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

Serguei Lvov (PI)
Mike Chung (co-PI)
Sridhar Komarneni (co-PI)
Zhicheng Zhang
Elena Chalkova
Sanjeev Sharma
Mark Fedkin
Chunmei Wang

The Pennsylvania State University

Project ID#: FC22

May 16, 2007

This presentation does not contain any proprietary, confidential, or otherwise restricted information
Overview

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

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 FY06: $140,000
- Funding for FY07: $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*
- 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°C RH 25-50%.

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°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°C and 50%RH
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.

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.
Technical Accomplishments

Task 1

Synthesis of Functionalized Fluoropolymers Using Functional Borane Control Radical Initiator

$$\text{CH}_2=\text{CF}_2 \quad \text{CF}_2=\text{CFCl} \quad \text{CF}_2=\text{CF}$$

$$\text{CH}_2 \quad \text{CH}_2$$

$$\text{Si(}\text{CH}_3\text{)}_2\text{-O-R}$$

Borane Initiator

$$\text{CH}_2=\text{CH-Si-(OR)}_3$$

$$\text{BH}_3 / \text{THF}$$

$$\text{O}_2$$

Silane functional groups
- interacting with inorganic particles
- crosslinking
Technical Accomplishments

Fabrication of the new inorganic/polymer composite

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

**Zr-phosphates:**

3-dimensional phase: \( \text{H}_3\text{OZr}_2(\text{PO}_4)_3 \) (ZrPh) 8.7 m²/g
2-dimensional phase: \( \alpha-\text{Zr(HPO}_4)_2 \cdot \text{H}_2\text{O} \) 11 m²/g
Amorphous Zr phosphate: \( \sim \text{ZrOHPO}_4\cdot\text{H}_2\text{O} \) 325 m²/g

**Characterization:** XRD, SEM and BET

**Flow Chart for the synthesis of \((\text{H}_3\text{O})\text{Zr}_2(\text{PO}_4)_3\)**

\[ \text{(NH}_4\text{)}\text{H}_2\text{PO}_4 + \text{ZrOCl}_2\cdot8\text{H}_2\text{O} + \text{H}_2\text{O} \]

\[ 92.45 : 22 : 3000 \text{ mMol} \]

1. Hydrothermal treatment 200°C, 48 hrs
   \( \text{(NH}_4\text{)}\text{Zr}_2(\text{PO}_4)_3 \)
2. Calcination 540°C, 6 hrs
   \( \text{HZr}_2(\text{PO}_4)_3 \)
3. Hydrothermal treatment 200°C, 24 hrs
   \( \text{(H}_3\text{O})\text{Zr}_2(\text{PO}_4)_3 \)

\( a \) - Three dimensional \( \text{HZr}_2(\text{PO}_4)_3 \) where \( \text{M} \) represents protons along with water molecules

\( b \) - Layered \( \alpha-\text{Zr(HPO}_4)_2\cdot\text{xH}_2\text{O} \) where exchangeable protons are present in the interlayers as OH.
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 H₂(SiTi₂O₇)(H₂O)₁.₅
  SSA: 70 m²/g

- Three-dimensional H₃O(SnxZr₂-x)(PO₄)₃
  SSA: 23 m²/g

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

SEM Images of: a - H₃O(SnxZr₂-x)(PO₄)₃, b - H₂(SiTi₂O₇)(H₂O)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°C

**Fabrication procedure:**

1. **Polymers** + **Acetone** → **Polymer solution** → **Stirring** → **Composite membrane**
2. **Thermal compressing** → **Solvent evaporating** → **Casting on a substrate**

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

Fabrication of the new inorganic/polymer composites

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

Exploring different avenues to obtain desirable membrane conductivity without Nafion:

- Sulfonation of inorganic phases:

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

P(VDF-CTFE-Sulfonated TMPS*):

- Introduction of sulfonic groups into side chains of copolymer:

  Crosslinkable P(VDF-CTFE-SiOR)

* - Trimethoxyl phenyl silane

TMPS

P(VDF-CTFE-SiOR-Sulfonated TMPS)
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-TFE)/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.
Testing Conductivity of Different Composite Membranes

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

<table>
<thead>
<tr>
<th>Additives</th>
<th>Conductivity @ 70%RH, mS/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al₂O₃</td>
<td>0.003ᵃ</td>
</tr>
<tr>
<td>α-Zr(HPO₄)₂·H₂O (α-ZrPh)</td>
<td>0.038ᵇ</td>
</tr>
<tr>
<td>MSᵈ</td>
<td>0.145ᶜ</td>
</tr>
<tr>
<td>HTiSiO₄</td>
<td>4.33ᶜ</td>
</tr>
<tr>
<td>ZrPh Amorph.</td>
<td>7.52ᶜ</td>
</tr>
<tr>
<td>Zr(HPO₄)₂·H₂O</td>
<td>9.40ᶜ</td>
</tr>
</tbody>
</table>

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

1. 30%VDF-CTFE/30%Nafion/40%Zr(HPO₄)₂·H₂O
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.

Zr(HPO₄)₂·H₂O is the most promising additive.

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
Technical Accomplishments

Exploring different avenues to obtain desirable membrane conductivity without Nafion:

- Sulfonation of inorganic phases:
  \[ \text{RO-Si(OH)}_{x} \text{SiOR} \rightarrow \text{RO-Si(OH)}_{x} \text{SiOR-SO}_{3}H \]

- Introduction of sulfonic groups into side chains of the copolymer:
  \[ \text{P(VDF-CTFE-SiOR-Sulfonated TMPS*)} \]
  * -Trimethoxyl phenyl silane

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
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
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.

Summary

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.

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.

Relevance

Approach

Future perspective