

# Improving Formation Efficiency of Lead Acid Battery using Hydrogen Peroxide as an Additive

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**Abstract:** Formation is one of the critical step in lead acid battery manufacturing process. The purpose of formation process is to convert the cured paste into electrochemically active porous paste i.e. lead dioxide as positive plate and sponge lead as negative plate respectively. In the present work we studied “ Improving formation efficiency of lead acid battery using hydrogen peroxide as an additive”. This additive is oxidizing in nature. When this additive is subjected to high temperature or dissolved in water, it releases nascent oxygen. The nascent oxygen reacts with semi-conductive lead monoxide and converts it as conductive lead dioxide. The presence of lead dioxide in cured paste thus increases conductivity of plate and reduces the formation energy required for conversion during formation. So, to establish the impact of this additive on lead dioxide conversion and formation energy, samples made with and without addition of hydrogen peroxide. From XRD analysis, conversion of formed paste and formed cell discharge capacity test, it was observed that this additive can reduce the formation energy potentially up to 20%.

**Keywords:** lead acid batteries, paste additive, oxidizing additive, formation efficiency, formation energy

## 1. Introduction

The process of formation can be conducted based on two basic methods namely, tank formation and container formation. In the earlier case, cured positive and negative plates are formed in large electrolytic tanks containing H<sub>2</sub>SO<sub>4</sub> of 1.08-1.10 relative density and then plates are assembled. Whereas in case of container formation, cured positive and negative plates are assembled into groups along with separator, which are then placed into the battery container and subjected to formation after filling with H<sub>2</sub>SO<sub>4</sub> [1-2]. In both the methods of formation processes conversion of positive plates consumes more time and energy than negative plates. Oxidation of bivalent lead compounds in the paste and formation of the lead dioxide positive active mass passes through a number of chemical reactions, some of which proceed at a low rate, which retards the technological process of formation of the positive plate. In an attempt to accelerate the formation process, various studies had been carried out to improve the rate of conversion of lead dioxide and to reduce the formation energy. Earlier studies include two shot formation in container formation process, acid recirculation formation process, pulse charging and paste additives which includes conductive, porous and electrolyte additives.

Generally two formation methods are applied in container formation, two shot and single shot formation. In the two shot formation, the battery is filled with H<sub>2</sub>SO<sub>4</sub> of relative density 1.08-1.15, after completion of formation the electrolyte is replaced with higher relative density H<sub>2</sub>SO<sub>4</sub> to achieve the required relative density this is the one of the efficient process to reduce the formation energy and formation cycle time [1-3]

The 0.2 wt% (Silica gel) of material addition resulted in improved capacity at both low and high rates. Although the addition of silica gel was not observed to cause significant physiochemical changes to the positive active-material; it is possible that silica gel promotes nucleation which consequently leads to a finer pore structure in the active

material. Since this form of silica is porous, the additive may act as an acid reservoir [4].

Acid recirculation formation process is the one of the solution for the formation of Flooded Automotive and Industrial batteries. The process permits to maintain the constant temperature all over the plates inside the batteries, highly reducing the cycle time and increasing the quality of the formation process [5].

Different conductive additives for positive plates to improve the formation efficiency includes Barium plumbate, Titanium oxide, Tin dioxide, Lead dioxide, Carbon and Conductive Polymers were studied [1]. D Pavlov studied the effect of read lead as a conductive additive to improve the formation efficiency [2]. K.R Bullock et al investigated the ozone treatment that enhances conductivity of positive material [6].

The patent - US 2,658,097 A, manufacture of positive plates for lead storage batteries issued Nov. 3, 1953 mentioned that The oxidizing solution may be applied to the positive plates by immersing the plates in the solution or by applying the solution by dipping, painting, spraying or other known method. We have found it convenient to immerse the plates in the solution for an interval of time sufficient to form a thin deposit of higher oxides of lead on the surface of the active material in the positive plates. [7].

The patent - US 4909955 A, Lead oxide paste mix for battery grids and method of preparation issued on 20 Mar 1990 mentioned that, battery grades of oxides of lead are mixed with a dilute solution of hydrogen peroxide, either alone or with additives and/or expanders. The resultant paste offers such advantages as reduced curing and drying times and/or the elimination of the need for curing and drying, lower dry active material weights and improved cohesion when compared to conventional pastes manufactured from leady oxides, sulfuric acid, and water [10].

The patent - US 5149606 A, method of treating battery electrode with per-sulfate issued on 22 September 1992, discloses that, Improved formation efficiencies for positive pasted plates used in lead-acid batteries are provided by treatment of the positive plates with a stabilized aqueous alkaline persulfate solution to effect the conversion of lead monoxide to lead dioxide. Use of the alkaline persulfate solution enhances both formation and initial performance of the fabricated batteries [8].

Pulse charging option is available for the formation, it is used together with constant voltage/current profiles to increase charge acceptance, improve the charging time and to potentially increase the life cycle of lead acids cells [9].

In the present study we focused mainly on oxidizing additive to reduce the formation energy, by mixing the additive with paste. The effect was studied after curing, drying and formation. The concept of using additive to improve formation efficiency has been explored as it is easy to adopt in manufacturing and economical.

## 2. Experimental

4.5" × 2.5" × 0.5" (H × W × T) Ca-Sn alloy based gravity casted grid was chosen for experimentation. Experiments were conducted with different percentages of additive as shown in the Table 2 with respect to the weight of leady oxide. Hydrogen peroxide is chosen as an additive for experimentation, it was added during paste mixing in positive active material considering the available active oxygen in it. Here onwards hydrogen peroxide and active oxygen are denoted as HP and AO respectively.

### 2.1 Material properties

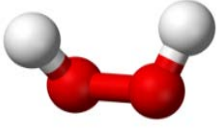
HP is a colorless free flowing liquid, slightly viscous than water. It is an oxidizing agent with solid source of AO. It is readily soluble in water and can easily decompose at elevated temperatures thus releases nascent oxygen. Physical and chemical properties of HP are described in the Table 1 [10].

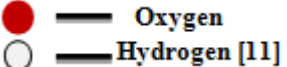
#### 2.1.1 Physical and chemical properties

**Table 1:** Physical and chemical properties

S. No	Property	UOM	50% H <sub>2</sub> O <sub>2</sub> (50 % H <sub>2</sub> O + 50% H <sub>2</sub> O <sub>2</sub> )
1	Molecular weight	g/mole	34.01
2	Appearance	-	Free flowing liquid
3	Water solubility @25 <sup>o</sup> C	g/l	Miscible
4	Density	g / ml	1.20
5	Active oxygen	%	23.54
6	pH	-	<3

#### 2.1.2 Chemical Structure

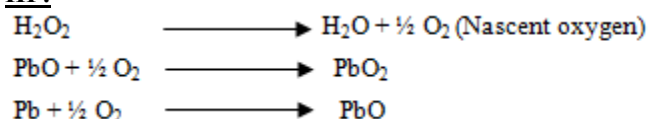
Chemical name	Chemical structure (ball and stick model)
Hydrogen peroxide	



### 2.2 Mechanism of HP

HP is a strong oxidizing agent with high percentage of active oxygen. But when it is dissolved in water or exposed to elevated temperatures, nascent oxygen gets evolved. This nascent oxygen has the potential to react with leady oxide in such a manner that both residual lead and lead monoxide in the leady oxide will get oxidized. The following reactions are expected to occur and to establish the below reactions experiment detailed in section 2.3.1 has been carried out [12].

#### HP:



### 2.3 Experimental procedure

#### 2.3.1 Leady oxide mixing with HP

To verify the above mechanism 5 g of laboratory reagent grade HP (50% H<sub>2</sub>O and 50% H<sub>2</sub>O<sub>2</sub>) is slowly (drop by drop) mixed with 50 g of Barton mill leady oxide in the laboratory with continuous stirring at room temperature for 15 minutes, followed by 20 hrs drying at 60°C and analysis was carried out to confirm the above mechanism. The results are discussed in 3.1.

#### 2.3.2 HP as an additive in paste

To study the effect of HP as an additive in paste mixing, curing and drying and formation, positive plates were prepared in the laboratory by mixing with different percentages of HP (50% H<sub>2</sub>O and 50% H<sub>2</sub>O<sub>2</sub>) as stated in the Table 2 in paste mixing. Samples were made by the below procedure. The results are discussed in 3.2 and 3.3.

**Table 2:** Hydrogen peroxide addition with respect to leady oxide

Sample (50%HP)	Leady oxide (g)
No additive (NA)	1000
1.07 g (0.3 g AO)	1000
2.14 g (0.6 g AO)	1000
5 g (1.17 g AO)	50

#### 2.3.3 Preparation of positive paste and plate

Positive paste was prepared by using Barton mill leady oxide (with 22-28 wt. % residual lead). Binder (poly ethylene terephthalate) was mixed with leady oxide and HP solution was introduced slowly into the leady oxide with different percentages as specified in Table 2 with good dispersion over the paste and mixing is carried out for 3 minutes. After mixing, water added as quickly as possible and uniformly mixed (wet mixing) for 3 minutes. After completion of wet mix, sulfuric acid (1.40 relative density) of battery grade was added to the mix in such a way that maintaining mix temperature below 60°C to form a specific paste morphology i.e., tri basic lead sulfates. Final mix was done for 3 minutes followed by the measurement of paste density.

Paste densities were adjusted to 4.20 g cm<sup>-3</sup>. Required quantity of paste weighed in a micro balance and manually

pasted on grid panel which is mentioned above. After pasting, panel was weighed and loaded into curing and drying oven. Plates were cured at 50°C by maintaining 95% relative humidity for 48 hours and dried at 60°C for 24 hours and plates were assembled in a commercial AGM battery case to form a dry unformed battery.

### 2.3.4 Cell formation

Required amount of chilled sulphuric acid (<15°C) with 1.290 relative density was filled into the dry unformed battery using vacuum filling. After soaking the plates in electrolyte for 1 hr, charging was conducted. Connecting cables were connected to the battery in series and then allowed for charging using constant current charging process with water circulation to control the temperature during formation. The Ah input during formation has been varied between 5 to 6 times of its designed rated capacity of the cell in order to evaluate the effect of additive on reduction in input formation energy and improve in conversion efficiency.

## 2.4 Analysis

Lead oxide without and with HP as explained in 2.3.1, was analyzed by dissolution and precipitation method and XRD.

Positive cured paste without and with HP (1.07 g and 2.14 g) was analyzed by XRD and SEM. Positive formed paste without and with HP was analyzed for lead dioxide content by dissolution and precipitation method and for initial capacity at 10 h rate.

### 2.4.1 Analysis of residual lead and lead dioxide content

#### 2.4.1.1 Residual lead content in lead oxide after mixing with HP

5 g of lead oxide without and with HP was dissolved in 5% acetic acid solution. Lead monoxide can effectively dissolve in acetic acid solution and the residual lead gets precipitated at the bottom; it is filtered, dried and weighed.

#### 2.4.1.2 Analysis of lead dioxide content in formed paste

The positive formed paste contains lead dioxide, lead sulfate and lead monoxide. Lead dioxide content in formed paste was determined by the following methodology.

5 g of positive formed paste was dissolved in 20% ammonium acetate solution. Lead sulfate and lead monoxide can effectively dissolve in this solution and lead dioxide gets precipitated at the bottom; it is filtered, dried and weighed.

### 2.4.2 XRD analysis (X-Ray Diffractometer)

The analysis of phase composition of the lead oxide and positive cured paste without and with HP was determined by using X-ray diffractometry. Samples collected after curing and drying was grinded into a fine powder and placed into a

standard aluminum glass-slide-back sample holder. RIGAKU ULTIMA-IV X-Ray diffractometer was used with Cu K $\alpha$  radiation. Scans were conducted in the 2 $\theta$  range of 10–90°, with a scan time of 4deg.min<sup>-1</sup>. Different phase compositions (3BS, PbO, Pb and PbO<sub>2</sub>) were analyzed and they are explained in 3.1.2 and 3.2.1.

### 2.4.3 Paste morphology

The analysis of paste morphology of positive cured paste without and with HP was determined by scanning electron microscopy (SEM). All samples were sputter coated with a thin layer of platinum, ~5 nm in thickness, to reduce charging and improve image quality. Examination was carried out in a JEOL JSM-6010PLUS low vacuum model SEM using a working distance of 12 mm, a spot size of 30, and an electron beam voltage of 10 kV.

### 2.4.4 Formed cell discharge capacity test

Initial capacity tests were performed on formed cell in which positive formed paste made with, without and with HP. Tests carried out at 10 h rate current by BITRODE LCN CIRCUIT, USA. The initial capacity test results are given in Table 5.

## 3. Results and Discussion

### 3.1 Lead oxide mixing with HP

#### 3.1.1 Residual lead after mixing

Residual lead percentage in lead oxide before and after mixing with HP (50% HP) was shown in Table 3. From the results reduction of 3.4% (average) of residual lead was observed after mixing with HP followed by drying. This indicates that, when lead oxide is mixed with HP, the residual lead gets partially oxidized to lead monoxide this results in residual lead reduction. This is in line with the earlier investigation of X.L. Wang et al [12]. Since, the effect of HP on oxidation of residual lead was already investigated (by X.L Wang et al), further experimentation was not detailed here.

**Table 3:** Oxidation of residual lead after treating with 50% HP

Sample	Lead oxide (g)	Residual lead (wt. %)	
		Before mixing	After mixing
5 g of 50% HP	50	26.6	22.8
		25.3	21.3
		27.2	24.2
		19.4	16.5

#### 3.1.2 Lead dioxide after mixing

XRD analysis was carried out on lead oxide without and with HP for lead dioxide peaks. Results were shown in Fig. 1 and Fig. 2. From the results, the additional lead dioxide peaks were observed when lead oxide mixed with HP and here  $\lambda$ ,  $\phi$  and  $\Theta$  are the lead monoxide, residual lead and lead dioxide respectively.

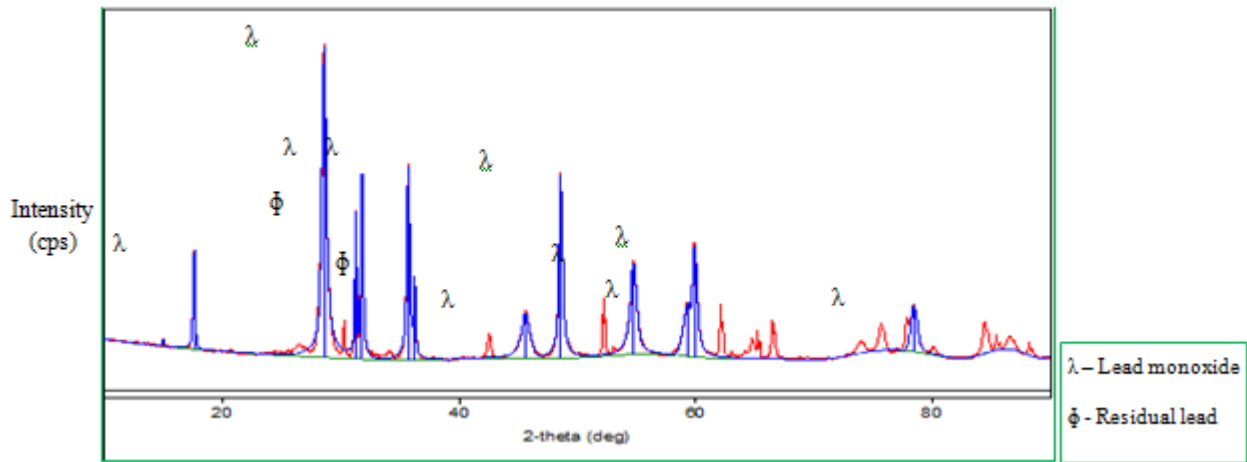


Figure 1: Lead oxide without HP addition

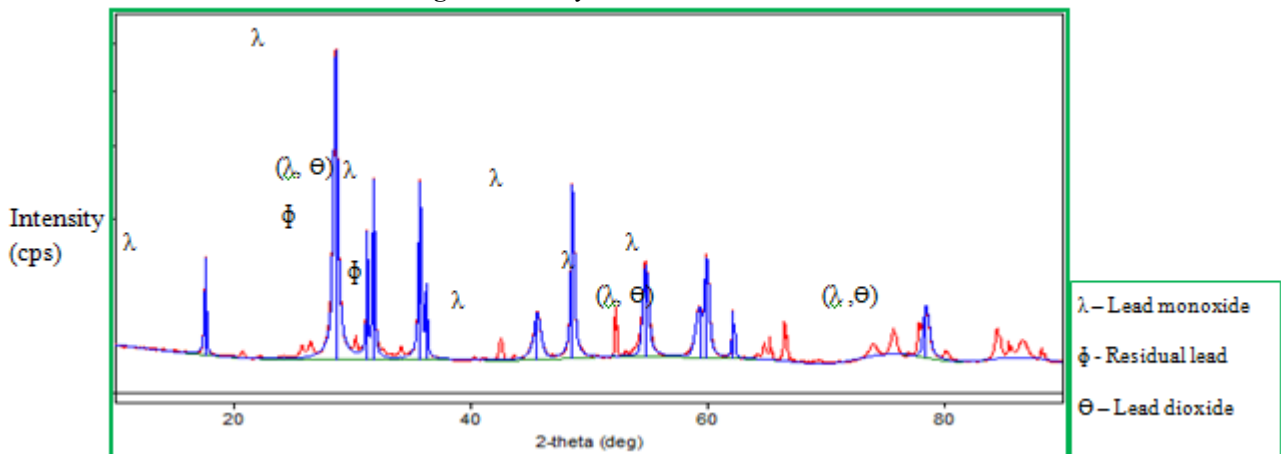


Figure 2: Lead oxide with HP addition

From the above XRD results, when lead oxide is mixed with HP, there is a slight reduction in residual lead percentage and at the same time lead dioxide phases were observed at  $2\Theta$  of 34.18, 59.28 and 77.82 degrees. So, the mechanism explained in 2.2 is expected to occur in this particular additive.

### 3.2 HP as an additive in paste

#### 3.2.1 XRD analysis

XRD analysis of positive cured paste without and with HP was carried out to check the reaction of HP in curing and

drying and for lead dioxide peaks. Results were shown in Fig. 3, 4 and 5. The characteristic lines of the substances are: tri basic lead sulfate, lead monoxide and lead dioxide. They are denoted by  $\gamma$ ,  $\lambda$  and  $\Theta$  respectively. So, in positive cured paste with HP, lead dioxide peaks were observed at  $2\Theta$  of 30.28, 45.63, 56.95, 59.92 and 77.86 degrees, after paste mixing, curing and drying process i.e., lead monoxide converts into lead dioxide due to availability of AO in the additive, as explained in chapter 2.2 Mechanism of HP.

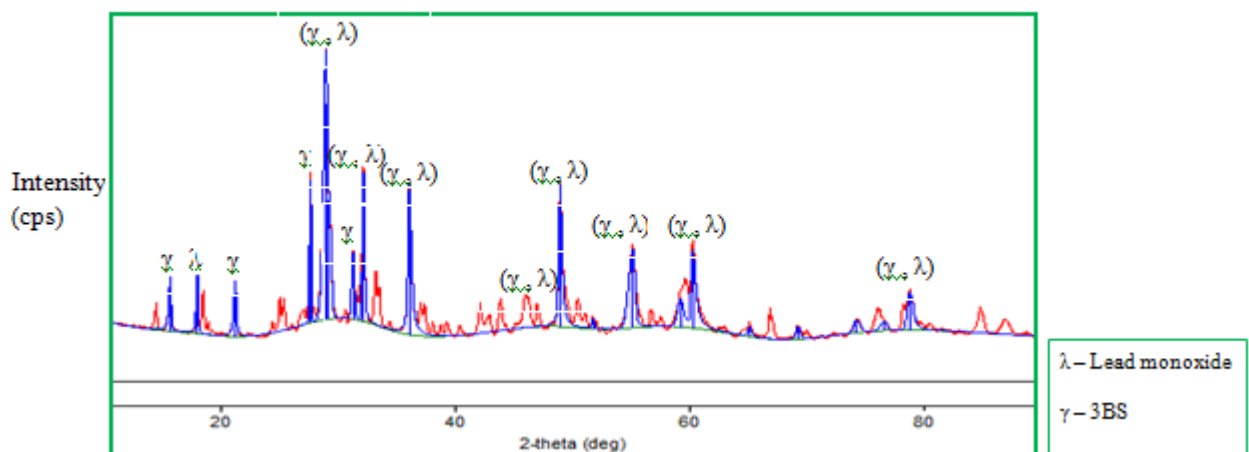


Figure 3: Without HP addition

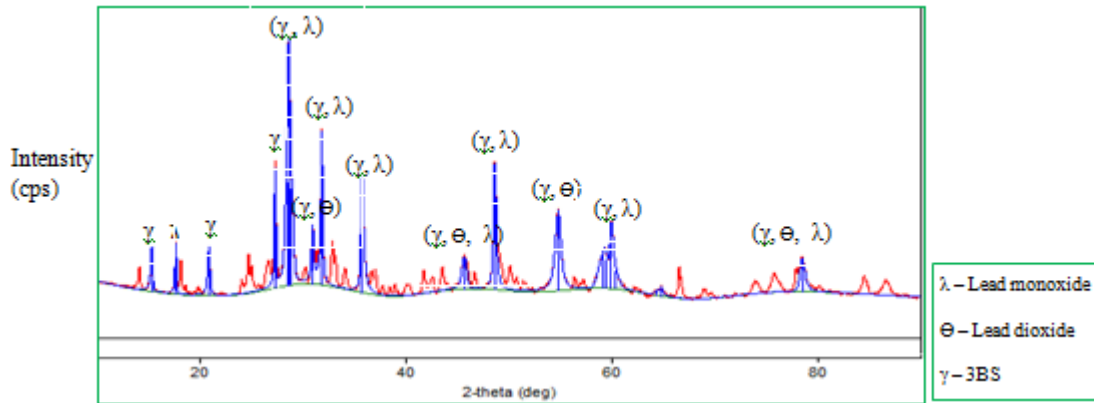


Figure 4: 1.07 g HP addition

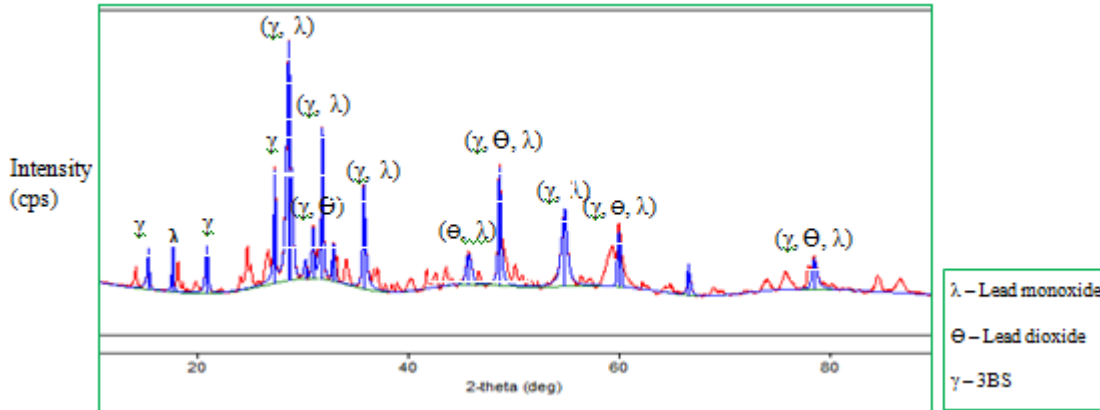
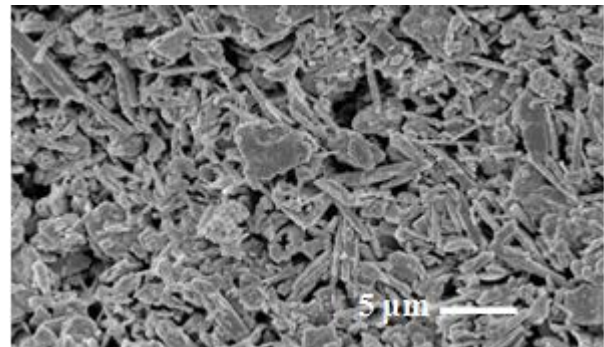


Figure 5: 2.14 g HP addition

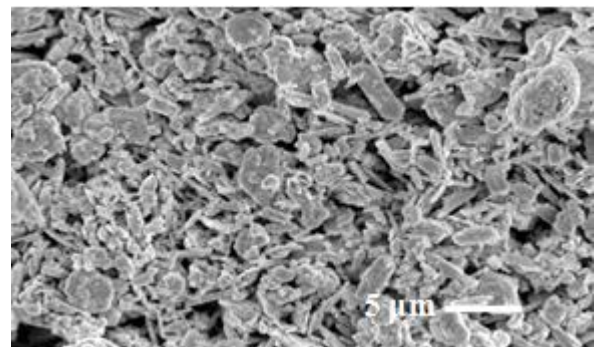
Due to the addition of small amount of HP lead dioxide peaks were observed in low intensity with lead monoxide peaks. Lead dioxide presence is evident from XRD analysis. This lead dioxide in the positive cured paste increases the conductivity during the formation process there by formation efficiency increased and formation energy reduced.

### 3.2.2 Paste morphology

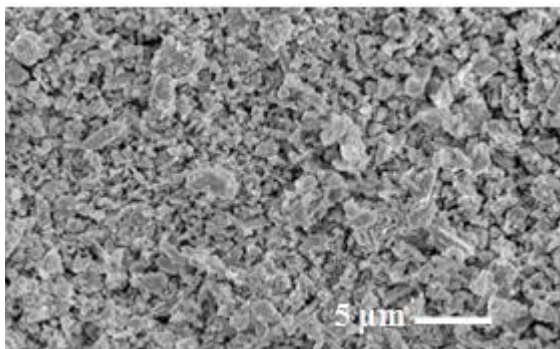
Scanning electron micrographs of positive cured paste without and with HP was carried out to check the paste morphology. Results were shown in Fig. 6. In both cured pastes lead monoxide agglomerates and cylindrical lead sulfate crystals were observed. Predominantly 3BS crystals were observed in positive cured paste without and with HP. From 3.2.1, in positive cured paste without and with HP, majority of the phases were 3BS and lead monoxide. This supports the cured paste micrographs.



(b) 1.07 g HP addition



(c) 2.14 g HP addition



(a) Without HP addition

Figure 6: Scanning Electron Microscope of cured paste with and without HP addition

### 3.3 Chemical analysis of formed paste

#### 3.3.1 Lead dioxide conversion level and Formation energy:

The conversion level of positive formed paste without and with HP obtained from different formation energies were shown in Table 4. In Table 4 all the samples were made with different formation input energies such as 5, 5.5 and 6 times the rated capacity and minimum required level of lead dioxide conversion is above 75%.

Adequate conversion of lead dioxide for positive formed paste without HP was achieved at 6 times rated capacity of formation input energy, whereas in 1.07 g HP paste required level of conversion is achieved in between 5-5.5 times of rated capacity of formation input energy and in 2.14 g HP paste at 5 times of rated capacity, required level of conversion is achieved. Thus, by the addition of this additive in positive paste during paste mixing, 20% of formation input energy can be reduced during formation.

**Table 4:** Lead dioxide content in formed paste

Sample	Input formation energy in rated capacity	Composition (wt. %)
		PbO <sub>2</sub>
NA	5	70
	5.5	73
	6	76
1.07 g HP (0.3 g AO)	5	75
	5.5	78
	6	82
2.14 g HP (0.6 g AO)	5	78
	5.5	83
	6	85

#### 3.3.2 Rate of conversion with formation energy

Rate of conversion of lead dioxide with formation input energy were shown in the Table 4. In positive formed paste without HP, conversion of lead dioxide at 5, 5.5 and 6 times rated capacity of formation input energy is 70%, 73% and 76% respectively. Rate of conversion from 5 to 5.5 times rated capacity of formation input energy is increased by 3% and from 5.5 to 6 times rated capacity of formation input energy, it is increased by 3%. So, rate of conversion is more or less same as formation input energy is increasing.

In positive formed paste with HP (1.07 g), conversion of lead dioxide at 5, 5.5 and 6 times rated capacity of formation input energy is 75%, 78% and 82% respectively. Rate of conversion from 5 to 5.5 times rated capacity of formation input energy is increased by 3% and from 5.5 to 6 times rated capacity of formation input energy, rate is increased by 4%. So, rate of conversion is more or less same for 1.07 g HP paste. However comparing positive formed paste without HP and 1.07 g HP paste, conversion rate is about 5-6% higher in 1.07 g HP paste. This indicates the presence of lead dioxide in cured paste accelerates the formation process.

In positive formed paste with HP (2.14 g), conversion of lead dioxide at 5, 5.5 and 6 times rated capacity of formation input energy is 78%, 83% and 85% respectively. Rate of conversion from 5 to 5.5 times rated capacity of formation input energy is increased by 5% and from 5.5 to 6 times

rated capacity of formation input energy, rate is increased by 2%. So, the rate of conversion in 2.14 g HP paste is slowly decreasing as formation input energy is increasing. This could be due to that, in 2.14 g HP paste the lead dioxide conversion has reached a maximum level. Similarly comparing 1.07 g HP paste with 2.14 g HP paste, conversion rate is about 3-5% higher in 2.14 g HP paste.

This indicates that the addition of HP and the resultant lead dioxide availability in the cured paste increases the rate of conversion of positive paste. Also, formation rate increases with increased addition of HP. The initial capacity test results are explained in the following paragraphs to supplement the lead dioxide conversion results.

#### 3.4 Formed cell capacity testing

Initial capacity test results of formed cell, in which positive formed paste is made without and with HP, were shown in Table 5. The required level of delivered capacity is greater than or equal to 100%.

In positive formed paste without HP, the capacity delivered at 5.5 times rated capacity of formation input energy is 103%. Whereas in 1.07 g HP paste, it is 105% and in 2.14 g HP paste is 109%. This is in corroboration with lead dioxide conversion level discussed in 3.3.2.

Comparing, 1.07 g HP paste at 5, 5.5 and 6 times rated capacity of formation input energy, delivered capacity is about 7-8% higher than positive formed paste without HP. Whereas in 2.14 g HP paste it is about 3-7% higher than 1.07 g HP. This data describes the mechanism explained in 2.2 i.e., during paste mixing, curing and drying lead monoxide reacts with HP gets oxidized to lead dioxide. The lead dioxide presence in the cured paste increases the conductivity and accelerates the formation process. So, paste with HP can improve the formation efficiency by reducing the formation input energy by 20%.

**Table 5:** Cell initial capacity (at C10 rate)

Sample	Input formation energy in rated capacity	Delivered capacity (%)
No additive (NA)	5	98
	5.5	103
	6	107
1.07 g HP (0.3 g AO)	5	105
	5.5	110
	6	115
2.14 g HP (0.6 g AO)	5	109
	5.5	117
	6	118

### 4. Conclusion

The following are the main observations from the present study:

- The use of HP can convert the residual lead to lead monoxide during paste mixing [12].
- The addition of HP in positive active material during paste mixing and subsequent curing and drying process leads to the creation of small amount of lead dioxide. This was evident from XRD analysis.

- The conductive lead dioxide present in the cured paste potentially increases the conductivity of the paste during formation, thus enables the paste to form with less formation input energy compared to without additive sample
- 2.14 g HP was shown the higher impact on lead dioxide conversion at all levels of formation input energy and adequate conversion is achieved at 5 times rated capacity of formation input energy.
- Potentially up to 20% of formation input energy can be reduced by the addition of 2.14 g HP.
- The other impact of this additive in lead acid battery performance need to be further studied.

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