Improved Membrane Materials for PEM Fuel Cell Applications

USM/DOE Cooperative Agreement
No. **DE-FG36-06GO86065**

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Project ID # FC11

Overview

Timeline

- Project start date: 6/1/2006
- Project end date: 11/30/07
- Percent complete: 65%

Budget

- Total project funding: $618,750
  - DOE share: $495,000
  - Contractor share: $123,750
- Funding received in FY06: $228,066
- Funding for FY07: $266,935

Partners

- USM only

Barriers

- A. Durability
  - Mechanical integrity, chemical stability, cycle stability, morphological stability
- B. Cost
  - Membrane/MEA manufacturing
  - Alternative membrane materials
- C. Performance
  - Power density, electrode/membrane interface, catalyst utilization, low/high temp conductivity

Targets

- Durability: 40,000 hrs (stationary) 5000 hrs (automotive)
- Cost: $20/m^2 (Alternative materials)
- Performance: > 0.1 S/cm amb. to 120 ^{o}C; 0.01 S/cm -20 ^{o}C

Objectives

- **Overall Goal**: To ascertain and integrate critical structure-property information in order to develop methods that lead to significant improvements in the durability and performance of PEMFC membrane materials. Specific objectives include:
  - Provide fundamental information regarding the origins of chemical and morphological degradation during accelerated chemical attack and PEMFC operation,
  - Investigate the effect of modifications in membrane and MEA processing parameters on performance and durability, and
  - Evaluate the role of controlled morphological features and reinforcing structures on membrane performance and durability.
  - In addition, we will explore the performance and durability of new hydrocarbon-based membrane materials as alternatives to the benchmark perfluorosulfonate ionomers.

- **Focus in 2006-07**: Investigations of membrane and MEA processing parameters on performance and chemical durability; use of dielectric spectroscopy to probe molecular motions impacted by degradation.

Approach

- **18-month project focused on the fundamental improvement of PEMFC membrane materials with respect to chemical, mechanical, and morphological durability, as well as the development of new membrane systems with alternative chemical structures and compositions.**
  - 80% effort focused on perfluorosulfonate ionomer membrane materials.
  - 20% effort focused on alternative hydrocarbon membranes
- **Task 1.0: Acquisition and installation of equipment** (complete)
  - Two fuel cell test stations
  - Dynamic mechanical analyzer
- **Task 2.0: Development of characterization methods to evaluate the effects of degradation and origins of performance characteristics** (75% complete)
  - Probes of chemical structure, morphology (over many length scales), molecular mobility, mechanical properties
  - As-received membranes used as controls
- **Task 3.0: Modifications of Nafion® Membranes and MEAs** (60% complete)
  - Membrane fabrication procedures
  - Post-processing treatments
  - MEA fabrication procedures
  - Inorganic modification of membranes
- **Task 4.0: Membrane Durability Studies** (35% complete)
  - Accelerated chemical attack (Fenton's reagent)
  - Fuel cell testing vs. time and/or conditions
- **Task 5.0: Evaluation of Alternative Membrane Systems** (10% complete)

Technical Accomplishments/ Progress/Results

- ❑ Our previous studies of chain dynamics in PFSIs during thermal treatment provide important insight related to processing-property relationships.

- ❑ Thermal treatment of H^+-form membranes may impact chemical stability.

- ❑ Control of electrostatic interactions and solvent-polymer interactions during solution-processing of membranes and MEA processing yields significant improvements in PEMFC performance.

- ❑ Dielectric spectroscopy has been used to demonstrate that relaxation time distributions are related to MWD, thermal history, and low level moisture content.

- ❑ Hydrophilic silicate nanoparticles have been successfully incorporated into the polar domains of Nafion®.

# Solvent Stability of Thermally-Annealed Dispersion Cast Nafion® NRE 212CS Membranes

Membranes in Boiling MeOH

Elapsed Time = 330sec

Sample	Condition	Water Uptake, λ	% Soluble in 50:50 EtOH/Water	Stability in Stirred MeOH (60 ºC)	Stability in Stirred MeOH (60 °C) Na$^+$-form Films
AR 112	As-received	17	1.3	Stable	Stable
NRE 212CS	As-received	43	7.3	Disintegrates < 1 min.	Disintegrates < 1 min.
NRE 212CS	Annealed 175 ºC with DMSO	15	1.9	Stable	Stable
SP 2 mil	Cast from DMSO at 180 ºC	51	2.3	Stable	Stable
NRE 212CS	Annealed 100 ºC	28	1.8	Disintegrates in 3 min.	Disintegrates in 3 min.
NRE 212CS	Annealed 125 ºC	26	1.8	Disintegrates in 5 min.	Disintegrates in 3 min.
NRE 212CS	Annealed 150 ºC	24	0.7	Disintegrates in 20 min.	Disintegrates in 5 min.
NRE 212CS	Annealed 175 ºC	16	0.6	Stable	Disintegrates in 5 min.
NRE 212CS	Annealed 200 ºC	15	0.4	Stable	Disintegrates in 5 min.

- ❑ **As-received NRE 212CS membranes tend to disintegrate in boiling MeOH.**
- ❑ **Annealing at elevated temperatures (above the α-relaxation) improves solvent stability. T_α (H$^+$) = 110 ºC; T_α (Na$^+$) = 220 ºC**
- ❑ **Annealing has no effect at temperatures below the α-relaxation (i.e. Na$^+$-form samples).**

# Effect of Thermal Annealing on the Crystalline Order in H⁺ and Na⁺-form NRE 212CS
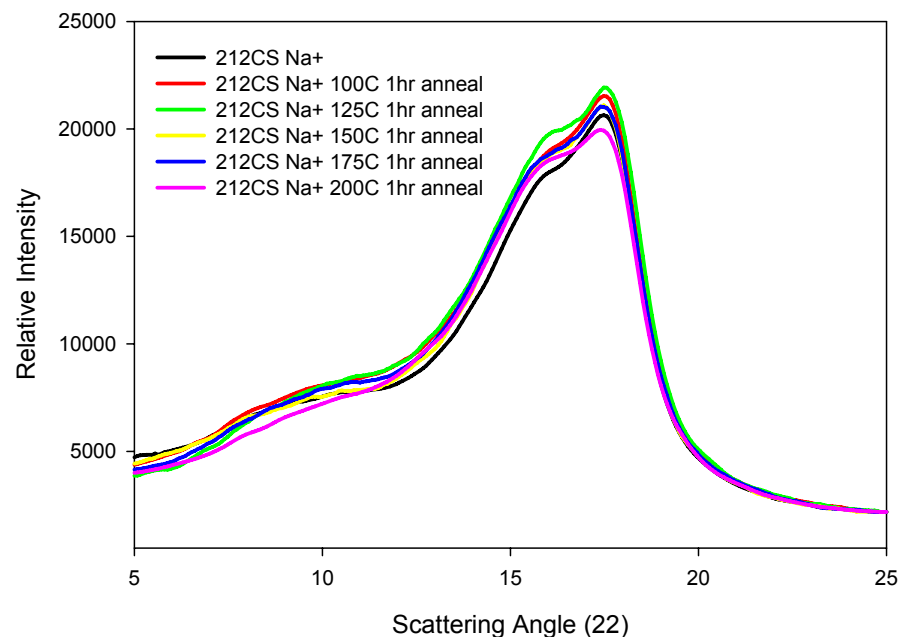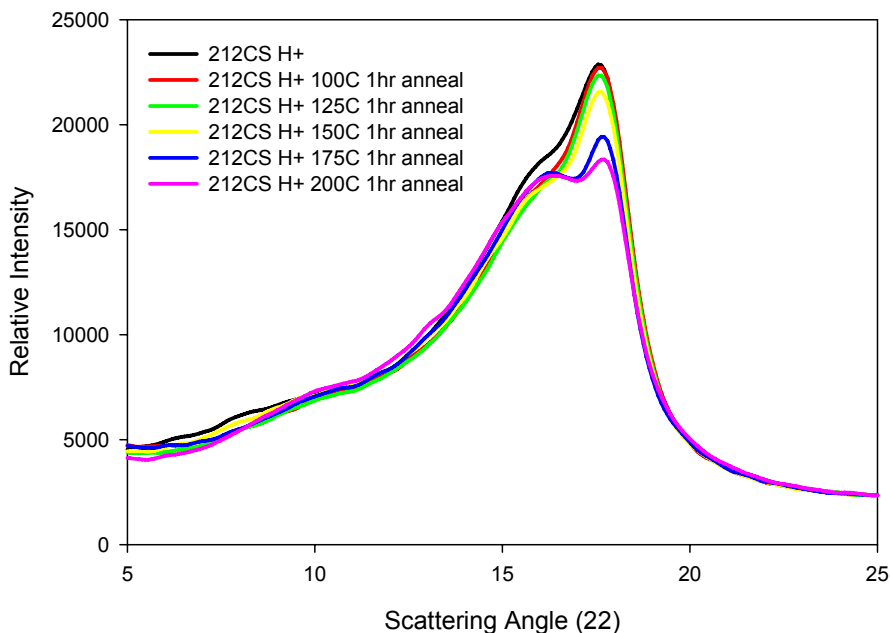
NRE212CS H+	Percent Crystallinity	FWHM of crystalline peak	FWHM of Amorphous Peak
Unannealed	12.67	1.59	3.84
100C	13.78	1.58	3.78
125C	13.58	1.56	3.73
150C	11.82	1.50	3.77
175C	7.06	1.25	3.82
200C	6.56	1.32	3.78

❏ **Thermal annealing above T_α (H⁺-form) apparently increases crystalline order.**

❏ **Thermal annealing has no effect on crystalline order in Na⁺-form samples.**

Effect of Membrane Thermal Treatment on PEMFC Performance
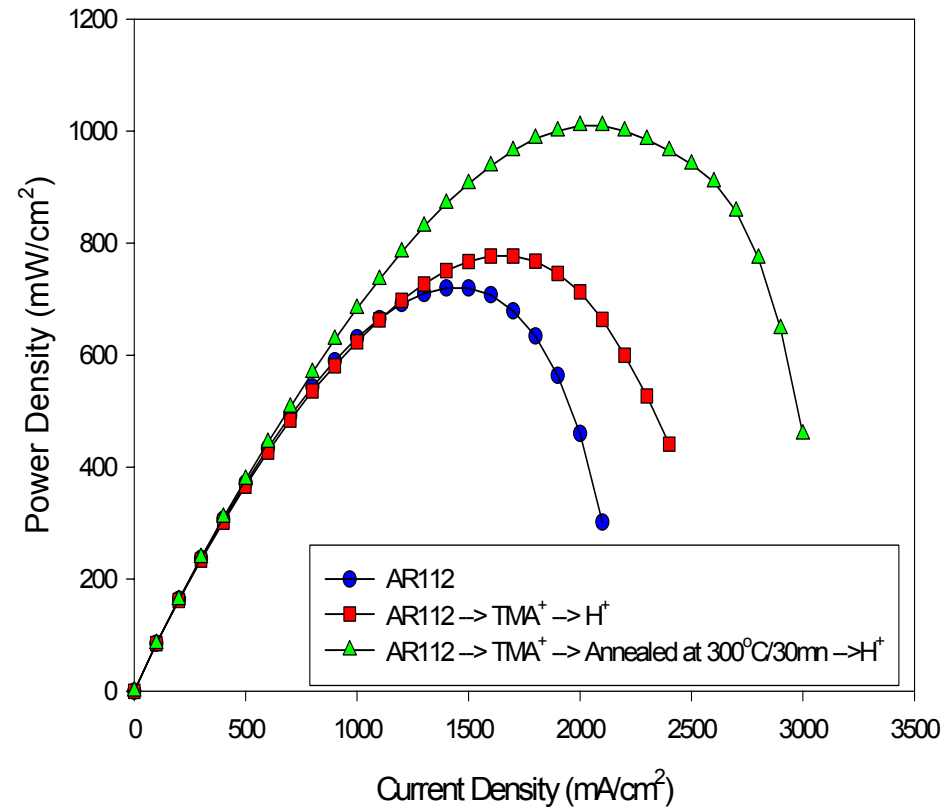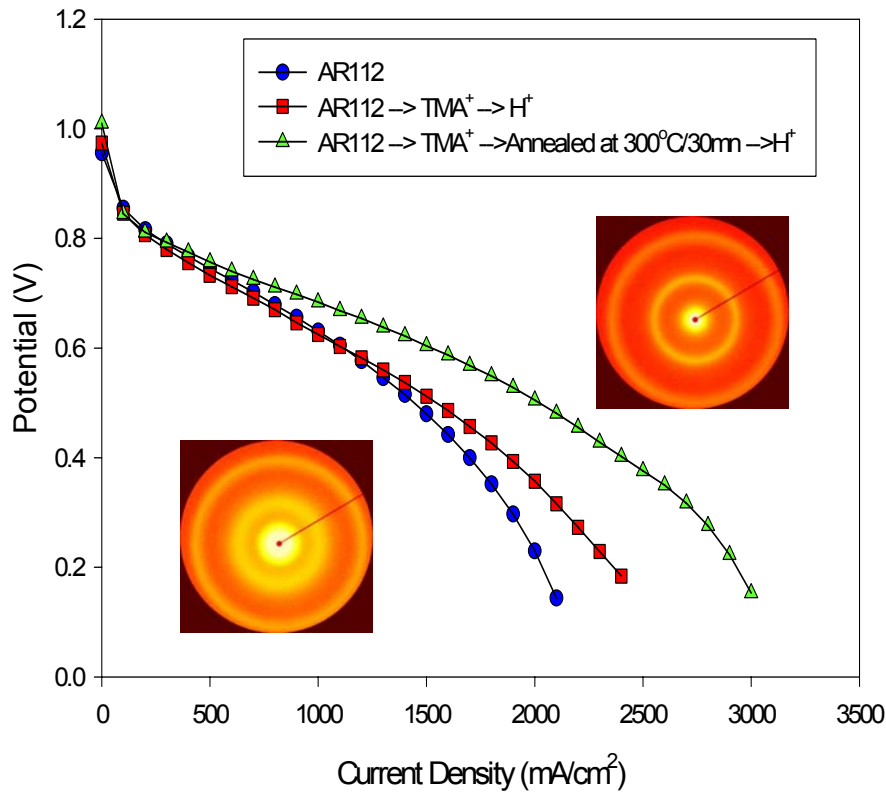
❏ **Thermal annealing above T_α significantly improves the order within the ionic domains, which consequently improves PEMFC performance.**

AR112 = as-received (extruded) 2 mil 1100 EW Nafion® membranes; 5 cm² cell; Pt loading = 0.5mg/cm² on anode and cathode (decal method); H_2/O_2 stoich = 1.5/2.0; T_{cell} = 60 °C, T anode humidifier = 70 °C (100% RH), T cathode humidifier = 55 °C (80% RH).

Fenton's Test on Annealed NRE 212CS

Samples	Dry weight (g)	15hr F- (ppm)	30hr F- (ppm)	45hr F- (ppm)	60hr F- (ppm)	75hr F- (ppm)	Dry wt after HCl wash	% wt loss
H+ Unannealed	0.352	2.82	6.64	8.07	7.46	6.93	0.349	0.68
H+ 212CS 100C 1hr	0.345	3.29	7.12	8.15	7.32	6.98	0.342	0.80
H+ 212CS 150C 1hr	0.340	9.05	13.24	13.71	13.29	12.01	0.334	1.69
H+ 212CS 200C 1hr	0.344	28.08	31.16	30.04	28.54	27.87	0.295	14.08
Na+ Unannealed	0.340	5.92	6.58	6.12	5.96	5.16	—	—
Na+ 212CS 100C 1hr	0.337	5.61	6.53	6.20	5.70	5.63	—	—
Na+ 212CS 150C 1hr	0.356	5.95	6.72	6.39	5.68	5.35	—	—
Na+ 212CS 200C 1hr	0.347	7.16	7.24	6.45	5.86	5.46	—	—

- H^+-form samples progressively darken with annealing temperature and time.
- For the H+ samples, this thermal degradation apparently enhances susceptibility to chemical attack.
- No thermal degradation observed for ionized Nafion® (Na^+-form), and the fluoride release remains relatively constant with annealing temperature.

Effect of Mixed Counterions Composition during Casting
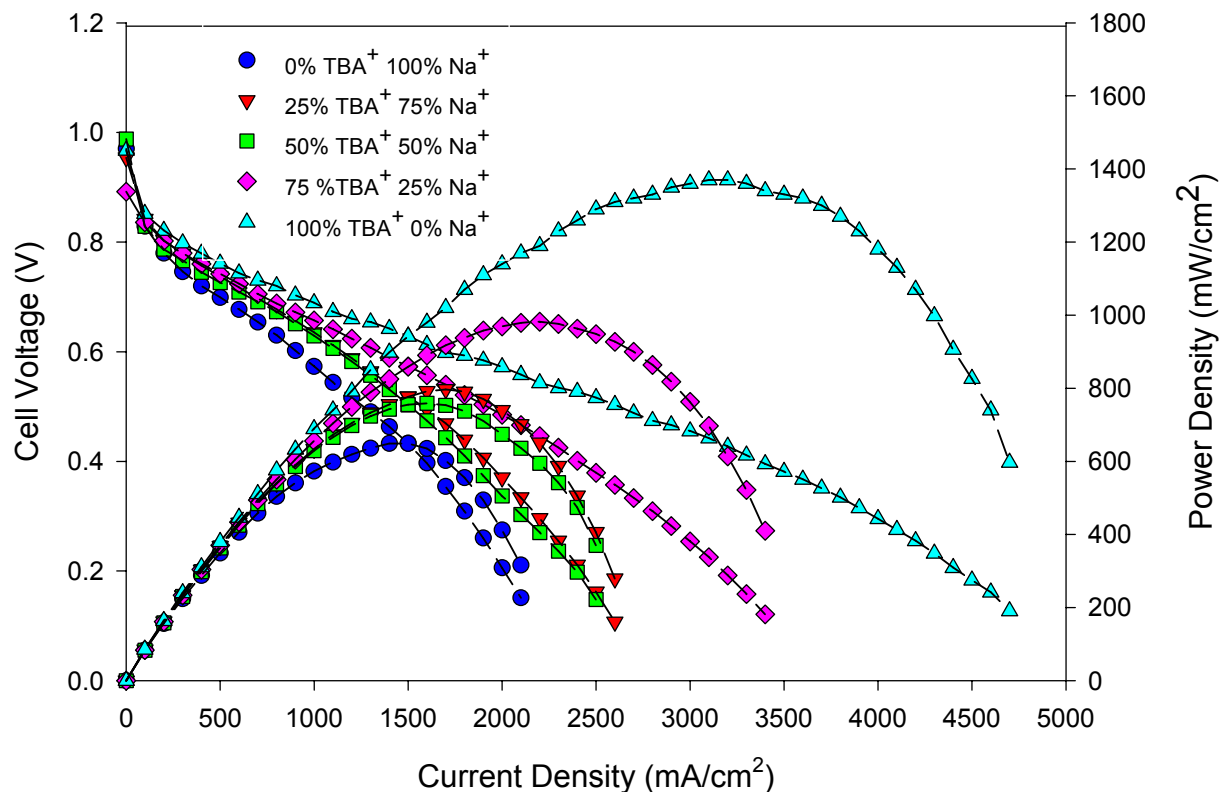
□ **Solution-processing above T_α (TBA$^+$-form) improves PEMFC performance, relative to casting below T_α (Na$^+$-form).**

Solution processed Nafion® membranes (180 °C) 2 mil thick 1100EW with mixed TBA$^+$ and Na$^+$ counterions, reacidified in 4M Sulfuric acid in Methanol; 5cm^2 cell; Pt loading=0.5 mg/cm^2 on anode and cathode (decal method); H$_2$/O$_2$ stoich.=1.5/2; T$_{cell}$=60°C, T$_{anode\ humidifier}$=70°C (100% RH), T$_{cathode\ humidifier}$=55°C (80% RH)

Effect of Membrane Casting Temperature (TBA$^+$ and Na$^+$ form Nafion®)
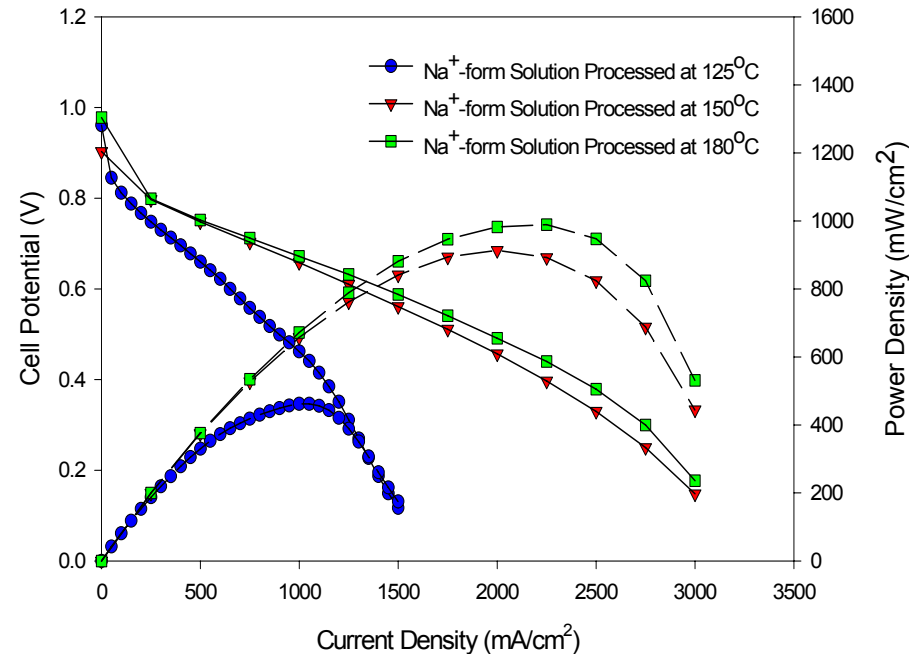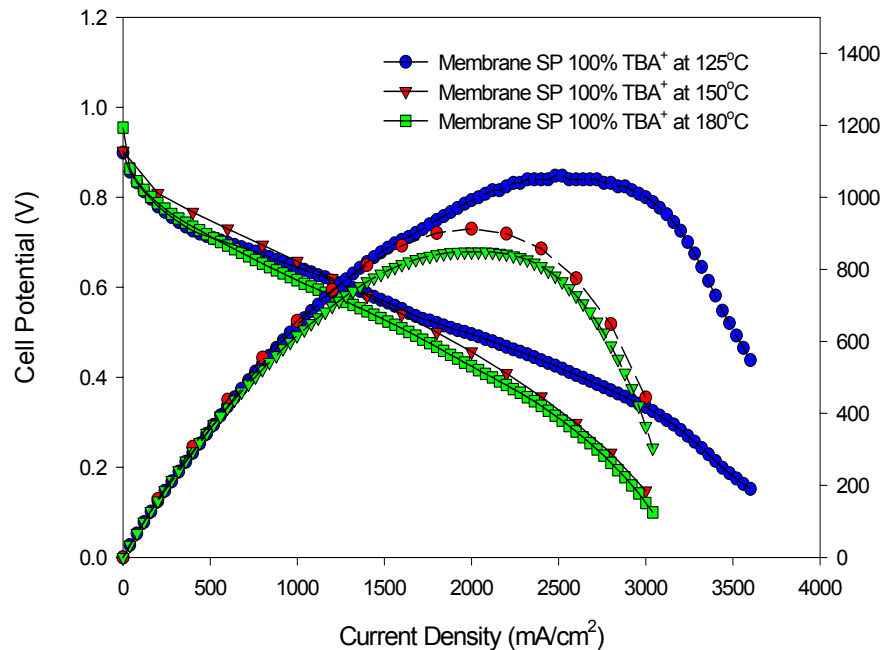
- ❑ **Casting above T$_\alpha$ (TBA$^+$-form), PEMFC performance decreases with increasing temperature.**

- ❑ **Casting below T$_\alpha$ (Na$^+$-form), PEMFC performance increases with decreasing temperature.**

Solution processed 2 mil thick 1100EW Nafion® membranes in Na$^+$ form, reacidified in 4M Sulfuric acid in Methanol; 5cm^2 cell; Pt loading=0.5 mg/cm^2 on anode and cathode (decal method); H$_2$/O$_2$ stoich.=1.5/2; T$_{cell}$=60°C, T$_{anode\ humidifier}$=70°C (100% RH), T$_{cathode\ humidifier}$=55°C (80% RH)
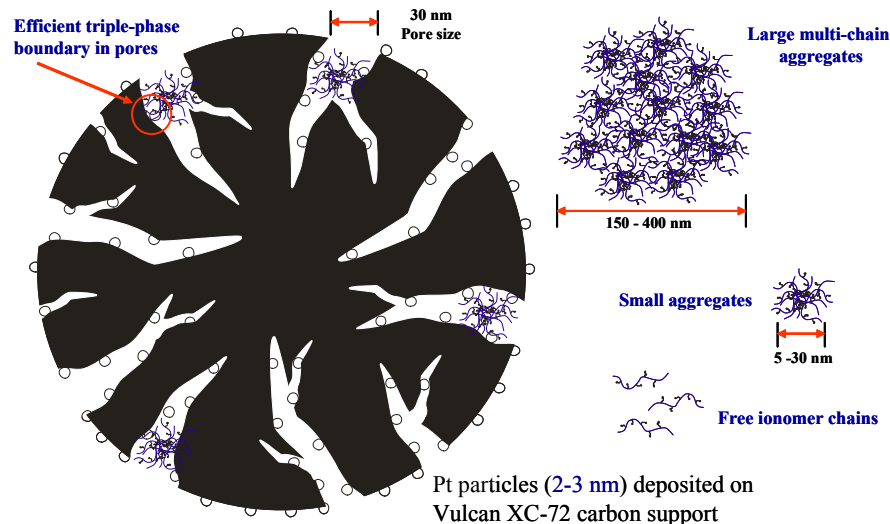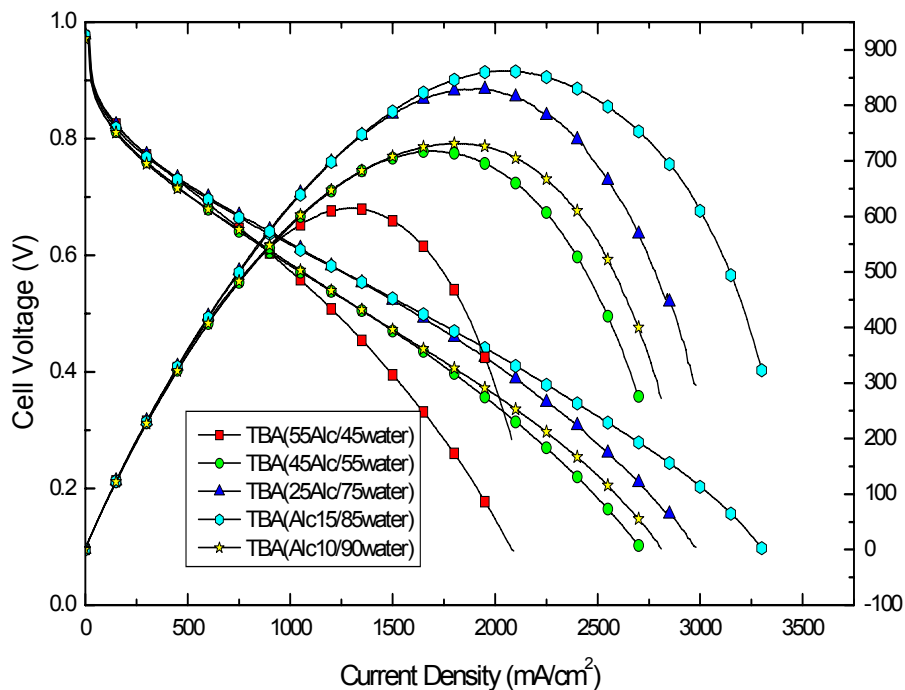
□ **Free chains and large aggregates in the dispersion (used in the ink) yield relatively poor performance.**

□ **Optimum performance observed when aggregate size matches pore size in carbon particle supports.**

AR112 = as-received (extruded) 2 mil 1100 EW Nafion® membranes; 5 cm^2 cell; Pt loading = 0.5mg/cm^2 on anode and cathode (ink painted on GDLs); H_2/O_2 stoich = 1.5/2.0; T_{cell} = 60 °C, T anode humidifier = 70 °C (100% RH), T cathode humidifier = 55 °C (80% RH); GDL: Toray TGP-H-090.

Dielectric Spectroscopy

ε_0

ε'

$\log_{10} f$

ε''

$\log_{10} f$
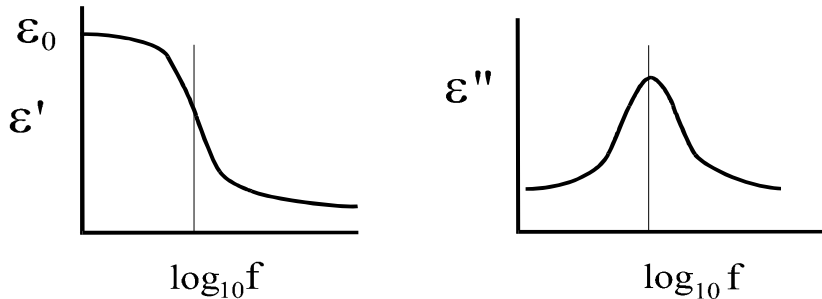
ε', ε'' = storage, loss components of complex dielectric permittivity:

$\varepsilon^* = \varepsilon' - i\,\varepsilon''$ f = frequency (10^{-3} - 10^9 Hz)

- fast, accurate, vast range of characteristic time scales

Single Relaxation Time = τ = $1/(2\pi f_{max})$

sample

v

i
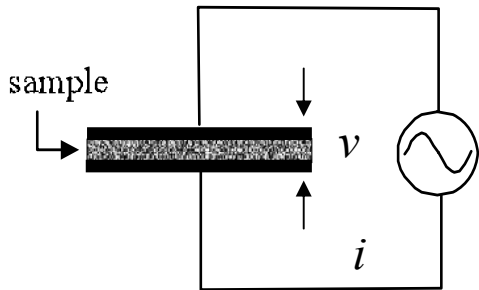
phase angle

between i and v

$\tan \delta = \varepsilon''/\varepsilon'$
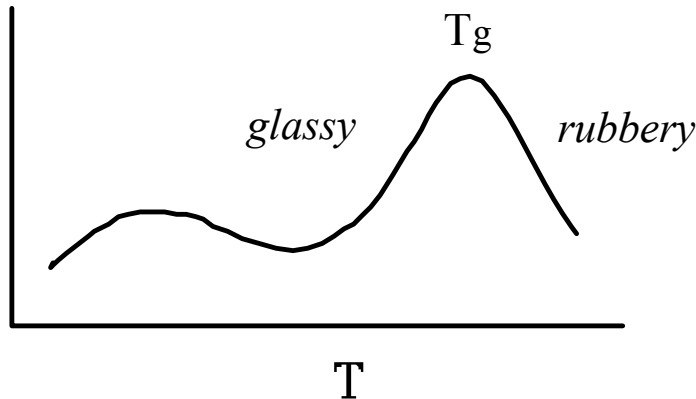
Observe polymer transitions

glassy

Tg

rubbery

T

Novocontrol
Broadband
Dielectric
Spectrometer

A Powerful Diagnostic Tool

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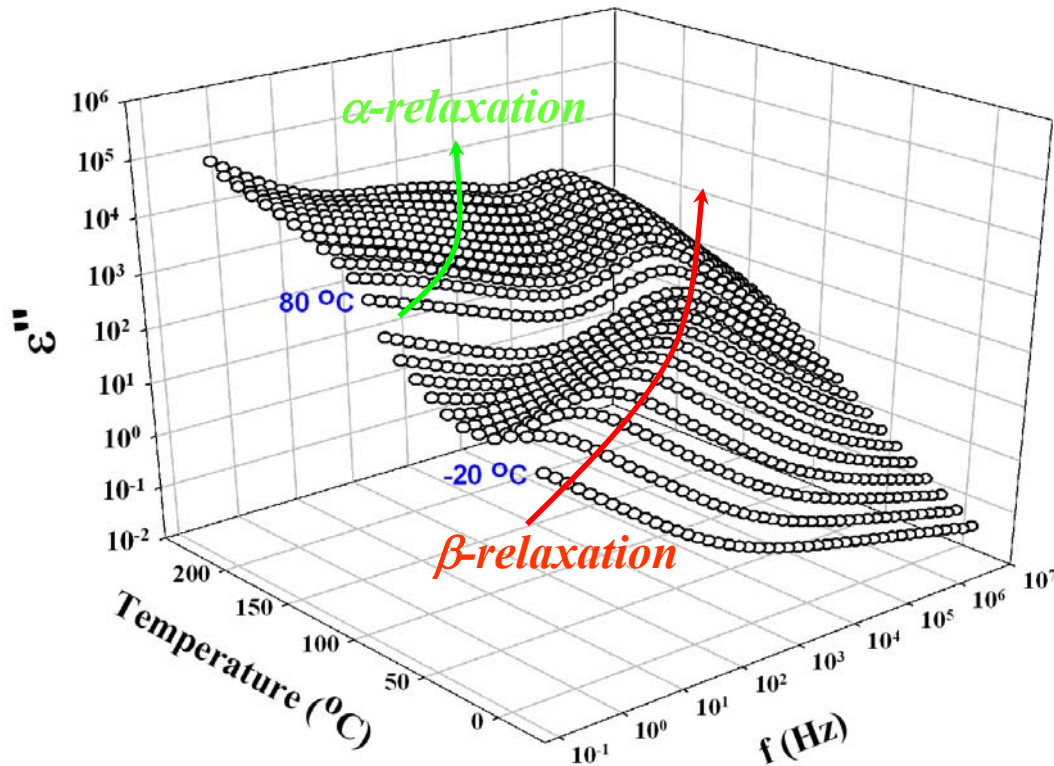
- Curves spaced 10 °C increments from -20 to 200 °C

- Characteristic Nafion® molecular motions occur along crests of 'hills' (peaks):

  β-relaxation with onset at -10 °C

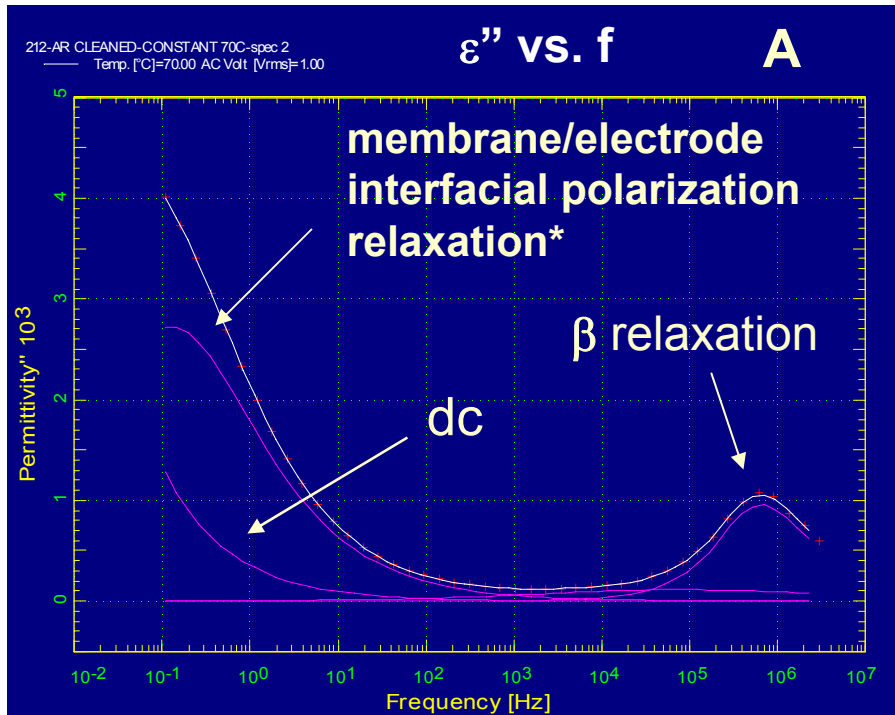 α-relaxation with onset at ≅ 80 °C

- What is the nature of these motions and how are they affected by degradation?

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DS Real Time Studies of Membrane Drying

AR Nafion® NRE 212 at T = 70 °C under N_2 with f-sweep iterations.
A) after ~ 2.5h and B) ~15h of testing.

Data fitted to Havriliak-Negami eqn   (conditioned in 6.4%RH for 4d before testing)
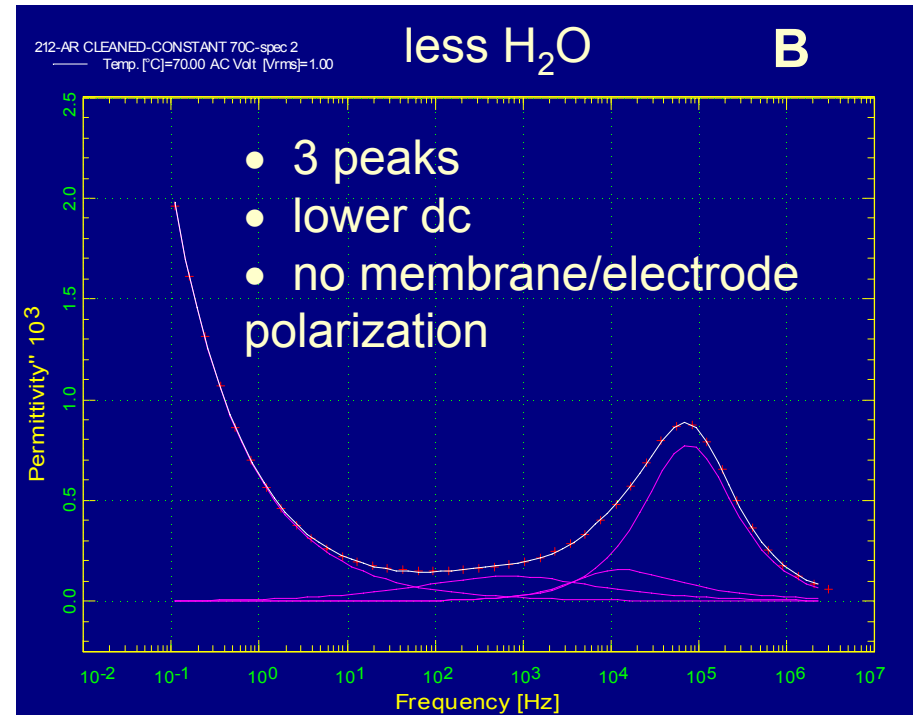
β Peak shifts to lower frequencies – longer relaxation time with dehydration

α Peak is off-scale →

Nafion® Degradation

- Four sample preparations:

  - As-received cleaned (HNO_3 reflux, DI water soak, dried)
  - Degraded 75h w/ Fenton's Reagent—no post degradation treatment
  - Degraded 75h w/ Fenton's Reagent—washed with HCl
  - Placed in Fenton's reagent soln w/o H_2O_2 (iron only)

- Samples stored < 0.2% RH 4d prior to dielectric spectroscopic testing:

  - Part 1. Constant T = 70 $^{\circ}$C for 7.5h w/ frequency sweep
  - Part 2. Temperature cycles from -130 to 200 $^{\circ}$C in 10 $^{\circ}$C temperature increments

- Objectives:

  - Understand bound moisture and Fe^+ ion incorporation
  - Understand/quantify Nafion® degradation

Dielectric Relaxation

As received—not modified

d.c.

f_{max} for β-relaxation
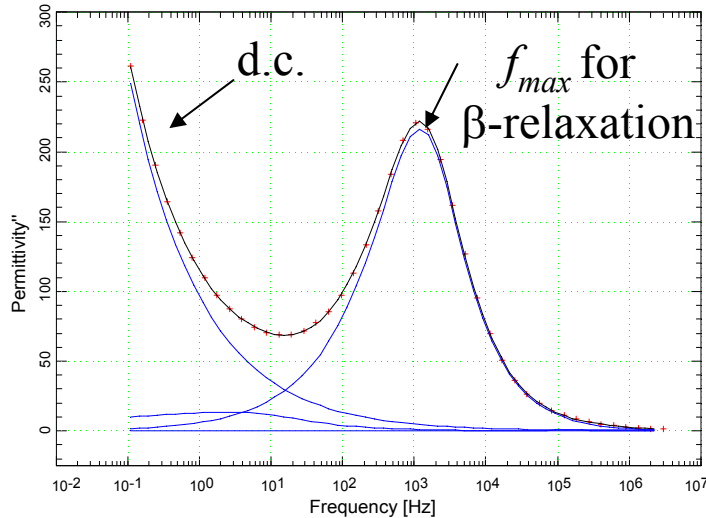
Degraded 75h – HCl cleaned

d.c.

2 β peaks
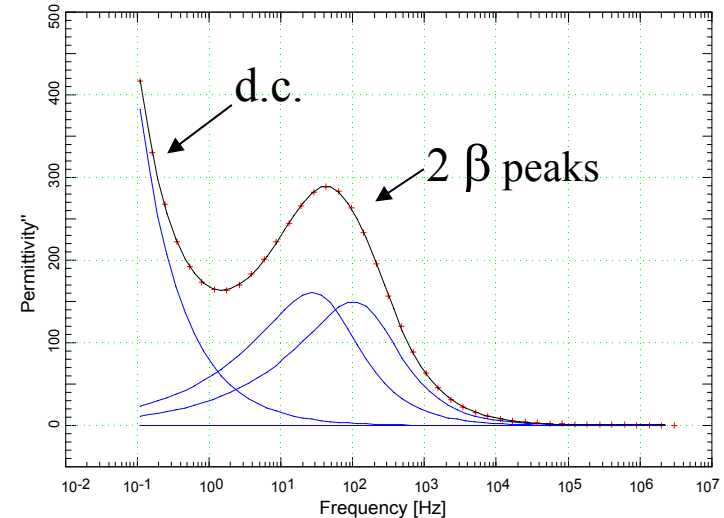
- Spectra after drying 7.5h/70 °C in spectrometer
- Specimens degraded 75h, then cleaned w/ HCl
  - Broader relaxation peak
  - Resolved into 2 components
  - Increased $\tau_{max} = 1(2\pi f_{max})$
  - → *broadened distribution of molecular environments*
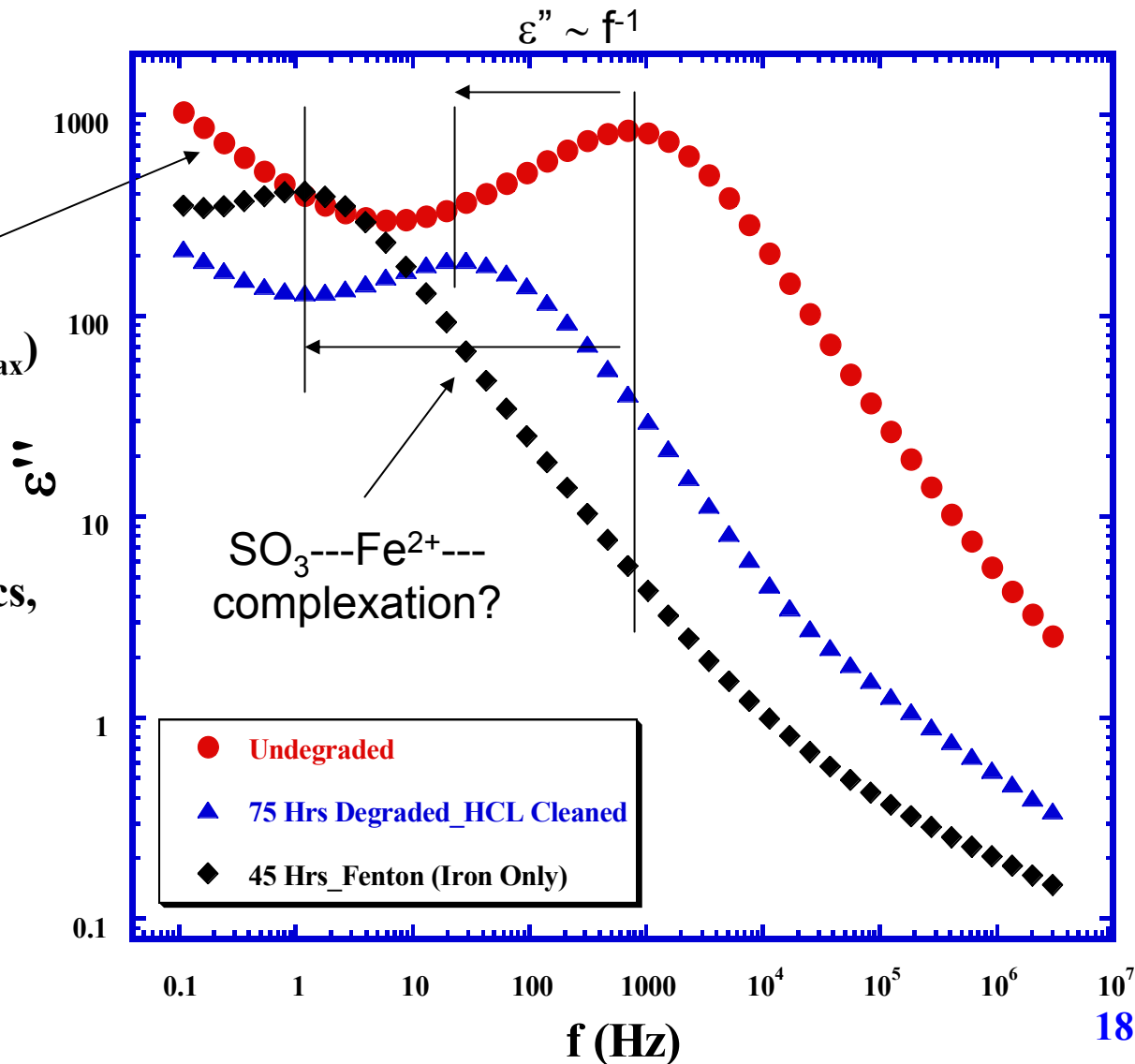
Degraded vs Non-degraded Nafion®: *Comparisons at 60 °C*
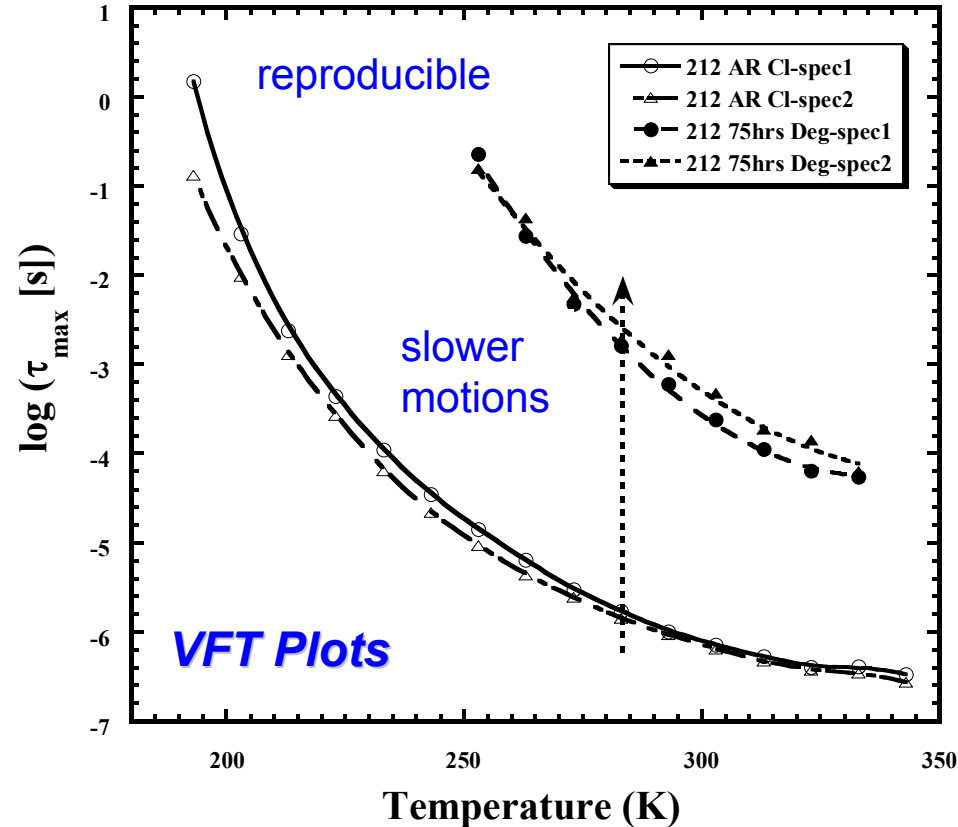
- **f_{max} with degradation**

- **Relaxation time (τ) = $1/(2\pi f_{max})$**

- **Chain conformation dynamics, T_g – related motions**

- **Slower motions with degradation**

dc conductivity slope ≈ 1

$\varepsilon'' \sim f^{-1}$

SO_3---Fe^{2+}--- complexation?

ε''

Legend:
- ● **Undegraded**
- ▲ **75 Hrs Degraded_HCL Cleaned**
- ◆ **45 Hrs_Fenton (Iron Only)**

f (Hz)

1000   100   10   1   0.1

0.1   1   10   100   1000 10^4 10^5 10^6 10^7

Nafion® NRE 212 H⁺ films degraded in Fenton's reagent 75h vs. untreated film
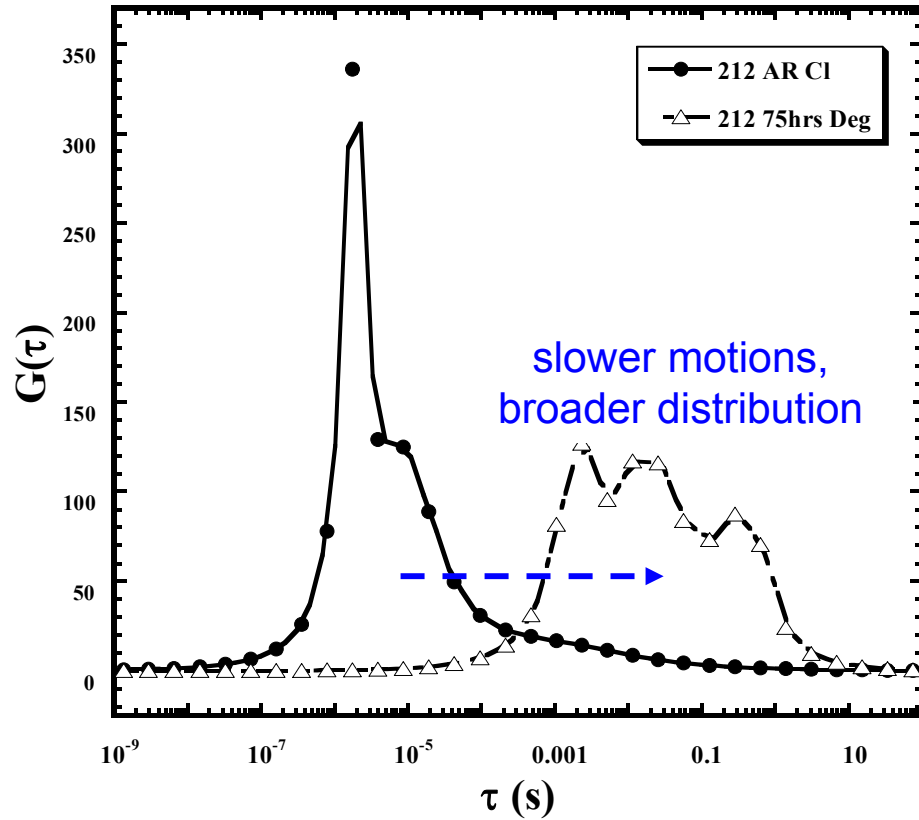
Leach out low molecular weight (M) fragments during Fenton treatment → average M increases

$$\tau \propto M^a : \text{Longer chains move slower}$$

# High temperature Nafion®/silicate Nanocomposite FC Membranes
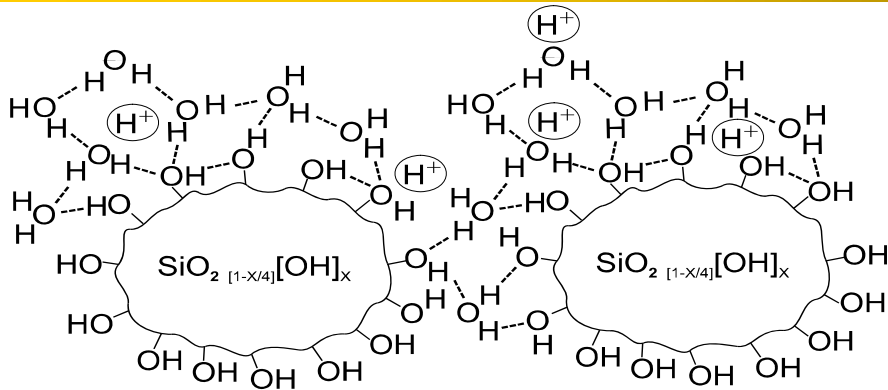

- ❑ Issues:
  - ❑ Molecular state of water - contiguous water pathways - proton conductivity
  - ❑ High temperature water retention

  - ❑ Sample pre-swollen in EtOH → immersed in TEOS / dibutyltin dilaureate / EtOH → membrane-*in situ* sol-gel process (no water)
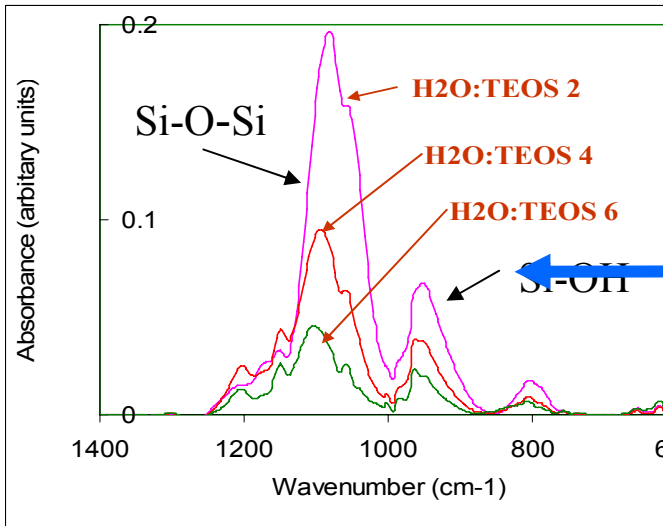
- ❑ Behavior
  - ❑ Monotonic increase in T_g with increase in silicate loading
  - ❑ Side-chains trapped in silicate cages?

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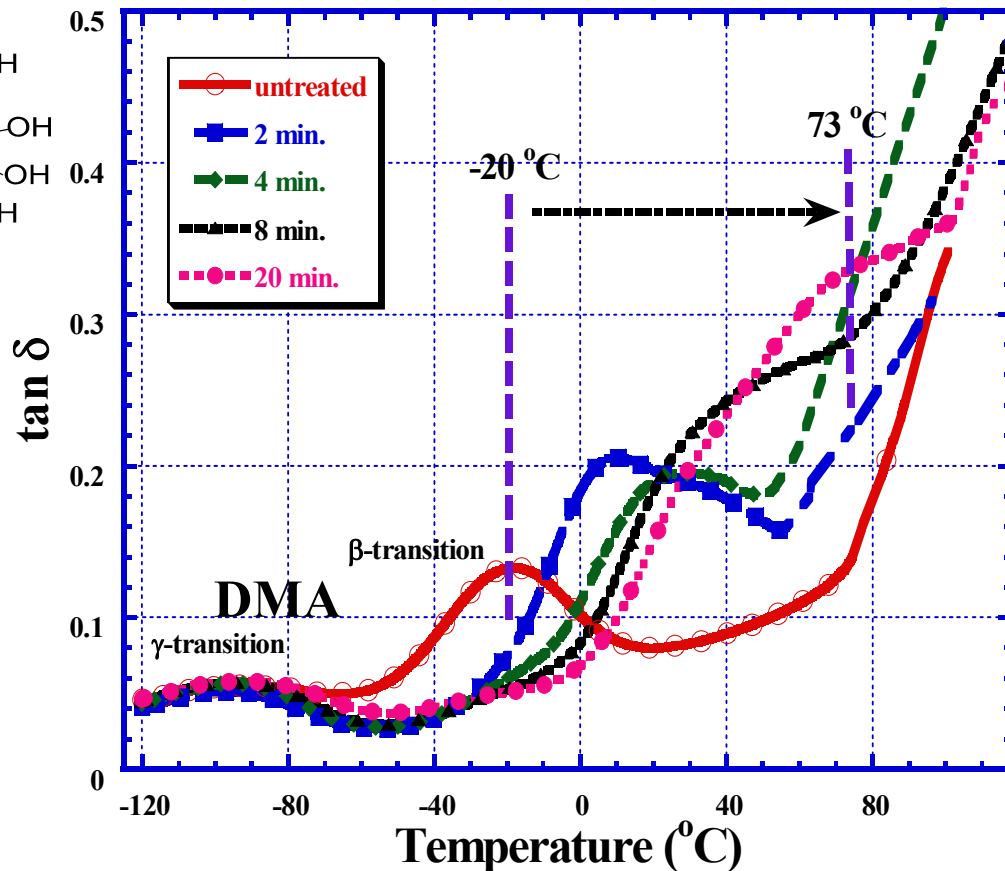
Inorganic Modification of Nafion Membranes: Effect of Water:TEOS Ratio
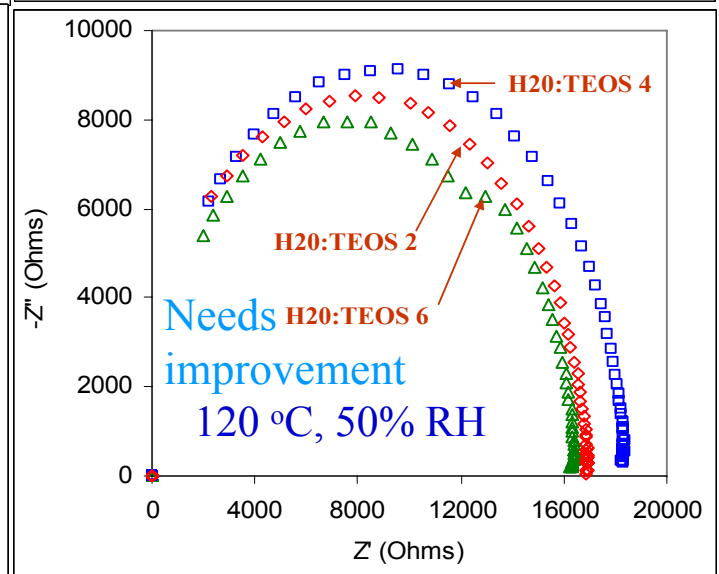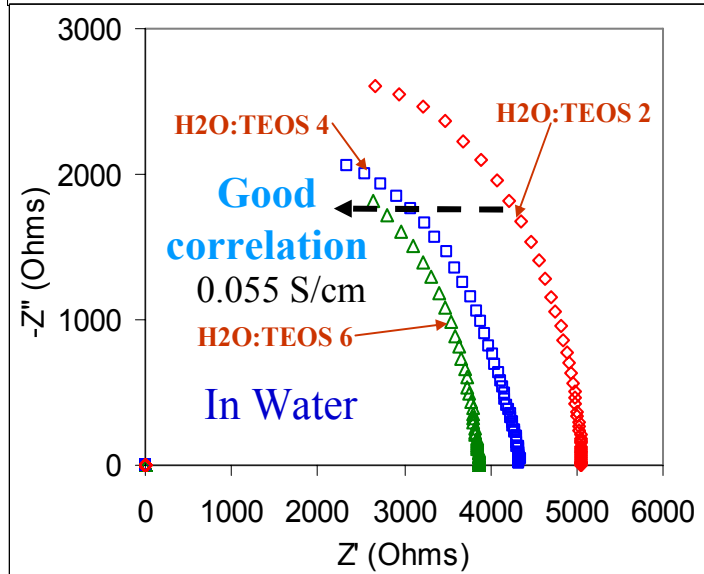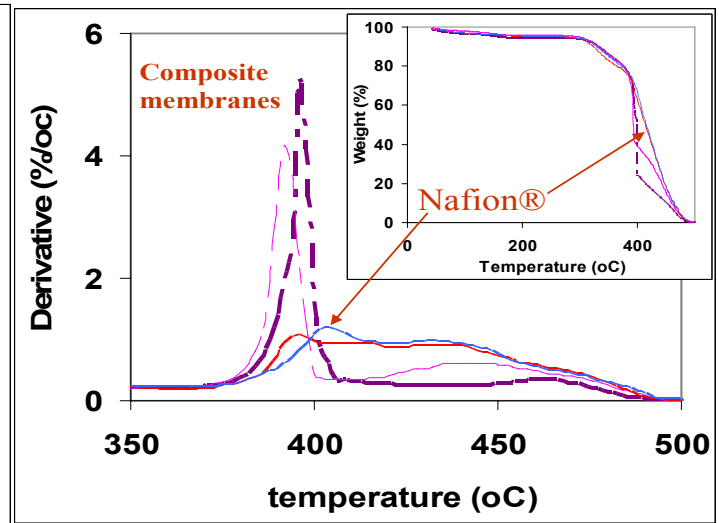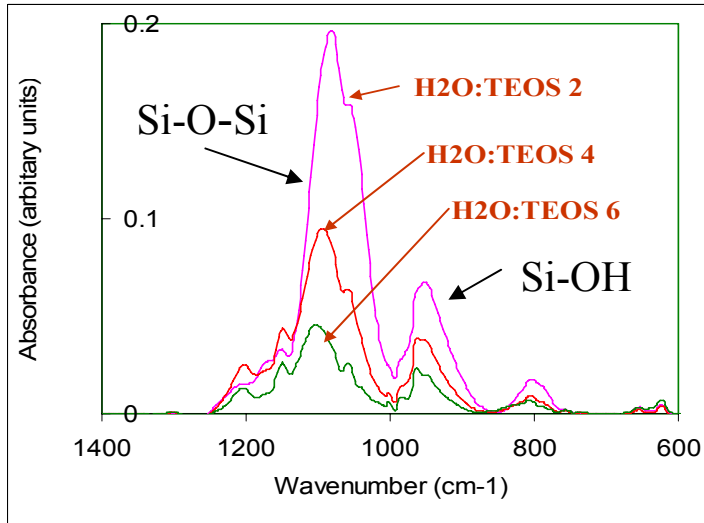
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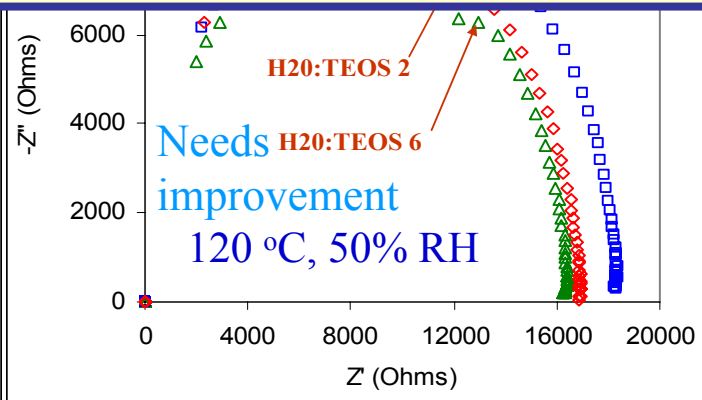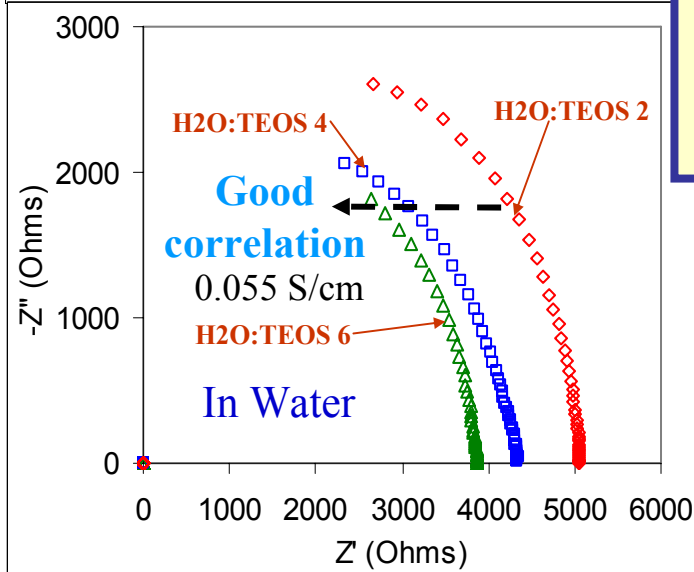

FTIR/ATR Spectroscopy

Effect of H_2O:TEOS

$A_{Si-OH} / A_{Si-O-Si}$

❑ Relative measure of hydrophilic groups on *in situ* – grown silicate nanoparticles

❑ Impart high temp. water retention

Future Work

- **Timeframe: May – November 2007**
- **Characterize structural/physical changes after chemical degradation**
  - **Spectroscopic analysis, titration, extraction/characterization of soluble components**
- **Optimize morphological parameters for performance and durability**
  - **Membrane processing with tailored morphological control**
  - **Post-processing treatments for enhancement of stable morphology**
- **Optimize MEA preparation procedures for performance and durability**
- **Characterize performance and durability of organic/inorganic composites**
- **Complete synthetic procedures for new hydrocarbon-based PEMFC membranes**

Summary

❑ **Chemical and physical properties are significantly affected by thermal treatments. Annealing enhances solvent stability, but may compromise chemical stability in H^+-form Nafion®.**

❑ **Solution-processing conditions have a significant effect on membrane and MEA performance.**
  - ▪ **Likely to be related to morphology**
  - ▪ **Durability of enhancements must be evaluated.**

❑ **Broadband dielectric spectroscopy: powerful tool in characterizing molecular motions in Nafion® and chemical degradation.**
  - ▪ **Connection between relaxation time distribution and degraded molecular weight distribution**
  - ▪ **Spectra sensitive to Nafion® thermal history and low level moisture content**

❑ **Hydrophilic silicate nanoparticles successfully incorporated in polar domains of Nafion®.**