



Fuel Cell & Hydrogen Technologies JP

SP2: Catalyst and Electrodes

Borovetz, Bulgaria

June 2nd and 3rd 2014

A step backward for a new approach to understand
and modelling LSM/YSZ composite cathodes

M.P. Carpanese, A. Giuliani, S. Congiu, E. Mercatelli, A. Sanson, A. Bertei, C.
Nicoletta, A. Barbucci

EERA FCH2-SP2 WORKSHOP in frame of EIA10

Bridging experimental and numerical research:

development and optimization of advanced characterization tools – Electrochemical Impedance Spectroscopy



Antonio Barbucci

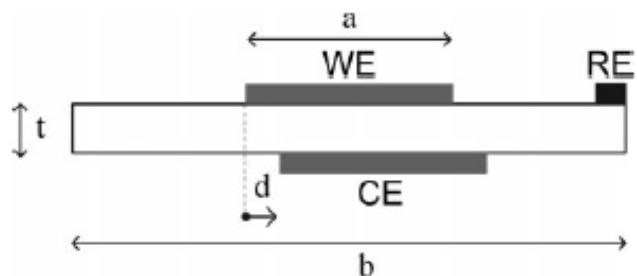
'University of Genoa, Italy

Why this study (1) : cell type and geometries

1st we wish to check some of our data and conclusions obtained in the past with a cell geometry that does not exactly match the suggestion for reliable impedance analyses

Reference electrode position

Electrodes misalignment



M. Cimenti et al., Fuel Cells, 5 (2007) 377-391

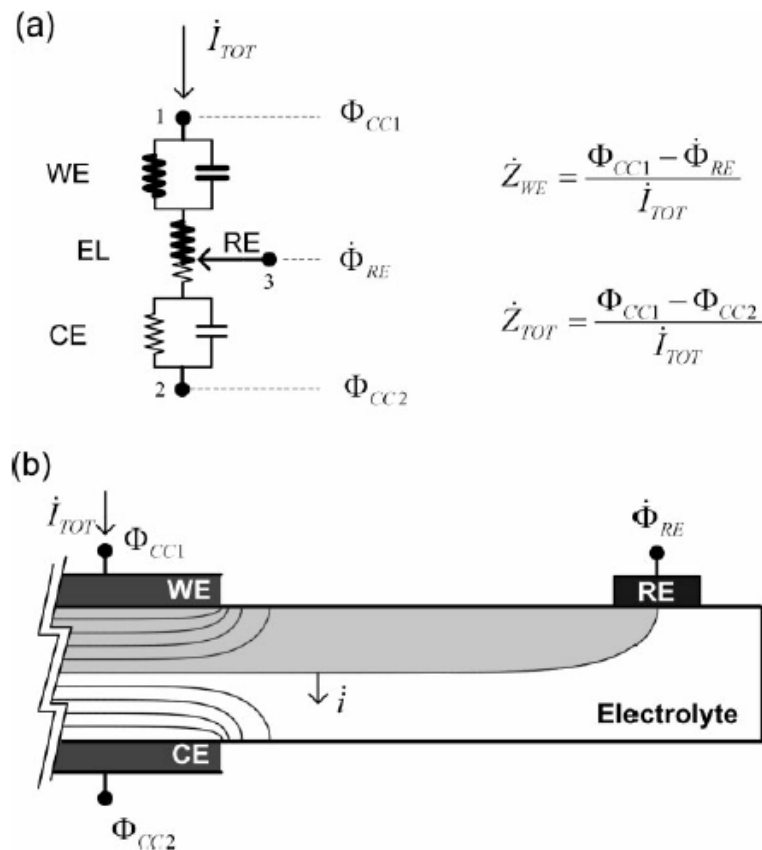


Fig. 2 Schematic (a) showing the network of ideal circuit elements electrically equivalent to a hypothetical SOFC and (b) the three-electrode configuration employed in a planar SOFC.

2nd we want to implement the experimental/theoretical studies we performed on composite cathodes [1, 2, 3],

producing **simulated EIS spectra** on the basis of a theoretical adjustable model.

To do this we need a base of experimental data on a **simplified system** (no composite, no MIEC) for a **validation of a theoretical model and code under study**.

This code [4] is based on the

- i. reconstruction of the electrode structure
- ii. quantification of effective properties (diffusivity, conductivities, ...)
- iii. simulation of the reaction process.

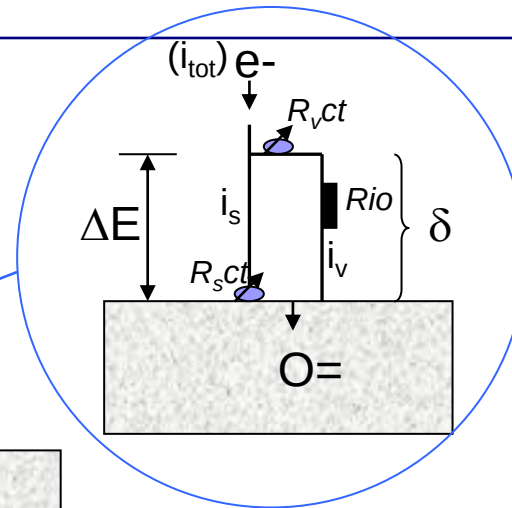
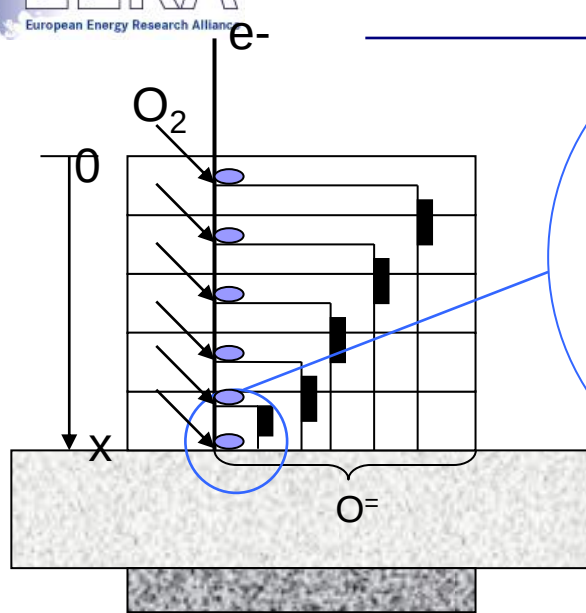
[1] Barbucci A, M.P. Carpanese, M. Viviani, N. Vatistas, C. Nicolella, *J. Appl. Electroch.* 39 (2009) 513–521.

[2] Nicolella C, A. Bertei, M. Viviani A. Barbucci, *Appl Electrochem* (2009) 39:503–511

[3] Bertei A, A. Barbucci, M.P. Carpanese, M. Viviani, C. Nicolella *Chemical Engineering J.* 207 (2012) 167

[4] Bertei A, B. Nucci and C. Nicolella, *Chemical Engineering Science*, 101, (2013), 175-190

Summary: mechanistic model on composite electrodes



-  R_{ct} charge transfer
-  R_{io} ionic resistance
- i_s surface current
- i_v volume current
(subscripts: s = surface; v = volume)

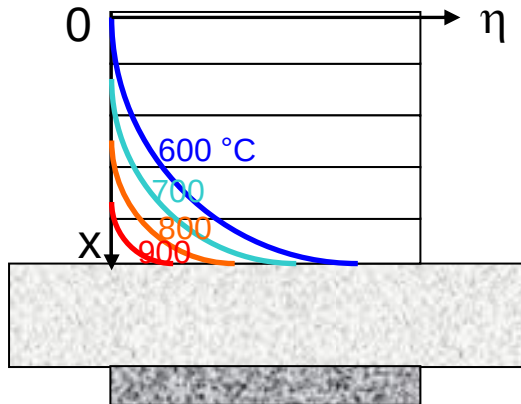
$$\Delta E = \eta_s = \eta_v + R_{io} i_v$$

- A) For **low overpotential** we have an analytical solution using low field Butler-Volmer equation $\eta/i = R_{ct} = RT/Fi_0$;
- B) For **medium-high overpotential** we should solve this equation numerically including the complete Butler-Volmer eq. for η .

$$\begin{aligned} \text{A) } \Delta E &= R_{ct}^s i_s = R_{ct}^v i_v + \rho_{io} \delta i_v A_c/A \\ i_{tot} &= i_s A_s + i_v A_c \\ i_{tot}/A &= \Delta E/R_{tot} \end{aligned}$$

A_c = reactive contact area into volume
 A_s = reactive area at the surface
 A = electrode area

Summary: result of the model and literature



$$R_{tot} = \frac{R_{ct}^s \left(\frac{R_{ct}^v}{a_c \delta} + \rho_{io} \delta \right)}{\left(\frac{R_{ct}^v}{a_c \delta} + \rho_{io} \delta \right) \frac{A_s}{A} + R_{ct}^s}$$

$$A_c = a_c \cdot V = a_c A \delta$$

A_c = reactive contact area into volume

A_c = reactive site per volume unit

A = electrode area

Δ = electrode thickness

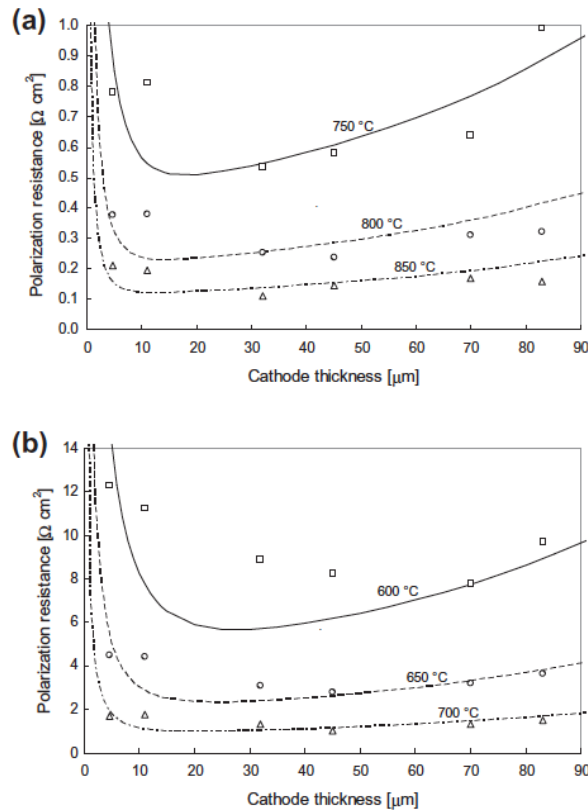
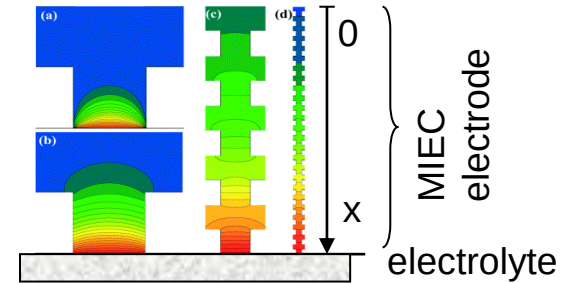


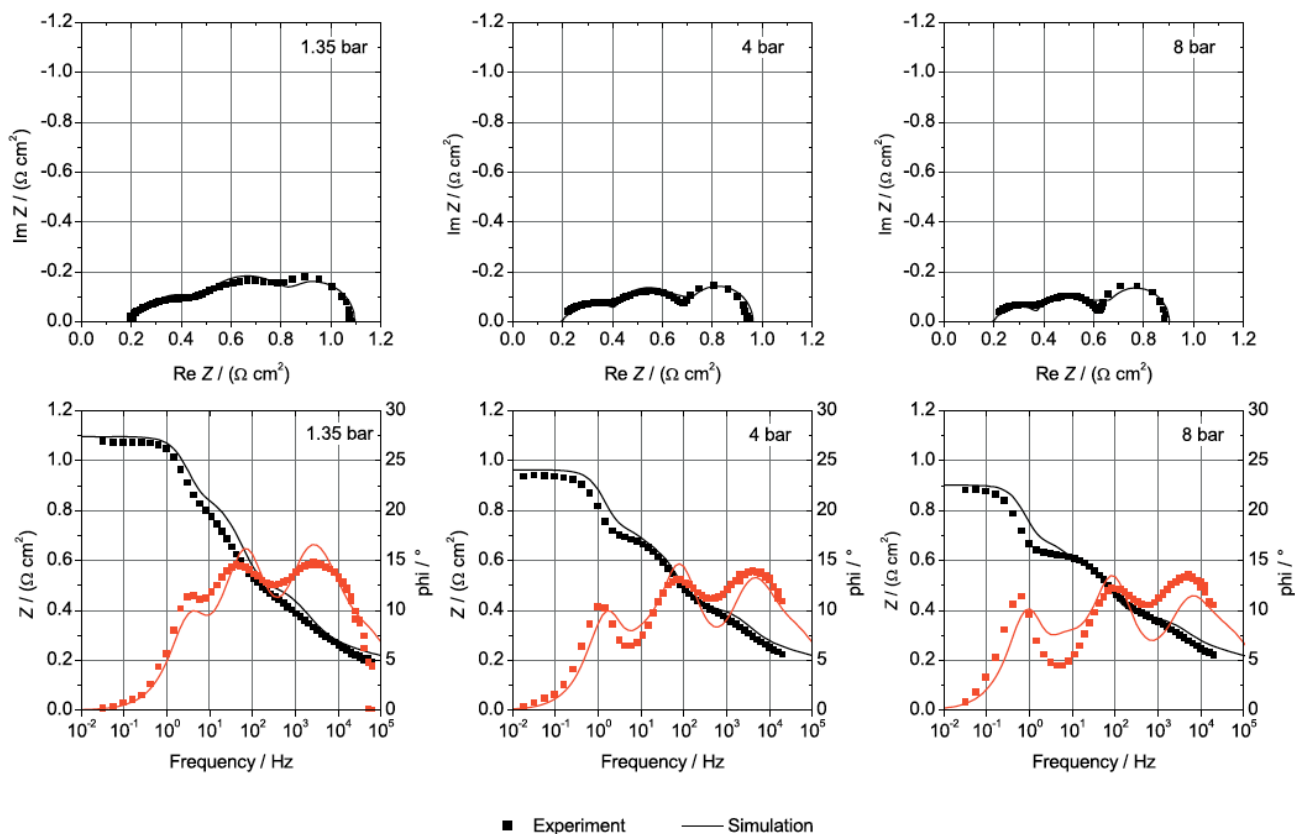
Fig. 3. Simulated and experimental [26] cathode polarization resistance in air as a function of thickness for different operating temperatures.



“For a fast oxygen surface reaction the oxygen incorporation mainly occurs close to the three phase boundary (a); ...If the resistance of the oxygen surface reaction increases, more and more particle layers contribute to the oxygen reduction reaction (c) and for very high values of the resistance (d) the entire cathode is active. ”

Model for MIEC: J. Fleig, J. Maier,
J. Europ. Ceramic Society, 24 (2004) 1343

Summary: Simulation of EIS and experimental (literature)



M. Henke, C. Willich, C. Westner, F. Leucht, J. Kallo, W.G. Bessler, K. A. Friedrich, FUEL CELLS 13, 2013, No. 5, 773–780.

- 3rd Many studies have been performed on pure LSM in the past, the **oxygen reduction reaction is however not clear**. We believe that this is a focal point. Probably not only TPB extension has to be considered for improve electrode performance.
- 4th Component **duration** is one of the main issue for SOFC development. In heavy loads SOFC or SOEC, LSM/YSZ cathode are still considered a good solution for their high chemical stability.

Looking for reliable electrochemical EIS data (electrolyte supported cells)

- **Electrolyte:** YSZ (TZ-8Y Tosoh) sintering 1500°C 1h. Pellets diameter 35 mm, thickness 3 mm.
- **Electrode:** Screen printed (AUR'EL 900, AUR'EL Automation S.p.A) $(\text{La}_{0.8}\text{Sr}_{0.20})\text{MnO}_{3-x}$ (Fuelcellmaterials) (squeegee speed = 0.12 m/s: squeegee load = 4.5 kgF, sintering: 1050 °C and 1150 °C for 2h, electrode thickness 5 μm).
- High precision mask to avoid electrode misalignment.
- **Cell A:** WE-RE distance > 3 x electrolyte thickness
- **Cell B:** WE-RE distance < 3 x electrolyte thickness

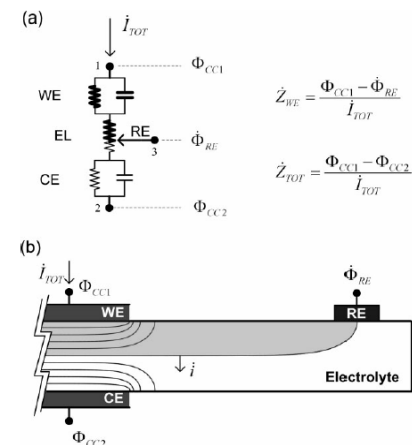
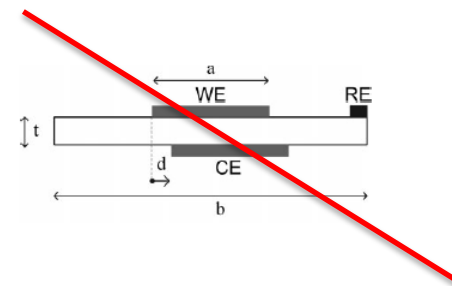
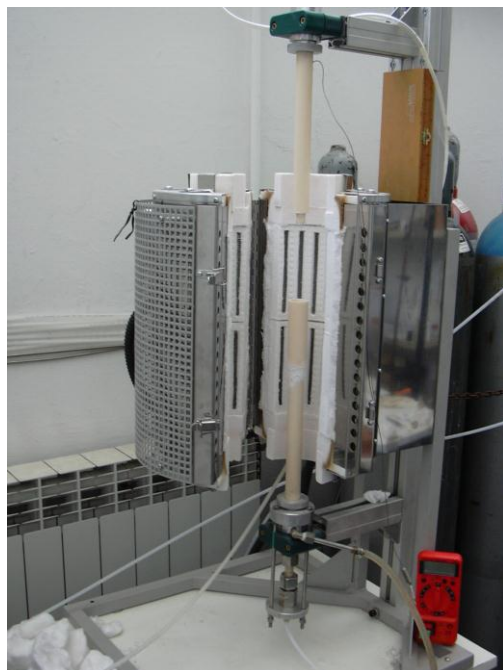


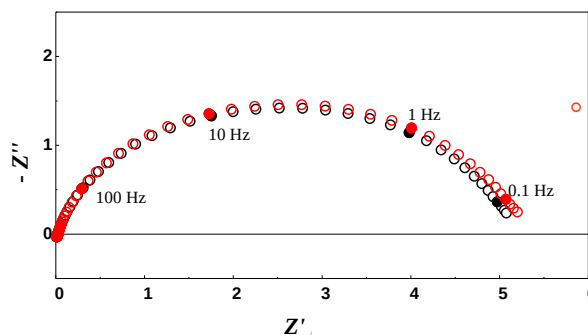
Fig. 2 Schematic (a) showing the network of ideal circuit elements electrically equivalent to a hypothetical SOFC and (b) the three-electrode configuration employed in a planar SOFC.

Looking for reliable electrochemical EIS data



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

- Check of memory effects:

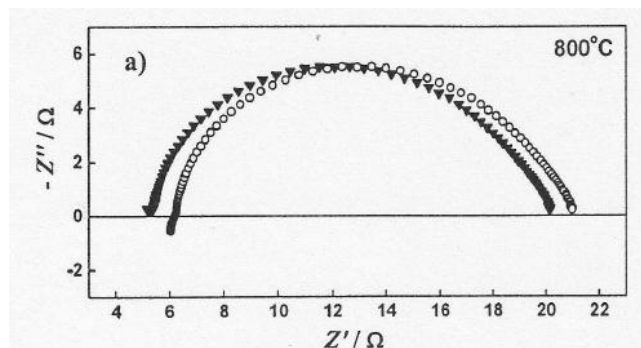


°Up (from high to low frequencies)

°Down (from low to high frequencies)

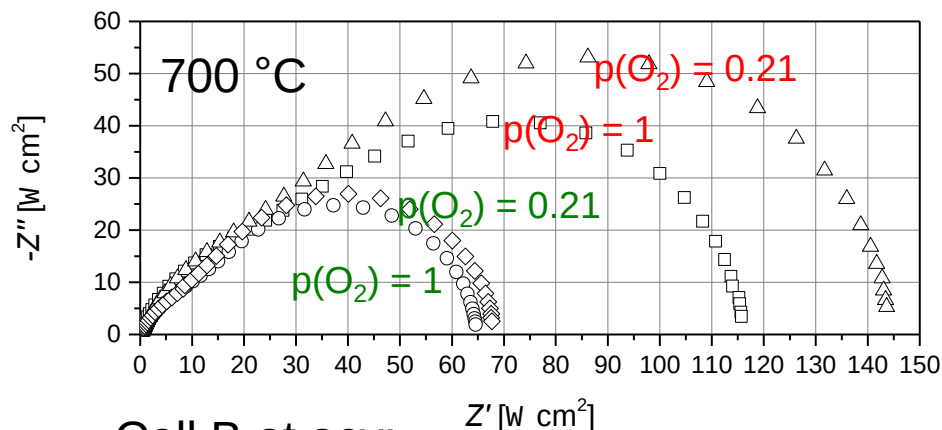
- Frequency density: 10 point per decade

- Correction of data for the parasitic inductance



□ uncorrected data

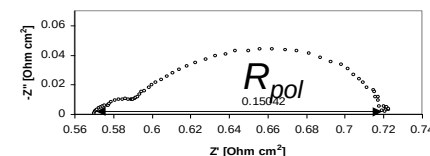
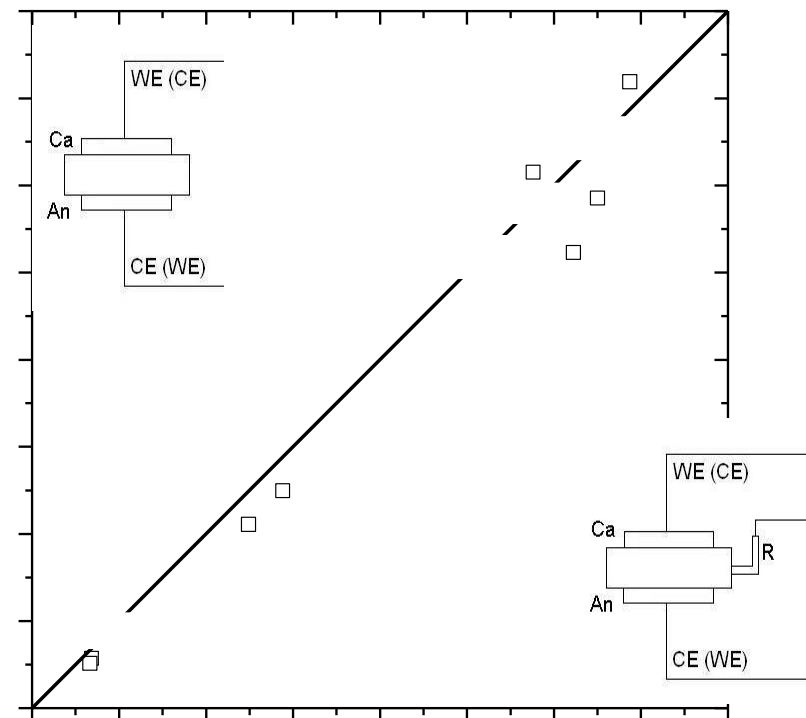
■ data corrected by system inductance



Cell B at ocv:

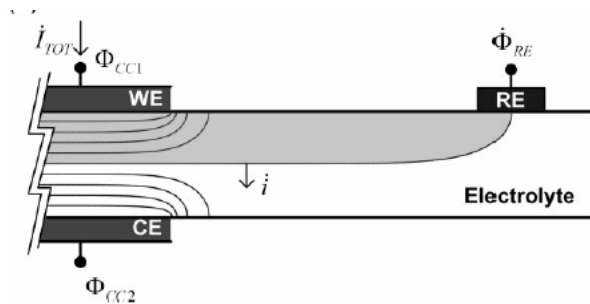
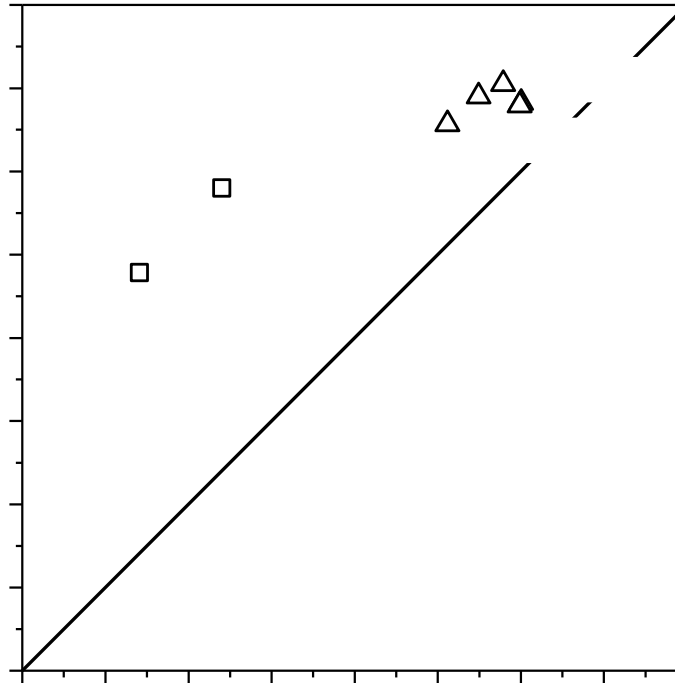
2- and 3-electrode configurations

1. Quite good agreement in this cell geometry (CELL B) at ocv and low η
2. Quite good symmetry of the cell; equal polarisation resistance of the two opposite electrodes
3. Characteristic shape of the frequency dispersion at ocv and low η



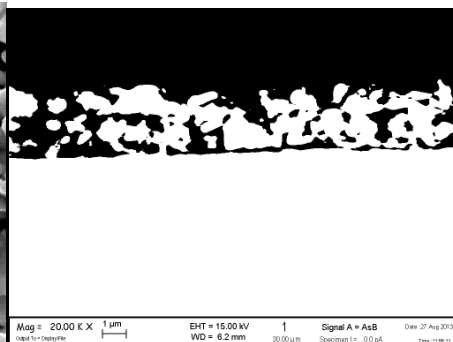
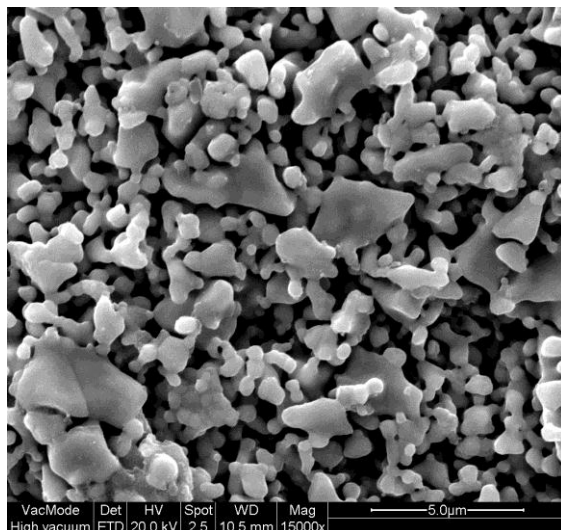
Example of R_{pol} evaluation

Results: Cell A and B geometries in comparison (3-electrode configuration)

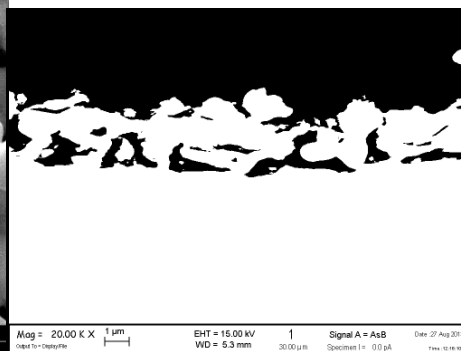
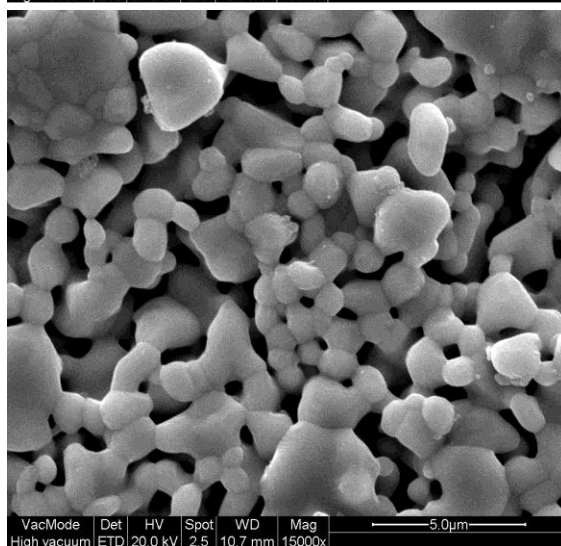


1. Quite good agreement in this cell geometry (CELL A and B) at ocv and low η
2. Cell A and B Deviations at higher η

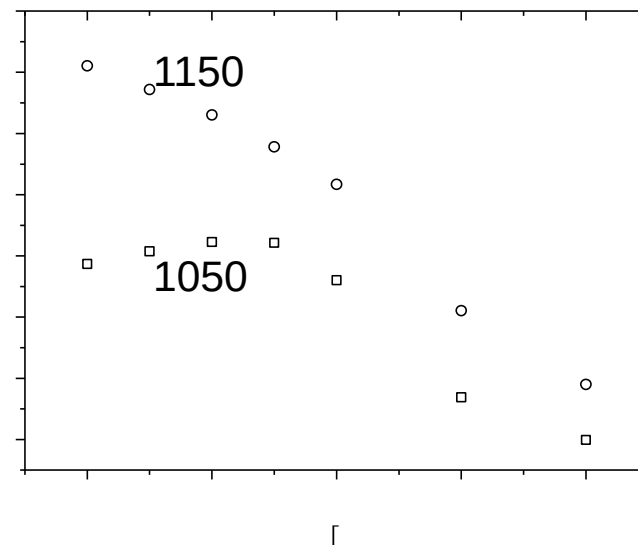
Electrode sintered at 1050 or 1150 °C



Porosity₁₀₅₀ = 49%
Avg particle size = 0.7 µm



Porosity₁₁₅₀ = 34%
Avg particle size = 2 µm

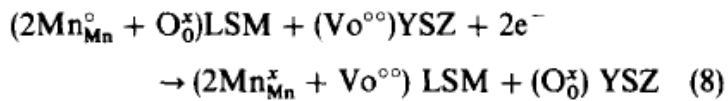


R_{pol} not normalised.
At high η the global reaction kinetic of the two electrodes get closer

From surface to bulk transport

(activation of a second path for reaction)

(b) In the overpotential range corresponding to the reduction of the LSM (around point C in Fig. 10), oxygen vacancies are created in the electrode material according to the following global electrode equation:

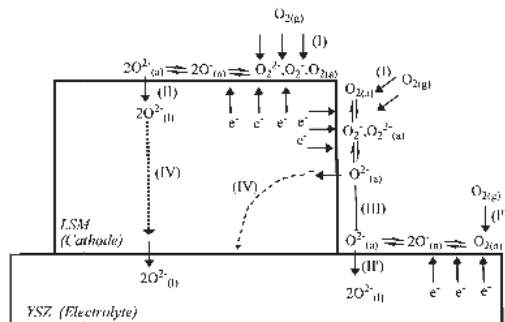


where $\text{Mn}_{\text{Mn}}^{\circ}$ represents a Mn^{4+} on a regular manganese crystallographic site and $\text{Mn}_{\text{Mn}}^{\times}$ a Mn^{3+} on the same site. The peculiar behavior observed in this transition zone could be associated with a significant contribution of this reaction to the overall current.

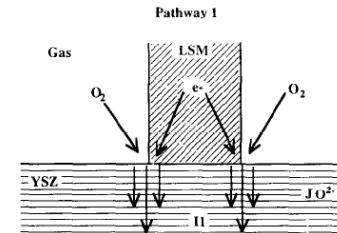
E. Siebert et al, El Acta 40 (1995) 1741
(with dense pin shaped LSM electrode)

V. Brichzin et al, Solid state Ionics 152 (2002) 499
(with dense circular microelectrode)

S.B Adler Chem Rew 104 (2004) 4821



low η



high η

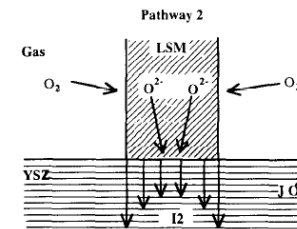
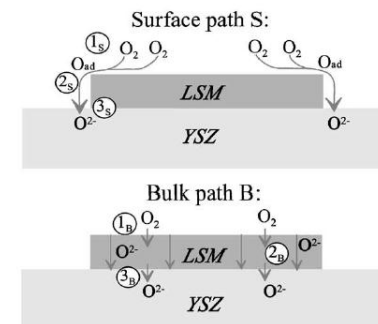


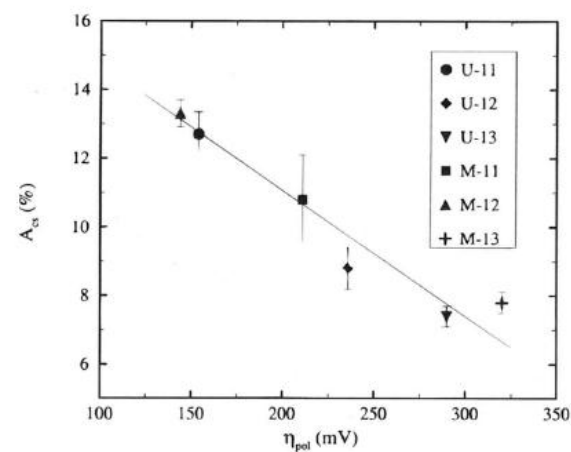
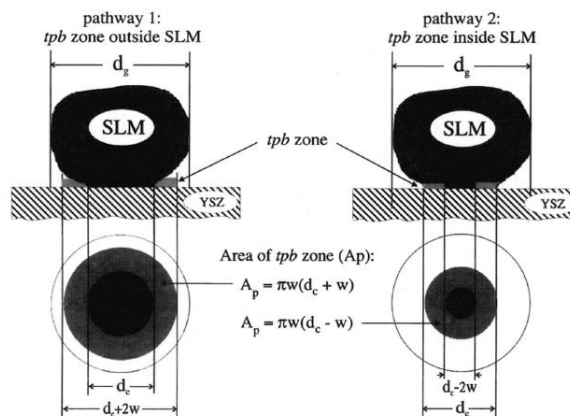
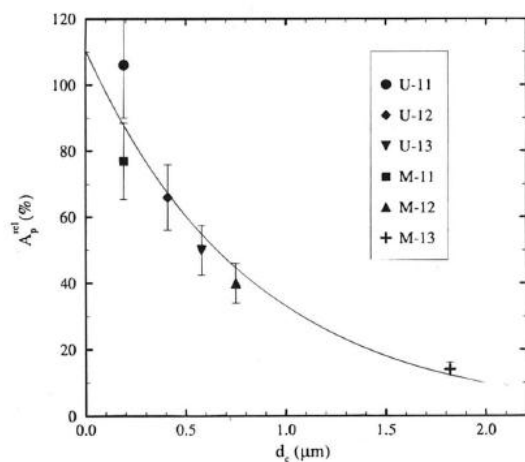
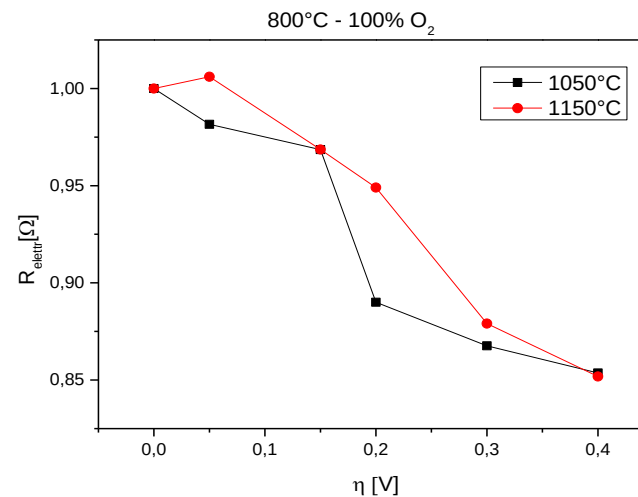
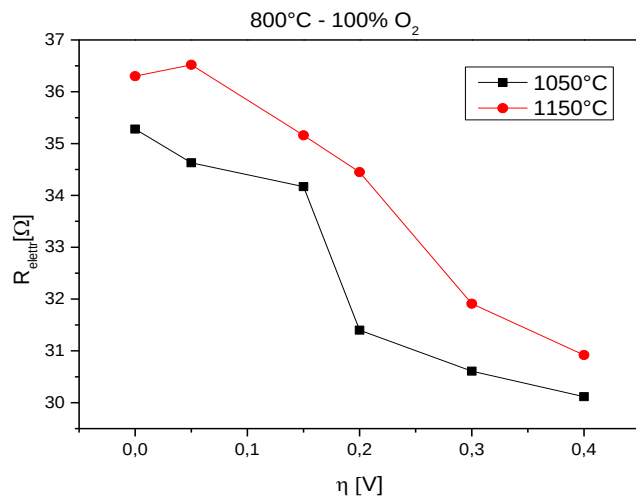
Fig. 13. Diagram of the oxygen reactions at an LSM-YSZ



H.T. Chen et al Langmuir 27 (2011) 6787
($\text{La}_{0.75}\text{Sr}_{0.25}\text{MnO}_{3-x}$ computational mod)

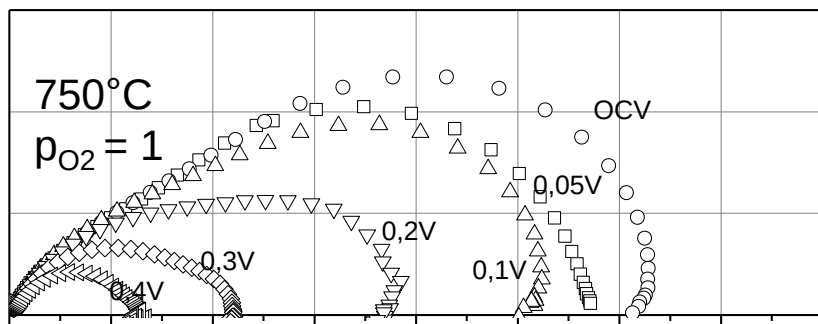
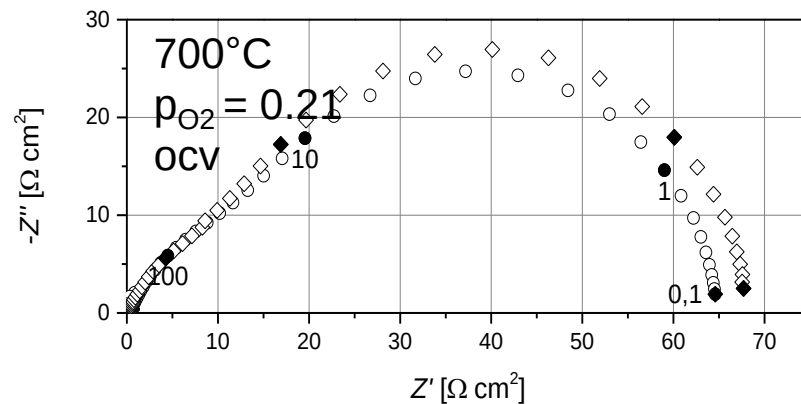
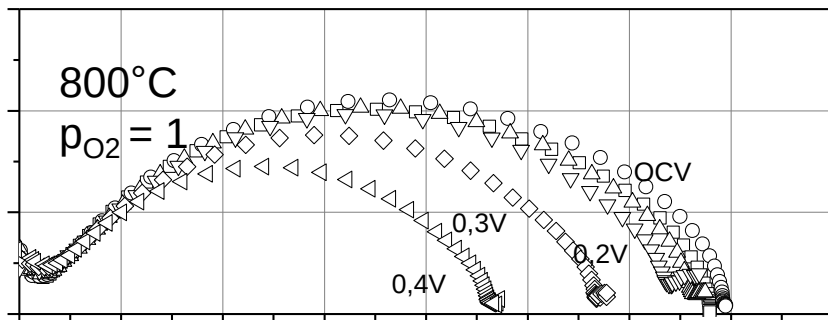
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From surface to bulk, looking at electrolyte resistance



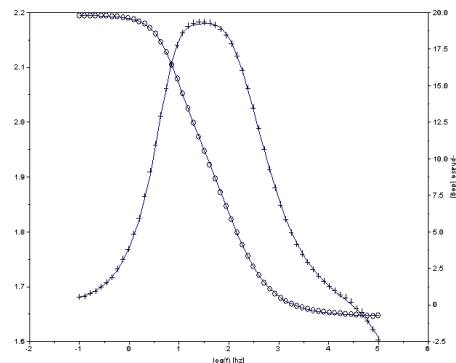
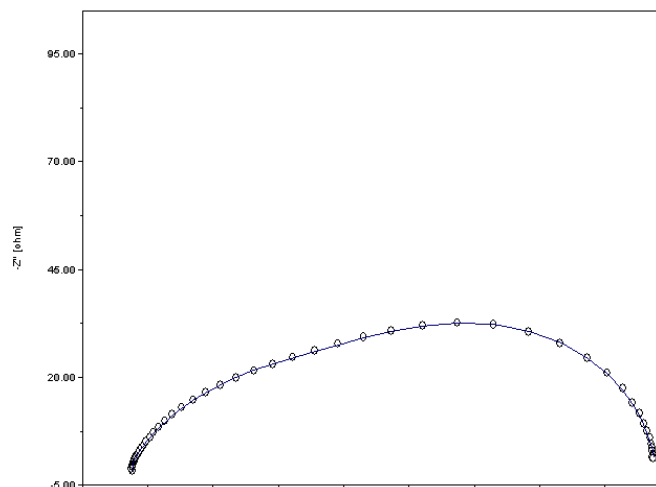
F. H. van Heuveln, H. J. M. Bouwmeester, F. P. F van Berkela J. Electrochem. Soc.144 (1997) 126

Some obtained Nyquist plots



Fitting analysis: Voigt type model

$$R_1(R_2Q)(R_3C)$$

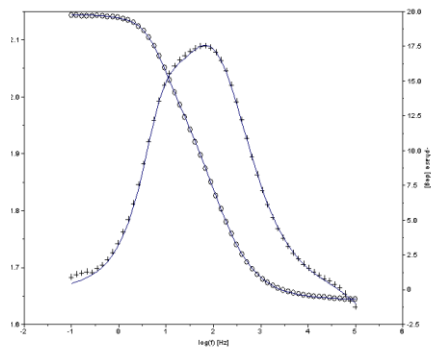


Good fitting with a widely used circuit for SOFC cathode*:

R_1 electrolyte resistance

(R_2Q) low frequency arc: to be ascribed

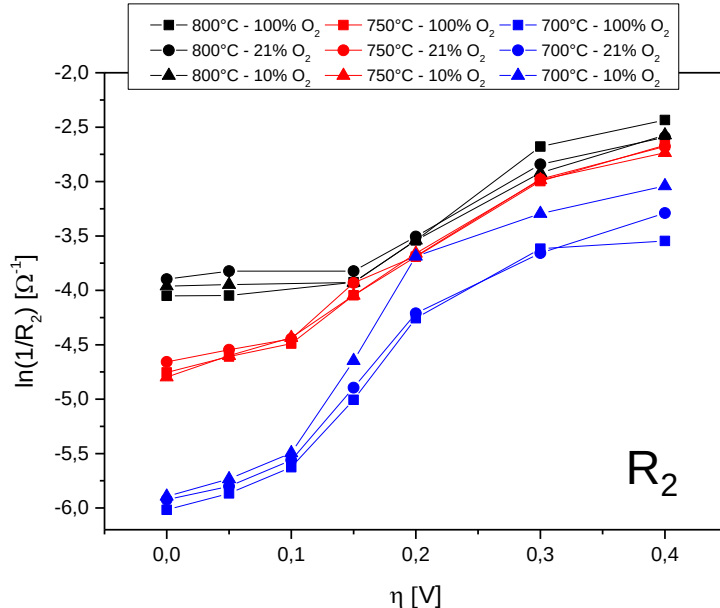
(R_3C) high frequency arc: to be ascribed



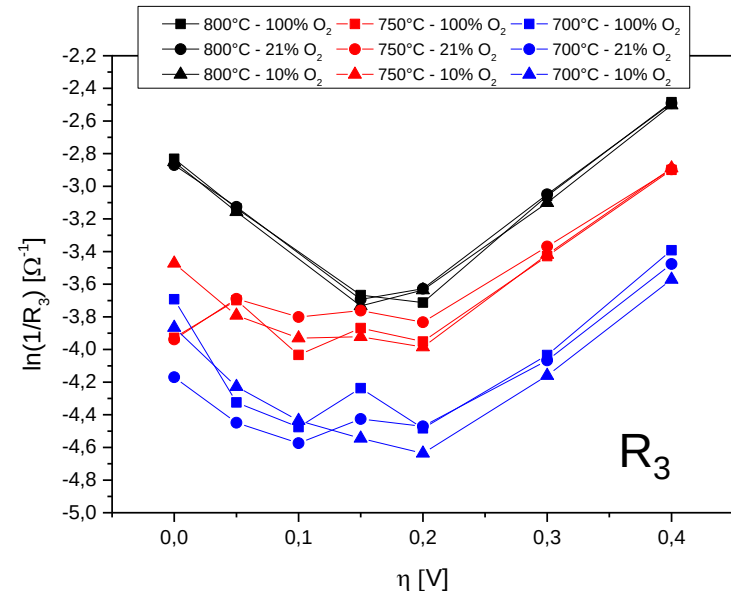
★

F. van Heuvelin, H. Bouwmeester J Electrochem. Soc. 144 (1997) 144
J. Fleig, H.R. Kim, J. Jamnik, J. Maier Fuel Cells 5 (2008) 330
S. Gamble, J.T.S. Irvine Solid State Ionics 192 (2011) 394

Fitting analysis $R_1(R_2Q)(R_3C)$



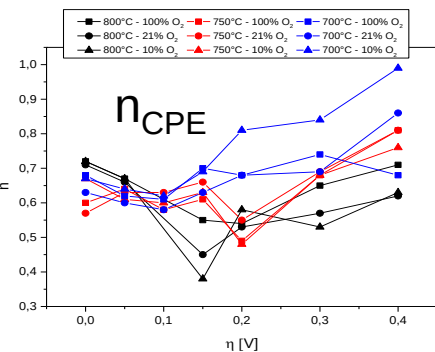
R_2 (low frequency arc)
shows a dependance on the
applied overpotential



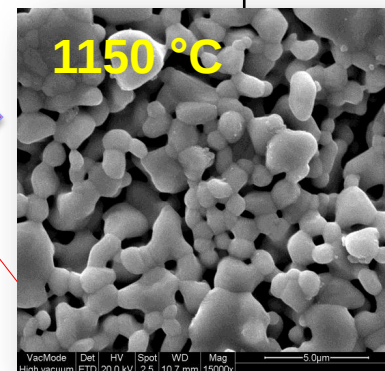
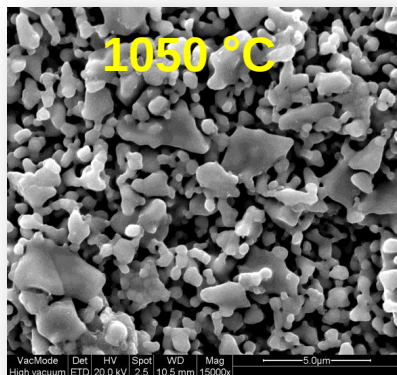
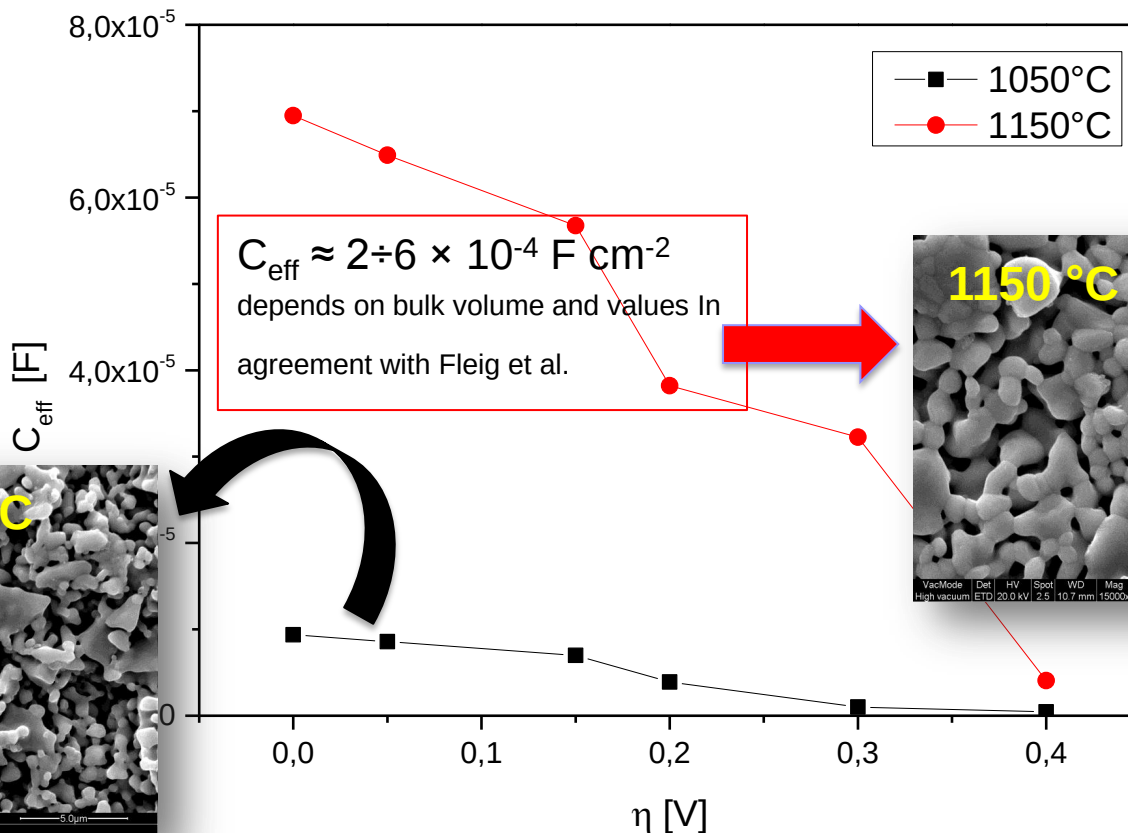
$\ln(1/R_3)$ shows a linear
dependance on η at medium-high
overpotentials

Effective capacitance of the R₂Q element

800°C - 21% O₂



Average n_{CPE} values 0,6

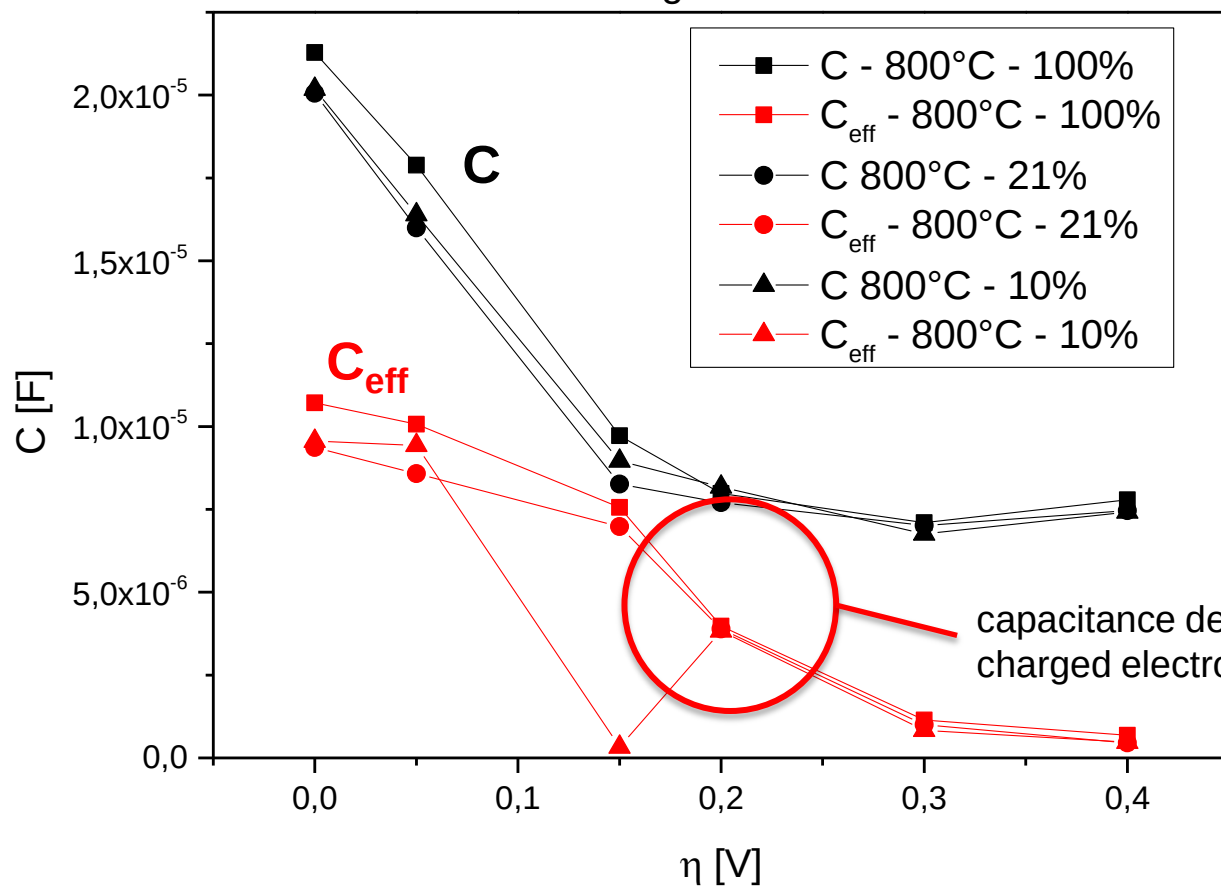


B. Hirschorn et al., *El Acta*, 55 (2010) 6218-6227
J. Fleig et al., *Fuel Cells*, 5 (2008) 330-337

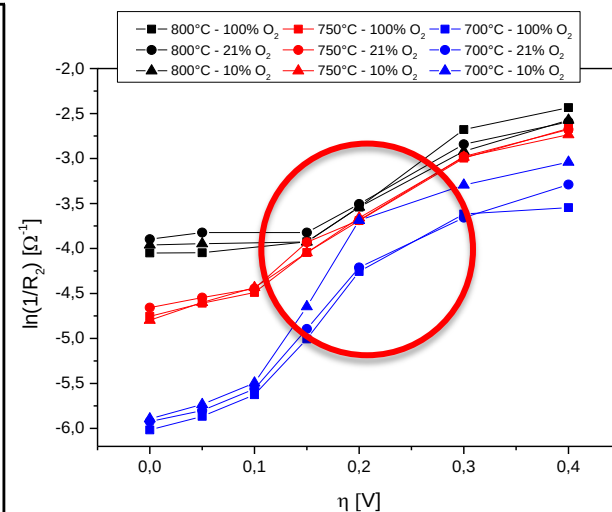
$$C_{eff} = Q^n R_2^{\frac{1-n}{n}}$$

Comparison between the effective and the electrostatic capacitance:

$$R_1(R_2Q)(R_3C)$$

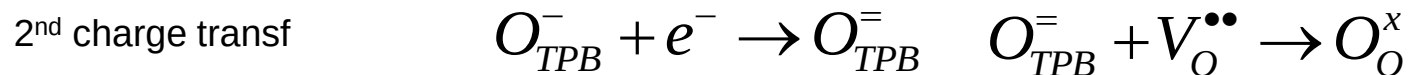
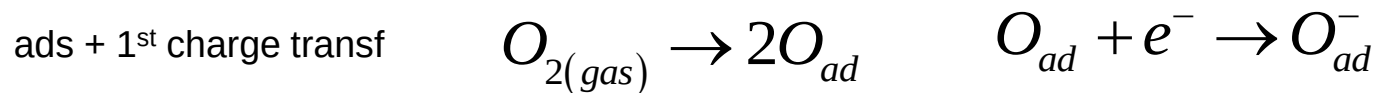


capacitance decrease due to faster charged electroactive specie transport

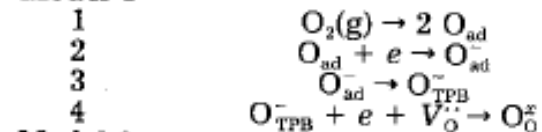


Overall reaction path: $O_{2(gas)} + 4e^- + 2V_O^{\bullet\bullet} \rightleftharpoons 2O_O^x$

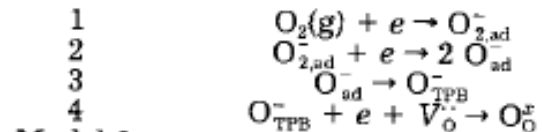
Possible reaction steps: J.D. Kim et al. *Solid State Ionics* 143 (2001) 379



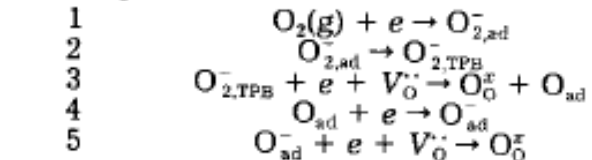
Model 1



Model 2

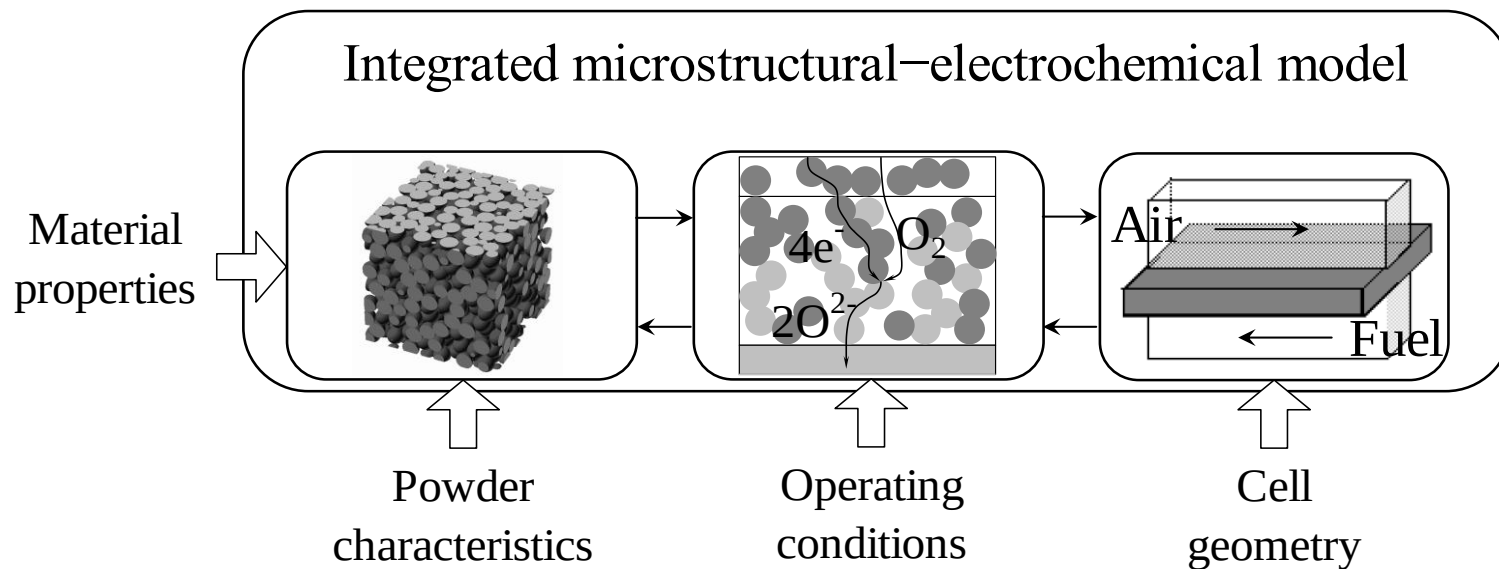


Model 3



F. H. van Heuvelin, H. J. M. Bouwmeester
J Electrochem. Soc., 144 (1997) 144

The prediction of transport properties and electrochemical performance in SOFC electrodes, is the approach we look at for helping the experimental interpretation.



1st. numerical construction of the electrode structure using a sedimentation algorithm, based on data extracted from morphological observation.

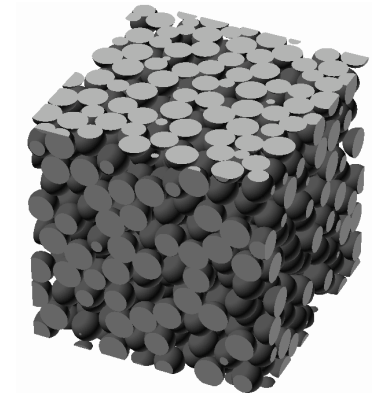
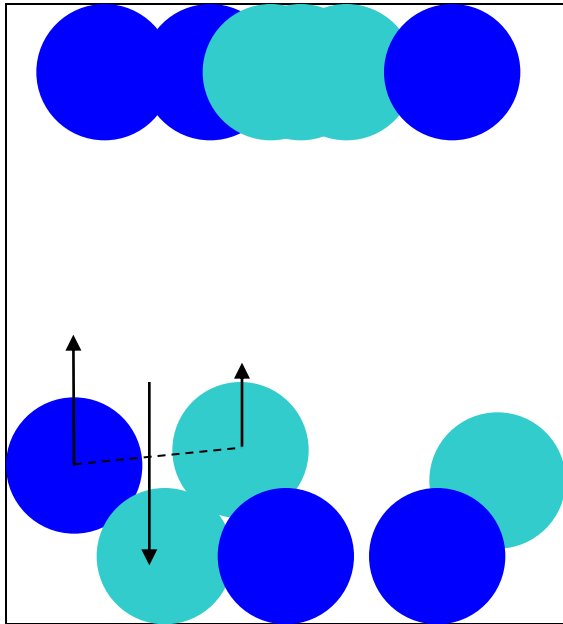
Simulated procedure

1 – Drop

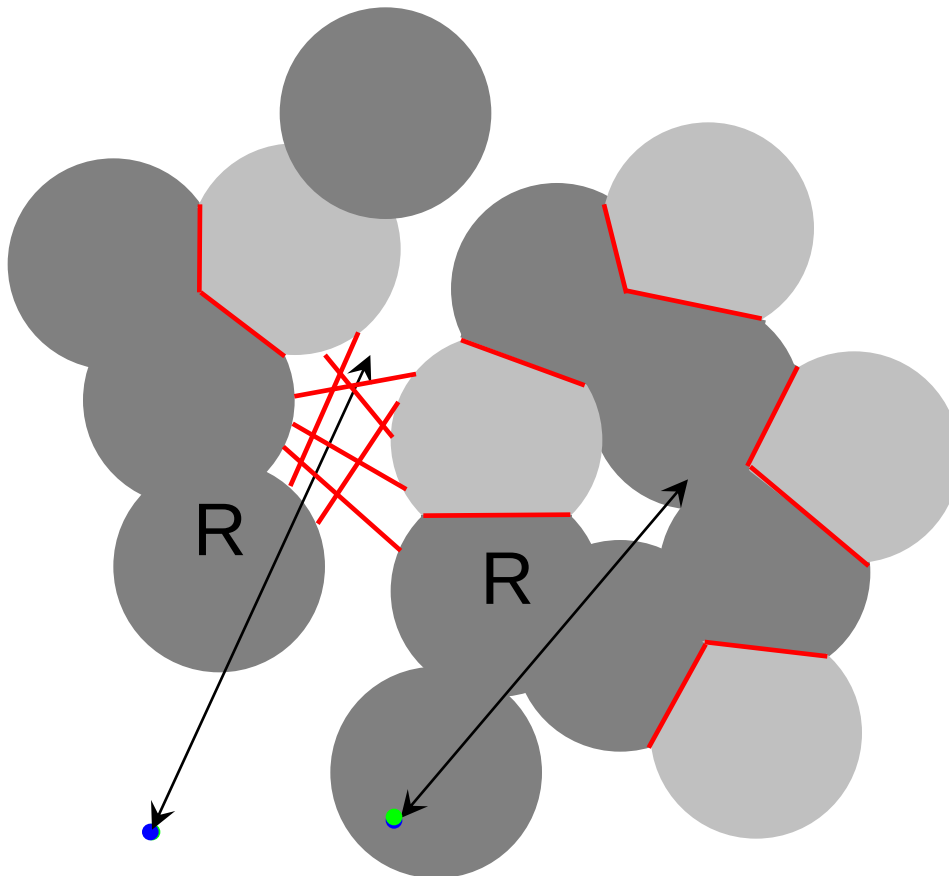
2 – Roll

3 – Stability

4 – Sintering



2nd. random walk Monte Carlo simulation used for calculation of effective properties (gas diffusivity, conductivities, TPB length).



$$D^{\text{eff}} = \langle R^2 \rangle / (6\Delta t)$$

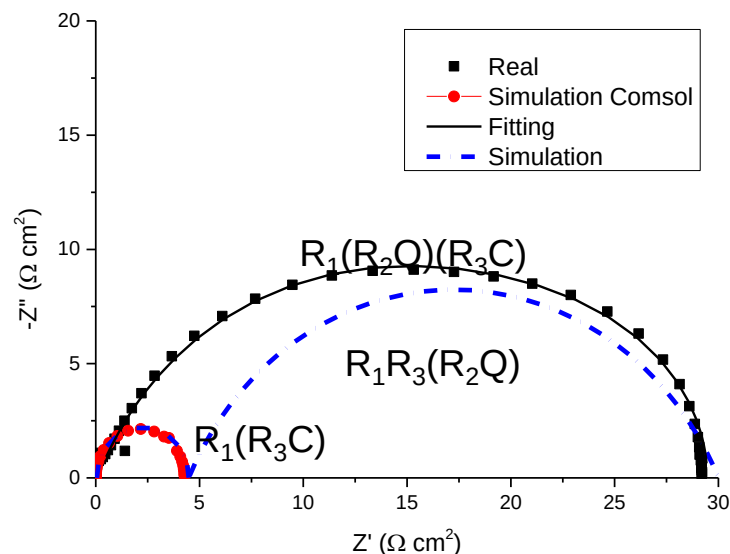
$$\sigma^{\text{eff}} = \langle R^2 \rangle / (6\Delta t)$$

TPB length

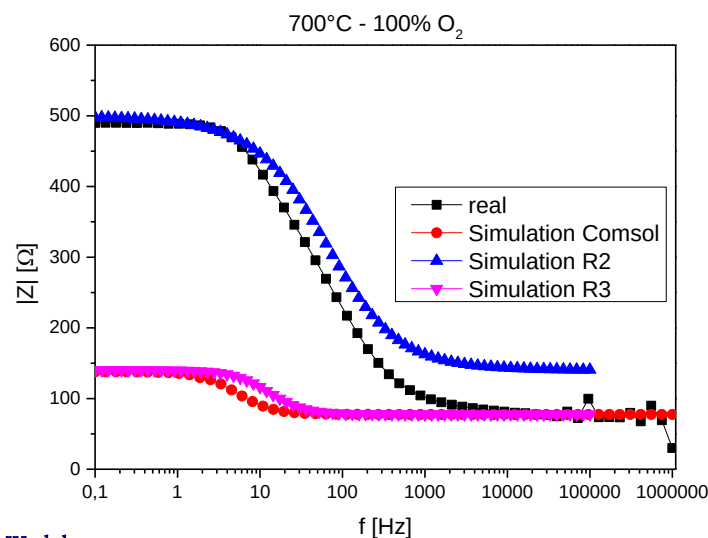
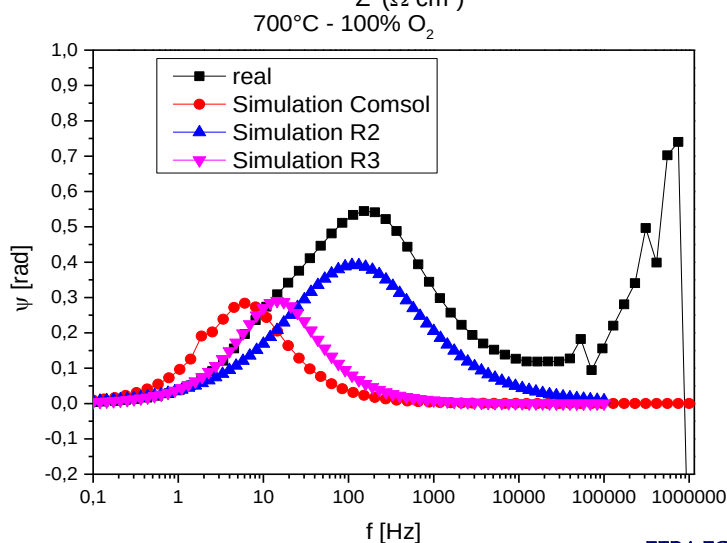
Pore size

EIS simulation

700°C - 100% O₂ - OCV



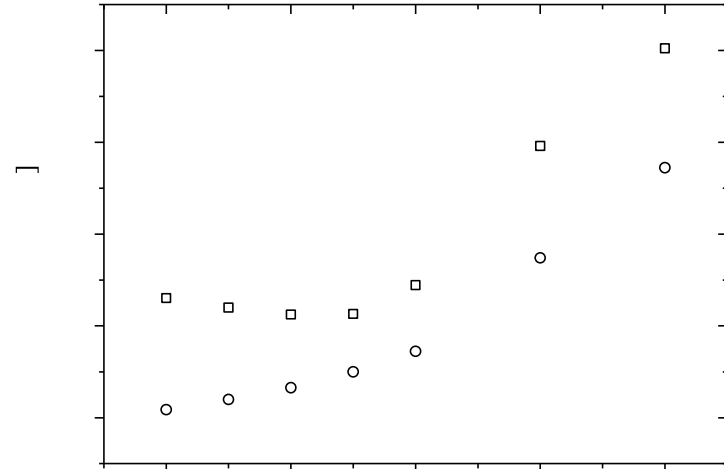
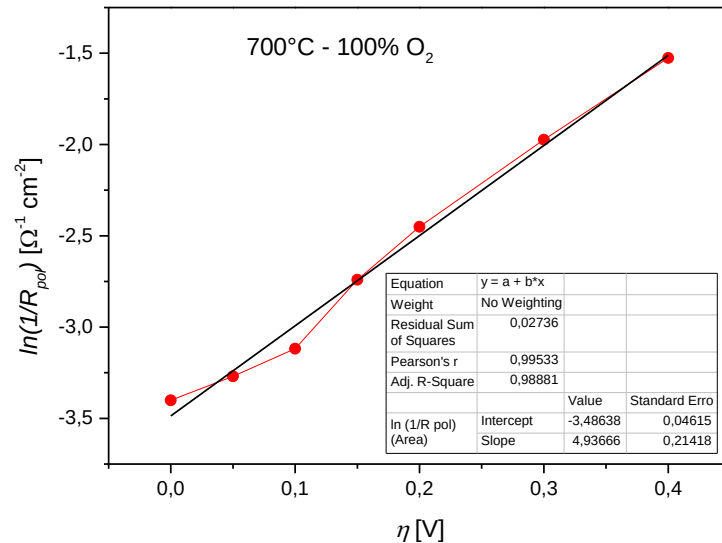
3rd. Application of a model able to produce simulated impedance spectra, which considers the influence of some parameters (external molar fraction of oxygen, working temperature...).



- The presented analysis is still preliminary and needs further validation, possibly also by methodology based on non arbitrary choices (e.g. DIA, ...).
- The code for the EIS simulation is under implementation, to take into account adsorption and surface or bulk transport of the electroactive specie.
- The results presented and the literature demonstrate that LSM is a complex system and we are still far to clearly understand its behaviour.
- This last consideration makes us think that there is room for further improvements of LSM/YSZ electrodes, that till now have been optimised mainly looking at TPB length.

it will be great that each presentation covers points like for example:

- Current problems and challenges
- Role of the EIA for advanced characterization of catalyst/electrode and what kind of information can give for models development and validation
- What we need to improve to develop further the experimental validation using EIS as an advanced characterization technique
- Anything else that you consider relevant to discuss...



Trend of $\ln(R_{pol})^{-1}$ versus overpotential at 800°C and $P(O_2) = 1\text{bar}$, square sample sintered at 1050°C, circle sample sintered at 1150°C.

If activation control

B-V eq hold:

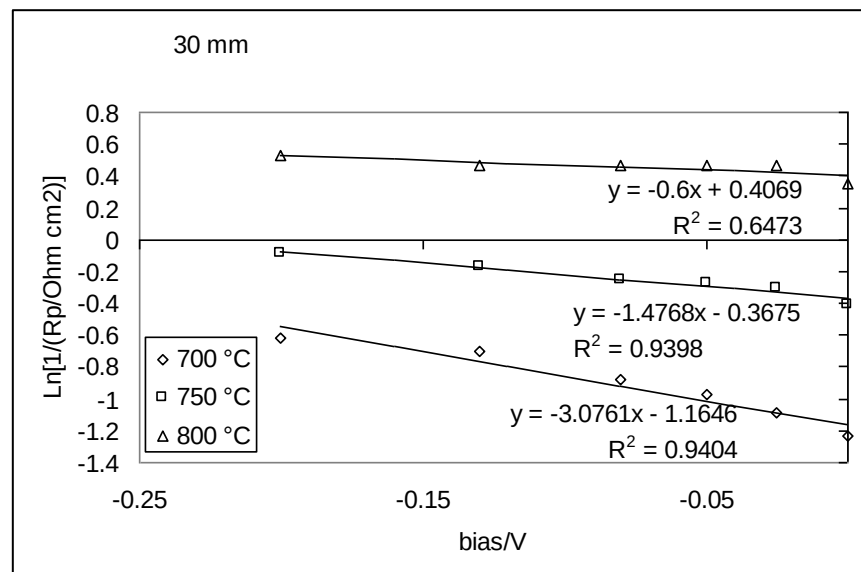
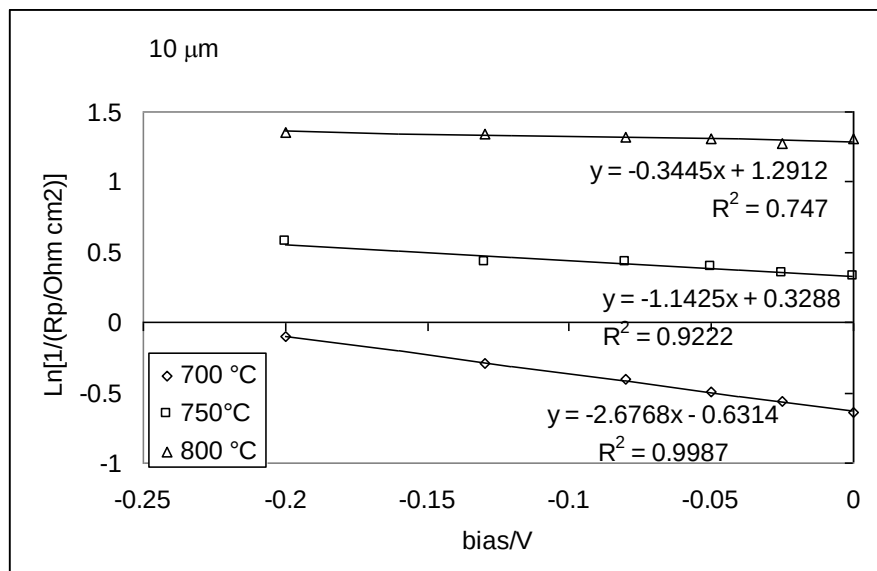
$$i = i_0 \left[\exp\left(\frac{\alpha_a n F}{RT} \eta\right) - \exp\left(\frac{-\alpha_c n F}{RT} \eta\right) \right]$$

then:

$$R = \frac{d\eta}{di} \Rightarrow \frac{1}{R} = \frac{di}{d\eta} = -i_0 \left(-\frac{\alpha_c n F}{R_g T} \right) \exp\left(-\frac{\alpha_c n F \eta}{R_g T} \right)$$

$$\ln \frac{1}{R} = \ln \frac{i_0 \alpha_c n F}{R_g T} - \frac{\alpha_c n F \eta}{R_g T} = A - B \eta$$

Composite cathode LSM/YSZ



normalisation
of raw data
play a role?

