V.L.7 Fuel Cell Coolant Optimization and Scale Up*

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Contract Number: 09EE0000278

Subcontractor:
Lehigh University, Bethlehem, PA

Project Start Date: September 1, 2009
Project End Date: August 31, 2011

*Congressionally directed project

Fiscal Year (FY) 2011 Objectives

The overall objective of this project is to optimize and scale up the process to make Dynalene FC fuel cell coolant with a great deal of reproducibility. Following are some specific objectives that would help to reach the overall goal of the project:

- Demonstrate the production of one key ingredient of the coolant (a nanoparticle) in 10 L, 20 L and 100 L batches in a pilot-scale operation and study the effect of various process parameters on the size and charge density of the particles.
- Produce the nanoparticles necessary for the fuel cell coolant, Dynalene FC, in a very consistent manner (i.e., particle size, charge density and yield).
- Optimize the filtration process for the nanoparticles to minimize the cleaning time for different scales of operation.

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:

(B) Durability
(C) Cost

Technical Targets

Dynalene FC is expected to help the fuel cell industry achieve their 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 -40°C, 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 deionizing 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.

Accomplishments

Dynalene FC has been demonstrated by field testing to maintain a very low electrical conductivity and stay stable over several years. This was possible due to the addition of a nanoparticle into the coolant. This project addresses the optimization and scale up of this nanoparticle ingredient. The main accomplishments in this project so far are the design and set up of 10 L, 20 L and 100 L reactor vessels, and optimization of the production of nanoparticles in the 10 L scale. Optimization in the 100 L scale is continuing now and it is expected to be finished by the project end date (August 31, 2011). Other accomplishments include the development and optimization of the filtration process for the nanoparticles and quality control procedures.

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 thermophysical properties, non-toxicity, and low electrical conductivity is desired for this application.

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). However, this coolant can only be produced in lab scale (500 ml to 2 L) due to problems in optimization and scale up of a nanoparticle ingredient. This project will optimize the nanoparticle production process in 10 L, 20 L and 100 L reactors, optimize the filtration process, and develop a high throughput production method for the final coolant formulation.

Approach

Before this project, Dynalene researchers were producing the nanoparticles ingredients used in the fuel cell coolant in 100 ml, 500 ml and 2 L reactors. At 100 ml scale, the nanoparticles were produced using magnetic stirring and the heating was provided by a constant temperature bath. At the 500 ml scale, the stirring mechanism was changed to a mechanical stirrer with impellers, while the heating mechanism was still through a constant temperature bath. At the 2 L scale, the stirring was through a mechanical stirrer whereas the heating was accomplished by pumping hot water through the jacket of the reactor. In this project (for 10 L and 100 L reactors), mechanical mixers with multiple impellers and heating systems using the jacket of the reactor will be used. Mixing/stirring mechanism as well as the heating method impacts the particle size, charge density and the yield of the reaction. Therefore, an understanding of the influence of these parameters is very essential to obtain the nanoparticles with reproducible properties. Dynalene and Lehigh University have partnered to develop the scale up criteria needed to go from a 2 L scale to a 10 or 20 or 100 L scale. The two types of emulsion polymerization methods used in this project to make the nanoparticles are batch and shot-growth methods.

Results

The batch style polymerization recipe at the 10 L scale did not produce the desired results (in terms of particle size and charge density). This method was abandoned in favor of optimizing the shot growth procedure which showed promise in the 2 L scale.

Shot growth polymerization is when a large portion of the reaction components are added to the reactor at the beginning of the reaction, the reaction is initiated, and the reaction is allowed to progress to 80 to 90% completion before a “shot” of co-monomers is added quickly to the reactor. This approach gives an added level of control to the reaction because the ratio of co-monomers in the shot has a large effect on the final particles.

The shot growth method has benefits over the batch method. The first is the large number of variables that can be altered to achieve the desired result. The following is a list of those parameters:

- Ratio of co-monomers
- Concentration of co-monomers
- Timing of shot
- Speed of shot
- Use of dip tube for shot addition
- Pre-emulsion of shot components

The shot growth method also has the benefit of a much higher solids concentration than the batch method. This higher concentration gives a much more efficient and cost-effective synthesis due to the increase in yield over the batch recipe. The optimum co-monomer concentrations and their ratio were determined at the 2 L scale and were left constant for the 10 L experiments. Experiments were also carried out to determine the correct timing of the shot, which was found to be between 2.5 and 3.0 hours after initiation of the reaction. All subsequent experiments were run with this timing.

Impeller position and the stirring speed were optimized next. Several reactions were run with the multi-impeller set-up in combination with the slower stirring speed. The scanning electron microscope (SEM) picture (Figure 1) showed a uniform, consistent particle size in the 200-250 nm range. Surface charge density was also within the expected range of 500-1,000 µeq/g (Table 1).

Optimization of cationic nanoparticle synthesis at 10 L scale was completed and the initial testing with the 100 L reactor begun. The testing started with dyed oil and water in which the oil represents the styrene. It is necessary to decrease the stirring speed when scaling up because the tip speed on the larger impellers is much greater at the same rotational speed. Too much shear creates unwanted

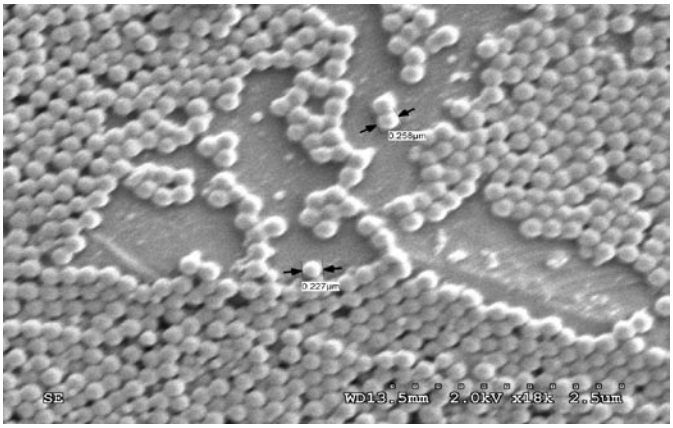

FIGURE 1. SEM Picture of the Cationic Particles Produced in 10 L Scale

TABLE 1. 10 L Scale Cationic Particle Experiments with Optimized Parameters

Experiment	Reaction type	Particle Size (nm)	Surface Charge Density (µeq/g)
JWM-0002-07	10 L shot growth	230	500-1,000
JWM-0002-10	10 L shot growth	225	500-1,000
JWM-0002-12	10 L shot growth	230	500-1,000
JWM-0002-14	10 L shot growth	235	500-1,000

results in the final latex, mostly coagulum and non-uniform particle distribution. The impellers were initially set up with geometric similarity to the final placement at the 10 L scale.

Testing was conducted at room temperature first to determine the minimum mixing speed to mix efficiently without high shear. It was not possible to achieve complete mixing at a speed low enough to eliminate vortexing at the initial reaction volume. It was necessary to either add another impeller or reduce the volume in the reactor to increase mixing efficiency. It was determined to decrease the reaction volume to better fit the reactor with the current number of impellers. The impeller spacing was altered to work with the decreased reaction volume.

Testing was resumed at room temperature with the new impeller placement and decreased volume concentration. It was possible with the new set-up to achieve complete mixing without the formation of a vortex. Photographs of the dyed oil/water mixing study can be seen in Figure 2.

Testing of the heating system also was carried out in conjunction with the mixing study. This testing included measuring the efficiency of the heating system while studying the effect of temperature on mixing efficiency. It was discovered at this time that the current heating system configuration was not able to heat the full volume of the 100 L reactor to the reaction temperature. A larger pump was installed in the heating system to increase the flow rate of the heating water through the reactor jacket. Testing was resumed and the reactor achieved the reaction temperature within two hours.

The impeller configuration and stirring speed were optimized at the 100 L scale with dyed oil and water at the initial reaction volume. Further testing is currently being done to optimize the stirring conditions with the addition of the shot to the reactor.

Conclusions and Future Directions

Dynalene has set up all the reactors for the nanoparticle production. After some preliminary testing, the 10 L reactor was used for the synthesis of the nanoparticles. The scale up criteria developed in collaboration with Lehigh University was verified. It was determined that a shot-growth approach was better suited than a batch synthesis. Shot addition time and the process as well as the speed of the stirrer were optimized to obtain the right size and surface charge of the particles. Nanoparticle synthesis in the 10 L scale was repeated several times and the particle size

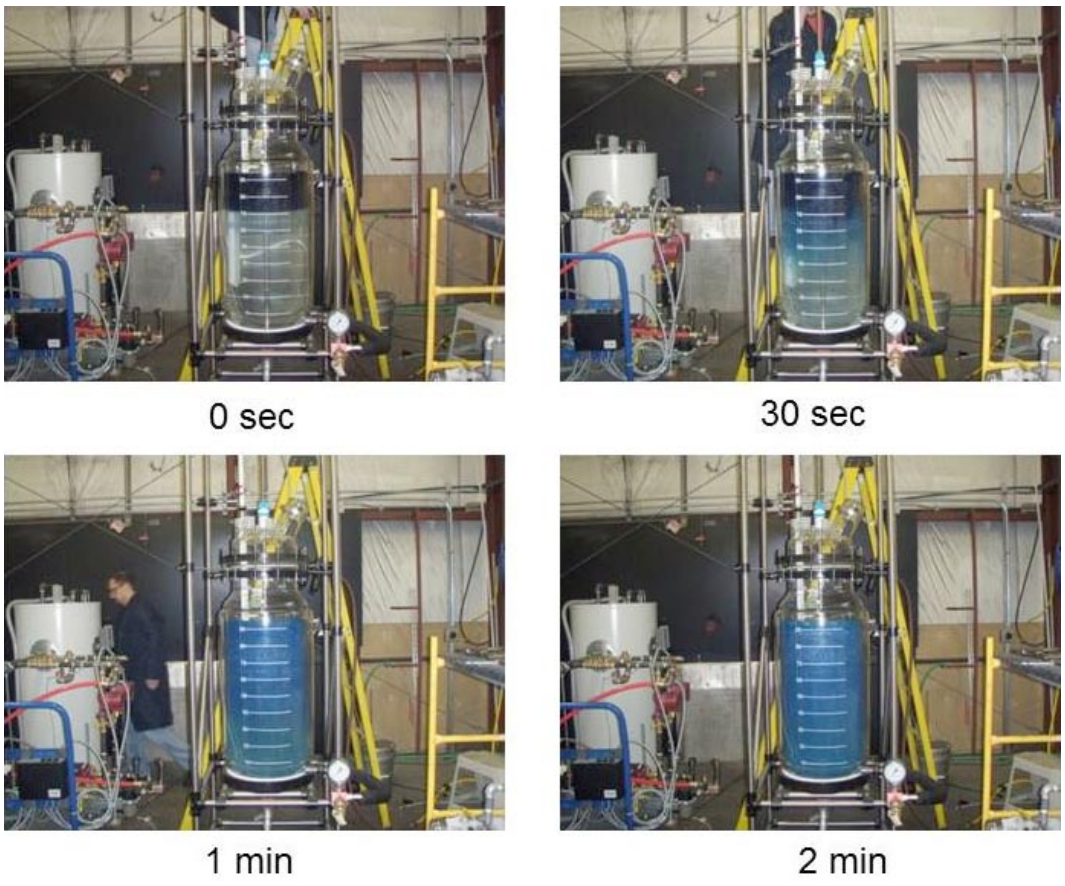

FIGURE 2. Oil/Water Study to Determine Mixing Parameters in the 100 L Glass Reactor

as well as the surface charge density was reproduced, thus making it a viable process for future commercial production. An oil/water study was conducted in the 100 L scale to optimize the stirrer position and the speed. In the future, nanoparticle synthesis will be performed at this scale, and filtration will be performed in 5 L scale to produce clean nanoparticles for subsequent production and testing of the fuel cell coolant.

FY 2011 Publications/Presentations

1. McMullen, P, Mock, J and S. Mohapatra, "Fuel Cell Coolant Optimization and Scale-up", Poster presented at the Annual DOE Hydrogen Program Review Meeting, May 2011, Washington, D.C.