Development of Metal Supported SOFC at DLR

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The DLR
German Aerospace Research Center
Space Agency of the Federal Republic of Germany
Sites and employees

5.100 employees working in 27 research institutes and facilities
  ■ at 8 sites
  ● in 7 field offices.

DLR Stuttgart
Possible growth of renewable electricity for EU-15 until 2050 - Scenario “Solar Energy Economy” -

Source: “Renewable Energies in Europe” DLR Stuttgart, to be published

- Photovoltaics
- Solarthermal
- Geothermal
- Wind
- Biomass
- Hydropower

System Analysis and Technology Evaluation

1) percentage of total generation
Low Temperature Fuel Cells
AFC, PEFC, DMFC

Fuel Reforming
MEA production

Competence and Activities
Segmented Cells for analysis and control

System Technology and Analysis
PEMA Test equipment

High Temperature Fuels
SOFC

Spray Concept
Plasma deposition process

SOFCs for APUs
Outline

1. Introduction
2. SOFC Spray Concept of DLR
3. Plasma Deposition Technologies
4. Development of Cells and Functional Layers
5. Metallic Substrate Support
6. Electrochemical Performance of Cells and Stacks
7. Spatially-Resolved Cell Characterisation
8. Conclusion
SOFC Development from 1st (1G) to 3rd Generation (3G)

1G
- LSM + YSZ
  - YSZ
  - Ni+YSZ

2G a
- LSM + YSZ
  - YSZ
  - Ni+YSZ

2G b
- LSCF
  - CGO
  - YSZ
  - Ni+YSZ

3G
- LSCF
  - CGO
  - YSZ/SSZ
  - Ni+YSZ
  - FeCr

- Improved power density
- Improved long-term stability
- Reduced operating temperature
Advantages of Metal Supported Cells (MSC)

- High electrical conductivity of the metal support
- High thermal conductivity of the metal support
- High stability of the cell during temperature changes
- High and homogeneous mechanical stability of the cell
- Application of conventional joining and sealing techniques
- Cost reduction for materials and fabrication technologies
Requirements for Metal Substrate Supports

- High electrical conductivity
- Adapted thermal expansion coefficient (10-12·10^{-6} K^{-1})
- High corrosion stability in oxidising and reducing, moist atmosphere
- Sufficient mechanical stability
- High gas permeability (porosity > 40 Vol. %)
- Flat surface area for plasma sprayed functional layers
SOFC Spray Concept of DLR

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

Objective of DLR Development:

Light-weight stack of 5 kW power with high performance, rapid heat-up and good thermal cycling properties
Cell Design for APU Application

Seals

MEA layers

Interconnect sheet (top)

Substrate

Interconnect sheet (bottom)

Cassette arrangement with integrated substrate and MEA
Principles of DC and RF Plasma Spraying
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, spherical</td>
<td></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>

![SEM images of powders](image-url)
Cross Section of Entirely Vacuum Plasma Sprayed Thin-Film MEA on a Porous Ni Felt

- Cathode (30 µm)
- Electrolyte (25 µm)
- Anode (35 µm)
- Porous Metallic Substrate (Ni felt)
Development of Nanostructured Anode Layer

Permeability coefficient \( (10^{-15} \text{ m}^2) \)

<table>
<thead>
<tr>
<th>VPS ref</th>
<th>APS conv.</th>
<th>Ni-C</th>
<th>Double Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>2</td>
<td>12</td>
<td>30</td>
<td>54</td>
</tr>
</tbody>
</table>
## Ferritic Alloys Studied for Porous Metallic Substrates

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Supplier</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ferrochrom (1.4742)</td>
<td>ThyssenKrupp</td>
<td>18% Cr, 0.9% Al, 0.9% Si, 0.69% Mn, 0.06% C</td>
</tr>
<tr>
<td>CrAl20 5 (1.4767)</td>
<td>ThyssenKrupp</td>
<td>19% Cr, 5.5% Al, 0.5% Si, 0.5% Mn, 0.05% C</td>
</tr>
<tr>
<td>FeCrAIY</td>
<td>Technetics</td>
<td>22% Cr, 5% Al, 0.1% Y</td>
</tr>
<tr>
<td>ZMG 232</td>
<td>Hitachi Metals</td>
<td>21% Cr, 0.08% Al, 0.43% Si, 0.47% Mn, 0.02% C</td>
</tr>
<tr>
<td>SUS 430 HA</td>
<td>Nippon Steel</td>
<td>16% Cr, 0.13% Al, 0.29% Si, 0.13% Mn, 0.05% C</td>
</tr>
<tr>
<td>SUS 430 Na</td>
<td>Nippon Steel</td>
<td>16% Cr, 0.01% Al, 0.29% Si, 0.56% Mn, 0.05% C</td>
</tr>
<tr>
<td>Crofer22 APU</td>
<td>ThyssenKrupp</td>
<td>22% Cr, 0.12% Al, 0.1% Si, 0.41% Mn, 0.16% Ni, 0.05% Ti, 0.08% La</td>
</tr>
<tr>
<td>IT 14</td>
<td>Plansee</td>
<td>26% Cr, &lt; 0.03% Al, &lt; 0.03% Si, Mo, Ti, Mn, Y₂O₃</td>
</tr>
</tbody>
</table>
Porous Metallic Substrates Used for the Plasma Spray SOFC Concept

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Felt</th>
<th>Foam</th>
<th>Knit fabric</th>
<th>Sintered plate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Material</td>
<td>Ni</td>
<td>Fe-22Cr-5Al-0,1Y</td>
<td>Fe-22Cr-0,5Mn</td>
<td>Fe-26Cr (Y₂O₃)</td>
</tr>
<tr>
<td>Thickness</td>
<td>~ 1,0</td>
<td>~ 1,8</td>
<td>~ 1,0</td>
<td>~ 1,0</td>
</tr>
<tr>
<td>Porosity</td>
<td>~ 85</td>
<td>~ 80</td>
<td>~ 90</td>
<td>~ 50</td>
</tr>
<tr>
<td>Supplier</td>
<td>Bekaert</td>
<td>Technetics</td>
<td>Rhodius</td>
<td>Plansee AG,</td>
</tr>
<tr>
<td></td>
<td>Belgium</td>
<td>USA</td>
<td>Germany</td>
<td>Austria</td>
</tr>
</tbody>
</table>
Interdiffusion of Fe, Cr and Ni Between Substrate and Anode

- Triple phase boundary (TPB)

FeO, Fe$_2$O$_3$
Experimental Approach For a Diffusion Barrier Layer at the Anode Side

Requirements

• Porous structure
• Adapted thermal expansion coefficient ($\alpha_{\text{tech.}} = 10^{-11} \times 10^{-6} \text{ K}^{-1}$)
• High electronic conductivity in reducing anode atmosphere [$\sigma = 1-3 \text{ S/cm, } p(O_2) = 10^{-16} \text{ bar}$]
• Chemical stability in reducing humid anode gas atmosphere
• Barrier effect for Fe, Cr und Ni species
• Electrochemical compatibility at cell operation (chemical inert behavior)
Plasma Sprayed Diffusion Barrier Interlayer

LaSrMnO$_3$-cathode

8YSZ-electrolyte

Ni/8YSZ-anode

Perovskite-type barrier layer

Porous sintered ferrite plate
I-V Characteristics of a VPS Cell with Improved Anode and Cathode Layers (LSM) as a Function of Different Operating Temperatures (0.5 $H_2$+0.5 $N_2$ / 2 Air)
Electrochemical Performance of VPS Cells With and Without Diffusion Barrier Layer in Operation with Simulated Reformate H2/N2 and Air

- **MSC without DBL**
  - Active cell area: 7.06 cm²
  - Degradation rate:
    - 0-1000 h > 20%
    - 1000-1500 h = 40%

- **MSC with DBL**
  - Active cell area: 7.06 cm²
  - Degradation rate:
    - 0-1000 h < 1%
    - 1000-2300 h = 30%
Redox Cycling Conditions

Gases switched off: Diffusion of Air to Cell

Gases switched on: Operation @ 200 mA/cm²

Time [h]

Cell Voltage [V]

Power density

Gas Flow

Cell voltage

[Graph showing redox cycling conditions with time, cell voltage, power density, gas flow, and redox cycling over time.]
Electrochemical Behaviour of a SOFC (12cm²) during 10 Redox Cycles (800°C, 0.5N₂+0.5H₂ / 2.0 Air, 200 mA/cm²)
I-V Characteristics of a VPS Cell with Improved Anode and Electrolyte Layers / LSM Cathode after Redox Cycling

![Graph showing I-V characteristics with different markers for different redox cycling conditions.]
Thermal Cycling Conditions

- **Current Voltage Curve**
  - Cell Voltage
  - Temperature
  - Power Density

- **Time [h]**
  - 212, 217, 222, 227, 232

- **Cell Voltage [V]**
  - 0, 0.2, 0.4, 0.6, 0.8, 1.0, 1.2

- **Power den. [mW/cm²]/Temp. [°C]**
  - 0, 200, 400, 600, 800, 1000, 1200

- **Current Voltage Curve**
  - 50 K / h
  - 200 K / h

- **DLR**
  - Deutsches Zentrum für Luft- und Raumfahrt e.V.
in der Helmholtz-Gemeinschaft
Electrochemical Behaviour of a SOFC (12 cm²) during 10 Thermo Cycles (800°C, 0.5N₂+0.5H₂ / 2.0 Air, 200 mA/cm²)
I-V Characteristics of a 4-Cell Stack in Cassette Configuration Operated at 800 °C with H₂/N₂-Air (12.5/12.5/80 smlpm/cm²)
The segmented approach of DLR

**Schematic of the metallic housing**

- Metallic housing
- Segment with air flow channels
- Wire for voltage measurements
- Thermocouple
- Isolation
- Wire for current measurement
- Segmented cathode
- Segmented anode
- Electrolyte
- Capillary for gas chromatography
- Segment with fuel flow channels
Cell Design and Test Rig

- "Simple" measuring device for cassettes
- More flexible housing, less disturbed impedance signals
- GC measurement
- Sealing and contacting
- All cell types applicable
- Improved contacting
- More reliable sealing
- Impedance measurements
- Reliable temperature measurement
Results – flow design
Plasma sprayed cell with LSCF (NT107B02)

- P und T distribution at standard gas flow rates:
  12,5/12,5//80 smlpm/cm² H₂/N₂//Air, 800°C, 0,6V,
  after 189h, counter flow
Results – flow design

Plasma sprayed cell with LSCF (NT107B02)

- P und T distribution at standard gas flow rates:
  12,5/12,5//80 smlpm/cm² H₂/N₂//Air, 800°C, 0,6V,
  after 193h, co flow

![Graph showing power density and temperature distribution](image)
Results – effect of leakage on voltage

Plasma sprayed cell with LSCF (NT107B02)

• V distribution at OCV with co and counter gas flow:
  L: 12,5/12,5//80 smlpm/cm² H₂/N₂//Air, 800°C, counter
  R: 12,5/12,5//80 smlpm/cm² H₂/N₂//Air, 800°C, co
Results – effect of leakage on the concentrations

Leaky pre-test cell (Te142)

- Gas concentration distribution at 800°C:
  Gas flow rates: 25%H₂, 25%CO, 50%N₂
  6,8/6,8/13,5//68 smlpm/cm² H₂/CO/N₂//Air
Determination of Steam Content at Operation with Reformate

- Voltage distribution at **standard flow rate**: 1.79 A/cm² current density equivalent, 50% H₂, 50% N₂ + 3% H₂O, 0.08 SlpM/cm² air

Nernst equation:

\[ U_{rev} = U_{rev}^0 - \frac{RT}{zF} \ln \left( \frac{P_{H2O}}{\sqrt{PO_2 \cdot PH2}} \right) \]

Chemically produced water:

S4: 0.61%, S8: 0.72%, S12: 0.78%, S16: 3.30%
Locally Resolved Power Density Distribution and Fuel Utilisation in Dependence of H$_2$ Concentrations
Comparison of Calculated and Measured H$_2$ Concentration by Gas Chromatography For a Segment Row
Conclusion

- World wide increasing interest on metal supported SOFC cells, particularly for mobile application
- Long-term stability of the metallic support is an important requirement for metal supported cell technology
- Improvement of long-term cell operation by applying plasma sprayed diffusion barrier layer
- An adequate cell and stack design for plasma sprayed cells in cassette configuration has been developed
- The development of the metal supported SOFC concept has a high potential for SOFC application in dynamic operation with multiple thermal and redox cycles
- Spatially-resolved measuring techniques are important analytical tools to optimise cell operation