On Degradation Issues in High-Temperature Electrochemical Devices

De Haart, L.G.J.; Holtappels, Peter

Publication date: 2016

Document Version
Peer reviewed version

Citation (APA):

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal

If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.
On Degradation Issues in High-Temperature Electrochemical Devices

EERA Conference 2016, November 24-25, 2016
Birmingham, UK
Session: Materials and their degradation modes
On Degradation Issues in High-Temperature Electrochemical Devices

JP Fuel Cells and Hydrogen

L.G.J. (Bert) de Haart
Forschungszentrum Jülich
Institute of Energy and Climate Research
Fundamental Electrochemistry (IEK-9)

Peter Holtappels
DTU ENERGY
Department of Energy Conversion and Storage
outlines

- 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)

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

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

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

fuel cell: electricity production

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

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

\[
\text{CO}(g) + \text{O}_2^- \text{(ad)} \rightarrow \text{CO}_2(g) + 2 \text{e}^-
\]
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>
</tr>
</thead>
<tbody>
<tr>
<td>conductivity</td>
<td>ionic purely</td>
<td>electronic</td>
<td>electronic</td>
<td>electronic</td>
<td>insulator</td>
</tr>
<tr>
<td></td>
<td></td>
<td>additional ionic</td>
<td>advantageous</td>
<td>purely</td>
<td></td>
</tr>
<tr>
<td>thermal expansion</td>
<td></td>
<td>adapted to electrolyte and</td>
<td>adapted to electrolyte and</td>
<td>adapted to electrolyte</td>
<td>adapted to electrolyte and</td>
</tr>
<tr>
<td>thermo-chemical</td>
<td></td>
<td>interconnect</td>
<td>interconnect</td>
<td></td>
<td>interconnect</td>
</tr>
<tr>
<td></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 atmospheres</td>
<td></td>
</tr>
<tr>
<td>micro-structure</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></td>
<td>impermeable for hydrogen</td>
<td>porous</td>
<td>porous</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

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
- Electrolyte: 8 mol% Y₂O₃ doped ZrO₂ (8YSZ)
- Anode: Ni / 8YSZ cermet

w/ (La,Sr)MnO₃ (LSM) cathode

- Cathode current collector: LSM
- Cathode: (La,Sr)(Co,Fe)O₃ (LSCF)
- Barrier: Gd₂O₃ doped CeO₂
- Electrolyte: 8 mol% Y₂O₃ doped ZrO₂ (8YSZ)
- Anode: Ni / 8YSZ cermet

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 of SOFC/SOEC structure]

- electrolyte: yttria stabilized zirconia (YSZ)
- anode: Ni / YSZ cermet
- cathode: (La,Sr)MnO₃ / YSZ
- cathode: (La,Sr)(Co,Fe)O₃
- anode contact layer: Ni-mesh
- cathode contact layer: (La,Sr)CoO₃
- interconnect and cell frame: Crofer 22 APU / ITM
- sealing: (Ba,Ca,Al) silicate glass

L.G.J. (Bert) de Haart, JÜLICH
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

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

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
parallel acting degradation processes are usually on different time-scales

this leads to different time-dependent observations:

- initial drop
- quasi linear
- progressive
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

Operation time / h
Voltage / V
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

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

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

\[
Cr_2O_3(s) + 2(\text{La,Sr})\text{MnO}_3 \rightarrow + \text{MnCr}_2O_4(s) + (\text{La,Sr})_2\text{MnO}_4(s) + 2O_2(g)
\]

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

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

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/cm$^2$ / 40% utilisation

operation time / h

voltage / V
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

(\textit{Mn,Cr}) spinel phases

post-test examination of recovered LSM cells

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

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

= insulator

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

Differences:
APS: MCF dense
WPS: MnOₓ porous

No gas phase diffusion for CrO₂(OH)₂ and drastically minimized solid state diffusion through MCF layer!

WPS coating on IC: 110-160 µg Cr/cm²

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

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

stack de-assembly and post-test analyses

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)
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$_2$

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

\[\text{NiO} \xrightarrow{\text{reduction}} \text{Ni} \xrightarrow{\text{oxidation}} \text{NiO}\]

- volume change: -41% for reduction, +70% for oxidation

- 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

L.G.J. (Bert) de Haart, JÜLICH
P. Holtappels, DTU Energy
On Degradation Issues in High-Temperature Electrochemical Devices
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 $\text{H}_2$

→ 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**: 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$_3$
- **Cathode**: (La,Sr)(Co,Fe)O$_3$
- **Barrier**: (Ce,Gd)O$_2$
- **Electrolyte**: (Zr,Y)O$_2$
- **Anode (+ substrate)**: Ni + (Zr,Y)O$_2$

Formation of an austenitic phase

- Cr(oxide-hydroxide) evaporation
- Manganese solid state diffusion
- Strontium(oxide) segregation
- Nickel(oxide-hydroxide) evaporation
- Nickel agglomeration

Cracking, secondary phases, decomposition, delamination
World Record SOFC

- **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
  - 101 Keynote & Invited Talks
  - 277 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..."

- **Facts**
  - 2-layer short stack
  - NiWZ protective layer
  - Glass-ceramic coating
  - LSCF with SP 000
  - ITI (Plansee)
  - moredata available

- **Start 6.8.2007**
  - Start of operation

- **Operation data**
  - 1000°C
  - 0.5 A/cm²
  - H₂ + 20% H₂O
  - uF = 0.6

- **Voltage behaviour**
  - 10.000 h
  - Continuous operation
  - 40,000 h
  - Continuous operation
  - 70,000 h
  - Continuous operation

- **Commission in 26.05.2008**
  - On degradation issues in high-temperature electrochemical devices
EERA Conference 2016
November 24-25, 2016
Birmingham, UK

L.G.J. (Bert) de Haart, JÜLICH
On Degradation Issues in High-Temperature Electrochemical Devices

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
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.
On Degradation Issues in High-Temperature Electrochemical Devices

thank you for your attention

L.G.J. (Bert) de Haart
Forschungszentrum Jülich
Institute of Energy and Climate Research
Fundamental Electrochemistry (IEK-9)

Peter Holtappels
DTU ENERGY
Department of Energy Conversion and Storage