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
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

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

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

**Fuel Cell Diagram**:
- **Oxidation**:  
  \( \text{H}_2(g) + \text{O}_2^- \text{(ad)} \rightarrow \text{H}_2\text{O}(g) + 2 \text{e}^- \)
- **Reduction**:  
  \( \text{CO}(g) + \text{O}_2^- \text{(ad)} \rightarrow \text{CO}_2(g) + 2 \text{e}^- \)

**Cell Reaction**:  
\( \text{O}_2 + 4 \text{e}^- \rightarrow 2 \text{O}_2^- \)
SOFC/SOEC: anode substrate cells (ASCs)

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

- cathode LSCF
- barrier Gd$_2$O$_3$ doped CeO$_2$
- electrolyte 8 mol% Y$_2$O$_3$ doped ZrO$_2$ (8YSZ)
- anode Ni / 8YSZ cermet

w/ (La,Sr)MnO$_3$ (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:**
- anode substrate
- anode layer
- electrolyte layer (< 10 µm)
- cathode layer
- interconnect
- anode contact layer
- cathode contact layer
- cell frame
- sealing

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

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

**Sealing:**
- Crofer 22 APU / ITM

**Contact layers:**
- anode contact layer
- cathode contact layer

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

*On Degradation Issues in High-Temperature Electrochemical Devices*
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 and degradation processes]
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

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

- F1002-132: ASC w/ LSCF cathodes and w/ LCC12 contact layer
- F1002-62: ASC w/ LSM cathodes and w/ LCC10 contact layer

- Operation 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

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

with LSM cathodes

reaction at the LSM/YSZ interface

\[ 2\text{CrO}_2(\text{OH})_2 (\text{g}) + 6\text{e}^- \rightarrow \text{Cr}_2\text{O}_3 (\text{s}) + 2\text{H}_2\text{O}(\text{g}) + 3\text{O}^{2-} \]

• in competition with the oxygen reduction reaction

• reaction with LSM to form (Mn,Cr) spinel phases

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

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

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

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

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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%)
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F1002-132
F1002-62

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

Post-test examination of recovered LSM cells

(Mn,Cr) spinel phases
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

\[
y \text{CrO}_\frac{2}{3} (\text{OH})_\frac{2}{3} (g) + (\text{La}_{1-x}\text{Sr}_x \| \text{Co,Fe})\text{O}_3
\rightarrow y \text{SrCrO}_4 (s) + (\text{La}_{1-x}\text{Sr}_{x-y} \| \text{Co,Fe})\text{O}_{3-y} + y\text{H}_2\text{O}(g)
\]

= insulator

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

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

SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-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
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 \(\rightarrow\) operation \(\rightarrow\) at EOL

interconnect steel
oxide scale on steel
protection layer

cathode contact

cathode

barrier

electrolyte

anode (+ substrate)

Fe, Cr(,Mn)

Cr\(_2\)O\(_3\)
(Fe,Cr,Mn)\(_3\)O\(_4\)
(Mn,Fe,Co)\(_3\)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\(_2\)

dense

delamination

Mn at grain boundaries

sponge-like secondary phases

Mn solid state diffusion (and possibly reduction)
(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

- 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%

volume change
-41%

volume change
+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) 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
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?
L.G.J. (Bert) de Haart, JÜLICH  On Degradation Issues in P. Holtappels, DTU Energy  High-Temperature Electrochemical Devices
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)

- 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

- dense
- porous
outlook

World Record SOFC

1. Milestone on 26.09.2008
10.000 h
Continuous operation

Facts
- 2-layer short stack
- WP2 protective layer
- Glass-ceramic spacers
- LSCF with SP 000
- IT1 (Plansee)
- |c|o|w|e|t|o|p|a|n|a|l

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

The SOFC success story
- 56 Power Blocks
- 186 Short Stack
- 64 Lightweight Design Stacks
- 95 Granted Patents
- 101 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..."

Produced electrical energy
During the 70,000 h
3.400 kWh

Start
6.8.2007
Start of operation

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

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

- 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

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

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thank you for your attention