



Characteristics of lithium-ion battery with non-flammable electrolyte

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ABSTRACT

To improve the safety of lithium-ion batteries, we studied non-flammable electrolytes made by adding several types of phosphazene-based flame retardants to conventional electrolytes and evaluated their conductivities, electrochemical characteristics, and the effects of flame retardants in terms of safety. Cell performance tests and abuse tests were also conducted using cylindrical test cells. The conductivity of electrolytes decreased when phosphazene-based flame retardants were added to the conventional electrolytes. The reason for this decrease in conductivity may be the increase in electrolyte viscosity caused by adding flame retardants. The conductivity decrease led to a decrease in cell capacity at high current density and at low temperature. However, the cell capacities at 0.2 CA (CA = 750 mA) and at 25 °C were almost the same as those of cells using conventional electrolytes. Flame tests showed that the electrolytes with flame retardants exhibited flame resistance consistent with UL-94V0. We also carried out several abuse tests to check the safety improvements. Both overcharge tests up to 10 V and heating tests up to 200 °C were completed without any extraordinary heat generation. Heating tests using a burner revealed the self-extinguishing properties of these electrolytes which were gushed out by venting. These results indicate that electrolytes with phosphazene-based flame retardants are effective for making lithium-ion batteries safe.

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1. Introduction

Compared with conventional lead acid batteries and alkaline secondary batteries, lithium-ion batteries have high-voltage and high-energy-density characteristics. Thanks to these features, they have found widespread use in small portable devices like camcorders and cell phones since their commercialization in 1991. Recently, much effort has been focused on developing large-capacity lithium-ion batteries for use in hybrid automobiles [1,2]. At the same time, much attention has also been paid to the safety of lithium-ion batteries to prevent cases of smoking, igniting or exploding.

In telecommunications, many battery systems are used to keep the services running reliably. Lead acid batteries with capacities of several hundred or several thousand ampere-hours (Ah) are used in the backup systems, and increases in the capacity of backup batteries or reductions in the volume of battery systems are expected as IP (Internet protocol) services make progress. Backup systems using lithium-ion batteries are expected to satisfy these demands. When lithium-ion batteries are used for various types of station-

ary applications in telecommunications, the cell capacity must be significantly higher than in batteries used in conventional portable devices, and several such high-capacity batteries are connected in series or parallel. This scenario calls for a higher level of battery safety such as self-extinguishing capabilities.

Most of today's lithium-ion batteries use an organic solvent as the electrolyte, and elevated cell temperature at an early stage of thermal runaway caused by the electrolyte burning is thought to play an important role in lithium-ion battery thermal runaway. Hence, if we can inhibit the burning of the electrolyte, we may be able to improve the safety of lithium-ion batteries.

In this paper, we report on our efforts to give electrolytes self-extinguishing characteristics equivalent to UL-94V0 by adding phosphazene-based flame retardants to conventional electrolytes. We evaluated the discharge characteristics and flame resistance of such electrolytes using 750 mAh cylindrical lithium-ion cells.

2. Experimental

2.1. Flame retardants

Flame-resistant electrolytes are classified as (1) organic electrolyte containing flame retardant, (2) flame retardant polymer electrolyte [3], (3) inorganic solid electrolyte (sulfide glass, etc.) [4],

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Table 1
Main flame retardant electrolytes used in lithium-ion batteries.

Type		Components	Ion Conductivity	Remarks
Aprotic organic electrolyte + flame retardant		Phosphoric-acid esters phosphazenes fluorine-based organic solvents		
Polymer electrolyte (polymer solid electrolyte)	Completely solid	Composite of polyethylene oxide and lithium salt	10^{-4} S cm $^{-1}$	Conductivity is low
	Gel-like polymer	Composite of polymer, organic solvent, and lithium salt	10^{-3} S cm $^{-1}$	Problems in securing strength when manufacturing large-capacity cells and in achieving adhesion between polymer and battery-plate interface
Inorganic solid electrolyte	Sulfide-based solid electrolyte	Sulfide glass	10^{-3} S cm $^{-1}$	Decomposition voltage is low (about 3 V)
Ionic liquid (ambient-temperature molten salt)		Various asymmetric quaternary ammonium-imide salts, etc.	–	Highly reactive with lithium
Aprotic organic electrolyte		Composite of organic solvent and lithium salt	$(5-10) \times 10^{-3}$ S cm $^{-1}$	At present, most are of this family

Table 2
Physical properties of phosphazene-based flame retardants used in this study.

	Flame retardant A	Flame retardant B	Flame retardant C
Viscosity (MPa s)	1.1	1.3	1.7
Boiling point (°C)	125	194	194
Density (g cm $^{-4}$)	1.49	1.37	1.5

and (4) ionic liquid, as listed in Table 1. In this study, we selected group (1) systems because a long shelf life, high current density performance, and low cost are necessary for telecommunication applications. This is because flame retardant polymer electrolyte has insufficient ionic conductivity for use in telecommunication applications. Ionic liquids also have insufficient conductivity because of their viscosity and still have the problem of reduction on the negative electrode to make undesirable solid electrolyte interphase [5,6]. On the other hand, alkyl phosphates are known to have problems with shelf life because a film that inhibits lithium ion transfer forms on the graphite electrode [7] and alkyl fluorides have issues related to solubility and viscosity, amount of added solvent, etc. [8]. Consequently, we chose phosphazene-based flame retardants because of their current research and commercialization level, availability, low cost, and other factors. Phosphazene-based flame retardants are known as flame retardants for plastics [9] and have high-voltage resistance. Up to now, the effect of adding phosphazene derivatives to electrolyte has been executed by thermal analyses [10]. Furthermore, only a flame test on electrolyte containing cyclo-phosphazene has been executed [11], and a burning test on a cell containing cyclo-phosphazene electrolyte has not previously been performed.

In this study, the three types of phosphazene-based flame retardants shown in Fig. 1 were used to investigate physical properties such as ionic conductivity and flame resistance. In the figure,

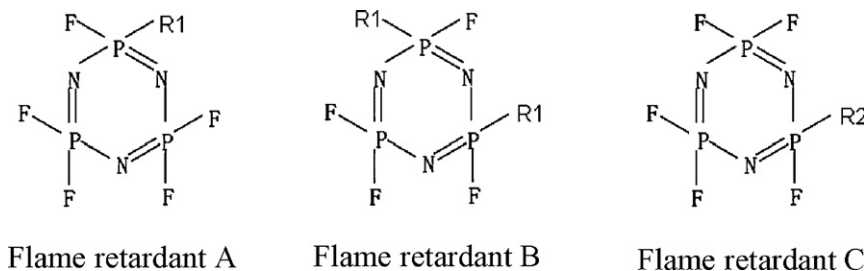


Fig. 1. Molecular structure of phosphazene-based flame retardants used in this study.

R1 and R2 are alkyl or aryl groups. The boiling points of these phosphazene-based flame retardants were optimized by partial fluorination and functional group substitution. The physical properties of phosphazene-based flame retardants are listed in Table 2.

2.2. Electrolyte preparation

A conventional electrolyte was made by dissolving LiPF₆ into a mixture of ethylene carbonate and dimethyl carbonate. A flame-resistant electrolyte was then made by mixing from 15 to 35 wt.% of phosphazene-based flame retardant into the conventional electrolyte in an Ar-filled dry box.

2.3. Evaluation of flame resistance of electrolytes

In telecommunications, valve regulated lead acid batteries are widely used. They have plastic battery cases that feature flame retardant properties in compliance with the UL-94V0 standard. Therefore, we referred to the UL-94V0 standard to evaluate the flame resistance performance of electrolytes. Namely, after immersing a piece of glass fiber cloth in an electrolyte and exposing it to a flame (spirit lamp) for 10 s, as shown in Fig. 2, the flame was removed and the time that the glass fiber cloth continued to burn was measured. This procedure was then repeated. Flame resistance criteria are also listed in Fig. 2.

2.4. Conductivity measurement

The conductivity of each electrolyte was measured with a Cyber Scan CON400 conductivity meter from Eutech Instruments after the electrolyte had been kept in an incubator at 25 °C for 16 h.

For N=5, all criteria must be satisfied

Item	Passing Criteria
Burning time after 10 s of ignition	≤ 10 s
Burning time after 10 s of second ignition	≤ 10 s
Completely burnt out	Unacceptable



Fig. 2. Test conditions and passing criteria.

2.5. Test cell production

Cylindrical cells (18 mm in diameter and 65 mm long) were prepared for electrochemical measurement and abuse tests. The cathode material was lithium manganese oxide spinel and the anode material was graphite. Cells were produced in a dry room where the relative humidity was under 0.2%. The nominal capacity of each cell was 750 mAh.

2.6. Overcharge test

Test cells were wrapped in a rubber heater and maintained at temperatures of 25, 50, and 80 °C to test overcharging up to 10 V at a constant current of 1 CA.

2.7. Heating test

Test cells were wrapped in a rubber heater and heated to the 200 °C level with the temperature rising at a rate of about 5 °C min⁻¹.

2.8. Burner test

Test cells were fully charged and set on a Bunsen burner and heated until they vented. After this venting occurred, the burner was turned off and the self-extinguishing properties of the electrolytes were evaluated.

3. Results and discussion

3.1. Effect of phosphazene-based flame retardants

An example of a test in progress is shown in Fig. 3. The electrolyte without flame retardant (blank sample) ignited instantaneously and was completely engulfed in flame. It continued to burn for

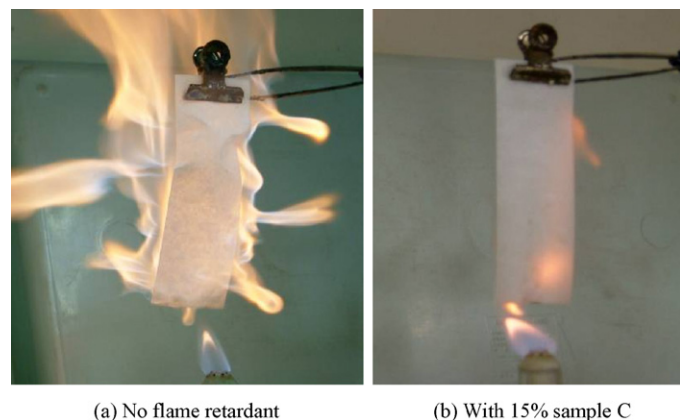


Fig. 3. Burning test conditions.

Table 3

Burning test results.

Sample	Self-extinguishing within 10 s (1st ignition)	Self-extinguishing within 10 s (2nd ignition)
A	20%	35%
B	15%	25%
C	15%	15%

more than 10 s after the removal of the spirit lamp until it completely burnt out (a). In contrast, the test sample with 15% of flame retardant C never became engulfed in flame after being exposed to a flame and stopped burning immediately the spirit lamp was removed, demonstrating its self-extinguishing properties (b). The kinds of electrolyte are summarized in Table 3. Here, sample A represents an electrolyte containing flame retardant A, and the percentages show the minimum content of flame retardant that enabled it to demonstrate self-extinguishing properties. When samples were ignited for a second time, the amount of flame retardant necessary for self-extinguishing within 10 s was found to be 35% for flame retardant A, 25% for flame retardant B, and 15% for flame retardant C.

The flame resistance mechanism of phosphazene-based flame retardants may be similar to that of alkyl phosphates. Namely, phosphazene-based flame retardants decompose at a high temperature to generate phosphate radicals, which scavenge reactants such as oxygen. Therefore, the decomposition temperature of a flame retardant and the stability of the phosphate radical may affect the flame retardant's performance. As shown in Fig. 1, flame retardants A, B, and C have the same phosphazene framework but different functional groups. This difference in functional group could govern the decomposition temperature; for this electrolyte system, the decomposition temperature of flame retardant C is suitable. In addition, the boiling points of flame retardants are also important. The flame retardants should have a boiling point that is compatible with that of the base electrolyte.

3.2. Conductivity of electrolytes

The conductivity of an electrolyte was decreased by adding phosphazene-based flame retardants because these retardants are viscous liquids, as shown in Table 2. The relationships between electrolyte conductivity and flame retardant content are shown in Fig. 4. The relationships show that when flame retardant was added, the drop in conductivity was roughly the same for flame retardants A, B, and C, and that the conductivity dropped linearly with increasing amount of flame retardant. Furthermore, when we compared electrolytes with enough added flame retardant to make self-extinguishing properties appear, we found that the electrolyte containing retardant C (sample C) was the most conductive.

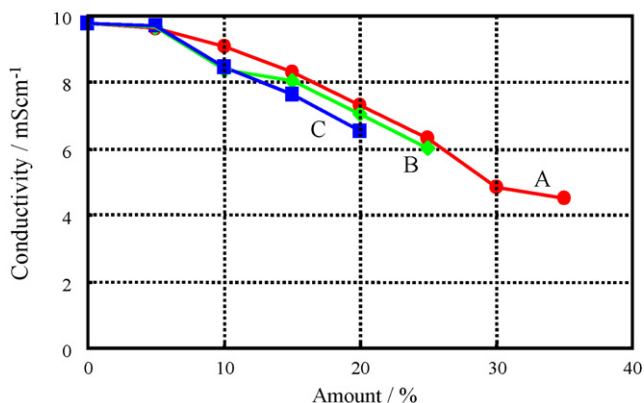


Fig. 4. Relationship between amount of flame retardant and conductivity.

3.3. Discharge characteristics

To investigate cell performance, we prepared cylindrical cells using three types of electrolyte determined from the flame tests described in Section 3.1. Electrolyte A contained 35% of flame retardant A, electrolyte B contained 25% of flame retardant B, and electrolyte C contained 15% of flame retardant C. We denoted the cells using electrolytes A, B, and C as 1-A, 1-B, and 1-C. We also denoted the cells using electrolytes without flame retardant as no flame retardant.

We conducted a discharge test at several current densities (0.2, 1, and 3 CA, where 1 CA = 750 mA) and at several temperatures (-10 , 0, 25, 45, and 50 °C). The dependence of relative capacity on current density at 25 °C is shown in Fig. 5, and discharge curves at a current density of 3 CA for test cells 1-A, 1-B, and 1-C are shown in Fig. 6. Compared with the results for the cell without flame retardant (no flame retardant), no remarkable decrease in capacity was observed up to 3 CA for 1-B and 1-C. On the other hand, 1-A showed a remarkable decrease in discharge capacity with increasing current density. At a current density of 3 CA, its capacity was only 25% of that at 0.2 CA. Discharge characteristics at 45 and 50 °C were similar to those at 25 °C.

The dependence of relative capacity on current density at 0 °C is shown in Fig. 7, and discharge curves at a current density of 3 CA for test cells 1-A, 1-B, and 1-C are shown in Fig. 8. At this temperature, a remarkable decrease in discharge capacity with increasing current density was observed for all cells. In particular, only about 10% of the discharge capacity at 0.2 CA was obtained for 1-A and 1-C at 3 CA. The voltages of cells 1-A and 1-C dropped rapidly in a linear manner for discharge at 3 CA, as shown in Fig. 8. The discharge capacity decreases at low temperature and at high current density were more remarkable in the -10 °C tests.

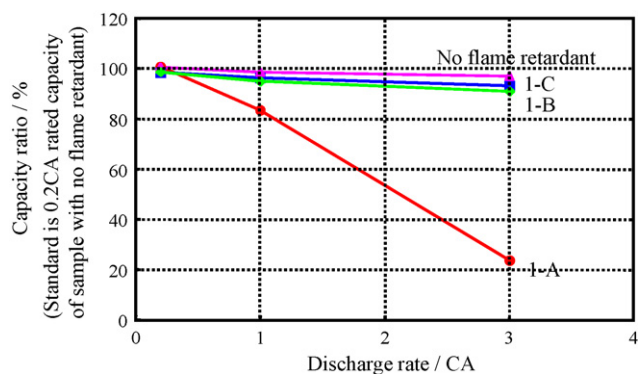


Fig. 5. Discharge characteristics for test cells using electrolyte with flame retardant.

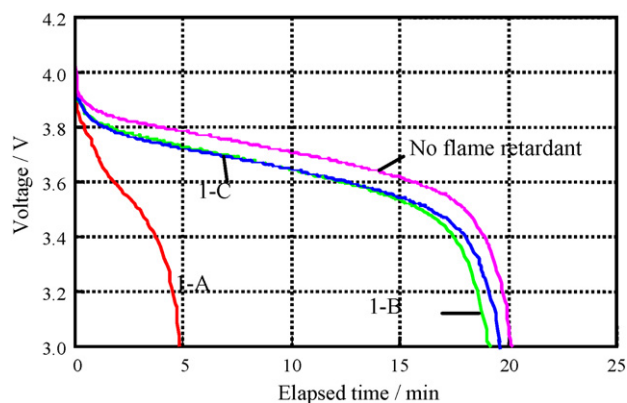


Fig. 6. 3 CA discharge curves for test cells using electrolyte with flame retardant (25 °C).

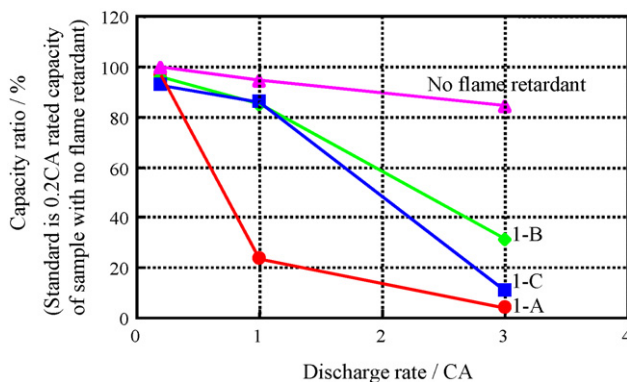


Fig. 7. Discharge characteristics for test cells using electrolyte with flame retardant (0 °C).

Figs. 4, 5, and 7 indicate that when phosphazene-based flame retardant was added, the electrolyte's conductivity decreased, resulting in a decrease in discharge capacity at high current density. This tendency was remarkable at low temperature below 0 °C, which suggests that the viscosity of the electrolytes was increased by adding the flame retardants. This was confirmed by viscosity measurement of electrolytes at -10 °C, as shown in Fig. 9. Viscosity was highest for flame retardant C and lowest for flame retardant A, as shown in Table 2. However, the self-extinguishing performance of flame retardant A was poorer than that of flame retardant C, so much more of flame retardant A had to be added to an electrolyte to provide self-extinguishing properties. This is why electrolyte A

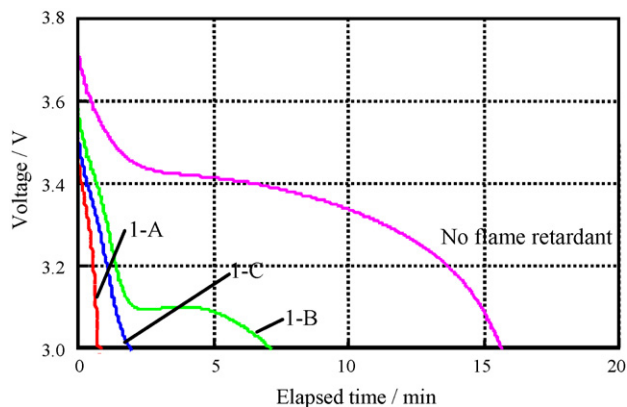


Fig. 8. 3 CA discharge curves for test cells using electrolyte with flame retardant (0 °C).

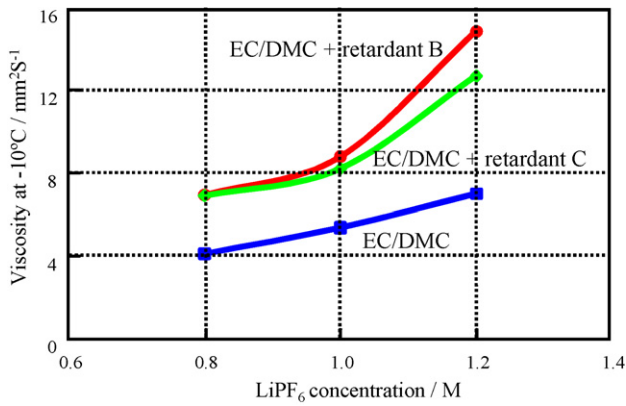


Fig. 9. Relationship between LiPF_6 concentration and viscosity.

was more viscous, resulting in it having poorer conductive than electrolyte C. On the other hand, the discharge capacity of test cell 1-B, which contains electrolyte B (flame retardant B) was higher than that of 1-C in spite of the conductivity of electrolyte B being lower than that of electrolyte C, as shown in Fig. 4. Unfortunately, the reason for this is not clear yet.

3.4. Overcharge test

The change in voltage and temperature over time at 25 °C is shown in Fig. 10. We tested three samples of each cell type: 1-A, 1-B, 1-C, and no flame retardant. The figure shows a representative value for the cells of each type. The cell voltage stayed relatively constant for about 10 min at the 4 V level. It then began to rise but became stable again at about 5 V for 1-C and at about 6.5 V for 1-A and 1-B. After an elapsed time of about 50 min, each of the test cells began to show a steep rise up to the charger's maximum output voltage of 10 V. The rate of the rise in cell temperature increased gradually, until the temperature eventually reached 120–130 °C, corresponding to separator shutdown. In this overcharge test, no ignitions or explosions were observed at any test temperature.

3.5. Heating test

For this test, we used three fully charged samples of each cell type: 1-A, 1-B, 1-C, and no flame retardant. During the heating, all of the cells maintained a voltage of about 4 V up to about 150 °C, and no ignitions, explosions, or other phenomena occurred during heating past that point up to about 200 °C. The results of this heating test for test cell 1-C are shown in Fig. 11, which shows a representative value for this cell type.

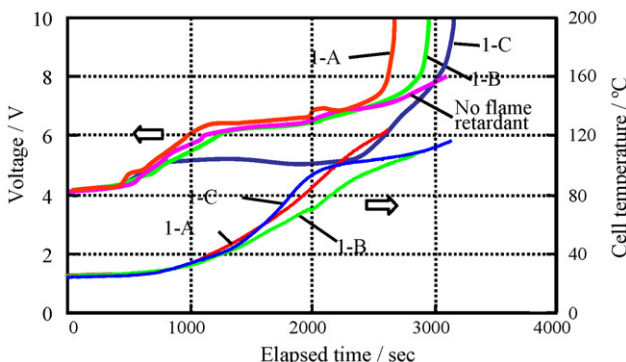


Fig. 10. Change in cell voltage and temperature during overcharge test.

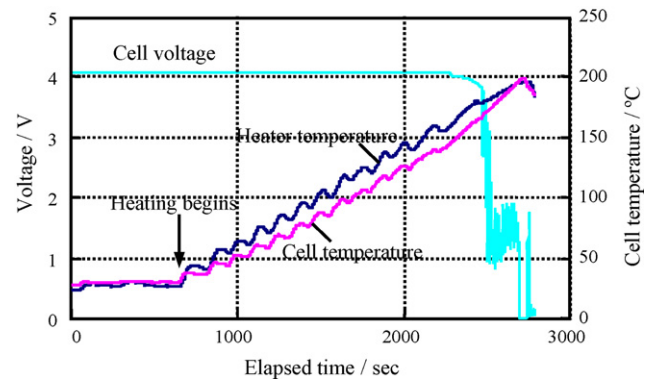


Fig. 11. Results of heating test for test cell 1-C.

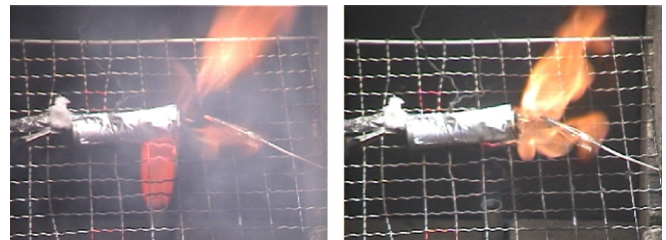
3.6. Burner test

We tested two samples of each cell type: 1-A, 1-B, 1-C, and no flame retardant. We heated the fully charged cells with the flame of a gas burner until venting occurred. Gas containing electrolyte was released by venting and caught fire after being ignited by the burner. Results for a cell without flame retardant are shown in Fig. 12. As the cell temperature rose, the safety valve was opened to release gas that quickly ignited and continued to burn even after the gas burner was turned off. Results for 1-A, 1-B, and 1-C, which contained flame retardant, are shown in Fig. 13. In all cases, the released gas had similar self-extinguishing properties. These results indicate that phosphazene-based flame retardants are effective at making lithium-ion batteries safe.

4. Summary

We have been developing flame-resistant lithium-ion batteries for telecommunication applications. In this work, flame-resistant electrolytes obtained by adding phosphazene-based flame retardants was prepared, and their applicability was investigated. The results can be summarized as follows.

- (1) Self-extinguishing properties in compliance with UL-94V0 were achieved by adding phosphazene-based flame retardants to conventional electrolytes.
- (2) The discharge capacity of test cells using flame-resistant electrolytes was almost the same as those of cells using conventional electrolyte at 25 °C or more. However, the discharge capacity was remarkably decreased at 0 °C and at 3 CA ($\text{CA} = 750 \text{ mA}$). This may be caused by the increase in viscosity of flame-resistant electrolyte produced by adding flame retardants.
- (3) No ignitions or explosions were observed in a continuous overcharge test at 1 CA or heating test up to 200 °C.



(a) Immediately after gas gushes out (b) After extinguishing burner flame

Fig. 12. Heating of test cell (without flame retardant) during the burner test.



(a) Test cell 1-A



(b) Test cell 1-B



(c) Test cell 1-C

From the left: immediately after gas gushes out, midway through, after extinguishing burner flame

Fig. 13. Heating of test cells (1-A, 1-B, and 1-C) during the burner test.

(4) The self-extinguishing properties of gas gushing out of cells with flame retardants were confirmed by a burner test.

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