A new method for charging and repairing Lead-acid batteries

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Abstract. With the rapid development of China's electric vehicle industry, the demand for vehicle-mounted lead-acid batteries is increasing, and higher requirements are put forward for their safety and reliability. There are some problems in lead-acid batteries, such as short service life and decreasing capacity. In this paper, a new method of charging and repairing lead-acid batteries is proposed. Firstly, small pulse current is used to activate and protect the batteries in the initial stage; when the current approaches the optimal current curve, the phase constant current charging is used instead, when the voltage is low. When the value is in stable state, the polarization and vulcanization phenomena of batteries in the earlier stage can be eliminated by using the composite resonant pulse repair technology. When the vulcanization and polarization phenomena are eliminated successfully, the REFLEXYM charging method is carried out immediately to protect the batteries, and the batteries can be controlled by intermittent charging at this stage. The phenomenon of temperature rise is helpful to prolong the life of the battery. Finally, it enters the floating charging stage, providing a very small trickle current to compensate for the self-loss of the battery, so that the battery can remain fully charged.

1. Background and significance of the research

The State Environmental Protection Administration, Ministry of Science and Technology and other departments jointly issued the Technical Policy on Pollution Prevention and Control of Waste Batteries, which clearly elaborated how to deal with scrap lead-acid batteries, how to improve the reuse rate of waste battery resources, and encouraged the development of related technology research [1]. With the development of environment-friendly and energy-saving automobiles, electric vehicles and related industries are growing, and the demand for lead-acid batteries is also increasing. Therefore, the safety and reliability of lead-acid batteries are also put forward higher requirements [2].

2. Research status at home and abroad

In China, according to the charging and discharging characteristics of lead-acid batteries, southwest jiaotong university has designed a repair system to eliminate polarization and vulcanization of lead-acid batteries. East China university of science and technology mainly studies the electrochemical characteristics of lead in electrolyte, explores the relationship between lead electrode and the characteristics of lead-acid battery in electrochemical reaction, and uses chemical methods to eliminate the vulcanization of lead-acid battery [3].

Edwards University of the United States has solved the problem of delamination of sulfuric acid
electrolyte in lead-acid batteries and the loss of active substances on the plates. Catholic University of America uses microcontroller to output PWM signal to control switching circuit and generate positive and negative pulses to repair lead-acid batteries [3].

Battery repair technology is a hot topic in recent years. Major universities and enterprises are striving to find better repair methods, reducing the amount of battery waste. Reducing the waste of resources is an important manifestation of building an environmental friendly society. Therefore, the problem of battery repair has received more and more research.

3. Vulcanization and polarization characteristics of lead-acid batteries and related solutions

3.1 Vulcanization characteristics of batteries

3.1.1 Definition of battery vulcanization

It means that during the discharge process, PbSO₄ is reduced to active substances Pb and PbO₂. If the lead-acid battery cannot be used correctly, such as insufficient charging or over-discharging, the surface of the internal negative plate of the battery is attached with a layer of white hard crystal. After charging, it is still impossible to strip the lead sulfate converted to the active material on the surface of the negative electrode plate, which is sulfation [4]. A cross-sectional view of a lead-acid battery is shown in Figure 1.

Figure 1. Cross-sectional view of lead-acid battery

3.1.2 The main cause of battery vulcanization

1. long-term over discharge will accelerate the vulcanization of lead-acid battery [5].
2. Insufficient electrolyte makes the liquid level of the electrolyte inside the battery lower, resulting in a part of the plate exposed, unable to contact with the electrolyte, making this part of the plate directly in contact with air, resulting in the vulcanization of the plate [6].
3. The battery is not fully charged for the first time, which will lead to the deterioration of the active substance's participation in the chemical reaction, which will reduce the charge and discharge capacity of the lead-acid battery, and will also lead to vulcanization [7].

3.1.3 Solutions to vulcanization

High frequency pulse method; High frequency pulse current was used to charge the battery, and the repair rate was about 60%. But this method takes a long time to repair (it can take tens of hours or even a week), low efficiency, serious "vulcanized" battery repair effect is not good. The method is simple and many devices are based on it.

the composite high frequency pulse method. A complex high frequency positive and negative pulse occurs through a special circuit structure. The pulse current value is appropriately controlled to charge the positive electrode plate with a small current density, and substantially no damage to the positive electrode plate is formed. It has the advantages of rapidity, high repair efficiency, low power consumption, no water loss of the battery, softening of the positive electrode plate and changing the
original structure of the electrolyte. The experimental verification shows that the repair rate can reach
more than 90%. The application of this technology reduces the number of discarded batteries and has
good economic and environmental benefits. The compound high frequency pulse method is adopted to
solve the problem of vulcanization.

3.2 Polarization characteristics of the battery

3.2.1 Definition of battery polarization
When the battery starts charging or discharging, there will be current passing through the battery. After
a period of time, the electromotive force of the battery will deviate from the original equilibrium value,
which will deviate from the original equilibrium electromotive force.[8].

3.2.2 Three common polarization phenomena
Ohmic polarization (U_o): It is caused by the resistance of each connected part of the battery. During the
charging process, the positive and negative ions in the electrolyte move to the two poles. During the
whole process, the conductive parts inside the battery (including the partition) are received. The
resistance generated by the electrolyte, etc., is called the ohmic internal resistance; this part of the
internal resistance is a fixed value and remains unchanged to some extent. In order to ensure the smooth
running of the charge, the additional charging voltage needs to be separated to overcome this resistance
to push the ions to move. This causes dispersion of the voltage, which is ohmic polarization. Ohmic
polarization follows Ohm's law, and as the charging current increases, the ohmic polarization increases;
and the temperature of the lead-acid battery rises [9]. When the charging current is zero, the ohmic
polarization will disappear, which provides a theoretical basis for setting the stop time during the
charging process.

Electrochemical polarization: It is caused by the retardation of electrochemical reaction on the
surface of the electrode. Lead ion in electrolyte needs to get or lose electrons for reductive oxidation
reaction. Usually, the speed of electron transmission is close to the speed of light, which is faster than
the electrochemical reaction in the electrolyte. Therefore, compared with the previous electrochemical
reaction, the electrons near the cathode will accumulate because the electrons can not react in time, and
the corresponding anode will have less electrons. The excess electrons near the cathode plate will cause
lead ions to be reduced at a faster rate, and the reduction of electrons on the anode will cause lead ions
to lose electrons at a faster rate and be oxidized, finally reaching a dynamic equilibrium. At the initial
stage of charging, the polarization phenomenon is weak. With the reaction proceeding and the charging
current increasing, the polarization will be enhanced. Polarization not only hinders the charging process,
but also reduces the acceptance of charging current for lead-acid batteries. The final result is that some
unreactable charges are used to electrolyze water, and the amount of gas evolution will increase. The
increase of the amount of gas evolution will cause the active substances on the plate to fall off and affect
the capacity and life of the battery.

Concentration difference polarization: is the formation and reaction of the material diffusion speed
is far less than the speed of chemical reaction, finally caused the electrolyte concentration near the plate
changes, electrolyte concentration distribution uneven phenomenon is called concentration difference
polarization. After the charging stops, the concentration of ions will eventually become even due to the
diffusion movement, and the concentration difference will gradually disappear. Because the diffusion
movement speed is relatively slow, the concentration difference polarization will not disappear
immediately [11].

3.2.3 Adverse effects of battery polarization on battery charging
(1) the battery is over potential and too much over potential, which will hinder the increase of charging
current, slow down the battery chemical reaction speed and reduce the efficiency of charging.

(2) In advance of electrolyzed water, a large amount of gas will be generated. The precipitation of
these gases will have a certain corrosive effect on the electrode plate. At the same time, the electrolyzed
water will generate a large amount of heat, so that the temperature of the electrolyte will continuously rise, and eventually the electrode plate will be heated. Deformation, causing the active material to fall off, resulting in battery failure.

(3) Polarization will cause waste of energy and reduce the efficiency of charging.

3.2.4 Solutions
The inevitable phenomenon of polarization occurs during the charging process. Adding a stop time or a negative pulse during the charging process is beneficial to reduce or eliminate the polarization. At the same time, there is a certain limit to the depolarization process. Don't waste time on depolarization. After achieving a certain degree of effect, you should immediately transfer to the normal charging process.

4. A new charge repair method for lead-acid battery

4.1 An understanding of J.A.Mas ’ law
In 1972, J. A. Mas, an American scientist, developed the famous three laws of charging. By controlling the gas evolution and temperature rise of batteries during charging, the optimal charging curve of a given current can be obtained, as shown in Figure 2.

![Optimal Charging Curve of Battery](image)

Figure 2. Optimal charging curve of the battery

The charging repair should conform to the three laws of mas charging, which means that the charging acceptance rate of the battery is inversely proportional to the square root of the discharge capacity of the battery, which is directly proportional to the logarithm of the discharge current. In the process of charging, a small amount of reverse pulse is given to discharge the battery, which can effectively improve the charging acceptability of the battery.

The formula of the optimum charging curve of the battery is as follows:

\[ I = I_0 e^{-\alpha t} \]

\( I_0 \) is the initial maximum charging current; \( \alpha \) is the reception rate of charging;

4.2 Establishment of a new method
Firstly, the traditional charging methods are studied. Through experiments, the methods of overcurrent charging, constant voltage charging, stage charging, pulse charging and intermittent charging are verified. Only when different charging methods are applied in different charging periods can this method achieve the maximum and optimal effect and finally realize the quick and friendly charging of the battery. A new method for charging and repairing lead-acid batteries is proposed.

4.2.1 Slow charging of small pulse current
The battery is charged with a small pulse current. A constant positive pulse small current is used to preliminarily charge the battery. Its function is to activate the electrolyte and the active substances in the
electrolyte and make it enter the chemical reaction state as soon as possible. Secondly, the temperature of the battery is controlled by pulse, so as to prevent the temperature of the battery from rising rapidly in the initial stage of charging, and to alleviate the polarization phenomenon and ensure the initial safety problems. Curve of slow charging of small pulse current, as shown in figure 3. After a period of time, when the actual size of the current catches up with the optimal charging curve of the battery, the next stage is entered.

\[
\begin{array}{c}
\text{Cycle} \\
\text{Time/(min)}
\end{array}
\]

\[
\begin{array}{c}
\text{Current} \\
\text{Charge Time}
\end{array}
\]

Figure 3. slow charging of small pulse current

4.2.2 Piecewise constant current charging
The batteries are charged rapidly by using sectional constant current charging and sectional high current. At this time, the high current will cause negative resistance breakdown dissolution of lead sulfate crystals. Sectional constant current charging divides the charging process into several constant current charging stages, and the current decreases step by step. This charging method was proposed by Tomohiko [12]. The charging process can be divided into charging stages according to time, battery voltage and battery capacity. Step-by-step adjustment of the charging current is affected by the type of battery and the ambient temperature. The state of charge cannot be accurately controlled. The charging current is adjusted according to the change of the battery voltage. The control method is simple, so that the active material can be better chemically reacted [13]. The piecewise constant current charging curve is shown in Figure 4. This stage plays an important role in the charging process of the lead-acid battery. However, at this stage, gas evolution also occurred, and it was only a temporary effect for eliminating vulcanization, and it was accompanied by an increase in polarization. Wait until this stage to achieve a relatively stable battery voltage, the next stage of battery repair.

In the literature [14], professor Ma Youliang used the capacity gradient method to conduct multi-stage constant current charging, and proved that this kind of charging current is close to the optimal charging curve, which can shorten the charging time, improve the charging efficiency and extend the battery life.

\[
\begin{array}{c}
\text{Charging rate/C} \\
\text{Charging current /A} \\
\text{Time t/s}
\end{array}
\]

\[
\begin{array}{c}
\text{Voltage curve of battery} \\
\text{Charging current curve}
\end{array}
\]

Figure 4. Segmented constant current charging

4.2.3 Compound resonant pulse repair technology
The composite resonant pulse repair technology can alleviate the gas precipitation and polarization and
vulcanization of the battery. In this stage, pulse charging is adopted, and the charging time is intermittent, which controls the temperature rise of the battery reaction. Reduce gas precipitation. Moreover, the high order harmonics in the pulse are used to resonate with the large lead sulfate crystal to eliminate the sulfurization of the battery in the repair process.

4.2.4 REFLEXYM charging method
The next stage is the REFLEXYM charging method [15], which includes three stages: forward pulse charging, reverse pulse discharging and stop charging. The main working process is in the charging process of the lead-acid battery. When the electrochemical reaction of the lead-acid battery reaches the gas-discharging voltage of the lead-acid battery during the charging process, it enters the discharge phase; the discharge phase causes the oxygen generated during the gassing and The hydrogen recombination is consumed; then the charging is stopped, and the charging, the instantaneous discharging, and the stopping charging process are alternately performed in sequence. The curve of the REFLEXYM charging method is shown in Figure 5. The stopping process slows down the cumulative effect of the battery polarization effect, and the electrochemical reaction can proceed smoothly. Therefore, the pulse charging method enables the battery to be charged quickly with a large current in the later stage of charging, thereby improving the charging efficiency, and intermittent charging can control the temperature rise of the battery. This is helpful for extending battery life.

![Figure 5. REFLEXYM charging](image)

4.2.5 Floating charge
The last stage adopts floating charging [16]. In the floating charge stage, the charger provides a small trickle current to compensate the self-loss of the battery, so that the battery is kept at full charge but not charged. The purpose is to supplement the capacity loss caused by the self-discharge of the battery and keep the sufficient power. Inhibit vitrification caused by recrystallization of active substances; Keep the battery voltage in the range of floating charge voltage, so that the plate corrosion in the slowest state.

5. Conclusion
After a great deal of experiments, the new charging method not only greatly reduced the required charging time, and can reduce or even eliminate the polarization in the process of charging and sulfide phenomenon, reducing the analysis of the gas volume in the process of charging, better to control temperature, increasing the rate of lead-acid battery current acceptable to improve the quality and performance of the lead-acid battery charging. The new charging system can repair the lead-acid batteries and prolong the deep cycle life of lead-acid batteries.

The new charging and repairing method is proposed to repair the polarization and vulcanization of the lead-acid battery during the charging process, control the temperature of the battery, and extend the service life of the battery without changing the material and its own structure.

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