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Carbon honeycomb grids for advanced lead-acid batteries. Part I: Proof of concept☆

Angel Kirchev*, Nina Kircheva, Marion Perrin

Laboratoire de Stockage de l'Electricté, Institut National de l'Energie Solaire, Commissariat à l'Energie Atomique et Energies Alternatives (CEA), 50 Avenue du Lac Léman – Lynx 3, BP332, 73377 Le Bourget du Lac, France

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ABSTRACT

The carbon honeycomb grid is proposed as innovative solution for high energy density lead acid battery. The proof of concept is demonstrated, developing grids suitable for the small capacity, scale of valve-regulated lead acid batteries with 2.5–3 Ah plates. The manufacturing of the grids, includes fast, known and simple processes which can be rescaled for mass production with a minimum, investment costs. The most critical process of green composite carbonisation by heating in inert, atmosphere from 200 to 1000 °C takes about 5 h, guaranteeing the low cost of the grids. An AGM–VRLA, cell with prototype positive plate based on the lead–2% tin electroplated carbon honeycomb grid and, conventional negative plates is cycled demonstrating 191 deep cycles. The impedance spectroscopy, measurements indicate the grid performance remains acceptable despite the evolution of the corrosion, processes during the cycling.

1. Introduction

In the past decade the huge variations in the oil prices along with the increasing demands for reduction of the CO_2 emissions renewed the interest in the electric "zero emission" transport. Due to its low cost, high safety and efficient recycling infrastructure, the valve-regulated lead-acid batteries (VRLAB) remained relatively strong market competitor of the concurrent nickel and lithium-ion based storage systems in applications like electric bicycles, scooters and small electric cars especially in countries with low average incomes. However, regarding the forthcoming electric vehicle (EV) and plug-in hybrid electric vehicle (PHEV) markets, the lead-acid battery was "thrown" out the competition due to its low energy density. The huge difference between the theoretical energy density of 168 Wh kg^{-1} and the typical values of about 35 Wh kg^{-1} are mainly due to the inefficient use of the lead and its components, which comprises about 67% of the total battery weight [1]. The grids of the positive and negative plates are the heaviest components serving only to support mechanically the active materials and to collect the electric current generated by the charge/discharge process. They comprise between 33 and 50% of the plate weight (active material to grid ratio varies from 1:1 to 2:1 depending on the particular technology). The utilisation of the active materials is also relatively low—typically between 40 and 50% of the lead or the lead dioxide can be converted to lead sulphate during a 10 h-rated discharge. As a result, 65–75% of the lead does not participate in the electrochemical reactions of energy storage and generation. Hence the improvement of the lead-acid battery energy density is still an open challenge.

In the past two decades several research teams proposed different types of carbon or carbon foams as a promising alternative to the classical cast or punched grids:

- Peterson and Ahlberg suggested that the monolithic glass-like carbon can serve as grid material without giving practical demonstration of the concept [2].
- Czerwiński and Żelazowska proposed Reticulated Vitreous Carbon (RVC®, glass-like carbon foam) as grid material in [3,4]. Further RVC® was used to develop grids by Gyegne et al. [5,6]. Recently, Czerwiński et al. compared the performance of bare RVC electrodes and Pb-electroplated ones, both types pasted with negative active material (NAM) [7,8]. The results of this comparison indicated that conductivity of the bare RVC is good enough to support charge/discharge currents in the range of $C_n/1$ h (where C_n is the electrode or cell nominal capacity in [Ah]).
- Kelley and co-workers proposed carbon foam lead-acid battery grid technology described in a series of patents applied by the start-up company Firefly Energy (presently Firefly International Energy) [9–12]. Despite that the company announced in 2008 the

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* Corresponding author. Tel.: +33 4 79 44 45 49; fax: +33 4 79 68 80 49.
E-mail address: angel.kirchev@cea.fr (A. Kirchev).

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launch of their OASIS^{TM} battery up to the moment no data about the performance of this technology can be found in the literature.
- Chen et al. published a series of papers on the development of small positive and negative pasted electrodes using pitch-based carbon foam [13–17].
- Jang et al. studied graphite foam electrodes pasted with positive active material (PAM) and negative active material (NAM) [18] indicating that the graphite foam material [19] has much better electric and thermal conductivity.

The main advantage of the foam-type current collectors is the large surface area making possible to decrease the so-called "γ" coefficient representing the ratio of the active material weight per unit of current collector surface area [20]. Since the hydrogen overvoltage on the above-mentioned carbon materials is relatively high and the process of hydrogen evolution does not have destructive impact on the carbon structure, the carbon foams of different types can be used without modifications as grid materials. However the direct use of carbon as a positive grid material is hardly possible up to now. The main reason is a destructive corrosion-like process of the carbon surface flaking caused by the process of oxygen evolution which proceeds in similar way and gives similar final result in acid, neutral and alkaline electrolytes [18,21–23]. Similar effect is observed when glass-like carbon surface is treated with Fenton solution, i.e. when the surface is chemically attacked by $OH^{\bullet}$ radicals [24]. As a result of this, if bare carbon structure (foam, spine, etc.) is pasted with basic lead sulphate paste, the process of oxygen evolution on the carbon surface runs in parallel with the positive plate formation and charge processes resulting in progressive detachment of the active material from the carbon current collector [18]. The usual strategy to employ the carbon foam as a positive grid material is to electroplate it with lead or lead–tin coating [5,6]. In this way, the pasted electrodes can withstand prolonged cycling because the lead metal coating resembles very well the surface of the classical lead-acid battery grids and works as a protective layer over the carbon.

2. Carbon honeycomb grid concept

Despite the excellent surface to volume ratio, which is the main advantage of the foam as a lead-acid battery grid material, there are several problems between the "foam grid concept" and the practical realisation of grids which can be employed in the existing schemes of lead-acid battery assembly. From one hand it is the pasting process where the paste should be forced into the foam pores—it supposes the combined use of foams with bigger cell-size and pastes with lower density/consistency resulting probably in poor performance in terms of cycle life and energy density. Because of the reticulated 3D structure of the foams, the pasting can be mechanically "difficult" and the foam could be crushed during this process. From the other hand at large-scale battery plates, foam grid alone cannot collect efficiently the current generated during the cycling. The solution of adding a massive frame and top-lug of lead bonded to the perimeter of the foam slab as proposed by Gyenge et al. [6] can be enough efficient. However combined with the electroplated lead, the grid weight becomes too high.

In attempt to propose an alternative of the carbon foam, the carbon honeycomb grid technology was developed at the Laboratory for Storage of the Electricity of the French Commission for Atomic and Alternative Energies (LSE—CEA) [25].

The composite honeycomb structures are well-known materials used in different constructions requiring very high strength to weight ratios [26]. When the composite honeycomb structure is constituted of suitable materials, for example cellulose-based paper impregnated with thermosetting resin [27] or pitch [28], it can be subjected to carbonisation by heating in inert atmosphere up to 1000–3000 °C. The resulting carbon/carbon composite structures retain the inherited honeycomb geometry obtaining some new properties, the most important of which is the electric conductivity.

The honeycombs alone are hardly useful as grids in the same manner as it was discussed above in the case of carbon foams. That's why the manufacturing scheme presented in Fig. 1 was developed. The first stage consists in the choice of suitable "green" composite honeycomb core with the desired dimensions. In the second stage a frame of thermosetting composite material is moulded along the honeycomb core keeping the honeycomb channels empty. Note that this process is compatible only with honeycomb core structures due to the unique parallel arrangement of the channels typical for these structures. After the hardening of the frame, the resulting block is cut to slices with a desired thickness during the third stage—these will be the "green" honeycomb grids. After the heat treatment procedures applied during stage 4, the resulting all-carbon/carbon composite grids consist of carbon honeycomb core connected to a massive carbon frame having a top-lug, resembling well the typical lead-acid battery grid. The frame ensures the mechanical stability of the grid and the efficient colleting of the electric current. The top-lug allows using the cast-on-strap process where the plates from the same polarity are connected in parallel within the lead-acid cell. The last manufacturing stage is the surface treatment of the carbon honeycomb grids. Here the main process is the lead electroplating. It may be preceded by chemical or electrochemical etching in order to improve the adhesion of the lead coating, however this step is optional.

The honeycomb grids offer several strategic advantages. The first one is the increase of the active materials utilisation. From one hand the decrease of the plate thickness enhances the sulphuric acid transport from the AGM separator (in the case of VRLA batteries) to the core of the plate, especially at high current discharge rates [29]. From the other hand the decrease of the grid mesh dimension (in the case of honeycomb grids this parameter is the half of the honeycomb cell size [26]) increases the active mass utilisation. This effect is first discussed in details by Faber in [30]. According to the data published by Faber, honeycomb grids with cell size in the range of 2–3 mm (grid mesh dimension 1–1.5 mm) should deliver 60–65% positive active mass utilisation or 135–145 Ah kg^{-1}. For cell size in the range of 1 mm the PAM utilisation is even 80%. The second advantage is the high γ-coefficient, due to the good surface to volume ratio of the honeycomb structures. The third advantage is the efficient use of the compression in the case of AGM–VRLAB technology. Fig. 2 illustrates a fragment of the active block assembly where the two AGM separator sheets exert a compression on both side of the honeycomb channel. It can be supposed "a priori" that even low levels of compression will maintain a good contact between the active material and the internal walls of the honeycomb channel. The same cannot be said for the carbon foam grids due to their reticulated 3D structure—in this case the compression will be "absorbed" rather by the foam instead of the active materials.

The aim of this work is to present the proof of carbon honeycomb grid concept demonstrating its capabilities as the positive plate current collectors.

3. Experimental

3.1. Honeycomb core and honeycomb block

The honeycomb core used in this work was prepared using the easiest available material for this purpose—a corrugated paperboard with two layers scavenged from waste packaging. The