On Degradation Issues in High-Temperature Electrochemical Devices

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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

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Forschungszentrum Jülich
Institute of Energy and Climate Research
Fundamental Electrochemistry (IEK-9)

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

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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)

fuel cell: electricity production

oxidation

2 $O^2^-$ (ad) $\rightarrow$ $O_2$(g) + 4 e$^-$

$H_2O(g)$ + 2 e$^-$ $\rightarrow$ $H_2$(g) + $O^2^-$ (ad)

$CO_2(g)$ + 2 e$^-$ $\rightarrow$ $CO(g)$ + $O^2^-$ (ad)

cathode

anode

$O_2$

$CO$

$H_2$

$H_2O$

electrolyte

$e^-$

$O_2^-$

$H_2^-$

$H_2O^-^+$

$voltage$

source

$e^-$

$I$

external

load

$e^-$

$I$

$voltage$

source

$O_2$

$CO$

$H_2$

$H_2O$

electrolyte

$e^-$

$O_2^-$

$H_2^-$

$H_2O^-^+$

fuel cell: electricity production

oxidation

$H_2(g)$ + $O^2^-$ (ad) $\rightarrow$ $H_2O(g)$ + 2 e$^-$

$O_2(g)$ + 4 e$^-$ $\rightarrow$ 2 $O^2^-$ (ad)

cathode

anode

$CO$

$CO_2$

$H_2$

$H_2O$

$e^-$

$O_2^-$

$H_2^-$

$H_2O^-^+$

$O_2$

$CO$

$H_2$

$H_2O$

electrolyte

$e^-$

$O_2^-$

$H_2^-$

$H_2O^-^+$
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 additional ionic advantageous</td>
<td>electronic additional ionic advantageous</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 and interconnect</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: yttria stabilized zirconia (YSZ)
Anode: Ni / YSZ cermet
Cathode: (La,Sr)MnO₃ / YSZ, (La,Sr)(Co,Fe)O₃

Fuel cell: electricity production

<table>
<thead>
<tr>
<th>Oxidation</th>
<th>Reduction</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{H}_2(g) + \text{O}^{2-} \text{(ad)} \rightarrow \text{H}_2\text{O}(g) + 2 \text{e}^- )</td>
<td>( \text{O}_2(g) + 4 \text{e}^- \rightarrow 2 \text{O}^{2-} \text{(ad)} )</td>
</tr>
<tr>
<td>( \text{CO}(g) + \text{O}^{2-} \text{(ad)} \rightarrow \text{CO}_2(g) + 2 \text{e}^- )</td>
<td></td>
</tr>
</tbody>
</table>
SOFC/SOEC: anode substrate cells (ASCs)

w/ (La,Sr)(Co,Fe)O₃ (LSCF) cathode

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

LSCF
Ni / 8YSZ cermet
Gd₂O₃ doped CeO₂
8 mol% Y₂O₃ doped ZrO₂ (8YSZ)
substrate
anode
electrolyte
 barrier to prevent formation of SrZrO₃

w/ (La,Sr)MnO₃ (LSM) cathode

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

LSM
cathode current collector
LSM / 8YSZ
cathode electrolyte
anode
Ni / 8YSZ cermet
Ni / 8YSZ cermet (ceramic metal)
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

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

interconnect
anode contact layer
cathode contact layer
cell frame
sealing

interconnect and cell frame
sealing
anode contact layer
cathode contact layer

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

Crofer 22 APU / ITM
(Ba,Ca,Al) silicate glass
Ni-mesh
(La,Sr)CoO₃
 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

![Diagram of current path through an interconnect and contact layers](image)
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

![Graph showing degradation observations](image)

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

**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

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

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

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

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

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 $\text{CrMn}$-spinel by Mn removal from LSM; change in cathode parameters

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

**Graph Details:**
- Voltage (V) versus operation time (h)
- ASC w/ LSCF cathodes and w/ LCC12 contact layer
- ASC w/ LSM cathodes and w/ LCC10 contact layer
- Conditions: 800 °C, $\text{H}_2 / \text{H}_2\text{O}$ (10%), 0.5 A/cm², 40% utilisation

**Figure Footnotes:**
- F1002-132
- F1002-62

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P. Holtappels, DTU Energy

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Degradation observations during durability tests

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

Operation time / h

Voltage / V

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

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

= 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

SOFC-Stack F1004-69, test-No. SK 595
FuE - Protection layer 2 x APS / 2 x WPS

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.
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

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

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)

at start >>> operation >>> at EOL

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%
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

Separation of Electrochemical activity
Electronic conductivity + gas transport

Allows for multiple materials combinations
Single cells test 16 cm²
Constant current

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
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

Fe, Cr, (Mn)
Cr$_2$O$_3$
(Cr, Mn)$_3$O$_4$
(Mn, Co, Fe)$_3$O$_4$
(La, Mn, Co, Cu)$_2$O
(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

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

interdiffusion
cracking
secondary phases
decomposition
delamination
outlook

World Record SOFC

1. Milestone on 26.09.2008
10,000 h
Continuous operation

Start
6.8.2007
Start of operation

Facts
- 2-layer short cell
- WP2-protective layer
- Glass-ceramic spacers
- LSCF with SP 000
- IT (Plansee)
- water vapor

Operation data
- 100°C
- 0.5 A/cm²
- H₂ + 0.5%H₂O
- 0.5 V = 40	μm

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 Stack
- 64 Light Weight Design Stacks
- 95 Granted Patents
- 101 Keynote & invited talks
- 277 Reviewed Papers
- 429 Conference Presentations
- 297 Proceedings Papers
- 9 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

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

- **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)

  **Average cell voltage / V**

  - **Operating time / kh**
  - **Operating time / year**

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

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

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

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

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thank you for your attention

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