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

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Fundamental Electrochemistry (IEK-9)
outline

- 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

\[
\begin{align*}
2 \text{O}_2^- \text{(ad)} & \rightarrow \text{O}_2(\text{g}) + 4 \text{e}^- \\
\text{H}_2\text{O}(\text{g}) + 2 \text{e}^- & \rightarrow \text{H}_2(\text{g}) + \text{O}_2^- \text{(ad)} \\
\text{CO}_2(\text{g}) + 2 \text{e}^- & \rightarrow \text{CO}(\text{g}) + \text{O}_2^- \text{(ad)}
\end{align*}
\]
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 CH\textsubscript{4}) 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>
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<tr>
<td><strong>thermal expansion</strong></td>
<td>adapted to electrolyte and interconnect</td>
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<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>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>
</tr>
</tbody>
</table>
SOFC/SOEC: materials, cells and stacks

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

Electrolyte: yttria stabilized zirconia (YSZ)
Anode: Ni / YSZ cermet
Cathode: (La,Sr)MnO₃ / YSZ (La,Sr)(Co,Fe)O₃

*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)O₃ (LSCF) cathode

- Cathode LSCF
- Barrier Gd₂O₃ doped CeO₂
- Electrolyte 8 mol% Y₂O₃ doped ZrO₂ (8YSZ)
- Anode Ni / 8YSZ cermet

w/ (La,Sr)MnO₃ (LSM) cathode

- Cathode current collector LSM
- Electrolyte LSM / 8YSZ
- Anode Ni / 8YSZ cermet
- Substrate

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

![Diagram of SOFC/SOEC cell](image)

 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
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
  • external
  reactions within / interactions between stack components
  operation conditions
  (temperature, current, fuel gas / air quality, …)
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

- current path
- interconnect
- anode contact layer
- cathode contact layer
- cell frame
- sealing
degradation observations during durability tests

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

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

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

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

degradation observations during durability tests

Phase 1:
formation of Cr$_2$O$_3$ at triple phase boundary = loss of active cathode

Phase 2:
equilibrium between Cr$_2$O$_3$-formation and re-evaporation

Phase 3:
formation of CrMn-spinel by Mn removal from LSM; change in cathode parameters

ASC w/ LSCF cathodes and w/ LCC12 contact layer

ASC w/ LSM cathodes and w/ LCC10 contact layer

800 °C
H$_2$ / H$_2$O (10%)
0.5 A/cm$^2$ / 40% utilisation

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**

**Operation Time / h**

- **Voltage / V**
  - 0.0
  - 1.2
  - 1.4
  - 1.6
  - 1.8

**Operation Conditions**

- **Temperature**: 800 °C
- **Fuel**: H₂ / H₂O (10%)
- **Current Density**: 0.5 A/cm² / 40% utilisation

**Post-Test Examination**

- SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
- Source: D. Röhrens et al., Ceram. Int. 42 (2016) 9467-74

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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

\[
y\text{CrO}_\frac{3}{2} \text{(OH)}_\frac{1}{2} (g) \rightarrow y\text{SrCrO}_\frac{4}{3} (s) \rightarrow y\text{SrCrO}_\frac{4}{3} (s) (\text{La}_{1-x}\text{Sr}_x \downarrow \text{Co},\text{Fe})\text{O}_3\]

\[
\rightarrow y\text{SrCrO}_\frac{4}{3} (s) + (\text{La}_{1-x}\text{Sr}_{x-y} \downarrow \text{Co},\text{Fe})\text{O}_{3-y} + y\text{H}_2\text{O} (g)
\]

= insulator

- no reaction sites at TPB blocked;
- 'merely' increased resistance of cathode contact layer
- 'quasi' linear degradation behaviour

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


formation of volatile Cr species

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

interconnect

Anode

Fuel

Air

Electrolyte

Cathode

vapour transport
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 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 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

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

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
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- secondary phase and pores at electrolyte grain boundaries
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SEM/EDX analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
degradation issue: Manganese diffusion

at start \(\rightarrow\) operation \(\rightarrow\) at EOL

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

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\(_4\)
(La,Sr)(Co,Fe)O\(_3\)
(Ce,Gd)O\(_2\)
(Zr,Y)O\(_2\)
Ni + (Zr,Y)O\(_2\)

Mn at grain boundaries
sponge-like secondary phases
delamination
cracks

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

- oxidation remains problematic, because of the volume changes

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

volume change
-41%

volume change
+70%

- 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%

[Images of bending cells at 700 °C and 800 °C]
degradation issue: Ni/YSZ cermet and re-oxidation

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

*SEM analyses: J. Malzbender. JÜLICH / IEK-2

possible alternative: doped SrTiO$_3$
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) CeO₂ (1 1 1)

- Separation of Electrochemical activity
  - Electronic conductivity + gas transport

- Allows for multiple materials combinations

- Single cells test 16 cm²
  - 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>Layer/Phase</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe, Cr, (Mn)</td>
<td>Chromium(-oxy-hydroxide) evaporation</td>
</tr>
<tr>
<td>Cr₂O₃ (Cr,Mn)₃O₄</td>
<td>Chromium(-oxy-hydroxide) evaporation</td>
</tr>
<tr>
<td>(Mn,Co,Fe)₃O₄</td>
<td>Chromium(-oxy-hydroxide) evaporation</td>
</tr>
<tr>
<td>(La,Mn,Co,Cu)₂O</td>
<td>Strontium(-oxide) segregation</td>
</tr>
<tr>
<td>(La,Sr)(Co,Fe)O₃</td>
<td>Strontium(-oxide) segregation</td>
</tr>
<tr>
<td>(Ce,Gd)O₂</td>
<td>Strontium(-oxide) segregation</td>
</tr>
<tr>
<td>(Zr,Y)O₂</td>
<td>Strontium(-oxide) segregation</td>
</tr>
<tr>
<td>Ni + (Zr,Y)O₂</td>
<td>Nickel(-hydroxide) evaporation</td>
</tr>
<tr>
<td>Ni + (Zr,Y)O₂</td>
<td>Nickel agglomeration</td>
</tr>
</tbody>
</table>

**Cracking**
- Secondary phases decomposition delamination

**Formation of an Austenitic Phase**
- Interdiffusion
- Manganese solid state diffusion
- Nickel(-hydroxide) evaporation
- Nickel agglomeration

**Formation of Secondary Phases**
- Decomposition delamination
- Interdiffusion
outlook

**World Record SOFC**

- **Start:** 6.8.2007
- **Continuous operation:**
  - **10,000 h**
- **Facts:**
  - 2-layer short stack
  - WP3-protective layer
  - Glass-ceramic sealant
  - LSCF with SP 000
  - IT 11 (Plansee)
  - Water electrolysis

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

- **The SOFC success story**
  - 55 Power Blocks
  - 183 Short Stacks
  - 64 Lightweight Design Stacks
  - 95 Granted Patents
  - 120 Keynote & Invited Talks
  - 277 Reviewed Papers
  - 420 Conference Presentations
  - 267 Proceedings Papers
  - 94 Poster

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

- **Voltage behaviour**

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

- **Milestone on 26.09.2008**
  - **10,000 h**
  - Continuous operation

- **World record on 23.08.2012**
  - 40,000 h
  - Continuous operation

- **World record all SOFC:**
  - 70,000 h
  - Continuous operation
in operation for nearly 80,000 h (9 years)
mean degradation rate less than 0.6 %/kh

4 layer short-stack
APS protective coating on Crofer 22 APU (TK)

2 layer short-stack
WPS protective coating on ITM (Plansee)

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

APS – atmospheric plasma spraying
WPS – wet powder spraying
acknowledgements

the authors would like to thank all co-workers at JÜLICH and DTU Energy (formerly Risø) for all efforts over the past years

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thank you for your attention

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