  - large
  - non-linear → SOFC are quasi-linear
  - non-steady state
  - semi-irreversible
  - distributed parameters
  - mass- and energy transfer take place



The TF approach needs a number of simplifications and assumptions, generalized in

BASIC WORKING HYPOTHESES

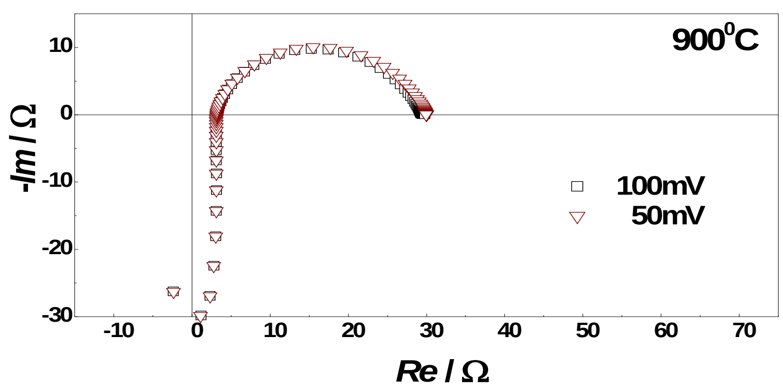
➢ Working hypotheses from system analysis point of view

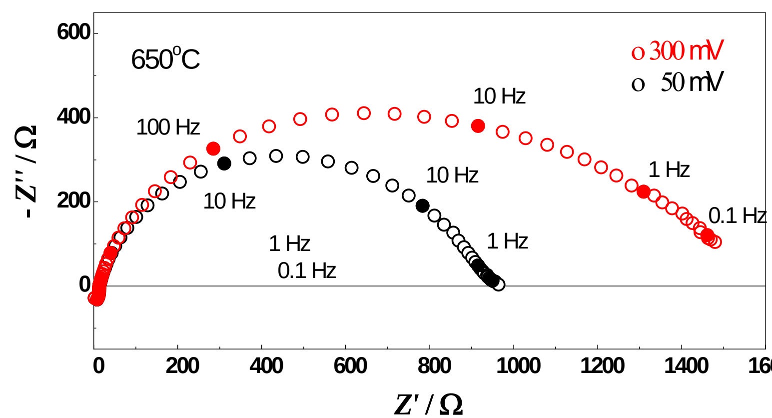
✓Linearity: the input perturbation signal should be small enough to keep the state of the investigated system unchanged.

The requirement for a small signal covers the potential, the current, as well as the quantity of electricity for half a period (very important at low frequencies!).

Experimental verification: Consecutive impedance measurements in the full frequency range with decreasing amplitude and analysis of the weighted differences.

YSZ electrolyte DC = 0 mV;



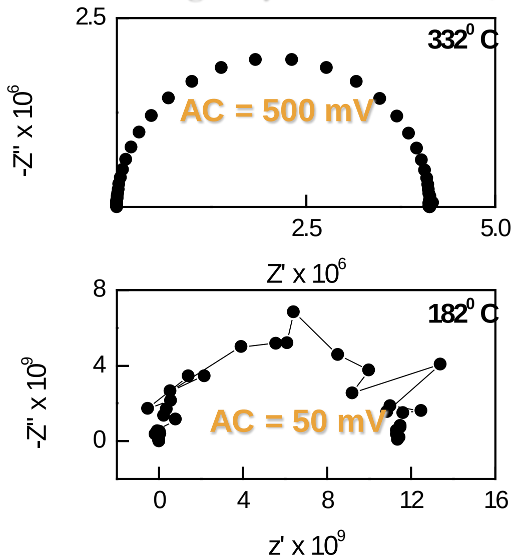


- Working hypotheses from system analysis point of view

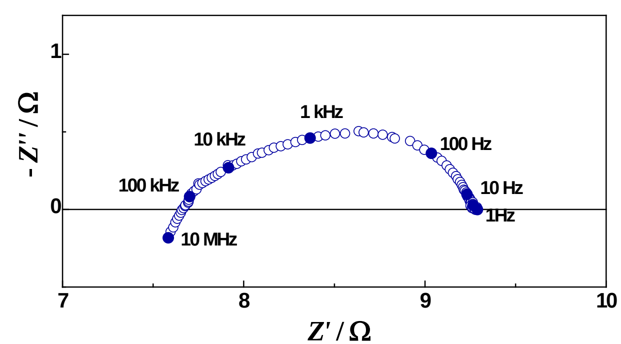
✓**Linearity:** the input perturbation signal should be small enough to keep the state of the investigated system unchanged.

Small signal : depends on the investigated system

YIG single crystal DC = 0 mV;



Composite LSM/YSZ
DC = 0 mV; AC = 50 mV



Dislocation free Ag single crystal
DC = 5 mV;
AC = 50 mV

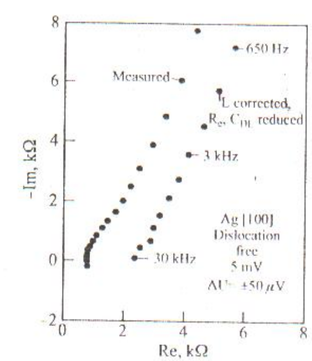
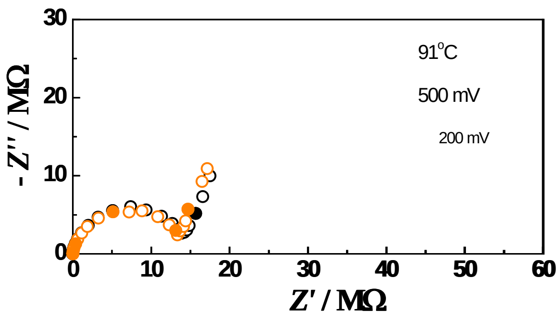


Fig. 3. Impedance plots

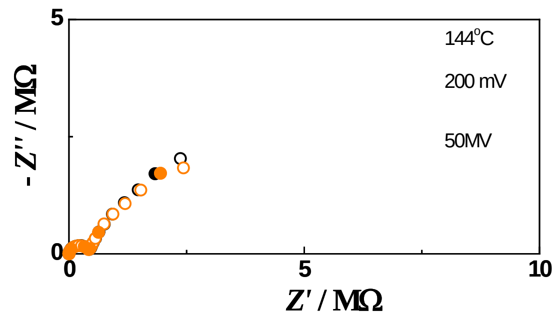
Small signal : depends on the investigated system

LSCF/YDC/LSCF
DC = 0 mV

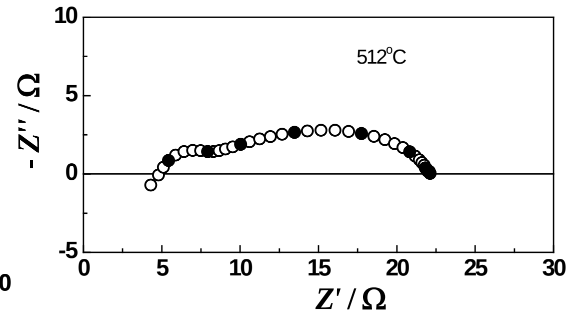
AC = 500 mV
AC = 200 mV



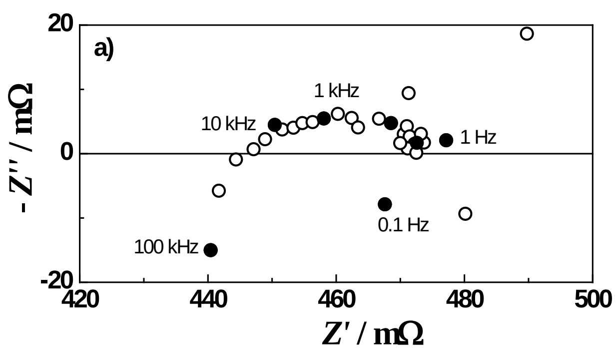
AC = 200 mV
AC = 50 mV



AC = 50 mV

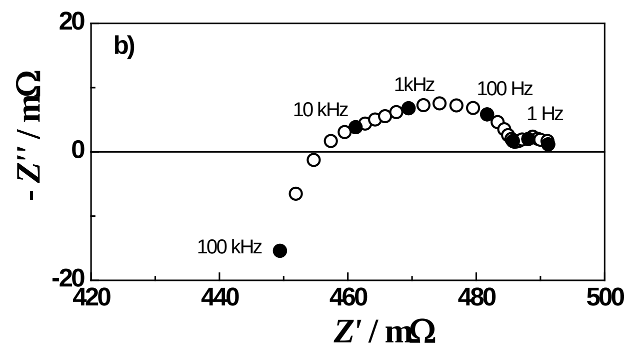


AC = 50 mV



719°C

AC = 20 mA

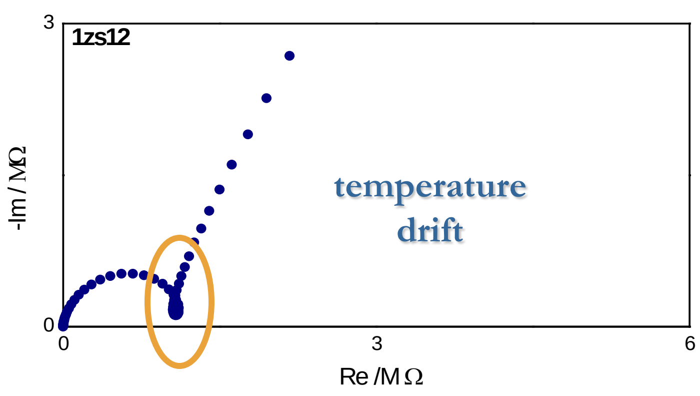


- Working hypotheses from system analysis point of view

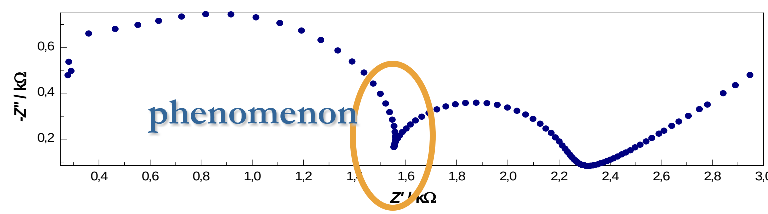
  - ✓ Single input, single output:

    achieved if the rest of the parameters (temperature, concentration, d.c. signal, pH etc.) are kept constant by passive or active conditioning.

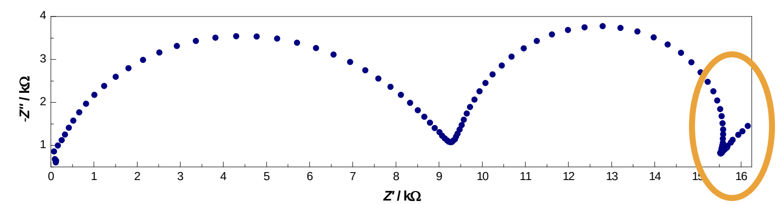
Oxygen conducting ceramic



Proton-conducting ceramic



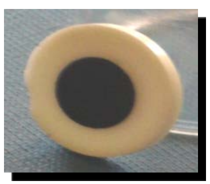
150°C

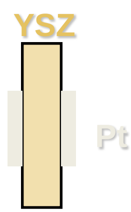


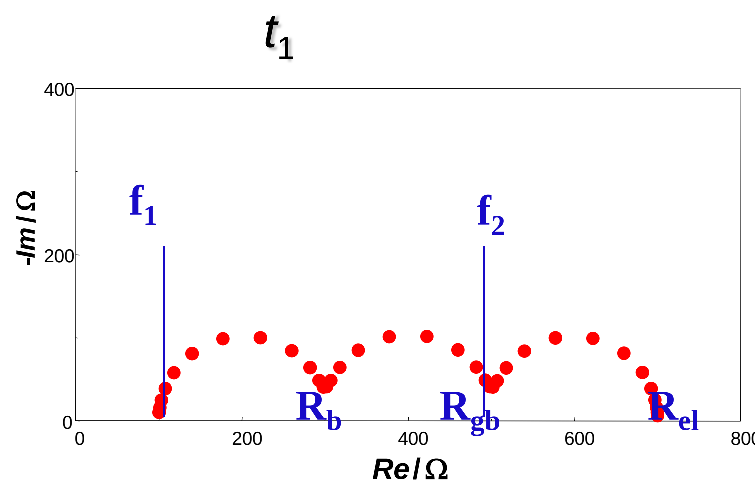
200°C

- Working hypotheses from system analysis point of view

  ✓ **Observability:**
  All the phenomena under study can be observed in the measured frequency range.







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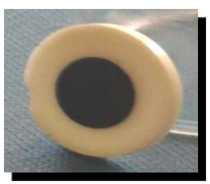
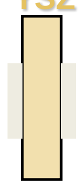
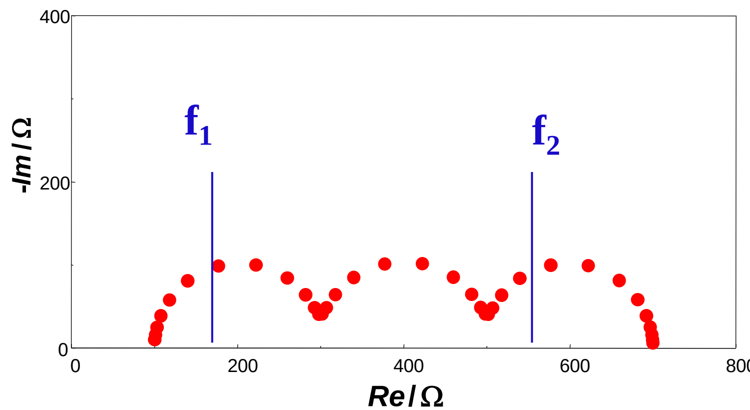




$t_2 > t_1$



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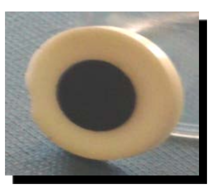
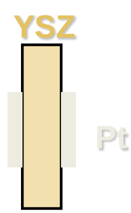
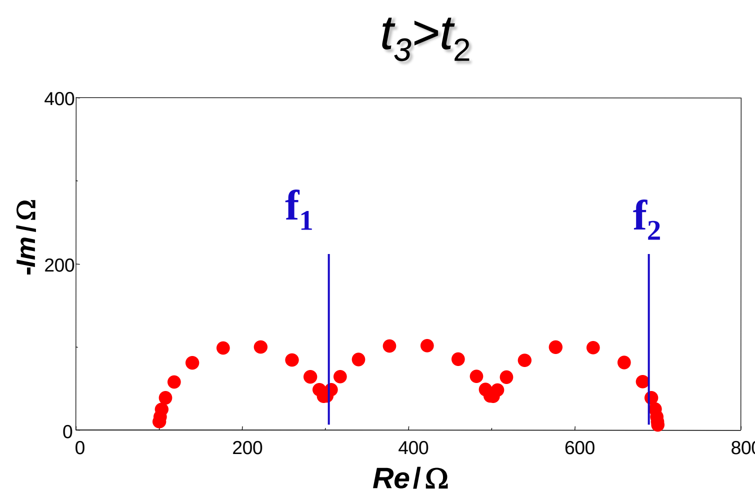
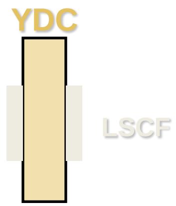


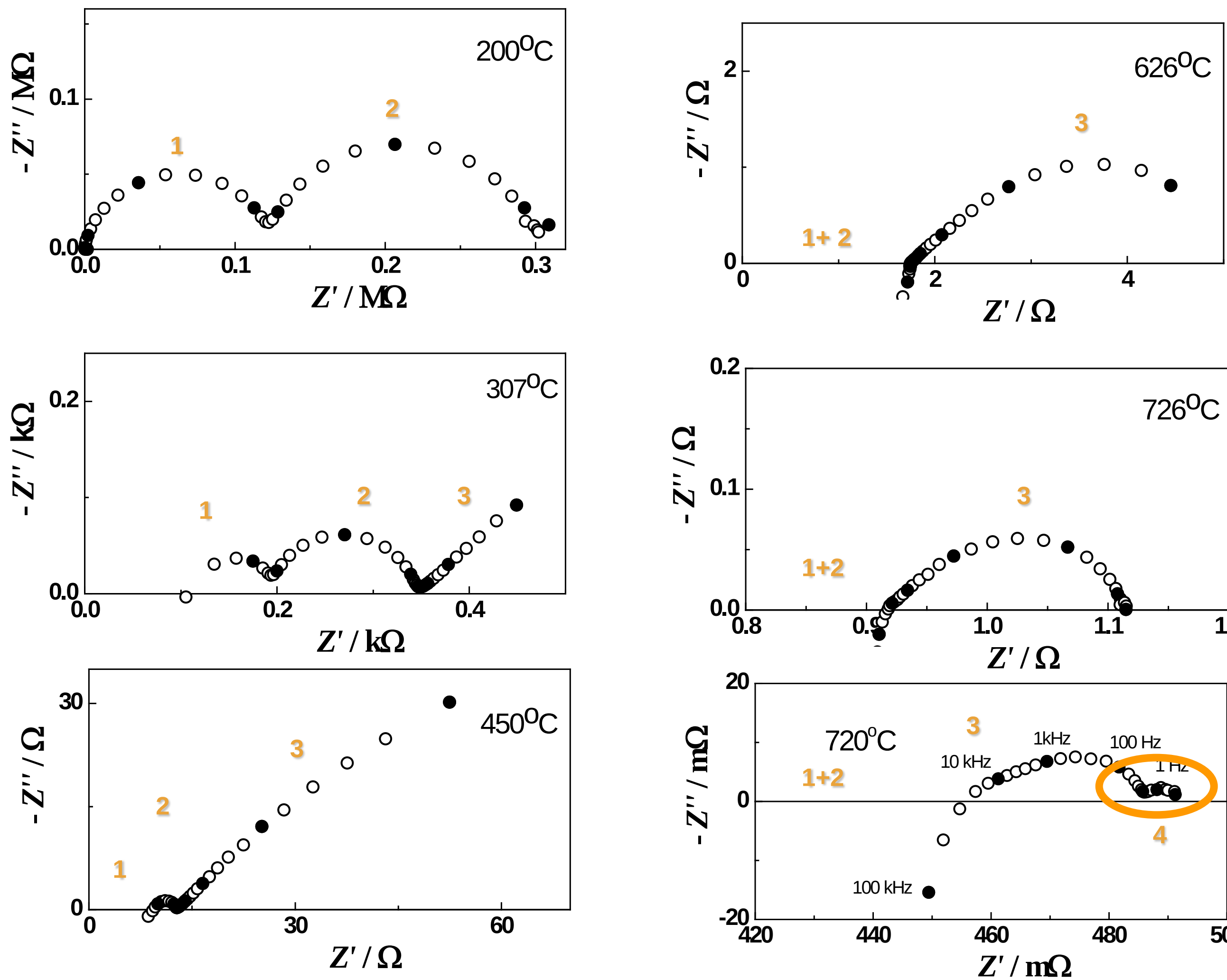






f_1 10 MHz
f_2 0,01 Hz

Both electrolyte (YDC) and electrode (LSCF) behavior become observable



ИМООД

➢ Working hypotheses from system analysis point of view

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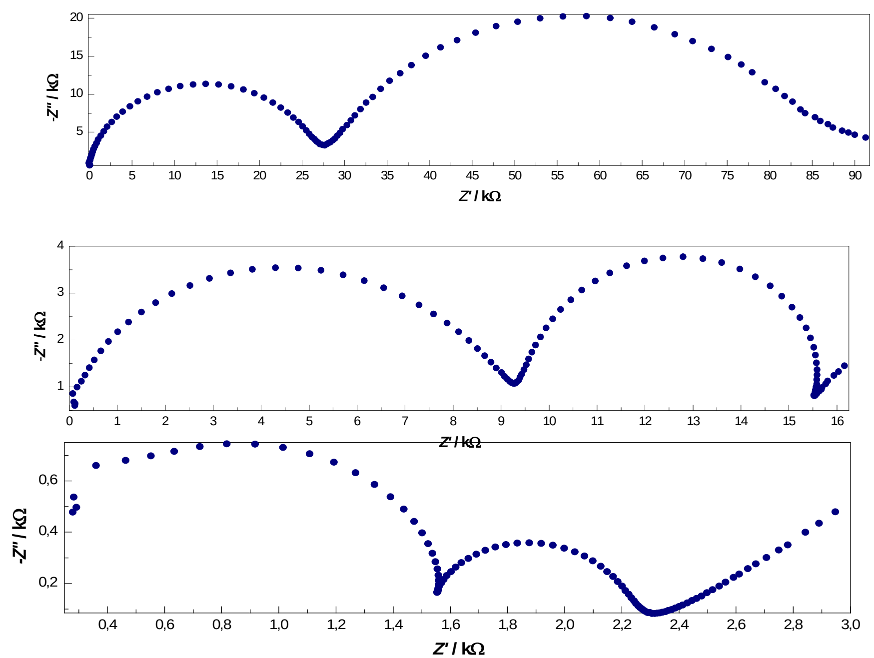


100°C

150°C

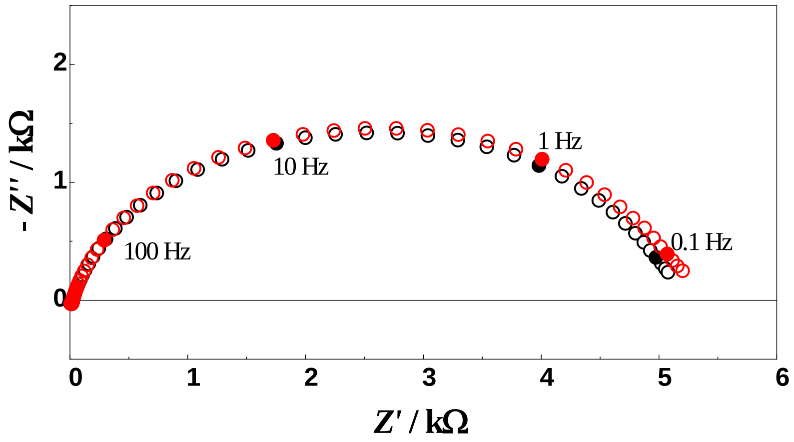
200°C

✓ Lack of memory effects:

the investigated system dos not "remember" the history of the experiment. That means that the result does not depend on the order of the measurements.

Experimental verification: measurements from high to low and then from low to high frequencies, + analysis of the weighted differences.

Recommendation: down-scanning



YSZ: 650° C

° Up (from high to low frequencies)

° Down (from low to high frequencies)

✓ For Systems that:

OBEY the working hypotheses

CAUSAL (all the changes are caused by the perturbation signal)

Hilbert Transform:

full description of the object with only with *Re* (or *Im*)

Experimental application: Kramers-Kronig Transform (KK)

$Im \rightarrow Re$ or $Im \rightarrow Re$

KK is valid ONLY for a class of electrochemical objects

- Working hypotheses from electrochemical point of view

  - ✓ Additiveness of the Faradaic current and the charging current of the double layer

  - ✓ Electrical neutrality of the electrolyte – the total density of the charges in every point of the solution is zero

  - ✓ Lack of convection and migration – i.e. there are no changes in the local concentration of the electrolyte

  - ✓ Lack of lateral mass and charge fluxes at the electrode surface.

- New Trends in the Electrochemical Impedance

✓ **AIM:** To overcome the restrictions of the working hypotheses:

- ☺ NON -LINEAR Impedance
- ☺ NON-STATIONARY Impedance
- ☺ MULTI-TRANSFER FUNCTION ANALYSIS – single input and multiple outputs

- Working hypotheses - Conclusions

  - ✓ **ONLY correct experimental conditions ensure**
    - ☺ accuracy
    - ☺ reliability of the measured impedance data

  - ✓ Correct experimental conditions depend on:
    - ☺ construction of the experimental cell + object configuration
    - ☺ measurement setup
    - ☺ correct combination of parameters and conditions *(small signal, scan from high to low frequencies, well defined working point – constant values of all the parameters)*

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   - Simple models
   - Identification

➢ Impedance monitoring

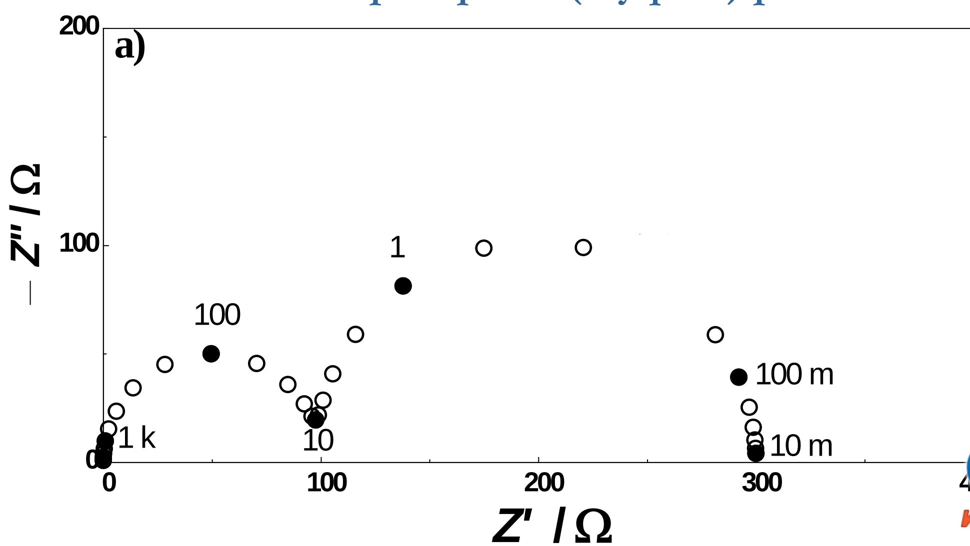
$Z(i\omega_i) = Y(i\omega_i) \,/\, X(i\omega_i) = U(i\omega_i) \,/\, I(i\omega_i)$ → complex number

→ 3D data set $Z(Re_i, Im_i, \omega_i)$

✓ Cartesian coordinates:

$Z(i\omega_i) = Re_i + iIm_i$; $i = (-1)^{1/2}$; $_i = 1, 2, \ldots, n$ – frequency range

Complex plane (Nyquist) plot



Coordinates: $x_i = Re$; $y_i = -Im$

Nd – frequency density; 3-5 for screening; 10-15 for precise measurements;

Data pre-processing: data quality improvement - correction of erroneous data

✓ **Polar coordinates:** $Z(i\omega_i) = |Z| \; e^{j\varphi_i}$ - **Bode Plots**

$|Z| = (Re_i^2 + Im_i^2)^{1/2}$ - modulus ; $\phi_i = \text{Arc tan}\,(Im_i / Re_i)$ - phase

Recalculated 3D set of data:

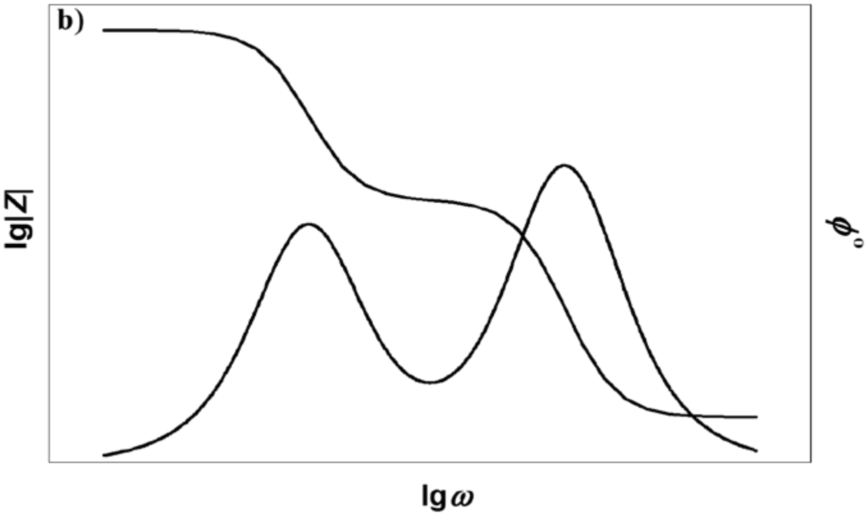
$D3\ [\,\omega_i,\ |Z|_i,\ \phi_i\,]$; $i = 1, 2, ..n$

Coordinates:

$x_i = \lg \omega_i$; $y1_i = |Z|_I$

$y2_i = \phi_i$

Bode Plots



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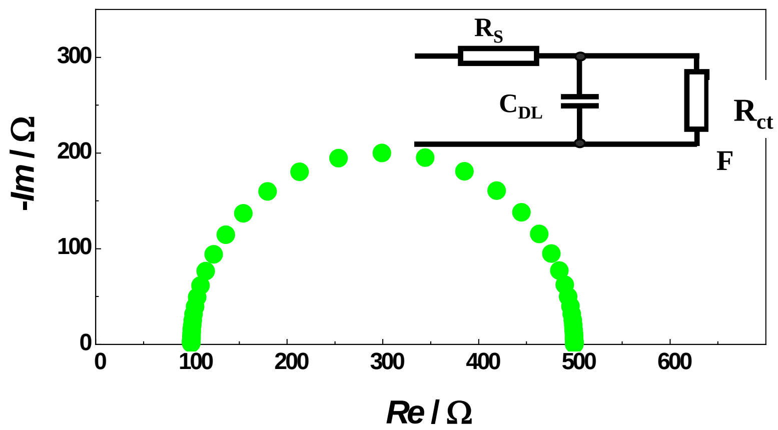
From one side the impedance (or admittance) functions contain all the information for the investigated system (if the working hypotheses are fulfilled at the selected working point).
From another side this information has to be extracted from the data, i.e. the data analysis is an identification procedure.
Advantage: The electrochemical impedance has the unique possibility to separate the kinetics of the different steps involved in the total process under investigation, because as a transfer function it is a local, linear an full description of the system under study. A number of processes are taking place, caused by the perturbation signal. The impedance, however, does not measure them, i.e. it is not a physical reality, but information property of the object.
Disadvantage: Since impedance is not a physical reality, the interpretation of the experimental data is based on the construction of a WORKING MODEL, following a preliminary working hypothesis, which should be identified. This introduces a subjective component in the analysis.

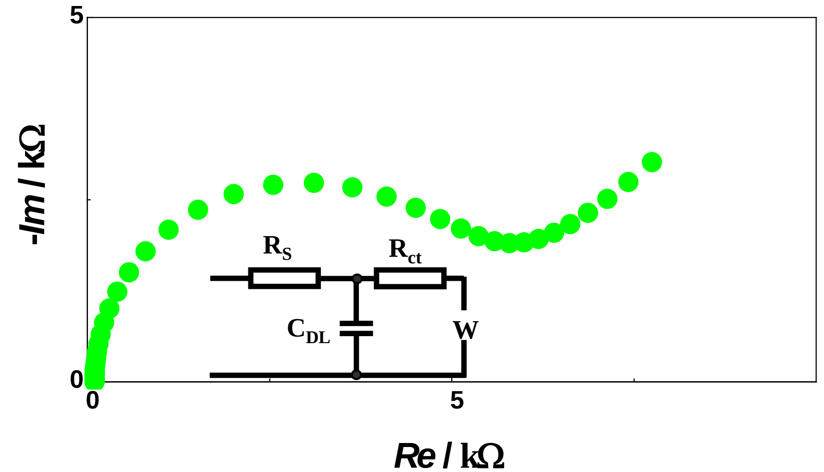
Impedance (as a Transfer Function) gives a local, linear an full description of the system under study.

- **Data analysis – construction of a model by identification procedure.**

  - ✓ **Theoretical (classical) identification approach**
    - construction of a working model(s), following a preliminary working hypothesis
    - verification of the model by parametric identification
  - ✓ **Structural identification approach**
    - no need of a preliminary working hypothesis
    - extracts the model structure + parameters from the experimental data (DIA)

➢ Model representation by equivalent circuits - construction of different elements connected under given laws





✓ The electrical circuit has a response identical to that obtained from the measurement of the investigated system.

✓ Every element describes part of the physical processes taking place

✓ If the model is not formal, the values of its elements could give a significant contribution to the physical understanding of the investigated system.

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- Lumped (electrical) elements – describe homogeneous systems (electrical elements)
  - ✓ resistance R;
  - ✓capacitance C;
  - ✓inductance L.
- Frequency dependent (electochemical) elements – describe frequency inhomogeneity (electrochemical processes)

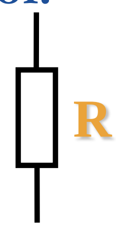
➢ Resistance *R*

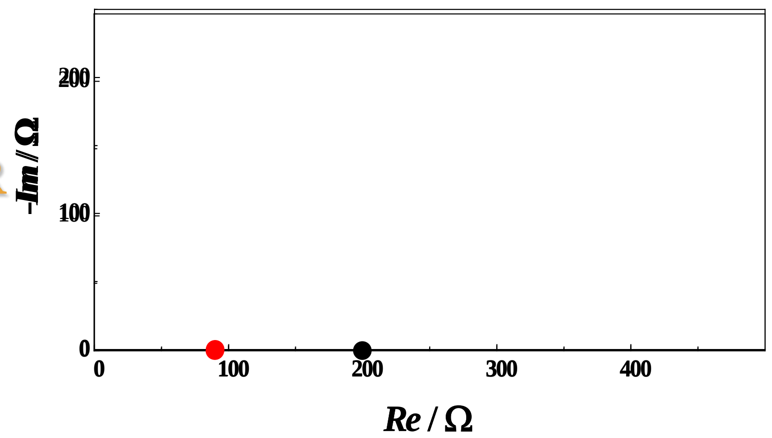
- ✓ In the time (t) domain – follows Ohm's Law: $U_R = R.I$
  Dimensions: ohm (Ω) = $VA^{-1} = m^2kgA^{-2}s^{-3}$

- ✓ In the frequency (w) domain: $Z_R\,(i\omega) = R$
  only real part ($Re = R$; $Im = 0$)

✓ Physical meaning: - description of:

energy losses;
dissipation of energy;
potential barrier;
electronic conductivity
conductivity of very fast carriers





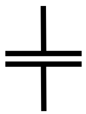
✓ Electrolyte resistance - $Zs(i\omega)$ = Rs for water based electrolytes

➢ Capacitance *C*

✓ In the time (t) domain
Dimensions: F = sΩ^{-1}

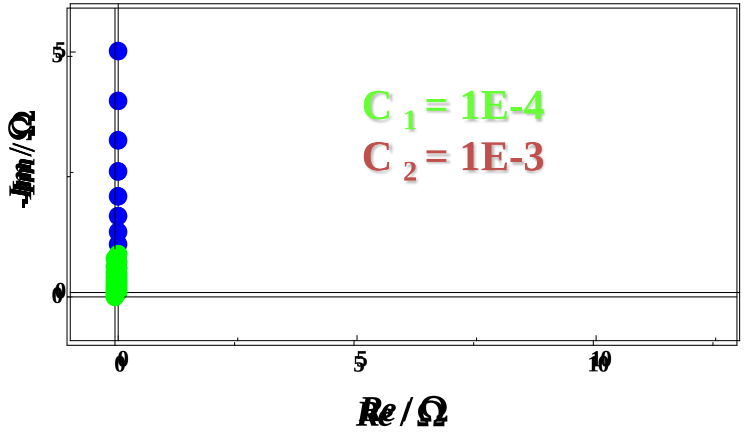
$$U_C = \frac{1}{C}\int_{t_o}^{t} i(t)dt + U_C(t_o)$$

$$Z_C(i\omega) = (i\omega C)^{-1} = -i(\omega C)^{-1}$$



C

✓ In the frequency (ω) domain:
only imaginary part (*Re* = 0)
90º phase retardation; Z ↓;ω↑



✓ Physical meaning: - modeling of:
mass and charge accumulation,
dielectric polarization,
integral relation between parameters

✓The impedance of the Double layer C_{dl} has a capacitive character.

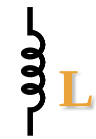
➢ Inductance *L*

- ✓ In the time (t) domain
  Dimensions: H = Ωs

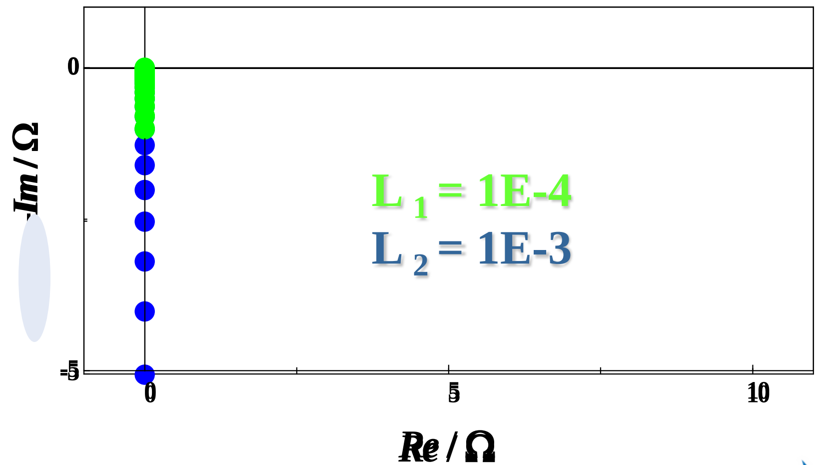
$$U_L = L\frac{di(t)}{dt}$$

- ✓ In the frequency (ω) domain:
  only imaginary part (Re = 0)
  90^o phase shift; Z ↑; ω↑

$$Z_L(i\omega) = \boldsymbol{i}\omega L$$



- ✓ Physical meaning: - modeling of:
  self inductance of the connecting cables, the measuring cell and investigated objects
  self inductance of current flow or of charge carriers movement;



- ✓ Represents accumulation of magnetic energy

Impedance elements

- Frequency dependent (electochemical) elements – describe frequency dependent behaviour

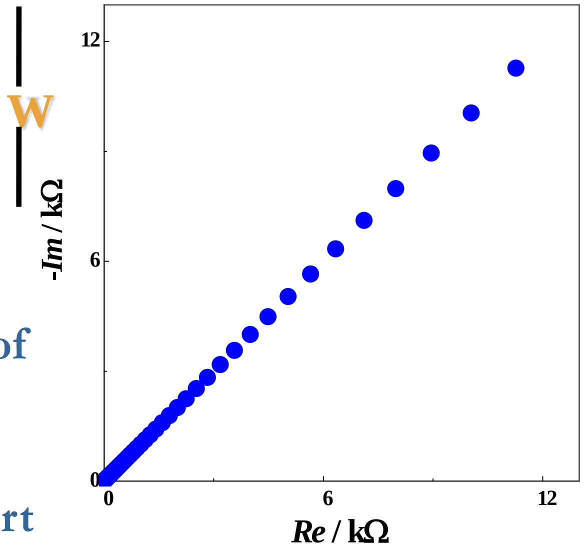
- **Warburg element (1896) *W* -** describes linear semi-infinite diffusion, which obeys the second Fick's low:

$$\partial c / \partial t = D(\partial^2 c / \partial x^2)$$

- ✓ In the time (t) domain
  Dimensions: $\Omega m^2 s^{1/2}$

$$Z_W(i\omega) = \sigma \omega^{-1/2}(1 - i)$$

- ✓ In the frequency (ω) domain:
  $Re = Im$ – phase shift = 45°



- ✓ Remark:

  the sin wave does not reach the end of the diffusion layer.

  Warburg impedance is a one port element – no introduction of another element after Warburg impedance

- **Constant Phase Element (CPE) – empirical relationship**
  - ✓ **CPE describes frequency dependent impedance caused by surface roughness or non-uniformly distributed properties of the irregular electrode surface.**

$$Z_{CPE}(i\omega) = A^{-1}(i\omega)^{-n}$$

A – proportional factor [$\Omega m^{-2} s^{n}$];

n – exponential coefficient (CPE exponent) that describes the phase shift

➢ Constant Phase Element (CPE) – empirical relationship

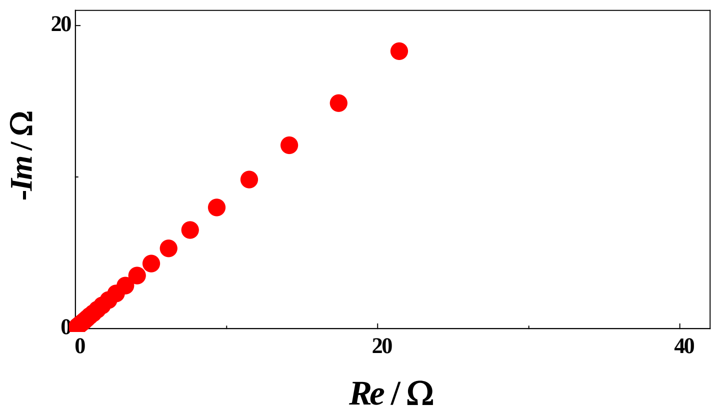
✓ CPE is a generalized element

n = 0.5 ± e (0 < e < 0.2) - diffusion with deviations from the second Fick's law;

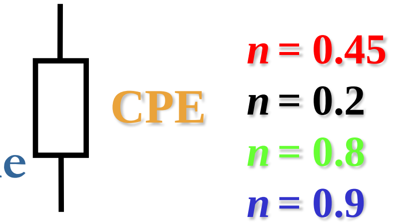
n = 0 ± e - distorted resistance (n < 0 is related to inductive energy accumulation);

n = 1 – e - distorted capacitance;

n = -1 + e - distorted inductance.



For integer values of n (n = 1, 0, -1) – lumped elements C, R and L.



✓ In general CPE is semi-infinite element. It models the impedance of a layer with a thickness bigger than the penetration depth of the perturbation signal.

✓ CPE has only an input with the exception in the cases when n = 1, 0, -1.

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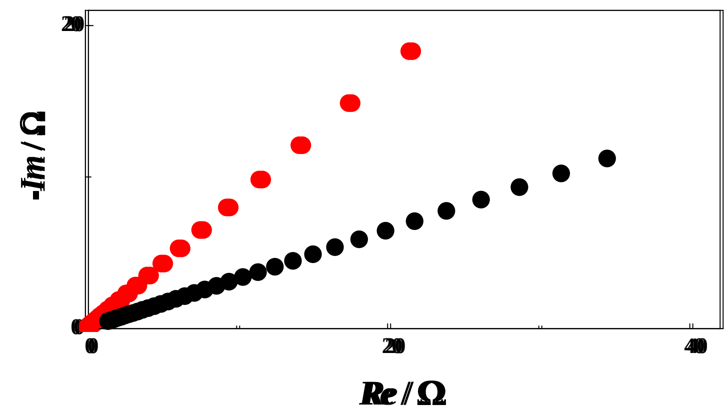

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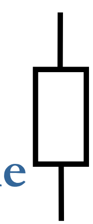

CPE

n = 0.45
n = 0.2
n = 0.8
n = 0.9

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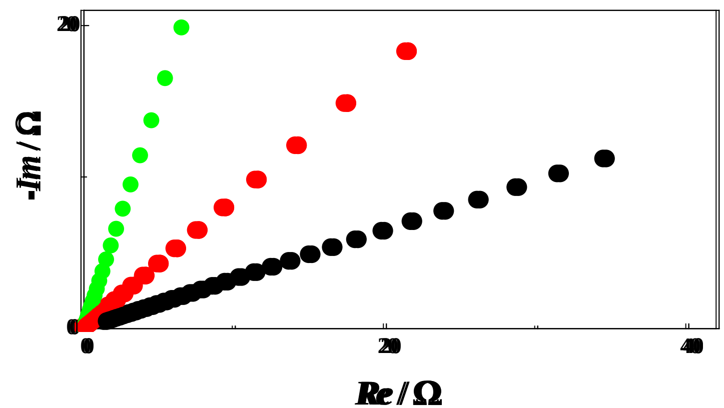

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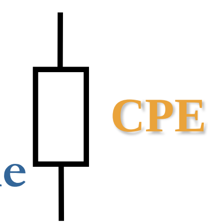

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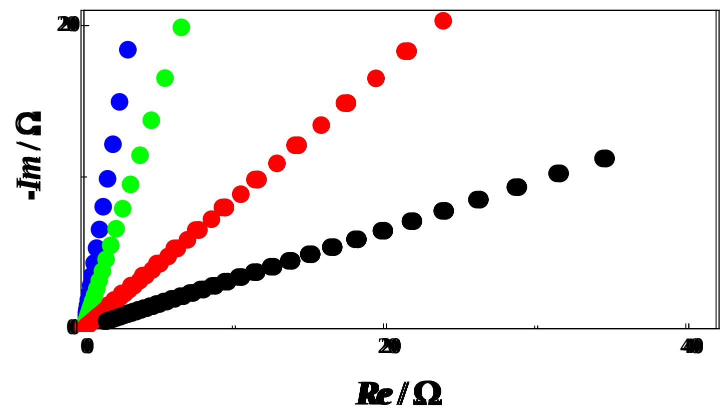

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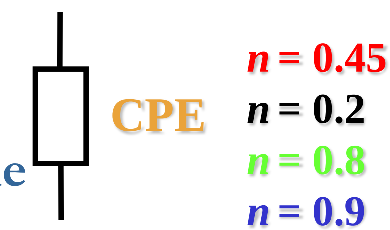


✓ In general CPE is semi-infinite element. It models the impedance of a layer with a thickness bigger than the penetration depth of the perturbation signal.

✓CPE has only an input with the exception in the cases when $n = 1, 0, -1$.

CPE- Physical Meaning

CPE may have direct physical meaning :

the generalized resistance n = 0 - 0.2 may model conductance of ionic clouds or conductance connected with accumulation of magnetic or electrostatic energy;

the generalized capacitance n = 0.8 - 1 may model surface roughness of the electrode or distribution of the charge carrier density, i.e. a double layer with complicated stricture;

The generalized Warburg n = 0.4 - 0.6 may present non-ideal geometry of the diffusion layer; presence of migration or convection; diffusion connected with energy loses or accumulation of charges; constrains of the host matrix to the diffusion of species,unhomogeneous diffusion;

CPE may be also used for formal better modeling of an external similarity with the measured impedance.

➢Bounded electrochemical elements

In real systems very often at low frequencies the perturbation signal penetrates to the end of the layer, which behaves as a layer with a finite thickness. For more precise modeling of such systems bounded electrochemical elements are introduced.

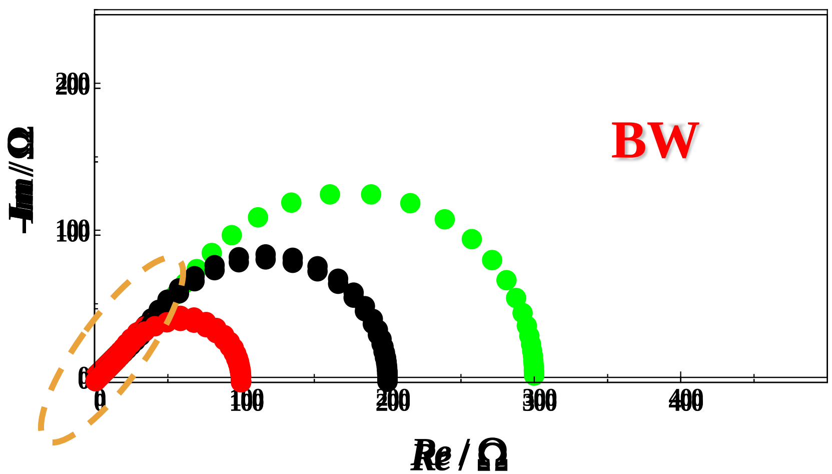
Bounded Warburg (BW)

- Bounded Warburg element describes the impedance of a linear diffusion in a homogeneous layer with finite thickness

$$Z_{\mathrm{BW}}(\mathrm{i}\omega) = \sigma(\mathrm{i}\omega)^{-1/2}\,\mathrm{th}\left(\frac{\mathrm{i}\omega R_0^2}{\sigma^2}\right)^{1/2}$$

R_0 is the total resistance [Ω] of the layer at ω= 0

At high frequencies $(\omega \to \infty)$ BW behaves as Warburg element.



R_0 = 100
R_0 = 200
R_0 = 300
σ = 0.01

➢ **Bounded Constant Phase Element (BCP)** - represents the impedance of a bounded homogeneous layer with CPE behaviour of the conductivity in the elementary volume and a finite conductivity R_0 at d.c. ($\omega \to 0$)

$$Z_{BCP}(i\omega) = A^{-1}(i\omega)^{-n}\,\mathrm{th}(R_0 A(i\omega)^n)$$

n and *A* are the CPE coefficients

$R_0 = 100$
$R_0 = 200$
$R_0 = 300$
$n = 0.45$
$A = 0,01$

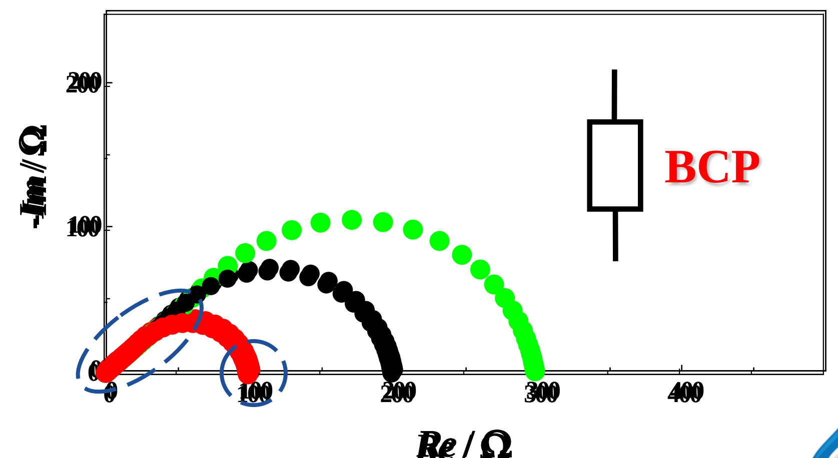
✓ **Properties** – the most generalized element:

for high enough frequencies tends to the classical CPE

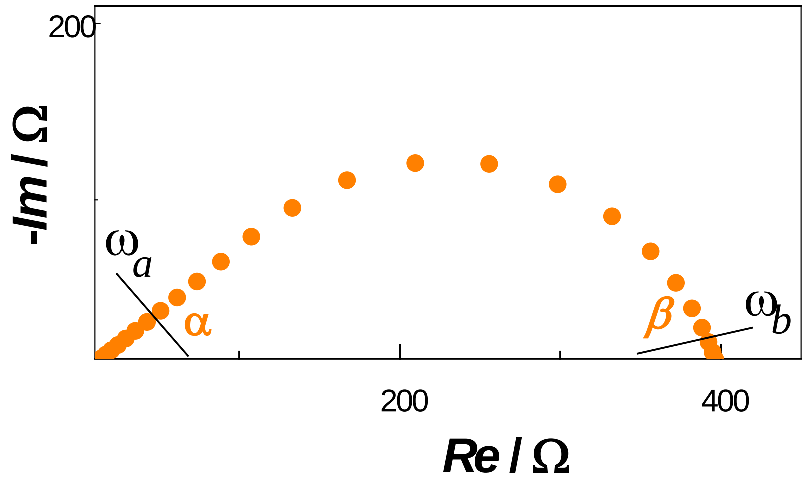
$$Z_{BCP}(\omega \geq \omega_a) = Z_{CPE} + \varepsilon$$

for low frequencies – pure resistance R_0

$$Z_{BCP}(\omega \leq \omega_b) = R_0 + \varepsilon$$

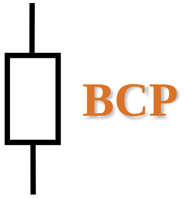


Criterion for verification of BCP:



a and b are the angles of the diagram's asymptotes respectively at low and high frequencies.

$$\beta = 2\alpha = (n\,\pi/2)$$



$R_o = 400$
A = 0.01
n = 0.3

➢Bounded Constant Phase Element (BCP)

$$Z_{BCP}(i\omega) = A^{-1}(i\omega)^{-n}\,th(R_0 A(i\omega)^n)$$

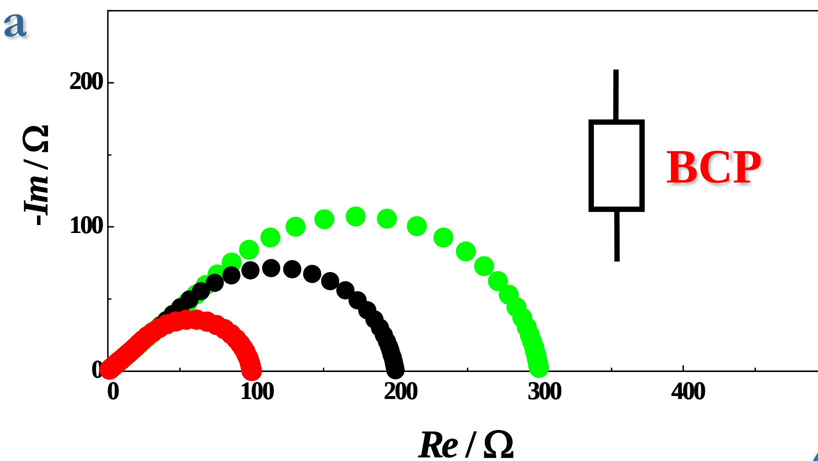
n and *A* are the CPE coefficients.

$R_0 = 100$
$R_0 = 200$
$R_0 = 300$
$n = 0.45$
$A = 0{,}01$

✓ **Remark:**

BCP can be applied for *n = 0 – 0.6* because of the initial assumption that the investigated object is regarded as a conductor.

Obviously at higher values for *n* the system demonstrates capacitive behaviour.



Electrical circuit model – construction of different elements connected under given lows

✓Lumped (electrical) elements

R →	$Z_R(iw) = R$	energy losses
L →	$Z_L(iw) = iwL$	accumulation of magnetic energy
C →	$Z_C(iw) = -i(wC)^{-1}$	accumulation of mass or charge

✓Frequency dependent (electrochemical)

W →	Z_W	semi-infinite diffusion
BW →	Z_{BW}	bounded diffusion
CPE →	Z_{CPE}	generalized, semi-infinite
BCP →	Z_{BCP}	most generalized, bounded

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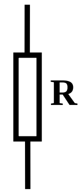
➢ Connections between elements:



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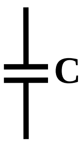
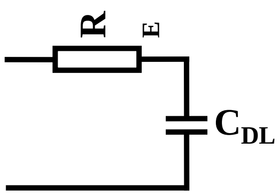


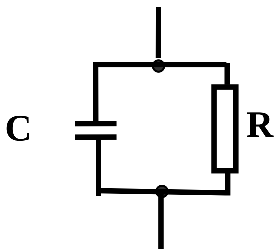
$Z_R(i\omega) = R$

$Z_C(i\omega) = -i(\omega C)^{-1}$

Series connection



Parallel connection:

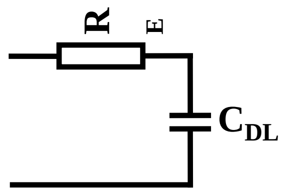


$Z_{IP}(i\omega) = Z_R(i\omega) + Z_C(i\omega)$

$1/Z(i\omega) = 1/Z_R(i\omega) + 1/Z_C(i\omega)$

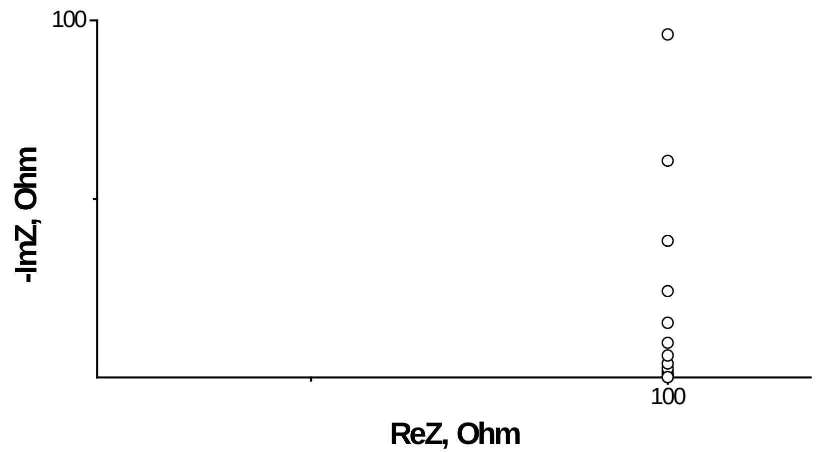
➢ Connections between elements:

Series connection



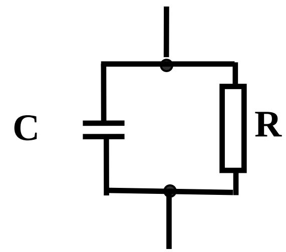
$$Z(i\omega) = Z_R(i\omega) + Z_C(i\omega) =$$

$$= R + (i\omega C)^{-1} = R - i(\omega C)^{-1}$$



- Connections between elements:

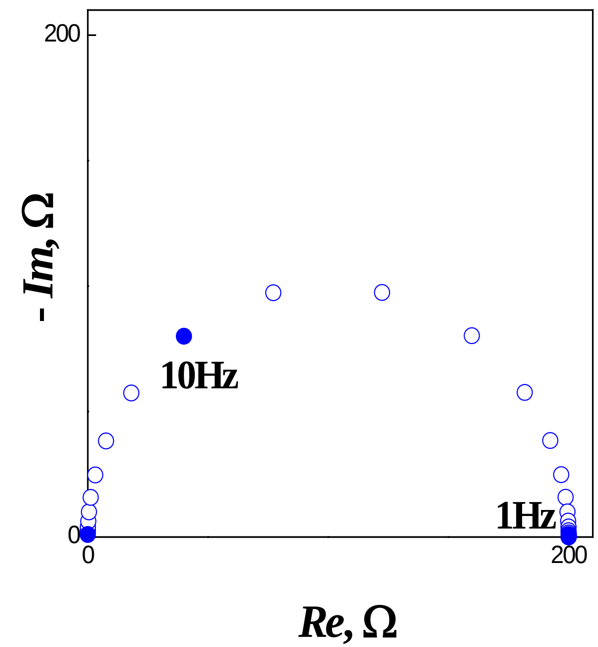
Parallel connection:



$1/Z(i\omega) = 1/Z_R(i\omega) + 1/Z_C(i\omega)$

$$\frac{1}{Z(i\omega)} = \frac{1}{Z_R(i\omega)} + \frac{1}{Z_C(i\omega)}$$

$T = R.C$



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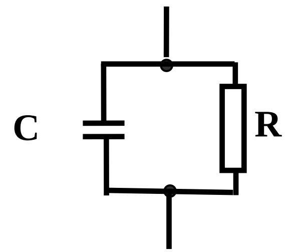
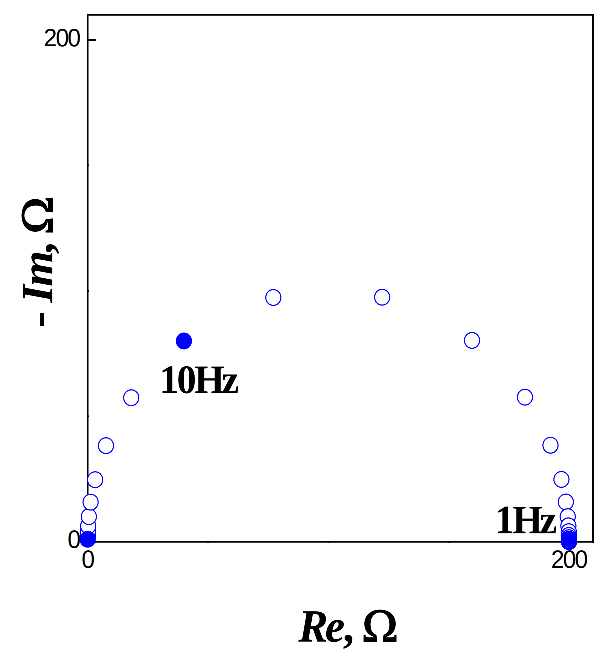


$1/Z(i\omega) = 1/Z_R(i\omega) + 1/Z_C(i\omega)$

$$\frac{1}{Z(i\omega)} = \frac{1}{Z_R(i\omega)} + \frac{1}{Z_C(i\omega)}$$

$$Z(i\omega) = \frac{R}{1+\omega^2T^2} + i\,\frac{\omega RT}{1+\omega^2T^2}$$

$$T = R.C$$



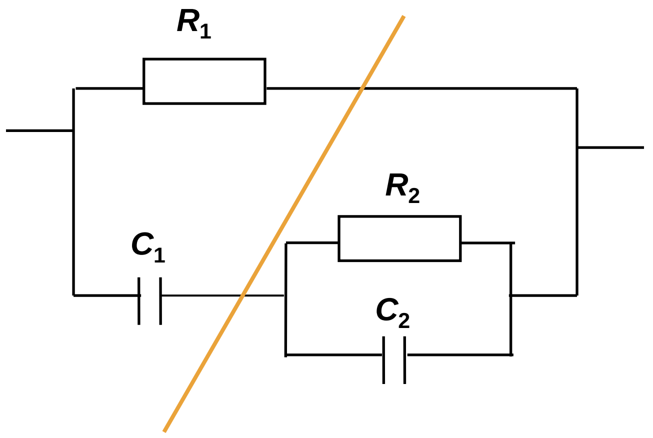
Main model structures:

- ✓ Ladder Structure – consists of a number of kernels corresponding to the modelled phenomena. The modeled phenomena occur consequently.

$$Z(i\omega) = Z_1(i\omega) + \{Z_2(i\omega) + [Z_3(i\omega) + Z_4(i\omega) + \ldots)^{-1}]^{-1}\}^{-1}$$

The model has typical "ladder" structure

Application for description of processes at the electrode interface

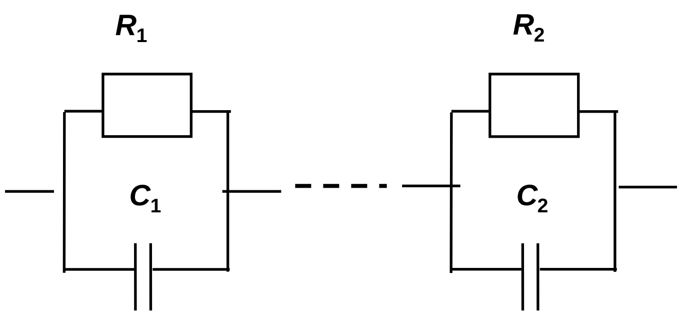


Main model structures:

- ✓ Voigt's Structure – consists of meshes with impedances $Z_k(i\omega)$, connected in series.

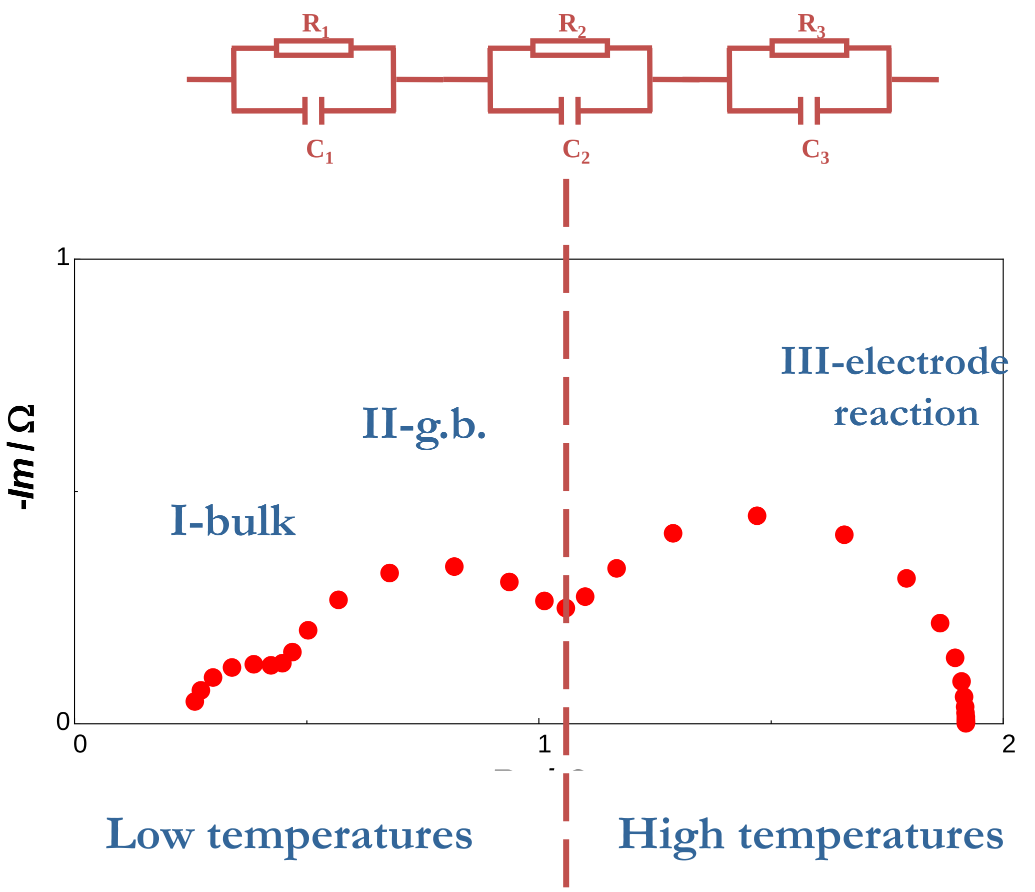
$$Z(i\omega) = \sum Z_k(i\omega)$$

The phenomena modeled by each mesh start instantaneously.
The flowing current is equal for all meshes.
The rates depend on their own time-constants.

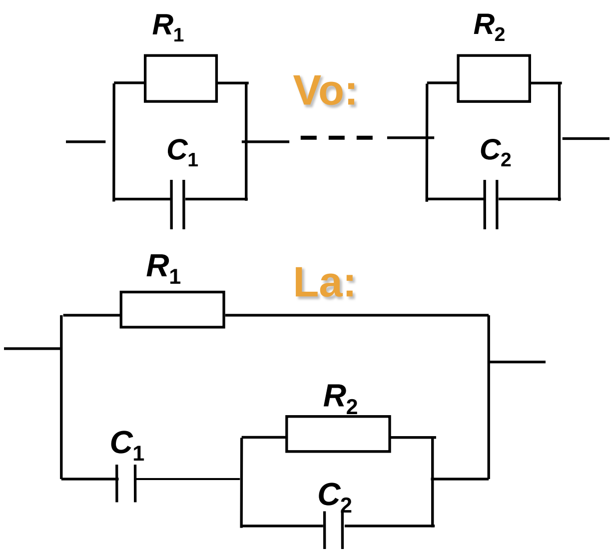


Voigt's model structure is applied for impedance description of solid state samples

- **Main model structures:** Voigt's model structure



➢ Model description conventions



✓ Structures:

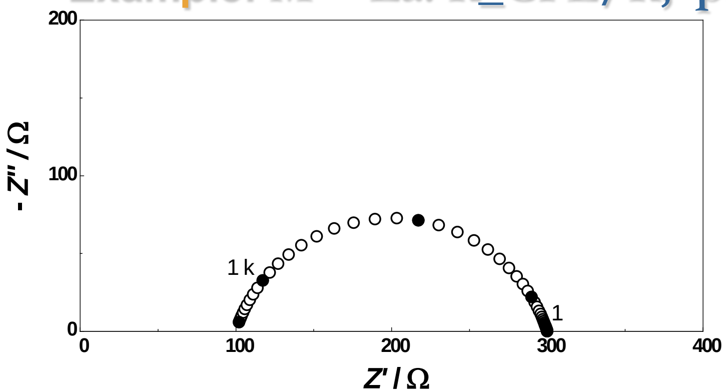
La: - ladder; Vo: - Voigt

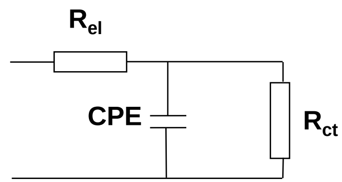
✓ Elements: R, C, L, W, BW, CPE, BCP

✓ Connections: “ “ in series; “/” in parallel

✓ Parameters: dimensions in SI ; delimiters “;”; multiple parameters separator – “\”

Example: M = La: R_CPE/R; par: 100; 10^{-3}\0.8; 200

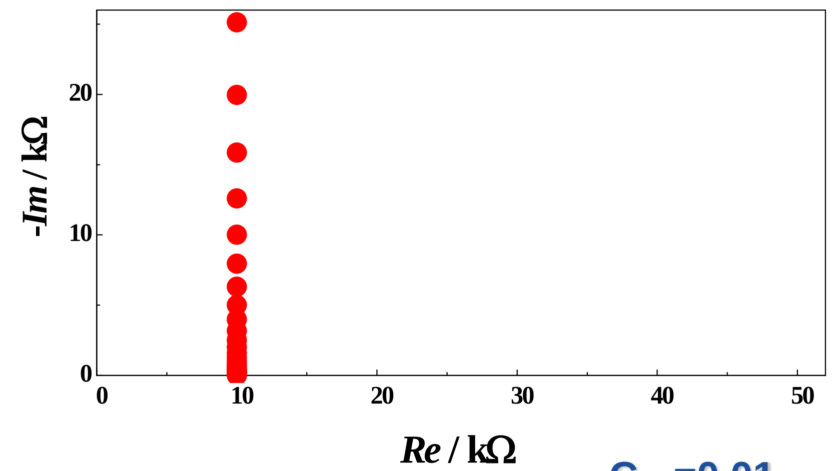




IUPAC project: Z. Stoynov (coordinator)
Ch. Brett, M. Orazem

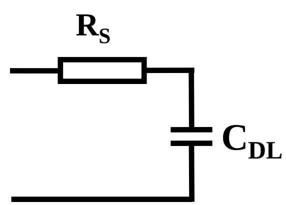
- ✓ **Ideally polarizable electrode (IPE)** La: $R_s\ C_{dl}$

describes a case when there is absence of any process at the electrode surface



C_{DL}=0.01
R_S=10E+3
R_S=20E+3
R_S=30E+3

Structure (equivalent circuit)



Impedance

$$Z_{IPE}\,(i\omega) = R_s - i(\,\omega C_{dl})^{-1}$$

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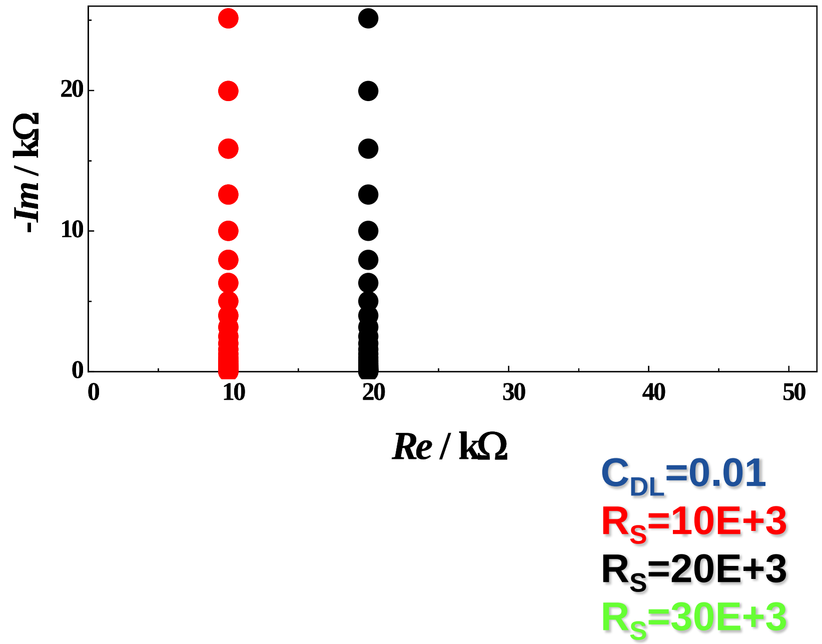

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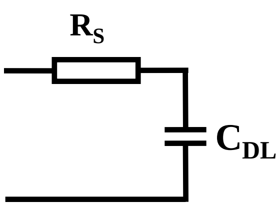

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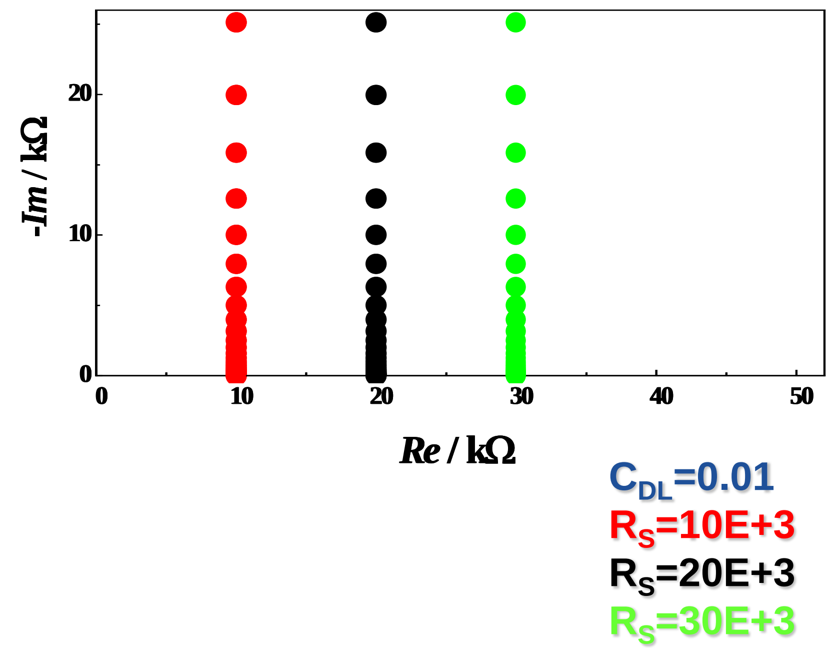

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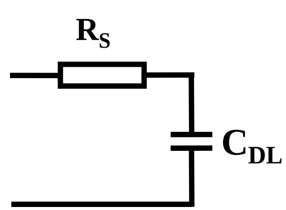


Impedance

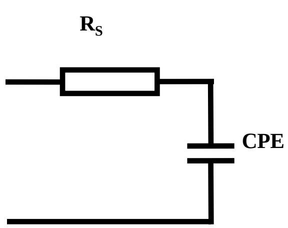
$$Z_{IPE}(i\omega) = R_s - i(\omega C_{dl})^{-1}$$

✓ **Modified Ideally polarizable electrode (MIPE)** La: R_s CPE_{dl}

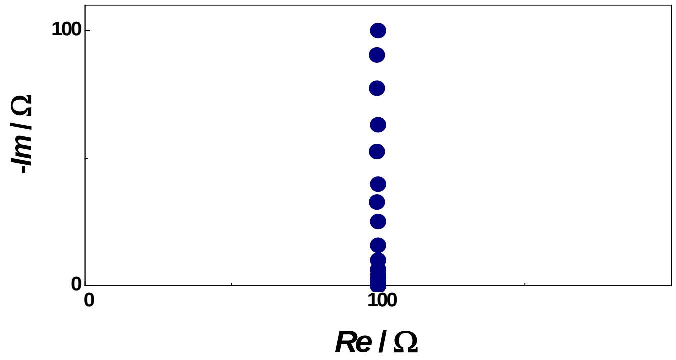
describes a case when the electrode surface is rough and inhomogeneous

Structure (equivalent circuit)

Impedance



$R_S = 100$
$A = 0.01$
$n = 1$
$n = 0.8$



$$Z_{MIPE}(i\omega) = Rs + A^{-1}(i\omega)^{-n}$$

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Structure (equivalent circuit)

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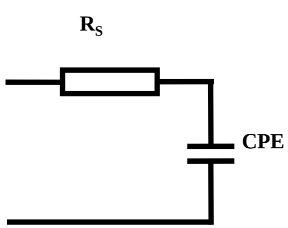
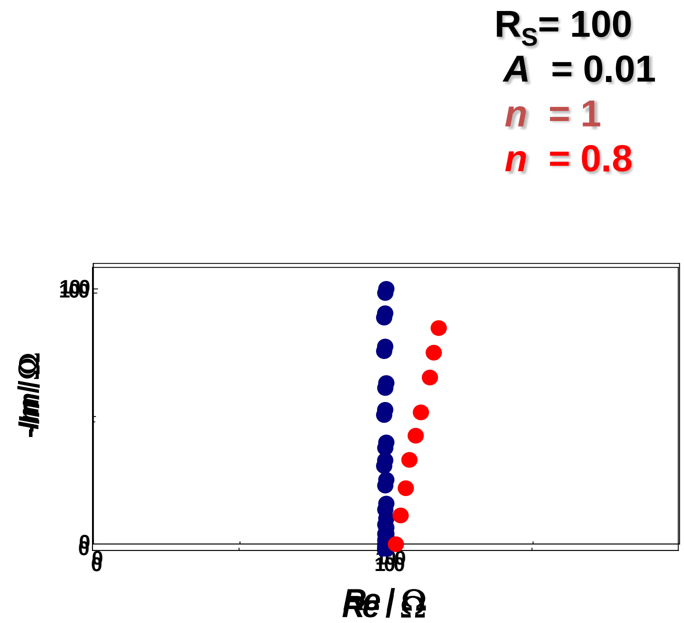




$$Z_{MIPE}(i\omega) = Rs + A^{-1}(i\omega)^{-n}$$

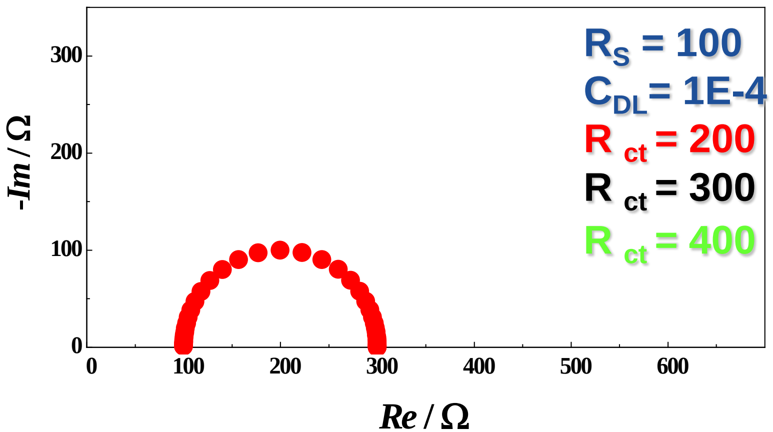
- ✓ Polarizable electrode (PE) (simple Faradaic reaction) La: R_s C_{dl}/R_{ct}

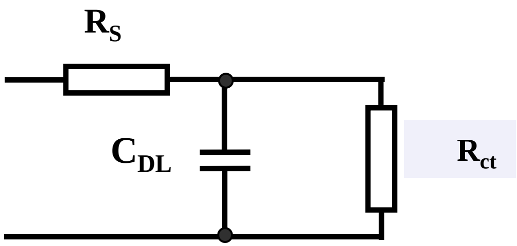
Describes a single step electrochemical reaction at the electrode surface

Additiveness of the Faradaic current and the charging current of the double layer

Structure (equivalent circuit)- physical meaning

Impedance





$$Z_{PE}(i\omega) = R_s + R_{ct}(1 + \omega^2 T^2)^{-1} - i\omega R_{ct} T (1 + \omega^2 T^2)^{-1}$$

$$(T = RC)$$

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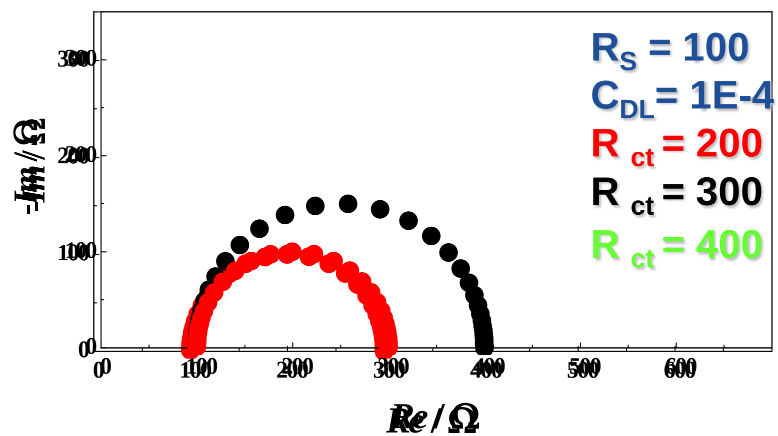

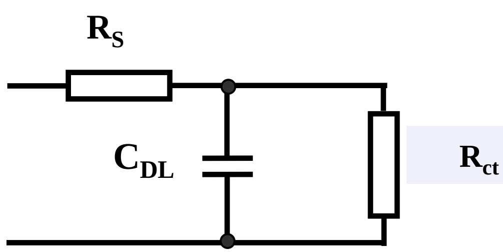

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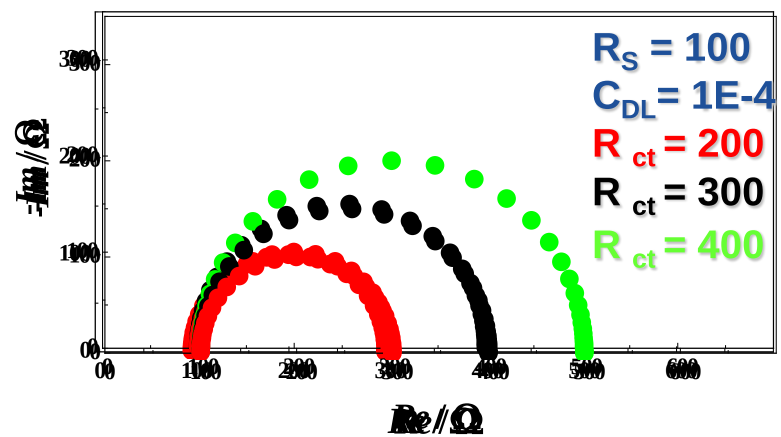
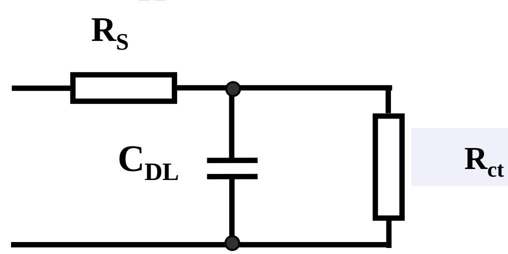




$$Z_{PE}(i\omega) = R_s + R_{ct}(1 + \omega^2 T^2)^{-1} - i\omega R_{ct} T(1 + \omega^2 T^2)^{-1}$$

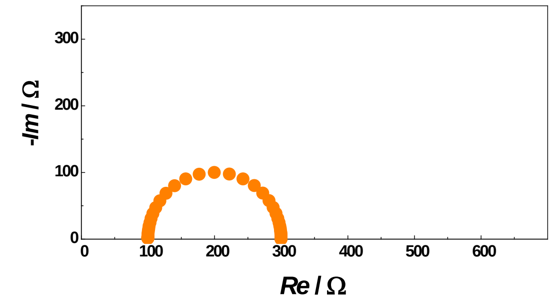
$$(T = RC)$$

Geometrically the impedance diagram is presented as an ideal semicircle with a diameter R_{ct};

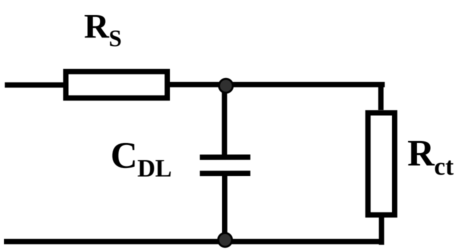
for $\omega \to \infty$ the semi-circle intercepts the real axis in R_s

for $\omega \to 0$ the intercept is in a point with value $R_s + R_{ct}$

the imaginary component reaches a maximum at the so called characteristic frequency ω_0



Impedance diagram in the frequency range 10^5-10 Hz



$R_s = 100$
$C_{DL} = 1E\text{-}4$
$R_{ct} = 200$

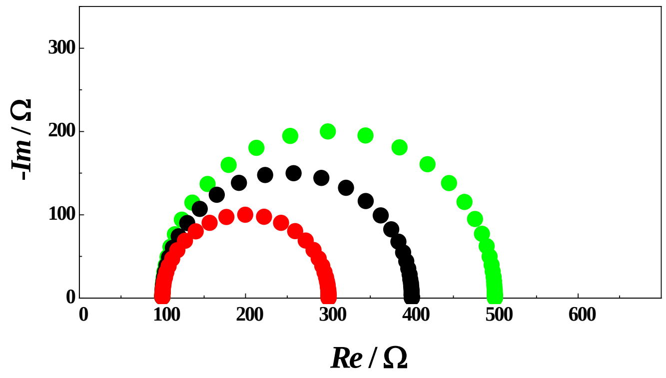
$$\omega_0 = (C_{dl}R_{ct})^{-1} = T^{-1}$$ (T is the time-constant)

$$Z_{PE}(i\omega) = R_s + R_{ct}(1 + \omega^2 T^2)^{-1} - i\omega R_{ct} T (1 + \omega^2 T^2)^{-1}$$

The structural parameters have direct physical meaning (R_s, R_{ct}, C_{dl}) for partially reversible charge transfer reaction at equilibrium

$R_{ct} = (RT/nF)(1/I_0)$ (I_0 - exchange current)

R_{ct} depends on the rate of reaction, which is potential dependent and thus R_{ct} varies with the potential, i.e.the diameter of the semi-circle changes.



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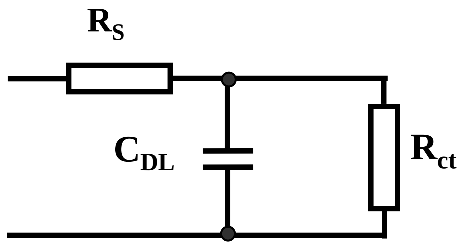
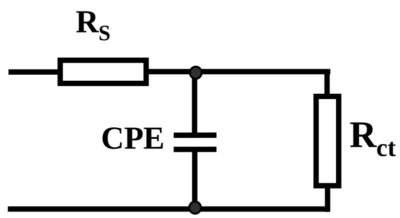
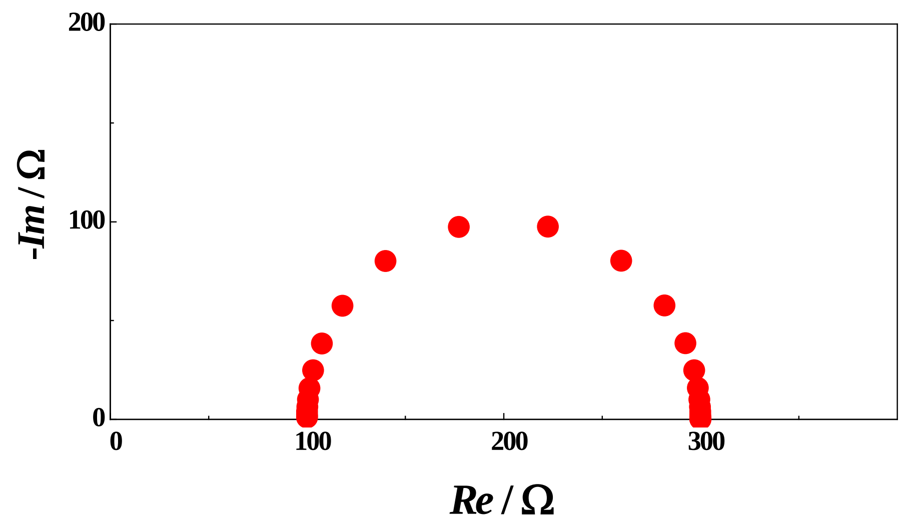


$R_S = 100$
$C_{DL} = 1E-4$
$R_{ct} = 200$
$R_{ct} = 300$
$R_{ct} = 400$
$R_{ct} = 500$

✓ Modified Polarizable electrode (MPE) La: R_s CPE_{dl}/R_{ct}



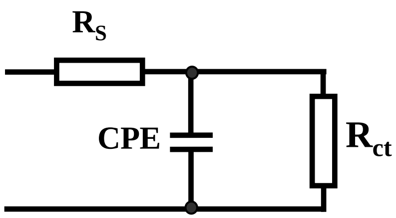
R_{EIS} = 100
R_{ct} = 200
A = 0.01
n = 1
n = 0.8



May give better Structure, but formal description of the investigated system

May have a physical meaning: description of the electrode's surface roughness

✓ Modified Polarizable electrode (MPE) La: R_s CPE_{dl}/R_{ct}



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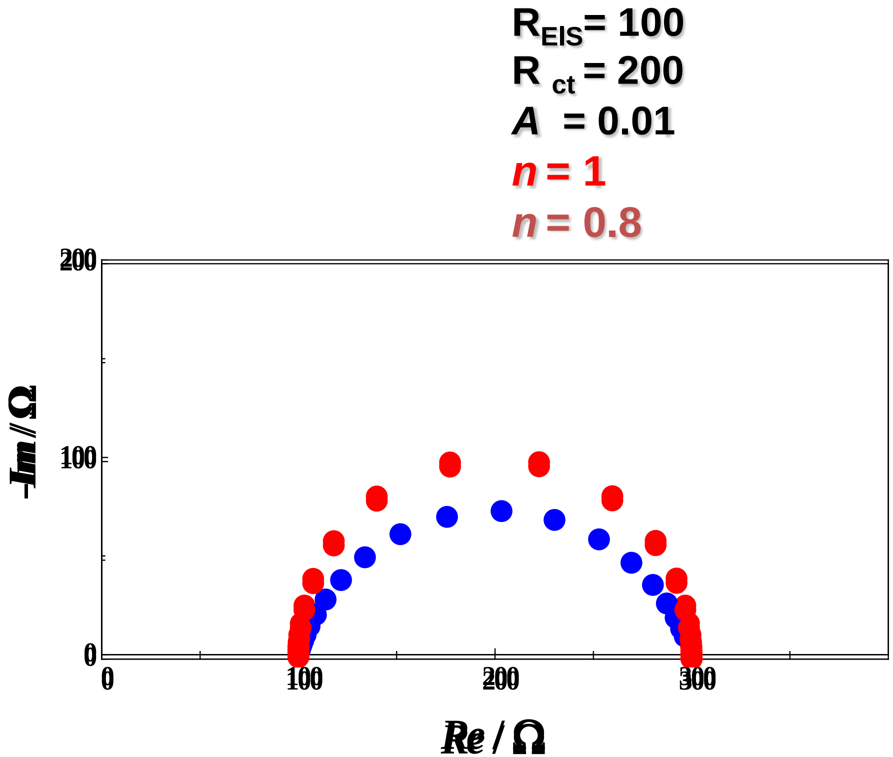
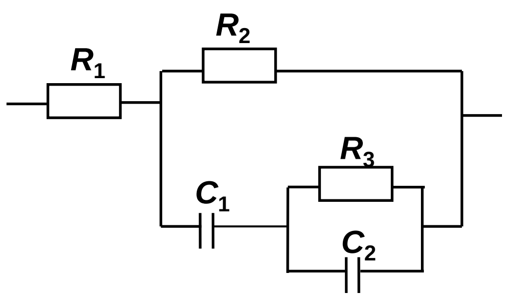
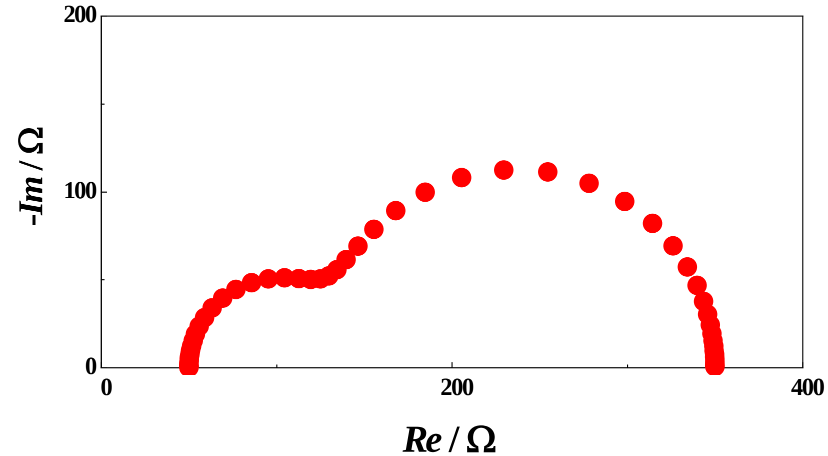


✓ Faradaic reaction with one adsorbed species La: $R_1\ C_1/R_2\ C_2/R_3$

Structure (equivalent circuit)





$R_1 = 50$
$R_2 = 100$
$C_1 = 1E\text{-}3$
$R_3 = 200$
$C_2 = 1E\text{-}2$
$C_2 = 3E\text{-}3$
$C_2 = 1E\text{-}3$

describes a heterogeneous reaction occurring in two steps with adsorption of the intermediate product X

B ⟶ X + e step I

X ⟶ P + e step II

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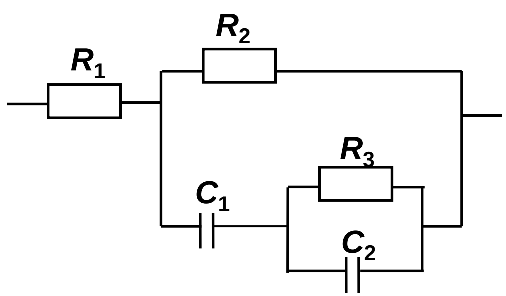

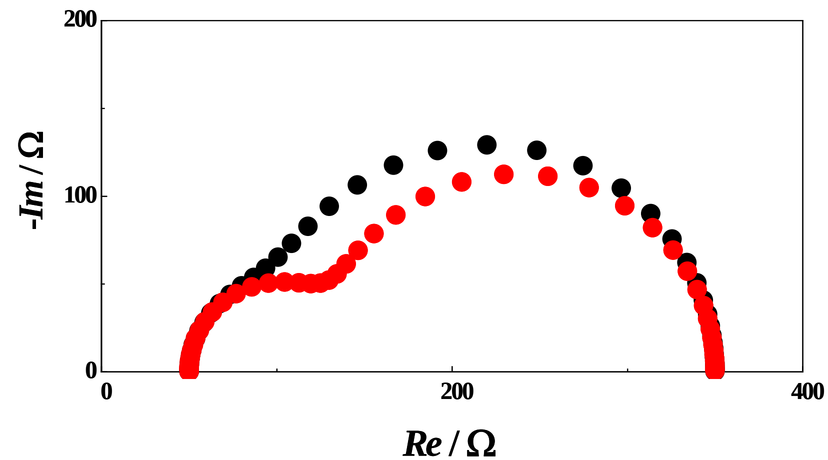

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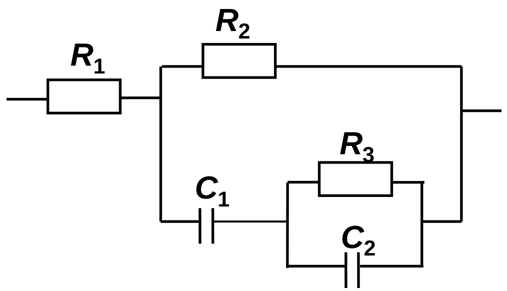

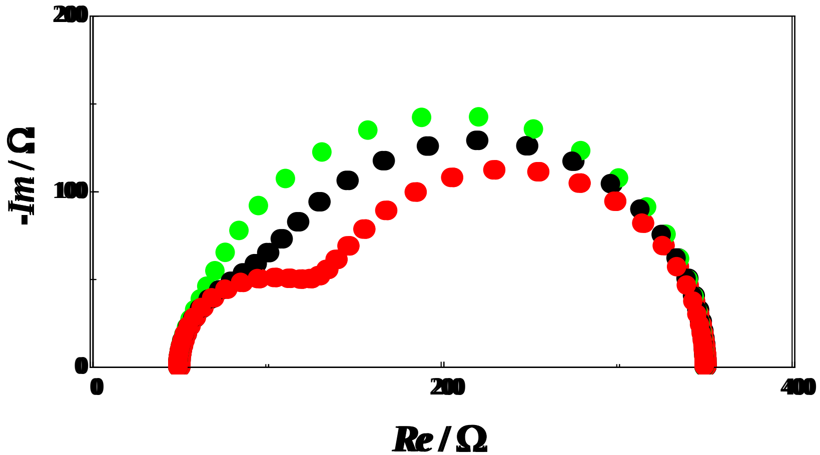

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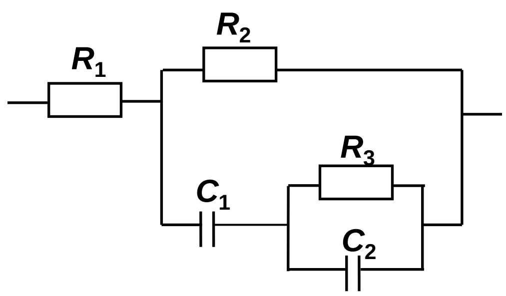

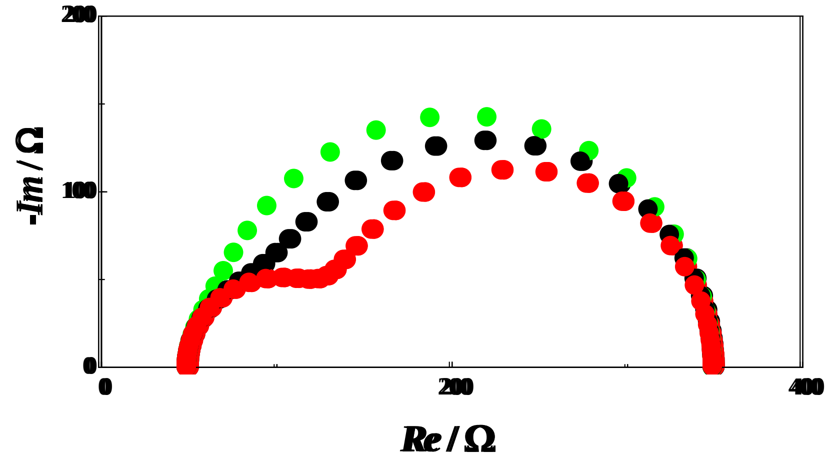

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$C_2 = 3E\text{-}3$
$C_2 = 1E\text{-}3$

The structural parameters have direct physical meaning:

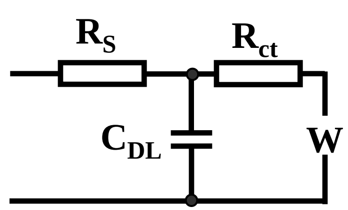
$R_1 = R_S$ $\qquad C_1 = C_{DL}$

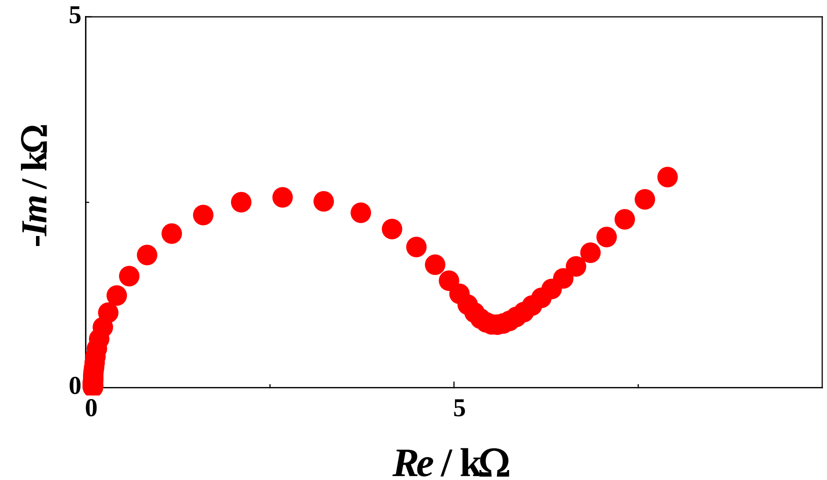
$R_2 = R_{ct}$ $\qquad C_2 = C_{ad}$

✓ Randles model La: $R_s\ C_{dl}/R_{ct}\ W$

Describes polarizable electrode with diffusion limitations

Structure (equivalent circuit)





R_S=100
R_{ct}= 5E+3
W = 100
C_{DL}=3E-4
C_{DL}=1E-3
C_{DL}=3E-3

Impedance

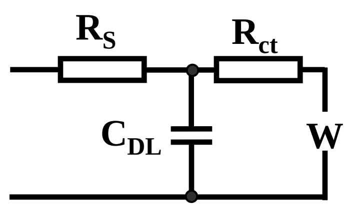
$$Z_{RNS}(i\omega) = R_S + [i\omega C_{dl} + (R_{ct} + \sigma\omega^{-1/2} - i\sigma\omega^{-1/2})^{-1}]^{-1}$$

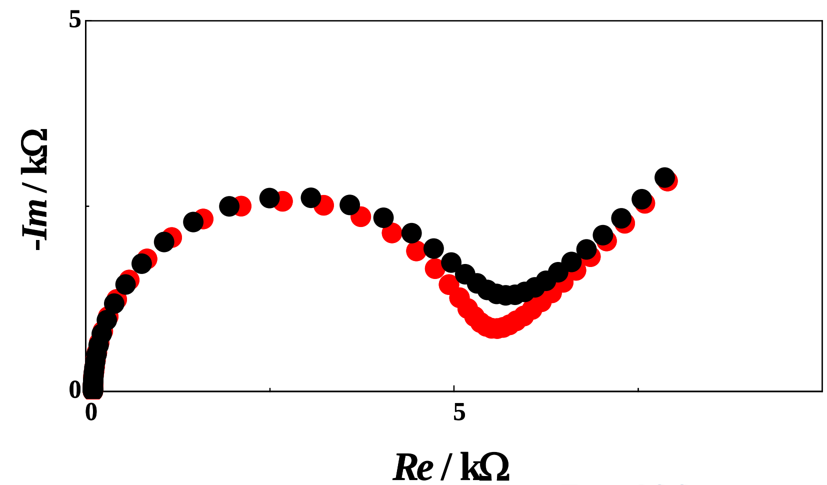
ИМООД

✓ Randles model La: $R_s\ C_{dl}/R_{ct}\ W$

Describes polarizable electrode with diffusion limitations

Structure (equivalent circuit)





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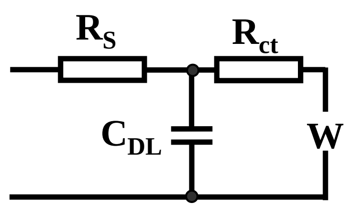

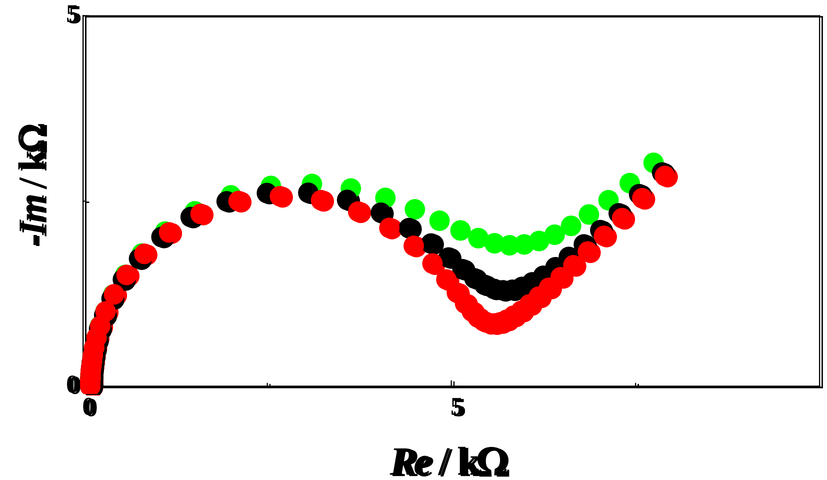

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Impedance

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Relation between the structural parameter σ and the electrochemical parameters:

$$W = R_{ct}[k_f(D_O)^{-1/2} + k_b (D_R)^{-1/2}]$$

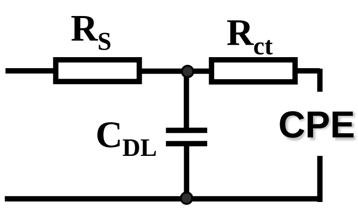
(k_f, k_b – reaction rates of the "forward" and "backward" reactions; D_O and D_R – diffusion coefficients of the species)

The structural model has 4 parameters, which can be determined from the impedance (R_S, R_{ct}, C_{dl}, W), while the electrochemical impedance model has 7 parameters (R_S, C_{dl}, I_0, k_f, k_b, D_R, D_O), which can not be determined directly)

✓ Modified Randles model

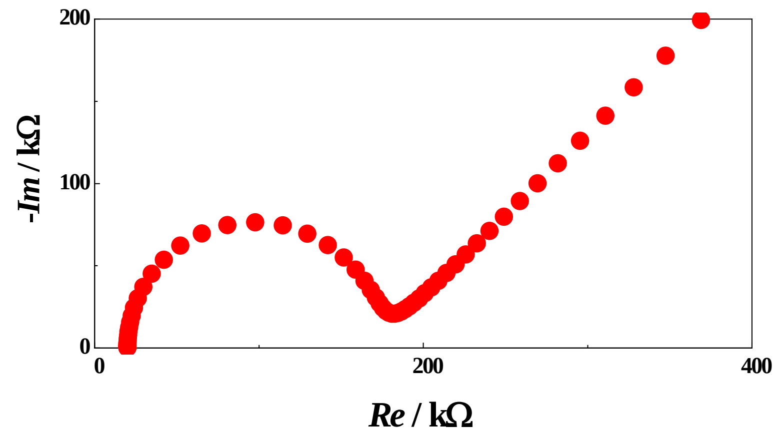
La: R_s C_{dl}/R_{ct} CPE

Structure (equivalent circuit)



Describes geometrical or activation inhomogeneity of the surface or deviations from the linear diffusion process.

That happens very often when the diffusion occurs in a diluted solution or in case that the diffusion does not obey Fick's



R_S=20

R_{ct}= 150

C_{DL}=1E-2

A = 0.1

n = 0.5

n = 0.45

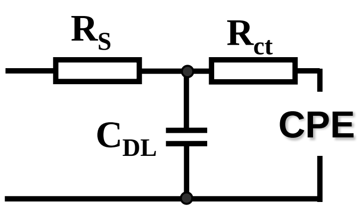
n = 0.4

ИМООД

✓ Modified Randles model

La: $R_s\ C_{dl}/R_{ct}$ CPE

Structure (equivalent circuit)



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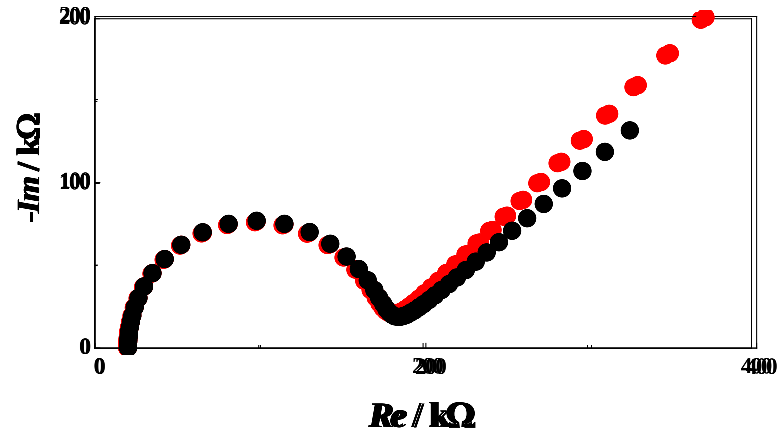
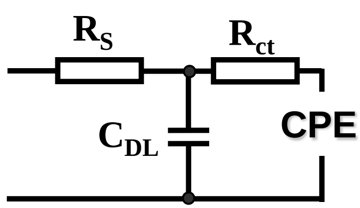


R_S=20
R_{ct}= 150
C_{DL}=1E-2
A = 0.1
n = 0.5
n = 0.45
n = 0.4

✓ **Modified Randles model** La: $R_s\ C_{dl}/R_{ct}$ CPE

Structure (equivalent circuit)



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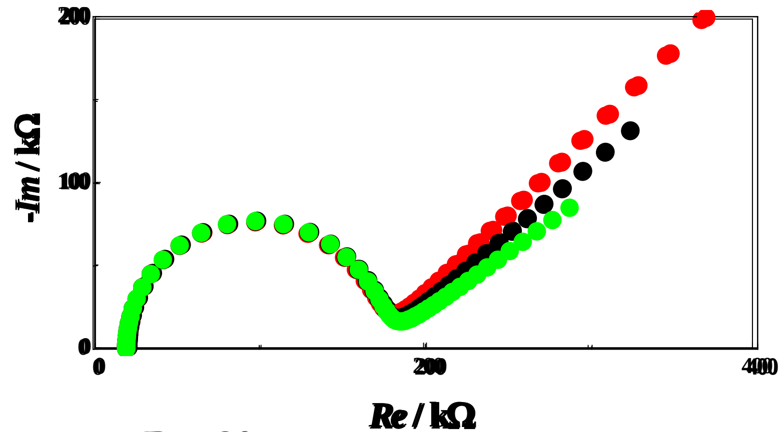


R_S=20
R_{ct}= 150
C_{DL}=1E-2
A = 0.1
n = 0.5
n = 0.45
n = 0.4

- ✓ Impedance does not measure directly a physical phenomenon
- ✓ Interpretation of experimental data - construction of an impedance model by identification procedure.

Parametric identification approach – confirmation of preliminary chosen hypothetical model(s)

Structural identification approach derives structure + parameters form experimental data

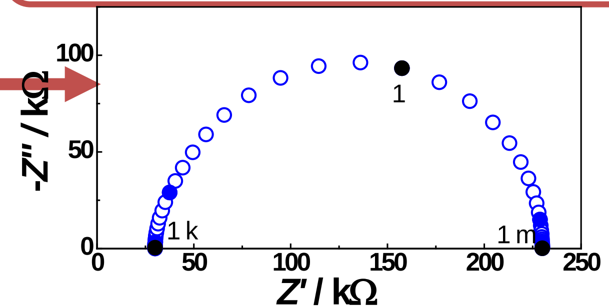
1. Why Impedance
2. What is impedance
3. Impedance measurements
   - Basic Working Hypotheses
4. Presentation of the experimental data
5. Interpretation of the measured data (data analysis)
   - Impedance elements
   - Simple models
   - Identification

STEP I

Organization of the experiment & measurement
Monitoring, data pre-processing

- Algorithm of one impedance experiment

D_3 [Re_i, Im_i, ω_i]

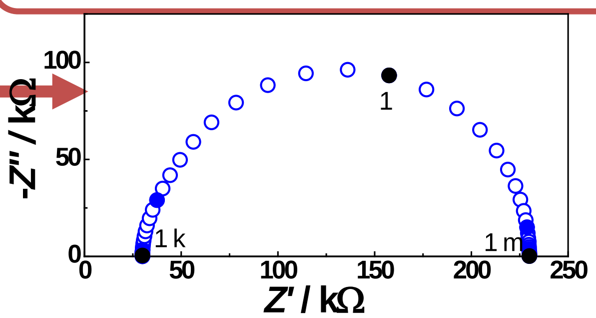


- Algorithm of one impedance experiment

STEP I

Organization of the experiment & measurement
Monitoring, data pre-processing

D_3 [Re_i, Im_i, ω_i]



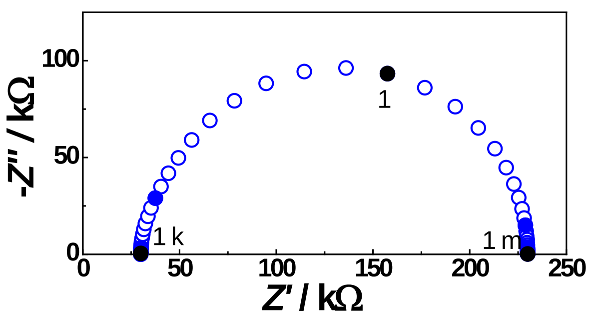
STEP II

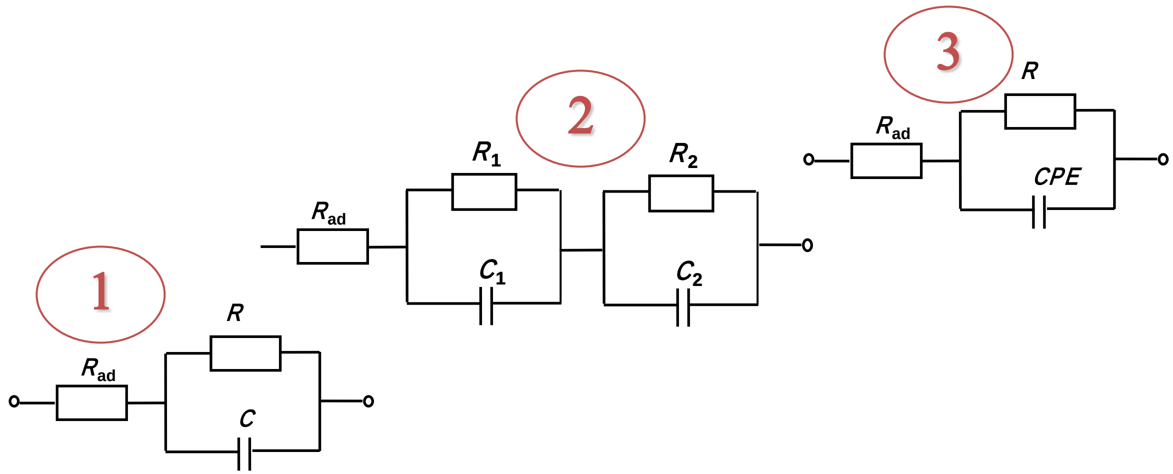
DATA ANALYSIS

Model Identification

Parametric Identification Approach

- Choice of a working hypothesis presented by one or few models





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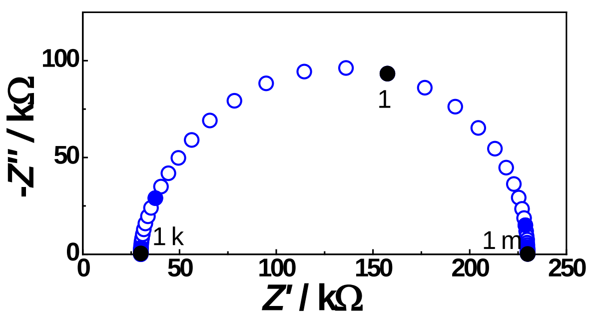
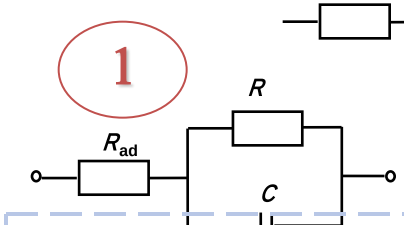
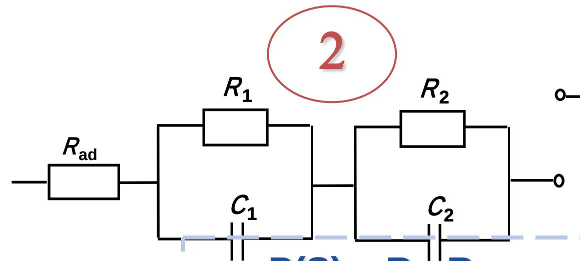
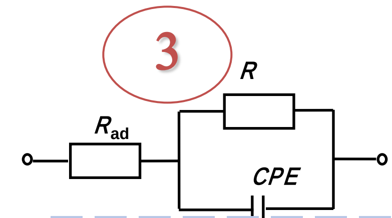




P(S) = R_1, R_2, C
(estimated values)



P(S) = R_1, R_2, C_1, R_3, C_2

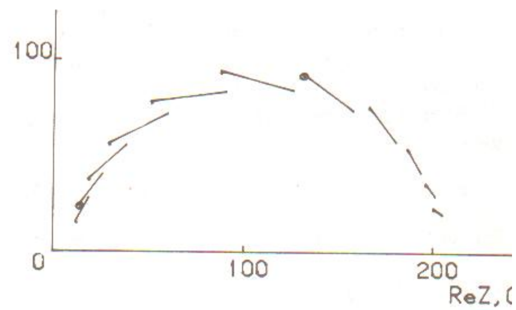


P(S) = R_1, R_2, CPE

- Parametric identification $\hat{P}_M = \boldsymbol{Par.Ident}.[\omega_i, \mathrm{Re}_i, \mathrm{Im}_i | S_M]$

- Model validation

- **Model validation**
  - ✓ **Model simulation:** $\hat{Z}(i\omega) = Simul.[\omega_i, \big| S_M, \hat{P}_M]$
  - ✓ **Selection of criterion for proximity** $\Delta_i(i\omega) = \Phi_i(\hat{Z}_i - Z_i)$
  - ✓ **Analysis of the residuals (adequacy)** $\Delta_i(i\omega) = f(\lg f)$



- **Selection of the best model**

- **Selection of the Best Model**

  Evaluation of the distance for "best fit "

$$\sum \Delta^2{}_i \Rightarrow \min$$

The most frequently applied algorithm for parametric identification

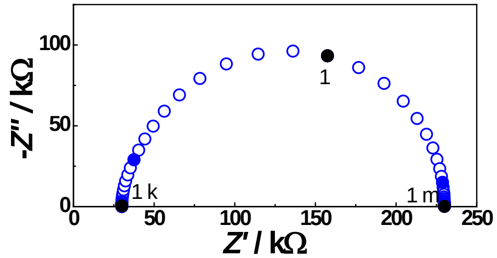
Complex Nonlinear Least Squires Method (CNLS).

Professional software tools are available for it !!!

D3 [Re_i, Im_i, ω_i]

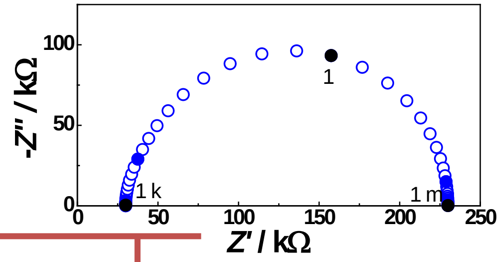
I. Measurement & Data Pre-Processing

II. Data Analysis



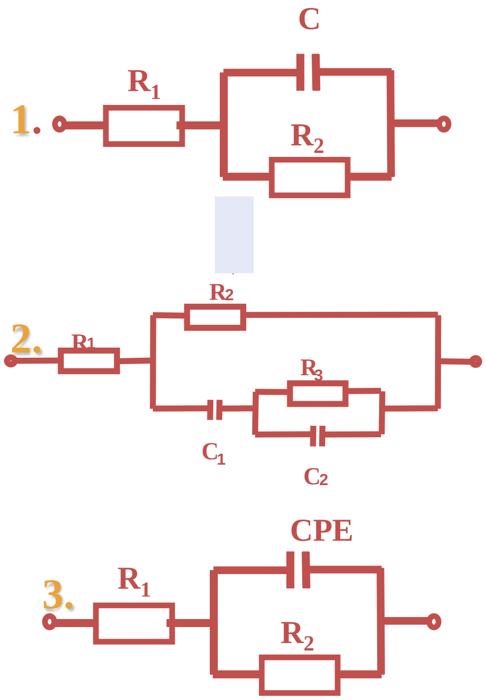
D3 [Re_i, Im_i, ω_i]

I. Measurement &
Data Pre-Processing



II. Data Analysis

1. Choice of Hypothetical model(s)



D3 [Re_i, Im_i, ω_i]

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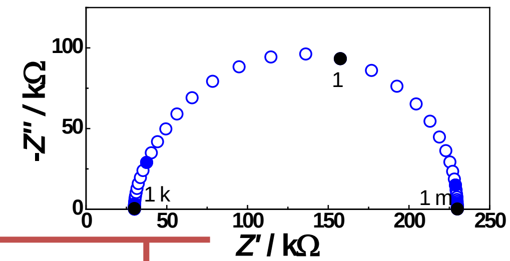
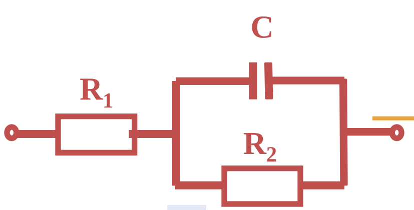


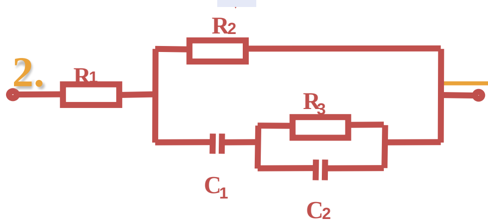
II. Data Analysis

1. Choice of Hypothetical model(s)

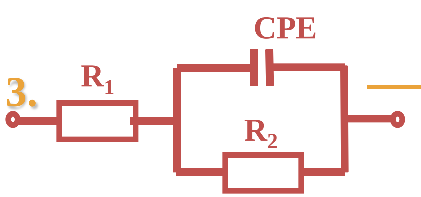
2. Parametric Identification & Validation (CNLS)

1.


$P_{(S)} = R_1, R_2, C$ *(estimated values)*

2.


$P_{(S)} = R_1, R_2, C_1, R_3, C_2$

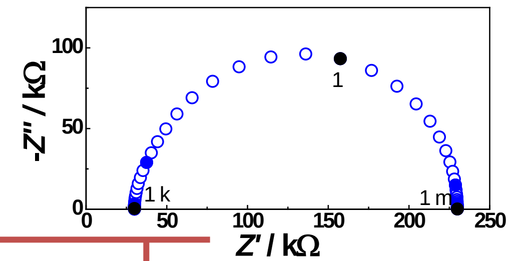
3.


$P_{(S)} = R_1, R_2, CPE$
No adequacy

ИМООД

D3 [Re_i, Im_i, ω_i]

I. Measurement & Data Pre-Processing



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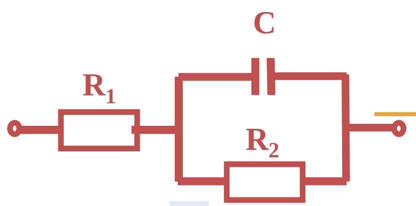

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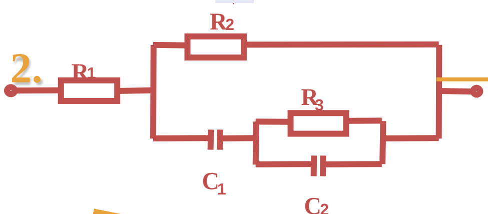

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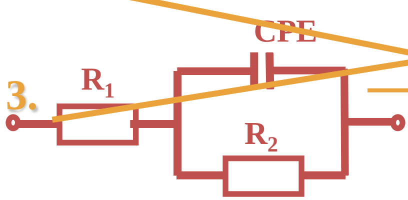
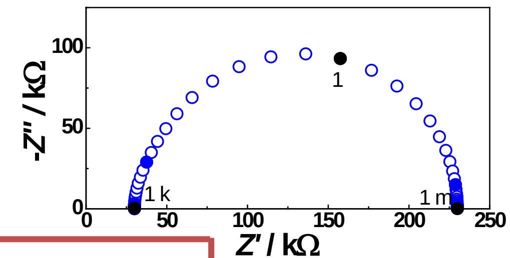


~~$P_{(S)} = R_1, R_2, CPE$~~
~~*No adequacy*~~

ИМООД

D3 [Re_i, Im_i, ω_i]

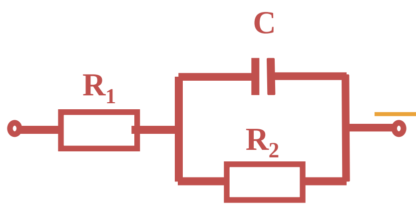
I. Measurement & Data Pre-Processing



II. Data Analysis

1. Choice of Hypothetical model(s)	2. Parametric Identification & Validation (CNLS)	3. Selection of the BEST Model – "best fit"

1.



$P_{(S)} = R_1, R_2, C$ *(estimated values)*

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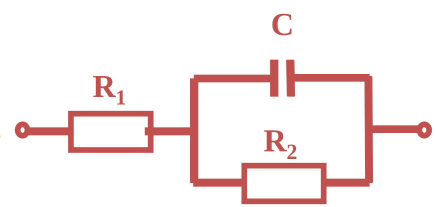
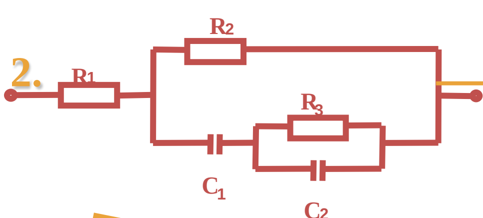


2.



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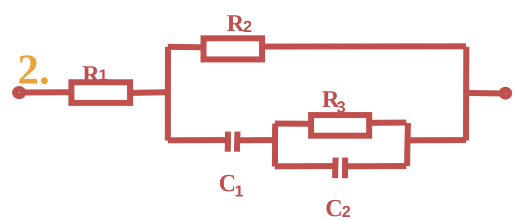
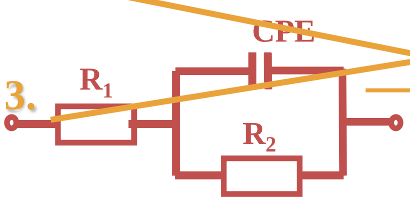


3.



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No adequacy

D3 [Re_i, Im_i, ω_i]

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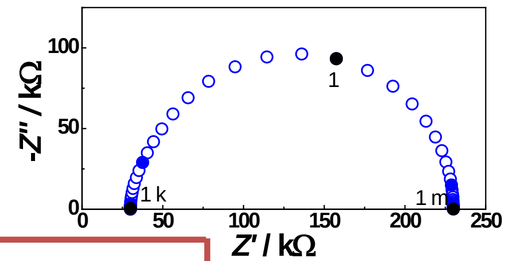

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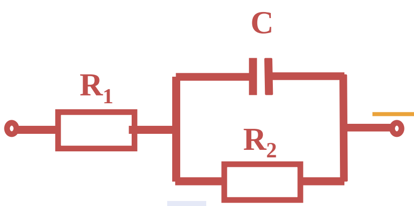

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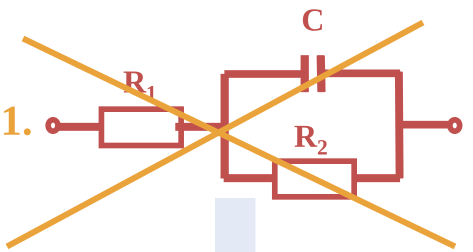
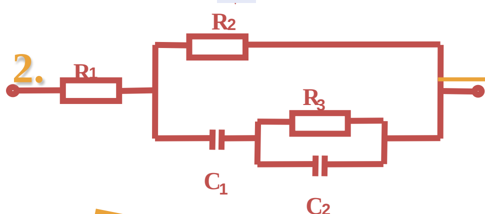
NO

1.


2.


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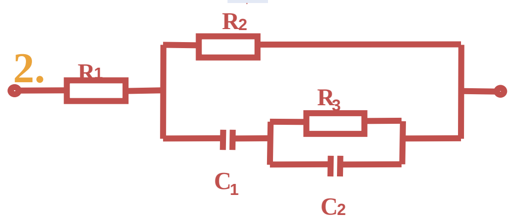
YES

2.


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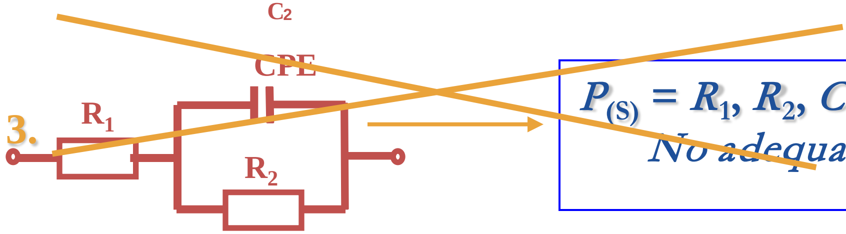

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INSTITUTE OF ELECTROCHEMISTRY AND ENERGY SYSTEMS
ACADEMICIAN EVGENI BUDEVSKI

D3 [Re_i, Im_i, ω_i]

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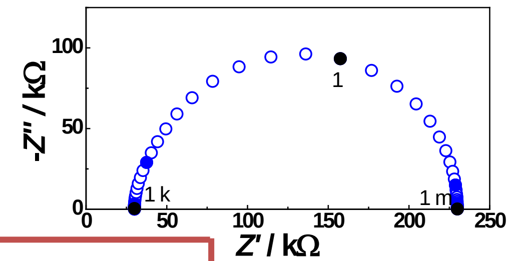

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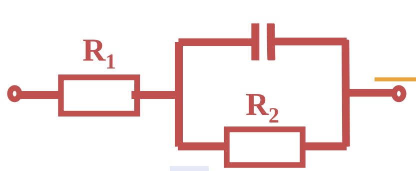

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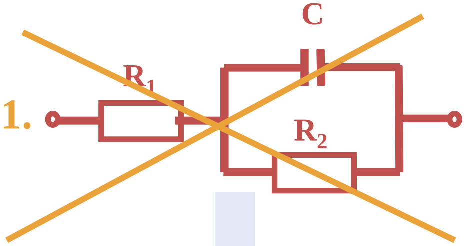
1.


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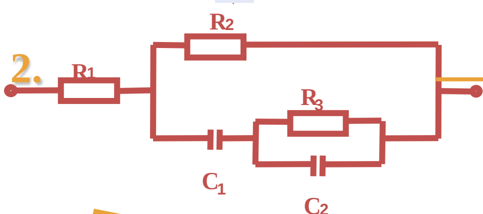
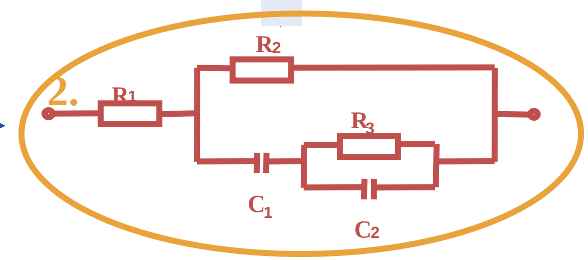


$P_{(S)}$ = R_1, R_2, C_1, R_3, C_2

YES

2.


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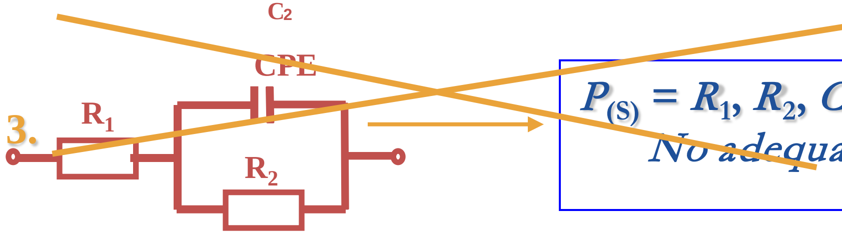

$P_{(S)}$ = R_1, R_2, CPE
No adequacy

ИМООД

- GENERAL Approaches for tailoring the materials properties (conductivity)

  ✓ Optimization of the composition (bulk properties)

  ideal stoichiometric structure
  defect structure
  additional phases
  composites

  ✓ Optimization of the microstructure (grain boundary properties)

  grain size
  inter-granular or intra-granular pores
  additional phases at the grain boundaries
  architecture of ordered internal structures

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    inter-granular or intra-granular pores
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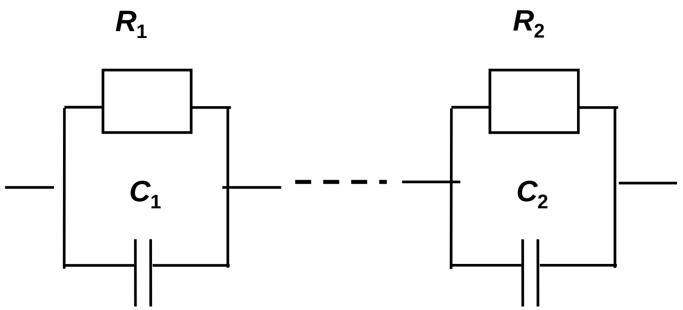
EIS Applications in Materials Science

Voigt's model structure is applied for impedance description of solid state samples

- ✓ Voigt's Structure – consists of meshes with impedances Z_k (iω), connected in series.

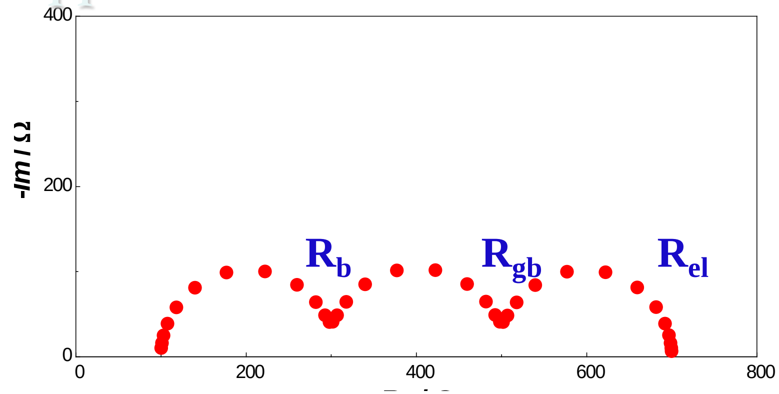
$$Z(i\omega) = \sum Z_k(i\omega)$$

The phenomena modeled by each mesh start instantaneously.
The flowing current is equal for all meshes.
The rates depend on their own time-constants.

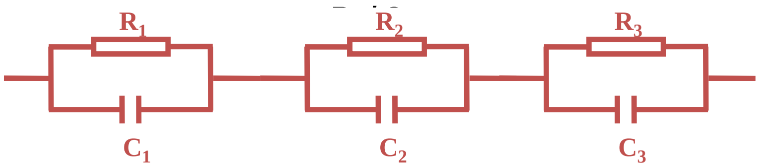


- Basic (idealized) Model

(~ 1970ths; Bauerle & Schouler)

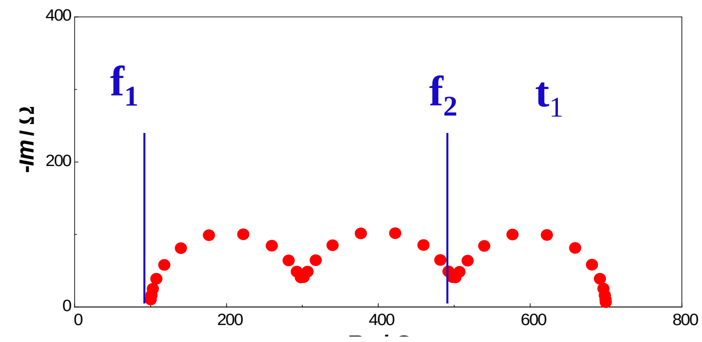


Voigt model structure
with 3 meshes



VISUALIZATION -
Depends on:
$f_1 - f_2$

temperature



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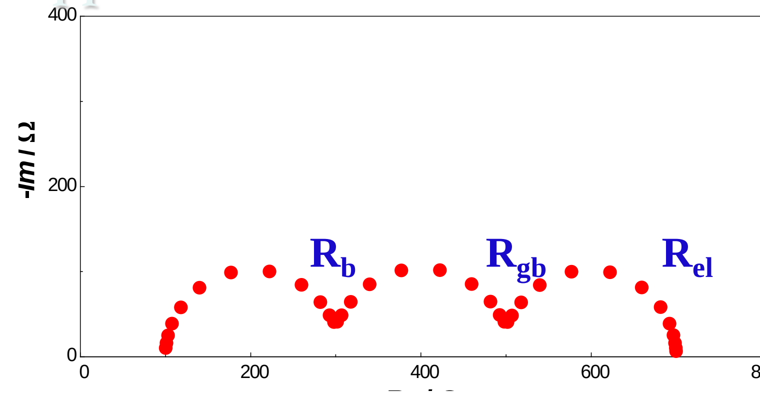

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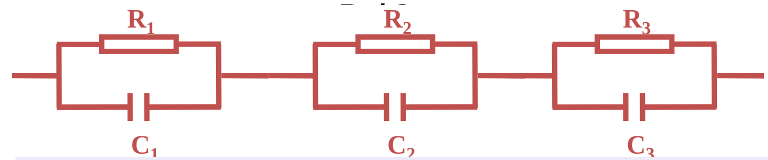

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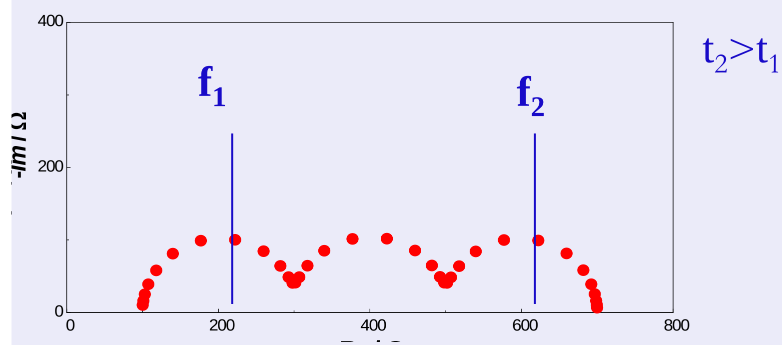
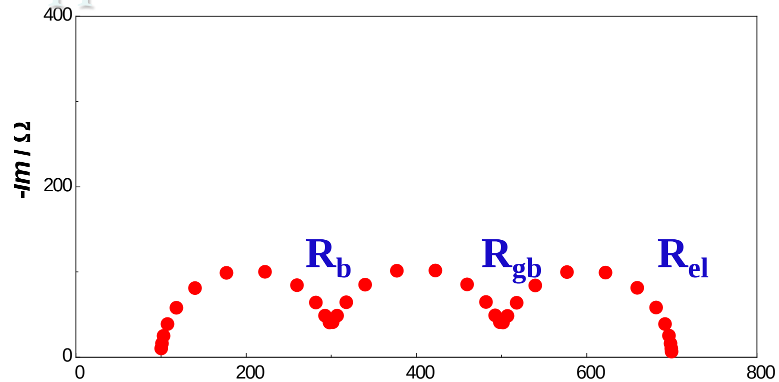
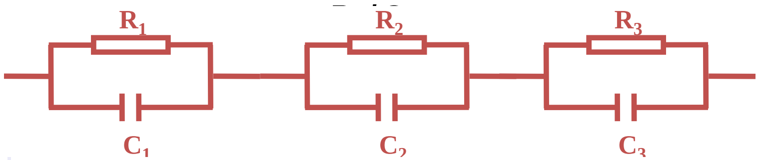


- **Basic (idealized) Model**

(~ 1970ths; Bauerle & Schouler)

Voigt model structure with 3 meshes





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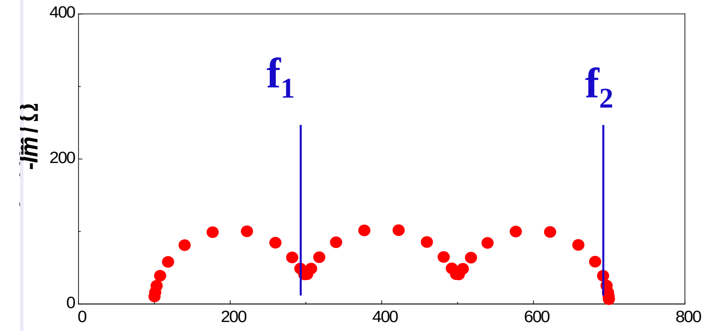

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Voigt model structure
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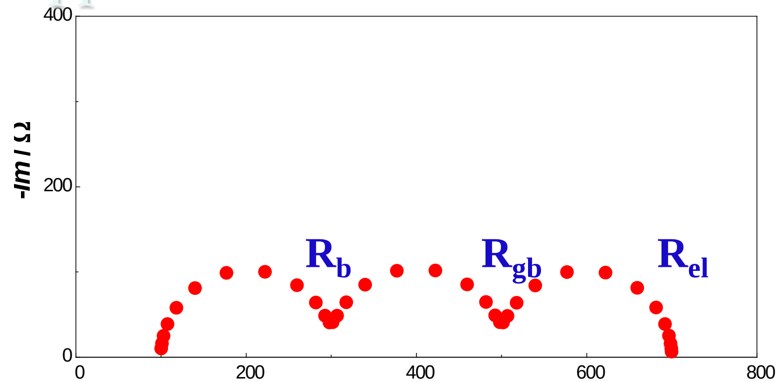

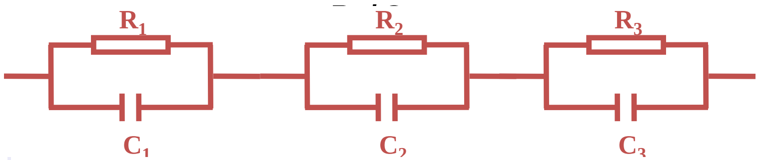

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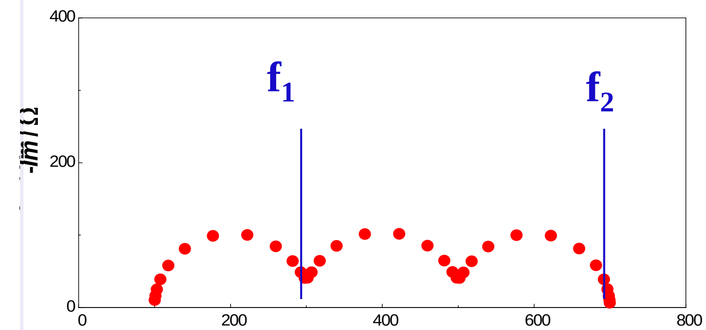
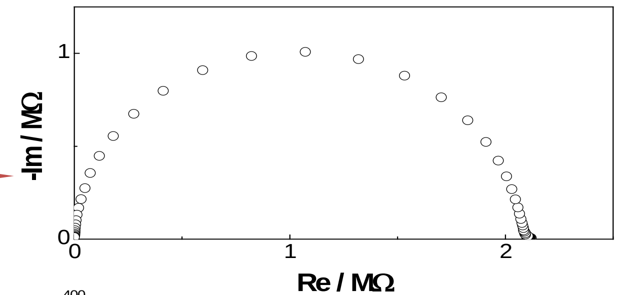
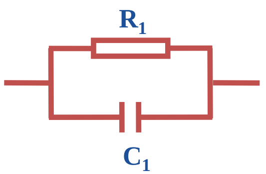


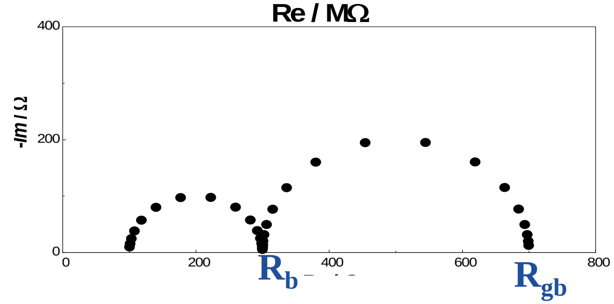
Single crystals — R_{bulk} →



→



Polycrystalline — $R_{bulk} + R_{g.b.}$ →



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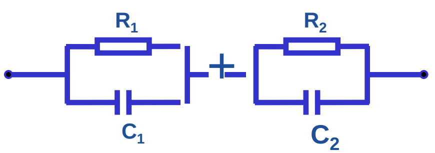
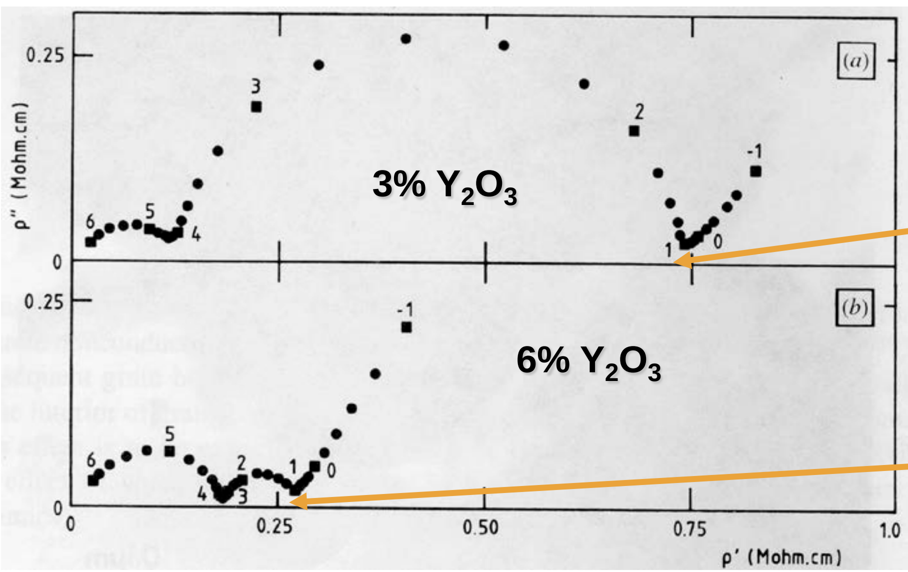


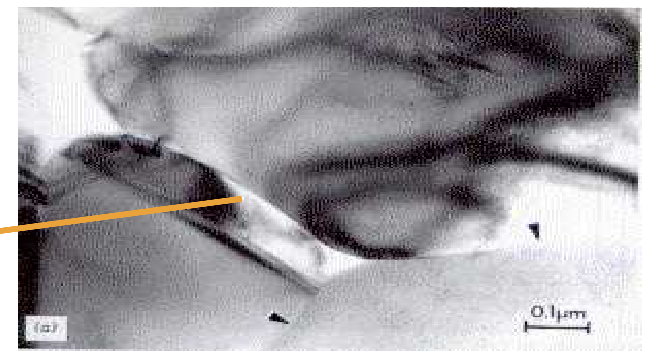
$R = f(T)$ — *Arenius plot* → $\square = \square_0 \exp(E_{\square}/kT)$ → $E_{\square}$ → bulk, g.b.

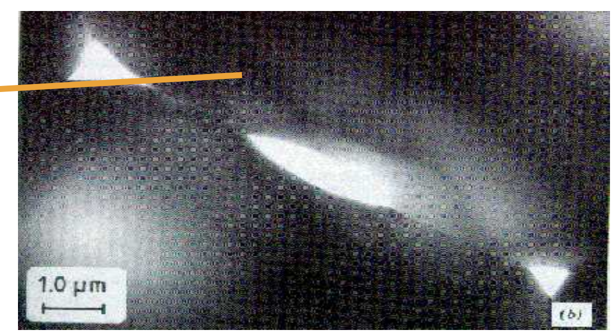
- ✓ Evaluation of $E_{\square}$
- ✓ Properties of the grain boundary
- ✓ Comparison of Ea_{gb} and Ea_{bulk}
- ✓ Conclusions for structure & conductivity mechanisms

ИМООД

- Conductivity characterization: bulk; grain boundaries







Zirconia ceramics: Impedance Spectroscopy, Emphasizing Solid Materials and Systems, ed. J.R. Macdonald, 1987, p.219

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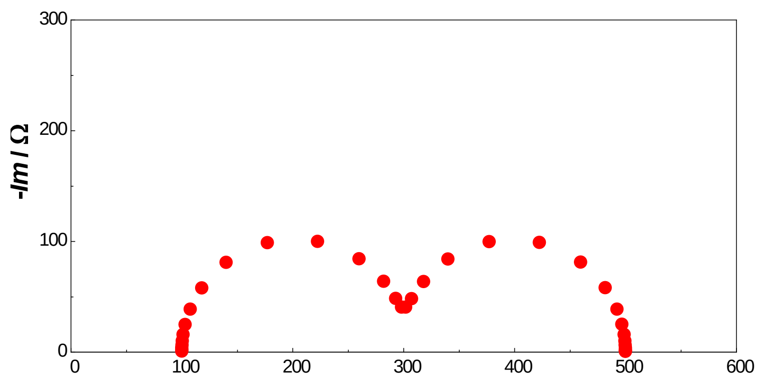
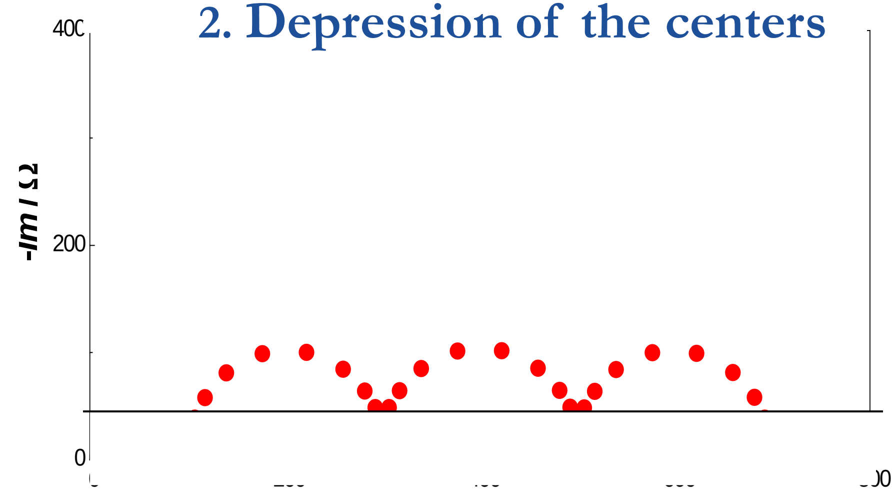
➢ Deviations in real systems from the Idealized Model

1. High degree of mixing of *T*



2. Depression of the centers



- **Deviations in real systems from the Idealized Model**

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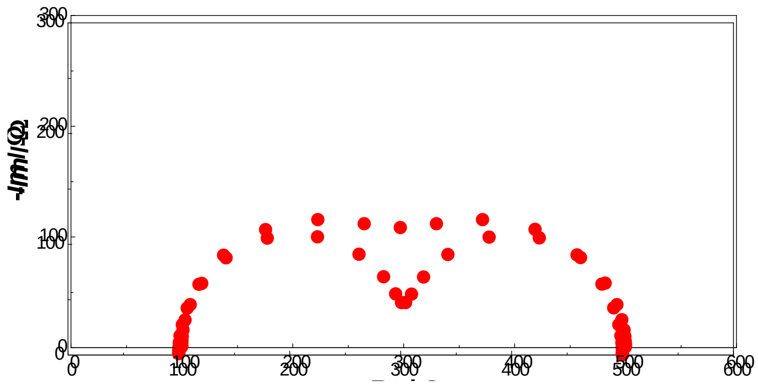

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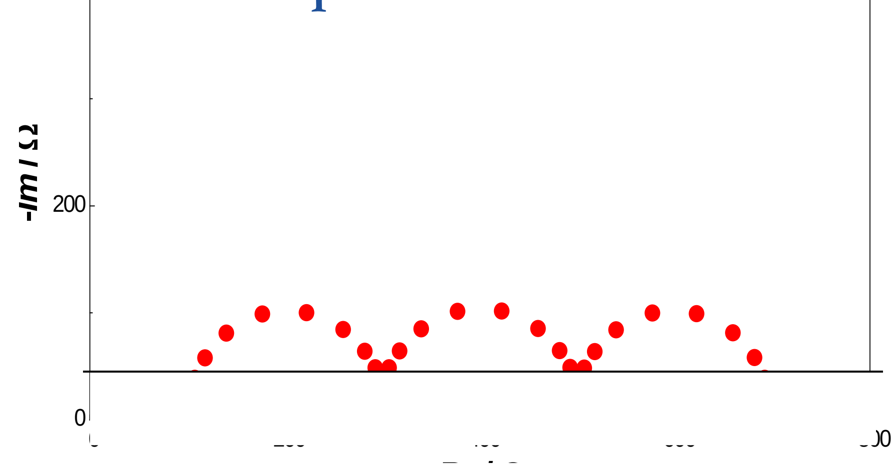

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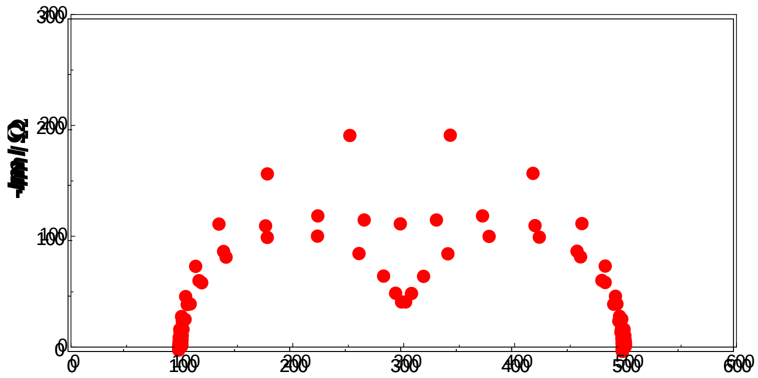

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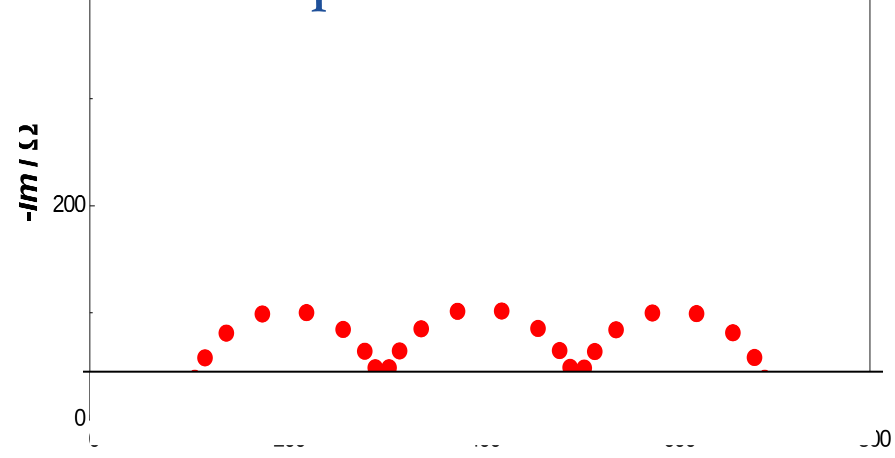
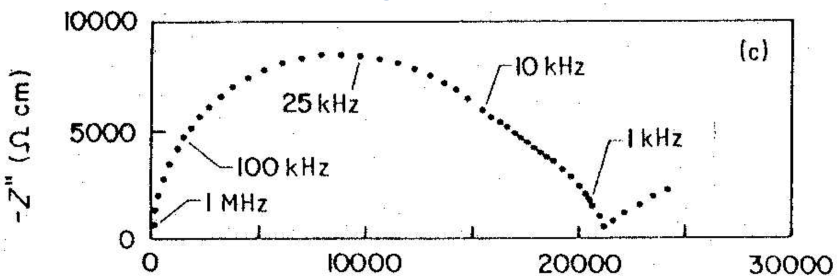


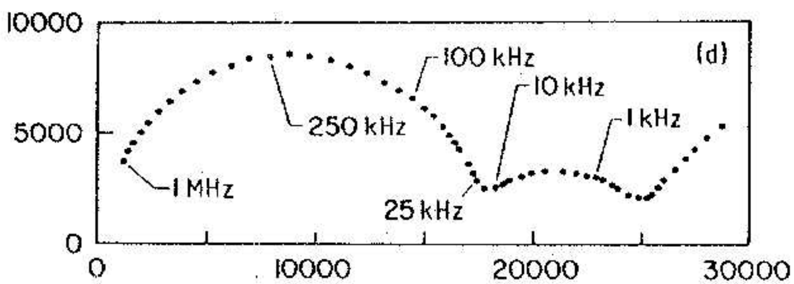
- Real Samples Impedance – MORE COMPLICATED

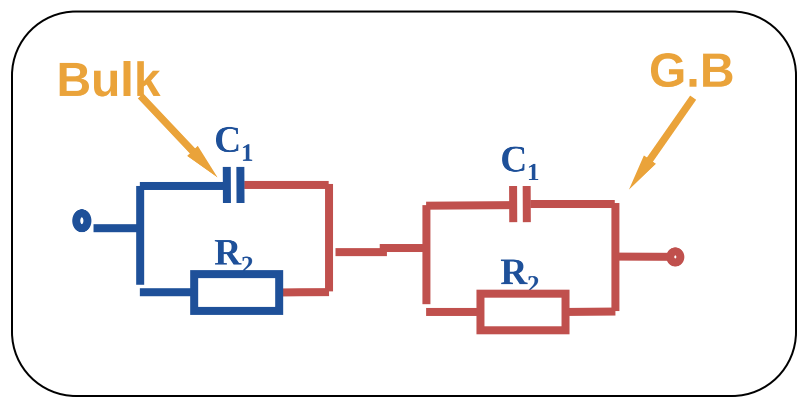
✓BULK - second phase (including pores); vacancy ordered structures; magnetic or electric domains;
✓G.B. – accumulation or depletion of space charge; impurities; defects; second phase;

YSZ – clean grain boundaries



YSZ grain boundaries with impurities





S.P.S. Badwal, J. Mater. Sci 19 (1984) 1767

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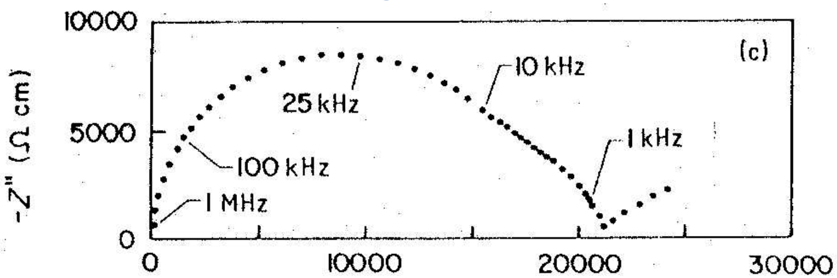

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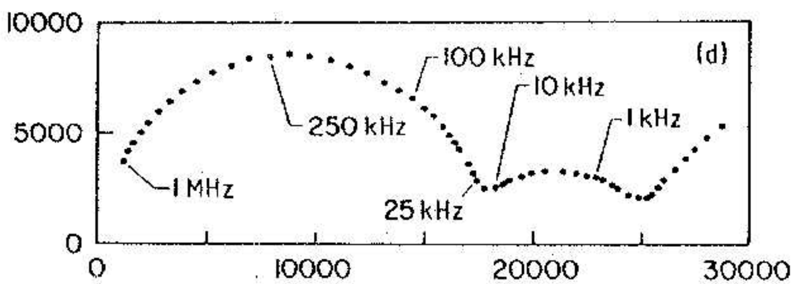

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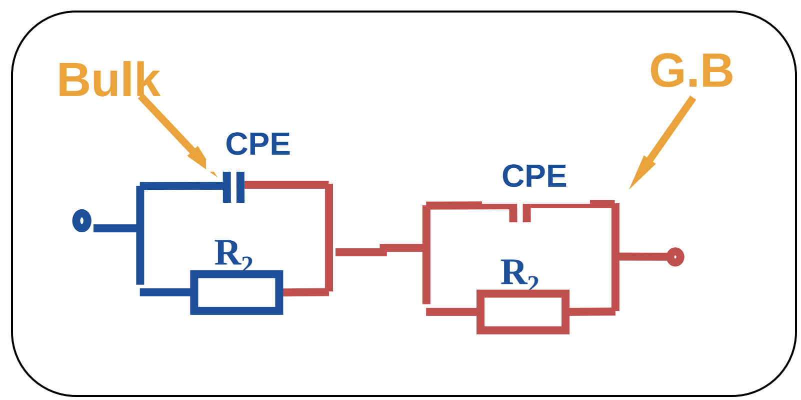


Basic (idealized) Model - interpretation

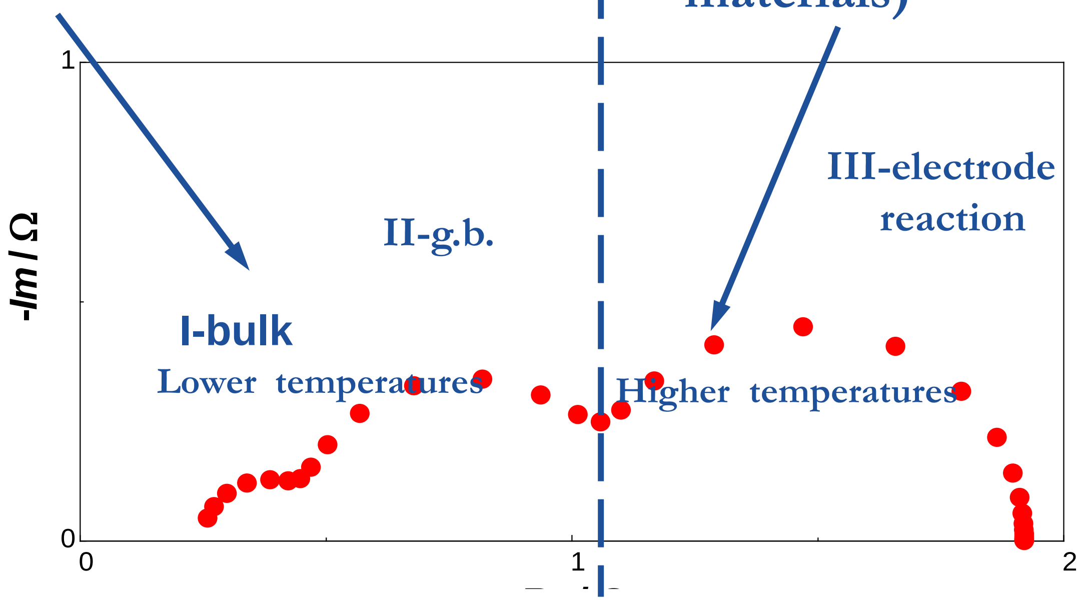
As Material (conductivity)

Influence of composition (BULK);

Influence of microstructure (GRAIN BOUNDARIES)

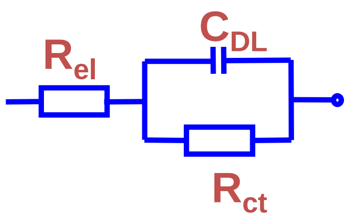
As component (electrode reaction)

Characterization the functionality of the material in a process (in combination with other materials)

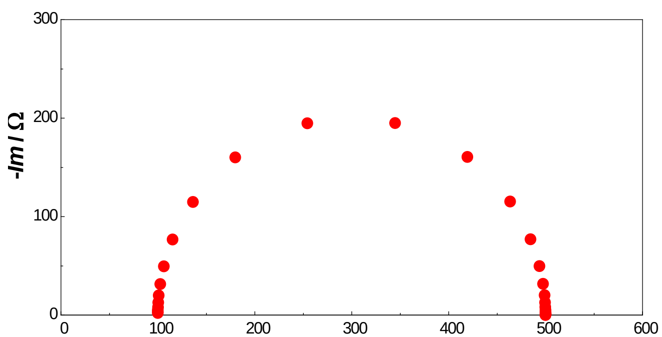


➢ Electrode reaction description

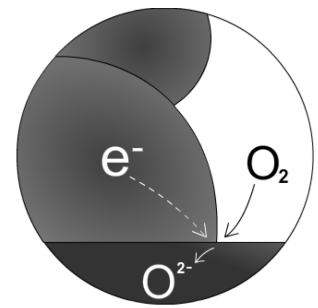
✓ Charge transfer approach (adopted from liquid Electrochemistry – idealized description



Idealized model



✓Assumption:



Electrochemical (charge transfer) reaction takes place at the three phase boundary (metal-electrolyte-gas)

➢ Electrode reaction description

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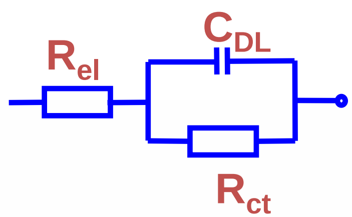
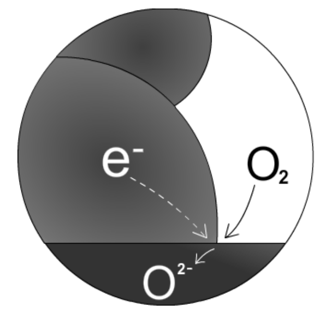
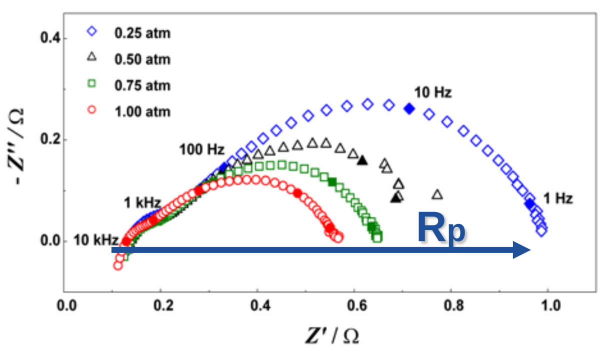


+ .....



Real data



P. Carpanese, A. Barbucci, G. Cerisola et all, Bulg. Chem. Communic. 38 (2006) 186

✓Assumption:

- Electrochemical (charge transfer) reaction takes place at the three phase boundary (metal-electrolyte-gas)
- Break down of the electrode reactions on individual steps involving : 2 D charge transfer, different diffusions, adsorption etc.

SUMMARY (1)

What can impedance give for SOFC studies

- **Materials and components**:
  - Electrolyte: R_b. $R_{g.b}$., optimization of microstructure
  - Electrodes: polarization resistance *R*p. quality of interface, rate limiting stage, quality of deposition;
- **Cells**: performance; separation of components influence, influence of water behaviour; gas flow, tempereratura

SUMMARY (2)

What else can impedance give :

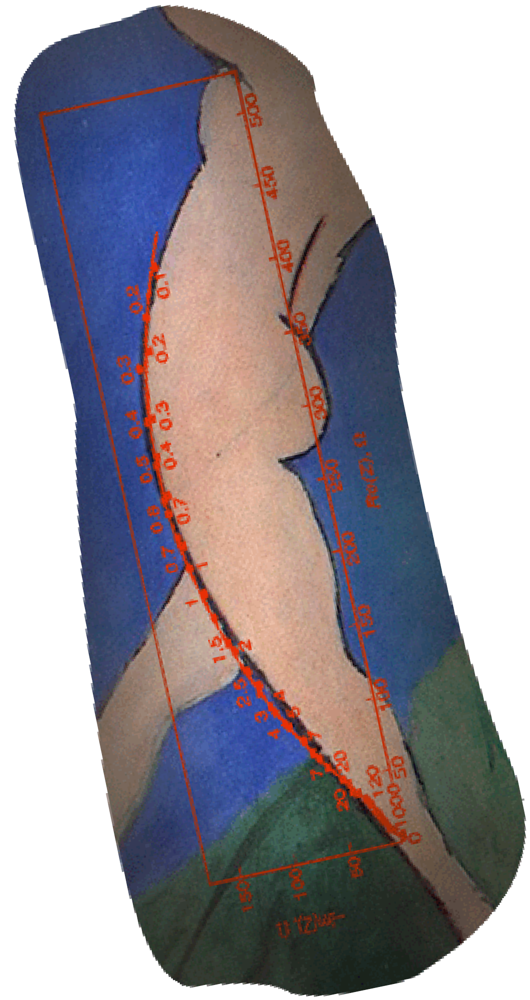
- PLEASURE and
- RELAXATION

Mattice: Dance 1

Impedance: Ferri-ferrocyanide System

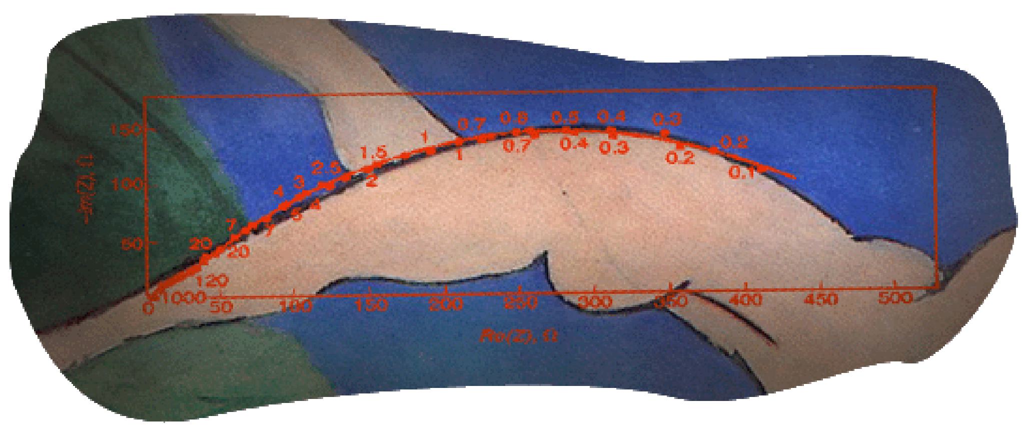
Mattice: Dance 1

Impedance: Ferri-ferrocyanide System



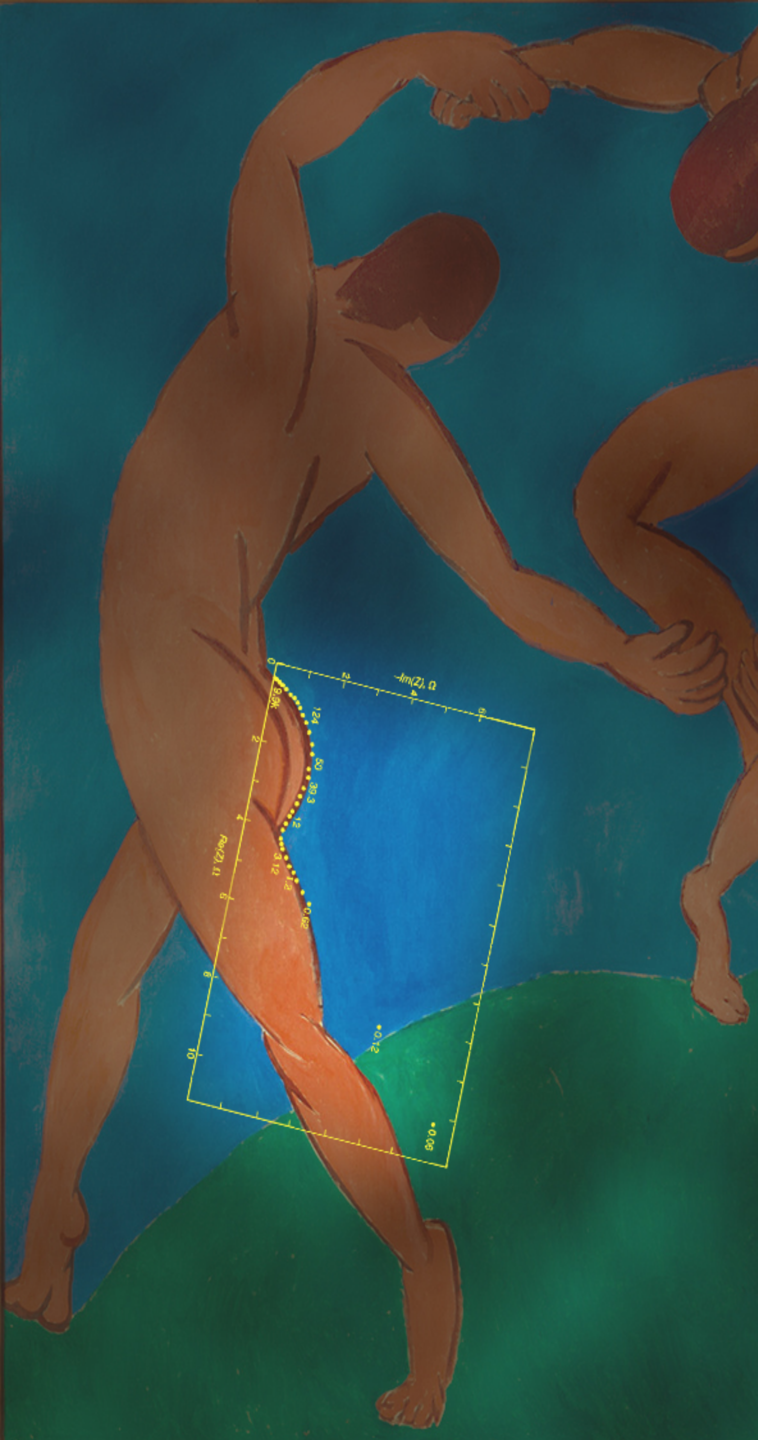
Mattice: Dance 1

Impedance: Ferri-ferrocyanide System



Mattice: Dance 2

Impedance: Armico iron/organic coating



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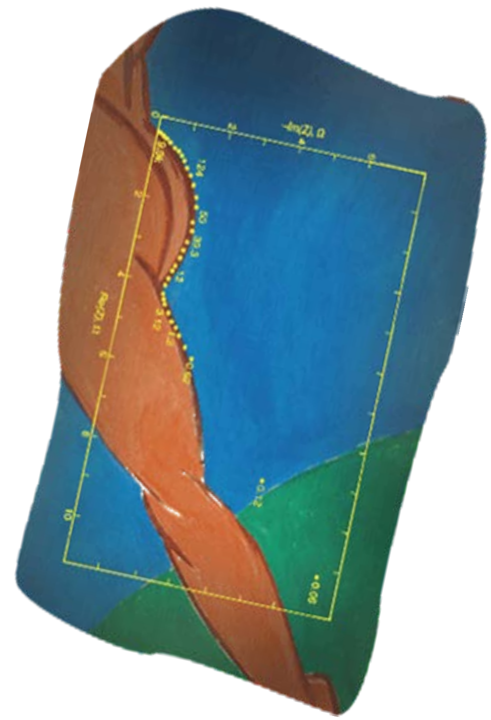

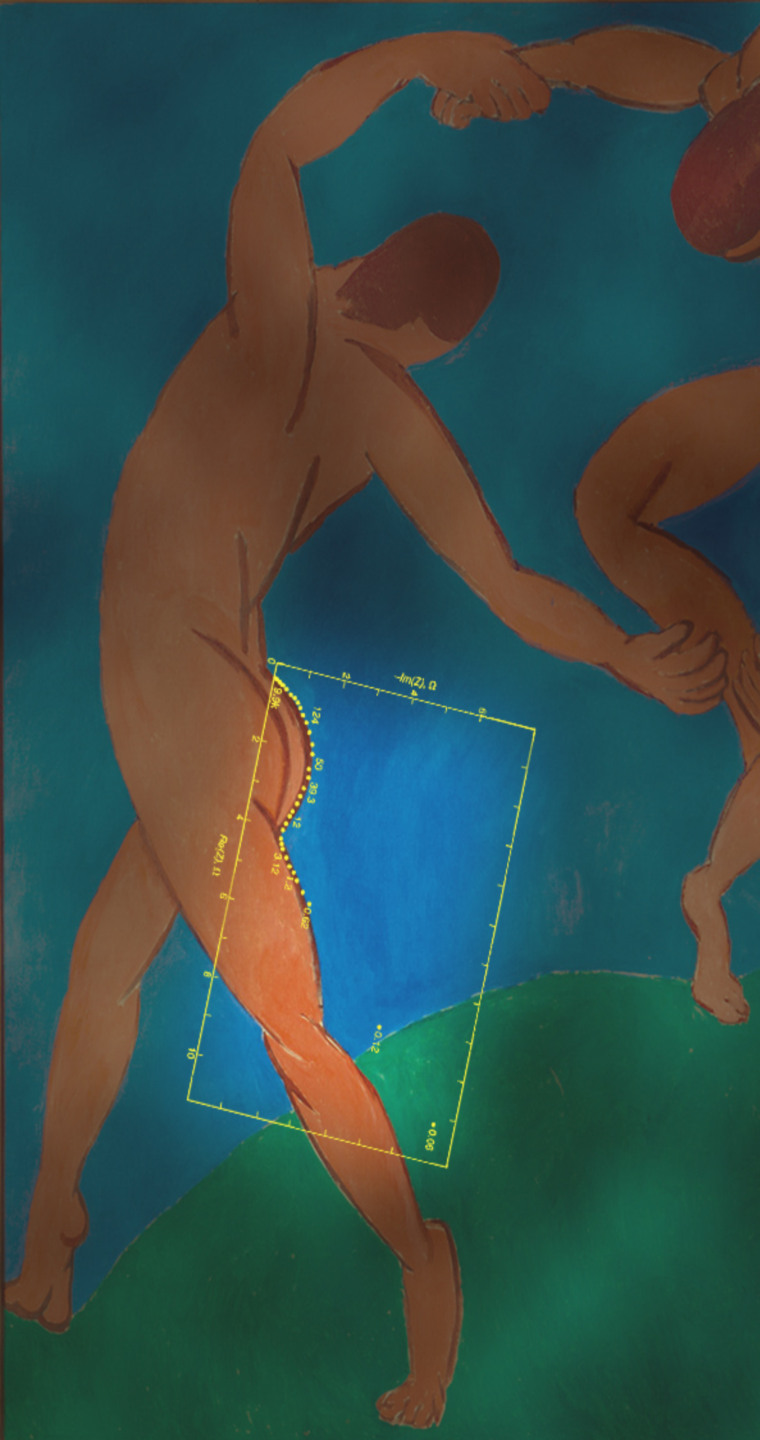

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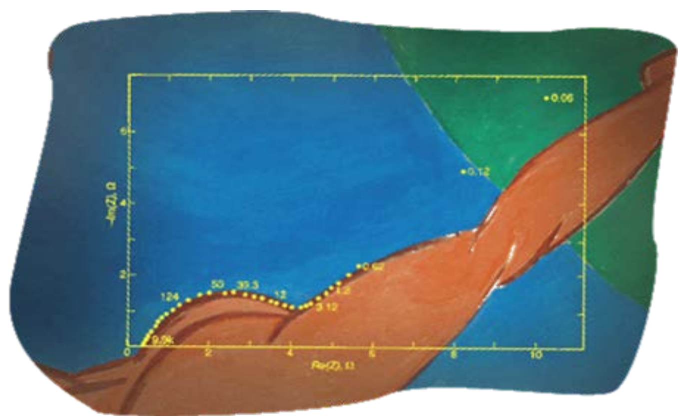

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ASKNOWLEGEMENTS

ИМООД

The e - course was prepared in the frames of the project:

"conductIvity and reversibility Mechanisms in an InnOvative design of sOlid oxiDe fuel cell" - IMOOD ;

"Изследване Механизмите на прОводимост и Обратимост в иновативен Дизайн на твърдооксидна горивна клетка" - ИМООД

funded under Grant Agreement No E02/3/2014 of the National Science Foundation – Bulgaria.