CARBOLEAD 2010

NOUVELLES GRILLES DE CARBONE POUR ACCUMULATEURS LEGERS A ELECTRODES EN PLOMB

IDENTIFICATION DU PROJET

Edition : 2010
Partenaire (organisme) coordinateur : CEA-LITEN
Autres partenaires (organismes) du projet : Institut Jean Lamour, STECO Power, Material Mates
Projet labellisé par les pôles de compétitivité : TENERRDIS, MATERALIA
Contact : Angel KIRCHEV mail : angel.kirchev@cea.fr
Date de début / date de fin du projet : 01 janvier 2011 / 31 décembre 2013

ELEMENTS FINANCIERS

Budget total du projet (M€)	dont Aide ANR (M€)	Nombre de personnes.an
0.801	0.398	4.67

RESUME DU PROJET

The aim of the project is the increase of the energy density of the lead-acid battery replacing the conventional lead alloy current collectors with conductive carbon honeycomb composite ones. In the beginning of the project the conductive carbon composite material will be developed, optimizing its cost in terms of time and energy consumption. Further the developed material will be electroplated with lead-tin alloy layer with proper thickness, optimal corrosion and mechanic resistance. After the optimization of the electroplating processes, all the obtained experience will be focused on the development of the prototype AGM valve-regulated lead-acid batteries (VRLAB) with honeycomb grids. The aimed energy density of 80Wh/kg and 150Wh/l will be achieved by both increase of the active material utilisation up to 70-80% due to the honeycomb grid structure and due to the low density of the carbon current collectors. One part of the prototypes will be tested under the electric vehicle and hybrid electric vehicle protocols, and another will be used for demonstration in commercially available electric scooter, replacing its original lead-acid batteries. A special study will be carried out on the structure of the interface between the carbon and the lead coating and its evolution during the battery ageing. The corrosion processes will be optimised. The management of the prototypes will be improved using integrated “low cost / long life) reference electrodes ($Ag/Ag_2SO_4/H_2SO_4$). They will work as electrochemical sensors inside the battery cells, allowing improving the duration and the security of the charge process keeping lower positive grid corrosion rates, and estimating State of Charge by innovative approaches.

PUBLICATIONS – COMMUNICATIONS MAJEURES

- A. Kirchev, N. Kircheva, M. Perrin, “Carbon honeycomb grids for advanced VRLAB negative plates”, lecture held by A. Kirchev during the 8th International Conference on Lead-Acid Batteries LABAT’2011, 7-10 June, Albena, Bulgaria
- A. Kirchev, “Evaluation of Carbon Honeycomb Grids for Positive and Negative Lead-Acid Battery Plates”, invited lecture during the 123rd Convention of Battery Council International, Miami, USA, 1-4 May 2011

ILLUSTRATIONS

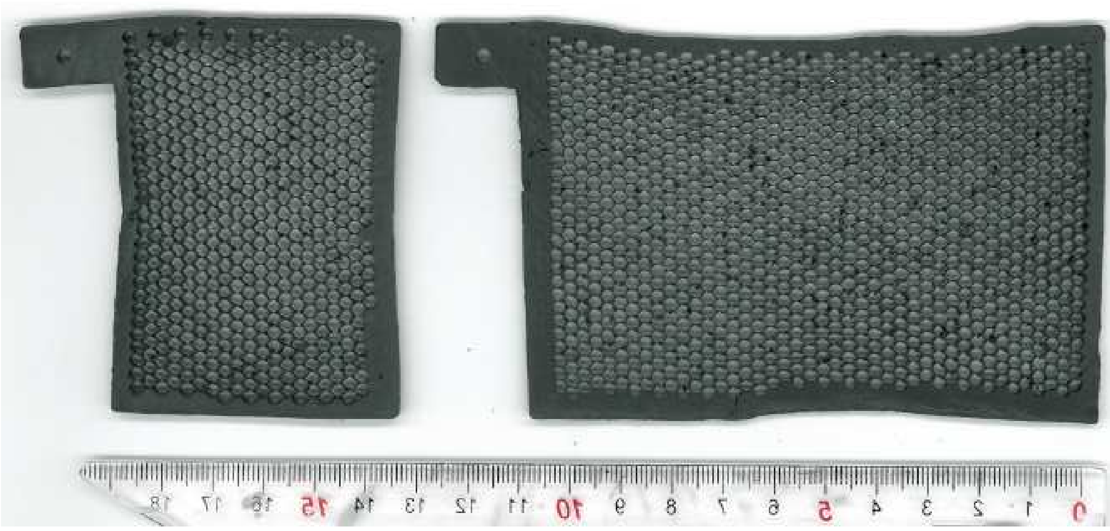


Fig. 1. Comparison between "¼" and "½" size carbon honeycomb grids before the lead-electroplating.

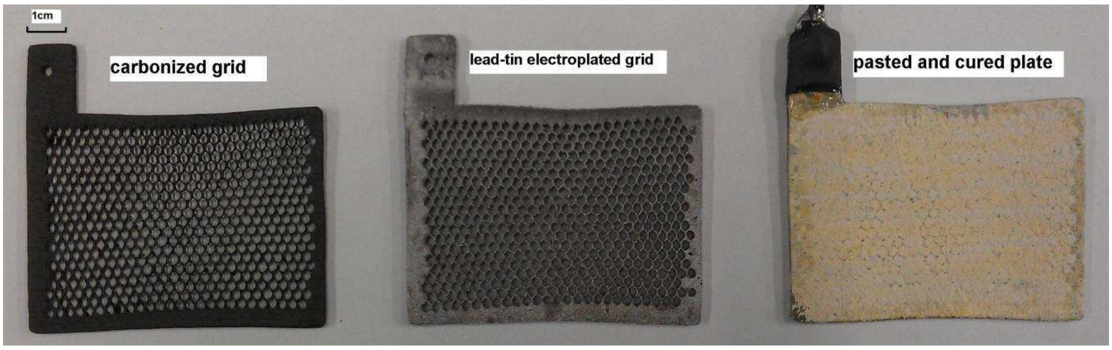
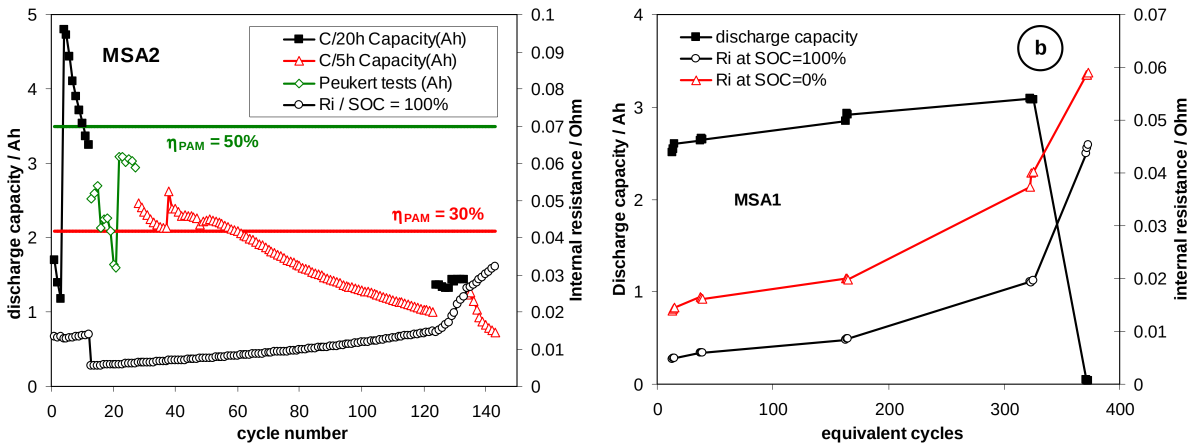


Fig. 2. "½" size carbon honeycomb grid before and after the electroplating and pasted plate with electroplated grid.



(a) (b)

Fig. 3. Results from the cycle life tests of two VRLA cells (~3Ah) with honeycomb positive plates under deep cycling with C/5h rated current (a) and at partial state of charge with current C/2h (b).

BREVETS

Three patent applications concerning this technology were deposed **prior to the start of the project**
- A. Kirchev, REFERENCE ELECTRODE, MANUFACTURING METHOD AND BATTERY COMPRISING SAME, International patent application WO2008090403 (A1) — 2008-07-31
- A. Kirchev, ELECTRODE FOR LEAD-ACID BATTERY AND METHOD FOR PRODUCING SUCH AN ELECTRODE, International patent application WO2009150485 (A1) — 2009-12-17
- A. Kirchev, N. Kircheva, ACID-LEAD BATTERY ELECTRODE COMPRISING A NETWORK OF PORES PASSING THERETHROUGH, AND PRODUCTION METHOD, International patent application WO2010115705 (A1) — 2010-10-14

FAITS MARQUANTS

During the first half of the project, the technology was validated providing prototype grids with ½ and ¼ sizes. Images of the carbonised structures are provided in Figure 1. Two types of honeycomb structures were successfully used as grid precursor materials – a “home-made” honeycomb core based on recycled corrugated paperboards (carton) and an industrial-grade honeycomb core based on Nomex® paper manufactured by Euro-Composites (Luxemburg). The applied heating rate corresponding to time of the carbonisation (200 – 1000°C) in the range of 4 to 12h indicate that this step will be industrially “affordable” resulting in grids with relatively low cost.
A series of ¼ size honeycomb grids were used to develop AGM-VRLA cells with positive and negative prototype plates (~3Ah nominal capacity) with thickness of 3-3.5mm (one prototype plate against two counter-plates cut from industrial positive and negative plates). The cells were equipped with $Ag/Ag_2SO_4/H_2SO_4$ reference electrodes for half-cell potential monitoring and active charge regulation. Grids from the same series were subjected to corrosion tests in order to evaluate the performance of the lead-tin coating applied to the carbon honeycomb substrate.
Figure 3 presents the cycle-life performance of two cells with positive honeycomb plates subjected to deep cycling (C/5h, Figure 3a) and partial state of charge cycling (C/2h at 50% state of charge, Figure 3a). The initial capacity of the cell MSA2 corresponds to 70% utilisation of the positive active material which demonstrates the potential to increase the lead-acid battery specific energy. Good cycle-life capabilities were observed in partial state of charge cycling (over 350 equivalent cycles). The performed corrosion tests showed that the compact structure of the coating is attacked by the corrosion process uniformly, which can be seen in Figure 4. During the same tests the project team from IJL found that the tin is absent in some of the samples which explains the rather early failure of the cells with positive honeycomb grids. These results were used to optimise further the lead-tin plating process.

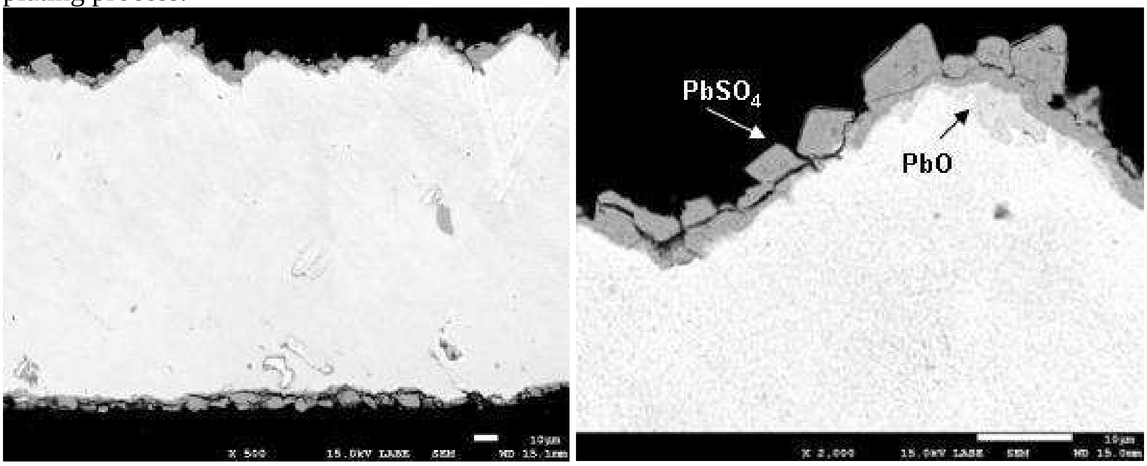


Fig. 4. SEM images of the honeycomb grid cross-section after “cycling” corrosion test.

Figure 5 presents the evolution of the internal resistance of the negative honeycomb prototype VRLA cells. The grids were electroplated with three types of coatings in order to evaluate structures with

different electric resistance. The negative grids are 2 to 3 times lighter (depending on the type of the coating) than the positive ones carrying approximately the same quantity of active material. It can be seen that for the selected plate and separator thickness the ohmic resistance of the cell is limited almost completely by the electrolyte and separator resistance. The final internal resistance values are in the range of 20-22mΩ (~3Ah cells) indicating that even at this plate thickness the cells can be used for high power applications (5C - 7C pulses can be applied). The initial cycling performance presented in Figure 6 is also similar – all 6 cells show almost the same behaviour at C/20h cycling. The initial capacity corresponds to about 60% utilisation of the negative active material indicating both the complete formation of the negative paste and the feasibility of the use of honeycomb grids for negative plates.
The results obtained from the testing of the prototypes with positive and negative honeycomb grids will be used further in the project tasks dedicated on the development of the management of this technology.

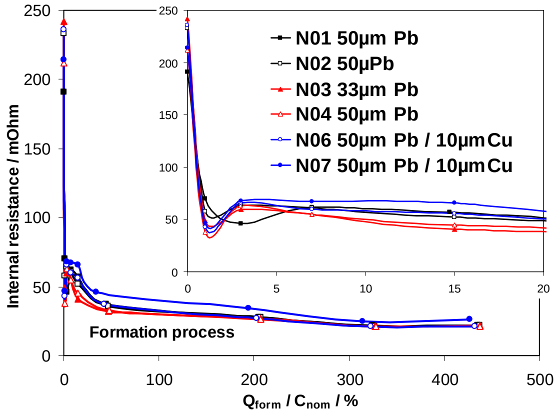


Fig. 5. Evolution of the internal resistance of the cells with negative plate prototypes during the formation process.

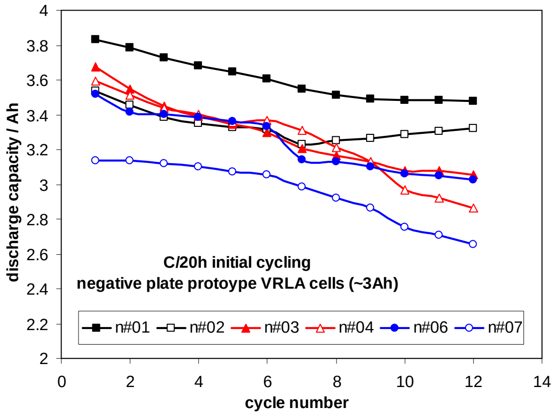


Fig. 6. Initial cycling of the cells with negative plate prototypes with C/20h rated current.

RETOMBEES PREVISIBLES

The development of the full-size prototype grids is ongoing and the two series of 170 positive and 230 negative girds are scheduled for the period Q1 2013. The grids will be pasted (manually) and cured by STECO Power. Further, 8 mono-block prototype batteries (12V / ~50Ah each) will be assembled for laboratory cycling and demonstration in an electric scooter.

VERROUS RESTANT A LEVER

The preliminary analysis of the compatibility between the new grids and the exsisting flooded SLI battery manufacturing equipment of STECO Power showed that the automatic pasting, the cast-on-strap (parallel connection of indentic plates within one cell) and the intercell connection technique are not directly compatible. In contrary, the assembly of AGM-VRLA 2V cells would be possible due to a lower mechanical stress applied on the cast-on strap connections.
However, some innovative alternatives of the cast-on-strap and the intercell connections including decrease of the metallic lead content were already dicussed by the consortium and the working “full-size” prototypes will be delivered during the third year of the project.