



## Fluorinated phosphazene co-solvents for improved thermal and safety performance in lithium-ion battery electrolytes



Harry W. Rollins\*, Mason K. Harrup, Eric J. Dufek, David K. Jamison, Sergiy V. Sazhin, Kevin L. Gering, Dayna L. Daubaras

Idaho National Laboratory, P.O. Box 1625, Idaho Falls, ID 83415, USA

### HIGHLIGHTS

- Fluorinated cyclic phosphazene electrolytes for lithium-ion batteries.
- Improved thermal and safety performance.
- Improved electrochemical window.
- Comparable rate capabilities at C/1 for up to 20 wt% phosphazene.

### ARTICLE INFO

#### Article history:

Received 5 March 2014

Received in revised form

3 April 2014

Accepted 4 April 2014

Available online 16 April 2014

#### Keywords:

Phosphazene

Electrolyte

Lithium-ion battery

Stability

Non-flammable

### ABSTRACT

The safety of lithium-ion batteries is coming under increased scrutiny as they are being adopted for large format applications especially in the vehicle transportation industry and for grid-scale energy storage. The primary short-comings of lithium-ion batteries are the flammability of the liquid electrolyte and sensitivity to high voltage and elevated temperatures. We have synthesized a series of non-flammable fluorinated phosphazene liquids and blended them with conventional carbonate solvents. While the use of these phosphazenes as standalone electrolytes is highly desirable, they simply do not satisfy all of the many requirements that must be met such as high LiPF<sub>6</sub> solubility and low viscosity, thus we have used them as additives and co-solvents in blends with typical carbonates. The physical and electrochemical properties of the electrolyte blends were characterized, and then the blends were used to build 2032-type coin cells. We have evaluated the performance of the electrolytes by determining the physical properties, thermal stability, electrochemical window, cell cycling data, and the ability to form solid electrolyte interphase (SEI) films. This paper presents our most recent results on a new series of fluorinated cyclic phosphazene trimers, the FM series, which has exhibited numerous beneficial effects on battery performance, lifetimes, and safety aspects.

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### 1. Introduction

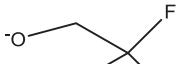
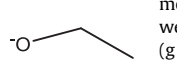
As lithium-ion batteries are being rapidly adopted for large format applications, the safety of these systems is receiving ever-increasing scrutiny. More stringent safety and energy density requirements make the development of electrolytes with lower flammability, larger electrochemical window, and higher operating voltages a necessity [1]. Most of the commercial electrolytes for lithium-ion batteries are LiPF<sub>6</sub> dissolved in a mixture of organic carbonate and/or ester solvents [2]. These electrolyte blends are highly volatile and highly flammable, with typical flash points of

around 30 °C or less. This presents serious safety concerns especially when utilized in large format cells or when the cells come under undue stress or physical damage. One approach to improve the safety performance of the electrolyte is to use additives and co-solvents to reduce the flammability of the organic carbonate and ester electrolytes. A variety of additives and co-solvents have been proposed, including sulfones, ionic liquids, phosphates, phosphonates, phosphazenes, siloxanes, fluorinated carbonates, and fluorinated ethers and mixtures thereof [3–10]. In addition to flammability suppression, additives have also been used to improve solid electrolyte interphase (SEI) formation [11], overcharge protection [12], and thermal stability [13]. Compared to other organophosphorous compounds and other additives, phosphazenes showed the least degradation in battery performance [14]. We have

\* Corresponding author. Tel.: +1 208 526 4066.

E-mail address: [harry.rollins@inl.gov](mailto:harry.rollins@inl.gov) (H.W. Rollins).

**Table 1**  
Pendant group distribution and properties of the FM series of phosphazenes.

Designation	# of 	# of 	Average molecular weight (g mol <sup>-1</sup> )	Density (g ml <sup>-1</sup> )
FM1	6	0	729.13	n.d. <sup>a</sup>
FM2	3	3	567.22	1.33
FM3	2	4	513.25	1.28
FM4	1	5	459.27	1.29

<sup>a</sup> Not determined.

focused our recent investigations on the use of novel low molecular weight phosphazenes as additives and co-solvents in lithium ion batteries [15–18]. This paper presents our results on a series of chemically similar, fluorinated cyclic phosphazene trimers, referred to as the FM series in this paper.

## 2. Experimental

### 2.1. Instrumentation

During the synthesis of the phosphazenes the reaction progress was followed by <sup>31</sup>P NMR using a Bruker Avance III 600 MHz spectrometer. To ensure the materials were dry, titrations were performed using a Mettler Toledo C30 Karl Fischer coulometer (in an argon glovebox). To ensure the samples were halide-free, samples were analyzed by ion-chromatography with a conductivity detector. Electrolyte blends containing the fluorinated phosphazenes, alkyl carbonates and LiPF<sub>6</sub> were prepared in an argon glovebox where the conductivity and viscosity were determined. The reported conductivities are the average of ten measurements obtained on a TOA CM-30R conductivity meter. The viscosities of the blends were determined using a Cambridge DL-4100 (falling bob) viscometer (average of 10 measurements). A portion of the sample was passed out of the glovebox, where the flash point and vapor pressure were determined. Closed-cup flash points were determined using a Setaflash 82000-0 (electric ignition) using a ramp determination method. Vapor pressures of the samples were determined from 15 °C to 60 °C in 1 °C increments using a Grabner Instruments Minivap VPXpert vapor pressure analyzer. Thermal stability experiments were run in an ESPEC BTU133 thermal chamber.

### 2.2. Reagents

Hexachlorocyclotriphosphazene was obtained from Molport.com and was purified by sublimation prior to use. Anhydrous ethanol, anhydrous 1,4-dioxane, dichloromethane, and sodium metal were obtained from Sigma–Aldrich and were used as received. 2,2,2-trifluoroethanol (Sigma–Aldrich) was distilled prior to use. Battery-grade LiPF<sub>6</sub>, ethylene carbonate (EC), ethyl methyl carbonate (EMC), and diethyl carbonate (DEC) were obtained from Kishida Chemical Co. and were used as received in an argon glovebox.

### 2.3. Synthesis of the fluorinated phosphazenes

We prepared a series of chemically similar fluorinated cyclic phosphazene trimers with varying number of fluorinated pendant groups. This series of compounds was prepared by the nucleophilic substitution of the reactive chlorines on hexachlorocyclotriphosphazene with ethoxy or 2,2,2-trifluoroethoxy

groups. The number of ethoxy and 2,2,2-trifluoroethoxy groups where varied as shown in Table 1. Fig. 1 shows the structure for FM2 as an example. Synthesis of this series of fluorinated phosphazenes were carried out in oven dried glassware under a blanket of nitrogen gas using Schlenk techniques. The synthesis of each of these materials were nearly identical, the details of the FM2 synthesis are given below.

#### 2.3.1. Sodium ethoxide

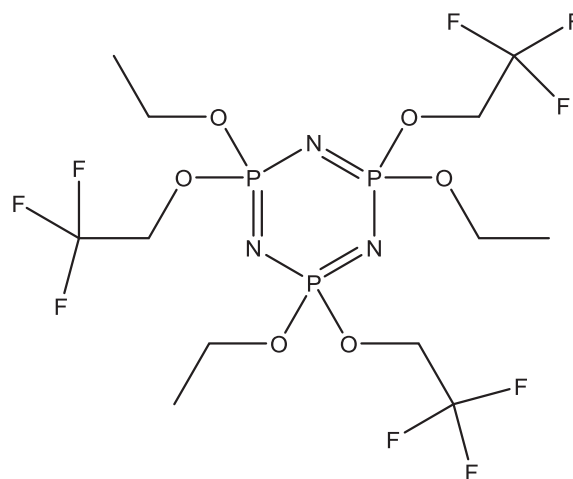
An oven-dried 1 L 3-neck flask was fitted with a dry nitrogen inlet, a reflux condenser and rubber septa. The dry nitrogen outlet was fitted to the top of the reflux condenser and passed through a bubbler filled with ~2 inches of silicon oil. The reactor was kept under a slow steady stream of dry nitrogen until the completion of the reaction. The flask was filled with ~700 ml of anhydrous dioxane and then 9.92 g sodium metal (0.431 mol) was added. To this a 60% excess of ethanol was added (40 ml, 0.685 mol). The reaction was heated at sub-reflux temperature until all of the sodium was consumed.

#### 2.3.2. Sodium trifluoroethoxide

An oven-dried, 2 L 3-neck flask was fitted with a dry nitrogen inlet, a reflux condenser and rubber septa. The dry nitrogen outlet was fitted to the top of the reflux condenser and passed through a bubbler filled with ~2 inches of silicon oil. The reactor was kept under a slow steady stream of dry nitrogen till the completion of the reaction. The flask was filled with ~700 ml of anhydrous dioxane and then 11.3 g sodium metal (0.49 mol) was added. Then 35.7 ml (0.49 mol) of the TFE was added. The reaction was heated at nearly reflux temperature until all of the sodium was consumed.

#### 2.3.3. Hexachlorocyclotriphosphazene substitution

In an oven dried 500 ml flask, 50 g (0.144 mol) of the hexachlorocyclotriphosphazene trimer was dissolved in ~300 ml anhydrous dioxane which was then added to the sodium ethoxide solution (under nitrogen at room temperature) and heated at sub-reflux for 5 h and the reaction progress was monitored by <sup>31</sup>P NMR. This solution was then cooled to room temperature and then added to the sodium trifluoroethoxide (at RT under nitrogen). This solution was heated to sub reflux for ~5 h. This reaction was also followed by <sup>31</sup>P NMR. When the reaction was complete, the solution was allowed to cool to room temperature and the excess ethoxides were quenched with water. The solution was neutralized with 2 M HCl. The solvent was removed by rotary evaporation leaving the FM product (a liquid) and undissolved solid sodium chloride. The



**Fig. 1.** Structure of the fluorinated phosphazene designated FM2.

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