



Fuel Cell & Hydrogen Technologies JP

SP2: Catalyst and Electrodes

Borovetz, Bulgaria

June 2nd and 3rd 2014

Analysis of superposed relaxation processes in
EIS spectra of High Temperature Fuel Cells in
order to individualize degradation phenomena

EERA FCH2-SP2 WORKSHOP in frame of EIA10

Bridging experimental and numerical research:

development and optimization of advanced characterization tools – Electrochemical Impedance Spectroscopy



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- Introduction to EIS in HTFCs
- Improving Data Quality
 - Minimizing Data Contamination
 - Deconvoluting EIS spectra
- Interpretation of Experimental Data
- Implementation in HTFCs
 - MCFCs
 - SOFCs
- Establishing Harmonized Testing Procedures
- Conclusions

Introduction to EIS in HTFCs

EIS is a very powerful technique in order to discern the various physicochemical processes occurring in the HTFCs.

But...

Data can be slightly contaminated

Measurements are affected by the *parasitic inductances* generated by the electrical wiring and other external devices (e.g. kiln).

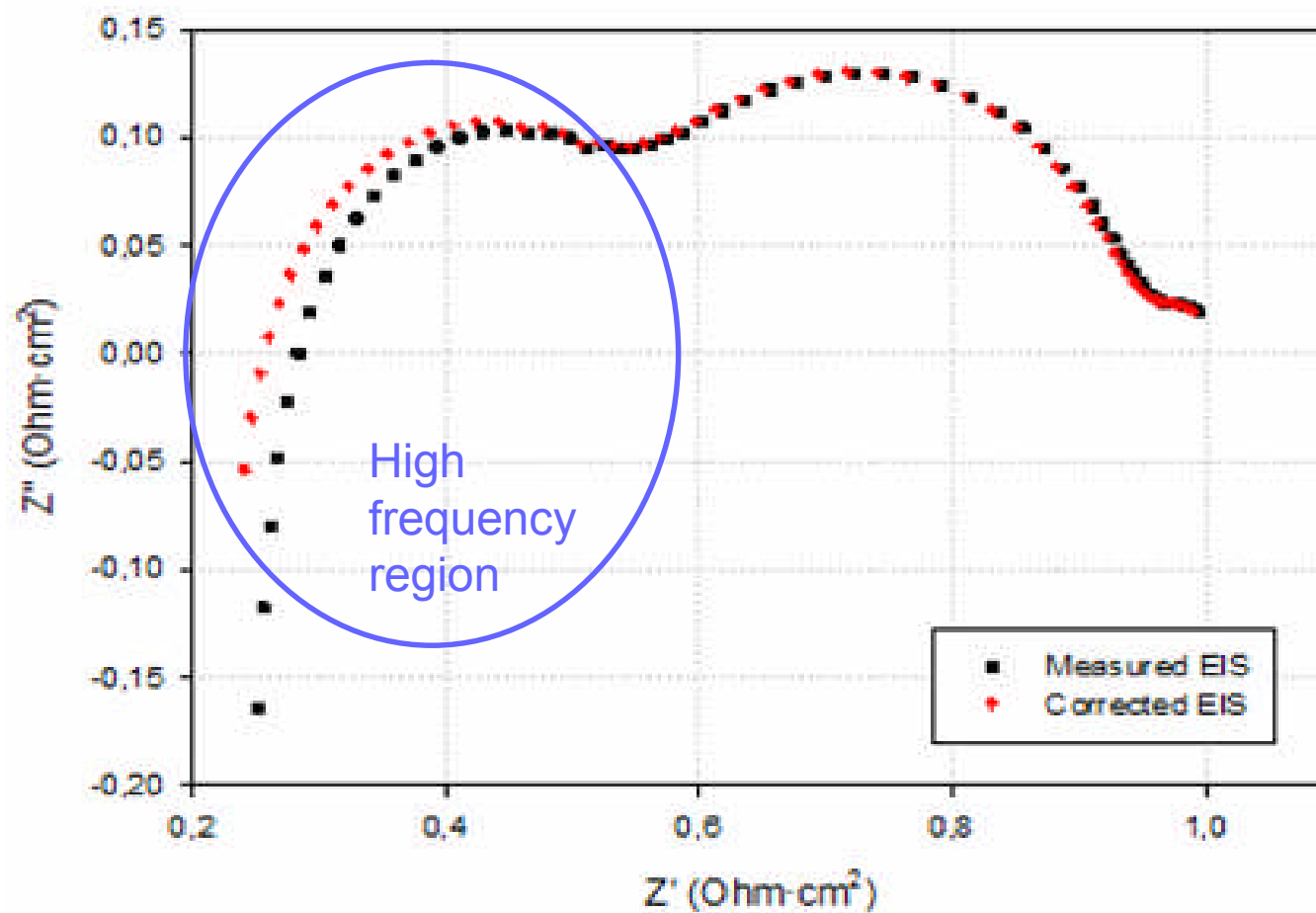
Relevant information can be hidden

Due to the nature of the electrochemical processes, the individual signals of these are often convoluted.



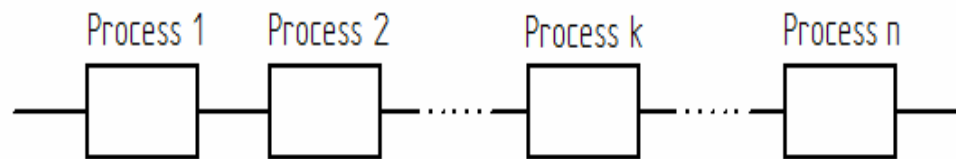
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Improving Data Quality



Towards EIS response deconvolution (DRT method)

The output signal of an electrochemical cell can be modelled as a sum of relaxator terms with different relaxation times and amplitudes ^[1].



The total impedance of a finite series of relaxator terms is:

$$Z_{tot} = \frac{1}{\sum_k \frac{1}{j\omega\tau_k c_k}}$$

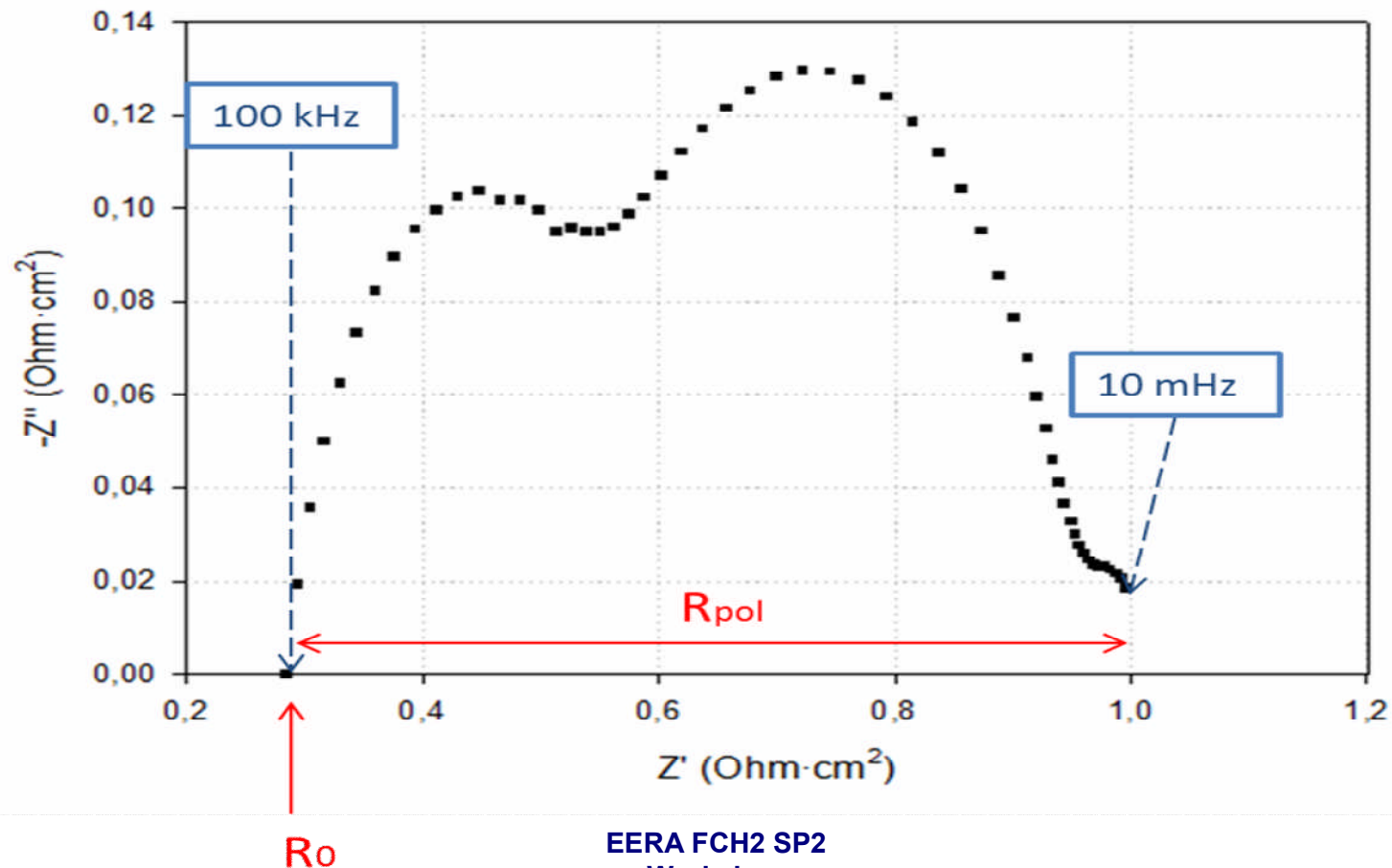
τ_k is the relaxation time of process k

c_k is the relaxation time distribution

[1] N. Link, S. Bauer, B. Ploss. Analysis of signals from superposed relaxation processes. J.Appl.Phys. 69, 2759 (1991); doi: 10.1063/1.348634

Improving Data Quality

$$Z^*(\omega_i) = R_0 + R_{pol} \sum_k \frac{1}{1 + j\omega_i \tau_k} c_k$$



Improving Data Quality

The relaxation time distribution function can be obtained from both the real and the imaginary part of the impedance equation. For instance, choosing the imaginary part:

$$\begin{array}{l} \backslash Z''_1 \backslash \\ \backslash Z''_1 \backslash \\ \backslash Z''_1 \backslash \\ \left\langle \begin{array}{l} Z''_1 \\ Z''_n \end{array} \right\rangle \end{array} \quad \begin{array}{l} / \frac{-\omega_1 \tau_1}{1 + (\omega_1 \tau_1)^2} \dots \dots \\ / \frac{-\omega_1 \tau_1}{1 + (\omega_1 \tau_1)^2} \dots \dots \\ / \frac{-\omega_1 \tau_1}{1 + (\omega_1 \tau_1)^2} \dots \dots \\ \left\langle \begin{array}{l} -\omega_1 \tau_1 \\ 1 + (\omega_n \tau_1)^2 \end{array} \right\rangle \dots 1 \end{array}$$

Ill-posed problem

**CANNOT BE SOLVED
DIRECTLY!**

It can be solved by regularization methods (e.g. Tikhonov) [2].

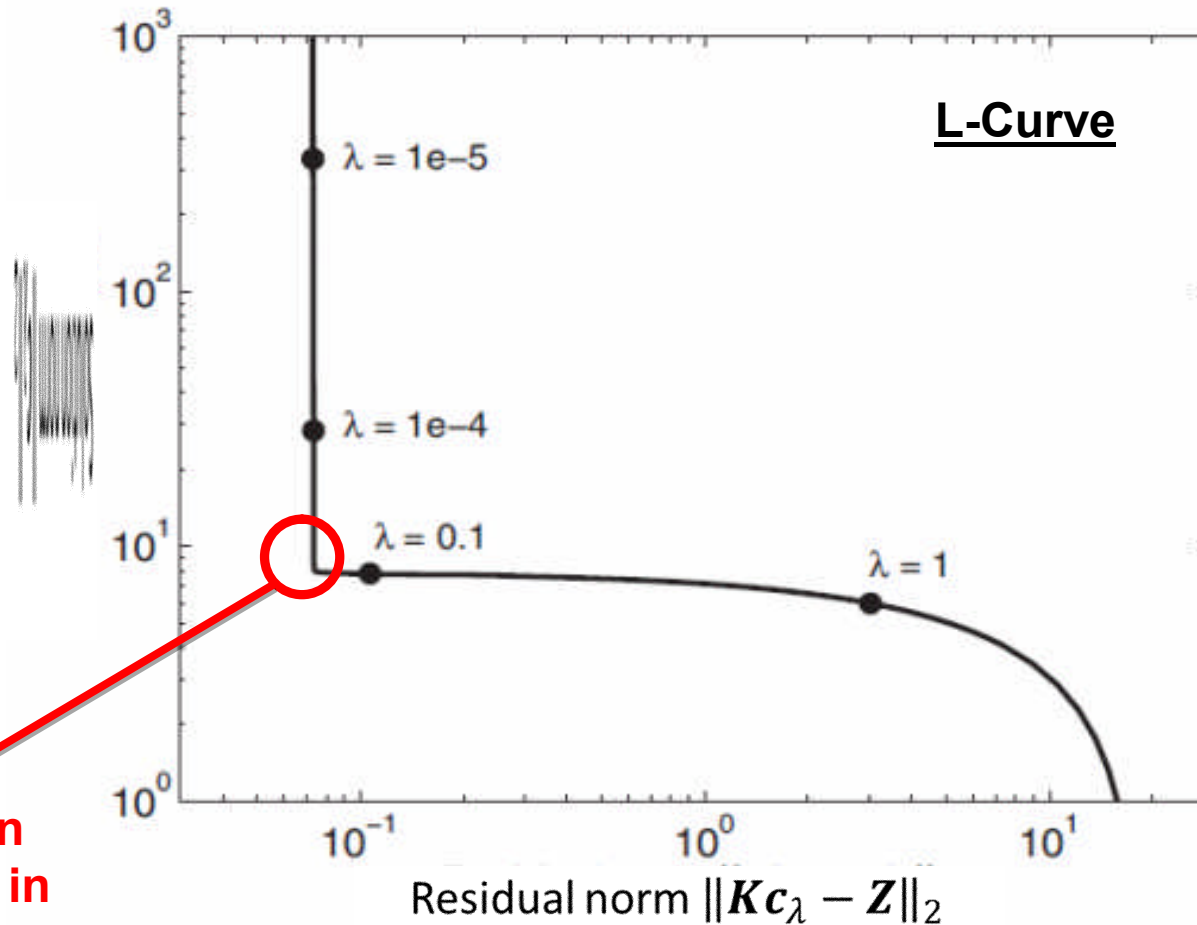
$$\min_c \{ \|Kc - Z\|_2^2 + \lambda^2 \|c\|_2^2 \} \longrightarrow c_\lambda = (K^T K + \lambda^2 I)^{-1} K^T Z$$

where λ is the regularization parameter
where λ is the regularization parameter

[2] A. Leonide, SOFC Modelling and Parameter Identification by means of Impedance Spectroscopy, PhD Thesis, KIT Scientific Publishing

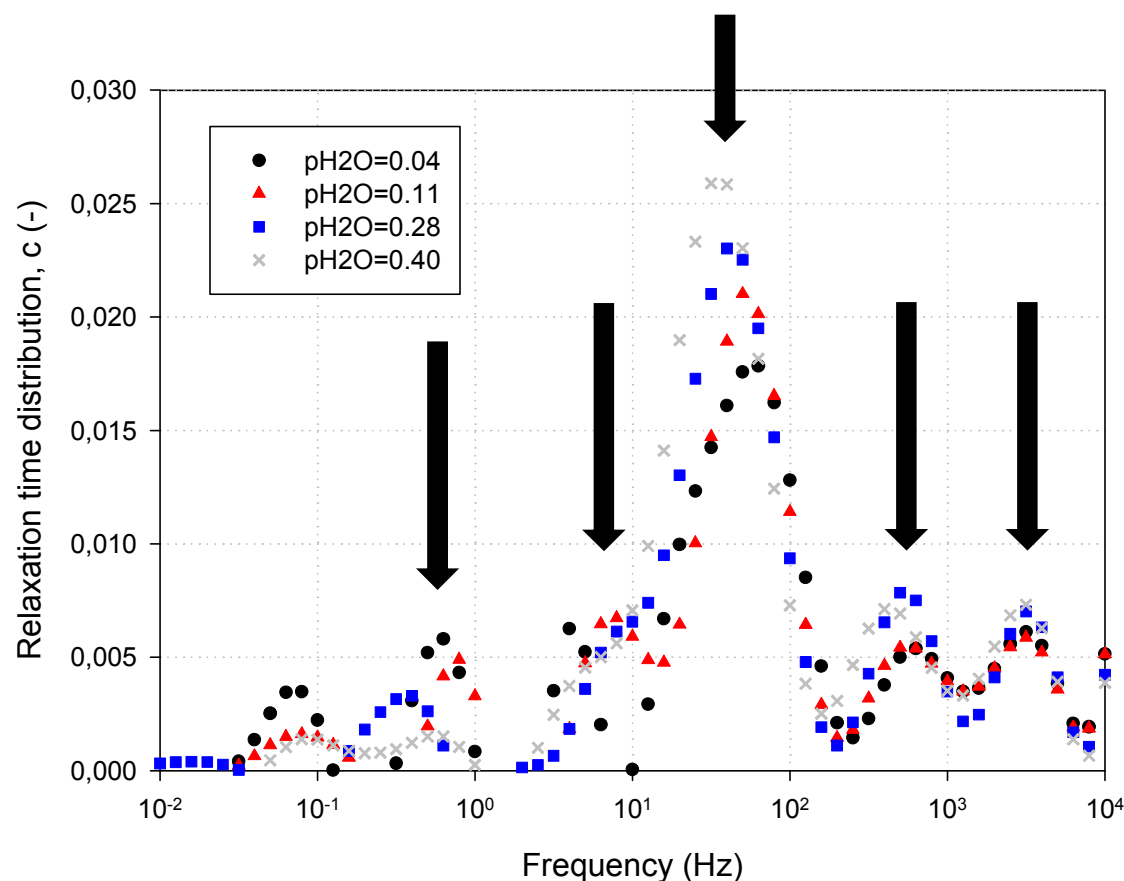
Improving Data Quality

$$c_\lambda = (K^T K + \lambda^2 I)^{-1} K^T Z$$



Optimum regularization parameter is in the “L-curve” corner

Interpretation of Experimental Data



DRT graph of an SOFC cell with a PRN-based cathode when varying the humidity content in the anode at 750°C

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Individual processes are clearly identified in the DRT graph whilst **convolution** of the EIS responses is **minimized**.

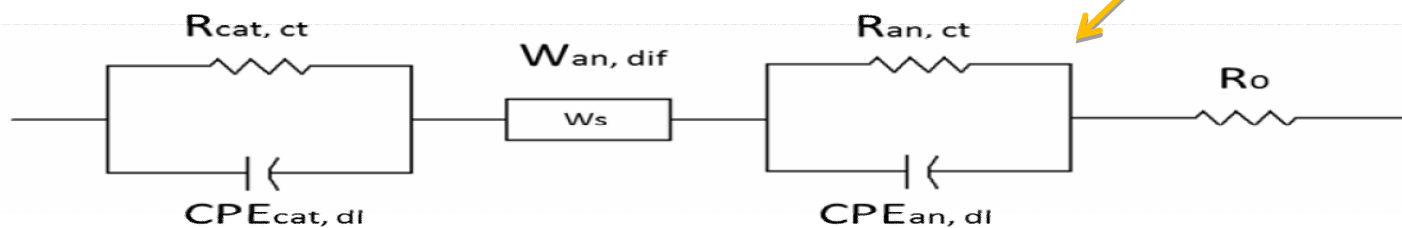
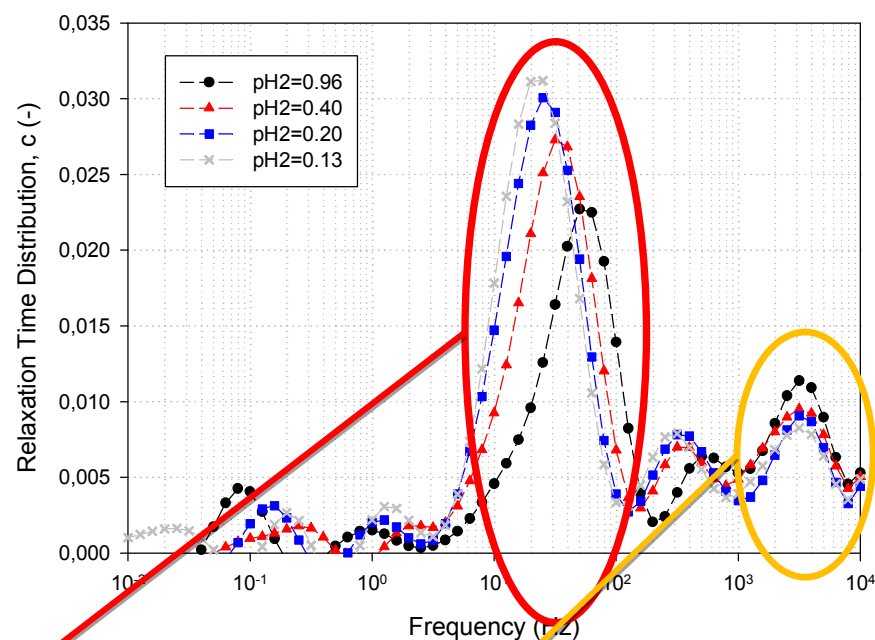
By varying one operational parameter of the cell (i.e. temperature, H_2 , H_2O , etc...) whilst maintaining the rest of them constant, **each peak can be associated to a physicochemical process**.

Time-consuming
Might induce degradation
slightly

Interpretation of Experimental Data

More realistic Equivalent Circuit Modeling (ECM) can be obtained.

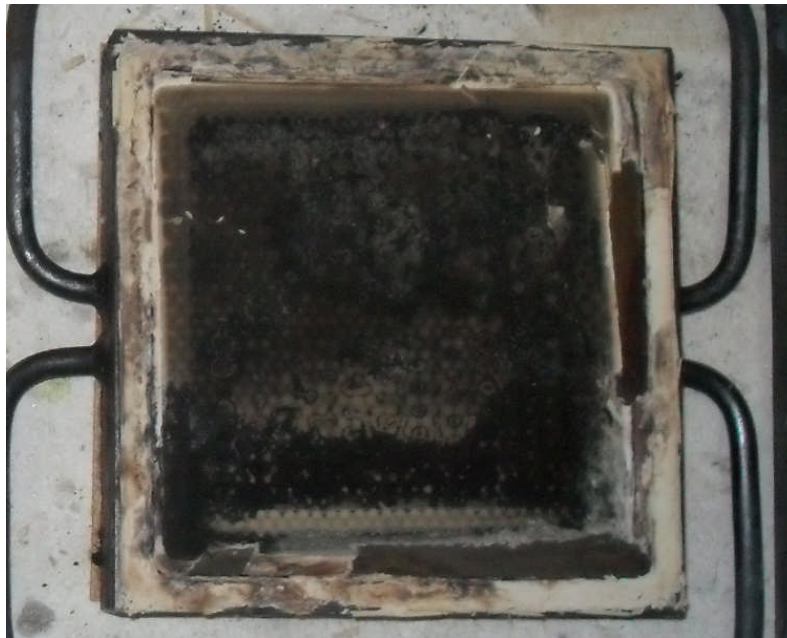
Each element can be associated with a peak.



Implementation in HTFCs

Molten Carbonate Fuel Cells (MCFCs)

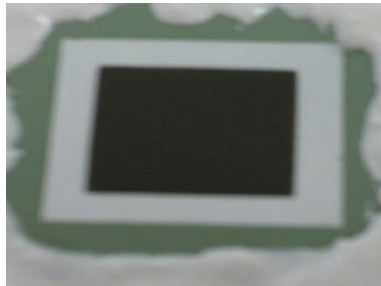
It has been experimentally demonstrated that introducing low concentration of SO₂ (1-20ppm) to the cathode side degrades the anodic side of the cell...**verified only after post-operando analysis.** (MCFC-CONTEX Project)



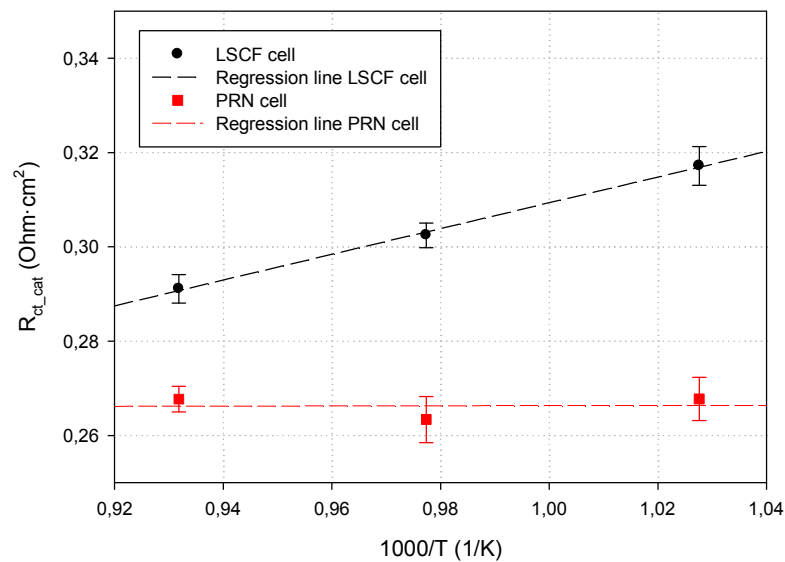
The **DRT** methodology paves the way to understanding the degradation mechanisms behind this loss in performance, being able to discern not only the affected layers, but also if this loss in performance is of physical (e.g. pore block) and/or chemical nature... and all of this **whilst in-operando!**

Implementation in HTFCs

Solid Oxide Fuel Cells (SOFCs)



Test the immediate and endurance performance of SOFC active layers (e.g. Cathodes) under different operative conditions.



Experimental



Modeling

$$r_{ct,cat} = \frac{d\eta_{act,cat}}{di} = \frac{RT}{i_{0,cat}^{pre}(p_{O_2})^{\gamma_{O_2}} \exp\left(-\frac{E_{act,cat}}{RT}\right) n_e F}$$

Establishing Harmonized Testing Procedures

The **SOCTESQA Project** (May 2014 – April 2017) will approach harmonized standard testing procedures on solid oxide cell (SOFC and SOEC) stacks as well as assuring the product's quality and safety.

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The International Electrochemical Commission (IEC) is committed to creating harmonized testing protocols for fuel cells.

Conclusions

- EIS data must be corrected to remove “noise” from the original measurement in order to obtain high quality results.
- Complementary analysis tools and techniques are **NEEDED** to boost EIS potential. Deconvolution of its spectra is regarded as a step beyond SoA analysis.
- In-depth study of degradation phenomena in HTFCs is needed, especially if information is obtained *in-operando*. EIS and DRT method combined can provide a powerful tool to attain this goal.

Thank you!