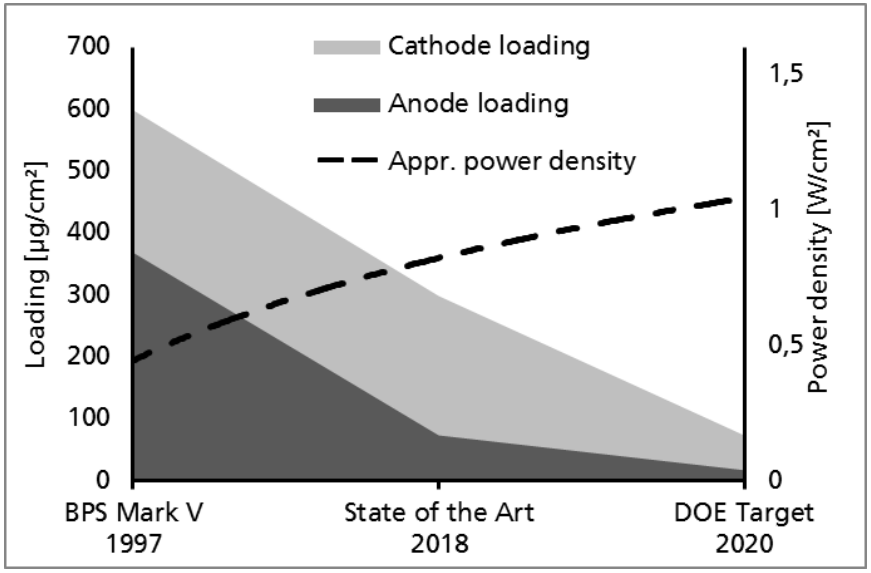
EFFECT OF FUEL IMPURITIES (CO, CO_2, H_2S) ON PEMFCS WITH ULTRA-LOW LOADED ANODIC CATALYST LAYERS



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FDFC 2019 / PEM Fuel Cell Degradations

Nantes, 12.02.2019

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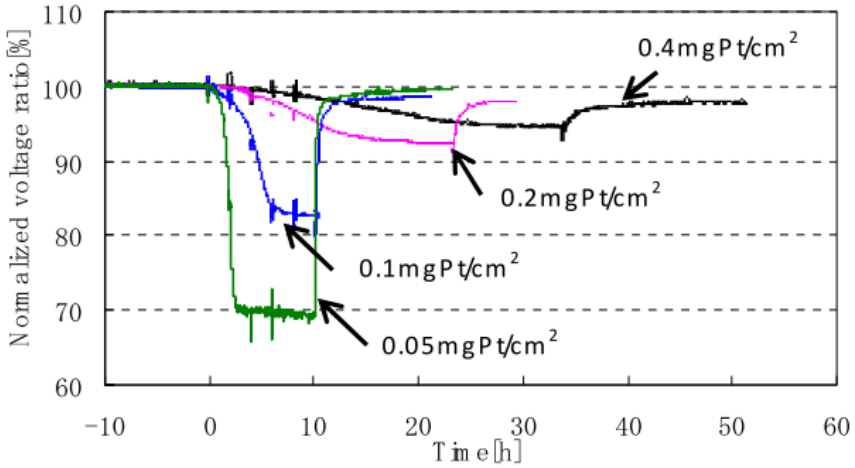
Background
Anodic catalyst loading and fuel impurities

- DOE Target (Stretch) for 2020: 0.125 (0.0625) g/kW$_{rated}$ PGM [1]
  - Loadings of 25 (15) µg/cm² on anode side
  - Lower loadings generally less tolerant vs. H_2 impurities [2]



Species		Limit [ppm]	Ef… Rev. FC	Irrev. FC	…ystem	Dilution
Carbondioxide	CO2	2	X			
Carbonmonoxide	CO	0.2	X			
Total sulfur compounds	-	0.004		X		
…missing in list: oxygen, water, halogenated compounds, hydroc…						

Arguably inert at low concentrations

Totally reversible but strong contaminant

Predominantly irreversible contaminant

[1] Kongkanand, A. et al. (2016). The priority and challenge of high-power performance of low Pt-PEMFCs. *The Journal of Physical Chemistry*, 7, 1127-1137.

[2] Hashimasa, Y. et al. (2010). Effects of Pt loading on PEFC power generation performance deterioration by CO in H2 fuel. *ECS Transactions*, 26 (1), 131-142.

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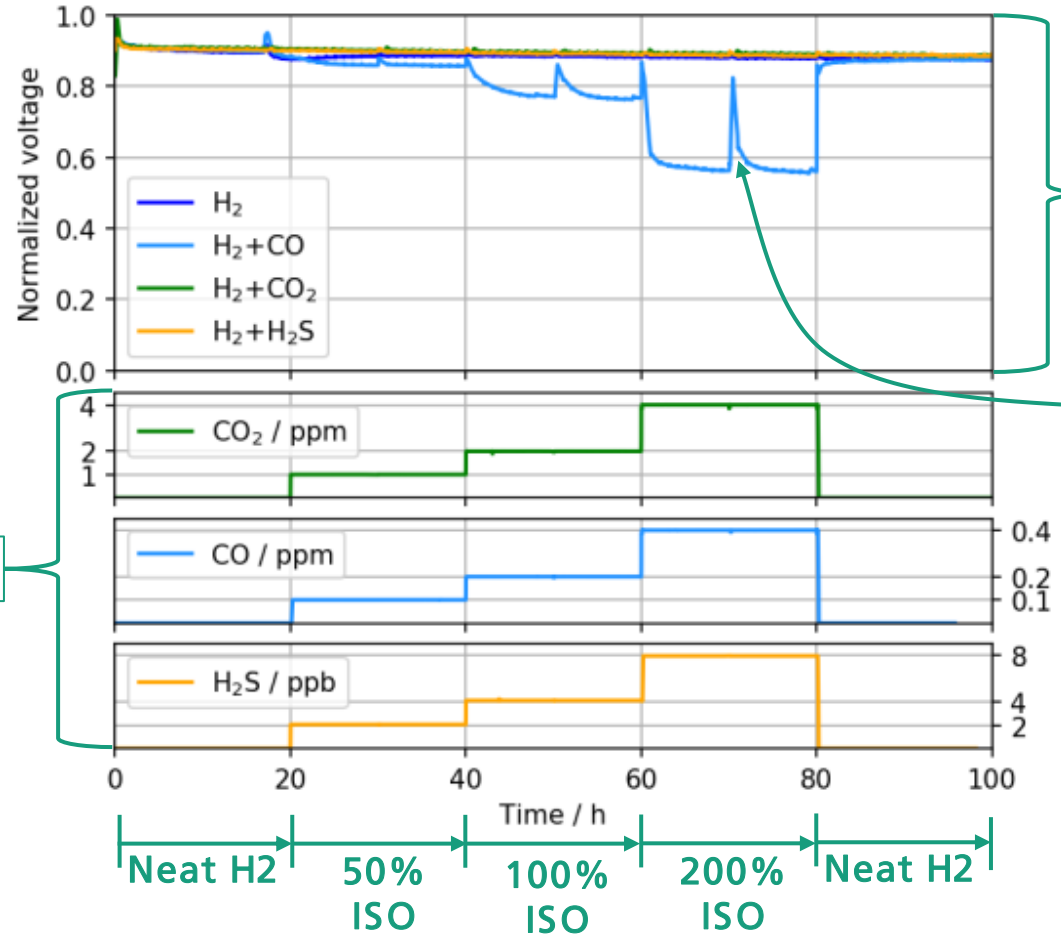
Experimental
Setup and testing procedure

- Mixture of high-purity H_2 and bottled H_2 / N_2 containing
  - 10 / 100 ppm CO / CO_2 in H_2
  - 0.5 ppm H_2S in N_2
- 100 hour galvanostatic operation
  - Voltage decay over time
- 3 CCMs from Greenerity
  - Kathode: 400 µg/cm² Pt/C
  - Anode: 15 / 25 / 50 µg/cm² Pt/C
  - Anode loading varied via thickness

Operating conditions & materials		
Current density	A/cm²	1
Cell temperature	°C	80
Fuel/air stoichiometry		12 / 14
Anode/Cathode RH	%	95 / 75
Pressure	bar	0.2
Active area	cm²	20.25

MEA	An / Ca loading [µg/cm²]
A	50 / 400
B	25 / 400
C	15 / 400

Experimental
Setup and testing procedure



Voltage decay

Anode bubbler refills → oxygen in water recovers voltage

Concentrations

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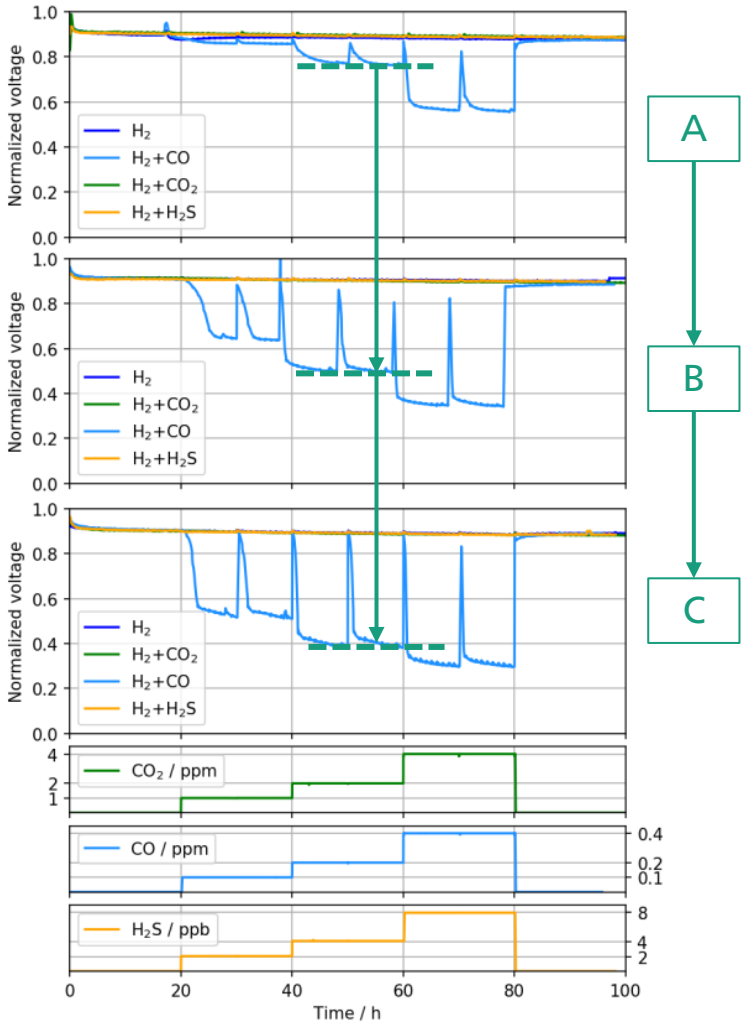
Effect of impurities on ultra-low Pt anodes
Contaminant and concentration variation

- Voltage losses observed
  - Carbon monoxide: increase from 8 to 40 to 50%
    - For comparison: ~5% @ 110 µg/cm² Pt/C [3]



[3] Matsuda, Y. et al. (2016). Adsorption behavior of low concentration carbon monoxide PEMFC anodes for automotive applications. *Journal of Power Sources*, 318, 1-8.

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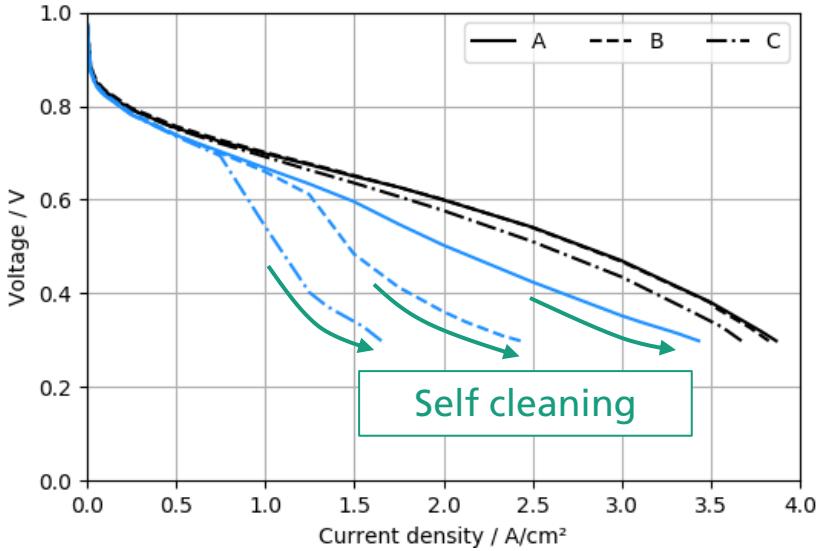
Carbon monoxide poisoning in detail
Effect of 0.2 ppm CO on UI-curves

- Polarization curves
  - Comparable using neat H_2 (black curves), MEA C slightly lower
  - Performance drops for lower anodic loadings (blue) due to CO adsorption (1)
- Self cleaning effect (2+3) at higher current densities, when anode overpotential reaches CO reduction potential ~0.55V [4], [5]



$$Pt + CO \Leftrightarrow Pt - CO \qquad (1)$$

$$Pt + H_2O \Leftrightarrow Pt - OH + H^+ + e^- \qquad (2)$$

$$Pt - OH + Pt - CO \Leftrightarrow CO_2 + H^+ + e^- + 2Pt \qquad (3)$$

[4] Wagner, N. et al. (2003). Change of electrochemical impedance spectra during CO poisoning of the Pt and Pt--Ru anodes in a PEMFC. *Electrochimica Acta*, 48, 3899-3907.

[5] Iezzi, R. et al. (2018). CO Tolerance and Stability of PEMFCs with Nafion® and Aquivion® Membranes and Mo-Based Anode Electrocatalysts. *Brazilian Chemical Society*, 29 (5), 1094-1104

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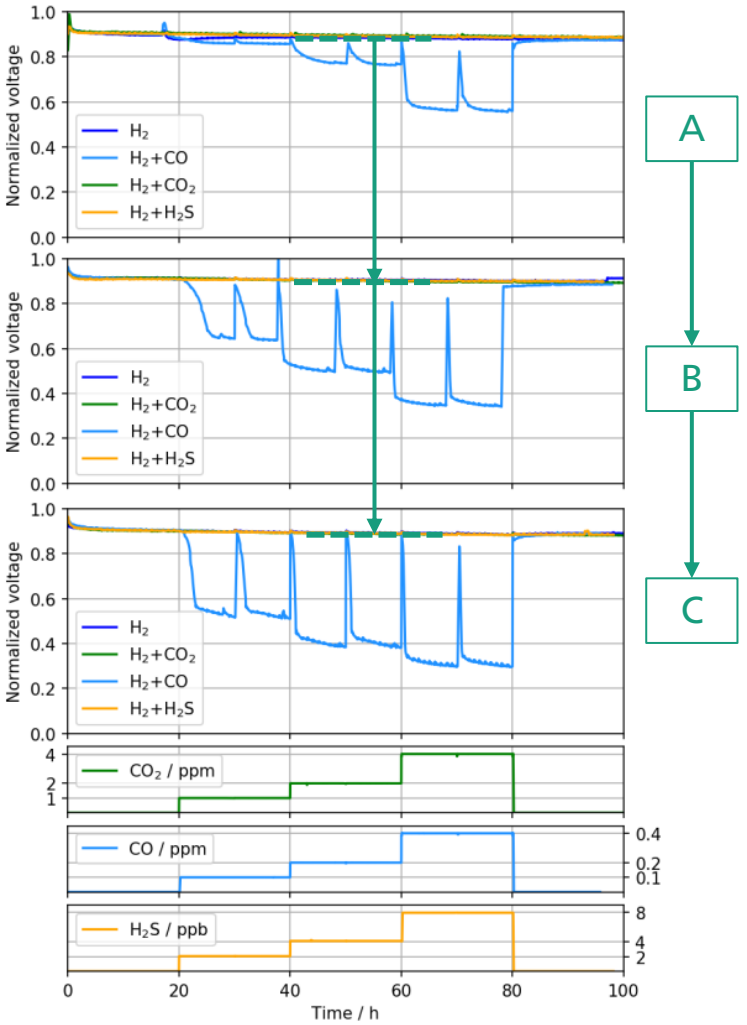
Effect of impurities on ultra-low Pt anodes
Contaminant and concentration variation

- Voltage losses observed
  - Carbon monoxide: increase from 8 to 40 to 50%
  - Hydrogen sulfide: no loss visible on these graphs
    - Literature: 30 mV loss after 100 h @ 100 µg/cm² Pt/C [6]



[6] Fuel Cell Technologies Office (2016). Hydrogen fuel quality specifications for PEMFCs in road vehivles, *U.S. Department of Energy*, DOE (p. 22, data provided by T. Rockward)

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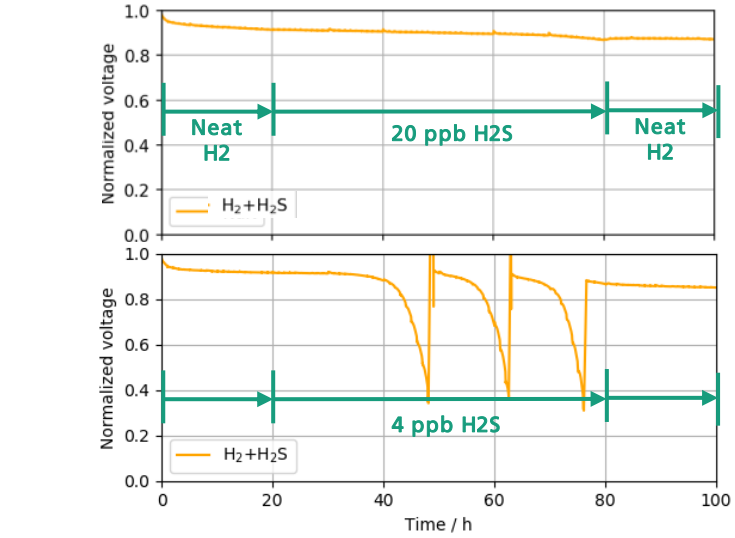
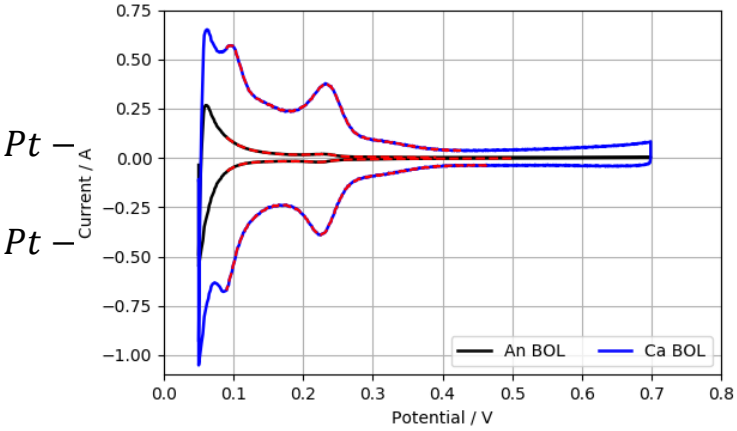
Hydrogen sulfide poisoning in detail

Effect of H_2S on 50 and 15 µg/cm² anodes

- H_2S poisoning cumulative with dissociative adsorbtion on Pt (4)
  - MEA A: ~2% loss @ 20 ppb a. 60h
  - MEA C: U-break downs @ 4 ppb
- Recovery of sulfur poisoning via
  - Oxidation (5+6) using anode CVs up to ~1.4 V [7], [8]
  - Shut-down and start-up, too?

	Anode ECSA [m^2/g_{Pt}]
BOL	65
After H_2S	47
After SD+SU	56





$Pt -$ (5)

$Pt -$ (6)

[7] Kakati, B. et al. (2016). Using corrosion-like processes to remove poisons from electrocatalysts: chemically regenerate irreversibly poisoned PEMFCs. *Electrochimica Acta*, 222, 888-897.

[8] Lopes, T. et al. (2011). The effects of hydrogen sulfide on the PEMFC anode catalyst: H2S--Pt/C interaction products. *Journal of Power Sources*, 196 (15), 6256-6263.

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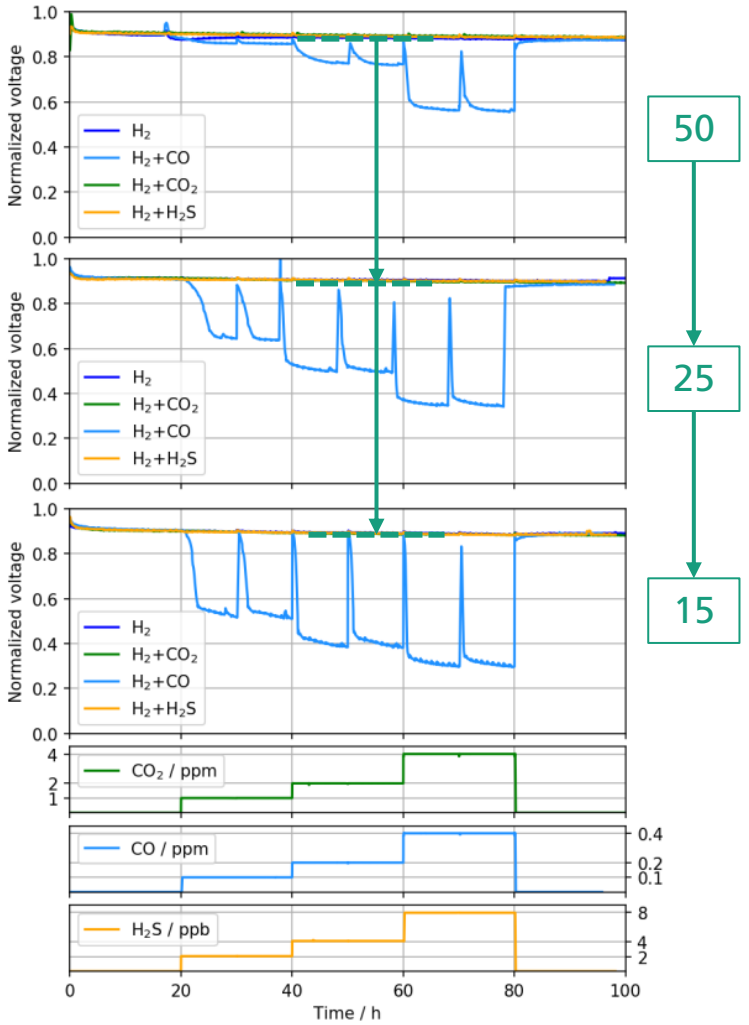
Effect of impurities on ultra-low Pt anodes
Contaminant and concentration variation

Anode loading [µg/cm²]

- Voltage losses observed
  - Carbon monoxide: increase from 8 to 40 to 50%
  - Hydrogen sulfide: visible at higher doses
  - Carbon dioxide: no loss visible → no reverse WGSR (7) at such low concentrations

$$CO_2 + 2Pt - H \Leftrightarrow Pt - CO + H_2O + Pt \qquad (7)$$

  - U-loss typically observed at higher CO_2 concentrations



[9] Jansen et al.- Carbon dioxide poisoning on proton exchange membrane fuel cell anodes, presented at *Fuel Cells Science and Technology* in Munich, 2004

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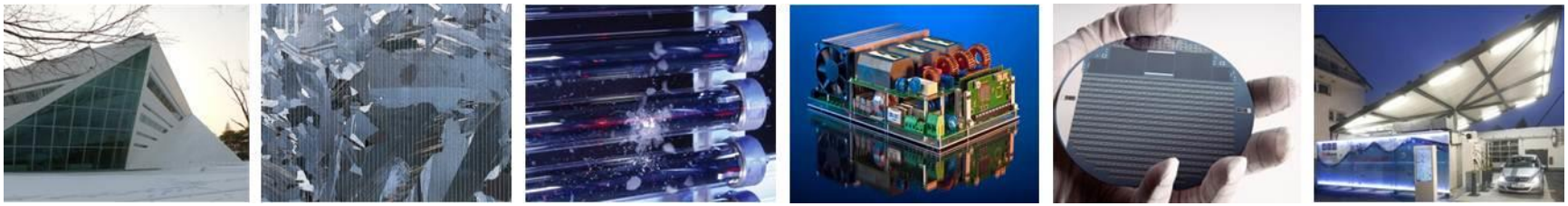
Summary

- Carbon monoxide severely poisons ultra-low loaded anodic CLs
  - ~50% performance drop for 15 µg/cm² pure Pt/C at ISO concentration (0.2 ppm)
- Hydrogen sulfide poisoning is sluggish and shows after many hours
  - Voltage break-downs in galvanostatic mode in shorter times with lower loaded anodic catalyst layers
  - Further research on „gentle“ recovery due to cell relaxation
- Carbon dioxide does not show poisoning character as it does for higher concentrations
- Contaminant tolerant catalyst materials are likely needed for ultra-low loaded anodic CLs

Thank you for your attention!



This project was funded by the Bundesministerium für Wirtschaft und Energie via. grant agreement: 03ET6098A.

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Bundesministerium für Wirtschaft und Energie

Projektträger Jülich Forschungszentrum Jülich

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Background

Hydrogen Quality Specification ISO 14687-2 (SAE J2719)

Species		Concentration max. [ppm]	Eff				
			Rev. FV	Irrev. FC			
Water	H2O	5					
Hydrocarbons	-	2	X				
Oxygen	O2	5				X	1.1 – 5.7
Helium	He	300					
Nitrogen/Argon	N2/Ar	100					
Carbondioxide	CO2	2	X		X		
Carbonmonoxide	CO	0,2	X				
Total sulfur compounds	-	0,004		X	X	X	0.000076 – 0.00033
Formaldehyde	H				X	X	<0.001
Formic acid	HC				X	X	<0.005
Ammonia	N				X	X	<0.001
Halogenated compounds					X	X	0.013 – 0.05
Particles	-	1 mg/kg			X	X	

Vernachlässigbar, Einfluss konnte meist erst bei höheren Vol.% festgestellt werden. Aber was ist mit ultra-low Pt-Beladungen?

Zellspannung 30-70 mV (~6-13%) Verlust bei 100 µg/cm² Pt/C [Rockward, DOE Report 2016 on H2 Quality Specs]

Zellspannung 29-50 mV (~5-8%) Verlust bei 50-110 µg/cm² Pt

[Matsuda, JPS 2016; 318: 1-8

Perez, JPS 2014; 258: 122-128]

HyCoRa – Hydrogen Contaminant Risk Assessment, Deliverable 3.2 Measurement of hydrogen quality variation at various HRS with different fuel feedstock, Author: Thor Anders Aarhaug (SINTEF), 30.9.2015