Lead Plating Processes and Their Application in Lightweight Grids for Lead-Acid Batteries

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Abstract：The "light weight and high energy" of lead-acid battery requires the development of light metal coated with lead instead of pure lead grid. Fluoroboric acid system, sulfamic acid system, citric acid system and methane sulfonic acid system can be applied in the process of lead/tin plating on the surface of light metal. The fluoride in the residual solution of fluoroboric acid system is difficult to be removed to meet the national standard. Sulfamic acid can form lead sulfate precipitation easily, and the stability of the bath and the quality of the coating will be affected. The high current density of citric acid system exerts great influence on the lead content of the coating; methane sulfonic acid system can work under high current density, and the wastewater treatment is reliable. The light-weight lead-plated grid material, coating lead or lead-tin alloy on low density copper, aluminum and carbon foam, plays an important role in the development of lightweight and high-energy technology in lead-acid batteries.

Key words：lead-acid battery；lightweight；lead plating process；lead-tin alloy

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As electrochemical energy storage devices, LABs show low cost, high safety, large market scale, almost all recycling rate (over 99.5%), and developed production technology. LABs have been widely applied in energy storage systems for electric mopeds, solar and wind power generation, start-up for vehicles, low-speed vans and other fields[1-6]. However, LABs' short cycle life and low specific energy density limit its further application in the fields of electric vehicles and large ships[7-9]. The weight of lead-based alloy grids accounts for nearly 25% of the total weight. Reducing the grid weight has become a key issue to improve the specific energy density of LABs[10-13].

The main way to reduce the grid weight is to replace the lead-based grid with lightweight materials. In order to meet its electrochemical role in the battery, it is necessary to plate lead or lead tin alloy on the surface of the materials by electroplating and hot dip plating[14-16]. Hot-dip plating of lead coating need a high working temperature (400-500 ℃), and the coating obtained is thick and uneven. In contrast, electroplating is usually facile, and the coating is thin and more uniform. This paper will briefly summarize these lead plating techniques of lead and lead tin and their application as lightweight grids for LABs.

1 Material of grid

In LABs, grids act as a carrier to support the active material and a current collector to make the current distribution uniform. The grid material is exposed to a sulfuric acid environment for a long time, and its corrosion resistance directly affects the cycle life of the battery. After being corroded and loses its effect, the battery will fail.

Currently, the most widely used grid materials are lead-antimony alloy and lead-calcium alloy[16-21]. The densities of these alloys are almost the same as that of pure lead grid (11.34 g·cm^{-3}), making it impossible to achieve lightweight. The lead-antimony alloy has good tensile strength, ductility, creep resistance and good casting performance. The grid is not easy to deform during the working process with simple production process, and the lead-antimony alloy has a good bonding force between the active materials. However hydrogen evolution is prone to occur at the negative electrode during working life[22]. Lead-calcium alloy has higher conductivity so that it shows better performance especially at lower temperature compared with lead-antimony alloy. Furthermore, its hydrogen evolution overpotential is about 200 mV higher than lead-antimony alloy, which can effectively inhibit hydrogen evolution and water loss at negative electrode during battery charge and discharge. The shortages of lead-calcium alloy are poor deep discharge cycle capability, poor creep resistance and short service life.

Lightweight grids use lightweight materials with a lead-plated surface to replace lead-based alloy grids[23-25]. Base materials for lightweight grid include copper[26-30]、aluminum[31-32]、titanium[33]、foam metal material[34-36]、carbon material[37]、glass fiber[38-39] etc. Tab.1 compares the physical and chemical properties of copper, aluminum, titanium and lead metals. The density of the first three metals is significantly lower than that of lead, and grids made from them will be lighter. The thermal and electric conductivity of copper and alumina is much higher, which means potential faster and more homogeneous conduction of heat and current.

Tab. 1 Physical and chemical properties of copper, aluminum, titanium and lead

Function	Cu	Al	Ti	Pb	Unit
Atomic number	29	13	22	82	
Atomic weight	63.55	26.98	47.87	207.2	g·mol^{-1}
Density	8.96	2.7	4.51	11.34	g·cm^{-3}
Melting point	1 083	660.2	1 678	327.4	℃
Linear expansivity	16.5	23.2	10.8	29.3	10^{-6}·K^{-1}
Thermal conductivity	401	237	15.2	34.9	W·m^{-1}·K^{-1}
Resistivity (20 ℃)	1.68	2.65	42.00	20.68	μΩ·cm
Electronegativity	1.90	1.61	1.54	2.33	

2 Lead plating or lead-tin alloy process

2.1 Lead plating or lead-tin alloy system

Lead and lead-tin coatings have good protection, solderability, corrosion resistance and wear resistance[40-41]. Lead-tin alloy coating with 4%-10% tin is used as protective coating for steel parts[42]. Lead-tin alloy coating with 6% to 20% tin is widely used in anti-friction coatings of bearings[43]. Lead-tin alloy coating with 60% -63% tin is widely used on printed circuit boards, because it has the advantages of less porosity, good welding performance and smooth surface[44]. In lightweight LABs, if the lead-plated light grid is used as a positive grid, it will be at a high potential and easily corroded, causing battery failure, so it is more suitable for negative grids[45].

The standard electrode potential of lead is –0.126 V, and the standard electrode potential of tin is –0.136 V. The close electrode potentials make the co-deposition of lead and tin easy. Lead-tin alloy coatings with different alloy components can be obtained by changing the composition of the plating solution. The lead of lead-tin alloy coating is the main component in LABs, the corrosion resistance of the coating improved and working life prolonged with the increase of tin content in the coating. However, due to the high tin content, the hydrogen evolution overpotential will be decreased causing water loss, thus the most suitable content of tin in coating is about 1%-2% for lightweight grid[22]. Electroplating is carried out in a plating tank filled with electroplating liquid. The electroplating bath usually includes main salt, additional salt,

complexing agent, stabilizer and additives. When electroplating lead or lead-tin alloy, in the electroplating solution, lead or lead-tin alloy is used as the anode, while the cathode is the substrate to be plated[46-48]. During the electroplating process, the composition of the plating solution, the type and content of additives, current density, operating temperature, type and quality of electrical grade boards and the intensity of stirring will all affect the quality of the coating. Due to the occurrence of side reactions, the current efficiency is difficult to reach 100%. Fig.1 is a schematic diagram of electroplating with lead electroplating as an example.
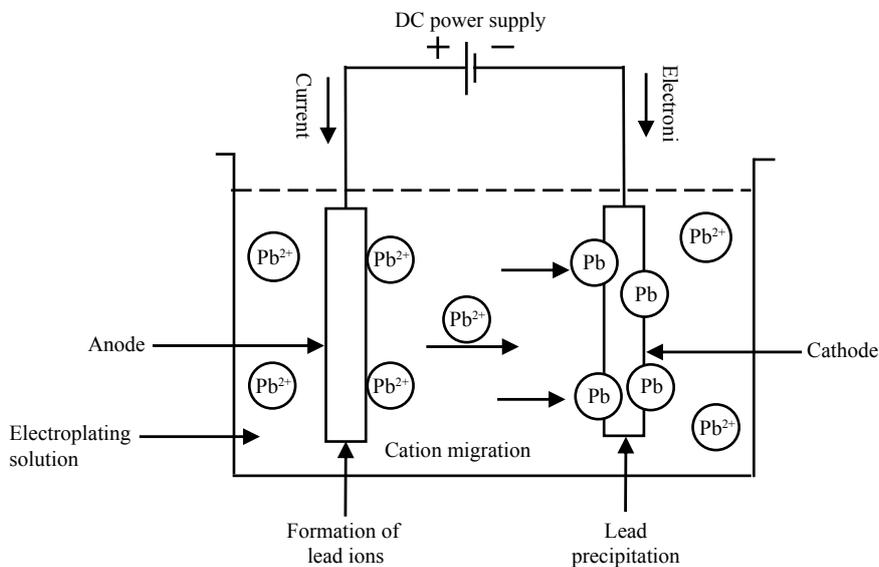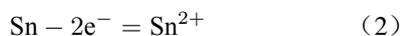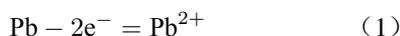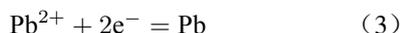

Fig. 1　Principle of Electroplating

After the current passes, the anode metal is dissolved and electrons deposited on the cathode are obtained. The electrochemical reaction formula for lead or lead-tin alloy plating is as follows (1-4):
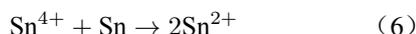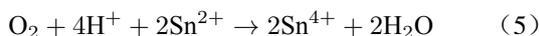
Anode

$$Pb - 2e^- = Pb^{2+} \qquad (1)$$

$$Sn - 2e^- = Sn^{2+} \qquad (2)$$

Cathode

$$Pb^{2+} + 2e^- = Pb \qquad (3)$$

$$Sn^{2+} + 2e^- = Sn \qquad (4)$$

In addition, the tin of the anode will have the following reactions in the plating solution:

$$O_2 + 4H^+ + 2Sn^{2+} \rightarrow 2Sn^{4+} + 2H_2O \qquad (5)$$

$$Sn^{4+} + Sn \rightarrow 2Sn^{2+} \qquad (6)$$

Both reactions are heterogeneous reactions. If there are oxidizing substances in the bath or contact with oxygen, the stannous ions will be converted into tin ions (5). The tin can react with tin ions to restrain the stannous ion's oxidation to Sn^{4+} (6). The main electroplating solution systems for lead or lead-tin alloy electroplating process include fluoroborate, phenol sulfonate (PSA)[49], sulfamate, citrate[50], tartaric acid[51], and alkyl sulfonate systems[52-55]. Fluoroboric acid system is the most widely used plating solution system. However, in recent years, the application of environmentally friendly and safe bath systems has been increasing. Among them, the methane sulfonic acid system (MSA) is considered to be the most promising bath system[56].

2.1.1　Fluoroboric acid system

The composition of the fluoroborate electroplating solution is simple, which includes lead fluoroborate, free fluoroboric acid, free boric acid, and additives.
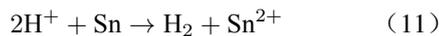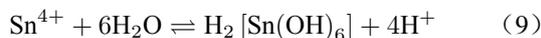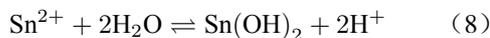
Fluoroborate plating solution is a traditional plating solution for lead plating, which can be used for electroplating materials such as bearing bushes, silicon wafers, and battery grids. Fluoroboric acid plating solution is facile to configure and to operate even at room temperature. The plating solution has

good stability, strong conductivity. The current efficiency of cathode and anode is close to 100% from 1 to 7 A·dm^{-2}. Tab.2 is a recipe for fluoroboric acid system.
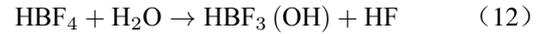
Tab. 2　Electroplating solution composition and process conditions (fluoroborate)[57]

Composition of electroplating solution	Content
Pb(BF$_4$)$_2$	200 g·L^{-1}
Dissociate HBF$_4$	60 g·L^{-1}
Gelatin	2 g·L^{-1}
Hydroquinone	3 g·L^{-1}
Sodium Ligninsulfonate	1 g·L^{-1}
Temperature	Ambiance
Current density	1 A·dm^{-2}

In the fluoroboric acid plating solution, fluoroboric acid is obtained by the reaction of hydrofluoric acid and boric acid (7). Fluoroboric acid is a strong monobasic acid. The excess presence of fluoroboric acid can restrain the stannous ion's oxidation to Sn^{4+} (In acidic solutions, divalent tin compounds may exist as stannous hydrate ions, but tin ion compounds generally hydrolyze to form precipitates) (8-9). The free fluoroboric acid ensures the normal dissolution of lead-tin alloy and supplements metal ions, which maintain the stability of the plating solution (10-11).

$$H_3BO_3 + 4HF \rightarrow HBF_4 + 3H_2O \qquad (7)$$

$$Sn^{2+} + 2H_2O \rightleftharpoons Sn(OH)_2 + 2H^+ \qquad (8)$$

$$Sn^{4+} + 6H_2O \rightleftharpoons H_2[Sn(OH)_6] + 4H^+ \qquad (9)$$

$$2H^+ + Pb \rightarrow H_2 + Pb^{2+} \qquad (10)$$

$$2H^+ + Sn \rightarrow H_2 + Sn^{2+} \qquad (11)$$

Boric acid is added to prevent hydrolysis of fluoroboric acid. Fluoroborate anions can be hydrolyzed to form boric acid and free fluoride ions (12-15), and fluoride ions will form lead fluoride precipitates with lead ions (16). In order to inhibit the hydrolysis of the fluoroborate anion, an excess of boric acid can be added to force the reaction (7) to proceed in the positive direction. The free boric acid acts to stabilize the fluoroboric acid, also stabilizing the lead fluoroborate.

$$HBF_4 + H_2O \rightarrow HBF_3(OH) + HF \qquad (12)$$

$$HBF_3(OH) + H_2O \rightarrow HBF_2(OH)_2 + HF \qquad (13)$$

$$HBF_2(OH)_2 + H_2O \rightarrow HBF(OH)_3 + HF \qquad (14)$$

$$HBF(OH)_3 + H_2O \rightarrow HB(OH)_4 + HF \qquad (15)$$

$$2F^- + Pb^{2+} \rightleftharpoons PbF_2 \qquad (16)$$

In the fluoroboric acid system, various proteins are used as additives, such as peptone, glue, gelatin and meat protein, in order to change the morphology of the coating. The lead or lead-tin alloy coating obtained is generally smooth and tight.

In this system, hydrofluoric acid and fluoroboric acid are highly corrosive and irritating, which can damage electroplating equipment and burn human skin. Industrial fluorine-containing wastewater treatment methods mainly include precipitation method, electrochemical method, adsorption method, ion exchange resin method, microbial defluoridation method, etc.[58]. The inorganic and organic pollutants in the wastewater greatly increase the difficulty of wastewater treatment, which requires more expensive equipment and operating costs according to the latest electroplating pollutant emission standards[59].

2.1.2　Sulfamic acid system

The sulfamate plating solution takes sulfamate as the main salt with free sulfamate, boric acid and additives.

Lead sulfamate and stannous sulfamate are prepared by chemical reaction similar to the method of preparing fluoroborate solution. Amino sulfonic acid and its salts are solid, non-volatile, no peculiar smell, low toxicity, low price, and easy to store and transport. However the aqueous solution of sulfamic acid has the same strong acidity as HCl and H$_2$SO$_4$, whose dust and solution can burn eyes and skin. Therefore, personal protection must be required during using it.
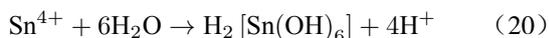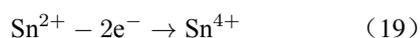
For the lead-tin alloy coating (9 : 1), the suitable current density range of the sulfamic acid system is between 0.7-2.0 A·dm^{-2}. The conductivity of the plating solution is great (72 mS·cm^{-1}). The

wastewater treatment is relatively simple and has little harm to the environment[60]. Tab.3 is a recipe for Sulfamic acid system.

Tab. 3   Electroplating   solution   composition   and   process conditions (sulfamic acid)[22]

Composition of electroplating solution	Content
$Pb(NH_2SO_3)_2$	70-100 g·L^{-1}
Dissociate H_2NSO_3H	60-100 g·L^{-1}
HBO_3	2 g·L^{-1}
Additive A	1-2 g·L^{-1}
Additive B	2-3 g·L^{-1}
Additive C	2-5 g·L^{-1}
Temperature	20-30 ℃
Current density	1-10 A·dm^{-2}

Sulfamic acid anions tend to be hydrolyzed into ammonia and sulfate radicals (17), which precipitates as lead sulfate (18), changing lead concentration. During the plating process, Sn^{2+} in the electroplating solution is easily oxidized to form Sn^{4+}, and Sn^{4+} is easily hydrolyzed to form a colloid and suspended in the electroplating solution (19-20).

$$HSO_3NH_2 + H_2O \rightarrow NH_3 + H_2SO_4 \qquad (17)$$

$$SO_4^{2-} + Pb^{2+} \rightarrow PbSO_4 \downarrow \qquad (18)$$

$$Sn^{2+} - 2e^- \rightarrow Sn^{4+} \qquad (19)$$

$$Sn^{4+} + 6H_2O \rightarrow H_2[Sn(OH)_6] + 4H^+ \qquad (20)$$

The oxidation and hydrolysis of Sn^{4+} will cause the loss of Sn^{2+} in the electroplating solution and bring about turbidity. Therefore, the long-term storage stability of the sulfamic acid is poor and its application is limited.

2.1.3   Citric acid system

The components of citric acid electroplating solution mainly include citric acid, EDTA or ammonium acetate, stannous chloride, lead acetate and additives.

Citrate ions can complex with a variety of metal ions, while EDTA only complexes with lead ions. Ammonium acetate can also form stable soluble coordination compounds. They ensure that all lead ions and stannous ions are complexed without being hydrolyzed. The excessive complexing agent maintains the coordination balance of metal

ions during the electroplating process. The pH of the bath needs to be maintained in the range of 4 to 5. The performance of the solution is stable, and after being left open for four months, it is still clear and   transparent[61].   The   solution   has   excellent dispersion and deep plating ability. Tab.4 is a recipe for Citric acid system.

Tab. 4   Electroplating   solution   composition   and   process conditions (citric acid)[62]

Composition of electroplating solution	Content
$C_6H_8O_7$	150-160 g·L^{-1}
CH_3COONH_4	100-120 g·L^{-1}
$SnCl_2$	30-35 g·L^{-1}
$Pb(CH_3COO)_2$	10-20 g·L^{-1}
HBO_3	30-35 g·L^{-1}
YDZ-7	12-16 mL·L^{-1}
YDZ-8	12-16 mL·L^{-1}
Temperature	10-35 ℃
Current density	0.5-2.5 A·dm^{-2}

Citric acid is a kind of fruit acid, non-toxic, raw materials from grain, and its use cost is lower than that of fluoroboric acid. In addition, citric acid is degradable under the action of microorganisms and heat, and using it will not damage the environment. Compared with organic acid, citric acid is weaker and less corrosive to production equipment.

However, as the current density increases, the content of lead in the coating will decrease, and once the current density is too large, hydrogen evolution will be serious. Therefore, the current density is generally controlled at 1-2.5 A·dm^{-2} under room temperature. The plating solution contains complexing agent, which can form water-soluble complexes with most metal ions. It will dissolve and release   the   heavy   metals   deposited   in   the environment, bringing harm to the environment. Moreover, Citric acid is an edible substance, and once mold in the air enters the plating solution, the mold will multiply quickly, showing mold clusters, or clusters and suspension in the plating solution, which will affect the performance of the plating solution.

2.1.4   Methane sulfonic acid system

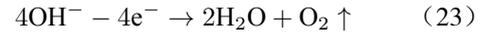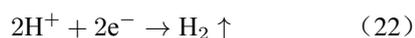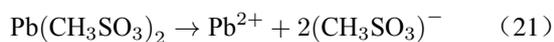In the alkyl sulfonic acid system, the alkyl

group usually contains 1 to 5 carbon atoms, of which the structure of methane sulfonic acid is the simplest. Among them, methane sulfonic acid is easier to produce, and its cost is relatively lower. Considering the treatment of wastewater, the length of the alkyl chain should be as short as possible. Therefore, Methane sulfonic acid plating solution has become the most used plating solution system among alkyl sulfonic acid plating solutions. The composition of the solution mainly includes lead methane sulfonate, methane sulfonic acid and organic additives.

Methane sulfonic acid system plating solution is stable, not affected by pH, and has low toxicity, whose solution is still clear and transparent after storage for 3 months. Methane sulfonic acid can improve the solubility of surfactants and organic additives as a complexing agent and stabilizer. The complex formed by it can inhibit the hydrolysis of lead methane sulfonate or stannous methane sulfonate. Meanwhile, it is difficult to cause the oxidation of various metal ions, which is very beneficial for metal electroplating in a multivalent state. Tab.5 is a recipe for Methane sulfonic acid system.

Tab. 5 Electroplating solution composition and process conditions (methane sulfonic acid)[63]

Composition of electroplating solution	Content
CH_4O_3S	100-140 $g\cdot L^{-1}$
$(CH_3SO_3)_2Pb$	10-20 $g\cdot L^{-1}$
$(CH_3SO_3)_2Sn$	20-30 $g\cdot L^{-1}$
Chlorobenzaldehyde	40 $mL\cdot L^{-1}$
Temperature	18-35 ℃
Current density	2-4 $A\cdot dm^{-2}$

Lead methane sulfonate dissociates lead ions in the plating solution, and is reduced at the cathode. At the same time, hydrogen ions overflow with hydrogen ion reduction (21-22). If the lead anode is passivated, oxygen will be released at the anode (23).

$$Pb(CH_3SO_3)_2 \rightarrow Pb^{2+} + 2(CH_3SO_3)^- \quad （21）$$

$$2H^+ + 2e^- \rightarrow H_2 \uparrow \quad （22）$$

$$4OH^- - 4e^- \rightarrow 2H_2O + O_2 \uparrow \quad （23）$$

The strong acidity of methane sulfonic acid brings about high conductivity and much higher operable current density of 2-40 $A\cdot dm^{-2}$[64]. The high current density supports fast plating, improving production efficiency and reducing energy consumption. Methane sulfonic acid shows low corrosivity for corrode glass, ceramics, etc. Compared with phenol sulfonic acid system, the total organic carbon (TOC) content in MSA is only 11.4% of PSA. Methane sulfonic acid can be biodegraded to eventually produce sulfate and carbon dioxide. It can be completely degraded within 24 days[65]. Therefore, the MSA system will greatly reduce the production of pollutants, which is conducive to environmental protection.

However methane sulfonic acid system uses many complex additives, which can be divided into stabilizers, dispersants, and brighteners according to their functions. They can stabilize the plating solution, improving the dispersion of the solution and the ability of deep plating, and making the coating dense and bright. Such as hydroquinone, phenol sulfonic acid, ascorbic acid, polyethylene glycol, Schiff base, etc., some of these additives are toxic and pollute the environment. Therefore, the preparation of high-quality additives is one of the future development directions of the methane sulfonic acid system. Tab.6 shows the physical and chemical properties, toxicity and selling price of fluoroboric acid, sulfamic acid, citric acid, and methane sulfonic acid. By comparison, it is concluded that the surface tension of methane sulfonic acid and fluroboric acid are relatively small, which is beneficial to the dispersion of the plating solution. Except for fluoroboric acid, sulfamic acid, citric acid and methane sulfonic acid are non-toxic or low-toxic. From the price point of view, the price of methane sulfonic acid is the highest, nearly $43 higher than the traditional fluoroboric acid bath. Except for the sulfamic acid system, the stability of the other three systems is very good. In terms of bath treatment, the treatment of fluoroboric acid is more troublesome, and the treatment of the other three is easier.

Tab. 6　Physical and chemical properties, toxicity and selling price of fluoroboric acid, sulfamic acid, citric acid, and methane sulfonic acid

| Function	Fluoroboric acid	Sulfamic acid	Citric acid	Methane sulfonic acid	Unit
Molecular formula	BF_3FH	H_3NSO_3	$C_6H_8O_7$	CH_4O_3S	
Molecular weight	87.81	97.09	192.12	96.11	
Density	1.38	2.12	1.54	1.48	$g \cdot mL^{-1}$
Surface tension	47	101.5	103.9	53.3	$dyne \cdot cm^{-1}$
Toxicity classification	Moderate toxicity	Low toxicity	nontoxic	Low toxicity	
Price (reagent grade)	205	91	83	248	$\$ \cdot kg^{-1}$
Stability	High	Low	High	High	
Can it be treated with biological methods?	NO	YES	YES	YES	

Note: Remark: 1\$=6.47￥.

2.2　Application of lead plating system in lightweight grid

　　Lightweight grids made of lead-plated materials with low density and high conductivity have a lot of progress. Various electroplating systems have been tried for electroplating different substrates, then, according to the nature of the base material, determine the best plating solution composition and process conditions. The following is the examples of electroplating systems that uses copper and titanium as a matrix to make grids. Furthermore, as for aluminum grid, if the dense lead layer is corroded by sulfuric acid, even a little bit, the aluminum substrate will be corroded and LABs will not work due to its high active type. Therefore lead-deposited aluminum grids are not feasible at negative electrodes of light-weight LABs from the viewpoint of commercial reliability[66].

2.2.1　Lead plating on copper substrate grids

　　Copper has a lower density than lead, having excellent conductivity and long life. The lead-acid battery using it could significantly improve specific energy and electrochemical performance. However, it is necessary to prevent lead exposure, excessive hydrogen evolution and tip dissolution. The fluoroborate system is used to lead-plated copper mesh. In the fluoroboric acid plating solution, copper is more inert than lead, and has poor activity. The pretreatment of electroplating is relatively simple, which only needs simple degreasing, derusting and activation. Fig.2 is the scanning electron microscope (SEM) image of lead plating on copper substrate, uniform and compact without pores, having better corrosion resistance.
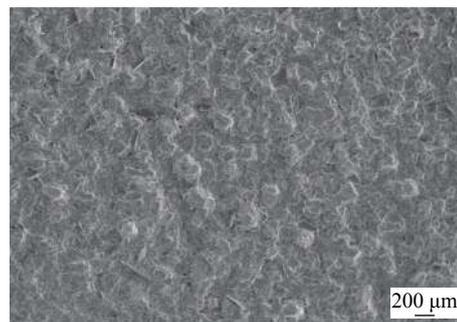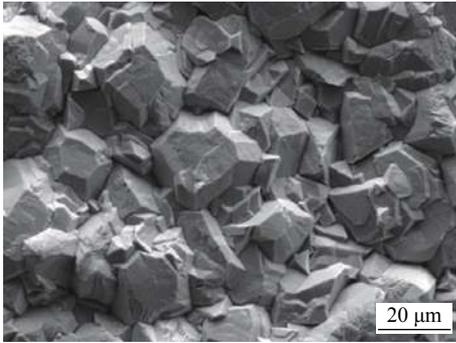

Fig. 2　SEM image of the coating for Pb on copper substrate

　　When the copper thickness is greater than 15 μm, the coating will not dissolve, and the actual weight ratio capacity can reach about 83 $Ah \cdot kg^{-1}$, while the specific weight of the lead-tin grid is only 50 $Ah \cdot kg^{-1}$[57].

2.2.2　Lead plating on titanium substrate grid

　　Titanium metal is called space metal, which shows low density and high strength. It is easy to form a dense oxide film on the surface, so that the titanium metal substrate needs to be treated before electroplating. Pre-treatment steps of polishing, degreasing, water washing.etc. are performed on the titanium substrate, which can remove the oxide film, ensure that the oxide film is no longer formed and increase the bonding force of the coating. Fig.3 is the SEM image of lead plating on titanium substrate, which is mostly large massive grains, with better corrosion resistance than small.

　　The two kinds of coating grids are used to assemble two bipolar LABs, and test their performance. As is shown in Fig.4, after 60 charge and discharge cycles, the discharge specific capacity
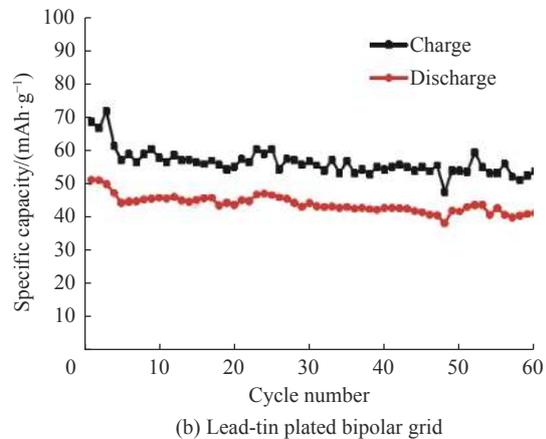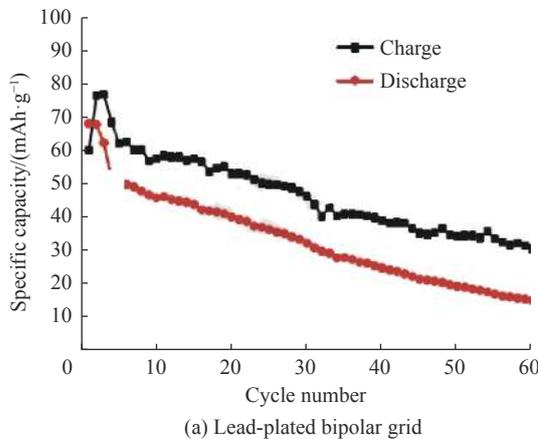
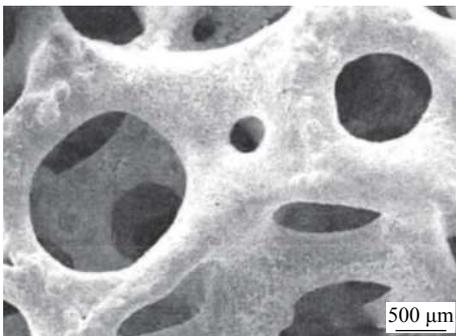**Fig. 3 SEM image of the coating for Pb on titanium substrate**

retention rate of the bipolar lead-acid battery assembled with the lead-tin alloy grids is 80.6%, which is far higher than that of the battery assembled with the lead-plated grid (22.5%). Therefore, the electrochemical performance of the lead-tin alloy coating is better than that of the lead coating[67].

2.2.3 Lead plating on foam metal grid

The lead foam grid has a three-dimensional

network structure, which has good conductivity and lighter weight owning large specific surface area. It can fill LABs with more active materials and increase battery capacity. It is an ideal electrode material for preparing high-performance LABs[68-72]. At present, the preparation methods of lead foam at home and abroad include casting method, plating method, spray deposition method, powder metallurgy method, etc.[73-74] Among them, the plating method is simple, having a good development prospect. The foamed lead is uniform, with high porosity and large specific surface area, whose substrates can be reticulated glassy carbon and foamed silicon carbide[75]. The fluoroboric acid system can be used for lead plating on carbon foam under certain conditions. As is shown in Fig.5, the carbon foam is completely covered by the lead plating layer outside and inside.

(a) Lead-plated bipolar grid

(b) Lead-tin plated bipolar grid

**Fig. 4 Capacity decay curve of bipolar lead-acid battery[67]**

Fig. 5 Microscopic morphology of electrodeposited nano-lead-carbon foam

Assemble LABs with lead-plated carbon foam and test the charge and discharge performance. As is shown in Fig.6, the battery has stable charge and

discharge capacity and cycle performance. The highest current efficiency is 65.7%, and the
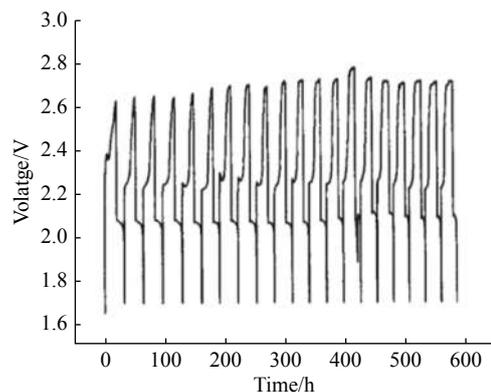
Fig. 6 Charge-discharge curve of lead-carbon foam cathode current collector lead-acid battery[76]

corresponding cathode active material utilization rate is 59% (Generally, only 48%-52% for LABs). Nano lead-carbon foam can be used as the positive current collector of LABs, and its performance is better than traditional lead grids, which can be used as a better lightweight grid material[76].

3　Conclusion

Light metals coated with lead or lead-tin alloy have good corrosion resistance applying in LABs, increasing the specific energy. For lead-tin alloy coating, the acid resistance of the coating will be improved with the increase of tin proportion, while the hydrogen evolution overpotential will be decreased under the higher proportion, causing water loss. The most suitable content of tin in coating is about 1%-2% applying in LABs.

As for the above plating systems, in the fluoroboric acid system, some components are highly toxic and the fluoride in the waste liquid is difficult to meet the national standards by treating. Generating lead sulfate precipitation in Sulfamic acid system easily will change the stability of the plating solution and the quality of the coating. The lead content of the coating in the citric acid system will be reduced with increase of current density. Due to using some of toxic additives in methane sulfonic acid solution, it can be optimized by improving the performance of additives. The overall performance of the methane sulfonic acid system is better than that of the other three, but the complete replacement of others still requires the significant lowering of the cost.

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（编辑　陈　红）

镀铅工艺及其在轻量化铅酸电池中的应用

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摘　要：铅酸电池"轻量高能"要求发展表面镀铅的轻质金属代替铅板栅。轻金属表面镀铅/锡工艺可以采用氟硼酸、氨基磺酸、柠檬酸和甲基磺酸体系镀液。氟硼酸体系中残液中的氟化物难以处理到符合国家规定标准；氨基磺酸易生成硫酸铅沉淀，影响镀液稳定性及镀层质量；柠檬酸体系镀液在高电流密度下对镀层铅含量的影响大；甲基磺酸体系能在高电流密度下工作，废水处理可靠。在轻金属铜、钛基体以及炭泡沫上电镀铅或铅锡合金，得到的轻型镀铅板栅材料在铅酸电池中轻量高能技术发展中具有重要地位。

关键词：铅酸电池；轻量化；镀铅工艺；铅锡合金

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