

## 2010 – 2012 Program Project Review

### Battery Science (4 projects)

---

#### **1012 A, Fundamental Research. Duration: 15 months. Status: Completed**

**Contractor:** Coolohm Inc., USA

**Project leader:** Dr. Kathryn Bullock

**Objective:** To perform a literature survey on studies that simulate carbon corrosion in PEMFCs and compare those with carbon corrosion in VRLA batteries to better understand the function of temperature, carbon types, and other variables. To summarize the mechanisms of carbon corrosion and the impact of electrical parameters on the oxygen cycle and battery cycle life in ALABC carbon studies and HRPSoC test results. The study is based on results obtained from fuel cells and lead-acid batteries.

**Results:** The study summarizes published corrosion data about carbon blacks, graphitized carbon black, highly-oriented pyrolytic graphite and other graphitic materials, carbon nanotubes, multiwall carbon nanotubes (MWNT) and nanocages in dilute sulfuric acid at temperatures between 25 and 80°C. Previous research has found that graphitic carbon materials have greater corrosion resistance compared to carbon blacks. Nano materials have high surface areas and those that have graphitized surfaces work well in PEMFCs. Graphitized submicron particles are the best material with high surface area and surface stability, and good conductivity.

The symptom of carbon corrosion is carbon dioxide and hydrogen formation. As a result, the internal resistance and the temperature of the cell can increase. Weight loss and negative plate sulfation during HRPSoC cycling can be other symptoms. To minimize these failure modes it is recommended to optimize the negative active mass composition and to improve vent design. An optimum negative to positive plate ratio is also recommended.

#### **1012 G, Fundamental Research. Duration: 12 months. Status: Ongoing**

**Contractor:** Bulgarian Academy of Sciences (IEES), Bulgaria

**Project leader:** Prof. Dr. Detchko Pavlov

**Objective:** Addition of different types of high surface area carbon materials to NAM markedly improves the cycle life in the HRPSoC regime. A parallel charge mechanism of lead-carbon electrodes was proposed. According to this mechanism the electrochemical reaction of charge ( $\text{Pb}^{2+} \rightarrow \text{Pb}$ ) proceeds on the surface of both lead and carbon phases. The processes involved in this mechanism will be influenced by the NAM pore system, specific surface area, and microstructure. These parameters of negative active mass are affected by the expander added to the negative paste during its preparation. The objective was to determine the influence of different expander components'

loading levels, as well as elucidating the influence of cycling conditions on the processes at the negative plates in the HRPSoC duty by disclosing the elementary processes that proceed during the seconds range charge and discharge events of the HRPSoC cycling mode, and revealing the mechanism of action of different carbon additives on the performance of the battery cycled at very high current rates. The following parameters of the cycling regime have been varied: state-of-charge, current rate, depth of discharge and rest (open-circuit) period length during the cycling test.

**Results:** Negative paste batches have been prepared with various concentrations of BaSO<sub>4</sub> and carbons. Testing comprised initial discharge capacity tests, Peukert dependence determinations, charge acceptance tests and HRPSoC cycling tests. The NAM microstructure was characterized by XRD, SEM, BET, Hg porosimetry and wet chemical analysis. Detailed conclusions were drawn about the benefits and drawbacks of various types of carbons used in different concentrations. Similarly, conclusions were drawn about the joint effect of expander composition and carbons on the performance off the negative plate. The studies of the influence of various charge pulse length on the cycleability of the negative plate at PSoC conditions showed that when cycling is conducted with short pulses, the dominating processes are capacitive charging and discharging of the electric double layer. The electrochemical and chemical reactions proceed at a low rate. They limit the cycleability within one cycle-set of the HRPSoC test. On cycling by longer pulses, the main processes which determine the electrical parameters of the cells are the electrochemical reactions of Pb oxidation and PbSO<sub>4</sub> reduction, and the chemical reactions of formation and dissolution PbSO<sub>4</sub>. The number of completed cycles within one cycle-set is dramatically smaller (by several factors) as compared to the cells with capacitively charged and discharged negative plates. During operation of the cells in the HRPSoC duty, parallel to the above charge and discharge processes also processes of PbSO<sub>4</sub> recrystallization proceeds which lead to progressive sulfation of the negative plates and thus limit the cycle life of the cells. Carbons added to the negative active material are included in the structure of NAM and alter the pore system of NAM. When the mean pore radius is about 1 μm the solution in the pores is alkalized and tetragonal PbO forms which impede the reaction of lead oxidation.

### **1012 H, Fundamental Research. Duration: 24 months. Status: completed.**

**Contractor:** Technical University of Brno, Check Republic.

**Project leader:** Dr. Karel Micka.

**Objective:** Estimate the influence of mechanical pressure applied to the active block of the cell (cell compression) on the power output and cycle life at high rate partial state of charge of model cells with carbon or TiO<sub>2</sub> added to the negative active mass.

**Results:** The results showed that, like in AGM valve regulated lead-acid cells without carbon additives, compression (0 to 6 N.cm<sup>-2</sup>) is very useful for achieving long cycle life in cells with carbon-added negative active material. The strongest effect was observed at 4 N.cm<sup>-2</sup>. The study showed also that adding TiO<sub>2</sub> to the NAM has a beneficial effect on charge acceptance like adding carbon, but on long cycling the benefits of carbon are stronger and last for larger number of cycles.

## **1012 L, Fundamental Research. Duration: 12 months. Status: completed.**

**Contractor:** EnerG2 Inc., Seattle, USA.

**Project leader:** Mr. Matt Maroon (left the company), replaced by Dr. Aaron Feaver.

**Objective:** Carbon additives to the negative active material can provide significant improvements to the performance of flooded and VRLA batteries in specific applications such as hybrid electric vehicles. The inclusion of various forms and combinations of carbon (graphite, carbon black, and activated carbon) has been shown to improve the performance of lead-acid batteries against all of these performance standards. However, some work has indicated that increased hydrogen gassing and thus failures associated with battery dry-out occur in some batteries. The purpose of this project was to perform fundamental electrochemical research into the hydrogen gassing behavior of carbon materials, independent of lead and expander, and to attempt to correlate the physical and chemical properties of the carbon with its hydrogen gassing behavior. The goal was also to help lead-acid battery manufacturers identify which carbon materials to specify and incorporate into their battery designs. In addition, this information can help manufacturers produce carbon with the right properties for maximum performance and minimal side reactions in the negative active material.

**Results:** Carbon samples (incl. carbon blacks, activated carbons and graphites) supplied by various producers and having different physico-chemical properties (particle size, specific surface area, porosity, impurity levels, ash content, pH), have been used for preparing carbon powder electrodes, testing and comparing their electrochemical properties shown during polarization in model cells. Voltammograms have been recorded in the potential area where the negative plate of lead-acid batteries is operating. Quasi-steady polarization tests have been used in order to build polarization plots (Tafel) for the process of hydrogen evolution. Hydrogen can be evolved electrochemically on conductive carbon particles staying in contact with both the lead metal electrode base and the electrolyte.

The results of this project show significant hydrogen gassing differences between the classes of carbon (graphite, carbon black, and activated carbon). The physical properties of each carbon type like impurity levels, particle size, surface area, pore size and pore volume, ash content, conductivity, pH, etc., can play an important role for the mechanism of hydrogen evolution on conductive carbon particles.