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Review

A Review of the Positive Electrode Additives in Lead-Acid Batteries

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Lead acid battery occupies a very important position in the global battery market for its high security and excellent cost-effective. It is widely used in various energy storage systems, such as electric vehicles, hybrid electric vehicles, uninterruptible power supply and grid-scale energy storage system of electricity generated by renewable energy. Lead acid battery which operates under high rate partial state of charge will lead to the sulfation of negative electrode. Lead carbon battery, prepared by adding carbon material to the negative electrode of lead acid battery, inhibits the sulfation problem of the negative electrode effectively, which makes the problem of positive electrode become more prominent. As a result, more and more researchers are working on ways to improve the performance of the positive electrode, such as adding additives to positive active material. In this paper, the positive additives are divided into conductive additive, porous additive and nucleating additive from two aspects: the chemical properties of the additives and the effect on the performance of the lead-acid battery. The effect and mechanism of different additives on the structure and properties of positive electrode are discussed.

Keywords: Lead-acid battery, positive electrode, conductive additive, porous additive, nucleating additive

1. INTRODUCTION

The development of new energy vehicle and non-fossil energy, protection of the earth's environment and reduction in carbon dioxide emissions have become the consensus of all the countries. Therefore, the research of energy storage systems such as lead-acid battery (LAB), sodium-ion battery, super capacitor, and so on have been attracting more and more attention [1-11]. LAB as a kind of traditional secondary battery, with its initial low cost, mature manufacturing technology and high recycling efficiency, etc., plays an irreplaceable role in electric vehicles (EVs), hybrid electric vehicles (HEVs), uninterruptible power supply and grid-scale energy storage system of electricity generated by renewable energy compared to other energy storage system [12-17].

LAB which operates at high rate partial state of charge (HRPSoC) will cause the negative electrode sulfation prematurely and lead to the battery failure. This problem has been effectively solved through the introduction of various carbon materials into negative electrode, as a result a new energy storage system called “Lead-Carbon” battery is produced [18]. Lam et al. worked in Japanese Furukawa company prepared 42 V automotive lead carbon battery [19]. The test results showed that the life of the battery under HRPSoC was four times of the ordinary LAB. They installed the battery on a Honda Insight hybrid car and placed it in a space where Ni-MH battery was placed before [20]. It had safely traveled 100 thousand miles after 9 months of actual operation. The test results demonstrated that the battery can satisfy the requirements of HEVs, and the performance was equivalent to Ni-MH battery, but the cost was far lower than the latter. This indicated that the lead carbon battery had a good application prospect in small or medium-sized EVs.

The improvement of the negative electrode cycle life leads to the highlighted problem which caused by the low coefficient of utilization and softening and shedding of the positive electrode active material (PAM) [21]. Therefore, how to improve the performance of the positive electrode is very important for LAB, which is directly related to the improvement of the whole battery performance. In order to solve the positive electrode problems, numerous researchers have been doing a lot of research to improve the performance of the battery positive electrode. It is found that the overall performance of the battery can be greatly improved with the use of suitable PAM additives. In this paper, the additives are divided into conductive additive, porous additive and nucleating additive according to the different mode of additive action on positive electrode.

2. FAILURE REASON OF THE POSITIVE ELECTRODE LAB

The PAM of the LAB are composed of a mixture of PbO and Pb_3O_4. During the process of curing, PAM is mainly transformed into two kinds of lead sulfate: $3PbO \cdot PbSO_4 \cdot H_2O$ (3BS) and $4PbO \cdot PbSO_4 \cdot H_2O$ (4BS). Based on the “crystal-gel” theory, 4BS would transforms into α-PbO_2 and 3BS would transforms into β-PbO_2 in the succedent formation process [22]. The crystal structures of these two kinds of PbO_2 are completely different. α-PbO_2 belongs to orthorhombic system and its grain size is larger. It could form a network of skeleton structure in the PAM, thereby improving the cycle life of the battery [23]. β-PbO_2 belongs to tetragonal system and its grain size is smaller [24]. It has better electrochemical activity, so that the battery has higher initial capacity [25]. Therefore, the battery's capacity is determined by α-PbO_2 and the cycle life of the battery is determined by β-PbO_2. Changing the content of α-PbO_2 and β-PbO_2 could directly influence the capacity and cycle life of the battery.

Structure and performance of PAM change in battery during charge/discharge cycle. The working principle of the positive LAB is shown in reactions (1) and (2) [26-28]. In the discharge process, PbO_2 positive plate accepts electrons to convert into $PbSO_4$. When the battery is charged, $PbSO_4$ is electrochemically converted into PbO_2 at the positive plate.

Discharge:

$$PbO_2 + 2e^- + SO_4^{2-} + 4H^+ \rightarrow PbSO_4 + 2H_2O \qquad (1)$$

Charge:

$$PbSO_4 + 2H_2O - 2e^- \rightarrow PbO_2 + SO_4^{2-} + 4H^+ \qquad (2)$$

In charge and discharge process, the material transformation between PbO_2 and $PbSO_4$ is reversible theoretically. However, α-PbO_2 can only form in weak acid or alkaline solution while β-PbO_2 is obtained in strong acid solution with pH below 2~3 [29]. The equilibrium potential of transforming β-PbO_2 to $PbSO_4$ is lower in electrolyte, compared with α-PbO_2 active material, so β-PbO_2 is more stable. Consequently, in the actual reaction, the content of α-PbO_2 in the newly prepared positive plate is higher than that of β-PbO_2, and the content of α-PbO_2 gradually decreases while the content of β-PbO_2 increases gradually with the cycle. This is due to the transformation from α-PbO_2 to β-PbO_2 during the cycling of the battery. At the same time, there's an irreversible side reaction occurs on the positive electrode that the non-conductive $PbSO_4$ accumulates on the positive plate [30].

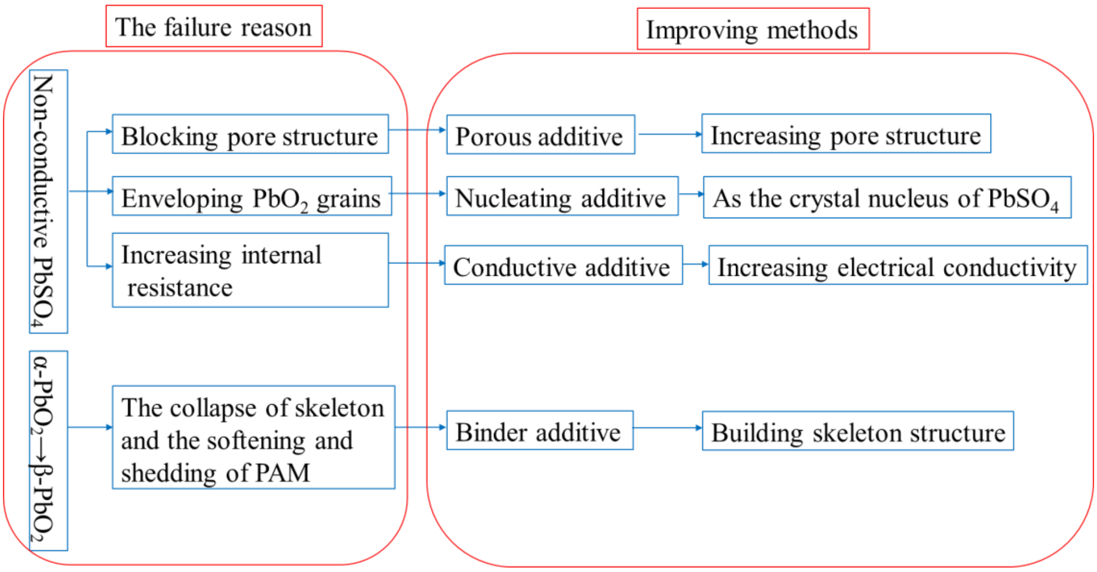

Figure 1. The failure reasons and improving methods of the battery.

The transformation of the PAM is responsible for the utilization of the active material and the structural integrity of the plate. The failure reasons and the improving methods of the positive electrode battery are shown in Fig. 1. The electrode reaction is preferentially carried out on the surface of the electrode, the reaction product $PbSO_4$ blocks the pore structure of the plate surface, so that the electrolyte cannot diffuse into the active material inside, and there are a lot of unreacted materials in the plate; $PbSO_4$ envelops the active material PbO_2, which makes the internal particles materials cannot participate in the reaction; $PbSO_4$ makes the internal resistance of the battery increase [31]. These reasons have led to a decrease in the utilization of active materials. The transformation from α-PbO_2 into β-PbO_2 will lead to the composition and structure changes of PAM. The β-PbO_2 exists in the form of small particles, which is hardly come together and easily lead to softening and shedding of the

PAM [32, 33]. Additives, such as conductive additive, porous additive, nucleating additive and binder additives, are adopted to enhance the performance of the active material by changing its (i) conductivity, (ii) porosity, (iii) crystal morphology and geometry, and (iv) mechanical strength [34]. Among these, the binder additive will be added in today's battery preparation process, which is not mentioned in this paper.

3. CONDUCTIVE ADDITIVE

The aim of conductive additive is to ensure a good charging and discharging performance of the plate. When a plate is made, a certain amount of conductive materials are usually added as the pathway that connects isolated PbO_2 to the Pb grid, and the micro current can be collected between the active materials and the grid [35]. At the same time, the migration rate of hydrogen ions in the active materials can also be effectively increased, so as to improve the charge and discharge efficiency of the electrode.

3.1. Carbon materials

Carbon materials are widely used as positive additive materials for LAB because of their high conductivity and insolubility in electrolyte [34, 36]. Dietz studied the addition of 0.2 wt. % carbon black additive in the positive electrode. With increasing formation time, the participation of carbon black improved the electronic conductivity, the α/β-PbO_2 ratio and the PbO/α-PbO_2 contact area, which resulted in an increasing amount of PbO directly transformed into α-PbO_2 [36]. This unusual effect was attributed to the expansion of α-PbO_2 which was formed during the early low-voltage stage [37].

Banerjee et al. added two kinds of additives, single-wall carbon nanotube (SWCNT) and multiwall carbon nanotube (MWCNT), to positive electrode respectively [38]. The addition of CNT enhanced the specific discharge initial capacity by increasing the amount of β-PbO_2 in the PAM and, at the same time, prolonged the cycle life by increasing the specific capacity due to lower cell resistance. Because to the reason that per unit weight percent in the active material, the SWCNT contained more discrete nanotubes than MWCNT. So that the multilayer structure of MWCNT did not contribute much to the stabilization and integration of the active material in positive plate, while the single-layer construction of SWCNT performed this successfully.

The effect of carbon fiber addition and specific surface area on the performance of the positive electrode LAB was investigated by Ren et al. [39]. It was found that the optimum dosage of carbon fiber in PAM was 0.5 wt. %, and the larger specific surface area was good for improving the battery performance. Carbon fiber could form conductive network in plate, enhance its mechanical strength and delay the softening and shedding of PAM. The conductive network formed by a small amount of carbon fiber could improve the conductivity of PAM and make the current distribution more uniform, which was beneficial to the positive plate formation and the improvement of the discharge performance of the battery.

3.2. Metallic elements

Rubha et al. indicated that titanium wire with 2.3 wt. % addition had the optimal effect of increasing the active material utilization by 12.3% (57 to 64% utilization) at the slow discharge rate, as well as a 13.6% improvement on active material utilization during the fast discharge rate without detrimental effects [35]. The result was correlated well with the 2D model of Edwards and Zhang [40]. The model predicted that, even at a low loading, a long conductive additive with 1 × 100 aspect ratio should raise the utilization from around 60% to between 65~70%.

Lam pointed out that adding 0.05 wt. % of bismuth in positive plate served to enhance the electrical connectivity, both between the individual agglomerates of the PAM and between this material and the grid member, which provided higher initial capacity and significantly faster attainment of full capacity [41]. Importantly, the battery doped with bismuth had a lower self-discharge rate and an appreciably longer cycle life [41]. The battery voltage made from Bi-bearing oxide had dropped from 6.52 to 6.39 V and the capacity from 4.82 to 3.67 Ah. Thus, the self-discharge rate was 0.6 mV or 5.3 mAh per day. However, both the voltage and the capacity of the battery made from factory oxide decreased more rapidly, giving a higher self-discharge rate of 1.2 mV or 18.6 mAh per day. Pavlov′s study also found that bismuth can improve the contact between PbO_2 particles and the sensitivity of the electrode to the density of active material [42, 43]. Furthermore, the doped of bismuth in the positive plate can accelerate the structure recovery of the PAM and slow down the early capacity decay of the positive plate [43].

Shiomi et al. found that the doping of the highest activity antimony in the PAM was beneficial to reduce the oxygen evolution current and increase the cycle life of LAB when the active material density was not less than 3.75 g/cm^3 [44]. In the process of formation, antimony generally remained in the PAM. It did not penetrate into the electrolyte or migrated to the negative active material, which can reduce the generation of the grid corrosion layer.

3.3. Metallic oxide

Tin dioxide, as a good conductive material, was used in positive plate in order to increase the electrical conductivity of the material by many researchers [45-48]. Zhou et al. reported that the addition of SnO_2 could change the structure of the active material and transform the spherical particles into a slender rod like structure [47]. This structure could enhance the strength of the active material and make the active material difficult to fall off during the charging process. Besides, the addition of SnO_2 enhanced the intensity of the diffraction peak of the β-PbO_2 and inhibited the formation of α-PbO_2.

Zhou et al. studied that the addition of a certain amount of ultrafine Sb_2O_3 increased the surface area, the reaction interface and the diffusion coefficient of the active material, weakened the polarization, improved the contact of particles, reduced the resistance, and enhanced the conductivity of the PAM [49]. The results also showed that the discharge capacity and the utilization ratio of PAM could be improved, the structure of the corrosion products in the grid could be changed, and the integrity of the structure of active material could be helped by adding 2~3 wt. % Sb_2O_3.

Ferg et al. demonstrated that the addition of 25 wt. % red lead (Pb_3O_4) to the PAM could improve the formation efficiency by producing β-PbO_2 during the initial stage and result in first discharge capacity that was close to the rated capacity of the LAB [50]. Wang et al. and Boden accounted that the addition of red lead could also enhance the initial formation and high-rate performance as well [51, 52].

Gao et al. concluded that the addition of Ti_4O_7 oxide of Magneli phase in the PAM could restrain the dissolution of water by increasing the over-potential of oxygen evolution, improve the active material utilization and inhibit irreversible sulfation. [53]. The results demonstrated that the discharge capacity and cycle life were increased by 11.72 % and 16.81 % when Ti_4O_7 at 0.5 wt. % and 0.2 wt. % respectively.

3.4. Organics

Lubentsov et al. reported that the introduction of conducting polymers in positive plate leaded to the increase of β-PbO_2 concentration, the growth of the specific surface and the formation of the micro-crystalline structure of the PAM [54]. When adding 1~2 % polyaniline additive in PAM, the capacity of LAB was increased about 30 % [54]. Kuzmenko et al. explained the mechanism of polyaniline (PANI) [55]. The initial protonated form of PANI turned into deprotonated form with less electro-conductivity during the soaking stage. After that H_2SO_4 ions diffused into the surface and middle layer of the positive plate, forming the medium acidic layer. However, H_2SO_4 had no time to reach inner layer of the positive plate, so that PANI stayed in left layer in a deprotonated form with relatively low electro-conductivity. When battery was charged, as the current flowed within layer of PAM, the PANI could form a conductive nanostructured cross-linking channels gradually. Therefore, the cycle life of LAB increased by two times.

Wei et al. found that the existence of butadiene (BD) in the positive plate was beneficial to the process of PbO_2 discharge [56]. Therefore, butadiene organic additive could greatly improve the capacity of LAB and positive electrode charge/discharge performance, as well as improve the utilization rate of PAM significantly. It was pointed out that BD could form the microstructure with more pores, thus improving the mass transfer process.

The effect of polyhydroxyl organic compounds (PA) on the positive electrode of LAB was studied by Chen et al. [57]. The experimental results showed that the organic additive could increase the utilization ratio of PAM by 15~18 wt. % at low rate discharge condition. The content of α-PbO_2 in the active material of the electrode decreased while the content of β-PbO_2 increased. The large and loose $PbSO_4$ crystals were generated during discharge, which decreased the diffusion resistance of H^+ in the PAM.

4. POROUS ADDITIVE

The pore structure of porous additive could adsorb sulfuric acid and accelerate the migration of electrolyte ions. It is a good ionic conductor. The researchers point out that porous additive increased the diffusion of HSO_4^- and also provided local reservoirs of the ion within the pores [58].

Foudia et al. found that the alumina-silicate ceramic additive, dispersed uniformly in the PAM, could work as acid reservoirs and facilitate the ionic diffusion [59]. The results showed that the use of the alumina-silicate ceramic improved the capacity and cycle life of the PAM. Moreover, the addition of alumina-silicate ceramic in the plate before oxidation influenced the composition and the crystal size of the PAM after oxidation. The authors concluded a prominent improvement of the discharge capacity of the PAM for an amount of additive ranging between 1 and 5 %.

Mcallister et al. found that the use of diatomaceous earth ($SiO_2 \cdot nH_2O$) could improve the discharge capacity and the utilization of the PAM [60]. They pointed out that the LAB had the best performance when diatomite with a 53~74 μm particle size and an optimal mass ratio of 3% was used. Under the condition with this particle size and mass ratio, the PAM utilization rate was increased by 12.7% and the specific capacity was increased by 9.3% at high rate discharge compared to control plate without diatomite. Wang et al. concluded that the additive SiO_2 in the positive plate could increase the plate porosity, while keeping the original plate chemical composition and crystal morphology [61]. When the amount of SiO_2 additive was about 3 wt. %, the plate had a good mechanical strength of the pore and could enhance acid supply in the plate during high-rate discharge, thus decreasing the capacity loss per cycle.

Processes had been developed to make nonconductive, porous hollow glass microspheres (PHGMs) which added in the PAM could further improve their specific energy performance through increasing electrolyte storage and diffusion [62-64]. Newell et al. produced PHGMs by etching commercially available borosilicate hollow glass microspheres using dilute HF solution [65]. They pointed out that PHGMs could be used to store more electrolyte in the plate and enhance the high rate energy storage of LAB [65]. Edwards et al. used a computer model to predict the performance of positive electrode doping with PHGMs [66]. The result demonstrated that the model helped to make the PHGMs clearer in both the medium and the high rate discharge, and improved the positive plate performance [66]. Mcallister et al. found that the introduction of PHGMs coated with lead dioxide in the PAM could significantly improve the PAM utilization and the specific energy of the LAB [67].

Chen et al. elucidated the mechanism of the function of bismuth compound as a positive plate additive in LAB [68]. The soluble bismuth compound reacts with sulfuric acid electrolyte, so that the Bi^{3+} leaves the active material and enters the electrolyte through chemical or physical transfer process. The transfer of bismuth compound produces plenty of micro-pores in the active material, therefore, a higher ratio of porosity in the PAM is resulted. The ‘pore-creating’ mechanism increases the utilization of the PAM. Luo confirmed the ‘pore-creating’ through the tests that the capacity and the cycle life of the positive electrode of LAB doping with 0.02 wt. % Bi_2O_3 were improved [69].

Liu et al. also pointed out that the addition of sodium sulfate (Na_2SO_4) in the positive plate, which was easy to dissolve and gradually transfer from the plate to the electrolyte, could increase the porosity and amount of electrolyte of the plate, and speed up the liquid mass transfer process [70]. Thus, the conductivity of the ions in the discharge termination period was effectively improved, which was beneficial to the further utilization of the active substance and the enhancement in the battery capacity.

Tokunaga et al. observed that adding anisotropic graphite to the positive plate could increase the capacity and cycle life of the battery, because graphite expansion increased the porosity of the

PAM [71, 72]. Baker et al. reported that the synthetic graphite increased porosity and decreased the consistency of structure when it was used as an additive to tubular positive plate [73]. This was due to the fact that graphite, as a loose dilatant, was greatly beneficial to the diffusion of H_2SO_4 into the interior of the electrode and, accordingly, reducing the concentration polarization. This result made both the surface structure and the inner structure of the PAM to generate the chemical reaction in a uniform way so that the coefficient of utilization was improved. At the same time, graphite was also able to raise the water absorptivity of the lead paste and decrease its density without increasing its consistency [74]. Ball et al. investigated that the addition of carbon fiber to the positive plate could improve the capacity by approximately 20% and significant prolong the cycle life [75].

Toussaint et al. validated that the ZSM-5 zeolite with a pore diameter about 0.5 nm as an additive to the positive plate increased the discharge capacity close to 20% whatever the discharge rate [76]. It has also been reported that the porous structure of zeolite could adsorb sulfuric acid and exchange cations. Adding 0.05 wt. % 20~70 μm zeolite into the PAM could increase the utilization ratio of active material, and then increase the capacity and the life of the LAB.

5. NUCLEATING ADDITIVE

Sulfate, such as $CaSO_4$ and $NaSO_4$ and so on, could act as nuclei for $PbSO_4$ growth in the discharge. Nucleating additive could suppress the growth of larger particles by forming a uniformly distributed small growth nucleus in the PAM. The addition of this kind of additive is beneficial to the discharge process and increase the discharge capacity.

The addition of 0.25~2 wt. % $CaSO_4$ in the PAM increased the voltage at all discharge rate [77]. The effect was more markedly at high rate of discharge, particularly at low temperature. The affixion of Na_2SO_4 in the PAM could reduce the 4BS crystal size during the curing process, which produced much smaller α-PbO_2 and β-PbO_2 crystals in the formation process [78, 79]. The refining grains made the PAM have a larger specific surface area and caused a higher initial capacity and average capacity per cycle for both testing methods: the initial and average capacity could be increased up to 4% in the standard cycle testing and up to 8% in the electric scooter driving pattern cycle testing. The additive $BaSO_4$ in the PAM improved the content of 4BS in the cured plate [80]. In the SEM test, the researchers found that the peak intensity of 4BS at 27.7^{o} was 350 counts without of $BaSO_4$, and increased to 1521 with the proportion of $BaSO_4$ up to 0.1%. The result showed that the content of 4BS phase increased with the increase of $BaSO_4$ dosage. The increased proportion of 4BS phase with the addition of $BaSO_4$ could be attributed to the high nucleation density of 4BS on the $BaSO_4$ crystal nucleus. 4BS would transform to α-PbO_2 in the subsequent formed plate, which contributes to the cycle life improvement. In addition, such as $SrSO_4$, $Bi_2(SO_4)_3$ and so on can also be used as a nuclear agent to improve the performance of the LAB.

4BS is also a common positive plate additive for LAB [81-83]. Many researchers believe that small particle 4BS has the higher formation conversion rate and the LAB can be easier to obtain good performance [84, 85]. A type of micro-nanostructure 4BS, which synthesized by the sol-gel method, was added to the PAM [86]. It would inhibited the fast growth of poor conductor $PbSO_4$ crystals during curing processing. The study showed that, with the increase of nanometer 4BS addition, the crystal was smaller and its distribution was very uniform. In the meantime, it formed a stable skeleton in the PAM and was firmly attached on the grid. The tests showed that the discharge specific capacity and discharge voltage plate did not decline sharply and the discharge platform was relatively more flat as the discharge rate increased. This certified that the positive plate with micro-nanostructure 4BS had a higher electronic conductivity speed and a lower polarization resistance.

The mechanism of sulfate in PAM is approximately the same. Take $CaSO_4$ as an example [77]. $CaSO_4$ is not isomorphous compounds of $PbSO_4$ and, its solubility is several orders of magnitude higher than that of $PbSO_4$, so that the discharge voltage cannot be affected by $CaSO_4$. The crystal polarization results in the accumulation of Pb^{2+} in the electrolyte near the grid, and promotes the formation of the $PbSO_4$ crystal nucleus after achieving supersaturation with the solubility product of HSO_4^-. At the same time, the $CaSO_4$ deposited in the micro-pores of the PAM acts as the seed of $PbSO_4$, which makes the $PbSO_4$ be deposited in the pores of the PAM. Although the porosity of PAM is reduced to some extent, the structure of active material is improved, and the integrity of it is not destroyed, so as to improve the utilization rate of PAM.

6. CONCLUSIONS

The sulfation of negative electrode and the softening and shedding of PAM have been the main problems restricting the application of LAB. The development of lead carbon battery solves the sulfation of negative electrode under HRPSoC, inhibits the occurrence of side reactions such as hydrogen evolution, and enhances the charge/discharge efficiency and cycle life. At present, we are leading the extension of the real LAB in the form of a lead carbon energy storage device.

In recent years, researchers have improved the performance of positive electrode via modifying the PAM of LAB by various kinds of positive additives, such as conductive additive, porous additive, nucleating additive and binder additive. However, the current research results show that the failure mode of LAB is the softening and shedding of PAM, and the cycle life is mainly limited to the positive electrode. Therefore, the continuous development of LAB is still facing a problem to be solved, which is of great significance for improving the performance of PAM of the LAB. It is believed that the LAB energy storage system modified by PAM additives can acquire better service performance through the researchers' systematic and in-depth research. At the same time, some electrolyte additives can be explored and combined with positive additives to improve the performance of the battery. It is foreseeable that LAB will have a good application and promotion in the field of start and stop system, power battery field, solar energy storage and other fields.

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