New Proton Conductive Composite Materials with Co-continuous Phases Using Functionalized and Crosslinkable VDF/CTFE Fluoropolymers

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Project ID#: FC22

Overview

Timeline

- Project start date: *May 1st, 2006*
- Project end date: *April 30th, 2011*
- Percent complete: *66%*

Barriers

- **Durability**
  -Thermal stability of PEMs
  - High temperature, low RH proton conductivity
- **Cost**

Budget

- Total project funding:
  >>DOE share: *$1,300,698*
  >>Contractor share: *$325,175*
- Funding received in FY07: *$300,000*
- Funding for FY08: *$300,000*

Partners

- **Prof. S. Lvov's group –** *The Energy Institute's Electrochemical Lab, PSU*
- **Prof. M. Chung's group –** *Department of Materials Science and Engineering, PSU*
- **Prof. S. Komarneni's group –** *Materials Research Institute, PSU*
- ***BekkTech LLC* –** *Fuel Cell Testing & Diagnostic Services*

PENNSTATE

Project Objectives

Overall

Contribute to DOE efforts in developing high temperature PEM for transportation applications.

Develop a new composite membrane material with hydrophilic inorganic particles and VDF/CTFE polymer matrix to be used in PEMFC at -20-120^{o}C RH 25-50%.

Year 1

- Synthesis of inorganic proton-conductive materials
- Chemistry development for preparing functionalized VDF/CTFE polymers
- Development of the membrane fabrication methods

Year 2

- Scaling up of the supply of inorganic proton-conductive materials and polymers
- Reaching the Milestone of proton conductivity of 0.07 S/cm at 25^{o}C and 80%RH.
- Selection of the best membrane based on test results and adjustment of the synthesis procedures

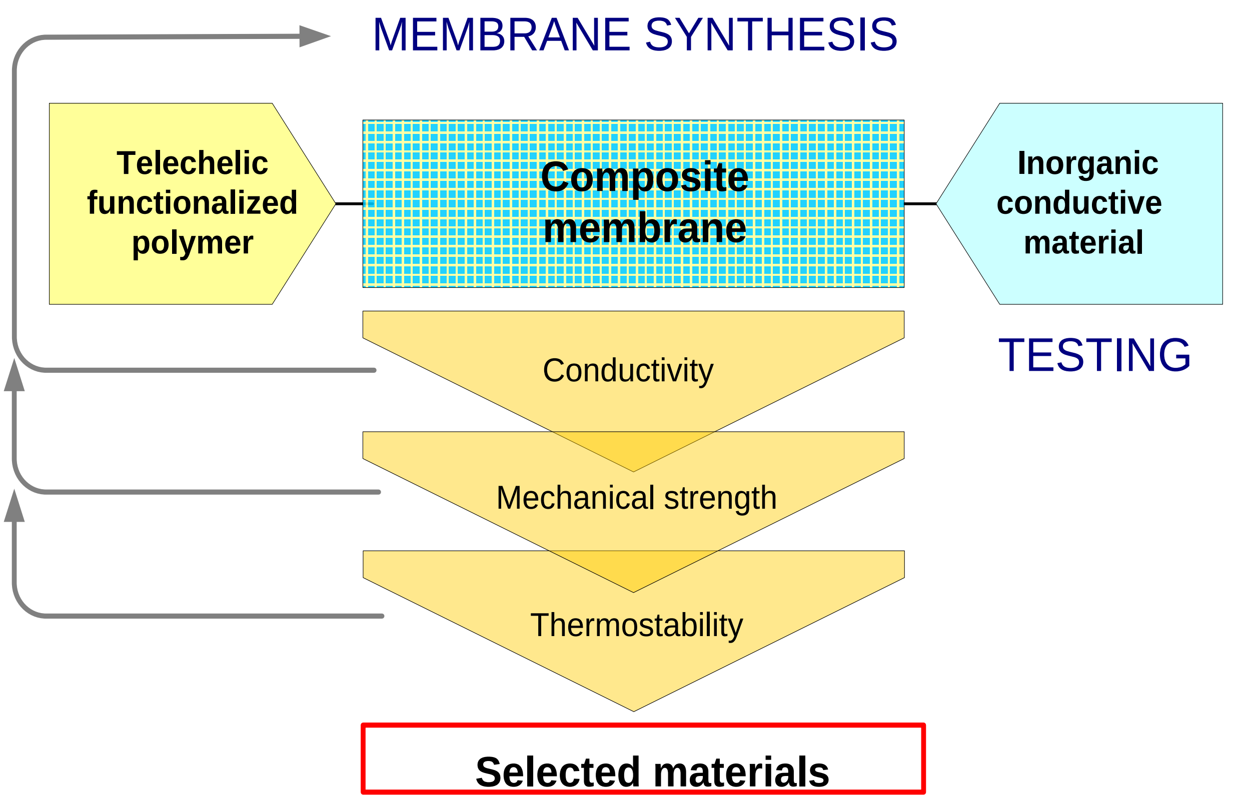
Year 3

- Membrane optimization based on test results and tuning the synthesis of polymers and inorganic additives.
- Reaching the Milestone of proton conductivity of 0.1 S/cm at 120^{o}C and 50%RH

Project Activities and Schedule

Task	Period of Performance	Milestones and GO/NO-GO Decisions
Task 1. Synthesis of functionalized polymers		
Development of the chemistry for preparing functionalized and crosslinkable TFE/VDF fluoropolymers.	1^{st} year	
Synthesis of the functionalized polymeric material for membrane fabrication and testing	2^{nd} year	
Improvement of the polymer structure and performance to achieve targeted properties	3^{rd} year	
Task 2. Synthesis of proton-conductive inorganic materials		
Synthesis and characterization of layered and network phosphates, mesoporous materials, and titanosilicates	1^{st} year	
Synthesis and characterization of mesoporous materials and titanosilicates	2^{nd} year	
Adjustment of synthetic techniques to achieve targeted particle properties	3^{rd} year	
Task 3. Membrane synthesis and characterization		
Development of membrane fabrication methods and preliminary testing	1^{st} year	
Membrane fabrication and conductivity testing. Selection of successful membrane materials and improvement of membrane properties	2^{nd} year	**Conductivity of 0.07 S/cm at 80% RH at 25^{o}C.**
Membrane fabrication and conductivity testing; selection of successful membrane materials and improvement of membrane properties to achieve targeted properties	3^{rd} year	**Conductivity of 0.1 S/cm at 50% RH at 120^{o}C. GO/NO-GO decision point**

Approach



Three PSU research groups focusing on

- ***Polymer synthesis***
- ***Inorganic particle synthesis***
- ***Membrane synthesis and characterization***

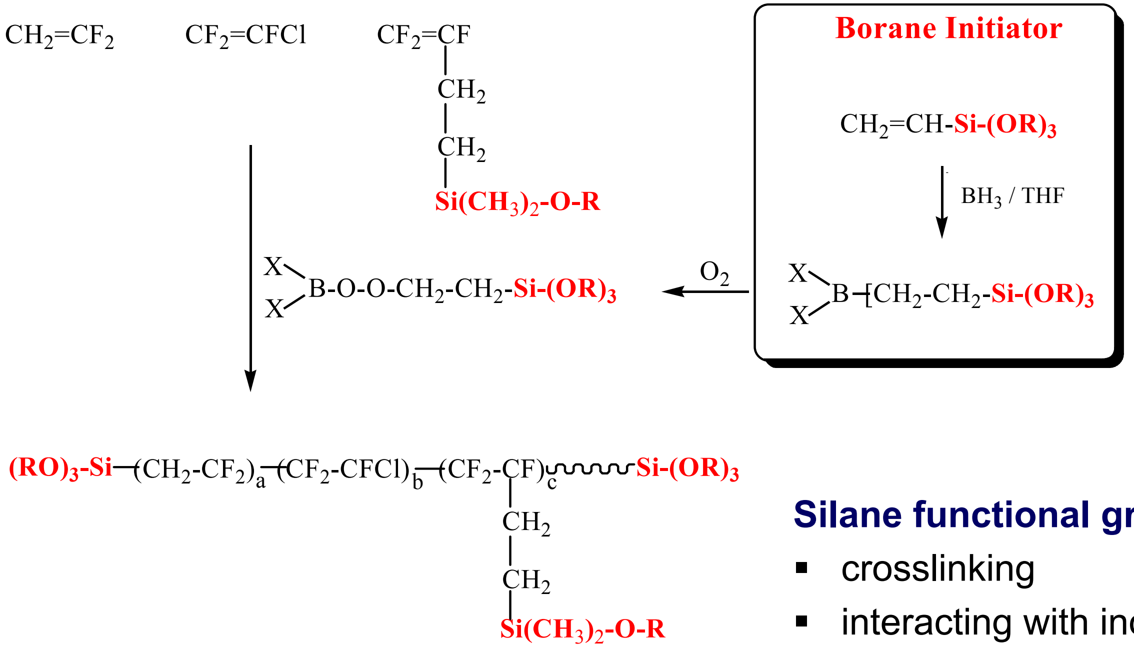
are involved in a loop of continuous feedback until the final product meets the target requirements.

The unique aspect of our approach is the development of a composite membrane with hydrophilic proton-conductive inorganic material and the polymeric matrix that is able to “bridge” the conduction paths in membrane by functionalized chain ends.

Technical Accomplishments

Task 1

Synthesis of Functionalized and Crosslinkable Fluoropolymer P(VDF-CTFE) Using Functional Borane Control Radical Initiator



Silane functional groups

- crosslinking
- interacting with inorganic particles

This fluoropolymer has an advantages of high copolymerization reactivity and wide molar ratio of VDF/CTFE to control polymer properties.

U. S. Patent 7,220,807

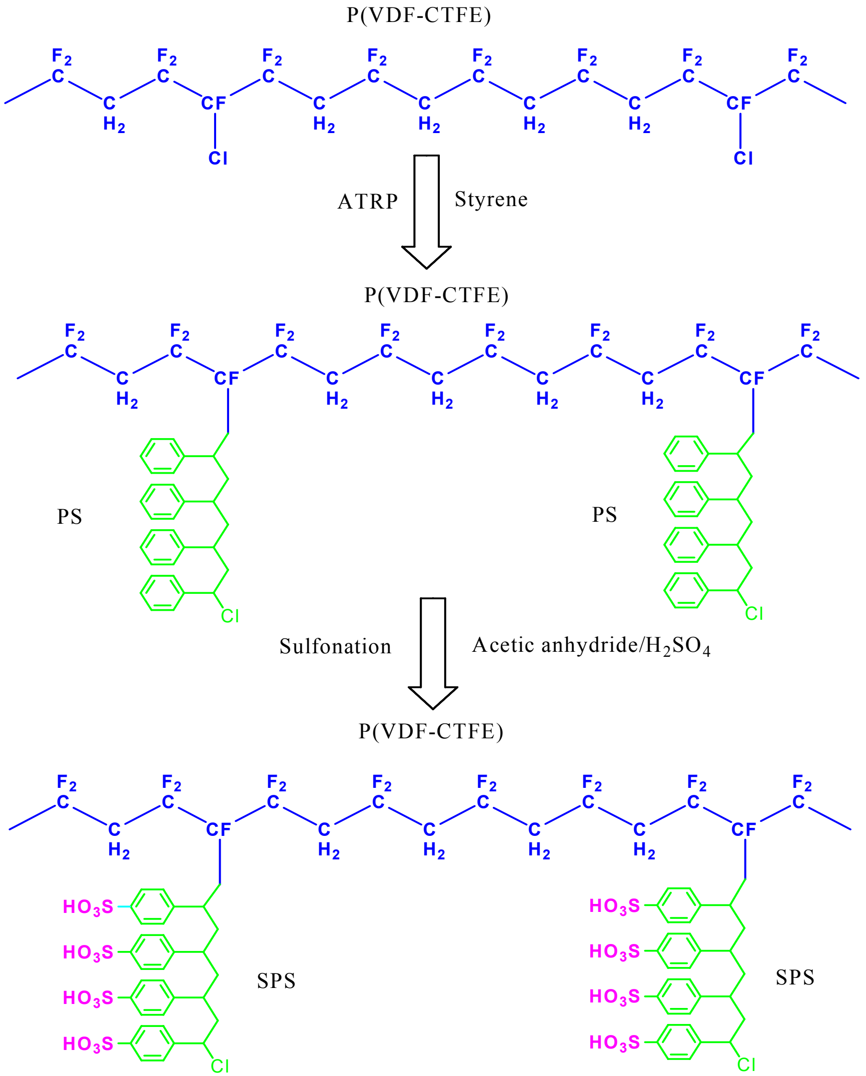
Technical Accomplishments

Synthesis of Sulfonated Styrene Grafted Fluoropolymer P(VDF-CTFE)-g-PS

Polymer properties requirements:

- Thermal and chemical stability
- Mechanical strength
- Compatibility with inorganic particulate phases
- Processibility to form uniform thin film
- Cost effectiveness and
- Sufficient proton conductivity

To obtain a desirable proton conductivity without Nafion, P(VDF-CTFE) copolymer was grafted with styrene via atom transfer radical polymerization (ATRP) followed by partial or the whole sulfonation of phenyl groups.

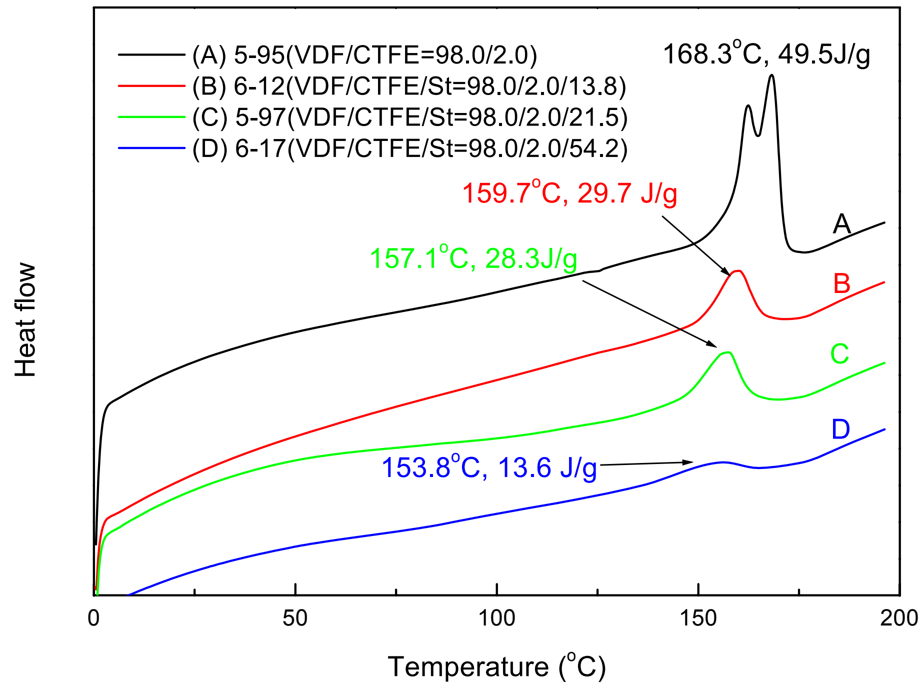


Technical Accomplishments

Relationship between composition and thermal properties of P(VDF-CTFE)-g-PSt Terpolymer

Composition (VDF/CTFE)	Tm (°C)	ΔH (J/g)
99.0/1.0	172.9	49.5
98.0/2.0	168.3	47.9
96.6/3.4	160.6	36.4
95.4/4.6	157.8	29.1
92.8/7.2	152.6	18.0

Effect of CTFE content on VDF/CTFE copolymer melting point and fusion heat

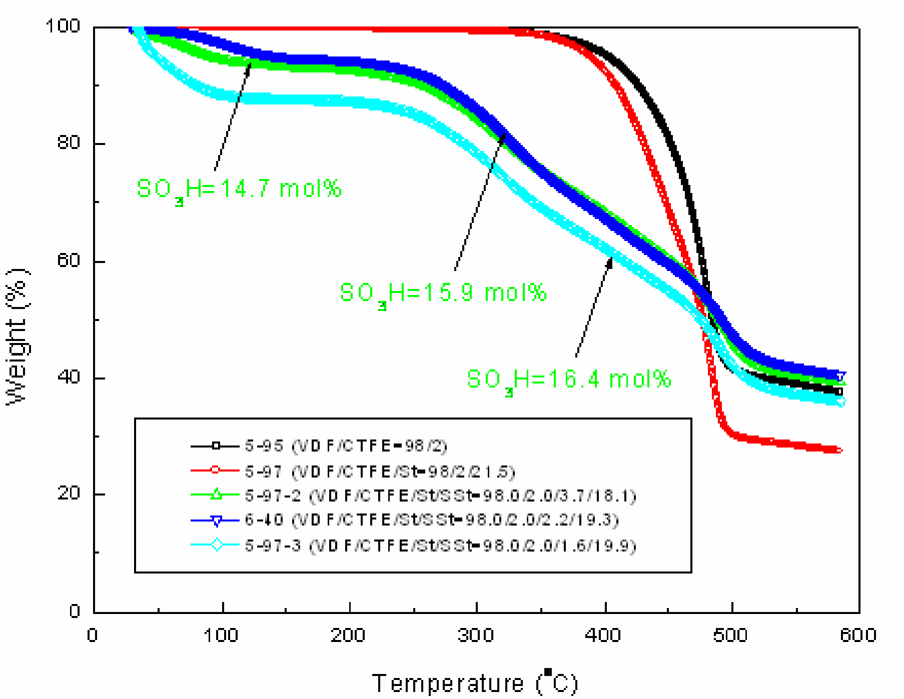


Effect of polysterene content on the DSC of P(VDF-CTFE)-g-PSt terpolymer

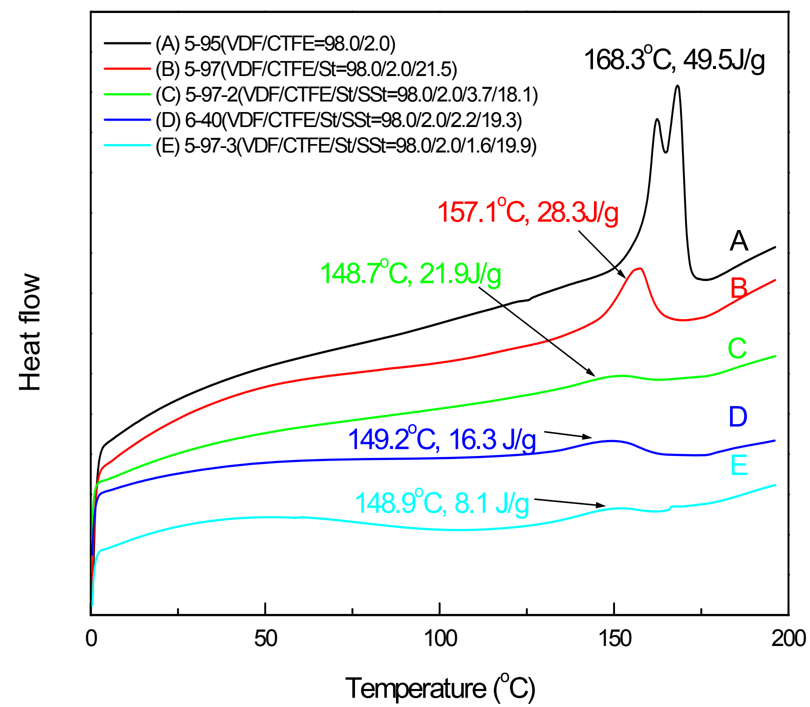
The increase in CTFE content and the introduction of polysterene (PSt) onto the side chains of P(VDF-CTFE) resulted in a slight decrease of the melting point and obvious drop of fusion heat indicating changes in membrane crystallinity.

Technical Accomplishments

The Relationship Between the Composition and Thermal Properties of P(VDF-CTFE)-g-PSt Terpolymer



TGA analysis of copolymer, terpolymer, and sulfonation products in comparison with Nafion.



Effect of sulfonation on DSC of P(VDF-CTFE)-g-PSt terpolymer

Compared to the VDF-CTFE copolymer and Nafion, decomposition temperature of terpolymer and sulfonated products was slightly reduced and weight loss was increased due to the lower stability.

The sulfonation slightly affected the melting point, but fusion heat value was dramatically reduced to almost zero indicating the loss of crystallinity.

Technical Accomplishments

Task 2

Improving Properties of Proton Conductive Polymers by Adding Proton Conductive Inorganics

A systematic study of different types of hydrophilic and proton conducting inorganics

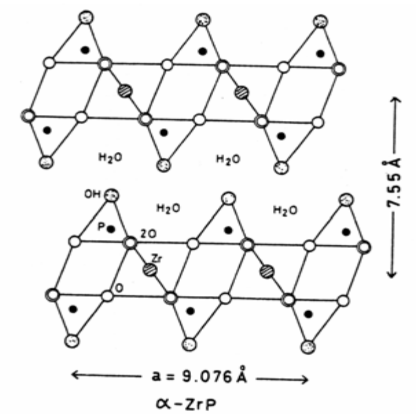
Zr-phosphates:

3-dimensional phase: $H_3OZr_2(PO_4)_3$	8.7 m^2/g
2-dimensional phase: α-$Zr(HPO_4)_2 \cdot H_2O$	11 m^2/g
Amorphous Zr phosphate: ~$ZrOHPO_4H_2O$	325 m^2/g

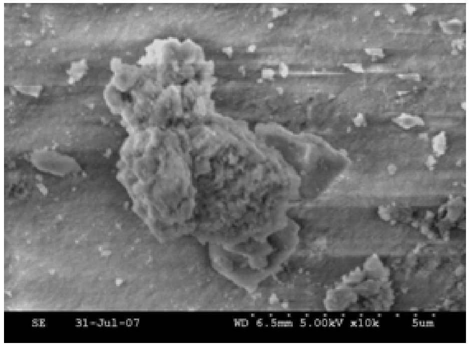
Sulfated Zirconia

Sulfated Zirconia Powder (ZrO2-P)	283 m2/g
Sulfated Zirconia Sol (ZrO2-S)	135 m2/g

***Characterization**: XRD, SEM and BET*



a



b

a - Layered α-$Zr(HPO4)_2.xH_2O$ where exchangeable protons are present in the interlayers as OH groups.

b - SEM of sulfated zirconia powder

Flow Chart for the synthesis of $(H_3O)Zr_2(PO_4)_3$

$(NH_4)H_2PO4$ +		*$ZrOCl_2.8H_2O$ +*		*H_2O*
92.45	*:*	*22*	*:*	*3000 mMol*

Hydrothermal treatment — *200^0C, 48 hrs*

$(NH_4)Zr_2(PO_4)_3$

Calcination — *540^OC, 6 hrs*

$HZr_2(PO_4)_3$

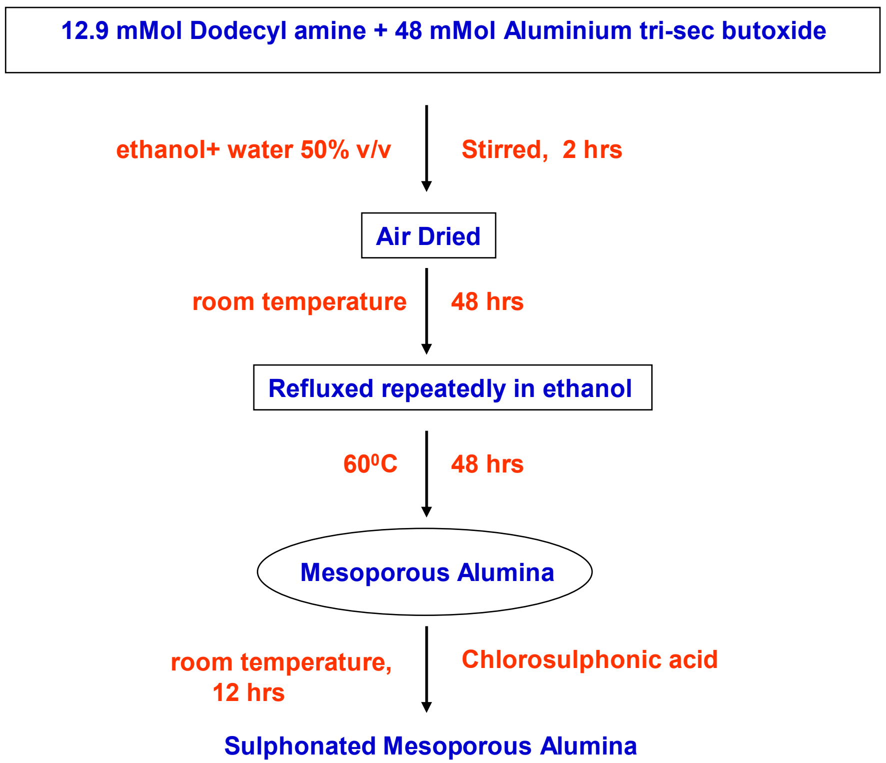
Hydrothermal treatment — *200^0C, 24 hrs*

$(H_3O)Zr_2(PO_4)_3$

Technical Accomplishments

Inorganic materials with high surface area and high conductivity, such as sulfonated mesoporous alumina and titania, were synthesized, and their effect on the composite membrane conductivity was investigated.

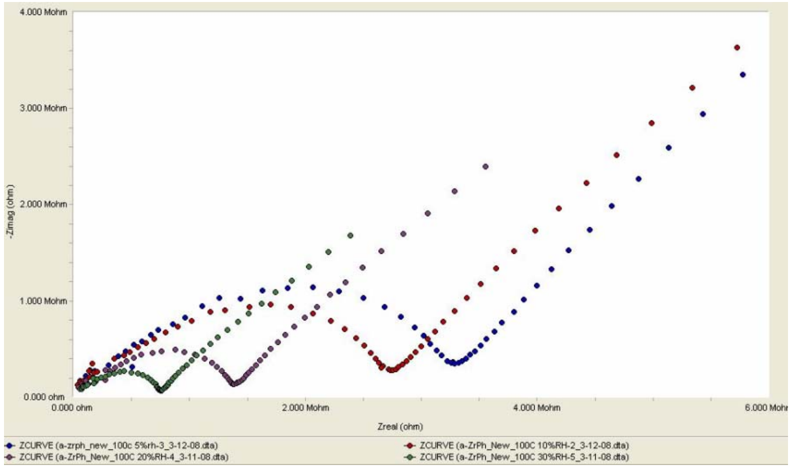
Schematic diagram for the preparation of sulphonated alumina



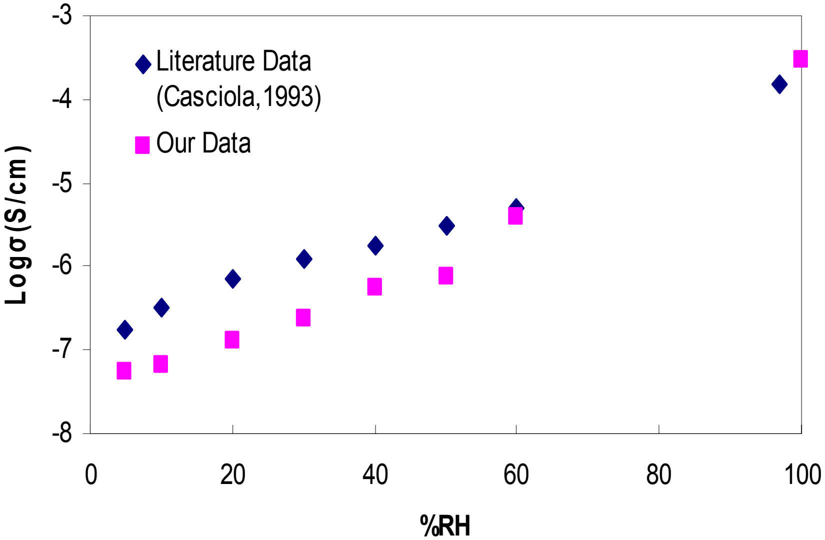
Technical Accomplishments

Characterization of proton conductive inorganic materials

Proton conductivity of Zr phosphates



Nyquist plots of α-ZrPh at different RH



Comparison of proton conductivity data for α-ZrPh at 100°C and different RH

- A system for measuring proton conductivity of inorganics (in pellet form) was constructed.
- Two-electrode impedance measurements were applied.
- Gamry electrochemical impedance spectroscopy system was used to measure AC conductivity.
- Inorganic pellets were fabricated by cold powder pressing.
- The pellets were sandwiched between two silver plates and assembled into BekkTech-type conductivity cell.
- The RH in the cell was achieved by feeding humidified nitrogen.
- Measurements were conducted between 25°C and 120°C at variable RH.

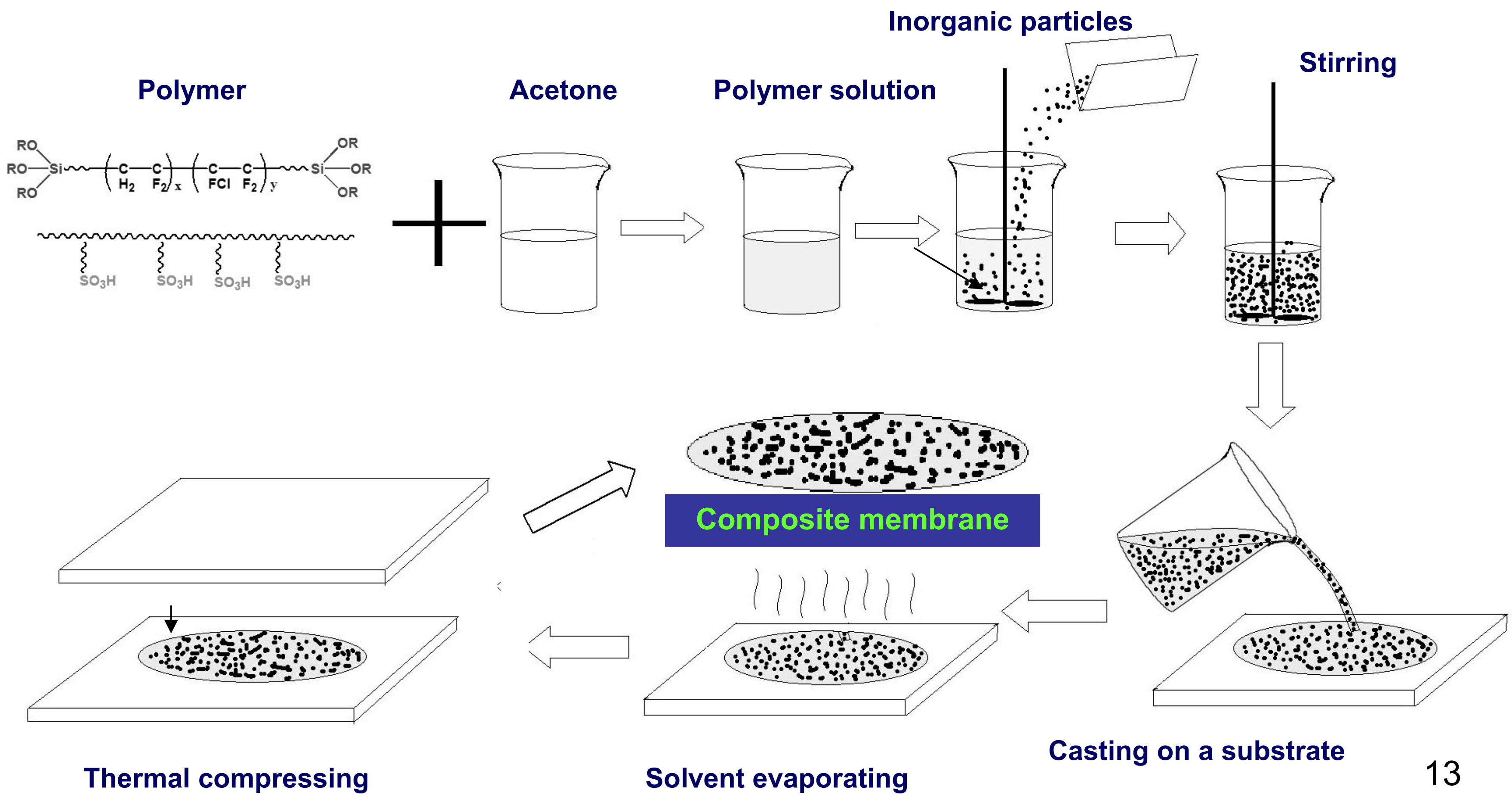
- At the same conditions, conductivities of α-ZrPh measured in our system are comparable to literature data.
- α-ZrPh is a surface conductor, and its conductivity depends on RH.
- The conductivity of high-surface-area sulfated zirconia and cesium phosphates will be studied as the next step.

Technical Accomplishments

Task 3

Fabrication of P(VDF-CTFE)-g-St Membranes and their Blends with Inorganic Particles

(Casting procedure with thermal compression)



Technical Accomplishments

Membrane Characterization

Conductivity

- *BekkTech* conductivity cell was assembled into an ElectroChem fuel cell hardware.
- The RH in the cell was achieved by feeding humidified nitrogen. To yield the desired RH in the conductivity cell, the temperatures of the cell and humidification column were controlled.
- The *BekkTech* Test Protocol was used for conductivity tests, including sample preparation and testing procedure.
- Gamry electrochemical impedance spectroscopy system was used.
- Measurements were conducted at 25^{o}C and 120^{o}C at variable RH.

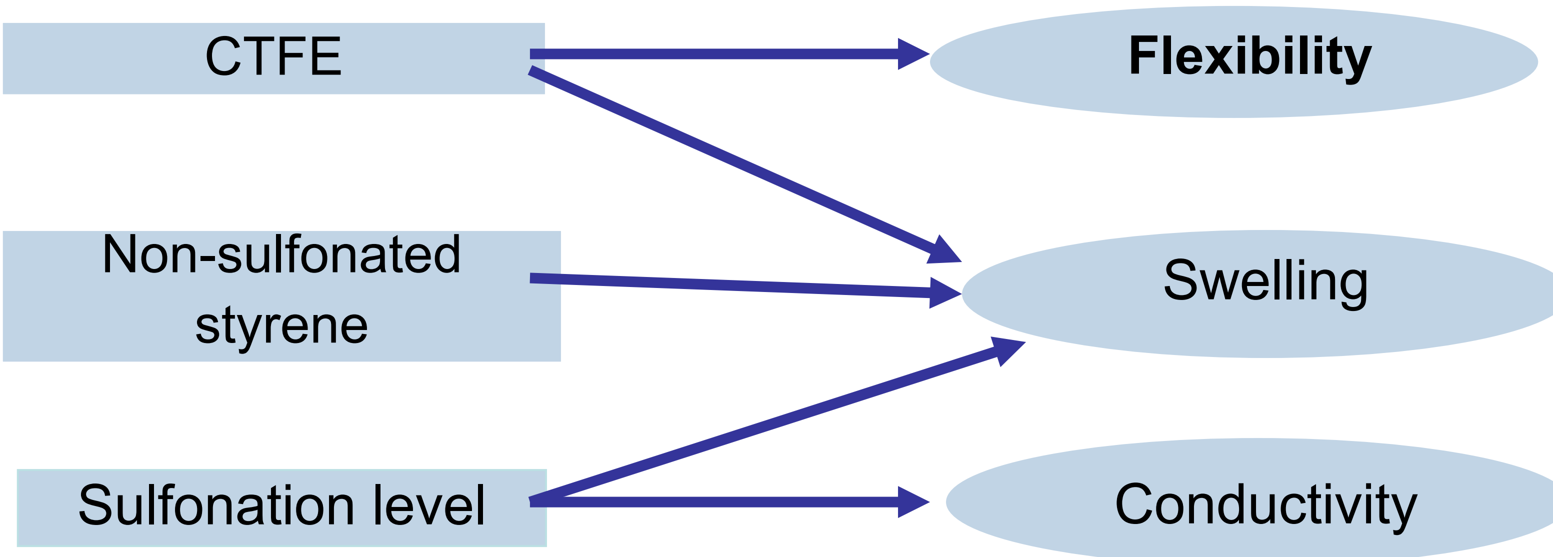
Swelling

Water swelling of membranes was measured at room temperature as the weight percent water per dry membrane weight in fully equilibrated membranes.

- **A series of sulfonated P(VDF-CTFE)-g-PS membranes with high proton conductivity was synthesized.**
- **For some membranes, measured conductivity values at 25^{o}C and 80%RH exceeded 0.07 S/cm (the second year Milestone).**
- **High swelling remains a challenge.**
- **Some membranes with good proton conductivity were brittle.**

Technical Accomplishments

Optimization of terpolymer P(VDF-CTFE)-g-PSt composition to balance proton conductivity, swelling, and membrane flexibility

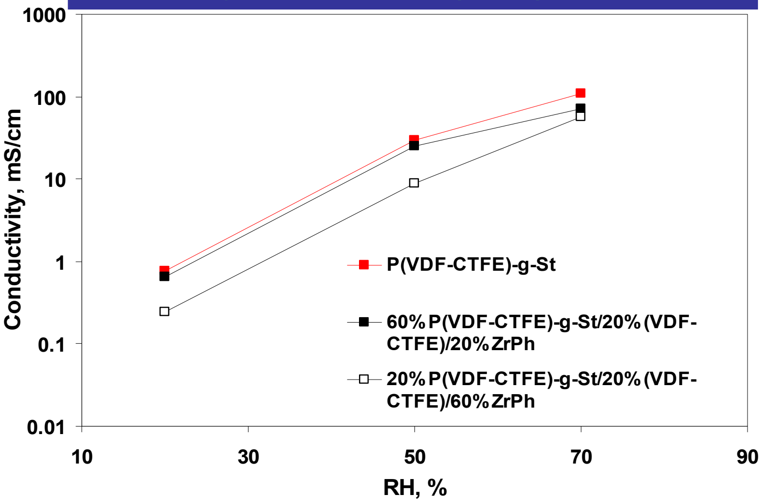


The increase in CTFE content from 1 to 3.4% substantially enhanced membrane flexibility. Membrane swelling, in general, correlated with sulfonation level, but it was also affected by CTFE and non-sulfonated amorphous styrene content. The high temperature conductivity (120^{o}C) correlates well with the sulfonation level.

Technical Accomplishments

Exploring different avenues to improve P(VDF-CTFE)-g-St membrane flexibility and swelling

Modification of P(VDF-CTFE) –g-St with Cross-linked Mother Polymer (VDF-CTFE) and Inorganic Particles (ZrPh)

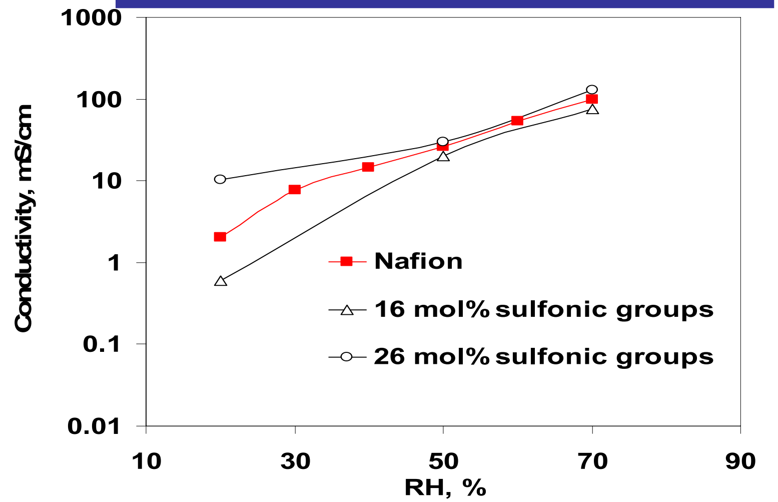


Conductivity of P(VDF/HFP/CTFE)-g-PS and (VDF-CTFE) and (VDF-CTFE)/ ZrPh modified membranes at 120^{o}C and different RH

Sample	Swelling,%
P(VDF-CTFE)-g-St	464
P(VDF-CTFE)-g-St/ (VDF-CTFE)/ZrPh 60/20/20	285
P(VDF-CTFE)-g-St/ (VDF-CTFE)/ZrPh 20/20/60	295

Addition of ZrPh improved membrane homogeneity and swelling, but swelling is still high and flexibility is low

Introduction of hexafluoropropylene (HFP)



Conductivity of P(VDF/HFP/CTFE)-g-St membranes with VDF/HFP/CTFE= 94.7/3.4/1.9 at 120^{o}C and different RH

Sample #	[SO3] Mol%	Swelling%.
1	16	126
2	26.1	300

Addition of HFP improved membrane flexibility and swelling without compromising the conductivity, but the swelling is still high.

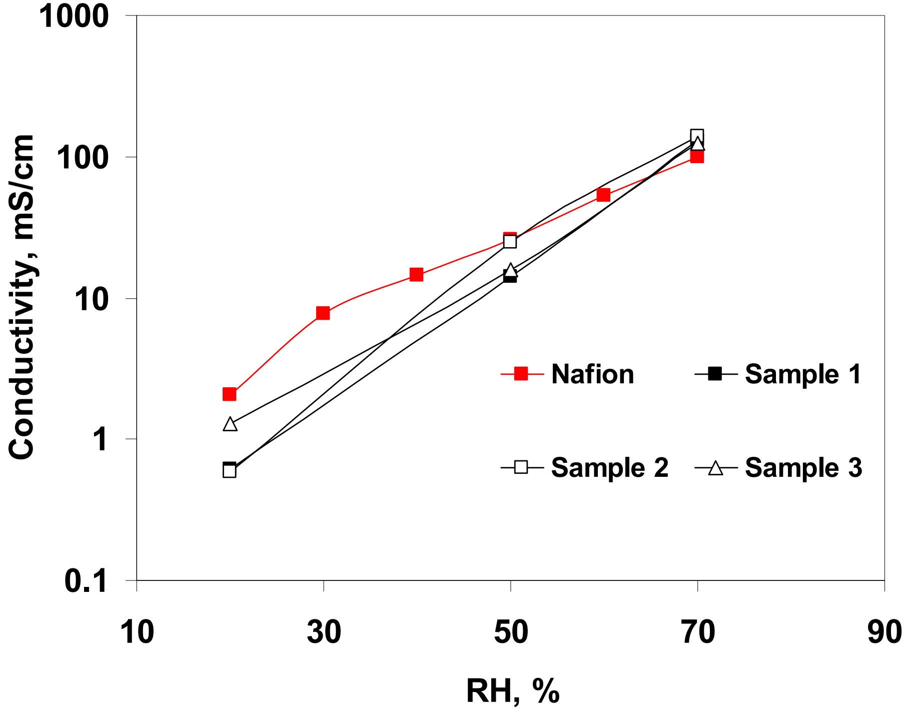
For some membranes measured conductivity values at 25^{o}C and 80%RH exceeded 0.07 S/cm (the second year Milestone).

Technical Accomplishments

Exploring different avenues to improve P(VDF-CTFE)-g-St membrane flexibility and swelling

Increase of molecular weight of (VDF-CTFE) copolymer

Properties of High Molecular Weight (HMW) Membranes



Conductivity of P(VDF-CTFE)-g-St HMW membranes at 120°C and different RH

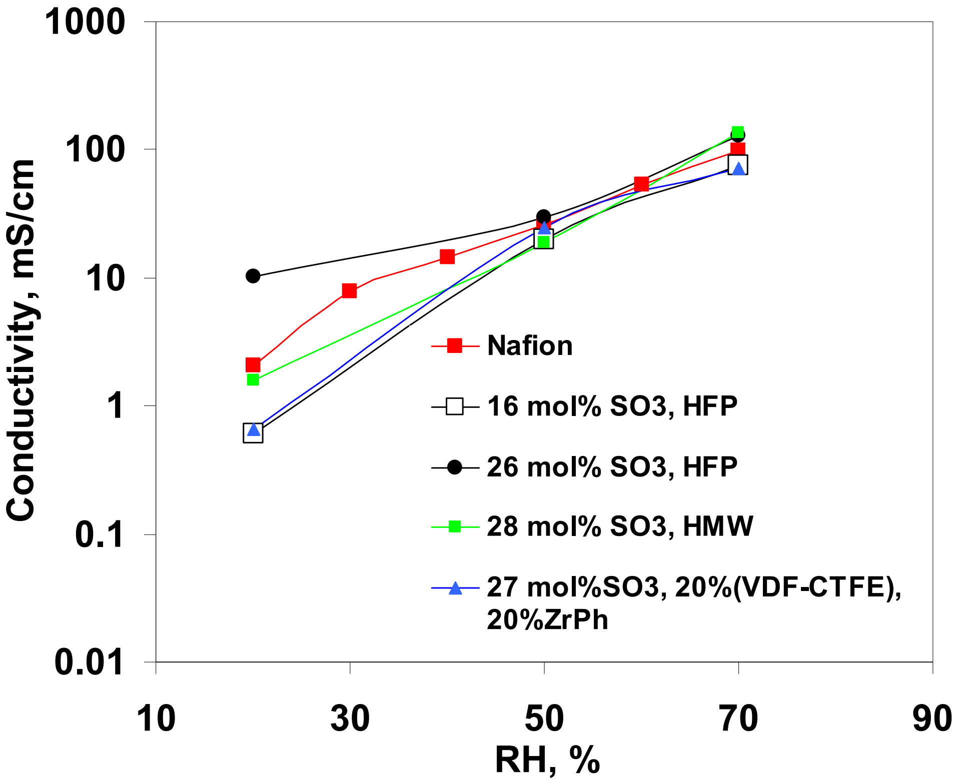
Sample #	$[SO_3]$ Mol%	Swelling%
1	20.3	190
2	20.8	220
3	27.8	220

- ❑ Membranes with high molecular weight (100,000) were synthesized
- ❑ Better flexibility was achieved
- ❑ High proton conductivity:

Milestone of Proton Conductivity 0.07 S/cm at 25°C and 80%RH was achieved

- ❑ Swelling was substantially improved.

Summary

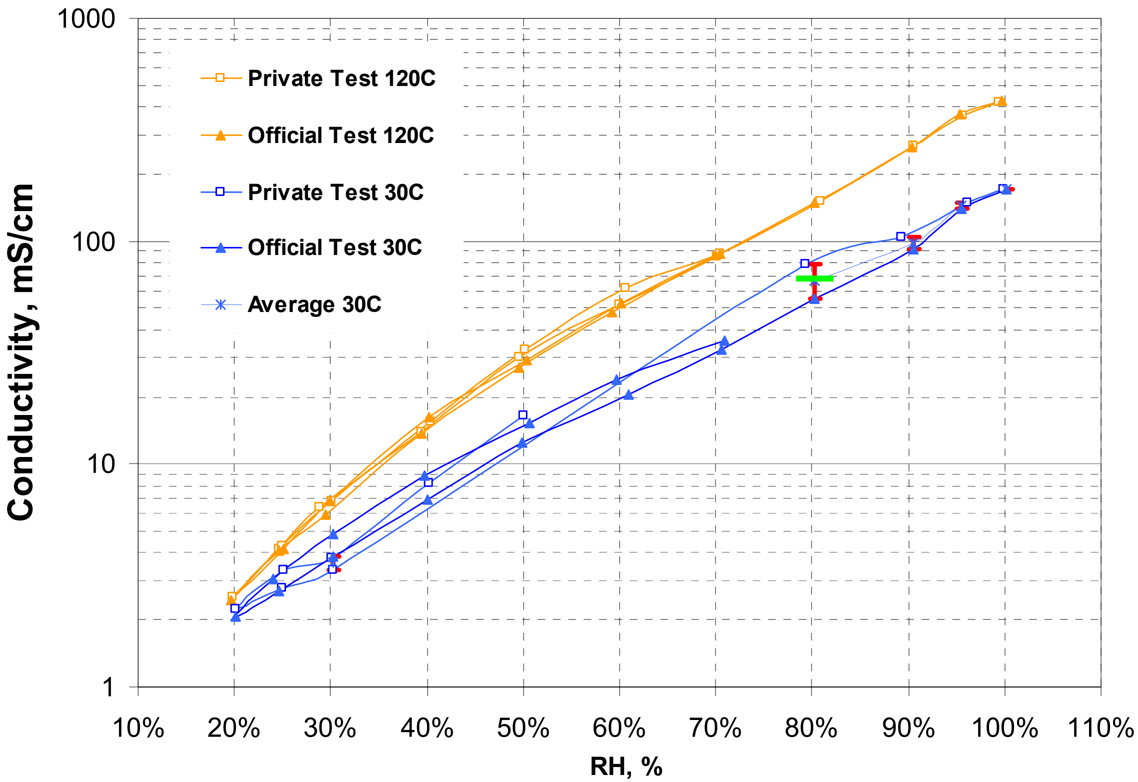


Conductivity of P(VDF/CTFE)-g-St membranes fabricated using different approaches at 120^{o}C and different RH

- Milestone of Proton Conductivity 0.07 S/cm at 25^{o}C and 80%RH was achieved for several types of membranes.
- Membranes with high proton conductivity at 120^{o}C were synthesized. Terpolymer with 26% SO_3^- groups, containing HFP, demonstrated conductivity higher than that of Nafion in the whole range of RH.
- Membrane flexibility was substantially improved.
- Membrane swelling was improved, but it is still high compared to Nafion.

Summary

Achieving of the first milestone of proton conductivity 70 mS/cm at 30°C and 80% RH



BekkTech Testing Results on PSU Sample 7-40-2

Membrane conductivity at 30 and 120°C

Conductivity Precision Measurement: at 30°C is in the range of 10-20%. Errors of membrane thickness (non-uniformity) can introduce errors of 30% or more.

The selected sample: 7-40-2

Composition: VDF/TrFE/CTFE/St/SSt = 94/5.2/0.8/0/38.5

Sulfonation: $[SO_3^-]$ = 27.8%

Conductivity at 30°C and 80% RH:

***(BekkTech* measurements)**

Official Test: 55.4 mS/cm

Private Test: 78.5 mS/cm

Average: (67.0 ± 11.5) mS/cm

Within the error of measurements the conductivity of the tested sample 7-40-2 matches up the first milestone of 70 mS/cm

Future Work

Year 3

- Use new highly conductive terpolymers containing HFP and terpolymers with increased molecular weight as a matrix
- Fabricate super acidic inorganic proton conductors with high water retention capability and proton conductivity comparable with polymeric matrix
- Produce "workable" hybrid membrane specimens for complete electrochemical, mechanical, and water uptake characterization
- Carry out characterization of the best membranes and based on the results, adjust membrane synthesis

GO/NO-GO decision