Poly(cyclohexadiene)-Based Polymer Electrolyte Membranes for Fuel Cell Applications

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Project ID # FC25

Overview

Timeline

- Start: April 2006
- End: April 2011
- 40% complete

Budget

- Total project funding
  - DOE share $1.5M
  - Contractor share $500K
- Funding received in FY07 $300K
- Funding for FY08: $300K

Barriers

- Barriers addressed
  - Thermal stability of PEMs
  - High temperature, low RH proton conductivity
  - Cost

Partners

- Univ. of Southern Mississippi
- ORNL

Objectives

- The objective of the work proposed herein is to synthesize and characterize novel neat and inorganically modified fuel cell membranes based on poly(1,3-cyclohexadiene) (PCHD).
- To achieve these objectives, a range of materials incorporating poly(cyclohexadiene) (PCHD) will be synthesized, derivatized, and characterized.
- Successful completion of this project will result in the development of novel potentially inexpensive PEM membranes engineered to have high conductivity at elevated temperatures and low relative humidity.

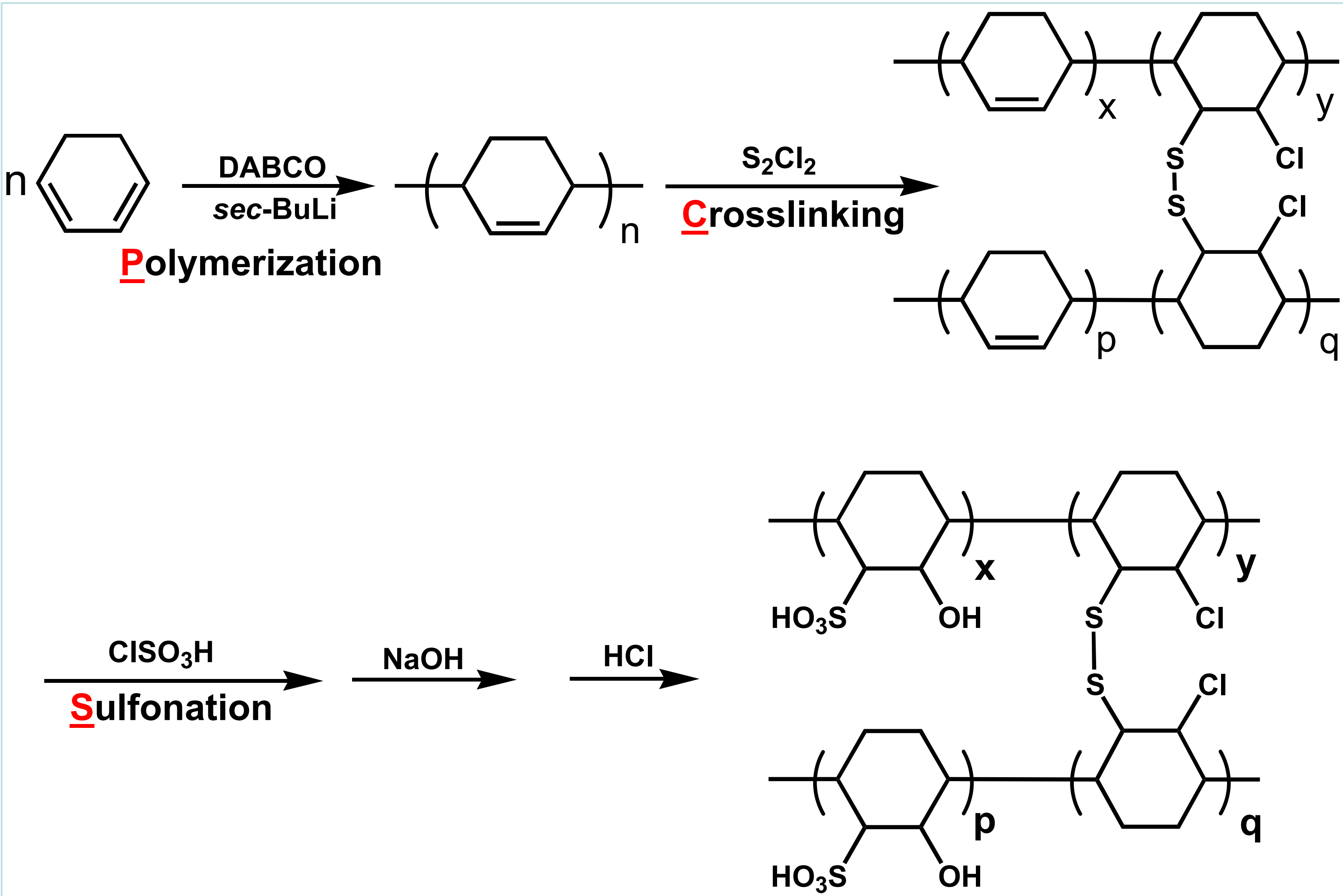
Key Milestones FY07-FY08

- Synthesis of 6 different crosslink type membranes (03/31/07)
- Meet initial conductivity milestone (0.07 S/cm at 80% RH) (01/01/08)
- Synthesis of multiblock copolymers (03/31/08) DOE target (σ > 0.1 S/cm at 50% RH at 120º C – Go/No Go Decision in 3rd quarter of Year 3)

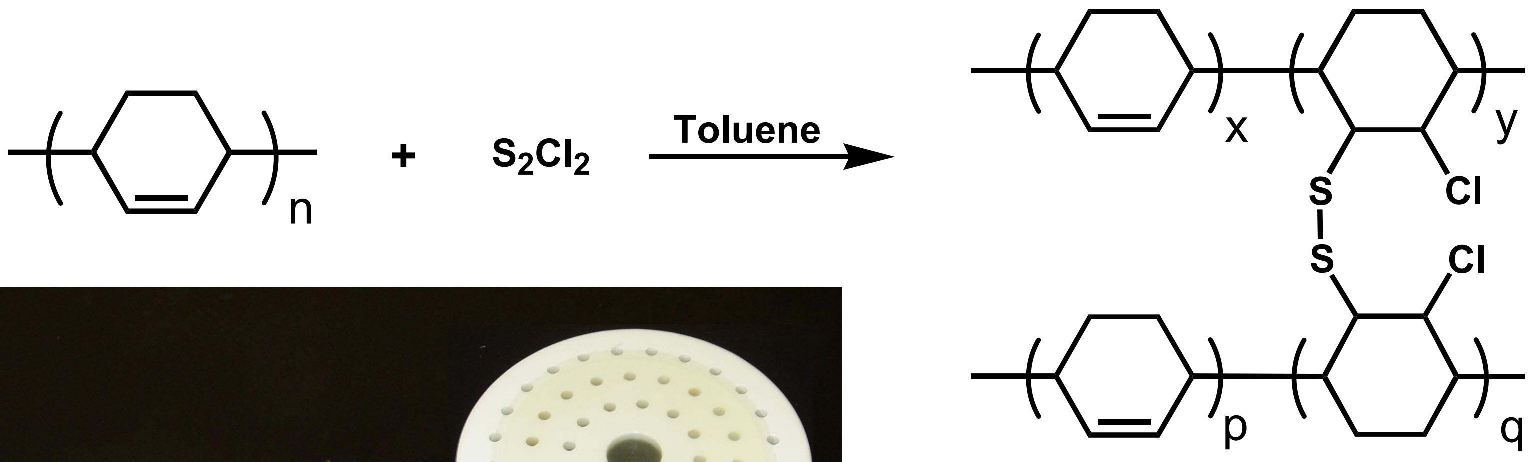
Approach

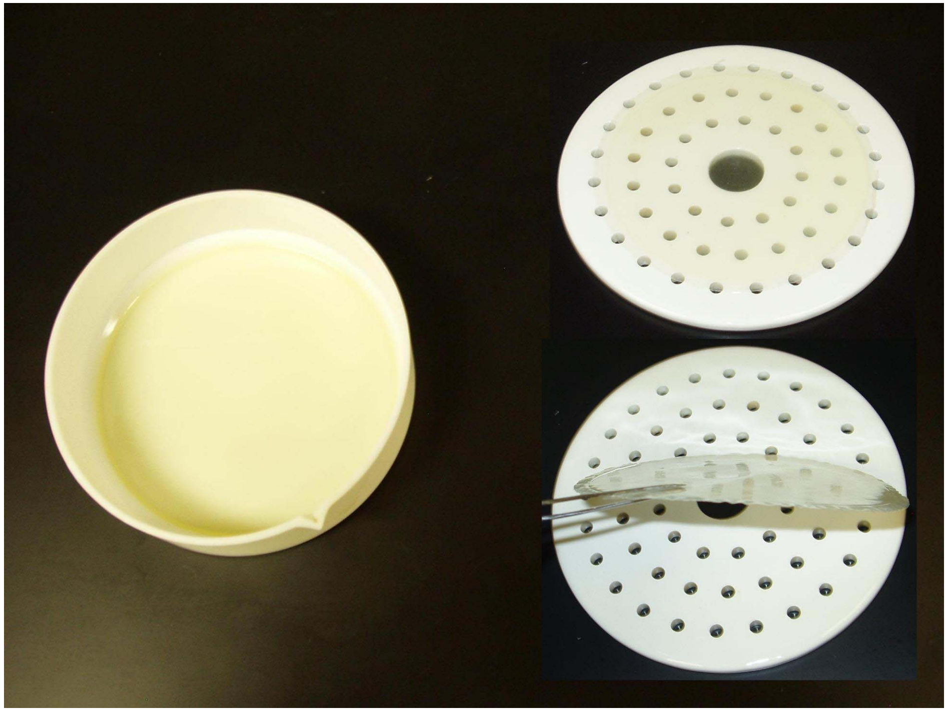
- Anionic polymerization and post-polymerization chemistry are utilized to synthesize novel thermally stable proton conducting membranes based on a potentially inexpensive hydrocarbon monomer, 1,3-cyclohexadiene.
- Inorganic modification of these novel membranes via a sol/gel process is used to enhance proton conductivity and thermal stability.
- Thorough characterization of the membranes is carried out to develop structure/property relationships.

RESULTS: PCS Approach



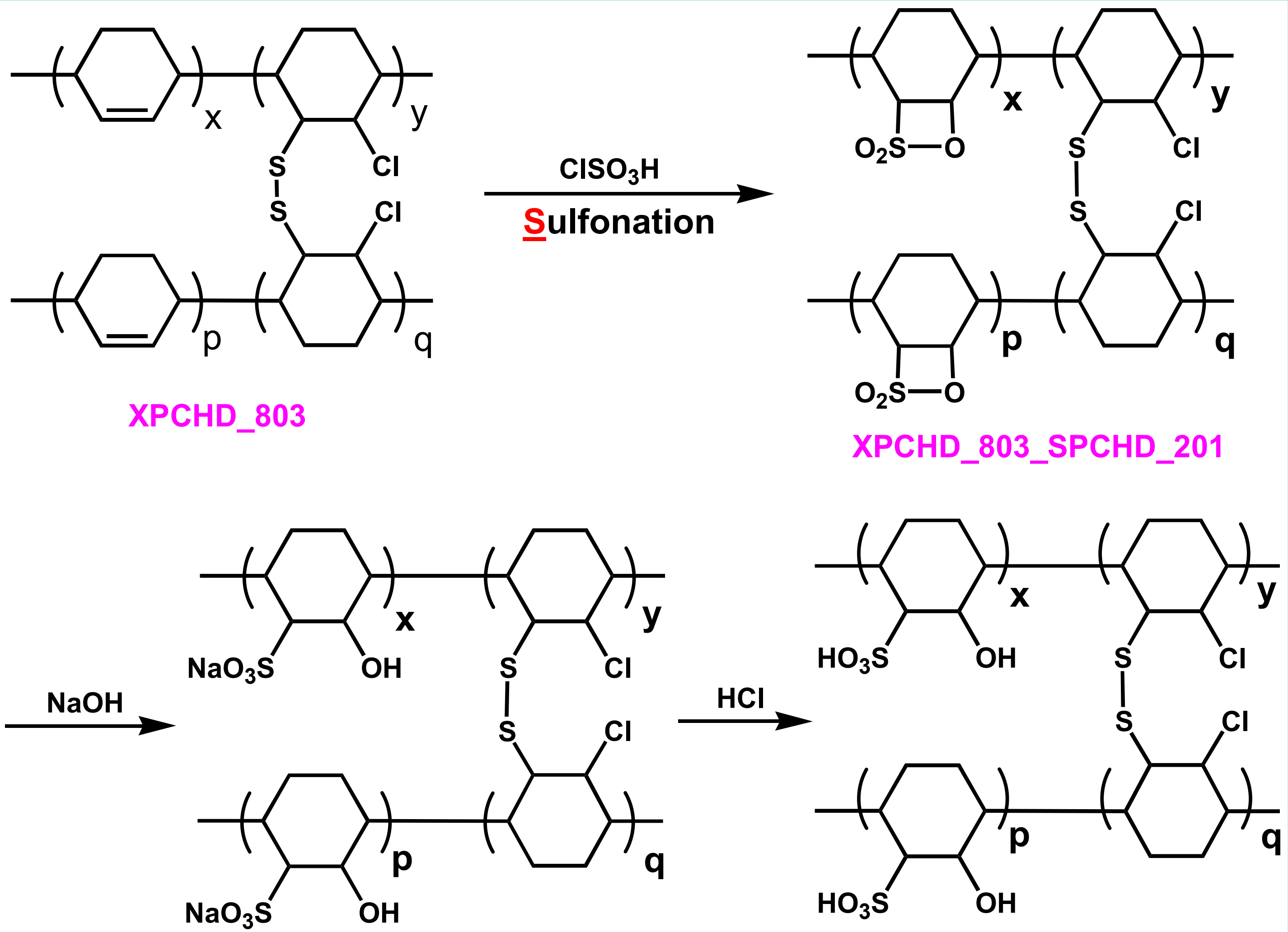
Crosslinking: Membrane Casting





- Choice of solvent
- Concentration of PCHD
- Molar ratio of S_2Cl_2
- Evaporation rate of solvent
- Temperature

Sulfonation: Formation of PEMs



XPCHD_803_SPCHD_202
Sodium Form

XPCHD_803_SPCHD_203
Acid Form

Elemental Analysis of Final Membranes

Sample	Expt. Content %	Calculated Formula	Yield
XPCHD_501	C: 84.24; H: 9.93; N: 0.50 S: 3.96; Cl: 2.15; O: 1.72	$C_6H_{8.43}N_{0.03}S_{0.11}Cl_{0.05}O_{0.09}$	5% Crosslinking S:Cl= 11:5
XPCHD_501_SPCHD_103	C: 45.30; H: 5.88 S: 11.89; Cl: 1.19; O: 31.12	$C_6H_{9.28}S_{0.59}Cl_{0.05}O_{3.09}$	48% sulfonation
XPCHD_803	C: 80.27; H: 9.28; N: 0.50 S: 6.09; Cl: 2.77; O: 1.62	$C_{6.00}H_{8.26}N_{0.03}S_{0.17}Cl_{0.07}O_{0.09}$	7% Crosslinking S:Cl= 17:7
XPCHD_803_SPCHD_203	C: 47.19; H: 5.49 S: 12.53; Cl: 1.03	$C_{6.00}H_{8.32}S_{0.60}Cl_{0.04}$	43% sulfonation
XPCHD_902	C: 87.81; H: 9.95 S: 3.81; Cl: 1.40	$C_{6.00}H_{8.10}S_{0.10}Cl_{0.03}$	3% Crosslinking S:Cl= 10:3
XPCHD_901_SPCHD_104	C: 72.09; H: 7.59 S: 6.34; Cl: 1.12; O: 10.12	$C_{6.00}H_{7.53}S_{0.20}Cl_{0.03}O_{0.63}$	10% sulfonation
XPCHD_902_SPCHD_103	C: 59.39; H: 7.16 S: 8.04; Cl: 0.26; O: 20.71	$C_{6.00}H_{8.62}S_{0.30}Cl_{0.01}O_{1.57}$	20% sulfonation
XPCHD_902_SPCHD_104	C: 49.70; H: 5.80 S: 9.73; Cl: 0.25; O: 29.88	$C_{6.00}H_{8.34}S_{0.44}Cl_{0.01}O_{2.71}$	34% sulfonation
XPCHD_902_SPCHD_108	C: 44.52; H: 6.53 S: 10.88; Cl: 0.21; O: 33.86	$C_{6.00}H_{10.49}S_{0.55}Cl_{0.01}O_{3.43}$	45% sulfonation
XPCHD_902_SPCHD_109	C: 66.13; H: 9.13 S: 9.50; Cl: 0.29; O: 26.36	$C_{6.00}H_{9.87}S_{0.32}Cl_{0.01}O_{1.80}$	22% sulfonation
XPCHD_902_SPCHD-113	C: 49.37; H: 6.66 S: 8.99; Cl: 0.19; O: 27.81	$C_{6.00}H_{9.64}S_{0.41}Cl_{0.01}O_{2.54}$	31% sulfonation

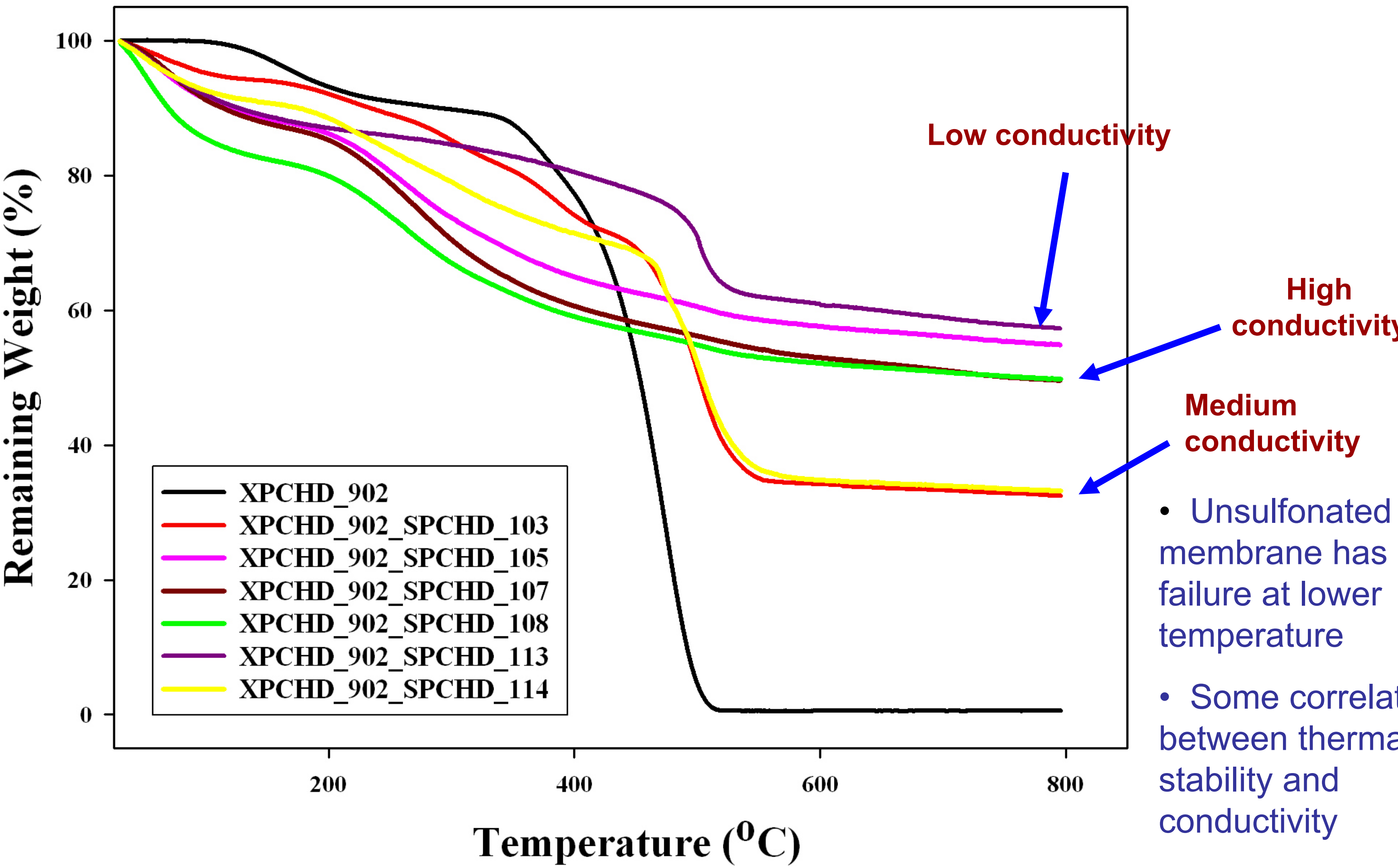
Conductivity Values for Different Samples (Early Batchs)

Sample	Conductivity (S/cm)
XPCHD_901_SPCHD_104	0.004 (low)
XPCHD_902_SPCHD_109	0.006 (low)
XPCHD_902_SPCHD_113	0.006 (low)
XPCHD_1001_SPCHD_103	0.005 (low)
XPCHD_902_SPCHD_103	0.032 (medium)
XPCHD_902_SPCHD_104	0.064 (medium)
XPCHD_902_SPCHD_114	0.043 (medium)
XPCHD_902_SPCHD_105	0.132 (high)
XPCHD_902_SPCHD_107	0.112 (high)
XPCHD_902_SPCHD_108	0.135 (high)
XPCHD_501_SPCHD_103	0.099 (high)
XPCHD_803_SPCHD_203	0.112 (high)

Conductivity Values for Different Samples (Recent Batchs)

Sample	Conductivity (S/cm)
XPCHD_1001_SPCHD_106	0.09
XPCHD_1001_SPCHD_112	0.09
XPCHD_1001_SPCHD_113	0.09
XPCHD_1001_SPCHD_115	0.12
XPCHD_1001_SPCHD_116	0.10
XPCHD_1001_SPCHD_118	0.09
XPCHD_1001_SPCHD_120	0.12
XPCHD_1001_SPCHD_122	0.09

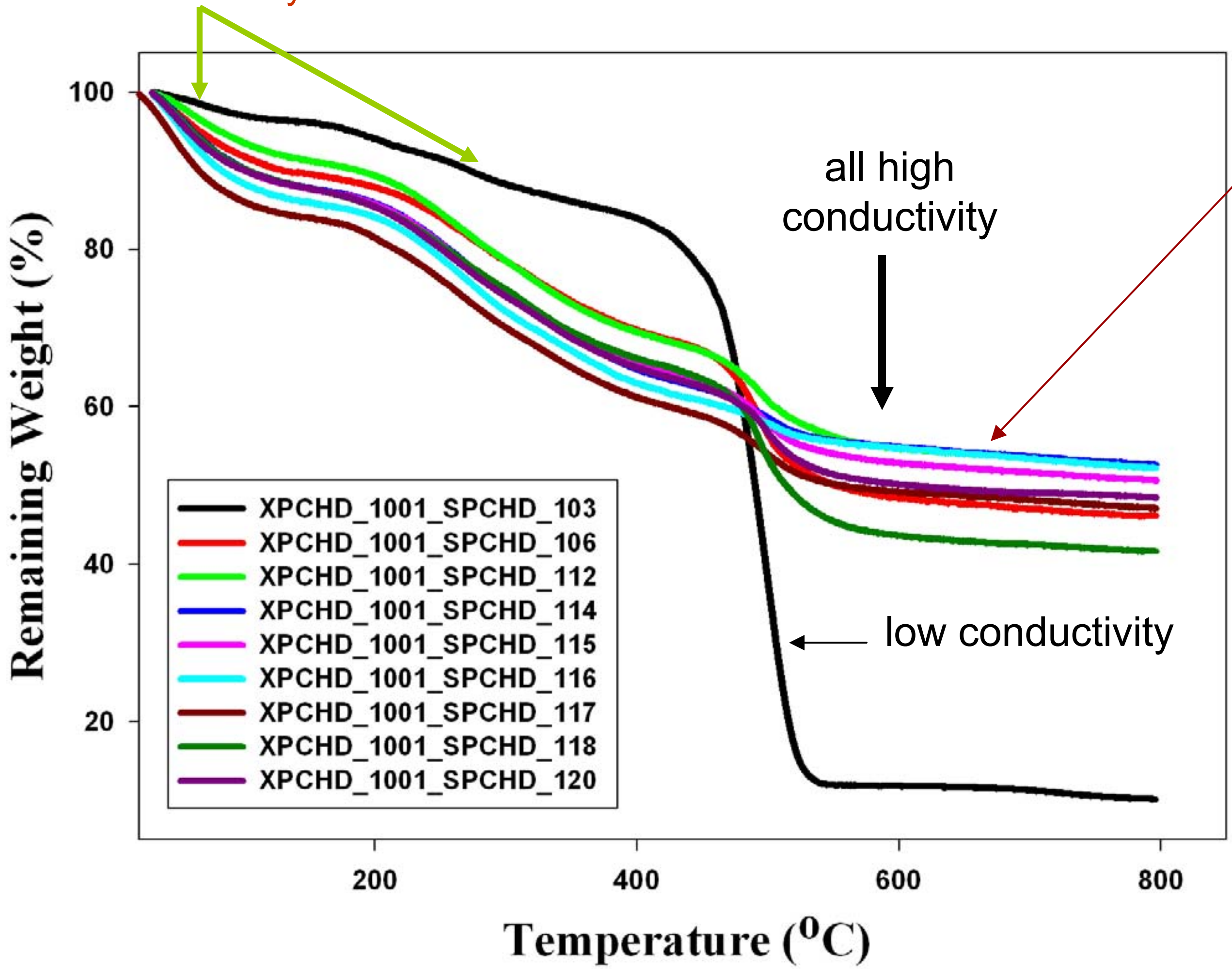
TGA Curves for Samples Having Different Conductivities



- Unsulfonated membrane has major failure at lower temperature
- Some correlation between thermal stability and conductivity

TGA for Recent Batch-High Conductivity

@ 95 ^{o}C, the polymer chain depolymerized until a more thermally stable unit on the polymer backbone was reached. The remaining backbone remained thermally stable until 200 ^{o}C

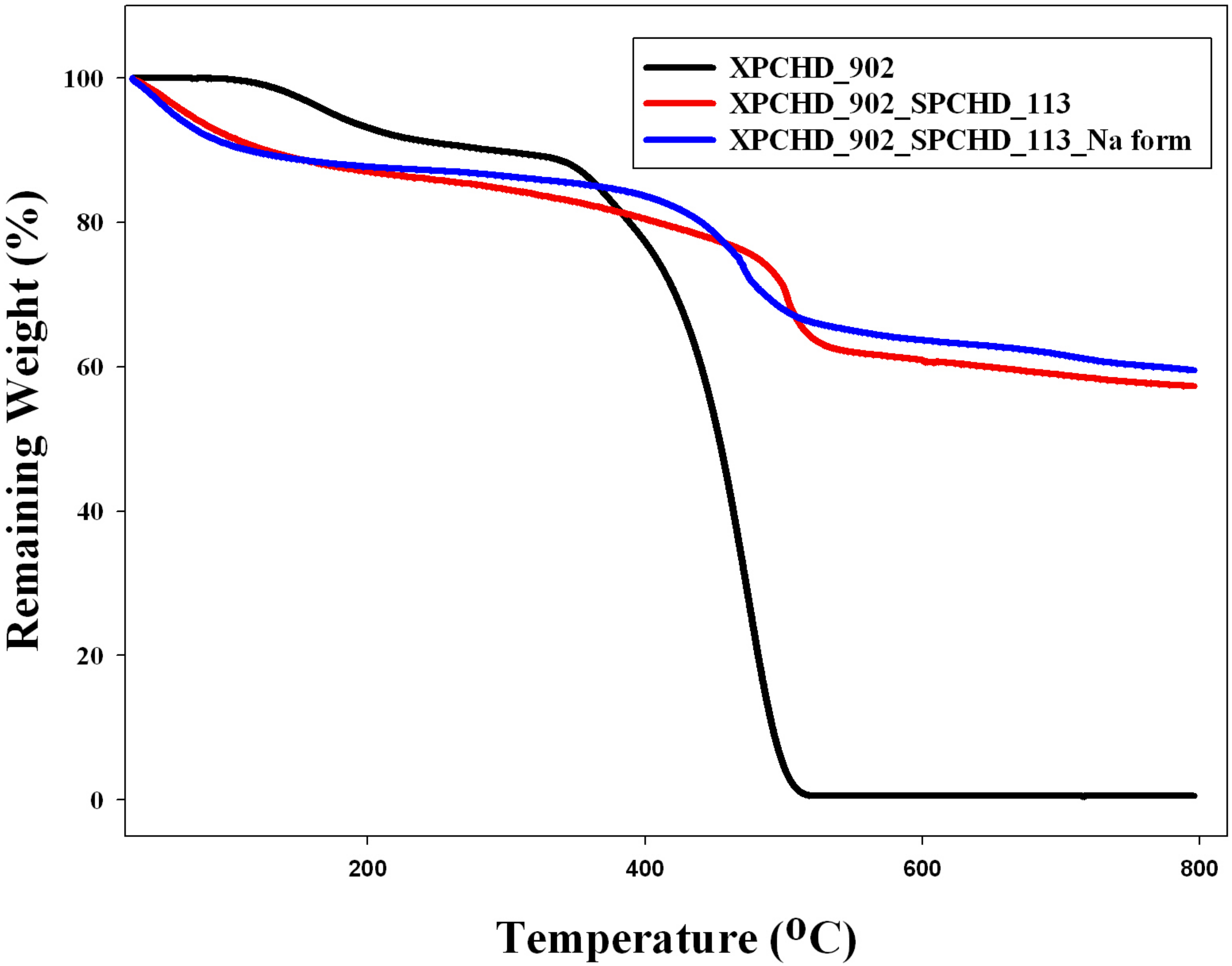


Carbonized compounds, formed from dehydrogenation of PCHD, regarded as *graphitic compounds* formed by carbonization of phenyl units

- Long, T. E. et. al. J. Polym. Sci.: Polym. Chem. **2003,** 41, 84.
- Natori, I.; Natori, S. Macromol. Chem. Phys. **2006,** 207, 1387.

TGA for SO_3H vs. Na Forms

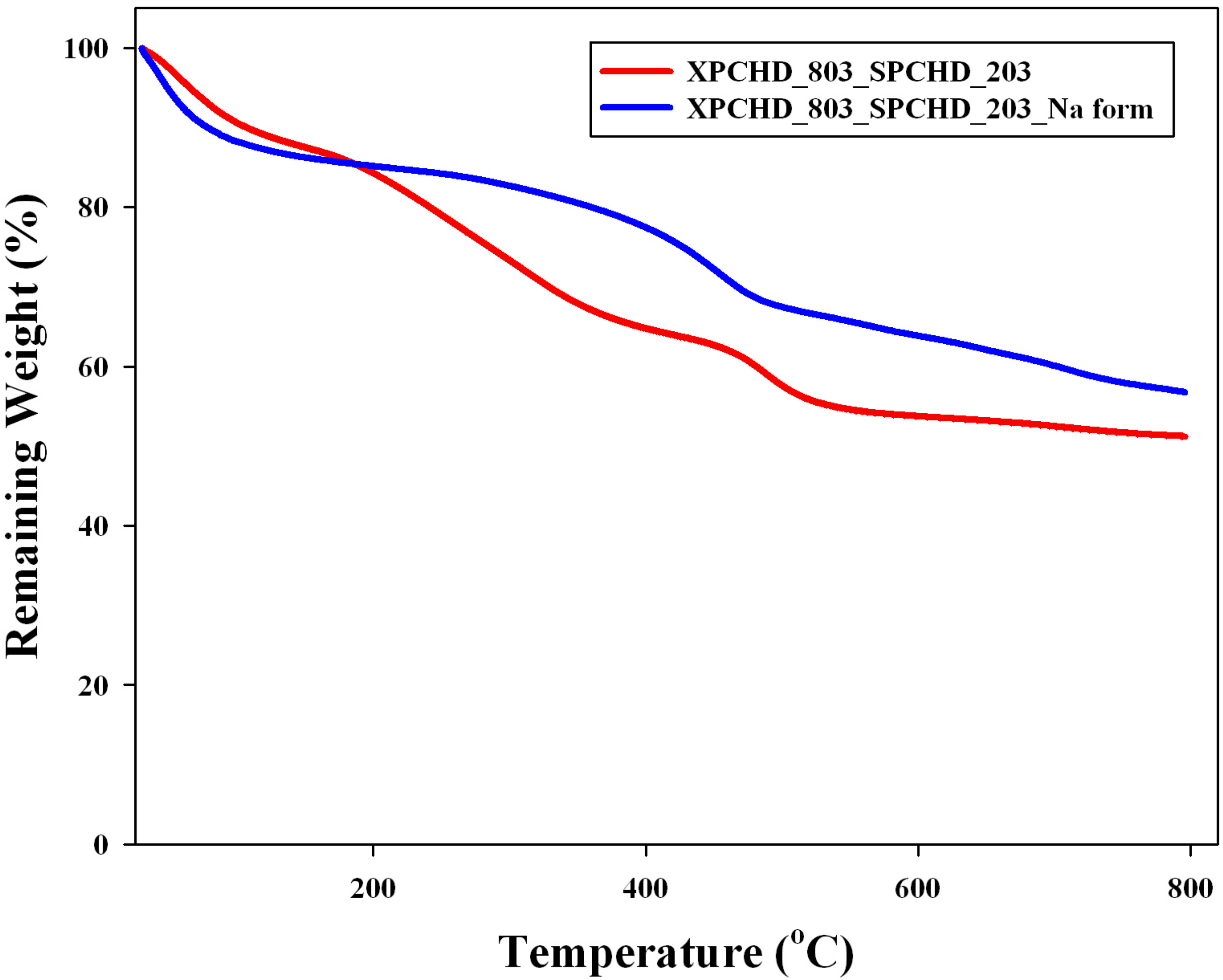
Low Conductivity Membranes



- Acid, sulfonate salt groups involved in stability at high temperature.
- Both forms behave almost the same in samples with low conductivity as concentration of $-SO_3H$ groups is low with weak interactions.

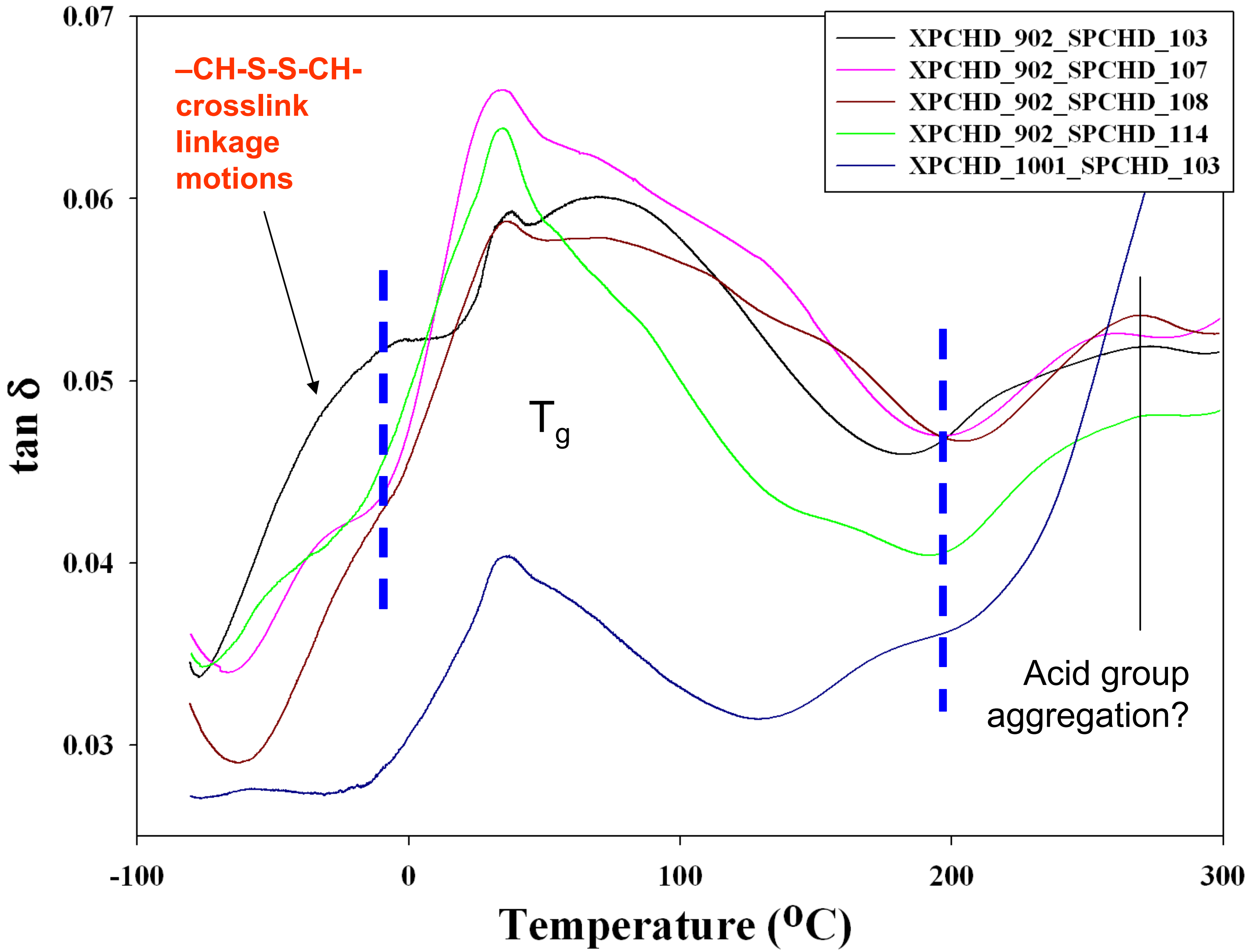
TGA for SO_3H vs. Na Forms

High Conductivity Membranes

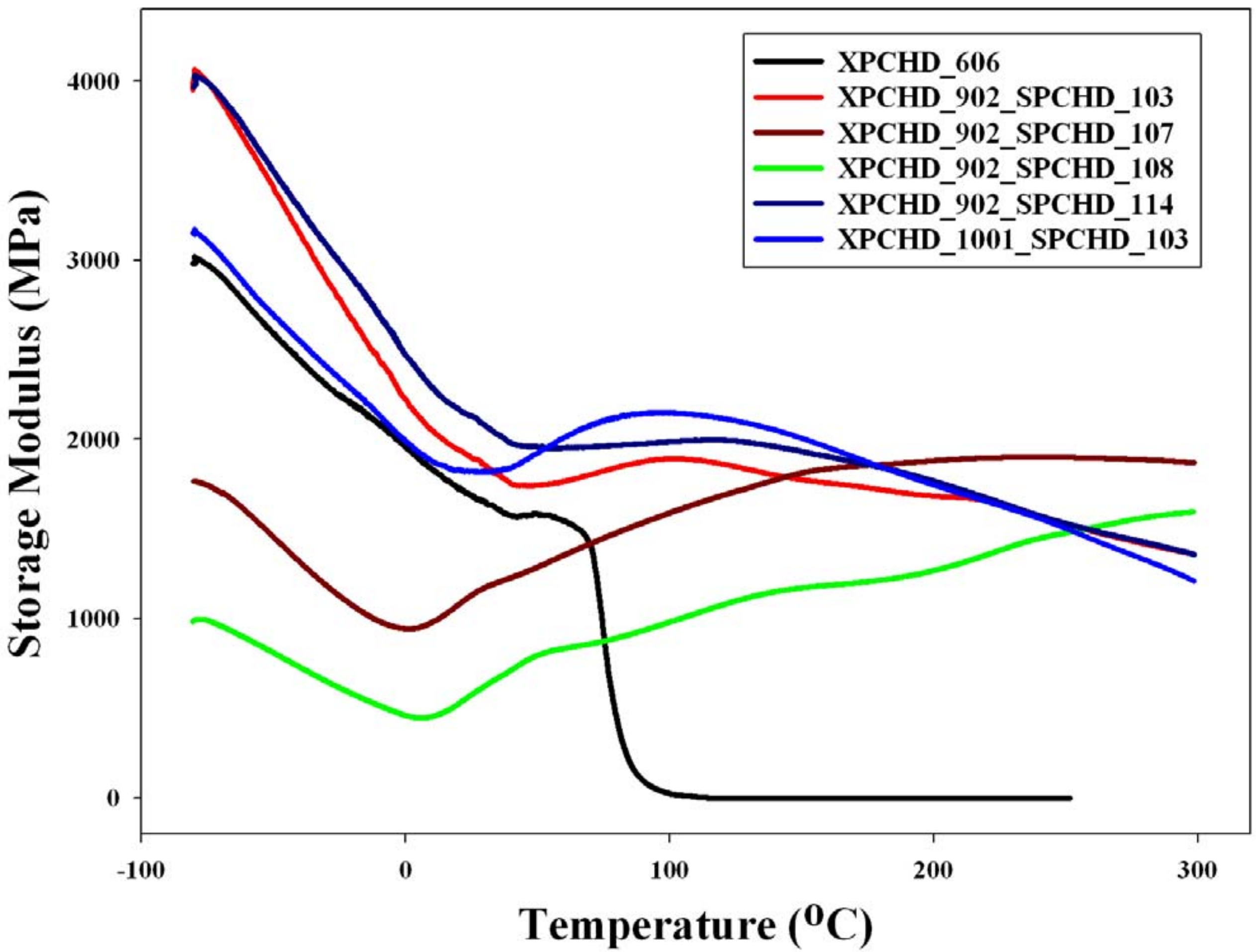


- Acid, sulfonate salt groups involved in stability at high temperature.
- Both forms behave differently with high conductivity as concentration of $-SO_3H$ groups is higher with strong interactions.

DMA for Recent Samples



DMA for Recent Samples

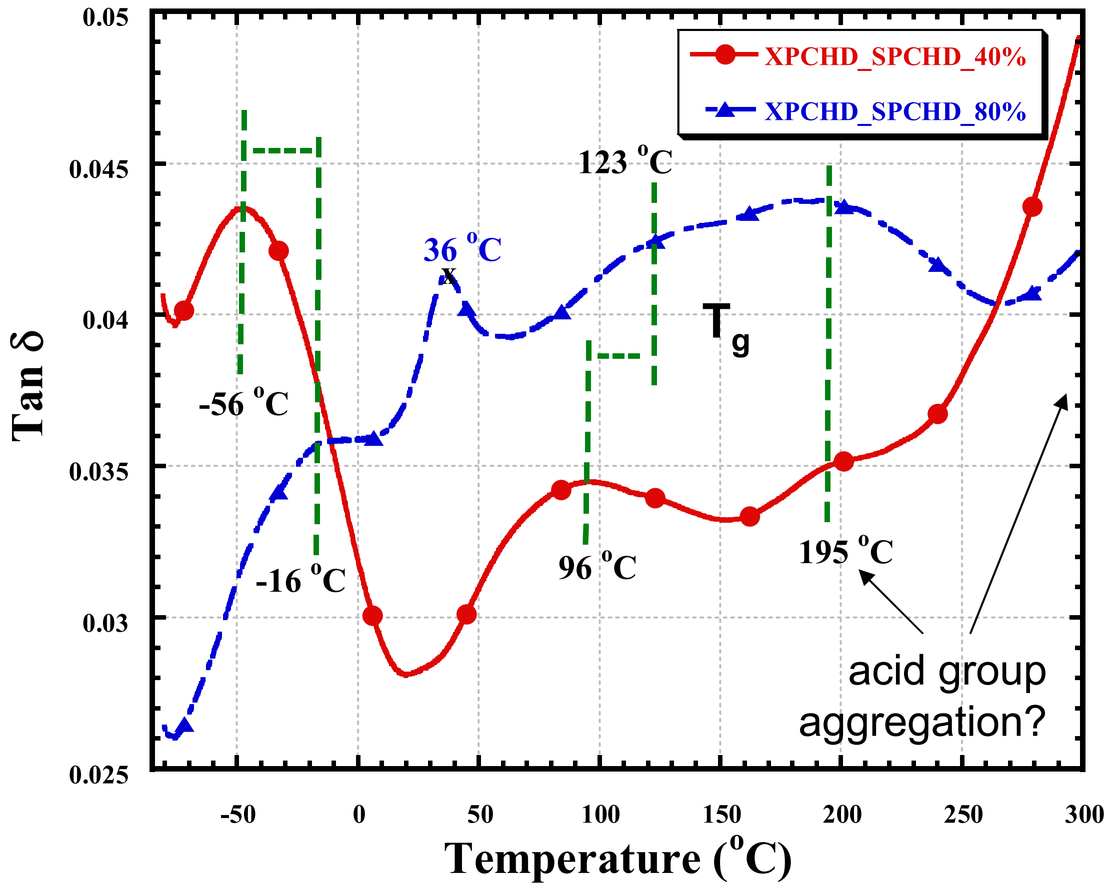


Storage modulus rises with temperature after decline - further reactions driven by heating?

Again, unsulfonated catastrophically fails early. Heat strengthening might bode well for mechanical durability.

Also, note activity ~ 100º C.

Tan δ vs. T for XPCHD_SPCHD with two degrees of sulfonation



- viscoelastic transition near FC operating temperatures- transport/durabililty implications?
- The lower temperature transition already activated before fuel cell operating temperatures.
- high temperature transitions might influence mechanical durability at high temp.
- higher temperature transitions involved with aggregations of sulfonic acid groups giving material cohesion.
- transition goes to higher temperature in passing from 40 to 80% sulfonation.

Future Work

- **Measure conductivity under different conditions. Key issue: DOE target (σ > 0.1 S/cm at 50% RH at 120º C – Go/No Go Decision in 3rd quarter of Year 3)**
- **Further optimize chemistry including sulfonation conditions. Key issue: conductivity-mechanical strength trade-off**
- **Degradation of membranes via Fenton's reagent and accelerated testing for chem/mech durability**
- **Continue inorganic modification to elevate the maximum temperature of water retention & enhance stability**
- **Fuel cell performance evaluation (polarization curves)**
- **OCV testing for durability, fuel crossover**
- **Oxygen permeability (crossover) using diffusion cells**
- **Dielectric spectroscopy to probe macromolecular motions**
- **Milestone for FY09 is to optimize the two best membrane formulations and complete testing demonstrating that the candidate membranes meet or exceed DOE targets.**

Summary

- **Flexible, potentially low cost and easily scaled up, PCHD-based membranes having proton conductivity as high as 0.135 S/cm and good mechanical strength have been successfully synthesized.**
- **Their crosslinked structure stabilizes (locks in) morphology.**
- **After some initial weight loss, membranes exhibit good thermal stability.**
- **Membranes can swell enough in water for inorganic sol-gel modification.**