Discrete carbon nanotubes increase lead acid battery charge acceptance and performance

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HIGHLIGHTS

- Molecular Rebar® lead negative is a NAM additive comprising discrete carbon nanotubes (dCNT).
- dCNT can increase the charge acceptance of lead acid batteries by >200%.
- dCNT reduce energy losses of lead acid batteries >15%.
- dCNT do not change NAM paste density or rheology.
- dCNT is easily implemented in existing manufacturing processes.

GRAPHICAL ABSTRACT
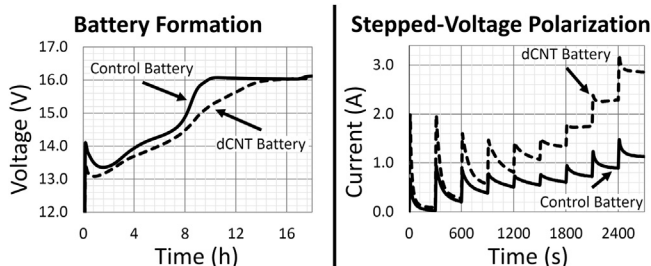
ABSTRACT

Performance demands placed upon lead acid batteries have outgrown the technology's ability to deliver. These demands, typically leading to Negative Active Material (NAM) failure, include: short, high-current surges; prolonged, minimal, overvoltage charging; repeated, Ah deficit charging; and frequent deep discharges. Research shows these failure mechanisms are attenuated by inclusion of carbon allotropes into the NAM. Addition of significant quantities of carbon, however, produces detrimental changes in paste rheology, leading to lowered industrial throughput. Additionally, capacity, cold-cranking performance, and other battery metrics are negatively affected at high carbon loads.

Presented here is Molecular Rebar® Lead Negative, a new battery additive comprising discrete carbon nanotubes (dCNT) which uniformly disperse within battery pastes during mixing. NS40ZL batteries containing dCNT show enhanced charge acceptance, reserve capacity, and cold-cranking performance, decreased risk of polarization, and no detrimental changes to paste properties, when compared to dCNT-free controls. This work focuses on the dCNT as NAM additives only, but early-stage research is underway to test their functionality as a PAM additive.

Batteries infused with Molecular Rebar® Lead Negative address the needs of modern lead acid battery applications, produce none of the detrimental side effects associated with carbon additives, and require no change to existing production lines.

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1. Introduction

As the uses and expectations for lead acid batteries evolve, so too do their modes of failure. Traditionally, the majority of failures were related to grid corrosion and softening in the Positive Active Material (PAM) however, in contemporary applications, these have

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been replaced by sulfation in the Negative Active Material (NAM), acid stratification, and short-circuit producing dendrite formation [1,2]. These "contemporary applications" are defined as any in which the battery experiences: frequent, short, high-current surges during charge and discharge (ex. micro-hybrid vehicles); minimal, but consistent overvoltage charging (ex. solar/photovoltaic cells); deficit charging caused by the increased energy demands of modern electronics (ex. automotive power); or, two to three deep cycles per day (ex. motive power). Recent studies suggest that such failure mechanisms can be averted by increasing the battery's charge acceptance, often through addition of excess carbon [3].

Carbon is added during NAM mixing as one, or a combination of, its carbon black, activated carbon, or graphite allotropes [4,5], and less commonly its graphene or nanotube allotropes. If restricted to 0.1–6.0% w.r.t. lead oxide weight, carbon is capable of doubling the battery's charge acceptance [6,7]. Throughout that range, however, carbon steadily increases the volume of water required for paste formation leading to decreases in paste density of up to 30% [6]. Reduced paste density lowers not only plate strength, battery capacity, and cold-cranking performance, but also production throughput. Consequently, a carbon allotrope capable of boosting charge acceptance at concentrations low enough to conserve paste density and plate strength is required.

Although the concept that carbon enhances charge acceptance is universally acknowledged, controversy exists regarding which allotrope produces the best effect, and in what concentration. In early studies, carbon black is preferred [3], but later studies describe the negative impact of carbon black additions over 0.5%, w.r.t. lead oxide weight, on formation [8]. Various forms of activated carbon have since proven more beneficial than common carbon black [9,10]. Analogous studies using 2% graphite, w.r.t. lead oxide weight, find decreases in charge acceptance, but addition of 1–2% carbon black in combination with the 2% graphite successfully produces performance gains [4]. Some authors find that carbon black or graphite loaded at 3% or 6%, w.r.t. lead oxide weight, respectively, improves charge acceptance but diminishes capacity and cold-cranking performance [6]. Regardless of the allotrope or concentration, the importance of a homogenous distribution of carbon throughout the paste/plate is understood [11]. This seemingly simple stipulation is often problematic given the poor dispersibility of many forms of carbon.

The mechanism by which carbon increases charge acceptance is also disputed. Some attribute the carbon's charge-acceptance enhancing properties to its ability to act as a fast-charging, intermediary capacitor between the source of energy and the more slowly charging lead [9,10,12,13]. Some of this capacitive effect may be due to the ability of carbon nanotubes to adsorb and reversibly store 0.1–10% hydrogen, w.r.t carbon weight, depending on temperature, pressure, and nanotube purity [14]. Hydrogen adsorption is fast, proceeding through the Volmer–Heyrovsky mechanism on carbon, and briefly delays hydrogen gas evolution to better handle overvoltage conditions [15]. Others suggest that high surface area carbon additives increase effective NAM surface area, increasing efficiency and decreasing polarization [7,16]. Carbon could also increase charge acceptance by blocking the growth of resistive lead sulfate deposits either sterically [17–20] or electrically [3], by acting as a conductive bridge around them, to improve lead reconversion rates. Alternate functions for carbon include providing additional surface area to facilitate the deposition of lead [8,21] or, in VRLA batteries, consuming PAM-produced oxygen to limit NAM sulfation and promote water oxidation [22]. In the battery, carbon likely participates in many of these roles to various extents.

The ideal carbon additive would be uniformly distributed throughout the paste and capable of boosting charge acceptance at concentrations low enough to avoid the decreases in paste density, cold-cranking performance, and reserve capacity experienced with current NAM additives. A recently developed carbon nanotube derivative, Molecular Rebar®, has the potential to fulfill this ideal [23]. The associated NAM additive, Molecular Rebar® Lead Negative (MRLead−), is provided as a pourable, aqueous fluid comprised of surfactant-stabilized, discrete, carbon nanotubes (dCNT). The highly dispersed nature of the fluid enables additive uniformity throughout the NAM to ensure the dCNT benefits are felt plate-wide.

Here, batteries formulated with and without dCNT/Molecular Rebar® in the NAM are compared based on their paste mixing profile, paste density, formation profile, reserve capacity, cold-cranking performance, and, most importantly, charge acceptance.

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 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 provides additional cleaning of the carbon nanotubes such that their residual catalyst content (Fe, Al, etc.) drops ∼80% from 5% by weight carbon to less than 1%, resulting in near pristine dCNT. Fig. 1 shows a comparison of stock carbon nanotubes and the dCNT known as Molecular Rebar® at a magnification low enough (5000×) to differentiate macrostructures. At higher resolution (>20,000×), the two samples are less distinguishable. Stock carbon nanotubes are used exclusively in paste distribution experiments and not included in any battery test.

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, or MRLead−.

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 instructions. 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%) [24].

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. Negative Active Material (NAM) paste mixing and analysis

dCNT are provided as an aqueous dispersion, MRLead−, allowing them to be uniformly distributed in NAM. During regular pasting procedures, a specific volume of water, X, is added to dry ingredients such that appropriate paste density specifications are met. To conserve paste consistency, the volume of MRLead−, Y, added to the paste is displaced from volume X to result in a remaining water allowance volume, Z, such that $X = Y + Z$. The MRLead− volume, Y, is added to the dry mixture first, followed by the remaining water allowance, Z, in order to maintain the liquid portion of the paste at volume X.

Large-scale paste mixes comprising 230 kg lead oxide and 1.4 kg Expander are combined mechanically as 27.0 L water (Control) or