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):
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

DTU Energy
Department of Energy Conversion and Storage
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)**

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

**fuel cell: electricity production**

\[
\begin{align*}
\text{H}_2(g) + \text{O}_2^- (\text{ad}) & \rightarrow \text{H}_2\text{O}(g) + 2 \text{e}^- \\
\text{O}_2(g) + 4 \text{e}^- & \rightarrow 2 \text{O}_2^- (\text{ad}) \\
\text{CO}(g) + \text{O}_2^- (\text{ad}) & \rightarrow \text{CO}_2(g) + 2 \text{e}^- 
\end{align*}
\]
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>Conductivity</th>
<th>Electrolyte</th>
<th>Anode</th>
<th>Cathode</th>
<th>Interconnect</th>
<th>Sealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ionic</td>
<td>Electronic</td>
<td>Electronic</td>
<td>Electronic</td>
<td>Electronic</td>
<td>Insulator</td>
</tr>
<tr>
<td>Purely</td>
<td>Additional</td>
<td>Advantageous</td>
<td>Purely</td>
<td>Purely</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermal Expansion</th>
<th>Electrolyte</th>
<th>Anode</th>
<th>Cathode</th>
<th>Interconnect</th>
<th>Sealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Adapted to electrolyte and interconnect</td>
<td>Adapted to electrolyte and interconnect</td>
<td>Adapted to electrolyte and interconnect</td>
<td>Adapted to electrolyte</td>
<td>Adapted to electrolyte and interconnect</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Thermo-chemical</th>
<th>Electrolyte</th>
<th>Anode</th>
<th>Cathode</th>
<th>Interconnect</th>
<th>Sealing</th>
</tr>
</thead>
<tbody>
<tr>
<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>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Microstructure</th>
<th>Electrolyte</th>
<th>Anode</th>
<th>Cathode</th>
<th>Interconnect</th>
<th>Sealing</th>
</tr>
</thead>
<tbody>
<tr>
<td>Impermeable for hydrogen</td>
<td>Porous open</td>
<td>Porous open</td>
<td>Porous open</td>
<td>Impermeable for hydrogen</td>
<td>Impermeable for hydrogen</td>
</tr>
</tbody>
</table>

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

On Degradation Issues in High-Temperature Electrochemical Devices

EERA Conference 2016
November 24-25, 2016
Birmingham, UK
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

\[
\begin{align*}
O_2(g) + 4 e^- & \rightarrow 2 O_2^- (ad) \\
H_2(g) + O_2^- (ad) & \rightarrow H_2O(g) + 2 e^- \\
CO(g) + O_2^- (ad) & \rightarrow CO_2(g) + 2 e^-
\end{align*}
\]

- OXIDATION
- REDUCTION

- anode supported cells (ASC)
- operation < 800 °C
- w/ internal reforming of CH₄
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: LSM
- Cathode current collector
- Electrolyte: LSM / 8YSZ
- Anode: Ni / 8YSZ cermet
- Substrate: Ni / 8YSZ cermet

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

EERA Conference 2016
November 24-25, 2016
Birmingham, UK

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

On Degradation Issues in High-Temperature Electrochemical Devices
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, (La,Sr)MnO₃ / YSZ, (La,Sr)(Co,Fe)O₃
- Cathode: (La,Sr)CoO₃

Interconnect and cell frame:
- Sealing: Crofer 22 APU / ITM, (Ba,Ca,Al) silicate glass, Ni-mesh, (La,Sr)CoO₃

Contact layers:
- Anode contact layer: Ni-mesh
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, ...)

- internal reactions within / interactions between stack components
- external 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
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

The observations --- durability tests

cell voltage

(time)

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/ LCC10 contact layer

- **ASC w/ LSM cathodes**
  - and w/ LCC12 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

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

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

Degradation observations during durability tests

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
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

(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

\[ y \text{CrO}_2(\text{OH})_2(g) + (1 - y) \text{La}_{1-x}\text{Sr}_x\text{Co,Fe}O_3 \rightarrow y \text{SrCrO}_4(s) + (1 - y) \text{La}_{1-x}\text{Sr}_x(\text{Co,Fe})\text{O}_{3-y} + y \text{H}_2\text{O}(g) \]

= 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.

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.
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

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

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

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

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

On Degradation Issues in High-Temperature Electrochemical Devices
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

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

- 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: NiO to Ni: −41% to +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 SrTiO₃

*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

source: M. Kurnatowska et al. / Applied Catalysis B: Environmental 148–149 (2014) 123–135

Electrochemical activity
Electronic conductivity + gas transport

Separation of
Electrochemical activity
Electronic conductivity + gas transport
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
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$_3$
(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
outlook

World Record SOFC

Start 6.8.2007
Start of operation

Operations data
- 100 bar
- 0.5 A/cm²
- H₂ + 0.1% H₂O
- uF = 4.0 k

Facts
- 2-layer short stack
- WP3-electrolyte layer
- Glass-ceramic sealant
- LSCF with SP 000
- IT11 (Plansee)
- weltover alrane

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

The SOFC success story
55 Power Blocks
184 Short Stacks
64 Light Weight Design Stacks
95 Graded Pallets
101 Keynote & invited talks
277 Reviewed Papers
429 Conference Presentations
257 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
outlook

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

- **APS** – atmospheric plasma spraying
- **WPS** – wet powder spraying

**Operating time / year**

- 4 layer short-stack APS protective coating on Crofer 22 APU (TK)
- 2 layer short-stack WPS protective coating on ITM (Plansee)

**Operating time / kh**

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

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

mean degradation rate less than 0.6 %/kh
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
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