Degradation behavior of MK35x stacks with chromium-based interconnects in steam electrolysis operation

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Fraunhofer IKTS

DLR

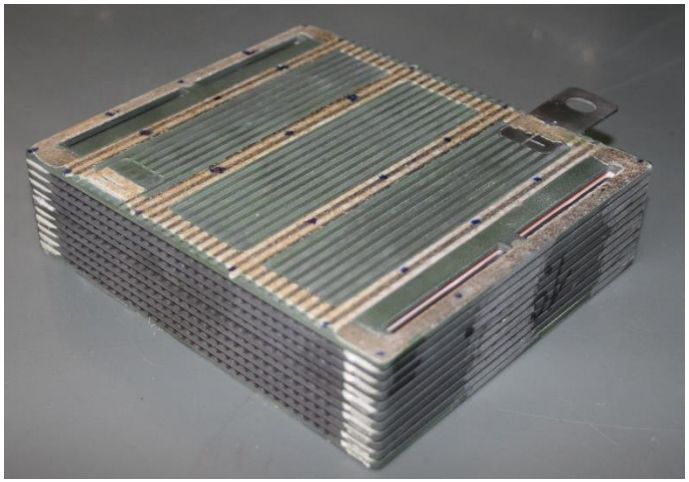
Motivation and aim of the work

- Reliable long-term operation is key for wide-scale adoption of solid oxide electrolysis (SOEL)
- Clean Hydrogen Joint Undertaking targets degradation rates <0.5 %/1000 h by 2030
- Long-term data beyond 1000 h of SOEL stacks are rare in literature
- Detailed understanding of the degradation behavior of individual repeat units (RUs) is often lacking

Research goals:

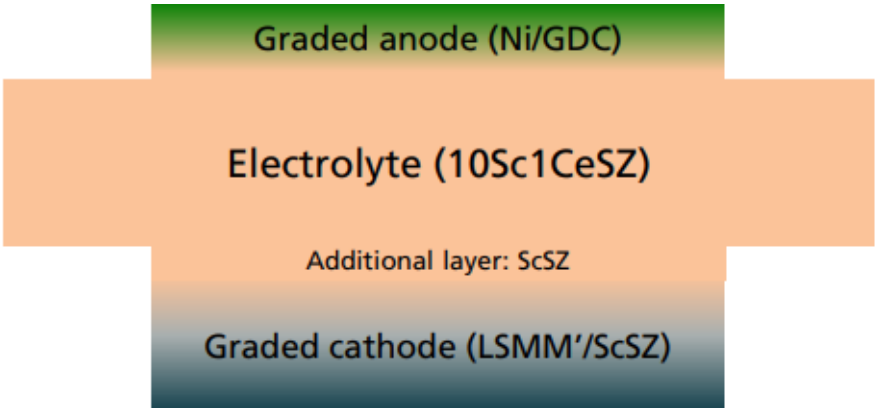
- Investigation of durability behavior of stacks developed by Fraunhofer IKTS for operation times >3000 h in SOEL
- In-depth examination of degradation of individual RUs

Methodology: MK35x stack platform



- 10-cell stacks of MK35x design developed by IKTS with active area of 127 cm^2
- Based on electrolyte-supported cells (ESC) with chromium-based interconnects

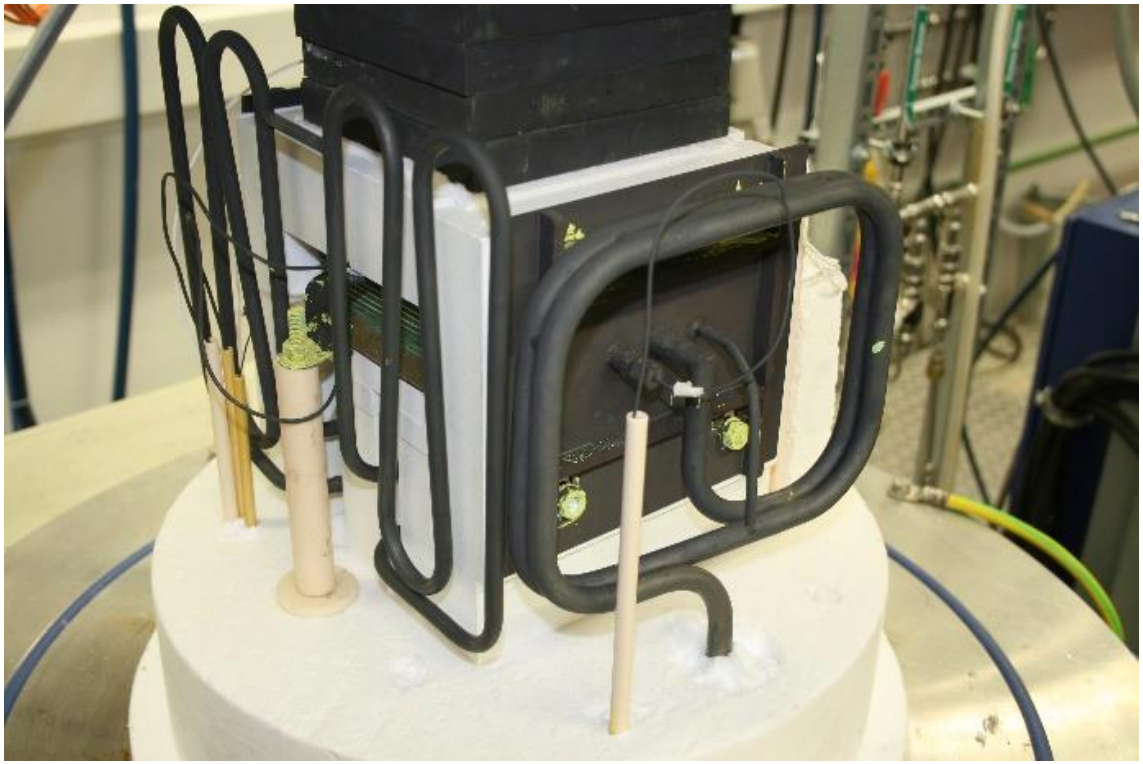
- Cell composition IKTSG5b:
  - LSMM' oxygen electrode
  - 165 µm thick 10Sc1CeSZ electrolyte
  - Ni/GDC fuel electrode



G5 cell

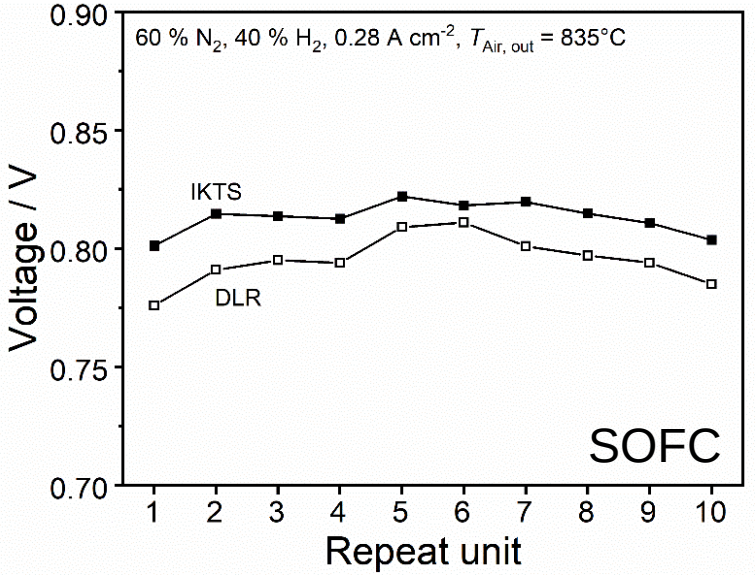
Methodology: Electrochemical characterization

- Long-term stack testing at DLR
- Operating conditions: 80 % H_2O, 20 % H_2, -0.6 A cm^{-2}, 75% steam conversion, oxygen side outlet temperature of 816°C
- Oven environment with constant temperature
- Before and after durability test: Electrochemical impedance spectroscopy at all individual RUs



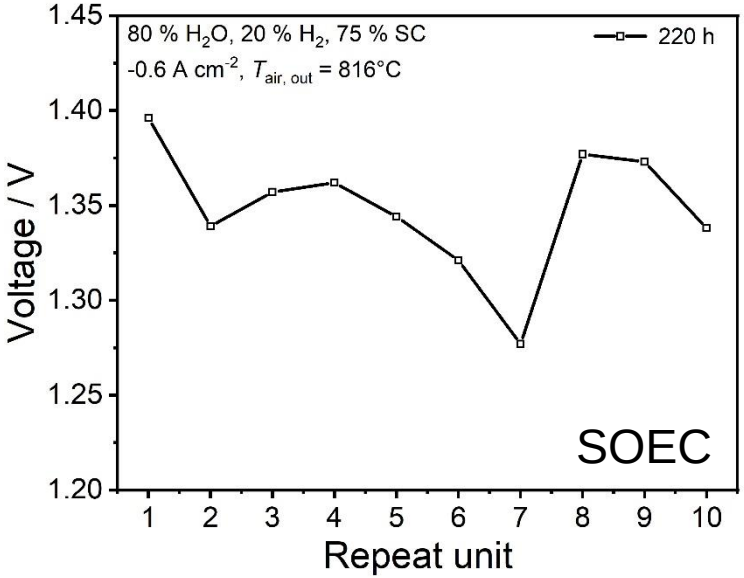
Results: Initial stack performance

60% N_2, 40% H_2, 0.275 A cm^{-2}, 75% FU, oxygen side outlet temperature of 835°C



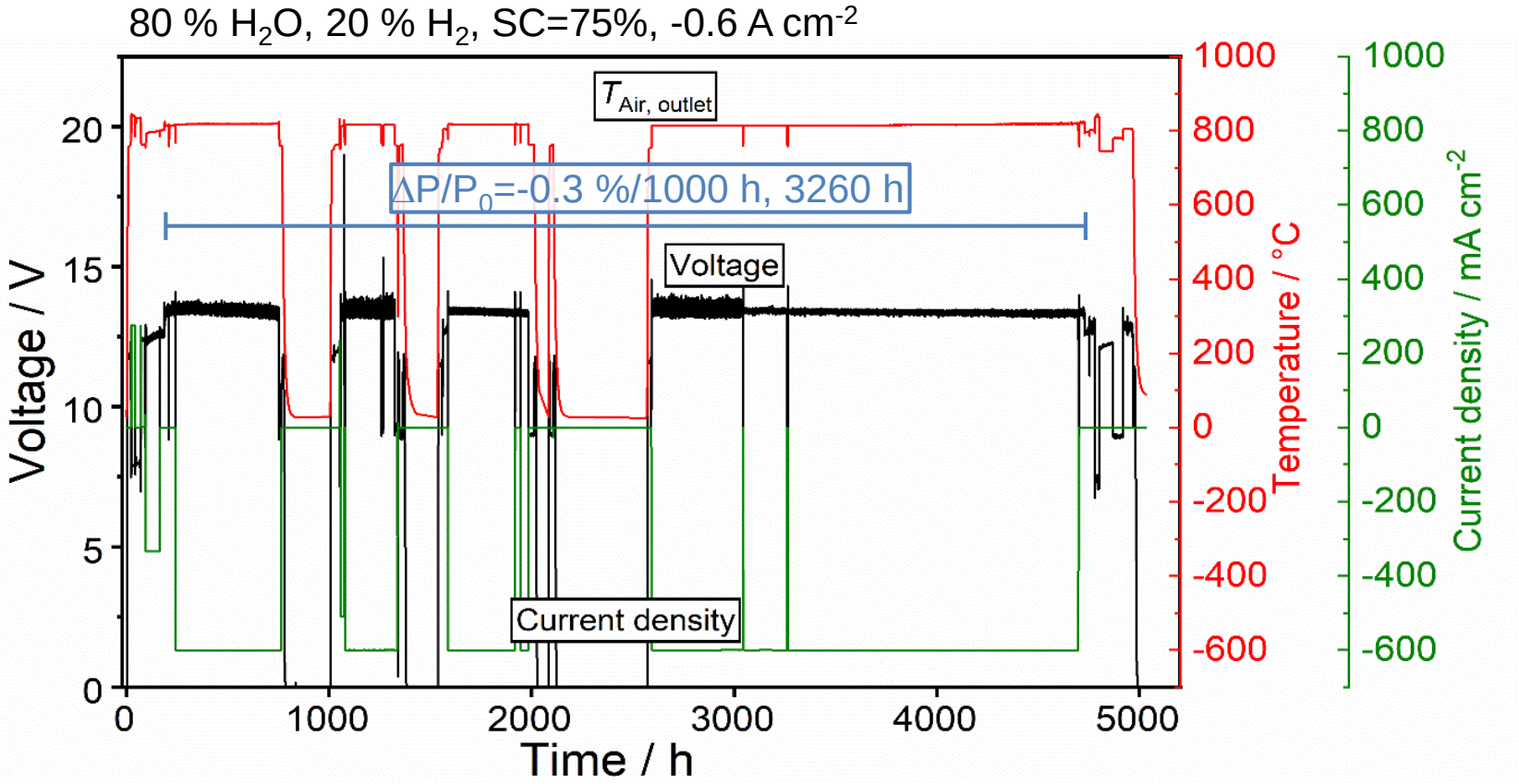
- Similar behavior at IKTS during joining and at DLR during initial characterization
- 15-30 mV difference, probably due to lower air preheater temperature at DLR
- Initial state: P = 0.28 kW, η_{el} = 53.4%

80% H_2O, 20 % H_2, -0.6 A cm^{-2}, 75% SC, oxygen side outlet temperature of 816°C



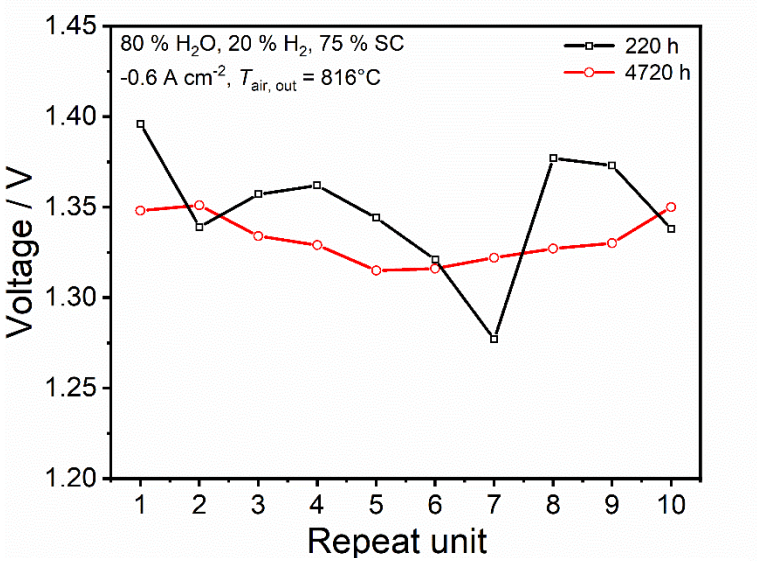
- Less pronounced edge effect
- Initial stack performance: P = 1.03 kW, η_{el} = 92.9%

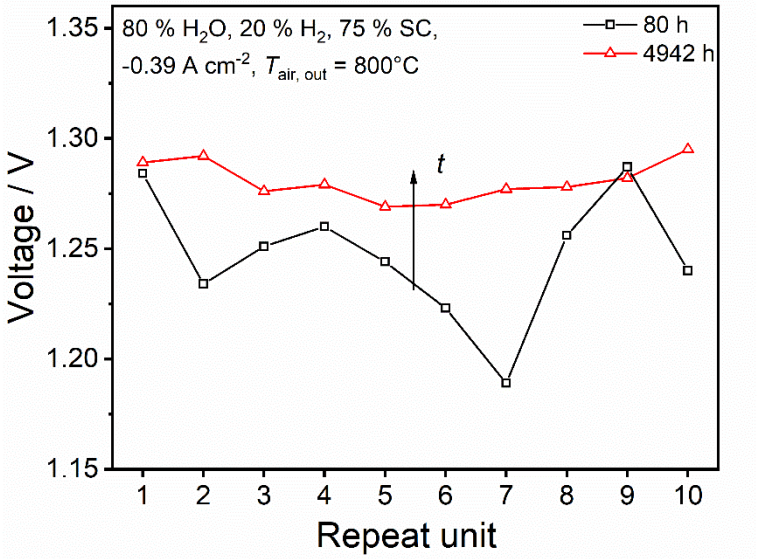
Results: Stack lifecycle



- Voltage oscillations during first half of experiment due to instable steam supply
- Improvement of stack voltage over the experiment
- Temperature change of <1 K

Voltage degradation over time

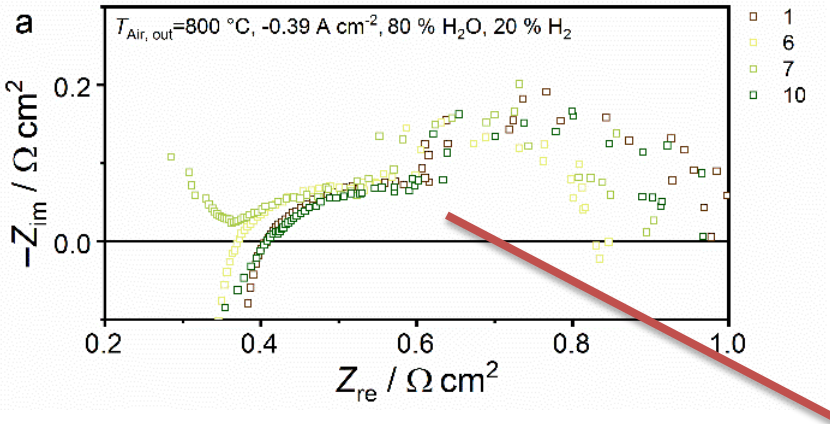


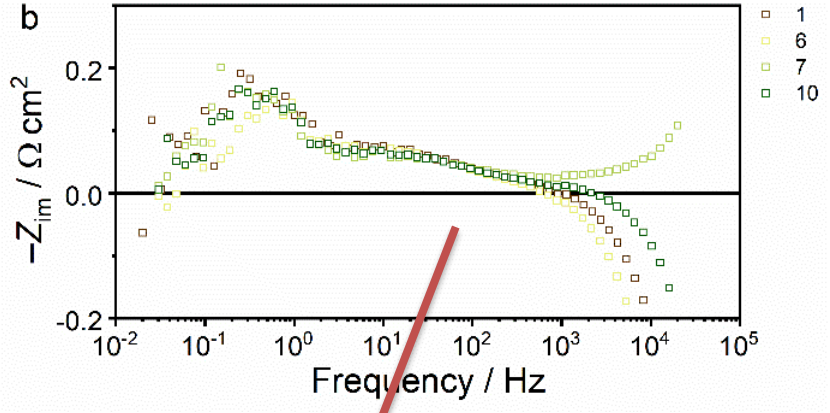


- Inhomogeneous degradation behavior
- Improvement of most RUs led to a negative overall degradation rate
- No reliable quantification of EIS data at operating point of long-term test due to low-frequency scattering

- 2nd reference point: -0.39 A cm^{-2}, 800°C
- Degradation for nearly all RUs and temperature increase of ~2 K
- Edge effect visible despite voltage values close to thermoneutral voltage
- Degradation rate has strong dependency on the operating conditions

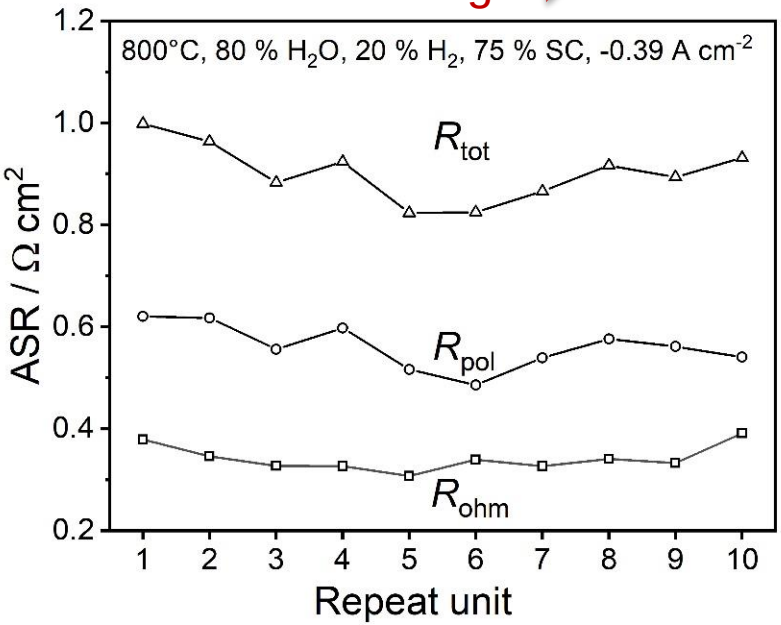
EIS analysis of initital SOEL stack performance



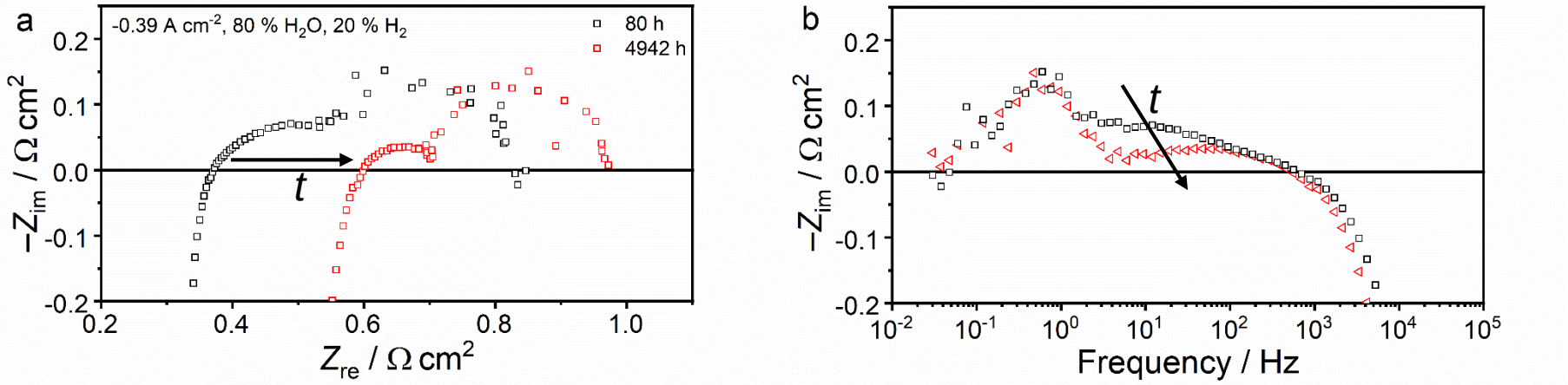


+ CNLS fitting

- Usage of -0.39 A cm^{-2}, 800°C as reference point
- Increased ohmic resistance at top and bottom layer
  →Contacting/temperature effect?
- Decreased low-frequency polarization resistance at 0.5 Hz → Increased gas supply?



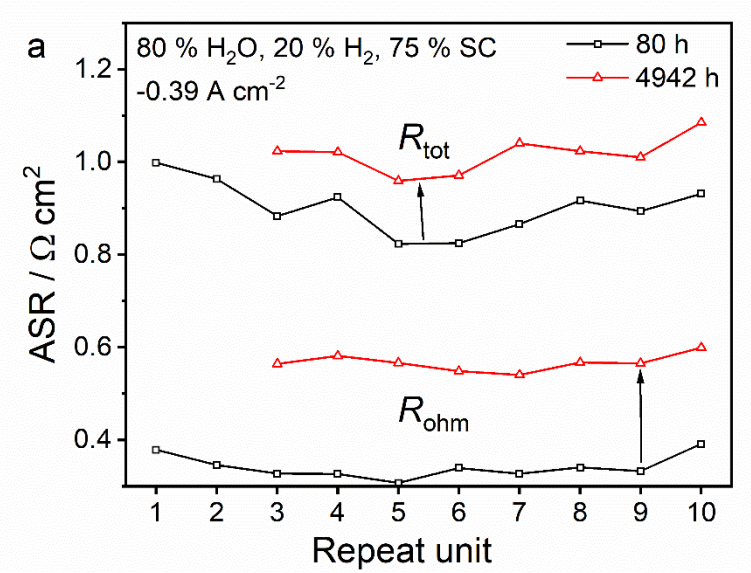
SOEL degradation analysis with EIS

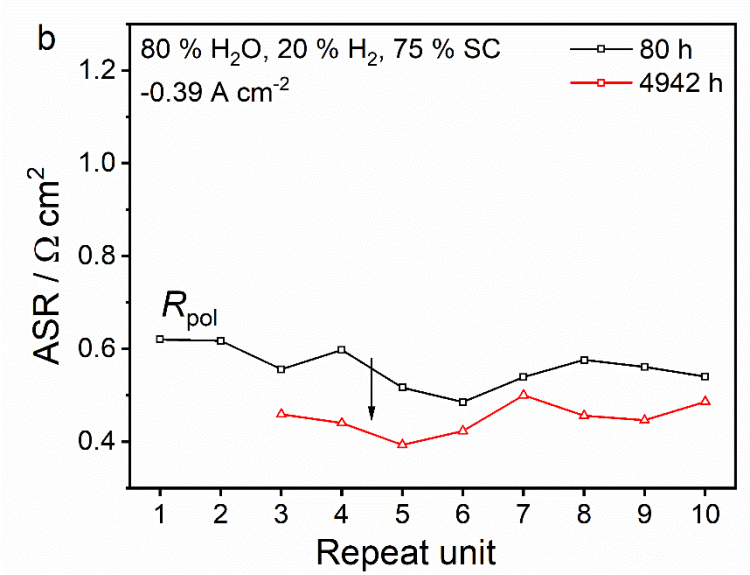


- Exemplary RU4 shows ohmic resistance increase over time
- Increase of R_{ohm} most likely due to decrease in electrolyte conductivity
- Decrease of polarization resistance at ~10 Hz

→ Attribution to LSMM‘ oxygen electrode process based on IKTS experience
→ Activation behavior of LSM electrodes due to oxygen vacancy formation is well-known

SOEL degradation analysis with EIS

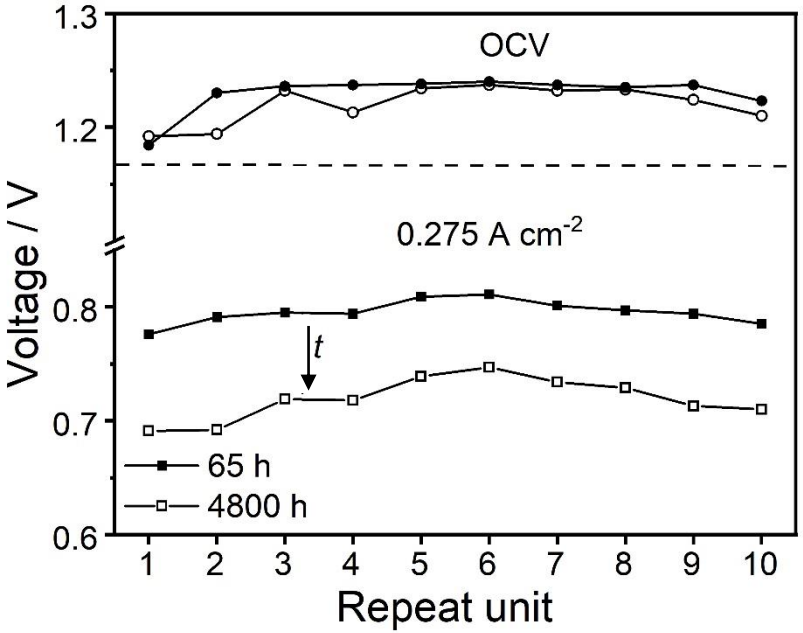


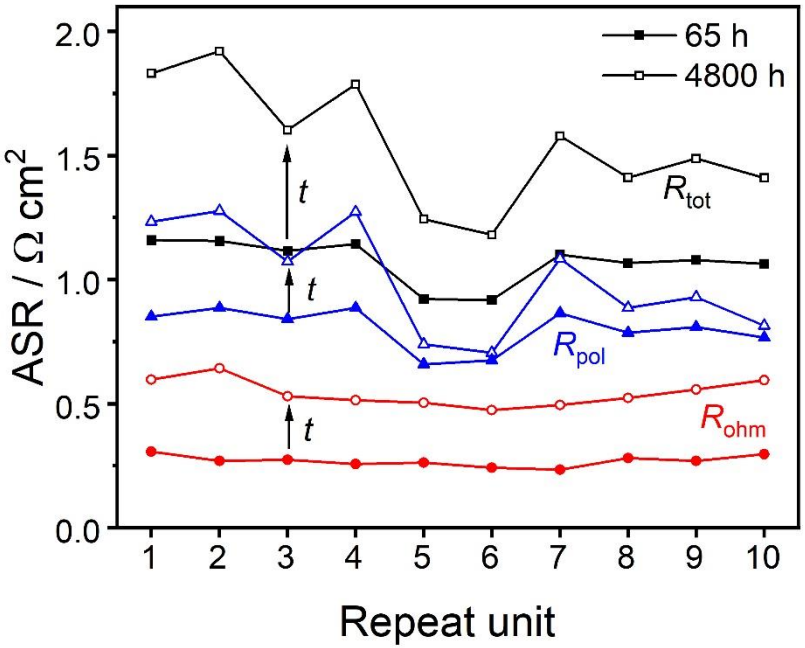


- 4942 h: Distorted EIS measurements at RU 1 & RU 2
- Considerable reduction of R_{pol} of RUs (oxygen electrode) partly compensates the ohmic resistance degradation at the EIS reference point
- This effect most likely overcompensates the ohmic resistance increase at the operating point

Degradation analysis in SOFC operation

i = 0.275 A cm^{-2}, $T_{air,\ out}$ = 835°C, 60% N_2, 40% H_2, FU = 75%

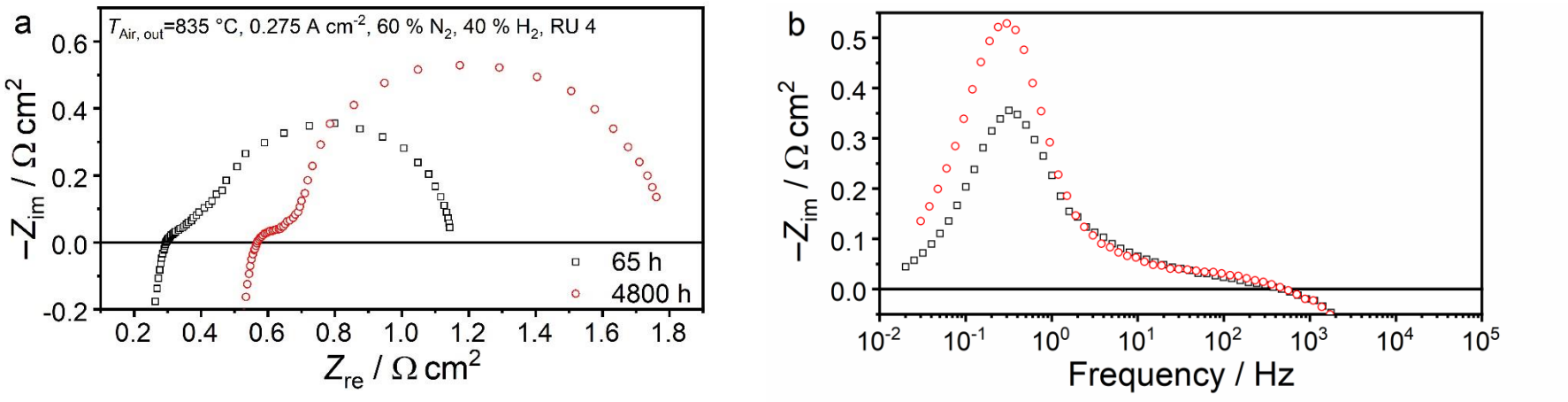




- Small decrease of OCV in some RUs → Negligible gas leakage
- Voltage decrease and ASR increase of all layers
- Increase of R_{ohm} and R_{pol}

Degradation analysis in SOFC operation

i = 0.275 A cm^{-2}, $T_{air,\ out}$ = 835°C, 60% N_2, 40% H_2, Fuel utilization = 75%



- Degradation of process at ~0.5 Hz → Change of gas conversion/additional process?

- Only small reduction of resistance in frequency range ~5 Hz

→ Major improvement of oxygen electrode process is only visible during electrolysis operation

→ Mechanistic explanation is unclear

Summary

- 10-cell MK35x stack from IKTS shows a reduction power in SOEL: $\Delta P/P_0$=-0.3 %/1000 h @-0.6 A cm^{-2} ,3260 h, *T*=816°C, SC=75%
- Increase of ohmic resistance, decrease of LSMM‘ polarization resistance
- Different degradation behavior at different operating points
- Oxygen electrode activation can skew degradation rates in stack tests until up to 5000 h
- Demonstration of value of EIS analysis on stack to obtain an in-depth understanding of degradation
- Next step: Correlation with post-mortem analysis results

Thanks for your attention

Federal Ministry
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and Research

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