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

Serguei Lvov (PI),
Mike Chung (co-PI),
Sridhar Komarneni (co-PI),
Elena Chalkova, and
Mark Fedkin

The Pennsylvania State University

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Project ID #
FCP 17

Overview

Timeline

- Project start date: May 1st, 2006
- Project end date: April 30th, 2011
- Percent complete: project just started

Budget

- Total project funding
  - DOE share: $1,300,698
  - Contractor share: $325,175
- DOE funding for FY2006: $150,000

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

Barriers

- Barriers:
  - Stability of membranes in the range of -20 – 120°C.
  - High conductivity and mechanical integrity of membranes at elevated T and low relative humidity
- Main targets:
  - Operating temperature to 120°C
  - Conductivity 0.01-0.1 S/cm
  - Inlet water vapor pressure 50-100 kPa
  - Cost 40 $/m^2

Objectives

<u>Overall</u>: Contribute to DOE efforts in developing high temperature PEM for transportation application. Develop a new composite membrane material with hydrophilic inorganic particles as a major component and TFE/VDF polymers as a matrix to be used in a PEMFC in the temperature range of -20-120^{o}C and relative humidity range of 25-50%.

<u>2006 - 2007:</u>

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

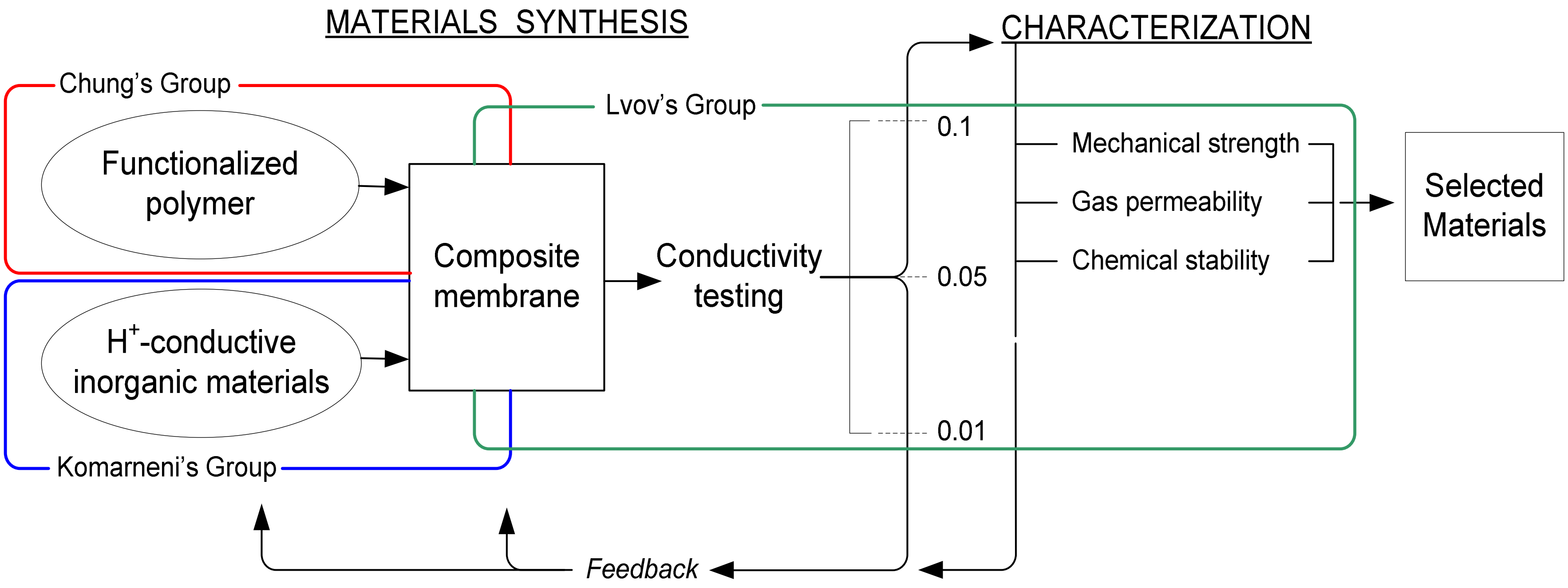
<u>2007 - 2008:</u>

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

<u>2008 - 2009:</u>

- Membrane optimization based on test results and adjustment of the synthesis of polymers and inorganic additives.
- Reaching the Milestone of proton conductivity of 0.1 S/cm at 120^{o}C and 25-50%RH

Approach



The main idea is to synthesize *mainly inorganic* membrane, which would include:

- 60-80% of highly hydrophilic proton-conductive inorganic material
- polymeric matrix that is able to "bridge" the conduction paths in membrane by functionalized chain ends.

Three research groups will be involved in a loop of continuous synthesis and serial testing until the final product meets the target requirements.

Technical Accomplishments

- We will synthesize a poly[vinylidene fluoride]-based polymer with chain–end functional groups which is highly compatible with the inorganic surfaces. The polymer can serve as an interfacial agent to bind the inorganic particles into a continuous membrane.
- A technological procedure will be developed to incorporate high loads of hydrophilic inorganic particles into the polymer. It involves direct mixing of the low molecular weight 3-D precursor, with inorganic particles followed by casting procedure. The recast films will be cured by a coupling agent to form crosslinking sites in 3-D polymer network (see Fig. 1).
- In our preliminary study, an inorganic/organic composite membrane containing 60% of 3-D structured $H_3OZr_2(PO_4)_3$ and 40% of functionalized poly[vinylidene fluoride] with Si- terminal groups and Si-OH functional groups was fabricated.

Technical Accomplishments

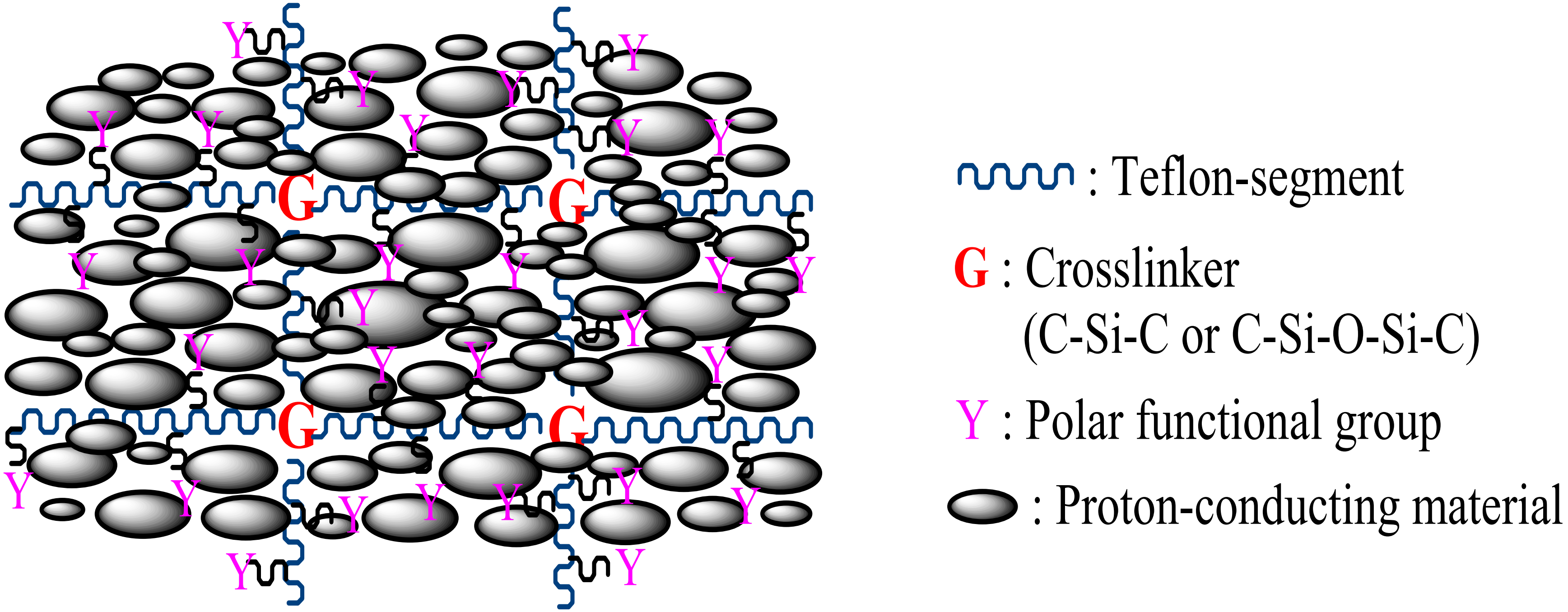


Fig. 1. Structure of the new inorganic/polymer composite

Technical Accomplishments

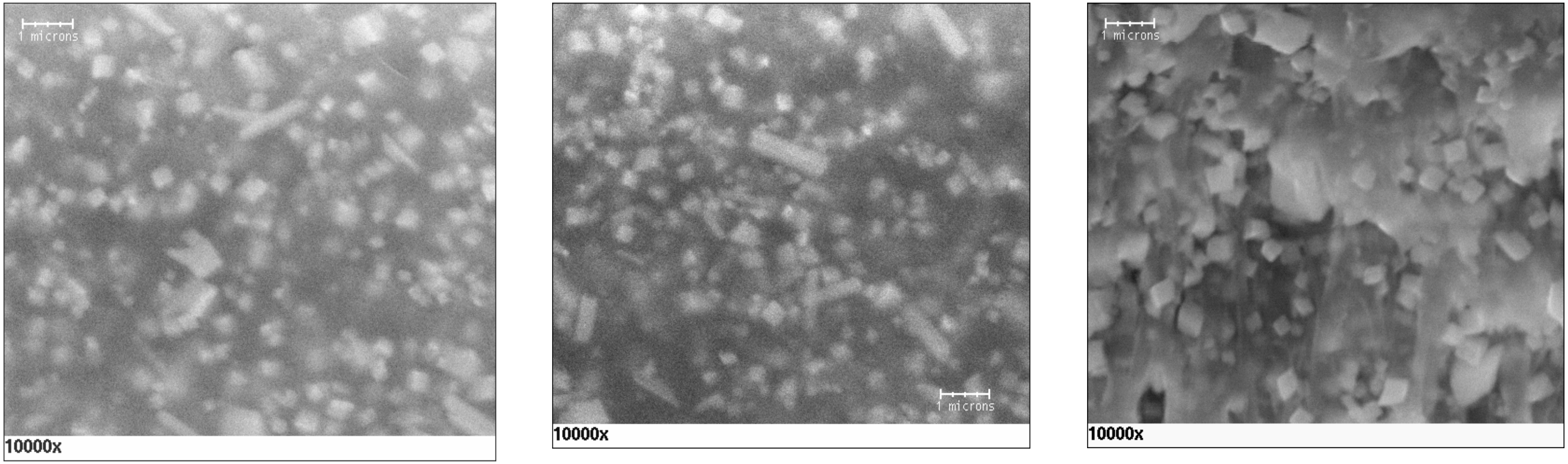
Conductivity (in water) and water uptake of the new composite membrane and Nafion for comparison

T, °C	Water uptake, wt.%	
	New composite material	Nafion®
23	0.9	28
100	1.1	27

T, °C	Conductivity, S/cm	
	New composite material	Nafion®
120	0.07	0.17
140	0.1	0.1

In contrast to Nafion, the composite membrane’s conductivity continued to grow as temperature increased from 120 to 140°C. At 140°C, it reached the same value as conductivity of a Nafion membrane. The new membrane has a very low water uptake (about 1%).

Technical Accomplishments



a b c

Fig. 2. SEM images of the new 60% $H_3OZr_2(PO_4)_3$ / 40% PVDF(Si) membrane: (a) and (b) show the surface on the opposite sides of the membrane and (c) is the cross-sectional image.

Based on the surface images the distribution of inorganic particles (300-500 nm in size) inside the membrane is uniform.

Technical Accomplishments

Properties of the new material suited to project goals:

- High proton conductivity at elevated temperature
- Minimal dependence on the availability of free water (highly promising for low RH operation)
- Chemical inertness (for both inorganic particles and polymer)
- Thermal stability to at least 150^{o}C
- Highly hydrophilic solids - once hydrated the particles can preserve a very thin surface layer of adsorbed water (within electrical double layer) up to temperatures above 200^{o}C even at very low RH.
- Bonding compatibility between the polymer and inorganic surfaces via inorganic crosslinkers, which also contribute to overall hydrophilicity of the material.

Future Work

- **Plan for the rest of FY06**
  - Develop chemistry for synthesis of functionalized and crosslinkable TFE/VDF polymers
  - Synthesize and perform surface and structural characterization of inorganic powders (Zr-phosphate phases, mesoporous alumina, titania, etc.) and find the most prospective inorganic materials
  - Fabricate a series of membrane specimens using existing technology and procedures for the first characterization loop
  - Test the membranes for conductivity
  - Reveal the potential technical issues and strategies to resolve them
- **Plan for FY07**
  - Scale up the supply of TFE/VDF polymers and inorganic additives
  - Produce “workable” membrane specimens for the complete electrochemical and structural characterization
  - Reach the conductivity criterion of 0.07 S/cm at target temperature and relative humidity by the end of the year.

    This will be 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 a composite

- **Expected results**

Main Characteristics	**Target**
Membrane conductivity	0.01 – 0.10 S/cm
Operating temperature	$\leq 120^{o}$C
Relative Humidity	25-50%
H_2/O_2 cross-over	2 mA/cm^2
Cost	40 \$/m^2
Survivability	to -40^{o}C
Thermal cyclablility w/condensed water	Yes

- **Future perspective:**

We plan to accomplish the transition from mainly polymeric membrane to mainly inorganic membrane. This will make it possible to minimize the reliance of membrane performance on liquid water stability and will make the PEMFC technology more adaptable to real life conditions.

Related Publications

Papers:

Fedkin, M.V., Chalkova, E., Komarneni, S., Wesolowski, D.J., and Lvov, S.N., Surface Electrochemistry of Composite Materials for High-Temperature PEM Fuel Cells, *Electrochem. Soc. Transactions*, 2006, (submitted).

Conference presentations:

Lvov S.N., Chalkova E. , Fedkin M.V., Chung M., Komarneni S., Sofo J., and Wesolowski D.J. Synthesis, Structure, and Surface Chemistry of New Inorganic-Organic Composite Materials for High-Temperature Proton Exchange Membrane Fuel Cells, *The Russian International Conference on Chemical Thermodynamics*, Moscow, August, 2005.

Chalkova E., Fedkin M.V., Komarneni S., Chung M., and Lvov S.N., Composite Materials for PEM Fuel Cells Operating at High Temperature and Low Relative Humidity, 208th ECS Meeting, Abstract # 933, Los Angeles, California, October, 2005.

Patents:

T.-C. Chung, S. Komarneni, E. Chalkova, and S.N. Lvov, Composite Membrane for Fuel Cell and Fuel Cell Incorporating Said Membranes. U.S. Provisional Patent Application Serial No. 60/670,186, Filed April 11, 2005.

Critical Assumptions and Issues

1. Conductivity of composite material

If composite membrane conductivity is not high enough to reach the Milestone of 0.07 S/cm at 80% RH at 25°C:

a) A polar hydrophilic functional group that is located in the side chains of the telechelic Teflon-based polymers can be replaced by a more polar group. We will investigate several polar hydrophilic functional groups, such as -OH, -$Si(OH)_3$, -$PO(OCH_3)_2$, -SO_3R, -NH_2. The concentration of functional groups in polymer can be also changed.

b) Matching the surface properties of the inorganic and organic phases can be improved. In particular, our approach takes into account the characteristics of the electrical double layer (EDL) on the hydrated surface of inorganic particles. We will use the surface charge and zeta potential data (measured at high temperatures) for the proposed inorganic and organic materials and surface charge adjustments to optimize the synthesis procedure.

c) Inorganic particle size and specific surface area, content of inorganic component in composite material can be also optimized.

Critical Assumptions and Issues

2. Membrane gas permeability and mechanical stability

We believe that the inorganic membranes (up to 80 mass % of inorganic solids) are promising candidates. However, if the amount of polymer is not sufficient to provide required mechanical robustness, the following factors can be manipulated to improve composite properties:

- inorganic/polymer ratio
- specific surface area of inorganic powder
- distribution of inorganic particles in the polymer matrix
- zeta potential and surface charge of the inorganic particles and polymeric matrix
- form of water and protons incorporated in the inner structure or adsorbed on the surface.