Design and Development of High-Performance Polymer Fuel Cell Membranes

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Overview

Timeline

Project start date:	4/2006
Project end date:	4/2011
Percent complete:	25%

Budget

Total project funding

DOE share:	$1.5M
GE share:	$0.5M

Funding received in FY06

DOE share:	$150k
GE share:	$50k

Funding for FY07

DOE share:	$300K
GE:	$100K

Barriers

Barriers addressed

- Membrane cost
- Membrane durability

Partners

GE Energy

imagination at work

Objectives

Design and develop novel polymer electrolyte membrane materials for fuel cell operation at high temperature (up to 120 °C) and low relative humidity (25-50 %RH)

FY06

- Design and synthesize new high performance polymer structures
- Design and synthesize hydrophilic organic additives
- Evaluate membrane performance with and without additives

FY07

- Design and synthesize cross-linked system
- Prepare high acid density PEM in porous supports
- Integrate hygroscopic inorganic additives
- Evaluate membrane performance at different relative humidity
- Improve chemical and thermal stability

FY08

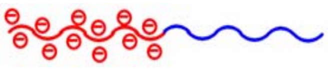
- Improve conductivity at low RH and high temperature (0.1S/cm 50%RH/120°C).

Approaches

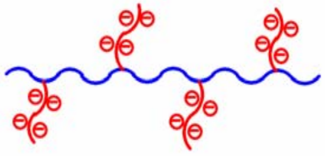
Copolymer architecture

- Thermally stable aromatic hydrocarbon polymers
- Balance proton conductivities, water uptake, and mechanical properties via material design

Gen 1



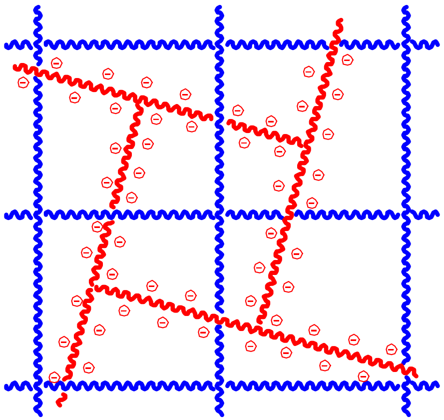
Gen 2



Gen 3

Cross-linked system in porous support

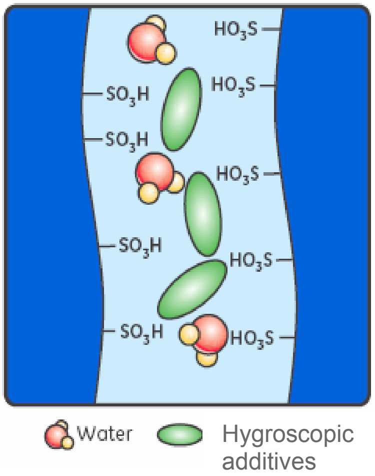
- High acid concentration with no leaching
- Cross-link chemistry design
- Control of the cross-link density
- Selection and fabrication of the porous supports
- Impregnation
- Evaluation of properties



Gen 4 : Cross-linked system in porous support

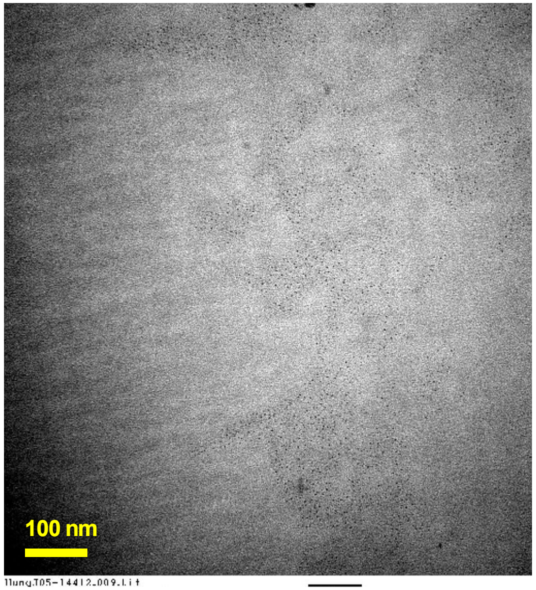
Introduction of the inorganic additives

- Improvement in the conductivity, especially at low RH



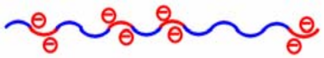
Gen 5 : with inorganic additives

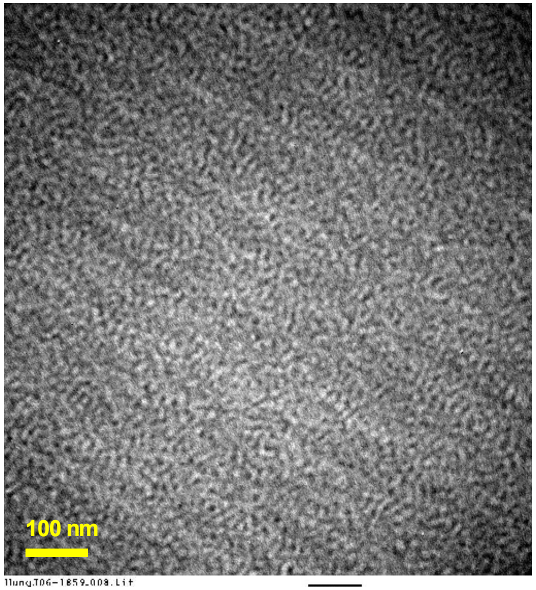
Control in copolymer architecture



Gen 1 : random copolymer

$\sigma \sim 10^{-3}$ S/cm (50 %RH)



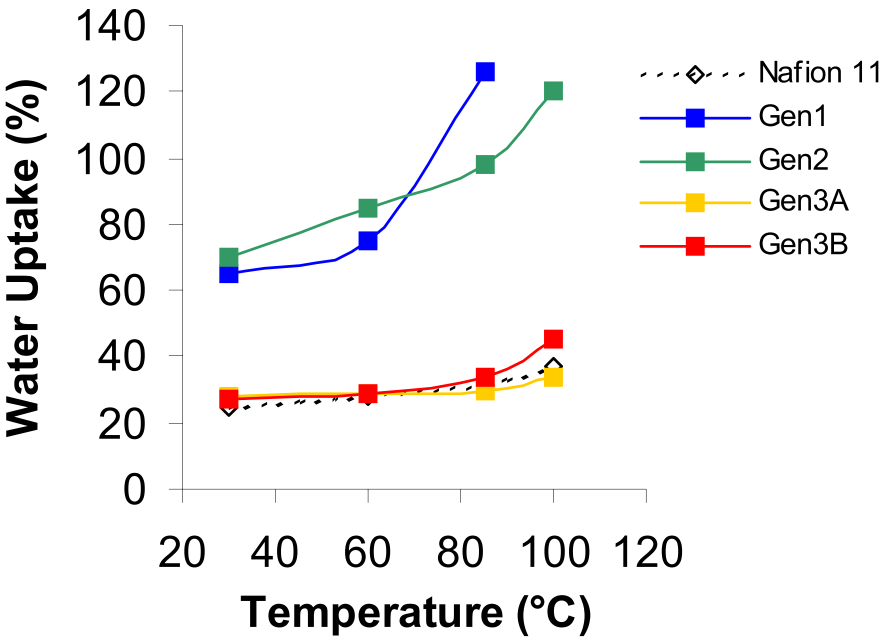


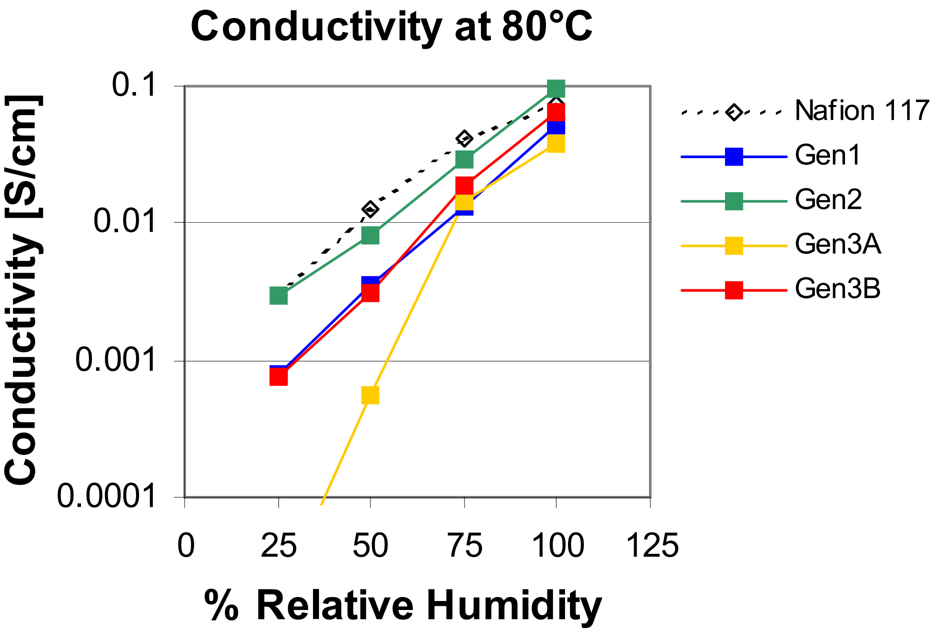
Gen 2 : block copolymer

$\sigma \sim 10^{-2}$ S/cm (50 %RH)

- Hydrophilic-hydrophobic phase separation is observed in Gen 2.
- The phase separated hydrophobic segment is expected to work as a scaffold and suppress the water uptake.
- Higher conductivity in Gen 2 through formation of efficient hydrophilic channels.

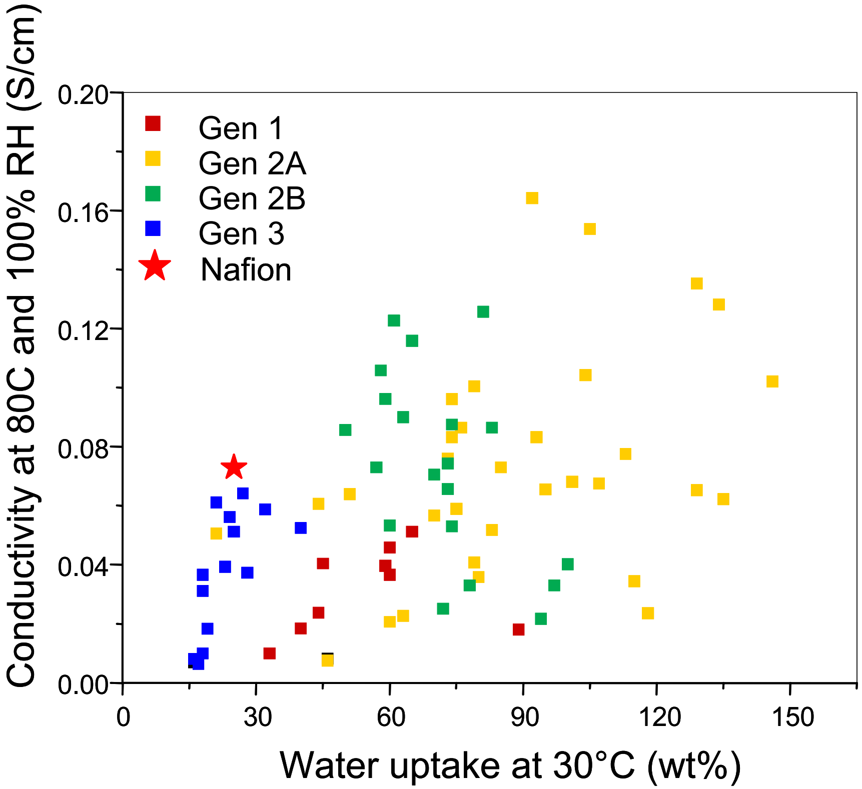
Water Uptake





- Water uptake was reduced in Gen3.
- Gen 2 demonstrated conductivity at the same level as Nafion.
- Within Gen 3, higher acid concentration resulted in the higher conductivity.

Conductivity vs. Water Uptake

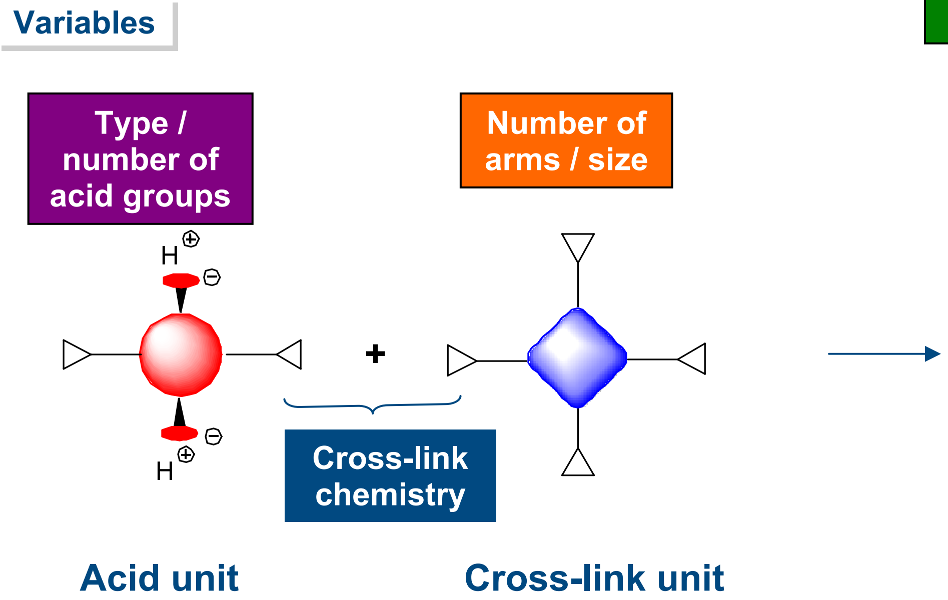


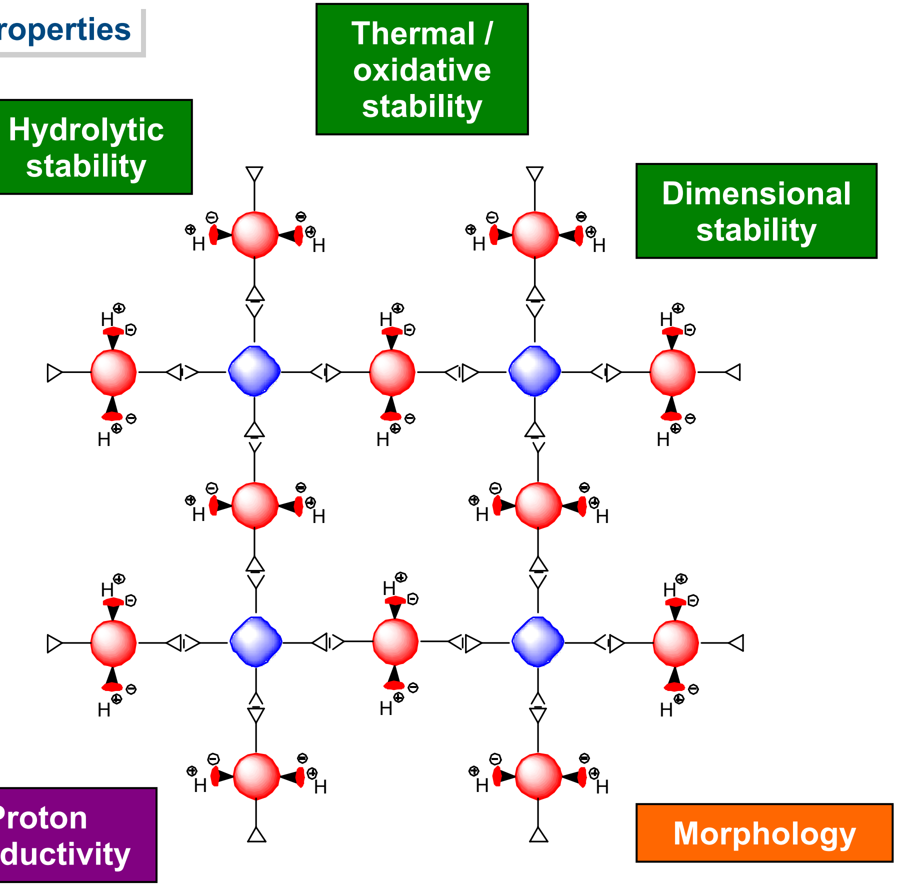
- Good balance of water uptake and conductivity was achieved in Gen3.
- Further increase in the conductivity is required to meet the Y3 DOE target (0.1S/cm 50%RH/120°C).
- However, higher increase in the acid groups make the polyelectrolyte soluble in water.
- New approaches (Gen 4 and 5) were investigated.

Selection of cross-linkable electrolyte units

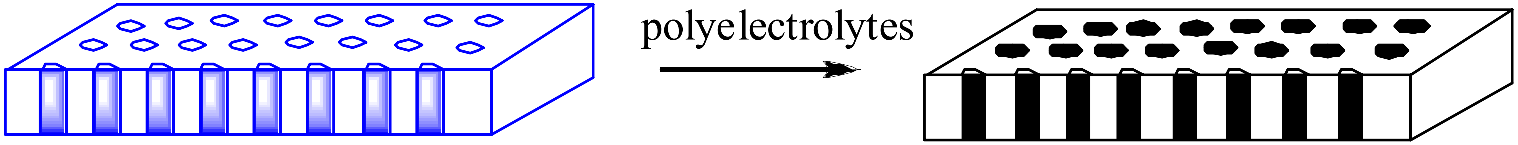
Critical factors for the electrolyte units

1. Thermal / oxidative stability
2. Acid density
3. Controllable cross-link density
4. Compatibility with the pore supports





Fabrication of cross-linked PEM in porous support



Cross-linked system provides :

1. Increase in acid concentration
2. Dimensional stability
3. Thermal stability

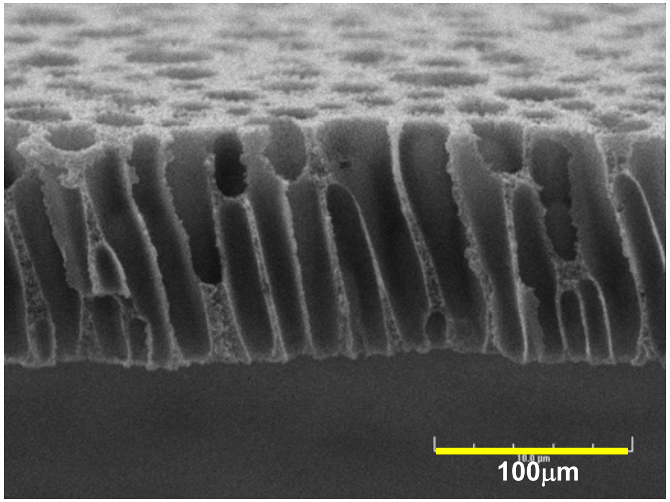
Porous support provides :

1. Mechanical strength
2. Dimensional stability
3. Thermal stability
4. Morphology (hydrophilic channel) control by template effect

Selection of porous supports

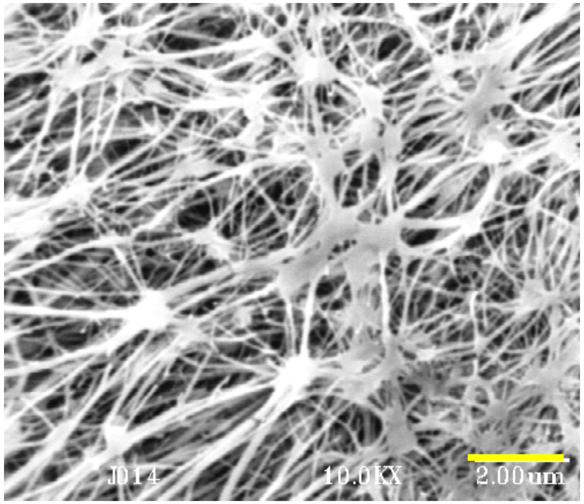
Critical factors	A	B
1. Mechanical strength	🔴	🟢
2. Thermal / oxidative stability	🟢	🟢
3. Porosity / pore size / surface area	🟡	🟢
4. Pore morphology	🟢	🟢
5. Compatibility with the polyelectrolytes	🟢	🟡
6. Scalability	🟡	🟢
7. Ease of handling	🔴	🟢
8. Cost	🟡	🟢

🟢	good
🟡	neutral
🔴	bad



Pore support A

Porosity ~45%

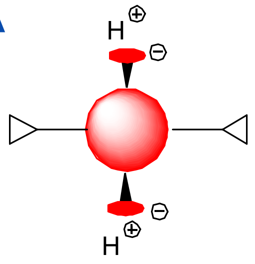


Pore support B

Porosity ~90%

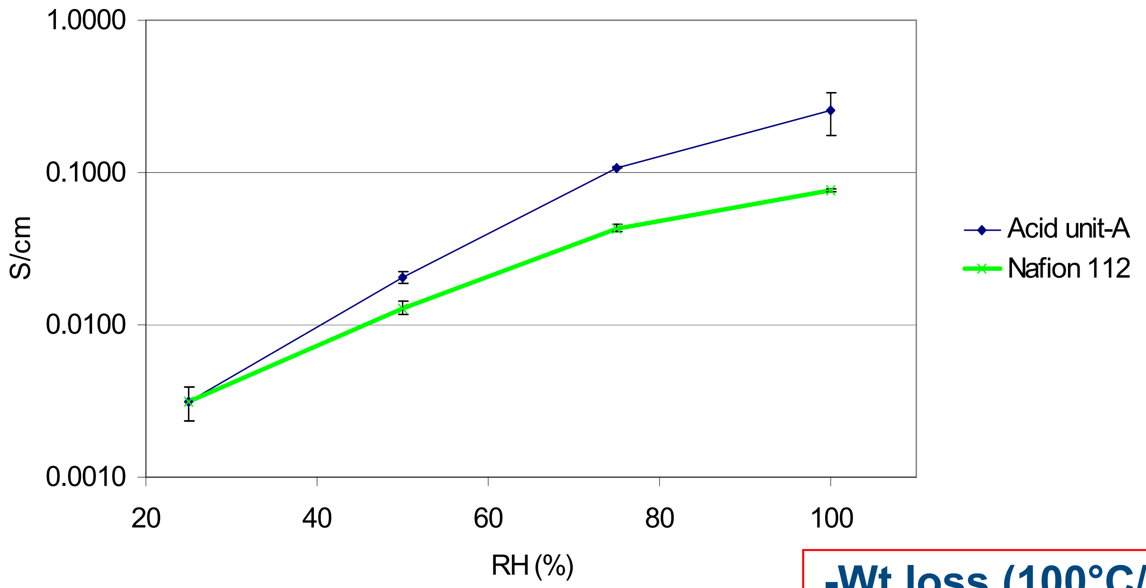
Control in the cross-link density – Gen 4A

- cross-link chemistry A / acid unit A -



Acid unit

Conductivity at 80 °C

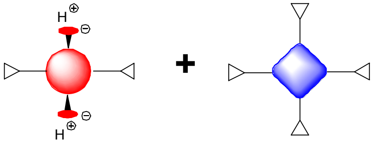


-Wt loss (100°C/2h) 70%

- Higher conductivity was obtained by incorporating acid units (100%) in a porous support.
- But the electrolyte was extracted out from the support by boiling for 2h due to the high acid concentration and the solubility in water.

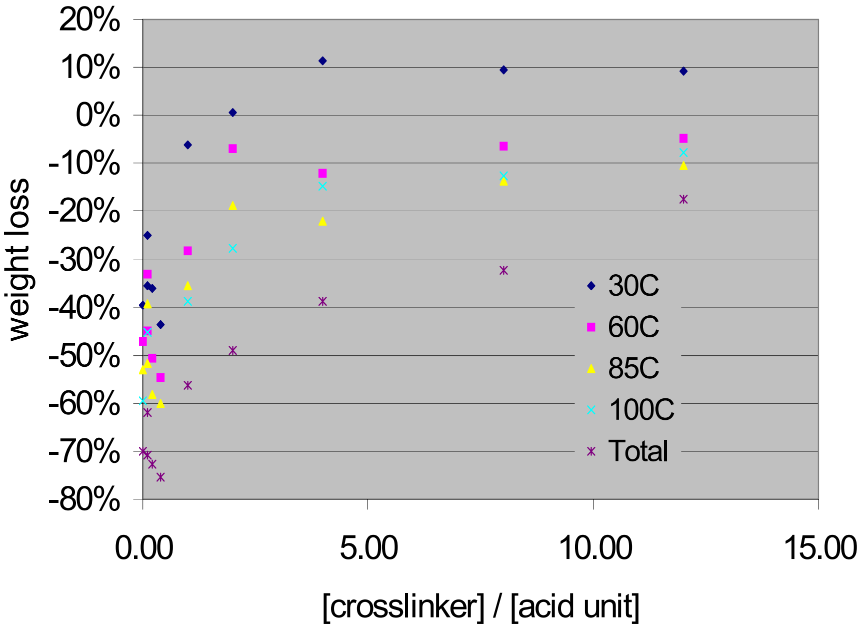
Control in the cross-link density – Gen 4A

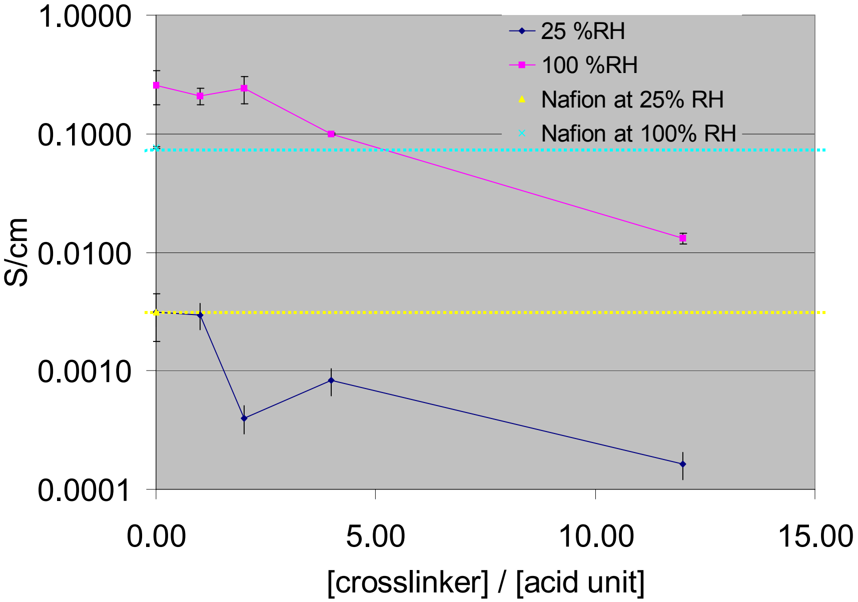
Effect of the cross-linker content on the leaching and the proton conductivity



Extraction at different temperatures

Conductivity at 80 °C

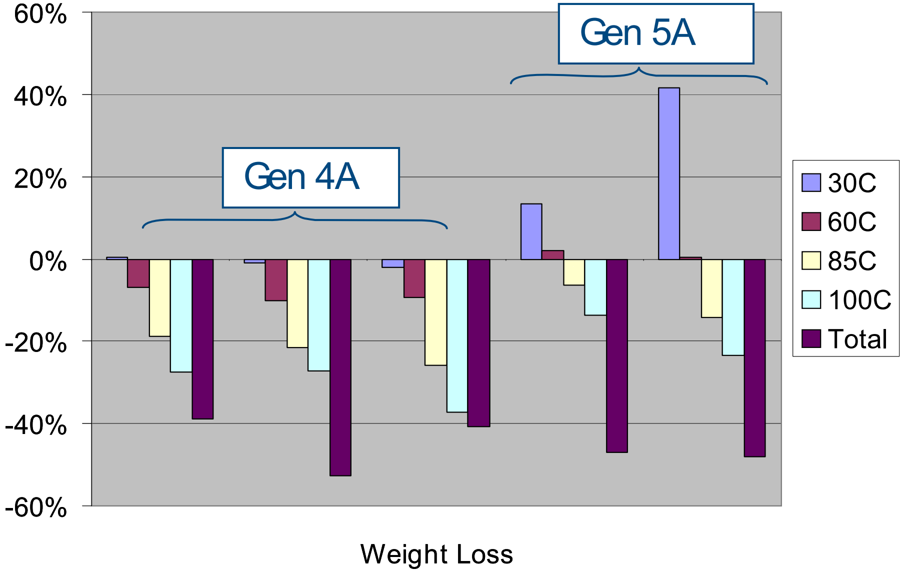




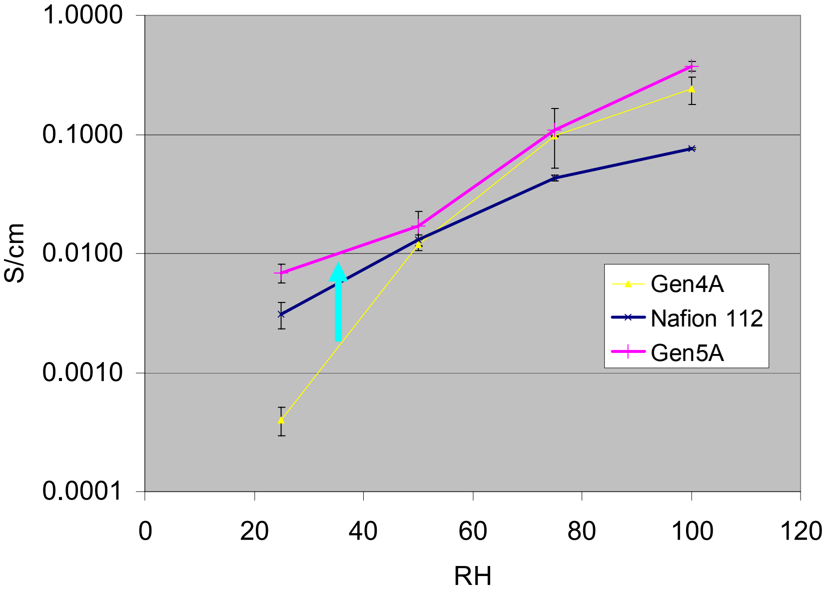
- Leaching was suppressed by increasing the cross-linker content.
- The decrease in conductivity with increase in cross-linker content is due to lower acid concentration.

Incorporation of inorganic additives – Gen 5A

Extraction at different temperatures



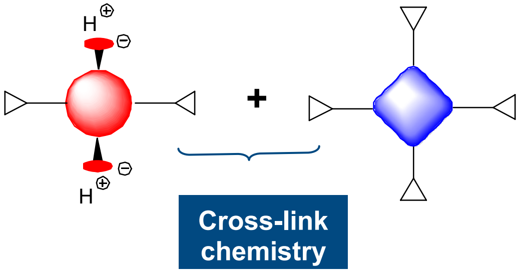
Conductivity at 80 °C



- Addition of the inorganic additive decreased acid group leaching at low temperatures.
- The conductivity improved with the inorganic additive, especially at low RH.

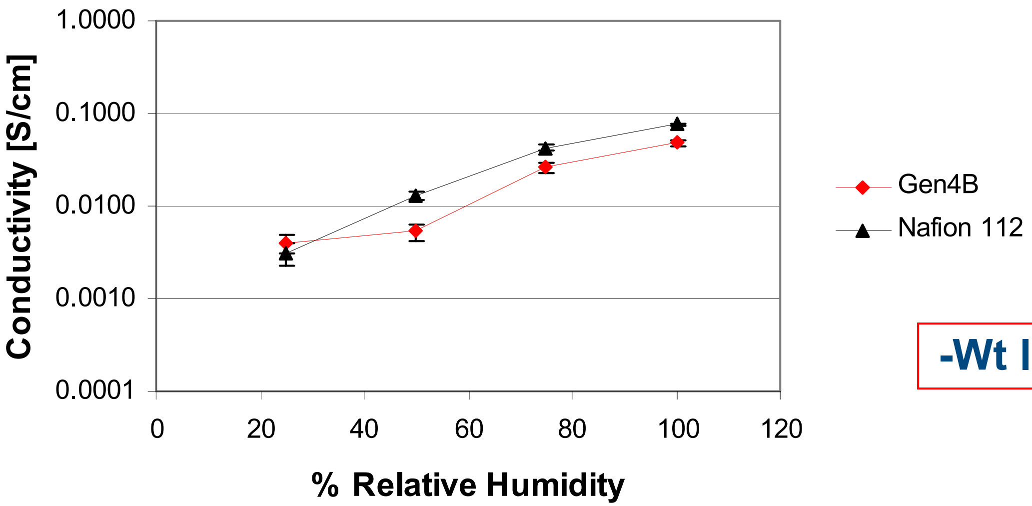
  (Exceeds the Y2 DOE target 0.07 S/cm at 80 %RH)
- Weight loss was still observed at high temperature and needs to be improved.

Alternative cross-link chemistry – Gen 4B



Cross-link chemistry was re-evaluated and optimized

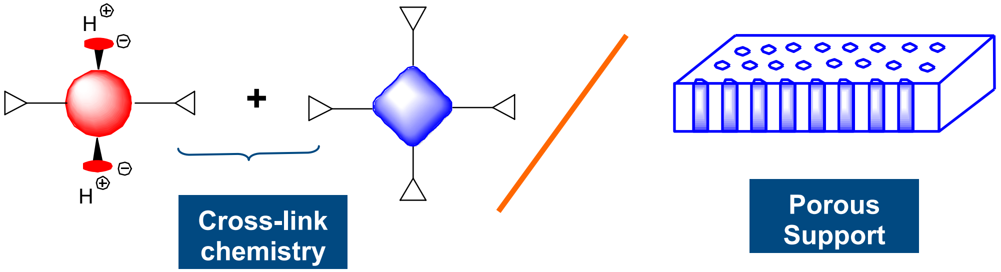
Conductivity at 80 °C



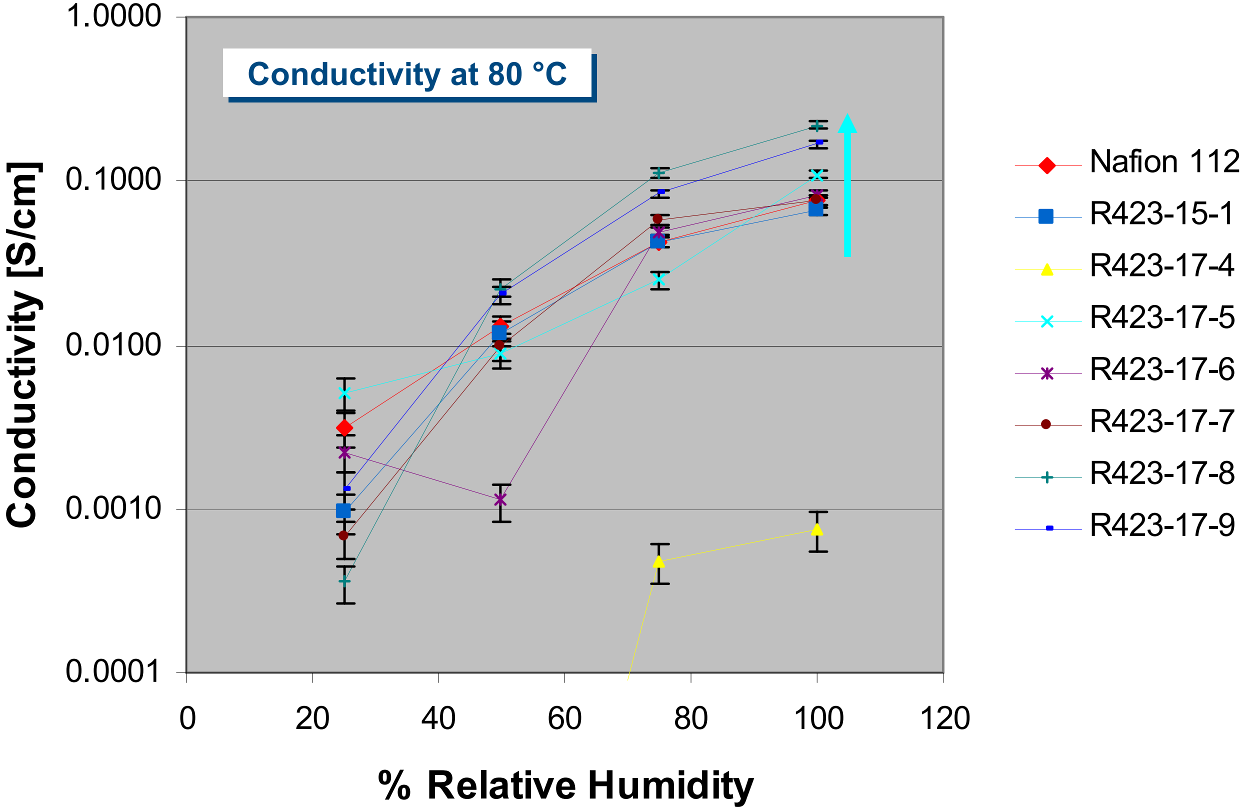
-Wt loss (100 °C/2h) 0%

- Membrane experiences no leaching.
- The conductivity is comparable to Nafion.

Alternative cross-link chemistry – Gen 4B



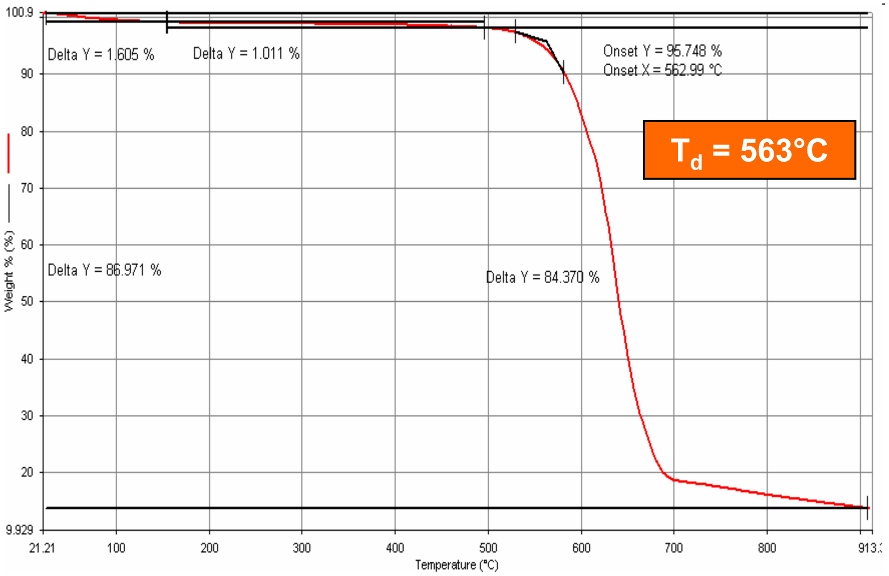
Optimization



- Membrane experiences no leaching.
- The conductivity exceeds Nafion.

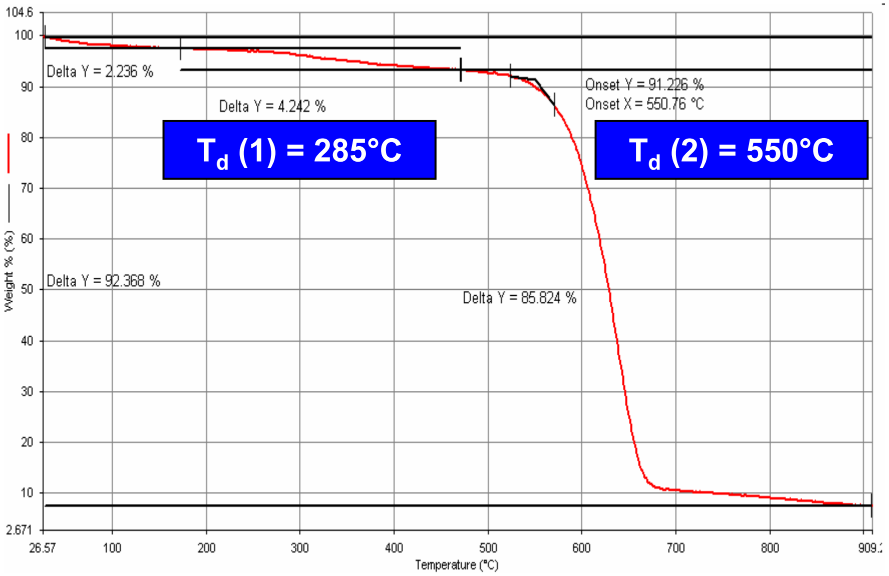
Alternative cross-link chemistry – Gen 4B

Before acidification



T_d = 563°C

After acidification



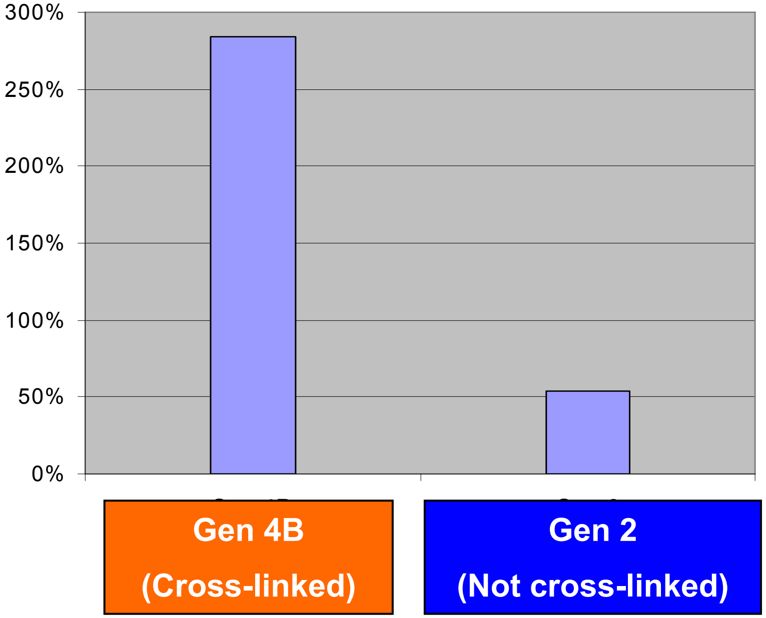
T_d (1) = 285°C

T_d (2) = 550°C

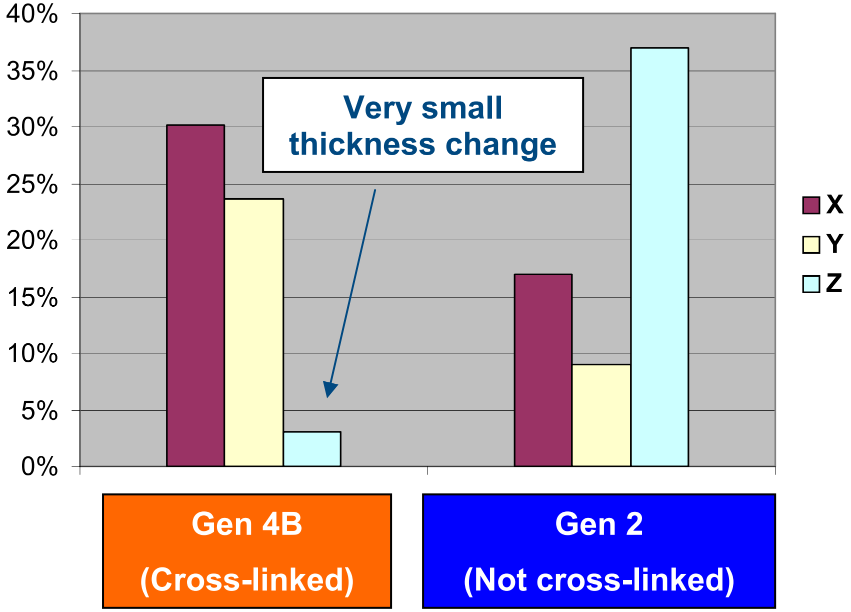
- Very high thermal stability (T_d = 550°C) was achieved.
- No T_g observed before decomposition.

Alternative cross-link chemistry – Gen 4B
water uptake and dimensional changes

Water uptake (30°C)



Dimensional changes (30°C)



- High water uptake in Gen4B compared to Gen2.
- Dimensional changes are at the same level as Gen2, but the thickness change for Gen4B is much smaller.

Future work FY07/FY08

Materials synthesis

- Demonstrate feasibility of cross-linked electrolytes in porous supports
- Evaluate the effect of acid/cross-linker ratios on the conductivity
- Study the effect of inorganic additives on the conductivity
- Evaluate the effect of pore size, porosity and thickness of porous supports on the conductivity

Membrane evaluation

- Evaluate membrane properties (proton conductivity, water uptake, mechanical properties)

Summary

Relevance : Apply new concepts in polymer membrane design to resolve challenging technical issues related to membrane performance over a wide range of temperatures and humidities.

Approach : Design and synthesize new polymer architectures by formation of the cross-linked electrolytes in porous supports with controlled structures. Explore hygroscopic additives to improve performance at high temperature, low RH.

Progress : Developed completely aromatic hydrocarbon based polymer architectures with concentrated proton conducting functionalities, demonstrating improved balance of water uptake and proton conductivity.

Developed cross-linked electrolytes in porous supports with or without hygroscopic inorganic additives. Demonstrated higher conductivity than Nafion over wide range of relative humidity.

Future research : Continue design and evaluation of new materials. Develop further understanding of the effect of membrane architecture on performance.

Summary Table

Results and DOE high temperature membrane targets

Parameters	FY06 target	FY06 results	FY07 target	FY07 results	
Conductivity (S/cm)	0.07	0.17	0.07	0.11	0.37
Temperature (°C)	rt	80	rt	80	80
RH	100%	100%	80%	80%	100%

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