

# Idaho Incubation Fund Program

## 3<sup>rd</sup> Quarterly Progress Report Form

**Proposal No.** IF12-014  
**Name:** Dr. Dean B. Edwards  
**Name of Institution:** University of Idaho  
**Project Title:** A High Performance, Horizontal Plate Battery for Plug-in Hybrid Electric Vehicles (PHEVs)

### Information to be reported in your progress report is as follows:

1. Provide a summary of project goals/milestones for the period just completed, accomplishments for the period just completed, and plans and goals for the coming quarter:

Because we only started working on this project in September, we have only spent about \$25k of the \$44k budget. However, during the third quarter we spent about \$14k whereas we had only spent about \$11k during the first two quarters due to the late start. The two month delay was a result of a lapsed agreement between the University of Idaho and the State Board of Education (SBOE). The budget summary shows that about \$19.5k remains to be spent in the budget during the final quarter while our "burn rate" last quarter was \$14k. However, the UI semester ends the first week in May so we will be able to use more of our student labor during the last two months of the project and we expect to finish the project by June 30, 2012.

In the last quarter we plan to paste and cure plates having porous, hollow, glass microspheres (PHGMs). We will then fabricate horizontal plate cells with these PHGM plates in specialized test chambers and test these cells in a starved electrolyte configuration. The test results from these cells having starved electrolyte, horizontal plates with the PHGMs will be compared with the test results from the same type of cells with standard plates not having PHGMs. With this comparison, we will be able to determine whether or not the PHGMs can work effectively in a starved electrolyte configuration which is the primary purpose for doing this work.

The schedule for the project and a summary for each of the project tasks is provided below:

#### Task 1. Fabrication of Horizontal Plate Test Chamber (HPTC)

The use of inexpensive, water-proof polypropylene containers that we modified for use as test chambers has proven to be successful. These containers cost about \$5.00 each and can be modified for our tests. The parts for fifteen of the new HPTCs have been fabricated and are ready for cell assembly. Figure 1 shows one of the HPTC containers in the environmental oven during testing. We have fabricated five horizontal test cells with these commercial, off-the-shelf containers and are presently testing cells in them. The HPTC have demonstrated good

performance with no indications of electrolyte leaking at the lugs. We will be testing additional cells having PHGM plates in a starved electrolyte configuration next quarter. (See Appendix A for more information)



**Figure 1** HPTC during testing

#### Task 2. Porous Hollow Glass Microsphere (PHGM) Plate Fabrication

In the 3<sup>rd</sup> quarter, we continued to fabricate more of the PHGMs required for this work from hollow glass microspheres (HGMs) supplied by 3M called S-38. We have fabricated enough PHGMs to make a batch of 15-20 horizontal plates containing 15% by solid volume of PHGMs. Cells containing these plates will be fabricated and tested next quarter. In addition to fabricating the PHGM plates and cells, we are continuing to develop models for these plates and cells in order to better understand how they can be used to increase plate porosity and performance. (See Appendix A for more information)

#### Task 3. Fabrication of Graphene Coated PHGMs

We are continuing to work on coating graphene on PHGMs, glass fibers, and diatoms. Although the graphene can be coated on these additives and appears to be stable even in the positive plate, the active material does not adhere well to the graphene. We are investigating methods for improving this adherence. Yuqun Xie, a previous graduate student at UI, observed that graphene coated diatomites did not increase positive electrode performance as predicted and reasoned that the hydrophobic forces between  $\text{PbO}_2$  (and/or  $\text{PbSO}_4$ ) and the graphene prevented a good interface from being created between them. As part of this project we are investigating a method for increasing the hydrophilic characteristics of graphene.

Figures 2 and 3 below show the graphene in aqueous solution before and after being treated. Before treating, almost all the graphene flakes were floating on the solution surface for at least 24 hours, as showed in Figure 2. Figure 3 shows graphene treated with  $\text{NaNO}_3/\text{H}_2\text{SO}_4$  mixture after different time scales. As the treating time increases, the amount of graphene flakes which float on the surface decreases. After treating for 1 hour, most of the graphene is either suspended in the

solution or sinks. We are excited about this result and believe this process will help the interface between the graphene and the active material.



Figure 2. Graphene from silicon wafer A in water, before oxidizing.

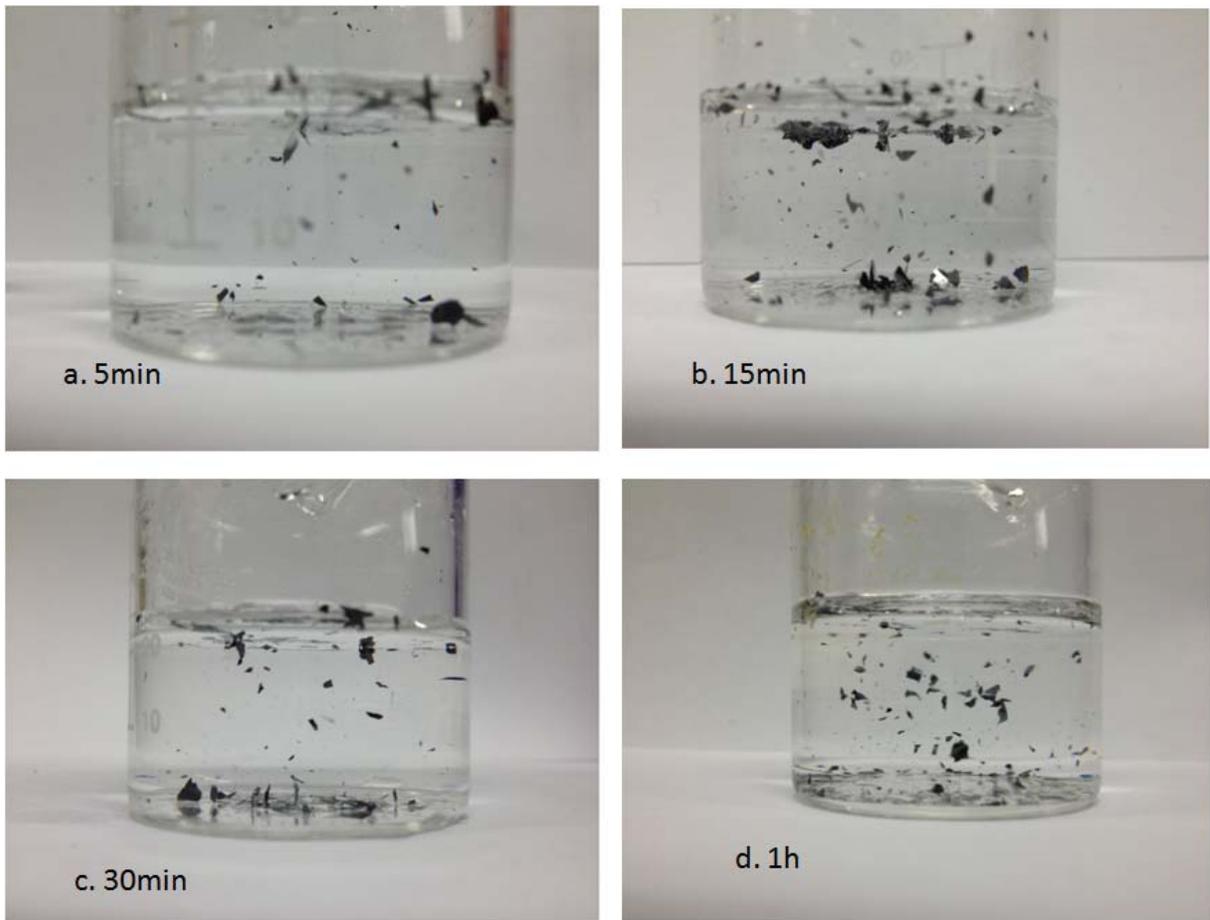


Figure 3. After oxidizing with 0.30g  $\text{NaNO}_3$  and 5ml 98% $\text{H}_2\text{SO}_4$  for a. 5 min, b.10 min, c.30min, d.1h, in dilute sulfuric acid (5 ml  $\text{H}_2\text{SO}_4$  +20 ml  $\text{H}_2\text{O}$ )

#### Task 4. Graphene Coated PHGM Plate Fabrication

Work on this task has been delayed until a method for improving the hydrophilic properties of graphene has been developed. We believe that once we have achieved this goal that a good interface between the graphene and active material can be created.

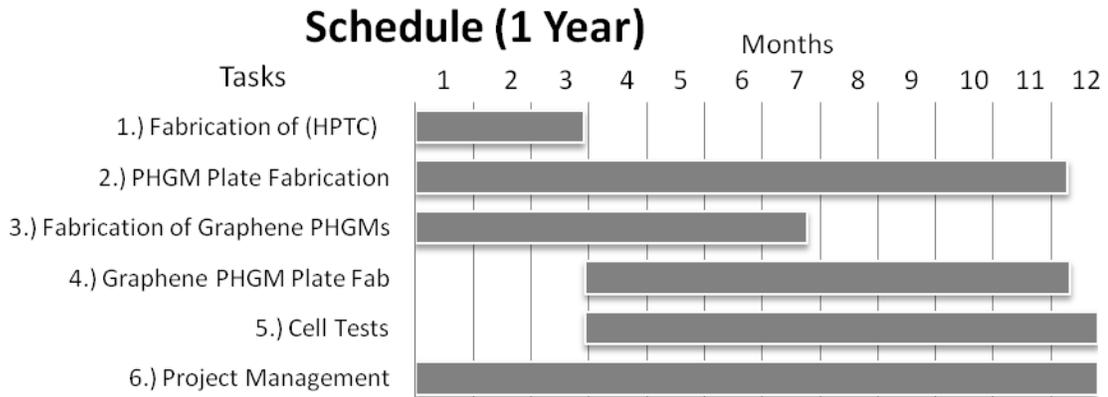
#### Task 5. Cell Tests

We have completed tests on six cells having conductive additives. We are in the process of analyzing the test data from these conductive additive plate cells but the initial analysis is consistent with our conductive additive models. (See Appendix A for more information)

Five test cells using production plates were assembled and successfully completed formation and cycling with a horizontal cell stack. Plates tested in the HPTC have demonstrated good performance with no indications of either electrolyte or air leaking into the HPTC. One of the test cells has over 57 cycles and had a peak utilization of 37%. This information on the production plates will be compared to data on cells using standard, hand pasted plates having no PHGM additives, and hand pasted plates having PHGM additives.

#### Task 6. Project Management

We are holding weekly project meetings and are making satisfactory progress on all the tasks. However, Task 4 has been delayed until the hydrophilic properties of graphene can be developed and tested as discussed above.



#### 2. Provide a summary of budget expenditures for the period just completed:

We are almost fully staffed for this work so the 2<sup>nd</sup> quarter cost of \$14k is closer to the burn rate that we expect for the next quarter. The budget summary shows that about \$19.5k remains to be spent in the budget during the final quarter which is greater than our “burn rate” last quarter (i.e. \$14k). However, the UI semester ends the first week in May so we will be able to use more of our student labor during the

last two months of the project and we expect to finish the project and the final \$19.5k by June 30, 2012.

**Organization:** FB2135 SBOE Horizontal Plate Battery

Account	Title	Adjusted Budget	YTD Activity	Encumbrances	Available Balance
01	Salaries	24,979.00	11,789.23	0.00	13,189.77
02	Fringe Benefits	6,894.00	4,633.36	0.00	2,260.64
03	Irregular Help	6,900.00	3,401.00	0.00	3,499.00
05	Other Expense	5,227.00	4,664.25	0.00	562.75
10	Trustee/Benefits	0.00	0.00	0.00	0.00
	<b>TOTALS:</b>	44,000.00	24,487.84	0.00	19,512.16

3. List patents, copyrights, plant variety protection certificates received or pending:

4. List invention disclosures, patent, copyright and PVP applications filed, technology licenses/options signed, start-up businesses created, and industry involvement:

A PCT/US2010/044269 titled "Method for Making Graphene" was filed 08/03/2010 and is some of the existing technology being used under this Gap funded project.

5. Include funding burn rate:

The present burn rate is about \$3000/month but work on the project was delayed and the project is not fully staffed. We anticipate the burn rate will be about \$4k per month.

6. Any other pertinent information:

Additional details on the work completed are provided in Appendix A that is shown below.

## Appendix A

In this appendix we provide additional details on the work being performed in our project, "A High Performance, Horizontal Plate Battery for Plug-in, Hybrid Electric Vehicles (PHEVs)." This additional explanation is provided below according to the task for which it was performed.

### Fabrication of Horizontal Plate Test Containers (HPTC)

#### Progress to date:

##### Cases

The original HPTC with cast lead terminals and a machined case have been replaced with a water and air-tight polypropylene container.

##### Terminals

The terminals used for the HPTC now use a  $5/16$ -18 flat head socket cap screw with a cast lead head. The cast lead head allows the lead strips from the cell stack to be spot welded to the brass screws. A plethora of spot welding attempts and weld inspections has shown that low compression force is required on the lead strip and cast lead head to produce a solid weld. If the compression force is too high, the soft lead joint does not provide adequate electrical resistance and the resulting spot weld attempt merely heats up the entire bolt rather than melting and fusing the lead at the weld site. After this realization, the use of low compression force has resulted in consistently good quality spot welds.

The terminals are secured to the container with a brass bolt and an o-ring provides for a leak proof seal. The two terminals of the same electrical polarity are connected together with a  $1/16$ " x  $3/4$ " strip of lead.

##### Glass Mat Measurements

The individual plates in each test cell are separated with a glass mat separator. A glass mat measurement apparatus, shown in Figure 4, was needed to reliably measure the thickness. The use of a  $1/2$  x  $1/2$  lead sheet along with the pressure from a spring loaded dial indicator provides 1.57 psi on the glass mat during the measurement. Current available thickness includes 0.042", 0.055" and 0.065".



Figure 4 Glass Mat. Measurements

### Cell Stack Design

The cell stack to be used for cycling positive plates in the HPTC will consist of 3 negative plates and two positive plates. Two layers of .035" glass mat separators will be used on each side of the negative plates for a total of six layers. With 3-5 psi of compression the mat is expected to have ~20% compression for a total separator thickness of .056". The thickness of the individual components and the total cell stack height is shown in the following table.

Item	Thickness	#	Totals
Negative Plate	.043"	3	.129"
Positive Plate	.063"	2	.126
Separator	.056"	6	.336
Total cell stack height .591"			

A trial cell stack using grids and the separator material was assembled and the spot welding techniques investigated. The method that produced the best results used lead strips between the plates with the spot welder to form a strap for connecting the individual plates together. This method helps maintain proper spacing on the grid tabs thus preventing excess deformation that would occur without the lead strips.

### Cell Stack Compression

Cell stack compression is accomplished by sandwiching the cell stack between two sheets of .022" thick polycarbonate sheets. Once the appropriate compression (3-5 psi) is applied to the cell stack a series of polypropylene zip ties are used to maintain the compression. This method has the advantage of rigidly holding the cell stack assembly together even when it is not in the HPTC which aids in stack assembly, spot welding, and making the connection to the terminals in the HPTC.

### **Modeling of Battery Cells with Additives, Progress to date:**

Two models are used to estimate the performance of the batteries and to aid in the design of new batteries. The conductivity model is a 2D (or 3D) nodal lattice model used to determine the critical volume fraction (CVF) of battery pastes with varying additives. The diffusion model is a 1D finite difference model to examine the discharge characteristics of batteries with varying additives and dimensions. Two very important parameters used to define the diffusion model are the critical volume fraction (obtained from the conductivity model), and the estimated porosity of the active material in the electrodes. As part of the most recent research, we have refined the mathematical models used to arrive at these estimates.

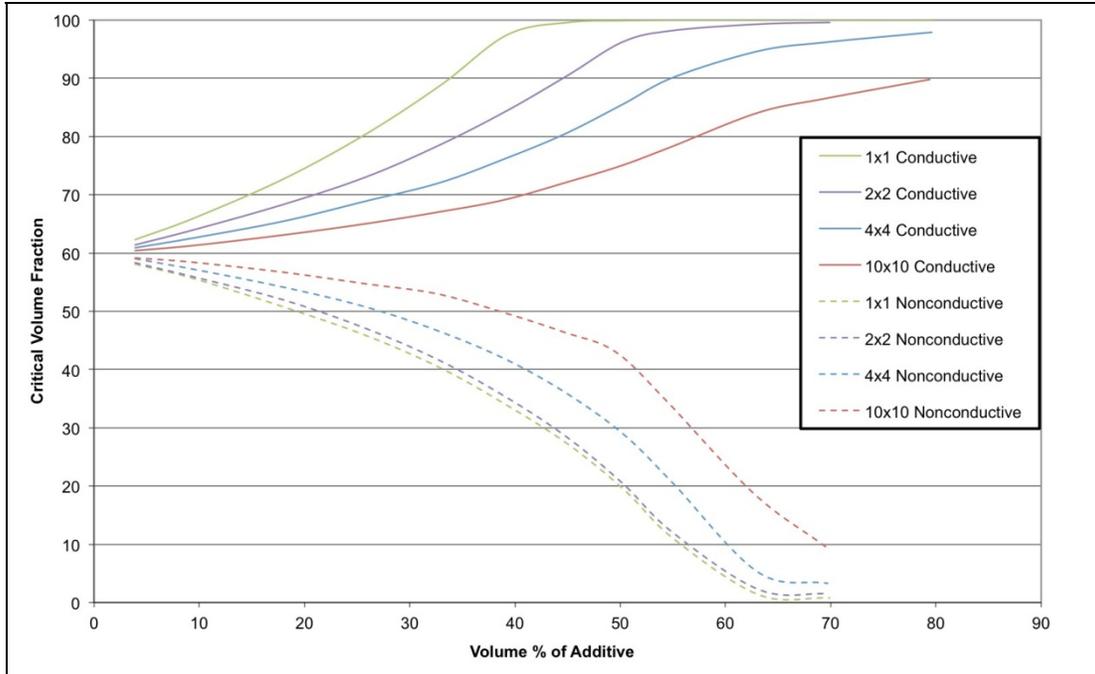


Figure 5. Conductivity model results for various additive sizes and loadings.

The major result of the conductivity model is shown in figure 5. It shows the critical volume fraction predicted by varying sized conductive and non-conductive additives. As more additives are placed in the mix, the effect on the critical volume is amplified. Conductive additives improve the CVF and non-conductive additives worsen the CVF. Due to the nature of the conductivity model, the critical volume fraction as seen in figure 5 is referenced to a *node volume percent* which is the fraction of nodes in the 3D matrix that are displaced by the additives. Two types of volume fractions are used to determine the *node volume percent*. The first is the *additive solid volume fraction*,  $f_s$ , which describes the amount of additives in the mix compared only to the volume of the solids and is given by the following equation:

$$f_s = \frac{V_{AD}}{V_{AD} + V_{AM}} \quad (1)$$

where  $V_{AD}$  is the true volume of the additives, and  $V_{AM}$  is the true volume of the active material. The second volume fraction that is used to determine the CVF is the *additive total volume fraction*,  $f_T$ . This fraction relates the volume of the additives to the total volume of the paste including the porosity and is found with the following equation:

$$f_T = \frac{V_{AD}}{V_T} \quad (2)$$

where  $V_{AD}$  is the volume of the additives, and  $V_T$  is the total volume of the paste in the plate.

As stated earlier, the critical volume fraction must be referenced to a *node volume percent* which takes into account any displaced porosity by the additive. Because the displaced porosity will depend on additive size, the node volume percent equation requires the use of both the above volume fractions. The following “Ad Hoc” equation was adopted to help estimate the percentage of nodes that would be replaced by the additives:

$$\frac{N_A}{N} = \frac{1}{n}f_s + \frac{n-1}{n}f_T \quad (3)$$

In eqn. (4),  $N_A$  is the number of nodes displaced by additives,  $N$ , is the total number of nodes in the plate,  $n$ , is the ratio of the average additive diameter to the active material node diameter, and  $f_S$  and  $f_T$  are the two volume fractions defined in eqns. (2) and (3).

The node volume percent value,  $N_A/N$ , varies with node size,  $n$ . The equation was developed so that when  $n = 1$ , and the additive size and node size are identical, the number of nodes replaced by the additives is the same volume as the additives. When  $n = 1$ , the number of additive nodes are equal to the number of active material nodes replaced, and the node fraction is equal to the *additive solid volume fraction*,  $f_S$ , as seen in the figure. When  $n$  is large (i.e.  $n \geq 10$ ), the additives are larger than the active material nodes and therefore displace porosity as well as active material nodes. Therefore, for large additives, the ratio of active material nodes replaced by additive nodes will be very close to the additive total volume fraction (i.e. if  $n \geq 10$  then,  $N_A/N \approx V_{AD}/V_T$ ). Assuming 50% porosity, large additives only displace half as many active material nodes as small additives with  $n = 1$ . Equation (3) therefore reduces to the approximate ratios expected for small additives ( $n = 1$ ) and for large additives ( $n \geq 10$ ).

From the results of eqn. (3) we can arrive at an estimate of the CVF, therefore we turn our attention to estimating the porosity. In order to estimate of the total porosity of PHGM additive plates,  $P$ , we first derive the porosity of the plate,  $P_A$ , where the internal volume of the PHGMs are not included. This porosity would be the same as if the PHGMs were HGMs. Using eqn. (3) we have arrived a the following equation for  $P_A$  :

$$P_A = \frac{V_P}{V_T} = \frac{P_{Std}}{1 + \frac{n-1}{n}f_s} \quad (4)$$

In eqn. (4),  $P_{Std}$  is the porosity of a standard plate,  $V_P$  is the pore volume inside the active material but does not include the porosity inside of the PHGMs,  $f_s$ , is the *additive solid volume fraction* as defined in eqn. (1) and  $n$  is the size ratio of the additives compared to the assumed active material nodes as seen in eqn. (3). Eqn. (4) provides the total porosity of the plate with additives not including any porosity inside of the additives (see Appendix A for a full derivation). We see when  $n = 1$ , that the porosity of the additive plate is equal to the porosity of a standard plate or  $P_A = P_{Std}$ . When  $n$  is large, the porosity is reduced because the additives also displace porosity and not just the active material. To find the total porosity,  $P$ , we also add the internal volume of the additives as in the following equation:

$$P = P_A + Zf_T \quad (5)$$

where  $Z$  is the porous fraction of the additive available for electrolyte storage. Although eqns. (4) and (5) are based on simple idealization so of the active material, experimental data agrees much closer to these equations than would be expected. Because these volumes found in eqn. (1) can be determined by dividing the mass of the additives or active material by their true density ( $V_{AD} = m_{AD}/\rho_{AD}$  and  $V_{AM} = m_{AM}/\rho_{AM}$ ), the *additive solid volume fraction*,  $f_S$ , is known at the time of mixing. The *additive total volume fraction*,  $f_T$ , is not known during mixing because the porosity is undetermined. The value of  $V_T$  may be estimated from the masses of the constituent parts of the paste once the plate has been cured. However, we may relate the additive total volume fraction,  $f_T$ , to the additive solid volume fraction,  $f_S$ , through a simple expression discovered during our research:

$$f_T = f_S(1 - P_A)$$

This new expression can be incorporated into our porosity equation (5) to give a function in one variable,  $f_S$ :

$$P = P_A + Zf_S(1 - P_A) \quad (6)$$

In figure 6, we compare the porosity estimation as derived from our simple models to porosity data derived from recent testing activity. The two solid lines are the model prediction given by eqns. (4) and (6). Porosity data from tested plates is represented on the graph with data points. The lower line (blue) which is the model given by eqn. (4) compares well with porosity data of HGM plates and PHGM plates where the internal volume of the additives is not included (triangular data points). The upper line (green) which is the model given by eqn(6) compares equally well with the total porosity data of PHGM plates (square data points).

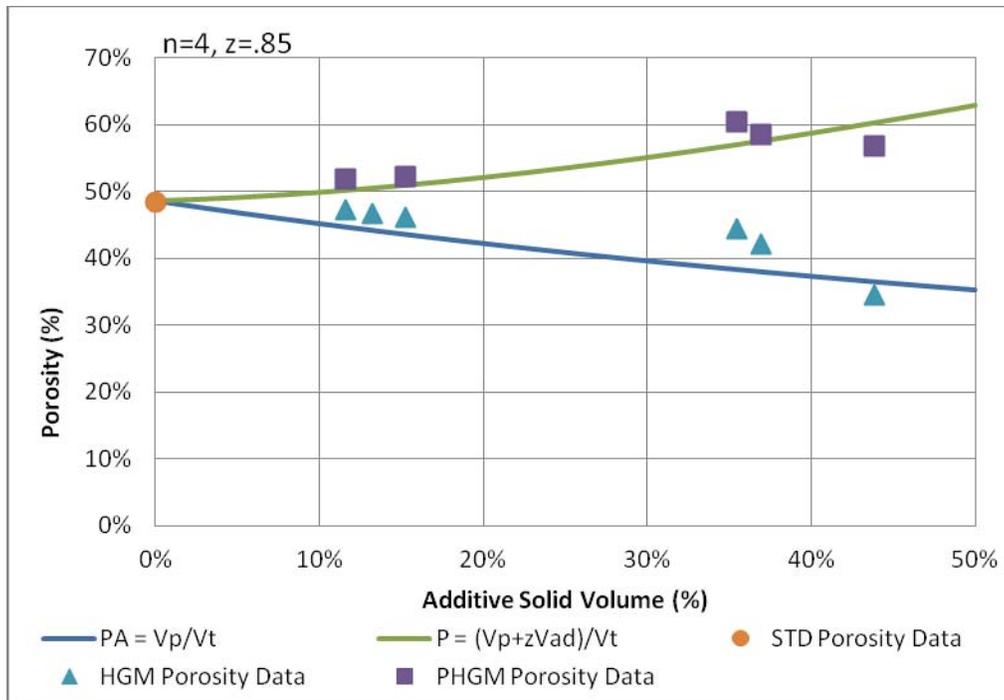


Figure 6. Comparison of the Porosity model to porosity data measured during recent testing.