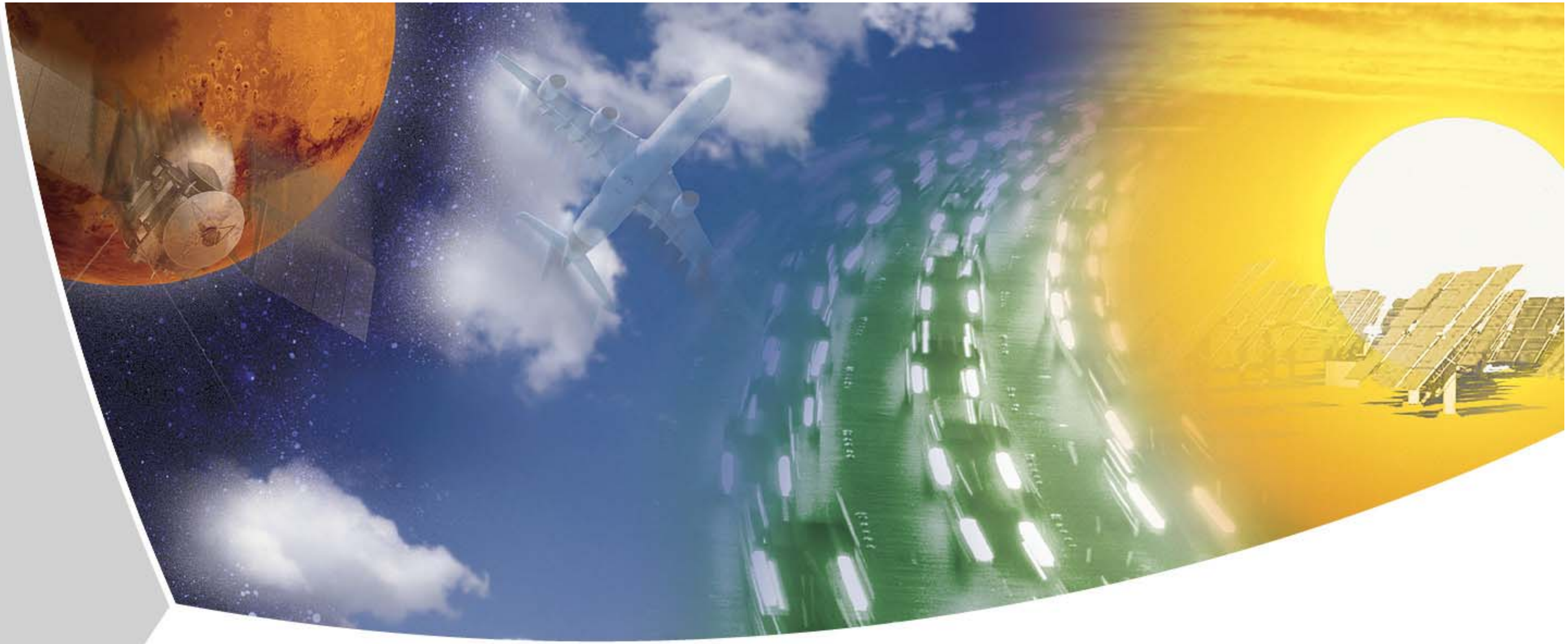


Progress in Metal-Supported Solid Oxide Fuel Cells

G. Schiller

German Aerospace Center (DLR)
Institute of Technical Thermodynamics

International Symposium on Energy Materials: Opportunities and Challenges (ISEM-2011), March 1-2, 2011, Kolkata, India

Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft

Outline

- Introduction
- Development of metal-supported SOFC by applying sintering techniques

    Ceres Power

    Lawrence Berkeley National Lab

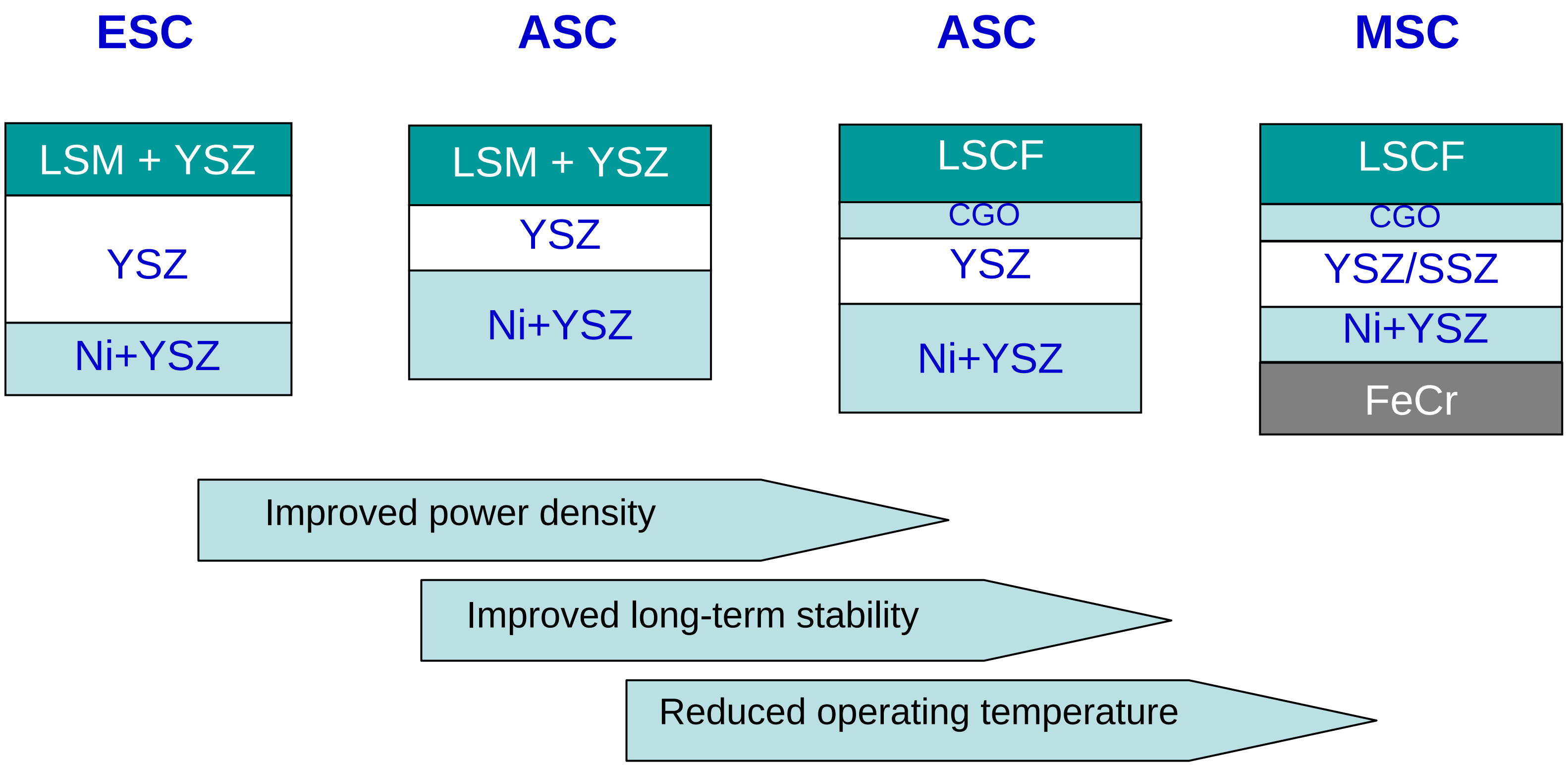
    Risoe / Topsoe Fuel Cells

- Development of metal-supported cells by applying plasma deposition techniques

    German Aerospace Center (DLR)

- Conclusions

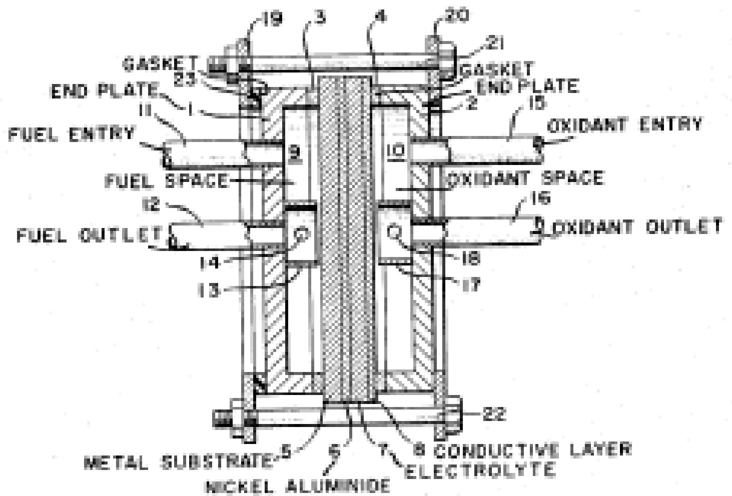
Development of Metal-Supported Cells



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**

Early Metal-Supported SOFC Work – 1960s-1970s

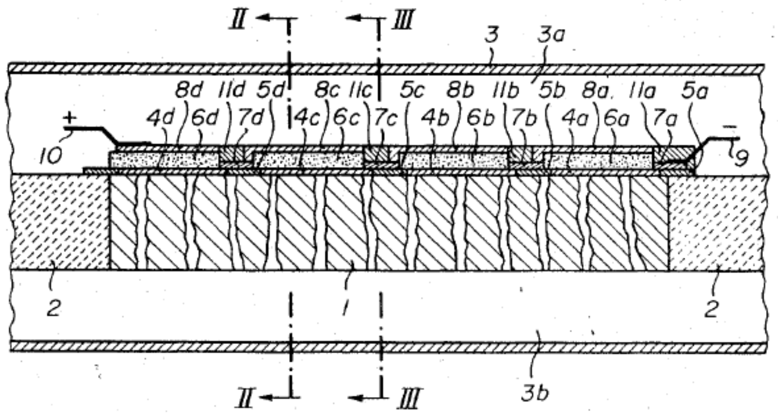


- Flame-sprayed ZrO2 electrolyte
- Sintered austenitic stainless steel support

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

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Berkeley Lab – 75 Years of World-Class Science 1931-2006

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)

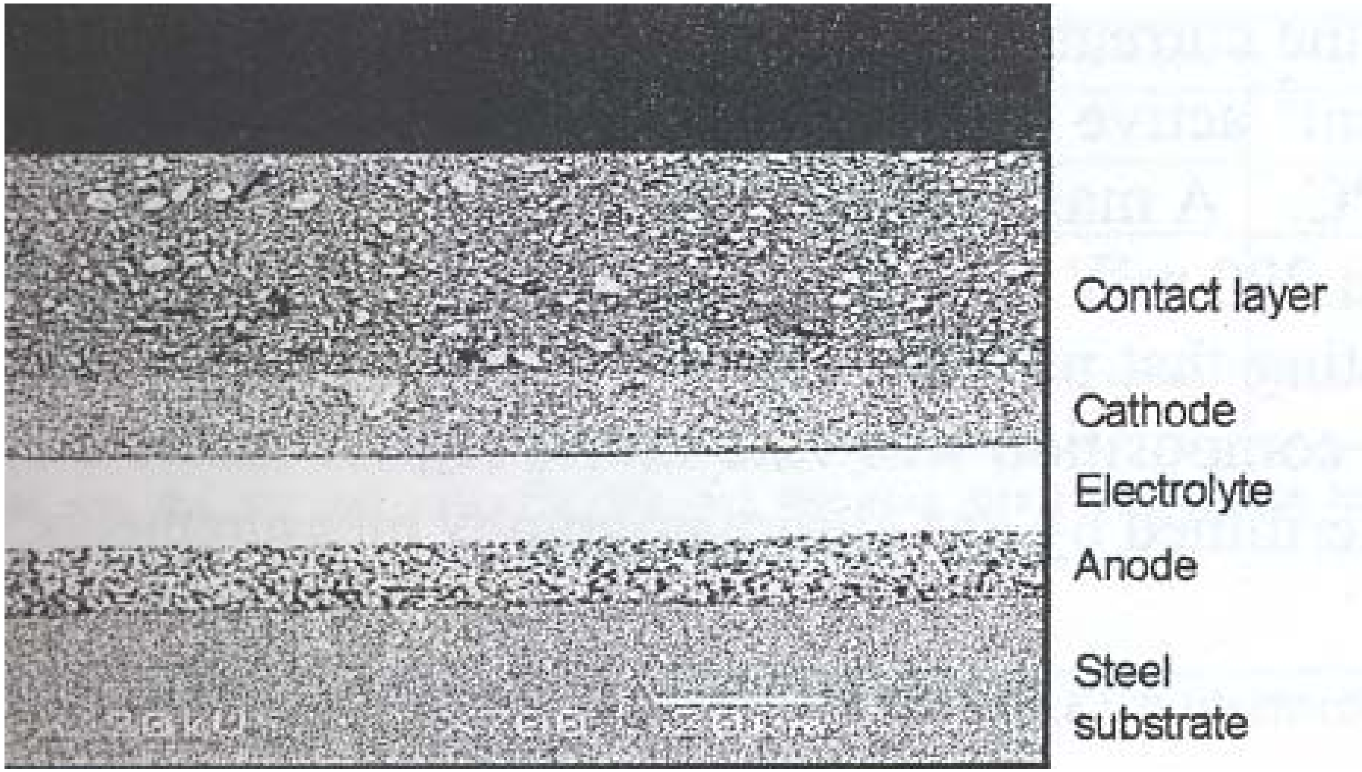
Requirements for Metal Substrate Supports

- High electrical conductivity
- Adapted thermal expansion coefficient ($10\text{-}12 \cdot 10^{-6}$ 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

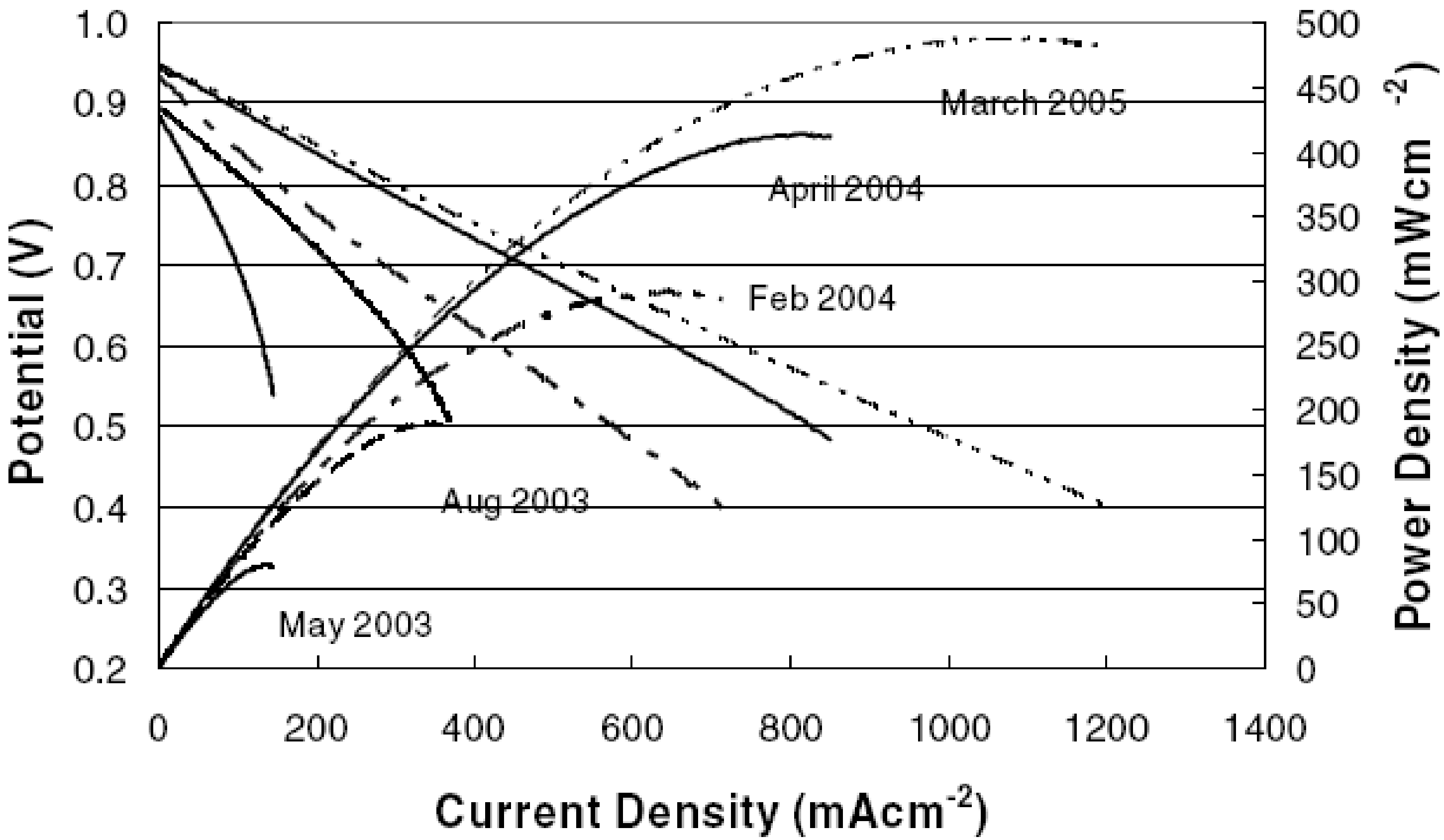
Alloy	Supplier	Composition
Ferrochrom (1.4742)	ThyssenKrupp	18% Cr, 0.9% Al, 0.9% Si, 0.69% Mn, 0.06% C
CrAl20 5 (1.4767)	ThyssenKrupp	19% Cr, 5.5% Al, 0.5% Si, 0.5% Mn, 0.05% C
FeCrAlY	Technetics	22% Cr, 5% Al, 0.1% Y
ZMG 232	Hitachi Metals	21% Cr, 0.08% Al, 0.43% Si, 0.47% Mn, 0.02% C
SUS 430 HA	Nippon Steel	16% Cr, 0.13% Al, 0.29% Si, 0.13% Mn, 0.05% C
SUS 430 Na	Nippon Steel	16% Cr, 0.01% Al, 0.29% Si, 0.56% Mn, 0.05% C
CroFer22 APU	ThyssenKrupp	22% Cr, 0.12% Al, 0.1% Si, 0.41% Mn, 0.16% Ni, 0.05% Ti, 0.08% La
IT 14	Plansee	26% Cr, < 0.03% Al, < 0.03% Si, Mo, Ti, Mn, Y_2O_3

Cross Section of a Metal-Supported Cell of Ceres Power



Lit.: Ceres Power, Electrochemical Society Proceedings, Vol. 2005-07, 113-122 (2005)

Development of Power Densities of Cells of Ceres Power (16 cm²) at 570 °C in Operation with H_2 + 3 % H_2O/Air



Lit.: Ceres Power, Proceedings 2005 Fuel Cell Seminar, 49-52 (2005)

Electrochemical Performance Data of Metal-Supported Cells of Ceres Power

Operation with reformate gas (73,8 % H_2, 7,1 % CO, 12,1 % CO_2, 7 % H_2O)

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 % H_2)

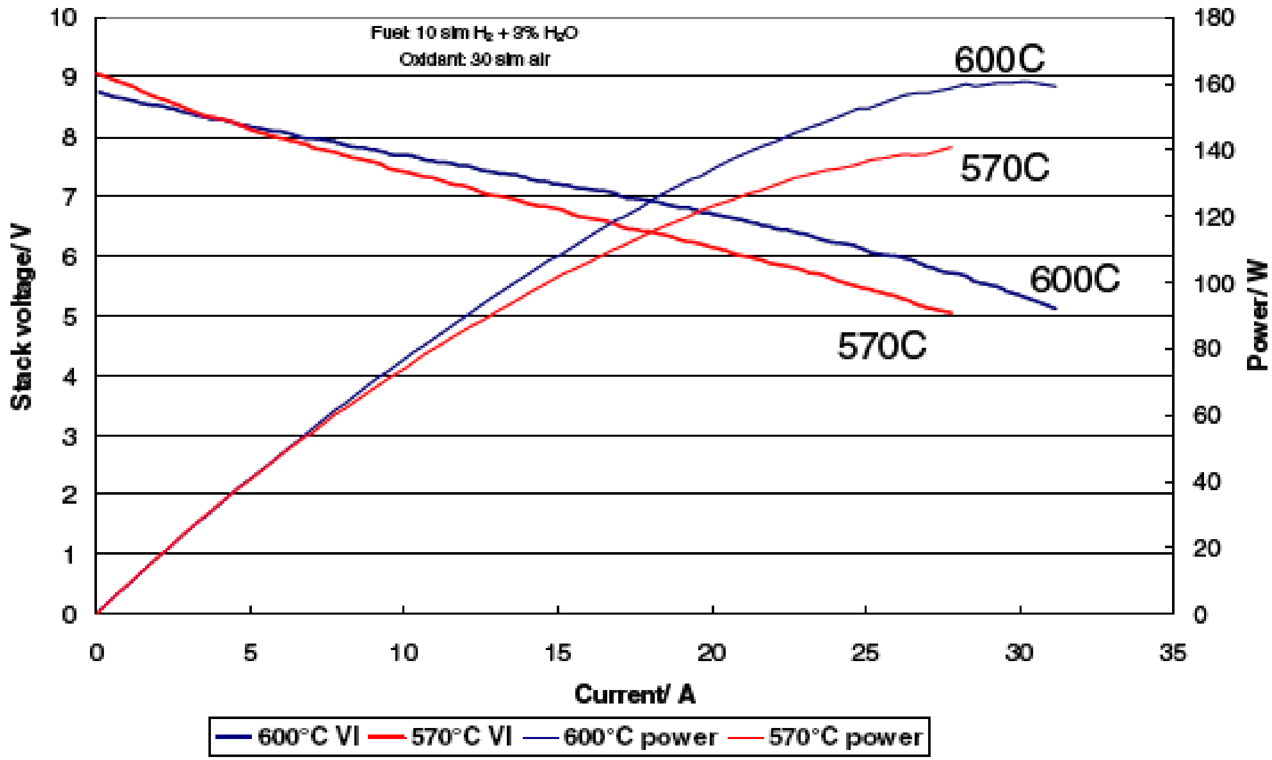
1000 hours of operation without degradation

8 Layers (32 Cells):

Thermal Cycling (RT/600 °C): 26 Cycles without degradation

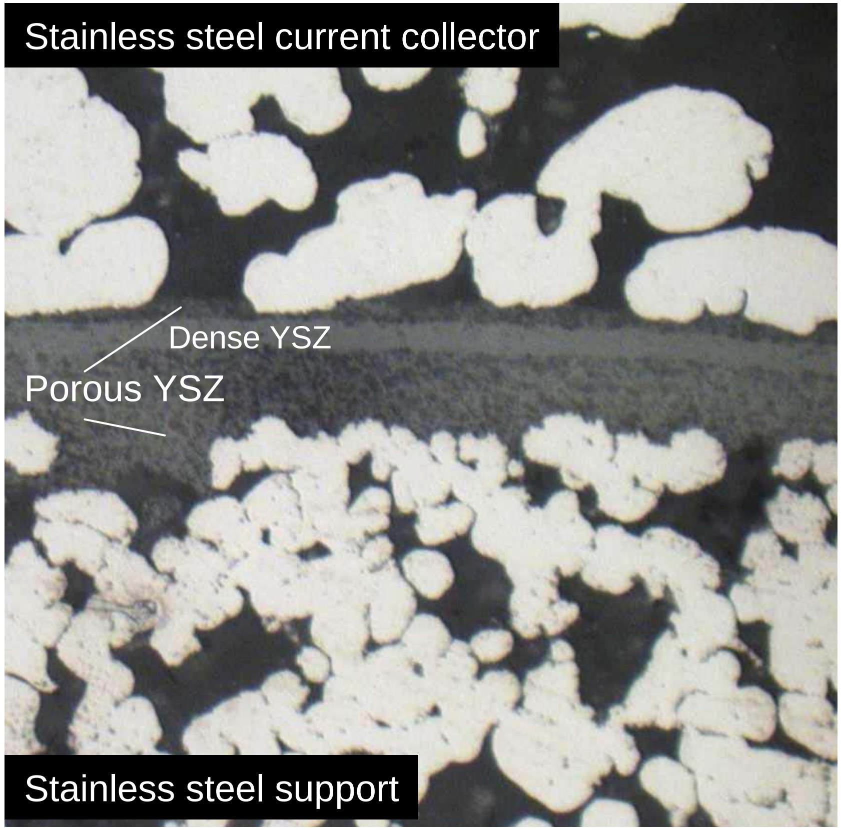
Long-term Operation: 2000 hours without degradation (1000 h with reformate)

I-V Characteristics and Power Density of a 40-Cells-Stack (10 Layers) in Operation with H_2+3% H_2O/Air at 570 °C and 600 °C



Lit.: Ceres Power, Proceedings 2005 Fuel Cell Seminar, 49-52 (2005)

LBNL Design: Co-Sintered YSZ Electrolyte



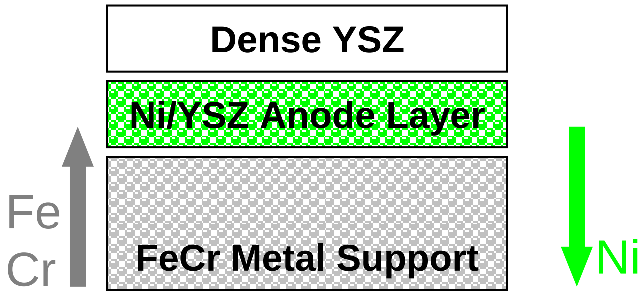
Colloidal spray electrolyte deposition
- inexpensive
- thin 10-20μm electrolyte
  - high performance at low temp

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

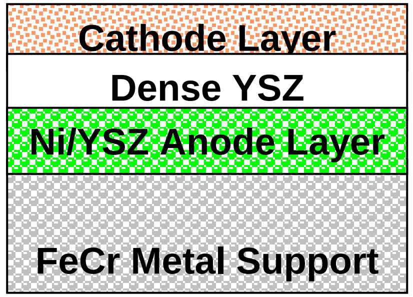


Interdiffusion of Ni and FeCr
Poor CTE match, lifetime of support
→ add barrier layer, but still:

- Coarsening of Ni
Poor performance of anode

→ move to Ceria-based anode

2. Add cathode 600-900 °C air



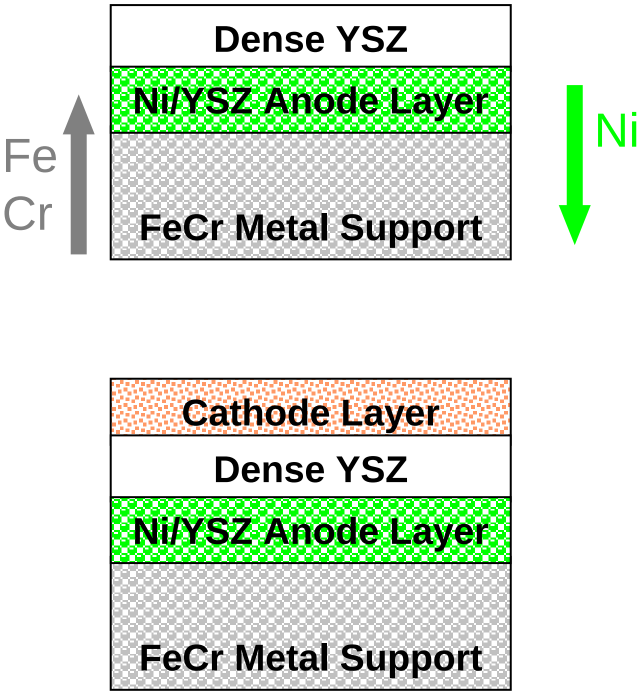
Low processing temperature limits choice of cathode
- LSCF or SSC
- worst choices for Cr tolerance
  - need coated current collector and BOP steel parts

→ move to infiltrated electrode architecture

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

Fuel Cell Fabrication Progress

Generation 1
Co-sintered support and Ni-YSZ

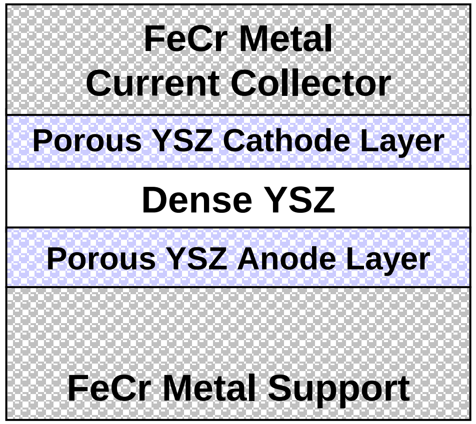


Poor CTE match, lifetime of support

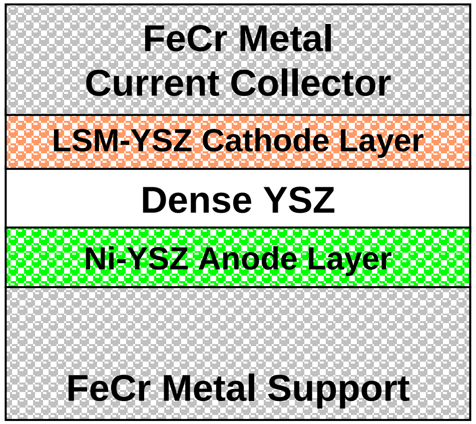
Poor performance of Ni

Generation 2
Infiltrated catalysts

1. 1300°C Reducing atmosphere



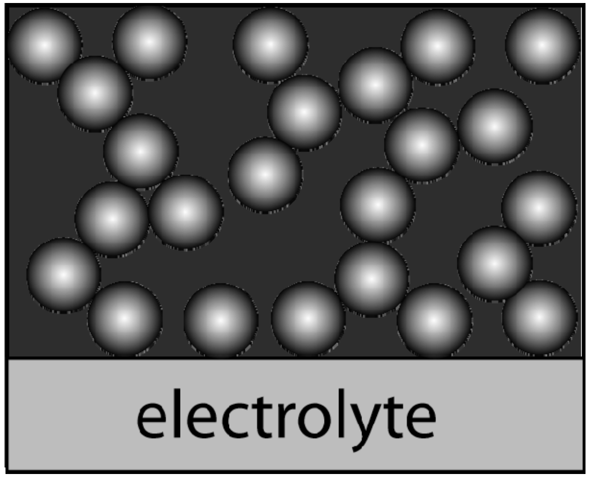
2. Infiltrate LSM, Ni 600-800°C air



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

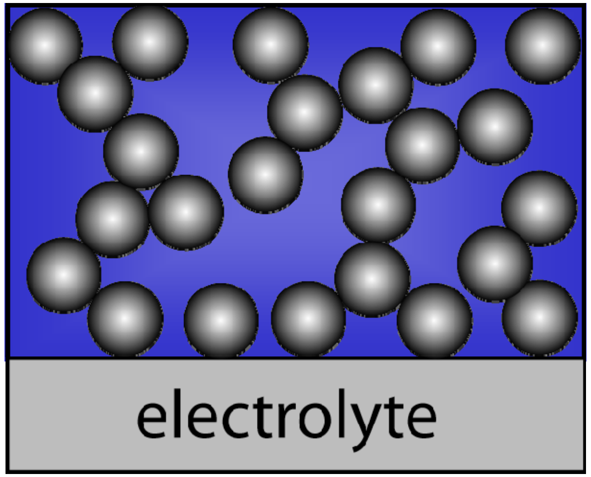
Catalyst Infiltration

Prepare porous YSZ structure with catalyst



1200-1400°C

Fill structure with catalyst precursor solution



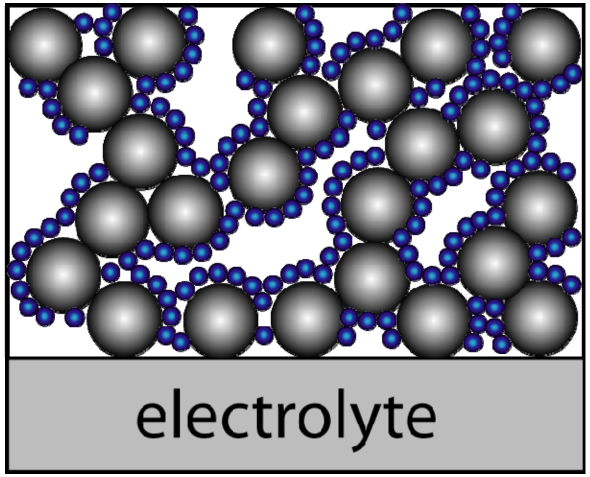
120°C

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

or

Ni-nitrate

Fire to produce nanoparticles of catalyst on surface of YSZ



600-800°C

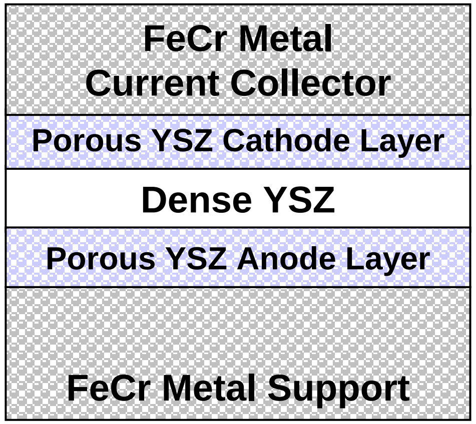
LSM ($La_{0.85}Sr_{0.15}MnO_3$)

or

Ni

Lit.: M. Tucker, Fuel Cell Seminar 2008

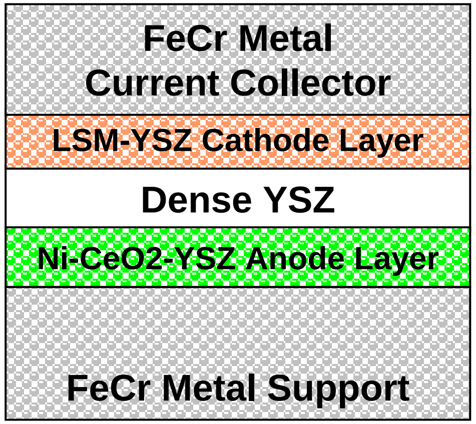
Infiltrated Catalysts Alleviate Processing Issues

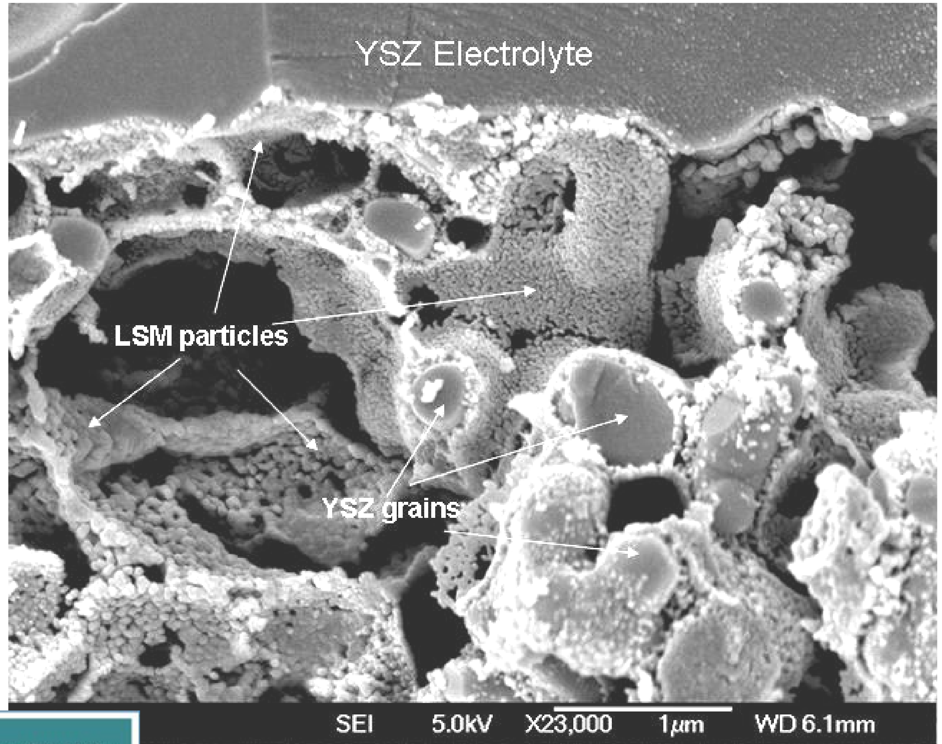


1. Sinter stainless steel and YSZ at 1300°C Reducing atmosphere

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

2. Infiltrate catalysts at <300°C air



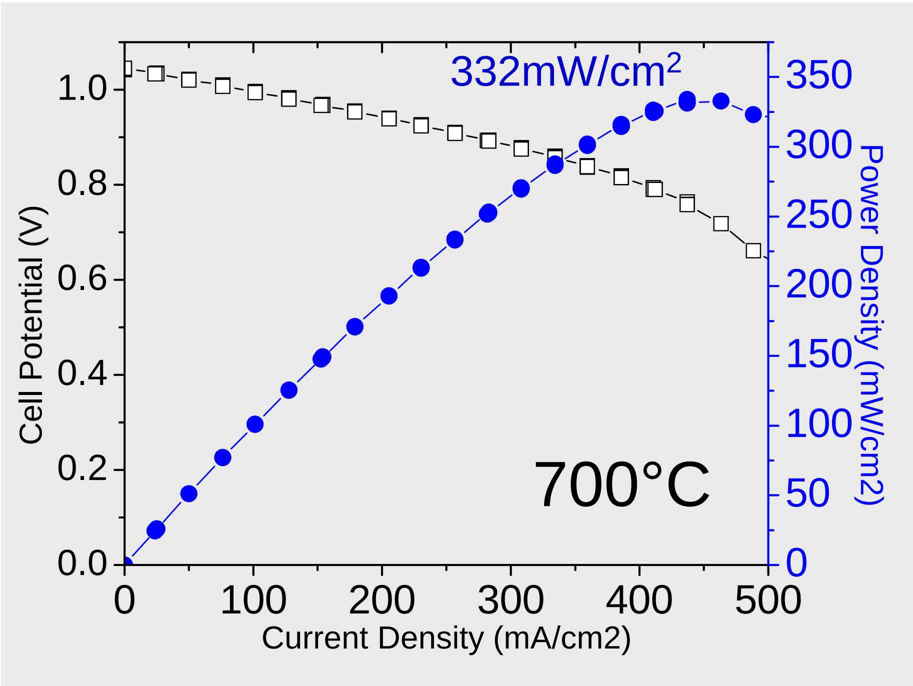


No FeCr/Ni interdiffusion
Wide choice of catalyst composition

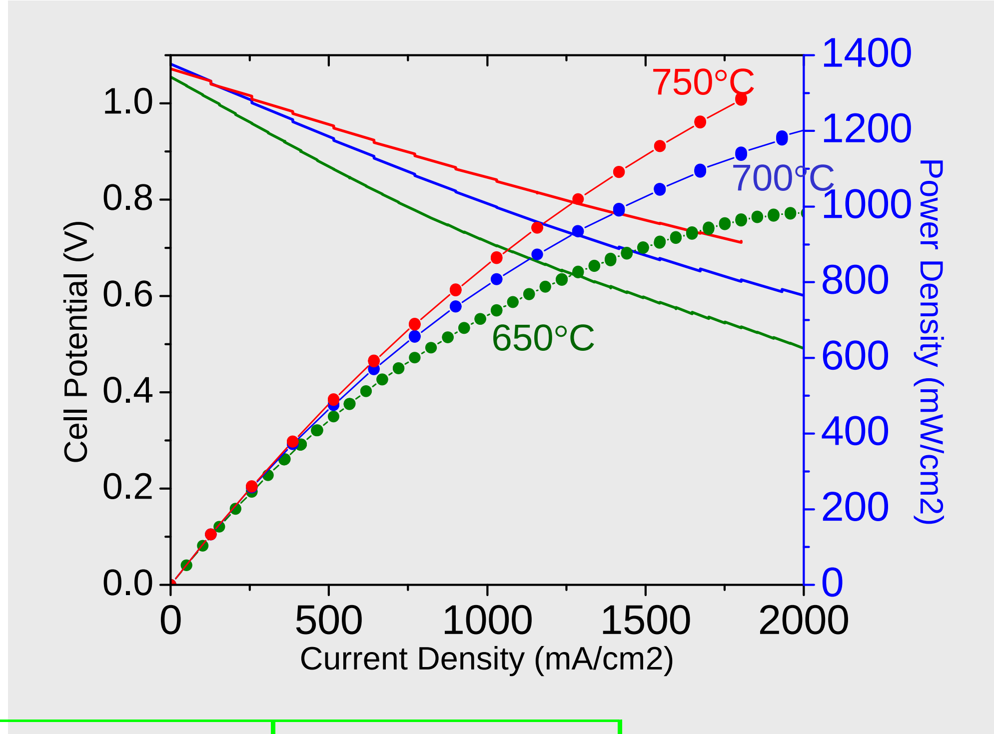
Lit.: M. Tucker, Fuel Cell Seminar 2008

Infiltrated Electrodes Support High Power Density

Air oxidant



Pure O_2 oxidant



H_2 –3%H_2O fuel

Temperature	Max Power (mW/cm2)	Power at 0.7V (mW/cm2)
650°C	982	726
700°C	>1300	993
750°C	>1300	>1300

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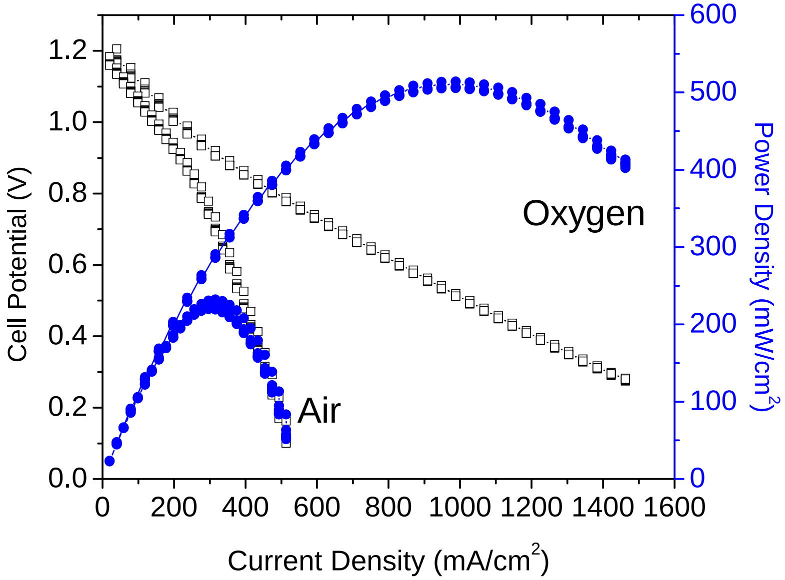
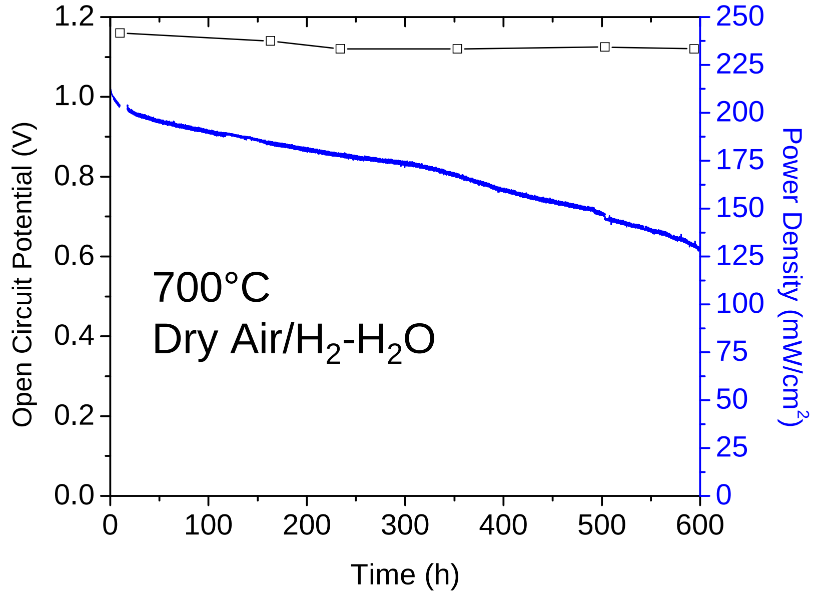
Lit.: M. Tucker, Fuel Cell Seminar 2008

Performance and Stability

Infiltrated Oxide Anode and LSM Cathode





> 500mW/cm² at 700°C

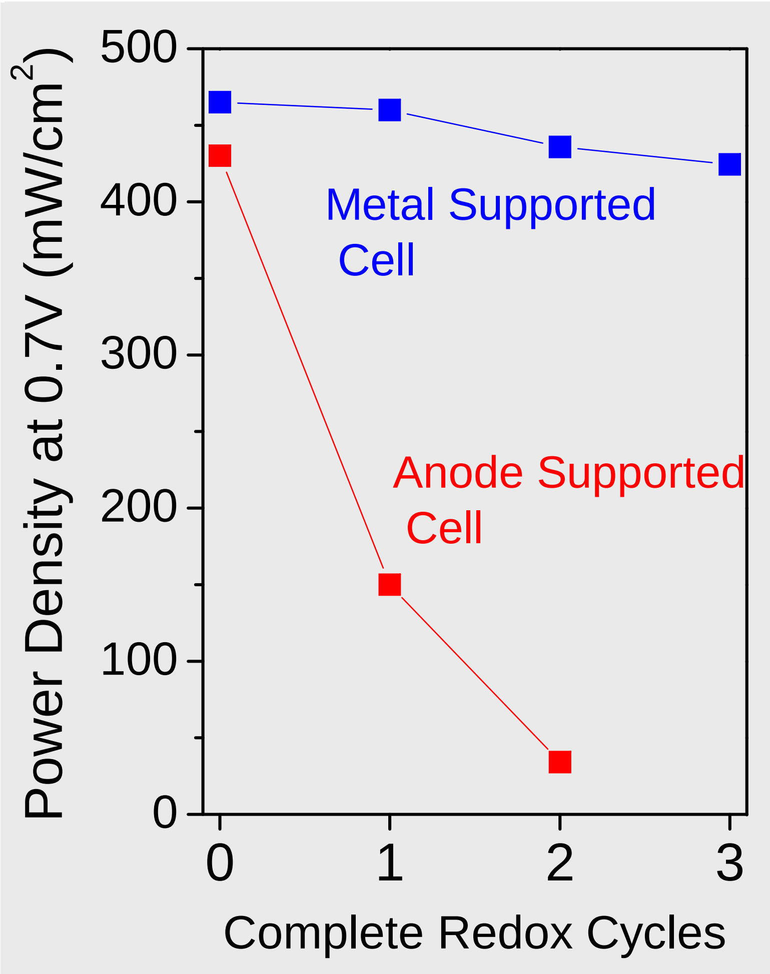
600 h operation demonstrated

Berkeley Lab — 75 Years of World-Class Science 1931-2006

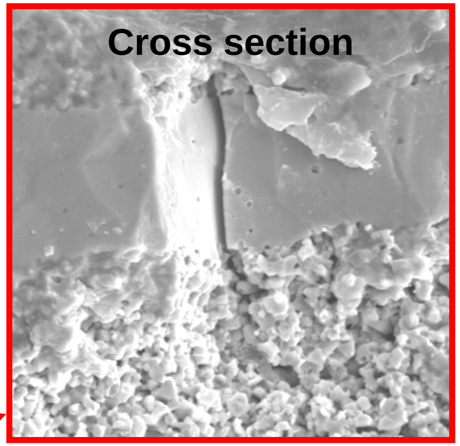
Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft

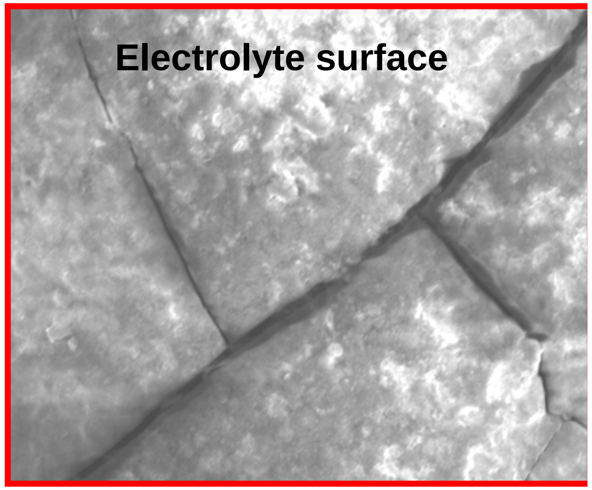
Lit.: M. Tucker, Int. Conf. on Advanced Ceramics and Composites, Daytona Beach 2010

Redox Cycling Tolerance



700°C, switching between H_2/H_2O and air
- Complete Ni ←→ NiO conversion each cycle

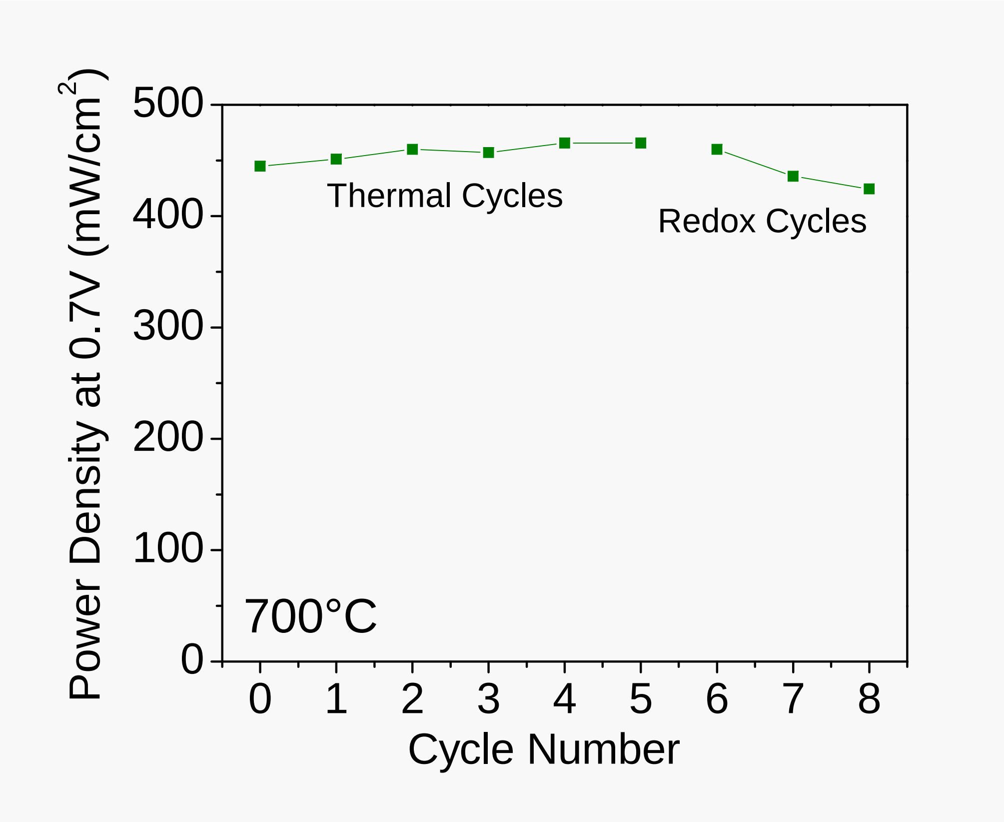




Anode supported cell fails after redox cycling
- Electrolyte cracks

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

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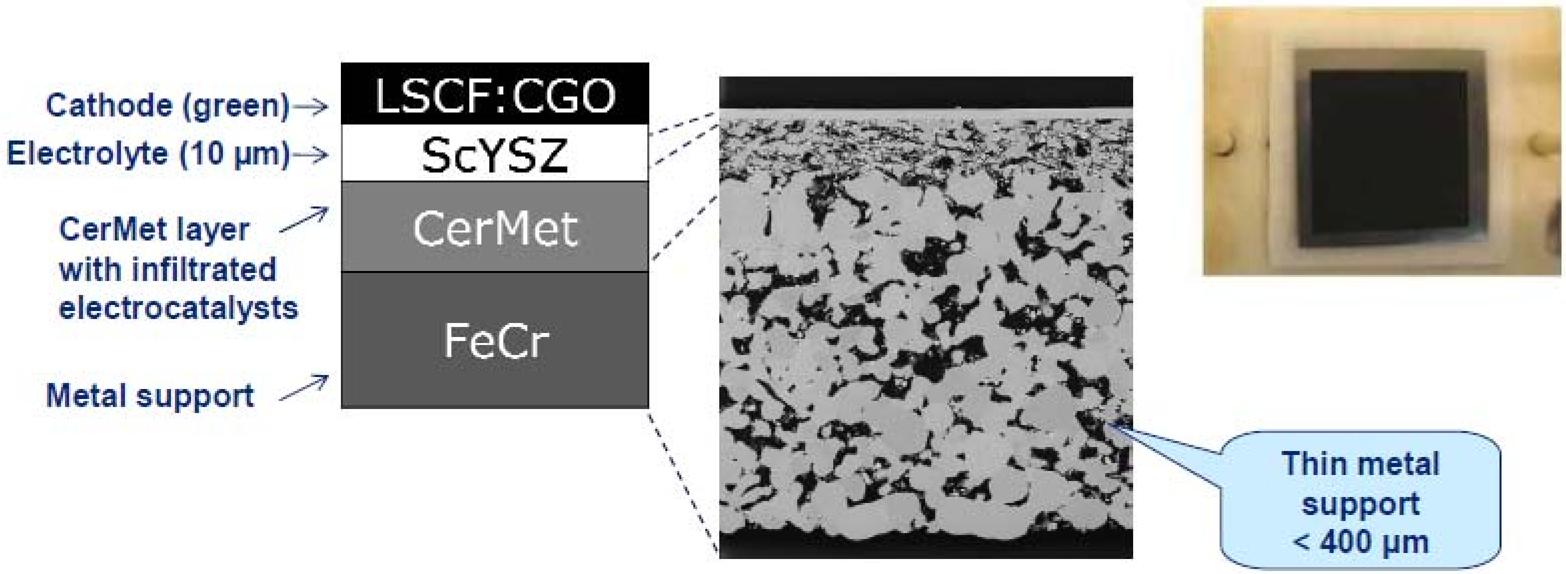
DLR Deutsches Zentrum für Luft- und Raumfahrt e.V. in der Helmholtz-Gemeinschaft

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

The Risø/TOFC Metal-supported Cell

TOPSOE FUEL CELL

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

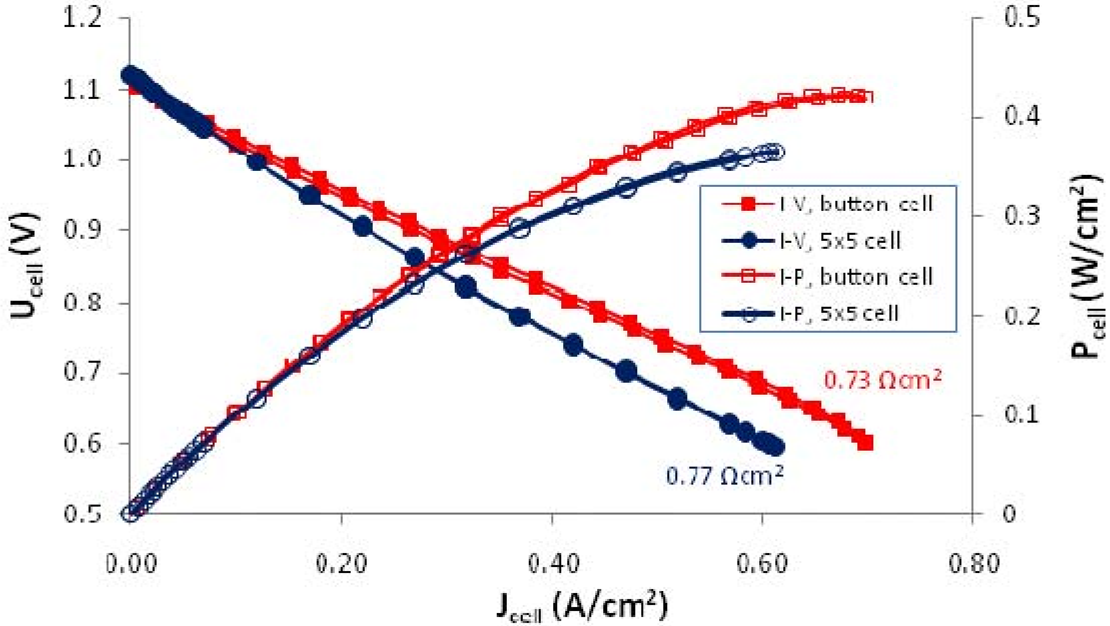


Cell design

- Tape cast powder metal porous support
- Co-fired half cell
- Infiltrated nano-structured electrodes

Performance of "METSOFC" Metal-Supported Cells

TOPSOE FUEL CELL

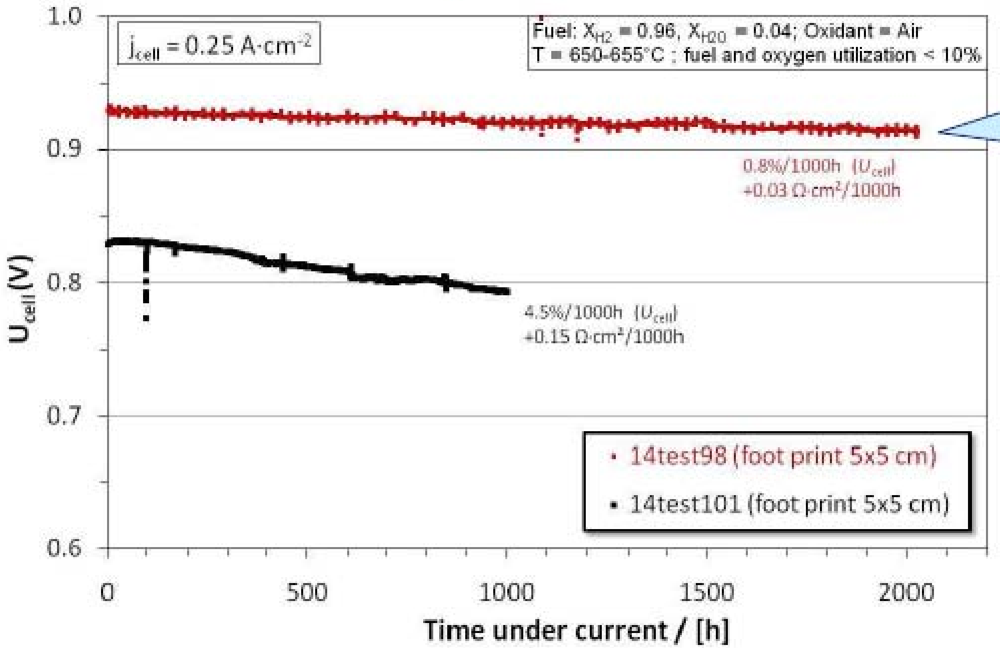


Button cel and 5x5 cm^2 tested at 650 °C
(fuel: 96% H2 with 4% H2O, oxidant: air).

Durability of Risø/TOFC Metal-Supported Cell

TOPSOE FUEL CELL

5x5 cm² cell footprint



0.8% / 1000 h
650 °C
0.25 A/cm²

SOFC Metal Supported Cell – DLR Concept

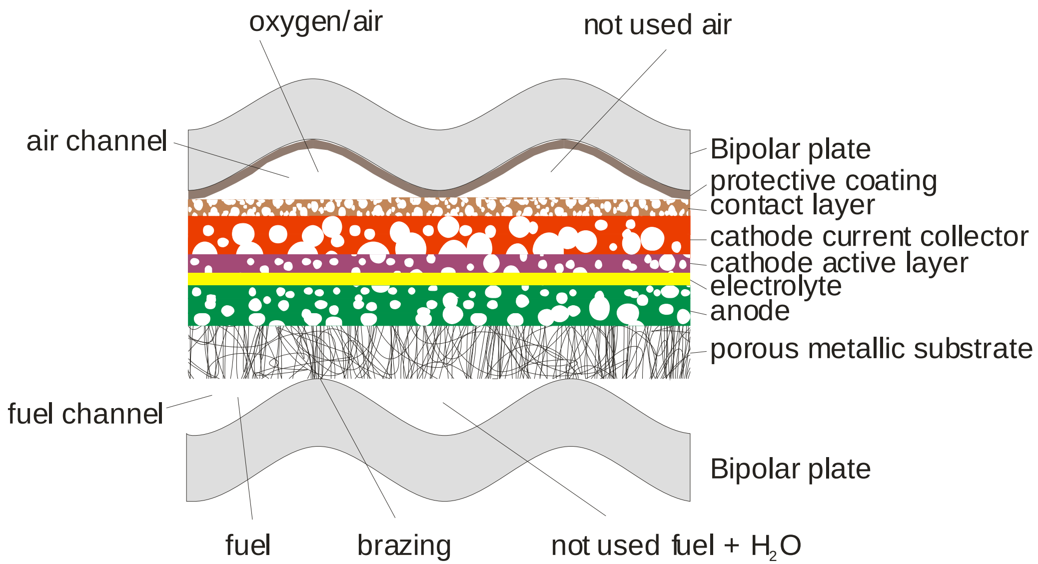
Plasma Deposition Technology

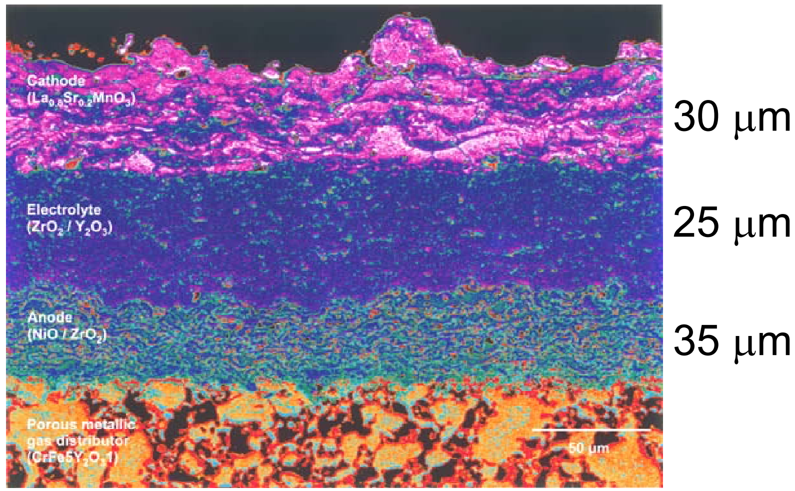
Thin-Film Cells

Ferritic Substrates and Interconnects

Compact Design with Thin Metal Sheet Substrates

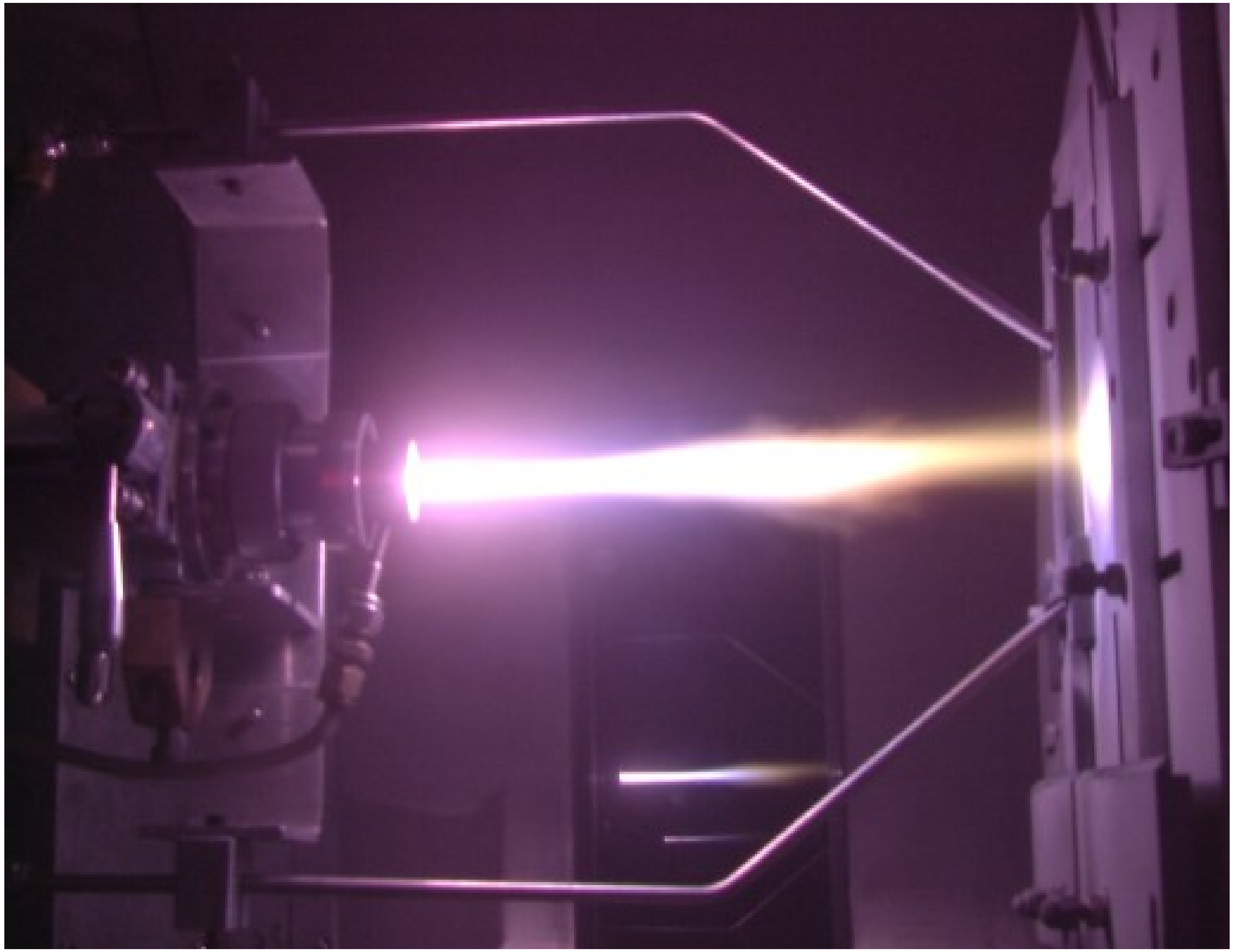
Brazing, Welding and Glass Seal as Joining and Sealing Technology



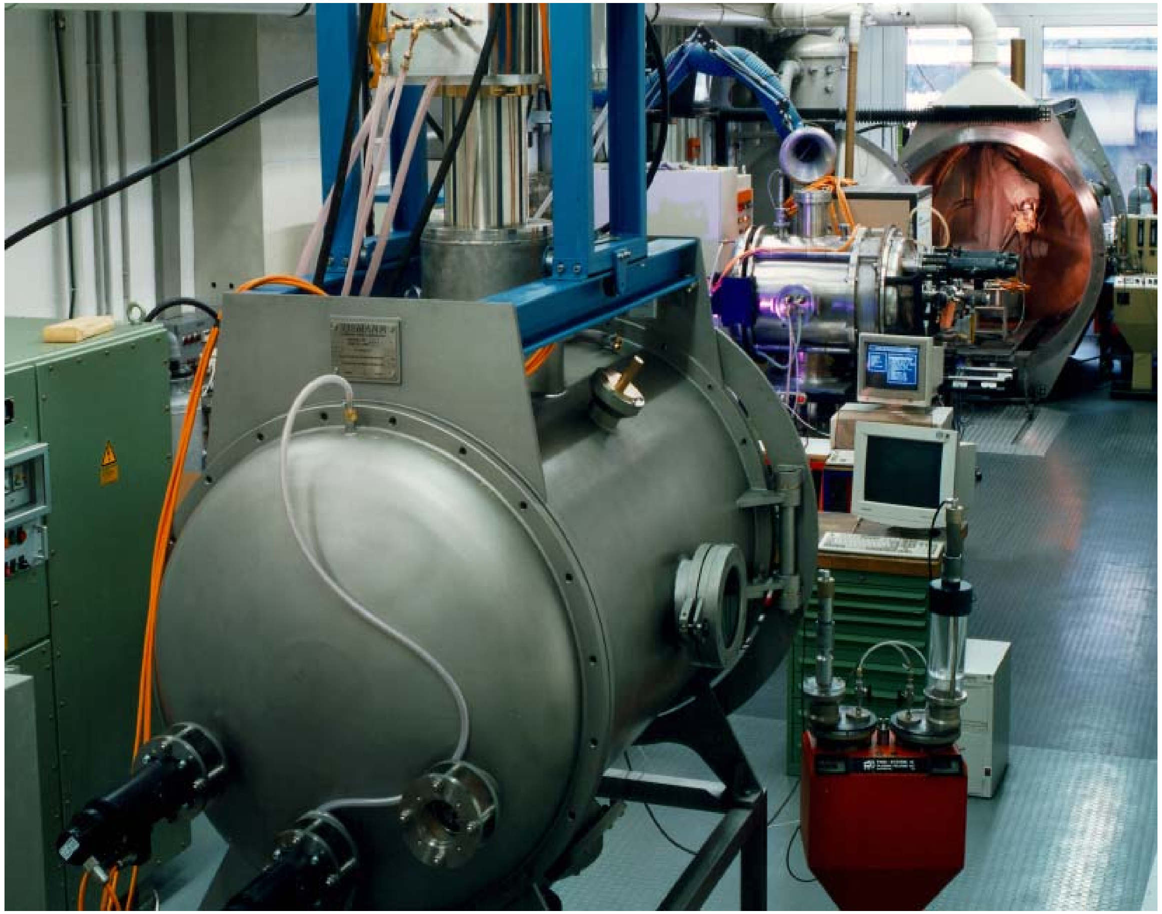


(not in scale)

Vacuum Plasma Spraying of SOFC Cells

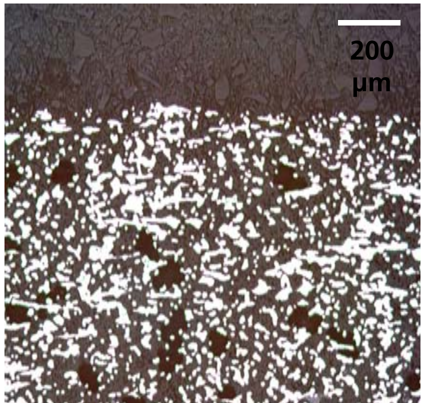


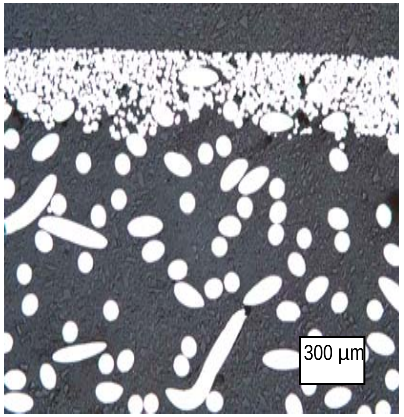
Plasma Spray Laboratory at DLR Stuttgart

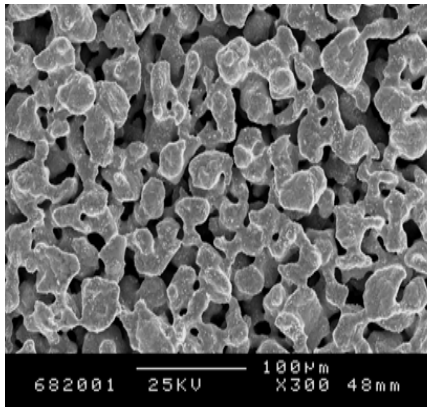


Porous Metallic Substrates Used for the Plasma Spray SOFC Concept

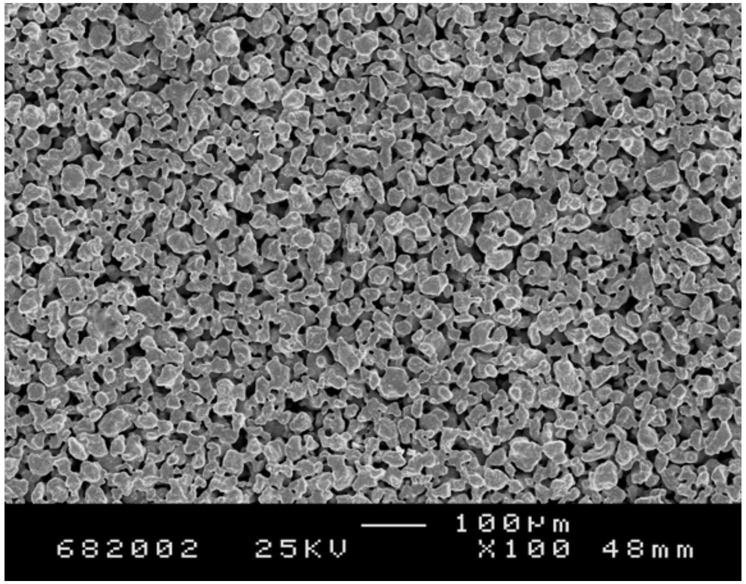
Substrate	Felt	Foam	Knit fabric	Sintered plate
Material	Ni	Fe-22Cr-5Al-0,1Y	Fe-22Cr-0,5Mn	Fe-26Cr (Y_2O_3)
Thickness	~ 1,0	~ 1,8	~ 1,0	~ 1,0
Porosity	~ 85	~ 80	~ 90	~ 50
Supplier	Bekaert, Belgium	Technetics, USA	Rhodius, Germany	Plansee AG, Austria

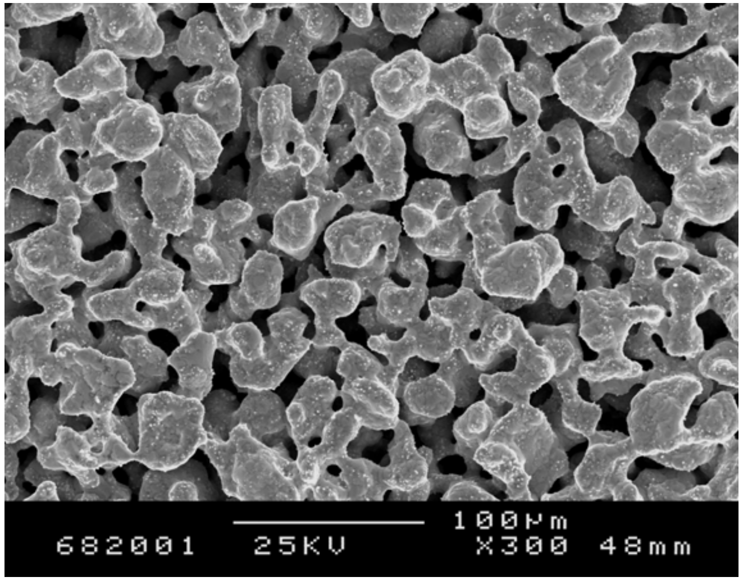






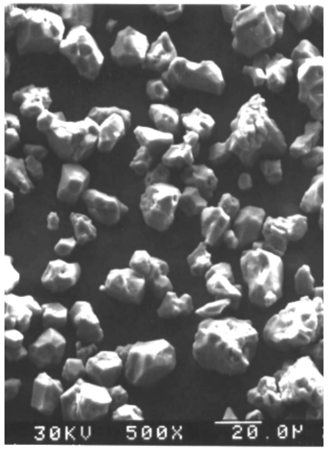
Morphology of Porous Metal Substrate PM Fe-26Cr-(Mo,Ti,Mn,Y_2O_3) of Plansee SE

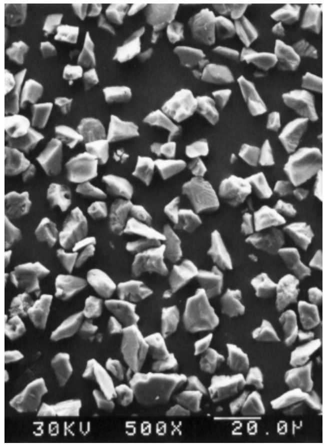


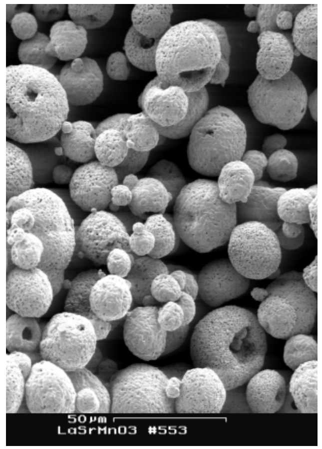


Powders Used for the Spraying of the Cells

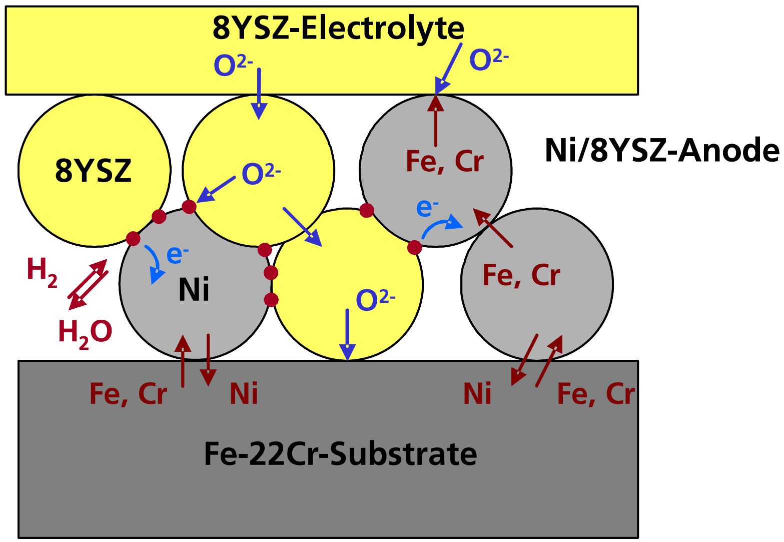
Powder	**NiO**	**ZrO_2- 7 mol %Y_2O_3**	**ZrO_2- 10 mol%Sc_2O_3**	**$(La_{0.8}Sr_{0.2})_{0.98}$ MnO_3**
Short name	NiO	YSZ	ScSZ	LSM
Morphology	sintered, crushed	sintered, crushed	sintered, crushed	sintered, spherical
Size distribution	10-25 µm	5-25 µm	2-35 µm	20-40 µm
Supplier	Cerac, USA	Medicoat, Switzerland	Kerafol, Germany	EMPA, Switzerland



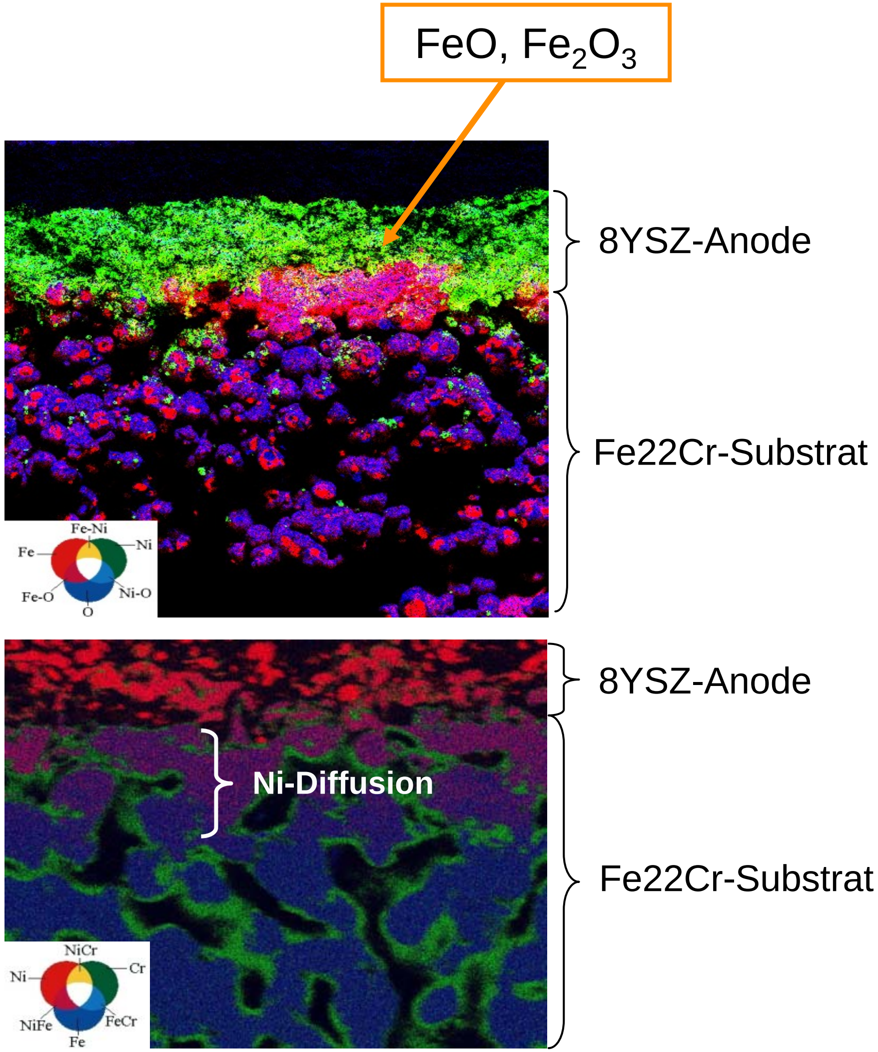




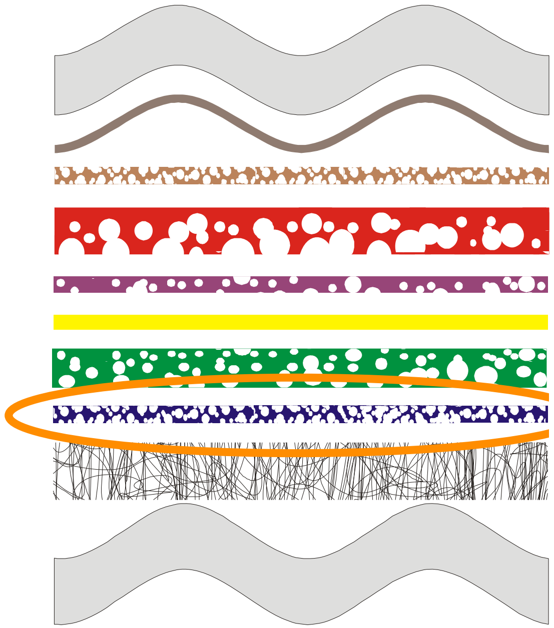
Interdiffusion of Fe, Cr and Ni Between Substrate and Anode



● Triple phase boundary (TPB)



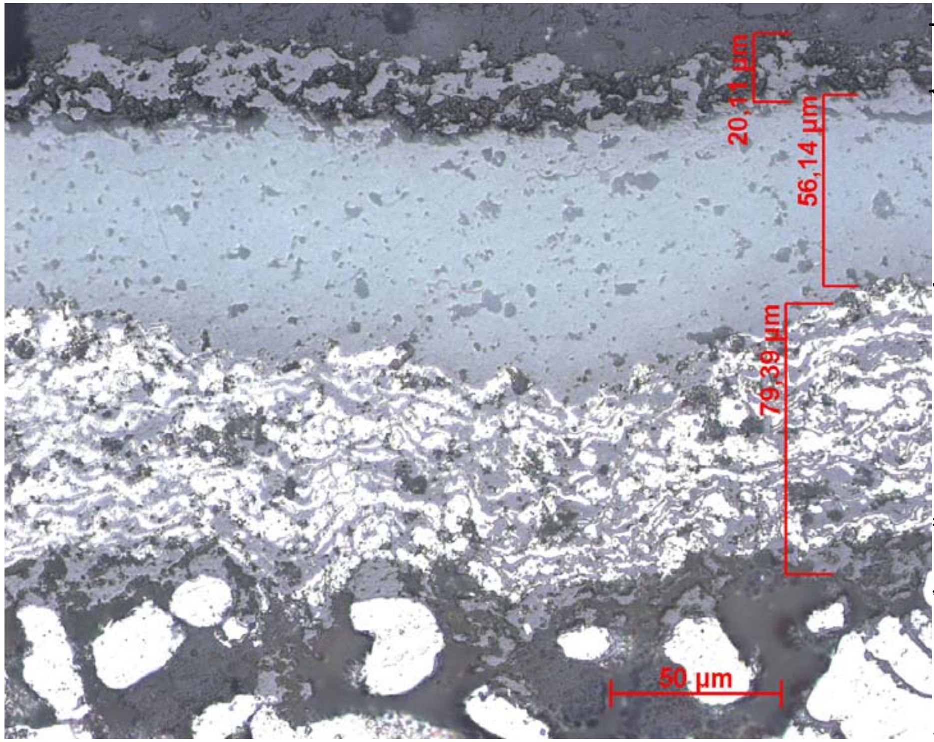
Experimental Approach For a Diffusion Barrier Layer at the Anode Side



Requirements

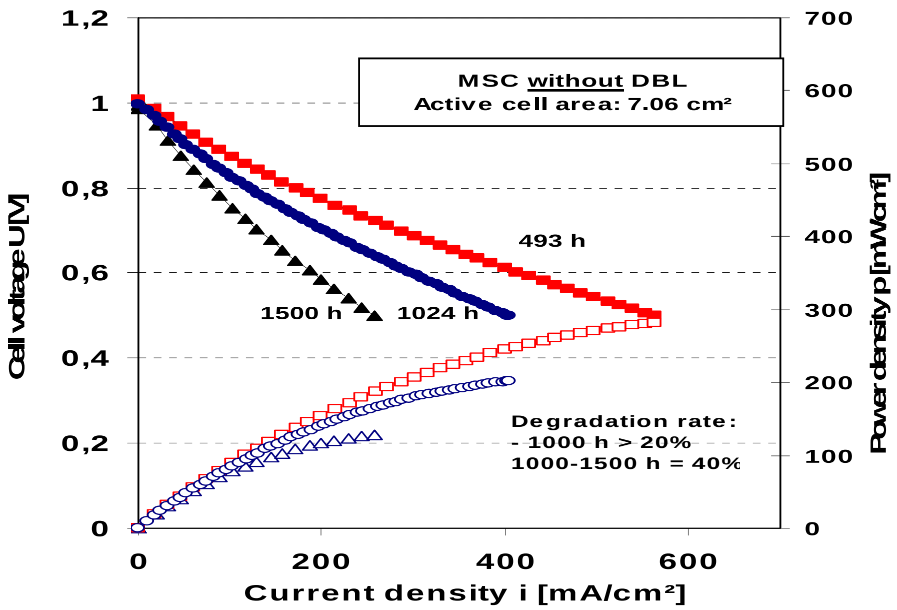
- Porous structure
- Adapted thermal expansion coefficient ($\alpha_{tech.}$= 10-11 x 10^{-6} K^{-1})
- High electronic conductivity in reducing anode atmosphere [σ = 1-3 S/cm, $p(O_2)$ = 10^{-16} bar]
- Chemical stability in reducing humid anode gas atmosphere
- Barrier effect for Fe, Cr und Ni species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

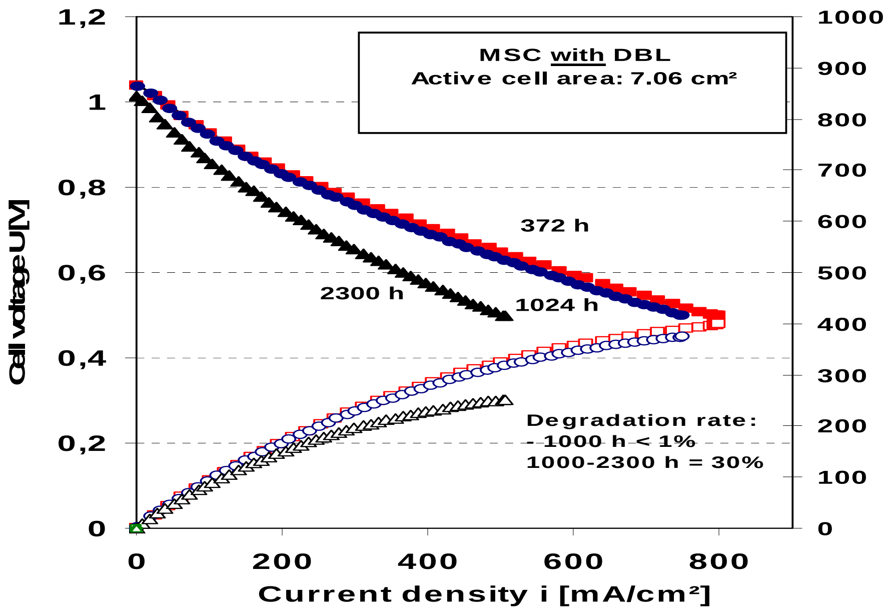
Metallographic Cross Section of MSC Cell



- $LaSrMnO_3$-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 H_2/N_2 and Air





Stack Assembly Based on Metal Supported Cell

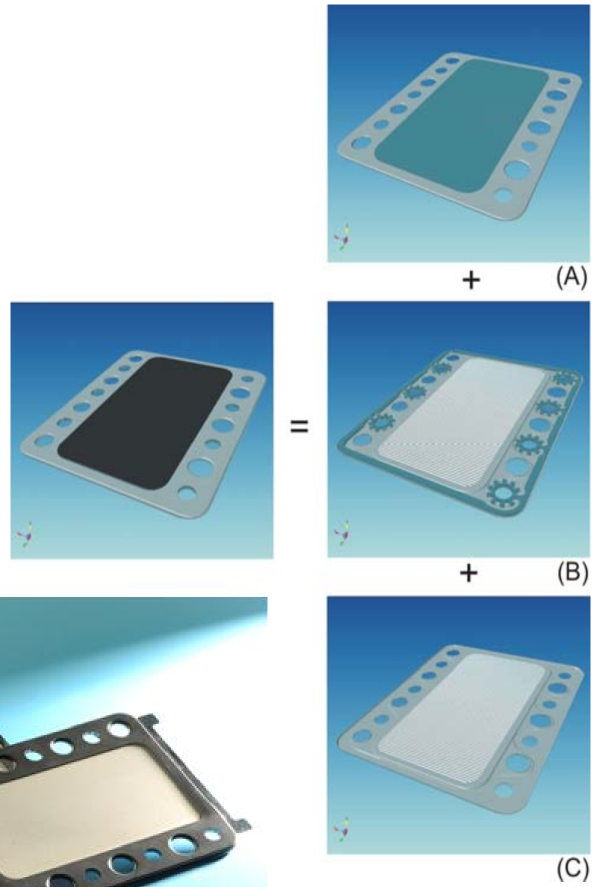
Current MS-SOFC Repeat Unit

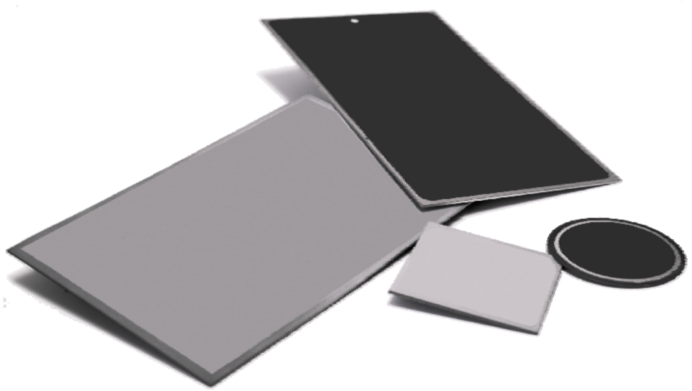
90x120 mm² footprint – ca 100 cm² cell area

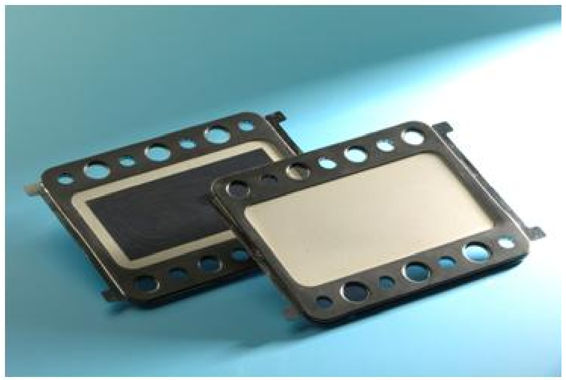
Counter flow design

Stamped sheet ferritic steel bipolar plate

Welded Fe-Cr substrate



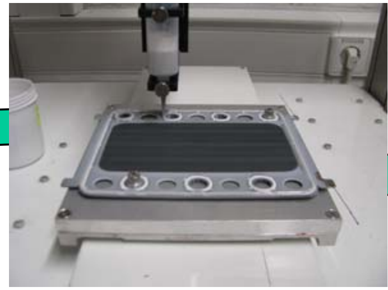




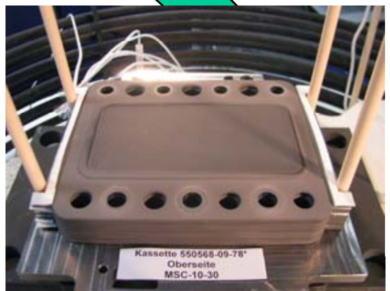
MSC Stack Integration

Cassette

Plasma coating



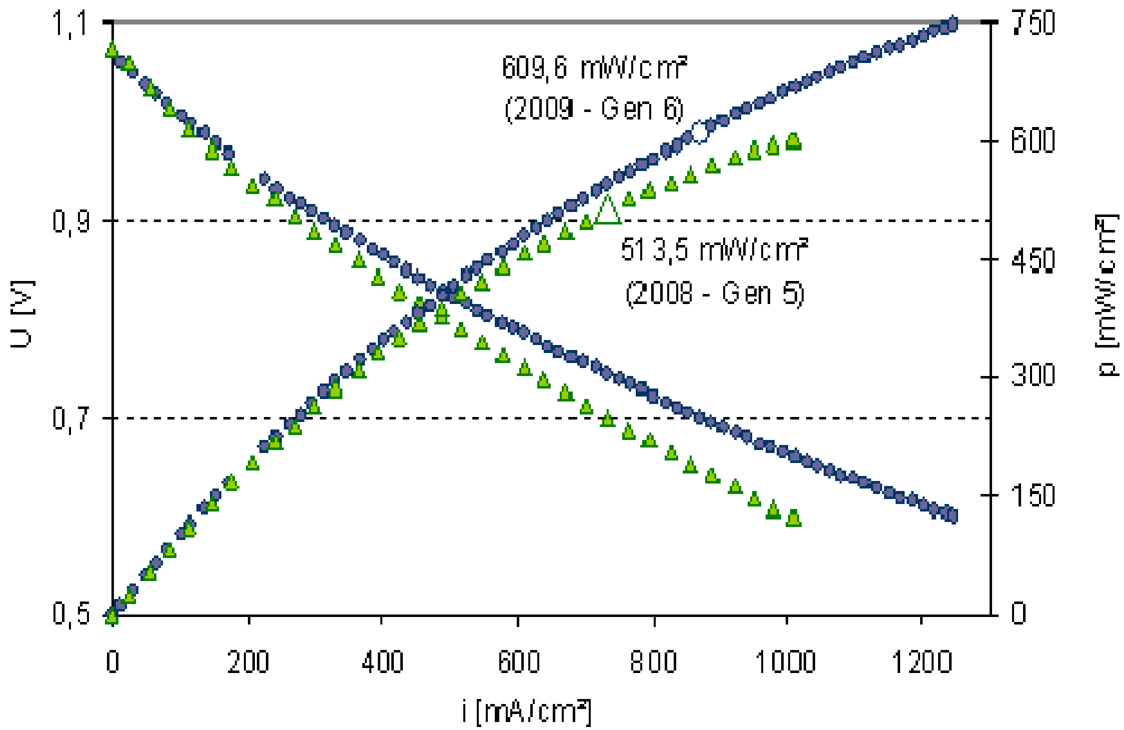
Application of seal



Assembly

Stack test

Performance of Plasma Sprayed MSC Single Cell



MSC Cell: 12.5 cm² cell at 800°C; H_2/N_2 and Air

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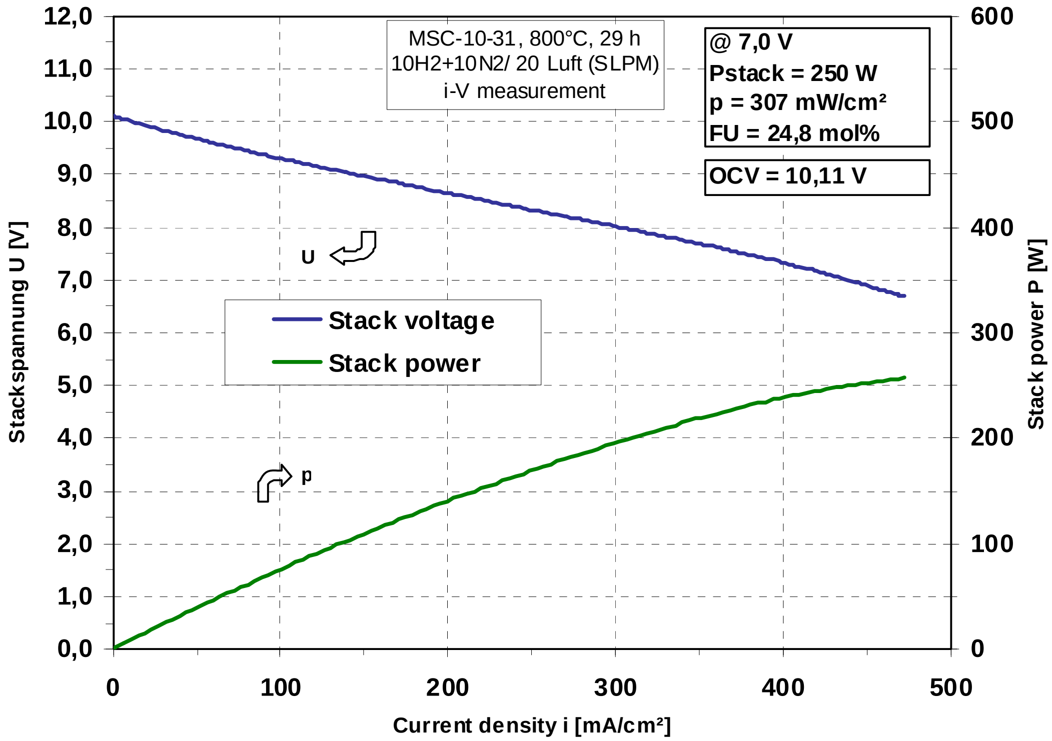
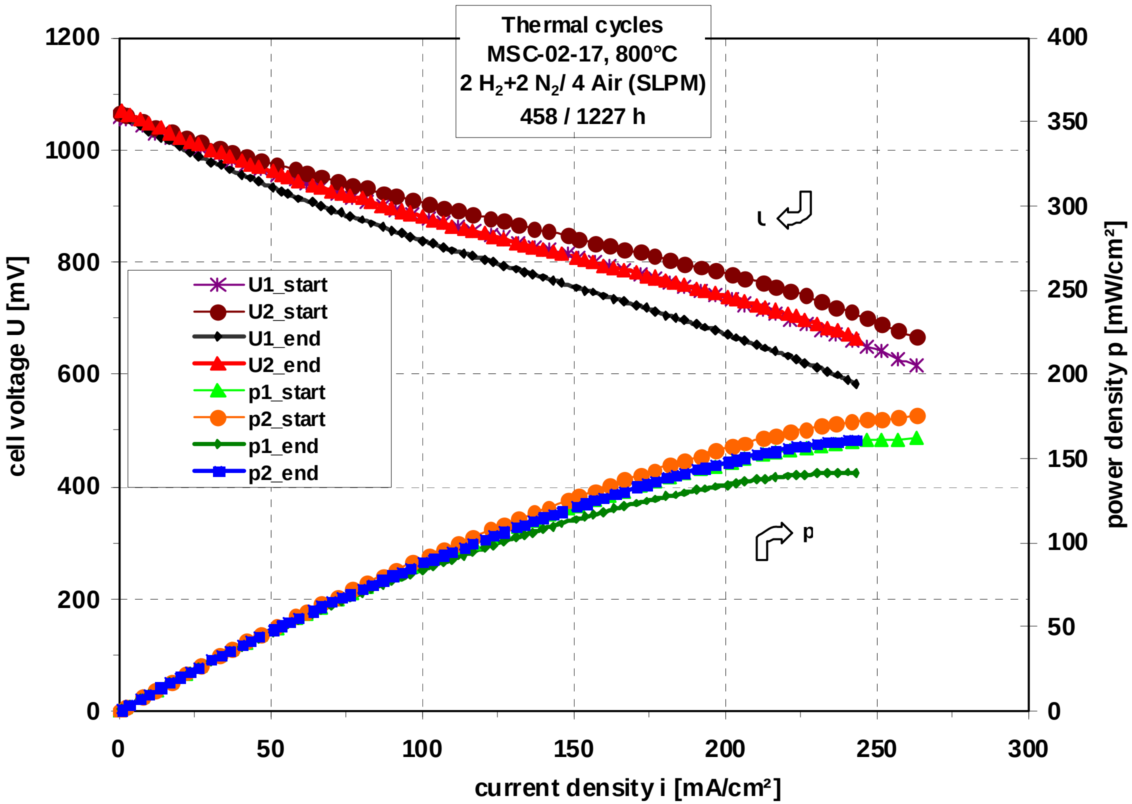
Performance of 10-Cells Stack



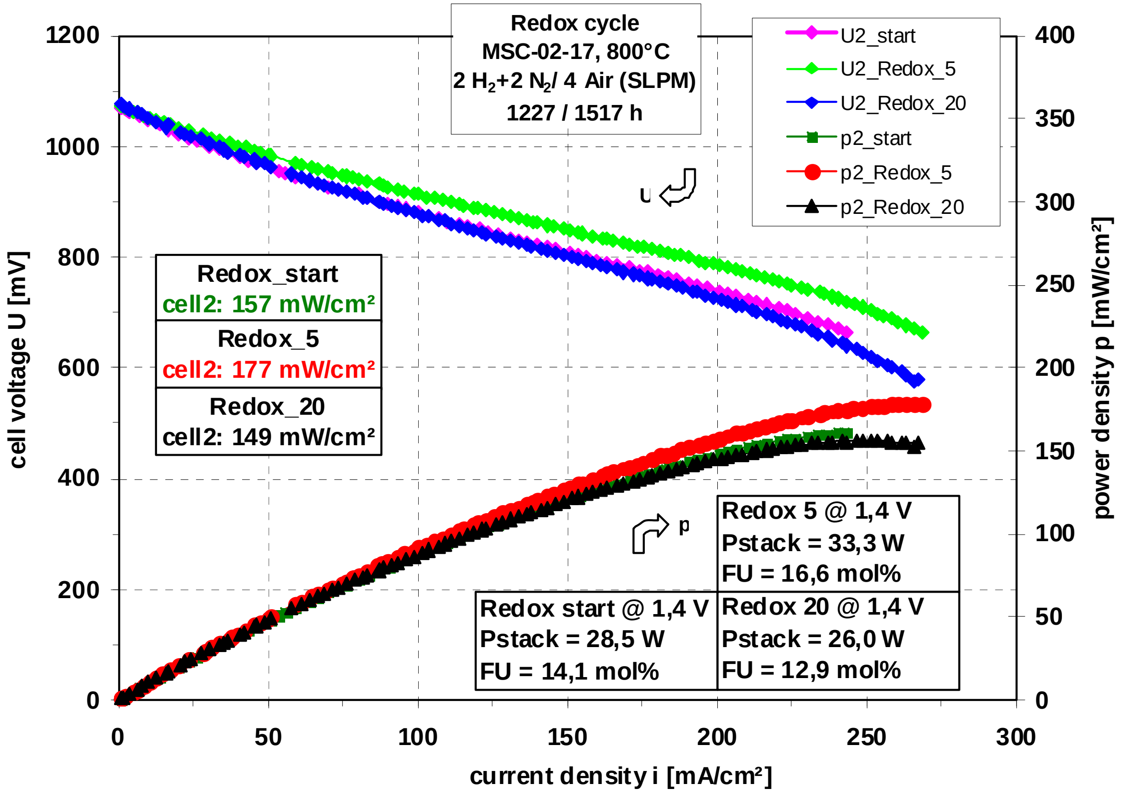
10-Cell Stack: 100 cm² single cells at 800°C; H_2/N_2; Air

Thermal Cycling



- 15 thermal cycles performed, 12 down to 350 °C and 3 to ambient temperature
- Degradation after thermal cycles was 10.3 %

Redox Cycling



- 20 forced redox cycles performed with 50 ml/min O_2 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

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