International Journal of Science and Research (IJSR)
ISSN (Online): 2319-7064
Index Copernicus Value (2015): 78.96 | Impact Factor (2015): 6.391

Recovery Process of Sulphated Flooded Lead-Acid Batteries with Organic Polymer Compounds as Activator

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Abstract: ***In this study, we examined the recovery of sulfated flooded battery with the help of organic polymer compounds asactivator. Battery samples,after having ensured that they were heavily sulfated were considered for the purpose of recovery.A desulphation revival solution was prepared with the selected polymer compounds and tested. The sulphated batteries were divided into two groups (Group A-Control, Group B-Trial) for optimization of desulfation solution parameters (concentration and volume of solution per cell) respectively. The effect of these two parameters on the recovery process was optimized by considering one parameter at a time. For this purpose, different concentrations of desulfation revival solution having different volumes were added to discharged sulfated batteries and the batteries were subjected to charging with C20 current up to 16V per batteryfor 12 hr. The control samples were subjected to similar charge regime but without desulfation revival solution added. Discharge capacity and charge/discharge cycle (endurance performance)behavior of the recovered batteries were investigated and compared with control sample.The electrode samples were characterized by XRD, SEM to understand the phase composition and crystal morphology of test samples before and after recovery process to assess the degree of capacity and active material restoration.***

Keywords: Lead acid sulfated battery, hard sulphation, sulphation recovery, activator,desulphation revival solution and recovery performance (R.P).

1. Introduction

Lead-Acid batteries can degrade due to various reasons, [1-9]: including Positive electrode corrosion, irreversible hard sulfation, water loss/dry-out, positive active mass softening/shedding, and electrolyte stratification, internal short-circuit, mechanical damage (current connector failure, case damage) and others (passive lead oxide film formation, thermal runaway) etc. They are often not independent from each other, further multiple failures can occur simultaneously. Lead-acid batteries are designed to minimize these effects as much as possible but both the manufacturing variations and operating environment can still result in performance degradation. Of all these, hard sulfation is one of the dominant aging mechanism and has received a significant attention from the LAB research community.

1.1. Sulphation

When a lead acid battery discharges or remains inactive, lead sulfate forms on the plates of the battery. When the battery is left in such a condition for a prolonged time period, this sulfate gradually accumulates and crystallized, and clogs the porous plates to the point where the battery will not accept or hold any charge. This process known as sulfation, happens in all lead acid batteries in every application e.g., standby power, automotive, trucking, mining, marine Industries and HEV. According to studies of International lead acid Battery Council, 60 to 70% batteries are replaced prematurely or scraped due to hard sulfation that occurs on lead plates.

1.2. Hard Sulfation

After hundreds of charge/discharge cycles, aging mechanisms decrease the capacity of batteries. Sulfation is often observed in cells that continually source small amounts of current or in cells that operate in the low SOC region for extended periods of time. In a fresh cell, the lead sulfate formed due to chemical reaction between the electrode materials and the sulfuric acid during normal discharge process is coarse and porous and it can be easily converted back to lead, lead dioxide, and sulfuric acid while recharge. A small fraction of lead sulphate remains un converted in each charge/discharge cycle's, and adheres to the battery plates changes it's crystal structure and become harder, finer and larger, significantly reduces the available surface area for electrochemical reactions. Thesesulphate crystals cannot be dissolved back into the lead, lead dioxide, and sulfuric acid through ordinary charging procedures.

As a result of which, a gradual loss of useful electrolyte and plate active material is evident.This phenomenon also causes the specific gravity of the electrolyte to drop. Lead sulfate has very weak electrical conductivity and act as an insulator and prevent current flow to the electrode surface on which they lie. The deposits of lead sulfate cover both electrodes and make them inactive so that the effective capacity of cell is limited to lower than 10% of the nominal capacity. As the discharge process continues,the internal resistance of cell increases due to the formation of $PbSO_4$. Irreversible lead sulfate increases in each cycle and after some cycles, the electrodes are completely sulfated.The outcome of entire process is, such batteries are declared as a "dead" battery and discarded.

Batteries with hard sulfation have the following characteristics:

- A General Lack of Capacity (Deliverable Power)
- An Increase in Battery temperature while charging & discharging
- An excessive use of water
- A rapid rise in battery voltage while charging

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- A sudden drop of Battery voltage and capacity while discharging

As mentioned above battery sulphation processes, hard sulfation is the most vulnerable processfor the healthy behavior oflead-acid batteries and finally makes them to scrap. Hard sulfation on the plates is found to be one of the major failure mechanisms for lead-acid flooded batteries and its recovery process will be of great interest in economical and commercial point of view. The sulfated lead acid batteries are discarded if not recoverable; a process which is harmful to the environment. Therefore, there is a general need in the art for an improved method of recovering sulphated lead acid flooded batteries.

Desulfation can restore some of the capacity lost due to hard sulfation.A literature search yields early attempts with various strategies for desulfation are: charge equalization or over charging [10], Pulse Width Modulation [11-23], Pressure Feedback [24-25], Resonant Frequency [26-30], Chemical Reaction [31-32] and Artificial Intelligent [33-38], Other Techniques [39-40] etc. These processes were successful at removing most of the deposits, but at a very high cost to the battery life span. Further, most of these published recovery methods are highly exothermic, results in heat generation thereby plate degradation and mechanical stress on cell Components. There are numerous examples of battery cells exploding as a result of equalization.

Most commercial battery chargers/desulfators conduct desulfation using a technique known as “pulse conditioning”, which consists of applying short, high-current pulses to a cell [41-44].

Lam et al. found pulsed charging to be a promising approach towards enhancing the cycle life of Pb-Sb and Pb-Ca-Sn cells [45]. Keyser et al. proposed to use high finishing currents and current- interrupt charging algorithm to minimize sulfation and gassing during cycling. Later a safer electronic charging process was developed. This improved technique is still unable to remove the oldest and most stable sulfate deposits from the plates. This process however happens to be energy intensive as large voltages and currents are required in the recovery process.

There also have been patents published about the recovery of sulfated lead-acid battery [10-11]. Palanisamy et al. recorded a patent [10] about an apparatus and a method for automatic recovery of sulfated lead acid batteries relying on monitoring battery voltage, current and internal resistance during battery charging. Only some of the sulfated lead-acid batteries which have been incompletely and locally sulfated can be recovered by this method. In this reference, the internal resistance was considered as a critical measurable parameter for the selection of charging current amount. Through this method, those batteries in which internal resistances are not lower than a critical limited can be recovered. The designed apparatus will automatically reject the sulfated batteries at lower internal resistances. Nevertheless, most of the lead-acid batteries which are discarded due to hard sulphation or fully sulfated and then the reported method cannot be applied to them.

Therefore, process to recover the sulfated flooded lead-acid batteries requires an eco-friendly environment, improved, cost effective and high performance method to provide a unique solution to this problem in the lead-acid battery world. In this work, we have selected many discarded flooded lead-acid batteries which they were discarded because of hard sulfation. Discarded batteries are treated with desulphation revival solution. With this method all locally and fully sulfated flooded batteries are recoverable.The investigated organic polymer compounds for this recoveryprocess were selected from functional homo-polymers and contains carboxylic acid as major functional group. One such polymer is,Sodium salt of polyacrylic acid (PAA). PAA is a water soluble dispersants and acts as an inorganic crystal growth modifier and findapplication in consumer products. This superabsorbent polymer has the ability to absorb as much as 200 to 300 times its mass in water.

2. Design of Experiments

2.1 Materials selected for this study

All materials and reagents used in these experiments were of industrial grade. The polymer compounds (ingredients) selected for desulfation purpose are in solid form. The investigated polymers and Sulfuric acid (98%) were supplied by Sigma-Aldrich Company and High-media chemicals. The experiments were conducted at room temperature in electrolytic solution of H_2SO_4 with 1.225 relative density. All the chemicals were used as received, unless otherwise stated.

2.2. Material properties

2.2.1. Physical and chemical properties

Property	UOM	Sodium polyacrylate (SPA)	Polyvinyl alcohol (PVA)
Appearance	-	White crystalline powder	White crystalline powder
Molecular weight	g/mole	Variable	100.46
Density	g / ml	1.334	1.19
Water solubility @25^0 C	-	form dispersion	Soluble in water
Chemical formulae	-	$(C_3H_3NaO_2)_x$	$(C_2H_4O)_x$

2.3 Desulfation revival solution (Test solution) preparation

About 1-5 grams of Sodium salt of poly acrylic acid (sodium polyacrylate) was added to 100 ml of 10 N sulfuric acid solution and sonicated for 15 min. It was then stirred with a magnetic stirrer at 40-50^{0}C for 30 min followed by slow addition of PVA (1-5gms). Then it was diluted by deionized water to make it 1000 ml in total and the reaction mixture was further stirred at 60^{0}C intensively for 15 min to yield desulfation revival solution. The total reaction mixture was cooled to room-temperature.

2.4 Test battery details

Around 15 No’s Batteries having identical histories are selected for present study purpose and they were sampled as

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test batteries.The test batteries used in this study were produced by Amara raja Battery manufacturing company (ARBL Group, India).The internal design details of test batteries are given in Table 2.

Table 2: Test batteries internal design information

Battery Parameter	*Information*
Capacity, voltage	65Ah, 12V
Model	DIN-65
Battery type	Flooded
Positive alloy	Pb-Sn-Ag
Negative alloy	Pb-Ca-Al
Separator used	PE Separator with glass mat
Total Number of electrode groups per battery	6
Plate count per electrode group	8 positive & 7 negative
Filling Acid Specific gravity	1.225

2.5 Instrumentals

Charge and discharge of sulphated flooded batteries during recovery process were done by a charge and discharge machine equipped with a computer to record data and apply a constant current. All measurements of voltage were done by digital multi meter FLUKE-179 (made byFluke Corporation-U.S.A).

A scanning electron microscopy from Jeol, JSM-6010 PLUS/L was used for characterization of the electrode active mass samples before and after recovery process. The structural studies and phase composition of the electrode active mass samples before and after recovery process with and without test solution were carried out by XRD (X-ray diffractometer) using Rigaku/DMAX 2400 diffractometer (Japan). The XRD spectra were recorded with CuKα (λ=1.5418 A^0) monochromatic radiation operating at 40 KV and 60 mA. XRD data were collected in the 2θ range from 10° to 80° and the results were analyzed by PDXL-2software.

2.6 Assessment of test batteries Failure mode

All Batteries used in this study were of flooded type and had the nominal capacity of 65 Ah and the nominal voltage of 12 V. Batteries which are used in this study and its design details are mentioned in Table 2. Batteries which are failed to render its useful service life in the field, upon request were received and taken up for this study. The reason for failure is not known at this stage. Upon receiving, the batteries were subjected to failure mode assessment as per the procedural manner listed below.

- Received batteries were subjected to physical verification to find out any possible signs of damage or not?
- Upon physical verification, once the batteries were found to be good, it's OCV's and acid specific gravities are measured.
- Boost charge the test batteries with C20 current up to 16V per battery for 12 hrs.
- A few batteries were randomly selected among the charged batteries for initial capacity (Ci) verification with constant current for 20 hrs. discharge up to end voltage reaches to 10.25V per battery.
- Those batteries which were delivered 20-30% capacity to its rated value in the initial capacity verification stage were considered for the purpose of failure mode assessment.
- Randomly selected batteries were subjected to tear down analysis for taking out the electrode groups from these batteries. While extracting out the electrode groups from these batteries, care should be take that without compromise the integrity of the batteries.Extracted electrode groups were subjected to analysis.
- Identified, the plates were fully sulphated and hard sulphation was the major failure mode on the electrodes. Other than sulphation, no other failure mode was observed. Fig.1 shows the image of positive and negative plates taken out from the extracted electrode group of tore down battery sample. The sulfated batteries are discarded and send for scrap, if not recoverable; a process which is harmful to the environment [13]. Therefore, there is a general need in the art for an improved, easily adoptable and cost effective method for recovery of flooded lead-acid batteries by the lead acid battery manufacturers and service providers.

2.6.1. Recovery process at electrode group level

Recovery process at electrode group level was done by constructing a group having 8 positive and 7 negative sulfated plates were washed with distilled water and utilized them to assemble in electrode group format with the nominal voltage of 2V and 65Ah.Like that six electrode groups are constructed. Out of that constructed six groups, one group was named as control sample and the remaining 5 groups were named as trial samples. The constructed electrode groups, as per experimental matrix are listed in Table.3, were used to investigate the effect of different concentration and volume range of desulphation revival solution on the recovery process of inactive sulfates.

Table 3: Experimental matrix for recovery at electrode group level having 2V and 65 Ah with different volume range of desulphation revival solution

Electrode Group Samples	Group details	Desulphation revival solution parameter	
		% Concentration of Solution	Volume of solution added per cell (ml)
Group-1	Control group	Nil	Nil
Group-2	Trial group	0.1	5
Group-3		0.2	10
Group-4		0.3	15
Group-5		0.4	20
Group-6		0.5	25

The trial group electrode samples were subjected to charging with C20 current up to 2.6V per electrode group for 12hrs. The charged electrode groups were subjected to final capacity (Cf) verification by discharge with C20 current up to 1.75 end voltage per plate group. The % improvement in capacity was noted and tabulated the obtained results. At each experimental step, the % improvement in capacity and the recovery performance (R.P) was calculated from the following equations:

% improvement in capacity = $(C_f - Ci/C_i) \times 100$

% Recovery performance (R.P) = $(C_f/C_n) \times 100$

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Where C_f is the discharge capacity (Ah) after recovery, C_i is the discharge capacity (Ah) before recovery and C_n is the nominal capacity (Ah) of the battery.

Based on the obtained capacity improvement data, the optimum desulphation revival solution parameters were finalized and implemented to battery level. Active material samples were taken from the positive and negative plates before and after recovery process for knowing the active material phase composition by Powder XRD analysis and morphology by SEM analysis.

2.6.2. Recovery Process at battery level

At final stage after selection of optimum test solution parameters for recovery of sulfated plates based on electrode group level performance, further studies were conducted on batteries with the nominal voltage of 12 V and the nominal capacity of 65 A h consisting of 8 positive and 7 negative plates. Recovery process at battery level was done as per the procedural manner carried out for sulphated electrode group's recovery. In this method, batteries which are exhibiting the initial discharge capacities in the range of 20-30% of nominal capacity (means sulphated heavily) were considered for improvement.Batteries which are fall under such capacity range were categorized into Group-A and Group-B. Group-A consists of five batteries (A, B, C, D and E) and they were named as control samples. Whereas Group-B consists of five batteries (F, G, H, I and J) and they were named as trial samples. Both control and trial group battery samples were subjected to recovery processto know the highest capacity (Ah) recovery, and recovery performance (R.P) among sulfated batteries before and after recovery process.

3. Results and Discussions

All batteries with identical histories were selected for present study purpose.To assure that, the batteries which are selected for this study are fully sulfated, several batteries were broken and fully sulfated plates were extracted out from them and used for this experiments. Figure.1 shows the sample image of selected positive and negative plates from the tore down battery plate groups.

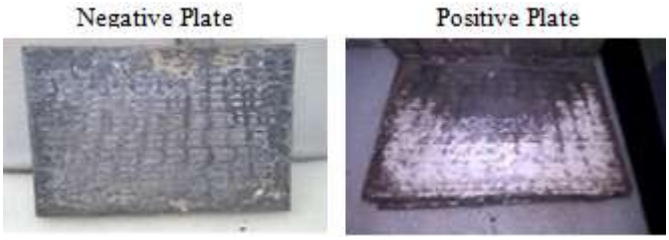


Figure 1: Sample image of the selected positive and negative sulfated plates from the sulphated battery for unit cell construction

As it is seen from Fig.1, most parts of the plates were covered with crystalline lead sulfates and a fine white/grey coating on the positive plate and a non-metallic luster on the negative plate. In most cases, the battery consists of such plates signifies the battery as not serviceable.

3.1. Optimization of test solution parameters

3.1.1. Recovery process at electrode group level

Firstly, to know the effect exerted by the addition of desulfation revival solution on the capacity recovery and active material restoration, 5 different concentrations of desulfation revival solution ranging from 0.1 to 0.5% and having different volume ranges from 5 to 25 ml per each electrode group extraced out from the randomly selected tore down batteries wereadded and tested as per the experimental matrix listed in Table.3.Table.4, shows the effect of solution parameters (concentrationand volume of solution added per each cell)on recovery of electrode group containing sulfated positive and negative plates with large crystals of inactive lead sulfate.

Table 4: Effect of desulphationrevival solution concentration (%) on the capacity (Ah) recovery and on % recovery performance (R.P) of constructed sulfated unit cell

Electrode group details	Test reagent parameters		Capacity recovery		% R.P
	Concentration (Wt. %)	Volume of solution added per group (ml)	Before recovery, C_i (Ah)	After recovery, C_f (Ah)	
Group-1	-	-	10	28.6	44
Group-2	0.1	5	12	48.6	74.6
Group-3	0.2	10	7	51.7	79.53
Group-4	0.3	15	13	57.8	88
Group-5	0.4	20	10	49.2	75.6
Group-6	0.5	25	16	43.3	66.76

As it is evident from the obtained results, 0.3% concentration having 15 ml of test solution, the rates of lead Sulphate crystal growth and nucleation are suitable for forming of active materials.

It is evident from the obtained results for discharge capacities shows that,test solution of 0.3% concentration having 15 ml for each electrode group is the best. It was observed that, the electrode group containing thisconcentration and volume of test solution, the recovery of active material was found to be above 80%. At this concentration, large crystalline lead sulfate crystals which are present on the surface of the plates are converted to active material form.

3.1.2. Scanning electron microscopic studies

The surface morphology of positive and negative paste under different experiemntal conditions were studied by scanning electron microscopy -JEOL, JSM-6010 PLUS low vacuum model using a working distance of 12 mm, a spot size of 30 and an electron beam voltage of 10 kV.SEM images were recorded and mapped to understand the role of

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desulphation revival solution on the morphology of the positive and negative active material. Electrode paste samples made for SEM analysis were prepared as follows: Firstly, the positive electrode samples were extracted out from the plate was washed with deionized water to pH of 6-7, then the electrodes were dried in a vacuum drying oven for 10 h at 85^0C. All samples were sputter coated with a thin layer of platinum, ~5 nm in thickness, to reduce charging and improve image quality. Lastly, the samples were tested with SEM.

3.1.2.1. Investigation of positive electrode

Fig.2, shows the morphology of positive electrode paste under different experimental conditions as follows. Paste morphology: after conventional charge without discharge, after charge and discharge and after charge with different concentrations of desulphation revival solution and discharge respectively. Fig.2a, shows the morphology of positive electrode paste after conventional charge without discharge. As it is seen from Fig. 2a, before recovery, there are many large and non-uniform lead sulfates crystals are available on the surface and in the inner layers of the conventionally charged positive electrode.

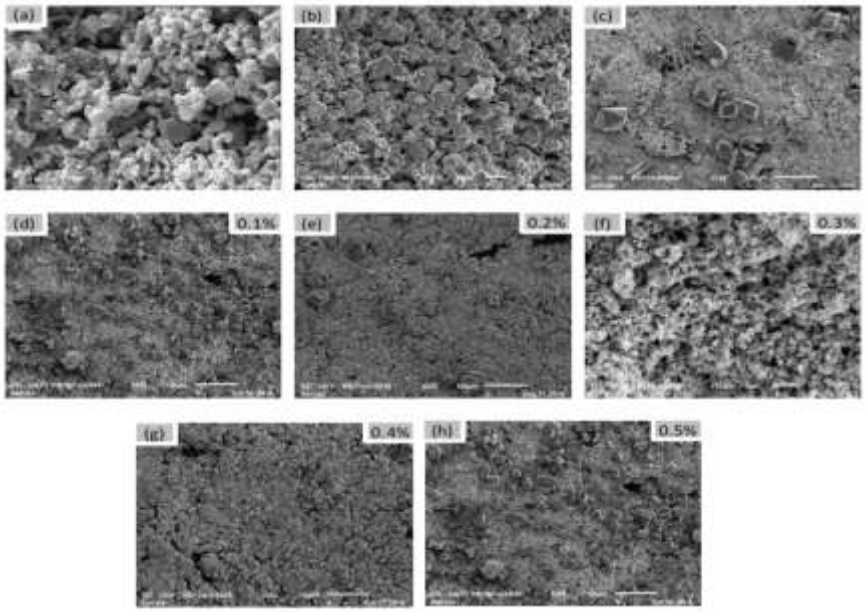


Figure 2: SEM images of positive electrode after conventional charge without discharge (a), after charge and discharge (b), after charge without test solution and discharge (c), after charge with different concentartions of test solution and discharge (d-h). All SEM images are in magnification of 1000x , 20kv

It is expected that, the large lead sulfate crystals cannot be converted into lead dioxide so that the unit cell consists of this positive electrodes be able to deliver very low capacity during initial capacity verification stage.Fig. 2b, shows SEM image of positive paste after discharge process for knowing of initial available capacity (Ci).It is evident from from Fig. 2b, during discharge process, lead dioxide of cathode was transformed to insoluble and irregular shape lead sulfate crystals. These lead sulfate crystals cannot be convert to lead dioxide with conventional method of charge process. Figure.2c, shows the SEM image of control positive electrode paste in discharge stage after recovery process. As can be seen from Fig.2c, the control sulfated positive plate after subjecting to recovery process, still possess many large lead sulfate crystals, particularly on the surface and inner layers of paste. So that the constructed unit cell consisting of this positive electrode be able to deliver very low energy at final discharge stage of capacity ($C_{f)}$ verification.

Where as the SEM images pertaining to recovery process in presence of different concentrations of desulphation revival solution is shown in Figfrom 2(d) to 2(h). As shown in Fig.2d, the SEM morphology of positive paste after charge with 0.1% concentartion of test solution and discharge. As it is seen from Fig. 2d, some part of crystalline lead sulfatewas converted to uniform small crystals which can be easily and more effectively transformed to lead dioxide at next charge process. It is evident from the SEM images from 2d to 2 h, the morpholy of crystalline lead sulfate has influenced by changing test solution concentration from 0.1 to 0.3% and the lead sulfate morholgy remains unaffected with further increase of test solution concentrion from 0.3-0.5% . As it is seen from Fig.2f, it is expected that, the positive electrode charged and discharged in presence of 0.3% concentration of test solution was able to successfully participate in the next charge/discharge electrochemical reaction process easily, so that the battery including these positive electrodes deliver high discharge capacity.

3.1.2.2. Investigation of negative electrode

As it is seen from Fig.1, of sample image of extracted negative plate from the tear down sulphated battery. It is evident from Fig.1, it is expected that the amount of crystalline lead sulfate available on the negative plate to be more than that on positive plate. Figure.3, shows the SEM surface morphology of paste on the negative plate at different states of recovery process. During normal discharge process of a lead acid storage battery, electrochemically active form of lead sulfate forms eventually on the plates of battery. When recharged immediately after discharge, the lead sulfate is converted back to electrode active materials. When this material gets fail to release from plates, upon cycling it begins to harden and crystallize and then the plates get sulfated. Hard

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sulfation is the prime cause of a battery losing its available capacity. This form of sulphates cannot be re-converted back to plate active materials during subsequent recharge. However this process continues, the plates containing hard and large sulphate crystals cannot accept charge and finally the battery is said to be dead and discarded for recycling.

The SEM morphology of sulfated negative plate after conventional charge without discharge is shownin Fig. 3a. As it is seen from Fig. 3a, the surface and also the inner layers of negative paste of fully sulfated plate is completely covered with large and non-uniform crystals of lead sulfate and it is expected that, the constructed unit cells containing this plate cannot support delivery of considerable amount of capacity during initial capacity verification stage.

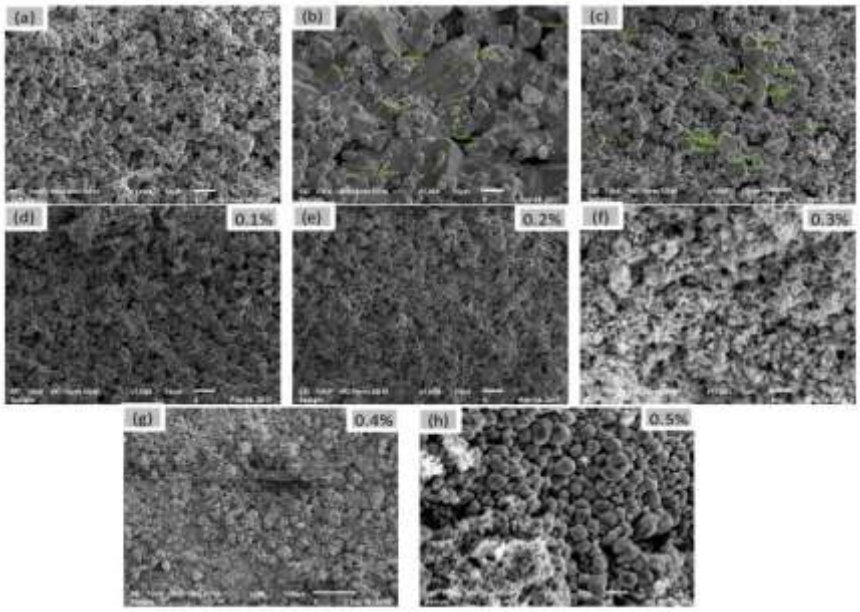


Figure 3: SEM images of negative electrode after conventional charge without discharge (a), after charge and discharge (b), after charge without test solution and discharge (c), after charge with different concentartions of test solution and discharge (d-h). All SEM images are in magnification of 1000x

The morphology of sulfated negative plate after conventional charge with discharge is shown in Fig. 3b. With comparison of Fig. 3cand 3b, after recovery, it is seen that only a few amount of crystalline lead sulfatewas transformed to active material. On the other hand, encounraging results were noticed when the sulphated negative plates were treated with different concentrations of test reagent. The morphology of fully sulfated negative plate after charging with different concentration of test reagent and discharge is seen in Fig. 3d to h. As it is seen from Fig. 3d to f, with increase of test reagent concentration and volume of solution added per cell, the major part of crystalline lead sulfateshas been converted to spongy lead. This conversion is more pronounced at 0.3% concentration of test reagent. It is expected that the unit cell treated with 0.3% concentration of test reagent can deliver high dischargeCapacity during final discharge verification. The negative plate charged with 0.3% test solution and discharged is shown in Fig. 3f, further corroborates this phenomenon that formed lead sulfate with small crystals was transformed into spongy lead, so that they can take part in next charge-discharge process effectively.

3.1.3. XRD analysis for the positive and negative paste before and after recovery

Each sample electrode paste was characterized by powdered XRD-RIR method to know the p hase components distribution (wt.%)before and after recovery process inpresence and inabsence of desulphation revival solution. The obtained XRD phase composition resultswere summerized in Table 5.It was observed that before conducting recovery experiment the constructed unit cells consisting of sulfated positive and negative plates have lead sulfate as a major component of paste as anticipated. After subjecting to recovery process by charging the disharged unit cells with different concentrations of test solution having different volume (ml) added per each unit cell , the major part of irreversible lead sulfate was converetd to lead dioxide and spongy lead on the positive and negative electrodes respectively. It is evident from the XRD phase composition results, at 0.3%concentration of test solution having 15 ml observes to be the optimal formulation. Under this optimal test condition, average lead sulfate conversion was found to be 80%. Further experimentation was carried out only with this optimal formulation.

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Table 5: XRD phase composition analysis for the positive and negative paste samples before and after recovery process with test reagent

Cell details	Sample	Test solution Parameters		Phase component (wt. %)			
		Conc. (Wt. %)	Volume of solution (ml) added per electrode group	PbO_2	PbSO4	PbO	Pb
Group -1 (Control)	Positive plate before recovery			46.0	46.12	4.34	-
	Negative plate before recovery			-	58.84	14.14	24.02
	Positive plate after recovery			53.4	37.14	1.83	-
	Negative plate after recovery			-	42.63	9.6	47.9
Group -2	Positive plate after recovery	0.1	5	64.0	27.14	8.64	-
	Negative plate after recovery			-	36.0	13.56	50.62
Group -3	Positive plate after recovery	0.2	10	76.57	17.63	5.98	-
	Negative plate after recovery			-	19.24	17.98	59.76
Group -4	Positive plate after recovery	0.3	15	89.30	9.40	1.24	-
	Negative plate after recovery			-	9.53	20.78	69.69
Group -5	Positive plate after recovery	0.4	20	64.98	26.21	9.86	-
	Negative plate after recovery			-	27.17	21.5	50.78
Group -6	Positive plate after recovery	0.5	25	43.7	42.56	14.14	-
	Negative plate after recovery			-	34	26.55	40

3.2. Recovery process at battery level

Before conducting recovery experiment on sulfated flooded batteries, we have ensured that all selected batteries were failed only because of hard sulfation on the plates and no other failure modes were associated in them. Charge and discharge process of the selectedtest samples (with the nominal voltage of 12 V and nominal capacity of 65Ah) were done in a manner listed in the preceding sections in this art. As shown in Table.6, the initial discharge capacity data before recovery was found to be lower than 25% of the nominal capacity of battery. Discharged batteries, after treating with desulphation revival solution as per the experimental matrix had been charged with C20 current up to 16V for 12 h.Charged batteries were re-examined for the discharge capacities through the application of the constant current 3.25A (20 h discharge rate) until reaching to 10.5V (cut off voltage). The control samples were subjected to similar charge and discharge regime but without desulfation revival solution added to these batteries. While, thecapacity of Group-B containing batteries after charging in presence of test solution was found to be higher than that of the capacity of Group-A containing batteries was noticed. Therefore, the capacity of Group-B batteries after charging with desulfating solution has increased significantly, which was more than twice of the initial value. The most efficient recovery interms of lead sulfate conversion into activematerials and recovery performance (R.P) w .r.t. %concentration and optimum volume in ml of test solution per each electrode groupwas identified and implemented. At each experimental step, the recovery performance (R.P) was calculated from the following equation:

$$\% \text{ Recovery performance (R.P)} = (C_f / C_n) \times 100$$

Where C_f is the discharge capacity (Ah) after recoveryand C_n is the nominal capacity (Ah) of the battery.

Table 6: Effect of test solution concentration (%wt) and volume of solution injected per cell (ml) on the capacity of sulfated flooded lead-acid batteries before and after recovery process

Battery group details	Battery symbol	Test solution Parameters		C_i (Ah)	C_f (Ah)	% R.P
		Conc. (Wt. %)	Volume injected per electrode group (ml)			
Group-A (Control samples)	A	Without test solution		10	28.6	44.0
	B			16	30	46.15
	C			9	34.9	53.69
	D			13	29.2	44.92
	E			8	32.8	50
Group-B (Trial samples)	F	0.1	5	12	48.6	74.76
	G	0.2	10	7	51.7	79.53
	H	0.3	15	13	57.8	88
	I	0.4	20	10	49.2	75.6
	J	0.5	25	16	43.3	66.76

Table.6 shows the effect of test solution parameters on recovery performance of large crystals of lead sulfate. The obtained results from the Table. 6 for discharge capacities of Group-B samples shows that, at 0.3% concentration having 15 ml of desulphation revival solution injected for each cell of the battery is the best and highest disharge capacity and highest recovery performance was observed. A drop in recovery performance and discharge capacity was noticed, further increase in concentration and volume of solution. we always focused on higher capacity (Ah) recovery at lower concentration and less er volume of solution per each cell of the sulfated battreies. The obtained results for discharge capacities show that, the battery sample treated with 0.3% concentration of test solution having 15 ml of such solution for each cell of the battery is expected to participate in more number of charge/discharge cycles during cycle life test. At this optimum parameters, the rates of lead sulphate crystal growth and nucleation are suitable for formation of respective electrodes active materials. At this concentration, the average recovery performance was 88%.

3.5 Cycling behavior of recovered batteries (Cycle life test)

After completion of recovery process, the recovered batteries were used for cycling (Endurance) test using Life

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cycle network battery testing device. Cycle life test was performed on the recovered batteries as per JIS standard test protocol. Discharging the battery with a current of 20 Amps for 1 hr. and charging at a constant current of 5 Amps for 5hr. After 25 cycles, the initial capacity of the battery was tested at a constant discharge current of 20 Amps with a cut-off terminal voltage of 10.2 V per battery (depth of discharge, DOD=30%).Figure.5,shows the number of completed chargedischargecycles per cycle set of the recovered batteries during cycle life test (temp = 40˚C). As it is seen from Fig.4, sulphated batteries which are not treated with test reagent have given only 50 cycles. The reason might be that, sudden internal short circuit happens due to the presence of large sized and more irreversible form of $PbSO_4$ crystals.

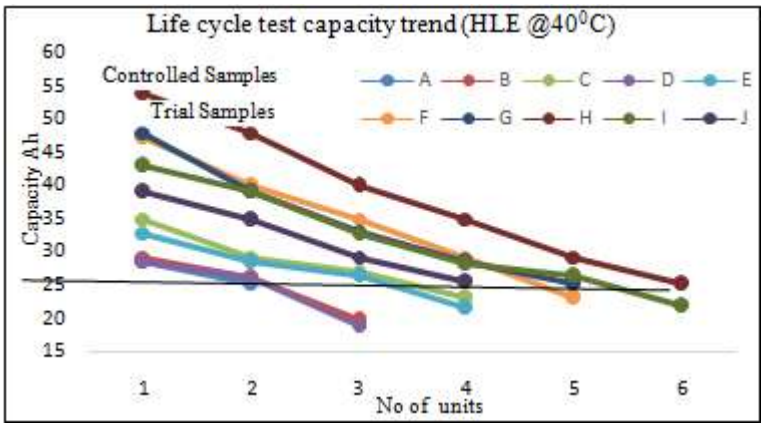


Figure 4: Comparison between discharge capacities of the recovered battery trial andControl samples duringlife cycle test. (Note: Each unit having 25 charge discharge cycles)

The presence of more irreversible $PbSO_4$ particles with larger crystal size causes the decrease of conductivity of electrode and then lead to the failure of the discharging during capacity verification of life cycle test. The obtained capacity results showed that the recovered batteries in presence of test solution in the electrolyte have cycle endurance of 50%more of the control battery samples.With the addition of 0.3% concentration (w/v) having 15 ml of desulphation revival solution in the electrolyte, the proportion of $PbSO_4$ large particles significantly decreased and the particles became fine and uniform, which was beneficial for the electrochemical performance. Under such conditions $PbSO_4$could be formed during the reduction reaction under the influence of polymer compound species which are dissolved in test solution may behaves as crystal growth modifier and also as crystal nuclei, resulting in the formation of smaller particles.This form of active mass structure allows the electrode to participate in more number of charge discharge reactions of life cycles test there by delivered maximum value of the discharge capacity.The cycle life test shows that the recovered batteries can be reused for a couple of months instead of buying a new battery in that place.

4. Conclusion

Results obtained from the current research shows the ability of organic polymer compounds as electrolyte additive added in diluted form as a simple, cheap and high performance method for the recovery of sulfated flooded lead-acid batteries. The selected polymer compounds falls under the category of polyelectrolytes and they were belongs to carboxylic acid group functional homo-polymers. The polymer containing monomer repeating units carries an electrolyte group and these electrolyte group dissociate in aqueous solution and makes the polymer molecule charged. The hydrophobic portion tends to adsorb on to the surface of growing crystal face in crystal lattice system and the hydrophilic portion promotes spread in water phase.In our: Pb/Pbo2/PbSO4 system, lead sulfate belongs to inorganic crystal category. These hydrophobic portion forms a charged layer on the surface of each growing lead sulfate particle and try avoid the recrystallization of lead sulafte particles. The created charged layer will generates electrostatic repulsive forces between the two lead sulfate particles and reduces the force of cohesion to form a big particle of lead sulfate.

Based on the scanning electron microscopy (SEM) and X-ray diffraction results showed that, various morphologies of active materials have been observed on the positive and negative paste of control and trail samples before and after recovery process.
It was found that the concentration of desulfation revival solution and volume of such solution in ml added per each cell were the most important parameters for morphological control of lead sulfate crystal. The effect of these parameters on the active material restoration, i.e. from lead sulfate to PbO_2 and spongy lead of respective electrode active materials, morphology and crystallization of lead sulfate can be attributed to their influence on the interaction between the carboxylic acid groups of sodium salt of poly acrylic acid (PAA-Na) and the crystal planes of lead sulfate particles.The flooded batteries which are failed only due to sulphation can be recoverable with this method. The Application of this method to fully sulfated batteries can recover them for over 75% of their nominal capacity. The recovered batteries can be reused for a couple of months rather than buying a new battery in that place. The presented method can be of very interest in economical and commercial views,because of the simplicity and reliability of this method at each battery manufacturing factory, battery repair and service stations can be adoptable.

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5. Acknowledgement

The Authors would like to thank the Management of Amara Raja Batteries Ltd., for their constant encouragement and valuable support for this work. The Authors would also like to thank Mr. Vijay, Mr. Muni Vishnu at the chemical lab and to Mr. Balaji at the electrical testing lab of R&D, Technology Centre, Amara Raja Batteries Ltd., for extending the experimental support and data analysis.

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