

PERFORMANCE ANALYSIS OF ALUMINUM SULFATE (ALUM) AS A LEAD-ACID BATTERY ELECTROLYTE

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Abstract. Lead-acid batteries play a crucial role in the automotive industry, often placed close to the engine, subjecting them to elevated temperatures during operation. These batteries rely on active materials such as lead (cathode), lead dioxide (anode), and the corrosive electrolyte solution sulfuric acid (H_2SO_4). In response to the need for safer alternatives, this research explores the potential of aluminum sulfate ($Al_2(SO_4)_3$), commonly known as alum, as a viable electrolyte for lead-acid batteries. The investigation encompasses solution preparation, Total Dissolved Solids (TDS) analysis, pH evaluation, charge-discharge assessments, and specific gravity measurements. The study includes six solution variations, comprising alum solutions at concentrations of 35%, 50%, and 100%, and alum 50% solutions augmented with H_2SO_4 at concentrations of 5%, 10%, and 15%. The findings reveal that the optimal molarity for the $Al_2(SO_4)_3$ solution is 2 M. With increasing concentrations of alum and H_2SO_4 , the electrical conductivity of the solution rises, whereas the pH levels decrease. Remarkably, the battery utilizing a 50% alum solution exhibited the highest capacity at 0.05 Ah, while the inclusion of 15% H_2SO_4 in the 50% alum solution resulted in an impressive capacity of 0.52 Ah. Moreover, the specific gravity of the alum solution decreases by 0.0013 for every 1-degree Celsius temperature increase, while the alum solution with added H_2SO_4 experiences a similar decrease of 0.0012. This research presents promising prospects for utilizing alum-based electrolytes in lead-acid batteries, offering enhanced safety and performance in high-temperature environments.

Keywords: Lead-acid batteries, Aluminum sulfate, and Battery performance

Abstrak. Baterai timbal-asam memainkan peran penting dalam industri otomotif yang sering ditempatkan dekat dengan mesin, sehingga menyebabkan suhu tinggi selama pengoperasian. Baterai ini mengandalkan bahan aktif seperti timbal (katoda), timbal dioksida (anoda), dan larutan elektrolit asam sulfat yang bersifat korosif (H_2SO_4). Menanggapi kebutuhan akan alternatif yang lebih aman, penelitian ini mengeksplorasi potensi aluminium sulfat ($Al_2(SO_4)_3$), yang umumnya dikenal sebagai tawas, sebagai elektrolit yang layak untuk baterai timbal-asam. Penyelidikan meliputi persiapan larutan, analisis Total Padatan Terlarut (TDS), evaluasi pH, penilaian muatan-pengosongan, dan pengukuran berat jenis. Penelitian ini meliputi enam variasi larutan, yang terdiri dari larutan tawas pada konsentrasi 35%, 50%, dan 100%, serta larutan tawas 50% ditambah H_2SO_4 pada konsentrasi 5%, 10%, dan 15%. Temuan menunjukkan bahwa molaritas optimal larutan $Al_2(SO_4)_3$ adalah 2 M. Dengan meningkatnya konsentrasi tawas dan H_2SO_4 , konduktivitas listrik larutan meningkat, sedangkan tingkat pH menurun. Hebatnya, baterai yang menggunakan larutan tawas 50% menunjukkan kapasitas tertinggi yaitu 0,05 Ah, sedangkan penambahan H_2SO_4 15% dalam larutan tawas 50% menghasilkan kapasitas yang mengesankan yaitu 0,52 Ah. Selain itu, berat jenis larutan tawas mengalami penurunan

sebesar 0,0013 untuk setiap kenaikan suhu 1 derajat Celsius, sedangkan larutan tawas yang ditambah H_2SO_4 mengalami penurunan serupa sebesar 0,0012. Penelitian ini menyajikan prospek yang menjanjikan untuk memanfaatkan elektrolit berbasis tawas dalam baterai timbal-asam, yang menawarkan peningkatan keamanan dan kinerja di lingkungan bersuhu tinggi.

Kata Kunci : Baterai timbal-asam, Aluminium sulfat, dan Kinerja baterai

1. Introduction

In recent years, energy storage systems have emerged as critical components across diverse domains, including vehicle technology, renewable energy setups, and portable electronic devices. Among these energy storage solutions, batteries hold the foremost position, with lead-acid batteries being a prominent example. These batteries, classified as secondary batteries, comprise lead (Pb) and lead dioxide (PbO_2) as electrode materials, with a sulfuric acid solution (H_2SO_4) serving as the electrolyte [1]. The presence of sulfuric acid as the electrolyte in lead-acid batteries can potentially yield negative consequences. Direct exposure to this substance poses hazards not only to human health but also to the surrounding environment [2]. Hence, in pursuit of a more eco-friendly electrolyte, researchers have been working on the development of alternatives using environmentally safer materials. One such candidate for use as an electrolyte is aluminum sulfate, scientifically referred to as $Al_2(SO_4)_3$ and commonly known as alum.

Alum, also known as aluminum sulfate ($Al_2(SO_4)_3$), is a substance that exists in the form of crystals, granules, or white powder. It readily dissolves in water but does not dissolve in alcohol [3]. Aluminum sulfate is a cost-effective, non-toxic, and safe substance, making it a more environmentally sustainable option compared to sulfuric acid [4]. When aluminum sulfate is dissolved in water, the salt dissociates into metal anions and cations [5]. The resulting ions can facilitate the flow of electric current within the solution, rendering aluminum sulfate solution a viable option for use as an electrolyte. Utilizing alum solution as an electrolyte can alter the electrochemical processes within the battery, consequently impacting key battery attributes like electrolyte-specific gravity, voltage, and battery capacity.

According to the findings of Chijioke *et al* in their study on incorporating alum as a supplement in the electrolyte of PbO_2 batteries, the research indicated that there wasn't a notable enhancement in the charge-discharge properties. This lack of improvement stemmed from the limited potential difference between the positive and negative terminals, leading to minimal charge-discharge cycling of the battery [6]. However, according to Zhengyang *et al*, alum can be used as an additive to PbO_2 battery electrolyte because it inhibits sulfation which can enhance battery performance [4]. In this research investigation, we will systematically prepare a range of alum-based solutions with varying molar concentrations. The primary objectives are to identify the optimal molarity of the alum solution, evaluate its electrolyte conductivity, assess pH levels, measure specific gravity, and thoroughly analyze the charge-discharge characteristics of lead-acid batteries utilizing alum-based electrolytes. Additionally, we will investigate the specific gravity of the alum solution as it pertains to its potential impact on battery performance.

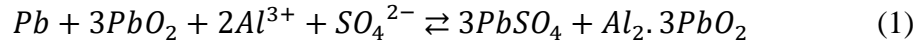
2. Material and Methods

2.1 Preparation of Alum Electrolyte Solution

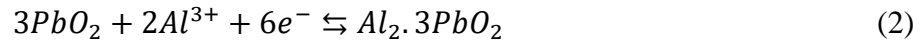
Alum electrolyte solution is made by mixing alum powder that has been filtered using mesh 200 with aquades stirred using a magnetic stirrer for 30 minutes at a temperature of $85^\circ C$ for every 200 mL of solution. Electrolyte solutions were prepared with

concentrations of 1 M, 2 M, and 3 M. Subsequently, the alum solution with optimum molarity that has been made is mixed with aquades with variations in the volume ratio of alum solution 35%, 50%, and 100% to aquades referred to as solution A, solution B, and solution C. Alum solution 2 M 50% is then mixed with aquades, followed by the addition of sulfuric acid with volume variations of 5%, 10%, and 15% relative to the alum, referred to as solution X, solution Y, and solution Z.

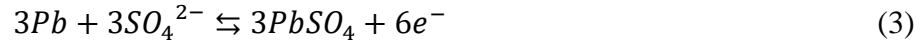
Chemical reactions that occur when alum ($\text{Al}_2(\text{SO}_4)_3$) is inside the lead-acid battery are as follows [6] :



At the cathode, the following reaction occurs:



The reaction that occurs at the anode is as follows:



2.2 Total Dissolve Solid and Conductivity Test

Total dissolved solid (TDS) in an electrolyte solution is measured using TDS (Total Dissolve Solid) meter brand Puretrex. Since ion concentration affects the electrical conductivity (EC) in water, EC can estimate TDS with a conversion factor of 0.64 which is a conversion factor that represents the average equivalent weight of salt commonly found in water [7]. The relationship between electrical conductivity and the amount of solute uses the following equation [8] :

$$\text{TDS} = \text{EC} \times 0.64 \quad (4)$$

$$\text{EC} = \frac{\text{TDS}}{0.64} \quad (5)$$

TDS, which stands for Total Dissolved Solids, quantifies the concentration of solute in parts per million (ppm), while EC, or electrical conductivity, is a measurement expressed in microsiemens per centimeter ($\mu\text{S}/\text{cm}$) at 25 °C.

2.3 pH test

pH testing is conducted using a pH meter from the Lutron brand. The testing process starts with the calibration of the pH meter using a calibration solution with pH values of 3 and 5. After calibration, the pH meter is immersed in the solution to be tested, and the displayed value is observed until it stabilizes.

2.4 Charge-Discharge Test

The charge-discharge testing on lead-acid batteries with alum electrolyte was conducted using the constant current charge and discharge method at 1.2 A. In testing discharge, 3 parallel arranged 12V/5 W motor brake lights are used as loads. The discharge process stopped at the cut-off voltage lead-acid battery i.e. 10.5 V. The obtained data were used for battery capacity calculations. Battery capacity is generally expressed in Ampere Hour (Ah) according to the equation below [9].

$$C = I \times \Delta t \quad (6)$$

where I is the current in Amperes (A) and t is the time in hours (h).

2.5 Specific Gravity Test

The solution is placed on a beaker wrapped using aluminum foil and heated using a hotplate magnetic stirrer with a temperature between 25°C – 120°C. For every 5°C increase in temperature, the specific gravity is measured using a hydrometer, and the temperature of the electrolyte solution is measured using a thermometer. Specific gravity measurement data needs to be corrected at the reference temperature of 80°F (26.7°C), using the following equation [10].

$$SG_{27} = SG + 0,0007 \times (27^{\circ}C - T) \quad (7)$$

SG_{27} refers to the specific gravity measured at the standard temperature of 27°C, while SG represents the specific gravity indicated by the tool. Additionally, T denotes the temperature of the electrolyte in degrees Celsius (°C).

3. Results and Discussion

3.1 Alum Electrolyte Solution

The aluminum sulfate electrolyte solution was prepared with variations in concentrations of 1 M, 2 M, and 3 M. As the concentration of the solution increases, it becomes more concentrated. The solution is made to a concentration of 3 M because at that concentration some alum is not completely soluble, resulting in the presence of solid particles. Therefore, the optimum concentration that can be used in research is a 2 M electrolyte solution.

3.2 Total Dissolve Solid of Alum Electrolyte Solution

Total dissolved solids are used for electrical conductivity calculations according to equation (5). Table 1 shows the amount of dissolved substances in the electrolyte solution.

Table 1. The TDS and the electrical conductivity of the electrolyte solution

Solution	Total Dissolve Solid (PPM)	Electrical Conductivity (S/cm)
Commercial	8958	1.40×10^{-2}
A	4468	6.98×10^{-3}
B	4626.1	7.23×10^{-3}
C	4958.7	7.75×10^{-3}
X	7355.9	1.15×10^{-2}
Y	8457.1	1.32×10^{-2}
Z	8852.8	1.38×10^{-2}

According to Table 1, the electrical conductivity of commercial electrolyte solutions is 1.40×10^{-2} S/cm, which aligns with theory [11]. Higher levels of alum and sulfuric acid lead to an increased concentration of dissolved substances. With a higher concentration of dissolved solids, there are more ions in the solution, resulting in greater electrical conductivity [12]. In this research, the electrical conductivity of alum is lower than that of sulfuric acid. This is because hydrogen ions are smaller than aluminum ions, leading to higher ion mobility.

3.3 pH of Alum Electrolyte Solution

pH measurement is carried out to determine the degree of acidity of the solution. Table 2 shows the pH of solutions at various concentration variations.

Table 2. pH of electrolyte solutions at various variations

Solution	pH
Commercial	0.32
A	3.7
B	3.59
C	3.3
X	1.57
Y	1.48
Z	1.38

Based on Table 2, the pH of the alum solution decreases as the alum concentration increases. This occurs because when alum reacts with water, the ions will dissociate to form Al^{3+} ions and hydrolyze with water molecules, generating hydrogen ions (H^+) which contribute to the pH reduction of the solution. As the alum concentration increases, the production of hydrogen ions also increases, leading to a decrease in the solution's pH. Alum solution with the addition of sulfuric acid exhibits a lower pH than pure alum solution because sulfuric acid increases the concentration of hydrogen ions in the solution, resulting in a lower pH. In commercial electrolyte solutions, the pH produced is very low at 0.32.

3.4 Charge-Discharge

Figure 1 shows a graph of the time to voltage of a lead-acid battery with alum electrolyte.

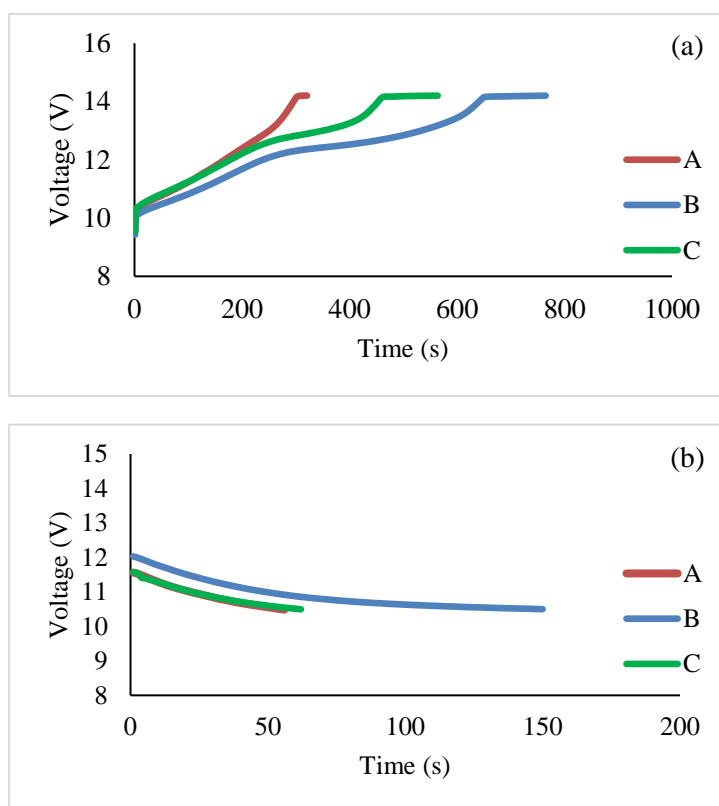


Figure 1. Graph of voltage (V) to time (s) lead-acid battery with alum electrolyte (a) charge; (b) discharge

The concentration of alum in the electrolyte directly affects the charging and discharging times of the batteries. Generally, as the alum concentration increases, the charging and discharging times also increase. However, there is an exception with Battery C, which has shorter charging and discharging times compared to Battery B. The discharging time is directly proportional to its discharging capacity. Battery B exhibits the highest discharging capacity, followed by Battery C and Battery A. Battery A has the lowest capacity because it contains fewer ions, resulting in fewer chemical reactions. However, Battery C experiences a decrease in capacity, despite having the highest alum concentration in. This decrease is caused by the formation of PbSO_4 crystals and $\text{Al}_2 \cdot 3\text{PbO}_2$ solids around the electrodes, which cover the active electrode surface. This precipitation hinders electrochemical reactions, resulting in suboptimal performance. Additionally, it also affects the working voltage of Battery C, causing it to decrease compared to Battery B. These findings align with previous research by Ghufroon *et al* [13] and Khairati [14], which explored the impact of sulfuric acid concentration (H_2SO_4) on lead-acid battery performance. Specifically, Battery B demonstrates the highest capacity among the tested batteries, reaching 0.05 Ah.

Figure 2 shows a graph of the time to voltage of a lead-acid battery with mixed electrolyte.

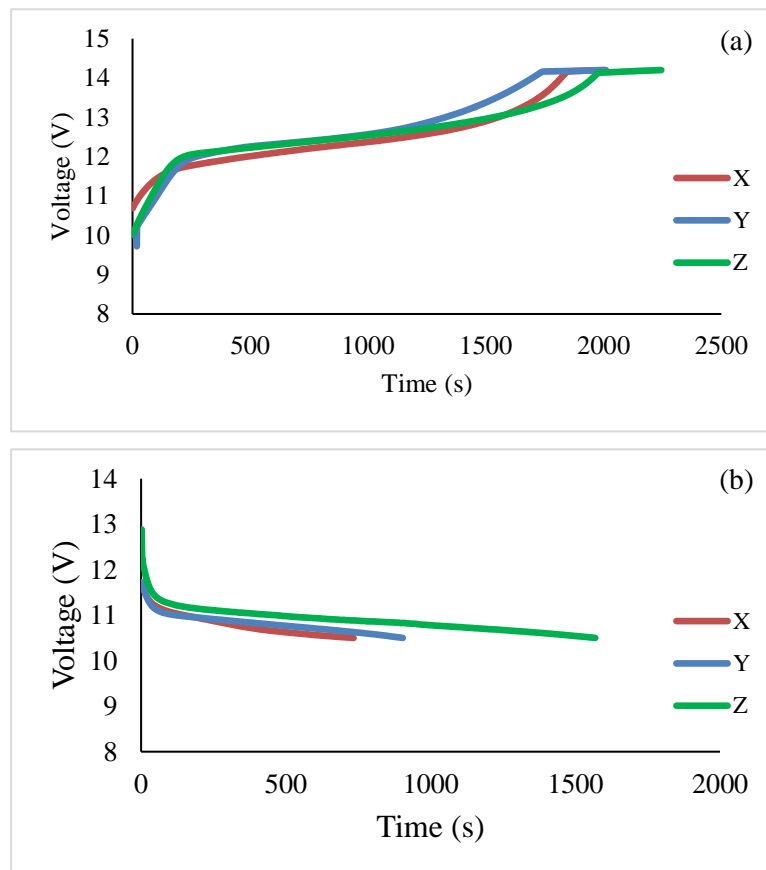


Figure 2. Graphs voltage (V) to time (s) lead-acid battery with mixed electrolytes (a) charge; (b) discharge

Based on Figure 2, the higher the addition of sulfuric acid, the longer it takes to charge and discharge the battery. Battery Z has the longest charge and discharge times compared

to others. This occurs because the increase in sulfuric acid concentration can enhance the chemical reactions within the battery and its energy storage capacity. The largest capacity is achieved by battery Z, which amounts to 0.52 Ah. Furthermore, a high working voltage is also generated by Battery Z because sulfuric acid can increase the number of freely moving ions in the solution.

3.4.1 Comparison with Commercial Lead-Acid Battery

In this study, battery B and Z were compared with commercial lead-acid batteries. Figure 3 shows a graph of the time-to-voltage relationship in lead-acid batteries.

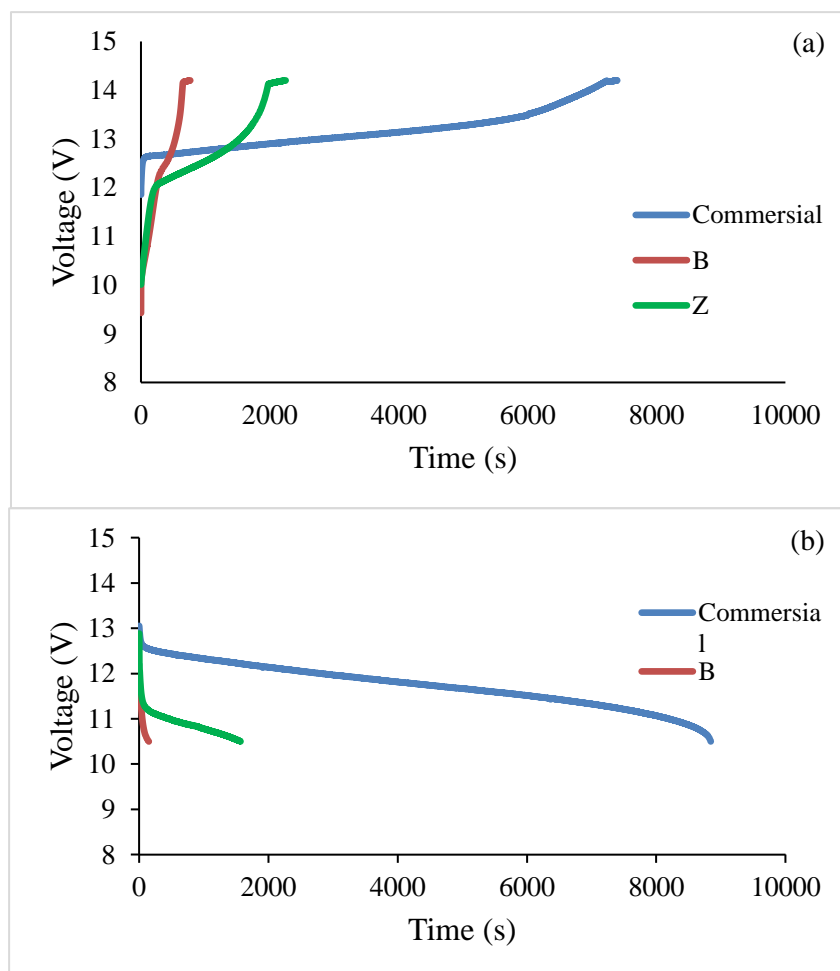


Figure 3. Graph of voltage (V) to time (s) of lead-acid battery (a) charge; (b) discharge

According to Figure 3, the charge and discharge times of B and Z batteries are shorter compared to commercial batteries. In addition, the initial charging voltage of B and Z batteries is lower than commercial batteries which can be affected by the limited ions in the electrolyte, resulting in a lower potential difference in the batteries. As a result, fewer particles can react during the charging process and the battery's ability to be loaded is smaller. Moreover, in battery systems B and Z, the formation of PbSO_4 and $\text{Al}_2.3\text{PbO}_2$ can inhibit contact between electrolyte and electrode. However, battery Z has a longer charge and discharge time compared to battery B because the addition of sulfuric acid can increase the number of ions that can react with the electrodes.

3.5 Specific Gravity Test

Specific gravity is tested on solution B, solution Z, as well as commercial solutions as shown in Figure 4.

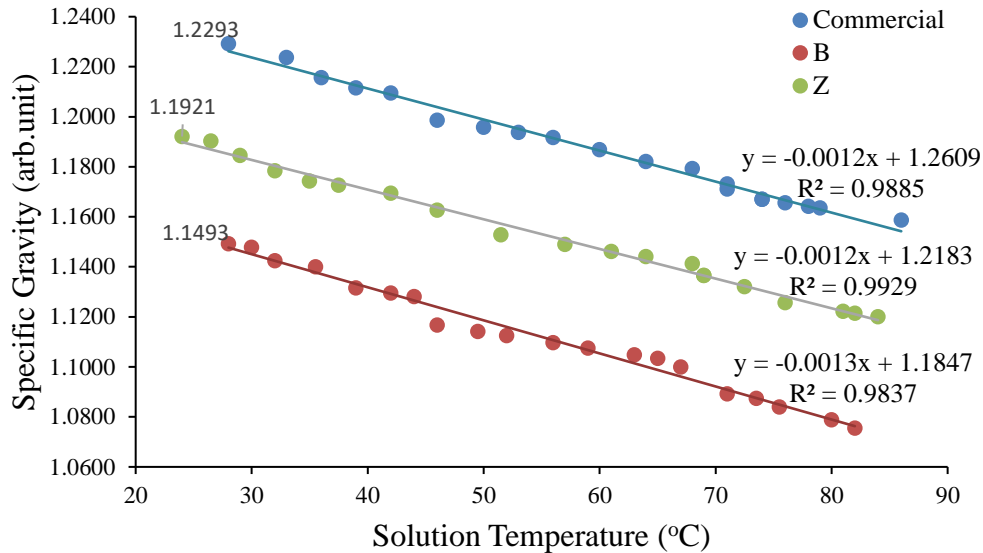


Figure 4. Graph of electrolyte-specific gravity to solution temperature

The specific gravity follows a descending order, with the commercial solution having the highest specific gravity, followed by Solution Z and Solution B. This difference is mainly due to the higher molarity of the commercial solution. Solution Z is Solution B by adding sulfuric acid, which increases the molarity and solute content so that the specific gravity is higher and closer to the commercial solution. A higher specific gravity has the potential to improve battery performance because a higher specific gravity correlates with a greater number of ions, resulting in higher conductivity.

Figure 4 displays a decreasing trendline, indicating an inverse relationship between specific gravity and temperature. As temperature rises, the specific gravity of the electrolyte solution decreases due to thermal expansion, causing the molecules to occupy more space while the mass remains relatively constant, resulting in reduced specific gravity. When applied to lead-acid batteries, high-temperature thermal expansion can enhance capacitance and reaction rates due to increased temperature. However, the downside is that high temperatures also accelerate degradation processes, limiting the battery's lifespan. The pure alum solution exhibits the most significant thermal expansion, with a specific gravity decrease of 0.0013, whereas sulfuric acid solution and alum solution with added sulfuric acid experience a smaller specific gravity decrease of 0.0012.

4. Conclusions

The optimum molarity of $\text{Al}_2(\text{SO}_4)_3$ alum solution that can be made is a solution with a concentration of 2 M because at a concentration above 2 M a solution that is not completely soluble is obtained which is characterized by the presence of precipitates. The electrical conductivity of the solution increases with the increase in alum and H_2SO_4 concentration. Meanwhile, the pH of the solution decreases as the increase of aluminum

sulfate (alum) and sulfuric acid. The largest capacity occurs in batteries with a 50% alum concentration, which is 0.05 Ah, and 50% alum + H₂SO₄ 15% batteries of 0.52 Ah. Alum solution decreased specific gravity by 0.0013 with every increase of 1 degree Celsius, while alum solution with the addition of H₂SO₄ decreased specific gravity by 0.0012.

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