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

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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\(^{-2}\)

- longest test
- highest ESC current density
- \(U_{\text{cell}} < U_{\text{th}}\) up to 2 years

<table>
<thead>
<tr>
<th>Duration</th>
<th>cell type</th>
<th>current density</th>
<th>degradation</th>
<th>temperature</th>
<th>feed humidity</th>
<th>steam convers.</th>
</tr>
</thead>
<tbody>
<tr>
<td>23,000 h (tot.)</td>
<td>ESC</td>
<td>-0.9 Acm(^{-2}) (20 kh)</td>
<td>(U_{\text{cell}}: 7.4 \text{ mV/kh (0.57 %kh)}) (\text{ASR: 8 m(\Omega) cm}^2/\text{kh})</td>
<td>850(^{\circ})C</td>
<td>75 %</td>
<td>50 %</td>
</tr>
</tbody>
</table>

ESC (Kerafol), 45 cm\(^2\)
- 6Sc1CeSZ electrolyte
- LSCF oxygen electrode
- Ni-GDC H\(_2\) electrode
- 75 \% feed AH

\(U_{\text{TH}}\) (800\(^{\circ}\)C)

-0.9 A cm\(^{-2}\) (847-51\(^{\circ}\)C)

H\(_2\)/H\(_2\)O electrode side (test end)

- impedance: degradation predominantly ohmic
- post test: Sr-Zirconate formation; partial delamination of O\(_2\) electrode; Si accumulation at H\(_2\) electrode

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\textsubscript{AC}

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

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

GrInHy system in Salzgitter (Germany)

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

**Operation principle**

- SOEC: No change in heat flow to/from cell in "ON" and "OFF" periods
- Zero heat flow for \( U_{cell} = U_{th} \) ("ON")

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

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**Thermodynamics**

\[
\begin{align*}
\Delta H \text{ (total energy demand)} \\
\Delta G \text{ (electric energy demand)} \\
Q = T \Delta S \text{ (Heat demand)}
\end{align*}
\]

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 sufficiently fast to limit temperature cycling in ceramic housing blocks
- asymmetrical “on/off” times ($t_{on}>t_{off}$) to facilitate comparison with steady-state “ON”

Open ceramic cell housing
- no sealing (issues)
- no poisoning from metal corrosion
- $H_2$ production measurable via temperature of TC2 ($H_2$ combustion)

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

Cell housing (45 cm$^2$ cell area)
- Al$_2$O$_3$ housing
- Oxygen electrode current collector
- Cell
- Steam/hydrogen electrode current collector
- Al$_2$O$_3$ housing

Steam supply with CEM
- (controlled evaporator mixer)
- H$_2$O (H$_2$)
- TC1
- TC2

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

WHEC 2018, “Fast Power Cycling at SOEC”, EIFER, 18/06/2018
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

ESC -0.7 Acm$^{-2}$
75 % feed AH
758°C (60% SC)
Current / power cycling in cell test (1/3)

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 H₂ electrode oxidation protection (via generated H₂)
• fast switching steps (no ramps)

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<tr>
<th>Power</th>
<th>“ON”</th>
<th>“OFF”</th>
</tr>
</thead>
<tbody>
<tr>
<td>W cm⁻²</td>
<td>-0.85</td>
<td>-0.062</td>
</tr>
<tr>
<td>%</td>
<td>100</td>
<td>7.3</td>
</tr>
</tbody>
</table>

(small U₉ transient neglected)
30 cycles/hour

- Voltage transients (~10 mV)

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 H₂); constant feed
- 60% steam conversion (“ON”); 6% (“OFF”)
- “OFF”: 40 mV above OCV

WHEC 2018, “Fast Power Cycling at SOEC”, EIFER, 18/06/2018
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

H₂ electrode side, dismantled cell

O₂ electrode side, dismantled cell

- no mechanical damage
- no delamination (scratches on O₂ electrode from dismantling - electrode sticking on contacting Pt grid
- post-test tbd
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)
Thank you for your attention!

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