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

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**The Pennsylvania State University**

**Project ID#: FC22**

**May 16, 2007**

# Overview

## Timeline

- Project start date: *May 1st, 2006*
- Project end date: *April 30th, 2011*
- Percent complete: *20%*

## Budget

- Total project funding:

  \>>DOE share: *$1,300,698*

  \>>Contractor share: *$325,175*

- Funding received in FY06: *$140,000*
- Funding for FY07: *$300,000*

## Barriers

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

## 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***
- **Oak Ridge National laboratory –** ***Chemical Sciences Division***

# 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 TFE/VDF polymer matrix to be used in PEMFC at -20-120$^{o}$C RH 25-50%.

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**Year 1**

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

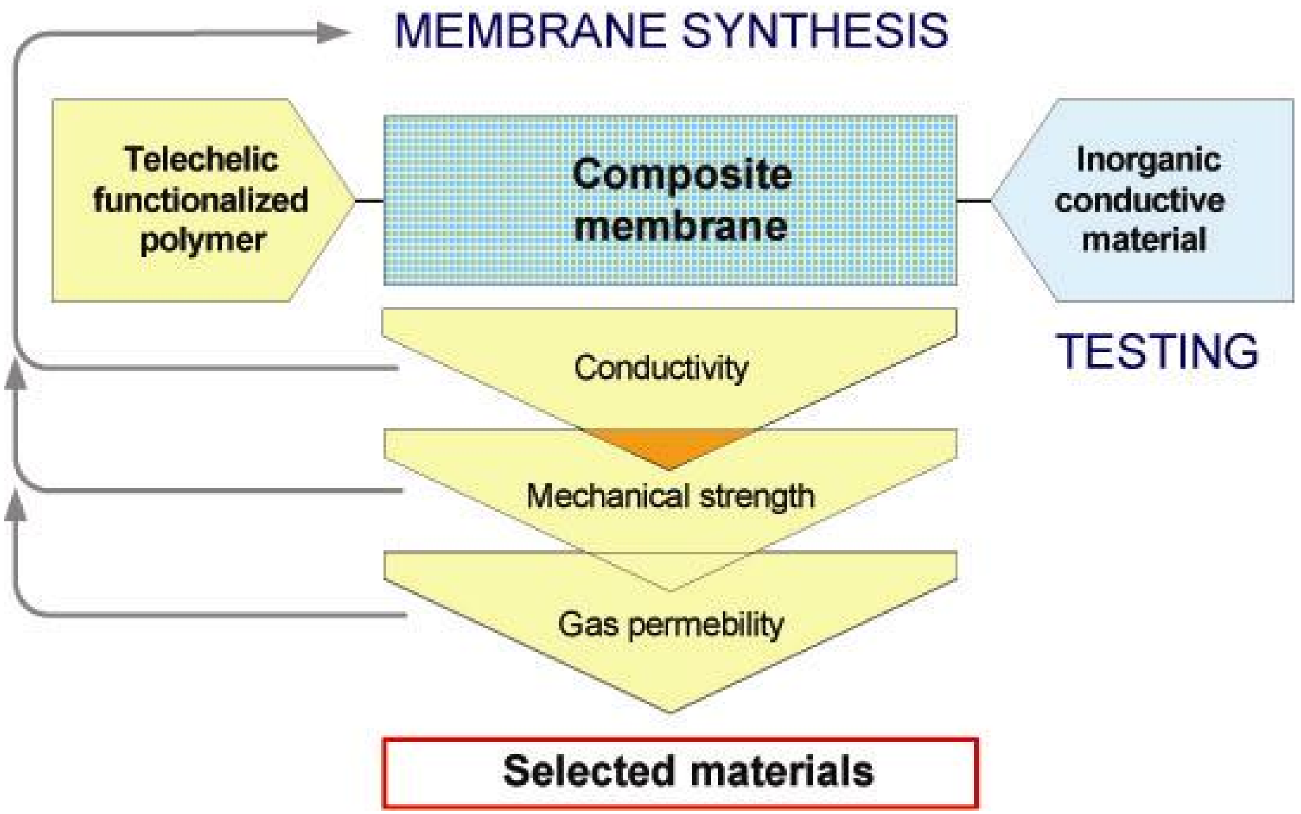
**Year 2**

- 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

# Approach



Three PSU research groups focusing on

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

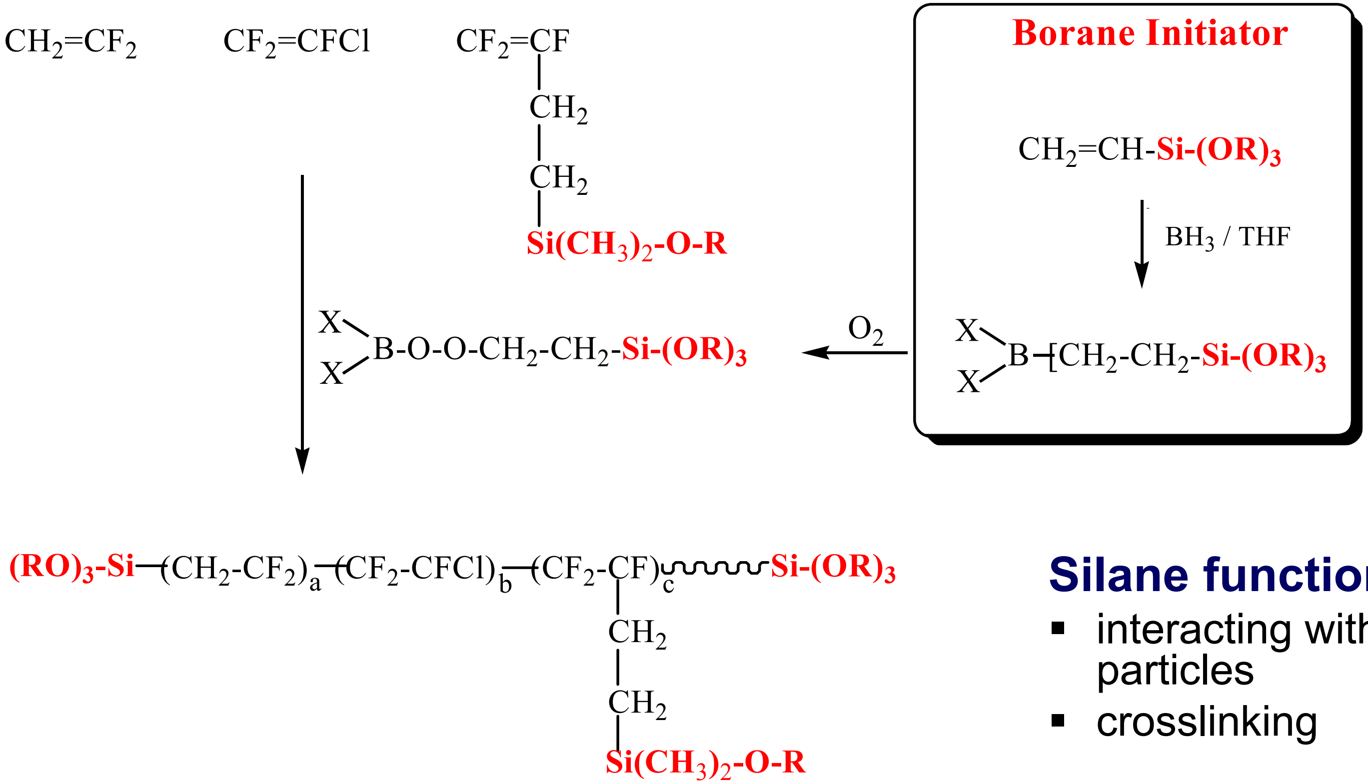
are involved in a loop of continuous feedback until the final product meets the target requirements.

**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 Fluoropolymers Using Functional Borane Control Radical Initiator



$CH_2=CF_2$ $\quad CF_2=CFCl$ $\quad CF_2=CF-CH_2-CH_2-Si(CH_3)_2-O-R$

**Borane Initiator**

$CH_2=CH-Si-(OR)_3 \xrightarrow{BH_3\ /\ THF} X_2B-[CH_2-CH_2-Si-(OR)_3$

$\xrightarrow{O_2} X_2B-O-O-CH_2-CH_2-Si-(OR)_3$

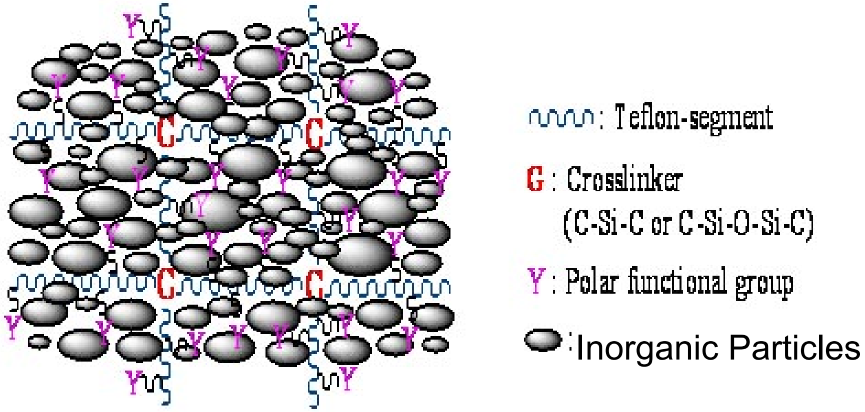
$(RO)_3-Si-(CH_2-CF_2)_a-(CF_2-CFCl)_b-(CF_2-CF(CH_2-CH_2-Si(CH_3)_2-O-R))_c\sim\sim Si-(OR)_3$

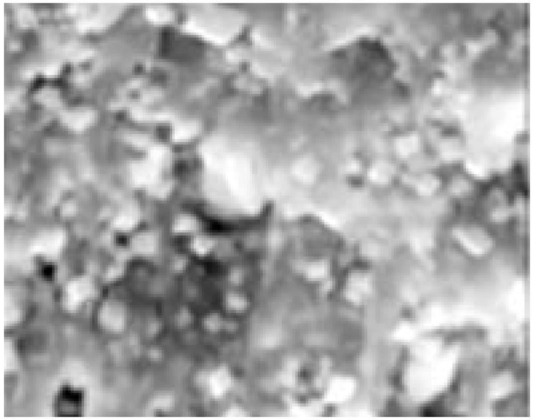
### Silane functional groups

- interacting with inorganic particles
- crosslinking

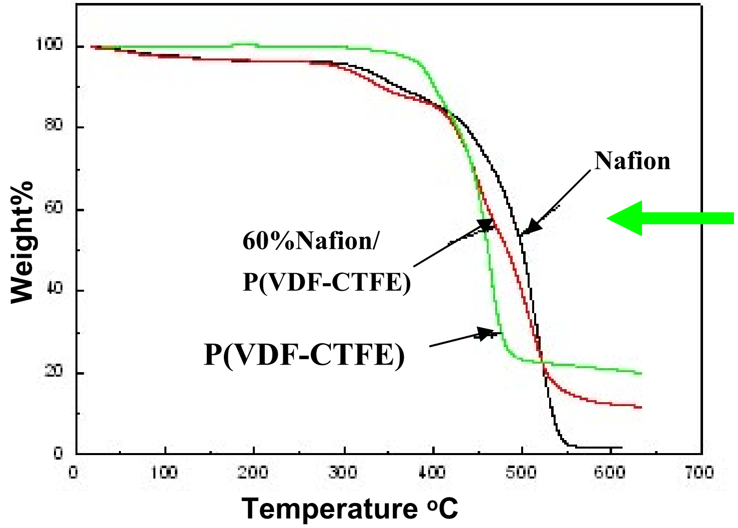
# Technical Accomplishments

## Fabrication of the new inorganic/polymer composite





**SEM Image of 40%PVDF/ 60% $H_3OZr_2(PO_4)_3$ composite with Si-terminal groups and Si-OH functional groups**



**TGA of Nafion, PVD, and 60%Nafion/PVDF blend**

**VDF, Nafion, and their blends showed similar thermostability**

- High proton conductivity was observed at elevated temperature in water, but not in water vapor.
- To increase proton conductivity in vapor, at the first step, Nafion was introduced inside the matrix as a model conductive substance.

# Technical Accomplishments

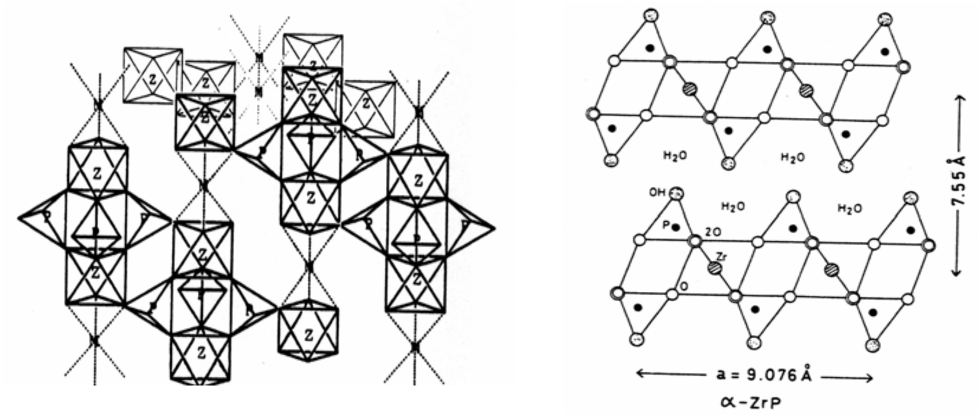
**Task 2**

## A systematic study of different types of Zr phosphates as proton conducting materials

**Zr-phosphates:**

| | |
|---|---|
| 3-dimensional phase: $H_3OZr_2(PO_4)_3$ (ZrPh) | 8.7 m²/g |
| 2-dimensional phase: α-$Zr(HPO_4)_2$ ~$H_2O$ | 11 m²/g |
| Amorphous Zr phosphate: ~$ZrOHPO_4H_2O$ | 325 m²/g |

**Characterization**: XRD, SEM and BET



a

b

a - Three dimensional $HZr_2(PO4)_3$ where M represents protons along with water molecules

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

**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 — 200⁰C, 48 hrs

$(NH_4)Zr_2(PO_4)_3$

Calcination — 540ᴼC, 6 hrs

$HZr_2(PO_4)_3$

Hydrothermal treatment — 200⁰C, 24 hrs

$(H_3O)Zr_2(PO_4)_3$

# Technical Accomplishments

## Other inorganic particulates

*Several classes of inorganic proton conductors with high water retention capability were synthesized for composite membrane fabrication:*

**Mesoporous materials, with a high specific surface area (wormhole-like channels) bearing proton containing groups:**

- Mesoporous alumina

  *Calcined at 540°C, SSA: 323 m²/g, Pore size: 8.5 nm*

- Mesoporous alumina (ethanol washed)

  *SSA: 450 m²/g, Pore size: 3.5 nm*

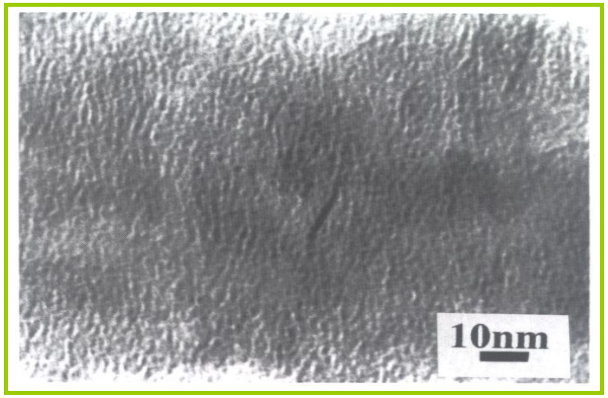
**Three-dimensional porous network phases with inside protons :**

- Titanosilicate with protons $H_2(SiTi_2O_7)(H_2O)_{1.5}$

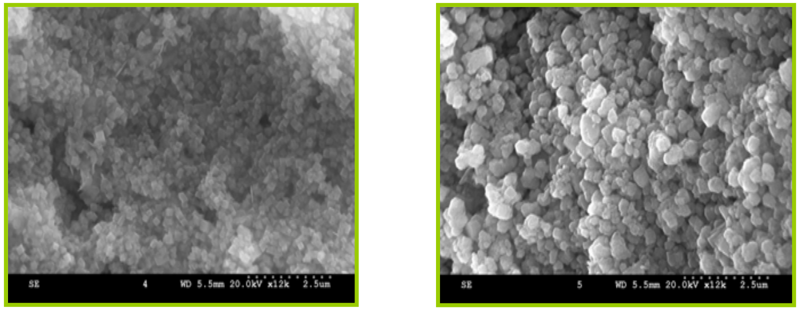
  *SSA: 70 m²/g*

- Three-dimensional $H_3O(Sn_xZr_{2-x})(PO_4)_3$

  *SSA: 23 m²/g*



TEM of calcined mesoporous alumina with worm-hole like pores where protons are located



a

b

SEM Images of: a - $H_3O(Sn_xZr_{2-x})(PO_4)_3$, b - $H_2(SiTi_2O_7)(H_2O)_{1.5}$

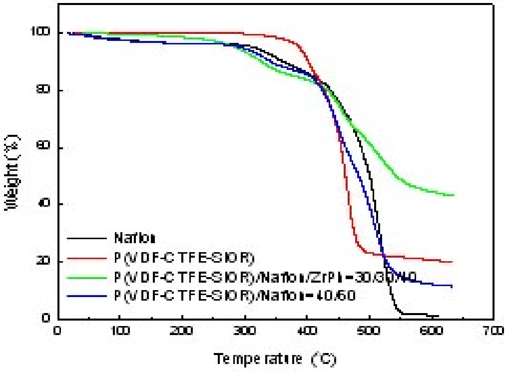
# Technical Accomplishments

## Fabrication of the new inorganic/polymer composites

**Task 3**

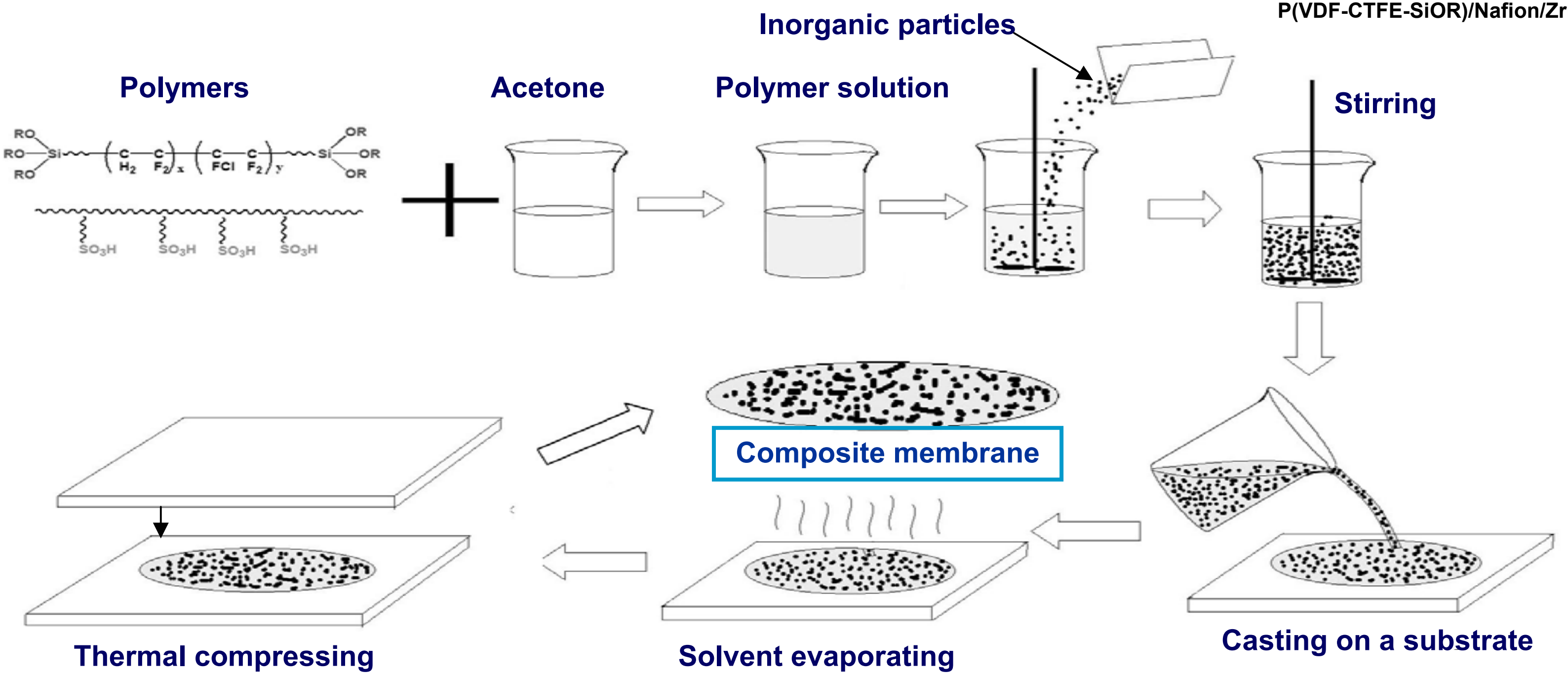
### P(VDF-CTFE-SiOR)/Nafion/ZrPh

*Newly synthesized polymer and its blends with Nafion and Nafion/ZrPh demonstrated high thermostability up to 400$^{o}$C*



**TGA of Nafion, P(VDF-CTFE-SiOR), P(VDF-CTFE-SiOR)/Nafion and P(VDF-CTFE-SiOR)/Nafion/ZrPh**

## Fabrication procedure:



**Polymers**

**Acetone**

**Polymer solution**

**Inorganic particles**

**Stirring**

**Casting on a substrate**

**Solvent evaporating**

**Composite membrane**

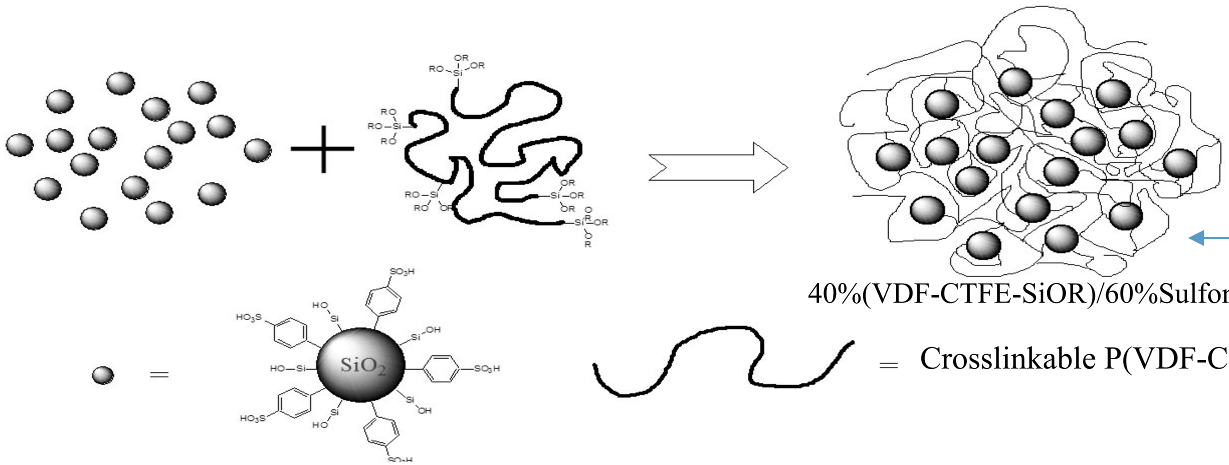
**Thermal compressing**

# Technical Accomplishments

## Fabrication of the new inorganic/polymer composites

**Exploring different avenues to obtain desirable membrane conductivity *without* Nafion:**

### P(VDF-CTFE-SiOR)/Sulfonated Silica:

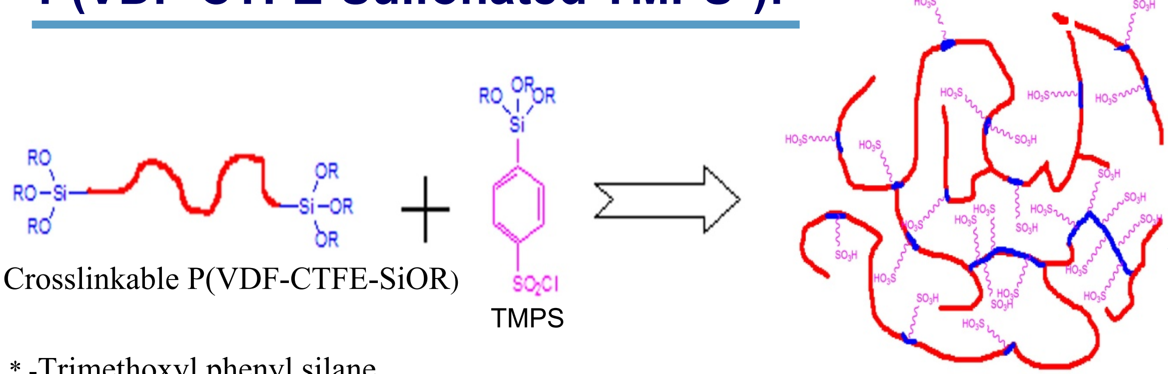


40%(VDF-CTFE-SiOR)/60%Sulfonated silica

= Crosslinkable P(VDF-CTFE)

- **Sulfonation of inorganic phases:**

### P(VDF-CTFE-Sulfonated TMPS*):



Crosslinkable P(VDF-CTFE-SiOR)

TMPS

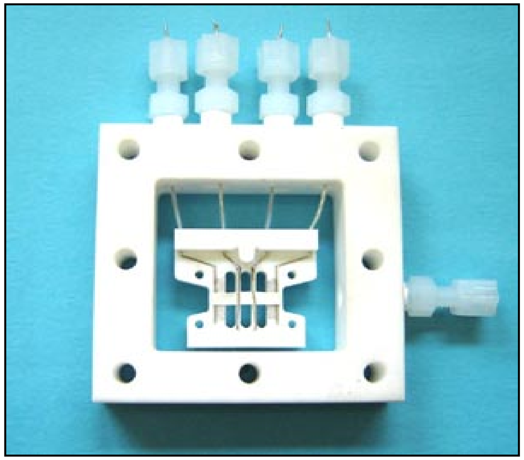
P(VDF-CTFE-SiOR-Sulfonated TMPS)

- **Introduction of sulfonic groups into side chains of copolymer:**

* -Trimethoxyl phenyl silane

# Technical Accomplishments

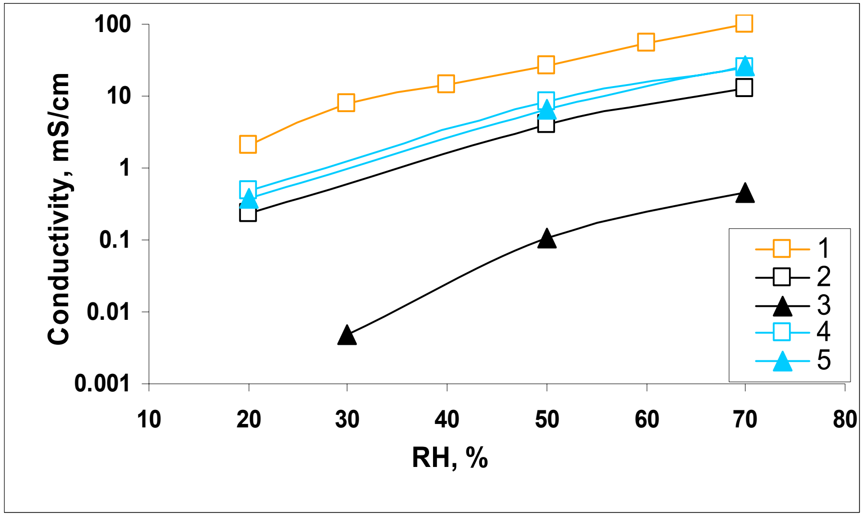
## Testing Conductivity of Different Composite Membranes



***BekkTech* Conductivity Cell**

- Four-electrode measurements using Electrochemical Impedance Spectroscopy
- Solid contact between a membrane and electrodes
- Access of moisture to both sides of a membrane
- Easy to handle a sample and operate
- Can be assembled into an available fuel cell hardware with use of their humidification system.

### (VDF-CTFE)/Nafion/ZrPh membranes



**Comparative performance of (VDF-CTFE)/Nafion and (VDF-CTFE/)Nafion/ZrPh membranes at 120°C.**

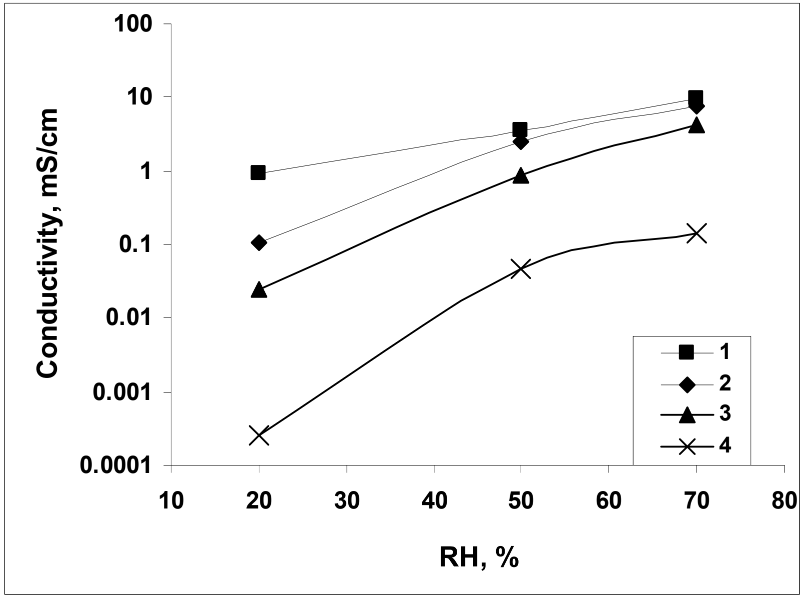
1 - Nafion 115; 2 - (VDF-CTFE)/60%Nafion; 3 - (VDF-CTFE)/40%Nafion;
4 - 20%(VDF-CTFE)/60%Nafion/20%ZrPh;
5 - 20%(VDF-TFE)/40%Nafion/40%ZrPh.

- ❑ Replacement of (VDF-CTFE) by ZrPh substantially increased the conductivity of composite.
- ❑ Membrane of 20%(VDF-TFE)/60%Nafion/20%ZrPh had the highest performance.

# Technical Accomplishments

## Testing Conductivity of Different Composite Membranes

### (VDF-CTFE)/Nafion/ZrPh membranes with different inorganic additives



**Conductivity of (VDF-CTFE)/ Nafion membranes with different inorganic additives at 120°C**

1. 30%VDF-CTFE/30%Nafion/40%$Zr(HPO_4)_2 \cdot H_2O$
2. 20%VDF-CTFE/20%Nafion/60%ZrPh Amorph.;
3. 30%VDF-CTFE/30%Nafion/40%HTiSiO4;
4. 30%VDF-CTFE/30%Nafion/40%MS.

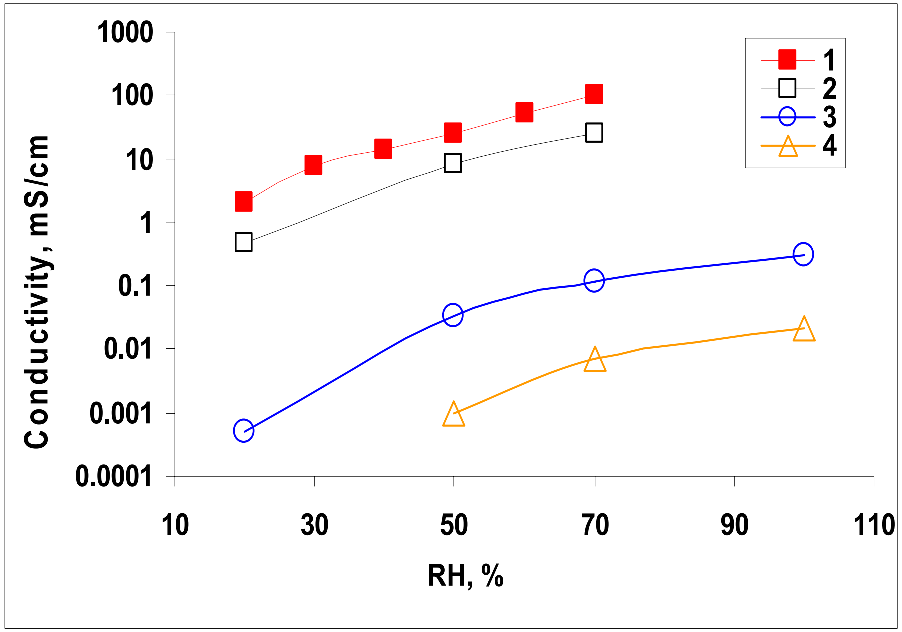
| Additives | Conductivity @ 70%RH, mS/cm |
|---|---|
| $Al_2O_3$ | 0.003[a] |
| $\alpha$-$Zr(HPO_4)_2 \cdot H_2O$ ($\alpha$-ZrPh) | 0.0389[b] |
| MS[d] | 0.145[c] |
| $HTiSiO_4$ | 4.33[c] |
| ZrPh Amorph. | 7.52[c] |
| $Zr(HPO_4)_2 \cdot H_2O$ | 9.40[c] |

a. 50%VDF/25%Nafion/25%Al2O3
b. 50%VDF/20%Nafion/30%α-ZrPh
c. Refer to Figure on the left
d. Molecular sieve

**$Zr(HPO_4)_2 \cdot H_2O$ is the most promising additive.**

# Technical Accomplishments

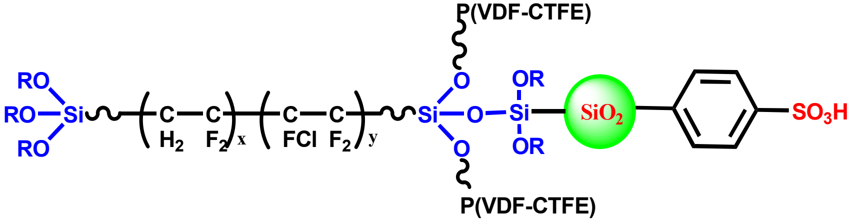
## Exploring different avenues to obtain desirable membrane conductivity *without* Nafion:



Conductivity of new composite materials compared to Nafion and 20%(VDF-CTFE-SiOR)/60%Nafion/20%ZrPH at 120°C.

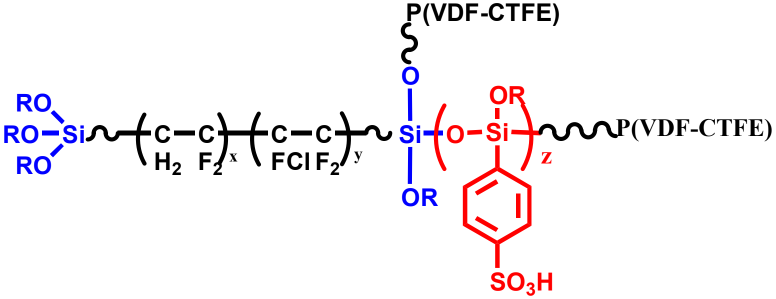
1. Nafion 115
2. 20%(VDF-CTFE-SiOR)/60%Nafion/20%ZrPh
3. P(VDF-CTFE-SiOR)-(Sulfonated TMPS)
4. 40%(VDF-CTFE-SiOR)/60%Sulfonated Silica

- ☐ Sulfonation of inorganic phases:



**40%(VDF-CTFE-SiOR)/60%Sulfonated silica**

- ☐ Introduction of sulfonic groups into side chains of the copolymer:



**P(VDF-CTFE-SiOR-Sulfonated TMPS*)**

* -Trimethoxyl phenyl silane

# Future Work

**Year 2**

- Develop chemistry for synthesis of functionalized and crosslinkable VDF/CTFE polymers
- Scale up the supply of VDF/CTFE polymers and inorganic additives. Fabricate a series of membrane specimens using existing technology and procedures for the characterization loop.
- Test the membranes for conductivity
- Reach the conductivity criterion of 0.07 S/cm at target temperature and relative humidity by the end of the year.
- Reveal the potential technical issues and strategies to resolve them

**GO/NO-GO decision**

**Year 3**

- Produce “workable” membrane specimens for complete electrochemical and structural characterization
- Select the best membrane based on test results, adjust membrane synthesis

**GO/NO-GO decision**

# Summary

**Relevance**

This project contributes to the development of energy economy on a wider scale, works towards cleaner and more efficient power generation, and promotes commercialization of PEM fuel cells.

A particular focus and novelty of this development is new conductivity mechanisms through the interfaces in composite materials.

**Approach**

Development of the composite membrane with highly hydrophilic proton-conductive inorganic material within the polymeric matrix that is able to “bridge” the conduction paths in membrane by functionalized chain ends. Exploration of different methods of functionalization of polymeric matrix.

**Future perspective**

We plan on developing several avenues to optimize the synthesis and to reach the target membrane properties:
- high surface area (mesoporous) inorganics will be used for enhanced water retention and functionalized (sulfonated) inorganics will be used to boost proton conductivity of the composites,
- functionalized (VDF-CTFE) will be used as matrix to provide more efficient charge transfer in the composite,
- Nafion component will be replaced with other conductors.