Comparison of Proton Exchange Membranes Degradation Rates Between Accelerated and Performance Tests

Marianne P. Rodgers, R. Paul Brooker, Nahid Mohajeri, Leonard J. Bonville, H. Russell Kunz, Darlene K. Slattery, James M. Fenton
University of Central Florida—Florida Solar Energy Center ♦ 1679 Clearlake Rd ♦ Cocoa ♦ Florida 32922

Introduction

- Lifetime tests
  - Usually V or I held for 100s or 1000s of hours
  - Non-steady-state tests are also important because loads vary
- Accelerated stress tests (ASTs)
  - Durability evaluation under normal operating conditions is impractical
  - Need to:
    - Activate targeted failure mode
    - Minimize confounding effects
  - Low RH, high temp, RH cycling, temp cycling, open circuit voltage (OCV)
    - OCV accelerates PEM chemical decomposition
    - RH cycling accelerates PEM mechanical decay
- Difficult to assess the extent to which ASTs accelerate membrane degradation

Strategy

- Goal:
  - To compare the effects of two types of tests on the durability of several standard MEAs
- Performance evaluation test (PET)
  - Assess CCM performance at conditions of interest to the DOE and industry
  - Will not significantly degrade the CCMs
  - 80-120 °C & 35-100% RH; stability for 64 h at 95 °C/83% RH, 400 mA/cm^2 (184 h total)
- OCV AST
  - Assess membrane chemical degradation
  - 100 h, H_2/air, 90 °C, 30% RH
- CCMs: NRE211® PEMs with 4 electrodes
  1. Pt/C + 32 wt% 1100 EW Nafion® ionomer
  2. PtCo/C + 32 wt% 1100 EW Nafion ionomer
  3. Pt/C + 28 wt% 825 EW 3M ionomer
  4. PtCo/C + 32 wt% 825 EW 3M ionomer

Table 1. Summary of performance evaluation test conditions for each day of testing. Numbers in the time period refer to Figure 1.

Time Period	Conditions
1	25 °C/100% RH, ambient pressure, N_2/N_2, then H_2/N_2 after ~5 min.; run LSV, CV
2	Heat to 80 °C/~100% RH, ambient pressure, H_2/N_2; run LSV, CV when cell reaches temperature
3	80 °C/~100% RH, ambient pressure, H_2/air; run performance curve
4	Switch to H_2/O_2 and wait until voltage is steady
5	80 °C/~100% RH, ambient pressure, H_2/O_2, run performance curve
6	Switch to H_2/air and wait until voltage is steady
7	80 °C/~100% RH, ambient pressure, H_2/air, run performance curve
8	Hold at 80 °C/~100% RH, ambient pressure, H_2/air overnight
9	Repeat Steps 2-7 at 80 °C/~100% RH, 0.5 atm backpressure
10	Repeat Step 8 at 80 °C/~100% RH, 0.5 atm backpressure
11	Repeat Steps 2-7 at 95 °C/83% RH, 0.5 atm backpressure
12	Repeat Step 8 at 95 °C/83% RH, 0.5 atm backpressure
13	Repeat Steps 2-7 at 120 °C/35% RH, 0.5 atm backpressure
14	Repeat Step 8 at 120 °C/35% RH, 0.5 atm backpressure
15	Repeat Steps 2-7 at 95 °C/83% RH, 0.5 atm backpressure
16	Cool to <50 °C, H_2/N_2, switch to N_2/N_2 after voltage drops
17	Repeat step 1
18	Repeat steps 2-7 at 95 °C/83% RH, 0.5 atm backpressure
19	Hold at 95 °C/83% RH, 0.5 atm backpressure, H_2/air for 64 h
20	Repeat steps 2-7 at 95 °C/83% RH, 0.5 atm backpressure
21	Repeat step 16

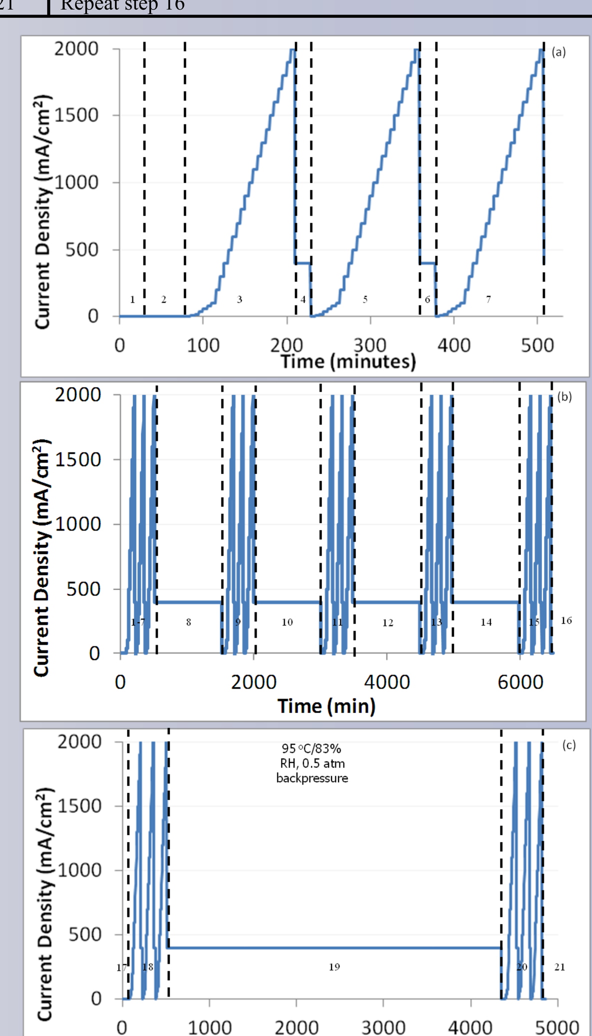


Figure 1. (a) Current density vs time for ~24 h of testing; (b) Current density vs time for the performance portion of testing; (c) Current density vs. time for the stability portion of testing. The cell is shutdown between the performance and stability portions of testing. Numbers refer to Table 1.

Results

Beginning of Life

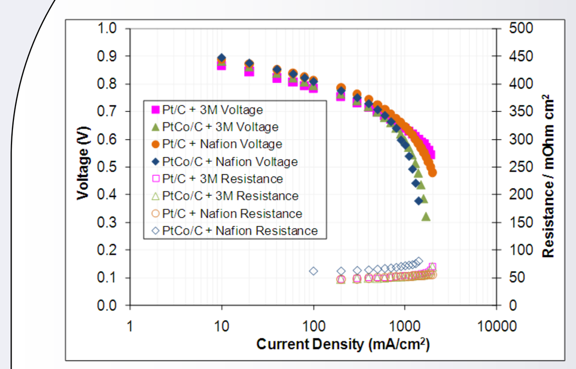


Figure 2. Performance at 80 °C/100% RH at BOL before PET

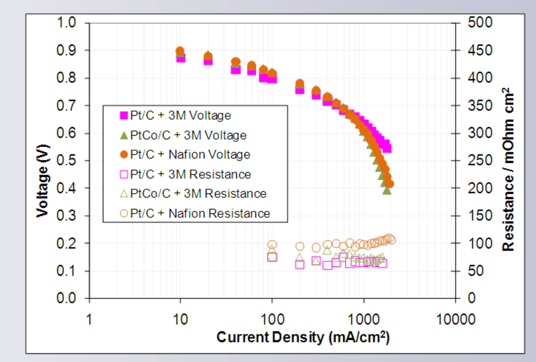


Figure 3. Performance at 80 °C/100% RH at BOL before OCV AST

Table 2. ECA, x-over and activity of each cell at the beginning of life

	Type of Test	ECA (m^2 Pt/g Pt)	x-over (mA/cm^2)	Activity (mA/cm^2)
Pt/C – 3M	PET	75.8	0.73	9.5
PtCo/C – 3M	PET	40.3	0.61	18.2
Pt/C – Nafion	PET	74.5	0.58	17.7
PtCo/C – Nafion	PET	44.9	0.96	26.0
Pt/C – 3M	OCV AST	76.5	0.73	14.8
PtCo/C – 3M	OCV AST	45.5	0.87	36.7
Pt/C – Nafion	OCV AST	73.9	0.78	19.1

*ECA and x-over were determined at 25 °C/100% RH under H_2/N_2 at ambient pressure; Activity was determined at 80 °C/100% RH under H_2/O_2 at ambient pressure

- All cells were in an acceptable condition at BOL

Durability

Table 3. Durability data for cells that were performance evaluation tested

	Pt/C + 3M	PtCo/C + 3M	Pt/C + Nafion	PtCo/C + Nafion
Average FER (μmol/h)*	4.7	0.66	3.7	0.82
Voltage Decay (mV/h)	1.6	0.22	1.7	0.35
Change in x-over (mA/cm^2/h)	0.027	0.0010	0.0057	0.0017
Change in ECA (m^2 Pt/g/h)	-0.21	-0.013	N.M.	0
Final thickness (μm, initial thickness ≈ 25 μm)	18	26	25	27

*Slope of the plot of total fluoride emission vs. time (Figure 4a)

Table 4. Durability data for cells that were OCV accelerated stress tested

	Pt/C + 3M	PtCo/C + 3M	Pt/C + Nafion
Average FER (μmol/h)*	0.070h + 1.64	0.0074h + 0.073	0.069h + 2.65
Voltage Decay (mV/h)	1.6	0.46	1.3
Change in x-over (mA/cm^2/h)	0.0017	0	0.0020
Change in ECA (m^2 Pt/g/h)	-0.076	0	-0.058
Final thickness (μm, initial thickness ≈ 25 μm)	23	26	19

*Slope of the plot of total fluoride emission vs. time (Figure 4b)

- X-over increased more for Pt/C cells than Pt/Co/C
- X-over of PET cells increased 3 to 16x compared to OCV AST
- ECA loss higher for Pt/C cells than PtCo/C
- ECA losses higher for the PET than OCV AST

Fluoride Emission

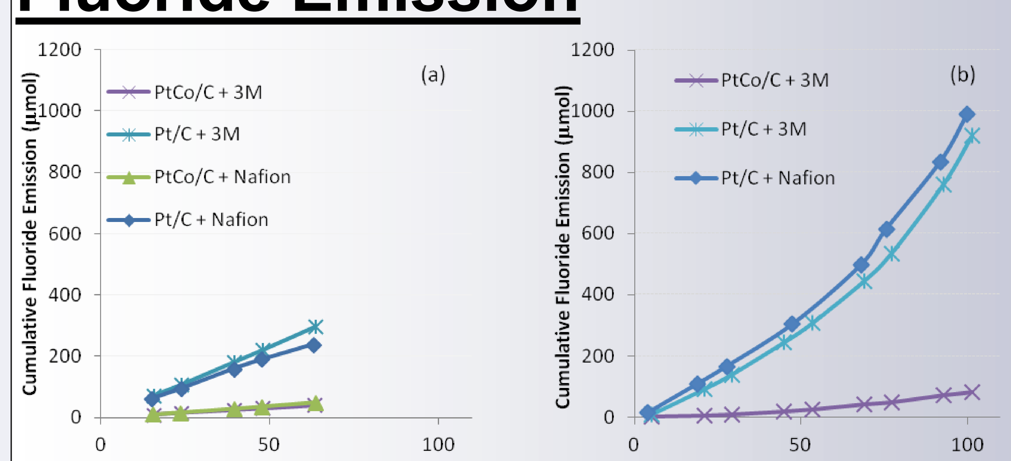


Figure 4 Cumulative fluoride emission for cells that were (a) PET & (b) OCV AST

- Cells with PtCo/C exhibited FERs an order of magnitude lower than cells with Pt/C
- OCV ASTs resulted in FERs that were several times larger than the PETs

OCV

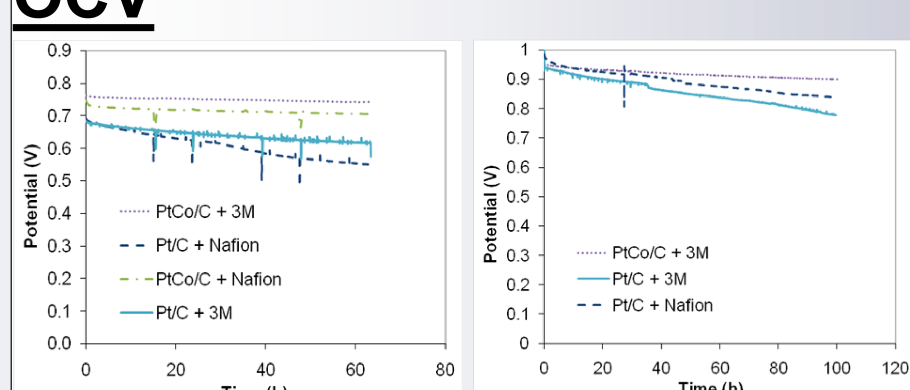


Figure 5. OCV for cells (a) PET and (b) OCV AST

- Voltage decay of PtCo/C cells 3 to 8x lower than Pt/C
- OCV AST increased voltage decay 100% for Pt/C + 3M cells
- Voltage decay from PET are more like drive cycle tests than steady-state tests

Localized Crossover Test

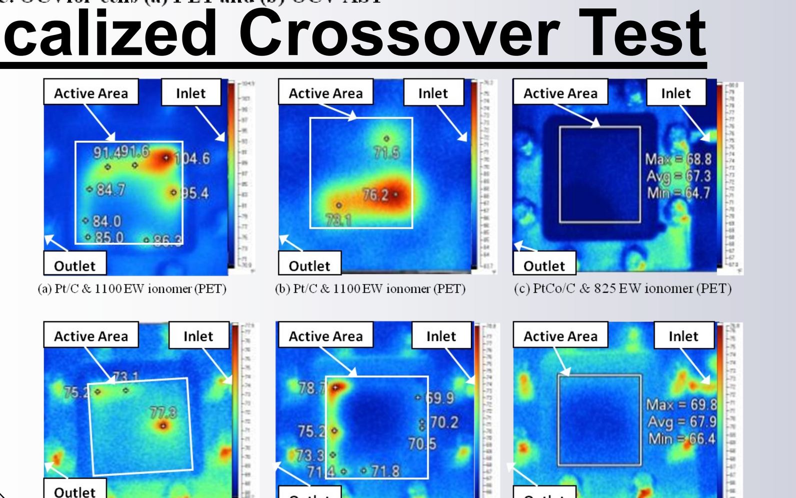


Figure 6. IR images of tested MEAs. Temperature increases are noted with approximate temperatures based on the emissivity of carbon.

- No temperature increases for PtCo/C cells
- Highest temperature increases for Pt/C + Nafion cell

Scanning Electron Microscopy

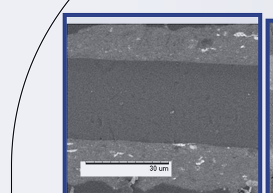
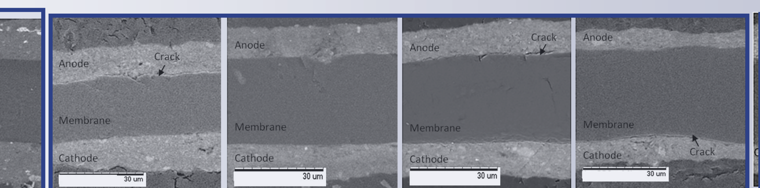
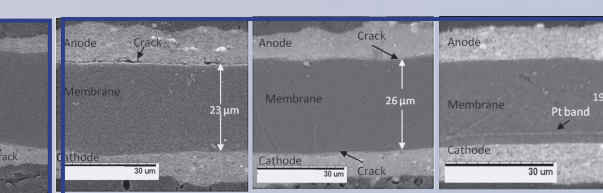


Figure 7. SEM image of an untested CCM



(a) Pt/C + 3M (b) PtCo/C + 3M (c) Pt/C + Nafion (d) PtCo/C + Nafion
Figure 8. SEM images of PET CCMs



(a) Pt/C + 3M (b) PtCo/C + 3M (c) Pt/C + Nafion
Figure 9. SEM images of OCV AST CCMs

- Cracks, thinning and Pt bands observed after testing

Transmission Electron Microscopy

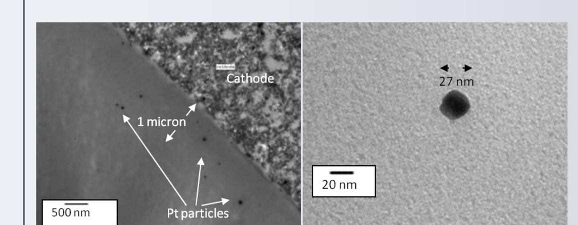


Figure 11. TEM images of a PET cell with Pt/C + 3M

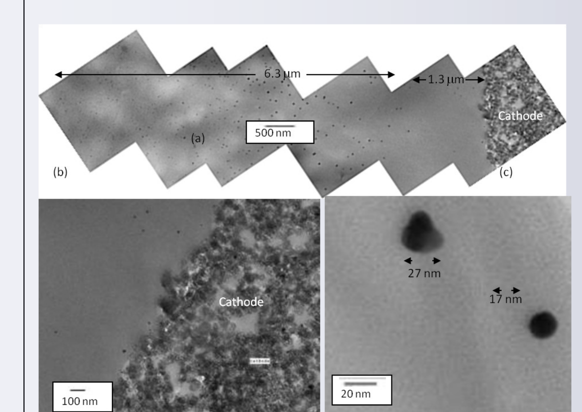


Figure 12. TEM images of PET cell with Pt/C + Nafion

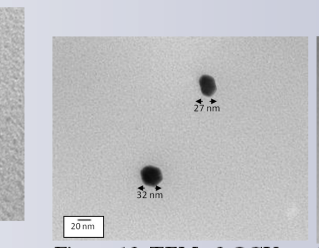


Figure 13. TEM of OCV AST cell with Pt/C + 3M

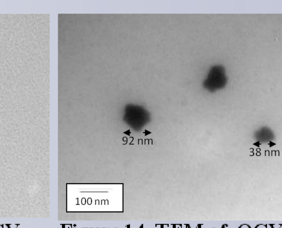


Figure 14. TEM of OCV AST cell with PtCo/C + 3M

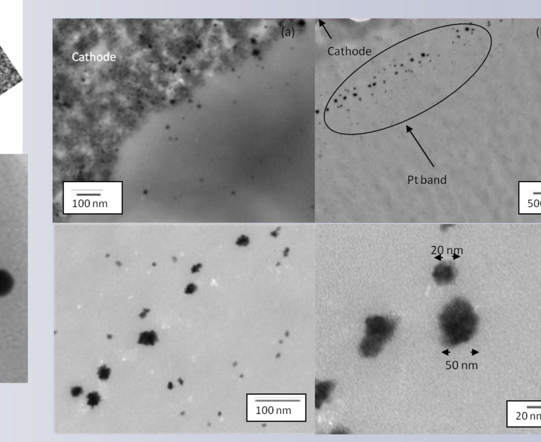


Figure 15. TEMs of OCV AST cells with Pt/C + Nafion

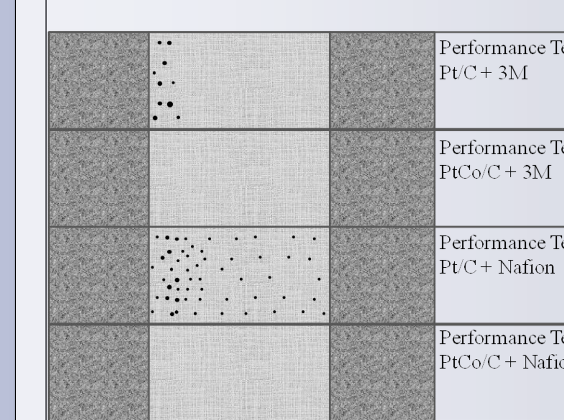


Figure 16. Schematic of Pt size, shape and distribution in membranes after PET

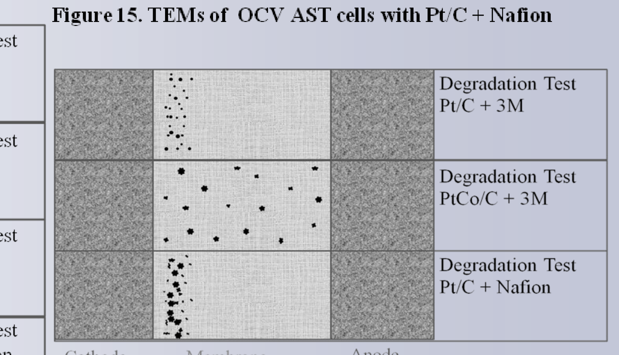


Figure 17. Schematic of Pt size, shape, and distribution in membranes after OCV AST

- No Pt in PEMs after PET of PtCo/C cells
- Pt in PEMs for all OCV AST cells
- Pt more diffuse in PEMs after OCV AST of PtCo/C cells
- Pt particle size & distribution differences explain differences in degradation
  - Pt band forms where radicals are produced → localized radical attack

Summary and Conclusions

- Similar decay modes for both types of tests
- Using PtCo/C rather than Pt/C improves durability by an order of magnitude
- FER can be used to project lifetimes
  - OCV ASTs accelerate degradation 4 to 9x over PETs
- Adopting a drive cycle as a baseline test would serve as a benchmark for future work

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Reference

M.P. Rodgers, P.B. Brooker, N. Mohajeri, L.J. Bonville, H.R. Kunz, D.K. Slattery, J.M. Fenton, Verification of the correlation between membrane/MEA degradation rate from accelerated and lifetime testing, *Journal of the Electrochemical Society*,159(7), F338-F352, 2012.