# PEM Fuel Cells Durability and Cost

**F.A. de Bruijn**

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ECN-L--09-177 December 2009

ECN

Energy research Centre of the Netherlands

# PEM Fuel Cells Durability and Cost

Frank de Bruijn

Oslo Nov 25th 2009

# Fuel Cell Vehicles are on the road!



Toyota FCHV: driving range of 780 km (EPA)
due to high fuel efficiency (> 80 mpge)

Honda Clarity
high fuel efficiency (74 mpge)
For lease for governments

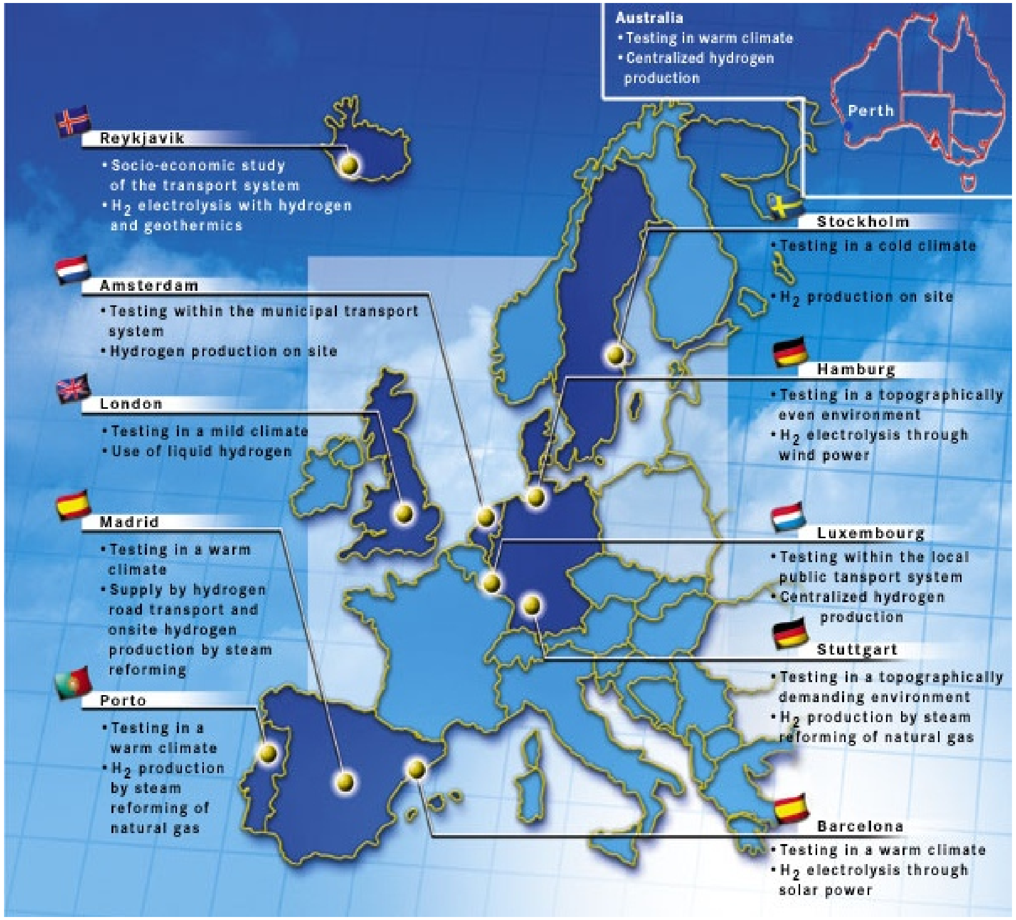
January 2007 first F-Cell >100,000 km and
2000 h without significant performance loss

## Field Trials


Coast to Coast USA,
4500 km


Simplon Pass,
2000 m altitude, - 9 °C

# Fuel Cell Busses




- 30 busses in 10 cities
- Various climate conditions
- Various options hydrogen production
- Availability fuel cell busses higher than diesel busses
- 1.8 million km and >116,000 h of operation by all Citaro busses by end February 2007

# Improvements needed on short and long term

**Short term: before large scale market introduction can take off**

Cost Reduction

Improvement of Life time and Durability

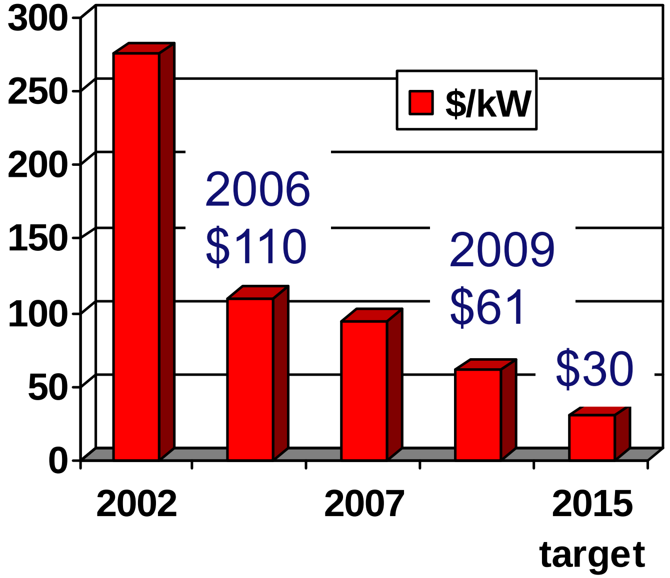
**Long term: further improvements needed for full market penetration**

Increase in Operating Temperature

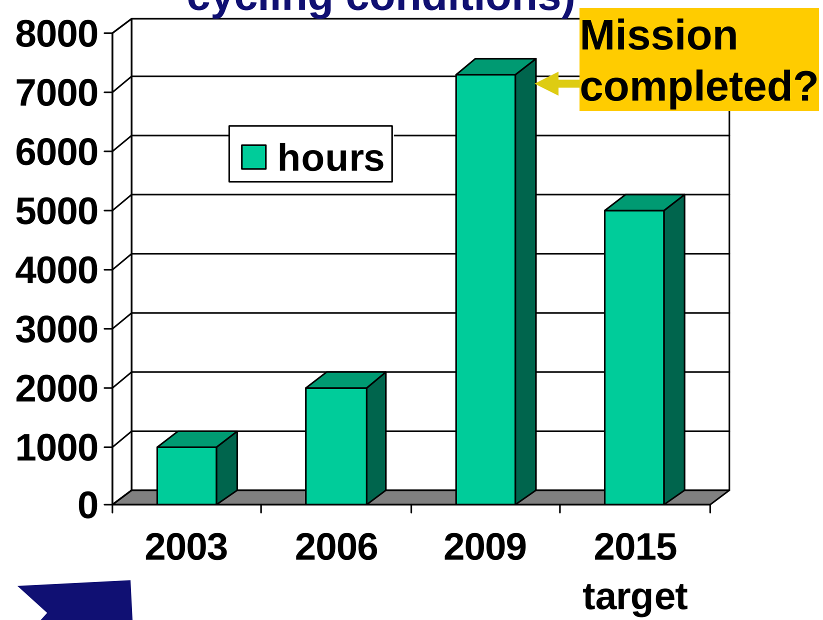
Operation at Reduced Water Content

# DoE analysis of the technology status versus the Targets

**Fuel cell system costs ***




**Durability (under voltage cycling conditions)**



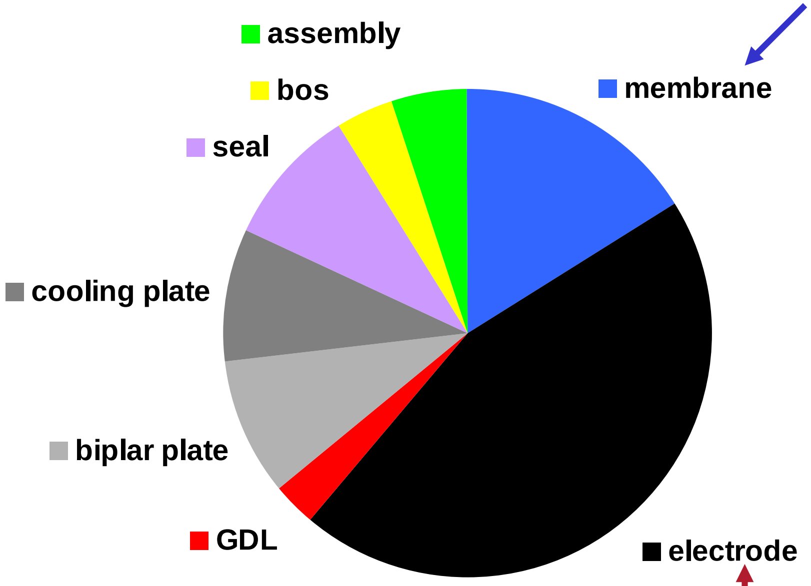

* for 500,000 vehicles, using a 80 kW system, produced per year

Cost reducing strategies could have a major impact on durability

S. Satyapal, Fuel Cells & Hydrogen Joint Undertaking General Stakeholders Assembly, Oct 27, 2009

# DoE analysis of Fuel Cell Stack costs

Carlsson , Fuel Cell Seminar 2005




Carlsson , Fuel Cell Seminar 2005

**Membranes: using thinner membranes leads to reduced materials costs but to increase of gas cross over, as well as to increased risk of damaging during MEA manufacturing**

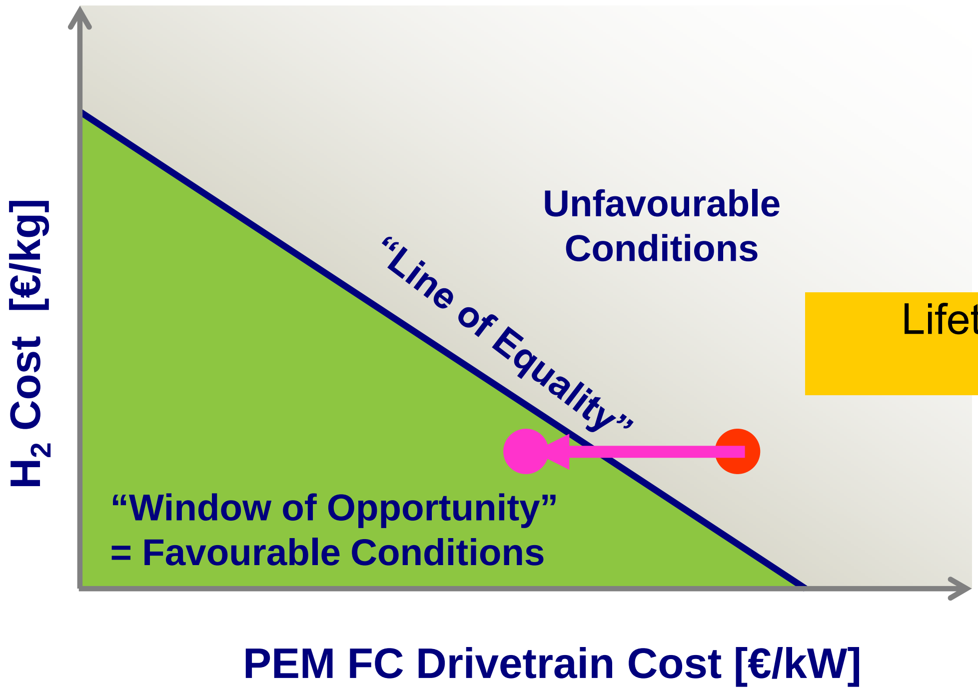
**Platinum: lowering its loading is viable, but how stable are these low loading electrodes?**

# Indirect effects of MEA performance and durability on vehicle cost

MEA lifetime is an important factor for maintenance costs, stack life (and maybe vehicle life?)

# Longer durability can make an application economically viable

- Specific Cost (reference vehicle) = Specific Cost (PEM FC vehicle)

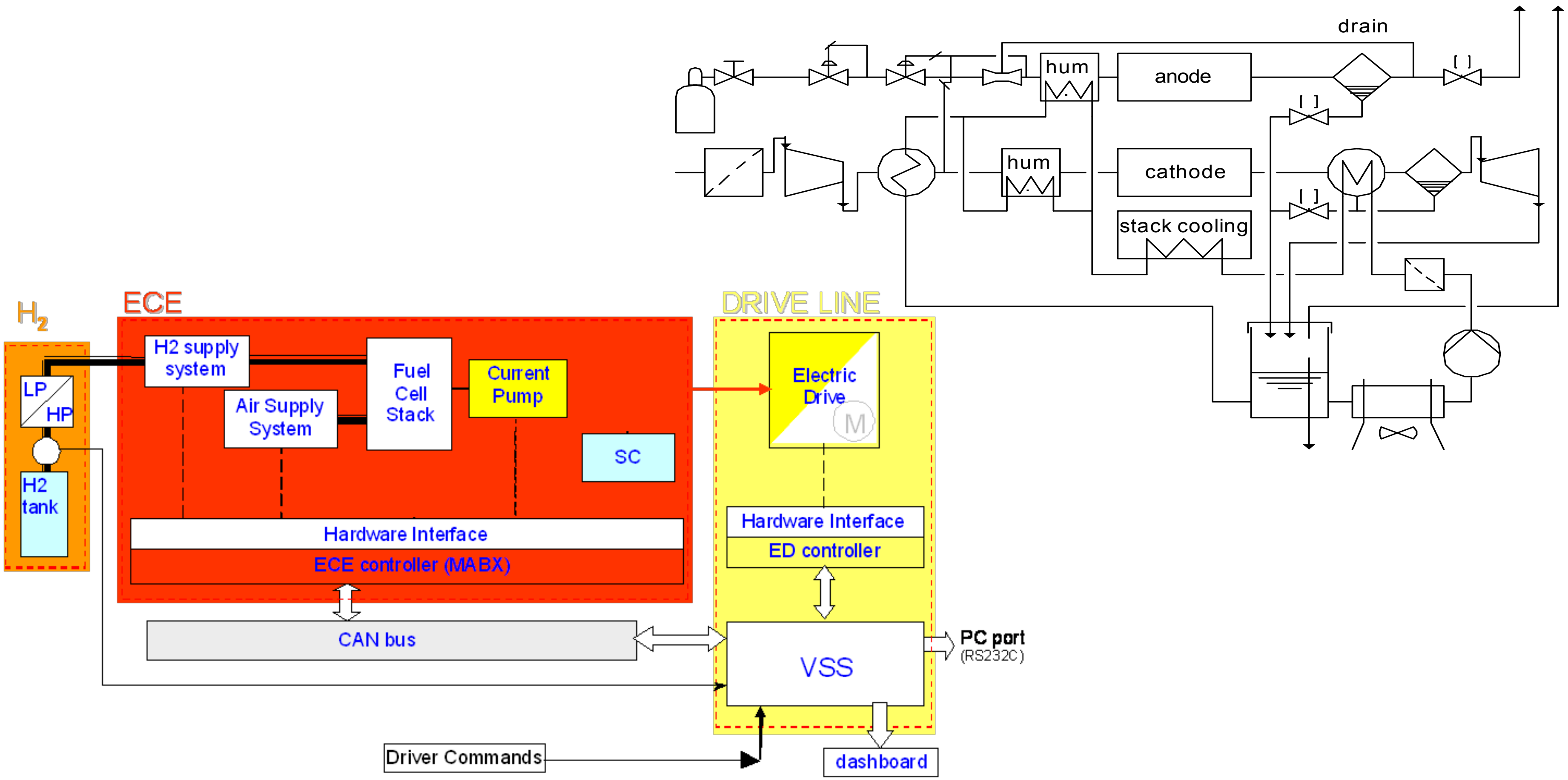



Lifetime (PEM FC stack) = 50%
→ PEM FC drivetrain cost + 40% !

P. Lebutch, Fuel Cell Seminar 2009 Results from Roads to HyCom

# Indirect effects of MEA performance and durability on vehicle cost

Operating window of present MEA leads to system complexity and size



# Increase in operating temperature

*Internal Combustion Engine*

- Heat removal 2/3 through tailpipe
- Engine works at 90 – 110 °C

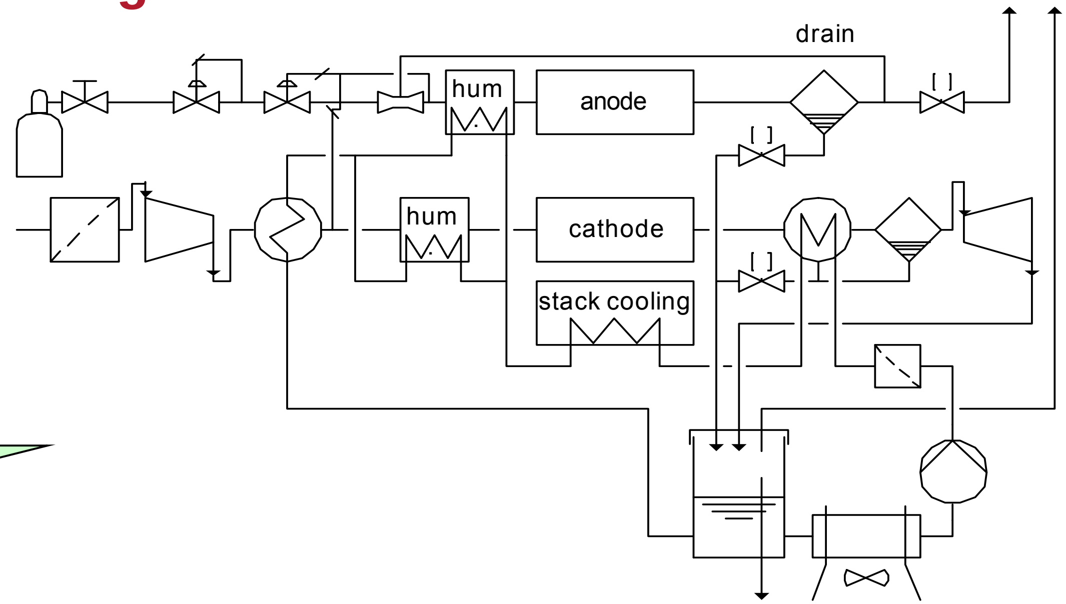
*Fuel Cells vehicles*

- Heat removal 100% through fuel cell coolant
- Fuel Cell works at 70 – 80 °C

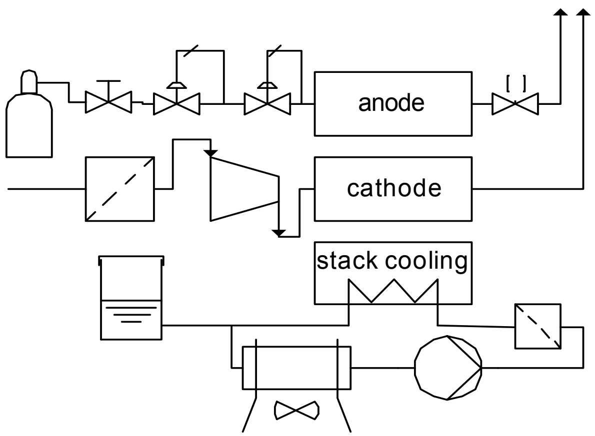
Cooling problem, which can only be solved
By applying big radiatiors

Radiator area
Doubles!

# Systems simplification: lowering the need for humidification




The system as it could have been, no water management…




The system as it is now, complex water management

F.A. de Bruijn, R.K.A.M. Mallant, R.C. Makkus, G.J.M. Janssen, Advances in Fuel Cells, vol 1, Chapter 5 (2007)

# Durability: capability to work under real life conditions

Freeze – thaw cycles

Load cycles

Cooling problems

## Durability issues for transport applications

- Under ideal conditions, using ideal materials: lifetime > 10,000 hrs

- Start-up/shut down can lead to extremely high catalyst potentials (up to 1.4 V)
  - Carbon corrosion / platinum dissolution

- High operating temperatures, unsaturated gases can lead to membrane degradation

- System must operate in wide window of conditions: –30 and + 40 ºC ambient

- High purity requirements lead to high hydrogen production and infrastructure costs
  - Contaminants in hydrogen and air can lead to catalyst and membrane poisoning

**When developing materials for more cost effective fuel cell systems, these must meet the durability requirements to enable 5000 hrs of operation !!**

↓

**Stability should be a selection criterion from the beginning!!!**

# A typical example

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

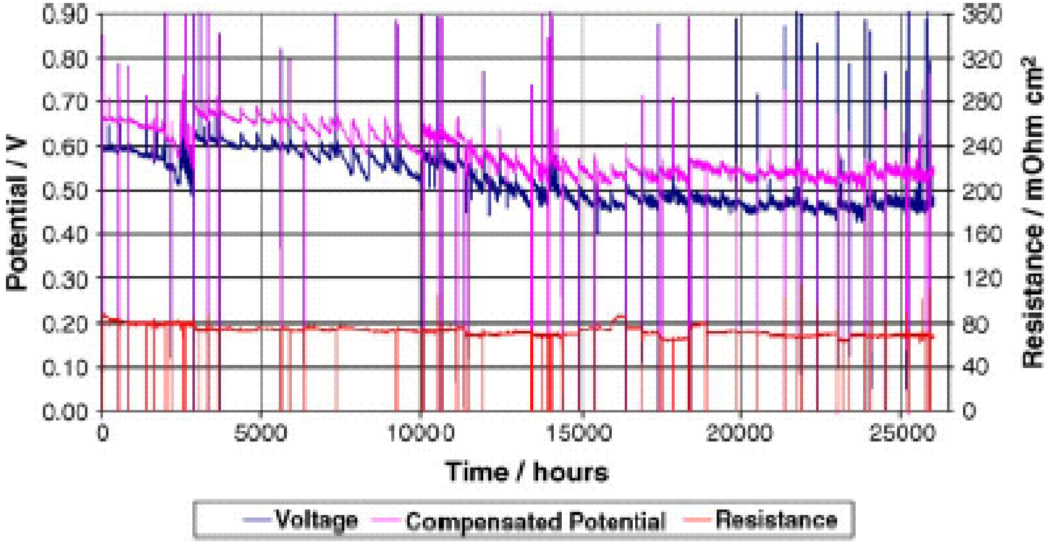



Fig. 1. Cell voltage, *iR* compensated cell voltage and cell resistance as a function of hours on load operated at constant current, 800 mA cm$^{-2}$ for the entire 26,300 h life test. Cell temperature 70 °C. Air: 2.0× stoichiometry, ambient pressure, 100% RH. Hydrogen: 1.2× stoichiometry, ambient pressure 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

## For development of more stable and robust materials we need:

Accelerated tests, which are still representative for PEMFC conditions

Characterization tools that can discriminate between various mechanisms

Isolation of the individual problems and components

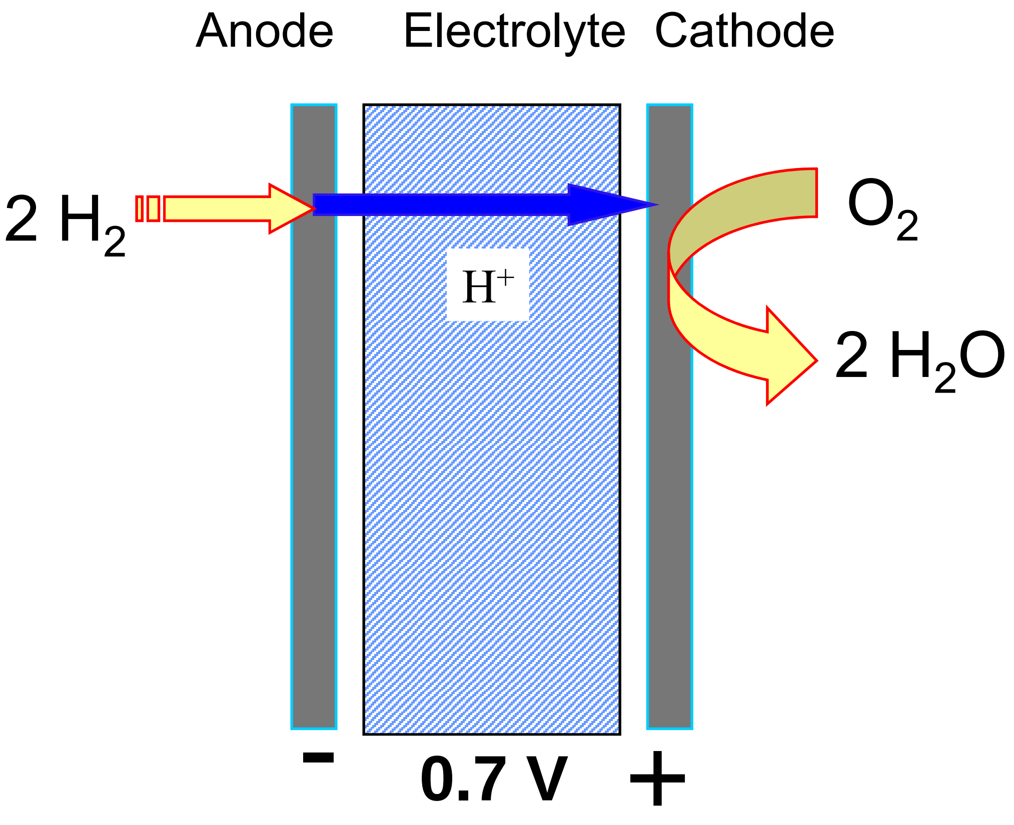
↓

With model electrochemical experiments study can be made of:

influence of potential & temperature on anode and cathode catalysts stability

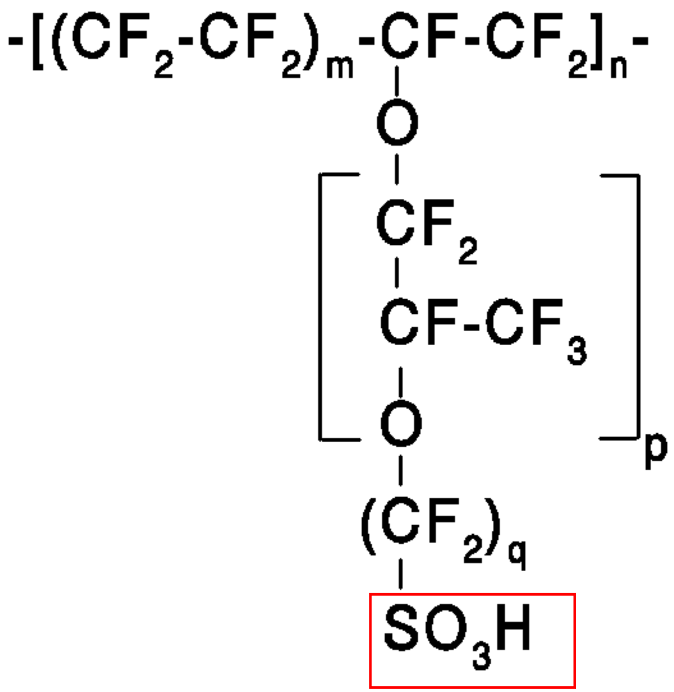
# Electrolytic Membranes : Functions

- Proton conductor
- Gas separator
- Electronic separator



# Electrolytic Membranes: the state-of-the-art

perfluorosulfonic acid/tetrafluoroethylene copolymers




| | |
|---|---|
| Advantage: | - chemically stable<br>- high proton conductivity |
| Disadvantage: | - expensive<br>- conductivity only when wet |

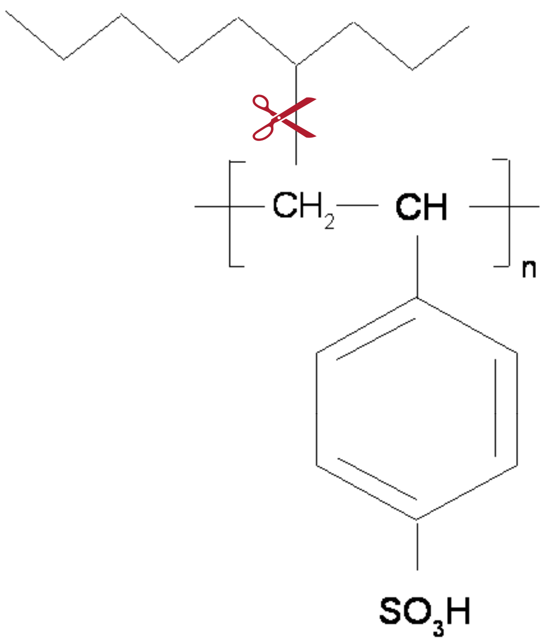
$m=5\text{-}15$

$n=1000$

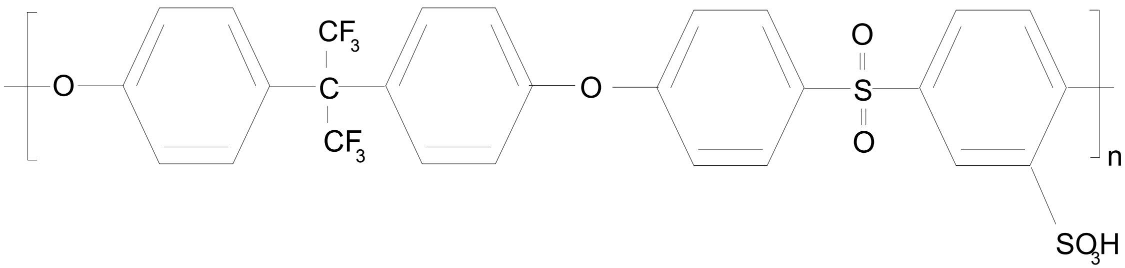
$p=0\text{-}1$

$q=2\text{-}5$

# Some alternatives that didn't make it: lack of stability

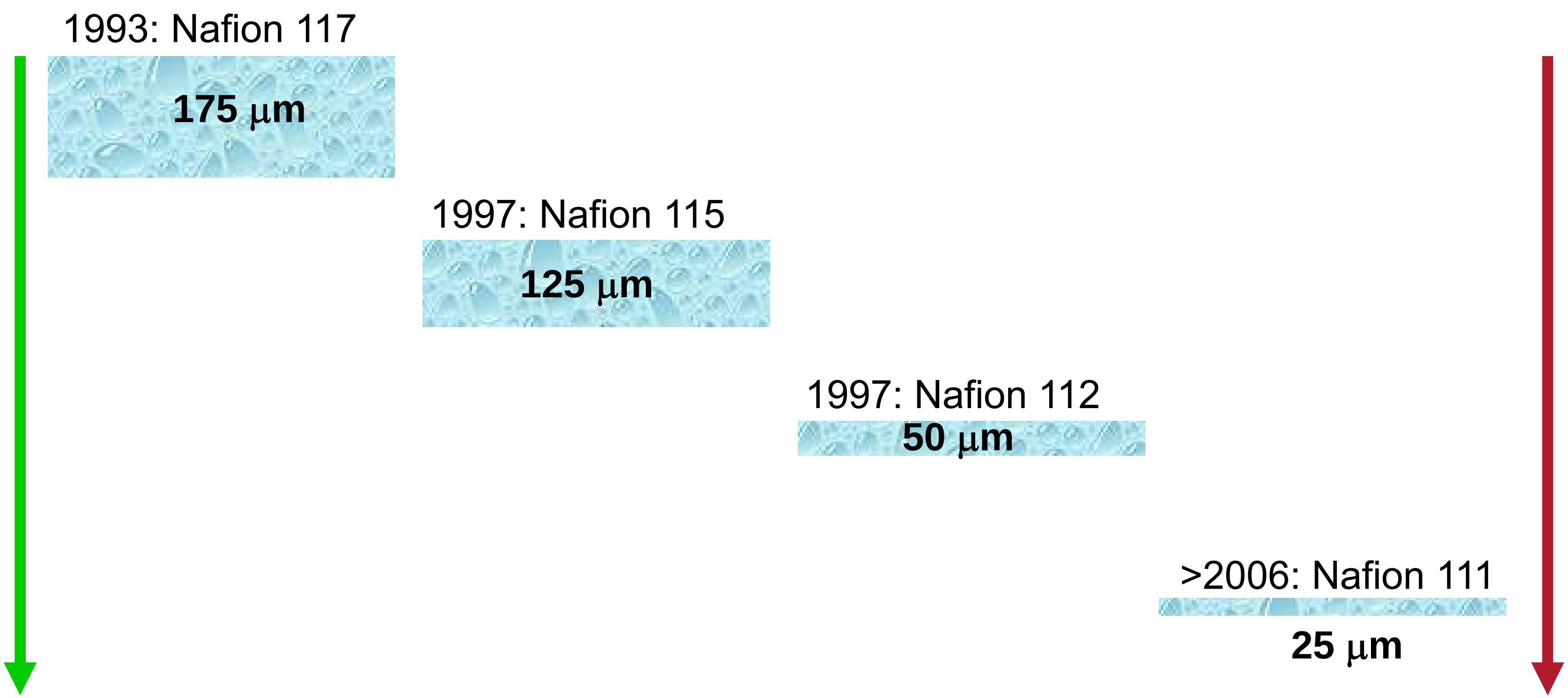



Damaging species during fuel cell operation:
$H_2O_2$, $HO_2^{\bullet}$




Sulphonated -PolyEtherSulfone

# Another way to reduce the cost of Nafion




\+ Restistance decreases
\+ Materials costs decreases
\+ Water management improves

\- Gas crossover increases
\- Mechanical strength decreases

# Fast voltage cycling: comparing MEAs with varying membrane thickness

Modification of DOE protocol;

80°C, 80% RH, ambient pressure

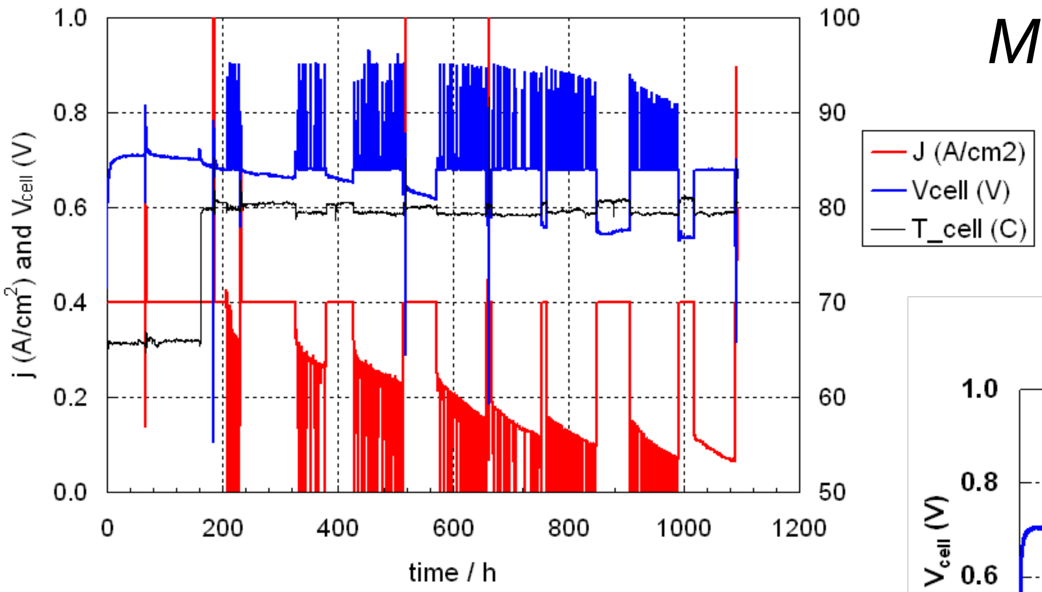
$H_2$/**Air**

Potential cycling between 0.7 and 0.9 V IR-corrected (or OCV )
(30 s hold at each)

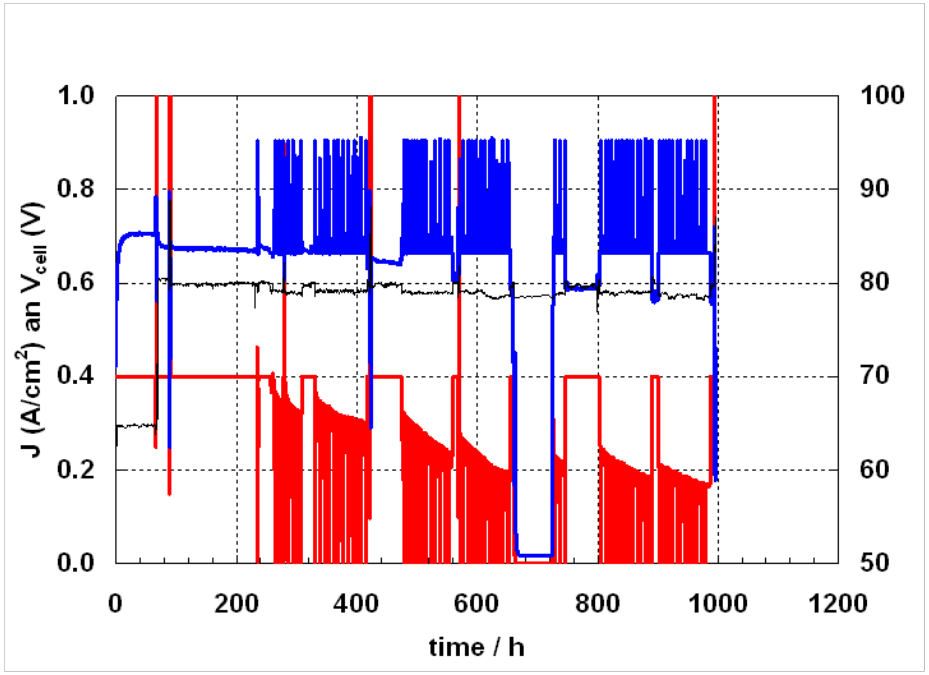
*MEA1: Hispec 9100, N:C=0.7, NRE211CS*

*MEA2: Hispec 9100, N:C=0.55, NRE212CS*

# Fast voltage cycles – load profile




*MEA1 (25 μm)*

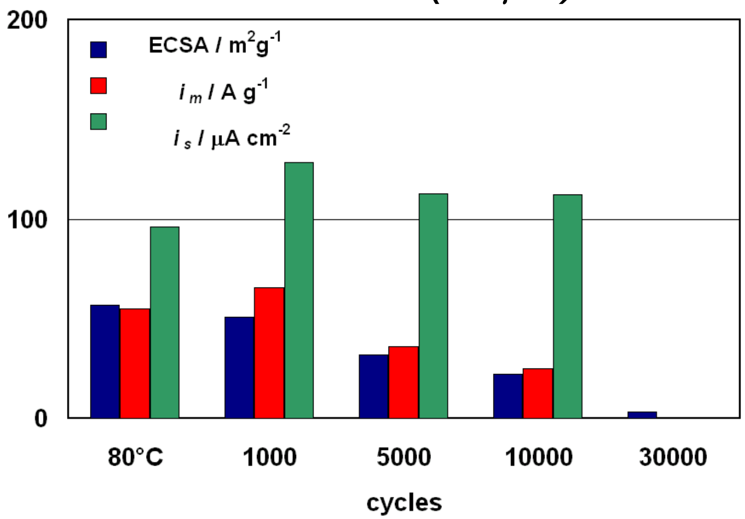



*MEA2 (50 μm)*

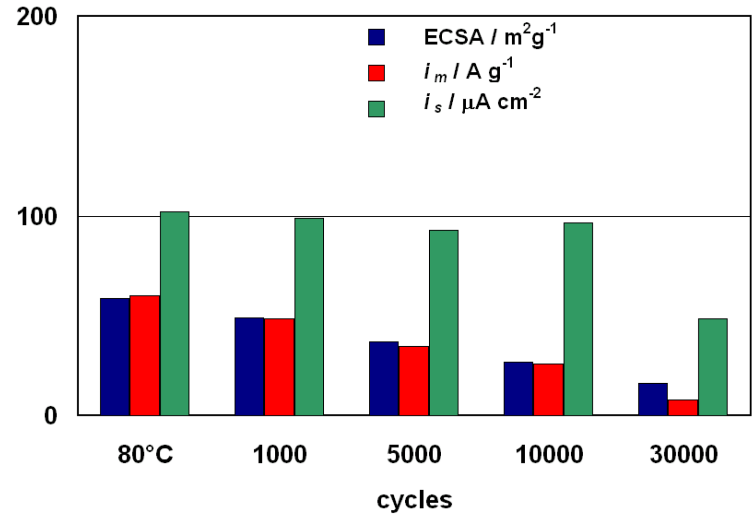
F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, R.C. Makkus, ECS Transactions, vol 25(1), 1835 - 1847 (2009)

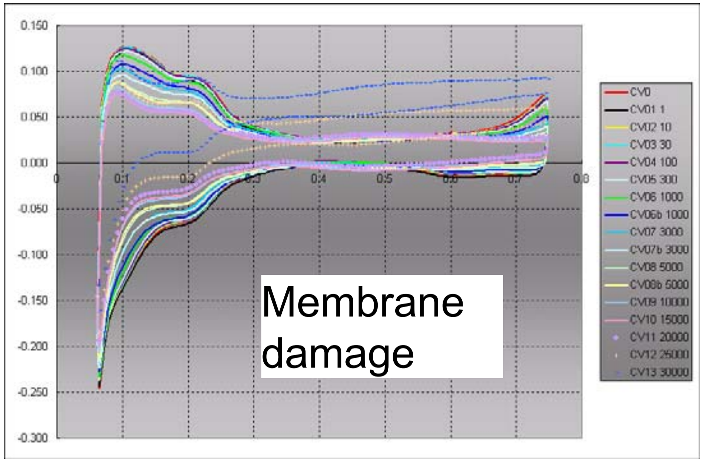
# Fast voltage cycling

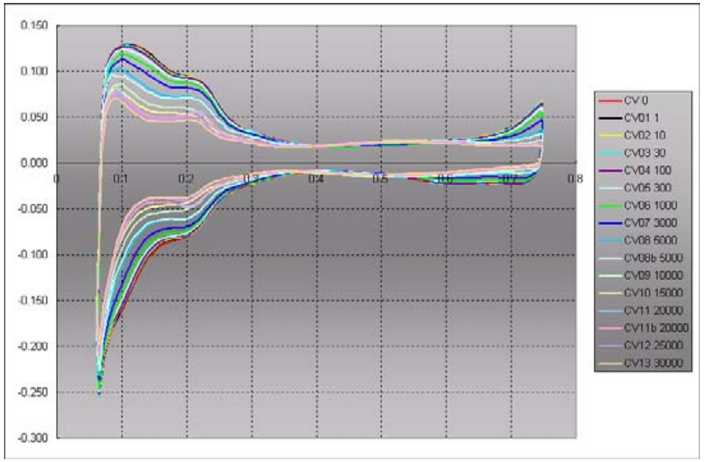
MEA 1 *(25 μm)*




MEA 2 *(50 μm)*



F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, R.C. Makkus, ECS Transactions, vol 25(1), 1835 - 1847 (2009)

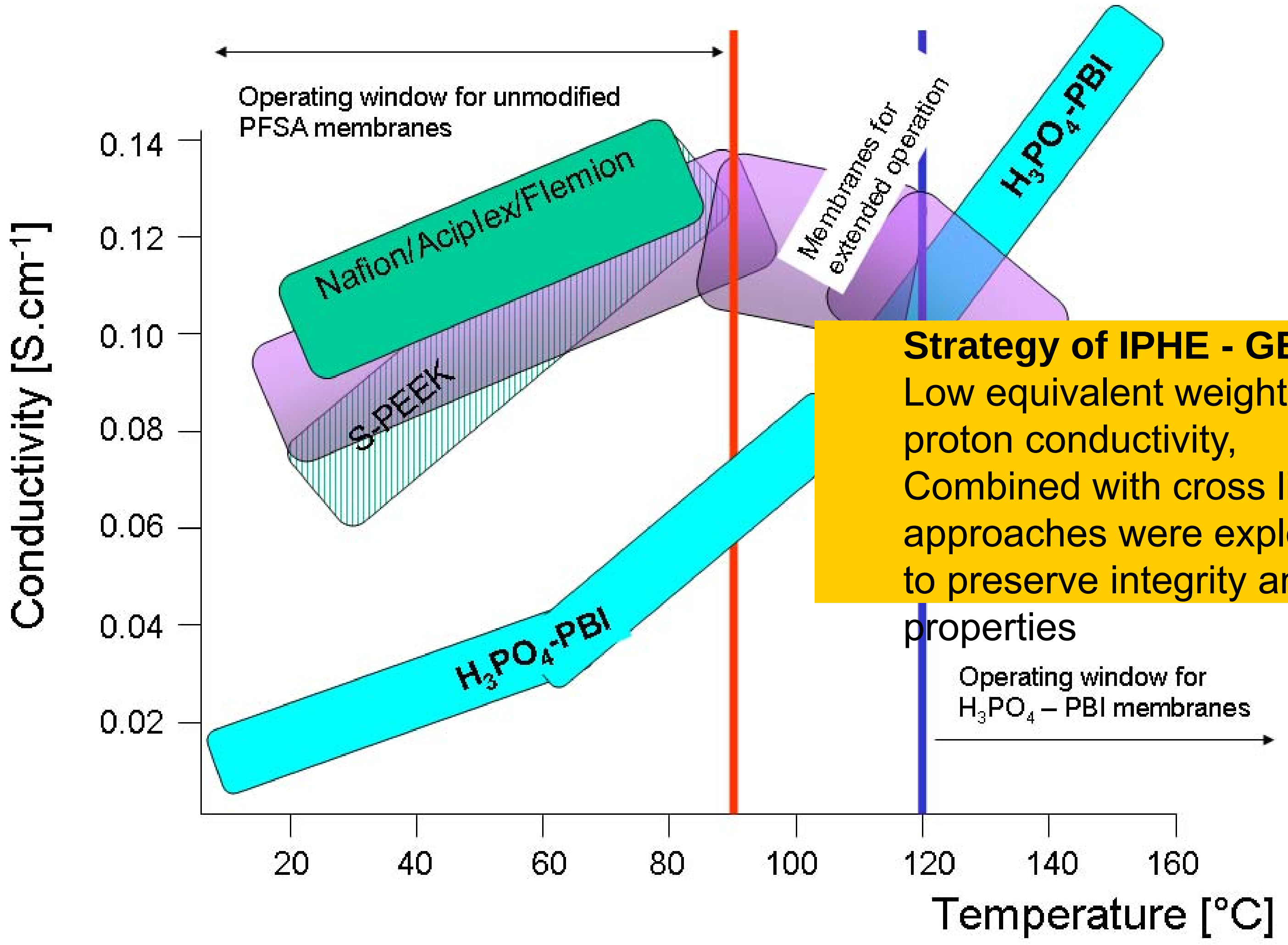
# Composite membranes enable the use of thin membranes without sacrificing mechanical strength

| Membrane | Tensile Strength Dry (MPa) | Tensile Strength Wet (MPa) | Shrinkage (%) |
|---|---|---|---|
| | | | |
| Nafion N117 (175 µm) | 30 MD<br>25 TD | 14 MD<br>10 TD | 11 MD<br>12 TD |
| Gore-Select (35 µm) | 34 MD<br>24 TD | 33 MD<br>18 TD | 3 MD<br>3 TD |

1996-1999:
The Solupor/Nafion composite membrane, now commercially available as a DSM Solutech product used by Ballard

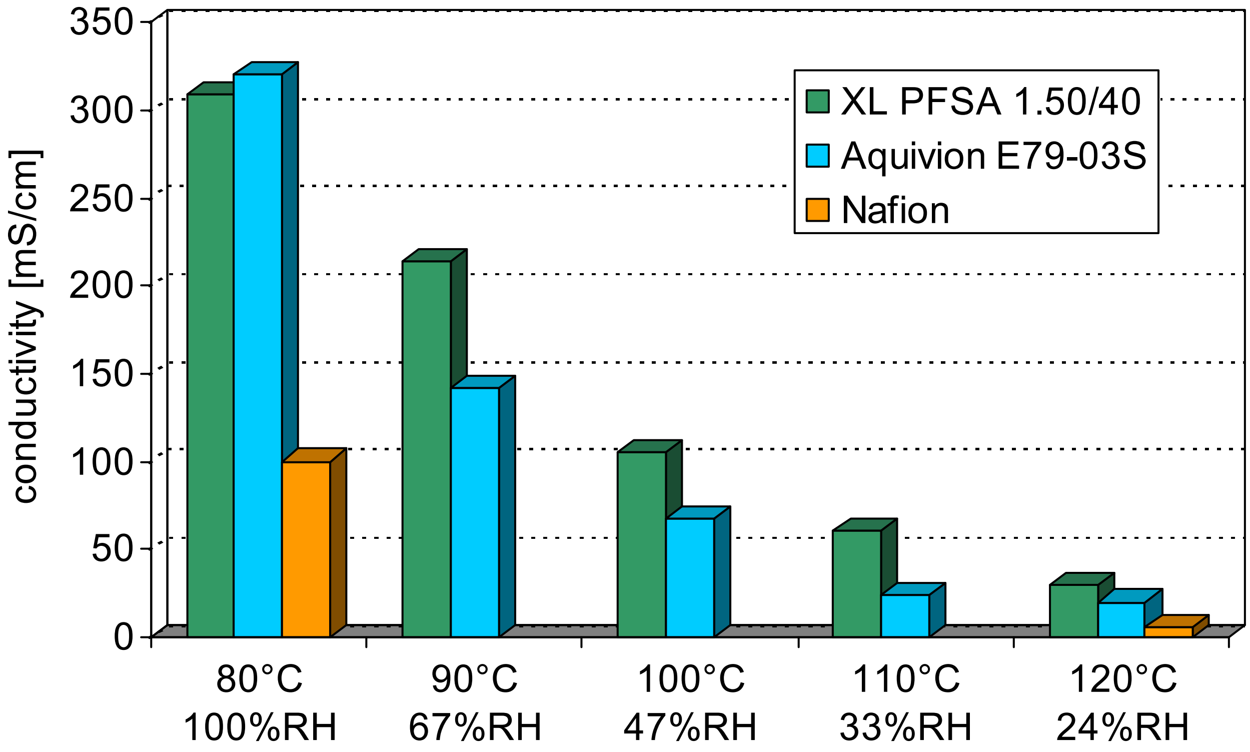
R.K.A.M. Mallant, F.A. de Bruijn, G.H.M. Calis, WO 98/20063

# Membranes for high T and low RH




**Strategy of IPHE - GENIE**
Low equivalent weight PFSA to enhance proton conductivity,
Combined with cross linking (several approaches were explored) and hybridization to preserve integrity and mechanical properties

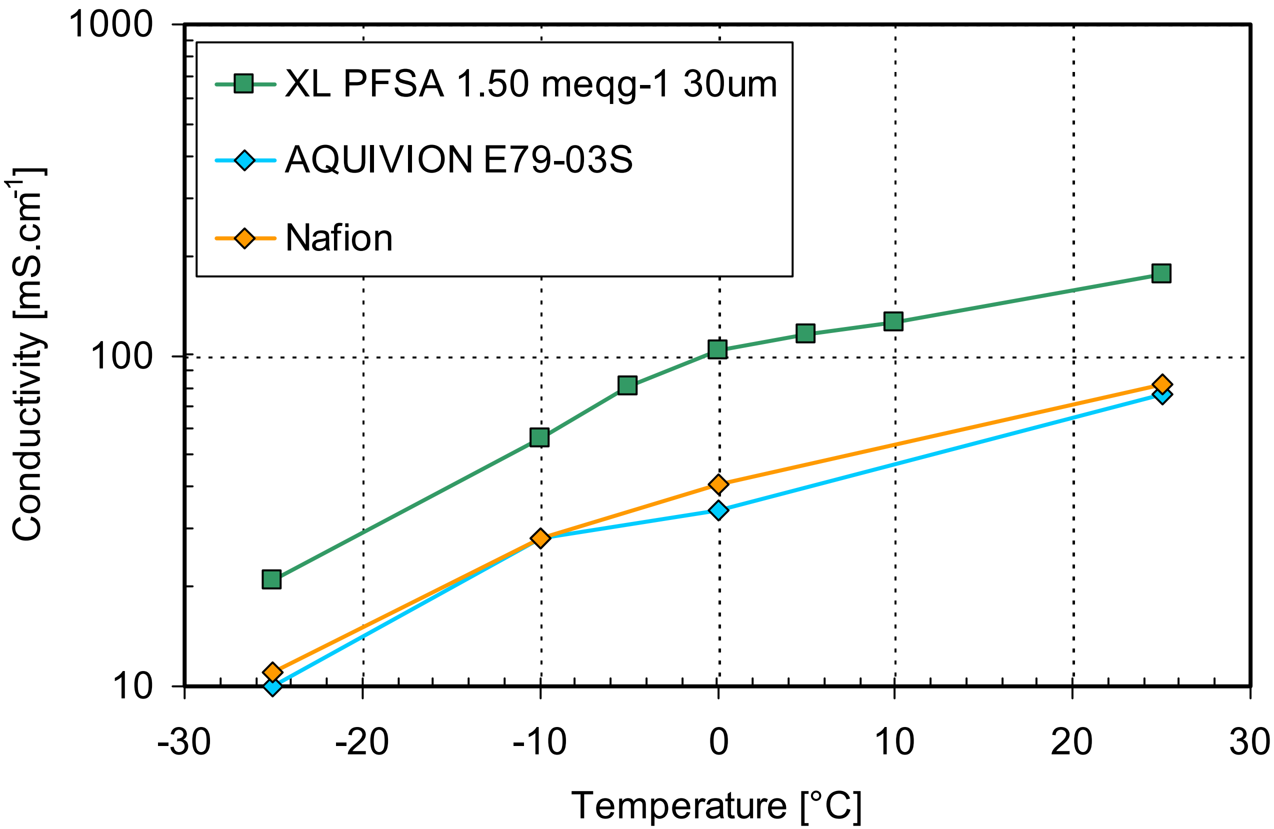
# High temperature conductivity




R.K.A.M. Mallant et al., Fuel Cell Seminar 2009 Results from IPHE-GENIE

ECN

# Low temperature conductivity




R.K.A.M. Mallant et al., Fuel Cell Seminar 2009 Results from IPHE-GENIE

# Platinum Loading vs Performance
## (Analysis by General Motors)

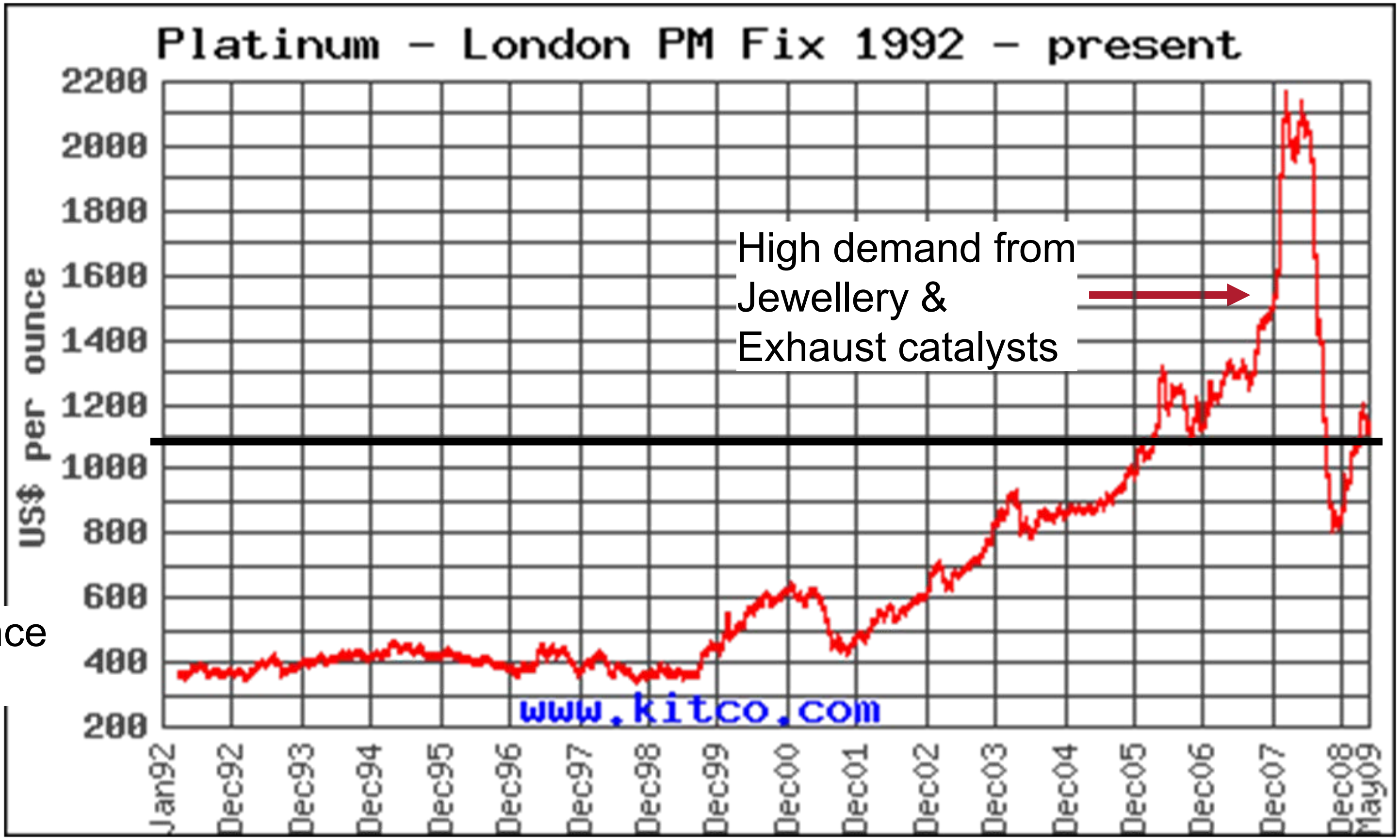
*2005 generation PEMFC*

Pt loading: 0.6 – 0.8 mg Pt.cm$^{-2}$ MEA
Power density: 0.7 W. cm$^{-2}$
Cell Voltage: 0.68 V eq to 58% cell efficiency

*Automotive target*

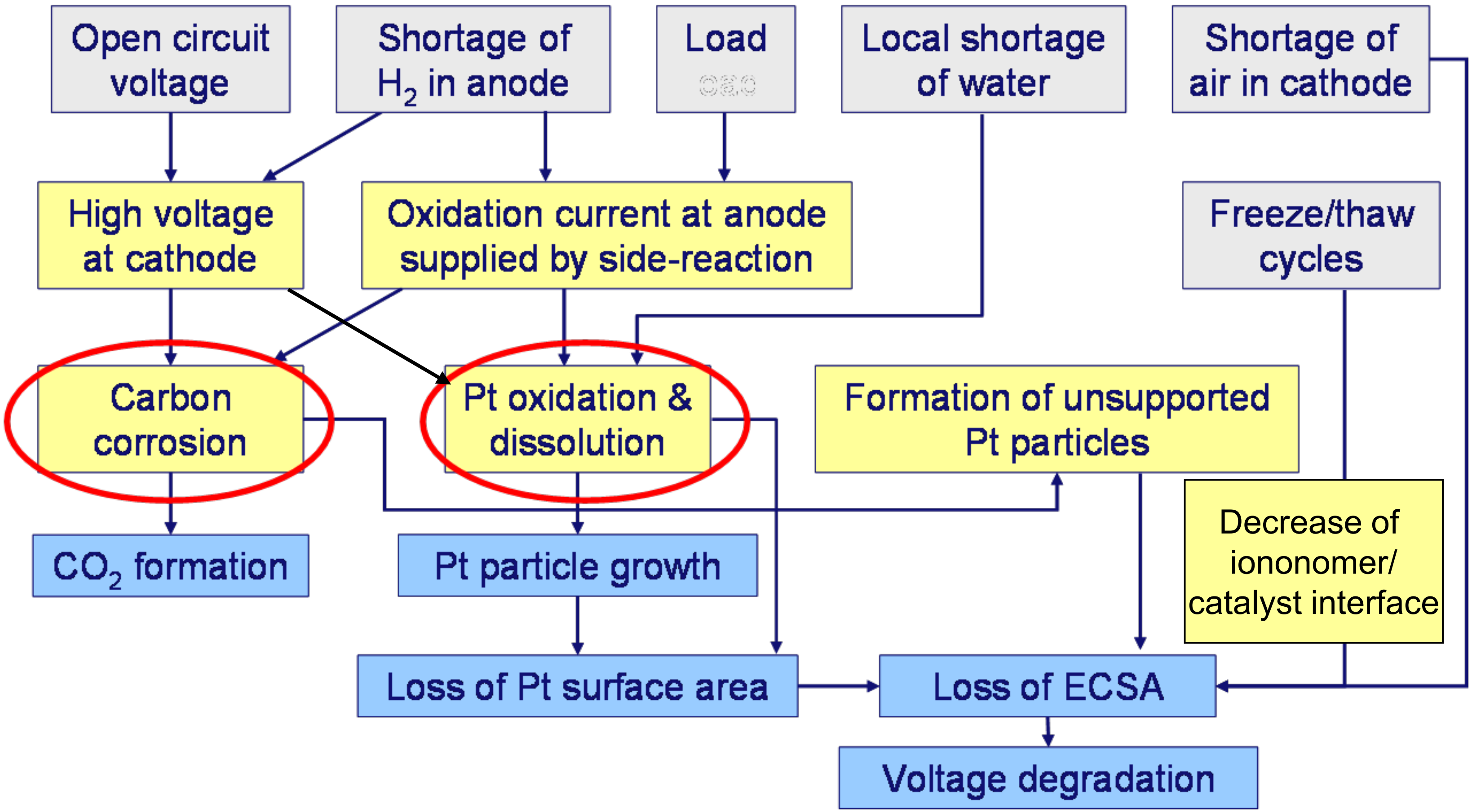
Pt loading: 0.2 mg Pt.cm$^{-2}$ MEA = **15 g Pt per 75 kW vehicle**
Power density: 0.8 – 0.9 W. cm$^{-2}$
Cell Voltage: > 0.65V eq to > 55% cell efficiency

# Platinum cost: a moving target
# platinum price increase over last years



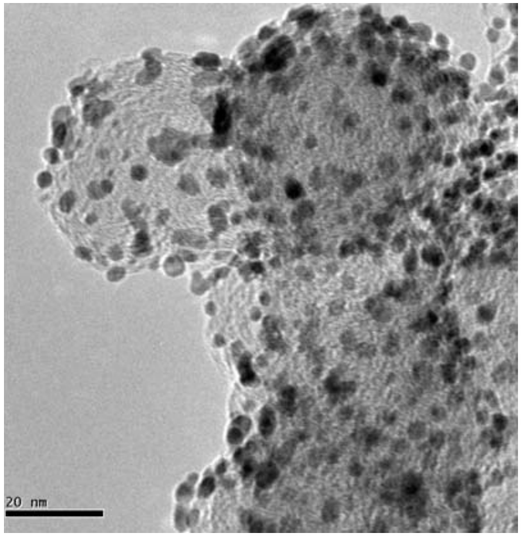

US$ per ounce
(31 g)

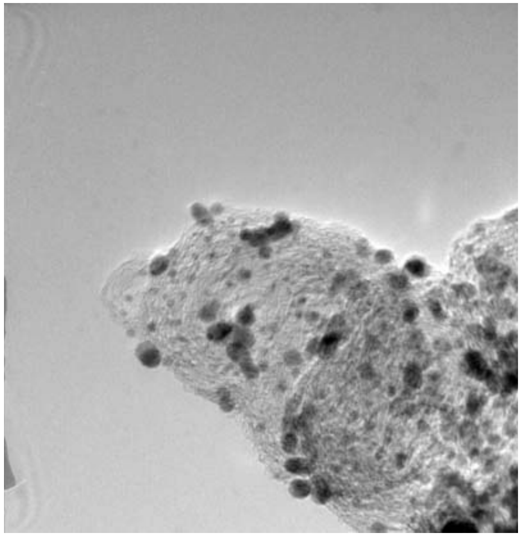
# Catalyst degradation in PEMFC

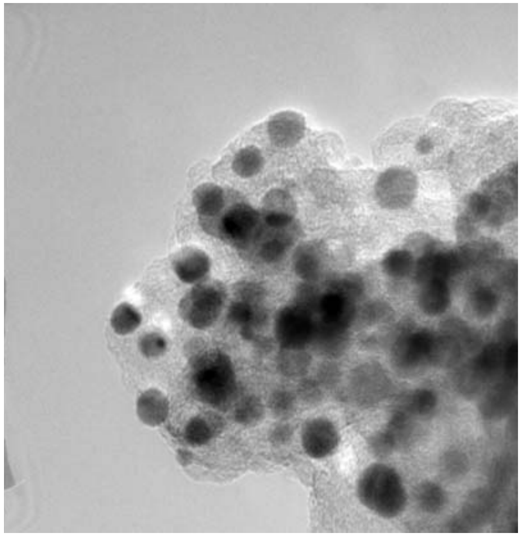



F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen,Fuel Cells, 2008, vol8, 3

## Effect of load cycling on Pt distribution in MEAs



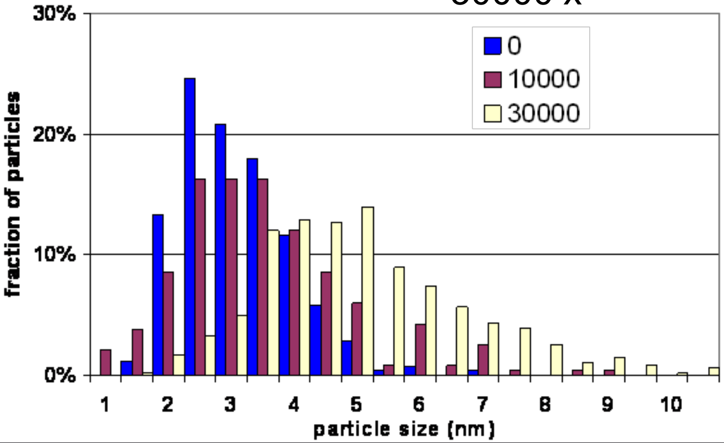





0 x

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, ECS Transactions, vol 25(1), 1835 - 1847 (2009)

# Effect of load cycling on Pt distribution in MEAs

After 30000 voltage cycles:

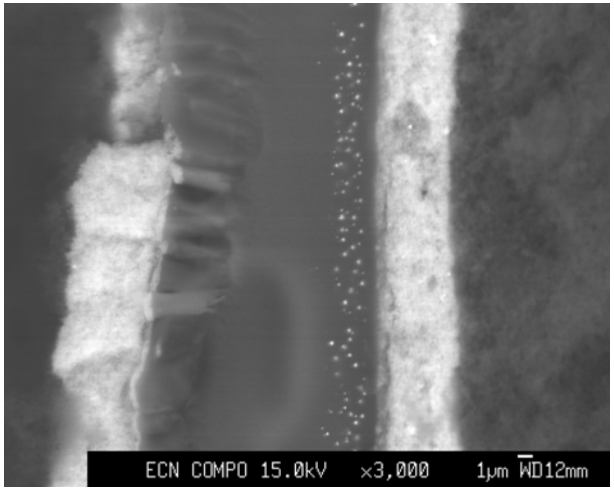
membrane thinning observed for NRE211CS (↓ 15 μm)

no significant electrode thinning

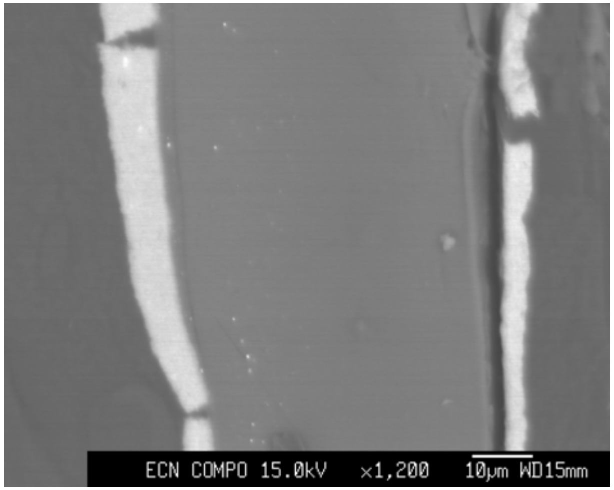
significant Pt deposition in NRE211CS near cathode

some Pt deposition in NRE212CS near anode

→ *ECSA loss is combined effect of Pt particle growth and dissolution*




*MEA 1 (NRE211CS)*

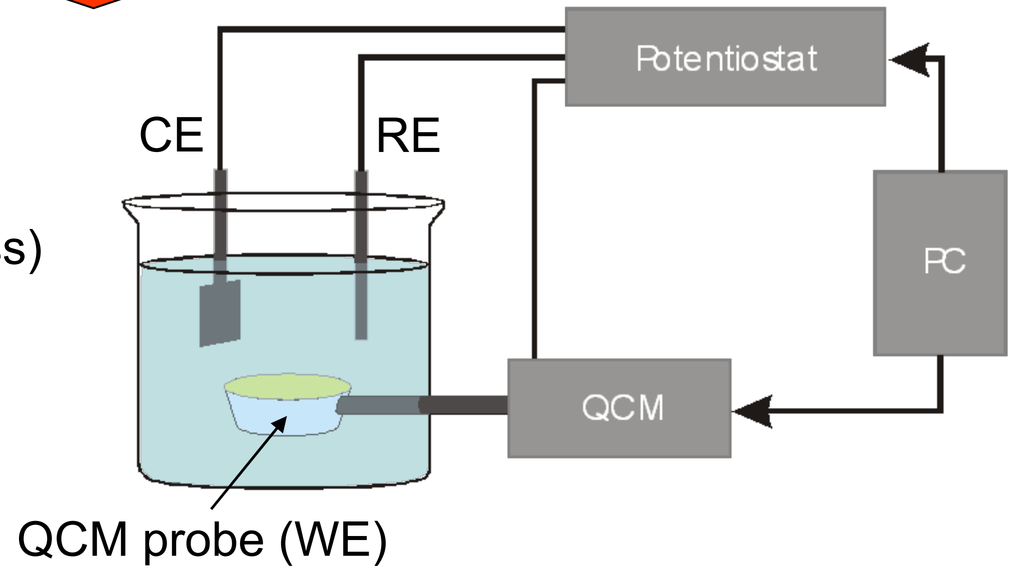



*MEA 2 (NRE212CS)*

F.A. de Bruijn, V.A.T. Dam, G.J.M. Janssen, R.C. Makkus, ECS Transactions, vol 25(1), 1835 - 1847 (2009)

# Ex-situ Electrochemical study of platinum and carbon stability

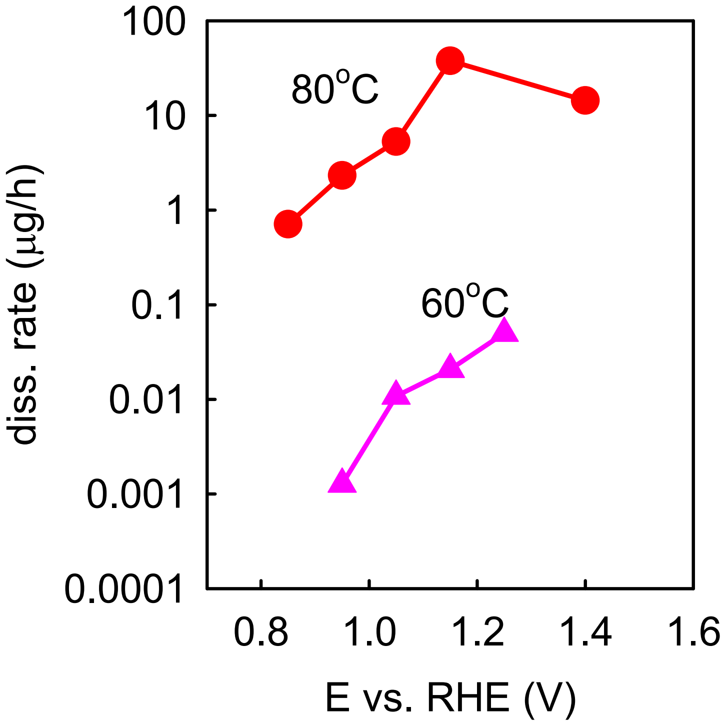
- Potentiostatic stability of Pt/C at operating conditions of fuel cell (elevated T, E)
- Real time monitoring of catalyst loss (Pt & C) by Quartz Crystal Microbalance (QCM) and Cyclic Voltammetry




- $\Delta$(frequency) = - K $\Delta$(electrode mass)
- High accuracy ~ 0.25 ng/cm$^2$
- Diversity of electrode materials

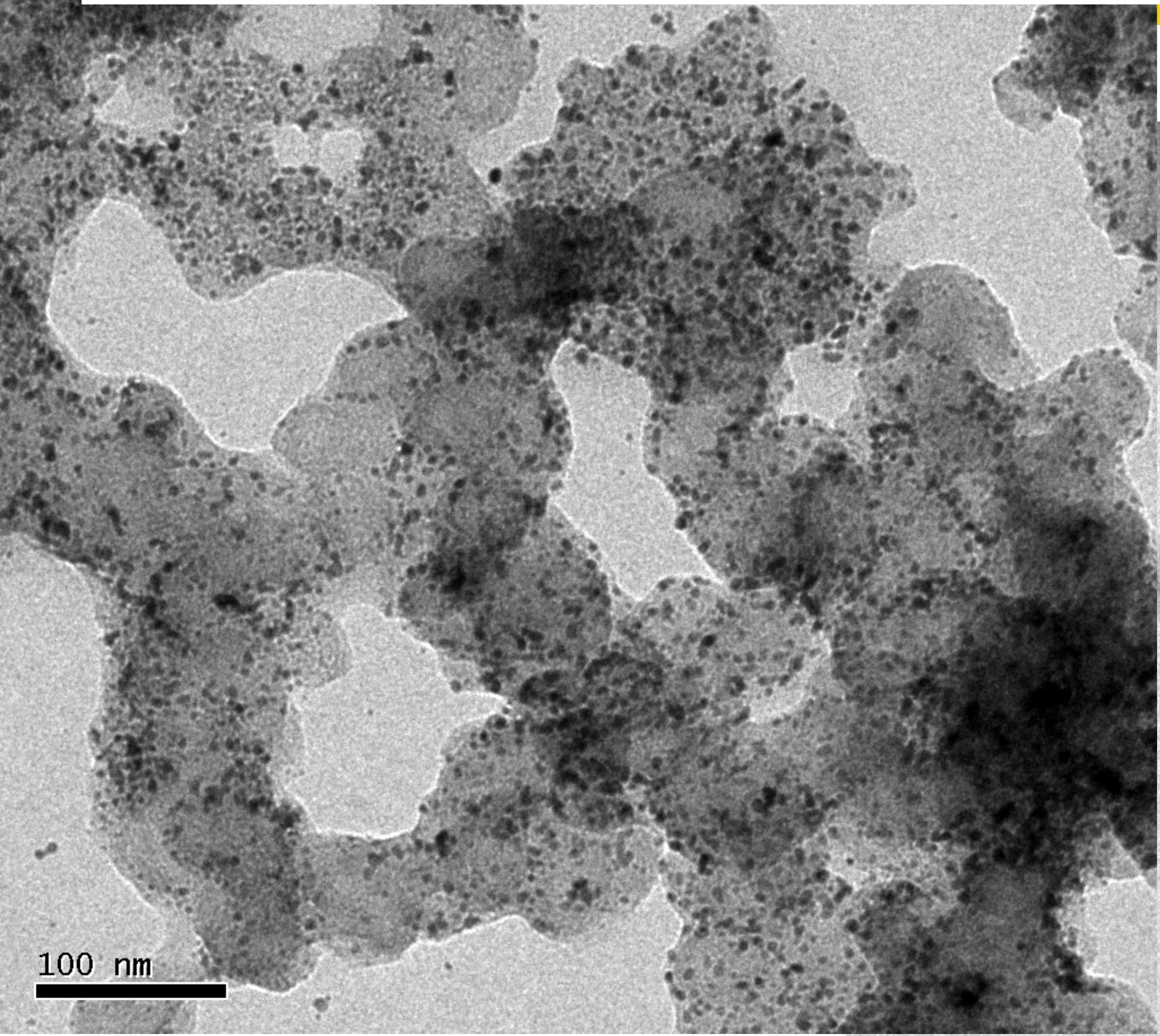
# Pt dissolution

- During dissolution, *first an oxide layer is formed*, which is further dissolved depending on T & E.
- The oxide layer is still continuously formed during dissolution.
- At E ≤ 1.15V, 80 ° C , log. of dissolution rate linearly depends on E (0.55 times / 0.1 V).
- At E > *1.15 V* and 80°C, the *dissolution rate decreases* due to passivating Pt oxide layer
- Dissolution rate *increases $10^3$* times when temperature increases from *60 to 80℃*.



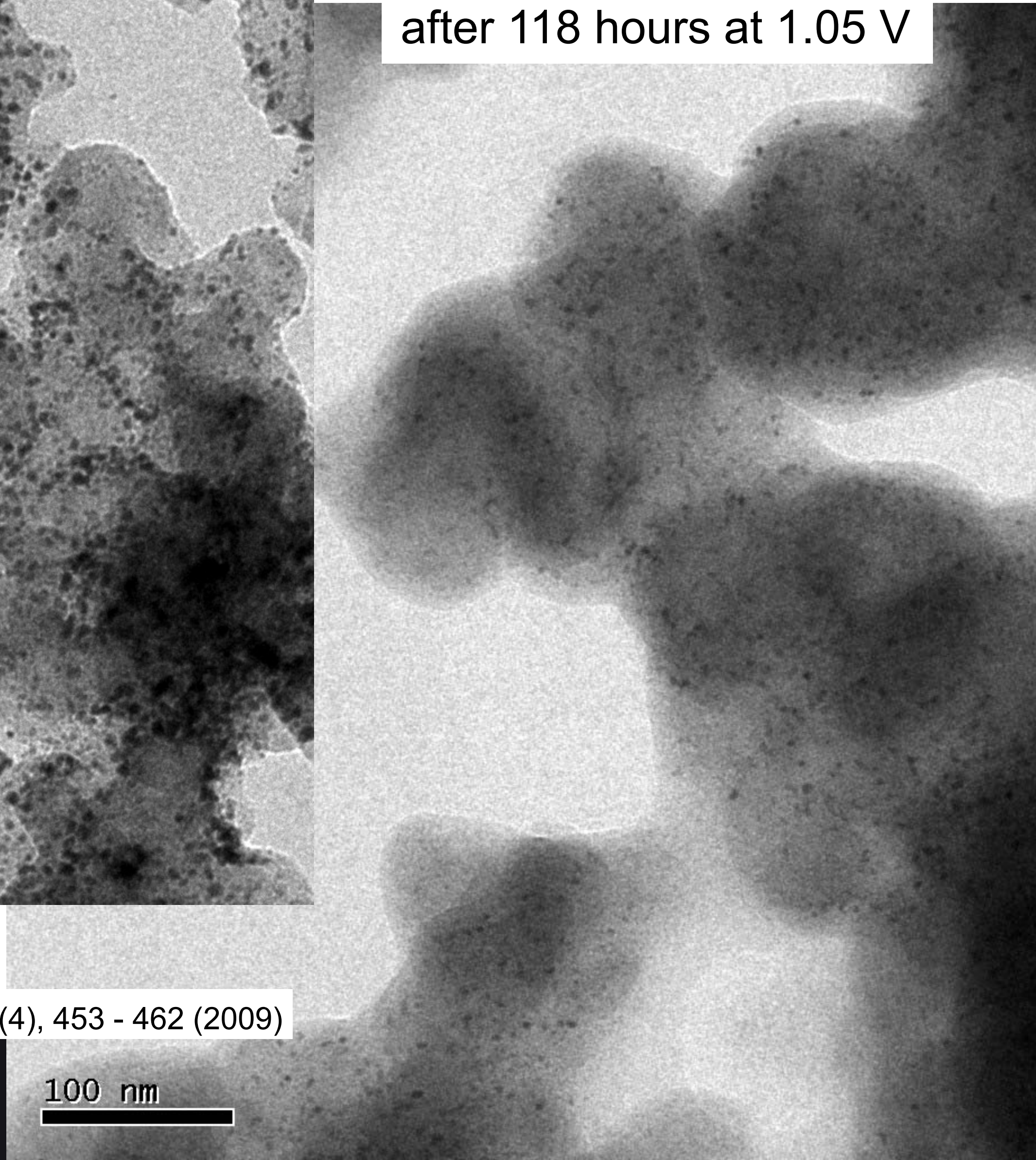

V. A. T. Dam, F. A. de Bruijn, *Electrochem. Soc.* **2007**, *154*, B494.

# Particle size in fresh Pt/C ink versus after 118 hrs, 1.05 V, 80 ºC



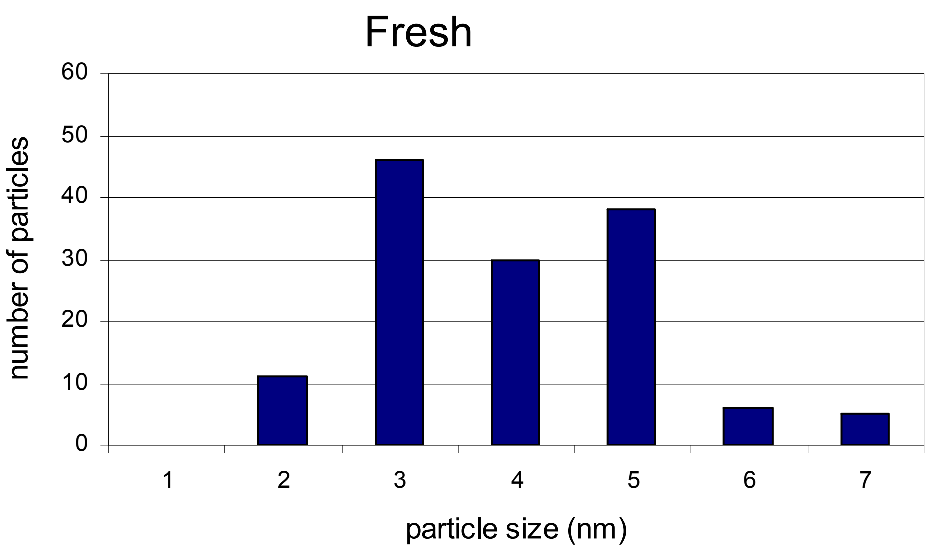

Fresh electrode

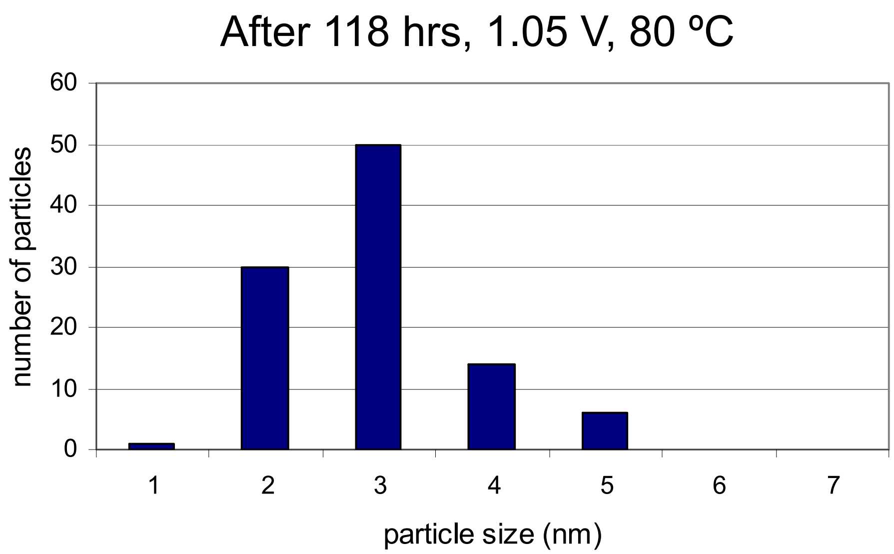
Electrode
after 118 hours at 1.05 V




V.A.T. Dam, K. Jayasayee, F.A. de Bruijn, Fuel Cells, 9(4), 453 - 462 (2009)

Particle size distribution in fresh Pt/C ink versus after 118 hrs, 1.05 V, 80 ºC




Average particle size: 4.0 ± 1.2 nm

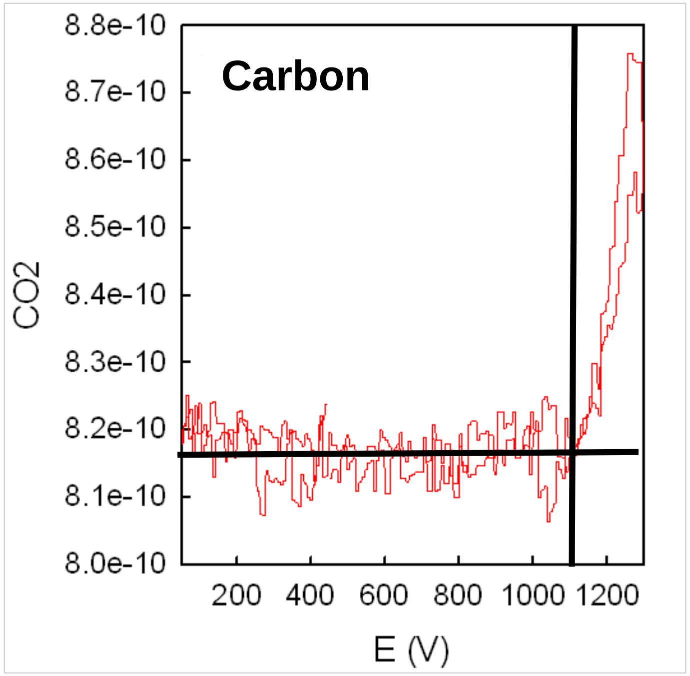
Average particle size: 3.0 ± 1.4 nm

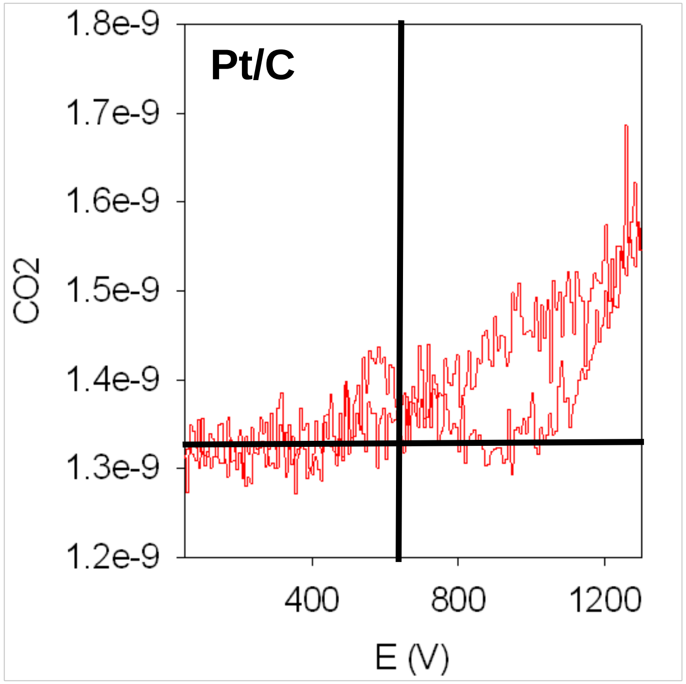
Compensating for decrease of average particle size:
85% loss of platinum!

V.A.T. Dam, K. Jayasayee, F.A. de Bruijn, Fuel Cells, 9(4), 453 - 462 (2009)

# Comparison of $CO_2$ formation on carbon and Pt/C during potential scan

$CO_2$ production on Carbon and Pt/C at 80$^o$C

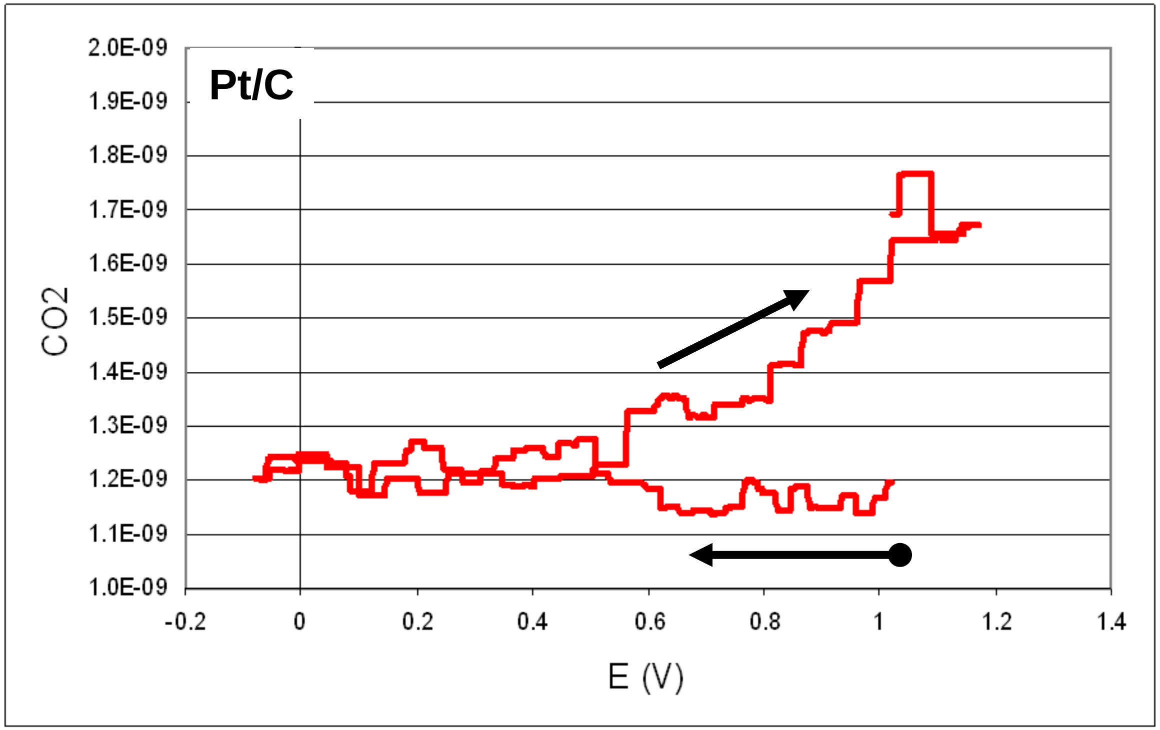



In the presence of Pt, carbon is oxidized at a lower potential

V.A.T. Dam, K. Jayasayee, F.A. de Bruijn, Fuel Cells, 9(4), 453 - 462 (2009)

# $CO_2$ formation on Pt/C after exposure to 1.15 V for 30 minutes

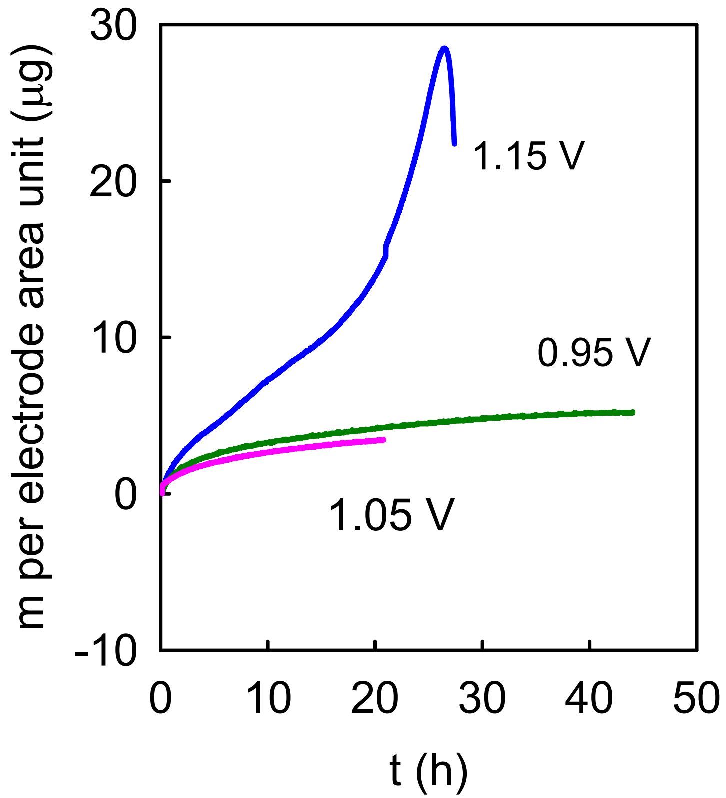



After 30 minutes at 1.15V, platinum is inactive for catalyzing carbon oxidation.
After its reduction during CV, $CO_2$ formation starts at 0.6 V

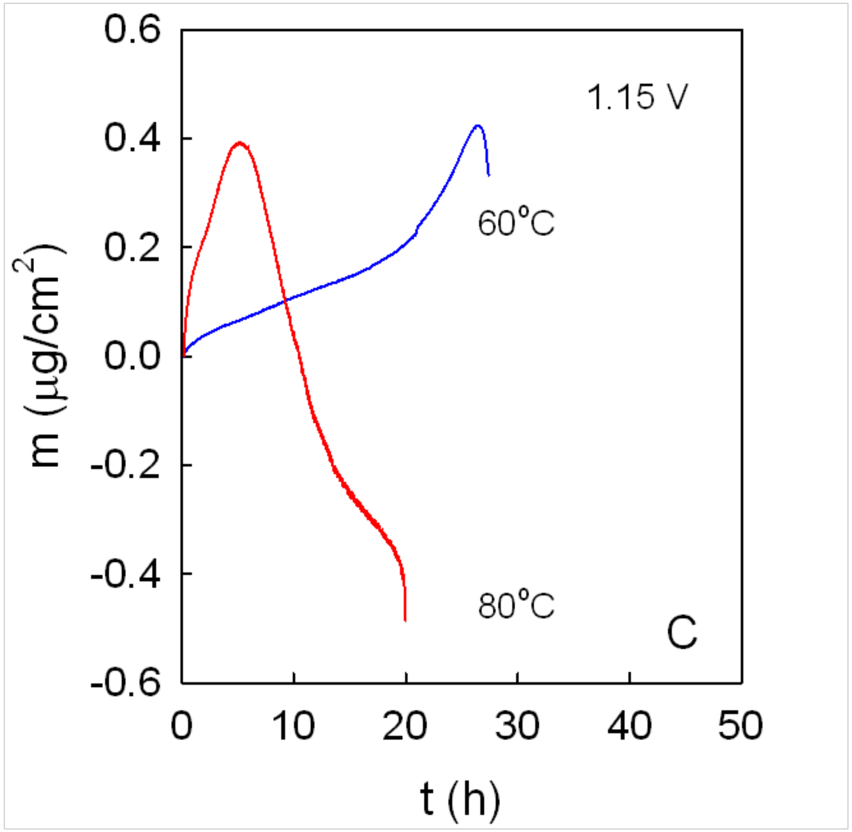
V.A.T. Dam, K. Jayasayee, F.A. de Bruijn, Fuel Cells, 9(4), 453 - 462 (2009)

# Stability of Carbon as function of temperature (Vulcan XC72R)

Increase in potential accelerates carbon corrosion




Increase in temperature accelerates carbon corrosion




V.A.T. Dam, K. Jayasayee, F.A. de Bruijn, Fuel Cells, 9(4), 453 - 462 (2009)

# Approaches to lower the platinum loading

**I Increase of catalyst (platinum) utilization**

improve electrochemical accessibility of platinum
remove transport barriers
increase platinum dispersion

For this structural optimizations, an understanding of the fundamental processes at the nano-scale are necessary (transport of protons, electrons and gases)

**II Apply alternative catalysts**

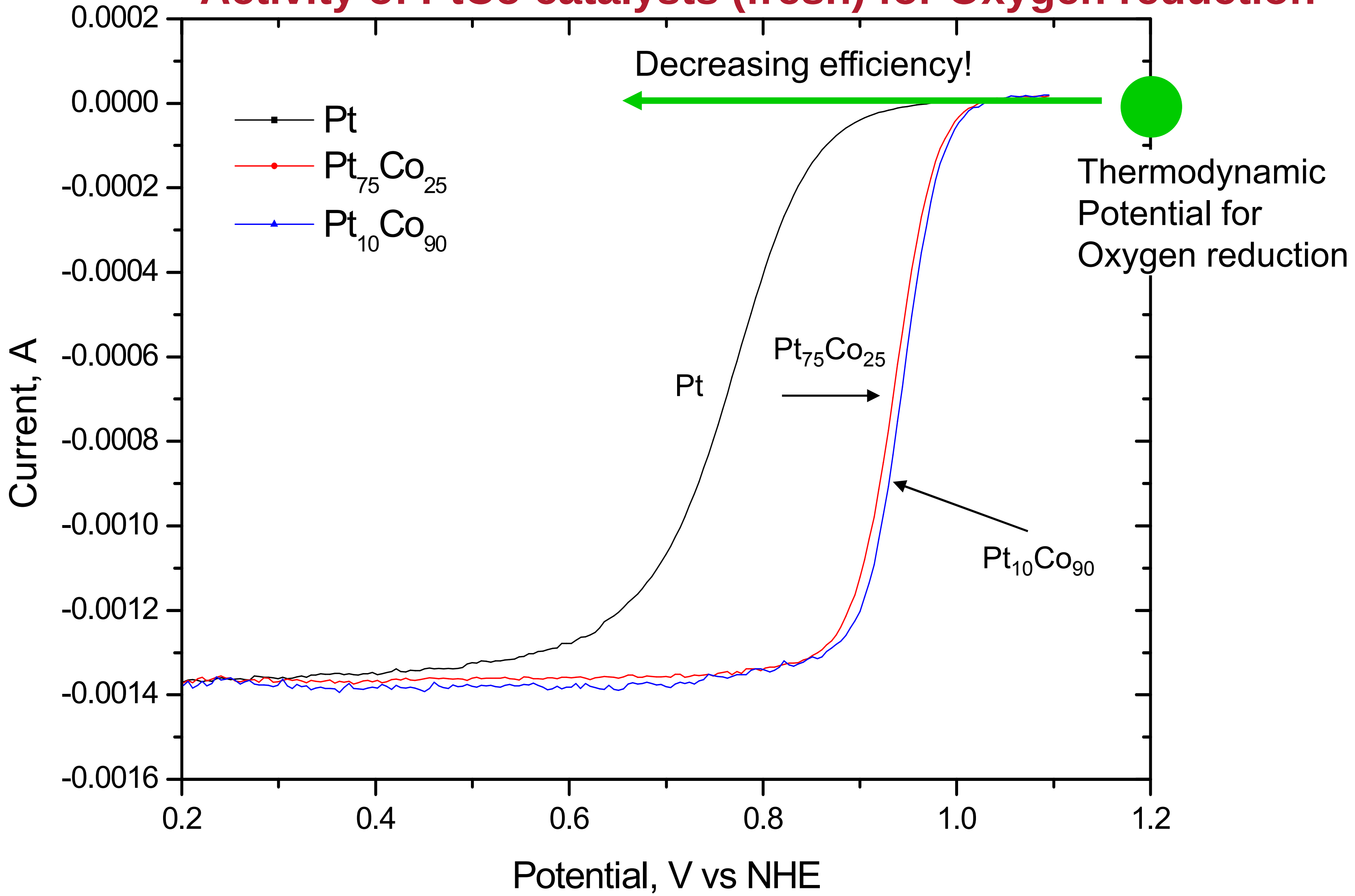
platinum free catalysts
**platinum alloys**

Until now, PEM fuel cells using platinum free catalysts have shown power densities approx. 10-100 fold lower than those using platinum. Lowering of power density leads to increase of other components costs!

**III Switch to anion exchange membranes (i.e. fixed alkaline electrolytes)**

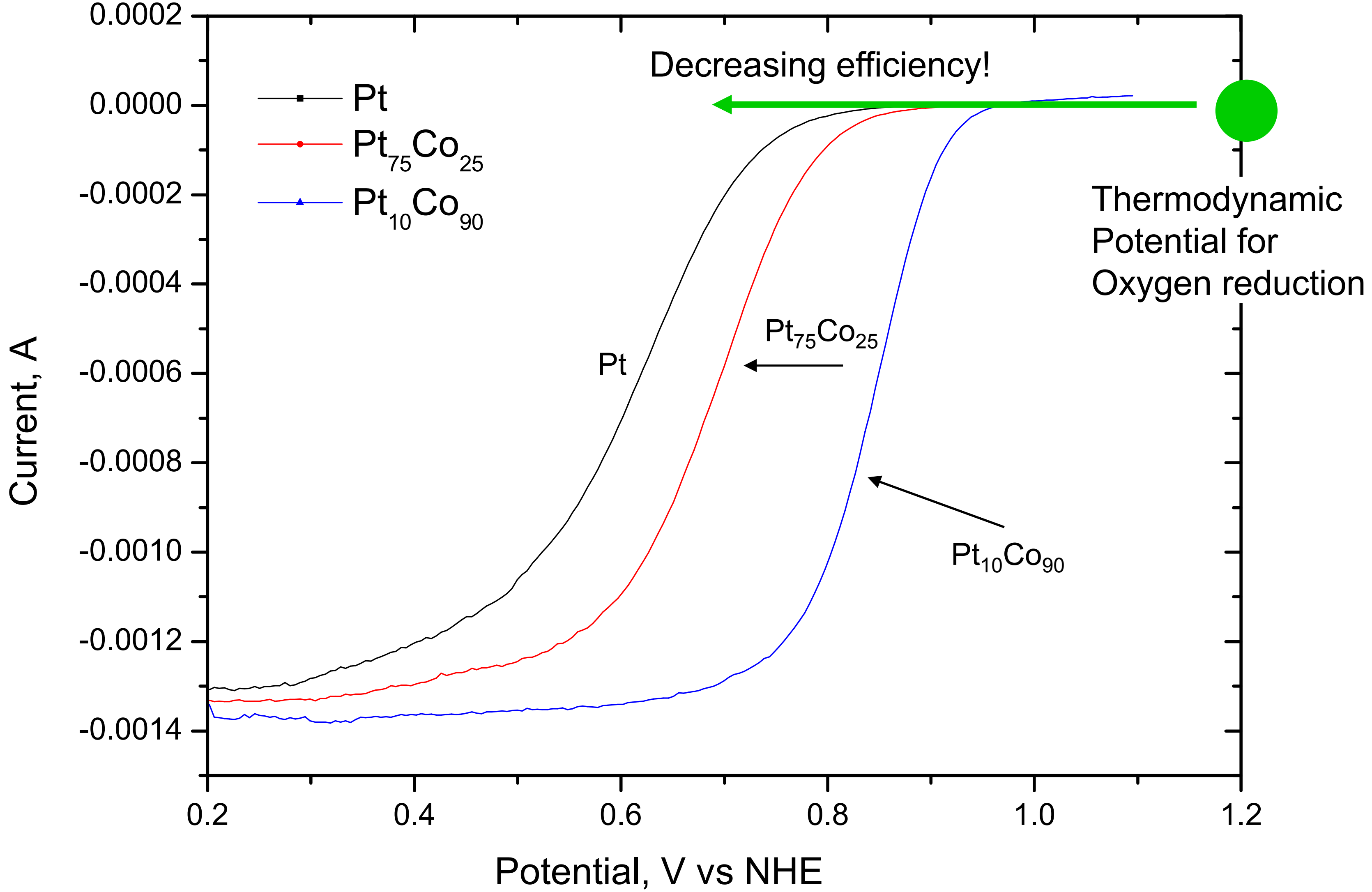
platinum free catalysts

# Activity of PtCo catalysts (fresh) for Oxygen reduction




K. Jayasayee, V.A.T. Dam, T. Verhoeven, F.A. de Bruijn, J. Phys.Chem. C, 113(47), 20371 (2009)

# Activity of PtCo catalysts (after 1000 voltage cycles)

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## Summary

MEA is key component which deserves much R&D attention :

- it's cost determines 30% of overall systems cost directly
- systems simplyfication and cost reduction only possible with advanced MEA
- stack and system durability determined by MEA durability

Standard cell materials not good enough from durability point of view

- Pt gets dissolved; can redeposit during cycling, but gets lost at potentiostatic hold
- most often used carbon gets corroded at high potential
- higher temperature accelerate these processes

The good news

- new membrane materials identified for extending temperature window, on low and high side
- new alloy formulations identified with low platinum ratio for enhanced activity & stability

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