Hammond Group researchers have analysed the way that PbO_2 conversion during formation can be overcome for cured positive plates with 4BS crystals. The research was led by Dr Marvin Ho with contributions from Thomas Wojcinski, Maureen Sherrick, Dave Petersen and Gordon Beckley.

Study of TTBLS seed crystals with treatments to improve formation efficiency

Modern applications demand that a battery delivers robust performance with increased cycle life. Typically, the life of the lead-acid battery is limited by the positive plate due to such factors as corrosion, active material shedding etc. Positive active material (PbO_2) with stronger structure is desired to extend the cycle life of lead acid batteries.

The structure of the PAM is determined by the phase composition, morphology of crystals and density of paste. Past research works have shown that positive paste containing tetrabasic lead sulfate crystals ($4PbO{\cdot}PbSO_4$, TTBLS or 4BS) has a stronger positive active material structure and longer life compared to paste with classical technology including tribasic lead sulfate crystals ($3PbO{\cdot}PbSO_4$, TBLS or 3BS).

4BS crystals in the positive active material ensure longer life performance of the battery, but they also reduce the conversion rate of PbO_2 during formation which leads to lower initial capacity of the battery. To compensate for the lower initial capacity caused by inefficiency of formation, longer formation is a typical method used by lead acid battery manufacturers.

But this method will reduce the production rate and add extra cost to the manufacturing process. Several approaches have been proposed to improve the PbO_2 conversion during formation. One of these approaches is to add an additive, such as red lead, to increase the conversion to PbO_2, however red lead is not readily available in all parts of the world.

Hammond's R&D team has developed a process of modifying their industry-proven 4BS seed crystal additive (SureCure®) to maintain the positive active material durability and consistency required for long service life in multiple applications such as: stop/start, renewable energy, golf car, e-rickshaw, etc. and to increase the formation efficiency of newly formed batteries.

OVERVIEW

Positive plates manufactured with Tetrabasic Lead Sulfate (TTBLS or 4BS) seed crystals have been studied and proven to improve the cycle life of the lead acid battery. But the more difficult PbO_2 conversion during formation is the key drawback of cured positive plates with 4BS crystals. The R&D team at Hammond Group has developed a process to apply treatments on 4BS seed crystals to increase PbO_2 conversion during formation and still maintain or extend the cycle life of the battery. This paper presents the data collected from the analysis of cured and formed plates in both controlled laboratory-scale experiments and in full production-scale battery trial.

Experiment and results

Hammond's 4BS crystal seed (Standard SureCure®) is made with a chemical process followed by a milling step to produce the specified particle size (~ 1 µm). This material is used as the base material in this study. Once the standard SureCure® material has been produced to within the proper particle size specification, a final finishing treatment is applied.

The purpose of treatment is to control the crystal growth of 4BS seeds (such as SureCure® crystals) during the curing process, while still providing seed sites to assist in the uniform controlled growth of 4BS crystals within the positive active material. There are two treatments (120 and 140) applied to the base SureCure® crystal and studied in this paper. These treated crystals are called Treated SureCure® 120 and Treated SureCure® 140 later in this paper.

Studies of crystal growth with different curing profiles were carried out in the laboratory. The curing profiles studied in this paper are 55°C with high humidity (>95% RH) for 48 hours and 75°C with high humidity (>95% RH) for 24 hours. Both profiles also include a 24-hour drying step after the high humidity step.

Samples were taken from the curing chamber over the course of the curing process and analyzed to characterize physical properties, phase composition and morphology of the positive active materials. Standard SureCure®, Treated SureCure® 120 and 140 were studied following this test plan, and the results are presented in this paper.

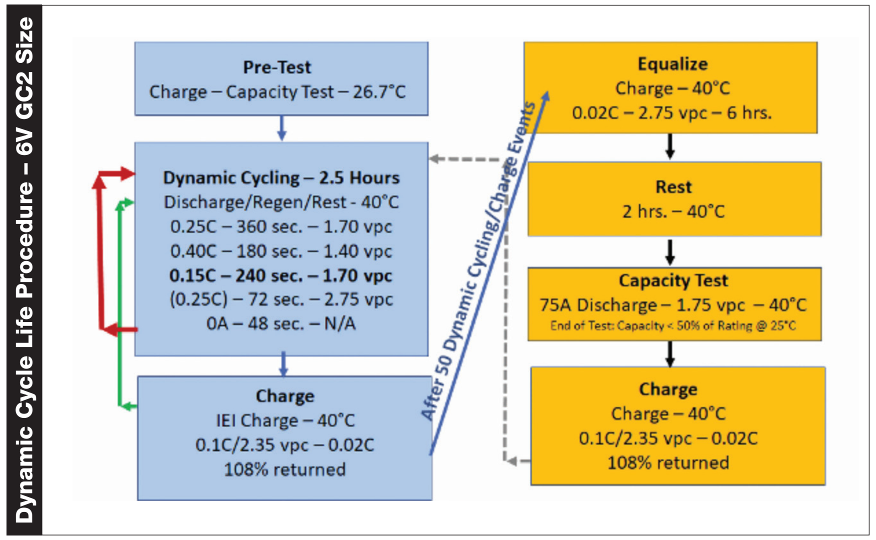
Battery trials were carried out as part of a production trial at a major battery manufacturing site. The Treated SureCure® was added to a standard mixer (2,400 lbs) with leady oxide, water, sulfuric acid and fiber to make the positive paste. Test plates were made with the paste described above. The addition rate of Treated SureCure® is 1% versus leady oxide.

The control plates were produced with 4BS crystal seeds from other sources besides Hammond and the same loading (1%). Both control and test plates were placed on racks and cured side by side in the same curing room to reduce variations during curing process.

The negative plates were collected from normal production and used in both control and test batteries. Then, both the control and test positive plates were assembled with negative plates into control and test batteries. The battery size is a typical 6V deep cycle battery (~230Ah at 20HR rate). All test and control batteries were formed at the same time to eliminate the variations from the process.

Cured plates were collected after the curing process and formed plates were collected from autopsying batteries after formation. These plates were analyzed in the lab employing techniques which focused on the chemical composition, phase composition, BET surface area and morphology of the active material mass. Electrical testing of the assembled batteries followed the dynamic load profile cycle life procedure as recommended by the BCI Deep Cycle and EV Battery Technical Committee in recent publications.

The detailed testing procedure is shown below:



Cured material characteristics from laboratory investigations

Positive plates containing Treated SureCure® will exhibit similar characteristics to plates containing Standard SureCure®. This includes a typically brighter orange hue and harder, more durable active material surface.

Figure 1

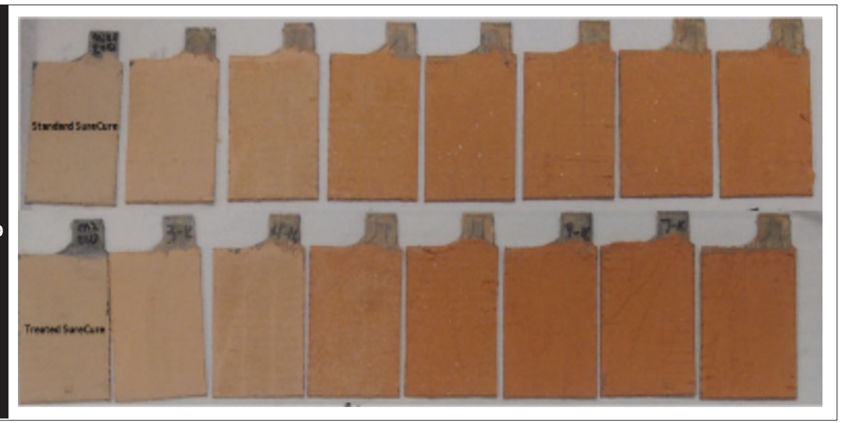


Figure 1: A comparison of Cured Positive plates sampled during the curing process for both Standard (Standard Hammond SureCure®) and Treated SureCure®120.

BENEFITS

The treatments and novel 4BS seed crystal materials developed by Hammond Group provide several benefits to battery performance:

- Increased PbO_2 conversion (or higher efficiency) with the same formation profile
- Produce cured material with similar or better PAM cohesion strength (drop test)
- Create higher BET surface area which leads to higher initial performance of the battery (initial capacity)
- Deliver longer cycle life with lower recharge factor (108%)
- Offer an optimized solution when combined with advanced expander for PSoC applications
- Certain treatments may slow the crystal growth and conversion of the active mass to 4BS at low temperature (≤55°C) curing profiles. Higher curing temperatures will resolve this issue.

By combining Treated SureCure® and advanced expander together into the battery's design, an optimized solution can be achieved for partial state of cycling (PSoC) applications.

Changes of phase composition during curing

Figures 2 and 3 on the following page show the X-ray diffraction analysis of active material from cured plates with the addition of Standard Hammond SureCure®, Treated SureCure® 120 and Treated SureCure® 140. Figure 2 shows the effect of various treatments on the conversion of tetrabasic lead sulfate (4BS) content in positive active material during the curing process at 55°C and 95% RH over the course of 48 hours plus drying. It is shown that Treated SureCure® 120 experiences delayed 4BS crystal conversion. Treated SureCure® 140 shows the same 4BS crystal conversion rate as standard SureCure®.

Conversely, Figure 3 illustrates the crystal growth of Standard SureCure®, Treated SureCure® 120 and Treated SureCure® 140 during curing at 75°C with the same RH conditions and a 24-hour wet phase

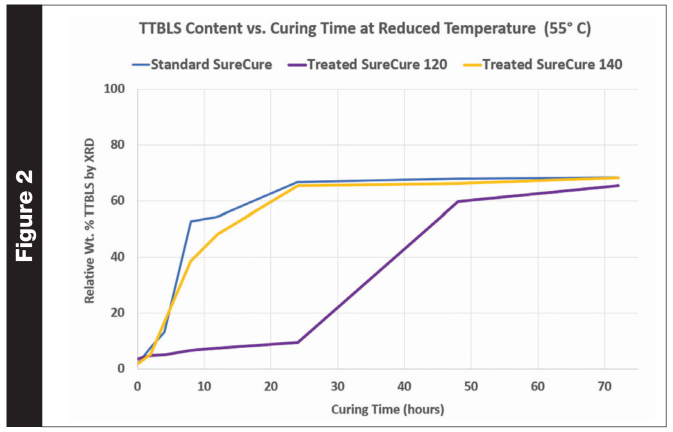


Figure 2: Phase changes of 4BS crystal growth during the curing process at 55˚C for both Standard SureCure® and Treated SureCure® Additives

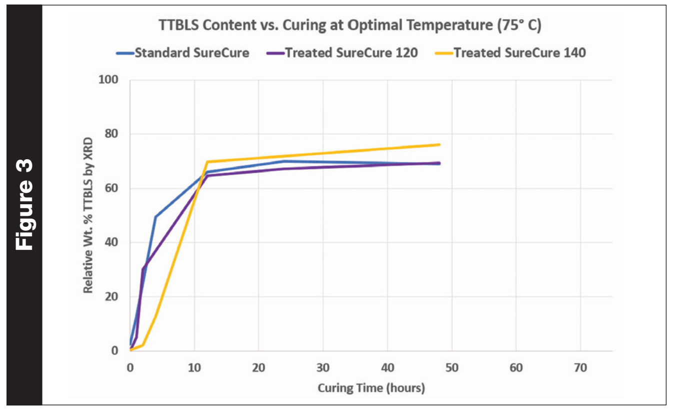


Figure 3: Phase changes of 4BS crystal growth during the curing process at 75˚C for both Standard SureCure® and Treated SureCure® Additives

plus drying. All three additives have similar crystal conversion rates when cured at 75˚C. These results demonstrate that the high temperature accelerates the crystal conversion (or crystal growth) and suppresses the delay experienced by Treated SureCure® 120. No steam is required which means most curing rooms can be set to properly cure positive plates using Treated SureCure®.

Figures 4-6 show the SEM pictures of positive active material from cured plates as produced with addition of Standard SureCure® (Figure 4), Treated SureCure® 120 (Figure 5) and Treated SureCure® 140 (figure 6). Both treatments (120 and 140) did change the way 4BS crystals grow and show different crystal appearance when compared to that seen in the Standard SureCure® additive.

Cured and formed active material characteristics from battery production trials

Cured plates from the battery production trial were collected after the curing process and analyzed in the Laboratory. Table 1 shows the characterization results of both control and Treated SureCure® 120 cured positive plates from this production trial. The control plate here is the plate with 4BS seed crystals from another source used by the manufacturer. The control material has a higher 4BS reading from XRD, lower BET surface area and slightly higher weight loss in drop testing.

Although the control material has a higher XRD reading, it does not ensure stronger cohesion inside the positive active material. These results give evidence to support that Treated SureCure® 120 did indeed change the way that the 4BS crystals formed during curing as seen initially in the laboratory trial. The treatment leads to higher surface area and stronger PAM even though the relative 4BS reading from the XRD measurement is lower.

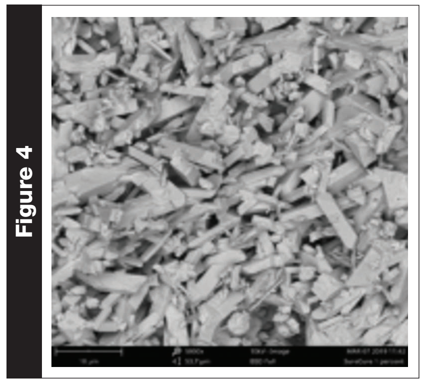


Figure 4: Standard SureCure® @75˚C

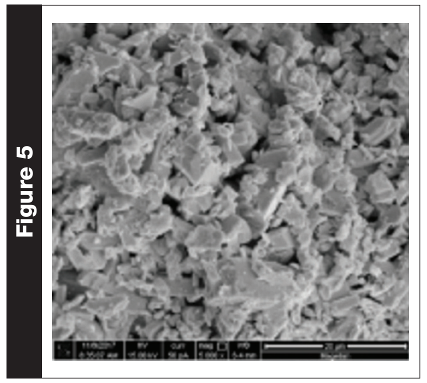


Figure 5: Treated SureCure® 120 @75˚C

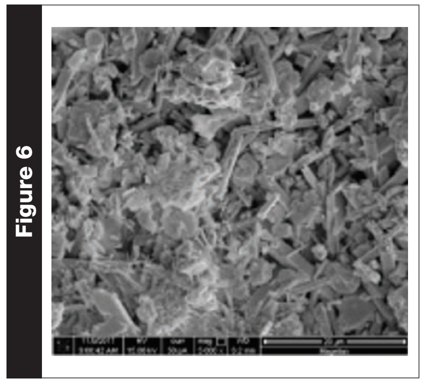


Figure 6: Treated SureCure® 140 @75˚C

Table 1. Analysis of cured plates from battery production trial

Test	Plate with Typical 4BS crystal seeds	Plate with Treated SureCure® 120
Weight Loss (%) from Drop Test	4.23	3.89
BET – SA (m²/g)	0.74	0.84
Relative Weight (%) of 4BS - XRD	78.8	65.5

Table 2 shows the results of formed plate characterization and initial battery testing results from test batteries constructed during the production trials. Positive plates with Treated SureCure® 120 demonstrate higher BET surface area, and PbO_2 conversion is shown to be more efficient when compared to the control plates. This explains the higher initial performance (capacity) of the battery with plates containing Treated SureCure® 120 as shown in the table.

These same samples of positive active material were then imaged using Hammond's on-site scanning electron microscopy (SEM) equipment. From Figures 7 and 8, a clear difference in the micro-crystal structure and ordering of the PAM particles between the samples is observed.

Cycle life test

Treated SureCure® was developed to increase cycle life performance through improved charging efficiency of the positive plate in conditions when high passive lead sulfate content is present. Both control and test batteries were placed into a constant temperature water bath and tested under the dynamic load profile cycle life procedure recommended by the BCI Deep Cycle and EV Battery Technical Committee.

Figure 9 shows the results of this cycling regime on both the control and test (with Treated SureCure® 120) batteries from the production trial. Both sets of batteries received 108% overcharge during cycling and received a full recharge before being capacity checked at a 75A discharge rate. As shown by the testing data, the test batteries delivered much longer cycle life compared to control batteries.

Since both batteries used the same negative plates from production, the extended cycle life is attributed to the change in the positive additive materials, specifically Treated SureCure® 120 in this case.

Also, this result provides further evidence that Hammond's treatment to the 4BS crystal seeds will provide additional benefit to overall performance at lower overcharge (108%) conditions. ■

Table 2. Analysis of formed plates from battery production trial

Test	Plate with Typical 4BS crystal seeds	Plate with Treated SureCure® 120
BET – SA (m²/g)	2.45	6.12
Weight (%) of Lead Sulfate	18.1	4.20
Weight (%) of PbO_2	81.1	94.6
Initial Capacity (Ah) @ 75A DCH before Cycle Test	99.4	117.5

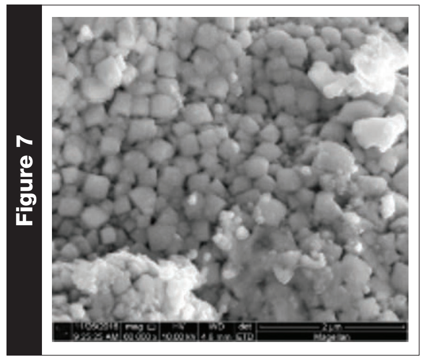


Figure 7: Positive Formed Material with Treated SureCure®120

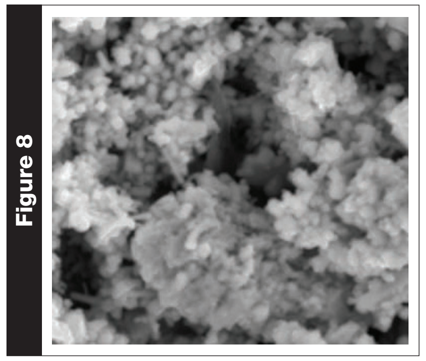


Figure 8: Positive Material with other 4BS Seed Crystals

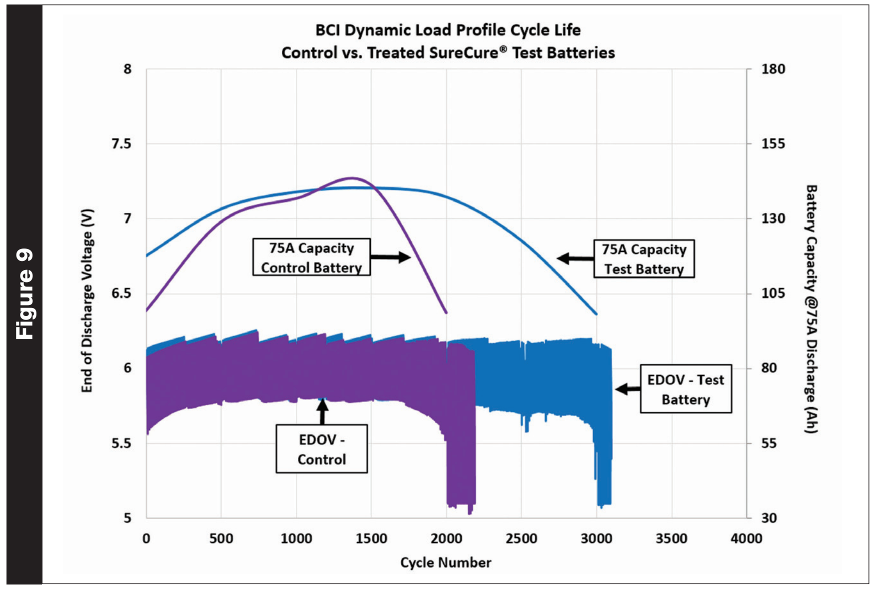


Figure 9: Cycling performance of control and treated SureCure®120 test batteries

Dr. Marvin Ho is Hammond's CTO and vice president of R&D responsible for the advancement of lead-acid battery electrochemistry through the development of innovative performance additives and lead oxides. He has over 25 years of experience in energy storage technologies such as fuel cells, nickel based and lead-acid battery systems, he has worked with leading research institutes including IEEES at the Bulgarian Academy of Sciences and Trinity College in Ireland.