



Fuel Cell & Hydrogen Technologies JP

SP2: Catalyst and Electrodes

Borovetz, Bulgaria

June 2nd and 3rd 2014



Advanced Impedance Techniques in SOFC Studies

EERA FCH2-SP2 WORKSHOP in frame of EIA10

Bridging experimental and numerical research:
development and optimization of advanced characterization tools based on Electrochemical Impedance Spectroscopy



Daria Vladikova, Zdravko Stoykov
IEES-BAS,

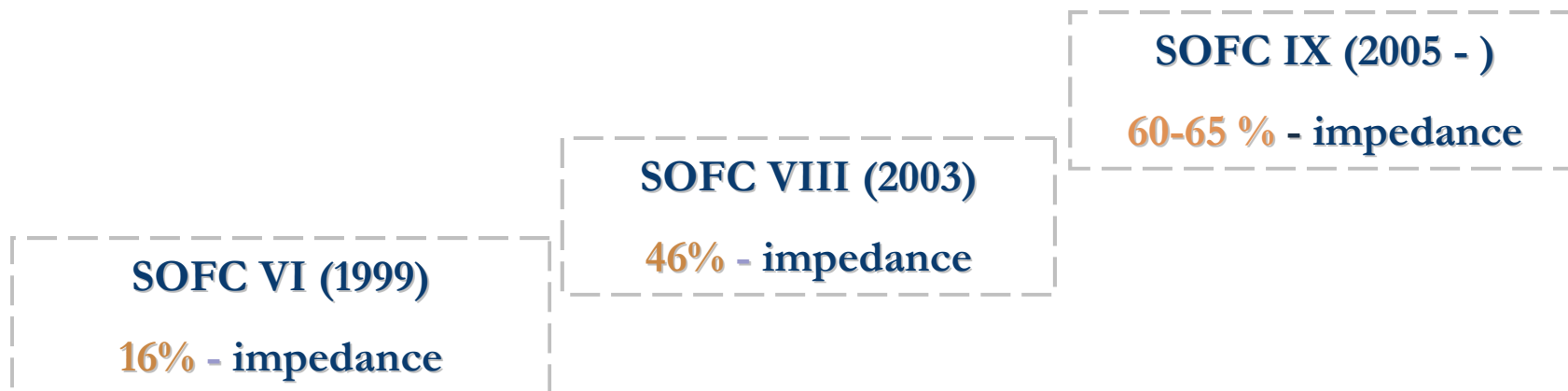
To present some simple approaches and tools for :

- Increase the information capability of Electrochemical Impedance
- Increase of the knowledge about the object by combination of EIS with other techniques
- Performance of some result-oriented studies
 - water formation and growth
 - Electrode degradation

IN FUEL CELLS (SOFC)

Impedance in SOFC:

➤ Solid Oxide Fuel Cell Conference (SOFC VI – XI) / Cathodes



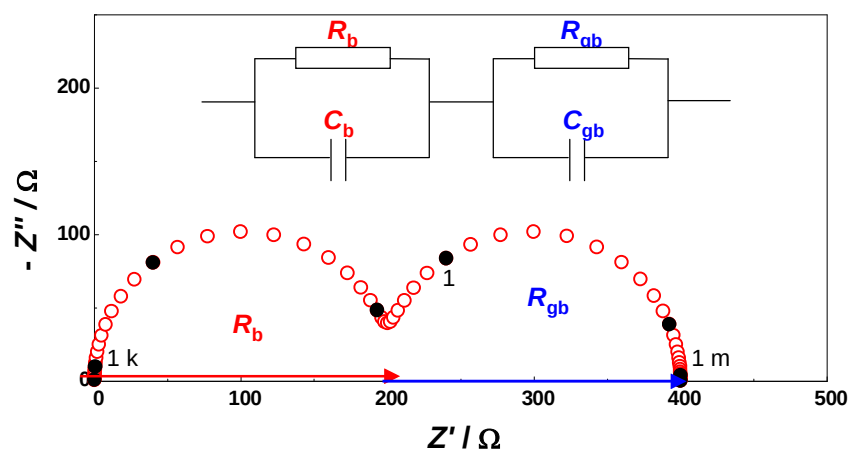
➤ European Fuel Cell Forum 2010 Proceedings: 10. Cathodes



- **UNIQUE ADVANTAGE:** to separate the kinetics of the different steps involved in the total process under investigation

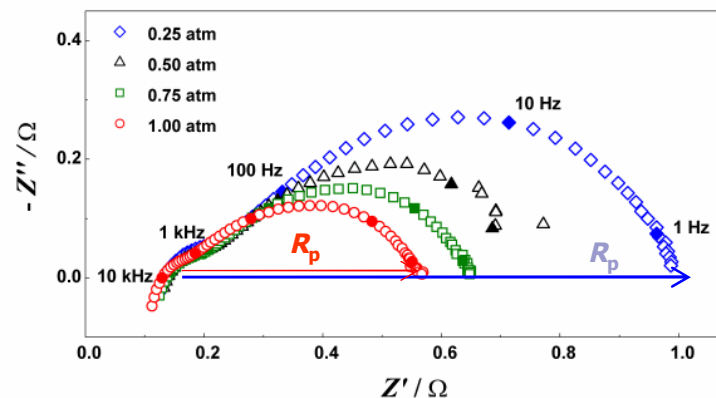
- **UNIQUE ADVANTAGE:** to separate the kinetics of the different steps involved in the total process under investigation

YDC15 electrolyte/200°C



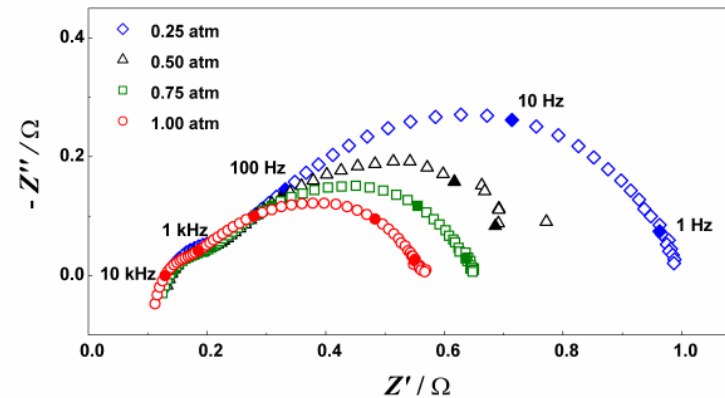
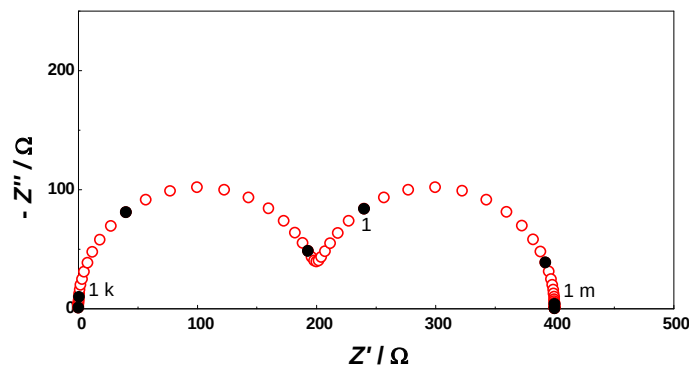
Z. Stoykov, D. Vladikova, Differential Impedance Analysis,
Prof. Marin Drinov Publ. House, Sofia, 2005

LSM cathode reaction/800°C



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

- **UNIQUE ADVANTAGE:** to separate the kinetics of the different steps involved in the total process under investigation



$$R = f(T)$$

Arenius plot

$$\rho = \rho_0 \exp(E_\rho / kT)$$

E_ρ → bulk
 E_ρ → g.b.
 E_ρ → reaction (steps/rate limiting one)

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

Impedance in SOFC: Specific problems

➤ **Low impedance at operating conditions**

➤ **Resistance: $M\Omega$ - $m\Omega$**

➤ **Multi-parametric working point**

- I_D
- Temperature
- Flow and pressure of O_2 and H_2
- H_2O contents;
- Impurities.

➤ **Fuzzy objects”**

- unpredictable distribution of parameters;
 - lack of knowledge based model for data analysis;
-

➤ **Low impedance at operating conditions**

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➤ **Multi-parametric working point**

- I_D
- Temperature
- Flow and pressure of O_2 and H_2
- H_2O contents;
- Impurities.

Measurement
and
Data Preprocessing
TOOLS

for
**Improved
Data
Quality**

➤ **Fuzzy objects”**

- unpredictable distribution of parameters;
- lack of knowledge based model for data analysis;

TOOLS for
**Improved
Data
Analysis**

➤ **Improved data quality**

- Improved measurement conditions
- Correction for the rig parasitic components
- Improved observability (searching a phenomenon)

➤ **Improved data analysis**

- Differential Impedance Analysis – structural approach
-

➤ **Improved data quality**

- Improved measurement conditions
- Correction for the rig parasitic components
- Improved observability (searching a phenomenon)

➤ **Improved data analysis**

- Differential Impedance Analysis

NO NEED
of a preliminary working
Hypothesis
*(the model is extracted
from the data)*

VERY HIGH:

- Selectivity
- Noise immunity
- Robustness

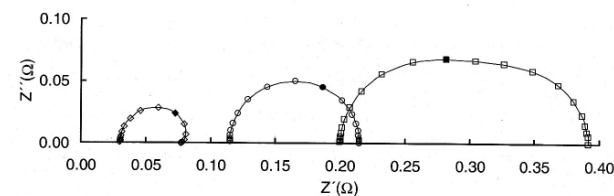
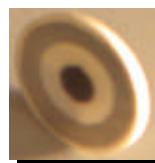
**DISTRIBUTION
Recognition
&
Characterization**

➤ Measurement configurations (“button cells”)

- symmetrical half cell ($2R_p$)



- three electrode half cell



Adler et al. J. Electrochem. Soc. 2002, 149, E166

- button cell (anode supported)



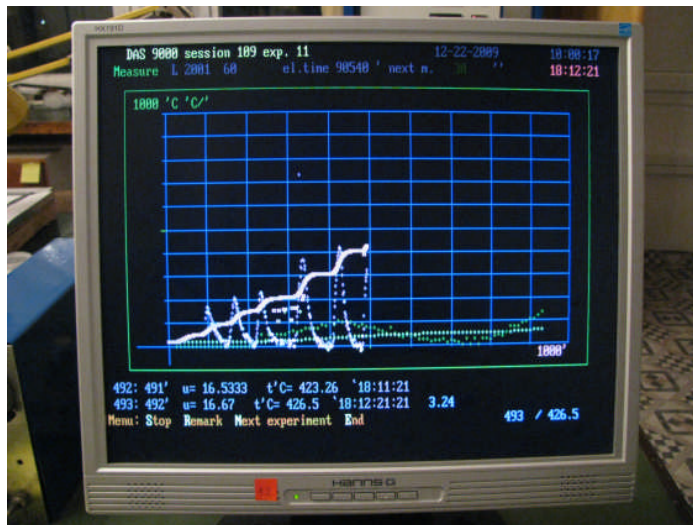
➤ Measurement conditions: AC amplitude; density (points/decade); Bias (DC); temp etc.

➤ Measurements:

- furnace with **D.C. power supply** (no erroneous data at 50, 100, 150, 250 Hz.)
- specialized sample rig

precise temperature
measurement and monitoring
(effective resolution 0.01°C)

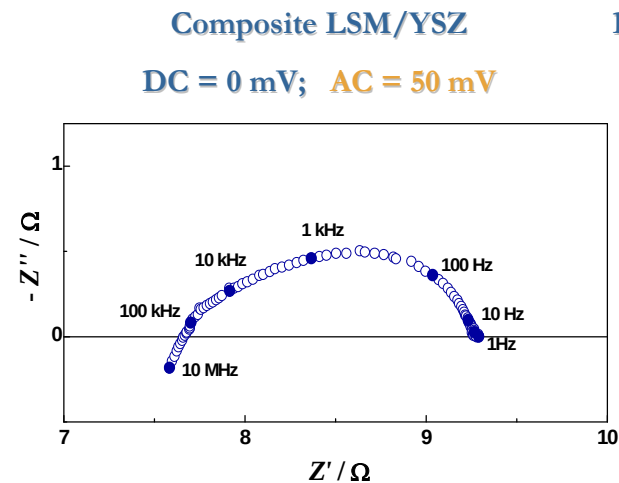
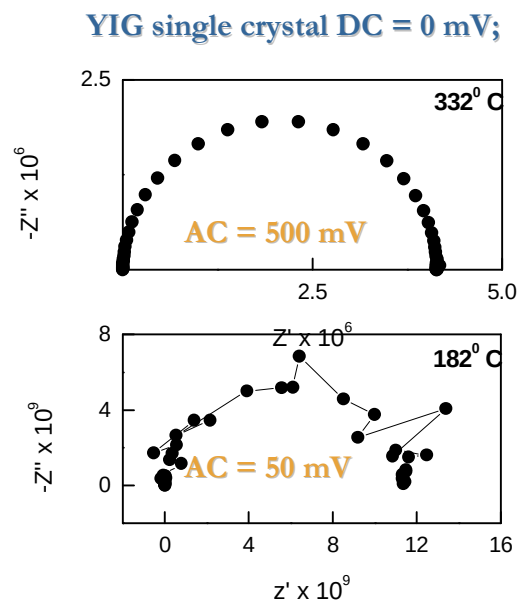
DC furnace (100A/15 V)



Improved Data Quality: Improved measurement conditions

✓ **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



Dislocation free Ag single crystal
DC = 5 mV;

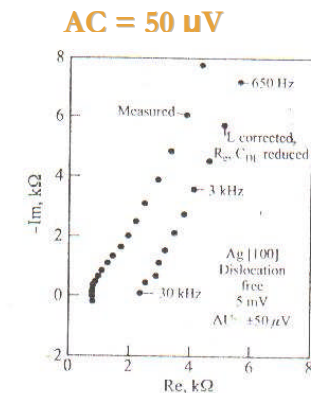


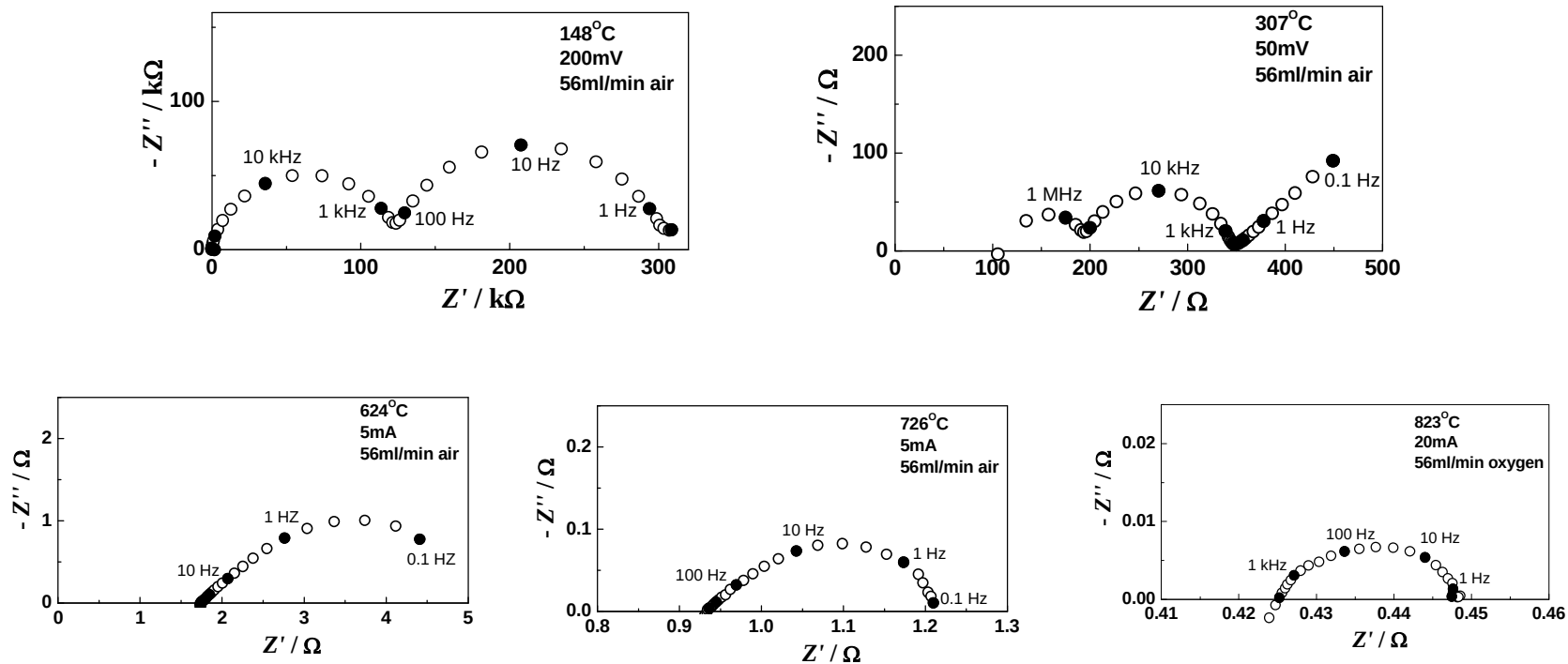
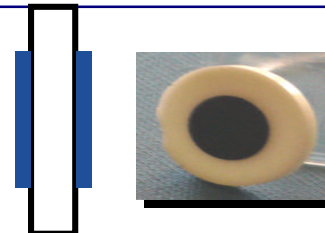
Fig. 3. Impedance plots

Improved Data Quality: Improved measurement conditions

➤ Measurements:

- **2 modes** (potentiostatic; galvanostatic);
- **changing amplitude**

LSCF/YDC15/LSCF

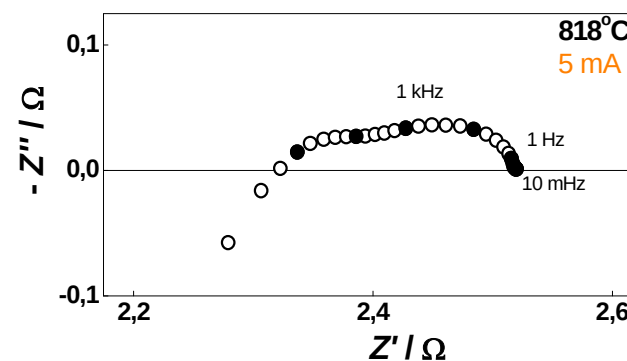
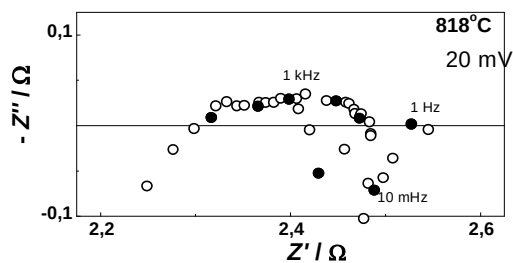


Measurements:

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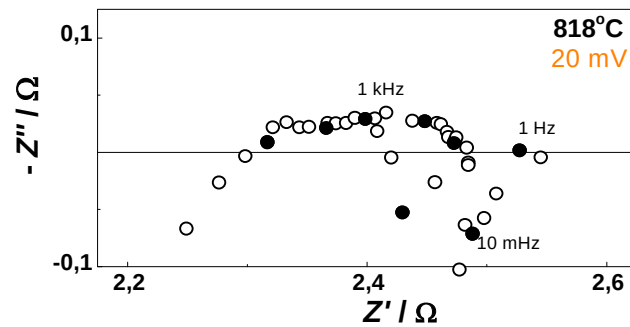
LSCF/YDC15/LSCF

Tape Casting

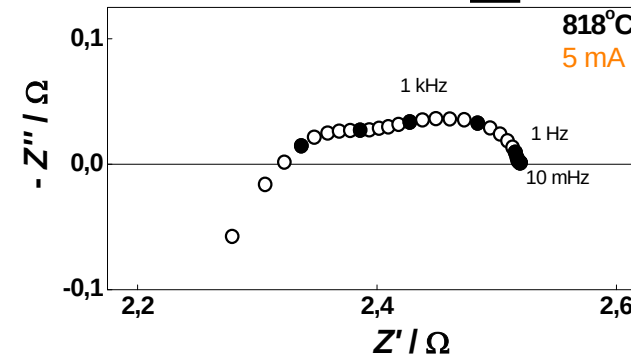


Measurements:

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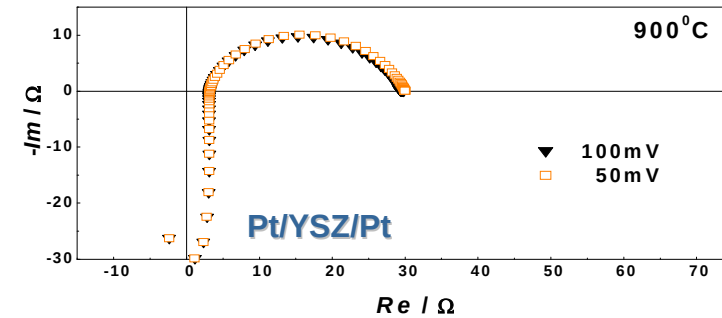
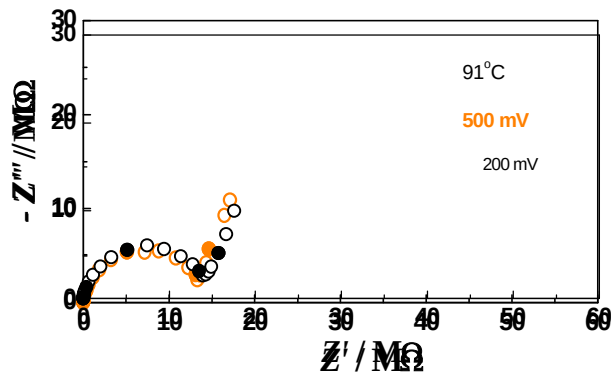


LSCF/YDC15/LSCF
Tape Casting



Testing for linearity

LSCF/YDC15/LSCF



➤ **Improved data quality**

- Improved measurement conditions
- **Correction for the rig parasitic components**
- Improved observability (searching a phenomenon)

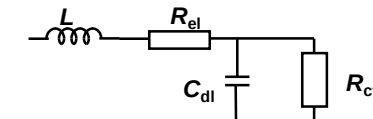
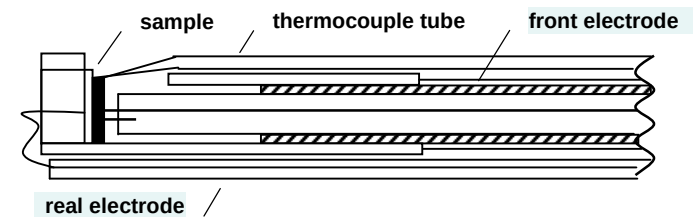
➤ **Improved data analysis**

- Differential Impedance Analysis

Analysis of inductance errors

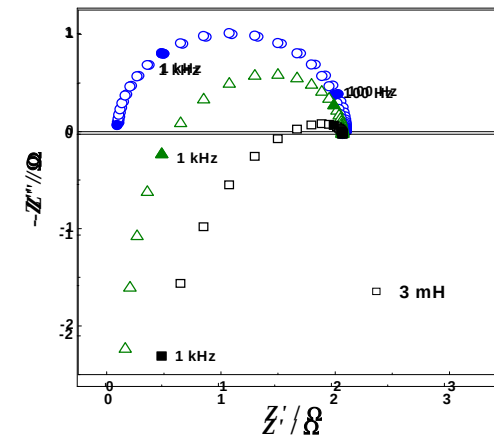
➤ Main Sources of Inductance Errors:

- Cabling
- Measurement cell
- Object
- Shunt



➤ Influence of L on the impedance data

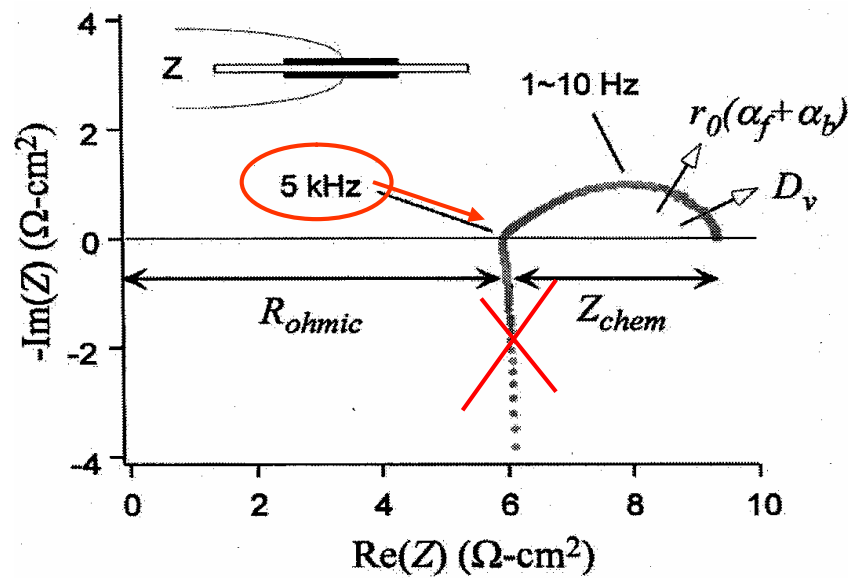
- Deformation of the impedance diagram (in size and in shape)
- Wrong parametric identification
- Decrease of the measurement frequency range



(L may influence even the low frequencies)

Analysis of inductance errors

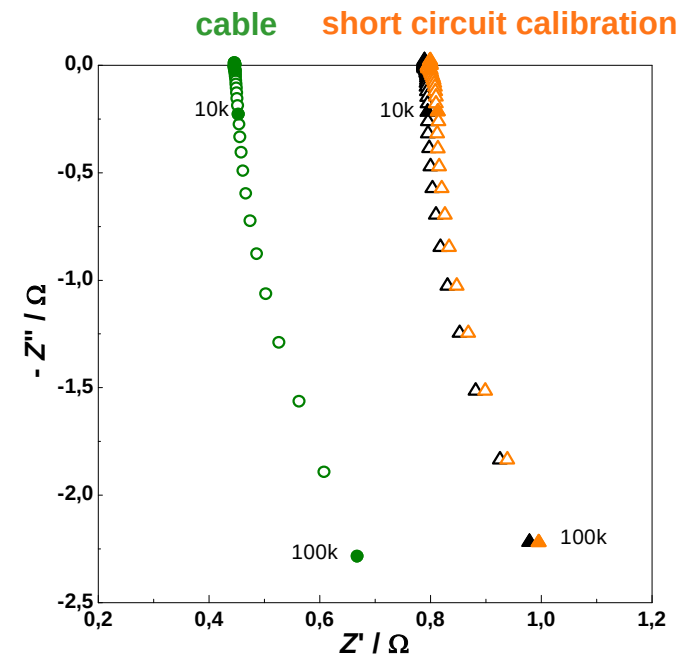
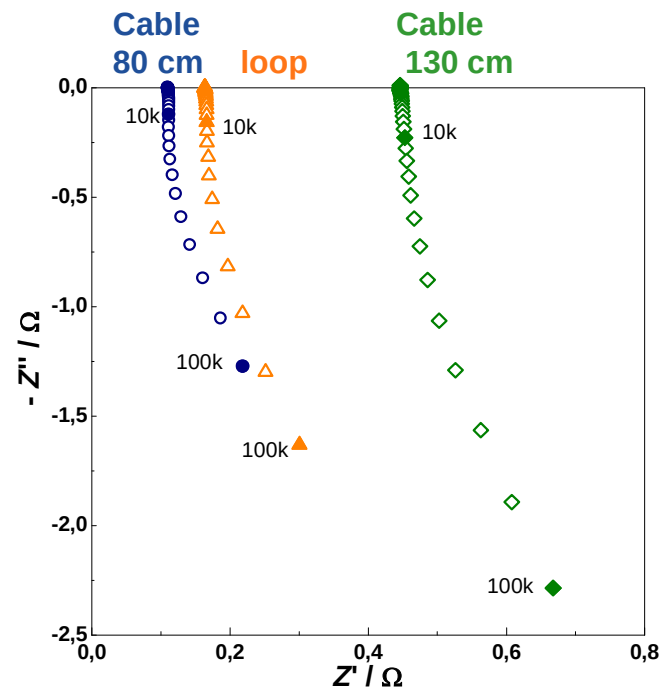
- Rejection of the Inductive tail or measurements at lower frequencies



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

Procedure for inductance & resistance errors correction

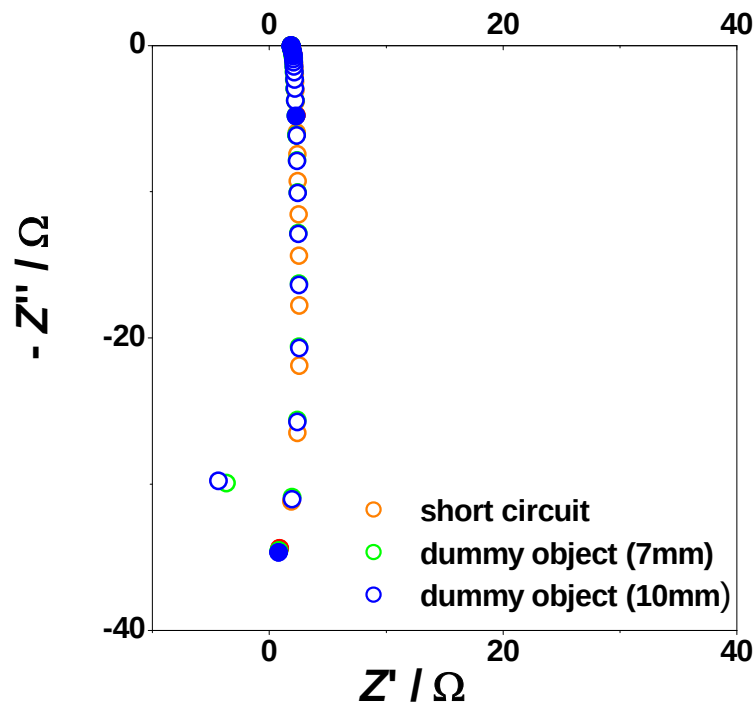
- **STEP 1: Short circuit calibration measurement - for evaluation of the cell's inductance and resistance (including the cables).**



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

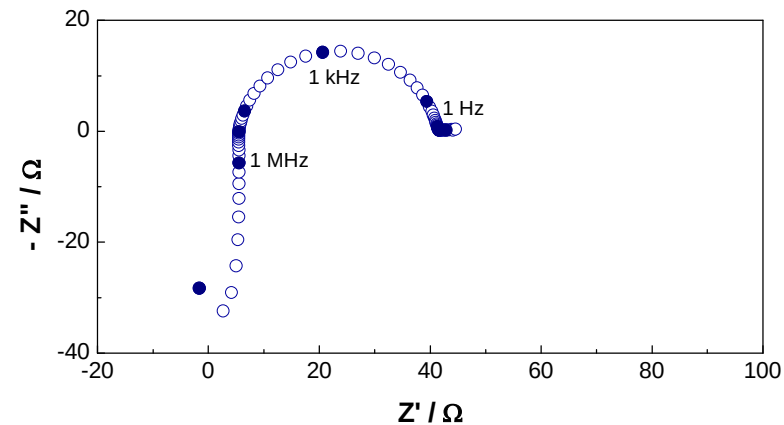
➤ **STEP 2: Measurement of Dummy Object** - takes into account the self-inductance of a sample with very low impedance



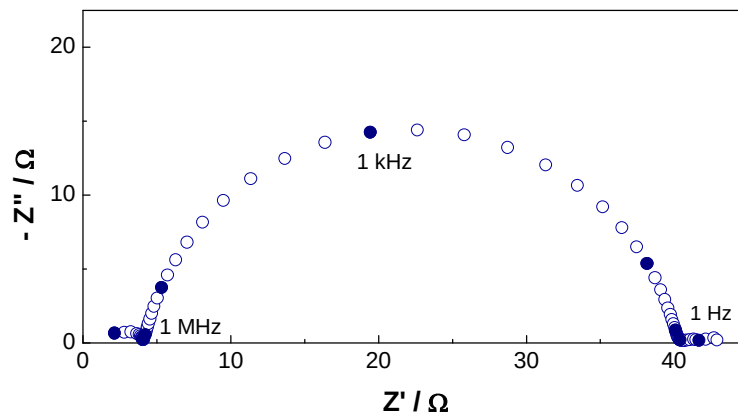
The measurement ensures evaluation of the object's inductance. Usually it is carried out using a metallic dummy object of the same shape and dimensions as the real one.

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.

➤ STEP 3: Measurement of the Investigated Object



➤ Step 4: Correction (calculations)



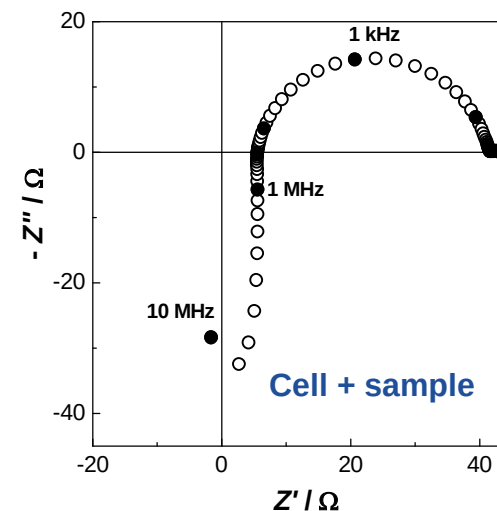
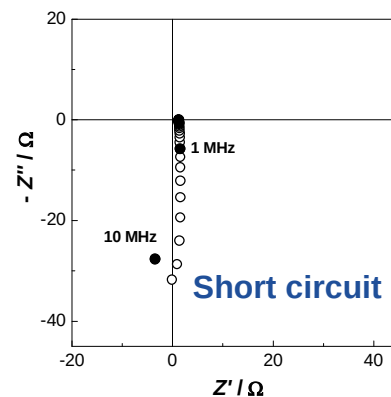
The procedure is performed:

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

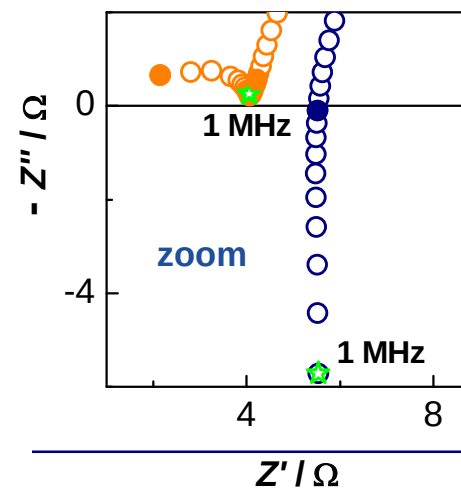
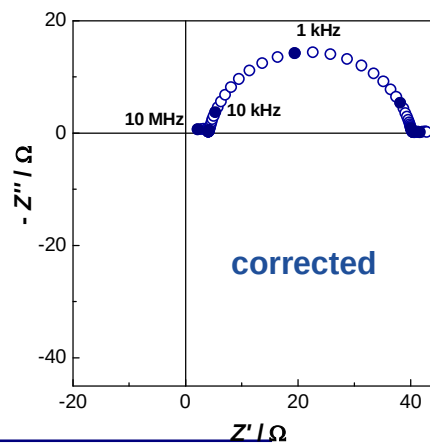
Procedure for inductance & resistance errors correction

➤ Object - YSZ

➤ Measurements

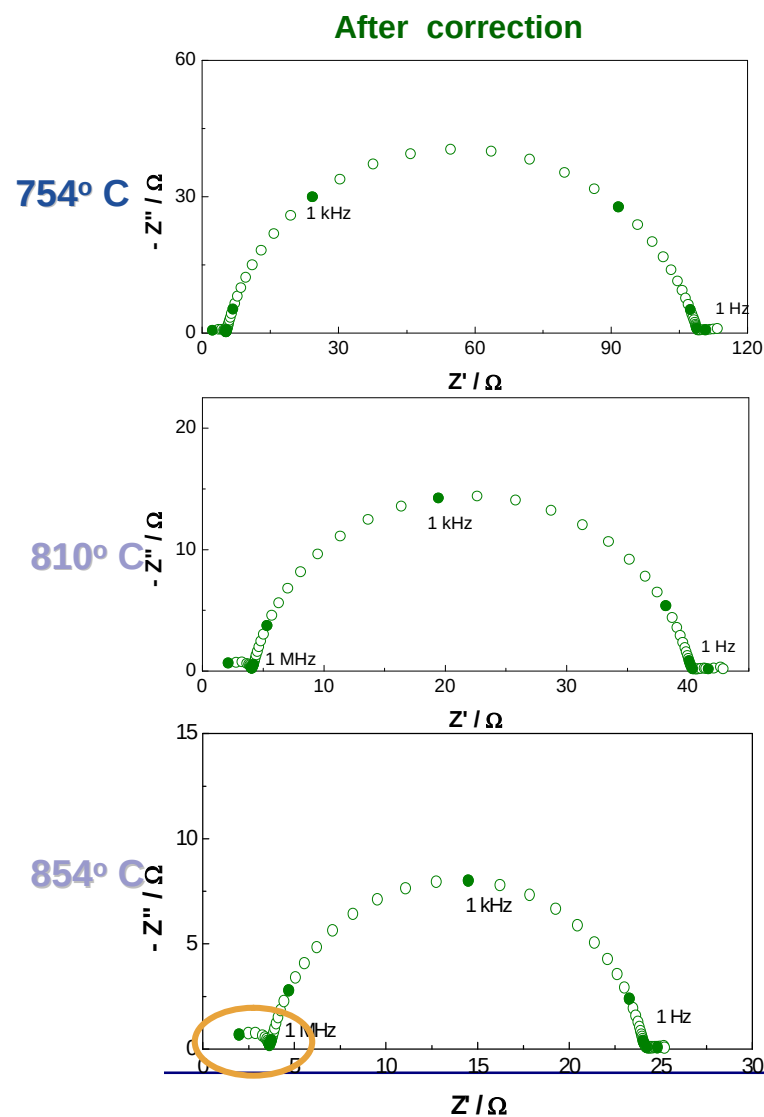
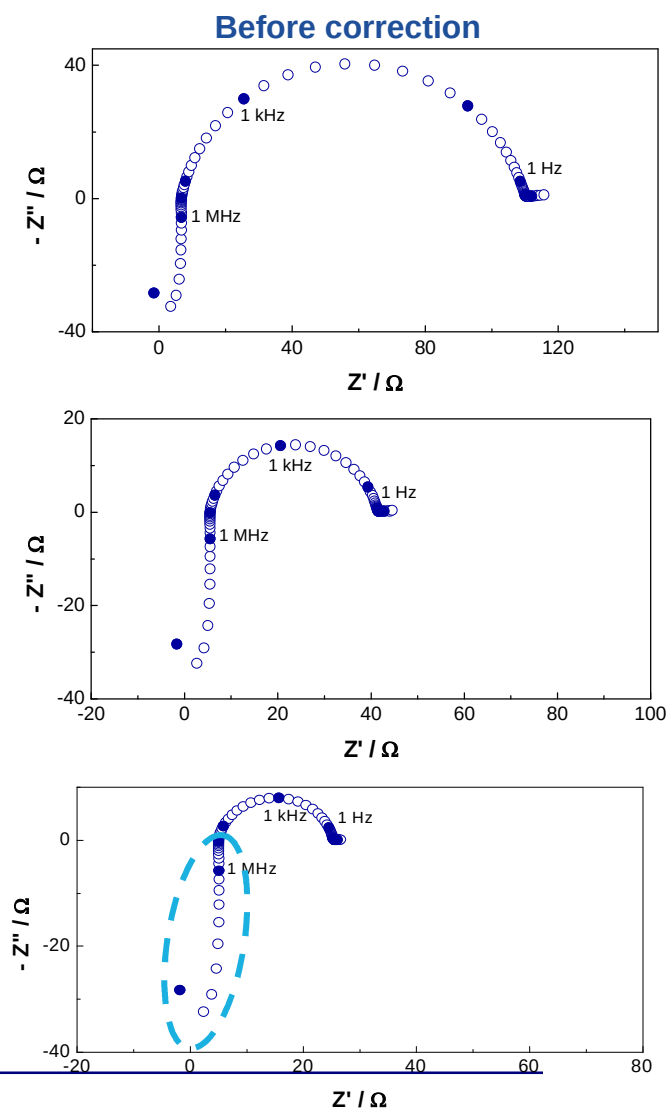


➤ Correction (calculations): under the assumption that Z_{error} and Z_{obj} are additive



Procedure for inductance & resistance errors correction

➤ Results



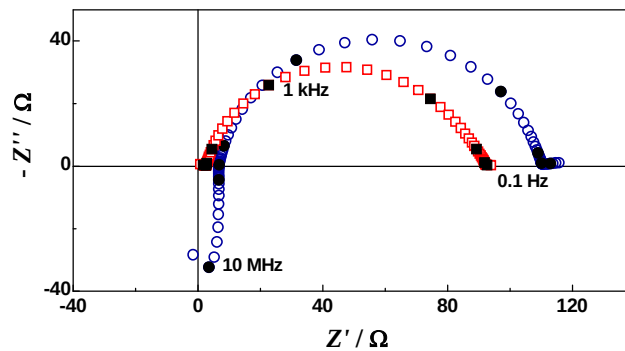
$$\varepsilon \approx KS^2$$



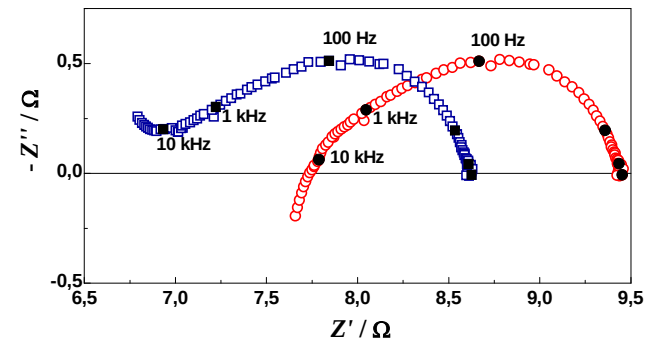
Procedure for inductance & resistance errors correction

➤ *L* Calibration and Correction

D. Vladikova, Z. Stoykov, G. Raikova, *Portable and Emergency Energy Sources*, Prof. Marin Drinov Academic Publishing House, Sofia, 2006



Pt/YSZ/Pt (793°C)



LSM+YSZ/YSZ/Pt (793°C);

A. Barbucci M. Viviani, P. Carpanese et al,
Electrochim. Acta 51 (2006) 1641

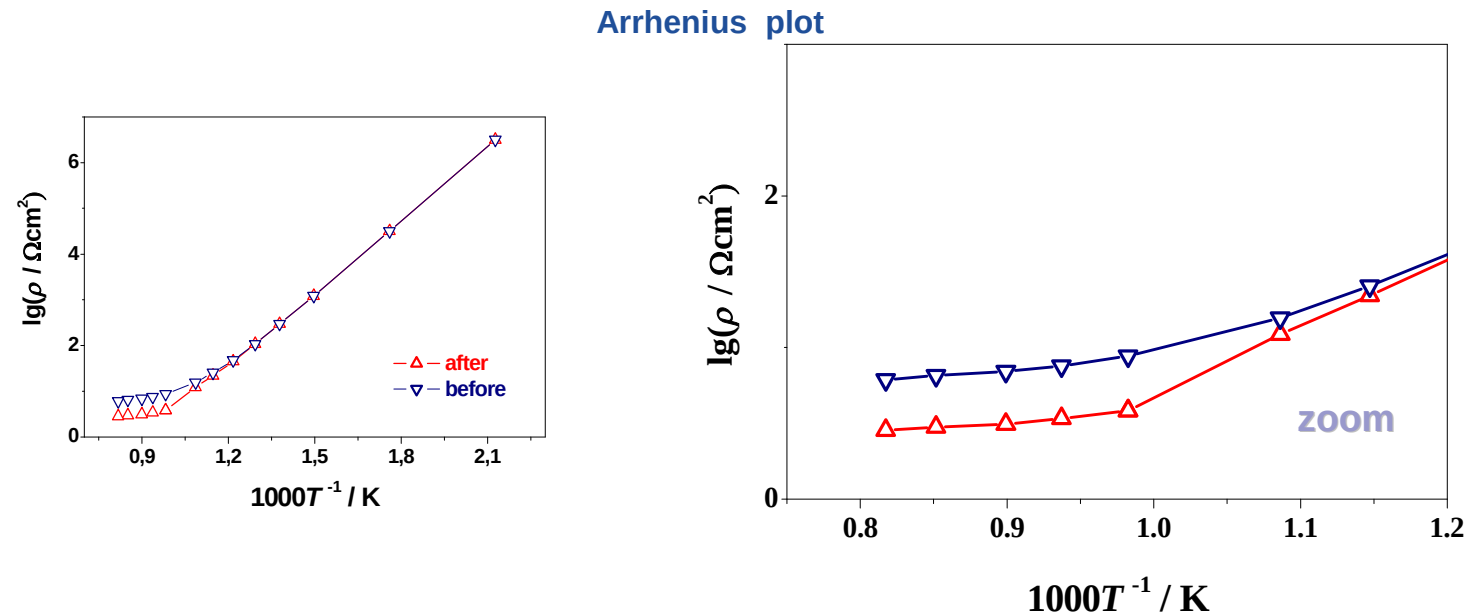
➤ Practical Conclusion:

Precise research experiments should be performed
on small cells with small electrode surface area

$$L \approx KS^{3/2}$$

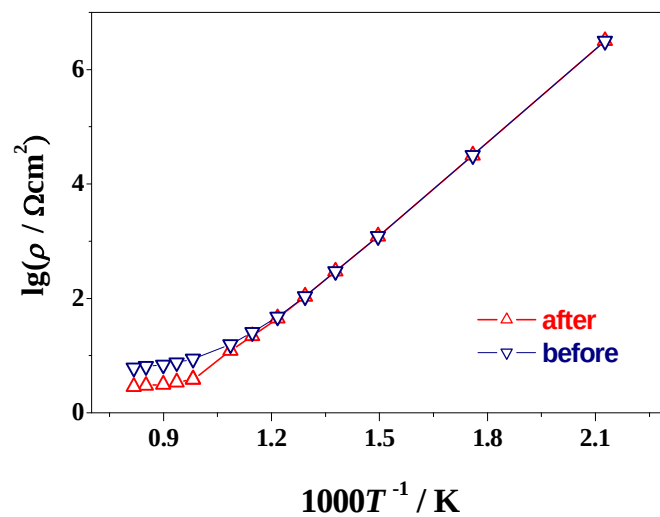
S – electrode surface area

➤ Results - YSZ

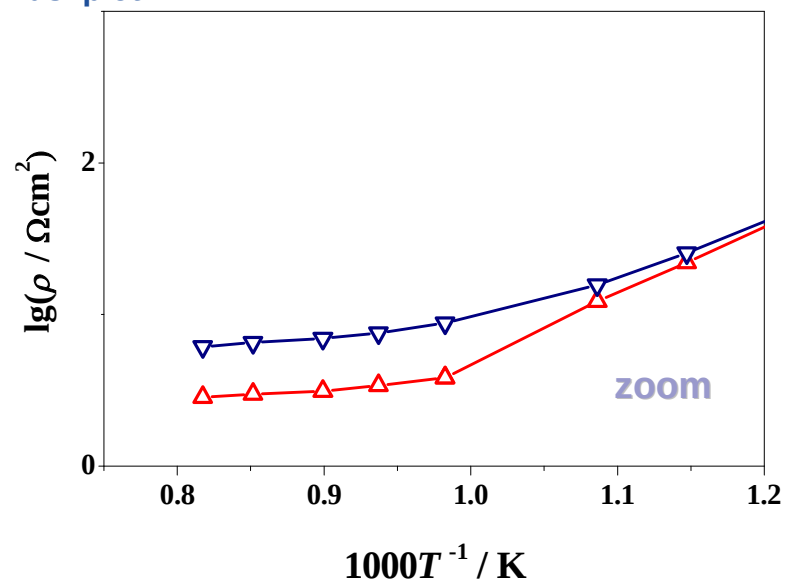


- Significant decrease of the corrected bulk resistance (at temperatures above 600°C)
- Change of the Arrhenius plots shape (smooth transition before the correction; sharp kink after the correction)
- Influence of the errors at lower frequencies (decrease of the corrected polarization resistance)

➤ Results - YSZ



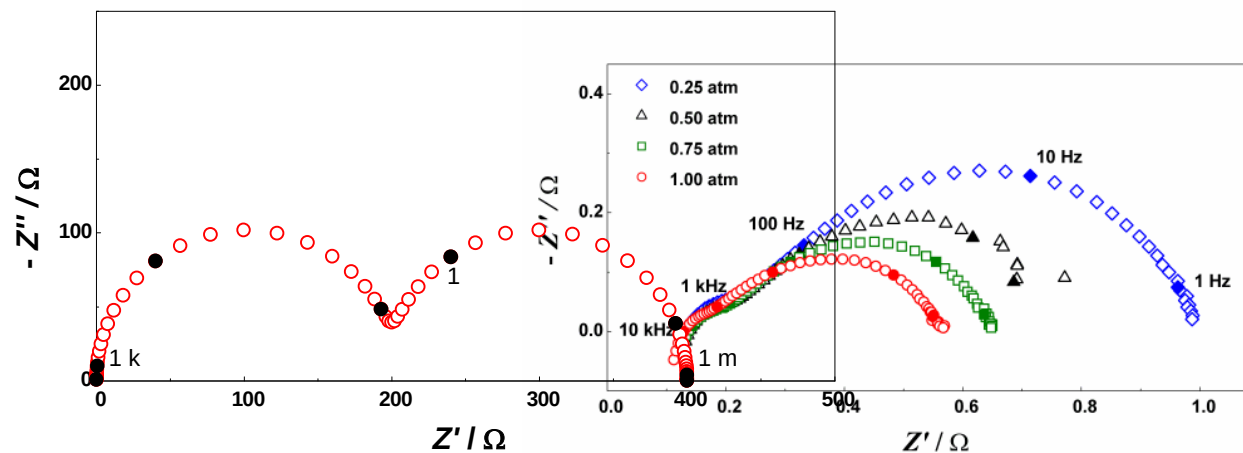
Arrhenius plot



Zahner Instrumental Approach - TOMORROW

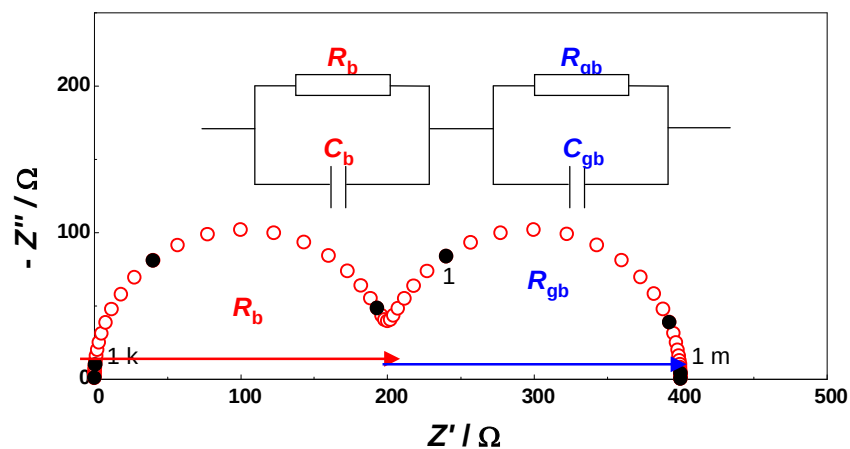
Impedance in SOFC: improved observability

- Improved measurement conditions
- Correction for the rig parasitic components
- **Improved observability (searching a phenomenon)**



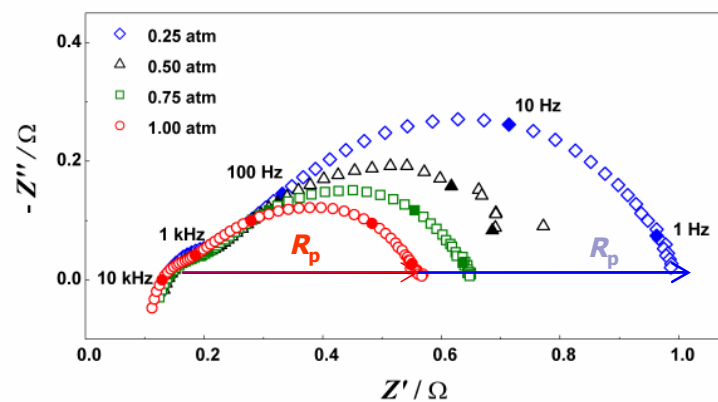
➤ CHANGING THE WORKING POINT

YDC15 electrolyte/200°C



Z. Stoyanov, D. Vladikova, Differential Impedance Analysis,
Prof. Marin Drinov Publ. House, Sofia, 2005

LSM cathode reaction/800°C



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

➤ **Observability** – searching a phenomenon

- frequency range
- appropriate “working point”
 - I_{DC}
 - temperature
 - Pressure and flow of O_2 and H_2
 - H_2O contents
 - Impurities.

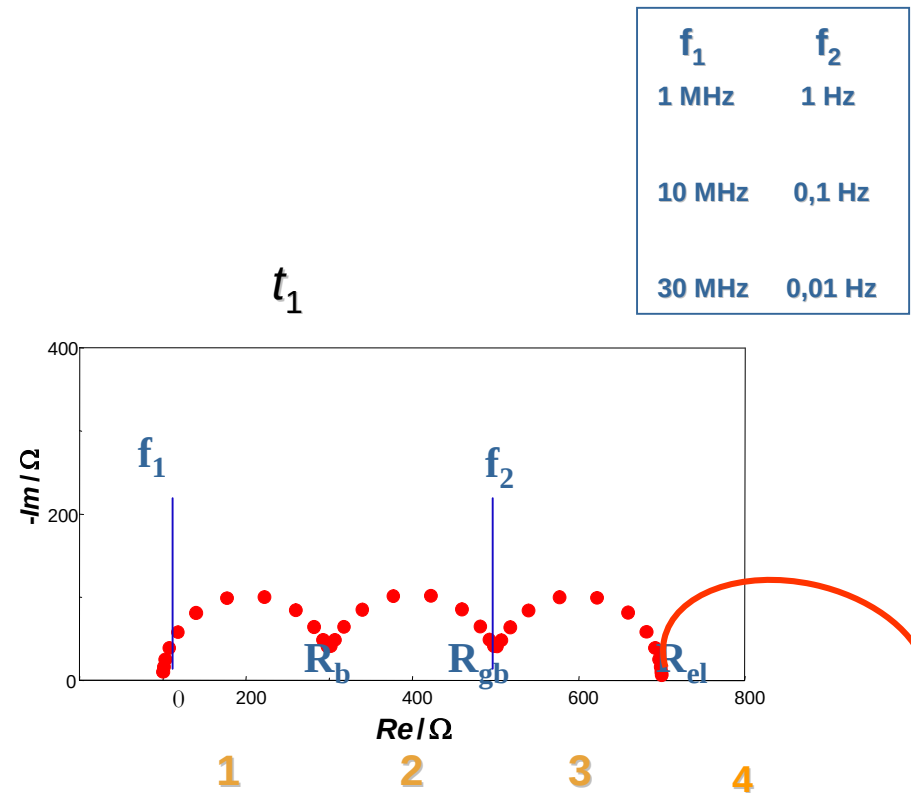
Impedance in SOFC: improved observability

□ All the phenomena under study can be observed in the measured frequency range.



How to increase the observability:

By changing the working point



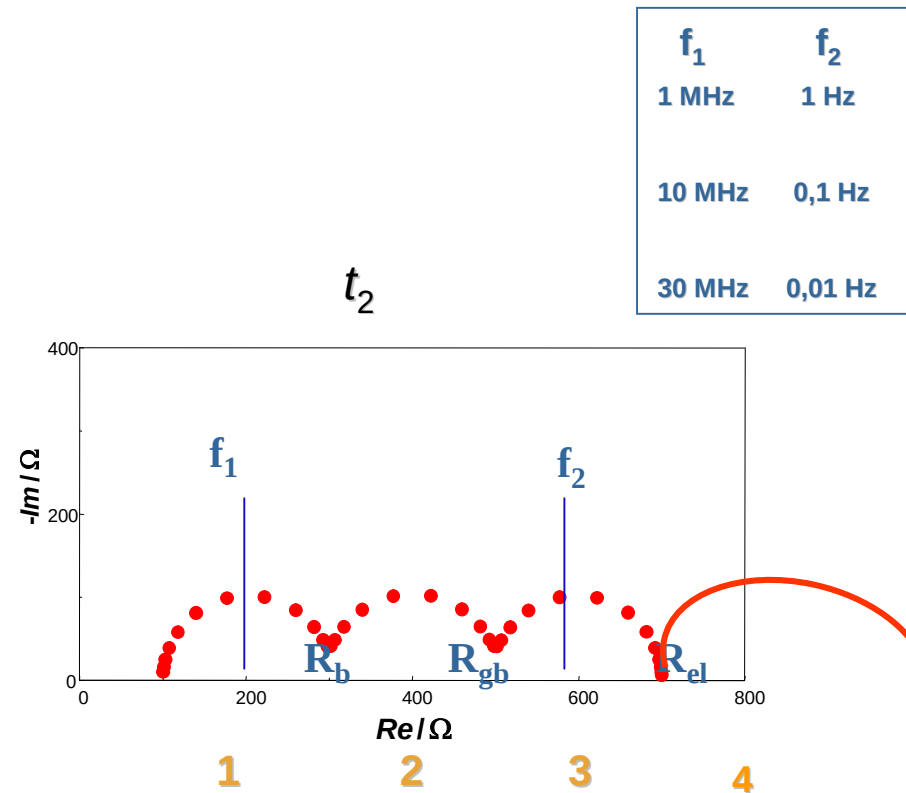
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Impedance in SOFC: improved observability

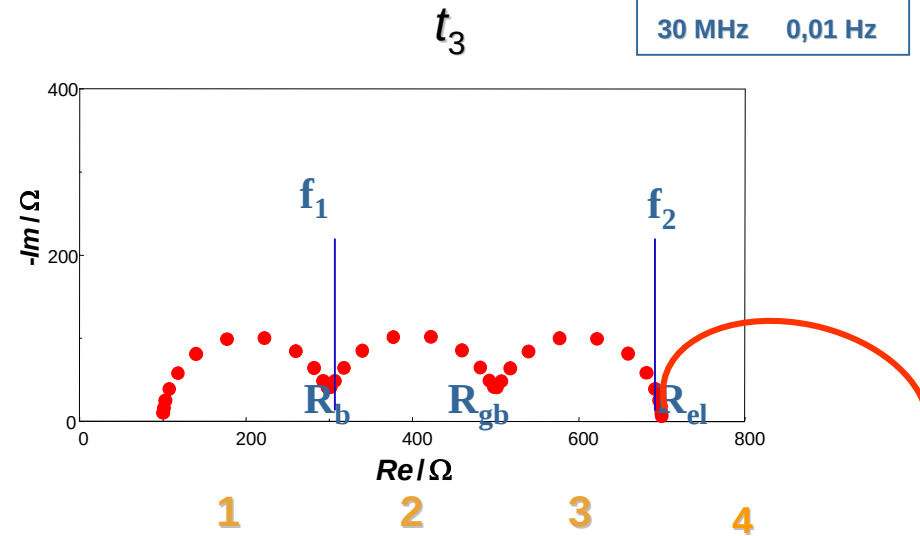
□ All the phenomena under study can be observed in the measured frequency range.



How to Increase the observability:

By changing the working point

f_1	f_2
1 MHz	1 Hz
10 MHz	0,1 Hz
30 MHz	0,01 Hz



Impedance in SOFC: improved observability

□ All the phenomena under study can be observed in the measured frequency range.

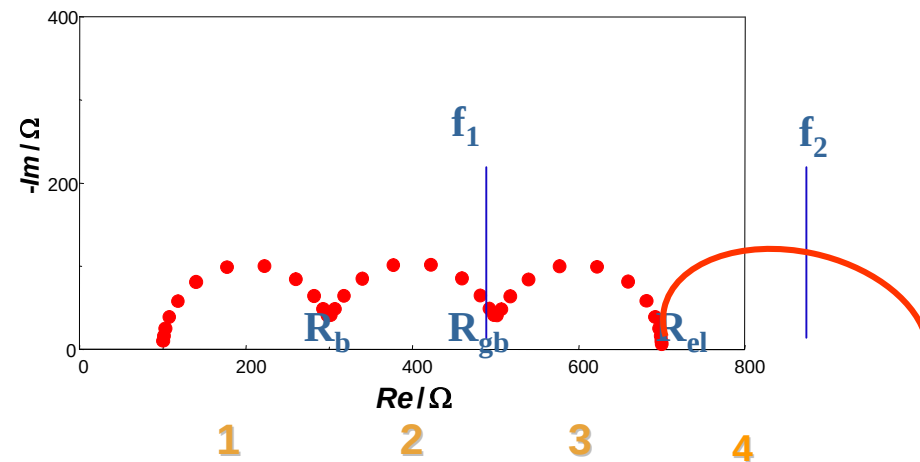


How to Increase the observability:

By changing the working point

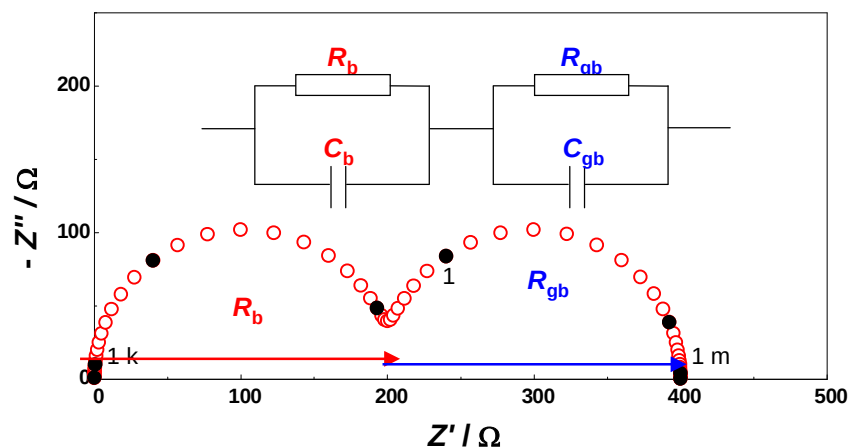
f_1	f_2
1 MHz	1 Hz
10 MHz	0,1 Hz
30 MHz	0,01 Hz

t_4



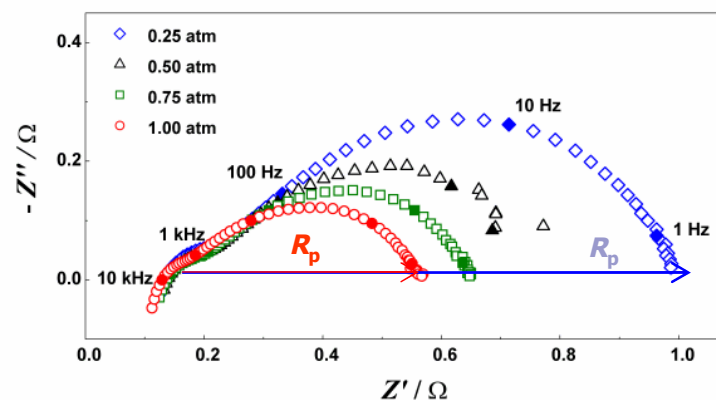
- Change of W.P.: Measurements in the wide temperature interval
- Combination with microstructure characterization

YDC15 electrolyte/200°C



Z. Stoykov, D. Vladikova, Differential Impedance Analysis,
Prof. Marin Drinov Publ. House, Sofia, 2005

LSM cathode reaction/800°C

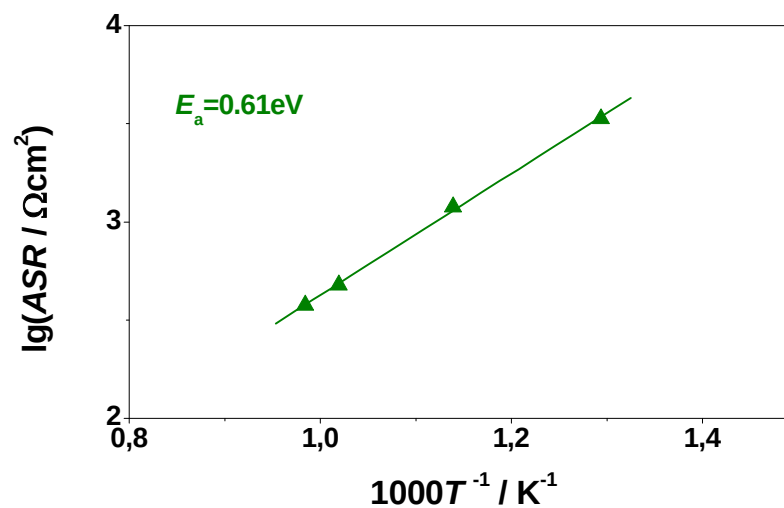
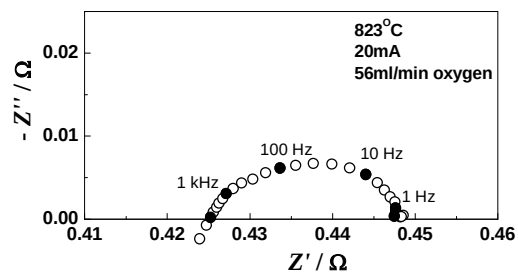
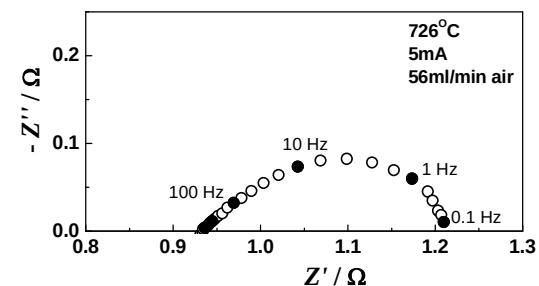
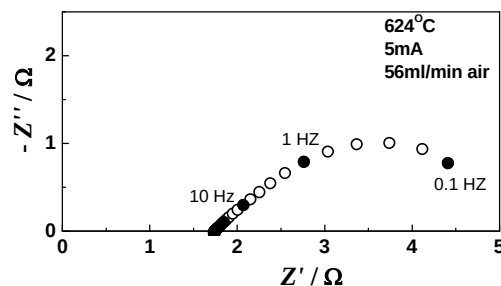
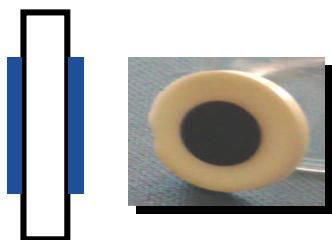


P. Carpanese, A. Barbucci, G. Cerisola et al,
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Example – anode BCY/Ni cermet studies

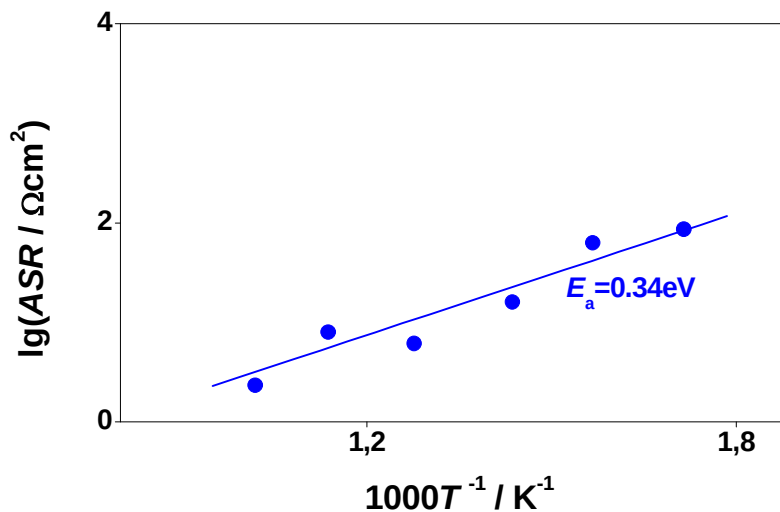
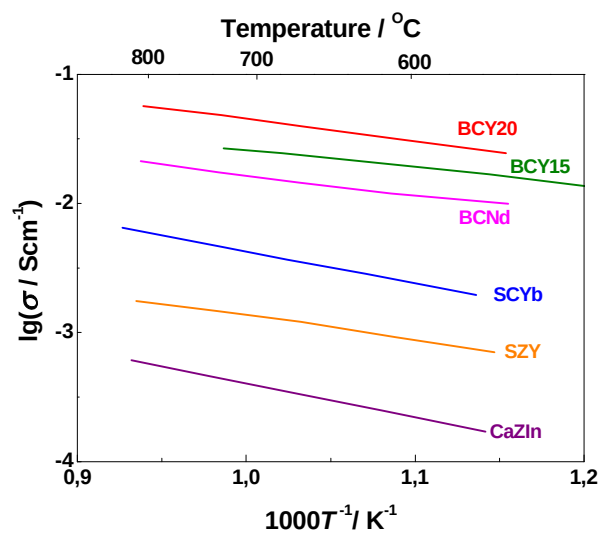
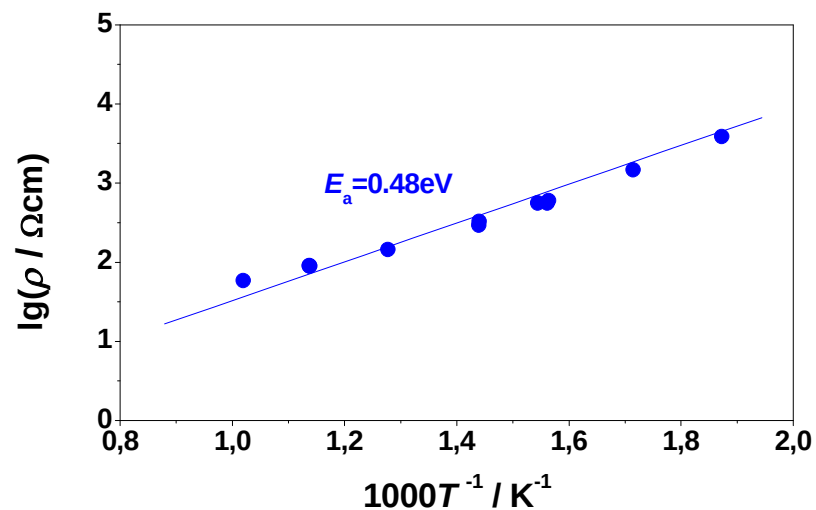
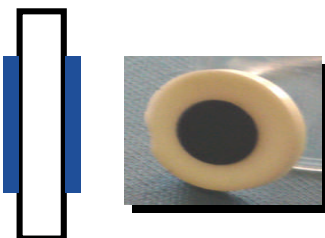
BCY15-Ni/BCY15/BCY15-Ni – classical measurement

1100°C



Example – anode BCY/Ni cermet studies

Ag/BCY15/Ag

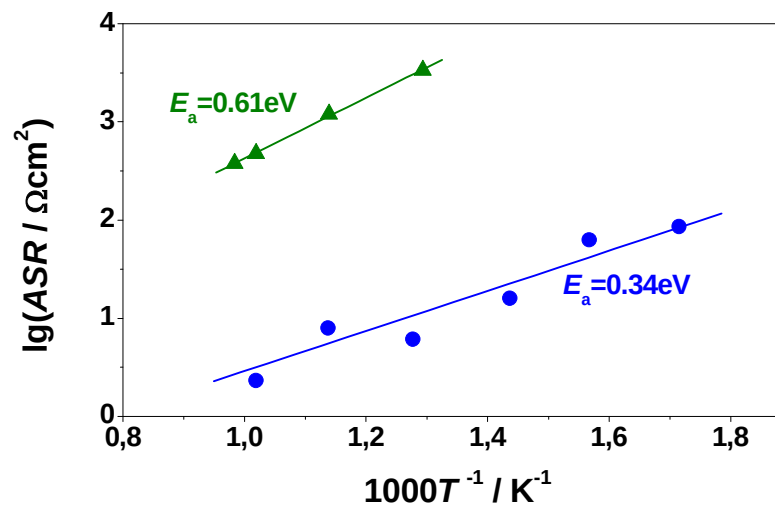
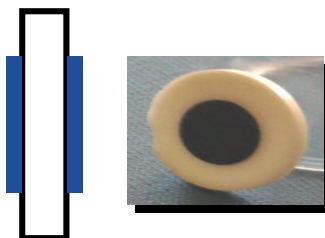


Example – anode BCY/Ni cermet studies

Ag/BCY15/Ag

BCY15-Ni/BCY15/BCY15-Ni

1100°C

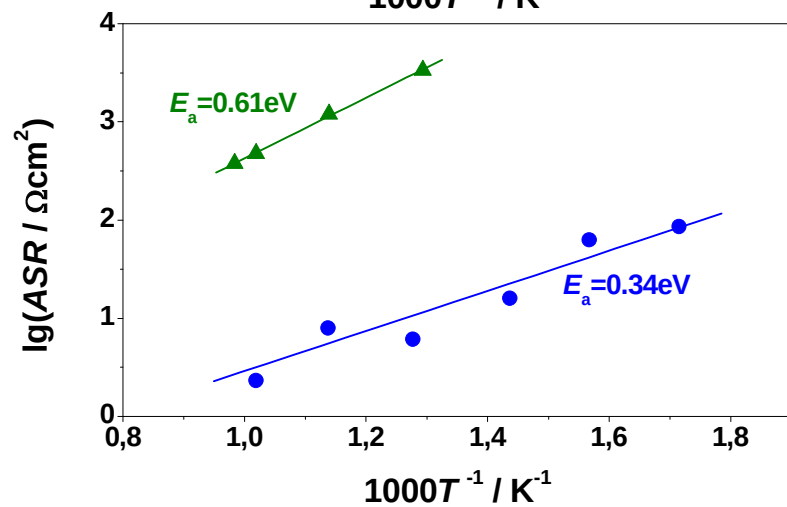
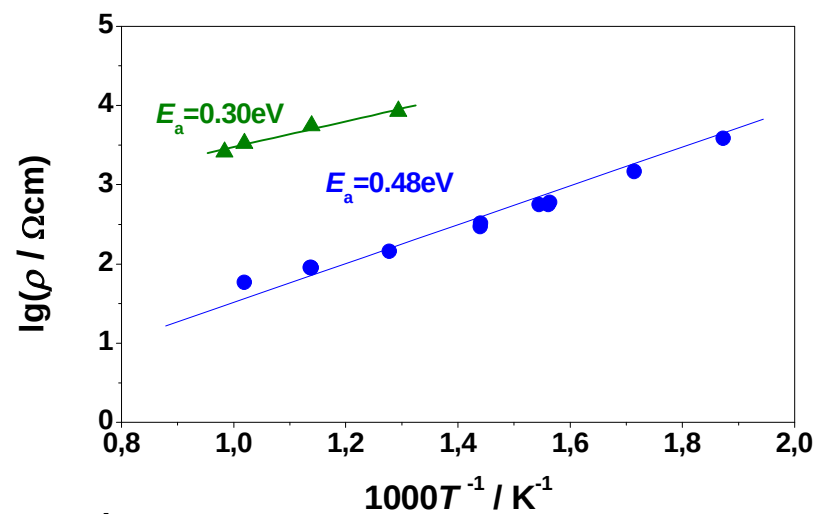
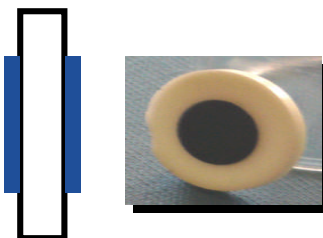


Example – anode BCY/Ni cermet studies

Ag/BCY15/Ag

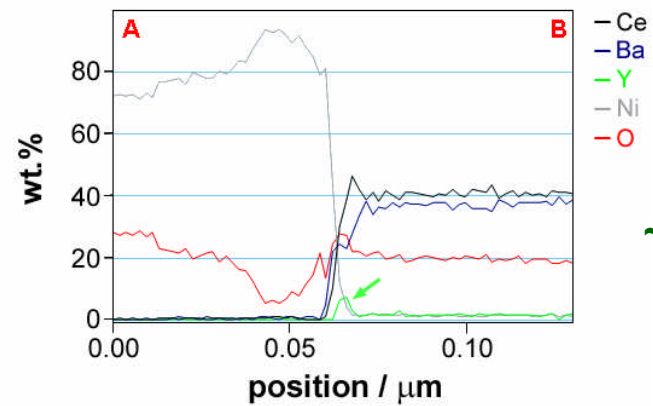
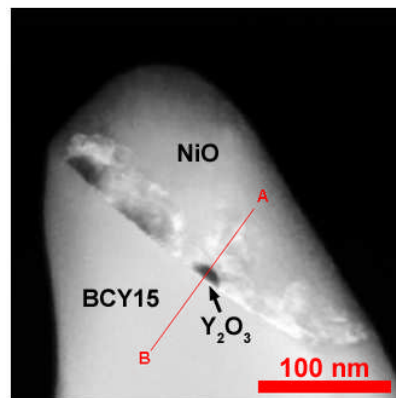
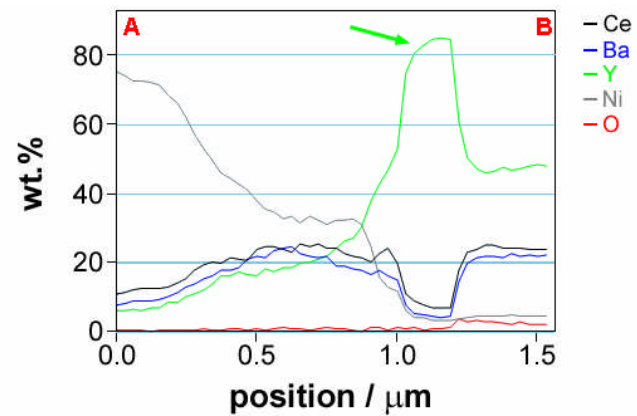
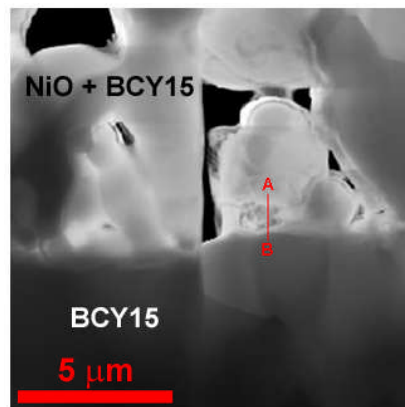
BCY15-Ni/BCY15/BCY15-Ni

1100°C



Example – anode BCY/Ni cermet studies

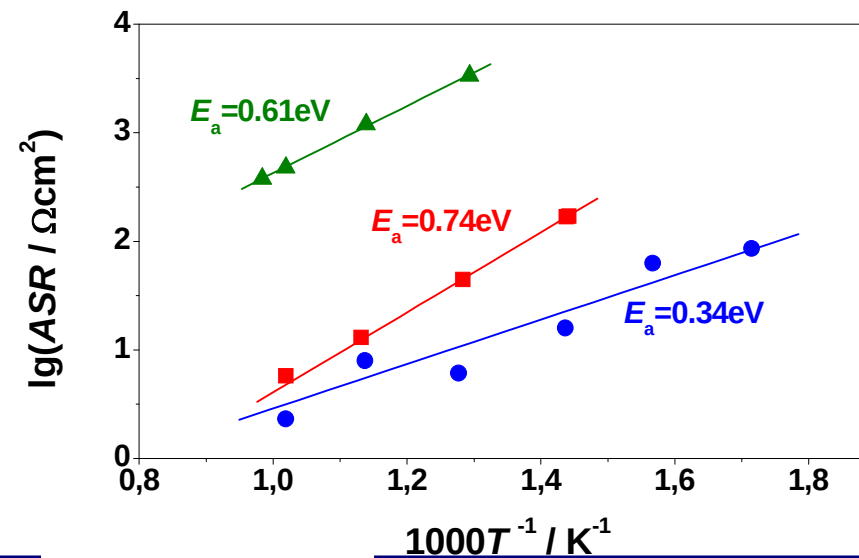
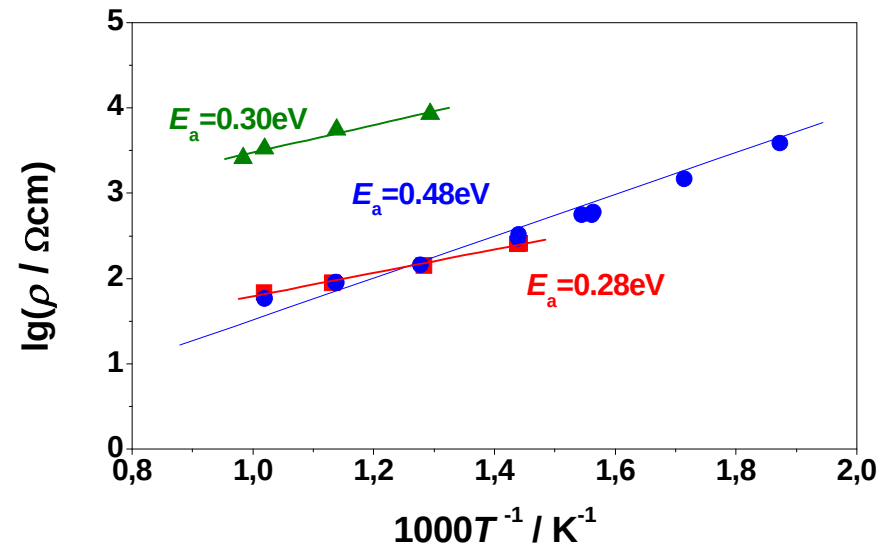
STEM-EDX Analysis



Example – anode BCY/Ni cermet studies

BCY15-Ni/BCY15/BCY15-Ni

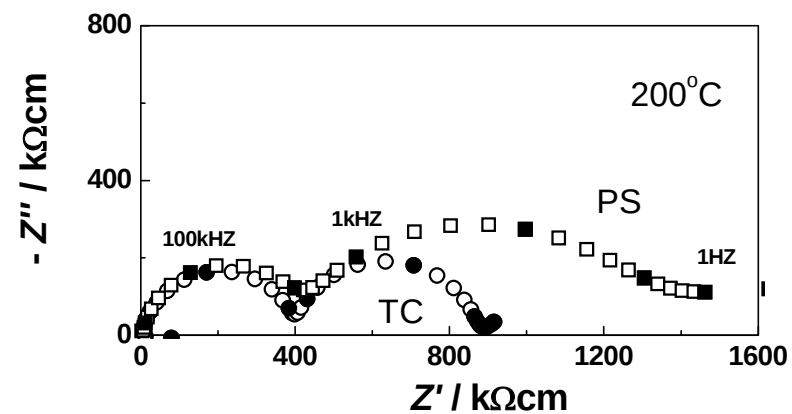
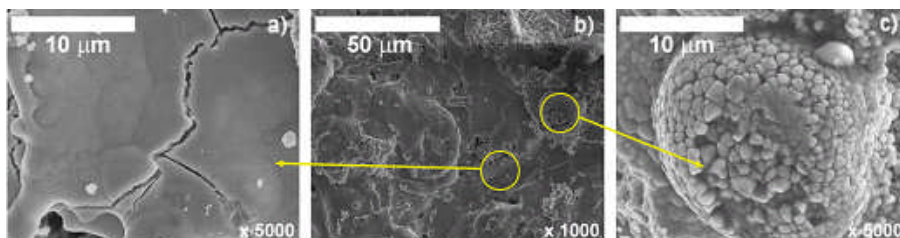
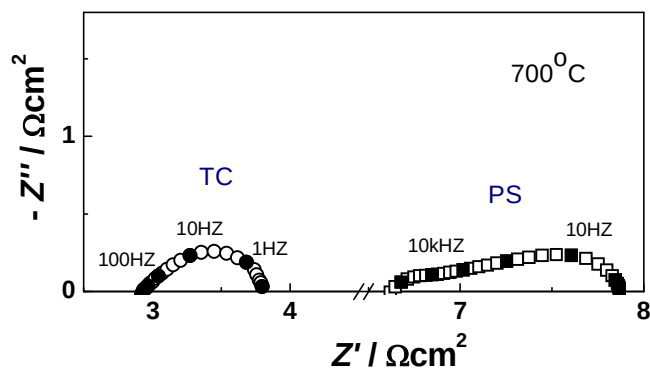
1350°C/2h



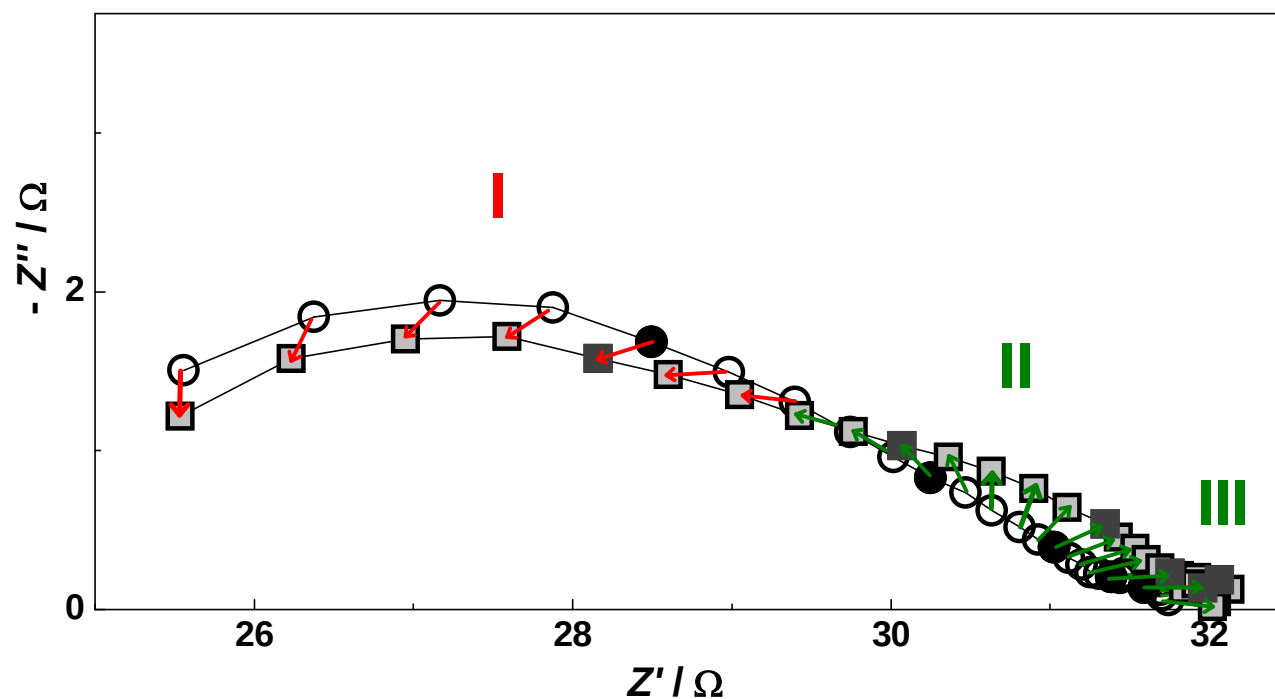
Example – Cathode deposition

➤ Tape Casting/ Plasma Spraying

LSCF48/YDC/LSCF48



➤ Iso-frequency Approach : Cathode/Anode contribution



I – anode

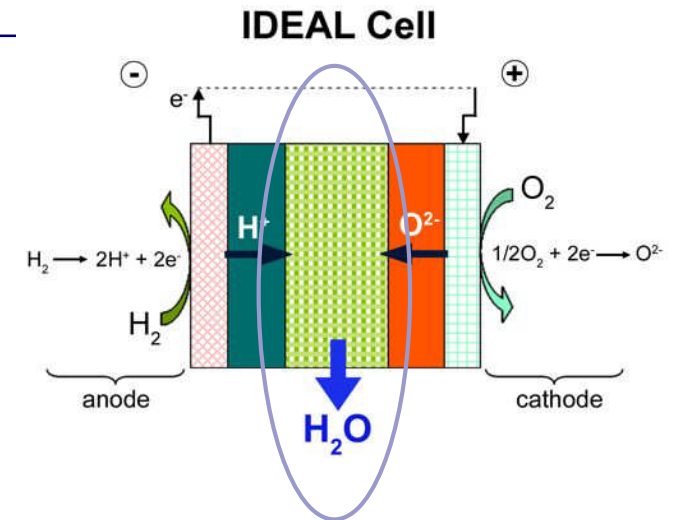
II - cathode

■ 20% H₂ / 20 % O₂

● 20% H₂ / 90 % O₂

➤ **Observability** – searching a phenomenon

- frequency range
- appropriate “working point”
 - I_{DC} (H_2O in CM)
 - temperature
 - Pressure and flow of O_2 and H_2
 - H_2O contents
 - Impurities.

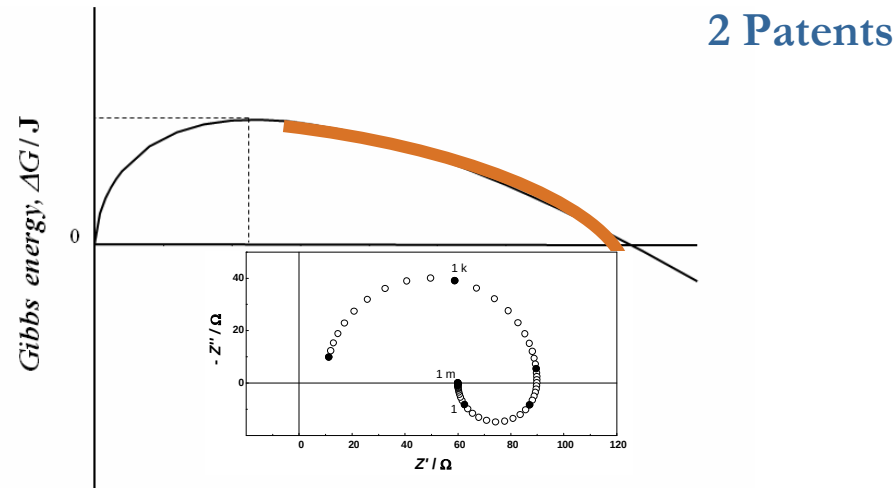
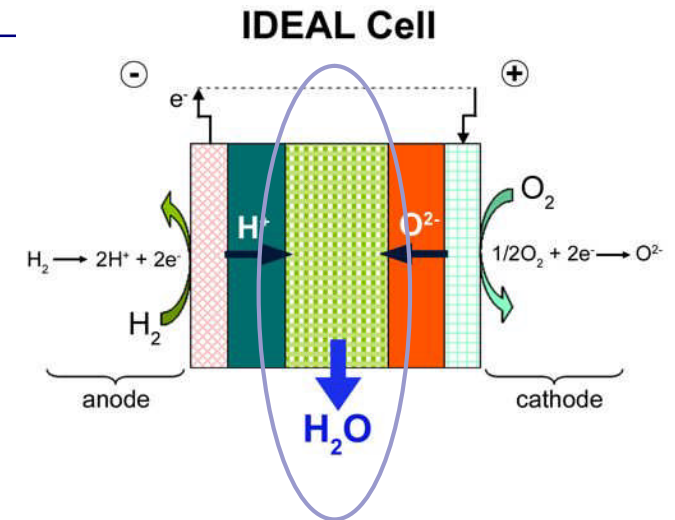


2 Patents

Improved Observability – new phenomenon (water formation)

➤ Observability – searching a phenomenon

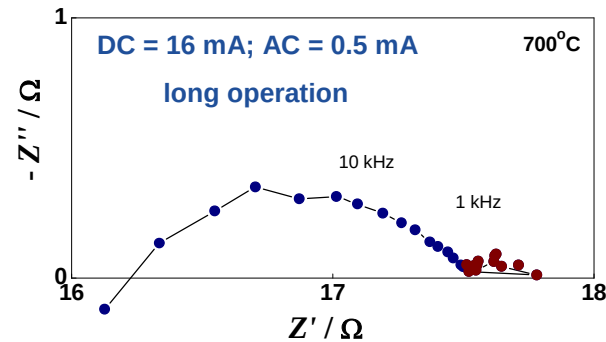
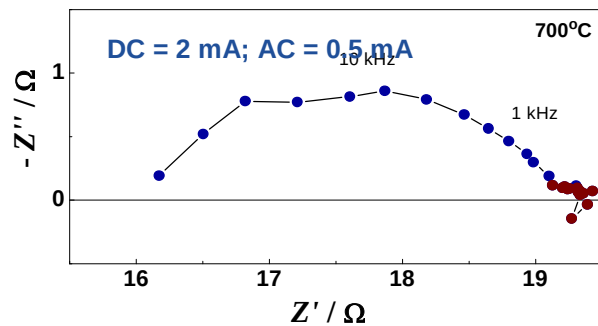
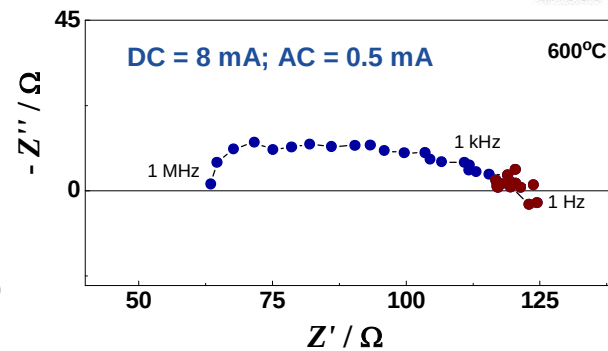
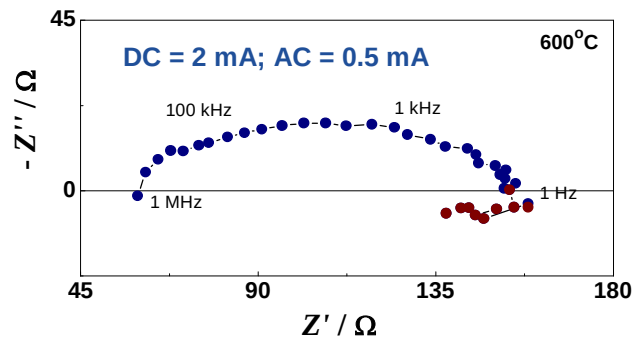
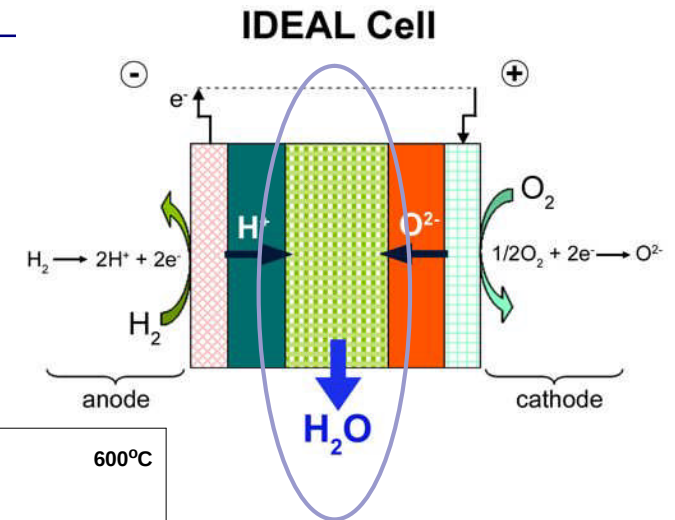
- frequency range
- appropriate “working point”
 - I_{DC} (H_2O in CM)
 - temperature
 - Pressure and flow of O_2 and H_2
 - H_2O contents



Improved Observability – new phenomenon (water formation)

➤ Observability – searching a phenomenon

- frequency range
- appropriate “working point”
- I_{DC} (H_2O in CM)

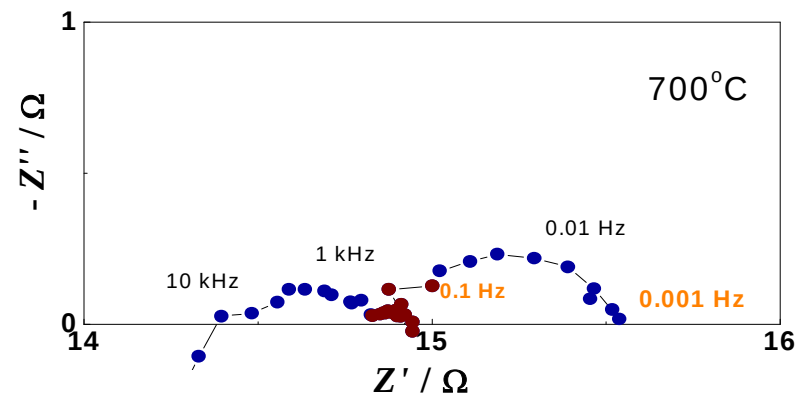
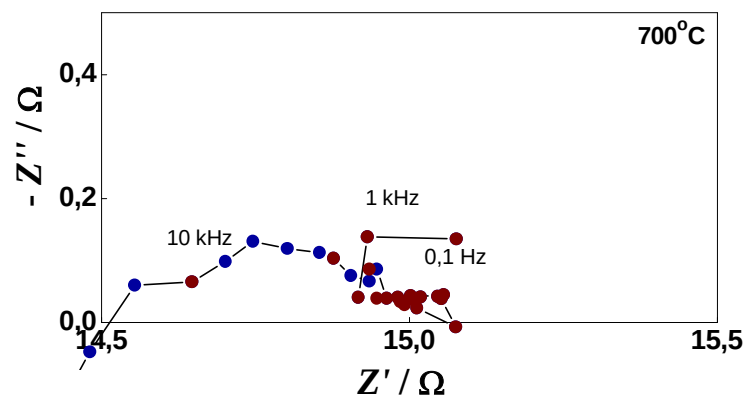
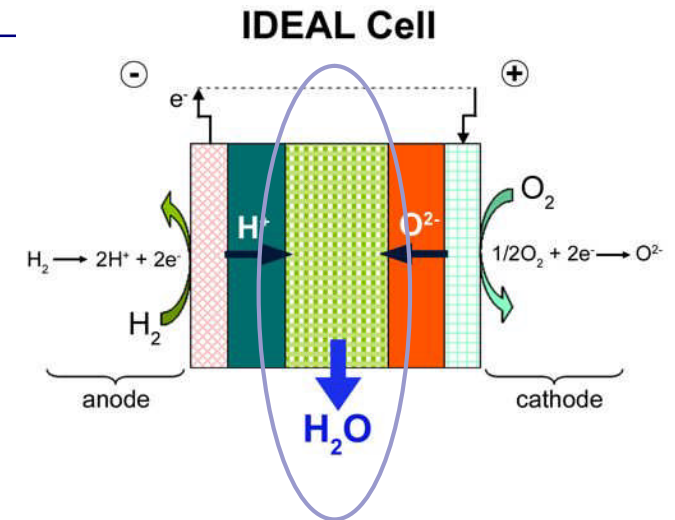


Improved Observability – new phenomenon (water formation)

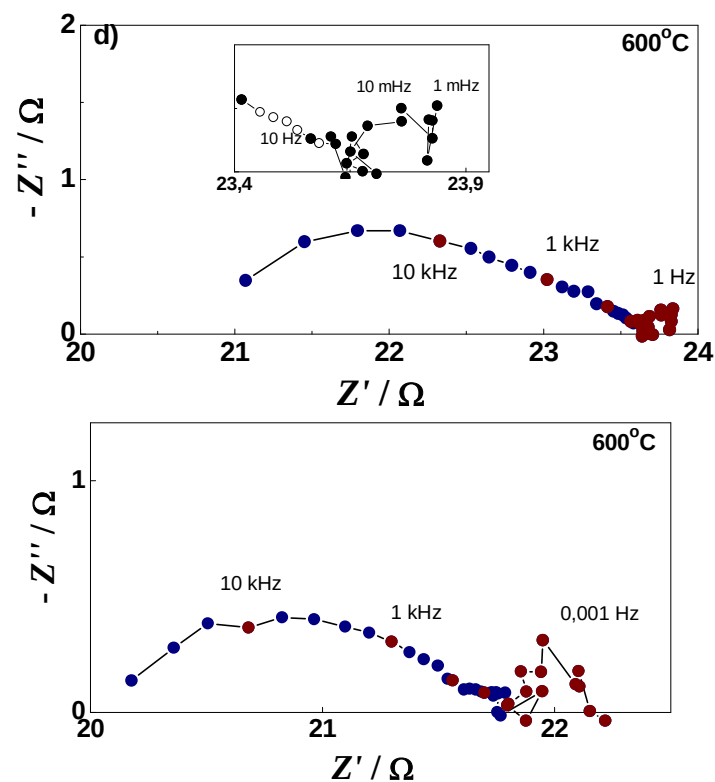
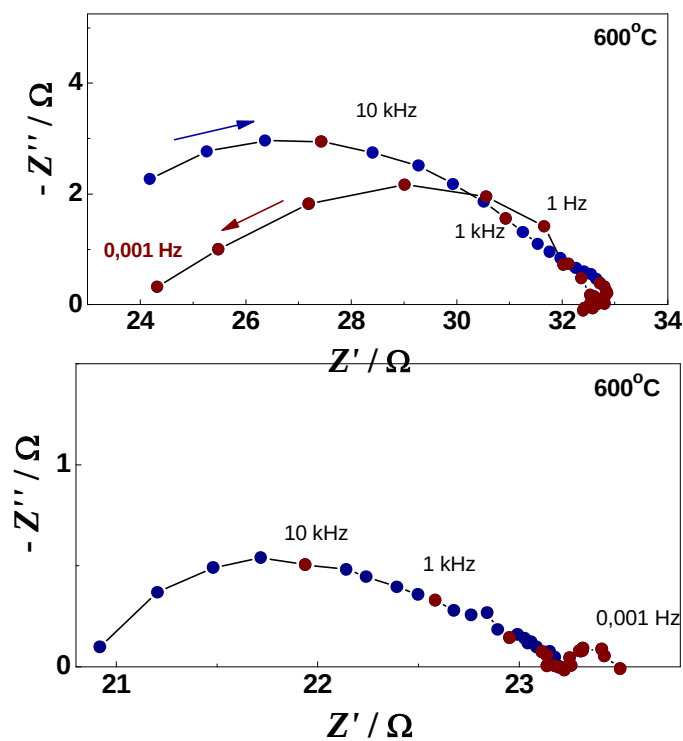
➤ **Observability** – searching a phenomenon

- frequency range
- appropriate “working point”

DC = 16 mA; AC = 0.5 mA (long operation)



- **Water formation**
- **Transport through the CM**
- **Observability** – increase of the l.f. range (1 MHz – 1 mHz)
- **Systematic survey** : DC = 16 mA; AC = 0,5 mA



What can impedance give for SOFC studies

- **Materials and components:**
 - Electrolyte: R_b , $R_{g,b}$, optimization of microstructure
 - Electrodes: R_p , quality of interface, rate limiting stage, quality of deposition;
- **Cells:** performance; separation of components influence, **influence** of water behaviour;
- **Degradation of electrodes - TOMORROW**



Thank you

✓ The people behind:



- Zdravko Stoyanov & Gery Raikova – IEES
- Alain Thorel, Anthony Chesnaud - ARMINES
- Massimo Viviani, Antonio Barbucci, Paola Carpanese. Sabrina Presto, - CNR
- Zeynep Ilhan - DLR

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