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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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)**

\[
\begin{align*}
2 \text{O}_2^{2-} \text{(ad)} & \rightarrow \text{O}_2\text{(g)} + 4 \text{e}^- \\
\text{H}_2\text{O}(\text{g}) + 2 \text{e}^- & \rightarrow \text{H}_2\text{(g)} + \text{O}_2^{2-} \text{(ad)} \\
\text{CO}_2\text{(g)} + 2 \text{e}^- & \rightarrow \text{CO}\text{(g)} + \text{O}_2^{2-} \text{(ad)}
\end{align*}
\]

**Fuel Cell: Electricity Production**

\[
\begin{align*}
\text{CO}(\text{g}) + \text{O}_2^{2-} \text{(ad)} & \rightarrow \text{CO}_2\text{(g)} + 2 \text{e}^- \\
\text{H}_2\text{(g)} + \text{O}_2^{2-} \text{(ad)} & \rightarrow \text{H}_2\text{O}(\text{g}) + 2 \text{e}^- \\
\text{O}_2(\text{g}) + 4 \text{e}^- & \rightarrow 2 \text{O}_2^{2-} \text{(ad)}
\end{align*}
\]
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
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<th>cathode</th>
<th>interconnect</th>
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<td>impermeable for hydrogen</td>
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**SOFC/SOEC: requirements for the components / materials**
SOFC/SOEC: materials, cells and stacks

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

**Electrolyte Layer (< 10 µm)**

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

**Diagram:**
- 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)O₃ (LSCF) cathode

- Cathode: LSCF
- Gd₂O₃ doped CeO₂ barrier
- 8 mol% Y₂O₃ doped ZrO₂ (8YSZ) electrolyte
- Ni / 8YSZ cermet anode
- Ni / 8YSZ cermet substrate

w/ (La,Sr)MnO₃ (LSM) cathode

- Cathode current collector: LSM
- LSM / 8YSZ cathode
- Gd₂O₃ doped CeO₂ barrier
- 8 mol% Y₂O₃ doped ZrO₂ (8YSZ) electrolyte
- Ni / 8YSZ cermet 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 CH$_4$
- metallic interconnect
- glass-ceramic sealing

- electrolyte: yttria stabilized zirconia (YSZ)
- anode: Ni / YSZ cermet
- cathode: (La,Sr)MnO$_3$ / YSZ
- (La,Sr)(Co,Fe)O$_3$

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

- metal interconnect
- glass-ceramic sealing
- anode support cells

- (Ba,Ca,Al) silicate glass
- Ni-mesh
- (La,Sr)CoO$_3$
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 current path through a stack with 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:
- initial drop
- quasi linear
- progressive

These lead to different time-dependent observations:

- Type A: linear 'progressive'
- Type B: linear 'progressive'
- Type C: 'initial drop'
- Type D: 'initial drop'

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

![Graph showing degradation observations during durability tests.](image)

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

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

- Operation time: 0 to 4000 hours
- Voltage: 0.0 to 1.8 V
- Temperature: 800 °C
- Atmosphere: 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

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

blocking reaction sites and changing the micro-structure 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

**Graph Details:**
- Voltage / V:
  - F1002-132: ASC w/ LSCF cathodes and w/ LCC12 contact layer
  - F1002-62: ASC w/ LSM cathodes and w/ LCC10 contact layer
- Operation time / h:
  - 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

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

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

= 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

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.
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 image>

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

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

- 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

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

dense
porous

Fe, Cr(,Mn)
Cr₂O₃
(Cr,Mn)₃O₄
(Mn,Co,Fe)₃O₄
(La,Mn,Co,Cu)₅O₇
(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)

delamination
sponge-like secondary phases

Mn at grain boundaries

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

- oxidation remains problematic, because of the volume changes

- 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%

700 °C

800 °C
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) 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 H$_2$

→ 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

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

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

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

dense
porous

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
World Record SOFC

Outlook

Start 6.8.2007
Continuous operation

1. Milestone on 26.09.2008
10,000 h
Continuous operation

Facts
- 2-layer short stack
- WP2-protective layer
- Glass-ceramic interlayer
- LSCF with SP 000
- ITI (Plansee)
- Water balance

Operations data
- 800 °C
- 0.5 A/cm²
- H₂ + 2.0% H₂O
- u₁ = 406

Autumn 2010
“We have to stop a comparable test — we hope the long-running test survives…”

The SOFC success story
- 55 Power Blocks
- 186 Short Stacks
- 64 Light Weight Design Stacks
- 95 Granted Patents
- 103 Keynote & Invited Talks
- 277 Reviewed Papers
- 428 Conference Presentations
- 267 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

Average cell voltage / V

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

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

Peter Holtappels
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