Effect of Equivalent Weight on Degradation of Perfluorosulfonic Acid Membranes Under Accelerated Stress Conditions

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Introduction

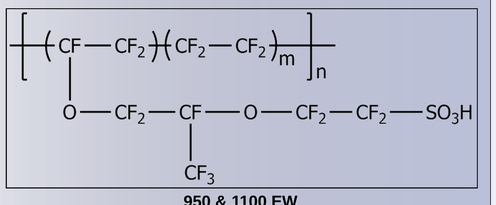
- Equivalent weight (EW) impacts properties of membranes Higher EW membranes have:
  - Higher crystallinity
  - Lower water content
  - Lower glass transition temperature
- Length of sulfonic acid side chains (SSCs) also impacts membrane properties; shorter SSC membranes have:
  - Higher crystallinity
  - Lower water content
  - Higher glass transition temperature
  - Similar gas permeability
  - Lower proton conductivity
- Mechanism of impact of EW and SSC length on durability is not fully understood
- Side chain attack by radicals is a major source of membrane degradation
  - » Hypothesis: Membranes with lower EW (more (SSCs) have lower durability

Strategy

Goal: To compare the effects of EW and side chain length on MEA durability

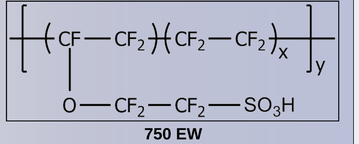
Membranes used:

- 950 EW (long SSC)
- 1100 EW (long SSC)
- 750 EW (short SSC)



950 & 1100 EW

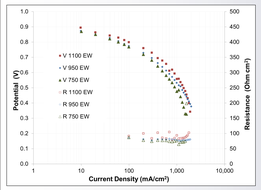
- Prepare CCMs by spraying on electrodes with Pt/C + 32 wt% 1100 EW Nafion ionomer
- Open-circuit voltage (OCV) accelerated stress test (AST)
  - Assess membrane chemical durability
  - 100 h, H_2/air, 90 °C, 30% RH



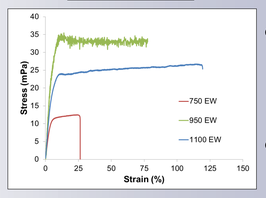
750 EW

Results

Pretest



Potential and resistance as a function of current density at 80 °C/~100% RH using H_2/air pretest



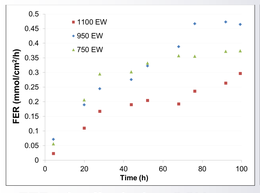
Mechanical properties of untested MEAs

EW (g/meq)	Strain at Break (%)	Modulus Of Elasticity (MPa)	Stress at Break (MPa)
750	27.6	328.6	13.3
950	85.0	654.5	31.6
1100	122.6	431.9	28.3

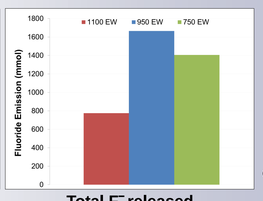
- Strain at break decreased with decreasing EW
- 950 EW membranes had the highest modulus of elasticity and stress at break
- All cells were in acceptable pretest condition

Post test

Fluoride Emission (FE)



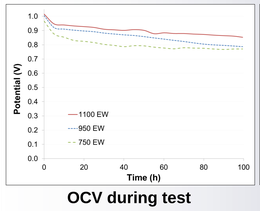
FER of cells during OCV test



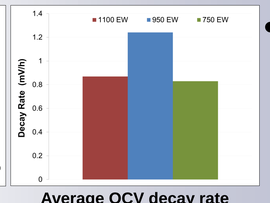
Total F^- released

- Post test fluoride emission rate (FER) of the 950 EW cell was 50% higher than the 1100 EW cell
- FE of 950 EW cell was >2x 1100 EW cell

OCV



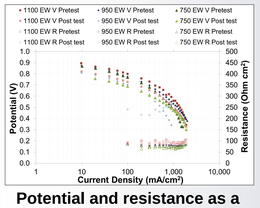
OCV during test



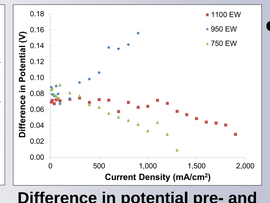
Average OCV decay rate

- The voltage degradation rate of the 950 EW cell was considerably higher than of the 1100 and 750 EW cells

Performance



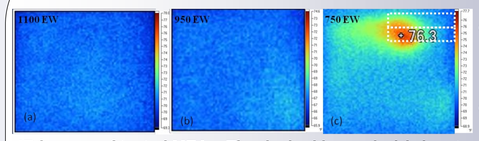
Potential and resistance as a function of current density at 80 °C/~100% RH using H_2/air pre– and post test



Difference in potential pre- and post test

- Resistances of the 950 EW cell tripled
  - » Decreased performance

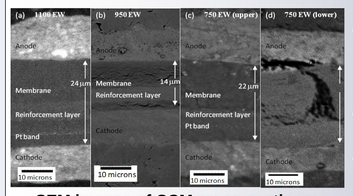
Localized Crossover Test



IR images of tested MEAs. The dashed boxes in (c) denote the areas of the cell from which SEM samples were cut

- 1100 and 950 EW cells had very little crossover
- 750 EW cells had increased crossover

Scanning Electron Microscopy



SEM images of CCM cross-sections; (c) and (d) are from the same CCM

- Pretest membrane thickness: ~25 µm
  - » 950 EW thinned considerably
- Pt band in 1100 and 750 EW
- Large crack in 750 EW
  - » Linked to temp. increase in IR image

Transmission Electron Microscopy (TEM)

1100 EW 750 EW
TEM images of tested CCMs

- In the 1100 EW MEA, Pt was only found in the Pt band
  - » Start: 2.5 µm from the cathode Width: 3.1 µm
- In the 750 EW MEA, Pt extended from the cathode 3.1 µm into the membrane
  - » Largest particles 2.1 µm from cathode
- Pt particle sizes were similar
  - » Range of 10 to 85 nm

Summary and Conclusions

- 1100 EW cell showed highest durability
  - » attributed to fewer sulfonic acid groups
- 750 EW cell showed areas of high localized crossover
- 950 EW cell showed the highest OCV decay rate, fluoride emission, loss in ECA and loss in performance
  - » lower degradation of 750 EW membrane attributed to shorter sulfonic acid side chains

Acknowledgements

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