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)**

- **oxidation**
  - $2 \text{O}_2^\text{- (ad)} \rightarrow \text{O}_2(g) + 4 \text{e}^-$
- **reduction**
  - $\text{H}_2\text{O}(g) + 2 \text{e}^- \rightarrow \text{H}_2(g) + \text{O}_2^\text{- (ad)}$
  - $\text{CO}_2(g) + 2 \text{e}^- \rightarrow \text{CO}(g) + \text{O}_2^\text{- (ad)}$

**fuel cell: electricity production**

- **oxidation**
  - $\text{H}_2(g) + \text{O}_2^\text{- (ad)} \rightarrow \text{H}_2\text{O}(g) + 2 \text{e}^-$
  - $\text{CO}(g) + \text{O}_2^\text{- (ad)} \rightarrow \text{CO}_2(g) + 2 \text{e}^-$
- **reduction**
  - $\text{CO}(g) + 2 \text{e}^- \rightarrow \text{CO}_2(g) + 4 \text{e}^-$
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>
<thead>
<tr>
<th></th>
<th>electrolyte</th>
<th>anode</th>
<th>cathode</th>
<th>interconnect</th>
<th>sealing</th>
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</thead>
<tbody>
<tr>
<td><strong>conductivity</strong></td>
<td>ionic</td>
<td>electronic</td>
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<td>electronic</td>
<td>insulator</td>
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<td>purely</td>
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<td><strong>thermal expansion</strong></td>
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<td>adapted to electrolyte and interconnect</td>
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<td>adapted to electrolyte</td>
<td>adapted to electrolyte and interconnect</td>
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<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
(La,Sr)MnO₃ / YSZ
(La,Sr)(Co,Fe)O₃

**Cathode**
(La,Sr)(Co,Fe)O₃

**Fuel cell: electricity production**

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

**Anode**

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
- 8 mol% Y₂O₃ doped ZrO₂ (8YSZ) electrolyte
- Ni / 8YSZ cermet anode
- substrate

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

w/ (La, Sr)MnO₃ (LSM) cathode

- LSM cathode current collector
- LSM / 8YSZ electrolyte
- Ni / 8YSZ cermet anode
- substrate

60 µm
15 µm
6...10 µm
7...10 µm
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
- (La,Sr)MnO₃ / YSZ
- (La,Sr)(Co,Fe)O₃

**Cathode**
- (La,Sr)CoO₃

**Interconnect and cell frame**
- sealing
- (Ba,Ca,Al) silicate glass
- Ni-mesh
- (La,Sr)CoO₃

**Cell frame**
- Crofer 22 APU / ITM
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, ...)

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
Degradation observations during durability tests

The observations --- durability tests

- Initial drop
- Quasi linear
- Progressive

Parallel acting degradation processes are usually on different time-scales:

- Initial drop
- Quasi linear
- Progressive

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

Supported by the European Commission under the 6th Framework Programme
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
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

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

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 $\text{CrMn}$-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
$\text{H}_2 / \text{H}_2\text{O}$ (10%)
0.5 A/cm² / 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

source: D. Röhrens et al., Ceram. Int. 42 (2016) 9467-74

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

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On Degradation Issues in
High-Temperature Electrochemical Devices
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

\[ y\text{CrO}_\frac{y}{2}(\text{OH})_\frac{y}{2} (g) + (\text{La}_{1-x}\text{Sr}_x \|\text{Co,Fe})\text{O}_3 \]

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

= Insulator

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

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

Crofer 22 APU


Crofer 22 H

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.

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

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

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

- oxidation remains problematic, because of the volume changes

  - single particle
  - reduction
  - NiO \rightarrow \text{Ni}
  - volume change \(-41\%\)
  - oxidation
  - Ni \rightarrow \text{NiO}
  - 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%
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)

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 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?

**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
**summary**

- **Interconnect steel**: Fe, Cr(Mn)
- **Oxide scale on steel**: Cr$_2$O$_3$, (Cr,Mn)$_3$O$_4$
- **Protection layer**: (Mn,Co,Fe)$_3$O$_4$
- **Cathode contact**: (La,Mn,Co,Cu)$_2$O
- **Cathode**: (La,Sr)(Co,Fe)$_3$O$_3$
- **Barrier**: (Ce,Gd)O$_2$
- **Electrolyte**: (Zr,Y)O$_2$
- **Anode (+ substrate)**: Ni + (Zr,Y)O$_2$

**Processes**

- **Cracking**
- **Secondary phases**
- **Decomposition**
- **Interdiffusion**

**Formation of an austenitic phase**

- Chromium(-oxy-hydroxide) evaporation
- Manganese solid state diffusion
- Strontium(-oxide) segregation
- Nickel(-hydroxide) evaporation
  - Nickel agglomeration
outlook

World Record SOFC

1. Milestone on 26.09.2008
10,000 h
Continuous operation

Facts
- 2 layer short stack
- WPS-protective layer
- Glass-ceramic sealant
- LSCF with SP 000
- ITI (Plansee)
- wettow alkane

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

The SOFC success story
- 55 Power Blocks
- 148 Short Stack
- 64 Light Weight Design Stacks
- 95 Granted Patents
- 101 Keynote & invited Talks
- 277 Reviewed Papers
- 420 Conference Presentations
- 267 Proceedings Papers
- 34 Poster

Spring 2012
“Degradation has slowed down – we have a good chance to get the world record…”

Start 6.8.2007
Start of operation

1. World record on 29.02.2012
in case of planar SOFC stacks
40,000 h
Continuous operation

10.10.2016
World record all SOFC: 70,000 h
Continuous operation

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

Operating time / year

Average cell voltage / V

Operating time / kh

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

APS – atmospheric plasma spraying
WPS – wet powder spraying

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

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