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.

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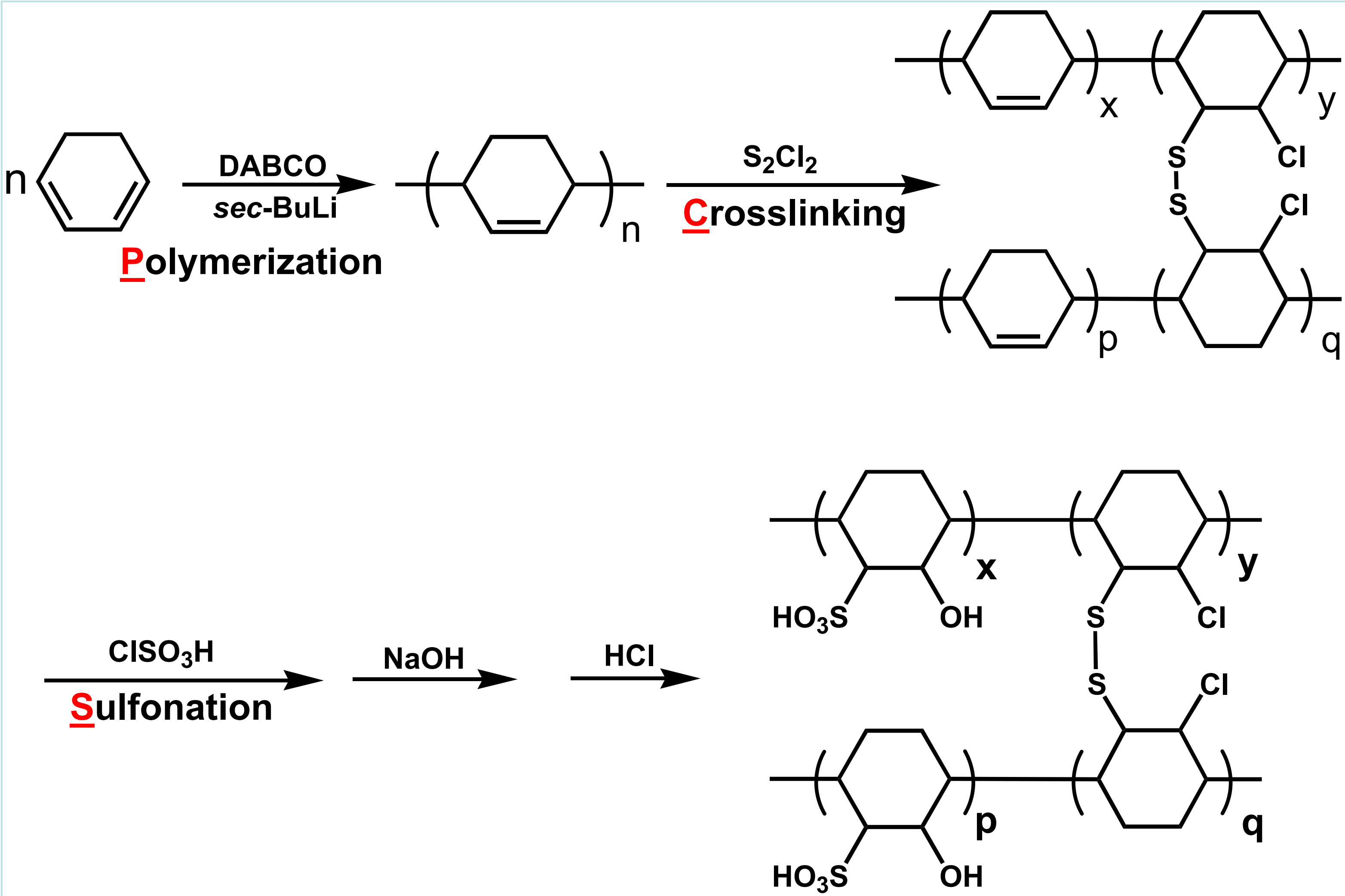
Key Milestones FY07-FY08

- 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)

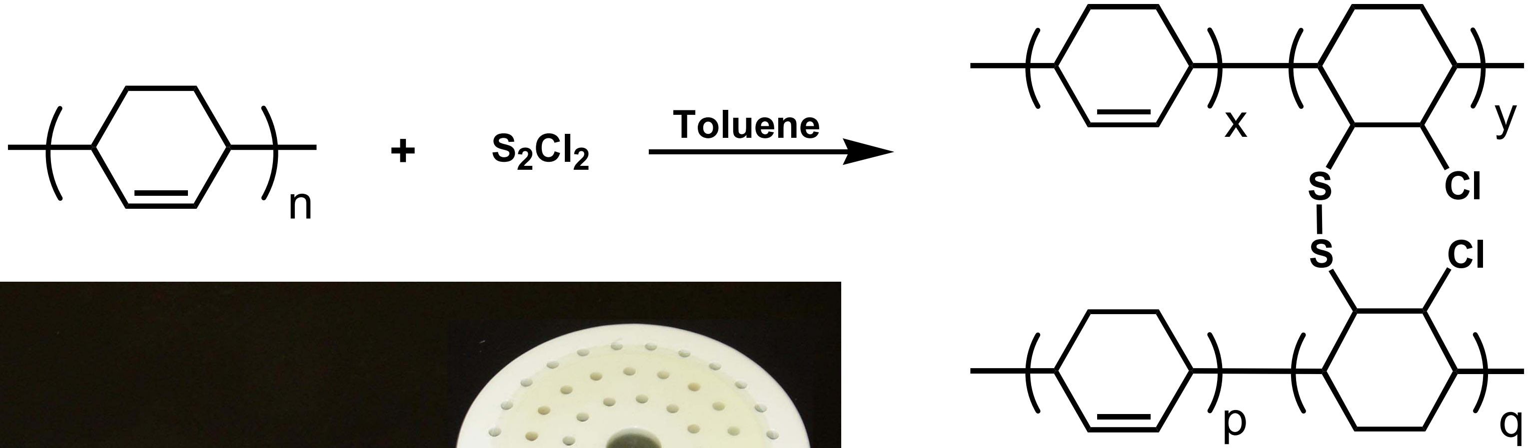
Approach

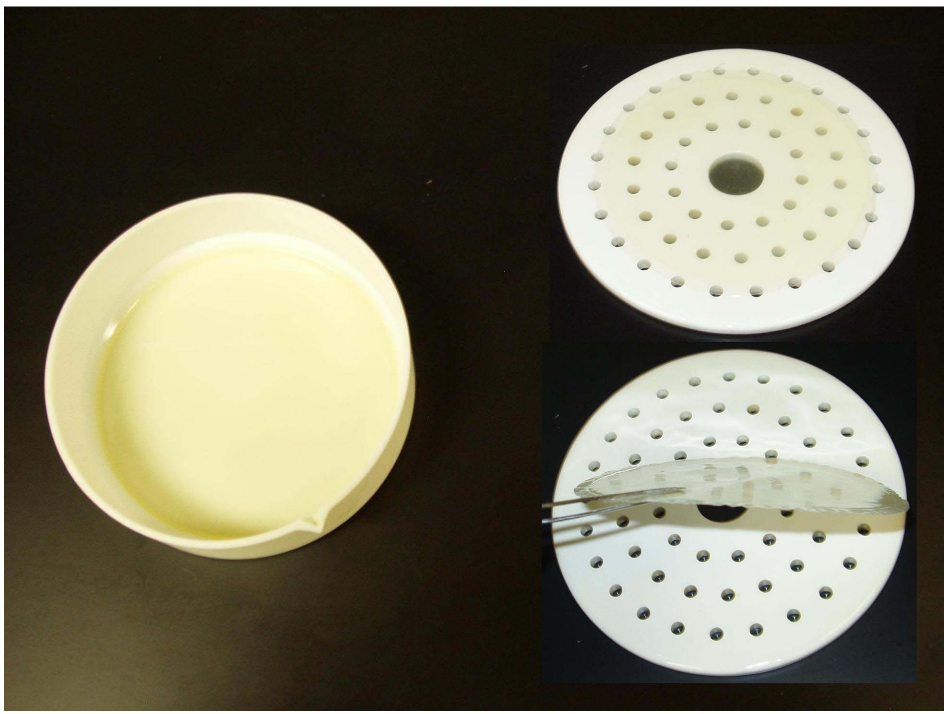
- Anionic polymerization and post-polymerization chemistry are utilized to synthesize novel thermally stable proton conducting membranes based on a potentially inexpensive hydrocarbon monomer, 1,3-cyclohexadiene.
- Inorganic modification of these novel membranes via a sol/gel process is used to enhance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

RESULTS: PCS Approach



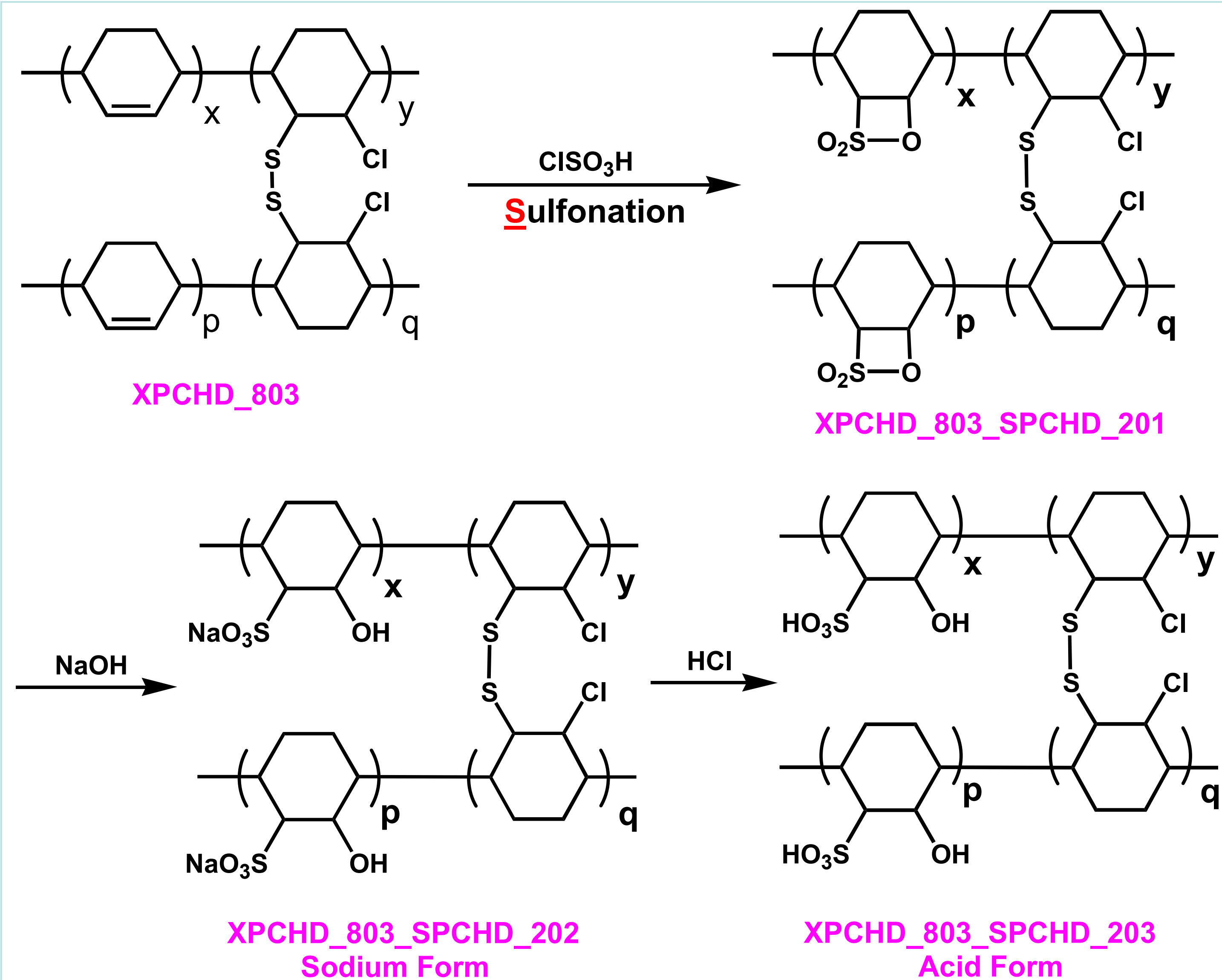
Crosslinking: Membrane Casting





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

Sulfonation: Formation of PEMs



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

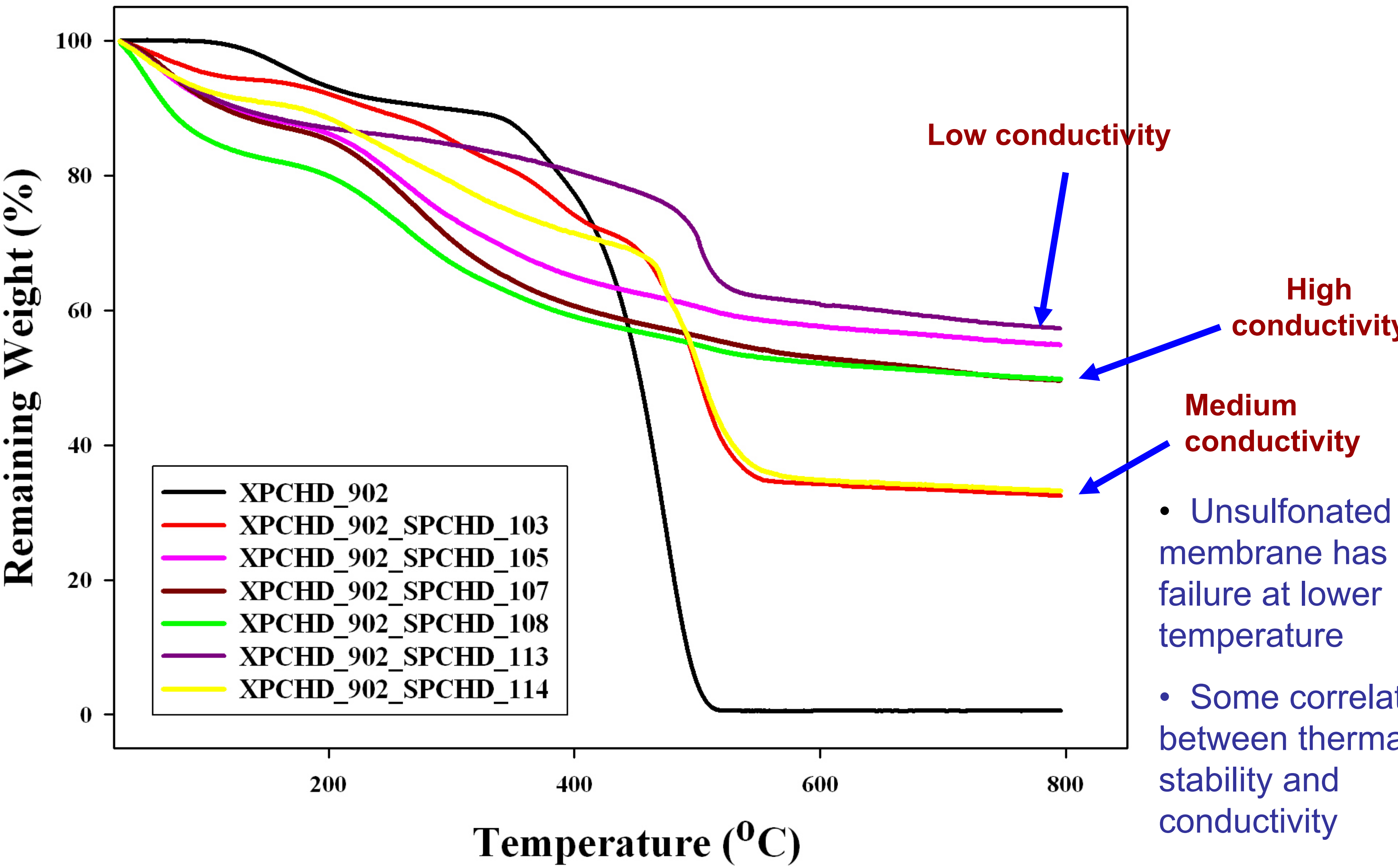
Conductivity Values for Different Samples (Early Batchs)

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

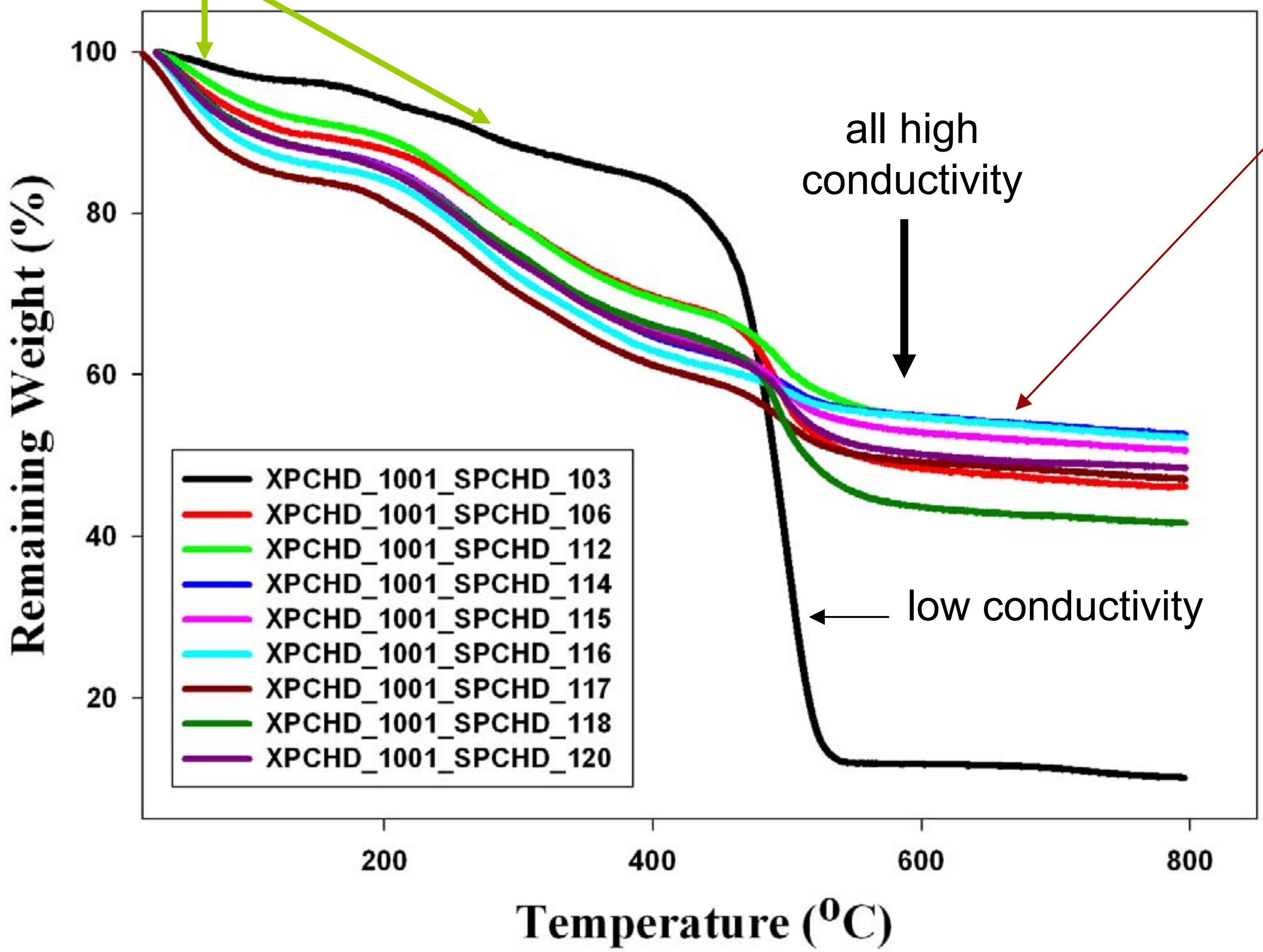
TGA Curves for Samples Having Different Conductivities



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

TGA for Recent <u>Batch-High Conductivity</u>

@ 95 °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 °C

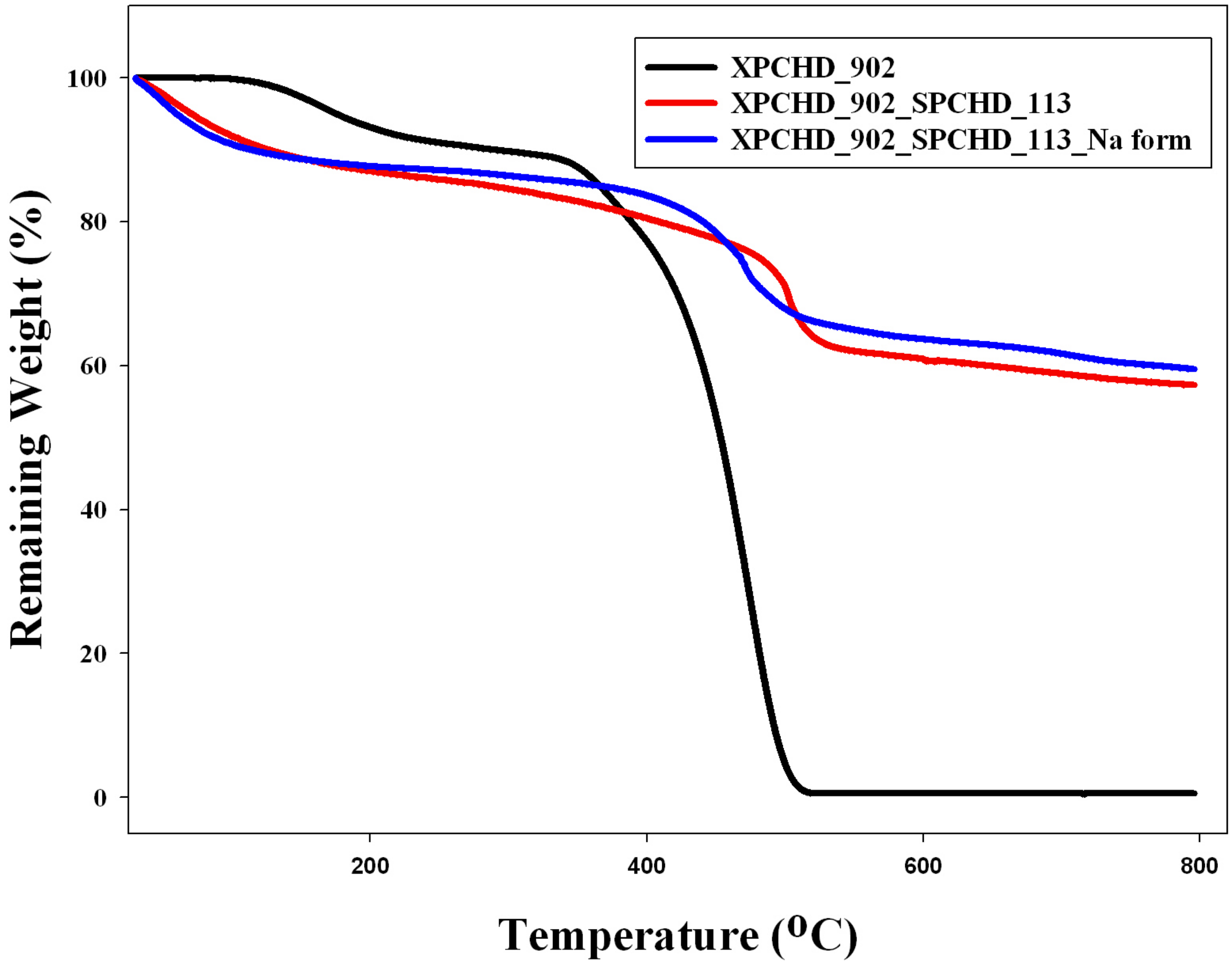


Carbonized compounds, formed from dehydrogenation of PCHD, regarded as *<u>graphitic compounds</u>* formed by carbonization of phenyl units

- 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

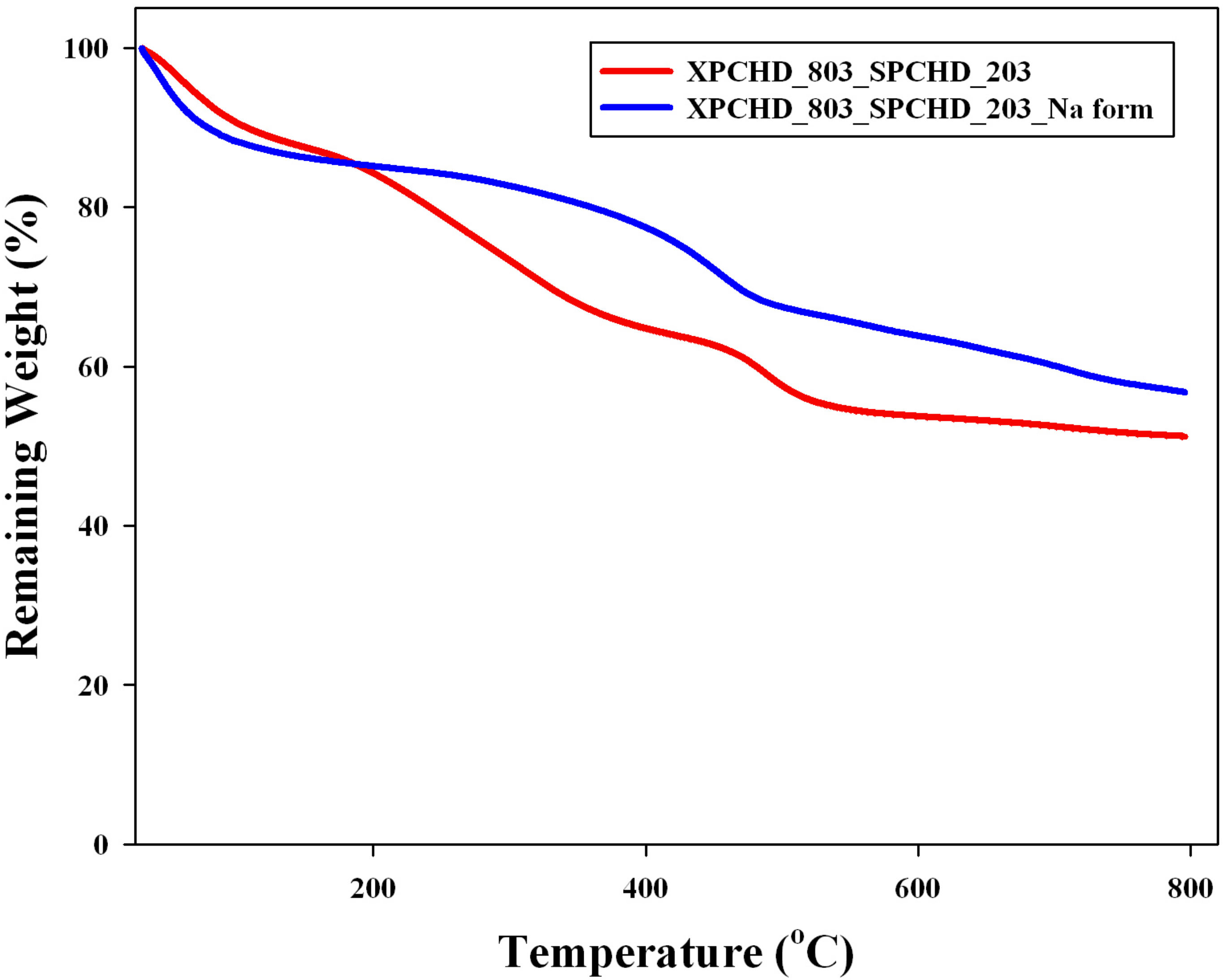
Low Conductivity Membranes



- 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.

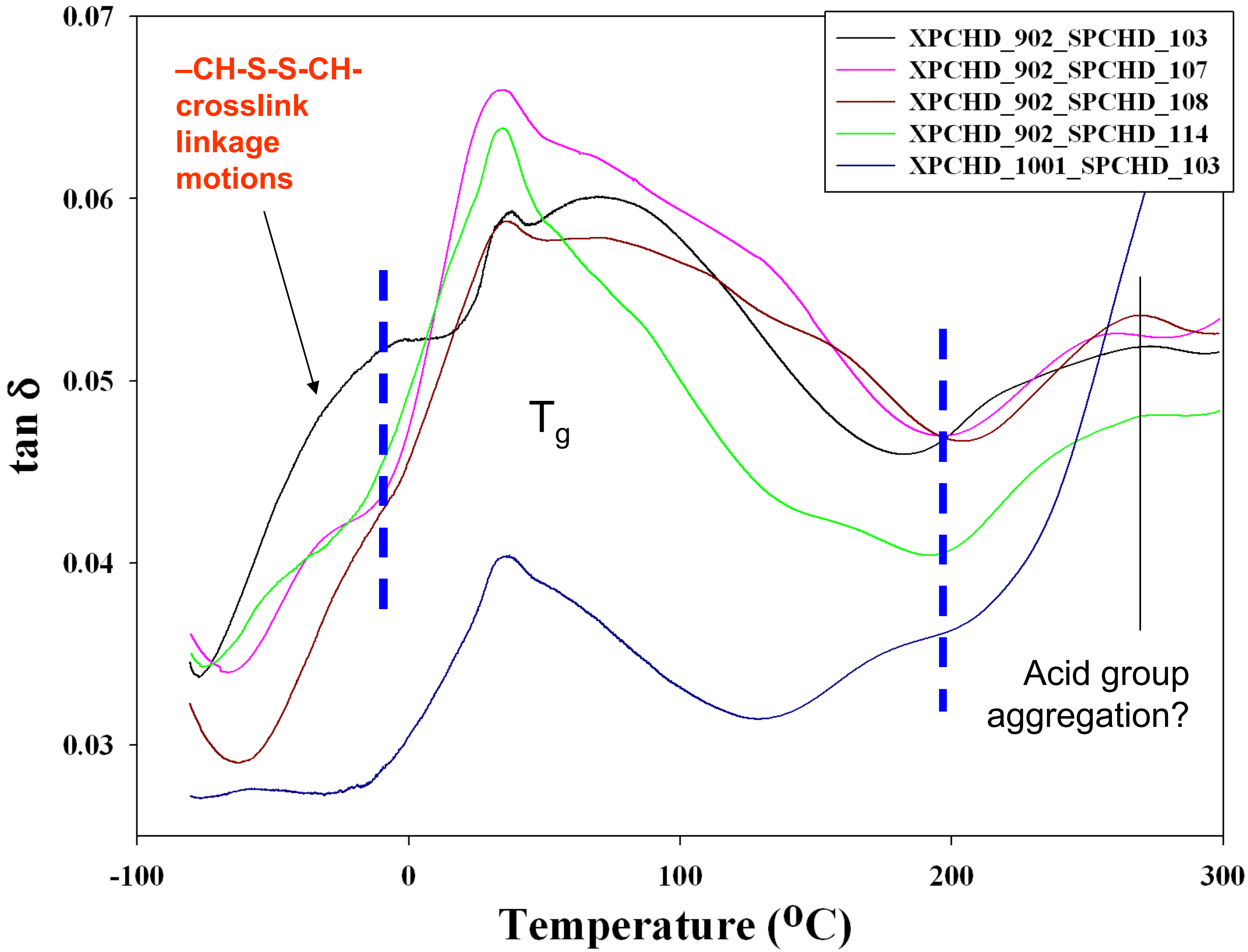
TGA for SO_3H vs. Na Forms

High Conductivity Membranes

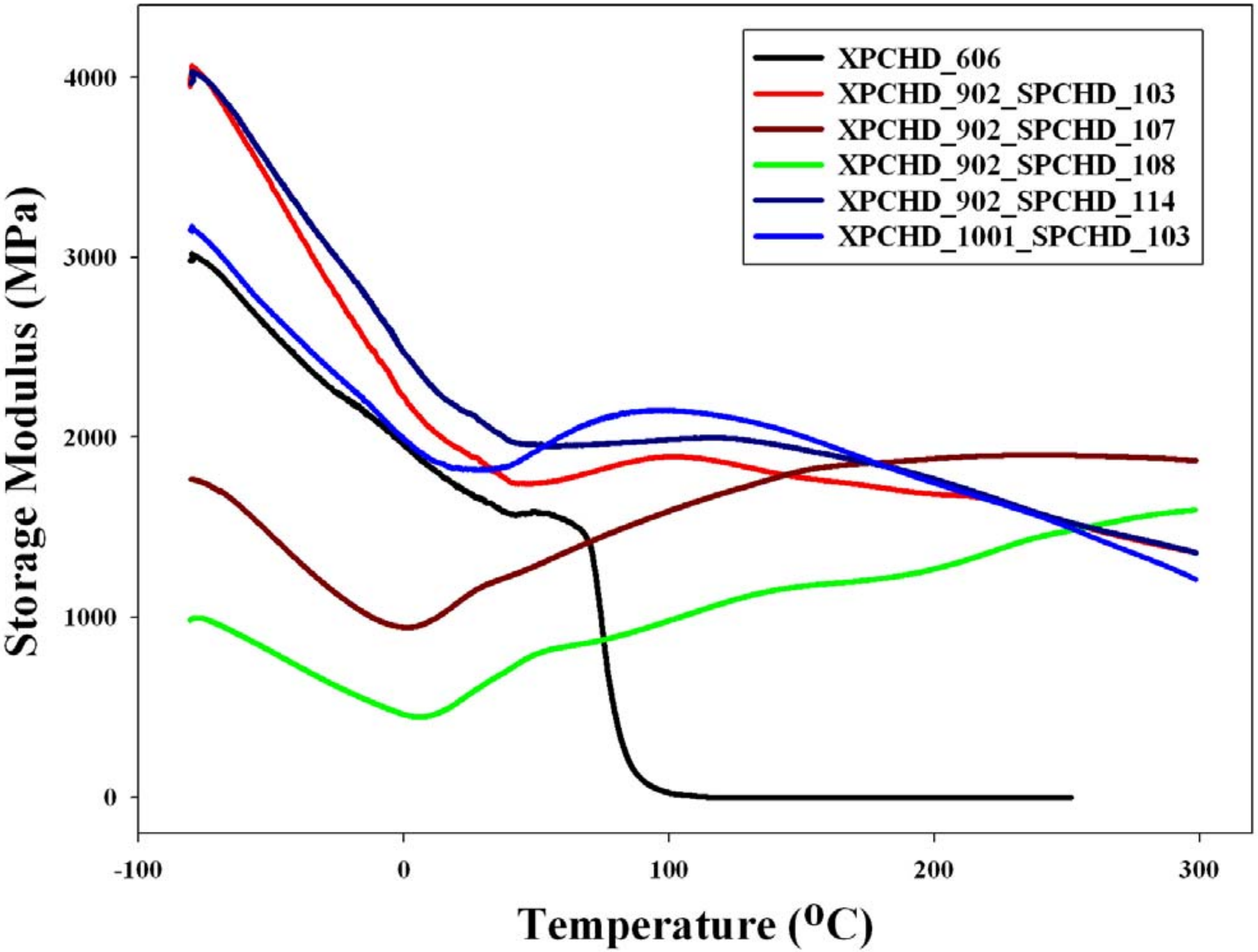


- Acid, sulfonate salt groups involved in stability at high temperature.
- Both forms behave differently with high conductivity as concentration of $-SO_3H$ groups is higher with strong interactions.

DMA for Recent Samples



DMA for Recent Samples

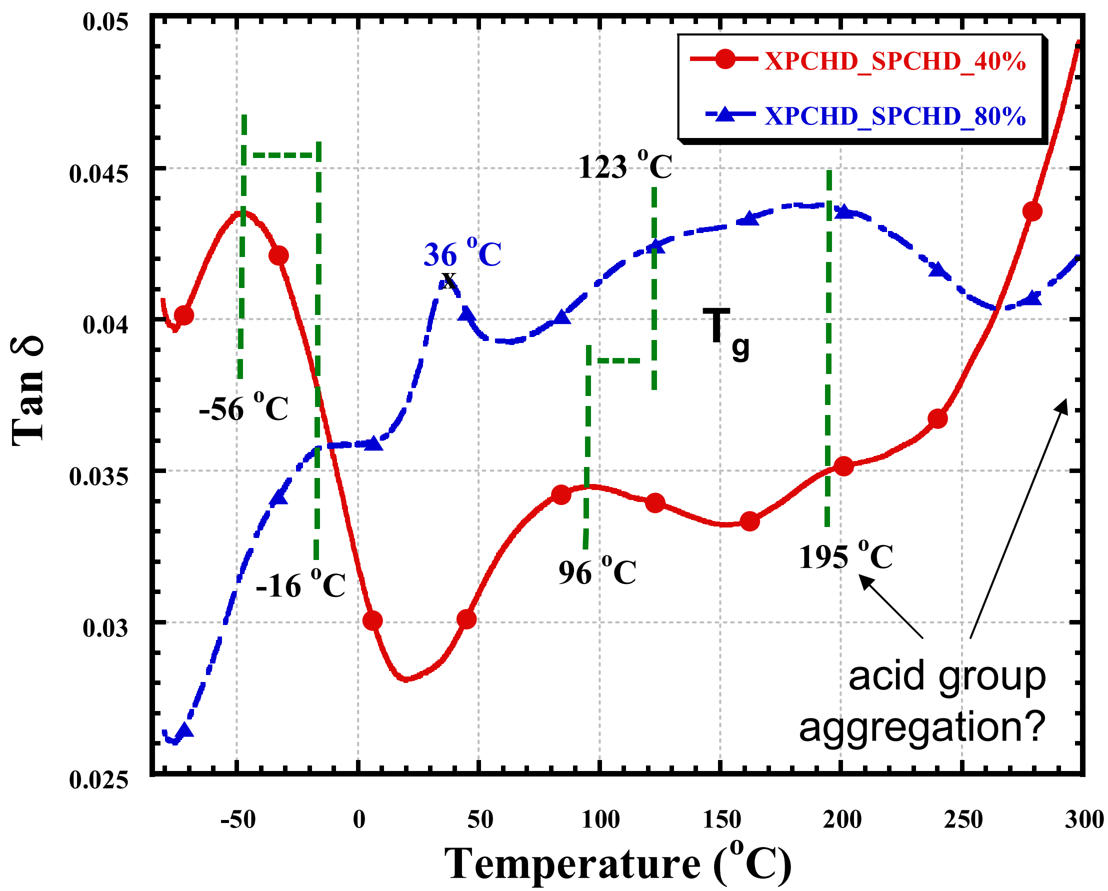


Storage modulus rises with temperature after decline - further reactions driven by heating?

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 – <u>Go/No Go Decision in 3rd quarter of Year 3</u>)**
- **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.