ABSTRACT

The adoption of aluminium sulfate and potassium sulfate as electrolyte additives were investigated to determine the possibility of enhancing the charge cycle of 2V/ 20AH lead acid battery with reference to the conventional dilute sulfuric acid electrolyte. The duration and efficiency of lead acid batteries have been a challenge for industries over time due to weak electrolyte and insufficient charge cycle leading to sulfation. This has affected the long-term production output in manufacturing companies that depend on lead acid batteries as alternative power source. Hence there is need to explore the use of specific sulfate additives that can possibly address this gap. The electrolyte solutions were in three separate charge and discharge cycles involving dilute sulfuric acid electrolyte, dilute sulfuric acid-aluminium sulfate mixed electrolyte and dilute sulfuric acid-potassium sulfate mixed electrolyte for one hour each. The total voltage after 30 minutes charge cycle was 2.3V, 2.35V and 5.10V for dilute sulfuric acid, aluminium sulfate additive and potassium sulfate additive respectively. The cell efficiency for dilute sulfuric acid, aluminium sulfate additive...
and potassium sulfate additive electrolytes are 77%, 77% and 33% respectively. The electrolyte sulfate additives were of no positive impact to the conventional dilute sulfuric acid electrolyte of a typical lead acid battery due to the low difference in potentials between the terminals.

Keywords: Charge cycle; discharge cycle; aluminium sulfate; potassium sulfate; lead acid battery.

1. INTRODUCTION

The invention of lead acid batteries dates to 1859 by French physicist Gaston Planté which is the oldest type of rechargeable battery that have gone through series of modifications, and improvements to make it have a better durability [1]. The competition from other renewable sources still haven’t surpass the reliability of lead acid batteries in the modern-day market especially for its wide range of application. Aluminium sulfate is a white crystalline solid when in its anhydrous state and is soluble in water but insoluble in organic solvents. It can also be produced by heating aluminium metal in a sulfuric acid solution. Aluminium sulfate which is sometimes known as alum is odourless and an ionic compound which is a combination of both positive and negatives ions. It has been established for years that aluminium sulfate has been the basic raw material in water treatment industry [2] used in purification of drinking and as coagulating agent in wastewater treatment plants and in paper industry. Amendment of poultry litter have been investigated which revealed that alum can allow more litter to be used before its removal in poultry flocks while decreasing the required cost of litter and environmental effect of regularly using litter [3]. It has been established that aluminium sulfate increases the drying shrinkage and improve the early strength on cement properties [4]. Potassium sulfate is a white odourless solid, an inorganic compound which has mineral form as arcanite but often rare and known as sulfate of potash. It naturally occurs in volcanic lava and salt lakes and has a saline like taste. Plants are essentially dependent on Potassium for good growth [5]. Potassium sulfate is often used as fertilizer because it doesn’t contain chloride which often cause damage to crop, and majority of these crops are tobacco, potatoes, watermelons, vegetables, and fruits [6]. Less sensitive crops sometimes need potassium sulfate for growth especially when chloride have been absorbed by the soil from irrigation water [7]. Research have shown that an increased application of Potassium sulfate in growth and development of cranberry plants resulted in decreased growth and yield parameters when subjected to irrigation methods [8]. It was discovered during an investigation on the influence of potassium sulfate on the character of the formation of Portland cement that it is useful additive because of its effectiveness as accelerator for slag Portland cement [9]. In the dissolution of potassium sulfate in aqueous solution, it was demonstrated that larger Potassium sulfate surface area improved the dissolution rate with its purity nearly 100% after purification process [10,11]. Lead acid batteries are configured to have an anode, a cathode, an electrolyte, and external casing. During the charging process, the anode act as the positive terminal where reduction (gain of electrons during reaction) occurs, and oxidation takes place at the negative terminal of the plate (cathode). For the discharge cycle, the excess electrons in the anode flows to the cathode where reduction occurs with the help of an applied external load with the cathode material also involved in the reduction reaction. The outcome of the oxidation reaction that took place at the anode during lead acid battery discharge are positive ions which is expected to flow to the cathode by the help of the electrolyte used. Similarly, the outcome of the reduction at the cathode are negative ions that will flow to the anode through the same electrolyte. The need to improve the efficiency of lead acid battery has been reported by some researchers and this investigation is driven to explore the use of sulfate additives as part of the electrolyte solution to resolve this research gap.

This research work is aimed at exploring the use of aluminium sulfate and potassium sulfate as electrolyte additives to enhance the charge cycle of lead acid battery. Comparing the charging and discharging cycles of dilute sulfuric acid electrolyte solution and mixed (sulfate) electrolyte solution will be used to determine if the addition of these salt additives improved the cycle life and efficiency of a 2V/20AH Lead Acid Battery.

2. MATERIALS AND METHODS

2.1 Materials Used

A 2V/20AH refillable lead-acid battery cell, stopwatch, connecting wires, distilled water,
electronic scale, measuring cylinder, digital D.C voltmeter, 6V 10.3W incandescent lamp, spatula, regulated 5V DC power supply, funnel, nose mask, moving coil voltmeter, hydrometer, 2ohms resistor, hand gloves, 33Vol% dilute sulfuric acid with specific gravity of 1.25, aluminum sulfate and potassium sulfate. Table 1 shows the amount of aluminum and potassium sulfate additives used in their respective electrolyte solution.

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) \[ \text{PbO}_2 + \text{Pb} + 2\text{H}_2\text{SO}_4 \rightleftharpoons 2\text{PbSO}_4 + 2\text{H}_2\text{O} \] \[ \text{(1)} \]

The discharge reactions of materials are as follows. \[ \text{PbO}_2 + \text{HSO}_4^- + 3\text{H}^+ + 2e^- \rightleftharpoons \text{PbSO}_4 + 2\text{H}_2\text{O} \] \[ \text{(2)} \]

Anode reaction,

\[ \text{Pb} + \text{HSO}_4^- \rightleftharpoons \text{PbSO}_4^- + \text{H}^+ + 2e^- \] \[ \text{(3)} \]

For Aluminium Sulfate Additive,

\[ 3\text{PbO}_2(s) + 2\text{Al}^{3+} + 6e^- \rightleftharpoons \text{Al}_2.3\text{PbO}_2(s) \] \[ \text{(4)} \]

For Potassium Sulfate Additive,

\[ \text{PbO}_2(s) + 2\text{K}^{+} + 2e^- \rightleftharpoons \text{K}_2\text{PbO}_2(s) \] \[ \text{(5)} \]

2.2 Methods

2.2.1 Experimental procedure for determination of charge and discharge voltages for each electrolyte solution

The experiment was set up with 400mL of dilute Sulfuric acid (33Vol% specific gravity of 1.25) 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 0minutes. Connection of the regulated 5V DC power supply was done at the beginning of the charging cycle. The charging voltage was read with a digital voltmeter and recorded after 5 minutes. This reading and recording of charging voltage was also done after 10 minutes, 15 minutes, 20 minutes, 25 minutes, and 30 minutes of the charging cycle. The power source was disconnected, and the voltage was read and recorded as discharge voltage at time 0 minutes. A 6V incandescent lamp (load) was connected at both terminals of the cell for the discharge cycle process. After a discharge time of 5 minutes, 10 minutes, 15 minutes, 20 minutes, 25 minutes and 30 minutes, 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. This charge and discharge cycle process was repeated two more times for aluminum sulfate additive with the refillable lead battery filled with 400mL sulfuric acid plus 168.1g of aluminum sulfate additive and for potassium sulfate additive containing 400mL sulfuric plus 139.4g potassium sulfate additive. The charging and discharging voltages for the two additive electrolyte solutions were also read and recorded after every 5 minutes until 30 minutes with 6V incandescent lamp connected at both terminals of the cell during the discharge cycle process. The battery efficiency for each electrolyte was also calculated.

3. RESULTS AND DISCUSSION

3.1 Charge and Discharge Voltage of Dilute Sulfuric Acid Electrolyte

Fig. 1 gives the summary of the charge and discharge cycle of a 2V lead acid battery using dilute sulfuric acid electrolyte solution. When a voltage is applied to the Lead Acid Accumulator which is greater than the battery’s voltage, a current will flow through the Lead Acid Accumulator in reverse direction to when it is supplying current, and the battery will 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. As seen from Fig. 1, 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 to other electrolyte solutions containing additives to check for improvement. On the discharge cycle, there was drop in the
voltage which caused the formation of lead sulfate crystals at both the negative and positive terminals. When it takes a longer time to fully discharge a lead acid battery, there is an improvement in the life of such battery. The voltage drop was more after 5 minutes of discharge cycle (0.3V) and less after 25 minutes (0.1V). 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. As the reference electrolyte solution, a total of 1.20V that was discharged during the 30 minutes discharge cycle and this will be used as yardstick to compare with the sulfate additives used.

Table 1. Experimental sample table for calculated mass of aluminium and potassium sulfate additives used

| Electrolyte Additive          | Molar Mass (g/mol) | Mass Required (g) | Mass used in 400mL of Dilute Sulfuric acid (g) |
|------------------------------|--------------------|-------------------|-----------------------------------------------|
| Aluminium Sulfate Additive   | 630.39             | 420.26            | 168.10                                        |
| Potassium Sulfate Additive   | 174.25             | 348.5             | 139.40                                        |

Fig. 1. Cycle plot for dilute sulfuric acid electrolyte (a) charge cycle & (b) discharge cycle
3.2 Charge and Discharge Voltage of Aluminium Sulfate Additive

Fig. 2 shows the charge and discharge cycle results for the aluminum sulfate additive mixed electrolyte solution of the same refillable lead acid battery. For the Aluminum Sulfate additive mixed solution, the charging voltage first increased after 5 minutes of the charge cycle, but a decrease after 10 minutes as shown below. There was an increase in charge voltage after 15 minutes which then maintained a steady decline to a final charge voltage of 2.35V after 30 minutes. From the graph, it is obvious that there was no consistency in the voltage increase across the charge cycle and this also implies that the mixed electrolyte solution of sulfuric acid-Aluminum sulfate additive yielded no significant improvement in charging cycle with reference to dilute sulfuric acid electrolyte. The discharge voltage decreases as the discharge time increases and the quantity of voltage discharged varies across different discharge time. The voltage drops between 5 minutes and 10 minutes yielded more (0.25V) while that between 0 minute and 5 minutes had the smallest voltage drop (0.05V). The decrease between 15-20 minutes and 20-25 minutes had a constant voltage (0.15V). The voltage drop was also not consistent across the 30 minutes of discharge cycle and therefore it will take less time to fully discharge and offers no improvement. The discharge voltage dropped from 2.0V to 1.2V as indicated in Fig. 2 within the 30 minutes discharge cycle.

Fig. 2. Cycle plot for aluminium sulfate additive. (a) charge cycle & (b) discharge cycle.
### 3.3 Charge and Discharge Voltage of Potassium Sulfate Additive

The summary of the charge and discharge cycle results for a refillable 2V lead acid battery using potassium sulfate additive electrolyte solution is illustrated in Fig. 2. The electrolyte solution of dilute sulfuric acid- potassium sulfate additive had a little increase in the charging voltage between 5 and 10 minutes and steady decrease after 15 minutes, 20 minutes and 25 minutes. This decrease in charge cycle voltage, stipulates that no positive change in the addition of Potassium Sulfate additives to dilute sulfuric acid electrolyte solution of the lead acid battery. The discharge cycle graph indicates that the changes in the discharge voltage is inversely proportional to the changes in the discharge time. As the discharge time increases, the discharge voltage decreases when a load of 6V incandescent lamp was applied to the potassium sulfate additive electrolyte solution. The highest voltage discharged was 0.15V between 5-10 minutes discharge time while the lowest was between 0-5 minutes of the discharge cycle process (0.04). 44% and 81% of the total discharged voltage (0.54V) were discharged after 15 minutes and 25 minutes respectively.

![Charge Cycle](image1)

![Discharge Cycle](image2)

**Fig. 3.** Cycle plot for potassium sulfate additive. (a) charge cycle and (b) discharge cycle
3.4 Cell Voltage Efficiency

The calculated voltage efficiency of the refillable lead acid battery for the three-electrolyte solution is illustrated in Fig. 4. The efficiency for the three electrolyte solutions is 77% for both dilute sulfuric acid and aluminum sulfate additive and 33% for potassium sulfate additive. The normal efficiency of a lead acid battery is 67% [13]. With reference to the efficiency of the lead acid battery using the conventional dilute sulfuric acid electrolyte solution (77%), there was no improvement in the application of potassium sulfate additive, while the efficiency of the battery using aluminum sulfate additive remained the same. The low voltage efficiency can be attributed to the low electromotive force during the charge and discharge cycles. This implies that the charge cycle had no significant improvement which ought to have prolonged the life of the battery.

3.5 Discussion

Additive effects of aluminium sulfate in the sulfuric electrolyte solution of lead acid battery had no improvement on the charge cycle and stability of the cathode with reference to the battery made of dilute sulfuric acid electrolyte. In a similar research, it was also discovered that sodium sulfate additive yielded no enhancement of the charge cycle and cathode stability of a refillable lead acid battery [14]. In addition, when investigating the impact of fluid solution additives, there was an extension of the life of a lead acid battery using mixed sulfates of copper, aluminum, cobalt, cadmium, magnesium, sodium, potassium, and deionized water [13]. Part of the reason for the no improvement while using aluminum sulfate additive electrolyte solution with reference to the sulfuric acid electrolyte battery was due to the high amount of voltage discharged (0.8V) during the discharge cycle and inconsistent charge cycle voltage. The charge cycle voltage was expected to have a steady increase and not a decrease with potassium sulfate additive electrolyte solution. Electrons were released, lead sulfate crystals were formed on both terminals and this resulted to the voltage drop. Similarly, this research illustrated that using potassium sulfate additive as part of the electrolyte solution neither improved the charge cycle nor the stability of the cathode of lead acid battery with reference to the dilute sulfuric acid electrolyte lead acid battery. It was also discovered that zinc sulfate additive added in the electrolyte solution of dilute sulfuric acid did not also improve a lead acid battery [15]. According to previous research, sodium sulfate as an electrolyte additive have positively influenced the performance of 12V/65AH lead acid battery [16]. This same idea was also reflected in the sodium sulfate effects on the electrochemical behaviors on commercial positive plates of lead acid batteries. In low concentration, sodium sulfate can be used as commercial additive for negative pastes and as additive for the positive plates of lead acid batteries [17]. It was shown that the battery filled with sulfuric acid solution and sodium sulfate prolonged the life cycle. The electrochemical
behavior of magnesium sulfate showed that its optimal concentration in the electrolyte solution will reduce the formation of hydrogen at the lead electrode terminal on lead electrodes. This reduction in the opposition to direct electric current of the electrode will decrease the resistance and further enhance the charge cycle and life of the lead acid battery [18]. The main reason for aluminium sulfate and potassium sulfate additives not being able to improve the conventional dilute sulfuric acid electrolyte solution is due to the low difference in potentials between the positive and negative terminals. This resulted to having no enhancement to the charge cycle of the refillable lead acid battery.

4. CONCLUSION

In terms of the voltage efficiency, there was no improvement in the efficiency of a lead acid battery when using aluminium and potassium sulfate additive solutions compared to that of dilute sulfuric acid electrolyte solution. For the life of 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. The addition of lithium sulfate salt to the sulfuric acid solution took 30 minutes to discharge 0.8V while 1.2V was discharged in only the dilute sulfuric acid solution lead acid battery. This implies that lithium sulfate additive in lead acid accumulator improved the stability of cathode and further enhancing the charge cycle by prolonging its life span. Finally, based on this research carried out on 2V refillable lead acid battery, it is safe to say that aluminium and potassium sulfate additives rendered no significant improvement to the conventional dilute sulfuric acid electrolyte battery because of the low electromotive force between the terminals of the plate.

COMPETING INTERESTS

Authors have declared that no competing interests exist.

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