



# Endurance of batteries and separators in automotive applications under high-temperature conditions

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## Abstract

Endurance tests under high-temperature conditions have been performed on three groups of automotive batteries. One group has been assembled with polyethylene pocket separators for the negative plates, another with polyethylene pocket separators with glass mats for the positive plates, and a third with leaf-type synthetic pulp separators with glass mats. Negative plates developed a sand-like appearance in the batteries assembled with the polyethylene pocket separators for the negative plates. Evidence of piercing shorts is found in batteries assembled with polyethylene pocket separators with glass mats for the positive plates. Also presented are the results of a structural analysis of failures in polyethylene separators after a series of cycle-life tests under high-temperature conditions, together with a theoretical examination of the deterioration process of the polyethylene pocket separators. It is concluded that battery assembly with polyethylene pocket separators with glass mat is an effective way to achieving good endurance (i.e., life extension at high temperature). On the other hand, the selection of leaf-type synthetic pulp separators with glass mats is the best approach for hot climatic conditions. © 1998 Published by Elsevier Science S.A. All rights reserved.

*Keywords:* Lead/acid batteries; Automotive batteries; Pocket separator; Glass mat; Polyethylene separator; Synthetic pulp separator

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## 1. Introduction

Recently, many industries world-wide have become very conscious in developing and producing environmentally-friendly products and those with a long service life to conserve further dwindling natural resources. It goes without saying that the battery is no exception, and to produce batteries with long service lives is one of the ways to attain the goal of energy sustainability.

Meanwhile, it is well established that the performance of plates and separators exerts a major influence on the service life of batteries. Accordingly, separator manufacturers are making efforts to develop separators which can prolong the life of plates and thus contribute to the extension of battery life.

In a previous work, Endoh [1] reported that one reason for the short life of batteries assembled with polyethylene pocket separators (called 'PE separator' hereafter) is the

development of internal short-circuits at the bottom part of the PE separator due to anodic corrosion causing active material to shed from the positive plates and leak through the separators. He also found that when synthetic pulp separators (called 'SP separator' hereafter) with glass mats (called 'GM' hereafter) are used, it is possible to not only restrain the shedding from positive plates, but also to protect the separators against intensive oxidation so that no internal short-circuits take place (Fig. 1). Therefore, he concluded that the use of SP separators with GM is required to produce long service-life batteries, especially in tropical regions. In the study presented here, we report test results from batteries assembled with PE separators for negative plates and with PE separators attached with GM for positive plates, together with a structural analysis of failed PE separators under high-temperature conditions (Fig. 2).

The authors' company, Nippon Muki, is the only general manufacturer of battery separators in the world to produce various types of separators, such as SP separators, PE separators, micro glass fibre separators (AGM) and GM for lead/acid battery applications. Thus, we believe it is not only necessary but also our duty to give our own

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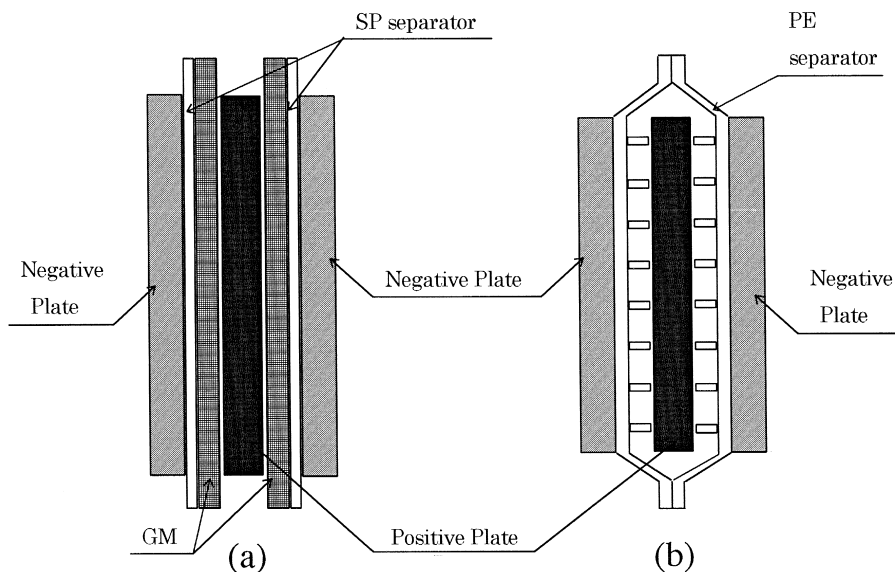


Fig. 1. (a) Schematic battery assembled with SP separators and glass mats. (b) Schematic of battery assembled with PE separators which envelope the positive plates.

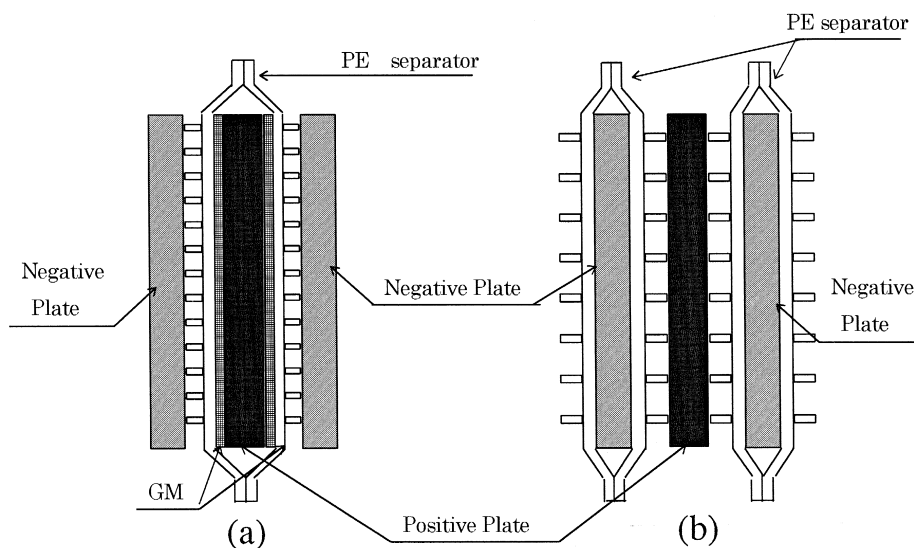


Fig. 2. (a) Schematic of battery assembled with PE separators and glass mats that envelope the positive plates. (b) Schematic of battery assembled with PE separators which envelope the negative plate.

Table 1  
Characteristics of battery separators

Separator parameter	Envelope separator		Leaf separator
	PE separator	PE separator with GM	SP separator with GM
Type	PA-A2500-1	PM-A2500-2	SP:LEWK
Overall thickness (mm)	1.10	0.60	
Web thickness (mm)	0.25	0.25	0.30
Rib height (mm)	0.85	0.35	
Rib pitch (mm)	12.0	5.0	
Electrical resistance ( $\Omega \cdot 100 \text{ cm}^2$ )	0.0009	0.0009	0.0007
Glass mat thickness (mm) (under 20 kg/100 cm <sup>2</sup> )		0.50	0.80

The 0.2 to 0.3 mm thick GM is often used as an attachment to the PE separators, but we suggest that such a thin GM will not restrain shedding but will only protect PE separators from anodic oxidation. Thus, 0.5 to 0.8 mm thick GM was used in this study.

Table 2  
Specifications of 55D23R battery

Dimensions $h \times w \times l$ (mm)	Capacity		High-rate discharge ( $-15^{\circ}\text{C}$ )				Reserve capacity (min)	JIS life-cycles
	5-h rate (A h)	20-h rate (A h)	Temperature ( $^{\circ}\text{C}$ )	Discharge (A)	Time (min)	V at 5 s (V)		
225 × 173 × 232 SAE standard	48	60	-15	300 356 <sup>a</sup>	1.9	8.0	99	315

<sup>a</sup>Cold-cranking amps at  $-18^{\circ}\text{C}$ .

view of the types of separator now in use in order to provide a guide to the selection of the correct type of separator for batteries to exhibit high performance and long service life in various applications and in different climatic conditions.

## 2. Experimental

### 2.1. Characteristics of PE separator

PM-A2500 type separators (UHMW PE) were used; the characteristics are given in Table 1.

### 2.2. Selection of test battery

A collaborative programme was set up with certain battery manufacturers in Japan to perform the tests on type 55D23R batteries which are the most popular type of automotive battery in Japan. The specifications of this battery are given in Table 2.

### 2.3. Type of grid

Expanded grids which are made from Pb–Ca–Sn alloy are often used in automotive batteries for both positive and negative plates. PE pocket separators are employed in these batteries.

In Japan, however, cast grids which are made from low-antimony alloy are often used for the positive plates, and Pb–Ca–Sn alloy for negative plates. In this study, cast grids were employed for both plate polarities in order to avoid the influence of grid type.

### 2.4. Test methods

The test methods are given in Table 3.

### 2.5. Classification of test batteries

Test batteries were marked separately as follows:

SPG = SP (with GM),  
PE = PE (without GM),  
PEG = PE (attached with GM),  
NPE = Negative plate in PE (without GM),  
Note: SP = leaf-type SP separator, PE = pocket type PE separator, G = GM.

## 3. Battery performance

### 3.1. $C_5$ capacity and reserve-capacity

$C_5$  capacity and reserve-capacity test results are listed in Table 4.

Table 3  
Test methods for automotive batteries

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		
● 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 20 A and 5 h charge at 5 A is one cycle. Count the cycles completed before the battery reaches 50% of $C_5$ capacity.	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 one 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

Table 4  
C<sub>5</sub> capacity and reserve-capacity performance

Battery performance	SPG Leaf separator with GM	PE PE separator without GM	PEG PE separator with GM	NPE PE separator without GM
C <sub>5</sub> capacity at 25°C (Ah)	46.6 (46.8)	46.8 (47.2)	46.3	47.5
Reserve-capacity at 25°C (min)	95.7 (95.8)	99.9 (99.6)	95.1	99.8
Reserve-capacity at 40°C (min)	135.7 (136.0)	136.2 (135.8)	135.6	136.2
Remarks	Fig. 1	Fig. 2	Fig. 3	Fig. 4

The values in parentheses have been reported previously [1].

### 3.2. Cold-cranking amperes

Cold-cranking amperes test results are presented in Table 5.

### 3.3. Cycle-life

Cycle-life data are shown in Table 6.

### 3.4. Analysis of battery performance

#### 3.4.1. C<sub>5</sub> capacity and reserve-capacity

As is well known, the capacity of a battery depends upon the quantity of both active material and electrolyte. Batteries without GM have a slightly larger amount of electrolyte than those with GM. This is because the latter types have more displacement of electrolyte due to the presence of GM. No effect of electrolyte limitation was observed, however, and every type of battery gave almost the same results because the batteries had sufficient amount of electrolyte for C<sub>5</sub> capacity.

In reserve-capacity tests, batteries without GM achieved a longer discharge time of about 5% than batteries with GM at 25°C. This is because the discharge current is 25 A and is about 2.5 times that at a discharge rate of 5 h. Both separator types gave the same discharge time at 40°C. Thus, it can be concluded that there is no problem under high-temperature conditions because the diffusion of electrolyte improves in proportion to the rising temperature and the necessary diffusion for the reserve-capacity is obtained at high temperature.

#### 3.4.2. Cold-cranking amperes

As reported before, the separator with GM is more disadvantageous than the separator without GM because

the viscosity of electrolyte increases at low temperatures, the electrolyte diffusion becomes poor, and composite electrical resistance of the separator becomes higher. On the other hand, the test results showed the same performance at 25°C. That is, the viscosity of electrolyte decreases as the temperature rises, the gas bubbles are released from the GM, the electrical resistance decreases and diffusion of electrolyte improves. Therefore, it can be concluded that there is no problem of cold-cranking amperes under high-temperature conditions.

#### 3.4.3. JIS cycle-life (heavy duty)

This test involves cycling to high depths-of-discharge (DODs). The results show (Fig. 3) that the presence of GM is effective in restraining shedding from positive plates for PEG type batteries at 25 and 65°C, but the life-cycles of PEG type batteries do not attain those of SPG type batteries. Furthermore, it is discovered that the NPE types behave differently: the capacity decreases sharply at 65°C.

#### 3.4.4. SAE cycle-life (light duty)

Although this SAE cycle-life test is conducted at a light load, it is found that the presence of GM is effective in restraining shedding from positive plates as found in JIS cycle-life tests at 25 and 65°C. By contrast, the cycle life of PEG type batteries is less than that of SPG type batteries (Fig. 4). Again, the NPE type displays different behaviour in that the terminal voltage falls suddenly (as observed in the JIS cycle-life test at 65°C).

### 3.5. Condition of batteries and separators after cycle-life testing

As shown in Table 7, evidence of piercing shorts due to anodic corrosion is found in PE and PEG types. Thus,

Table 5  
Cold-cranking amperes (CCA) performance

Battery performance	SPG Lead separator with GM	PE PE separator without GM	PEG PE separator with GM	NPE PE separator without GM
CCA at -18°C (A)	428 (432)	445 (443)	425	445
CCA at 25°C (A)	461 (459)	457 (460)	450	458
Remarks	Fig. 1	Fig. 2	Fig. 3	Fig. 4

The values in parentheses have been reported previously [1].

Table 6  
Cycle-life performance

Battery performance	SPG Leaf separator with G	PE PE separator without GM	PEG PE separator with GM	NPE PE separator without GM
JIS cycle-life at 25°C (cycles)	279	195	242	197
JIS cycle-life at 65°C (cycles)	183 (185)	106 (103)	140	92
SAE cycle-life at 25°C (cycles)	11 910 (12 100)	9540 (9400)	10 300	8650
SAE cycle-life at 65°C (cycles)	4410 (4380)	2610 (2590)	3500	2480
Remarks	Fig. 1	Fig. 2	Fig. 3	Fig. 4

The values in parentheses have been reported previously [1].

Table 7  
Battery failure modes

Failure mode	SPG Lead separator with GM	PE PE pocket separator without GM	PEG PE pocket separator with GM	NPE PE pocket separator without GM
Separator				
short at vertical part at 25°C	N	N	L	N
at 65°C	N	N	H	N
short at bottom part at 25°C	N	M	L	N
at 65°C	N	H	M	N
tear or cracks	N	M	L	N
Positive plate				
grid corrosion	M	M	M	M
shedding of active material	L	H	M	H
Negative plate				
sand-like PbSO <sub>4</sub>	N	N	N	M
Others				
short at upper parts of plate	N	L	L	N

M = several; H = many; N = none; L = few.

although thicker GM (more than 0.5 mm) has been used in the PEG type battery, the effectiveness of this GM is not sufficient at 65°C. By contrast, no evidence of piercing shorts could be found in SPG and NPE types. Thus, the method employed to envelope the positive plates with the PE separators will determine battery failure. Furthermore, an abnormal appearance is found on negative plates of the NPE type which does not occur on the other combinations such as SPG, PE and PEG types.

### 3.6. Comparative analysis of separators after SAE cycle-life test

In order to understand the deterioration of the separator, a comparative analysis was performed on both types of separator, namely, SP (synthetic pulp separator) and PE

(extracted film separator), that were used for positive plates. The following methods were used.

#### 3.6.1. SEM analysis (FE type scanning electron microphotograph)

The micrographs presented in Figs. 5 and 6 show the surface appearance of the separators before and after a series of SAE cycle-life tests under high-temperature conditions.

There was no noticeable change in the construction of the SP separator (Fig. 7) before and after cycle-life testing; evidently, the PE fibres survived (Fig. 5).

With PE separators, there is an uneven surface composed of glassy PE resin spheres before testing but a gritty surface after testing. It is concluded that PE resin is

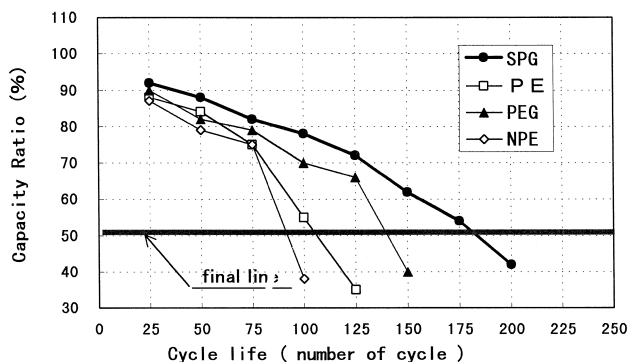


Fig. 3. JIS cycle-life test at high temperature (65°C); charge: 5 A, 5 h; discharge: 20 A, 1 h.

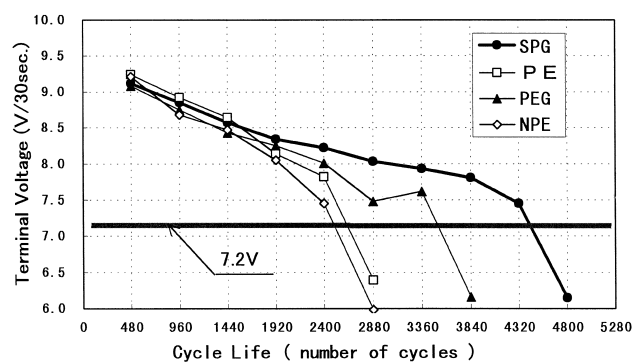


Fig. 4. SAE cycle-life test at high temperature (65°C); charge: 14.8 V (maximum 25 A), 10 min; discharge: 25 A, 4 min; rest period: 56 h.

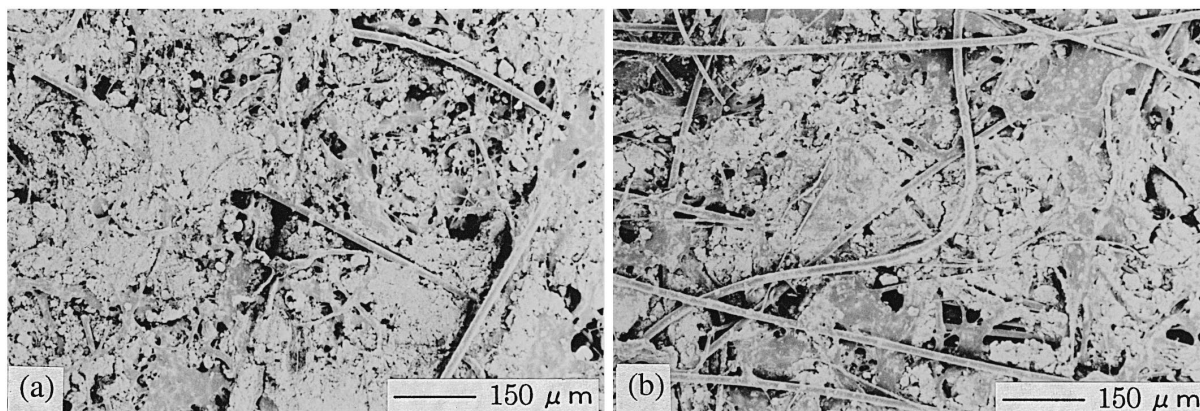


Fig. 5. Electron micrographs of SP separator: (a) before cycle-life test; (b) after cycle-life test.

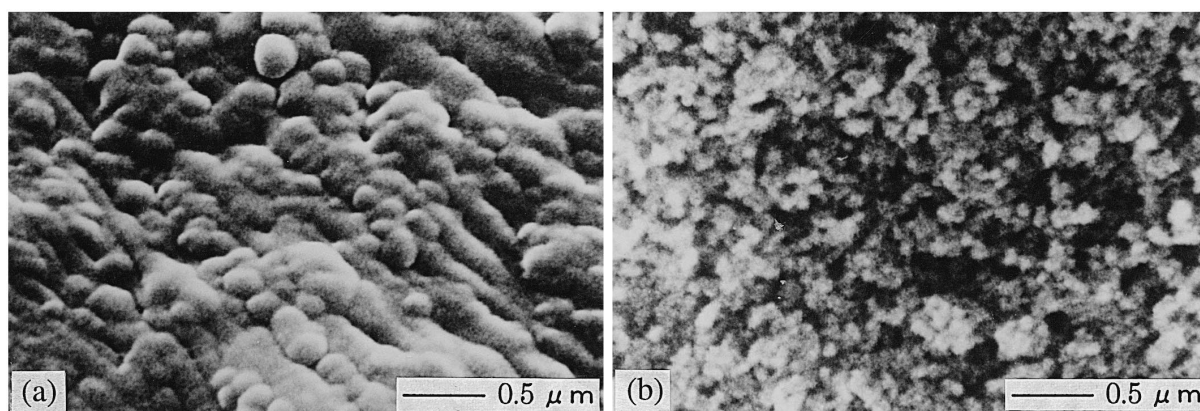


Fig. 6. Electron micrographs of PE separator: (a) before cycle-life test; (b) after cycle-life test.

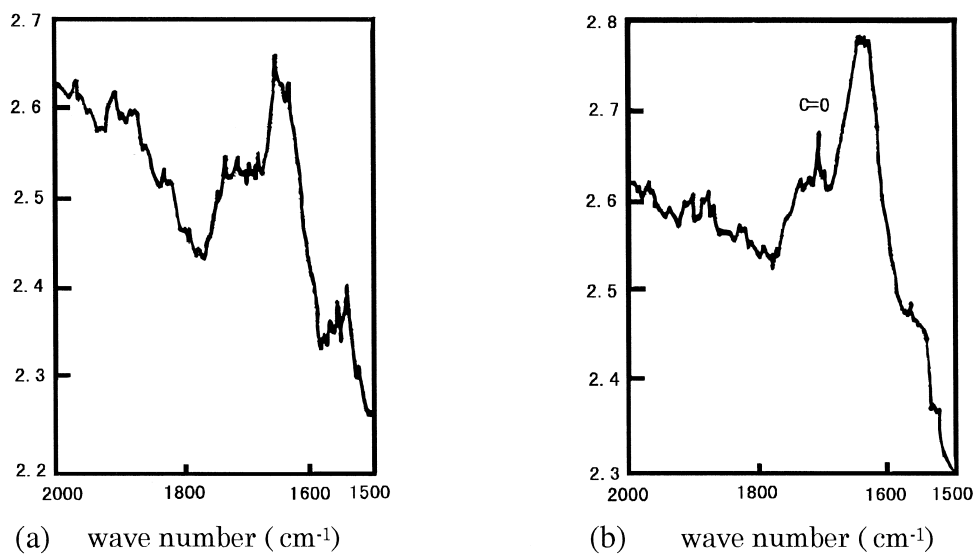


Fig. 7. FT-IR spectra for PE separator: (a) before cycle-life test; (b) after cycle-life test.

Table 8  
ESR measurement of radical numbers in PE separators

Item	Before cycle-life test	After cycle-life test
number of radicals ( $\times 10^{-4}$ spins/g)	5.61	34.85

consumed by anodic oxidation during the cycle-life test to produce the gritty surface.

### 3.6.2. Analysis by FT-IR (FT type infrared spectro-photometer: ART method)

The FT-IR scans in Fig. 7 are an infrared absorption spectrum for surface of the PE separator after a series of SAE cycle-life tests under high-temperature conditions.

The peak of the carbonyl group (C=O) is present in the FT-IR spectrum for the surface of the PE separator after the cycle-life test, but there is no such peak on the F-IR spectrum before the cycle-life test.

The carbonyl group (C=O) does not exist in PE resin itself. Thus, this carbonyl group is the functional group made from oxidation of the PE in battery reactions. PE resin is certainly oxidized and assists the deterioration in practical battery reactions.

### 3.6.3. Examination by ESR (electron spin resonance analyzer)

Table 8 shows the number of radicals in a PE separator before and after cycle-life testing. It is seen that the number of radicals is increased by about 6.2 times after the cycle-life test. This indicates the extent of the severance of molecular bonds in the PE resin.

### 3.6.4. Examination by NMR (nuclear magnetic resonance analysis)

There is a marked overlap of the NMR spectra taken for a PE separator before and after cycle-life testing (Fig. 8). An increase was found in the non-crystalline part in the methylene chain ( $-\text{CH}_2-$ ). This indicates the creation of free radicals in the PE resin due to the severance of PE molecular bonds. Therefore, these results are in accordance with the increase in radical numbers as revealed by ESR analytical results.

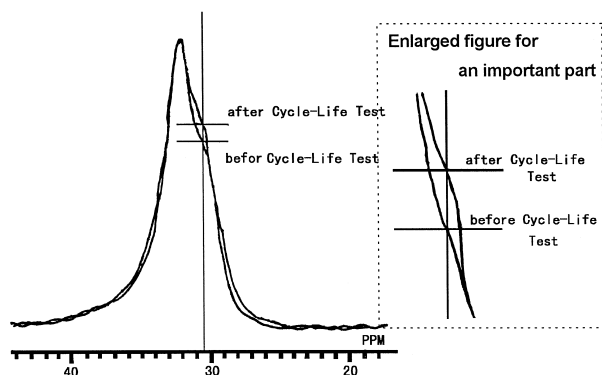


Fig. 8. NMR spectra for PE separator.

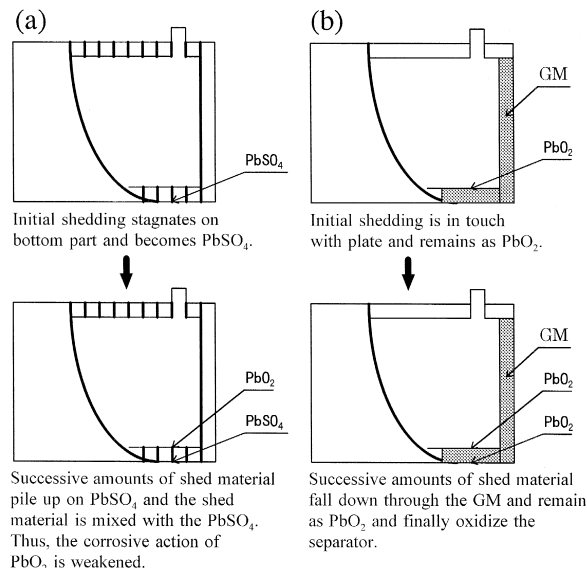


Fig. 9. (a) Schematic diagram in case without GM. (b) Schematic diagram in case with GM.

## 3.7. Discussion of battery test results

### 3.7.1. Enveloping for positive plate

Evidence of anodic corrosion was found on the vertical position of the PE separator attached with GM. It is concluded that the presence of GM inside the pocket provides a mediator between the positive plate and the PE separator for bridge shorts. Another problem is the oxidation by shed active material that is displaced from the positive plate and trapped in the GM. Gradually, this material falls down through the GM to the bottom of the PE separator, where it remains active because it is still connected to the positive plate. The processes by which shed material piles up at the bottom part of the pocket separator are shown schematically in Fig. 9(a) and (b).

For a PE separator without GM, the separator is severely corroded by the active material which falls from the positive plates, but the attack of the PE separator is expected to be less that of PEG (with GM). The reason for this phenomenon is believed to be the gradual accumulation of shed positive active-material at the bottom part of the pocket separator, and reaction with  $\text{H}_2\text{SO}_4$  to produce  $\text{PbSO}_4$ . The latter mixes with further shed material, piles up at the bottom of separator (as shown in the Fig. 9(a)) and the deposit loses its severe corrosive action. In the presence of GM, however, the shed material will not fall down so easily (Fig. 9(b)). Rather, the material falls down gradually to the bottom of the PE separator and will maintain its active life as long as it is in contact with positive plate. Thus, the PE separator will be corroded by highly activated shed material ( $\text{PbO}_2$ ).

### 3.7.2. Enveloping for negative plate

The NPE type separator showed a sudden decline in performance in the cycle-life test at  $65^\circ\text{C}$ . Moreover, the negative plates had a sand-like appearance—a condition

that was often found in failed batteries which were used in high temperature and concentrated electrolyte conditions.

Since an abnormal phenomenon was found in negative plates but the positive plates were normal, it is conceived that the negative plates are exposed conspicuously under these severe conditions. As generally known, discharge reaction produces the water on the positive side in battery reaction. So, when the positive plates are enveloped, the reaction of positive plates with sulfuric acid is sluggish and never produces concentrated sulfuric acid because the sulfuric acid on charging is diluted by the water immediately.

But when the negative plate is enveloped, the chemical reaction with sulfuric acid takes place easily because the sulfuric acid around the negative plate on charging gradually becomes concentrated  $H_2SO_4$  and the negative active materials are converted to lead sulfate ( $PbSO_4$ ). This is because the negative active materials consist of pure lead metal and react with sulfuric acid easily, this reaction is faster under high-temperature conditions. As mentioned above, the lead sulfate which is created by such chemical reaction is called irreversible lead sulfate and has a sand-like texture; it is different from the lead sulfate produced by the battery reaction and it cannot be converted to negative active material by charging.

When good circulation of electrolyte around the negative plate is accomplished, it is unlikely that the negative plate will develop irreversible lead sulfate. Rather, this undesirable state is created by the enveloped negative plate. That is to say, little of the sulfuric acid produced around the negative plate on charging diffuses into the outer electrolyte due to the presence of the PE pocket separator which has an extremely small pore size of  $0.05 \mu$  and, thereby, resembles a diaphragm.

Therefore, the rate of diffusion of sulfuric acid in the PE pocket separator is very slow because sufficient circulation cannot take place. The sulfuric acid is compelled to diffuse only by way of permeation diffusion. The concentrated sulfuric acid becomes stagnated inside the PE pocket separator and the negative plate 'suffocates.' The sand-like sulfation of negative plates takes place with the serious result that the battery fails very quickly, especially at high temperatures.

#### 4. Theoretical examination of polyethylene separator

##### 4.1. General properties of main material for PE separators

The material used in thin, flexible and porous separators are composed of organic substances that are resistant to both acid and oxidation. Nevertheless, it is usual that such organic compounds cannot withstand strong acid, oxidation and moisturized air conditions.

Polyethylene resin is an olefin and has a normal chain structure  $\{(-CH_2-CH_2-CH_2-)_n\}$ . Since it is a durable

resin against chemicals, it is considered to be a suitable resin for battery separator material.

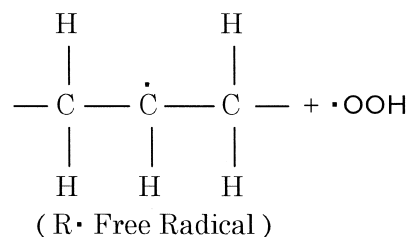
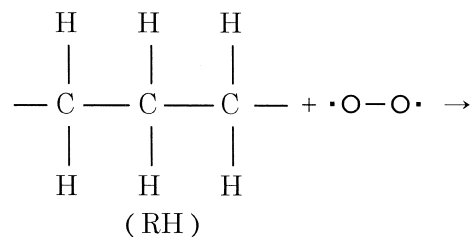
Polyethylene resin is synthesized from ethylene gas in the presence of a catalyst. There are three types of synthesis methods, namely, low pressure, middle pressure, and high pressure. The low-pressure or middle-pressure polyethylene resins have less branches and there are less radicals in the structure. Therefore, these materials are often used for battery separators and it is reported that larger molecular weight polyethylene resin is more resistant to chemical action and oxidation.

##### 4.1.1. Characteristics of polyethylene resin

The general characteristics of polyethylene resin are given in Table 9.

##### 4.1.2. Mechanism of oxidation process for polyethylene

As mentioned before, organic substances are influenced by the oxidation conditions of battery reactions. The mechanism of oxidized deterioration of PE material in battery separators is as follows.



The produced radical reacts again with oxygen and becomes a peroxy radical, i.e.,

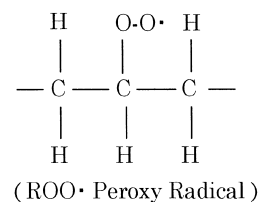
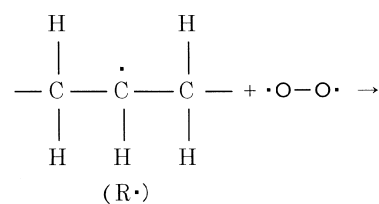
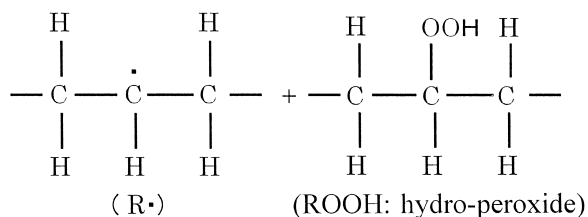
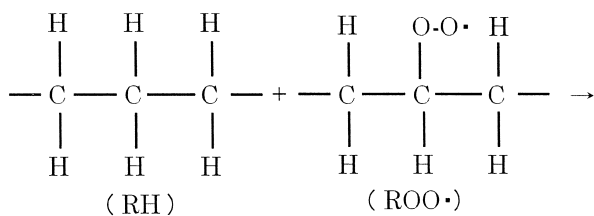




Table 9  
General characteristics of polyethylene resin

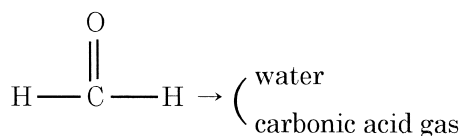
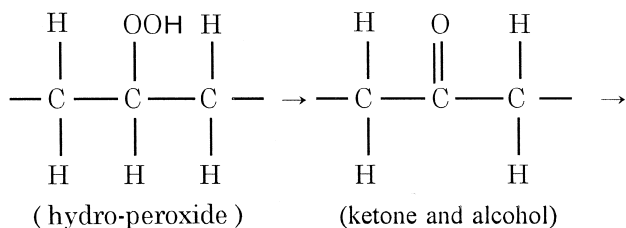
Type of PE resin Application	High molecular PE SP separator (PE pulp fibre)	Ultra high molecular PE PE separator (PE powder)	Test method
Average molecular weight ( $\times 10^6 \text{ g mol}^{-1}$ )	0.2 ~ 1	1 ~ 6	viscosity or GPC
Density ( $\text{g cm}^{-3}$ )	> 0.955	> 0.935	ASTM D 1505
MI (g per 10 min)	> 0.05		ASTM D 1238
Yield point tensile strength ( $\text{kg cm}^{-2}$ )	< 300	> 400	ASTM D 638
Methyl radical	> 3200	< 300	C:carbon
Vinyl radical	> 60	< 30	C:carbon

The peroxy radical reacts with  $-\text{H}-$  in the polymer and produces a hydro-peroxide and a radical, i.e.,



The hydro-peroxide is decomposed to an alkoxy-radical ( $\text{RO}\cdot$ ) and a hydro-oxyradical ( $\cdot\text{OH}$ ).

The alkoxy-radical and hydro-radical attack the original substance again and produce a radical. Accordingly, once this reaction begins, the reactions trigger chain reactions.



(formaldehyde and carbonic acid condensation product)

The hydro-peroxides in the above reactions are decomposed into water and carbonic acid gas, and are finally consumed.

Above sequence is for PE resin which has a normal chain structure  $[(-\text{CH}_2-\text{CH}_2-\text{CH}_2-)_n-]$ . Thus, it has substantially no branches and no radicals. That is, there is almost no starting point for oxidation. Other synthetic resins have many branches and radicals, such as vinyl or methyl radicals, in their structures. Therefore, this is the reason why polyethylene resin is very resistant to chemicals and oxidation.

#### 4.2. Factors that influence separators in lead/acid batteries

The separators in a lead/acid battery deteriorate when exposed to nascent oxygen or touched with positive active material as a peroxide. Finally, the separators disintegrate. This deterioration is more advanced at high temperatures. We have not discussed the influence of the negative plate because it is reductive material and, in general, its effect on separators is negligible.

##### 4.2.1. Influence of positive plate

Positive active-material gradually becomes fine particles during charge and discharge cycles and active materials are turned alternatively into  $\text{PbO}_2$  (charge) and  $\text{PbSO}_4$  (discharge). Furthermore, the volume of active material expands gradually and, subsequently, softening of the material takes place. Therefore, organic substances around positive plates are oxidized by the active material. There are no organic substances that can withstand this oxidation.

In these oxidizing circumstances, the  $-\text{C}-\text{H}-$  structure in the main material of the separator becomes unstable and  $-\text{H}-$  (hydrogen) in the organic substance is pulled out by  $-\text{O}-$  (oxygen) because  $-\text{O}-$  has a strong affinity to  $-\text{H}-$ . The organic substances are disintegrated and finally become water and carbonic acid gas, Fig. 10.

The above behaviour suggests that the separator should be kept away from positive plates in order to prolong its service life. One way to achieve this is to include ribs on the positive-plate side of separator but the shedding of corrosive positive active material is unavoidable. Thus, the application of inorganic material such as GM on the

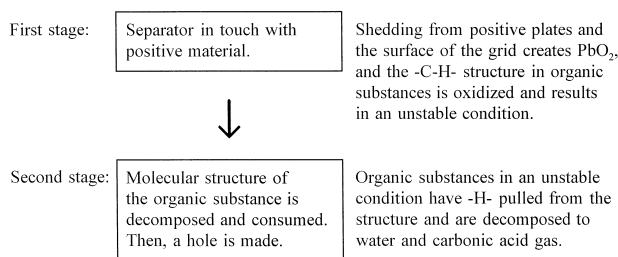


Fig. 10. Separator deterioration caused by oxidation.

positive side of the separator is an excellent way to keep the separator away from positive plate.

#### 4.2.2. Influence of electrolyte

The electrolyte originally consists of sulfuric acid and pure water. The electrolyte is decomposed by electrolysis in the final stages of charge and it loses water. Water loss also occurs through evaporation and this increases as the temperature is raised. The subsequent increase in acid concentration can result in separator deterioration, Fig. 11.

On the other hand, when a battery is discharged, the concentration of the acid in the electrolyte decreases almost to water due to the reaction of the acid with the active material of both plate polarities to form  $PbSO_4$ .

#### 4.3. Comparison of the structures of SP and PE separators

Cycle-life tests at high temperature show that the extruded type PE separator is of inferior quality compared with the paper type SP separator. The main material of both separators is PE resin. In order to clarify the differences between the two separators, a comparison of their structures is presented in Table 10.

As shown in Table 10, the extruded PE separator is made of ultra high molecular weight PE, and the SP separator of high molecular weight PE. Accordingly, the PE separator has superior quality. The manufacturing method for SP and PE separators is different we have concluded that there is a structural difference between the two types. The extruded PE separator is composed of aggregates of spheres that themselves consist of silica particles enclosed in this PE films; the pore size is extremely small ( $\sim 0.05 \mu\text{m}$ ), Table 10. By contrast, the SP

separator is constructed from PE fibre which is covered with silica particles; the pore size is relatively large ( $\sim 1.5 \mu\text{m}$ ) and is made by the fibres crossing each other at random, Table 10. Consequently, the PE separator has a very large specific surface area, and the volume is more exposed to the very strong oxidation conditions in practical battery usage.

#### 4.4. Other approaches to improving separator endurance

##### 4.4.1. Application of anti-oxidant

As mentioned above, PE resin can be oxidized and when the normal mass of hydro-peroxide accumulated in PE resin is exceeded, self-oxidation begins and this reaction triggers chain reactions. Anti-oxidants are often added to PE separators, but these sometimes influence battery performance or are extracted during separator manufacture. Thus, although it is possible to impregnate a phenolic anti-oxidant into the pores of the extruded type of PE separator, its inhibitive efficacy becomes null and void in a short period.

##### 4.4.2. Increase of mineral oil

Mineral oil is an olefinic compound, like polyethylene. It is possible to use mineral oil to protect PE separators from attack by nascent oxygen because the oil is a viscous liquid and makes a film around the grains of PE in the separator. But its effectiveness is expected only for a certain period, however, because it has very low molecular weight and can be easily oxidized compared with PE.

Further, when the amount of mineral oil is increased, the electrical resistance becomes higher because the pores of the PE separator become obstructed by the oil. Moreover, the oil creates a black scum which is made from organic expander, carbon and other suspended material in electrolyte. As a result, contamination of the electrolyte takes place, and the level of electrolyte cannot be confirmed through the container. If the battery has a vent plug with a filter, oily scum will block the filter and impair battery performance. In our experience, the amount of mineral oil must not exceed 20 wt.% of the PE separator.

##### 4.4.3. Increase of absolute amount of PE

Increasing the absolute amount of PE is effective in retarding the time for the hydro-peroxide to reach the regular mass because the oxygen partial pressure decreases and delays the oxygen absorptive velocity so that the decomposition time is retarded. For batteries of the same capacity, the amount of active materials are equal, and thus the produced nascent oxygen is also the same. To provide the same cycle life, the absolute amount of PE should be equal. In practice, however, when the absolute amount is increased, the electrical resistance of the PE separator becomes high, and the cost of PE separators becomes prohibitive. Further, even if the ratio of polyethylene to silica is increased to compensate for any loss in endurance when using a thinner back-web, the absolute amount of PE

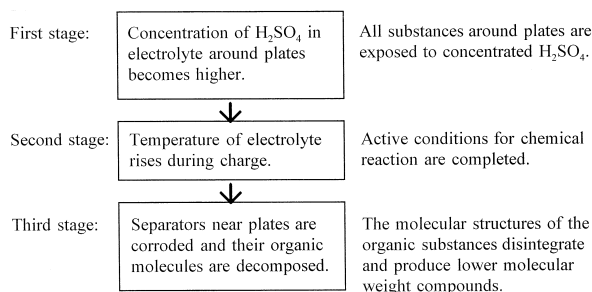

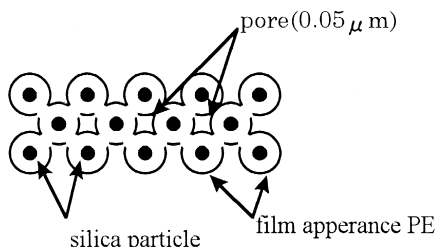
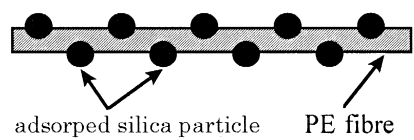
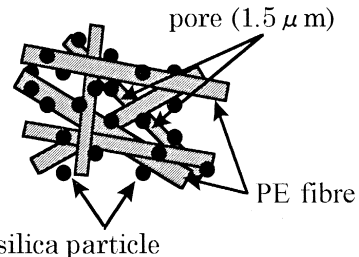


Fig. 11. Separator deterioration without oxidation.

Table 10  
Comparison of the structures of SP and PE separators

	Extruded type PE separator	Synthetic pulp type separator
Material	① Ultra high molecular weight PE. ② Fine silica powder ③ Mineral oil (used for plasticizer and pore making material)	① High molecular weight PE pulp ② Fine silica powder ③ PP fibre or glass fibre. (used for reinforcement material)
Manufacturing method	① Mix PE, fine silica and mineral oil to make a mixture. ② Mixture is extruded and pressed by extruder and forming rollers. ③ Extract mineral oil by solvent to make a PE porous sheet.	① Adsorb the silica to PE pulp and other fibre, and disperse in water. ② Make paper sheet by paper-making machine and produce continuous sheet. ③ Heat-set the paper by heating oven and press rollers.
Structure	① Single element  <p>This sphere seemed a silica particle wrapped with thin PE film.</p> ② Construction of PE sheet 	① Single element  ② Construction of PE paper 

in the separator is not always increased. Thus, though the cost of the PE separator may decrease, its endurance is not improved.

#### 4.4.4. Application of GM

GM is an inorganic substance that is both acid and oxidation proof and is never eroded by sulfuric acid or by nascent oxygen. It also has sufficient void to allow the gas to pass through easily. Attaching GM to the PE separators is an effective way to protect separators from oxidation but the results of battery tests show that the GM impedes the smooth falling down of shed material from the plates and produces bridges between the plates and the PE separators and thus creates a harmful effect and shortens battery life.

When the GM is used with the separator, the GM must be pressed tightly against the surface of the positive plate, first to prevent shedding of the positive active-material and, second, to prevent the separator from being in direct

contact with the positive plates. It should also be noted that the above tests were conducted on test batteries in a static condition. If the batteries are used on rough roads, more care should be given to the problem of battery vibration as a greater degree of positive active-material shedding will occur.

## 5. Conclusions

To meet the requirements of battery manufacturers world-wide for most types of the separators, we consider it our duty to provide a guide for the proper application of SP and PE separators. This is especially important for automotive batteries that are required to have long service lives particularly in high-temperature environments.

The following conclusions can be drawn from this study of separators: (i) a long service life cannot be expected even if GM is attached in the PE pocket separators; (ii) GM of at least 0.5 mm in thickness is necessary to restrain shedding from positive plates; (iii) PE pocket separators can be used for negative plates but another problem occurs, particularly under high-temperature conditions; (iv)

the application of leaf-type SP separators with GM is particularly suitable in high-temperature conditions.

### **References**

- [1] H. Endoh, *J. Power Sour.* 59 (1996) 51–55.