Degradation Testing - Quantification & Interpretation

2nd International Workshop on Degradation Issues of Fuel Cells
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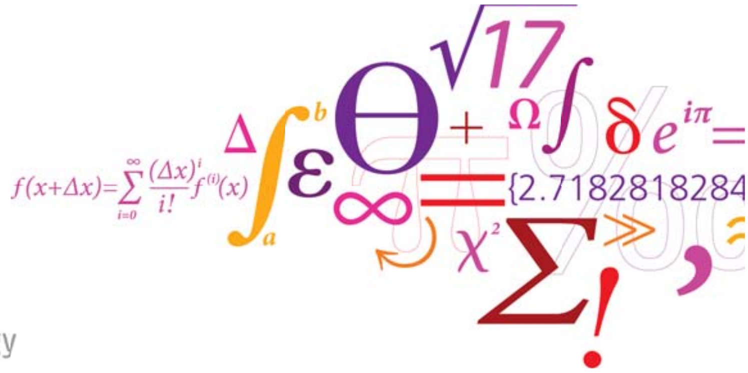

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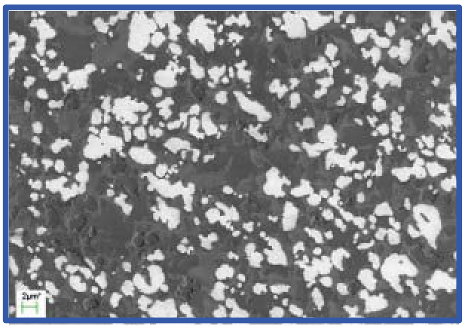
Outline

- Ways of Viewing Degradation
- Limits of Safe Operation
- Cell Performance Metrics (ASR)
- Degradation Rates determined from Current - Voltage Data
- Lifetime - Degradation Rate - Testing Considerations
- Summary and Conclusion

Types of Degradation in SOFCs (I)

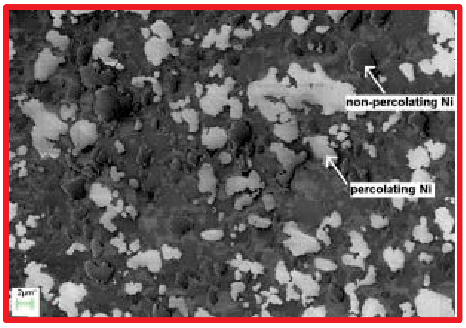
- **Irreversible Degradation**
  - <u>Microstructural coarsening</u>
  - Decomposition
  - Reactions
  - Interdiffusion
  - Delamination...
  - ...

- **Reversible** (Passivation / Re-activation)
  - S poisoning / S oxidative removal (anode)
  - Instantaneous effect of H_2O on LSM cathodes
  - exsolution / re-dissolution of metal ions (cathode)
  - ...



Ni-coarsening and reduction of connectivity within Ni-phase in anode cermet

from aging experiments at 884 °C in dilute H_2



M. Pihlatie *et al*; *Solid State Ionics,* 2011, 189, 82

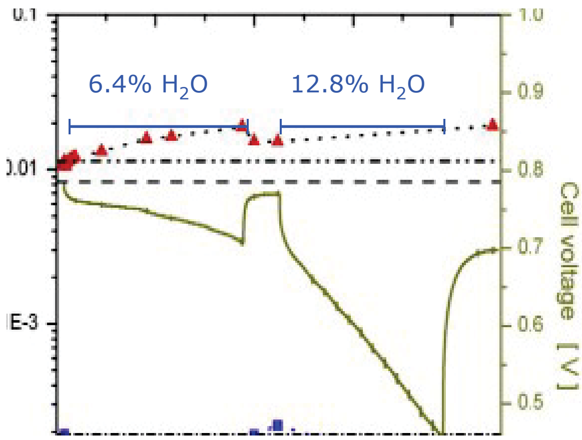
Types of Degradation in SOFCs

- **Irreversible Degradation**
  - Microstructural coarsening
  - Decomposition
  - Reactions
  - Interdiffusion
  - Impurity accumulation at TPBs...
  - ...

- **Reversible** (Passivation / Re-activation)
  - S poisoning / S oxidative removal (anode)
  - Instantaneous effect of H_2O on LSM cathodes
  - exsolution / re-dissolution of metal ions (cathode)
  - ...

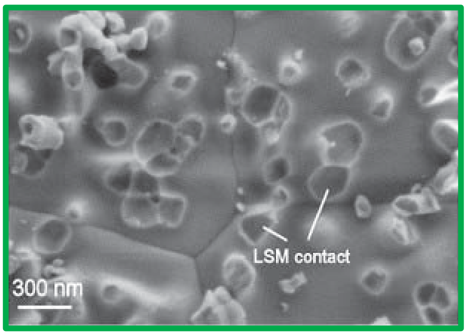
Influence of water vapour on LSM-YSZ cathode from test on anode-supported SOFC under operation at 0.41 A cm^{-2} and 750 °C.

Passivation is observed along with some extent of irreversible degradation.



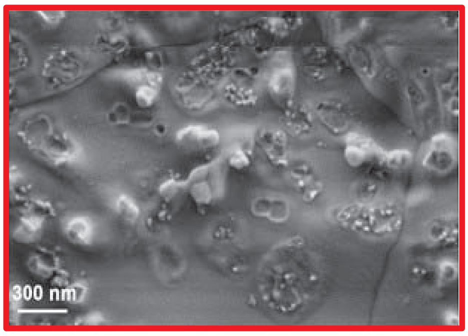
Nielsen *et al*; *Solid State Ionics,* 2011, 189, 74

Types of Degradation in SOFCs



Secondary phase formation in anode supported SOFC tested at for 1500 h at 0.75 A cm^{-2} and 750 °C leading to reduced TPB.

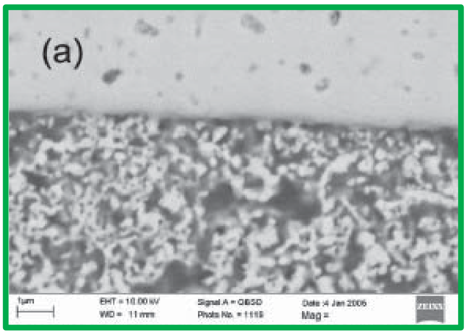
Reference Cell



Y.-L. Liu *et al*; *Solid State Ionics,* 2009, 180, 1298

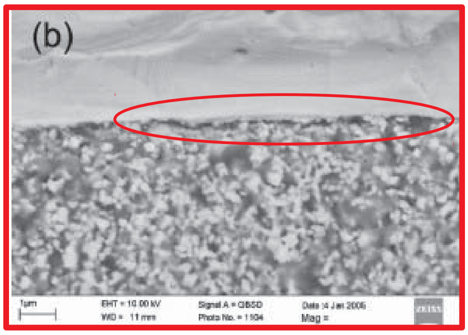
- **Chemical Degradation**
  - Interdiffusion of components
  - Reactions between components (secondary phase formation)
  - Poisoning (Cr, S, ...)
- **Physical Degradation**
  - Microstructural Coarsening
  - Cracking (e.g. as a result of redox...)
  - Delamination

Types of Degradation in SOFCs



Cell with LSM-YSZ cathode tested at high current density

Cell with LSM-YSZ cathode tested at low current density



A. Hagen *et al*; *J. Electrochem. Soc,* 2006, 153, A1165

- **Chemical Degradation**
  - Interdiffusion of components
  - Reactions between components (secondary phase formation)
  - Poisoning (Cr, S, ...)
- **Physical Degradation**
  - Microstructural coarsening
  - Cracking (*e.g.* as a result of re-oxidation of Ni...)
  - Delamination

Types of Degradation in SOFCs

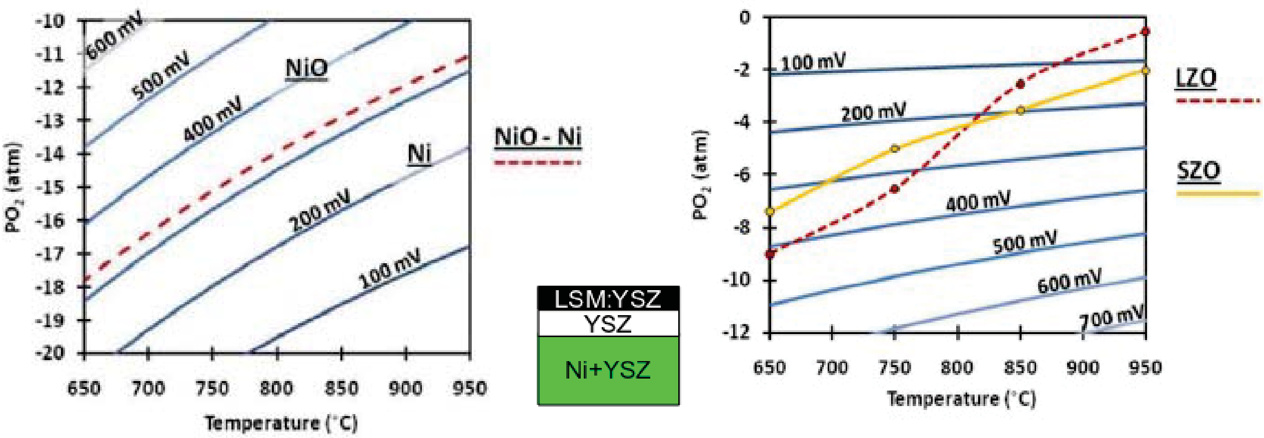
- **Intrinsic** degradation
  - Microstructural coarsening
  - Interdiffusion
  - Impurities in raw materials
  - Decomposition
  - ...

- **Extrinsic** degradation
  - Gas phase impurities (S, Si, Cr...)
  - "Unsafe" operating conditions
    - leading to redoxing
    - leading to carbon deposition
    - leading to secondary phase formation
    - ...

For establishing the maximum lifetime of a cell
the rate of **irreversible** & **intrinsic** degradation is a good place to start

→ This represents the "base" degradation rate of the cell
and corresponds to the unavoidable part of the degradation
of the cell

Limits of Safe Operation



Max anode overvoltage
~ 300 mV
for Ni-based cermet anodes

Max cathode overvoltage
temperature dependent.
Ranges from ~ 50 mV to 300 mV
for LSM25 and 8YSZ.

Measurements of the intrinsic (and irreversible) degradation rate should take place within limits of safe operation to avoid harmfully high overvoltages (high/low pO_2) and additional "extrinsic" degradation

Y.-L. Liu *et al*; *Solid State Ionics,* 2009, 180, 1298
R. Knibbe *et al*; *Green,* 2011, 1, 141

Cell Performance Metrics - ASR

ASR = area specific resistance ($\Omega \cdot cm^2$)

Secant ASR

$$ASR_{sec} = \frac{emf - U_{cell}}{j_{cell}}$$

Takes leaks into account

$$ASR_{sec} = \frac{OCV - U_{cell}}{j_{cell}}$$

Correction for reactant utilization

$$ASR_{sec,corr} = \frac{\overline{OCV} - U_{cell}}{j_{cell}}$$

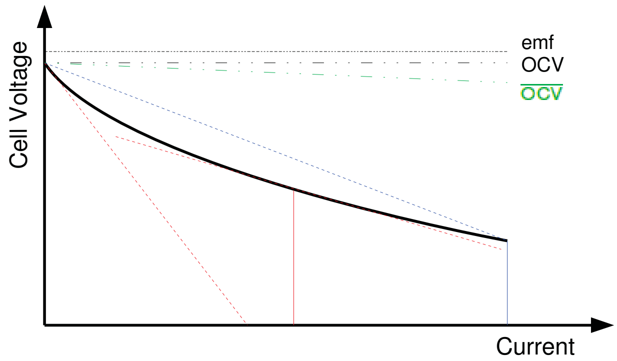
Tangential ASR

$$ASR_{\tan} = \frac{U_1 - U_2}{j_1 - j_2} = \frac{\Delta U_{cell}}{\Delta j_{cell}}$$

Differential ASR

$$ASR_{diff} = \frac{dU}{dj}$$

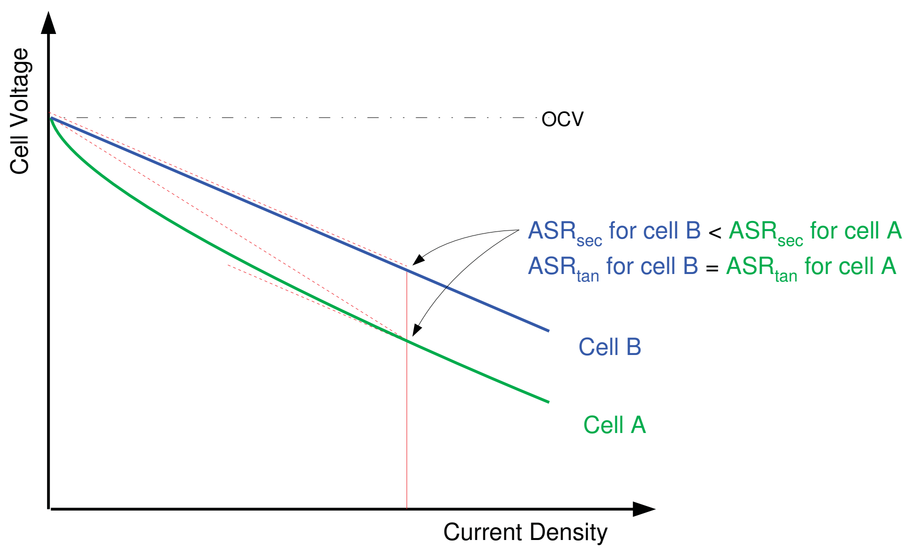
corresponds to real part of cell impedance...



P.V. Hendriksen and M. Mogensen; *in "High temperature SOFC", ed. S.C. Singhal and K. Kendall, Elsevier, 2003*

Cell Performance Metrics - ASR

Tangential vs Secant Resistance

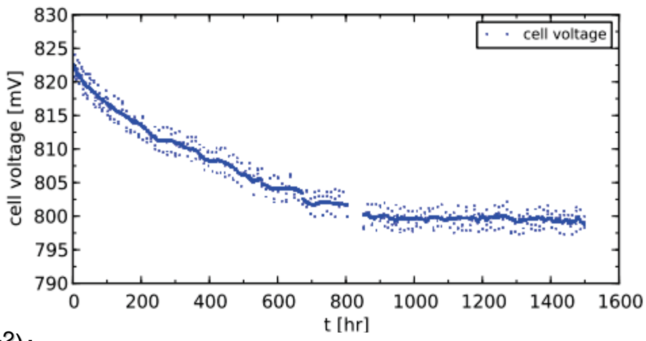


Recommendation: Use secant ASR!
For correlation with EIS - Use tangential ASR

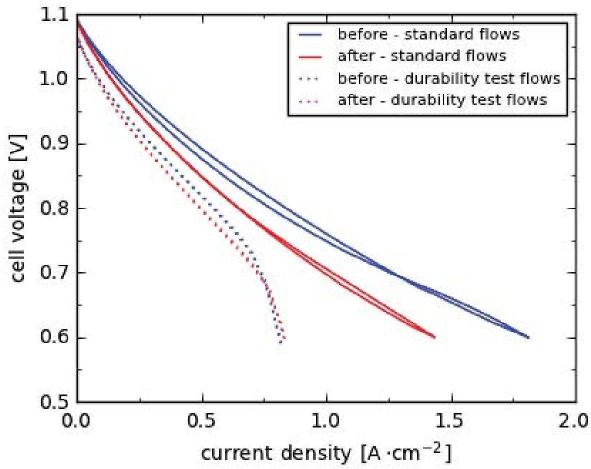
R.S. Gemmen *et al*; *J. Power Sources,* 2008, 184, 251

Degradation Rate from Polarisation Curves

Test data from a durability test of an anode supported SOFC at constant current (**0.5 A cm^{-2}**)



Polarisation Curve:	$ASR_{sec,corr}$ (at 0.5 A·cm^{-2}):
before test (std. flows)	0.33 Ω·cm^2
after test	0.38 Ω·cm^2
before test (dur. flows)	0.29 Ω·cm^2
after test	0.34 Ω·cm^2



➡ $\Delta ASR_{sec,corr}$ at 0.5 A·cm^{-2} = +*50* mΩ·cm^2 during 1500 h operation → +*33* mΩ·cm^2 kh^{-1}

➡ This overall degradation rate takes into account initial performance drop

Degradation Rates from Cell Voltage Data

Defining a degradation rate:

- *Usually given as a change of cell voltage or cell resistance with time*
- *Often given as a normalized change with time (operating point dependent)*
- *Desirable with an unambiguous measure for degradation (not operating point dependent)*

$$U_{cell}(j,t)=OCV(t)-i(t)R_{sec}(t)=OCV(t)-j(t)ASR_{sec}(t)$$

$$OCV(t)=const.$$

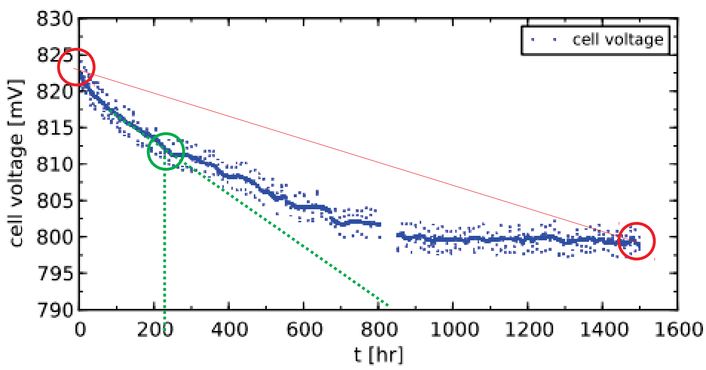
$$j(t)=const.$$

Instantaneous degradation rate:

$$\frac{d(U_{cell}(t))}{dt}=\frac{-d(ASR_{sec}(t))}{dt}j$$

Normalized Instantaneous Degradation Rate:

$$\frac{d(U_{cell}(t))/dt}{U_{cell}(t_0)}=\frac{-d(ASR_{sec}(t))}{dt}j$$

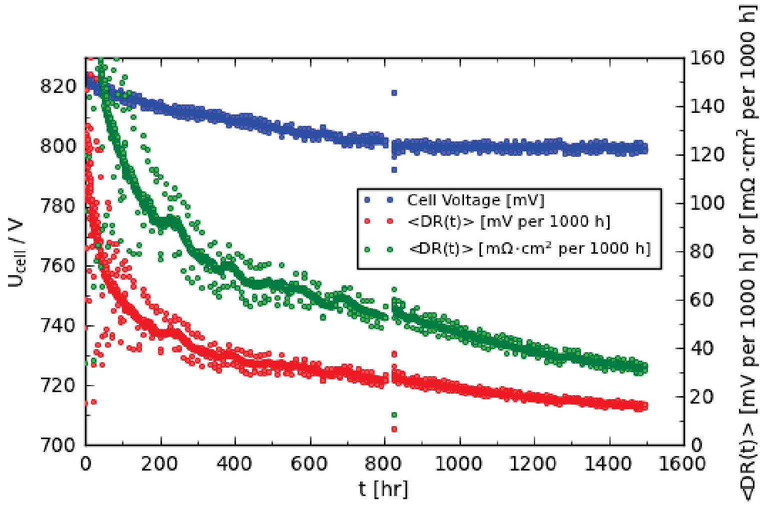


Average / Linearized degradation rate(s)

R.S. Gemmen *et al*; *J. Power Sources,* 2008, 184, 251
I. Vinke, Proc. Workshop on Degradation, Crete, Greece, Sept 20, 2007

Degradation Rates from Cell Voltage Data

Average degradation rate calculated from $U_{cell}(t_0)$ and $U_{cell}(t)$



$$\overline{DR(t)} = \frac{U_{cell}(t) - U_{cell}(t_0)}{(t - t_0)}$$

$$\overline{DR(t)} = \frac{U_{cell}(t) - U_{cell}(t_0)}{U_{cell}(t_0)(t - t_0)}$$ mV· h^{-1}

→ ~31 mΩ·cm^2 kh^{-1}
(under the assumption that OCV was constant)

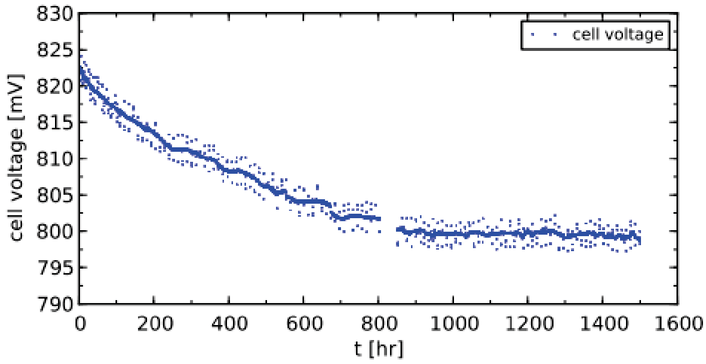
$$\overline{DR(t)} = \frac{U_{cell}(t) - U_{cell}(t_0)}{j_{cell}(t - t_0)}$$ mΩ·cm^2 h^{-1}

→ ~33 mΩ·cm^2 kh^{-1}
(from polarisation curves, $\Delta ASR_{sec,corr}$ at 0.5 A cm^{-2})

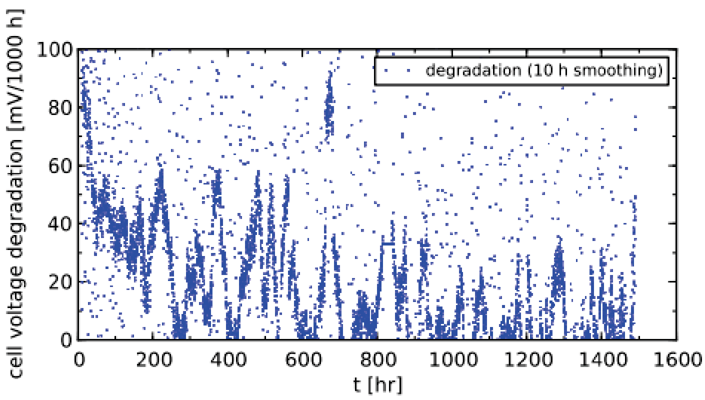
Instantaneous Degradation Rate

Test data from a durability test of an anode supported SOFC at constant current (0.5 A cm^{-2})

Data is noisy due to periodic impedance measurements...



$$\frac{d(U_{cell}(t))}{dt} = \frac{-d(ASR_{sec}(t))}{dt} j$$



Instantaneous degradation rates difficult to determine without some form of “filtering” *e.g.*

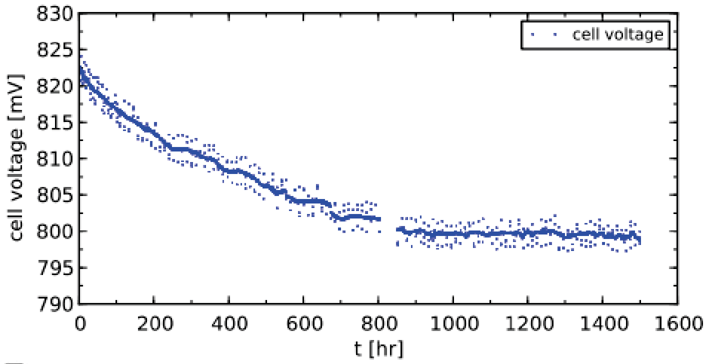
- averaging

- linearization

Local Linear and Averaged Degradation Rates

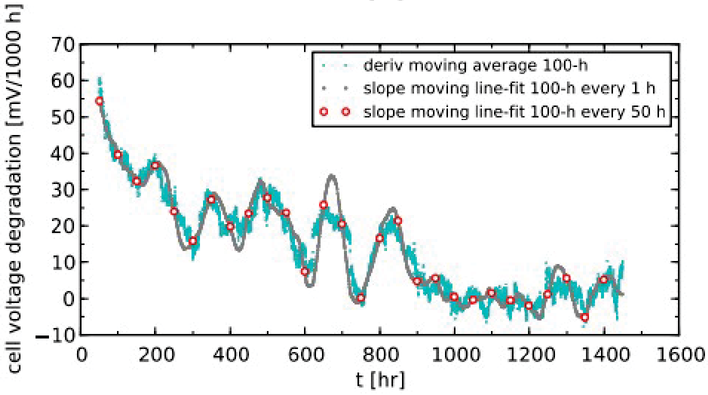
Test data from a durability test of an anode supported SOFC at constant current (0.5 A cm^{-2})

Data is noisy due to periodic impedance measurement.



Moving Average

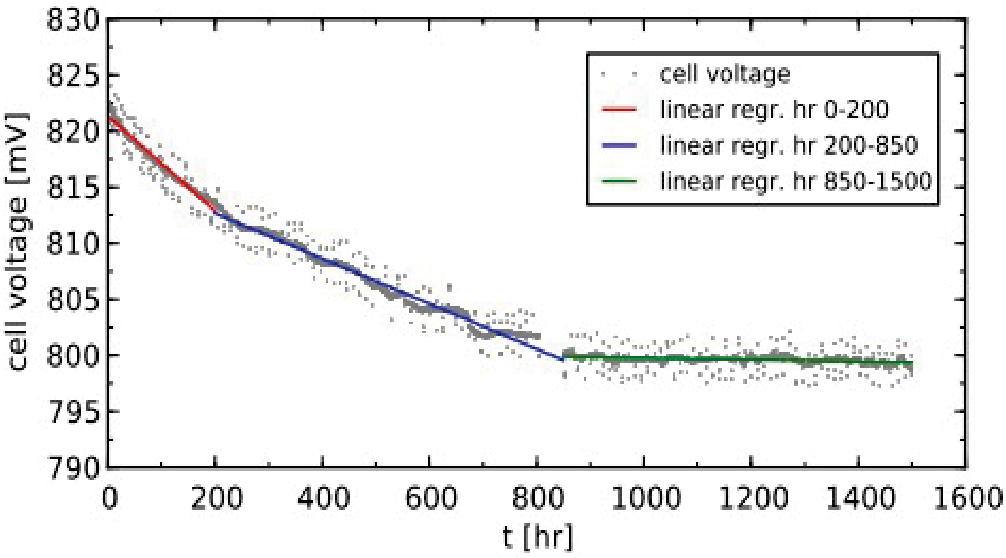
Moving Linear Fits



➡ Degradation rate approaching ~ 5 mV kh^{-1} or ~ 10 mΩ·cm^2 kh^{-1} but longer test time needed to overcome noise!

Moving Linear Fits, see → I. Vinke, Proc. Workshop on Degradation, Crete, Greece, Sept 20, 2007

Linearized Degradation Rates



→ ~42 mV kh^{-1} 84 mΩ·cm^2 kh^{-1}

→ ~20 mV kh^{-1} 40 mΩ·cm^2 kh^{-1}

→ ~0.8 mV kh^{-1} 1.6 mΩ·cm^2 kh^{-1}

Initial degradation

"Long-term degradation"
(although is the measurement time sufficient?)

Degradation - Lifetime - Test Time

Lifetime: 5 years = 43800 h

For example:

OCV = 1.1 V

j_{cell} = 0.5 A·cm^{-2}

$ASR_{cell}(t = 0)$ = 200 mΩ·cm^2

10% decrease in U_{cell} over 40000 h

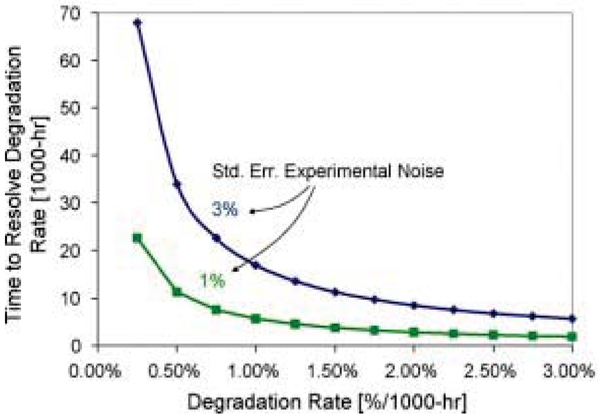
$U_{cell}(t = 0\ h)$ = 1.0 V

$U_{cell}(t = 40000\ h)$ = 0.9 V

$ASR_{cell}(t = 40000\ h)$ = 400 mΩ·cm^2

$DR_U(t)$ = 2.5 mV kh^{-1} ↔ 0.25% per 1000 h

$DR_{ASR}(t)$ = 5 mΩ·cm^2 kh^{-1}

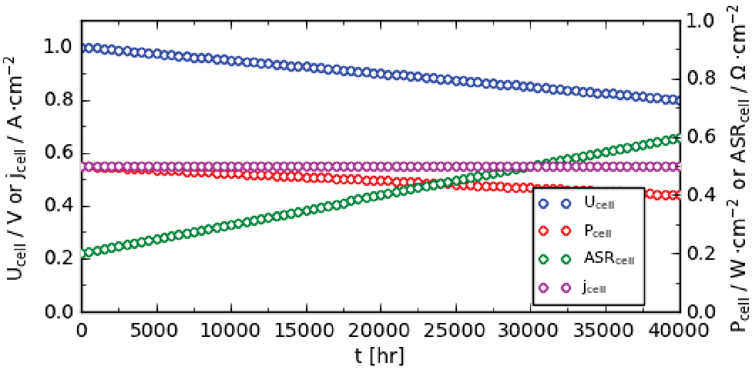


R.S. Gemmen *et al*; *J. Power Sources,* 2008, 184, 251

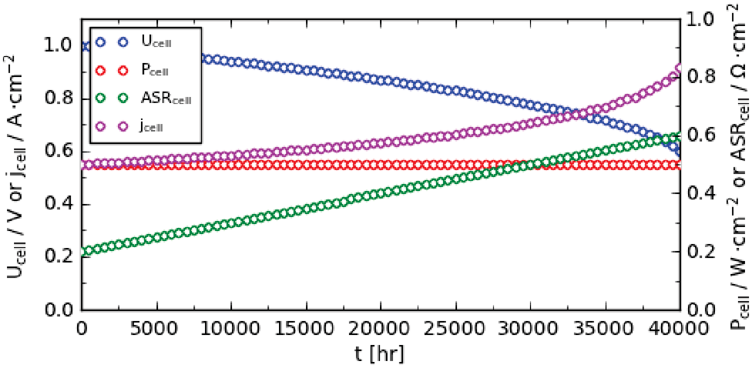
Decreasing degradation rates demands longer test times (or acceleration...)

Stationary Conditions

Many processes are strongly influenced by the thermodynamic state (overpotential, pO_2) at the electrodes. Will change with electrode resistance.



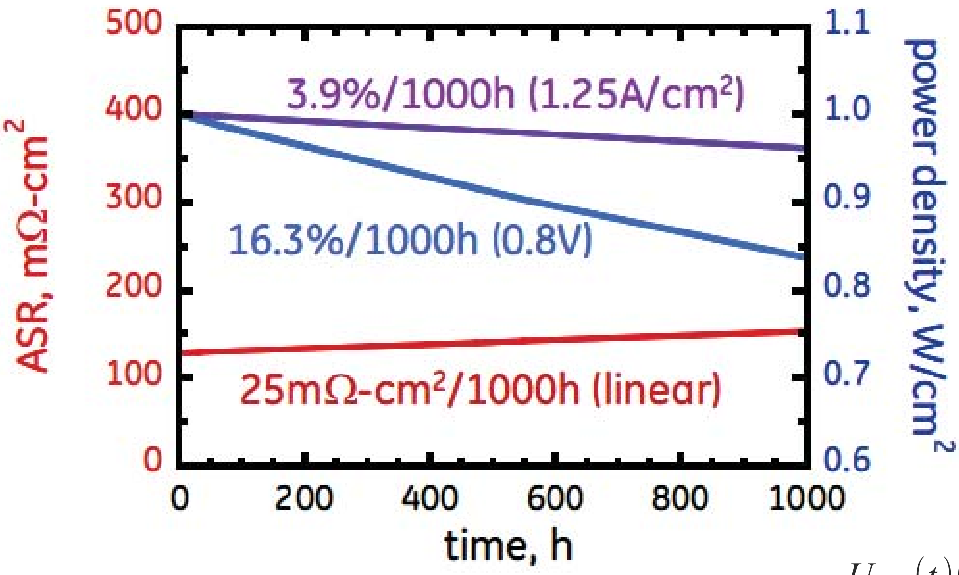
Degradation testing at "stationary conditions" carried out at **constant current** (and pressure, temperature) avoids further change in conditions due to that the current density and reactant utilization is kept constant with time - unlike the situation when constant power or constant voltage is used.



OCV = 1.1 V; $ASR_{cell}(t = 0)$ = 200 mΩ·cm^2
degradation rate = 10 mΩ·cm^2 / 1000 h

R.S. Gemmen *et al*; *J. Power Sources,* 2008, 184, 251

Degradation Metrics - Operating Mode



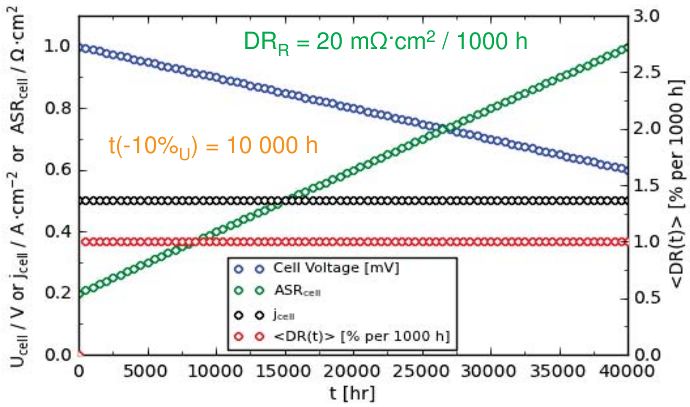
$$P_{U=const} = \frac{U_{cell}(t)(OCV - U_{cell}(t))}{ASR}$$

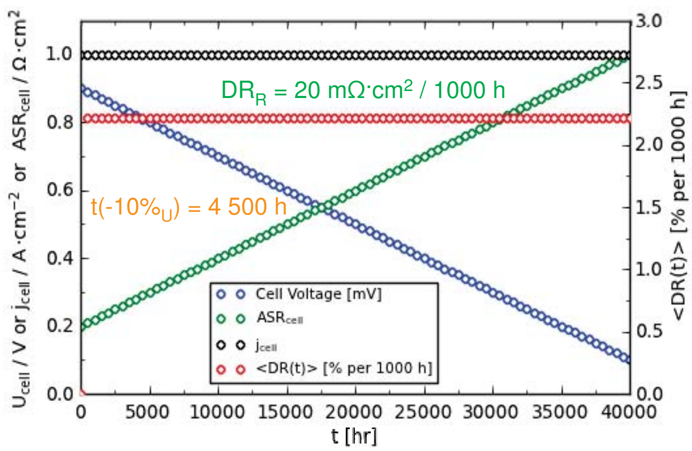
$$P_{j=const} = OCV - ASR * j_{cell}$$

M. J. Alinger, SECA Final Report, August 2009

➡ ASR is the most useful metric for quantification and understanding of degradation...

Degradation Rates & Lifetime





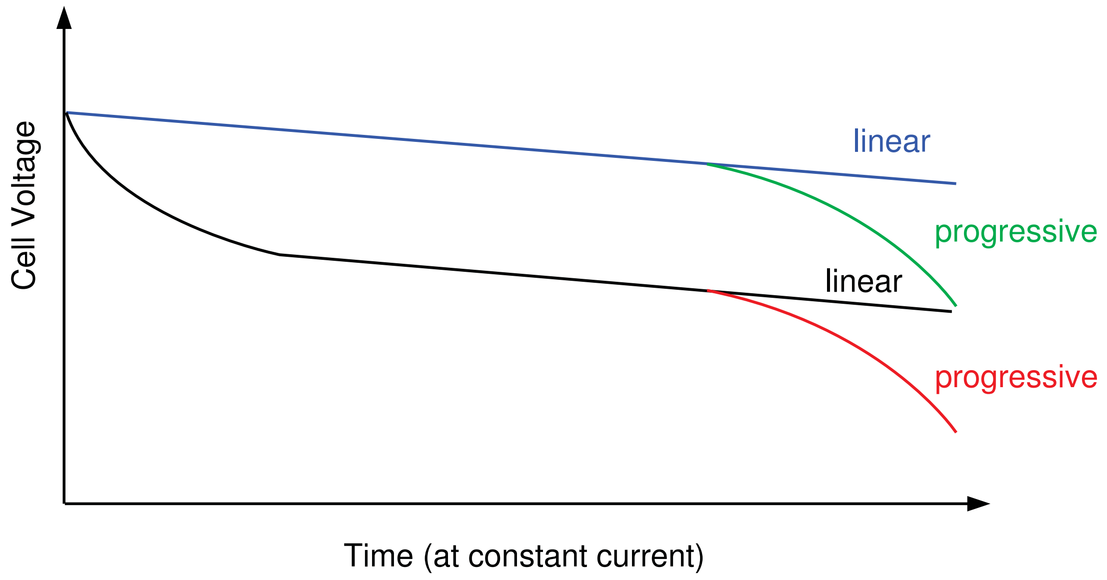
"Lifetime" at a given acceptable loss in cell voltage or power output depends on the current density and the cell resistance

The relative degradation rate is different for the same resistance degradation at different current densities

Absolute ASR degradation rate the most useful degradation metric.

OCV = 1.1 V; $ASR_{cell}(t = 0)$ = 200 mΩ·cm²
degradation rate = 20 mΩ·cm² / 1000 h

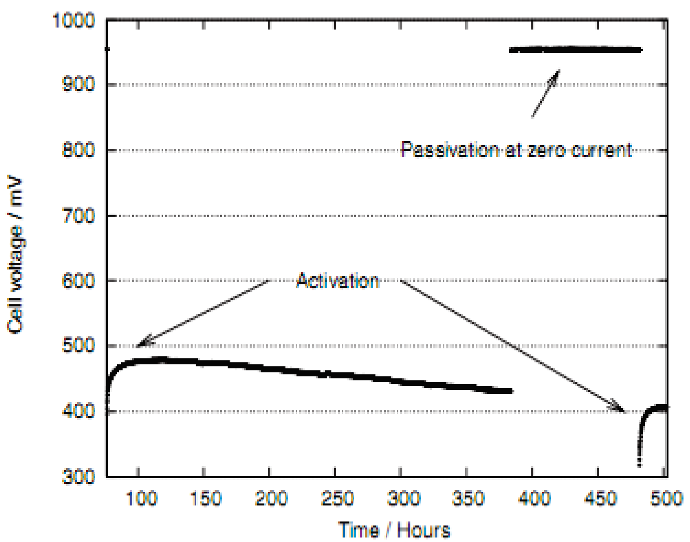
Trends in Cell Voltage Data

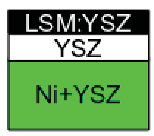


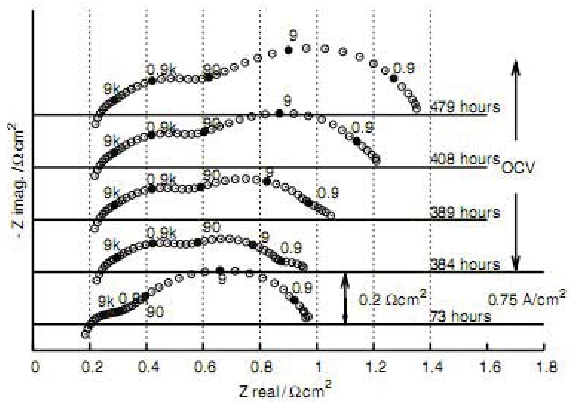
Progressive or accelerating degradation - no steady-state long-term degradation can be determined. Important to identify root causes of degradation.

L.G.J. De Haart *et al*; Fuel Cells, 2009, 09, No 6, 794-804

Degradation Testing - Pitfalls





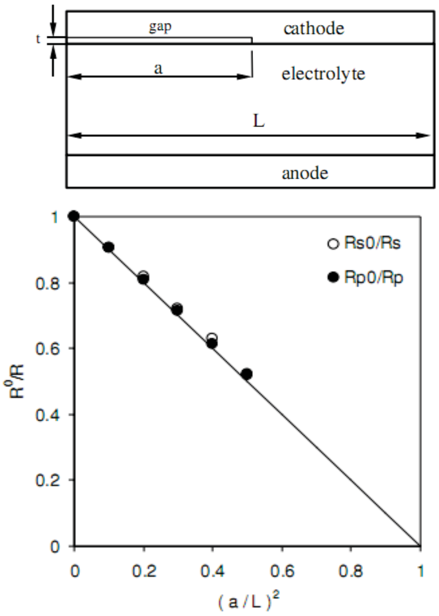


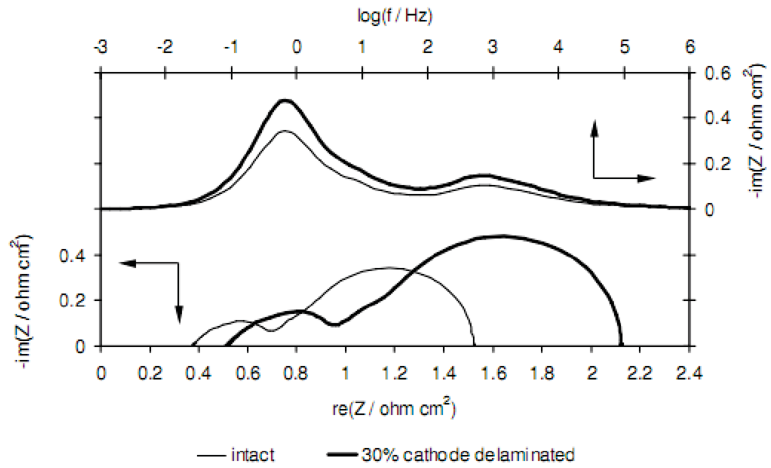
Performance measurements carried out before / after test does not yield a correct value for the degradation when such activation / passivation occurs

S. Koch *et al*, Fuel Cells, 2006, 06, No. 2, 117–122

Delamination - In Cells and Stacks

delamination = physical (mechanical) degradation
delamination or formation of insulating layer at electrode/electrolyte interface,
contact loss at interconnect / electrode interface





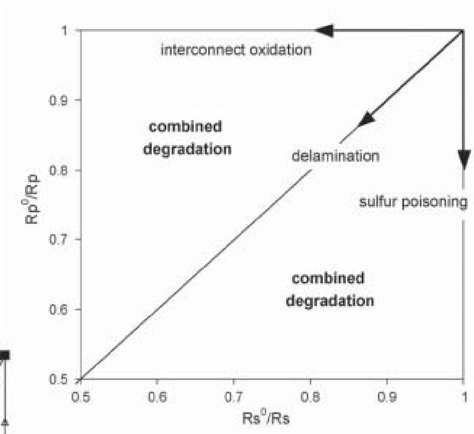
Electrode delamination - ionic path interrupted

Interconnect detachment from electrode - electronic path interrupted (less severe R_0/R change)

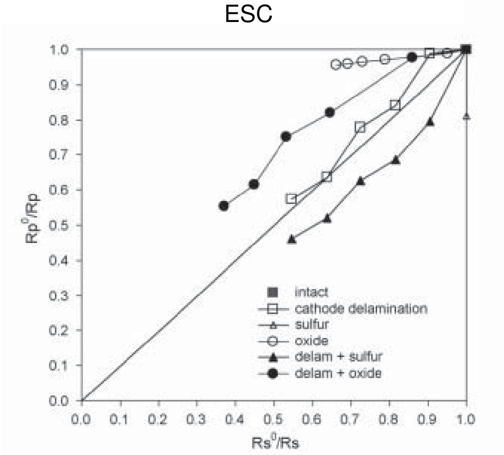
J.I. Gazzarri *et al*, Journal of Power Sources 2007, 167, 100
J.I. Gazzarri *et al*, Journal of Power Sources 2007, 167, 430
J.I. Gazzarri, PhD thesis, University of British Columbia, Canada (2007)

Detection of Multiple Degradation Modes

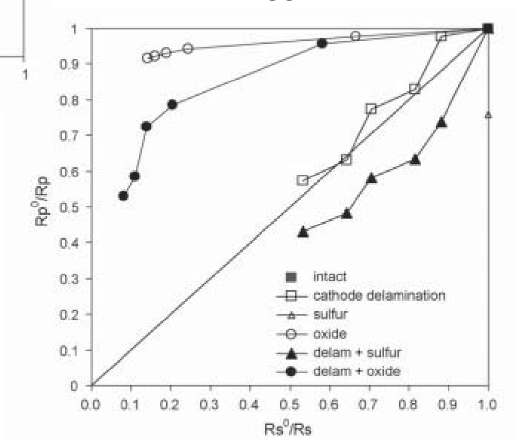
2D Model for Short Stack SRU
- both ESC and ASC



ESC



ASC



J.I. Gazzarri *et al*, Journal of Power Sources 2008, 176, 138
J.I. Gazzarri *et al*, Journal of Power Sources 2007, 176, 155
J.I. Gazzarri, PhD thesis, University of British Columbia, Canada (2007)

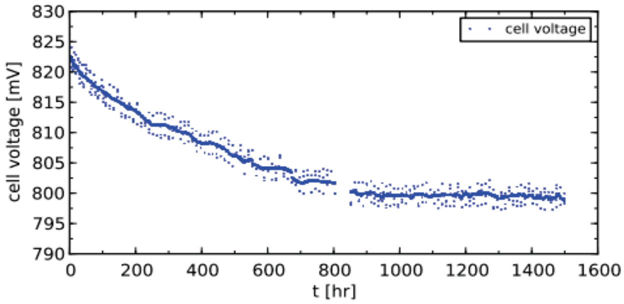
Summary

- **How can Degradation be Described?**
  Useful to identify the type of degradation studied

- **Degradation Quantified**
  Performance loss over time
  Important to define the performance metric used
  Avoid using only relative degradation rates!
  Degradation should be expressed as an intrinsic property (ASR)
  Avoid pitfalls - degradation rate should correspond to observed changes under operation

- **Degradation & Lifetime**
  SOFC degradation rates have reached values of 1% / 1000 h or lower → need to consider measurement time and data quality

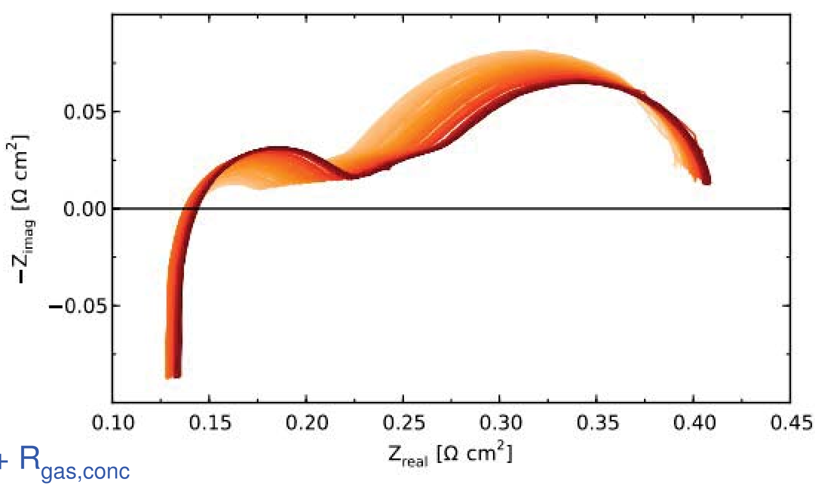
Concluding Remarks



Deconvolution of losses into component and process specific contributions during operation to identify major contributions to degradation, increase understanding, and focus mitigation strategies and development work on critical issues.

ASR is the most useful metric for describing and understanding degradation.

'Normalized' series (R_s^0/R_s) and polarisation (R_p^0/R_p) also valuable parameters.



$R_{cell} = R_s + R_p =$
$R_{aux} + R_{electrolyte} + R_{anode} + R_{cathode} + R_{gas,conc}$

Acknowledgements

Colleagues at the Fuel Cells and Solid State Chemistry at Risø DTU

Christopher Graves for work on averaging, moving linear fits etc

- Topsoe Fuel Cell A/S
- Danish Energy Authority
- Energinet.dk
- EU Framework Programmes
- Danish National Advanced Technology Foundation
- DONG Energy
- Danish Research Councils

Thanks for your attention!

Questions?