V.G.1 Large-Scale Testing, Demonstration and Commercialization of the Nanoparticle-Based Fuel Cell Coolant (SBIR Phase III)

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Contract Number: EE00004532

Subcontractors:

- University of Tennessee, Knoxville (UTK), TN
- Protonex Inc., MA

Project Start Date: October 1, 2010
Project End Date: September 30, 2013

Overall Objectives

- Understand coolant durability requirements by working with different fuel cell companies.
- Optimize coolant property in order to maintain low electrical conductivity and other thermo-physical properties for over 5,000 operating hours.
- Demonstrate materials compatibility of the fuel cell components with the coolant.
- Develop a system for long-term durability and diagnostics testing of nano-particle fuel cell coolant.

Fiscal Year (FY) 2013 Objectives

- Increase the nano-particle surface charge to >500 µeq/g for both cationic and anionic particles.
- Examine the compatibility of different coolants with the components of a typical fuel cell system over the course of 5,000 hours.
- Validate efficiency of corrosion inhibition abilities of Dynalene coolants at high temperature.
- Determine the effect of nano-particles on the surface of fuel cell components through various testing.
- Perform and compare short-term (100 hrs) and long-term (1,000 hrs) performance of coolants in the fuel cell (with or without applied voltage) in order to determine optimal coolant configuration.
- Achieve successful commercialization of the Dynalene Fuel Cell (Dynalene FC) coolant.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(A) Durability

(B) Cost

(C) Performance

Technical Targets

Dynalene FC is expected to help the fuel cell industry achieve the durability, cost, and performance targets. The current findings can be summarized as:

- Durability: coolant designed to have shelf life of 5,000 hrs. Immersion testing demonstrated minimal corrosion, and superior compatibility with system materials thereby extending the durability of the fuel cell system components such as the pump, the radiator, valves, seals/gaskets, and any other components coming in contact with the coolant.
- Cost: the projected selling price of coolant as production scales up (>100,000 gal/year) is about $10 per gallon, which is close to the price of the current automotive coolants.
- Performance: Dynalene LC and FC showed low electrical conductivity (<2 µS/cm) with high boiling point (>100°C), high thermal conductivity and low viscosity. The fluid is freeze tolerant under extremely cold conditions (<-40°C) which will assist both transportation and stationary fuel cells to quickly warm up during cold starts.

FY 2013 Accomplishments

Following are the accomplishments from July 1, 2012 to June 30, 2013:

- Surface charge of reformulated nano-particle has been increased to 890 µeq/g.

- Compatibility and thermal degradation studies of polymers and metals have been performed at 80°C for 5,000 hours.
- Corrosion inhibitors have been validated for metals at 80°C using electrochemical set-up.
- Coolants have been tested in working fuel cell in 100-hour tests with or without applied voltage.
- Freeze/thaw tests completed and confirmed that particles remain stable in coolant.
- More than 10 companies testing and some of them purchasing Dynalene FC and LC coolants.

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INTRODUCTION

This project addresses the goals of the Fuel Cell Technologies Office of the DOE to have a better thermal management system for fuel cells. Proper thermal management is crucial to the reliable and safe operation of fuel cells. A coolant with excellent thermo-physical properties, non-toxicity, and low electrical conductivity is desired for this application.

An ideal coolant must be durable for >5,000 hrs of operation, and therefore, the coolant must be tested for such duration. Electrical conductivity of the coolant should be less than 10 μS/cm throughout the testing period and the coolant must be compatible with all the materials (metals, plastics, rubbers, and composites) at the highest operating temperature (up to 120^{o}C). Current automotive coolants do not satisfy the electrical conductivity criteria due to the presence of ionic corrosion inhibitors in them. Water/glycol solutions without inhibitors can have low starting electrical conductivity, but it can increase rapidly due to corrosion of metal components leading to build-up of ions in the coolant. Fuel cell developers are using water or water/glycol mixtures with a de-ionizing filter in the coolant loop. The filter needs to be replaced frequently to maintain the low electrical conductivity of the coolant. This method significantly increases the operating cost and also adds extra weight/volume to the system. Dynalene Inc. has developed and patented a fuel cell coolant with the help of DOE Small Business Innovation Research Phase I and Phase II funding (Project # DE-FG02-04ER83884). This technology has been patented in the U.S., Canada, and Europe. The technical feasibility of this coolant was demonstrated in short-term tests using a dynamic re-circulating loop.

APPROACH

Conductivity of the reformulated nano-particles dispersed in bioglycol-distilled water was measured as NaCl solution was gradually added to it. Corrosion inhibitors for metals and polymers validated via immersion testing in different formulations of Dynalene coolants at 80°C for 5,000 hours. Coolant properties were monitored at regular intervals and the components were characterized using scanning electron microscopy and energy dispersive X-ray spectroscopy for any signs of degradation and inhibition. High-temperature electrochemical testing on metals was done to study the corrosion inhibitive properties of the coolants. UTK researchers performed 100 hrs testing of Dynalene coolants in their fuel cell systems at 70°C with applied voltage varying between 0-35 V.

RESULTS

Dynalene reformulated the nano-particles and achieved a surface charge of 890 μeq/g, which further helped in scavenging the stray ions in the system. Figure 1 shows the change in conductivity on addition of NaCl solution. The particles exhibited very low electrical conductivity till they were saturated with the salt solution.

Change in the electrical conductivity of the fluids in presence of metals and polymers is an important deciding factor for materials selection for fuel cells, as a considerable increase in the conductivity might indicate that ions might be leaching from the immersed materials and contaminating the fluids. Based on the 5,000 hr-80°C immersion studies, a list of materials have been recommended for Dynalene LC as shown in Figure 2. Scanning electron microscopy and energy dispersive X-ray spectroscopy studies on the metal samples showed presence of inhibitive surface layer in presence of the inhibited coolants. Surface cracks and swelling on the polymers were much less in the inhibited coolants compared to the uninhibited fluid.

Electrochemical corrosion studies of aluminum at 50°C and 80°C showed that in presence of the inhibitors the corrosion resistance improved due the formation of the inhibitive layer. For the coolants with inhibitor, on increasing the incubation period from two hours to four days, the corrosion rate dropped further. The electrochemical corrosion rate for Al in Dynalene LC at 50°C is shown in Figure 3.

UTK researchers tested different formulations of Dynalene coolants in their fuel cell stack at 70°C. The electrical conductivity of the fluid did not show any appreciable fluctuation. When the applied voltage was as high as 35 V, a slight decrease in the electrical conductivity was seen, it is postulated that the fuel cell was acting as a deionizer and pulling the ions from the fluid. Separately, inductively coupled plasma analysis performed on the tested coolants showed negligible leaching of ions in to the coolants from the fuel cell components.

To see the effect of nano-particles on the fuel cell, a high concentration of nano-particles and surfactant was deliberately added to one of the coolants, which caused

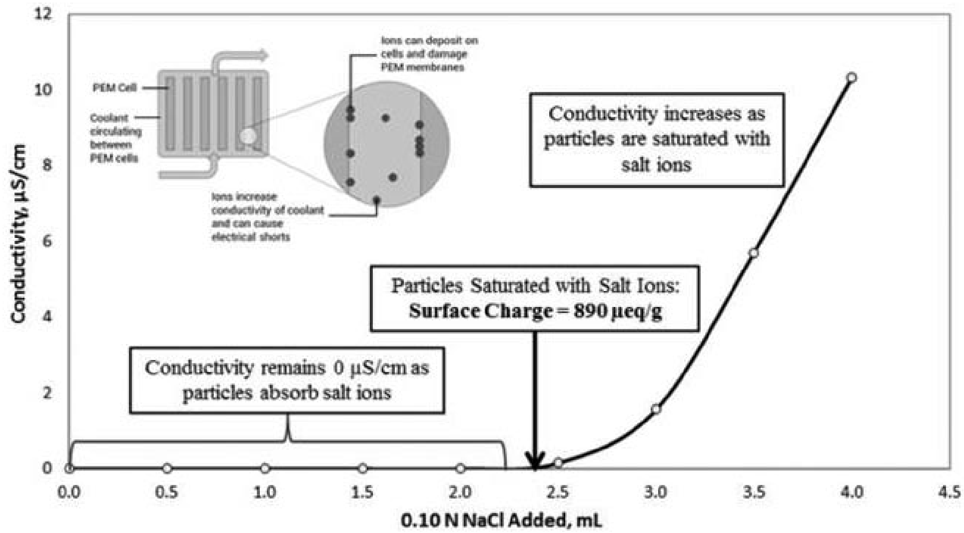
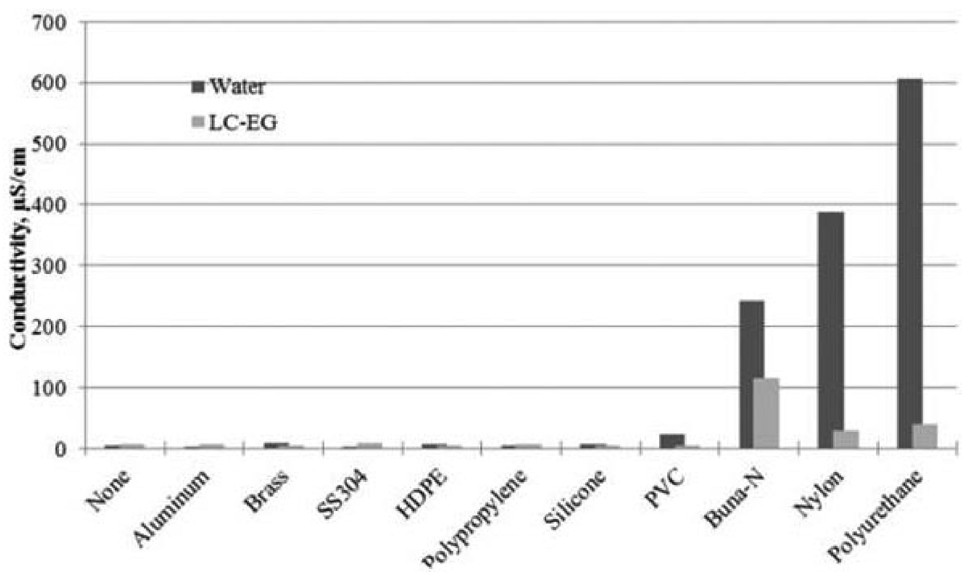


FIGURE 1. Change in electrical conductivity of reformulated nano-particle containing bioglycol-distilled water on addition of 0.10 N NaCl solution.



HDPE - high-density polyethylene; PVC - polyvinyl chloride

FIGURE 2. Change in electrical conductivity of materials subjected to 5,000 hour immersion testing in LC at 80°C.

bursting of pipes and blocked the coolants channels. On the other hand, Dynalene FC with an optimized concentration of nano-particles and surfactant was successfully circulated in the fuel cell stack.

CONCLUSIONS AND FUTURE DIRECTIONS

- Surface charge of the nano-particles increased to 890 µeq/g which surpassed the target of 500 µeq/g.
- Long-term material compatibility testing (5,000 hours) was completed for control glycol water, Dynalene LC, Dynalene FC and glycol water containing the individual components.
- The corrosion inhibitors were validated for both accelerated (electrochemical) and long-term (immersion) testing.
- UTK researchers completed and compared 100 hrs of testing of Dynalene fuel cell coolants in their working fuel cell with or without voltage application.
- The coolants showed a small change in electrical conductivity in the UTK fuel cell. Inductively coupled

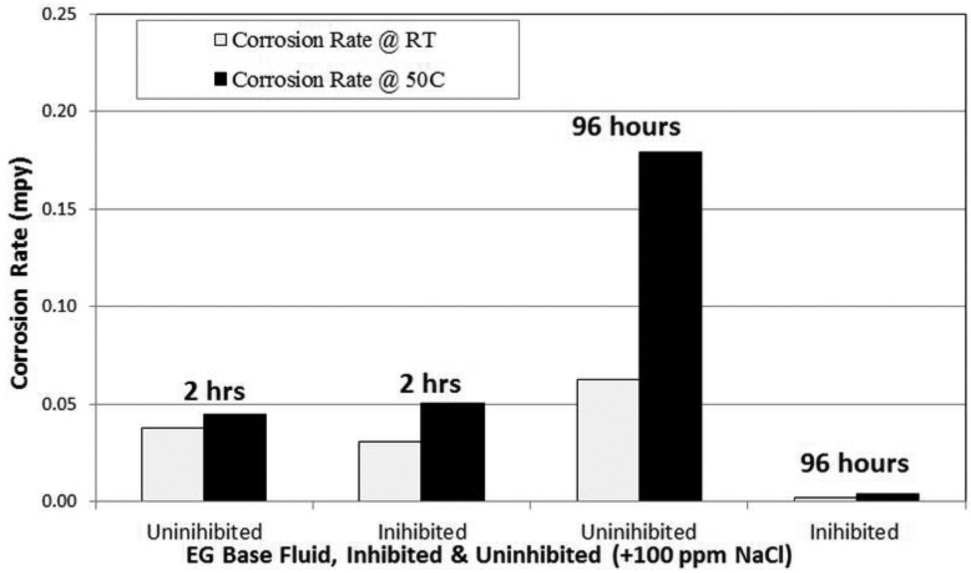


FIGURE 3. Effect of immersion time and temperature on the electrochemical behavior of Al alloy in inhibited and control glycol-water solution.

plasma analysis confirmed minimum leaching of ions in to the coolants.

- Dynalene is producing and selling Dynalene FC and LC to fuel cell companies.

Future work planned for the rest of the fiscal year:

- Continue surface and elemental characterization of the multiple fuel cell components that completed 5,000 hrs of testing.
- Continue high performance liquid chromatography and ion chromatography studies on the high-temperature treated glycol-water coolants to understand the degradation and breakdown of the glycols in to the component acids.
- On-going high-temperature testing of the nano-particles and surfactant at 110°C for 1,000 hrs to study their thermo-physical and degradation properties.
- Continue voltage testing with metal plates in nano-particles containing coolants to understand the coating effect of the nano-particles on the fuel cell plates.
- Perform 1,000 hrs of long-term testing with the coolants in the UTK fuel cell system.

FY 2013 PUBLICATIONS/PRESENTATIONS

1. Y. Garsany, S. Dutta and K.E. Swider-Lyons,"The Poisoning and Recovery of Pt/VC Electrocatalysts Contaminated with Glycol-Based Coolant Formulations" oral presentation at Pacific RIM Meeting, Honolulu, Hawaii, Oct. 7–12th 2012.

2. S. Dutta, K. Coscia, S. Mohapatra and P. McMullen, "Materials Compatibility and Corrosion in Glycol-Based Fuel Cell Coolants for Automotive Applications" poster and Symposium paper for Fuel Cell Seminar & Exposition 5–8th Nov. 2012, Uncasville, CT.

3. B.D. Gould, Y. Garsany, S. Dutta and K. Swider-Lyons, "Deactivation and recovery of polymer electrolyte fuel cells with commercial glycol-based coolants" paper submitted to 23rd North American Catalysis Society Meeting, June 2nd–7th, 2013, Louisville, Kentucky.