V.D.1 Lead Research and Development Activity for DOE’s High Temperature, Low Relative Humidity Membrane Program

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4) of the Hydrogen, Fuel Cells and Infrastructure Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability
(C) Performance

Technical Targets

FSEC has been developing and evaluating new polymeric electrolyte PTA composite membranes to increase conductivity. FSEC is also developing standardized experimental methodologies to:
(1) measure conductivity (in-plane and through-plane);
(2) characterize mechanical, mass transport, and surface properties of the membranes; and (3) predict durability of the membranes and their membrane electrode assemblies.

The primary goal was for the membranes to meet the following DOE targets:

- A non-Nafion® membrane with a demonstrated conductivity of 0.07 S/cm at 80% RH at room temperature by the third quarter of year two.
- A membrane with a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa water vapor partial pressure (50% RH measured at room temperature). This is a Go/No-Go decision point for the third quarter of year three.

Accomplishments

- Demonstrated conductivity of >0.07 S/cm at 80% RH at 30°C for the FSEC-3 membrane (exceeded Year 2 third quarter milestone).
- Achieved conductivity of 0.08 S/cm at 120°C and 1.5 kPa water vapor partial pressure (0.02 S/cm below Go/No-Go decision point milestone).
- Provided in-plane conductivity measurements for ten HTMWG teams and developed through-plane conductivity measurement method.
- Developed protocol for standardized testing of performance.
- Verified protocol in-house and distributed to HTMWG members at the May 2009 HTMWG meeting.

Objectives

- Demonstrate conductivity of 0.07 S/cm, at 30% relative humidity (RH), 25°C using new polymeric electrolyte phosphotungstic acid (PTA) membranes.
- Demonstrate conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack.
- Standardize methodologies for in-plane and through-plane conductivity measurements.
- Provide High Temperature Membrane Working Group (HTMWG) members with standardized tests and methodologies.
- Organize HTMWG biannual meetings: http://www1.eere.energy.gov/hydrogenandfuelcells/htmwg.html
Introduction

Proton exchange membrane fuel cells (PEMFCs) have increasingly received worldwide attention due to their potential use in the hydrogen economy. Generally, two regimes of PEMFC operation exist: the typical operating temperatures between 60-80°C, and elevated temperatures higher than 100°C. The ability for current automotive radiators to reject heat is insufficient at continuous full power waste heat loads for 60-80°C fuel cell stack temperatures. Running the stack at 120ºC under full load would allow the use of radiators similar to those available in automobiles today. This has driven the need for development of high-temperature membranes and membrane electrode assemblies that could operate at temperatures of up to 120°C, low RH and near atmospheric pressure.

The objective of the current project is to develop a fuel cell membrane material that meets the goals outlined by the DOE in the multi-year plan. Additional goals are: operation at elevated temperatures (up to 120°C), with a demonstrated conductivity of >0.1 S/cm at 120°C and 1.5 kPa inlet water vapor partial pressure to the fuel cell stack (50% RH measured at room temperature). The material needs to operate over a range of operating conditions from -20 to 120°C because conductivity at the lower temperature is necessary to achieve both quick start-up from cold temperatures and efficiency targets. Inlet water pressures of 25 kPa today are acceptable, but 1.5 kPa at the end of this five-year project is required. The membrane electrode assemblies (MEAs) fabricated from the membranes must meet durability targets in the aggressive environment of a fuel cell; i.e., the material must have good chemical stability and be resistant to oxidation by radicals produced in the cell during operation.

Approach

FSEC is a development leader, as well as a membrane developer. As development leader, FSEC develops and provides protocols, conducts standardized tests on samples from the group members, and provides fuel cell training with yearly hands-on “Short Courses” on conductivity and fuel cell performance testing. As a membrane developer, FSEC was developing membranes based on poly(perfluorosulfonic acid) (PFSAs) and on sulfonated poly(ether ether ketone) (SPEEK/SPEKK). New composite membranes containing small particle stabilized phosphotungstic acid were fabricated using non-Nafion®-based PFSAs of equivalent weight (EW) lower than 1100, SPEEKS with various sulfonation degrees, or SPEKK as the proton-conducting component in a blend with either poly(ether sulfone) or SPEKK with different sulfonation levels. The FSEC team, along with subcontractors BekkTech, LLC, and Scribner Associates, working with the fuel cell community, are developing standardized experimental methodologies to: (1) measure conductivity as a function of RH and mechanical properties of membranes; (2) characterize mechanical, mass transport and surface properties of the membranes; and (3) predict durability of the membranes and their membrane electrode assemblies, which have been fabricated by the FSEC team for the in-house research program and that will be fabricated for membranes provided by the HTMWG. FSEC will develop and provide the DOE’s HTMWG with standardized tests and methodologies, along with short course education offerings on these test methodologies and membrane electrode assembly fabrication techniques so that all research program members will be able to understand and reproduce these processes in their own facility. An easily implemented protocol and rapid test apparatus for evaluating the through-thickness conductivity (or resistance) of membranes over a broad range of conditions has also been developed.

Results

The Go/No-Go milestone occurred late in this contract year. To support the effort for the HTMWG members, conductivity measurements were made on membranes supplied by Fuel Cell Energy, Case Western Reserve University, University of Tennessee, Vanderbilt University, Virginia Polytechnic Institute and State University, Penn State University, Colorado School of Mines, Clemson University, and Giner, Inc. The results of these tests can be seen in Figure 1.

Over the first three years of the project, FSEC has evaluated five composite membranes: FSEC-1, FSEC-2, FSEC-3, FSEC-4, and FSEC-SLR. The first four membranes are poly(perfluorosulfonic acid)-phosphotungstic acid composite membranes, while the FSEC-SLR is a SPEEK-phosphotungstic acid...
composite membrane. The FSEC-1 membrane is a 25-30 µm thick composite membrane, prepared using a solution of an 1100 EW ionomer and PTA, cast on a thin, porous Teflon® support. The FSEC-1 membrane has been shown to be more durable than Nafion®-like membranes because of the support material, the presence of hetropolyacids, which decompose free radical oxidizing agents formed during fuel cell operation, and a higher temperature fabrication process that improves durability. The FSEC-2 membrane uses a 950 EW ionomer in place of the 1100 EW ionomer, and the FSEC-3 membrane uses a 750 EW ionomer. While the manufacturing processing steps are the same in the fabrication of FSEC-1, -2, and -3, the process conditions for the manufacture of FSEC-1 have been optimized to obtain maximum conductivity and durability. Since the conductivity of early FSEC-3 membranes showed substantial improvements over both the FSEC-1 and -2 membranes, FSEC-2 was not optimized. While some optimization process development of FSEC-3 has been completed, the lower EW PFSA ionomer has proven to be more sensitive to changes in the process variables than the higher EW ionomer. The improvements in conductivity that occurred as a result of the changes to the process can be seen in Figure 2. Manufacturing process changes, including the use of high-boiling solvents, modified drying times, stabilization with cesium, and adjusted heat-treat conditions for the 750 EW ionomer/PTA composite membrane, have shown conductivities (measured at FSEC) between 75 and 80 mS/cm, and are shown as FSEC-4 in Figure 2.

While significant conductivity improvements over Nafion® were achieved in the FSEC series of membranes, the Go/No-Go milestone was not achieved. As a result, the membrane development under this project has been halted.

The official conductivity measurements that were made under this project were made using the in-plane method. However, conductivity in an operating fuel cell is through-plane. As a result, a new novel method for making through-plane measurements was developed. A comparison of the two methods was made by measuring the conductivity of a number of standard Nafion® membranes. As can be seen in Figure 3 for Nafion® NRE-212, the conductivities were very similar for the two methods.

The DOE goal of this project is to meet the conductivity target at 120°C and 50% RH, but additional targets must also be met; for example, chemical and mechanical stability, cycle life of over wide ranges of operating temperature, minimal gas crossover, cost, tolerance to condensed water, and ability to be started from -40°C are also important. Meeting all of these membrane targets, as well as MEA targets, will ultimately be required to achieve the DOE-outlined 2015 goals. In preparation for the next two years of the project, FSEC has developed a standard protocol for performance testing of MEAs that will be constructed from membranes supplied by the HTMWG members remaining after the Go/No-Go milestone. FSEC has verified this protocol using commercial MEAs, as well as MEAs with FSEC series membranes. This protocol was distributed to the working group at the meeting in May 2009. An additional protocol has been written for accelerated endurance testing and is being verified.

Conclusions and Future Directions

- Significant progress has been made in improving the conductivity and performance of membranes.
- In accordance with the DOE decisions after the Go/No-Go Review, membrane development under this project has been halted.
- Verification of the accelerated endurance test protocol will be completed.
- Membrane electrode assemblies will be prepared from team member membranes.
- Performance testing of MEAs will be conducted.
FY 2009 Publications/Presentations


