

Nobel High Current Pulse Charging Method for Prolongation of Lead-acid Batteries

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Abstract

A new method for prolonging the life of lead-acid batteries was invented devised by charging the batteries with a high current pulse of a particular pulse width special wavelength. The effectiveness of the new method was verified by prototyping a prototype circuit and conducting charging-discharging cycle tests in a laboratory. The device was named the "High current pulse activator". Moreover, it was experimentally proven that this device was even more effective when used with batteries filled with a polymer additive supplied by ITE.

Keywords

high current pulse, charging-discharging, lead-acid battery, polymer activator, PbO_2 , $PbSO_4$

1. INTRODUCTION

Mass-production and mass-consumption have progressed in recent years alongside worldwide industrialization, most notably in the already industrially advanced nations. This has spurred a sharp increase in hazardous substances that have adverse affects on the environment and people, and have consequently degraded the environment. One of these hazardous substances is lead. Lead diffuses into the environment via illegal dumping of batteries used in automobiles and forklifts. If the lead from these batteries infiltrates the human body, the lead concentration in the blood rises, possibly resulting in neurological disorders including loss of perception and behavioral problems. In children, it can stunt growth, cause brain damage and mental retardation.

Currently, in Japan, there are about 70 million vehicles registered between an approximate 50 million passenger cars and an approximate 20 million commercial vehicles. Though depending on the conditions of use, currently used automobile batteries deteriorate in 2 to 3 years and are subsequently disposed of. If one in every five batteries is replaced in a year, it adds up to 15 million batteries a year. In other words, 15 million batteries (120,000 ton) are discarded every year in Japan alone. However, the manufacturers recycle only one-third of that amount. Another one-third is waiting to be disposed of. In addition, the remaining one-third is illegally dumped in wooded areas, rivers and other places, which is causing serious environmental pollution. China and other Asian nations that are rapidly motorizing are late

in establishing recycle laws, prompting concern that the processing of spent batteries may become a big issue in the future. A major reason for the increase in spent batteries is the short life of lead-acid batteries.

Moreover, the large batteries used with electric forklifts are very expensive, costing between ¥400,000 and ¥1.5 million, hence they must be ordered. Preventing deterioration of this type of battery and prolonging its life to that or more of an automobile battery would have a high economical effect.

In this study, it was thought possible to prolong battery life by charging the battery with a pulse current to activate the electrodes. This type of pulse activator has been made and sold for some time, but it applies a low current to the battery. It is difficult to say that its effectiveness has been sufficiently proven [Law, 1995]. Nevertheless, a method for prolonging the life of a battery that was charged with a high current pulse while keeping both the charging current duty cycle and average charging current low was developed [Minami et al., 2004]. With the method described in this paper, sulfation does not occur in the battery electrodes and particularly the negative electrode because the battery is charged and discharged with a high current pulse superimposed to the DC charge and discharge currents. Whereas earlier activators used a 1 μ s pulse width and approximate 100mA current, this method flows approximately 30A to a battery of 30AH capacity at 100 μ s to prevent sulfation.

Moreover, it has been shown in recent years that the ITE polymer activator is effective towards prolonging the life of lead-acid batteries [Kozawa et al., 2002; Kozawa et al., 2003]. The compounded effect of combining these two methods was also experimentally

proven.

2. THEORY OF LEAD STORAGE BATTERY ACTIVATION

Lead storage batteries are typical rechargeable batteries and the most widely used batteries for automobiles today. They use a Pb (lead) anode, PbO₂ (lead dioxide) cathode, H₂SO₄ electrolyte of a 1.2 specific gravity, and a separator between the electrodes.

The lead dioxide (PbO₂) - the active material of the positive electrode - is an n-type semiconductor and has both the α and β crystal form. When a solution of low specific gravity is used with α-PbO₂, often a thick plate is used, but the content is less than 50%. When a solution of high specific gravity is obtained by oxidizing lead sulfate and used with β-PbO₂, the plate is often thin. An electrode plate of the high α-PbO₂ content tends to last longer, while a plate of high β-PbO₂ content tends to be high capacity. Under charging and discharging, the α-PbO₂ decreased and turns into β-PbO₂.

The active material of the positive electrode is made of minute grains of small pore size and has a specific surface area of 5-10m²/g. In the charge-discharge cycling, it transforms into a coral-like structure with the specific surface area decreasing to 2-5m²/g. The active material of a large pore size has a high coefficient of use and large capacity, but cycle life tends to be short.

The active material of the negative electrode uses spongy lead of a specific surface area of 0.4-0.8m²/g, which is about one-tenth that of the active material of the positive electrode. Accordingly, both grain size and pore size are considerably larger than with the negative electrode and, in charge-discharge cycling as in the case of a storage cell, the specific surface area decreases to 0.2-0.4m²/g and discharge performance declines.

The active material of the negative electrode contains lignin, barium sulfate and carbon powder. Generally, lignin is extracted from waste pulp because of its characteristics as an ion exchange resin and wetting agent, but it decomposes and gradually disintegrates as the storage cell is used. The lignin then adheres to the surface of the active material of the positive electrode whereby reducing the surface area and preventing shrinking (contraction that occurs because of the lost surface area). Furthermore, it is believed to temporarily trap Pb²⁺ ions during charging and discharging, and thus improves quick discharge performance at low temperature, however electrical input density inversely declines because the hydrogen overvoltage increases. The barium sulfate comes as a minute insoluble powder in dilute sulfuric acid and is the source of lead sulfate crystals that form during discharge. It prevents service capacity from decreasing and the active material from shrinking. The

carbon improves electrical input density by slightly reducing the hydrogen overvoltage, absorbing the lignin, contributing conductivity and facilitating formation.

To prevent self-discharging, corrosion of the grid and deterioration of the plates with lead storage batteries, it is preferable to minimize the impurities in the dilute sulfuric acid of the electrolyte.

With porous lead dioxide (PbO₂) as the active material of the positive electrode and spongy lead (Pb) as the active material of the negative electrode, discharge occurs because of the reaction of these materials with the sulfuric acid (H₂SO₄) of the electrolyte. The electrochemical reaction of the positive electrode, negative electrode and battery as a whole is as follows (Figure 1).

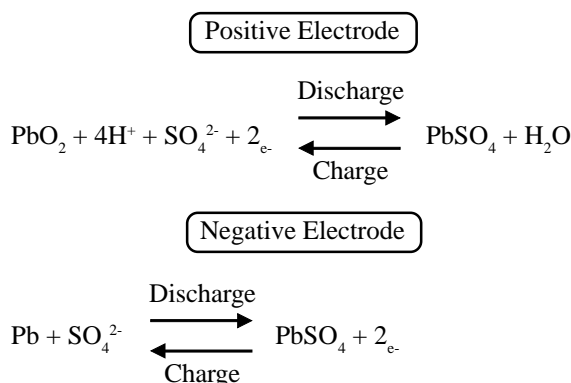


Fig. 1 Charging and discharging reactions of Lead-acid battery

In other words, PbSO₄ forms on both the positive electrode and negative electrode during discharge, hence consuming H₂SO₄. If charged, the PbSO₄ returns to Pb, PbO₂ and H₂SO₄. Accordingly, current is carried inside the electrolyte by H⁺ and SO₄²⁻.

The electrolysis reaction is reversible so the reaction should go on indefinitely. However, in actuality, the charge current eventually stops flowing even when voltage is applied. This is because of internal resistances other than hypercharge reaction of the electrolyte. As charging and discharging repeats, this internal resistance increases to the point that, at a certain current level, the voltage between terminals suddenly shoots up whereby releasing H₂ and O₂ gas. In short, the battery cannot store sufficient capacity to end charging. That being the case, a major factor behind this internal resistance is said to be sulfation, caused by the crystallization of PbSO₄ produced during discharge.

Because of discharging, PbSO₄ forms on both electrodes. This PbSO₄ should break back down into Pb²⁺ ions and SO₄²⁻ when the charge reaction starts, but some of it does not, whereby remaining as an inactive crystal and depositing on the electrode plates. This crystal gradually

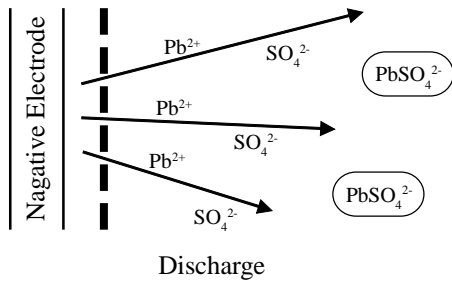


Fig. 2 Discharge reaction of electrode

covers the plates (active material grain) and decreases the electrolysis reaction area (Figure 2). Moreover, because the active material of the positive electrode has many pores that are smaller than those of the active material of the negative electrode, the small pores readily clog (Figure 3). Though, before discharge, the electrolyte sufficiently spreads between the active materials, as $PbSO_4$ crystal accumulate and increase in size, they block electrolyte penetration and further decrease the reaction area.

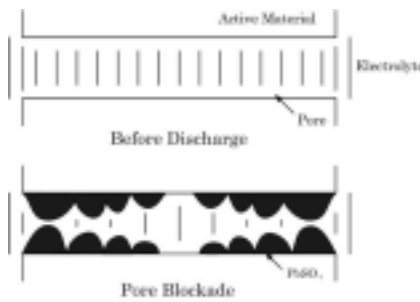


Fig. 3 Pore blockage by sulfation

As such, the crystallization of $PbSO_4$ lowers the specific gravity of the electrolyte as a whole. For the aforementioned reason, the electrolysis reaction shuts down and current stops flowing. As a result, internal resistance increases.

3. EXPERIMENT

3.1 Method of experiment

In this section, the switching timing of the charge relay and discharge relay in terms of trigger voltage and description of the circuit used to do this is explained.

In order to identify the deteriorated condition of a test battery, the battery is repeatedly charged and discharged within a specific voltage range, and the battery voltage and current are measured during that process. The charging final voltage specified in JIS (Japanese Industrial Standards) is 14.5V. Because hydrogen gas forms above this level, charging was ended at this voltage in accordance with JIS and switched over to discharging. In discharging as well, the final voltage was set at 10.5V

because JIS specifies to discharge the battery from a full charge at a constant current and assess performance in terms of time and capacity until reaching 10.5V.

Figure 4 shows an example of experiment results. When charging started, the voltage rose, and when discharging started, the voltage dropped. It was seen that the discharge time per cycle decreased as the number of cycles increased. This occurred because internal resistance rose as the battery deteriorated even though discharge current was kept constant. For this reason, battery voltage dropped drastically in proportion to the magnitude of internal resistance until the time it took to discharge to 10.5V became short. In other words, the change in internal resistance of a battery, that is to say, the deteriorated condition of a battery can be understood from the change in discharge time per cycle.

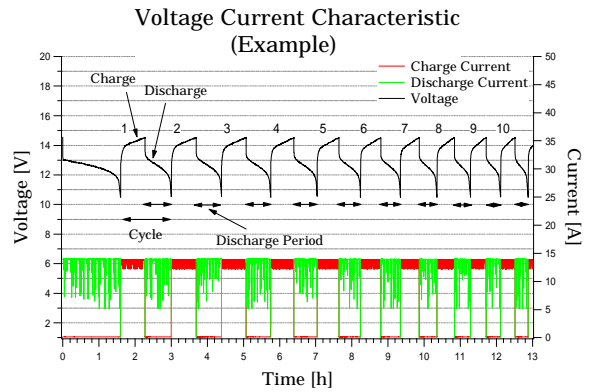


Fig. 4 Voltage and current characteristics in charging and discharging

3.2 Experimental setup

Figure 5 shows the basic circuit for charging and discharging.

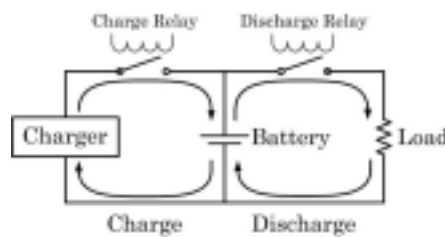


Fig. 5 Conceptual view of charging-discharging device

The schematic illustration basic circuit for charging and discharging is shown in Figure 5.

This figure illustrates the device used to repeatedly charge and discharge the battery. In charging, the charge relay is on and the discharge relay is off, therefore the charge current flows from the charger to the battery. In discharging, the charge relay is off and the discharge

relay is on, therefore discharge current flows to the load. Relay circuits are used to control charging and discharging. The charge relay and discharge relay controlled control current so operation switched is altered to be over to discharging when battery voltage reached 14.5V, and back to discharging when battery voltage reached 10.5V.

3.3 Charging-discharging device

Figure 6 shows the charging-discharging device that controlled voltage between the terminals. This experimental device is a basic circuit that constantly read the voltage between battery terminals using a meter relay. The end of the discharging is set to be 10.5V, while the end of charging is set to be 14.5V. Charging was kept at a constant current, whereas discharging was kept at a constant voltage.



Fig. 6 A photograph of charging-discharging device for controlling voltage between terminals

3.4 Pulse charging experiment

The mainstream in conventional batteries is to charge using DC. Nonetheless, thoughts were directed at finding a different method of charging that would prevent battery deterioration. As a result, it is thought possible to stimulate the battery electrodes and thereby prevent battery deterioration, by intermittently using a pulse current during battery charging and discharging. The effectiveness can be verified by experiment. Unlike commercially available pulse activators, the newly developed activator stimulates the electrodes by charging and discharging the battery with a high current pulse from the battery approximately every 500 μ s during ordinary DC charging and discharging. It is thought that this pulse current would be effective towards activating the electrodes because it is a high current. That effect was verified in comparative experiments between the newly developed pulse activator and commercially available pulse activators.

4. PULSE ACTIVATOR EXPERIMENTS

At present, there are commercially available pulse activators that eliminate sulfation, but the newly developed pulse activator uses high current and it was thought important to use this high current, therefore that effectiveness was verified by experiment.

4.1 Overview of pulse activator

This newly invented pulse activator flow draws a discharge current of several 10s of A (more than 1C) from the battery whose pulse width of several 100 μ s and immediately thereafter returns the discharge current to the battery. During an experiment, the charging and discharging current are kept to 14A to the 28AH capacity battery. However, the pulse activator works differently by performing discharging and charging from the battery (Figure 7). It was thought that using a high charge current and high discharge current of several 10s of A for this would be effective towards activating the electrodes.

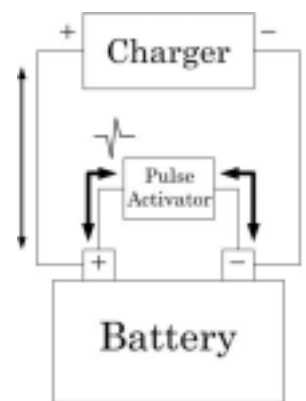


Fig. 7 Current flow between charger and pulse activator

This newly developed pulse activator first discharges the battery using a high current, then immediately thereafter charges it using a high current. This sequence is important as the active material of the electrodes is first dissolved by high current discharge to concentrate the Pb^{2+} ions near to electrodes. Then immediately after charging starts before those Pb^{2+} ions disperse to return active material to the electrodes. For that reason, it is important that with the new pulse activator charging comes after discharging.

Moreover, normal DC of about 14A uses only the shallow reaches of the active material on the electrode surface, but by discharging with a high current, discharging can use active material from deeper strata of the electrode. This approach dissolves more active material from the electrode than just using DC. The dissolved active material becomes Pb^{2+} ions by reaction and concentrates near the electrodes (Figure 8).

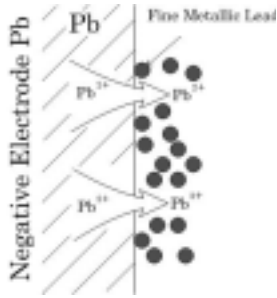


Fig. 8 Model of active material dissolution by high current discharging

Because the Pb^{2+} ions generated by discharging immediately disperse to the outer areas of the electrolyte, ion concentration decreases. Therefore, the charging reaction is started immediately after discharging ends in order to prevent Pb^{2+} ion dispersal and consequently reduce the Pb^{2+} ions to the electrode active material, Pb as shown in Figure 9.

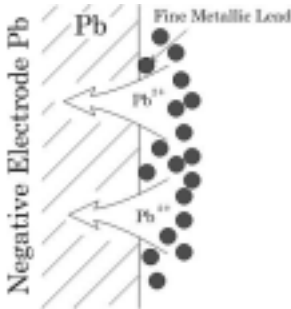
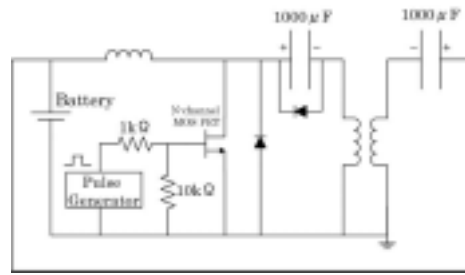


Fig. 9 Model of active material electrode position by high current charging

By repeating this process of dissolving and immediately thereafter electrodepositing the electrode's active material, the electrodes are activated.

To materialize this pulse activator, the circuit shown in Figure 10 was made. The N-channel FET at the center is controlled by a pulse generator. This pulse generator changes pulse width and duty to determine pulse interval. The magnitude of the pulse current can be changed by changing the number of turns on the primary and secondary sides of the transformer. The advantage of this pulse activator is that the electrodes can be activated by returning the same current drawn from the battery back to the battery; it works using the battery itself as a power source.

Figures 11 and 12 show the battery current behavior when using this pulse activator. With this pulse activator, the maximum discharge current is 28A, while the maximum charge current is 20A. However, because the pulse activator continuously charges and discharges the battery in addition to and in-between the 14A DC current used in ordinary charging and discharging, the total



N-channel MOS FET

Manufacturer: TOSHIBA

Model: 2SK2267

Gate source voltage maximum rating: 20V

Drain current maximum rating: 60A

Timing generator

Manufacturer: TOKYO APPLE CORP.

Model: 23900

Frequency: 0-20 MHz

Fig. 10 The circuit of the pulse activator

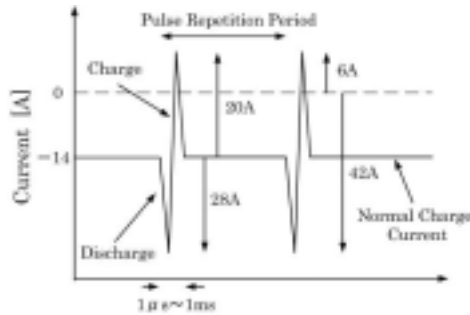


Fig. 11 Pulse current and charge current in discharging and charging

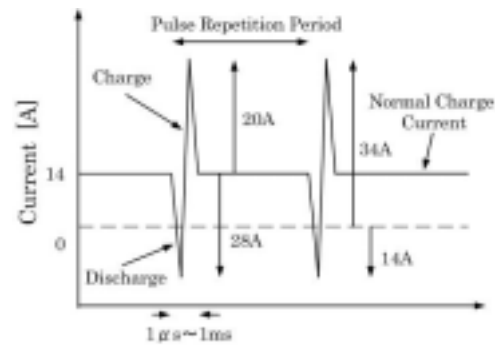


Fig. 12 Waveform of the current in this activator experiment and pulse current and charge current in charging

of the battery's discharge current and charge current differs between charging and discharging. While discharging the battery, the total sum of the current from the battery and pulse activator is 42A in any given instant. After that, the electrodes are reduced using a 6A charge current. During charging, the discharge current is 14A and the charge current is 34A.

4.2 Results of experiment

Before testing the performance of the newly developed pulse activator, the effectiveness and characteristics of commercially available pulse activators were investigated. Figure 13 shows the commercially available PR-012, while Figure 14 shows the voltage waveform and current waveform of the PR-012 in actual use.



Fig. 13 PR-012

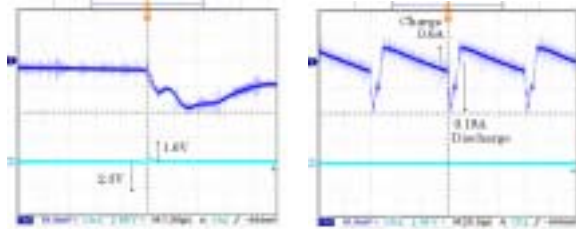


Fig. 14 Voltage and current waveforms of PR-012

The left chart is the current flow to the battery, while the right chart is the voltage waveform. Discharge current was 0.18A and charge current was 0.6A. This pulse current was repeated at 60µs intervals. The PR-012 operates only while the battery is charging, therefore current flowed as indicated in Figure 13 when the voltage between terminals was 14V and higher.

Figure 15 shows the newly developed pulse activator. The waveforms of the current and voltage are shown in Figure 16.

The newly developed pulse activator exhibited a discharge current of 28A and a charge current of 20A, both of which were completely different in magnitude from the currents of the commercially available PS-012. It



Fig. 15 Newly developed pulse activator

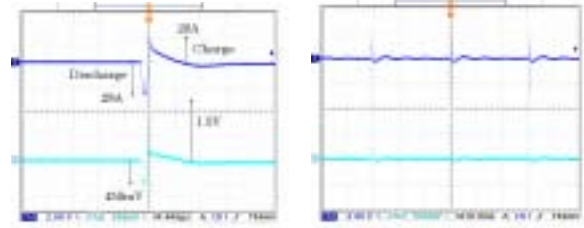


Fig. 16 Voltage and current waveforms of newly developed pulse activator

was deliberately developed to generate this level of current because a high discharge current was needed to dissolve the electrodes.

Table 1 lists the specifications of the test battery.

Table 1 The specification of the battery used for this experiment

Manufacturer	GS Yuasa Battery
5 hr capacity	28 Ah
Model	40B19R(L)
Length	187 mm
Width	127 mm
Height	227 mm
Weight	9.0 kg

In this experiment, a unique charging-discharging method is used (Hou *et al.*, 2005). This device was capable of constant current charging and constant current discharging; charging and discharging were performed at a constant current as charge current and discharge current did not change because of the battery's internal resistance. Effectiveness of the pulse activator was verified using a brand new battery. This was done because it was known that it would be difficult to form PbSO₄ again once sulfation dissolved. It was considered important for demonstrating the effectiveness of the pulse activator to constantly activate the electrodes so that crystallization would not occur.

Charge current and discharge current were both set at 14A, while the final charging voltage was set at 14.5V, and the final discharging voltage was set at 10.5V. The method for assessing the effectiveness of the pulse activator was to count the number of cycles up until the discharge time per cycle reached 720s. This was done so that a comparison could be made when service capacity decreased to 10% (2.8Ah) of the initial battery capacity of 28Ah. In other words, when discharged at a constant current of 14A, discharge time would eventually reach 720s.

Figure 17 shows the discharge characteristics in normal charging by the PR-012 and the newly developed pulse activator. Normal charging usually allows 11 discharge cycles and still the PR-012 attained only 10. However,

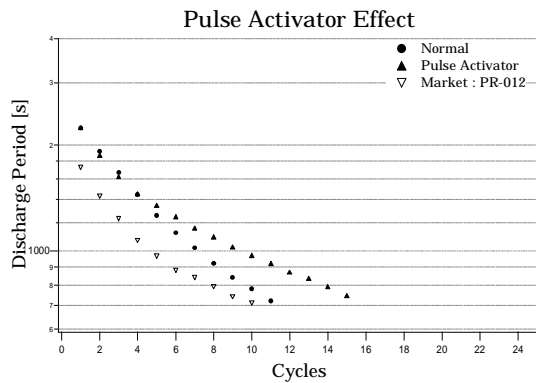


Fig. 17 Performance comparison between commercially available PR-012 and newly developed pulse activator

the newly developed pulse activator was able to discharge the battery for up to 15 cycles. Therefore, the newly developed pulse activator was effective in preventing deterioration and consequently prolonged battery life. It was discovered that charging and discharging with a low pulse current of 1A or less as with the PR-012 has almost no effect on preventing battery deterioration, whereas a high current pulse charging and discharging as with the newly developed pulse activator was effective.

5. CONCLUSIONS

In this study, the new pulse activator differed from commercially available products in that it used high current pulse charging [Minami et al., 2004] developed on the belief that charging and discharging at high current would prevent battery deterioration, and its effectiveness was experimentally verified. Moreover, the effectiveness of additives thought effective towards preventing battery deterioration was also verified and experiments were conducted to identify the compounded effect of using these additives in conjunction with the newly developed pulse activator.

The charge current and discharge current of commercially available pulse activators is low at 0.6A and 0.18A, respectively, and has little effect on preventing deterioration. The newly developed pulse activator discussed in this paper charges and discharges using a high current and, using a physical mechanism that is completely different from existing products, eliminates sulfation, refreshes the negative electrode and prolongs battery life. This new pulse activator can produce a maximum charge current of 20A and a maximum discharge current of 28A, which were believed sufficiently effective towards activating electrodes of an approx. 30Ah passenger car battery using pulse current. In experiments, a commercially available pulse activator lasted 10 cycles before discharge time reached 720s, which was similar to ordi-

nary charging, but the new pulse activator lasted 15 cycles, verifying its effectiveness in preventing battery deterioration.

The experiments conducted in this study involved continuous charging and continuous discharging at a constant 0.5C which are far harsher conditions than seen with automobiles and forklifts. From these experiments, the combined use of the pulse activator and additive can more than doubled the life of a battery, which is said to last 1-3 years, therefore it can be expected to prolong battery life up to 4-9 years by using this method. This should further slow the amount of waste with current used batteries, reducing the total amount of discarded batteries per year.

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