V.I.2 Large Scale Testing, Demonstration and Commercialization of the Nanoparticle-Based Fuel Cell Coolant (SBIR Phase III)

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Subcontractors:
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Protonex Inc., MA

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Project End Date: September 30, 2013

Fiscal Year (FY) 2012 Objectives

The overall objective of this Phase III Small Business Innovation Research project is to demonstrate the 5,000 hr durability of the nanoparticle-based coolant fluid developed in Phase I and II, and perform further research into how durability is affected and how to improve it. The specific objectives in 2012 are listed below:

- Build, install and validate two fuel cell coolant test systems: one at University of Tennessee, Knoxville and the other, a Protonex fuel cell system, at Dynalene location.
- Study the effect of nanoparticle properties on its durability under severe conditions such as high temperature (up to 120ºC), thermal cycling, high electric field and presence of contaminants.
- Determine the efficiency of corrosion inhibitors in long-term tests under severe conditions as well as electrochemical tests.
- Increase the nanoparticle surface charge to >500 μeq/g for both cationic and anionic particles.
- Perform testing of the coolant samples by fuel cell companies and begin commercialization.

Technical Barriers

This project addresses the following technical barriers from the Fuel Cells section (3.4.4) of the Fuel Cell Technologies Program Multi-Year Research, Development and Demonstration Plan:

(A) Durability

(B) Cost

Technical Targets

Dynalene's fuel cell coolant (Dynalene FC) is expected to help the fuel cell industry achieve its durability and cost targets to some degree. First of all, the coolant itself is being designed to have a life of 5,000 hrs. It is also expected to have excellent compatibility with the system materials and inhibit corrosion in the coolant loop. This will help in 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. The coolant is also designed to work at -40ºC, which will assist both transportation and stationary fuel cells to quickly warm up during cold starts.

The cost target for the coolant (in plant-scale production) is about $10/gallon, which is very close to the retail price of current automotive coolants. This coolant will also eliminate the de-ionizing filter and other hardware associated with it (i.e. fittings, valves). It is also being designed to work with cheaper, lighter and thermally efficient components such as aluminum radiators (instead of stainless steel) and brass heat exchangers.

FY 2012 Accomplishments

Following are the accomplishments from October 1, 2011 to June 30, 2012:

- Scale up and Optimization:
  - Scaled up the nanoparticle production to 100 L
  - Developed quality assurance/quality control methods for the coolant
  - Reduced final fluid cost
- Completed design and fabrication of two separate fuel cell systems:
  - University of Tennessee, Knoxville (UTK) fuel cell being tested at its facility
  - Protonex fuel cell being tested at Dynalene

- Dynalene has performed short-term immersion testing (pH and electrical conductivity) of the coolants at temperatures between 80-100ºC to demonstrate preliminary fluid-material compatibility.
- Electrochemical Corrosion Study:
  – Corrosion rate of aluminum decreased when exposed to Dynalene LC (low conductivity, without nano-particles) and FC (with nano-particles) as compared to ultra-pure distilled water (UP-DW) and 65% bio-glycol-35% distilled water (BG-DW). Dynalene LC was formulated with glycol, water and corrosion inhibitors.
  – Dynalene FC and LC showed better corrosion protection for shorter immersion time (1 hr) as well as improved corrosion resistance for longer immersion times (4 days) as compared to the base fluids.

Introduction

This project addresses the goals of the Fuel Cell Technologies Program 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 hr 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 120ºC). 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. 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. The nanoparticles used in the coolant were optimized for size and surface charge density.

Approach

In this Phase III project, Dynalene's plan is to validate the durability of the coolant fluid by developing long-term test plans in-house as well as in subcontractor locations. Two test systems were built (one at University of Tennessee, Knoxville and the other at Dynalene) and are currently being used for testing various coolant compositions. Direct current corrosion testing (open circuit potential, potentiodynamic and polarization resistance experiments) was performed on the Al 3003 alloy in different coolants using a Gamry Potentiostat. A range of metals and polymers were immersed in UP-DW, BG-DW and the two Dynalene coolants (LC and FC) at temperatures between 80-120ºC for up to three weeks. Dynalene performed measurements of electrical conductivity in these fluids as well as base fluids. Scanning electron microscopy and energy dispersive X-ray spectroscopy were used to characterize the metal surfaces and the inhibitive layers.

Results

UTK researchers performed elevated temperature (70ºC) testing for 100 hrs with Dynalene LC and FC coolants in chamber-integrated and insulated fuel cell system (Figure 1). FC and LC showed a slight increase in average conductivity rate @ 0.005 µS/cm-h. Dynalene conducted short-term testing with one of the Protonex fuel cells in-house (Figure 2). While the coolants were circulated in the fuel cell loop, it was observed that the FC attained steady state faster compared to the other fluids and also demonstrated lowest conductivity change. Dynalene will also start 5,000 hour testing on selected coolant formulations shortly. The other fuel cell will be tested at the Protonex facility for 2,000 to 3,000 hours.

Change in the electrical conductivity of the fluids in presence of metals and polymers, is an important deciding

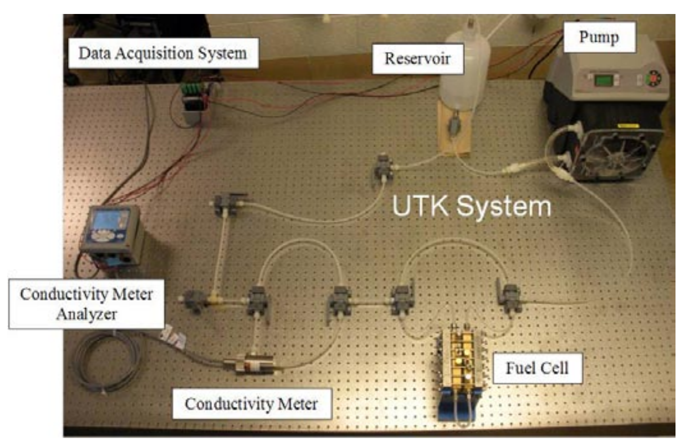

FIGURE 1. Fuel Cell Set-Up at UTK

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. Metals (brass and aluminum) and polymers (high-density polyethylene and silicone) showed smaller change in the electrical conductivity in the Dynalene coolants LC and FC when compared to UP-DW and BG-DW, as shown in Figure 3. All the base fluids/coolants were also heated up to 120ºC for a period of two weeks to study their degradation behavior. The coolants showed discoloration and a significant change in the pH and electrical conductivity due to break down of the glycol at higher temperature. The data is tabulated in Table 1.

Corrosion Rate was derived from the potentiodynamic/Tafel plots. Aluminum exposed to FC and LC after short immersion time (1 hr) demonstrated a lower corrosion rate compared to UP-DW and BG-DW, and after longer immersion times (4 days), FC and LC showed marked improvement in the corrosion protection behavior of aluminum (Figure 4).

Scanning electron microscopy and energy dispersive X-ray spectroscopy characterization on the metal coupons

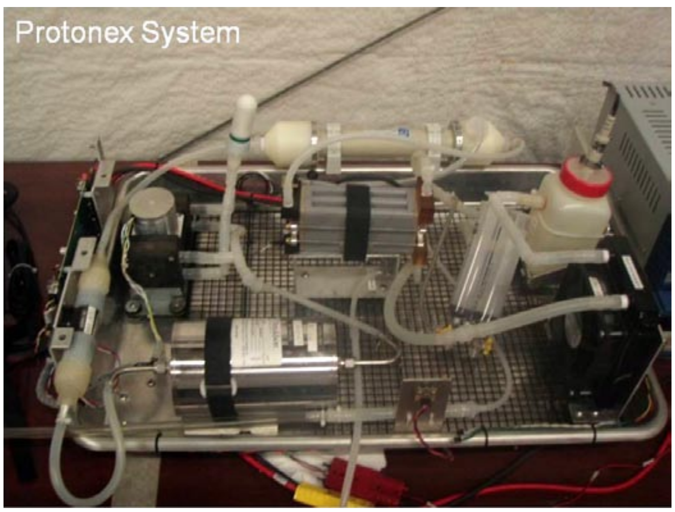

FIGURE 2. Protonex Fuel Cell System at Dynalene

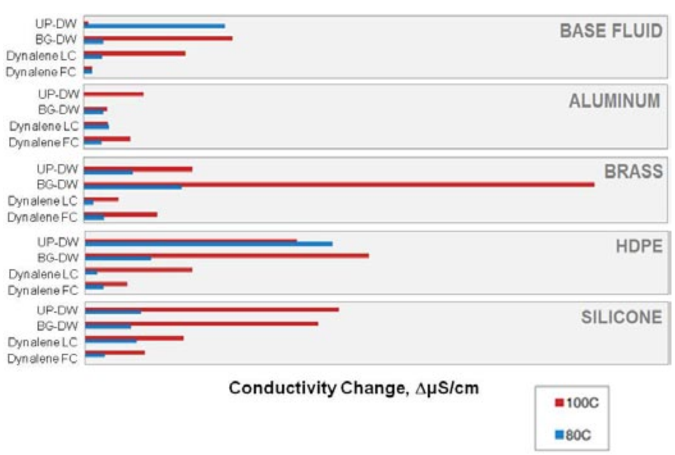

FIGURE 3. Electrical conductivity of materials in various fluids after 250 hour tests at 80°C and 100°C in Teflon® jars

TABLE 1. Base Fluid Properties after Two weeks at 120°C

Appearance of Fluids	Initial pH	Final pH	Initial Conductivity (μS)	Final Conductivity (μS)
UP-DW 	5.87	6.12	1.11	2.50
BG-DW 	4.56	3.91	1.85	10.23
LC 	4.59	3.87	1.85	10.69
FC 	6.22	3.9	0.75	13.6

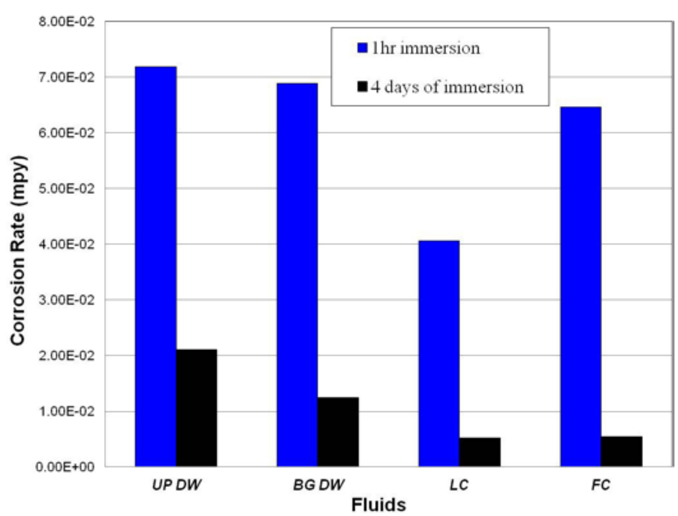

FIGURE 4. Corrosion Rate of 3003 Al immersed for different times in the fluids, derived from the potentiodynamic experiments

exposed to BG-DW, LC and FC at 88ºC for two weeks showed oxide rich corrosion layer in presence of BG-DW, organic inhibiting layer (rich in nitrogen and carbon) when exposed to LC, and a much cleaner metal surface when exposed to FC. The coolants are playing a role in inhibiting corrosion in the metals but further studies are needed to confirm their contribution.

Conclusions and Future Directions

Summary of the work done so far this year:

- The fuel cell coolant optimization and scale up has been completed and Dynalene is capable of producing Dynalene FC coolant in large quantities.
- The fuel cell coolant testing skids at Dynalene and the University of Tennessee, Knoxville have been completed, performed successful short-term testing and are ready for long-term testing.
- The corrosion inhibitors were validated in short-term testing using immersion and electrochemical methods.

Future work planned for rest of the FY:

- Validate corrosion inhibitors in 5,000 hour tests.
- Increase of anionic particle surface charge to match cationic at 500 μeq/g.
- Perform compatibility and thermal degradation studies at temperature exceeding 100ºC.
- Perform 5,000 hour testing of final coolant formulation in two fuel cell systems.
- Characterize samples after immersion testing with scanning electron microscopy and energy dispersive X-ray spectroscopy to understand the inhibitive effect of the coolant.

FY 2012 Publications/Presentations

1. S. Mohapatra, P. McMullen, S. Dutta and K. Coscia, "Fuel Cell Coolant Optimization and Scale-up", Presented at the Annual DOE Hydrogen Program Review Meeting, May 2012, Washington, D.C.

2. Y. Garsany, S. Dutta and K. E. Swider-Lyons, "Effect of Glycol-based Coolants on the Suppression and Recovery of Platinum Fuel Cell Electrocatalysts" *J. Power Sources,* 2012, 216, 515-525.

3. 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.

4. K. Coscia, S. Dutta, S. Mohapatra and P. McMullen, "Materials Compatibility and Corrosion in Glycol-Based Fuel Cell Coolants for Automotive Applications" manuscript accepted for Fuel Cell Seminar & Exposition 2012, Uncasville, CT.