



Unsaturated phosphazenes as co-solvents for lithium-ion battery electrolytes



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HIGHLIGHTS

- Unsaturated cyclic phosphazene electrolytes for lithium-ion batteries.
- Improved thermal and safety performance.
- Comparable discharge capacity at loading up to 10%.

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ABSTRACT

This paper covers the synthesis and use of a related family of cyclic phosphazene solvents containing terminal unsaturations that are being considered as electrolyte additives in lithium-ion cells. A brief synopsis on the synthesis and purification of these compounds is given. Data will be presented that covers physical and chemical properties of the phosphazenes as well as the properties when blended at various levels with representative organic carbonate baseline solvents. Electrochemical cycling data will be presented using commercially available electrode couples as well as studies focusing on cell performance at early lifetime as well as after repeated cycles. Conclusions regarding the effect of the unsaturated phosphazene compounds and their interaction with various alkyl carbonates, and their effect on cell performance will be presented.

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1. Introduction

Lithium ion batteries are currently in widespread use for a broad range of mobile power needs. However, in order to move lithium ion technology into long-term larger format applications, such as vehicle technologies and stationary power, there still remain significant challenges that must be addressed. Perhaps the most urgent of these issues is safety concerns with the electrolyte. As most commercial electrolytes employ LiPF_6 as the lithium salt dissolved in a mixture of organic carbonates and/or esters [1] this mix brings several intrinsic problems. These solvents are highly volatile as well as highly flammable. Also, they and their combustion products can be toxic. This presents a serious safety problem in situations where the battery is under abuse or if one (or more) of the individual cells in a pack design begins a thermal runaway, leading to propagation to the other cells. While this concern is partially mitigated in small

single cell power sources such as those that power small electronics, the problem rapidly grows in magnitude as battery sizes and the numbers of individual cells in a pack grow. In order to have meaningful commercial adoption of such larger format batteries, this problem must be addressed.

The search for alternative solvents to serve as replacements for the current generation of alkyl carbonate-based solvents has received much attention in recent years. This is important not only from a safety standpoint but from a performance standpoint as the alkyl carbonates are known to have poor oxidative stability above 4.7–4.8 V [2]. Approaches to address these issues under study include the use of sulfones [3] and most recently ionic liquids [4,5]. However it may be some time into the future before carbonates and esters may be entirely replaced. As a practical interim strategy, improvements in the performance and safety record of the current generation of electrolytes may be realized through the use of additives [6]. Additives have been the subject of research since the early 1990's [7] and continue to enjoy ever-increasing interest, especially in the past few years. Additive research has taken several forms to address various challenges in lithium ion batteries. Some

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have employed additives to improve solid electrolyte interphase (SEI) formation [8], overcharge protection [9], and flammability suppression [10]. Others have employed additives not as co-solvents but rather through the use of novel salts to achieve improved thermal stability [11]. Some of the classes of compounds originally investigated as complete replacements for the carbonates are undergoing a resurgence by employing them as co-solvents, such as ionic liquids [12].

There has been interest in the use of inorganic compounds for this purpose, particularly with the use of phosphorus compounds. Recent studies have employed phosphates as SEI improving additives [13], phosphites as additives [14], as well as phosphorus–nitrogen compounds to improve safety [15]. Previous work from our laboratories has shown that cyclic phosphazenes continue to exhibit real promise to improve both the safety and performance of conventional electrolytes [16–19]. This work reports on the behavior of novel liquid unsaturated phosphazene-based co-solvents for lithium ion batteries. This new class of phosphazene derivatives was chosen for study as it is well known that the incorporation of unsaturated moieties aids in SEI formation and subsequent battery performance [8].

2. Experimental

2.1. Instrumentation

All NMR analyses were performed on a Bruker Ascend Avance III 600 MHz spectrometer. Viscosity measurements were performed using a Cambridge DL-4100 (falling bob) viscometer, in an argon glovebox, the data presented is the average of 10 individual measurements. Conductivity measurements were performed using a TOA CM-30R conductivity meter in an argon glovebox, the data presented is the average of 10 individual measurements. Flash point determinations were performed using a Setaflash 82000-0 (electric ignition) using a ramp determination method, the data reported is the average of 3 individual determinations, all with fresh sample. Vapor pressure measurements were made on a Grabner Instruments Minivap VPXpert. Trace water determinations were performed on a Mettler Toledo C30 Karl Fischer coulometer (in an argon glovebox), the data presented is the average of 3 individual measurements. Electrochemical measurements were made on a Solartron SI 1260 impedance/phase gain analyzer with a Solartron SI 1287 electrochemical interface. Coin cells (type 2032) were tested using a Maccor Series 4000 5V/5A full range tester. Thermal stability experiments were run in an ESPEC BTU133 thermal chamber.

2.2. Reagents

Hexachlorocyclotriphosphazene was obtained from [Molport.com](#) and was purified via sublimation immediately prior to use. All pendant groups were obtained from Aldrich Chemical Company, allyl alcohol was distilled and stored in Schenk bulb containers prior to use. Isopropanol and ethanol were obtained as anhydrous grade and used as received. Sodium metal was obtained from Aldrich Chemical Company and the kerosene was rinsed off with hexanes and blotted dry with a laboratory wipe before use. Sodium hydride (95%, dry) was obtained from Aldrich Chemical Company and used as received. 1,4-Dioxane was obtained from Aldrich Chemical Company as anhydrous grade and used as received. Dichloromethane was obtained from Aldrich Chemical Company and used as received. Nanopure water (18.4 M Ω cm) was generated in the laboratory using a Barnstead NANOpure II water purification system. Ethylene carbonate, ethyl methyl carbonate, diethylene carbonate, and lithium hexafluorophosphate were all obtained as

battery grade reagents from Kishida Chemical Co. and used as received.

2.3. Phosphazene synthesis

Synthesis of all of the phosphazenes followed a similar synthetic pathway employing Schlenk techniques. The specific formulation described here is for the synthesis of AL-6. Sodium hydride (5.33 g, 222 mmol) was placed into an oven dried 2 L three-neck flask fitted with a reflux condenser, a dry nitrogen inlet, and a septum stopper. The dry nitrogen outlet issued from the top of the reflux condenser into an oil bubbler apparatus charged with approximately two inches of silicon oil. 1,4-Dioxane (700 ml) was cannulated into the flask and the reaction was stirred using a magnetic stirbar. Freshly distilled allyl alcohol (11.7 ml, 222 mmol) was cannulated into the reaction vessel and the reaction, which forms an allyl alkoxide solution, was allowed to proceed at room temperature overnight. In a separate 1 L three-neck flask outfitted as the first flask was placed sodium metal (5.95 g, 222 mmol) 1,4-Dioxane (350 ml) was cannulated into the flask followed by addition of anhydrous ethanol (16.0 ml, 274 mmol) and the reaction was stirred using a magnetic stirbar. The reaction was brought to a gentle reflux and allowed to proceed overnight. Hexachlorocyclotriphosphazene (25.0 g, 72 mmol) was placed in a 500 ml oven dried round bottomed flask fitted with a septum stopper. 1,4-Dioxane (200 ml) was cannulated in and the solution stirred magnetically. After dissolution was complete, the trimer solution was cannulated into the allyl alkoxide reaction solution. The reaction was brought to a gentle reflux and reaction progress was monitored by ^{31}P NMR until it was determined that the reaction was complete, which took approximately 2 h. When the ethoxide solution was determined to be complete evidenced by complete consumption of the sodium metal, that reaction mixture was added to the main reaction and the mix heated to a gentle reflux for 2 h. Completion of the reaction was confirmed by ^{31}P NMR and the reaction was cooled to room temperature. The excess nucleophile was quenched with 250 ml of water and brought to neutral pH with 2.0 M HCl. The volume of the reaction mixture was reduced on a rotary evaporator to a final volume of 300 ml. This solution was transferred to a 2 L separatory funnel and 500 ml of dichloromethane was added, forming two phases. These were separated and the dichloromethane phase was retained. This was returned to the separatory funnel where it was subsequently washed seven times with fresh aliquots of nanopure water (500 ml each). The final product was obtained by the removal of the dichloromethane solvent by rotary evaporation to yield a clear, slightly yellow oil. The oil was dried in a vacuum/argon oven at 80 °C, 25 mTorr Ar for a minimum of 72 h. Yield was 25.2 g, 78%. ^{31}P NMR: 17.5 ppm (m).

2.4. Coin cell build and testing

Full cell evaluation of each of the electrolyte chemistries of interest was performed using CR 2032-type coin cells. Prior to building cells all non-separator components were dried overnight at 90 °C under vacuum. Separators were dried overnight at 60 °C under vacuum overnight. All cells were built under an Ar atmosphere with oxygen and water content below 0.1 ppm. Cells were constructed using a G8 (Conoco-Phillips) graphite based anode and a proprietary blended $\text{Li}_{1.06}\text{Mn}_{1.94}\text{O}_4 + \text{Li}_{1.1}\text{Ni}_{0.33}\text{Mn}_{0.33}\text{Co}_{0.33}\text{O}_2$ cathode. Both the anode and cathode materials were calendared to a uniform thickness prior to use; the geometric area of each electrode was 1.43 cm². Consistent loading of the active materials onto the current collectors was confirmed by weighing same-area electrode samples, which showed very close agreement in

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