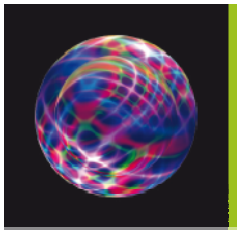
Josef Schefold, Annabelle Brisse

Long-term Steam Electrolysis with Solid Oxide Cells with up to 23 000 h Operation



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(Shortened) Presentation from the **7th World Hydrogen Technology Convention** in Prague, Czech Republic, 9 - 12 July 2017.

Steam Electrolysis with Solid Oxide Cells

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Our focus: cell (& stack) testing; mainly long-term

- *at interface applied science // development*
- *no own cell or stack development*
- *data (comparison) for different structures and from different suppliers*
- *lab test benches: 4x cells; 1x short-stack; 2x stack (1-10 kWel)*
- *milestones (23 000 h with Kerafol ESC……)*
- *degradation analysis (in-situ with impedance spectroscopy)*

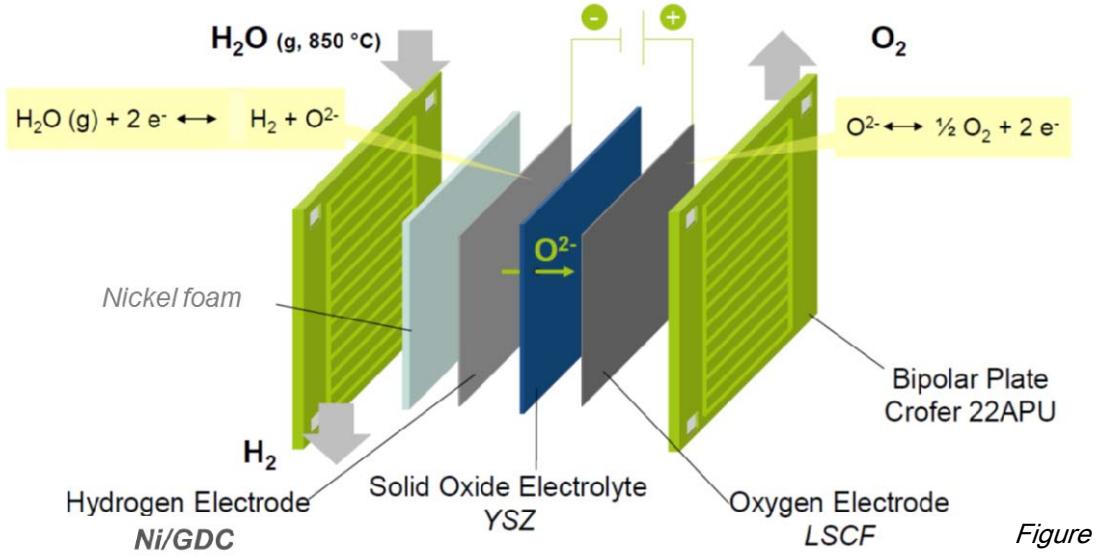


Figure from GrInHy project

Related Research Projects

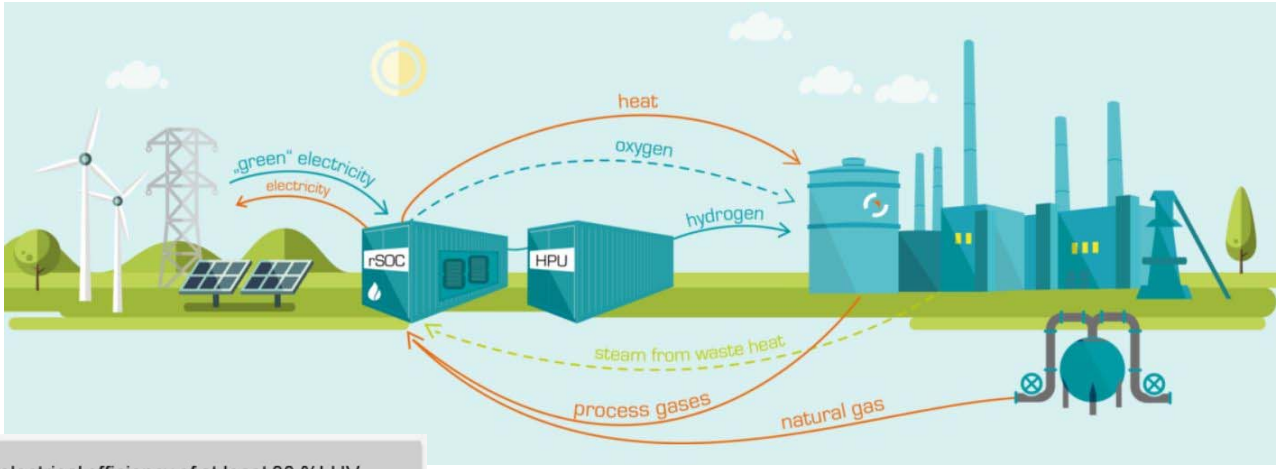
‘Sunfire’ (2012 - 16): Power-to-Liquid with SOEC (D); 10 kW_{el}

‘GrInHy’ (2016 - 19) on Reversible SOC (EU); 120 kW_{el}

GrInHy
Green Industrial Hydrogen

FCH
FUEL CELLS AND HYDROGEN JOINT UNDERTAKING

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



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

SOEC:120 kW_{el}

Cell/stack testing by

- ***company Sunfire and by***
- ***EIFER***

GrInHy Reversible SOC Installation (06/2017)

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Fig. 1. GrInHy system in Salzgitter (D)

Fig. 2. Container of the Reversible Solid Oxid Cells
(1440 rSOCs in 6 modules)

GrInHy
Green Industrial Hydrogen

SOEC: 120 kW_{el}

SOFC: 30 kW_{el}

Outline

1. **Introduction**
   - *influence of temperature & electrochemical kinetics*
   - *overview on our long-term cell data*
   - *electrolysis with electrode and with electrolyte supported solid oxide cells*
2. **23,000 h steam electrolysis benchmark test**
   - *cell (voltage) degradation*
   - *impedance (degradation)*
   - *post-test data*
3. **Recent long-term work**
   - *increase in current density & steam conversion*
   - *lower temperature*
   - *(industrial cells / cyclic operation)*

Temperature Influence in Fuel Cell & Electroysis Operation

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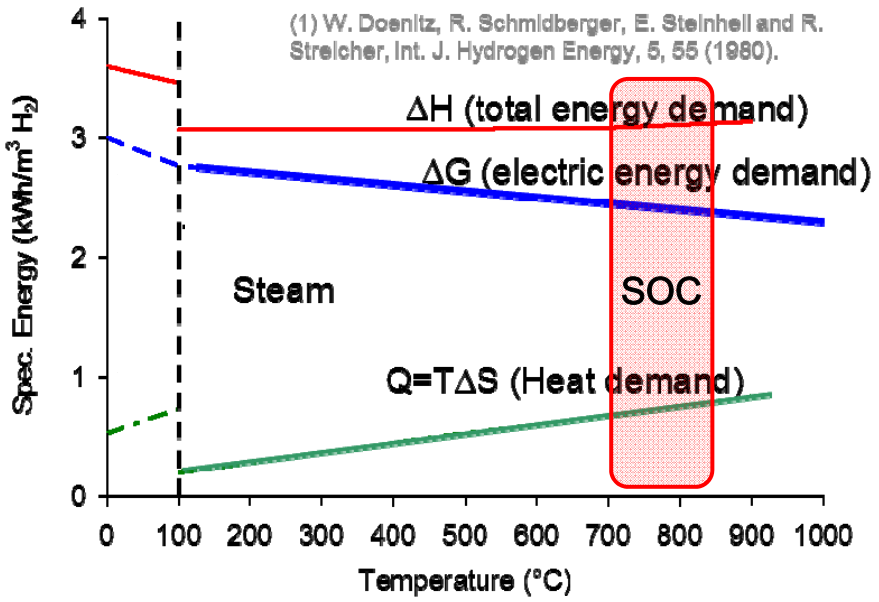
A Thermodynamics (1)



B Electrochemical kinetics : *Faster reaction kinetics at high temperature*

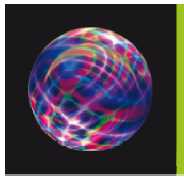
SOEC vs. PEM/Alkaline

- lower equilibrium cell voltage (thermodyn.)
- lower losses (kinetics)

SOC (SOFC & SOEC)

- largely fixed electrode potentials
- suitable for **reversible operation**
- similar **degradation** expected

Selected long-term cell tests 2011-2016



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Test duration	cell type (project)	date	current density	degradation	tempera-ture	feed humidity	steam convers.	equiv. time [a] (-0.5 Acm-2)	comment
9300 h	CSC* -	2010-2011	-1 Acm-2 (9000 h)	tot: 40 mV/kh min: 19 mV/kh	780°C	80 %	36 %	**18000 h**	many incidents
6100 h	CSC* (Horizont)	2012	-0.75 Acm-2	10 mV/kh (0.8 %/kh)	780°C	80 %	40%	**9150 h**	1st with acceptable stability

Test duration	cell type (project)	date	current density	degradation	tempera-ture	feed humidity	steam convers.	equiv. time [a] (-0.5 Acm-2)	comment
23000 h	ESC** (Sunfire)	2013-2016	-0.9 Acm-2 (20000 h)	7.4 mV/kh (0.6 %/kh)	850°C	75 %	50 %	**40000 h**	milestone

* Ni/8YSZ-8YSZ-LSCF (Research Centre Juelich, Germany)

** Ni/GDC-6Sc1CeSZ-LSCF (company Kerafol, Germany)

[a] Time for identical total charge flow assuming 0.5 Acm^2 current density as typical in SOFC testing)

9300 h CSC:

J. Schefold, A. Brisse, F. Tietz, *JES*, **159** (2012) A137-44.

23000 h ESC:

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

Experimental: cells for steam electrolysis (cells are established as fuel cells)

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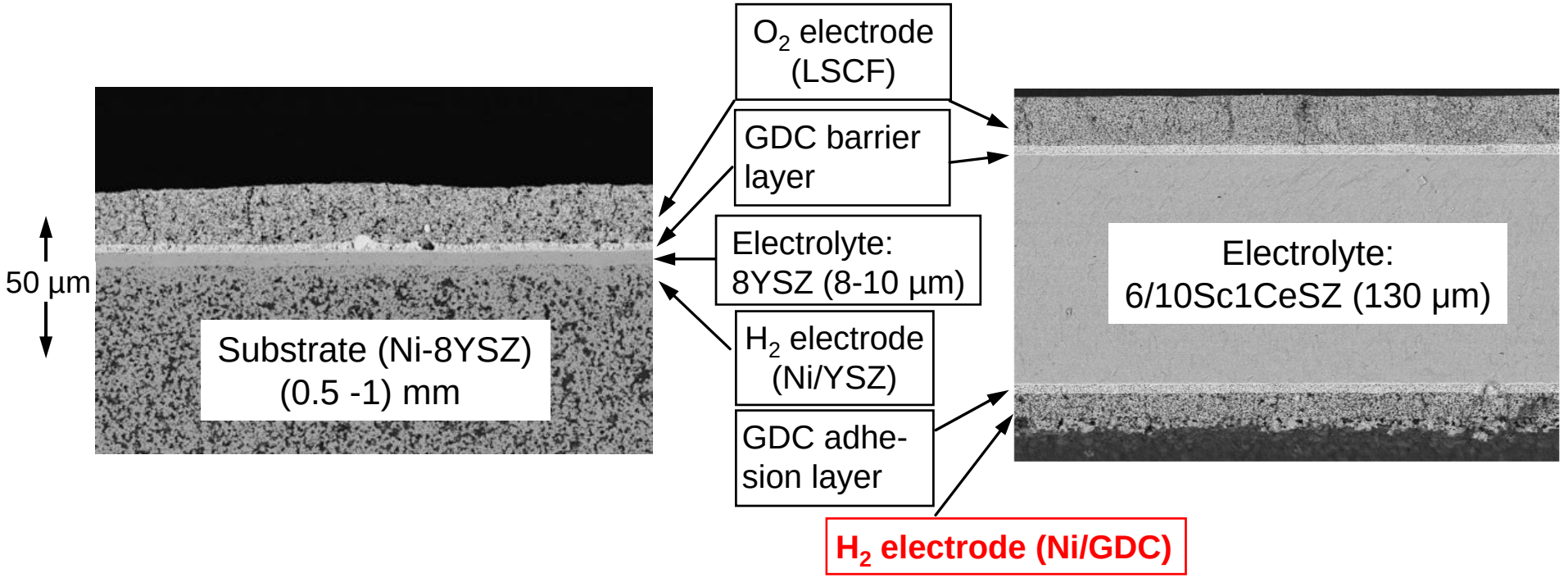
H_2 electrode supported cell

Electrolyte supported cell



700-800°C

800-860°C

Figures from Sunfire project

GDC: gadolinia doped ceria
LSCF: lanthanum strontium cobaltite ferrite

Experimental: cell mounting & operation

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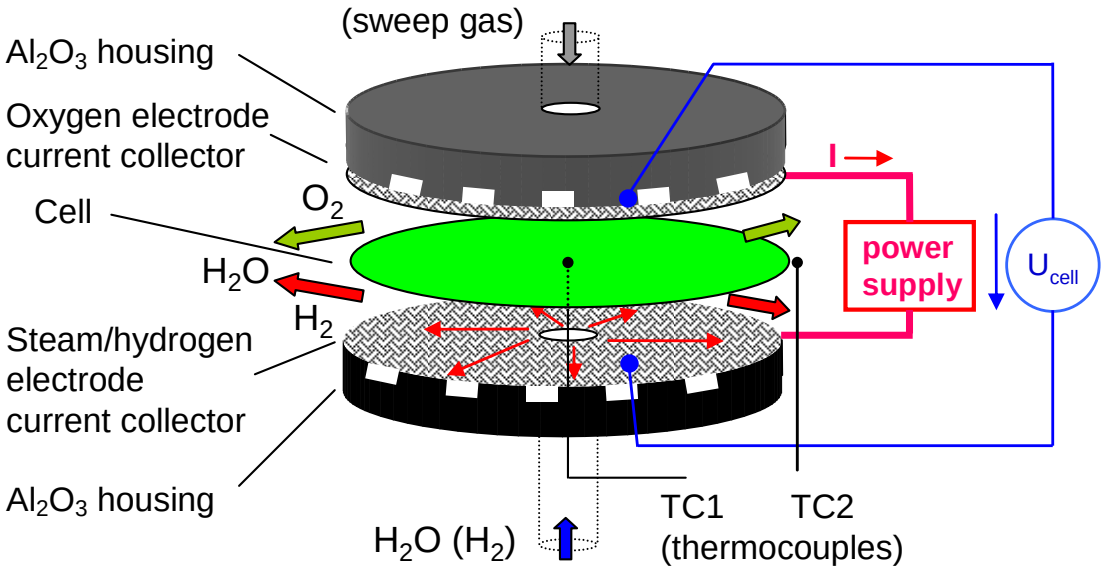
Cell housing (45 cm² cell area)



Steam supply with CEM
(controlled evaporator mixer)

Open cell housing

- no sealing (issues)
- no poisoning due to metal corrosion (Cr….)
- H_2 production qualitatively measurable via temperature rise at TC2 (H_2 combustion)

→ Suitable for long-term degradation work

Impedance spectroscopy

- equipment is implemented
- ***in-situ*** (no DC current interruption or change)
- typical sampling sequence: hours to days

SOEC degradation / H_2 electrode supported cells

H_2 electrode supported cells (CSCs) with Ni/YSZ cathode

- strong degradation increase above (0.7 to 1) Acm^{-2}, found by different groups (1,2,...)
- reason: interface instability electroyte/H_2 electrode (Nickel loss)
- ***this degradation is a major development issue for the SOEC application***

Consider **electrolyte supported cells (ESCs)**, preferably with different cathode materials

(1) D. The, S. Grieshammer, M. Schroeder, M. Martin, M. Al Daroukh, F. Tietz, J. Schefold, A. Brisse, *J. Power Sources*, **275**, 901 (2015).

(2) Q. Fang, L. Blum, N.H. Menzler, *J. Electrochem. Soc.*, **162**, F907 - F912 (2015).

Current densities in SOEC mode / ESC vs. CSC

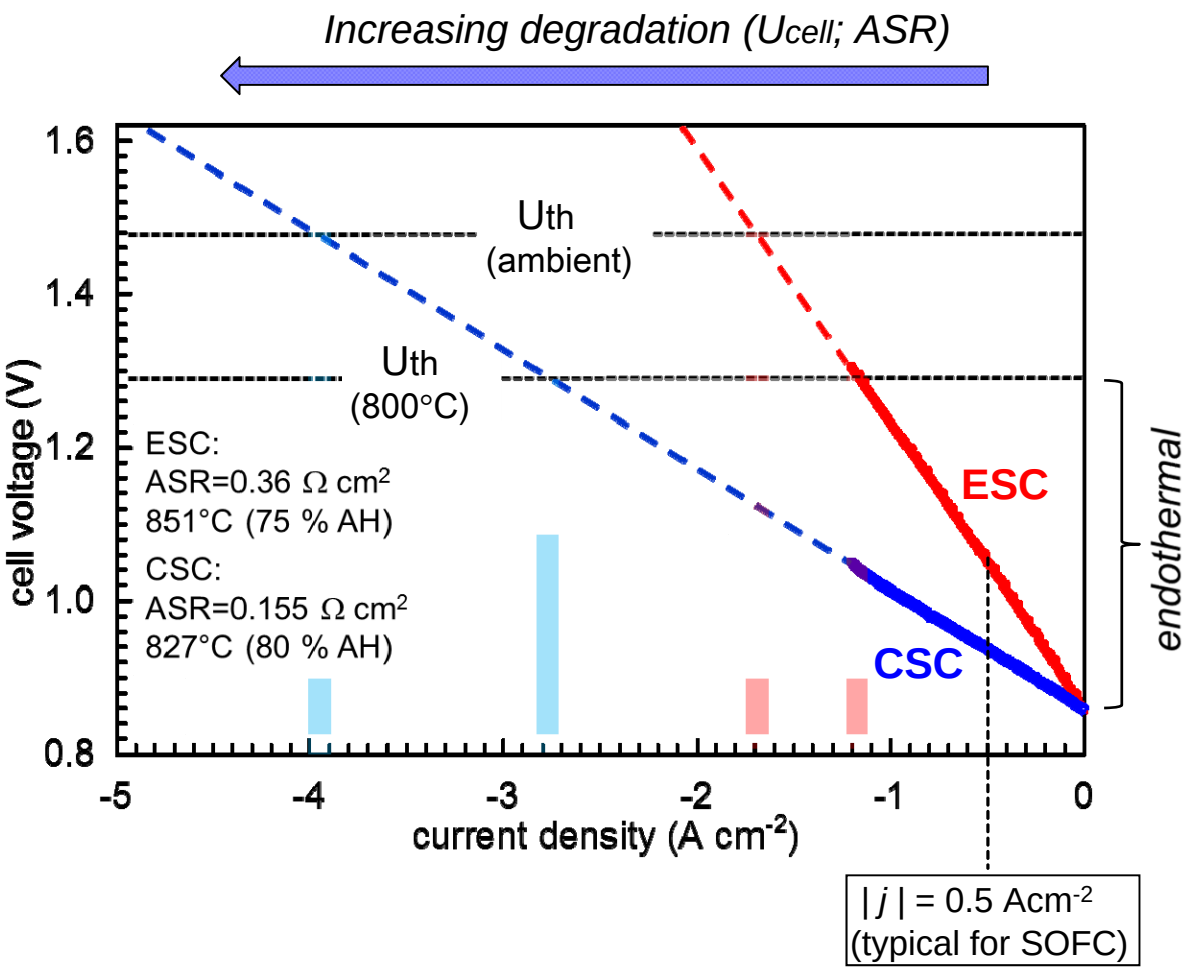


Figure: J. Schefold, A. Brisse, H. Poepke, Electrochim. Acta **179** (2015) 161.

CSC: cathode (H_2 electrode) supported cell
ESC: electrolyte supported cell
AH: absolute feed humidity (%)

Both cell types allow a large increase in current density $|j|$ compared to the typical SOFC operation, while maintaining $U_{cell} < U_{th}$

Measured CSC with up to $j = -6$ Acm^{-2} (*U-j* curve close to the one in the figure):
A. Wood, H. He, T. Joia, M. Krivy, D. Steedman, *JES* **163**, F327 - F329 (2016).

Electrolyte supported cell: 20,000 h @ -0.9 Acm^{-2}

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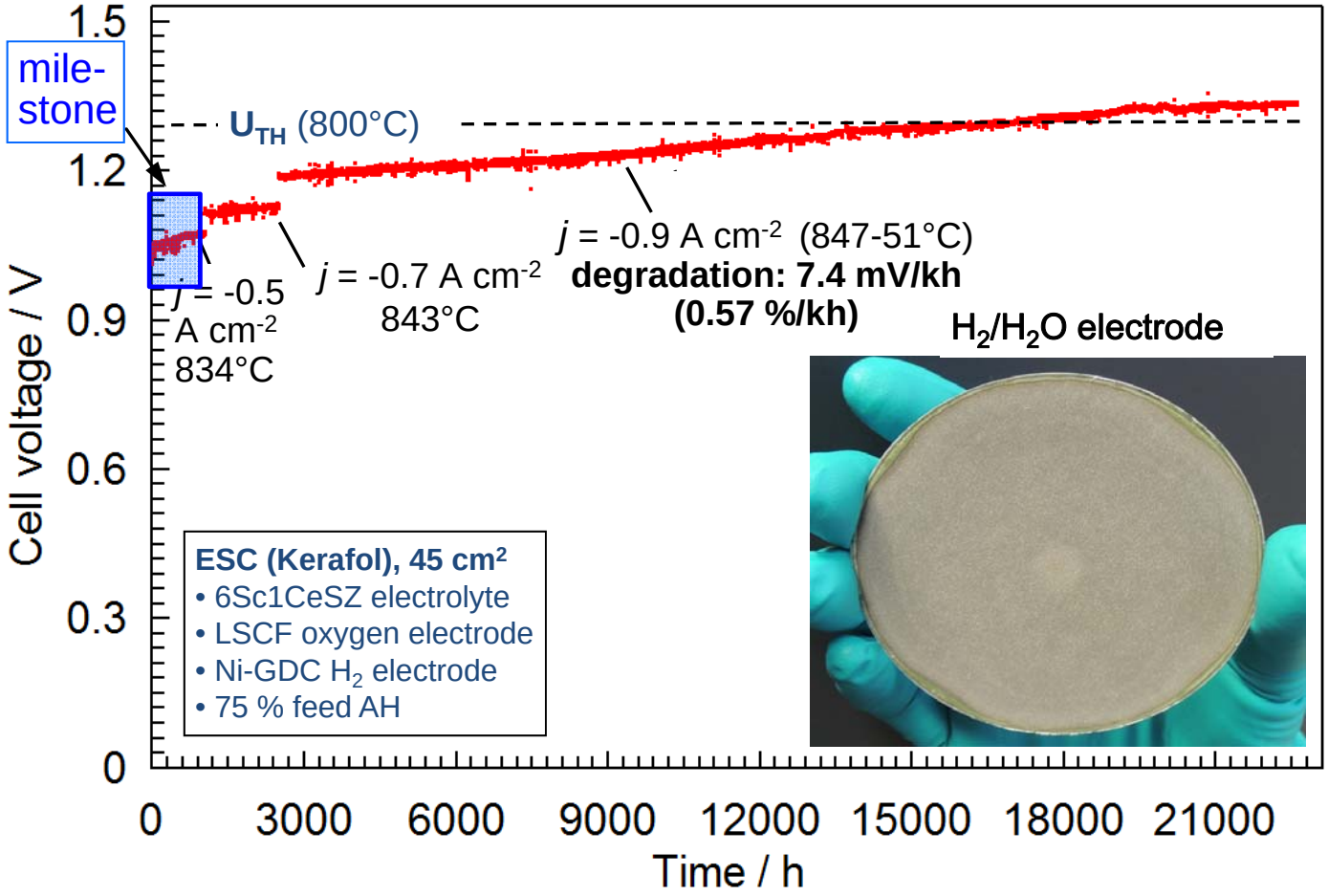
Cell voltage vs. time



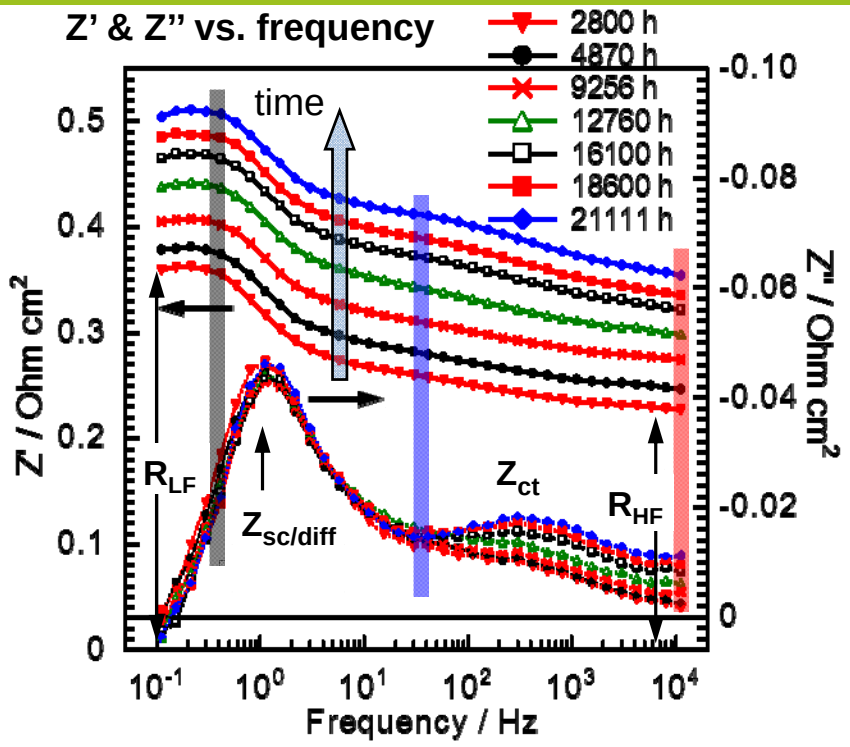
- longest reported test
- highest reported ESC current density

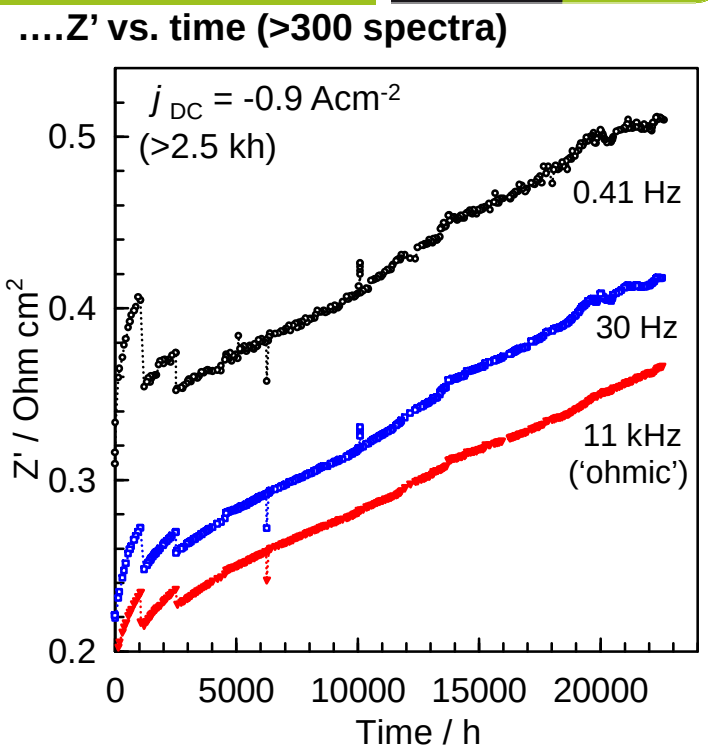
- OCV unchanged
- about linear *U-j* curves (fast kinetics)

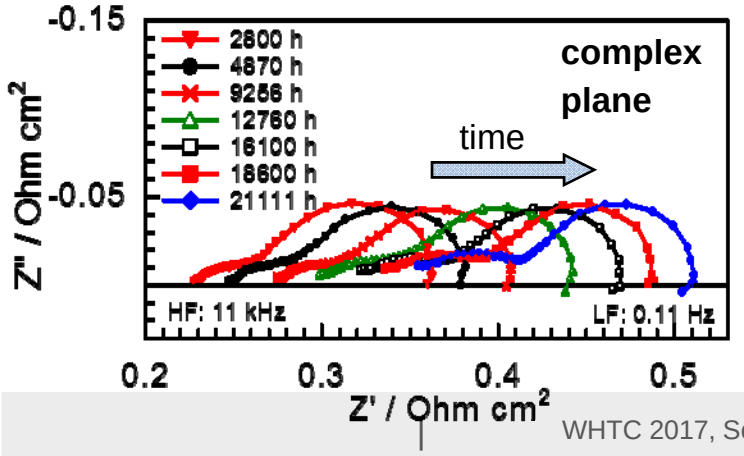
$U_{cell} < U_{th\ (800°C)}$ during 2 years (→ operation at theoretical efficiency limit with steam supply)

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

Impedance of ESC during 20,000 h @ -0.9 Acm^{-2}





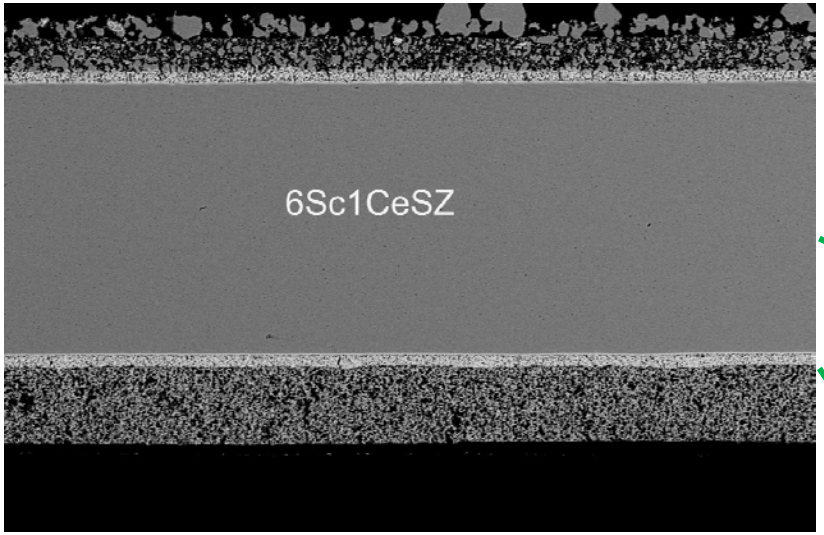


Degradation:

- largely ohmic, from electrolyte (avg. rise: 7 mΩcm^2/kh or 6.3 mV/kh)
- fast initial rate & rate decrease
- non-ohmic electrode contributions: from Z differences HF/IF/LF → ***very low electrode degradation***

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

Post test: Structure of aged cell



H_2-electrode (cathode):
Ni(coarse)/$(Ce,Gd)O_{2-\delta}$ (~10 µm)
Ni(fine)/$(Ce,Gd)O_{2-\delta}$ (~20 µm)

Adhesion layer:
$(Ce,Gd)O_{2-\delta}$ (~ 5 µm)

Electrolyte:
$(Zr,Sc,Ce)O_{2-\delta}$ (~ 120 µm)

Diffusion barrier layer:
$(Ce,Gd)O_{2-\delta}$ (~ 5 µm)

O_2-electrode (anode):
$(La,Sr)(Co,Fe)O_{3-\delta}$ (~ 40 µm)

Cell after dismantling:

- largely intact cell structure
- Sr-Zirconate formation at interface electrolyte/oxygen electrode
- Si accumulation at H_2/H_2O electrode, most likely coming from impurities in the steam supply (1)

(1) Q. Fu et al., presented at *ICE-2017*, Copenhagen, 12-15 June 2017

Increase in current density (ESC)

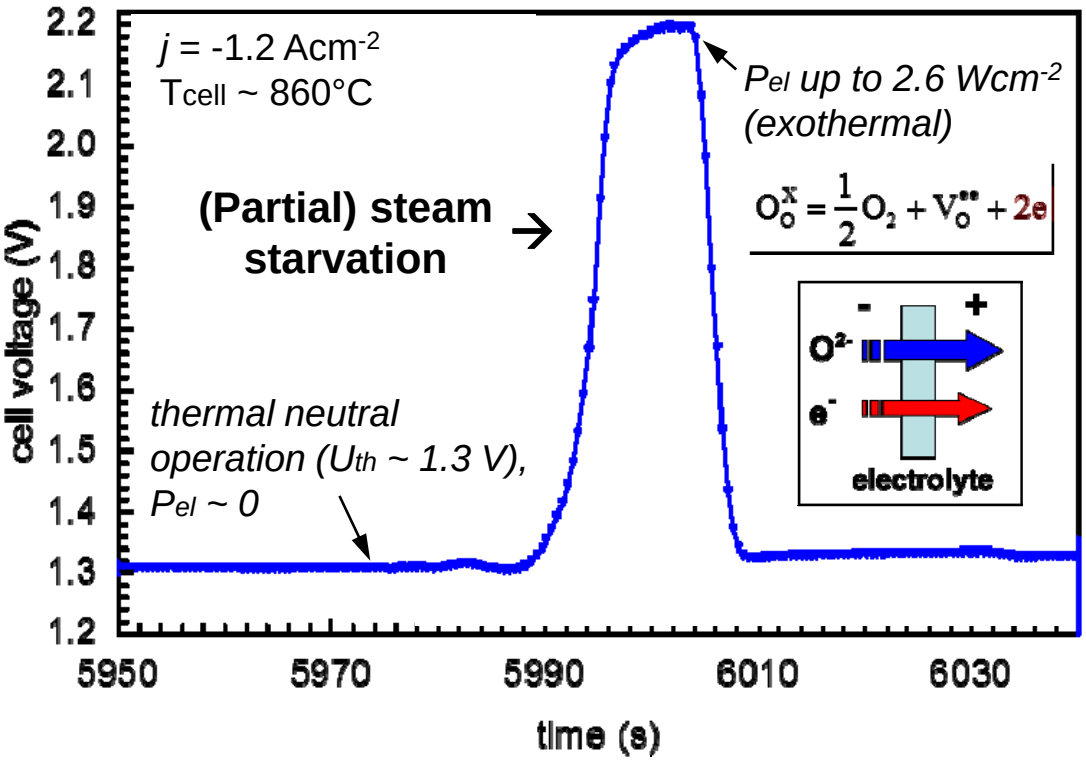
- **Cell with 6Sc1CeSZ electrolyte**
- **-1.2 Acm^{-2} current density**
- **60 % steam conversion**

- Ca. 5 kh linear degradation, then accelerated due to anode delamination (total ~10 kh at -1.2 Acm^{-2})
- degradation in linear range: 11 mV/kh
- no limitation evident from H_2 electrode (cathode)

→ higher current density at least feasible for intermediate time periods.

Steam starvation incident (-1.2 Acm^{-2})

Cell voltage vs. time



Steam starvation (failure of evaporator and of voltage safety):

- → Increase in cell voltage up to 2.2 V (limited by electronic conduction in electrolyte)[1]
- → High thermal stress ($P_{el,cell}$ up to 2.6 Wcm^{-2}, depending on degree of starvation) → accelerated delamination ?

[1] J. Schefold, A. Brisse, M. Zahid, *J. Electrochem. Soc.* **156** (2009) B897.

Decrease of operation temperature to 780°C

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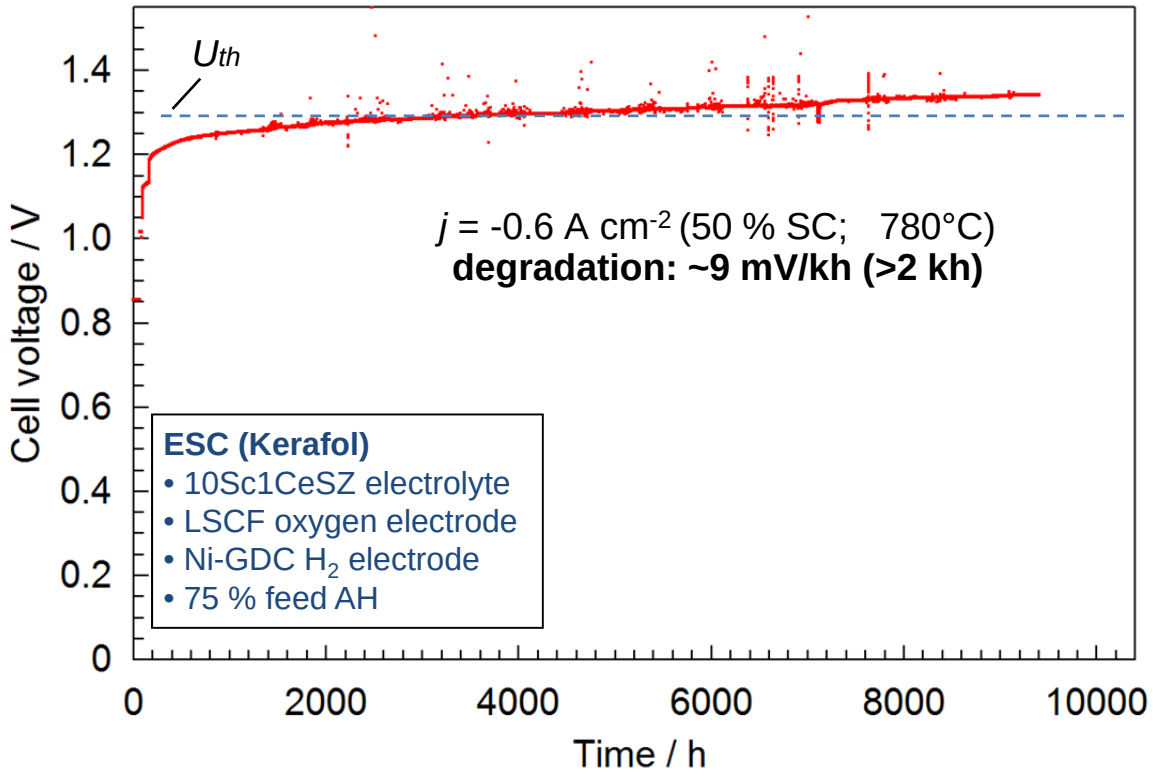
Cell voltage vs. time



- current density 20 % above typical SOFC values
- **cell voltage (1.25 – 1.35 V) close to thermal neutral voltage U_{th}**
- **low degradation**

Summary

Background

- *SOC allow highest energy-conversion efficiencies and reversible operation*
- *Electrode supported cells (CSCs): current-density increase so far limited by degradation*

Long-term testing (I): 23,000 h with electrolyte supported cell (ESC)

- *20,000 h with j = -0.9 Acm^{-2} → 7.4 mV/kh (0.57 %/kh) voltage degradation*
- *degradation predominantly ohmic; small electrode degradation*
- *post test work:*
  - *Sr-Zirconate formation (well-known from SOFC)*
  - *some delamination of the oxygen electrode*
  - *Si accumulation at H_2 electrode*

Long-term testing with ESC (II):

- *~10,000 h with high current density (-1.2 Acm^{-2})*
- *~10,000 h (running) at lower temperature (780°C)*
- *Outlook / ongoing work: commercial cells (3YSZ…..); cyclic operation; co-electrolysis, increase in steam-conversion rate…..*

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Thank you for your attention!

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