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Journal of Power Sources 59 (1996) 51–55

JOURNAL OF POWER SOURCES

Separators for automotive lead/acid batteries: selection of suitable types for different climate zones

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Received 12 November 1995; accepted 28 November 1995

Abstract

World climates are divided broadly into cold, temperate and tropical zones. It is well known that the performance of automotive batteries under cold, warm or hot conditions is determined by the characteristics of the chosen separators. In the battery tests reported here, polyethylene envelope separators are found to be beneficial in cold environments. By contrast, leaf-type, polyethylene, synthetic pulp separators with glass mat give better results in warm conditions and very good peformance at high temperatures. Therefore, it is concluded that polyethylene envelope separators are suitable for cold climates, while leaf-type, polyethylene, synthetic pulp separators with glass mat are more appropriate for warm and hot climates.

Keywords: Lead/acid batteries; Automotive batteries; Envelope separators; Polyethylene; Glass mat

1. Introduction

Lead/acid batteries are important components for automobiles; they are used not only for cranking, but also to power all the electric equipment on the car. Thus, car owners expect reliable performance and good life from the batteries in any climate zone.

The separators used in the batteries are also required to give reliable and sustainable performance. It is commonly acknowledged that a battery is affected by the temperature of operation. In particular, temperature is a primary contributor towards deterioration of the separator. Both battery manufacturers and separator manufacturers are well aware of this fact and, therefore, are conducting research and development to provide battery technology that is compatible with any climate zone.

Nippon Muki Co., Ltd. has performed extensive research on separators for lead/acid batteries during the 60 years that the company has been in existence. Needless to say, the separator material has changed in accordance with the evolution of battery technology during this period. The separator materials have included: wood, rubber, cellulose, synthetic pulp and polyethylene. More recently, an improved polyethylene synthetic pulp separator has been developed with a very thin base in order to lower the electrical resistance. Nippon Muki is the only separator manufacturer in the world to produce all types of separators, i.e., polyethylene synthetic pulp, polyethylene envelope, micro glass-fibre, and glass mat.

2. Functions of the separator

The thin porous separators are not related directly to the electrochemical reactions that take part in the battery. In fact, the separators are placed between the positive and negative plates in storage cells to prevent short circuits and to maintain smooth electrochemical reactions. Separators are very important components for lowering the electrical resistance and making the battery compact. The principal functions and necessary criteria for separators are as follows:

1. to separate the positive and negative plates, both mechanically and electrically;
2. to allow free passage of ions, but to obstruct fine particles of lead;
3. to have good diffusion characteristics and low displacement of electrolyte;
4. to have good resistance to acidic and oxidative attack, and free from soluble harmful substances, and
5. to have diverse characteristics that respond to different kinds of batteries.

Four main types of separator are used frequently in automotive batteries; these are shown in Table 1.

It is an inevitable fact that separators are influenced by temperature because they consist mainly of organic materials and are always exposed to attack by sulfuric acid, as well as by anodic oxidation, via the electrochemical reaction in the cell. Therefore, it is very important to select separators that are sustainable in any of the climate zones in the world.

Elsevier Science S.A.
SSDI 0378-7753(95)02300-3

Table 1
Separator types for automotive batteries

Separator	Manufacturing process	Feature
Cellulosic separator	Paper type products, made from cotton lint or craft pulp and then coated by phenolic resin for acid resistance and strength	1. Comparatively large mean pore size 2. High electrical resistance 3. Poor acid and anodic oxidation
Sintered PVC separator	Made from mixture of PVC and silica fine powder, and then mixture sintered on stainless-steel belt in furnace	1. Medium average pore size 2. High electrical resistance 3. Decomposed easily by anodic oxidation and Cl_2 gas released
Synthetic pulp separator with glass mat	Paper type products, made from polyethylene synthetic pulp, synthetic fibre and fine silica powder, and then heat treated	1. Acid and anodic oxidation proof 2. Fine pore size and very low electrical resistance 3. Flexible characteristics 4. Long service-life at high temperature
Polyethylene envelope separator	Film type products, made from mixture of UHM PE powder, fine silica powder and mineral oil. Then mixture is extruded as a film and made porous by extracting the mineral oil	1. Acid and oxidation proof 2. Excessive fine pore size 3. Very low electrical resistance 4. Very large specific surface area 5. Very good flexible characteristics

3. Test methods

There are many test methods for separators, e.g., JIS, SAE and DIN standards. The tests that are largely related to temperature are listed in Table 2. The author's company has cooperated with certain battery manufacturers in Japan to perform such tests on a type 55D23R hybrid battery. This is the most popular type of automotive battery in Japan. The design specifications of the 55D23R unit are given in Table 3.

Separators made from cotton lint or craft pulp, as shown in Table 1, cannot meet the operational requirements of present batteries in terms of either high-rate discharge or maintenance-free performance. Poly(vinyl chloride) (PVC) separators are equally unsuitable for maintenance-free performance. As a result, polyethylene envelope (PE) separators and polyethylene synthetic pulp (SP) separators are gradually becoming the most popular. Accordingly, a PE separator and an SP separator with glass mat (GM) were chosen for the above battery tests. The PE separator was the PM-A2500 type (ultra-high molecular weight (UHM) polyethylene separator) manufactured by the author's company. The characteristics of the PE and SP separators with GM are given in Table 4.

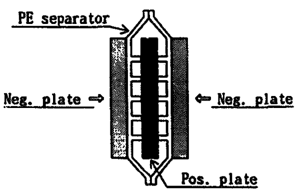

Fig. 1. Schematic of battery assembled with PE separators.

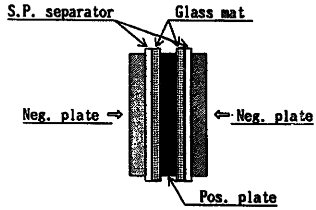

Fig. 2. Schematic of battery assembled with SP separators and glass mat.

There are two battery-assembling methods with the PE separator, i.e., one is a positive-plate envelope, the other is a negative-plate envelope. In the tests reported here, the positive-plate envelope was used; the upper cross section is shown in Fig. 1. For the SP separator, the glass mat was contacted with the positive plate and the separator was positioned on the negative side; the upper cross section is shown in Fig. 2.

4. Results and discussion

The tests were carried out in 1994 through 1995 for the batteries with PE separators or SP separators with GM. The performance data of these batteries are shown in Tables 5–9 and Figs. 3 and 4.

4.1. C_5 capacity and reserve-capacity tests

The capacity at the $C_5/5$ rate depends on the quantity of both active material and electrolyte. In these tests, the batteries had the same composition of active materials and the same plate weights. The batteries with PE separators had a slightly larger amount of electrolyte than those with SP separators

Table 2
Test methods for automotive battery separators

Test	Outline	Purpose
C_5 capacity	Capacity at $C_5/5$ discharge	Basic performance
Reserve capacity	Discharge time at 25 A discharge	Reserve capacity
High-rate discharge		
constant-current discharge	Voltage at 5 or 30 s at fixed current	Cranking ability
cold-cranking amperes (CCA)	Amperes for discharge voltage to 7.2 V at 30 s	Cranking power
Cycle-life		
Heavy duty (JIS)	1 h discharge at 40 A and 5 h charge at 10 A is 1 cycle Count the cycles when battery reaches 40% of C_5 capacity (Apply 0.5 of above current for batteries smaller than 24 Ah)	Presumed life for deep-cycle use in commercial cars
Light duty (SAE)	4 min discharge at 25 A and 10 min charge at 14.4 V constant voltage (max. 25 A) is 1 cycle. High-rate discharge at fixed current after 56 h stand after every 480 cycles. Count the cycles for terminal voltage to fall below 7.2 V	Presumed life for light-cycle use in private cars

Table 3
Specifications of 55D23R battery

Dimension	Capacity		High-rate discharge				Reserve capacity	JIS life
$h \times w \times l$ (mm)	5 h (Ah)	20 h (Ah)	Temperature (°C)	Discharge (A)	Time (min)	V at 5 s (V)	(min)	(cycles)
225 × 173 × 232	48	60	−15	300	1.6	7.5		300
SAE standard	CCA = −18 °C, 356 A						99	
Dimensions of plate (mm)	Positive: 144 (w) × 110 (h); thickness: 2.7 Negative: 144 (w) × 110 (h); thickness: 2.4							
Number of plates	5 positive/6 negatives							

Table 4
Characteristics of battery separators

Separator parameter	Envelope separator (PE separator)	Leaf separator (SP separator with GM)
Type	PM-A 2500 (Nippon Muki)	Lewk (Nippon Muki)
Overall thickness (mm)	1.10	1.10
Web thickness (mm)	0.25	0.30
Rib height (mm)	0.85	
Rib pitch (mm)	12.0	
Electrical resistance (Ω 100 cm²)	0.0009	0.0007
Mean pore size (μm)	0.1	0.2
Glass mat thickness (mm)		0.80
Main materials	Ultra-high molecular weight PE/fine silica powder	Polyethylene synthetic pulp/acid and oxidation resistant synthetic resin fibre/fine silica powder

Table 5
C_5 and reserve-capacity tests

Battery performance	Envelope separator (PE separator)	Leaf separator (SP separator with GM)
C_5 capacity at 25 °C (Ah)	47.2	46.8
Reserve capacity at 25 °C (min)	99.6	95.8
Reserve capacity at 40 °C (min)	135.8	136.0

Table 6
JIS test [a]

Battery performance	Envelope separator (PE separator)	Leaf separator (SP separator with GM)
Voltage at 5 s (V)	9.11	9.08
Discharge time (s)	133	132

[a] Test curve is shown in Fig. 3.

Table 7
Cold-cranking amperes test

Battery performance	Envelope separator (PE separator)	Leaf separator (SP separator with GM)
CCA at − 18 °C (A)	443	432
CCA at 25 °C (A)	460	459

Table 8
Cycle-life tests

Battery performance	Envelope separator (PE separator)	Leaf separator (SP separator with GM)
JIS cycle-life at 65 °C	103	185
SAE cycle-life at 25 °C	9400	12100
SAE cycle-life at 65 °C [a]	2590	4380

[a] Cycle-life test curve is shown in Fig. 4.

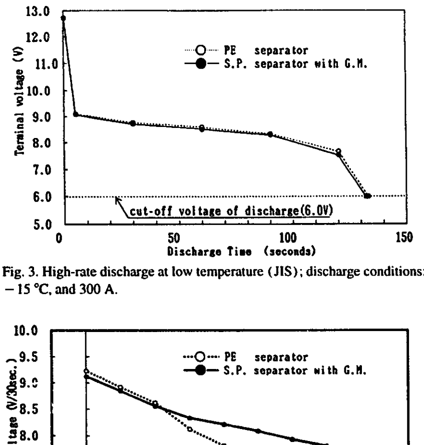

Fig. 3. High-rate discharge at low temperature (JIS); discharge conditions: − 15 °C, and 300 A.

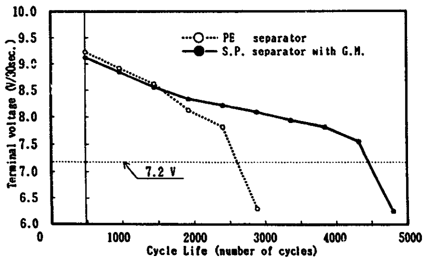

Fig. 4. SAE cycle-life test at high-temperature charge: 14.8 V (maximum 25 A), 10 min; discharge: 25 A, 4 min; rest period: 56 h, and temperature: 65 °C.

and GM. This is because the latter types had more displacement of electrolyte due to the presence of the glass mat. Nevertheless, the batteries had more than 120% of the electrolyte required for the $C_5/5$ discharge. Thus, it was considered that this quantity of electrolyte is sufficient for the $C_5/5$ test, and that there was no effect of electrolyte limitation. As expected, the separator types yielded similar results (Table 5).

In the reserve-capacity test, the capacity again depends on the the quantity of both active material and electrolyte, but the discharge current is 25 A which is about 2.5 times that used at the $C_5/5$ rate. Thus, an adequate supply of electrolyte is necessary for the active materials; in particular, excess electrolyte around the positive plates is advantageous. Therefore, since the PE separator has less displacement, it is more beneficial than the SP separator with GM.

The test results showed that the PE separator delivered about 5% more discharge time at 25 °C (Table 5). Both separator types gave the same time at 40 °C. Thus, the diffusion of electrolyte improves in proportion with the rising temperature and the necessary diffusion for the reserve-capacity is obtained at high temperatures.

4.2. High-rate discharge tests

4.2.1. JIS high-rate discharge test at low temperature

The discharge time in this test is not influenced by separator performance (Table 6), but it is anticipated that the voltage after 5 s is related to the electrical resistance, especially for the separators with GM. The 5 s voltage is very similar, however, for both types of separator, despite the fact that the SP separator itself has a lower electrical resistance. This is because of the added electrical resistance of the GM. The viscosity of the electrolyte increases at low temperatures and the electrolyte diffusion becomes poor, so that gas bubbles trapped in the glass mat are hardly released and the flow of ions is obstructed. Thus, the electrical resistance becomes higher.

The viscosity of the electrolyte decreases as the temperature rises, the gas bubbles are released from the GM, and the electrical resistance becomes lower. Accordingly, there is no difference in the initial high-rate voltage for these test separators. The discharge time is the same for both types of separator under all test conditions.

4.2.2. Cold-cranking amperes test

This test method is a comparatively new idea and determines the maximum discharge rate (in A) that will sustain a minimum terminal voltage of 7.2 V for 30 s. If the battery displays a large fall in voltage, the maximum discharge rate will be small. The electrical resistance of the separator influences the voltage-drop performance of the battery. The lower the electrical resistance of the separator, the better the cold-cranking amperes (CCA) performance. Therefore, PE separators should be more advantageous than SP separators with GM, as expected above for the JIS high-rate discharge test.

The test results confirmed that the PE separator gives an excellent maximum discharge rate at − 18 °C, but displays almost the same maximum discharge rate at 25 °C as the SP separator with GM (Table 7).

Table 9
Battery failure modes [a]

Battery performance		Envelope separator (PE separator)	Leaf separator (SP separator with GM)
Separator	shorts through cracks	M	N
Positive plate	grid corrosion;	M	Y
	shedding of active material	H	L
Others	shorts at upper parts of plate	L	N

[a] M: several; H: many; N: none, and L: few.

4.3. *Cycle-life tests*

The results from JIS and SAE cycle-life tests at 65 and 25 °C, respectively, are given in Table 8. The failure modes of the test batteries at 65 °C are listed in Table 9.

4.3.1. *JIS, heavy load, cycle-life test*

This is a cycle-life test to high depths-of-discharge. Thus, the failure mode is expected to be shedding of active material from the positive plates. The presence of GM should ameliorate this problem. This was confirmed on disassembling the cells after testing. It was also found that the GM prevented oxidation of the separator. On the other hand, it was revealed that the batteries assembled with PE separators failed through piercing short-circuits in the top parts and sediment short-circuits in the bottom parts.

The piercing short-circuits arose through penetration of the PE separator with active material. This was because the PE separator was extended and curved by the high temperature so that the separator web came into direct contact with the positive active-material. From oxidation by the positive active-material, the separator developed cracks in the web along the ribs.

The sediment short-circuit at the bottom parts was due to leakage of sediment. These sediments came from shedding of the positive active-material and accumulated at the bottom of PE separators. As a result, the separators were eroded and cracks were produced at the folded parts inside the bottom of the separators.

4.3.2. *SAE, light load, cycle-life test*

This is a cycle-life test at shallow depths-of-discharge. Thus, shedding of positive active-material should be negligible. The cycle life of batteries with PE separators without glass mat decreased suddenly at a certain stage at 65 °C. It was found that short-circuits had developed by passage of active material through cracks along the ribs of the PE separators, in a similar manner to that observed in the JIS life test. The shed material had also piled up on the upper edges of the positive plates and, thereby, had created short-circuits between the positive plates and the connecting strap of the negative plates. It was concluded that this phenomenon resulted from the fine powder of the sediments being thrown up by convection of electrolyte and piling up on the top of the positive plates because the convection in this region is restricted to the inside of the PE envelope separators.

5. Summary of test results

1. For low-rate discharge, e.g. $C_5/5$ rate, batteries assembled with either PE separators or SP separators with GM gave equivalent performance.
2. In reserve-capacity tests, the batteries assembled with PE separators delivered superior power at low temperatures. By contrast, batteries assembled with SP separators and GM gave the same power as those assembled with PE separators at higher-than-normal temperatures.
3. In high-rate discharge tests, batteries assembled with PE separators provided better performance at low temperatures, but batteries using SP separators with GM gave a similar high performance to those assembled with PE separators at higher-than-normal temperatures.
4. In cycle-life tests, batteries with PE separators displayed shorter lifetimes at high temperature, but batteries assembled with SP separators with GM gave remarkably long cycle lives under medium- and high-temperature conditions.

6. Conclusions

The appropriate selection of separators for automotive batteries in different climate zones is as follows:

- cold zone: PE separator
- temperate zone: SP separator with GM; but PE separators can be used if there are very cold temperatures during the four seasons, and the road conditions are good
- tropical zone: SP separator with GM