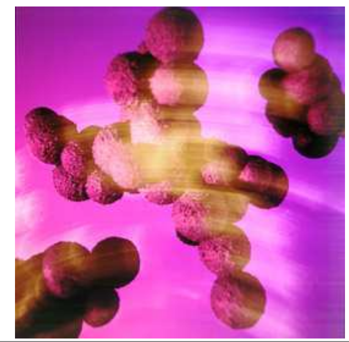

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DMFC Durability and Performance Degradation Mechanisms

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Material and Component Contributions to Performance Decline

- Cathode Pt particle stability.
- Anode PtRu alloy particle stability.
- Optimum surface coverage of cathode GDL carbon phases with fluoropolymer.
- Electrode quality (chemical stability of ionomer and structural integrity of catalyst layer).
- Interfaces between electrodes and membrane (mechanical integrity of interfaces and CCM preparation method).
- Key examples of component interaction and performance losses:
  - Ru corrosion (from PtRu anode), migration through the membrane, and deposition on the cathode negatively impacts cathode's ORR activity.
  - Cathode Pt dissolution, precipitation, and sintering causes significant ECSA loss, which increases electrode diffusion limitations (in turn, impact of cathode GDL flooding on cell performance is increased).
  - Ionomer degradation changes water transport and saturation characteristics of CCM (water drag, methanol crossover, etc.), which affects water management characteristics of GDLs.

Reversible and Irreversible Contributions to Performance Decline

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Key Reversible Losses

- Cathode PtO / PtOH Formation (V_{cell} > ~0.4 V).
- Cathode Flooding (GDL and/or Catalyst Layer).
- Ionomer Dehydration.
- Adsorbed CO on Pt.

Irreversible Losses

- ECSA Decline.
- Ru Crossover to Cathode.
- Pt Dissolution and Recrystallization (Cathode Activity Losses).
- Cathode GDL Hydrophobicity Loss (Carbon Surface Corrosion).
- Electrode/Membrane Interfacial Delamination (Ohmic Losses).
- Chemical Degradation of PFSA Ionomer.

Ex-situ Durability Test Protocol

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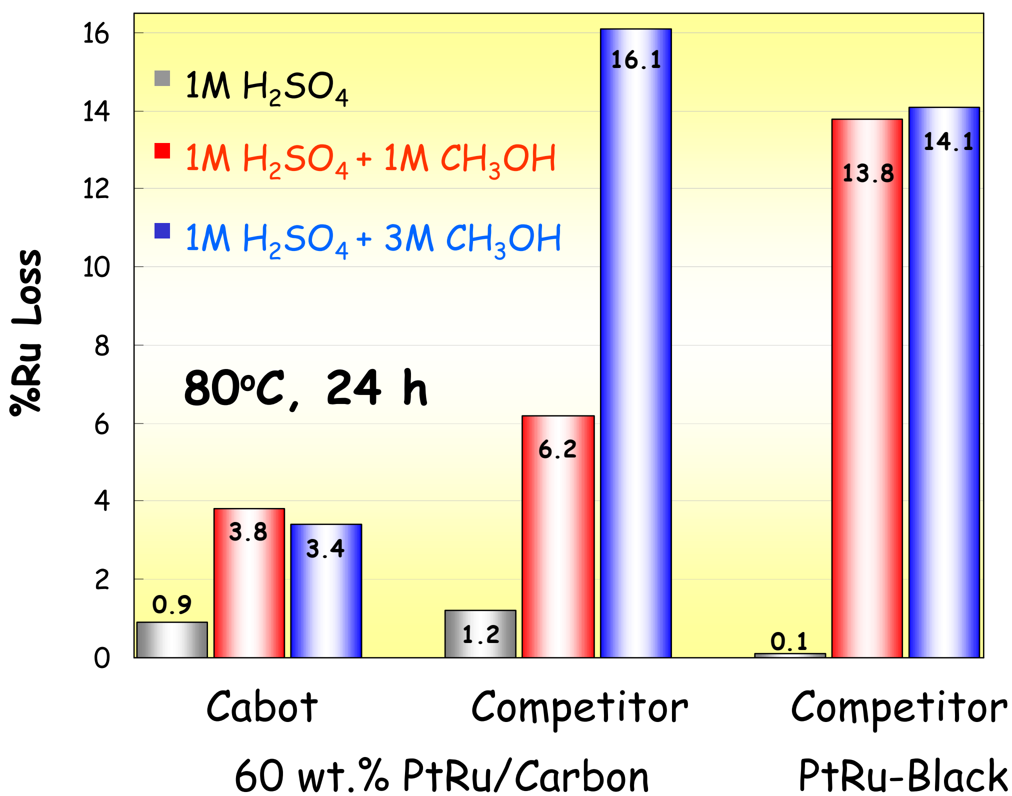

- Ru leaching/crossover and subsequent re-depositing on cathode is believed to be one of key root causes for DMFC performance degradation.
- Ex-situ durability evaluation protocol was developed to evaluate Ru loss outside of fuel cell.
- Samples were leached in 1M H_2SO_4, 1M H_2SO_4/1M methanol and 1M H_2SO_4/3M methanol, respectively. Ru and Pt loss was determined by ICP analysis of the leaching solution.
- For each ex-situ durability experiment ICP samples were collected after 24 hr at 80°C.

Single-Cell Durability – Accelerated Life Test

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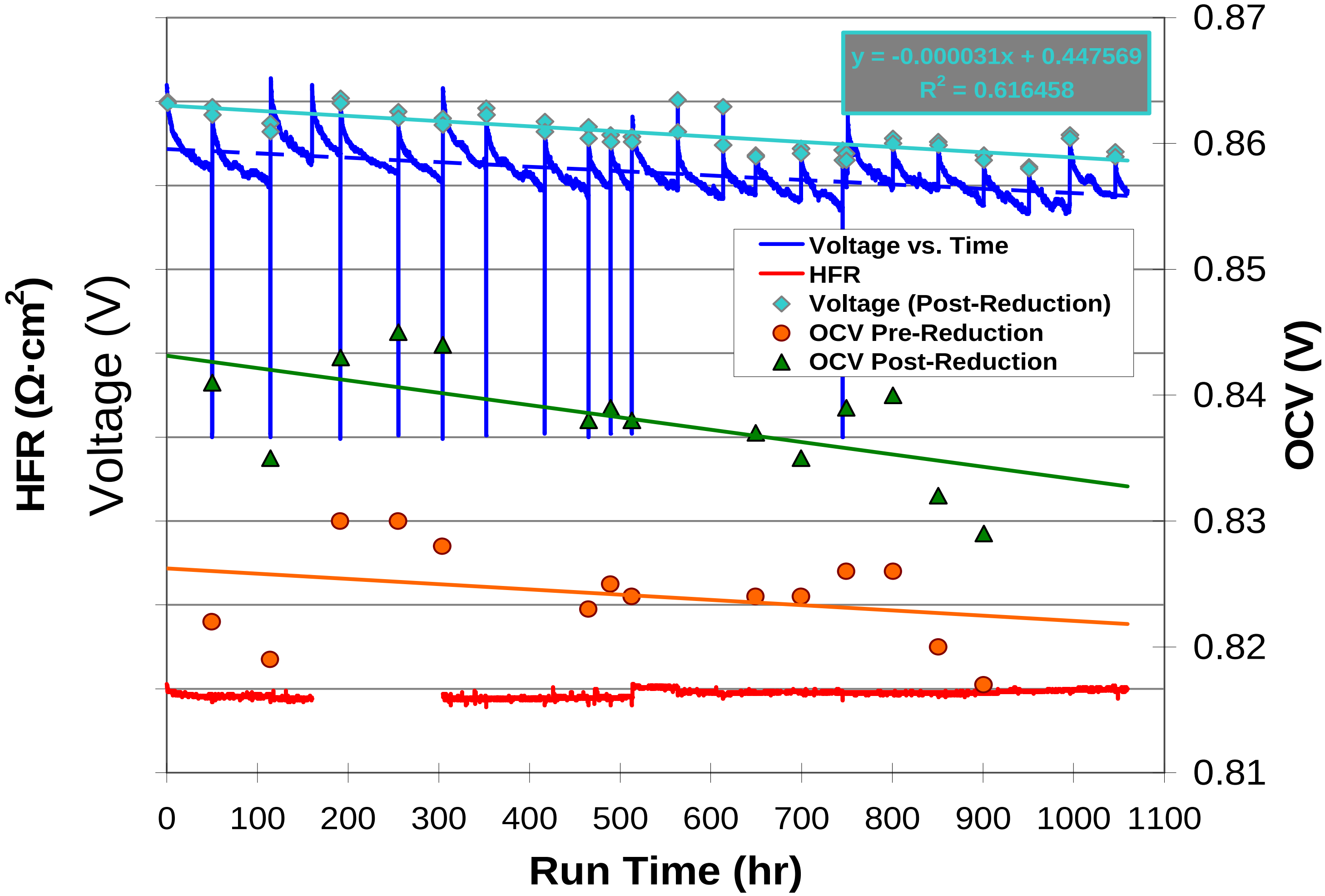
Accelerated Life Test

- All samples were tested after activation (break-in) period.
- Accelerated Life Test was defined by cell temperature, methanol concentration, anode/cathode flow rates.
- Single cell was operated at constant current density (steady state).
- Cell voltage and HFR were monitored as a function of time.

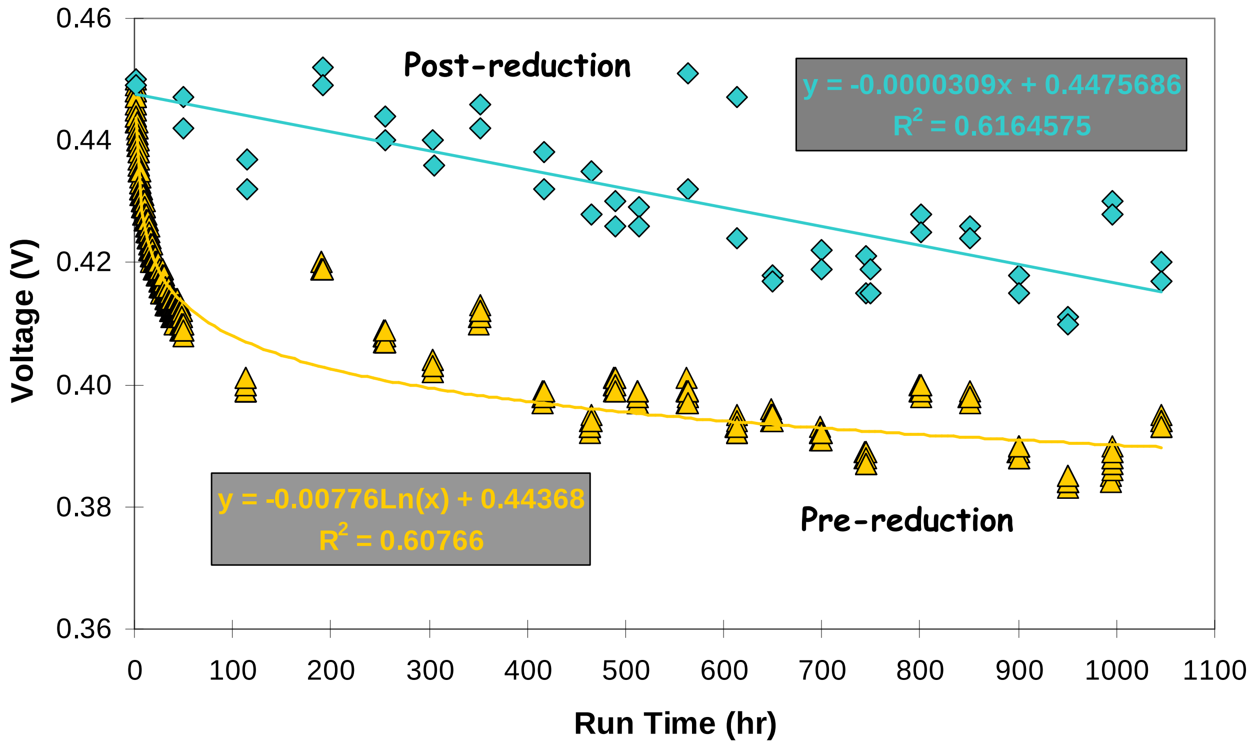
Durability Test and Separation of Recoverable Loss

- Load interruption: From operation current density to OCV (pre-reduction OCV).
- Cathode polarization: From OCV to cell voltage (considering that PtO reduction is dominated by electrochemical potential).
- From previous cell voltage (responsible for reducing PtO) back to OCV (post-reduction OCV).
- Subsequently, resume life test at constant current density.

Accelerated Life Test: Data Illustration



Lifetime Prediction: Example



- Pre-reduction logarithmic method is weighted towards effects of recoverable losses.
- Post-reduction linear method is weighted towards effects of irrecoverable losses.
- Overall linear decay not weighted and is least accurate.

Lifetime Predictions
(Neglecting Membrane Failure)

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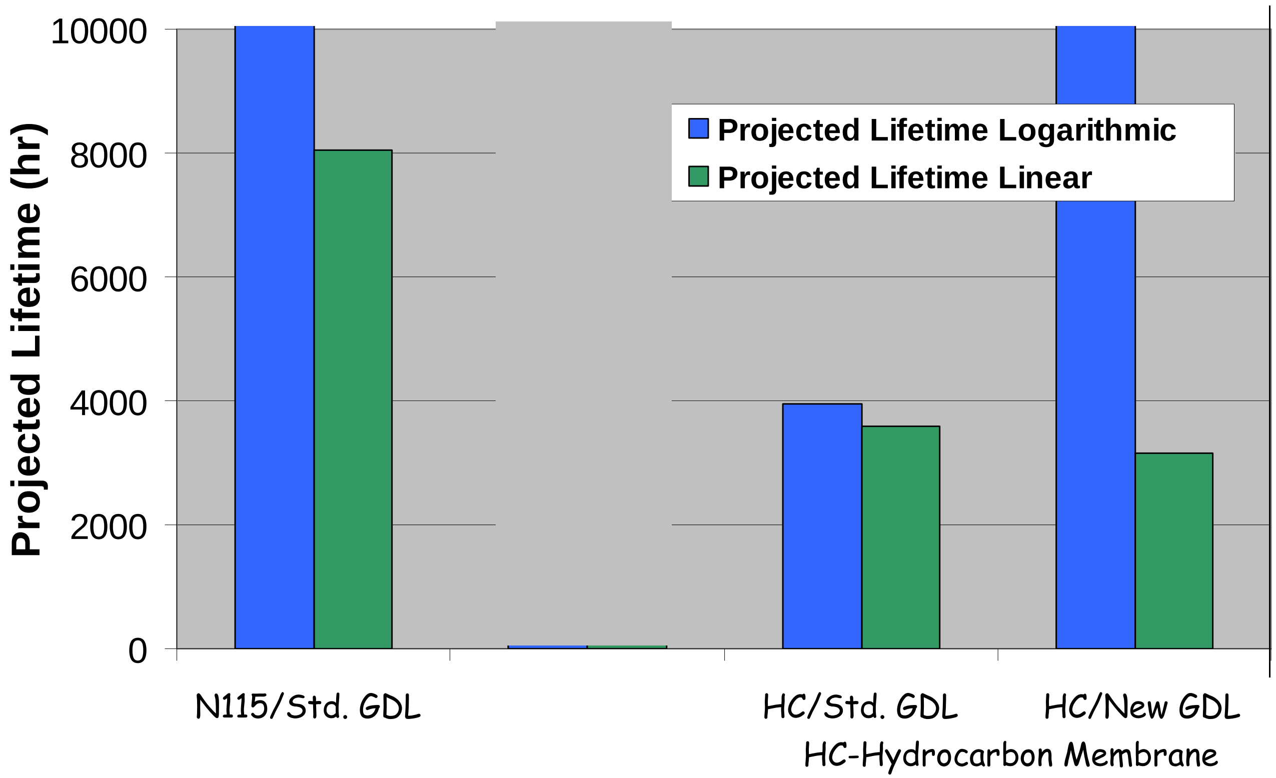

- Equivalent lifetime predictions for combinations of N115/Std. GDL and HC/New GDL.
- HC/Std. GDL cell had shortest lifetime prediction for logarithmic fit to data.
- These data indicates that MEA design/optimization should not be approached as mix-and-mach effort.

Before/After Anode XRD Comparison (N115 vs. HC Membrane)

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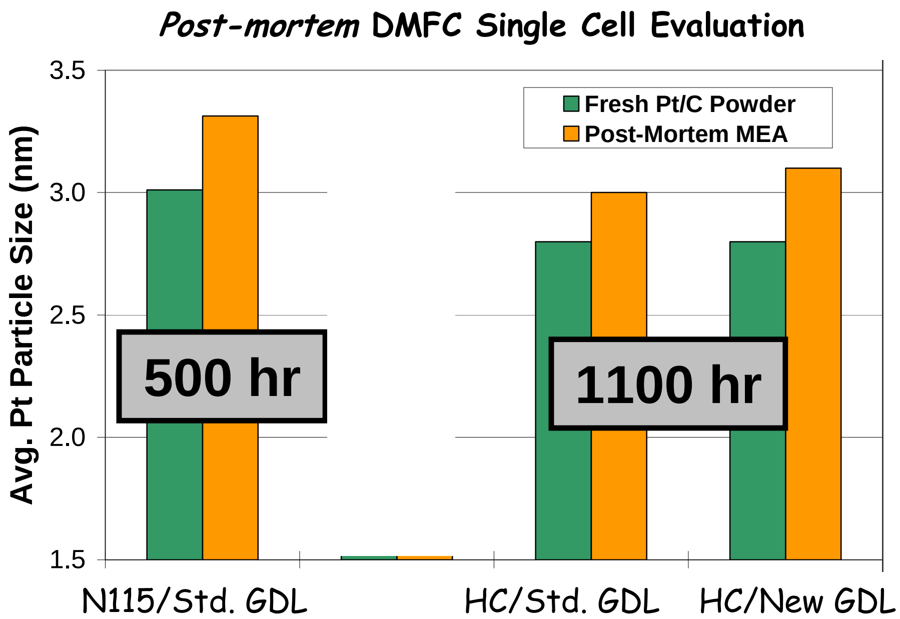

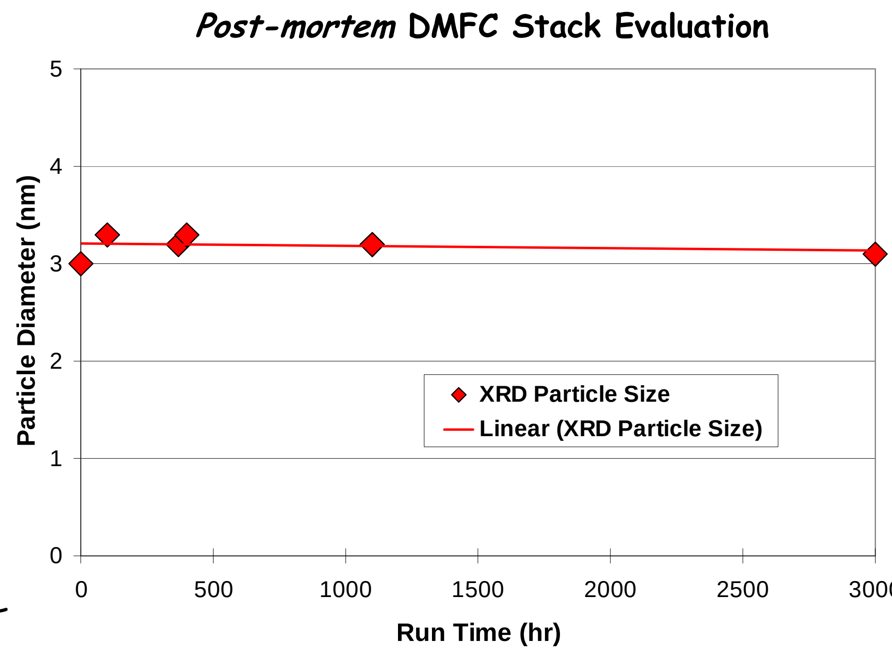

- No substantial change in PtRu particle size for MEA with N115 through 500 hr or with HC membrane through ~1100 hr.
- Data agrees with ECSA data and DMFC post-mortem stack data.

Before/After Cathode XRD Comparison (N115 vs. HC Membrane)

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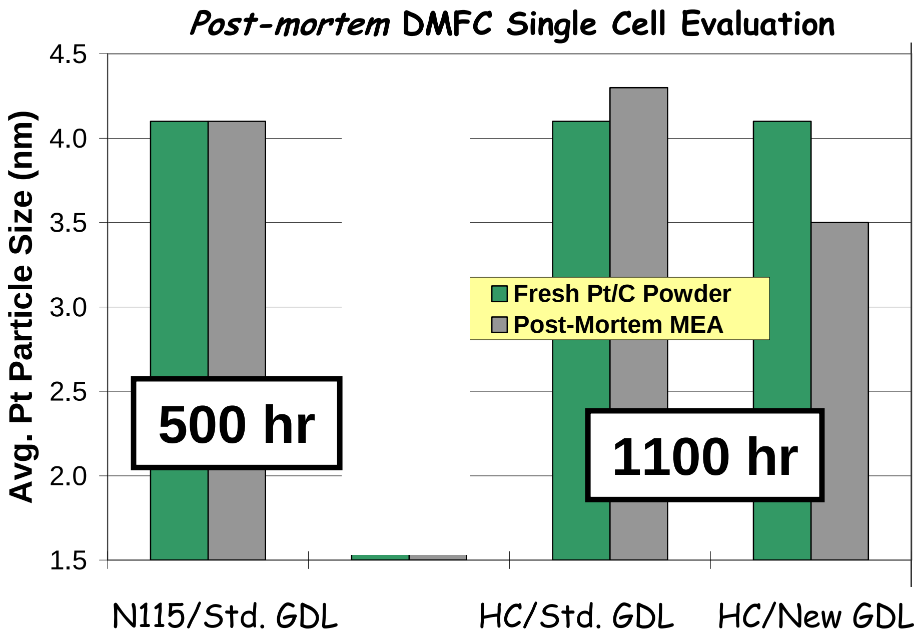
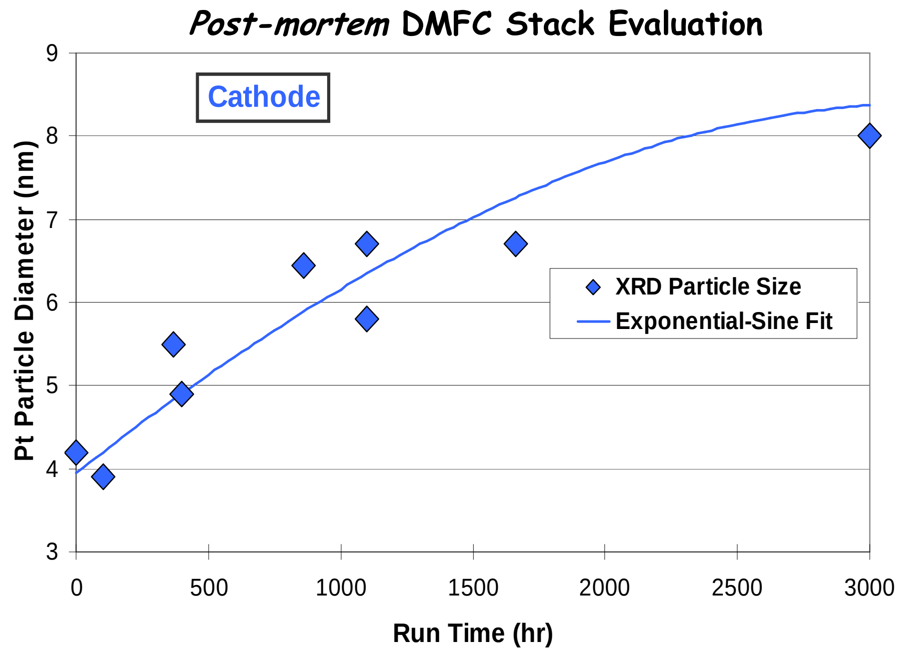
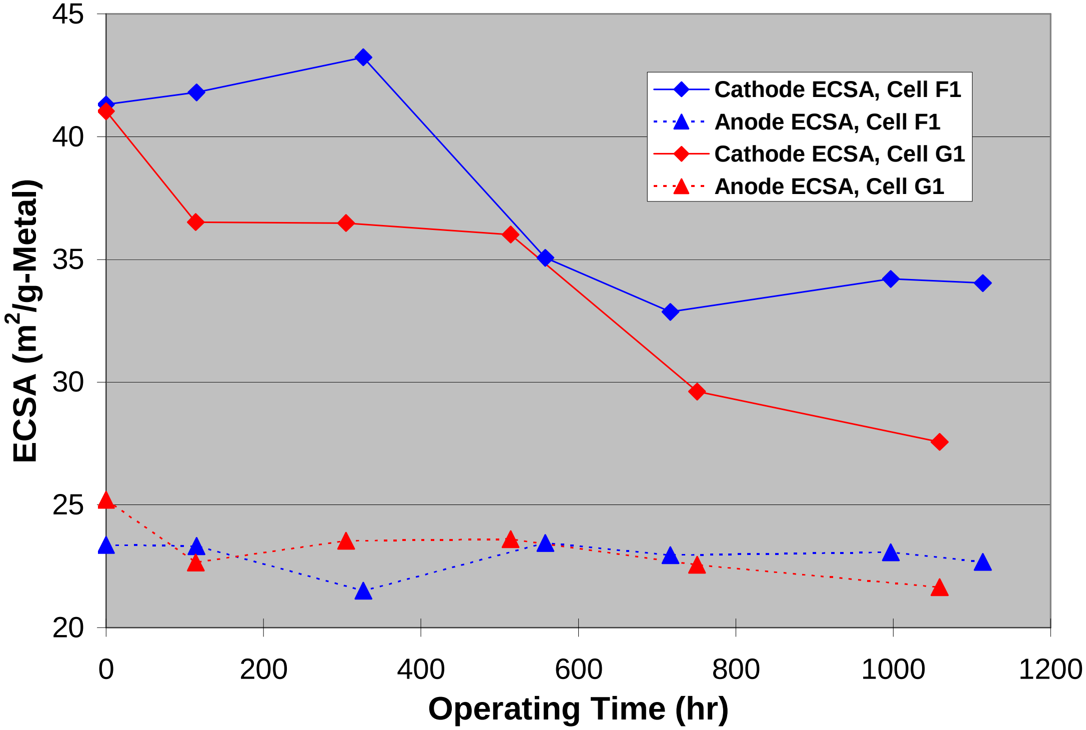




- New GDLs offset effects of possible Pt dissolution and higher rate of loss of ECSA.

ECSA vs. Operating Time (Std. vs. New GDLs)



- Cathode ECSA was better preserved with Std. GDLs than New GDLs (65 vs. 127 cm^2/g-Pt/hr degradation, respectively), despite equal/lower durability performance.
- Anode ECSA was similar and remained unchanged in both cases.

Cathode Performance Parameters vs. Operating Time (Std. vs. New GDLs)

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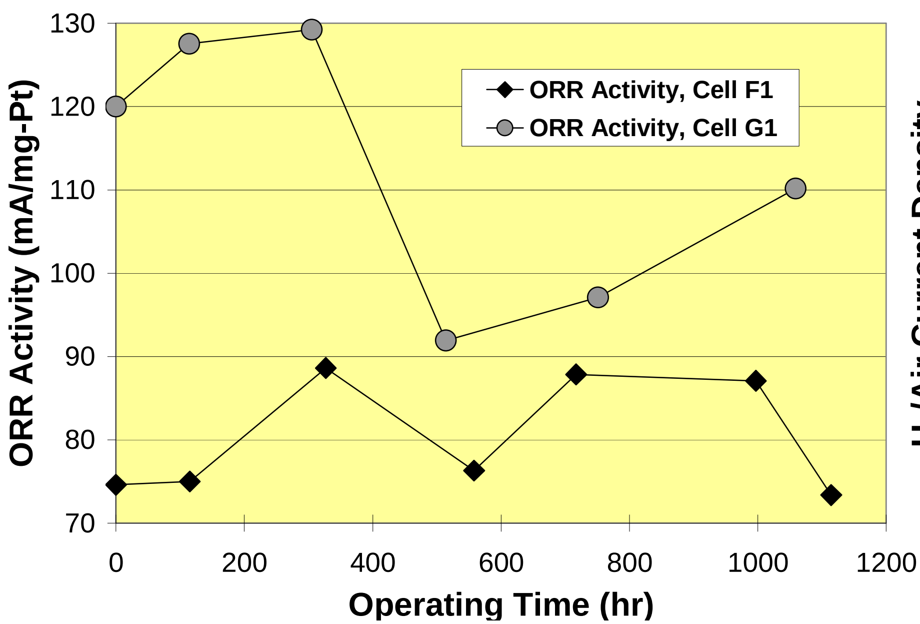
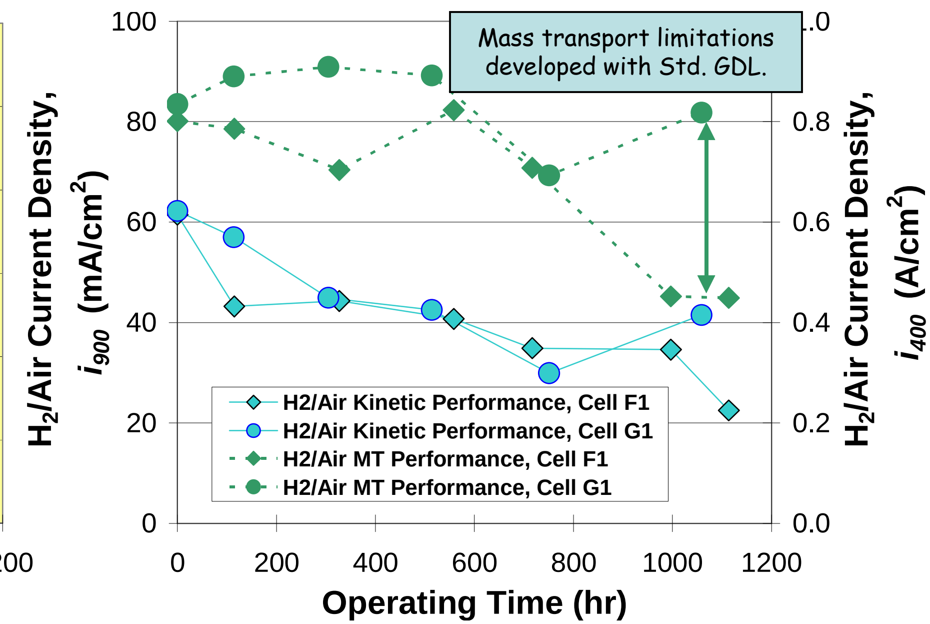
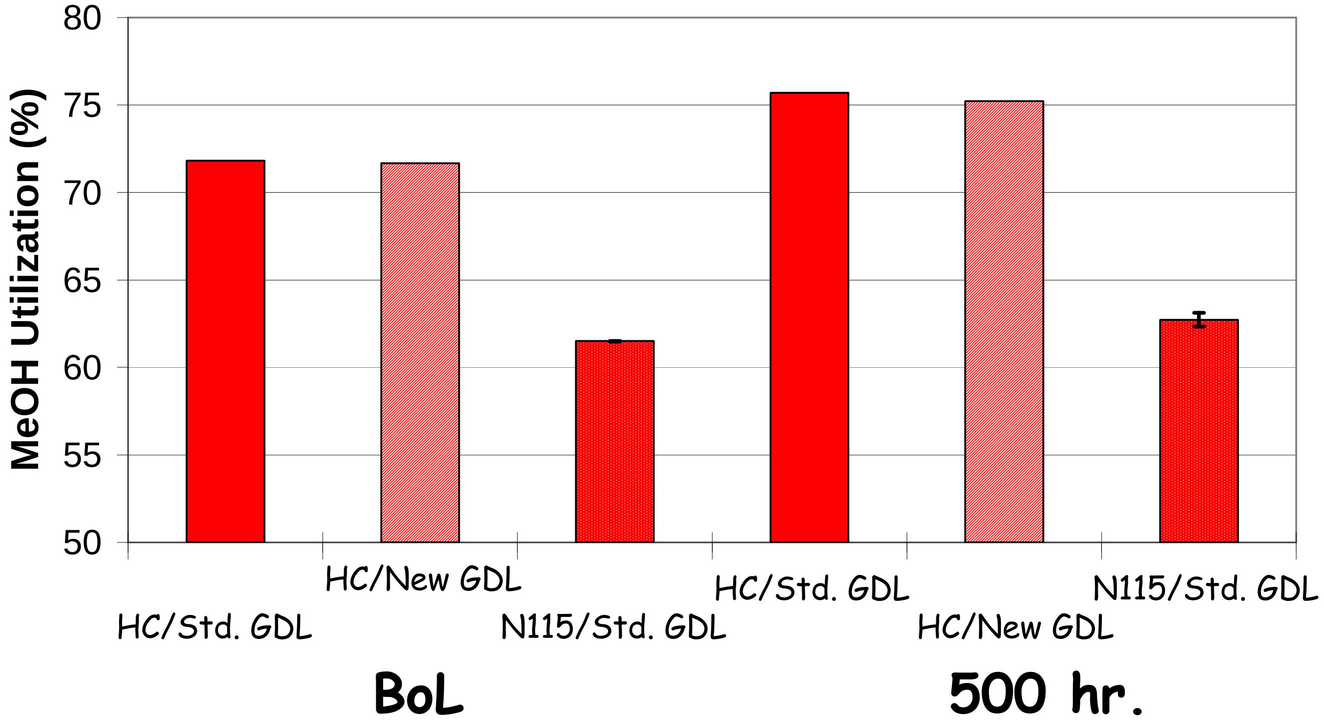




- Diffusion limitations developed in cell F1 (Std. GDLs), which could have contributed to significantly different measured ORR activities.
- BOL activity for cell G1 (New GDLs) was 60% higher than cell F1 (Std. GDLs) showing effect of GDL on catalyst activity measurement.
- No difference in H_2/Air i_{900} performance between cells until EOL.

Comparison of MeOH Utilization after ~500 hr (Nafion N115 vs. Hydrocarbon Membrane)



- Fuel utilization increased slightly for HC membrane after 500 hr.
- No change in utilization for N115 membrane over same operating period, but the overall values were significantly lower (17%) than for HC membrane.

Water and MeOH Crossover Rates Through ~500 hr (Nafion N115 vs. HC Membrane)

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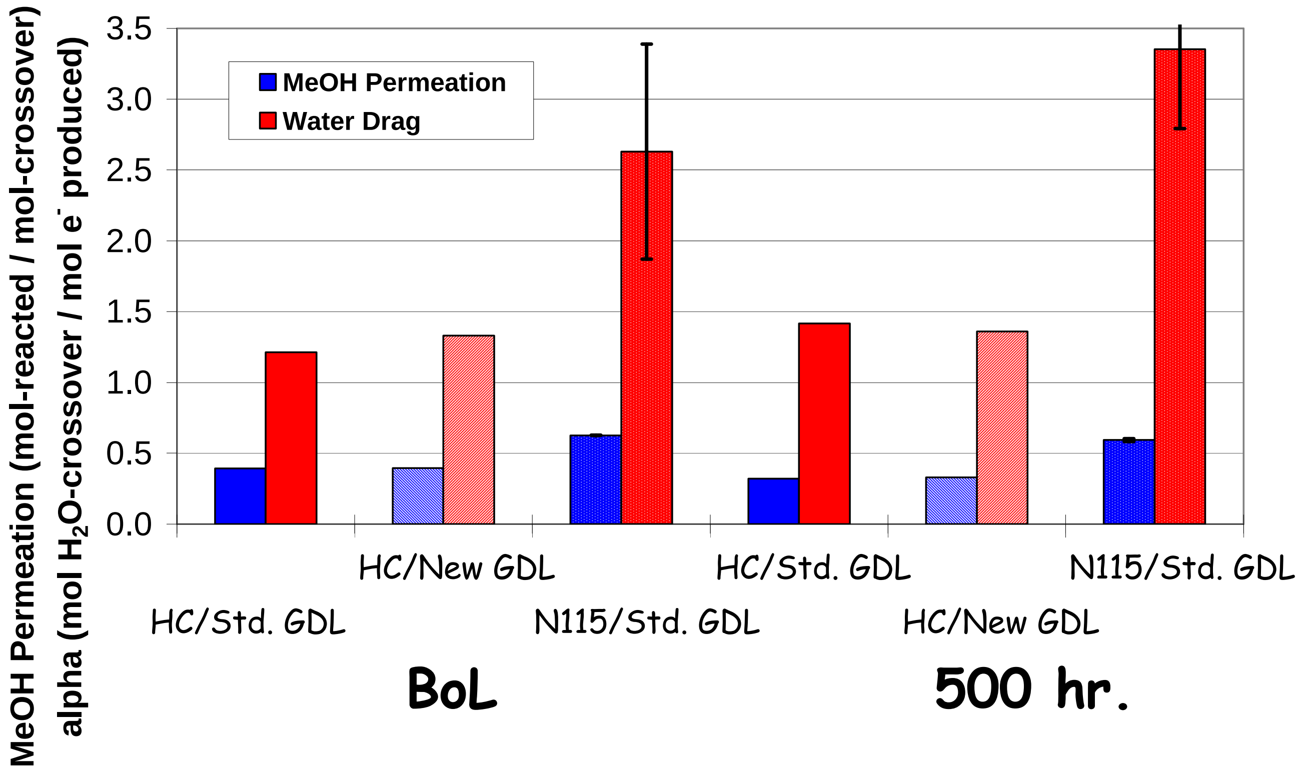

- Little change in electro-osmotic drag for either HC or N115 membranes through 500 hr.
- But water drag for N115 was 2.4× that of HC membrane after 500 hr.
- Similar trend for MeOH permeation.

⇒ Similar performance and durability for both membrane types, but much better system parameters for HC membrane.

Summary

- In general, performance deterioration of DMFC occurs as a result of negative phenomena taking place on both anode, cathode and cathode GDL.
- Cabot's anode catalysts demonstrate superior durability and stability under accelerated durability tests, shifting the origin of performance deterioration to the cathode side (loss of ECSA close to BoL and subsequently to loss of cathode GDL hydrophilicty approaching the EoL).
- MEA integration is not a simple mix-and-match effort, but requires MEA component compatibility optimization.
- Cabot was also able to achieve excellent durability with hydrocarbon membrane, which to our knowledge was not demonstrated before.