Effects of Various Additives on Anodes and Cathodes of Lead-acid Batteries (6)

Shoichiro Ikeda [1], Makoto Yoshida [2], Satoshi Iwata [3], Satomi Sakuragi [4], Shosuke Kita [5], Ryoichi Yamamoto [6], Yu Liu [7], Hideo Ono [8], Shinji Ono [9], and Akiya Kozawa [10]

[1] *Environmental Technology and Urban Planning, Nagoya Institute of Technology, ikedas@nitech.ac.jp*
[2] *Environmental Technology and Urban Planning, Nagoya Institute of Technology*
[3] *Environmental Technology and Urban Planning, Nagoya Institute of Technology*
[4] *Environmental Technology and Urban Planning, Nagoya Institute of Technology*
[5] *Shion Co.,Ltd., nanoca@shion.co.jp*
[6] *Shion Co.,Ltd.*
[7] *Shion Co.,Ltd.*
[8] *Shion Co.,Ltd.*
[9] *Shion Co.,Ltd.*
[10] *ITE Battery Research Institute, kozawa-akiya@mwb.biglobe.ne.jp*

Abstract
We have been investigating the prolongation of the life-time of lead-acid batteries in the view point of environmental aspects and material resources. Since 1997, we have been working on the activators for lead-acid batteries. We developed various activators using composite organic polymers with solid powder, organic polymers, etc. The effects of prolongation of life-time have been compared between our activators and the other commercially available additives, using actual 6 V batteries for motor cycles. The change in the internal resistance of batteries has been measured during discharge-charge cycles to clarify the deteriorating mechanism. Organic polymer P is useful for prolongation of the life-times of lead-acid batteries if it is used with a suitable amount. The solution of electrolyzed carbon particles with 2.00 mS/cm is also effective for enhancement of the battery performance, and more effective if it is used together with a small amount of organic polymer. The internal resistance of the battery becomes a good index of deterioration of the battery.

Keywords
reuse, activator, additives, electrolyzed carbon, organic polymer

1. INTRODUCTION
We have been investigating the prolongation of the life-time of lead-acid batteries in the view point of environmental aspects and material resources. Since 1997 [Kozawa et al., 1998], [Ikeda et al., 2000], [Kozawa et al., 2000] and [Kozawa et al., 2000], we have been working on the activators for lead-acid batteries. We developed various activators using composite organic polymers with solid powder, organic polymers, etc. The effects of prolongation of life-time have been compared between our activators and the other commercially available additives, using actual 6 V batteries for motor cycles. The change in the internal resistance of batteries has been measured during discharge-charge cycles to clarify the deteriorating mechanism.

2. EXPERIMENTAL
2.1 Materials
The effects of prolongation of life-time have been compared between our activators and the other commercially available additives, such as organic-Ge, Sulfates, etc., using 6 V-4 Ah batteries for motor cycles (GS; 6N4-2A-4). The each cell of the battery was filled with 60 mL of 5.5 M (M=mol/dm^3) H_2SO_4 aqueous solution at first in order to penetrate the electrodes, then 6.7 mL of each additive solution was added to each cell. The additives' solutions were mainly added 10% by volume to the electrolyte solutions. The total volume was 200 mL in each battery.

2.2 Method
Initially, batteries were charged by CC-mode of 0.8 A (2 *C*) for 5 hr (Cut off: 8.5 V) and discharged at 1.0 A (2.5 *C*) to 4.5 V using a battery tester (Hokuto Denko, HJ-101SM6).
In the case of battery added organic polymer (P), the charging voltage soon reached the cut off one, so the charging and discharging currents were changed to 1 *C* and 1.25 *C*, respectively.
The performances of batteries added without and with the electrolyzed carbons of different concentrations (Nano-A, B, and C) and Nano-B plus organic polymer

Table 1 Characteristics of additives used in the long-life tests-1.

Additive	Contents	Characteristics
Nano-0	Electrolyzed carbon particles	Mean dia. 515 nm (Sion)
Nano-0 + P	Electrolyzed carbon particles + Organic polymer	Nano-0:P = 8 : 2 (by volume)
Organic Ge	Ge compound	(Takehara)
P	Organic polymer	Special blend (ITE)
Chelete	Sulfate	(Takeaway)

Table 2 Characteristics of additives used in the long-life tests-2.

Additive	Contents	Specific properties
Nano-A	Electrolyzed carbon particles	1.65 mS/cm
Nano-B	Electrolyzed carbon particles	2.00 mS/cm
Nano-C	Electrolyzed carbon particles	3.15 mS/cm
Nano-B + P	B + Organic polymer	P: 0.067 g/cell
Nano-B + 2(P)	B + double amounts of Organic polymer	P: 0.134 g/cell
Non-added	None	-

(P) were also investigated by charging-discharging cycle test. In this case, they were charged by CC-mode at 0.8 A for 5 hr until the terminal voltage was under the cut off of 7.8 V, and above it, CV-mode at 7.8 V was taken up to 4 Ah using a battery test system (Toyo System, TOSCAT-5200K). The internal resistances of these batteries were measured by AC 4-probe low-resistance meter (Tsuruga, Model 3566) mainly before the discharge.

3. RESULTS AND DISCUSSION

It has been found that the CC and cut-off mode for the charging was not suitable for some additives because of early increase of the terminal voltage due to the high overvoltage in the charge-period causing a low state of charge (SOC). Namely, at early stage, the terminal voltage of the battery added organic polymer (P) was rapidly increased in the charging-period, so the charge capacity was decreased to almost zero in the case of CC and cut-off mode. So, the charging rate was decreased to 1 *C* for this battery, then the capacity gradually increased and after 150 cycles it became almost full (1.6 Ah) as shown in Figure 1 and Figure 2 until 300cycles (In these figures, the values for polymer (P) are presented by 2 times in the vertical axis. Namely, the adsorbed polymer covered the surface of electrodes may gradually be oxidized and removed during charging and discharge cycles [Ikeda et al., 2004].

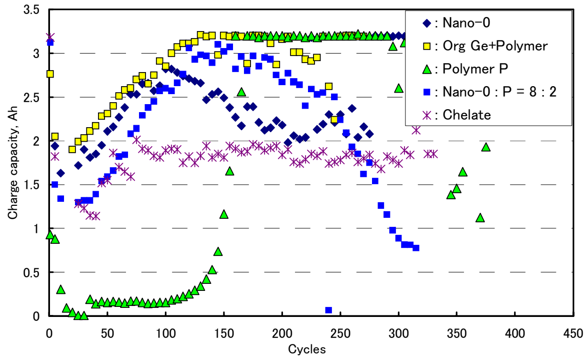

Fig. 1 Change capacities of the lead-acid batteries added with and without various additives during charge-discharge cycles. (The charge capacity of the battery added with Polymer P is multiplied by 2.)

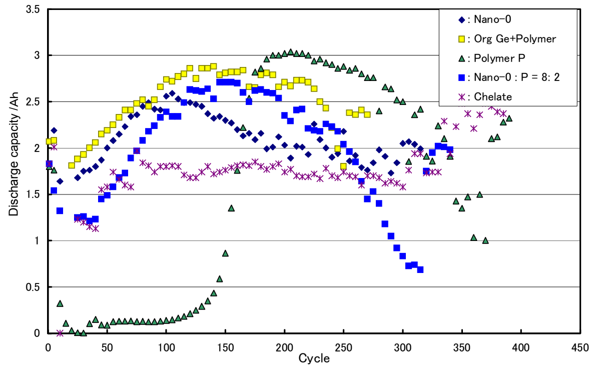

Fig. 2 Discharge capacities of the lead-acid batteries added with and without various additives during charge-discharge cycles. (The charge capacity of the battery added with Polymer P is multiplied by 2.)

Although the organic-Ge containing an organic polymer showed a good performance at first, it caused a high overvoltage and almost zero-SOC when it was used after about 6 months in the next test. The reason, however, is not clear. The increases in the charge capacities of batteries except for Polymer-P in early period have been thought due to they were not the electrolyte filled type but the ready-to-use type after filling with the sulfuric acid electrolyte solution. Namely the oxide layer covering electrodes of batteries produced in the storage period may be partially removed by reduction and the performance of the battery was gradually recovered during the charge-discharge cycles and [Ikeda et al., 2005]. In the case of the long-run test 2 shown in Figure 3, and Figure 4 the battery with non-additive showed the lowest charge and discharge capacities indicating the faster deterioration. It was found that the concentrations of carbons in additives also affected the cycle life of batteries. Although the lowest concentration of the addi-

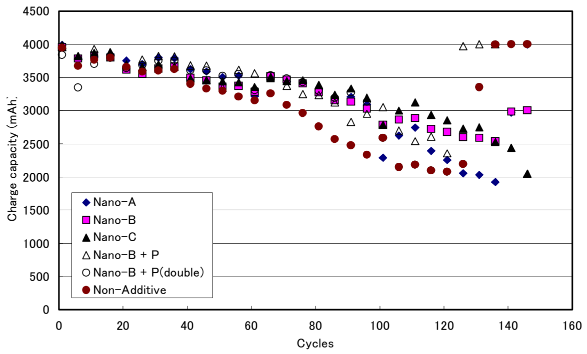

Fig. 3 Charge capacities of the lead-acid batteries added with and without various additives during charge-discharge cycles.

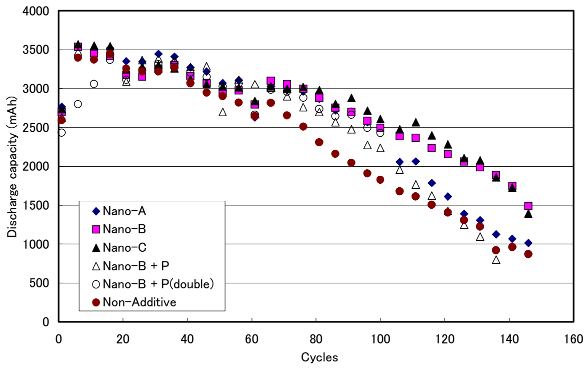

Fig. 4 Discharge capacities of the lead-acid batteries added with and without various additives during charge-discharge cycles.

tive was effective until 100 cycles, its ability abruptly decreased over 100 cycles suggesting the carbons may be consumed by oxidation at the electrodes. Namely, the thicker the carbon solution, the better performance would be obtained. The production cost and the risk of the short circuit between the electrodes, however, will increase. Consequently, the conductivity of electrolyzed carbon solution is enough at 2.0 mS/cm.

As shown in Figure 5, the internal resistances of batteries added with additives gradually increased with cycles, although that of no-addition abruptly increased after 180 cycles consistent with the decrease in the discharge capacity of the battery. So the internal resistance of batteries would also become a good indicator of the deterioration.

The solution of electrolyzed carbon particles, Nanocaloid, would be promising to reactivate quickly and to re-use the deteriorated lead-acid batteries as reuse batteries.

4. CONCLUSION

Several kinds of additives have been tested using prac-

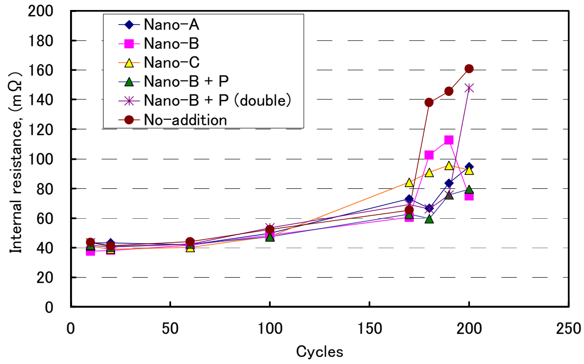

Fig. 5 Change in the internal resistance of the lead-acid batteries added with and without various additives during charge-discharge cycles.

tical lead-acid batteries. The following results were confirmed.

Organic polymer P is effective for prolongation the lifetime of lead-acid battery if it is used with a suitable amount and a charging-mode.

The solution of electrolyzed carbon particles with 2.00 mS/cm is also effective for enhancement of the battery performance, and more effective if it is used together with a small amount of organic polymer, such as 0.1 % (weight/volume).

The change in the internal resistance of the lead-acid battery during charge-discharge cycles coincides with that of the discharge capacity of the tested battery, so the internal resistance would become a good index of deterioration of the battery.

The solution of electrolyzed carbon particles, Nanocaloid, would be promising to reactivate the deteriorated lead-acid batteries used as reuse batteries, if it is used together with a suitable amount of organic polymer, such as P.

Acknowledgements

The authors would like to thanks to Ministry of Economy, Trade and Industry, Chubu Bureau of Economy, Trade and Industry for authorizing a business “Nanoca” “ecologist members service” of Shion Co.,Ltd. as one of new cooperation plans of 2005.

References

Ikeda, S., H. Oka, S. Iwata, Y. Suzui, S. Sakuragi, Y. Mori, M. Maeda, M. Ohta, Y. Liu, H. Ono, S. Ono, and A. Kozawa, Effects of Additives on Positive and Negative Electrodes of Lead-Acid Batteries (3), *Abstract of 72th Annual Meeting of ECSJ*, 1J33, 285, Kumamoto, April 1, 2005.

Ikeda, S., H. Oka, Y. Mori, M. Maeda, M. Ohta, S. Ono, and A. Kozawa, Effects of Additives on Positive and Negative Electrodes of Lead-Acid Batteries, *2004*

Joint International Meeting on Electrochemistry (206th Meeting of The Electrochemical Society) in Hawaii, Abstract, No. 467, October 3, 2004.

Ikeda, S., T. Kamibayashi, R. J. Brodd, and A. Kozawa, Voltammetric Studies of Organic Polymers for Lead-Acid Battery Activator, *ITE Letters*, Vol. 1, No. 1, 120-127, 2000.

Kozawa, A., M. Yamashita, S. Ikeda, J. C. Nardi, and J. Brodd, Comparison of Methods for Reactivating Deteriorated Lead Acid Batteries, *ITE Letters*, Vol. 1, No. 3, 382-390, 2000.

Kozawa, A., S. Ikeda, J. Broadhead, and R. J. Brodd, New Additives for Extending Lead Acid Battery Life Two to Three Times, *ITE Letters*, Vol. 1, No. 1, 128-131, 2000.

Kozawa, A., S. Mase, and M. Sano, New activators for lead-acid batteries, *Kagaku Kogyo*, Vol. 49, No. 1, 73-76, 1998.

(Received December 2, 2005; accepted December 5, 2005)