Experimental Study on the Optimum Density of ITE Additives for a Lead-acid Battery's Life Prolongation

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Abstract

Lead-acid batteries have been used as a starter for tens of millions of cars in the world. They are also used as a cheap way to store energy for electric-powered vehicles, EV's. Life prolongation of these batteries is an important issue for resource conservation and the reduction of environmental contamination caused by discarded batteries. For this purpose, an organic battery activator named ITE (International Technology Exchange) activator has been exploited since 1996. This additive is an organic battery activator. The results of high-precision bench-tests, which are conducted in order to find an optimization of the activator's density, are described in this paper. The test results show that the best life-prolongation is achieved when an activator of 5Wt% with 10cc/cell is added for a starting battery of engine, 28Ah (10hrs).

Keywords

ITE Battery activator, lead-acid battery, organic polymer, sulfation, life prolongation, optimization of density

1. INTRODUCTION

ITE battery activator is a type of additive for lead-acid batteries manufactured and sold by ITE (International Technology Exchange). Its dominant component is PVA. The ITE battery activator's superb performance has been proved in its use for lead-acid batteries. [Brodd, 2005; Kozawa, 2002a, 2002b, 2002c; Kozawa, 2003a, 2003b; Kozawa, 2004a, 2004b; Kozawa, 2005a, 2005b; Minami, 2003b, 2003d, 2004e] Research into chargers and charging methods has been conducted in order to extend battery-life. [Hou, 2005; Ikeda; 2004, 2005; Minami; 2002; Minami, 2003a, 2003c; Minami, 2004a, 2004b, 2004c, 2004d] Thus it is very important to determine experimentally the optimum value for an ITE activator's amount of supply in terms of the life prolongation of lead-acid batteries. Experiments are conducted by repeating the charge and discharge of batteries into which the additive is added in order to determine the deterioration property. A high-precision bench-test device is used for the experiments.

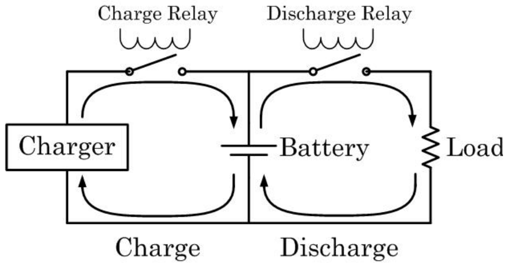


Fig. 1 Conceptual view of charging and discharging process

As shown in Figure 1, the test battery is monitored and charge-discharge is conducted as the current flows through the Charger and Charge Relay in this experiment. Charging is stopped as soon as the battery voltage reached 17.0V, and then it is discharged through a Discharge Relay with resistance (0.7Ω) or through a constant current electric load (14A). When the battery voltage reached 10.5V, discharging is stopped and charging is restarted. HITACHI's 38B19L (28Ah/5h) batteries, which are used as automobile starters, are utilized in all of the experiments. The discharging current is passed through 0.7Ω, and the discharge is done at an almost constant flow of current. The current is equivalent to approximately 0.75C.

In the case of internal voltage measurement as shown in Figure 16-20, a constant-current power-supply is used for charging, and the charging current is set for 14A (0.5C). When the inner electrical resistance of the batteries is measured, an electric load device is used and the discharge is conducted at a constant current (14A). Normally, the charging limit voltage of batteries is around 14V. However, when additives are put in, charging will not be completed unless the end-point voltage is made more than 16V. Thus the charging limit voltage is set for 17V in the experiments. Since battery property is largely influenced by differences of temperature, the battery case is placed in water, and the temperature of the water is controlled by an electric heater to keep it at 30°C during the experiments.

2. BASIC PRINCIPLES OF THE ADDITIVE'S PERFORMANCE

The ITE Battery Research Institute has developed a battery-additive to put into lead-acid batteries. [Kozawa et al. 2003b; Minami et al. 2004e] This additive consists of particles of μm, of which the main body is an organic polymer. These particles make a difference to an electrolyte solution during charging and discharging. Detailed studies of the charge and discharge behavior of batteries show that each charge and discharge goes through a 2-stage reaction, and an additive has effects on these stages. The 2-stage reaction of charge and discharge will be explained first in order to describe the effects of the additive.

As soon as discharge has taken place, Pb, an active material of the negative electrode, is resolved to Pb^{2+} ions and electrons. The resolved Pb^{2+} ions exist around the negative electrode at the beginning, and they diffuse and move to the offshore of the electrolyte solution. The diffused Pb^{2+} bind with SO_4^{2-} ions at the offshore and remain in the electrolyte solution as $PbSO_4$ during discharging (Figure 2). The chemical equations of the 1st Step and the 2nd Step are shown in Eq. (1) and Eq. (2), respectively.

Discharge Process
1st step: $Pb \rightarrow Pb^{2+} + e^-$ (1)
2nd ste: $Pb^{2+} + SO_4^{2-} \rightarrow PbSO_4$ (2)

Charge Process
1st step: $PbSO_4$ ® $Pb^{2+} + SO_4^{2-}$ (3)
2nd step: $Pb^{2+} + e^- \rightarrow Pb$ (4)

When a charge has begun, $PbSO_4$ at the offshore of the electrolyte solution resolves and becomes Pb^{2+} and SO_4^{2-} ions. Pb^{2+} ions, which are needed for the reaction, are concentrated around the negative electrode. They bind with electrons and become Pb, an active material of the negative electrode (Figure 3). The chemical equations of the 1st Step and the 2nd Step are shown in Eq.(3) and Eq.(4), respectively.

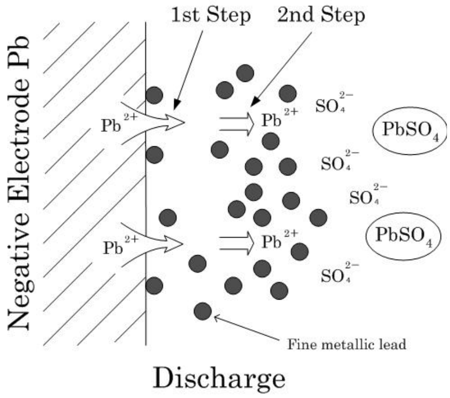


Fig. 2 Discharging reaction at the negative electrode

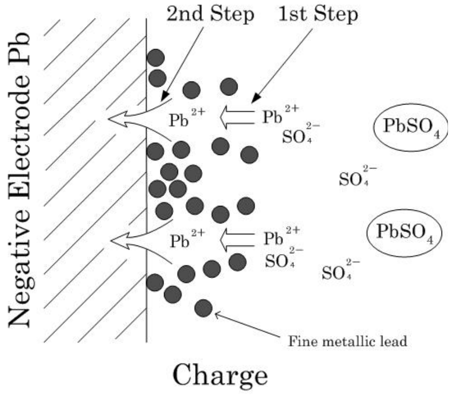


Fig. 3 Charging reaction at the negative electrode

When an electrolyte solution is infused with particles of μm, such as this additive, during this 2-stage reaction, the particles suppress the diffusion of Pb^{2+} ions. These particles prevent the diffusion of Pb^{2+} ions to the offshore during discharging. Because of this, Pb^{2+} ions are constantly concentrated around the electrodes. The number of diffused Pb^{2+} ions decreases, and this prevents the 2nd step (Equation 2) of the discharge from happen-

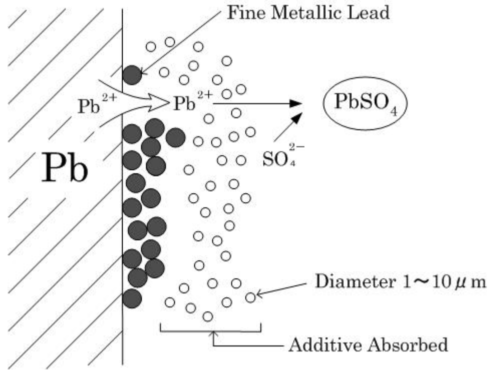


Fig. 4 Mechanism to reduce $PbSO_4$, the cause for sulfate, by injecting the additive with the illustration of the movement of particles contained in the additive

ing and reduces the number of generated $PbSO_4$. That is, this reduces $PbSO_4$, which is a cause of sulfate (Figure 4). If the amount of the additive put in is excessive, it will be resolved since it is water-soluble. But two problems will occur: (1) Because the hydrogen overvoltage increases, charging by an ordinary charged voltage will be insufficient; (2) Lead sulfate, which already exists, diffuses and prevents itself from becoming lead. Thus infusing an excess amount of the additive deteriorates the batteries.

An appropriate amount of additive has been suggested according to various capacities of batteries by the ITE Battery Institute, as is shown in Table 1. In this study, experiments are conducted to determine an optimum value, and the device used for this study is a bench-test with high reproducibility.

Table 1 Amount of additive suggested by the ITE Battery Research Institute

Method: 2.5W% of resolved fine particles, of which the main body is an organic polymer, is added into each cell of batteries once a year, in the following amounts.	
30 – 50Ah	5cc/cell (30cc/battery)
75 – 90Ah	10cc/cell (60cc/battery)
120 – 150Ah	20cc/cell (120cc/battery)
190 – 250Ah	30cc/cell (180cc/battery)
350 – 450Ah	50cc/cell (300cc/battery)

3. EXPERIMENTAL RESULTS

Experiments are conducted by repeating the charge and discharge with different amounts of ITE activator. Figure 5 shows the relations between the experimental times and the discharge periods in the experiments. Figure 6 plots the results with the number of charges as the horizontal axis.

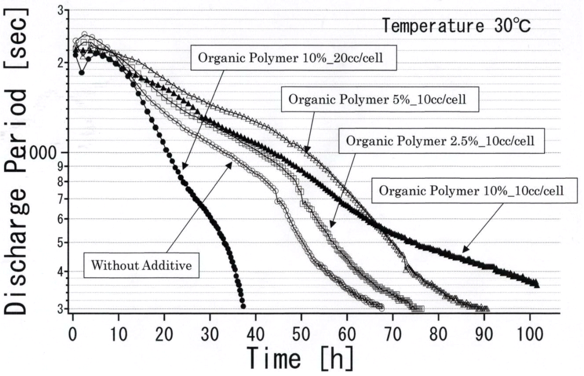


Fig. 5 Characteristics of charge and discharge in relation to the amount of added activator (Time required for experiments vs. discharge period)

Other experiments are conducted to reveal the effect of the ITE activator. The same kind of test with charge and discharge currents is at first conducted without using the activator. Then, after a certain period of time (15h, 26h, 50h, 63h), the activator is added and its effect on the discharge period is studied. Figure 7 shows the results. The horizontal axis shows the period after the experiment began, and the vertical axis shows the discharge period. (This result proves that the performance of the battery improved every time when the additive is added and the life prolongation is extended up to a certain range for the amount of additive.)

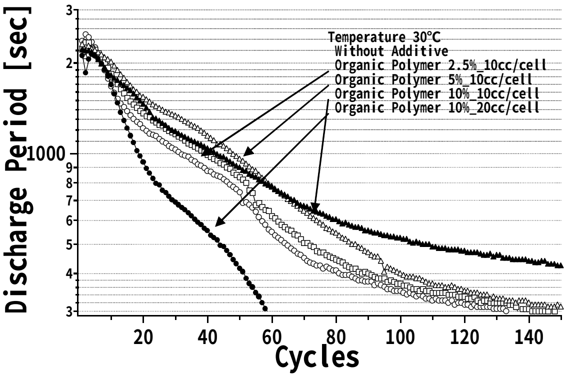


Fig. 6 Plot of characteristics of charge and discharge with the frequency of charging as the horizontal axis

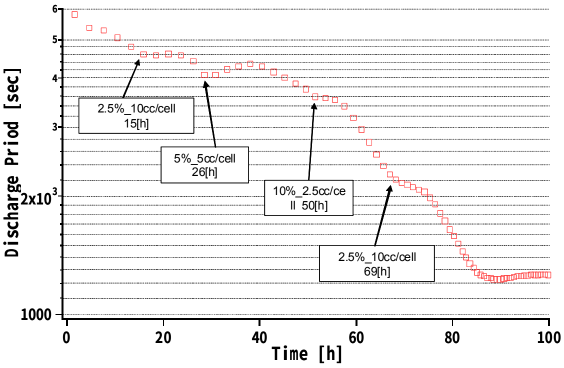


Fig. 7 Results of experiments to study the effect on the discharge period when activator is added 15 hours, 26 hours, 50 hours and 69 hours after discharge without injection of activator

4. DISCUSSION AND CONCLUSIONS

Experiments to find the optimization of density of the ITE activator for injection are conducted by using a bench-test. The temperature of the batteries is controlled to keep them at a constant temperature, so that the performance would not be influenced by temperature changes inside the batteries or by climate changes. The results in Figure 7 show that the battery's lifespan can be prolonged by injection of the activator. Experiments are conducted twice under the same conditions in order to study differences of density of the activator. As indicated in Figure 5 and 6, the experimental data show almost the same results, and it is revealed that differences in the batteries themselves will have no impact on the results. From the experiments, it is concluded that the best performance for a battery of 28Ah is achieved when an additive of 5W%10cc/cell is added.

When a battery is added with an additive of 10W%, 20cc/cell, the lifespan deteriorated significantly. In order to analyze the reason, the inner voltage of the battery is measured by the following method. As shown in section 2, an excess amount of additive increases hydrogen over-voltage and the generation of lead ions is suppressed. As a result, the inner resistance of the battery increases.

A device to study the deterioration of batteries has been developed. By using this device, information about changes in the inner resistance of batteries can be obtained while conducting a test on the characteristics of the charge and discharge of batteries and studying the inner voltage of batteries in real time. [Hou et al., 2005] In order to measure the changes of inner resistance in the repetitive charging-discharging cycles in real time, charge-discharge is stopped for approximately 60ms at every 5 or so seconds. Furthermore, the voltage between the ends of the battery, when the current is not flowing, is made sample-and-hold and this is recorded. Figure 8 shows the pulse when the current is turned off and the pulse waveforms for the samples of the terminal voltage. The voltage changes of the battery at lower trace are fast enough and the duration at off-pulse is long

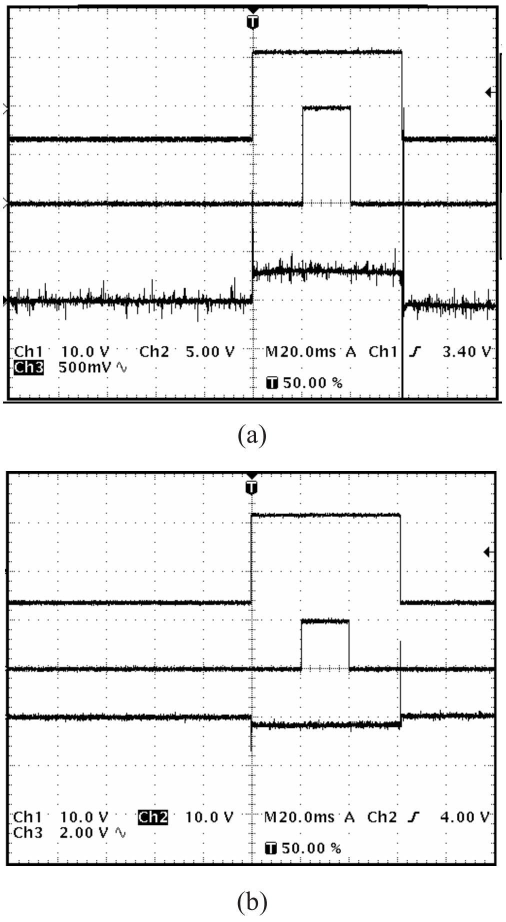
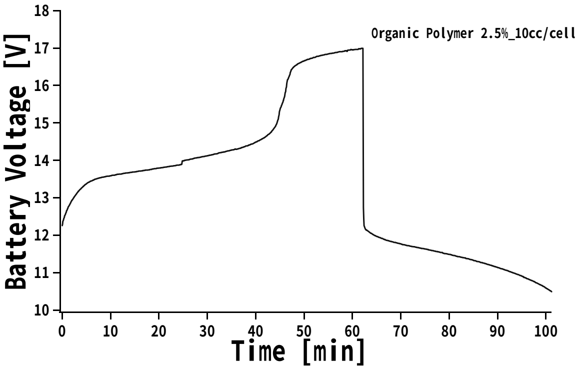
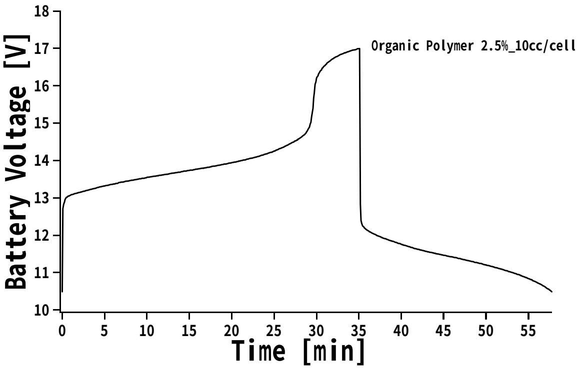


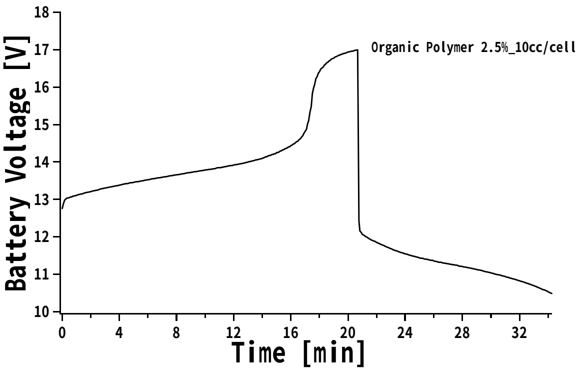
Fig. 8 Waveforms of the current-off-pulse and the sampling pulse for: (a) during the discharging time, (b) during the charging time (upper trace: off-pulse, middle trace: sampling pulse, lower trace: voltage change of the battery voltage)



(a) Organic polymer 2.5W%10cc/start



(b) Organic polymer 2.5W%10cc/24 hour



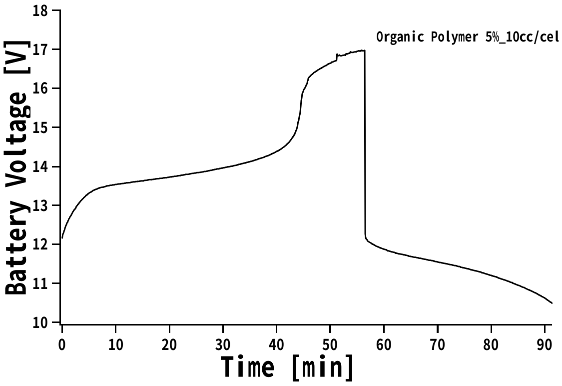
(c) Organic polymer 2.5W%10cc/48 hour

Fig. 9 Charge-discharge waveforms when additive of 2.5W%10cc/cell is added enough. This method to measure the inner voltage of the battery is called a pulsed-current-off method.

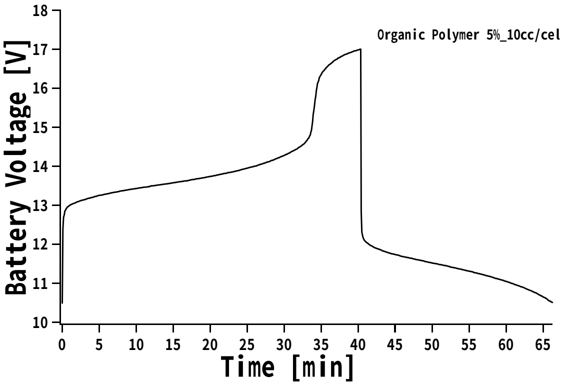
Figure 9 shows the waveforms of the charge and discharge at different periods of time when an additive of 2.5W%10cc is added into each cell. Figure 10 shows the case with a 5W%10cc/cell, Figure 11 with a 10W%10cc/cell, and Figure 12 with 10W%20cc/cell. In order to reveal the characteristics of the charge and discharge waveforms, waveforms which are normalized between discharges are shown in three categories: at the moment of first cycle charge-discharge (Figure 13), 24 hours after the experiment (Figure 14), and 48 hours after the experiment (Figure 15). In the case of an additive of 10W%20cc/cell, normalized waveforms did not accurately appear. The reason for this is that the time variation of the charging-discharging process caused by the deterioration of the battery is too fast for the time (5s) between samplings used for measuring. Thus the waveforms cannot be measured satisfactory.

As described in section 2, the hydrogen over-voltage is increased and the generation of lead ions will be suppressed by adding an excess amount of additive. Furthermore, because of this, the inner resistance of the battery is increased. An experiment to measure the inner resistance of batteries is conducted to reveal these points.

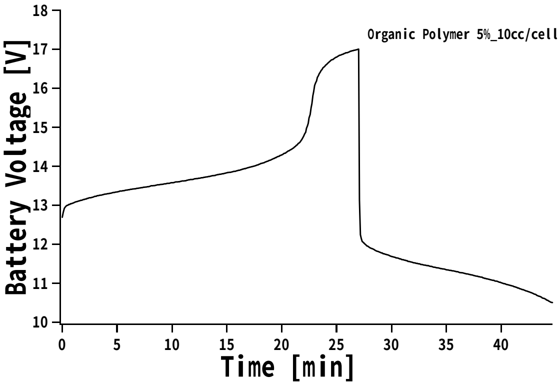
Through applying this method, changes in the inner volt-



(a) Organic polymer 5W%10cc/start

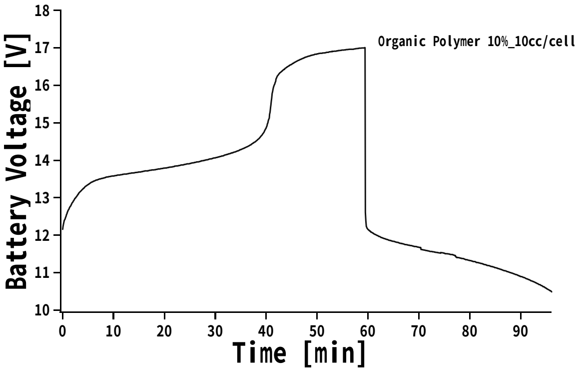


(b) Organic polymer 5W%10cc/24 hour

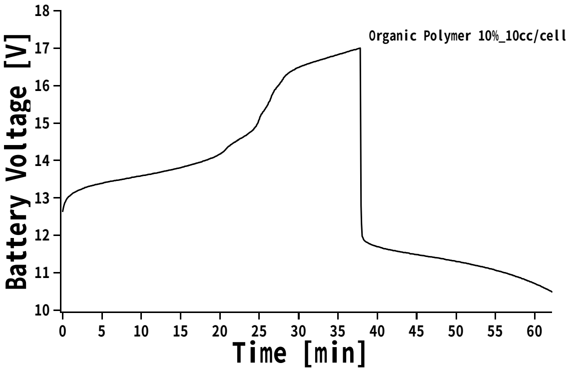


(c) Organic polymer 5W%10cc/48 hour

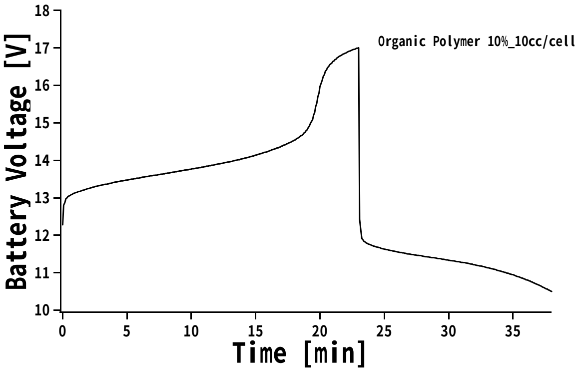
Fig. 10 Charge-discharge waveforms when additive of 5W%10cc/cell is added



(a) Organic polymer 10W%10cc/start

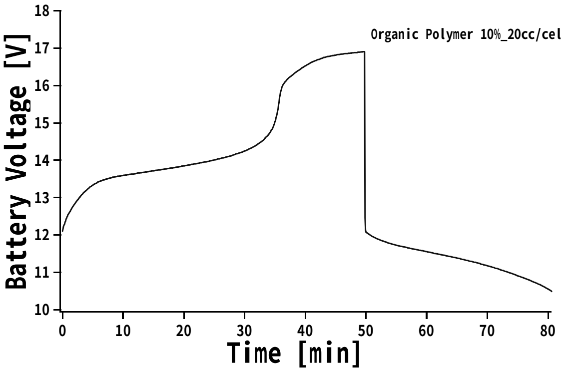


(b) Organic polymer 10W%10cc/24 hour

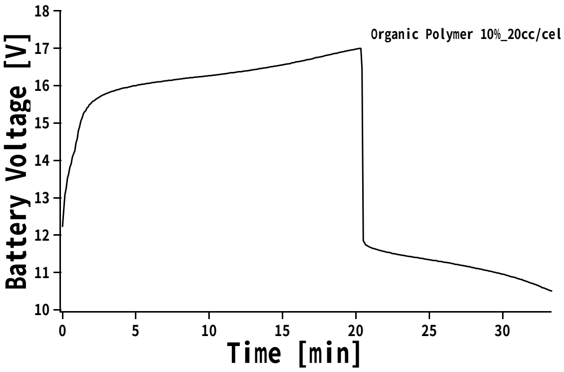


(c) Organic polymer 10W%10cc/48 hour

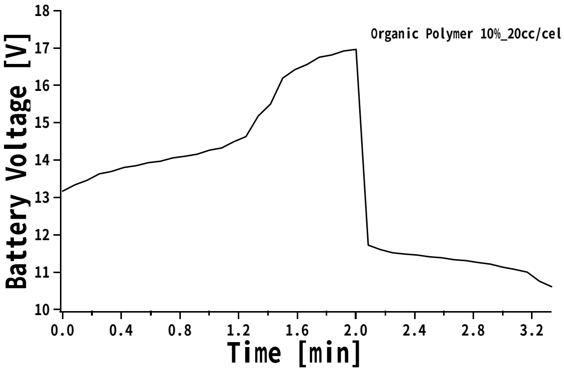
Fig. 11 Charge-discharge waveforms when additive of 10W%10cc/cell is added



(a) Organic polymer 10W%20cc/start



(b) Organic polymer 10W%20cc/24 hour



(c) Organic polymer 10W%20cc/48 hour

Fig. 12 Charge-discharge wave forms when additive of 10W%20cc is added

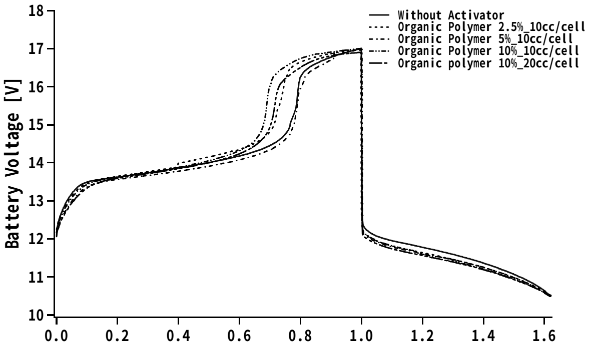


Fig. 13 Waveforms normalized by charging at the moment of first cycle charge-discharge

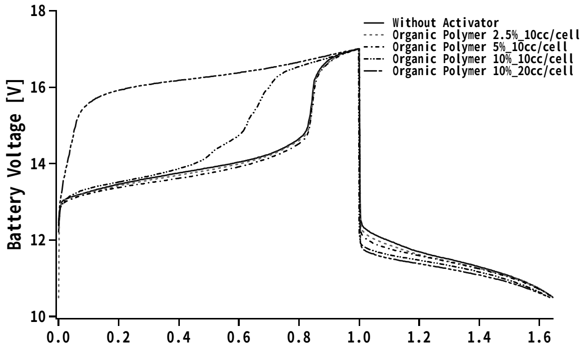


Fig. 14 Waveforms normalized by charging time 24 hours after the experiment

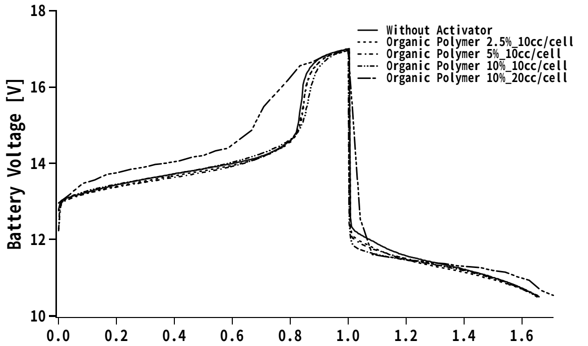


Fig. 15 Waveforms normalized by charging time 48 hours after the experiment

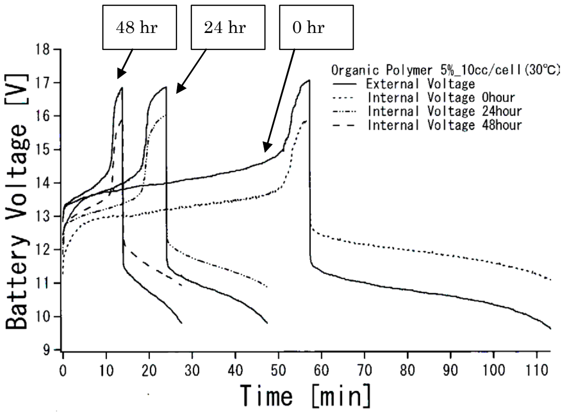


Fig. 16 Time variation of charge-discharge waveforms when additive of 5W%10cc/cell is added

age as well as the outer voltage are measured for cases when additives of 5W%10cc/cell and 10W%20cc/cell are added. Figure 16 shows the charge-discharge waveforms at different times when an additive of 5W%10cc/cell is added. Figure 17 shows the charge-discharge wave forms at different times for the case with 10W%20cc/cell. The normalized waveforms between charges are shown in three categories: at the moment of first cycle charge-discharge (Figure 18), 24 hours after the experiment (Figure 19), and 48 hours after the experiment (Figure 20).

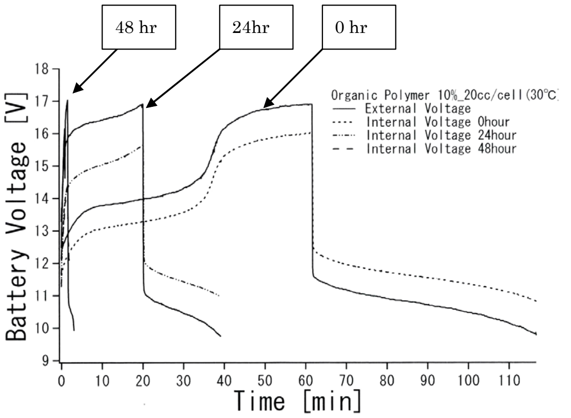


Fig. 17 Time variation of charge-discharge waveforms when additive of 10W%20cc is added

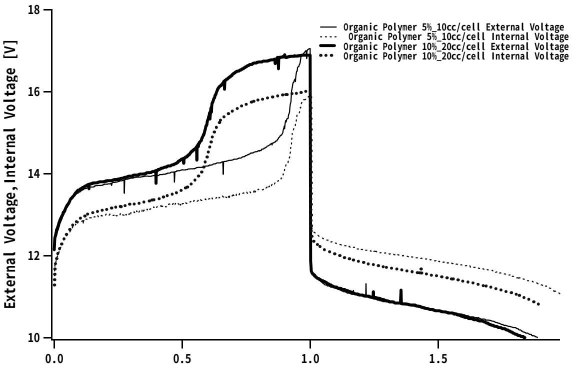


Fig. 18 Waveforms normalized by charging (at the moment of first cycle charge-discharge)

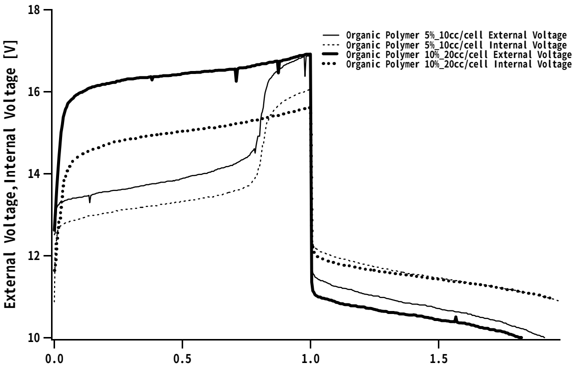


Fig. 19 Charge-discharge waveforms normalized between charging times (24 hours later)

Figures 18, 19 and 20 show that the difference between the inner and outer voltages is significantly large when an additive of 10W%20cc/cell is added, in comparison to when an additive of 5W%10cc/cell is added. That is, when the charge is started, because the voltage drop caused by the inner resistance and charge current (14A constant) is the biggest, the outer voltage reaches 17V, which is the end-point voltage, without having charged adequately. As a result, the period of discharge is shortened. Abe et al. [2001] shows that when carbon particulates are added into lead-acid batteries as an additive, the carbon entered the negative electrode and increased the effective surface area and increased performance. At the same time, the excess amount of carbon prevented Pb-Pb particles at electrodes from contacting, and it increased the resistance at the whole electrodes and decreased the structural strength of the negative electrode.

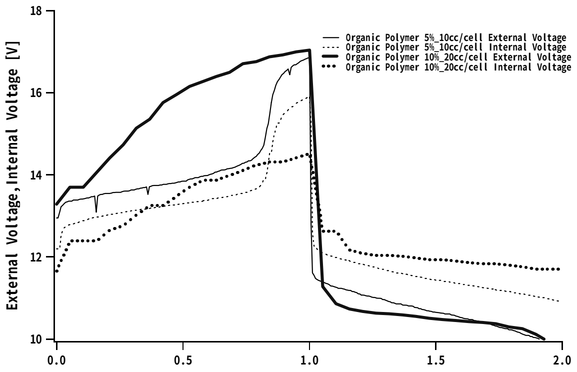


Fig. 20 Charge-discharge waveforms normalized between charging times (48 hours later)

In the case with this additive made of an organic polymer, too, the difference is the biggest when a large amount of additive is added, because the generation of Pb ions is suppressed at the negative electrode and $PbSO_4$ is deposited at the electrodes, and this increases the inner resistance. This paper reveals that the additive of 5W%10cc/cell is the optimum density for a 28Ah battery.

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