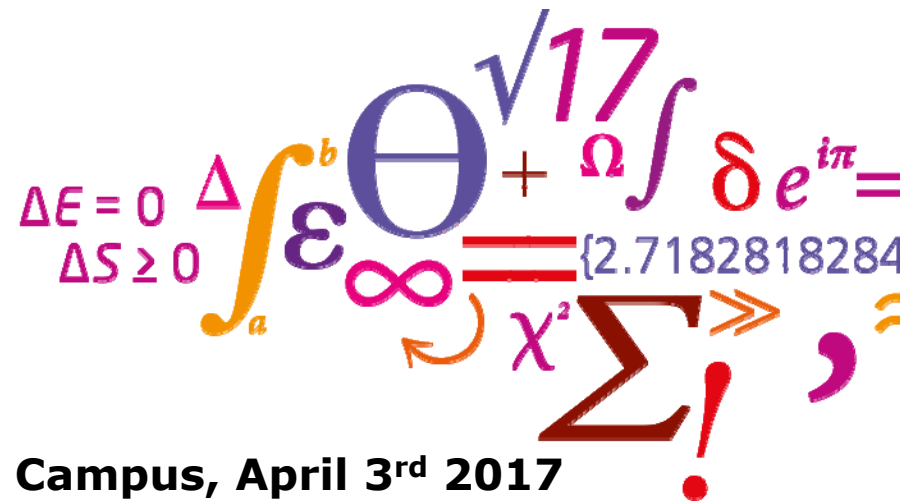


Electrolysis for energy storage

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Acknowledgements to
 colleagues at DTU
 Energy Conversion

Joint Gas Workshop
Building 424, Room 025, DTU Lyngby Campus, April 3rd 2017



$$\Delta E = 0 \quad \Delta S \geq 0 \quad \int_a^b \varepsilon \Theta + \Omega \int \delta e^{i\pi} = \{2.7182818284\}$$

Introduction

- **At DTU Energy we have been doing R&D on all the three main types of electrolyzer cells for some years**
 - **Solid Oxide Electrolysis Cell (SOEC) since 2002**
 - **Alkaline Electrolysis Cell (AEC) since 2009**
 - **Polymer Electrolyte Membrane Electrolysis Cell (PEMEC) since 2015**
- **We spend more than 50 man-years per year on electrolysis R&D because we think that a world based on renewable energy needs electrolysis**

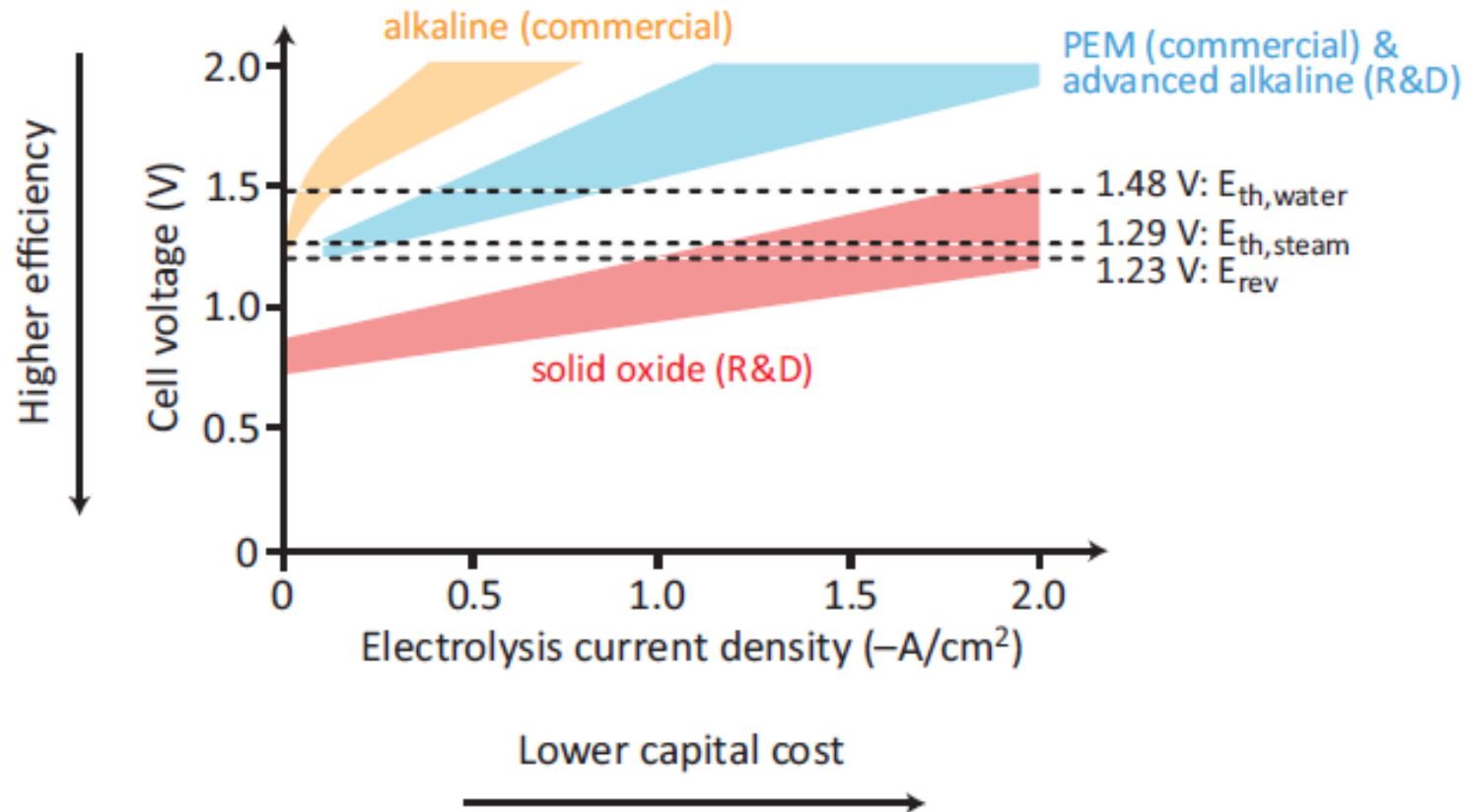
We need electrolysis because:

- **Many technical principles suitable for energy conversion + storage:**
 - **pumping of water to high altitudes**
 - **batteries**
 - **superconductor coil**
 - **flywheels**
 - **Thermo-chemical looping**
 - **Solar Thermal Electrochemical**
 - **Photo-electrochemical HER and CO₂ reduction**
- **All are very important! But: first 4 are not for long distance (> 500 km) transport like cars, trucks, ships, airplanes. 3 last are early stage research - may prove efficient in the far future.**
- **Therefore, within a “foreseeable” future (10 years): **Electrolysis is necessary in order to get enough renewable fuels!****

Electrolyser status I

- **Two types commercialized Alkaline (AEC) and polymer electrolyte (PEMEC), i.e. you can buy them. Both have operation temperature around 60 - 120 °C.**
- **None of them are commercial from an energy conversion and storage point of view in today's energy markets**
- **If significant amounts of green fuel to be produced via electrolysis in near future (the next few years) - only AEC is available multi MW scale**
- **Compact and expensive PEMEC popular for demo-projects – noble metals**
- **Several other types are under development**
- **SOEC is in demo phase – e.g. Sunfire (DE), Haldor Topsøe A/S (DK)**

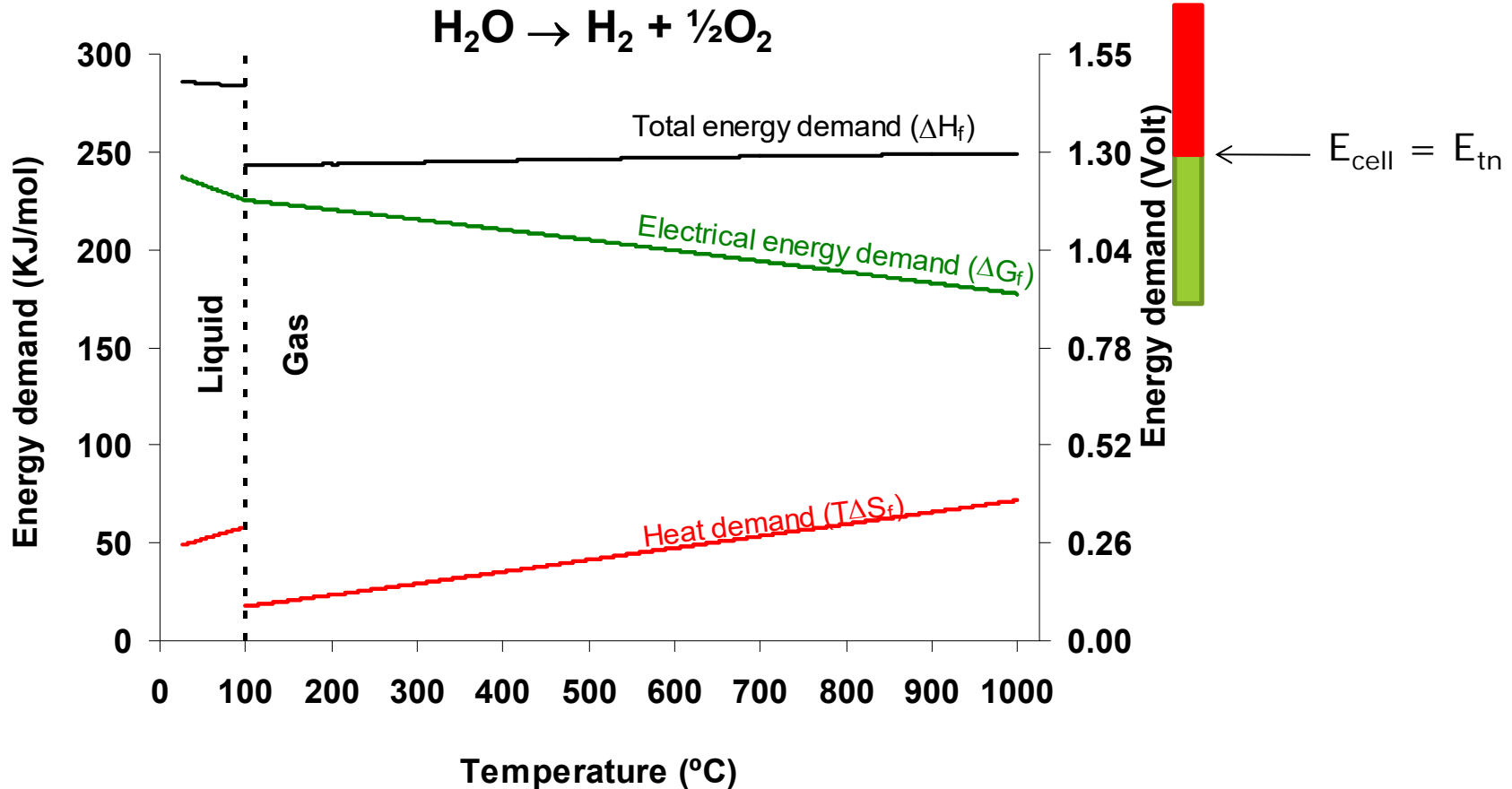
Electrolyser status II



Typical ranges polarization ranges for state-of-the-art water electrolysis cells. $E_{th,water}$ and $E_{th,steam}$ are the thermoneutral voltages. E_{rev} is the reversible voltage at standard state.

C. Graves, S. D. Ebbesen, M. Mogensen, K. S. Lackner, *Renew. Sustain. Energy Rev.*, 15 (2011) 1–23

Thermodynamics



Energy ("volt") = Energy (kJ/mol)/2F

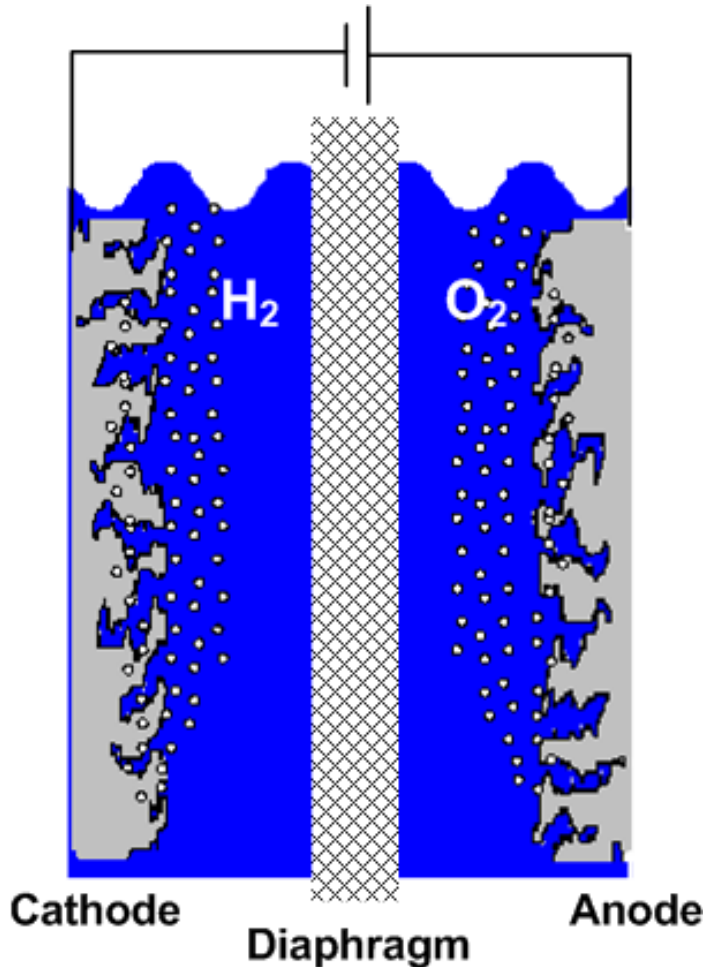
$i \propto E_{\text{cell}} - \Delta G/2F$

$E_{\text{tn}} = \Delta H/2F$

Price $\propto 1/i$ [A/cm²],

$\Delta H/\Delta G > 1$, $\eta = 100\%$ at $E = E_{\text{tn}}$ (no heat loss)

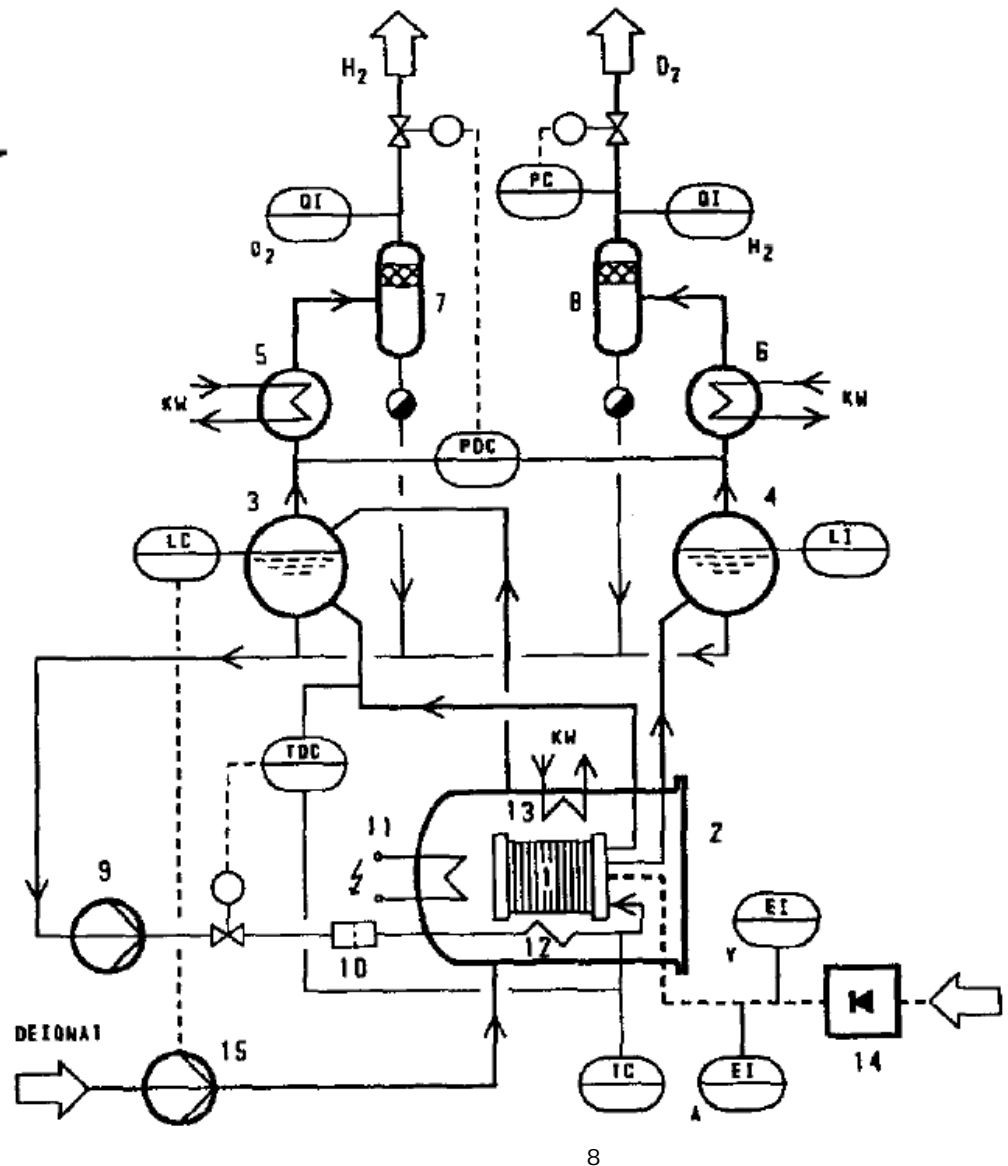
Classical Alkaline Electrolysis



- **Anode (+):** $2\text{OH}^- \rightarrow \frac{1}{2}\text{O}_2 + \text{H}_2\text{O} + 2\text{e}^-$
- **Cathode (-):** $2\text{H}_2\text{O} + 2\text{e}^- \rightarrow \text{H}_2 + 2\text{OH}^-$
- **Very simple reaction, which may be carried out in practice at a temperature as low as 60 °C**
- **Even so, it shows up that systems are not that simple**

Process flow diagram of a modern electrolyzer

- 1 Electrolytic cells
- 2 Electrolyzer pressure vessel
- 3 Hydrogen-electrolyte separator
- 4 Oxygen-electrolyte separator
- 5 Hydrogen cooler
- 6 Oxygen cooler
- 7 / 8 Condensate separators
- 9 Electrolyte circulating pump
- 10 Electrolyte filter
- 11 Electric heater
- 12 Electrolyte heater/cooler
- 13 Water cooler
- 14 Rectifier unit
- 15 Electrolyte feed pump



Hydrogenics Alkaline system



From Hydrogenics' homepage:

HySTAT® 10 – 10

10 Nm³H₂ h⁻¹, 5.4 kWh/Nm³ H₂

High temperature high pressure alkaline electrolysis cell (HTP-AEC) at DTU Energy

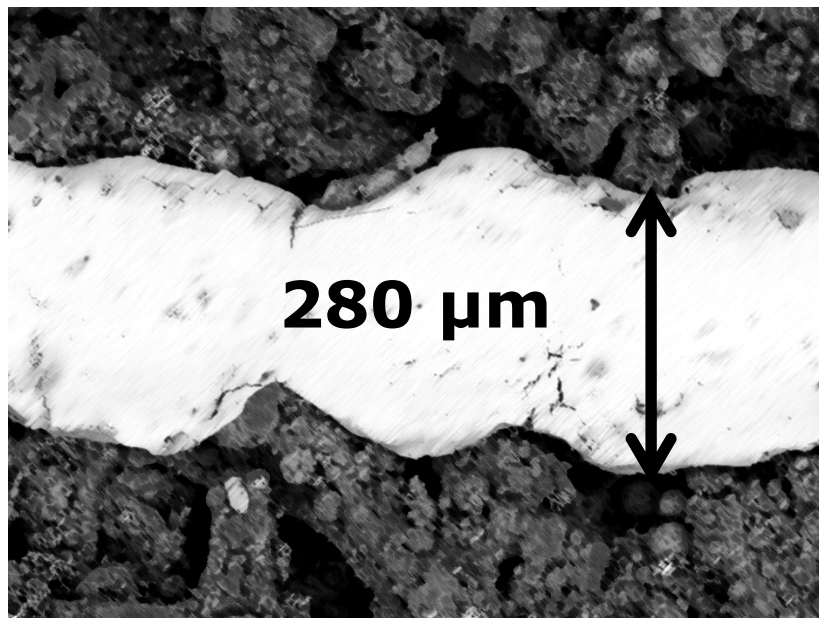
Advantages of operating at $T \sim 150-300 \text{ }^\circ\text{C}$, $P \sim 20-100 \text{ atm}$:

1. **Increased electrolyte conductivity.**
(Reduced ohmic losses. Lower operating cost)
2. **Improved electrode performance.**
(Reduction of capital and operating cost)
3. **Use of aq. KOH electrolyte with gas diffusion electrodes.**
(Improved mass transport. No need for electrolyte degassing. Reversible operation)
4. **System simplification and increased efficiency arising from improved performance.**
(No need for cooling and electrolyte circulation)
5. **Production of pressurized H_2 (and O_2). No/reduced compression need.**
(Reduction of capital and operating cost)
6. **Decreased footprint arising from improved performance.**
(Reduction of capital cost)
7. **Reduced electricity demand. Possibility to use "waste" heat.**
(Reduction of operating cost)

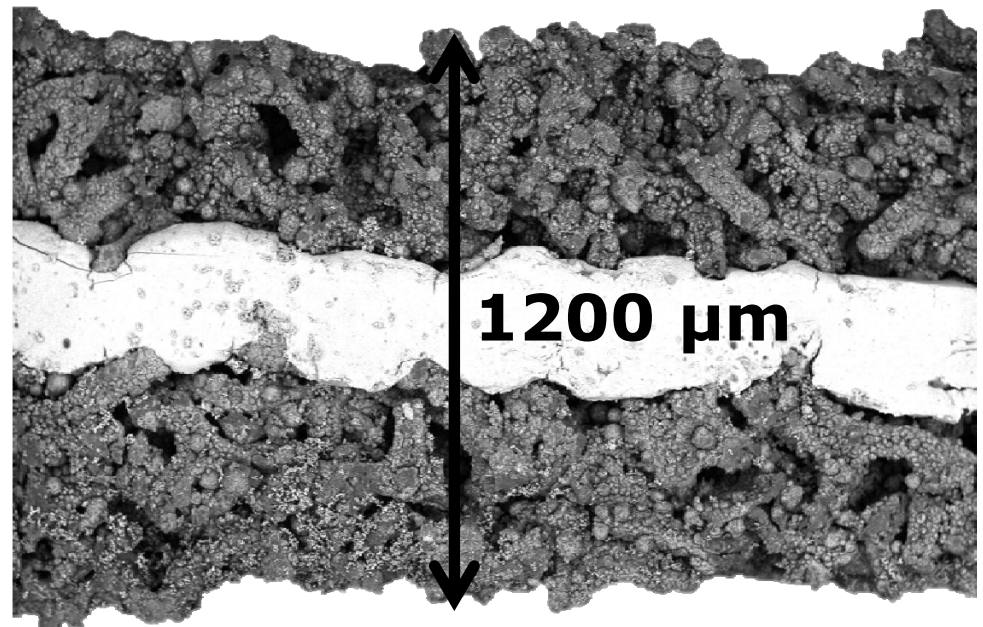
High temperature alkaline electrolysis

Design and upscaling

- NiFeCrAl foam (oxygen electrode)
- Tape cast porous YSZ as electrolyte (soaked with concentrated KOH aq.)
- Inconel foam (fuel electrode)
- Cell size: \varnothing 4.8 cm (circular); 5 x 5 cm² (rectangular)

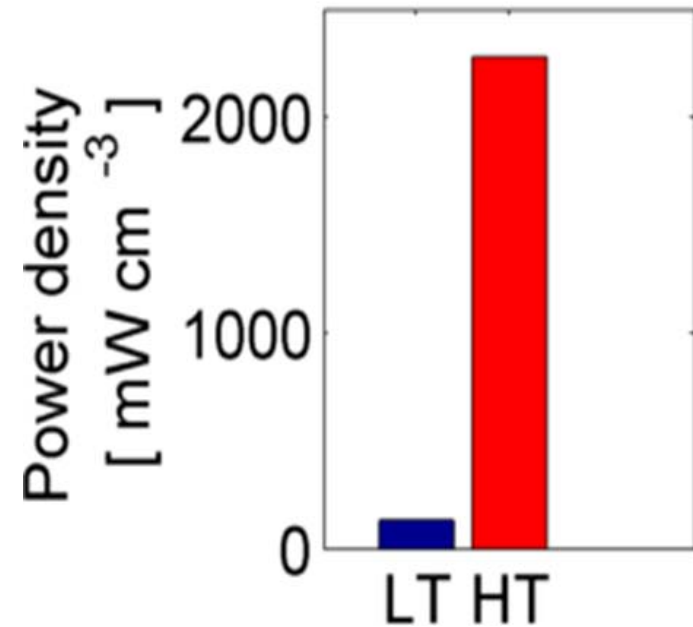
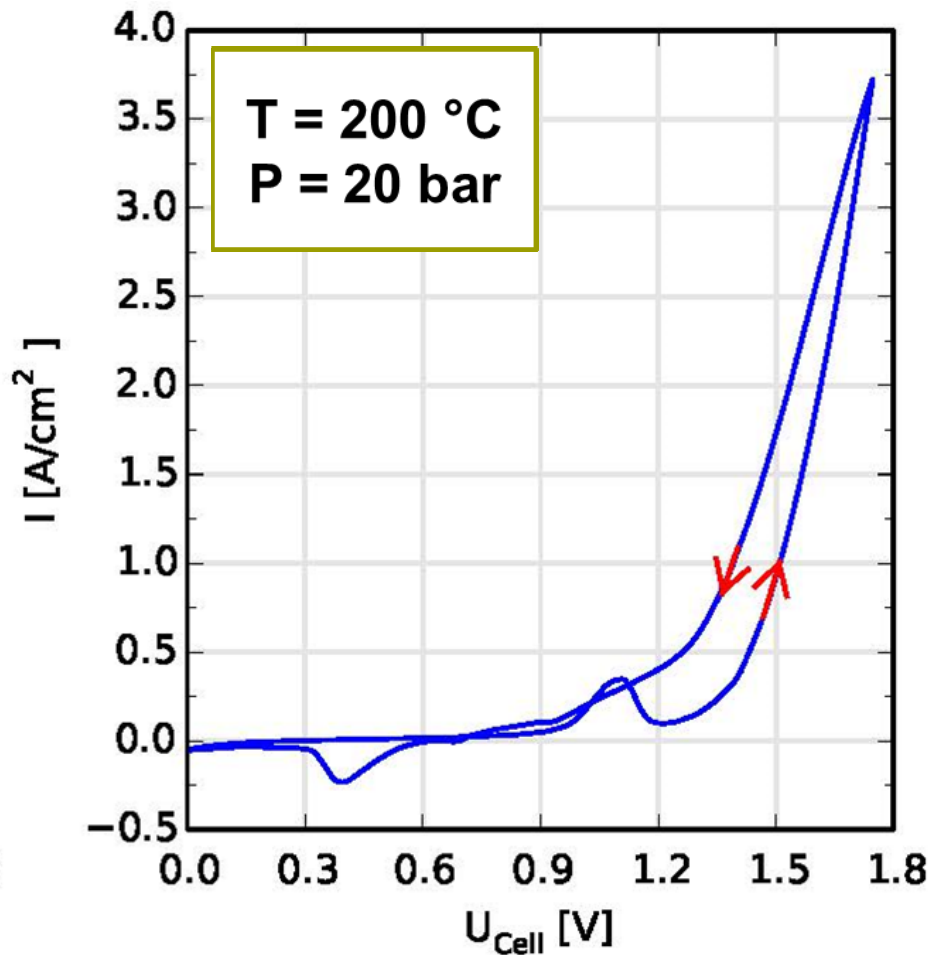


Cell#6_0009 2014-08-21 N D5.3 x300 300 um



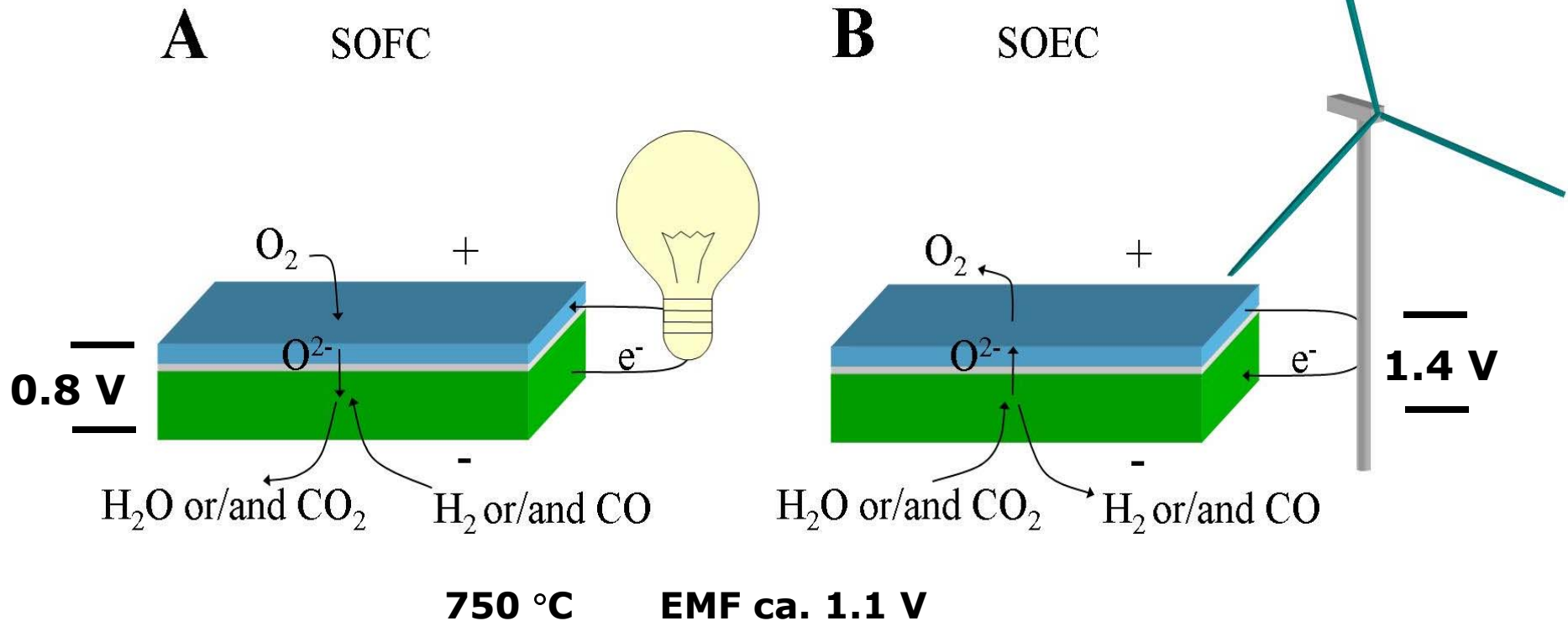
C. Chatzichristodoulou, F. Allebrod, and M. B. Mogensen, High Temperature Alkaline Electrolysis Cells with Metal Foam Based Gas Diffusion Electrodes, *J. Electrochem. Soc.*, 163(11): F3036-F3040, 2016.

HTP-AEC performance and comparison with Low Temperature AEC



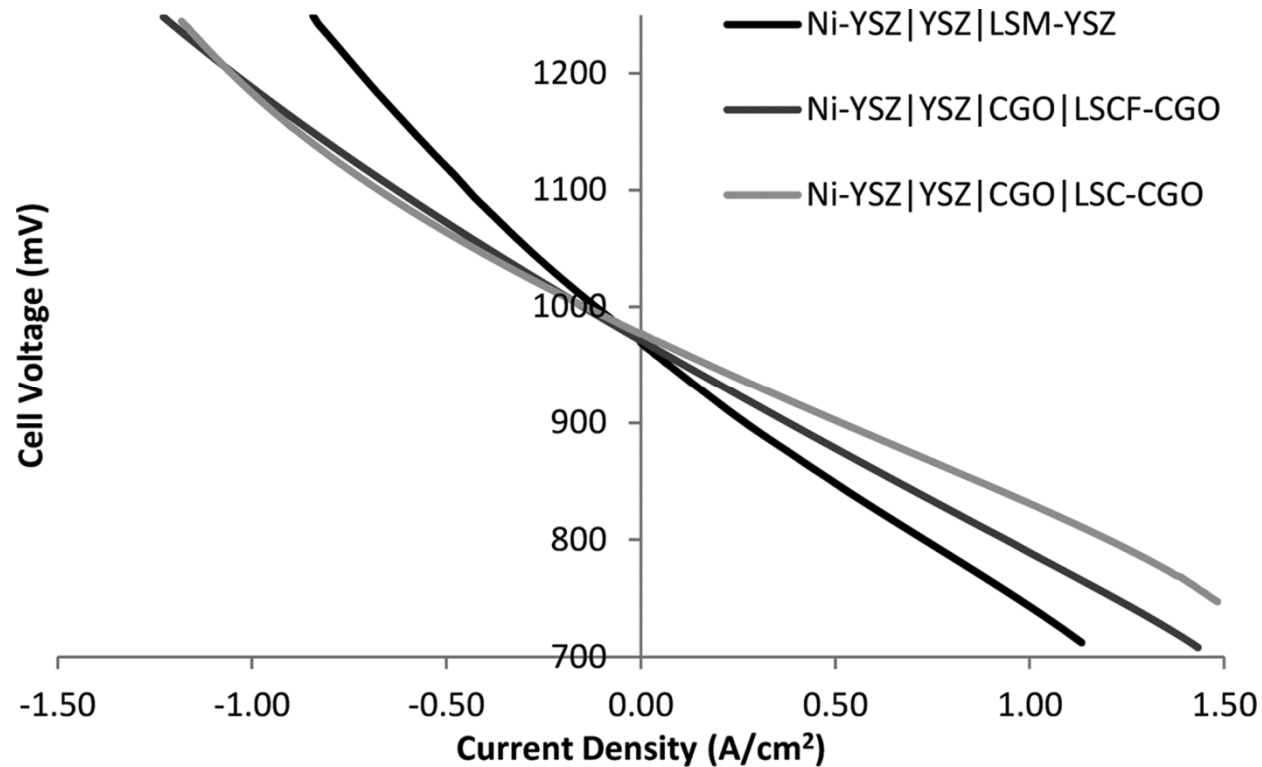
C. Chatzichristodoulou, F. Allebrod, and M. B. Mogensen, *J. Electrochem. Soc.*, 2016, 163, F3036

Principle of solid oxide electrolysis and fuel cells (SOC)



Working principle of a reversible Solid Oxide Cell (SOC). The cell can be operated as a SOFC (A) and as a SOEC (B).

DTU Energy - Reversible SOC performance

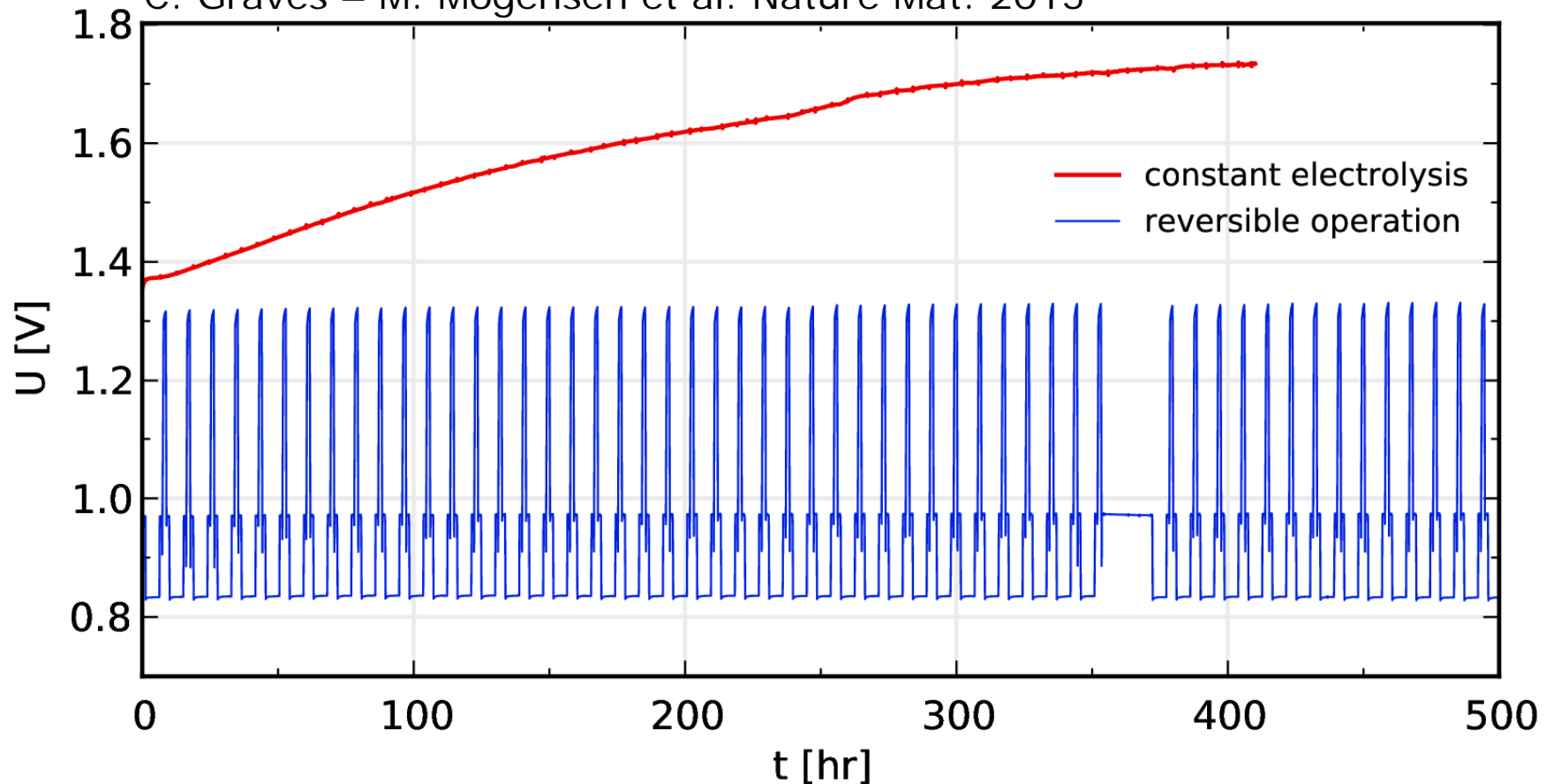


Polarization characterization for the planar Ni-YSZ based cells: Ni-YSZ|YSZ|LSM-YSZ, Ni-YSZ|YSZ|CGObarrier|LSCF-CGO, and Ni-YSZ|YSZ|CGObarrier|LSC-CGO. Conditions: 800 °C, 50% H₂O–50% H₂, pure O₂ at O₂-electrode

S. D. Ebbesen, S. H. Jensen, A. Hauch, M. B. Mogensen, *Chemical Reviews*, 114 (2014) 10697

Reversible operation

C. Graves – M. Mogensen et al. Nature Mat. 2015



SOC stability during constant current density (-1 A cm^{-2}) electrolysis test compared to reversible cycling test of 1 h EC (-1 A cm^{-2}) + 5 h FC ($+0.5 \text{ A cm}^{-2}$). During open-circuit and FC mode, $\sim 25 \text{ L/h}$ of $\text{pH}_2/\text{pH}_2\text{O} \approx 50/50$ and EC mode $\sim 13 \text{ L/h}$ of $\text{pH}_2/\text{pH}_2\text{O} \approx 10/90$ gas was supplied. Pure O_2 at the O_2 -electrode.

Summary

- **PEMEC: very high power densities at high cell voltage – high costs of materials - relative low energy efficiency- commercial available**
- **LT- AEC: low cost - low power density – commercial available**
- **HTP-AEC: potential low cost, very high power density, high efficiency – not commercial available, early stage**
- **SOEC: potential low cost, very high power density, high efficiency – demo can be ordered**
- **Lifetime seems promising for all three types**
- **Still huge potentials for improvements by R&D**