

# Characterization of PEMFC Membrane Durability

**Robert B. Moore and Kenneth A. Mauritz**

The University of Southern Mississippi

*DuPont Fuel Cells Subcontract*

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Project ID #  
**FCP 19**

# Overview

## Timeline

- Start – Oct. 1, 2003
- Finish – Sept. 30, 2006
- Percent complete – 75%

## Budget

- Total project funding
  - DOE share
  - \$200K
  - Contractor share
  - \$50K
- Funding received in FY05
- \$100K
- Funding for FY06
- \$50K

## Barriers

- Barriers addressed
  - Membrane Durability
  - Membrane Cost
- Targets
  - Durability: 5000 hrs. (transportation); 40,000 hrs. stationary

## Partners

- DuPont Fuel Cells

# Objectives

Overall	To produce lifetime improvements of low-temperature Proton Exchange Membranes (PEM) by seeking technologies that prevent premature membrane failure.
2005	To develop characterization methods (based on control studies of 2004) to evaluate the chemical and physical effects of chemical degradation on membrane properties.
2006	To extend the developed methods in the characterization of “used” membrane electrode assemblies subjected to accelerated-degradation operating conditions (i.e., post-mortem analysis).

# Approach

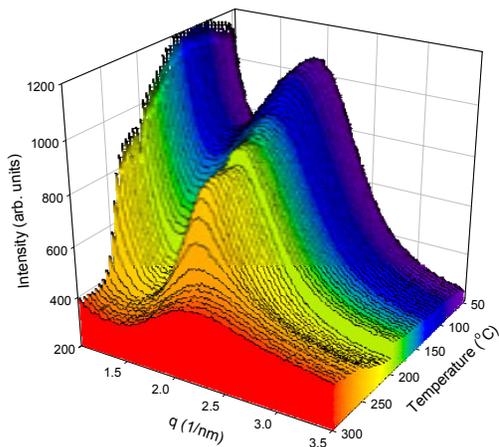
- Development and use of advanced characterization methods for membranes subjected to accelerated chemical degradation (85% complete).
  - Morphology
    - ESEM, TEM, AFM
    - SAXS, WAXD
  - Chemical composition/structure
    - $^{19}\text{F}$  SSNMR, FTIR
    - EDX
  - Mechanical/electrical properties
    - Tensile testing
    - DMA (counterion effects)
    - Dielectric spectroscopy
  - Transport properties
    - $\text{H}^+$  conductivity
    - Water diffusion (PFGSE NMR) and solvent swelling
    - Ionic mobility and gas transport
- Correlate structure/property information with control virgin characteristics to elucidate degradation mechanisms (45% complete). Provide input to DuPont for the stimulation of membrane improvements.

# Technical Accomplishments/ Progress/Results

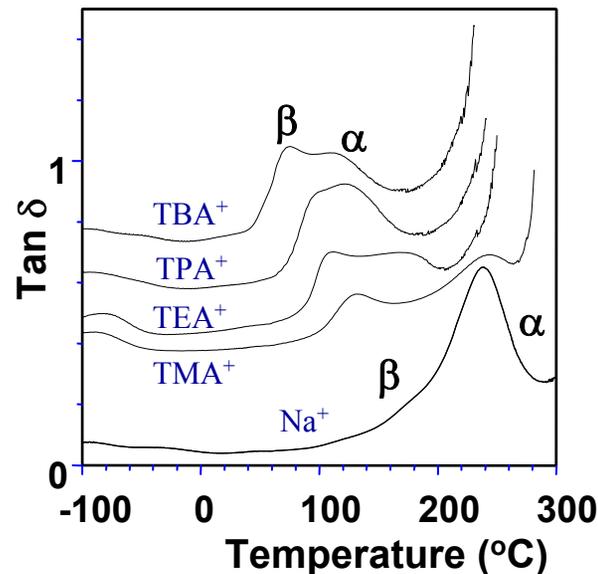
- Identification of the molecular and morphological origins of dynamic relaxations in PFSA membranes. Changes in the relaxations found to be characteristic of degradation.
- Discovery of the  $T_g$  of H<sup>+</sup>-form Nafion<sup>®</sup> at ca. -20 °C. Operation at temperatures above the  $\alpha$ -relaxation (ca. 100 °C) can cause morphological changes over time.
- Peroxide degradation using Fenton's reagent has the tendency to produce large voids (bubbles) in the membrane that may be linked to mechanical failure (cracks, pinholes) in FC operations.
- Dielectric spectroscopy is found to be particularly sensitive to molecular-level changes that occur in the membrane upon degradation.
- Broad-based characterization suggests that degradation affects the PFSA molecular weight distribution.

# Variable Temperature Studies of Morphological and Molecular Relaxations in Nafion<sup>®</sup>

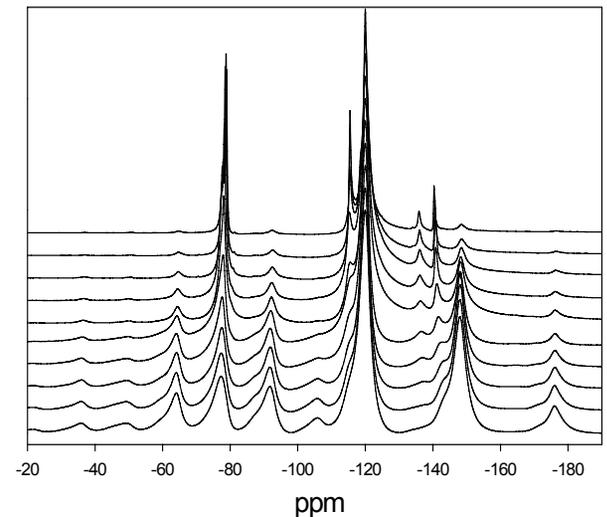
VT SAXS



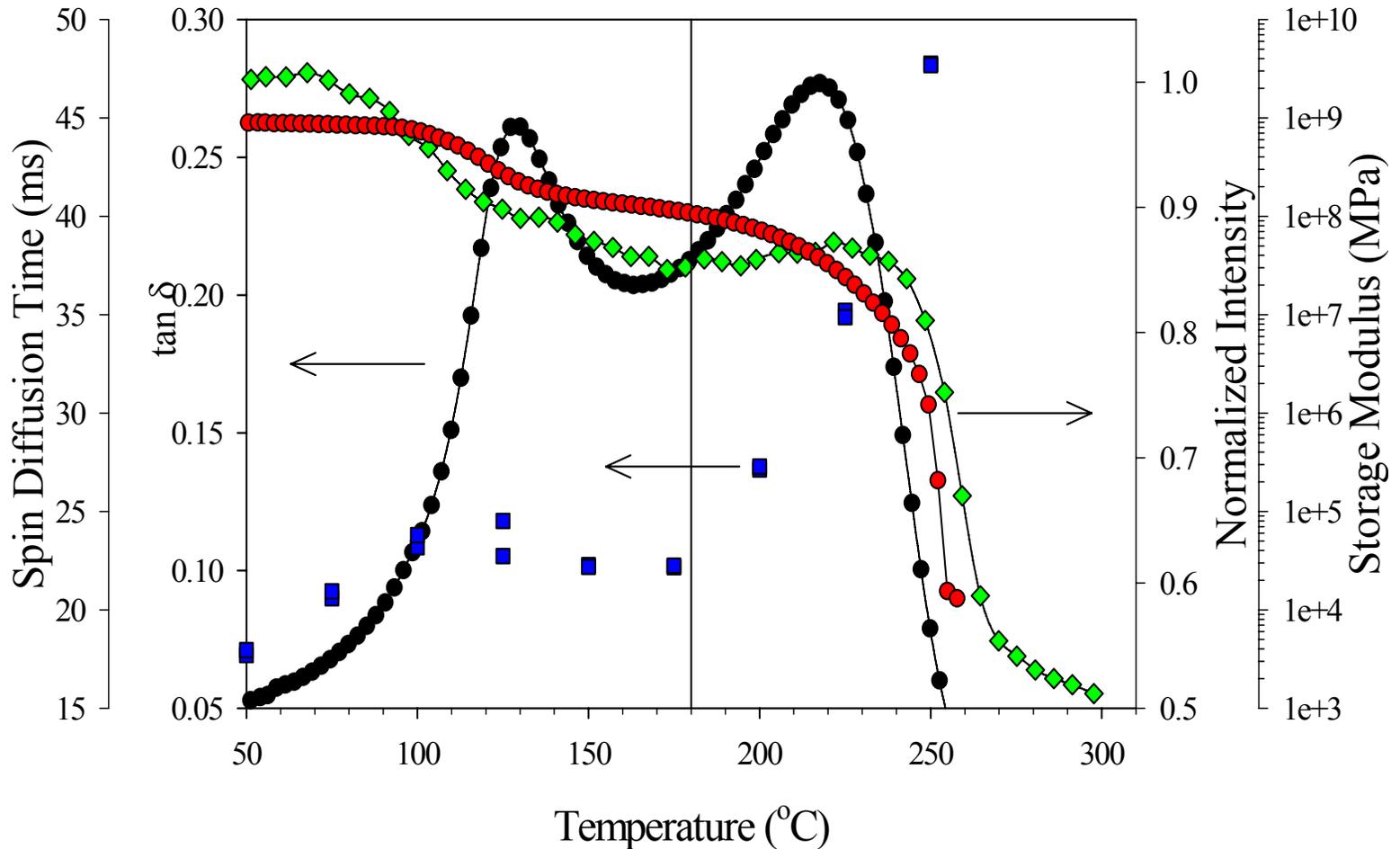
DMA



VT SS-NMR

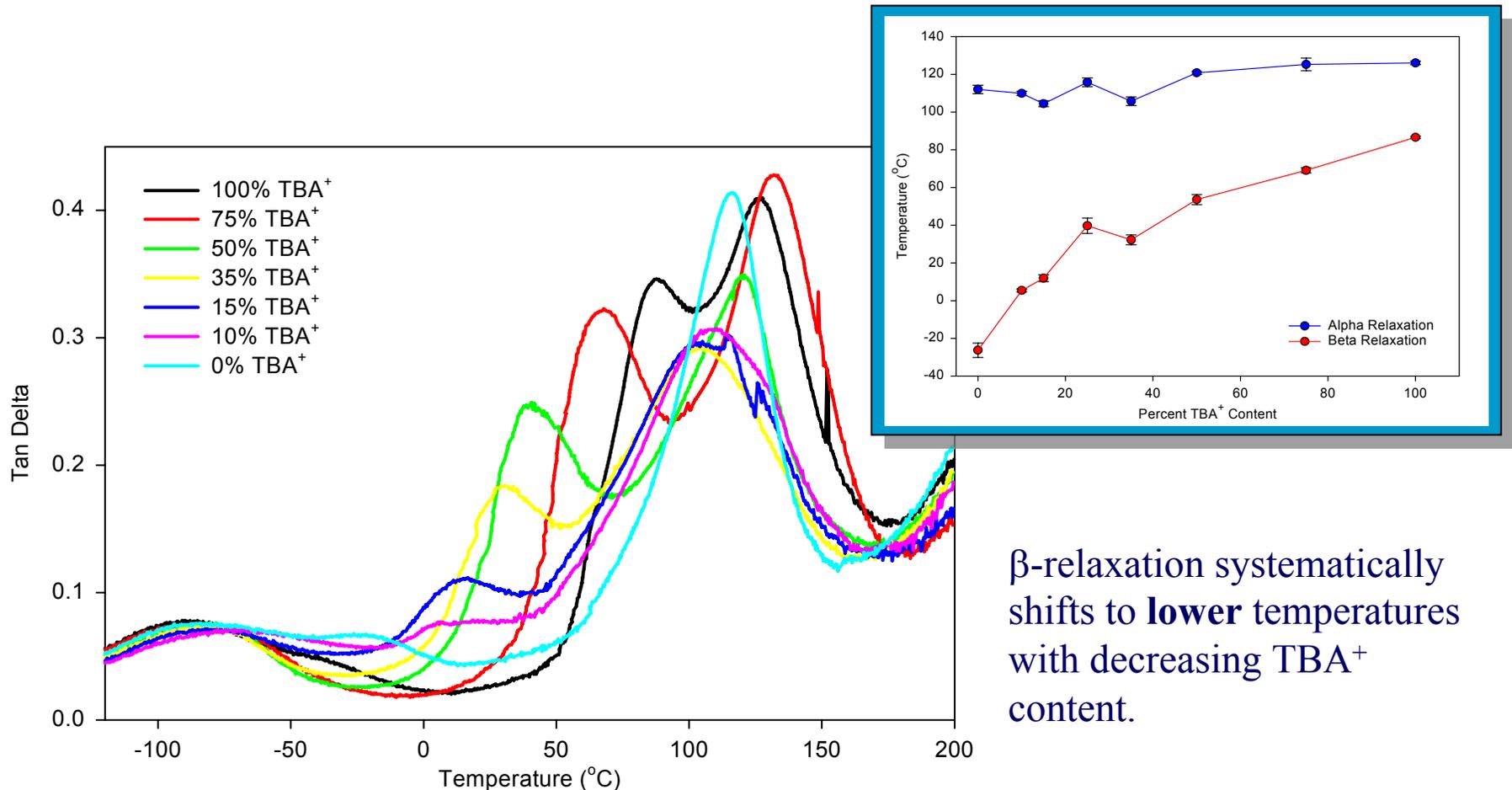


# Correlation of DMA, SAXS, and NMR Results for TMA<sup>+</sup> Nafion<sup>®</sup>

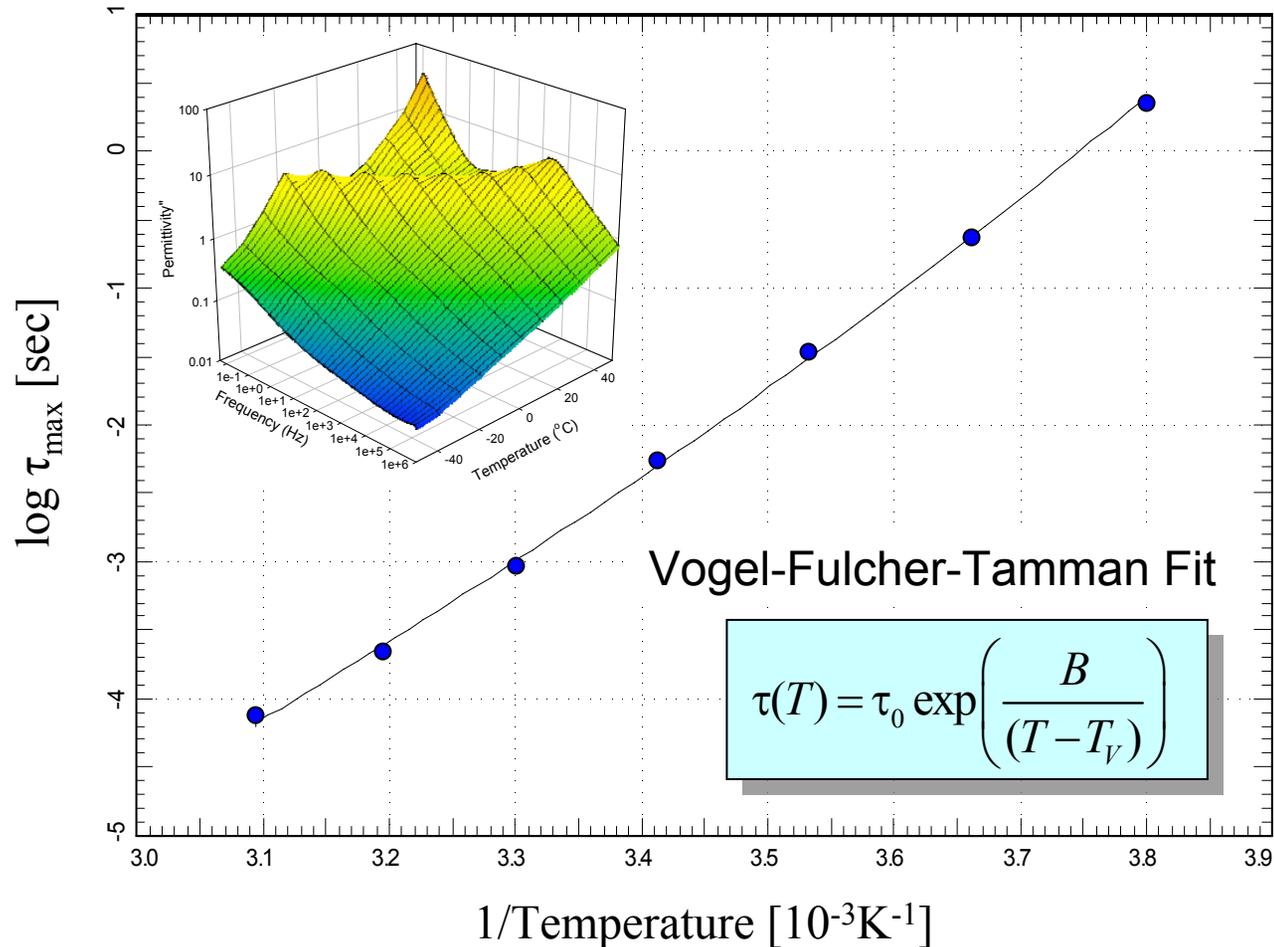


# DMA of Partially-Neutralized Nafion<sup>®</sup>

## (Variable H<sup>+</sup>/TBA<sup>+</sup> Compositions)



# VFT Behavior of the $\beta$ -Relaxation in H<sup>+</sup>-form Nafion<sup>®</sup> Using Dielectric Spectroscopy

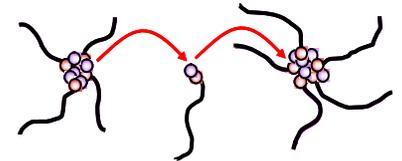


# Current Understanding of the Molecular Dynamics of Nafion<sup>®</sup>

The  **$\beta$ -relaxation** is attributed to the onset of segmental motions of the polymer chains within a static electrostatic network. This relaxation may be assigned to the genuine  $T_g$  of Nafion<sup>®</sup>.

The  **$\alpha$ -relaxation** is attributed to the onset of long-range mobility of chains/sidechains as a result of destabilization of the electrostatic network (i.e., chain motions within a dynamic electrostatic network).

The chain motions at the  **$\alpha$ -relaxation** also involve a significant contribution from the ion-hopping processes.

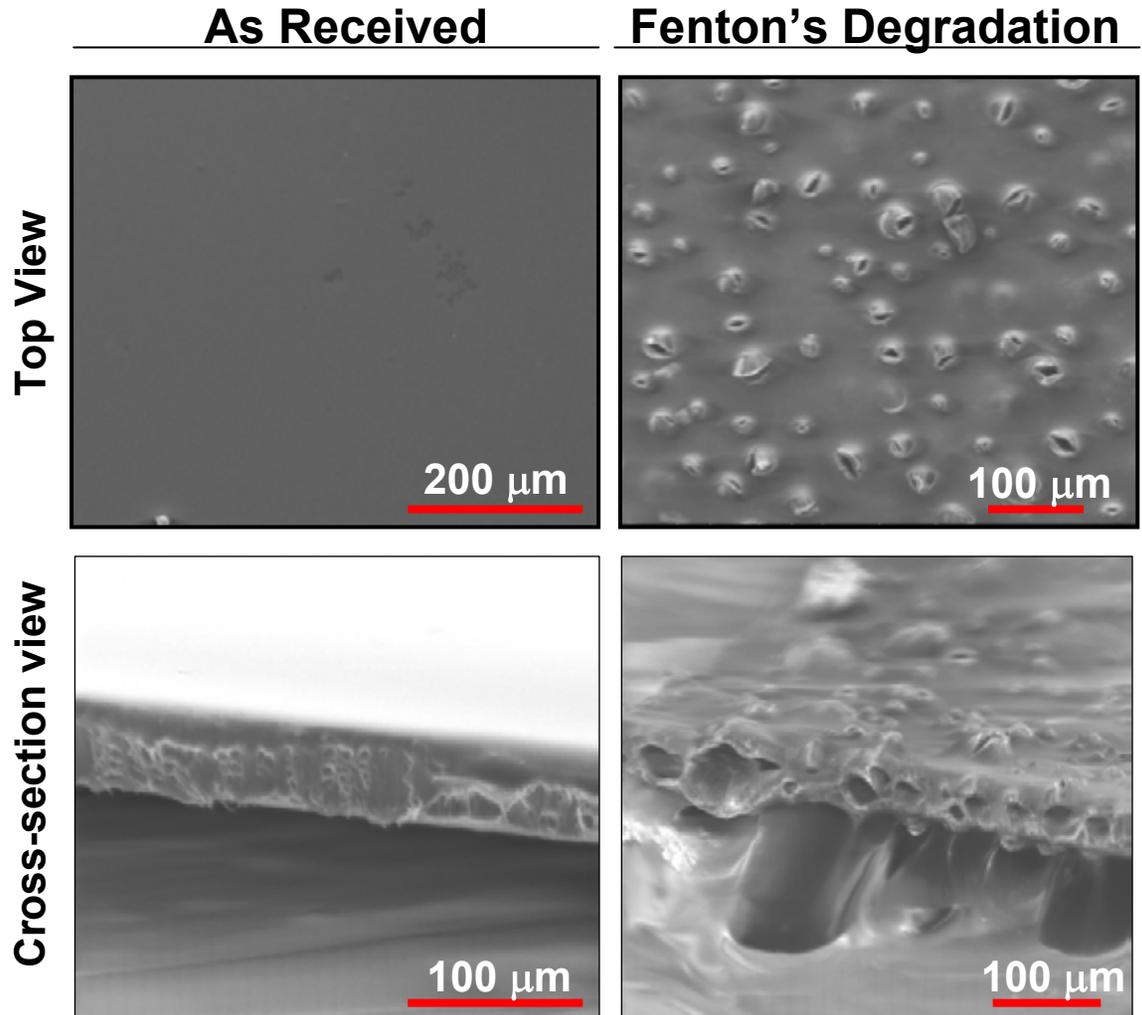


**Overall Conclusion:** Due to the dominance of the electrostatic network, the  $T_g$  for Nafion<sup>®</sup> is usually not the principle relaxation process. At temperatures above the  $\alpha$ -relaxation, significant morphological reorganization may occur.

# Degradation of Nafion NR 112

## Scanning Electron Microscopy

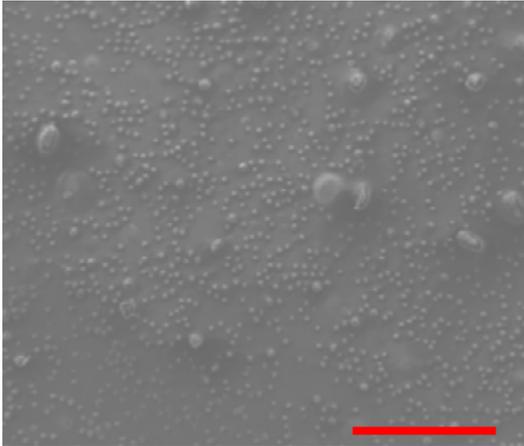
- As-received samples are smooth
- Degraded samples are rough
  - Ruptured bubbles (gas origin?)
  - Crack in bubble (mechanical failure nuclei?)



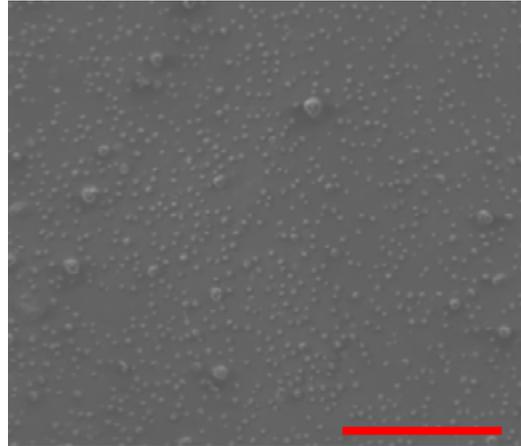
# Degraded Nafion Samples

## Scanning Electron Microscopy

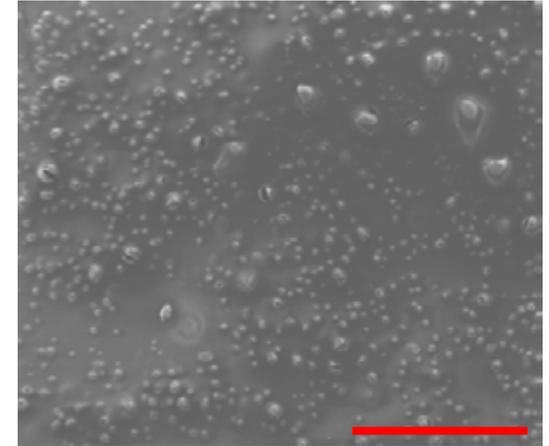
NR-111



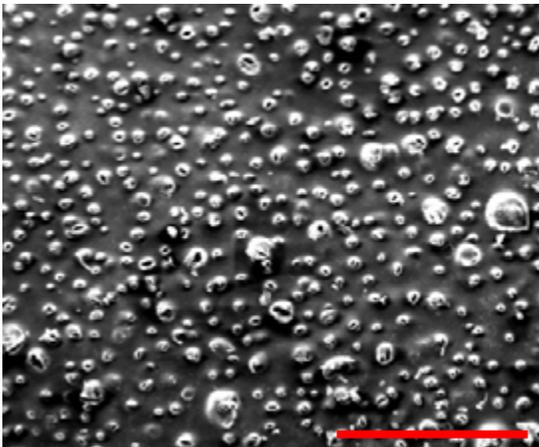
NRE-211



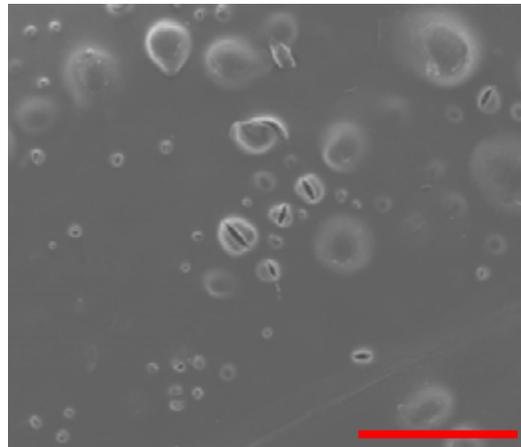
NRE-211-CS



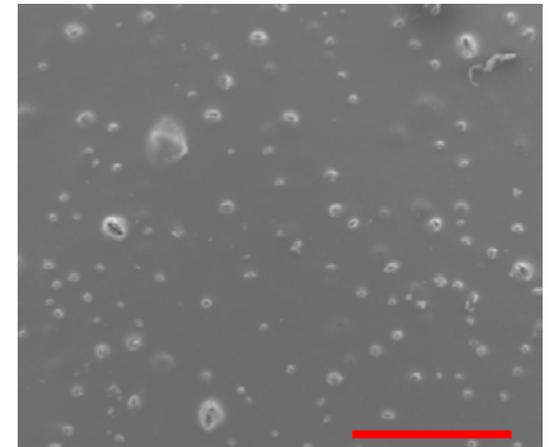
NR-112



NRE-212



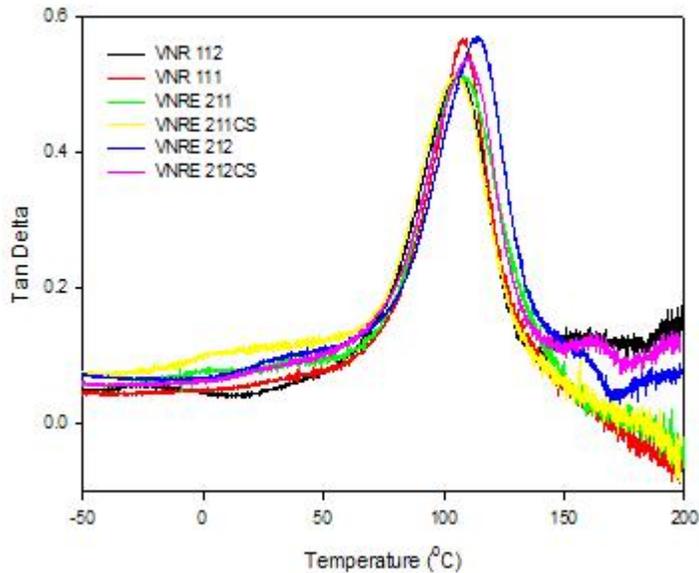
NRE-212-CS



Scale bar = 500  $\mu\text{m}$

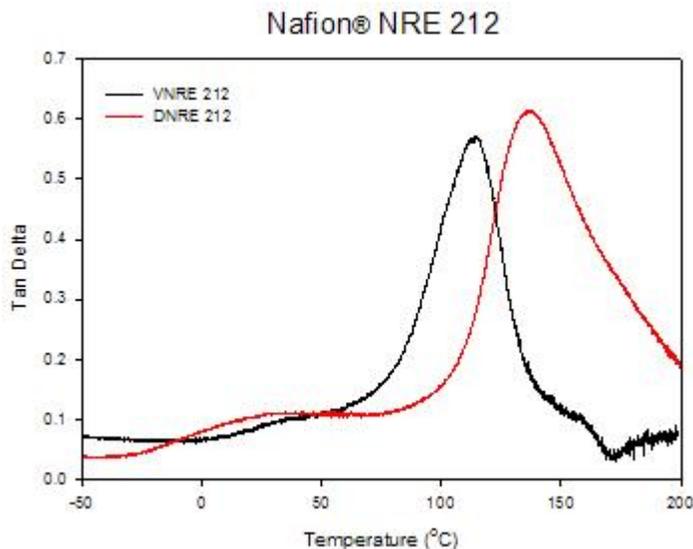
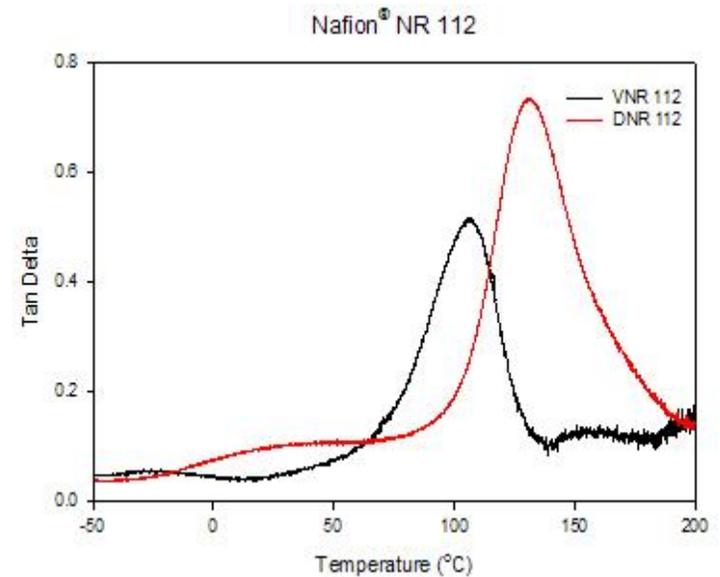
**Conclusion: Bubble formation not prevented by CS.**

# DMA of As-received and Degraded Membranes

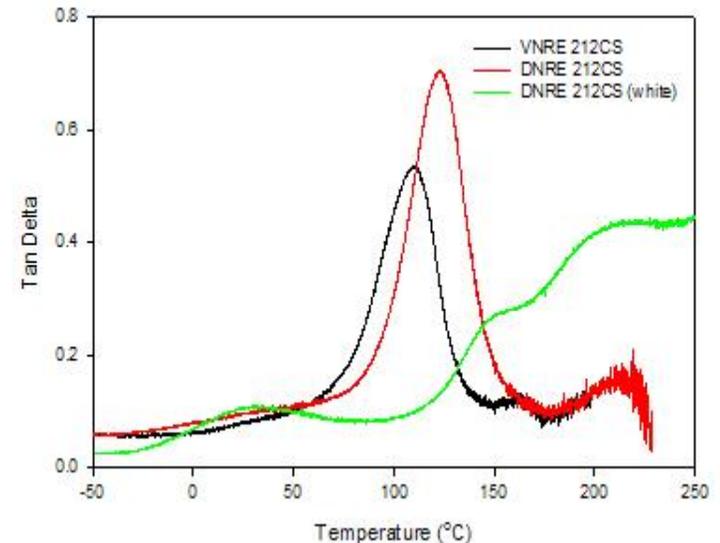


**The  $\alpha$  relaxation of the virgin membranes are all quite similar.**

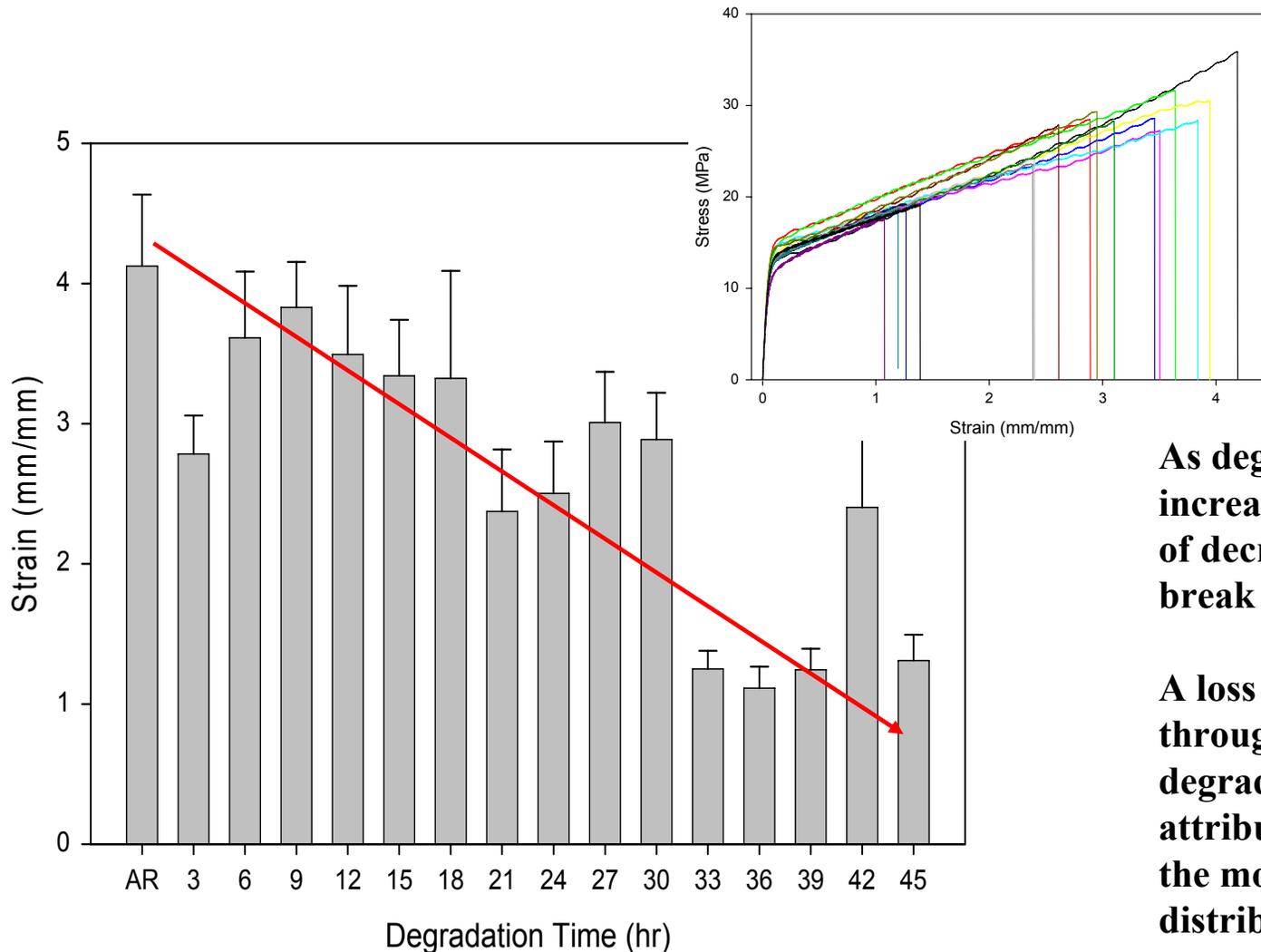
**With degradation, the  $\alpha$  relaxation shifts to higher temperatures.**



**Portions of the CS membranes are less susceptible to this behavior; however, other regions are greatly affected – this indicates some heterogeneity in the CS membranes.**



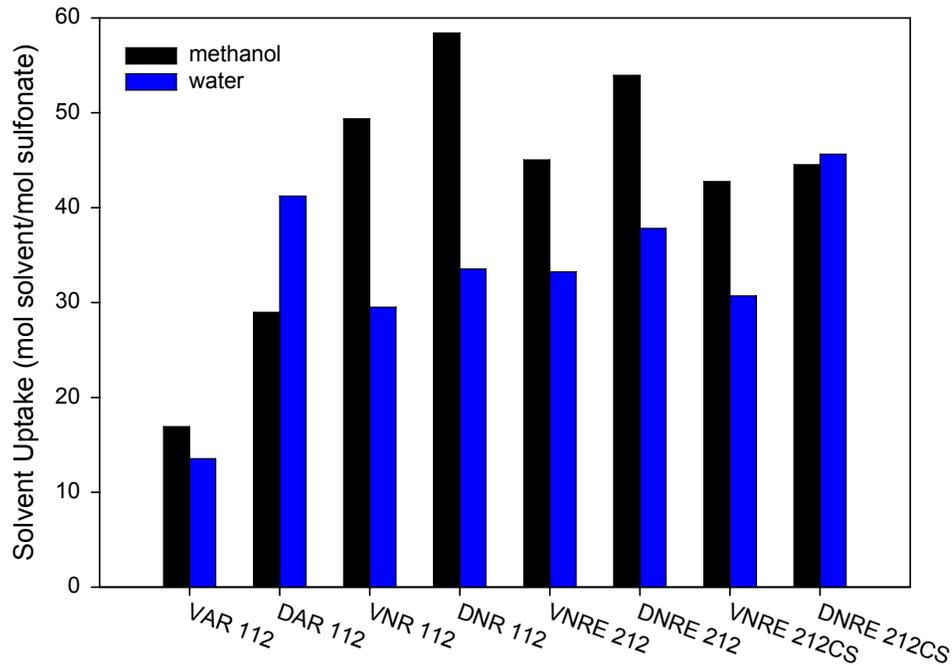
# Effects of Chemical Degradation on Tensile Properties of NRE 212



**As degradation time increases a general trend of decreasing strain at break is observed.**

**A loss of toughness through chemical degradation may be attributed to a change in the molecular weight distribution.**

# Methanol and Water Uptake After Chemical Degradation



Membrane	Solubility (MeOH Boil, 1hr)
VAR 112	Stable
VNR 112	Completely dissolved upon boiling ↓
VNRE 212	
VNRE 212CS	
DAR 112	Stable, weak film
DNR 112	Partially dissolved after 1 hr
DNRE 212	Disintegrated into gel-like particles after 1 hr
DNRE 212CS	

**AR = As-received (Extruded)**

**V = Virgin**

**D = Degraded**

**CS = Chemically Stable**

**Significant increase in methanol and water uptake from extruded to solution cast membranes**

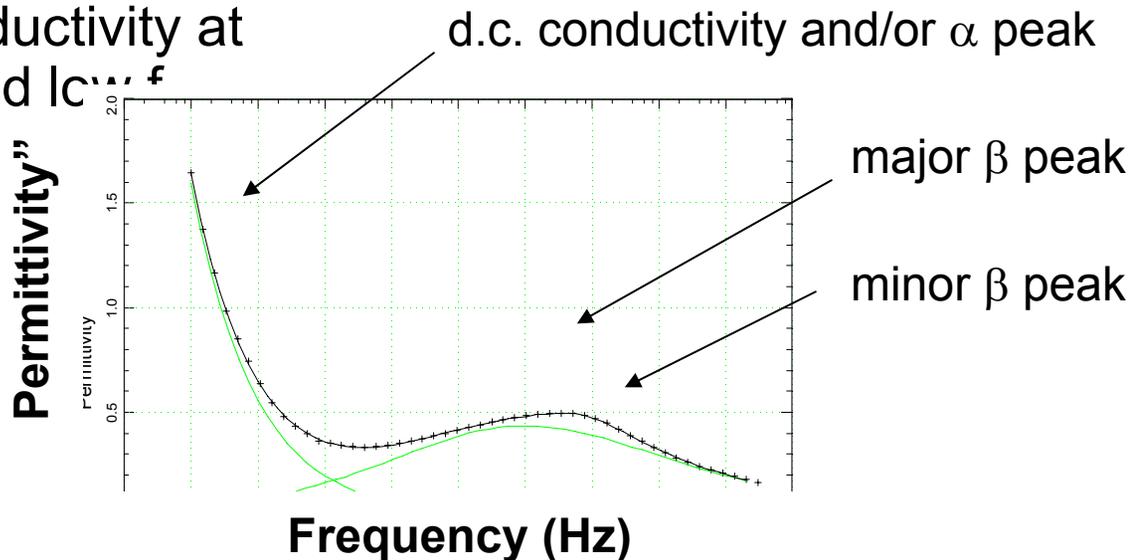
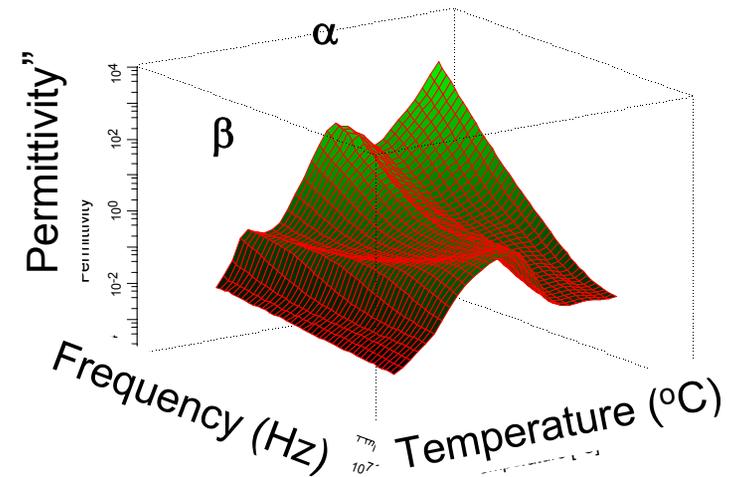
**Slight increase in methanol and water uptake upon degradation in solution cast films, except CS membranes**

**Stability of degraded films toward dissolution in boiling methanol suggests crosslinking during degradation**

# Dielectric Spectra: Signature of Molecular Motions

## Relaxation Peaks:

- 2  $\beta$  peaks at lower temp.  
Major and minor  $\beta$  peak components change with moisture
- $\alpha$  peak at higher temp.
- d.c. conductivity at high T and low  $f$



# Degraded vs. Non-degraded NRE 212 Samples

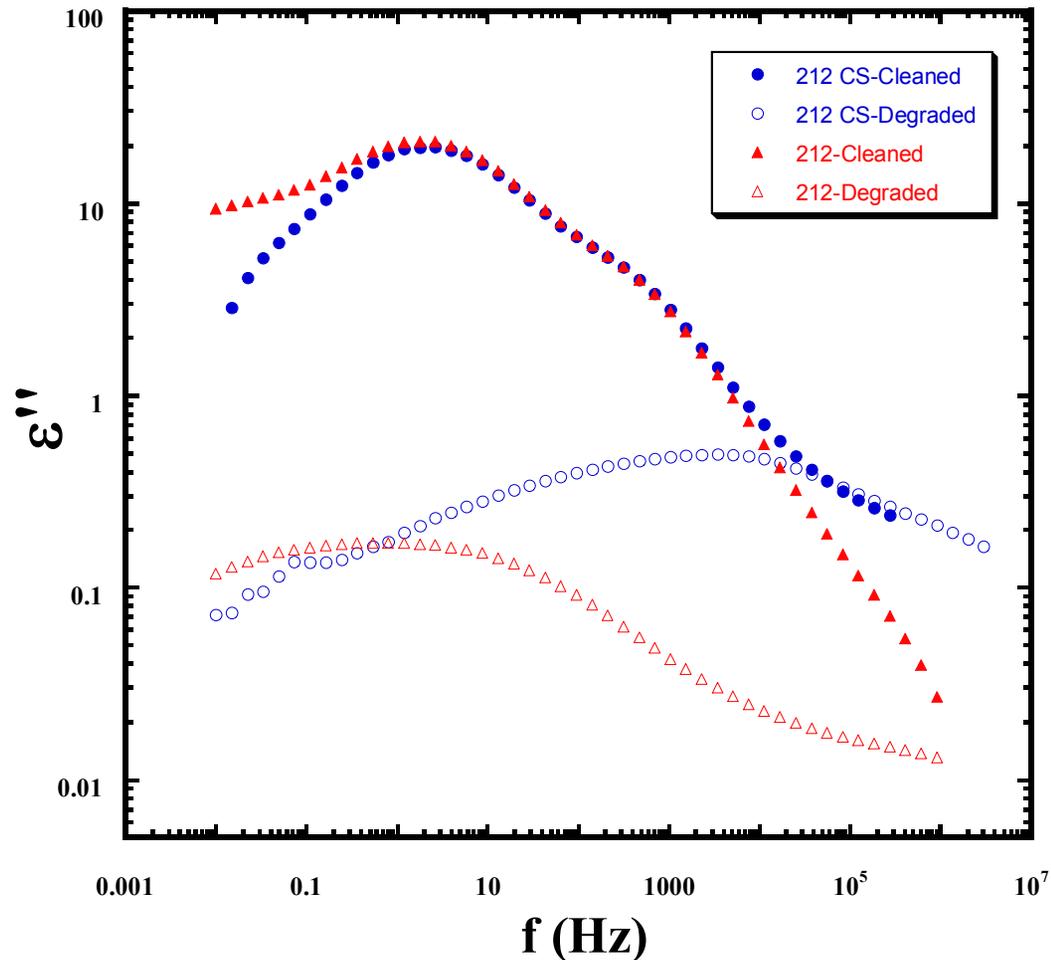
CS vs. non-CS  $\beta$  peak

- no difference in  $f_{\max}$

Degraded CS vs.  
degraded non-CS  $\beta$   
peak

-Upward shift in  $f_{\max}$   
w/ degradation

Commensurate with a  
broader distribution of  
smaller chain lengths  
upon degradation



# Future Work

- Expand chemical structure analysis (before and after degradation) using high temperature  $^{19}\text{F}$  SSNMR.
  - Technique found to yield extremely high resolution structural information in as-received/as-degraded membranes.
- Complete method development with dielectric spectroscopy – correlation with molecular level information from spectroscopy
- Correlate our solid-state characterization data with DuPont's solution-state data for elucidation of a refined mechanism fo chemical degradation.
- Begin processing history – performance study for continuing projects.

# Summary

- **Beta relaxation assigned to the Tg of PFSIs, while the higher temperature alpha relaxation attributed to the onset of longrange chain motions in a dynamic network.**
- **SEM shows chemical degradation which produces bubbles that become cracked – mechanical failure nuclei**
- **Bubble formation not prevented by CS**
- **DMA displays increase in alpha relaxation temperature with chemical degradation**
- **Strain at break decreases with degradation time**
- **Stability of degraded films in methanol suggest possible crosslinking**
- **Dielectric spectroscopy (DS) is diagnostic of chemical degradation**
- **Degradation broadens distribution - modes less distinct – shift toward faster motions**
  - *Interpretation: broadened molecular weight distribution of shorter chain lengths.*

# Publications

- Phillips, A.K.; Moore, R.B. “Mechanical and Transport Property Modifications of Perfluorosulfonate Ionomer Membranes Prepared with Mixed Organic and Inorganic Counterions,” *J. Polym. Sci., Part B: Polym. Phys.* **2006**, in press.
- Page, K.A.; Cable K.M.; Moore, R.B. “SAXS Analysis of the Thermal Relaxation of Anisotropic Morphologies in Oriented Nafion® Membranes,” *Macromolecules* **2006**, in press.
- Page, K.A.; Cable K.M.; Moore, R.B. “Molecular Origins of the Thermal Transitions and Dynamic Mechanical Relaxations in Perfluorosulfonate Ionomers,” *Macromolecules* **2005**, 38, 6472.
- Mauritz, K.A.; Moore, R.B. “State of Understanding of Nafion,” *Chemical Reviews* **2004**, 104(10), 4535.
- Page, K.A.; Moore, R.B. “Influence of Electrostatic Interactions on Chain Dynamics and Morphological Development in Perfluorosulfonate Ionomer Membranes,” *Mater. Res. Soc. Symp. Proc.* **2005**, 856E, BB6.4.1. **Trophy Award**
- Phillips, A.K.; Moore, R.B. “Morphological Manipulation and Plasticization of the Electrostatic Network in Perfluorosulfonate Ionomers,” *Mater. Res. Soc. Symp. Proc.* **2005**, 856E, BB8.11.1.
- Osborn, S.J.; Moore, R.B. “Effects of Humidity and Partial Neutralization on the Mechanical Properties of Perfluorosulfonate Ionomer Membranes,” *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)*, **2005**, 46(2), 597.

# Presentations

- “Probing the Molecular and Morphological Origins of Dynamic Behavior in Nanostructured Membrane Systems,” Department of Chemistry, Virginia Tech, Blacksburg, VA, March, 23, 2006.
- “Probing the Glass Transition of Perfluorosulfonate Ionomers,” Department of Macromolecular Science and Engineering, Case Western Reserve University, Cleveland, OH, February 17, 2006.
- “Molecular and Morphological Origins of the Mechanical Behavior of Nanostructured Perfluorosulfonate Ionomers,” DuPont Fuel Cells, Wilmington, DE, September 27, 2005.
- “Correlations between Spectroscopic, Morphological, and Dynamic Mechanical Information to Determine the Molecular Origins of Thermal Relaxations in Perfluorosulfonate Ionomer Membranes,” Department of Chemistry, University of North Carolina, Chapel Hill, NC, September 21, 2005.
- “Alteration of membrane properties of Perfluorosulfonate Ionomers using Solution and Melt Processing Procedures,” 2005 Fall ACS Meeting, Washington, DC, September 1, 2005.