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

Peter Holtappels
DTU ENERGY
Department of Energy Conversion and Storage

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

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

![Electrolysis Diagram]

**fuel cell: electricity production**

![Fuel Cell Diagram]
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><strong>conductivity</strong></td>
<td>ionic purely</td>
<td>electronic purely</td>
<td>electronic purely</td>
<td>electronic purely</td>
<td>insulator</td>
</tr>
<tr>
<td><strong>thermal expansion</strong></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>adapted to electrolyte and 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 Layer**: yttria stabilized zirconia (YSZ)

**Anode Layer**: Ni / YSZ cermet

**Cathode Layer**: (La,Sr)MnO₃ / YSZ (La,Sr)(Co,Fe)O₃

**Fuel cell: electricity production**

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

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

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

**Anode Supported Cells (ASC)**: operation < 800 °C

w/ internal reforming of CH₄
SOFC/SOEC: anode substrate cells (ASCs)

\[\text{w/ } (\text{La},\text{Sr})(\text{Co},\text{Fe})\text{O}_3 \text{ (LSCF) cathode} \]

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

\[\text{cathode} \quad \text{LSCF} \quad \text{Gd}_2\text{O}_3 \text{ doped CeO}_2 \quad \text{LSM} / 8\text{YSZ} \quad \text{barrier} \quad \text{8 mol% Y}_2\text{O}_3 \text{ doped ZrO}_2 \text{ (8YSZ)} \quad \text{anode} \quad \text{Ni} / 8\text{YSZ cermet} \quad \text{electrolyte} \quad \text{substrate} \quad \text{Ni} / 8\text{YSZ cermet} \quad \text{ceramic metal} \]

\[\text{to prevent formation of SrZrO}_3 \]

\[\text{LSM} \quad \text{cathode current collector} \quad 60 \mu m \]

60 µm
15 µm
6...10 µm
7...10 µm
600...1000 µm

\[\text{substrate} \quad \text{anode} \quad \text{electrolyte} \quad \text{cathode} \quad \text{cathode current collector} \quad \text{ceramic metal} \]

SEM analyses: D. Sebold, N.H. Menzler, JÜLICH / IEK-1
SOFC/SOEC: materials, cells and stacks

- anode supported cells (ASC)
- operation $< 800 \, ^\circ C$
- w/ internal reforming of CH$_4$
- metallic interconnect
- glass-ceramic sealing

![Diagram of SOFC/SOEC components]

**Electrolyte Layer**
- Yttria stabilized zirconia (YSZ)

**Anode**
- Ni / YSZ cermet
- (La,Sr)MnO$_3$ / YSZ
- (La,Sr)(Co,Fe)O$_3$

**Cathode**
- (La,Sr)CoO$_3$

**Interconnect**
- Crofer 22 APU / ITM
- (Ba,Ca,Al) silicate glass
- Ni-mesh
- (La,Sr)CoO$_3$
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, ...)

<table>
<thead>
<tr>
<th>interconnect</th>
<th>anode contact layer</th>
<th>cathode contact layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>cell frame</td>
<td>sealing</td>
<td></td>
</tr>
</tbody>
</table>
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

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

Operational conditions:
- Temperature: 800 °C
- Gas mixture: H₂ / H₂O (10%)
- Current density: 0.5 A/cm²
- Utilisation: 40%
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

blocking reaction sites and changing the microstructure of the triple phase boundary region

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

degradation observations during durability tests

![Graph showing voltage vs. operation time with phases and conditions.

Phase 1: formation of Cr₂O₃ at triple phase boundary = loss of active cathode
Phase 2: equilibrium between Cr₂O₃-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 conditions:
- 800 °C
- H₂ / H₂O (10%)
- 0.5 A/cm² / 40% utilisation

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

Institute of Energy and Climate Research

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
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

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

= 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

Cr-/Mn-spinel

CrO₂

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

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

stack autopsy: P. Batfalsky, JÜLICH / ZEA-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

SEM/EDX 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
degradation issue: Manganese diffusion

at start ▶▶ operation ▶▶ at EOL

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

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$_2$

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

![NiO reduction to Ni oxidation](image)

- volume change: -41% for NiO to Ni, +70% for Ni to NiO

- 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

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)

Separation of Electrochemical activity
Electronic conductivity + gas transport

Allows for multiple materials combinations
Single cells test 16 cm$^2$
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 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**
- **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

**dense**

**porous**

**cracking**

**secondary phases**

**decomposition**

**delamination**

**formation of an austenitic phase**

**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
- 62 Lightweight Design Stacks
- 344 Invited Talks
- 273 Review Paper
- 429 Conference Presentations
- 267 Proceedings Papers
- 94 Posters

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

Operation data
- > 100,000
- 0.5 A/cm²
- H₂ + 5% H₂O
- uF = 4006

Facts
- 2 layer short stack
- WPZ protective layer
- Glass ceramic sealant
- LSCF with SP 000
- ITI (Plansee)
- wet cellulose anode

1. World record on 23.08.2012 in case of planar SOFC stacks
40,000 h
Continuous operation

1. Milestone on 26.09.2008
10,000 h
Continuous operation

Start 6.8.2007
Start of operation

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
outlook

in operation for nearly 80,000 h (9 years)
mean degradation rate less than 0.6 %/kh

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)

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

Operating time / kh

Average cell voltage / V

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

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