WORKSHOP:

FROM BASIC TO APPLIED RESEARCH TOWARDS DURABLE AND RELIABLE FUEL CELLS

Lucerne, Switzerland, 5 July 2022

Online THDA for rSOC diagnostic:

Illustration for reactants depletion

G. Hammerschmid[1,2], H. Moussaoui[1*], J. Van herle[1], V. Subotić[2]

hamza.moussaoui@epfl.ch

[1]Group of Energy Materials, École Polytechnique Fédérale de Lausanne, Switzerland

[2]Institute of Thermal Engineering, Graz University of Technology, Austria

Contents

Context

Main limitation of solid oxide cells:

- Durability insufficient for large-scale deployment
- Critical conditions cause premature failure or irreversible degradation

Solution:

- Early detection & identification of critical cond.
- Mitigation and recovery
- No irreversible degradation

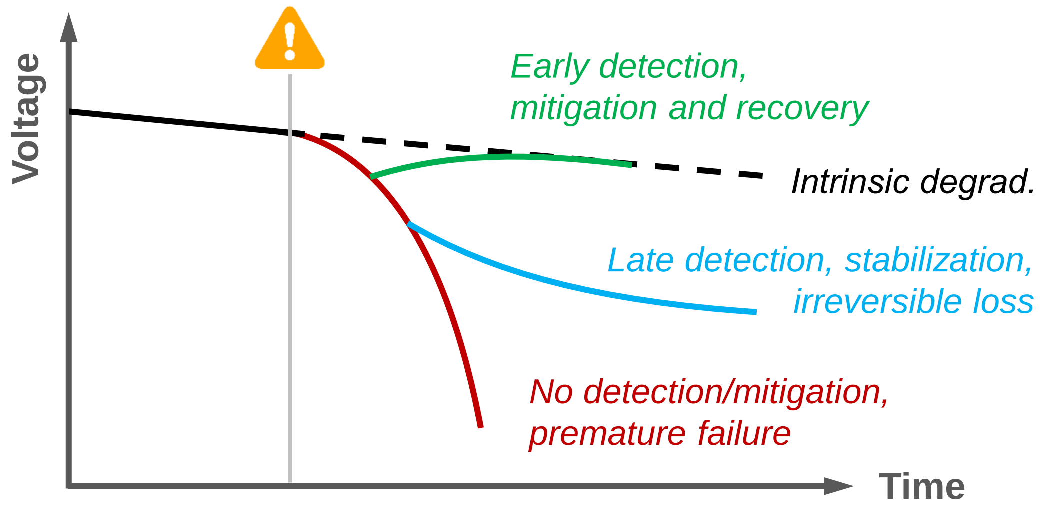


Fig.1: *Voltage evolution and possible degradation pathways under failure.*

SCOPE

Experimental investigation of fuel and steam starvation:

- Polarization curves (jV)
- Electrochemical Impedance Spectroscopy (EIS) and Distribution of Relaxation Times (DRT)
- Total Harmonic Distortion (THD)

2D, steady-state **simulation model** with MATLAB

Electrochemical Impedance Spectroscopy (EIS)

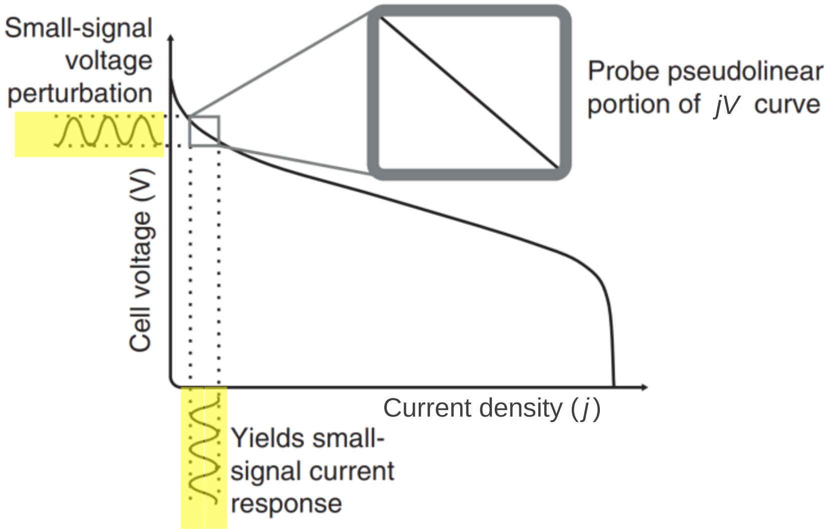


Fig.2: *EIS method from "Fuel Cell Fundamentals" (O'Hayre et al., 2016).*

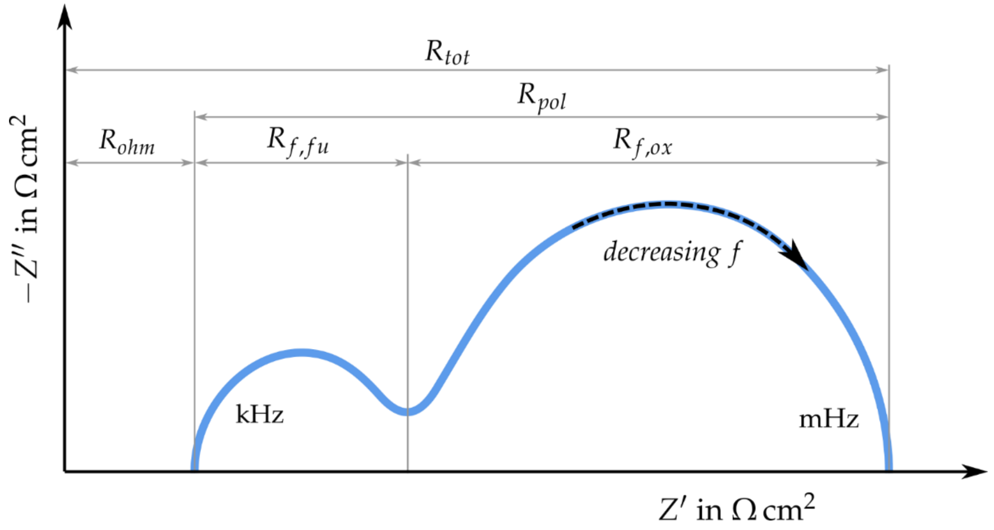


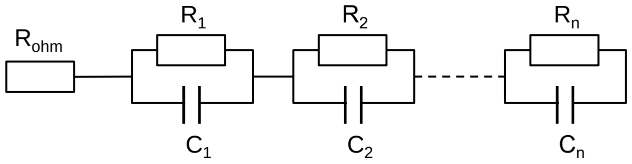
Fig.3: *Schematical representation of an impedance spectrum as Nyquist plot.*

Impedance: $$Z(\omega) = \frac{U(t)}{j(t)} = \frac{\hat{U}\sin(\omega t+\phi)}{\hat{j}\sin(\omega t)} = \frac{\hat{U}e^{i(\omega t+\phi)}}{\hat{j}e^{i\omega t}} = \hat{Z}e^{i\phi} = \hat{Z}(\cos\phi + i\sin\phi)$$ Eq. (1)

DRT (Distribution of Relaxation Times)**:**

$$Z_{\mathrm{DRT}}(\omega) = R_{ohm} + \int_{-\infty}^{\infty} \frac{\gamma(\ln\tau)}{1+i\omega\tau}\, d(\ln\tau)$$

Eq. (2)



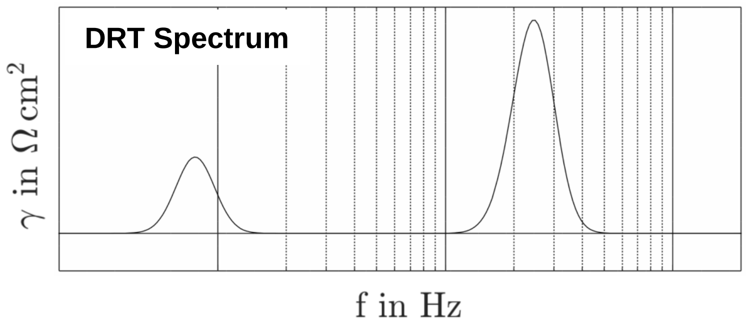
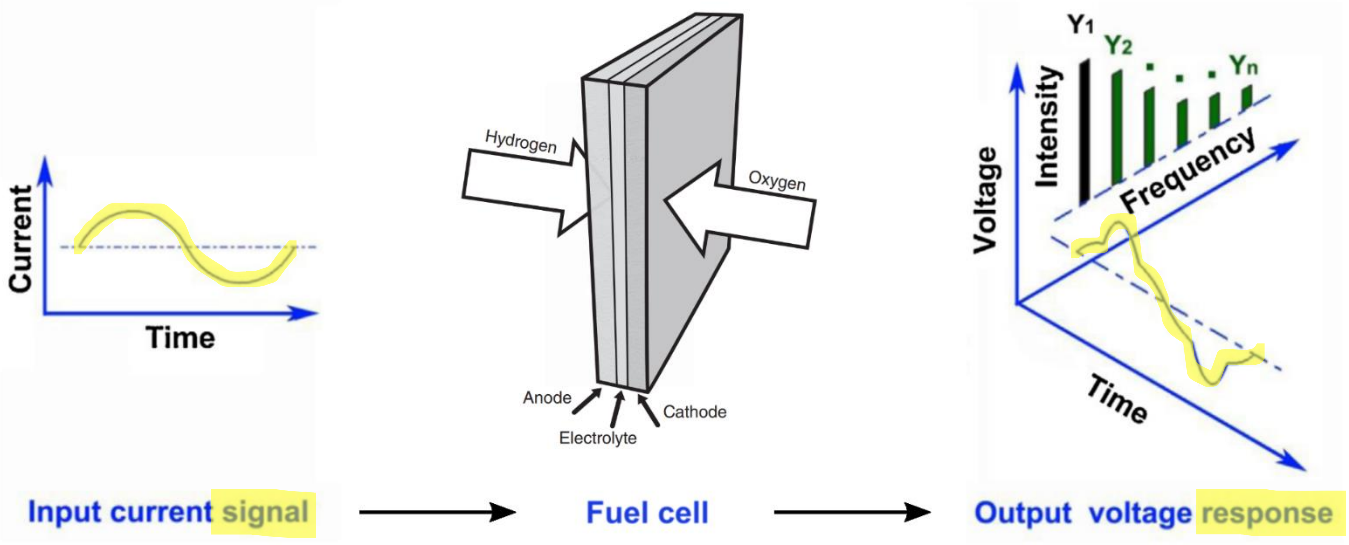


Fig.4: *Schematical representation of a DRT spectrum.*

❖ Well established but still a **laboratory tool** (sophisticated to implement in a commercial context)

Total Harmonic Distortion (THD)



$$\mathrm{THD} = \frac{\sqrt{\sum_{n=2}^{\infty} Y_n^2}}{Y_1} \qquad \text{Eq. (1)}$$

Y_1 amplitude of fundamental frequency (= frequency of excitation signal)

$Y_2 \ldots Y_n$ amplitudes of higher harmonics

***Fig.5:** Schematic voltage response to a sinusoidal current signal in time and frequency domain from “Total harmonic distortion analysis of oxygen reduction reaction in proton exchange membrane fuel cells” (Mao and Krewer, 2013).*

- Quantifies the **non-linearity** (no sinusoidal response)
- Deconvolution of response into **harmonics** (via Fourier transform)
- **Hypothesis:** Identification of critical conditions via frequency-specific distortion (compared to healthy, linear state)

- At const. operation, **THD index** dependent on:
  - f_1 frequency of excitation signal
  - j_{AC}, U_{AC} amplitude of excitation signal
  - n number of harmonics used

Single Cell Setup and Test Rig

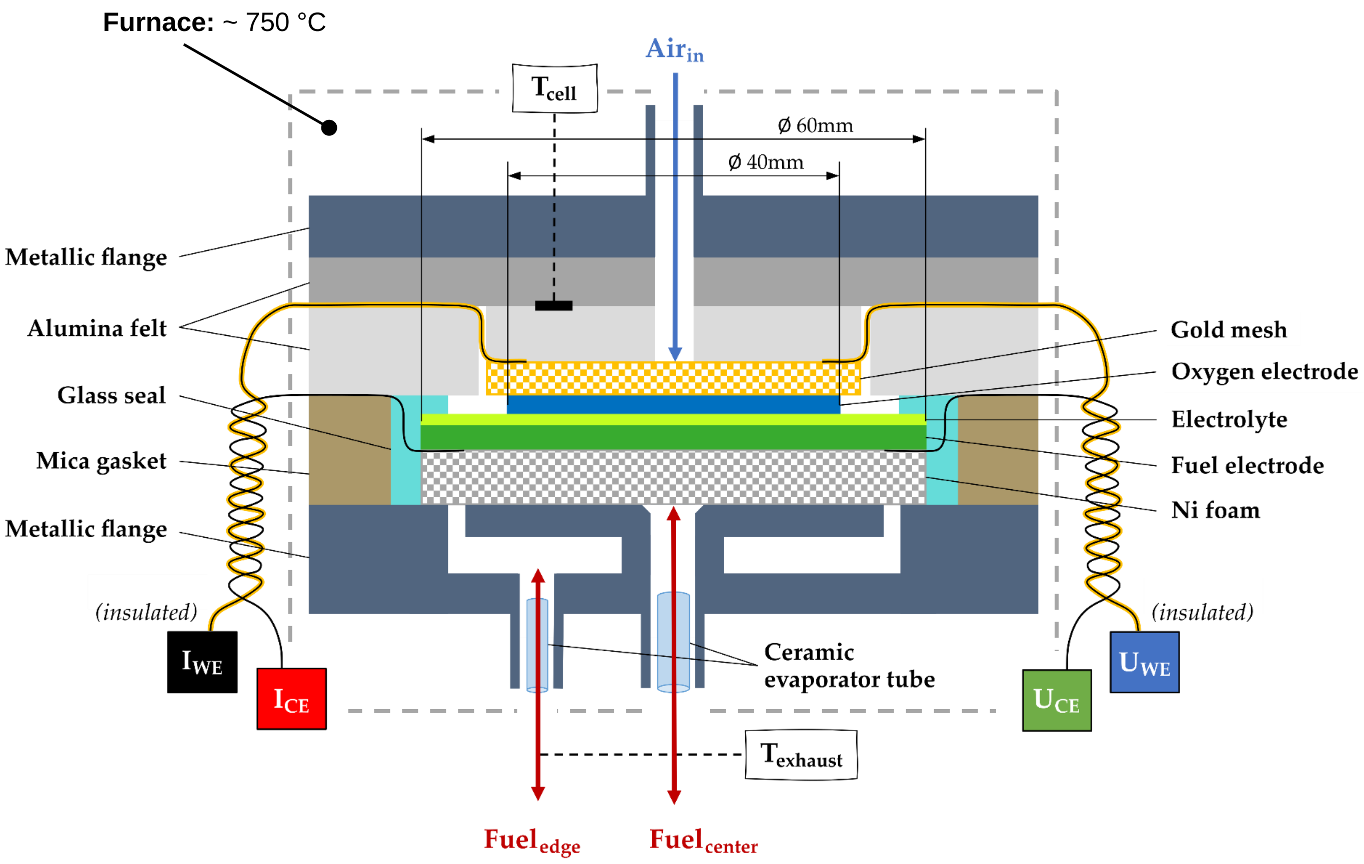


Fig.6: Schematic representation of the single cell setup.

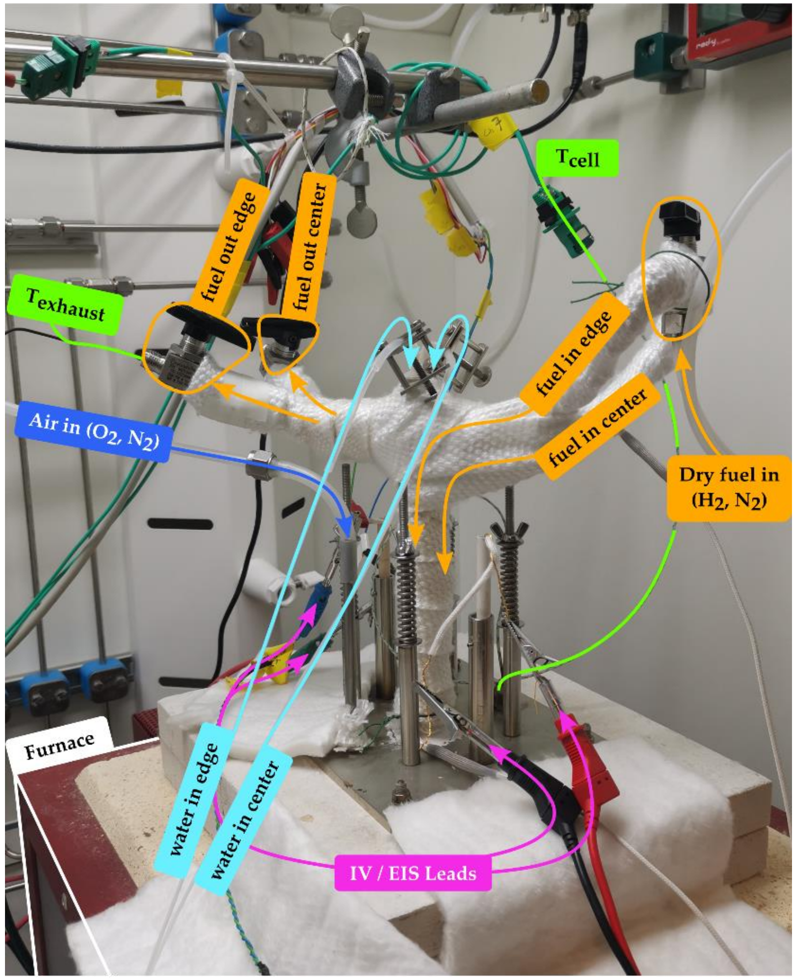


Fig.7: Photo of the experimental test rig.

Modeling

Fitted to experimental data

Nernst: but considering parasitic losses $j_{leak} \rightarrow p^{e}_{i,in}$

$$OCV = -\frac{\Delta_r G(T, p^{\ominus})}{z_e F} - \frac{RT}{z_e F} \ln\left(\prod_i \left(\frac{p^{e}_{i,in}}{p^{\ominus}}\right)^{\nu_{st,i}}\right) \quad \text{Eq. (3)}$$

Charge transfer: Butler-Volmer

$$j = j_0 \left\{ \exp\left(\frac{\alpha z_e F \eta_{act}}{RT}\right) - \exp\left(-\frac{(1-\alpha) z_e F \eta_{act}}{RT}\right) \right\} \quad \text{Eq. (4)}$$

$$j_0^0 = \gamma e^{-\frac{E_a}{RT}} \quad \text{Eq. (5)}$$

jV Model: $U(j) = OCV - \eta_{act} - \eta_{ohm} - \eta_{conc}$ Eq. (2)

Charge transport: Ohm's law

$$\eta_{ohm} = j R_{ohm} = j R_{ohm,0} e^{\left(\frac{E_{a,ohm}}{RT}\right)} \quad \text{Eq. (6)}$$

Change in electrochemical potential:

$$\eta_{conc} = \frac{RT}{z_e F} \ln\left(\prod_i \left(\frac{c_{i,j\neq 0}}{c_{i,j=0}}\right)^{\nu_{st,i}}\right) \quad \text{Eq. (7)}$$

→ Correction factor *C* for η_{conc}

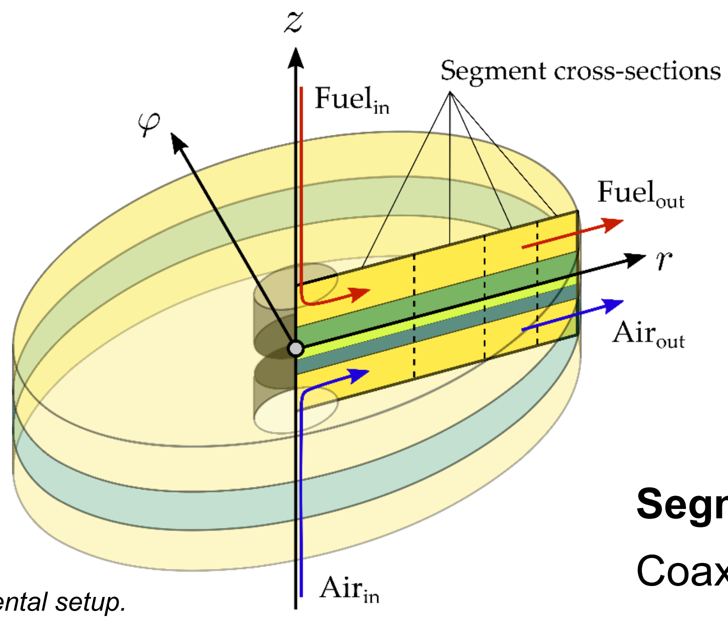


Fig.8:
Computational domain based on the experimental setup.

Segmentation:

Coaxial cylinders with equal active area

Fuel Starvation (SOFC)

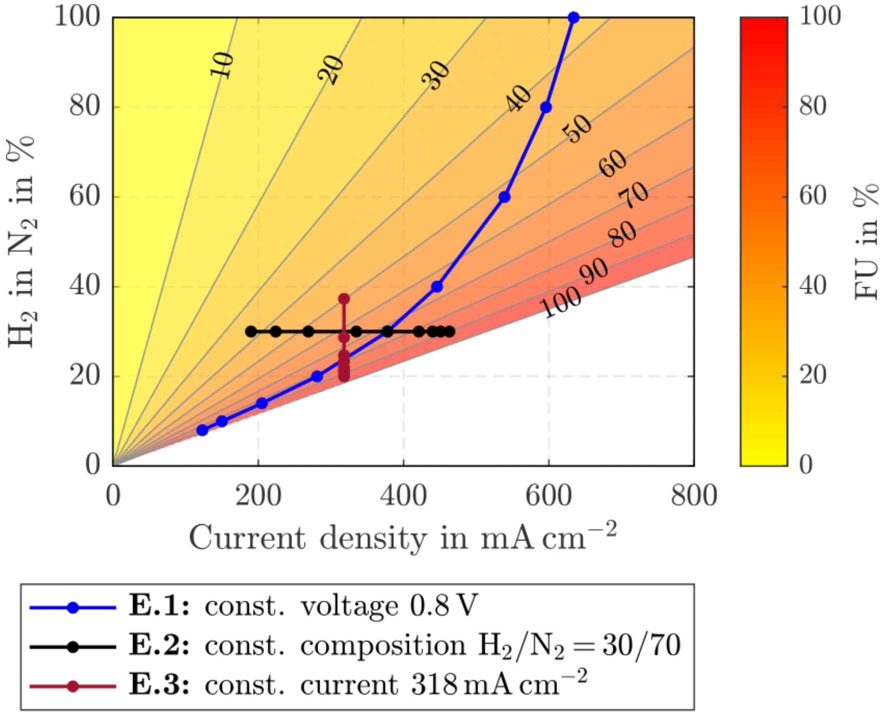


Fig.9: *FU with current density and composition (150 Nml min⁻¹, 12.57 cm²).*

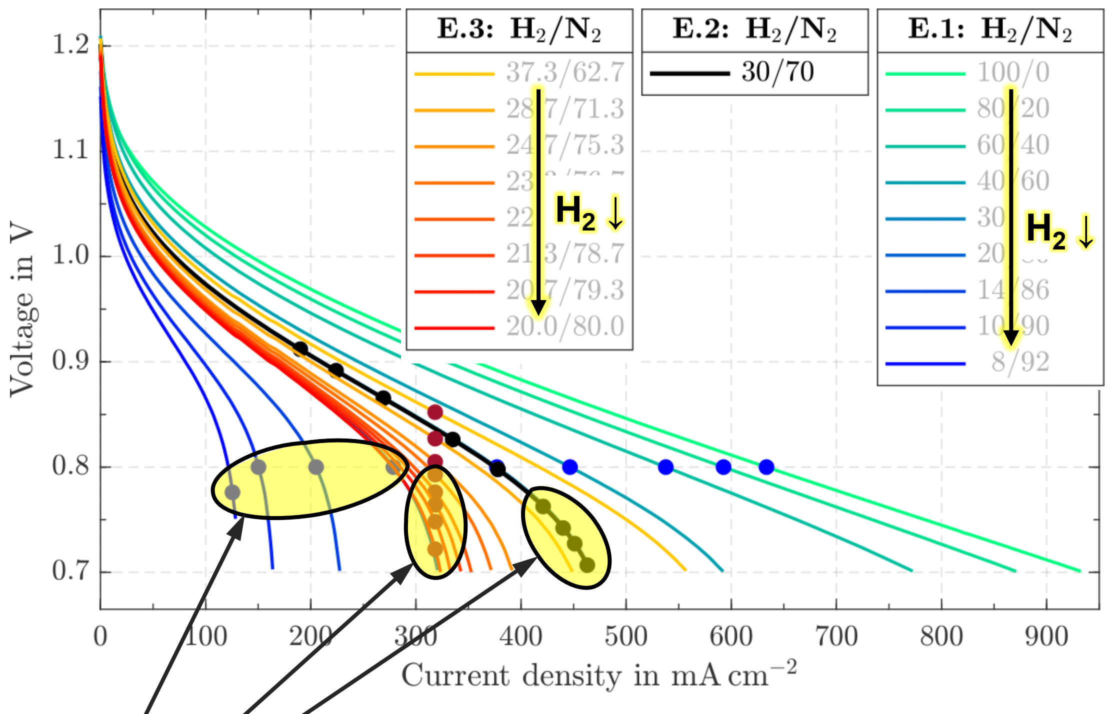


Fig.10: *jV curves of fuel starvation. The dots indicate operating points of EIS and THD measurements.*

Fuel Utilization: $\mathrm{FU} = \dfrac{jA_{cell}}{z_e F \dot{n}_{H_2}}$ Eq. (8)

- For **FU > 80%** significant voltage drop (↑ η_{conc})

Fuel Starvation (SOFC)

No	E.3) FU %	E.1) FU %	E.2) FU %
1	50	37	37
2	65	43	43
3	75	52	52
4	80	65	65
5	84	74	74
6	87	82	82
7	90	86	86
8	93	88	88
9		90	90
H_2 / N_2 =	20.7 / 79.3	8 / 92	30 / 70

- R_{ohm} and high-frequency semicircle ≠ f(FU)
- R_{pol} and low-frequency semicircle ↑↑ as FU ↑
- For same FU, impedance ↑ for diluted fuel and low *j* than for H_2 rich fuel and high *j*

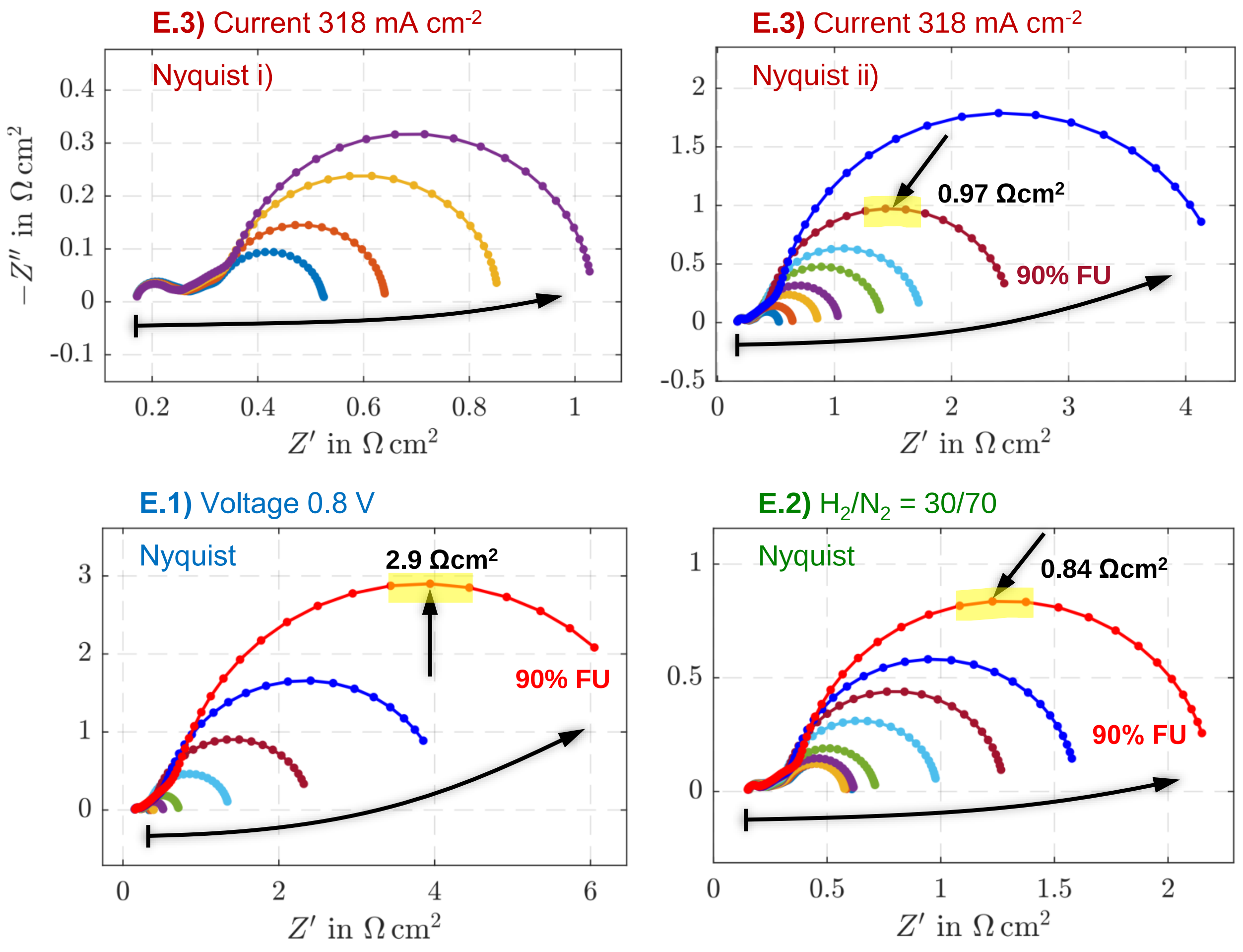


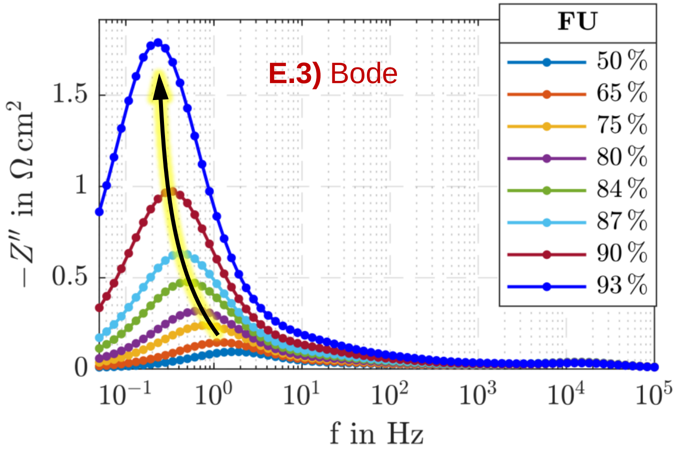
Fig.11: Nyquist plots of experiments on fuel starvation.

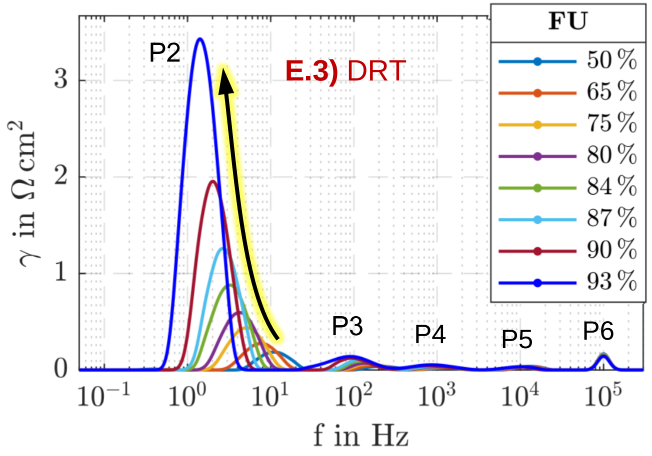
Fuel Starvation (SOFC)

E.3)

No	FU %
1	50
2	65
3	75
4	80
5	84
6	87
7	90
8	93
9	

- **Bode:** Low-frequency peak ↑ and shifts to lower frequencies as FU ↑
- **DRT:** Gas conversion peak P2 ↑ and shifts from 10^1 to 10^0 as FU ↑
- **THD:** THD ↑ the ↓ the frequency and ↑ FU, for f < 2 Hz
  THD above 1% threshold (healthy state) for FU > 80%
  max THD 9.3% at 87mHz for 93% FU





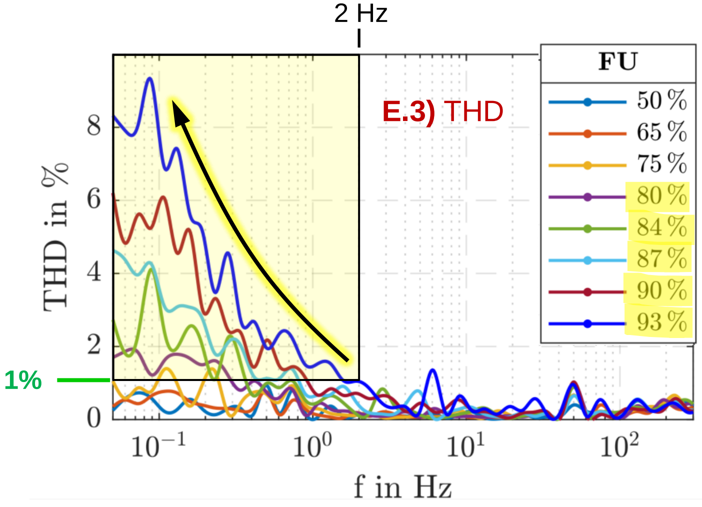


***Fig.12:** Bode, DRT, and THD plot of experiment 3 on fuel starvation.*

Steam Starvation (SOE)

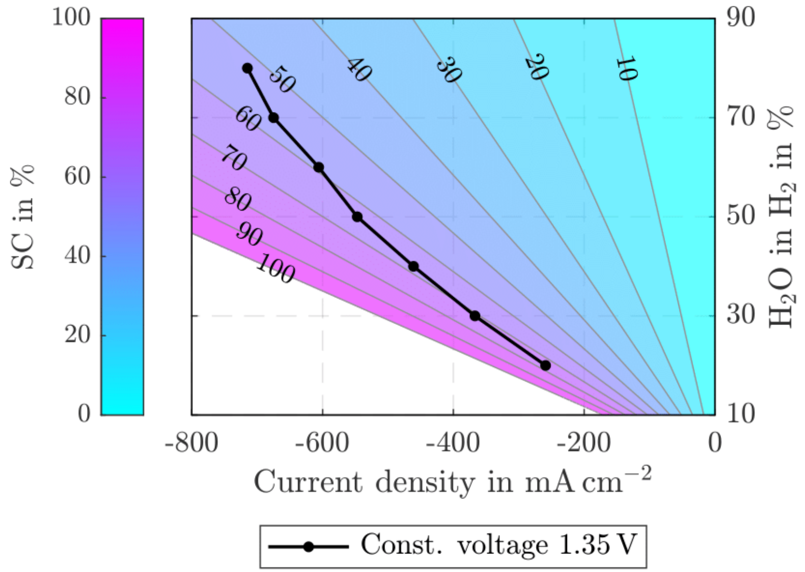


Fig.13: *SC with current density and composition (150 Nml min^{-1}, 12.57 cm^2).*

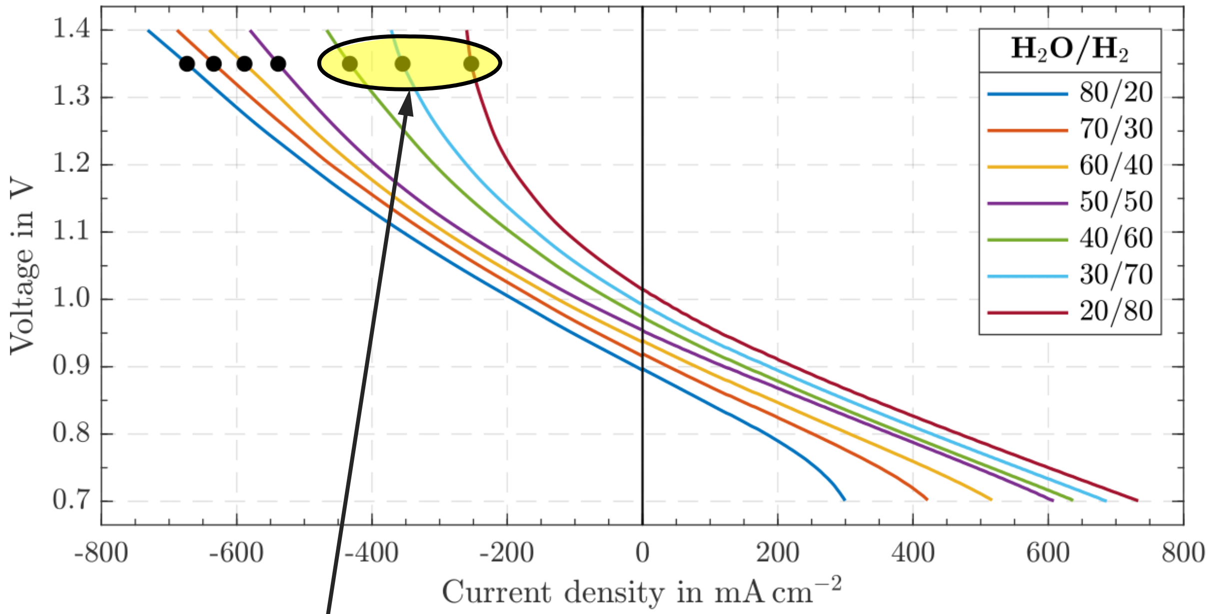


Fig.14: *jV curves of steam starvation. Dots indicate operating points of EIS/THD measurements.*

Steam Conversion: $\mathrm{SC} = \frac{jA_{cell}}{z_e F \dot{n}_{H_2O}}$ Eq. (9)

- For **SC > 67%** significant voltage rise (↑ η_{conc})

Steam Starvation (SOE)

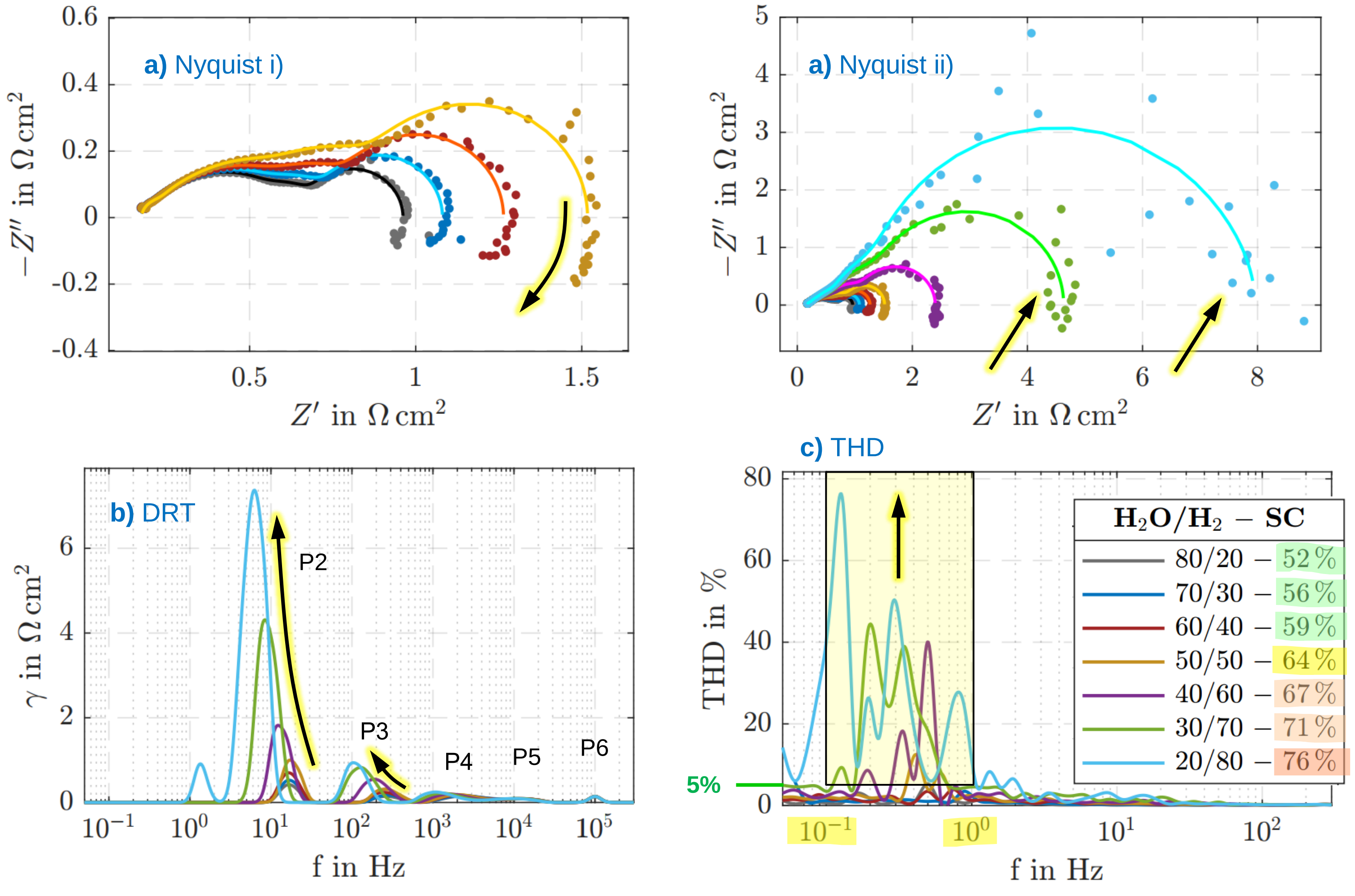


***Fig.15:** EIS, DRT, and THD results of steam starvation at 1.35V, Amp = 50mV.*

- **Nyquist:**

  "Pseudo-inductive" loop;

  For SC ≥ 71% (H_2 ≤ 30%) immense fluctuations in raw data

- **DRT:**

  P2 and P3 ↑ and shift to lower freq. as SC ↑

- **THD:**

  Threshold ≈ 5%,

  THD ↑↑ between 0.1–1Hz as SC ↑;

  Max THD 76% at 125mHz for 76% SC

THD – Number of Harmonics

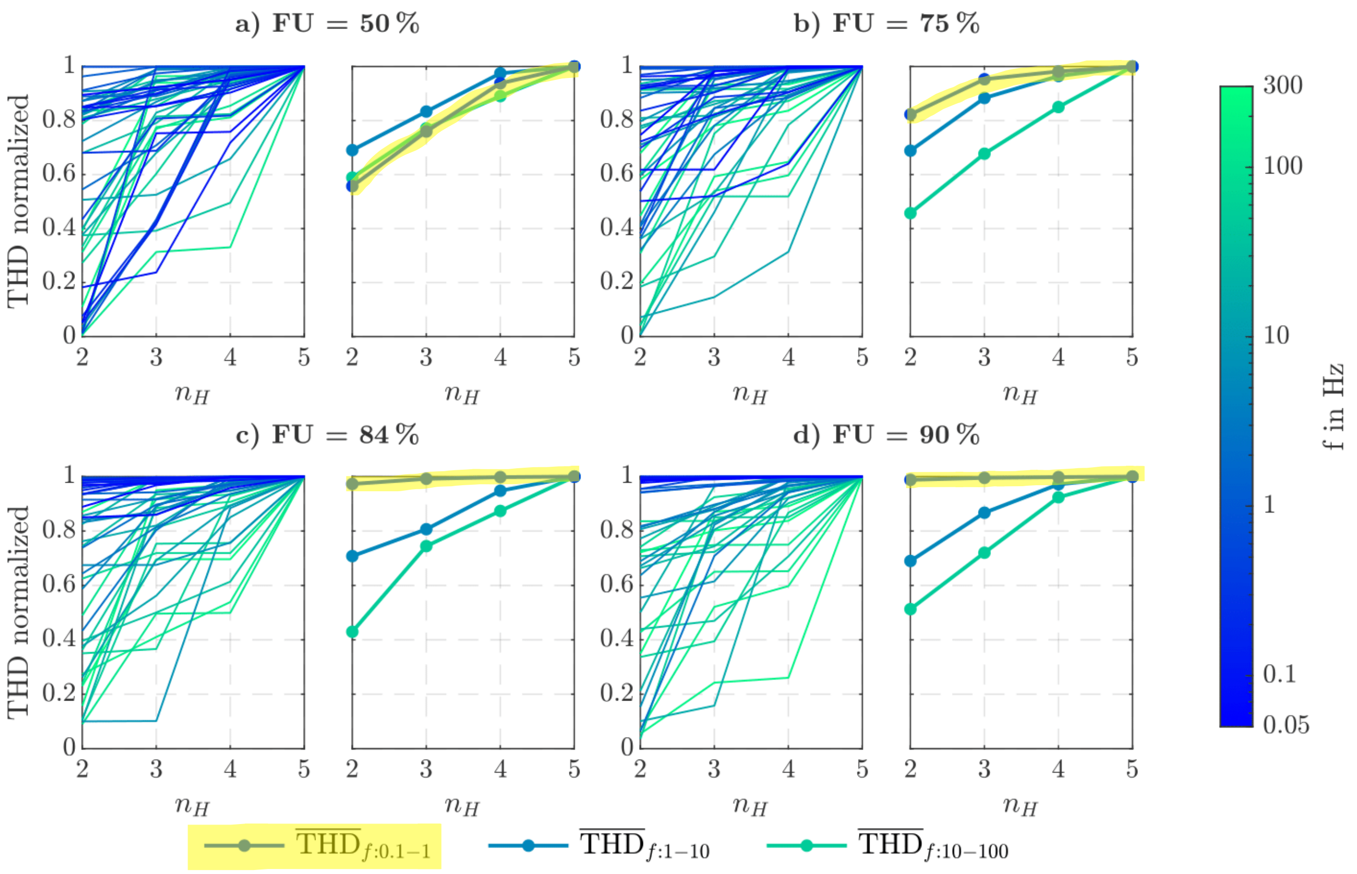


Fig.16: *Evolution of THD index with harmonics used, normalized to highest THD(n_H = 5). Operating points from E1.3 (const. current 318 mA cm^{-2} and Amp = 5%).*

The increase in THD at low frequencies (< 2 Hz) due to fuel starvation stems almost exclusively from the **2nd harmonic**.

All others are negligible.

Model Validation

- Introduction
- Exp. method
- Modeling
- Exp. results
- **Model results**
- Conclusion

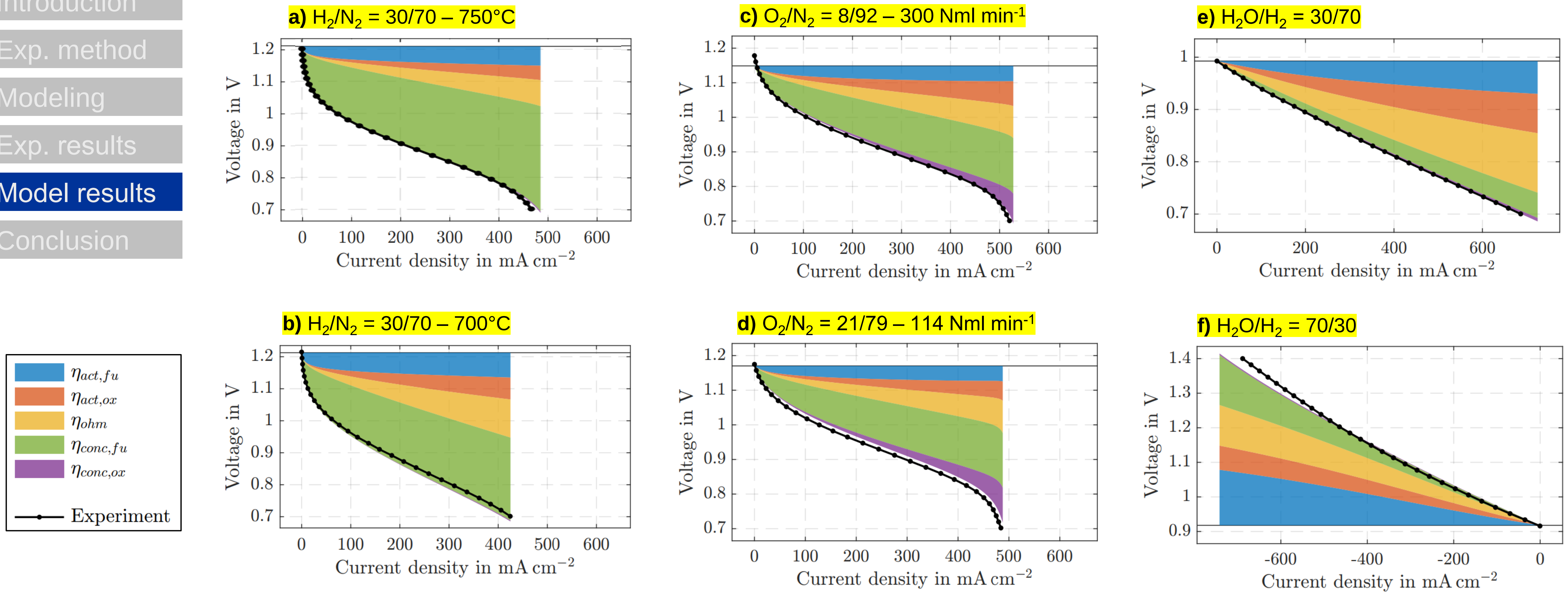


Fig.17: *Simulation versus measurements a) fuel starvation, b) temperature, c) and d) air starvation, e) and f) humid fuel.*

Simulation

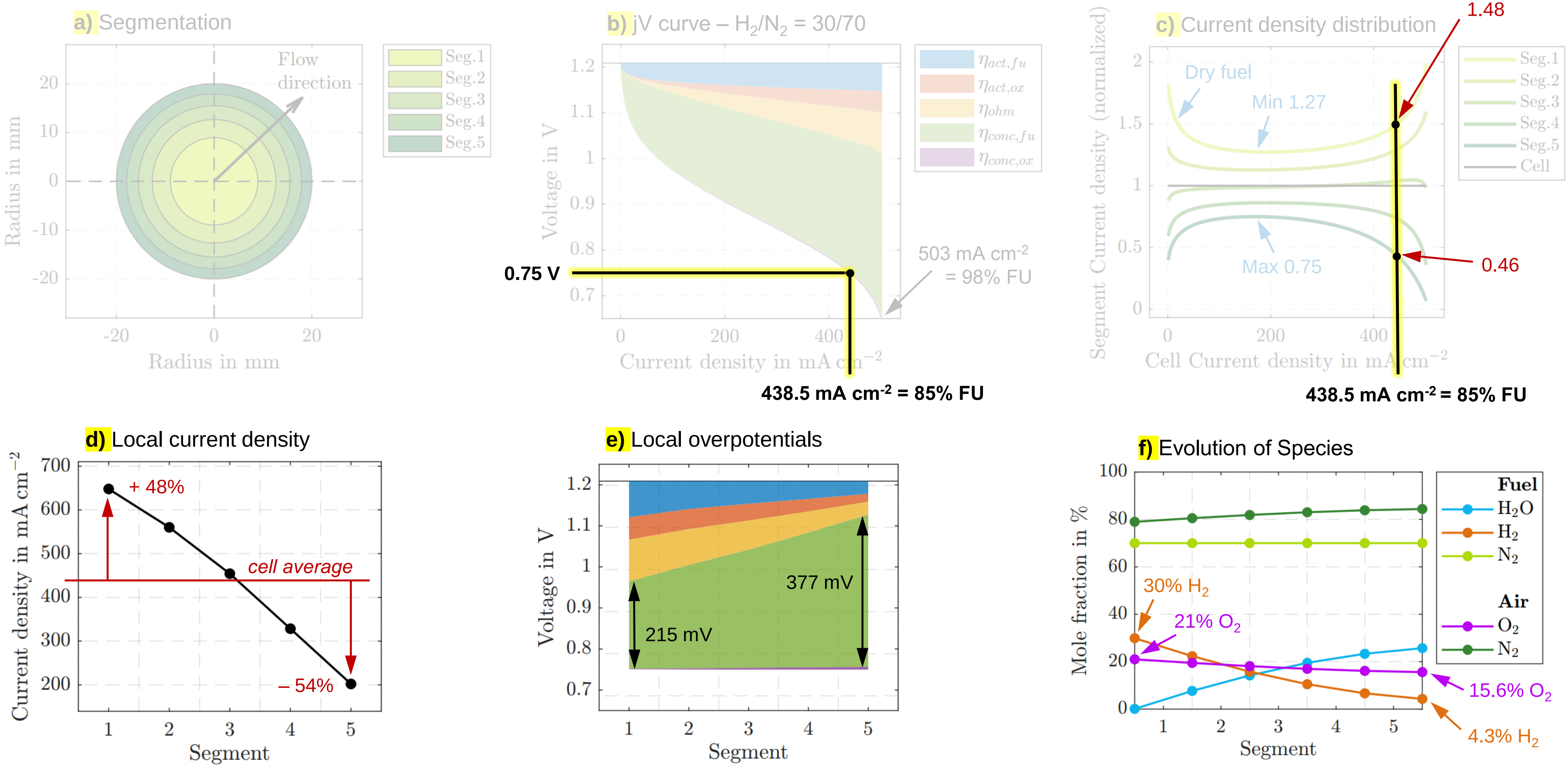


Fig.18: *Simulation for H_2/N_2 = 30/70, 150 Nml min^{-1} fuel flow rate, O_2/N_2 = 21/79, 300 Nml min^{-1} air flow rate, 750°C cell temperature, outward fuel flow.*

Conclusion

- **Experimental**
  - Extensive characterization of reactants starvation in SOFC and SOE modes
  - Tools: Polarization curve, EIS & DRT, and THD (each having advantages & drawbacks)
- **Modeling**
  - 2D steady-state model → Large local disparities during critical conditions

➢ **EFCF Presentation**
by Gerald Hammerschmid
On Friday 10:15

- **Impact**
  - **Understanding** of critical conditions and **how to detect** them (novelty THD)
  - Improve State-of-Health monitoring → Prevent degradation → **Increase lifetime**
  - Use model to propose **safe operating points** free of local extremes
- **Outlook**
  - Accelerated Stress Tests
  - Other failure modes
  - Stacks & systems
  - Transient model

THANK YOU

This work has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking (now Clean Hydrogen Partnership) under grant agreement N° 101007175 (REACTT), 875047 (RUBY) and 825027 (AdAstra) and Hydro-Québec Research Institute (IREQ). This Joint Undertaking receives support from the European Union’s Horizon 2020 research and innovation program, Hydrogen Europe and Hydrogen Europe research.

Comparison of Tools

BACKUP SLIDE

	jV	EIS & DRT	THD
Information	Global performance/SoH No identification of individual processes	In-depth characterization Deconvolution of processes by time charact. Identification of criticalities and causes	Severity of monitored criticalities Limited to certain criticalities
Time	**Fast** (< 3min)	**Slow** (> 15min) to obtain sufficient spectrum	**Fast** (1-2min) to monitor relevant frequencies
System Availability	Interrupted	In steady-state mode OK In dynamic mode not possible	In steady-state mode OK In dynamic mode not possible
Main Purpose	Characterization	Characterization	Monitoring
Application	Commercial	Laboratory	Emerging Commercial
Reliability / Reprod.	Very Good	Good	Fairly Good
Equip. Requirements	Low	High	High(er)
Usability	Simple	Sophisticated	Sophisticated

Working Principle

BACKUP SLIDE

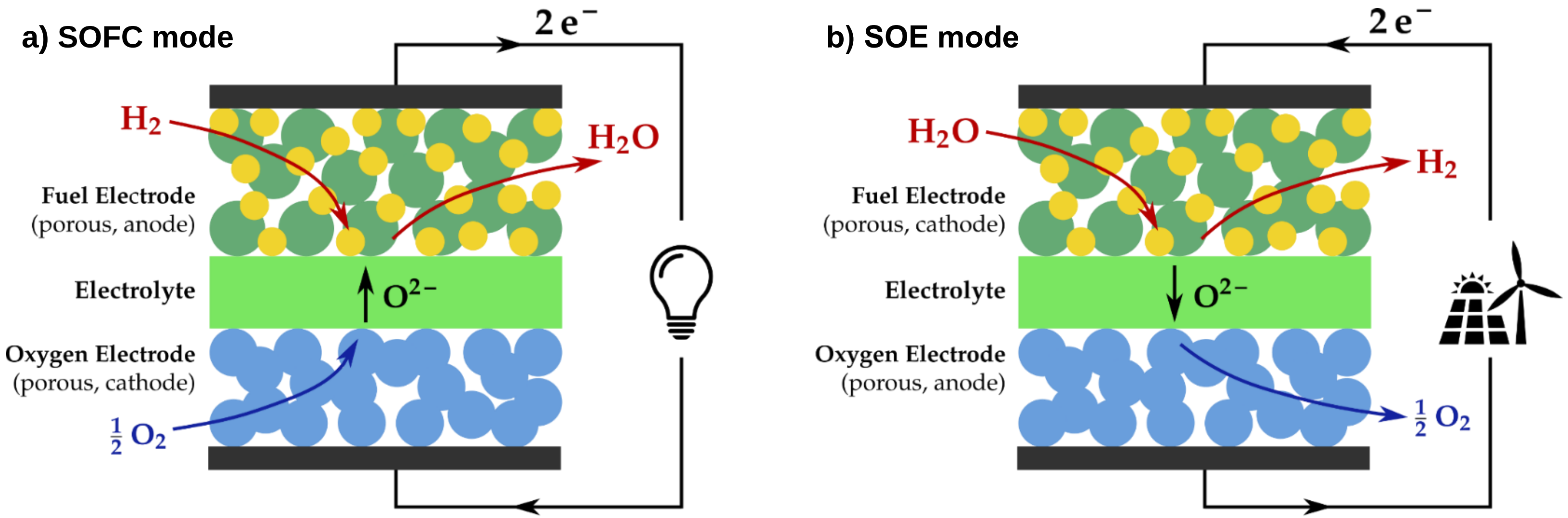


Fig.3: *Schematic representation of the working principle of a SOC in a) SOFC mode and b) SOE mode.*

- Temperature: 600 – 1000°C
- Reactions: at triple-phase-boundary (TPB)
- Fuel flexibility: H_2, NH_3, CO, CH_4 …
- Reversibility: fuel cell ↔ electrolyzer mode

- Dense, ceramic electrolyte: YSZ
- Porous electrodes
  - Fuel side: Ni-YSZ
  - Air side: LSM, LSM-YSZ, LSCF, LSCF-GDC

Causes for Failure and Degradation

BACKUP SLIDE

- **Causes for failure:**

current	*temperature*	*leakage*	*unpredicted shut-down*
voltage	*gas composition*	*load-cycles*	*defects in balance-of-plant (BoP) …*

- **Degradation:** Deterioration of cell performance over time

Fuel Electrode:

- *Ni-oxidation*
- *Ni-agglomeration*
- *Carbon deposition*
- *Poisoning: S, Cl, Si, Na, Al*

Oxygen Electrode:

- *Delamination of electrode/electrolyte interface*
- *Secondary phases: $SrZrO_3$, Cr_2O_3*
- *Cr evaporation*

Electrolyte:

- *Decomposition of YSZ*
- *Reduction of YSZ*

SCOPE

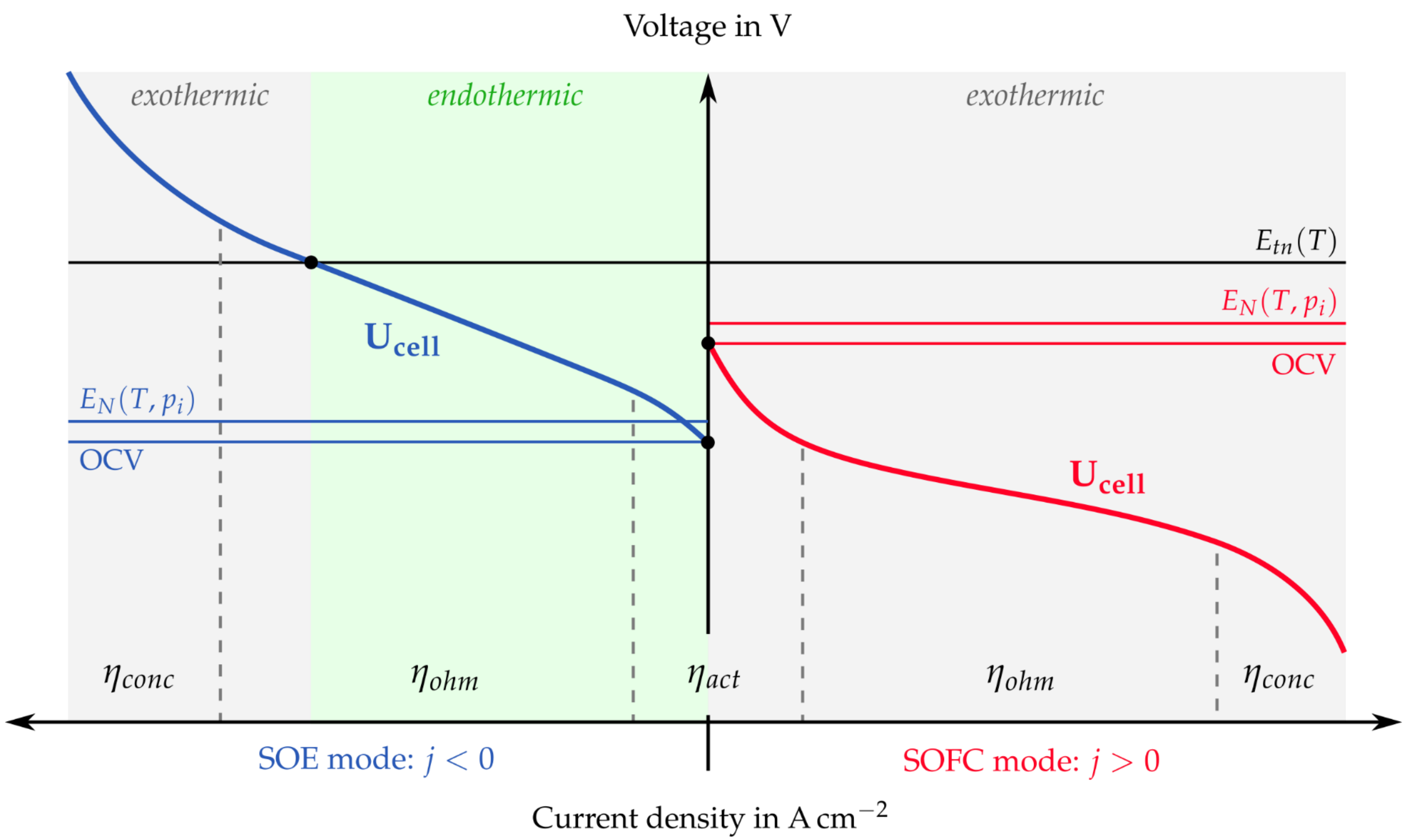
Experimental investigation of fuel-, air-, steam starvation:

- Polarization curves (jV)
- Electrochemical Impedance Spectroscopy (EIS) and Distribution of Relaxation Times (DRT)
- Total Harmonic Distortion (THD)

2D, steady-state **simulation model** with MATLAB

Polarization Curve (jV)

BACKUP SLIDE



$$E_{tn} = -\frac{\Delta_r H(T)}{z_e F} \quad \text{Eq. (1)}$$

$$E_N = -\frac{\Delta_r G(T,p^0)}{z_e F} - \frac{RT}{z_e F}\ln\left(\prod_i \left(\frac{p_i}{p^0}\right)^{\nu_{st,i}}\right) \quad \text{Eq. (2)}$$

$$U_{cell} = \mathrm{OCV} - \eta_{act} - \eta_{ohm} - \eta_{conc} \quad \text{Eq. (3)}$$

$$\mathrm{ASR}_{local}(j^*) = \left.\frac{dU}{dj}\right|_{j=j^*} \quad \text{Eq. (4)}$$

Fig.2: *Typical current-voltage (jV) characteristic known as polarization curve.*
(Note: Same temperature but different gas composition in each mode, therefore different Nernst voltage.)

(STP: 25°C, 1.01325 bar)

Electrochemical Impedance Spectroscopy (EIS)

BACKUP SLIDE

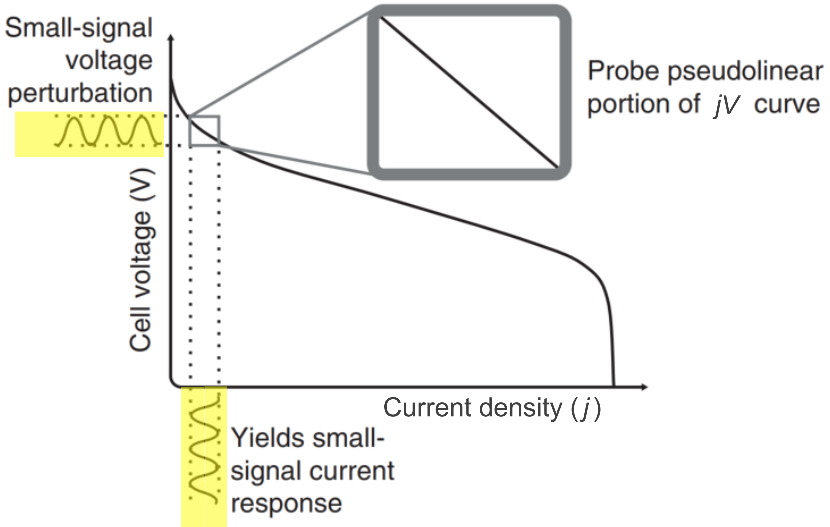


Fig.5: *EIS method from "Fuel Cell Fundamentals" (O'Hayre et al., 2016).*

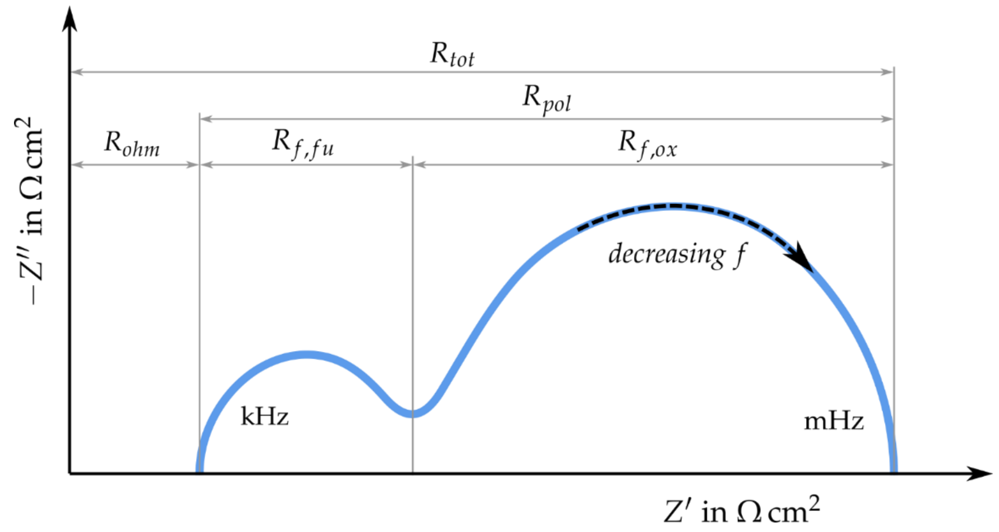
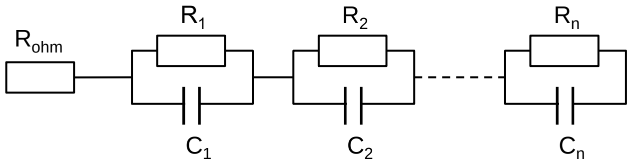


Fig.6: *Schematical representation of an impedance spectrum as Nyquist plot.*

Impedance: $$Z(\omega) = \frac{U(t)}{j(t)} = \frac{\hat{U}\sin(\omega t+\phi)}{\hat{j}\sin(\omega t)} = \frac{\hat{U}e^{i(\omega t+\phi)}}{\hat{j}e^{i\omega t}} = \hat{Z}e^{i\phi} = \hat{Z}(\cos\phi + i\sin\phi)$$ Eq. (1)

DRT (Distribution of Relaxation Times)**:**

$$Z_{\mathrm{DRT}}(\omega) = R_{ohm} + \int_{-\infty}^{\infty} \frac{\gamma(\ln\tau)}{1+i\omega\tau}\, d(\ln\tau)$$ Eq. (2)



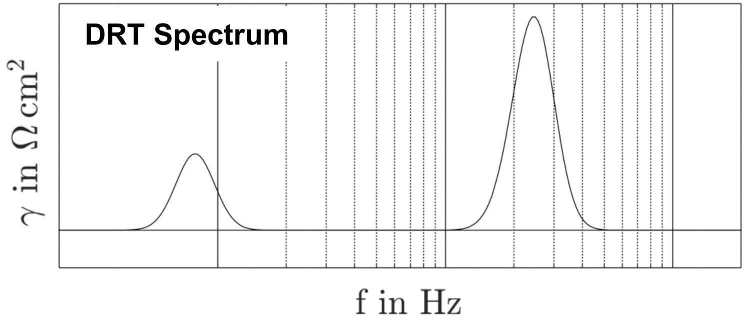


Fig.7: *Schematical representation of a DRT spectrum.*

Test Rig

BACKUP SLIDE

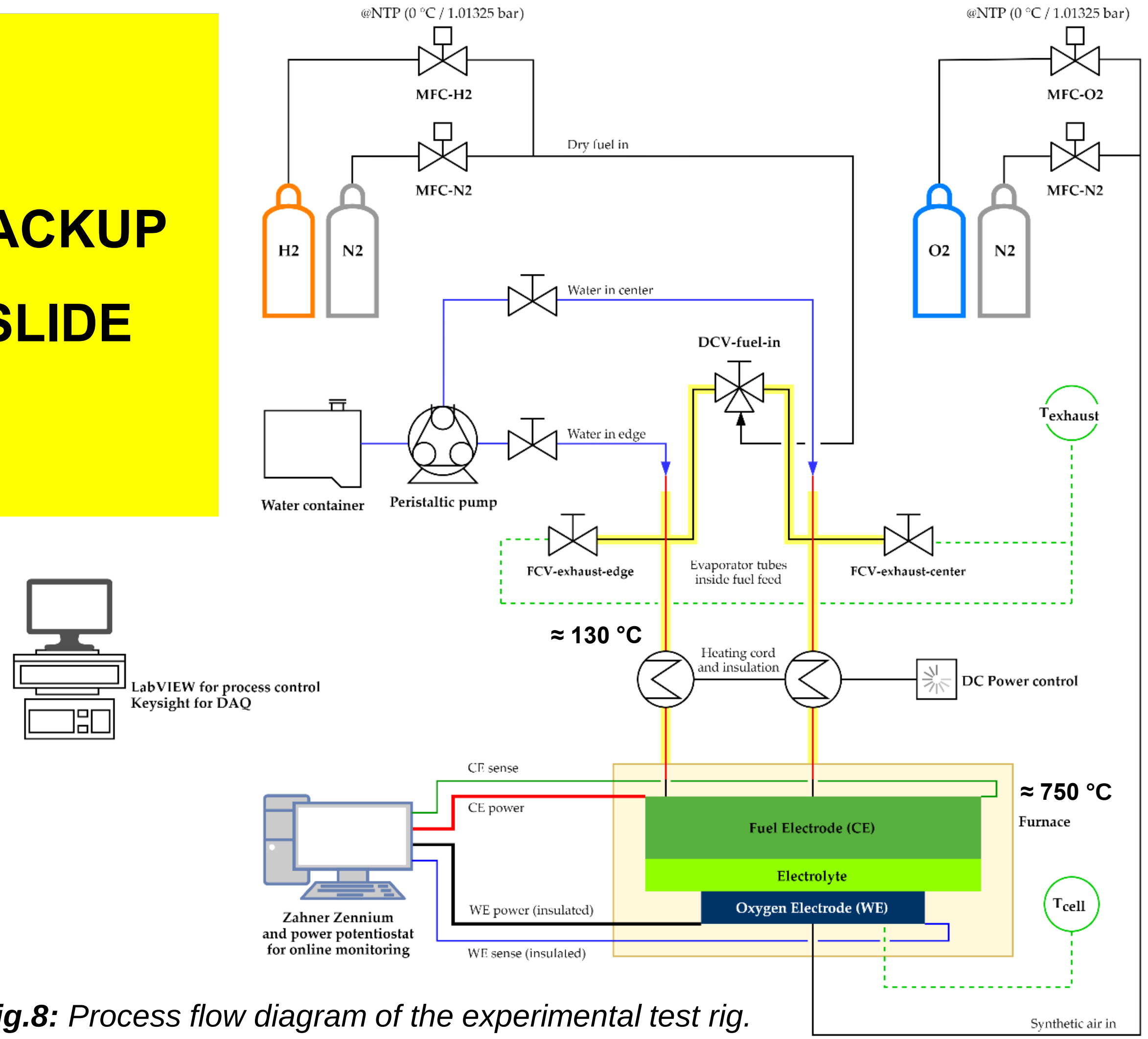


Fig.8: *Process flow diagram of the experimental test rig.*

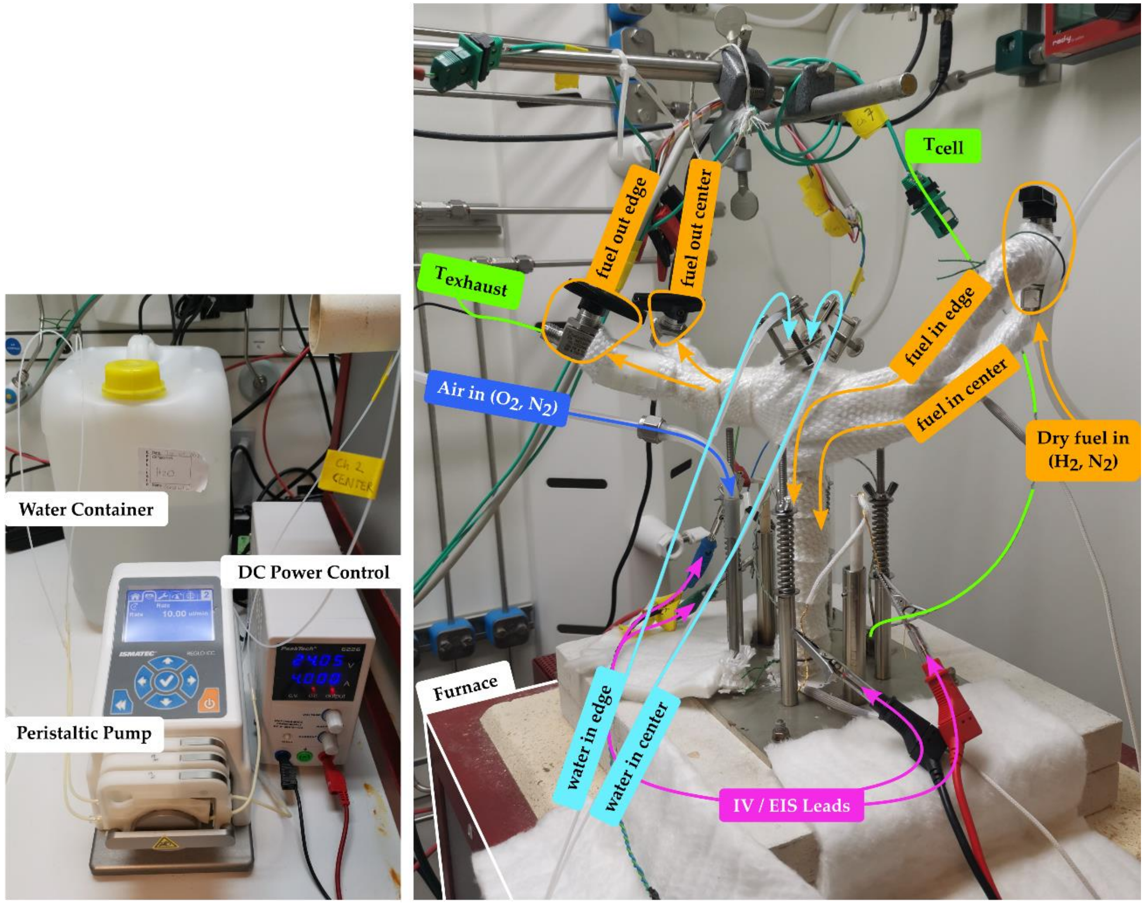


Fig.9: *Photos of the experimental test rig.*

Test Rig Modifications

BACKUP SLIDE

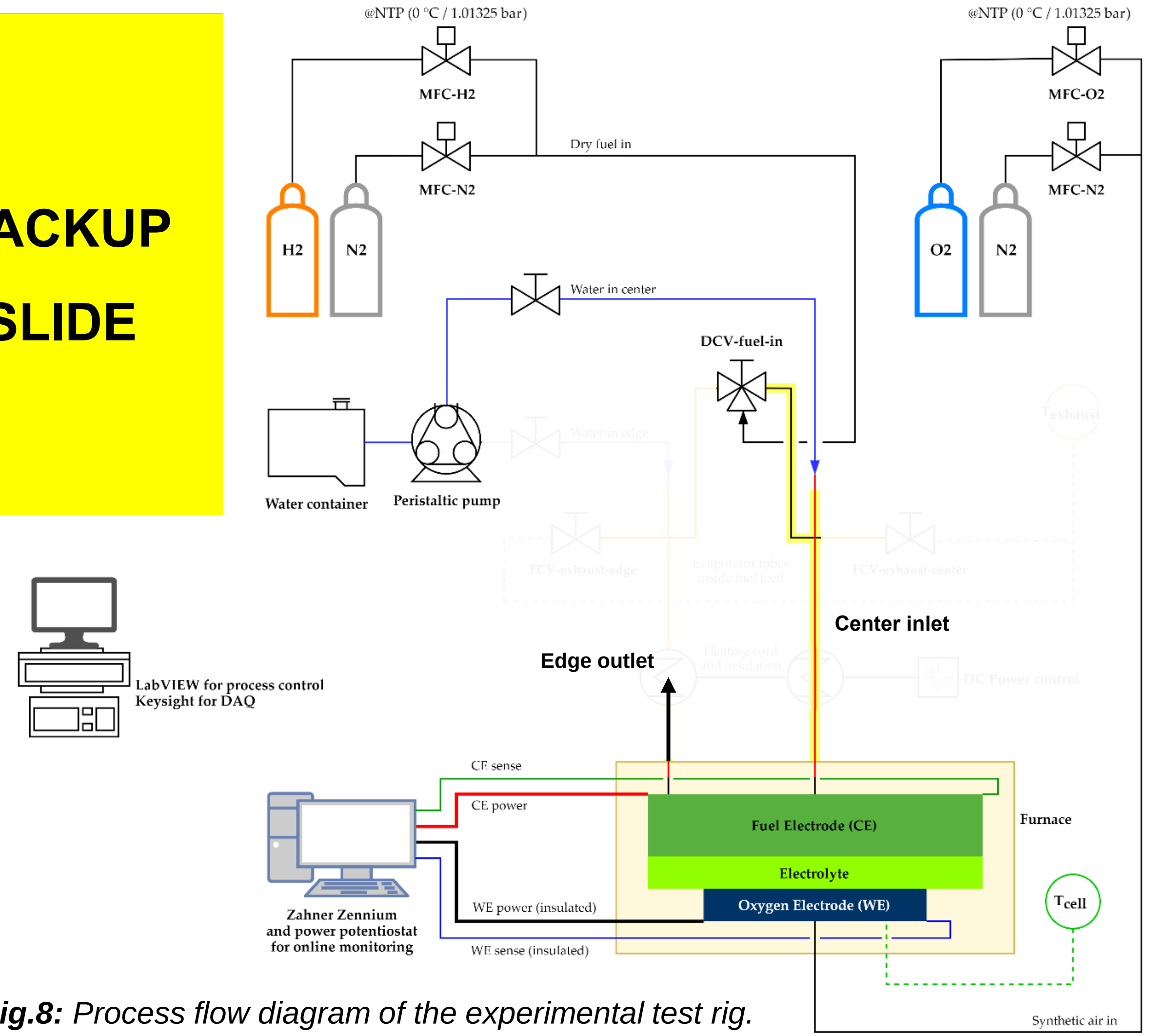


Fig.8: *Process flow diagram of the experimental test rig.*

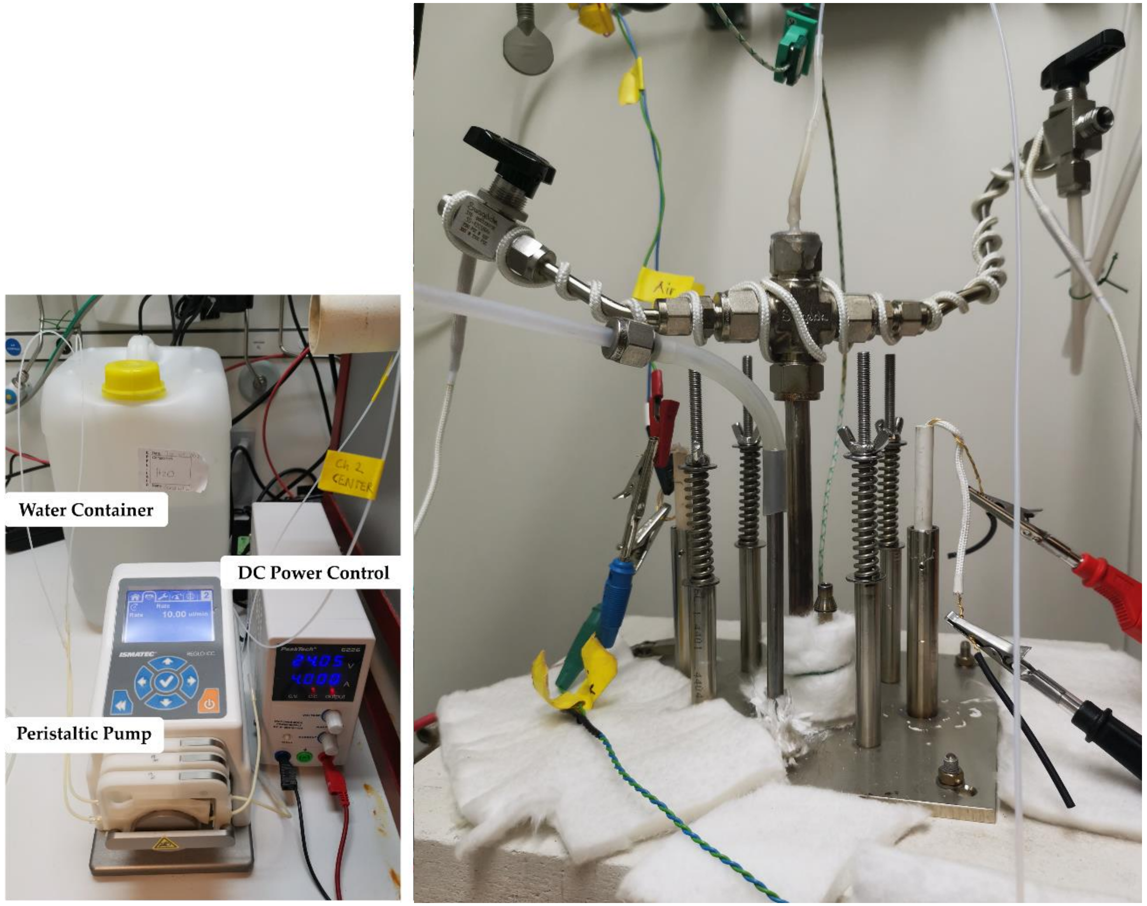


Fig.9: *Photos of the experimental test rig.*

Design of Experiments

BACKUP SLIDE

Tab.1: *List of experiments.*

	No	Name
I. Failure mode	1	Fuel Starvation
	1.1	Constant Voltage
	1.2	Constant Composition
	1.3	Constant Current
THD Settings	2	THD Sensitivity
	2.1	Signal Amplitude
	2.2	Number of Harmonics
Operating conditions	3	Temperature
	4	Flow Direction
II. Failure mode	5	Air Starvation
	5.1	Varying Air Composition
	5.2	Varying Air Flow Rate
III. Failure mode	6	Steam Starvation

Tab.2: *Default experiment parameter values.*

Default:

- 750°C
- outward fuel flow
- 150 Nml min^{-1} fuel flow rate
- 300 Nml min^{-1} air flow rate
- $H_2/N_2/H_2O$ fuel composition
- O_2/N_2 = 21/79 air composition
- 4 mV s^{-1} jV sweep rate
- EIS galvanostatic in SOFC mode
- EIS potentiostatic in SOE mode
- 50mHz lower frequency limit
- 100kHz upper frequency limit
- 12 steps per decade
- 12 measure periods
- THD of first five harmonics

Modeling

BACKUP SLIDE

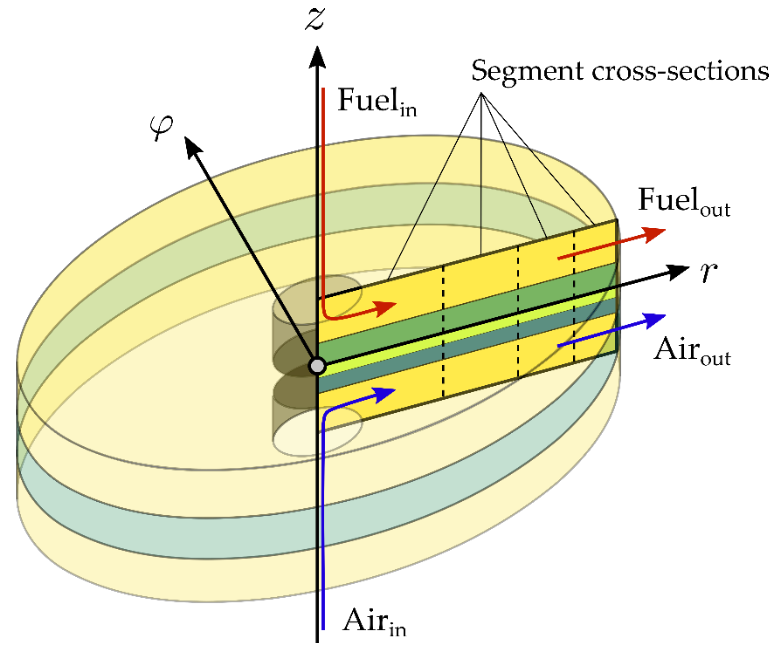


Fig.10: *Computational domain based on the experimental setup.*

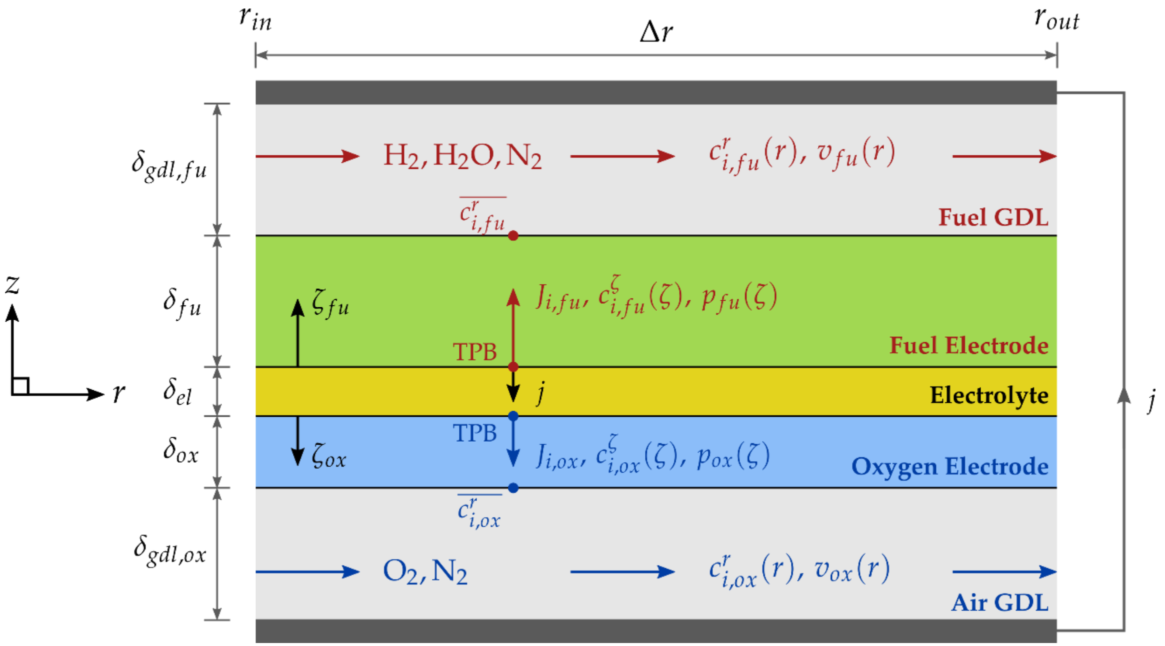


Fig.11: *Schematic illustration of a segment cross-section.*

- **Segmentation:**
  - Coaxial cylinders
  - Radial discretization such that all have same active area

- **Species balance in the GDL:**

$$\frac{1}{r}\frac{\partial}{\partial r}\left(r c_i^r v\right) = \frac{J_i}{\delta_{gdl}} \qquad \text{Eq. (16)}$$

- **Species balance in the Electrodes:**
  Dusty Gas Model (DGM)

$$\sum_{\substack{j \\ j\neq i}} \frac{c_j^\zeta J_i - c_i^\zeta J_j}{c^\zeta D_{ij}^e} + \frac{J_i}{D_{iK}^e} = -\frac{\partial c_i^\zeta}{\partial \zeta} - \frac{B_g c_i^\zeta}{\mu D_{iK}^e}\frac{\partial p}{\partial \zeta} \qquad \text{Eq. (17)}$$

Solution Algorithm

BACKUP SLIDE

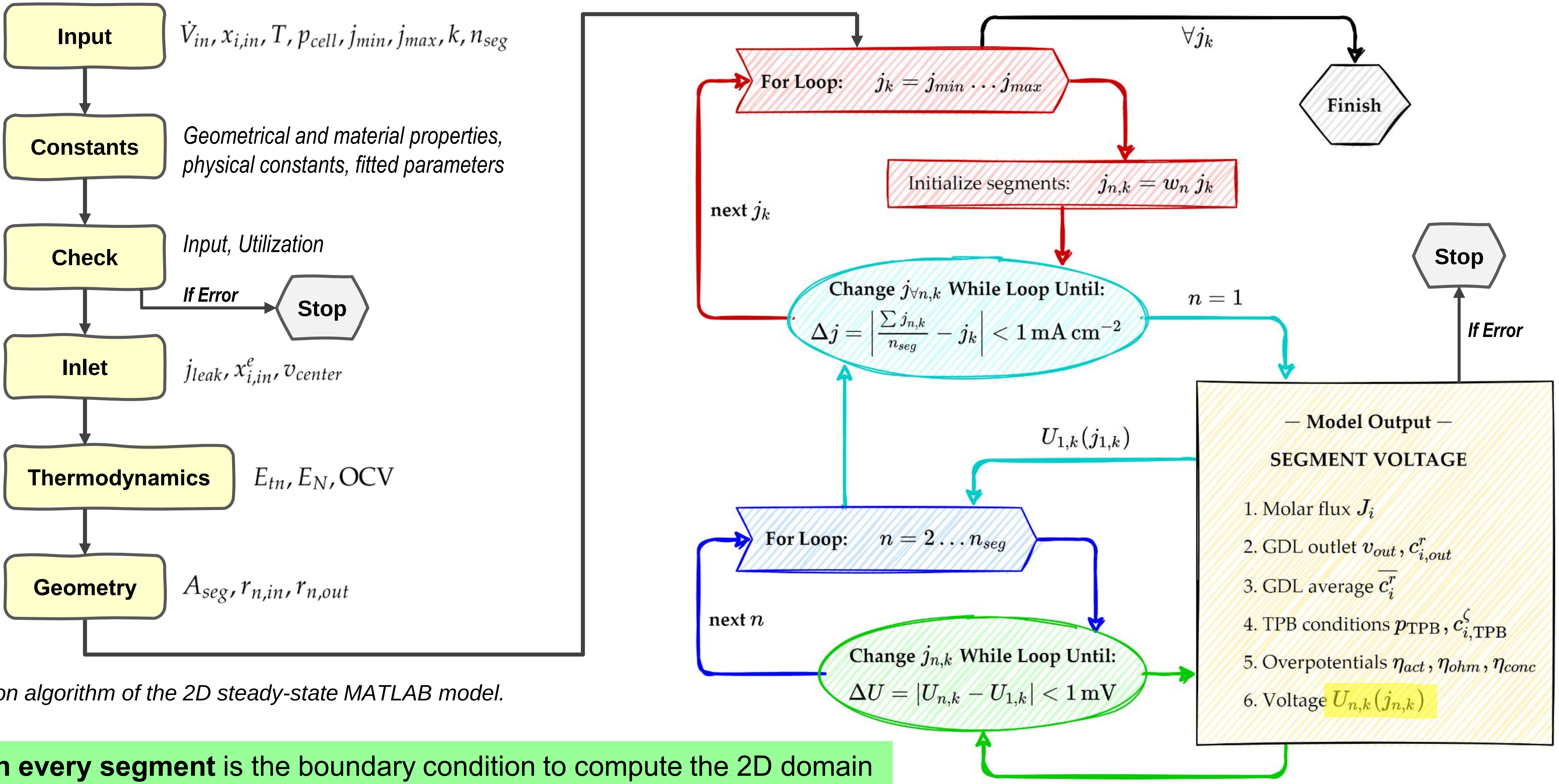


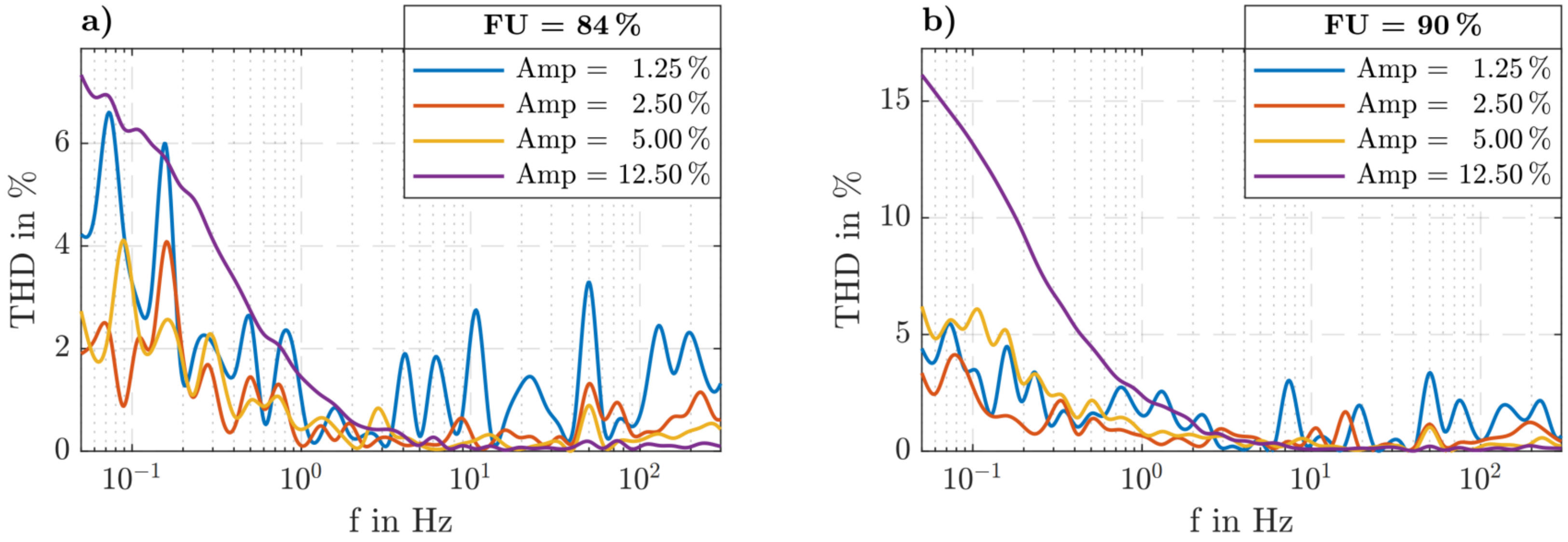
Fig.12: *Flow chart of solution algorithm of the 2D steady-state MATLAB model.*

The **same voltage in every segment** is the boundary condition to compute the 2D domain

THD – Excitation Signal Amplitude

BACKUP

SLIDE



j_{DC} = 4 A = 318 mA cm^{-2}

j_{AC} = 50, 100, 200, 500 mA

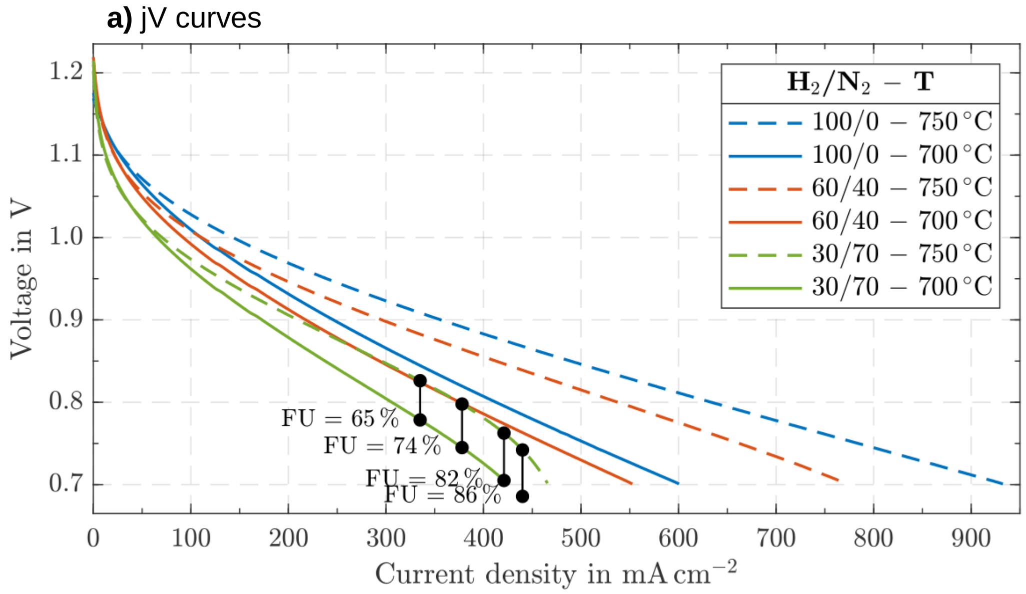
***Fig.15:** THD plot for different excitation signal amplitudes. Two operating points from E1.3 (const. current at 318 mA cm^{-2}).*

- If amplitude small → signal to noise ratio low and THD output corrupted by noise
- If amplitude high → non-linear operation *per se*, high distortion not necessarily from critical condition but due to measurement setting
- Recommendation → **approximately 5%**

Temperature

BACKUP

SLIDE



- η_{ohm} ↑ and R_{ohm} ↑ if T ↓
- high-frequency semicircle ↑ if T ↓
- low-frequency semicircle ≠ f(T)
- Charge transfer peaks P5 and P6 ↑ if T ↓
- Gas conversion peak P2 ≠ f(T)
- THD pattern similar

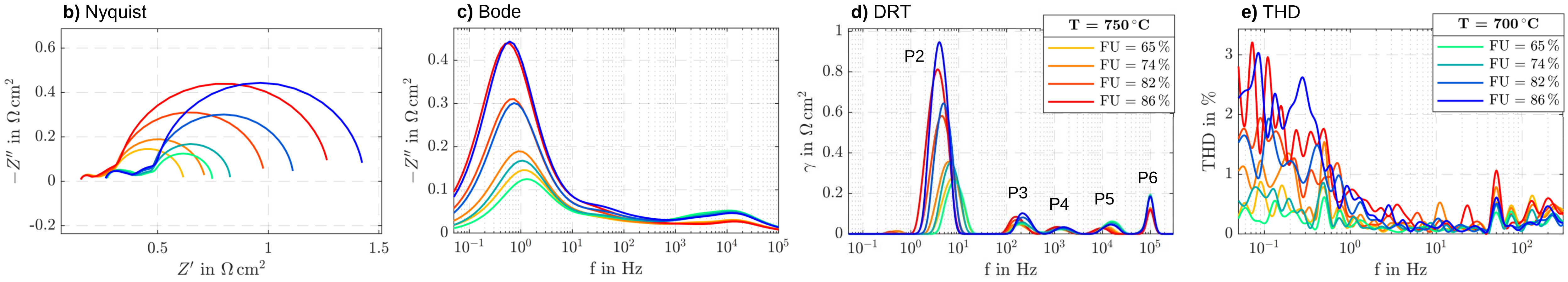


Fig.17: *Comparison of 750 and 700°C cell temperature. jV curves of three compositions from E1.3 and EIS/THD measurements for four operating points from E1.2.*

Flow Direction

BACKUP SLIDE

- OCV ↓ and T ↑ in inward flow
- η_{conc} ↑↑ in inward flow
- EIS, DRT, THD results of 48% inward ≈ 90% outward

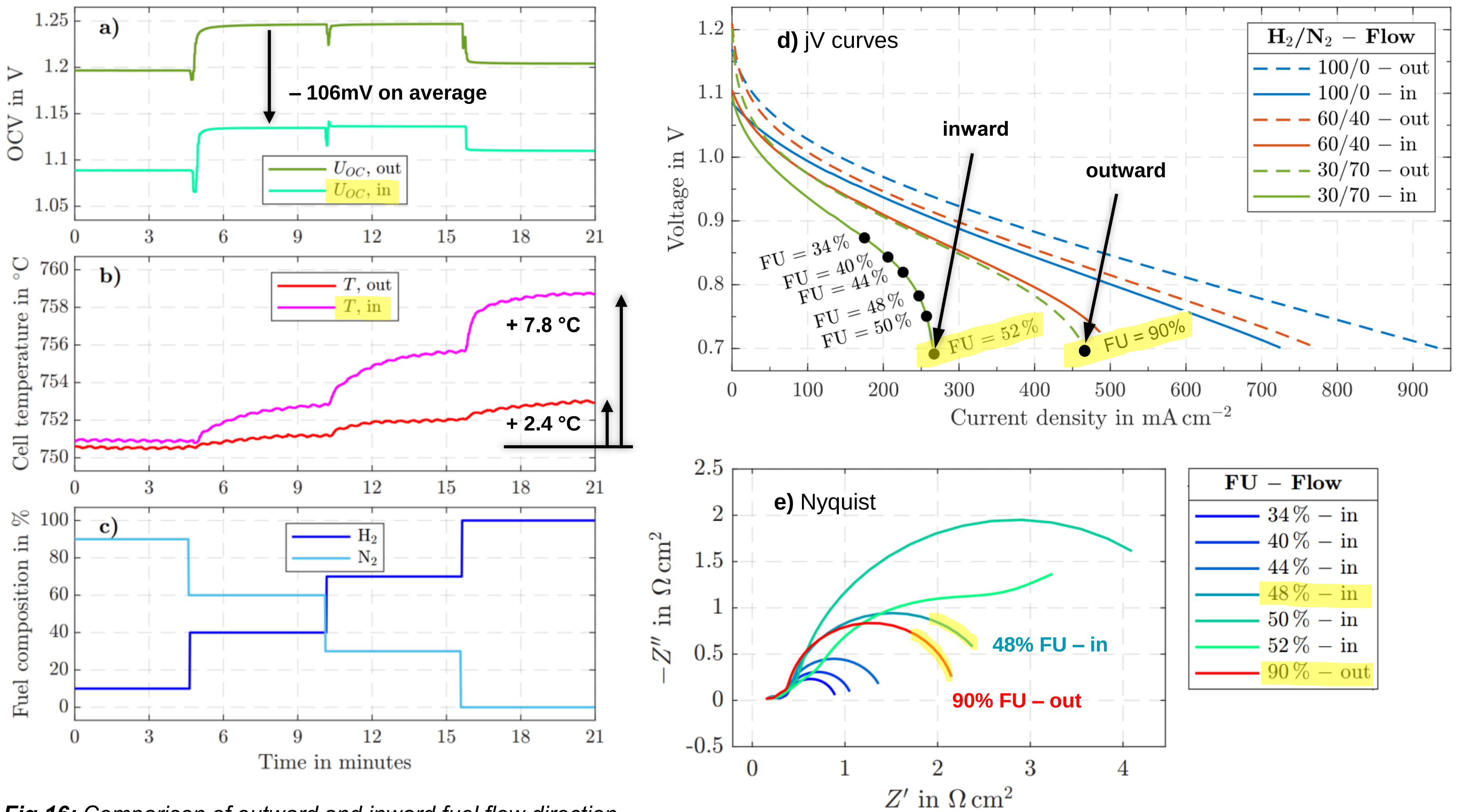


Fig.16: *Comparison of outward and inward fuel flow direction.*

Air Starvation

BACKUP SLIDE

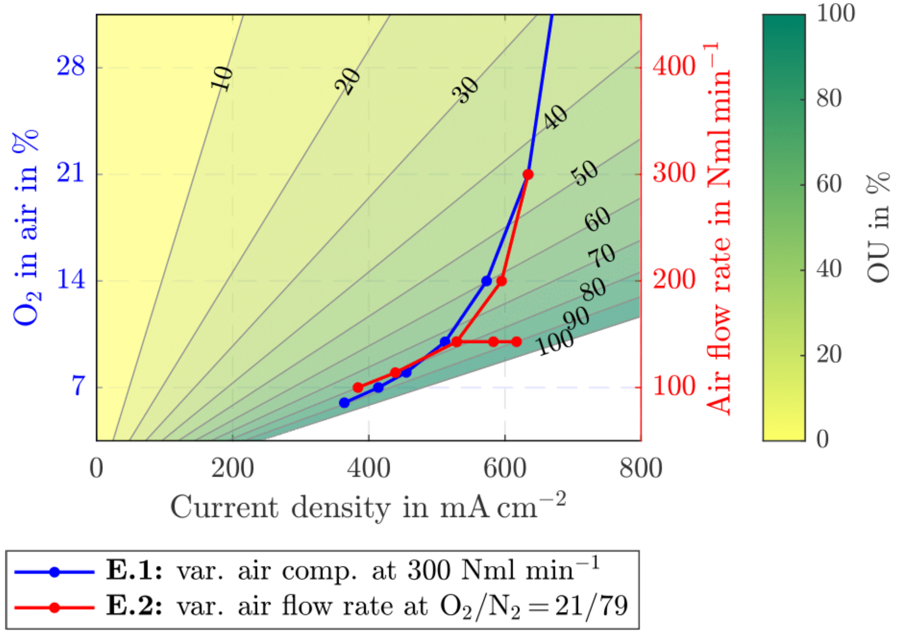


Fig.11: *OU with current density, composition and air flow rate (12.57 cm^2, 150 Nml min^{-1} fuel flow rate, 100% H_2).*

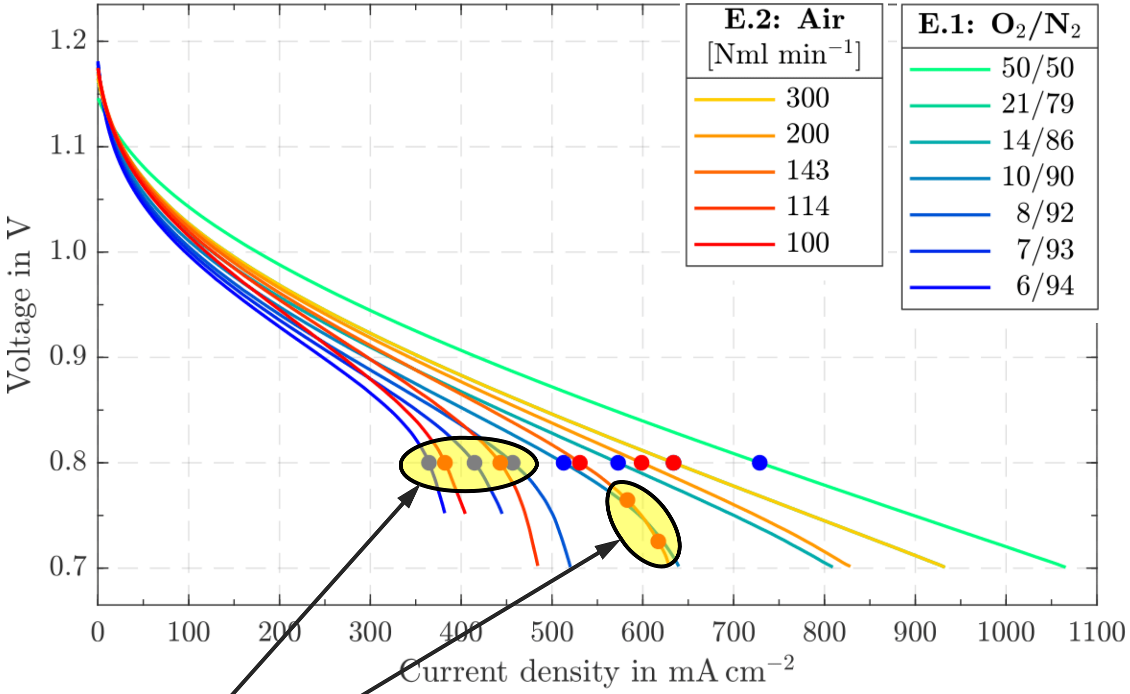


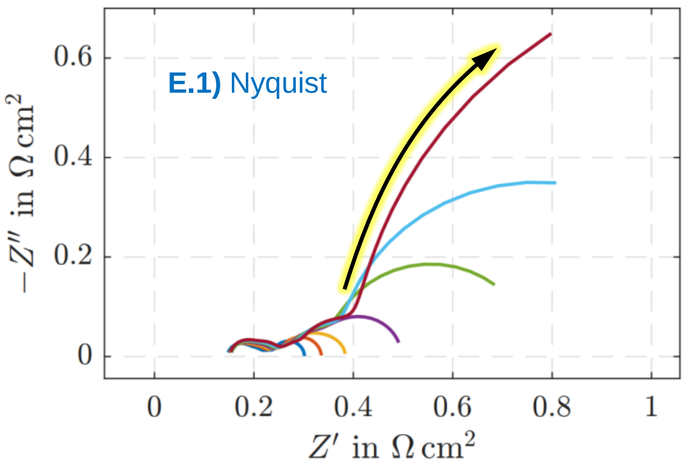
Fig.12: *jV curves of air starvation. The dots indicate operating points of EIS and THD measurements.*

Oxygen Utilization: $$\mathrm{OU} = \frac{jA_{cell}}{2z_e F\dot{n}_{O_2}}$$ Eq. (12)

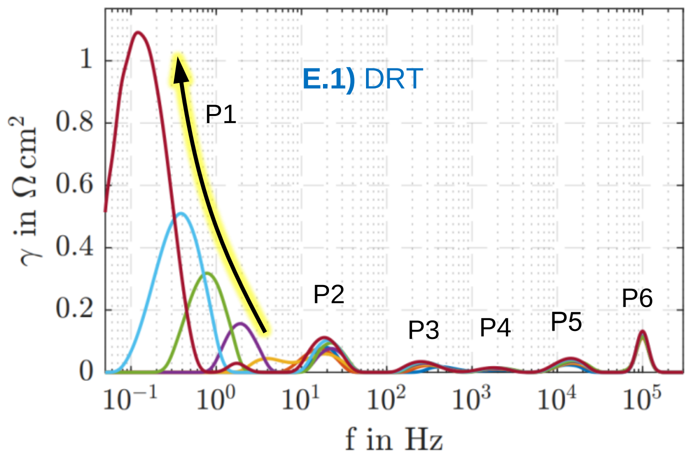
- For **OU > 80%** significant voltage drop (↑ η_{conc})

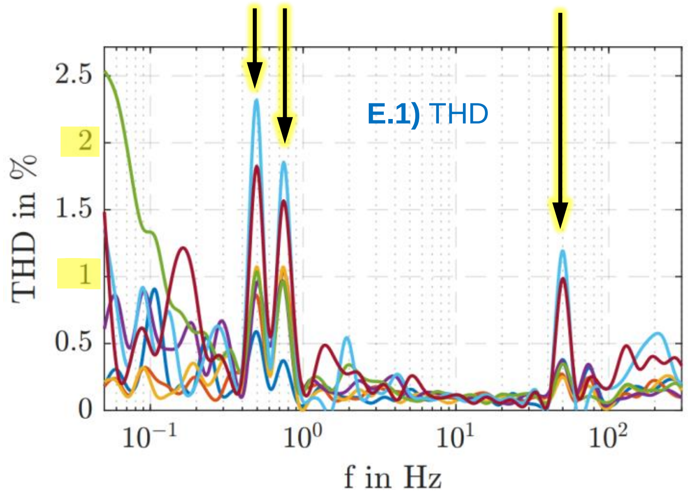
Air Starvation

BACKUP SLIDE



- **Nyquist:** 3rd semicircle at low frequencies for OU > 75%; Same behavior found in planar cells (Subotić et al, 2020, On the origin of degradation in fuel cells and its fast identification by applying unconventional online-monitoring tools)
- **DRT:** New peak P1 for OU > 75% (oxygen electrode diffusion)
- **THD:** Peaks at 500mHz, 750mHz, and 50Hz, but < 2.3% low
  → also visible in fuel starvation but overshadowed
  → setup-specific noise (e.g. furnace heating)





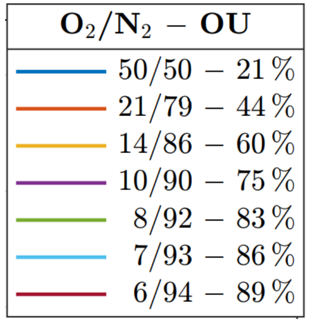


Fig.13: *EIS, DRT, and THD results of air starvation E.1 with varying composition (O_2/N_2) at constant air flow rate of 300 Nml min^{-1}.*

Steam Starvation

BACKUP SLIDE

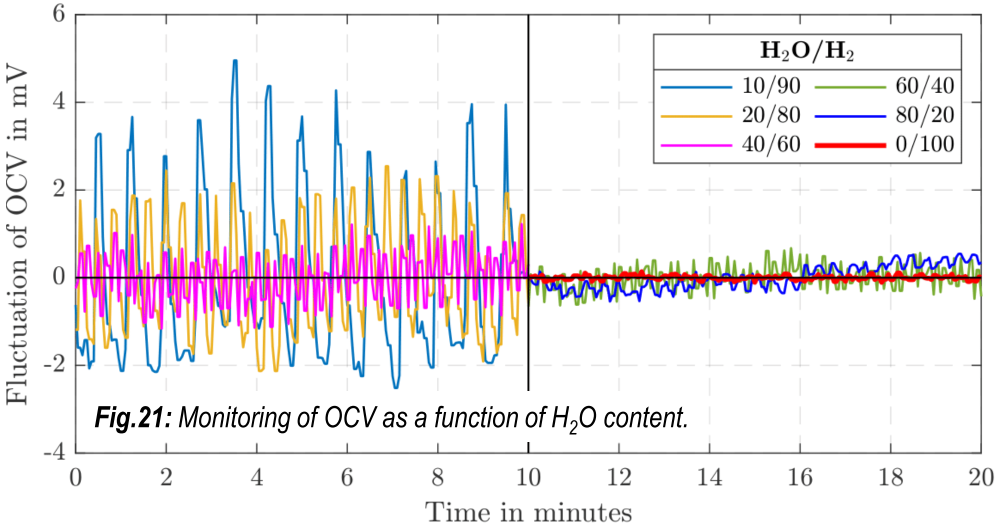


Fig.21: *Monitoring of OCV as a function of H_2O content.*

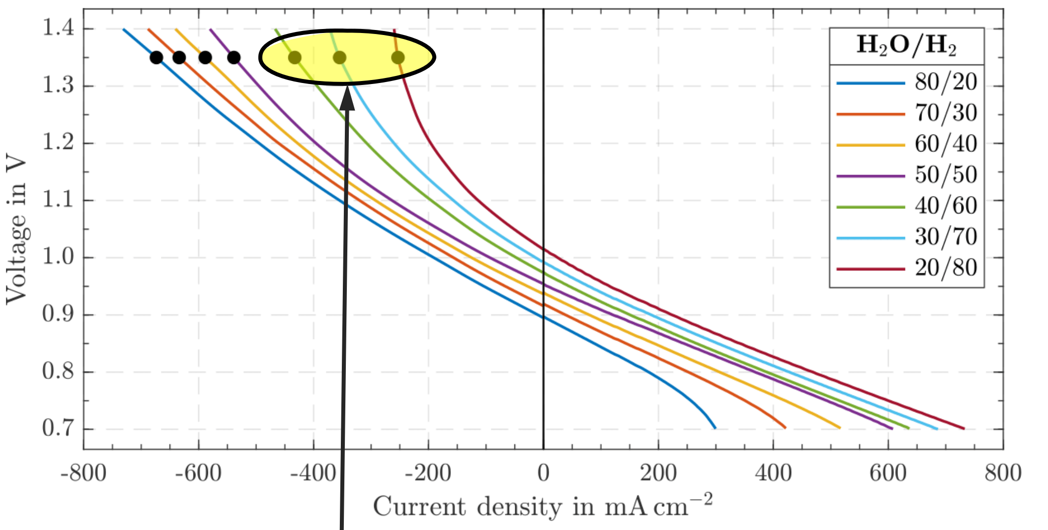


Fig.23: *jV curves of steam starvation. Dots indicate operating points of EIS/THD measurements.*

- OCV more stable if H_2O flow rate higher

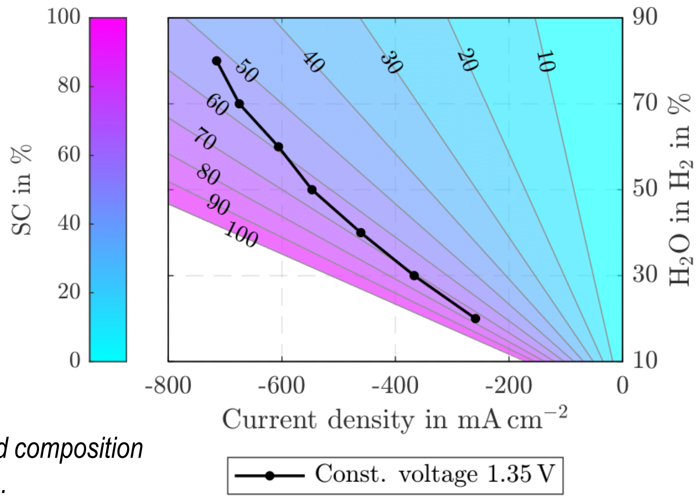


Fig.22:
SC with current density and composition (150 Nml min^{-1}, 12.57 cm^2).

- For **SC > 67%** significant voltage rise (↑ η_{conc})

Steam Conversion:

$$SC = \frac{jA_{cell}}{z_e F \dot{n}_{H_2O}} \quad \text{Eq. (18)}$$

Model Parameter Fitting

BACKUP SLIDE

- Ohmic resistance R_{ohm}
- Parasitic losses j_{leak}
- Exchange current density $j^0_{0,fu}$, $j^0_{0,ox}$
- Correction factor for concentration overpotential η_{conc}

Relative reactant depletion:

$$x_{i,dep} = \frac{x_{i,\mathrm{TPB}}}{\sqrt{x_{i,in}}} \qquad \text{Eq. (21)}$$

$$\eta_{conc,fu} = \eta_{conc,fu}\, C_{Fuel} \qquad j > 0 \qquad \text{Eq. (22)}$$

$$= \eta_{conc,fu}\, C_{Steam} \qquad j < 0 \qquad \text{Eq. (23)}$$

$$\eta_{conc,ox} = \eta_{conc,ox}\, C_{Air} \left(\frac{300}{\dot{V}_{air}}\right) \qquad j > 0 \qquad \text{Eq. (24)}$$

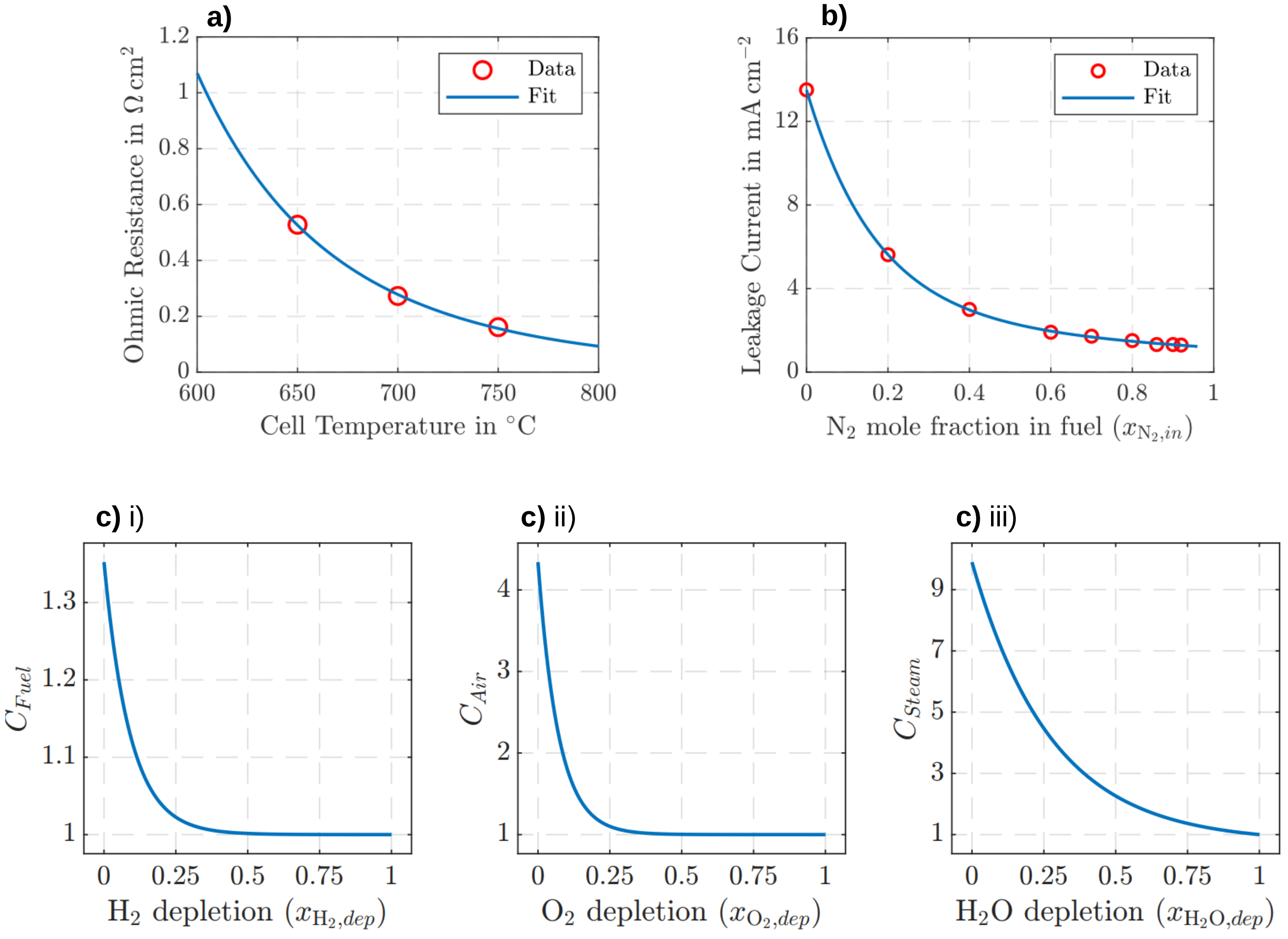


***Fig.28:** Fitting of a) ohmic resistance, b) parasitic losses, and c) correction factor for η_{conc}.*