EUROPEAN COMMISSION

Community Research

Measurements of Low-Impedance Objects

Inductance and Resistance Error Correction

P5

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IDEAL Cell
Innovative Dual mEmbrAne fueL Cell

SEVENTH FRAMEWORK PROGRAMME

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Specific problems coming from SOFC nature

Problems: / **Decisions:**

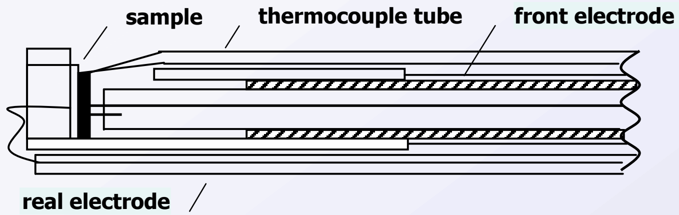
- SOFC are objects with very low impedance:
  - Parasitic Inductance *L* and resistance *R* — *L* & *R* correction

- This talk discusses:
  - The sources of parasitic inductance/resistance errors
  - The deformation of the impedance diagrams caused by the parasitic elements and its influence on the accuracy of the analysis
  - Approaches for parasitic inductance/resistance errors correction

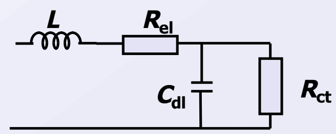
- A procedure for calibration and parasitic inductance/resistance errors correction is offered

- The procedure is demonstrated on impedance studies of cathode and electrolyte materials for SOFC

Analysis of inductance errors – general observations

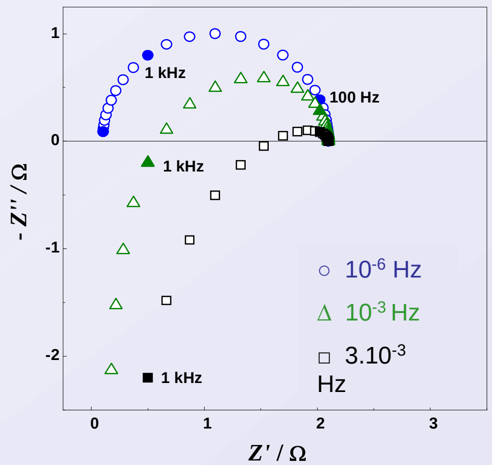


- Main Sources of Inductance Errors:
  - Cabling
  - Measurement cell
  - Object
  - Shunt



- Influence of *L* on the impedance data
  - Deformation of the impedance diagram (in size and in shape)
  - Wrong parametric identification
  - Decrease of the measurement frequency range

  (*L* may influence even the low frequencies)

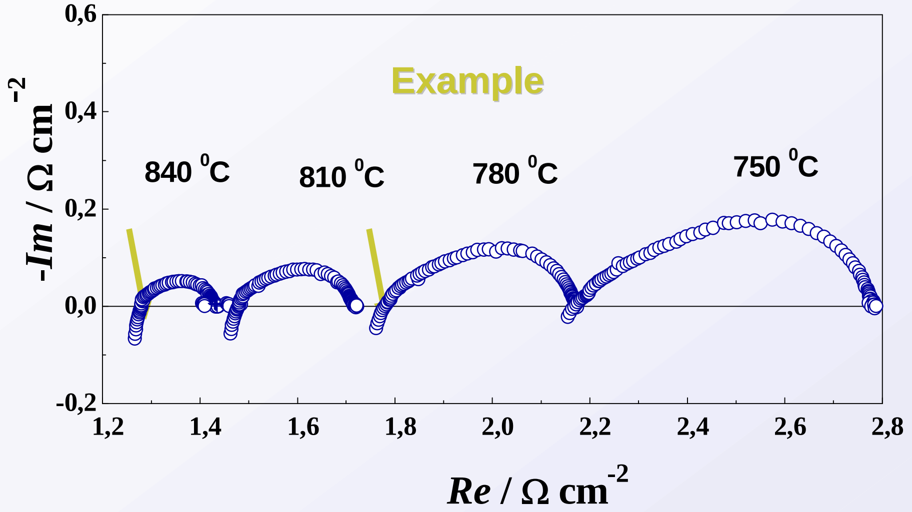


- INDUCTANCE ERRORS MAY BRING TO WRONG MODEL RECOGNITION
- INDUCTANCE ERRORS CORRECTION IS NEEDED

Analysis of inductance errors – experimental observations

➢ **Inductance errors (Z-plot deformations) increase with:**

- **Decrease of the object's resistance:** ***energy sources are low resistance systems (few Ω – 100 μΩ)***
- **Increase of the object's size**
- **Increase of the electrode surface area**



The increase of the temperature brings to:

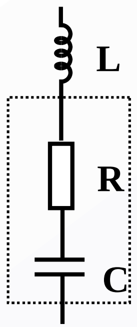
- **Decrease of the resistance**
- **Increase of the frequency range where the inductance is dominating**

Impedance diagrams of cathode polarization on composite LSM/YSZ at different temperatures

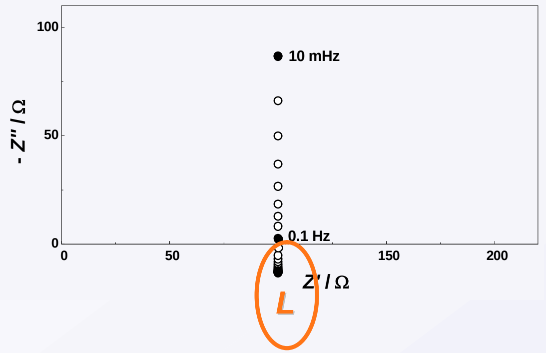
A. Barbucci et all, Electrochim. Acta 51(2006) 1641

Quantitative evaluation of inductance errors by simulation

➢ General simplified representation of an electrochemical system



$$Z(i\omega) = R + i(\omega L - \frac{1}{\omega C})$$



An electrochemical system can be presented simply by an equivalent circuit consisting of: parasitic inductance *L*, measured resistance *R* and capacitance *C* in series.

$$\varepsilon_L = \frac{Z_{Im}^L - Z_{Im}}{Z_{Im}} = -\omega^2 LC$$

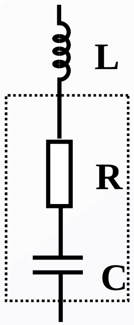
The relative inductance error ε_r can be estimated by comparison of the imaginary component which includes the inductance term Z_{im}^L with that of an ideal system of zero inductance Z_{im} .

Practical conclusion:

- Small electrodes ⟹ small *C* ⟹ small ε_r (noticeable at very high frequencies)
- Large objects ⟹ large *C* ⟹ big ε_r (significant even at lower frequencies)

Quantitative evaluation of inductance errors by simulation

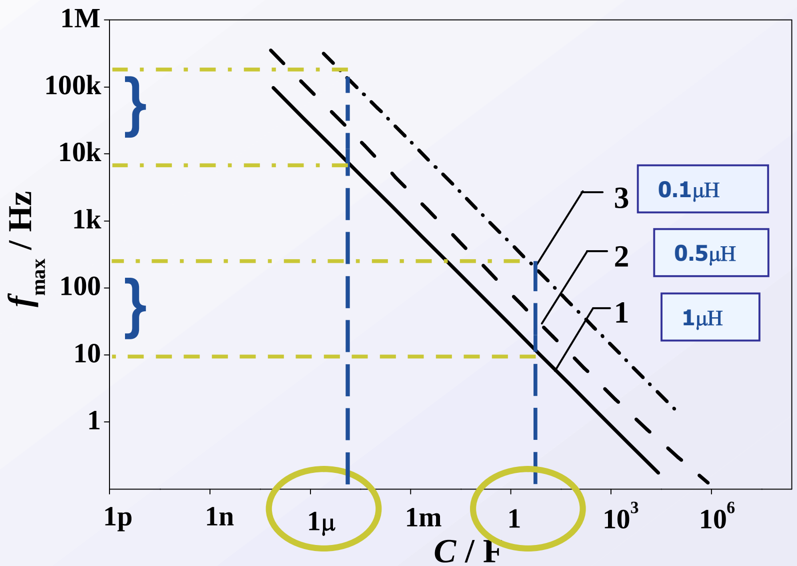
➢ General simplified representation of an electrochemical system



$$\varepsilon_L = \frac{Z^L_{Im} - Z_{Im}}{Z_{Im}} = -\omega^2 LC = 1\%$$

$$f_{max} = \frac{1}{2\pi}\left(\varepsilon_L / LC\right)^{1/2}$$

If we assume an acceptable value for ε_L (for instance 1%) and some reasonable values for *L* (0,1 μH ÷ 1 μH) , then we can evaluate the high frequency limit f_{max} which ensures acceptable inductance errors for measurements of samples with different capacitance.

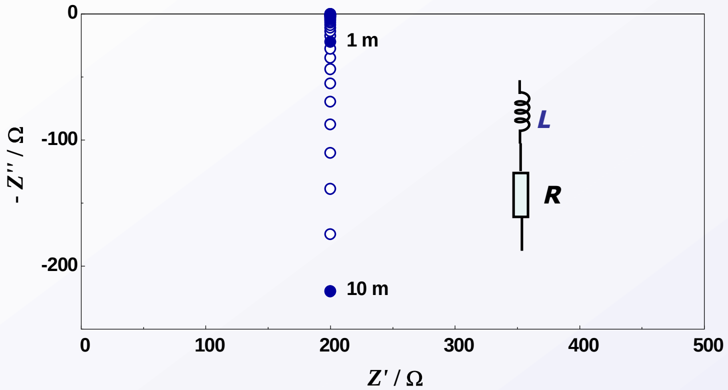


- Systems with capacitance 50-100 μF can be measured correctly within the high frequency range down to 10KHz
- For big objects with effective capacitance about 10 F, the frequency limit decreases to few Hz

Quantitative evaluation of inductance errors by simulation

➢ **Ideally Non-polarizable Electrode with inductance**

$$Z(i\omega) = R + i\omega L$$



The reaction taking place on the electrode surface is ideally reversible, R_{ct} = 0 and the model of a Faradaic reaction degrades down to a simple resistance, corresponding to that of the electrolyte R_{el} (*reasonable for aqueous electrolytes within a large frequency range - up to 1 ÷ 5 MHz*).

$$\varepsilon_L = \frac{Z_{Im}^L - Z_{Im}}{Z_{Im}} = -\omega^2 LC$$

Phase error: $\varepsilon_\varphi^L \approx \omega L / R$

Modulus error: $\varepsilon_M^L = \left[\left(\omega^2 L^2 + R^2 \right)^{1/2} / R \right] - 1$

Quantitative evaluation of inductance errors by simulation

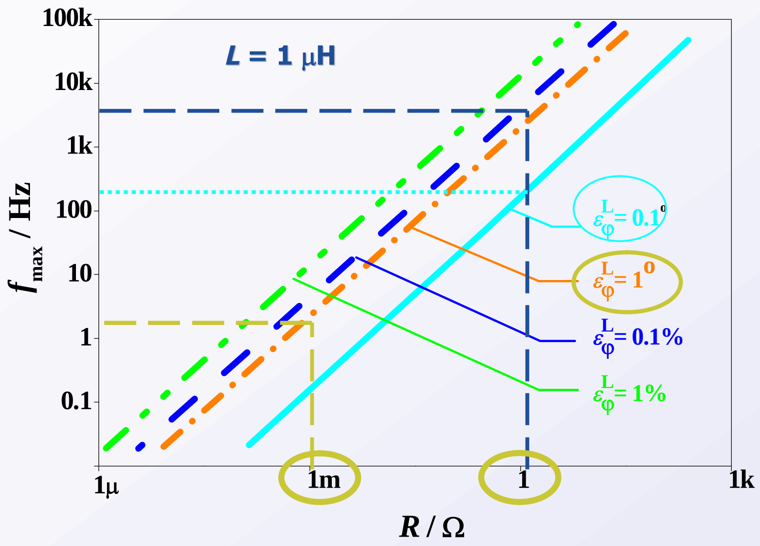
➢ Ideally Non-polarizable Electrode with inductance

$$\varepsilon_L = \frac{Z_{Im}^L - Z_{Im}}{Z_{Im}} = -\omega^2 LC$$

High frequency limit f_{max}:

$$f_{max} = \frac{R}{2\pi L}\varepsilon_\varphi^L$$

$$f_{max} = \frac{R}{2\pi L}\left(\varepsilon_M^2 + 2\varepsilon_M\right)^{1/2}$$



There is available information about different groups of energy sources objects :

- *L* – few nH ÷ above 1μH
- *R* – few mΩ ÷ few Ω

Thus we can evaluate f_{max} for good quality measurements as a function of *R*.

Quantitative evaluation of inductance errors by simulation

- **Dependence of the inductance error on the cell's and sample's shape and size - semi-quantitative evaluation:**

The cell is considered to be a single loop circuit, which coincides with the mean current line determined by the cell configuration. It includes the electrode under study, the electrolyte, the reference electrode and at least part of their leads.

$$\varepsilon^{L}_{obj} = \frac{\beta K_1}{T r_0}\left[S^{1.5}(0.5 \ln S + \ln \frac{2K_2}{d} + \log \beta) \right] \Rightarrow \varepsilon^{L}_{obj} \approx S^2 \qquad L \approx KS^{3/2}$$

S – electrode surface area
(smaller electrodes – smaller error)

Electrochemical parameters:

$T = C_{dl}R_{ct}$

r_0 - specific resistance

Geometric parameters: S, K_1, K_2, d, β

The influence of the cell's inductance on the measured impedance can be reduced by optimization of the cell's and the sample's shape and size.

For more information: D. Vladikova, Z. Stoynov, G. Raikova, *Portable and Emergency Energy Sources*, Prof. Marin Drinov Academic Publishing House, Sofia, 2006,p. 383

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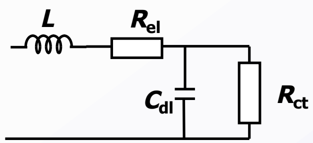
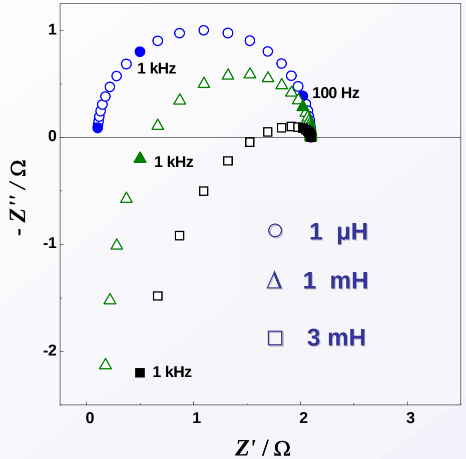
Quantitative evaluation of inductance errors by simulation

Structural deformations in a Simple Faradaic Reaction

$$Z(i\omega) = R_{el} + i\omega L + \left(\frac{1}{i\omega C_{dl} + 1/R_{ct}}\right)$$





Simulated data: R_{el} = 0.1 ohm

R_{ct} = 2 ohm

C_{dl} = 0.001 F

L = 1mH – 3 mH

The increase of L in reasonable limits (1 μH ÷ 3 mH) causes drastic changes in the impedance diagram in size and shape, which hampers the modeling procedure (parametric identification).

The errors in the determination of R_{ct} (ε_{ct}) and R_{el} (ε_{el}) can be evaluated by the characteristic frequency ω_L at which the inductive and capacitive parts of Z_{Im} are equal.

$$\omega_L L - \frac{\omega_L R_{ct} T}{1 + \omega_L^2 T^2} = 0$$

$T = R_{ct} C_{dl}$ is the time-constant

$$\omega_L = \frac{1}{T}\sqrt{T R_{ct} / L - 1}$$

$$\Delta_L = \frac{R_{ct}}{1 + \omega_L^2 T^2}$$

$$\varepsilon_{ct}^{L} = -\frac{\Delta_L}{R_{ct}} = -\frac{L}{R_{ct} T}$$

$$\varepsilon_{el}^{L} = \frac{\Delta_L}{R_{el}} = \frac{L}{R_{el} T}$$

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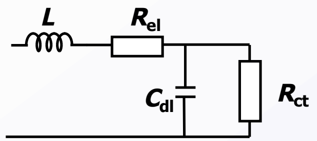
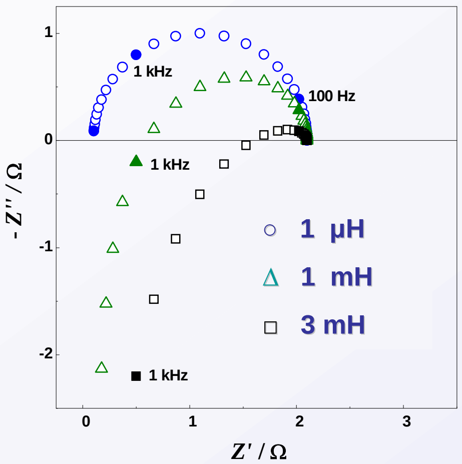
Quantitative evaluation of inductance errors by simulation

➢ Structural deformations

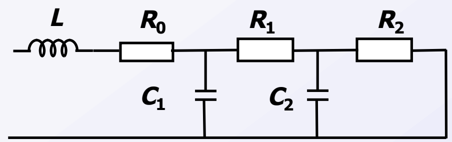
Simple (one step) Faradaic Reaction



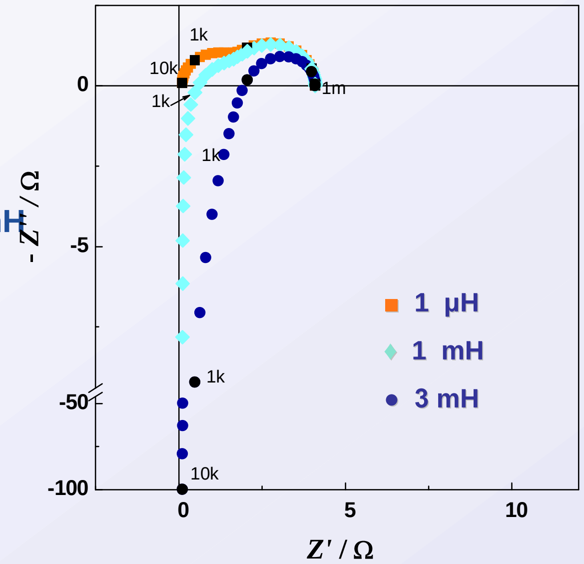
Simulated data: R_{el} = 0.1 ohm
R_{ct} = 2 ohm
C_{dl} = 0.001 F
L = 1mH – 3 mH



Two-step Faradaic Reaction



Simulated data: R_{el} = 0.1 ohm
R_1 = R_2 = 2 ohm;
C_1 = 0.001 F; C_2 = 0.01 F
L = 10^{-5} H – 3.10^{-3} H



L deforms first the high frequency semicircle, which disappears, followed by deformation of the second semicircle.

The blue curve (•) for the two-step Faradaic reaction is similar in shape to the green curve (△) for the one-step Faradaic reaction.

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Quantitative evaluation of inductance errors by simulation

➢ Summary of the observations & obtained results

- ✓ Change of the impedance diagram
  - In shape
  - in size
- ✓ Limitations of the measurement frequency range
  - at high frequencies
  - at intermediate frequencies
  - at low frequencies

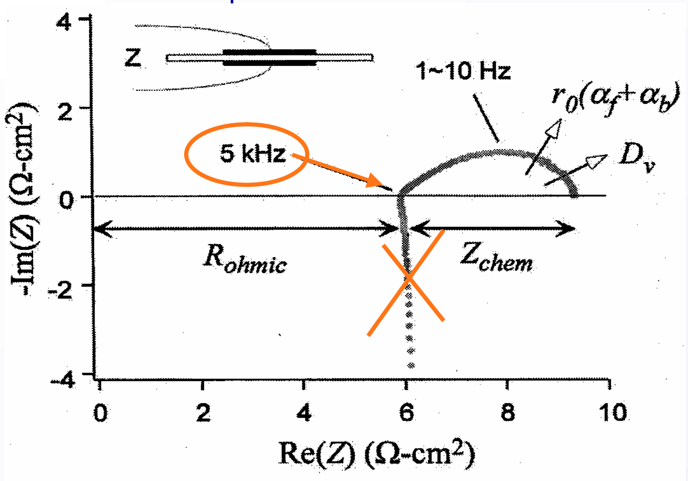
→ Wrong Parametric Identification

➢ Practical Conclusions

- ✓ Use of small cells with small electrode surface area
- ✓ Correction of the inductance error

Approaches for inductance errors correction

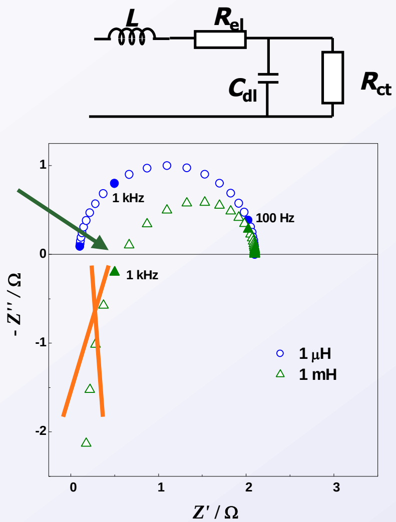
➢ **Rejection of the Inductive tail or measurements at lower frequencies**



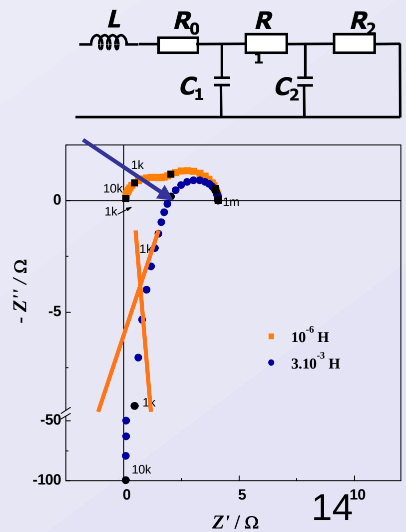
S.B. Adler, Solid State Ionics 135 (2000) 603

The most simple way to eliminate the impedance tail caused by the parasitic inductance is to reject it, which is often used. However, that is not a real correction, but just a formal elimination, because:

- **the rejected data may include necessary information;**
- **the deformed shape may bring to incorrect parametric identification and modeling .**

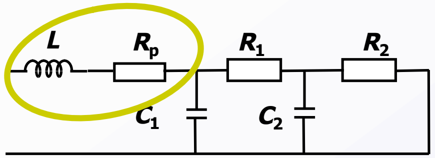


The green and the dark blue curves from the 2 diagrams are similar is shape, but they correspond to two different models.

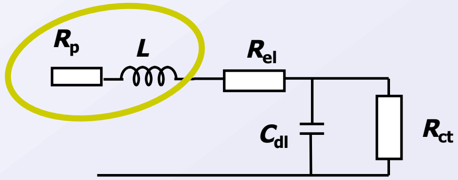


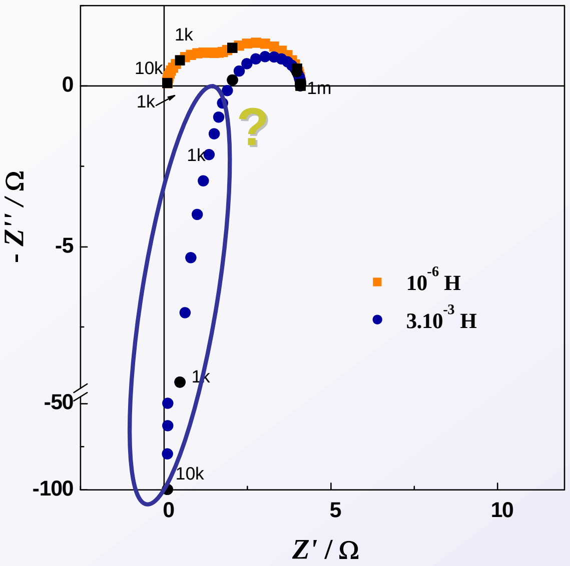
Approaches for inductance errors correction

➢ Identification including parasitic modeling elements (L or $L + R_{cell}$)



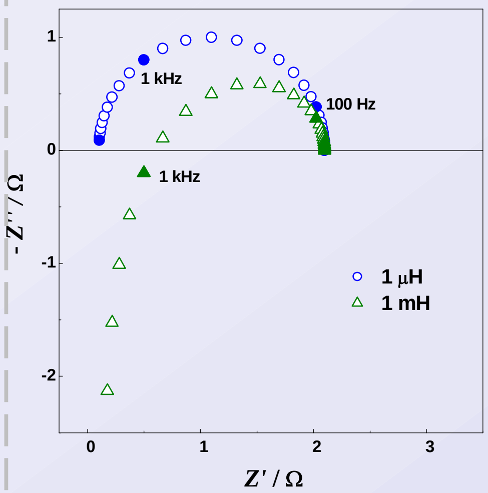
The parasitic elements R_p and L are introduced in the modeling working hypotheses





➢Valid only for lumped L (in real systems the parasitic element(s) are usually frequency distributed)

➢ The distortion of the shape may bring to incorrect modeling (if the experimental results describe <u>the dark blue curve</u> on the left side diagram, it is more difficult to predict the correct two step reaction, than the simple Faradaic reaction (the right side diagram).



Approaches for inductance errors correction

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Combination of High Current Interrupt Technique with EIS

- Applied for Fuel Cells
- Extends the high frequency range
- A set-up is available

This technique does not use the principle of the inductance error correction, but it ensures reliable information about the object at high frequencies.

Fore information see:

C-A. Schiller, W. Stunz, N. Wagner, F. Richter, http://accessimpedance.iusi.bas.bg, *Impedance Contributions Online* 4 (2006) p5-1;

Bulg. Chem. Communic. 39 (2007) 211

Approaches for inductance errors correction

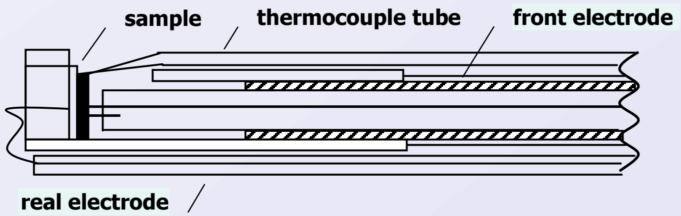
➢ Calibration and Parasitic Inductance & Resistance Errors Correction

- For more information see:

  D. Vladikova, Z. Stoynov, G. Raikova,

  Portable and Emergency Energy Sources, Prof. Marin Drinov Academic Publishing House, Sofia, 2006

- Nature of *L (and R) errors*
  - connecting cables
  - cell
  - object
  - shunt

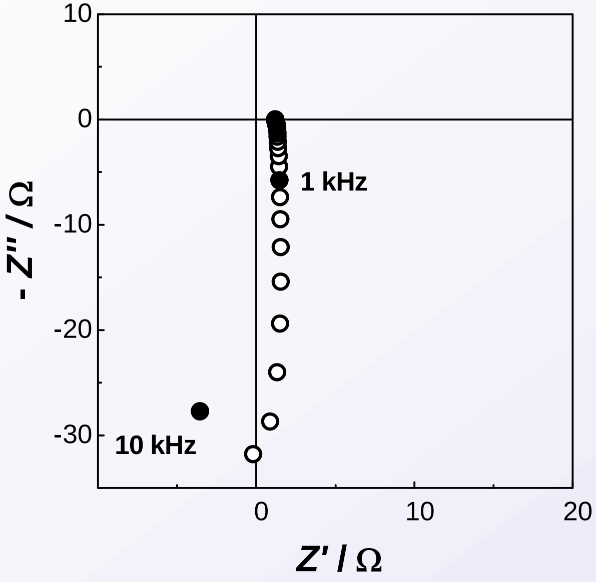


Cell for testing SOFC components

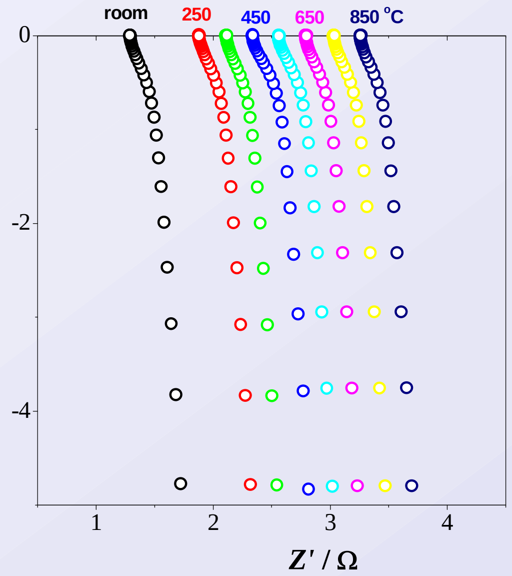
Procedure for inductance & resistance errors correction

The correction procedure includes several steps, in which different calibration measurements are performed, aiming at evaluation of the type and the values of the cell parasitic components.

➢ STEP 1: Short circuit calibration measurement - for evaluation of the cell's inductance and resistance (including the cables).

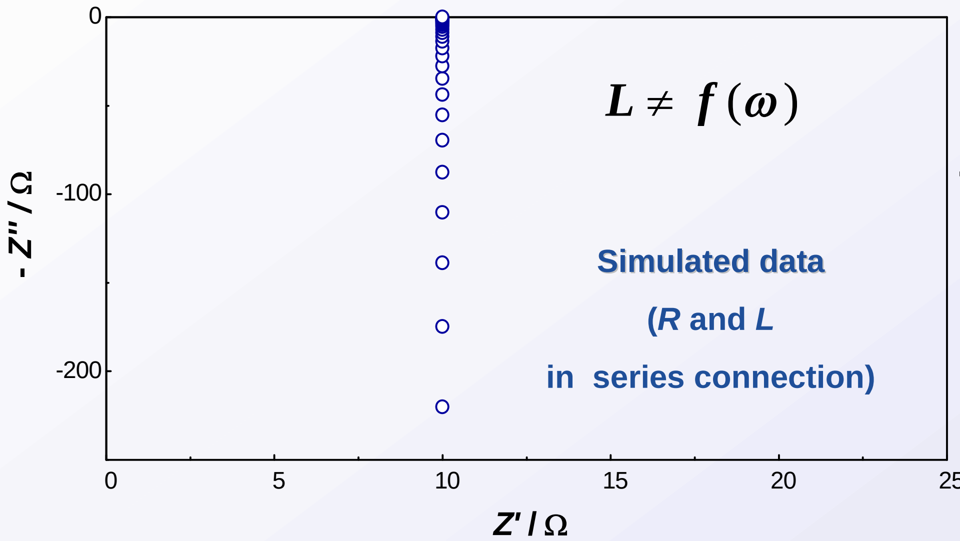


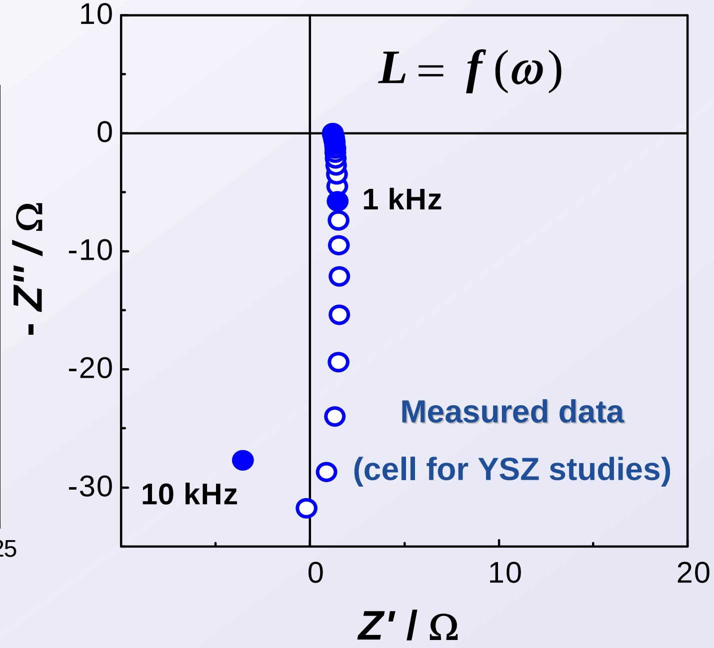
- The contacts are connected in a short circuit (no object!).
- The measurement is performed at the same conditions (frequency range and density) as the object's measurements.
- The measurement is carried out at every working temperature (the resistance of the metal parts is temperature dependent).



Procedure for inductance & resistance errors correction

➢ **STEP 1: Short circuit calibration measurement - for evaluation of the cell's inductance and resistance (including the cables).**

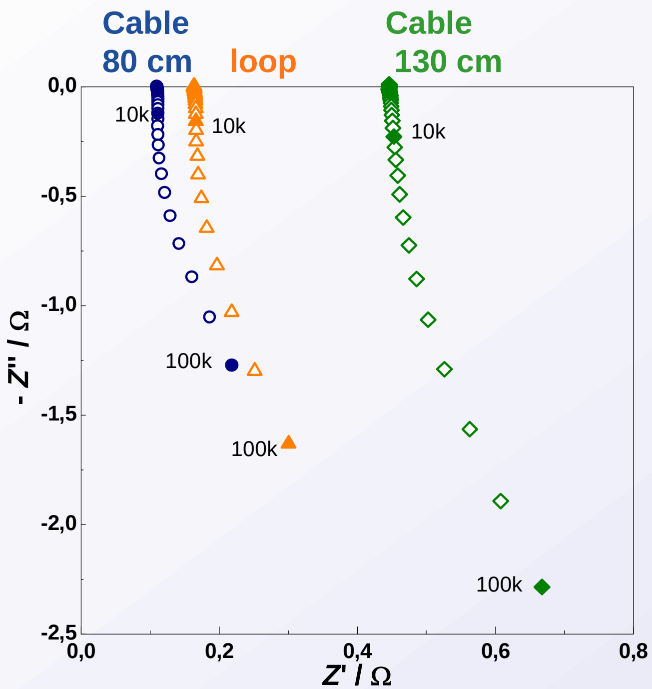


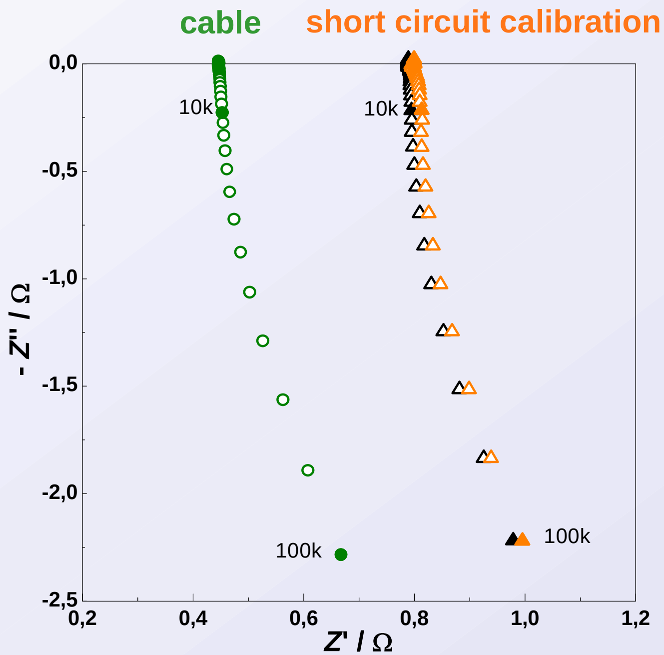


The *"pipe-shaped inductive tail"* of the short circuit measurement (right diagram) demonstrates the frequency dependent inductive behaviour of the cell.

Procedure for inductance & resistance errors correction

- STEP 1: Short circuit calibration measurement - for evaluation of the cell's inductance and resistance (including the cables).

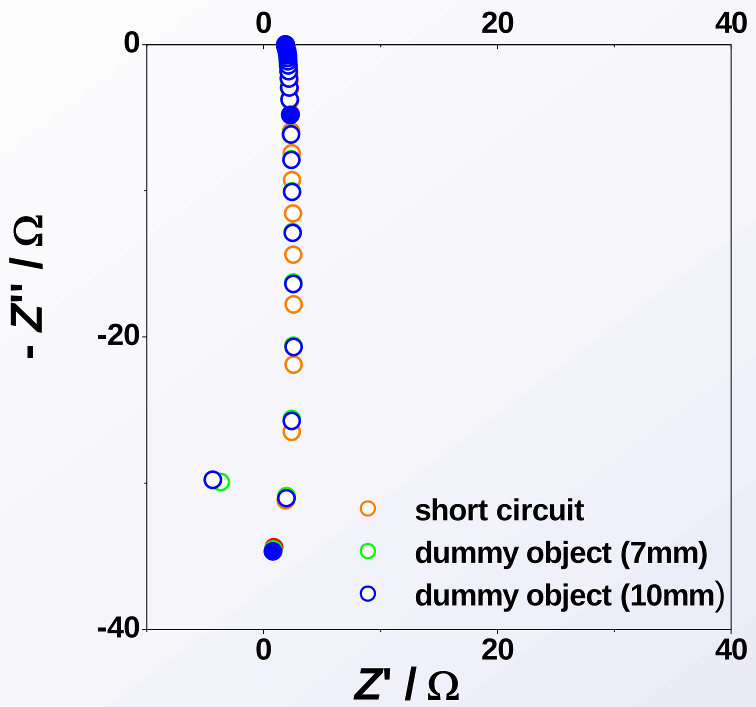




The calibration measurements should be carried out with a fixed configuration of the measurement cell and cables, which should be the same during the measurements of the investigated object.

Procedure for inductance & resistance errors correction

➢ STEP 2: Measurement of Dummy Object - takes into account the self - inductance of a sample with very low impedance

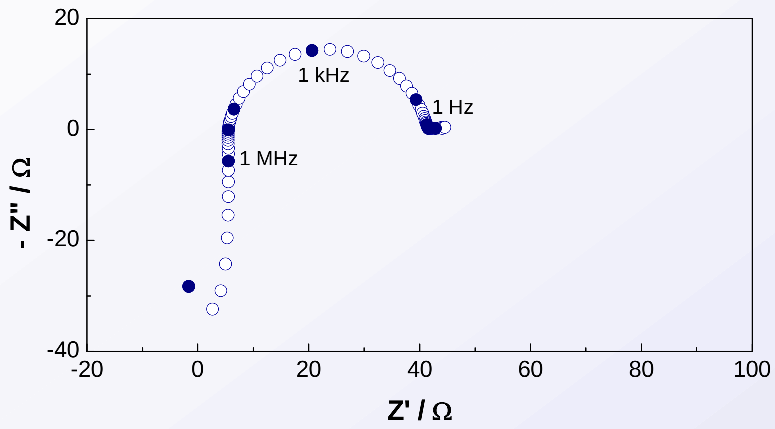


The measurement ensures evaluation of the object's inductance. Usually it is carried out using a metallic dummy object of the same shape and dimensions as the real one.

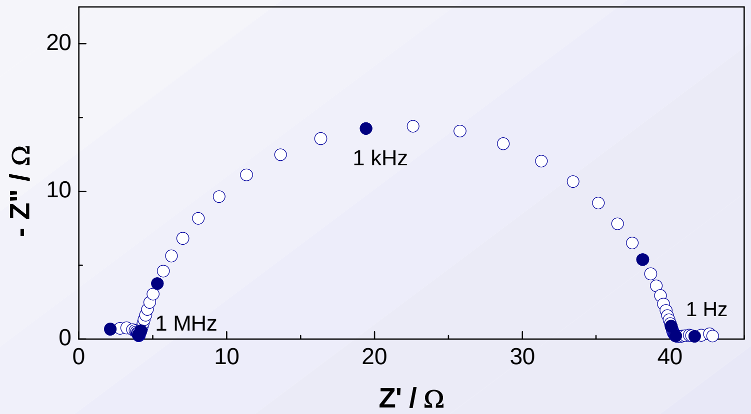
Experimental results show that for small samples (discs with diameter 7-10 mm and thickness few mm) the object's inductance is insufficient and can be neglected.

Procedure for inductance & resistance errors correction

- STEP 3: Measurement of the Investigated Object



- Step 4: Correction (calculations)



The procedure is performed:

- For every working frequency
- Under the assumption that the impedances of the parasitic components and of the object are additive.

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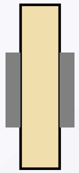
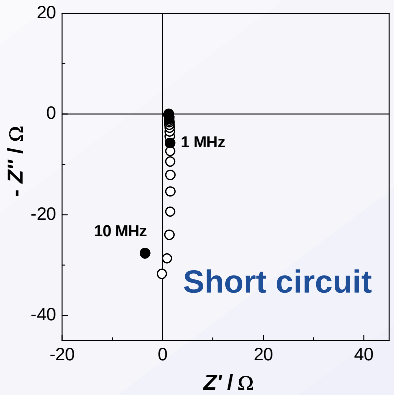
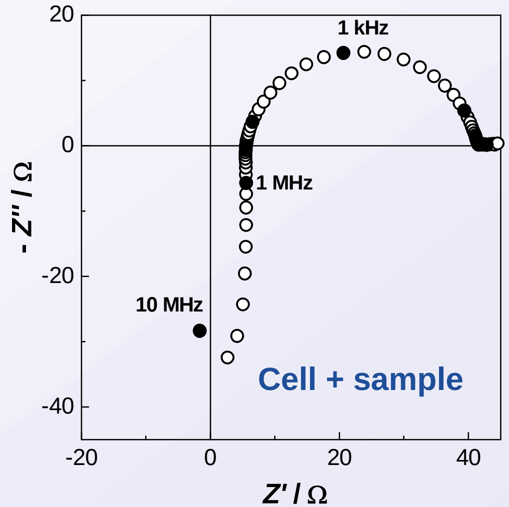
Inductance & resistance errors correction in YSZ studies

- **Object**

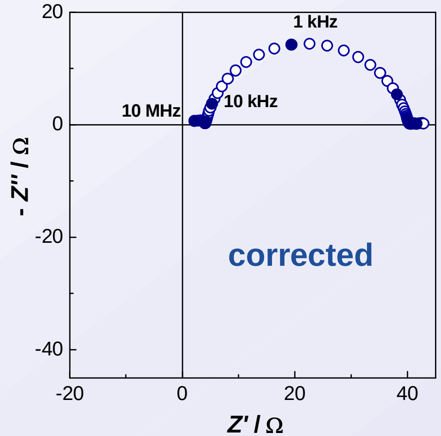


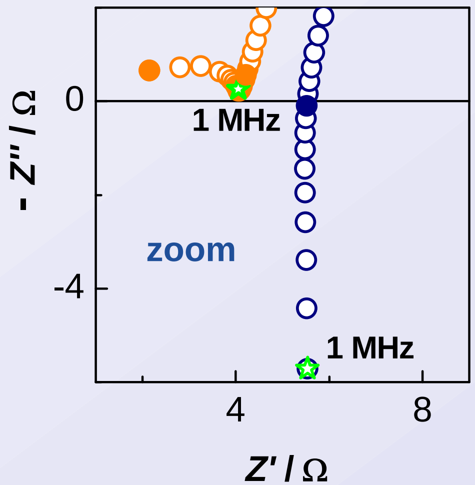
- **Measurements**





- **Correction (calculations): under the assumption that *Z*error and *Z*obj are additive**





Inductance & resistance errors correction in YSZ studies

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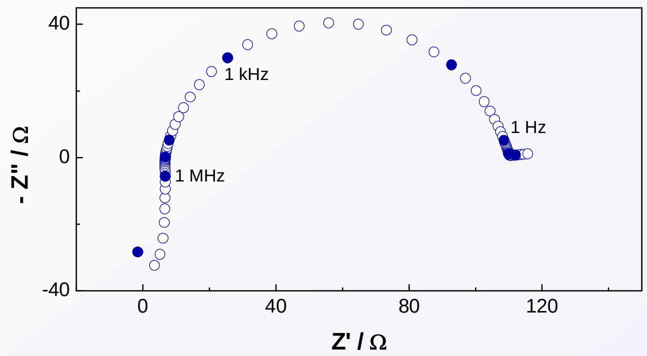
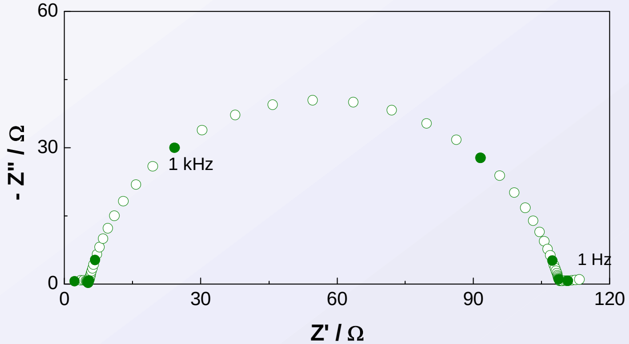
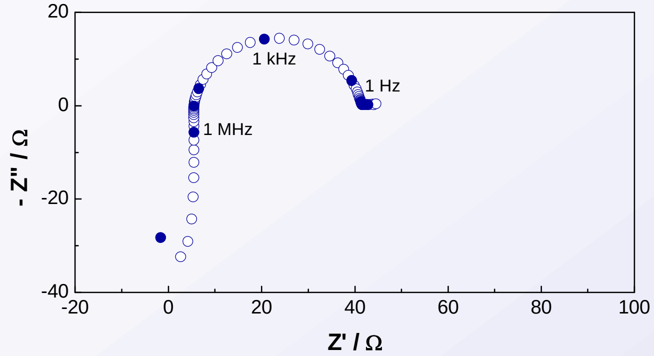
➢ Results

Before correction | **After correction**

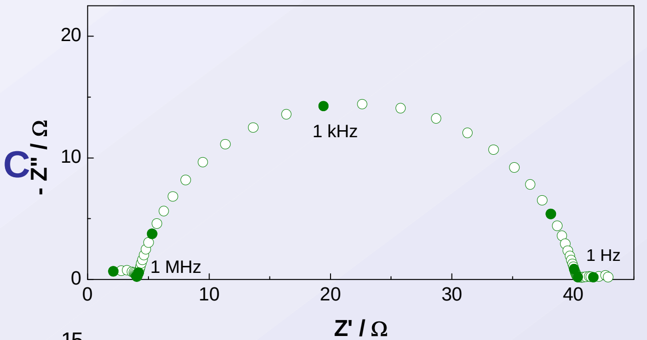


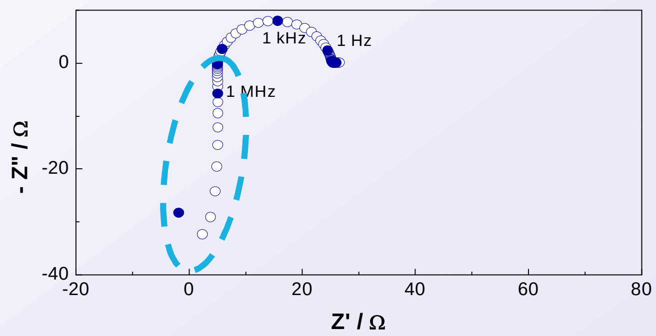
754º C



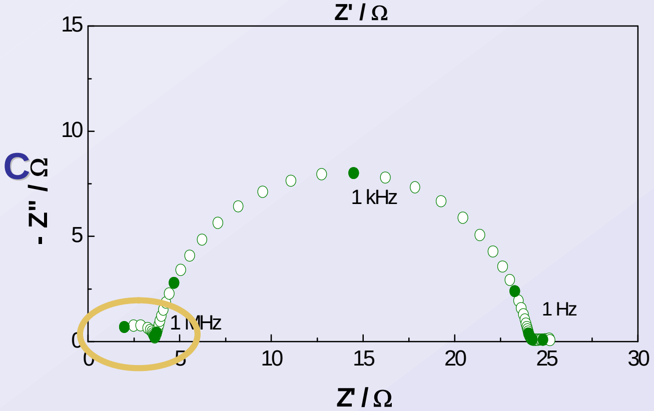


810º C



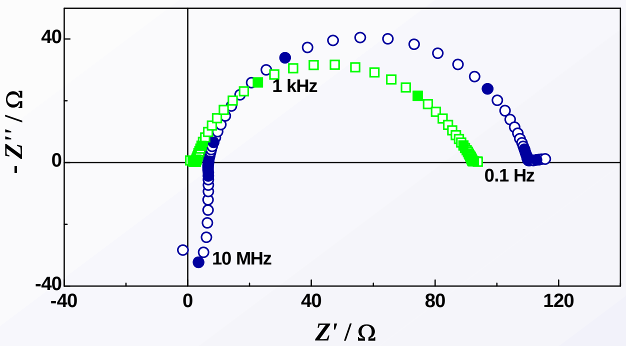


854º C

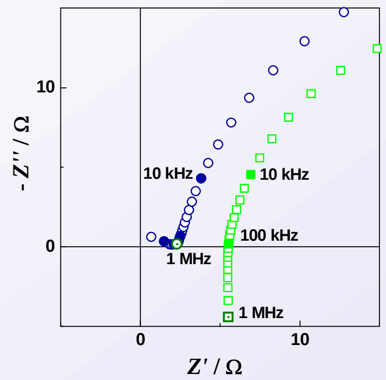


Inductance & resistance errors correction in YSZ studies

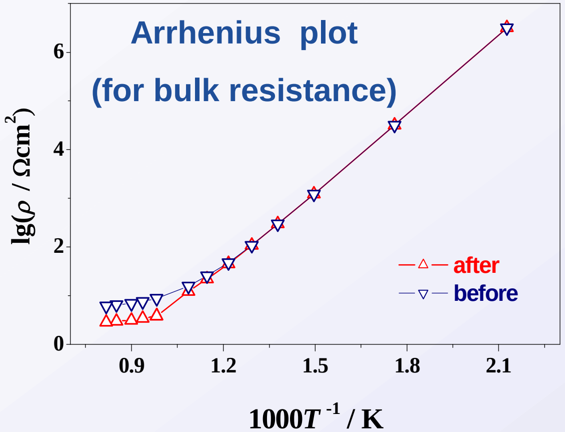
➢ Results

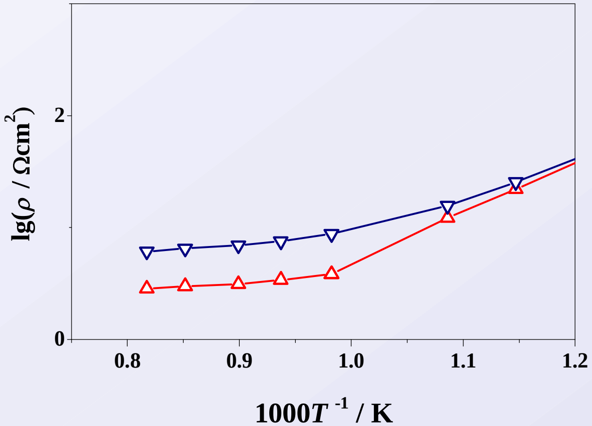


754º C



zoom





zoom

- Significant decrease of the corrected bulk resistance (at temperatures above 600ºC)
- Change of the Arrhenius plots shape (smooth transition before the correction; sharp kink after the correction)
- Influence of the errors at lower frequencies (decrease of the corrected polarization resistance)

Inductance & resistance errors correction in LSM/YSZ studies

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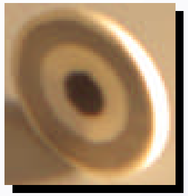
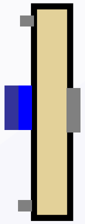
- **Object**





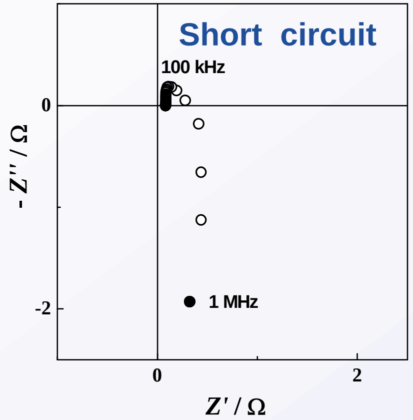
electrolyte support

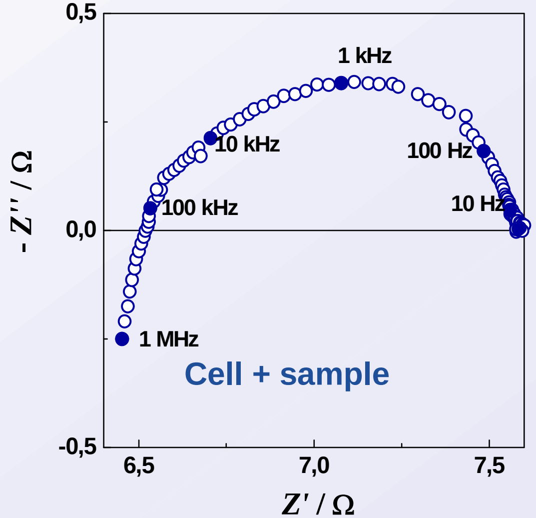
LSM/YSZ cathode

LSM current collector

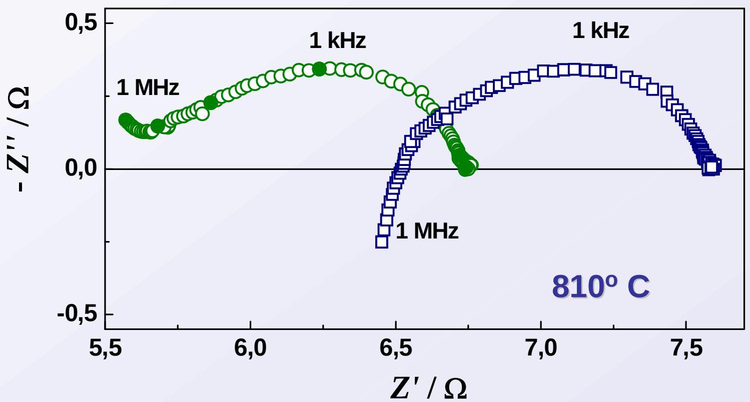
CE and RE – Pt ink (painted and sintered at 900 °C/1h)

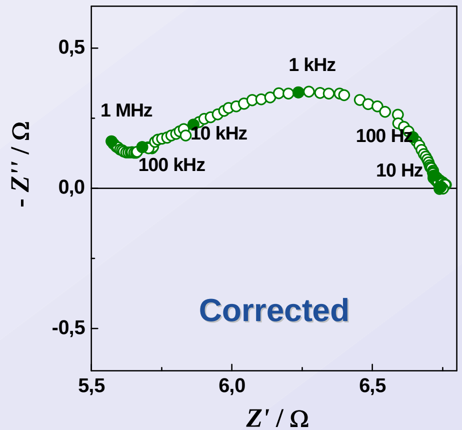
- **Measurements**





- **Correction (calculations):** under the assumption that Z_{error} and Z_{obj} are additive





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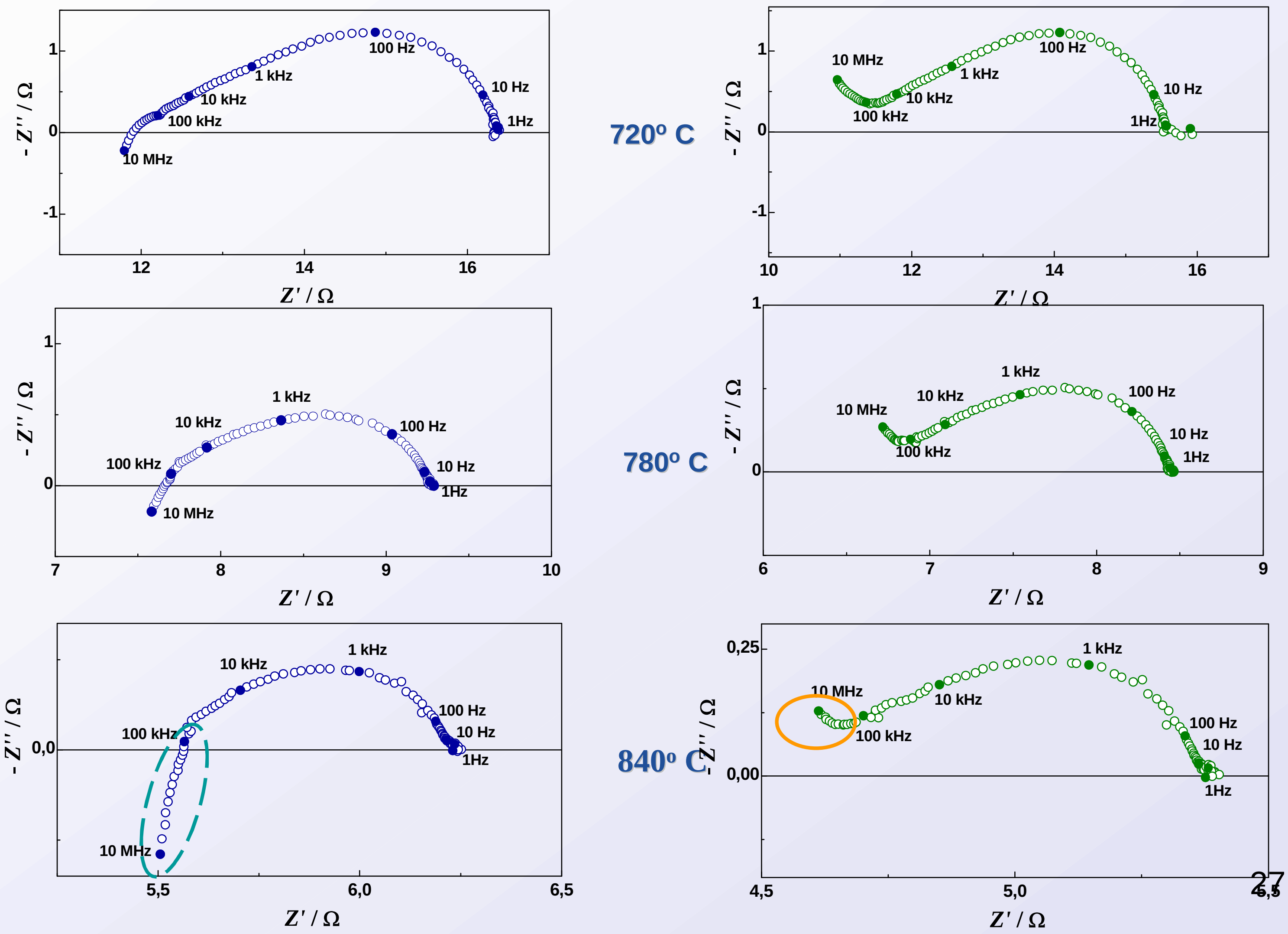
Inductance & resistance errors correction in LSM/YSZ studies

➢ Results

Before correction | **After correction**



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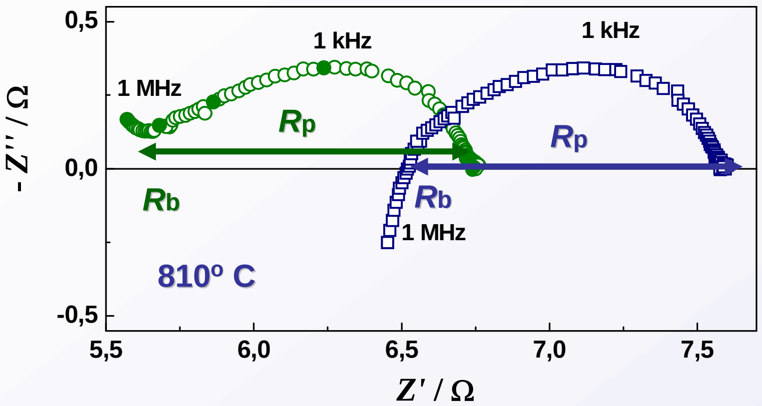
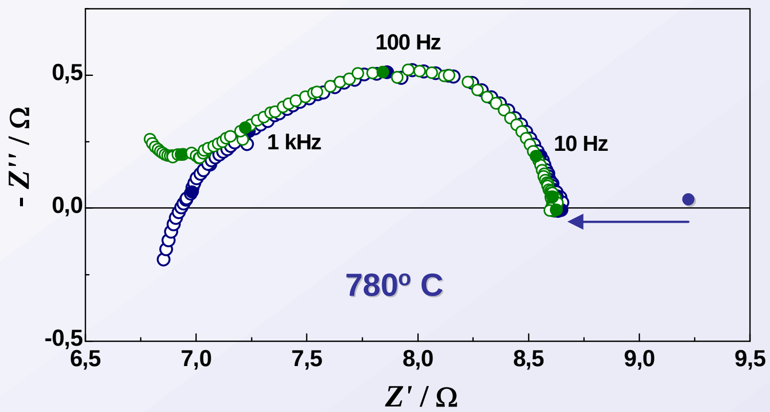
Inductance & resistance errors correction in LSM/YSZ studies

➢ **Results**

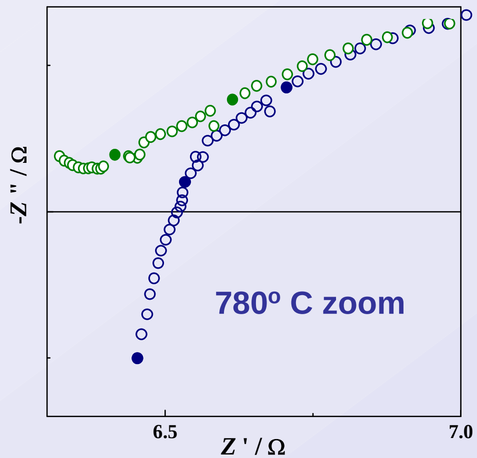




- Significant decrease of the corrected bulk resistance *R*b (at temperatures above 690ºC)
- Similar values of the polarization resistance before and after the correction,

but

- Differences in the impedance shape of the capacitive arc in its high frequency part (i.e. different modeling)



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CONCLUSIONS

- The proposed procedure for calibration and correction of the parasitic inductance and resistance increases the accuracy and information capability of EIS in studies of low impedance objects as fuel cells.
- Although more pronounced at higher frequencies, in low impedance objects the inductive errors have significant effect in the middle and even in the low frequency range. At some experimental conditions the interesting from research point of view phenomenon could be entirely masked by the parasitic inductance (and resistance) of the measurement system.
- The calibration and sample's measurements should be performed at the same experimental conditions (configuration of the cell and cables, temperature, frequency range and density).
- The correction (calculation) procedure is performed under the assumption that the impedances of the parasitic components and of the object are additive.

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