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Creating Energy Independence

Evaluation of Platinum Band Formation in PEM Fuel Cells

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Durability in PEM Fuel Cells

- Lack of long term stability in PEM fuel cells limits commercialization
- Automotive fuel cell systems need to be as durable & reliable as internal combustion engines
  - 5,000 hours by 2017
  - Operate -40 to +40 °C with < 5% performance loss
  - Operate without external humidification
- Stationary fuel cells
  - 60,000 hours by 2020

Membrane Chemical Failure Mechanisms

- Membrane is limiting factor in fuel cell longevity
- Membrane chemical decomposition caused by:
  - Reactant gas crossover
  - Radical formation and movement
  - Recrystallized Pt particles
  - Metal ion contaminants
- Radicals form at both electrodes and within the membrane
  - Requires H_2, O_2, and Pt (or certain other metals)
- Generation of radicals within membrane compromises integrity, leading to embrittlement and H_2-crossover

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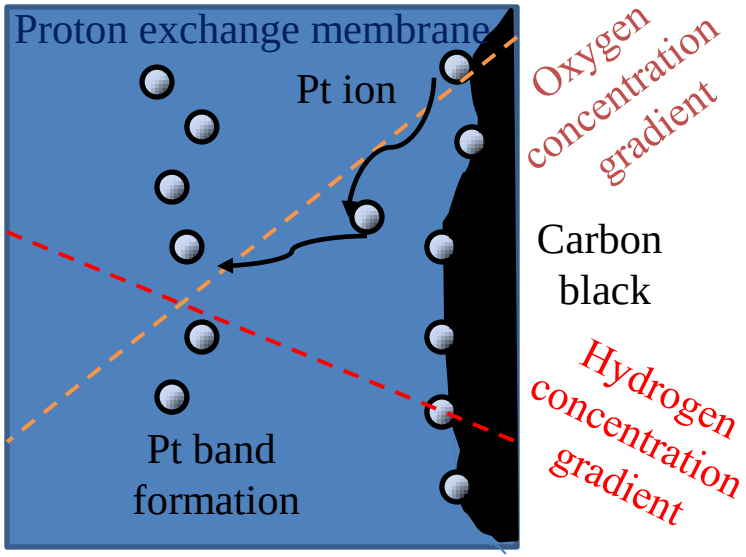
Impact of Pt on Membrane Failure

- Pt dissolves at high cathode potential and precipitates in the membrane through reduction by H_2
- The effect of Pt in the membrane is under debate
  - Decreases degradation[1,2]
    - Scavenges H_2O_2 and radicals
  - Accelerates degradation[3,4,5]
    - Radicals form on the Pt surface from crossover H_2 and O_2
    - Radicals attack PEM through chain unzipping and scission mechanisms



- Contrasting effects of Pt on degradation due to differences in size and distribution of particles

1. Hagihara, H. et al. *Electrochim. Acta* **2006**, *51*, 3979.
2. Endoh, E. et al. J. *ECS Trans.* **2007**, *11*, 1083.
3. Atrazhev, V. V. et al. *J. Electroanal. Chem.* **2007**, *601*, 251
4. Stucki, S. et al. *J. Appl. Electrochem.* **1998**, *28*, 1041
5. Zhao, D. et al. *J. Power Sources* **2010**, *195*, 4606.

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Effect of Size and Distribution of Pt in the Membrane on Degradation

- Location
  - Reactant x-over is stoichiometrically favorable for $OH^{\bullet}$ in the same location where the Pt band preferably forms[1]
- Size
  - Large particles → Radicals escape more slowly[1]
  - Small particles[1]
    - Far apart: fewer radicals
    - Close together: membrane degradation ↓ with ↑ particle size
- Density
  - O_2 is more efficiently reduced to H_2O with increased Pt density[2]

1. Gummalla, M.; Atrazhev, V. V.; Condit, D.; Cipollini, N.; Madden, T.; Kuzminyh, N. Y.; Weiss, D.; Burlatsky, S. F. *J. Electrochem. Soc.* **2010**, *157*, B1542.
2. Bonakdarpour, A.; Dahn, T. R.; Atanasoski, R. T.; Debe, M. K.; Dahn, J. R. *Electrochem. Solid-State Lett.* **2008**, *11*, B208.

Accelerated Stress Testing in Fuel Cells

- Evaluation of membrane durability under normal operating conditions is not practical
- Examining MEAs under accelerated testing gives indication of degradation behavior
- Accelerated tests need to:
  - Activate targeted failure mode
  - Minimize confounding effects
- Low humidities, high temperatures, humidity cycling, temperature cycling, open circuit voltage (OCV)
  - OCV operation accelerates membrane chemical decomposition

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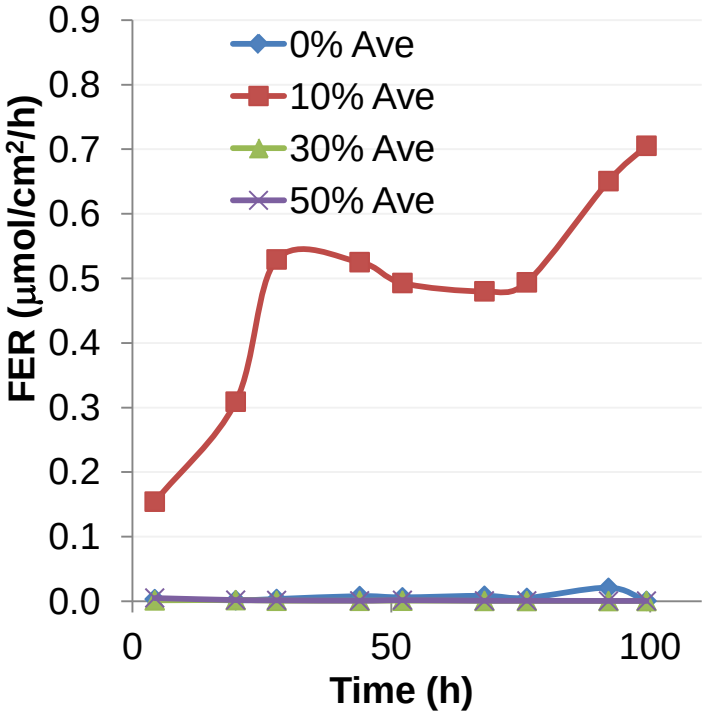
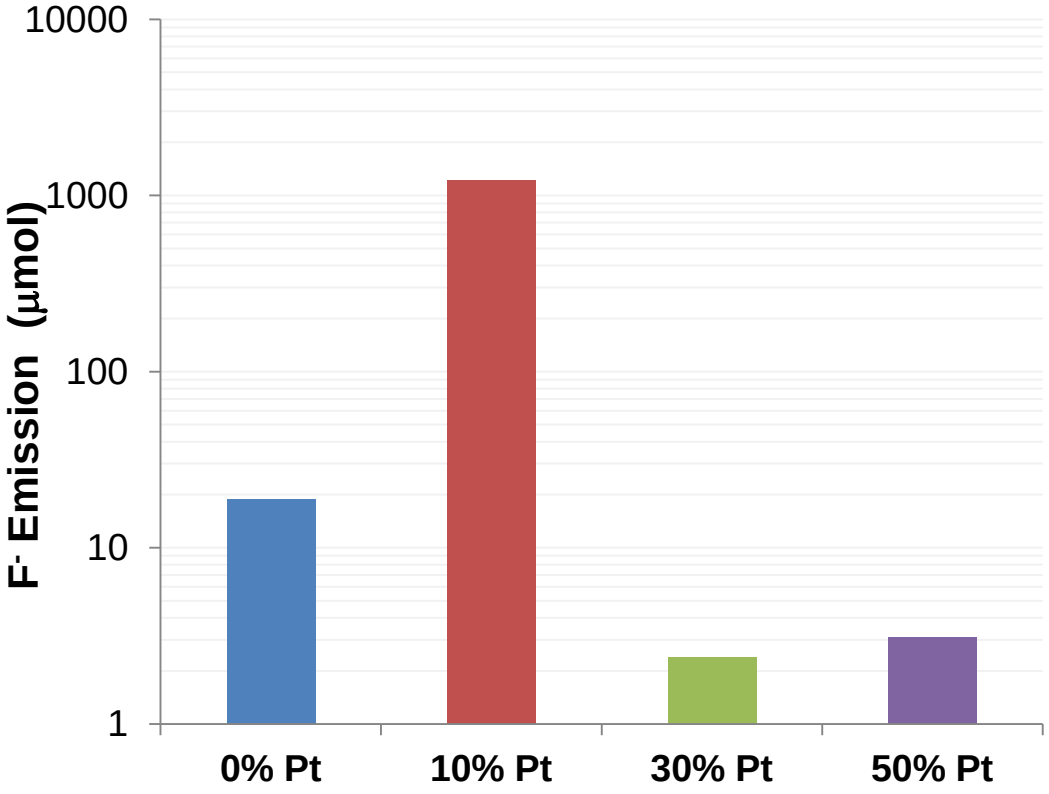
Strategy

- Goal:
  - To investigate the effect of Pt in the membrane on durability
    - Hypothesize that concentration of Pt in the membrane will impact the magnitude of degradation
- Impregnated NRE211® with 0, 10, 30, and 50 mol% Pt
  - No electrodes were applied to the membranes
- Compare the durability of cells with each Pt loading
  - 100 h, H_2/air, 90 ^oC, 30% RH
  - Monitor fluoride emission rate during test
  - Compare electron microscopy images before and after testing

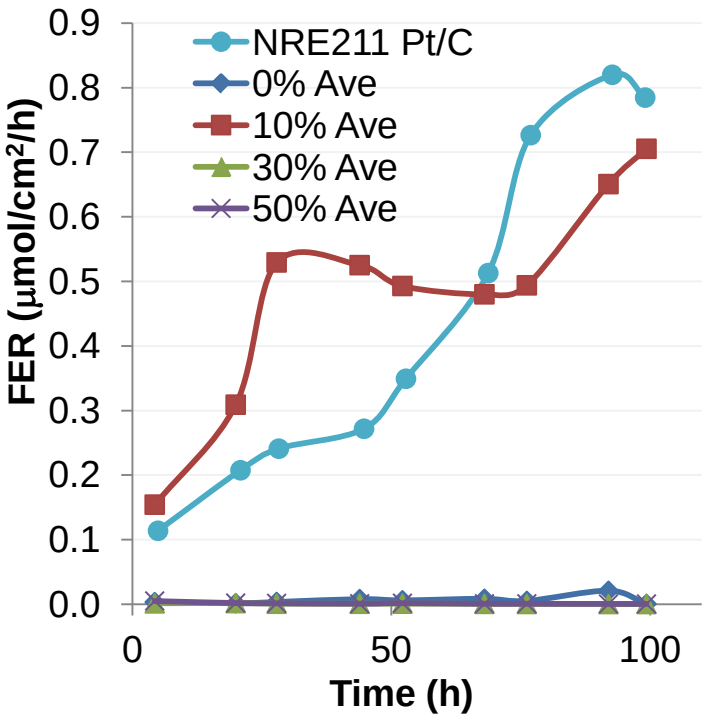
Results: Fluoride Emission Rate (FER)

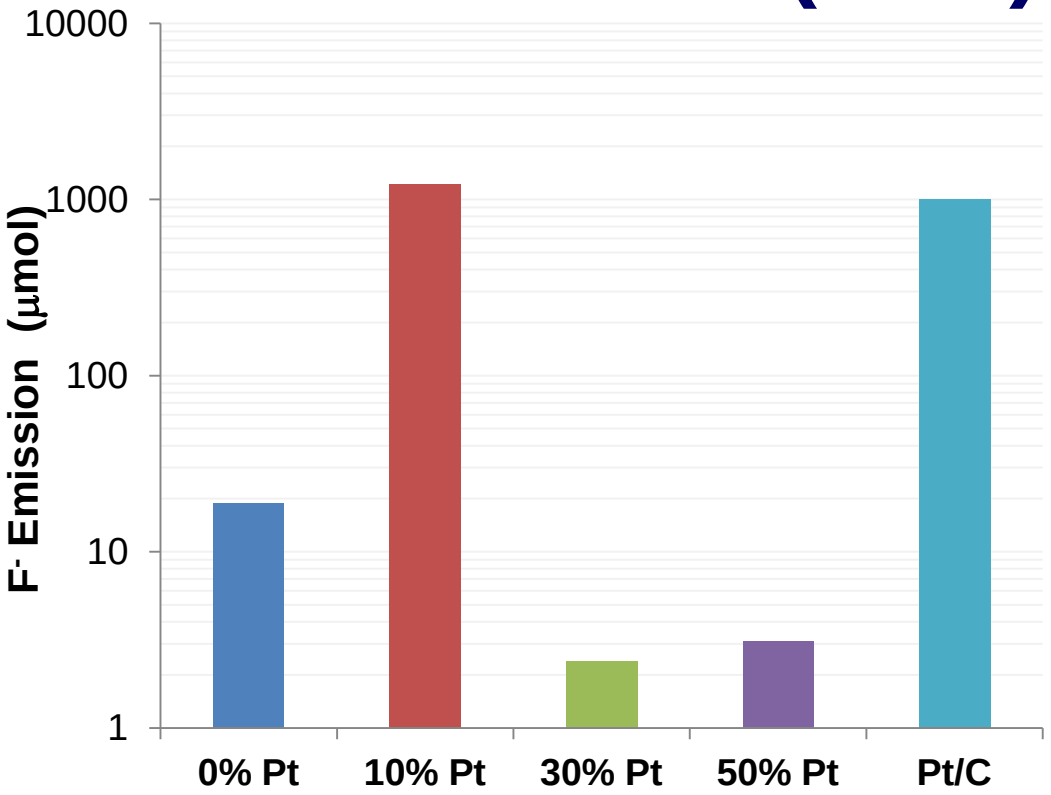




- The total fluoride emission of the 10 mol% Pt cell is >2 orders of magnitude higher than all other cells

Results: Fluoride Emission Rate (FER)





- The total fluoride emission of the 10 mol% Pt cell is >2 orders of magnitude higher than all other cells
- The results with 10% Pt are comparable to a standard cell with a NRE211® membrane and a Pt/C electrode

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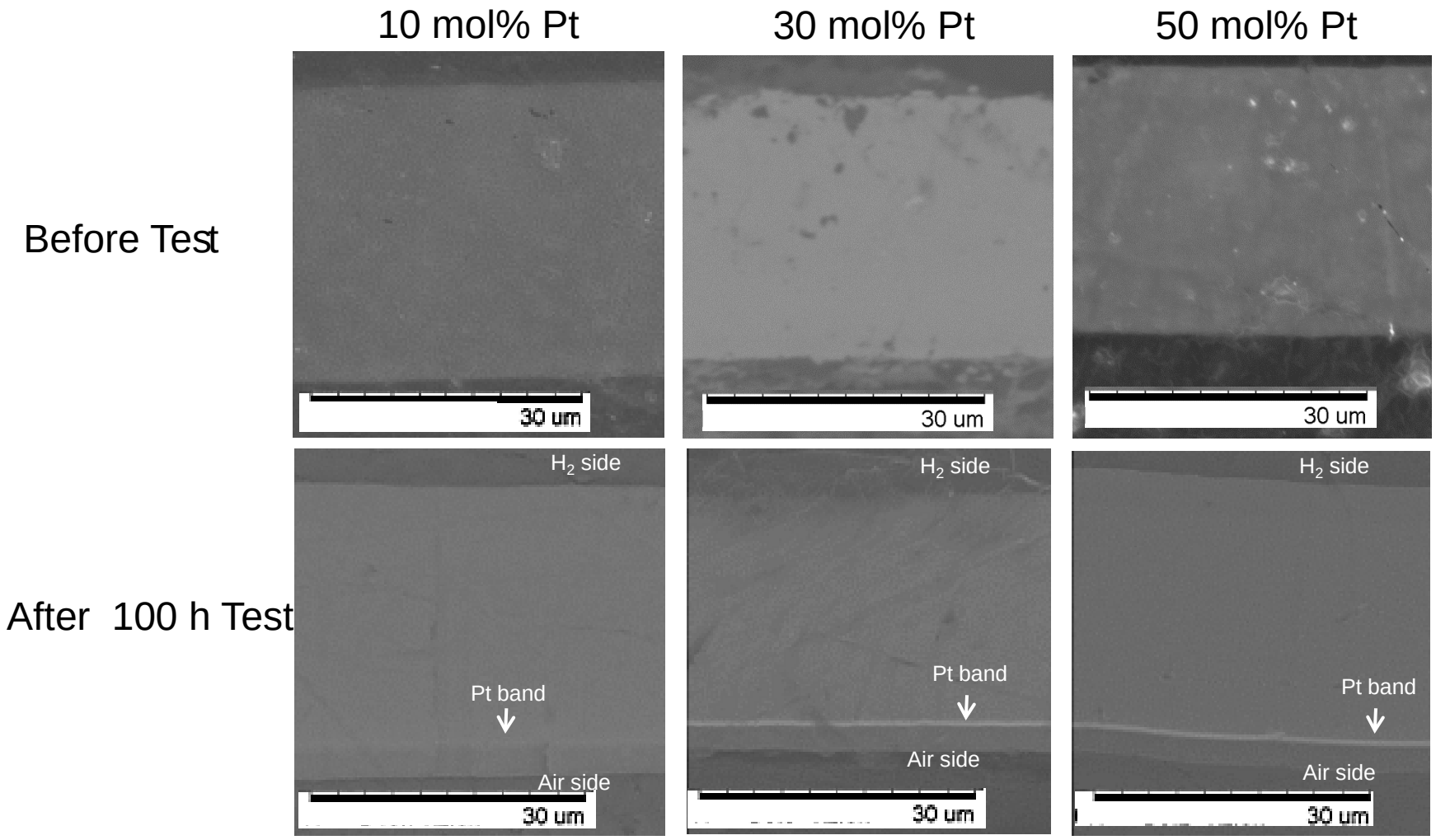
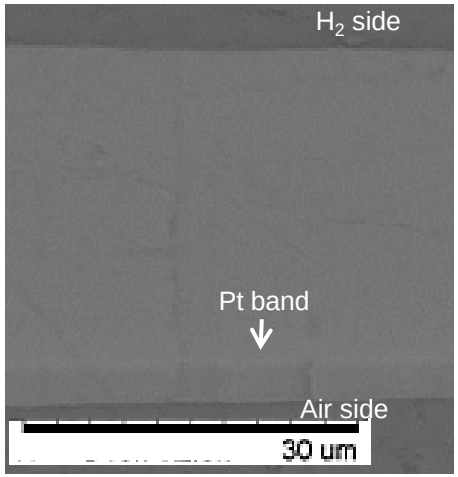
Results: SEM



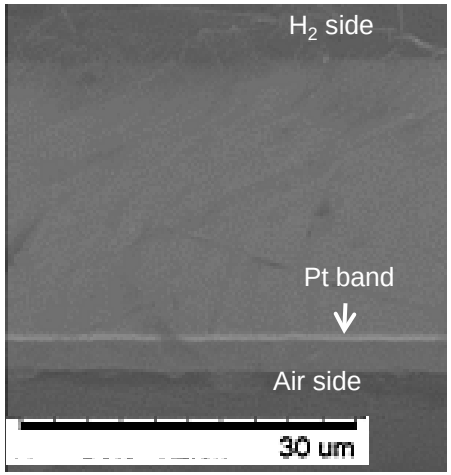
- All cells show a Pt band after testing located ~3 microns from air side

Results: SEM

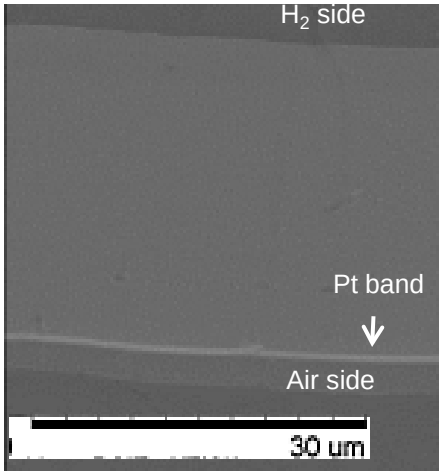
10 mol% Pt



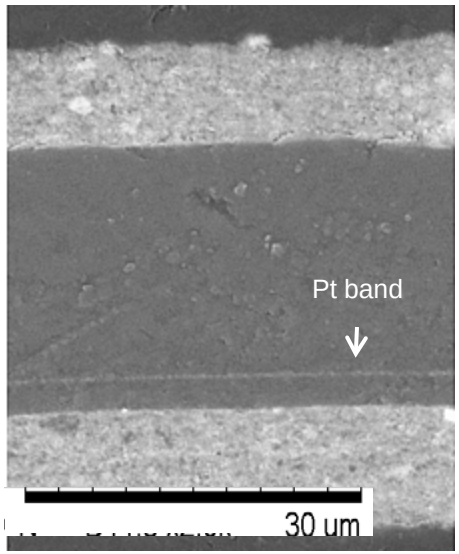
30 mol% Pt



50 mol% Pt



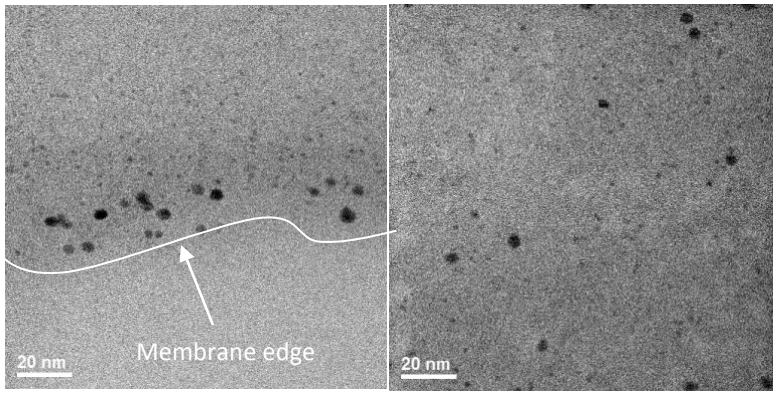
NRE211 with Pt/C electrodes



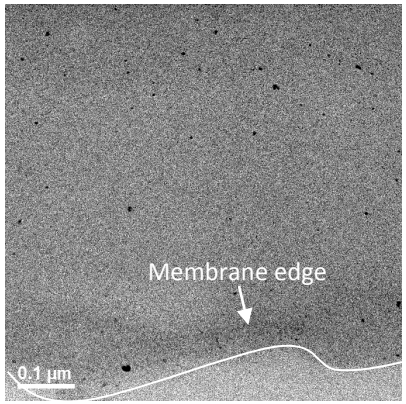
- All cells show a Pt band after testing located ~3 microns from air side
- Similar to a conventional CCM

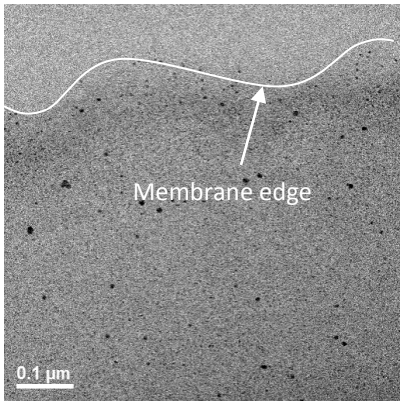
Results: TEM of PEMs: 10 mol% Pt

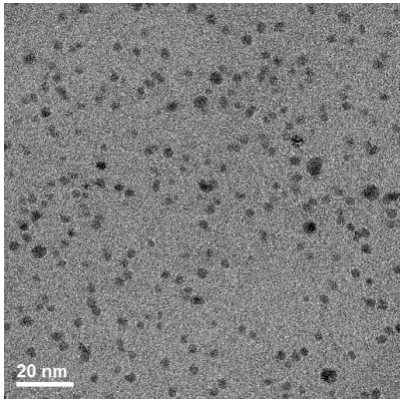
Before Testing



After Testing







- Before test:
  - Higher concentration of Pt near edge
  - Pt particles in the membrane evenly distributed
    - 44 nm average distance between particles
    - 2.9 nm average particle size
    - 0.6% area coverage by particles
- After 100 h test:
  - Edge effect is gone
  - Pt particles evenly distributed
    - 10 nm average distance between particles
    - 2.4 nm average particle size
    - 6.4% area coverage by particles

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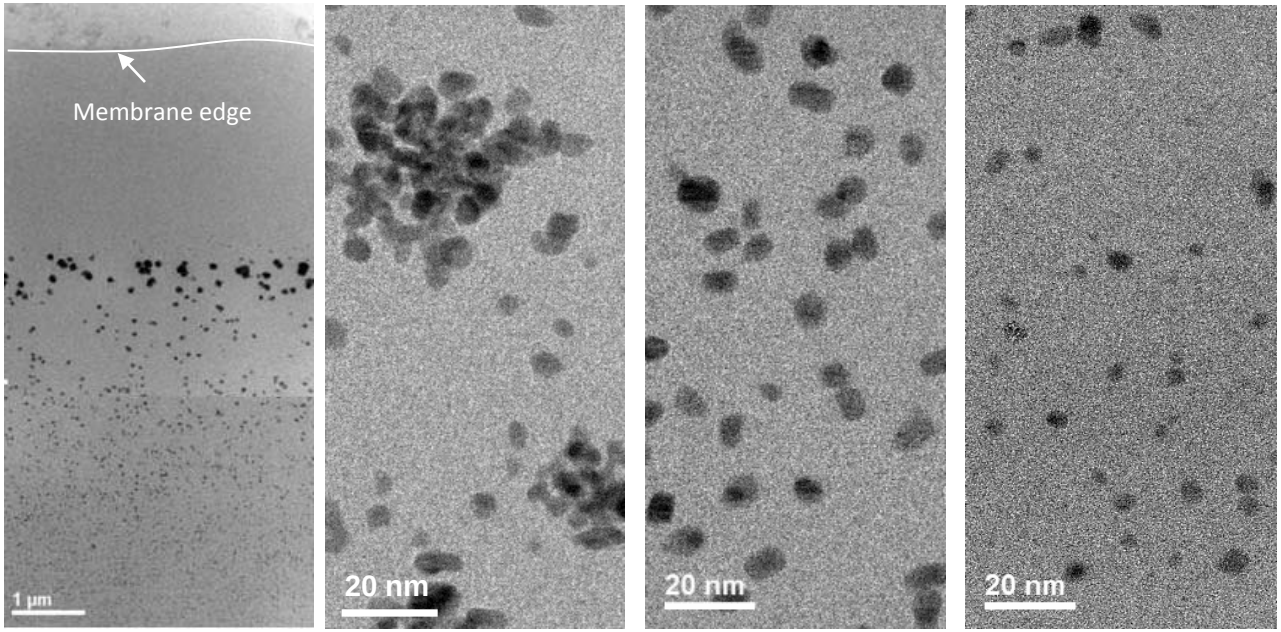
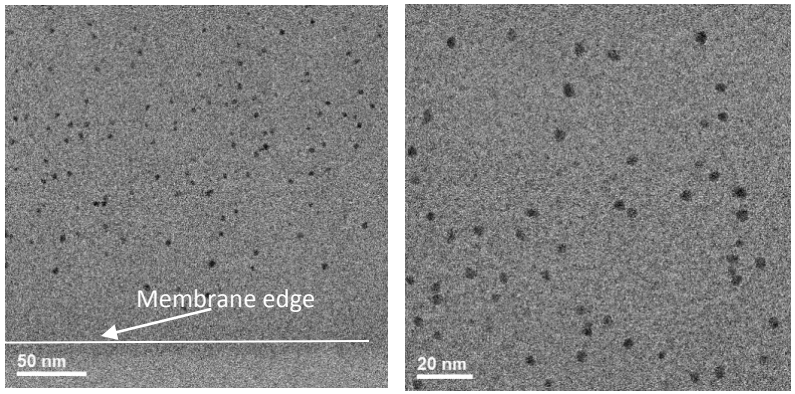
Results: TEM of PEMs: 30 mol% Pt



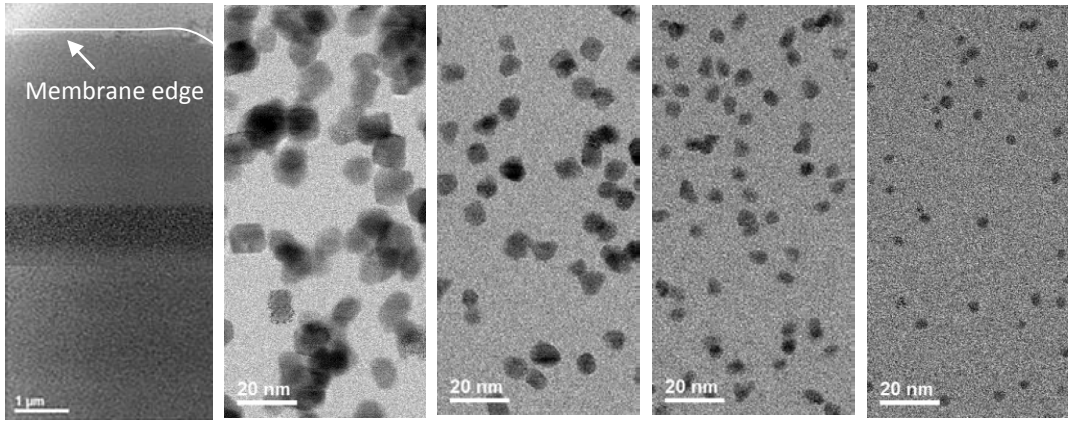
- After 100 h test:
  - Pt band has formed
    - More than 5 μm wide located 2.6 μm from air side
    - 18 to 20 nm average distance between particles (↑ with distance from air side)
    - 3.7 to 6.8 nm average particle size (↓ with distance from air side)
    - 3.3 to 14% area coverage by particles (↓ with distance from air side)

Results: TEM of PEMs: 50 mol% Pt

Before Testing



After Testing



- Before test:
  - Homogenous distribution of Pt
    - 24 nm average distance between particles
    - 3.4 nm average particle size
    - 2.2% area coverage by particles
- After 100 h test:
  - Pt band has formed
    - 0.9 µm wide 3.2 µm from air side
    - 14 to 18 nm average distance between particles (↑ with distance from air side)
    - 2.5 to 11 nm average particle size (↓ with distance from air side)
    - 3.3 to 40% area coverage by particles (↓ with distance from air side)

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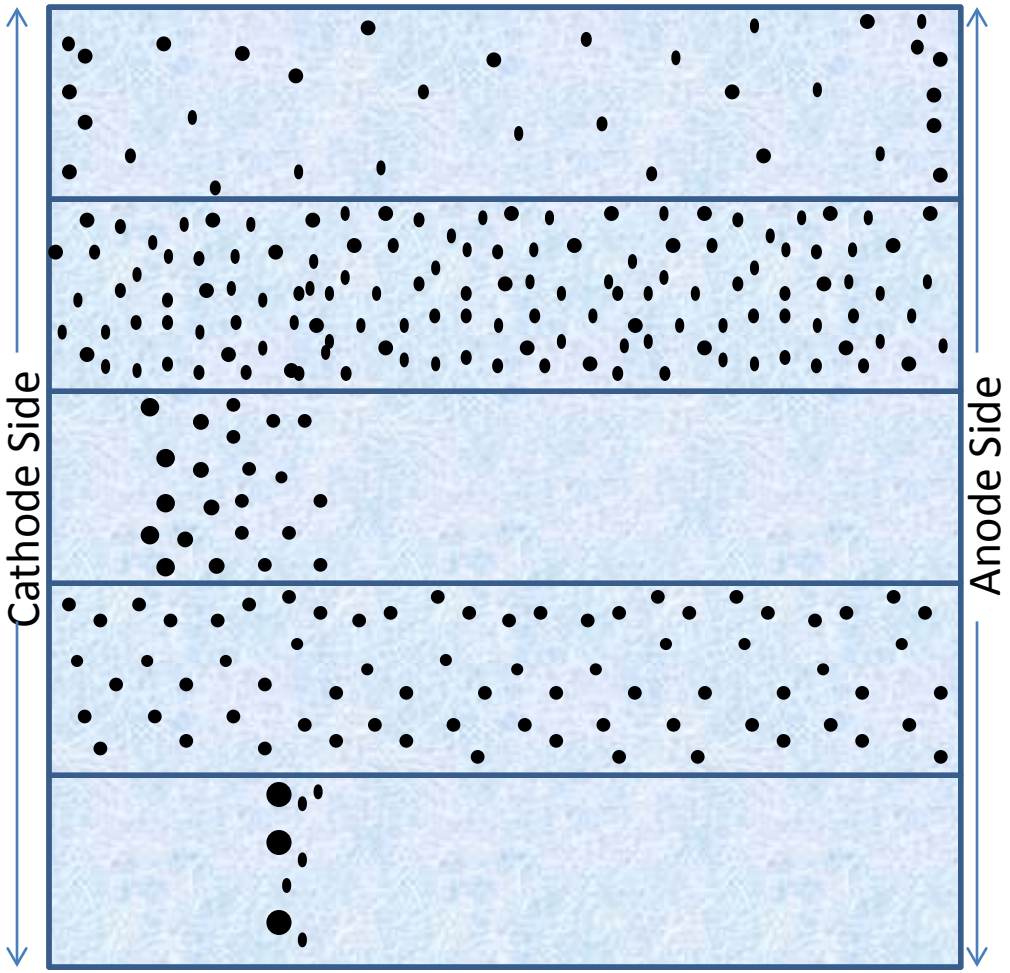
TEM Summary



10 mol% Pt before 100 h test

10 mol% Pt after 100 h test

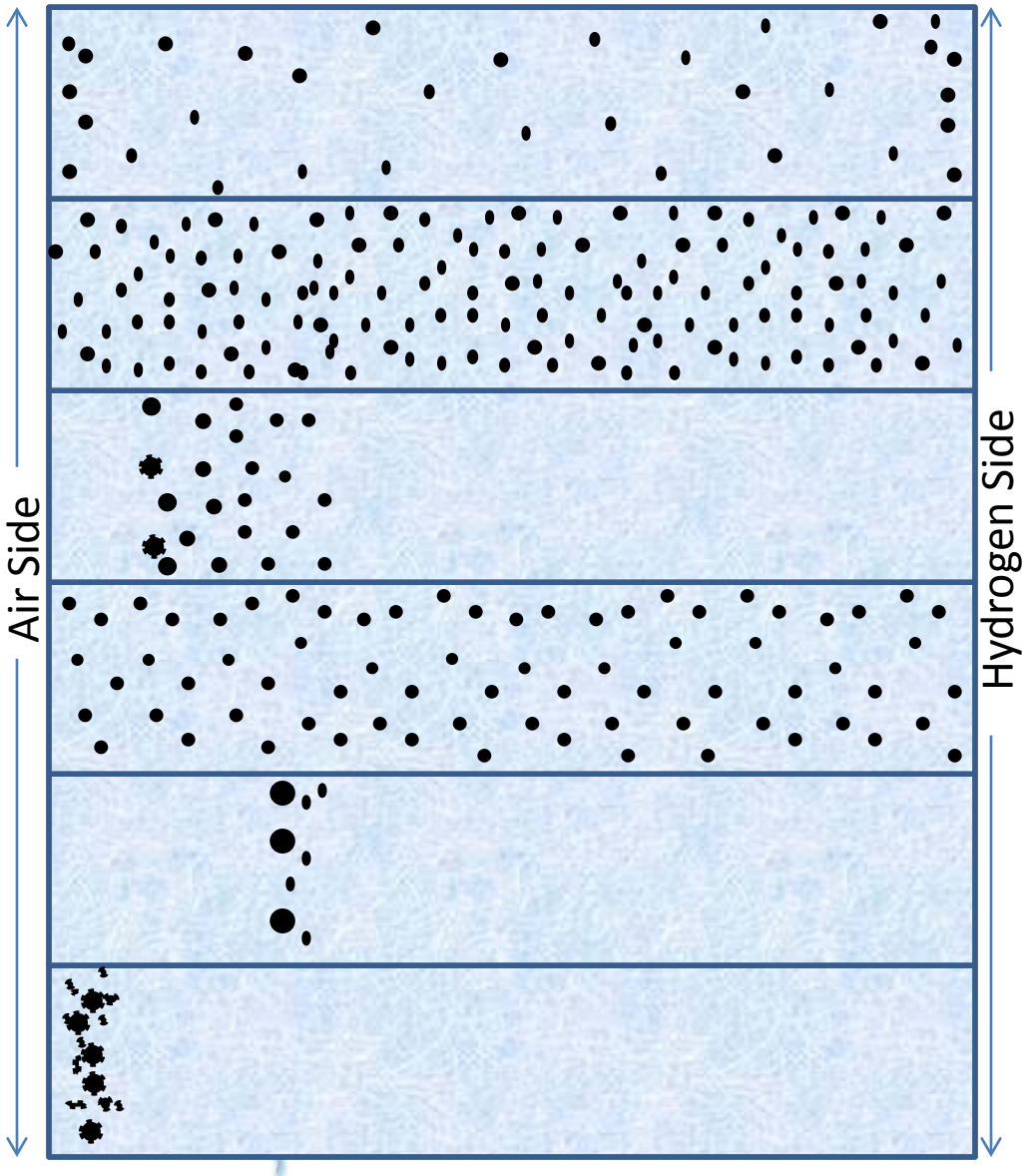
30 mol% Pt after 100 h test

50 mol% Pt before 100 h test

50 mol% Pt after 100 h test

- After testing, 10 mol% Pt had smallest particle distance and size, and the greatest overall Pt coverage

TEM Summary



10 mol% Pt before 100 h test

10 mol% Pt after 100 h test

30 mol% Pt after 100 h test

50 mol% Pt before 100 h test

50 mol% Pt after 100 h test

NRE211 with Pt/C electrodes after 100 h test

Summary and Conclusions

- Impregnated NRE211 with 0, 10, 30, and 50 mol% Pt, supplied H_2/air and examined degradation and Pt size and distribution
- Although Pt bands formed with 30 and 50 mol% Pt, degradation was negligible
- Highest degradation observed with 10 mol% Pt
  - Attributed to higher concentration of small particles, which has been shown to result in increased degradation[1]

1. Gummalla, M.; Atrazhev, V. V.; Condit, D.; Cipollini, N.; Madden, T.; Kuzminyh, N. Y.; Weiss, D.; Burlatsky, S. F. *J. Electrochem. Soc.* **2010**, *157*, B1542.

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ShaRE
Shared Research Equipment User Facility
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TEM of NRE211 Pt/C after 100 h OCV, 90 °C/30% RH, H_2/air