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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Fundamental Electrochemistry (IEK-9)

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DTU ENERGY
Department of Energy Conversion and Storage

DTU Energy
Department of Energy Conversion and Storage
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>
</tr>
</thead>
<tbody>
<tr>
<td><strong>conductivity</strong></td>
<td>ionic purely</td>
<td>electronic purely additional ionic advantageous</td>
<td>electronic purely 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</td>
<td>adapted to electrolyte and interconnect</td>
<td></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></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>
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<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>
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</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

- Oxidation: O₂(g) + 4 e⁻ → 2 O₂⁻ (ad)
- Reduction: H₂(g) + O₂⁻ (ad) → H₂O(g) + 2 e⁻, O₂(g) + 4 e⁻ → 2 O₂⁻ (ad)

- O₂(g) + H₂(g) → H₂O(g) + 2 e⁻
SOFC/SOEC: anode substrate cells (ASCs)

w/ (La,Sr)(Co,Fe)O$_3$ (LSCF) cathode

50 µm

7 µm

6...10 µm

7...10 µm

600...1000 µm

50 µm

7 µm

6...10 µm

7...10 µm

600...1000 µm

w/ (La,Sr)MnO$_3$ (LSM) cathode

60 µm

15 µm

6...10 µm

7...10 µm

600...1000 µm

LSM / 8YSZ cathode current collector

Ni / 8YSZ cermet

8 mol% Y$_2$O$_3$ doped ZrO$_2$ (8YSZ)

Gd$_2$O$_3$ doped CeO$_2$

LSCF

Ni / 8YSZ cermet

(ceramic metal)

substrate

anode

electrolyte

barrier
to prevent formation of SrZrO$_3$

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

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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

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<th>Cathode</th>
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<td>Yttria stabilised zirconia (YSZ)</td>
<td>Ni / YSZ cermet</td>
<td>(La,Sr)MnO₃ / YSZ</td>
</tr>
<tr>
<td></td>
<td></td>
<td>(La,Sr)(Co,Fe)O₃</td>
</tr>
</tbody>
</table>

- interconnect and cell frame sealing
- anode and cathode contact layers
- 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, ...)

current path

interconnect
anode contact layer
cathode contact layer
cell frame
sealing
degredation 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

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

F1002-132
ASC w/ LSCF cathodes
and w/ LCC12 contact layer

F1002-62
ASC w/ LSM cathodes
and w/ LCC10 contact layer
degradation issue: Cr evaporation, cathode poisoning

formation of volatile Cr species from oxide scale of interconnect

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

with LSM cathodes

reaction at the LSM/YSZ interface

\[
2\text{CrO}_2(\text{OH})_2 \text{(g)} + 6 \text{e}^- \\
\rightarrow \text{Cr}_2\text{O}_3 \text{(s)} + 2\text{H}_2\text{O} \text{(g)} + 3 \text{O}^{2-}
\]

• in competition with the oxygen reduction reaction

• reaction with LSM to form (Mn,Cr) spinel phases

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

Degradation observations during durability tests

- **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

Graph showing the degradation test results:
- ASC w/ LSCF cathodes and w/ LCC12 contact layer
- ASC w/ LSM cathodes and w/ LCC10 contact layer

Conditions:
- 800 °C
- H$_2$ / H$_2$O (10%)
- 0.5 A/cm$^2$ / 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

Operation time / h vs. voltage / V

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

(Mn,Cr) spinel phases

Post-test examination of recovered LSM cells

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

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degradation issue: Cr evaporation, cathode poisoning

formation of volatile Cr species

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

with LSCF cathodes

no reaction at the LSCF/YSZ interface

instead reaction at the LSCF / contact layer interface

\[
y CrO_{\frac{y}{2}} (g) + (La_{1-x}Sr_x)(Co,Fe)O_3 \rightarrow y SrCrO_{\frac{y}{2}} (s) + (La_{1-x}Sr_{x-y})(Co,Fe)O_{3-y} + yH_2O(g)
\]

= 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

Visibility 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

cross-section at cell #2

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

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

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
Mn solid state diffusion (and possibly reduction) (across grain boundaries through dense layers)

at start \[\rightarrow\] operation \[\rightarrow\] 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

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

- 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%

[Images of bending at 700 °C and 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)

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

Ni/CGO
Ru/CGO

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

Summary

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

Key elements:
- Fe, Cr(,Mn)
- Cr₂O₃
- (Cr,Mn)₃O₄
- (Mn,Co,Fe)₃O₄
- (La,Mn,Co,Cu)₂O₃
- (La,Sr)(Co,Fe)O₃
- (Ce,Gd)O₂
- (Zr,Y)O₂
- Ni + (Zr,Y)O₂

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
outlook

World Record SOFC

1. Milestone on 06.09.2008
10.000 h
Continuous operation

Start
6.8.2007
Start of operation

Operational data
- 1000°C
- 0.5 A/cm²
- H₂ + 0.05% H₂O
- uF = 4000

Facts
- 2-layer short stack
- WP2-protective layer
- Glass-ceramic sealant
- LSCF with SP 003
- IT (Plansee)
- wetted anode

Autumn 2010
"We have to stop a comparable test—we hope the long running test survives..."

The SOFC success story
- 50 Power Blocks
- 186 Short Stacks
- 64 Lightweight Design Stacks
- 90 Granted Patents
- 103 Keynote & Invited Talks
- 277 Reviewed Papers
- 420 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

40,000 h
Continuous operation

70,000 h
Continuous operation

1. Milestone on 26.09.2008
Voltage behaviour

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outlook

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

mean degradation rate less than 0.6 %/kh

Average cell voltage / V

Operating time / year

Operating time / kh

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

4 layer short-stack
APS protective coating
on Crofer 22 APU (TK)

2 layer short-stack
WPS protective coating
on ITM (Plansee)

APS – atmospheric plasma spraying
WPS – wet powder spraying

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

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thank you for your attention

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