Development and Characterisation of Metal-Supported Solid Oxide Fuel Cells

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Outline

- Introduction
  - German Aerospace Center (DLR)
  - SOFC Activities at DLR

- Development of Metal Supported SOFC Concept of DLR
  - Development of Functional Layers and Cells
  - Electrochemical Cell Performance

- Advanced Characterisation Techniques
  - Spatially Resolved Cell Characterisation
  - New Imaging Methods for SOFC Characterisation

- Conclusions
DLR
German Aerospace Center

- Research Institution
- Space Agency
- Project Management Agency

Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft
6700 employees across 33 institutes and facilities at 13 sites.

Research Areas

- Aeronautics
- Space
- Transport
- Energy
- Space Agency
- Project Management Agency
DLR Site Stuttgart

Employees: 560
Size of site: 25 860 m²
Research institutes:

- Institute of Structures and Design
- Institute of Vehicle Concepts
- Institute of Technical Physics
- Institute of Technical Thermodynamics
- Institute of Combustion Technology
Characterization of Short Stacks and Stacks (ASC, MSC)

SOFC Activities at DLR

Development of Metal Supported Cells (MSC)

SOFC Diagnostics

SOFC Modeling

System Technology

Fuel gas

Air

Cell current, voltage, impedance

Detailed 2D model of MEA, channel, interconnector

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Segment voltage, impedance

Segment current

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in der Helmholtz-Gemeinschaft

ISAEST-9, December 2-4, 2010, Chennai, India
Development of Metal Supported Cells

Advantages of MSC:

- High robustness
- High resistance against thermal and redox cycling
- Good integration into interconnects (bipolar plates)
- Low cost of metal support and cell materials (thin layers)
SOFC Metal Supported Cell

Plasma Deposition Technology

Thin-Film Cells

Ferritic Substrates and Interconnects

Compact Design with Thin Metal Sheet Substrates

Brazing, Welding and Glass Seal as Joining and Sealing Technology

Air channel

- Bipolar plate
- Protective coating
- Contact layer
- Cathode current collector
- Cathode active layer
- Electrolyte
- Anode
- Porous metallic substrate

Fuel channel

- Bipolar plate
- Not used fuel + H₂O

Oxygen/air

- Not used air

(not in scale)
Vacuum Plasma Spraying of SOFC Cells
Plasma Spray Laboratory at DLR Stuttgart
### Powders Used for the Spraying of the Cells

<table>
<thead>
<tr>
<th>Powder</th>
<th>NiO</th>
<th>ZrO$_2$-7 mol %Y$_2$O$_3$</th>
<th>ZrO$_2$-10 mol%Sc$_2$O$_3$</th>
<th>(La$<em>{0.8}$Sr$</em>{0.2}$)$_{0.98}$MnO$_3$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short name</td>
<td>NiO</td>
<td>YSZ</td>
<td>ScSZ</td>
<td>LSM</td>
</tr>
<tr>
<td>Morphology</td>
<td>sintered, crushed</td>
<td>sintered, crushed</td>
<td>sintered, crushed</td>
<td>sintered, spherical</td>
</tr>
<tr>
<td>Size distribution</td>
<td>10-25 µm</td>
<td>5-25 µm</td>
<td>2-35 µm</td>
<td>20-40 µm</td>
</tr>
<tr>
<td>Supplier</td>
<td>Cerac, USA</td>
<td>Medicoat, Switzerland</td>
<td>Kerafol, Germany</td>
<td>EMPA, Switzerland</td>
</tr>
</tbody>
</table>

![Scanning Electron Microscopy (SEM) images of powders](image1.png)

![Scanning Electron Microscopy (SEM) images of powders](image2.png)

![Scanning Electron Microscopy (SEM) images of powders](image3.png)

![Scanning Electron Microscopy (SEM) images of powders](image4.png)
Morphology of Porous Metal Substrate PM Fe-26Cr-(Mo,Ti,Mn,Y2O3) of Plansee SE
Metallographic Cross Section of MSC Cell

- Porously sintered ferrite plate
- 8YSZ-electrolyte
- Ni/8YSZ-anode
- LaSrMnO$_3$-cathode
- Perovskite-type barrier layer
- 8YSZ-electrolyte
- LaSrMnO$_3$-cathode
Stack Assembly Based on Metal Supported Cell

Plasma-spayed cell with sealing by laser welding

1 = Metallic lower plate
2 = Active cell on substrat
3 = Metallic frame
4 = Cassette
5 = Stack
Stack Assembly Based on Metal Supported Cell

Current MS-SOFC Repeat Unit

90x120 mm² footprint – ca 100 cm² cell area

Counter flow design

Stamped sheet ferritic steel bipolar plate

Welded Fe-Cr substrate
Performance of Plasma Sprayed Metal Supported Cell

MSC Cell
12.5 cm² cell at 800°C; H₂/N₂ and Air

3-Cell Stack
100 cm² single cells at 800°C; H₂/N₂; Air
Thermal Cycling

15 thermal cycles performed, 12 down to 350 °C and 3 to ambient temperature
Degradation after thermal cycles was 10.3 %
20 forced redox cycles performed with 50 ml/min O₂ on the anode side per layer
Increase of power density after 5 cycles
Degradation of the stack was 9.1 % after 20 redox cycles
Investigation of Degradation and Cell Failures

- Insufficient understanding of cell degradation and cell failures in SOFC
- Extensive experimental experience is not generally available which would allow accurate analysis and improvements
- Long term experiments are demanding and expensive
- Only few tools and diagnostic methods available for developers due to the restrictions of the elevated temperatures
„Sophisticated“ (non-traditional) In-situ Diagnostics

- Electrochemical impedance spectroscopy on stacks
- Spatially resolved measuring techniques for current, voltage, temperature and gas composition
- Optical imaging
- Optical spectroscopy
- Acoustic emission detection
- X-ray tomography
Motivation for Spatially Resolved Cell Characterisation

Problems:

- Strong local variation of gas composition, temperature, and current density

This may lead to:

- Reduced efficiency
- Thermomechanical stress
- Degradation of electrodes

Effects are difficult to understand due to the strong interdependence of gas composition, electrochemical performance and temperature
Measurement Setup for Segmented Cells

- 16 galvanically isolated segments
- Local and global i-V characteristics
- Local and global impedance measurements
- Local temperature measurements
- Local fuel concentrations
- Flexible design: substrate-, anode-, and electrolyte-supported cells
- Co- and counter-flow
Modelling and Simulation

- Electrochemistry: Elementary kinetics
- Porous electrodes: Mass and charge transport
- Channels: Transient Navier-Stokes conservation equations (Mass, momentum, particles, energy)
- Interconnects: energy conservation

Segmented Cells

- Anode supported cells:
  Segmented cathode
  (H.C. Starck/InDEC)

- Electrolyte supported cells:
  Segmented cathode and anode
Test Rig
OCV Voltage Measurement for Determination of Humidity

- Voltage distribution at standard flow rates:
- 50% H₂, 50% N₂ + 3% H₂O, 0.08 SlpM/cm² air

Nernst equation:

\[ U_{rev} = U^0_{rev} - \frac{RT}{zF} \ln \left( \frac{P_{H2O}}{\sqrt{P_{O2}P_{H2}}} \right) \]

Produced water:
- S4: 0.61%, S8: 0.72%,
- S12: 0.78%, S16: 3.30%
Power Density Distribution under Conditions of High Fuel Utilisation

Counter-flow

Anode: 33% H₂, 1% H₂O, 66% N₂

Cathode: air

T = 800 °C

Cell voltage: 0.59 V

F_u = 80%

Lit.: Fuel Cells, 10 (3), 411-418 (2010)
Assessment of Local Performance with Segmented SOFCs

**Experiment**

![Image of segmented SOFCs](image)

16 segments

**Model**

![Block diagram of model](image)

**Global behavior**

![Graph showing global behavior](image)

**Local behavior**

![Graph showing local behavior](image)

Cell can be locally in critical conditions!
Variation of Load - Reformate

Anode supported cell, LSCF cathode, 73.96 cm², gas concentrations (current density equivalent): 54.9% N₂, 16.7% H₂, 16.5% CO, 6.6% CH₄, 2.2% CO₂, 3.2% H₂O (0.552 A/cm²), 0.02 SlpM/cm² air
Alteration of the Gas Composition at 435 mA/cm²
Alteration of the Gas Composition at 100 mA/cm²

Metallic housing, anode substrate, active area 73.78 cm²
Anode: 542 µm NiO/YSZ, Electrolyte: 14 µm YSZ + YDC,
Cathode: 28 µm LSCF
Operation conditions: 0.10 A/cm² - Anode λ = 5.52
(54.9% N₂, 16.7% H₂, 16.5% CO, 6.6% CH₄, 2.2% CO₂, 3.2% H₂O
0.08 Nlpm/cm² Air, 800°C)
Potential for Optical Spectroscopies

- Raman spectroscopy
- Laser Doppler Anemometry (LDA)
- Particle Image Velocimetry (PIV)
- Fast-Fourier Infrared (FTIR)
- Coherent Anti-Stokes Raman Spectroscopy (CARS)
- Electronic Speckle Pattern Interferometry (ESPI)
Setup for 1D-Raman Spectroscopy

- 3 double pulse Nd:YAG PIV 400 laser systems
- $\lambda = 532$ nm
- Repetition rate: 10 Hz
- Single pulse: $E \leq 350$ mJ / $\sim 7$ ns
- Pulse energy: $6 \times 300$ mJ
- Pulse length: $\sim 380$ ns
  - (temporal resolution)
Transparent Flowfield for SOFC

Top view

Side view
Experimental Setup for Raman Spectroscopy Measurements
Cell Housing with Transparent Flowfield in Hot Furnace
Preliminary Results

- Large scatter in detected signal
- Improvement of S/N ratio needed

- $\text{H}_2 + 3\% \text{H}_2\text{O}$
- $850 \, ^\circ\text{C}$
Preliminary Results

- Measurements and evaluation still in progress
- Tendencies of the species concentration profiles can be seen

- $\textbf{H}_2 + 3\% \textbf{H}_2\textbf{O}$
- $850 \degree \textbf{C}$
Setup for In-Situ Optical Microscopy
Conclusions

- The development of the metal supported SOFC concept has a high potential for SOFC application in dynamic operation with multiple thermal and redox cycles.
- Scale-up to a full size cassette with adequate cell performance is under way.
- In-situ diagnostic techniques allow for a largely extended insight into fuel cell processes.
- The obtained experimental data using a segmented cell setup that allows for the measurement of local i-V characteristics, gas composition and temperature can be used for modeling and simulation.
- Strong gradients of gas concentrations and current density particularly at operation with high fuel utilisation may result in locally critical operating conditions.
- Additional in-situ diagnostic methods such as optical microscopy and gas-phase Raman Spectroscopy can provide further information for the understanding of cell reactions and processes.
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Locally Resolved Power Density Distribution and Fuel Utilisation in Dependence of H₂ Concentrations