Electrolysis

Construction and implementation of experimental set-ups for high pressure electrolysis

Analysis of differences impedance spectra

Risø DTU
National Laboratory for Sustainable Energy

ADIS
Analysis of Differences in Impedance Spectra

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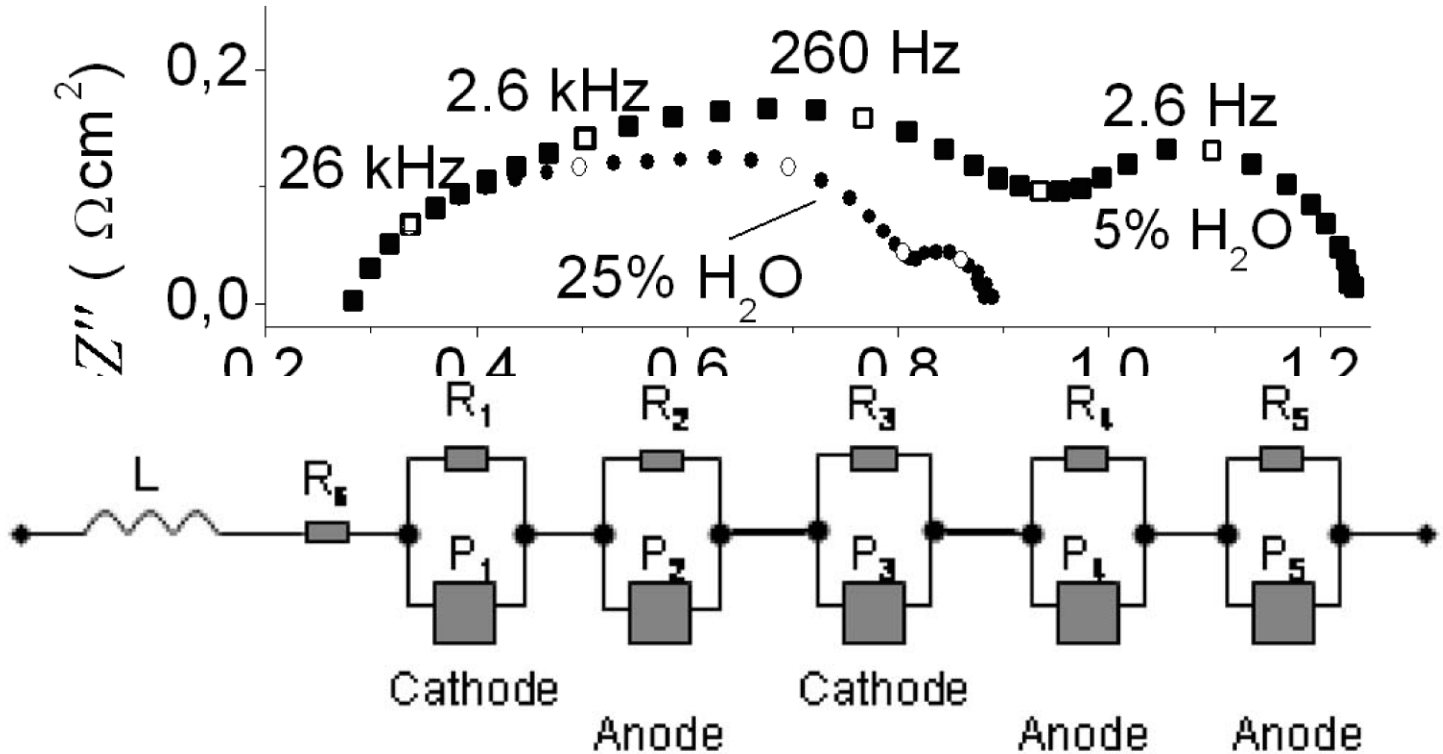

The cell impedance obtained for an Ni/YSZ|YSZ|LSM/YSZ at 750ºC
Fuel gas composition of 95% H_2-5% H_2O (squares) and 75% H_2-25% H_2O (circles)
Air is used as cathode gas.

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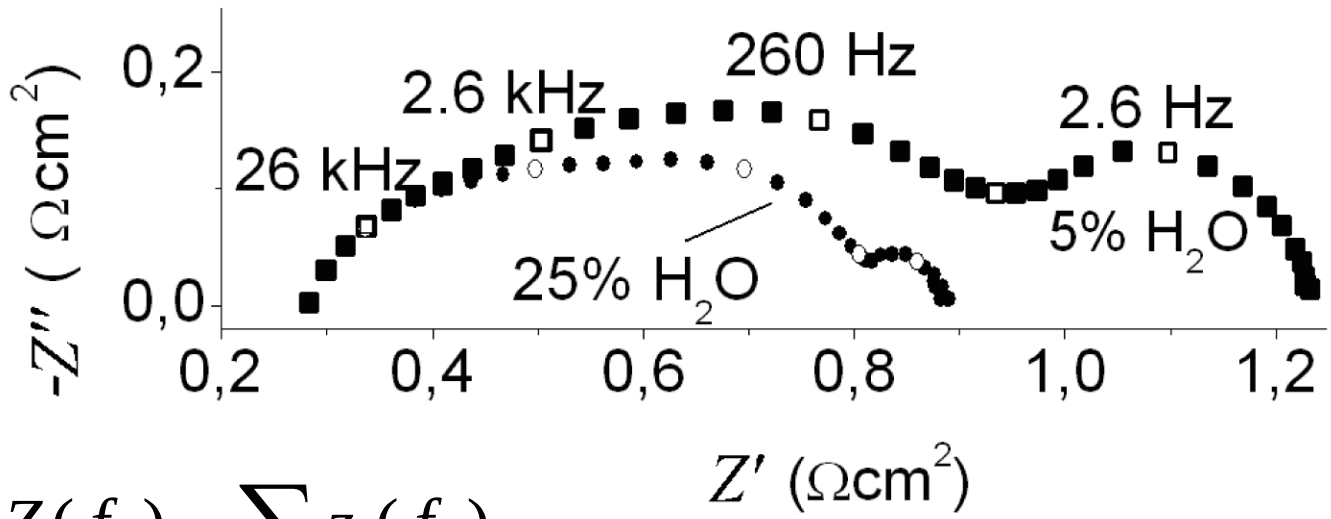

$$Z(f_n) = \sum_i z_i(f_n)$$

$$\Delta \dot{Z}'(f_n) \cong \frac{\left[Z'(f_{n+1}) - Z'(f_{n-1})\right]_{\alpha} - \left[Z'(f_{n+1}) - Z'(f_{n-1})\right]_{\alpha'}}{\ln\left(f_{n+1}/\mathrm{Hz}\right) - \ln\left(f_{n-1}/\mathrm{Hz}\right)}$$

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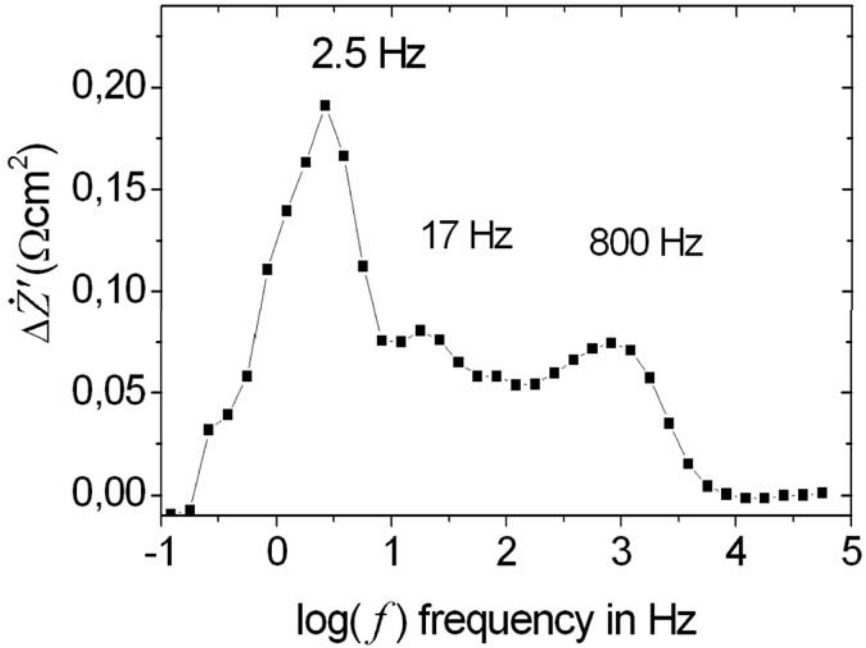

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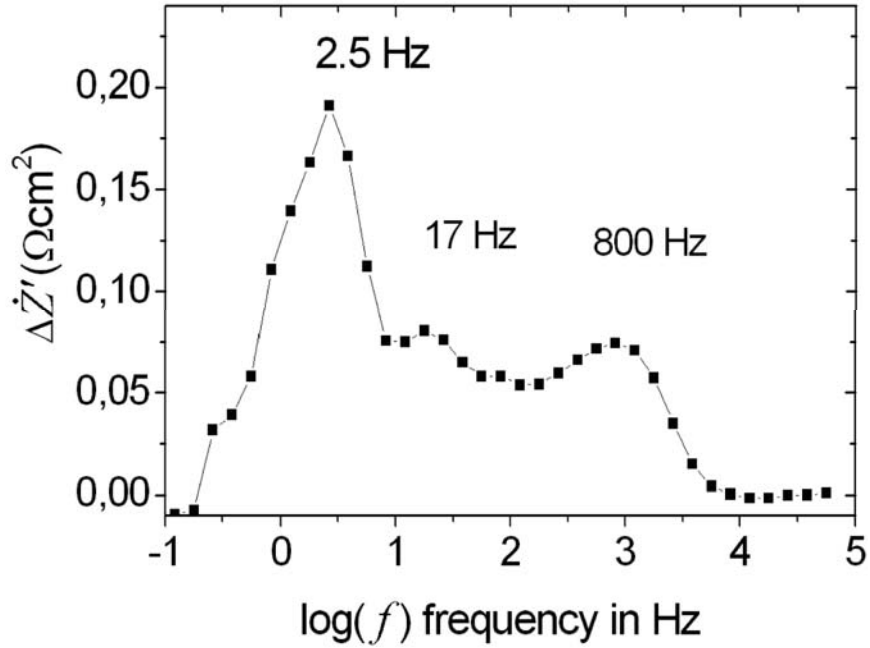

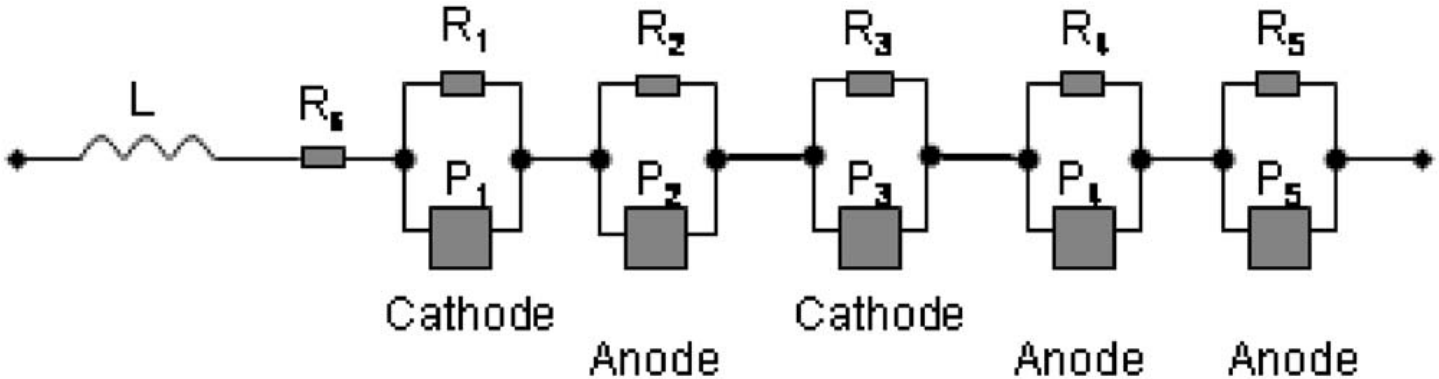

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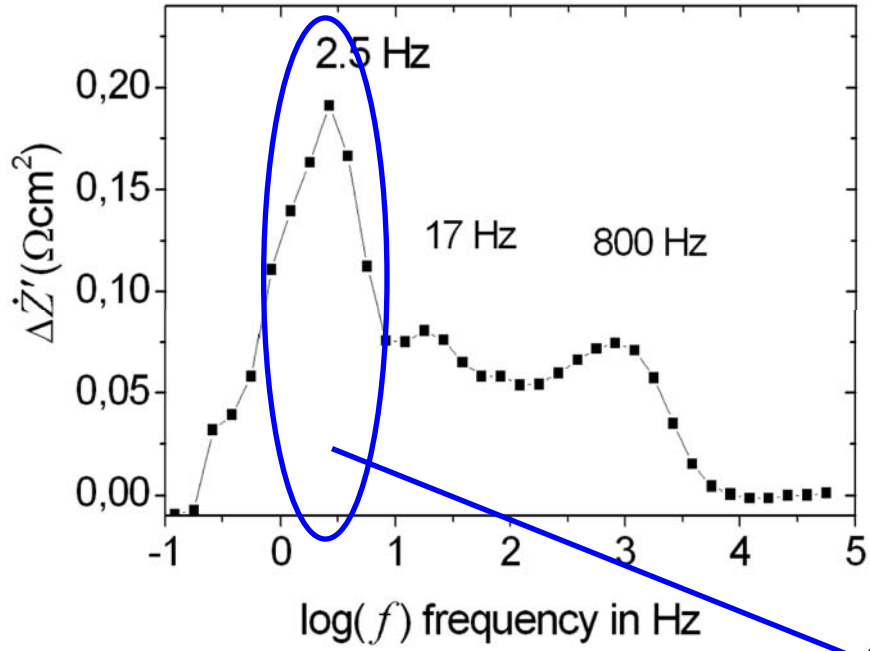

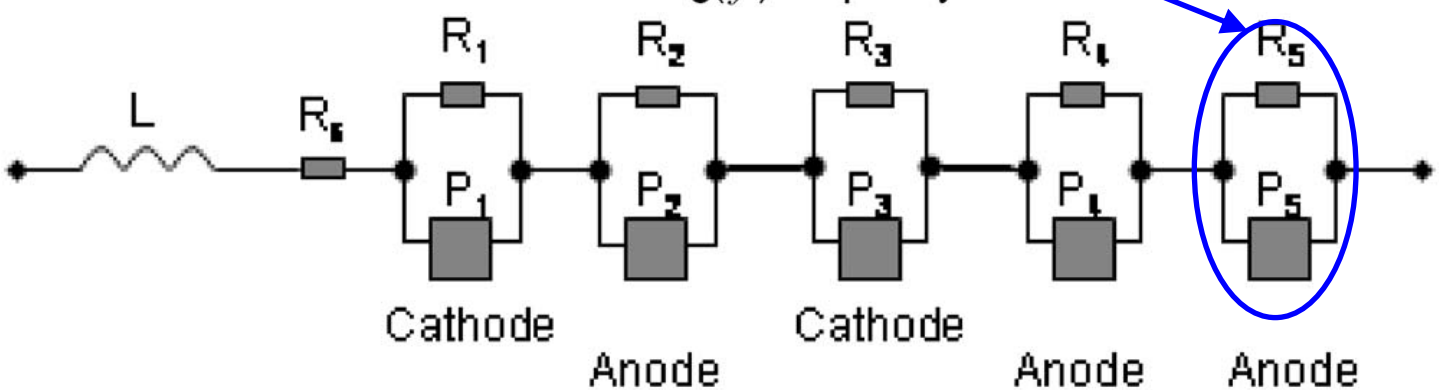

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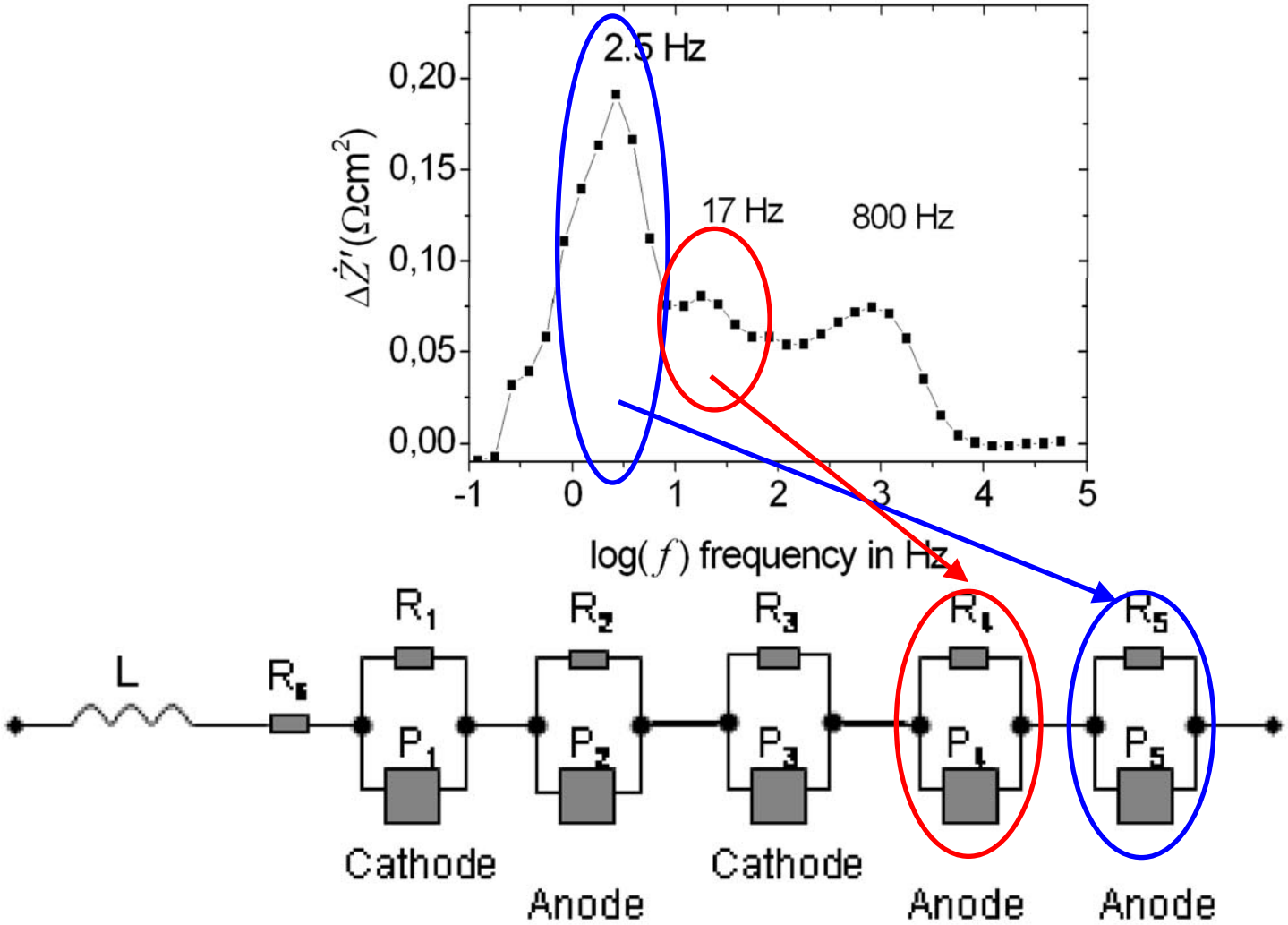

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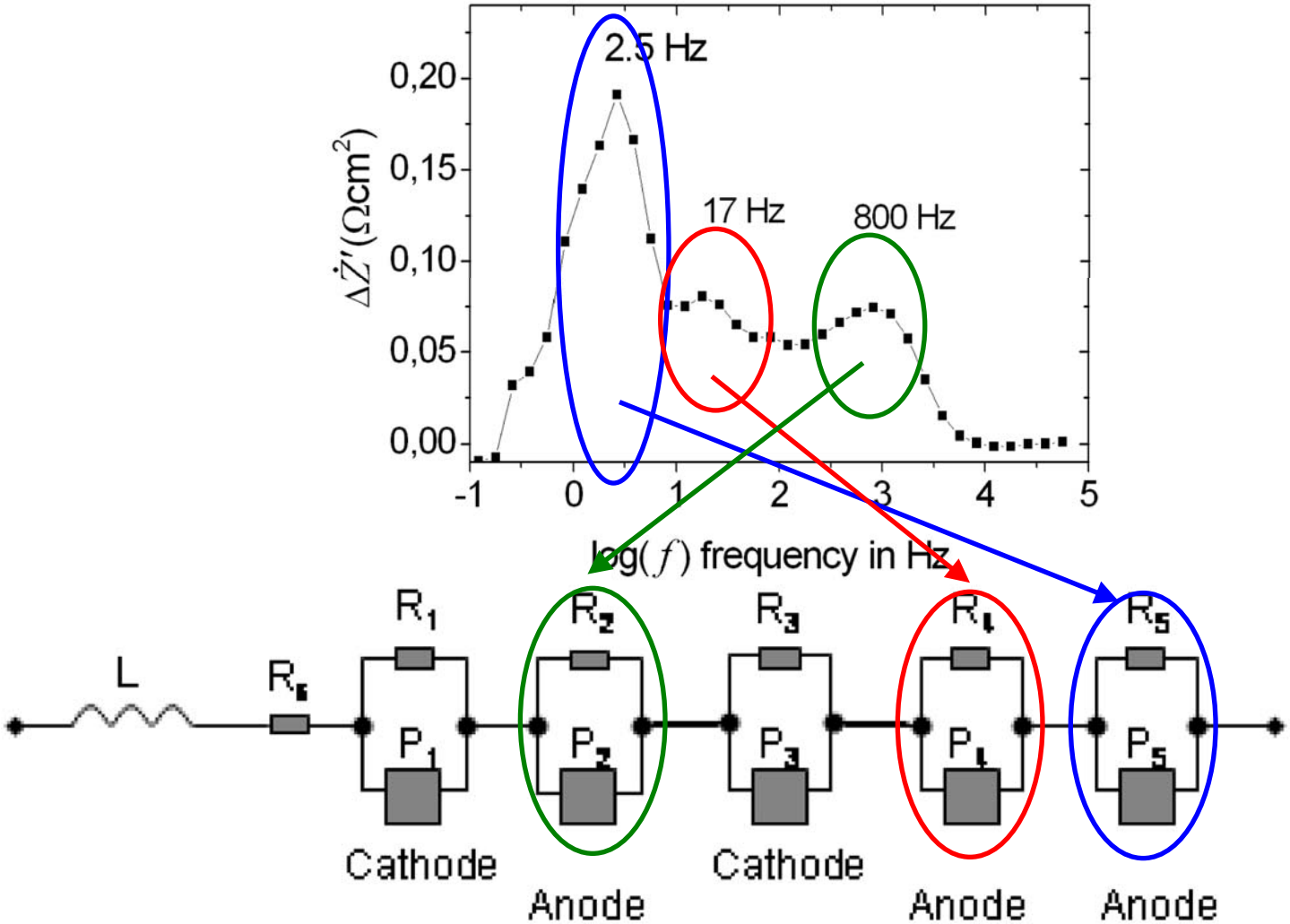

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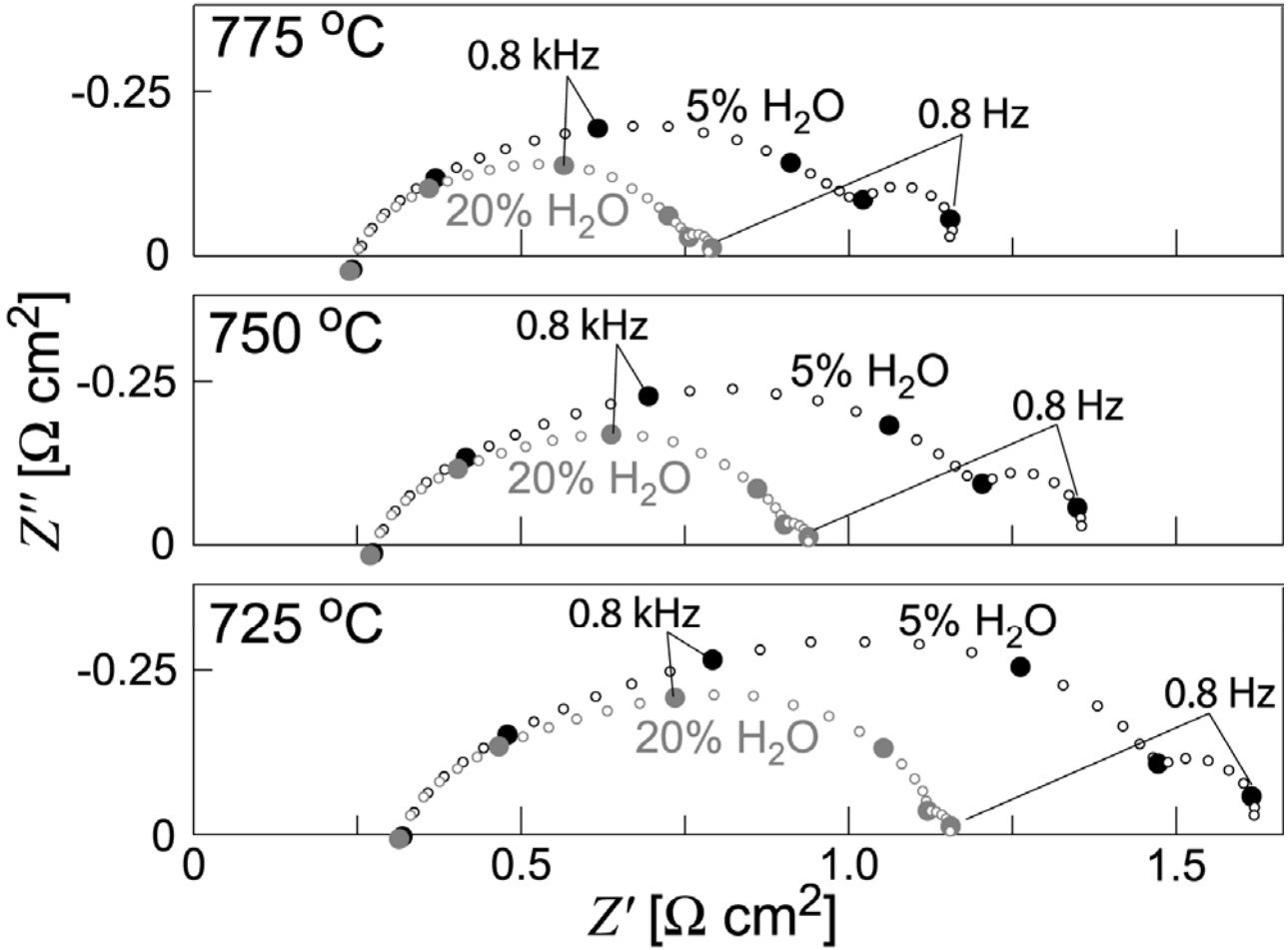

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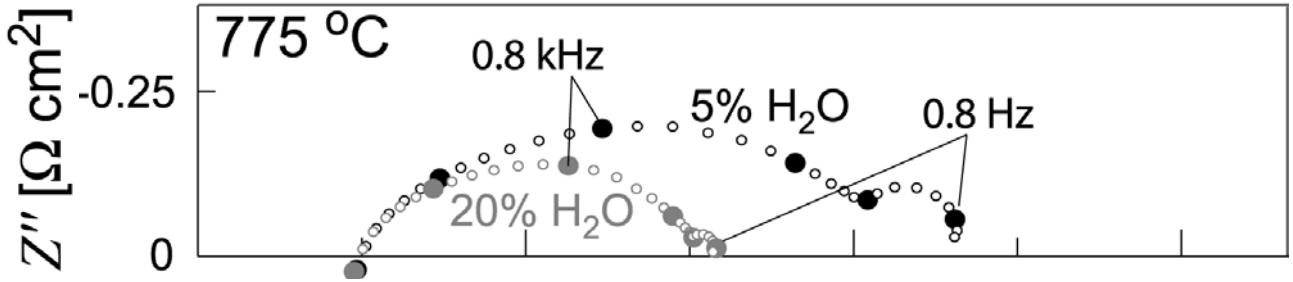

$$Z_{\text{cell}} = Z_{\text{An}} + Z_{\text{Elyt}} + Z_{\text{Cat}}$$

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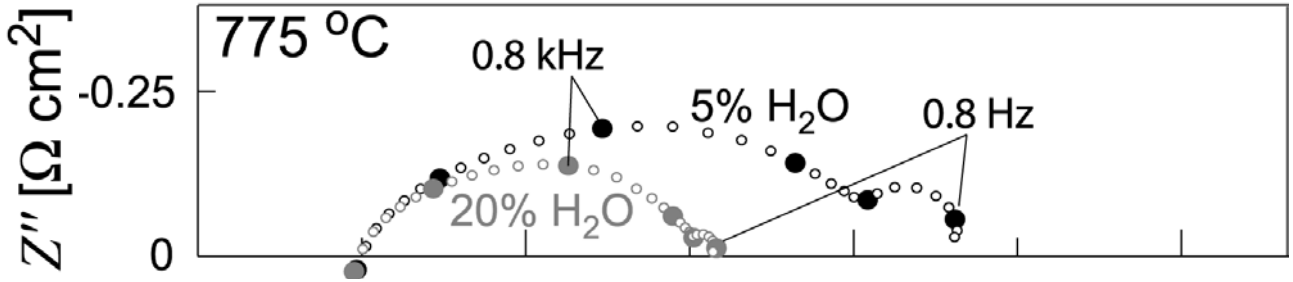

$$z_{\text{cell}} = z_{\text{An}} + z_{\text{Elyt}} + z_{\text{Cat}}$$

$$\Delta Z = \left(z_{\text{Aux}} + z_{\text{An}} + z_{\text{Elyt}} + z_{\text{Cat}} \right)\Big|_{95/5} - \left(z_{\text{Aux}} + z_{\text{An}} + z_{\text{Elyt}} + z_{\text{Cat}} \right)\Big|_{80/20}$$

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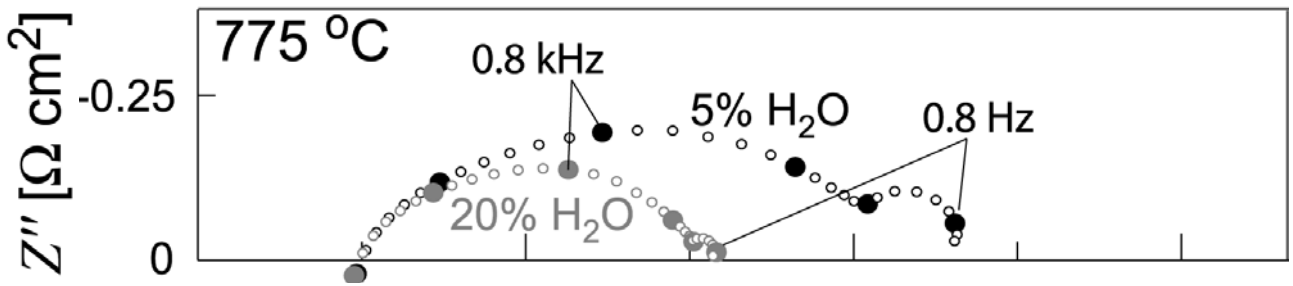

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$$= z_{\text{An}}\Big|_{95/5} - z_{\text{An}}\Big|_{80/20} = \Delta z_{\text{An}}$$

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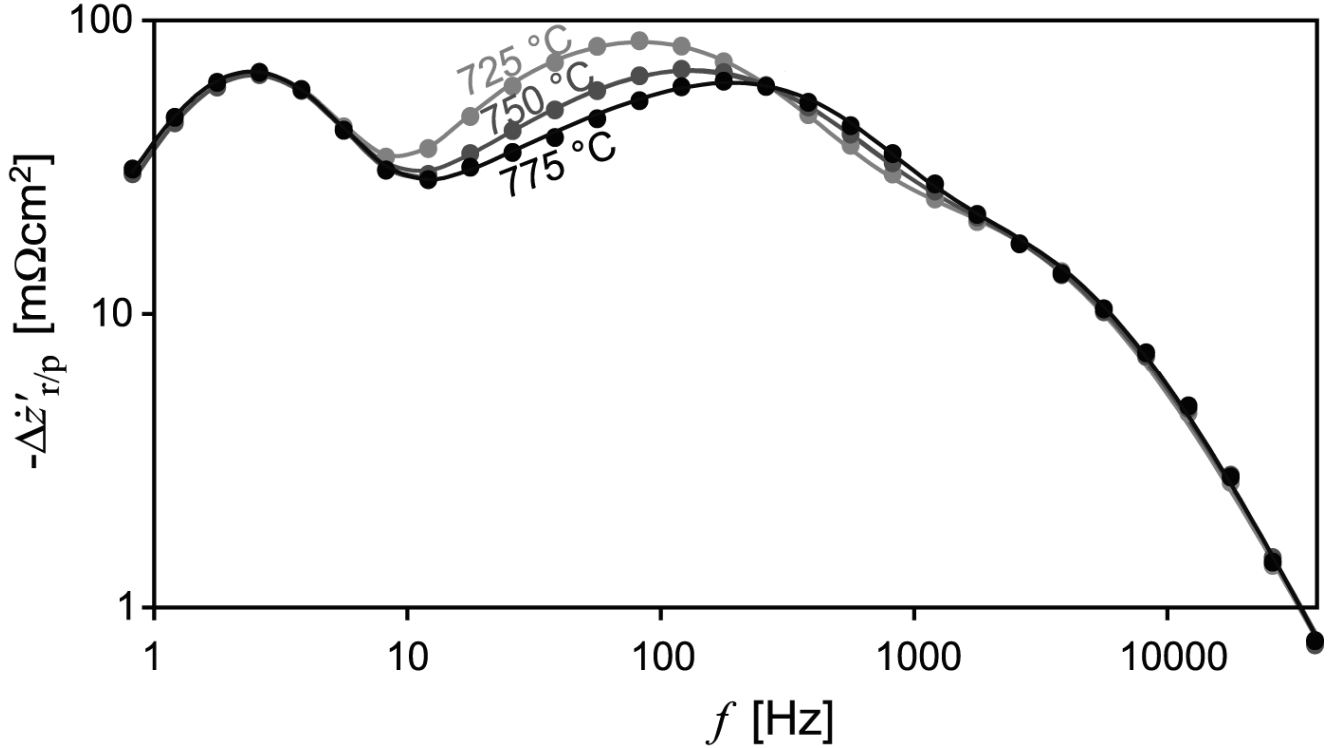

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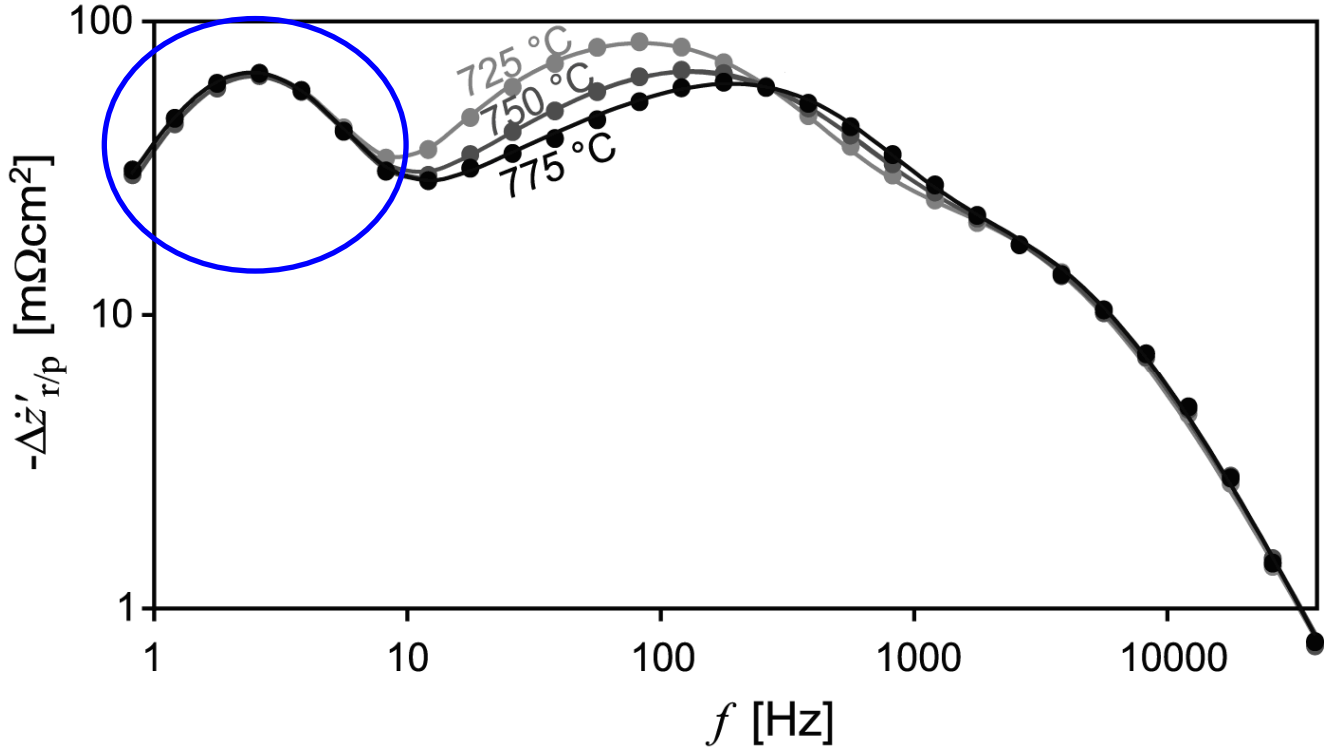
Independent of operation temperature



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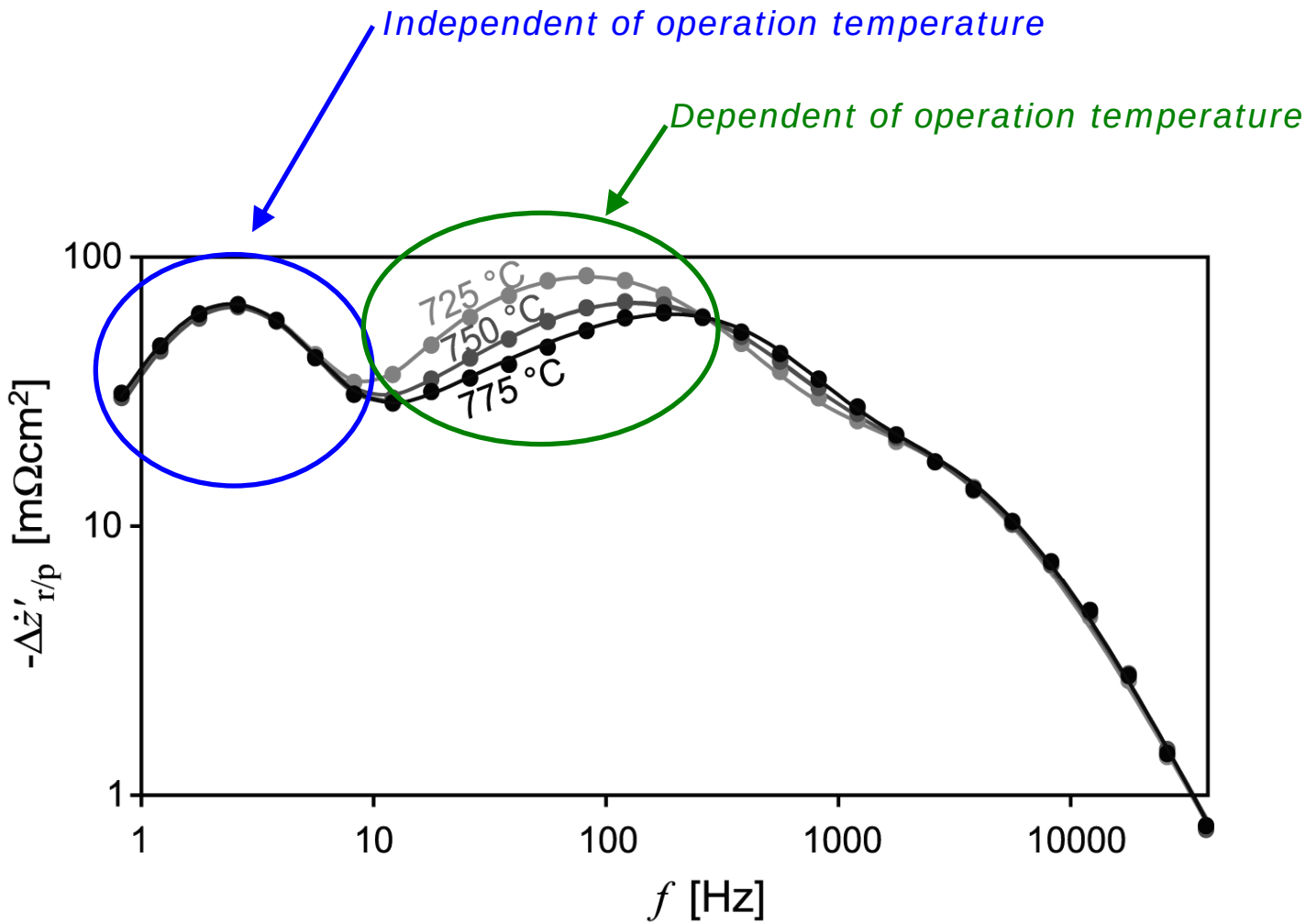

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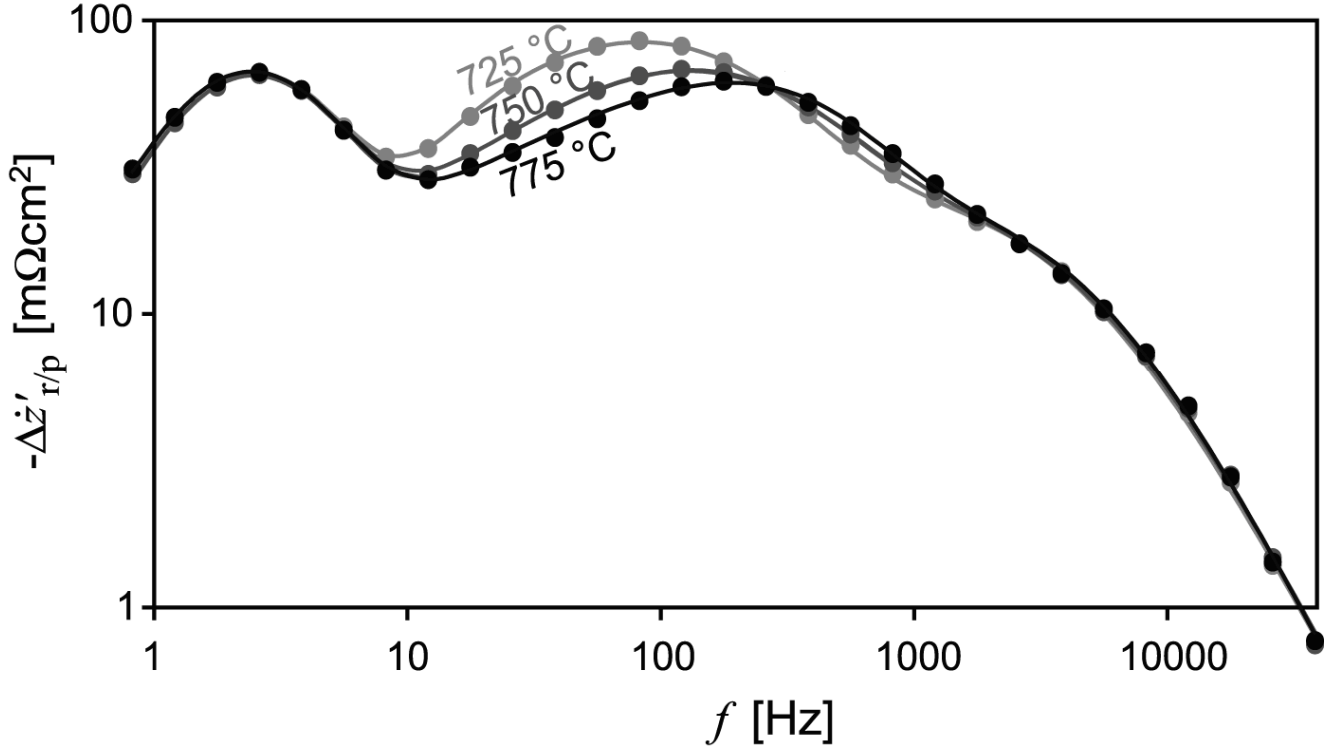
Difference calculated as $\Delta\dot{z}'_{r/p,T}$

This will give information on the processes which are dependant on both r/p and T only



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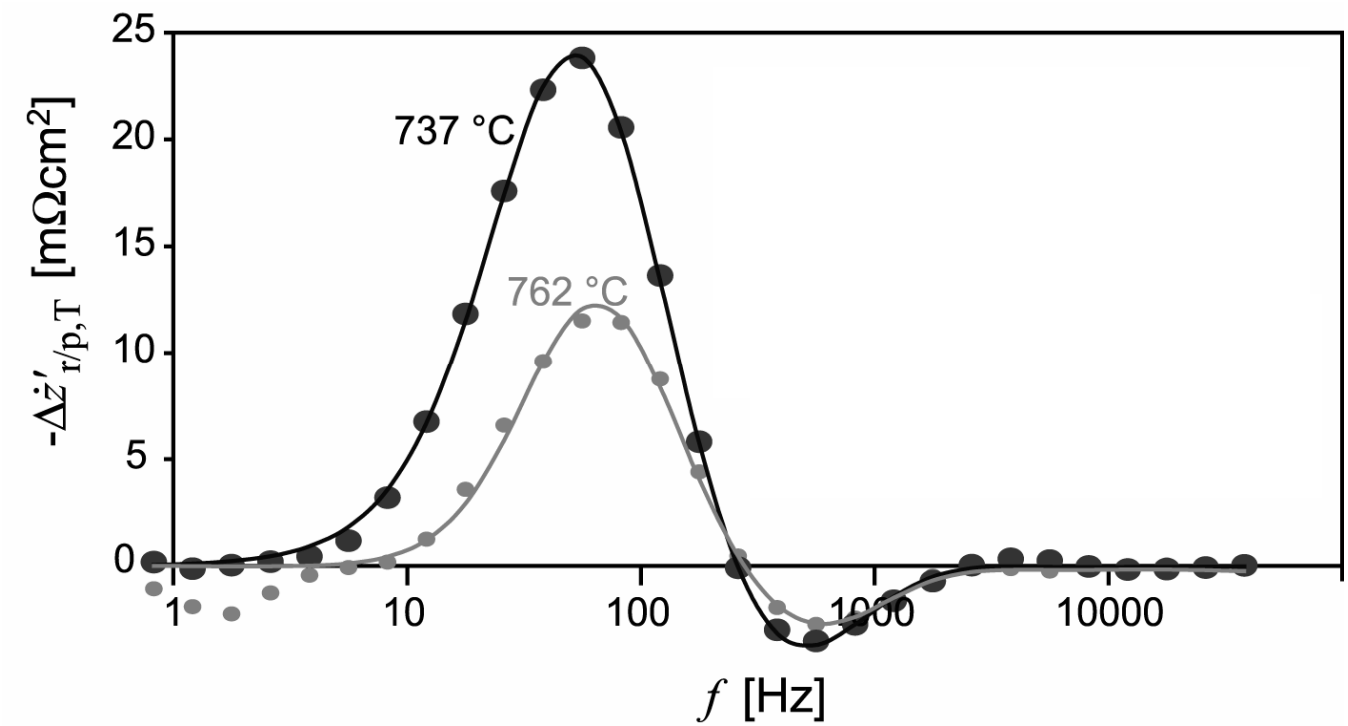

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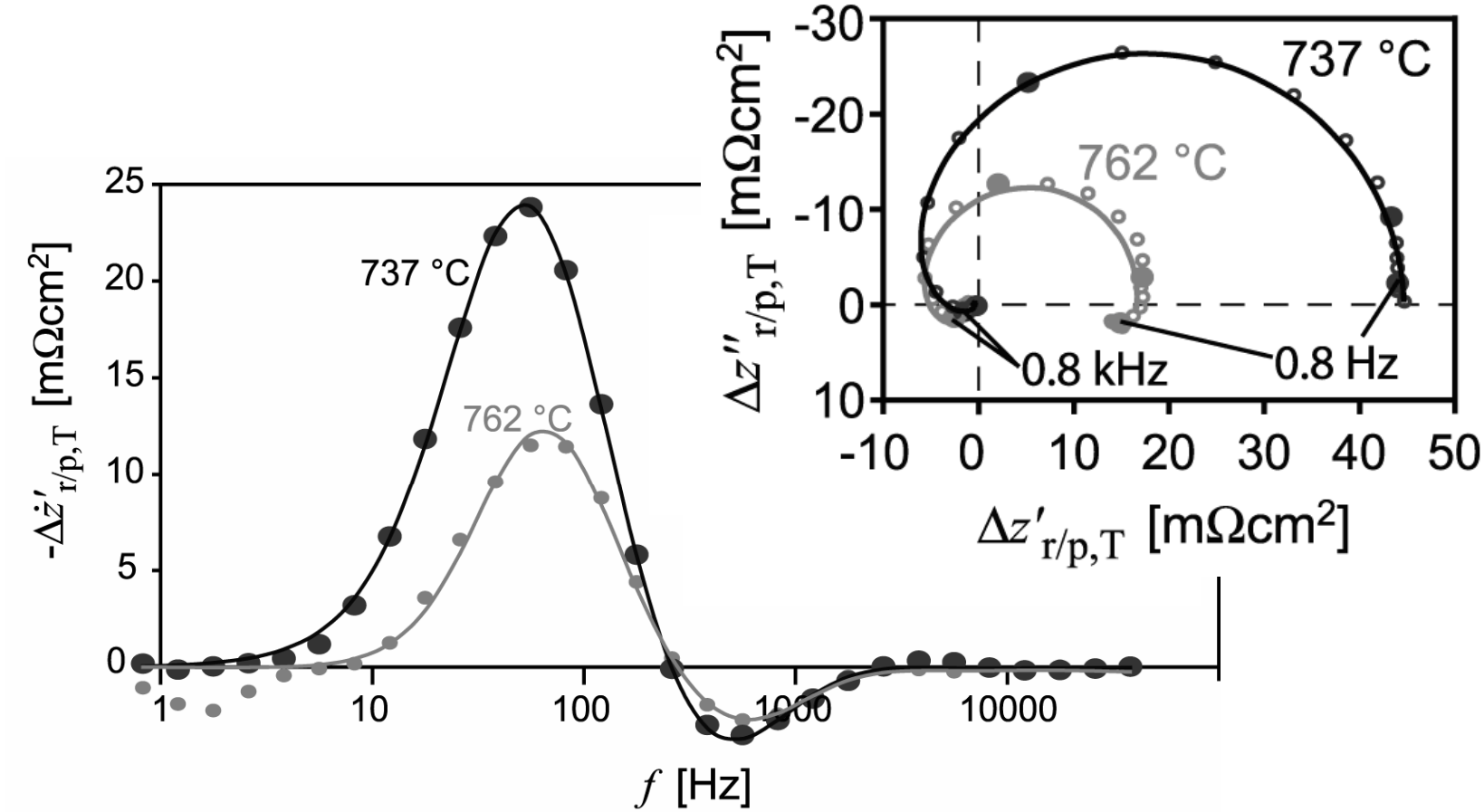

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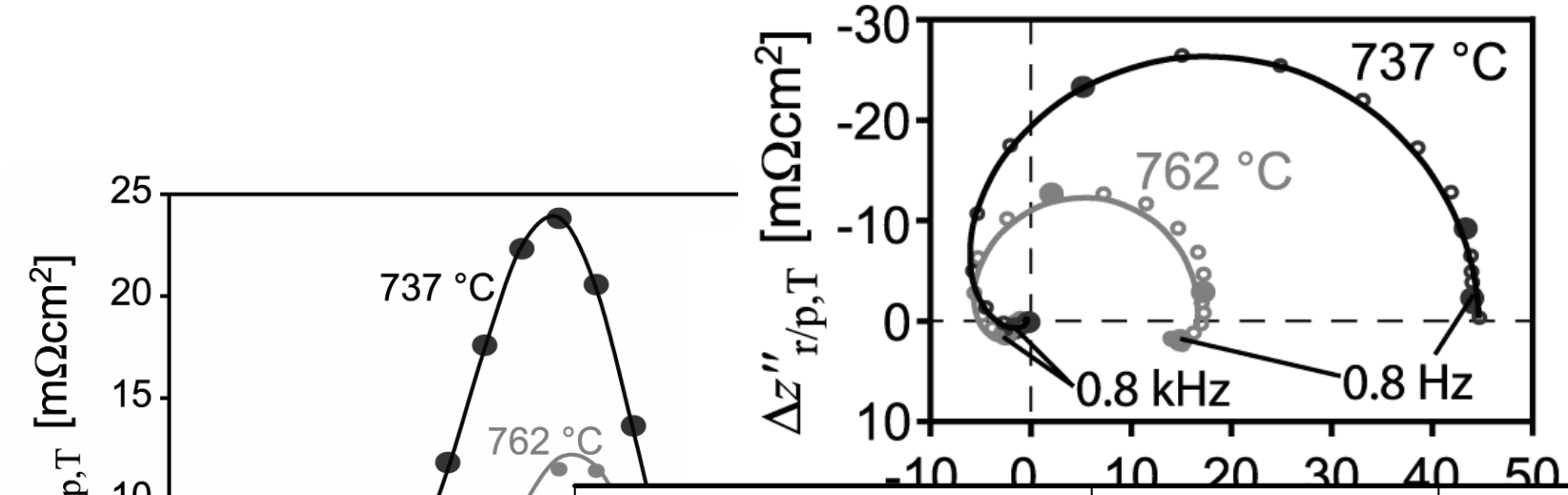

Operating condition	$f_s = \frac{\omega^o_{av}}{2\pi}$ [Hz]	n_{av}
762 °C, 10% H_2O/90% H_2	58 ± 8	0.38 ± 0.01
737°C, 10% H_2O/90% H_2	36 ± 4	0.39 ± 0.01

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- **Powerful tool to separate single process contributions to the full fuel cell impedance**

- **Powerful graphical tool where no model assumptions, filtering, or extrapolations are needed**

- **Provide information on the nature of the underlying process contributions and improve the resolution of overlapping processes in impedance spectra**

High Pressure Electrolysis
Thermodynamics

H_2O + electric energy (ΔG) + heat ($T\Delta S$) $\rightarrow$ $H_2 + \frac{1}{2}O_2$

CO_2 + electric energy (ΔG) + heat ($T\Delta S$) $\rightarrow$ $CO + \frac{1}{2}O_2$

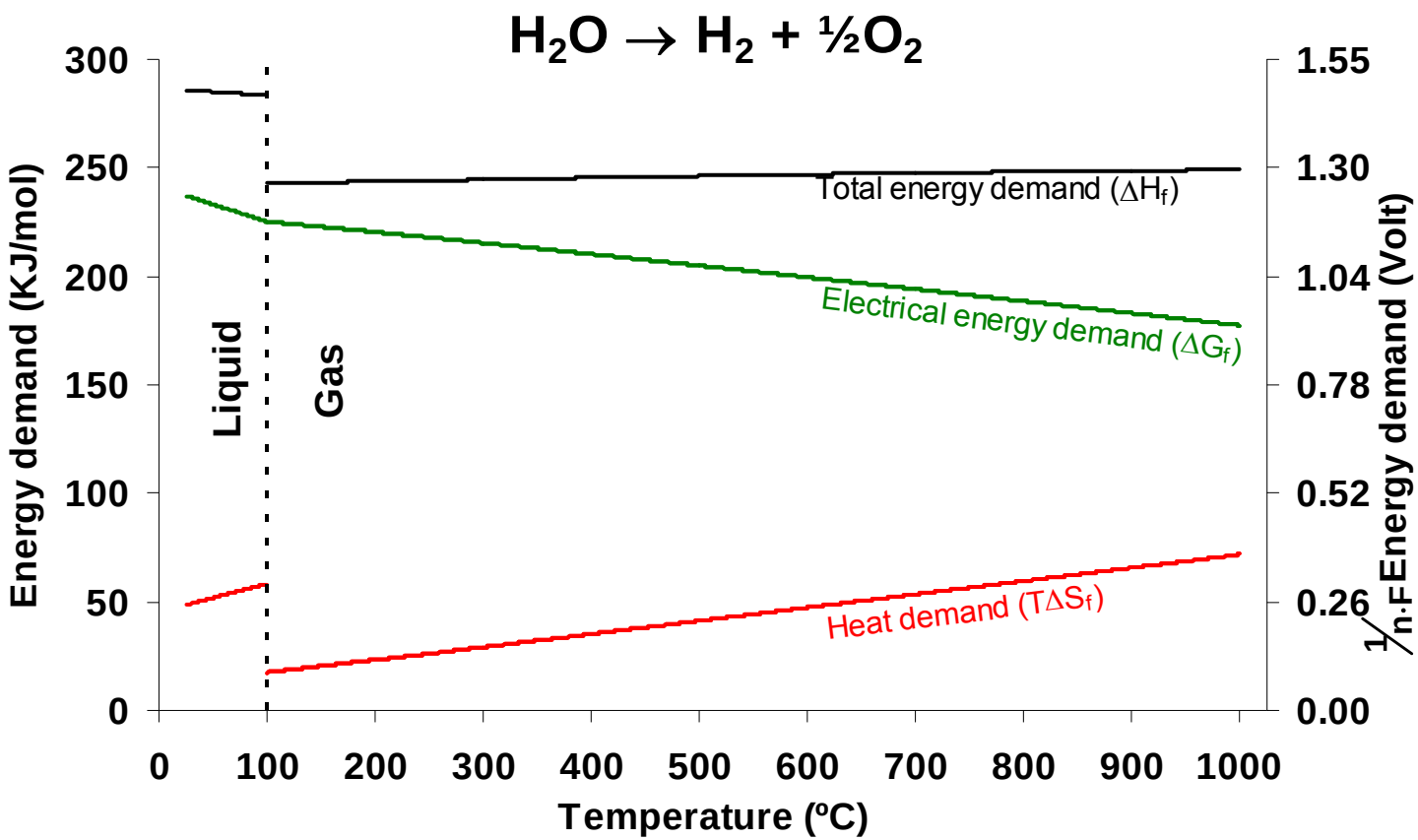
$$\Delta H_f = \Delta G_f + T \cdot \Delta S_f$$

$$E_{tn} = -\frac{1}{n \cdot F} \cdot \Delta H_f \text{ (Thermo neutral voltage)}$$

$$E^{\theta}_{rev} = \frac{1}{n \cdot F} \cdot \Delta G^{\theta}_f \text{ (Reversible voltage)}$$

$$E_{rev} = \frac{1}{n \cdot F}\Delta G^{\theta}_f - \frac{1}{n \cdot F} R \cdot T \cdot \ln Q, \quad Q = \frac{P_{H_2O}}{P_{H_2} \cdot P_{O_2}^{1/2}} \text{ or } \frac{P_{CO_2}}{P_{CO} \cdot P_{O_2}^{1/2}}$$

High Pressure Electrolysis
Thermodynamics (1 atm.)

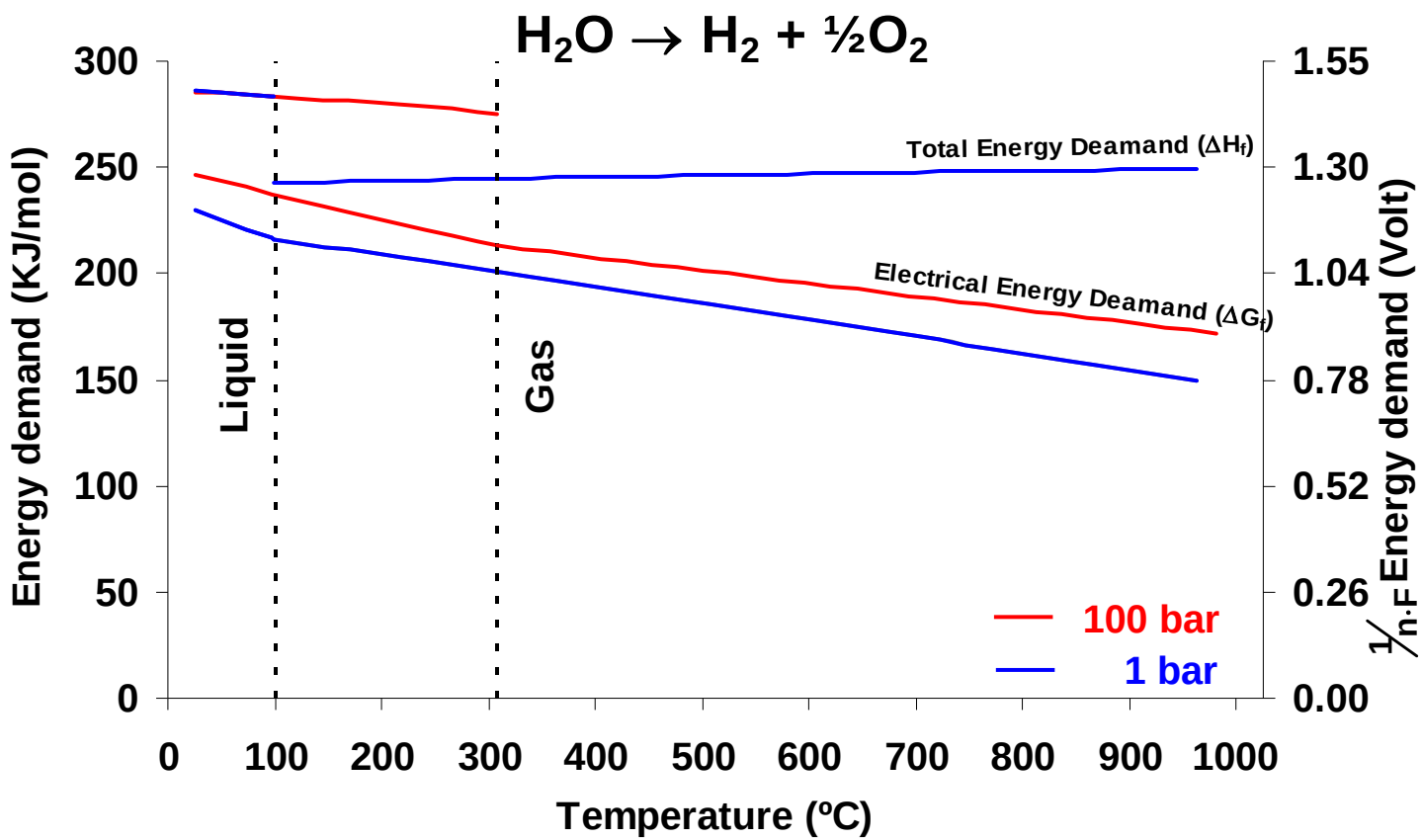


Water electrolysis at 25 ºC: E_{tn} = 1.48 V

Steam electrolysis at >100 ºC: E_{tn} = 1.29 V

High Pressure Electrolysis

Thermodynamics, effect of pressure



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High Pressure Electrolysis

How does high pressure influence on…

- Negative effect on the thermodynamic of electrolysis
- In general positive effect on catalyst kinetics and conversion
- ??? SOEC kinetic
- ??? SOEC durability

…experiments will tell…

Increase in pressure was shown to decrease the polarisation resistance for SOFC

A. V. Virkar, K. Fung, and S. C. Singhal,
Proceedings of the International conference on ionic and mixed conducting ceramics, 1998, 113-124.

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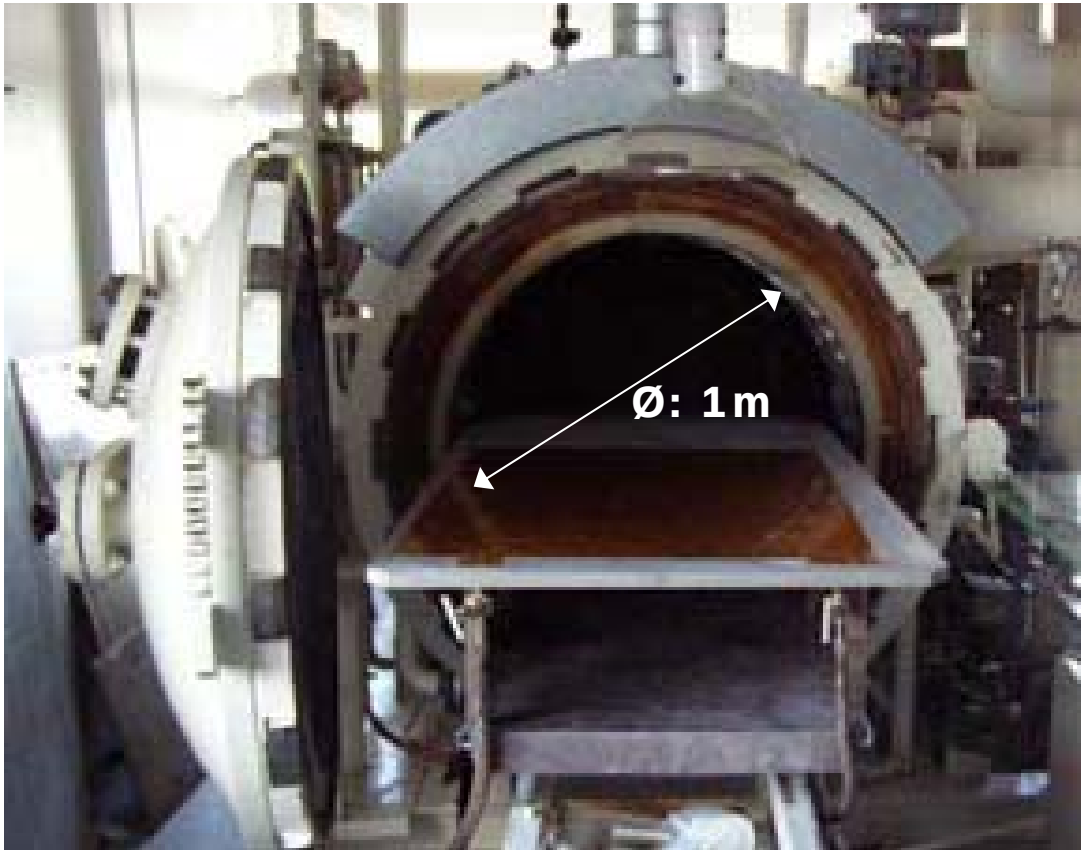
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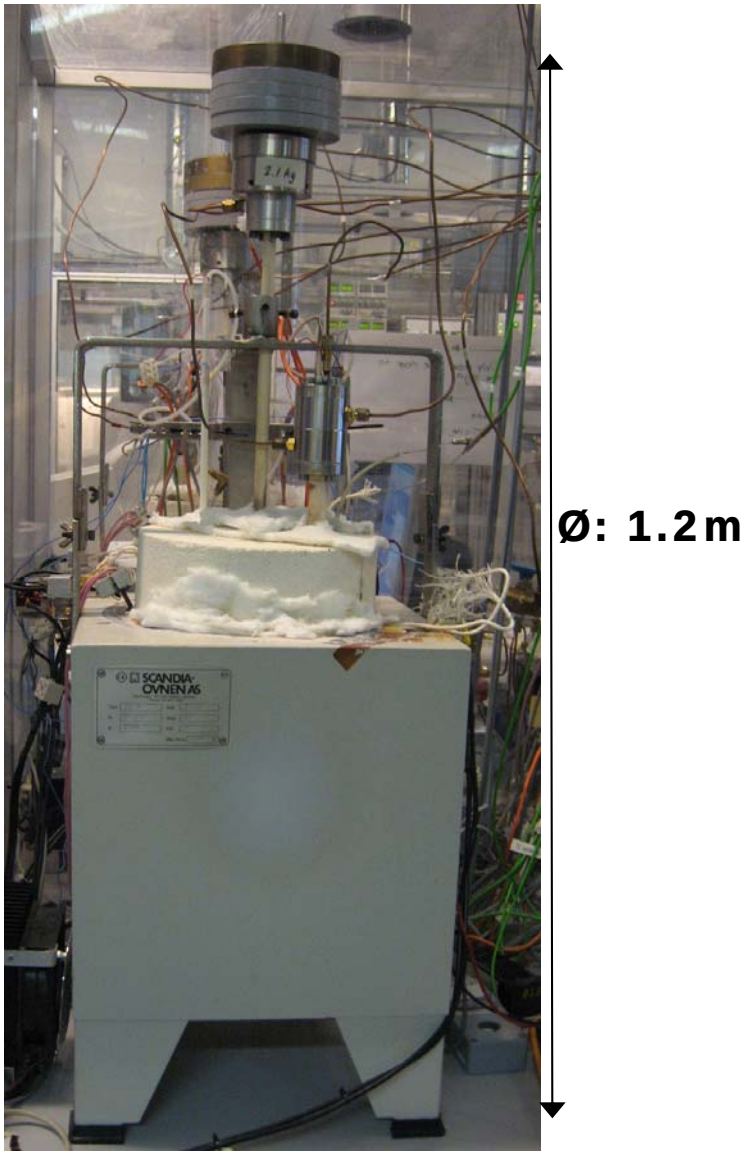
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Any further questions…

Please send Søren Højgaard an e-mail

soeren.hoejgaard.jensen@risoe.dk

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