On Degradation Issues in High-Temperature Electrochemical Devices

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On Degradation Issues in High-Temperature Electrochemical Devices

JP Fuel Cells and Hydrogen

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Fundamental Electrochemistry (IEK-9)
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)

```
O2 + 4e^- → 2O2^- (ad)
H2O + 2e^- → H2 + O2^- (ad)
```

fuel cell: electricity production

```
H2 + O2^- (ad) → H2O + 2e^- 
O2 + 4e^- → 2O2^- (ad)
```

Electrolysis: The reaction at the cathode is the reduction of oxygen to form water, while at the anode, water is oxidized to form oxygen and electrons.

Fuel cell: The reaction at the anode is the oxidation of hydrogen to form water and electrons, while at the cathode, oxygen is reduced to form water and electrons.
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 purely</td>
<td>Electronic additional ionic advantageous</td>
<td>Electronic additional ionic advantageous</td>
<td>Electronic purely</td>
<td>Insulator</td>
</tr>
<tr>
<td><strong>Thermal Expansion</strong></td>
<td>Adapted to electrolyte and interconnect</td>
<td>Adapted to electrolyte and interconnect</td>
<td>Adapted to electrolyte and electrolyte</td>
<td>Adapted to electrolyte and electrolyte</td>
<td>Adapted to electrolyte and interconnect</td>
</tr>
<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>Microstructure</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>
</tr>
</tbody>
</table>
SOFC/SOEC: materials, cells and stacks

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

![Diagram of SOFC/SOEC components]

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

**Fuel cell: electricity production**

- **Oxidation**
  - H₂(g) + O²⁻ (ad) → H₂O(g) + 2 e⁻
  - O₂(g) + 4 e⁻ → 2 O²⁻ (ad)

- **Reduction**
  - CO(g) + O²⁻ (ad) → CO₂(g) + 2 e⁻
SOFC/SOEC: anode substrate cells (ASCs)

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

- 50 µm cathode
- 7 µm LSCF
- 600...1000 µm substrate
- 8 mol% Y$_2$O$_3$ doped ZrO$_2$ (8YSZ) electrolyte
- Ni / 8YSZ cermet anode
- Gd$_2$O$_3$ doped CeO$_2$ barrier
to prevent formation of SrZrO$_3$

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

- 60 µm cathode current collector
- 15 µm LSM
- 600...1000 µm substrate
- Ni / 8YSZ cermet (ceramic metal)
- Gd$_2$O$_3$ doped CeO$_2$ barrier
to prevent formation of SrZrO$_3$

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

<table>
<thead>
<tr>
<th>Component</th>
<th>Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolyte</td>
<td>Yttria stabilized zirconia (YSZ)</td>
</tr>
<tr>
<td>Anode</td>
<td>Ni / YSZ cermet</td>
</tr>
<tr>
<td>Cathode</td>
<td>(La,Sr)MnO₃ / YSZ</td>
</tr>
<tr>
<td>(La,Sr)(Co,Fe)O₃</td>
<td></td>
</tr>
<tr>
<td>Anode substrate</td>
<td></td>
</tr>
<tr>
<td>Anode layer</td>
<td></td>
</tr>
<tr>
<td>Electrolyte layer (&lt; 10 µm)</td>
<td></td>
</tr>
<tr>
<td>Cathode layer</td>
<td></td>
</tr>
<tr>
<td>Interconnect</td>
<td>Crofer 22 APU / ITM</td>
</tr>
<tr>
<td>Anode contact layer</td>
<td>(Ba, Ca, Al) silicate glass</td>
</tr>
<tr>
<td>Cathode contact layer</td>
<td>Ni-mesh</td>
</tr>
<tr>
<td>Cell frame</td>
<td>(La,Sr)CoO₃</td>
</tr>
</tbody>
</table>
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, ...).

Diagram showing the current path through various components such as interconnect, anode contact layer, cathode contact layer, cell frame, and sealing.
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
degradation observations during durability tests

![Graph showing voltage vs. operation time for different cathode materials and contact layers.]

**F1002-132**
- ASC w/ LSCF cathodes and w/ LCC12 contact layer

**F1002-62**
- ASC w/ LSM cathodes and w/ LCC10 contact layer

Conditions:
- 800 °C
- H₂ / H₂O (10%)
- 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

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

Blocking reaction sites and changing the microstructure of the triple phase boundary region

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

![Graph showing degradation observations](image)

- **ASC w/ LSCF cathodes** and w/ LCC12 contact layer
- **ASC w/ LSM cathodes** and w/ LCC10 contact layer

**Conditions:**
- Temperature: 800 °C
- Gas: H$_2$ / H$_2$O (10%)
- Current density: 0.5 A/cm$^2$
- Utilisation: 40%

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

post-test examination of recovered LSM cells

(Mn,Cr) spinel phases

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{3}{2}}\text{OH}_2(g) + (\text{La}_{1-x}\text{Sr}_x \)_{Co,Fe})_O_3
\rightarrow y\text{SrCrO}_{\frac{3}{2}}(s) + (\text{La}_{1-x}\text{Sr}_{x-y} \)_{Co,Fe})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

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%H₂-2%H₂O, 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
WPS: wet powder spraying

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

APoS 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.
Hypothesis:
Ni transport via gaseous Ni(OH)$_x$ along the p(H$_2$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!)

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

cross-section at cell #2

- 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

stack autopsy: P. Batfalsky, JÜLICH / ZEA-1

L.G.J. (Bert) de Haart, JÜLICH
P. Holtappels, DTU Energy

On Degradation Issues in High-Temperature Electrochemical Devices
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
degradation issue: Manganese diffusion

at start → operation → at EOL

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

Fe, Cr(,Mn)
Cr₂O₃
(Cr,Mn)₃O₄
(Mn,Co,Fe)₃O₄
(La,Mn,Co,Cu)₂O₃
(La,Sr)(Co,Fe)O₃
(Ce,Gd)O₂
(Zr,Y)O₂
Ni + (Zr,Y)O₂

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

Mn at grain boundaries
sponge-like secondary phases
delamination
Cracks

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

- oxidation remains problematic, because of the volume changes

  ![Diagram of NiO reduction and oxidation with volume changes](image)

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

  ![Images of bending cells at different re-oxidation temperatures](image)

  - 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 SrTiO₃

*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)

source: M. Kurnatowska et al. / Applied Catalysis B: Environmental 148–149 (2014) 123–135

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?

SYT (FZJ)
Infiltrate agglomeration occurring during the first operation of the anode
Remains apparently unchanged during further operation

STN94
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
interconnect steel
oxide scale on steel
protection layer
cathode contact
cathode
barrier
electrolyte
anode (+ substrate)
dense
porous

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$_2$

formation of an austenitic phase
Chromium(-oxy-hydroxide) evaporation
Manganese solid state diffusion
Strontium(-oxide) segregation
Nickel(-hydroxide) evaporation
Nickel agglomeration

cracking
secondary phases
decomposition
delamination
interdiffusion
outlook

World Record SOFC

Autumn 2016

“We have to stop a comparable test – we hope the long running test survives...”

The SOFC success story

55 Power Blocks
189 Short Stacks
64 Light Weight Design Stacks
95 Granted Patents
110 Keynotes & Invited Talks
277 Reviewed Papers
429 Conference Presentations
267 Proceedings Papers
19 Poster

Spring 2012

“Degradation has slowed down – we have a good chance to get the world record...”

EERA Conference 2016
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L.G.J. (Bert) de Haart, JÜLICH
P. Holtappels, DTU Energy

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outlook

- 4 layer short-stack APS protective coating on Crofer 22 APU (TK)
- 2 layer short-stack WPS protective coating on ITM (Plansee)

in operation for nearly 80,000 h (9 years)
mean degradation rate less than 0.6 %/kh

Operating time / year

700 °C
0.5 A/cm²
H₂ + 20% H₂O; uᵣ = 40%

Operating time / kh

Average cell voltage / V
acknowledgements

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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