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Charging operation with high energy efficiency for electric vehicle valve-regulated lead–acid battery system

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Abstract

A new, high-energy-efficiency charging operation with as little amount of overcharge as possible is proposed to improve the energy efficiency and the cycle life for an EV valve-regulated lead–acid battery. Under this operation, the EV battery system is charged with 105% of amount of the preceding discharge five out of six times and once with 115% in order that it is fully charged. The cycle lives were estimated using a valve-regulated lead–acid battery system of 12 modules connected in series, by SFUDS79 pattern discharging and measurement of the amount of discharge every 50 cycles. Three-step constant current charging with 115% of amount of the preceding discharge required more than 5 h with the final charging step of more than 210 min, with coulomb efficiency of only 87% and energy efficiency of 74%. On the other hand, under the high-energy-efficiency charging operation, three-step charging with 105% shortens the final charging time to 132 min. It was completed in less than 4 h with coulomb and energy efficiency of 95% and 84%, respectively. This operation increased the energy efficiency from 74% to 83% on average in six chargings, and extended the cycle life by about 30% to more than 400 cycles. Decreasing the amount of charge by as much as possible suppressed the corrosion of the grids in the positive plate and the heat evolution in batteries due to shortening of the final charging step. Although the high-energy-efficiency charging operation led to the accumulation of inactive $PbSO_4$ at the upper part of the negative plate, possibly due to the decreasing amount of overcharge, this operation could prolong the cycle life. Full charging once every six times is though to be effective in suppressing degradation caused by the accumulation of inactive $PbSO_4$ in the negative plate due to the shortage of charge. © 2000 Elsevier Science S.A. All rights reserved.

Keywords: Valve-regulated lead–acid battery; Charge condition; Energy efficiency; Electric vehicle; Multi-step constant current charging

1. Introduction

The popularization of electric vehicles (EVs) is expected as a result of efforts to alleviate problems related to the global environment and for the efficient utilization of energy. One of the main issues of concern in electric power supply management is how to increase the night-

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time electric load for the purpose of utilizing electric power generation equipment with high efficiency. For the popularization of EVs, the conditions for charging EV batteries with available current patterns should allow complete charging in less than 5 to 8 h, and effectively increase the electric load during the period of minimum use between 2:00 and 5:00 am in Japan [1]. In 1995, 10 Japanese electric power companies and the Central Research Institute of Electric Power Industry (CRIEPI) started a 3-year collaborative investigation of battery systems for EVs [2–5].

Some vehicle manufacturers have proposed the production and sale of a new EVs battery, e.g., a Ni/MH battery or lithium-ion battery, these years. Battery types for EVs should be selected considering the cost, safety and performance of energy density, power density and cycle life. A lead–acid battery may become popular in the near future due to the benefits of cost performance, safety and ease of maintenance [6,7]. However, it has lower energy efficiency on discharge/charge than the Ni/MH battery or the lithium-ion battery. It is therefore necessary to determine new operating conditions with high-energy efficiency for the lead–acid battery to be used as an EV battery.

In previous papers [4,5], the multi-step constant current method was discussed for EV valve-regulated lead–acid batteries. The new charging method with a four-step constant current appears to be completed in less than 5 h and prolongs the cycle life of batteries in the system. An appropriate charging current of around 0.5CA for the first-step constant current is expected to further prolong the cycle life. Therefore, four- or six-step constant current methods with the first-step constant current of 0.5CA could shorten the charging time to less than 5 h as well as yield higher energy efficiency and enhanced cycle life. Clarification of the degradation mechanism of the batteries revealed that the conditions for multi-step constant current methods suppressed heat evolution and water loss during charging. In the next step, we should investigate a new charging method, which completes charging in a shorter time with high-energy efficiency on discharge/charge.

It is very important to enhance the energy efficiency on discharge/charge under daily operation of EVs. We should discuss the charging method for decreasing amount of charge by as much as possible to enhance energy efficiency and shorten charging time with a long cycle life.

In this paper, a new charging operation of three-step constant current charging with as little amount of overcharge as possible is proposed to realize high energy efficiency with longer cycle life.

2. Experimental

2.1. Valve-regulated lead–acid batteries

Two battery systems were constructed using 12 valve-regulated lead–acid batteries (12 V/60 Ah, type-B standardized by JEVS) in series connection. The battery systems were set in battery boxes with fans, which simulated the battery arrangement under the floors of EVs [4,5].

2.2. Discharge patterns

Discharge with SFUDS79-pattern [8] was regulated by the conditions of a capacity of 48 A h or voltage of 84 V for cycle tests. Two kinds of discharge for the measurement of capacity were performed every 50 cycles. One was discharge with a constant current of 1/3CA (20 A) under 118.8 V (9.9 V/module), and the other was subjected to a SFUDS79-pattern discharge to less than 84 V. In these measurements, the systems were charged by the two-step constant current method with the first constant current of 0.2CA (12 A) to a predetermined voltage (172.8 V) and the second constant current of 0.05CA (3 A) at a capacity corresponding to the preceding discharge capacity [5].

2.3. Charge patterns

The charge conditions were set in order to achieve complete charging of the battery systems in less than 8 h during the nighttime. The battery systems were charged by the three-step constant current method with constant currents of 0.5CA + 0.2CA + 0.05CA (30 A + 12 A + 3 A). The battery system should be charged with 115% of the preceding discharge capacity to achieve longer cycle life due to the suppression of degradation by the shortage of charge [5].

In this study, a new operation with control of the amount of charge, as in a weekly operation, is proposed. The battery system was charged with only 105% of amount

Table 1
Charging conditions for HEEC operation and normal charging operation

	Charging pattern	Amount of charge	Frequency
HEEC operation	Three-step constant current charging (30 A + 12 A + 3 A)	105% of amount of the preceding discharge	five times per six chargings
		115% of amount of the preceding discharge	once per six chargings
Normal charging operation	Three-step constant current charging (30 A + 12 A + 3 A)	115% of amount of the preceding discharge	every time

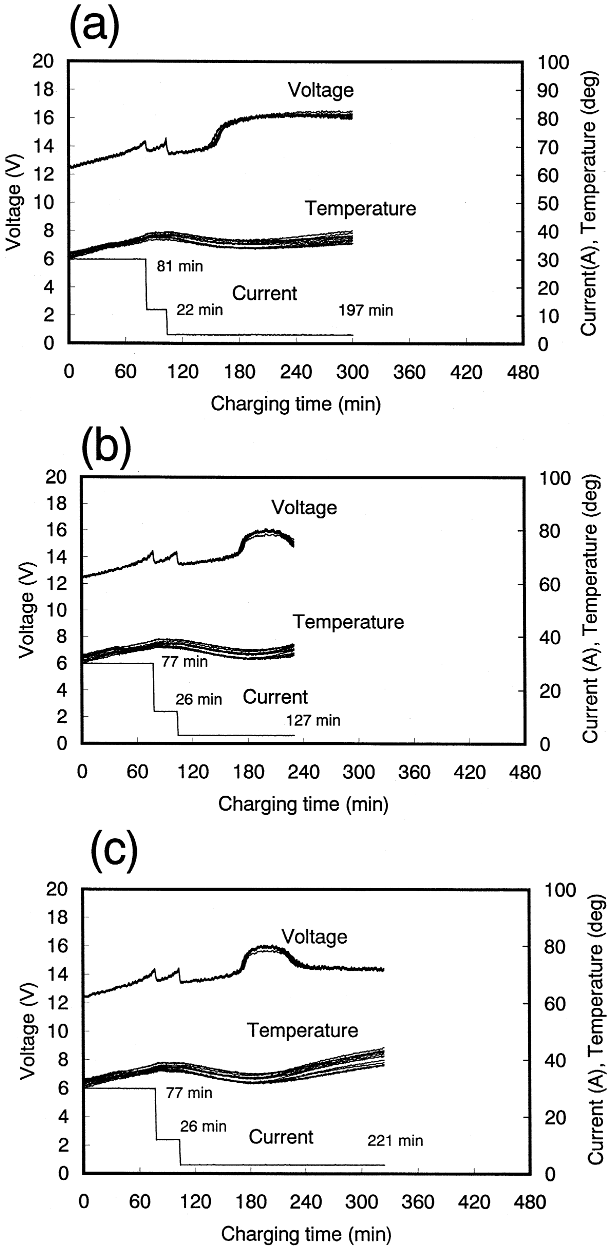

Fig. 1. Charging profiles with voltage, current and temperature under the HEEC operation: (a) with 115% of amount of the preceding discharge at the 9th cycle, (b) with 105% of amount of the preceding discharge around the 100th cycle, (c) with 115% of amount of the preceding discharge around the 100th cycle.

of the preceding discharge five times and once with 115%, as a weekly operation. The charging method with 115% of the preceding discharge capacity was termed the "normal charging operation", and that with both 105% five times and 115% once was termed the "higher-energy-efficiency charging operation (HEEC operation)." The system was charged by the three-step constant current method with 0.5CA + 0.2CA + 0.05CA (30 A + 12 A + 3 A) by regulating amount of charge. Each step was regulated by a voltage of 172.8 V, except the final step of 3 A in Table 1.

2.4. Definition of cycle life

In this study, the cycle life of the battery system is judged by the three parameters of battery voltage and two types of discharge capacities with the SFUDS79 pattern and constant current. The cycle life test was stopped when any battery showed a voltage decrease to zero on discharge during the cycle test, the amount of discharge measured from the SFUDS79 pattern every 50 cycles decreased to less than 80% of the first amount of discharge, or that obtained with constant current decreased to less than 48 A h [3–5].

On completion of the cycle life test, some batteries were disassembled and analyzed by XRD, SEM, EPMA and chemical analysis methods, in order to elucidate their degradation mechanism.

3. Results and discussion

3.1. Cycling test

The charging profiles with voltage, current, and temperature and charging time for each step under both HEEC and normal operations are shown in Figs. 1 and 2, respec-

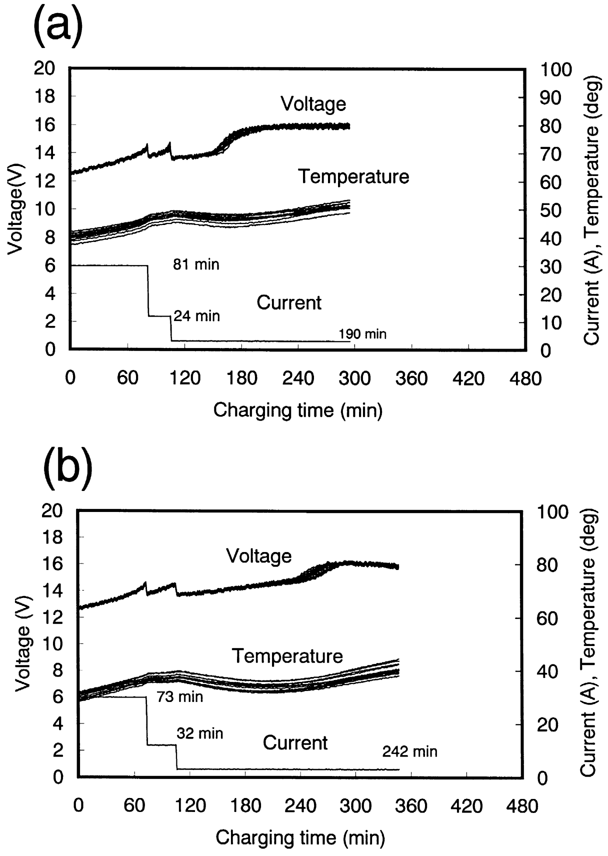

Fig. 2. Charging profiles with voltage, current and temperature under the normal operation: (a) with amount of charge of 115% of the preceding discharge capacity at the 9th cycle, (b) around the 100th cycle.

Table 2
Energy efficiency and cycle life for high-energy-efficiency and normal operations around the 100th cycle

	Amount of charge (%)	Charging time (min)	Average charging voltage (V)	Energy efficiency (%)	Average energy efficiency (%)	Cycle life
HEEC operation	105	230	160.1	83.6	82.5	431
	115	324	160.8	76.0		
Normal charging operation	115	347	167.7	73.7	73.7	310

tively. The results for cycle tests are summarized for the charging time around the 100th cycle, the energy efficiency and the cycle life, in Table 2. The coulomb and energy efficiencies are defined as the ratio of amounts of SFUDS79-pattern discharge per that of the preceding charge, respectively, in this study.

Under the HEEC operation, three-step charging with 105% of amount of the preceding discharge was completed in 230 min, with the final charging step lasting only 132 min, with coulomb efficiency of about 95% and energy efficiency of 84% (Fig. 1b). In contrast, charging with 115% of amount of the preceding discharge once per six chargings was completed in 324 min with the final charging step requiring more than 210 min, with coulomb and energy efficiencies of only 87% and 76%, respectively, as shown in Fig. 1c. The decrease of amount of charge by 10%, i.e., about 5 A h, directly shortened the final charging time by 80 min (Fig. 3). After charging only with 105% under the HEEC operation, the battery system could complete SFUDS79-pattern discharge until 80% DOD sufficiently. The HEEC operation presents the energy efficiency of about 83% on average.

On the other hand, three-step charging under the normal charging operation required 5 h and 47 min, as shown in Figs. 2 and 3. The energy efficiency on discharge/charge was calculated the energy efficiency of 74% with coulomb efficiency of 87% during the normal charging operation. This HEEC operation could increase the energy efficiency from 74% to 83% and shorten the charging time from 347 min (about 6 h) to 246 min (about 4 h) on average in six chargings. The energy efficiency under the normal charging operation proved to be lower by 2% than that under HEEC operation because charging profiles under HEEC operation showed lower voltage than that under the normal one.

Figs. 1 and 2 show the profiles of charging with each voltage, temperature and current, under the HEEC operation and the normal charging operation. Under the HEEC operation, the voltage profiles showed a small peak in the final step charging. However, no such voltage change could be observed under the normal charging operation. It is a characteristic feature of the HEEC operation.

The marked small peak in the voltage profile during the final step charging was present at the same position of charging time under HEEC operation in the cycling test (Fig. 1). Under the normal operation, the appearance of voltage evolution was delayed with respect to charging

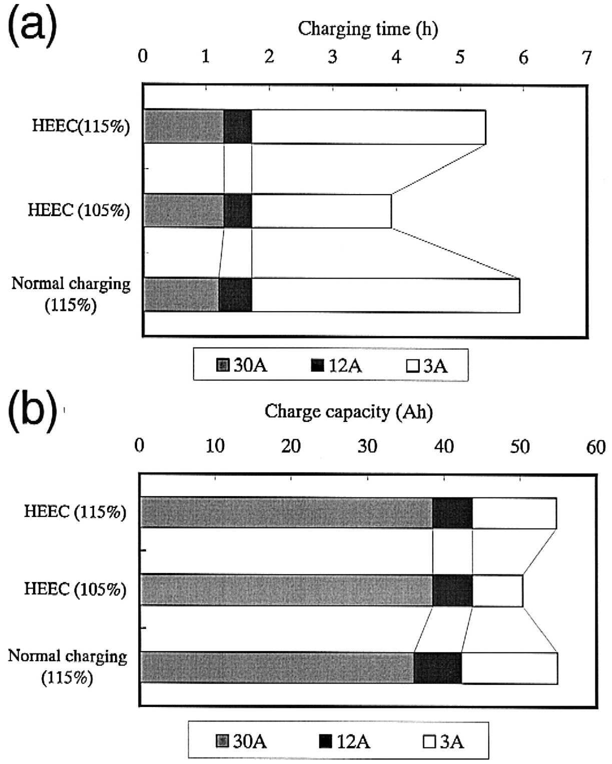

Fig. 3. Charging time and amount of charge for each step under the high-energy-efficiency operation and the normal charging operation: (a) charging time, (b) amount of charge.

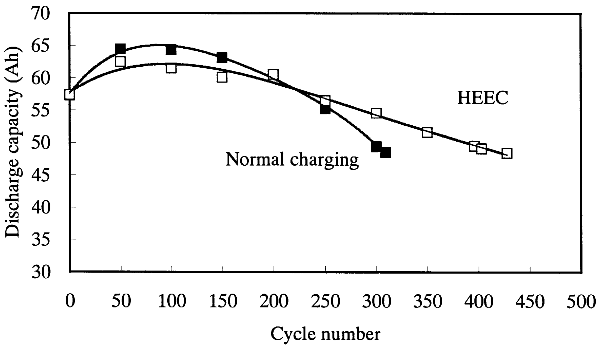

Fig. 4. Cycle life test with discharge capacity by constant current of 1/3 C (20 A): open squares; HEEC operation; closed squares; normal charging operation.

Table 3
Discharge capability (limited electrode) with low and high rates for the cells in the batteries during each cycle and after the cycle test under high-energy-efficiency and normal charging operation

	Discharge rate (cycle number)	Limited electrode				
		0	200	310	370	431
HEEC operation	low rate (1/3C)	Both	Negative	–	Positive	Negative
	high rate (3C)	Both	Negative	–	Positive	Negative
Normal charging operation	low rate (1/3C)	Both	Negative	Positive		
	high rate (3C)	Both	–	Positive		

time, as the cycle testing progressed, because the active material became active due to charging with amount of overcharge (Fig. 2). The voltage falls around the end of charging, due to heat evolution by hydrogen recombination on the negative plate. In HEEC operation, the active material was not active due to less amount of overcharge. This inactive material becomes highly resistant on charging, so that the marked small peak of voltage in charging was observed during the third step.

Under the normal charging operation, the amount of discharge increased to about 65 A h around the 100th cycle and decreased to below 48 A h after the 300th cycle, as shown in Fig. 4. In contrast, the HEEC operation prevented the amount of discharge from rising and it tended to remain almost constant. As a result, the cycle life could be extended to more than 400 cycles.

3.2. Degradation mechanism

To elucidate the degradation mechanism for battery modules during a cycling test, two modules were examined at the 200th cycle in the two systems. Other modules were analyzed after the cycle test for both systems. Additionally, another module was examined at the 370th cycle for the system under the HEEC operation.

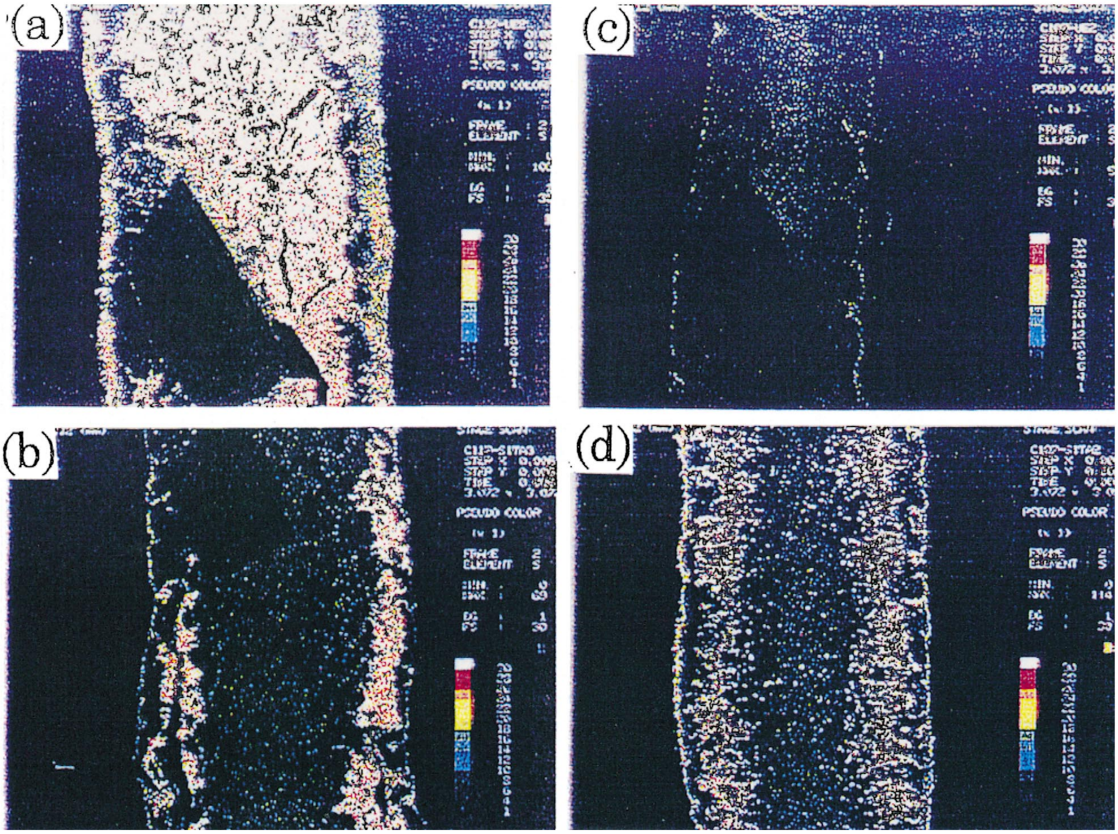

Fig. 5. The EPMA image for the distribution of sulfur on the negative plate charged under HEEC operation and normal charging: (a) a part at the top, and (b) the bottom of the negative plate of the battery under HEEC operation, (c) a part at the top, and (d) the bottom of the negative plate under normal charging.

From the results of the measurement of the discharge voltage of the cells using $Cd/CdSO_4$ as the reference electrode, the reduction in amount of discharge was found to be attributed to the capacity loss of the negative plate at the 200th cycle under both operations. Near the end of the cycle life, the capacity loss of the positive plate reduced the amount of discharge (Table 3). Measurement of the discharge voltage of the cells using the reference electrode showed that a change in the potential of the negative plate caused a marked change in the voltage in the final step of three-step charging under HEEC operation.

By means of EPMA observation (Fig. 5), the presence of sulfur was found only at the upper part of the negative plate in the cells charged at the 200th cycle under the HEEC operation. In many cases, sulfation at the lower part of the negative plate occurs due to the shortage of amount of charge and reduces the discharging capability of modules. Full charging once every six times is thought to be effective in suppressing degradation due to the accumulation of sulfur, inactive $PbSO_4$. The presence of sulfur at the upper part of the negative plate is characteristic of the HEEC operation, and it could cause a marked voltage change in the final charging step under the HEEC operation.

EPMA observation of the negative plate at the 370th cycle revealed the presence of sulfur at both its lower and upper part. This result suggested the degradation tendency of the battery due to sulfation of the lower part of the negative plate near the end of the cycle life, while the reduction in amount of discharge was attributed to the capacity loss of the positive plate, as shown in Table 3. It is therefore important to analyze the battery after the cycle test to elucidate the degradation mechanism of battery modules.

On comparing the charging times for the three-step method with 115% under both operations, normal charging was found to take longer than the HEEC operation, by approximately 20 min (Figs. 1 and 2). The presence of $PbSO_4$ at the upper part of the negative plate could prevent the voltage from rising quickly under the HEEC operation. Therefore, the system obtained a much larger amount of charge in the first charging step with 0.5CA (30 A) and a higher energy efficiency by 2% under this operation than under the normal charging operation.

Fig. 6 shows an increasing amount of corrosion of the grid in the positive plates during the cycle test under both operations. The amount of corrosion of the grid under HEEC operation was 40% less than that under the normal charging operation. The HEEC operation suppresses degradation due to corrosion of the grid, in addition to keeping the battery temperature low, because the charging with as little amount of overcharge as possible shortens the final charging step.

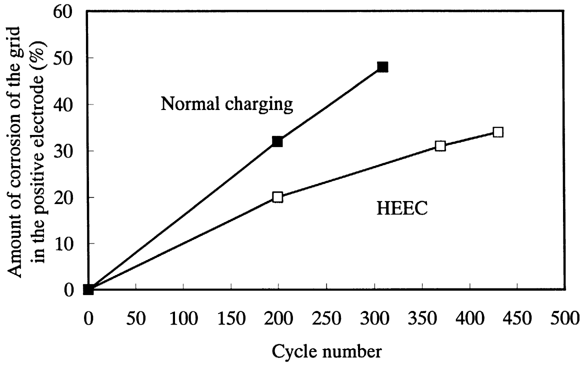

Fig. 6. Amount of corrosion in the grid of the positive plate: open squares; HEEC operation; closed square; normal charging operation.

4. Conclusion

It is important, for the popularization of EVs, to propose a beneficial charging method for the battery system in order to achieve high-energy efficiency without shortening the cycle life. In this paper, a new HEEC operation of three-step constant current charging with as little amount of overcharge as possible was proposed to improve the energy efficiency and the cycle life. Under this operation, the EV battery system was charged with 105% of the preceding discharge capacity five out of six times and once with 115%, in order to be fully charged. Under HEEC operation, three-step charging with 105% required a shorter time for the final charging step. It was completed in less than 4 h with the final charging step lasting only 132 min, with coulomb and energy efficiencies of 95% and 84%, respectively. This operation increased the energy efficiency from 74% to 83% on average in six chargings, and extended the cycle life by about 30%, to more than 400 cycles. Decreasing amount of charge by as much as possible suppressed the corrosion of the grids in the positive plate and the heat evolution in batteries due to shortening of the final charging step.

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References

[1] E. Hayashi, T. Inasaki, F. Anan, Proc. of EVS12 at Anaheim, USA vol. 2 (1994), p. 148.

[2] T. Iwahori, Y. Ibi, F. Anan, Proc. of EVS13 at Osaka, Japan vol. 1 (1996), p. 97.

[3] T. Ikeya, M. Iwasaki, S. Takagi, Y. Sugii, M. Yada, T. Sakabe, E. Kousaka, H. Tsuchiya, M. Kanetsuki, H. Nasu, M. Ono, H. Narisoko, Y. Mita, K. Nishiyama, K. Adachi, T. Iwahori, J. Power Sources 69 (1997) 103.

[4] T. Sakabe, K. Ishihara, K. Nishiyama, S. Nishino, S. Muta, Proc. of EVS14, dialog poster session at Orlando, Florida, USA,1997.

[5] T. Ikeya, N. Sawada, S. Takagi, J. Murakami, K. Kobayashi, T. Sakabe, E. Kousaka, H. Yoshioka, S. Kato, M. Yamashita, H. Narisoko, Y. Mita, K. Nishiyama, K. Adachi, K. Ishihara, J. Power Sources 75 (1998) 101.

[6] J.F. Cole, J. Power Sources 40 (1992) 1.

[7] P.T. Moseley, J. Power Sources 67 (1997) 115.

[8] G.H. Cole, Proc. of EVS9 at Toronto, Canada,1988, EVS88-078.