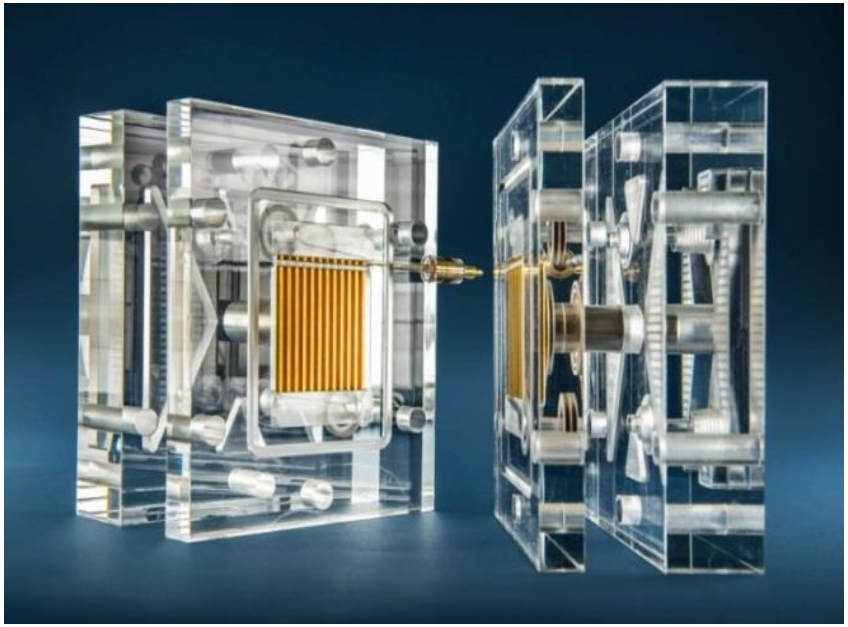
Electrochemical impedance spectroscopy (EIS) and half-cell potential measurements as tools for degradation analysis and AST development within PEM water electrolysis test cells



Thomas Lickert, Claudia Schwarz, Arne Fallisch, Anatolij Friske, Tom Smolinka

Fraunhofer Institute for Solar Energy Systems ISE

WHEC 2018, Session C3-2

Rio De Janeiro, 20.06.2018

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Outline

- Motivation
- Development of AST protocols
- Test equipment at Fraunhofer ISE
- In-situ characterization method development
- Conclusion

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Motivation
Why do we need ASTs?

- PEM electrolysis cells are electrochemically stable, degradation occurs slowly

  → Investigation of the degradation on materials is cost intensive
- Cheaper and more efficient stacks are required in the future
- New materials are needed, where degradation behaviour is unknown

  → Fast screening of these materials and profiles necessary

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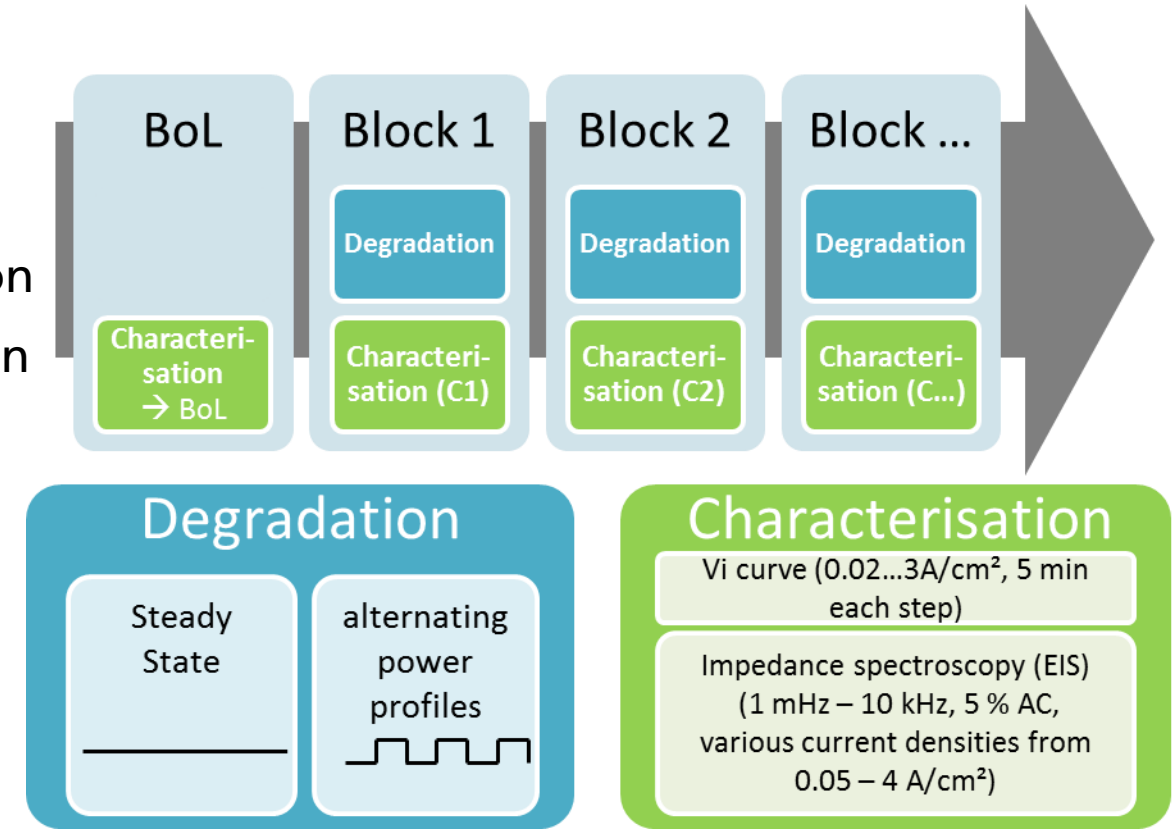
Development of AST protocols
Our Approach for characterization

- Operating conditions:
  - Current density
  - Temperature
  - H_2O contamination
  - Dynamic operation
  - Pressure



Development of AST protocols
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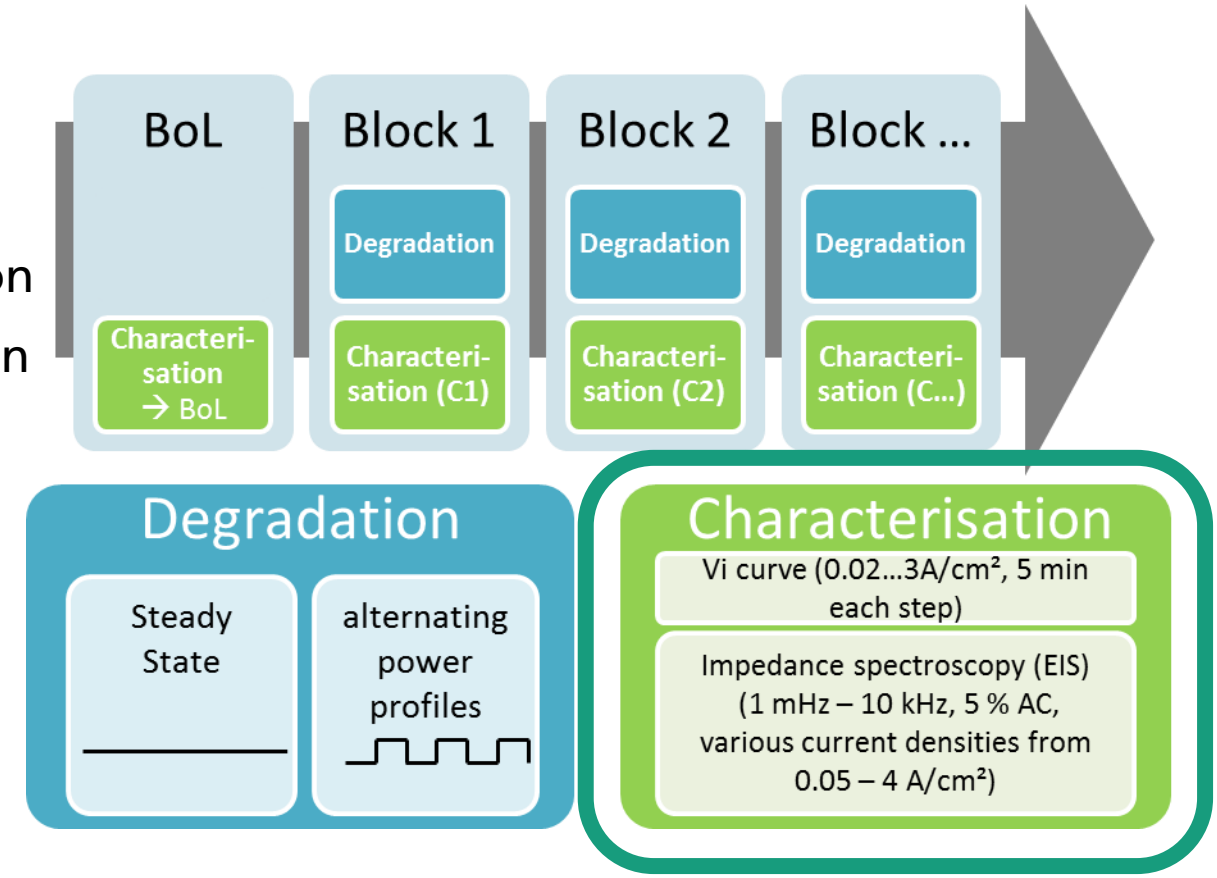

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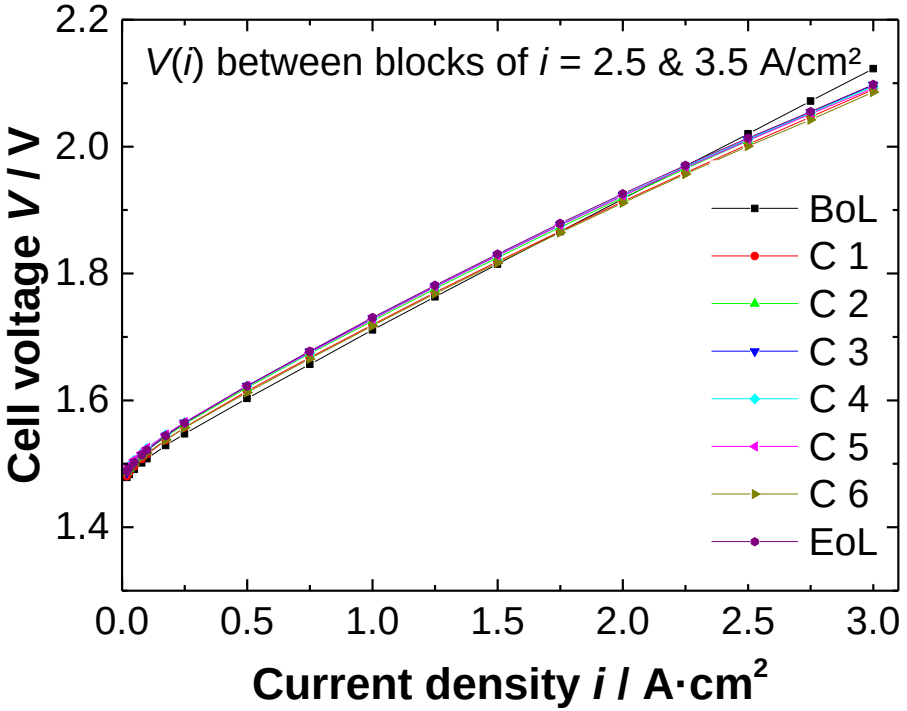
Development of AST protocols

Why do we need in-situ charactization methods?

- *Vi*(*t*) changes are rather small (within ≈ 340 h)
- Information content in *Vi* is limited



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Development of AST protocols

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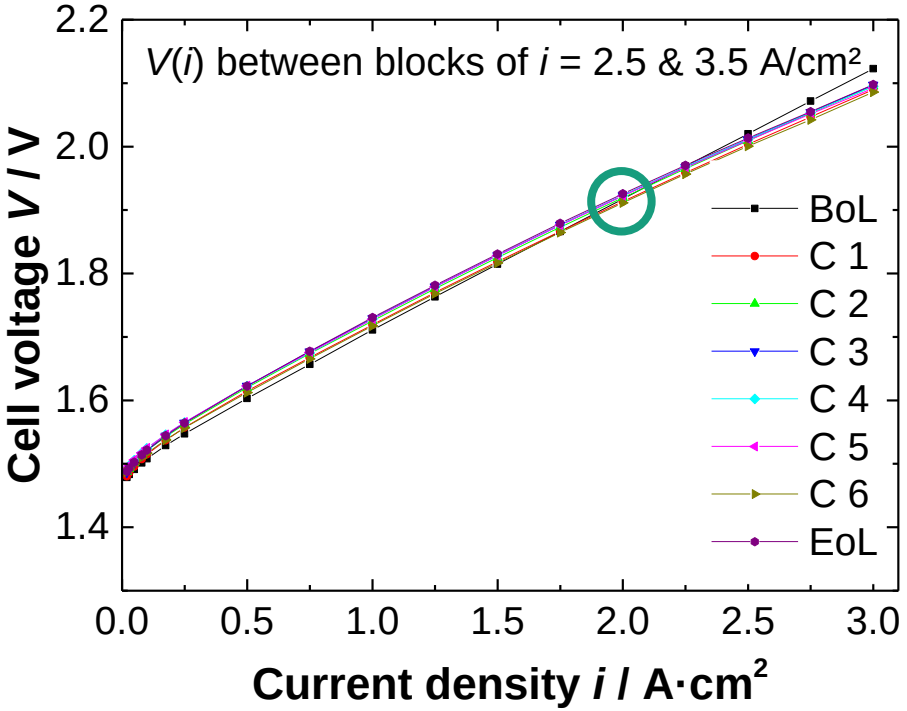

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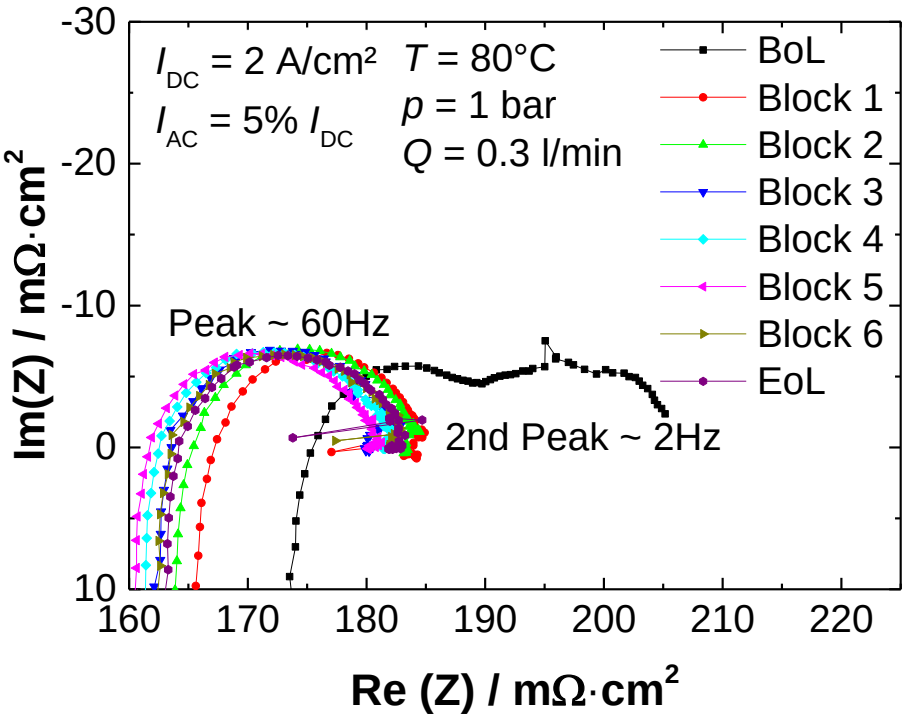
Development of AST protocols

Why do we need in-situ charactization methods?

- *Vi*(*t*) changes are rather small (within ≈ 340 h)
- Information content in *Vi* is limited
- Information content in EIS more comprehensive

→ Further characterization method development is very important



Fraunhofer ISE

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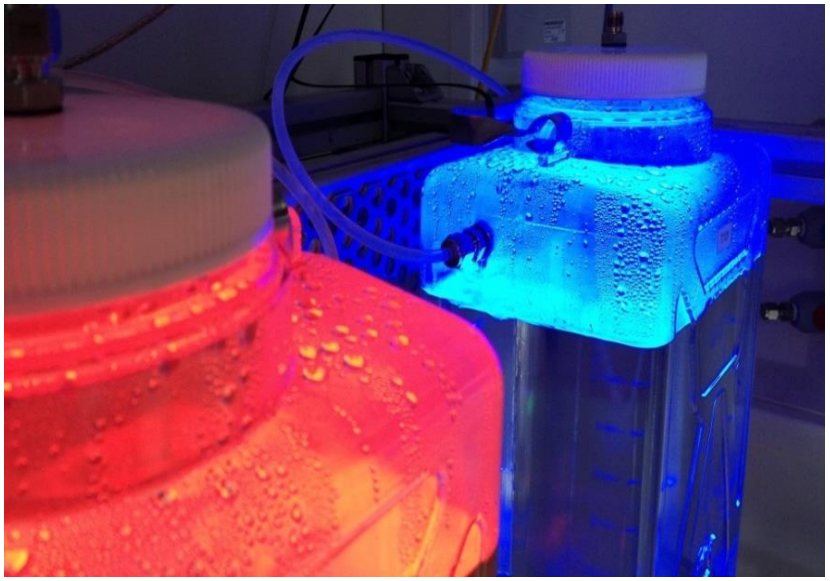
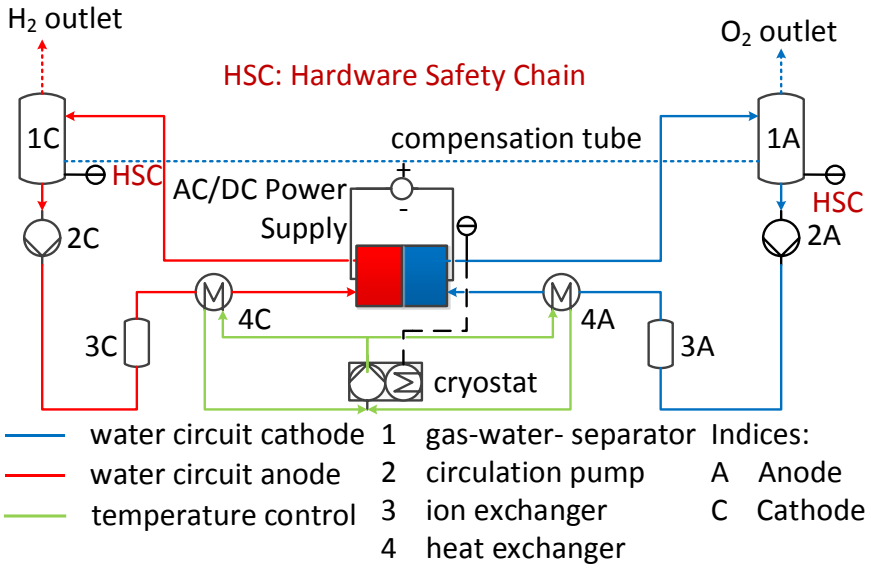
Test equipment at Fraunhofer ISE

Non-automated, unpressurized test bench



- Impedance spectroscopy
  - up to i_{DC} = 4 A/cm² (25 cm²)
  - f = 0.1 Hz – 10 kHz

- Operation temperature up to 80°C
- Ivium 4 channel potentiostat + 100 A Ivium booster



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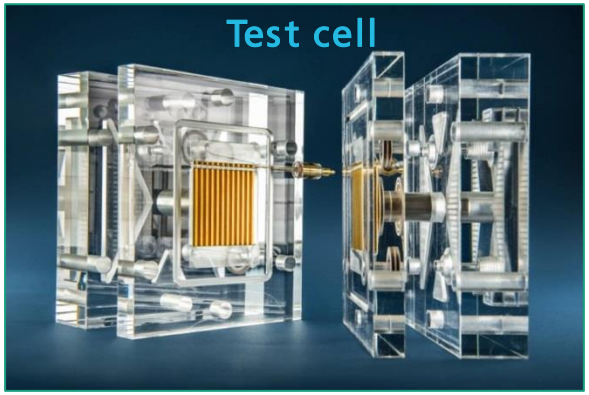
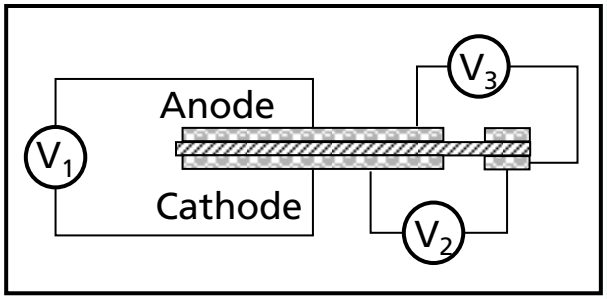
Test equipment at Fraunhofer ISE

Cell setup with in-situ overpotential measurement

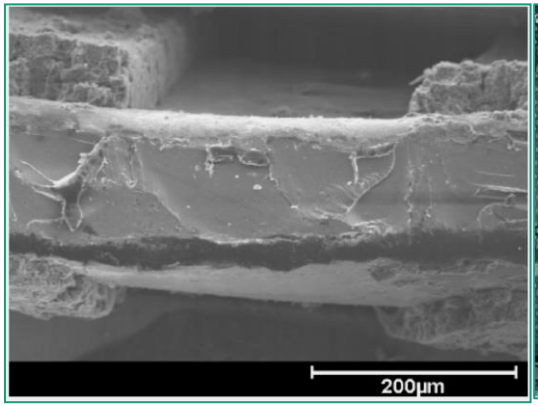
- Investigation of anodic and cathodic over-potentials
- Reference electrode made by laser ablation
- Pressurized measurements up to 50 bar
- Cell area of 25 cm² (including reference electrode)

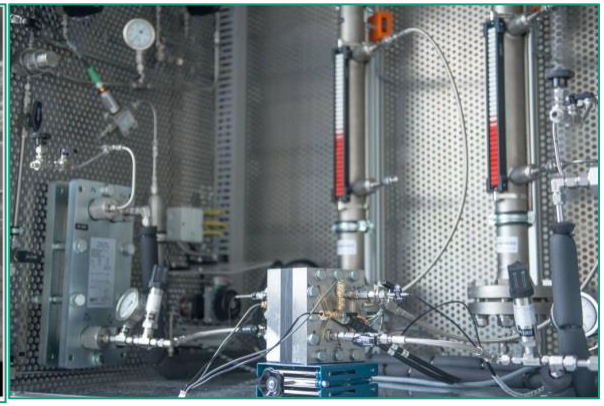


Test bench



Cross-section of a laser ablated CCM





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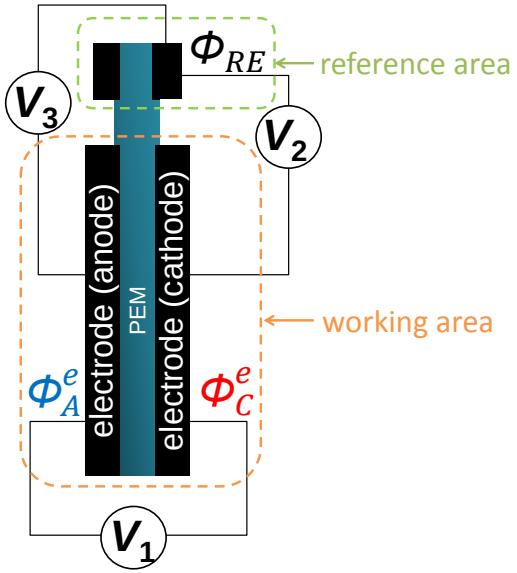
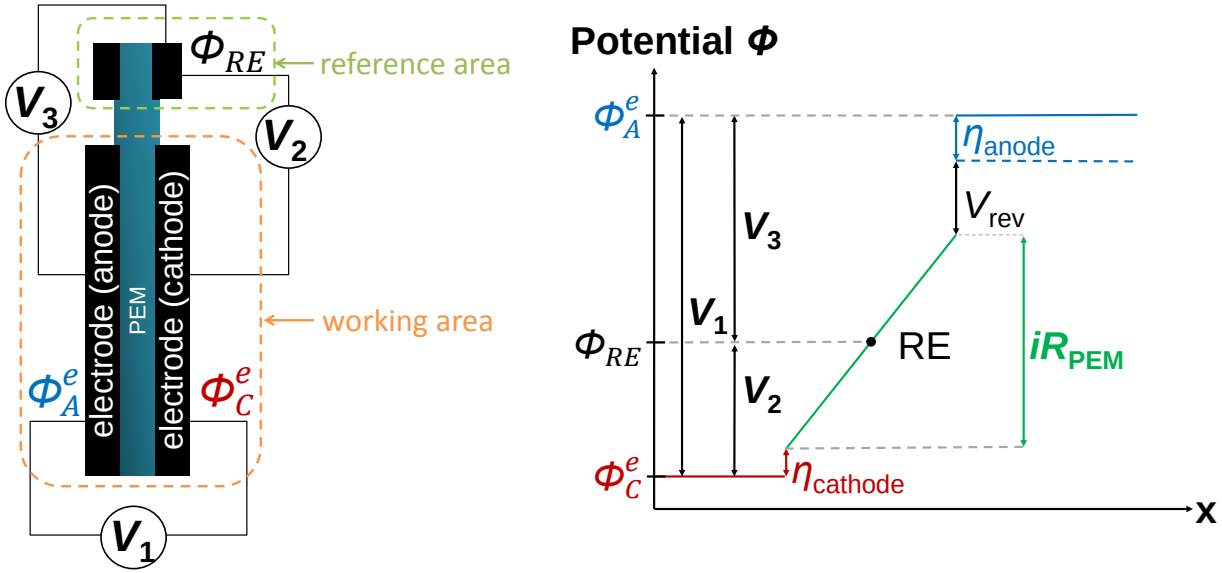
In-situ characterization method development
Reference Electrode (RE)



In-situ characterization method development
Reference Electrode (RE)

- Assumption that potential in the middle of the membrane is measured



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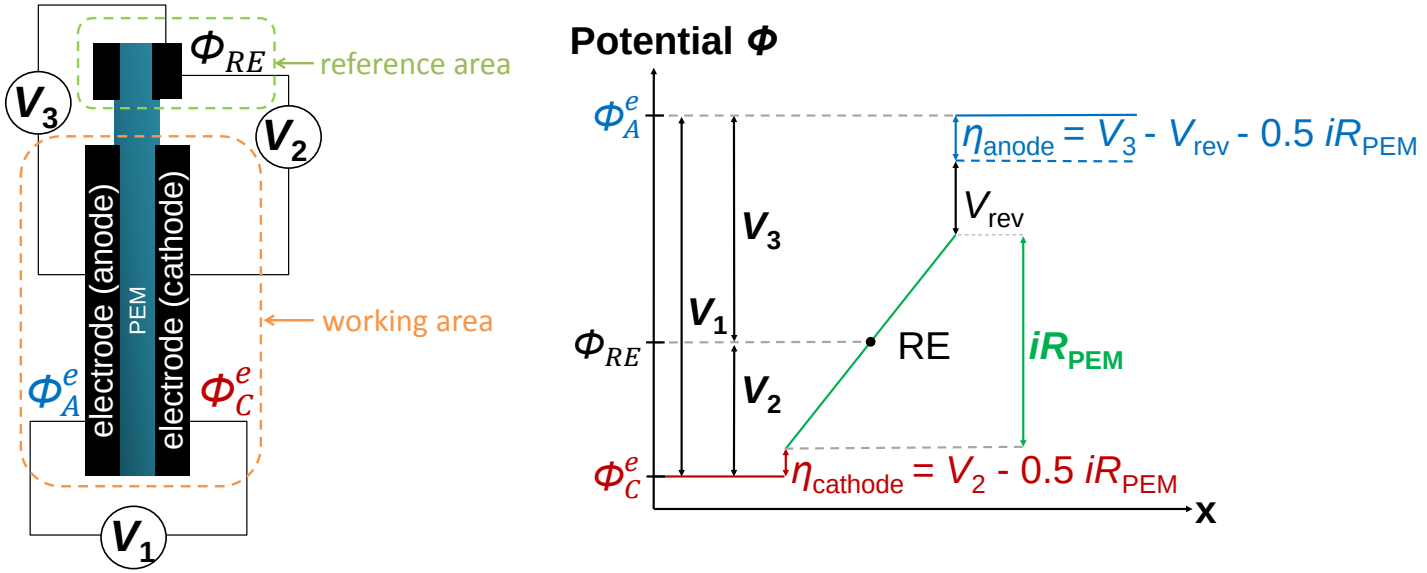

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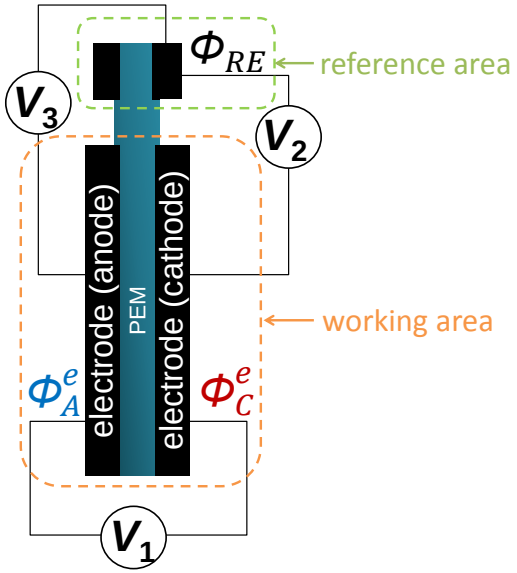
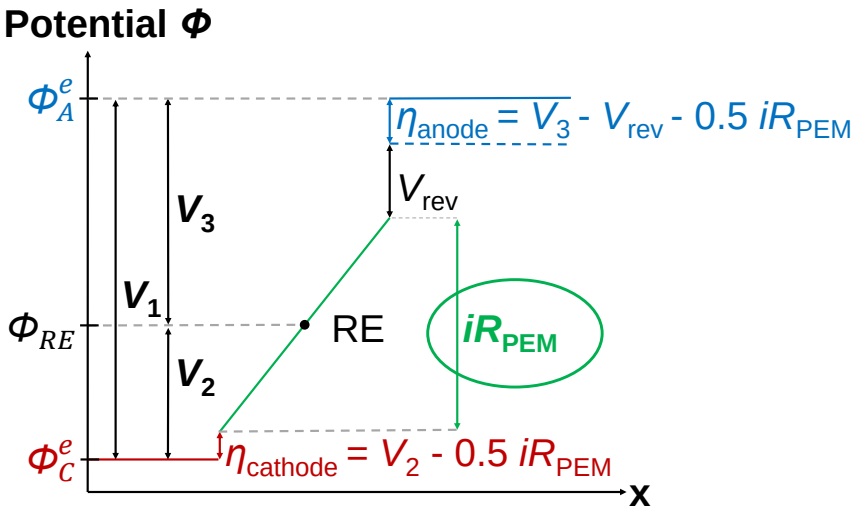
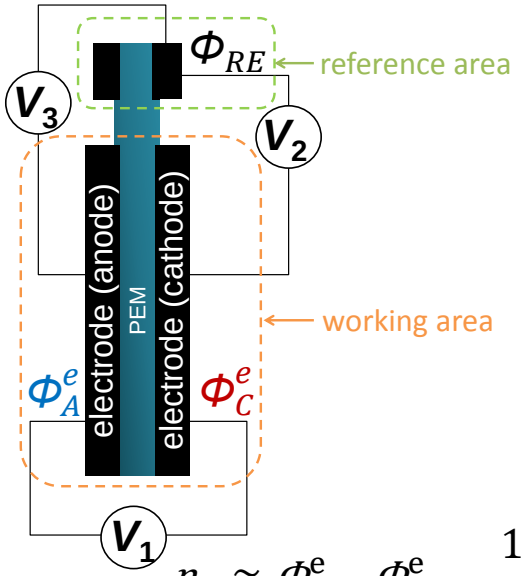
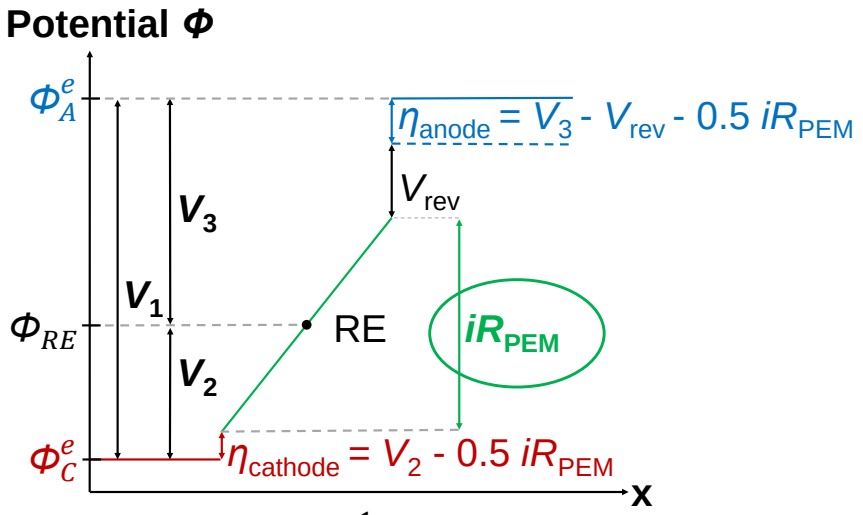




In-situ characterization method development
Reference Electrode (RE)

- Assumption that potential in the middle of the membrane is measured
- High frequency resistance (HFR) is measured by impedance spectroscopy





$$\eta_A \approx \Phi_A^e - \Phi_{RC}^e - \frac{1}{2} i_{cell} Z_1^* - V_{rev} = V_3 - \frac{1}{2} i_{cell} Z_1^* - V_{rev}$$

$$\eta_C \approx \Phi_C^e - \Phi_{RC}^e - \frac{1}{2} i_{cell} Z_1^* = V_2 - \frac{1}{2} i_{cell} Z_1^*$$

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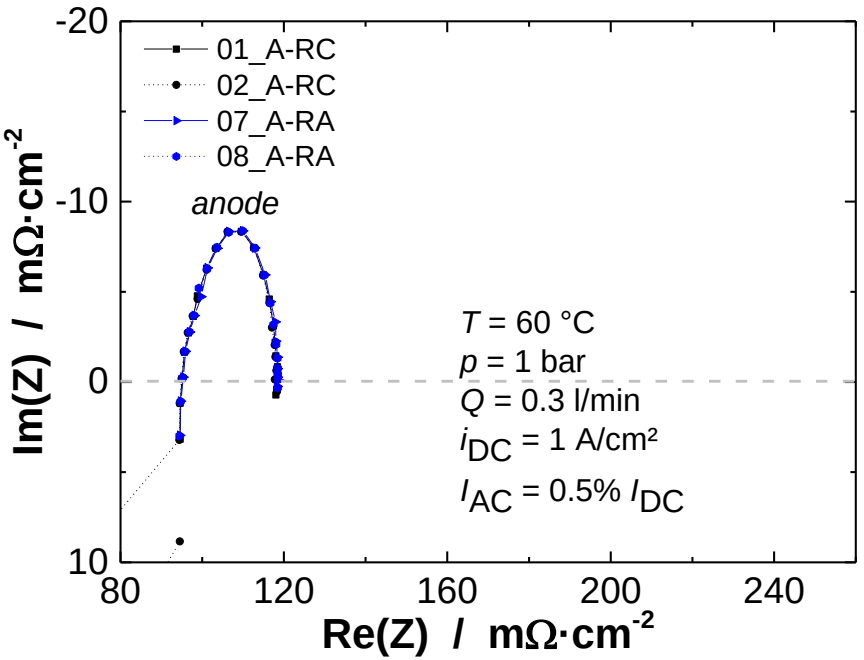
In-situ characterization method development
Reference Electrode (RE) – half cell spectra

- Half-cell spectra as tool to determine location of RE-potential



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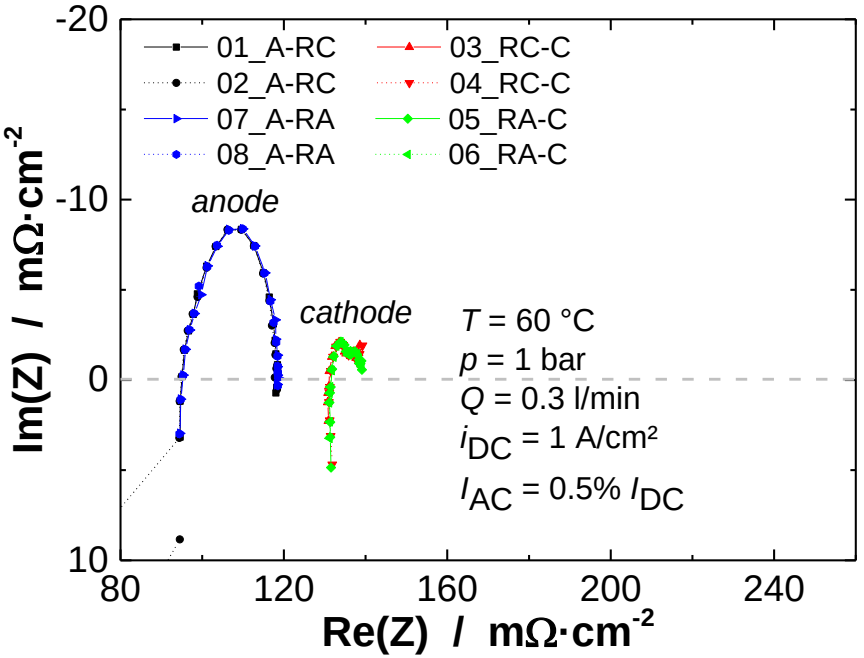
In-situ characterization method development
Reference Electrode (RE) – half cell spectra

- Half-cell spectra as tool to determine location of RE-potential
- Cathode limitation is not neglectable



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In-situ characterization method development
Reference Electrode (RE) – half cell spectra

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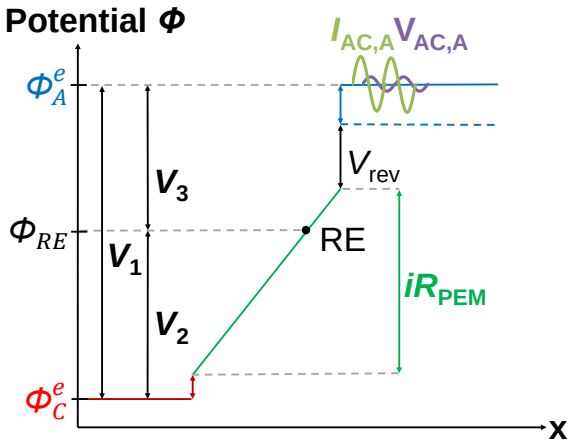
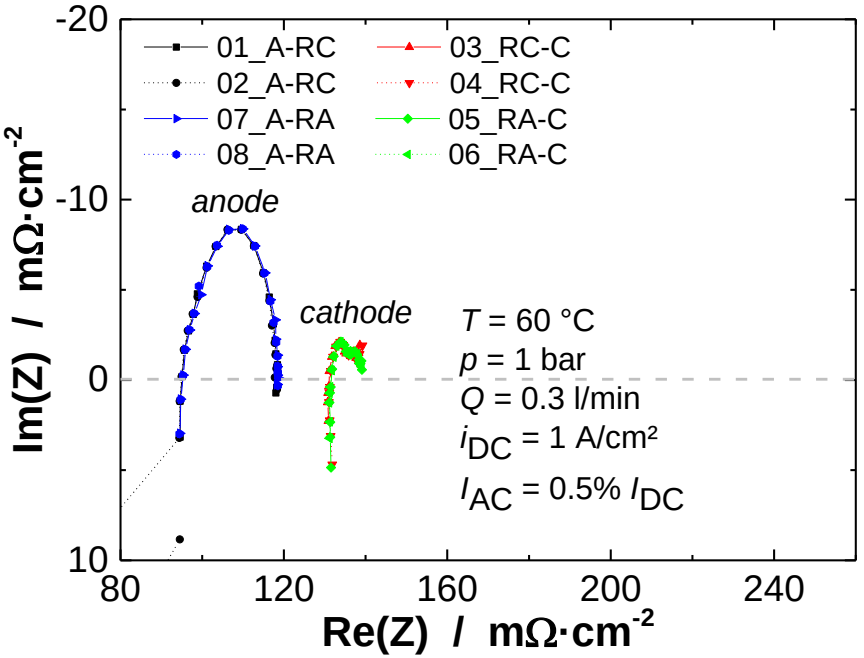
- RE potential is shifted away from the middle towards the anode





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In-situ characterization method development
Reference Electrode (RE) – half cell spectra

- Half-cell spectra as tool to determine location of RE-potential
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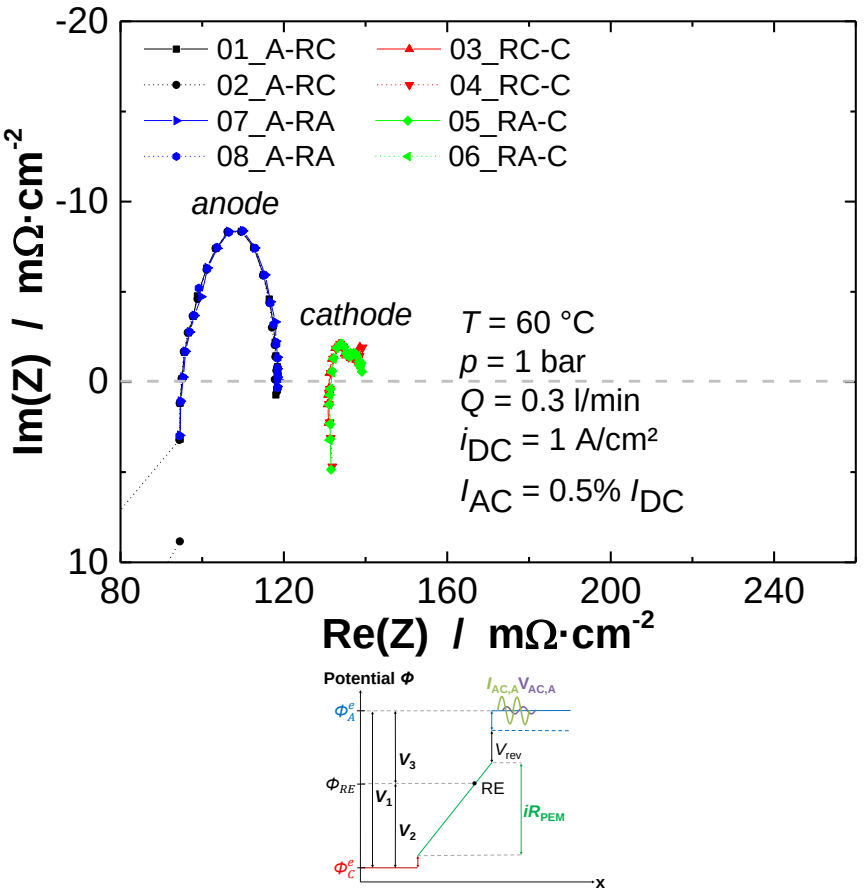
- Factor in calculation of overpotential which is not 1/2

f (?)

$$\eta_A = V_3 - \frac{1}{2} i_{cell} Z_1^* - V_{rev}$$



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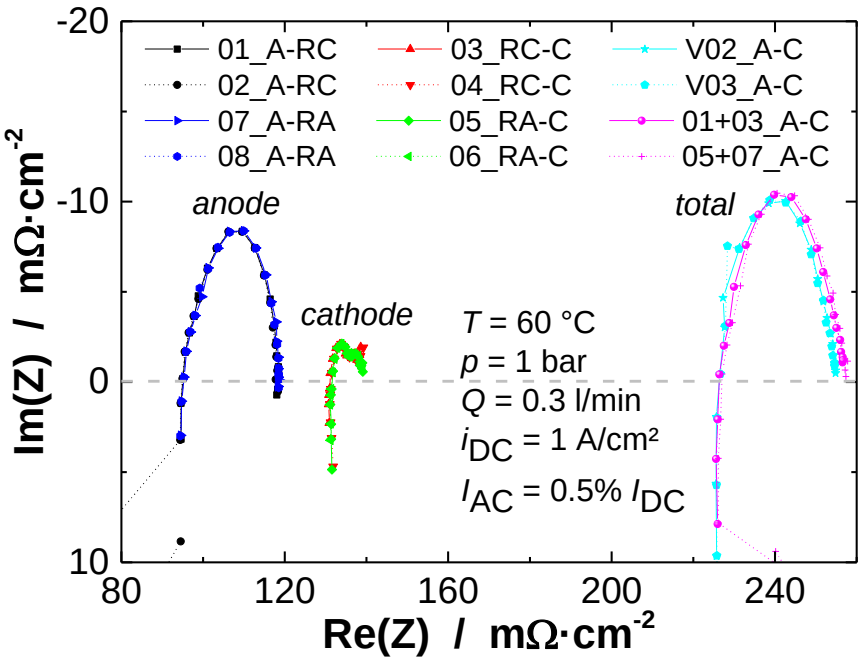

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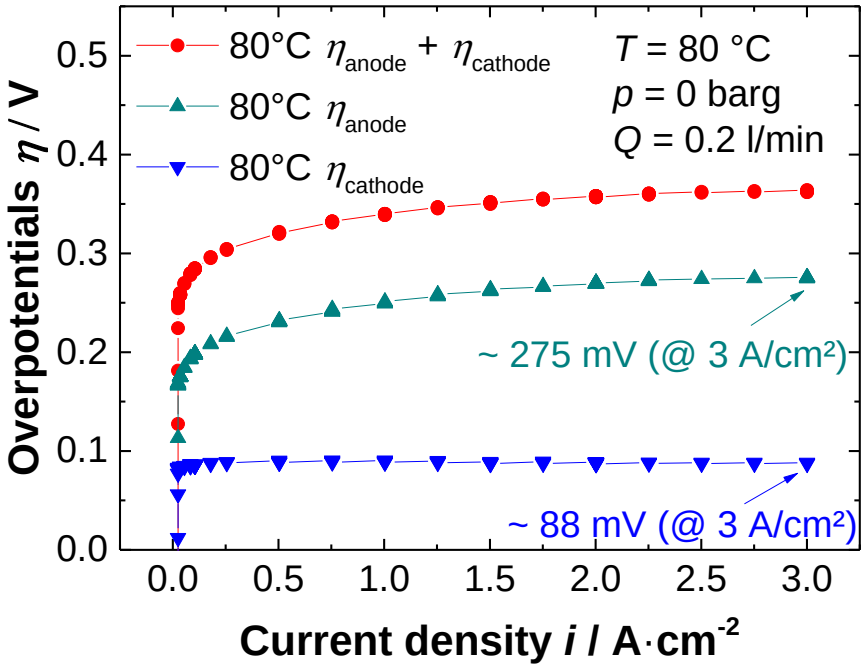
In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Half-cell spectra as tool to determine location of RE-potential
- Separate examination of anodic and cathodic overvoltages
  - Separate degradation analysis
- E.g.: overpotentials @ 3 A/cm²
  - Anode ≈ 275 mV
  - Cathode ≈ 88 mV

  → Separate anode and cathode in AST developement



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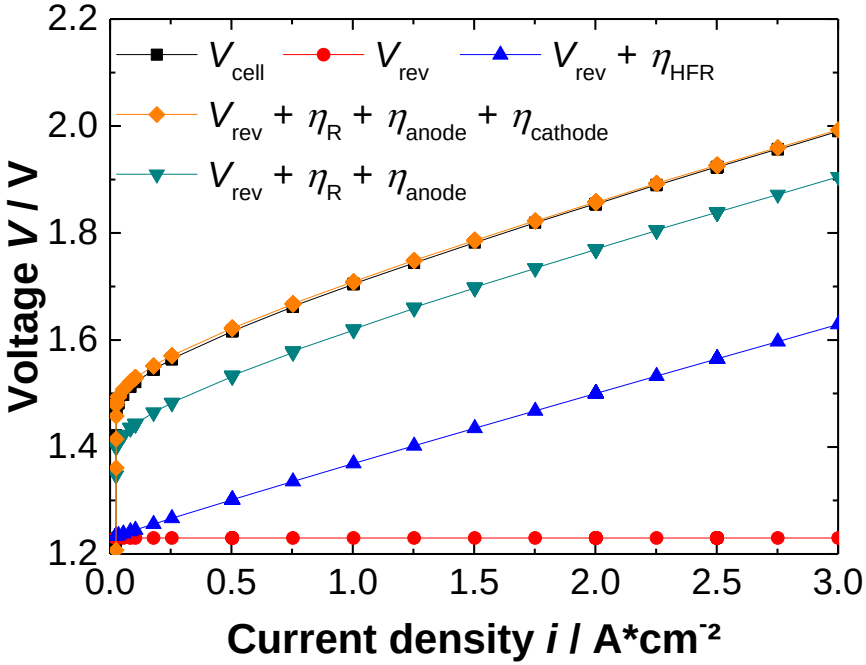

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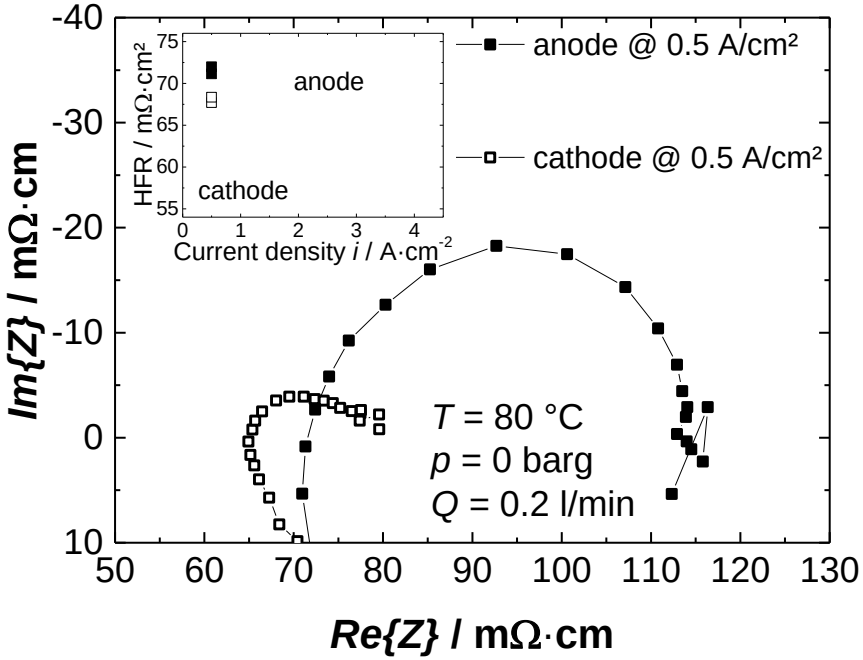
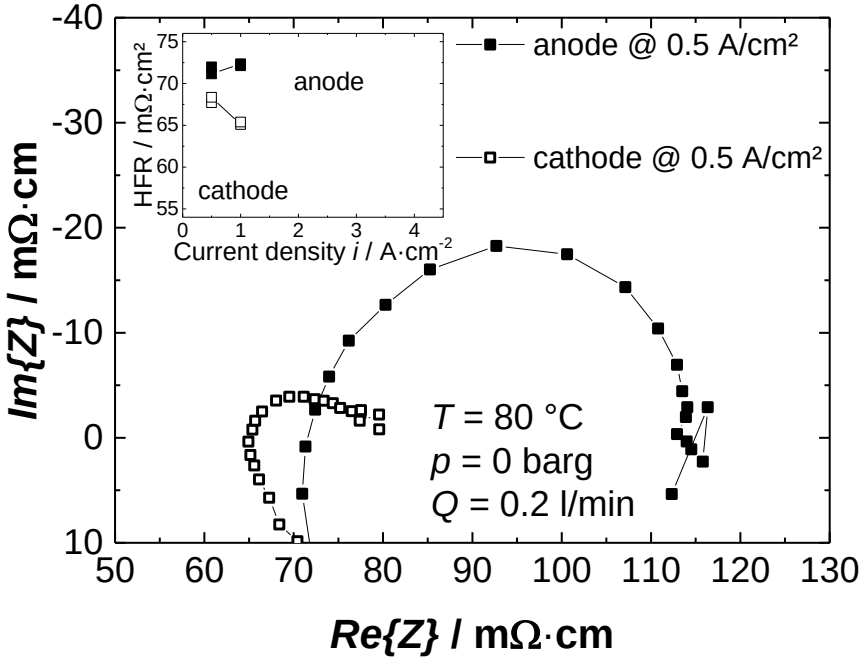
In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Half impedance spectra to extract HFR of anode and cathode



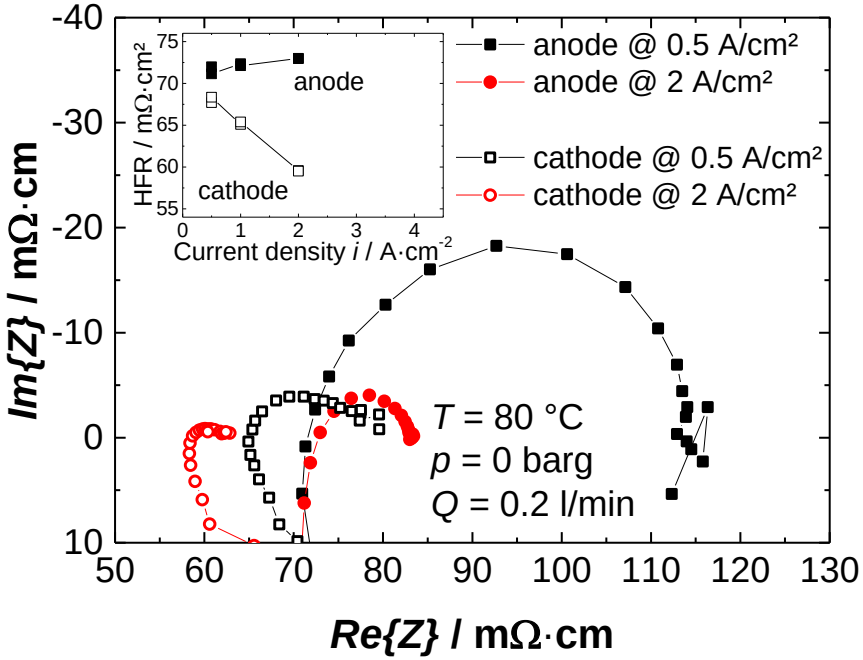
In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Half impedance spectra to extract HFR of anode and cathode
- HFR is current dependant



In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Half impedance spectra to extract HFR of anode and cathode
- HFR is current dependant
- Cathode HFR decreases



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In-situ characterization method development
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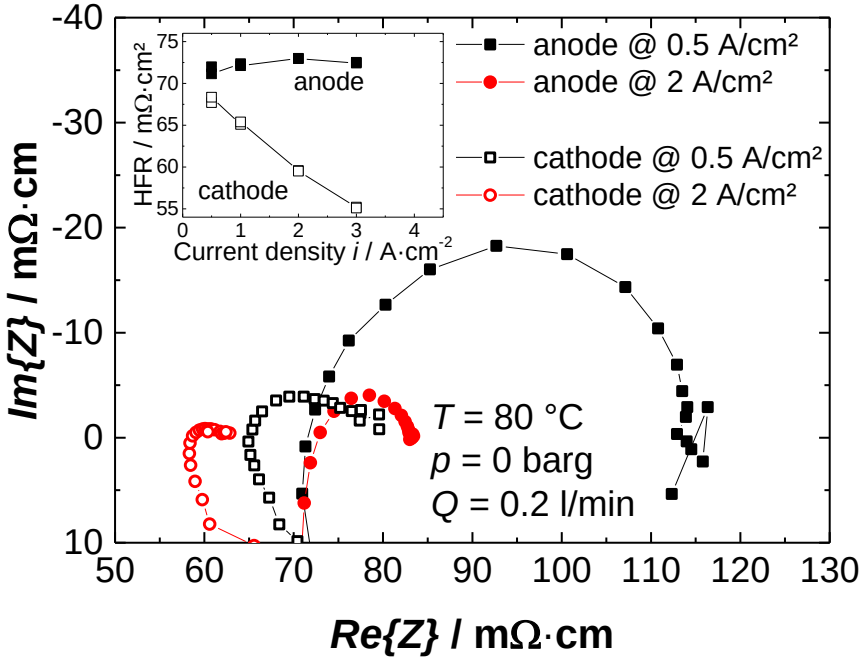
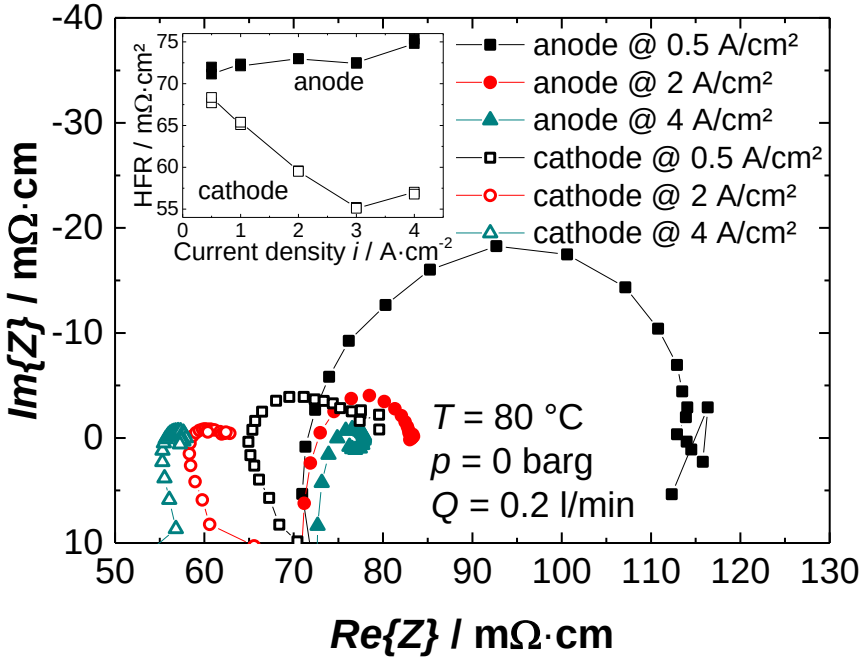


In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Half impedance spectra to extract HFR of anode and cathode
- HFR is current dependant
- Cathode HFR decreases
- Anode HFR slightly increases
- Factor to calculate overvoltages is dependent on current

$$f_{RE}(i) \downarrow \quad \eta_A = V_3 - \frac{1}{2} i_{cell} Z_1^* - V_{rev}$$



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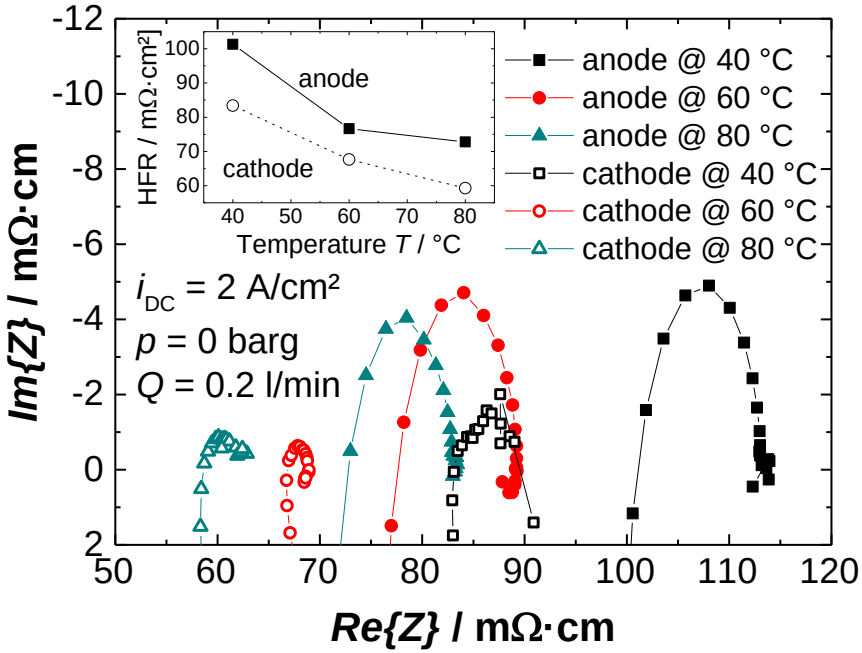
In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Half impedance spectra to extract HFR of anode and cathode
- HFR is temperature dependant
- Cathode and anode HFR decreases
- Factor to calculate overvoltages is also dependent on temperature

$$\mathrm{f_{RE}}(i,T) \downarrow \quad \eta_{\mathrm{A}} = V_3 - \frac{1}{2} i_{\mathrm{cell}}\, Z_1^* - V_{\mathrm{rev}}$$



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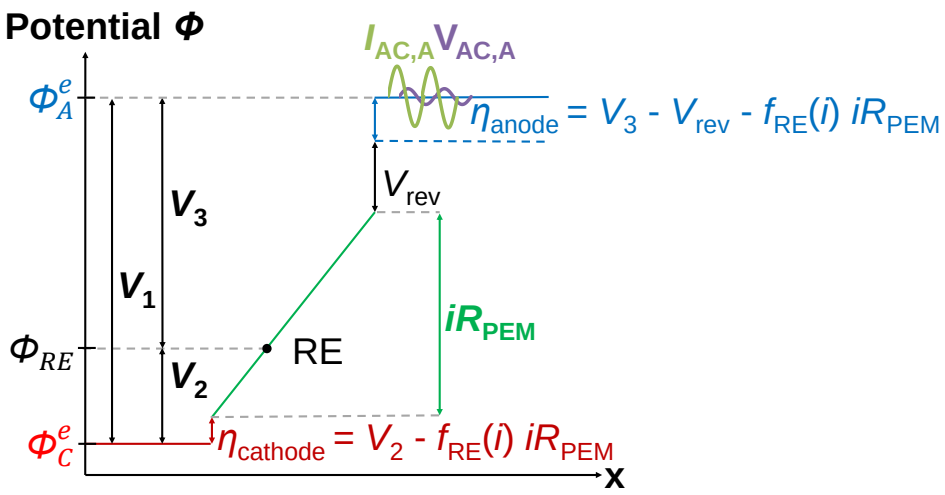
In-situ characterization method development
Reference Electrode (RE) – PEM behavior → AST

- Reduction of *HFR* with increasing *I* and *T* coming mainly from cathodic side
  - Heat production on anodic side might influence PEM behavior
- Possible gradient in *T* inside the PEM individual *HFR* shifts?
- Possible gradient in water content (*λ*) inside the PEM?

  → AST development for PEM possible



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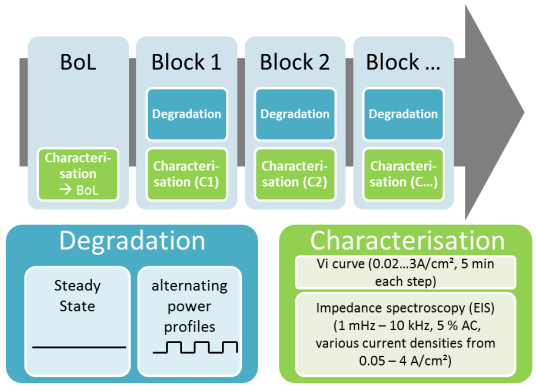
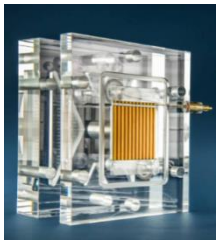
Conclusion
Summary

- Comprehensive understanding of in-situ characterization methods is necessary for AST development
  - RE-method for local separation of degradation effects
  - EIS for separation of transient behavior of degradation effects
  - Half-cell EIS for more insight and verification of both methods
- Evaluation of different operating profiles and their influence on degradation can be investigated more substantially
- Let's test different profiles



Acknowledgements



- All members of the departments “Chemical Energy Storage” at Fraunhofer ISE

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  - Project “POWER-MEE” - contract n° 03SF0536D

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Thank you for your attention!

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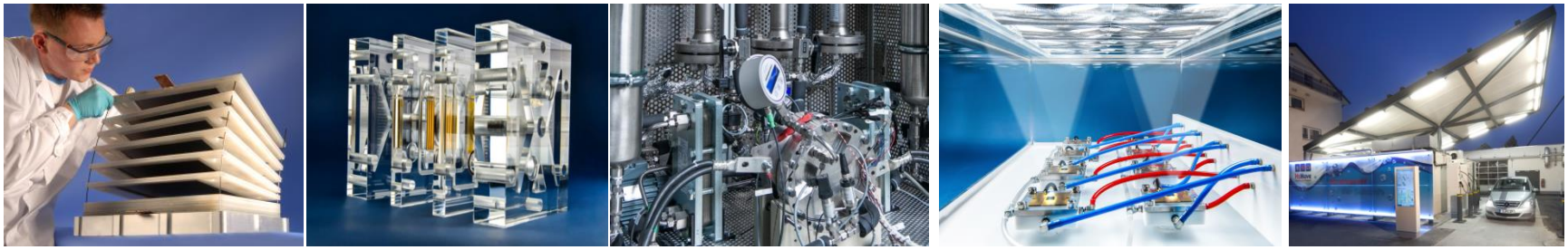

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