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)

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

- **Reduction**
  - $\text{CO}(g) + \text{O}_2^- (\text{ad}) \rightarrow \text{CO}_2(g) + 2 \text{e}^-$
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>
<thead>
<tr>
<th></th>
<th>electrolyte</th>
<th>anode</th>
<th>cathode</th>
<th>interconnect</th>
<th>sealing</th>
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<tbody>
<tr>
<td><strong>conductivity</strong></td>
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<td>electronic</td>
<td>electronic</td>
<td>electronic</td>
<td>insulator</td>
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<td>purely</td>
<td>purely</td>
<td>additional ionic advantageous</td>
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<td><strong>expansion</strong></td>
<td></td>
<td>interconnect</td>
<td>interconnect</td>
<td>electrolyte</td>
<td>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

Fuel cell: electricity production

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

Substrate

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

<table>
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<tr>
<th>Electrolyte</th>
<th>Ni / YSZ cermet</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode</td>
<td>(La,Sr)MnO₃ / YSZ</td>
</tr>
<tr>
<td>Cathode</td>
<td>(La,Sr)(Co,Fe)O₃</td>
</tr>
</tbody>
</table>

- anode substrate
- anode layer
- electrolyte layer (< 10 µm)
- cathode layer

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

- anode contact layer Ni-mesh
- cathode contact layer (La,Sr)CoO₃

- interconnect and cell frame sealing
- Crofer 22 APU / ITM (Ba,Ca,Al) silicate glass

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

EERA Conference 2016
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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
  - external

causes for their occurrence can be

- reactions within / interactions between stack components
- operation conditions (temperature, current, fuel gas / air quality, ...)

interconnect
anode contact layer
cathode contact layer

current path

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
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

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

operation time / h

voltage / V

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

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

formation of volatile Cr species from oxide scale of interconnect

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

with LSM cathodes

reaction at the LSM/YSZ interface

\[
2CrO_2(OH)_2 (g) + 6 e^- \\
\rightarrow Cr_2O_3 (s) + 2H_2O(g) + 3 O^{2-}
\]

• in competition with the oxygen reduction reaction
• reaction with LSM to form (Mn,Cr) spinel phases

\[
Cr_2O_3 (s) + 2 (La,Sr)MnO_3 \\
\rightarrow + MnCr_2O_4 (s) + (La,Sr)_2MnO_4 (s) + 2O_2 (g)
\]

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 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

Operation time / h

Voltage / V

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

(FM,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

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

with LSCF cathodes

no reaction at the LSCF/YSZ interface

instead reaction at the LSCF / contact layer interface

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

\[
\rightarrow y\text{SrCrO}_4 (s) \rightarrow (\text{La}_{1-x}\text{Sr}_{x-y} \quad \text{Co,Fe})\text{O}_{3-y} + y\text{H}_2\text{O} (g)
\]

= 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

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)\textsubscript{x} along the p(H\textsubscript{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

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

- 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)

Manganese diffusion (and possibly reduction) (across grain boundaries through dense layers)

- 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$_2$

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

- oxidation remains problematic, because of the volume changes
  
  ![Diagram showing single particle reduction and oxidation with volume changes](image)

  - 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 cells at 700 °C and 800 °C](images)
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)

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

Cell voltage / mV

Time / h

Operational changes
54% H₂O

OCV

850°C

0.25 A cm⁻²

Ru/CGO

CGO

Ni/CGO

50% H₂O/H₂; air; i = 0.125 A cm⁻²

0 50 100 150 200 250 300 350 400

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0 50 100 150 200 250 300 350 400
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
L.G.J. (Bert) de Haart, JÜLICH  On Degradation Issues in High-Temperature Electrochemical Devices

Fe, Cr(,Mn) oxide scale on steel
(Mn,Co,Fe)₃O₄ protection layer
(La,Mn,Co,Cu)₂O₃ cathode contact
(La,Sr)(Co,Fe)O₃ cathode
(Ce,Gd)O₂ barrier
(Zr,Y)O₂ electrolyte
Ni + (Zr,Y)O₂ anode (+ substrate)

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

interdiffusion
World Record SOFC

Outlook

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 Stacks
- 64 Light Weight Design Stacks
- 95 Granted Patents
- 101 Keynote & invited talks
- 277 Reviewed Papers
- 230 Conference Presentations
- 267 Proceedings Papers
- 94 Poster

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

Operational data
- 1000°C
- 0.5 A/cm²
- H2 + 0.5% H2O
- uF = 4 Ohm

Facts
- 2 layer short stack
- WO2 protective layer
- Glass-ceramic sealant
- LSCF with SP 000
- IT 11 (Plansee)
- Metal clad anode

1. Milestone on 26.09.2008
10.000 h Continuous operation

1. World record on 29.02.2012
40,000 h Continuous operation

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

Start
6.8.2007
Start of operation

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

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

financial support from various sources is greatly acknowledged
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thank you for your attention

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