



# Methoxyethoxyethoxyphosphazenes as ionic conductive fire retardant additives for lithium battery systems

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## ABSTRACT

The current highly flammable configurations for rechargeable lithium batteries generate safety concerns. Although commercial fire retardant additives have been investigated, they tend to decrease the overall efficiency of the battery. We report here ionically conductive, non-halogenated lithium battery additives based on a methoxyethoxyethoxyphosphazene oligomer and the corresponding high polymer, which can increase the fire resistance of a battery while retaining a high energy efficiency. Conductivities in the range of  $10^{-4}$  S  $\text{cm}^{-1}$  have been obtained for self-extinguishing, ion-conductive methoxyethoxyethoxyphosphazene oligomers. The addition of 25 wt% high polymeric poly[bis(methoxyethoxyethoxy)phosphazene] to propylene carbonate electrolytes lowers the flammability by 90% while maintaining a good ionic conductivity of  $2.5 \times 10^{-3}$  S  $\text{cm}^{-1}$ .

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## 1. Introduction

Lithium batteries are among the most widely used primary and secondary modern energy storage devices. Lithium metal and lithium ion batteries are electrochemical devices that generate electricity from lithium sources based on either metallic lithium or intercalation compounds such as lithium–cobalt/lithium–magnesium complexes. The main advantage of lithium batteries is the high energy density, which makes them smaller and lighter than other batteries such as nickel–cadmium devices. As such, lithium batteries are especially suitable for applications where lightweight or compact power sources are required, such as portable electronic devices and electrical vehicles.

On the other hand, one of the biggest drawbacks of rechargeable lithium batteries is their flammability. The high energy density of lithium batteries is accompanied by the high reactivity of their metallic or composite lithium components and by the flammability of their small-molecule, organic solvent-based electrolytes. This makes them susceptible to combustion or even explosions under certain conditions such as short circuits caused by defects or physical damage. Numerous lithium–battery related fires have been reported in recent years, leading to recalls and restrictions [1]. Although various protective devices have been designed, accidents

are still possible. This is an especially important problem for energy storage in electrical automobiles due to the large batteries that are required. The avoidance of secondary damage after accidents or short circuits is especially important for such an application [2].

A number of strategies have been implemented to improve the fire safety of secondary lithium batteries [3,4]. In addition to methods such as reducing the amount of flammable components in the battery, a major challenge is the development of fire retardant additives. Fire retardant materials include those that are truly non-flammable and which can physically contain a fire, and those that inhibit exothermic reactions via chemical reactions to prevent a fire [5,6]. Many fire retardant species contain phosphorus compounds [7–11] because organophosphorus molecules are efficient radical scavengers and flame quenching materials. Combustion processes are essentially exothermic free-radical reactions, and the existence of radical stabilizers impedes combustion by quenching the mechanism. Other types of fire retardants include nitrogen-containing compounds that release inert gaseous by-products to form a highly porous char that provides thermal insulation and prevents the combustion from spreading [12,13]. Most fire retardant additives for lithium batteries are integrated into either the electrode or the electrolyte. However, because such additives cannot contribute to the electrochemical reaction, they usually have a negative effect on the battery efficiency. Other important concerns for practical additive materials include electrochemical stability under actual operational conditions, as well as a straightforward synthesis procedure suitable for scale-up.

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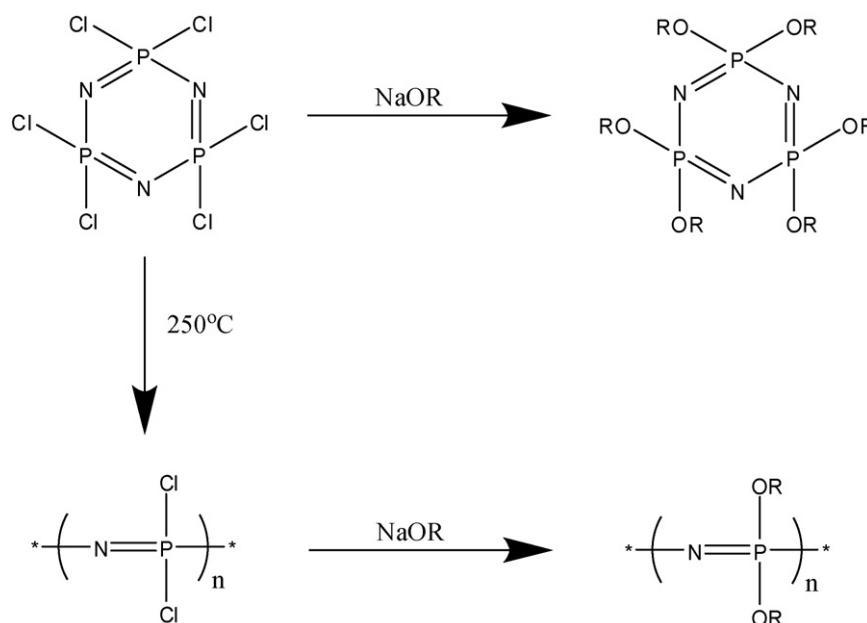


Fig. 1. General synthesis scheme of cyclic and polymeric phosphazenes.

Phosphazenes are a group of small-molecule cyclic or high polymeric linear phosphorus–nitrogen compounds with the general structure shown in Fig. 1. In addition to their versatility in reaction chemistry and overall stability in electrochemical environments [14,15], one of the most important advantages of many phosphazene compounds is their flame resistance or fire retardance properties [16]. This makes phosphazenes particularly good candidates for fire retardant materials in batteries. In other applications, studies have shown that phosphazene crosslinkers in polyurethanes cause the originally highly flammable material becomes self-extinguishing [17]. Other phosphazenes are effective as fire retardants for wood-based materials, where the weight loss during burning was cut in half by the application of a cyclic triphosphazene coating [18]. The currently available phosphazene fire retardant additives are mostly -amino or -oxy derivatives of methyl or phenyl substituted cyclic trimers. These compounds are relative easy to synthesize and have been reported to have useful fire retardant properties [19,20]. This is particularly evident for amino derivatives. However, when used in batteries these molecules lower the electrochemical efficiency of the cell. For aminophosphazene compounds there is also the problem of spontaneous degradation under typical electrochemical working conditions. Thus, the need exists for new fire retardant additives that will maintain or enhance the ionic conductivity of the cell, retain a high energy density, and increase the safety of lithium batteries.

An attractive solution is the incorporation of ionically conductive fire retardant additives into the organic electrolyte. Previous studies have shown that certain phosphazene compounds are themselves suitable as electrolytes for lithium batteries due to their acceptable ionic conductivities. For example, linear polyphosphazenes with oligo-ethyleneoxy side groups have ionic conductivities above  $10^{-5} \text{ S cm}^{-1}$  when used as a gum (solvent-free) electrolyte [14,22] (Fig. 2). It was also reported that these polymers have a high onset temperature of thermal degradation (235 °C) together with a modest heat release capacity [23]. Moreover, small molecule cyclic phosphazenes with the same ethyleneoxy side groups have been used either as stand-alone electrolytes or as plasticizers for gel electrolytes, and they are known to function well as solvents and as additives that increase the

ionic conductivity of the base macromolecular electrolyte [24,25] (Fig. 2). Related studies showed that, when used as a plasticizer for poly(ethylene oxide) electrolytes, or additives for organic carbonate solvents, the flammability of the electrolyte was lowered below the combustion standard while increasing the conductivity from  $\sim 10^{-5}$  to  $\sim 10^{-3} \text{ S cm}^{-1}$  at 50 °C [26]. By using these species as pure electrolytes or additives to organic solvent electrolytes, it should be possible to construct a fire-resistant lithium battery with a high energy density [27]. Moreover, small-molecule liquid cyclic phosphazenes that bear oligo-ethyleneoxy side groups should be useful as electrolyte additives or as stand-alone liquid electrolytes without decreasing the overall efficiency of the battery. High molecular weight, long-chain species can be used as the basis of gel electrolytes or as semi-solid spacer matrix materials,

In this work, we have performed in-depth studies of the performance of two phosphazene compounds as liquid electrolyte additives, gel electrolyte additives, and stand-alone electrolyte components. The main focus of this study is on the fire retardant

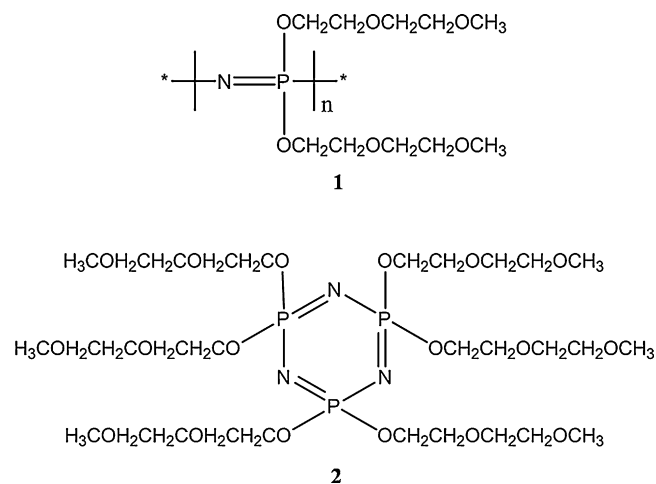


Fig. 2. Examples of phosphazenes with ethyleneoxy side groups. Compound 1: polymeric methoxyethoxyethoxyphosphazene (MEEP). Compound 2: cyclic trimeric phosphazene with methoxyethoxyethoxy side groups (MEE trimer).

properties and electrochemical performance of both the pure compounds and their mixtures with classical organic solvent-based electrolytes. For fire retardant properties, we analyzed the combustion properties of the electrolytes through direct burning tests modified from ASTM standard procedures. For the electrochemical evaluations, we prepared lithium salt electrolytes of each material and carried out alternating current impedance ionic conductivity experiments for different salt concentrations. Lithium triflate–propylene carbonate system have been selected as the model base electrolyte for better comparison with earlier phosphazene studies.

## 2. Experimental

### 2.1. Materials

Hexachlorocyclotriphosphazene,  $(\text{NPCl}_2)_3$ , was obtained from Fushimi Chemical and Pharmaceutical Co. Ltd., Japan. The compound was purified by recrystallization from heptane, and sublimation at  $40^\circ\text{C}$  and 0.05 mmHg vacuum. Celite, sodium metal, lithium trifluoromethylsulfonate ( $\text{LiCF}_3\text{SO}_3$ ), di(ethylene glycol)methyl ether, and propylene carbonate were obtained from Aldrich. Grade 691 glass microfiber filter paper, diethyl ether, hexanes, tetrahydrofuran (THF), and methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) were purchased from VWR. Di(ethylene glycol) methyl ether and propylene carbonate were purified by vacuum distillation. The diethyl ether, hexanes, THF, and  $\text{CH}_2\text{Cl}_2$  were purified through copper/silica catalytic drying columns. All other chemicals were used as received. Nextel 312 aluminum–silicon–boron oxide fiber was obtained from 3M.

### 2.2. Characterization

Molecular characterization was carried out by  $^1\text{H}$  and  $^{31}\text{P}$  NMR spectroscopy with use of a Bruker AMX-360 instrument. Conductivity measurements were made using a HP-4192A impedance analyzer and a two-point liquid conductivity cell. The cell constant was calibrated with a set amount of standard sodium chloride solutions of various concentrations. The cell containing the sample was dried under reduced pressure for 24 h and was refilled with dry nitrogen before measurements.

### 2.3. Syntheses

MEE trimer (**2**) and MEEP polymer (**1**) were synthesized using previously reported procedures [23], with improvements to the purification processes.

#### 2.3.1. Hexa(methoxyethoxyethoxy)cyclotriphosphazene (MEE trimer) (**2**)

Di(ethylene glycol) methyl ether (68 ml, 0.57 mol) was added to a suspension of sodium metal (6.55 g, 0.28 mol) in THF (400 ml), and the mixture was stirred and heated gently until all the solid sodium was consumed. The fully reacted mixture was then added to a solution of hexachlorocyclotriphosphazene (15 g, 0.043 mol) in THF (100 ml). The reaction mixture was stirred and heated gently for 16 h, then cooled to room temperature. The THF was removed under reduced pressure, and the remaining mixture was re-dissolved in  $\text{CH}_2\text{Cl}_2$  and purified via a water extraction. The solvent was then removed, the product was re-dissolved in an ether–hexane mixture at the maximum possible concentration, and the solution was stored at low temperature ( $-65^\circ\text{C}$ ) until a clear phase-separation was obtained. The lower portion was separated and dried, re-dissolved in  $\text{CH}_2\text{Cl}_2$ , mixed with activated carbon to remove colored impurities, and filtered with a short Celite column, followed by a final removal of  $\text{CH}_2\text{Cl}_2$  under reduced pressure. The product was

a clear, slightly yellow oil. Yield: 77.9%.  $^{31}\text{P}$  NMR: 17.7311 ppm (s, 3P, NPN).  $^1\text{H}$  NMR: 3.282 ppm (s, 3H,  $\text{OCH}_3$ ); 3.449 ppm (t, 2H,  $\text{MeOCH}_2$ ); 3.553 ppm (m, 4H  $\text{CH}_2\text{OCH}_2$ ); 4.006 ppm (t, 2H,  $\text{POCH}_2$ ).

#### 2.3.2. Poly[bis(methoxyethoxyethoxy)phosphazene] (MEEP) (**1**)

This synthesis was carried out by a previously published procedure [14,20].

### 2.4. Flammability test procedures

#### 2.4.1. Wick test

A 2 g electrolyte sample was contained in a small glass cup, and a  $1\text{ cm} \times 1\text{ cm}$  glass fiber paper (VWR Grade 691 glass microfiber filter paper) was soaked in the electrolyte for 1 min. The paper was then supported vertically by the side of the cup, and was ignited by a butane flame held in contact with the edge of the paper until either a free-standing flame was observed, or 10 s had passed, whichever was shortest. Once the ignition source was removed, the flame was timed until it self-extinguished.

#### 2.4.2. Fiber test

This test was a modified procedure based on ASTM D-5306: A 12-cm length of 3M Nextel 312 aluminum–silicon–boron oxide fiber (900 Denier Ply-twisted 2.7 twist per inch 3/4 yarn, 390 yds  $\text{lb}^{-1}$ ) was weighed and soaked in the electrolyte solution for 1 min. The yarn was then tensioned via weights at both ends and pretreated by a standard method, weighed to calculate the average amount of electrolyte absorbed per unit length, then suspended horizontally and ignited from one end. The flame was allowed to burn over 1 cm before the timing was started, and the timing ended either when the flame self-extinguished or when the flame had traveled 5 cm, whichever came first. The flame propagation was calculated by dividing the actual distance the flame traveled by the time taken for the flame to travel. The average fuel consumption rate was calculated by multiplying the electrolyte weight per length by the flame propagation rate.

### 2.5. Electrolyte solution preparation

Two alternative methods were employed for electrolyte preparation.

#### 2.5.1. Solvent-free electrolytes

The conductivity measurements for the electrolyte solutions of MEE trimer/ $\text{LiCF}_3\text{SO}_3$  salt were carried out for samples of various concentrations by adding  $\text{LiCF}_3\text{SO}_3$  to a 2:1 THF:MEE trimer mixture and removing the THF later in vacuum. Liquid MEE trimer (3.5771 g, 3 ml), pre-dissolved in THF (5 ml), was mixed with  $\text{LiCF}_3\text{SO}_3$  in 1.3, 2.6, 3.7, 6, 9.3, 11.3, 28.7, 37.7, and 44.7 wt% ratios [14,20,23,25]. Stirring was applied to ensure proper mixing. The solvent was then removed from the resulting mixture at reduced pressure. Polymeric MEEP gum electrolyte samples were prepared using the same procedure and weight ratios, but the MEEP polymer was pre-dissolved in THF (5 ml) before mixing.

#### 2.5.2. Electrolytes containing propylene carbonate

Propylene carbonate-based samples were prepared using the same total sample weight in each case: a base of propylene carbonate–phosphazene blend was mixed with  $\text{LiCF}_3\text{SO}_3$  in 1.3, 2.6, 3.7, 6, 9.3, 11.3, 28.7, 37.7, and 44.7 wt% ratios. For propylene carbonate–MEE trimer mixtures and 75:25 weight ratio propylene carbonate–MEEP polymer mixtures,  $\text{LiCF}_3\text{SO}_3$  was first blended with propylene carbonate in predetermined amounts to maintain the final concentrations as described above. MEE trimer or MEEP polymer were then added to the solution until the components formed a homogeneous solution. For propylene carbonate–MEEP

mixtures of 25:75 and 50:50 weight ratios, the polymer was first dissolved with the lithium salt in THF to form a homogeneous solution. The solvent was then removed under reduced pressure. The resultant solid electrolyte was then allowed to absorb propylene carbonate at ratios described above for 2 weeks under an inert atmosphere until a uniform gel electrolyte was formed.

### 3. Results and discussion

#### 3.1. Fire retardant properties

##### 3.1.1. General aspects

The fire retardant behavior of these compounds is of major interest. Although no commonly accepted tests are available for flammability of electrolytes, a number of methods are possible based on previous research [10–12,15,19,28]. However, our attempts to test various phosphazene systems showed that many of the methods employed previously caused samples to self-extinguish too quickly to allow the detection of differences between various compositions. Thus, we have modified existing methods so that we can artificially sustain a flame by introducing a larger surface area, so that the variations between different samples can be examined thoroughly. In addition, we believe that both the self-extinguish time and the flame propagation behavior are important indicators of fire retardant behavior, although the latter is rarely reported. Similarly, the consumption rate of the electrolytes may also give some insight into the nature of the actual combustion process. As such, we have chosen methods which used non-flammable matrices that absorb the electrolyte samples in order to provide stable platforms for all three measurements.

##### 3.1.2. Self-extinguishing rate

The self-extinguishing time measurements using a glass fiber wick method were performed with a container of electrolyte ignited from a piece of glass fiber supported by the side of the glass cup container, and the extinguish time of the resulting flame was timed (Fig. 3). While it is not possible to compare MEEP flammabil-

ity directly with other samples, because MEEP is a gum rather than a liquid, and it cannot be readily absorbed into the wick during combustion, it is still possible to estimate through the performance of phosphazene–propylene carbonate mixtures. The flammability of samples with higher phosphazene content was found to be lower in all the electrolyte types we have investigated. Interestingly, the experimental results with MEEP–PC show lower flammability than for MEE trimer–PC, with a significantly shorter self-extinguish time (Fig. 4). This is probably due to the lower volatility of MEEP, which decreases the overall vapor pressure of flammable species, effectively reducing the flammable fuel supply with a higher energy barrier. It was also observed that samples with a high content of phosphazene materials tend to produce large amounts of char after combustion, which is consistent with the radical stabilization effect of organic phosphorus fragments, which are expected to hinder exothermic chain reactions, thus lowering the temperature of the flame and promoting char formation. This may be one of the reasons for the difference in self-extinguishing behavior between different samples: MEE trimer–PC mixtures had lower viscosities and thus had less efficient coating capacities than the MEEP–PC mixtures. On the other hand, the charring effect of the phosphazenes still caused the samples to self-extinguish after a short period of time compared with clean-burning pure PC (Fig. 4).

##### 3.1.3. Linear flame propagation

Flame propagation tests using ceramic fibers are adapted from hydraulic fluid characterization methods (ASTM D-5306), where the speed of an ignited flame traveling from one end of the fiber to another is used to compare flammability (Fig. 5). Our results show that the addition of phosphazene components indeed reduces the average flame propagation rate in a PC electrolyte, and increases in the amount of PC in the mixture increases the flammability as expected. Higher concentrations of the non-flammable  $\text{LiCF}_3\text{SO}_3$  component also decreased flame propagation, although it shows a much reduced effect after a certain point (Figs. 6 and 7). The results are promising since the phosphazene additives not only lower the flammability significantly, but the optimal concentration range of  $\text{LiCF}_3\text{SO}_3$  (where the fire retardant effect levels off) for all samples overlap with the optimal range for conductivity. On the other hand, the results show no significant difference between the MEE trimer and MEEP in terms of its impact on linear flame progression.

##### 3.1.4. Fuel consumption rate

Conversion of flame progression data to fuel consumption was done by dividing weight of absorbed electrolyte over flame propagation speed, and the results show some interesting differences between the two data sets despite use of the same method. At lower salt concentrations, the addition of MEEP seemed to induce

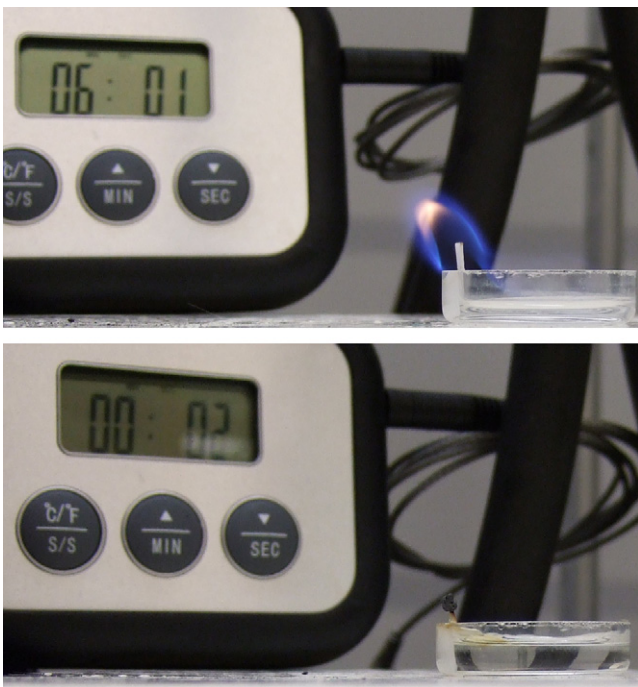


Fig. 3. Self-extinguish time experiment setup. Above: sustaining flame of pure PC. Below: rapidly self-extinguished flame of MEE trimer.

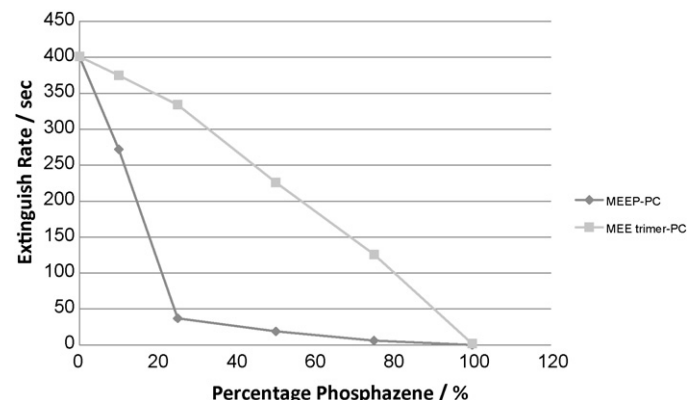


Fig. 4. Results of self-extinguishing test.

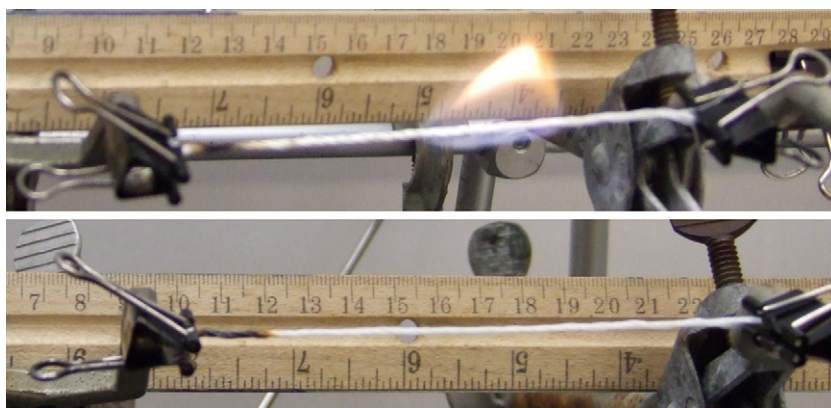


Fig. 5. Experimental setup for linear flame propagation test. Above: rapid progressing flame of PC sample. Below: self-extinguished MEE trimer sample.

a similar fuel consumption rate just as in the linear flame propagation, but at very high salt concentrations the electrolyte appeared to be consumed faster (Figs. 8 and 9). Although the difference is relatively minor, such a result suggest that the variation at the high  $\text{LiCF}_3\text{SO}_3$  salt concentrations compared to wick tests could be related to the viscosity of the electrolyte solution, as higher viscosity would lead to a thicker coating of the electrolyte on the ceramic fiber, and the difference in the amount of absorbed electrolyte per unit length would impact the effective surface area and thus the fuel consumption rate. In fact, with higher viscosity sam-

ples it was sometimes observed that parts of the electrolyte were melted and dripped from the fiber rather than being consumed by the flame, which could also contribute to the difference. Similarly, the trend of flammability at higher concentrations reverses slightly for MEE trimer versus MEEP when the percentage of MEEP is large in the mixture, again closely tied to the apparent viscosity. As such, more investigation will be required to find a more appropriate test to compare with the results of existing methods for a clear picture.

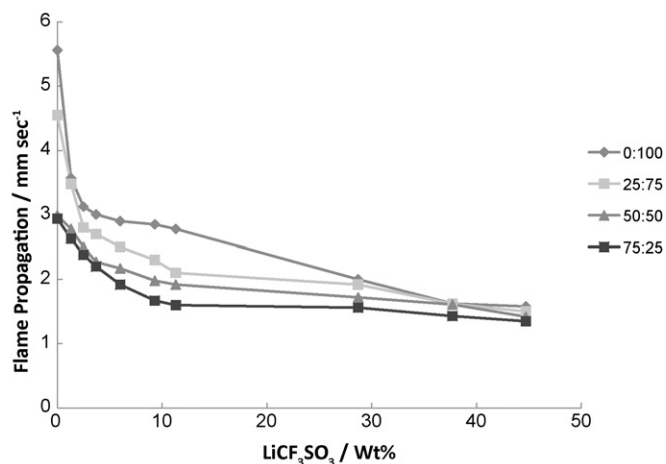


Fig. 6. Linear flame propagation of MEEP-PC mixtures.

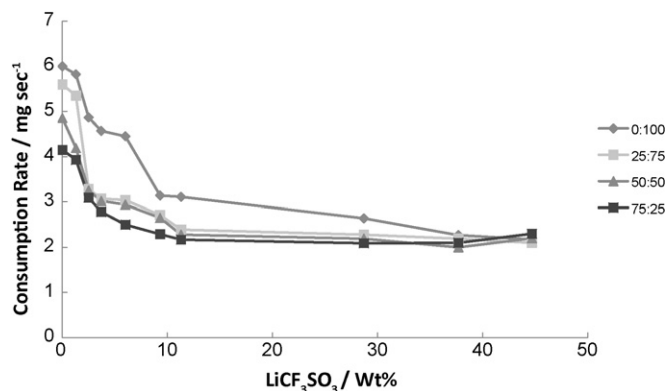


Fig. 8. Fuel consumption rates of MEEP-PC mixtures.

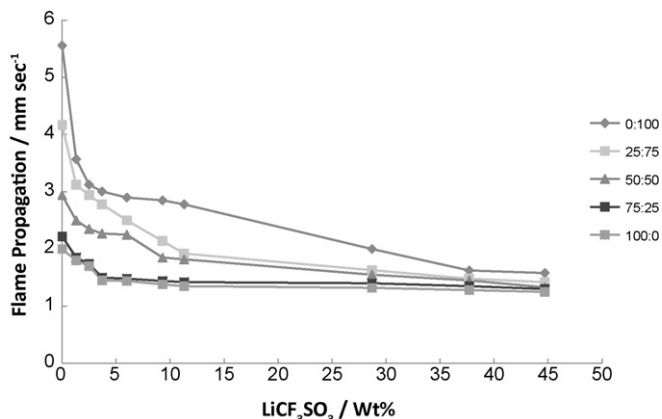


Fig. 7. Linear flame propagation of MEE trimer-PC mixtures.

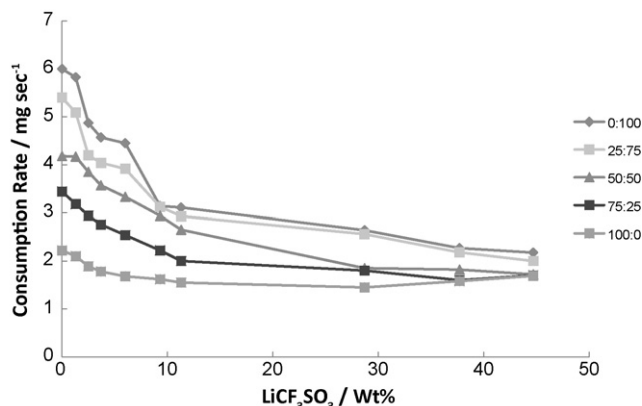
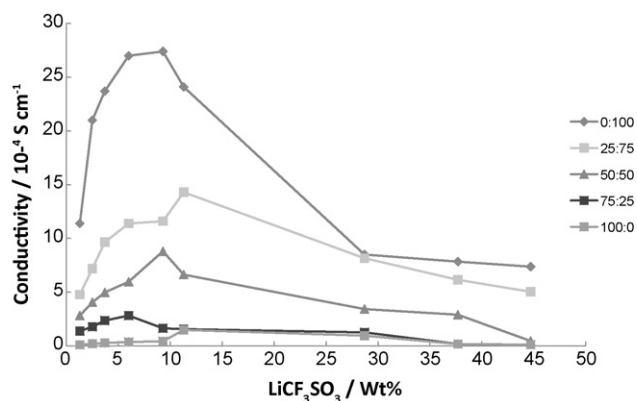


Fig. 9. Fuel consumption rates of MEE trimer-PC mixtures.



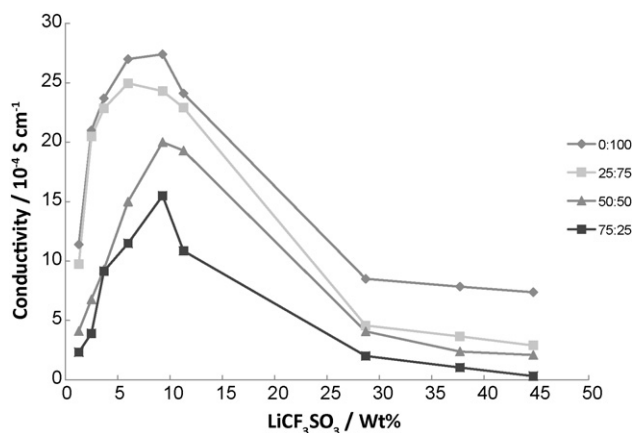
**Fig. 10.** Conductivity data of MEE trimer-PC mixtures for different phosphazene:PC weight ratios.

### 3.2. Ionic conductivity

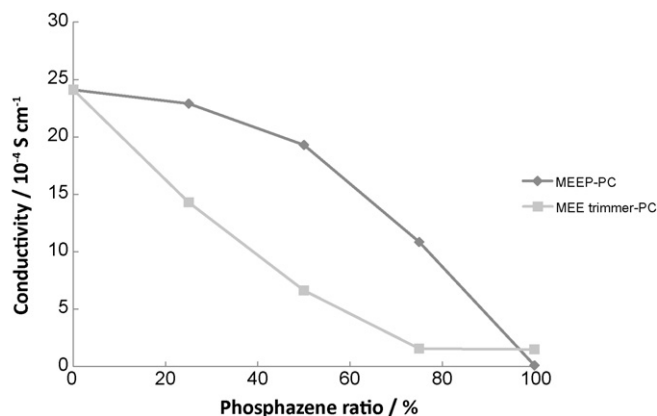
The second part of this project was focused on comparative conductivity studies of electrolytes that contain methoxyethoxyethoxy polymeric- or small molecule cyclic phosphazenes. As before, the abbreviations MEEP polymer and MEE trimer refer to the compounds shown in Fig. 2 as structures 1 and 2.

The conductivity results are shown in Figs. 10 and 11. The salt concentrations were chosen to approximate to 0.1–1 M values in the liquid electrolyte at lower ranges, while the Li:O atomic ratios were targeted to 1:4–1:8 at the higher ranges in accordance with previous solid electrolyte experiments [14,20,23,25]. The  $1.5 \times 10^{-4} \text{ S cm}^{-1}$  maximum conductivity of the MEE trimer electrolyte was in agreement with other liquid phosphazene electrolytes reported previously.

Mixtures of both methoxyethoxyethoxyphosphazenes with propylene carbonate generally had higher ionic conductivities than the pure phosphazene compounds, as shown in Figs. 10 and 11. This is not unexpected, because the addition of a highly ion-conductive, low viscosity liquid plasticizer should increase the ion mobility. Thus, both polymeric and cyclic trimeric methoxyethoxyethoxyphosphazenes are acceptable additives to propylene carbonate, since their existence does not significantly compromise the conductivity of the organic carbonate-based electrolyte system even at relatively high weight ratios. However, an unexpected result is that the polymeric MEEP-PC mixtures had higher ionic conductivities than comparable MEE trimer-PC mixtures. The addition of PC to MEEP had a significant effect on the



**Fig. 11.** Conductivity data of MEEP-PC mixtures for different phosphazene:PC weight ratios.



**Fig. 12.** Comparison of ionic conductivity around the optimal  $\text{Li}^+$  concentration.

conductivity, while, for MEE trimer, the increase was not obvious until the amount of PC was raised to approximately 50 wt% (Fig. 12). Because similar numbers have been reported in the past for MEEP-PC mixtures [23], the possibility of conductive contamination can probably be ruled out. However, considering that pure MEEP has a lower ionic conductivity and higher viscosity than MEE trimer, this result still requires investigation and explanation, especially for the samples with low PC content where the viscosities of the MEEP-PC mixtures are higher than those of MEE trimer-PC mixtures.

A possible explanation for the behavior of the high polymer is that the “swinging-arm” ion transport mechanism often invoked for a branched polymer electrolyte is applicable to this system. The mechanism supposes that the ions can be transported between side chains through their random thermal movements, and that this process is actually assisted by the existence of a continuous, flexible polymer backbone if the matrix is swollen by a compatible ion-conducting liquid medium. A possible additional effect is the preservation of the ion transport properties of propylene carbonate within a larger molecular framework of MEEP polymer. Instead of a homogeneous mixture of solvent molecules that encase the ions, as in the case of propylene carbonate alone or MEE trimer-propylene carbonate systems, the MEEP chains may form large coils or a supporting matrix when suspended in etheric solvents. Such a system can be viewed as islands or webs of MEEP floating in a sea of propylene carbonate, essentially providing ion conductive channels through a solution that is composed mainly of propylene carbonate. On the other hand, polymers that have a lower compatibility with propylene carbonate may still form an entangled matrix that is swollen by PC instead, and the ionic conductivity would be hindered by the solid matrix. However, both of these assumptions require additional proof by comparing our results to liquid solvent compatible gel systems that are known to have low ionic conductivities.

### 4. Conclusions

We have developed fire-retardant electrolyte systems based on the methoxyethoxyethoxy-substituted phosphazene polymer and oligomer systems and have developed testing methods to estimate their flame retardant ability and measure their ionic conductivity behavior. As a stand-alone electrolyte the methoxyethoxyethoxyphosphazene cyclic trimer has shown very good self-extinguishing behavior with acceptable conductivity. When mixed with propylene carbonate solvent, both the cyclic oligomer and MEEP polymer showed good compatibility with the organic medium and a significant reduction of flammability while retaining good ionic conductivity. Additional tailoring of

the side groups attached to the phosphazene skeleton should further improve the fire safety of lithium battery electrolyte systems. Future research will be focused on the in-depth electrochemical study geared toward assembled commercial batteries, including CV studies of component stabilities as well as the effect of different salt types.

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