Progress in Metal-Supported Solid Oxide Fuel Cells

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Outline

- Introduction
- Development of metal-supported SOFC by applying sintering techniques
  - Ceres Power
  - Lawrence Berkeley National Lab
  - Risoe / Topsoe Fuel Cells
- Development of metal-supported cells by applying plasma deposition techniques
  - German Aerospace Center (DLR)
- Conclusions
Development of Metal-Supported Cells

Advantages of MSC:

• High robustness with resistance against shock and transient conditions
• High resistance against thermal and redox cycling
• Good integration into interconnects (bipolar plates)
• Low cost of metal support, cell materials (thin layers) and sealing

Improved power density
Improved long-term stability
Reduced operating temperature
Early Metal-Supported SOFC Work – 1960s-1970s

1964    Shell Oil, Williams et al  US 3,464,861
- Flame-sprayed ZrO2 electrolyte
- Sintered austenitic stainless steel support
Temperature: 700-800°C
Fuel: hydrogen, methanol, and kerosene
115 mW/cm² at 750°C

1970    Tannenberger et al  US 3,525,646
- Plasma-sprayed cell layers
- Sintered metal support
## Developments in MSC Technology

### 1990s:
- **Fuji Electric, Japan**  
  Plasma sprayed ZrO$_2$ electrolyte, MCrAlY support
- **DLR, Germany**  
  Plasma sprayed cells on porous metal support

### 2000s:
- **Ceres Power, GB**  
  Wet processing of CGO electrolyte, stainless steel support, dense CGO after 1000 °C firing, operation at 500-600 °C
- **LNBL, USA**  
  Colloidal spray electrolyte deposition (10-20 µm), co-sintered YSZ, infiltrated electrodes, porous stainless steel
- **Risoe/Topsoe, Denmark**  
  Co-fired half-cell, infiltrated nanostructured electrodes, tape cast powder metal porous support
- **Ikerlan, Spain**  
  Tubular, co-sintered YSZ
- **ElringKlinger, Germany**  
  Plasma sprayed layers on porous metal substrate (DLR)
- **Plansee, Austria**  
  Wet powder processing and sintering (FZJ)
Requirements for Metal Substrate Supports

- High electrical conductivity
- Adapted thermal expansion coefficient \((10-12 \cdot 10^{-6} \text{ K}^{-1})\)
- High corrosion stability in oxidising und reducing, moist atmosphere
- Sufficient mechanical stability
- High gas permeability (porosity > 40 Vol. %)
- Flat surface area for plasma sprayed functional layers
# 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, Y$_2$O$_3$</td>
</tr>
</tbody>
</table>
Cross Section of a Metal-Supported Cell of Ceres Power

Development of Power Densities of Cells of Ceres Power 
(16 cm²) at 570 °C in Operation with H₂ + 3 % H₂O/Air

Electrochemical Performance Data of Metal-Supported Cells of Ceres Power

**Operation with reformate gas** (73.8 % H₂, 7.1 % CO, 12.1 % CO₂, 7 % H₂O)
600 °C: max. 500 mW/cm²
570 °C: Operation over 2500 hours without degradation

**Thermal Cycling**
RT → 600 °C → RT: 500 cycles without degradation

**Stack Operation**
10 Layers (40 Cells)
585 °C: 100 W at operation with reformate (55 % H₂)
   1000 hours of operation without degradation
8 Layers (32 Cells):
Thermal Cycling (RT/600 °C): 26 Cycles without degradation
Long-term Operation: 2000 hours without degradation (1000 h with reformate)
I-V Characteristics and Power Density of a 40-Cells-Stack (10 Layers) in Operation with H₂ + 3% H₂O/Air at 570 °C and 600 °C

LBNL Design: Co-Sintered YSZ Electrolyte

- Colloidal spray electrolyte deposition
  - inexpensive
  - thin 10-20μm electrolyte
    - high performance at low temp

- Porous stainless steel current collector on anode AND cathode side
  - rugged
  - no expensive wire or mesh
  - no contact paste or compliant interconnect

Lit.: M. Tucker et al., ECS Transactions, 25(2) 673-680 (2009)
Cosintering Fabrication Issues

1. 1300°C Reducing atmosphere

- Interdiffusion of Ni and FeCr
- Poor CTE match, lifetime of support → add barrier layer, but still:
  - Coarsening of Ni
  - Poor performance of anode

→ move to Ceria-based anode

Lit.: M. Tucker et al., ECS Transactions, 25(2) 673-680 (2009)

2. Add cathode 600-900 °C air

- Low processing temperature limits choice of cathode
  - LSCF or SSC
  - worst choices for Cr tolerance
    - need coated current collector and BOP steel parts

→ move to infiltrated electrode architecture
Fuel Cell Fabrication Progress

Generation 1
Co-sintered support and Ni-YSZ

1. 1300°C Reducing atmosphere
   - Porous YSZ Cathode Layer
   - Dense YSZ
   - FeCr Metal Support

2. Infiltrate LSM, Ni 600-800°C air
   - LSM-YSZ Cathode Layer
   - Dense YSZ
   - Ni-YSZ Anode Layer
   - FeCr Metal Support

Poor CTE match, lifetime of support
Poor performance of Ni

Generation 2
Infiltrated catalysts

Lit.: M. Tucker et al., Fuel Cell Seminar 2008
Catalyst Infiltration

Prepare porous YSZ structure with catalyst

Fill structure with catalyst precursor solution

Fire to produce nanoparticles of catalyst on surface of YSZ

1200-1400°C

electrolyte

120°C

electrolyte

600-800°C

electrolyte

0.85 La-nitrate
0.15 Sr-nitrate
1.0 Mn-nitrate

LSM (La_{0.85}Sr_{0.15}MnO_{3})

or

Ni-nitrate

or

Ni

# Infiltrated Catalysts Alleviate Processing Issues

1. Sinter stainless steel and YSZ at 1300°C Reducing atmosphere

<table>
<thead>
<tr>
<th>FeCr Metal Current Collector</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous YSZ Cathode Layer</td>
</tr>
<tr>
<td>Dense YSZ</td>
</tr>
<tr>
<td>Porous YSZ Anode Layer</td>
</tr>
<tr>
<td>FeCr Metal Support</td>
</tr>
</tbody>
</table>

2. Infiltrate catalysts at <300°C air

<table>
<thead>
<tr>
<th>FeCr Metal Current Collector</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM-YSZ Cathode Layer</td>
</tr>
<tr>
<td>Dense YSZ</td>
</tr>
<tr>
<td>Ni-CoO2-YSZ Anode Layer</td>
</tr>
<tr>
<td>FeCr Metal Support</td>
</tr>
</tbody>
</table>

No FeCr/Ni interdiffusion
Wide choice of catalyst composition

Easy to infiltrate
LSM, LNF, LSCF, CGO, Cu, Ni, Co, many others

Infiltrated Electrodes Support High Power Density

Air oxidant

Pure O₂ oxidant

H₂ – 3%H₂O fuel

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Max Power (mW/cm²)</th>
<th>Power at 0.7V (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>650°C</td>
<td>982</td>
<td>726</td>
</tr>
<tr>
<td>700°C</td>
<td>&gt;1300</td>
<td>993</td>
</tr>
<tr>
<td>750°C</td>
<td>&gt;1300</td>
<td>&gt;1300</td>
</tr>
</tbody>
</table>

Performance and Stability
Infiltrated Oxide Anode and LSM Cathode

$> 500 \text{mW/cm}^2$ at 700°C
600 h operation demonstrated

Lit.: M. Tucker, Int. Conf. on Advanced Ceramics and Composites, Daytona Beach 2010
Redox Cycling Tolerance

700°C, switching between H₂/H₂O and air
- Complete Ni ↔ NiO conversion each cycle

Anode supported cell fails after redox cycling
- Electrolyte cracks

Metal-supported cell does not fail
- Ni is not a structural element

Thermal and Redox Cycling Tolerance

Thermal Shock:
150-735°C, ~500°C/min

Full Redox:
Switch between air and fuel at 700°C

Metal-supported cell tolerates
- redox cycling
- rapid thermal cycling

Lit.: M. Tucker et al., ECS Transactions, 25(2) 673-680 (2009)
The Risø/TOFC Metal-supported Cell

New design and components developed (to avoid interdiffusion of Ni, Fe, Cr):

Cell design
- Tape cast powder metal porous support
- Co-fired half cell
- Infiltrated nano-structured electrodes
Performance of “METSOFC” Metal-Supported Cells

Button cell and 5x5 cm² tested at 650 °C
(fuel: 96% H2 with 4% H2O, oxidant: air).
Durability of Risø/TOFC Metal-Supported Cell

5x5 cm² cell footprint

- $j_{cell} = 0.25 \text{ A/cm}^2$
- Fuel: $X_{H_2} = 0.96$, $X_{CH_4} = 0.04$
- Oxidant: Air
- $T = 650-655°C$ : fuel and oxygen utilization = 19%

Decline: 0.8% / 1000 h
650 °C
0.25 A/cm²

- 0.8%/1000h \( U_{cell} \)
- 0.03 \( \Omega \text{ cm}^2/1000h \)

Decline: 4.5%/1000h \( U_{cell} \)
- 0.15 \( \Omega \text{ cm}^2/1000h \)

- 14test98 (foot print 5x5 cm)
- 14test101 (foot print 5x5 cm)
SOFC Metal Supported Cell – DLR Concept

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

[Diagram of SOFC cell layers and dimensions]
Vacuum Plasma Spraying of SOFC Cells
Plasma Spray Laboratory at DLR Stuttgart
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, Belgium</td>
<td>Technetics, USA</td>
<td>Rhodius, Germany</td>
<td>Plansee AG, Austria</td>
</tr>
</tbody>
</table>
Morphology of Porous Metal Substrate PM Fe-26Cr-(Mo,Ti,Mn,Y$_2$O$_3$) of Plansee SE
### 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>
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)
Metallographic Cross Section of MSC Cell

- LaSrMnO₃-cathode
- 8YSZ-electrolyte
- Ni/8YSZ-anode
- Perovskite-type barrier layer
- Porously sintered ferrite plate
Electrochemical Performance of VPS Cells With and Without Diffusion Barrier Layer in Operation with Simulated Reformate H₂/N₂ and Air
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
MSC Stack Integration

1. Plasma coating
2. Application of seal
3. Assembly
4. Stack test
Performance of Plasma Sprayed MSC Single Cell

MSC Cell: 12.5 cm² cell at 800°C; H₂/N₂ and Air
Performance of 10-Cells Stack

10-Cell Stack: 100 cm² single cells at 800°C; H₂/N₂; Air

@ 7.0 V
P_{stack} = 250 W
p = 307 mW/cm²
FU = 24.8 mol%
OCV = 10.11 V
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
Conclusions

- The development of metal-supported cells – both sintered cells with infiltrated electrodes and plasma sprayed cells – show good progress achieving high power density.

- Metal-supported cells prove rugged behaviour, such as:
  - fast start / thermal cycling
  - redox tolerance
  - mechanical strength

- Low-cost materials expect low-cost manufacturing at low and high volume.

- The development of the metal-supported SOFC concept has a high potential for SOFC application in dynamic operation with multiple thermal and redox cycles.

- Metal-supported SOFC is an opportunity to transcend barriers to SOFC commercialisation.
Acknowledgment

I'd like to thank Michael C. Tucker from Lawrence Berkeley National Lab and Niels Christiansen from Topsoe Fuel Cells for providing slides on their MSC development.

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