Preparation and characterization of metal supported solid oxide fuel cells with screen-printed electrodes and thin-film electrolyte

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Content

Introduction of SOFCs

Processing of planar SOFCs

MSC with screen-printed electrodes and thin-film electrolyte

Summary & Perspectives
Repetition of Basic Principle

Air / $O_2$

Cathode

Electrolyte

Anode

Fuel gas

$O_2 + 4e^- \rightarrow 2O^{2-}$

$H_2 + O^{2-} \rightarrow H_2O + 2e^-$

$CO + O^{2-} \rightarrow CO_2 + 2e^-$

Oxidation

Reduction

Source: L.G.J. de Haart, IEF-3, FZJ
Motivation: towards the next generation SOC

1st gen.

ESC
- Limited power density
- Robustness
- Stationary
- Transportation

2nd gen.

ASC
- High power density
- Sulfur poisoning
- Fast thermal cycling
- Redox Cycling
- Stationary
- Transportation

3rd gen.

MSC
- High power density
- Sulfur poisoning
- Fast thermal cycling
- Redox Cycling
- Stationary
- Transportation

4th gen.

MSC
- High power density
- Sulfur resistant
- Thermal cycling
- Redox Cycling
- Low cost
- Stationary
- Transportation

Flexible architecture for multiple applications
Which materials for the next generation of SOCs?
Potential Advantages of Metal Supported Cells

**MSC** (Metal Supported Cell):
- High robustness
- High resistance against thermal and redox cycling
- Good integration into interconnects (bipolar plates) via brazing or welding
- Low cost of metal support and cell materials (thin layers)
- High electronic and thermal conductivity

- To Replace ceramic components by metals
- Operating temperature > 600 °C
- Atmosphere: Hydrogen / or Synthetic Gas, Air
- Reversible operation
Manufacturing Route (conventional ASC)

- **Substrate**
  - Tape casting
  - Cold/warm pressing
  - Extrusion

- **Anode**
  - Screen printing
  - Vacuum slip casting
  - Wet powder spraying

- **Electrolyte**
  - Cofiring of anode and electrolyte
  - 1400°C

- **Cathode**
  - Dense-sintered electrolyte

- **Current Collector**
  - Screen printing
  - Wet powder spraying

- **Solid Oxide Fuel Cell**
  - Laser-cutting

Alternatives without sintering: plasma spraying, PVD

M. Bram, IEF-1, FZJ
SEM fracture surface of anode-supported SOFC

Anode

Electrolyte

Sr-barrier layer

Cathode

\( \text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) (LSCF)

Ce\(_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta} \) (CGO)

8mol% \( \text{Y}_2\text{O}_3\)-\( \text{ZrO}_2 \) (8YSZ)

NiO / 8mol% \( \text{Y}_2\text{O}_3\)-\( \text{ZrO}_2 \) (8YSZ)

Sintered single cell

50mm x 50mm
**Screen Printing**

**origin:** printing industry (non-paper prints, e.g. CD etc.) to print letters and graphics

**ceramic applications:** large screen opening (50-70% open area) easy to create contured coatings

**thickness of dried layer** $\sim 1/4..1/2$ of wet layer (spreading and drying) => $5..100 \, \mu m$ feasible

![Printing scheme](image)

![Screen mesh and wet film](image)

threads by polymer, steel, or liquid crystal polyarylates
Screen Printing Paste Preparation

Paste for Energy Devices at DLR
1. SOFC/SOEC
2. PEMFC/PEMEC
3. Battery
4. Thermoelectric Generator
5. Gas Separation Membrane

Paste for SOFC functional layers
1. Anode: NiO-YSZ, NiO-GDC, NiO-BCZY, LST-NiO
2. Cathode: LSM-YSZ, LSCF, LSC
3. Electrolyte: YSZ, GDC, BCZY
4. Contact layer: LSCF
5. Sealing: glass sealant

Contact coating for Bi-polar plate
Demonstration of the feasibility of the cell concept and design

Development of metal supported SOFCs without nickel as structural components, improving redox cycling stability and sulfur tolerance.

Deposition of gas-tight thin-film electrolyte (~3 μm thick) layers

Apply perovskite based materials for anode functional layer in MSC
Material Selection

• Improving durability of the metallic substrate
  ➢ Implementing alumina forming alloys (NiCrAl)

• Enhancing sulfur tolerance and redox stability at the anode
  ➢ Perovskite based anode materials

• Ensuring the electrolyte with good gas tightness and electrical property
  ➢ Multi-layered thin film

• Avoiding High T sintering and reducing atmosphere
  ➢ low T (max. 1000 °C) processing in air

La_{0.1}Sr_{0.9}TiO_{3-α}

screen printing
Materials and Architecture

Cathode: $La_{0.4}Sr_{0.6}Co_{0.2}Fe_{0.8}O_{3-\alpha}$ (LSCF)
Electrolyte: 8YSZ / GDC10
Composition of the anode: GDC10-LST (w/o 5-10%Ni)

Metallic substrate at the fuel side

Type 1

- Porous steel
  - pore size <50µm

Type 2

- Metal foam (NiCrAl)
  - pore size 450µm
- $La_{0.1}Sr_{0.9}TiO_{3-\alpha}$
- $NiO + La_{0.1}Sr_{0.9}TiO_{3-\alpha}$ (50:50)
Processing at reduced temperature

Pretreatment of metal substrates

Substrate → Anode deposition → Electrolyte deposition → Cathode deposition

- Firing air 1000°C
- Infiltration of catalytic Nickel (ca. 5wt%)
- Electrochemical Testing

Fabrication options for electrolyte:
1. PVD
2. Plasma-spray (VPS)
3. Sintering
4. Sol-gel
A Way to Thin Electrolyte

Sketch of cell design

Electrolyte

Anode

NiCrAl Metal foam

LST

YSZ

GDC

Anode: LST+GDC

NiCrAl Metal foam

LST

Anode: LST+GDC
MSC with ITM Substrate (Type 1)

Porous metal
MSC with Metal Foam Substrate (Type 2)
Hermiticity of the electrolyte

Compared to DLR Plasma Sprayed MSCs:
Gas tightness improved by 1 order of magnitude
Material consumption reduced

- PVD: 1,2mg/cm² of YSZ + 1,5mg/cm² of CGO
- PS MSCs: 20-30 mg/cm² of YSZ
Performance Cell type 1

*ITM (w 5-10wt%Ni) – 16cm²*

@ 750°C 1slpm H₂ / 2slpm air

OCV: 1,03V
Power density at 0,7 V ca. 430 mW/cm² (520 mW/cm² @ 800°C)

No OCV drop after 10 redox cycles
Performance Cell (Type 2)
NiCrAl + LST + NiO – (w 5-10wt%Ni)

@ 750°C 1slpm H₂ + 3% water / 1 slpm air
OCV: 1,03V
Power density at 0,7 V ca. 430 mW/cm²
OCV drop of less than 2% (50cycles)

- good tolerance toward redox cycles
- Performance enhancement with addition of catalytic nickel

![Graph showing OCV drop comparison between ASC (5x) and MSC (50x)]
MSC with thin-film electrolyte vs. ASC with sintered YSZ

**0.9 W/cm²**
- LSCF >1000 °C
- SP GDC 1300 °C
- SP YSZ 1400 °C
- Ni-YSZ AFL
- Ni-YSZ Substrate

**1.2 W/cm²**
- LSCF >1000 °C
- PVD GDC 800 °C
- SP YSZ 1400 °C
- Ni-YSZ AFL
- Ni-YSZ Substrate

**1.6 W/cm²**
- LSCF >1000 °C
- PVD GDC 800 °C
- NS YSZ 1400 °C
- Ni-YSZ AFL
- Ni-YSZ Substrate

**0.32 W/cm²**
- LSCF <850 °C
- PVD GDC 600 °C
- NS YSZ 700 °C
- NS YSZ 950 °C
- LST-GDC AFL
- Metal Substrate

**0.43 W/cm²**
- LSCF <850 °C
- PVD YSZ 600 °C
- NS YSZ 700 °C
- NS YSZ 950 °C
- LST-GDC AFL
- Metal Substrate

- **Operated@750°C & 0.7V**
- **Poor redox stability**
- **Good redox stability**
Up-scaled cells for stacks

- Size up to 90 mm x 100 mm
- Laser cut substrate
- Infiltrated Ni catalyst

- Leak rate moderate or poor
- Stackable cells 8 pcs
- Needs for LT sealing solution
Conclusion & Perspectives

- MSCs cell with various substrates (Stainless Steel & NiCrAl) delivered fair Power density despite low nickel content (< 10wt%)
- OCV drop of less than 2% for 50 forced redox cycles (30min in Oxygen) at 750°C
- Thin film electrolyte technology developed and demonstrated
- Estimated cost reduction: 20 Euro for a 10cm²x10 cm² cell (10 MW per year)

- LST based anode materials can operate without pre-reduction at high temperature (>1000°C)
- Without addition of catalysts in LST based anode is performance limited

- Degradation issue at the cathode
- Operando migration of cobalt from the cathode size in the electrolyte layer

- Improvement of the cathode performance
- Development of appropriate low T sealing (750°C) solutions
- Implementation in Single Repeat Unit and Test for completing Assessment
- Assessment against Sulfur Poisoning
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