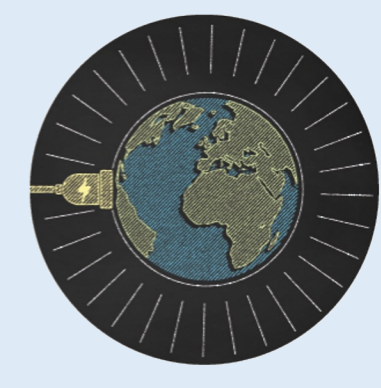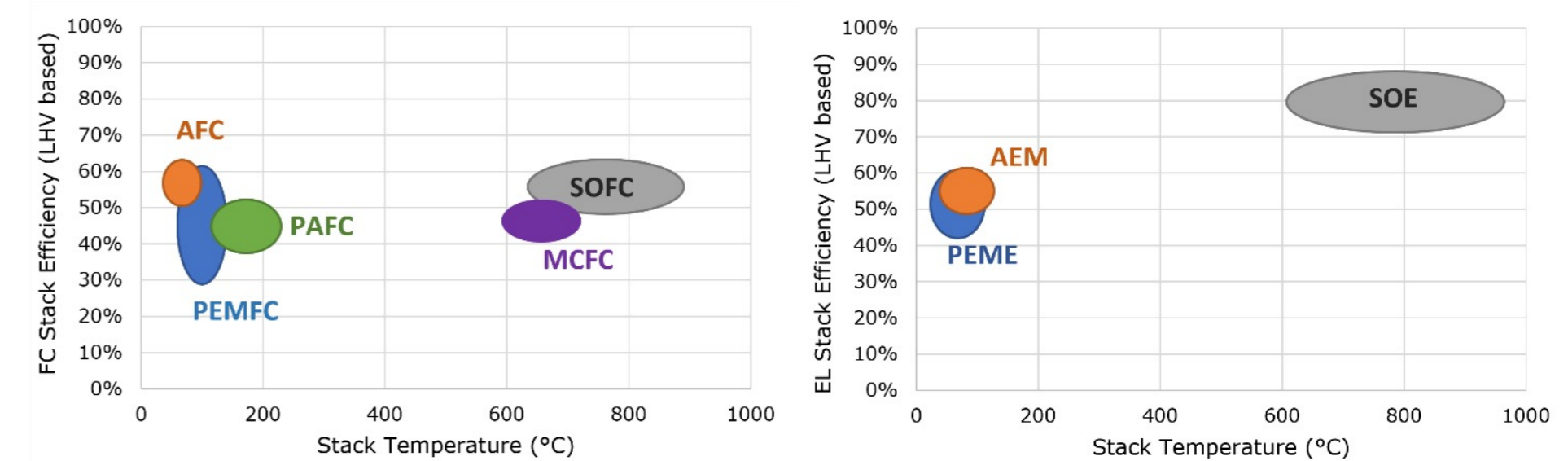# Analysis of Polarization Losses in commercial-size Solid Oxide Cells by Electrochemical Impedance Spectroscopy and Distribution of Relaxation Times

Dr. A. Staffolani[a], Dr. A. Baldinelli[a], Prof. F. Nobili[b], Prof. L. Barelli[b]

[a]Università di Camerino, School of Science and Technology – Chemistry Division, Camerino, Italy.
[b]Università degli Studi di Perugia, Department of Engineering, Perugia, Italy
e-mail: antunes.staffolani@unicam.it

INTRODUCTION

Solid Oxide Fuel Cells (SOFCs) are advanced electrochemical systems with a wide range of applications in energy generation and storage. SOFCs show several advantages with regard to their competitors: higher efficiency, modularity and environmental sustainability. Real operation of SOFCs implies cyclic temperature variation (following the need to shut the SOFC down periodically), as well as exposure to fuel gases containing carbon compounds and impurities[1]. These extrinsic factors are responsible for undesired side reactions involving the SOFC materials and ending in a loss of performances[2]. In order to investigate the main issues attempting the long lifetime of SOFC materials, diagnosis techniques to observe on real time the specific physicochemical process are necessary. **Electrochemical impedance spectroscopy (EIS)** and its **distribution of relaxation times (DRT)** is a powerful and non-destructive tool to address the processes occurring inside the cell, as well as modification in the membrane electrode assembly.

AIM OF THE WORK

To build an **equivalent circuit model (ECM)** suitable for real-time diagnosis based on EIS measurement. In order to find the proper ECM, we have performed a wide experimental campaign on a commercial SOFC by changing several working parameters such as: **temperature** (640-820°C), **fuel flow** (25 mL min^{-1} < Q_{FE} < 50 mL min^{-1}) and its **composition** by H_2 and H_2O binary mixtures and H_2, H_2O, and N_2 ternary mixtures, and air electrode gas composition (0.05 < pO_2 < 0.21).
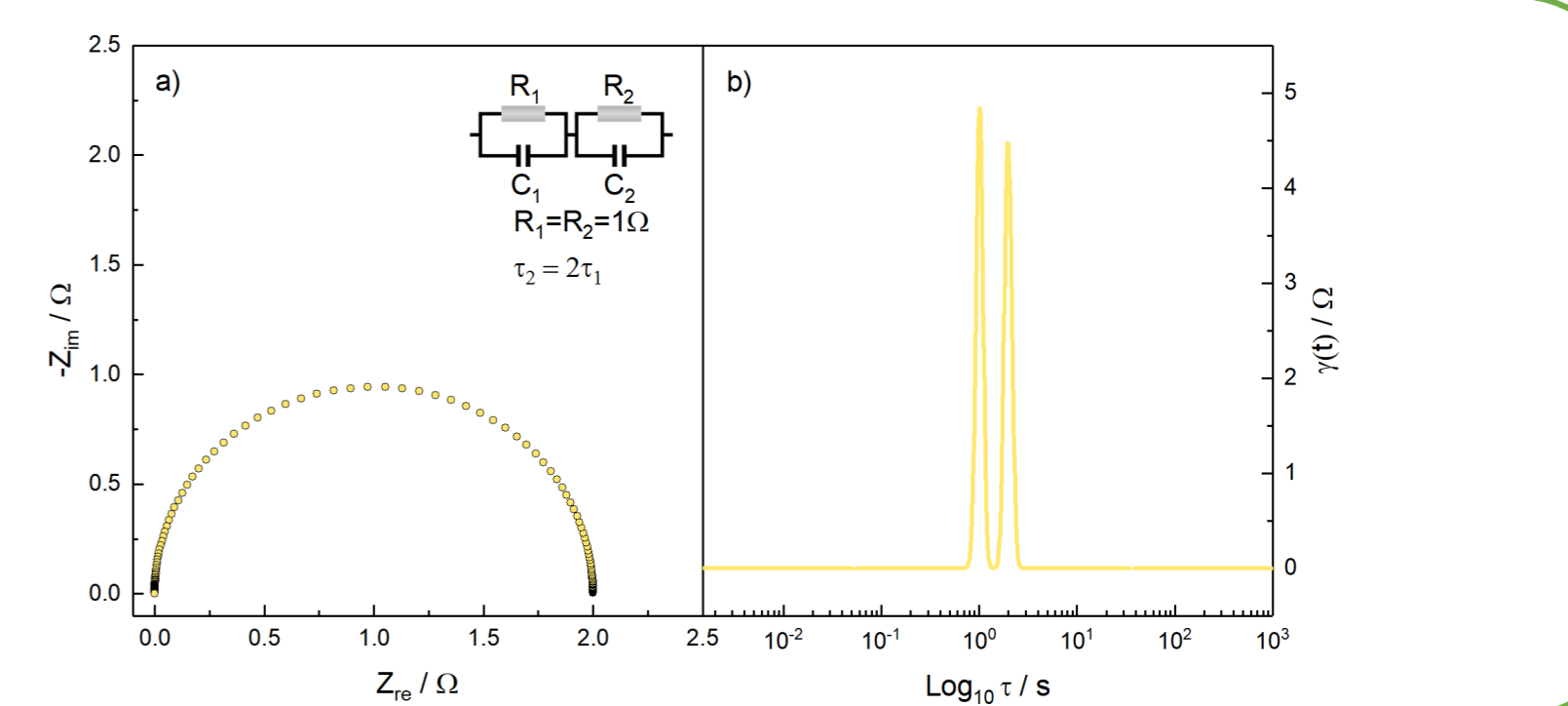
DISTRIBUTION OF RELAXATION TIME

DRT is a function correlated with the complex impedance by the expression at Eq.1, where R_{pol} stands for the polarization resistance and $\gamma(\tau)$ represent the **distribution function**.

$$Z_i(\omega) = -R_{pol}\int_0^\infty \frac{\gamma(\tau)}{1+(\omega\tau)^2}d\tau \qquad \textbf{Eq. 1}$$
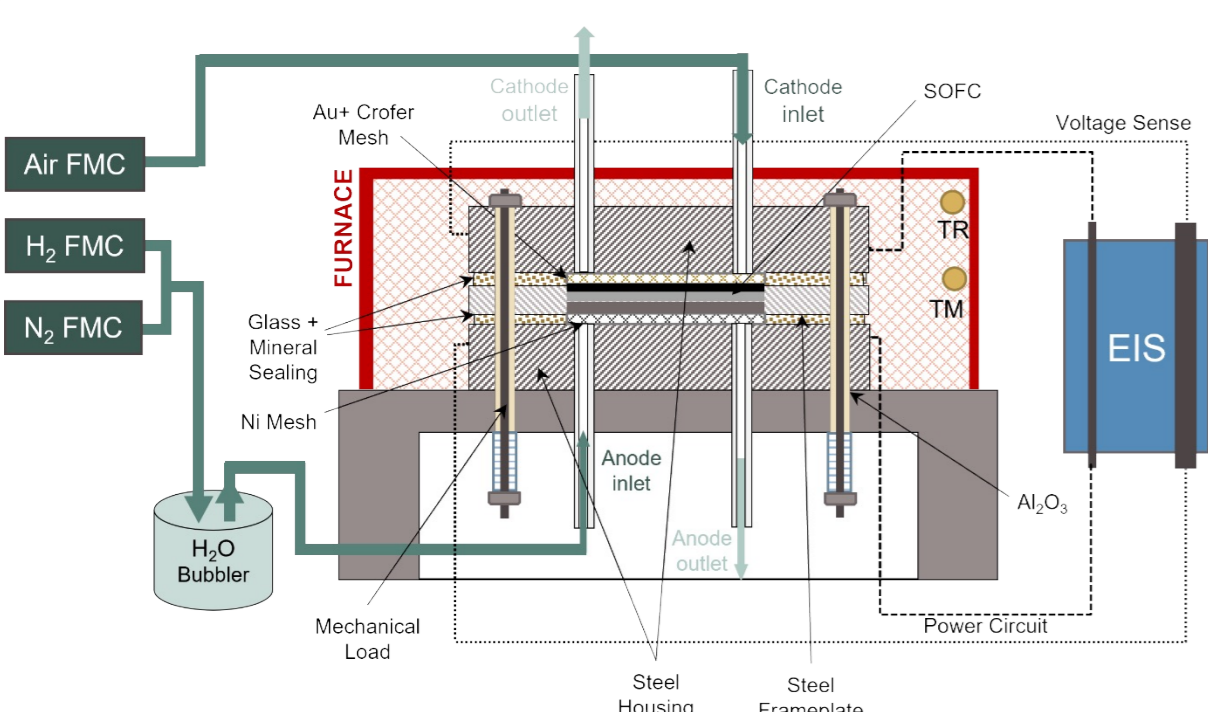
With:

$$\int_0^\infty \gamma(\tau)d\tau = 1 \qquad \textbf{Eq. 2}$$

In this work, **Tikhonov Regularization** has been used for the calculation of the DRT function[3].
In this way, all the physicochemical processes occurring inside the cell can be split according to their characteristic relaxation time
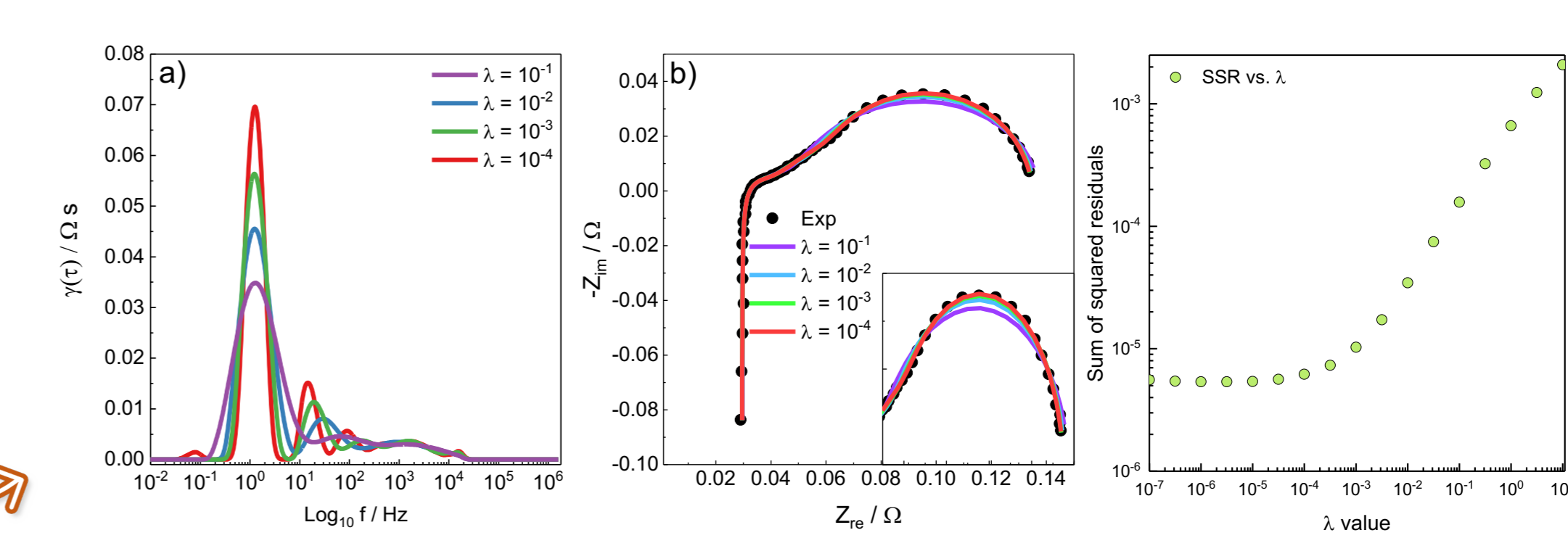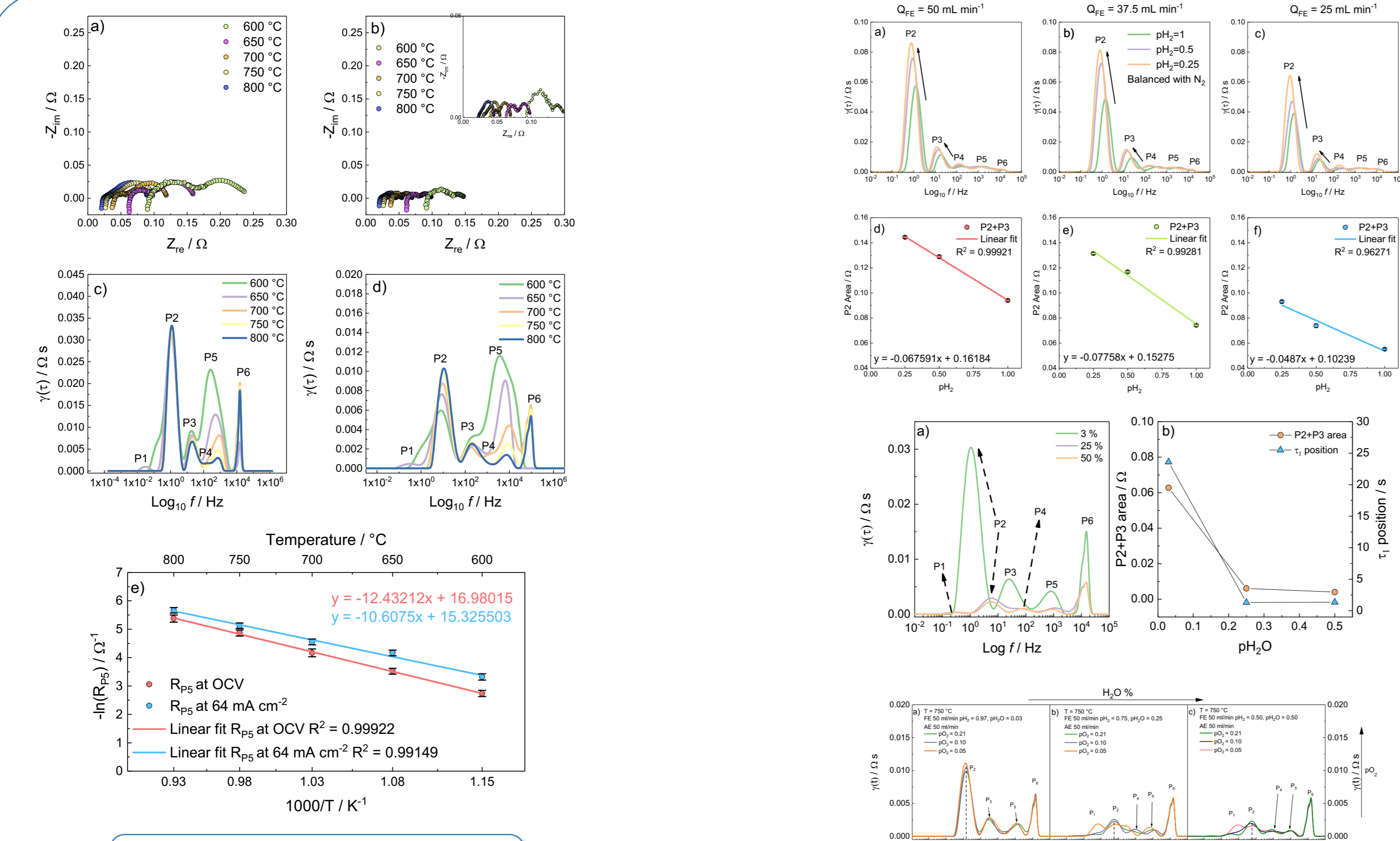

EXPERIMENTAL

SOFC test rig scheme: mechanical and electrical connection, measurement hardware.

Optimization of the regularization parameter λ

RESULTS AND DISCUSSION - DRT

The peak P5 has a a thermally activated behavior in the Arrhenius plot, thus it was assigned to a charge-transfer process

The peaks P2 and P3 are connected to the same process, i.e.: gas diffusion in the fuel electrode. It can be modeled by a finite-length Warburg and its DRT function is characterized by multiple peaks with decreasing intensities (**Eq. 3**)
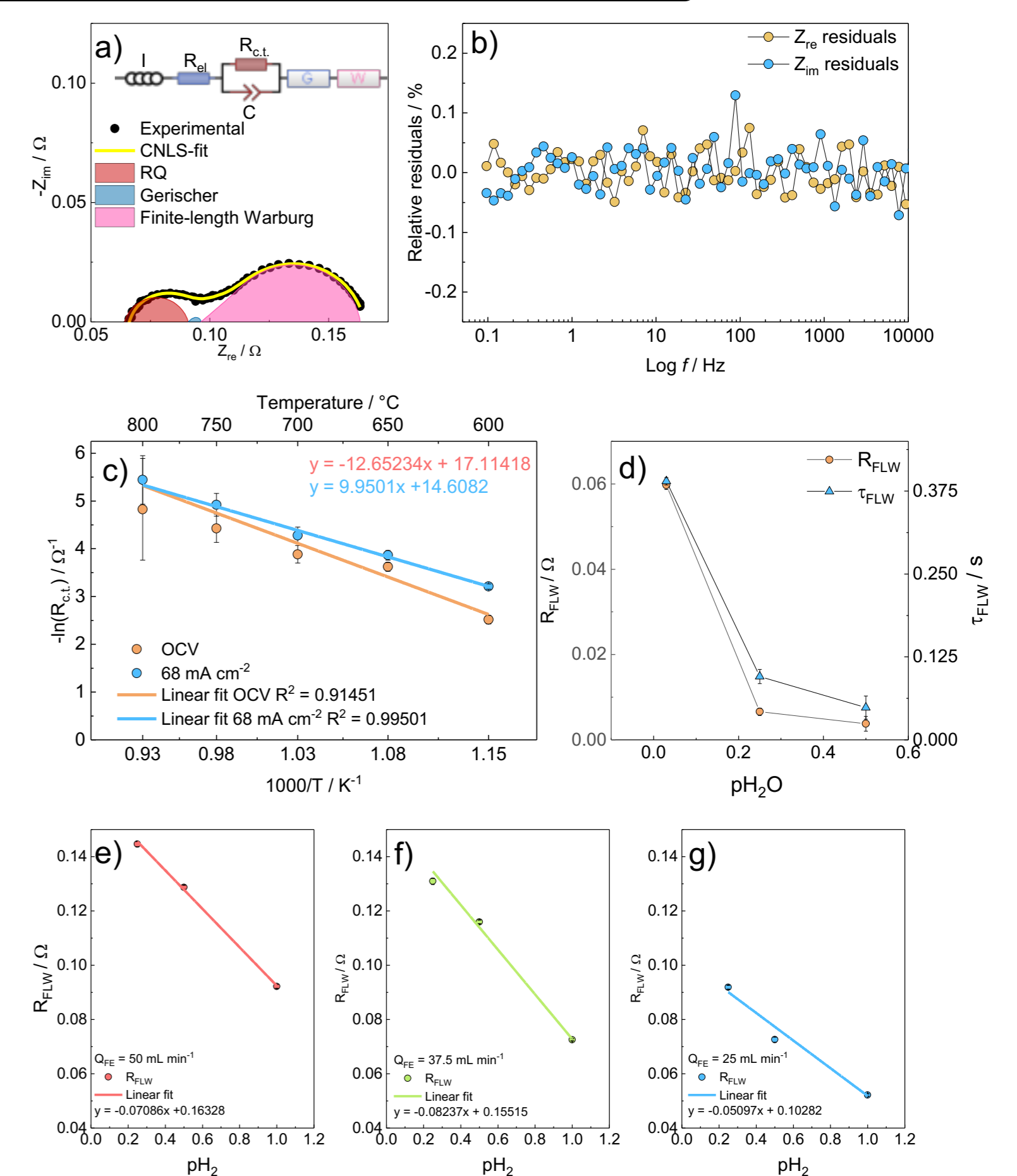
$$\tau_k = \frac{\tau_0}{\pi^2(k-0.5)^2}, k = 1, 2, 3, \dots \qquad \textbf{Eq. 3}$$

The diffusion cannot be modeled the Fick's 2° law of diffusion because the fuel is a multicomponent mixture, thus the Stefan-Maxwell diffusion must be used (**Eq. 4-5**)

$$R_W = \left(\frac{RT}{2F}\right)^2 \frac{l}{PD_{H_2,H_2O}}\frac{\kappa}{\varphi}\left(\frac{1}{pH_2}+\frac{1}{pH_2O}\right) \qquad \textbf{Eq. 4}$$

$$R_W = \left(\frac{RT}{2F}\right)^2 \frac{1}{P}\frac{\kappa}{\varphi}\left[\frac{1}{x_{H_2O}}\left(\frac{x_{H_2}}{D_{H_2,H_2O}}+\frac{x_{H_2O}}{D_{H_2,H_2O}}+\frac{x_{N_2}}{D_{H_2O,N_2}}\right)+\frac{1}{x_{H_2}}\left(\frac{x_{H_2}}{D_{H_2,H_2O}}+\frac{x_{H_2O}}{D_{H_2,H_2O}}+\frac{x_{N_2}}{D_{H_2,N_2}}\right)\right] \qquad \textbf{Eq. 5}$$

- The peak P1 is visible only at low pO_2 and thus it was assigned to the gas diffusion in the air electrode.
- The peak P4 has been assigned to the oxygen surface exchange and diffusion in bulk LSCF in the cathode.

RESULTS AND DISCUSSION – CNLS-fit

a linear relationship between the $\ln(R^{-1})$ and 1000/T was found, suggesting a thermally activated behavior [42]. The activation energy has been calculated by using the slope of the linear fit and Arrhenius equation[42] (**Eq. 6**):

$$\ln\left(\frac{1}{R_{ct}}\right) = A - \frac{E_a}{k_bT} \qquad \textbf{Eq. 6}$$

Technique	E_a	
	j = OCV	j = 68 mA cm^{-2}
DRT	E_a = 1.07132 ± 0.0851 eV	E_a = 0.90674 ± 0.07104 eV
CNLS-fit	E_a = 1.09029 ± 0.19247 eV	E_a = 0.76992 ± 0.03505 eV

CONCLUSIONS

This work presents an experimental methodology to identify the main processes behind polarization losses in SOFCs by varying the operating and temperature, anode feeding gas flow rate and quality, and cathode gas coposition. The experimental trials are used to build an adaptive ECM suitable for real-time diagnosis based on DRT analysis of EIS measurement. The ECM for the cell analysed is a $LR_{el}(R_{ct}Q)GW_{FLW}$, where R_{el}, R_{ct} Q correspond to the electrolyte resistance, charge-transfer resistance and its related capacitance, respectively. A further (RQ) parallel can be added when performing experiments at pO_2 << 0.21 to model the gas diffusion in the air electrode. Moreover, gas diffusion at the anode is modelled with a W_{FLW} and G stands for diffusion on the cathode.

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