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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EERA Conference 2016
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Birmingham, UK
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)

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

fuel cell: electricity production

\[
\text{H}_2 \text{(g)} + \text{O}^2- \text{(ad)} \rightarrow \text{H}_2\text{O} \text{(g)} + 2 \text{e}^- \\
\text{O}_2 \text{(g)} + 4 \text{e}^- \rightarrow 2 \text{O}^2- \text{(ad)} \\
\text{CO} \text{(g)} + \text{O}^2- \text{(ad)} \rightarrow \text{CO}_2 \text{(g)} + 2 \text{e}^- 
\]
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>
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<th>electrolyte</th>
<th>anode</th>
<th>cathode</th>
<th>interconnect</th>
<th>sealing</th>
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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  
- (La,Sr)MnO₃ / YSZ  
- (La,Sr)(Co,Fe)O₃

**cathode**  
- (La,Sr)MnO₃ / YSZ

**fuel cell: electricity production**

\[
	ext{O}_2 (g) + 4 \text{e}^- \rightarrow 2 \text{O}_2^{-} (ad)
\]

\[
\text{H}_2(g) + \text{O}_2^{-} (ad) \rightarrow \text{H}_2\text{O}(g) + 2 \text{e}^- 
\]

\[
\text{H}_2(g) + \text{O}_2^{-} (ad) \rightarrow \text{H}_2\text{O}(g) + 2 \text{e}^- 
\]

\[
\text{CO}(g) + \text{O}_2^{-} (ad) \rightarrow \text{CO}_2(g) + 2 \text{e}^- 
\]

\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + \text{O}_2^{-} (ad)
\]

\[
\text{CO}_2 \rightarrow \text{CO} + \text{O}_2^{-} (ad)
\]
SOFC/SOEC: anode substrate cells (ASCs)

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

- 50 µm
- 7 µm
- 6...10 µm
- 7...10 µm
- 600...1000 µm

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

- Ni / 8YSZ cermet
- Gd$_2$O$_3$ doped CeO$_2$
- LSM / 8YSZ
- 8 mol% Y$_2$O$_3$ doped ZrO$_2$ (8YSZ)
- (La,Sr)(Co,Fe)O$_3$ (LSCF) cathode

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:**
- anode substrate
- anode layer
- electrolyte layer (< 10 µm)
- cathode layer
- interconnect
- anode contact layer
- cathode contact layer
- cell frame
- sealing

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

**Interconnect and Cell Frame Materials:**
- 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 reactions within / interactions between stack components
- external operation conditions (temperature, current, fuel gas / air quality, ...)

Current path

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

![Graph showing the performance of different fuel cell types](image)

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

![Graph showing voltage vs. operation time for ASC with different cathodes and contact layers.]

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

**Operating 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

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

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

degradation observations during durability tests

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

**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:**
- **ASC with LSCF cathodes and LCC12 contact layer**
- **ASC with LSM cathodes and LCC10 contact layer**

**Conditions:**
- 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

Operation time / h vs. Voltage / V graph showing:
- ASC w/ LSCF cathodes and w/ LCC12 contact layer
- ASC w/ LSM cathodes and w/ LCC10 contact layer

Post-test examination of recovered LSM cells.

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

(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

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On Degradation Issues in High-Temperature Electrochemical Devices
degradation issue: Cr evaporation, cathode poisoning

formation of volatile Cr species

\[
Cr_2O_3(s) + 2H_2O(g) + \frac{3}{2}O_2(g) \rightarrow 2CrO_2(OH)_2(g)
\]

with LSCF cathodes

no reaction at the LSCF/YSZ interface

instead reaction at the LSCF / contact layer interface

\[
yCrO_{\frac{y}{2}OH}(g) + (La_{1-x}Sr_x)(Co,Fe)O_3 \rightarrow ySrCrO_{\frac{y}{2}s}(g) + (La_{1-x}Sr_{x-y})(Co,Fe)O_{3-y} + yH_2O(g)
\]

= 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 $p(H_2O)$ 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

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

stack de-assembly and post-test analyses

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
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

- 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

- 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)

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

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

Mn at grain boundaries
sponge-like secondary phases
delamination

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
Probe Nr. 2459-3-2

800 °C
Probe Nr. 2459-3-1
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?

STN94

SYT (FZJ)

FZJ / IEK1 2013
EHT = 15.00 kV Detector = InLens WD = 6 mm

FZJ / IEK1 2013
EHT = 15.00 kV Detector = InLens WD = 6 mm
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
L.G.J. (Bert) de Haart, JÜLICH  On Degradation Issues in High-Temperature Electrochemical Devices

**summary**

- **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**
- formation of an austenitic phase
- 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$_2$
World Record SOFC

Outlook

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 Stack
- 64 Lightweight Design Stacks
- 95 Granted Patents
- 121 Keywords & Invited Talks
- 177 Review Papers
- 429 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

Facts
- 2-layer short stack
- WP2 protective layer
- Glass-ceramic spacer
- LSCF with SP 000
- IT1 (Plansee)
- Water electrolysis

Operation data
- 1000°C
- 0.5 A/cm²
- H₂ + 0.5H₂O
- uₐ = 4006

1. Milestone on 26.09.2008
10,000 h
Continuous operation

1. World record on 23.02.2012
40,000 h
Continuous operation

15.10.2015
World record all SOFC: 70,000 h
Continuous operation

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In operation for nearly 80,000 h (9 years)

Mean degradation rate less than 0.6 %/kh

Operating time / year

Average cell voltage / V

Operating time / 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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