On Degradation Issues in High-Temperature Electrochemical Devices

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Session: Materials and their degradation modes
On Degradation Issues in High-Temperature Electrochemical Devices

JP Fuel Cells and Hydrogen

L.G.J. (Bert) de Haart
Forschungszentrum Jülich
Institute of Energy and Climate Research
Fundamental Electrochemistry (IEK-9)

Peter Holtappels
DTU ENERGY
Department of Energy Conversion and Storage

DTU Energy
Department of Energy Conversion and Storage
High-Temperature Electrochemical Devices
- operation and requirements
- materials, cells and stacks

Degradation Issues
- degradation processes
- examples
  - Chromium poisoning
  - Manganese diffusion
  - Nickel evaporation

Summary and Outlook
operation of high-temperature electrochemical devices

In an electrochemical device, like a fuel cell, chemical energy (contained in a fuel) is converted into electrical energy, or, *vice versa*, in an electrolyser electricity is converted into a fuel.

**Electrolysis: electricity storage (as fuel)**

- **Fuel Cell: electricity production**

\[
\begin{align*}
2 \text{O}^{2-} \text{(ad)} & \rightarrow \text{O}_2(g) + 4 \text{e}^- \\
\text{H}_2\text{O}(g) + 2 \text{e}^- & \rightarrow \text{H}_2(g) + \text{O}^{2-} \text{(ad)} \\
\text{CO}_2(g) + 2 \text{e}^- & \rightarrow \text{CO}(g) + \text{O}^{2-} \text{(ad)} \\
\end{align*}
\]
SOFC/SOEC: basic characteristics and requirements

The Solid Oxide Fuel Cell (SOFC) and Solid Oxide Electrolysis Cell (SOEC) are characterised by / require:

- A ceramic oxygen-ion conductor as the electrolyte
- Requires operating temperatures above 600 °C
- Non-noble metal and metal oxides as catalysts for the electrochemical reactions
- Allows the use of carbon (as carbon monoxide CO and methane CH₄) containing fuels
- Requires catalysts for methane/steam reforming in/at the fuel electrode
- Produces useable heat in the off-gas, next to electricity
# SOFC/SOEC: requirements for the components / materials

<table>
<thead>
<tr>
<th></th>
<th>electrolyte</th>
<th>anode</th>
<th>cathode</th>
<th>interconnect</th>
<th>sealing</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>conductivity</strong></td>
<td>ionic</td>
<td>electronic</td>
<td>electronic</td>
<td>electronic</td>
<td>insulator</td>
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<tr>
<td></td>
<td>purely</td>
<td>additional ionic advantageous</td>
<td>additional ionic advantageous</td>
<td>purely</td>
<td></td>
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<tr>
<td><strong>thermal expansion</strong></td>
<td></td>
<td>adapted to electrolyte and interconnect</td>
<td>adapted to electrolyte and interconnect</td>
<td>adapted to electrolyte</td>
<td>adapted to electrolyte and interconnect</td>
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<tr>
<td><strong>thermo-chemical</strong></td>
<td>stable in oxidising and reducing atmospheres</td>
<td>stable in reducing atmospheres</td>
<td>stable in oxidising atmospheres</td>
<td>stable in oxidising and reducing atmospheres</td>
<td>stable in oxidising and reducing atmospheres</td>
</tr>
<tr>
<td></td>
<td>stable in contact with anode, cathode, sealing and interconnect</td>
<td>stable in contact with electrolyte and interconnect</td>
<td>stable in contact with electrolyte and interconnect</td>
<td>stable in contact with anode, cathode and sealing</td>
<td>stable in contact with electrolyte and interconnect</td>
</tr>
<tr>
<td><strong>micro-structure</strong></td>
<td>impermeable for hydrogen</td>
<td>porous open</td>
<td>porous open</td>
<td>impermeable for hydrogen</td>
<td>impermeable for hydrogen</td>
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</tbody>
</table>
SOFC/SOEC: materials, cells and stacks

- anode supported cells (ASC)
- operation < 800 °C
- w/ internal reforming of CH₄

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>Anode</th>
<th>Cathode</th>
</tr>
</thead>
<tbody>
<tr>
<td>yttria stabilized zirconia (YSZ)</td>
<td>Ni / YSZ cermet</td>
<td>(La,Sr)MnO₃ / YSZ</td>
</tr>
<tr>
<td>(La,Sr)(Co,Fe)O₃</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Fuel cell: electricity production

\[
\begin{align*}
\text{OXIDATION} & : \\
\text{anode} & : \text{H}_2(g) + O^{2-} \text{ (ad)} \rightarrow \text{H}_2\text{O}(g) + 2 e^- \\
\text{cathode} & : \text{O}_2(g) + 4 e^- \rightarrow 2 \text{O}^{2-} \text{ (ad)} \\
\text{REDUCTION} & : \\
\text{anode} & : \text{CO}(g) + O^{2-} \text{ (ad)} \rightarrow \text{CO}_2(g) + 2 e^- \\
\text{cathode} & : \\
\end{align*}
\]
SOFC/SOEC: anode substrate cells (ASCs)

w/ (La,Sr)(Co,Fe)O$_3$ (LSCF) cathode

- Cathode: LSCF
- Electrolyte: 8 mol% Y$_2$O$_3$ doped ZrO$_2$ (8YSZ)
- Anode: Ni / 8YSZ cermet
- Barrier: Gd$_2$O$_3$ doped CeO$_2$
- Substrate: 600...1000 µm

w/ (La,Sr)MnO$_3$ (LSM) cathode

- Cathode: LSM
- Electrolyte: LSM / 8YSZ
- Anode: Ni / 8YSZ cermet
- Substrate: 600...1000 µm

SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
SOFC/SOEC: materials, cells and stacks

- anode supported cells (ASC)
- operation < 800 °C
- w/ internal reforming of CH₄
- metallic interconnect
- glass-ceramic sealing

- electrolyte: yttria stabilized zirconia (YSZ)
- anode: Ni / YSZ cermet
- cathode: (La,Sr)MnO₃ / YSZ (La,Sr)(Co,Fe)O₃

Interconnect and cell frame
- sealing
- anode contact layer
- cathode contact layer

- Crofer 22 APU / ITM
  - (Ba,Ca,Al) silicate glass
  - Ni-mesh
  - (La,Sr)CoO₃

- anode substrate
- anode layer
- electrolyte layer (< 10 µm)
- cathode layer

- interconnect
- anode contact layer
- cathode contact layer
- cell frame
- sealing

- anode contact layer Ni-mesh
- cathode contact layer (La,Sr)CoO₃

- cell frame
- sealing
- interconnect
- anode contact layer
- cathode contact layer

- electrolyte
- anode
- cathode
degradation processes

- increase the resistance for the passage of the electrical current
- increase the over-potential for the electrochemical reactions
- causes for their occurrence can be
  - internal reactions within / interactions between stack components
  - external operation conditions (temperature, current, fuel gas / air quality, ...)

Interconnect
Anode contact layer
Cathode contact layer
Cell frame
Sealing
Current path
degradation processes

- can be caused by various parallel acting processes and therefore issues a highly convoluted problem

- de-convolution is complicated but necessary for their mitigation
The observations --- durability tests

Parallel acting degradation processes are usually on different time-scales. This leads to different time-dependent observations:

- Initial drop
- Quasi linear
- Progressive

Source: L.G.J. de Haart et al., Fuel Cells 9 (2009) 794 - 804
degreadation observations during durability tests

![Graph showing voltage vs. operation time for ASC with LSCF cathodes and LCC12 contact layer compared to ASC with LSM cathodes and LCC10 contact layer.](image)

- **F1002-132**: ASC with LSCF cathodes and LCC12 contact layer.
- **F1002-62**: ASC with LSM cathodes and LCC10 contact layer.

- **Conditions**:
  - Temperature: 800 °C
  - Gas mixture: H₂ / H₂O (10%)
  - Current density: 0.5 A/cm² / 40% utilisation
Degradation issue: Cr evaporation, cathode poisoning

Formation of volatile Cr species from oxide scale of interconnect

\[
\text{Cr}_2\text{O}_3 (s) + 2\text{H}_2\text{O}(g) + \frac{3}{2}\text{O}_2 (g) \rightarrow 2\text{CrO}_2(\text{OH})_2 (g)
\]

With LSM cathodes

Reaction at the LSM/YSZ interface

\[
2\text{CrO}_2(\text{OH})_2 (g) + 6 \text{e}^- \rightarrow \text{Cr}_2\text{O}_3 (s) + 2\text{H}_2\text{O}(g) + 3\text{O}^2- 
\]

- In competition with the oxygen reduction reaction
- Reaction with LSM to form (Mn,Cr) spinel phases

\[
\text{Cr}_2\text{O}_3 (s) + 2(\text{La},\text{Sr})\text{MnO}_3 \\
\rightarrow + \text{MnCr}_2\text{O}_4 (s) + (\text{La},\text{Sr})_2\text{MnO}_4 (s) + 2\text{O}_2 (g)
\]

L.G.J. (Bert) de Haart, JÜLICH  On Degradation Issues in High-Temperature Electrochemical Devices

**Degradation observations during durability tests**

- **Phase 1:** formation of $\text{Cr}_2\text{O}_3$ at triple phase boundary = loss of active cathode
- **Phase 2:** equilibrium between $\text{Cr}_2\text{O}_3$-formation and re-evaporation
- **Phase 3:** formation of CrMn-spinel by Mn removal from LSM; change in cathode parameters

---

Institute of Energy and Climate Research

source: D. Röhrens et al., Ceram. Int. 42 (2016) 9467-74
degradation observations during durability tests

ASC w/ LSCF cathodes and w/ LCC12 contact layer

ASC w/ LSM cathodes and w/ LCC10 contact layer

800 °C
H₂ / H₂O (10%)
0.5 A/cm² / 40% utilisation

(Mn,Cr) spinel phases

post-test examination of recovered LSM cells

SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
source: D. Röhrens et al., Ceram. Int. 42 (2016) 9467-74
degradation issue: Cr evaporation, cathode poisoning

formation of volatile Cr species

\[
\text{Cr}_2\text{O}_3 (s) + 2\text{H}_2\text{O}(g) + \frac{3}{2}\text{O}_2 (g) \rightarrow 2\text{CrO}_2(\text{OH})_2 (g)
\]

with LSCF cathodes

no reaction at the LSCF/YSZ interface

instead reaction at the LSCF / contact layer interface

\[
y\text{CrO}_\frac{y}{2}(\text{OH})_\frac{y}{2}(g) + \left( \text{La}_{1-x}\text{Sr}_x\right)_\frac{x}{2}(\text{Co,Fe})\text{O}_3 \rightarrow y\text{SrCrO}_y (s) + \left( \text{La}_{1-x}\text{Sr}_{x-y}\right)_\frac{x}{2}(\text{Co,Fe})\text{O}_{3-y} + y\text{H}_2\text{O}(g)
\]

= insulator

• no reaction sites at TPB blocked;

• 'merely' increased resistance of cathode contact layer

• 'quasi' linear degradation behaviour
degradation issue: Cr evaporation, cathode poisoning

ferritic steels with 0,4 % Mn limit Cr-evaporation by formation of (Cr,Mn) spinel

Cr-/Mn-spinel

Cr$_2$O$_3$

this Cr-evaporation can be further reduced by applying protective layers containing Mn

Fig. 5. BSE images of (a) Crofer 22 APU and (b) Crofer 22H after exposure in simulated anode gas, Ar-4%H$_2$-2%H$_2$O, for 1000 h at 800 °C.

degradation issue: Cr evaporation, cathode poisoning

- 2 layers w/ APS protective layer (Mn,Co,Fe)Ox
- 2 layers w/ WPS protective layer MnOx

APS: atmospheric plasma spraying
dense layer
WPS: wet powder spraying porous layer

visibly enhanced degradation rate for the layers with WPS protective coating compared to the ones with APS coating

source: N.H. Menzler et al.
degradation issue: Cr evaporation, cathode poisoning

APS coating on IC: 2.5-3 μg Cr/cm²

WPS coating on IC: 110-160 μg Cr/cm²

Differences:
APS: MCF dense
WPS: MnOₓ porous

No gas phase diffusion for CrO₂(OH)₂ and drastically minimized solid state diffusion through MCF layer!

source: N.H. Menzler et al.
degradation issue SOEC: Ni-transport in the fuel electrode

Hypothesis:
Ni transport via gaseous Ni(OH)$_x$ along the pH$_2$O gradient

degradation issue: Sulphur exposure on Ni-cermet based electrodes

Overpotential dependent degradation:
Low overpotential: reversible
High overpotential: irreversible

degradation issue: Manganese diffusion

constant current (0.5 A/cm²) operation @ 700 °C w/ H₂ + 20% H₂O (u_f = 40%) and air
average voltage degradation rate: 0.2 %/kh
total operation time: 34507 h  (4 years!)

SOFC-Stack F1004-21, test-No. SK430 Long term constant current operation @ 700°C
Fue

stack test graphs: U. de Haart, JÜLICH / IEK-3

cell #2 shows progressive degradation over the last 7000 hours of operation
degradation issue: Manganese diffusion

stack de-assembly and post-test analyses

- delamination of electrolyte+barrier+cathode from substrate (only for cell #2!)
- cracks in cathode contact layer

SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1

Cross-section at cell #2

cell

gas channel

contact layer

interconnect rib

Delamination of electrolyte + barrier + cathode from substrate (only for cell #2!)

Cracks in cathode contact layer

Stack autopsy: P. Batfalsky, JÜLICH / ZEA-1
degradation issue: Manganese diffusion

stack de-assembly and post-test analyses

- delamination of electrolyte+barrier+cathode from substrate (only for cell #2!)
- cracks in cathode contact layer

• secondary phase and pores at electrolyte grain boundaries
• electrolyte cracking along grain boundaries
• sponge-like secondary phase formation at electrolyte / anode delamination area

SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
degradation issue: Manganese diffusion

stack de-assembly and post-test analyses

- secondary phase and pores at electrolyte grain boundaries
- electrolyte cracking along grain boundaries
- sponge-like secondary phase formation at electrolyte / anode delamination area

SEM/EDX analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
degradation issue: Manganese diffusion

at start operation at EOL

Mn solid state diffusion (and possibly reduction) (across grain boundaries through dense layers)

dense porous

interconnect steel oxide scale on steel protection layer cathode contact cathode barrier electrolyte anode (+ substrate)

Fe, Cr, (Mn)

Cr$_2$O$_3$

(Cr,Mn)$_3$O$_4$

(Mn,Co,Fe)$_3$O$_4$

(La,Mn,Co,Cu)$_2$O$_4$

(La,Sr)(Co,Fe)O$_3$

(Ce,Gd)O$_2$

(Zr,Y)O$_2$

Ni + (Zr,Y)O$_2$

Mn delamination cracks sponge-like secondary phases

after N.H. Menzler, JÜLICH / IEK-1
degradation issue: Ni/YSZ cermet and re-oxidation

- oxidation remains problematic, because of the volume changes

\[
\text{NiO} \quad \xrightarrow{\text{reduction}} \quad \text{Ni} \quad \xrightarrow{\text{oxidation}} \quad \text{NiO}
\]

- volume change: -41% for reduction, +70% for oxidation

- depends on (strength of) the YSZ matrix how the cermet (substrate) is affected

bending of unconstrained cells at different re-oxidation temperatures;
degree of re-oxidation = 70%
degradation issue: Ni/YSZ cermet and re-oxidation

crack formation in the YSZ electrolyte layer after uncontrolled re-oxidation

possible alternative: doped SrTiO$_3$

*SEM analyses: J. Malzbender. JÜLICH / IEK-2
Degradation phenomena: nano structured Sr-Ti based anodes

Strong Metal-Support interaction (SMSI)?
The unique resistance of Ru to sintering is assigned to a special epitaxial orientation Ru (0 0 2) CeO$_2$ (1 1 1)

Separation of
Electrochemical activity
Electronic conductivity + gas transport

Allows for multiple materials combinations
Single cells test 16 cm$^2$
Constant current

source: M. Kurnatowska et al. / Applied Catalysis B: Environmental 148–149 (2014) 123–135
Degradation hypothesis: Surface reconstructions in Ni/CGO infiltrated nano structures?

Infiltrate agglomeration occurring during the first operation of the anode

Remains apparently unchanged during further operation

CGO surface reconstruction?

→ less active surface in H₂

→ reduced facetting

→ affected by NiO skin on Ni?
Degradation test: micro CHP load profile on Sr-Ti based anodes

SOFC cells
LSCT/Ru-CGO infiltrated anode, ScSZ electrolyte and LSM cathode tested in reformed pipeline natural gas w/o de-sulphurizer

Electrode micro-structure after 1400 h operation
# Summary

<table>
<thead>
<tr>
<th>Component</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interconnect steel</td>
<td>Formation of an austenitic phase</td>
</tr>
<tr>
<td>Oxide scale on steel</td>
<td>Chromium(-oxy-hydroxide) evaporation</td>
</tr>
<tr>
<td>Protection layer</td>
<td>Manganese solid state diffusion</td>
</tr>
<tr>
<td>Cathode contact</td>
<td>Strontium(-oxide) segregation</td>
</tr>
<tr>
<td>Cathode</td>
<td>Nickel(-hydroxide) evaporation</td>
</tr>
<tr>
<td>Barrier</td>
<td>Nickel agglomeration</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Cracking, secondary phases, decomposition, delamination</td>
</tr>
<tr>
<td>Anode (+ substrate)</td>
<td></td>
</tr>
<tr>
<td>Dense</td>
<td></td>
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<tr>
<td>Porous</td>
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<table>
<thead>
<tr>
<th>Layer</th>
<th>Material Type</th>
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<tbody>
<tr>
<td>Fe, Cr(Mn)</td>
<td>Cr$_2$O$_3$</td>
</tr>
<tr>
<td></td>
<td>(Cr,Mn)$_3$O$_4$</td>
</tr>
<tr>
<td>Oxide scale on steel</td>
<td>(Mn,Co,Fe)$_3$O$_4$</td>
</tr>
<tr>
<td>Protection layer</td>
<td>(La,Mn,Co,Cu)$_2$O</td>
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<tr>
<td>Cathode contact</td>
<td>(La,Sr)(Co,Fe)O$_3$</td>
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<tr>
<td>Cathode</td>
<td>(Ce,Gd)O$_2$</td>
</tr>
<tr>
<td>Barrier</td>
<td>(Zr,Y)O$_2$</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Ni + (Zr,Y)O$_2$</td>
</tr>
</tbody>
</table>

**Formulas and Terms:**
- Chromium(-oxy-hydroxide)
- Manganese solid state diffusion
- Strontium(-oxide) segregation
- Nickel(-hydroxide) evaporation
- Nickel agglomeration
- Cracking, secondary phases, decomposition, delamination
- Formation of an austenitic phase
- Interdiffusion

**Materials:**
- Fe, Cr(Mn)
- Cr$_2$O$_3$
- (Cr,Mn)$_3$O$_4$
- (Mn,Co,Fe)$_3$O$_4$
- (La,Mn,Co,Cu)$_2$O
- (La,Sr)(Co,Fe)O$_3$
- (Ce,Gd)O$_2$
- (Zr,Y)O$_2$
- Ni + (Zr,Y)O$_2$
outlook

World Record SOFC

1. Milestone on 26.09.2008
10,000 h Continuous operation

2. Milestone on 23.08.2012
40,000 h Continuous operation

3. Milestone on 10.10.2015
70,000 h Continuous operation

Voltage behaviour

Facts
- 2-layer short stack
- WP5-protective layer
- Glass-ceramic spacers
- LSCF with SP 000
- IT11 (Plansee)
- wet/wet shunt

Operational data
- 100 mV
- 0.6 A/cm²
- H₂, 4.0% H₂O
- uF = 40 kΩ

Autumn 2010
"We have to stop a comparable test - we hope the long running test survives..."

The SOFC success story
- GG Power Blocks
- ASO Short Shocks
- LW Lightweight Design Shocks
- D2D Stacked Piles
- 2D Keynote & invited talks
- 277 Conference Presentations
- 278 Proceedings Papers
- 94 Poster

Spring 2012
"Degradation has slowed down - we have a good chance to get the world record..."

Produced electrical energy
During the 70,000 h
3,400 kWh
**outlook**

- **Operating time / year**

<table>
<thead>
<tr>
<th>Operating time / kh</th>
<th>Average cell voltage / V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>1.0</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
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<td>4</td>
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<tr>
<td>6</td>
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<tr>
<td>8</td>
<td>0.2</td>
</tr>
<tr>
<td>10</td>
<td>0.0</td>
</tr>
</tbody>
</table>

**Operating Conditions:**
- **700 °C**
- **0.5 A/cm²**
- **H₂ + 20% H₂O; u_F = 40%**

**Coatings:**
- **APS protective coating** on Crofer 22 APU (TK)
- **WPS protective coating** on ITM (Plansee)

**Performance Summary:**

- **In operation for nearly 80,000 h (9 years)**
- **Mean degradation rate less than 0.6 %/kh**
the authors would like to thank all co-workers at JÜLICH and DTU Energy (formerly Risø) for all efforts over the past years

financial support from various sources is greatly acknowledged
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thank you for your attention

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Forschungszentrum Jülich
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