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Research Article

Biofuel Technology: A Review

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Abstract- Electrochemical batteries are rapidly gaining widespread application in the electric utility sector as well as in transportation systems and accurate battery models are needed during the design phase of such systems to predict future performance. Most Valve Regulated Lead Acid (VRLA) batteries on the market or in production today are AGM batteries. The electrolyte is immobilized by a micro fiber glass mat. Their usable life is usually between 5 and 10 years and cycle life is between 200 and 500 cycles (80% DOD). Their lifespan is restricted by an increase in internal resistance and consequently a decrease in capacity. Alongside lead acid batteries, AGM batteries will be more prominent in the future. AGM batteries are widely used thanks to their maintenance-free and high safety standards. The use of AGM batteries is increasing day by day by evaluating battery performance with various studies and models. Compared to flooded batteries, they have lower levels of electrical resistance and electrolyte stratification. It also provides a more flexible usage area due to its high gas efficiency. AGM batteries with long discharge depth will provide various benefits to the user in the current technology and in the future.

Keywords: Lead Acid Battery, Absorbed Glass Mat, Battery, Lead Acid.

I. INTRODUCTION

In contemporary times, the rapid advancement of technology has significantly increased the demand for energy. While traditional energy sources play a crucial role in meeting this demand, their environmental impact and finite nature make them unsustainable. At this juncture, renewable energy sources come into play. Unlike fossil fuels, renewable energy sources can be continuously harvested from nature and are environmentally friendly. The development of renewable energy sources is vital for ensuring the sustainable progression of technology. However, due to issues related to the intermittency of these energies, energy storage systems become necessary. Energy storage systems store energy produced at times when it is not needed, making it available when required. These systems ensure the continuity of energy supply, meeting the needs of modern life and contributing to the sustainability of human existence. Therefore, the development and widespread implementation of energy storage systems are critical for the efficient use of renewable energy sources and the uninterrupted continuation of human life. At this point, batteries become crucial. Batteries are fundamental devices that store produced energy and make it available when needed. By storing energy obtained from renewable sources such as solar panels or wind turbines, they enable this energy to be used continuously and reliably. Particularly in applications such as electric vehicles, portable electronic devices, and emergency power supplies, batteries are key to energy storage. Therefore, the development and widespread use of batteries play a critical role in ensuring the efficient use of renewable energy sources and the continuity of energy supply. As the storage capacity and efficiency of batteries increase, they become an indispensable component for the sustainability of modern life. The integration of energy storage technologies, especially batteries, with advancing technology and renewable energy sources, emerges as a fundamental requirement for the sustainability of human life.

Batteries are considered one of the most important and efficient ways to store electrical energy. The ability to store electrical energy plays a critical role in almost every aspect of modern life. Therefore, many types of batteries with different electrode and electrolyte combinations have been developed. Various battery types are used in applications with high energy storage requirements, such as electric vehicles (EVs).

Lead-acid (Pb-acid) batteries are one of the oldest and most widely used types of batteries. They are commonly used to provide starting power for automobiles. Lead-acid batteries remain popular due to their low cost and reliability, although their energy density is relatively low. Absorbent Glass Mat (AGM) batteries are a type of lead-acid battery in which the electrolyte (sulfuric acid) is absorbed into a glass fiber mat. This structure makes the battery more durable, reliable, and maintenance-free.

Nickel-Cadmium (Ni-Cd) batteries are known for their durability and long lifespan. They are resistant to high discharge rates and are used in many industrial applications. However, due to the environmental hazards of cadmium, their use is decreasing.

Nickel-Metal Hydride (NiMH) batteries are more environmentally friendly compared to Ni-Cd batteries and offer higher energy density. Therefore, they are widely used in hybrid vehicles and various electronic devices.

Zero Emission Battery Research Activity (Zebra) batteries are based on sodium-nickel chloride technology. These batteries have high energy density and are known for their ability to operate at high temperatures. They are being investigated as a potential alternative for electric vehicles.

Lithium-ion (Li-ion) batteries are one of the most widely used energy storage solutions today. Due to their high energy density, low weight, and long lifespan, they are used in a wide range of applications from portable electronic devices to electric vehicles. Lithium-ion batteries are divided into various subtypes:

- ‘Lithium-Cobalt-Oxide (LCO) batteries’ are known for their high energy density and are commonly used in electronic devices such as mobile phones and laptops.
- ‘Lithium-Manganese-Oxide (LMO) batteries’ possess high thermal stability and are utilized in power tools and electric bicycles.
- ‘Lithium-Titanate (LTO) batteries’ are noted for their fast charging and discharging capabilities and long lifespan, making them ideal for applications requiring rapid charging.
- ‘Lithium-Nickel-Manganese-Cobalt (NMC) batteries’ offer balanced performance and are widely used in electric vehicles.
- ‘Lithium-Nickel-Cobalt-Aluminum (NCA) batteries’ provide high energy density and long lifespan, and are used by electric vehicle manufacturers such as Tesla.
- ‘Lithium-Iron-Phosphate (LFP) batteries’ are known for their high safety and long lifespan, making them popular in electric vehicles and energy storage systems.

Sodium-ion (Na-ion) batteries have been developed as an alternative to lithium-ion batteries. They are expected to be low-cost and environmentally friendly, but have not yet become commercially widespread.

Lithium-air (Li-air) batteries theoretically offer very high energy density. They are in the research phase and could potentially provide a solution for long-range electric vehicles in the future.

Lithium-sulfur (Li-sulfur) batteries attract attention with their high energy density and low-cost advantages. They are currently in the research and development stage.

Zinc-air (Zn-air) batteries are known for their high energy density and low costs, and are typically used in small electronic devices such as hearing aids.

The development of battery technologies for electric vehicles can be represented in a timeline, showing the progress of these types over time. Each battery type offers different energy storage capacities, safety features, costs, and environmental impacts suitable for specific applications. The development and widespread use of batteries are crucial for sustainable energy solutions and meeting the energy requirements of modern life.

In this context, the focus will be on AGM (Absorbed Glass Mat) batteries.

1.1 Lead-Acid Battery Theory

The lead-acid battery was invented in 1859 by the French scientist Gaston Planté. Despite being the first type of battery developed, lead-acid batteries continue to remain relevant today. They are the oldest and most widely used type of battery. Lead-acid batteries are devices that store electrical energy as chemical energy and convert it back to electrical energy when needed. These batteries are widely used in automobiles, renewable energy systems, and uninterruptible power supplies. During charging and discharging in lead-acid storage, the reaction products at the electrodes are described by the "double sulfate theory." The double sulfate theory explains the chemical reactions occurring in lead-acid batteries. According to this theory, the formation and dissolution of sulfate occur at both the positive and negative electrodes during the charging and discharging processes of the battery. Sulfuric acid (H_2SO_4) plays a critical role in the operation of these batteries. The fundamental structure and working principle of lead-acid batteries rely on the chemical reactions between sulfuric acid and lead electrodes. The double sulfate theory is a fundamental chemical process for understanding the working principle of lead-acid batteries. Figure 1 illustrates the structure of a lead-acid battery. The reactions occurring within the battery are generally summarized by the following reaction:

$$PbO_2+Pb+2H_2SO_4 \xleftrightarrow[\text{charging/discharging}]{} 2PbSO_4+2H_2O \qquad [1]$$

Since the concentration of sulfuric acid changes significantly with conversion, extensive research has been conducted on its thermodynamics. Since 1954, these studies have been expanded with various explanations, which can be summarized as follows:

- The discovery of two forms of PbO_2 in active materials, α-PbO_2 and β-PbO_2, reveals that while the modifications in PbO_2 result in slight differences in free energies, the entropies vary significantly.

- The electrochemistry of materials found between the defined phase boundaries can be explained. The width of the phases affects the potential.
- A lead-acid battery uses a combination of lead plates or grids with an electrolyte. The cells, consisting of diluted sulfuric acid, convert electrical energy into potential chemical energy.
- A galvanic cell is a combination of two electrodes and an electrolyte where a chemical reaction generates electricity. There are two types of cells: primary and secondary (or accumulators). An accumulator is an energy storage device that directly converts electrical energy into chemical energy during charging.
- The positive electrode or plate of a cell is cathodic during discharge, allowing electrons to enter the cell to cause a chemical reduction. During charging, an anodic reaction or oxidation occurs, and electrons leave the plate.
- Cells or batteries have a nominal capacity rated in ampere-hours (Ah) and a standardized nominal voltage of 2.0V per cell for lead-acid batteries.

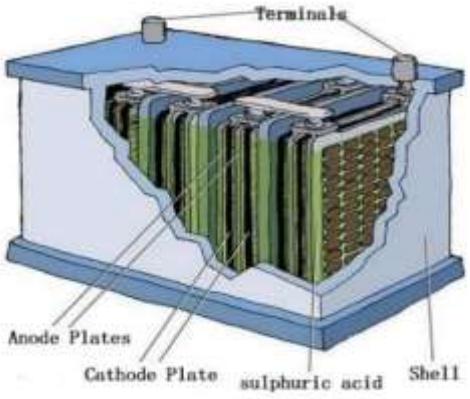

Figure 1. Structure of a lead acid battery [1]

1.2 Advantages of AGM (Absorbed Glass Mat) Batteries

Absorbent Glass Mat (AGM) batteries contain a matrix made of thin glass fibers designed to hold a sufficient amount of electrolyte. This matrix ensures that the electrolyte remains in place throughout the battery's lifespan. The mat made of thin glass fibers does not absorb the acidic electrolyte nor is it chemically affected by it. During the manufacturing process, the matrix is saturated with acid and then compressed by 2-5% to achieve a higher acid storage capacity and prevent leakage. Compared to traditional batteries, AGM batteries are lighter and exhibit high resistance during charge-discharge cycles. These characteristics make them ideal for use in vehicles with start-stop technology. They do not suffer from performance loss during charging and discharging processes. Additionally, they have a long shelf life due to the absence of the sulfation problem.

II. AGM BATTERY PERFORMANCE

2.1 Accurate Circuit Model

To accurately predict the performance of AGM batteries, the development of an appropriate circuit model is necessary. AGM batteries are valve-regulated, recombinant gas, and absorbed electrolyte lead-acid batteries. These batteries offer various advantages due to their inherent properties.

In AGM batteries, the cells are sealed with a pressure relief valve that prevents gases inside the battery from escaping. This valve releases excess gas when the internal pressure reaches a certain level. The positive and negative plates are tightly placed between glass mat fibers saturated with liquid. These glass mat fibers have over 90% saturation with the electrolyte but are not fully saturated by design, containing some gas. This design allows the electrolyte to move and gases to be properly managed. Figure 2 illustrates the O_2 recombination process in AGM cells. This process is critical in valve-regulated lead-acid (VRLA) batteries, especially in AGM and gel batteries. Oxygen recombination enhances the efficiency and lifespan of the battery.

Another important feature of AGM batteries is their very low self-discharge rate and minimal water loss. This allows the battery to retain its charge even when not in use for extended periods and reduces the need for maintenance.

However, the escape of gases such as hydrogen and oxygen from the battery can pose serious safety issues. If these gases are not properly ventilated, risks such as explosions or fires can arise. Therefore, it is vital to implement proper ventilation and safety measures in systems using AGM batteries.

These characteristics make AGM batteries ideal for vehicles with start-stop technology and other energy storage applications. Developing an accurate circuit model is critical for predicting their performance and ensuring their safe use [2].

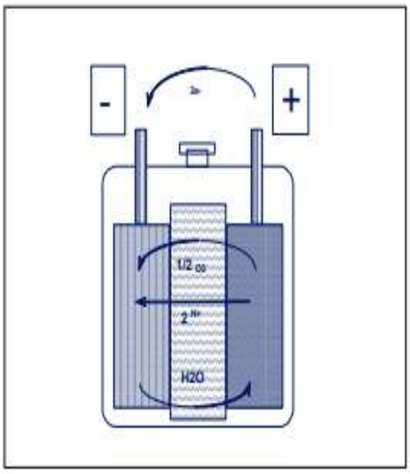

Figure 2. O_2 Recombination in AGM Cells [4]

Experiments have been conducted to reduce gassing and water loss by replacing antimony lead alloy with calcium lead alloy. However, this change has led to a reduction in cycle life and the loss of deep cycle properties.

Low acid concentration reduces the capacity at the top of the plates, while high acid concentration causes corrosion at the bottom of the plates, shortening the battery's lifespan. Stratification can be minimized by increasing the charging voltage to agitate the electrolyte with the increased gas, but this also increases water loss and the frequency of water replenishment.

The selected battery has a nominal voltage of 12V and a capacity of 89Ah at a 24-hour rate. The circuit model for this battery was designed using both the manufacturer's handbook data and test results. This approach is necessary because discharging the battery to a very low State of Charge (SOC) level can damage the internal components of the battery and permanently reduce its service life; this also affects the test results of the same battery. Considering SOC and Depth of Discharge (DOD), deep discharge (DOD) is the percentage of the discharge capacity of a fully charged battery.

The non-linear relationship between the State of Charge (SOC) and the open-circuit voltage (VOC) of the battery should also be considered. The values of the circuit parameters were obtained using the curves provided in the manufacturer’s data sheet and simple laboratory tests conducted on a 12-volt, 89 ampere-hour battery. Figure 3 shows the necessary test equipment.

Comparisons were made between the responses of various charge/discharge cycles measured and simulated using Matlab/Simulink, demonstrating that the proposed battery model has an adequate degree of accuracy. The battery function aligns closely within an acceptable error range between experimental data and simulation results [2].

Figure 3. Test Equipment [2]

2.2 AGM: Electrolyte Immobilization in Glass Fibers

AGM separators consist of a paper-like arrangement of glass fibers with a thickness ranging from 1 to 4 mm. The diameter of these glass fibers ranges from 0.5 µm to 3 µm. Due to their hydrophilic properties, diluted sulfuric acid is retained by the glass fibers. In an AGM separator, the larger pores remain open until 100% saturation is reached, and when drying begins, these larger pores are the first to open. Figure 4 illustrates the liquid distribution dependent on surface tension.

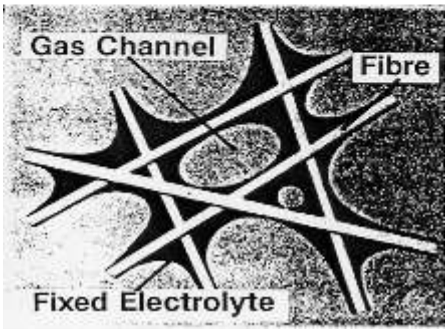

Figure 4. Liquid Distribution Dependent on Surface Tension [3]

The concentrated acid produced during charging sinks due to gravitational force, leading to acid stratification. The smaller the pores and fiber diameters, the fewer the problems related to acid stratification. AGM cells do not contain extra microporous separators; thus, the AGM separator is the only separator between the plates. To prevent damage to the separator during cell production, which could later cause short circuits, organic binders are used in thinner AGM separators. Figure 5 shows the bonds between particles. The AGM electrolyte immobilization structure is chemically composed of SiO_2. The early exposure of AGM to drying as an active material has serious consequences on internal resistance and capacity reduction. As water is lost, the separator shrinks, reducing the contact between the plates and the separator, thereby increasing impedance [3].

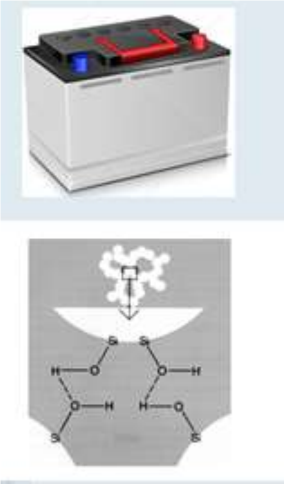

Figure 5. Bonds Between Particles [3]

6V 68Ah AGM blocks were used. As shown in Figure 6, these blocks were artificially aged by overcharging them until they lost 10% of their water content. To simulate heat transfer to the environment or to create a situation with a large battery in a small room, a charging voltage of 2.60V per cell was applied to increase heat generation in the cells. In AGM batteries, oxygen recombination is equivalent to a current of approximately 10A. In AGM cells, the six-fold increase in heat generation causes the temperature to rise to 100°C after 5 hours.

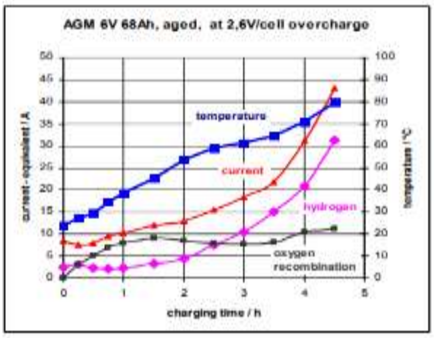

Figure 6. Thermal Runaway Simulation of AGM, Temperature Variation Immobilization During Charging and Current-Discharging [4]

Figure 6 presents the thermal runaway simulation of AGM, illustrating temperature variation immobilization during charging and current-discharging. These simulations are tests conducted to evaluate the overheating risk of batteries. These tests analyze how batteries heat up under certain conditions and whether this heating can be controlled. Temperature variation immobilization during charging and current-discharging means keeping the temperature changes during these processes under control. This is critical to ensure the safe and efficient operation of batteries. The SiO_2 chains in AGM, with a diameter of 1 µm, have 100 times different battery characteristics. The temperature change in AGM cells demonstrates a 100-fold increase in immobilization [4].

2.3 The Effect of Electrolyte Stratification on AGM Batteries

Electrolyte stratification is a common failure in flooded lead-acid batteries. During discharge, water is produced from the plates and tends to rise as it is lighter than the surrounding electrolyte. During charging, sulfuric acid is released from the plates and moves downward as it is heavier than the solution. Therefore, the electrolyte at the bottom of a cell tends to be more concentrated than at the top, especially during discharge [5,6]. Electrolyte stratification can be overcome by strong gassing during prolonged overcharge at regular intervals, causing the electrolyte to mix. Some studies have proposed a two-dimensional model. The experimental results in the proposed model are consistent with theoretical data. Here, it was predicted that electrolyte stratification causes sulfation and leads to early capacity loss. In AGM batteries, electrolyte stratification is considered in two aspects: electrolyte concentration and saturation. Concentration stratification in the electrolyte shows that it leads to uneven usage of the active material. Early in the discharge process, the usage of active material at the bottom is earlier than at the top, resulting in a higher current discharge at the bottom. This leads to the formation of more and finer $PbSO_4$ crystals at the negative electrode at the bottom, causing passivation of the negative plate and reducing the usage of active material and further discharge [7,8]. According to the simulation results, concentration stratification increases sulfate formation at the negative plate, while saturation stratification reduces sulfate formation at the negative plate. Additionally, self-discharge and self-recharge processes in resting batteries increase sulfate formation at the negative plate. Figure 7 shows the SEM (Scanning Electron Microscopy) image of fully loaded active material in cells simulated with saturation stratification.

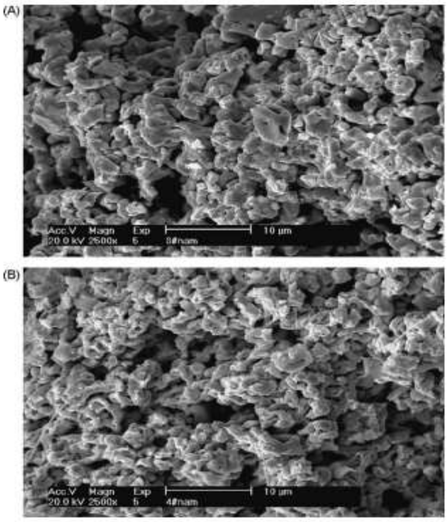

Figure 7. SEM of Fully Loaded Active Material in Cells Simulated with Saturation Stratification. (A) 93% and (B) 100% Saturation [4]

III. EFFECTS OF DİFFERENT ADDİTİVES ON THE ELECTROLYTE OF AGM BATTERİES

The release of hydrogen and oxygen at the negative and positive electrodes of AGM batteries is one of the main causes of self-discharge. Self-discharge is the loss of charge by a battery over time even when it is not in use. This occurs due to chemical reactions within the battery. Self-discharge prevents the battery from retaining its charge for long periods and increases the need for more frequent charging. Self-discharge occurs at the negative electrode of a battery. It can occur through two different reactions, shown below as reactions 2 and 3. Here,

$$Pb + HSO_4^{-} \longleftrightarrow PbSO_4 + H^{+} + 2e^{-} \qquad [2]$$

$$2H^{+} + 2e^{-} \longleftrightarrow H_2 \qquad [3]$$

The overvoltage of hydrogen affects the self-discharge process. High acid concentration accelerates gas formation [9]. These processes cause AGM batteries to lose charge over time. The release of hydrogen and oxygen gases is a significant factor influencing the self-discharge rate of these batteries. Therefore, minimizing this gas release is crucial for ensuring the efficiency and longevity of AGM batteries. Various additives affect self-discharge, and in another study, the effects of boric acid, stearic acid, and sodium sulfate on AGM batteries were examined. Boric and stearic acids were predicted to be the most significant additives that reduce the battery's self-discharge [10]. Figure 8 examines the effect of these additives on voltage.

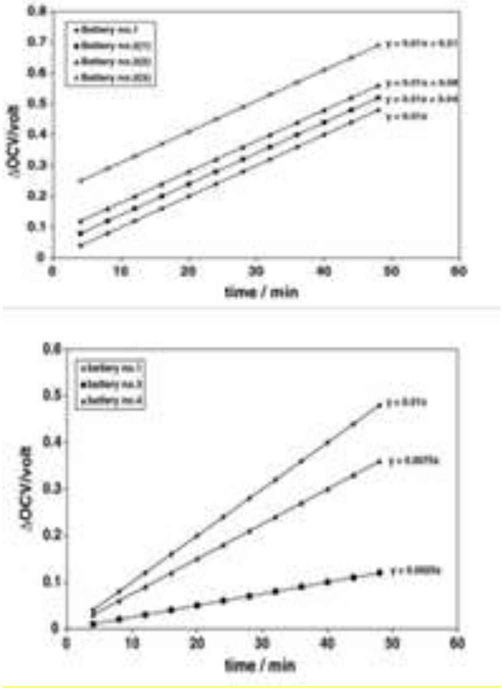

Figure 8. Na_2SO_4 and Boric Acid Variation [9]

In another study, AGM batteries prepared with different compositions were stored for 48 days, and their open-circuit voltages were measured daily using a multimeter. The different additives used in the compositions are listed in Table 1.

Table 1. Compositions Used in Experiments [9]

Battery Number	Electrolyte Composition
1	%35 (a/a) H_2SO_4
2	%35 (a/a) H_2SO_4 %5 (a/a) H_2SO_4 + 7, 1, 9.94 ve 21
3	%36 (a/a) H_2SO_4 %36 (a/a) H_2SO_4 + 4g 1 boric acid
4	%35 (a/a) H_2SO_4 + 3g 1 citric acid
5	%35 (a/a) H_2SO_4 + 0.7 ve 1g stearic acid

As seen in Figure 8, boric acid and stearic acid reduced the self-discharge rate of the battery from 0.01 to 0.0025 volts and 0.005 volts, respectively. Boric acid alters the accumulation of PbO_2 without reducing the formation efficiency of $PbSO_4$. Boric acid inhibits the formation of insulating $PbSO_4$ phase, thereby reducing the self-discharge of the resulting PbO_2 [10]. The adsorption of stearic acid on PbO_2 and the subsequent formation of concentrated stearic acid layers at the electrolyte-electrode interfaces reduce the self-discharge rate. When comparing batteries containing 35% H_2SO_4 with batteries containing different concentrations of additives (sodium sulfate, boric acid, citric acid, and stearic acid), it is shown that boric acid and citric acid are effective in reducing self-discharge. Sodium sulfate was found to be ineffective and even increased self-discharge.

IV. CONCLUSION-DISCUSSION

AGM batteries have widespread usage due to their maintenance-free nature and high safety standards. With various studies and models evaluating battery performance, the use of AGM batteries is increasing day by day. Compared to flooded batteries, they have lower electrical resistance and electrolyte stratification. Additionally, their high gas efficiency provides more flexible usage areas. AGM batteries with a long depth of discharge will offer various benefits to users with current and future technologies.

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