V.B.20 Fluoroalkylphosphonic-Acid-Based Proton Conductors

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Contract Number: DE-FG36-06GO16031

Subcontractors:
University of Utah, Salt Lake City, UT

Start Date: April 2006
Projected End Date: March 2011

Objectives

- Synthesize and characterize new proton-conducting electrolytes based on the fluoroalkylphosphonic acid functional group.
- Create and apply new computer models to study protonic conduction in fluoroalkylphosphonic acid-based electrolytes.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4.2) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(D) Thermal, Air and Water Management

Technical Targets

The following technical targets from Table 3.4.12 from the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan are relevant to this project:

- Membrane ionic conductivity >0.10 S/cm at <120°C and water partial pressure of 1.5 kPa for transportation applications (2010 target)
- Membrane ionic conductivity >0.10 S/cm at >120°C for stationary applications

We will seek to prepare new electrolyte membranes that will meet or exceed these targets. The electrolytes will be based on the fluoroalkylphosphonic acid functional group, which offers good prospects for enabling proton conduction under high-temperature, low-humidity conditions while also being compatible with low-temperature, high-humidity conditions as would be expected in a transportation (e.g. automotive) fuel cell.

The project is in a very early stage so no results are yet available that would enable comparison with these technical targets.

Approach

We will follow a dual approach involving synthesis and characterization of new electrolytes focusing on ion conduction under a wide range of conditions of temperature and water content (humidity), coupled with computer modeling work that will help explain whether and how proton transport can be facilitated by a Grotthuss-like hopping mechanism, and how the membrane morphology/cluster structure is important in proton transport.

The work will be pursued in seven task areas, as follows:

1. Synthesize new fluoroalkylphosphonic-acid-based electrolytes.
   - Small-molecules, trifluorovinyl ether (TFVE) monomers, ionomer membranes
2. Characterize new fluoroalkylphosphonic-acid-based electrolytes.
   - Structure/purity, conductivity, ion self-diffusion
3. Demonstrate conductivity of at least 0.07 S/cm at 80% relative humidity (RH) at ambient temperature.
4. Demonstrate conductivity of at least 0.10 S/cm at 50% RH at 120°C.
5. Simulations of fluoroalkylphosphonic-acid-based electrolytes.

- Classical force fields, multi-state empirical valence bond (MS-EVB) models

6. Simulations of fluoroalkylphosphonic acid electrolyte/heterocycle/water mixtures.
7. Project management and reporting.

Accomplishments

Work has begun on Task 1 aiming to synthesis some model compounds, in advance of studies with ionomer membranes. Figure 1 presents a summary of the synthetic methodology being used. Synthesis of hundreds of milligrams of a fluoroalkylphosphonic acid with the fluoroalkyl group (Rf) = $CF_3CF_2CF_2$- has been accomplished, and synthesis of several other variants using different fluoroalkyl groups is in progress.

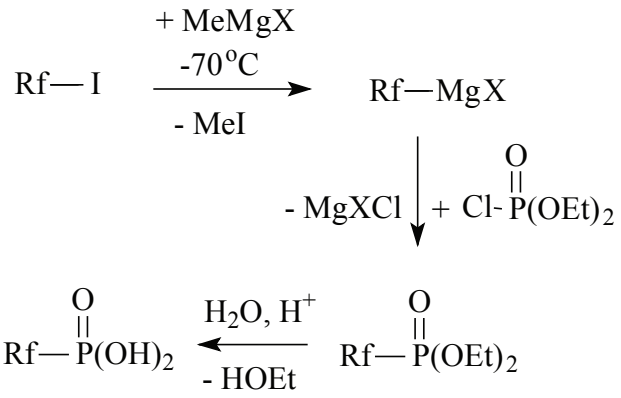

FIGURE 1. Scheme for Synthesizing Fluoroalkylphosphonic Acids from Fluoroalkyl Iodides

A variable-temperature, variable-pressure chamber with integrated liquid conductivity cell is being fabricated. A schematic diagram of the cell is shown in Figure 2. This cell will be used to study conductivity in mixtures of fluoroalkylphosphonic acid electrolytes with water under pressurized conductions at temperatures up to 150°C.

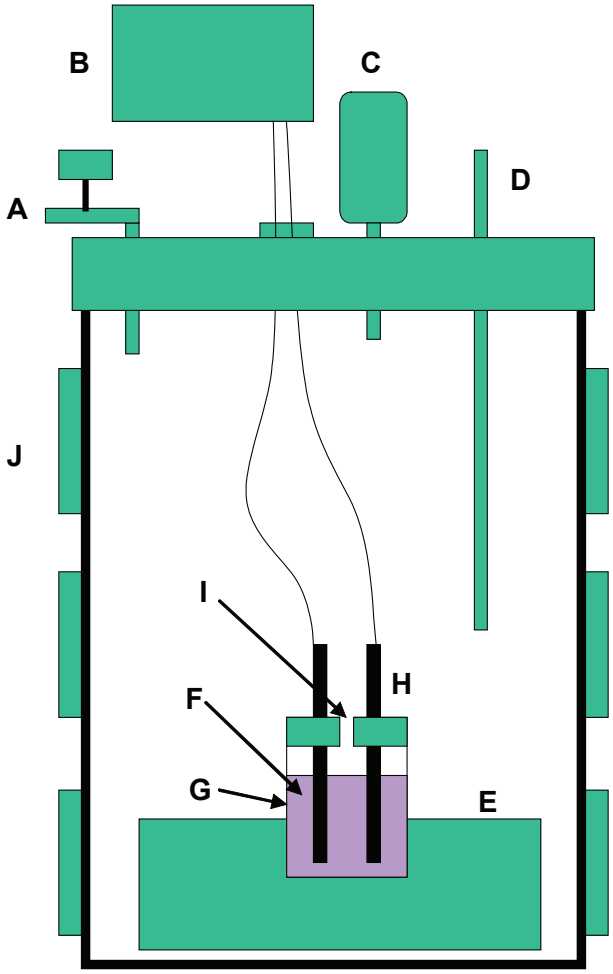

FIGURE 2. Diagram of a Conductivity Cell for Study of Fluoroalkylphosphonic Acid Electrolytes Parts are as follows: A. Vacuum/gas inlet/outlet B. Impedance analyzer C. Pressure transducer D. Thermocouple E. Cell holder F. Liquid electrolyte (acid plus water plus additives) G. PEEK cell body H. Platinized platinum rod electrodes I. Pressure equalization hole (very narrow) J. Heating tape for temperature control