New Polymer/Inorganic Proton Conductive Composite Membranes for PEMFC

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The Pennsylvania State University

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Project ID#: FC_03_lvov

Overview

Timeline

- Project start date: *May 1st, 2006*
- Project end date: *April 30th, 2009*
- Percent complete: *100%*

Barriers

- **Durability**
  Chemical and mechanical stability of PEMs
- **Performance**
  High temperature, low RH proton conductivity
- **Cost**

Budget

- Total project funding:
  >>DOE share: *$900K*
  >>Contractor share: *$325K*
- Funding received in 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

Project Objectives and Tasks

Objectives

The main project objectives of the last year:

- Development of a proton conductive inorganic/polymeric membrane for PEMFC operating at elevated temperatures up to 120 ^{o}C and significantly reduced relative humidity
- Durability, improved fuel cell performance

Task 1

Synthesis and characterization of functionalized polymeric materials suitable for the desirable composite membranes.

Task 2

Synthesis and characterization of inorganic proton conductive materials suitable for the desirable composite membranes.

Task 3

Fabrication and characterization of composite membranes and MEAs for PEMFC in automotive applications.

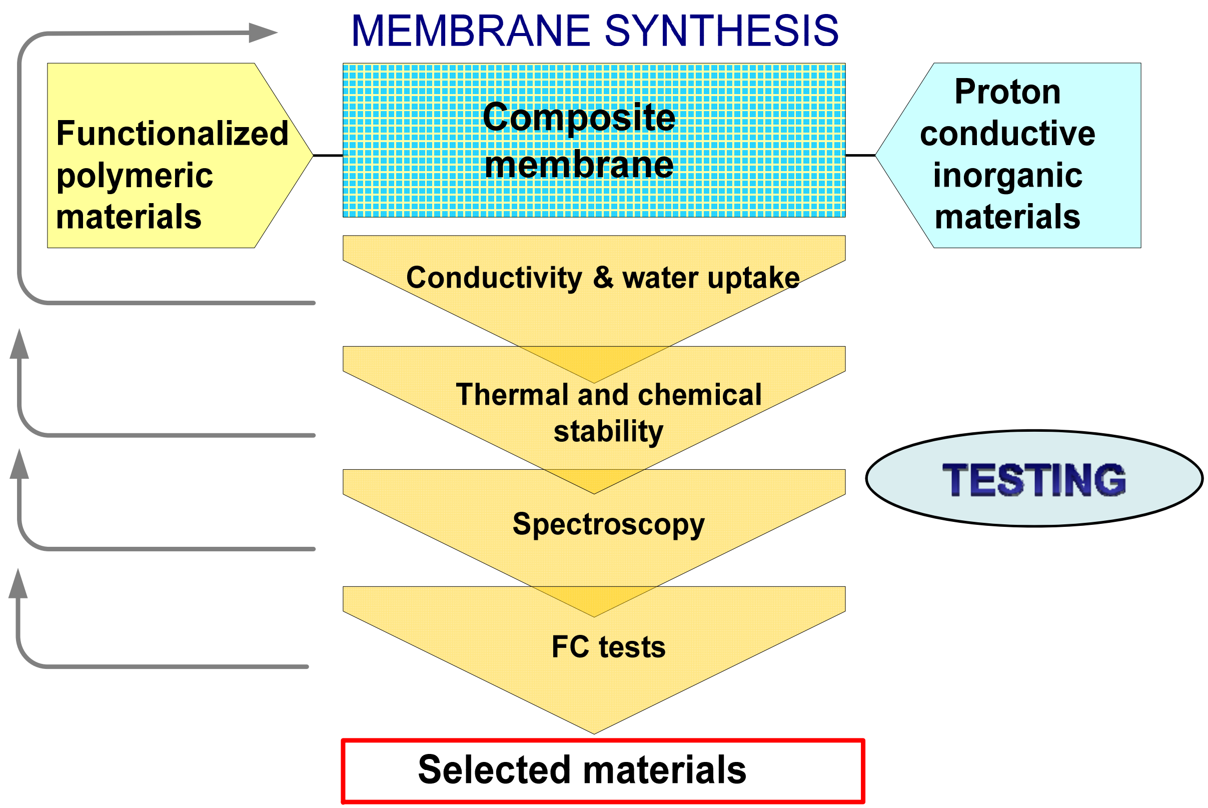
Project Relevance to DOE Objectives

This membrane development effort addresses the DOE research and development objective to provide membranes that allow operation at high temperatures. High-temperature polymer electrolyte membranes (PEMs) are desirable for transportation applications (to facilitate thermal management) as well as for stationary applications (higher value heat in combined heat and power and/or CO-tolerance).

The project addresses DOE conductivity milestones:
70 mS/cm at 30^{o}C, 80% RH and 100 mS/cm at 120^{o}C, 50%RH and DOE high-temperature membrane 2010 and 2015 targets: a membrane capable of operating at inlet water vapor partial pressure <1.5 kPa.

The project focuses on the barriers in the development of PEMs such as high temperature low RH conductivity and durability.

Approach



The unique aspect of our approach is the use of hydrophilic highly proton conductive additives to hold on to water more tightly than the ionomer and increase membrane conductivity at higher temperature and low RH. These additives provide water-rich surfaces inside the membrane to attract the hydrophilic portions of the ionomer.

The approach addresses the barriers in the development of PEMs such as high temperature low RH conductivity and durability and DOE conductivity milestone of 100 mS/cm at 120^{o}C, 50%RH

Technical Accomplishments and Progress

Task 1

Previously presented accomplishments include the synthesis of Sulfonated Styrene Grafted Fluoropolymer P(VDF-CTFE)-g-PS via atom transfer radical polymerization and membrane testing.

P(VDF-CTFE)-g-PS had high thermostability, high proton conductivity, exceeding Nafion® at 120°C and 50, 70% RH at high sulfonation degree. Substantial lowering of excessive swelling and improvement of membrane flexibility were reached by the introduction of hexafluoropropylene (HFP) and increase of molecular weight of VDF-CTFE copolymer (HMW) without of compromising conductivity (Fig.1), but swelling was still very high in comparison with Nafion®

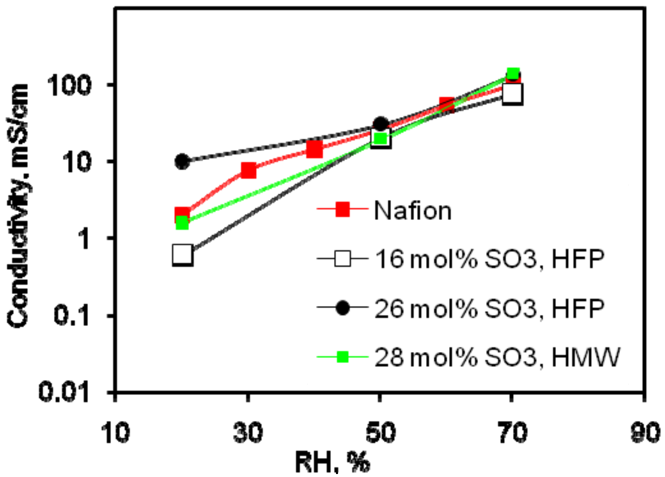
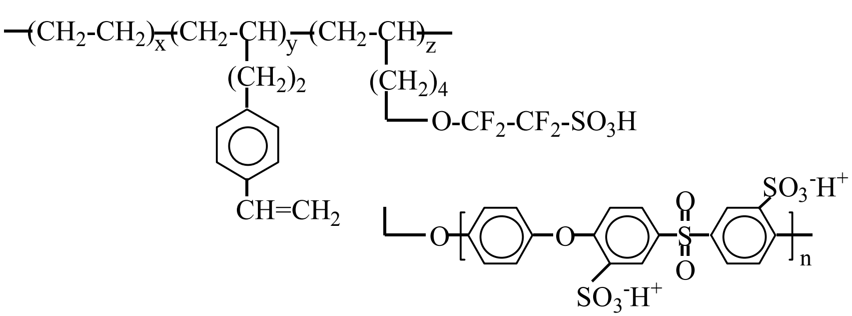


Figure1. Conductivity of P(VDF-CTFE)-g-PS membranes with addition of HFP and using VDF-CTFE of HMW at 120°C and different RH

Synthesis of new polyolefin based proton conductors:

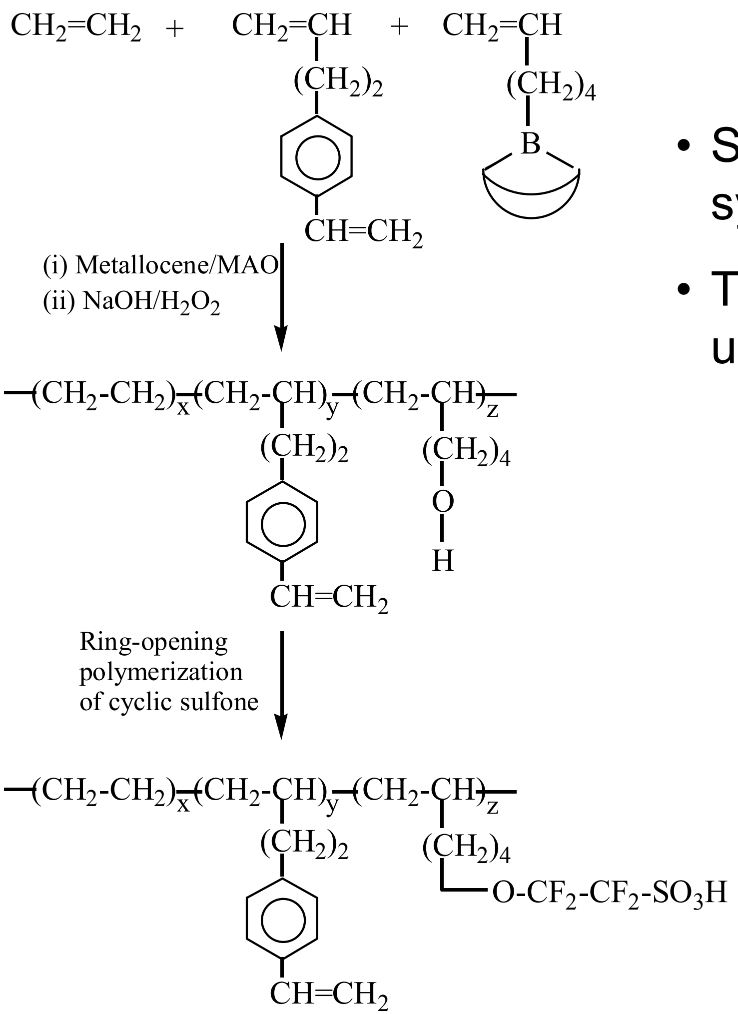
- very stable under free radical conditions
- semicrystalline thermoplastics with excellent mechanical strength
- have co-continuous hydrophobic and hydrophilic phase separated morphology
- cross-linkable



New polyethylene based proton conductor (PE)

Task 1

Synthesis of Sulfonated PE PEMs



- Sulfonated PE polymers successfully synthesized
- The major hurdle is in the processing of uniform PEM films

New approach to prepare the hydroxylated and crosslinked PE film before sulfonation

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Technical Accomplishments and Progress

Task 2

Synthesis and Characterization of Proton Conductive Inorganic Materials

Synthesis of new inorganics with different structures was developed and a number of inorganics including sulfonic acid functionalized porous materials were synthesized and characterized by X-ray diffraction (phase purity) and SEM (morphology and particle size) .

Inorganic:

Layered

α-$Zr(HPO_4)_2 \cdot H_2O$

$Sn(HPO_4)_2 \cdot H_2O$

3-dimensional

$H_3O\ Zr_2\ (PO_4)_3$

$H_2(SiTi_2O_7) \cdot 1.5H_2O$

2-dimensional

SBA-15

MCM-41

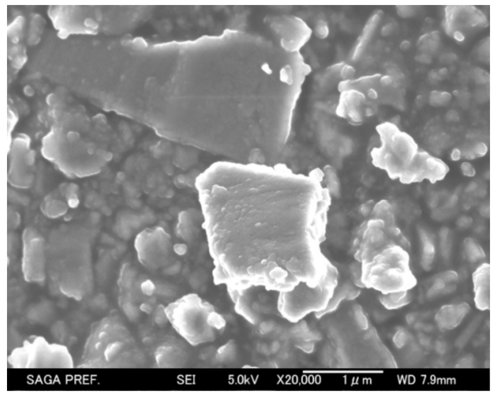
Sulfated

S-SiO_2

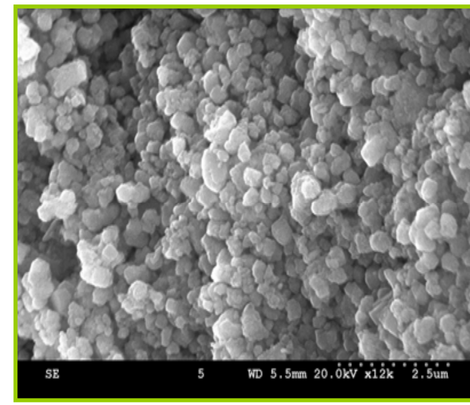
S-ZrO_2

Phosphated

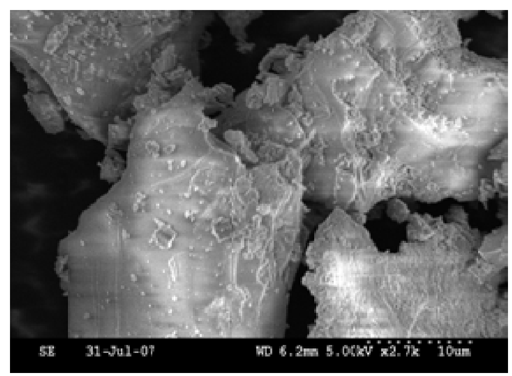
P_2O_5-SiO_2 gel



SEM Image of $Sn(HPO_4)_2$.



SEM Image of $H_2(SiTi_2O_7)(1.5H_2O)$



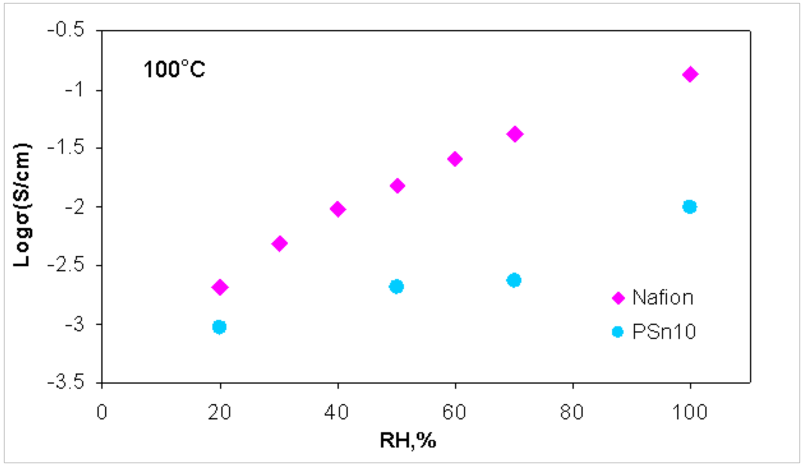
SEM Image of S-ZrO_2

Technical Accomplishments and Progress

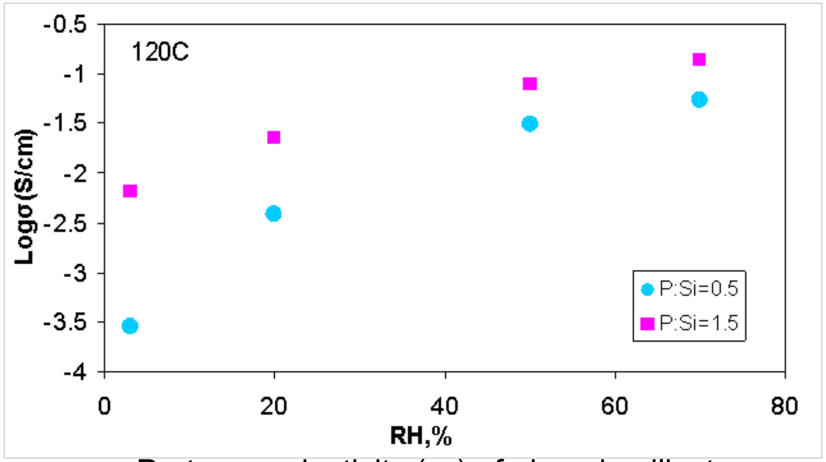
Task 2

Conductivity of New Inorganic Materials

- *Two-electrode through-plane measurements, EIS*
- *Inorganic pellet sample preparation*
- *Characterization for porosity and BET surface area*
- *BekkTech conductivity hardware*



Proton conductivity (**σ**) of $Sn(HPO_4)_2$ vs. Nafion® at 100°C and different RH.



Proton conductivity (**σ**) of phosphosilicate gels at 120°C and 3% to 70% RH.

- **σ** reached 0.01S/cm at 120 °C
- low dependence on RH (σ changed within one order of magnitude a range of RH from 20% to 70%
- the structure of stannic phosphate can provide water retention at 120 °C and reduced RH.

- **σ** of gel with a P/Si mole ratio of 1.5 reached 0.1 S/cm at 120 °C 70%RH, which is higher than for Nafion®.

The inorganics can be used in composite membranes to achieve DOE technical targets and milestone of 100 mS/cm at 120°C and 50% RH.

Task 3

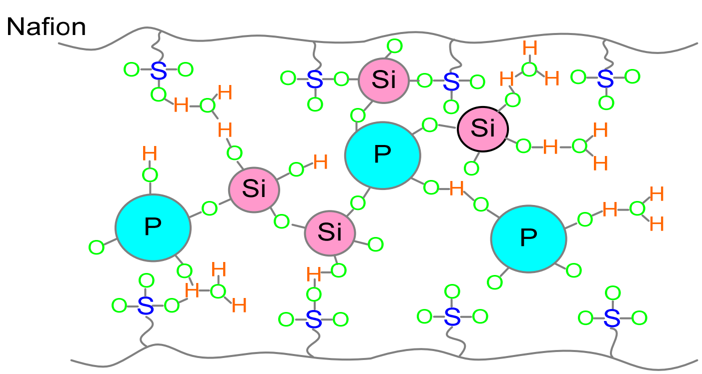
Polymer/Inorganic Composite Membranes

In the last year, the effect of newly synthesized inorganic materials and membrane fabrication techniques on composite membrane conductivity was tested in Nafion®/ Inorganic composite membranes to select the best candidates for future sulfonated PE/inorganic composite membranes to meet DOE conductivity milestone 100 mS/cm at 120°C, 50% RH and fuel cell needs on durability, mechanical and chemical stability

Inorganic tested

- Sulfated SiO_2
- Sulfated ZrO_2
- Phosphosilicate gel
- SBA - 15
- MCM - 41

Schematic of a Nafion®/ phosphosilicate membrane



Preparation

- Blending inorganic particles with 5% Nafion® solution followed by casting and annealing
- In situ formation of inorganic particles from precursor in a Nafion® film
- In situ formation of inorganic particles from precursor in 5% Nafion® solution followed by casting and heat treatment

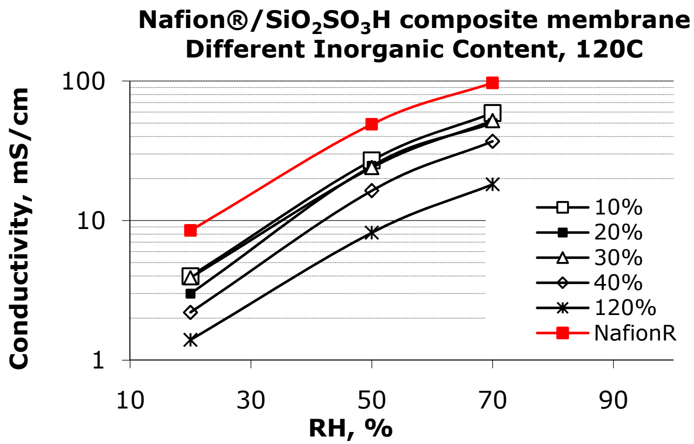
Technical Accomplishments and Progress

Task 3

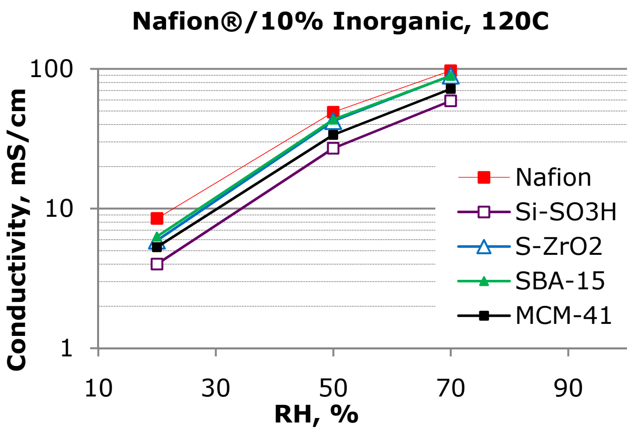
Polymer/Inorganic Composite Membranes
Blending technique
Conductivity

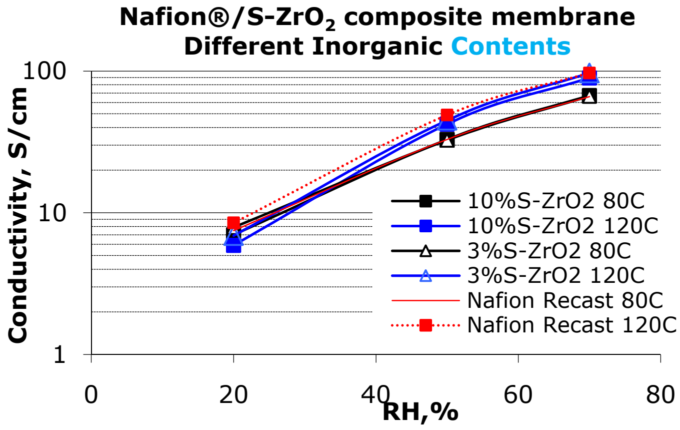
- The nature of inorganic additive affects the conductivity of the composite membrane
- No enhancement in conductivity of polymer matrix was reached by addition of inorganic by blending technique.
- High doping level (>20%) lowered the conductivity.

Different Inorganic Content



Performance of Different Inorganics





Technical Accomplishments and Progress

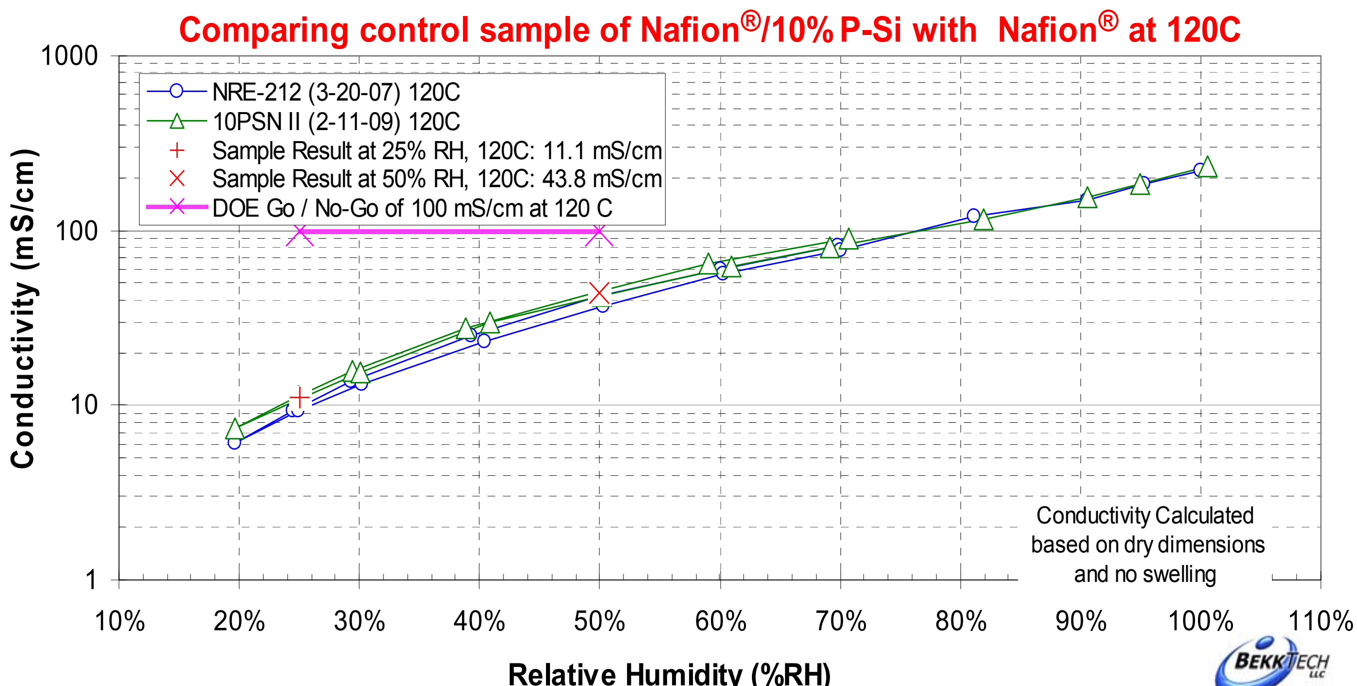
Task 3

Polymer/Phosphosilicate Gel Composite Membranes

In situ formation technique

Conductivity

- The best performance demonstrated the membrane prepared using in situ formation in Nafion® solution.
- P:Si ratio (from 0.2 to 1.5) did not affect membrane performance.
- Conductivity of Nafion®/10% P-Si gel membrane was slightly higher than Nafion® at all conditions.



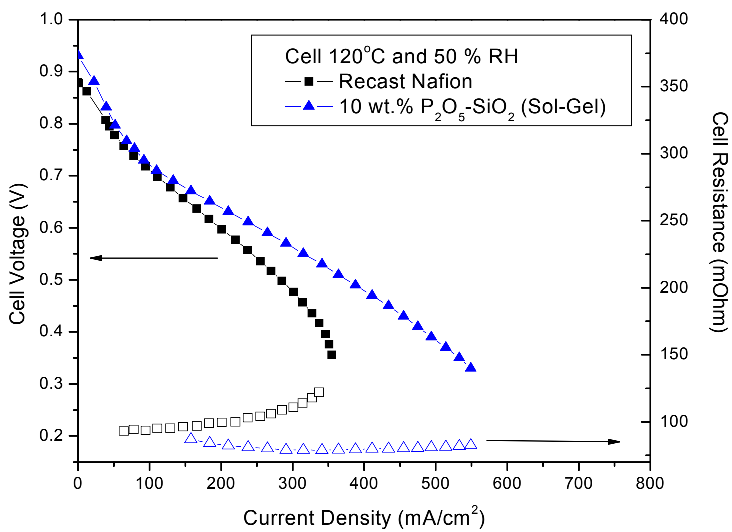
Technical Accomplishments and Progress

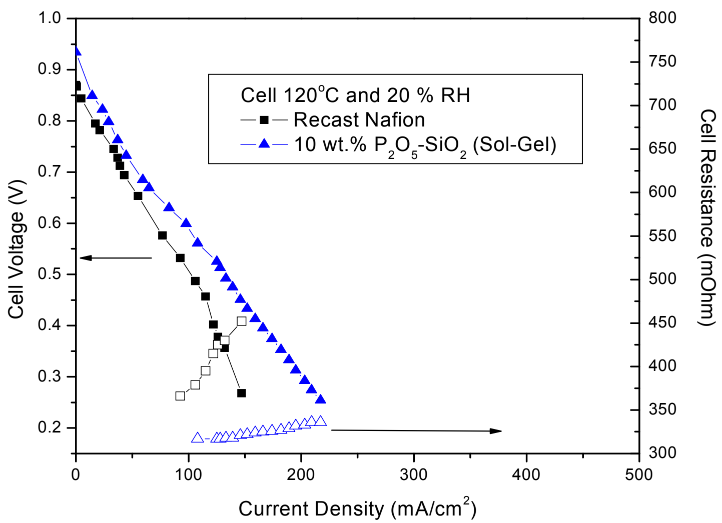
Task 3

Polymer/Phposphosilicate Gel Composite Membranes

Fuel Cell Performance

At 120 °C and 50 and 20% RH, resistance of Nafion®/ 10% P-Si gel membrane in a fuel cell 40-50% less and limiting current 40-50% higher than that of Nafion® membrane.





Performance and FC Resistance of Nafion®/10%P-Si Gel Membranes in H_2/Air Fuel Cell at 120 °C and Different RH

Collaborations

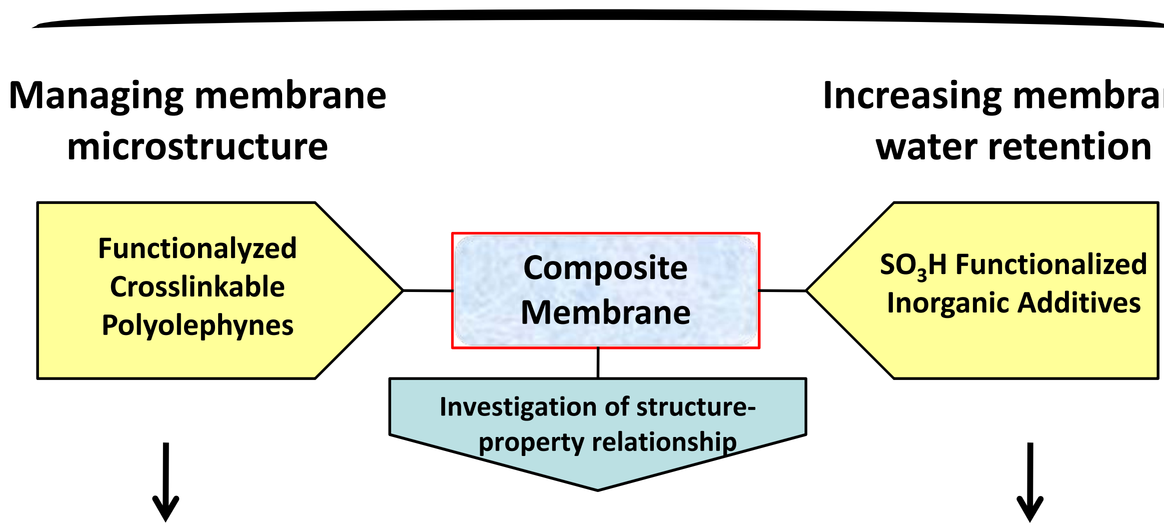
Partner: ***BekkTech LLC***

- Fuel Cell Testing & Diagnostic Services
- Within of the DOE H_2 Program
- Control Measurements of New Samples Conductivity

Possible Future Work

Our approach to achieve DOE goals on membrane conductivity

- 100 mS/cm at 120°C and 50% RH
- 100 mS/cm at ≤120°C and inlet water vapor partial pressure < 1.5 kPa



Controllable membrane structure with pure hydrophobic hydrocarbon backbone, higher concentration fluorinated sulfonic acid groups, and crosslinkable functional groups.

Increase water retention at low RH, enhance composite membrane conductivity by providing alternate proton conduction path, provide water-rich surfaces inside membrane changing the membrane structure.

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Project Summary

Relevance: Development of high temperature membrane necessary for energy efficient PEM fuel cell implementation

Approach: Composite membrane based on functionalized polymeric material and hydrophilic proton conductive inorganic capable to hold water more tightly than the ionomer and to increase membrane conductivity at higher temperature and low RH.

Technical Accomplishment and Progress: Synthesis of new chemically and mechanically stable cross-linkable polyolefin based proton conductors; synthesis and characterization of highly conductive inorganics; selecting the technique for composite membrane fabrication; fabrication of Nafion®/phosphosilica gel composite membrane with enhanced conductivity and substantially improved fuel cell performance

Collaborations: *BekkTech LLC,* fuel cell testing and diagnostic service

Possible Future Research: Development of composite membrane based on new chemically and mechanically stable cross-linkable polyolefin proton conductors and highly conductive inorganic to increase membrane water retention and conductivity up to the level necessary to meet the DOE milestones.