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Carbon honeycomb grids for advanced lead-acid batteries. Part III: Technology scale-up

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HIGHLIGHTS

- Scaling-up of the carbon honeycomb grid technology using industrial grade precursors.
- Improved lead-acid battery negative active material to grid ratio.
- Demonstration of the technology using electric scooter.

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ABSTRACT

The carbon honeycomb grid technology employs new carbon/carbon composites with ordered 3D structure instead of the classic lead-acid battery current collectors. The technology is laboratory scaled up from small size grids corresponding to electrodes with a capacity of 3 Ah to current collectors suitable for assembly of lead-acid batteries covering the majority of the typical lead-acid battery applications. Two series of 150 grids each (one positive and one negative) are manufactured using low-cost lab-scale equipment. They are further subjected to pasting with active materials and the resulting battery plates are assembled in 12 V AGM-VLRA battery mono-blocks for laboratory testing and outdoor demonstration in electric scooter replacing its original VRLAB pack. The obtained results demonstrate that the technology can replace successfully the state of the art negative grids with considerable benefits. The use of the carbon honeycomb grids as positive plate current collectors is limited by the anodic corrosion of the entire structure attacking both the carbon/carbon composite part and the electroplated lead-tin alloy coating.

1. Introduction

The use of carbon materials for lead-acid battery current collectors has been a subject of growing interest since more than a decade [1–6]. The usual technology route is typically based on the lead electroplating of various carbon structures obtaining current collectors with electric resistance comparable with the actual state of the art grids, reduced weight and an architecture enhancing the active materials utilization. The latter can be expressed as low γ-coefficient (grams of active material per square centimeter of current collector area, often denoted also as "surface loading") [7] and low grid mesh size [8]. The use of carbon materials like foams of composite honeycombs allows to decrease these two current collector parameters down to 0.15–0.2 g cm^{-2} for the γ-coefficient and 0.5–1 mm for the grid mesh size, which is hardly possible for lead-acid battery grids manufactured by casting, strip punching or strip expanding where these parameters are in the range of 2–2.5 g cm^{-2} and 3–5 mm. Despite their strong sides, the industrialization of the carbon-based current collectors is still a problem under consideration. The aim of this work is the development and testing of carbon honeycomb current collectors with size matching the mainstream lead-acid battery grids, i.e. those intended for automotive applications. Apart from the car engine starting (cranking), the lead-acid batteries within this size range are often used in many other systems as electric scooters, low-speed electric vehicles, uninterruptible (emergency or reserve) powers supplies

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or small scale stand-alone renewable energy storage. The specific power demands (or the so-called C-rate) in these systems is considerably lower in comparison with the engine cranking, making the use of lighter carbon-based current collectors attractive alternative of the lead alloy grids.

2. Experimental

2.1. Honeycomb grids preparation

Detailed description of the precursor materials and the processes of grids and plates laboratory manufacturing can be found in Part II of this series [9]. The composite honeycomb precursor was block of the type "ECA 3.2–144" supplied by Euro-Composites (Luxemburg) with dimensions of 132 × 181 mm and thickness of 280 mm (it coincides with the length of the honeycomb channels). It was placed in a mold with dimensions of 135 × 185 mm and height of 280 mm in order to add a composite frame with current collecting tab around the honeycomb block. Totally 11 honeycomb composite blocks have been molded and cut to slices by a wood-cutting band-saw equipment. Two of the blocks have been cut to slices with an average thickness of 2.2–2.3 mm. The rest of the blocks have been cut to slices with an average thickness of 2.9–3.0 mm. The thermal treatment of the composite was divided in two stages: "drying" in air atmosphere up to 200 °C with heating rate of 0.2 °C/min, followed by "pyrolysis" up to 1000 °C in nitrogen atmosphere using a heating rate of 1.2 °C/min. The capacity of the laboratory muffle furnace with a volume of 8 dm^3 allowed to carbonize 20–22 grids with thickness of 2.9 mm and 25–30 grids with thickness of 2.3 mm.

The carbonized grids have been electroplated with Pb–Sn2% in two steps at room temperature of 22 ± 1 °C. The "top lead" part of the grid (the tab and the adjacent top frame) was plated fist with 30 mA cm^{-2} for 30 min (for negative grids) or 1 h (for positive grids). The electrochemical baths were equipped with a peristaltic pumps with a debit of 300 cm^3 min^{-1} for constant electrolyte steering. After the top lead plating, the whole grid was electroplated with the same current density and duration, washed with tap and deionized water and left to dry at 60 °C overnight.

2.2. Plates preparation and battery assembly

A total number of 300 positive and negative honeycomb grids have been subjected to manual pasting. The applied paste batch compositions are listed in Table 1. The paste components are identic to those used previously [9]. The curing and drying processes were comprised of 48 h stay in fan-assisted oven at 60 °C resulting in homogeneous appearance of the dried paste.

The X-ray diffraction patterns of the lead oxide and both dried pastes can be found in the Supplementary materials (S1), together with the corresponding phase analysis results (S2) and scanning electron micrographs (S3).

Each plate was connected to 2 mm thick lead wire which was passed through the hole located in the tab zone of the plate. The connection was carried out using electric soldering iron and lead-tin solder (60%Pb/40%Sn). The tab and the lead wire were covered with thermoplastic PVC glue using a hot glue gun and the whole ensemble was sealed by a thermo-shrinkable tube in order to prevent the access of the electrolyte to the welding spot.

Each plate was enveloped with AGM (absorptive glass-mat) separator with a thickness of 1.3 mm @ 10 kPa provided by Bernard Dumas (France). Thus prepared, the plates and the separators were arranged in seven 12 V battery mono-blocks with cell configuration "three positive plates vs. two negative plates" and one 12 V battery mono-block with cell configuration "two positive plates vs. three negative plates" using boxes from type "LB1" provided by Accumalux (Luxemburg). The boxes were sealed by custom designed polycarbonate lids and epoxy resin. The holes of the lead wire outlets have been sealed by thermoplastic PVC glue using a hot glue gun. The lids were equipped with automotive VRLA battery M18 valves provided by Accumalux (Luxemburg). The current collecting lead wires of each plate were soldered to lead-tin plated copper bus-bars fixed to the lid, obtaining the corresponding parallel/series connections typical for each 12 V lead-acid battery mono-block. Each mono-block was also equipped with a custom designed system for external stack compression.

2.3. Formation and testing of the battery mono-blocks

The cells were filled with a sulfuric acid electrolyte with specific gravity of 1.21 g cm^{-3} (3.57 mol dm^{-3}) up to the top edge of the AGM separator (so-called "water mirror" filling with electrolyte). The first four mono-blocks were left for 72 h soaking prior to the start of the formation process. The second series of four mono-blocks were left for 16 h soaking. The formation algorithm employed multi-step constant current sequence with a total charge accumulation of 130 Ah. The formation and the further tests have been carried out at temperature equal to 22 ± 1 °C in thermostated water bath using Digatron battery test system.

After a series of 10–15 initial cycles, four of the mono-blocks have been selected for out-door test as onboard storage system of electric scooter E-max 110S having the following technical specifications: 4 kW DC brushless motor limited to 2.5 kW (48 V/50 A); weight without the battery pack equal to 95 kg; maximum speed limited to 45 km/h; no regenerative braking. The original pack of the scooter is comprised of four 12 V AGM-VRLAB mono-blocks with 20 h-rated capacity of 75 Ah. The scooter was equipped with onboard system for battery monitoring (current, temperature, voltage of the four mono-blocks connected in series). The remaining four mono-blocks have been laboratory tested under the above-mentioned conditions.

Table 2 lists the average active materials electrochemical equivalent in each prototype mono-block.

Table 1
Batch composition of the positive and the negative pastes.

Component	Positive paste	Negative paste
Lead oxide	1 kg (4.484 mol)	1 kg (4.484 mol)
Deionized water	125 mL	140 mL
H_2SO_4 solution (50%wt.)	52 ml (0.375 mol pure H_2SO_4)	52 ml (0.375 mol H_2SO_4)
Vanisperse-A	–	2 g
MCF Toho-Tenax 100 μm	–	25 g
Target density	4.20 g/mL	4.05 g/mL
Measured density	4.15 g/mL	4 g/mL