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Short Communication

Experiment Study on Effect of Different Parameters Pulses on the Battery Plate Sulfuration

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Sulfuration of lead-acid battery negative plates is main fault which cause batteries failure. For this failure mechanism, pulse maintenance method is given. But experiment study on effect of pulses on the battery plate sulfuration is lack. In this paper, the effect of pulses on the battery plate sulfuration is found by using adjustable pulse parameter maintenance devices designed independently and some test means and methods. At last, the effect can provide bases to define parameters of battery maintenance devices.

Keywords: lead-acid battery; Sulfuration; pulse maintenance; experiment study

1. INTRODUCTION

Lead-acid batteries have developed for about a hundred years and become the most widely used chemical energy in world. Although lead-acid batteries are interior to new batteries in specific capacity and specific power, but they have several advantages such as good reversibility, safety, low cost, long life and other characteristics and are still going on technological innovation and development[1]. One of the lead-acid battery technology development trend is to extend the service life. To extend the service life there are online maintenance technology and sulfidation repair technology[2-3]. And these two technologies are based on the pulse method[4]. In this article, effect of different parameters pulses on the battery plate sulfuration is researched through experiment.

2. THE SULFIDATION FAILURE MECHANISM OF LEAD-ACID BATTERY PLATE AND PULSE REPAIR TECHNOLOGY

The following reactions of lead-acid battery occur during charge and discharge courses:

Positive plate: $PbO_2 + 3H^+ + HSO_4^- + 2e \underset{charge}{\overset{discharge}{\rightleftharpoons}} PbSO_4 + 2H_2O$ (1)

Negative plate: $Pb + HSO_4^- \underset{charge}{\overset{discharge}{\rightleftharpoons}} PbSO_4 + H^+ + 2e$ (2)

From reaction (1) and (2), during the battery discharging the active substance is converted to lead sulfate by chemical reaction. The lead sulfate shows loose sponge-like texture in microcosmic, and the plate is in a high potential state. If lead-acid batteries are not charged in time and place too long in the state of power loss, the lead sulfate on the plates will shift from unstable state of high potential to stable state of low potential. And the polycrystal tends to decrease the surface free energy. So the porous lead sulfate crystals in the dual role gradually transformed into sulfide layer composed by coarse lead sulfate crystals. The large crystals have more solubility than small crystals, resulting in failure of the active material on the plates. Since the oxygen atom of the positive plate produced in the charging process has strong oxidation ability, lead sulfate is oxidized to the original active substance. So the sulfuration occurs only on negative plate[5].

3. THE DESIGN OF PULSE MAINTENANCE DEVICE

Battery maintenance device hardware system consists of a pulse DC/DC module, detection module, signal indication module, controller module, boost module and MOS transistor module, as shown in Fig 1.The workflow of the device is shown in Fig 2[6-7].

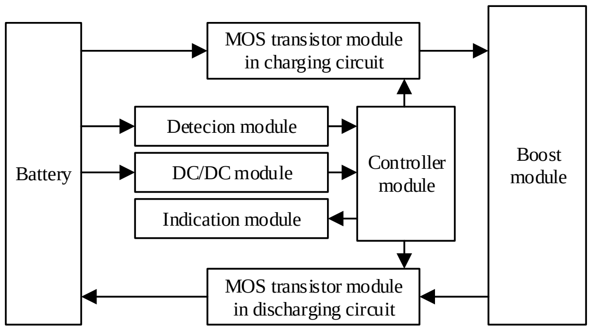


Figure 1. Pulse maintenance device hardware system chart

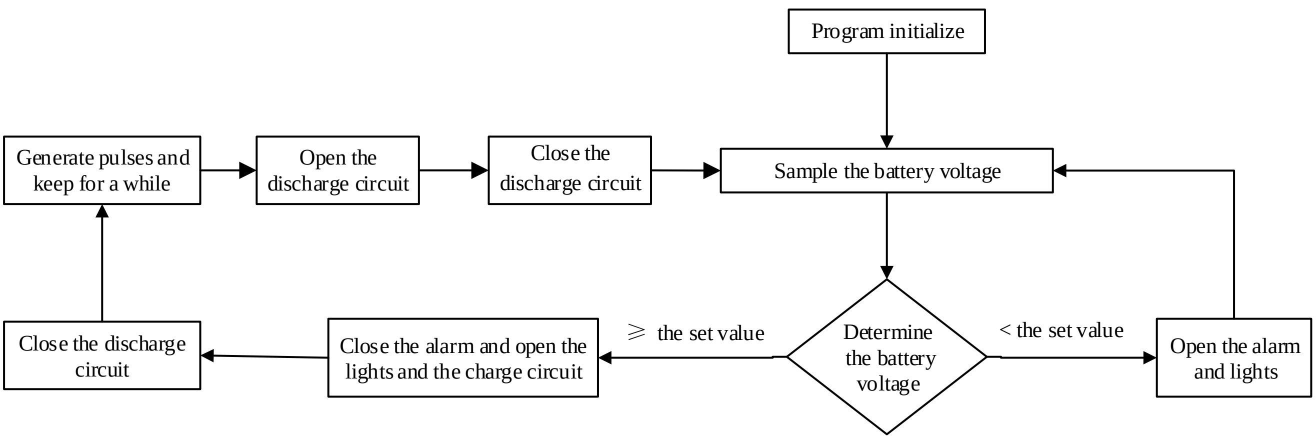


Figure 2. Pulse maintenance device workflow chart

The pulse maintenance device uses battery as energy. Workflow is as follows, firstly the battery voltage is sampled and determined, when the voltage is normal, it is boosted by the boost module, then charge the capacitor, after waiting some time, the energy flows through the discharge circuit to the battery. This is a complete process. The controller module control MOS transistors in the charging and discharging circuit to adjust the frequency of the pulse. And the amplitude of the pulse is adjusted by changing the feedback resistance of the boost module. When the battery voltage is too low, the battery power is low and the device can produce sound and light alarm, prompting operators to charge the battery in time.

4. EXPERIMENT METHOD

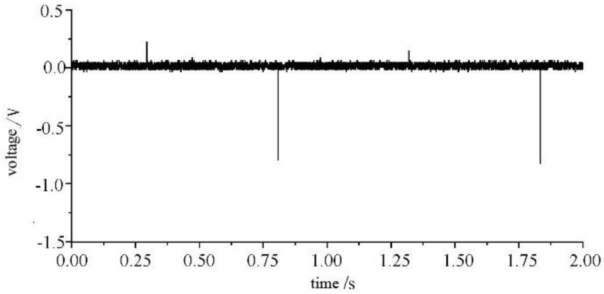
In order to explore effect of different parameters pulses on the battery plate sulfuration, we need maintenance devices with different parameters to experiment. Different frequencies and amplitudes pulse can be get through adjusting the feedback resistor and control program. A kind of 12V30Ah battery was studied in the experiment. When the voltage is boosted too large the power consumption of the device itself will increase and affect the battery performance. So the boosted voltage is not too large.

During the experiment several devices with different combinations of the pulse amplitude and pulse frequency were tested. When the parameters are very close the results are very close too and are not easy to distinguish. Therefore, some devices with results of the relatively large difference were chosen to study. Their parameters are shown in Table 1.

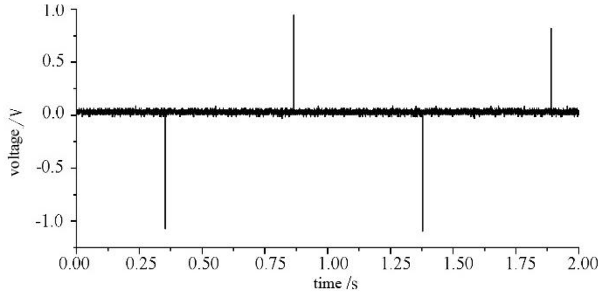
Table 1. Maintenance pulse parameters

Frequency (Hz)	Boost voltage (V)	Battery voltage (mV)		Current of the device (A)	
		Up	Down	Charge	Discharge
1	14	250	750	10	2.5
1	25	900	1100	15	7
1000	14	250	250	2.5	2.5
1000	25	900	700	9	6

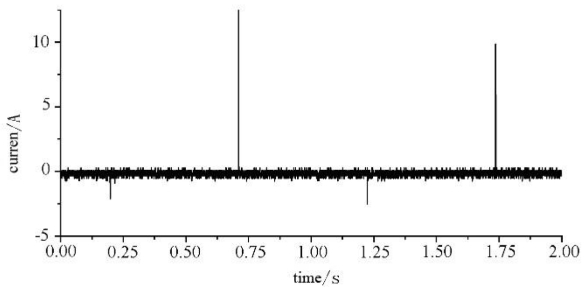
Table 1 indicates that when the boosted voltage is 14V and 25V at 1Hz and 1000Hz pulse, in fact the battery voltage rises 250mV, 900mV at both 1Hz and 1000Hz and drop 750mV, 1100mV at 1Hz pulse and 250mV, 700mV at 1000Hz. This is due to the internal resistance of the battery is lower than the MOS transistor drain-to-source on-resistance. The higher boosted voltage, the more power consumption of the MOS trasnsistors. The voltage drop is caused by the discharge of the battery. The charge and discharge current flow between the device and the battery when the device generate pulses. Actual voltage and current waveforms are shown in Fig 3 and Fig 4.



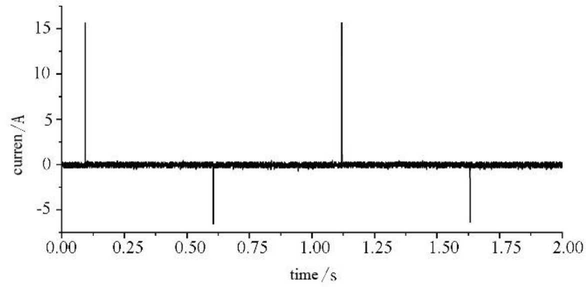
Voltage waveform of 14V boosted voltage at 1Hz



Voltage waveform of 25V boosted voltage at 1Hz

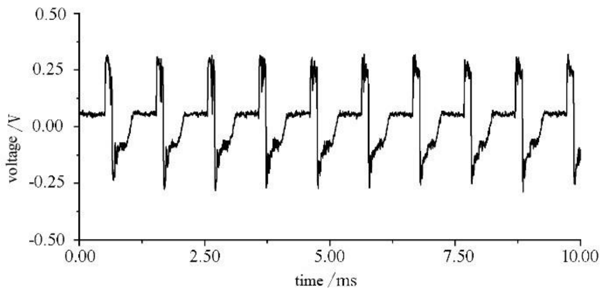


Current waveform of 14V boosted voltage at 1Hz

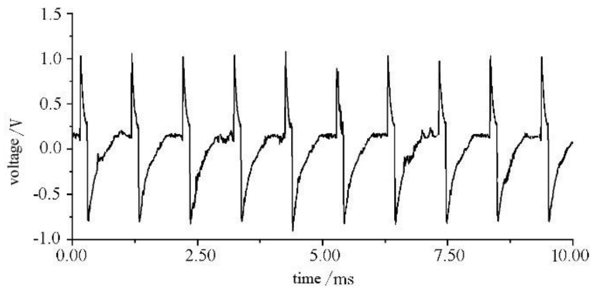


Current waveform of 25V boosted voltage at 1Hz

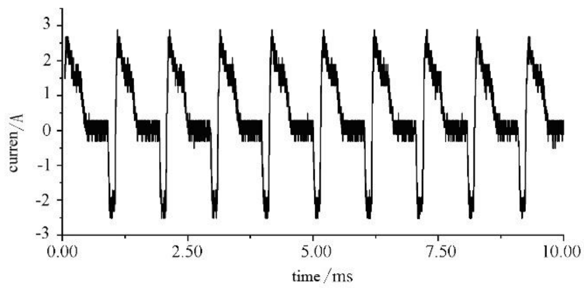
Figure 3. Voltage and current waveforms of 14V and 25V boosted voltage at 1Hz



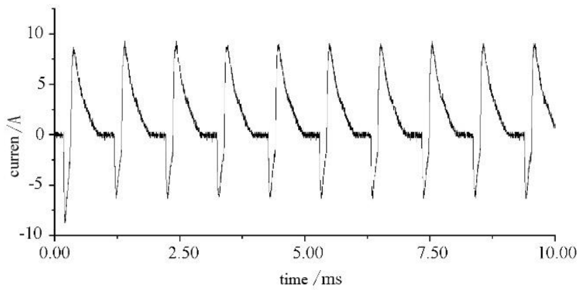
Voltage waveform of 14V boosted voltage at 1000Hz



Voltage waveform of 25V boosted voltage at 1000Hz



Current waveform of 14V boosted voltage at 1000Hz



Current waveform of 25V boosted voltage at 1000Hz

Figure 4. Voltage and current waveforms of 14V and 25V boosted voltage at 1Hz

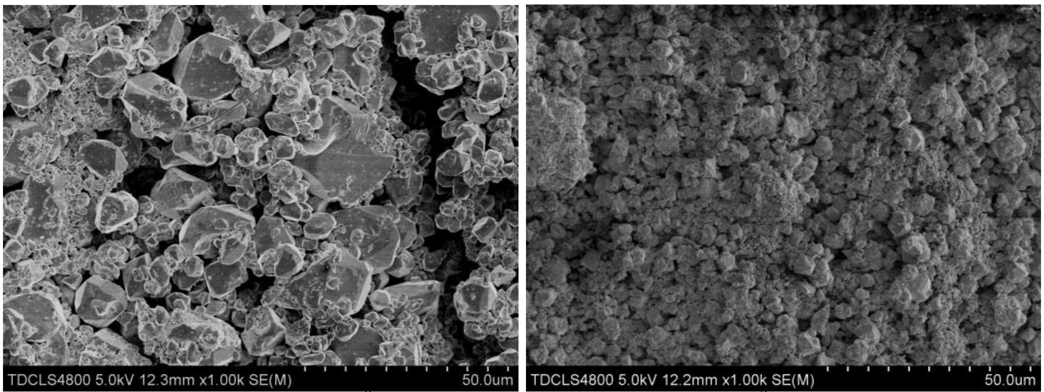
When the boost voltage is constant, as the pulse frequency increases from 1Hz to 1000Hz, the pulse amplitude decreases gradually, while the charge and discharge current of the device reduces. This is because as the pulse frequency increases, the period of charging and discharging is shorten. But the switching frequency of the boost circuit is constant, thus the number of switches in each cycle is reduced. Thereby the boost voltage and current is reduced gradually.

As the active substance in the plate of the new battery is not recrystallized in initial phase, the sulfuration occurs by the crystals accumulating gradually. So the test cycle of inspecting maintenance of the device is very long. To solve this problem, according to the law of temperature change will accelerate the process of crystallization, a method of the environment temperature alternating is proposed to shorten the test cycle. Multiple comparison tests conducted under the same conditions to eliminate the influence of environmental change on the active substance crystallization. Batteries connected the maintenance were placed in 40 ^{0}C and -20 ^{0}C environment for 90 days with three days of a cycle. After 90 days, the active substance on the plate was sampled and researched.

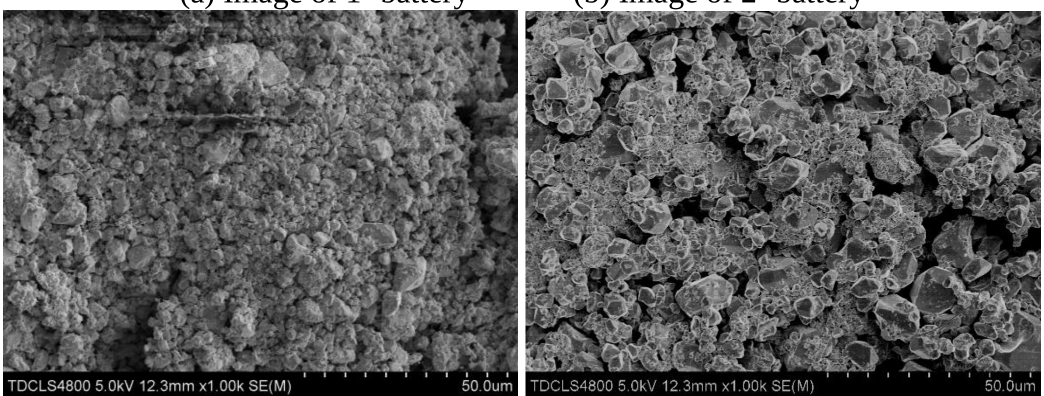
The size magnitude of the lead sulfate crystals is 10^{-6} meters and the electron microscope can be used to observe crystal size and determine effect of different parameters pulses on the battery plate sulfuration[8]. In experiments, the scanning electron microscopy TDCLS4800 is used to observe crystals.

5. RESULTS AND ANALYSIS

After 90 days, the active substance samples in the same position of the battery plates were taken and observed using the SEM. Fig 5 and Fig 6 show the images of the samples from $1^{\#}$ to $4^{\#}$ battery in the 1000 magnification and 5000 magnification.

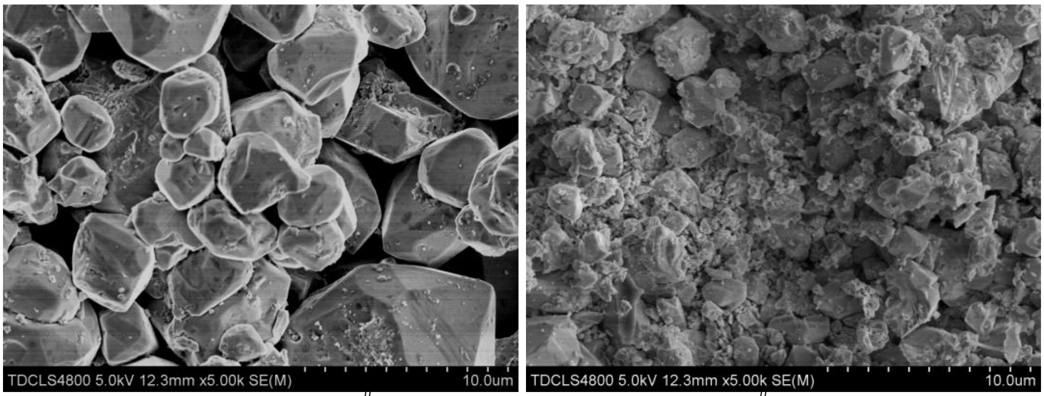


(a) Image of $1^{\#}$ battery (b) Image of $2^{\#}$ battery

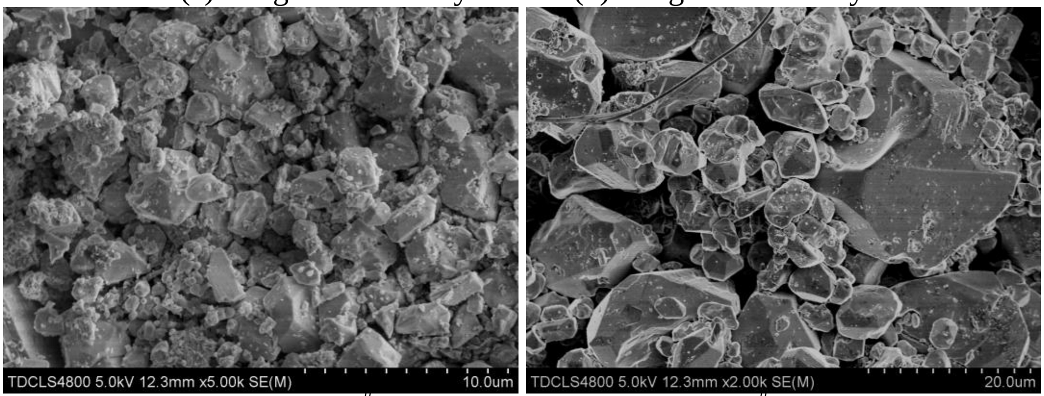


(c) Image of $3^{\#}$ battery (d) Image of $4^{\#}$ battery

Figure 5. Images of batteries in 1000 magnification



(a) Image of $1^{\#}$ battery (b) Image of $2^{\#}$ battery



(c) Image of $3^{\#}$ battery (d) Image of $4^{\#}$ battery

Figure 6. Images of batteries in 1000 magnification

Parameters of the maintenance device used in $1^{\#}$ battery and $2^{\#}$ battery are 14V boost voltage, 1Hz and 14V boost voltage, 1000Hz. As can be seen from Fig 5(a), Fig 6(a) and Fig 5(b), Fig 6(b) the active substance in the plate of $1^{\#}$ battery crystallized very seriously. But the active substance in the plate of $2^{\#}$ battery crystallized individually. Parameters of the maintenance device used in $3^{\#}$ battery are 25V boost voltage and 1000Hz. As can be seen from Fig 5(b), Fig 6(b) and Fig 5(c), Fig 6(c) crystals of $2^{\#}$ battery and $3^{\#}$ battery are very similar in size. Parameters of the maintenance device used in $4^{\#}$ battery are 25V boost voltage and 1Hz. As can be seen from Fig 5(a), Fig 6(a) and Fig 5(d), Fig 6(d) crystals of $1^{\#}$ battery are bigger than crystals of $4^{\#}$ battery. So $1^{\#}$ and $4^{\#}$ battery have sulfuration but the $1^{\#}$ is more serious.

From the above analysis, the amplitude and frequency of the pulse have a great impact on the maintenance effect. When the pulse amplitude is same and the pulse frequency is different, the higher the frequency, the better the maintenance effect. When the pulse amplitude and frequency is similar, the maintenance effect is similar. When the pulse frequency is same and the pulse amplitude is different, the higher the amplitude, the better the maintenance effect. But as the pulse amplitude increases, the average current of the circuit and the power consumption of the device increase. In this way, it does not meet low-power requirement. Therefore, the high frequency and low amplitude pulse should be used.

6. CONCLUSION

Experimental on effect of different parameters pulses on the battery plate sulfuration were carried out by using the maintenance device independently designed whose pulse amplitude and frequency can be changed by adjusting the circuit and program and SEM through the method of the environment temperature alternating. The main conclusions are as follows:

(1) The higher the pulse amplitude the better the maintenance effect and the greater the power consumption of the device. Hence the appropriate pulse amplitude is needed to minimize the performance impact on batteries.

(2) The higher the pulse frequency the better the maintenance effect. By the pulse frequency increasing the power consumption increasing is not obvious. However, the frequency of the circuit can be achieved is limited, excessive frequency will affect the stability of the circuit. Hence the appropriate frequency is needed.

(3) Through experiment research, the maintenance device should adopt a high frequency and low amplitude pulse. In this way, the device can maintain the battery and minimize the performance impact on the battery.

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