



Enhanced performance of starter lighting ignition type lead-acid batteries with carbon nanotubes as an additive to the active mass



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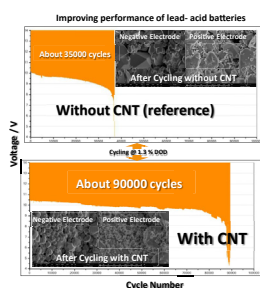
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HIGHLIGHTS

- Enhancement of the electrical conductivity of lead-acid battery electrodes by adding CNT.
- Homogeneous distribution throughout the electrode matrix due to well dispersed CNT.
- Enhanced conductivity avoids the sulfation mechanism in lead-acid batteries.
- Prolonged cycle-life has been achieved by minimizing the sulfation problem.

GRAPHICAL ABSTRACT



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ABSTRACT

Addition of various carbon materials into lead-acid battery electrodes was studied and examined in order to enhance the power density, improve cycle life and stability of both negative and positive electrodes in lead acid batteries.

High electrical-conductivity, high-aspect ratio, good mechanical properties and chemical stability of multi-wall carbon nanotubes (MWCNT, unmodified and modified with carboxylic groups) position them as viable additives to enhance the electrodes' electrical conductivity, to mitigate the well-known sulfation failure mechanism and improve the physical integration of the electrodes.

In this study, we investigated the incorporation-effect of carbon nanotubes (CNT) to the positive and the negative active materials in lead-acid battery prototypes in a configuration of flooded cells, as well as gelled cells. The cells were tested at 25% and 30% depth-of-discharge (DOD). The positive effect of the carbon nanotubes (CNT) utilization as additives to both positive and negative electrodes of lead-acid batteries was clearly demonstrated and is explained herein based on microscopic studies.

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1. Introduction

Lead-acid batteries were invented during the 19th century [1,2]. These batteries are the most widely used rechargeable systems.

Even today in the 21st century, lead-acid batteries share about 50% of the rechargeable batteries market. Though lead-acid systems were studied and developed over 150 years, research continues to enhance their performance in terms of rate capability, stability, cycle life and durability [3,4]. In this study, we demonstrate modifications in flooded lead-acid start light ignition (SLI) batteries. The standard use of SLI flooded batteries is based on very shallow depth

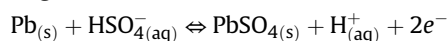
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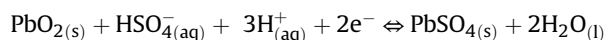
of discharge. The use of SLI batteries in deeper depth-of-discharge (DOD) leads to a pronounced capacity fading and too short life. The main failure modes of SLI type batteries are sulfation and shedding [5–7]. Sulfation is related to the formation of too large crystals (or crystal agglomerates) of PbSO_4 . This salt is the product of both lead metal oxidation at the negative electrode and lead oxide reduction at the positive electrode. PbSO_4 is not conductive and the larger crystals are not soluble during cycling. Evolution of large crystals of PbSO_4 reduces the recyclable lead content, what degrades cell performance [8,9].

Due to physical, morphological and chemical changes ($\text{Pb} \rightleftharpoons \text{PbSO}_4 \rightleftharpoons \text{PbO}_2$) at the positive and negative electrodes, they are mechanically degrade, losing contact and causing short-circuits. Lead-acid battery chemistry is based on the following reactions [10]:

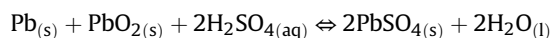
Negative electrode side:



Positive electrode side:



Over all reaction:



Other failure modes in flooded cells are related to grid corrosion and acid stratification which are not discussed in the present paper.

The increasing demand from lead-acid batteries to operate in deeper depth-of-discharge namely 20–30% DOD, emphasizes further the above described problem of sulfation. Due to sulfation, SLI batteries are planned to work at a shallow DOD. Their cycle life becomes very limited when they are forced to operate at 20–30% DOD. In order to solve the sulfation problem in deep cycling of SLI batteries, carbon materials were added into the active-masses of their electrodes [5]. It is universally accepted that carbon materials as additives enhance the performance of these batteries in terms of higher charge-acceptance, which is the key metric for addressing the sulfation problem. However, controversy arises regarding the preference of carbon allotrops, which renders the best performance. Graphitic powder, carbon black, various activated carbons are already introduced by several industries and their use as additives indeed enhances performance. Apart from that, carbon-based nano materials like single-walled carbon nanotubes (SWCNT), multi-walled carbon nanotubes (MWCNT) and graphenes are envisaged as most efficient materials, because of their ordered structures and consequently high intrinsic electrical conductivity. However, exploring the use of carbon-based nano-materials in lead-acid batteries was very limited so far. In any event, it is clear that extending battery life cycling at both low and high DOD values definitely remains one of the most important challenges for this battery technology.

We report here for the first time the use of CNT in both negative and positive electrodes of lead acid batteries in order to improve the cycle life of these batteries, especially at relatively high DOD. In this publication we describe how the use of carbon nanotubes (CNT) as a component in the composite electrodes improves the performances of flooded lead-acid cells.

The use of CNT in these systems was reported already by several groups [11–14]. For instance, reference [14] reports on the use of CNT called “Molecular rebar” in both positive and negative plates of practical lead acid batteries produced by a commercial company. It is clear that the CNT used in the present work (in both negative and positive electrodes), are different than those used in the studies described before. Hence, we accumulate results coming from

several groups, showing clearly the improvement that can be reached for this important battery technology, by adding CNT to the active mass of both anodes and cathodes of L-A battery systems. It was important to realize that the results presented herein, obtained with new types of commercial CNT, were fully coherent with previous findings (reported in references [11–14]).

The presence of CNT in the electrodes improves the electrical conductivity between the active mass particles though preventing thickening and the growth of large PbSO_4 particles [15]. This improvement is naturally attributed to the formation of a stable conductive active mass matrix that enables the delivery and distribution of current to all the active material homogeneously. This modified active mass consists of composites made of CNT conformably coated with lead salts. By enabling a uniform current distribution, and subsequently well distributed electrochemical redox reactions throughout the electrode matrix, arrested the formation of too large PbSO_4 particles [16].

The presence of CNT is supposed to improve both the mechanical stability and electrical integrity of the electrodes [17,18] and to induce uniform changes in the active mass during the complicated conversion reactions during cycling. We expect that the CNT in the electrodes will affect the electrical integrity of the active mass and should lead to the formation and existence of small enough particles, thus facilitating effective charge-transfer interactions [19–21].

2. Experimental

Two sets of SLI type electrodes were fabricated by Vulcan Automotive Ind. using their standard processes (see a description below). The electrodes were in two sizes: 1 cm^2 for laboratory cells and 150 cm^2 for full plate electrodes as are used in commercial batteries. The laboratory cells' capacity varied from 60 to 100 mAh while the large, industrial electrodes had capacities in the range 13–16 Ah. Reference sets of electrodes were based on standard SLI positive and negative electrodes. Other sets of positive and negative electrodes were modified with CNT.

We tested the following cells combinations: (1) positive and negative electrodes without CNT as reference, (2) Positive electrode with CNT and negative electrode without CNT, (3) Positive electrode without CNT and negative electrode with CNT, (4) Positive electrode with CNT and negative electrode with CNT. All sets were cured and aged in similar curing processes and were confirmed to be tri-basic lead sulfate (3BS). The CNT which were used during the tests were:

- i MWCNT from Arkema Inc., having a diameter of 10–15 nm, 1–10 microns long.
- ii MWCNT having diameter of 40–60 nm, about 15 microns long, purchased from Hongwu Nanometer Inc., China.

The same MWCNT as in (ii), modified with carboxylic groups (–COOH). These CNT contained carboxylic groups that were bound to their surface, obtained via oxidation process with an aqueous nitric acid solution (by the manufacturer). The concentration of the carboxylic group was estimated as 6% by weight. In general, immersing the CNT in a concentrated solution of HNO_3 at elevated temperature (e.g. 80°C), leads to an obvious oxidation of their surface, thus forming surface carboxylic groups. Their concentration depends on the immersion time and temperature.

Laboratory electrodes contained 0.008–0.02% CNT by weight. Large format electrodes also contained 0.008–0.02% of CNT by weight. It was found that dispersing CNT in the electrodes' active mass in this range of concentration was suitable for reaching a desirable improvement in performance. With such a low amount of CNT required, the effect on the price of the batteries is negligible.

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