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

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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 Buses**

- 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 *

<table>
<thead>
<tr>
<th>Year</th>
<th>Cost ($/kW)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2002</td>
<td>$300</td>
</tr>
<tr>
<td>2006</td>
<td>$110</td>
</tr>
<tr>
<td>2007</td>
<td>$94</td>
</tr>
<tr>
<td>2015</td>
<td>$30</td>
</tr>
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</table>

Durability (under cycling conditions)

<table>
<thead>
<tr>
<th>Year</th>
<th>Hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>2003</td>
<td>1000</td>
</tr>
<tr>
<td>2006</td>
<td>2000</td>
</tr>
<tr>
<td>2015 target</td>
<td>5000</td>
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</table>

* for 500,000 vehicles produced per year

Cost reducing strategies could have a major impact on durability

DoE analysis of Fuel Cell Stack costs

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
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 μV.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 °C 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**
- Accelerated tests which are still representative for conditions in PEMFC applications
- Characterization tools that can discriminate between various contributions
- Quantitative data on degradation
- Life-time predictions
- Post test information

**Ex situ**
- Model studies on components and materials at well-defined conditions
- Advanced techniques for mechanistic studies
- Understanding of degradation
- Mitigation strategies
- Improved materials
Content of this Work

In situ
MEA testing under stressing conditions
  MEA potential and load cycling
  MEA freeze/thaw cycles

Characterization by polarisation curves, EIS, CV, chronoamperometry
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 (N₂/H₂) → catalyst
- OCV hold → membrane
- Potential hold (≥1.2 V) → carbon support

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

Load or potential (H₂/air) cycling:
- Variations in potential → Pt dissolution, Pt particle growth, carbon corrosion
- Exposure to H₂/air(O₂) → 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

\[ V_{cell}(j) = E^{0} - \eta_{\Omega}(j) - \eta_{ORR}(j) - \eta_{transport}(j) \]
\[ = E^{0} - j \cdot R_{hf} - \log \left( \frac{j}{i_{m} m_{Pt} P_{O_2}} \right) - f(R_{p}, P_{m}, j) \]

\[ \Delta \eta_{air}(j) = \Delta \eta_{\Omega} + \Delta \eta_{ORR} + \Delta \eta_{transport} \]
\[ = j \cdot \Delta R_{hf} + \log \frac{i_{m}^{1}}{i_{m}^{2}} + f(\Delta R_{p}, \Delta P_{m}, j) \]

\[ \Delta \eta_{O_2}(j) = j \cdot \Delta R_{hf} + \log \frac{i_{m}^{1}}{i_{m}^{2}} + f(\Delta R_{p}, j) \]

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

- H₂/O₂,
- Under load
- High frequency
  real axis intercept for
  Ohmic resistance
- Nyquist arc: cathode

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

(C<sub>dl</sub> from cyclic voltammetry)

Linear part:
Fast voltage cycles – load profile

H₂/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**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>80°C</th>
<th>1000</th>
<th>5000</th>
<th>10000</th>
<th>30000</th>
</tr>
</thead>
<tbody>
<tr>
<td>ECSA / m²g⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Im / A g⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Is / μA cm⁻²</td>
<td></td>
<td></td>
<td></td>
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**MEA 2**

<table>
<thead>
<tr>
<th>Temperature</th>
<th>80°C</th>
<th>1000</th>
<th>5000</th>
<th>10000</th>
<th>30000</th>
</tr>
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<tbody>
<tr>
<td>ECSA / m²g⁻¹</td>
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<tr>
<td>Im / A g⁻¹</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Is / μA cm⁻²</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Membrane damage
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 $\Delta V^{\text{air}} @ 0.4 \text{ A cm}^{-2}$

Loss ECSA & activity

<table>
<thead>
<tr>
<th></th>
<th>MEA 1</th>
<th>MEA 2</th>
</tr>
</thead>
<tbody>
<tr>
<td>10000 c</td>
<td>61%</td>
<td>55%</td>
</tr>
<tr>
<td>ECSA</td>
<td>54%</td>
<td>57%</td>
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<tr>
<td>activity</td>
<td>95%</td>
<td>73%</td>
</tr>
<tr>
<td>30000 c</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ECSA</td>
<td>95%</td>
<td>73%</td>
</tr>
<tr>
<td>activity</td>
<td>87%</td>
<td></td>
</tr>
</tbody>
</table>

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

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
Load on/off cycles: break down of $\Delta V_{\text{air}}$ @ 0.4 A cm$^{-2}$


After 5 x 10 cycles / 600 hr at 80$^\circ$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

ECSA / m² g⁻¹

R₀ / Ohm cm²

iₓ / mA cm⁻²

Rₑ / Ohm cm²

# cycles

# cycles

# cycles

# cycles
Break down of $\Delta V^{\text{air}}$ @ 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 H₂ 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

\[ \Delta \text{(frequency)} = - K \Delta \text{(electrode mass)} \]

- High accuracy ~ 0.25 ng/cm²
- Diversity of electrode materials

QCM probe (WE)
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 $E \leq 1.15 \text{V}$, $80^\circ \text{C}$, log. of dissolution rate linearly depends on $E$ (0.55 times / 0.1 V).
- At $E > 1.15 \text{V}$ and $80^\circ \text{C}$, the dissolution rate decreases due to passivating Pt oxide layer
- Dissolution rate increases $10^3$ times when temperature increases from 60 to 80°C.

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 → CO₂ 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
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 \( \sim 0.14 \mu g/h \) or \( 0.01 \mu g/h \cdot cm^2 \)
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 °C

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

<table>
<thead>
<tr>
<th>Rate of Pt area change (cm² Pt/ cm² Ptfresh.hr⁻¹)</th>
<th>60 °C / 1.05 V</th>
<th>80°C / 1.05 V</th>
<th>80°C / 1.05 V</th>
<th>80°C / 1.15 V</th>
<th>80°C / 1.15 V</th>
<th>80°C / 1.15 V</th>
<th>80 °C / 1.25 V</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.0016</td>
<td>-0.00849</td>
<td>-0.0072</td>
<td>-0.30044</td>
<td>-0.014</td>
<td>-0.015</td>
<td>-0.0779</td>
<td></td>
</tr>
</tbody>
</table>

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
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