Parametrization and Validation of a 2D, Transient, Two-Phase MEA Model with EIS Capability

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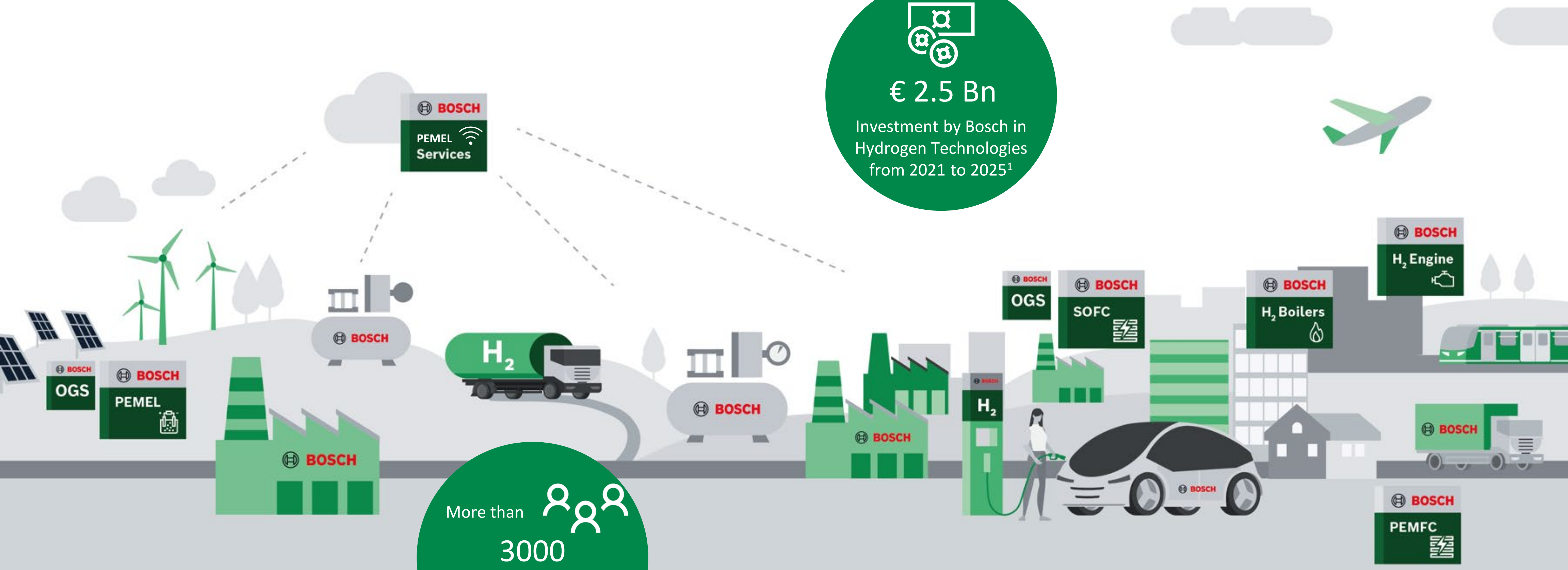
25.10.2023 – User Presentations: Fuel Cells

BOSCH

Bosch and the Hydrogen Economy



€ 2.5 Bn

Investment by Bosch in Hydrogen Technologies from 2021 to 2025[1]

More than

3000

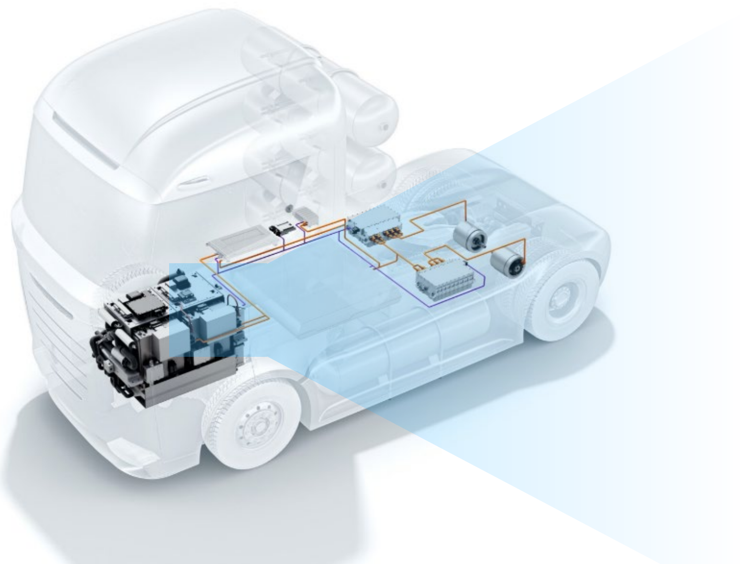
Bosch Employees

Work on Hydrogen technologies[1]

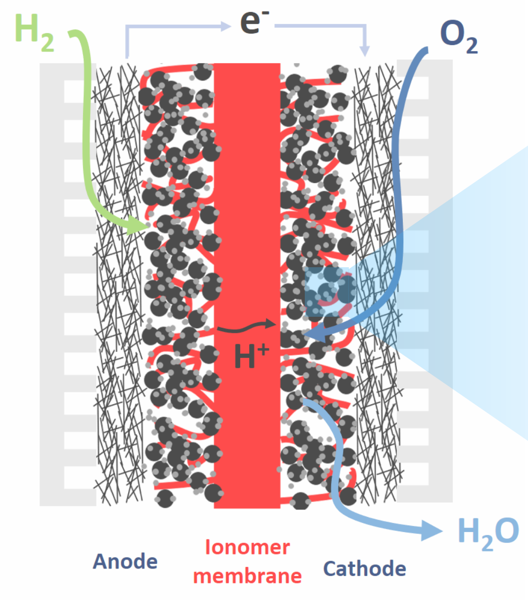
[1] Source: Press release 13.07.2023

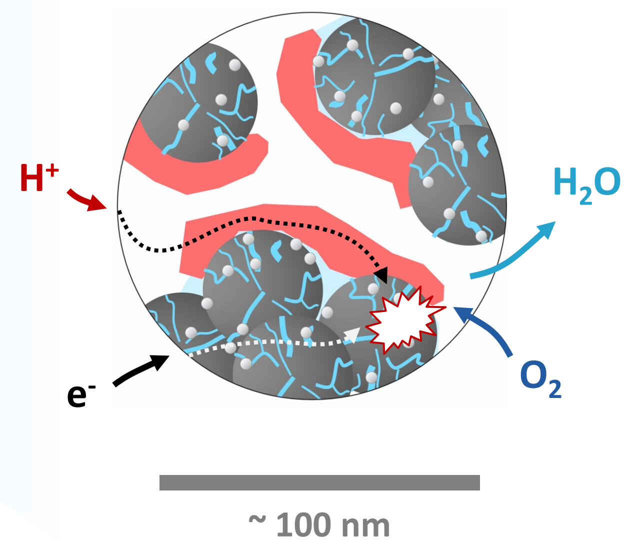
PEMEL = Polymer electrolyte membrane electrolysis; PEMEL Services: Electrolysis services
OGS = Optical Gas Spectrometer; SOFC = Solid oxide fuel cell; PEMFC = Polymer electrolyte membrane fuel cell

From Macro to Micro



From: bosch-mobility-solutions.com



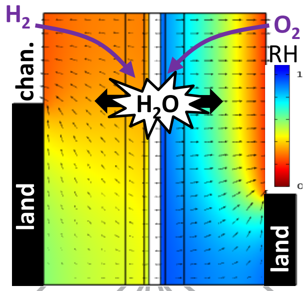


Physical MEA Model: 2D, Transient, Two-Phase

General structure: 10 PDE's of the form:

$$\frac{\partial C_\zeta}{\partial t} + \nabla j_\zeta = S_\zeta$$

- storage term [6]: $\frac{\partial C_\zeta}{\partial t}$
- flux: j_ζ
- source term: S_ζ
- ζ: field variable

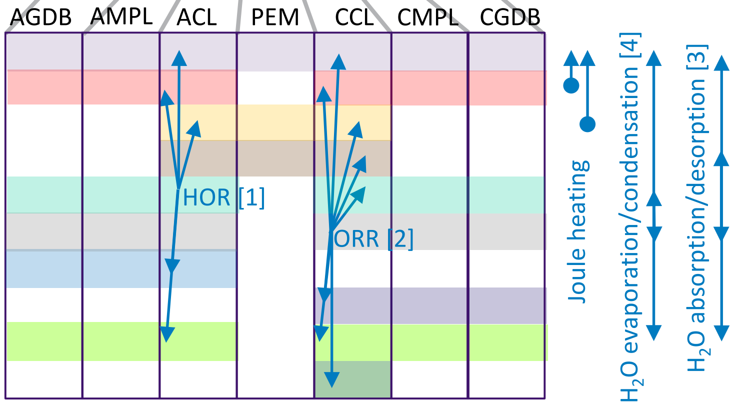


Main references:

[1] Gerling *et al.*, JES 169, 14503 (2022)
[2] Gerling *et al.*, JES 170, 14504 (2023)
[3] Pant et al., JES 168, 74501 (2021)
[4] Vetter, Schumacher, JPS 438, 227018 (2019)
[5] Jahnke, Baricci, JES 169, 94514 (2022)
[6] Goshtasbi *et al.*, JES 166, F3154 (2019)

Physical assumptions	Field variables	Boundary conditions
Fourier heat cond. [4]	temperature T	heat transfer at lands
Ohmic electron conduction	electron potential ϕ_e	cell current or voltage
conc. solution theory [3]	ionic potential ϕ_p	
(vapor-equilibrated only)	chem. pot. of sorbed H_2O ϕ_λ	
Darcy flow [3]	liquid H_2O pressure p_l	breakthrough condition [3]
mixture-averaged	H_2O vapor mole fraction x_{H2O}	relative humidity of fuel gases
Fick diffusion	H_2 mole fraction x_{H2}	H_2 mole fraction anode gas
(+ film res. in CCL [5])	O_2 mole fraction x_{O2}	O_2 mole fraction cathode gas
& convection (Darcy flow)	gas pressure p_g	channel gas pressure
PtOx model [2]	free Pt site coverage θ_{Pt}	

Modeling domains — blue: Couplings (source terms)



A/C = anode/cathode, GDB = gas diffusion backing, MPL = microporous layer, CL = catalyst layer, PEM = polymer electrolyte membrane.

We use a full macro-homogeneous physical 2D model, with physics and material laws largely based on state-of-the-art literature.

Overview of Partial Differential Equations

Heat conduction	$\frac{\partial(c_p T)}{\partial t} + \nabla\cdot(-k\nabla T) = S_T$	Fourier heat conduction
Electron Transport	$\frac{\partial\left(C_{dl}(\phi_e - \phi_p)\right)}{\partial t} + \nabla\cdot(-\sigma_e\nabla\phi_e) = S_e$	Ohm's law
Proton Transport	$\frac{\partial\left(C_{dl}(\phi_e - \phi_p)\right)}{\partial t} + \nabla\cdot\left(-\sigma_p\nabla(\phi_p + k_{drag}\phi_\lambda)\right) = S_p$	Ohm's law + Electro-osmotic drag
Dissolved H_2O transport	$k_\lambda \frac{\partial(\phi_\lambda)}{\partial t} + \nabla\cdot\left(-\sigma_p\xi\nabla\phi_p - (F^2\alpha_{g,I,eff} + \sigma_p\xi^2)\nabla\phi_\lambda\right) = S_\lambda$	Electro-osmotic drag + concentration gradient
Liquid H_2O transport	$\epsilon_p \frac{\partial(\rho_{H_2O}s)}{\partial t} + \nabla\cdot\left(-\frac{M_{H_2O}D_s}{V_{m,H_2O}}\nabla p_l\right) = S_\lambda$	Darcy Law
H_2O vapor flux	$-\frac{\partial\left((1-s)\epsilon_p\chi_{H_2O}\right)}{\partial t} + \nabla\cdot(\boldsymbol{J}_{H_2O}) + \nabla\cdot(\chi_{H_2O}c\boldsymbol{u}) = S_{H_2O}$	Maxwell-Stefan + Knudsen diffusion
H_2 flux	$-\frac{\partial\left((1-s)\epsilon_p\chi_{H_2}\right)}{\partial t} + \nabla\cdot(\boldsymbol{J}_{H_2}) + \nabla\cdot(\chi_{H_2}c\boldsymbol{u}) = S_{H_2}$	Maxwell-Stefan + Knudsen diffusion
O_2 flux	$-\frac{\partial\left((1-s)\epsilon_p\chi_{O_2}\right)}{\partial t} + \nabla\cdot(\boldsymbol{J}_{O_2}) + \nabla\cdot(\chi_{O_2}c\boldsymbol{u}) = S_{O_2}$	Maxwell-Stefan + Knudsen diffusion

Our aim is to predict **performance** for upscaling, detect **flooding** and understand **transient behavior**.

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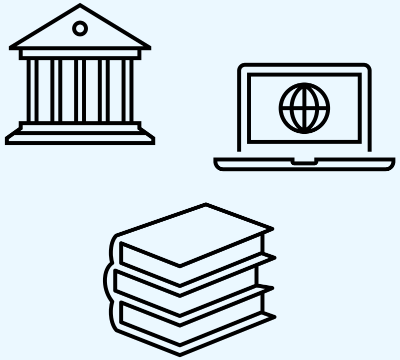
Parametrization Workflow

From Literature to In Situ Measurements

Literature

Parametrization

- Supplier Data (GDL…)
- State of the art
- …



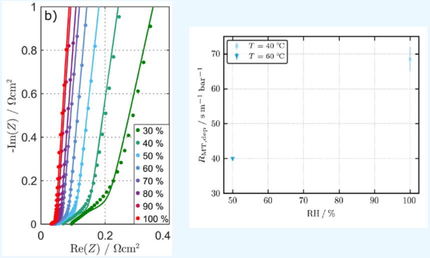
Ex Situ Measurements

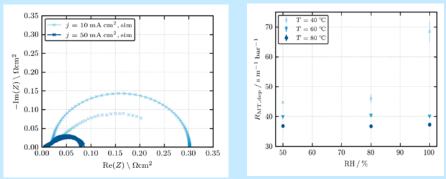
Parametrization

- Mercury Porosimetry
- XRF, XRD, SEM
- …

In Situ Measurements

Parametrization

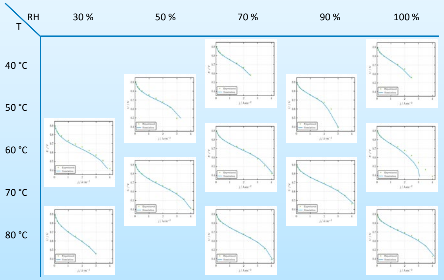




Validation

Global Fit

Parametrization



Validation

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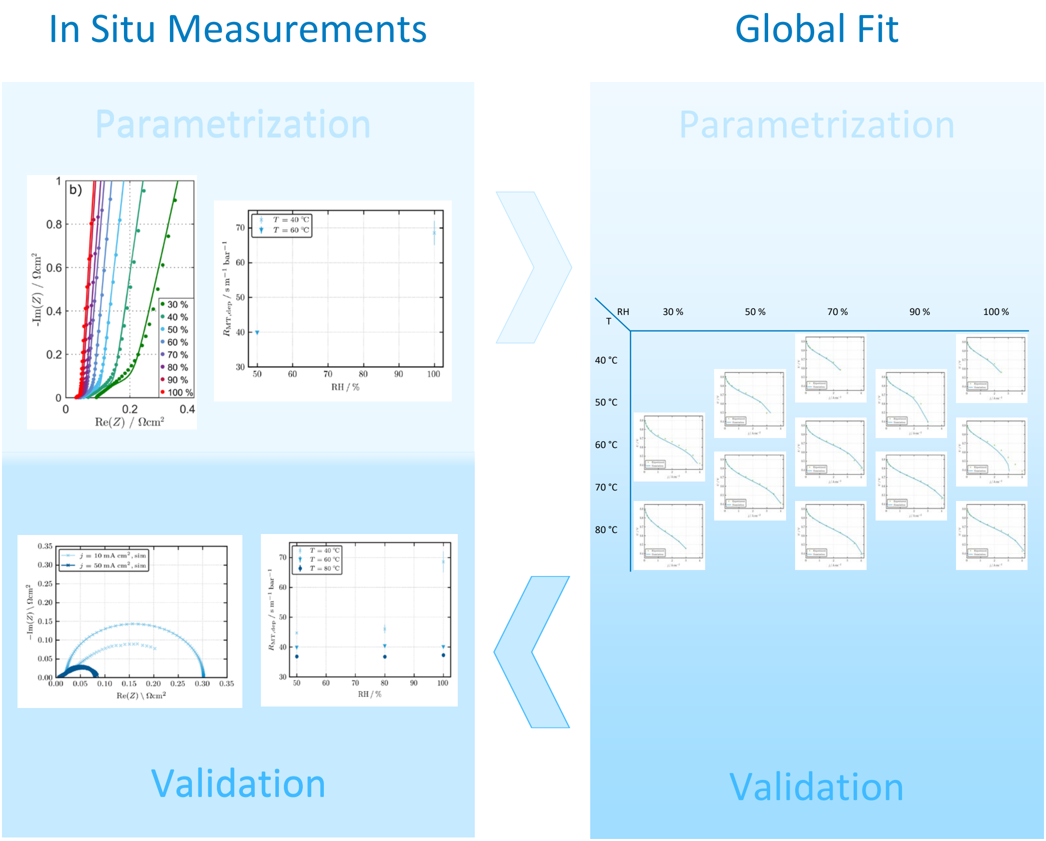
Parametrization Workflow
Parametrization and Validation



Parametrization Workflow
Parametrization and Validation

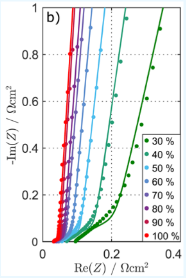
EIS	Limiting Current	Global Fit
Parametrization	Parametrization	Parametrization
Validation	Validation	Validation

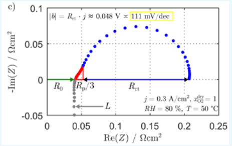
Parametrization

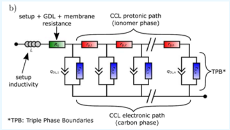
Electrochemical Impedance Spectroscopy

EIS

Parametrization







Validation

Limiting Current

Parametrization

Validation

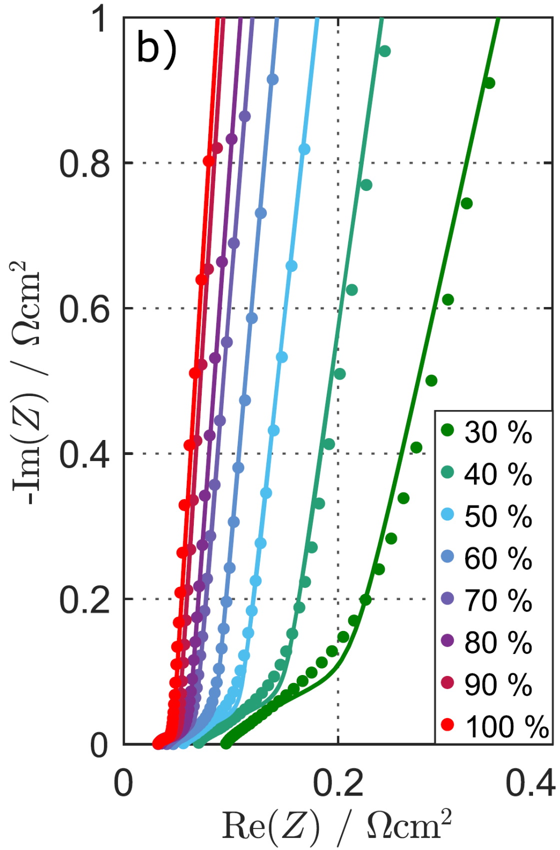
Global Fit

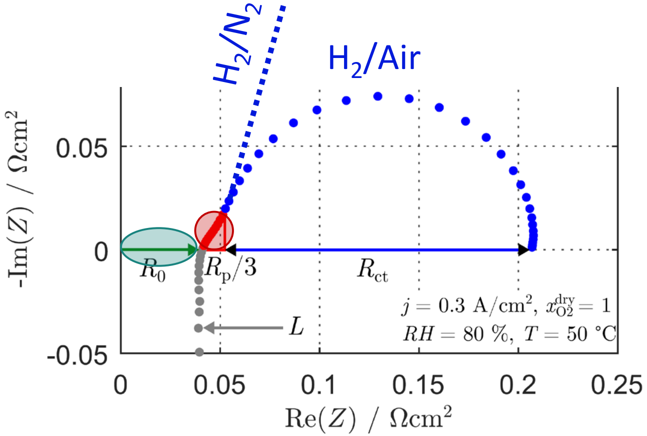
Parametrization

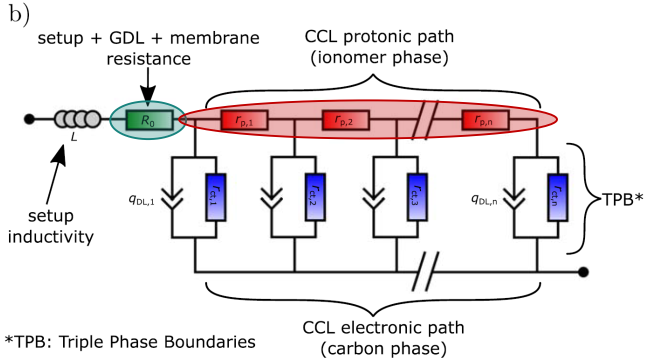
Validation

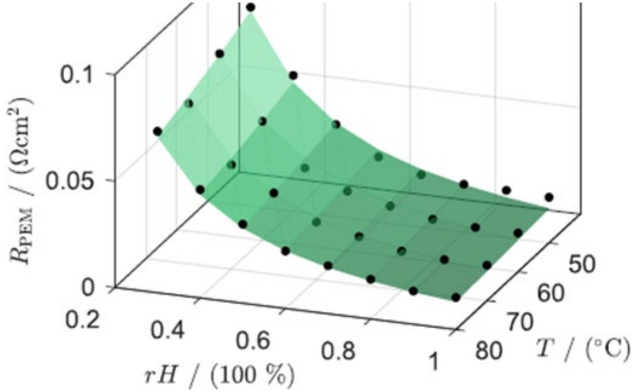
Electrochemical Impedance Spectroscopy

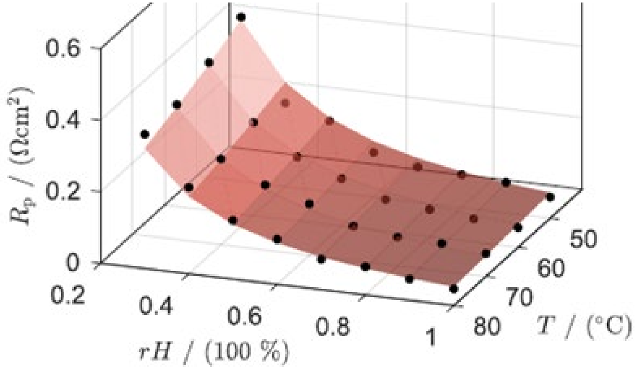
HFR and Protonic Sheet Resistance under OCV for Parametrization











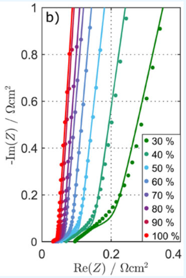
Gerling *et al.*, JES 168, 84504 (2021); *ibid.* 169, 14503 (2022); *ibid.* 170, 14504 (2023).

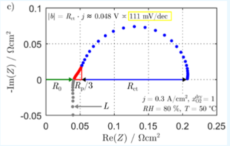
Parametrization

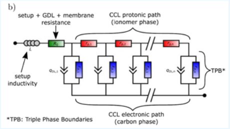
Electrochemical Impedance Spectroscopy

EIS

Parametrization







Validation

Limiting Current

Parametrization

Validation

Global Fit

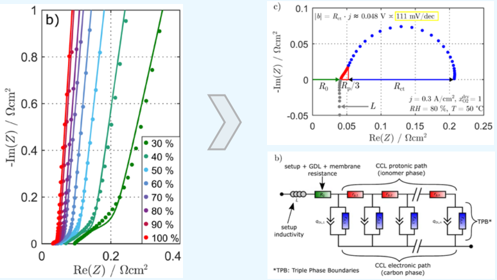
Parametrization

Validation

Parametrization
Limiting Current

EIS

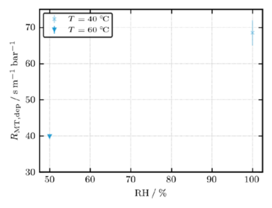
Parametrization

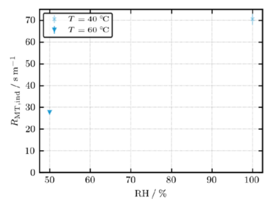


Validation

Limiting Current

Parametrization





Validation

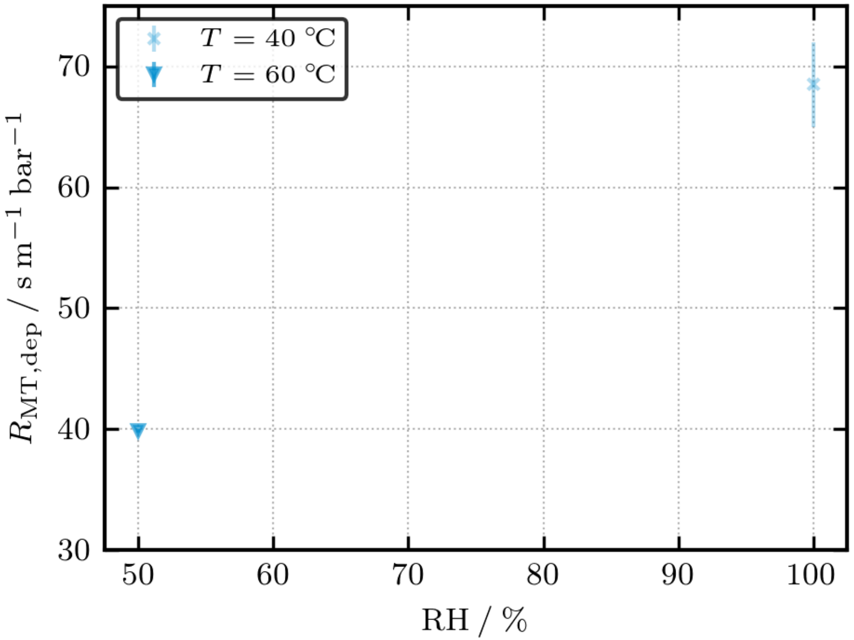
Global Fit

Parametrization

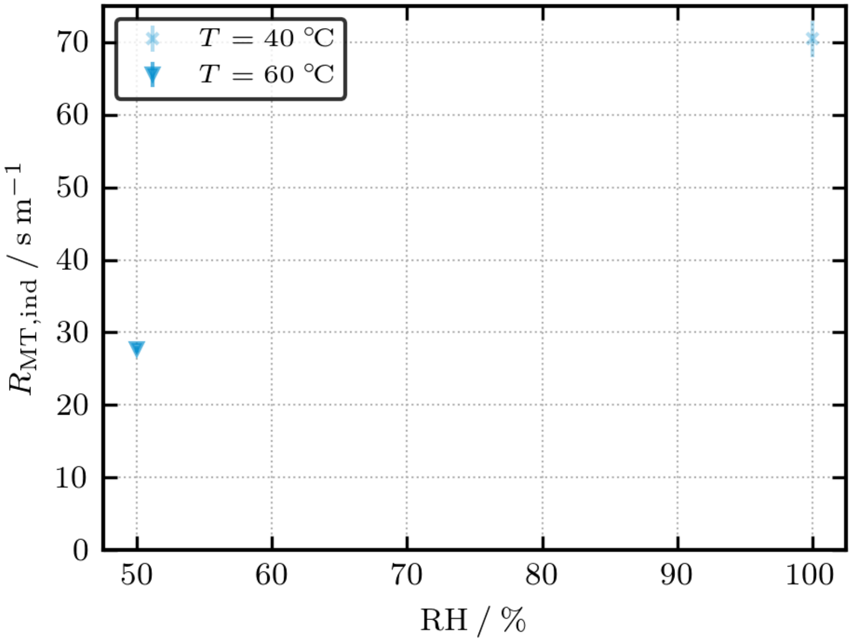
Validation

Limiting Current
Only Selected Conditions Used for Parametrization

Pressure-**dependent** MTR



Pressure-**independent** MTR



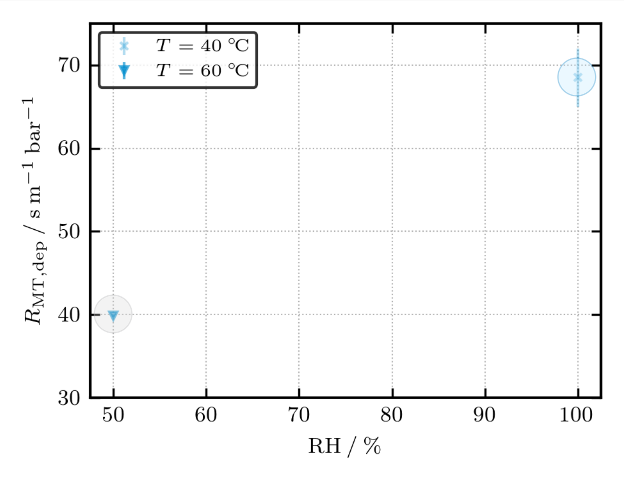
MTR = Mass transport resistance

Limiting Current

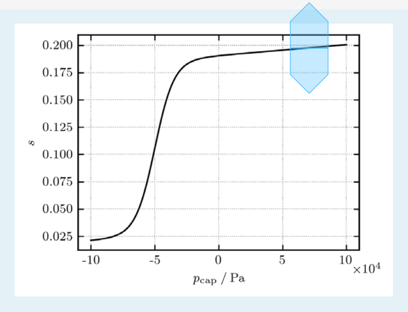
Wet and Dry Limiting Current to Parametrize Diffusion Properties

Fit **GDB** diffusion properties

Pressure-**dependent** MTR



WRC **GDB**



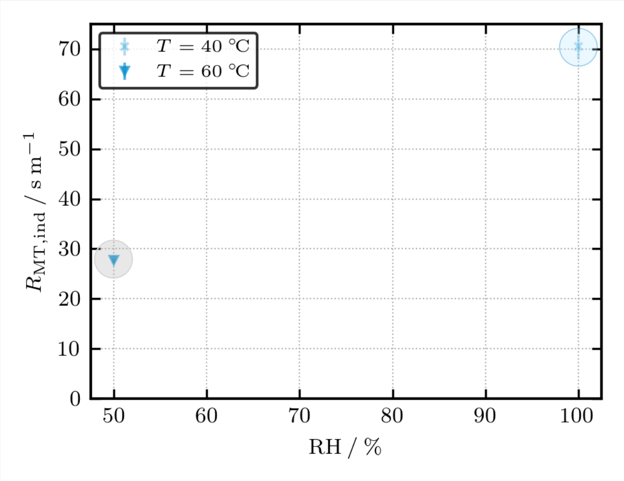
Fit to wet MTR

$$M_{p,GDB} = M_{p,GDB,fac}\left(\epsilon_p(1-s)\right)^{2.5}$$

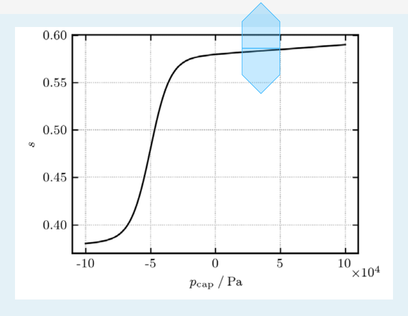
Fit to dry MTR

Fit **CL** diffusion properties

Pressure-**independent** MTR



WRC **CL**



Fit to wet MTR

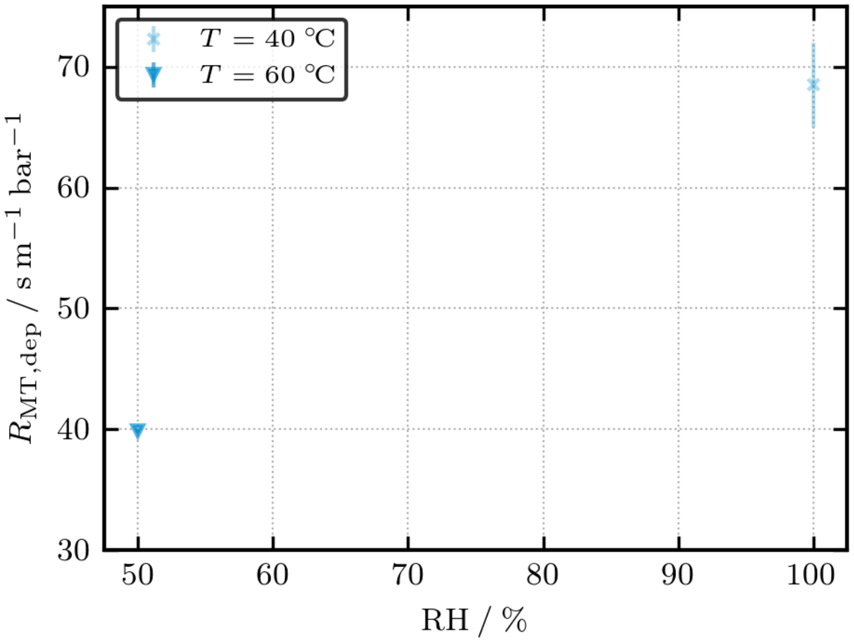
$$M_{p,CL} = M_{p,CL,fac}\left(\epsilon_p(1-s)\right)^{2.5}$$

Fit to dry MTR

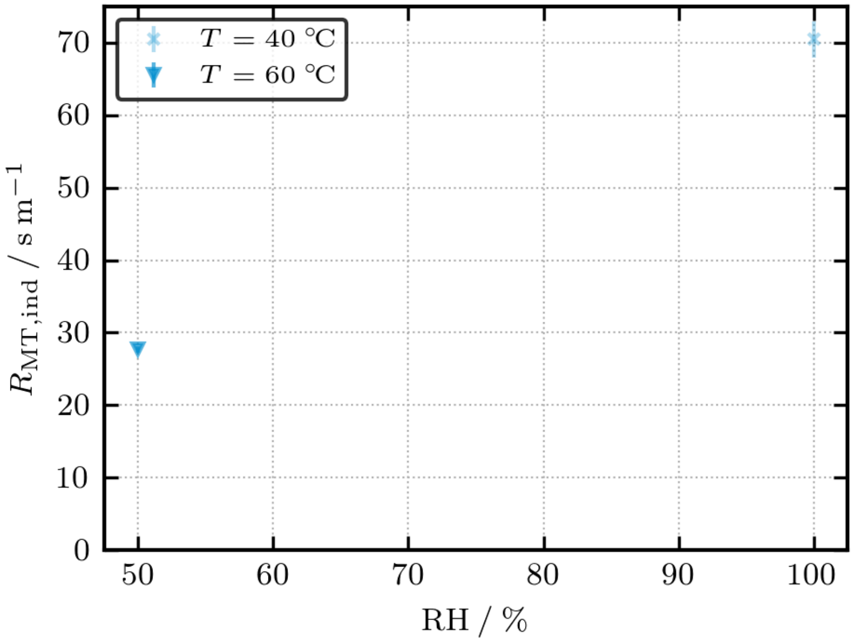
MTR = Mass transport resistance, GDB = Gas diffusion barrier, WRC = Water retention curve, CL = Catalyst Layer

Limiting Current

Pressure-**dependent** MTR



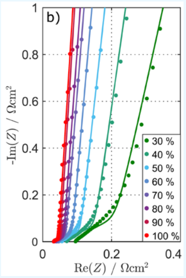
Pressure-**independent** MTR

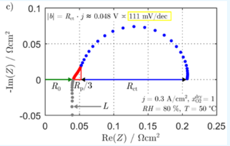


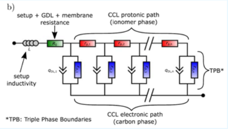
Parametrization
Limiting Current

EIS

Parametrization



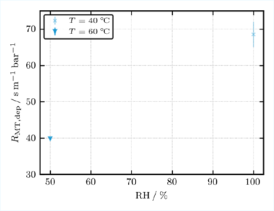


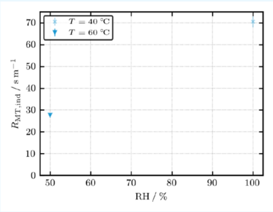


Validation

Limiting Current

Parametrization





Validation

Global Fit

Parametrization

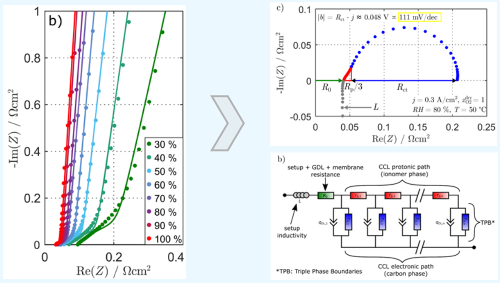
Validation

BOSCH

Validation/Parametrization
Polarization Curves

EIS

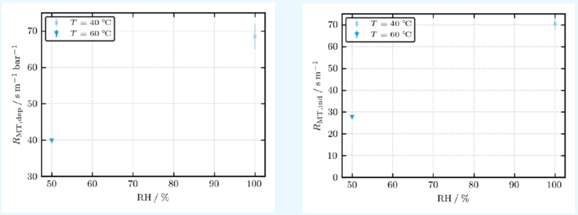
Parametrization



Validation

Limiting Current

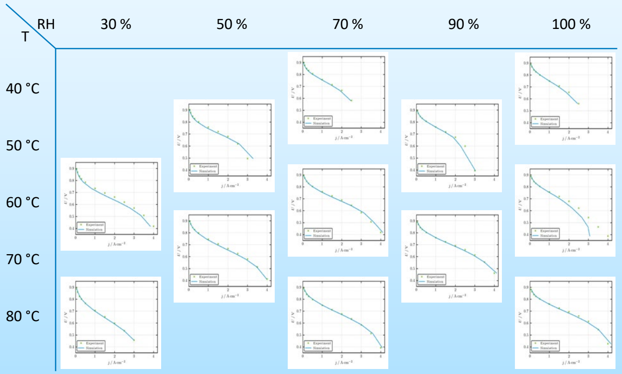
Parametrization



Validation

Global Fit

Parametrization

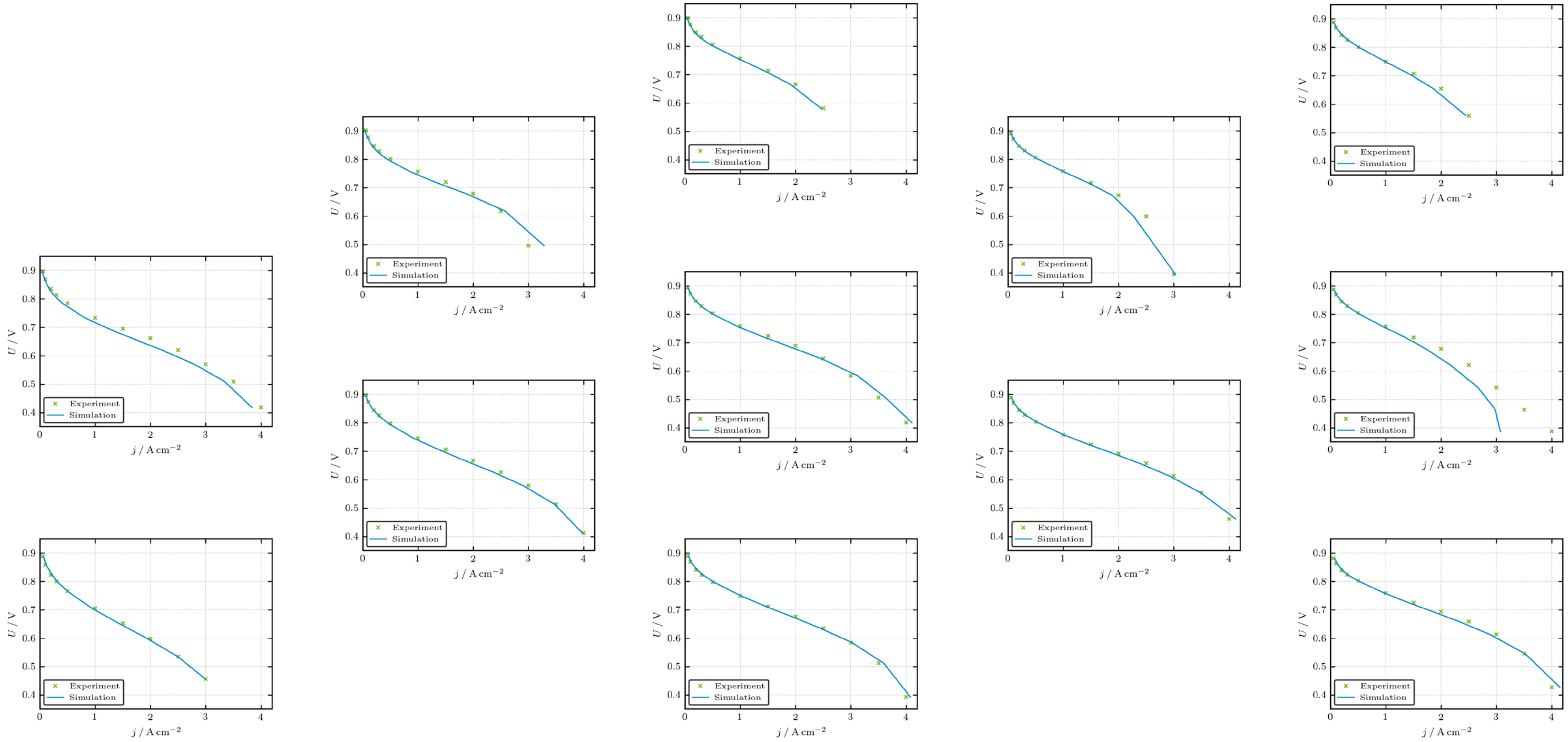


Validation

Polarization Curves

Full Factorial DOE under Hydrogen/Air

T \ RH	30 %	50 %	70 %	90 %	100 %
40 °C					
50 °C					
60 °C					
70 °C					
80 °C					



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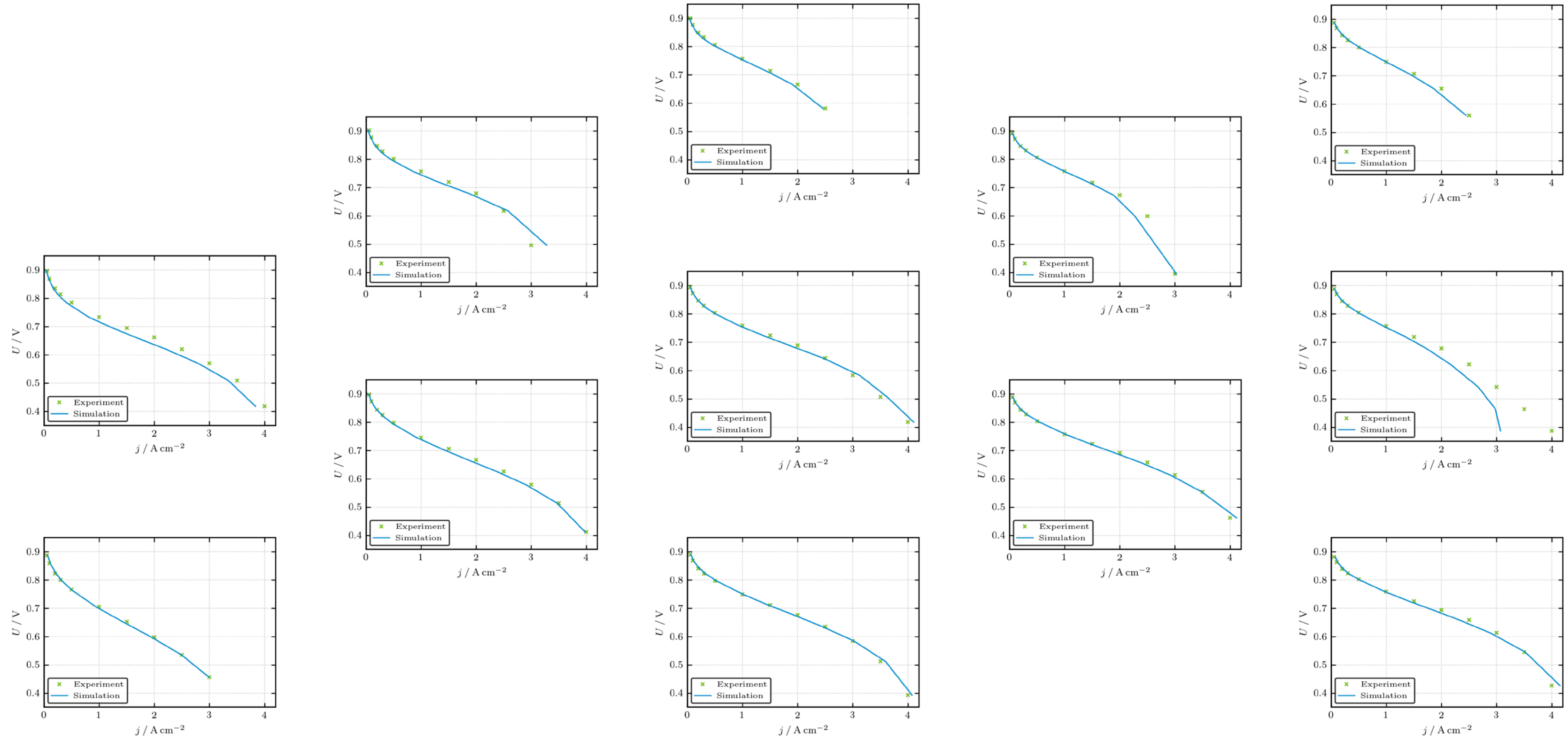
Polarization Curves

Full Factorial DOE under Hydrogen/Air

RH: 30 % | 50 % | 70 % | 90 % | 100 %

T: 40 °C | 50 °C | 60 °C | 70 °C | 80 °C



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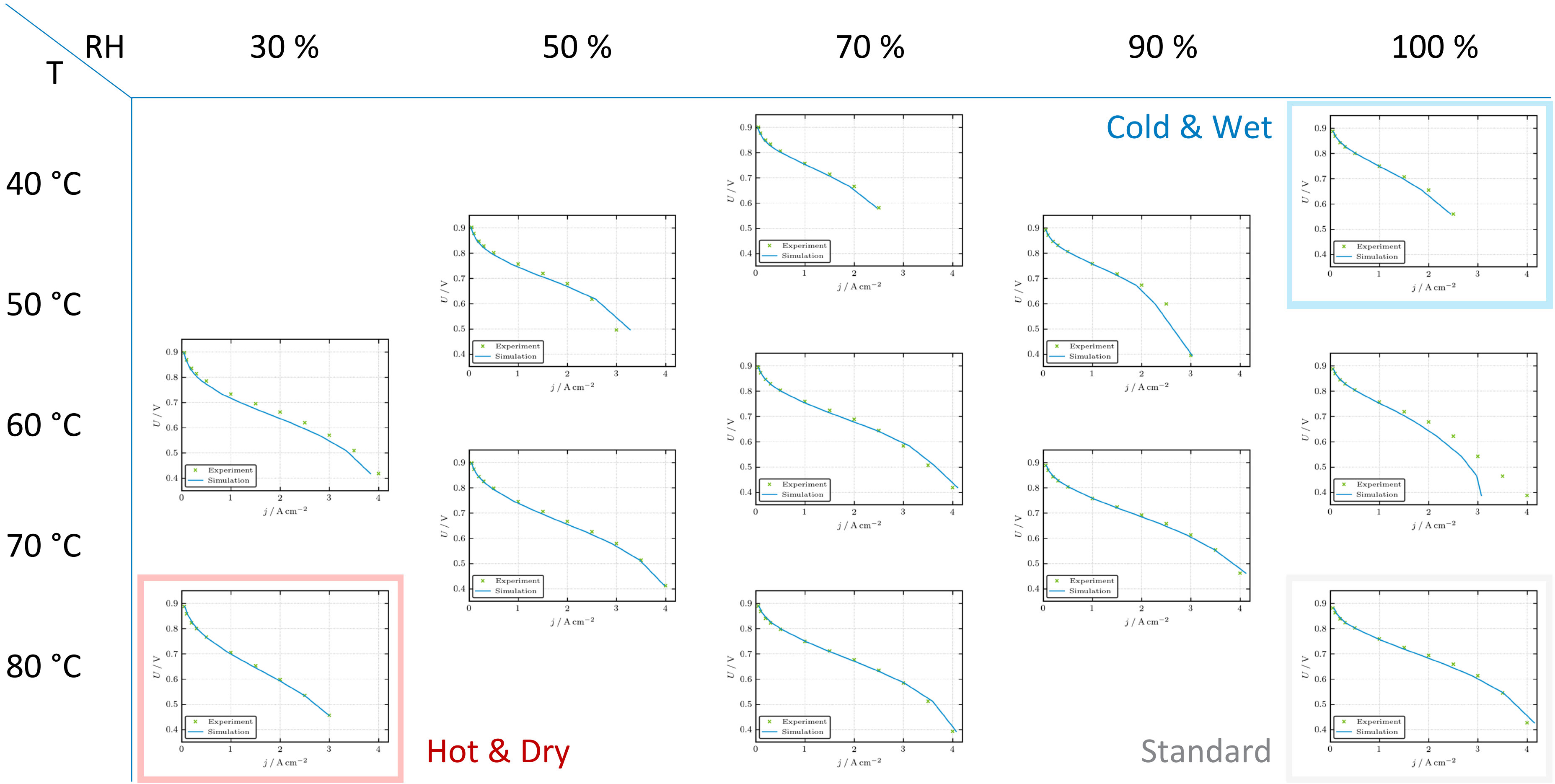
Polarization Curves

Focus on Extreme Conditions: Standard, Cold/Wet & Hot/Dry



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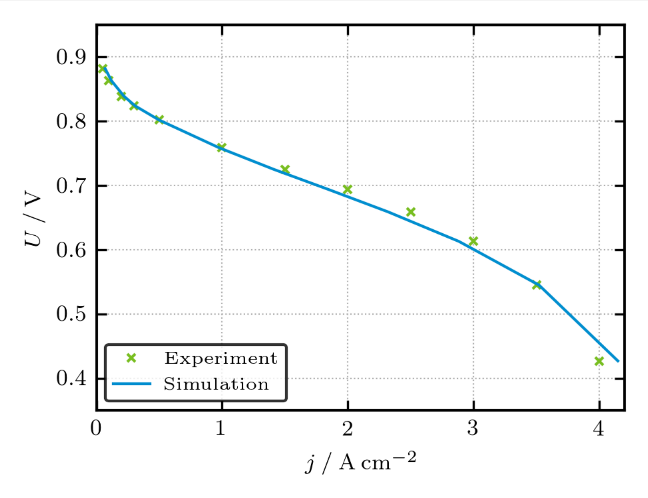
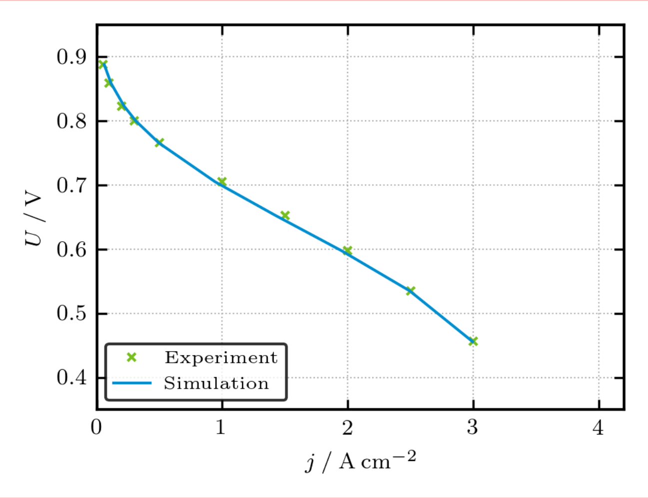
Polarization Curves

Standard, Hot & Dry, Cold & Wet with Excellent Agreement

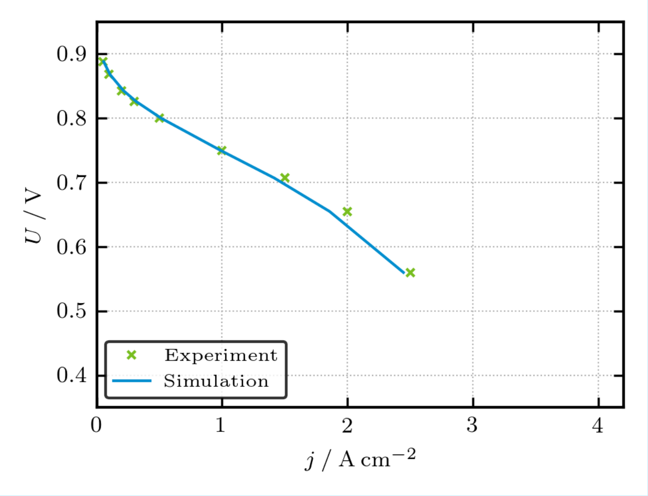
Standard



Hot & Dry



Cold & Wet



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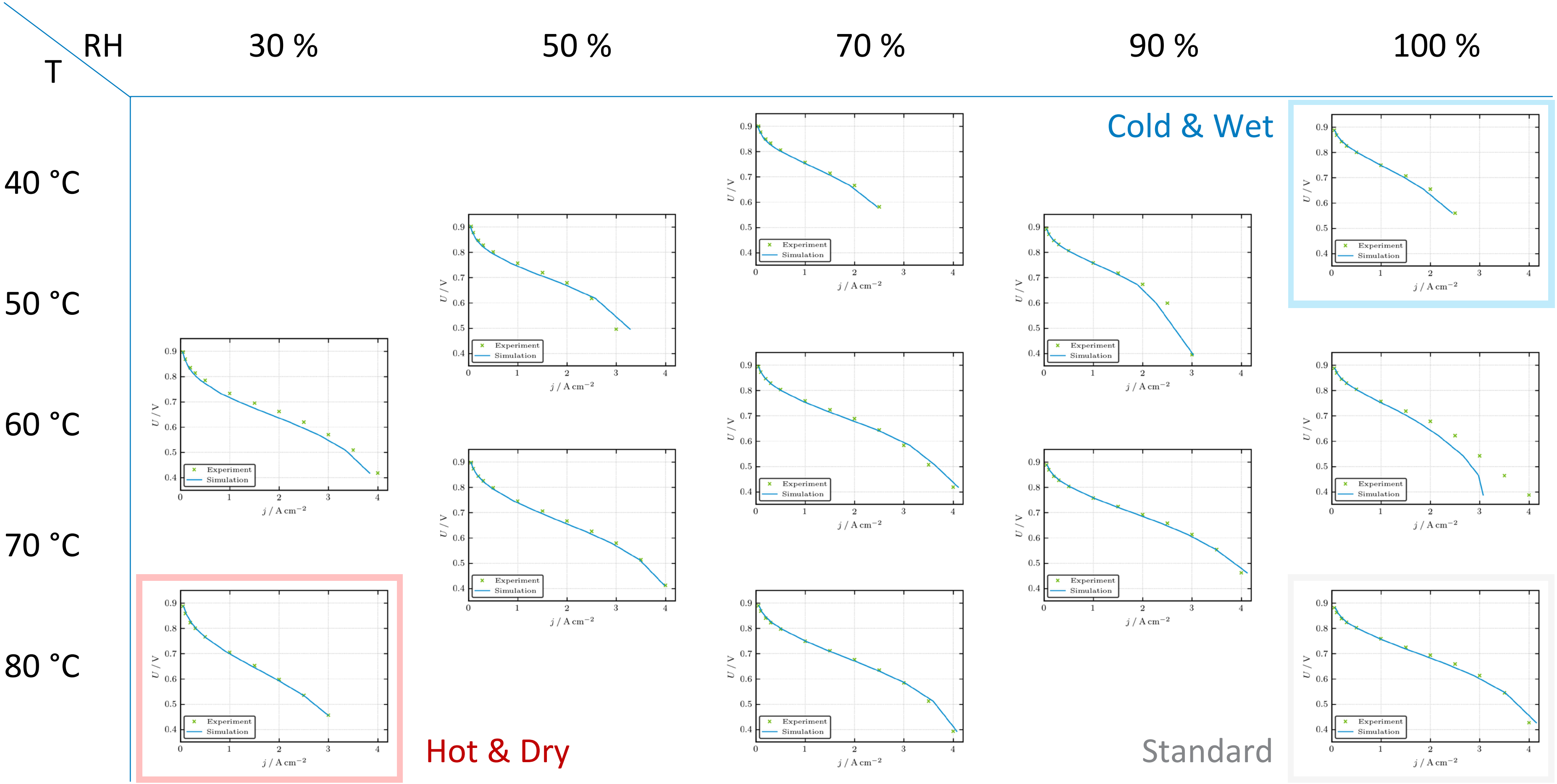
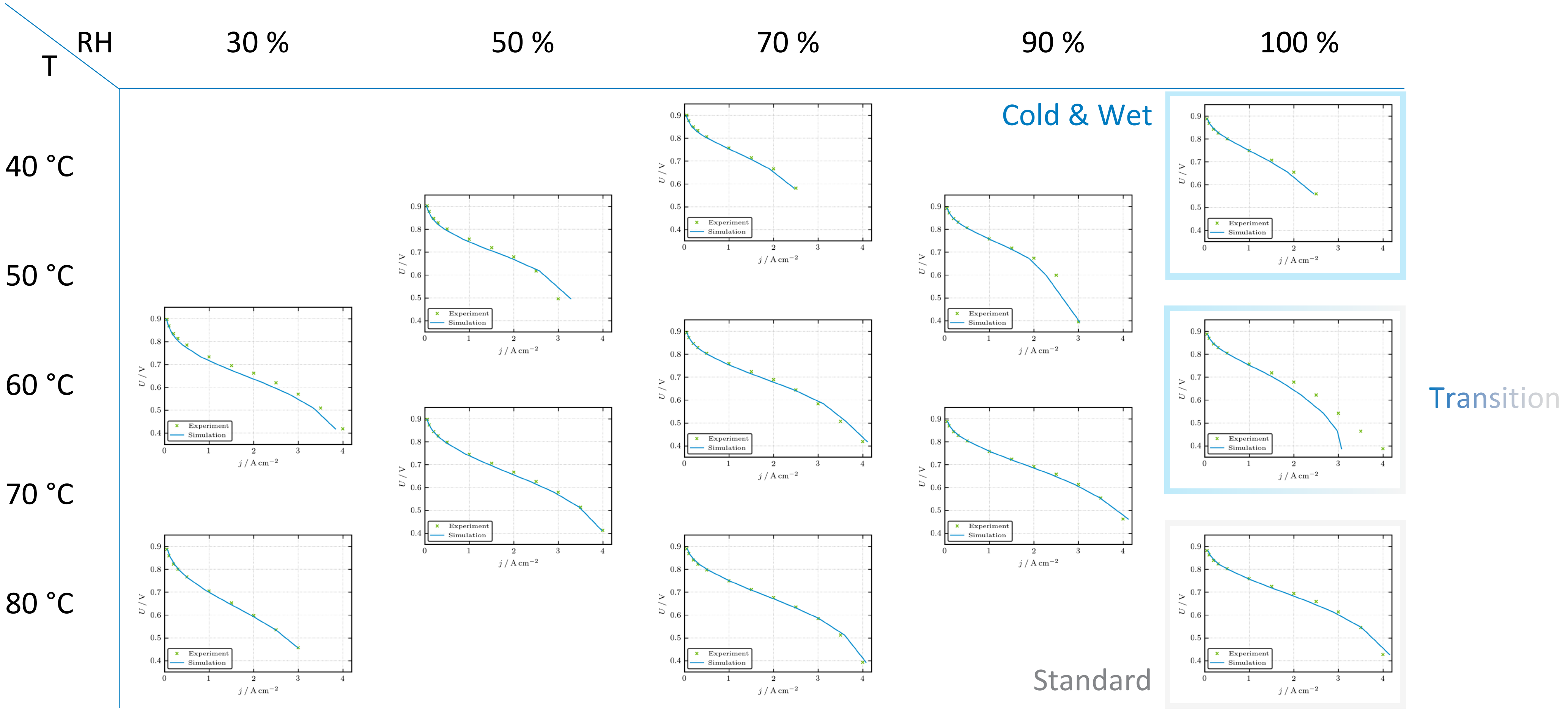
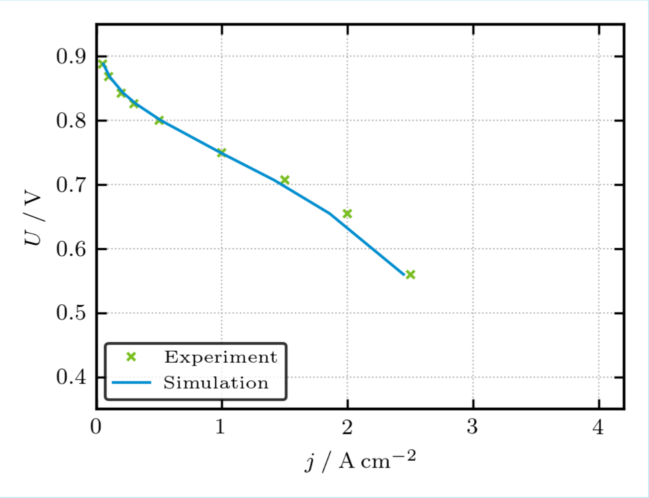
Polarization Curves
Focus on Extreme Conditions



Polarization Curves
Focus on Transition Conditions

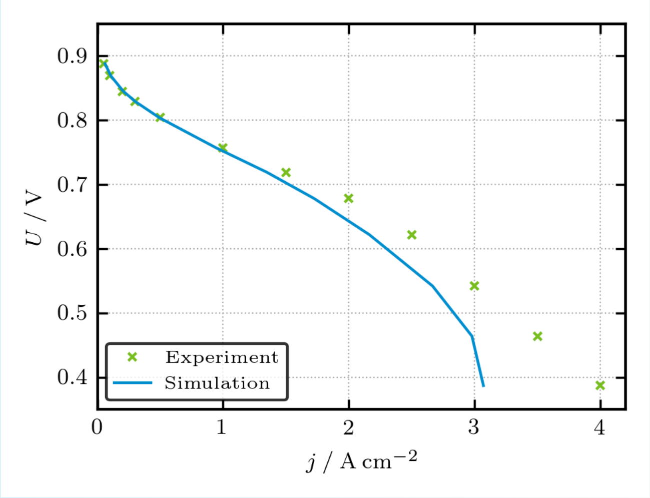


Polarization Curves
Model Overestimates Flooding under Transition Conditions

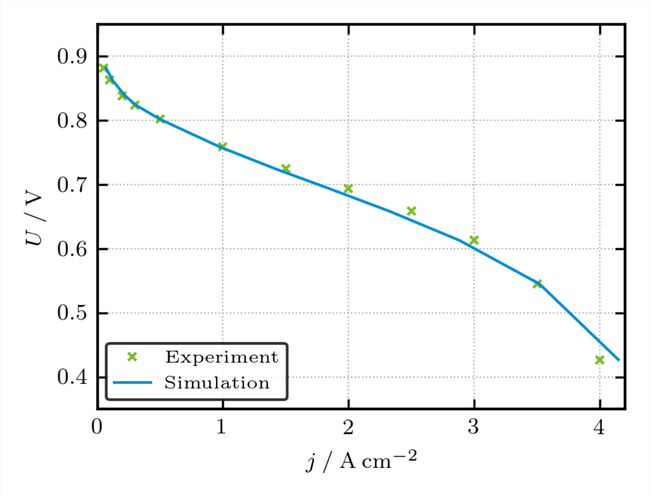


Cold & Wet

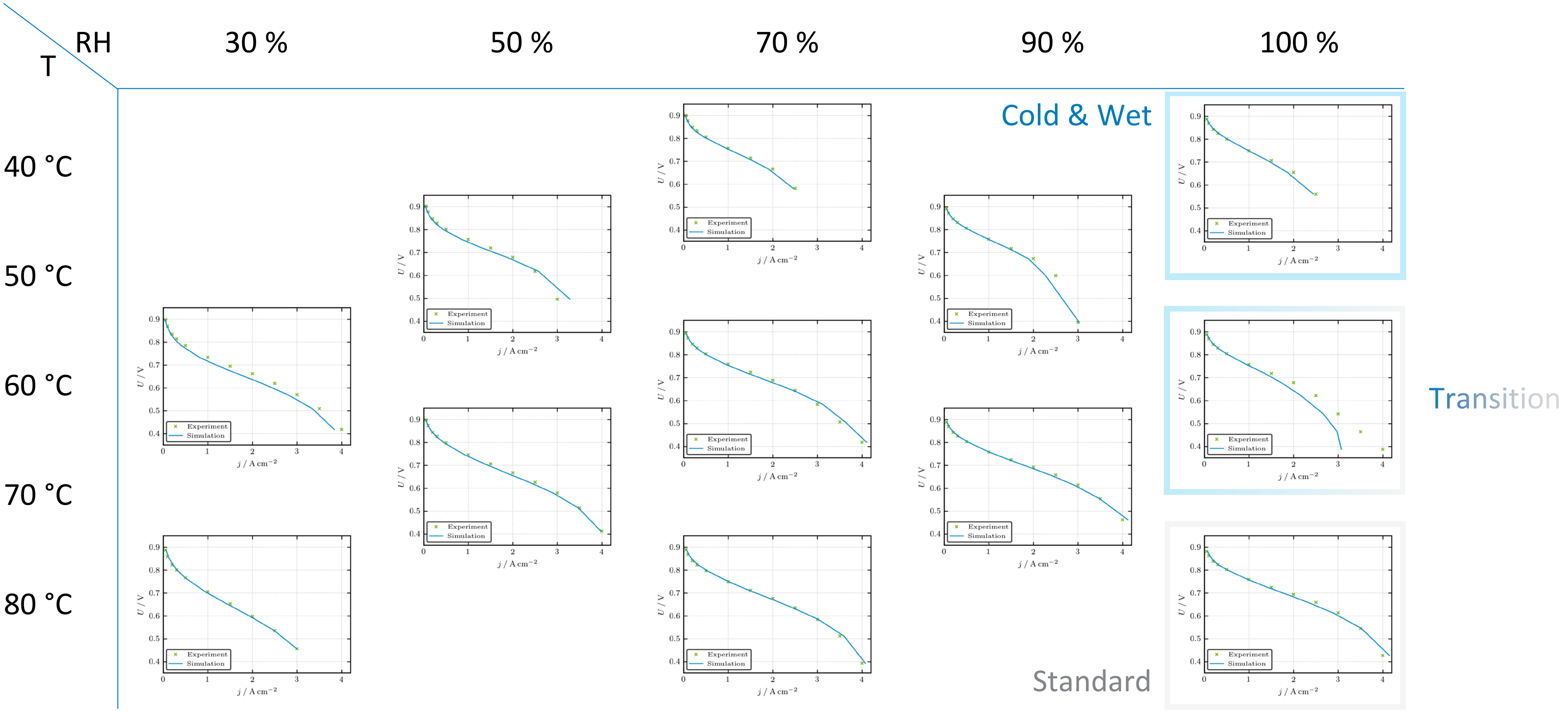
Transition



Standard

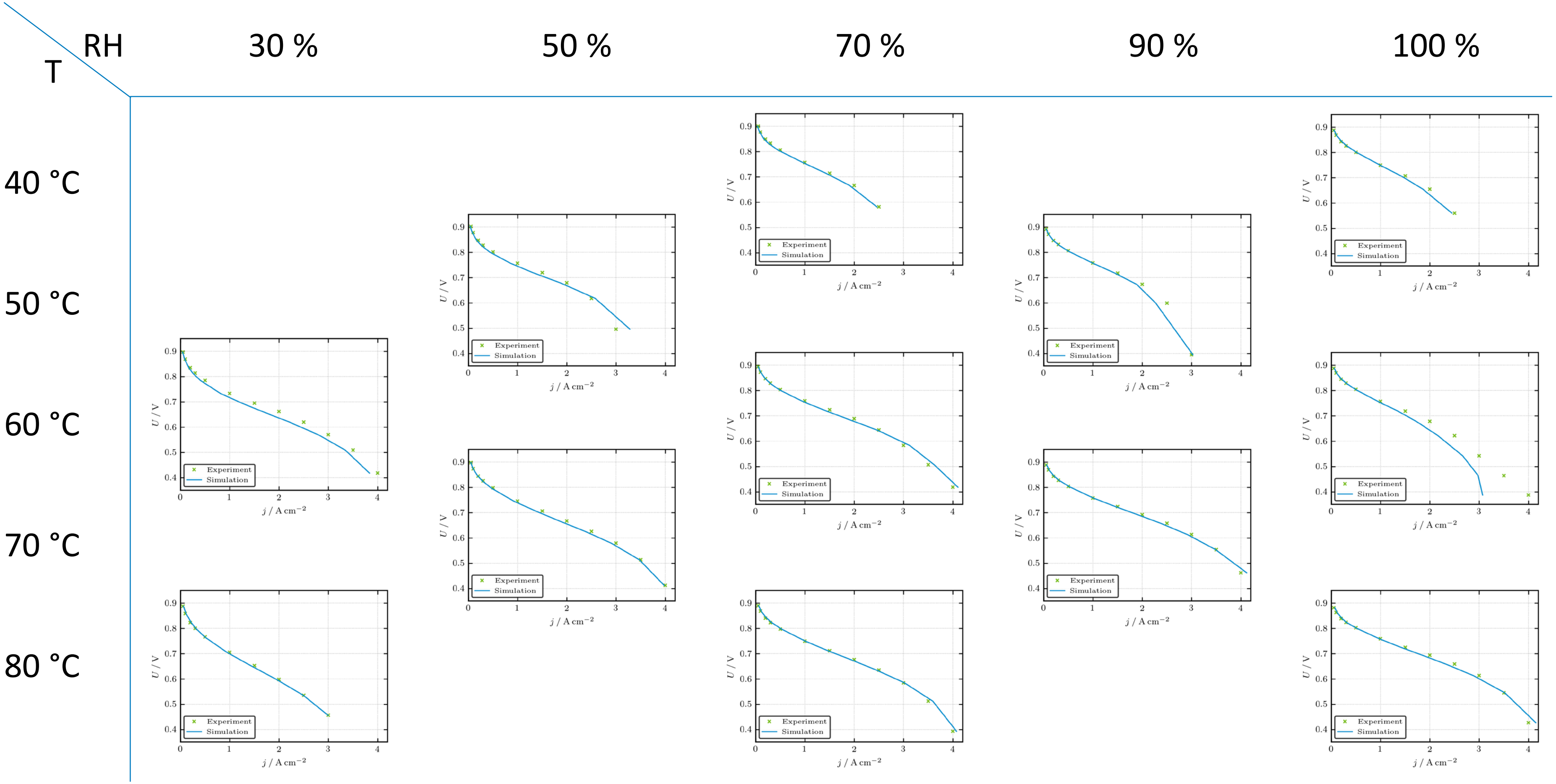


Polarization Curves
Focus on Transition Conditions



Polarization Curves

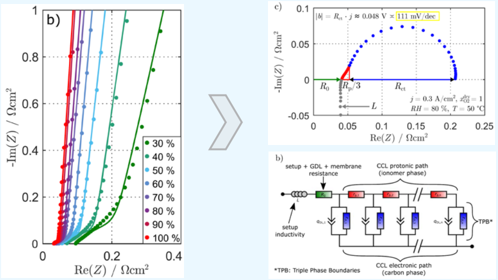
Full Factorial DOE under Hydrogen/Air



Validation/Parametrization
Polarization Curves

EIS

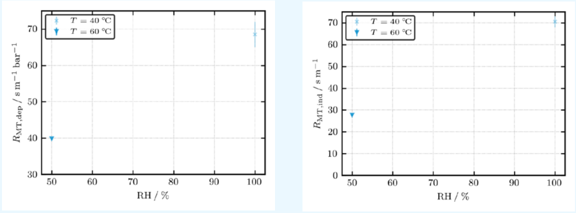
Parametrization



Validation

Limiting Current

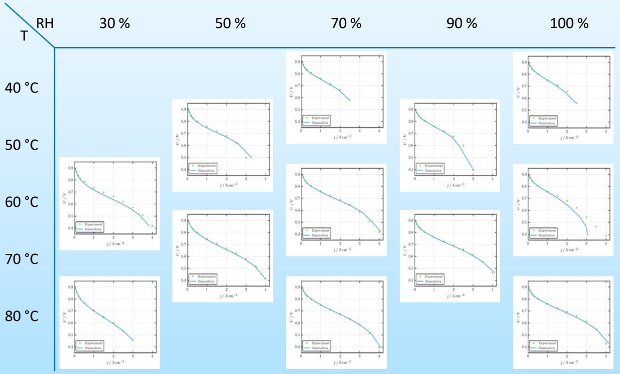
Parametrization



Validation

Global Fit

Parametrization



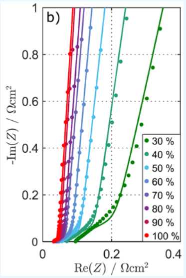
Validation

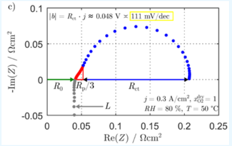
BOSCH

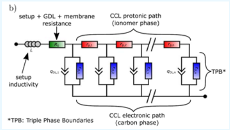
Validation
Limiting Current

EIS

Parametrization



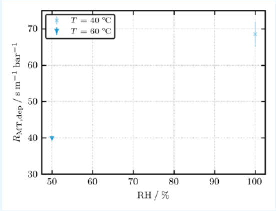


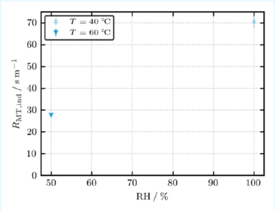


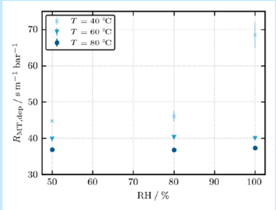
Validation

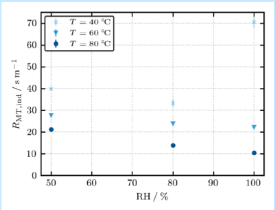
Limiting Current

Parametrization





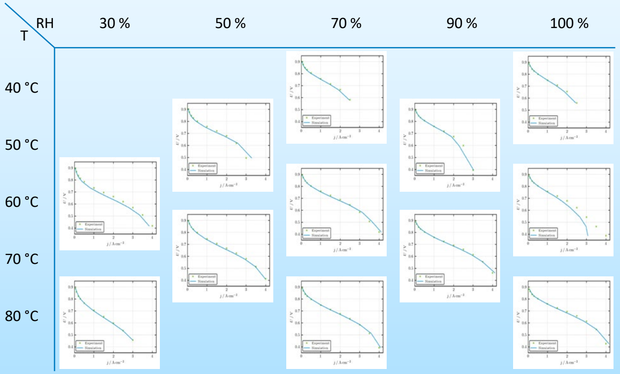




Validation

Global Fit

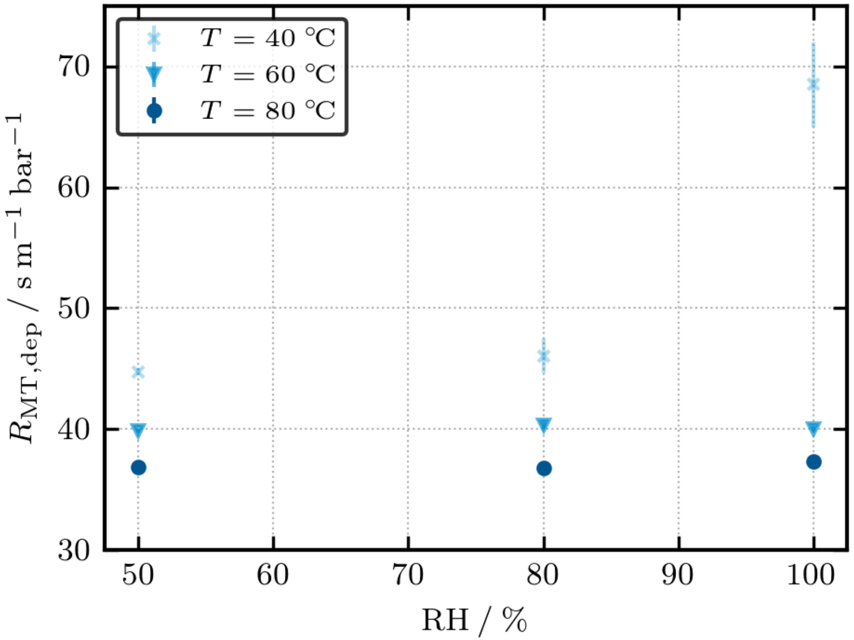
Parametrization



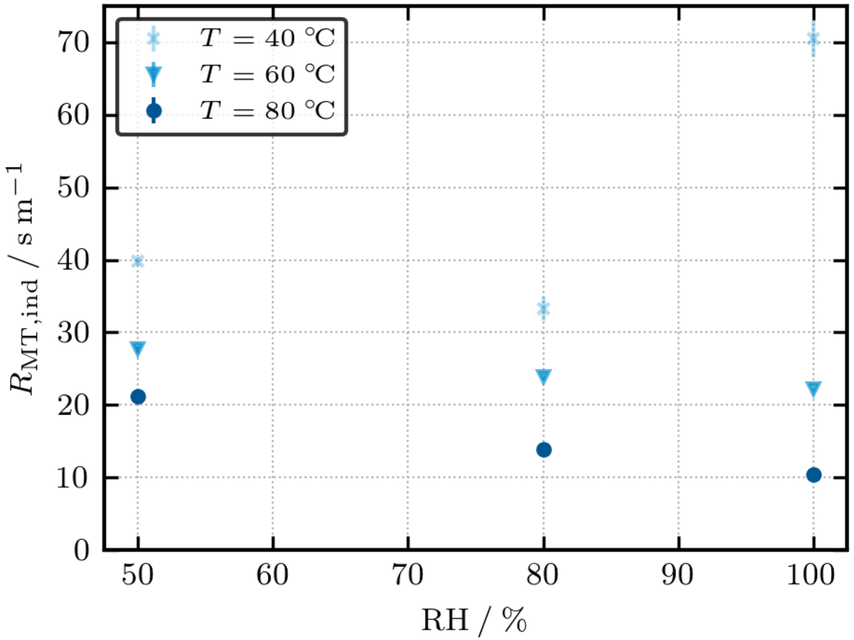
Validation

Limiting Current
Full Factorial DOE for Validation

Pressure-**dependent** MTR

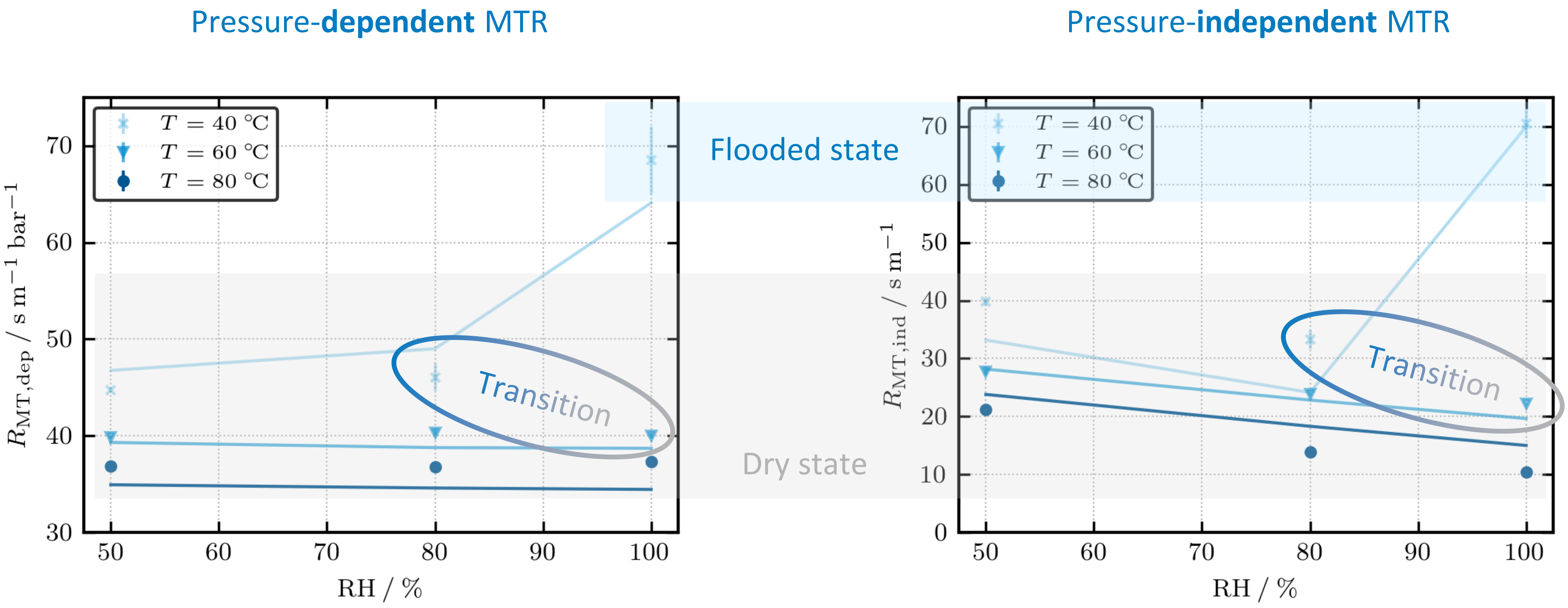


Pressure-**independent** MTR



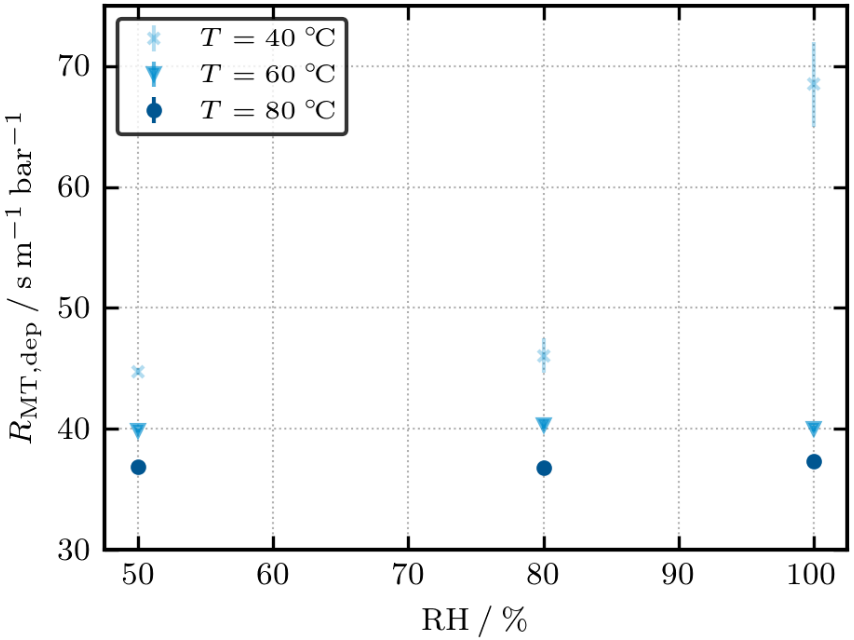
Limiting Current

Good Model Agreement, Problems at Transition Regions

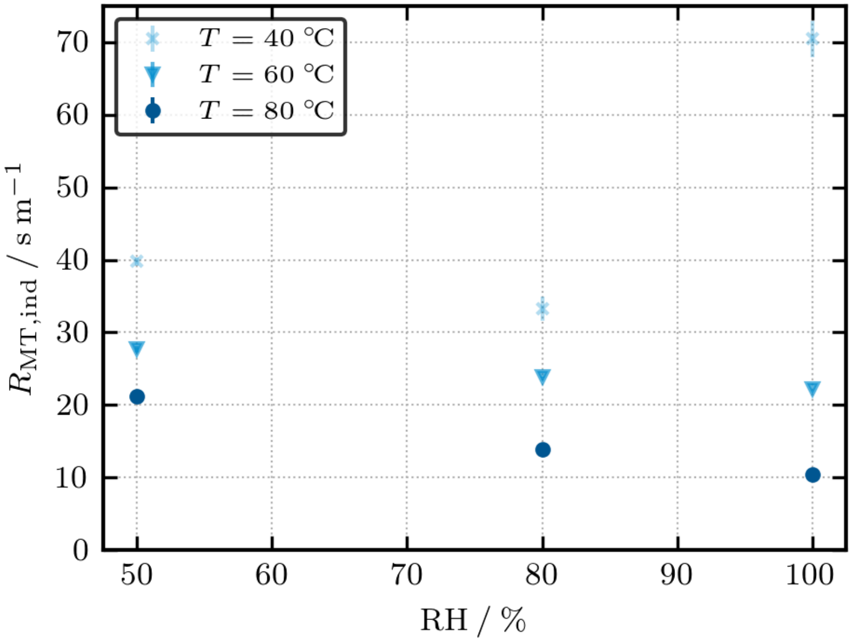


Limiting Current
Full Factorial DOE for Validation

Pressure-dependent MTR



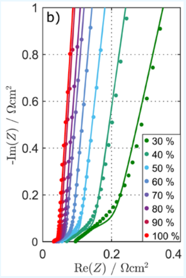
Pressure-independent MTR

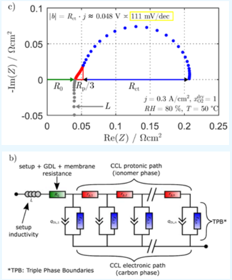


Validation
Limiting Current

EIS

Parametrization

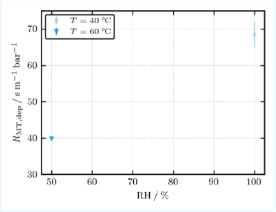


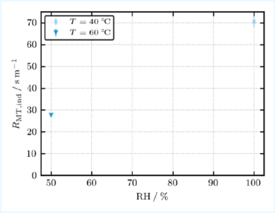


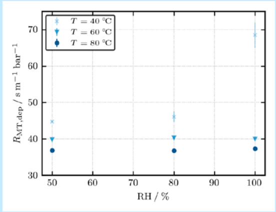
Validation

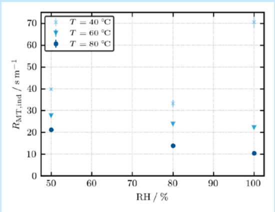
Limiting Current

Parametrization





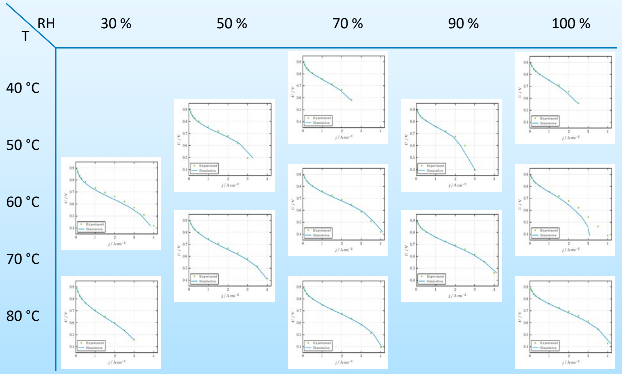




Validation

Global Fit

Parametrization



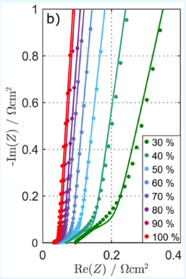
Validation

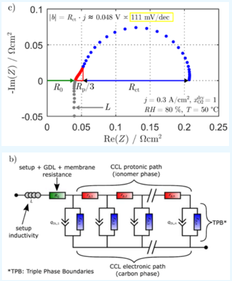
Validation

Electrochemical Impedance Spectroscopy

EIS

Parametrization





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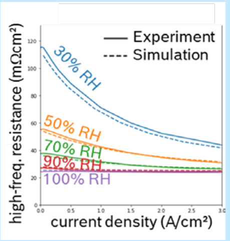
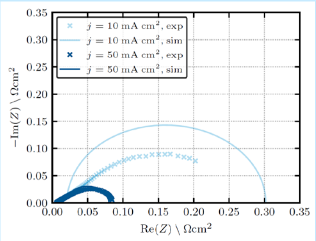
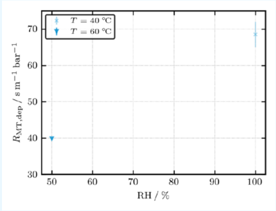
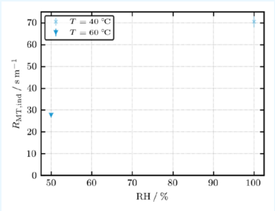




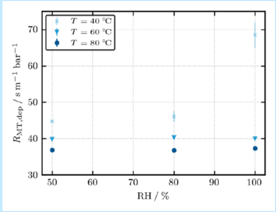
Limiting Current

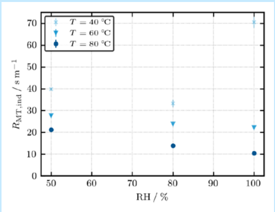
Parametrization





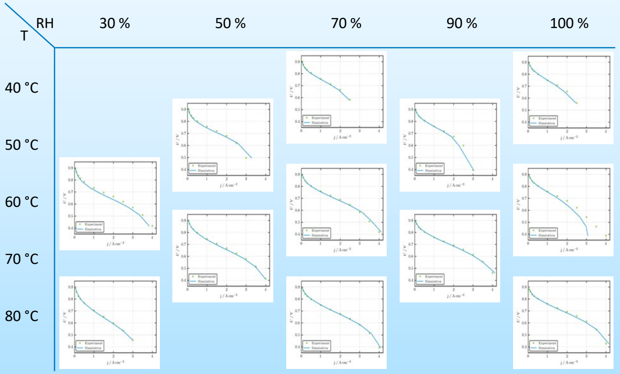
Validation





Global Fit

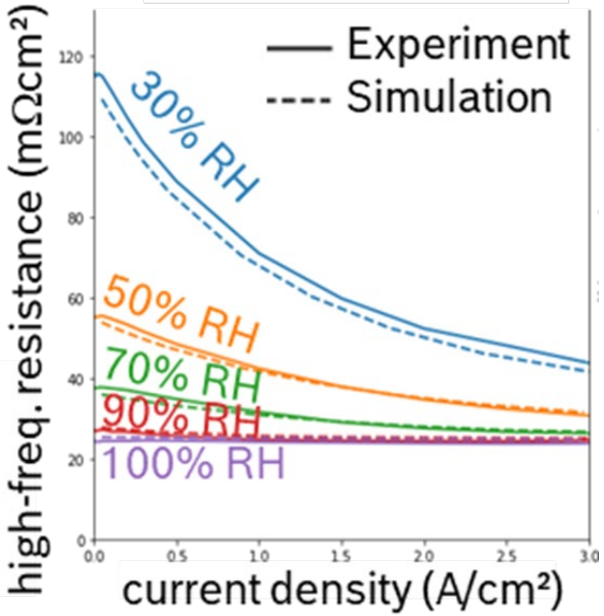
Parametrization



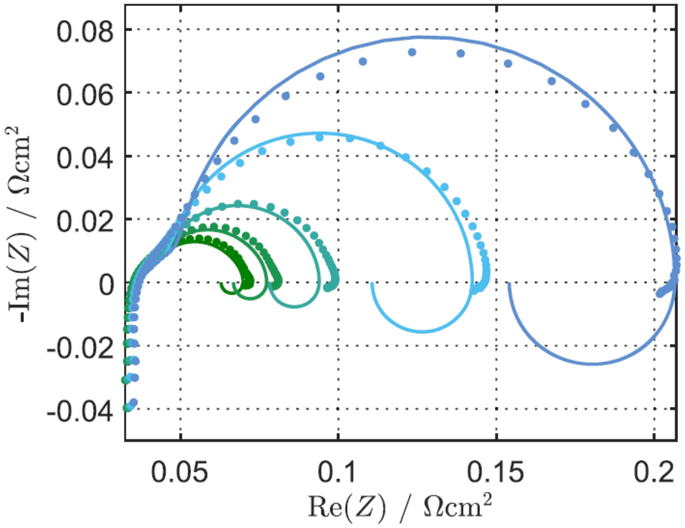
Validation

Electrochemical Impedance Spectroscopy

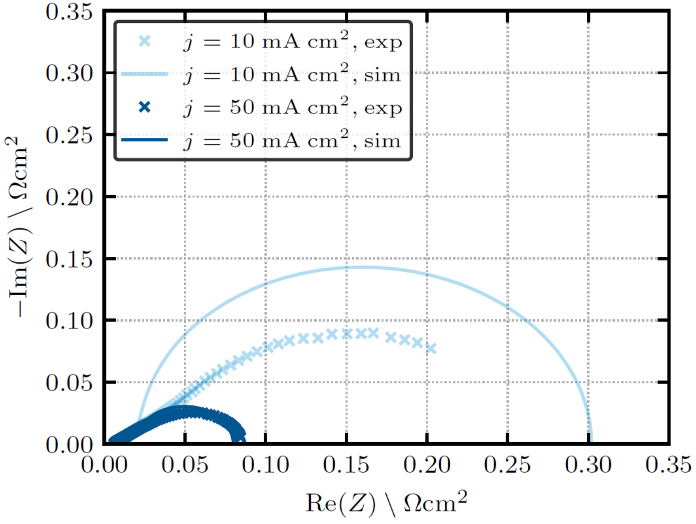
Validation using HFR and Complete Impedance Spectra



EIS validation with **simplified 1D model**



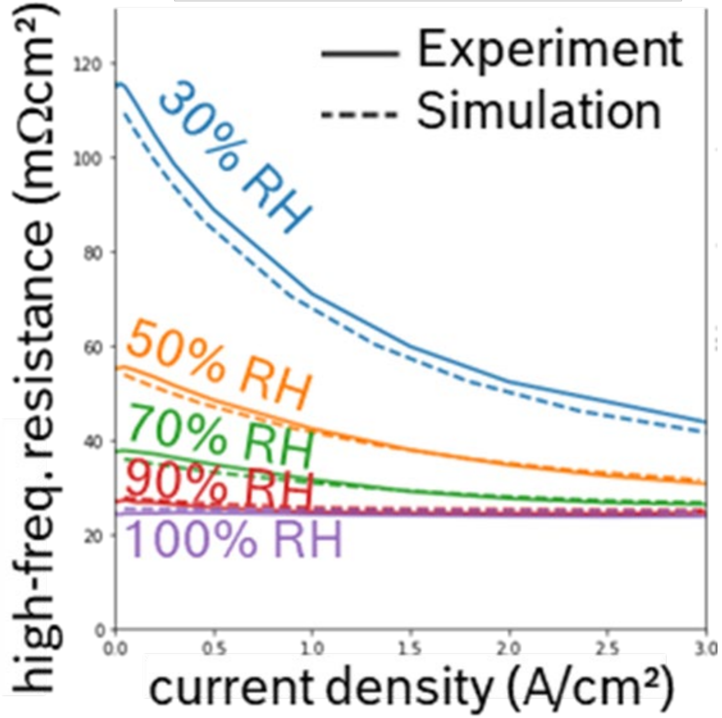
EIS validation with **Full 2D model**

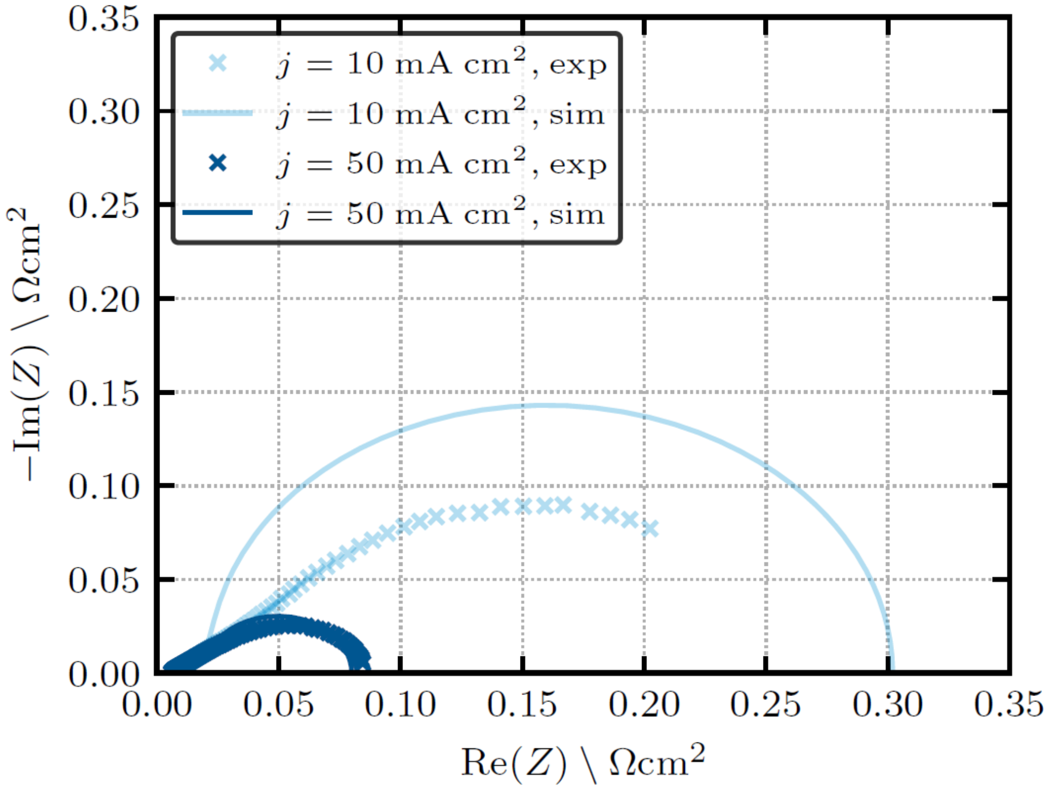


Gerling *et al.*, JES 170, 14504 (2023)

Electrochemical Impedance Spectroscopy

Validation using HFR and Complete Impedance Spectra

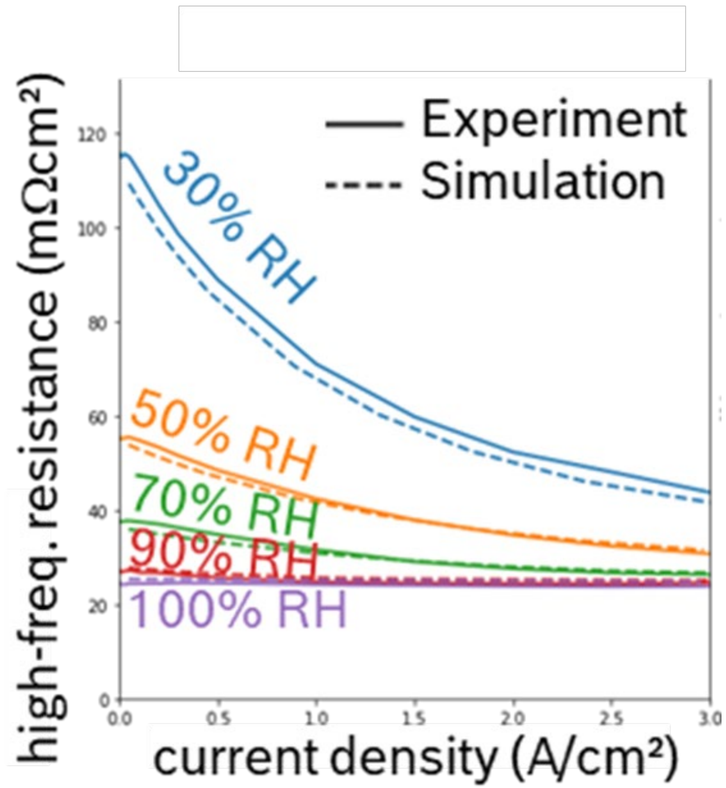


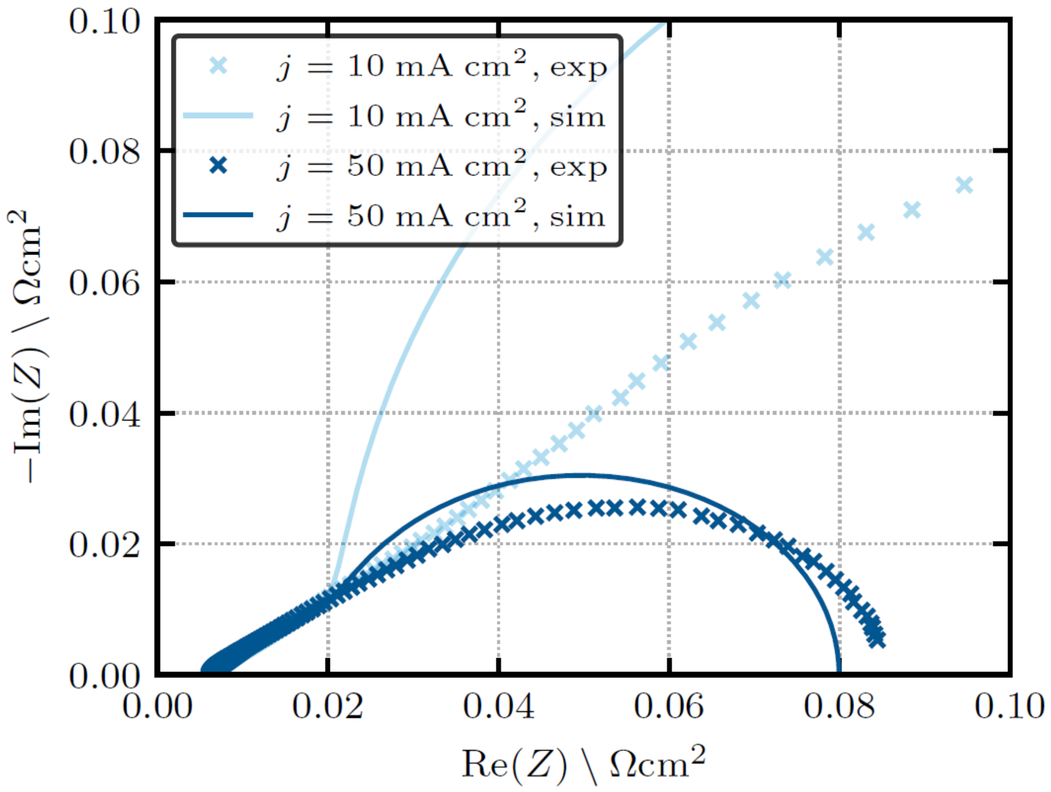


Charge Transfer too large at low current density due to crossover + short circuit.

Electrochemical Impedance Spectroscopy

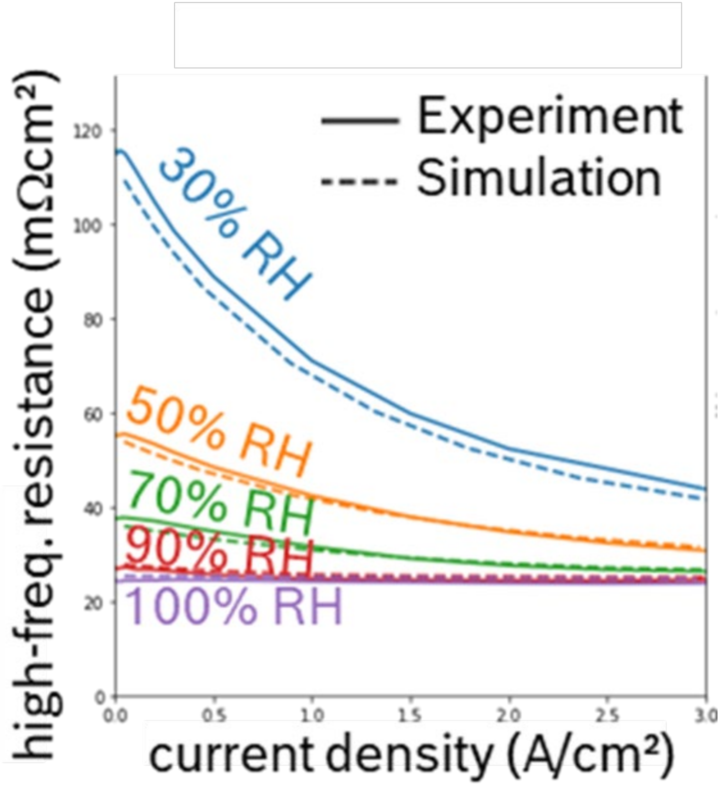
Closer Match at Higher Current Density, but Still Open Questions

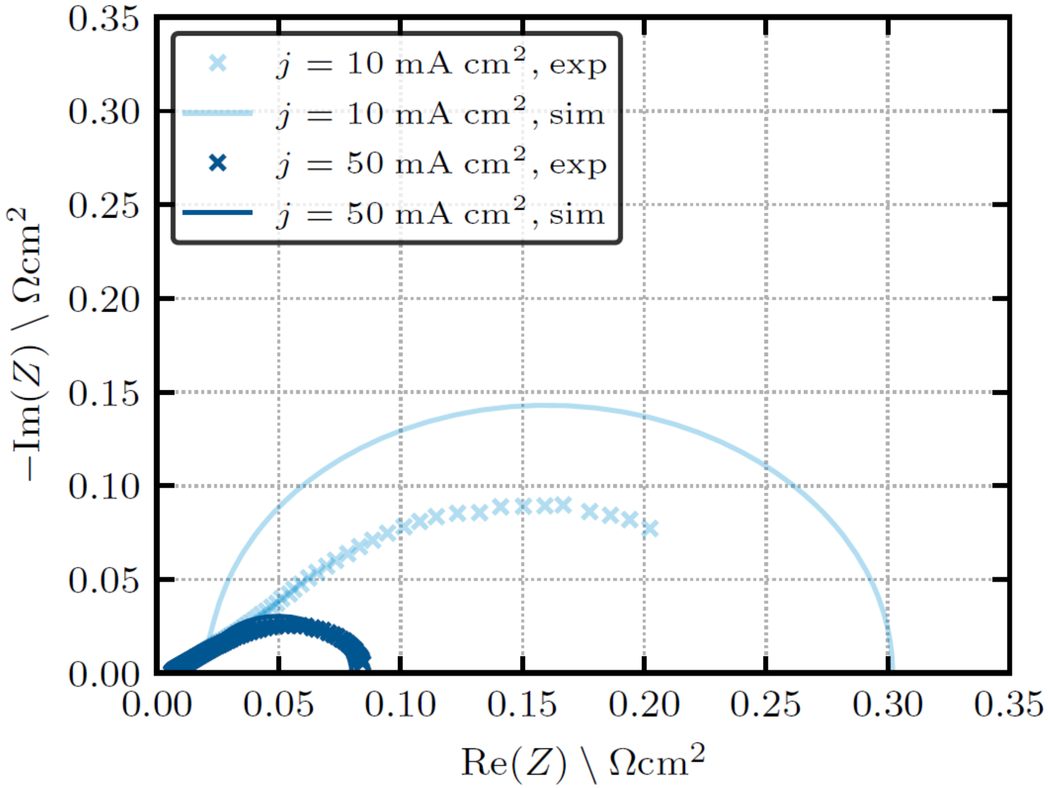




BOSCH

Electrochemical Impedance Spectroscopy
Validation using HFR and Complete Impedance Spectra





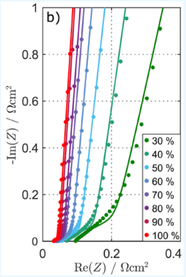
BOSCH

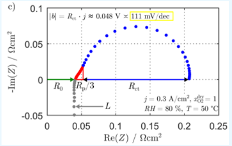
Validation

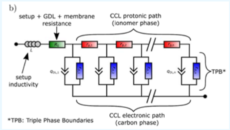
Electrochemical Impedance Spectroscopy

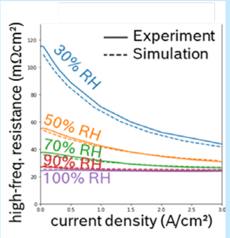
EIS

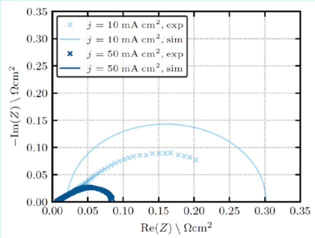
Parametrization







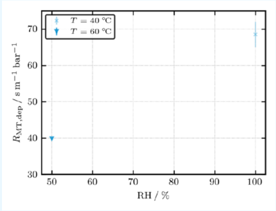


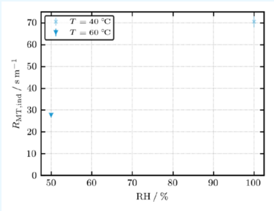


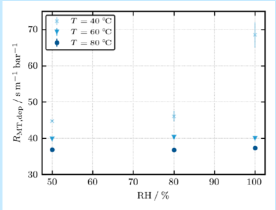
Validation

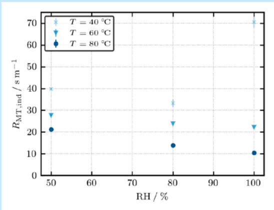
Limiting Current

Parametrization





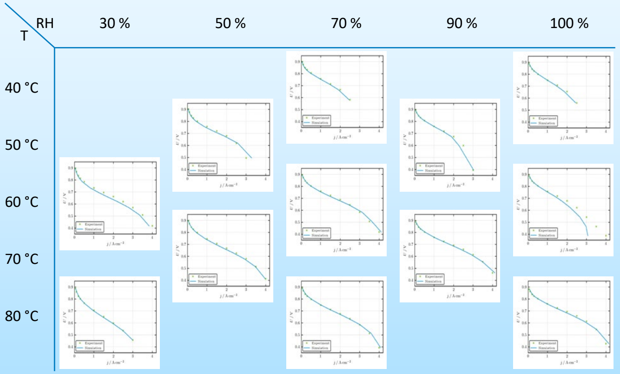




Validation

Global Fit

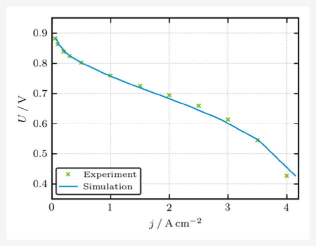
Parametrization

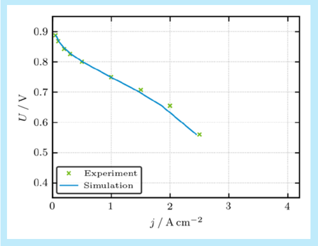


Validation

BOSCH

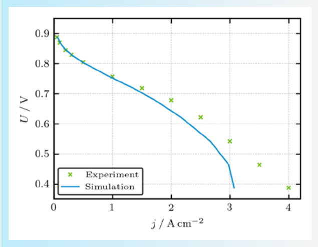
Key takeaways





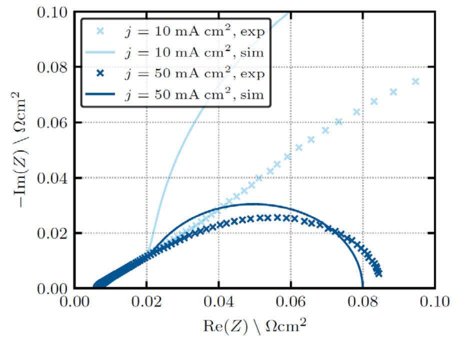
Performance

- Can be predicted for broad field of RH, T and j.
- Prediction quality already sufficient for industrial use + upscaling.



Flooding

- Can be parametrized using few limiting current measurements.
- Requires deeper understanding under transitional areas (net water transfer[1], segmented cells[2]).



Transient Effects

- Quantitative models required for slow dynamical effects (e.g. Pt oxides[3])
- Ongoing: Direct validation of dynamics using impedance spectra

THANK YOU FOR YOUR ATTENTION!

1) Bligny *et al.*, JPS 560, 232719 (2023); 2) Schmitt *et al.*, JES 169, 124505 (2022); 3) Gerling *et al.*, JES 170, 14504 (2023)

Further Questions? Get in Touch Via Mail / LinkedIn!

Looking for a Job? Several Openings at Bosch Research in Stuttgart!

SCAN ME

AST Expert Electrolysis

Coating Expert Electrolysis

SCAN ME

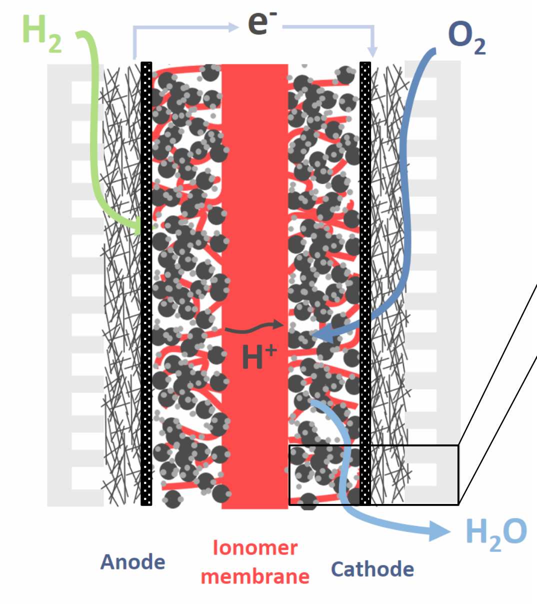
Please get in touch!

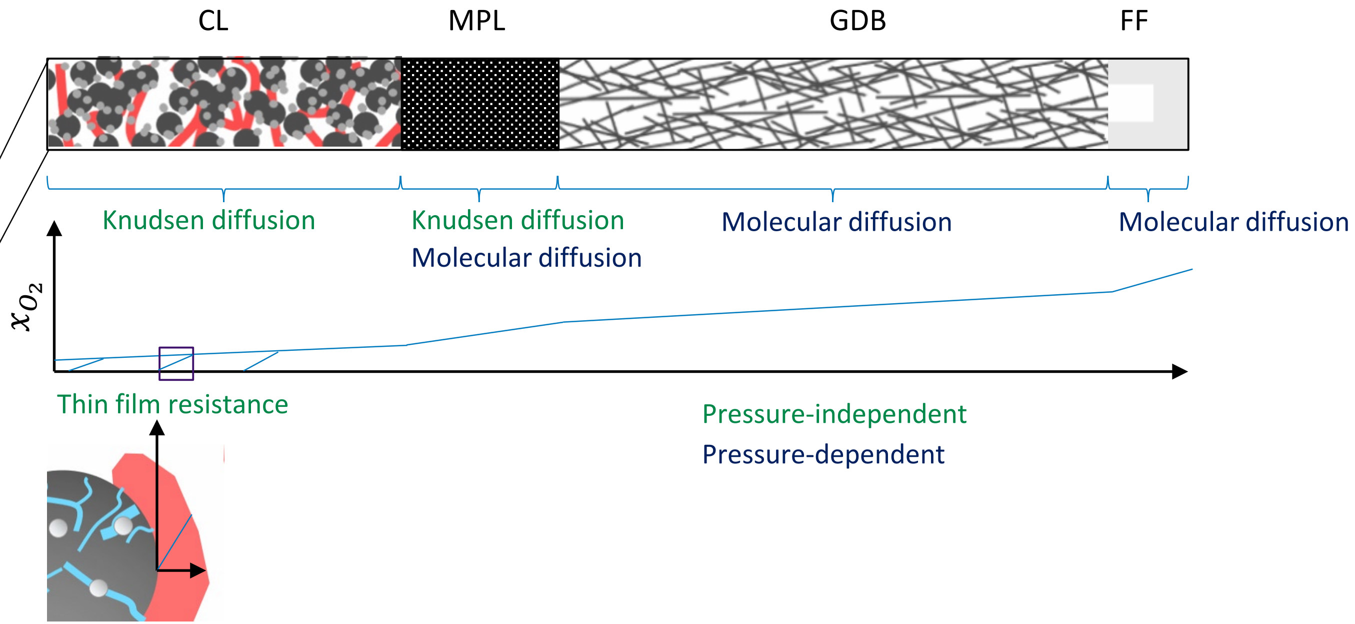
SCAN ME

Backup

Overview of Mass transport resistance contributions

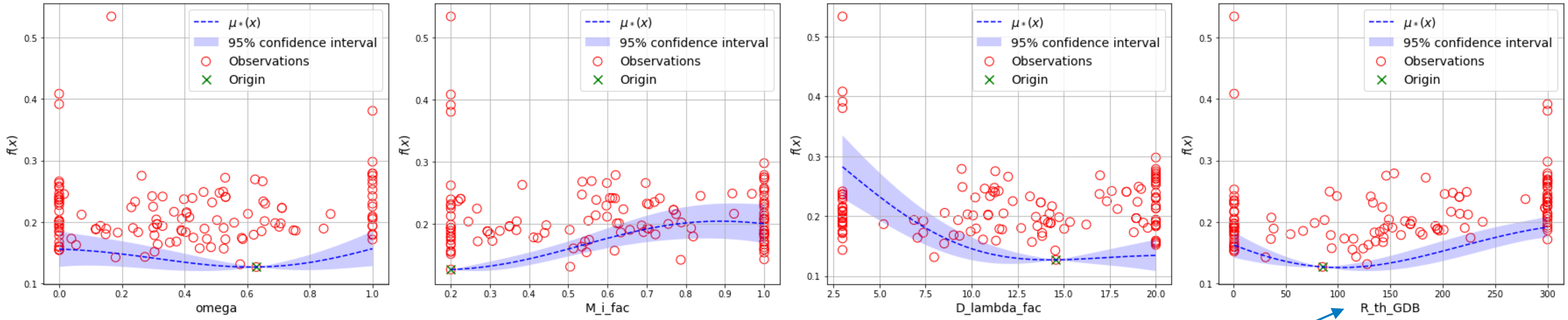
Molecular diffusion, Knudsen diffusion and thin film resistance

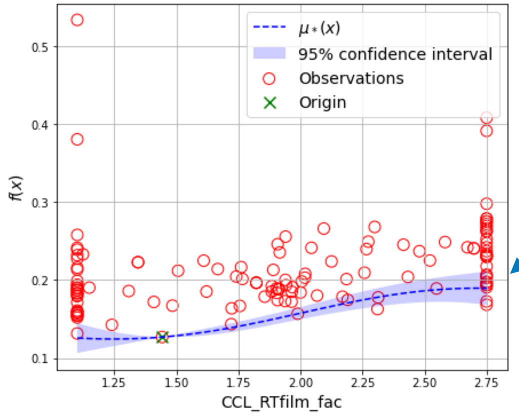




Parametrization

Five factors are fitted globally using 180 Polcurve points





- R_th_GDB: Thermal contact resistance between GDB and flowfield land: one of the key factors that determine when flooding occurs – difficult to measure
- CCL_Rtfilm_fac: We have fitted the proportion of pressure-independent MTR from the platinum-near film vs Knudsen diffusion in the CL
- Optimum for almost all parameters does not lie on the edge – quality criteria