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Study on the Influence of Anode Additives in the Negative Electrode of Lead-Carbon Batteries

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Abstract. With the increasing demand for energy in the society, energy storage devices are more widely used. As one of the main energy storage devices in the past, lead-acid batteries are characterized by low cost, relatively long life and relatively simple maintenance. In particular, it is a highly favored, risk-free option for energy storage and vehicle starting due to its mature structural design, controllable reaction mechanism, and flawless recycling system, as well as the chemical stability of its aqueous electrolyte. Nevertheless, when lead-acid batteries are charged at a high rate, large, insoluble lead sulfate particles tend to form on the electrode surfaces. As the cycle progresses, these particles accumulate, preventing the electrolyte from penetrating the plates and reducing the active substance's utilization rate. The lead-acid battery's negative electrode sulfation is permanent and makes it unsuitable for energy storage applications. To make lead-carbon batteries, which are an improvement over lead-acid batteries and a solution to the sulfation problem, carbon materials are added to the negative electrode of the battery. The use of carbon material has the dual benefit of enhancing battery performance and preventing sulfation, but it also introduces the issue of excessive hydrogen precipitation. In this regard, this paper researches and discusses the hydrogen precipitation problem of lead-carbon batteries, analyzes the key role of the hydrogen precipitation inhibitor and its influence on the battery performance, and explores the performance of the battery materials.

Keywords: lead-acid battery, negative electrode, carbon material

1. Introduction

Traditional fossil fuels are becoming increasingly scarce, and pollution is on the rise, as a result of modern society's fast economic expansion. The majority of people rely on cars for transportation, which means they contribute to air pollution through the combustion of fossil fuels. Consequently, new energy vehicle development can lessen pollution by decreasing usage of conventional fossil fuels. A key component of the government's response to energy policy and the sustainable growth of the automotive sector is the research and development of new energy vehicles [1]. The longevity, reliability, and security of a new energy vehicle's batteries—the lifeblood of its driving system—are intimately connected. Battery types such as nickel-metal hydride, lithium, lead-acid, and fuel cells are widely available and employed. On the other hand, lead-acid batteries offer a number of benefits, such as being inexpensive, safe, having technology that is both mature and stable, performing well without maintenance, and having a high recycling rate [2-4]. As a cheap substitute for energy storage and electrical system operation, it continues to rule the worldwide battery industry [5]. Due to its low cost, excellent safety, and strong high and low temperature performance, lead-acid batteries are often utilized as a beginning power source for autos in modern energy vehicle systems. Compared with lithium batteries, which have poor low-temperature performance, lead-acid batteries can still maintain good starting ability at low temperatures, and good low-temperature resistance is very important for automobiles in cold regions [6].

As a result, lead-acid batteries frequently use carbon compounds such graphite, activated carbon, carbon nanotubes, and carbon black as additions to the negative electrode in order to fulfill the needs of maintenance-powered automobiles. In this paper, it is studied that the battery with carbon added will enhance the utilization rate of negative active material (NAM) and alleviate the sulfation problem; give super capacitance effect and enhance the charging acceptance; optimize the negative conductive network and enhance the electrochemical performance and other values, but the low hydrogen precipitation overpotential of carbon leads to the aggravation of hydrogen precipitation in batteries, which affects the service life of the batteries.

This paper focuses on the optimization of the anode performance of lead-carbon batteries, focusing on the core mechanism of lead-carbon batteries, existing problems and the performance enhancement of hydrogen precipitation inhibitor composite additives, and analyzes the enhancement of the performance of the battery by the composite additives of hydrogen precipitation inhibitors.

2. Lead-carbon battery and lead-acid battery

Lead-carbon batteries are not a "subversive innovation" to lead-acid batteries, but a "precise upgrade" based on the traditional technological framework - solving the core defects of lead-acid batteries through the introduction of carbon materials and By introducing carbon materials to solve the core defects of lead-acid batteries, while retaining its mature, low-cost, high-safety advantages, and ultimately realize the balance of "performance improvement - cost control - process compatibility", which has become a key technology path for lead-acid batteries to expand to the application of "long-life, high-multiplication, wide range of scenarios".

2.1. Lead-acid battery

In 1859, the lead-acid battery was conceived by the French physicist Planté. A two-way conversion system between chemical and electrical energy was successfully built by the original lead-acid battery, which used lead plates as the positive and negative stages, a rubber separator in the intermediate, and diluted H_2SO_4 (10%) as the electrolyte. In 1880, Faure proposed to mix water, H_2SO_4, and lead oxides to make a paste, and then apply the mixed lead paste to the lead grid [7]. By 1881, Swan had replaced lead sheets with lead grids, which could be used to increase the capacity of the grids by changing the direction of the electrolytic current [8]. In 1970, Dveiff created the first valve-regulated lead-acid battery with a liquid-poor structure. 1971, Gates replaced the rubber spacer with fine glass fiber (AGM).

Lead sulfate (H_2SO_4) reacts with the plate-based active material to produce lead sulfate ($PbSO_4$) when lead-acid batteries are discharged.At the positive electrode of the battery, PbO_2 is reduced by the H_2SO_4 electrolyte during the discharge process, and at the same time, the hydrogen ions in the system combine with the oxygen to produce water, releasing electrons, which are passed through the external circuit to form an electric current, thus realizing the power supply of the external equipment. The specific discharge process is as follows [9] :

Positive pole: PbO_2+2e-+SO_4^{2-}+4H^+→$PbSO_4$+2H_2O(1)

Negative: Pb+SO_4^{2-}→$PbSO_4$+2e^-(2)

Total reaction: PbO_2+Pb+2H_2SO_4=2$PbSO_4$+2H_2O(3)

When charging, the $PbSO_4$ generated by discharge will be decomposed into PbO_2, Pb and H_2SO_4. The reaction process is as follows:

Positive pole: $PbSO_4$+ 2H_2O→PbO_2+4H^+ +SO_4^{2-}+2e^- (4)

Negative: $PbSO_4$+2e^- →Pb+SO_4^{2-} (5)

Total reaction: 2$PbSO_4$+2H_2O=PbO_2+Pb+2H_2SO_4 (6)

However, in practice, lead-acid batteries cannot be charged for a long time, the $PbSO_4$ on the pole plate is easy to recrystallize when the temperature changes, resulting in insoluble $PbSO_4$ gradually accumulated on the pole plate, forming an insulating layer, preventing the reaction from proceeding further, resulting in a significant reduction in battery capacity and cycle life.

2.2. Shallow battery

Carbon material additives can boost battery capacity and prolong cycle life, according to studies [10]. Increasing the utilization rate of NAM and providing more active sites by adding high specific surface carbon materials to the negative electrode of the battery inhibits the formation of big lead sulfate grains. There are three distinct types of lead-carbon batteries that can be classified according to the methods used to mix the carbon materials. The first type is the externally-parallel lead-carbon battery, which uses a double-layer capacitor formed by lead electrodes and capacitive carbon electrodes connected in parallel as a complete negative electrode. The second type is the internally-parallel lead-carbon battery, which uses ordinary lead sponge plate for half of the negative electrode and carbon supercapacitors, also called supercells, for the other half. Finally, there is the internally-hybrid lead-carbon battery, which adds carbon with a mass fraction of 0.2% to 5% to the negative lead paste as a negative additive or component [11]. The internal mixed lead-carbon battery has found widespread market use due to its relative ease of production process control.

2.2.1. Carbon material action mechanism

Adding carbon elements to lead-acid batteries improve battery performance and reduces sulfation, two of the several benefits of lead-carbon battery technology. The NAM of lead-carbon batteries is home to two electrical systems: one uses a double electric layer to facilitate the charge/discharge reaction, which mostly takes place on the carbon surface; the other uses electrochemistry and chemical reactions to oxidize Pb to $PbSO_4$ and then reduce it to lead. Carbon additives are used for the following purposes.

The negative plate of a lead-acid battery becomes covered in dense, non-conductive $PbSO_4$ crystals during the discharge process, which reduces the active material's use. The lead-acid battery's cycle life can be prolonged by increasing the carbon content in the negative plate while operating in a partially charged condition. This is because the negative plate acts as an effective inhibitor of $PbSO_4$ accumulation [12].

Some carbon compounds can increase the capacitance contribution in lead-acid batteries by creating a supercapacitor effect in the negative electrode [13]. When the battery is being charged, the carbon materials in the lead-carbon electrodes work as supercapacitors, enhancing the battery's ability to receive charges and decreasing the production of irreversible lead sulfate.

When discussing lead-acid batteries, the term "spatial site resistance effect" is most often used to describe how the arrangement and interaction of ions in the electrolyte and electrodes might impede specific chemical reactions occurring inside the battery. Because of this consequence, the battery's responsiveness and performance are compromised. While holes on the negative electrode plate allow electrolyte to flow into the NAM, they can also cause $PbSO_4$ crystals to develop into enormous particles if the holes are too big.

In NAM, $PbSO_4$ reduction on carbon surfaces is possible by means of the Pb electrodeposition technique. Adding carbon to Pb-carbon composite electrodes may improve the charge transfer performance of the $Pb/PbSO_4$ redox pair by providing an additional electrochemically active surface to the Pb surface [14].

2.2.2. Hydrogen precipitation reaction in lead-carbon batteries

An electrochemical adsorption stage, an electrochemical desorption step, and a complicated desorption step are typically involved in lead-carbon batteries when it comes to the precipitation of hydrogen on the electrode material's surface:

Volmer reaction: $H^+ + M + e^- \leftrightarrow M\text{-}H^*$ (7)

Heyrovsky reaction: $M\text{-}H^* + H^+ + e^- \leftrightarrow M + H_2$ (8)

Tafel reaction: $2M\text{-}H^* \leftrightarrow 2M + H_2$ (9)

The negative electrode causes the cell to lose more water because it forms hydrogen, stores it at the top, and then dissipates it as heat. The HER can be suppressed by introducing high hydrogen precipitation overpotential materials into the negative electrode using methods such as physical mixing or chemical deposition, e.g., the addition of high overpotential metal atoms such as Bi, Ga, and In can effectively slow down the rate of hydrogen precipitation from the negative electrode plate, and improve the cycling performance of the battery. The negative electrode's charge uptake ability and the battery's suppression of hydrogen precipitation were both enhanced with the addition of 2% MXene and 0.2% carbon black by Kang et al [15].

3. Application of negative electrode additives in lead-carbon batteries

3.1. Mechanism of CF action in batteries

As an anode additive for lead-carbon batteries, the unique structural characteristics of layered porous carbon (CF) play a key role in improving the performance of the batteries. Due to its highly porous and mesoporous structure, CF may achieve porosities of over 65%. This allows the electrolyte to penetrate and diffuse through the material, and it also helps the negative electrode active material (NAM) come into full contact with the electrolyte. Results demonstrated a 50% increase in electrolyte infiltration rate and an 85% increase in NAM utilization rate when 2% CF by mass fraction was applied to the negative electrode plate, in comparison to the blank group [16].

When it comes to preventing sulfation, CF really shines. Large $PbSO_4$ crystals readily develop on the negative electrode surface of lead-acid batteries during rapid discharge; these crystals are difficult to fully transform during charging and progressively accumulate to provide an insulating layer. The spatial site resistance effect of CF can limit the growth of $PbSO_4$ crystals, which can be dispersed in the form of nanoscale particles. It was observed by scanning electron microscopy that the diameter of surface $PbSO_4$ particles on the CF-added negative plate was about 50 - 100 nm after 100 cycles, while the blank group showed massive crystals with a diameter of more than 500 nm [11]. This well-dispersed $PbSO_4$ is more easily reduced to sponge Pb during charging, thus maintaining the capacity stability of the battery.

The high degree of graphitization (up to 80% graphitization) of CF provides excellent conductivity and can form an efficient conductive network in the NAM. The AC impedance test showed that the charge transfer resistance (Rct) of the CF-added battery was 15 Ω, which was much lower than that of the blank group (35 Ω), implying that the kinetics of electrochemical reaction was significantly enhanced [13]. Meanwhile, the addition of CF significantly extended the cycle life of the battery. Under 1C-fold charging and discharging conditions, the capacity retention rate of the battery with 2% CF was still 70% after 500 cycles, whereas the capacity of the blank group decreased to less than 50% after 200 cycles.

Recent studies have further explored the potential of CF. Lin Haibo's team at the School of Chemistry, Jilin University, innovatively utilized rice husk to prepare high-performance CF materials for lead-carbon batteries [17]. Rice husk is widely available and inexpensive, and the CF obtained after special treatment not only retains a rich pore structure, but also has unique surface functional groups. It was shown that the cycle life of lead-carbon batteries with rice husk-based CF was 20% higher than that of ordinary CF additive batteries in partially charged state (PSoC), and the capacity retention rate was still higher than 80% after 400 cycles [17].This success opens the door to a new source of inexpensive raw materials for the industrial scale use of CF additives, which should encourage the widespread use of lead-carbon batteries for a variety of applications.

3.2. Mechanism of BiOCl/Bi_2WO_6 in batteries

As a new type of hydrogen precipitation inhibitor, BiOCl/Bi_2WO_6 composites show unique advantages in solving the problem of hydrogen precipitation in lead-carbon batteries. The Bi element has a high hydrogen precipitation overpotential (-1.2 V vs. SHE), and when BiOCl/Bi_2WO_6 is added to the negative electrode, Bi^{3+} acquires electrons preferentially to H^+ in the acidic electrolyte, forming metallic Bi deposited on the surface of the carbon material, thus occupying the hydrogen precipitation active site [15]. The hydrogen precipitation rate of the cell with 1% BiOCl/Bi_2WO_6 was measured to be 0.5 mL/(h g), which is only 30% of that of the unadded group.

The layered structure of BiOCl/Bi_2WO_6 also contributes to the improvement of the cell performance; the lamellar structure of BiOCl/Bi_2WO_6 increases the contact area with the electrolyte, and the oxygen vacancies on the surface of BiOCl/Bi_2WO_6 adsorb H intermediates, which further inhibits hydrogen precipitation. x-ray photoelectron spectroscopy analysis shows that the concentration of oxygen vacancies on the surface of the composite material is 12%, which is a defective structure with significantly enhanced adsorption of H X-ray photoelectron spectroscopy analysis showed that the oxygen vacancy concentration on the composite surface reached 12%, and this defect structure significantly enhanced the adsorption of H [14].

Inhibiting sulfation is another beneficial function of BiOCl/Bi_2WO_6. The addition of this composite greatly reduced the generation of large-particle $PbSO_4$ on the surface of the electrode plate of the battery, according to high-rate discharge experiments. After 50 cycles, the $PbSO_4$ coverage on the surface of the electrode plate was only 20%, while the blank group reached 60%. This was because Bi^{3+} could enhance the reduction reaction of $PbSO_4$, and the cyclic voltammetry curve showed a 40% increase in the reduction peak current compared to the blank group, suggesting that the $PbSO_4$ reduction kinetics were improved [9].

Adding BiOCl/Bi_2WO_6 also makes the battery more stable during cycles. After 300 cycles in the 2C high-rate cycling test, the battery with 1% BiOCl/Bi_2WO_6 added had a capacity retention rate of 65%, 25% higher than the unadded group. Hydrogen precipitation was a major cause of electrolyte depletion, but the battery's water loss rate was reduced by 50% and performance was improved.

Recent research has attempted to compound BiOCl/Bi_2WO_6 with other materials to further optimize its performance. One team composite BiOCl/Bi_2WO_6 with carbon nanotubes (CNTs) to form a ternary additive system [18]. CNT can synergize with BiOCl/Bi_2WO_6 due to its good electrical conductivity and mechanical properties. The experimental results showed that the lead-carbon battery with the addition of this ternary composite had a cycle life exceeding 400 cycles at 1C charge/discharge multiplication and a capacity retention rate of 75%, which was 33% and 15% higher than that with the addition of BiOCl/Bi_2WO_6 alone, respectively [18]. Meanwhile, the internal resistance of the battery was reduced by 20%, and the hydrogen precipitation rate was further decreased to 0.3 mL/(h g), which showed better overall performance and provided a new idea for the design of anode additives for lead-carbon batteries.

4. Conclusion

In comparison to other electrode plates, those made of CF exhibit better electrochemical performance, including lower hydrogen precipitation rates, smaller impedances, and greater capacitances. CF is a layered porous carbon structure that contains oxygen and carbon. Since CF has a higher graphitization degree than AC, it is easier for CF to form a conductive network in NAM, which improves the anode plate's electrochemical performance. Additionally, CF has many micropores and mesopores, which allow the electrolyte and NAM to react completely. With their layered structure, BiOCl/Bi_2WO_6 composites effectively inhibit hydrogen precipitation. This is due to the fact that Bi has a high hydrogen precipitation overpotential and the oxygen vacancies created by the acidic electrolyte occupy the carbon material's active sites of hydrogen adsorption.

In the future, lead-acid batteries can be developed in the direction of developing carbon materials compatible with lead or metals with high hydrogen precipitation overpotential and environmentally friendly new biomass-based porous carbon composites to achieve better battery performance. In addition, more efficient ones with low environmental impact and recyclability are selected to meet the changing market demand and environmental protection requirements in order to improve the utilization rate and life of lead-acid battery negative electrodes. With the continuous development of lead-acid battery technology and the advancement of actual production technology, the application of lead-carbon batteries will be more widely used.

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