V.C.1 Complex Coolant Fluid for PEM Fuel Cells

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Subcontractors:

Lehigh University, Bethlehem, PA
The Pennsylvania State University, University Park, PA

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Project End Date: July 2007

Objectives

- Optimize nanoparticle chemistry for dispersion and thermal stability in the coolant medium.
- Optimize corrosion inhibitors type, concentration and combination.
- Perform long-term tests (>1,000 hours) in the dynamic test skid.
- Perform tests in real fuel cells.

Technical Barriers

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

(E) System Thermal and Water Management

Technical Targets

This project is developing an advanced coolant that will demonstrate an electrical conductivity of less than 2 μS/cm in a real proton exchange membrane (PEM) fuel cell for a period of 3,000 hours.

Accomplishments

The best coolant developed so far has maintained electrical conductivity of less than 10 μS/cm for a period of 1,000 hours.

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Introduction

Current automotive coolants do not meet the electrical conductivity criteria set forth by fuel cell manufacturers. The recommended electrical conductivity of a fuel cell coolant is less than 2 μS/cm, whereas, the automotive coolants have three orders of magnitude higher electrical conductivity.

Fuel cell developers are currently using water or glycol/water mixture 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 of the fuel cell. PEM fuel cell developers also use stainless steel and polymers to minimize the amount of ions coming into the fluid. Due to light weight, lower cost and better thermal conductivity, aluminum will definitely replace stainless steel radiators in the future fuel cells. The de-ionizing filters used today will not be able to handle the excessive amount of aluminum ions in the fluid if the coolant itself is not designed to substantially buffer the ion build-up. Therefore, a different approach for the fuel cell coolant is being pursued in this project.

Approach

The proposed complex coolant fluid (CCF) consists of a base compound (glycol/water mixtures) and an additive package [1]. The base compound mixture has a freezing point less than –40°C, is non-flammable for transportation purposes, and can be used at temperatures up to 122°C. The additive package consists of non-ionic corrosion inhibitors and ion-suppressing compounds (ion-exchange nanoparticles) to maintain the electrical conductivity of the coolant at a low level. Use of this type of coolant will enable the fuel cell manufacturers to eliminate the de-ionizing filter they are using to maintain a low electrical conductivity of the glycol/water-based coolants.

The technical approach to developing the complex coolant fluid includes the development of the nanoparticles and the corrosion inhibitors, and studying the fluid performance (electrical conductivity vs. time) in short-term as well as long-term tests utilizing a dynamic

test loop. Ultimately, the fluid will be tested in real fuel cell systems by the developers of PEM fuel cells.

Results

Dynalene's subcontractor, Lehigh University, has prepared and provided ion-exchange nanoparticles with an average diameter of about 80 nm and 350 nm. These particles were used for the formulation of propylene glycol coolant tested in the dynamic test stand in the Dynalene laboratory. Dynalene also installed a stack into its test skid to simulate the flow of coolant through the channels inside a stack of cells in a PEM fuel cell.

A comparison between de-ionized (DI) water, propylene glycol/water and propylene glycol/water containing nanoparticles were carried out to determine the rate of change of electrical conductivity at 70°C when they are pumped continuously in the test skid. For DI water, the rate came out to be about 0.16 μS/cm-hr. For propylene glycol/water solution, this rate was about 0.03 μS/cm-hr. Finally, for propylene glycol/water with a corrosion inhibitor and nanoparticles, this rate came out to be 0.009 μS/cm-hr (carried out for 1,000 hours). These results have been duplicated, and in some cases carried out three times to verify the reproducibility of the results. Using the results for propylene glycol/water with corrosion inhibitor and nanoparticles, for over 3,000 hours of operation, the conductivity of the solution would have gone up to about 27 μS/cm-hr. We are continuing our optimization to bring this level down by an order of magnitude (which is accepted by almost all the fuel cell manufacturers).

Penn State University (a subcontractor in this project) carried out the mathematical modeling and simulation of particle deposition process on the electrode surfaces of a fuel cell. When ion-exchange nanoparticles with surface charges flow in the coolant channels and between the electrodes, they will be attracted towards the surface because of electrokinetic forces (Figure 1).

Penn State researchers used a coupled multiphysics modeling program, COMSOL Multiphysics, to create a computational fluid dynamics (CFD) coupled physicochemical model of the nanoparticle deposition process. This requires the coupling of the heat transfer and hydrodynamic equations, as well as electrochemistry. The fluid properties depend on temperature, and charged particle deposition depends on the phase potential of the coolant channel surface. The overall goal of the model is to provide a fundamental first-principles-based tool to design a coolant that will operate in a fuel cell stack for 2-3 years without replacement of the coolant.

The flow cell simulation predicted a significant amount of deposition on the electrode surfaces if the particles are not sterically stabilized (Figure 2). It was shown that the deposition would be maximum at the outlet and minimum at the inlet. Dynalene, at the request of Penn State, installed a single channel flow cell with voltage across the plates. The coolant containing ion-exchange nanoparticles was allowed to pass through the flow cell for for four hours. Then the flow-cell was disassembled and sent to Penn State for surface analysis. This process was repeated with different voltage and flow rate combinations. Without any voltage, there was insignificant amount of particle deposition on the electrodes. However, with voltage applied (i.e., 60 and 300 mV) across the plates, particles could be observed on the electrodes (Figure 3) and significant deposition was observed when the coolant was allowed to flow for 24 hours (Figure 4).
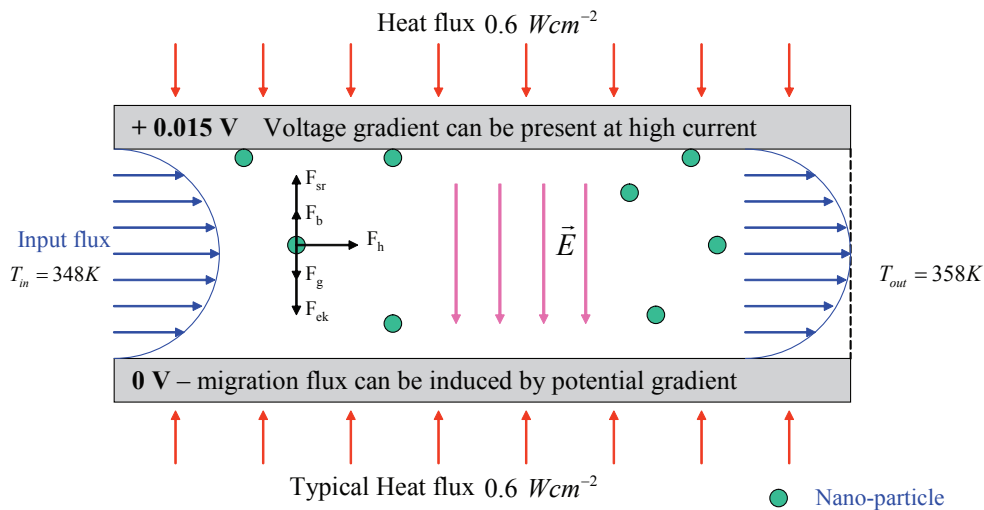

FIGURE 1. A Schematic Diagram of a Coolant Flow Channel Showing the Nanoparticles (Circles) and the Forces Acting on Them
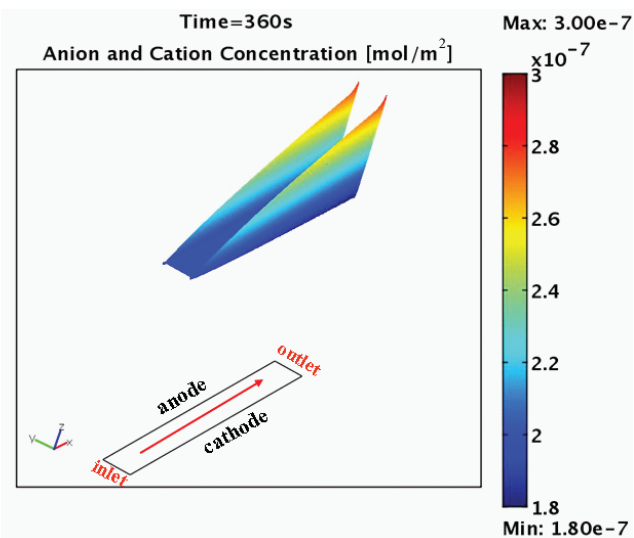
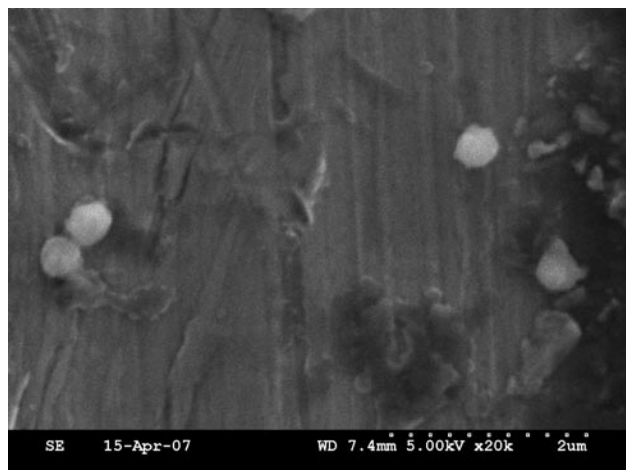**FIGURE 2.** Particle Concentration (Z-Axis) as a Function of Flow Channel Geometry at 360 Seconds

FIGURE 3. Scanning Electron Microscopy Image of Deposition within 1 mm Thick Channels and 60 mV Applied for 4 Hours – No Significant Deposition Observed

Dynalene also concentrated its effort to develop a non-ionic corrosion inhibitor package that could be used with a variety of metals such as stainless steel, carbon steel, aluminum, copper and brass. We have created a package consisting of two types of inhibitors. One is designed for steel and aluminum and the other is designed for copper and brass. The corrosion rates for steel and aluminum at 60°C are 4 and 3 μm/year, respectively. This is one order of magnitude lower than the corrosion rates observed without any inhibitor. The inhibitor used for copper and brass has shown two orders of magnitude reduction in the corrosion rate as compared with a coolant without the inhibitor (6 to 8 mm/year for uninhibited versus <0.1 mm/year for inhibited).
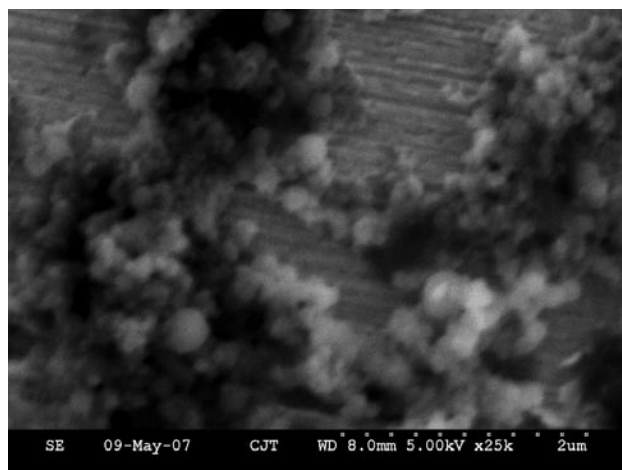

FIGURE 4. Scanning Electron Microscopy Image of Deposition within 5 mm Thick Channels and 300 mV Applied For 24 Hours – Particle Flocculation Observed Indicates Unsuccessful Steric Stabilization

Conclusions and Future Directions

- A coolant containing non-ionic corrosion inhibitors and ion-exchange nanoparticles demonstrated three times lower rate of increase in the electrical conductivity compared a coolant without the additives.

- Modeling and simulation of the nanoparticle deposition process on the electrode walls has demonstrated that there could be significant deposition of particles near the outlet of the flow channels if the particles are not properly stabilized. Experimental data also proved this. Work is currently underway to optimize the steric stabilization method.

- Non-ionic corrosion inhibitors were developed and tested in the coolant fluid using electrochemical tests. Corrosion rates for stainless steel and aluminum were one order of magnitude lower, and for copper and brass, two orders of magnitude lower compared to the coolant without inhibitor.

- This project will officially end in July 2007. However, Dynalene has committed to fund Lehigh University to continue the research work to optimize the nanoparticle chemistry and develop a steric stabilization method that will prevent flocculation of the particles.

- Dynalene is also building a facility to produce sample quantities of the coolant fluid by the end of 2007. Several fuel cell developers have requested Dynalene to supply samples.

FY 2007 Publications/Presentations

1. Modeling Electrodeposition of Charged Nanoparticles onto Fuel Cell Coolant Flow Channel Wall. Jiangtao Cheng, Kendra Sharp, and Matthew M. Mench. Annual COMSOL Conference, Boston, MA, October 2006.

2. A nanoparticle-based coolant for PEM fuel cells, Satish Mohapatra, Daniel Loikits, Larry Chiang, Su Jeong Han, Kevin Bian, Eric Daniels, Victoria Dimonie, E. David Sudol, and Andrew Klein. Fuel Cell Seminar, Honolulu, HI, November 2006.

3. Complex Coolant Fluid for PEM Fuel Cells. Satish Mohapatra. DOE Annual Hydrogen Program Review, Washington, D.C., May 2007.

References

1. *Fuel Cell and Fuel Cell Coolant Composition*. Satish Mohapatra. U.S. Patent # 7,138,199.

Special Recognitions/Patents Issued

1. *Fuel Cell and Fuel Cell Coolant Composition*. Satish Mohapatra. U.S. Patent # 7,138,199.