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SOFC Degradation

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European SOFC Stack Technologies

Variety of manufacturers and design types

- planar stacks
 - higher performance
 - compact design
 - mechanically robust
 - simple manifolding
 - lower cost
- tubular stacks
 - resistant to high temperature gradients (*)
 - mechanically robust (*)
 - low power density





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Variety of SOFC Cell Concepts



Specific properties with different application opportunities



Application Requirements

	Lifetime	Thermal cycles	Redox cycles	Efficiency	Weight
APU road vehicles	5000 - 10000 h	2500 – 5000	5000 – 10000	(ŋ _{el} >30%)	1–4 kg/kW
APU aircraft / ships	20000 – 100000 h	5000 – 20000	10000 – 40000	η _{el} >40%	1 kg/kW
Residential	> 40000 h	100 - 5000	(100-,5000	η _{el} >35% η _{tot} >90%	n/a
Commercial	> 40000 h	100-5000	(100-,5000	η _{el} >45% η _{tot} >85%	n/a
Power Generation	100000 h	100-5000	(100-,5000	η _{el} >50%	n/a
Portable	<2500 h	500 – 5000	500 – 5000	η _{el} >30%	n/a



Performance of ,Conventional' Products

Service life

- vehicles >10 years (5.000 to 10.000 operating hrs)
- heating boilers (residential power) >10 years (20.000 to 40.000 hrs, frequent cycles possible)
- power generating equipment 10 30 years (40.000 to 200.000 operating hours)

Other

- vibration and shock (road vehicles)
- acceleration (aircraft)
- simple coupling to natural gas supply (boilers/engines)



• you can even drop them ...



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SOFC Development Challenges

- improved durability under static, transient and cycling conditions
 - redox stability
 - thermal cycling capability
- stack lifetime in excess of 40.000 hrs. (stationary & la loss of power at end of life <20%)
- high performance, high efficiency
- arbitrary switch-off and start-up cycles (several 100 t)
- tolerance against fuel impurities
- operation without external water supply
- robustness to vibration and mechanical shock
- design of large units and hybrid power plants
- lower cost, increased system compactness, simplification of technology

topics in joint materials, design and systems development



Priorisation (results of 2007 Crete workshop)

- high priority:
 - thermodynamics and kinetics of material stability
 - anode and cathode, including re-oxidation & chromium poisoning
 - protective layer & sealants
 - re-oxidation of anode
 - testing (incl. ALT), predictive models
- medium priority:
 - rapid start-up
 - fuel contaminants
- low priority:
 - steel oxidation etc.
 - load cycling



HEXIS: Comparison of ZIP Stack Generations (2000/2002)





Long-term Test Topsoe Fuel Cells



material copyright TOFC

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Development Status in SOFC

- stack lifetime of 2 to 4 years shown (proven?)
- single cell lifetime of >> 2,5 years shown
- degradation of well below 1% / 1000 hrs. shown for more than 10 000 hours, but depends on operating conditions



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Proof of Concept Stack FZ Juelich

- 700°C, 500 mA/cm², 40% f_u
- CroFer22APU steel with APS protective coating
- LSCF cathodes







How do we quantify 'Degradation'?





Long-term degradation behaviour in stacks



source: Bert de Haart, FZJ

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Degradation types

- 1. Baseline (continuous, steady) degradation
 - initialisation phase (sintering, saturation)
 - constant slope phase
 - progressive degradation phase (EoL)
- 2. degradation from transients
 - thermal cycle
 - redox cycle
- 3. degradation after ,incidents' (failures)
 - malfunction of BoP components
 - malfunction of control
 - external influence (shock, grid outage etc.)



Definitions of Degradation

 $\Delta U = U(t_2) - U(t_1) |_{t2 = t1 + 1000 \text{ h}}$

 $\Delta t = t_2 - t_1 = 1000 \text{ h}$

 $d_{\%} = \Delta U / U$ [%/1000 h] (relative to start value)

d $_{V} = \Delta U / \Delta t \text{ [mV/1000 h]}$ (average over interval)

- 1. problem: reference value for $d_{\%}$?
- 2. people just don't stop using $d_{\%}$...







'Current Dependance' of Degradation



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Degradation in I-V-Curve





Evolution of Polarization Resistance of Ni-YSZ Anode







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Real-SOFC Endurance testing: sensitivity matrix

	Real-SOFC	G1 FZJ F1002-60 / FZJ 🏾 ü			= standard WT4.1 conditions
	WT1.2.2 CEA	G1	stack generation		
	WT1.2.4 FZJ	FZJ	stack manufacturer		= benchmark G2 conditions
	WT1.2.7 EBZ	F1002-60	stack number		
	WT1.3.1 FZJ	/ FZJ	testing partner		= benchmark G3 conditions
		°ü	test running / performed		(alternative: G2 w/ temp <800 °C)
		fuel		temperature	
		hydrogen + 3 % water vapour		800 °C	
	current density	fuel utilisation	%		
	mA/cm ²	10	40) 60) 75
	300	G1 FZJ F1002-60 / FZJ ü	G1 FZJ F1002-62 / FZJ ü		
	400				
*			G1 FZJ F1002-56 / FZJ Ü		C2 E7 E1002-88 / E7
	5 00		G2 FZJ F1002-68 / FZJ ü	G2 FZJ F1002-79 / CEA °	G2 FZ F F 1002-00 / FZ F
			G3 FZJ F1002-xx / FZJ		G2 FZJ F1002-69 / FZJ
REAL	600				
	700		G2 FZJ F1002-87 / FZJ °	G2 FZJ F1002-83 / CEA	G3 FZJ F1002-xx / FZJ
SOF	800				
	1000	l			
*		fuel		temperature	
		methane (internal reforming) S	S/C=2.0	800 °C	
	current density	fuel utilisation	%		
	mA/cm ²	10	40) 60) 75
	300		G1 FZJ F1002-61 / FZJ ü		
	400		G1 FZJ F1002-53 / EBZ ü		
	500		G1 FZJ F1002-57 / FZJ ü		G2 FZJ F1004-11 / EBZ [•]
	600				
	700		G2 FZJ F1002-xx / FZJ	G2 FZJ F1004-12 / EBZ	G3 FZJ F1004-yy / EBZ
	800				
	900				
	1000				



Real-SOFC Stack Generations: Progress by Materials



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Sensitivity to Current Flow & Fuel Utilisation



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Long-Term Stack Operation

- >42 000 hours of operation on load
- 700°C, 500 mA/cm², 40% f_u
- Plansee ITM steel with standard protective coating
- LSCF cathodes





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Evaluating Degradation Rates





Degradation Phenomena Overview

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Variety of Degradation Phenomena





Variety of phenomena (2)

Types

- changes in single layers or components (independent of others)
- changes at interfaces
- interaction of materials (e.g. transport of species)

Driving forces

- temperature
- current flow
- overpotential
- partial pressures of oxygen, hydrogen, water etc.
- pressure
- etc.



Degradation Mechanisms

- changes in morphology and phase with consequences for
 - gas transport
 - resistivity
 - mechanical strength
 - reduction of active surface area
- interdiffusion with consequences for
 - corrosion resistance
 - loss of activity
 - resistivity
- transport of species with consequences for
 - poisoning / de-activation
 - build-up of layers / scales
- corrosive interaction
- build-up of corrosion scales with consequences for
 - dimensional changes (e.g. swelling)
 - resistivity
 - cycling capability



Overview of Degradation Mechanisms

Cathode side	Electrolyte	Anode side	
Three phase boundary reduction by - Cr poisoning - Particle sintering Phase changes Interdiffusion Contact degradation	Phase instabilities Interdiffusion	Ni-agglomeration Ni-coarsening S poisoning Interdiffusion Destruction by re-oxidation Contact loss by - by sintering - by seal swelling - temp. gradient Resistivity	
Resistivity Cr transport			
Interconnect: - Cr evaporation - Corrosion cracking - Inner oxidation		Interconnect: - Scale resistance - Embrittlement by carburization - Corrosion cracking	
Ceramic glass sealant Interaction with gaseous s Interaction between comp Leakage or short circuit d Degradation due to impur 	species/ contamir conents luring thermal cyc rities in raw mater	nants ling ials	



SRU Cross-Section

Mechanism
Corrosion perforation
Carburisation (embrittlement)
Scale resistivity
Coating/scale resistivity
Contact loss (sintering)
Contact loss (seal swelling)
Contact loss (dT/dx, dT/dt)
Poisoning / low- σ phases by contact layer
Coking
Ni sintering
Redox at high j and/or Uf
S-poisoning
S-poisoning
Ni sintering (TPB reduction)
Interdiffusion (low- σ phase formation)
Phase instability (ageing)
Interdiffusion (low- σ phase formation)
Phase changes, demixing
Particle sintering (TPB reduction)
Cr-poisoning
Interdiffusion
Contact loss (sintering)
Contact loss (seal swelling)
Contact loss (by dT/dx, dT/dt)
Cr evaporation / cathode poisoning
Coating/scale resistivity
Corrosion perforation (H assisted)
Cr evaporation / cathode poisoning

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Conductivity Degradation of Electrolyte



caused by phase separation and re-ordering in micro-domains, impurities, etc.

Source: IWE Slide 32/77 JESS 2 / 2012

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Electrolyte Degradation by Diffusion of Mn



- after 20 000 hours of operation: failure of cell
- Mn enrichment along grain boundaries 5-10 at.%)



Electrode-Electrolyte Interface during Manufacturing

- 1. formation of low-conductive products such as $La_2Zr_2O_7$ and $SrZrO_3$ during cell sintering and SOFC operation, especially with LSCF cathodes
- 2. segregation of material impurities at TPB's
- 3. solution of Ni in YSZ



Processes at the Cathode-Electrolyte Interface

- 1. segregation of materials impurities at TPB's
- 2. very low SiO₂ content (~100 ppm) in the raw materials affects the microstructure of interfaces and grain boundaries in SOFC.



M. Mogensen / Proc. 26th Risø Int. Symp.

Y.L. Liu, C. Jiao / Solid State Ionics 176(2005)435

Cathode Materials: Stability

thermodynamical stability and kinetics: perovskites ABO₃



 $(La,Sr)MnO_3$ (La,Sr)FeO₃ $(La,Sr)CoO_3$ $(La,Sr)(Co,Fe)O_3$ $(La_{0.9}, Sr_{0.1})MnO_3$ $(La_{0,7},Sr_{0,3})MnO_{3}$ $(La_{0,7},Sr_{0,3})_{0,99}MnO_{3}$ $(La_{0.7}, Sr_{0.3})MnO_{3+\delta}$ $(La_{1-x}Sr_x)_vFe_{1-z}(Ni,Cu)_zO_{3-\delta}$

source: Yokokawa, EMPA

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Cathode Materials: Volatility



Sr deposition

source: Tietz/Mai

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Nickel Anode Volatility

volatilisation of nickel (NiOH) in high water content fuel gases – loss of active surface



Source: IWE Slide 38/77 JESS 2 / 2012

Anode Substrate: Particle Agglomeration



- temperature-induced tendency of metals to decrease free energy, i.e. to minimize the surface area and agglomerate
- examples: anode substrate Ni-YSZ cermet



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Microstructure characterization



SEM images of anode surface (70 wt% Cu + 30 wt% SDC)



secondary electron mode

backscattering mode

For good distinguishability of different phases their backscattering coefficients should be different.

Source: IHTE Slide 40/77

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Three-Dimensional Characterisation





J.R. Wilson et al. / Nature Materials 5(2006)541

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Chromium Volatilisation



Fig. 6. Cr transport at the cathode side of a SOFC.





K. Hilpert / J. Electrochem. Soc. 143(1996)3642

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Impact of Chromium on Cathode Performance





Chromium Poisoning: Microscopic Findings



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Without current Cr is only located within the $La_{1-x}Sr_xMnO_3$ layer, forming $(Cr,Mn)_3O_4$ spinel crystals. If a current passes through the cell the Cr is mainly deposited near the TPB near the YSZ electrolyte. Chromium is clearly found along the perimeter of the pores on the surface of the YSZ, thereby decreasing the number of active sites necessary for oxygen reduction.

S.P.S. Badwal / Solid State Ionics 143(2001)39



Konysheva et al. Journal of The Electrochemical Society, 153 (4) A765-A773 (2006)

Steinberger: SOFC Degradation

Electrochemical tests with the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_3$ cathode under current clearly show Cr poisoning at 800°C. Significant formation of SrCrO₄ crystals was detected on the surface of the cathode layer.

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Redox Cycling Requirements

- redox cycles:
 - after stack shut-down air will flow to the fuel electrode
 - Ni in Ni-YSZ anode will re-oxidise to NiO₂
 - NiO₂ has higher volume and will cause mechanical damage to cell
- goals:
 - no gas leakages from stack (safe operation)
 - rapid start-up (30 minutes for road APU)



T. Klemenso et al. / Electrochem. Solid-State Lett. 9(2006)A403

Redox stability of Ni–YSZ cermet



- cyclic reduction and oxidation leads to large volume change of Ni to NiO
- microstructure of Ni/YSZ bulk is affected
- performance degradation due to change in Ni particle surface, or
- catastrophic (mechanical) failure of cermet, or
- cracking of electrolyte layer





Anode – Redox-Stability



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Anode Redox Stability – SrTi Anode





Sulphur Poisoning – The Phenomenon





Sulphur Poisoning – The Phenomenon (2)



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Sulphur Poisoning



H₂S concentration:

Coal syngas – 100-300 ppm Biogas – 50-200 ppm Natural gas – up to >1%

Chemosorption:

 $H_2S=HS(ad)+H(ad)=S(ad)+2H(ad)$

Chemical reactions:

 $H_2S=H_2+S$ (at 1100 K 8.6% H_2S is decomposed) Ni+H₂S=NiS+H₂

 $3Ni+xH_2S=Ni_2Sx+xH_2$ (at 800°C required level for sulfides formation is 1% H₂S)

Electrochemical reactions:

 $H_2S+3O^{2-}=H_2O+SO_2+6e^{-}$ $H_2S+O^{2-}=H_2O+S+2e^{-}$ $S+2O^{2-}=SO_2+4e^{-}$

<u>1st step (reversible)</u>: Fast adsorption of sulfur occurs in minutes upon exposure to H_2S , which blocks reaction sites and leads to rapid performance degradation. 90% coverage may occur at 1000 K for a low H_2S concentration (10 ppm).



Sulphur Poisoning: Microscopic Findings





Coking – Carbon Buildup in Internal Reforming

carbon build-up due to hydrogen and oxygen stochiometry mismatch (Boudouard Reaction)



Fig. 4. The morphology of carbonaceous deposits on the surface of an anode containing 10 wt % CeO2 and 20 wt % Cu after long-term testing in n-butane at 1173 K.

figures courtesy of Jörger & He

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Methane Conversion Reactions

```
equilibrium (i≈0)
          CH_{4} = C + 2H_{2}(1)
steam reforming (endothermic)
          CH_4 + H_2O = CO + 3H_2 (2)
partial oxidation
          CH_4 + 1/2O_2 = CO + 2H_2 (3)
water-gas shift reaction
          CO + H_2O = CO_2 + H_2 (4)
Boudouard reaction
          2CO = CO_2 + C(5)
direct oxidation
          CH_{4} + O^{2} = CO + 2H_{2} + 2e^{-} (6)
          CH_4 + 4O^{2-} = CO_2 + 2H_2O + 8e^{-}(7)
oxidation
          C + O^{2-} = CO + 2e^{-}(8)
          C + 2O^{2-} = CO_2 + 4e^{-}(9)
          CO + O^{2-} = CO_2 + 2e^{-}(10)
          H_2 + O^{2-} = H_2O + 2e^{-}(11)
```



Interconnect Corrosion: Scale Cross-Sections

Microstructures of oxide scales after 1000 h discontinuous oxidation at 800°C in air





Steel Corrosion - Interconnects





*k*_p–dependence on specimen thickness

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Metal Corrosion: Nickel Mesh





Degradation of Interconnect Steels

Ferritic stainless steels are Fe–Cr alloys. To be considered "stainless", the alloys must contain at least 12-14% Cr for aqueous corrosion. Even more Cr is required if the alloy is to be able to selectively oxidize the Cr to form a continuous, protective layer of Cr_2O_3 .

Chromia (Cr_2O_3) forming ferritic stainless steels have similar coefficient of thermal expansion with the oxide components of the SOFC. Electrical conductivity requires that the oxide that forms at the interconnect surfaces be conductive at operating temperatures. Chromia forming alloys meet this requirement; as Cr_2O_3 is a semiconductor at elevated temperatures.

chemical composition of the anoys used								
Alloy	Fe	Cr	Mn	Tì	Si	Al	Re-el.	Ni
Crofer22APU-1st	Bal.	22.6	0.4	0.06	0.1	0.1	La-0.1	0.2
JS-3	Bal.	23.3	0.4	0.05	< 0.01	< 0.01	La-0.1	-

P. Batfalsky et al. / Journal of Power Sources 155 (2006) 128-137

Chemical composition of the alloys used







P. Batfalsky et al. / Journal of Power Sources 155 (2006) 128-137

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Interaction of Glass Sealant and Ferritic Interconnect





- optimal matching of steel and sealing materials is vital:
 - good adhesion = chemical interaction
 - but: no excessive corrosion



Degradation due to Contacting problems

Contact trace on cathode

high local current due to narrow contacting ,ridge'



820 mV - 336 mA/cm²

770 mV - 336 mA/cm²

880 mV - 298 mA/cm²



Thermo-Mechanics

low strength of steels at high temperatures







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Thermal Cycling Requirements

- thermal cycles:
 - 'cold start' 20°C ... 200°C, 'warm start' >400°C up to 600 ... 750°C
- goals:
 - no gas leakages from stack (safe operation)
 - rapid start-up (30 minutes for road APU)





FEM Analysis of Critical ThermoMechanical Stress



leakages





- identification of critical locations in stack
- implementation of global model
- passing of boundary conditions to more detailed sub-model
- prediction of strain
- improvement of design

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Impact of Failing Element in a Stack



If a single cell in a stack exhibits higher resistance than the rest of the cells, stack failure often initiates at such a cell. The cell is then exhibits lower voltage than the rest of the cells, and often even a negative voltage. It is necessary that cell-to-cell characteristics be as uniform as possible including contact between repeat units.

If a cell exhibits a negative voltage, the oxygen chemical potential within the electrolyte can exceed that in the oxidant, and/or can drop below that in the fuel. This can lead to high internal oxygen partial pressure resulting in electrode cracking and delamination, and/or very low oxygen partial pressure leading to local electrolyte decomposition. Both situations can lead to cell and stack degradation.



Modelling of degradation processes

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Analysis Approach

- correlating cause and effect (phenomena and ensuing degradation)
- modelling of effects
- understanding and influencing mechanisms
- improving materials with less sensibility to degradation and/or deterioration

not only to be worked on in sequence, but also in parallel



Modelling Approach to Degradation Effects



The quantification and prediction of single contributions with respect to their behaviour over time is the key expected outcome of this project



Correlated percolation model

In the model monosized particles are located on a face-centered cubic lattice and sintering between two metal particles occur with a certain probability. The model gives an insight in the development of active bonds in the anode, the density of three phase boundaries and the transport resistance in anodic materials.





Fig. 3. Variation of the number of active bonds with time, $n_s(t)$, obtained for the composition which maximizes $n_s(0)$. Lines: effective medium theory; points: Monte Carlo simulation. The effect of the probability of pore opening in each sintering act, λ : (a) 0, (b) 0.5, (c) 1. The curves and points correspond to the indicated values of the minimum number, n_s of non-electrolyte neighbors of the bond between two metal particles which allows their fusion.

A. Ioselevich et al. / Solid State Ionics 124 (1999) 221-237



Approaches to SOFC Accelerated Lifetime Testing

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Accelerated durability testings





 Increase stress (e.g., voltage or pressure) to make degrading units fail more quickly.

These types of acceleration may work in combination (e.g. electrochemical reactions)

Acceleration of a failure mechanism must mimic actual occurrence of the failure mode(s)

William Q. Meeker

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Accelerating Degradation Effects





Accelerating Degradation Effects





Mapping in Time

- Cell voltage can be written as
 E(t) = E(t=0) X(t)
- degradation phenomena are generally functions of
 - T, p(O₂), p(H₂O), j, overpotential, concentration gradients etc.
 - in the form $X(t) = f(T, p(O_2), j, t, ...)$
- a mapping has to be found where

 $X^{\cdot}(t) = X(a \cdot t)$

where a > 1 is an acceleration coefficient

• prerequisite:

the acceleration must not change the principal effect

• the mapping is not necessarily linear



A Lifetime Prediction Model

- stack test results are too complicated to analyse
- full set of parameters to equip a ,full' stack model (including degradation) does not exist
- a disaggregated model of single degradation mechanisms could be suitable for evaluation of the single effects
- a complete model could then be achieved by reaggregating results
- this also might lend itself to introducing accelerated testing





Thank you for your attention! If there's any questions ... go ahead.

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