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Study and application of several-step tank formation of lead/acid battery plates

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Abstract

A several-step tank formation method and related charging equipment have been developed for automotive lead/acid batteries. This process offers the advantages of reduced energy requirements, increased charging efficiency and reduced environmental problems. Results also suggest that several-step formation ameliorates the problem of premature capacity loss and extends the useful service-life of automotive batteries. This is thought to be due to the production of greater amounts of α-PbO_2 in the positive plates.

Keywords: Lead/acid batteries; Several-step formation; Positive plates; Efficiency; Charging

1. Introduction

Usually, formation methods include tank formation, battery formation and plate-group formation. Tank formation is suitable for dry-charged automotive batteries, and usually involves a constant-current method. In China, most battery manufacturers use a one-step formation with constant current; only a fewer use a two-step formation. Recently, two manufacturers have imported formation equipment and technology for a four-step process. Some large manufacturers are studying several-step tank formation, others have abandoned it. The application difficulties with several-step formation are as follows:

1. Several-step formation requires longer time to achieve the same efficiency as given by one- or two-step formation.
2. There is a large rise in the temperature of batteries when the acid solution is added to the cells. After filling, the battery cannot be used for 20 min. Otherwise, the formation efficiency is poor.
3. The voltage of a battery prepared via several-step formation is lower.
4. Formation chargers cannot be controlled automatically, and the current has to be changed manually.

Guangzhou Storage Battery Enterprises Co., Ltd. has overcome the above difficulties and has employed six- to ten-step tank formation since May 1995. There are some advantages with several-step tank formation, e.g., both the performance and the quality of the batteries are improved, the cost of the batteries is lower, environmental pollution is reduced.

2. Basic mechanism of several-step tank formation

One-step tank formation with constant current is the conventional method. It produces, however, large amounts of oxygen gas at the positive plates and hydrogen gas at the negatives. The gases dispel electrolyte from the active materials, contacting areas of electrolyte and active materials are reduced, and resistance to ion diffusion is increased [1]. Moreover, formation efficiency is reduced and excessive gas evolution may loosen the active materials from the plates.

In the ideal situation, formation should produce less oxygen and hydrogen gas at the end than at the beginning of the process. Several-step tank formation approximates to the ideal current curves for constant-voltage charging, see Fig. 1. By contrast, the current for conventional formation is shown in Fig. 2. At the beginning and final stages of conventional formation, the constant-current curve differs markedly from the ideal curve. This lowers the current efficiency compared with several-step formation.

3. Results and discussion

Test results for plates prepared by several-step formation and conventional formation are given in Table 1. The time

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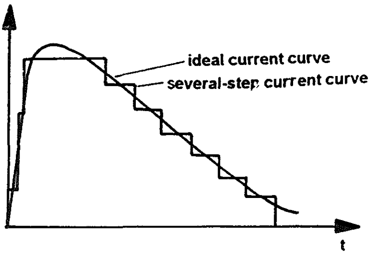

Fig. 1. Current curve of several-step formation.

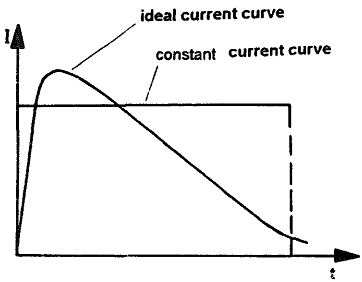

Fig. 2. Current curve of conventional formation.

for the several-step formation is 20 h, but the time for conventional formation is 22 h. Because the charge efficiency of the negative plates is not the controlling factor and the PbO content is influenced by the drying conditions, it is not necessary to consider the PbO content of the negative plates. The efficiency of the formation can be assessed from the PbO_2 content of the positive plates. The efficiency of several-step formation is satisfactory, but the charge capacity is lower. Nevertheless, this formation can save greater amounts of energy when thicker plates are used. The PbO_2 content of the different positive plates increases marginally with several-step formation. On summer days, the temperature at 20 min after acid filling rises from 31 to 34 °C. Several-step formation provides plates with a good dry-charge, automobile-starting capability.

Different batteries were produced with plates D^1_2 to D^9_{10}. Plastic-cased batteries of 60 and 80 Ah capacity and rubber-cased batteries of 105 Ah capacity were tested according to the Chinese National Standard GB 5008.1-91. The performance of these batteries reached the specifications of the standard. Several-step formation endowed batteries with a better starting capability during the later stages of their cycle life; the voltages at 30 s after 96 cycles are given in Table 2.

The phase composition of the positive active-material was determined by X-ray diffraction phase-analysis. The results are shown in Table 3. The current density in the several-step formation is less than that used in the conventional method. Accordingly, more α-PbO_2 (and, hence, less β-PbO_2) is produced in the several-step process [2]. The α-PbO_2 is composed of large particles and has a small surface area. Thus, it gives a less capacity. On the other hand, the structure of the α-PbO_2 is stronger and this provides a longer battery cycle life. The particles of β-PbO_2 are smaller and have a higher surface area. Consequently, β-PbO_2 promotes a greater battery capacity. The structure of the β-PbO_2 is weaker, how-

Table 1
Influence of different plate-formation methods

Plate type	Positive-plate thickness	Conventional formation			Several-step formation			
		PbO_2 content of positive plate	Temperature at 20 min after acid addition	Discharge time	PbO_2 content of positive plate	Temperature at 20 min after acid addition	Discharge	$\frac{I_st_s}{I_ct_c}$ [a]
	(mm)	(%)	(°C)	(s)	(%)	(°C)	(s)	(%)
D^1_2	2.30	89.88	34.0	248	90.54	33.5	253	80.5
D^3_4	1.80	89.21	33.0	98	89.72	33.0	102	86.3
D^5_6	1.65	89.94	33.0	206	91.25	32.5	208	89.6
D^7_8	1.55	88.23	32.0	203	89.64	32.0	207	89.9
D^9_{10}	1.40	88.38	31.0	198	88.59	31.0	202	91.3

[a] I_st_s: several-step capacity; I_ct_c: conventional capacity.

Table 2
Results of discharge test during late stages of battery cycle life

Battery type/formation method	60 Ah (plastic)		80 Ah (plastic)		105 Ah (rubber)	
	Conventional	Several-step	Conventional	Several-step	Conventional	Several-step
Voltage at 30 s (V)	8.39	8.54	8.11	8.37	7.31	7.53

Table 3
Influence of formation methods on phase composition (wt.%)

Component	Conventional	Several-step
α-PbO_2	11	23
β-PbO_2	79	68
Others	10	9

ever, and the material can shed more easily from the plates. During cycle service, α-PbO_2 is converted gradually into β-PbO_2 [3], i.e.:

(i) discharge:

$$\alpha\text{-}PbO_2 + HSO_4^- + 3H^+ + 2e^- \rightarrow PbSO_4 + 2H_2O \quad (1)$$

(ii) charge:

$$PbSO_4 + 2H_2O \rightarrow \beta\text{-}PbO_2 + HSO_4^- + 3H^+ + 2e^- \quad (2)$$

Although the content of α-PbO_2 decreases on cycling, it still remains in the skeleton of the positive active-material to form a 'backbone' that maintains the integrity of the positive active-material structure [4,5]. Pavlov [6] supports the view that α-PbO_2 strengthens the skeleton of the positive active-material and prevents premature capacity loss (PCL). According to the above concepts, since several-step formation produces more α-PbO_2, it can strengthen the skeleton of the positive active-material and ameliorate PCL effects.

Pavlov [7] has reported that soaking prior to formation ensures good and stable battery performance characteristics. During the soaking period, there are changes in the structure and the morphology of the crystals in the cured paste. After soaking, the skeleton of the active mass becomes quite strong. Soaking can also prevent PCL. The initial charge current in several-step formation is much lower than that in conventional formation. Therefore, it has some correspondence with the soaking process prior to formation, i.e., there is more soaking action with several-step formation than with conventional formation. Consequently, it is concluded that PCL can be prevented by several-step formation. This has been demonstrated by using batteries in cars. The statistics (according to drivers) have shown that the starting capability of batteries with conventional formation plates decreases after six months of battery service. By contrast, batteries with several-step formation plates still provide stable and good starting after eight months. Most of the drivers have been satisfied with the batteries assembled from several-step formation plates.

4. Formation chargers

4.1. Requirement of chargers for several-step formation

The key problem for application of several-step formation is to improve formation chargers. Because the charge current and charge voltage are changed at different stages, it is inconvenient to do this by hand. In particular, some processes cannot be carried out at all, such as the automatic compensation of ampere-hours. A charger controlled by a single chip processor not only solves these problems, but also provides other special functions, such as on-line programming, error alarm, displayed working hours. Although the different battery manufacturers have their own formation method and technology, it is usual to change the following control parameters: time, current, voltage and temperature. Thus, the requirements of the charger are as follows: (i) flexible programming of formation time; (ii) sufficient space for numerous steps in the formation process; (iii) ability to vary the formation current; (iv) ability to control formation voltage; (v) measurement of charge (ampere-hours) and automatic compensation; (vi) memory function to prevent loss of data during power outages, and (vii) the program must be able to work from the interrupted point when power is returned.

4.2. Principle and realization

The main circuit of the charger uses a transformer to convert voltage and then adopts a thyristor inverter circuit system. The control circuit uses a 8031 processor, and a 2764 EPROM is used for the program memory, a 2864A for the data memory, a 0832 as a D/A converter, a 0809 as an A/D converter, and a 8155 as an I/O interface. A key pad is used to input data and LED provides the display messages. The output of the D/A is the set value of the constant-current regulator. The output of the regulator is the control signal to the pulse board. The pulses are used to control the on/off status of a three-phase thyristor bridge. A block diagram of the circuit is presented in Fig. 3.

In order to program on-line and input technical parameters easily, 2864A is used as a data memory. If incorrect data are input, the error can be corrected immediately. This method

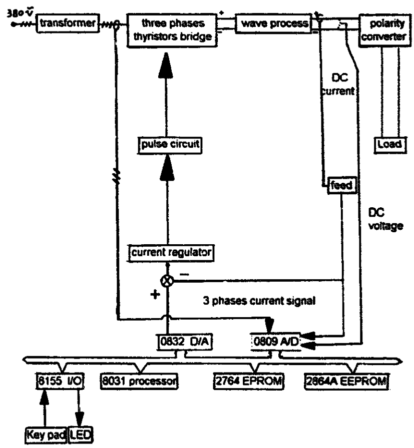

Fig. 3. Block diagram of charger controlled by 8031.

is more convenient than that of putting the technical parameters and the control monitor program together in the 2764 EPROM. An individual development machine is required for inputting the program to the 2764 EPROM. It becomes necessary to erase the program or parameters. On the other hand, the retention characteristics of the 2864A are adopted. When the power is off, the relative information of the charge process is put into the corresponding area of the 2864A by an interrupted service program, and a flag byte is set. This important information remains within the 2864A while the power is off. The program is able to continue to run from the interrupted point when the power is returned. This method differs from that of conventional microprocessor systems, which use RAM as data memory in addition to using batteries to maintain information. The use of the 2864A improves the reliability of the control system.

An LED used to display the charger working time, the step number in the several-step formation, current, voltage, charge mode, ampere-hours, etc. It is easy for the operator to observe the status of chargers. A direct-current feed signal adopts the constant-current control, and the voltage feed signal is used for voltage regulation. The three-phase a.c. current is for the single-chip processor to monitor the status of the transformer current. Should the combined signal of these three phases be larger than one value, it is possible that some of thyristors in the bridge could become broken. The unbalanced current would make the transformer heat quickly. Thus, the processor should send a zero pulse signal to cut out thyristors in order to protect the circuit. The direct signal can be also used to monitor any broken welding of the plates during formation. If the welding is broken, there is an alarm to alert the operator to take corrective action. The chargers meet the requirements of several-step formation. They have been operating for five months and are performing well.

5. Conclusions

Several-step tank formation has been applied since May 1995 with the following results:

1. Several-step tank formation produces more α-PbO_2 than the conventional process. The α-PbO_2 is changed gradually into β-PbO_2 on battery charge/discharge cycling and it may strength the skeleton of the positive active-material and prevent premature capacity loss. There is more soaking action with several-step formation compared with conventional formation. This can also help automotive batteries maintain stable and good starting capability during later stages of service.
2. The charge ampere-hours for several-step tank formation are about 15% less than those required by the conventional method. Several-step formation increases the charging efficiency and reduces atmospheric pollution.
3. Chargers have been developed to apply the several-step tank formation. Formation time, current and voltage can be changed and controlled. Charge ampere-hours can be monitored and compensated automatically. The charger has a memory function when the power is off.

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