Estimation of area specific resistance corrected to fuel utilization as universal characteristic for cell performance

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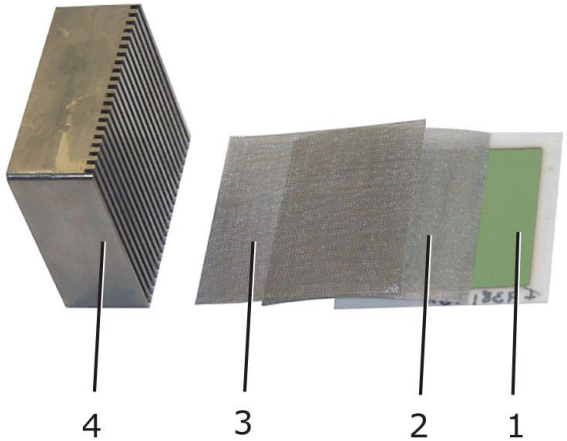
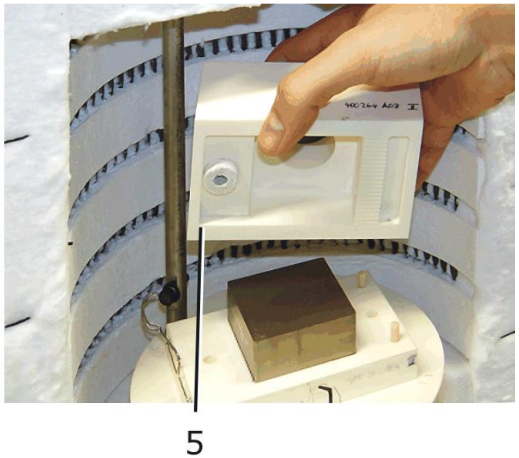
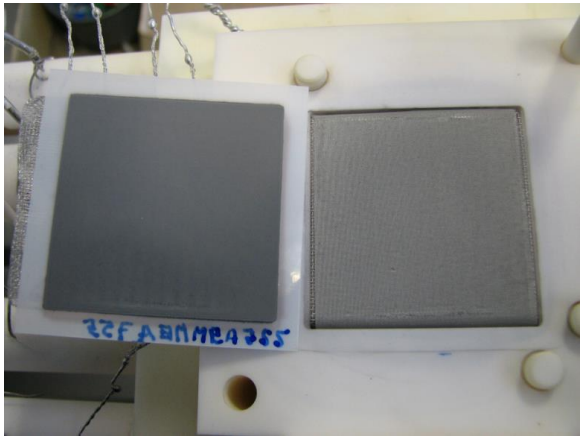
Outline

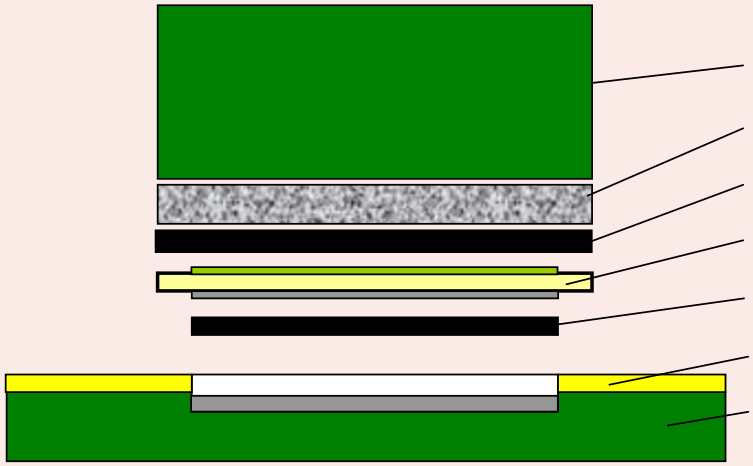
- MEA characterization
- Nernst voltage and polarization Losses
- Estimation of ASR corrected to Fuel Utilization
- Challenges
  - Fuel utilization
  - Current density
- From I-V-Characteristic to Area Specific Resistance
- Summary







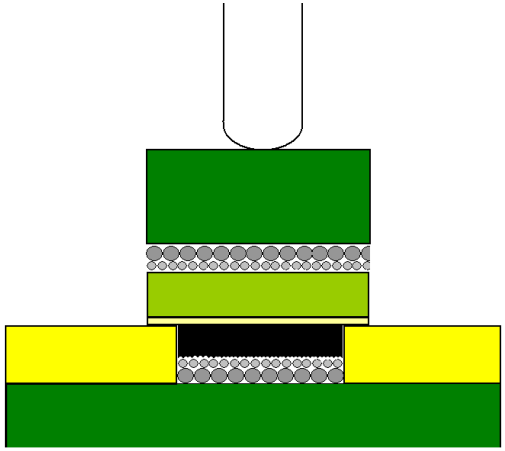
MEA Characterization



1 Stamp for mechanical loading
2 Nickel mesh (coarse)
3 Nickel mesh (fine)
4 MEA
5 Pt-mesh (fine)
6 Tightening ceramic plate
7 Cathode manifold mit Pt-mesh (coarse)

Important parameters for cell integration:

- Cathode thickness
- Pt-mesh (fine + coarse) thickness
- Tightening ceramic plate thickness
- Mechanical load

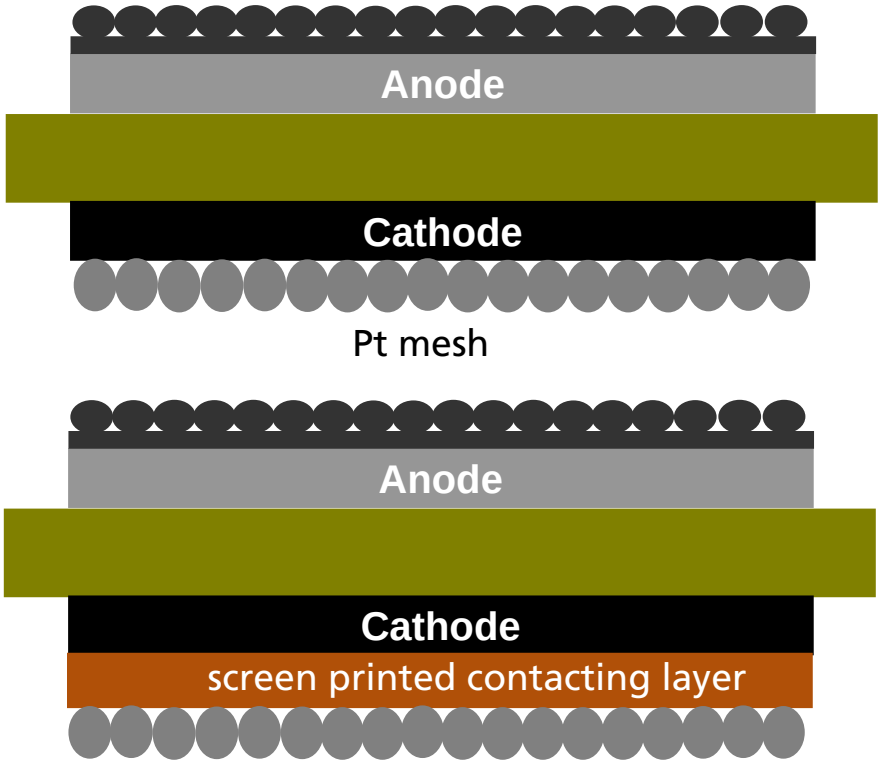


MEA Characterization

Test procedure:

- Anode reduction at 900÷950°C
- Cell activation at 300 mA/cm^2
- Cool down to 850°C
- Cell activation at 300 mA/cm^2
- U/I-Characteristic and EIS at 850°C (H_2:H_2O=1:1 and/or (H_2:H_2O:N_2=40:5:55)
- Cool down to 800-700°C
- U/I-Characteristics and EIS at 800-700°C (H_2:H_2O=1:1 and/or (H_2:H_2O:N_2=40:5:55)

- MEA contacting in ceramic housing:



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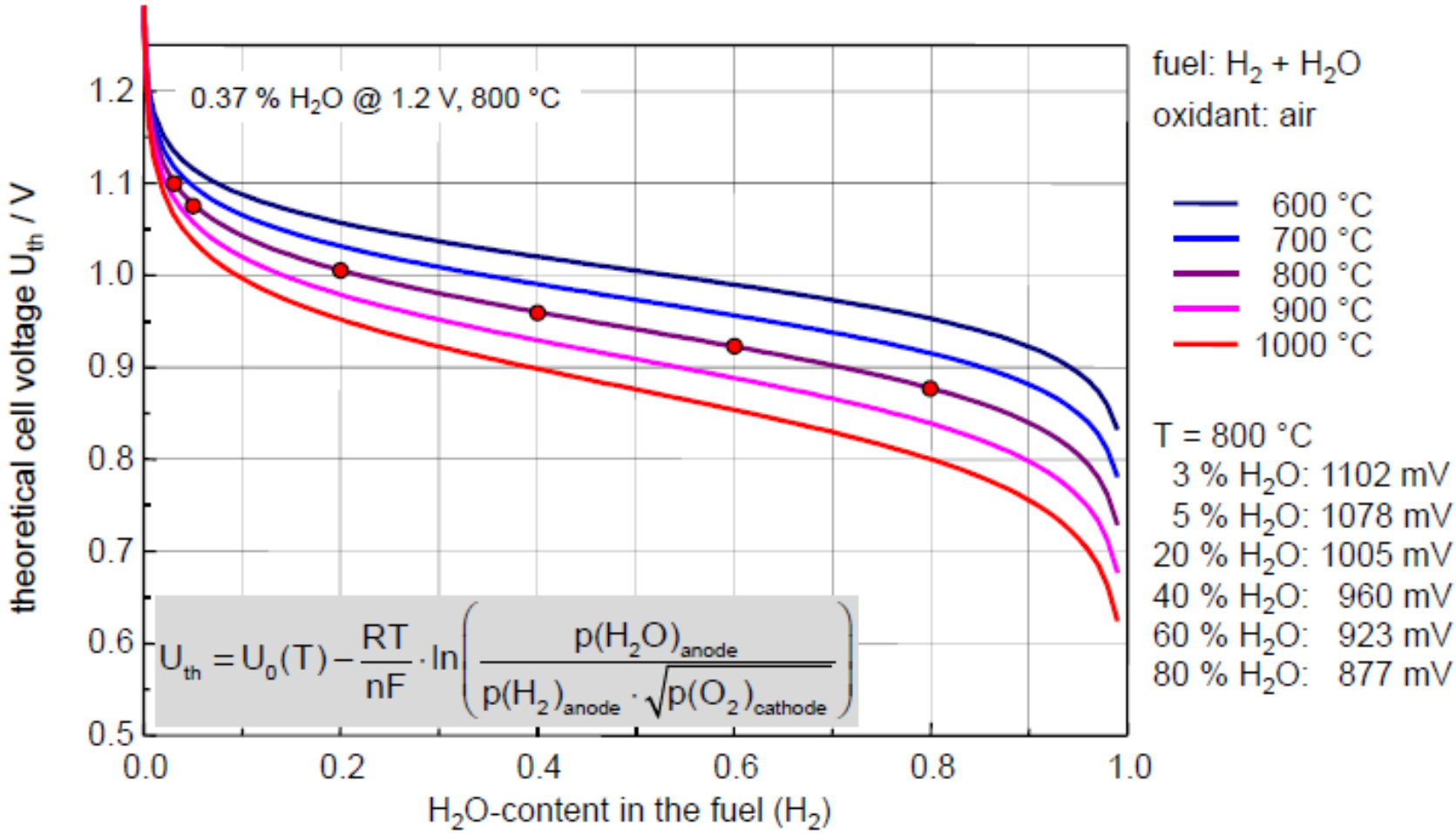
Nernst Voltage



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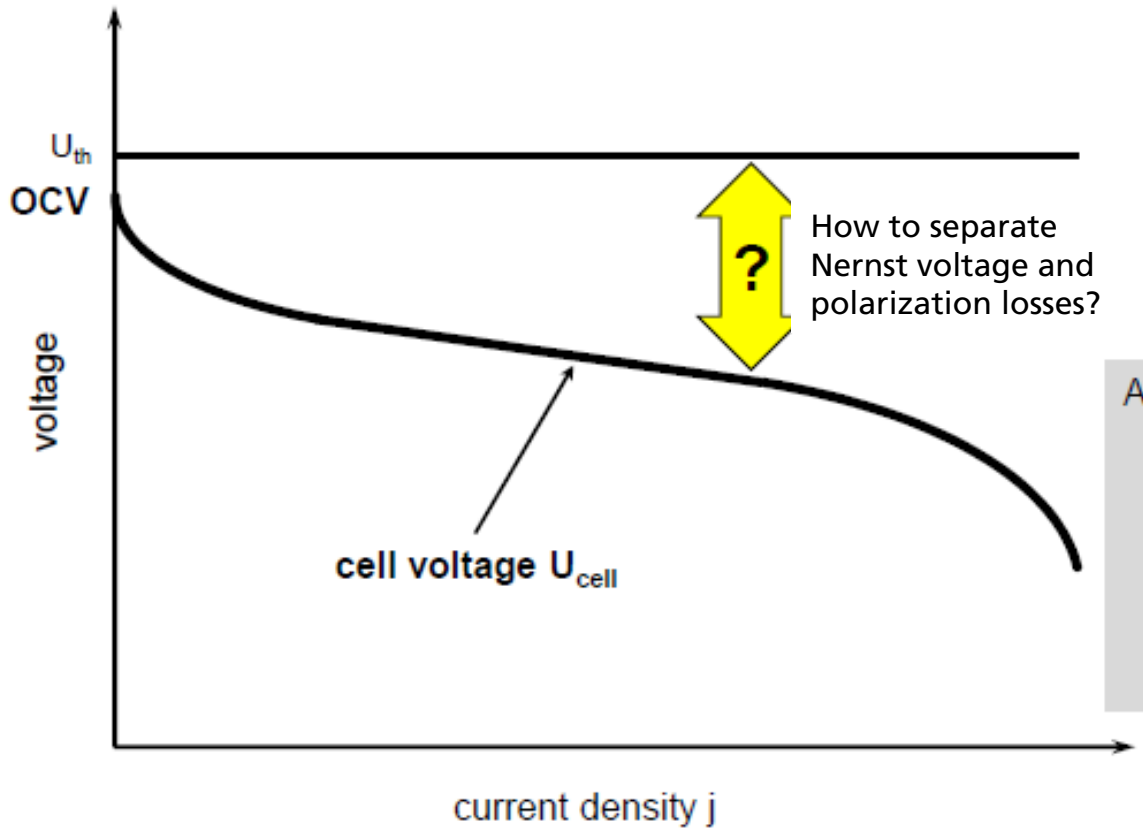
Nernst Voltage and Polarization Losses



Area specific resistance **ASR**:

$$ASR = \frac{\Sigma U_{loss}}{j} = \frac{OCV - U_{cell}}{j}$$

$$ASR = \frac{\Delta U}{\Delta j} = \frac{100\,mV}{j(0.65\,V) - j(0.75\,V)}$$

ASR = f(j,T,gases,...)

OCV: open circuit voltage [V, mV]

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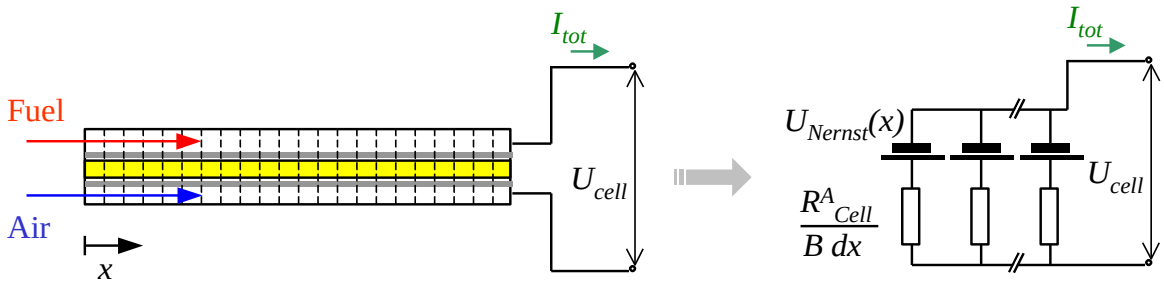
Estimation of ASR corrected to Fuel Utilization

Model:

Geometry



local growth of current flow

$$\frac{\partial}{\partial x} I(x) = \frac{B}{R^A_{cell}} \cdot \left(\underbrace{\frac{R \cdot T}{2F} \cdot \left(\ln \frac{\dot{N}_{H2,in} - \frac{I(x)}{2F}}{\dot{N}_{H2O,in} + \frac{I(x)}{2F}} + 0.5 \cdot \ln \frac{\dot{N}_{O2,in} - 0.5 \cdot \frac{I(x)}{2F}}{\dot{N}_{air,in} - 0.5 \cdot \frac{I(x)}{2F}} \right)}_{U_{Nernst}(p,T,X_i(x))} + U_{Nernst,0}(p,T) - U_{cell} \right)$$

Total current:

$$I_{tot} = \int_0^L \frac{B}{R^A_{Cell}} \cdot \left(U_{Nernst}(x) - U_{Cell} \right) \cdot dx = \frac{B \cdot L}{R^A_{Cell}} \cdot \left(\underbrace{\frac{1}{L} \cdot \int_0^L U_{Nernst}(x) \cdot dx}_{\hat{U}_{Nernst}} - U_{Cell} \right)$$

Approxiation for average Nernst voltage:

$$\hat{U}_{Nernst} \cong U_{Nernst}\left(p,T,\{\hat{X}_k\}\right) \cong U_{Nernst}\left(p,T,\left\{\dot{N}_{k,in} + \nu_k \cdot \frac{\Delta \dot{N}}{2}\right\}\right) = U_{Nernst}\left(p,T,\left\{\dot{N}_{k,in} + \frac{\nu_k}{2F} \cdot \frac{I_{tot}}{2}\right\}\right)$$

Nernst voltage at $I_{tot}/2$

Estimation of ASR corrected to Fuel Utilization

Correction

Relationship between Nernst voltage and fuel composition $X_{k,in}$

$$\frac{dI(x)}{dx} = \frac{b}{R_A} \cdot \left[\overbrace{\frac{R \cdot T}{2F} \cdot \left(\ln\left(\frac{X_{H_2O,in}}{X_{H_2,in}} \cdot \frac{2F \cdot X_{H_2,in} \cdot \dot{N}_{fuel,in} - I(x)}{2F \cdot X_{H_2O,in} \cdot \dot{N}_{fuel,in} + I(x)} \right) + 0.5 \cdot \ln\left(\frac{1}{X_{O_2,in}} \cdot \frac{4F \cdot X_{O_2,in} \cdot \dot{N}_{air,in} - I(x)}{4F \cdot \dot{N}_{air,in} - I(x)} \right) \right)}^{\Delta U(I(x))} + U_{N,0}(p, T, X_{k,in}) - U_{cell} \right]$$

Deviation of Nernst-Voltage from Open Circuit Voltage

Open Circuit Voltage

Total current after integration over MEA length:

$$I_{tot} = \frac{b \cdot L}{R_A} \cdot \left(\frac{1}{L} \cdot \int_0^L \Delta U(I(x)) \cdot dx + U_{N,0}(p, T, X_{k,in}) - U_{cell} \right)$$

Transformation of integral

$$dx \rightarrow dI \quad \int_0^L \Delta U(I(x)) \cdot dx = \int_0^{I_{tot}} \frac{\Delta U(I)}{I'} \cdot dI$$

$$I_{tot} = \frac{b \cdot L}{R_A} \cdot \left(\frac{R_A}{L \cdot B} \cdot \int_0^{I_{tot}} \frac{\Delta U(I) \cdot dI}{\Delta U(I) + U_{N,0}(\ ) - U_{cell}} + U_{N,0}(\ ) - U_{cell} \right)$$

Estimation of ASR corrected to Fuel Utilization

$$I_{tot} = \frac{b \cdot L}{R_A} \cdot \left(\frac{R_A}{L \cdot B} \cdot \int_0^{I_{tot}} \frac{\Delta U(I) \cdot dI}{\Delta U(I) + U_{N,0}(\ ) - U_{cell}} + U_{N,0}(\ ) - U_{cell} \right) = \boxed{\int_0^{I_{tot}} \frac{\Delta U(I) \cdot dI}{\Delta U(I) + U_{N,0}(\ ) - U_{cell}}} + \boxed{\frac{b \cdot L}{R_A} \cdot \left(U_{N,0}(\ ) - U_{cell} \right)}$$

- ASR

$$R_A = \frac{b \cdot L}{I_{tot}} \cdot \frac{U_{N,0}(\ ) - U_{cell}}{1 - \boxed{\frac{1}{I_{tot}} \cdot \int_0^{I_{tot}} \frac{\Delta U(I) \cdot dI}{\Delta U(I) + U_{N,0}(\ ) - U_{cell}}}}$$

Final expression:

$$R_A = b \cdot L \cdot \frac{U_{N,0}(\ ) - U_{cell}}{\int_0^{I_{tot}} \frac{U_{N,0}(\ ) - U_{cell}}{\Delta U(I) + U_{N,0}(\ ) - U_{cell}} \cdot dI}$$

Approximation for integration: Taylor approximation at $I = I_{tot} / 2$

$$\int_0^{I_{tot}} \frac{U_{N,0}(\ ) - U_{cell}}{U_{N,0}(\ ) - U_{cell} + \Delta U(I)} \cdot dI = \int_0^{I_{tot}} f(I) \cdot dI = \int_0^{I_{tot}} \left[f\left(\frac{I_{tot}}{2}\right) + \frac{1}{2} f'\left(\frac{I_{tot}}{2}\right) \cdot \left(I - \frac{I_{tot}}{2}\right) + \frac{1}{2} f''\left(\frac{I_{tot}}{2}\right) \cdot \left(I - \frac{I_{tot}}{2}\right)^2 + \right] \cdot dI$$

Estimation of ASR corrected to Fuel Utilization

$$R_A = b \cdot L \cdot \frac{U_{N,0}(\ ) - U_{cell}}{\int_0^{I_{tot}} \frac{U_{N,0}(\ ) - U_{cell}}{\Delta U(I) + U_{N,0}(\ ) - U_{cell}} \cdot dI}$$

- Integral:

$$\int_0^{I_{tot}} \frac{U_{N,0}(\ ) - U_{cell}}{U_{N,0}(\ ) - U_{cell} + \Delta U(I)} \cdot dI = \frac{U_{N,0} - U_{cell}}{U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)} \cdot I_{tot} \cdot \left(1 + K_1 \cdot I_{tot}^2 + K_2 \cdot I_{tot}^4 + \ldots\right)$$

Correction factors:

$$K_1 = -\frac{\left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right) \cdot \Delta U''\left(\frac{I_{tot}}{2}\right) - 2 \cdot \left(\Delta U'\left(\frac{I_{tot}}{2}\right)\right)^2}{24 \cdot \left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right)^2}$$

$$K_2 = \frac{1}{80} \cdot \left[\frac{\Delta U'\left(\frac{I_{tot}}{2}\right)^4}{\left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right)^4} - \frac{3 \cdot \Delta U'\left(\frac{I_{tot}}{2}\right)^2 \cdot \Delta U''\left(\frac{I_{tot}}{2}\right)}{2 \cdot \left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right)^3} + \frac{\Delta U''\left(\frac{I_{tot}}{2}\right)^2}{4 \cdot \left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right)^2} + \frac{\Delta U'\left(\frac{I_{tot}}{2}\right) \cdot \Delta U'''\left(\frac{I_{tot}}{2}\right)}{3 \cdot \left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right)^2} - \frac{\Delta U''''\left(\frac{I_{tot}}{2}\right)}{24 \cdot \left(U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)\right)} \right]$$

Estimation of ASR corrected to Fuel Utilization

- corr. expression for calculation of R_A:

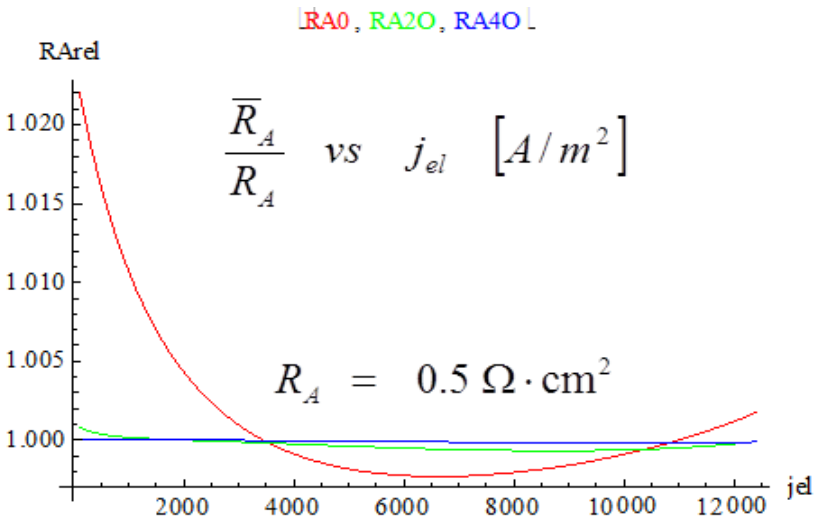
$$R_A = b \cdot L \cdot \frac{U_{N,0} - U_{cell} + \Delta U\left(\frac{I_{tot}}{2}\right)}{I_{tot}} \cdot \frac{1}{1 + K_1 \cdot I_{tot}^2 + K_2 \cdot I_{tot}^4 + \ldots}$$

Simple model
→ 0th order correction

Corr. Factors K_1 and K_2
→ 2nd and 4th for order correction

$$R_A = b \cdot L \cdot \frac{U_{N,0} + \frac{R \cdot T}{2F} \cdot \ln\left(\frac{X_{H_2O,in}}{X_{H_2,in}} \cdot \frac{2F \cdot X_{H_2,in} \cdot \dot{N}_{fuel,in} - \frac{I_{tot}}{2}}{2F \cdot X_{H_2O,in} \cdot \dot{N}_{fuel,in} + \frac{I_{tot}}{2}}\right) + 0.5 \cdot \ln\left(\frac{1}{X_{O_2,in}} \cdot \frac{4F \cdot X_{O_2,in} \cdot \dot{N}_{air,in} - \frac{I_{tot}}{2}}{4F \cdot \dot{N}_{air,in} - \frac{I_{tot}}{2}}\right) - U_{cell}}{I_{tot} \cdot \left(1 + K_1 \cdot I_{tot}^2 + K_2 \cdot I_{tot}^4 + ..\right)}$$

Estimation of ASR corrected to Fuel Utilization



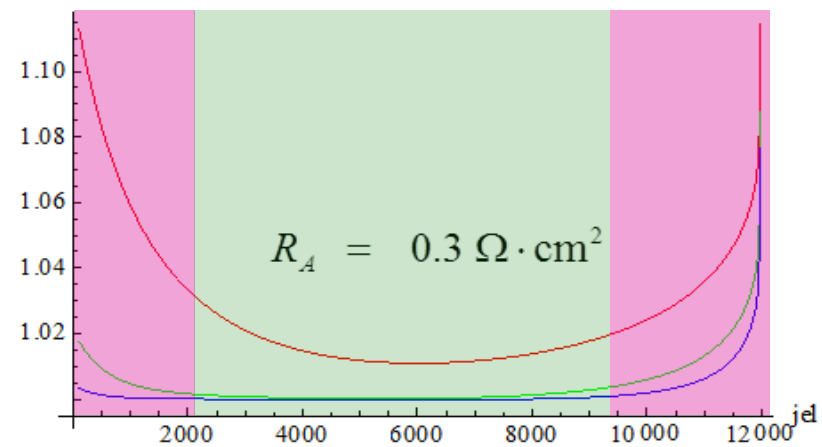
$\Delta R^{0.O}{}_{A,rel} < 2.2\ \%.$

$\Delta R^{2.O}{}_{A,rel} < 0.1\ \%.$

$\Delta R^{4.O}{}_{A,rel} < 0.00?\ \%.$

[A/m²]

L= B=	40x40	mm^2
dN_{air}/dt=	60	Nl/h
T=	850	°C
R_A=	0.1;0.3;0.5	$\Omega\ cm^2$
x_{H2} =	40	%
x_{H2O} =	5	%
x_{N2} =	55	%
dN_{H2}/dt=	11	Nl/h
dN_{fuel}/dt =	27.5	Nl/h



$\Delta R^{0.O}{}_{A,rel} < 11.0\ \%.$

$\Delta R^{2.O}{}_{A,rel} < 2.0\ \%.$

$\Delta R^{4.O}{}_{A,rel} < 0.5\ \%.$

[A/m²]

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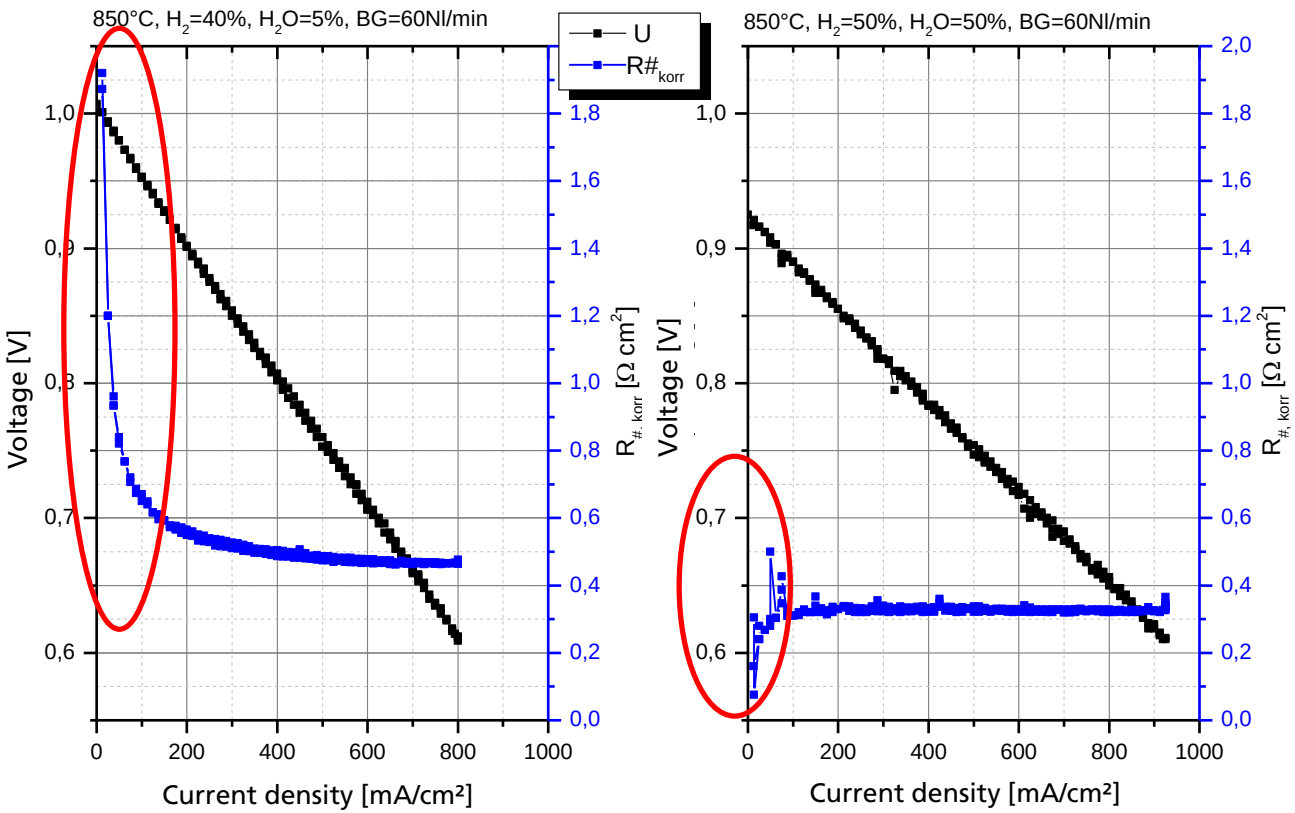
Challenges

L= B=	40x40 mm^2	
dN_{air}/dt=	60	Nl/h
T=	850	°C

0th order



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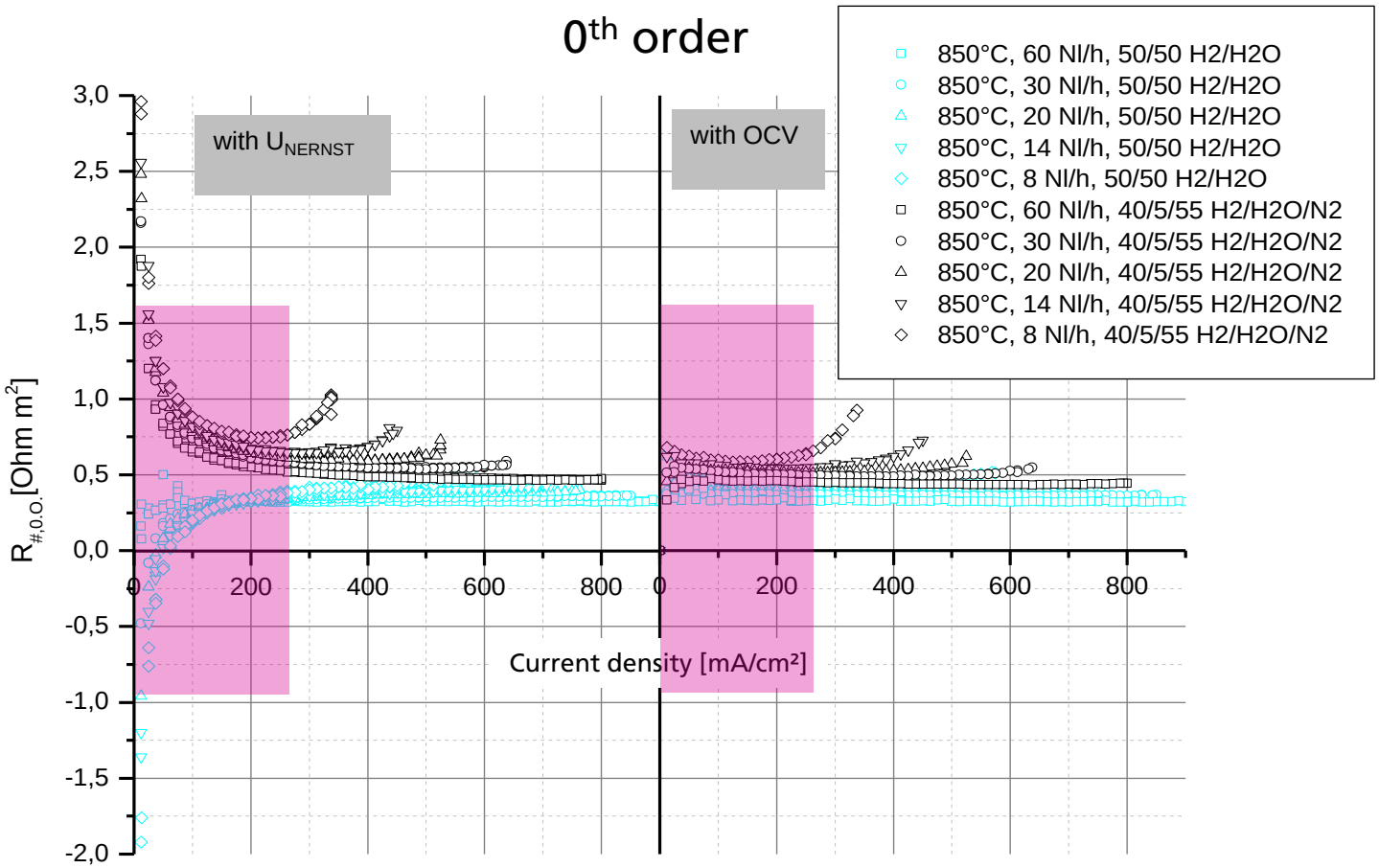
Challenges



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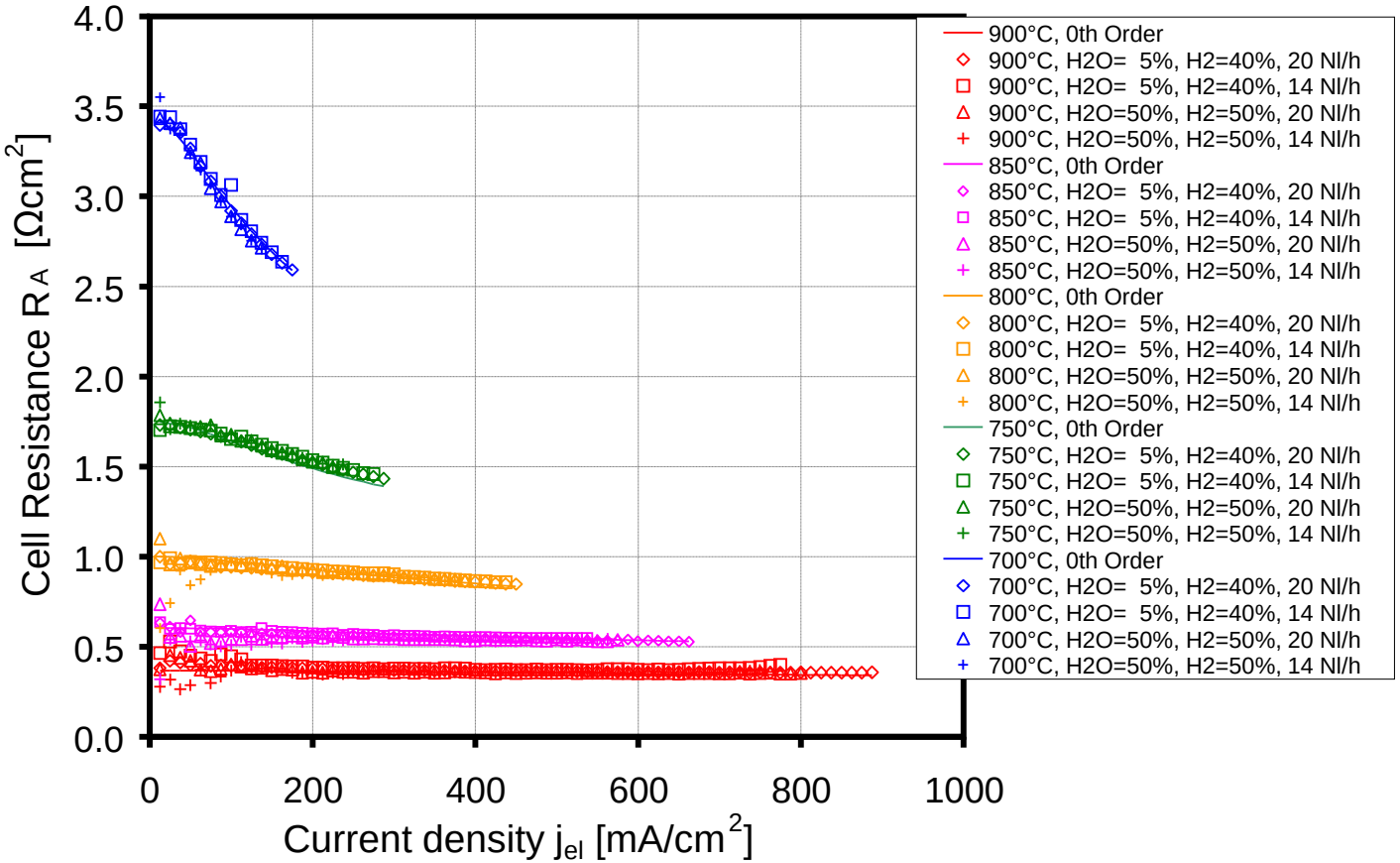
Challenges

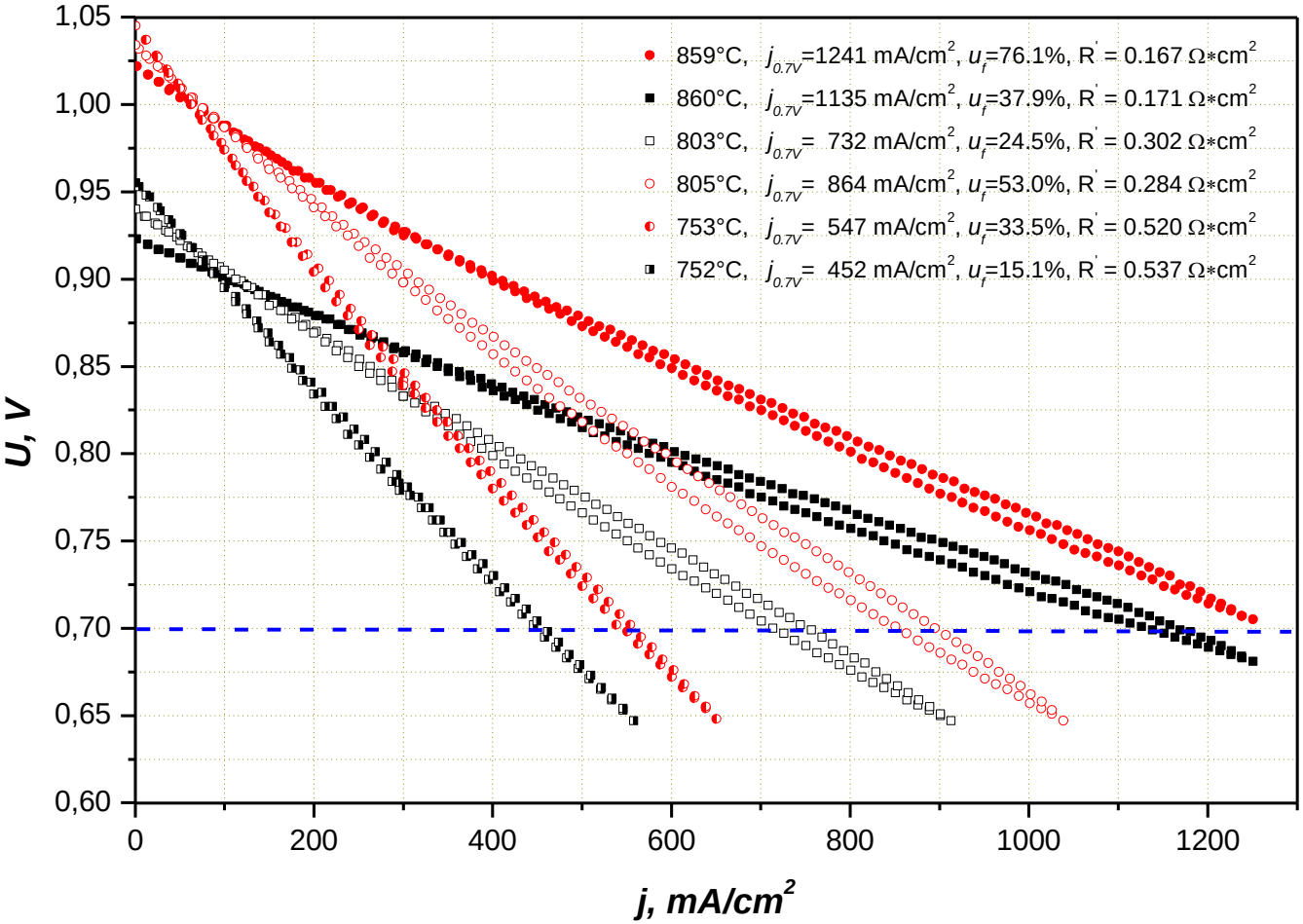
Example of 3YSZ electrolyte supported cells

0th order correction



From I-V-Characteristic to Area Specific Resistance

MEA based on 10Sc1CeSZ substrate (210µm), H_2:N_2:H_2O:=40:55:5 and H_2:H_2O:=50:50) with KS1 as contact layer: correction done by 0th order approximation at 300 mA/cm²



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Influence of measurement method

MEA based on 10Sc1CeSZ substrate (210µm), H_2:H_2O:=50:50)

with KS1 as contact layer: correction done by 0th order approximation at 300 mA/cm²

Initial adjusted Temperature °C	R_A from stationary operation Ωcm²	R_A from EIS Ωcm²	R_A from I-V-curve Ωcm²
850	0.213 (851°C)	0,226 (851°C)	0,171 (860°C)
800	0.356 (801°C)	0,373 (801°C)	0,302 (803°C)
750	0.612 (752°C)	0,594 (752°C)	0,537 (752°C)

- Isothermal measurement at stationary conditions gives most accurate results
- ASR obtained from EIS show deviation from calculated corrected ASR value
- ASR calculation from I-V-curve has following challenges
  - Temperature change during measurement
  - Hysteresis of I-V-curve
  - Result depends on averaging algorithm

Summary

- ASR corrected to fuel utilization is nearly independent on fuel composition and can be considered as universal electrochemical cell characteristic
- Measurement in H_2:H_2O = 50:50 at moderate current density under stationary operation conditions allows the simplest estimation of corrected ASR value
- By measurements in “dry” fuel
  - Current density must be high enough to come into linear region of U-I-characteristic (region of moderate steam content (30-70%)
  - More complex calculation algorithm (4th order correction) should be applied for correction
- Best reproducibility has the calculation of ASR at constant current density under conditions of moderate hydrogen humidification at fuel outlet and use of OCV (not the Nernst voltage) for calculation (isothermal conditions)
- ASR corrected to fuel utilization allows accurate calculation of cell degradation and resolving of degradation mechanisms and can be applied to stacks.

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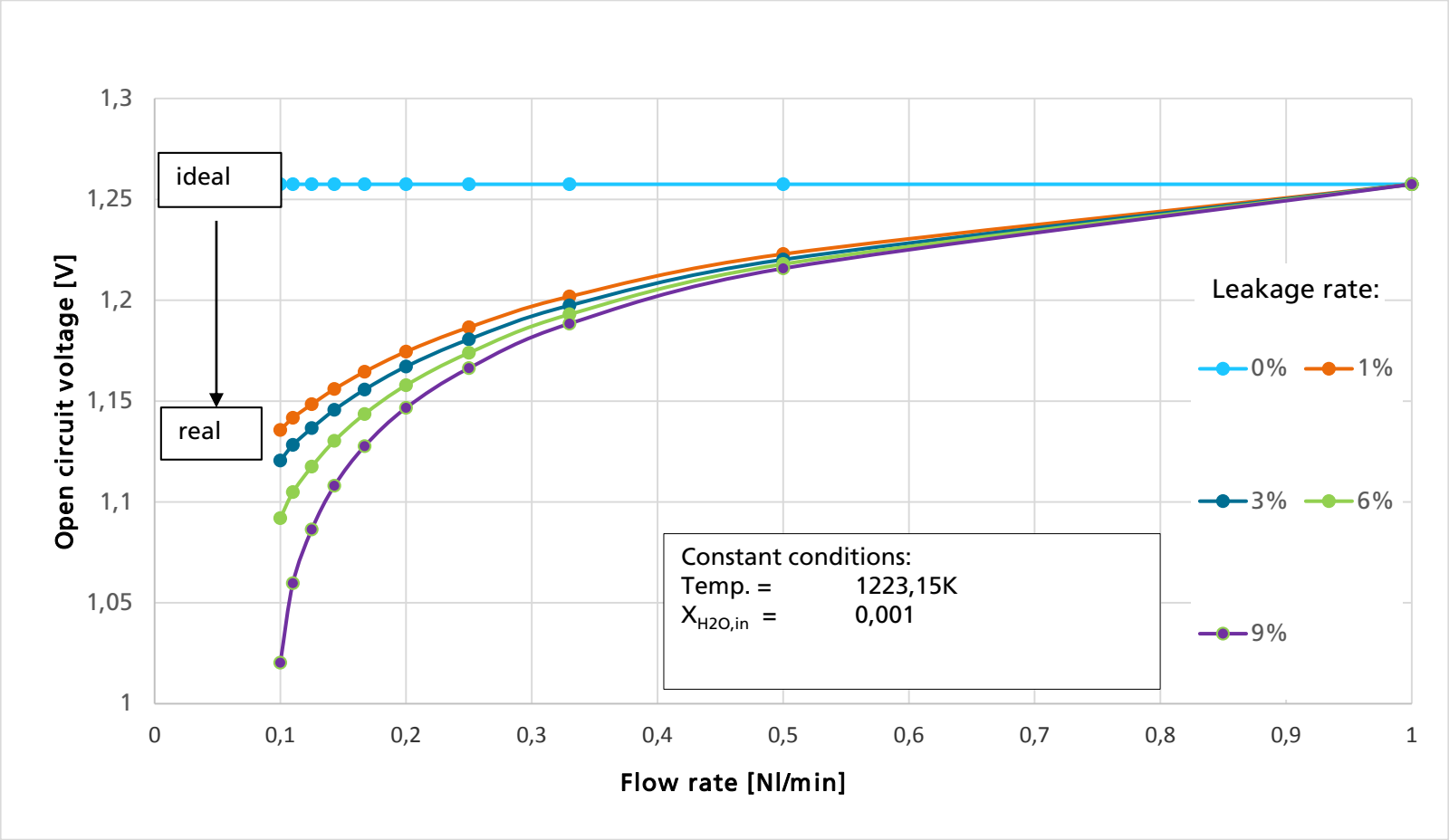
Challenges



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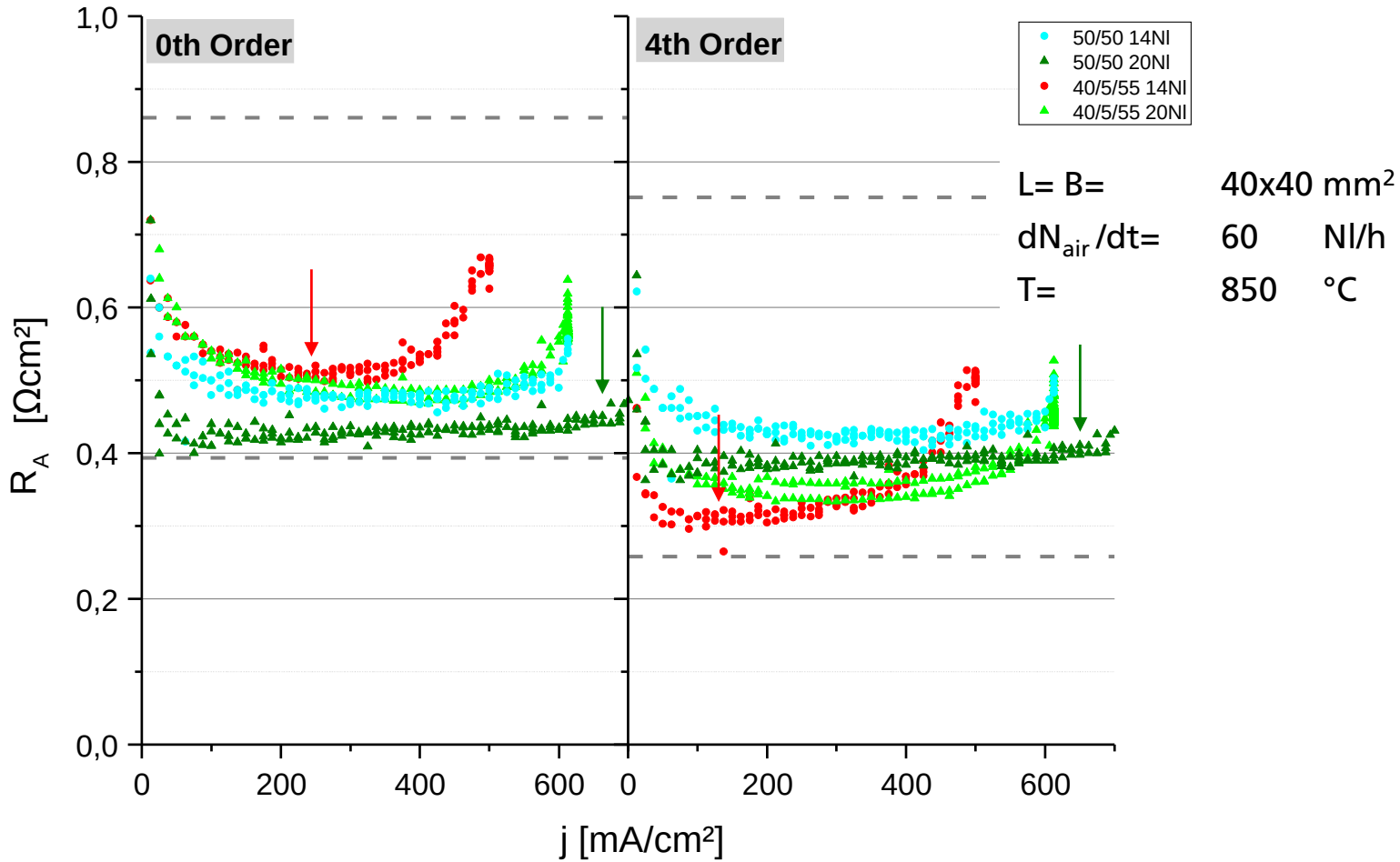
Challenges

Comparison of ASR correction



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