On Degradation Issues in High-Temperature Electrochemical Devices

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Session: Materials and their degradation modes
On Degradation Issues in High-Temperature Electrochemical Devices

JP Fuel Cells and Hydrogen
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

**2 O^{2-} (ad) → O_2(g) + 4 e^{-}**

**H_2O(g) + 2 e^{-} → H_2(g) + O^{2-} (ad)**

**CO_2(g) + 2 e^{-} → CO(g) + O^{2-} (ad)**

**H_2(g) + O^{2-} (ad) → H_2O(g) + 2 e^{-}**

**O_2(g) + 4 e^{-} → 2 O^{2-} (ad)**

**CO(g) + O^{2-} (ad) → CO_2(g) + 2 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 CH\(_4\)) containing fuels
- requires catalysts for methane/steam reforming in/at the fuel electrode
- produces useable heat in the off-gas, next to electricity
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SOFC/SOEC: materials, cells and stacks

- anode supported cells (ASC)
- operation < 800 °C
- w/ internal reforming of CH₄

**Diagram: SOFC/SOEC cell components**
- anode substrate
- anode layer (Ni / YSZ cermet)
- electrolyte layer (< 10 µm) (yttria stabilized zirconia (YSZ))
- cathode layer ((La,Sr)(Co,Fe)O₃)

**Fuel cell: electricity production**

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

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

**Chemical reactions**

- 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)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
- Substrate: Ni / 8YSZ cermet (ceramic metal)

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

- Cathode: LSM
- Cathode current collector
- Electrolyte: LSM / 8YSZ
- Anode: Ni / 8YSZ cermet
- Substrate: Ni / 8YSZ cermet (ceramic metal)

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 CH$_4$
- metallic interconnect
- glass-ceramic sealing

- electrolyte: yttria stabilized zirconia (YSZ)
- anode: Ni / YSZ cermet
- cathode: (La,Sr)MnO$_3$ / YSZ (La,Sr)(Co,Fe)O$_3$

- cell frame
- sealing
- interconnect
- anode contact layer
- cathode contact layer

- anode substrate
- anode layer
- electrolyte layer (< 10 µm)
- cathode layer
- interconnect
- anode contact layer
- cathode contact layer

- 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, ...)

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.
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

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

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

Institute of Energy and Climate Research

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/ LCC12 contact layer

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

post-test examination of recovered LSM cells

(Mn,Cr) spinel phases

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

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

= 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$_2$O) gradient
degradation issue: Sulphur exposure on Ni-cermet based electrodes

Overpotential dependent degradation:
Low overpotential: reversible
High overpotential: irreversible

Figure 9. a) Sketch of high overpotential without YSZ-Hi.

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!)

SOFC-Stack F1004-21, test-No. SK430
Long term constant current operation @ 700°C

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

cross-section at cell #2

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P. Holtappels, DTU Energy

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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

interconnect steel
oxide scale on steel
protection layer
cathode contact

cathode
barrier
electrolyte

dense porous

anode (+ substrate)

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

Mn at grain boundaries
sponge-like secondary phases

delamination

cracks

after N.H. Menzler, JÜLICH / IEK-1
**degradation issue: Ni/YSZ cermet and re-oxidation**

- oxidation remains problematic, because of the volume changes

  ![Diagram showing the conversion of NiO to Ni and then NiO, with volume changes indicated.]

  - reduction: NiO
  - oxidation: Ni
  - volume change: 
    - NiO → Ni: -41%
    - Ni → NiO: +70%

- 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 showing the bending of cells at 700 °C and 800 °C.]
  - 700 °C
  - 800 °C
  - Probe Nr. 2459-3-2
  - Probe Nr. 2459-3-1
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)

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 cm$^2$
Constant current

Electrochemical activity
Electronic conductivity + gas transport

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

Electrochemical activity
Electronic conductivity + gas transport

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

Fe, Cr(Mn)

Cr$_2$O$_3$
(Fe, Cr)$_3$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

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 stack
- WPS-protective layer
- Glass-ceramic barrier
- LSCF with SP 000
- IT 11 (Plansee)
- Wenketal anode

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 Granted Patents
- 121 Keynote & invited talks
- 777 Reviewed papers
- 128 Conference presentations
- 267 Proceedings Papers
- 94 Poster

Spring 2012
“Degradation has slowed down – we have a good chance to get the world record…”

1. World record on 23.02.2012
40,000 h
Continuous operation

10.10.2015
World record all SOFCs:
70,000 h
Continuous operation

Produced electrical energy
During the 70,000 h
3,400 kWh
In operation for nearly 80,000 h (9 years)
mean degradation rate less than 0.6 %/kh
acknowledgements

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On Degradation Issues in High-Temperature Electrochemical Devices

thank you for your attention

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Department of Energy Conversion and Storage