Industrial Validation of Lead-plated Aluminum Negative Grid for Lead-acid Batteries

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Abstract. Aluminum metal grids as lightweight substitutes for lead grid are promising to achieve the overall weight reduction of lead-acid battery for increasing energy density without sacrificing charge/discharge and cyclic performance. In this paper, a dense lead layer with an average thickness of 40 μm is industrially electro-deposited onto aluminum grid with a pre-plated nickel interlayer as the negative electrode for lead-acid battery. The charge/discharge tests with such an grid as negative plates show that the false welding between the lead-plated aluminum grid and lead busbar is an important challenge due to the thin plated lead layer, which would be a potential long-term risk for the charge step and sulfation. From dissection of the failed battery, it is found that the dense lead layer is partially corroded by sulfuric acid and aluminum substrate is partially dissolved into the electrolyte. Sulfation at such a negative electrode brings about a dense and sticky layer composed of the mixed PbSO₄ and Al₂(SO₄)·18H₂O, which is the main failure mode of the lead-acid battery. This industrial validation demonstrates that lead-deposited aluminum grids are not feasible at negative electrodes of light-weight lead-acid batteries from the viewpoint of commercial reliability.

1. Introduction

Electrochemical energy technologies, such as lithium-ion batteries, fuel cells, and lead-acid batteries are widely used in energy storage and conversion applications such as portable electronics, electric vehicles and stationary power stations [1-8]. Compared with other types of batteries, rechargeable lead-acid batteries (LABs) have been recognized as the most mature, reliable, safe, and cost-effective as well as recyclable type (>99% of recycling efficiency of the spent batteries). These advantages make them the largest battery market among different batteries [7, 8]. However, two major disadvantages including insufficient energy density and cycle-life have limited their applications in some fields. With respect to this, increasing both energy density and cycle-life should be the major efforts in the development of LABs. Regarding increasing energy density of LABs, reducing the weight of electrode grids has become one of the approaches by exploring lighter metal and carbon materials. In general, the commercialized LAB adopts lead mesh as the electrode grids, which are
embed into the active material pastes to form both positive and negative electrodes. Lead grids can serve as both the frame to support the active material pastes and the current collectors. They have important impacts on the total weight of the LAB, the usage of active materials, the charge and discharge performance, and the cycle-life [9, 10]. Due to the high gravity of lead metal, lead grids can contribute a considerable weight to LABs, leading to heavy LABs with low energy densities (30-50 Wh·kg⁻¹). These values of energy density are much lower than those of Lithium-ion batteries (100-300 Wh·kg⁻¹) [1, 3]. Therefore, in recent years, the development approaches of LABs are focused on reducing weight by exploring light materials as the grids to replace lead grids for increasing energy density. In this regard, many types of electrically conductive materials such as lead-antimony alloy, lead-calcium alloy, meshed lead-calcium aluminum alloy, meshed resin carbon, and lead-plated polymer, etc. have been explored [11-14]. The results obtained with materials lighter than lead have shown some progress in terms of internal resistance reduction, mechanical strength increase, and energy density increase compared with traditional lead grids [15-17].

Among different non-lead LAB grids explored, aluminum (Al)-/aluminum alloys(Al alloys)-metal based grids have shown some advantages than other metal materials in terms of high electrical conductivity, lightness, and high toughness/plasticity. The physical and chemical properties of aluminum compared with lead are shown in Table 1. Furthermore, Al and Al alloys are relatively inexpensive and suitable for large-scale industrial production [18]. However, Al is a high-chemically active metal that has a strong affinity for oxygen [19, 20]. Under natural conditions, a thin and dense oxide film can be quickly formed on aluminum surface. This oxide film can protect the underneath Al from corrosion in neutral media such as water. However, in harsh environments, such as industrial waste-water, corrosive media like acids, alkalines, salts, etc., Al and its alloys are easily corroded and prone to inter-granular corrosion [21]. Therefore, in such media, a protective electroplate lead layer need be prepared onto the surface of Al or Al alloy grid to improve the corrosion resistance [22, 23]. In this study, the Al grid would be deposited with lead layer and adopted as the negative electrode grids for 6-DZM-20Ah LAB cells in order to validate the commercial reliability in industrial scale.

### Table 1. Comparison of physical and chemical properties of aluminum and lead.

| Function                        | Al  | Ni  | Pb  | (unit)  |
|---------------------------------|-----|-----|-----|---------|
| Atomic number                   | 13  | 28  | 82  |         |
| Atomic weight                   | 26.97| 58.69| 207.2| g/mol   |
| proportion (20 °C)              | 2.680| 8.902| 11.3437| g/cm³   |
| Melting point                   | 660.2| 1453.0| 327.4| °C      |
| Linear expansion coefficient    | 24.58| 13.30| 29.1| 10⁻⁶/°K |
| Thermal Conductivity            | 237  | 82.9 | 34.8| W/M·K   |
| Resistivity (20 °C)             | 2.65 | 6.84 | 20.6| μΩ·cm   |
| Electronegativity               | 1.5  | 1.91 | 2.33|         |

2. Experimental

Nickel was first used as the coating of Al grid made through an electroless plating process to introduce a conductive layer. Electroless nickel plating was cooperatively completed using a mass production line in Shanghai Rensheng Fastener Manufacture Co., Ltd. After that, lead was plated on the top of the Ni coating layer using a standard fluoroborate system. The lead fluoroborate solution was obtained through the reaction between lead carbonate and excess fluoboric acid With Gelatin as an additive for the electroplating solution. The lead electroplating process was controlled at 45°C with a typical current density of 1-2 A·dm⁻². To measure the microstructure, small pieces of plated grids were mounted with heat-curing epoxy and followed with a grinding processing with abrasive slurry. The metallography microstructure was observed with an Olympus microscope.

To validate the Al grid-based negative electrodes for 6-DZM-20Ah, the electrode with a geometric size of 135 mm × 65 mm was assembled into a lead-acid battery. In prepare the electrodes, the active
materials for both negative and positive electrodes were taken from the mass production line of Chilwee Group Co., Ltd. The Al-based grid plated with a lead layer was then pasted with such an active materials as the negative electrode, and the conventional Pb-Ca alloy-based grid coated with active paste was adopted as the positive electrode, respectively. The grid ears of four positive at the left and five negative electrodes at the right were staggered and aligned respectively. An AGM (absorptive glass-microfibre) separator paper was placed between the positive and negative electrodes to prevent them from contact. The formed stack with four positive electrodes and five negative electrodes was then mounted into a plastic tank. Then, a proper amount of H₂SO₄ electrolyte with a gravity of 1.260 g·cm⁻³ was dripped into the tank. This tank was sealed and evacuated to form a lead-acid battery.

For performance measurements, the assembled lead-acid battery was placed onto the battery tester with both the positive and negative electrodes connected to the corresponding ports. The upper limit charge voltage and lower limit discharge voltage were 2.35V and 1.8V, respectively. Then the charge and discharge currents was set to 2A, and then the number of cycles were recorded. After cycling test, the battery was dissected and the appearance of each plate was recorded, and the Pb contents in the upper, middle and lower parts of the plates were measured. The separator papers were also peeled off to measure the acid content.

3. Results and discussion
The Al grids, lead-plated Al grids, and the active material pasted negative electrode are shown in Figure. 1a, Figure. 1b, and Figure. 1c, respectively. Before nickel coating by chemical deposition, the possible oil and aluminum oxide film on the surface of Al grids were all completely removed with the pretreatment steps in the production line. These pretreatment steps are highly important for the deposition quality of the nickel layer. Similarly, the quality of nickel layer is also important for lead electro-plating to form the uniform lead layer. Otherwise, Al grid corrosion by sulfuric acid electrolyte may take place firstly at the defects of lead layer.

Figure 1. a: aluminum substrate grid. b: aluminum substrate grid after lead plating. c: aluminum substrate grid coated with active material.

Figure 2. SEM images of aluminum plated with lead layer.
To observe the micro-structure of the lead-plated surface of Al grid, SEM (SEM: Hitachi S-3400N) was used in this work, as shown in Figure.2a and Figure.2b. It can be seen that a dense and uniform lead layer has coated onto the Al grid through electro-plating processing. No cracks and pinholes can be found on the lead coating layer. This dense lead layer is expected to provide a good protection from corrosion of acidic electrolyte.

Figure 3. Metallographic pictures of the aluminum substrates after lead plating.
3a, pole ear; 3b, frame bone; 3c, center bone of aluminum grid.

To examine the uniformity of the lead coating layer on Al grid, metallographic images were taken on the cross section of lead-plated pole ear, frame bone, and the center of bone of the Al grid, the obtained images are shown in Figure.3a, Figure.3b, and Figure.3c, respectively. It can be measured that the thickness of the lead plating layer is about 40 μm. Even though the thickness of the layer is not very homogeneous, it is basically uniform without cracks or pinholes found in the cross-section images.

As identified, the thickness of lead layer is important for the welding between pole ear and busbar. For pure lead grid, false welding usually does not appear but for lead coated grid, welding upon pole ear is not easy. Figure. 4 shows the conventional intense welding (A) and a typical false welding (B).

Carry out capacity tests on batteries of the same type assembled from the false welding lead coated grids (B) and conventional lead grids, evaluate their battery performance at different time rates (C20, C10, C5, C2). The Peukert constant of the false welding lead coated grids cell was 1.34, which was higher than the conventional lead grids cell. The results show that the false welding lead coated grids batteries have poor high-rate discharge performance. The false welding lead coated grids cell dragged battery rate discharge performance[24].

The reason for false welding is that the melting point of Al substrate lead is more than 300 °C higher than that of lead coating, as shown in Table 1. During welding, Al grid ear does not melt and take part in welding process. Furthermore, if considering the thin Ni interlayer with a melting point at 1453 °C, there will be even more difficulty for an intense welding.

Figure 4. A: Intense welding between lead grid and lead busbar; B: False welding between lead-plated grid and lead busbar.
Table 2. Electrical performance test data of the tested battery.

| Number batch | Acid volume | Discharge time | Coulomb efficiency | Cycle number |
|---------------|-------------|----------------|--------------------|--------------|
| normal /     | 210±2ml    | 125min         | 98.14%             | 130 (processing) |
| Group A 1     | 225±2ml    | 98min          | 88.41%             | 43times (die) |
| Group B 1     | 215±2ml    | 107min         | 91.40%             | 57times (die) |
|              |            | 118min         | 95.7%              | 73times (die) |

Table 2 summarizes the performance of the lead acid battery with Al grid negative electrodes (Labelled with Group A). It can be seen that the discharge time can only reach 98 minutes and the coulomb efficiency can only reach 88.41%. It can be seen that even though the initial capacity of the battery is acceptable, the inner electric resistance is increased with increasing the charging and discharging cycles. During the cycling, it was also observed that sulfate accumulate at negative side happened and the active material was gradually fell off, resulting in a die of the battery at the 43 cycles. To further improve the performance, some improvements were applied as follows: 1) adopting flux during ear welding; 2) keeping the pole ear of the negative plate slightly longer for giving more welding area; 3) increasing the tin content in busbar; and 4) enclosing the additive material surface of the negative plate with a plastic thin film to avoid paste scattering before and during the curing. The thin film could prevent the paste edge of the negative plate from smearing, increasing the adhesion of the lead paste onto the negative plate. After the improvement, experiments show that these measures are well helpful for the fabrication of batteries. As shown in Table 2, the data after the measures (marked by Group B in Table 2) are better than those of Group A. The discharge time can go 118 minutes and the coulomb efficiency can reach to 95.7%.

Unfortunately, Table 2 shows that the initial capacity and Coulomb efficiency of Group B are still relatively lower than those with pure Lead grid negative electrode. In experiments, it could be observed that the cell voltage was increased rapidly during the charging process, and its initial and final voltages were both relatively too high. The final charging voltage could reach to 2.90 V/single cell. The voltage increases rapidly during the charging process and the voltage was also dropped rapidly during the discharging process too. That is, it dropped to the termination voltage too early because the capacity is significantly low.

![Figure 5](image5.png)  
Figure 5. Anatomy of the cleaned grid of Group B test battery.

![Figure 6](image6.png)  
Figure 6. Aluminum substrate grid bars is exposed after dissection.

To understand the failure mechanism, the battery was disassembled after the cycling tests. Figure 5 shows the dissection of Group B batteries after cycling. It can be seen that there are white spots which indicate the accumulation of sulfate on the surface of negative plates. Normally, the negative
plate should be grayish white (normally gray). However, after cycling, the surfaces of the negative plates look coarsen, hard and sandy, indicating that a severe sulfation has taken place on the surface. In general, these sulfates cannot be restored to activity under normal conditions. It is concluded that the degradation of the battery performance is mainly caused by the sulfation of the plates.

From the accumulated experiences during the past decade, Chilwee Research Institute and their cooperators have summarized the formation reason of white spots of plate sulfation as follows: 1) lead-acid battery is initially charged insufficiently, or the initial charge is interrupted for a long time; 2) the battery is not fully charged for a long time; 3) failure to charge in time after discharge; 4) frequent over-discharge or low-current deep discharge; 5) if the electrolyte density is too high or the temperature is too high, lead sulfate will be deeply formed and difficult to recover. 6) the batteries have a long shelf life and are not used for a long time without regular charging. 7) localized short-circuit, local action or water on the surface of the battery causes leakage. and 8) the electrolyte is impure and self-discharge is large. In the case of normal use of lead-acid batteries, most of the active substances (PbO₂ and Pb) on the positive and negative plates are converted into small-grained lead sulfate grains. These soft, small-grained lead sulfate grains are uniformly distributed in a porous state. The active material is easy to contact with the electrolyte during charging to restore the original substances PbO₂ and Pb. If the above-listed improper use occurs, the active material on the electrode plate gradually forms large sulfate crystal grains, generating died sulfate grains.

Generally, during the solidification of the electrode plate, the oxidation of lead on the surface of the grid, or the process of forming a good corrosion layer on the surface of the grid, is the essential factor that can make the active material tightly and firmly combined with the grid [25]. After the surface of the grid is oxidized, lead oxide deposits on the surface of the grid, grows and enters the lead paste, thereby creating a very strong connection between the lead paste and the grid, ensuring that the active material is tightly attached to the grid thereafter [26, 27]. If the adhesion between the active material and the grid surface is not strong enough, the expansion and contraction of lead paste volume during charge and discharge will detach the active material from the grid ribs, forming a gap. When electrolyte is infiltrated and the battery is in a discharged state, preferential discharge will occur around the grid bars, generating a PbSO₄ barrier layer to increase battery internal resistance, and finally causing severely insufficient discharge capacity [28].

In this research, the substrate metal of grid is Al, which has high metal activity. The corrosion of the negative electrode strip will cause the aluminum substrate to be exposed. Aluminum can react with sulfuric acid to produce aluminum sulfate. The impurity element is determined from the used electrolyte of Group B battery. The electrolyte with aluminum grid shows an Al element content of 0.0023%, as compared with 0.0002% for a conventional lead grids, which means that ten times of Al element dissolves into the electrolyte from aluminum grid. After the ultrasonic stripping, some aluminum substrate is exposed out, as shown in Figure 6. It can be seen that the lead coating is peeled off by sulfuric acid electrolyte and the aluminum substrate is partially corroded during the charge and discharge cycles. Even though the lead layer of Al grid is dense shown in Figure 2, their may be some unclear pine holes or other defects which are corroded firstly. Whatever, it is unreliable to industrially produce completely perfect protecting lead layer. The chemical reaction between Al surface and H₂SO₄ can be expressed as Equation (1):

\[
2\text{Al} + 3\text{H}_2\text{SO}_4 \rightarrow \text{Al}_2(\text{SO}_4)_3 + 6\text{H}_2
\]

Aluminum sulfate (Al₂(SO₄)₃) can absorb a large amount of water to generate Al₂(SO₄)₃·18H₂O, which will harden the interface electrolyte to lose fluidity, which was confirmed by on-site anatomy of the tested batteries in this work. These coarse and hard aluminum sulfate crystals are bulky and poorly conductive, and inactive for charging and discharging. They can also block the pores of the active material of the electrode plate, making the electrolyte penetration and diffusion harder, and then increase the internal resistance of the battery. Furthermore, Reaction (1) can produce hydrogen gas, which is also a harmful thing for lead-acid battery.
Table 3. Chemical composition of the tested battery.

| Group | batch | Acid volume | Physical and chemical testing |
|-------|-------|-------------|-----------------------------|
|       |       |             | PbO₂ content (%) | Separator acid density (g/cm³) |
|       |       |             | up  | middle | down | up  | middle | down |
| normal | /     | 210±2ml    | 91.7 | 91.7  | 91.2 | 1.327 | 1.326  | 1.335 |
| Group A | 1     | 225±2ml    | 88.3 | 87.5  | 86.6 | 1.297 | 1.301  | 1.305 |
| Group B | 1     | 215±2ml    | 90.5 | 90.2  | 89.9 | 1.311 | 1.314  | 1.319 |
|        | 2     | 215±2ml    | 91.5 | 91.4  | 91.2 | 1.320 | 1.318  | 1.325 |

Due to the produced harden Al₂(SO₄)₃·18H₂O, during charge, the crude and hard lead sulfate mixed with aluminum sulfate is not easily converted into PbO₂ and Pb, causing a significant performance degradation of the battery. Table 3 shows that the PbO₂ content of Group A and Group B are all lower than that of conventional lead grid battery. If it takes too long, those coarse and hard lead sulphate will lose reversibility, and as a result, the quantity of active material and the discharge capacity will be reduced.

In this work, experimental improvements on battery preparation, the discharge capacity of the Al grid negative electrode based lead-acid battery have been made, the coulomb efficiency can research to 95.7%, and effective cycle-life to 73 times, as listed in Table 2. The lead-acid battery produced in this experiment is the existing model 6-DZM-20Ah in the market. The production process and the evaluation of battery performance are completed under the reference of GB/T 22199.1-2017 in china, which specifies in the state that the capacity retention rate is above 90%, the number of cycles is not less than 350 about battery life. It is concluded that the application of aluminum-based lead-plated negative grids in 6-DZM-20Ah lead-acid batteries does not meet various operating standards.

4. Conclusions

The aluminum negative grids are plated with a dense lead layer in order to completely protect the aluminum grid from the sulfuric acid corrosion. The lead-plating and battery assembly are both manufactured according to the production standard as closely as possible. It is found that the false welding is not easy to avoid due to the thin plated lead layer, which is a potential long-term risk for the charge step. Aluminum substrate generation on the aluminum grid surface even with full lead coverage can still be partially corroded by sulfuric acid during charging and discharging cycles. The produced Al₂(SO₄)₃·18H₂O can accelerate the serious hardening of the negative plates and then deep sulfation, which dramatically reduces battery capacity.

As a conclusion, the lead-plated aluminum grid could not be used as a negative plate for power-regulated lead-acid batteries with mature mass production processes after evaluating the production process and the battery performance.

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