Fuel Cell Coolant Optimization and Scale-up

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Overview

Total project funding

- DOE share: $351K
- Contractor share: $88K
- All funds obligated in FY 2009

Timeline

- Project start date: 09-01-2009
- Project end date: 08-31-2011
- Percent Complete as of 3/31/11: 75%

Barriers addressed

- System thermal management
    - Durability
    - Cost

Interactions/ collaborations:

- Lehigh University (Subcontractor)

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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 to improve the durability and reduce the cost of fuel cell systems.

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.

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Background

Development of a Nanoparticle Based Coolant for Application in PEM Fuel Cells

- Began in 2004 with an SBIR grant from the DOE.

- Expectations
  - Low electrical conductivity over 5000 hours of operation
  - Exceptional thermo-physical properties – similar to current automotive coolant

- 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:
  - Durability
  - Cost

- SBIR Phase I and Phase II
  - Provided a good recipe for a coolant fluid that demonstrated low electrical conductivity in short term tests.

- Current DOE Grant
  - Scale up of the manufacturing of the coolant has taken center stage to reduce the cost of production and increase the availability of samples.
  - In 2010, a pilot plant was completed and production began on semi-large scale of 10 L nanoparticle batches, which translated into 600 gallons of finished coolant.
  - In 2011, scale-up will grow another order of magnitude to 100 L nanoparticle batches, which translates to 5000 gallons of finished coolant.

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Technical Targets

Dynalene FC fuel cell coolant is expected to help the fuel cell industry achieve their durability and cost targets.

- **Durability**
  - Designed to have a life of 5000 hrs.
  - Excellent compatibility with the system materials and inhibit corrosion in the coolant loop.
    - 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 ^{o}C
    - Assisting both transportation and stationary fuel cells to quickly warm up during cold starts.
- **Cost**
  - Target (in plant-scale production) is about $10/gallon
    - Close to the retail price of current automotive coolants
  - Eliminate the deionizing filter and other hardware associated with it (i.e. fittings, valves)
  - Designed to work with cheaper, lighter and thermally efficient components
    - Aluminum radiators (instead of stainless steel) and brass heat exchangers

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Characteristics of the Coolant

- The Dynalene FC fuel cell coolant consists of a base compound (glycol/water mixtures) and an additive package.
- The base compound mixture has a freezing point less than –40 ^{o}C, is non-flammable, and can be used at temperatures up to 122 ^{o}C.
- The additive package consists of corrosion inhibitors and ion-suppressing compounds to maintain the electrical conductivity of the coolant at a low level.

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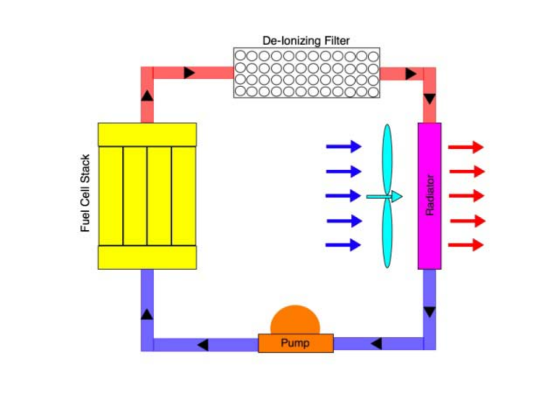
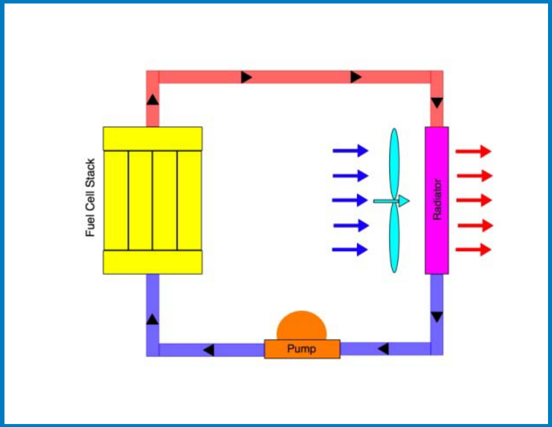
Dynalene FC in a PEM Fuel Cell

Typical DI Water Fuel Cell Cooling System



- Needs De-ionizing Filter
- Heavier
- More Maintenance
- Clogging
- Higher Pressure Drop (Large Pump)
- Possible Corrosion Problems

Dynalene FC Fuel Cell Cooling System



- No De-Ionizing Filter
- Higher Performance
- Lower Cost
- Lighter Weight
- No Clogging
- Less Pressure Drop (Smaller Pump)
- Less Corrosive

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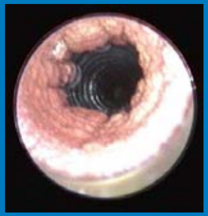
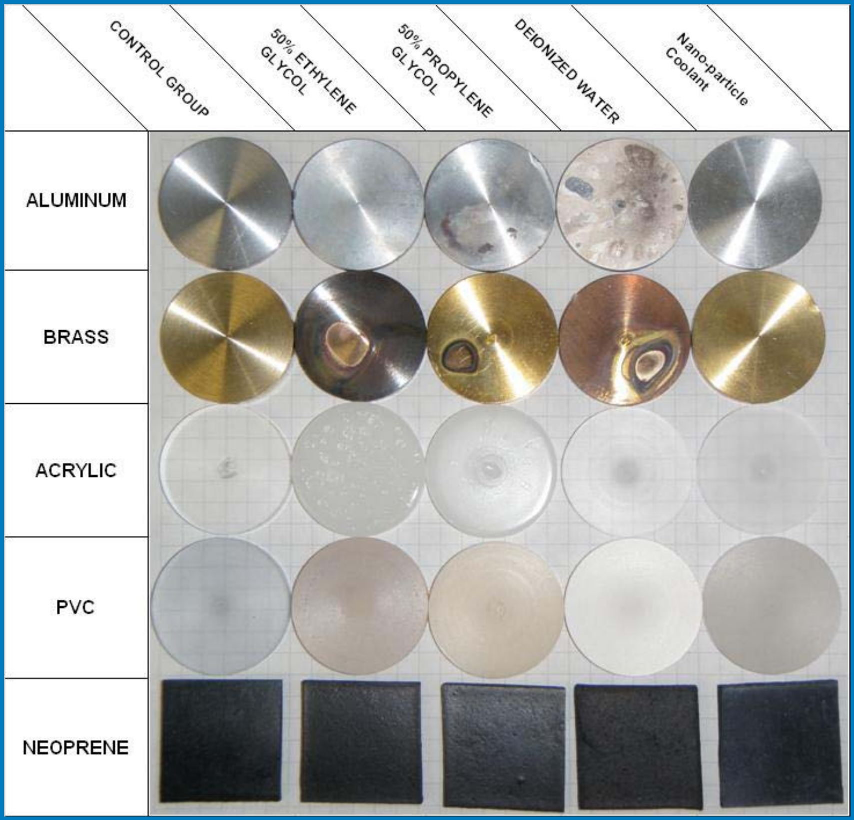
Corrosion Studies



EG/DI Water (corrosion debris)

EG/DI Water with a Cation Exchange Bed

Dynalene FC (no deposits or corrosion debris)



Corrosion/Degradation after 700 Hours at 80 ^{o}C

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Conductivity Study

Materials	Coolant Conductivity in µS/cm			
	DI water	EG 50/50	PG 50/50	Dynalene FC
Initial Conductivity	0.8	2.6	2.4	0.7
SS Alloy 316	218	59.6	28.9	7
Aluminum Alloy 2017	95.7	49	29.2	7.9
SS Alloy 304	172.9	47.4	17	8.2
Brass Alloy 360	66.7	92.5	46	7.6
Polypropylene	162.5	42.5	19	7.5
Extruded Acrylic	189	34.2	19.8	11.7
PVC (Type I)	135.1	64.3	52	7.6
HDPE	148.8	34.5	40.9	8.2
Neoprene	213	89.7	44.8	14.5
EPDM Rubber	224	57.8	48.7	12.1
Silicone	119.6	35.7	22.8	8.9

Test Conditions: 700 Hours at 80^{o}C, 3 Sq in of wetted surface with 250 ml fluid volume.

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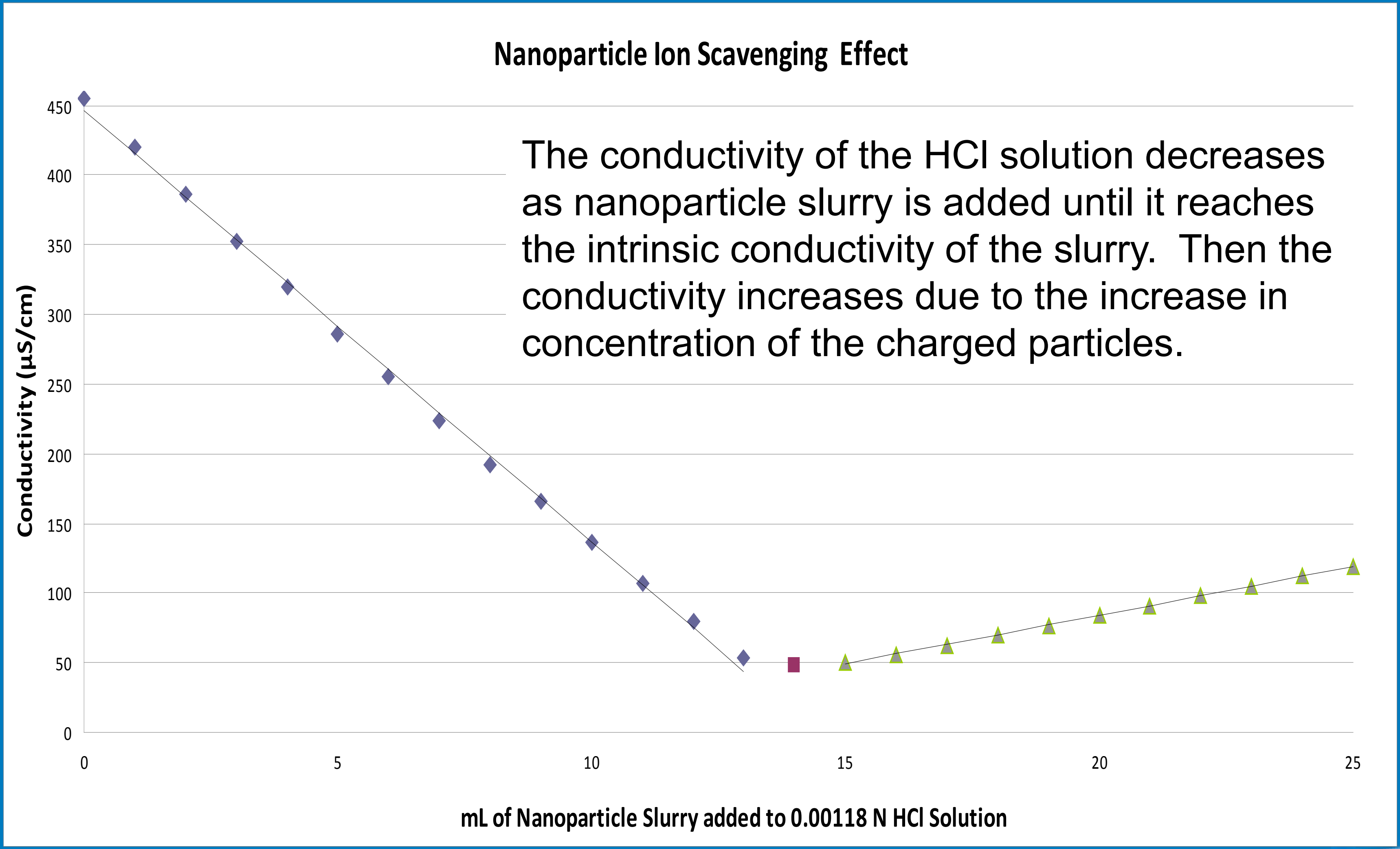

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Objectives

- Optimize and Scale up with Reproducibility:
  - 100 Liter Batches of Nanoparticles in Pilot Plant Scale (Dynalene and Lehigh University)
  - Effects of Various Parameters on the Size and Charge Density of the Particles (Dynalene and Lehigh University)
- Optimize Two-step Filtration Process (Dynalene)
- Develop Blending and QC Procedure (Dynalene)

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Key Technical and Economic Questions to be Answered

- What effect will the impeller type, mixing speed, number of baffles in the reactor, temperature, and the recipe have on the nanoparticle properties?
- What filtration process could be used to remove unwanted chemical species from the nanoparticle slurries?
- How to blend the coolant in large quantities (thousands of gallons)?
- What are the quality control issues with the nanoparticle based coolant and how to solve them?
- How will the large scale pilot plant production affect the cost of the coolant?

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Approach

Dynalene researchers have been producing the nanoparticles ingredients used in the fuel cell coolant in 100 ml, 500 ml and 2 L reactors. The main parameters that contribute to the quality of the nanoparticles are size and surface charge density. Another important factor needs to be optimized is the yield from the production as well as cleaning/filtration. 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.

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Accomplishments in 2010

Dynalene FC fuel cell coolant has been demonstrated by field testing to maintain a very low electrical conductivity and stay stable for over 3000 hours of operation. This was possible due to the addition of a nanoparticle and a corrosion inhibitor package into the coolant. This project addresses the optimization and scale up of the nanoparticle ingredient to improve durability and reduce the cost of the coolant.

Following is a list of accomplishments in 2010:

- Finalized recipe for targeted nanoparticle size and surface charge density (proprietary)
- Increased yield of nanoparticle production by 100% which reduced the cost of coolant
- Optimized the number of impellers and baffles, temperature, and stirring speed
- Produced nanoparticles in 10 L batches with optimum size and charge density
- Developed two-step filtration system (proprietary)
- Blending final product in 55 gallon batch size and supplying to end users
- Began optimizing 100 L batch process. At this scale the cost of the coolant will decrease by 60%

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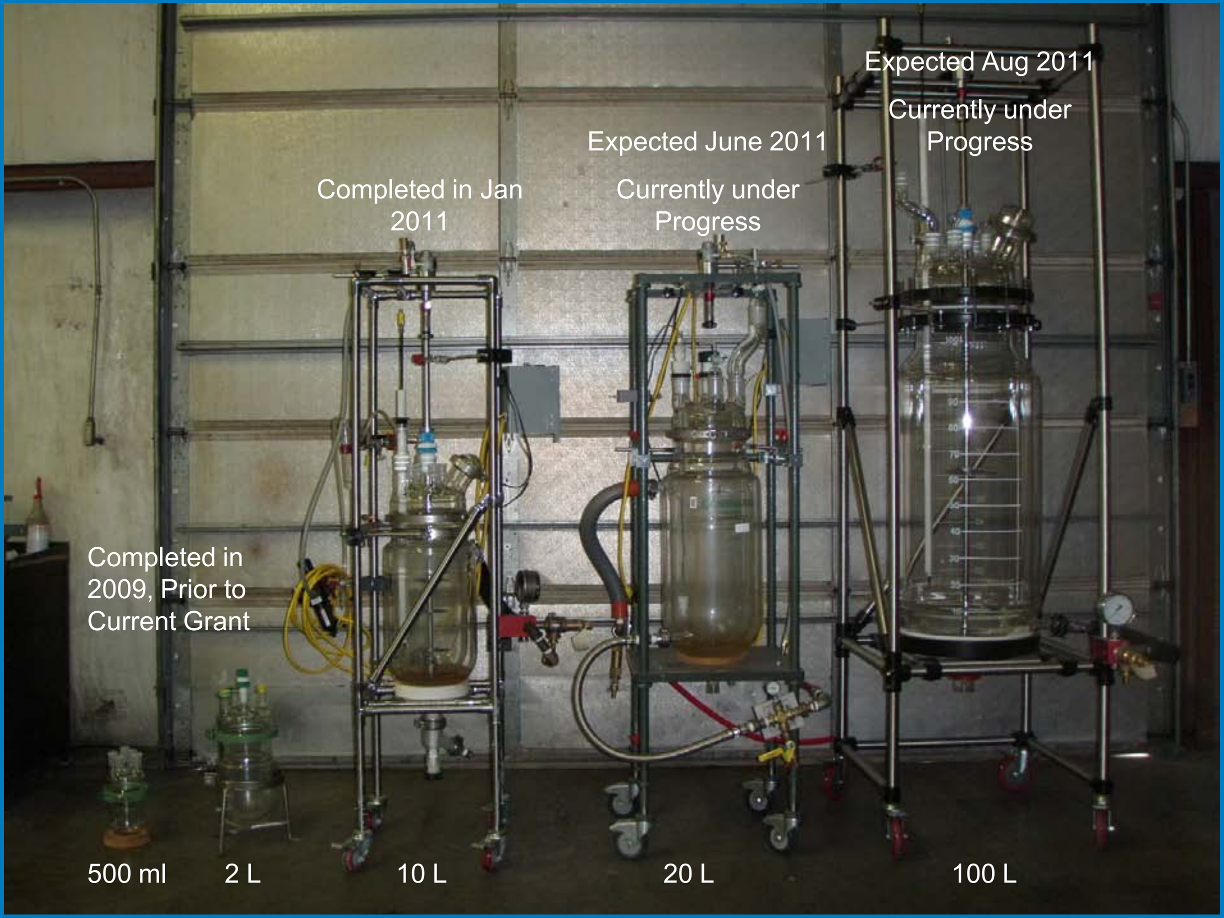
Scale-up Timeline



Glass Reactors Used in the Scale-up of Nanoparticle Production from 500 mL to 100 L Batches

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Parameters Studied for Scale-up

Independent Variables	Dependent Variables	Goals
Mixer RPM	Coagulum Concentration	Reduce Coagulum Concentration
Impeller Location/ Number of Impellers	Particle Size	Optimum Size (200-250 nm)
Shot Addition* (Timing, Rate, Location)	Surface Charge Density	Maximize Surface Charge Density
Filtration (Type, Materials, Pressure)	Filtration Time	Reduce Filtration Time

* The shot is added during the synthesis to improve the surface charge density of the nanoparticles.

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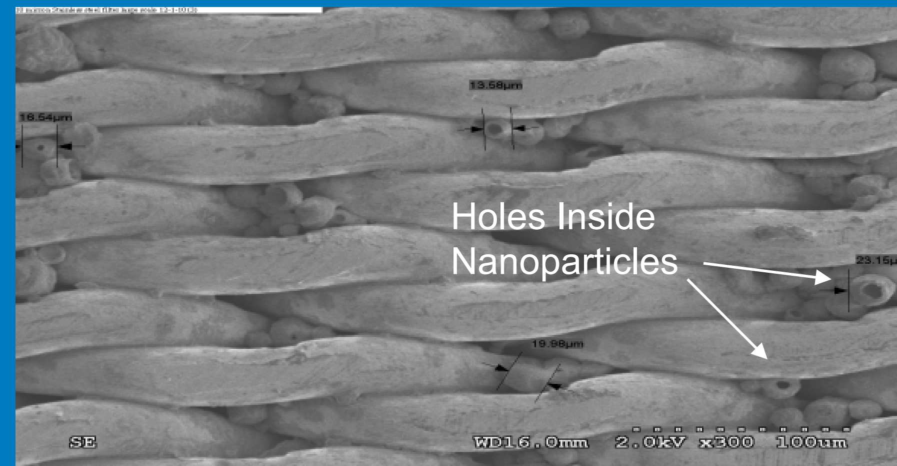
Effects of Mixer RPM

Effect of High RPM of the Impeller:
As seen in the picture above, there is coagulum forming on the impeller, caused by the effect of the high shear.



Effect of High RPM on the Nanoparticle: As seen in the picture above, the nanoparticles are forming with a hole. This is caused by the particles forming around air bubbles.

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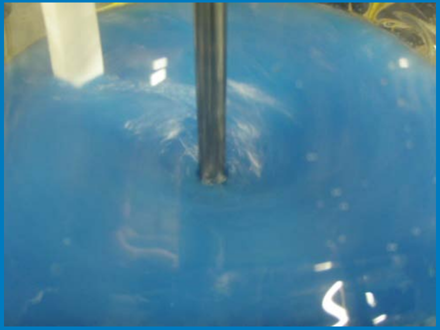
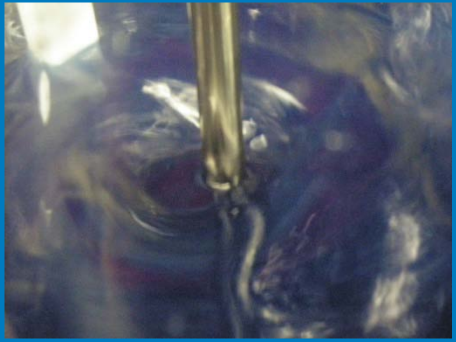
Effects of RPM Cont.



Higher RPM

- **Large Vortex**
- **Air Bubble Entrapment**
- **Coagulum Formation on Shaft**
- **Non-uniform Particle Size**



Lower RPM

- **Incomplete Emulsion**
- **Reaction Gradient**
- **Thermal Gradient**
- **Large Coagulum Formation**

Optimum RPM

- No Air Bubble Entrapment
- Negligible Coagulum
- Uniform Particle Size
- Complete Emulsion Formation

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Oil/Water Mixing Test

0 sec

~30 sec

~1 Min

>2 Min

The oil water study is conducted to maximize impeller placement and number of impellers at a desired mixing RPM. The placement and location must be optimized so the mixing can be uniform to reduce the amount of coagulum and increase the efficiency of the reaction. If these are not correctly adjusted, a layering effect occurs and the components of the reaction will not mix properly causing large amounts of coagulum.

Coagulum from Improper Mixing

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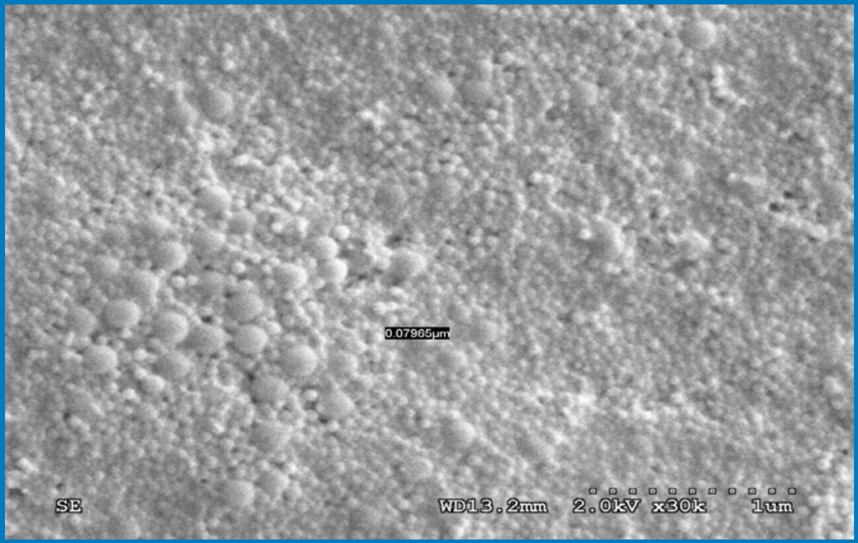
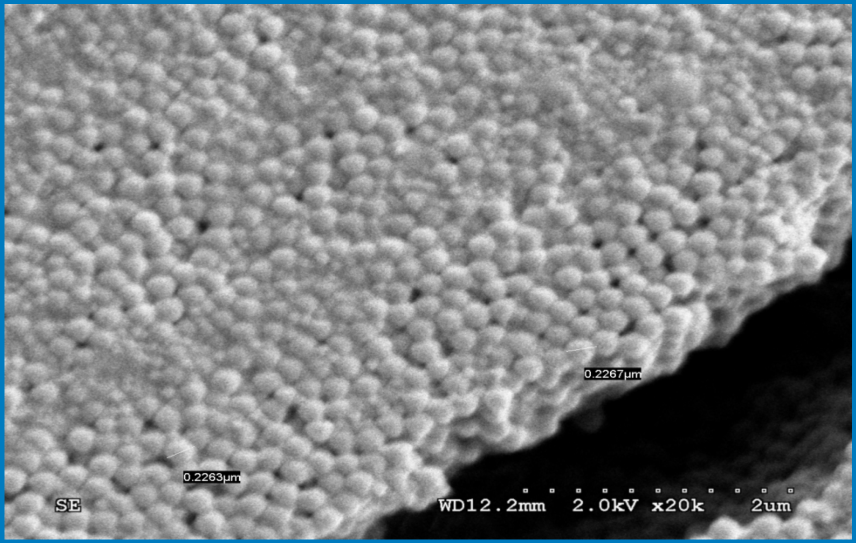
Effects of Shot Addition





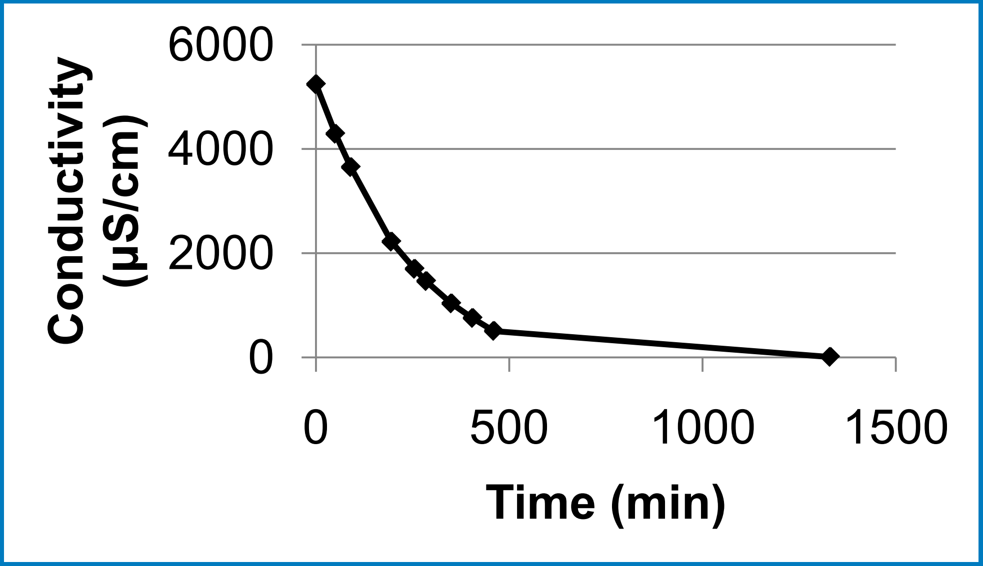
Early Addition Timing:
- Secondary Nucleation
- Non-Uniform Particle Size
- 50% Reduction of Surface Charge

Optimum Addition Timing:
- No Secondary Nucleation
- Uniform Particle Size
- Maximum Surface Charge

When late addition timing is used the reaction is already completed. There is no effect by the shot.

Filtration

The stainless steel filter shown on left collapsed during filtration due to pressure build up. This was a result of large particle forming during synthesis and poor filter selection. This problem was addressed by optimizing the mixing process during synthesis and selecting the right filter.



The graph demonstrates the effect of removing all the unwanted ionic materials (during filtration) that are not nanoparticles. What is left is the nanoparticle slurry with a low electrical conductivity.

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Particle Size and Surface Charge Density of Cationic Nanoparticles in 10 L Batches

<table>
<tr><th>Experiment</th><th>Di*
nm</th><th>Dv*
nm</th><th>Dn*
nm</th><th>PDI**</th><th>Surface Charge Density of nanoparticles
(µeq/g)</th></tr>
<tr><td>DOE1JWM08</td><td>477.1</td><td>583.6</td><td>479.3</td><td>1.00</td><td>280.2</td></tr>
<tr><td rowspan="2">EED-DOE-C-02</td><td>81.0</td><td>69.1</td><td>67.6</td><td>1.20</td><td rowspan="2">313.3</td></tr>
<tr><td>343.1</td><td>351.9</td><td>341.6</td><td>1.00</td></tr>
<tr><td>EED-DOE-C-04</td><td>274.1</td><td>269.3</td><td>261.5</td><td>1.05</td><td>152.6</td></tr>
<tr><td>EED-DOE-C-05</td><td>299.0</td><td>299.0</td><td>274.7</td><td>1.09</td><td>702.0</td></tr>
<tr><td>EED-DOE-C-6+8+10</td><td colspan="4">Multiple Particle Populations</td><td>359.9</td></tr>
<tr><td rowspan="2">EED-0001-06</td><td>181.0</td><td>169.9</td><td>164.8</td><td>1.10</td><td rowspan="2">377.7</td></tr>
<tr><td>542.2</td><td>557.4</td><td>542.2</td><td>1.0</td></tr>
<tr><td>JWM-0002-07</td><td>400.9</td><td>457.8</td><td>403.4</td><td>1.01</td><td>498.8</td></tr>
<tr><td rowspan="2">JWM-0002-10</td><td>186.0</td><td>175.9</td><td>170.9</td><td>1.09</td><td rowspan="2">1010.8</td></tr>
<tr><td>536.9</td><td>553.1</td><td>536.9</td><td>1.00</td></tr>
<tr><td rowspan="2">JWM-0002-12</td><td rowspan="2">621.6</td><td>171.4</td><td>162.0</td><td rowspan="2"></td><td rowspan="2">434.2</td></tr>
<tr><td>638.7</td><td>621.6</td></tr>
<tr><td>JWM-0002-14</td><td>403.0</td><td>416.2</td><td>405.2</td><td>1.01</td><td>450.4</td></tr>
</table>

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*Di, Dv, Dn are intensity, volume, and number average particle diameter, respectively

** PDI: Polydispersity index

Tasks being Performed in 2011

Task 4: Scale-up Nanoparticle Production in 100 L Reactor (20% completed)

Task 5: Develop Blending Procedure for Coolant (50% completed)

Task 6: Create QA/QC Protocols for the Coolant (50% completed)

Tasks 4-6 will be completed by August, 2011.

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Summary

- The fabrication of the pilot plant to produce nanoparticles is complete.
- Nanoparticle production has been optimized at 10 L scale. Effects of mixer RPM, shot addition timing, and mixer placement were optimized to obtain uniform particle size and high surface charge density.
- Filtration has been optimized at 2 L scale.
- Coolant has been successfully produced and shipped in 55 gallon drum quantities. It has reduced the cost of production by more than 60%.

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