2010 – 2012 Program Project Review

Battery Technology (7 projects)

1012 J, Technology Development. Duration: 30 months. Status: completed.

Contractors: Hammond, USA, Lignotech, USA, Moura Batteries, Brazil.

Project leader: Dr. Matt Spence (left the company), replaced by Dr. David Boden.

Objective: Optimization of the traditional lead-acid battery to meet the new demands of Idle-Stop-Start micro-hybrid vehicles and stationary photovoltaic (PV) systems. For micro hybrid vehicle batteries the duty will call for a battery design that is able to repeatedly supply warm cranking currents, power the in-car systems with reserve capacity and rapidly accept recharge. For photovoltaic systems the demands are somewhat different, requiring a much deeper cycling duty and resilience to possible periods of undercharge.

The project examines the effects of several organic additives to the NAM on negative plate performance. The most commonly used organic expander, Vanisperse A, was included as control reference, and cells with no organic expander were included as blank references. Oxylignin derivatives from the Borregaard-Lignotech (BL) wood pulping process were selected based on pre-existing work. In total 14 variables were studied.

Results: The project was conducted in two phases: additive screening by testing of 2V model cells with standard automotive test methods comprising reserve capacity, charge acceptance, recharge-ability, and cold cranking; and building and testing of automotive and PV batteries with the best additives found in the first phase. The experimental data showed strong correlation between both the type of organic expander and its dosage level in the initial paste mix. Further analysis of the data revealed that both reserve capacity and cold cranking performance exhibit quadratic concentration dependencies over the dosing range studied. Curve fitting gave optimal concentrations and expected maximum performances. Several of the organic compounds tested outperformed the industry standard lignosufonate for cold cranking and reserve capacity. Full size commercial batteries have already been built from the plate-stock produced in Phase 1. These are being cycle tested in Phase 2.

1012 M, Technology Development. Duration: 24 months. Status: Completed.

Contractor: Exide, Spain

Project leader: Mr. Melchor Fernandez

Objective: To develop a 6V/10Ah VRLA Spiral Wound Battery with optimized negative active mix (10 new carbon types) for mild hybrid vehicle applications by redesign of the already existing 6V/24Ah modules.

Results: Study results showed that carbon additives are not a universal remedy for lead-acid batteries. Some carbon additives substantially increase battery performance in pulse applications at normal and elevated temperatures. Others reduce the performance at slow discharge and at low temperatures, and/or cause higher water losses. Gaining control over the controversial influence of various carbons and their amounts requires a deep understanding of how different carbons work in the negative plate of the battery.

Five types of carbon were tested in test cells were produced. Peukert and Tafel plots were built, and tests of discharge at high rate and at low temperature (-18ºC), of discharge power at different state of charge (SoC), and of charge acceptance were conducted. The variety of carbons exerted little influence on Peukert plots due to the changes in NAM structure (local distortions) they created. Carbon additives are not beneficial for high-rate discharge at low temperature, they can be even harmful. Using specific combinations of some carbon types can keep the performance as high as in the controls. Carbon additives are very beneficial, however, for the discharge power at room and elevated temperatures, and for charge acceptance, especially at higher SoC, what is a key feature in hybrid electric vehicles. Microstructure tests of unformed paste have shown that carbon additives have little effect on porosity but can affect pore size, especially of micro pores (below 300 nanometers). Carbon additives influence (increase) most significantly the specific surface area (SSA) of the paste which is then transferred to the formed NAM. This effect is directly related to increased charge acceptance and other battery parameters.

1012 E (ISOLAB), Technology Development. Duration: 8 months. Status: Discontinued, a design project launched.

Contractors: Banner Batteries, Austria, Teck, Canada, Focus Consulting and Provector, UK

Project leader: Dr. Geoffrey May, Mr. Norbert Maleschitz

Objective: The project was a continuation of the ISOLAB project. A special type of 2V / 6 Ah valve regulated lead-acid cells with carbon-added negative active mass and optimized for higher energy and power output grid and cell design (new grid design, terminals placed at opposite sides of the box) were designed for production by Banner and used further for assembling a battery capable to replace (by volume and performance) the originally used Ni-MH battery in a mild hybrid electric vehicle (Honda Inside, Generation II).

Results: The grids were punched from Pb-Ca-Sn foil by Cominco and delivered for assembly to Austria. The first batch of batteries was produced by Banner. The cells were tested electrically. The initial results were encouraging, but most of the cells had electrolyte leaks around the terminals. As a result, they were losing capacity. After a couple of unsuccessful trials to fix the leaks a smaller was designed to adjust the design and eliminate the leaks (**Project 1012 KD**). After fixing the leaks problem, the necessary amount of cells will be produced and connected into a battery. The project is ongoing. New grids have been produced. Battery production is in preparation and is expected to be completed by the end of February 2013. Subsequently, cell testing can be initiated. The battery will be tested in the vehicle during the final stage of Project 1012 KB.

0709 SPSoC1, Technology Development. Duration: 24 months, continuation from 2007-2009. Status: Completed.

Contractor: CEA-INES, France, BAE – Germany, AmerSil - Luxembourg

Project leader: Dr. Elizabeth Lemaire, replaced by Dr. Sylvie Genies, final report by Dr. Sven Zarske

Objective: To enhance the performance and cycle life of deep discharge tubular lead-acid batteries (both OPzS (flooded) and OPzV (valve regulated, gel)) for PV application by varying the electrolyte (silica added to the flooded cells and phosphoric acid to the VRLA ones), the negative active mass (adding carbon), and the cell design (by varying the separator and gauntlet material). In addition, a pulse profile for faster and more efficient recharge was tested along with regular CC-CV and CC1-CC2 profiles.

Results: Some of the batteries under test have reached over 2000 cycles at 40^{o}C, which corresponds to ≥ 4,000 cycles at room temperature, and were still functioning well. Assuming one cycle per day, this result is equivalent to 11 years with the same battery without replacement – a success which offers excellent new market possibilities for lead-acid batteries in PV systems. After further optimization, the target of 15 years appears realistic. This study is further proof that lead-acid batteries offer the best cost-value-ratio in PV applications.

Capacity (C/10, C/20 and C/100) measurements at 25^{o}C and 40^{o}C were used for demonstrating the influence of the design parameters. The recharge profiles were evaluated by energy efficiency and water losses. The results show that the reinforced non-woven gauntlets of AmerSil can be utilized as an alternative to woven gauntlets. Because of the smaller pore size, less mass shedding was observed. The ribbed separator DWT also performed very well. Addition of silica to the electrolyte in OPzS cells increased cell voltage and capacity. It also improved recovery after electrolyte stratification. For both cell designs – OPzS and OPzV - optimum recharge remains the regular IU charge. Pulsed charge decreases recharge time but requires more energy and can result in battery heating and water loss.

0709 C1.2A, Technology Development. Duration: 15 months, continuation from Program 2007-2009. Status: Completed.

Contractor: Exide, Spain

Project leader: Mr. Melchor Fernandez

Objective: To increase the performance of VRLA batteries to the point of becoming a real alternative to NiMH and Li-ion ones in hybrid electric vehicle applications. To reach this goal, it was necessary to improve both charge/discharge power as well as the so called “power assist” cycle life. Charge and discharge specific power should be in the range around 500 $W.kg^{-1}$, Power Assist Cycle life should be increased to values in the range 300,000- 400,000 cycles corresponding to 10,000 capacity turnovers.

In previous ALABC projects (C1.2), values of Power Assist Cycle life in the range 200,000-220,000 cycles have been obtained for different negative active material formulations that included additions of different types of graphites, and for combinations of activated carbon + graphite. Specific charge and discharge power close to 500 $W.kg^{-1}$ were obtained. In Project C1.2, it was found that Power

Assist Cycle life is limited by the negative plate that becomes heavily polarized during charge, increasing battery voltage to values above 16 V, clearly deleterious by promoting positive grid corrosion and water consumption. In order to compensate for this fact, the more specific target of this project was to implement the supercapacitor effect inside the battery. To do so it was necessary to focus on the negative plate because it limits the total capacitance value of the battery. (Its surface area is about five times lower than this of the positive plate). The key factor that determines electrochemical capacitance is the Specific Surface Area of the plate. In order to implement the supercapacitor effect, it is necessary to increase it as much as possible by adding high SSA materials like activated carbons or graphites.

Results: Carbons of high SSA were added to the negative mix. Four batches of batteries were assembled. All tests were performed with Exide's ORBITAL 6V/24Ah Spiral wound modules. Impressive charge acceptance values were obtained with batteries that had activated carbon in their negative mix. The increase for some cells was up to 80 - 120%, for others with a different combination of carbons it was up to 100 to 150%. Considering the weight of the batteries, specific charge acceptance values in the range 300-500 $W.kg^{-1}$ were observed. The specific discharge power was in the same range, being less dependent of the use of carbon.