THE IMPACT OF Na_2SO_4 and $MgSO_4$ AS ELECTROLYTE ADDITIVES ON THE EFFICIENCY AND CYCLE LIFE OF LEAD ACID BATTERIES

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Abstract - *The Lead acid batteries are type of secondary batteries. Its ability to supply high surge currents and because of low cost these are attractive for automotive applications. Sulphation of the negative electrode remains a serious failure in these batteries. The influence of Na2SO4, MgSO4 additives were investigated. Charging and discharging cycles were carried out separately for Existing electrolyte, Electrolyte + Na2SO4, Electrolyte + MgSO4 for each one hour. The cycle test is evidence that the addition of Na2SO4 improved the cycle life and efficiency of 12V/100 AH lead-acid battery, while MgSO4 addition showed little improvement in cycle life compared to Na2SO4. Battery cycle life increases with reduced acid concentration, extended discharge time, and increased efficiency.*

***Key Words*: Lead-acid batteries, Sulphation, Chemical additives, lead- sulphate.**

1.INTRODUCTION

The Lead acid battery is a type of rechargeable battery first invented in 1859 by French physicist Gaston Plantae. It is the first rechargeable battery ever created. Compared to modern rechargeable batteries lead-acid batteries have relatively low density. Despite this, their ability to supply high surge current means that the cells have a relatively large power-to weight ratio. These features, along with low cost, make them attractive for use in motor vehicles to provide the high current required by starter motors [1].

As of now the usage of LAB can be categorized into:

1.Immobile applications:

Inverter applications, such as UPS; [2] Power storage device in electrical vehicles(EV) [3]. Power source in hybrid electrical vehicles and grid-scale energy storage component of electricity generated by renewable sources (solar/wind etc) [4].

2.Mobile applications:

Automotive or vehicular batteries used for starting in vehicle, lighting and ignition (SLI) [5,6].

1.1. Working of Lead-acid Batteries

The storage battery or secondary battery is such a battery where electrical energy can be stored as chemical energy and this chemical energy is converted into electrical

energy as and when required. The conversion of electrical energy into chemical energy by applying external electrical source known as charging of battery. Whereas conversion of chemical energy into electrical energy for supplying the external load is known as discharging of secondary battery.

However, the failure of LAB becomes the key barrier for its further development and application. Therefore, understanding the failure modes and mechanism of LAB is of great significance. The failure modes of LAB mainly include two aspects: failure of the positive electrode and negative electrode. The degradations of active material and grid corrosion are the two major failure modes for positive electrode, while the irreversible sulfation is the most common failure mode for the negative electrode [8]. Sulfation is the process of recrystallisation of PbSO4. In battery operation, it is desirable for the lead sulfate to form small crystals that readily redissolve during the charging process, allowing the active materials to revert to their original form. The lead sulfate crystals can grow larger, however, making it difficult to convert back to the active material. The growth of the nonconductive lead sulfate on the negative electrode during discharge can lead to the formation of the passive PbSO4 film, result- ing in the loss of battery capacity over time. In the operation of lead-acid batteries, if the battery operating conditions enable it to easily recharge to PbSO4, the process is called "soft sulfation"; if the recharge is difficult, the process is called "hard sulfation" [9]. The formation of "hard" sulphate is said to occur when the normally rechargeable lead sulphate crystals produced during discharge undergo a prolonged and/or elevated temperature ageing process. The lead sulphate crystals apparently undergo a recrystallisation process which results in an enlargement of the sulphate crystals. [10]

1.2.Lead–acid battery problems related to environment

Lead consumption in LAB production is about 86% of the world's total lead production. That is, it is mainly used for energy storage from automobiles, PV cells and wind turbines[11]. Batteries contains large amounts of lead as solid metal or lead-oxide powder. The average lead acid battery can contain up-to 10 kg of lead. Despite its widespread use, the use of lead is not without its problems and limitations. Lead is a highly toxic substance that attacks almost every organ in the body, and the nervous system is the area most affected by lead toxicity in both children and adults. Long-term exposure can lead to cognitive decline in tests that measure nervous system function. This can lead to behavioral problems, lack of learning, and a decline in IQ. Infants and children are particularly vulnerable due to their disproportionate exposure to toxins, their immature metabolic pathways, their delicate growth phase, and their long onset. Lead accounts for almost 1% of the world's disease burden and is the largest burden in developing regions [12] The main ways of lead exposure and ingestion are inhalation, ingestion, and lesser extent to skin contact. For people who use lead, inhalation of smoke and the dust are primary ways of exposure to the lead. Toddlers spend a lot of time in one place, tend to play on the floor, and move frequently from hand to mouth, which can be especially exposed to contaminated soil and dust in the air. Lead has no obvious physiological function and it has an affinity for sulfhydryl groups, other organic ligand in proteins and can copy other biologically essential metals such as zinc, iron and especially calcium.

• Effects on the digestive system

Due to the frequent gastrointestinal side symptoms of lead toxicity, a person who has been exposed may initially seek medical help. The side effects include a metallic aftertaste in the mouth, nausea, vomiting, constipation, abdominal pain or discomfort, and loss of appetite accompanying weight loss.

• Cognitive effects

The nervous system as a whole is toxic by lead. Particularly in young children, lead poisoning can result in life threatening encephalopathy. In adults, encephalopathy is less frequent. The first symptoms are sporadic vomiting, appetite loss, aggressive behavior changes, irritability, and agitation, headache, clumsiness, and sporadic sleepiness. Continued ataxia, vomiting, seizures, serious cerebral edoema, coma, and even death could result from this.

• Cardiovascular

Even at exposure levels below 10 g/dL, lead exposure is linked to an elevated risk of hypertension in adults and in pregnant women. Blood pressure and lead levels in bone have been discovered to have significant, albeit minor, relationships. The higher correlation with the bone lead suggests that the rise in blood pressure is linked to the long term consequences of early lead exposures.

• Hematological

Anaemia results from prolonged exposure to lead because it inhibits the synthesis of hemoglobin, which is essential for creation of red blood cells. Hemoglobin is required for the creation of cytochrome c, which is crucial for cellular respiration and may contribute to the neurotoxicity, therefore interfering with its synthesis also has additional detrimental effects [13].

2. MATERIALS AND METHODS

2.1 Materials Used

1. Lead-acid Batteries
2. Charging and Discharging Equipment
3. Sodium Sulphate
4. Magnesium Sulphate
5. Aluminium Potassium Sulphate
6. Digital Multimeter
7. Hydrometer
8. 3W DC Bulb
9. Weighing balance
10. De-ionised battery
11. Battery Acid
12. Glass beakers, conical flasks, glass rods, funnel
13. Hand Gloves, Face shield

2.2 Methods

2.2.1 Charge and the Discharge cycles for battery before addition of any additive

▪ The batteries were undergone through load test to know about the battery condition.
▪ Experiment was setup as shown in the diagram.
▪ The refillable lead acid batteries were filled with de-ionized water up to the mark.
▪ Initial specific gravity of the electrolyte and initial voltage was measured before
connecting to charge cycle and noted down. It is considered as charging voltage at time zero minute. Connecting the charger machine to power supply was done to start the charging cycle.
▪ 12V and 6A set to begin the charge cycle in charger.
▪ The charging voltage was noted with the help of digital multimeter and recorded
after 3 mins.
▪ The reading & recording of charging voltage was also done after 6mins, 9mins, 12mins, 15mins upto 30 mins within a intervals of 3 mins of the charging cycle.

▪ Discharge cycle was carried in the same equipment by setting to 12V and 6A and then it is connected to the battery.
▪ The voltages were read and noted down as discharge voltages after 3 mins.
▪ The respective discharge stages at 6 minutes, 9 minutes, 12 minutes up to 30 mins were all noted as the discharge voltage.
3.2.2 Charge and the Discharge cycle for Sodium sulphate blended electrolyte solution
▪ One of the flooded battery was taken & the electrolyte was withdrawn using a dropper to a beaker.
▪ Weigh exactly 4261.2 grams of sodium sulphate and mix with electrolyte.
▪ The mixed electrolyte solution was then gently poured in to the battery using a funnel.
▪ The voltage at this point is noted down as initial voltage using digital multimeter.
▪ Specific gravity of the solution measured using hydrometer and recorded.
▪ The charging equipment which is connected to power supply is connected to the battery to initiate the charging cycle.
▪ Charging done at 12V and 6A.
▪ After 3minutes, the charging voltage was read and noted down.
▪ The charge cycle was carried till thirty minutes. Charging voltages at 6 mins, 9mins, 12mins up-to 30 minutes within a interval of 3 minutes of charging cycle were all noted down.
▪ At the end of 30 minutes cycle, the voltage was read and recorded.
▪ The specific gravity of each cell was checked using hydrometer and noted down.
▪ For discharging, the battery was connected to charging equipment and the mode
was changed to discharging.
▪ Discharging was done by setting voltage to 12 V and 6A.
▪ Initial voltage was read and recorded.
▪ After 3 mins of discharge voltage was recorded with the help of digital multimeter.
▪ The discharge voltages at 6minutes, 9 minutes, 12 minutes upto 30 minutes within intervals of 3 minutes were recorded.

2.2.2 Charge and discharge cycle for Sodium sulphate mixed electrolyte solution

▪ One of the flooded refillable battery was taken and the electrolyte was withdrawn using a dropper to a beaker.
▪ Weigh exactly 4261.2 grams of sodium sulphate and mix with electrolyte.
▪ The mixed electrolyte solution was then gently poured in to the battery using a funnel.
▪ The voltage at this point is noted down as initial voltage using digital multimeter.
▪ Specific gravity of the solution measured using hydrometer and recorded.
▪ The charging equipment which is connected to power supply is connected to the battery to initiate the charging cycle.
▪ Carried out the charging and discharging cycles for about 30 minutes and noted down the voltages at intervals of 3 minutes each.
▪ The above procedure was repeated for Magnesium sulphate.

3. RESULTS AND DISCUSSIONS

3.1 Battery – 1 for Sodium sulphate Additive

Table 3.1.1: Charge and Discharge Voltages before addition of Sodium sulphate

Time in minutes	Charge voltage(V)	Discharge voltage(V)
0	13.44	12.66
3	14.40	12.27
6	14.60	12.22
9	14.68	12.14
12	14.63	12.09
15	14.73	12.01
18	14.73	12.01
21	14.73	12.04
24	14.73	12.04
27	14.71	12.06
30	14.71	12.06

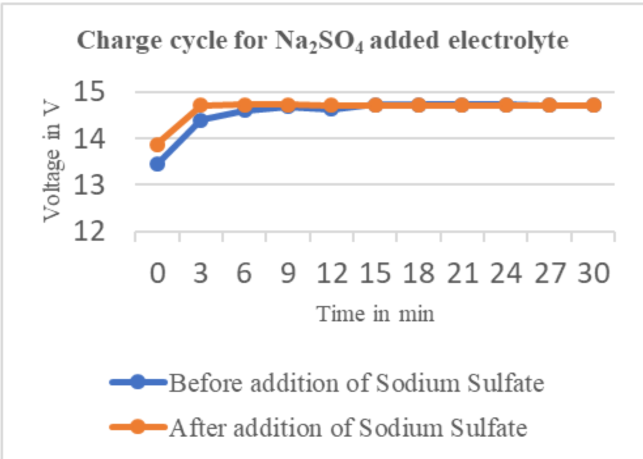

Chart – 1: Charge cycles for Battery – 1

Table 3.1.2: Charge and Discharge Voltages after addition of Sodium sulphate.

Time in minutes	Charge Voltage(V)	Discharge Voltage(V)
0	13.87	12.63
3	14.71	12.35
6	14.73	12.30
9	14.73	12.24
12	14.71	12.19
15	14.71	12.11
18	14.71	12.06
21	14.71	12.01
24	14.71	12.01
27	14.71	12.01
30	14.71	12.06

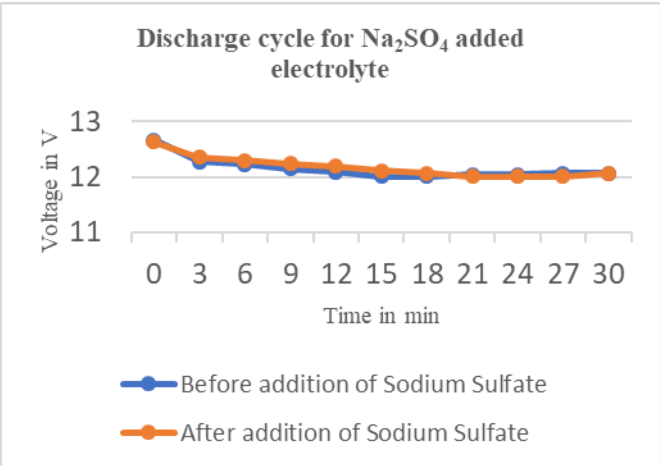

Chart – 2: Discharge cycles for Battery – 1

3.2 Battery – 2 for Magnesium Sulphate additive

Table 3.2.1: Charge and Discharge Voltages before addition of magnesium sulphate.

Time in minutes	Charge Voltage(V)	Discharge Voltage(V)
0	12.68	12.60
3	13.13	12.45
6	13.15	12.41
9	13.16	12.38
12	13.16	12.36
15	13.17	12.33
18	13.18	12.30
21	13.19	12.27
24	13.19	12.22
27	13.20	12.17
30	13.21	12.13

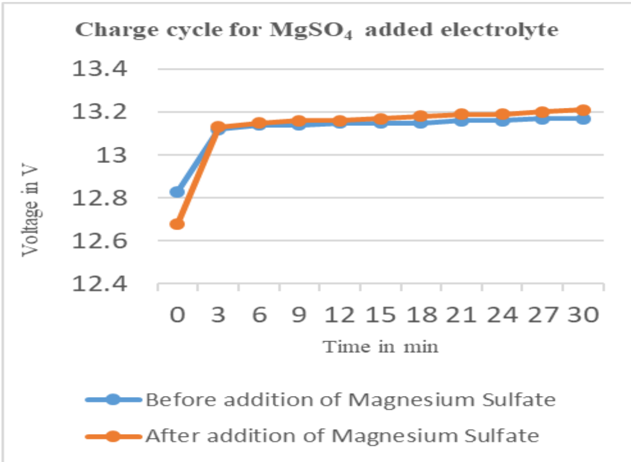

Chart – 3: Charge cycles for Battery – 2

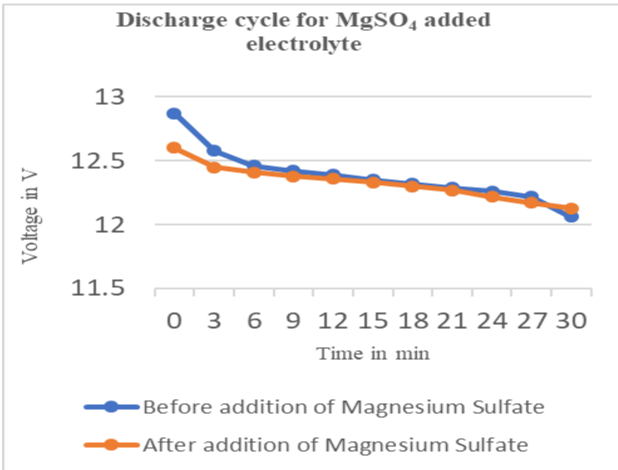

Chart – 4: Discharge cycles for Battery - 2

Table 3.2.2: Charge and Discharge Voltages after addition of magnesium sulphate.

Time in minutes	Charge Voltage(V)	Discharge Voltage(V)
0	13.10	12.87
3	13.84	12.58
6	14.14	12.46
9	14.68	12.42
12	14.68	12.39
15	14.68	12.35
18	14.73	12.32
21	14.76	12.29
24	14.73	12.26
27	14.73	12.22
30	14.73	12.06

4.CONCLUSIONS

Charging and the discharging cycles carried out on three flooded lead - acid batteries, found that the presence of the sodium sulphate additive in existing electrolyte of a lead acid battery provided small improvement to both the cycle life and the performance of the lead acid battery.

The service life of a lead-acid battery can be clearly explained because the one-cycle test is much shorter than the total life of battery, but time required to fully discharge can be used to infer the extension of life.

Small quantity of voltage was discharged during discharge cycle, which was less with the addition of Sodium sulphate to the existing electrolyte as compared to only the electrolyte of lead acid battery have the ability of extending the battery lifespan.

REFERENCES

[1] Https://en.wikipedia.org/wiki/lead-acid-battery

[2] J. Power Sour. 144 (2) (2005) 494– 504.

[3] C.C. Chan, E.W.C. Lo, W.X. Shen, J. Power Sour. 87 (2000) 201–204.

[4] Ioannis Hadjipaschalis, Andreas Poullikkas, Venizelos Efthimiou, Overview of current and future technologies for applications, Renewable and Sustainable Energy Rev. 13 (6–7) (2009) 1513–1522,

[5] https:// doi.org/10.1016/j.rser.2008.09.028. [5] R. Marom, B. Ziv, A. Banerjee, B. Cahana, S. Luski, D. Aurbach, J. Power Sour. 296 (2015) 78–85.

[6] P. Reasbeck, J.G. Smith, Batteries for Automotive Use, Research Studies PressLtd, Baldock, Hertfordshire, England, 1997.

[7] https://www.electrical4u.com/working- of-lead-acid-battery-lead-secondary- battery/ energy electric storage power

[8] Review on the research of failure modes and mechanism for lead–acid batteries

[9] Jun Yang, Chen Hu, Hao Wang, Kai Yang, Jing Bing Liu, Hui Yan, 2016

[10] Joey Jung, Lei Zhang, Jiujun Zhang, Lead-Acid Battery Technologies: Fundamentals, Materials, and Applications (2016), CRC Press, (International Standard Book Number – 13:978-1-4665-9223-0). [10]. Sulphation in discharged lead-acid batteries, I. K. Gibson and k. Peters Chloride technical ltd., wynne avenue, swinton, manchester (gt. Britain)1982

[11] W.W.W.UNEP.ORG

[12] W.W.W.NCBI.NLM.NIH.GOV

[13] Recycling used batteries, WHO

[14] Arup Bhattacharya, Indra Narayan Basumallick, Effect of mixed additives on lead-acid battery electrolyte, Department of electrochemistry, Journal of Power Sources, vol 113, 2003, pp 382-387.

[15] Chengwei Chen, Yongchuan Liu, Yuanqiang Chen, Xin Li, Jian Cheng, Sujing Chen, Junhong Lin, Xiangxin Zhang, Yining Zhang, Effect of polyaniline-modified lignosulfonate added to the negative active material on the performance of lead – acid battery, Fujian Normal University, Electrochimica Acta, Feb 2020.

[16] Chijioke Elijah Onu, Nnabundo Nwabunwane Musei and Philomena Kanwulia Igbokwe, Exploring the additive effects of aluminium and potassium sulfates in Enhancing the charge Cycle of Lead Acid Batteries, Department of chemical engineering, Asian Journal of Chemical Sciences 10(3), 2021, pp 11-19.

[17] C. Snydersa, E.E. Ferga, T.Van Dyl, The use of polymat material to reduce the effects of sulphation damage occurring in negative electrodes due to the partial state of charge capacity cycling of lead acid batteries ,Journal of Power Sources 200, 2012, pp 102-107.

[18] D. G. Enos, S. R. Ferreira, H. M.Barkholtz, W.Baca and S. Fenstermacherd, Understanding Function and Performance of Carbon Additives in Lead-acid batteries, Journal of Electrochemical Society 164, 2017, pp 3276-3284.

[19] Detchko Pavlova, Vesselin Naidenova, Yovka Milushevaa, Sasho Vassileva, Toshio Shibaharab, Masatoshi Tozukab, Benzyl Benzoate as an inhibitor of the sulphation of negative electrodes in lead-acid batteries, Journal of Energy storage 17, 2018, pp 336-344.

[20] Hai-Yan Hu, Ning Xie, Chen Wang, Li-Ya Wang, Robert M. Privette, Hau-Fei Li, Ming Pan, Fan Wu, Xiao-Ling Yan, Bang-Bang Jiang, Marvin H, Enhanced Performance of E-Bike Motive Power Lead-Acid Batteries with Graphene as an additive to the Active mass, ACS Omega, 2018, pp 7096-7105.

[21] Hai-Yan Hu1, Ning Xie 2, Chen Wang 1, Robert M. Privette, Hau-Fei Li, Ming Pan 1, Fan Wu 1, Xiao-Di Wang 1, Marvin H, Wu 4, K.Vinodgopal 5, Enhancing the Performance of Motive Power Lead-acid batteries by High surface Area Carbon Black Additives, Applied sciences,2019.

[22] Hassan Karami 1. Abbas Yaghoobi 1, Ali Ramazani, Sodium sulphate Effects on the Electrochemical Behaviors of Nanostructured Lead Dioxide and Commercial Positive Plates of lead-acid batteries, International Journal of Electrochemical Scioence 5, 2010, pp 1046-1059.

[23] Jakub Lach & Kamil Wrobel 1 & Justyna Wrobel &Piotr Podsadni & Andrzej Czerwinski, Apllications of carbon in lead-acid batteries: a review, Journal of solid state Electrochemistry, 2019.

[24] Jun Yang, Chen Hu, Hao Wang, Kai Yang, Jing Bing Liu, Hui Yan, Review on the research of failure modes and mechanism for lead- acid batteries.2016.

[25] Jiayuan Xiang, Ping Ding, Hao Zhang, Xianzhang Wu, Jian Chen, Yusheng Yang, Beneficial effects of activated carbon additives on the performance of negative lead-acid battery electrode for high-rate partial-state-of-charge operation, Journal of Power Sources 241, 2013. pp 150-158.