Short communication

Sodium sulfate as an efficient additive of negative paste for lead-acid batteries

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Abstract

This paper is devoted to the effect of sodium sulfate as negative paste additive on the performance of the lead-acid battery. Six different percentages of sodium sulfate were added to negative paste. The effect of sodium sulfate on discharge capacity, cycle life and cold cranking ability of the sealed lead-acid batteries were investigated. Batteries containing sodium sulfate in negative plates at low amount (0.1 wt%) showed a remarkable electrical behavior during the test. Results indicate that negative electrodes containing 0.1 wt% sodium sulfate exhibit discharge capacity of the more than 3% and 12% with respect to negative electrodes without sodium sulfate before and after cycling test, respectively. Addition of sodium sulfate also increases the time of reaching to cut off voltage of 6 V at cold cranking test more than 17%. The main effect of sodium sulfate is to increase the cycle life of the lead-acid batteries to more than 18%. Scanning electron microscopy (SEM) was used for the investigation of paste morphology.
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1. Introduction

Lead-acid technology currently remains the most reliable, safe and affordable power source. None of the new developed battery types (e.g. Li-ion and Ni-MH batteries) has so far reached the commercial success of the lead-acid battery. Lead-acid batteries have many applications such as starting-lighting-ignition (SLI) in vehicles, tractions, telecommunications, children tools etc.

It is well known that the performance of the negative plates of lead-acid batteries is strongly influenced by the presence of some substances such as expanders, conductive additives and others which are added to the negative active material during paste making.

Additives are added to the negative pastes of lead-acid batteries to improve their performance in cycle life. Two types of additives were used in negative paste of lead-acid batteries including organic and inorganic additives. For example, barium sulfate as a common inorganic expander provides nucleation sites of lead sulfate during discharge process. Barium sulfate has similar unit cell dimensions to lead sulfate during battery discharge. This similarity of structures facilitates the formation of small crystals of lead sulfate in the negative active material in preference to the formation of large crystals that are difficult to recharge. Organic additives such as humic acid, lignin and lignin derivates like lignosulfonate are strongly adsorbed on the surface of the active material and induce fine, porous crystal structure and increase the specific surface area from 0.2 to $0.8\,m^2\,g^{-1}$ [1–3]. Increasing surface area reduces the effective current density during discharge and thereby, increases utilization of the active material. This effect is particularly important at low temperatures and at high rates of discharge and is the principle reason why automotive battery expanders use high dosage of lignosulfonate.

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Additives in the negative electrode of lead-acid batteries promote the development of fine crystal sponge lead upon formation and preserve the high surface area structure upon cycling [2,4–6].

The effects of such additives mainly concern the performance at high rates of discharge and cyclability, but they also exert other beneficial actions on the overall behavior of the negative plate [7–11]. Although the mechanism of action of the additives is very complex and not yet completely understood, it is commonly accepted that adsorption of such substances on crystals is of fundamental importance for their behavior [12–17]. In fact, the expanders adsorbed on lead seem to facilitate a dissolution-precipitation mechanism for lead sulfate formation, thus preventing passivity by a solid-state reaction [18–22]. According to Ritchie [15,16], and Willihnganz [14], the effects of additives are simply explained by considering that a porous lead sulfate is formed during discharge as a consequence of the partial coverage of the lead surface by adsorption of the additive substances, while a limitation of the size of lead crystals occurs during charging.

As already mentioned, the presence of additives can also affect other aspects of the negative plate behavior. In fact, the adsorption of such substances on lead modifies the electro-chemical cathodic behavior of lead by affecting the hydrogen evolution reaction, and thus yields a possible inhibiting action on the effects of impurities [23–30].

The function of the carbon black is to increase the conductivity of the negative active material to assist in the initial charging of the lead-acid battery (formation). Until recently, it has been thought that once the active material has been charged (lead sulfate converted to lead), the carbon has little influence on its behavior. This belief has been challenged recently by the discovery that high dosages of carbon and/or graphite in the negative plate have a beneficial effect on battery life [31].

Some researchers have investigated the role of sodium sulfate. This additive is added in powder form to the electrolyte in amounts of about 1% of its weight. Sodium sulfate acts by the common ion effect to prevent the harmful depletion of sulfate ion, which is a danger in the discharge of acid-starved batteries. The addition of sodium sulfate provides an 'inventory' of sulfate ions that are available without increasing grid corrosion [32–34].

Another investigation is about using sodium sulfate in the positive electrode. Jenn-Shing Chen studied the effect of sodium sulfate on the performance of sealed lead-acid cells and found that 4BS crystal size can be reduced in the cured positive plates, and thus furnishes a larger surface area which helps the user to have a better performance and cyclability at high temperatures [35].

This study develops previous studies dealing with performance of lead-acid cells particularly for increasing the specific energy and cycle life. In this work, sodium sulfate was investigated as a new, cheap and efficient additive of negative paste for lead-acid batteries. Sodium sulfate improves capacity, cold cranking ability and cycle life of the lead-acid batteries. Several practical production examples are carried out about prepared paste batches with the addition of 0–4% of new additive to the negative active materials. Pastes made with the additive of sodium sulfate had higher capacity, better cold cranking ability (CCA) and cycle life performance compared to the batteries without sodium sulfate. All experiments were repeated two times before finalizing the results.

2. Experimental

2.1. Reagent and material

All materials and reagents used in experiments were industrial grade and all of them were obtained from Iranian companies. The inorganic additive employed in this study was sodium sulfate from Merck. All sealed lead-acid batteries 35 A h used in the study were produced by Sepahan Battery Industrial Complex (SBIC, Isfahan, Iran). The specification of the batteries has been summarized in Table 1.

2.2. Instrumental

Provision of low temperature ($-18\,^{\circ}$C) was carried out by industrial freezer (ARMDFB, Iran). Cold cranking tests were performed by discharge instrument (HEW1500-12, Digatron, Germany). The capacity and cycle life tests were performed by charge and discharge instrument (UBT150/75-018-5, Digatron, Germany). Morphological studies were carried out by scanning electron microscopy (SEM, Philips XL30).

2.3. Methods

The experimental variable was the amount of sodium sulfate including 0.1, 0.5, 1, 2 and 4 wt% based on the weight of lead oxide in the negative paste. In addition, the reference (blank) batteries with 0% of sodium sulfate were produced. The hydrophilic nature of sodium sulfate makes paste mixing difficult in the dosage more than 4%.

Normal amounts of Vanisperse A (organic expander), barium sulfate, carbon black and stearic acid were used with each inorganic variable. Two similar batteries containing the same amount of active material and additives for each dosage of sodium sulfate were produced.

The batteries built and tested in this study were specifically designed of the negative electrode and its additives. Thus, the batteries do not represent standard SBIC production. Six positive plates accompanied with three negative plates to forming one

Table 1
The specifications of the experimental batteries

No.	Parameter	Amount or type
1	Nominal voltage (V)	12
2	Nominal capacity (A h)	35
3	CCA (A)	280
4	Grid	Expanded lead-calcium-tin alloy
5	Plate ratio in cell (positive: negative)	6:3
6	Active mass ratio (positive: negative)	2:1

cell, so that the ratio of positive active mass (PAM) to negative active mass (NAM) in each cell ratio was 2:1. This is done to assist in establishing the cause of failure and to verify whether the negative electrode was in fact the limiting electrode. Twelve batteries were selected. Six of them were used for capacity test and cold cranking test and the next six were used for cycling test. The conditions for the production of the two groups were the same.

The low rate capacity and cold cranking of the batteries were tested according to both Deutsche Industrie-Norm (DIN) [36] and Europe Norm (EN) [37] protocols.

For the EN cold cranking test, the voltage after 10 s of discharge at 280 A and −18 °C was measured with an additional extension of discharge after 10 s rest at 168 A to determine the time in seconds to reach cut off voltage of 6.0 V. For the DIN capacity, the batteries were discharged to 10.5 V at the rate of 2.5 A.

Cycle life was evaluated according to the International Electrical Component (IEC) [38] and Iranian National Standard [39] protocol at 40 °C, which was modified as follows.

Each battery was charged for 5 h at the constant current of 7 A and then discharged at the rate of 10 A to reach in 10.5 V; this procedure was repeated until the battery capacity reach to 15 A h (or 50 A h kg^{-1}). To monitor capacity after the cycle life tests, each battery was discharged at the rate of 2.5 A to reach in 10.5 V. After failure and before further testing, the batteries were charged until the battery voltage stabilized.

After life cycle test and recharging, the batteries were dissected and the condition of the positive electrodes, the negative electrodes and the separator were noted. The morphology of the negative paste of each battery was studied by SEM before and after cycle life.

3. Results and discussion

3.1. Discharge capacity and cold cranking ability

It is expected that sodium sulfate is dissolved in sulfuric acid solution in paste making step. After curing and drying steps, sodium sulfate precipitates as very small particle on the surface of lead sulfate and other species of the negative paste. Sodium sulfate precipitation particle was not detected by SEM at cured paste. Therefore, it can be concluded that either the size of these particle was very small or the precipitation as a thin film was taken place on the surface of the other species. After dipping of the pasted electrodes in battery electrolyte, the precipitated sodium sulfate dissolves in the electrolyte and leaves some holes in the negative paste. These holes facilitate the diffusion of electrolyte into the paste and maintain the porosity of negative paste after charge/discharge cycles. They also turn prevent decreasing the active surface area during charge/discharge cycles. For the determination of discharge capacity, different batteries were discharged with current of 2.5 A to cut off voltage of 10.5 V. Voltage-time behavior of the prepared batteries with different amounts of sodium sulfate is shown in Fig. 1. As it is seen, the discharge time for the battery containing 0.1 wt% of sodium sulfate is the highest. The first discharge capacities for these bat-
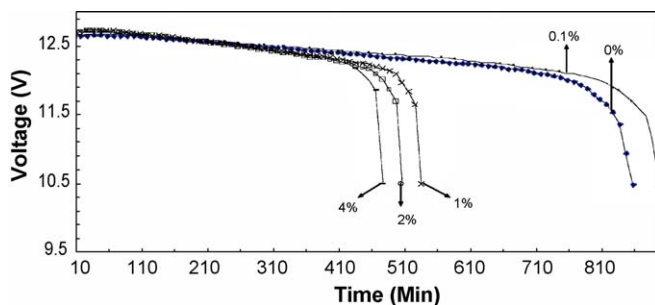

Fig. 1. Voltage/time curves for different percentages of sodium sulfate as a negative paste additive during first discharge process by constant current of 2.5 A.
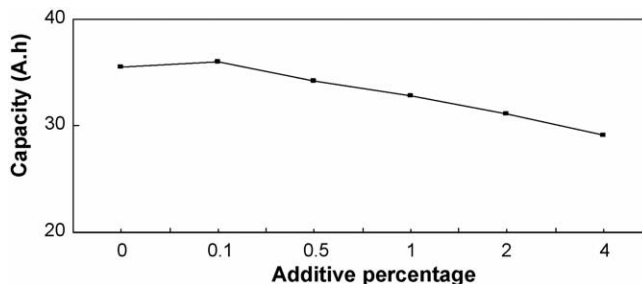

Fig. 2. First discharge capacities for the different percentages of sodium sulfate as a negative paste additive at discharge current of 2.5 A.

teries were calculated and shown in Fig. 2. As Fig. 2 shows, the battery with sodium sulfate content of 0.1 wt% has the highest discharge capacity. The use of sodium sulfate with weight percent of 0.1 wt% causes 3% increase in first discharge capacity with respect to the negative paste weight. These results can be explained by increasing the active surface area of active material in the presence of 0.1 wt% sodium sulfate. At higher amounts of sodium sulfate, the interconnection of paste particles is probably broken. Thus, the sodium sulfate weight percentage of 0.1% is the optimum value.

All the prepared batteries were used in cold cranking test. The time of reaching to cut off voltage of 6 V was used as a parameter for comparison of the batteries. The results of cold cranking tests are shown in Fig. 3. As it is obvious, as well as discharge capacity, the time of reaching to final voltage of 6 V in cold cranking test can be increased from 64 to 72 s (17%) by using 0.1 wt% sodium sulfate.

The highest capacity and cold cranking ability for the battery with 0.1 wt% of sodium sulfate can be related to a good
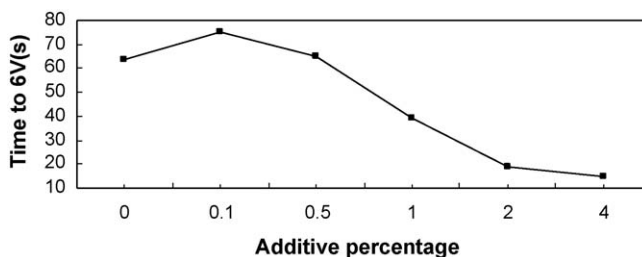

Fig. 3. Cold cranking result (time of reaching to cut off voltage of 6 V) for different percentages of sodium sulfate as a negative paste additive ($I_{dis} = 280$ A).
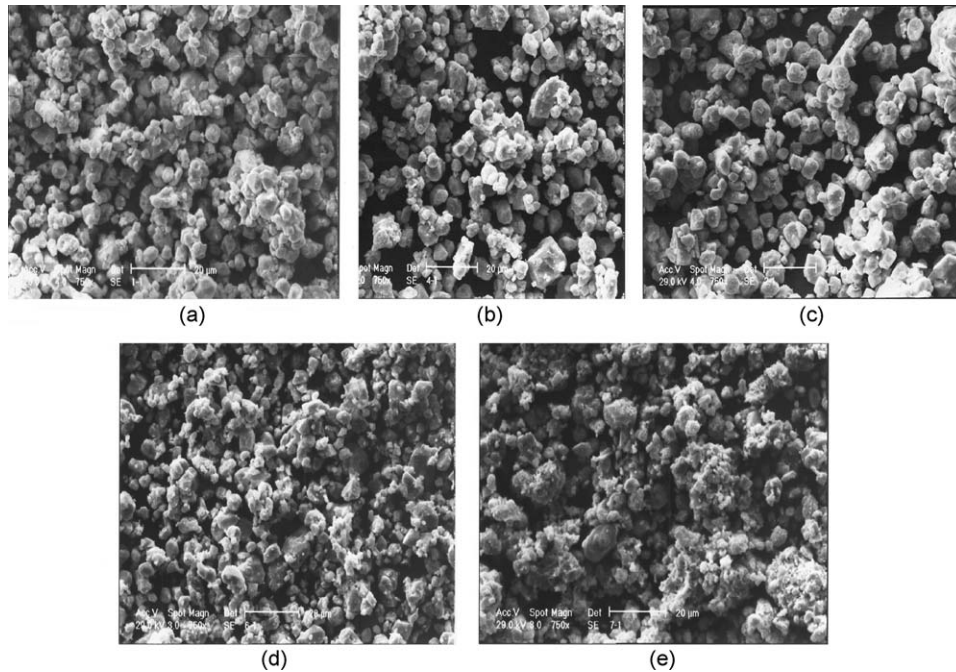
Fig. 4. SEM micrograph of negative paste with different weight percentages of sodium sulfate 0% (a), 0.1% (b), 0.5% (c), 2% (d) and 4% (e) at 40 °C.

connectivity between particles as well as high surface area and available active sites. At higher amounts of sodium sulfate, the porosity of negative paste can be increased, but the connectivity between active particles decreased. For evaluation of this idea, scanning electron microscopic images of the negative electrodes are shown in Fig. 4. As Fig. 4b shows, the negative paste containing 0.1 wt% sodium sulfate has more porosity as well as good connectivity between active particles. The active surface area for electrochemical reactions can be increased, when the porosity of paste increases.

3.2. Cycle life

After first discharge capacity and cold cranking tests, all the batteries were tested for the cycle life. For the cycle life test, each battery possessed some charge/discharge cycles until discharge capacity decreased to the final discharge capacity of 15 A h (or 50 A h kg^{-1}). The obtained results are shown in Fig. 5. As Fig. 5

shows, the battery assembled with the negative paste containing 0.1 wt% sodium sulfate possesses the maximum cycle life. This effect can be due to the fact that in the negative paste containing 0.1 wt% sodium sulfate, enough porosity and good connectivity between active particles are retained during charge–discharge cycles.

Fig. 6 shows the variation of discharge capacities during 25 cycles of charge/discharge processes for the different batteries at discharge current of 10 A. As it is seen, the capacity drop for 0.1 wt% sodium sulfate is the lowest during charge/discharge cycles. The cells containing no sodium sulfate additive or high dosage of this additive showed very poor cycle life at 40 °C, but 0.1% of sodium sulfate additive improved cycle life. Sodium sulfate is soluble in sulfuric acid and thus after addition to the paste mixture and immersion in sulfuric acid, it is dissolved in the electrolyte causing the production of a porous paste. This ability helps the negative active material to tolerate the pressure from shrinkage and expansion in the charge and discharge cycles. These results showed that the discharge capacity of the battery
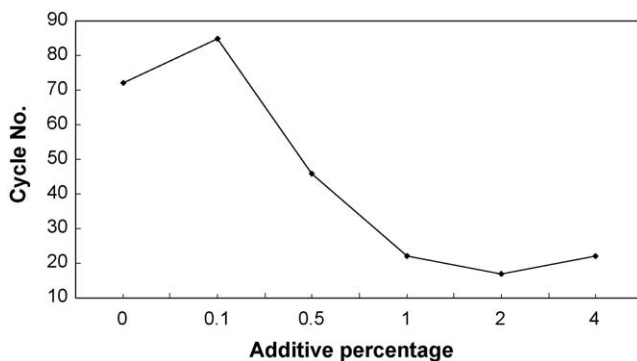

Fig. 5. The passed discharge cycles to reach final capacity of 15 A h for different percentages of sodium sulfate as a negative paste additive at 40 °C.
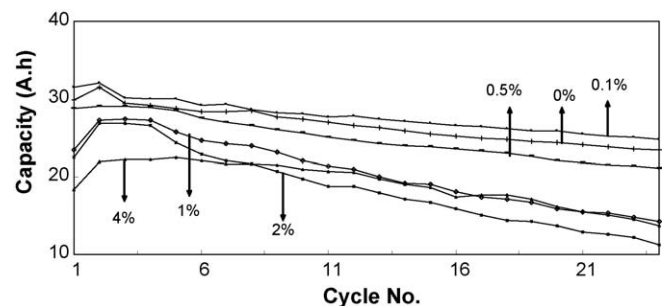

Fig. 6. Variation of discharge capacity at cycle life test for different percentages of sodium sulfate as a negative paste additive during 25 cycles at discharge current f 10 A.
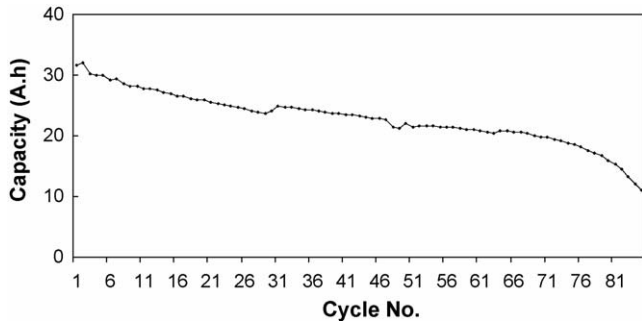
Fig. 7. The variation of discharge capacity during 85 charge–discharge cycles for the battery assembled with negative paste containing sodium sulfate of 0.1 wt% at discharge current of 10 A to reach the final capacity of 15 A h.

At the end of cycle life test, the morphology of negative paste was studied by a scanning electron microscopy (SEM). SEM images for several dosages of sodium sulfate are shown in Fig. 8. As it is seen, at the end of cyclelife, the SEM images show that the active material has become denser. In good agreement with the surface area studies, sodium sulfate makes the greatest surface area also creates the finest grained most porous structure. Sodium sulfate changed the morphology to a large crystal of metallic lead. The large size of these crystals is consistent with slow growth giving support to the idea that self-discharge is responsible for at least part of the capacity loss during cycling.

All the obtained results including first discharge capacity, cold cranking time; number of cycles and discharge capacity after cycle life test are summarized at Table 2. As it is seen at Table 2, the use of sodium sulfate with weight ratio of 0.001 (0.1 wt%) with respect to weight of initial lead oxide can increase the first discharge capacity, cold cranking ability, cycle life and discharge capacity at the end of cycle test to more than 3%, 17%, 18% and 12%, respectively. These results show that the use of sodium sulfate has an excellent effect on cold cranking ability and cycle life of the negative electrodes of lead-acid batteries.

with sodium sulfate of 0.1 wt% at the end of cycle life test is 12% more than battery without sodium sulfate.

For further investigation of the effect of sodium sulfate at charge–discharge cycles, the battery with 0.1 wt% sodium sulfate was charged and discharged during 85 cycles. The variation of discharge capacities during 85 charge–discharge cycles are shown in Fig. 7. As it is seen from Fig. 7, the battery with sodium sulfate content of 0.1 wt% shows the excellent cycle life.
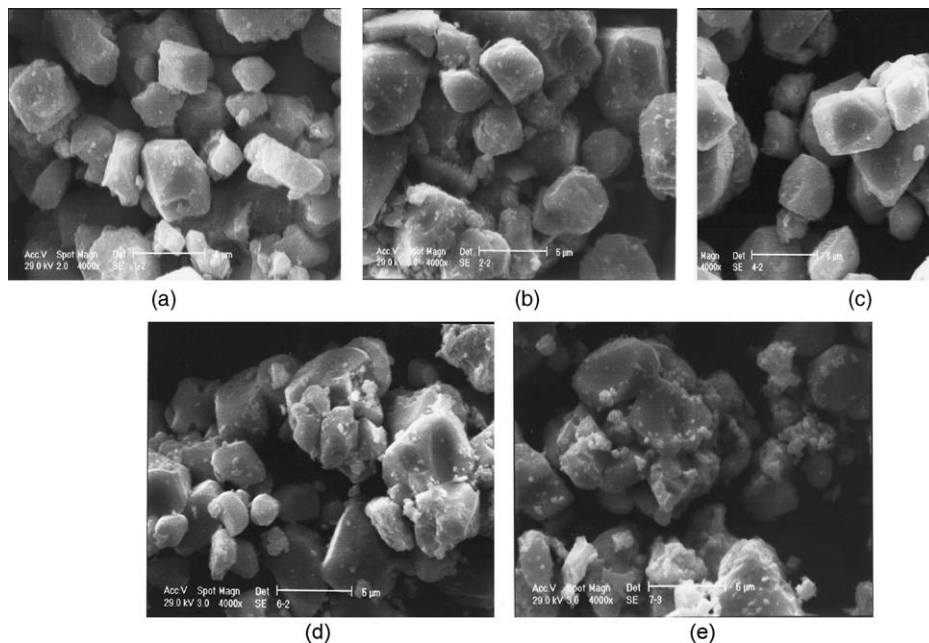

Fig. 8. SEM micrograph of cycled negative pastes with different percentages of 0% (a), 0.1% (b), 0.5% (c), 2% (d) and 4% (e) of sodium sulfate, at 40 °C.

Table 2
Summary of all test results of the prepared batteries

Na$_2$SO$_4$ dosage	0	0.1	0.5	1	2	4
NAM initial discharge capacity (A h)	34.9	35.99	34.22	32.8	31.1	29.1
NAM initial discharge capacity (A h kg^{-1})	169.49	174.05	158.8	155.01	153.05	149.51
Time of reaching to 6 V in cold cranking test (s)	64	75	65	39	19	15
NAM discharge capacity at the end of life cycle (A h)	25.31	28.47	21.71	20.18	16.67	18.35
NAM discharge capacity at the end of life cycle (A h kg^{-1})	123.55	140.02	107.03	95.339	80.112	86.69
Number of cycles in life cycle test (until reaching to 15 A h or 50 A h kg^{-1})	72	85	46	22	17	22

3.3. Tear down observation for life tests at 40 °C

Densification was evident by the many shrinkage cracks in the negative active material (NAM). The size of the cracks and their distribution was varied with the sodium sulfate amounts, and more cracks were seen in the negative plates without sodium sulfate or with the high dosage of it.

The negative active material (NAM) exhibited limited surface shedding and was in overall good condition excluding high dosage of additive (40–50% shedding in the 4% of sodium sulfate). For 0.1% wt of sodium sulfate, the negative grids were in good shape and flexible. There was good adhesion between the negative material and the grid structure porosity. In addition, corrosion was not seen in the grids.

4. Conclusions

Batteries containing sodium sulfate show a remarkable electrical behavior during the test. With respect to active material utilization, sodium sulfate gave the best performance at a weight percent of 0.1% with respect to lead oxide weight. Sodium sulfate as a pore forming agent with dosage of 0.1% increases the initial capacity up to 3%, cycle life up to 18%, discharge capacity after cycling up to 12% and cold cranking ability of the negative material up to 17%. Sodium sulfate can be considered as a very cheep and very efficient additive for negative paste of lead-acid batteries.

Acknowledgement

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