The performance of Pb-Cu binary alloys used in lead-acid batteries

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Abstract. In this paper, a series of Pb-Cu binary alloys with different copper content are synthesized and the electrochemical performance is investigated by electrochemical working station. Results show that the introduction of Cu to the pure lead alloy can reduce the hydrogen evolution potential, and the addition of Cu is beneficial for the formation of Pb (IV) oxide, which can increase the overall conductivity of the plate. Besides, the corrosion property testing also shows that the Pb-Cu alloys possess good anti-corrosion properties compared with pure lead.

Keywords: hydrogen evolution performance, alloy, lead-acid battery

1. Introduction

Nowadays, the lead-acid batteries is still the main batteries used in the electric bicycle in the market, especially the valve regulated lead-acid batteries (VRLA). Lead alloy is the important part for the lead acid batteries, while it determined most of the performance relating to the anti-corrosion, gas evolution potential, cycling performance, etc. The current used lead-alloys for VRLA are mainly low Sb-Pb alloy and Pb-Ca alloy, while the Pb-Sb alloy cannot satisfy the maintenance-free demand of the lead acid batteries, and the Pb-Ca alloy is extensively used. At the same time, in order to overcome the loss of the calcium during the producing process, some factories often add some elements such as Sn and Al. However, Al is easily precipitated in the grain, which lead a poor cohesive properties between the positive plate and the active material, leading to the poor anti-corrosion properties of the battery.

The cupper is very hard, tough, wear-tolerance, both the heat-conducting property and the electrical conductivity are all very well. So in this investigation, the element of the Cu is used as the additive and the performance of the Pb-Cu binary alloys is investigated.

2. Experimental Section

2.1 Sample preparation

The pure Pb was placed in a vertical heating furnace in which the temperature was kept at 450°C, then adding the Cu to the molten lead under continuous stirring. The added amount of Cu of different samples were listed in Table 1. The mixture was stirred for several hours and then quickly poured into two moulds, one cylindrical mould was 8.0mm in diameter and 16.0mm in length, and the dimension of the other square mould is 20mm×20mm×2mm.

2.2 Sample characterization

A three-electrode cell was used to test the electrochemical performance, while the Hg/Hg_2SO_4 electrode was used as the reference electrode and high-area platinum sheet was used as the counter electrode. For making the working electrode, the as-prepared cylindrical alloys were welded to the copper wire, then wrapped with epoxy resin to prevent any touch with electrolyte solution, leaving only one end exposed. Before the electrochemical testing, the working electrode was mechanically polished and washed with ethyl alcohol and distilled water several times. The simulated cell was added in a certain 1.28g cm^{-3} H_2SO_4 solution.

For evaluate the electrochemical performance of the samples, linear scanning voltammetry (LSV), electrochemical impedance spectroscopy and corrosion test were employed by using a CHI660D electrochemical workstation (Shanghai CH Instrument Company), Autolab electrochemical working station(ECOEchemie, B.V., Holland) as well as Hyelec DC power supply (Hangzhou haiyi company, China). All the test above-mentioned were performed at Room Temperature.

The corrosion tests were conducted in 1.28g cm^{-3} H_2SO_4 solution, while the Pb-Cu electrodes were used as the postive electrode and the pure Pb as the negative electrode, respectively. After charged with 100mA constant current for 30 days, the simulated cells were dismissed, washed, dried and ovserved by Scanning electron microscopy (SEM).

Table 1 element proportion in the alloys

Numble	Pb	Cu
1#	1	0
2#	1	6ppm
3#	1	16ppm
4#	1	58ppm
5#	1	110ppm
6#	1	570ppm

3. Results and Discussion

3.1 Hardness of the Pb-Cu alloys

Fig.1 shows the hardness of the Pb-Cu binary alloys, it can be seen that the hardness of each alloy increase as the copper amount increase in the alloy, indicating that the addition of Cu can increase the hardness of pure lead, which is beneficial for the processing forming in the alloy fabrication process.

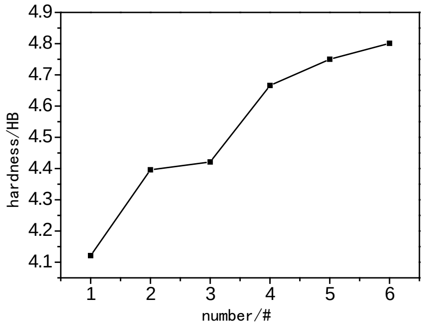

Fig.1 Hardness of the alloys after casted for 10 days

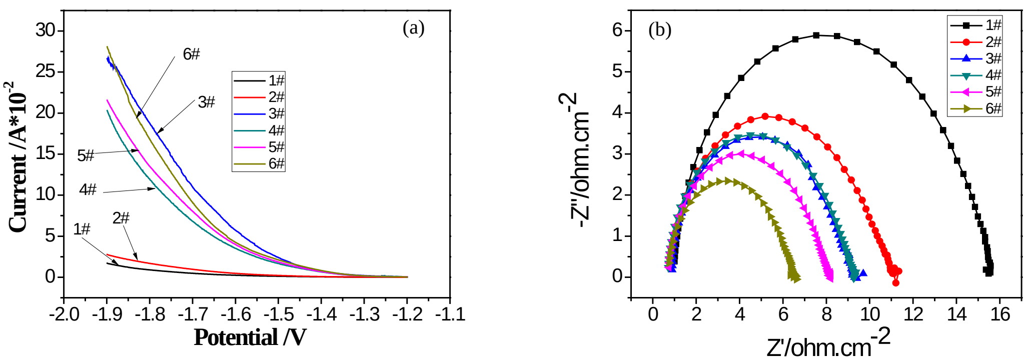

Fig.2 (a) Linear sweep voltammograms obtained on different electrodes with a cathodic potential range of -1.2 to -1.9V in 1.28 g·cm^{-3} H_2SO_4 solution; (b) The Nyquist plot obtained for Pb-Cu electrodes at a potential of -1.75V in 1.28 g·cm^{-3} H_2SO_4 solution, following oxidization at-1.75V for 1h.

3.2 Hydrogen evolution performance

Fig.2(a) and 2(b) show the hydrogen evolution performance by linear sweep voltammogram as well as by electrochemical impedance spectroscopy (EIS), respectively. As shown in Fig.2(a), it's clearly that the pure lead process the highest hydrogen evolution over-potential. Fig.2(b) shows the EIS results which were performed at a constant potential of -1.75V, the impedance diagram shows a single semicircle at high frequency, indicating the hydrogen evolution is controlled by a single charge transfer process. The diameter of the semicircle indicates the resistance of the hydrogen evolution reaction, while the pure lead exhibits the highest hydrogen evolution reaction resistance, indicating the pure lead possess the highest hydrogen evolution over-potential, this result is accordance with that from Fig.2(a)

3.3 Impacts of the Cu additve to the growth of PbO_2

Fig.3 shows the change of the open circuit potential of Pb-Cu binary alloy after oxidating at 1.3V for 1h in 1.28g cm^{-3} H_2SO_4 with time. Since 1.3V is the formation potential of PbO_2, the plat (EF) formed at around 1.12V is corresponding to the amount of the PbO_2. The different length of the platforms relfect the amount formed on the alloys at 1.3V. It can be seen that there's a optimun addtion amount of Cu, under which the formation of PbO_2 is the maximum. Since PbO_2 possess excellent electrical conductivity, it can be obtained that the Cu added with a optimum amount can improve the conductivity of the discharge plate, which is beneficial for increasing the charge acceptance of the battery.

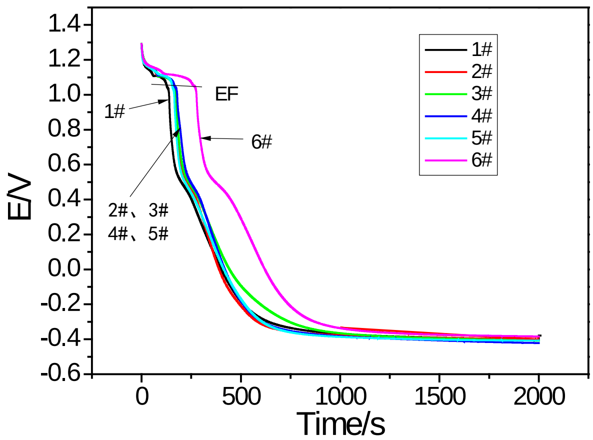

Fig.3 The open circuit decay curves for the self-discharge of Pb–Cu electrodes after 1 hour charging at 1.3V in 1.28g·$cm^{-3}$$H_2SO_4$ solution.

3.4 Impacts of the Cu additve to the corrosion layers

To furrther investigate the effect of Cu additive to the lead alloys, we performed corrosion tests on the square lead alloys. The testing procedure was presented in the experimental part. It can be seen from the SEM images of the corroded alloys in Fig.4, the corrosion products are very different in shape. With the addition of Cu to the alloys, some noodle-like products emerged in the corrosion products. Which may increase the contact degree and increase the strength of the corrosion product, making the contact between the corrosion products and the alloys better, thus increasing the cycling performance of the battery.

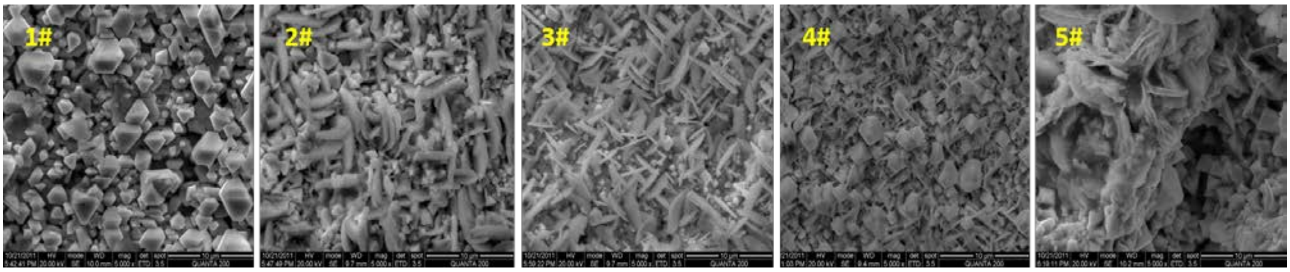

Fig.4 Morphology of corrosion layers on the surface of different Pb-Cu alloys

4. Summary

The performance of the Pb-Cu binary alloys was investigated in this paper. Results show that the addition of Cu to the pure Pb can increase the hardness of the alloy, reduce the hydrogen evolution over-potential and increase the conductivity of the corrosion film. Corrosion test shows that the addition of Cu can increase the anti-corrosion properties of the pure lead.

5. References

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