



# Influences of carbon materials and lignosulfonates in the negative active material of lead-acid batteries for microhybrid vehicles



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## ARTICLE INFO

### Article history:

Received 14 November 2016

Received in revised form 18 January 2017

Accepted 31 January 2017

Available online 26 April 2017

### Keywords:

Lead-acid batteries  
Micro-hybrid vehicles  
Cyclability  
Carbon materials  
Lignosulfonates

## ABSTRACT

Lead-Acid batteries have been in continuous upgrade as they are required for new applications, such as stop-start function and regenerative braking for Micro-Hybrid vehicles. These issues are closely linked to cyclability and charge acceptance whose failure is directly related to a high sulfation of the negative plates. Carbon materials can be added to the negative active material to delay this sulfation, and other organic compounds, such as lignosulfonates, take part also in the improvement of these features. In this study, different types of carbon materials and lignosulfonates were used as additives for the negative active material, and negative plates have been prepared to assembly 2V/1 Ah small lead acid cells. The cells performed several electrical tests: capacity, cold cranking, initial charge acceptance test, negative polarization study and cycling life in Partial State of Charge. At the same time, continuous physicochemical analyses of negative plates were carried out in order to evaluate their structure and composition. As a conclusion, those carbon materials that were able to be introduced into the lead skeleton showed performance on charge acceptance by acting as super-capacitors, and on cycle life by reducing negative plate sulfation. The carbon material that was able to remain on the lead surface was able to increase charge acceptance, but failed to complete the cycle life test due to a high sulfation on its negative plates. The type of lignosulfonate and the electrochemical surface area supplied with the carbon materials had a strong influence on hydrogen evolution.

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## 1. Introduction

Micro-Hybrid vehicles have become a new opportunity for reducing fuel consumption and air pollution. Its technology is based on automatic start and stop functions and brake energy regeneration. In order to achieve this goal, 12V batteries, denominated Enhanced Flooded Batteries (EFB), are continuously introducing new design changes [1]. EFB must be prepared to work at a High Rate Partial State of Charge (HRPSoC), taking into account that this condition provokes formation of big lead sulfate ( $\text{PbSO}_4$ ) crystals, in the negative plates, which can't be converted efficiently to lead (Pb) leading to battery failure [2]. This sulfation is partially avoided by a group of additives denominated *expanders*: *lignosulfonate, carbon and barium sulfate*. In some cases, batteries also have to recover energy from braking; where charge acceptance becomes a critical parameter which also is limited by sulfation in the negative plate.

On the one hand, lignosulfonates avoid continuous formation of a  $\text{PbSO}_4$  layer, acting as a surface active polymer [3]. They also take part in carbon degradation by oxygen from positive plate, which is strongly associated with water consumption [4]. Two types of lignosulfonates, with different dosages, are utilized in this paper. On the other hand, carbon materials are able to confer some properties to the Negative Active Material (NAM), such as increasing conductivity and/or surface area [5].

Due to the addition of carbon materials, the NAM electrochemical surface area is increased and the creation of isolated  $\text{PbSO}_4$  crystals is facilitated, preventing the formation of a  $\text{PbSO}_4$  continuous layer and increasing cycle life at HRPSoC. Increasing overall conductivity of NAM involves an increase of charge acceptance due to proper current flow through the plate. Furthermore, the addition of carbon materials with high specific surface area enhances charge acceptance by introducing a super-capacitor effect of the carbon [6,7].

Moseley et al. [5] also indicate that carbon materials act as an electroosmotic pump facilitating acid diffusion in the inner NAM. D. Pavlov et al. [8] establish that these additives must have high affinity for lead in order to be involved in battery performance.

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They can be incorporated into the NAM by two ways: into the bulk of lead skeleton branches or on the lead phase surface, depending on particle size and concentration in NAM, respectively. Both ways can result beneficial for battery performance if these parameters are relatively low [8]. In addition, it has been proposed that electrochemical reduction of lead ions to lead in sulfuric acid is preferentially performed on electrochemically activated carbon surface [3].

Reactions of carbon materials [4] in Valve-Regulated Lead-Acid (VRLA) batteries indicate that at HRPSoC conditions, carbon can compete with lead to react with oxygen (oxygen cycle in positive plate) and water. As a result of carbon oxidation, the NAM electroconductive system is lost (when carbon is incorporated into the bulk) and charge acceptance is impaired [8]. Products of the above reaction can be used to produce hydrogen (and raise water consumption) or recharge lead sulfate in the negative plate [4].

The addition of carbon materials can lower hydrogen evolution reaction (HER) overpotential in the negative plate [2], leading to water loss, which finally accelerates battery failure. For this reason, adequate type and dosage of the carbon materials are an important factor for water consumption prevention. Some studies based on activated carbon and carbon black addition, demonstrate the existence of an optimized dosage of carbon, which shows the best battery performance working at HRPSoC [7,9].

Different types of carbon materials at several concentrations have been tested as additives for the negative plate, confirming that both, the amount and the type of carbon material, are decisive for providing beneficial effects to the negative plates [10]. CSIRO laboratories in Australia have demonstrated that carbon black at concentrations from 0.2 to 2.0 wt.% in the negative plates increases the conductivity by some five orders of magnitude [11]. Low concentrations of graphite (1 wt.%) [12] and mixtures of flake graphite and carbon black [13] enhance cycle life at Partial-State of Charge (PSoC). However, flake graphite with low surface area does not improve cycle life at PSoC [7]. Differences between carbon black and graphite as additives for the negative plate have been studied by P.T. Moseley. This study shows better performance on HEV duty by those cells which contain graphite at 2.0 wt.% [14]. Other study shows that the optimum amount of expanded graphite is 1.50 wt.%, which makes possible to double the PSoC life of the battery by increasing charge acceptance [15]. New materials called Pb@C [2], made by high adhesion of Pb to carbon, are able to restraint hydrogen evolution while improving performance of the battery. Among other types of carbon materials, discrete Carbon NanoTubes (dCNT) have been used as an additive for NAM. They enhance charge acceptance, but hamper capacity and cold cracking performance; furthermore, a proper dispersion of this additive is completely necessary for a good performance [16]. Multi Wall Carbon Nano Tubes have also been tested as NAM additive for flooded lead acid battery Start Light Ignition (SLI). They are able to double the cycle life of real batteries [17].

In this paper, six mixtures that combine different types of carbon materials and two lignosulfonates were prepared in order

to study the influence of NAM in 2V/1 Ah small lead acid cell performance. The electrical and structural characterizations were made and the different mixtures were compared depending on their performance on capacity, cold-cracking ability, charge acceptance, water consumption and cycle life at PSoC tests.

## 2. Experimental

### 2.1. Carbon additives and lignosulfonates to the negative active material

Five different carbon materials and two lignosulfonates (LS1 and LS2) were selected for this experiment. The BET Specific Surface Area (BET SSA) and particle size characteristics of the carbon materials and the sulfonation degree of the lignosulfonates were summarized in Table 1. Finally, six mixtures were selected in order to study their performance as NAM electrodes (Table 2). Also, BET SSA for the unformed negative plates of the different mixtures was included in Table 2.

### 2.2. Preparation of negative plates

Negative plates were prepared using lead oxide powder, Polyacrylic fiber (PAC), barium sulfate, deionized water, H<sub>2</sub>SO<sub>4</sub> (1.40 g cm<sup>-3</sup>), and different amounts of each carbon and lignosulfonate types; see Table 2. The weight percentage of Pb in leady oxide was 28 ± 4%. Contents of PAC fiber, barium sulfate, deionized water and H<sub>2</sub>SO<sub>4</sub> (1.40 g cm<sup>-3</sup>) were 0.22 wt.%, 1 wt.%, 11.62 wt.% and 5.4 wt.% (weighted percentage is related to leady oxide), respectively. Paste preparation was carried out in a laboratory mixing machine. The procedure was as follows: firstly, leady oxide, PAC fiber, lignosulfonate and carbon material were stirred for a few minutes; then, deionized water was added and mixed for 5 min. Finally, H<sub>2</sub>SO<sub>4</sub> was added to the mixture dropwise, and deionized water was used to adjust the consistency of the lead paste. A certain amount of paste was coated on a concast Pb-Sn grid with an area of around 10 cm<sup>2</sup> to prepare the negative plates. In order to complete the process, negative plates were introduced in a curing chamber for 24 h at 55 °C and 85% of relative humidity, during the first stage. In a second stage, temperature and relative humidity were set to 30 °C and 100%, respectively, for 24 h. After that, plates were dried at room temperature.

### 2.3. Assembly and formation of test cells

2V/1 Ah small lead acid cells were prepared by one negative, and two positive plates, and a glass mat separator. All plates were compressed between two methacrylate sheets, and this assembly was partially submerged in H<sub>2</sub>SO<sub>4</sub> (1.28 g cm<sup>-3</sup>). The formation process was carried out at 40 °C, and was composed by an initial charge at constant current (0.35 A) for 13 h followed by several charges and discharges (–0.12 A/4.7 h, 0.24 A/3.0 h, 0.16 A/6.3 h, –0.24 A/2.5 h, 0.24 A/3.2 h, 0.12 A/4.2 h), in order to complete the

**Table 1**  
Characteristics of the carbon materials and lignosulfonates added to NAM.

Carbon material	BET specific surface area/m <sup>2</sup> g <sup>-1</sup>	Mean particle size D <sub>50</sub> /μm	Conductivity
C1	18	28.0	Excellent
C2	25	11.6	Outstanding
C3	125	14.4	High
C4	120–180	11.0	Low
C5	1300–1550	<1	Low
Lignosulfonate		Degree of sulfonation <sup>a</sup>	
LS1		1.4	
LS2		0.9	

<sup>a</sup> Number of sulfonic acid groups per 1000 unit weight lignin.

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