SOFC Degradation

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European SOFC Stack Technologies

Variety of manufacturers and design types

• planar stacks
  - higher performance
  - compact design
  - mechanically robust
  - simple manifolding
  - lower cost

• tubular stacks
  - resistant to high temperature gradients (*)
  - mechanically robust (*)
  - low power density

(*) thermo-mechanical stability greatly depends on SIZE, not so much on concept
Variety of SOFC Cell Concepts

<table>
<thead>
<tr>
<th>Electrolyte supported</th>
<th>Anode supported</th>
<th>Metal supported</th>
<th>Thin films on thin substrate</th>
</tr>
</thead>
<tbody>
<tr>
<td>~ 300µm</td>
<td>600 µm – 1 mm</td>
<td>~ 1 mm</td>
<td>~ 300 µm</td>
</tr>
<tr>
<td>LSM</td>
<td>LSCF</td>
<td>LSCF</td>
<td>LSC/xSCF</td>
</tr>
<tr>
<td>YSZ</td>
<td>CGO</td>
<td>CGO</td>
<td>CGO</td>
</tr>
<tr>
<td>Ni + YSZ</td>
<td>YSZ/SSZ</td>
<td>YSZ/SSZ</td>
<td>SSZ</td>
</tr>
<tr>
<td>Ni + YSZ</td>
<td>Ni + YSZ</td>
<td>Ni + SSZ</td>
<td></td>
</tr>
</tbody>
</table>

Electrolyte supported: ~ 300µm
Anode supported: 600 µm – 1 mm
Metal supported: ~ 1 mm
Thin films on thin substrate: ~ 300 µm

1000 °C Temperature 700 °C 700 °C 400 °C

Specific properties with different application opportunities
# Application Requirements

<table>
<thead>
<tr>
<th></th>
<th>Lifetime</th>
<th>Thermal cycles</th>
<th>Redox cycles</th>
<th>Efficiency</th>
<th>Weight</th>
</tr>
</thead>
<tbody>
<tr>
<td>APU road vehicles</td>
<td>5000 - 10000 h</td>
<td>2500 - 5000</td>
<td>5000 - 10000</td>
<td>$\eta_{el}&gt;30%$</td>
<td>1- 4 kg/kW</td>
</tr>
<tr>
<td>APU aircraft / ships</td>
<td>20000 - 100000 h</td>
<td>5000 - 20000</td>
<td>10000 - 40000</td>
<td>$\eta_{el}&gt;40%$</td>
<td>1 kg/kW</td>
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<tr>
<td>Residential</td>
<td>&gt; 40000 h</td>
<td>100 - 5000</td>
<td>100 - 5000</td>
<td>$\eta_{el}&gt;35%$</td>
<td>n/a</td>
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<tr>
<td>Commercial</td>
<td>&gt; 40000 h</td>
<td>100 - 5000</td>
<td>100 - 5000</td>
<td>$\eta_{el}&gt;45%$</td>
<td>n/a</td>
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<tr>
<td>Power Generation</td>
<td>100000 h</td>
<td>100 - 5000</td>
<td>100 - 5000</td>
<td>$\eta_{el}&gt;50%$</td>
<td>n/a</td>
</tr>
<tr>
<td>Portable</td>
<td>&lt;2500 h</td>
<td>500 - 5000</td>
<td>500 - 5000</td>
<td>$\eta_{el}&gt;30%$</td>
<td>n/a</td>
</tr>
</tbody>
</table>
Performance of 'Conventional' Products

Service life

• vehicles >10 years (5,000 to 10,000 operating hrs)
• heating boilers (residential power) >10 years (20,000 to 40,000 hrs, frequent cycles possible)
• power generating equipment 10 – 30 years (40,000 to 200,000 operating hours)

Other

• vibration and shock (road vehicles)
• acceleration (aircraft)
• simple coupling to natural gas supply (boilers/engines)
• you can even drop them …
SOFC Development Challenges

- improved durability under static, transient and cycling conditions
  - redox stability
  - thermal cycling capability
- stack lifetime in excess of 40,000 hrs. (stationary & large units, loss of power at end of life <20%)
- high performance, high efficiency
- arbitrary switch-off and start-up cycles (several 100 to 1000)
- tolerance against fuel impurities
- operation without external water supply
- robustness to vibration and mechanical shock
- design of large units and hybrid power plants
- lower cost, increased system compactness, simplification of technology

topics in joint materials, design and systems development
Priorisation (results of 2007 Crete workshop)

• high priority:
  - thermodynamics and kinetics of material stability
  - anode and cathode, including re-oxidation & chromium poisoning
  - protective layer & sealants
  - re-oxidation of anode
  - testing (incl. ALT), predictive models

• medium priority:
  - rapid start-up
  - fuel contaminants

• low priority:
  - steel oxidation etc.
  - load cycling
Long-term Test Topsoe Fuel Cells

- average 2% / 1000 h
- 750°C, 250 mA/cm²
- several thermal cycles
Development Status in SOFC

• stack lifetime of 2 to 4 years shown (proven?)
• single cell lifetime of >> 2.5 years shown
• degradation of well below 1% / 1000 hrs. shown for more than 10 000 hours, but depends on operating conditions
Proof of Concept Stack FZ Juelich

- 700°C, 500 mA/cm², 40% $f_u$
- CroFer22APU steel with APS protective coating
- LSCF cathodes
How do we quantify ‘Degradation’?

800°C new protective coating
Long-term degradation behaviour in stacks

voltage vs. time behaviour

- 'initial drop' for type A
- 'linear' for type B and type C
- 'progressive' for type C

source: Bert de Haart, FZJ
Degradation types

1. Baseline (continuous, steady) degradation
   - initialisation phase (sintering, saturation)
   - constant slope phase
   - progressive degradation phase (EoL)

2. degradation from transients
   - thermal cycle
   - redox cycle

3. degradation after 'incidents' (failures)
   - malfunction of BoP components
   - malfunction of control
   - external influence (shock, grid outage etc.)
Definitions of Degradation

\[ \Delta U = U(t_2) - U(t_1) \mid t_2 = t_1 + 1000 \text{ h} \]

\[ \Delta t = t_2 - t_1 = 1000 \text{ h} \]

\[ d\% = \frac{\Delta U}{U} \%/1000 \text{ h} \] (relative to start value)

\[ dV = \frac{\Delta U}{\Delta t} \text{ mV/1000 h} \] (average over interval)

1. problem: reference value for \( d\% \)?

2. people just don’t stop using \( d\% \) ...
Lifetime Requirements

solutions:
- lower temperatures
- more stable materials

achievement:
- 2 .. 7 mV / kh over 17000 hours (JÜLICH, ongoing)

2 .. 4 mV / kh

15 – 25%

40000

end of life (EoL)
‘Current Dependence’ of Degradation

Assuming that degradation shows as an increase in $R_i$ (or ASR),

$U_1 > U_2$

and

$\Delta U_1 < \Delta U_2$

therefore

$\Delta U_1/U_1 < \Delta U_2/U_2$
Degradation in I-V-Curve
Evolution of Polarization Resistance of Ni-YSZ Anode

- $\text{pH}_2\text{O} = 3\%$
- $\text{pH}_2\text{O} = 30\%$
- $\text{pH}_2\text{O} = 60\%$
- $\text{pH}_2\text{O} = 90\%$

Electrical circuit diagram with resistors $R_1$, $R_2$, and $R_3$ connected through switches $Q1$ and $Q2$. Graph showing the evolution of polarization resistance with time and different humidity conditions.

- $\text{pH}_2\text{O} = 3\%$
- $3\%$
- $30\%$
- $45\%$
- $60\%$
- $75\%$
- $30\%$

Graph with lines indicating high and low polarization resistances.
### Real-SOFC Endurance testing: sensitivity matrix

<table>
<thead>
<tr>
<th>Real-SOFC</th>
<th>G1 FZJ F1002-60 / FZJ</th>
<th>FZJ</th>
<th>G1</th>
<th>stack generation</th>
<th>stack manufacturer</th>
<th>stack number</th>
<th>testing partner</th>
<th>test running / performed</th>
<th>= standard WT4.1 conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>WT1.2.2 CEA</td>
<td>G1</td>
<td>FZJ</td>
<td>F1002-60</td>
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<td>WT1.2.4 FZJ</td>
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<tr>
<td>WT1.2.7 EBZ</td>
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<tr>
<td>WT1.3.1 FZJ</td>
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</tbody>
</table>

- WT1.2.2 CEA: Standard WT4.1 conditions
- WT1.2.4 FZJ: Benchmark G2 conditions
- WT1.2.7 EBZ: Benchmark G3 conditions
- WT1.3.1 FZJ: Test running / performed (alternative: G2 w/ temp <800 °C)

<table>
<thead>
<tr>
<th>fuel temperature</th>
<th>hydrogen + 3 % water vapour</th>
<th>current density mA/cm²</th>
<th>fuel utilisation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
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<td>300</td>
<td>10</td>
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<td>1000</td>
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</tbody>
</table>

<table>
<thead>
<tr>
<th>fuel temperature</th>
<th>methane (internal reforming) S/C=2.0</th>
<th>current density mA/cm²</th>
<th>fuel utilisation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>800 °C</td>
<td></td>
<td>300</td>
<td>10</td>
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Real-SOFC Stack Generations: Progress by Materials

- **G1** at 800°C with LSM electrode
- **G2**
- **G3** at 700°C with LSCF electrode

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**Durability Tests**
- G1, G2, G3

**Temperature**
- 800 °C
- 700 °C

**Fuel Gas**
- Hydrogen

**Fuel Utilisation**
- 40%

**Current Density**
- 0.5 A/cm²
Sensitivity to Current Flow & Fuel Utilisation

- Temperature: 700 °C, 800 °C
- Fuel gas: Hydrogen
- Fuel utilisation: 40%, 75%
- Current density: 0.5 A/cm², 0.7 A/cm²

Comparison of baseline vs benchmark for durability tests G3:

- G3 --- baseline 700 °C
- G3 --- benchmark 800 °C
- G3 --- benchmark 700 °C
Long-Term Stack Operation

- >42,000 hours of operation on load
- 700°C, 500 mA/cm², 40% \( f_u \)
- Plansee ITM steel with standard protective coating
- LSCF cathodes
Evaluating Degradation Rates

![Graph showing degradation rates over run time](image)
Degradation Phenomena Overview
Variety of Degradation Phenomena

- Fuel impurities
- Contacting
- Cathode poisoning
- Anode re-oxidation
- Corrosion

Graph showing voltage and current over time.
Variety of phenomena (2)

Types
- changes in single layers or components (independent of others)
- changes at interfaces
- interaction of materials (e.g. transport of species)

Driving forces
- temperature
- current flow
- overpotential
- partial pressures of oxygen, hydrogen, water etc.
- pressure
- etc.
Degradation Mechanisms

- changes in morphology and phase with consequences for
  - gas transport
  - resistivity
  - mechanical strength
  - reduction of active surface area
- interdiffusion with consequences for
  - corrosion resistance
  - loss of activity
  - resistivity
- transport of species with consequences for
  - poisoning / de-activation
  - build-up of layers / scales
- corrosive interaction
- build-up of corrosion scales with consequences for
  - dimensional changes (e.g. swelling)
  - resistivity
  - cycling capability
# Overview of Degradation Mechanisms

<table>
<thead>
<tr>
<th><strong>Cathode side</strong></th>
<th><strong>Electrolyte</strong></th>
<th><strong>Anode side</strong></th>
</tr>
</thead>
<tbody>
<tr>
<td>Three phase boundary reduction by</td>
<td>Phase instabilities</td>
<td>Ni-agglomeration</td>
</tr>
<tr>
<td>- Cr poisoning</td>
<td></td>
<td>Ni-coarsening</td>
</tr>
<tr>
<td>- Particle sintering</td>
<td>Interdiffusion</td>
<td>S poisoning</td>
</tr>
<tr>
<td>Phase changes</td>
<td></td>
<td>Interdiffusion</td>
</tr>
<tr>
<td>Interdiffusion</td>
<td>Destruction by re-oxidation</td>
<td></td>
</tr>
<tr>
<td>Contact degradation</td>
<td>Contact loss by</td>
<td></td>
</tr>
<tr>
<td>Resistivity</td>
<td>- by sintering</td>
<td></td>
</tr>
<tr>
<td>Cr transport</td>
<td>- by seal swelling</td>
<td></td>
</tr>
<tr>
<td></td>
<td>- temp. gradient</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Resistivity</td>
<td></td>
</tr>
<tr>
<td>Interconnect:</td>
<td>Interconnect:</td>
<td></td>
</tr>
<tr>
<td>- Cr evaporation</td>
<td>- Scale resistance</td>
<td></td>
</tr>
<tr>
<td>- Corrosion cracking</td>
<td>- Embrittlement by carburization</td>
<td></td>
</tr>
<tr>
<td>- Inner oxidation</td>
<td>- Corrosion cracking</td>
<td></td>
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<tr>
<td>Ceramic glass sealant</td>
<td></td>
<td></td>
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<tr>
<td>- Interaction with gaseous species/ contaminants</td>
<td></td>
<td></td>
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<tr>
<td>- Interaction between components</td>
<td></td>
<td></td>
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<tr>
<td>- Leakage or short circuit during thermal cycling</td>
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<td></td>
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<tr>
<td>- Degradation due to impurities in raw materials</td>
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<td></td>
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</table>
SRU Cross-Section

<table>
<thead>
<tr>
<th>Mechanism</th>
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<tbody>
<tr>
<td>Corrosion perforation</td>
</tr>
<tr>
<td>Carburisation (embrittlement)</td>
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<tr>
<td>Scale resistivity</td>
</tr>
<tr>
<td>Coating/scale resistivity</td>
</tr>
<tr>
<td>Contact loss (sintering)</td>
</tr>
<tr>
<td>Contact loss (seal swelling)</td>
</tr>
<tr>
<td>Contact loss (dT/dx, dT/dt)</td>
</tr>
<tr>
<td>Poisoning / low-σ phases by contact layer</td>
</tr>
<tr>
<td>Coking</td>
</tr>
<tr>
<td>Ni sintering</td>
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<tr>
<td>Redox at high j and/or Uf</td>
</tr>
<tr>
<td>S-poisoning</td>
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<tr>
<td>S-poisoning</td>
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<tr>
<td>Ni sintering (TPB reduction)</td>
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<tr>
<td>Interdiffusion (low-σ phase formation)</td>
</tr>
<tr>
<td>Phase instability (ageing)</td>
</tr>
<tr>
<td>Interdiffusion (low-σ phase formation)</td>
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<tr>
<td>Phase changes, demixing</td>
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<tr>
<td>Particle sintering (TPB reduction)</td>
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<tr>
<td>Cr-poisoning</td>
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<tr>
<td>Interdiffusion</td>
</tr>
<tr>
<td>Contact loss (sintering)</td>
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<tr>
<td>Contact loss (seal swelling)</td>
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<tr>
<td>Contact loss (by dT/dx, dT/dt)</td>
</tr>
<tr>
<td>Cr evaporation / cathode poisoning</td>
</tr>
<tr>
<td>Coating/scale resistivity</td>
</tr>
<tr>
<td>Corrosion perforation (H assisted)</td>
</tr>
<tr>
<td>Cr evaporation / cathode poisoning</td>
</tr>
</tbody>
</table>
Conductivity Degradation of Electrolyte

8YSZ

caused by phase separation and re-ordering in micro-domains, impurities, etc.

Source: IWE
Electrolyte Degradation by Diffusion of Mn

- after 20,000 hours of operation: failure of cell
- Mn enrichment along grain boundaries 5-10 at.%
Electrode-Electrolyte Interface during Manufacturing

1. formation of low-conductive products such as $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{SrZrO}_3$ during cell sintering and SOFC operation, especially with LSCF cathodes

2. segregation of material impurities at TPB’s

3. solution of Ni in YSZ
Processes at the Cathode-Electrolyte Interface

1. segregation of materials impurities at TPB’s
2. very low SiO\textsubscript{2} content (~100 ppm) in the raw materials affects the microstructure of interfaces and grain boundaries in SOFC.

M. Mogensen / Proc. 26th Risø Int. Symp.  
Cathode Materials: Stability

thermodynamical stability and kinetics: perovskites $\text{ABO}_3$

$\sqrt{2a} = 2r(A) + 2r(O)$

$\alpha = 2r(B) + 2r(O)$

- $(\text{La},\text{Sr})\text{MnO}_3$
- $(\text{La},\text{Sr})\text{FeO}_3$
- $(\text{La},\text{Sr})\text{CoO}_3$
- $(\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3$
- $(\text{La}_{0.9},\text{Sr}_{0.1})\text{MnO}_3$
- $(\text{La}_{0.7},\text{Sr}_{0.3})\text{MnO}_3$
- $(\text{La}_{0.7},\text{Sr}_{0.3})_{0.99}\text{MnO}_3$
- $(\text{La}_{0.7},\text{Sr}_{0.3})\text{MnO}_3 \delta$
- $(\text{La}_{1-x}\text{Sr}_x)_y\text{Fe}_{1-z}(\text{Ni},\text{Cu})_z\text{O}_{3-\delta}$

source: Yokokawa, EMPA
Cathode Materials: Volatility

source: Tietz/Mai
Nickel Anode Volatility

Volatilisation of nickel (NiOH) in high water content fuel gases – loss of active surface

Performance plot

Long term measurements
Operation time: 700 ... 1000 h
Temperature: 950 °C
Oxidant: air

Aim: <1 mV/1000h

Degradation rates in mV/1000h


Source: IWE
Anode Substrate: Particle Agglomeration

• temperature-induced tendency of metals to decrease free energy, i.e. to minimize the surface area and agglomerate
• examples: anode substrate Ni-YSZ cermet


Source: ICE-FORTH
Microstructure characterization

SEM images of anode surface (70 wt% Cu + 30 wt% SDC)

secondary electron mode  backscattering mode

For good distinguishability of different phases their backscattering coefficients should be different.

Source: IHTE
Three-Dimensional Characterisation

- FIB/TEM analysis
- reconstruction of 3-D structure from 'slices'

Chromium Volatilisation

Impact of Chromium on Cathode Performance
Chromium Poisoning: Microscopic Findings

- LSM/YSZ
- \((\text{CrMn})_3\text{O}_4\) (spinel)
- Electrolyte (YSZ)
Without current Cr is only located within the \( \text{La}_{1-x}\text{Sr}_x\text{MnO}_3 \) layer, forming \((\text{Cr, Mn})_3\text{O}_4\) spinel crystals. If a current passes through the cell the Cr is mainly deposited near the TPB near the YSZ electrolyte. Chromium is clearly found along the perimeter of the pores on the surface of the YSZ, thereby decreasing the number of active sites necessary for oxygen reduction.

Electrochemical tests with the \( \text{La}_{0.58}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_3 \) cathode under current clearly show Cr poisoning at 800°C. Significant formation of \( \text{SrCrO}_4 \) crystals was detected on the surface of the cathode layer.

Konysheva et al.  
Redox Cycling Requirements

- redox cycles:
  - after stack shut-down air will flow to the fuel electrode
  - Ni in Ni-YSZ anode will re-oxidise to NiO$_2$
  - NiO$_2$ has higher volume and will cause mechanical damage to cell
- goals:
  - no gas leakages from stack (safe operation)
  - rapid start-up (30 minutes for road APU)

Redox stability of Ni–YSZ cermet

- cyclic reduction and oxidation leads to large volume change of Ni to NiO
- microstructure of Ni/YSZ bulk is affected
- performance degradation due to change in Ni particle surface, or
- catastrophic (mechanical) failure of cermet, or
- cracking of electrolyte layer

solutions:
- system control of temperature and fuel flow
- robust cells
Anode – Redox-Stability

starting state:
oxidized
NiO + ZrO$_2$($+$Y$_2$O$_3$)
Anode Redox Stability – SrTi Anode

disadvantage: low electrochemical performance due to low electrical conductivity
Sulphur Poisoning – The Phenomenon

![Graph showing voltage and time relationship](image-url)
Sulphur Poisoning – The Phenomenon (2)

![Graph showing the effect of different concentrations of H₂S on voltage over time at 1000°C and 200mA/cm².](image)
**Sulphur Poisoning**

**H$_2$S concentration:**
- Coal syngas – 100-300 ppm
- Biogas – 50-200 ppm
- Natural gas – up to >1%

**Chemosorption:**
H$_2$S = HS(ad) + H(ad) = S(ad) + 2H(ad)

**Chemical reactions:**
- H$_2$S = H$_2$ + S (at 1100 K 8.6% H$_2$S is decomposed)
- Ni + H$_2$S = NiS + H$_2$
- 3Ni + xH$_2$S = Ni$_2$S$_x$ + xH$_2$ (at 800°C required level for sulfides formation is 1% H$_2$S)

**Electrochemical reactions:**
- H$_2$S + 3O$^{2-}$ = H$_2$O + SO$_2$ + 6e$^-$
- H$_2$S + O$^{2-}$ = H$_2$O + S + 2e$^-$
- S + 2O$^{2-}$ = SO$_2$ + 4e$^-$

**1st step (reversible):** Fast adsorption of sulfur occurs in minutes upon exposure to H$_2$S, which blocks reaction sites and leads to rapid performance degradation. 90% coverage may occur at 1000 K for a low H$_2$S concentration (10 ppm).
Sulphur Poisoning: Microscopic Findings

- Bulk material deposition
  - Reduction of porosity
  - Passivation of catalytically active Ni

- Surface deposition
  - Passivation of catalytically active Ni
Coking – Carbon Buildup in Internal Reforming

carbon build-up due to hydrogen and oxygen stochiometry mismatch (Boudouard Reaction)

\[
\begin{align*}
CH_4 + O_2 & \rightarrow CO_2 + H_2O \\
CH_4 + H_2O & \rightarrow CO + H_2 \\
C + H_2O & \rightarrow C + H_2 \\
C + O_2 & \rightarrow C + O \\
\end{align*}
\]

figures courtesy of Jörger & He
Methane Conversion Reactions

equilibrium (i=0)
\[ \text{CH}_4 = \text{C} + 2\text{H}_2 \] (1)

steam reforming (endothermic)
\[ \text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \] (2)

partial oxidation
\[ \text{CH}_4 + \frac{1}{2}\text{O}_2 = \text{CO} + 2\text{H}_2 \] (3)

water-gas shift reaction
\[ \text{CO} + \text{H}_2\text{O} = \text{CO}_2 + \text{H}_2 \] (4)

Boudouard reaction
\[ 2\text{CO}=\text{CO}_2+\text{C} \] (5)

direct oxidation
\[ \text{CH}_4 + \text{O}^{2-} = \text{CO} + 2\text{H}_2 + 2\text{e}^- \] (6)
\[ \text{CH}_4 + 4\text{O}^{2-} = \text{CO}_2 + 2\text{H}_2\text{O} + 8\text{e}^- \] (7)

oxidation
\[ \text{C} + \text{O}^{2-} = \text{CO} + 2\text{e}^- \] (8)
\[ \text{C} + 2\text{O}^{2-} = \text{CO}_2 + 4\text{e}^- \] (9)
\[ \text{CO} + \text{O}^{2-} = \text{CO}_2 + 2\text{e}^- \] (10)
\[ \text{H}_2 + \text{O}^{2-} = \text{H}_2\text{O} + 2\text{e}^- \] (11)
Interconnect Corrosion: Scale Cross-Sections

Microstructures of oxide scales after 1000 h discontinuous oxidation at 800°C in air

Commercial Si-containing steel

Ni-coating

Oxide scale

SiO₂

alloy

5µm

Si + Laves phase forming elements

Ni-coating

Oxide scale

alloy

5µm
Steel Corrosion - Interconnects

Cyclic Oxidation of Ferritic Steel Crofer 22 APU in Air at 900°C

Weight change (mg/cm²) vs. Time (h)

- 0.1 mm (breakaway)
- 0.3 mm (breakaway)
- 0.5 mm
- 2 mm

$k_p$–dependence on specimen thickness
Metal Corrosion: Nickel Mesh

Ni-coating

Ni-mesh

Ni-mesh

100 μm

100 μm
Degradation of Interconnect Steels

Ferritic stainless steels are Fe–Cr alloys. To be considered “stainless”, the alloys must contain at least 12-14% Cr for aqueous corrosion. Even more Cr is required if the alloy is to be able to selectively oxidize the Cr to form a continuous, protective layer of Cr$_2$O$_3$.

Chromia (Cr$_2$O$_3$) forming ferritic stainless steels have similar coefficient of thermal expansion with the oxide components of the SOFC. Electrical conductivity requires that the oxide that forms at the interconnect surfaces be conductive at operating temperatures. Chromia forming alloys meet this requirement; as Cr$_2$O$_3$ is a semiconductor at elevated temperatures.

Chemical composition of the alloys used

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Fe</th>
<th>Cr</th>
<th>Mn</th>
<th>Ti</th>
<th>Si</th>
<th>Al</th>
<th>Re-el.</th>
<th>Ni</th>
</tr>
</thead>
<tbody>
<tr>
<td>Crofer22APU-1a</td>
<td>Bal.</td>
<td>22.6</td>
<td>0.4</td>
<td>0.06</td>
<td>0.1</td>
<td>0.1</td>
<td>La-0.1</td>
<td>0.2</td>
</tr>
<tr>
<td>JS-3</td>
<td>Bal.</td>
<td>23.3</td>
<td>0.4</td>
<td>0.05</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>La-0.1</td>
<td>–</td>
</tr>
</tbody>
</table>

Under SOFC stack conditions rapidly growing oxide nodules were observed bridging the 200 mm seal gap between the metallic components. These oxide nodules, rich in iron, gave rise to local short-circuiting effects eventually resulting in stack failure.

optimal matching of steel and sealing materials is vital:
- good adhesion = chemical interaction
- but: no excessive corrosion
Degradation due to Contacting problems
Contact trace on cathode

high local current due to narrow contacting 'ridge'

820 mV - 336 mA/cm²  
770 mV - 336 mA/cm²  
880 mV - 298 mA/cm²
Thermo-Mechanics

low strength of steels at high temperatures
Thermal Cycling Requirements

- **thermal cycles:**
  - ‘cold start’ 20°C … 200°C, ‘warm start’ >400°C up to 600 … 750°C
- **goals:**
  - no gas leakages from stack (safe operation)
  - rapid start-up (30 minutes for road APU)

**FEM-simulation of this part**

measured temperatures

minimal calculated temperature

795°C

leakages

highest tensile stress

**solutions:**
- strong sealings
- robust design
- compliant design

**achievement:**
- 100 to 250 cycles > 25°C
  (JÜLICH, ElringKlinger)
FEM Analysis of Critical ThermoMechanical Stress

- identification of critical locations in stack
- implementation of global model
- passing of boundary conditions to more detailed sub-model
- prediction of strain
- improvement of design
Impact of Failing Element in a Stack

If a single cell in a stack exhibits higher resistance than the rest of the cells, stack failure often initiates at such a cell. The cell is then exhibits lower voltage than the rest of the cells, and often even a negative voltage. It is necessary that cell-to-cell characteristics be as uniform as possible including contact between repeat units.

If a cell exhibits a negative voltage, the oxygen chemical potential within the electrolyte can exceed that in the oxidant, and/or can drop below that in the fuel. This can lead to high internal oxygen partial pressure resulting in electrode cracking and delamination, and/or very low oxygen partial pressure leading to local electrolyte decomposition. Both situations can lead to cell and stack degradation.
Modelling of degradation processes
Analysis Approach

• correlating cause and effect (phenomena and ensuing degradation)
• modelling of effects
• understanding and influencing mechanisms
• improving materials with less sensibility to degradation and/or deterioration

not only to be worked on in sequence, but also in parallel
The quantification and prediction of single contributions with respect to their behaviour over time is the key expected outcome of this project.
Correlated percolation model

In the model monosized particles are located on a face-centered cubic lattice and sintering between two metal particles occur with a certain probability. The model gives an insight in the development of active bonds in the anode, the density of three phase boundaries and the transport resistance in anodic materials.

*Fig. 3. Variation of the number of active bonds with time, $n(t)$, obtained for the composition which maximizes $n(t)$. Lines: effective medium theory; points: Monte Carlo simulation. The effect of the probability of pore opening in each sintering act. $X$: (a) 0, (b) 0.5, (c) 1. The curves and points correspond to the indicated values of the minimum number, $n$, of non-electrolyte neighbors of the bond between two metal particles which allows their fusion.*

Approaches to SOFC Accelerated Lifetime Testing
Accelerated durability testings

Types of Acceleration

• Increase the use-rate of the product (e.g., test a toaster 200 times/day). Higher use rate reduces test time.

• Use elevated temperature or humidity to increase rate of failure-causing chemical/physical process.

• Increase stress (e.g., voltage or pressure) to make degrading units fail more quickly.

These types of acceleration may work in combination (e.g. electro-chemical reactions)

Acceleration of a failure mechanism must mimic actual occurrence of the failure mode(s)
Accelerating Degradation Effects

![Graph showing the relationship between hours and voltage for E(t).]
Mapping in Time

- Cell voltage can be written as
  \[ E(t) = E(t=0) - X(t) \]

- degradation phenomena are generally functions of
  - T, p(O_2), p(H_2O), j, overpotential, concentration gradients etc.
  - in the form \[ X(t) = f(T, p(O_2), j, t, ...) \]

- a mapping has to be found where
  \[ X'(t) = X(a \cdot t) \]
  where \( a > 1 \) is an acceleration coefficient

- prerequisite:
  the acceleration must not change the principal effect

- the mapping is not necessarily linear
A Lifetime Prediction Model

- stack test results are too complicated to analyse
- full set of parameters to equip a 'full' stack model (including degradation) does not exist
- a disaggregated model of single degradation mechanisms could be suitable for evaluation of the single effects
- a complete model could then be achieved by re-aggregating results
- this also might lend itself to introducing accelerated testing
Thank you for your attention!
If there’s any questions … go ahead.

Acknowledgments go to
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