

# Influence of Carbon and Interaction of Carbon and Lignosulfonate on Dynamic Charge Acceptance of Flooded (Enhanced) Lead Acid Batteries

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**Abstract:** Lead acid batteries are being developed to suit automotive micro hybrid (stop-start) applications that demands, cycling continuously at high rate of discharge and charge in partial state of charge (HRPSoC) mode. High rate of discharge is necessary for engine cranking and acceleration, while high rate charge associated with regenerative braking. In Lead acid, enhanced flooded battery is a cost effective solution for above such vehicles. Various studies reported that, flooded lead acid batteries operated in HRPSoC mode loses capacity on cycling, because of sulfation of negative plates. In order to suppress this process, the rate of charge process or the dynamic charge acceptance (DCAT) during PSoC cycling need to be enhanced. Numerous studies reported the improvement on DCAT and its impact of improved cycle life using increased level of carbon in negative active material and also with high surface area carbon materials [1]. In this study, we have used conventional carbon black and high surface area carbon at different levels along with varied level of lignosulfonate to understand the impact comprehensively on dynamic charge acceptance and high rate discharge performance. Results show that increase in carbon and high surface area carbon improves the dynamic charge acceptance, however the level of lignosulfonate also influences this performance. Increase in the lignosulfonate addition affects the high surface area carbon influence and hence affects the charge acceptance also. This indicates that the ratio of carbon to lignosulfonate need to be adjusted and extent of high surface area carbon addition to be made very carefully by assessing the other impacts on battery performance.

**Keywords:** Lead acid batteries, carbon additives, Lignosulfonate, dynamic charge acceptance, cold cranking amperes

## 1. Introduction

Lead acid battery (LAB) has been playing an active role with a long history of more than 150 years. Approaching legislation to control carbon dioxide emissions towards climate change control, combined with a continuing rise in oil based fuel prices has encouraged the introduction of various type of hybrid electric vehicles (HEVs) to the automotive market place with an ultimate aim of electric vehicles (EVs) and 'zero emission'. LABs particularly enhanced flooded battery (EFB) are considered as cost effective solution for micro hybrid type HEVs. Micro hybrids typically with an improved 12V LAB (enhanced flooded lead acid Battery, EFB or VRLA) provides a stop-start function and usually recover energy through regenerative braking. Mild hybrids add to this basic scheme the ability to make a contribution to the vehicle motive power from an electric motor-the 'power assist' system and in order to achieve this capability; they incorporate a battery with a higher voltage. At the top end of the HEV range, is the full hybrids that uses a battery at a voltage of above 100V typically. While LABs (EFB/VRLA) are active in micro hybrid, other systems (Ni/MH, Li-Ion) are under active development for mild and full hybrid vehicles as well as EVs [2-3]

The task for battery becomes more demanding through the series micro, mild to full hybrid, but in all cases the requirements is to operate from partial-state-of-charge (PSoC), so that regenerative braking energy can be accepted efficiently. From this baseline the battery is called upon far more frequently than SLI (starting, lighting and ignition) predecessor. Discharge and charge events typically involve only a small fraction of the battery capacity but they occur continuously and do take place at very high rates. Conventional lead acid batteries, such as those designed for

SLI quickly accumulate lead sulfate on the negative plate under such regime. Over the past few years it has emerged that the incorporation of elevated levels of carbon/high surface area carbon materials into the negative plate of lead acid batteries can overcome the problems in HRPSoC cyclability and led to the developments in LABs for micro hybrid vehicles such as enhanced flooded lead acid battery (EFB) and improved valve regulated lead acid batteries [3-4].

When the battery is in partially discharged state during cycling, which creates favorable conditions for a PbSO<sub>4</sub> recrystallization process to proceed, i.e. small lead sulfate crystallites dissolve and precipitate onto big lead sulfate crystals. This leads to progressive sulfation of the negative plates. On the positive plates, the discharge processes proceed in hydrated zones of PbO<sub>2</sub> particles through a series of chemical reactions which retard substantially the formation and growth of big PbSO<sub>4</sub> crystals. Moreover, the process of sulfation is impeded by the small pore radii in the lead dioxide active mass. Hence, the sulfation is confined to the negative plates only. The charge process should be accelerated to such an extent that the whole amount of sulfate formed during discharge could be converted back to lead [1].

M. Saravanan et al have studied in situ generated carbon as integrated conductive additive for hierarchical negative plate of lead-acid battery. Enhances the electrochemical performance mainly due to its low ohmic resistance between lead particle to lead particle contacts. Moreover, this contact makes the charge/discharge reaction much easier even at high rates and leads to the better charge acceptance [2].

Nakamura, Shiomi et al. have found that introduction of increased amounts of carbon black to the negative paste retards substantially the sulfation of the negative plates on

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HRPSoC cycling and the number of completed micro-cycles increases to about 5000. The authors explain the observed effect of carbon black with the formation of a conductive network of carbon around the PbSO<sub>4</sub> crystals, which is evidenced by scanning electron microscopy of the negative active mass (NAM). Hollenkamp et al. have established, within a project of the Advanced Lead-Acid Battery Consortium (ALABC) program, that addition of graphite or carbon black to the negative paste improves notably its conductivity and lowers the charge voltage of the cells. Calabek et al. have proved that the presence of carbon in NAM reduces its pore radii and thus impedes the continuous growth of PbSO<sub>4</sub> crystals, sustaining formation of small crystallites of high solubility and hence efficient charge process. Newnham et al. have found that the specific surface area of NAM is an important parameter as it sustains the potential of the negative plates below the hydrogen evolution potential. However, not all carbon forms that increase the specific surface of NAM contribute to improvement of battery cycle life on HRPSoC operation. Moseley assumes that carbon acts as an electro-osmotic pump that facilitates acid diffusion in the inner NAM volume at high rate of charge and discharge. Lam et al have created an ultra-battery with a conventional PbO<sub>2</sub> positive plate and a negative plate comprising two parts: half of it is a carbon electrode and the other half is a regular negative plate (with sponge lead active material) [1].

While most of the investigations are done with respect to carbon and its effect on HRPSoC cycling, we attempted a comprehensive study with carbon and lignosulfonate on the impact on typical battery characteristics that are relevant to application. In the present study we focused mainly on conventional carbon black at elevated level, high surface area

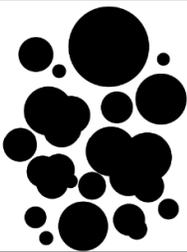
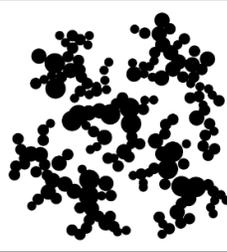
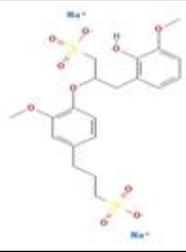
carbon addition along with lignosulfonate to improve the dynamic charge acceptance. Also, focused on the interaction of carbon and lignosulfonate. The effect was studied after curing, drying and formation through performance tests like DCAT and CCA. The material efficiency also evaluated by capacity performance test. The paste morphology of negative active material is observed after formation.

## 2. Experimentation

Experimentation was done using a lead alloy (Pb-Ca) grid of dimensions approx. 4.5" x 5.7" x 0.04" (H x W x T) for negative plate. These grids were pasted with negative active mass prepared with a typical flooded lead acid negative active material recipe, except varying the carbon material, its level and lignosulfonate level. Two types of carbon materials were used, conventional carbon black and a high surface area carbon, as explained in *Table 1* along with lignosulfonate material commonly used in automotive LABs. Here onwards it will be noted as CB (carbon black) and HC (high surface area carbon). Typical flooded type positive plate of similar dimension used. Positive and Negative plates are sandwiched with polyethylene separator of 1.0mm thickness over negative plate to form a group. Dry unformed battery was made by using those plate groups placed in a polypropylene container. Dry unformed batteries were filled with a diluted sulfuric acid gravity of 1.225 and then placed for charging under constant current mode with input capacity of 5-6 times the rated capacity of the battery.

### 2.1 Material Properties

**Table 1:** Carbon and Lignosulfonate physical, chemical properties and Structure

Property	Carbon Black (CB)	High Surface Area Carbon (HC)	Lignosulfonate
Appearance	Fine Powder	Fine Powder	Fine Powder
Ash Content (%)	5-10	3-4	<23
Moisture (%)	<10	<5	< 7
pH (10% solution)	7-9	7-9	7-8
Particle Size (µm)	6-8	< 3	0.2-0.3
Surface Area (m <sup>2</sup> /g)	<80	>500	-
Structure			

### 2.2 Mechanism of Carbon and Lignosulfonate additives

PbSO<sub>4</sub> is an insulator which does not accept current well during charging and carbon particles acts as conductive medium between these PbSO<sub>4</sub> crystals. The uniform distribution of carbon particles are necessary to get this benefit by creating more pores and this porous structure acts as reservoirs for acid in the bulk to avoid sulfation.

Lignosulfonate is an organic additive used in negative active material. It helps in increasing the low temperature high rate

discharge performance. Lignosulfonate is a polymer containing phenyl propane groups building a three-dimensional mesh-like structure. The structure of lignosulfonates comprises various structural groups with micropores in-between. These micropores allow transfer of ions through the layer of Lignosulfonates adsorbed on the metal surface. Lignosulfonates form a layer of polyelectrolyte on the lead surface, which impedes the formation of a passivating PbSO<sub>4</sub> layer on the negative electrode. Thus,

through their structural properties, lignosulfonates protect the negative plates from passivation [7 - 8].

## 2.3 Experimental Procedure

### 2.3.1 Preparation of negative paste with carbon material

Negative active material was prepared by using ball mill leady oxide (with 25-30 wt. % residual lead). Binder (polyethylene terephthalate) was mixed with leady oxide. Additives, barium sulfate (kept constant), lignosulfonate and carbon was added slowly and mixed thoroughly for about 3 minutes with varied levels as explained in *Table 2*, different paste mix batches were made accordingly, water and sulfuric acid was added to the above dry mix each and the contents are thoroughly mixed for about 20 minutes. The temperature of the mix was maintained below 60°C and the paste density was adjusted to 4.50 +/- 0.05 g/cc. The required weight of the paste is weighed in micro balance and applied to the grid. After pasting, the plates were again weighed to confirm the exact amount of paste applied and then loaded into curing and drying chamber. Plates were cured at about 50±5°C by maintaining >90 % humidity for about 24 hours and then dried at 60°C for 24 hrs.

**Table 2:** Negative plates with carbon

Additive/ description	CB (Wt. % of Leady Oxide)		HC (Wt. % of Leady Oxide) + 0.2Wt. % of CB			
	0.2	0.5	0.1	0.2	0.1	0.2
Carbon	0.2	0.5	0.1	0.2	0.1	0.2
Lignosulfonate	0.5	0.2	0.5	0.5	0.6	0.6
Experimental Sample – ID	CB1	CB2	HC1	HC2	HC3	HC4

### 2.3.2 Battery Samples Assembly and Formation

These negative plates which are enveloped with polyethylene separator were assembled with regular positive plates and are placed in typical flooded lead acid battery plastic container made with polypropylene copolymer. Dry-unformed batteries were filled with chilled electrolyte (sulfuric acid) of 1.225 relative density. After soaking the plates in electrolyte for 30 minutes, charging given under constant current process with an input capacity of 5-6 times the rated capacity of the battery. Adequate water circulation is provided so that electrolyte temperature is well within 60°C. Formed batteries had an open circuit voltage of 12.80 +/- 0.05V and electrolyte relative density of 1.270. In each combination 4 samples were prepared (1 for formed negative active material analysis, 3 for electrical performance characteristics evaluation) to ensure the consistency in results. The samples are labeled as indicated in *Table 2*.

## 2.4 Analysis

The formed negative plate samples were analyzed for paste morphology using SEM (scanning electron microscope) and XRD (X-ray diffraction) to understand the impact of carbon. Formed battery samples subjected to electrical performance characterization using programmable life cycle testers. The evaluation done initially for specific capacity, followed by dynamic charge acceptance test, cold cranking test and charge characteristics test at 14V and 16V.

### 2.4.1 Paste Morphology

The analysis of paste morphology of negative active material (NAM) with CB and HC was determined by scanning electron microscopy (SEM). All negative plates were thoroughly washed (immediately after cut open) in demineralized water, then in acetone and dried in cold environment to prevent lead oxidation. The samples were sputter coated with a thin layer of platinum, 5nm 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 12mm, a spot size of 30 and an electron beam voltage of 10KV.

### 2.4.2 X-Ray Diffraction

The phase composition of negative active material (prepared and dried as explained in 2.3.1) with CB and HC was determined using RIGAKU ULTIMA-IV X-Ray diffractometer, with Cu K $\alpha$  radiation. Scans were conducted in the 2 $\theta$  range of 10–90°, with a scan time of 4deg.min-1.

### 2.4.3 Electrical Performance Characteristics

The electrical performance characteristics of the CB and HC samples were analyzed by using LCN-Bitrode (USA), life cycle testers.

#### 2.4.3.1 Specific capacity test (SCT)

The battery discharged at a constant current I<sub>20</sub> = Rated Capacity/20, until the battery terminal voltage falls to 10.5V. The duration t is recorded. The capacity is arrived by multiplying current (A) and duration (Hour).

#### 2.4.3.2 Cold Cranking Performance test (CCA)

The battery is stored in a cold chamber at temperature of (-18 ± 1) °C until the acid temperature in a centre cell reaches (-18 ± 1) °C, Afterwards, the battery is discharged at the associated test current for low temperature for a duration of 30seconds. The 30 second voltage is recorded.

#### 2.4.3.3 Dynamic Charge Acceptance test (DCAT)

Full charged battery is soaked at (25±2°C) for 6 hours. The battery is discharged with current of I<sub>20</sub> for 2 hours at the same temperature to reach SOC of 90%. Then, battery is charged at (14.0±0.05) V with current limited to 100 A for 10 sec at (25±2°C). The current over time is recorded during this charging step.

#### 2.4.3.4 Charge Characteristics test (CCS)

Fully charged battery charged at 16V, 2 x I<sub>20</sub> current limit for 24 hours the current and ampere hour (Ah) data is recorded during charging. Similarly battery is charged at 14V, 2 x I<sub>20</sub> current limit for 24 hours the current and ampere hour (Ah) recorded.

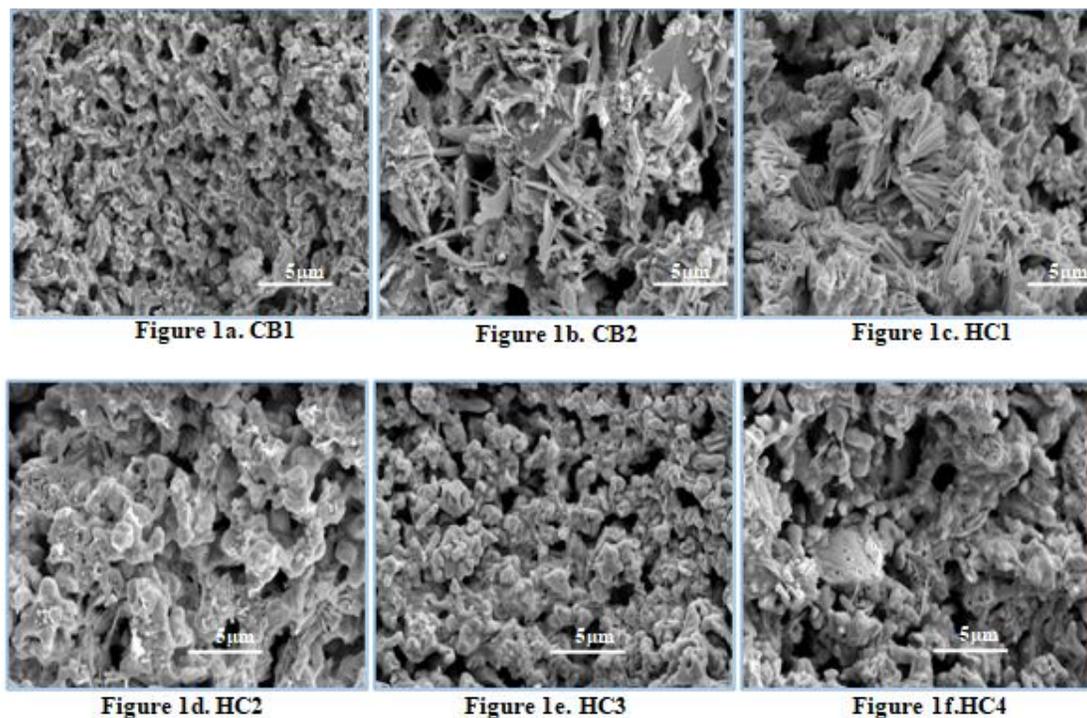
## 3. Results & Discussion

### 3.1 Paste Morphology

SEM analysis of formed negative active material samples is carried out to check the impact of CB and HC on paste morphology. Results are shown in *Figure 1*. The basic sponge lead skeleton formed out of tribasic lead sulfate observed in all the samples. Increase in the carbon black addition and thus reduction in lignosulfonate (CB2) to the negative active material increases the carbon particles adsorption on skeleton

structure. Similar change observed between HC1 and CB1, i.e. when high surface area carbon added over carbon black. This explains the carbon particles adsorption over the spongy lead structure when carbon content increases. This is in line

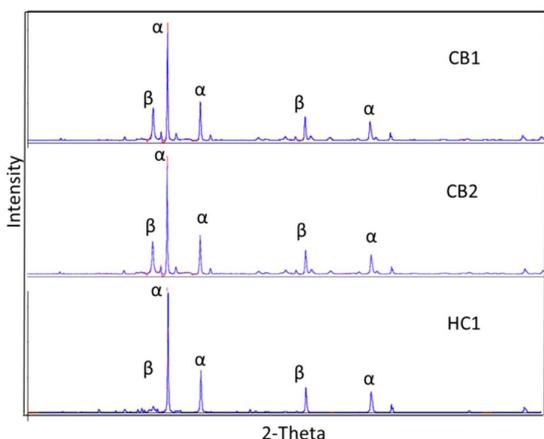
to the observation from *D. Pavlov et al [1]*. From the SEM pictures of HC1 and HC3, opposite effect is evident when lignosulfonate is increased.



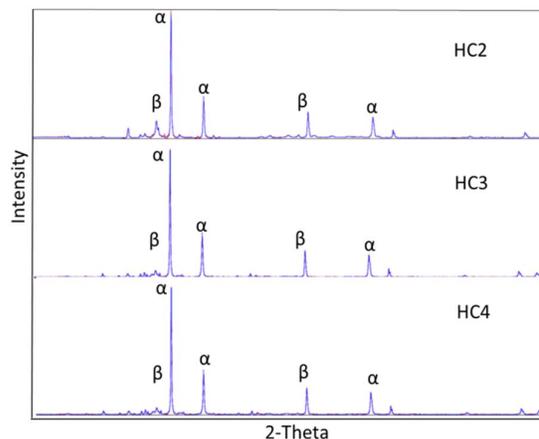
**Figure 1:** Formed negative active material SEM

### 3.2 X-Ray Diffraction Analysis

XRD analysis is performed on formed negative active materials made with CB and HC. Results were shown in *Figure 2*. The characteristic lines of the substances are sponge lead and lead oxide which were denoted by  $\alpha$  &  $\beta$  respectively. Sponge lead (Pb) peaks were obtained at 2-theta values of 31.2, 36.2 & 62.1 whereas lead oxide peaks were obtained at 2-theta values of 29.0 & 52.2. Peak intensity versus diffraction angle ( $2\theta$ ) plots for all the experimental samples looks similar, which indicates sponge lead conversion is similar in all the experimental samples ranging from CB1 to HC4.



**Figure 2a**



**Figure 2b**

**Figure 2:** Formed negative active material XRD analysis

### 3.3 Formed Battery Electrical Performance:

Electrical performance was tested for all the experimental samples mentioned in *Table 2*.

#### 3.3.1 Specific Capacity Test (SCT)

All the experimental samples given similar specific capacity output which is presented in *Figure 3*, which indicates there is no impact in specific capacity if the carbon content in the negative active material is varied or high surface carbon is

added to the negative active material to an extent as shown in Table 2.

### 3.3.2 Cold Cranking Performance Test (CCA)

Cold cranking test results for all the experimental samples were given in Figure 4, sample made with increased carbon black (CB2) resulted in the reduced cold cranking performance compared with CB1. Samples made with high surface area carbon and with increased lignosulfonate quantity (HC3 & HC4) have shown higher cold cranking performance compared with the other samples, implies the significant linear effect of lignosulfonate over low temperature performance. These results are in agreement with the findings of *shandong jinkeli power sources technology co., ltd, china* [5]. Samples made with high surface area carbon without increasing the lignosulfonate quantity (HC1 & HC2) resulted in the reduced cold cranking performance in comparison with that of HC3 & HC4.

### 3.3.3 Dynamic Charge Acceptance Test (DCAT)

The charge acceptance current (specific current) for all the experimental samples were plotted in Figure 5. CB2 accepted around 1.09 times higher current than CB1 because of increase in the carbon black addition. Addition of high surface area carbon along with carbon black in HC1 & HC2 which provides more surface area, thus HC1 & HC2 accepts around 2.4 times more current than that of CB1 & CB2. Compared to carbon black, the high surface area carbon has significant effect on DCAT. This observation is also explained by *J. Settlein, J.Oehm, B. Bozkaya, et al* [6] studied that the charging currents can dramatically be improved with carbon additives with a high external surface area or small primary particles. In HC3 & HC4 where lignosulfonate content also increased along with the addition of high surface area carbon, HC3 & HC4 accepts around only 1.4 times higher current than that of CB1, the addition of increased lignosulfonate content affects the DCAT and decreases the current acceptance lower than HC1 & HC2.

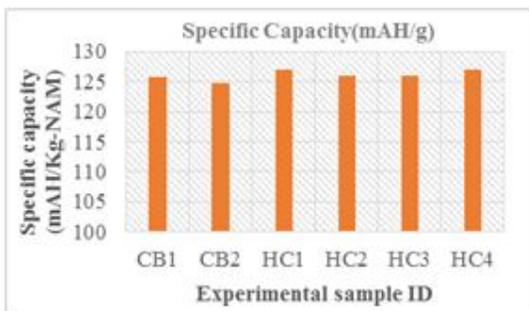


Figure 3

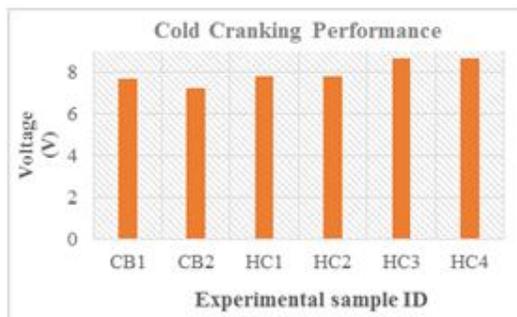


Figure 4

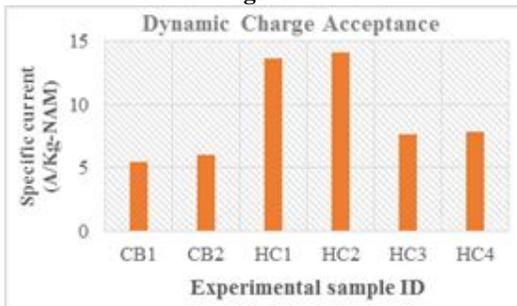


Figure 5

### 3.3.4 Charge Characteristics Test (CCT)

Fully charged batteries were over charged at a constant voltage of 14V/15A. Plots were given in Figure 6 and Figure 7. All the test samples charging behaviors look similar and charge current rate doesn't change at 14V charging, which indicates that at lower charging voltages increase in carbon black (CB2), addition of high surface carbon (HC1 & HC2) and addition of high surface area carbon along with increased lignosulfonate (HC3 & HC4) doesn't result any impact over the charge characteristics at 14V.

Fully charged batteries were over charged at a constant voltage 16V/15A. At 16V charging batteries made with increased carbon black doesn't show any significant change in a given point of time. Whereas the charge characteristics of batteries made with high surface area carbon (HC1 & HC2), i.e. the ampere hour input (Ah) is about 1.3 times higher than CB1 & CB2. The batteries made with high surface area carbon and an increased lignosulfonate (HC3 & HC4) resulted in increase of only about 1.2 times higher Ah input in comparison with that of CB1 & CB2. The higher Ah input indicates the battery is drawing more current at a given point of time when charged from 100 % SOC. It clearly shows that at higher voltages high surface area carbon and lignosulfonate have significant impact on the charging characteristics of the battery. Higher addition of high surface area carbon results in the overcharge of the batteries which may potentially lead to higher corrosion of the grid and water loss.

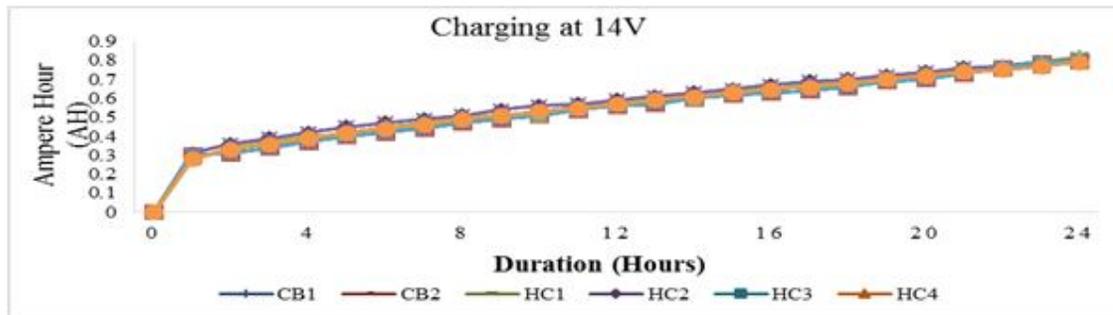


Figure 6

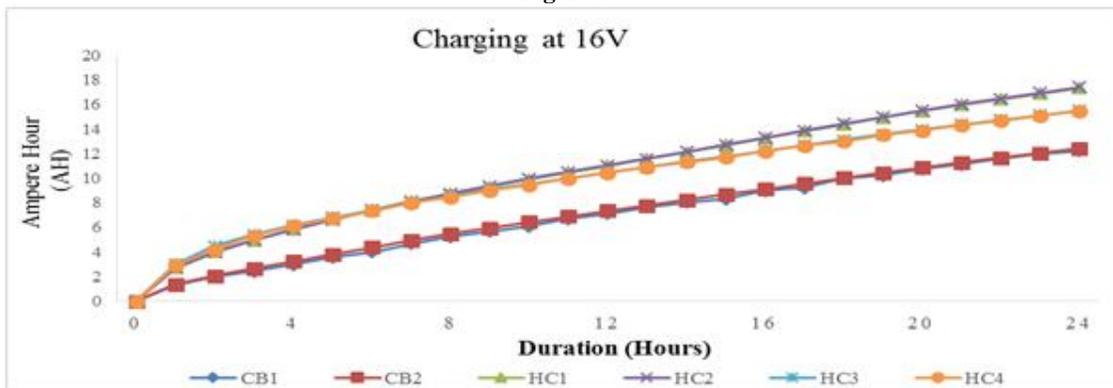


Figure 7

#### 4. Conclusions

- Increase in the carbon black addition and reduction in the lignosulfonate to the negative active material increases carbon particles adsorption on skeleton structure. This composition doesn't impact specific capacity, but results in the reduced cold cranking performance of the battery. It slightly (1.09 times) increases the dynamic charge acceptance of the battery.
- Addition of high surface area carbon along with carbon black results in more coverage of skeleton structure. This addition of high surface area carbon shows dramatic increase in the dynamic charge acceptance of the battery, and it slightly improves the cold cranking performance. When charging at 100 % SOC at higher voltages, this addition of high surface area carbon to the negative active material resulted in higher current input comparatively, which can have a negative impact on battery, particularly grid corrosion and water loss.
- Addition of high surface area carbon and proportionately increasing the lignosulfonate to the negative active material results in significant increase of cold cranking performance of the battery and reduced dynamic charge acceptance in comparison with that of HC1 & HC2. This effect also seen in charging behavior at 100 % SOC.
- Hence, an optimal blend of carbon black, high surface area carbon along with lignosulfonate gives better cold cranking, dynamic charge acceptance and charge characteristics of the battery.
- Further studies on PSoc cycling test and vehicle fleet testing, will lead to more understanding.

#### 5. Acknowledgements

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