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Research Article

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The Impact of Sodium Sulfate Additive on the Cycle Life of Lead Acid Battery

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Abstract Sodium sulfate as an additive in the electrolyte solution of a 2V/20AH lead acid battery to determine the effect on the cycle life and performance of the battery has been investigated. The electrolyte solution was a combination of sulfuric acid and sodium sulfate with charge and discharge cycle processes carried out for 30 minutes each. The two different electrolyte solutions (dilute sulfuric acid and sulfuric acid-sodium sulfate additive) for the battery were done separately at negligible temperature change with an incandescent lamp of 6V, 10.3W applied as load for each of the discharge cycle process. The total quantity of voltage discharged by the sodium sulfate additive electrolyte (0.80V) was less than that of the dilute sulfuric acid electrolyte (1.20V) and this implies that the additive slightly improved the cycle life of the battery. The additive offered minimal positive impact to an already existing dilute sulfuric acid electrolyte of a typical lead acid battery. The effect of sodium sulfate additive on the life of the battery was discussed.

Keywords charge cycle; discharge cycle, sulfuric acid, sodium sulfate, Lead acid battery

Introduction

Lead acid batteries have been known for several years as the best reliable source of power for automotive and industrial use. It has also been established as the dominant in market use among other rechargeable batteries because of its economic value, the availability of raw materials, the unlimited recycling ability and the low energy. A lot of research has been carried out to improve the performance of the lead acid battery processes by looking at the positive and negative electrodes, type of electrolyte, composition of the terminals and other components of the battery [1]. The nature of positive and negative plates of a lead acid battery is synonymous to how the battery performs electrically which go through different changes. Adding sulphate salts to the electrolyte of lead acid batteries to decrease solubility of lead sulfate also decreases the inefficiency arising from the effects of deeply discharging the battery [2]. Several efforts have also been made to address the limitation of low specific energy in lead acid batteries which is as a result of inadequate use of the positive active material and presence of too much atomic weight in lead [3]. Other studies have concentrated on making the charge acceptance and cycle life of lead acid battery more efficient through the removal of sulfation (accumulation, crystallization of sulfate to state of not being able to charge) found in the negative electrode [3-5]. The removal of this sulfation in the negative electrode by adding more carbon and in the process prolonged the life of the lead acid batteryhave been achieved by Nakamura, et al [6]. This added carbon played the role of an additive which also had a positive impact on the material [7-15]. Sodium sulfate has a variety of areas where it has been used for years to enhance the life of lead acid batteries. It has been established that some additives help to influence the effectiveness of the negative plates of lead acid batteries. Sodium sulfate is an inorganic type of additives applied on the negative paste of lead acid batteries [16].

On the establishment that additives are very key in helping to improve the capacity, cycle life, charge acceptance, electrical performance of the battery and electrochemical aspect of the plates, in this paper, an effort has been tried using sodium sulfate in the electrolyte solution of dilute sulfuric acid of a 2V/20AH lead acid battery.

2. Materials and Methods

2.1. Materials

For this study, a 2V/20AH refillable Lead Acid Battery was used which was sourced from Ariria Market Aba in Nigeria. 33 vol% of dilute sulfuric acid with specific gravity=1.25, sodium sulfate salt. A digital voltmeter was used for measuring the voltage and a 6V incandescent lamp acted as the load applied.

The basic lead-acid chemical reaction in a sulfuric acid electrolyte, where the sulfate of the acid is part of the reaction, is:

(Overall reaction) [17]

discharge

$$PbO_2 + 2Pb + 2\,H_2SO_4 \rightleftharpoons 2PbO_4 + 2H_2O \qquad (1)$$

charge

The discharge reactions of materials are as follows, [6]

Cathode reaction,

$$PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbO_4 + 2H_2O \qquad (2)$$

node reaction,

$$Pb + HSO_4^- \rightarrow PbSO_4 + H^+ + 2e^- \qquad (3)$$

For Sodium Sulfate

$$PbO_{2(s)} + 2Na^+_{(aq)} + 2e^- \rightleftharpoons Na_2PbO_{2(s)} \qquad (4)$$

From equation (4), 2 moles is required and therefore mass of sodium sulfate required

$$2 * 142.04 = 284.08g$$

Mass of Sodium Sulfate required in 400mL of dilute H_2SO_4

$$284.08 * 0.4 = 113.63g$$

2.2. Methods

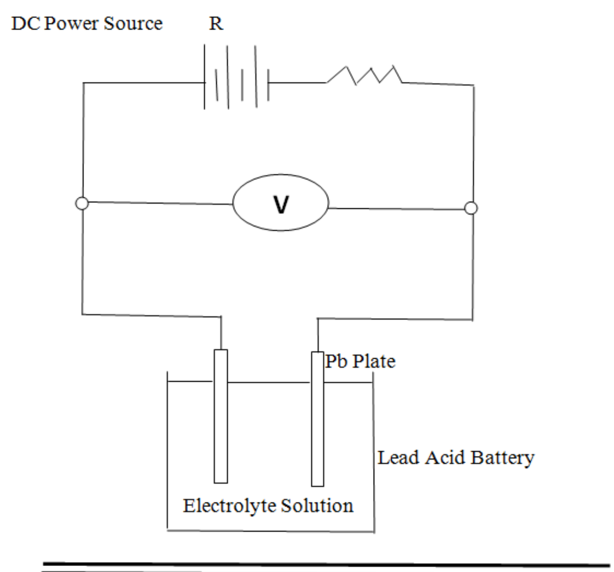

Figure 1: Experimental Set up (Circuit Diagram)

2.2.1 Charge and Discharge Cycle for Dilute Sulfuric Acid Electrolyte Solution

The experiment was set up as shown in the circuit diagram. 400mL of dilute Sulfuric acid (33Vol% specific gravity of 1.25) was measured with weighing cylinder and gently poured into the empty refillable 2V Lead Acid Accumulator with the help of a funnel. The voltage was read and recorded as charge voltage at time 0minute.

Connection of the regulated 5V DC power supply was done for beginning of the charging cycle. The charging voltage was read with a digital voltmeter and recorded after 5minutes. This reading and recording of charging voltage were also done after 10minutes, 15minutes, 20minutes, 25minutes and 30minutes of the charging cycle.

The power source was disconnected, and the voltage was read and recorded as discharge voltage at time 0minutes. A 6V incandescent lamp was connected at both terminals of the cell for the discharge cycle process. After a discharge time of 5minutes, 10minutes, 15minutes, 20minutes, 25minutes and 30minutes, the discharge voltages were all read and recorded. A moving coil voltmeter was used to check the accuracy of the digital voltmeter in reading the voltages.

2.2.2 Charge and Discharge Cycle for Mixed Electrolyte Solution

The refillable lead acid battery with distilled water, was emptied and cleaned with distilled water and another 400mL of dilute Sulfuric Acid was measured and gently poured into the battery. 113.6g of sodiumsulfate salt was weighed with the electronic scale and gently poured into the battery with the help of a spatula. The voltage at this time was read with a digital voltmeter and recorded under time 0 minutes. The regulated 5V DC power source was connected for start of the charging cycle. After 5 minutes, the charging voltage was read with a digital voltmeter and recorded. This charging cycle continued until 30 minutes. The charging voltages at 10 minutes, 15 minutes, 20 minutes, 25 minutes and 30 minutes were also read and recorded.

At the end of the charging cycle, the power supply was disconnected, and the voltage was read and recorded. The 6 V incandescent lamp was connected at the positive and negative terminals of the Lead Acid Accumulator with the help of connecting wires.

After 5 minutes of discharge, the voltage was read and recorded as the discharge voltage after 5 minutes and this discharge cycle was continued till the 30^{th} minute. The respective discharge voltage at 10 minutes, 15 minutes, 20 minutes, 25 minutes and 30 minutes were all read and recorded as the discharge voltages after those time intervals.

The molecular weight of the additive and the mole fraction in the reaction equation were the parameters that made up mass of additive used. A moving coil voltmeter was used to checkmate the accuracy of the digital voltmeter in reading the charge and discharge voltages.

3. Results and Discussion

3.1. Dilute Sulfuric Acid Electrolyte Solution

Figure 2 and Figure 3 shows the results of the charge and discharge cycle respectively for dilute sulfuric acid electrolyte solution of a 2V lead acid battery. As seen from the charge cycle graph, the charging process of lead acid battery using dilute sulfuric acid electrolyte solution had constant charging voltage between the 0-5 minutes and had a slight increase after 5 minutes (0.15V). There was no further voltage increase after 10 minutes of the charging cycle which led to consistent drop to 2.30V while the charging voltage after 25 minutes and 30 minutes were constant. The electrolyte solution of dilute sulfuric acid is being used as a reference base for the other electrolyte solutions containing additives to check for improvement.

As expected, for the discharge cycle after the application of 6 V incandescent lamp, the discharge time increases as the voltage keeps dropping steadily. The voltage drop was more after 5 minutes of discharge cycle (0.30V) and less after 25 minutes (0.10V). The quantity of voltage discharged after 15 minutes and 25 minutes, accounted for 58% and 92% respectively of the total discharged voltage of the discharge cycle process. This resulted to a total of 1.20V that was discharged during the 30 minutes discharge cycle and this value indicates that there was significantly no improvement on the life of this lead acid accumulator. The drop during the discharge cycle was inconsistent.

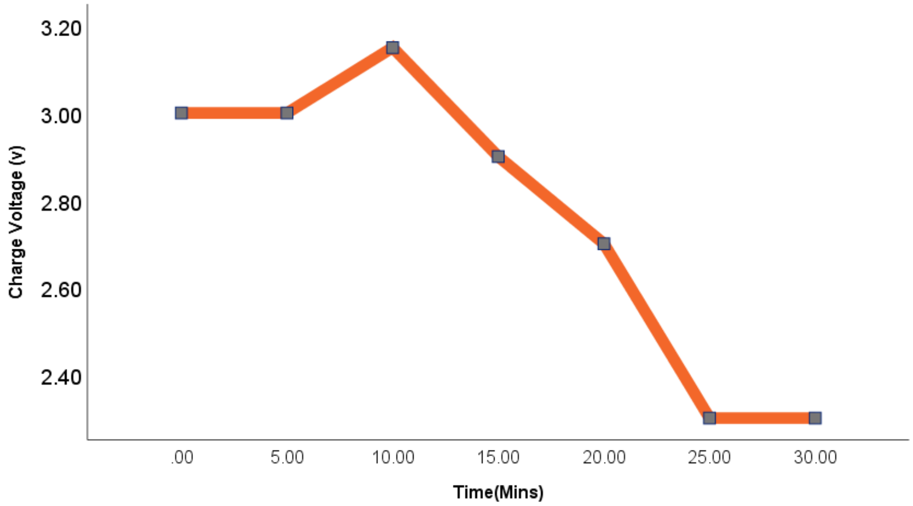

Figure 2: Plot of Charge Cycle for Dilute H_2SO_4 Electrolyte Solution

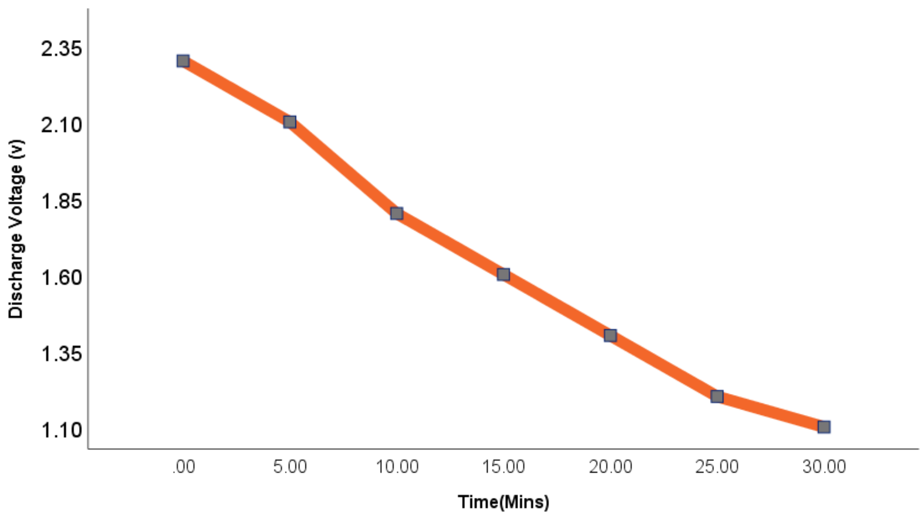

Figure 3:Plot of Discharge Cycle for Dilute H_2SO_4 Electrolyte Solution

3.2. Sulfuric Acid-Sodium Sulfate Mixed Electrolyte Solution

Figure 4 shows the result of the charge cycle while Figure 5 graphically illustrates the discharge cycle results for sodium sulfate additive mixed electrolyte solution of a 2V lead acid battery. For the charge cycle, as the time increases the voltage also increased but the change was constant between the 10-15 minutes and 20-25 minutes mark with a total increase in voltage of 0.25V which resulted in final charge voltage of 3.10V after 30 minutes. The highest increase was between 0-5 minutes (0.10V) while the lowest increase was 0.05V. The total increased voltage after 15 minutes (0.20V) accounted for 80% of the total increased voltage of the entire charging cycle respectively.

The application of 6 V incandescent lamp for the discharge cycle yielded decreased voltage from 1.30V to 0.5V with more of the decrease between discharge time of 5-10 minutes and 20-25 minutes (0.20V) of discharge cycle. The quantity of voltage discharged after 15 minutes (0.40V) and 25 minutes (0.70V) is equivalent to 50% and 88% of the total discharged voltage (0.80V) of the discharge cycle respectively.

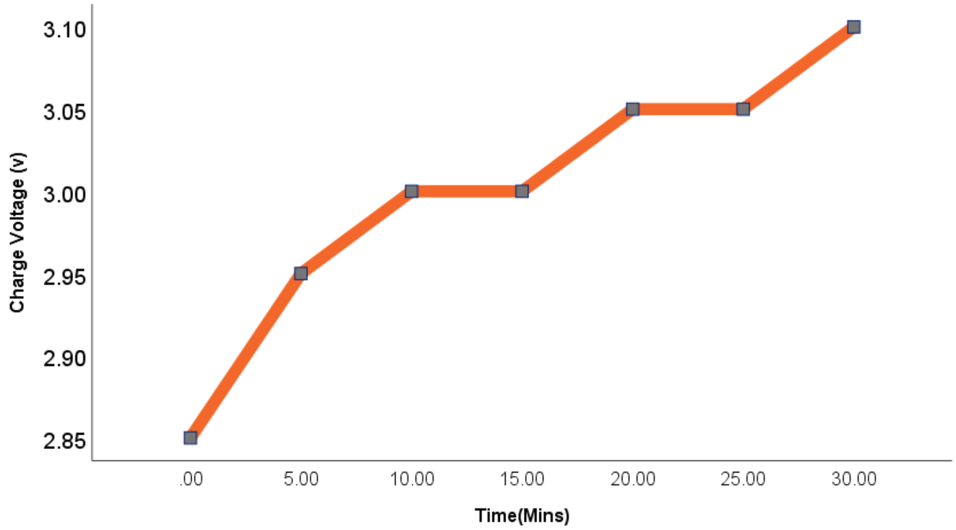

Figure 4: Plot of Charge Cycle for H_2SO_4+Na_2SO_4 Electrolyte Additive Solution

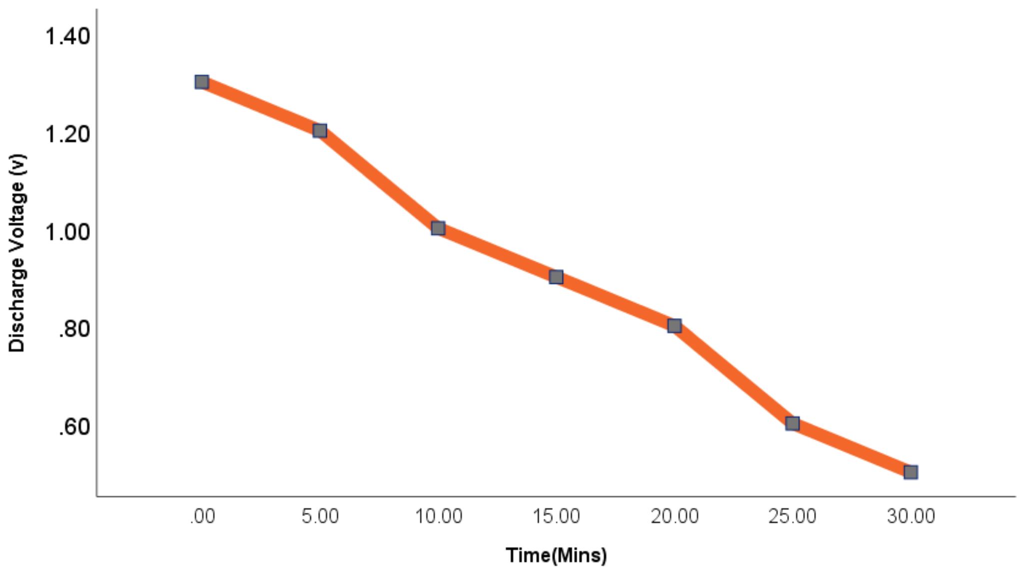

Figure 5:Plot of Discharge Cycle for H_2SO_4+Na_2SO_4 Electrolyte Additive Solution

3.4. The Effect of Sodium Sulfate Additive

A normal lead acid battery has dilute sulfuric acid as the electrolyte solution and this will be compared to that of the mixed electrolyte solution involving sulfate additive ((H_2SO_4 + Na_2SO_4).

In most cases as a voltage is applied to the lead acid battery which is always greater than the battery's voltage, a current is expected to flow through the lead acid battery in opposite direction to when it is supplying current and this makes the battery to charge. The rate of charge or current that will flow, depends on the difference between the battery's voltage and the voltage that is applied to it.

In an ideal charge cycle, as the charge time increases, the charge voltage also increases which end up creating an improvement on the lead acid battery. However, for discharge cycle of a typical lead acid battery, the discharge voltage decreases as the discharge time increases which bring about the formation of lead sulfate crystals at both terminals (positive and negative) of the battery. If the time to fully discharge a lead acid battery takes a much longer duration, it signifies that the life of the battery has been prolonged, and the efficiency improved. There was no consistency in the charging cycle process for the dilute sulfuric acid solution of 2V lead acid batter as observed in the charge voltage and in the same way, for the sulfuric acid-sodium sulfate mixed solution, the increase in voltage during the charge cycle showed more consistency.

Moreover, the total increased voltage during the charge cycle process shows the quality of the cycle life of such lead acid battery and therefore prolong the life of the battery. In this case, the sodium sulfate additive electrolyte delivered little increased Ampere-Hour rating and made significant improvement to the 2V lead acid battery as compared to the dilute sulfuric acid electrolyte solution. For the discharge cycle process in which a 6V incandescent lamp was applied with result as shown, the discharge voltage after 30 minutes for dilute sulfuric acid electrolyte solution was more than that of the mixed electrolyte solution. The decrease in voltage was more consistent in the sulfuric acid-sodium sulfate mixed solution than in dilute sulfuric electrolyte solution as illustrated in the graphs above. The total quantity of voltage discharged in the lead acid battery after 30 minutes of discharge cycle for dilute sulfuric acid was more than that of the sodium sulfate mixed electrolyte solution. The mixed additive solution had better polarity as compared to the sulfuric acid electrolyte solution and yielded little improvement with less discharged voltage after 30 minutes discharge cycle. This implies that a lead acid battery made up of dilute sulfuric acid electrolyte solution will discharge faster during the discharge cycle than that of a sulfuric acid-sodium sulfate mixed electrolyte solution. This signifies that for lead acid batteries with sulfuric acid-sodium sulfate electrolyte solution will take less time to discharge the same quantity of voltage compared to a battery of dilute sulfuric acid electrolyte.

A similar work by Rekha et al [1], discovered that addition of sodium sulfate to determine its electrical and electrode effects on a 12V-65Ah lead acid battery limited the large formation of sulfates which help to resist the challenges associated with sulfation. It was also stated that the quantity and concentration of the additive is dependent on what the lead acid battery is intended for and there is need for subsequent perseverance. Karami et al [2] shared the same view as the effects of sodium sulfate on the electrochemical behaviors of nanostructured lead dioxide were investigated. It was established that with a concentration of $1x10^{-5}$M, sodium sulfate is a very suitable additive for lead acid battery by carrying out a cyclic voltammetry and battery tests. It can serve as additives for both the negative paste and positive plates of lead acid batteries which will be productive for commercial use. Titanium dioxide and carbon additives in the positive and negative material properties with the effect on the performance of a lead acid battery was investigated by Rekha et al [7]. The titanium dioxide in the positive material helped to improve the tetra basic lead sulfate and subsequently prolonged the life of the battery while the activated carbon in the negative electrode enhanced the capacity [7]. According to an investigation, the addition of discrete carbon nanotubes to both electrodes also enhanced and improved the performance and cycle life of a lead acid battery [14]. These carbon nanotubes were incorporated to increase acceptance and cycle life with no change to paste density and without impeding the manufacturing process. The nanotubes treated lead acid battery showed little change to reserved capacity, improved cold cranking and enhanced overall system efficiency [14].

The sodium sulfate additive introduction into the battery cell due to the cohesive nature of the product resulted in particle shedding which in the traditional dilute sulfuric acid electrolyte always causes difficulty in the separators and electron effluent. The input and output qualities are improved and reduction in the heat produced. Therefore, a 2 V lead acid battery of sulfuric acid-lithium sulfate mixed electrolyte solution (H_2SO_4 + Na_2SO_4) offers better performance compared to a battery made of only sulfuric acid electrolyte solution.

4. Conclusion

The charge-discharge cycle carried out on the lead acid battery, established the fact that the presence of sodium sulfate additive in dilute sulfuric acid solution of a lead acid battery offered little improvement to the cycle life and performance of the battery.

For the life of the lead acid battery, the one cycle test carried is quite short compared to the overall life of a battery to make a clear statement, but the life improvement can be inferred from the length of time it took to fully discharge. Less quantity of voltage was discharged with the addition of sodium sulfate salt to the sulfuric acid solution as compare to only the dilute sulfuric acid solution lead acid battery. It was concluded that sodium sulfate additive in lead acid battery have the potential of prolonging its life span.

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