Nedstack
PEM FUEL CELLS
To be sure.

PEMFC Lifetime and Durability an overview

Thessaloniki, September 21 2011

Frank de Bruijn

We are dedicated to designing and producing the best value for money PEM fuel cell stacks in the market.

PEMFC in real life

2007
Passenger vehicle: 2,375 hrs operated on 1 stack

Daimler in DoE programme

2011
City Bus > 10,000 hrs in operation on original stack

UTC AC Transit

2011
Base load > 11,000 hrs in operation on original stack

Nedstack at Akzo Nobel

Technical requirements differ (1/2)

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	Automotive	Bus Fleet	Backup power	Power generation
System Cost per kW	$ 30	$50 - $70	$1000 - $2000	$1000 - $2000
Stack Power density kW/l	2	0,5 – 2	Not relevant	Not relevant
Start up time	5 s at 20°C 30 s at -20°C	300 s at 20°C 300 s at -20°C	Immediate	< 30 min.
Hours in operation	5,000 incl. start/stops	18,000 incl. start/stops	1500 - 4000 incl. start/stops	40,000 – 90,000

Technical requirements differ (2/2)

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	Automotive	Bus Fleet	Backup power	Power generation
Operating cell voltage	0.5 – 0.7 V	0.6 – 0.7 V	0.6 – 0.65 V	0.7 V
Current density	> 1 $A.cm^{-2}$	0.6 – 1 $A.cm^{-2}$	> 1 $A.cm^{-2}$	< 0.6 $A.cm^{-2}$
Voltage cycles (OCV – load)	45,000* - 1,200,000	>12,000* - 1,800,000	1000 - 4000	< 100
Cold starts	> 15000	> 4000	1000 - 4000	< 100
Freezing	Yes	Yes	Yes	Exceptional
Fuel Quality	High	High	High	Depends on source

* Assuming optimized hybridization

Gap between present status and commercialization


	Automotive	Bus Fleet	Backup power	Power generation
System Cost per kW	Too high	Too high	OK	Depends on feed-in tariff (> 10 ct/kWh)
Stack Power density kW/l	OK	OK	OK	OK
Start up time	OK	OK	OK	OK
Hours in operation	Projections OK for presently used components	Projections OK for presently used components	OK	OK, but economics improve with further extension

Work ahead

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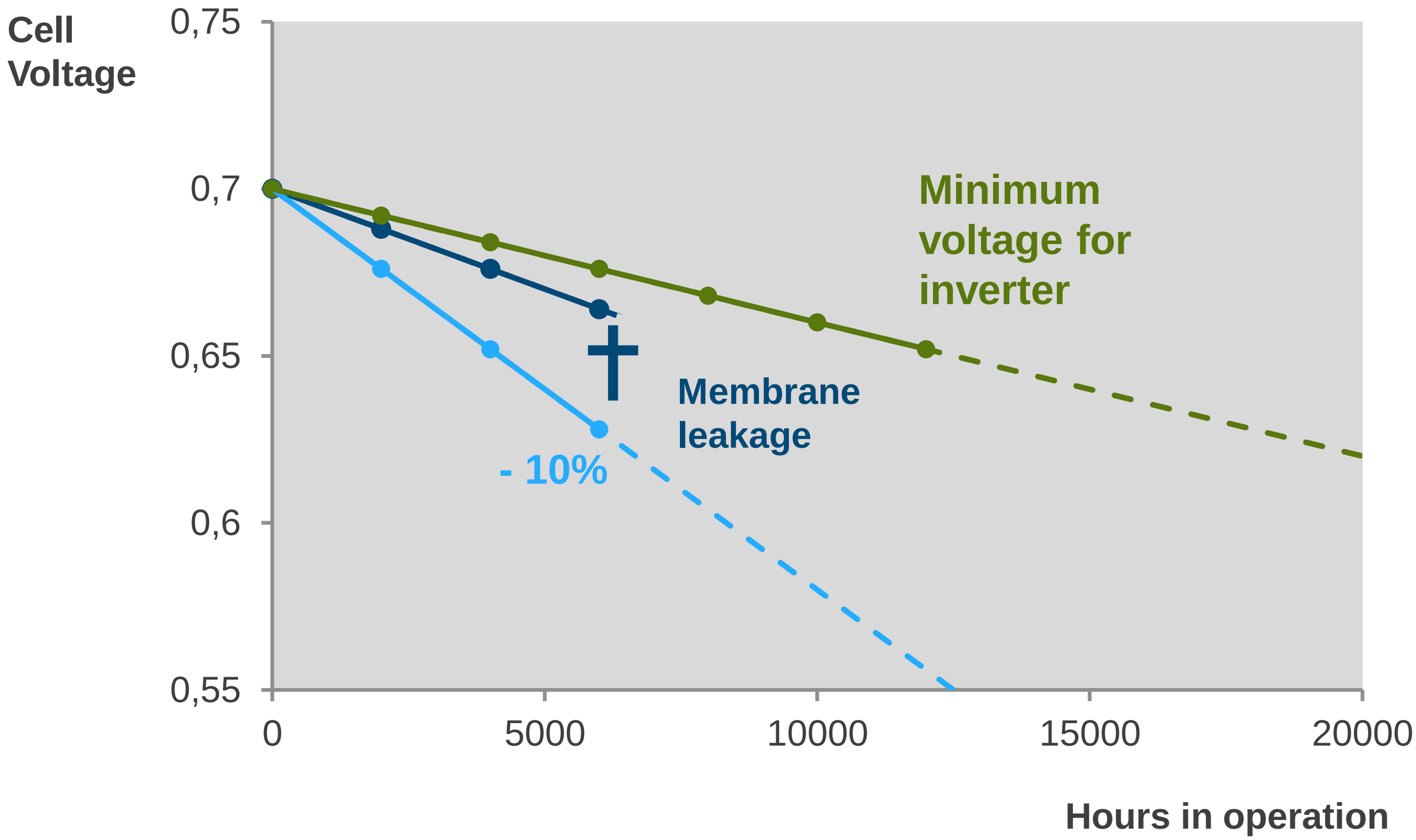
Transportation
Reduce costs while maintaining achieved lifetime and durability

Demonstrate lifetime on stack and system level

Stationary
Increase lifetime of stacks to > 40,000 hours without increasing costs

What determines end of life ?



From the laboratory to real life

Laboratory testing

- Well defined load profile
- Well defined gas flows and humidity level
- Well defined temperature
- Clean hydrogen and air, or well controlled added contaminants
- Easy to collect run hours (24/7)
- "Academic" definition of end-of-life

versus

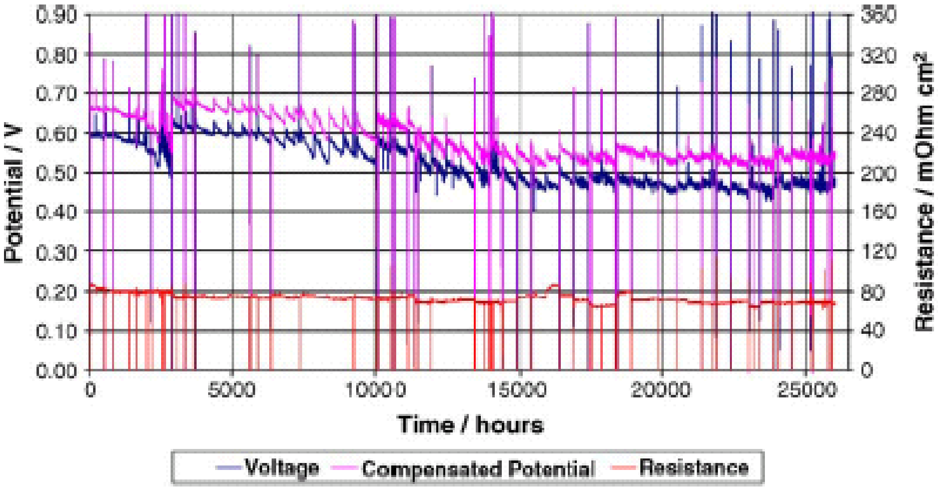
Real life testing and use

- Varying load profile, user specific
- Limited control of gas flows and humidity level
- Frequent temperature variations
- Hydrogen and air quality vary in Time and are not logged
- Data collection can take many years
- Economic decision for end of life or cell failure

There is no dominant degradation mechanism

Conditions:
load operated at constant current,
800 mA cm^{-2} for the entire 26,300 h life test.
Cell temperature 70°C.

Air: 2.0 x stoichiometry, ambient pressure, 100% RH.
Hydrogen: 1.2 x stoichiometry, ambient pressure and 100% RH.



Observed MEA changes:

- Loss of water removal efficiency
- Detoriation of seals
- Loss of Pt surface area in cathode
- Thinning of membrane
- Increased hydrogen cross-over

1) S.J. C. Cleghorn et al. J.Power Sources, 2006, vol158, 446

PEMFC component durability

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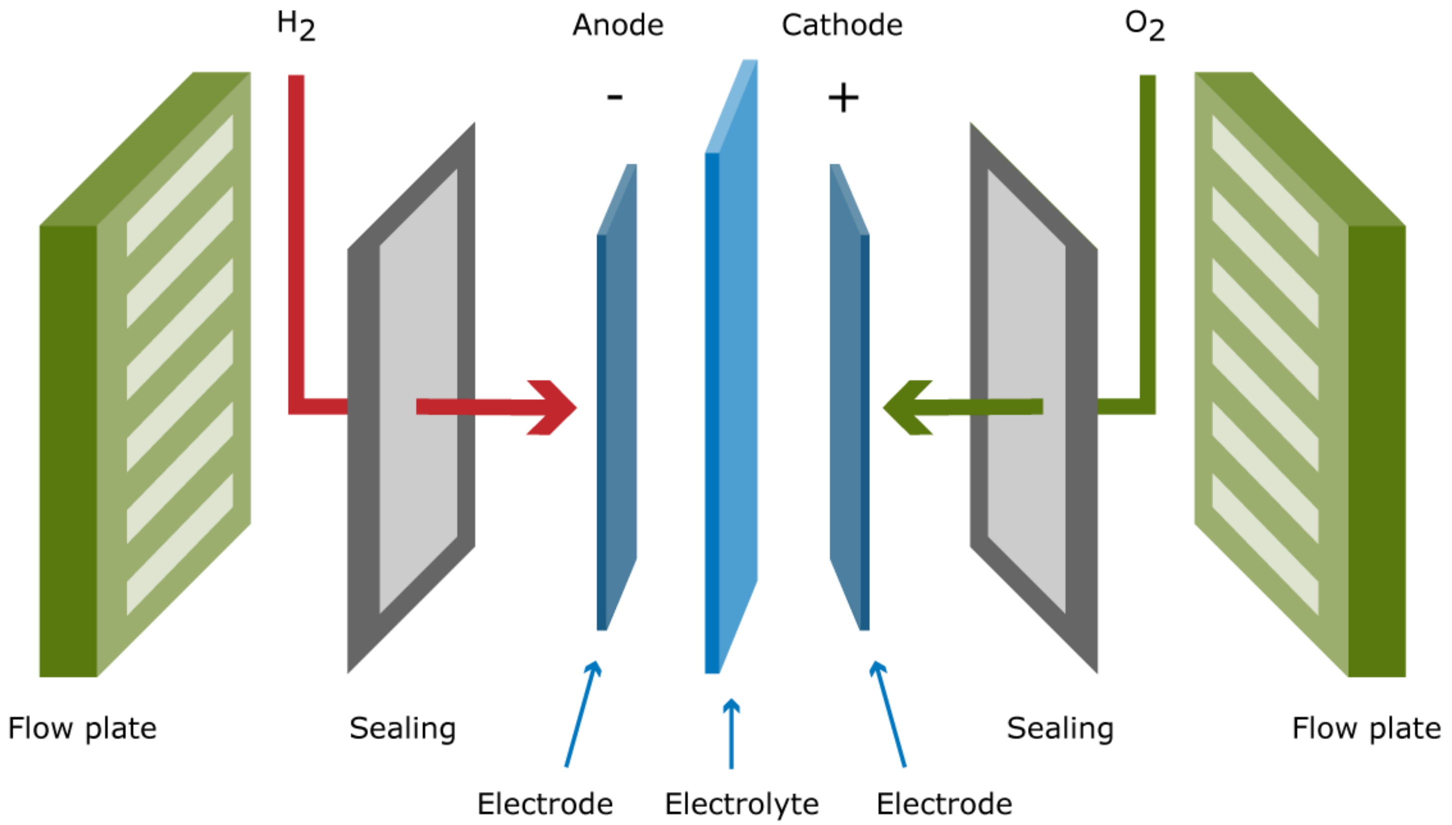
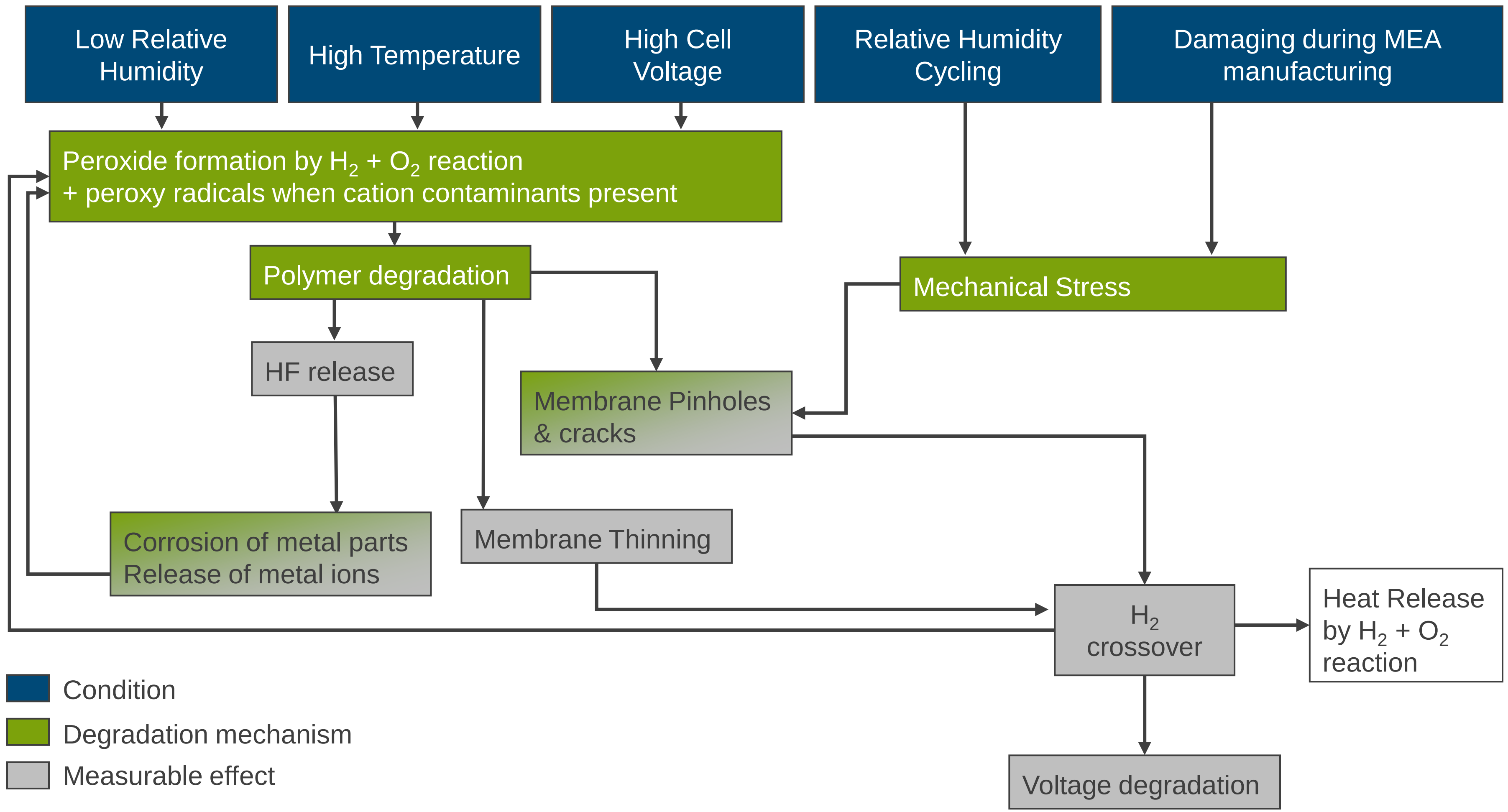
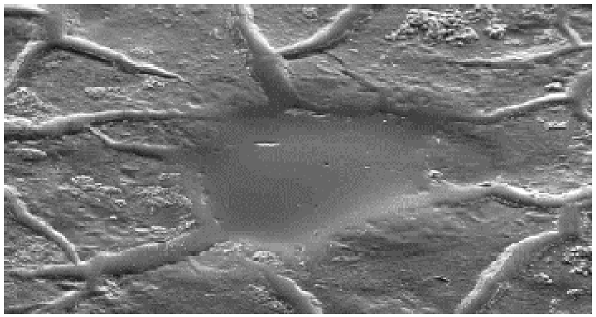


Membrane degradation in PEMFC

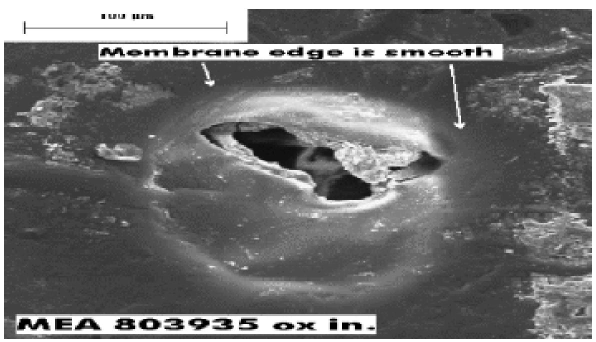


F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, Fuel Cells, 2008, vol8, 3

PEMFC membrane thinning and rupture



Membrane is thinning in discrete areas



Reduced physical strength – leads to rupture

Reinforced membranes have proven to prevent crack propagation, and decrease interfacial stress between membrane and electrodes

C. Stone and G. Calis, Fuel Cell Seminar 2006, p265 - 267

Wrinkled non-reinforced PFSA membrane

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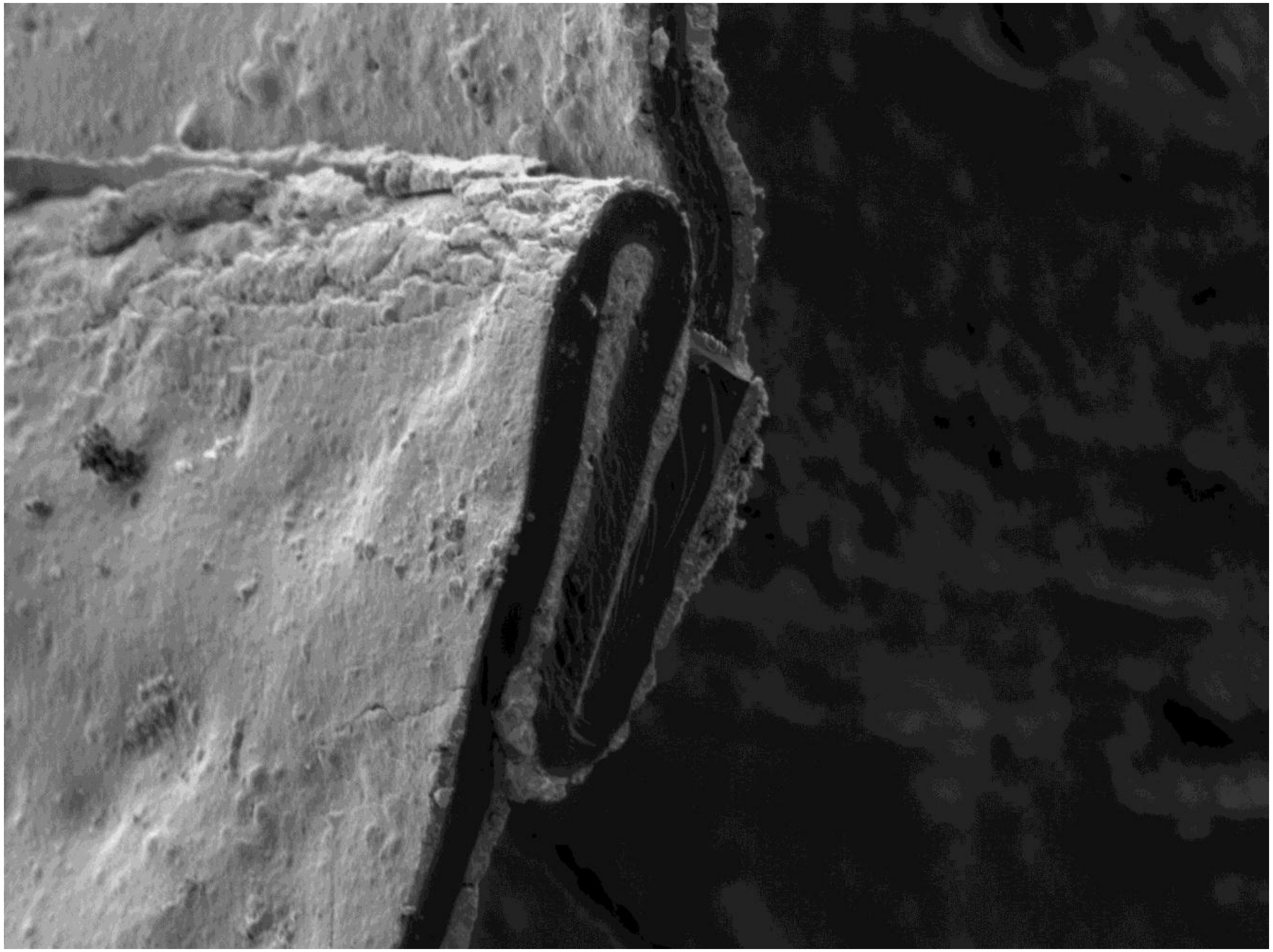
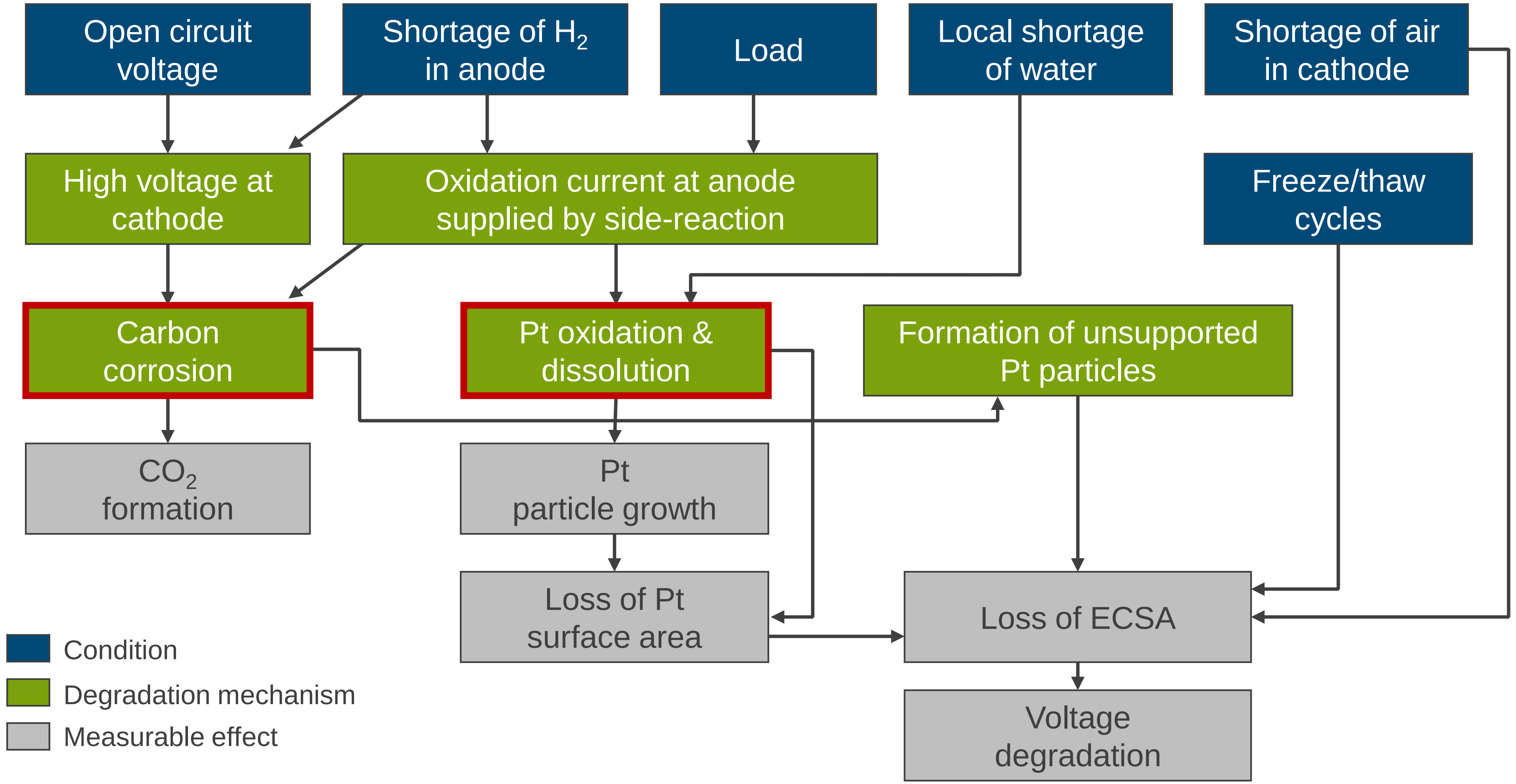


Scanning Electron Microscope image of a wrinkle in the catalyst coated membrane

Electrode degradation in PEMFC



F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, Fuel Cells, 2008, vol8, 3

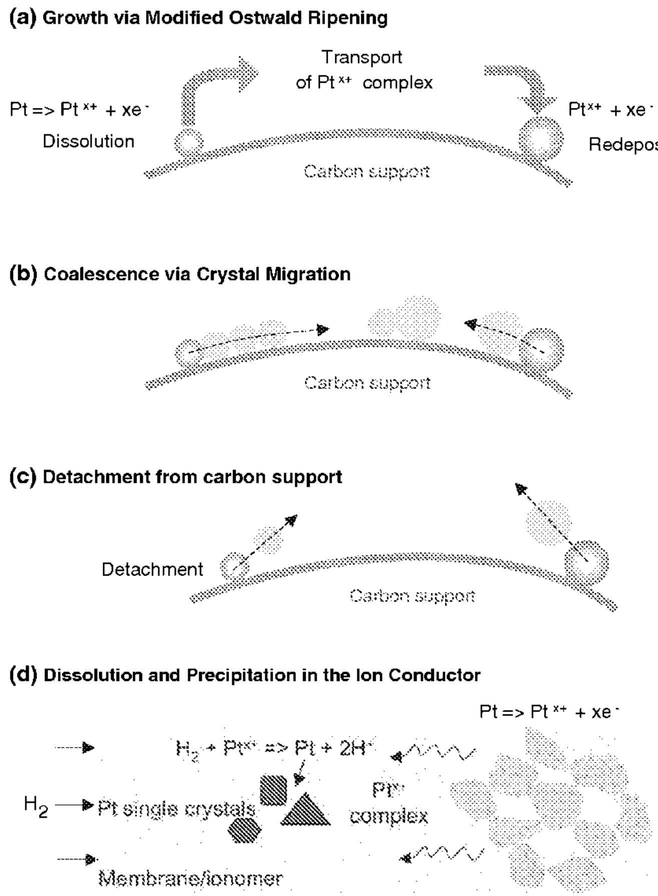
PEMFC electrode issues
Degradation: Pt

Pt nano-particles (3-4 nm) are not stable
- Coarsening
- dissolution

Loss of active surface area
- increased kinetic losses

Accelerating factors:
- elevated potential
- varying potential (oxide growth/dissolution)
- support corrosion

Mitigation:
- low humidity
- large initial particles



Shao-Horn, Top. Catal. 46 (2007) 285

PEMFC electrode issues

Degradation: Carbon

Surface oxidation	$C + H_2O \rightarrow CO_{surf} + 2H^+ + 2^e$	E > 0.3 V vs RHE
Oxidation to CO_2	$CO_{surf} + H_2O \rightarrow CO_2 + 2H^+ + 2^e$	E > 0.8 V vs RHE, Pt catalysed

Sluggish kinetics but accelerated by potential > 1.2 V

- Cathode: During start stop or local fuel starvation
  - H2/air front at anode from air leaching-in or cross-over
- Anode: During fuel starvation (cell reversal)

Monitor: CO2 in exhaust

- Effect: electrode thinning, loss of active area, increased hydrophilicity
- Mitigation: more graphitic carbon → less surface area, fewer Pt particles per weight unit C

Pt dissolution / re-deposition

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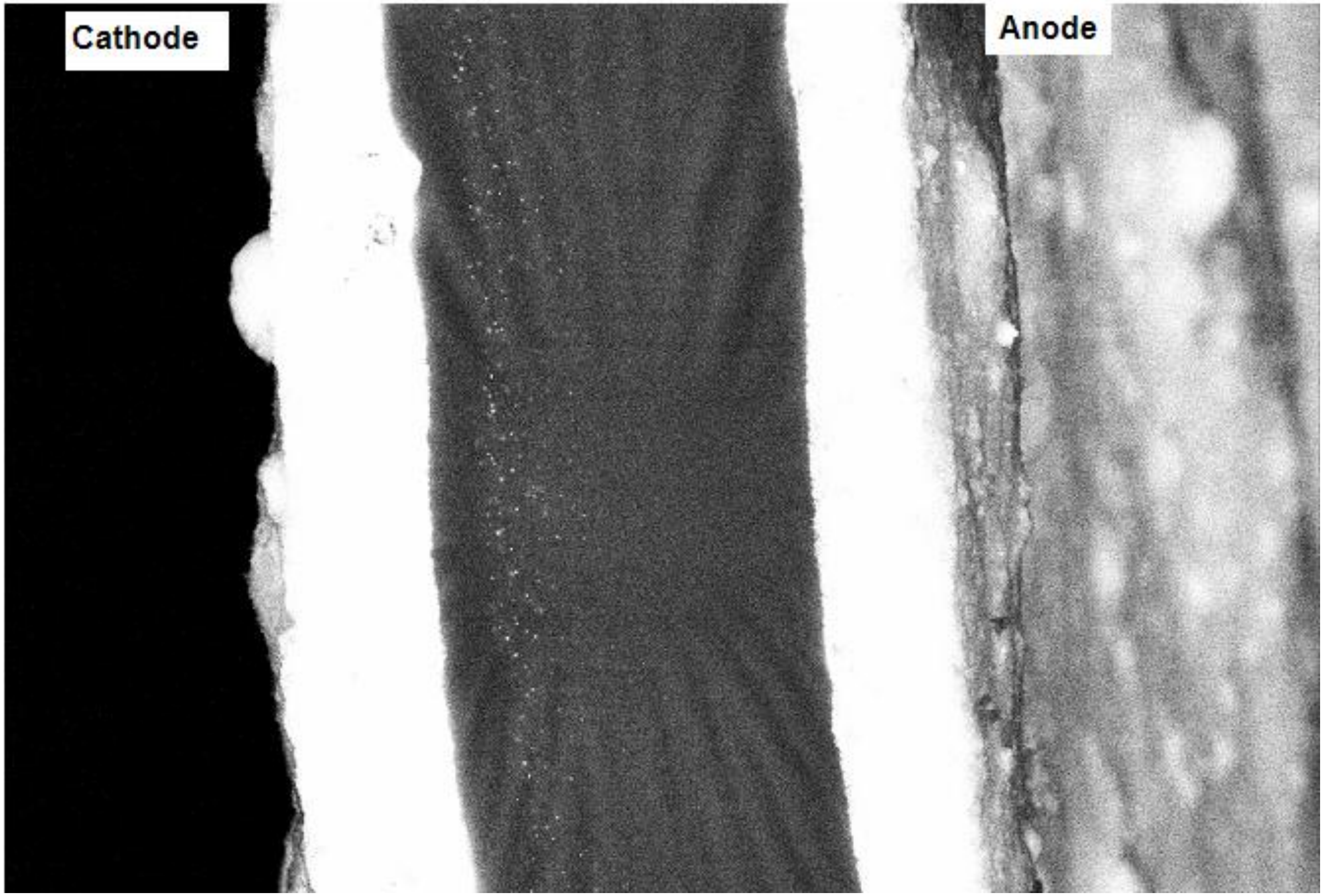
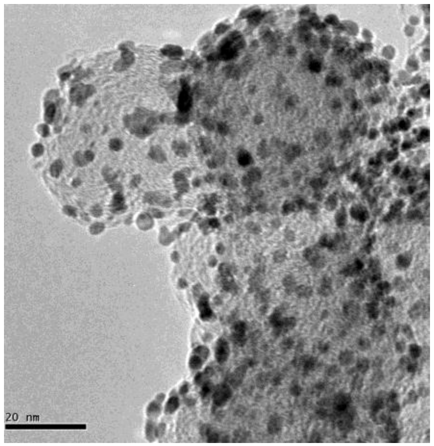
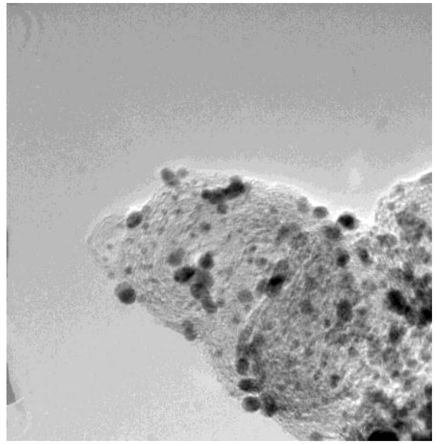


SEM in back scatter mode:
Cross section of MEA;
Visible is the band of light Pt spots near the cathode catalyst layer, as confirmed with EDX analysis

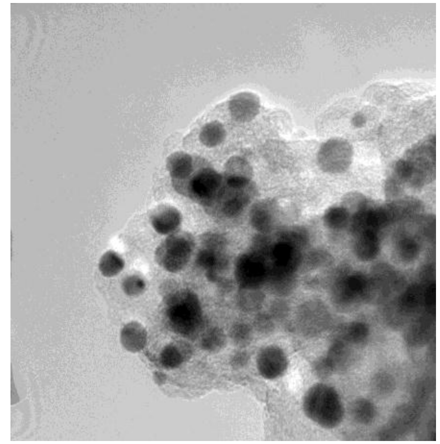
Pt dissolution / re-deposition upon voltage cycling



0 x



10000 x



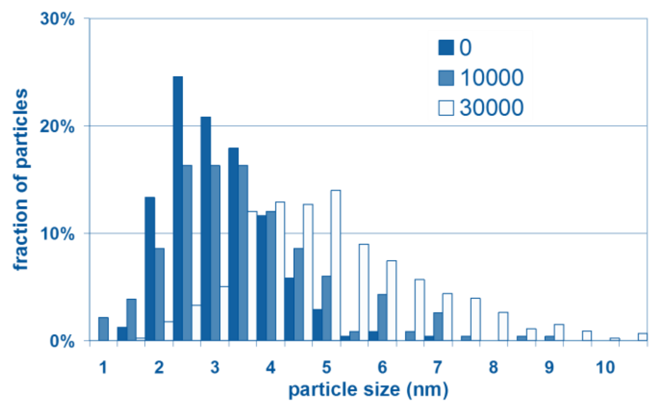
30000 x

Pt particle coarsening

d 0 2.4 nm - SA loss 0%

d10000 3.8 nm - 38%

d30000 5.8 nm - 55%



F. A. de Bruijn, V.A.T. Dam, G.J. M. Janssen, R. C. Makkus, 216th ECS meeting, Vienna, Oct 2009.

Contaminants - anode

Large scale production of H_2 : quality can be best controlled;
Gas will be dry, low CO content, but there is a relation between purity and cost per kg H_2 (including infrastructure cost)

Local production of H_2 : quality is less controlled;
Gas will contain CO, NH_3 , aromatics in the ppm range
CO_2, N_2, CH_4 on %-level

Local production of H_2 with electrolyzers: primary product is saturated with water. Other contaminants that can be present: NH_3, Formaldehyde, Formic acid, Sulfur

$SO_2 \rightarrow$ can be tolerated to ~ 10 ppb
$H_2S \rightarrow$ can be tolerated to ~ 8 ppb
HCHO $\rightarrow$ can be tolerated to ~ 0.6 ppm
$CH_4 \rightarrow$ can be tolerated to > 1000 ppm

Composite Data Products, http://www.nrel.gov/hydrogen/cdp_topic.html#performance

Contaminants - cathode

$CO \rightarrow$ oxidised by O_2 ; can be tolerated to ~ 250 ppm

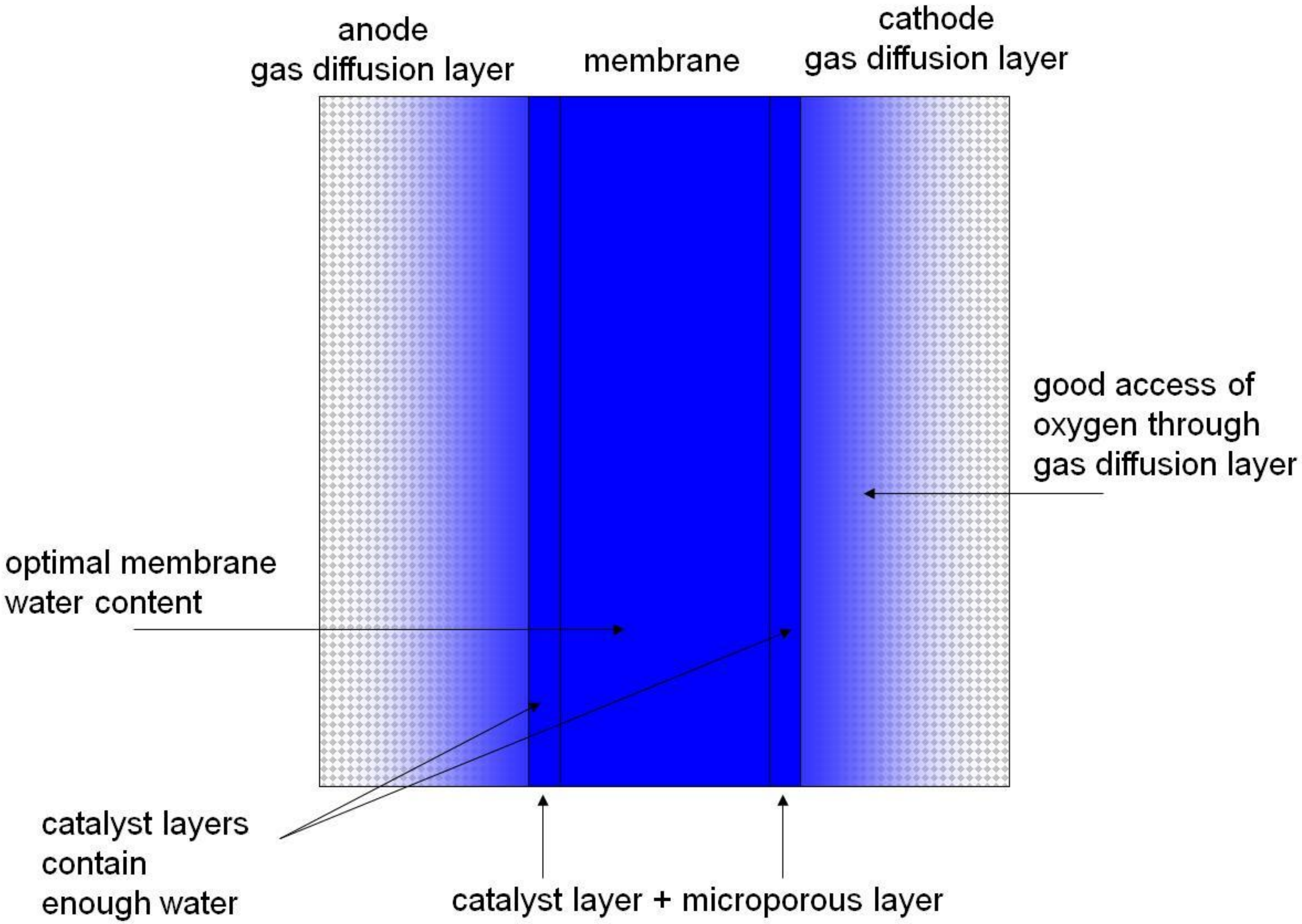
$NO_2 \rightarrow$ partially oxidised by O_2 ; can be tolerated to ~ 3 ppm

$SO_2 \rightarrow$ partially oxidised by O_2 ; can be tolerated to ~ 2 ppm

$NH_3 \rightarrow$ oxidised by O_2 ; tolerance level unclear

Narusawa, K, Myong, K, Murooka, K, & Kamiya, Y (2007) A Study Regarding Effects of Proton Exchange Membrane Fuel Cell poisoning due to impurities on fuel cell performance, SAE Technical Paper Series, pp. 2007-01-0698

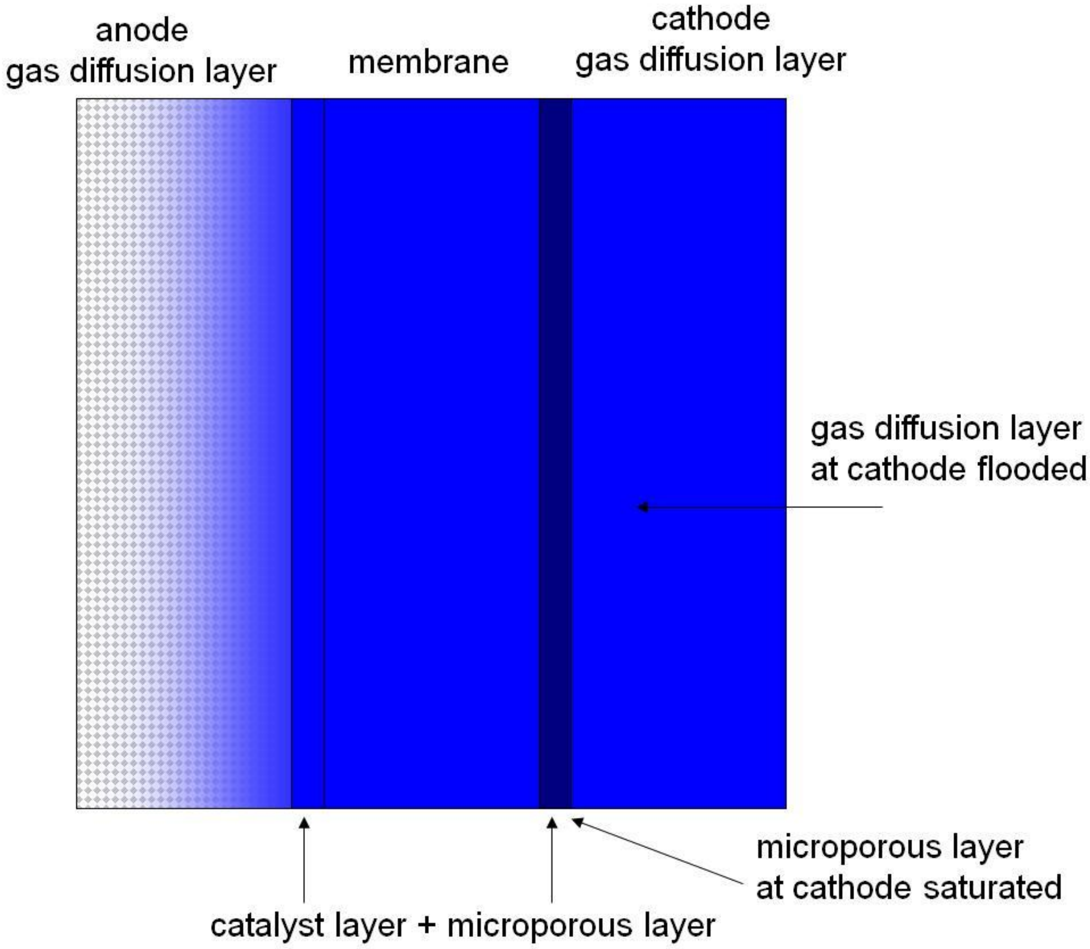
Gas Diffusion Media are extremely important for the performance of the PEMFC



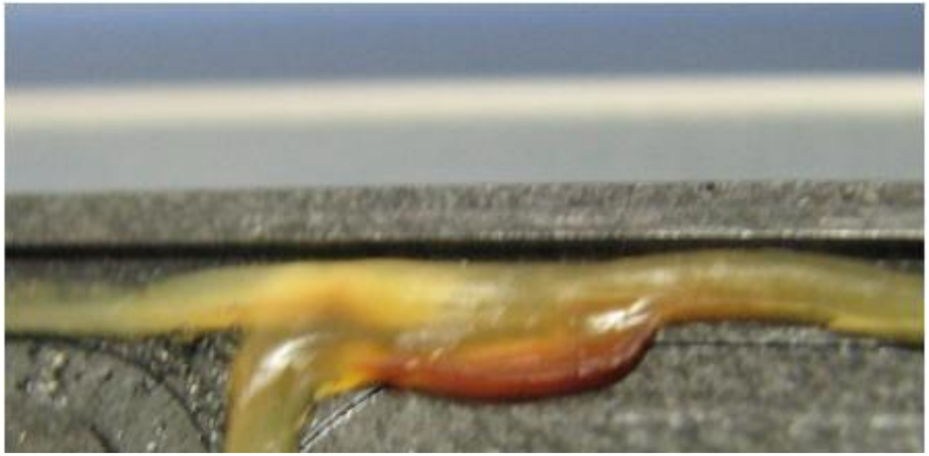
Loss of hydrophobicity can have a large impact on water management

Carbon oxidation in microporous layer similar to in electrodes
- oxidation
- corrosion

Conditions:
- elevated potential
- fuel starvation (anode & cathode)



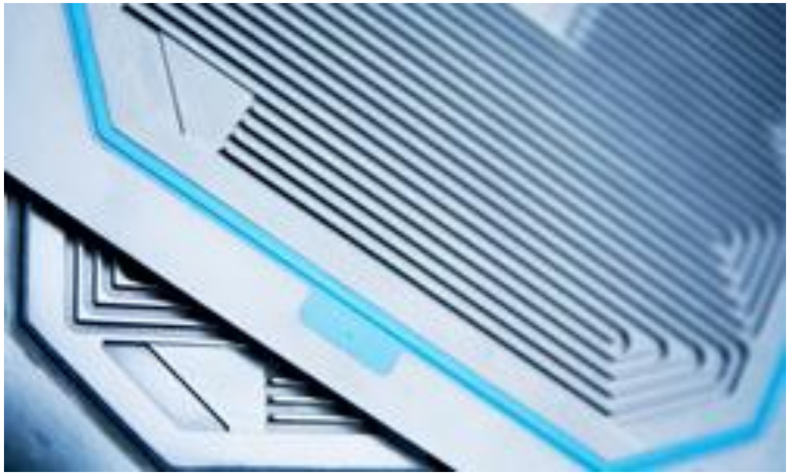
Seal degradation in PEMFC



- Seals prevent external and internal leakage
- Set compression force on MEA
- Materials choice is crucial for preventing seal degradation
- Processibility is more important than materials costs

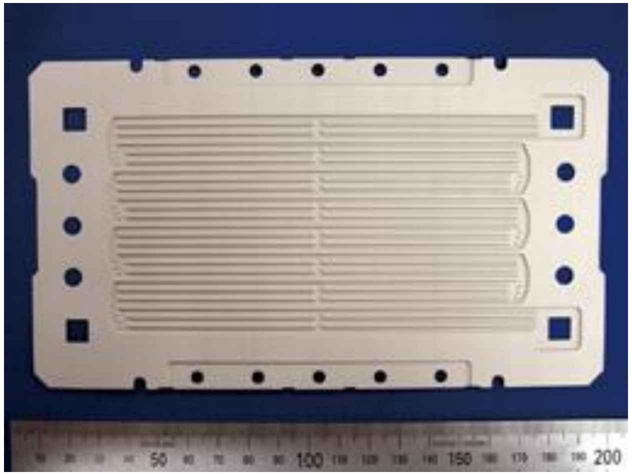
PEMFC cell plate issues

Carbon composite plates



- Mostly applied in fuel cells for long life applications where power density is not crucial
- Under most fuel cell conditions, no relevant degradation issues (plates are more durable than GDM and electrodes)

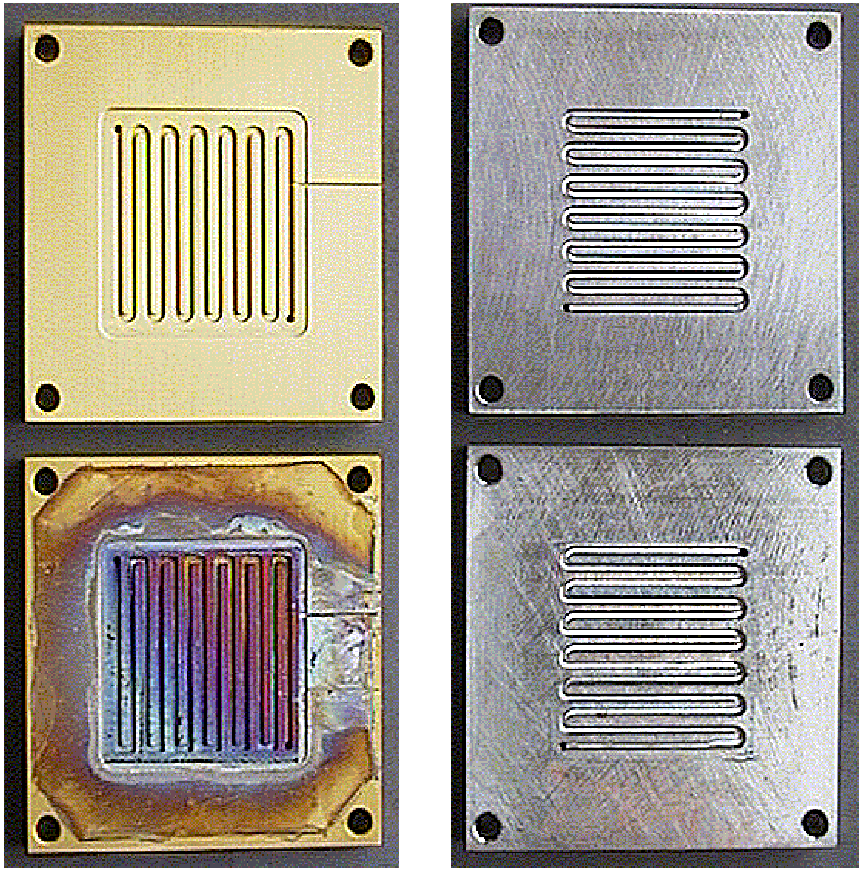
Metal plates



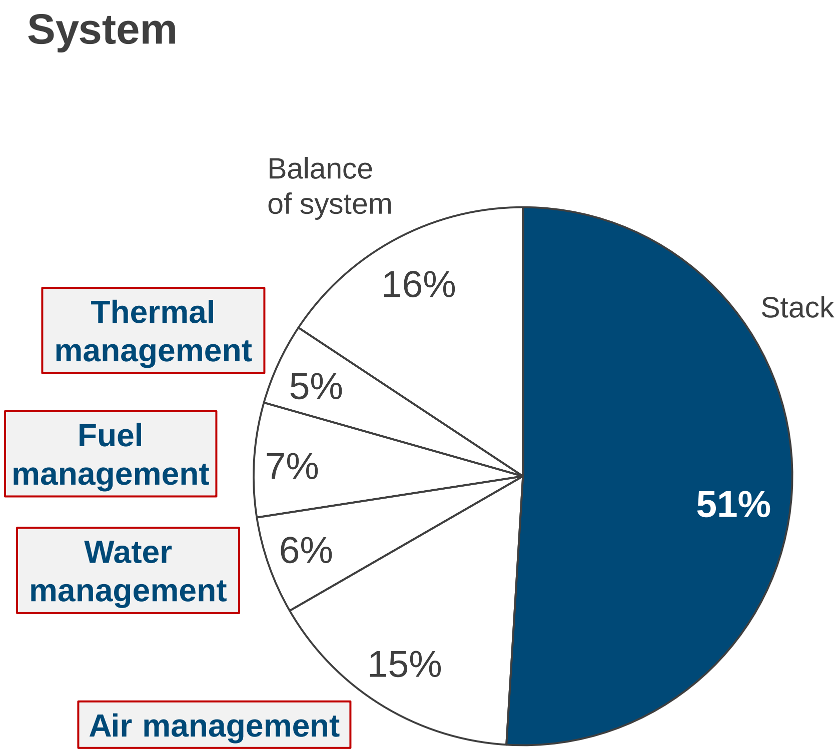
- Applied by automotive OEM’s for obtaining very high stack power density (~ 2 kW/l)
- Under fuel cell conditions, only a very limited number of materials are suitable

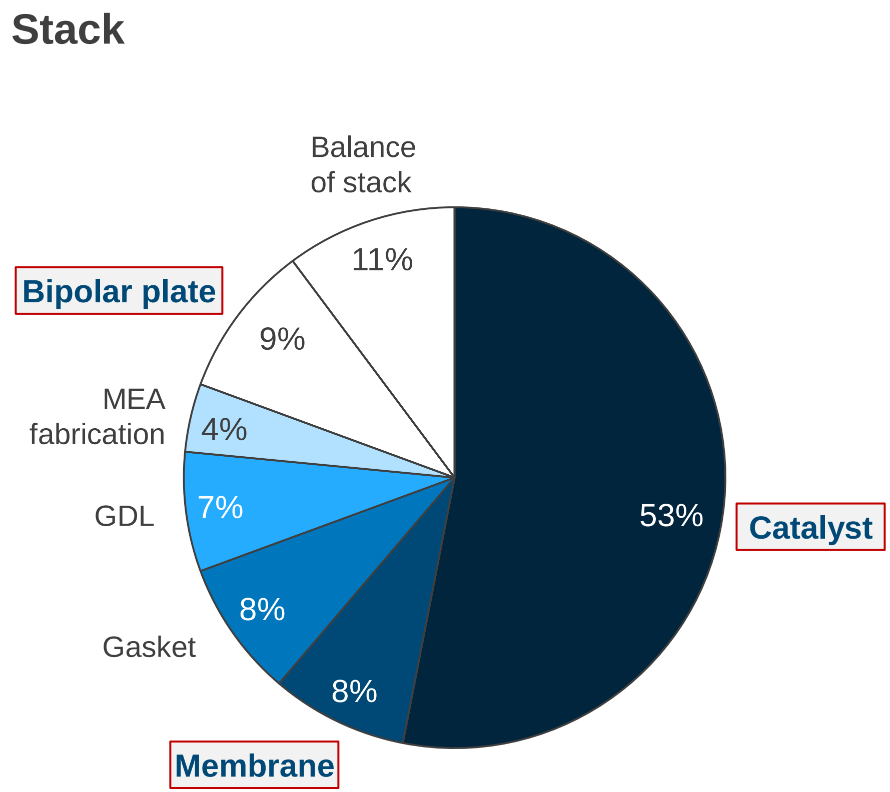
Flow plate degradation in PEMFC

	Titanium Nitride	316 L
Before fuel cell operation		
After fuel cell operation		



Driving the cost down can jeopardize achieved durability and lifetime





Source: DoE

Durability is especially dependent on the MEA

MEA components	Main degradation mechanism	Direct Effect	Most stressing Icondition[2]
Electrode	Loss of Pt surface area Carbon corrosion	Lower output over full I range	High cell voltage Contamination Starvation
GDL	Loss of hydrophobicity	Increased flooding, lower output at high I Instability	High cell voltage Starvation
Membrane	Membrane thinning, rupture, pinholes	Gas crossover, external leaks: lower output at low I	Low RH High T RH cycles
Seal	Loss of compression characteristics	Internal and external leakage Poisoning of MEA	Direct contact with electrolyte
Flow plates	Composites: Corrosion	Flow field detoriation, leading to instability	Extreme oxidative potentials
	Metal based: Corrosion (anode) Passivation (cathode)	Membrane resistance Contact resistance	High cell voltage High cell voltage

Our PEM Power Plant at AkzoNobel Delfzijl has proven durability in practice

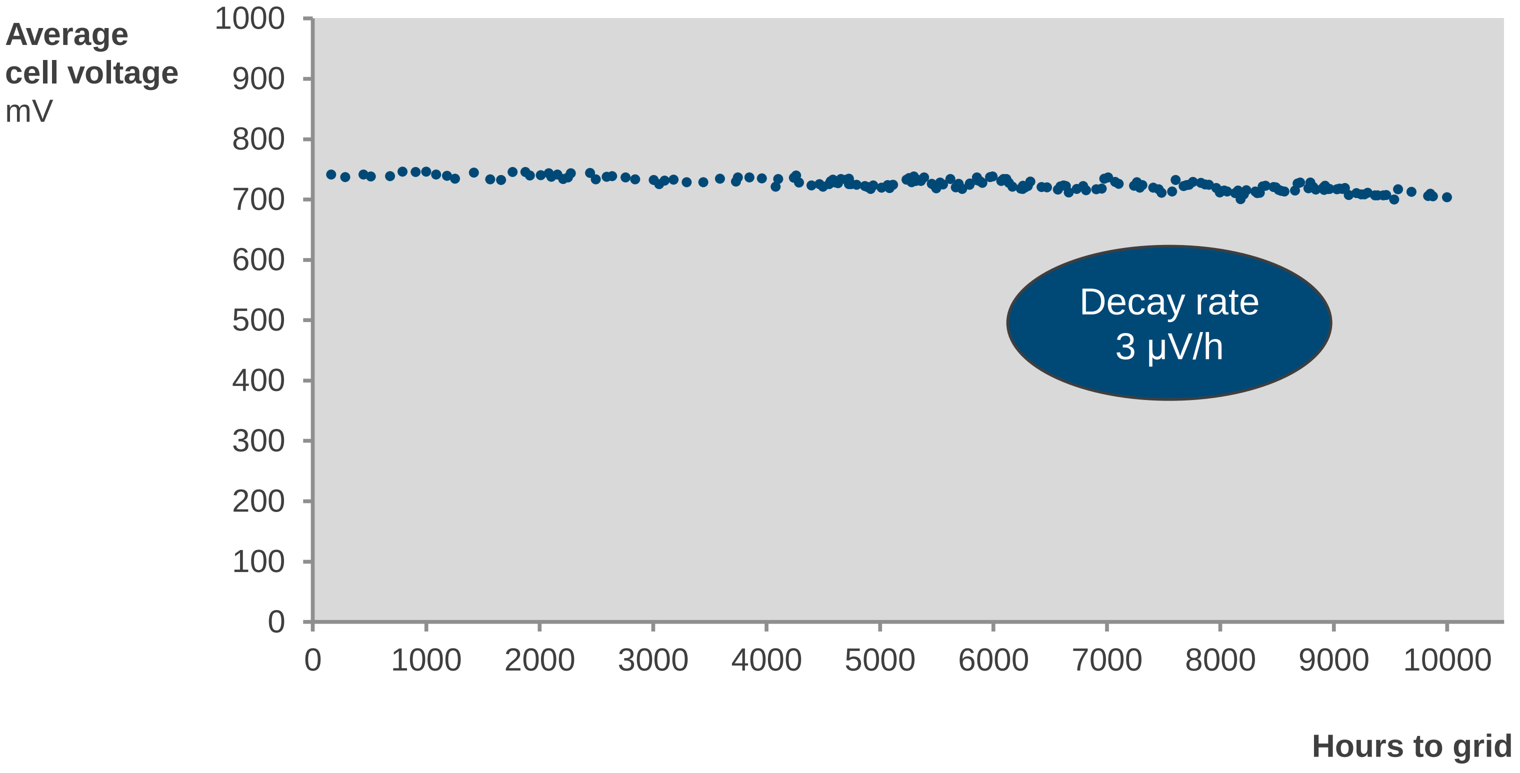
23,000 hours on the grid:

- Up time since Jan 2011 > 90%
- Low maintenance costs
- Stacks has proven lifetime > 11,000 hrs

Since start-up:
99 stacks
7425 MEAs

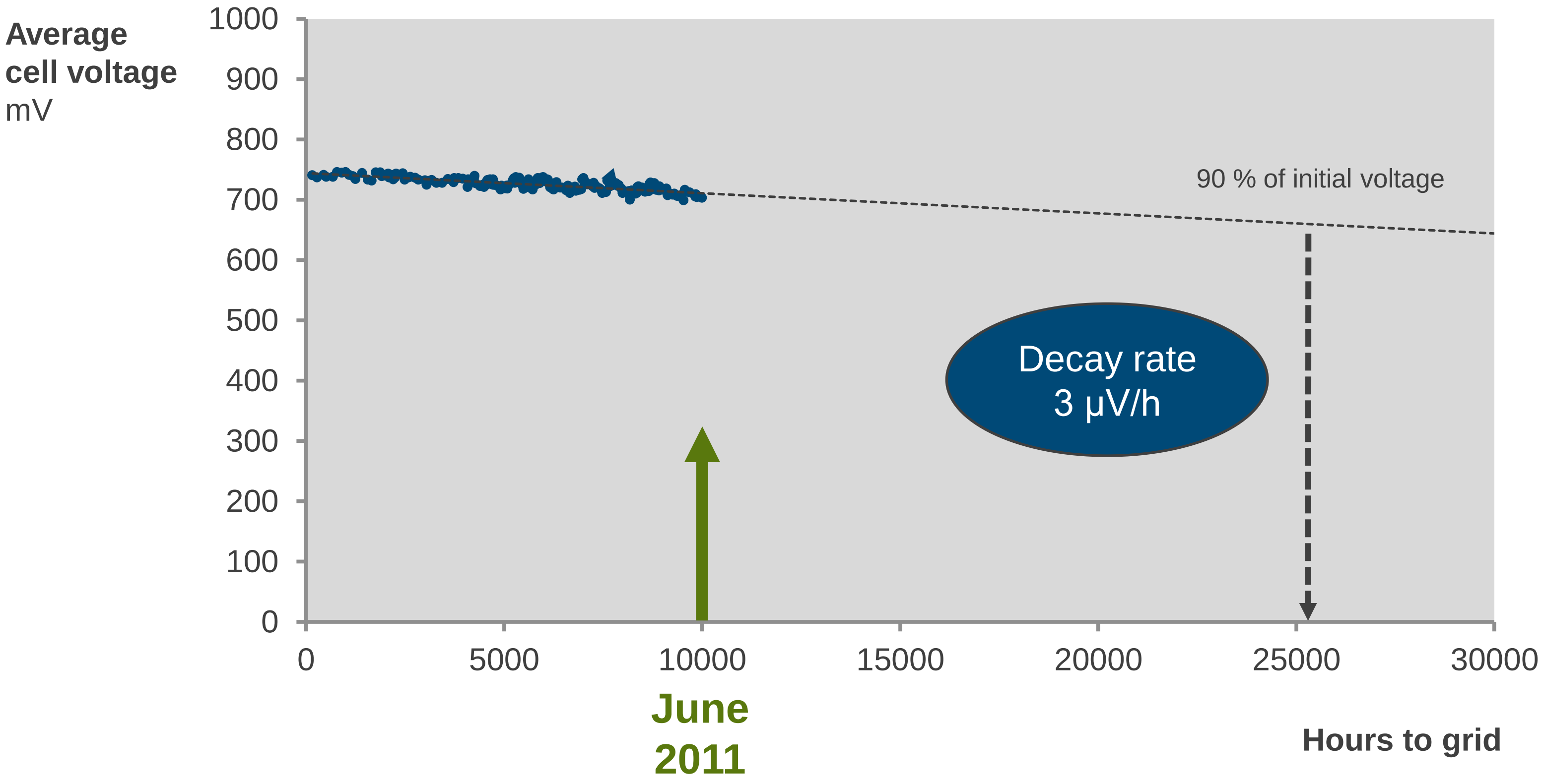
Nedstack has proven stack lifetime of 10,000 hours

Actual measurements at AkzoNobel Delfzijl



Current decay rates suggest Nedstack's stacks will survive over 20,000 hours

Extrapolation of actual measurements at AkzoNobel Delfzijl PEM Power Plant



Cell – cell variation does not increase, proving predictable degradation

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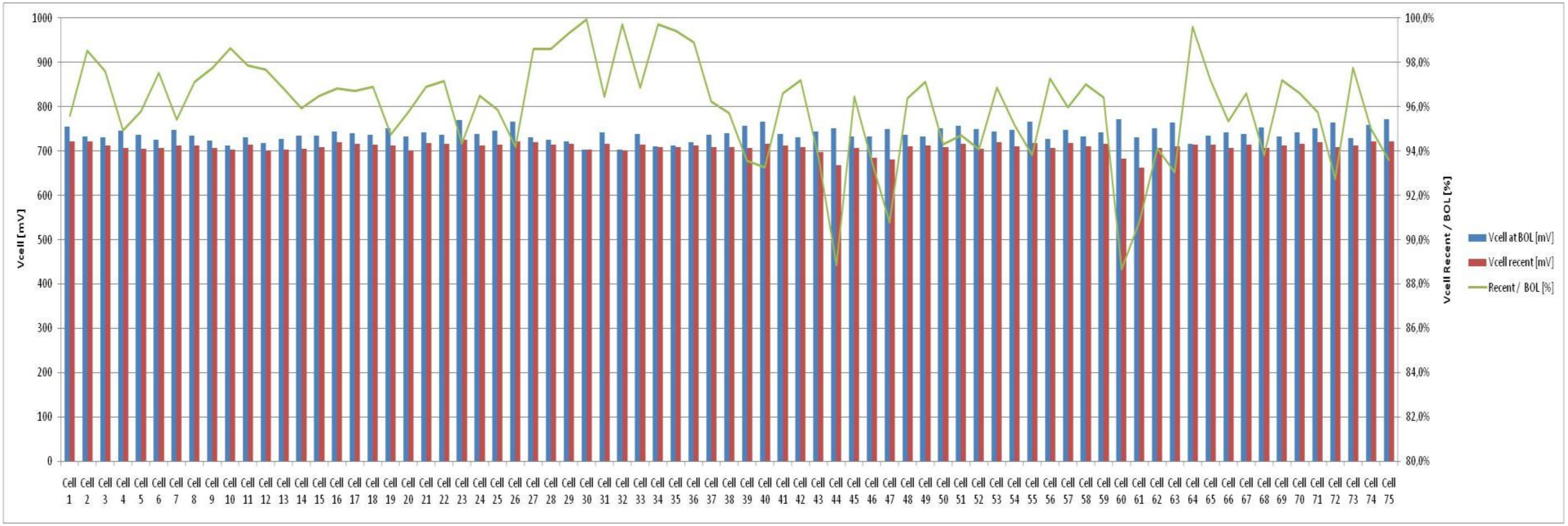
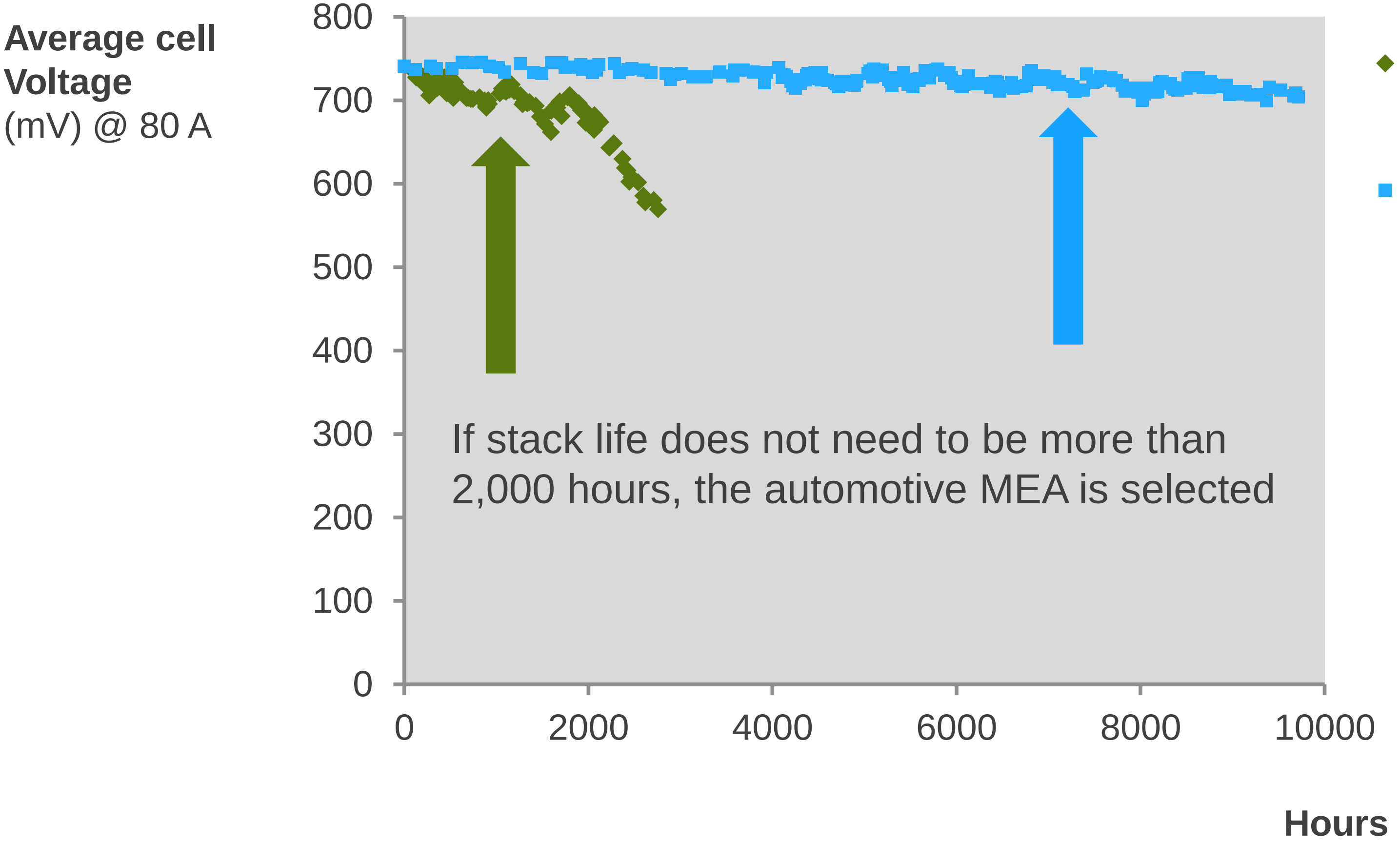
Hourly averaged cell voltage at 80 A



	Average cell voltage	Highest cell voltage	Lowest cell voltage
Beginning of Life	739 ± 15 mV	771 mV	703 mV
At 10,500 hrs	710 ± 11 mV	725 mV	663 mV

Nedstack offers fit for purpose stacks



Conclusions

1. There are many ways to damage PEMFC components

2. Proper selection and integration of materials can lead to MEAs and stacks that show low decay rates and long life, but might conflict with cost targets

3. The way that MEAs and stacks are operated are determining factors for decay and lifetime (see conclusion 1)

4. Contaminants are a complicating factor with a long term effect that is not well understood/investigated

5. The translation from the component to the stack to the system level is crucial for creation of end-user acceptance

Acknowledgements

The FCH-JU is greatfully acknowledged for financial support through the STAYERS project – FCH JU 256721