



# Material Challenges in Proton Exchange Membrane Fuel Cells

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**DuPont Fuel Cells**

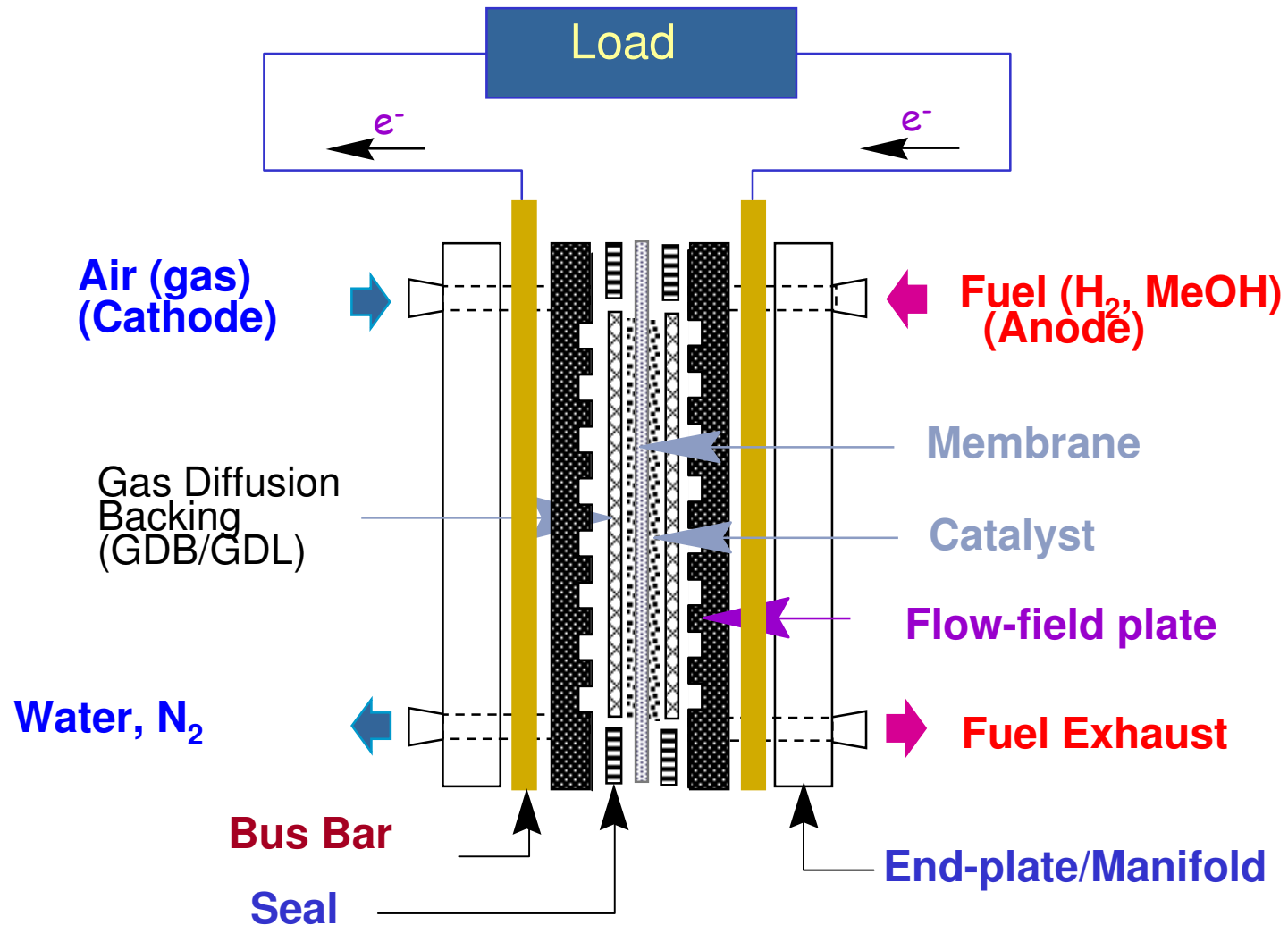
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# PEM Fuel Cell - Basic Single Cell Structure



# Material Challenges for Fuel Cell Components

## Membrane

- Proton conductivity
- Low RH operation
- Chemical Stability
- Mechanical Stability
- Low gas permeability
- Low Solubility / Swelling

## Bipolar Plates

- Electrical conductivity
- Zero leaching
- Chemical Stability
- Mechanical Stability
- Low gas permeability
- High flow property
- Good sealing

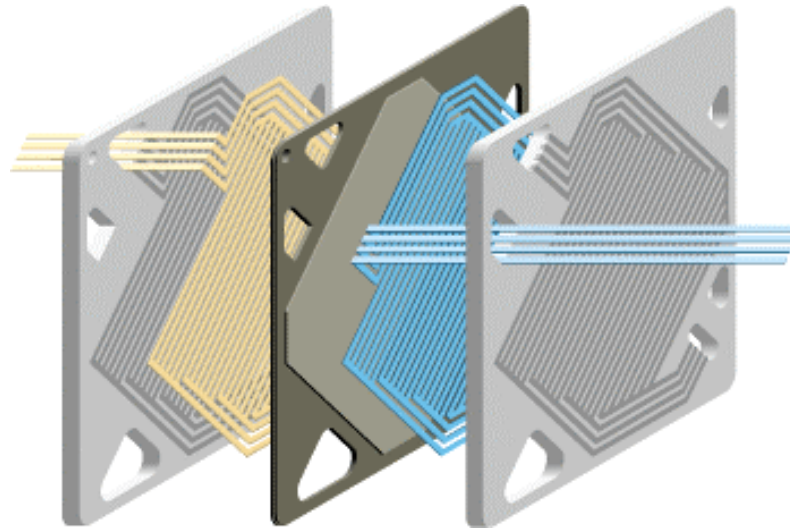


Figure: Courtesy of Ballard Power Systems

## Gas Diffusion Barrier

- Carbon Corrosion
- Good Mechanical Property
- Good Mass Transport
- High Electrical Conductivity

## Electrodes

- Electrical conductivity
- Proton conductivity
- Chemical Stability
- Good mass transport
- Platinum Dissolution
- Platinum Agglomeration
- Carbon Corrosion
- Catalyst Poisoning

## Seal Material

- Electrical insulation
- High compressibility
- Chemical Stability
- Low creep behavior

**System & BOP Challenges**



## Challenges - Fuel Cell Industry

Fuel Cell Durability is one of the most critical requirements for the successful commercial feasibility of PEM fuel cell technology.

### Opportunities for MEA durability improvements include:

- Chemical stability of the membrane material to peroxide attack.
- Loss of conductivity and mechanical failure of the PEM.
- Stability of the gas diffusion layer against carbon oxidation.
- Catalyst support resistance to corrosion.
- Catalyst surface area stability against agglomeration, dissolution and poisoning.
- Catalyst migration through the polymer electrolyte membrane.

# Reliability and Durability Requirements

Significant material improvements are required to meet durability goal for commercial implementation of Fuel Cell Systems.

## Typical lifetime requirements

- Automotive applications: 5,000 - 6,000 hrs
- Bus applications: 20,000 - 40,000 hrs
- Stationary applications: 40,000 hrs

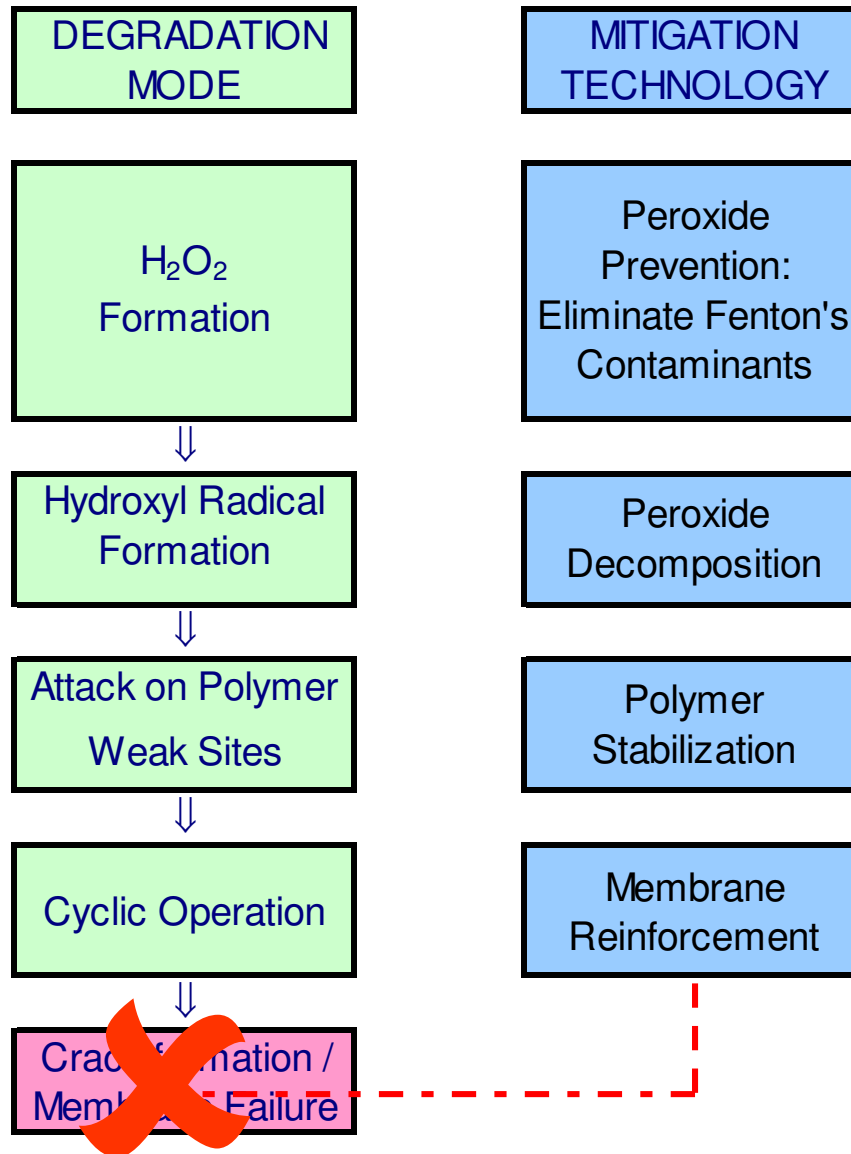


# DuPont Fuel Cells - History & Milestones

- Early 1960's** - Provided initial PEM membrane to NASA space program
- 1995** - Alternative Energy R&D program started
- 2001** - Accelerated efforts in Product / Process Development
- 2002** - Films and Dispersions - "Pipeline" of improvements
- 2003** - Achieved commercial status with MEA3 and MEA5
- 2004** - First fruits from increased PEMFC durability efforts
- 2005** - Transition to chemically stable product line



# Approach for Membrane Durability Enhancement



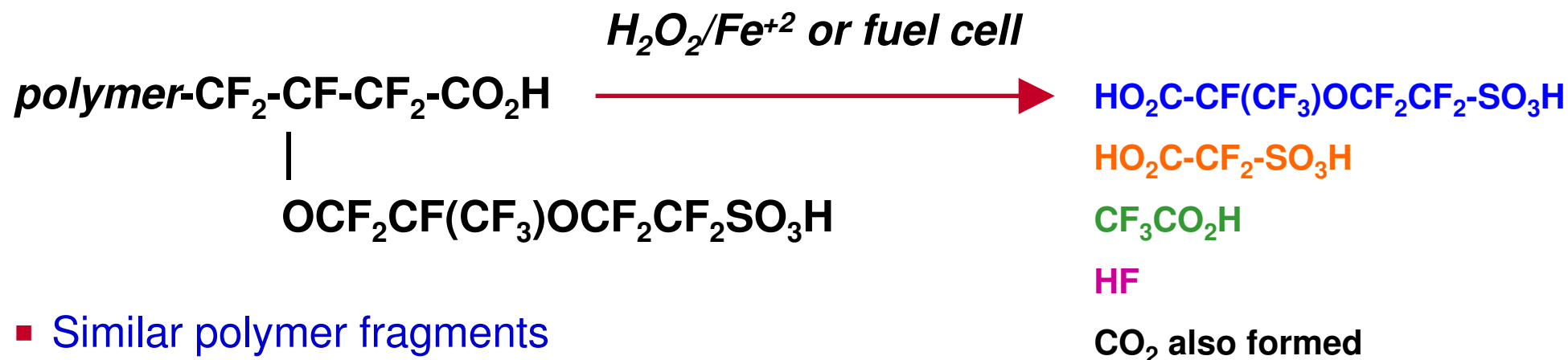
# Understanding the Chemical Degradation of Nafion<sup>®</sup> Membrane

## Chemical Degradation of Membrane

- $\text{H}_2\text{O}_2$  is generated by the reaction of the crossover oxygen with the hydrogen from anode side.
- $\text{H}_2\text{O}_2$  decomposes in presence of Fenton's cations to produce  $\cdot\text{OH}$  or  $\cdot\text{OOH}$  radicals.
- These radicals preferentially attack reactive end groups of the polymer and initiate chain scission reactions leading to the degradation of the polymer backbone

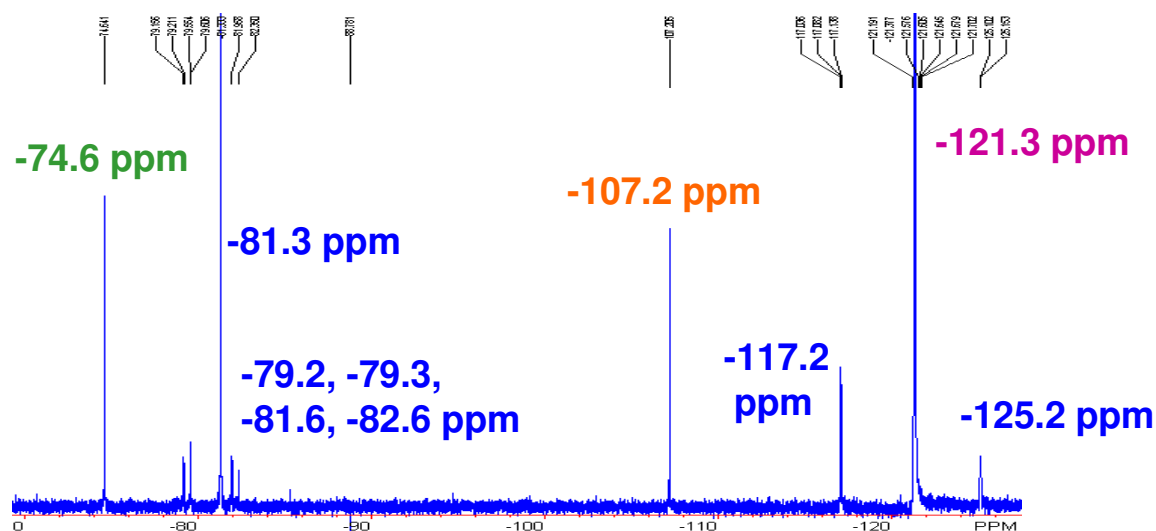


# Reactive End Groups : Polymer Degradation

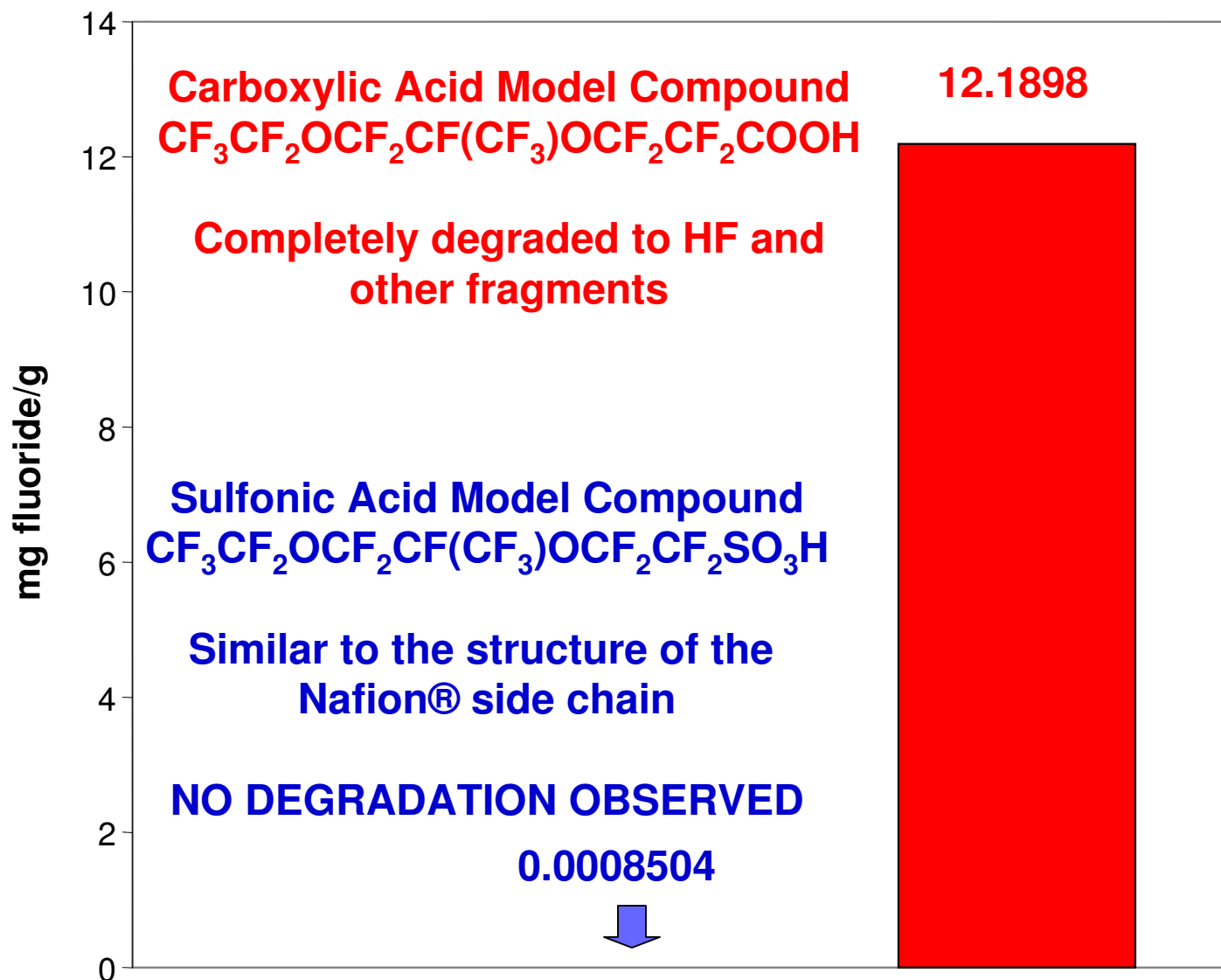


- Similar polymer fragments found in ex-situ Fenton's test and fuel cell test suggest similar degradation mechanisms under both conditions.
- Fragments are consistent with a step-wise degradation mechanism from unstable polymer end-groups.

<sup>19</sup>F-NMR of Cathode Product Water - OCV Test

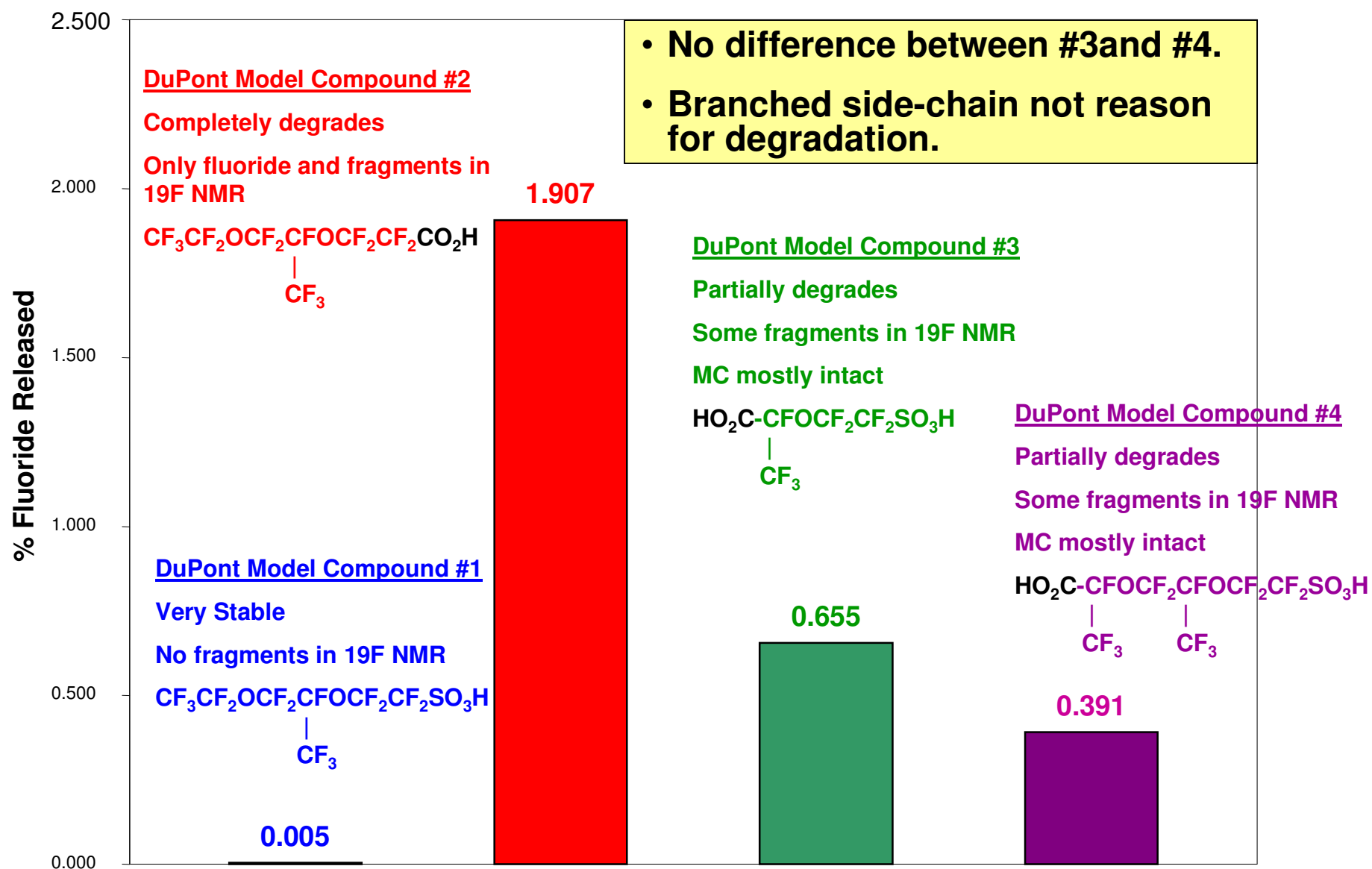


# Reactive End Groups : Model Compound Study

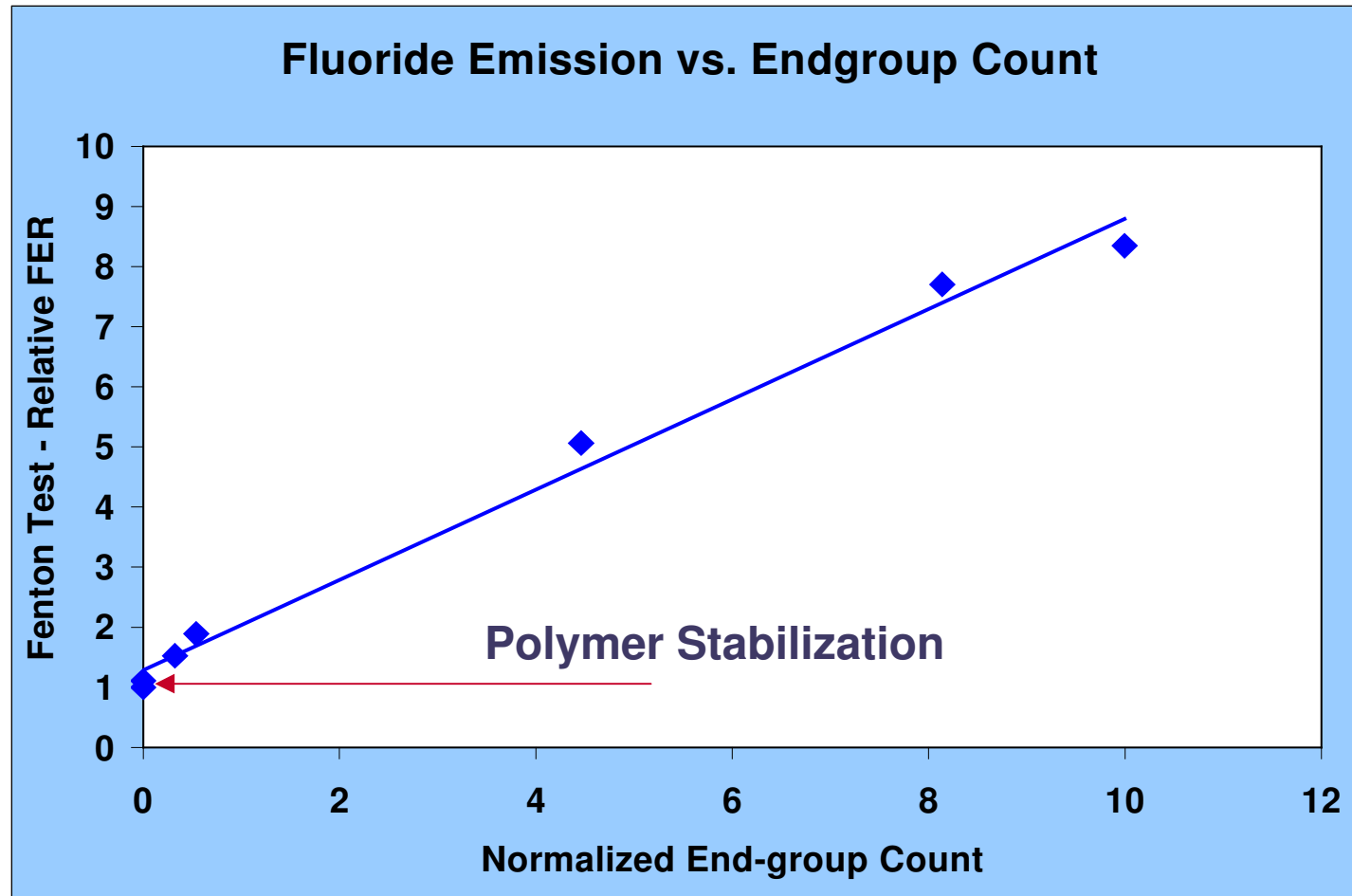


- Polymer backbone associated with -SO<sub>3</sub>H group is stable, while that with -COOH group decomposed completely.

# Reactive End Groups : Model Compound Study



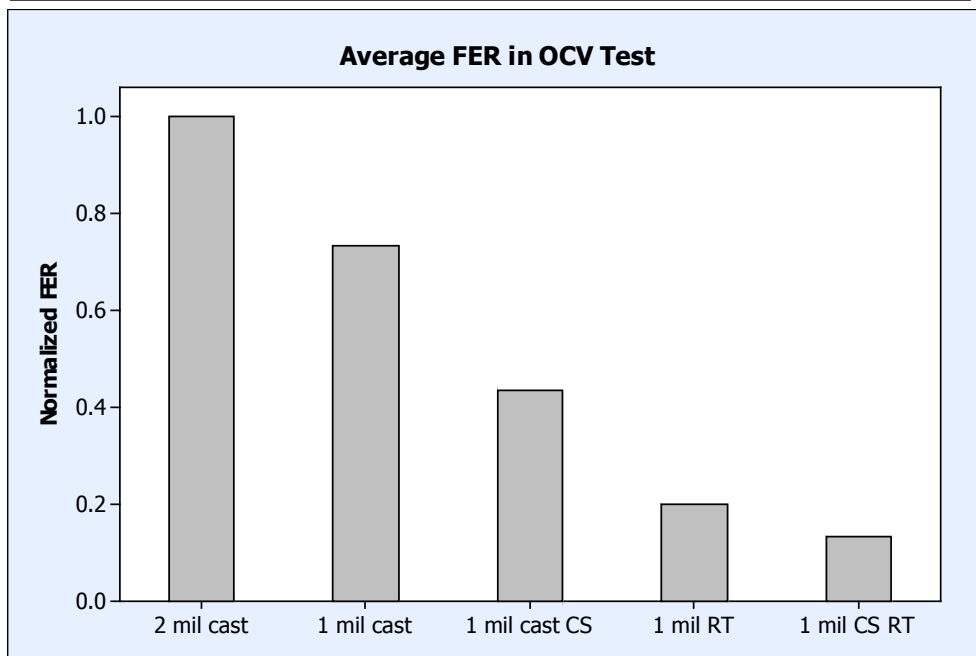
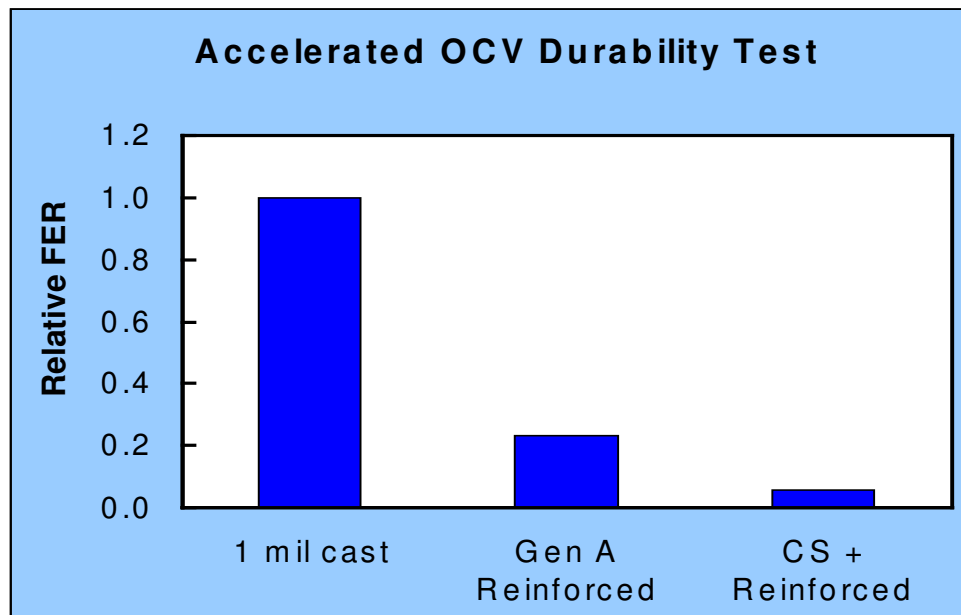
# Polymer Degradation : Correlation with End Groups



- PFSA ionomer is stabilized by reducing reactive polymer end-groups
- Fluoride emission in the Fenton's test is **8X lower** for the stabilized polymer

# Understanding the Mechanical Strength Requirements of Nafion<sup>®</sup> Membrane

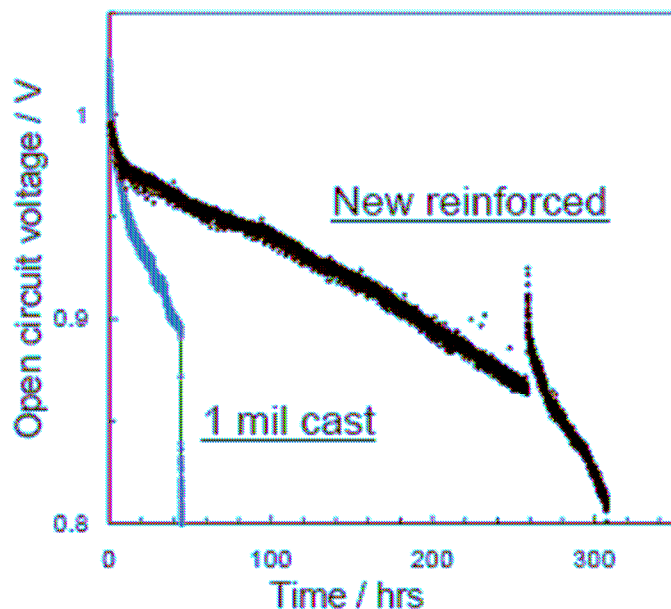
# Membrane Performance : Accelerated Durability Test



- Our selected reinforced membrane prototypes show significant lower FER than the baseline materials.
- CS/Reinforced membrane shows lowest FER
- We have successfully combined our mechanical and chemical stability strategies in a series of prototype membranes
- Different reinforced membrane structures including stabilized ionomer (CS) show good performance in our accelerated durability tests.

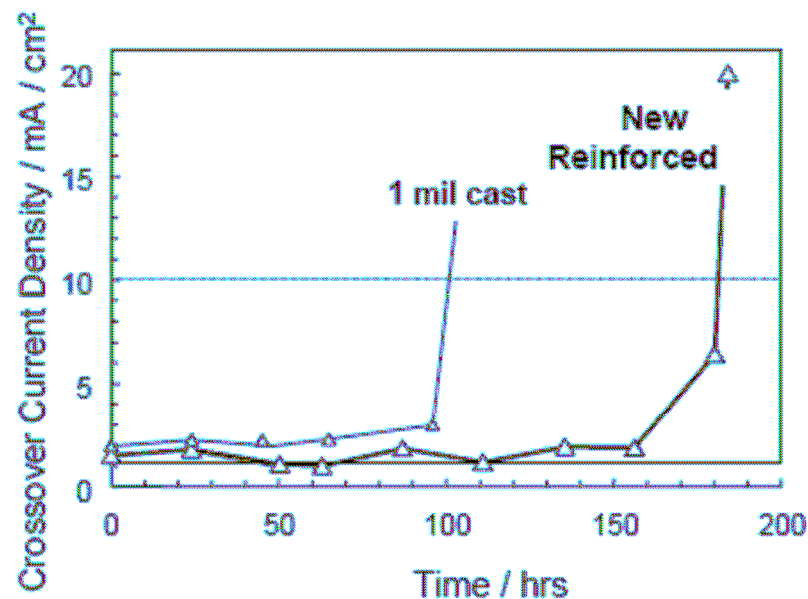
## UTC Single Cell Testing of Gen A Reinforced Membrane

*New membrane shows increased chemical and mechanical stability*



**OCV hold**  
• lifetime, fluoride release

- 7x increase in OCV hold lifetime
- Substantial chemical stability
- Does not yet include CS ionomer, UTC peroxide mitigation



**RH-load cycle**  
• lifetime

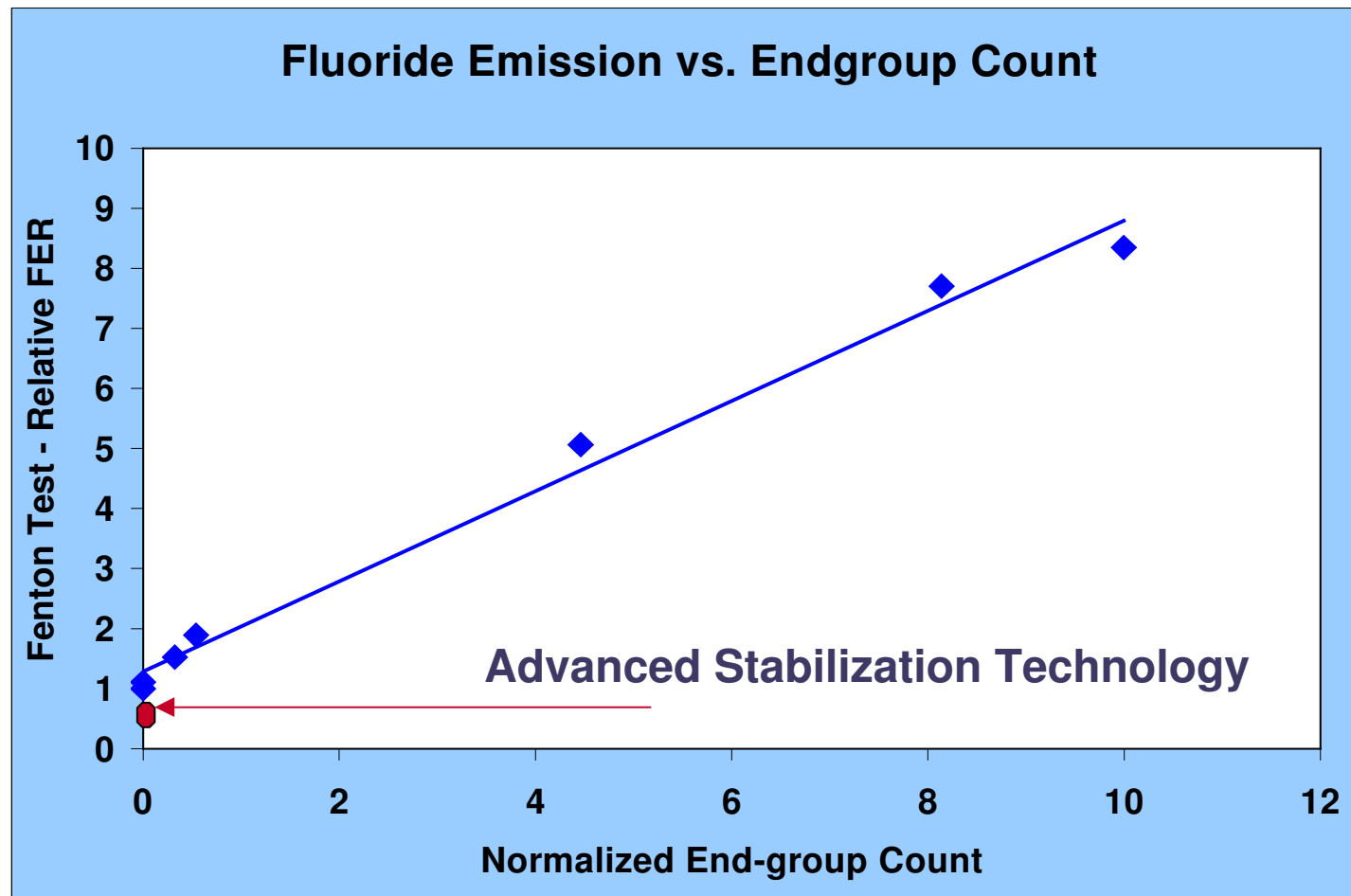
- ~2x increase in RH-load cycle lifetime
- Improved mechanical properties improve durability in a fuel cell

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[http://www.hydrogen.energy.gov/pdfs/review05/fc9\\_escobedo.pdf](http://www.hydrogen.energy.gov/pdfs/review05/fc9_escobedo.pdf)

# Further Improvements of Chemical Stability of Nafion<sup>®</sup> Membrane

# Polymer Degradation : Correlation with End Groups



- PFSA ionomer is stabilized by reducing reactive polymer end-groups
- Fluoride emission in the Fenton's test is 8X lower for the stabilized polymer
- **Further reduction in FER is achieved by incorporating DuPont's advanced stabilization technology.**

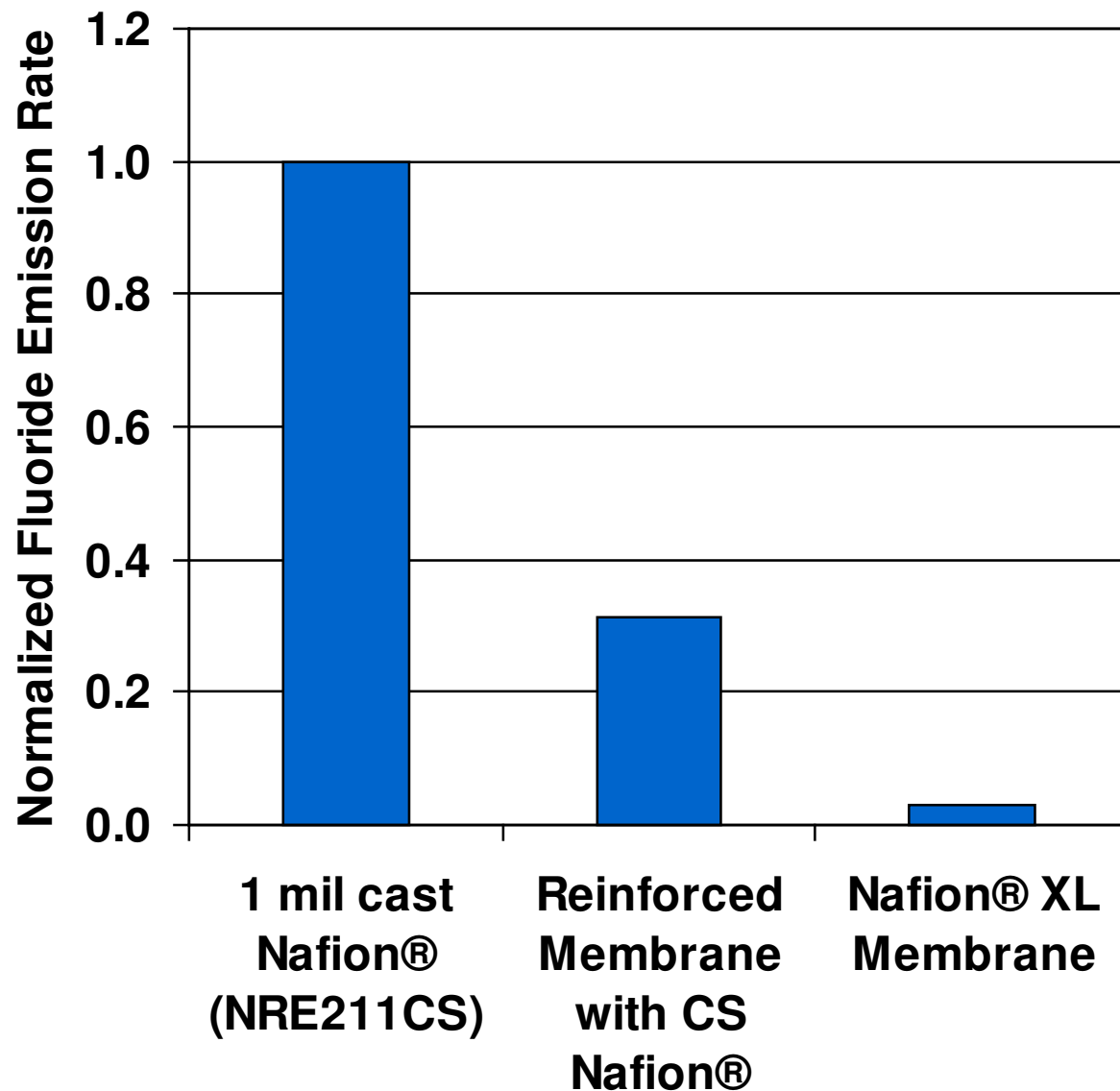


## Nafion® XL Membrane

- Nafion® XL membrane incorporates DuPont's most recent advances in chemical stabilization technology.
- A fundamental understanding of PEM degradation mechanisms has enabled DuPont to develop proprietary technologies to enhance the chemical stability of Nafion® membranes.
- Nafion® XL membrane demonstrates improvements beyond the benefits already provided by our chemically stable (CS) ionomer.

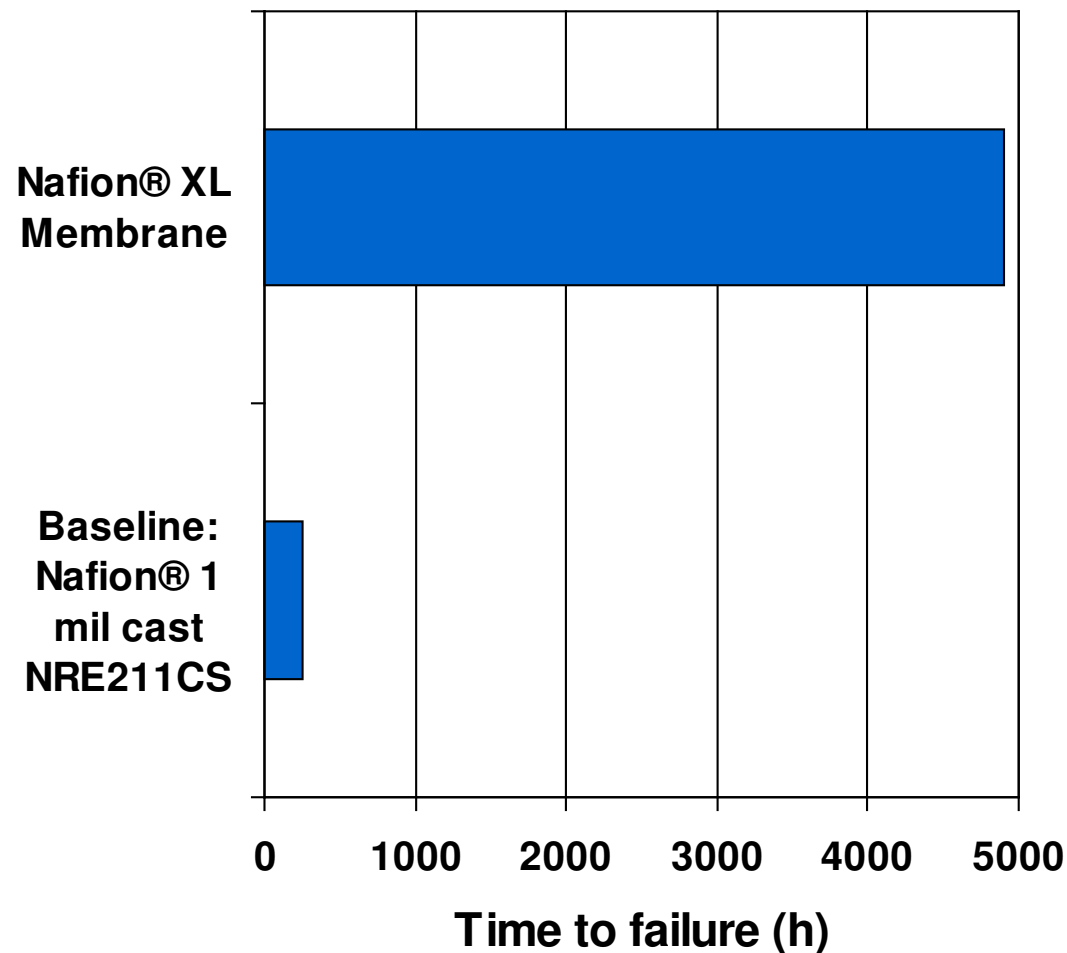


## Fluoride Emission : Accelerated Durability Test



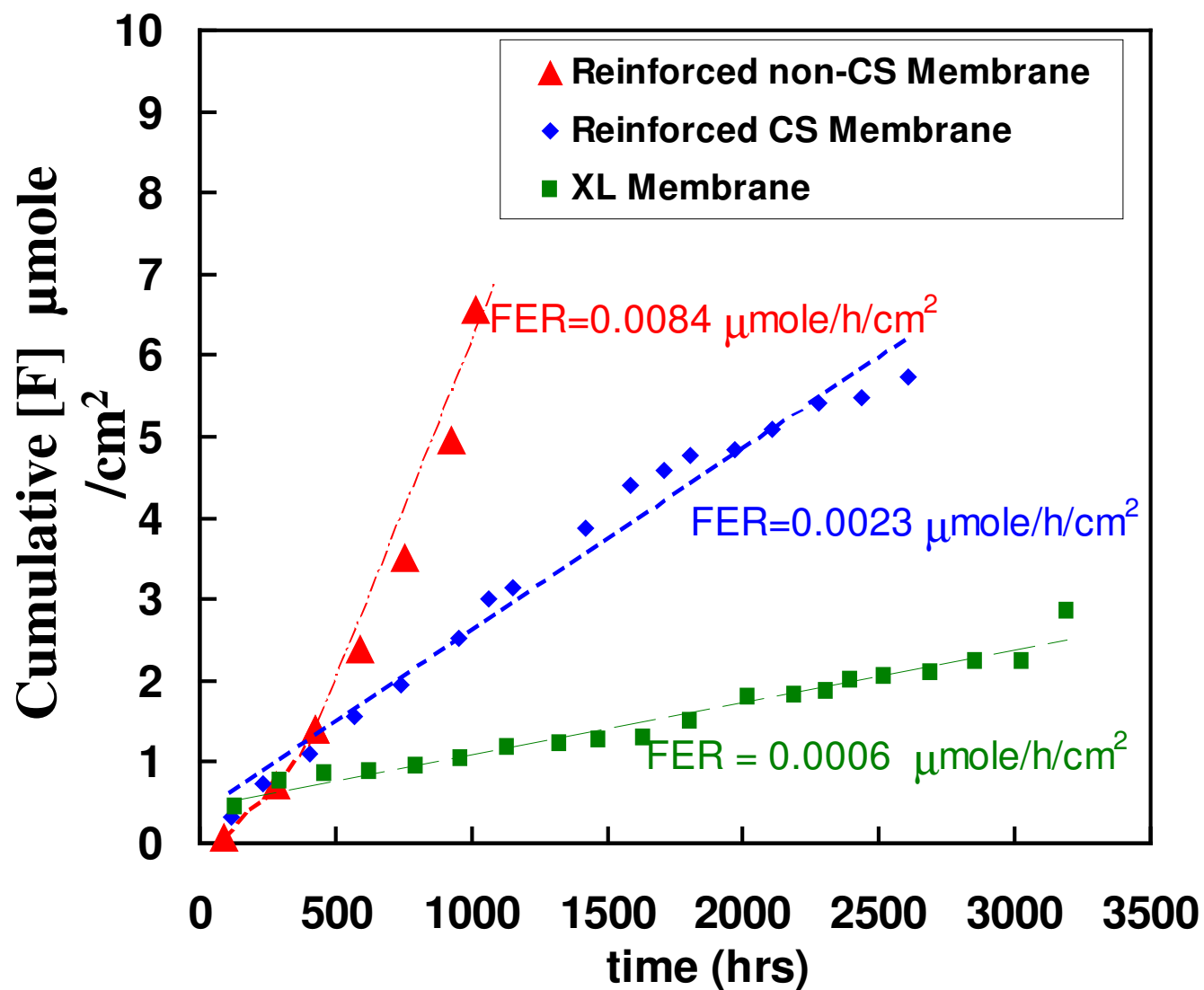
Nafion® XL Membrane enables a **40-50x** reduction in Fluoride Emission Rate (FER)

## Durability : Load & Humidity Cycling Test



Nafion® XL Membrane lasts **20x** longer in demanding load & humidity cycling test

# Fluoride Emission : Automotive Load Cycling Test



Nafion<sup>®</sup> XL Membrane shows **14x** lower FER than standard reinforced PFSA membrane

## Conclusions

- DuPont has made significant advancements in enhancing the durability of Fuel Cell Membrane.
- The advancements were made through careful understanding of material problems and developing appropriate mitigation technologies.
- Model compound studies and the identification of degraded polymer fragments have enabled a better understanding of PFSA degradation strategies and mitigation strategies.
- PFSA ionomer stabilized by reducing reactive polymer end-groups showed 8X reduction in FER.
- A combination of chemically stabilized polymer with reinforcement shows 5-6X reduction in FER under accelerated OCV test and 3-4X improvement in accelerated load/humidity cycling test



## Conclusions

- Nafion<sup>®</sup> XL membrane offers a step change towards meeting the PEM durability requirements for automotive applications.
- Nafion<sup>®</sup> XL membrane possessing advanced stabilization technology achieves a **40x reduction** in fluoride emission in the OCV test over chemically stabilized cast membrane.
- Nafion<sup>®</sup> XL membrane also shows other significant improvements in the drive cycle test:
  - **14X lower Fluoride Emission Rate (FER)**
  - **>3X longer lifetime**

# Acknowledgements

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