A Study of the Effect of Lead Sulphate on the Efficiency of Lead-Acid Storage Battery

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A field study of the effect an addition of lead sulphate ($PbSO_4.nH_2O$) in an automotive lead acid battery has been worked out. The results indicate that there is a significant improvement in the capacity of the lead storage battery; it prolongs the service life. A new electrochemical method for preparing this compound ($PbSO_4$) has been introduced.

The main objective of the present work is to investigate the possibility of using lead sulphate as a reinforcer (or service life prolonger) for the maintenance of SLI (starting, lighting and ignition) lead-acid batteries. Several articles have appeared in literature [1-7] concerning the chemical factors that influence the characteristics of these batteries but the influence of lead sulphate addition has not been reported.

During the cyclic life of lead-acid battery [8], layers of Pb and PbO_2 are smoothly desposited upon charging. At the end of this stage, lead ions are converted up to 98%. The acid concentration increases to the original value. In the course of discharge, the deposit of active mass is redissolved layer by layer and the $PbSO_4$ is formed and stored as a precipitate. Kubes [9] compared samples of pure $PbSO_4$ and the active mass collected from lead storage battery plates; he reported that the $PbSO_4$ is a constitutent part of the active masses produced by the current in the battery. A common mode of failure of these batteries in many applications - from standby power to automotive starting - is the corrosion of the positive plate [10]. This mainly arises from the gradual decrease in cohesion arising from the change of volume, (50% increase in the volume from PbO_2 to $PbSO_4$); more PbO_2 particles are disengaged from the mass as cycling is prolonged [11].

If one can increase the quantity of the active material, the capacity of the battery can definitely be improved. In the present study, an attempt has been made to use $PbSO_4$ as a reinforcer for failed lead-acid battery - the battery which cannot meet the demands of starting an automibile engine as a result of its low capacity.

According to the literature, there is no direct method for preparing $PbSO_4$ from Pb and H_2SO_4. It is always prepared by the reaction of lead(II) ion - PbO and $Pb(NO_3)_2$ - with SO_4^{-2} ion [12-14]. A new direct method for preparing $PbSO_4$ has been developed in the present work.

EXPERIMENTAL

Method of Preparing Lead Sulphate ($PbSO_4.nH_2O$)

The lead electrodes were prepared in an appropriate size from lead alloy scrap. An electrochemical cell of the type Pb/ CH_3COOH(dil), H_2SO_4 /Pb was constructed. The electrolyte was 3.5 M

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CH_3COOH. A potential of 12-20 V was applied at a current density of 40-50 $mA.cm^{-2}$. Hydrogen gas evolved as bubbles at the cathode. Sulphuric acid was added (causing a detectable increase in the electrical current). The lead sulphate precipitated as a white solid product. After a while (depending on the volume of the electrolyte and the number of the electrodes), the H_2SO_4 was consumed and the electrical current decreases. Then, an additional amount of H_2SO_4 was added in a manner similar to the previous one. The addition of H_2SO_4 was continued till the lead anodes were consumed. The product was collected by filtration and then washed several times with distilled water. The electrolyte was cycled to the cell for further use. It should be noted that H_2SO_4 can also be continuously added at a controlled rate, probably using a separating funnel.

Method of adding Lead Sulphate ($PbSO_4.nH_2O$) to the Lead Storage Battery

Lead Sulphate ($PbSO_4.nH_2O$), (60g) was suspended in distilled water (60ml). During charging operation, about 10 ml of this was added through a vent hole to each cell of a commercial battery. The charging operation can be carried out overnight by a conventional battery charger. The charging operation can also be carried out directly when the car engine worked for at least three hours. The capacity was estimated by high rate discharge through a resistor using a Battery Tester Model PB-12.

RESULTS AND DISCUSSION

The capacity of the battery can be increased by increasing the quantity of active material on the plates. This can be applied by addition of lead sulphate into the cells; this should be converted to the active material to enhance the battery capacity; this is the essential idea of the present work.

In order to avoid the precipitation of lead sulphate at the bottom of the battery container, the addition must be carried out during the charging operation; the released gases under such conditions can keep $PbSO_4$ suspended in the electrolyte and also can give more chance for the redox reactions of lead sulphate at the electrodes.

Since the battery capacity decreases by 1.0% (from its standard capacity) for each 1.0°C decrease in temperature, the work has been carried out during of late autumn and early winter - when temperature is low). The use of failure battery in this research can provide definitive results; Any improvements in the capacity of the failure battery is more detectable than the standard battery.

Fig.1 illustrates schematically the effect of the addition of lead sulphate to the capacity of lead-acid battery. Such relationship has been obtained from the addition of $PbSO_4.nH_2O$ separately to a failure battery (60Ah, 12V) in a bad state that could not start a motor car even if it is left two hours after charging. It has been recongnized clearly that there is a significant improvment in the capacity of the battery for each 10g $PbSO_4$ and when the amount reached 50-60g, it became capable of starting the electric motor of car in the morning and even 36 hours after charging. Each added amount of $PbSO_4$ has been followed by charging for six hours at a current density of 0.8-0.9 $mA.cm^{-2}$ and then the period can definitly be considered as a function of the capacity and therefore it has been employed in Fig.1. Since the charging operation can also alter the capacity, a

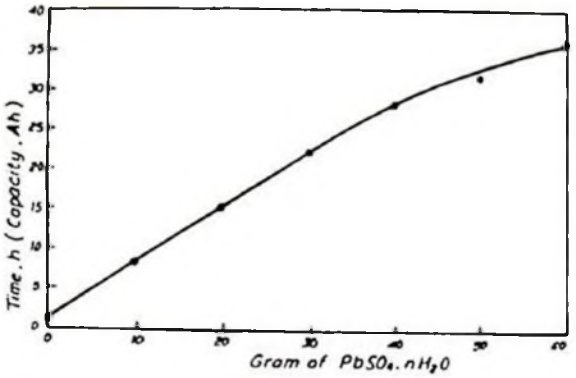


Fig. 1, A Schematic Plot Illustrating The Relationship Bet The Added Amount Of $PbSO_4$ And The Capacity Of Battery.

similar treatment has been carried out preliminary to verify this effect from the effect of lead sulphate. Thus, there is a clear proportion between the amount of $PbSO_4$ and the capacity of the battery.

In order to obtain more definitive results, a field study has been made by adding $PbSO_4$ to 33 failure batteries and the observed results are listed in Table 1. Interestingly, a significant improvement has been observed in the capacity of the lead acid batteries. Addition prolongs the service life for a period ranging from one to three months for the added 60g of $PbSO_4$. It is not surprising because the battery plates are manufactured from basic lead sulphate. The plates were prepared by mixing PbO with a sufficient amount of H_2SO_4. (It is recently evident that chemically prepared PbO_2 can be used for the manufacture of positive plates for lead acid batteries [15]).

The mechanism of conversion of added $PbSO_4$ to the active material can be presented as follows:

At positive plate (cathode)

$$PbSO_4 \longrightarrow Pb^{+2} + SO_4^{-2}$$
$$Pb^{+2} \longrightarrow Pb^{+4} + 2e^-$$
$$Pb^{+4} + 2\,OH^- \longrightarrow PbO_2(s) + 2H^+$$
$$2H_2O \longrightarrow 2\,OH^- + 2H^+$$

$$PbSO_4 + 2H_2O \longrightarrow PbO_2\,(s) + 2e^- + SO_4^{-2} + 4H^+$$

At negative sponge lead plate (anode):

$$PbSO_4 \longrightarrow Pb^{+2} + SO_4^{-2}$$
$$Pb^{+2} + 2e^- \longrightarrow Pb(s)$$

$$PbSO_4 + 2e^- \longrightarrow Pb(s) + SO_4^{-2}$$

Table 1

The Results of Field Study of Reviving Failed Batteries

60 g of $PbSO_4.nH_2O$ added and charged Total observations made = 33

No. studied	Observation	Percent
25	can start the car in the morning	75.8
6	improved significantly but can not start the car	18.18
2	No recognisable difference	6.0
0	Became worse	0.0

The overall reaction is;

$$2PbSO_4(s) + 2H_2O \longrightarrow PbO_2(s) + Pb(s) + 2H_2SO_4$$

Thus, the added $PbSO_4$ undergoes redox reactions which enlarge the surface of active material and contribute to increasing the capacity of the battery. Because the battery plates are very close to each other, the suspended $PbSO_4$ particles are usually in contact with the surface of the plate and then (upon charging) they will be oxidized or reduced in a manner similar to that of the formed $PbSO_4$ during discharging operation. Furthermore, Bagheb et al. [16] indicated that there are two additional processes occuring in the lead-acid battery which are significant for the formation and enlargement of the capacity of lead electrodes, especially as they contribute to enlarging the active lead surface. These processes have arisen from the solubility of $PbSO_4$ in diluted H_2SO_4. A common feature in the above equations is the consistency of the overall reaction with that of lead-acid battery which are identically the same.

The results in Table 1 show that two samples (6.0%) deviate from others. Both samples have no recognizable difference in the capacity after the addition of the solution of lead sulpahte. Such deviation can arise when a some type of contact takes place between the negative and positive plates, resulting in internal (or self) discharge and from some damages in the structure of the lead acid battery that can occur during its cycle life. It should be noted that only rechargable batteries which have a shortage in their capacities have been used in such treatment, while, batteries suffering from hard lead sulphate are excluded. Further developments should be made for making the addition of lead sulphate more applicable by mixing it with some additives such as expander, catalyst and so on.

From the method of preparing lead sulphate, it is necessary to introduce the electrochemical reactions taking place in the electrolytes and at the electrodes during the preparation process. When the cell operates, the reactions may be presented as following.

Anode:

$$Pb(s) + 2CH_3COO^- \longrightarrow Pb(CH_3COO)_2(\text{soluble}) + 2e^-$$

$$Pb(CH_3COO)_2(\text{soluble}) + SO_4^{2-} \longrightarrow PbSO_4(s) + 2CH_3COO^-$$

Cathode:

$$2H^+ + 2e^- \longrightarrow H_2(g)$$

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overall reaction:

$$Pb(s) + H_2SO_4 \longrightarrow PbSO_4 + H_2(s)$$

Thus, the acetic acid acts in a catalytic manner, or as an intermediate in which it absence can lead to cover the lead anode with porous nonconducting $PbSO_4$. In other words, the high resistance of $PbSO_4$ produces a *sulphate barrier layer*, which can lead to certain failure. So, the acetic acid reacts with Pb ion and form soluble lead acetate which reacts with sulphuric acid to reform acetic acid and lead sulphate.

Attention must be paid seriously to avoid any contamination of $PbSO_4$ with acetic acid (the product must be washed perfectly with distilled water). The latter can harm the battery and lead to eventual negative effect [17].

CONCLUSIONS

On the basis of our results we can conclude that the addition of lead(II) sulphate can lead to a positive effect on the efficiency of the battery. Lead(II) sulphate can be used as a reinforcer and service life prolonger for lead-acid batteries. It may also be used in the maintenance of such batteries in a similar way to that of adding approved water at regular intervals to ensure that the electrolyte level is kept at the specified point. The relationship between the amount of added $PbSO_4$ and the efficiency (Fig.1) suggests that the battery efficiency can not reach the normal or typical state, whatever the amount of added $PbSO_4$ is.

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