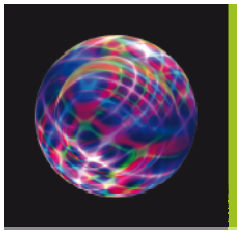
Josef Schefold, Annabelle Brisse

Long-term Fast Current/Power Cycling at Solid-Oxide Electrolyser Cells



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Steam Electrolysis with SOC in EIFER

Focus: solid-oxide cell & stack testing (*up to 10 kWel)*; mainly long-term

- *no own cell/stack development → data for different suppliers*
- *at interface applied science // development*
- *lifetime milestones (23,000 h / -0.9 Acm^{-2} with Kerafol ESC)*
- *in-situ degradation analysis (impedance spectroscopy)*
- *current work: electrolyte supported cells with Ni/GDC and LSCF electrodes*

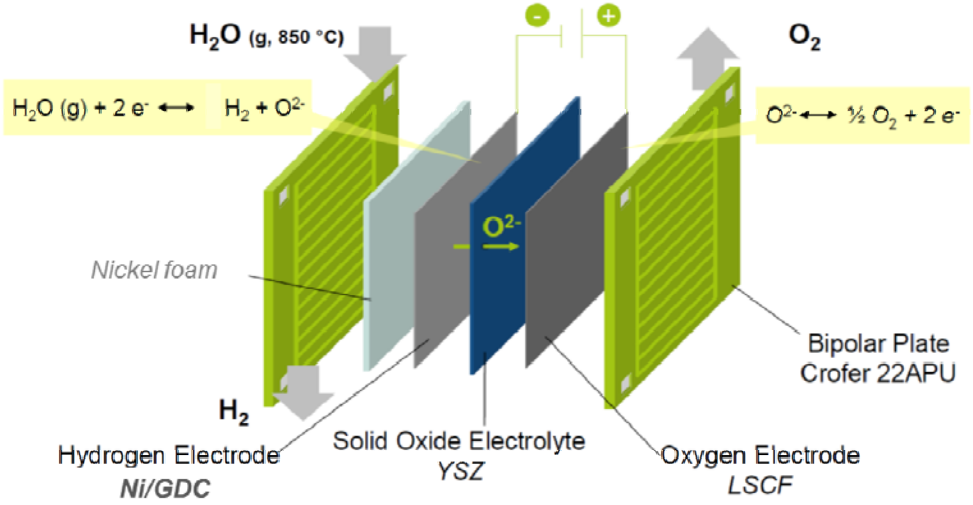

Figure from GrInHy project

Long-term benchmark: 20,000 h @ -0.9 Acm^{-2}

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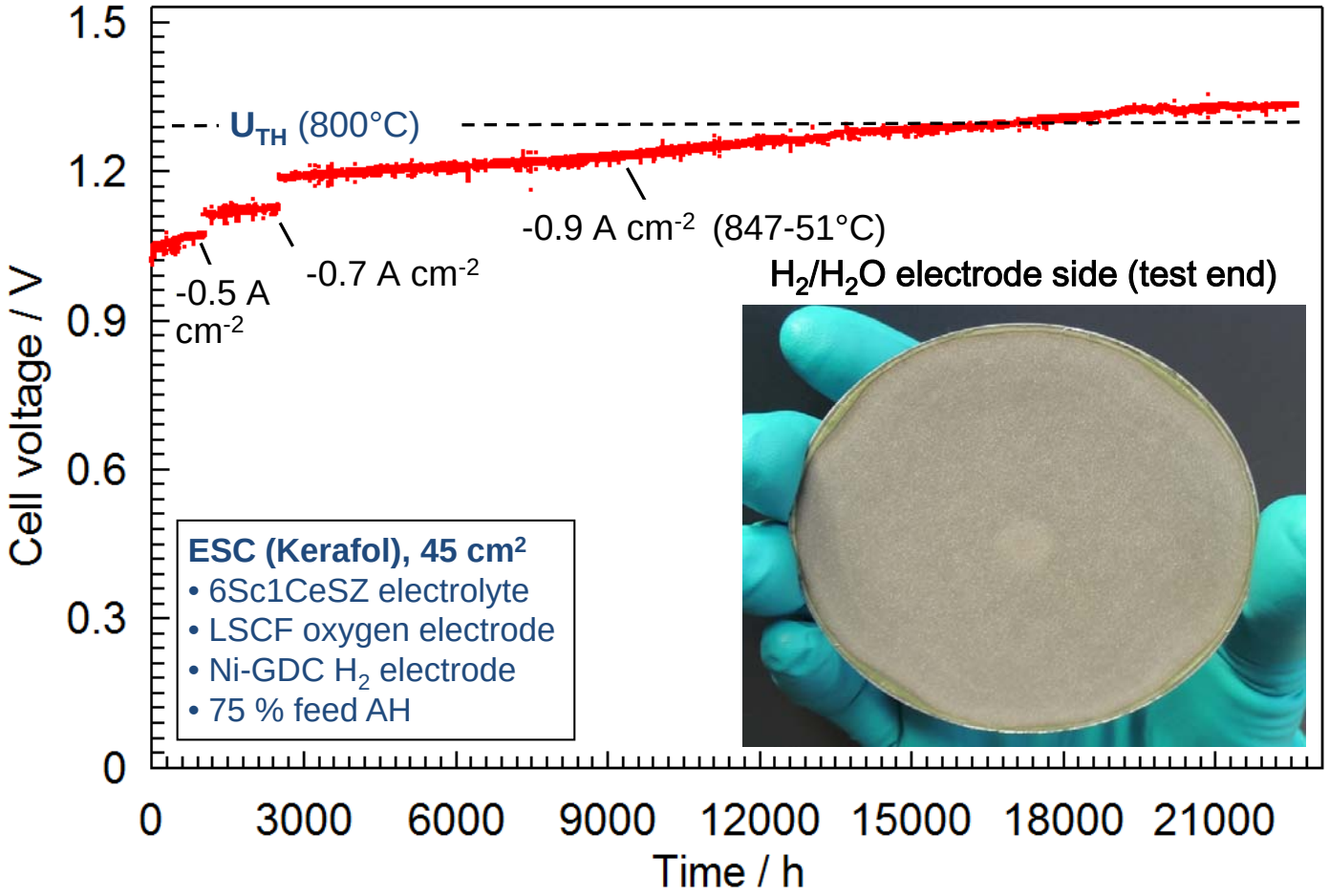
Duration	cell type	current density	degradation	temperature	feed humidity	steam convers.
23,000 h (tot.)	ESC	-0.9 Acm^{-2} (20 kh)	U_{cell}: 7.4 mV/kh (0.57 %/kh) ASR: 8 mΩ cm^2/kh	850°C	75 %	50 %



- longest test
- highest ESC current density
- $U_{cell} < U_{th}$ up to 2 years

- *impedance: degradation predominantly ohmic*
- *post test: Sr-Zirconate formation; partial delamination of O_2 electrode; Si accumulation at H_2 electrode*

J. Schefold, A. Brisse, H. Poepke, *Int. J. Hydrogen Energy* **42** (2017), 13415-26.

Outline

1. **Introduction**
   - *participation in "GrInHy" project – reversible SOC operation*
   - *need for electrolyser power variation (in largely different time windows)*
2. **"On/Off" switching at SOEC for load variation (thermal neutral mode)**
3. **The test: 80,000 cell switching cycles during >8,000 h operation**
   - *experimental set-up; cell*
   - *switching cycle*
   - *cell degradation during cycling vs. steady-state operation*
   - *impedance / dismantling*
4. **Summary / Outlook**

Research Project ”GrInHy” (European Union) on Reversible SOC Operation; 150 kW_{AC}

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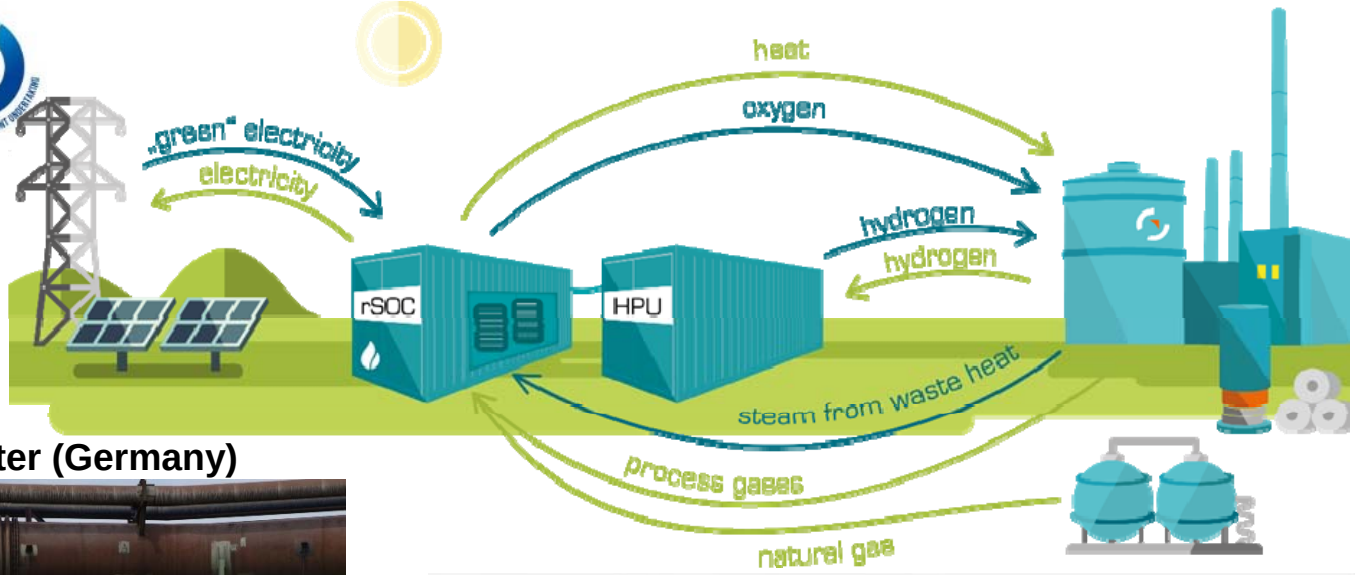
GrInHy Green Industrial Hydrogen

http://www.green-industrial-hydrogen.com

System operation: (Proceedings of) European Fuel Cell Forum (Lucerne, Switzerland, 07/2018)



GrInHy system in Salzgitter (Germany)

Efficiency	proof of reaching an overall electrical efficiency of at least 80 %LHV
Upscaling	SOEC unit to a DC power input (stack level) of 120 kW_{el}
Operation	at least 7,000 h of operating the system
Lifetime	greater than 10,000 h with a degradation rate below 1 %/1,000 h
Reversible Operation	higher capacity utilization for stronger business cases
Costs	development of dependable data on system costs and cost reductions
Exploitation Roadmap	reversible high-temperature electrolyzer as a marketable product

Current / Power Cycling: Context

- Industrial electrolysis: reliable operation for years
- **But:** published long-term cell data beyond a few kh are scarce and refer to constant current operation
- Coupling to Renewables **(“Power-to-X“)** requires capability for load variation (seasonal; day/night; wind profiles; electrical grid services….)

Goals of this (cell) work:

- several 10,000 ‘‘On/Off‘‘ cycles in kh timescale, using
  - ➢ thermal neutral operation (unique at SOEC), and
  - ➢ fast switching times (instantaneous in electrochemical scale)
- steady-state ’’On’’ operation for comparison
- testing with typical values for current density and feed conditions
- in-situ diagnostics (impedance spectroscopy)

Current / Power Cycling: Concept

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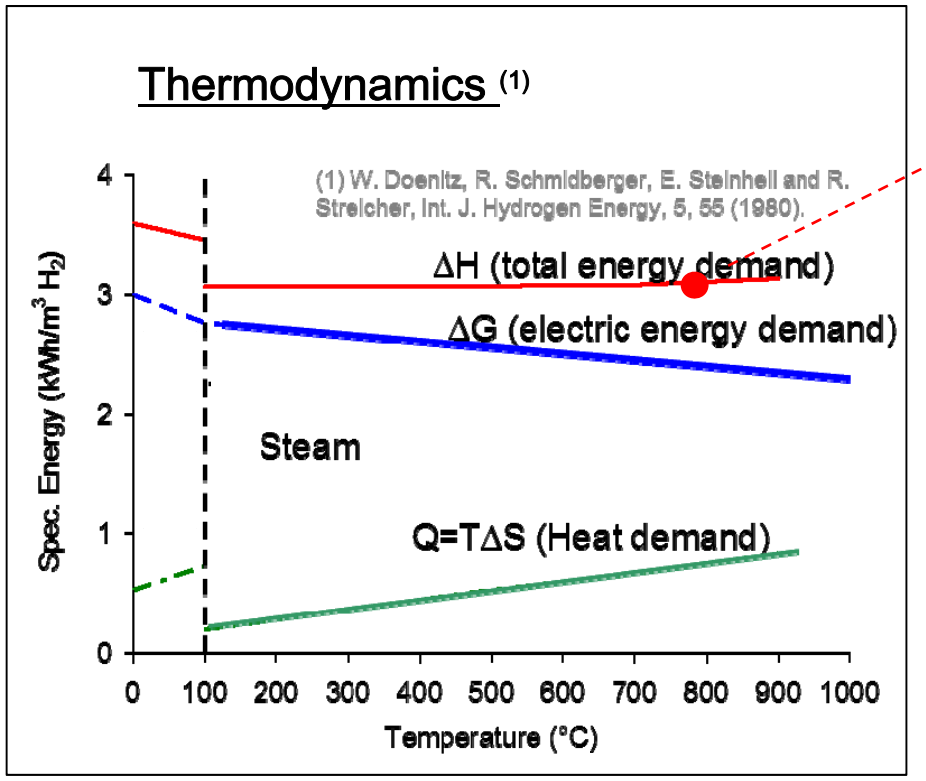
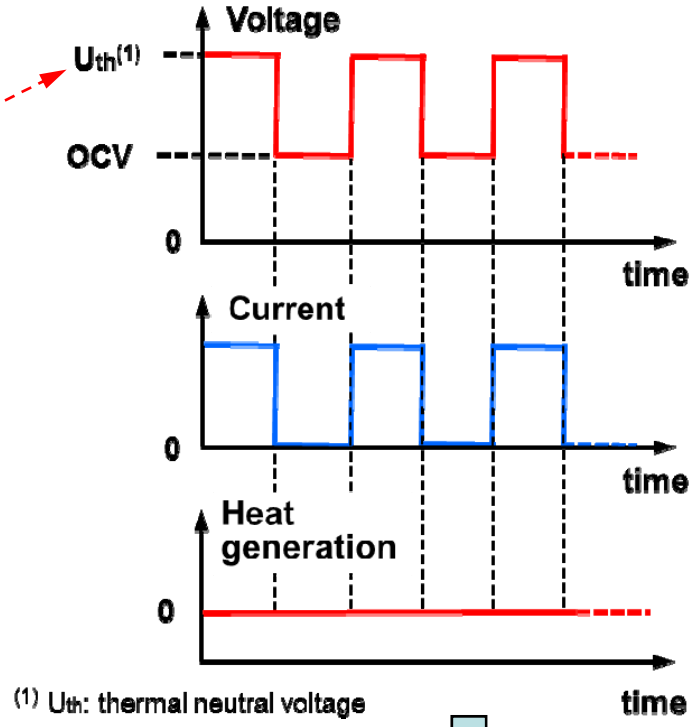
Thermodynamics (1)



Operation principle



- **Favourable for stack operation; no specific efforts for thermal management**
- **Cell stability (changing heat flows inside cell) ?**

- SOEC: No change in heat flow to/from cell in ”ON” and ‘’OFF” periods

- Zero heat flow for $U_{cell} = U_{th}$ (“ON“)

Experimental: Cell mounting & current/power cycling in open cell housing (1/2)

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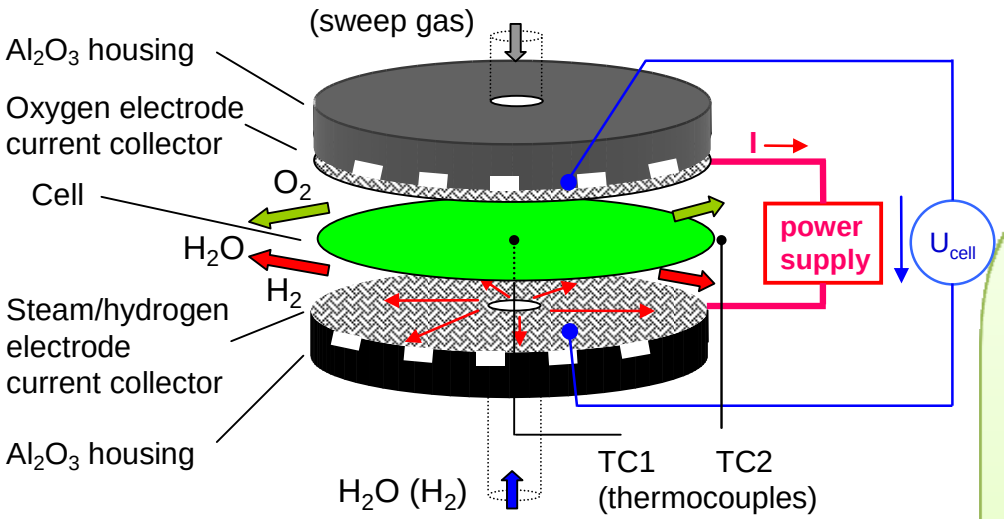
Cell housing (45 cm² cell area)



Steam supply with CEM
(controlled evaporator mixer)

Impedance spectroscopy implemented

Cell from company sunfire (Germany)

- electrolyte supported (3YSZ; d = 90 µm)
- Ni/GDC H_2 electrode + CGO adhesion layer
- LSCF air electrode + CGO barrier layer

Open ceramic cell housing

- no sealing (issues)
- no poisoning from metal corrosion
- H_2 production measurable via temperature of TC2 (H_2 combustion)

Difficulties for cyclic operation

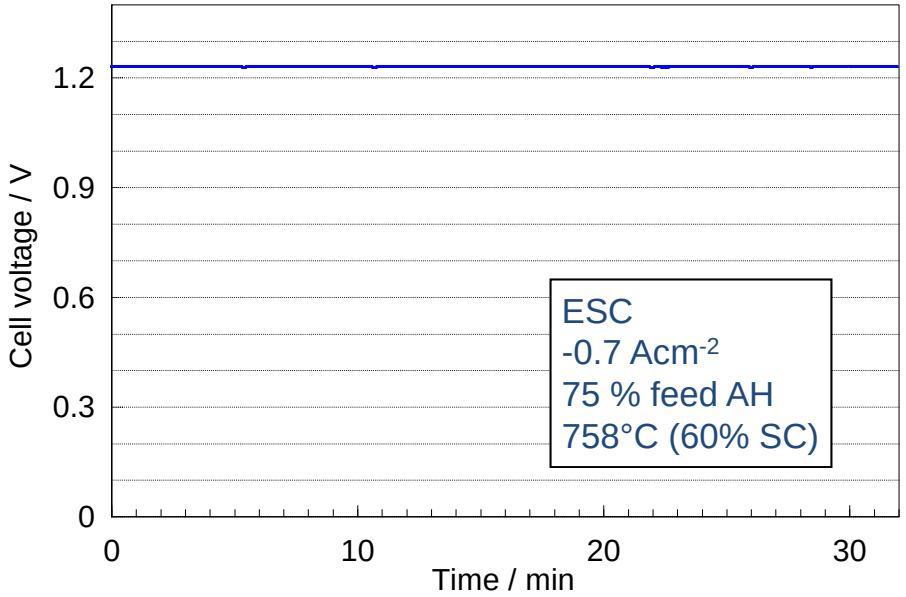
- higher contacting resistance compared to stack → increased temperature variations (ohmic heating)
- (cyclic) heating from H_2 combustion
- *ceramic housing blocks do not withstand larger fast temperature gradients*

Testing approach

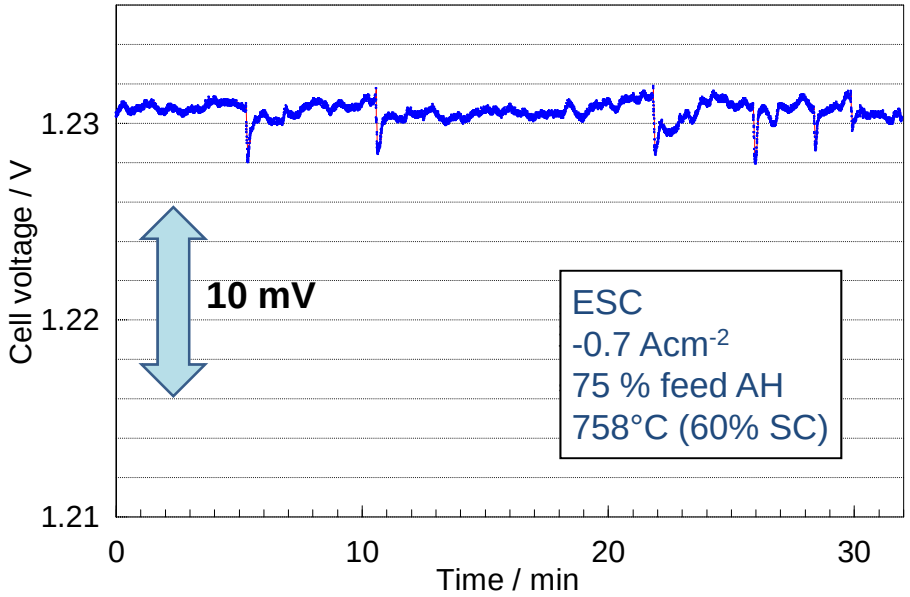
- cycling time **sufficiently slow** for voltage equilibration
- cycling time **sufficently fast** to limit temperature cycling in ceramic housing blocks
- asymmetrical "on/off" times (t_{on}>t_{off}) to facilitate comparison with steady-state "ON"

Experimental: Cell voltage noise from steam generator (2/2)

Cell voltage, full scale



Cell voltage, zoom



- Some instability in steam generation with CEM (mass flow rate of water is controlled)
- Pulses of up to 5 mVpp (typical 2 – 3 mV) for the used CEM
  → noise band in U_{cell} vs. time for longer times
  → noisy impedance at lower frequencies

Current / power cycling in cell test (1/3)

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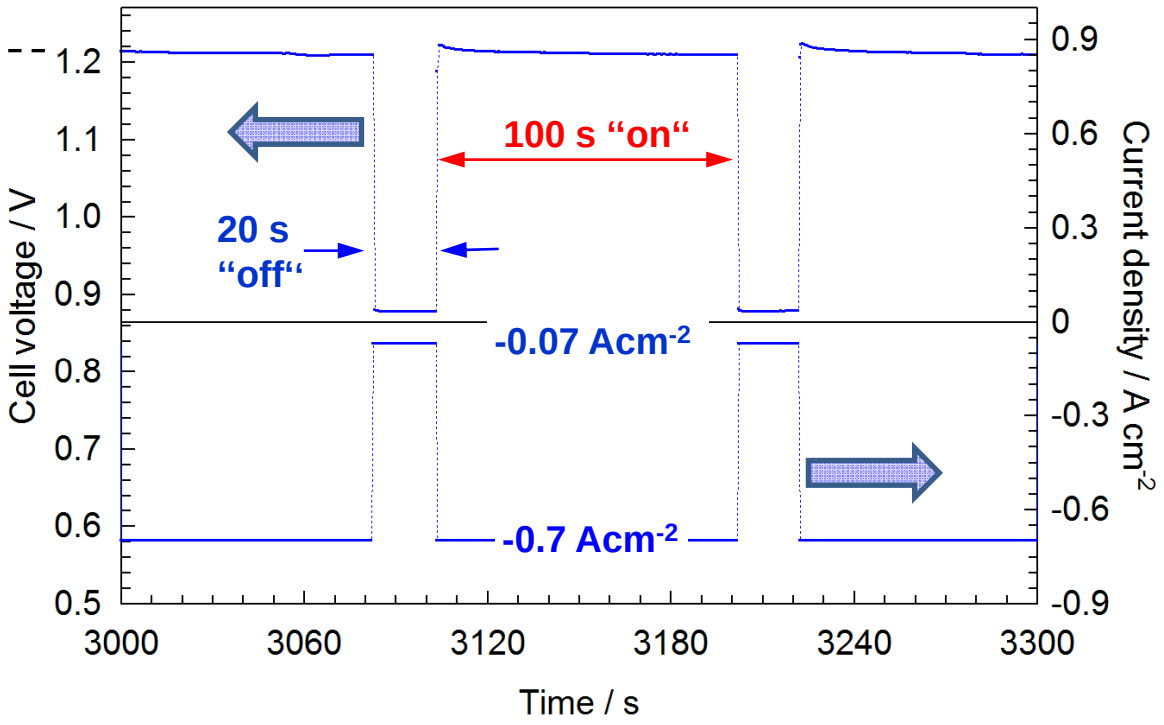
Cycle definition

- 2 min cycle time (100 s on/20 s off)
- **“ON“ = close to thermal neutral voltage**
- “OFF“ = small current density (10 %) left for H_2 electrode oxidation protection (via generated H_2)
- **fast switching steps (no ramps)**

- Sunfire ESC
- 852°C
- 75 % H_2 feed humidity
- 60 % steam conversion (“ON“)
- constant gas supply

Power	‘’ON”	“OFF”
W cm^{-2}	-0.85	-0.062
%	100	7.3

(small U_{cell} transients neglected)



Current / power cycling….. (2/3)

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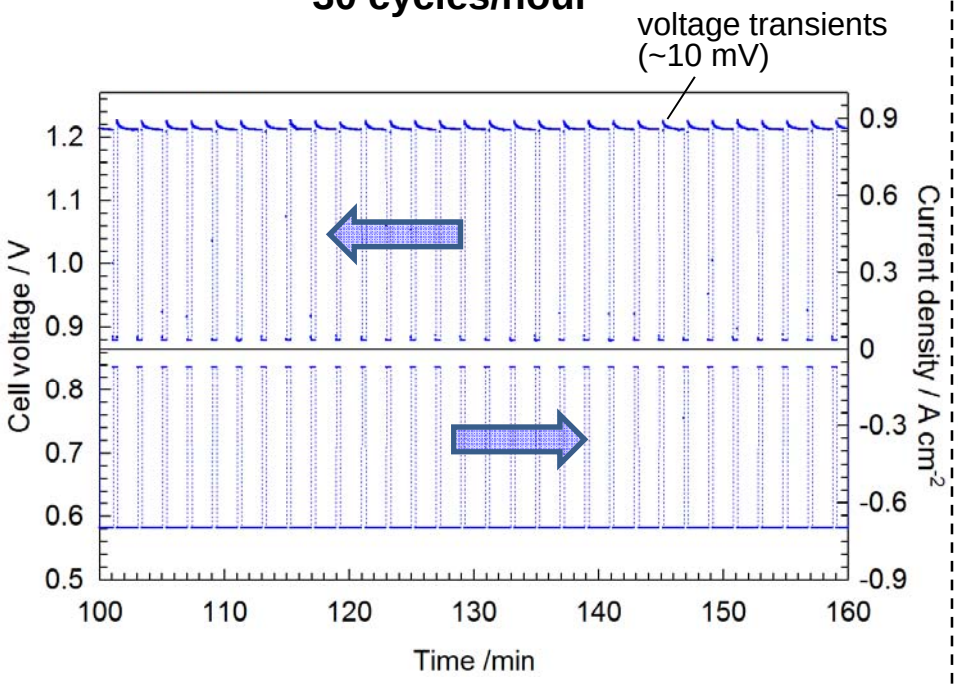
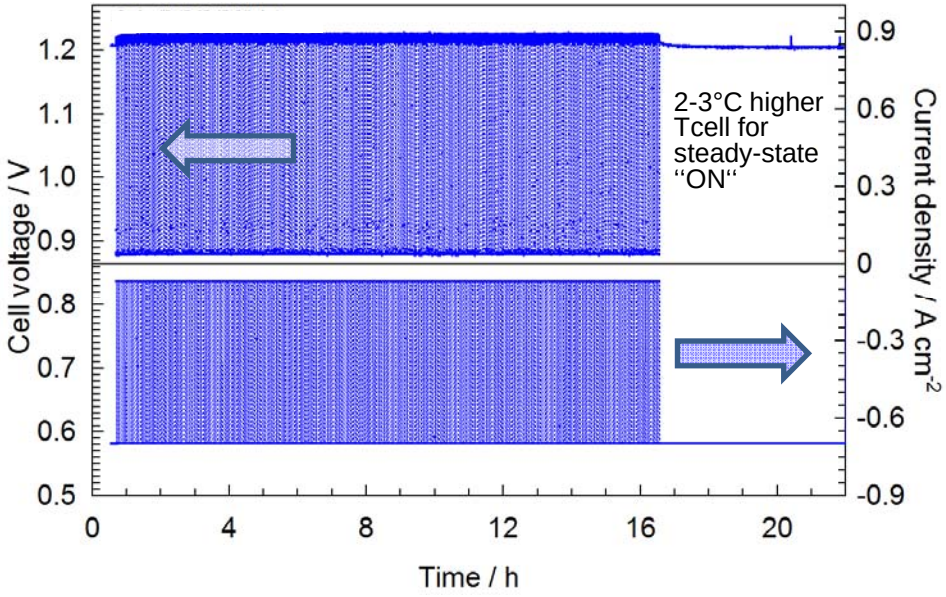
30 cycles/hour

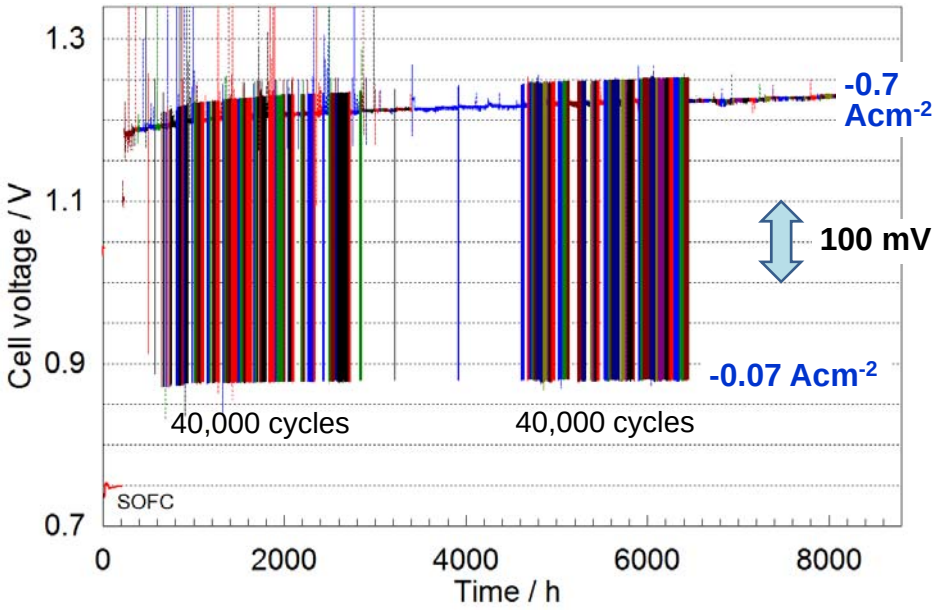


400 - 700 cycles/day
(with steady-state "ON" for comparison)



- Sunfire cell (3YSZ/Ni-GDC/LSCF)
- 852-53°C (switching) / 855°C (steady state "ON")
- 75 % abs. feed humidity (in H_2); constant feed
- 60 % steam conversion ("ON"); 6 % ("OFF")
- "OFF": 40 mV above OCV

Current / power cycling – long-term (3/3)



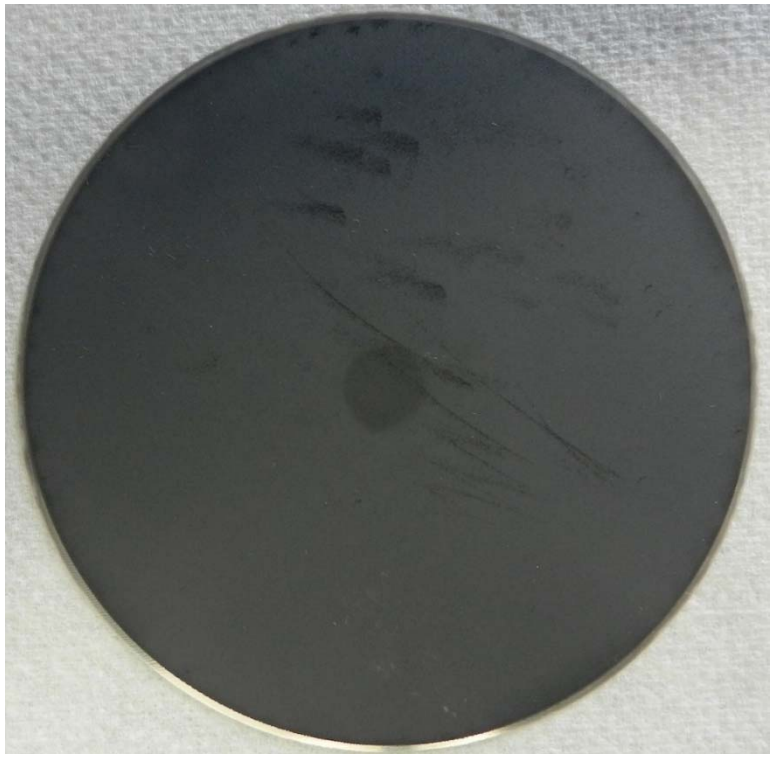
- 2 cycling blocks with 40,000 cycles each (total 2666 h cycling; 444 h ‘‘Off‘‘)
- steady-state ‘‘ON‘‘ periods for comparison
- low linear voltage degradation of 3.8 mV/kh or 0.3 %/kh (raw data >1 kh)
- >1000 h required to reach about linear range

- temperature correction (+0.4°C/kh): **1.2 mV/kh**
- temperature corrected voltage degradation: **5.0 mV/kh (0.38 %/kh)**
- **no notable change in degradation due to cycling**

Cell after dismantling

H_2 electrode side, dismantled cell

O_2 electrode side, dismantled cell



- no mechanical damage
- no delamination (scratches on O_2 electrode from dismantling - electrode sticking on contacting Pt grid
- post-test tbd

Summary / Outlook

- Concept of ‘‘On/Off‘‘ current switching presented; ‘‘On‘‘ close to the thermal neutral voltage
- *>8000 h cell test done with ESC, with 80,000 ‘”On/Off” cycles integrated (2 min each)*
- Small voltage degradation (5 mV/1000 h @-0.7 Acm^{-2}, temperature corrected)
- *Cell degradation:*
  - independent of cycling
  - no physical damage such as delamination
  - impedance spectroscopy: degradation mainly ohmic; small contribution from electrode deactivation (similar to earlier work with the used cell structure)

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Thank you for your attention!

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