Energy Efficient Production of Pressurized Hydrogen - E2P2H2

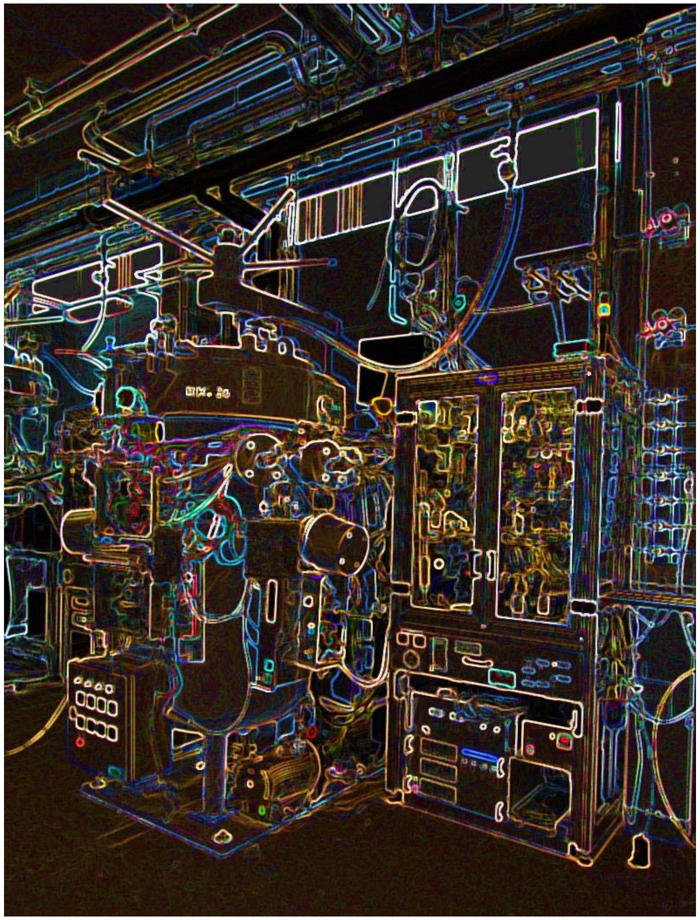
(EUDP project commenced by DTU Energi in collaboration with HTAS, 2014-2016)

Workshop, April 4th 2017

Søren Højgaard Jensen

Department of Energy Conversion and Storage, Technical University of Denmark, Roskilde, Denmark.

shjj@dtu.dk

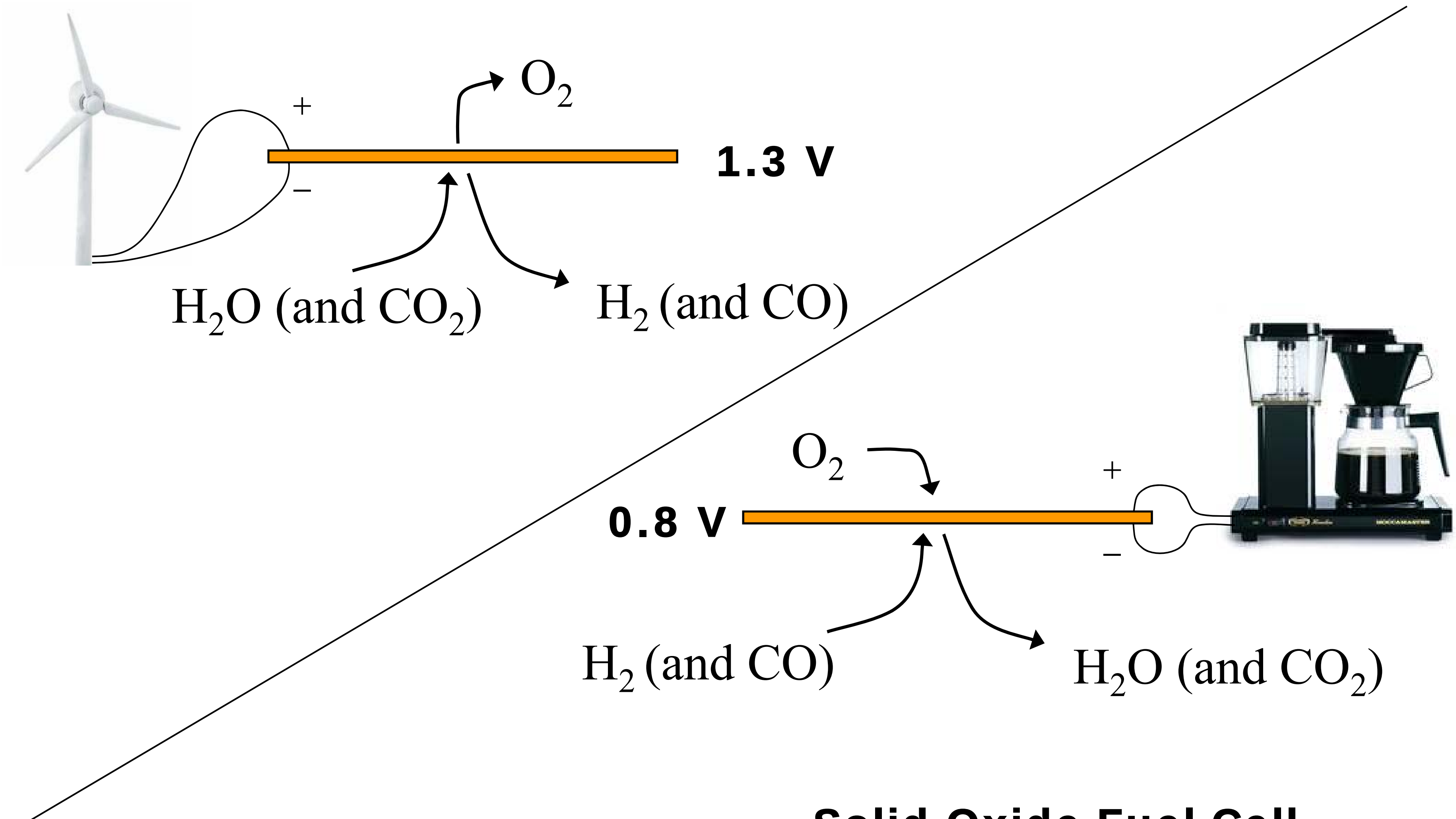


Cover on *FUEL CELLS* **16** (2) 2016

DTU Energy
Department of Energy Conversion and Storage

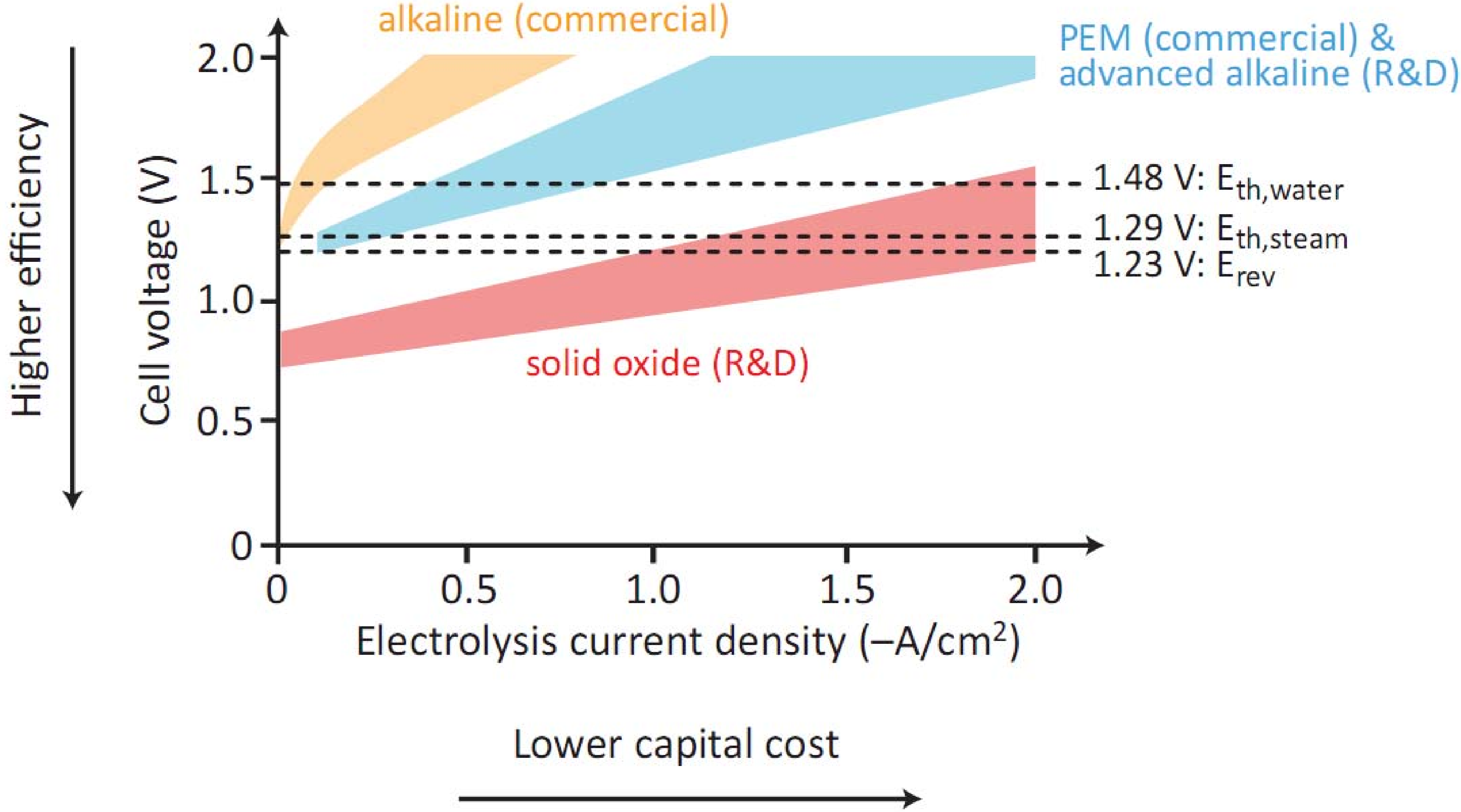
The Solid Oxide Cell

Solid Oxide Electrolysis Cell



Solid Oxide Fuel Cell

Why Are Solid Oxide Electrolysers Interesting?



C. Graves, S.D. Ebbesen, M. Mogensen, K.S. Lackner, *Renewable and Sustainable Energy Reviews*. 15 (2011) 1–23

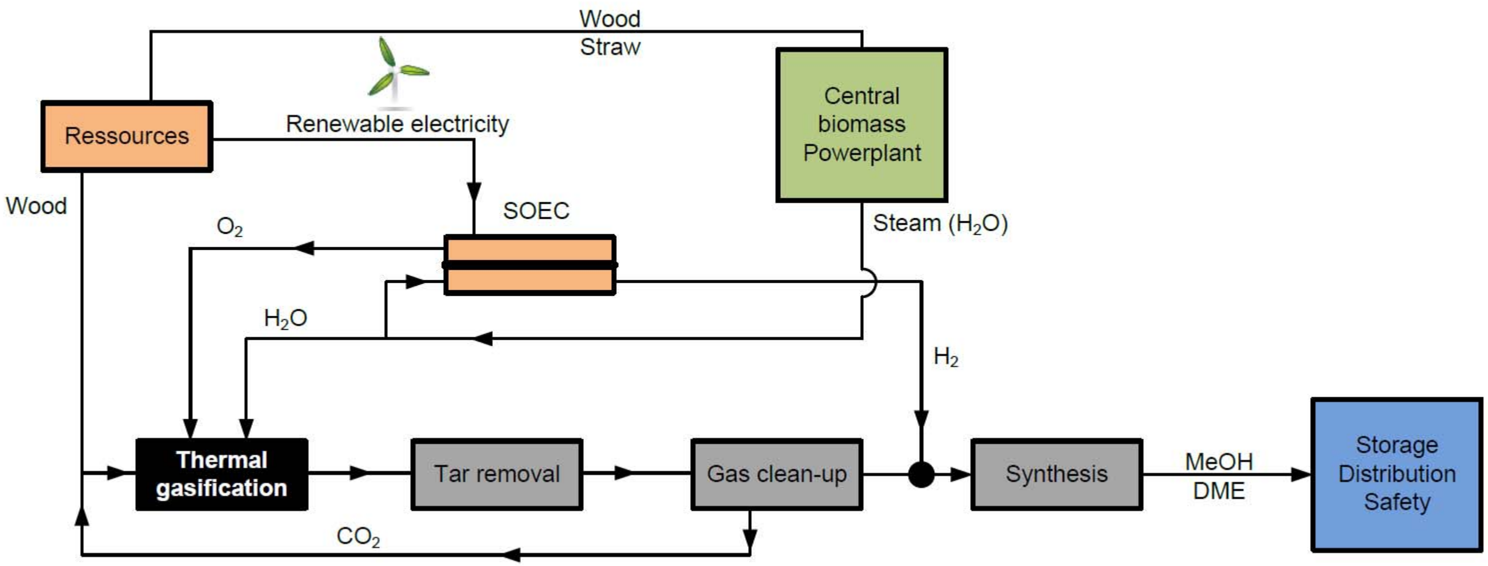
Synergy with utilization of biomass

- Biogas from biomass consist mostly of CO_2 (40%) and CH_4 (60%)
- If CO_2 in the biogas can react with H_2 we can generate app. 50% more CH_4

Photo: Mikael Kau/

http://www.chamco.net/Gasification.htm

SOEC Operating Strategy

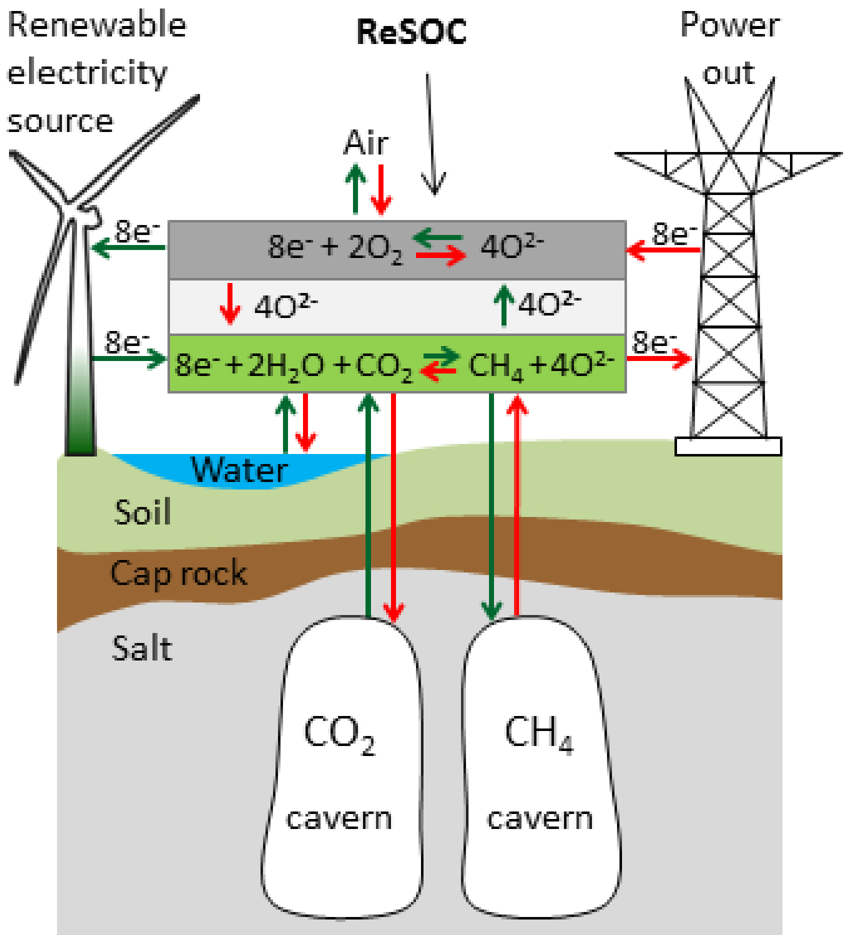


Two operating strategies

1. Always at optimal H-C ratio for the synthesis step
2. SOEC operates at 1/3 of nominal power at high electricity prices (generates enough O_2 for gasification)

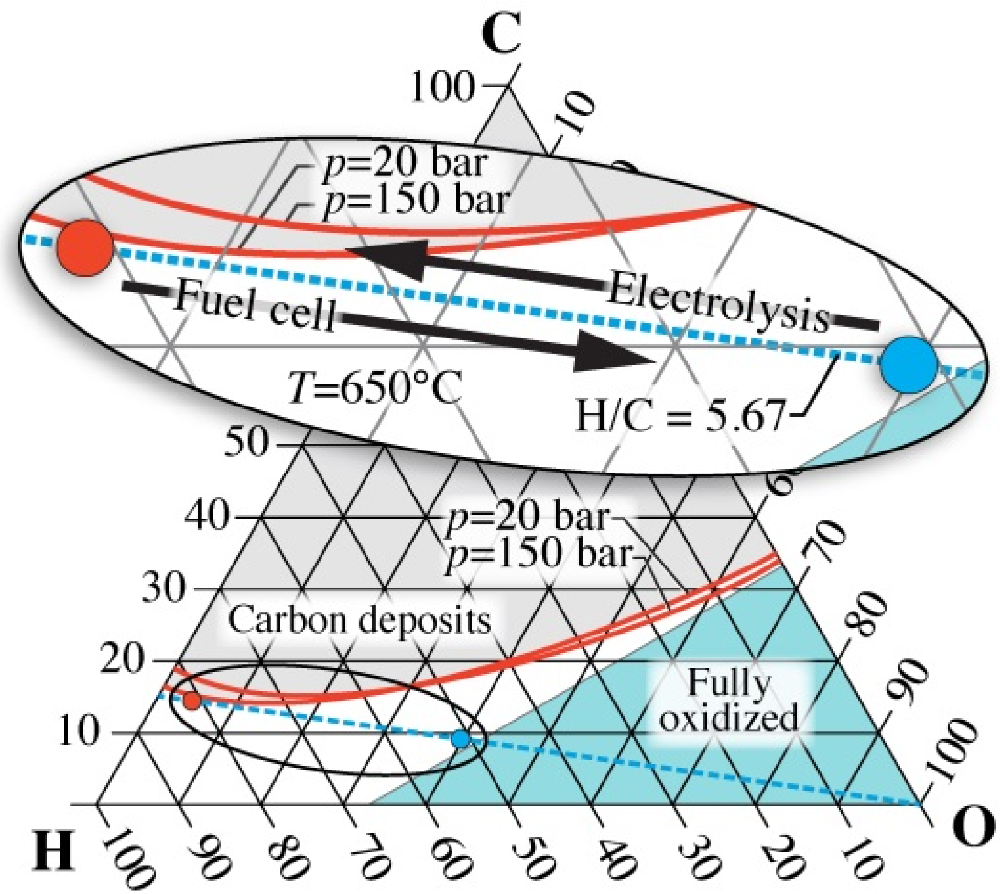
GreenSynFuels Report: http://www.hydrogennet.dk/groennesynfuels/

Pressurized SOCs for large-scale electricity storage



S. H. Jensen, C. Graves, M. Mogensen, C. Wendel, R. Braun, G. Hughes, Z. Gao and S. A. Barnett, *Energy and Environmental Science* **8** (2015) 2471

Pressurized SOCs for large-scale electricity storage



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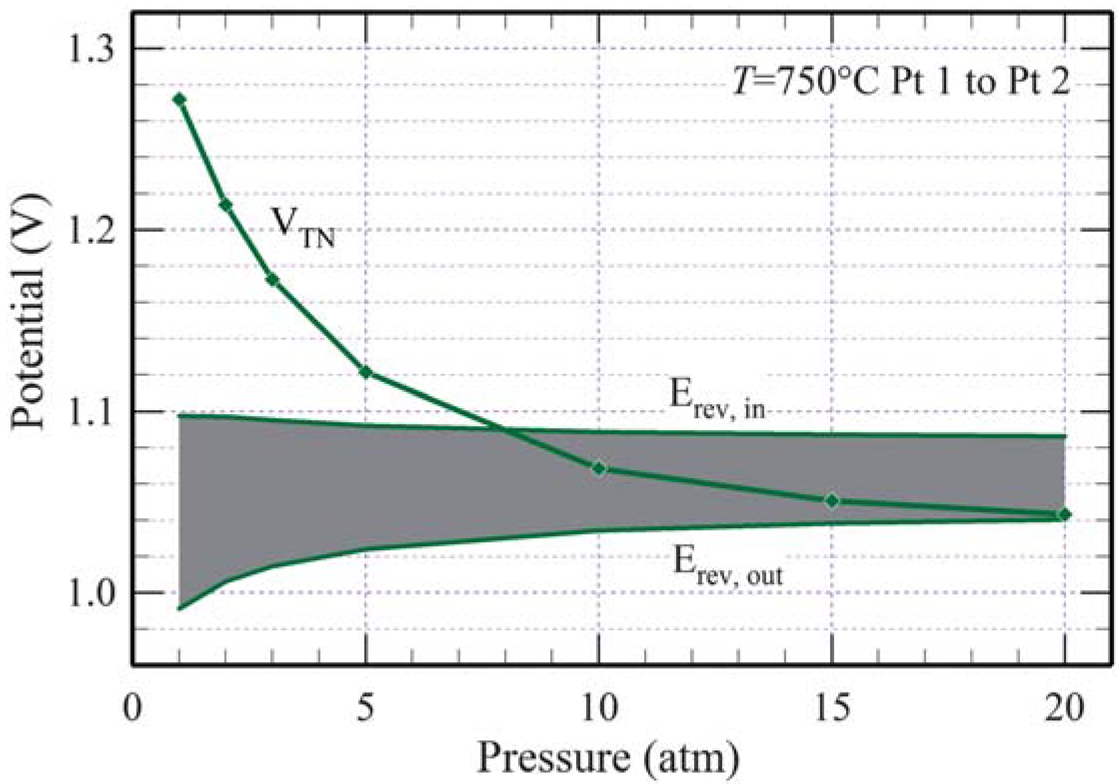
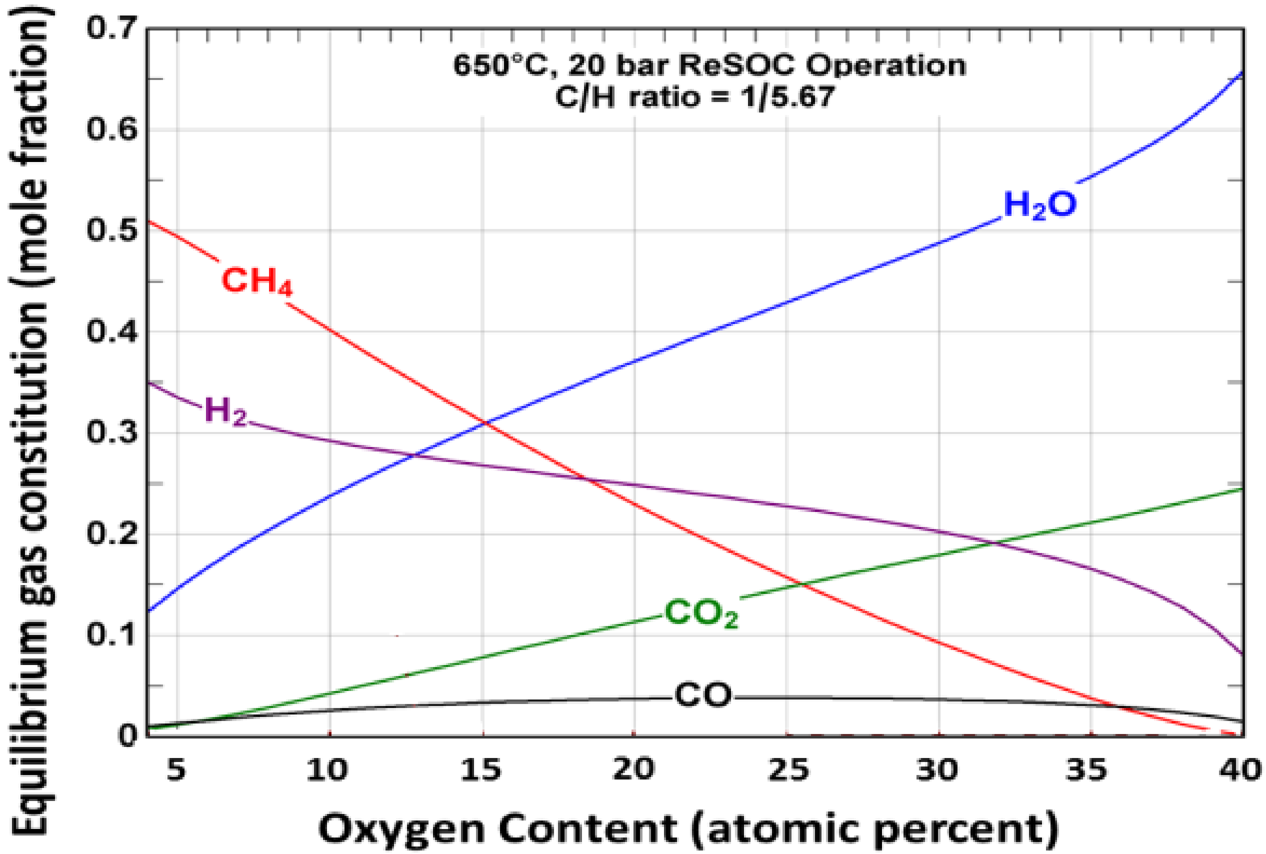


Thermal-neutral potentials versus P at T ¼ 750 C for a cell operating over a fuel composition range from pt 1 to pt 2 (Fig. 3). Shown for comparison are the Nernst potential ranges for fuel compositions from pt 1 to pt 2 and oxygen at the other electrode.

Energy Environ. Sci., 2011, 4, 944–951

Pressurized SOCs for large-scale electricity storage



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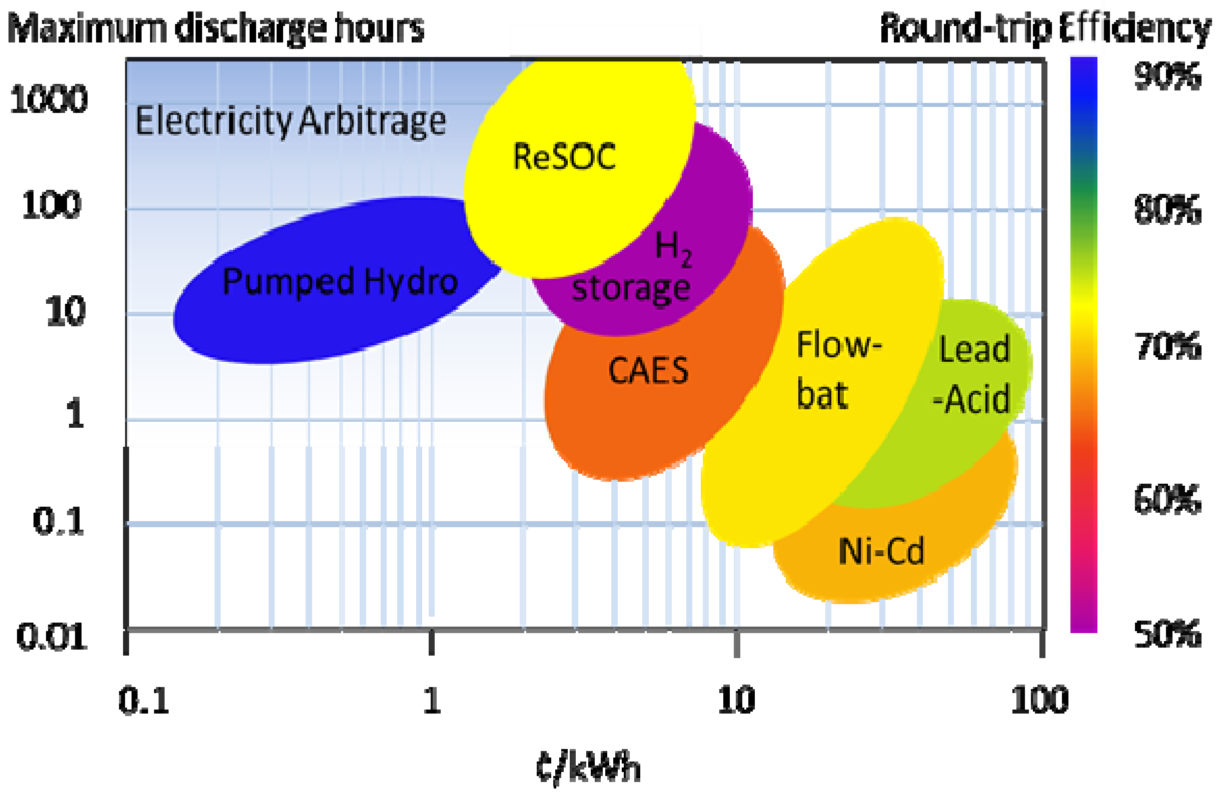

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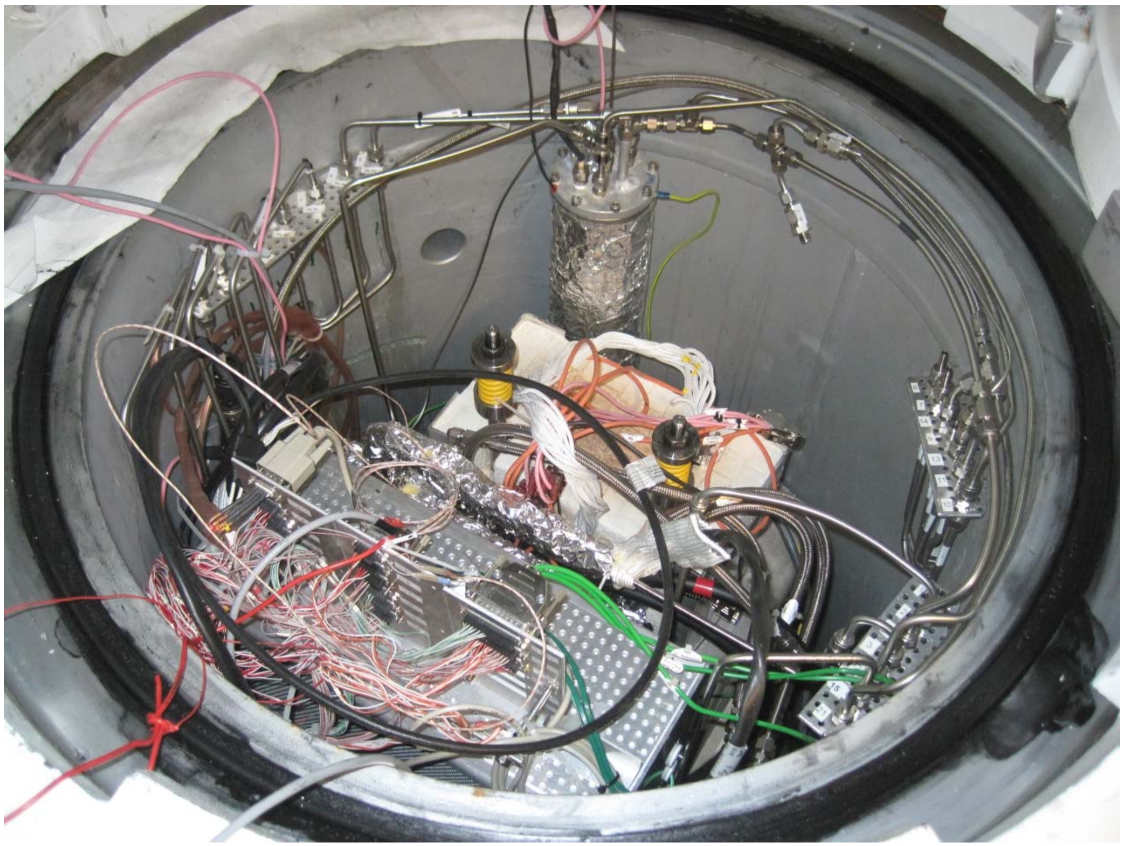
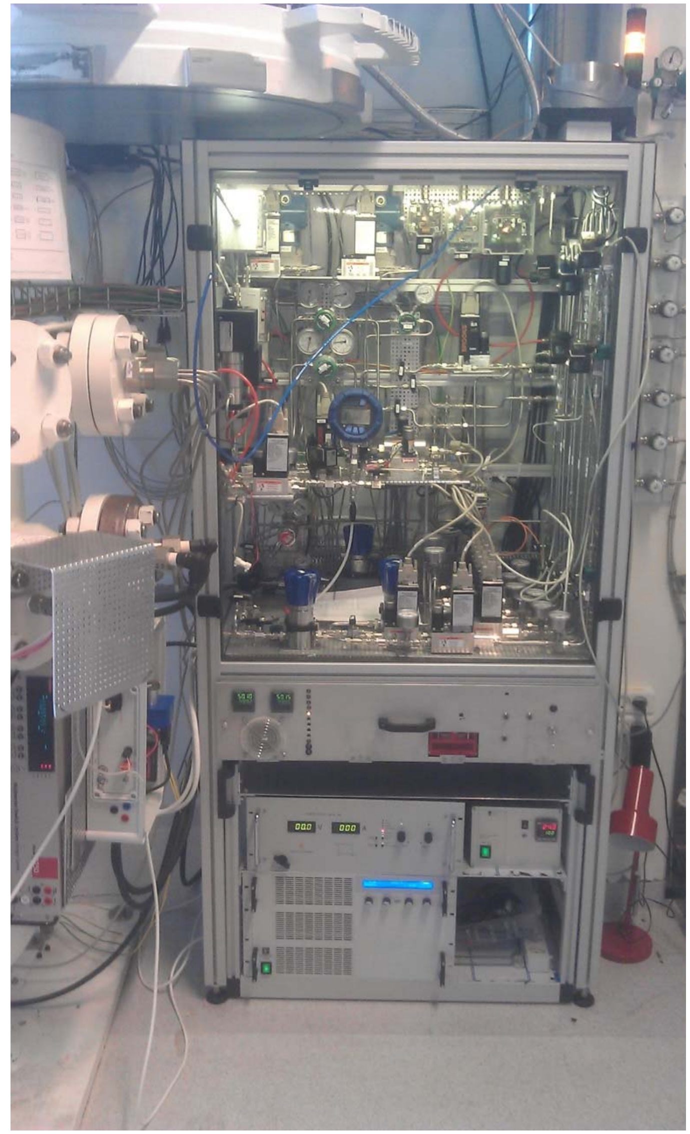
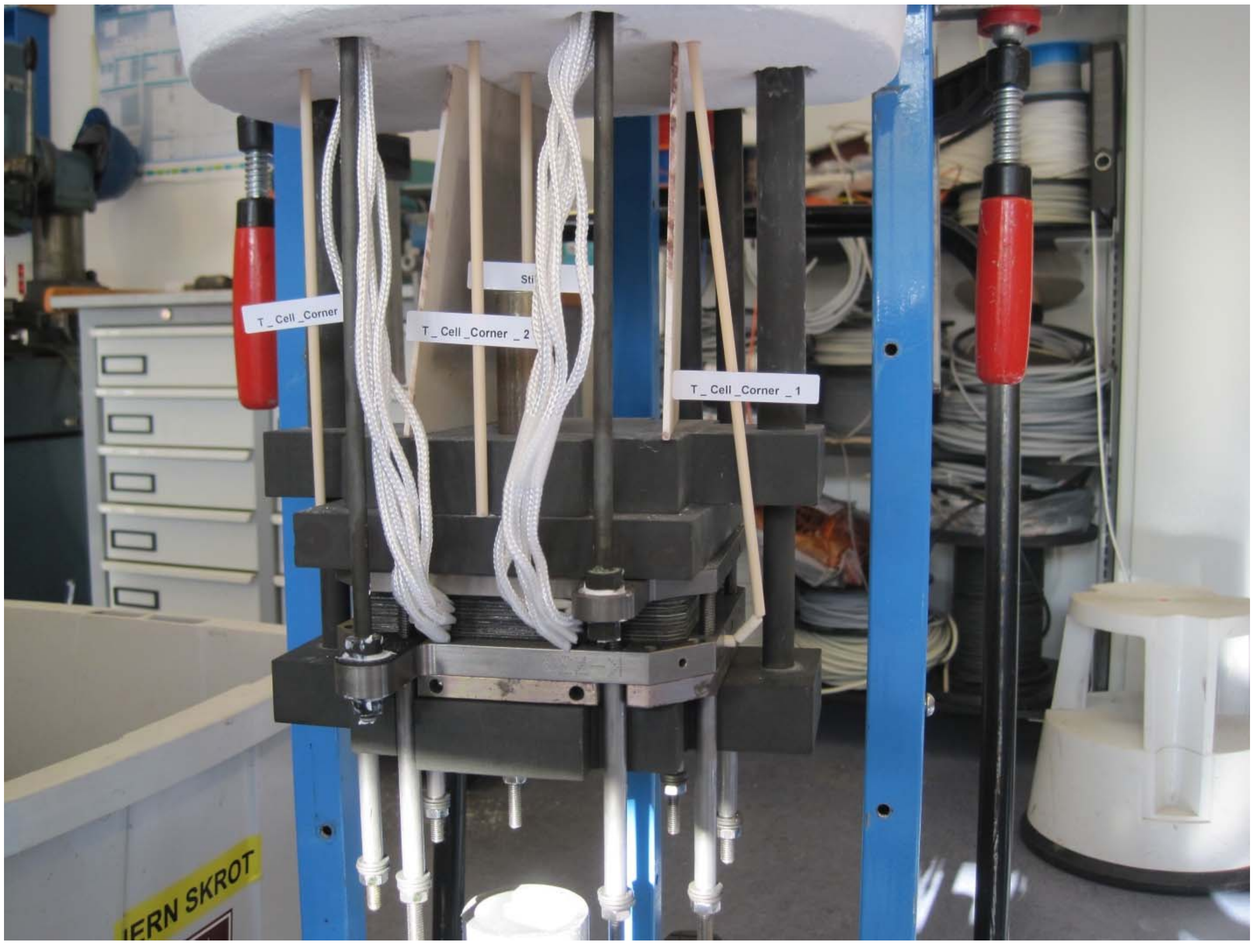
Pressure Test Setup

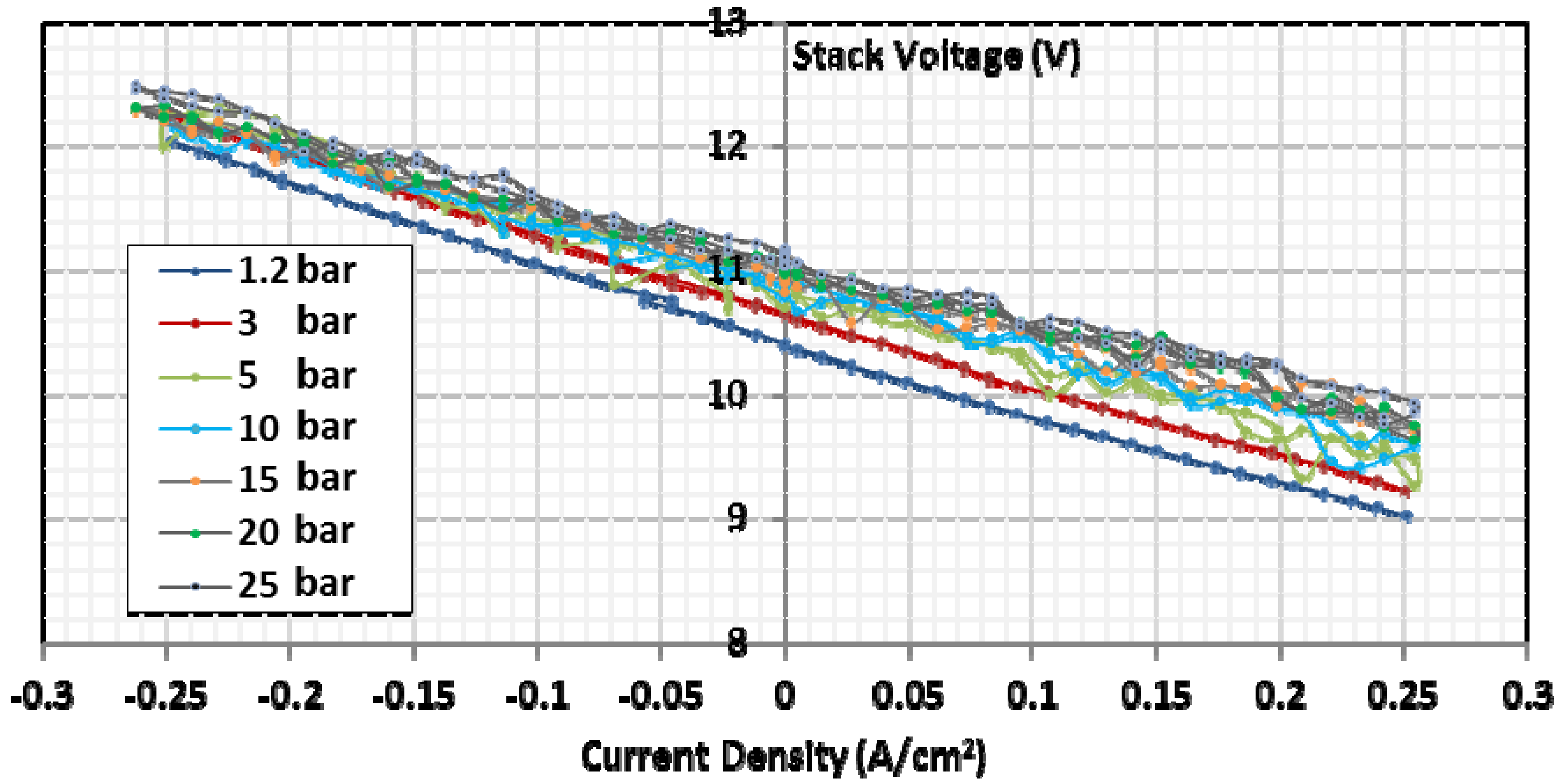




1 kW SOEC Stack from HTAS



iV curves vs Pressure



S. H. Jensen, X. Sun, S. D. Ebbesen, M, Chen,
Fuel Cells ***16*** *(2) 2016 205-218*,
DOI: 10.1002/fuce.201500180

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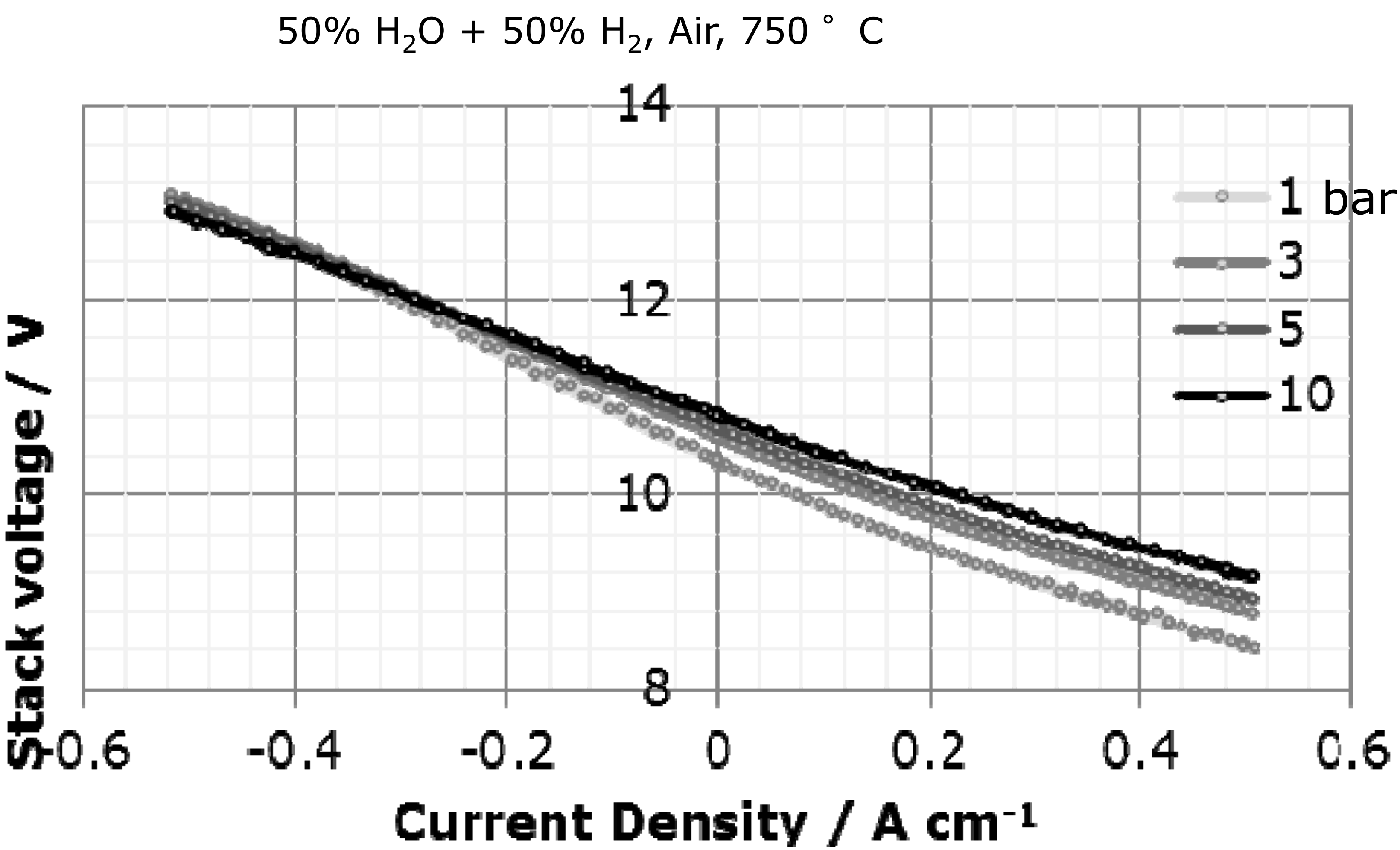
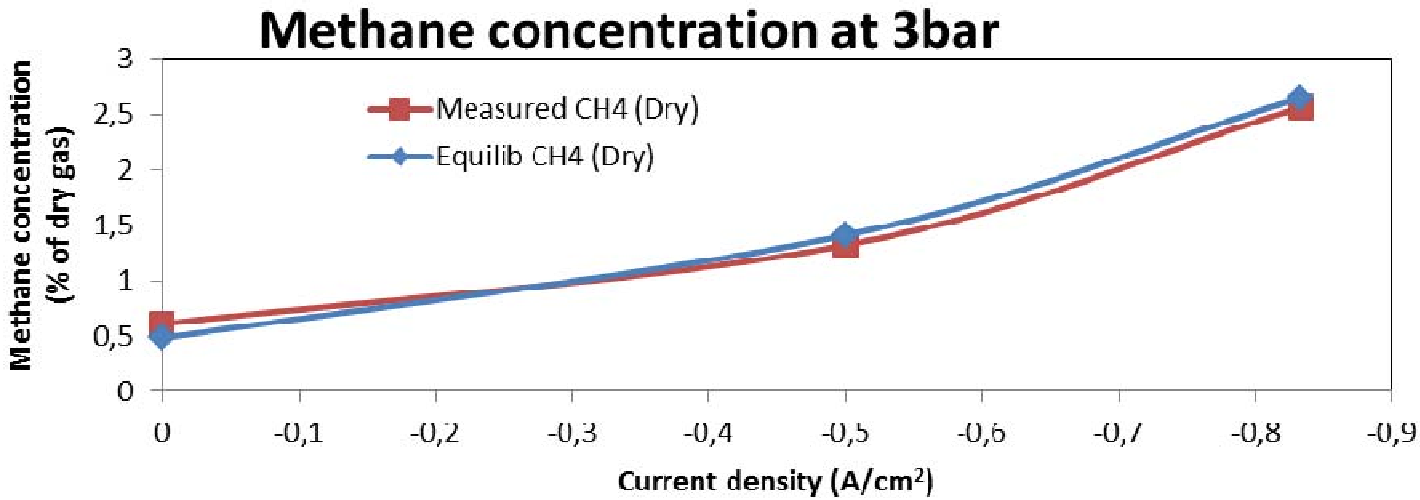


S. H. Jensen, M, Chen, X. Sun, C. Graves, J. B. Hansen *To be published in J. Electrochem. Soc*

Internal Methane production in a Planar SOEC



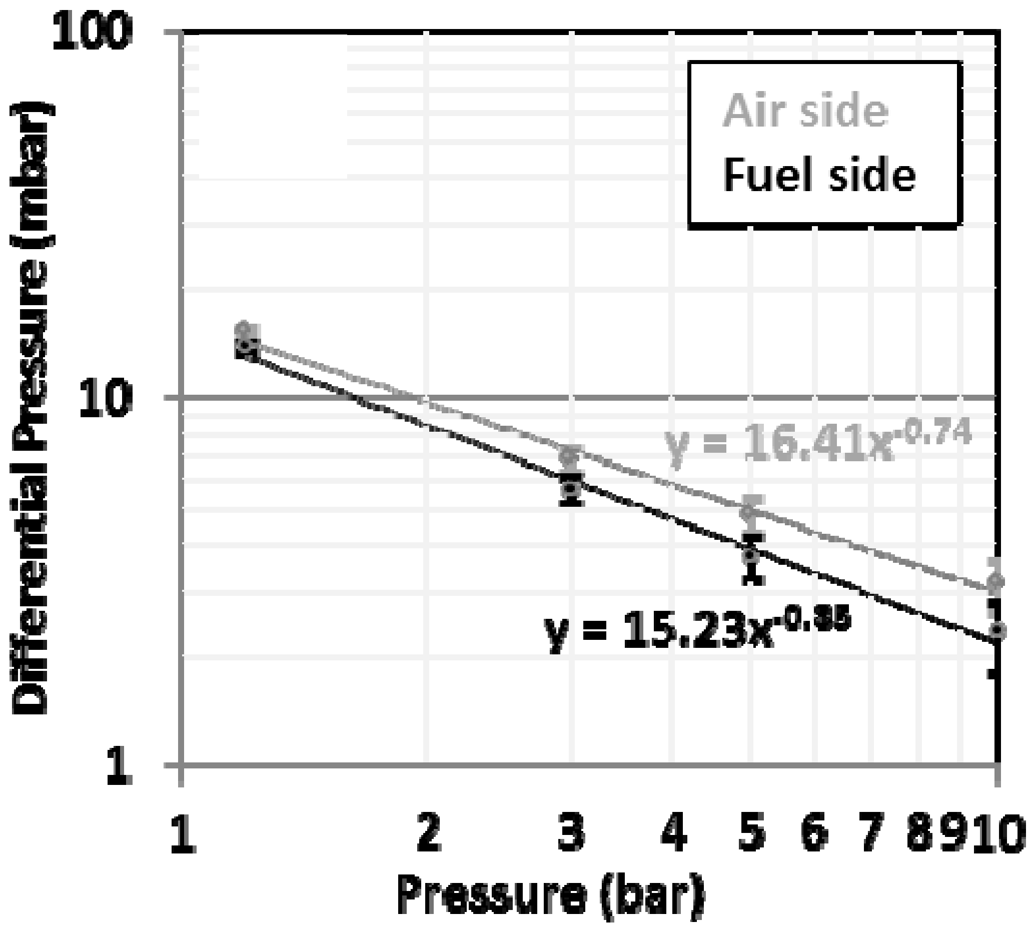
SOEC operating conditions:

- 750°C
- 20 L/h of 50% H_2 + 25% H_2O+25% CO_2 to the fuel electrode
- 50 L/h air to the oxygen electrode

S. H. Jensen, *et al. unpublished work*

Gas Pressure Drop Across the Stack

Operating conditions: 400 l/h Air. 200 l/h H_2 + 200 l/h H_2O. 750 ° c



ΔP across stack and heat exchangers as a function of the gas pressure

Assuming an **isentropic expansion** of the gas through the stack, the **theoretical exponent** for **ΔP** is **-0.71** for air **-0.75** for 50% H_2 + 50% H_2O

S. H. Jensen, X. Sun, S. D. Ebbesen, M, Chen, *Fuel Cells **16** (2) 2016 205-218*, DOI: 10.1002/fuce.201500180

Conclusions

Pressurized operation of Planar SOC stacks demonstrates that:

- Gas pressure drop across the stack decreases with pressure ~ (adiabatic) $P^{-0.8}$
- Stable SOEC/SOFC operation with small steam/stack-voltage fluctuations demonstrated at elevated pressure
- ASR decreases with pressure (electrode resistance ~$P^{-0.3}$)
- Long-term operation at high pressure does not show increase in the degradation rate, although the short test period for the stack test makes this statement a bit uncertain
- Internal Methane Formation is the new black ;-)

Acknowledgement

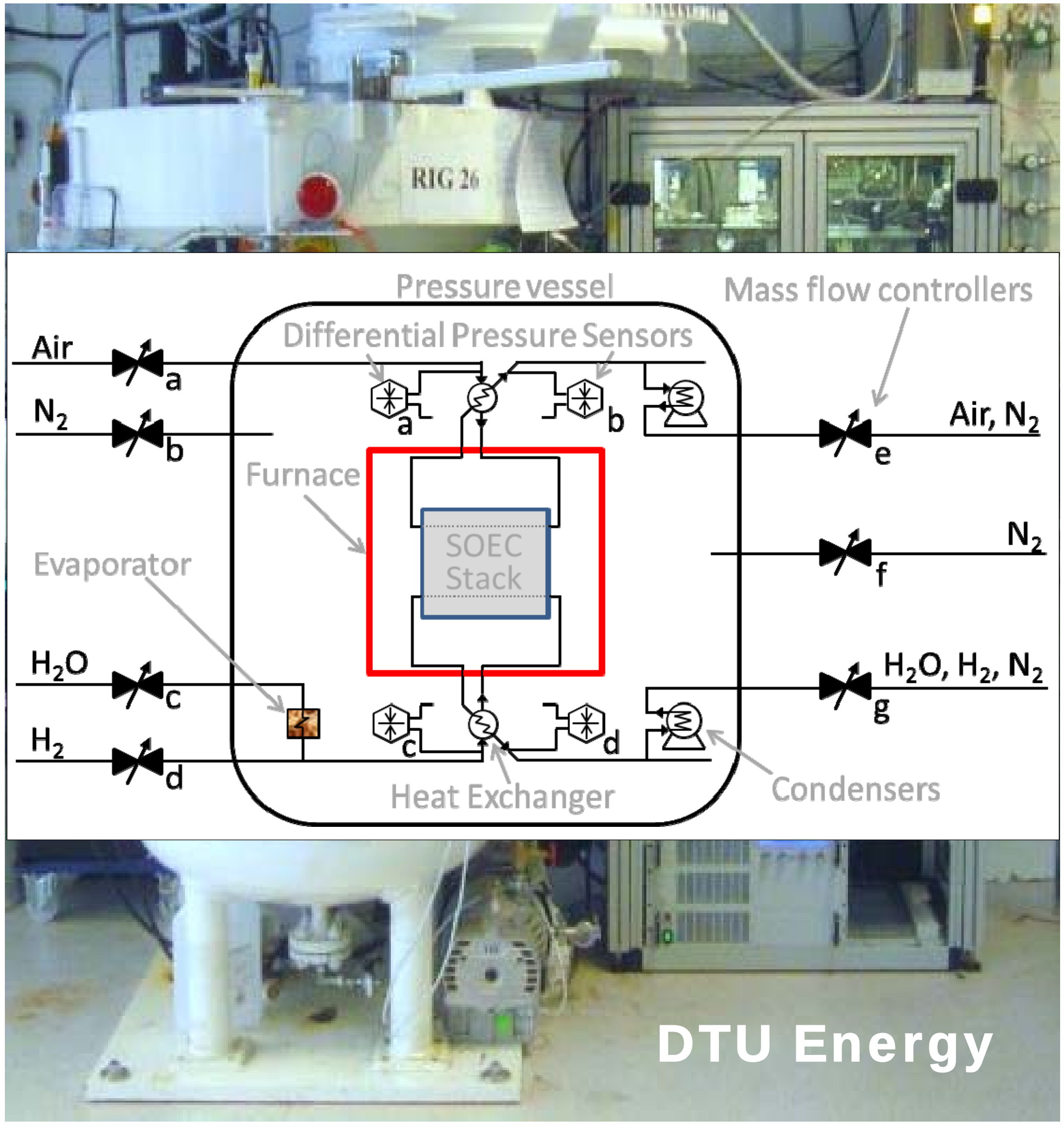
Thank You For Your Attention

Sponsor Organizations	Projects and Centres
Det Strategiske Forskningsråd	SERC, 2104-06-0011
ENERGINET.DK	Solid Oxide Electrolysis for Grid Balancing, 2013-1-12013 and "SOFC4RET", 2014-1-12231
norden Nordic Energy Research	CO_2 Electrofuel, 40000
EUDP	Green Natural Gas, 64011-0036 Energi Effektiv Produktion af Tryksat Brint, 64013-0583

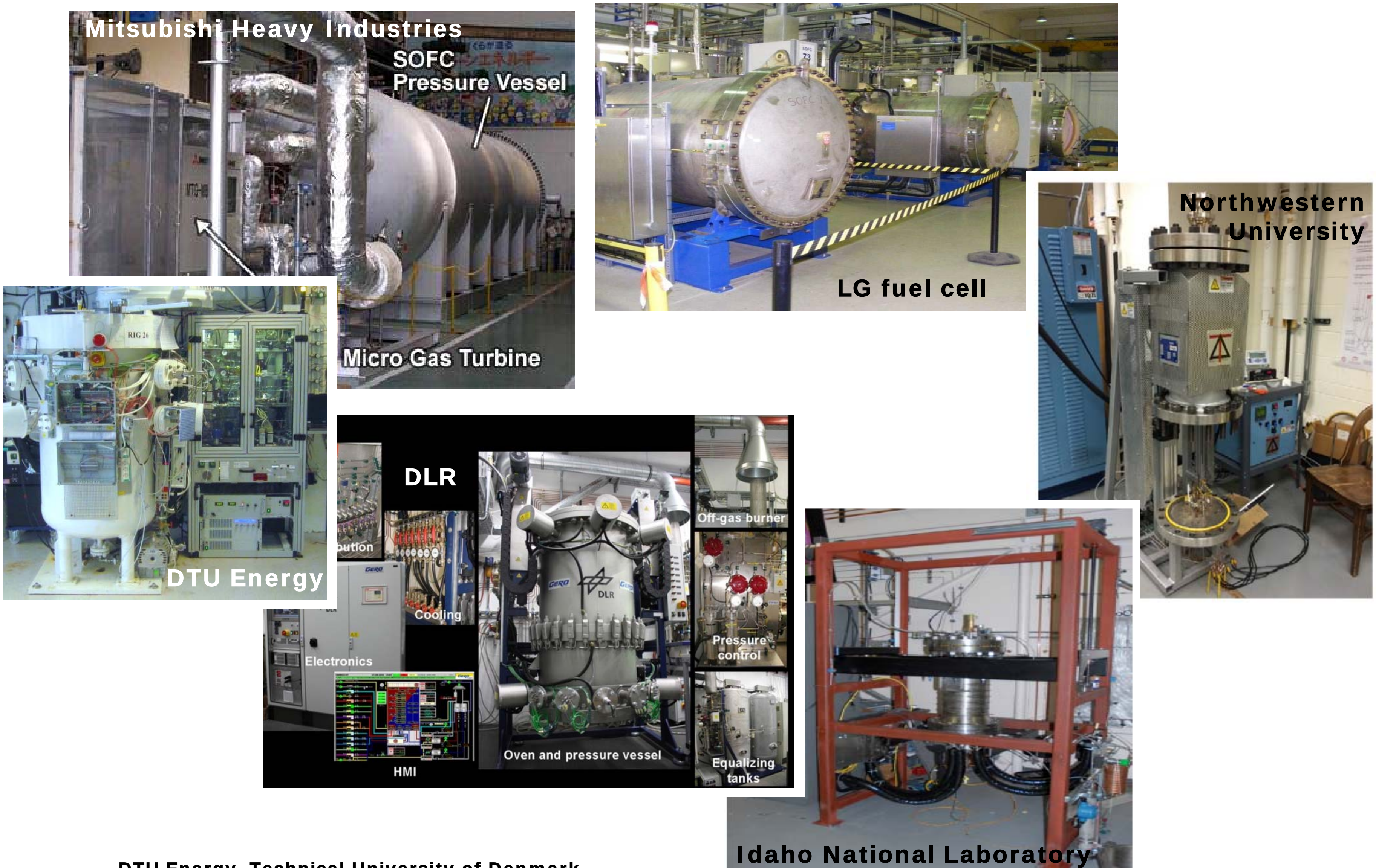
SOEC Stack — HALDOR TOPSØE, CATALYSING YOUR BUSINESS

Extra Slides

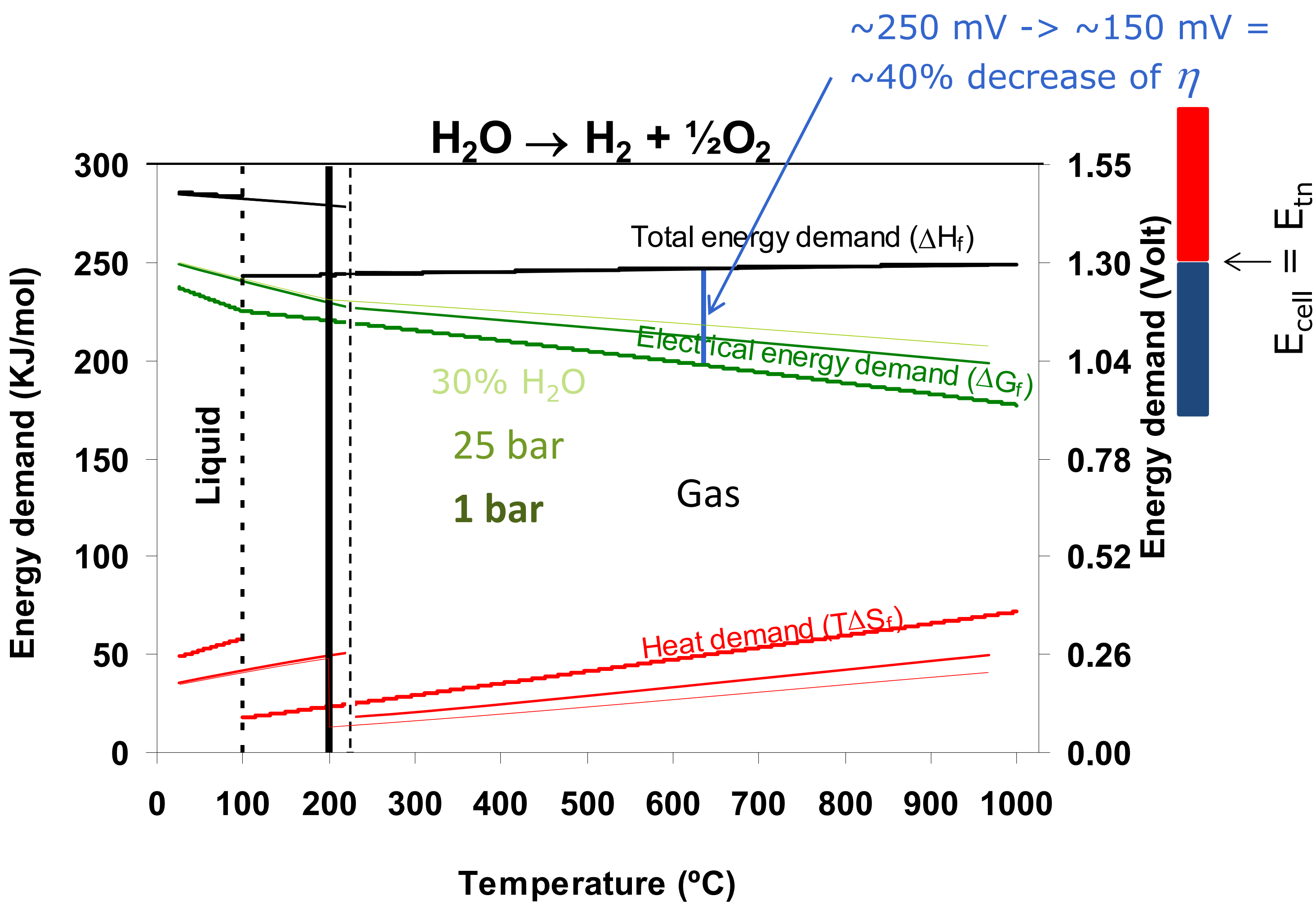
Pressure Test Setup



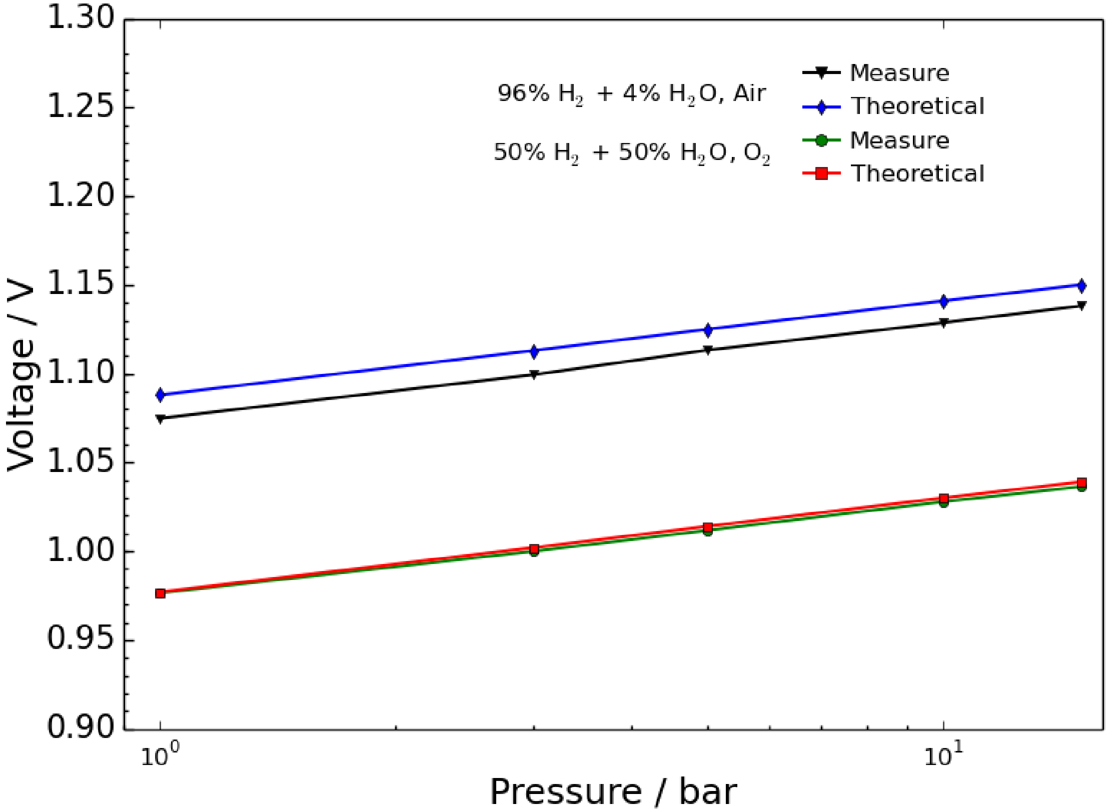
Pressurized SOC activites around the world



Steam Electrolysis Thermodynamics



Steam Electrolysis at Elevated Pressure



The cell voltage is given by the Nernst equation…

$$E = E_0 + \frac{RT}{2F} \ln\left(\frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}}\right)$$

…the cell voltage increases with linearly with $\ln$ gas pressure

X. Sun *et al.* submitted to *Fuel Cells*

Electrode Reaction Kinetic

$$H_2 + O^{--} \underset{\nu_b}{\overset{\nu_f}{\leftrightarrows}} H_2O + 2e^-$$

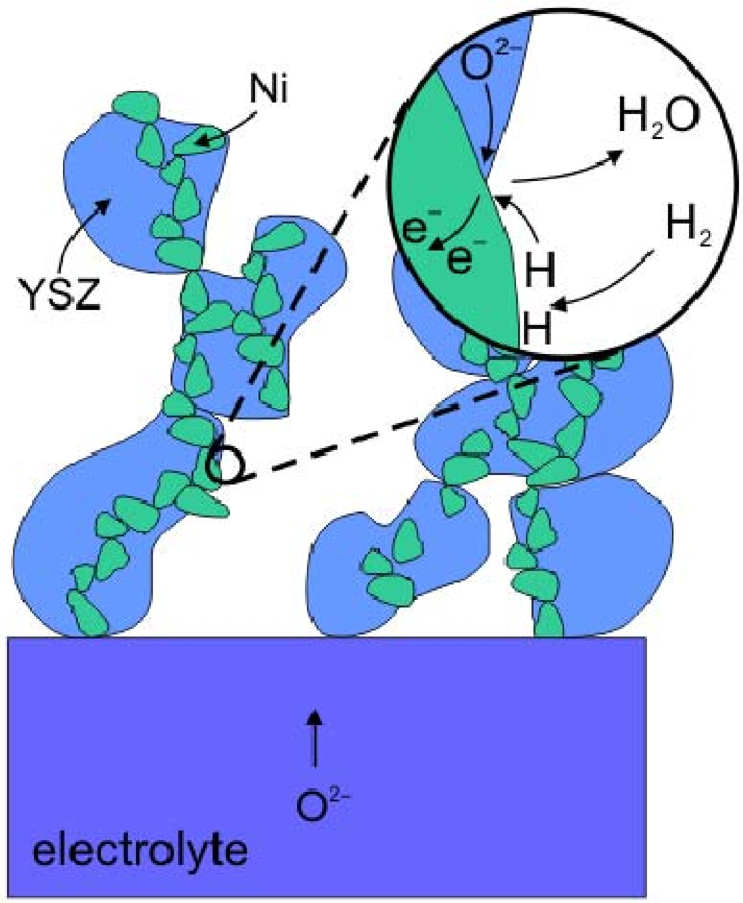
$$\frac{1}{2}O_2 + 2e^- \underset{\nu_b}{\overset{\nu_f}{\leftrightarrows}} O^{--}$$

Exhange rates increases with pressure

↓

Gas-solid reaction resistance decreases with pressure

$$R = k(P)^{-n}$$



Pressure and Performance

- J. Høgh have reported n ~ 0.27 (P_{H2O} dependence) for DTU Energy Ni/YSZ electrodes*

- Thomsen *et al.* have reported n ~ 0.25 for composite LSM/YSZ electrodes**

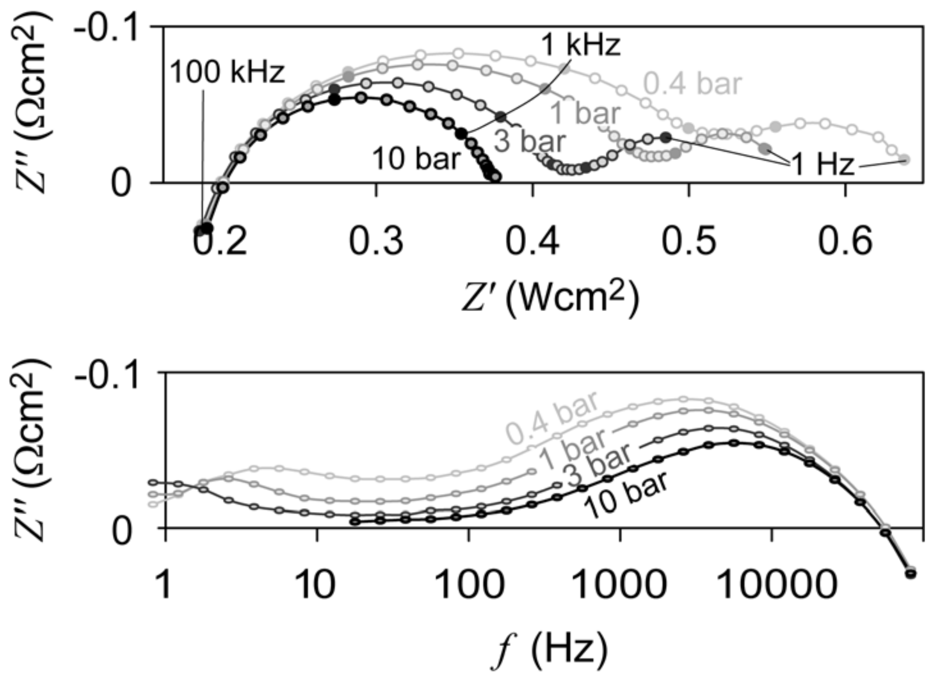
* J. Høgh, *Influence of impurities on the H2/H2O/Ni/YSZ electrode*, Risø National Laboratory, Roskilde, Denmark (2005)

** *E.C. Thomsen et al. J. Power Sources **191** (2009) 217–224*

$$R = k(P)^{-n}$$

Pressure and Performance

- 750 °C
- Negative Electrode: 20% H_2O + 80% H_2
- Positive Electrode: O_2



Jensen, Sun, Ebbesen, Knibbe, Mogensen. *Int. J. Hydrogen Energy* **35** (2010) 9544

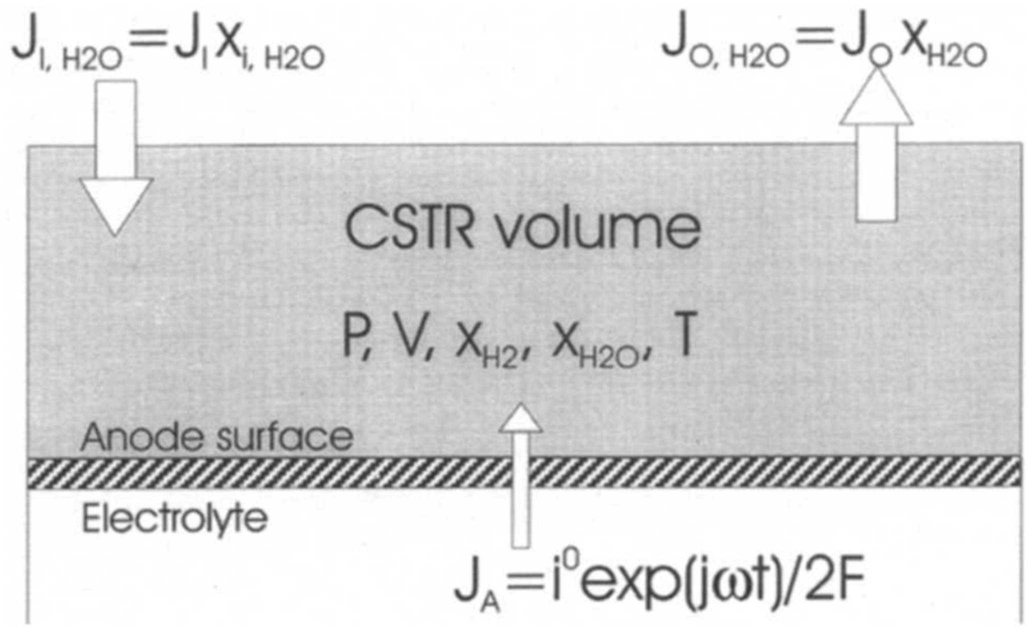
Gas Conversion Impedance

Primdahl and Mogensen. *J. Electrochem. Soc* **145**, 2431 (1998)

$$R_g = \frac{RT}{4F^2 J_i}\left(\frac{1}{x_{i,H_2O}} + \frac{1}{x_{i,H_2}}\right)$$

$$C_g = \frac{4F^2 PV}{(RT)^2 A}\frac{1}{\frac{1}{x_{i,H_2O}} + \frac{1}{x_{i,H_2}}}$$

$$f_g = \frac{J_i ART}{2\pi PV}$$

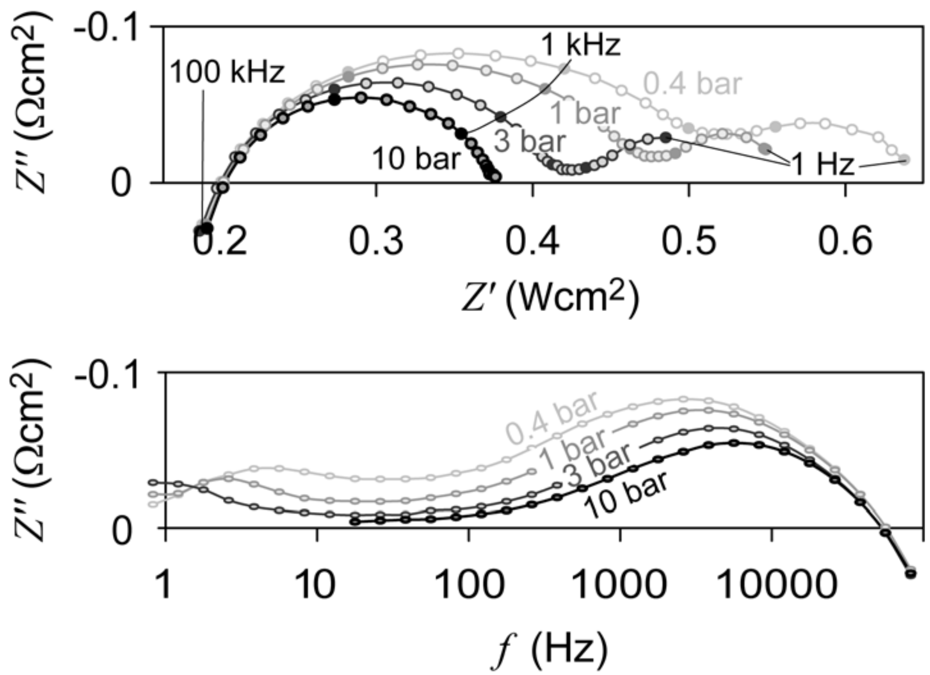


$$J_I = J_O + J_A$$

$$H_2 + O^{--} \rightarrow H_2O + 2e^-$$

Pressure and Performance

- 750 ºC
- Negative Electrode: 20% H_2O + 80% H_2
- Positive Electrode: O_2



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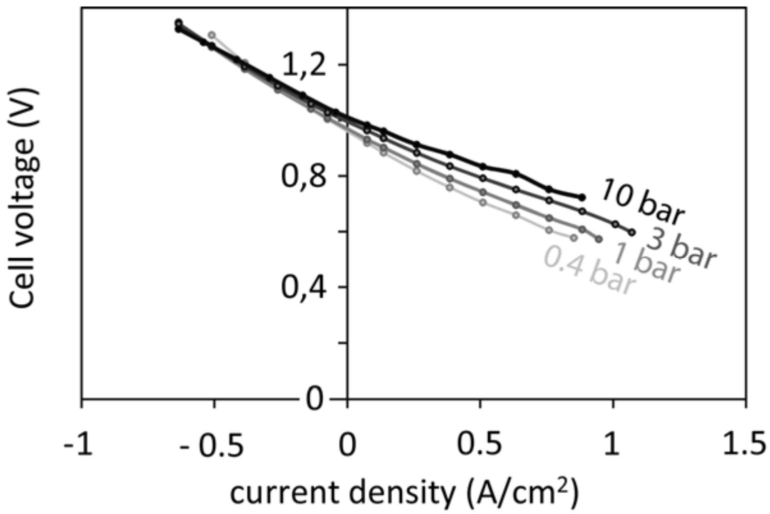

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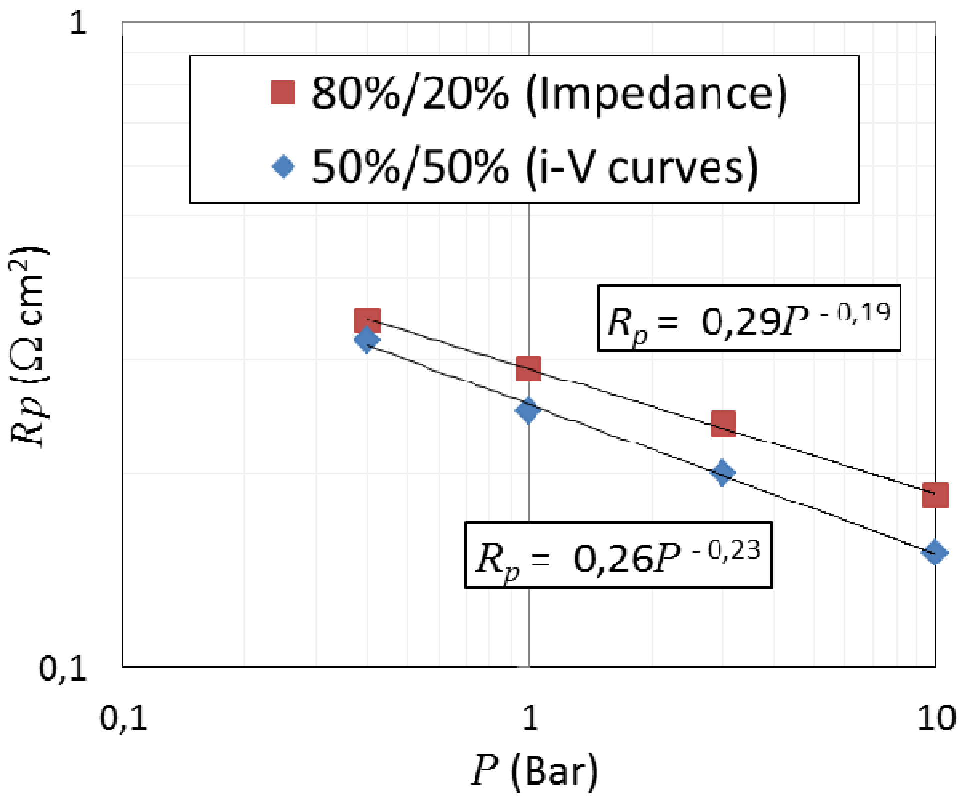
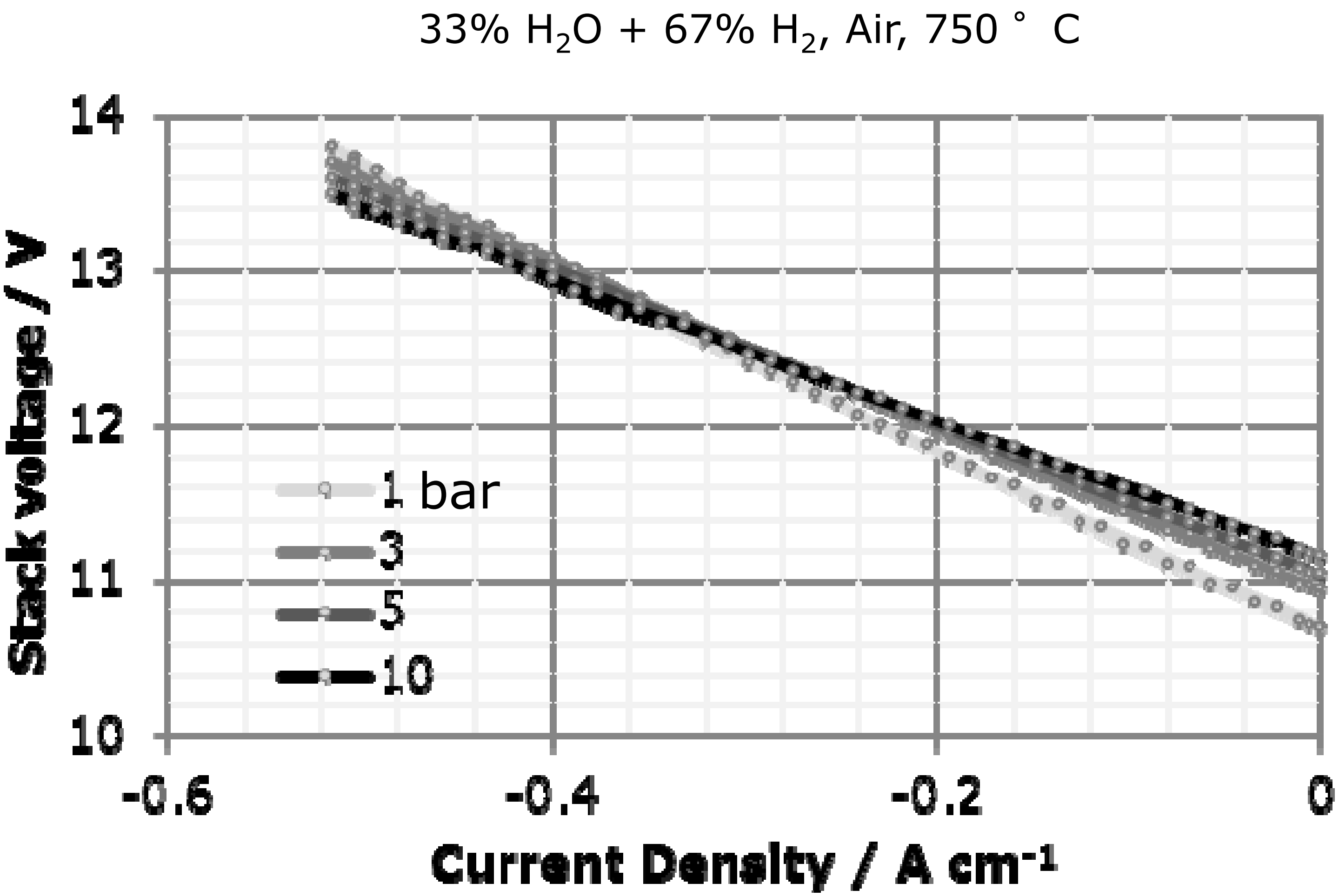
Int. J. Hydrogen Energy **35** (2010) 9544

Assuming 70 mΩcm^2
gas conversion



”Charge transfer limited reactions involving dissociatively adsorbed oxygen at low Coverage” *E.C. Thomsen et al. J. Power Sources **191** (2009) 217–224*

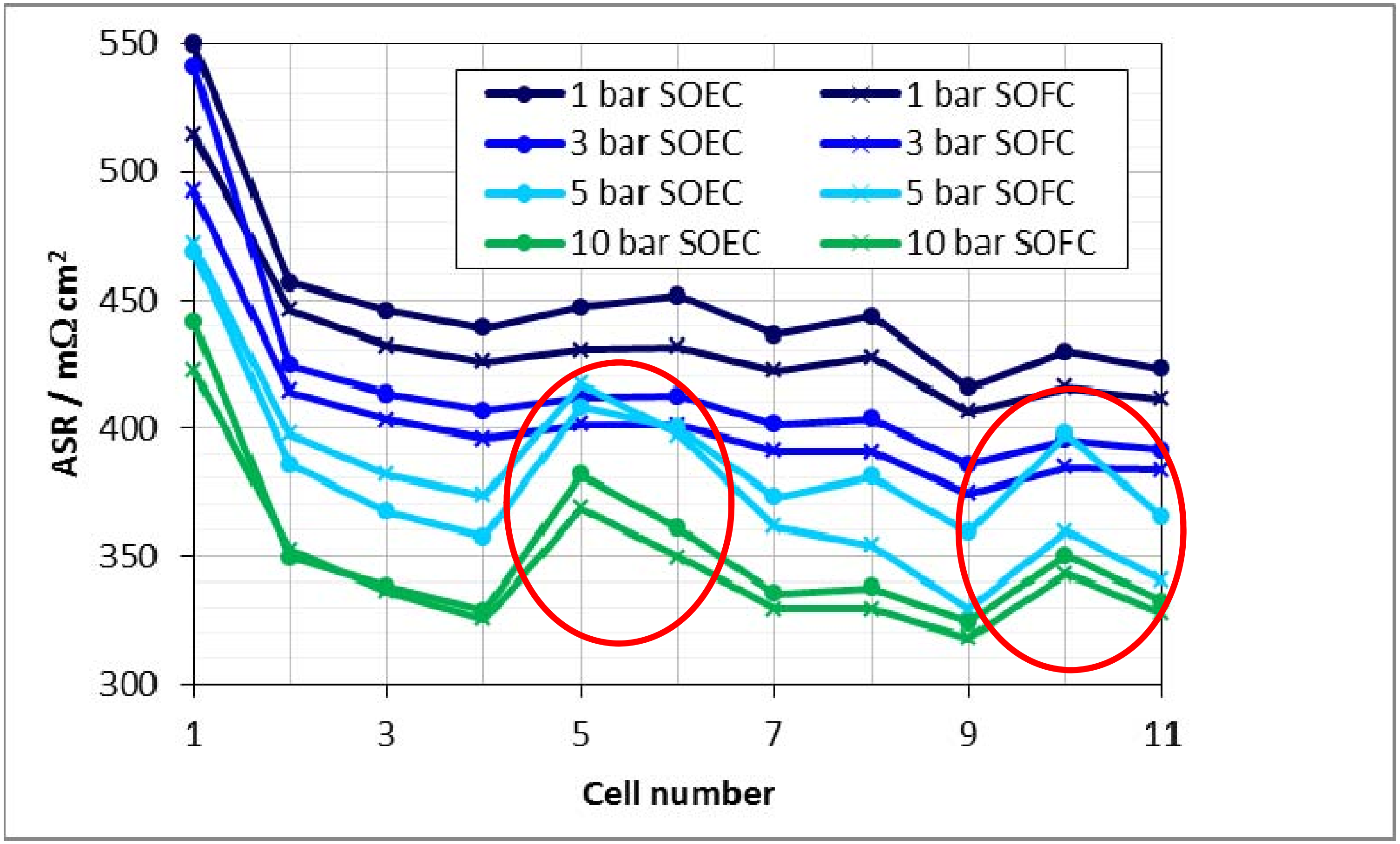
iV curves vs Pressure



S. H. Jensen, M, Chen, X. Sun, C. Graves, J. B. Hansen *To be published in J. Electrochem. Soc*

ASR vs pressure

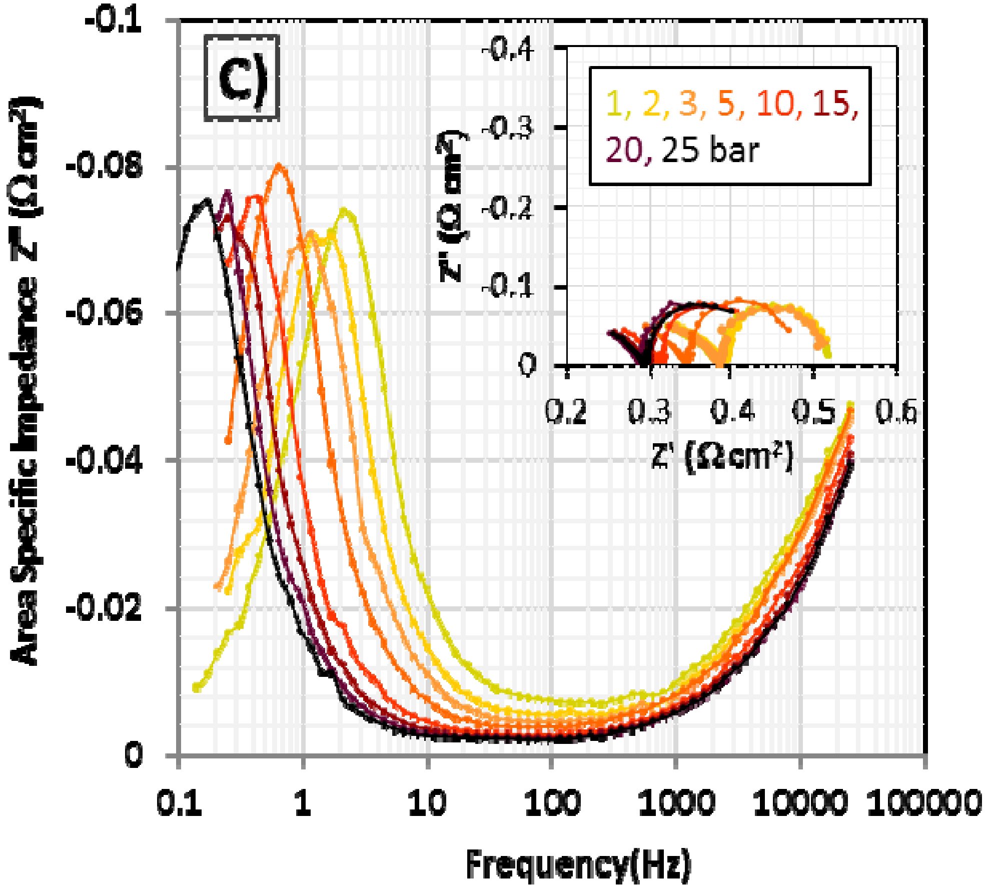
50% H_2O + 50% H_2, Air, 750 ° C



Air starvation during IV curve recorded between 3 and 5 bar

S. H. Jensen, M, Chen, X. Sun, C. Graves, J. B. Hansen *To be published in J. Electrochem. Soc*

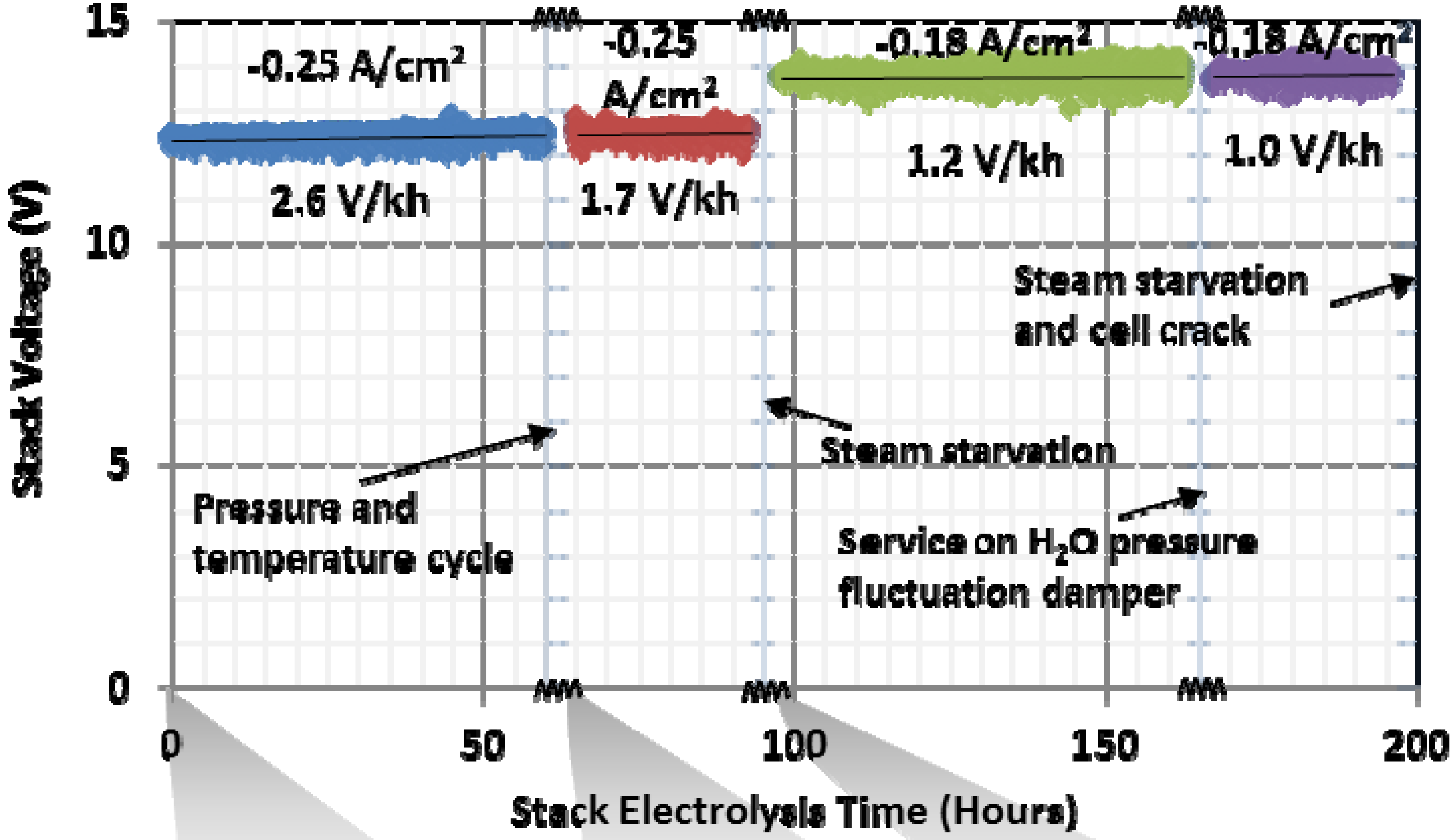
Stack Impedance vs Pressure



- Low frequency summit frequency decreases with pressure
- The size of the high-frequency arc decreases with pressure

S. H. Jensen, X. Sun, S. D. Ebbesen, M, Chen, *Fuel Cells **16** (2) 2016 205-218*,
DOI: 10.1002/fuce.201500180

Durability Test at 10 bar



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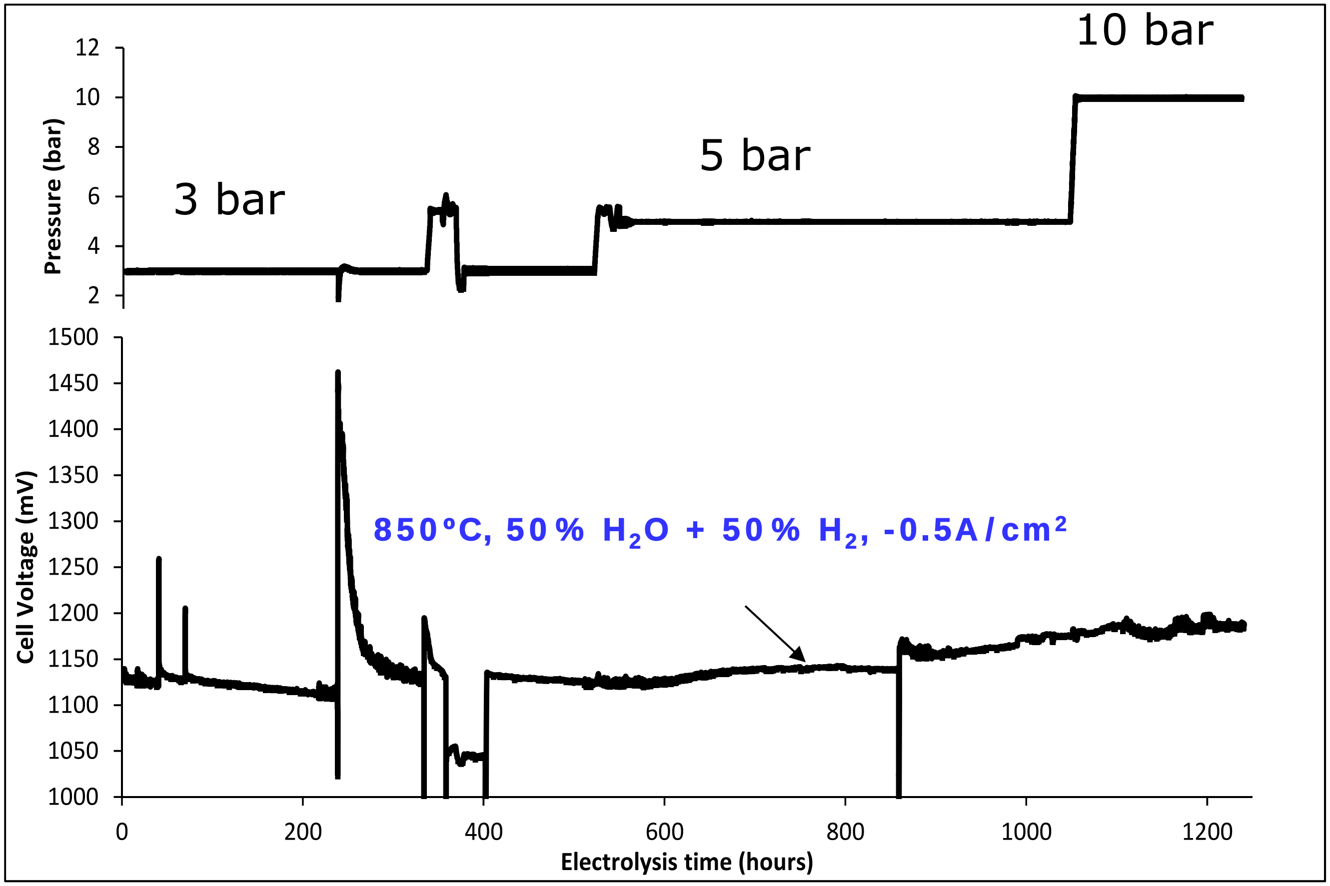
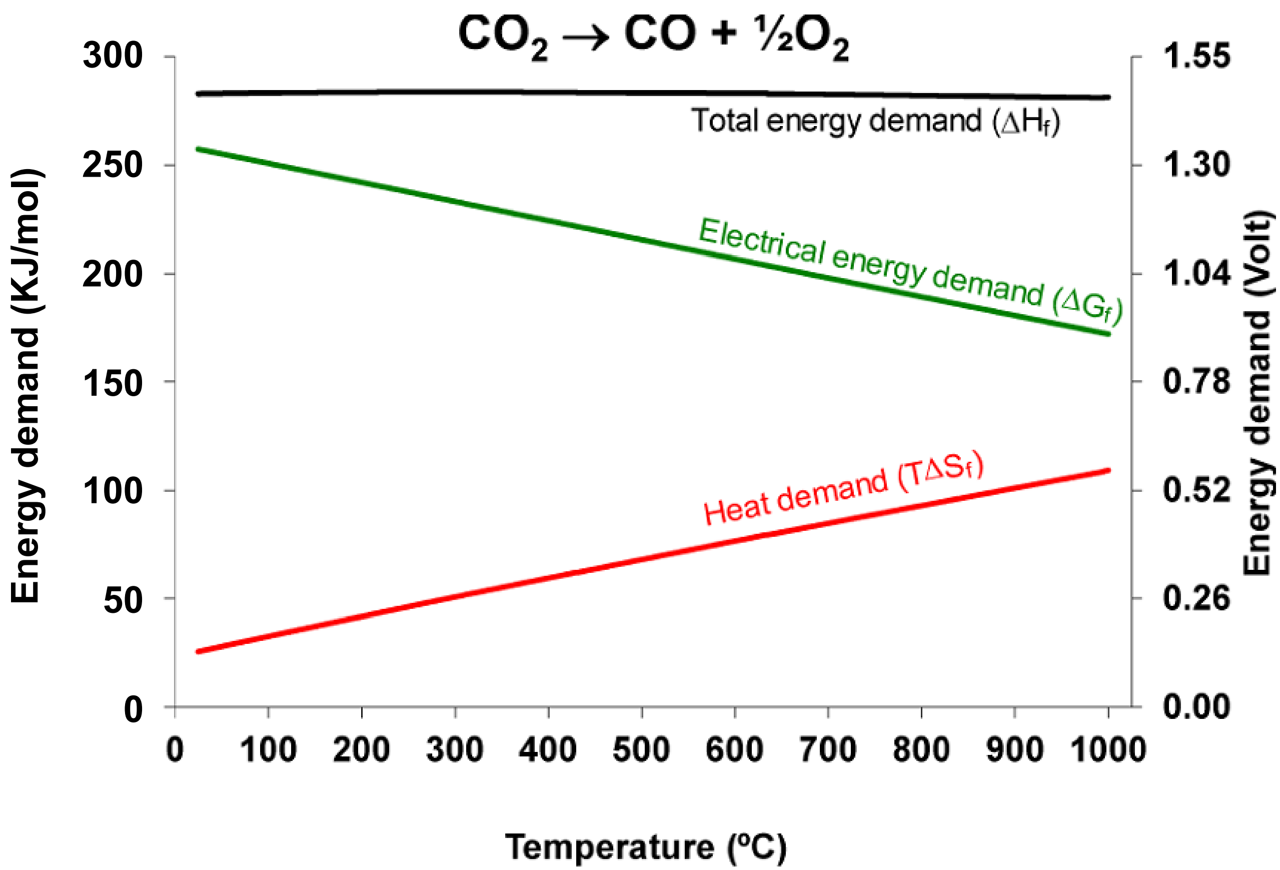


S. H. Jensen, *et al. unpublished work*

CO2 Electrolysis Thermodynamics



CH4 Formation Thermodynamics