



Lead acid battery performance and cycle life increased through addition of discrete carbon nanotubes to both electrodes



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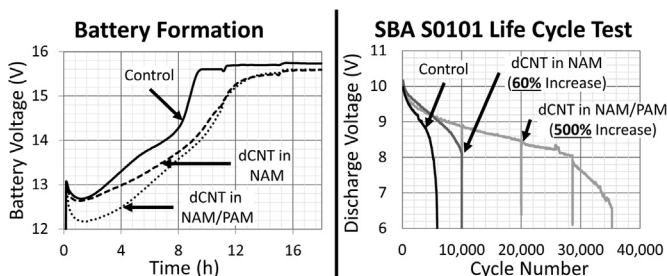
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HIGHLIGHTS

- Molecular Rebar[®] (discrete carbon nanotubes, dCNT) are formulated NAM/PAM additives.
- dCNT have no effect on paste density, rheology, or manufacturing processes.
- dCNT improve battery formation, maintain Reserve Capacity, and boost Cold-Crank.
- dCNT increase HRPSoc cycle life >60% and decrease water loss per cycle >19%.
- dCNT increase SBA S0101 cycle life >300% and decrease water loss per cycle >20–50%.

GRAPHICAL ABSTRACT



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ABSTRACT

Contemporary applications are changing the failure mechanisms of lead acid batteries. Sulfation at the negative electrode, acid stratification, and dendrite formation now precede positive electrode failures such as grid corrosion and active material shedding. To attenuate these failures, carbon has been explored as a negative electrode additive to increase charge acceptance, eliminate sulfation, and extend cycle life. Frequently, however, carbon incorporation decreases paste density and hinders manufacturability.

Discrete carbon nanotubes (dCNT), also known as Molecular Rebar[®], are lead acid battery additives which can be stably incorporated into either electrode to increase charge acceptance and cycle life with no change to paste density and without impeding the manufacturing process.

Here, full-scale automotive batteries containing dCNT in the negative electrode or both negative and positive electrodes are compared to control batteries. dCNT batteries show little change to Reserve Capacity, improved Cold Cranking, increased charge acceptance, and enhanced overall system efficiency. Life cycle tests show >60% increases when dCNT are incorporated into the negative electrode (HRPSoc/SBA) and up to 500% when incorporated into both electrodes (SBA), with water loss per cycle reduced >20%. Failure modes of cycled batteries are discussed and a hypothesis of dCNT action is introduced: the dCNT/H_{ad} Overcharge Reaction Mechanism.

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1. Introduction

In order to meet the demands of modern lead acid battery applications, the technology must provide higher levels of charge acceptance to boost system efficiency and delay common failure mechanisms such as sulfation or dendritic growth [1,2]. For example, in the modern automobile, advanced systems such as navigation, heating, and air conditioning can increase electrical energy consumption beyond that which the alternator can replenish during normal vehicle operation. The battery system therefore operates at a detrimental energy deficit. In order to maintain batteries at higher states of charge and avoid irreversible sulfation, modern applications demand increased charge acceptance. As a second example, batteries operating in hybrid-electric automobiles as well as some grid storage applications must be able to effectively accept charge in quick, high-current bursts or risk negative electrode passivation. If these challenges can be surmounted, lead acid batteries will remain competitive with other chemistries in the automobile, storage, and telecom markets, amongst others.

Carbon has been added to the Negative Active Material (NAM) during paste preparation in a variety of forms including carbon black, activated carbon, and more recently developed varieties including graphite and carbon nanotubes [6–8]. When incorporated at 0.1–6% w.r.t. lead oxide, carbon increases the charge acceptance of a battery by more than 200% but at the cost of paste rheology and paste density [3–5]. Reductions in paste density directly lead to decreased active material adhesion to the grids, decreased battery capacity which requires higher active material masses to reach specification, and insufficient cold-cranking performance [4]. New paste processing machinery is often required to overcome some of the issues brought on by high carbon loading. A further drawback to the use of carbon as a NAM additive is the potential to introduce gas-evolving impurities into the electrode. If the carbon additive is particularly high in iron residuals remaining from its production, for example, gas evolution and water loss will increase, leading to premature battery failure [9]. An abundance of literature studies discuss carbon allotropes, or mixtures thereof, in relation to the formation improvements [10] and charge acceptance boosts [6] they produce, but the detrimental effects of these carbon additives, namely paste property changes and gas evolution increases, remain consistent.

Our previous report introduced discrete carbon nanotubes (dCNT) as novel additives for the negative electrode [11]. The dCNT, also known as Molecular Rebar[®], are cleaned, functionalized, individualized, multi-walled, carbon nanotubes which are easily incorporated into battery pastes as a concentrated, pourable fluid [12]. The fluid replaces a portion of the water used during the paste mixing process, requiring no alteration to existing industrial production lines. When combined with traditional paste ingredients (lead oxide, expander, fiber, water, and acid) at 0.16% w.r.t. lead, dCNT offer prolonged increases in charge acceptance and more efficient battery usage with no detrimental effect to paste rheology or Reserve Capacity (RC), and an augmented Cold-Cranking Ability (CCA).

In this work, lead acid batteries incorporating dCNT into the negative electrode or both the negative and positive electrodes are compared to dCNT-free control batteries across various performance metrics. Addition of carbon additives to the positive electrode is typically avoided, with few exceptions [13], because of fears that the highly oxidizing environment of the positive electrode

would result in degradation of the carbon to carbon dioxide. Here, the stability of dCNT in such an environment is tested (See [supp. info.](#)) and the benefits of their inclusion in the Positive Active Material (PAM) is revealed. Full-scale, control batteries are compared to full-scale, experimental batteries containing 0.16% dCNT in the NAM or 0.16% dCNT in both the NAM and PAM. Pasting properties, basic performance (formation, reserve capacity, and cold temperature performance), advanced performance (polarization and triple electrode studies), gassing, cycle life (HRPSoC and SBA models), and battery failure mechanisms are presented.

dCNT provide additional benefits if added to both electrodes instead of the negative electrode alone. Batteries containing dCNT benefit from improved formation profiles, charge acceptance boosts of >200%, and elongated cycle life. Theories regarding the hydrogen adsorptive functionality of dCNT are introduced as a potential mechanism of action and grounds for future experimentation.

2. Experimental

2.1. Materials

Discrete carbon nanotubes (dCNT), also known as Molecular Rebar[®], are manufactured in Austin, Texas, by Molecular Rebar Design, LLC through a proprietary process that disentangles and functionalizes commonly available stock carbon nanotubes. Functionalization includes addition of carboxylic acid groups to the surface of the tubes and an increase in the number of open ends. The process also cleans the carbon nanotubes such that their residual catalyst content (Iron, Aluminum, etc.) drops ~80% from >5% by weight carbon to less than 1%, resulting in near pristine dCNT. A comparison of stock, non-processed carbon nanotubes and the dCNT can be found in our previous work [11].

The process by which the dCNT are prepared for use in lead acid batteries involves a surfactant coating step employing a high-intensity mixer. This produces a final, fluid dispersion of dCNT, surfactant, and water at a final concentration of 3% w/v dCNT at pH 7. This fluid is named Molecular Rebar[®] Lead Negative (MRLead⁻) or Molecular Rebar[®] Lead Positive (MRLead⁺) depending on its intended electrode, differentiated by processing methods and formulation.

Lead oxide (70% PbO/30% Pb) is manufactured onsite at Pacific Batteries, Ltd from 99.97% pure lead.

Hammond Expander is purchased directly from Hammond and used as per the manufacturer's instruction. Here, expander appropriate for SLI battery formulations is used (HEM-4640). The product includes proprietary amounts of barium sulfate (40–60%), sodium lignosulfate (25–40%), and carbon black (10–20%) [14].

All water used in the battery making process adheres to BS 4974:1975 standards.

Battery grade sulfuric acid (1.40 sp gr.) is used during paste mixing.

2.2. Scanning electron microscopy

High resolution scanning electron microscopy is accomplished with a Jeol JSM-6010LV instrument.

Battery plates are prepared for SEM analysis by removing them from their battery casings, washing them with distilled water until the runoff is pH neutral, and then drying them under vacuum at 30–40 °C. Samples are obtained by carefully pushing the dried

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