Micro-solid oxide fuel cells running on reformed hydrocarbon fuels

Barbara Scherrer¹,², Anna Evans¹, Alejandro J. Santis-Alvarez³, Bo Jiang⁴, Julia Martynczuk¹,⁵, Henning Galinski⁶, Michel Prestat¹, René Tölke¹, Anja Bieberle-Hütter¹, Dimos Poulakakos³, Paul Muralt⁴, Philippe Niedermann⁷, Alex Dommann⁷, Thomas Maeder⁸, Peter Heeb⁹, Valentin Straessle⁹, Ludwig J. Gauckler¹,¹⁰ and Claude Muller⁷

¹ Nonmetallic Inorganic Materials, ETH Zurich, Zurich, Switzerland
² Australian Centre of Microscopy and Microanalysis, The University of Sydney, Sydney, Australia
³ Laboratory of Thermodynamics in Emerging Technologies, ETH Zurich, Zurich, Switzerland
⁴ Ceramic Laboratory, EPFL, Lausanne, Switzerland
⁵ Electron Microscopy ETH Zurich, ETH Zurich, Zurich, Switzerland
⁶ Applied Physics, Harvard School of Engineering and Applied Sciences, Cambridge, US
⁷ Centre Suisse d'Electronique et Microtechnique, CSEM, Neuchâtel, Switzerland
⁸ Laboratory of Microengineering for Manufacturing, EPFL, Lausanne, Switzerland
⁹ Institute for Micro- and Nanotechnology, NTB, Buchs, Switzerland
¹⁰ International Institute for Carbon Neutral Energy Research (WPI-I2CNER), Kyushu University, Fukuoka, Japan
Sources for mobile energy

Advantages of micro-SOFC:
- high efficiency
- high energy density
- fuel flexibility
- geographically independent

Challenges of micro-SOFC:
- high temperature

Horizon Minipack is a recharging system based on PEMFC
http://www.horizonfuelcell.com

Adapted from: Manhattan Scientifics & L. Livermore National Laboratories and Sulzer Hexis, 2002.
Micro-fuel cell systems for battery replacement

Assembly of glass carrier, reformer and micro-SOFC chip

micro-SOFCs on Si chip (Pt/YSZ/Pt)

micro reformer (2 wt% Rh/Ce$_{0.5}$Zr$_{0.5}$O$_2$)

functional glass carrier

glass frit

cement

anodic

reformer

(gas supply and heater)
Functional glass carrier

- Fabrication of carrier:
  - Schott AF 32®
    - \( T_G = 717^\circ C \)
  - Glass frit bonding
    - \( H = 100 \mu m \)

- Fabrication of heaters:
  - Pt and Ag heaters
  - Screen printed heaters
    - Height < 50 \( \mu m \)
  - Heater A: bottom of MR
  - Heater B: before MR inlet
Assembly of glass carrier, reformer and micro-SOFC chip

- **micro-SOFCs on Si chip (Pt/YSZ/Pt)**
- **glass frit**
- **anodic cement**
- **functional glass carrier**
- **micro reformer (2 wt% Rh/Ce_{0.5}Zr_{0.5}O_2)**
- **(gas supply and heater)**
Micro reactor

- Conversion of \( \text{C}_4\text{H}_{10} \) is higher
- \( \text{H}_2 \) production from \( \text{C}_4\text{H}_{10} \) is higher
- **n-Butane**: \( \text{C/O} = 0.7 \) and \( \text{C/O} = 0.8 \) are best dilutions
- **Propane**: \( \text{C/O} = 0.8 \) is best dilution

<table>
<thead>
<tr>
<th>( \phi )</th>
<th>( \eta )</th>
<th>( x_{\text{CH}_4} )</th>
<th>( \psi_{\text{H}_2} )</th>
<th>( \psi_{\text{CO}} )</th>
<th>( \psi_{\text{syngas}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>n-Butane</strong></td>
<td>0.7</td>
<td>Average ± ( \sigma ) [%]</td>
<td>95.2 ±0.1</td>
<td>0.18 ±0.0</td>
<td>66.7 ±0.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outlet flow rate [( \mu \text{mol/s} )]</td>
<td>0.06 ±0.01</td>
<td>0.24 ±0.01</td>
<td>4.43 ±0.14</td>
</tr>
<tr>
<td><strong>Propane</strong></td>
<td>0.8</td>
<td>Average ± ( \sigma ) [%]</td>
<td>84.3 ±0.4</td>
<td>0.16 ±0.0</td>
<td>55.4 ±0.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Outlet flow rate [( \mu \text{mol/s} )]</td>
<td>0.31 ±0.01</td>
<td>0.32 ±0.01</td>
<td>4.33 ±0.01</td>
</tr>
</tbody>
</table>
Micro reactor

- Temperature increase behavior during testing
  - Reaction starts > 300 °C

- Higher flow rate results in higher temperature.

Characterization of micro reformer

... in the furnace

... on the carrier with integrated heaters
Results of gas analysis

- Less even temperature distribution results in lower yield, conversion and selectivity for the integrated heater setup.

- Better insulation will improve it again.

\[ T_{\text{set}} = 550^\circ\text{C}, \, T_{\text{op}} = 565^\circ\text{C} \]
\[ T_{\text{set}} = 350^\circ\text{C}, \, T_{\text{op}} = 560^\circ\text{C} \]

![Bar chart showing results of gas analysis](chart.png)
Assembly of glass carrier, reformer and micro-SOFC chip

micro-SOFCs on Si chip (Pt/YSZ/Pt)

micro reformer (2 wt% Rh/Ce$_{0.5}$Zr$_{0.5}$O$_2$)

functional glass carrier

gas supply and heater
Micro-SOFC fabrication

- Si Wafer (380 µm), LPCVD-Si$_3$N$_4$ (200 nm) on both sides
- Window opening (900 µm): photolitho + RIE of Si$_3$N$_4$
- Si wet etching: KOH 20%, 90 °C
- YSZ deposition: AA-CVD, PLD, spray pyrolysis
- Release of the YSZ membrane by reactive ion etching
- Top-side electrode deposition
- Back-side electrode deposition

Top-view light micrographs

- 390 µm
- comp. stress
- tens. stress
Micro-SOFC fabrication

- Test chip: 30 free-standing micro-SOFC membranes
- Membrane yield (%): number of surviving membranes / 30 \* 100
- Membrane yield target: \( \sim 100 \% \)

Membrane side length: 390 μm
Thermomechanical stress

$T_{\text{dep}} = 25 \, ^\circ\text{C}$

Partially crystalline as-deposited film (PLD)

Yield after free-etching: ca. 100%

Tensile stress (flat membrane)

$T_{\text{dep}} = 700 \, ^\circ\text{C}$

Fully crystalline as-deposited film (PLD)

Yield after free-etching: ca. 100%

Compressive stress (buckled membrane)

**Thermomechanical stress**

- **$T_{\text{dep}} = 25 \, ^\circ\text{C}$**
  - Crystallization during heating $\gg$ tensile stress
  - Membrane rupture (low yield: $< 10\%$)

- **$T_{\text{dep}} = 700 \, ^\circ\text{C}$**
  - Buckling «apparently» unchanged during heating
  - Robust membrane (high yield: 100%)

---

Residual stress in free-standing YSZ membranes

Different stresses $f(T_{\text{depo}})$:
- Tensile and too much compressive stress result in membrane rupture.

ASR of Pt in fuel cell conditions

Pt thin films tested on YSZ single crystal
- ASR of the electrodes are stable over heating and cooling
- Microstructure is different depending on the seen environment
Assembly of glass carrier, reformer and micro-SOFC chip

- micro-SOFCs on Si chip (Pt/YSZ/Pt)
- functional glass carrier
- reformer
- micro reformer (2 wt% Rh/\text{Ce}_{0.5}\text{Zr}_{0.5}\text{O}_2)
- glass frit
- cement
- anodic
- functional glass carrier
- (gas supply and heater)
Assembly of glass carrier, reformer and micro-SOFC chip

- Functional glass carrier
- Micro re-former (2 wt% Rh/Ce\textsubscript{0.5}Zr\textsubscript{0.5}O\textsubscript{2})
- Contact wires from the cells to the impedance analyzer
- Gas supply and heater
Assembly of glass carrier, reformer and micro-SOFC chip

- Thermocouple placed on top of the sample
- Insulation with WDS-Ultra blocks and fiberfrax® ceramic paper
- Heating tracks connected to power supply
- Gas inlet connected to the air and butane gas lines, gas outlet not connected
- 2 individual micro-SOFC membranes contacted with Pt wires and connected to impedance device (Zahner IM6)
Temperature program

- Heating ramp done by increasing voltage
- Temperature measurement on the sample is accurate
Temperature program

- Self sustained reaction of the reformer heats the assembly further
  - Increasing flow results in increasing temperature
- Almost stable temperature reached after 2 min
Cell voltage and power density

- Theoretical open circuit voltage was achieved!
  - Gas-tight membranes
- Maximum power density of about 50 mW/cm² at 565 °C!
- All membranes survived the testing program (maximal temperature of 596 °C)!
Strange curve shape at ~0.7 V, most likely due to excess water at the gas outlet.
Cell voltage and power density – decrease in OCV

- Long-term testing not possible due to instable Pt-electodes
  - Cathode agglomerates more severe most likely due to the surface roughness of the electrolyte layer
- Gas leak of ceramic paste results in lower OCV
Summary

- Assembly of the glass carrier, reformer and micro-SOFC chip works.

- The heater was able to heat up the assembly till the self sustained reaction of the reformer sets in.

- Further heating was achieved by increasing the flow of butane and air.

- Theoretical OCV and a maximum power density of about 50 mW/cm² at 565 °C was achieved.
Outlook

- Excess of water results in unstable current-voltage curve.

- Integration of more stable (and active) electrode materials in order to achieve a better stability and higher power density
  - Metal alloys: Pt-Y-Al
  - Ceramics: LSC, LSMC

- Cement paste starts to leak at 550 °C, which resulted in an unstable temperature due to complete combustion of the fuel.

- Current collection of the membranes should be improved
  - On the chip with connection path
  - To the out side with wire bonding
Acknowledgements

Thank you for your attention!

Support:
- Electron Microscopy Center of the ETH Zurich (EMEZ)
- I²CNER, Kyushu University

Funding:
- Swiss National Science Foundation (SNSF), Switzerland
- Korean-Swiss Science and Technology Cooperation