Alternative Fuel Cell Membranes for Energy Independence

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Project ID #fcp_10_mauritz

Overview

Timeline

- Project start date 8/01/2008
- Project end date 1/31/2010
- Percent complete 25%

Budget

- Total funding share
  - DOE share $984,000
- Funding received in FY08
  - $984,000
- Funding for YR09/10
  - $951,000

Barriers

Barriers addressed

- Synthesis of bisphenol monomer with tethered ion exchange site has been hampered by availability and high cost of fluorinated reagents.
- Challenge to tailor and test membranes for good proton conductivity at high temperatures over a range of RH.
- Challenge to balance excellent chemical and mechanical durability with excellent fuel cell performance.

Partner

Interactions/Collaborators

- Prof. Vijay Ramani, Illinois Institute of Technology, Chicago (unfunded)

Project Objectives - Relevance

- Synthesize stable aromatic hydrocarbon polymers containing acid ion-exchange groups tethered to the backbone via fluorinated side chains

- Synthesize benchmark aromatic hydrocarbon membranes for properties comparisons and refinement of synthetic methods

- Establish Nafion® benchmark data to which novel hydrocarbon membrane data can be compared on an all-other-things being equal basis

- Establish hydrocarbon membrane structure-property, proton conductivity characterizations and fuel cell performance data as relating to the Hydrogen Program proton conductivity technical achievement milestones.

Project Objectives - Approach
(a/p current reported segment)

- Condense phenol with acid-functionalized perfluorinated ketone to create bisphenol monomer with tethered ion exchange site; polymerize bisphenol monomer with aromatic dihalide using nucleophilic aromatic substitution.

- Benchmark aromatic hydrocarbon membranes will by synthesized and processed using literature methods.

- Nafion[®] benchmark property data will be established to compare with data for hydrocarbon membrane data on an all-other-factors being equal basis.

Milestones

| Task Number	Project Milestones	Task Completion Date			Percent Complete	Progress Notes
		Original Planned	Revised Planned	Actual		
1.0	Acquisition of Equipment	03/31/09			95%	On-Track.
2.0	Polymer Synthesis	1/31/10			34%	On-Going
2.1	Monomer Synthesis	1/31/10			34%	On-Going
2.2	Polymer Synthesis and Characterization	1/31/10			34%	On-Going
3.0	Establishment of Standard Membrane Benchmark Data	3/31/09			70%	On-Track

Technical Accomplishments and Progress

- A key monomer precursor, 2-oxo-1,1,3,3,3-pentafluoropropane phosphonic acid diethyl ester, was synthesized and purified for condensation with phenol

- 4,4'-Dichlorodiphenyl)sulfone 3,3'-disulfonc acid was prepared for benchmark hydrocarbon resin synthesis

- OCV decay curves for degraded Nafion® MEAs established for comparison w/ degraded hydrocarbon MEAs

- MEA preparation shown to improves Nafion® mechanical modulus at 80° C, 100% RH

- Stress-strain curves of OCV-degraded samples at 80° C, 100% RH show MEA modulus decreases w/ increasing OCV degradation-failure at very low strain-poor ductility due to decrease in polymer molecular weight, loss of entanglements.

- Contractile stress vs. time experiment for RH drop at 80° Cfor constrained membranes show control and degraded MEA fail. Related to mechanical durability with RH cycling.

- Mechanical creep tests show degraded MEA deformation lower than that of control MEA – fewer chain entanglements due to shorter chains.

- SEM micrographs of OCV-degraded creep samples show cracks instead of crazing as is the case for non-degraded creep samples.

- Broadband dielectric spectroscopy analysis show shifts in time scales of characteristic polymer chain motions that infer changes in molecular weight with degradation.
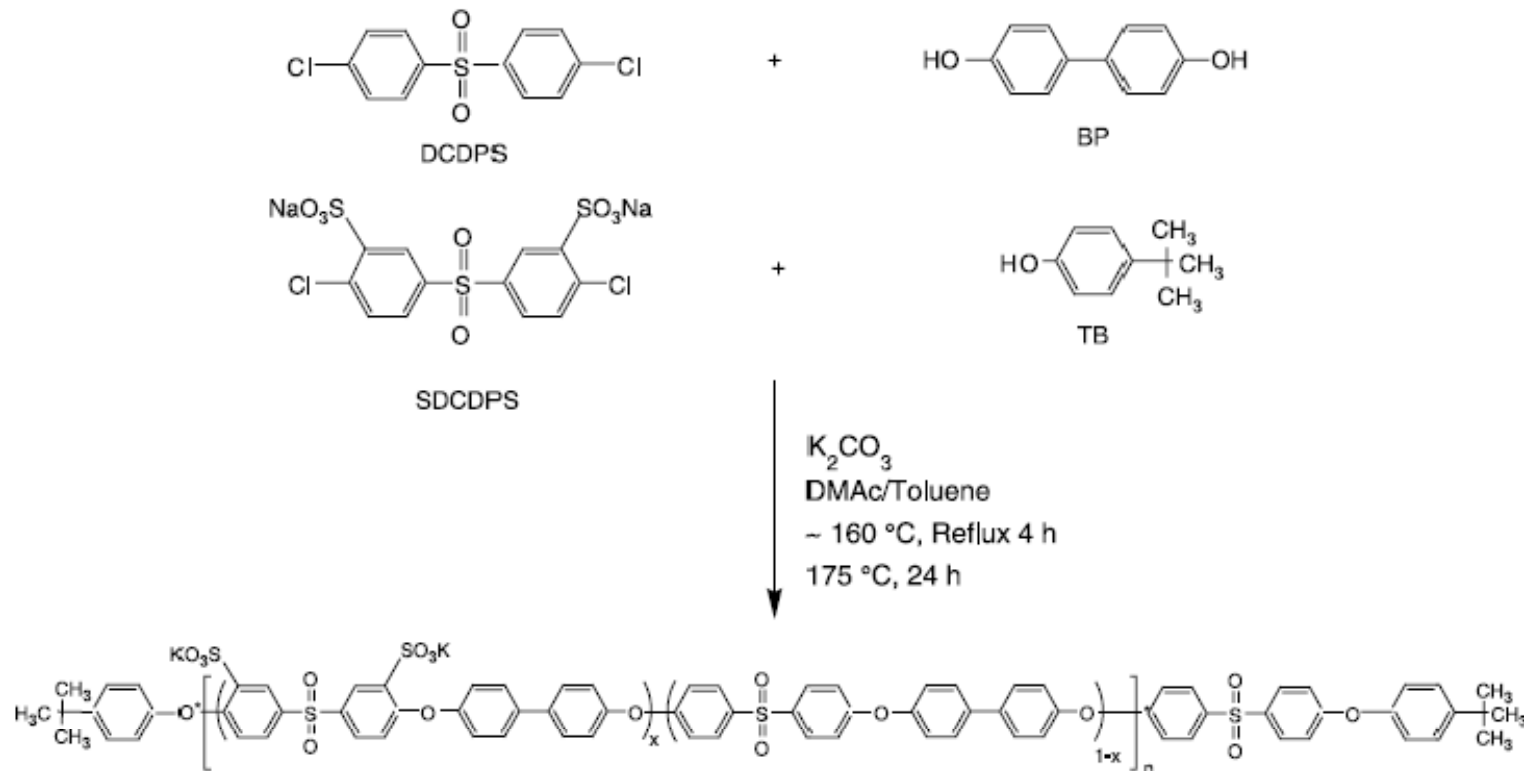
Organic Membrane Synthesis

Proposed membrane polymers created using step-growth polymerization via nucleophilic aromatic substitution
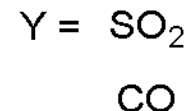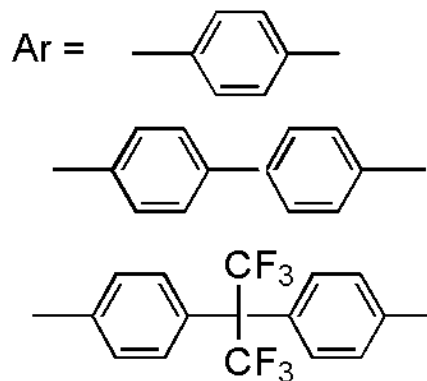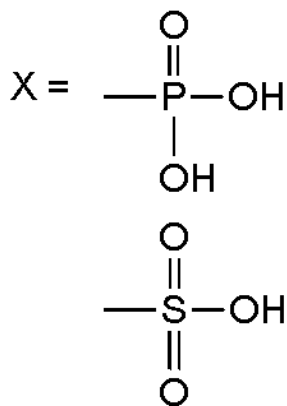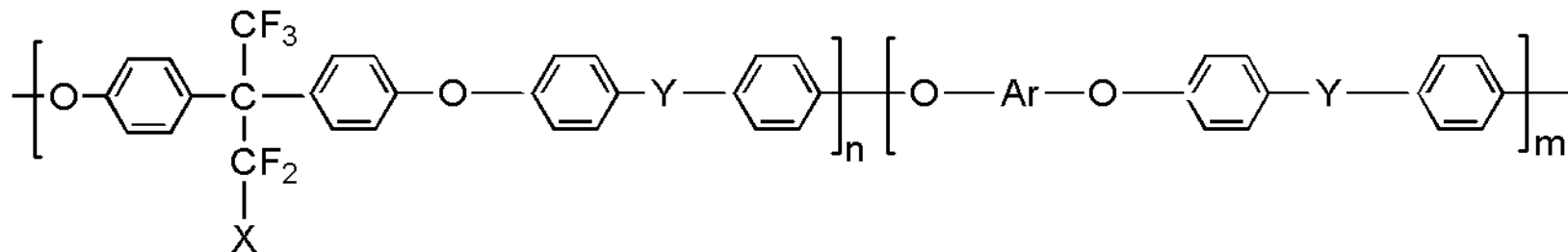
Synthesis of Benchmark Aromatic Hydrocarbon Membranes

(pertaining to Subtask 2.2: Polymer Synthesis)

- sPAES has been successfully synthesized (need GPC to determine molecular weight).

- Suspected low MW sPAES batch appears to be water soluble. Low MW is believed to be due to NaCl impurity in SDCDPS.
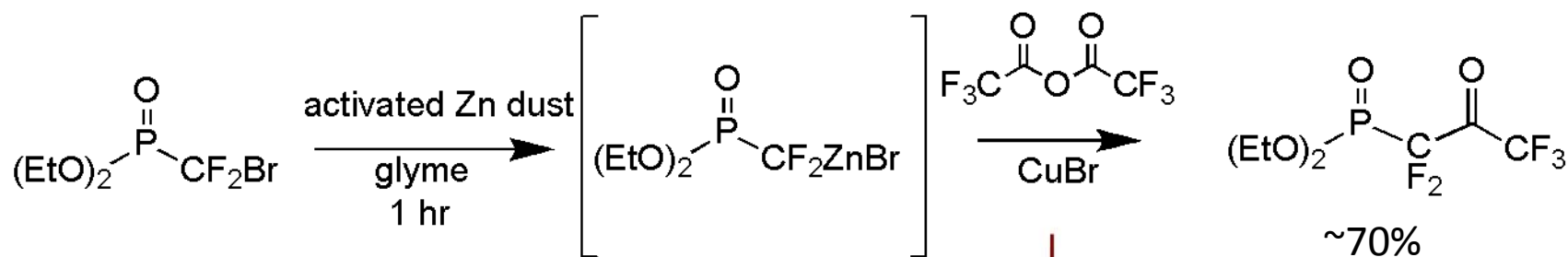
McGrath et al, *Polymer* **2006**, *47*, 4210

Synthesis of Phosphonic Acid-Tethered Monomer
(pertaining to Subtask 2.1: Monomer Synthesis)

2,2 bis(4-hydroxyphenyl) perfluoropropane phosphonic acid
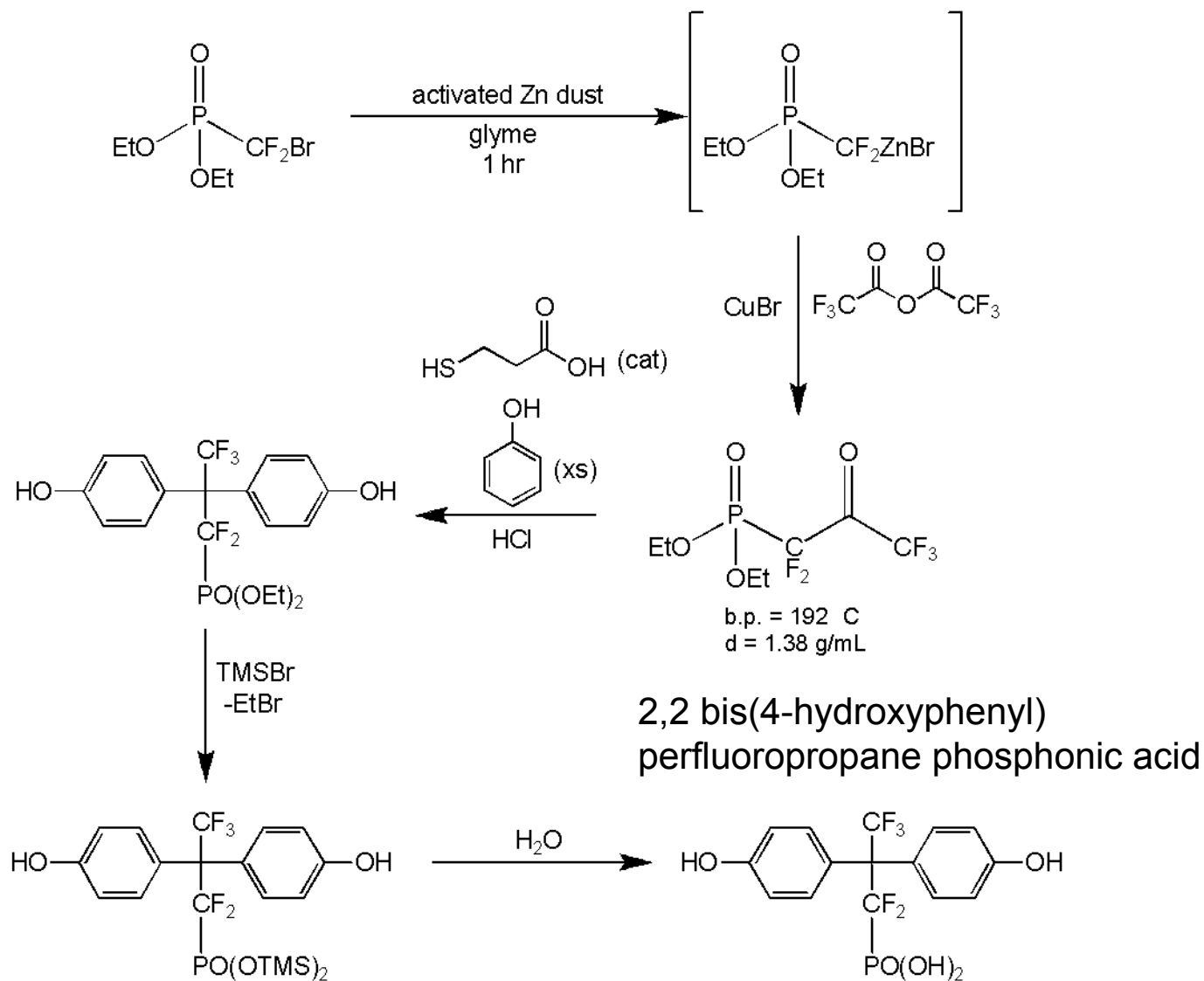
Synthesis of $(EtO)_2P(O)CF_2C(O)CF_3$
(Subtask 2.1)

Alkylation readily occurs with trifluoroacetic anhydride

^{1}H NMR shows ethoxy protecting groups

^{1}H NMR in CDCl$_3$, 200 MHz, RT

~70%

Pasternak et al *J. Fluorine Chem*. **2004**, *125*, 1853
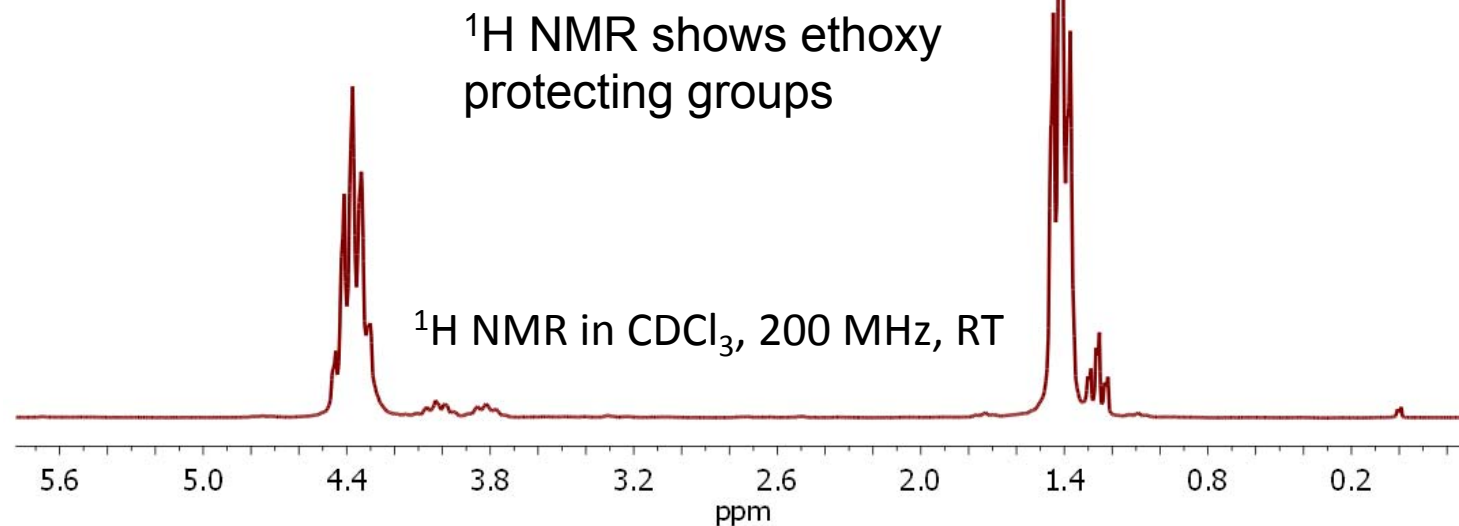
$^{13}C\{^{1}H\}$ NMR of $(EtO)_2P(O)CF_2C(O)CF_3$

C=O

CF_2 dt, $^{1}J_{C-F}$ = 278 Hz, $^{1}J_{C-P}$ = 192 Hz

CF_3 dq, $^{1}J_{C-F}$ = 289 Hz, $^{3}J_{C-P}$ = 13 Hz

No $^{3}J_{C-F}$ coupling observed
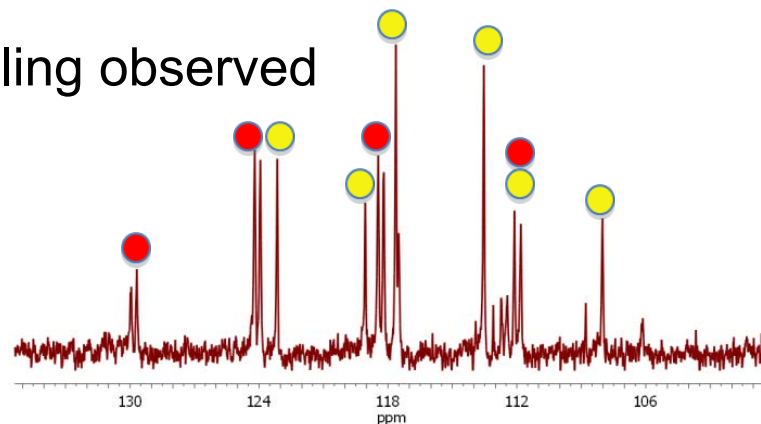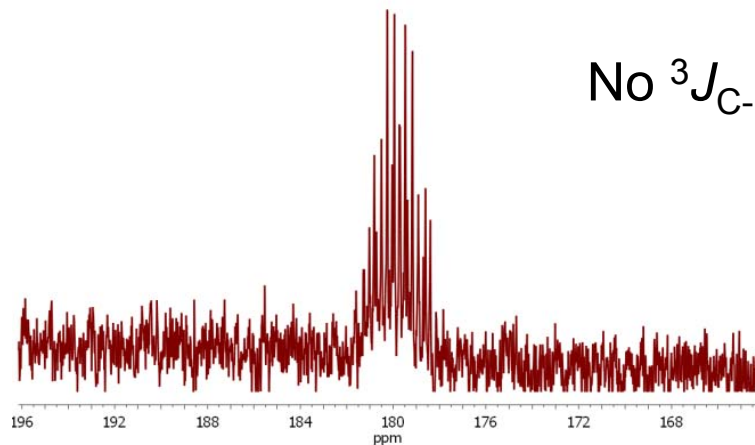
OCH_2CH$_3$ d, $^{2}J_{C-P}$ = 7 Hz
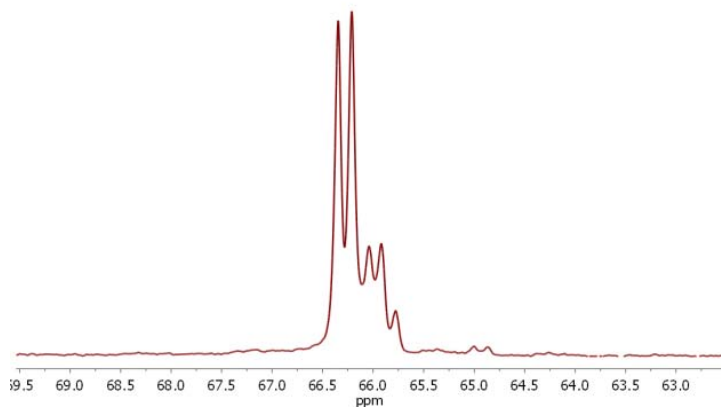
OCH$_2$$CH_3$ d, $^{3}J_{C-P}$ = 5 Hz
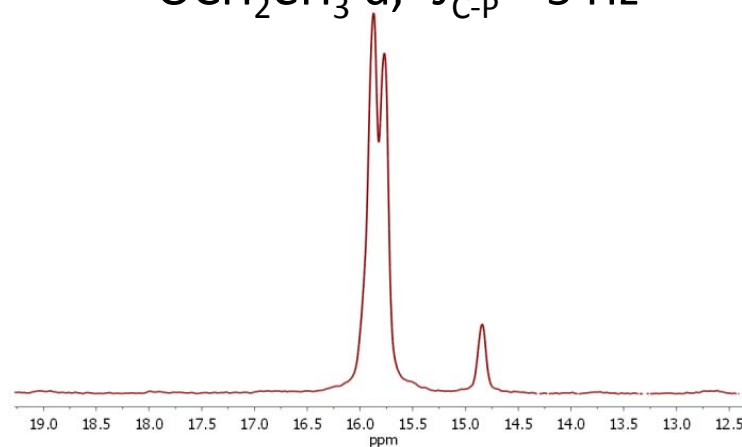
$^{31}P\{^{1}H\}$ and ^{19}F NMR of $(EtO)_2P(O)CF_2C(O)CF_3$

(Subtask 2.1)

tq, $^{2}J_{P-F}$ = 94 Hz

$^{4}J_{P-F}$ = 5 Hz

○ $(EtO)_2P(O)CF_2H$

Side product formed in the presence of adventitious water

^{31}P and ^{19}F NMR confirm addition of $C(O)CF_3$ unit
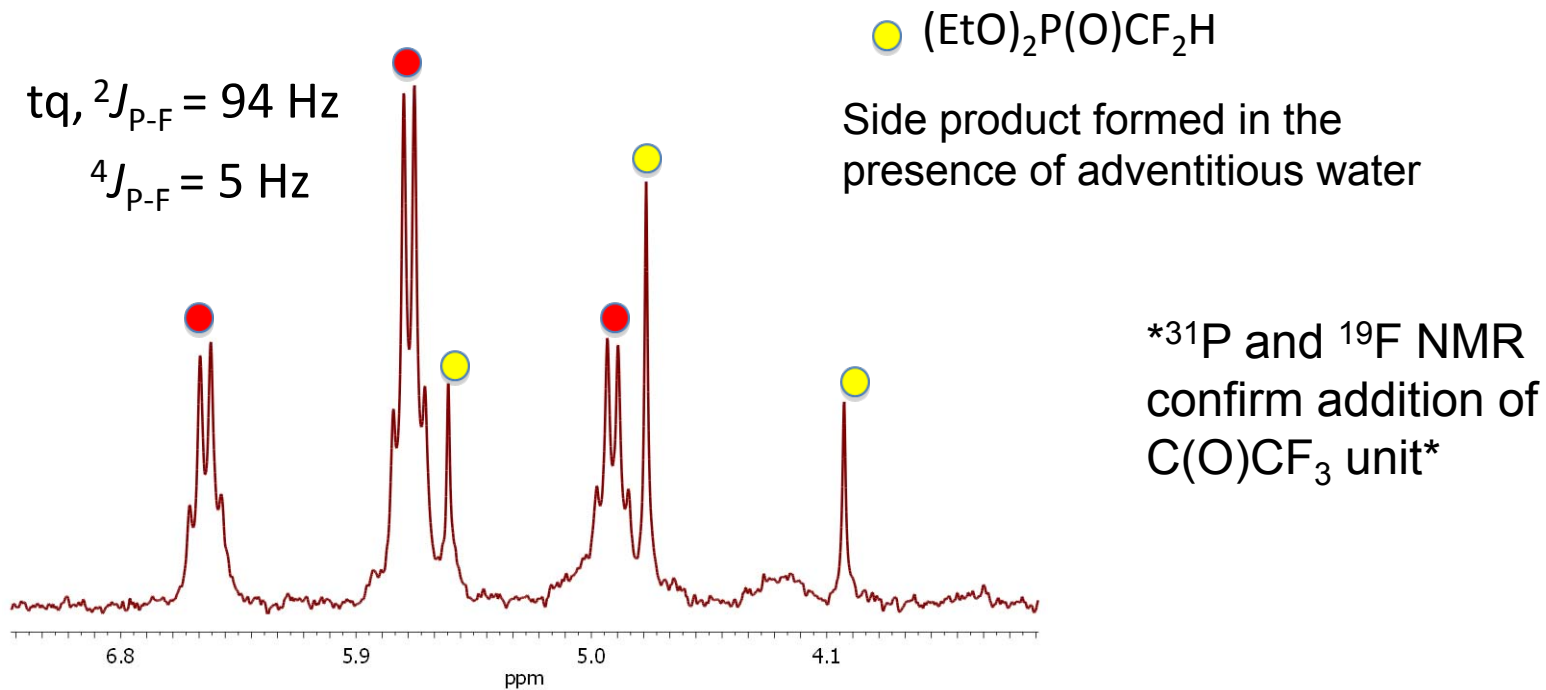
^{19}F NMR of $(EtO)_2P(O)CF_2C(O)CF_3$

(Subtask 2.1)

● CF_3

dt, $^4J_{F-P}$ = 5 Hz

dt, $^4J_{F-F}$ = 12 Hz
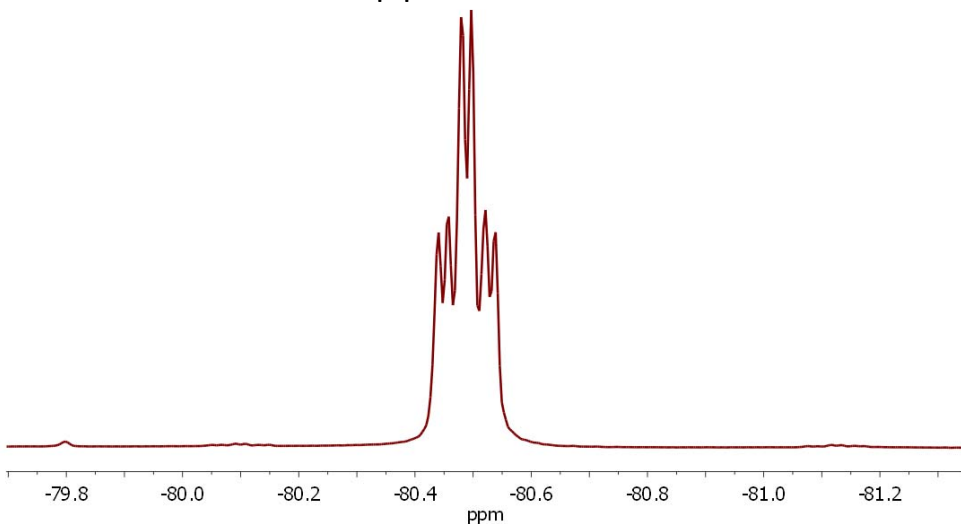
● CF_2

dq, $^4J_{F-F}$ = 12 Hz

dq, $^2J_{F-P}$ = 94 Hz
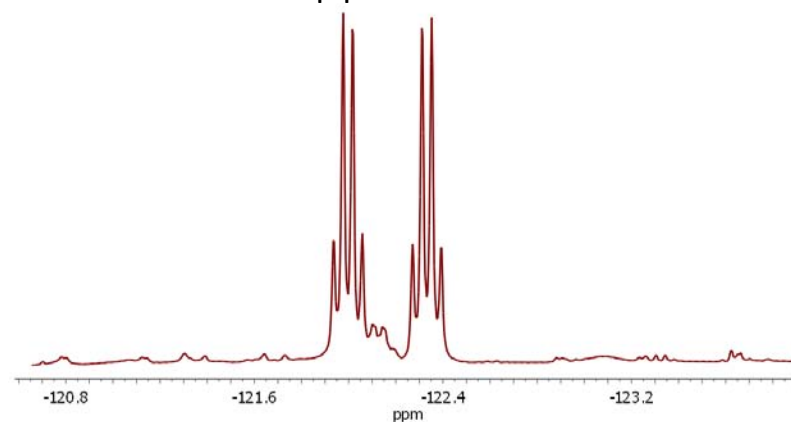
## Task 3.0 Establishment of Standard Membrane Benchmark Data

Data collected on Nafion® membranes *prepared under the same conditions as hydrocarbon membranes* as Nafion® is the benchmark for comparison.

I*n situ*, *ex situ* membrane degradation studies, generation of polarization profiles:

1. Effect of degradation on mechanical properties of membranes
2. Dielectric spectroscopy characterization of membrane degradation

OCV decay curves for degraded MEA samples
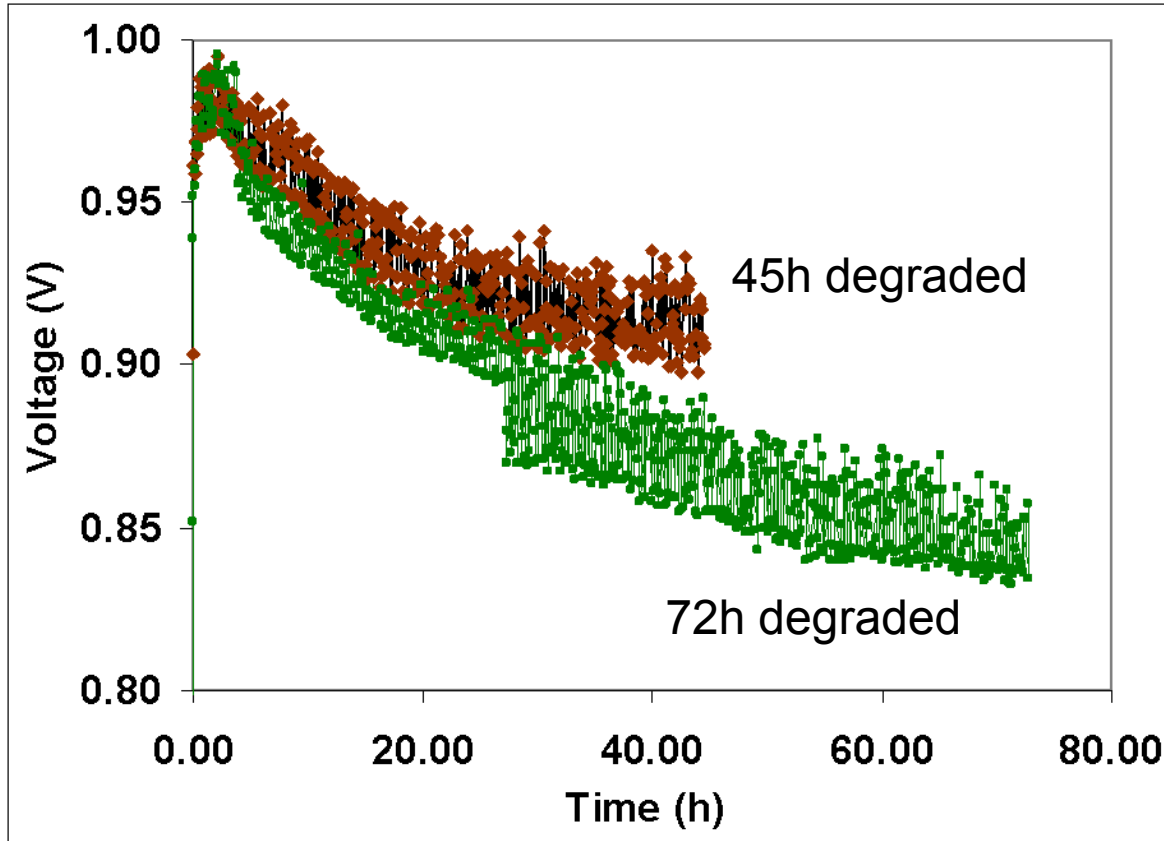
- 90° C, 30% RH, 25 cm² MEA
- Catalyst loading 0.4 ± 0.01 mg/cm²

- Increased fuel cross over with time due to membrane degradation results in gradual decrease in cell voltage.
- Sudden drop in 72h degraded MEA due to pinhole formation?

Mechanical properties

at 80° C, 100% RH

sample prep	Modulus	Linear expansion	Strain-at-break	Stress-at-break
	MPa	%	mm/mm	MPa
Acid cleaned	24.8 ± 5.7	15.1 ± 3.4	4.8 ± 0.7	15.6 ± 1.5
Control MEA	38.2 ± 4.7	8.2 ±1	4.82 ± 0.5	15.74 ± 1
45h degraded MEA	22.8 ± 8.1	6.3 ± 1.9	0.2 ± 0.03	2.6 ± 0.7
72h degraded MEA	19.5 ± 4.8	7.2 ± 2.3	0.17 ± 0.05	1.8 ± 0.3

MEA preparation process improves membrane modulus - due to high processing temperature, increased crystallinity?

OCV degradation severely deteriorates membrane mechanical properties. Modulus reduction + reduced ductility – polymer molecular weight lowering causes fewer chain entanglements
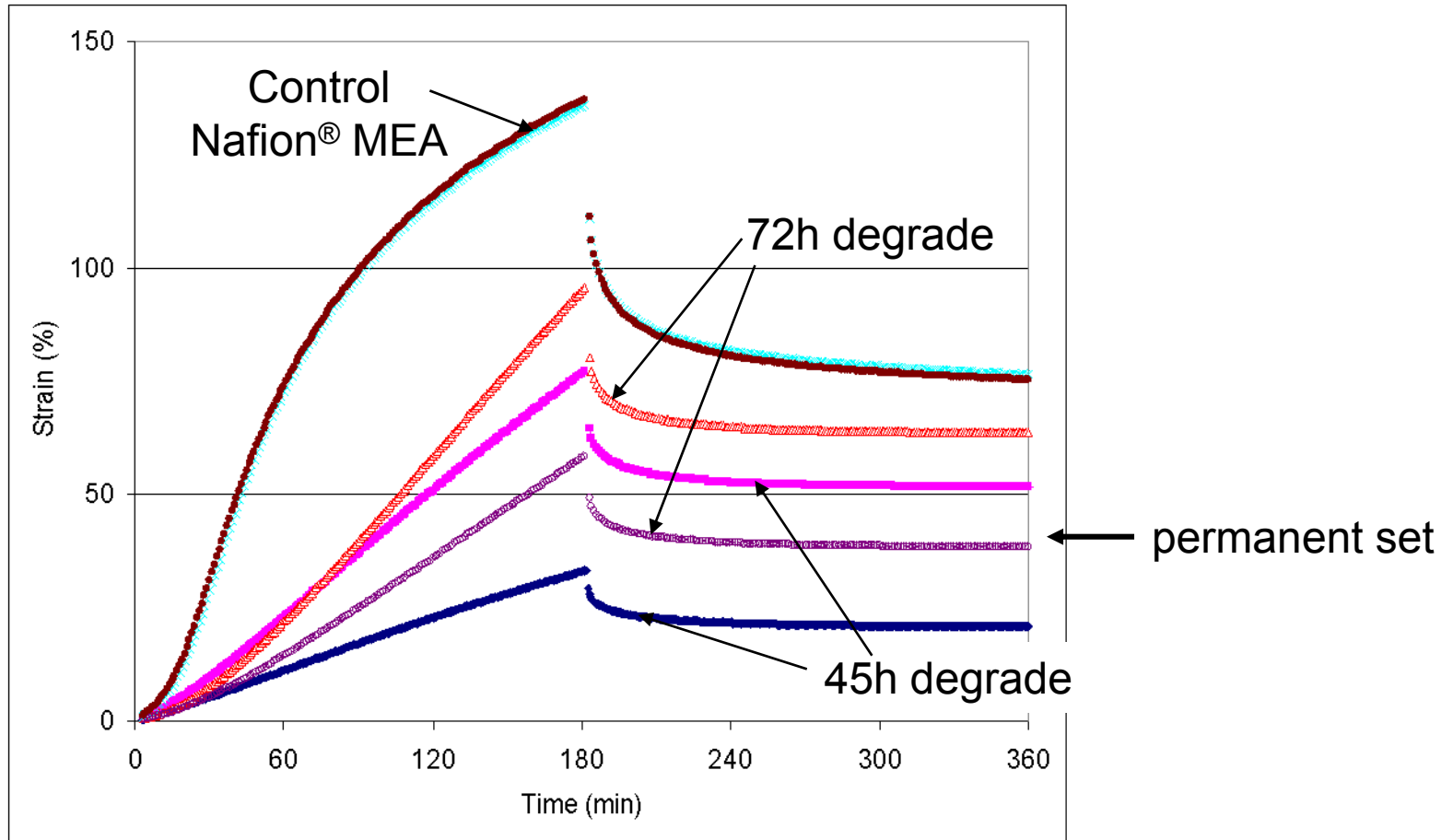
# Contractile stress response to humidity change from 100 down to 0% RH at 80° C
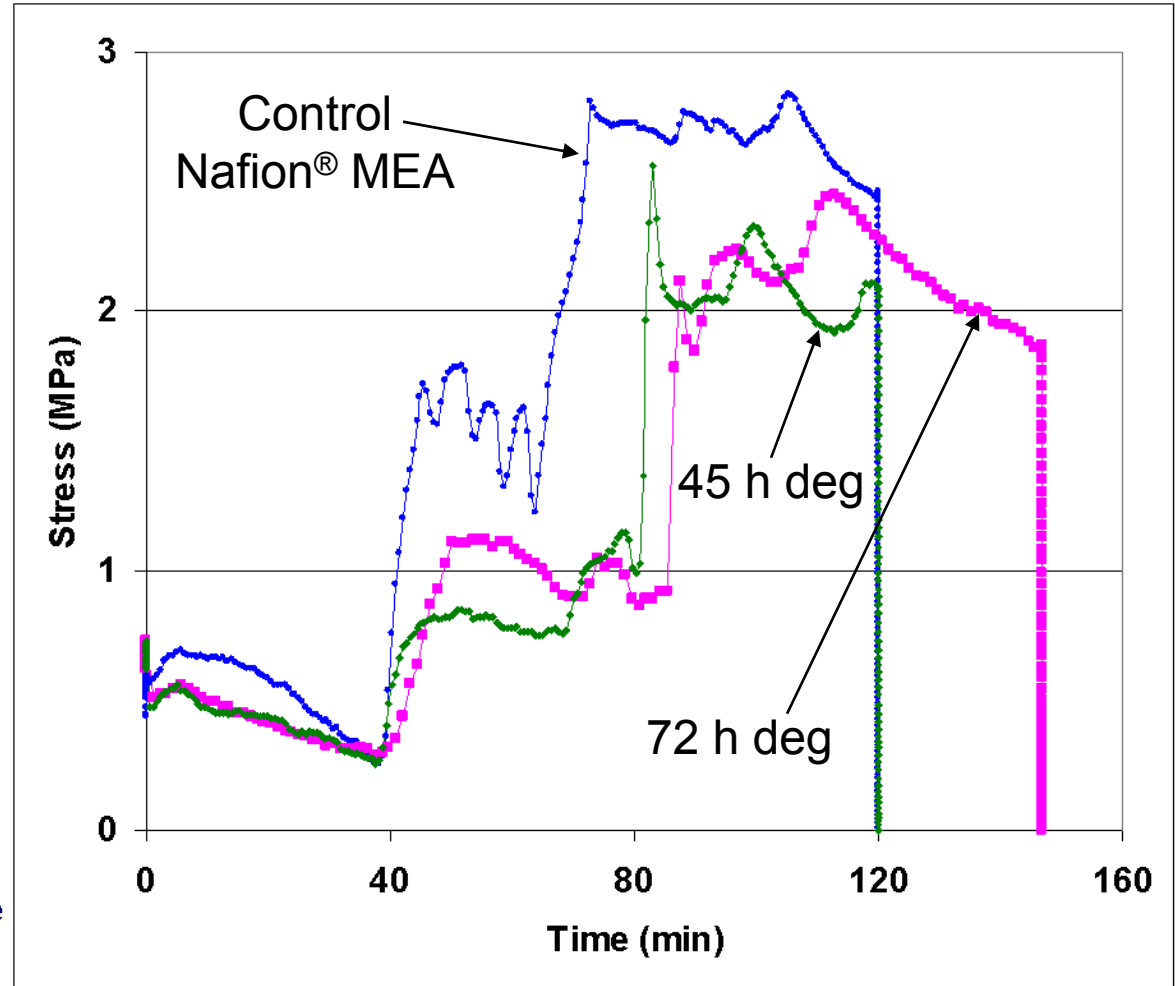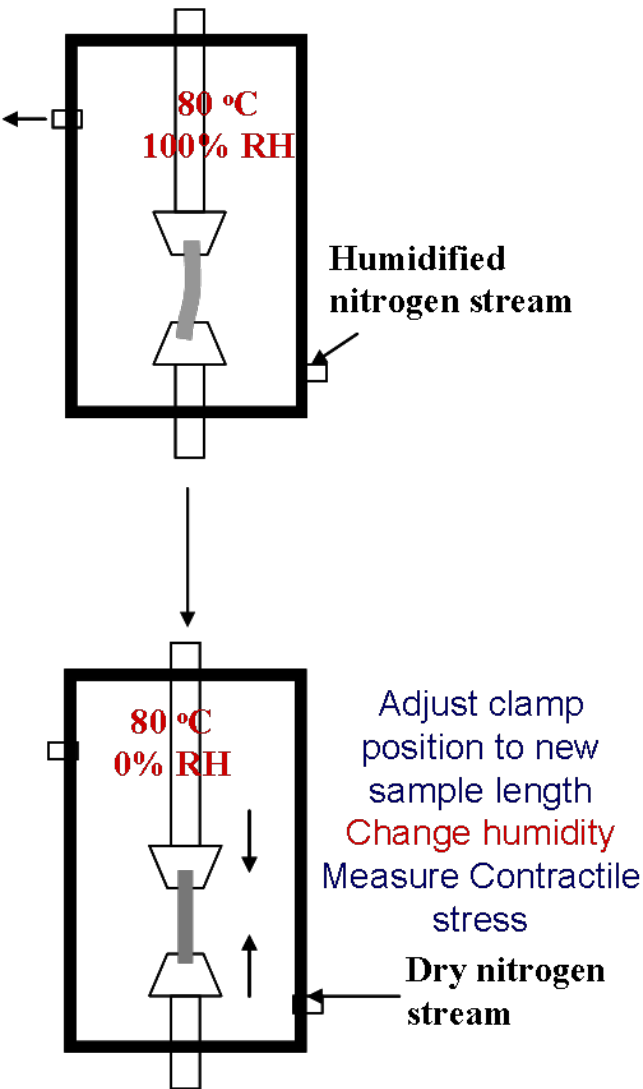
- Control as well as degraded MEA fails when subjected to stresses resulting from humidity change

Creep response to 10 MPa stress at 80° C

- Degraded MEA deformation lower than that of control MEA – fewer chain entanglements due to shorter chains
- SEM micrographs of creep samples: wide cracks suggesting failure instead of deformation
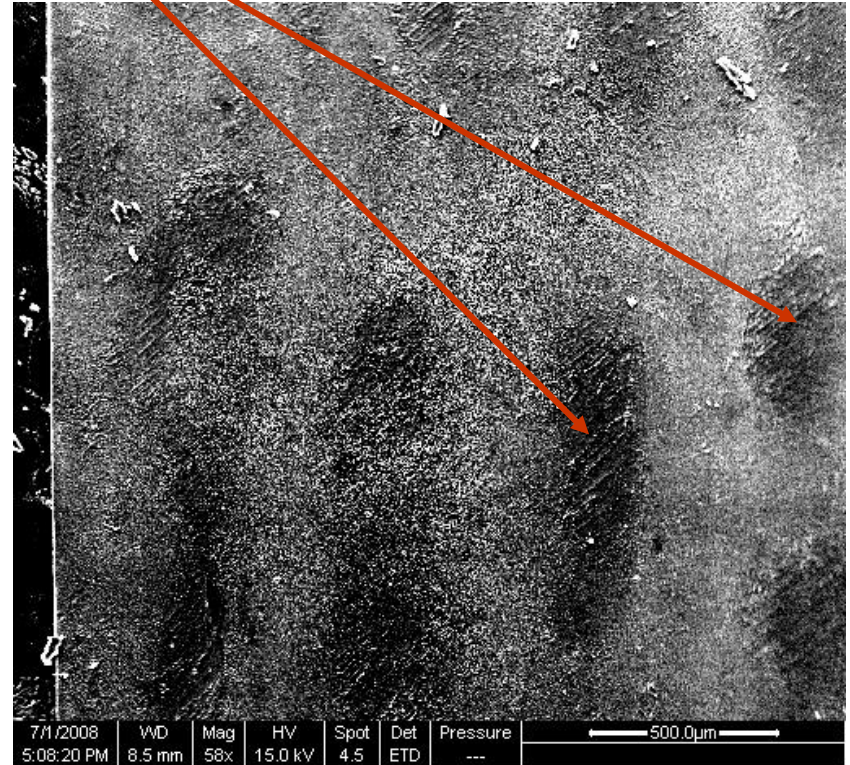
72h degraded MEA micrograph after creep
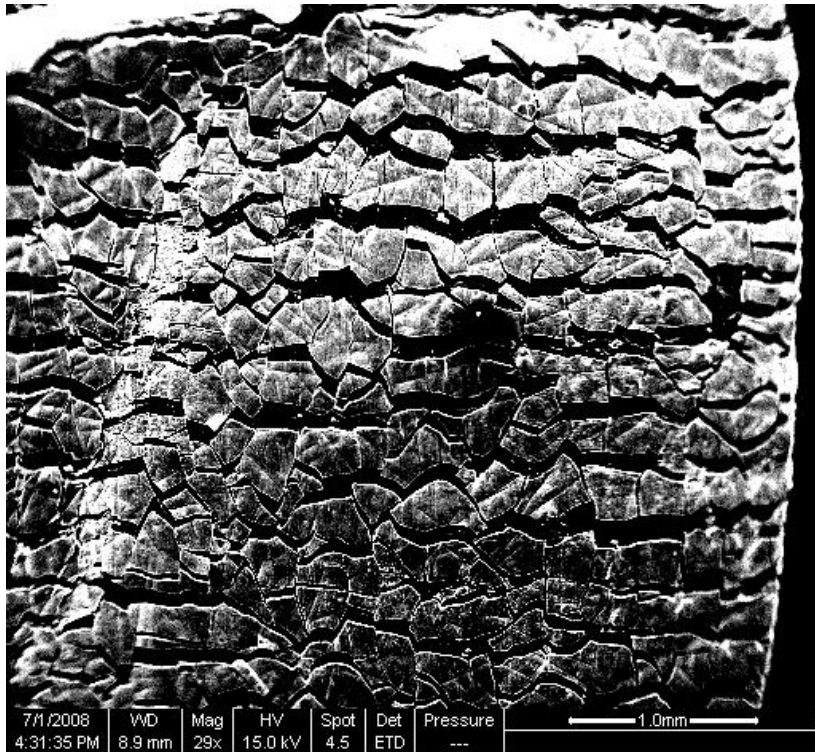
72h OCV - degraded MEA shows wider cracks over entire surface than 45h degraded MEA. Cracks extend over entire surface.

Control (non-degraded) MEA micrograph after creep deformation

failure regions
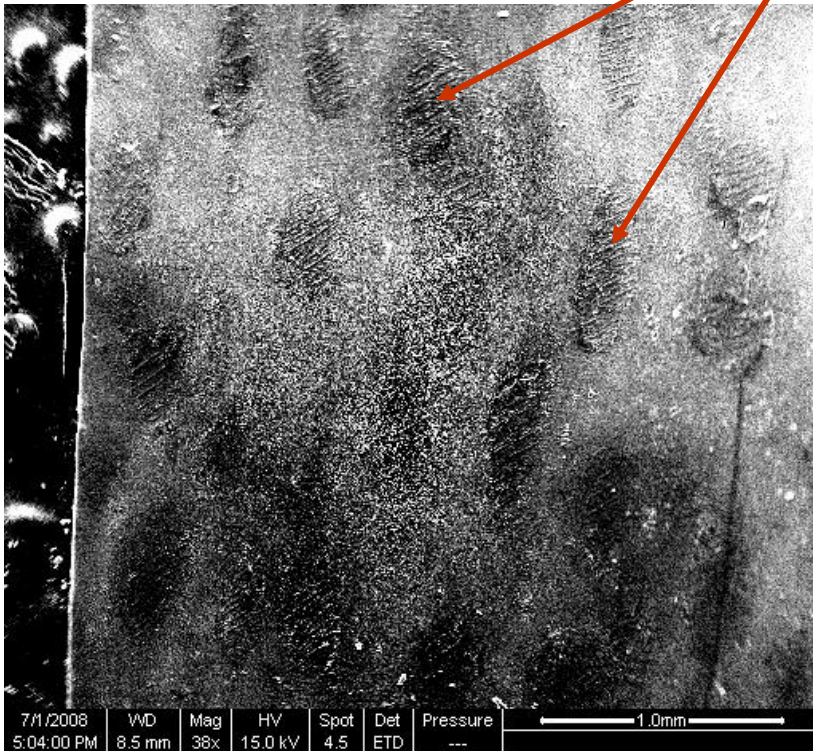
Control MEA shows no wide cracks as for degraded samples, but crazes which could be spots for failure initiation

Creep response to 20 MPa stress at 80°C

Subject to 20 MPa stress control MEA is intact but degraded MEAs break; reduced ability to withstand stress – fewer polymer chain entanglements

Membrane Degradation Strategy for Broadband Dielectric Spectroscopy Analysis

Fenton Reagent Degradation (*ex-situ*)
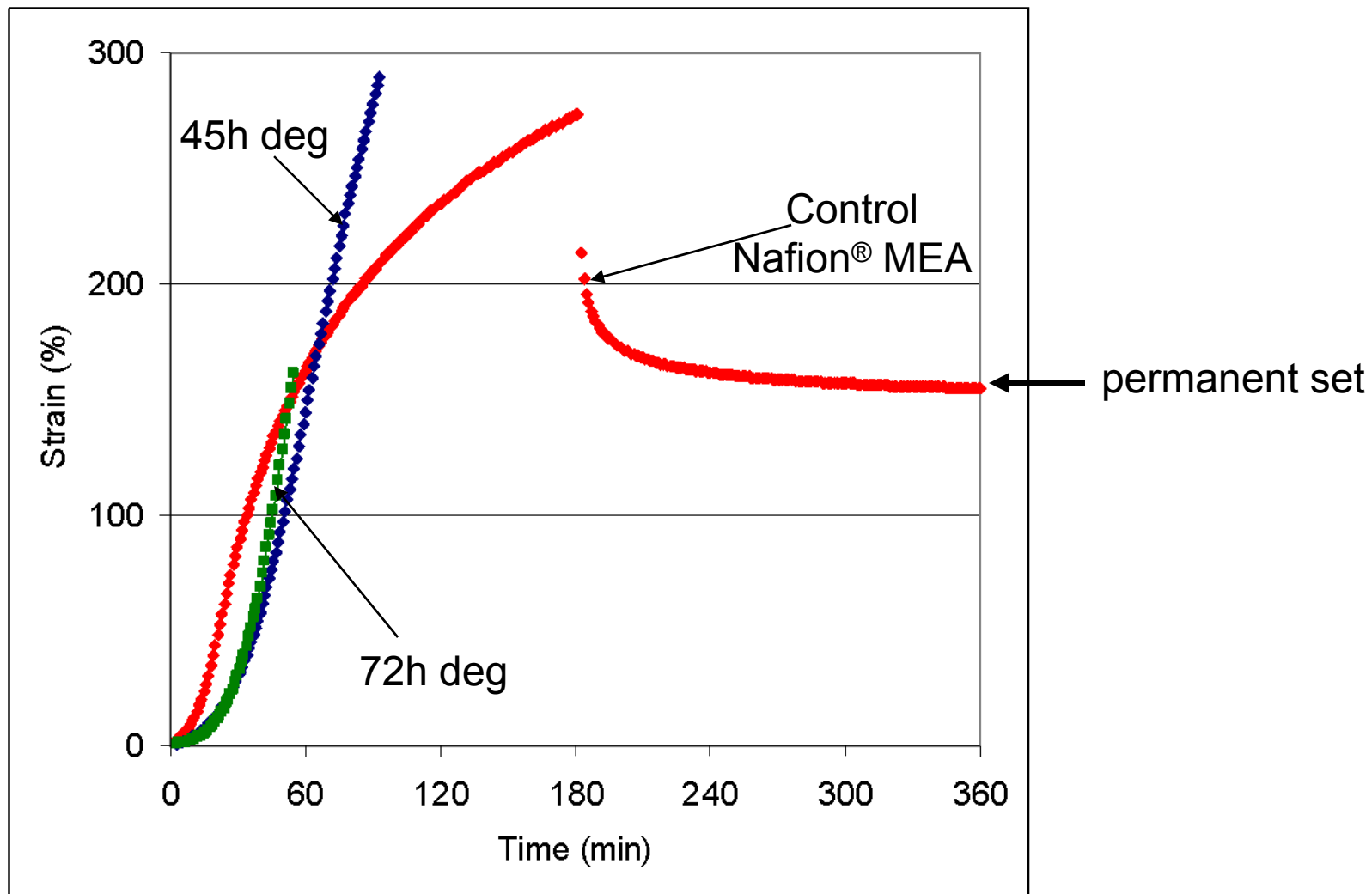**(FeSO$_4$/H$_2$O$_2$- 0.005 g/g polymer + 30% H$_2$O$_2$) @ 80° C**

FC Degradation-OCV (*in-situ*)

- **Membranes degraded up to 200h**

- **Degraded membranes cleaned w/ 2M HCl to convert [SO$_3^-$]$_{2,3}$ Fe^{+2}/Fe^{+3} coordination back to SO$_3$H groups**

- **Membranes tested with dielectric spectroscopy in forms of degraded films and film made by solution re-cast**

-**Catalyst layer removed by mixing with EtOH/H$_2$O (50:50)**

-**Membranes dissolved in DMAc and re-cast directly on dielectric electrodes**

$\varepsilon'' - f - T$ response surface for *undegraded* Nafion® acid film. Curves spaced at 10° C increments from onset of β relaxation up to 200° C. Arrows show crests of peaks

Broadband Dielectric Spectroscopy

α-relaxation   β-relaxation

ε'' = dielectric loss permittivity

0 °C
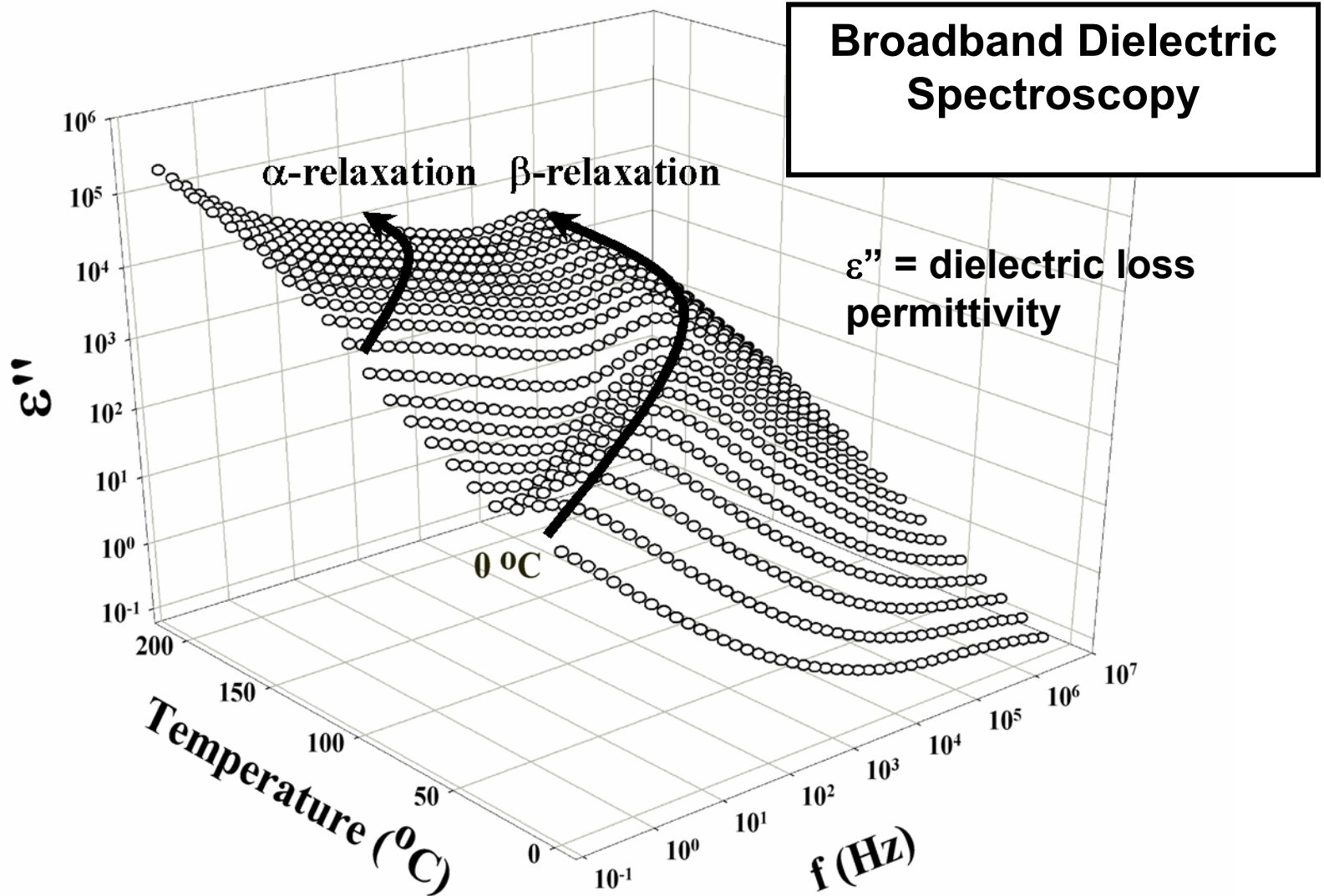
$\varepsilon'' - f - T$ response surface for NRE 212 degraded 75h in Fenton reagent

Degraded film cleaned w/ 2M HCl → dissolved → re-cast from DMF at 180° C

Relaxation crests shift and an extra peak (pink arrow) appears in the low temperature region.

Signatures of change in membrane molecular motions with degradation.
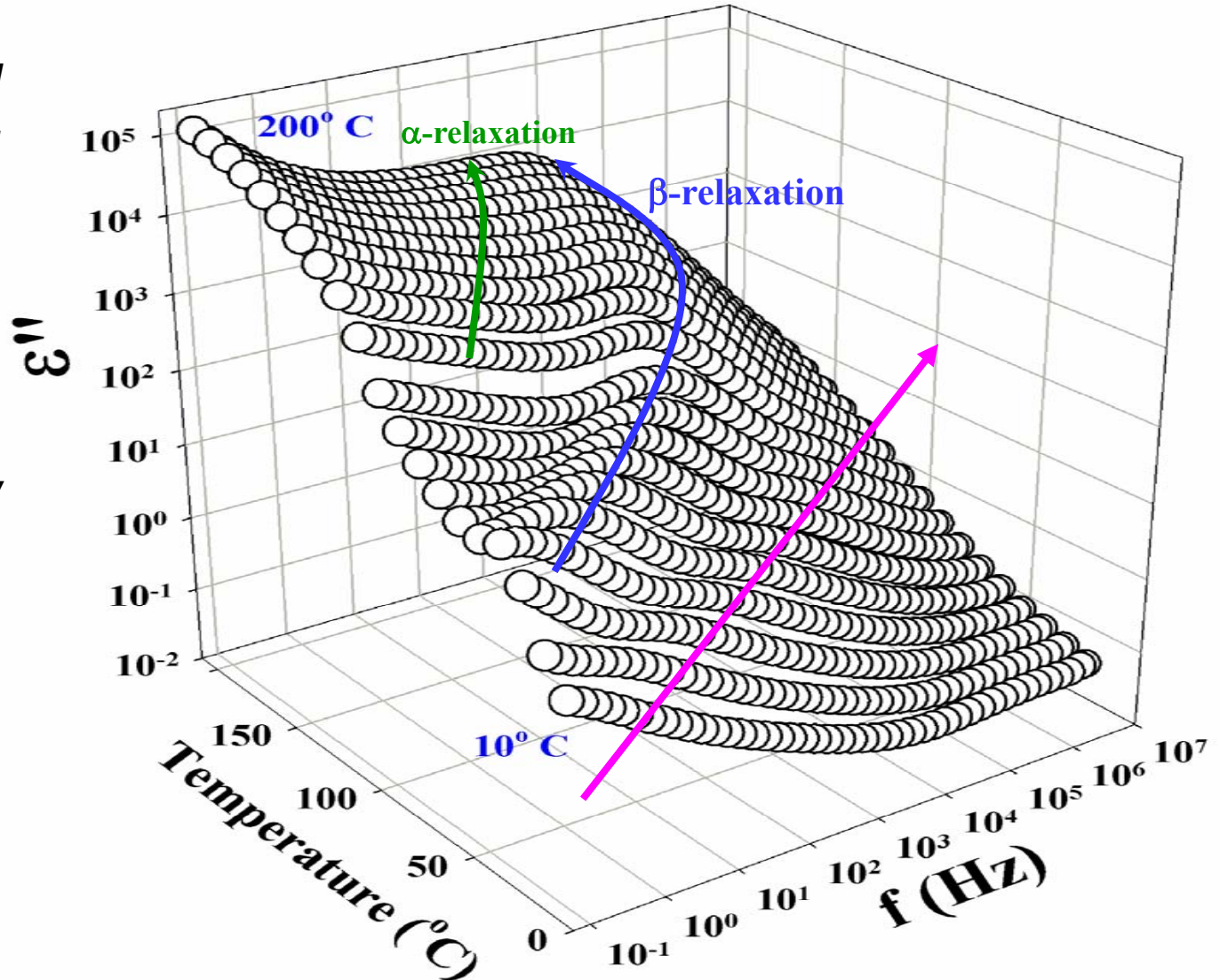
NRE 212_75h Degraded in Fenton Reagent
Comparison at 70° C

β *relaxation slower w/ degradation: Out-leaching low MW chains?*

Extra peak for degraded samples in high f range. Emergence of additional polymer motions.

extra peak -faster motions

Collaborations

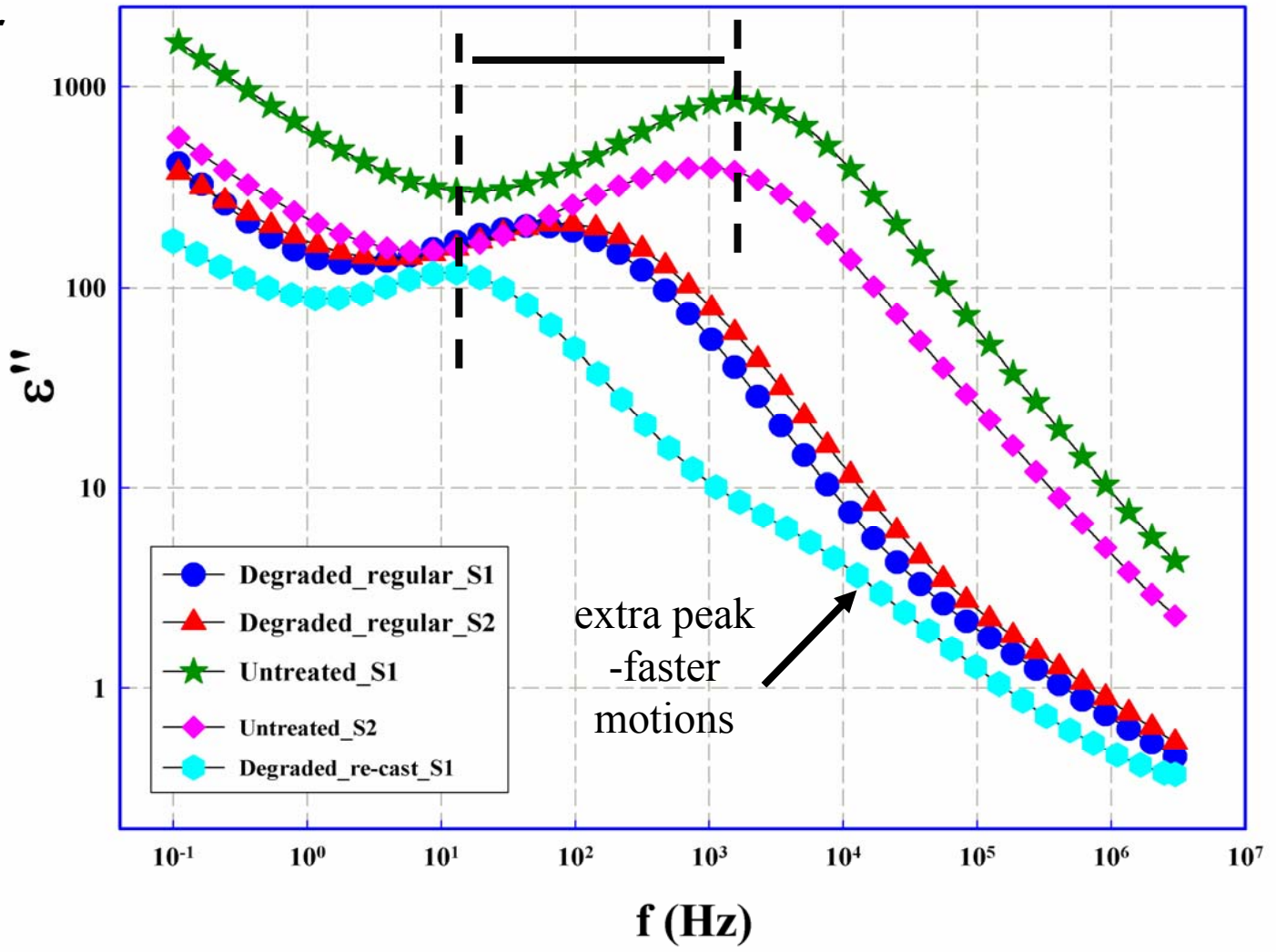- Prof. Vijay Ramani, Illinois Institute of Technology, Chicago.

Proposed Future Work

- Condensation of phosphonic acid ketone with phenol; polymerization of resulting 2,2-bis(4-hydroxyphenyl) perfluoropropane phosphonic acid with aromatic dihalide vis NAS.

- Synthesis of sulfonic acid ketone with phenol and subsequent polymerization.

- Solution cast hydrocarbon membranes will be prepared for structure-property-conductivity characterization and MEAs for fuel cell testing.

- *Ex-situ* tests of hydrocarbon membrane durability will be performed.

- Inorganic modification of synthesized hydrocarbon membranes for enhanced durability. Battery of structure-property-performance tests.

- Extension of dielectric spectroscopy studies to the gigahertz region.

Summary Slide

- Relevance: Attain DOE goal of high temperature proton exchange membrane fuel cells for automotive applications.
- Approach: Synthesize novel stable hydrocarbon membrane polymers that are economical. Characterize structure-properties and fuel cell performance of novel membranes.
- Technical Accomplishments and Progress:
  - A key monomer precursor, 2-oxo-1,1,3,3,3-pentafluoropropane phosphonic acid diethyl ester, was synthesized and purified for condensation with phenol
  - 4,4'-Dichlorodiphenyl)sulfone 3,3'-disulfonc acid was prepared for benchmark hydrocarbon resin synthesis
  - Open circuit voltage (OCV) decay curves for degraded Nafion® MEAs established for comparison w/ degraded hydrocarbon MEAs. Mechanical studies of degraded samples, related to mechanical durability with RH cycling, were conducted.
  - Scanning electron microscopy of OCV-degraded creep samples show cracks rather than crazes as is the case for non-degraded creep samples.
  - Dielectric spectroscopy analysis show shifts in polymer chain motions with degradation.
- Collaborations: Professor Vijay Ramani, IIT, Chicago.
- Proposed Future Research:
  - Condensation of phosphonic acid ketone with phenol; polymerization of resulting 2,2-bis(4-hydroxyphenyl) perfluoropropane phosphonic acid with aromatic dihalide vis NAS.
  - Synthesis of sulfonic acid ketone with phenol and subsequent polymerization.
  - Solution cast hydrocarbon membranes will be prepared for structure-property-conductivity characterization and MEAs for fuel cell testing.
  - *Ex-situ* tests of hydrocarbon membrane durability will be performed.
  - Inorganic modification of synthesized hydrocarbon membranes for enhanced durability. Battery of structure-property-performance tests.
  - Extension of dielectric spectroscopic characterization to the gigahertz region.

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