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

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Outline

- Motivation
- Electrolytes
- Cell concept
- Electrochemical testing equipment
- $\text{H}_2\text{O}$ electrolysis
- Summary
- Outlook
Motivation - Sustainability

- 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 $T \sim 100-300 \, ^\circ\text{C}$, $P \sim 10-100$ 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)*
Motivation – Some facts

- 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 ($CO + 3 H_2 \leftrightarrow CH_4 + H_2O$) between 200 – 450 °C at 30 bar

- $(CH_3)_2O$ synthesis on Cu/ZnO/Al$_2$O$_3$ catalyst ($2 CO + 4 H_2 \leftrightarrow (CH_3)_2O + H_2O$) between 200 - 300 °C at ca. 50 bar, very similar for synthesis of CH$_3$OH

- Electrochemistry under pressure of 30 - 50 bar and temperatures of 200 – 300 °C ⇒ intimate thermal integration of electrochemistry and catalysis is possible
Electrolytes – The Norby gap

Electrolytes – Possibilities

- **45 wt% KOH immobilized in ca. 50 % porous ceramics:** 0.84 S cm\(^{-1}\) at 200 °C and 25 bar  
- **15 wt% K\(_2\)CO\(_3\)(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, CsH\(_2\)PO\(_4\):** ca. 10\(^{-2}\) S cm\(^{-1}\) at 240 °C (“the limit”).  
- **Acceptor doped metal phosphorous oxides such as Ce(PO\(_3\))\(_4\) and CeP\(_2\)O\(_7\) - high initial conductivity – not stable over time > 100 h**  
- **BaCe\(_x\)Zr\(_y\)Y\(_z\)O\(_{3-\delta}\)** 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 CO\(_2\)
Electrolytes – Immobilized KOH (aq.)

Cell concept

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

Ceramic powder, e.g. SrTiO$_3$, forming a mesoporous matrix

Proton conducting (solid acid) electrolyte:

H$^+$
e-
e-
H$_2$O
O$_2$, H$_2$O
CO$_2$
CH$_3$OH, H$_2$O, CO$_2$, …

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Alkaline (KOH) electrolyte (water electrolysis):

OH$^-$
e-
e-
O$_2$
O$_2$
H$_2$O
H$_2$

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OH$^-$
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O$_2$
H$_2$O
H$_2$
**H₂O electrolysis - Performance**

**Graph:**
- Current density vs. Applied Cell Voltage
- Conditions: 240 °C, 40bar

<table>
<thead>
<tr>
<th>Current density [A·cm⁻²]</th>
<th>1.5 V</th>
<th>1.75 V</th>
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<tr>
<td>Ag-Ni-foam / Inconel-foam</td>
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<td>2.00</td>
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<td>Ni-foam / Inconel-foam</td>
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<td>2xAg-Ni-foam / 2xInconel-foam</td>
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<td>2xNi-foam / 2xInconel-foam</td>
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</table>

**Electrodes:**
- **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 Inconnel foam

**Electrolyte:**
45 wt% KOH (aq.)
immobilized in mesoporous SrTiO₃

**O₂ electrode:**
Co-activated Ni foam

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F. Allebrod et al., J. Power Sources 255 (2014) 394-403
H₂O electrolysis - Degradation

Electrolysis time t [h] at I = const = 640 mA cm⁻²
**H₂O electrolysis - Upscaling**

- Continuous production of mesoporous YSZ layer has been achieved by tape casting
- Layer thickness 300 μm → full cell height can be < 1 mm
- A 5x5 cm² cell corresponds to ~100 W at η_{el} = 85 % → H₂ production of > 25 L/h
• 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 HₓCᵧOᵢ with similar type electrochemical reactors
Outlook

• Use of oxide based electrocatalysts for the $\text{O}_2$-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
Acknowledgements

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Thank you for your attention!