Idaho Incubation Fund Program

Final 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 final report is as follows:

1. Provide a summary of overall project accomplishments to include goals/milestones met, any barriers encountered, and how the barriers were overcome:

Plug-in hybrid electric vehicles (PHEVs) which have a 30-50 mile electric vehicle range are increasingly being manufactured and marketed. Unfortunately, the present Li-ion batteries being used in most of these vehicles are expensive and are limiting the number of PHEVs and other HEVs being sold. However, material innovations and improved battery designs developed at the University of Idaho and with collaborators elsewhere can provide a high performance, cost effective battery for PHEVs and other HEVs.

Porous, hollow, glass microspheres (PHGMs) is one of the key technologies needed to create this high performance, cost effective battery. One example of a PHGM is shown in Figure 1. Using PHGMs in special horizontal plates in a starved electrolyte, lead-acid battery design would provide the needed performance at a reduced cost for a PHEV. Although the performance improvement of having PHGMs in electrodes used in flooded cells has been shown, the use of PHGM electrodes in starved cells has not been adequately investigated. The concern is that filling the PHGM with electrolyte in a starved configuration may be more difficult than in a flooded design. The ability of these PHGMs to store electrolyte inside the spheres when the batteries operate in a starved electrolyte configuration may therefore be compromised.

PHGM Research Results

The major objective of the project was to determine if PHGMs (i.e. porous, hollow, glass microspheres) could be used effectively in starved, horizontal plate, lead acid cells. In Figure 2, the utilization of the active material at the one hour rate (i.e. 1C rate) is shown for a number of starved electrolyte cells having different amounts of PHGMs in their plates. All the data is normalized to the amount of active material so that all the results can be compared directly. As can be seen from the figure, the utilization of the plates containing PHGMs have similar performance to the production plates and better performance than the hand pasted plates having no PHGM additives. This data confirms that the PHGMs can be used effectively in starved electrolyte cells.

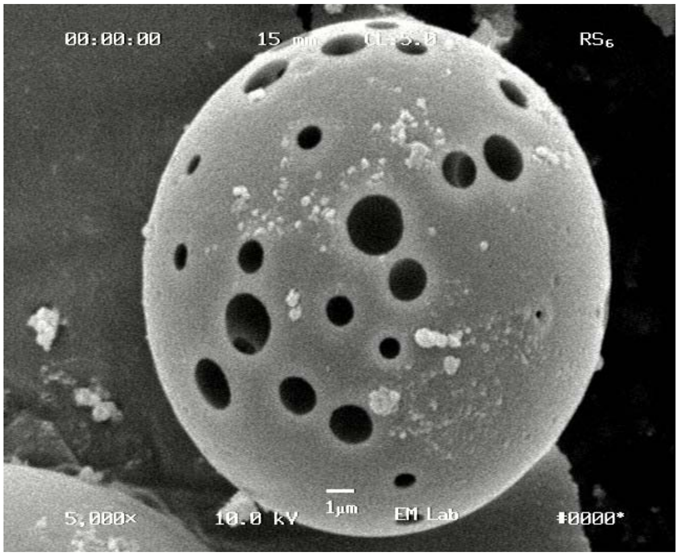

Figure 1 Porous hollow glass microsphere (PHGM)

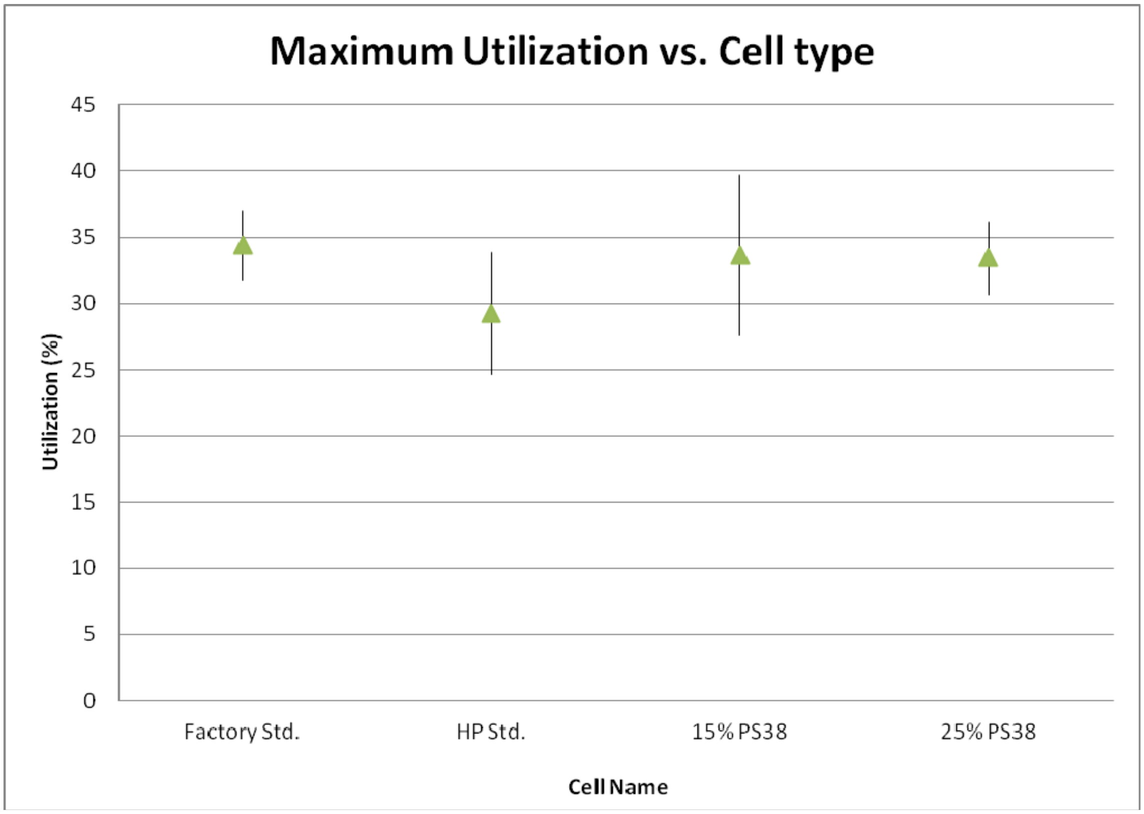

Figure 2 Utilization at the 1C rate for different cell types

The reason for including the data on the production plates in the figure is that they are made by machines in a more controlled and accurate manner than the hand pasted plates.

As shown in Figure 2, the hand pasted plates with no additives did not perform as well as the production plates. However, the hand pasted plates having additives need to be compared to the hand pasted plates without additives to see the effect that the PHGMs have on the high rate performance of the cells.

Figure 3 shows the results from our model for cells having different additive loadings (i.e. 0% to 40%) and at three discharge rates (i.e. 1C, 2C, and 4C rate correspond to the 1 hour, half hour, and 15 minute discharge rate). An increase in additives will increase the porosity of the active material and improve the diffusion of electrolyte in the battery. We note that the limiting factor for discharges on standard and low additive plates is diffusion. This is the reason that discharging at lower rates return higher utilizations. At high additive loadings, the limiting factor is the conductivity of the active material. The addition of non-conductive additives increases active material resistance and reduces utilization. This leaves a peak for each discharge rate that returns an optimal additive loading for a design discharge rate. Note that 20% PHGM loading is close to the optimal amount for both the 1C and 2C rate, which is the discharge rate that PHEV batteries would operate.

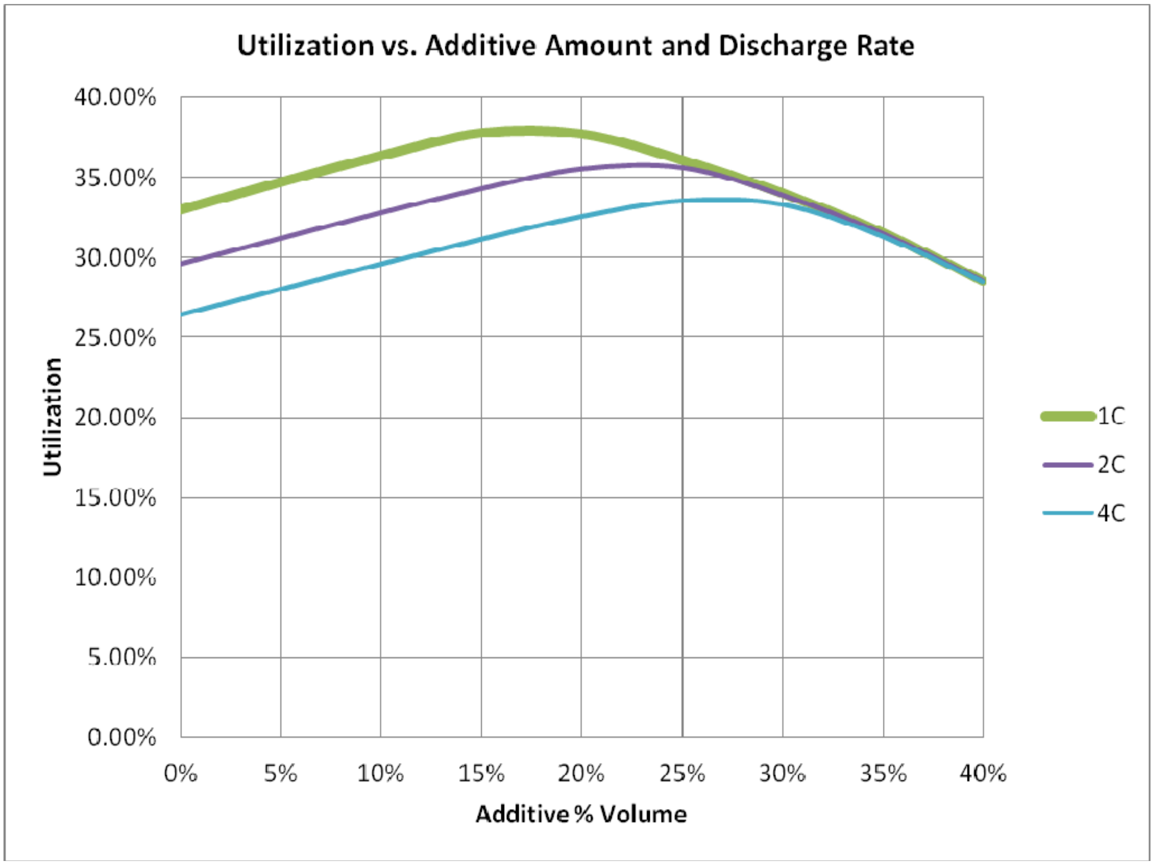

Figure 3 Model Results for Utilization vs. Additive Loadings at Different Discharge Rates

In Figure 4, all of the utilization plots have been removed for better clarity except for the 1C rate plot. The crosses are the expected 1 hour rate utilization for each of the additive loadings that we tested. The data from the hand pasted test cells are shown with the circles, and factory produced standard is marked with a square. This data represents the average of the 10 best discharges of the test cells. We note that the model predicts the factory production plate very accurately at the 1C rate. Also, the model over predicts the performance for all the hand pasted plates by about the same amount, which we believe is an artifact of the difficulty in making plates by hand. For production plates with PHGMs, we would expect the data to follow the predicted 1C rate line.

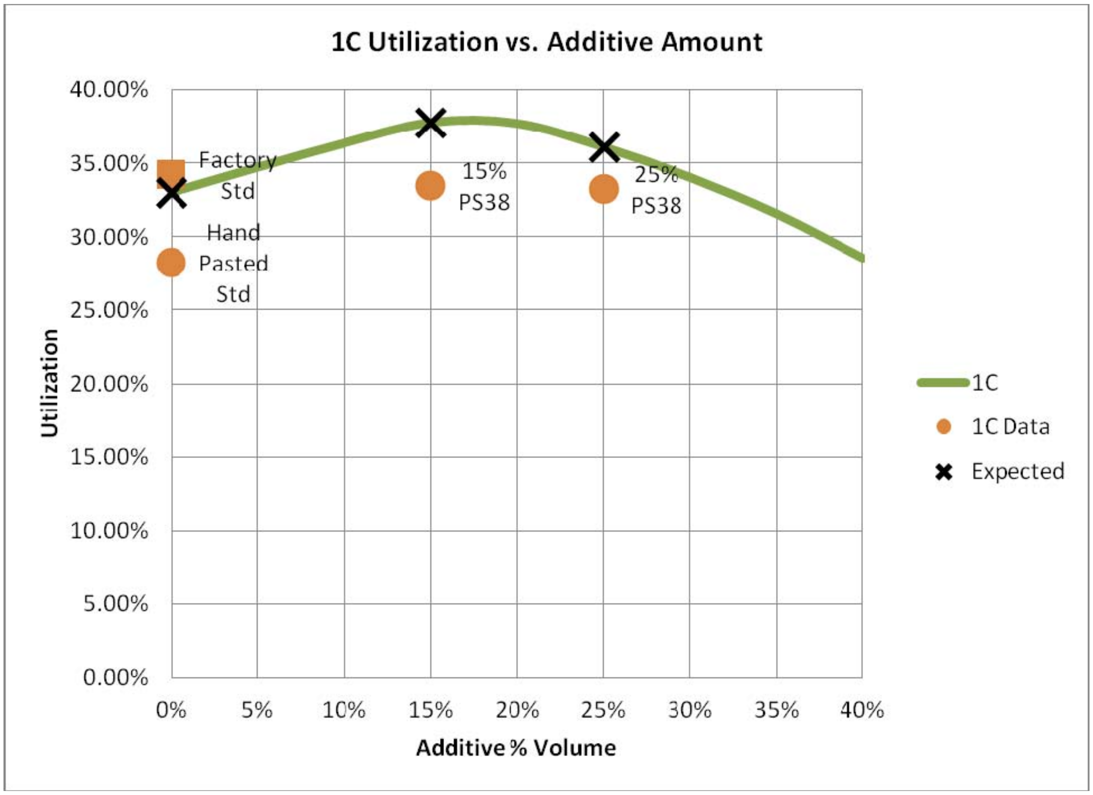

Figure 4 Expected Model and Experimental Results at 1C Rate

In addition to demonstrating that the PHGMs could be used effectively in sealed, starved electrolyte batteries, we also investigated methods for improving the yield of making PHGMs from HGMs. Using a mixture of HF and NaF solution, we were able to increase yields of PHGMs from around 8-10% to approximately 65%, a notable improvement. Although the breakage was somewhat higher, we are investigating methods for separating intact microspheres from broken ones to solve this problem.

Graphene Research Results

The graphene obtained from the procedure we use at the UI is more disordered than other types and appears to have superior corrosion resistant characteristics. For these reasons we have started to refer to our graphene as GUITAR, “Graphene from University of

Idaho Thermolyzed Asphalt Reaction." GUITAR coated glass fiber was synthesized in a crucible. An SEM of graphene coated glass fiber is shown in Figure 5. The non-conductive part of the glass fibers is white and the grey areas are the coated fibers.   . From the SEM, the glass fibers appear to be well coated with at least 60% of the glass fibers being coated.

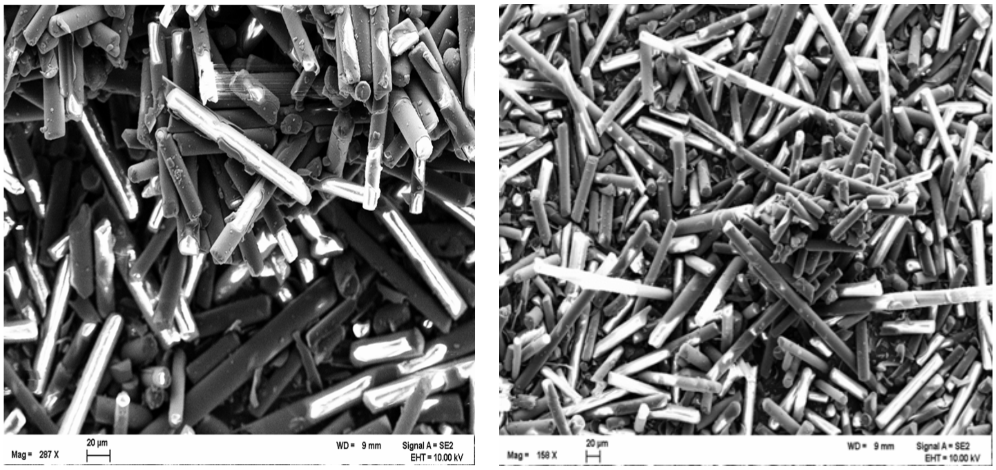

Figure 5. SEMs of GUITAR Coated Glass Fiber Scanning electron micrographs-SEMs were obtained with a Zeiss Supra 35 Scanning Electron Microscope (Carl Zeiss, Germany).

Conductivity tests were made on the GUITAR coated glass as well as the GUITAR coated glass fiber after acid treatment to make the graphene more hydrophilic. Electrical measurements of conductivity were performed with an Arbin. The average conductivity of GUITAR coated glass fiber was 2.955 siemens/m (1st batch), 4.530 siemens/m(2nd batch), 15.205siemens/m(3rd batch), 18.835siemnes/m(4th batch), 8.042siemens/m(6th batch) and 7.011siemens/m(Ox 5&6th batch). Ox 5&6th refers to the procedure where GUITAR glass fiber from the 5&6th batch were also treated in an acid/oxidizing environment. Conductors having conductivity from 0.1-25 siemens/m are classified as medium conductors. All the GUITAR coated glass fibers can be regarded as medium conductors, including the more hydrophilic treated GUITAR glass fiber. The conductivity of PbO_2 is about 3.675 Siemens/m and PbO is nearly zero following the same testing method. Because PbO_2 provides the conductivity for the positive paste, additives with higher conductivity than PbO_2 will improve battery performance at any state of charge.

During earlier testing, it was observed that GUITAR graphene coated diatomites did not increase the positive electrode performance of lead acid batteries as predicted. Our analysis suggested that the hydrophobic forces between PbO_2 (and/or $PbSO_4$) and graphene was responsible for the poorer than expected performance. As part of our work, we developed a method to increase the hydrophilic characteristics of graphene. This method was observed to be successful as the treated graphene now sinks in water where before it simply floated. From the conductivity tests, the treated grahene's conductivity is still adequate. Only the corrosion resistance of the treated graphene needs to be evaluated before beginning tests of graphene coated additives in plates.

Summary of Research Results

The most important result of our work was the demonstration that electrodes containing PHGMs could be used effectively in sealed, starved electrolyte batteries. In addition, we demonstrated methods for improving the yield of making PHGMs from HGMs. Our work also included investigating the use of graphene to increase the conductivity of both the negative and positive electrodes to boost battery performance. Because the hydrophobic forces between PbO_2 (and/or $PbSO_4$) and graphene was responsible for the poor interface between them, we developed a method to increase the hydrophilic characteristics of graphene. This method was observed to be successful as our treated graphene now sinks in water whereas before it simply floated. From conductivity tests, the treated grahene's conductivity is still adequate for our purposes. Only the corrosion resistance of the treated graphene needs to be evaluated before beginning tests of graphene coated additives in both the negative and positive electrodes.

2. Describe the current state of the technology and related product/service:

   The projections for PHEV, HEV, and EV batteries continue to show strong growth in demand with the number of batteries sold for these vehicles expected to increase by a factor of three by 2018. However, the present Li-ion batteries being sold for many of these vehicles are expensive and are limiting the number of PHEVs and other HEVs being sold. The GM volt stopped production earlier this year because of a lack of demand. The Department of Energy (DOE) just recently announced plans to try to reduce the cost of these batteries. Our battery and material innovations are timely as they are already addressing both the cost and performance issues of these batteries.

3. List the number of faculty and student participants as a result of funding:

   Professors: Dean B. Edwards, I. F. Cheng
   Graduate Student: Haoyu Zhu
   Undergraduate Students: Heinrik Gottesche, Henry Cross, Robert Heine, Frank Ramirez
   Post Doc: John Canning
   Research Eng: Tom Bean

4. What are the potential economic benefits:

   The potential economic benefits are large as the cost of our battery would be 1/5 to 1/10 the cost of an equivalent Li-ion battery. In addition, our research brings in significant money to the University of Idaho and the State. A potential spin-off company using this technology and located in Idaho could also bring in significant economic benefits to the State.

5. Description of future plans for project continuation or expansion:

   A spin-off company has been formed called "Advanced Hybrid Power Systems, LLC" that will use UI technology to sell a complete system for converting older

Prius vehicles into PHEVs. This system would include our battery technology. The company is developing a business plan to raise capital and compete for funding from the State of Idaho. In addition, UI researchers will be submitting applications to DOE to demonstrate our technology for reducing the costs of these PHEV batteries.

6. Please provide a final expenditure report (attached) and include any comments here:

7. 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. A start-up company has been created called “Advanced Hybrid Power Systems, LLC” which is also interested in signing a technology license with the University of Idaho. We have also been interacting with different battery companies including Axion Power International, Inc.

8. Any other pertinent information:

   We believe that the business opportunity for our technology will greatly improve over the next year.

FINAL EXPENDITURE REPORT

A. FACULTY AND STAFF		
Name/Title	$ Amount Requested	Actual $ Spent
Thomas Bean, Research & Development Engineer	10158.72	9,810.99

B. VISITING PROFESSORS		
Name/Title	$ Amount Requested	Actual $ Spent
N/A		

C. POST DOCTORAL ASSOCIATES/OTHER PROFESSIONALS		
Name/Title	$ Amount Requested	Actual $ Spent
John Canning, Post doctoral fellow	8190.00	10,336.82

D. GRADUATE/UNDERGRADUATE STUDENTS		
Name/Title	$ Amount Requested	Actual $ Spent
Graduate Assistant (never able to hire one)	6630.28	0
Temp undergrad research assts: Henry Cross, Heinrik Goettsche, Robert Meine, Francisco Ramirez	3900.00	9460.76

E. FRINGE BENEFITS		
Rate of Fringe (%)	$ Amount Requested	Actual $ Spent
Salary @ 37%	6789.00	7851.89
IH 1% school year/ 9% summer	105.00	690.85
PERSONNEL SUBTOTAL:	**35773.00**	38151.31

F. EQUIPMENT: (List each item with a cost in excess of $1000)		
Item/Description	$ Amount Requested	Actual $ Spent
1. Grids -1000 pieces	4175.00	6747.51
2.		
3.		
4.		
EQUIPMENT SUBTOTAL:	**4175.00**	6747.51

G. TRAVEL		
Description	$ Amount Requested	Actual $ Spent
1.N/A		
2.		
3		
TRAVEL SUBTOTAL:	0	0

H. PARTICIPANT SUPPORT COSTS:			
Description		$ Amount Requested	Actual $ Spent
1. Grad RA tuition		4052.00	0
2.			
3			
PARTICIPANT SUPPORT COSTS SUBTOTAL:		4052.00	0
I. OTHER DIRECT COSTS:			
Description		$ Amount Requested	Actual $ Spent
1.N/A			
2.			
3.			
OTHER DIRECT COSTS SUBTOTAL:		0	0
TOTAL COSTS (Add Subtotals):		44,000.00	44,898.82
TOTAL AMOUNT REQUESTED:			44,000.00
TOTAL AMOUNT SPENT:			44,898.82