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Sodium Sulphate as an Electrolyte Additive and its Influence on the Performance of the Lead Acid Battery

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Abstract: ***The sodium sulphate in the electrolyte and its influence on the electrochemical characteristics such as capacity, reserve capacity, cold cranking ampere, high rate discharge and charge acceptance of the lead acid battery have been investigated. The studies have been carried out on the 12V-65Ah automotive flooded type battery. The structural and morphological characteristics by X-ray diffraction and Scanning Electron Microscopy are performed respectively in order to understand the influence of modified electrolyte on the positive plate properties of the charged battery. The XRD spectral analysis reveals that lead based compounds PbO_2 and $PbSO_4$ have been found to be in acceptable range when the additive percentage closer to 2.0%. Further, the morphology of the PbO_2 particles are found to be uniform compared to standard sample as evidenced from the SEM. The morphological studies on the positive plate and electrical characteristics of the batteries in the modified electrolyte were found to be sensitive to percentage of dosage of the sodium sulphate. The small dosage has beneficial on the properties of electrode performance of the battery. Thus, the influence of sodium sulphate on the electrical and electrode properties on the charged battery were studied and the results were correlated and discussed.***

Keywords: Sodium sulphate, Capacity, X-ray diffraction, Scanning Electron Microscopy and Lead acid battery

1. Introduction

Lead acid battery technology is being used for several years and remains as the most reliable power source for automotive and industrial applications. Unlike other rechargeable batteries, this technology is the most economical and competitive to other rechargeable batteries, thus it continues to dominate in the market. The abundance of raw materials, extensive reuse of recycled lead further boost the widespread use of this technology. However, the specific energy of the technology is relatively lower , thus considerable research efforts are going on to improve the performance of the technology by addressing the electrodes, electrolyte, grids, terminal compositions and also passive components such as separator, poly containers vent caps, etc., of the battery. These constituent ingredients in mentioned items were addressed to achieve desired results of the lead acid battery for meeting the requirement for the electric/hybrid vehicles and other demanding applications.

The electrical performance of the battery is closely related to the structure of positive and negative electrodes which undergo chemical changes during discharge and charge processes respectively. The chemical reaction processes should be 'reversible and stable' for several cycles of charge/discharge thereby to guarantee the life of the battery. In case of any irreversible processes occurring in the battery, the kinetics of the electrode reactions get slower which obviously impair the performance and life of the battery. During discharge, the specific conductivity of electrolyte decreases and internal resistance of the battery increases due to the formation of $PbSO_4$ both of these aspects limiting the cell capacity [1]. The problem gets aggravated in the deep discharged conditions as the so formed sulphated crystals become too hard to get dissociated during subsequent charging process. In order to control the size and shape of the sulphated crystals, several approaches were adopted in the past and one of the ways to improve the performance is to add additive in the respective positive, negative electrode paste recipes and /or electrolyte of the battery.

An extensive research has been carried out in this direction to mitigate the failure and to meet the design life of the battery. The role of inorganic additives such as phosphoric acid, boric acid, soluble metal sulphates, polymers, mixed additives and also different ions in the electrolyte have been investigated by several researchers and these studies infer a remarkable improvement in the performance of the battery [2-13]. The most beneficial additive is observed to be the phosphoric acid which improves the cyclic life under deep discharge but with a downside effect of capacity drop [2, 3].The beneficial role of phosphoric acid was attributed to increase in oxygen over-potential of the positive electrode, reduction in shedding, irreversible sulphation in the PAM and also lower self-discharge characteristic of the battery. The advantage of citric acid in the sulphuric acid electrolyte favourable to the charge /discharge process was reported by Wei et al, [4]. However, an increase in dosage of citric acid has adverse impact on the oxygen and hydrogen gas evolution at the positive and negative electrodes respectively. There is an interesting report on the deferred softening of the positive active mass and inhibition of stratification of electrode plate and significant improvement of battery life with the presence of $H_3PO_4$and colloidal silica in the electrolyte [5]. In another report, it is mentioned that the addition of $SnSO_4$ in sulphuric acid electrolyte improves the re-chargeability and capacity under deep discharge cycling. The improvement of charge acceptance and reduced water loss have also been reported by presence of $SnSO_4$ in the electrolyte [6-8]. The benefit of the mixed additives such as phosphoric acid -boric acid, phosphoric acid- tin sulphate when introduced into the electrolyte reported to reduce corrosion of the positive grids and the lugs of negative grids. In a study on the influence of varying ions comprising Sn^{2+}, Sb^{3+}, Co^{2+}, Mg^{2+} and Al^{3+} on the formation of PbO_2 particles, while certain types of ions exhibited remarkable

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influence on the structure of positive active material, other metal ions helped to enhance the capacity [9-11]. Fengliang et.al reported that the effect of inorganic positive ions such as Al^{3+}, Mg^{2+}, Ca^{2+}, and traces of Cd^{2+} improve the electrode behaviour and accordingly the service life of lead acid batteries [12]. The presence of Li+ ions in the electrolyte exhibited a favourable impact on the discharge capacity of the positive electrode [13]. Presence of sulphate salts to the battery electrolyte to reduce the solubility of lead sulphate reduces the number of failures from shorting when the battery is deeply discharged or stored with minimal electrolyte. [14-17].

Thus, the authors understand that the additives are of considerable interest to improve the electrochemical activity of the electrodes as well as electrical performance of the battery. Thus, the sodium sulphate (Na_2SO_4) is chosen for the study.

2. Design and Battery Testing

2.1 Preparation of Electrolyte

The modified electrolyte was prepared with different concentrations of sodium sulphate by adding to aqueous electrolyte. The dosage of sodium sulphate maintained at x% where x = 0%(Standard), 0.5%, 0.75%, 1.0%, 2.0%, 4.0%, 6.0%, 8.0% and 10.0% .The corresponding battery samples were labelled as A, B, C, D, E, F, G, H and I respectively. The electrolyte with sodium sulphate, here after referred to as the modified electrolyte. The density of the electrolyte is expected to vary by the presence of sodium sulphate in the electrolyte, and the same was measured using Anton Paar Density meter (Model: DMA 35). The test batteries (12V-65Ah) were manufactured by adopting the automotive battery manufacturing method.

2.2 Test battery design

The flooded battery consists of 8 positive and 7 negative plates. The average apparent density of positive and negative plates was4.25g/cc and 4.4g/cc respectively. The polyethylene with glass mat leaf was used as a separator. The aqueous sulphuric acid with 1.225 relative density was used as filling electrolyte and considered as standard electrolyte in this experiment. It is usual that battery manufacturers maintain a maximum of 1.28 relative density of sulphuric acid for fully charged battery. Keeping this in mind and in view of the fact that the addition of sodium sulphate increases the relative density of the sulphuric acid, a relatively lower gravity i.e. 1.225 was chosen in the present study so that end of charge acid concentration does not cross the threshold value of 1.280.The assembled LAB group was subjected to galvano-static multi-step pulsed mode of charge formation technique by jar formation method until it receives 250% of its rated (theoretical) capacity. The effect of different wt. % addition of sodium sulphate on the electrical performance of the batteries was studied by introducing it into the electrolyte as desired. The experimental plan was tailored systematically by varying the concentration (wt. %) of sodium sulphate as electrolyte additive.

2.2.1 Electrical studies

The electrical studies on the flooded type battery (12V-65Ah) were carried out. The electrical characteristics such as reserve capacity, capacity, cold cranking ampere, high rate discharge and charge acceptance were studied as per JIS D5301. The battery life cycle tester (Make: Bitrode, USA) was used to pursue the studies and data related to voltage, current and discharge time was captured automatically i.e., with the help of computer controlled software.

2.3 Surface area

The electrochemical properties of the electrode depend on its surface area. The higher surface area facilitates greater electrochemical activity of the battery and it is of interest to study this parameter. The representative sample of active mass was collected as shown in Fig.1 and estimated its surface area by the Brunauer-Emmett-Teller (BET) surface area analyser (Make: Coulter SA3100). The data analysis was carried out using an in-built software.

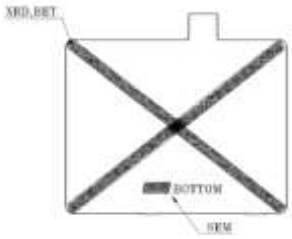

Figure 1: Positive active material Sample collection for BET, XRD and SEM analysis

2.4 Studies by X-ray diffraction (XRD)

The active mass of the positive plate that is collected from different parts of the plate as shown in the Fig.1, was washed thoroughly with distilled water in order to remove the adsorbed electrolyte and then dried for 12hrs. The dried active mass was then grounded into fine powder using a mortar and pestle. The resultant powder was used for analysis by X-ray diffraction (XRD) Ultima IV X-ray diffractometer RIGAKU Corporation, Japan. The XRD spectra were recorded on 2θscale in the range of 10-90°with a scan rate of 4°per minute using Cu K α Radiation (λ=1.54Å).

2.5 Morphological Studies by Scanning Electron Microscopy (SEM)

The size and shape of the electrode particles do influence the electrode stability and therefore justifies the need for understanding this parameter when sodium sulphate is introduced into the electrolyte. The collected samples for SEM analysis were initially subjected to platinum sputtering in order to facilitate conductive surface which in turn improve the image clarity significantly. The SEM images were recorded at 10 kv with working distance of 11-12 mm. The morphology of the active mass was obtained by SEM-EDX using JSM6010PLUS, JEOL, Japan.

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3. Results &Discussion

3.1 Influence of the Na_2SO_4 on the density of the electrolyte

As mentioned earlier the electrical performance of the battery strongly depends on the electrolyte characteristics i.e.,having direct impact on the component properties, particularly the grid corrosionthat increases with increase of concentration of the electrolyte. The sodium sulphate in the aqueous sulphuric acid electrolyte acts as buffer solution and also expected to improve the reversibility of redox reaction in the lead acid battery. Further, the density of the electrolyte changes with Na_2SO_4concentration in the electrolyte and the same is depicted in Fig.2.

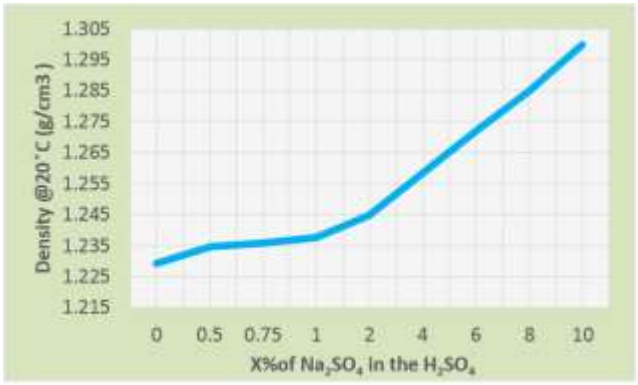

Figure 2: Influence of the Na_2SO_4 content on the density of H_2SO_4

As evident, that the density of the electrolyte changes with increase of the sodium sulphate percentage in the electrolyte. The variation in the density of the electrolyte with additive dosage was categorized into two regions. In the region-I, the change in the density of the electrolyte with addition of the Na_2SO_4 up to 2.0%is observed to be marginal. The increase of the Na_2SO_4 from 2.0% to 10% in the electrolyte (Region II) is found to increase density linearly. The solubility of the lead sulphate depends on the concentration of Na_2SO_4in electrolyte and higher concentration is expected to decrease the solubility of $PbSO_4$ which impede the charging process of the battery [18].

3.2 Electrical studies

The electrical studies were carried out as per JIS D 5301. The sample batteries are subjected to full state of charge and allowed to stand for 1 hour prior to studying various battery characteristics such as reserve capacity, capacity at 5h, cold cranking, high rate discharge, charge acceptance. The results were reviewed from view point of electrolyte concentration and properties of the positive plate.

3.2.1 Reserve Capacity

The test was carried out in an ambient environment controlled at 25.0˚C ±2.0˚C. The battery was discharged with a current of 25.0 Amps until the terminal voltage falls to 10.5Vand noted down the duration of the discharge. The obtained discharge time as expressed in minutes is shown in the Fig.3. From figure, it was found that all the samples met the JIS requirement, except sample -I. Further, a very interesting trend was apparent that the reserve capacity fell initially with addition of 0.5 Wt.% salt and then slowly risen to reach the value of standard sample when the salt concentration reached 1% and then again dropped continuously with further increase in the salt concentration.

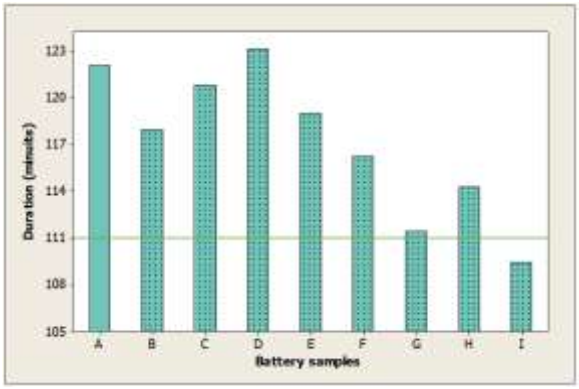

Figure 3: Influence on Na_2SO_4 concentration in Reserve Capacity.

3.2.2 Capacity at 5h rate

The capacity depends on the quantity of both active material and electrolyte. Samples are placed in a water bath maintained at a temperature of 25.0˚C ±2.0˚C. The battery was discharged with 5hr current until the terminal voltage falls to 10.5V and measured duration of the discharge. The capacity was derived with input current and operation duration of the time. The observed test results are shown in the Fig.4. It is evident that both standard and modified electrolyte samples met the JIS requirement. Nevertheless, the modified samples exhibited a marginal drop in capacity compared to standard sample inferring non significance of higher salt concentrations.

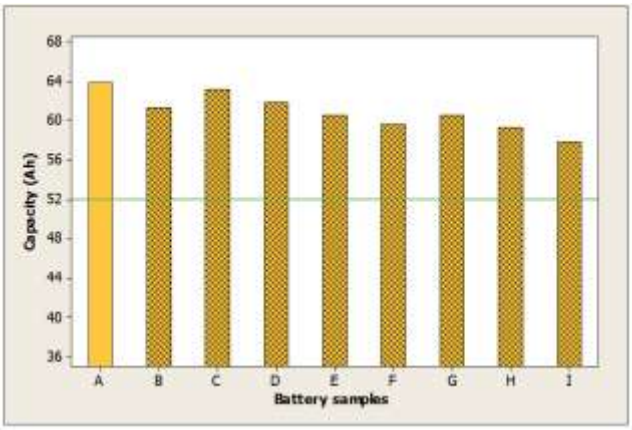

Figure 4: Influence on Na_2SO_4 concentration in 5h capacity

3.2.3 Cold Cranking Ampere (CCA)

The samples were placed in an environmental chamber maintained at temperature at -18˚C ±1˚C for 24hrs. At the end of soaking period, the samples were subjected to cold cranking test and measured the 30th sec discharge voltage of the battery. The observed test results are shown in the Fig.5. Itis observed thatall the samples met the JIS requirement. Further, the negative impact of Na_2SO_4 was evident, particularly when Na_2SO_4concentration exceeded 0.75 Wt. % and the impact became more pronounced with increasing concentration.

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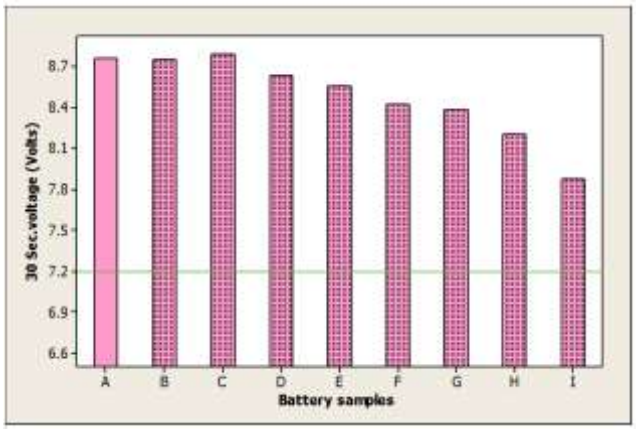

Figure 5: Influence on Na_2SO_4 concentration in CCA at -18˚C.

3.2.4 High Rate Discharge (HRD)

The samples were placed in an environment chamber maintained at temperature 0of -15˚C±1˚C for 16hrs and then the batteries are discharged with current until the terminal voltage falls to 6V and recorded the 5th sec discharge voltage and duration in minutes. The results are presented in the Fig.6a &6b respectively. Comparison of results, infer that the samples met performance requisites of JIS standard. Further it isof interest to note the 5th sec voltage increased marginally particularly at1% concentration and even more interesting phenomenon is yield time exhibiting an improvement in the concentration rang of 6to10%

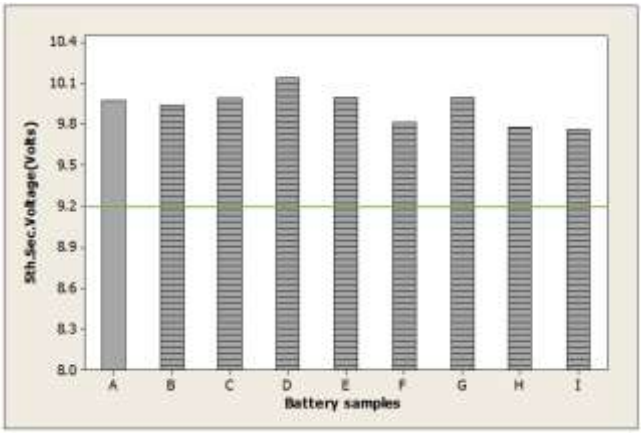

Figure 6 (a): Influence on Na_2SO_4concentration in HRD at voltage

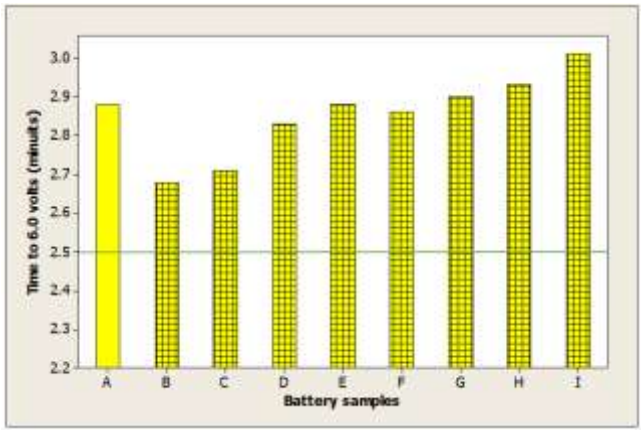

Figure 6 (b): Influence on Na_2SO_4concentration in HRD at yield time

3.2.5 Charge Acceptance

The batteries are soaked at 0˚C ±1˚C for 12hrs and then charged the battery at a constant voltage of 14.4V±0.1V and measured the 10th minute current from the start of charging of the battery. The observed results are presented in the Fig.7. The results infer the charge acceptance of samples comply the requirement of JIS standard but increasing in addition of Na_2SO_4exhibiting a negative impact on charge acceptance. The results are in agreement with reported literature (19).Pavlov et.al. Explained the charge acceptance of the battery declines at higher acid concentrations, because of low $PbSO_4$ solubility. While adding Na_2SO_4 in acid electrolyte, the concentration of sulphate ion increases therefore the solubility of $PbSO_4$ decreases, which in turn reduces the charge acceptance.

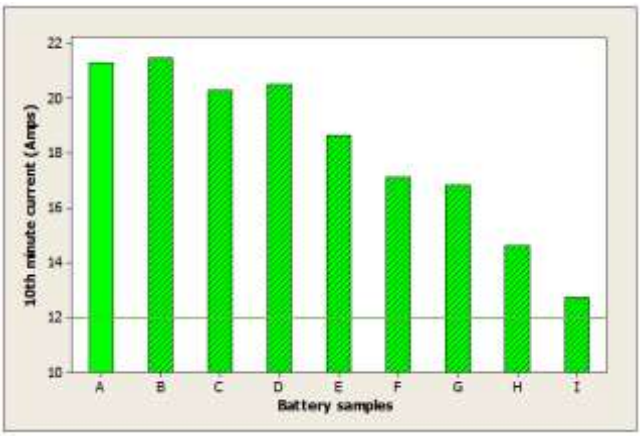

Figure 7: Influence on Na_2SO_4concentration in Charge acceptance

In summary, the study of short term electrical performance of the batteries does not show any significant advantages with increasing concentrations of Na_2SO_4 addition. The endurance performance must be considered for complete understanding considering the fact that dendritic growth of lead sulphate crystals is strongly influenced by Na_2SO_4 concentration in the electrolyte which in turn exhibits a profound impact on battery life.

3.3 Surface area of PAM

The surface area is one of the factors in improving the electrochemical activity of the active mass and also electrical performance of the battery. The surface area is related to particle size of theactive mass, smaller the particles larger is the surface area. The surface area of the positive plate for the samples is shown graphically in the Fig.8.

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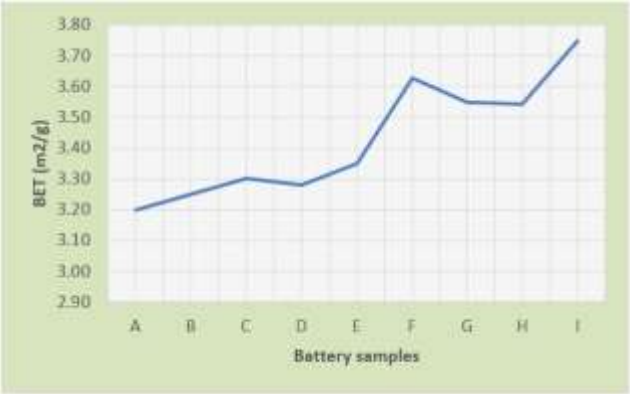

Figure 8: BET Surface area of the formed Positive active material

From the figure, it is observed that the samples,namely, A to E are found to be consistent and the average surface area of A to E samples is 3.3 m^2g^{-1} whereas this values happens to be 3.61 $m^2g^{-1}$for samples F to I. The increased surface area from F to I samples is attributed to smaller PbO_2 particles as evident from micrographs of the SEM. However, such an improvement has not shown any improvement in high rate electrical performance of the battery (Figs. 3.2.3&3.2.4).In this context, the understanding of influence of Na_2SO_4 on the negative plate properties is needed to get further insight into the subject. In high discharge current applications, the available surface of the electrodes coupled with high pore volume becomes importantas acid that freely flow into the porous material to react with the inner active sites [20].

3.4 Structural Studies by X-Ray Diffraction (XRD)

The electrode stability is one of the factors for enhanced electrical characteristics of the lead acid battery. The structure stability of the positive electrode in the standard and modified electrolyte with different dosage of the sodium sulphate were investigated by X-ray diffraction (XRD). Obtained XRD spectra profiles from A to I samples are shown in Fig.9.

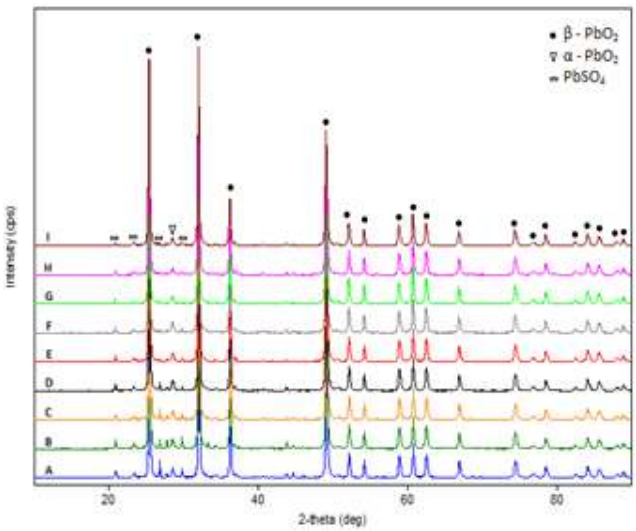

Figure 9: XRD patterns for tear down battery positive active mass samples as a function of sodium sulphate content in the electrolyte

From the Fig.9, all detected peaks were identified to be α-PbO_2, β-PbO_2, and $PbSO_4$ although no differences in the spectra were obtained, changes in peak intensity were clearly detected. As the result of comparison for presented in the Table2. The XRD analysis reveals that the formation of well-defined crystals in the positive electrode as evidenced from the sharp peak of the sample. The higher percentage of the PbO_2 means better is electrochemical activity of the plate. The qualitative analysis of A to I samples, the formation of PbO_2 is more when the Na_2SO_4 concentration is optimal. It means that the lead sulphate percentage decreases proportionally at optimal concentration.

Table 1: XRD phase composition data for the positive active mass samples

Battery samples	wt. % of Na_2SO_4	Phase component (wt. %)		
		β-PbO_2	$PbSO_4$	α-PbO_2
A	0	76.2	17.9	5.89
B	0.5	80	13.1	6.84
C	0.75	85.7	8.2	6.06
D	1	84.2	9.1	6.66
E	2	86.5	8.3	5.2
F	4	84.6	11.1	4.29
G	6	83.1	11.8	5.1
H	8	82	12	6.26
I	10	78.6	15	6.12

3.5 Morphology of Positive electrodes by Scanning Electron Microscopy [SEM]

The influence of sodium sulphate on the plate morphology of the lead compounds such as PbO_2 and $PbSO_4$ were examined (Fig.10) in the charged state by Scanning Electron Microscopy (SEM) coupled with Energy Dispersive Spectroscopy (EDX).The SEM analysis showed that the additive has a significant influence on the growth of PbO_2 and $PbSO_4$particles. The presence of $PbSO_4$ and PbO_2 crystals for A to I are captured at low (200X) and high (10Kx) magnifications. Further, the images at higher magnifications are indexed as A1 to I1 for greater visibility.It can be observed that a few $PbSO_4$ crystals are noticed for samples A&B, also a few of the $PbSO_4$ crystals possessing small holes and indentations in their surfaces. The absence of $PbSO_4$ crystals was evident in case of samples C and E. The observations are in agreement with literature i.e. the crystals of $PbSO_4$hardlydiscernible in case of charged state of the plate. However, the trend is changed with increase in additive concentration i.e. from E to I samples where the formation of $PbSO_4$crystals is observed. According to Le Chatelier's hypothesis state that the presence of additives, one of the common ions from additive or other compound will shift to the reaction to left thereby reduce the solubility of the solid and to maintain the equilibrium.

Analysis was also undertaken to understand the crystallites size and distribution of PbO_2crystals (Ref to A1toI1). The study reveals that the size of the PbO_2 grains increase with Na2SO4concentration up to 1 Wt. % (A1 to D1) and tend to form agglomerates when the concentration is increased further (E1 to I1). Therefore, that the sodium sulphate concentration is to be chosen carefully for well controlled

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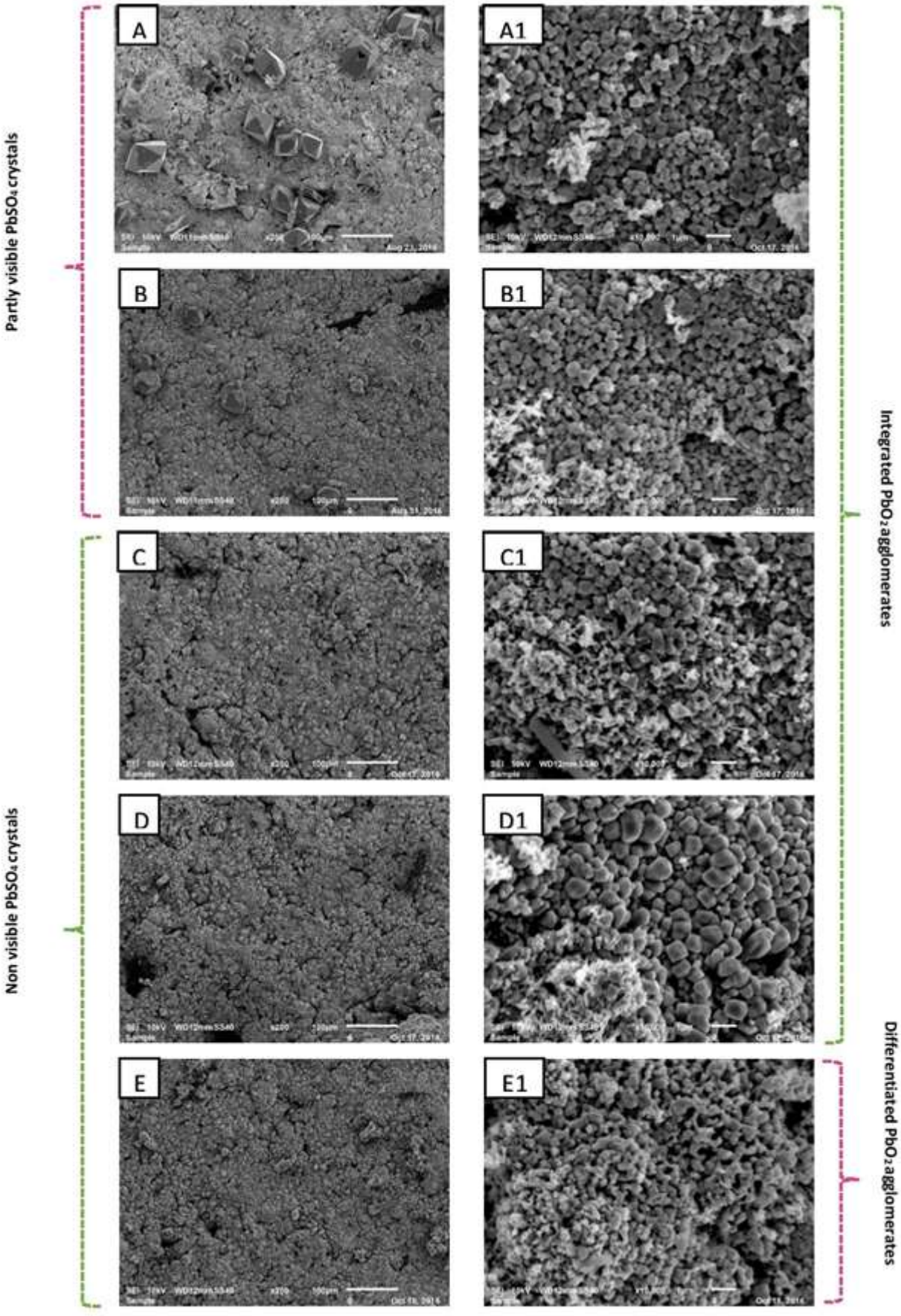
$PbSO_4$/ PbO_2crystals and for balancing the electrical and electrode properties to obtain better performance of the battery.



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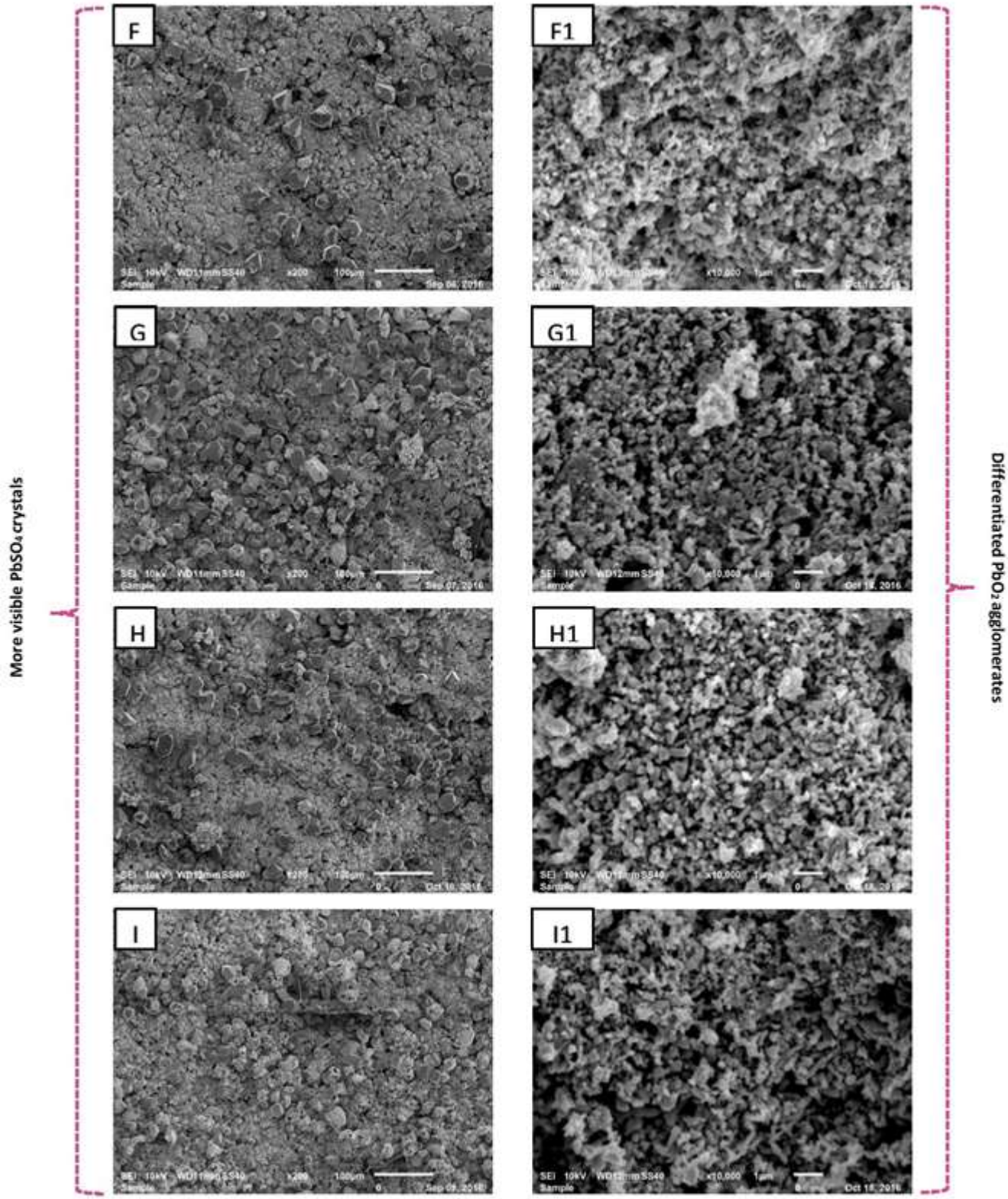

Fig.10. SEM images of the Positive active material with standard and modified electrolyte, all Images from A to I magnification (200X) Images from A1to I1 (10000X)

4. Conclusions

The flooded type lead acid battery with rated configuration of the 12V-65Ah was evaluated for its electrochemical performance in the standard and modified electrolyte. The positive electrode consists of predominately β-PbO_2 and its concentration is observed to be dependent on additive dosage as evidenced from XRD spectral analysis. The optimal additive concentration restrain formation of larger particles of sulphates as evidenced from SEM and help in overcoming sulphation phenomenon. The short term electrical performance study infers a mixed trend i.e. Na_2SO_4 act a facilitator depending on its concentration and the parameter under study. It is therefore, its concentration is to be chosen based on the application for which the battery

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is intended. Further, endurance performance must be considered for complete understanding of the subject.

5. Acknowledgments

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