



Fuel Cell & Hydrogen Technologies JP

SP2: Catalyst and Electrodes

Borovetz, Bulgaria

June 2nd and 3rd 2014

Intermediate temperature and pressure electrochemical reactors

EERA FCH2-SP2 WORKSHOP in frame of EIA10

Bridging experimental and numerical research:

development and optimization of advanced characterization tools – Electrochemical Impedance Spectroscopy



Christodoulos Chatzichristodoulou

Technical University of Denmark, Department of Energy Conversion and Storage

- Motivation
- Electrolytes
- Cell concept
- Electrochemical testing equipment
- H₂O electrolysis
- Summary
- Outlook

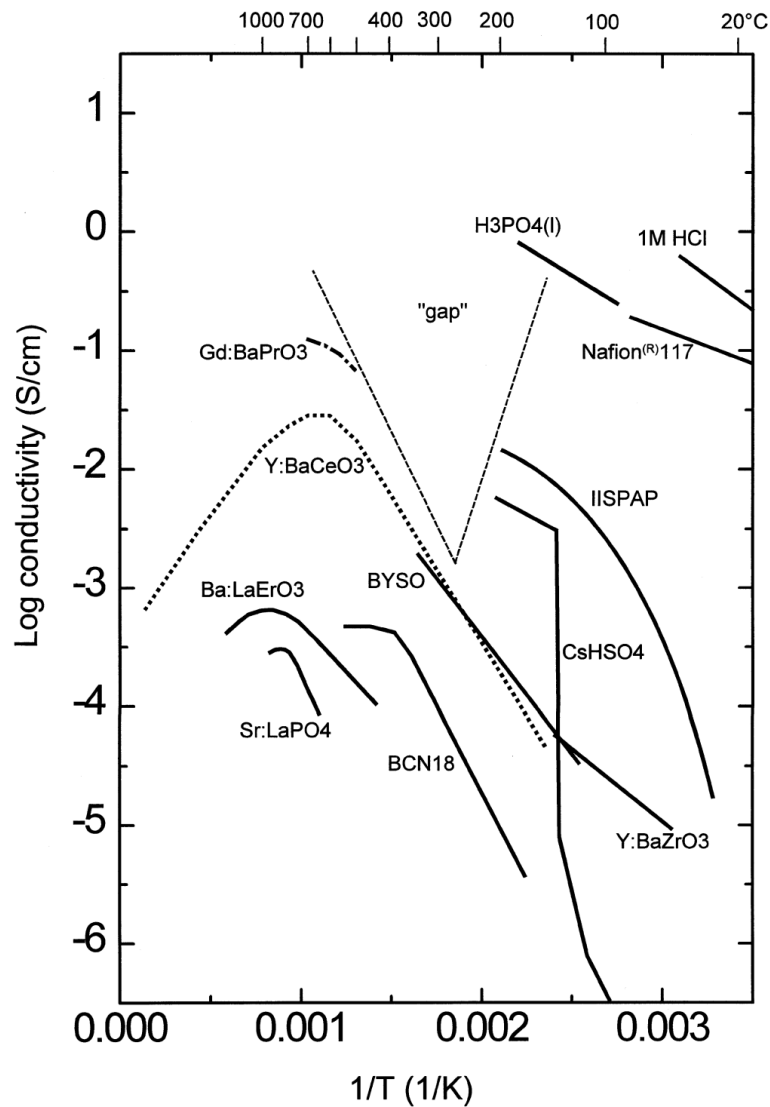
- Increasing need for large scale, efficient and affordable storage of intermittent renewable energy
- Need for sustainable production of fuels for transportation
- Need for sustainable production of chemicals
- Oxygenates (MetOH, EtOH, DME) offer high energy density and ease of storage (as liquids)

Advantages of operating at $T \sim 100\text{-}300\text{ }^{\circ}\text{C}$, $P \sim 10\text{-}100\text{ atm}$:

1. Incorporation of electrolysis and fuel synthesis in a single component.
(System simplicity, reduction of capital cost, intelligent heat management)
2. Improved electrode performance. No need for expensive electrocatalysts.
(Reduction of capital and operating cost)
3. Production of pressurized fuel (and O_2). No need for compressor.
(Reduction of capital cost)
4. Use of aqueous electrolytes with gas diffusion electrodes.
(Improved mass transport. Reversible operation)
5. Increased electrolyte conductivity.
(Reduced ohmic losses)
6. Reduced thermal strain, inter-diffusion and catalyst coarsening as compared to SOEC.
(Durability and lifetime improvement. Easier integration with RE sources)

- Many $H_xC_yO_z$ are thermodynamically stable up to about 300 °C and very few are stable at much higher temperature
- CH_4 may be synthesised using a Ni catalyst ($CO + 3 H_2 \rightleftharpoons CH_4 + H_2O$) between 200 – 450 °C at 30 bar
- $(CH_3)_2O$ synthesis on Cu/ZnO/ Al_2O_3 catalyst ($2 CO + 4 H_2 \rightleftharpoons (CH_3)_2O + H_2O$) between 200 - 300 °C at ca. 50 bar, very similar for synthesis of CH_3OH
- Electrochemistry under pressure of 30 - 50 bar and temperatures of 200 – 300 °C $\Rightarrow$ intimate thermal integration of electrochemistry and catalysis is possible

Electrolytes – The Norby gap



T. Norby, *Solid State Ionics*, 125 (1999) 1

- **45 wt% KOH immobilized in ca. 50 % porous ceramics: 0.84 S cm⁻¹ at 200 °C and 25 bar**

F. Allebrod, C. Chatzichristodoulou, P.L. Mollerup, M.B. Mogensen, *Internat. J. Hydrogen Energy*, 37 (2012) 16505, and Proc. of 4th EFCF, paper A0705

- **15 wt% K₂CO₃(aq.): 0.57 S cm⁻¹ at 200 °C measured, ca. 0.3 S cm⁻¹ expected for immobilized electrolyte**

P.L. Mollerup, A.S. Christiansen, N. Bonanos, M.B. Mogensen, submitted for publication 2013

- **Solid acid, CsH₂PO₄: ca. 10⁻² S cm⁻¹ at 240 °C (“the limit”).**

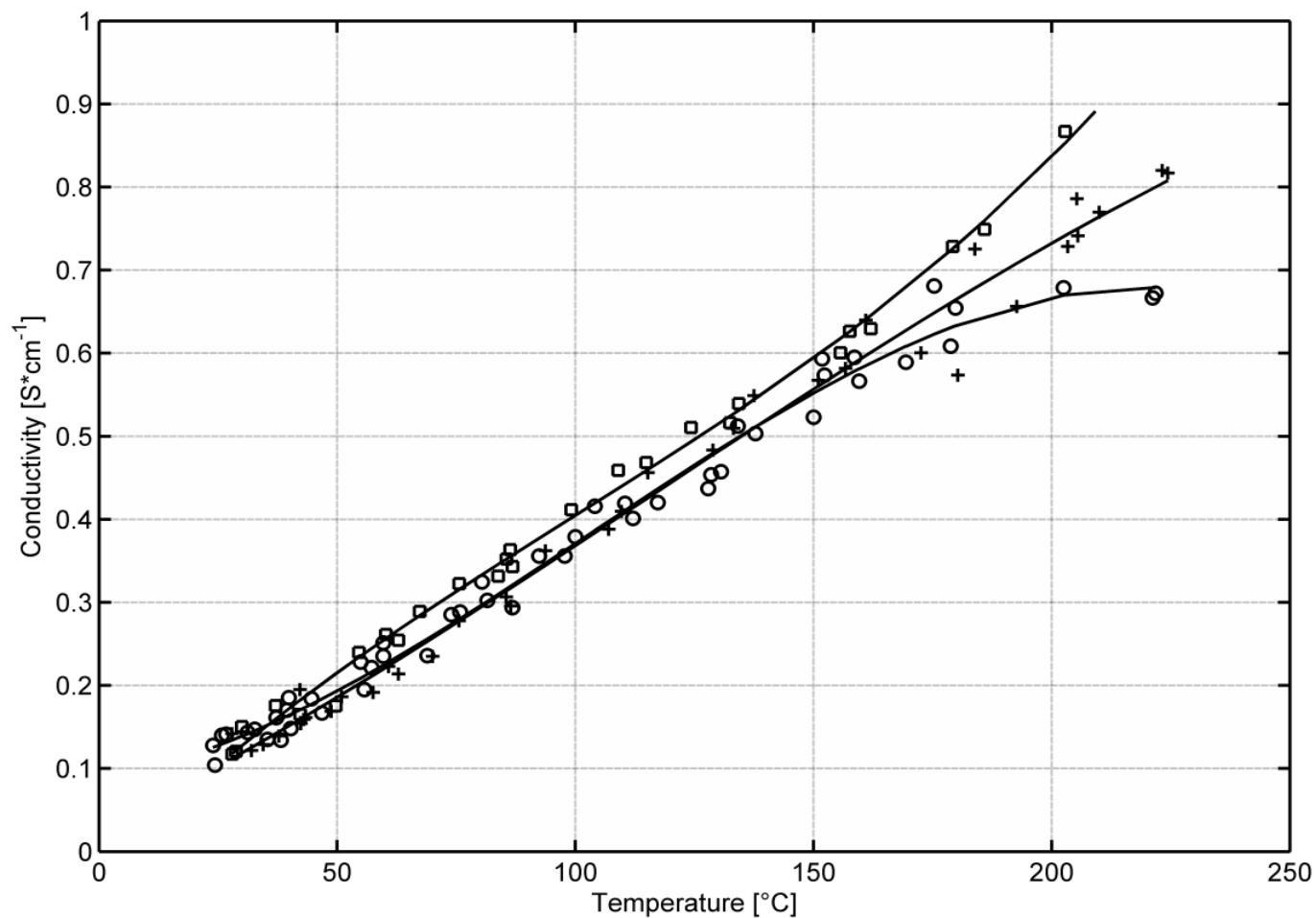
S.M. Haile, C.R.I. Chisholm, K. Sasaki, D.A. Boysen, T. Uda, Solid acid proton conductors: from laboratory curiosities to fuel cell electrolytes, *Faraday Discussions*, 134 (2007) 17

- **Acceptor doped metal phosphorous oxides such as Ce(PO₃)₄ and CeP₂O₇ - high initial conductivity – not stable over time > 100 h**

C. Chatzichristodoulou, J. Hallinder, A. Lapina, P. Holtappels, M. Mogensen, *J. Electrochem. Soc.*, 160 (2013) F1

- **BaCe_xZr_yY_zO_{3-δ} might be possible at 300 °C if its grain boundary resistance could be reduced – it can by adding ceria, which makes the material degrade fast in CO₂**

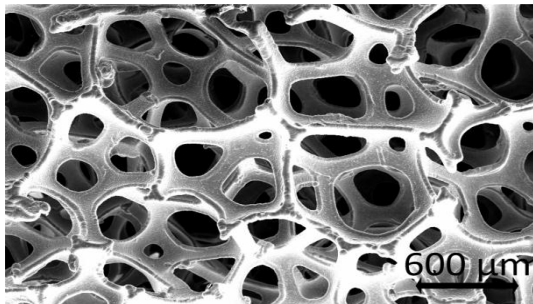
Electrolytes – Immobilized KOH (aq.)



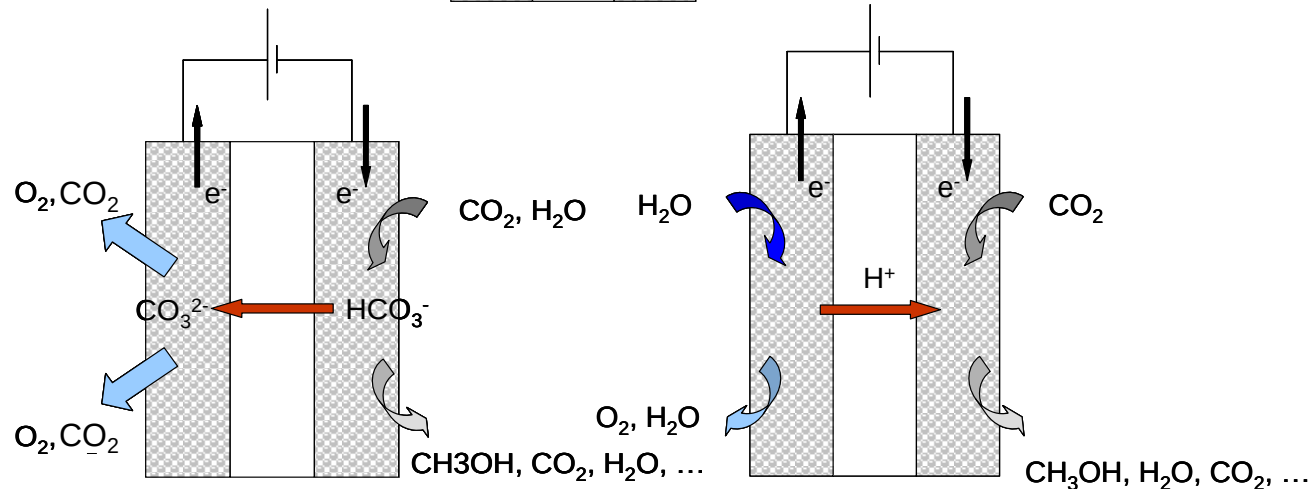
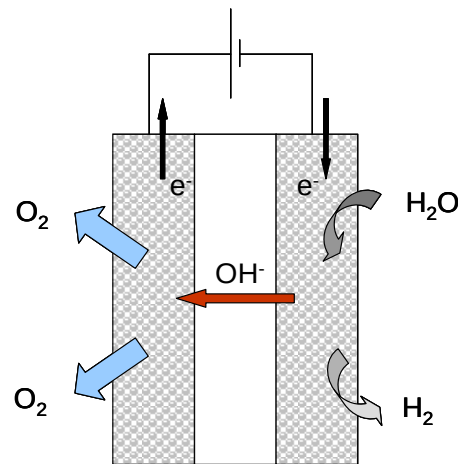
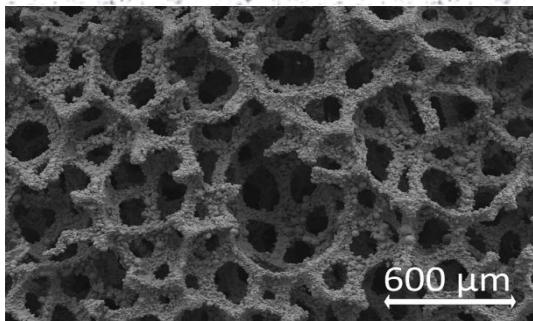
F. Allebrod *et al.*, *Internat. J. Hydrogen Energy*, 37 (2012) 16505

Cell concept

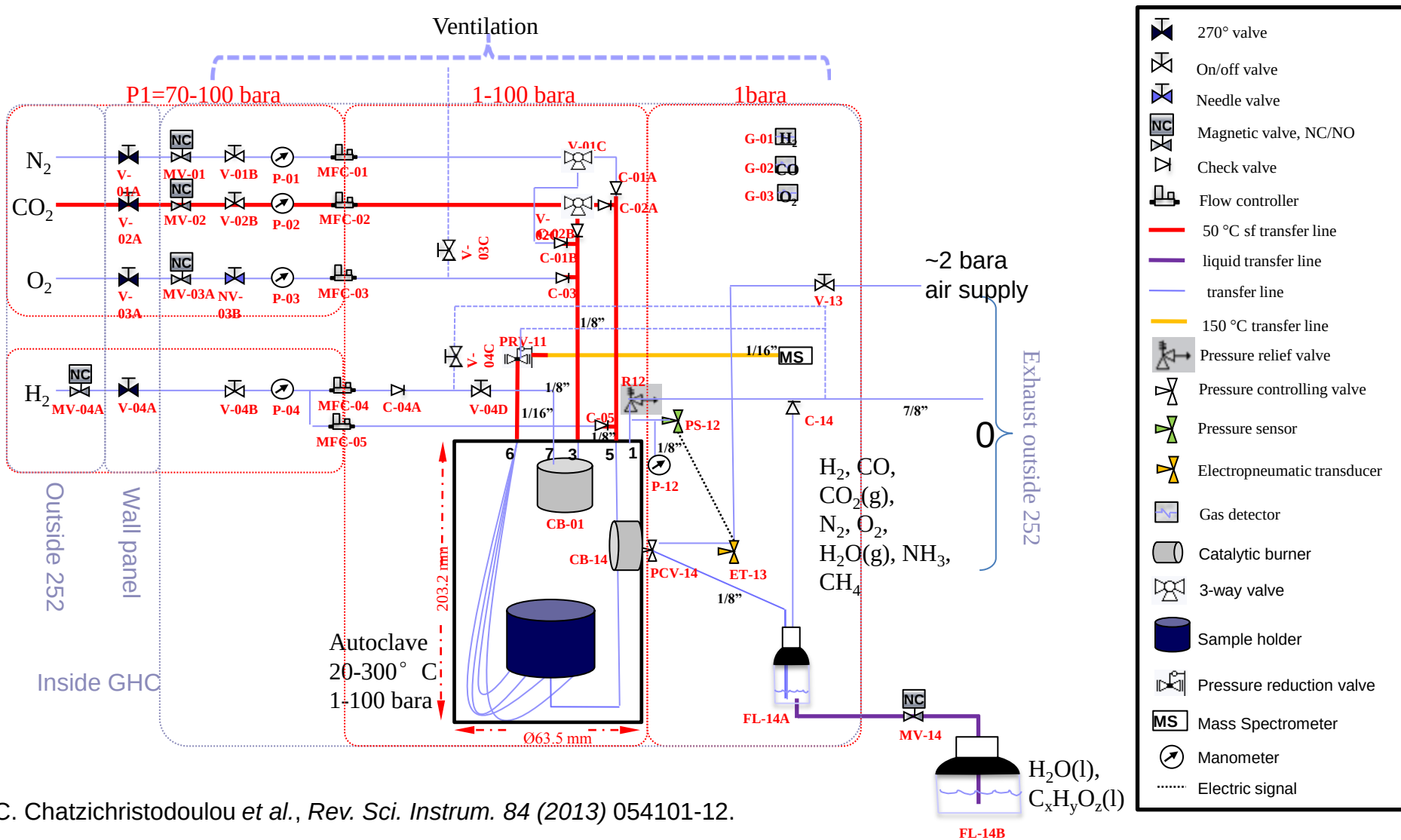
- Aq. electrolyte immobilized in mesoporous ceramic matrix
- Gas diffusion electrodes



Ceramic powder, e.g. SrTiO_3 , forming a mesoporous matrix

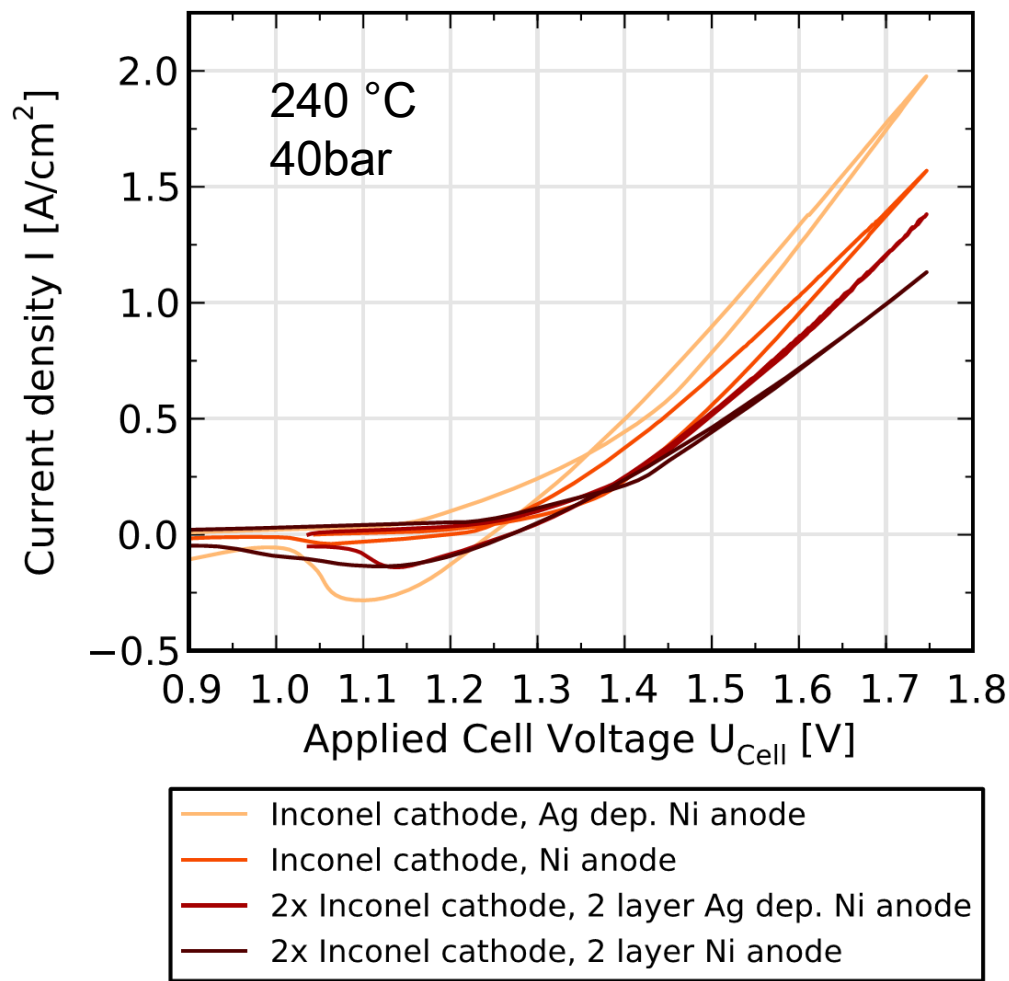


Electrochemical testing equipment – Intermediate temperature and pressure rigs



C. Chatzichristodoulou et al., Rev. Sci. Instrum. 84 (2013) 054101-12.

H₂O electrolysis - Performance



	Current density [A•cm ⁻²]	
	1.5 V	1.75 V
Ag-Ni-foam / Inconel-foam	0.9	2.00
Ni-foam / Inconel-foam	0.68	1.58
2xAg-Ni-foam / 2xInconel-foam	0.52	1.38
2xNi-foam / 2xInconel-foam	0.46	1.1

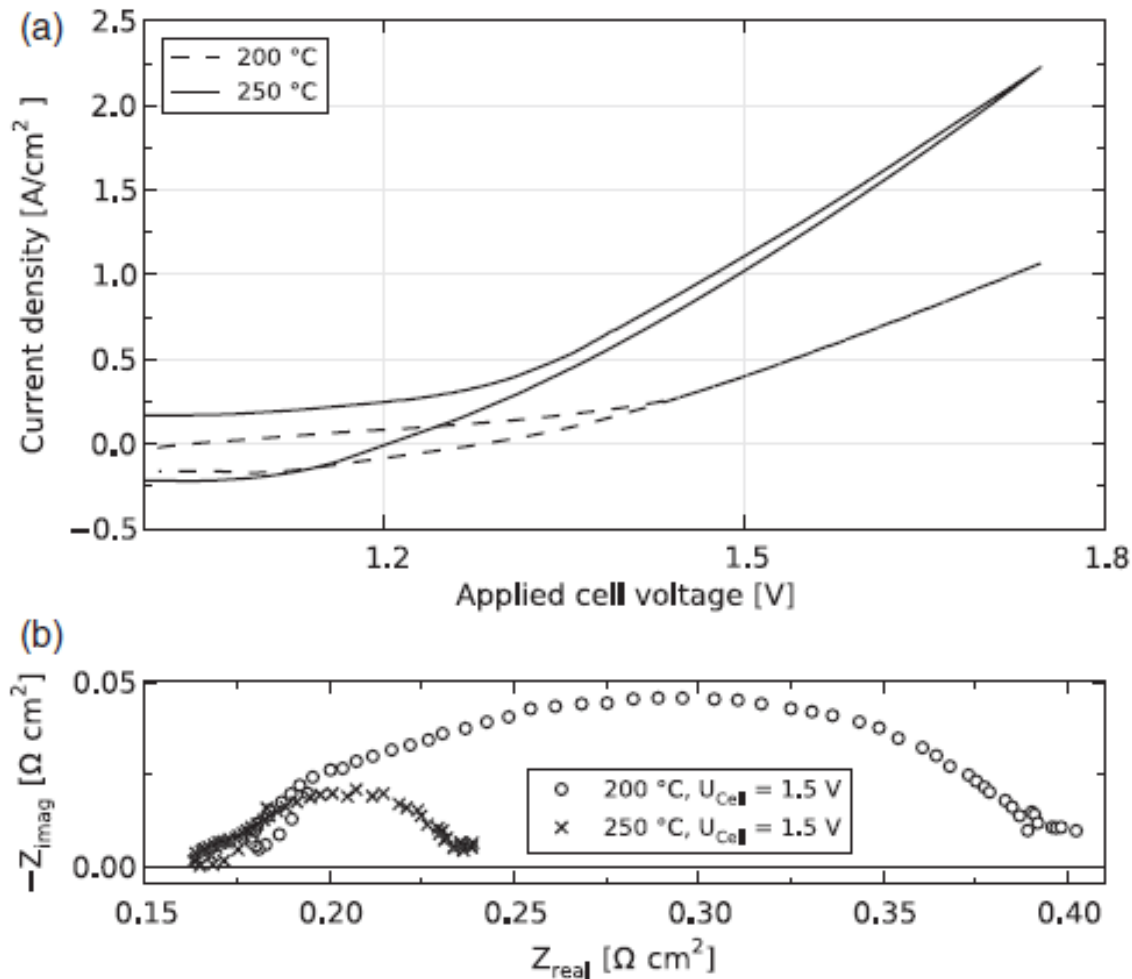
H₂ electrode: Inconel foam based

Electrolyte: KOH (aq.)

O₂ electrode: Ni foam based

F. Allebrod *et al.*, *J. Power Sources* 229 (2013) 22-31

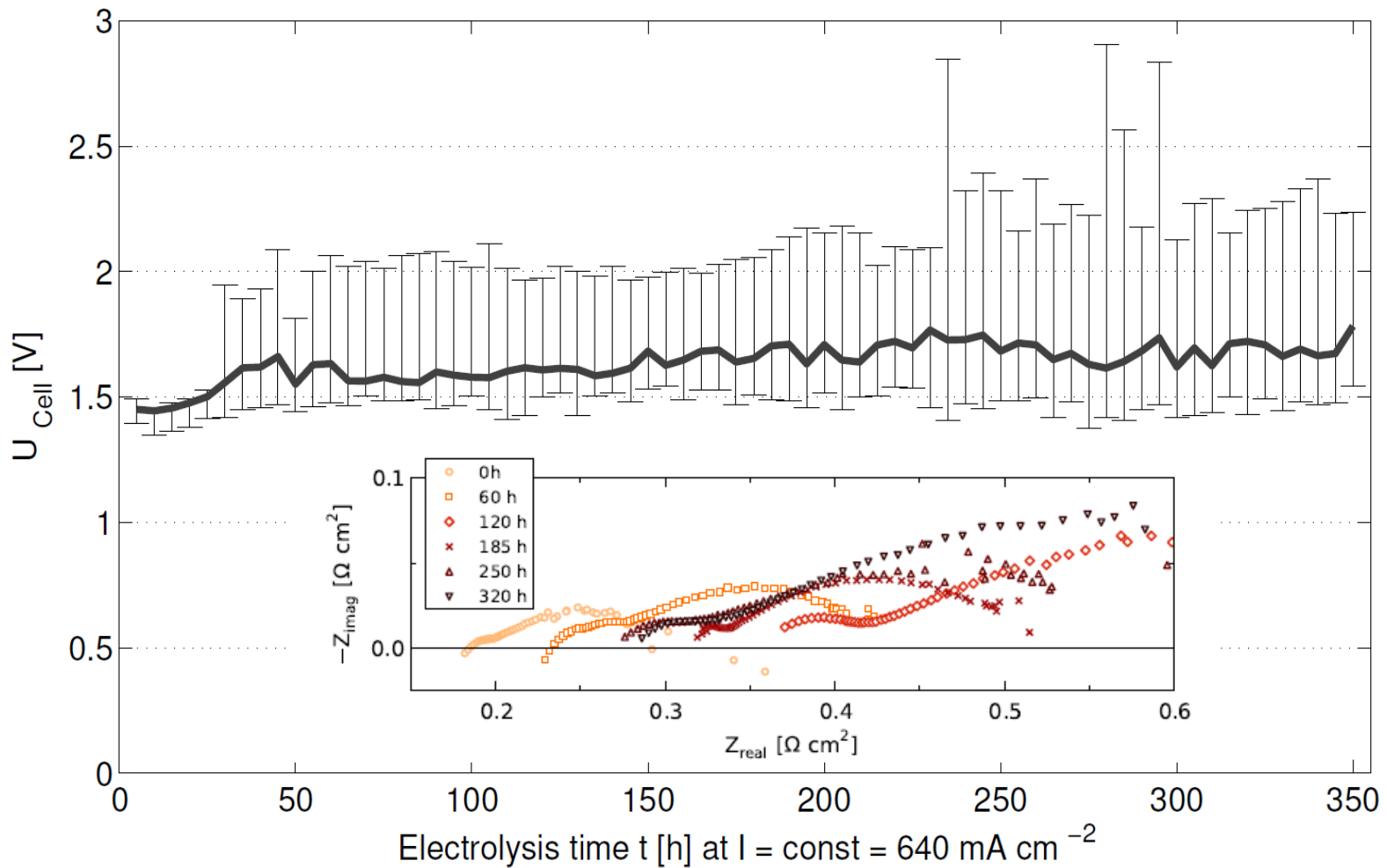
H₂O electrolysis - Performance



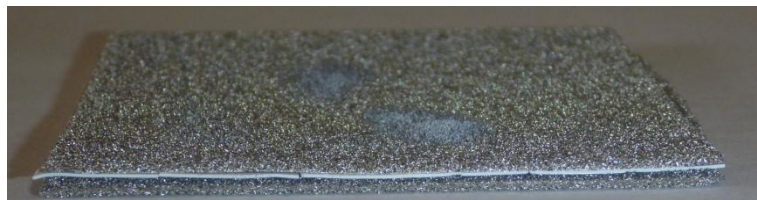
H₂ electrode:
Mo-activated Inconel foam
Electrolyte:
45 wt% KOH (aq.)
immobilized in mesoporous
SrTiO₃
O₂ electrode:
Co-activated Ni foam

F. Allebrod *et al.*, J. Power Sources 255 (2014) 394-403
C. Chatzichristodoulou *et al.*, Rev. Sci. Instrum. 84 (2013) 054101-12.

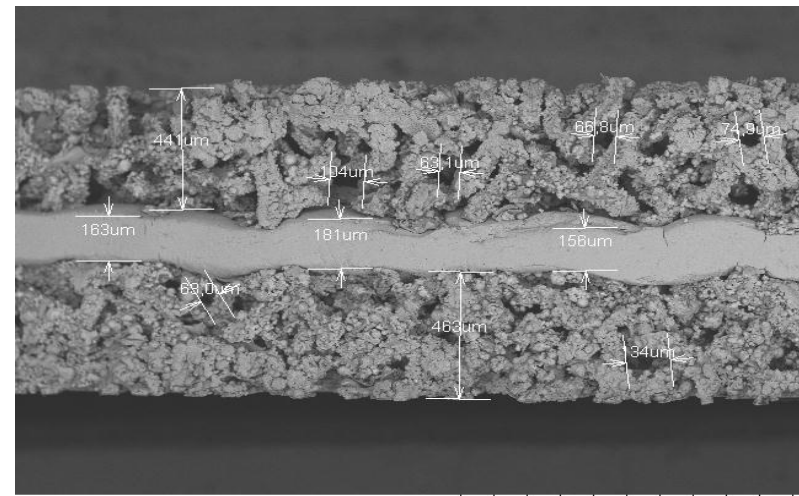
H₂O electrolysis - Degradation



H₂O electrolysis - Upscaling



- Continuous production of mesoporous YSZ layer has been achieved by tape casting
- Layer thickness 300 μm
→ full cell height can be < 1mm
- A 5x5 cm² cell corresponds to ~100 W at $\eta_{\text{el}} = 85 \%$
→ H₂ production of > 25 L/h



Inc_YSZ-0007 2013-10-14 H D5,5 x100 1 mm
YSZ-fkal-01 + Inc electrodes

- Electrochemical reactors operating at ca. 100-300 °C and 10-100 bar appear very promising
- Immobilized liquid electrolytes can fill the Norby gap (0.84 S/cm at 200 °C)
- Encouraging results achieved with H₂O electrolysis (2.3 A/cm² at 1.75 V)
- Efforts to upscale production have begun
- Potential for synthesis of H_xC_yO_z with similar type electrochemical reactors

- Use of oxide based electrocatalysts for the O₂-electrode (DFT + advanced characterization)
- Model assisted electrode development work
- Advanced characterization of GDE functionality
- Corrosion resistant materials for interconnects, current collectors, stack housing
- Up-scaling fabrication
- Testing of cells, single repeating units and small stacks
- Stack design and testing
- System design

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- The 2nd generation alkaline electrolysis project, EUDP 63011-0200
- The Department of Energy Conversion and Storage, DTU

Thank you for your attention!