Electrode Degradation in PEM Fuel Cells in Model Systems and PEMFC Testing

F.A. de Bruijn

V.A. Dam

G.J.M. Janssen

R.C. Makkus

Presented at the 16th ECS Meeting Fall 2009, 4-9 October 2009, Vienna, Austria

ECN-L--09- 174 December 2009

ECN

Energy research Centre of the Netherlands

TU/e

Electrode Degradation in PEM Fuel Cells in Model Systems and PEMFC Testing

Frank de Bruijn[1,2], Van Anh Dam[2], Gaby Janssen[1], Robert Makkus[1]

[1] Energy research Centre of the Netherlands ECN , Petten, NL

[2] Inorganic Chemistry and Catalysis Group, Eindhoven University of Technology, Eindhoven, NL

216th ECS Meeting Fall 2009 Vienna, Austria

Fuel Cell Vehicles are on the road!

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

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

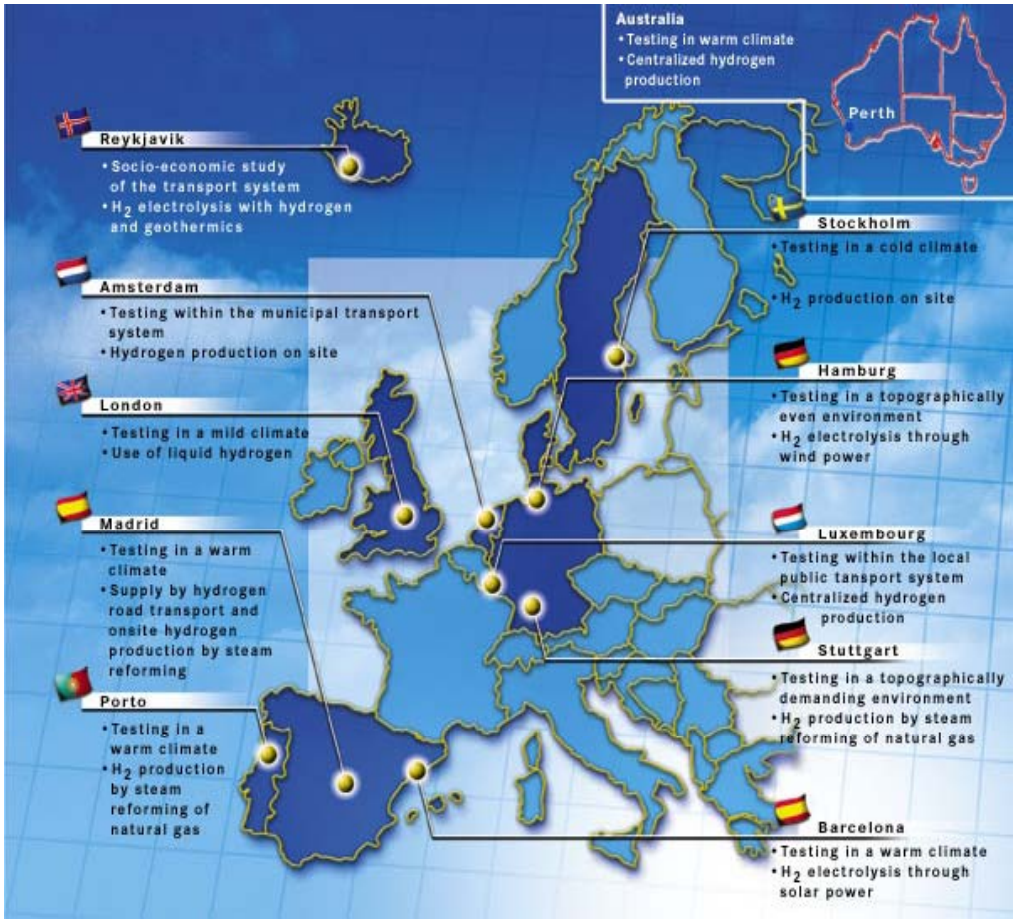
January 2007 first F-Cell >100,000 km and
2000 h without significant performance loss

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

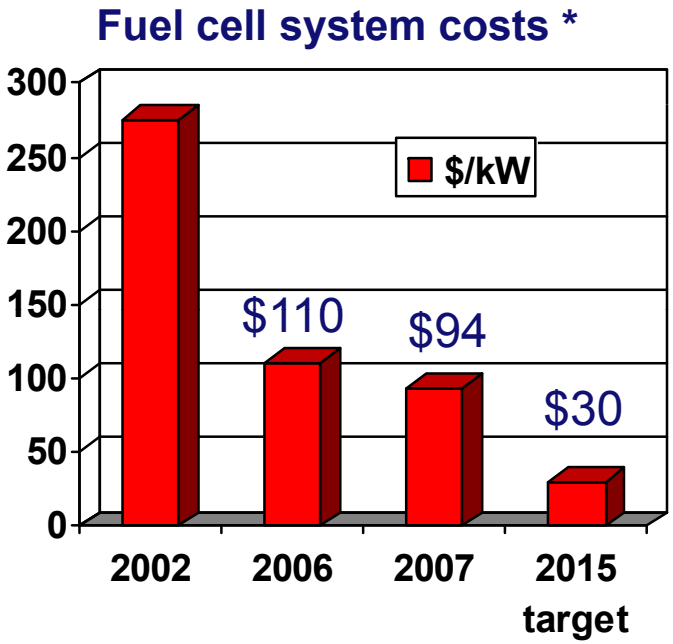
Improvement of Life time and Durability

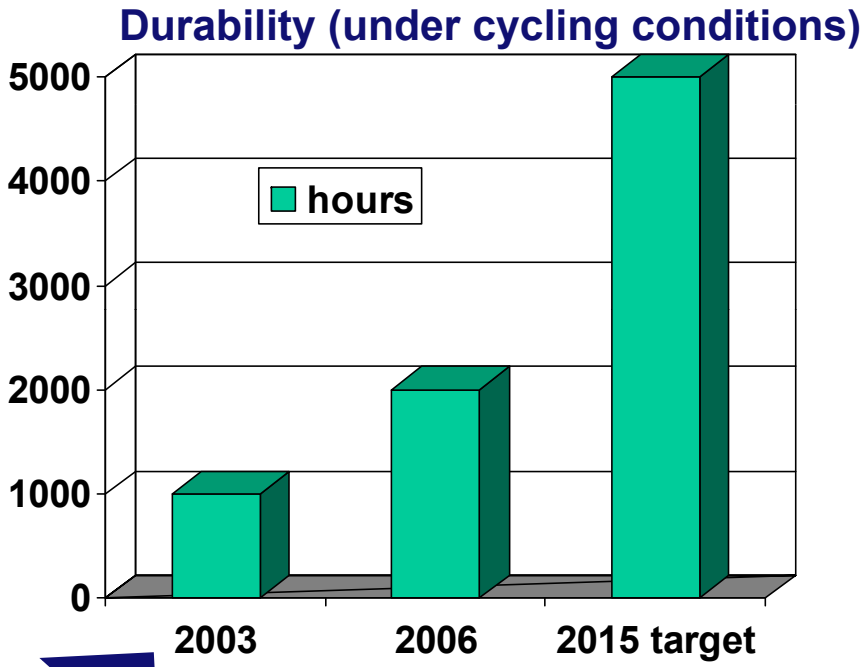
Long term: further improvements needed for full market penetration

Increase in Operating Temperature

Operation at Reduced Water Content

DoE analysis of the technology status versus the Targets





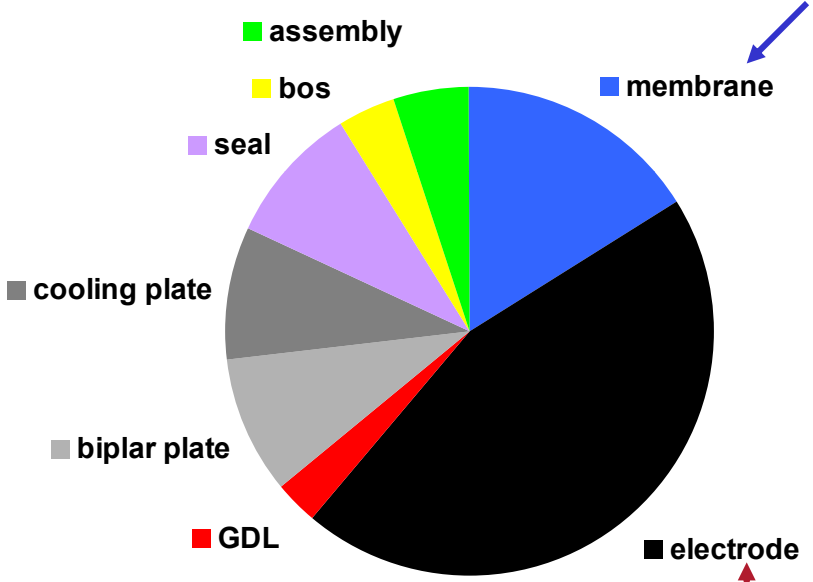
* for 500,000 vehicles produced per year

Cost reducing strategies could have a major impact on durability

J. Milliken et al., Hydrogen Technologies for the Developing World Forum, Moscow 2008

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?

Durability: capability to work reliably under real life conditions

Freeze – thaw cycles

Load cycles

Cooling problems

PEMFC degradation: literature review

*F.A. de Bruijn et al. Fuel Cells, **8** (2008) 3*

Analyzing published long term PEMFC operation, we concluded that fuel cell degradation varies strongly with conditions:

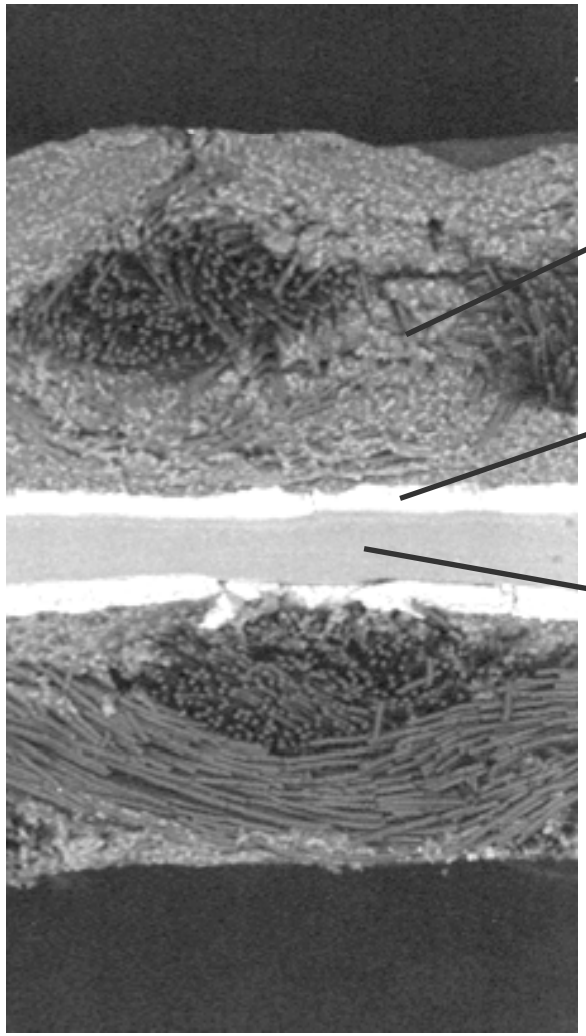
Ideal conditions: RH = 100%; T = 75 °C; no cycling
Materials: membranes ~ 125 µm; no ultralow Pt loadings

voltage decay: 1-2 $\mu V.hr^{-1}$
lifetime: > 10,000 hrs

Voltage decay generally increases when:

thin membranes are used
RH < 100%, but strongly depends on flow field design
voltage cycling is applied, especially when OCV is included
T > 75 °C
freeze/thaw cycles are applied

PEMFC degradation



SEM cross section of PEMFC MEA

GDL

Loss of hydrophobicity

Pt/C catalyst

Carbon corrosion; Platinum sintering; Platinum dissolution; Catalyst fouling

electrolyte

Chemical degradation:
Membrane thinning; pinhole formation; Ion exchange by metal ions

Durability issues for transport applications

- Load (voltage cycling) accelerates platinum dissolution/coarsening

- Start-up/shut down can lead to extremely high cathode 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 costs for hydrogen production and infrastructure
  Contaminants in hydrogen and air can lead to catalyst and membrane poisoning

When developing components 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!!!

For development of more stable and robust PEMFCs we need:

In situ	*Ex situ*
Accelerated tests which are still representative for conditions in PEMFC *applications*	Model studies on components and materials at well-defined conditions
Characterization tools that can discriminate between various contributions	Advanced techniques for mechanistic studies
⇓	⇓
Quantitative data on degradation	Understanding of degradation
Life-time predictions Post test information	Mitigation strategies Improved materials

Content of this Work

In situ

MEA testing under stressing conditions

MEA potenial and load cycling

MEA freeze/thaw cycles

Characterization by polarisation curves, EIS, CV, chronoamparometry

Post test analysis (TEM,SEM)

Ex situ

Potentiostatic studies on Platinum, and Carbon Platinum/Carbon electrodes

Characterization by Quartz Crystal Microbalance, CV

Post test analysis TEM

In Situ Accelerated Stress Tests

Qualify materials:

- Potential cycling (N_2/H_2) → catalyst
- OCV hold → membrane
- Potential hold (≥1.2 V) → carbon support

Qualify MEAs → membrane, catalyst, support, ionomer phase, GDL

Load or potential (H_2/air) cycling :

- Variations in potential — Pt dissolution, Pt particle growth, carbon corrosion
- Exposure to H_2/air(O_2) — membrane/ionomer chemical degradation
- Humidity variation — shrinkage/swelling of membrane/ionomer
- Fuel starvation — carbon corrosion

and coupling effects!

Freeze/Thaw cycling includes

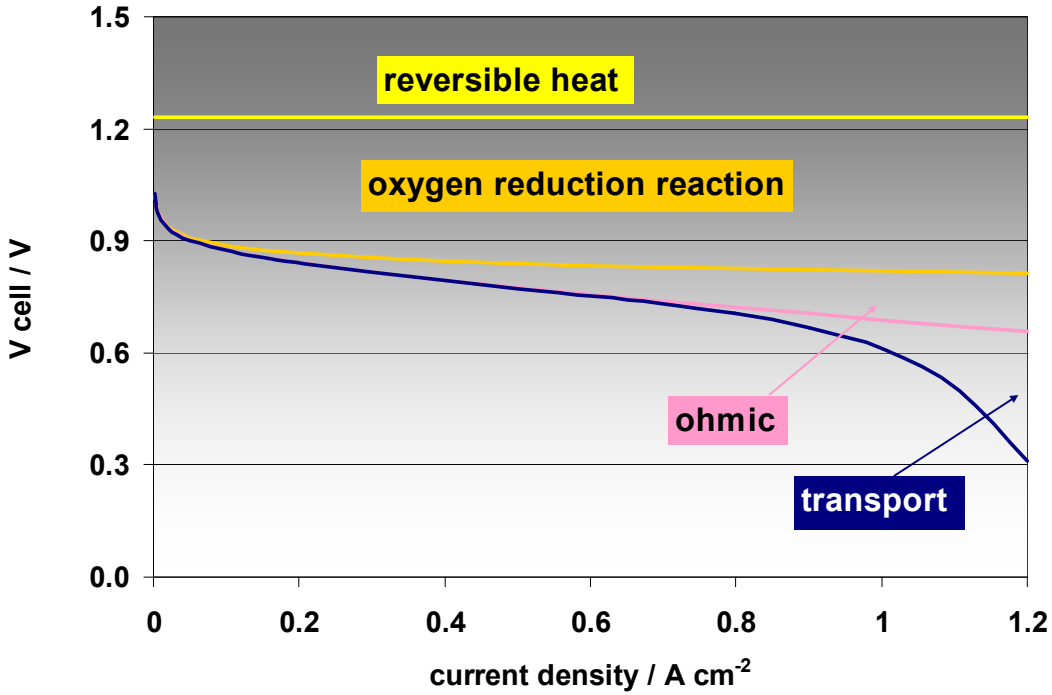
- Ice formation — electrode delamination, GDL damage

AST with break-down of cell voltage losses

$$V_{cell}(j) = E^0 - \eta_{\Omega}(j) - \eta_{ORR}(j) - \eta_{transport}(j)$$
$$= E^0 - j \cdot R_{hf} - b\log\left(\frac{j}{i_m m_{Pt} pO_2}\right) - f(R_p, P_m, j)$$

$$\Delta\eta_{air}(j) = \Delta\eta_{\Omega} + \Delta\eta_{ORR} + \Delta\eta_{transport}$$
$$= j \cdot \Delta R_{hf} + b\log\frac{i_m^1}{i_m^2} + f(\Delta R_p, \Delta P_m, j)$$

$$\Delta\eta_{O2}(j) = j \cdot \Delta R_{hf} + b\log\frac{i_m^1}{i_m^2} + f(\Delta R_p, j)$$



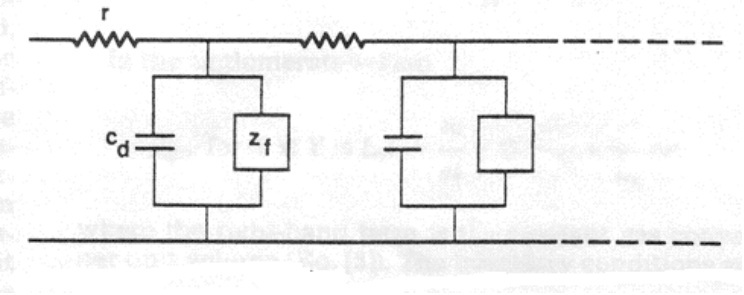
Transport losses depend on R_p and P_m, contributions difficult to separate

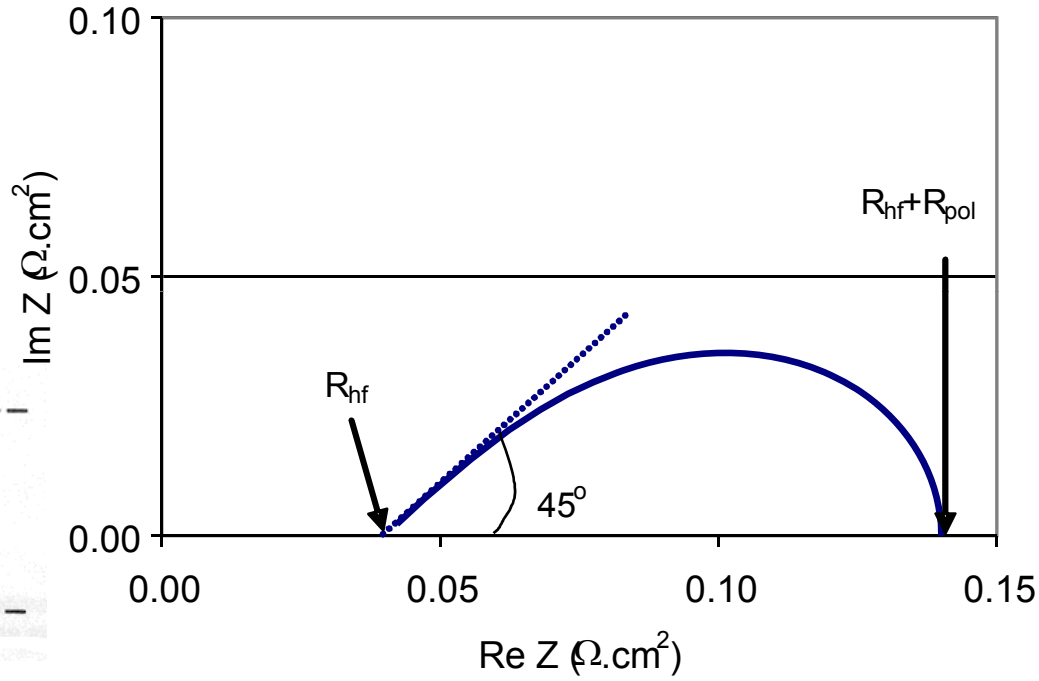
Transport loss in pure O_2 dominated by R_p

R_p can be measured by EIS

Electrochemical Impedance Spectroscopy

- H_2/O_2,
- Under load
- High frequency real axis intercept for Ohmic resistance
- Nyquist arc: cathode





Linear part:

$$Z(\omega) = R_{hf} + \sqrt{\frac{R_p}{\omega C_{dl}}}\exp\left(-i\frac{\pi}{4}\right)$$

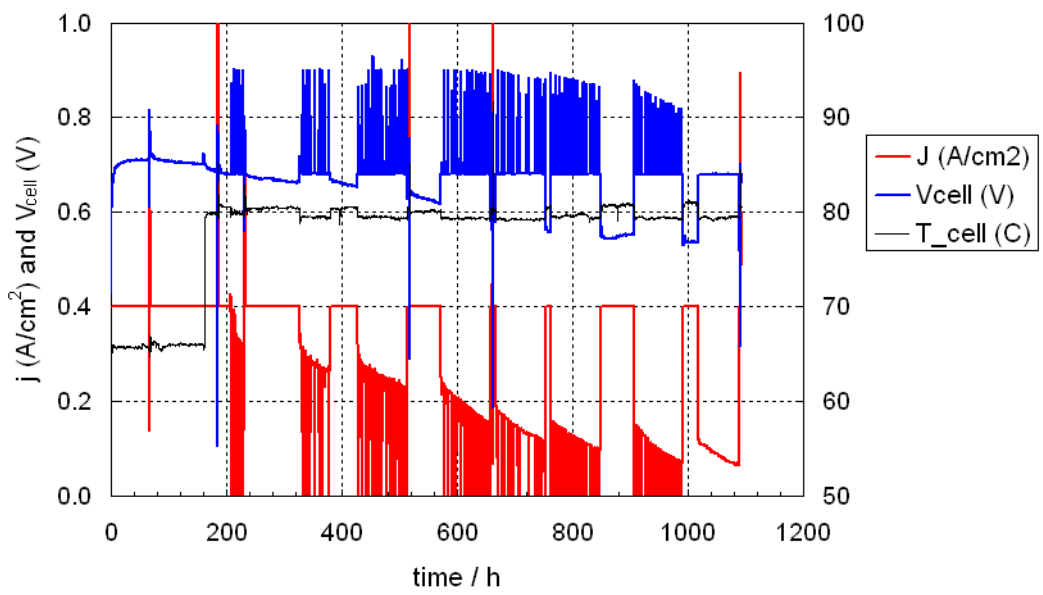
(C_{dl} from cyclic voltammetry)

Fast voltage cycles – load profile

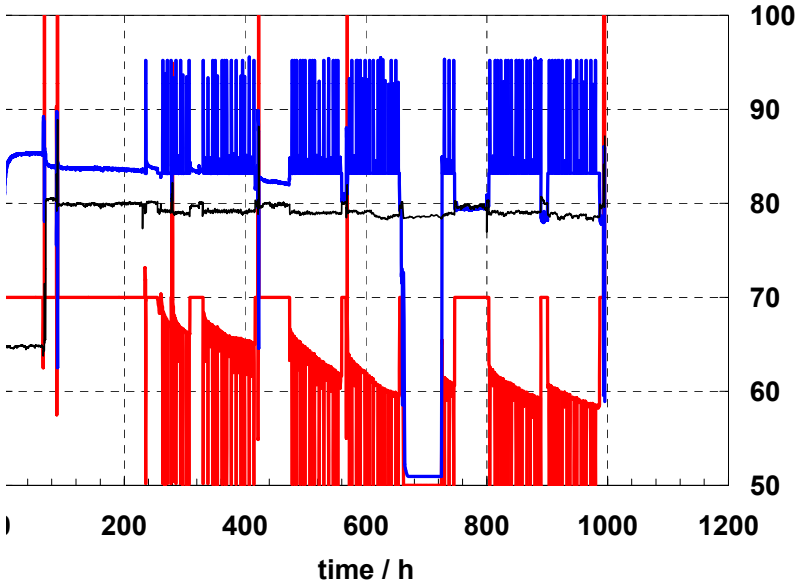
H_2/Air,80°C, 80% RH, ambient pressure

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

Full characterization after 0, 1000, 5000, 10000, 30000 cycles



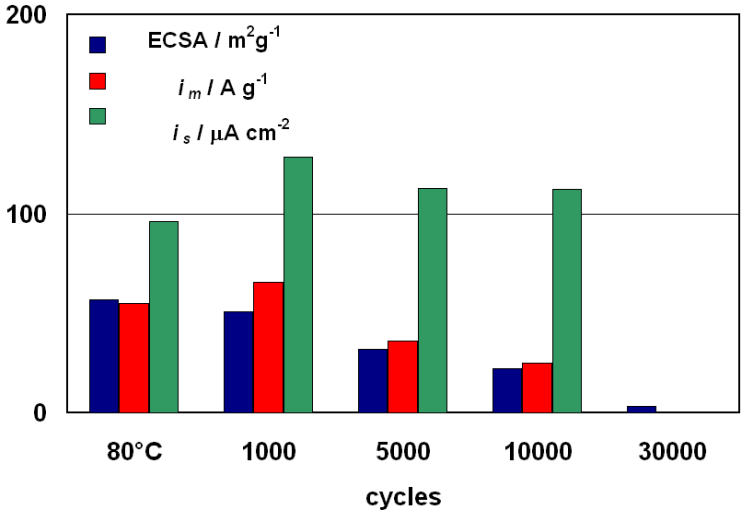
MEA1: Hispec 9100, N:C=0.7, NRE211CS



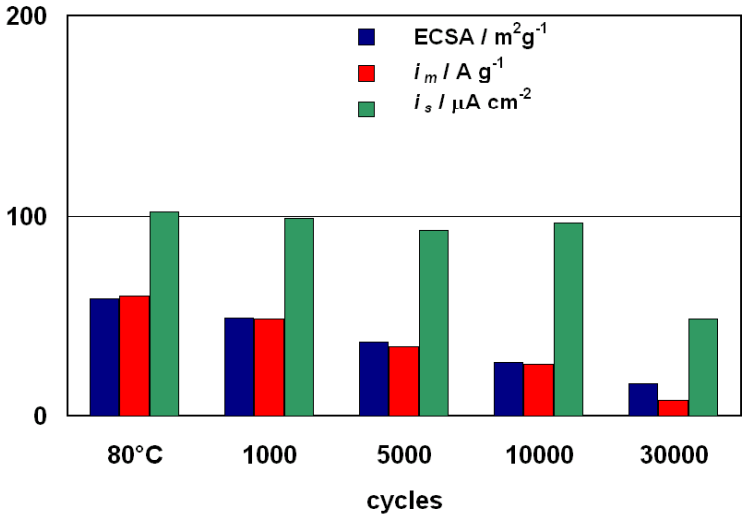
MEA2: Hispec 9100, N:C=0.55, NRE212CS

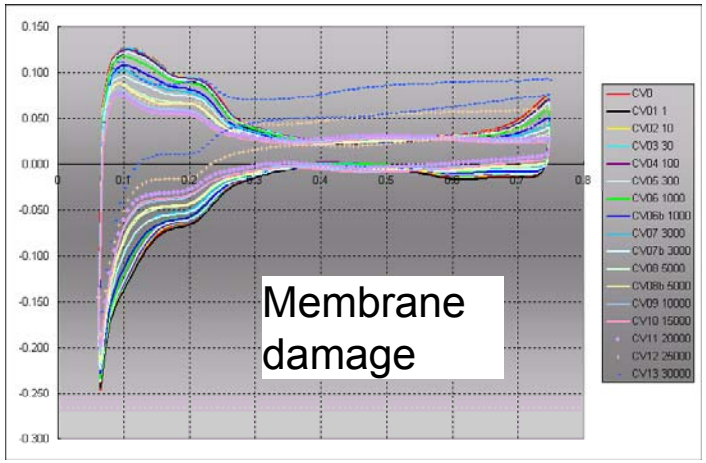
Fast voltage cycling

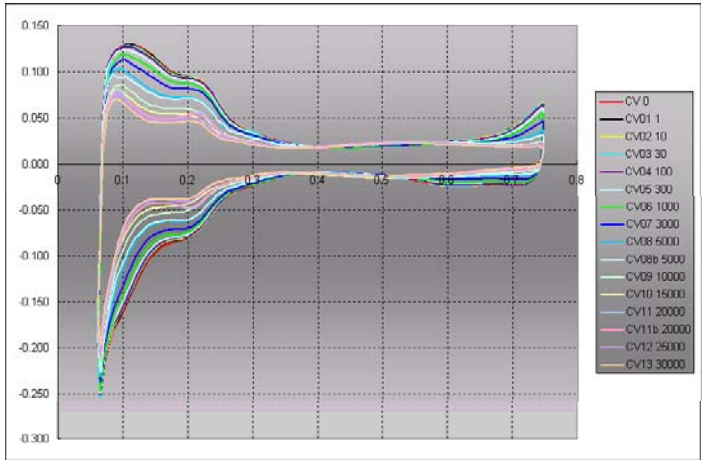
MEA 1



MEA 2

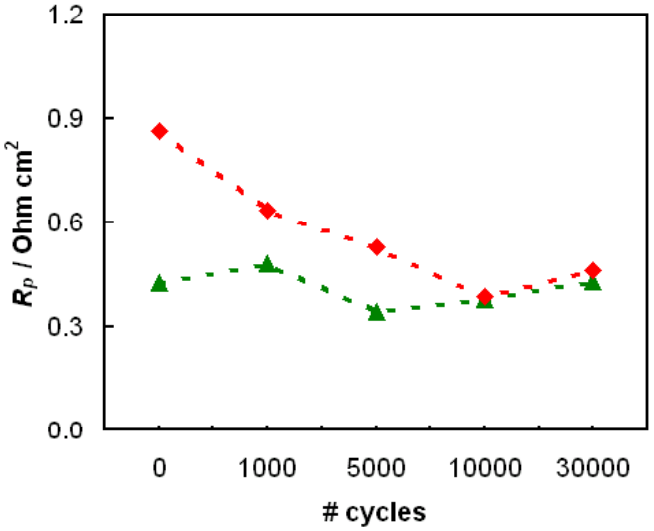






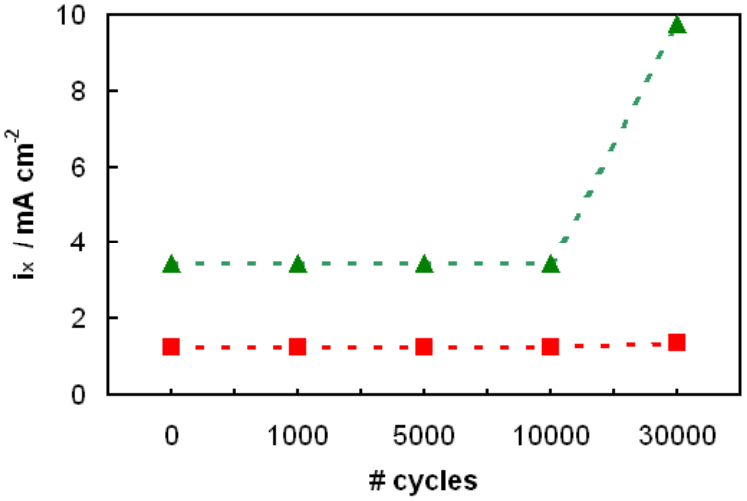
Fast voltage cycling

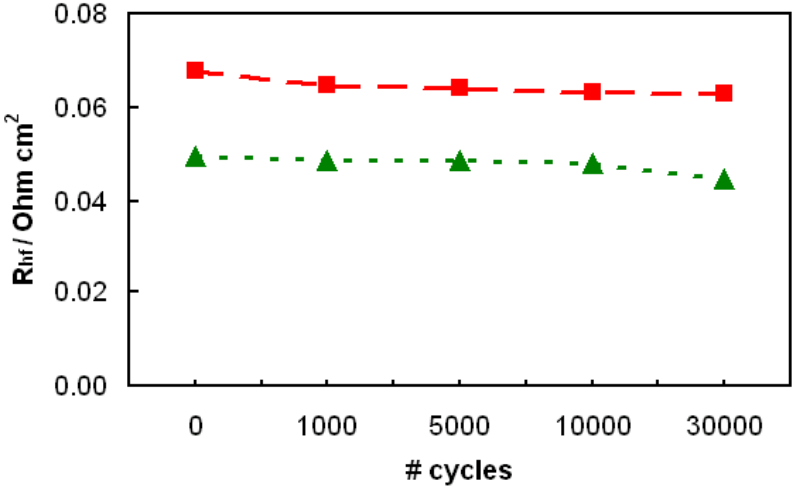
Low ionomer content:
R_p decreases



NRE211CS: damage
NRE212CS: stable

Green MEA 1
Red MEA 2





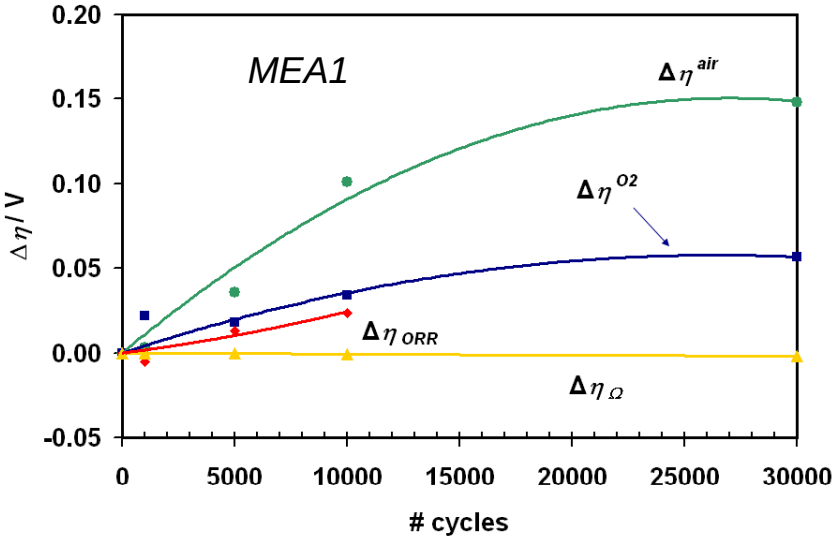
Fast voltage cycling: break down of ΔV^{air} @ 0.4 A cm^{-2}

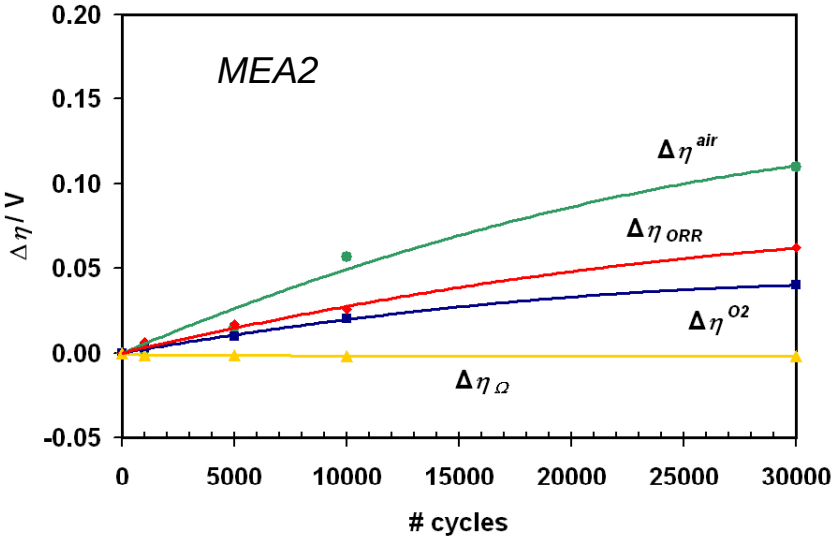
Loss ECSA & activity

	MEA 1	MEA 2
10000 c		
ECSA	61%	55%
activity	54%	57%
30000 c		
ECSA	*95%*	73%
activity		87%

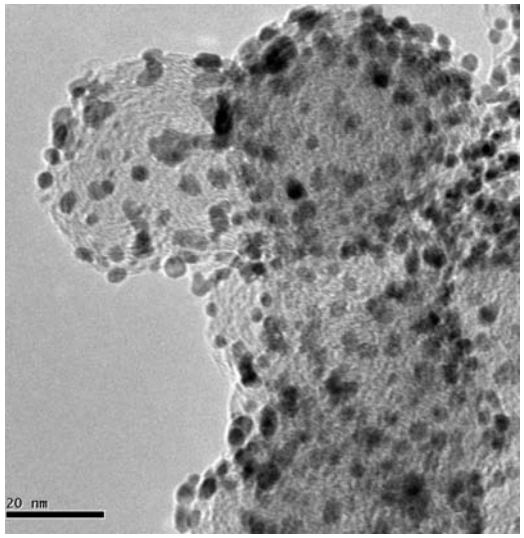
After 30000 fast cycles

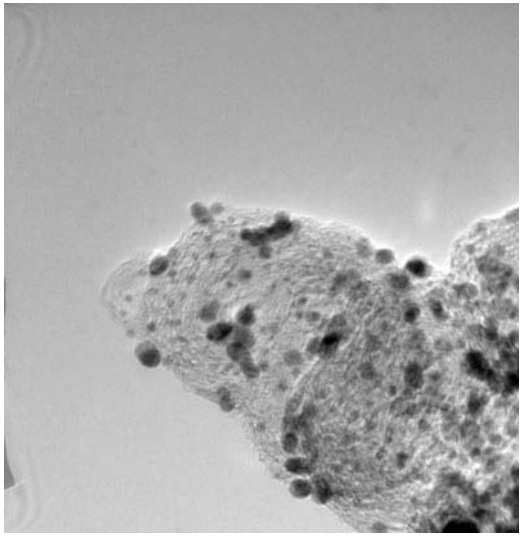
- slight decrease of ohmic losses and increase of kinetic losses
- change in in oxygen gain large contribution; depends on ionomer content
- substantial decrease of permeability (P_m) suspected

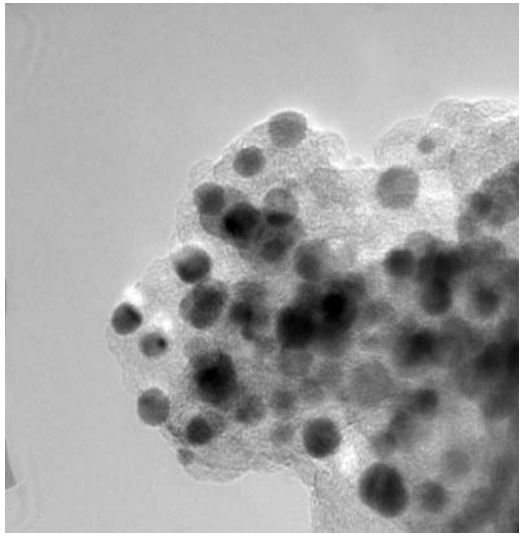




Post test analysis – TEM cathode catalyst







0 x

10000 x

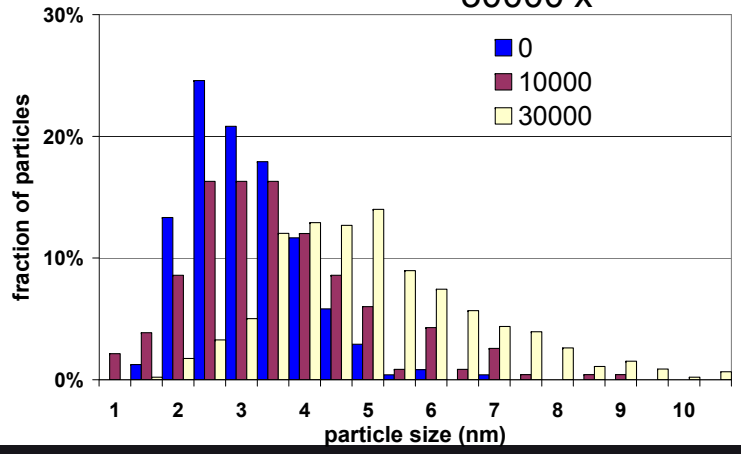
30000 x

Pt particle coarsening

d 0 2.4 nm - SA loss 0%

d10000 3.8 nm - 38%

d30000 5.8 nm - 55%



Post test analysis – SEM MEA cross section

After 30000 voltage cycles:

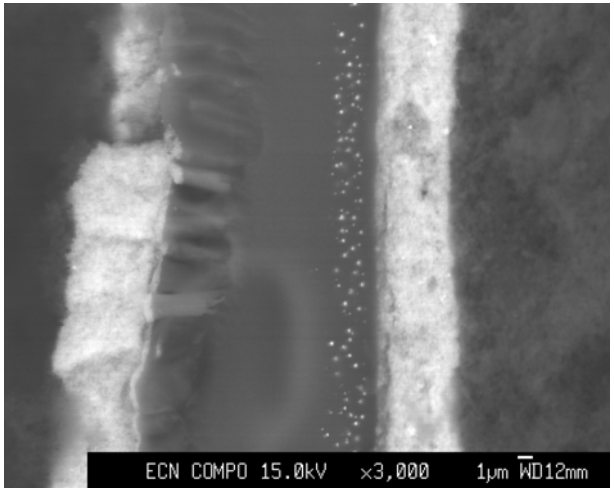
membrane thinning observed for NRE211CS (↓ 15 µm)

no significant electrode thinning

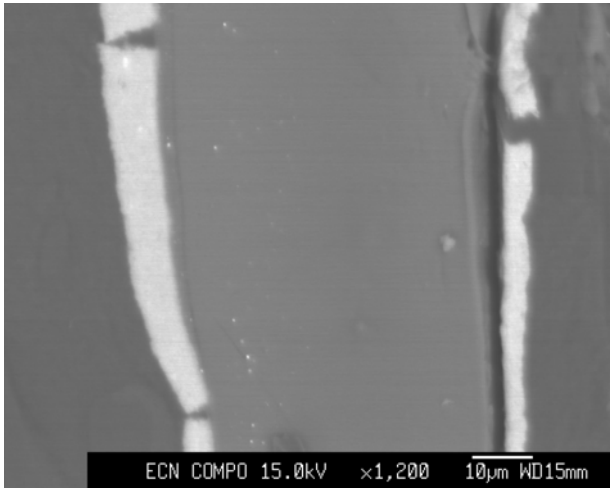
significant Pt deposition in NRE211CS near cathode

some Pt deposition in NRE212CS near anode

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



MEA 1 (NRE211CS)

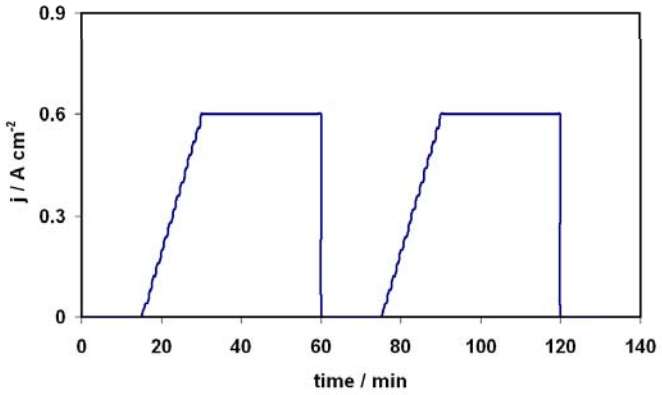


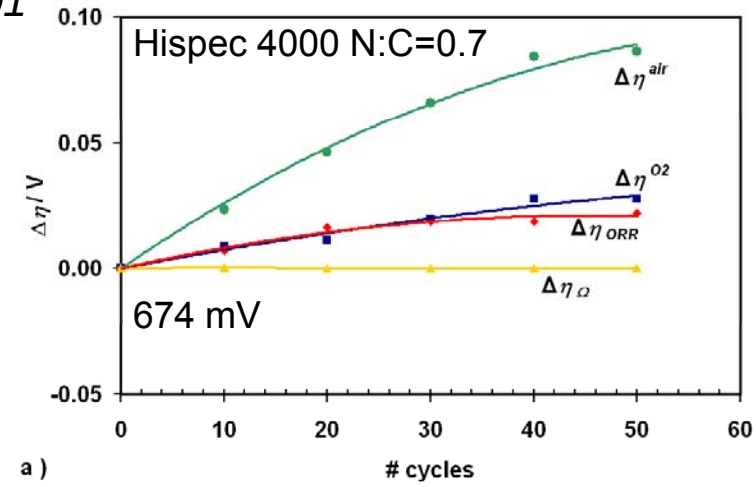
MEA 2 (NRE212CS)

Load on/off cycles: break down of ΔV^{air} @ 0.4 A cm^{-2}

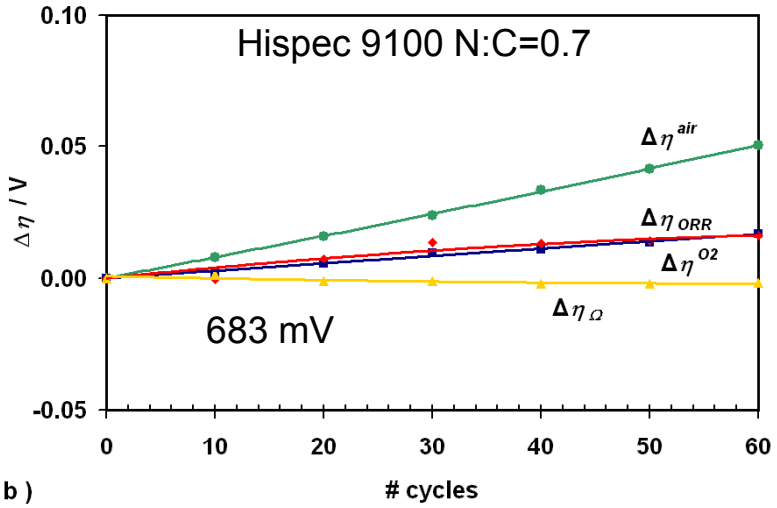
*G.J.M. Janssen et al., J. Power Sources **191** (2009) 501*

After 5 x 10 cycles / 600 hr at 80°C

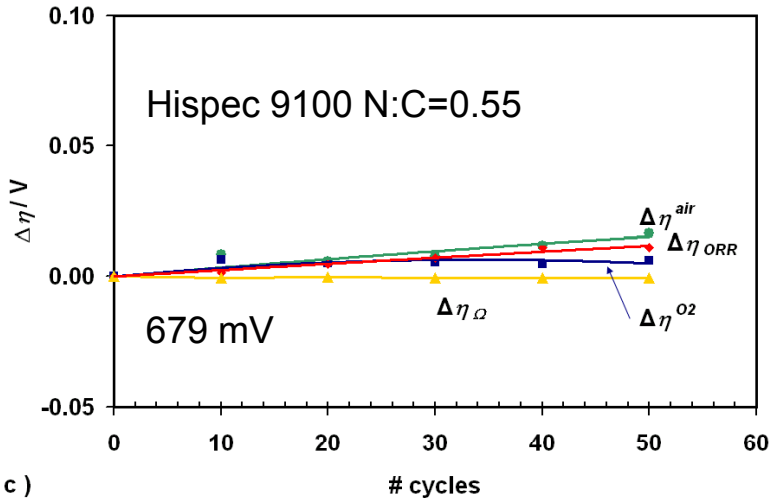




a)



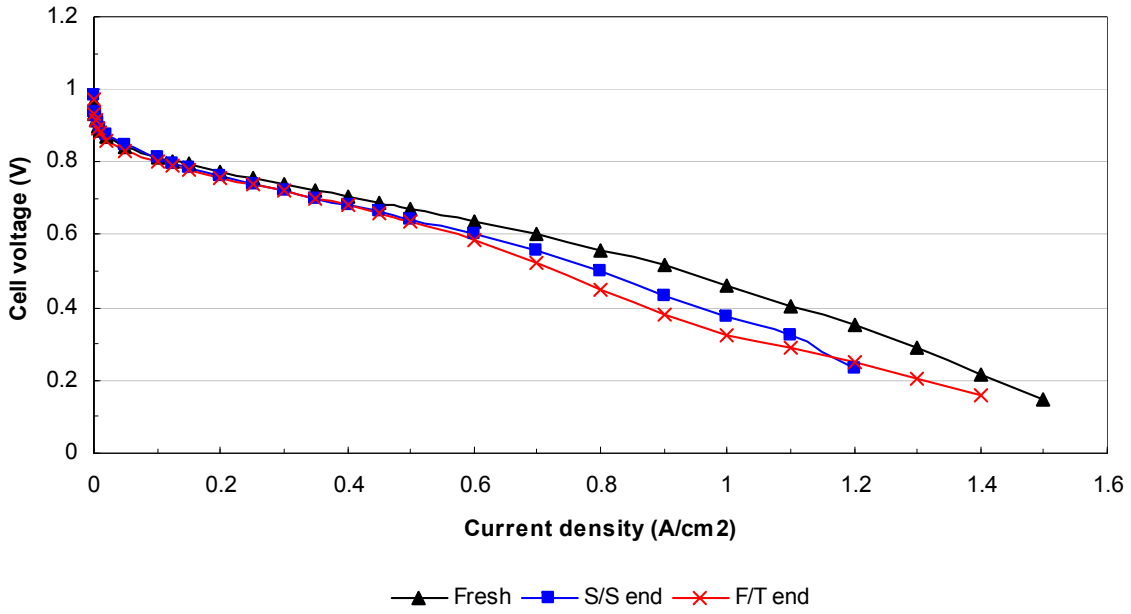
b)



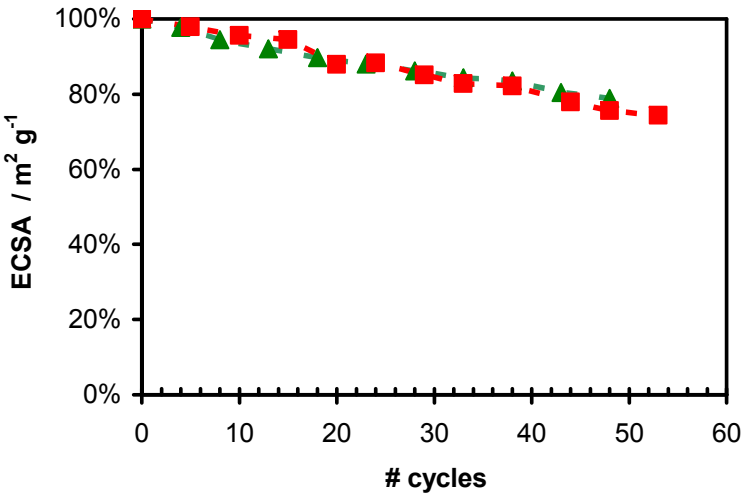
c)

In situ AST

- Freeze/thaw experiments
  - -20 °C/ 65 °C
  - no water removal
  - gas supply shut off
- Start /Stop
  - 5 °C/ 65 °C
  - gas supply shut off
- 58 cycles, each 4th cycle characterisation

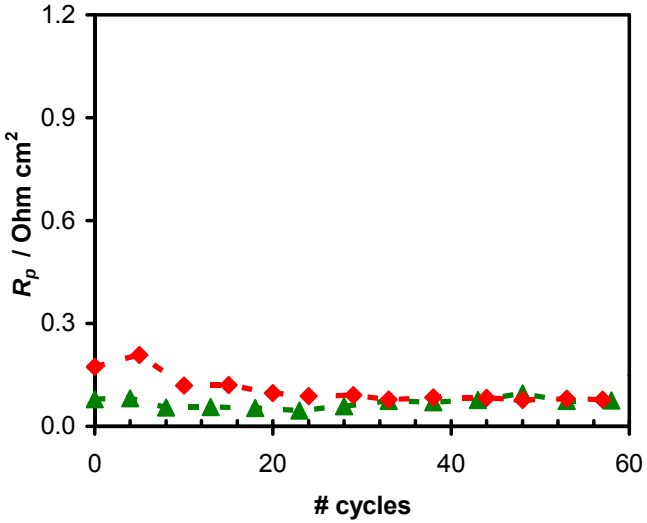


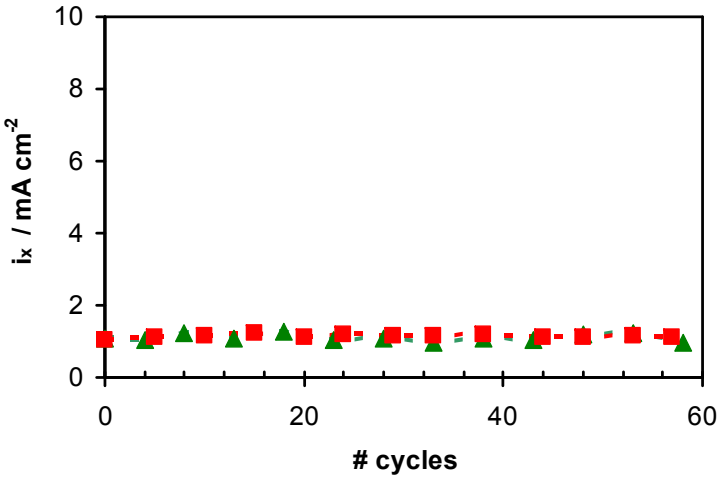
F/T & S/S cycling

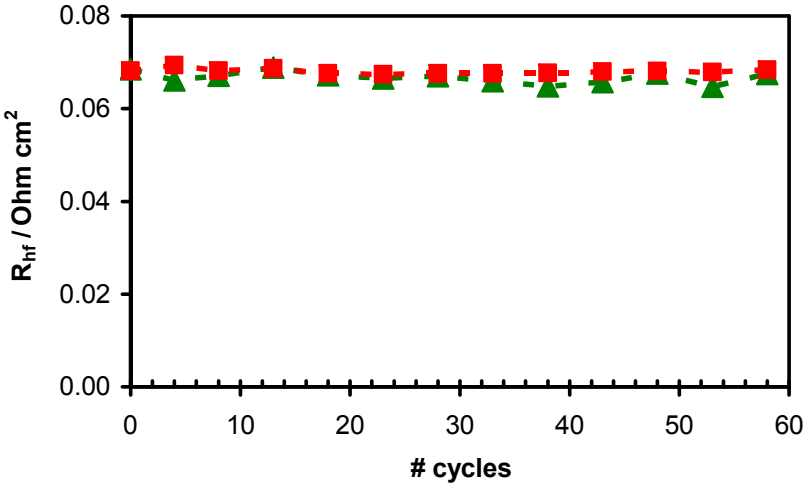


Green S/S

Red F/T



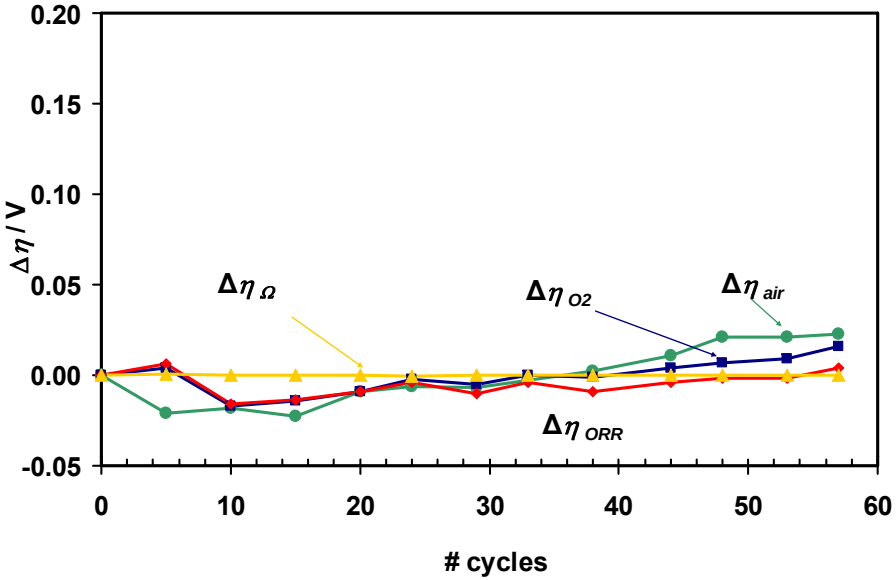




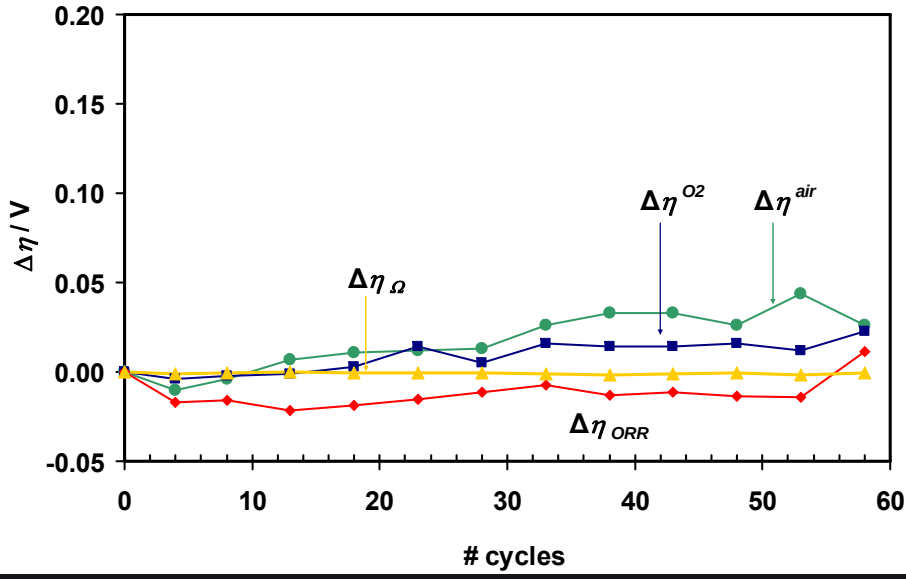
Break down of ΔV^{air} @ 0.4 A cm^{-2}

F/T

Slight changes in transport losses only



S/S

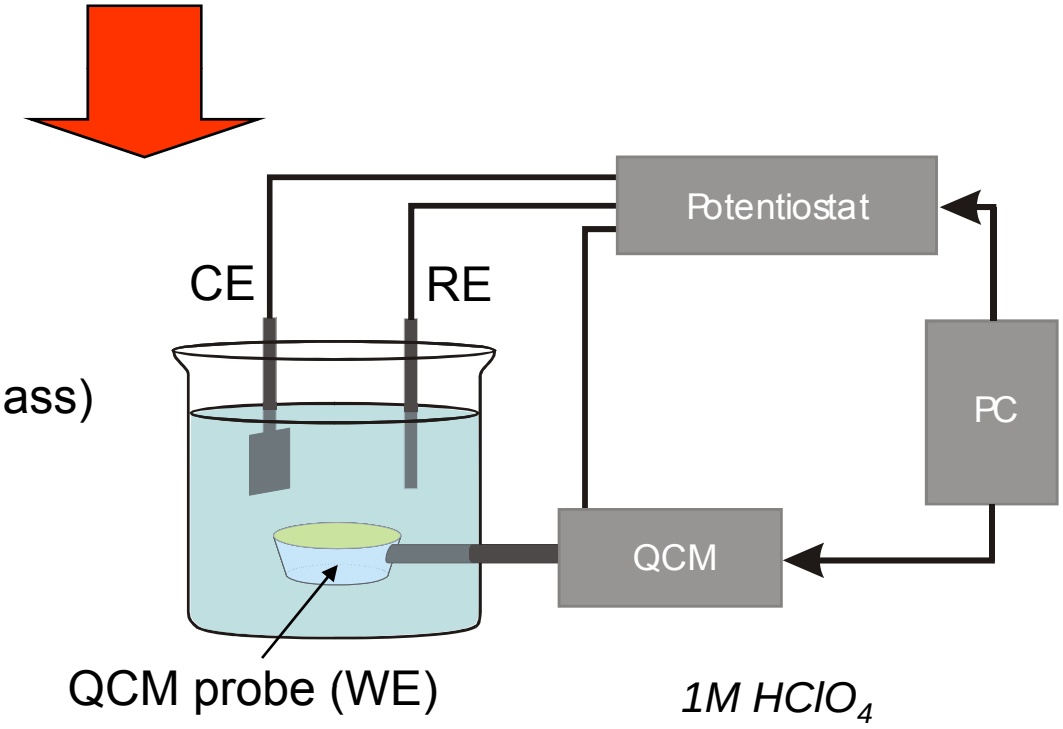


Conclusions *in situ* tests

- Potential and load cycles at 80°C with breakdown of cell losses show
  - Ohmic losses: constant although membrane damage could be observed (thinning, increased H_2 cross-over) for 25 μm membranes
  - Kinetic losses increase due to decreased mass activity (Pt growth and dissolution)
  - Transport losses *dominate* cell voltage loss and are strongly affected by catalyst layer composition
    - Protonic resistance electrode stable or decreasing, depending on ionomer content
    - Oxygen permeability seems strongly reduced (increased hydrophilicity?)
  - No significant carbon corrosion observed (potentials ≤ OCV)
- F/T cycles and S/S show:
  - No membrane damage
  - Slight increase in mass transport losses

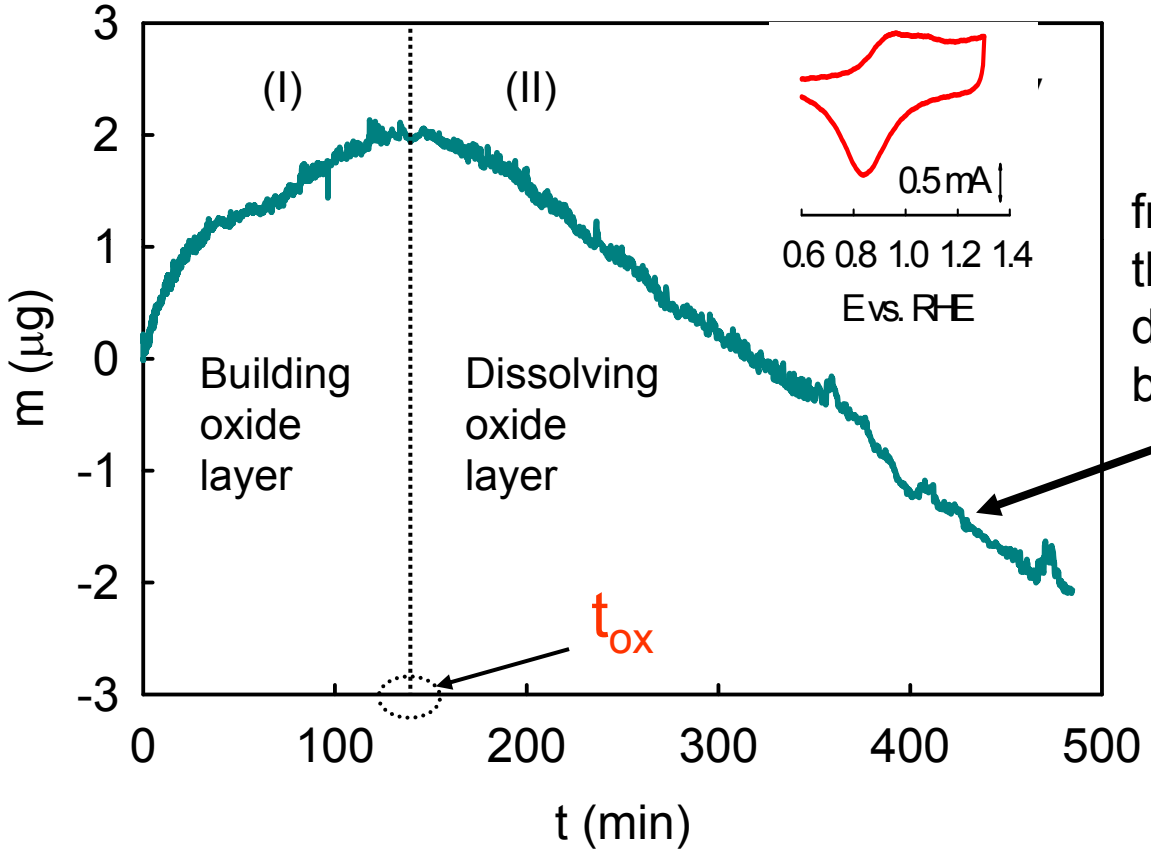
Ex Situ Electrochemical study of platinum and carbon stability

- Stability of Pt, C, and 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



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

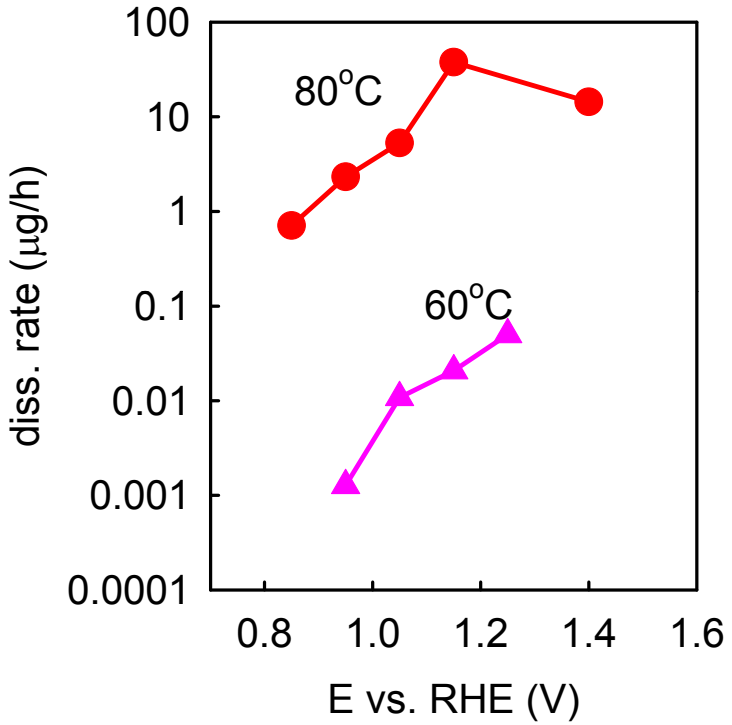
Pt thin film mass change at 0.85V & 80°C



from the slope, the net platinum dissolution rate can be calculated

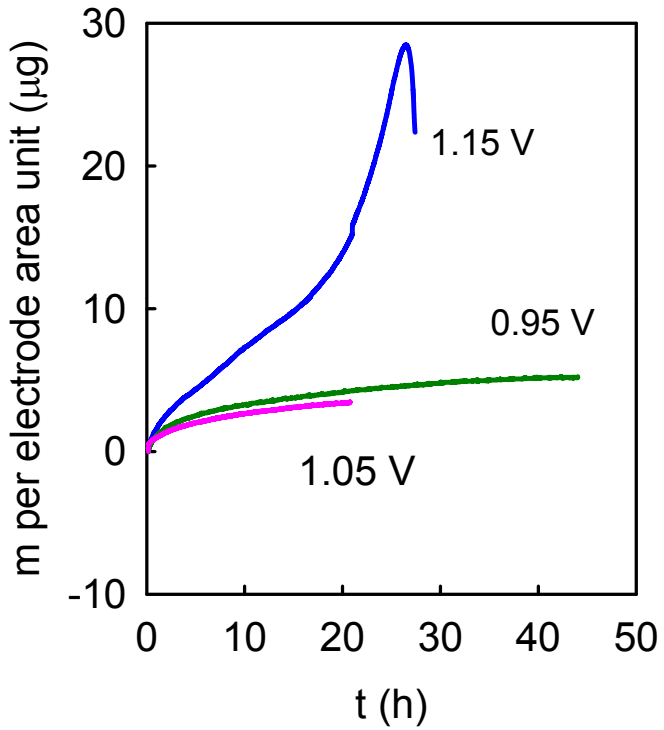
Pt thin film dissolution

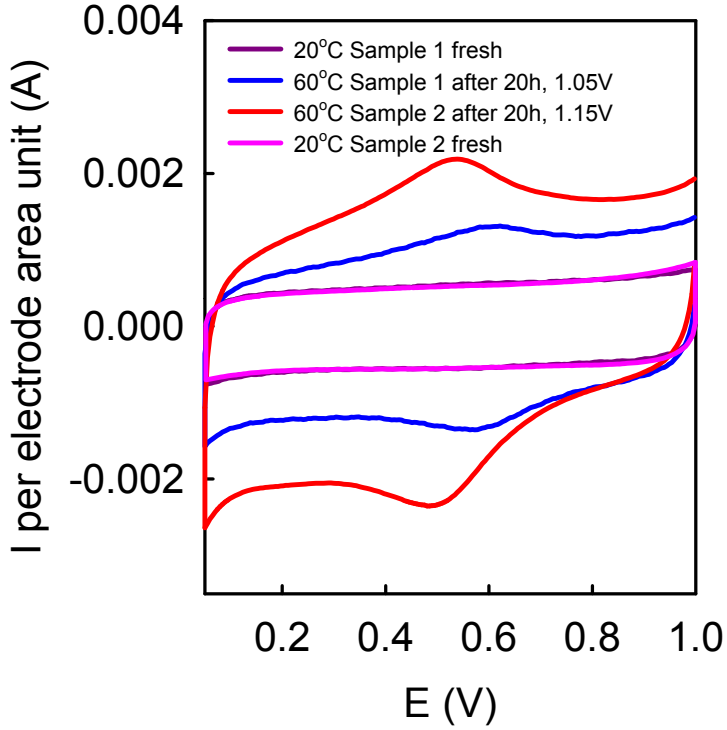
- During dissolution, *first an oxide layer is formed*, which is further dissolved depending on T & E.
- The oxide layer is still continuously formed during dissolution.
- At E ≤ 1.15V, 80 ° C , log. of dissolution rate linearly depends on E (0.55 times / 0.1 V).
- At E > *1.15 V* and 80°C, the *dissolution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



Dam and De Bruijn, J. Electrochem. Soc. ***154*** *(2007) B494*

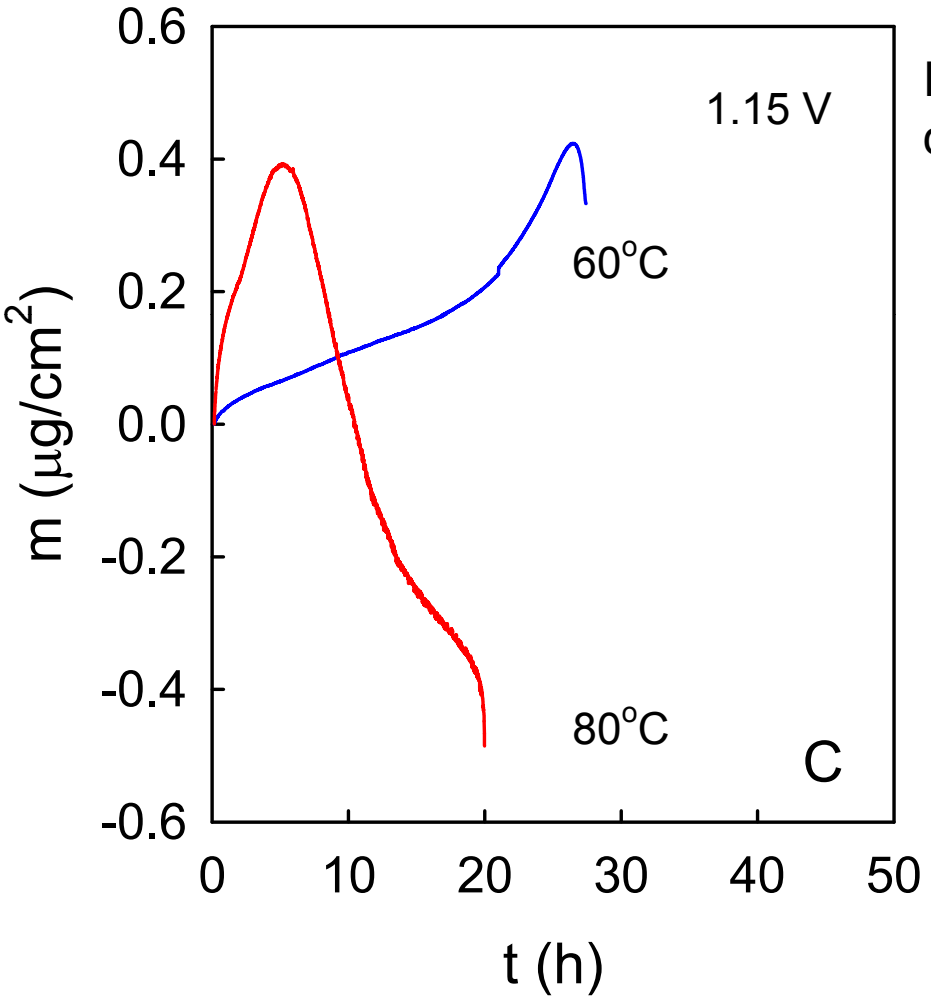
Carbon corrosion at 60°C (Vulcan XC72R)





- At 0.95 & 1.05V, mass increase corresponds to water uptake
- At E = 1.15V, mass decrease can be observed → CO_2 formation (OLEMS)
- Quinone/hydroquinone production increases with the potential.

Stability of Carbon as function of temperature (Vulcan XC72R)

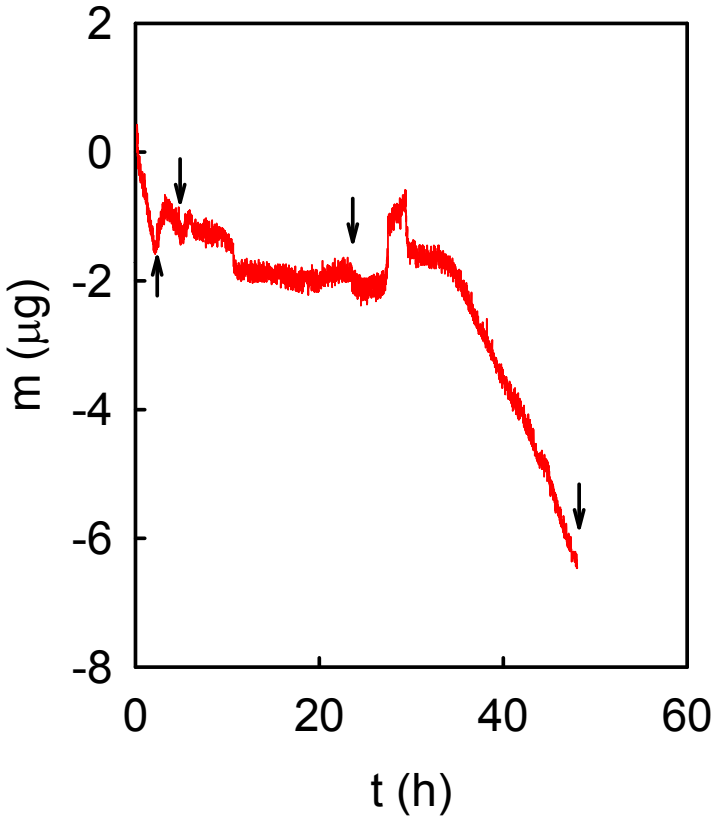


Increase in temperature accelerates carbon corrosion

V.A.T. Dam et al., Fuel Cells ***9*** *(2009) 453*

Platinum/Carbon catalysts

Pt/C mass change at 1.05V & 80°C

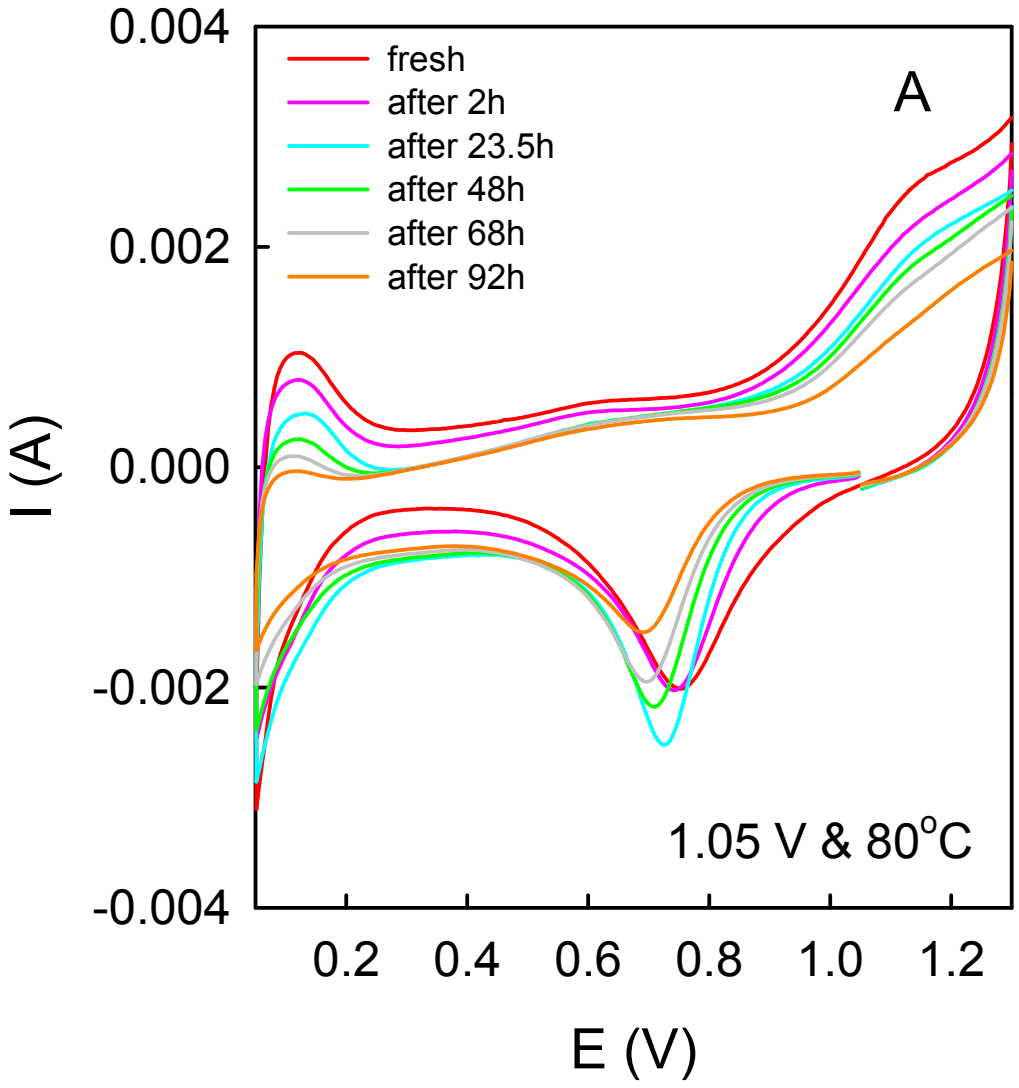


At 80°C, a complex picture is observed which could be caused by:

- platinum oxidation and dissolution
- carbon oxidation and corrosion
- combinations of these processes

How can we discriminate between these processes??
At indicated time intervals, cyclic voltammograms are recorded

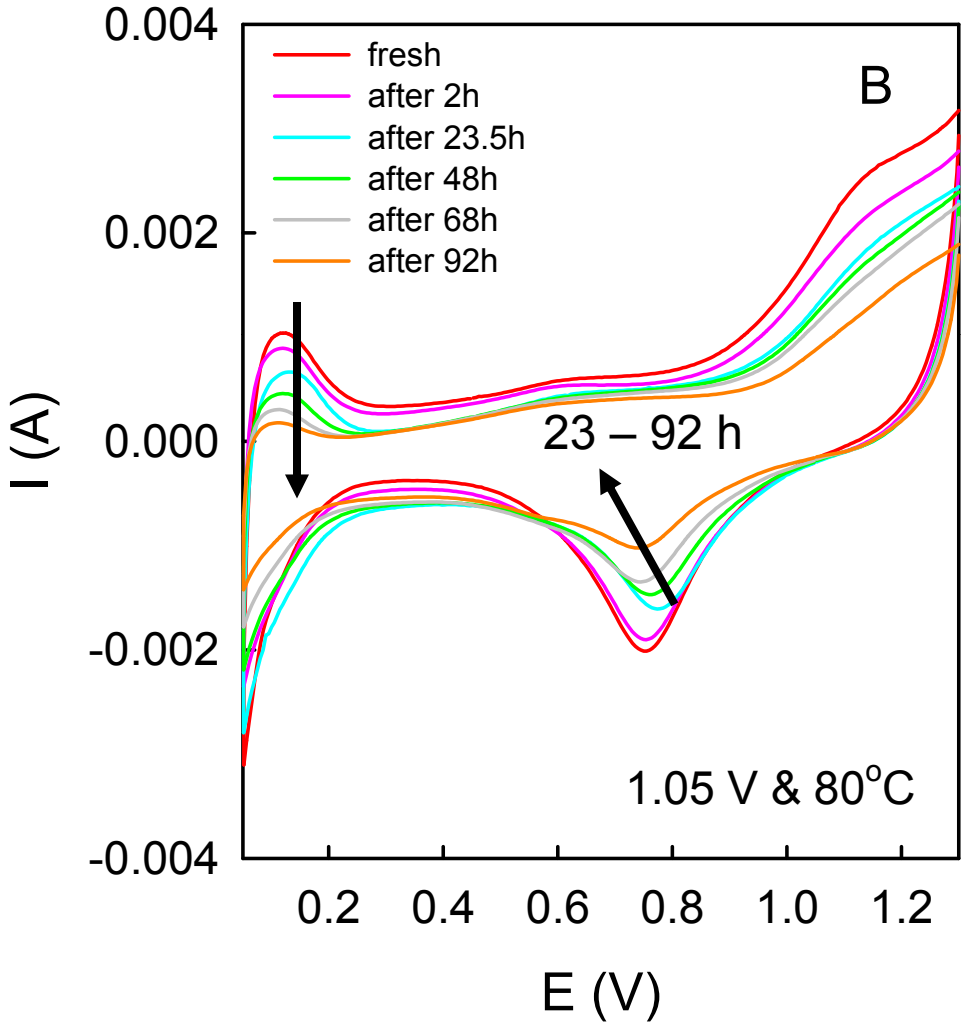
Pt/C dissolution at 1.05V & 80°C



First cyclic voltammograms taken at various intervals during exposure to 1.05 V and 80°C.

Deep oxides are formed during exposure to 1.05 V

Pt/C dissolution at 1.05V & 80°C

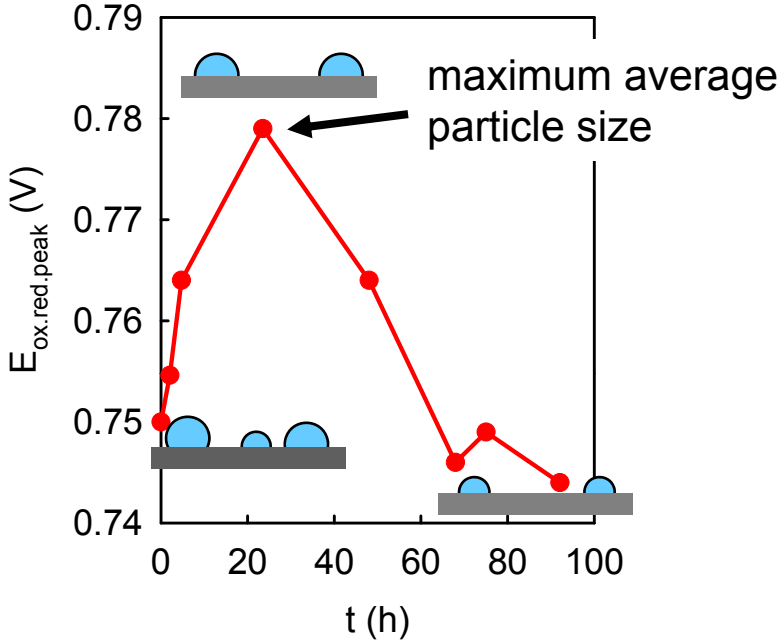


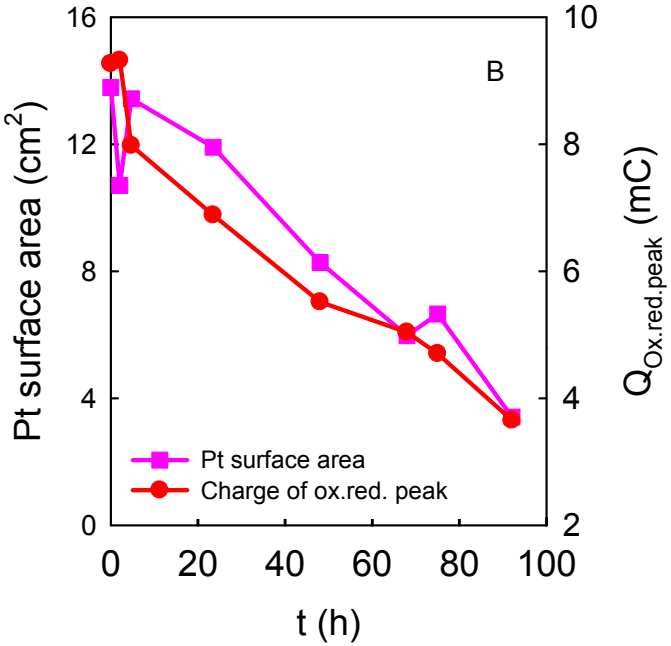
Second cyclic voltammograms taken at various intervals during exposure to 1.05 V and 80°C.

Pt surface area continuously decreases during potential hold

Platinum oxide reduction potential shifts first to slightly more positive but then to more negative values

Pt/C dissolution at 1.05V & 80°C



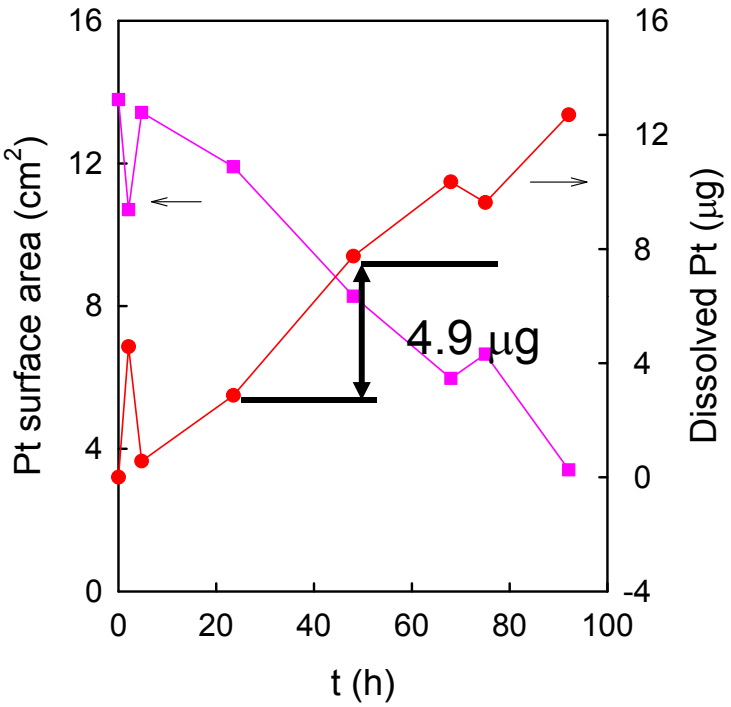


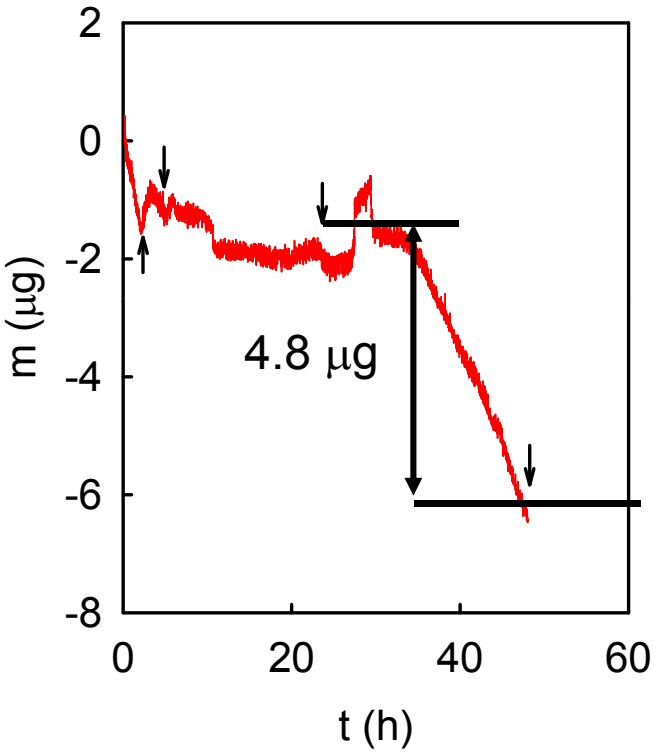
From the second CVs:

- In the first 23 hours, averaged Pt particle size increases, then decreases.
- Pt surface area decreases with time.

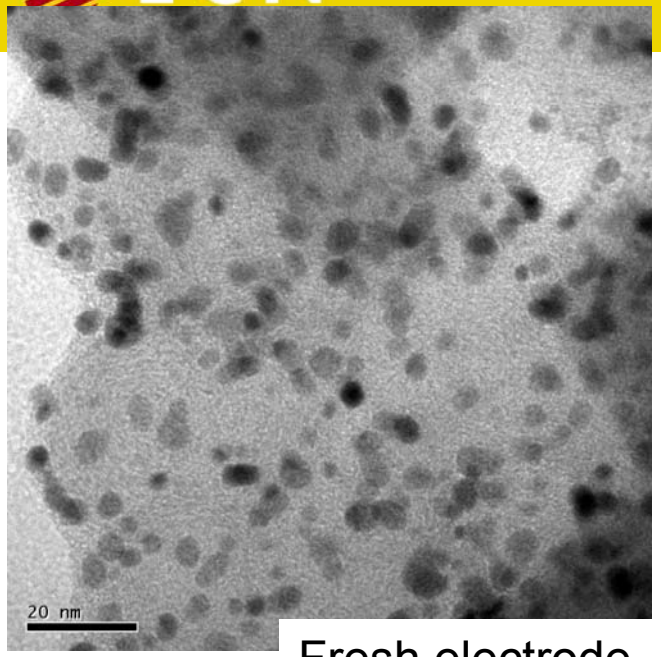
It is very unlikely that Pt redeposition occurs at E = 1.05 V
Surface area decrease can be attributed to shrinking of particles

Pt/C dissolution at 1.05V & 80°C

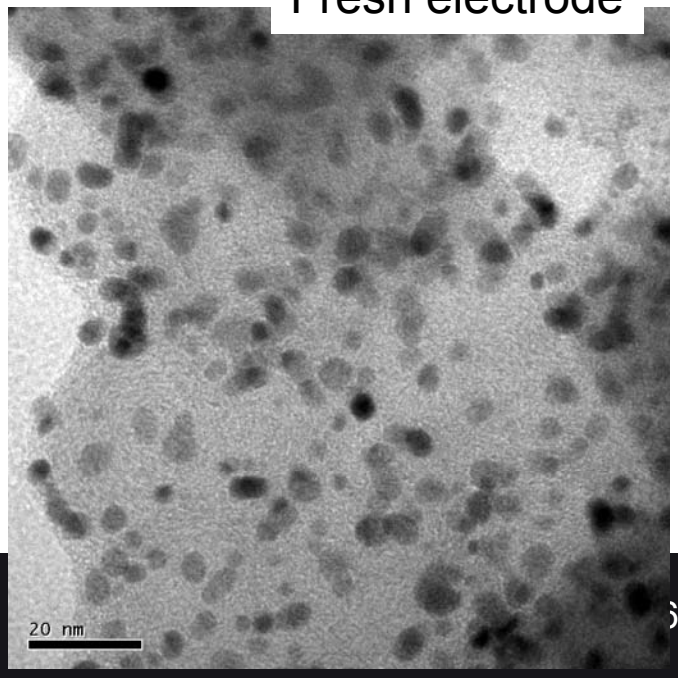




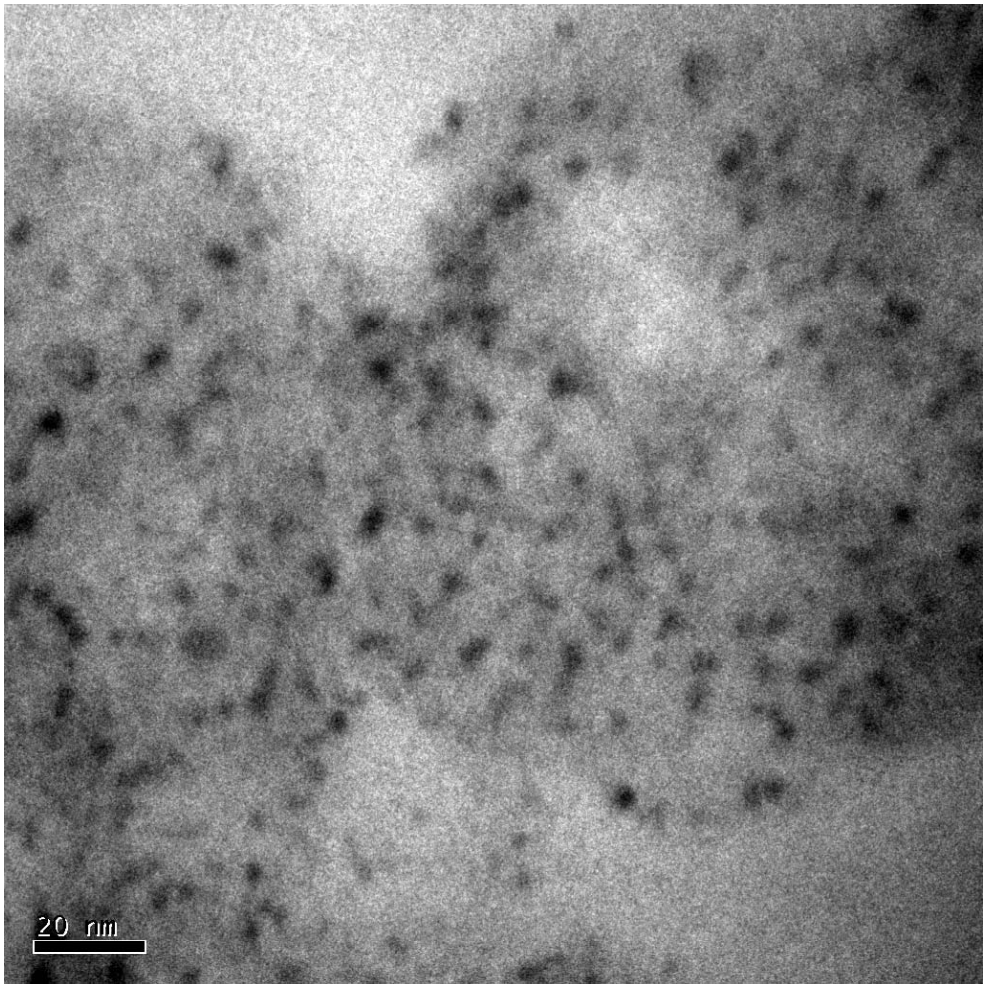
- Pt loss determined from cyclic voltammetry data (assuming spherical particles) is in agreement with QCM mass loss in same time span
- Pt dissolution rate ~ 0.14μg/h or 0.01μg/h.cm^2

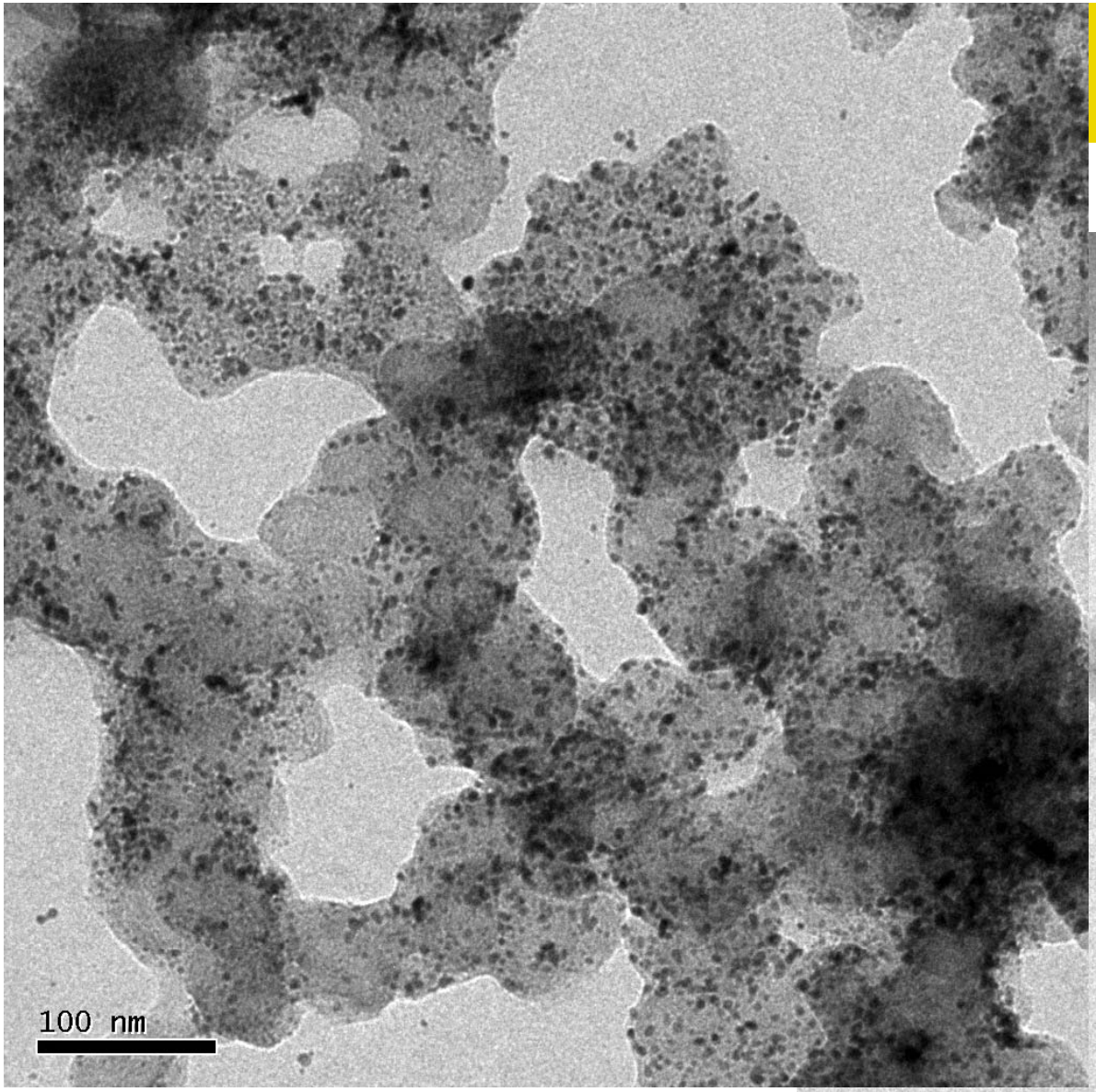


Fresh electrode



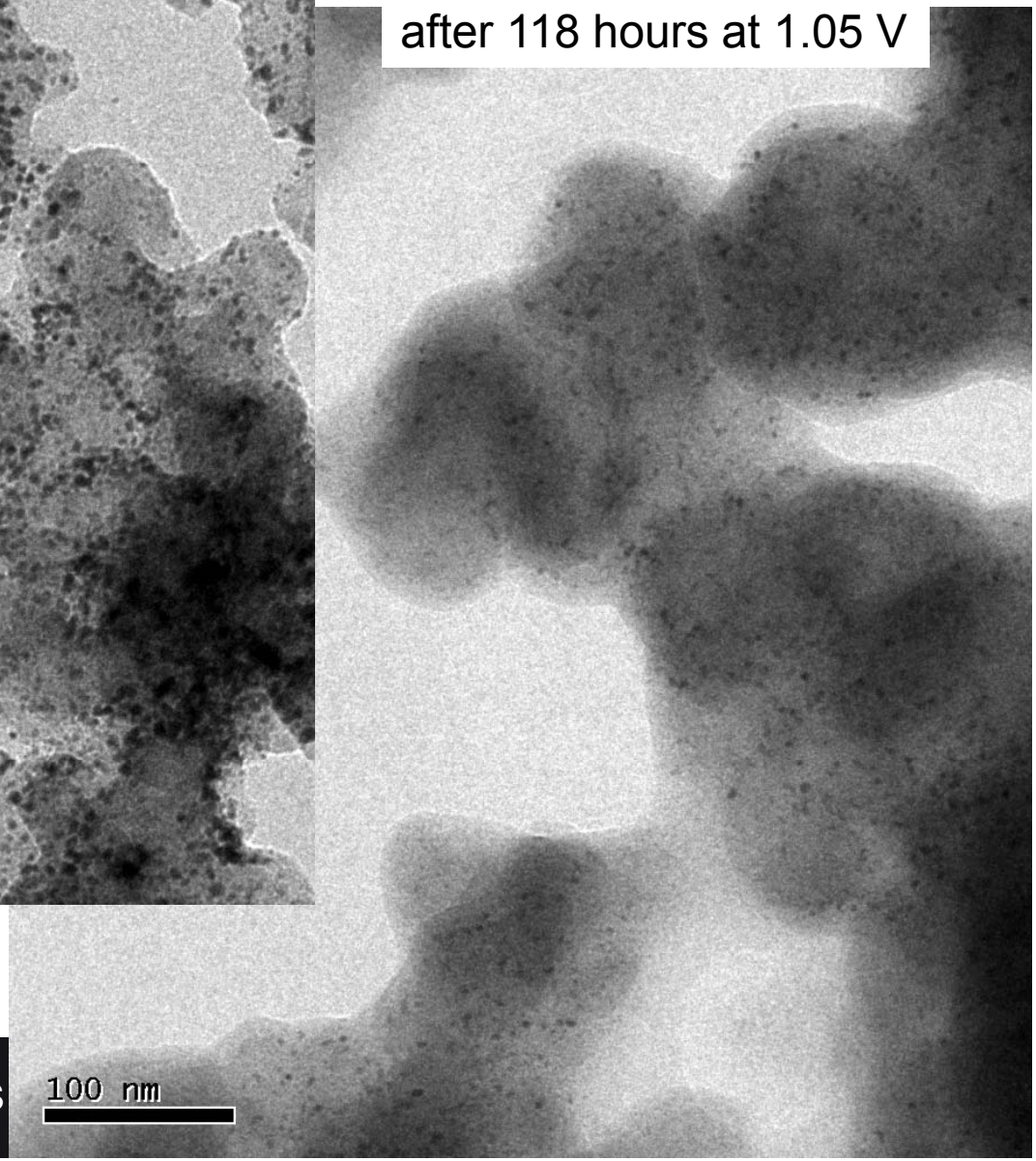
Electrode
after 118 hours at 1.05 V



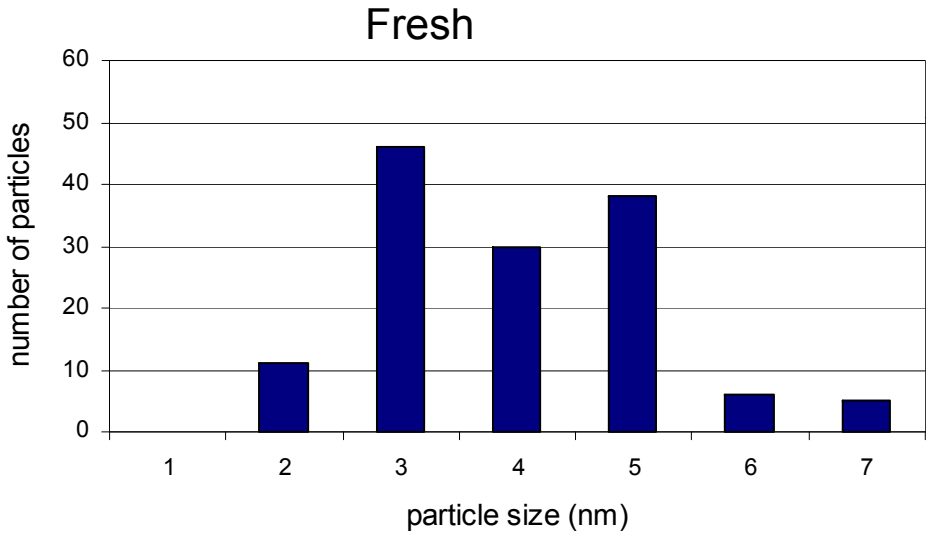


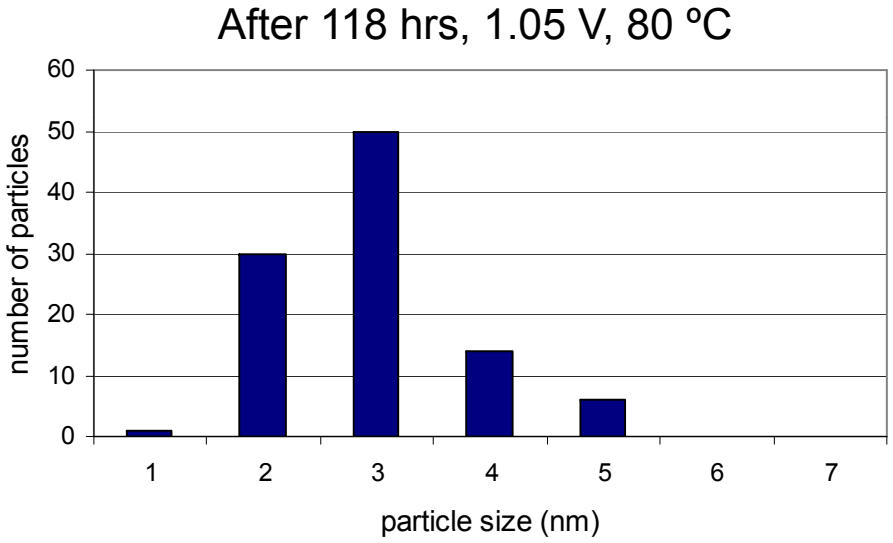
Fresh electrode

Electrode
after 118 hours at 1.05 V



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





Average particle size: 4.0 ± 1.2 nm

Average particle size: 3.0 ± 1.4 nm

V.A.T. Dam et al., Fuel Cells ***9*** *(2009) 453*

Pt surface area loss

	60 °C / 1.05 V	80°C / 1.05 V	80°C / 1.05 V	80°C / 1.15 V	80°C / 1.15 V	80°C / 1.15 V	80 °C / 1.25 V
Rate of Pt area change (cm^2 Pt/ cm^2 Ptfresh.hr^{-1})	-0.0016	-0.00849	-0.0072	-0.30044	-0.014	-0.015	-0.0779
Total Loss of Pt surface area observed (as % of original area)	40% in 262 hours	71% in 92 hours	83% in 118 hours	90% in 6 hours	24% in 17 hours	30% in 20 hours	85% in 6 hours

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

Conclusions *ex situ* tests

Potentiostatic hold at 1.05 V and higher leads to considerable loss of Platinum surface area. Platinum dissolution is dominant mechanism.

> Note: high potentiostatic potential and high electrolyte volume prevents redeposition

Potentiostatic hold at 1.15 V and higher leads to carbon corrosion. Increase in temperature accelerated corrosion. Quinone formation preceeds corrosion, and takes place at lower potentials as well.

Decreasing temperature can prevent loss of platinum by dissolution by orders of magnitude

Overall conclusions

- Ex situ electrochemical model studies explain in situ MEA observations:
  - Under conditions applied during potential cycling platinum can dissolve, leading to a large loss of electrochemical surface area
  - Potentials during potential cycling are too low for carbon corrosion, which takes place at 1.15 V and higher
  - Formation of quinone groups might explain increased hydrophilicity of electrodes

- Automotive durability targets are not met with present generation components:
  - Electrode properties change considerably
  - Membranes contribute less to voltage decay, but still a concern

Acknowledgements

The authors wish to thank

- E.F. Sitters, A.J. Grootjes and M. de la Rie (ECN) for MEA preparation and testing.
- K. Jayasayee and S. Celebi (TU/e) for electrochemical tests and TEM characterization
- A. Pfrang (JRC-IE) for TEM analysis
- M. Roos (ECN) for SEM analysis

This work was part of the Dutch EOS-LT PEMLIFE project, contract no.EOSLT01029, and EOS-LT Consortium PEMFC, contract nos. EOSLT 06005 and EOSLT 07005 supported by the Dutch Ministry of Economic Affairs.