Use of phosphoranimines to reduce organic carbonate content in Li-ion battery electrolytes

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ABSTRACT

The use of phosphoranimines (PAs), a class of linear, monomeric phosphazenes, as electrolytes for Li-ion battery applications has been investigated as a route to improve safety and stability for Li-ion batteries. Of the potential PAs for use in battery applications, this work focuses on the initial synthetic preparation and analysis of N-trimethylsilyl-P,P-bis((2-methoxyethoxy)ethoxy)-P-ethylphosphoranimine (PA-5). PA-5 has high $LiPF_6$ solubility in excess of 2 M, high thermal stability with a melting point below -80° C and high thermal stability as a neat compound to at least 250° C. As part of electrolyte blends, the inclusion of PA-5 shifts the onset of thermal degradation by close to 40° C at 35% loading and by 20° C at a 10% loading, improves the low temperature performance of the electrolyte, and when used as a primary solvent leads to increases in the flash point (by 20° C) when compared to more traditional EC:EMC blends. Cycling capabilities of full-coin cells with graphite negative electrodes and $Li_{1+w}[Ni_{0.5}Mn_{0.3}Co_{0.2}]_{1-w}O_2$ positive electrodes using PA-5:EC:EMC electrolyte blends are comparable with the performance seen for traditional EC:EMC blends. Analysis of the impact of the use of additives such as vinylene carbonate in PA-5:EC:EMC blended electrolyte results in enhanced capacity retention and improved coulombic efficiency.

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1. Introduction

Currently, organic carbonates serve as primary solvent components in electrolytes for Li-ion batteries (LIBs). For low to medium voltage applications, carbonates are effective, yet for high voltage use and use in extreme conditions, issues arise with the overall safety and stability of carbonate-based electrolytes. As small, highly oxygenated organic compounds, carbonates have high volatility and are combustible. This is a combination which is ill-suited for applications where a high level of safety is desired, such as in electric vehicles. Additionally, carbonate electrolytes begin to degrade at temperatures as low as 50° C and exhibit significant reduction in conductivity if exposed to temperatures greater than 80° C for more than 10 h [1,2]. Degradation inherently leads to shortened battery life and increases in cell impedance, in addition to safety issues such as increased heat generation associated with the higher impedance. Several routes have been proposed to improve the safety of liquid electrolytes for LIBs including the use of a host of different co-solvents and additives [3].

A significant number of chemical classes and types of compounds have been proposed for improving liquid electrolyte properties. These include room temperature ionic liquids, esters, nitriles, silicon-containing compounds, ethers, sulfones and sulfoxides in addition to multiple combinations of Li salts [3]. Phosphorus-containing compounds [4–16], including phosphazenes [7,8,13,14,17–19], have received significant attention due to their flame retardant nature and high thermal stability. The use of phosphazenes in battery systems has primarily focused on cyclotriphosphazenes (CTPs) as electrolyte components [7,13,14,17]. Similar, yet slightly higher molecular weight CTPs and linear polyphosphazenes have also been investigated as electrode components including binders [20,21]. While some promise is shown in the use of CTPs to improve the safety of LIB electrolytes, CTP inclusion in electrolytes is limited by the amount which can be loaded into the electrolyte without increasing viscosity to a point where performance declines. As an example, at a 20% (by volume) CTP loading the viscosity of electrolyte solutions nearly doubles and the observed capacity at a C/1 rate declines by roughly 25% of what was observed at a C/10 rate [14]. Recently, Wu et al., reported the use of phosphorimidic compounds (triethoxyphosphazen-N-phosphoryldiethylester, PNP) which has lower molecular weight than CTPs, but which contain two phosphorus

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and a singular nitrogen atom [13]. The reported data indicate that the PNP compounds have reasonable cycling ability at low loading levels (10% by volume) when using LiFePO$_4$ and LiMn$_2$O$_4$ [13].

The work described below continues the investigation of lower molecular weight (below 450 g mol^{-1}) phosphazene compounds with an analysis of phosphoranimines (PAs). Like the PNP compounds, PAs have a single P=N unit, however PAs lack the additional phosphoryl pendant and its associated lone pairs on the O. Instead, the present PAs (Fig. 1) contain a silyl moiety on the N as a means to reduce viscosity for use at higher loading levels and to reduce the strength of the interaction between the Li and the different lone pairs in the vicinity of the phosphazene N. Other silyl compounds have recently received attention as electrolytes for similar reasons [22,23]. Additionally, when compared to CTPs the PAs, have lower molecular weights and remain as liquids at room temperature [24,25]. As such they provide an option as electrolyte additives which reduce impact on viscosity while still providing the advantageous safety aspects of CTPs. As a first investigation of feasibility, this work looks to identify areas which need to be improved upon for further expansion PAs and other small phosphazenes.

2. Experimental

2.1. Chemical Synthesis

The synthesis of PA-5 used established methods by Neilson and Wisian-Neilson [20,22–26] as shown in Fig. 1. This route provides the opportunity, through the formation of mixed silylaminophosphines, for the production of mixed silylphosphoranimines [23–26]. As shown in Fig. 1, the synthesis of the silylaminophosphine involves reaction of lithium bis(trimethylsilyl)amide (LiN (SiMe$_3$)$_2$) with alkyldichlorophosphine (RPCl$_2$) to give the analogous halo(silylamino)phosphine. The aminophosphine product (1) was isolated via vacuum distillation at this stage. Following isolation of the silylaminophosphine the PA compound was generated by an oxidation step using bromine [20,24–26]. This was done using the starting aminophosphine for PA-5 [(Me$_3$Si)$_2$N P (Et)Cl] (Fig. 1). Subsequently, the bromine(s) were displaced with an alkoxide, sodium 2-(methoxyethoxy)ethanoxide, to give the desired phosphoranimine. Following synthesis, PA-5 which was a clear low viscosity liquid at room temperature, was characterized using ^{31}P, ^{1}H, and ^{13}C NMR.

2.1.1. (CH$_3$)$_3$SiN = P(Et)(OCH$_2$CH$_2$OCH$_2$CH$_2$OCH$_3$)$_2$, (PA-5) [N-Trimethylsilyl-P,P-di(2-methoxyethoxyethoxy)-P-ethylphosphoranimine)

[30% overall yield, boiling point 120–125 °C at 0.07 mm Hg, ^{31}P NMR δ (CDCl$_3$) = (s) 23.6; ^{1}H NMR δ (CDCl$_3$) = (broad doublet, JPH = 10.2 Hz) 3.95-4.11, (m) 3.55-3.64, (m) 3.45-3.51, (m) 3.35-3.29, (multiplet) 1.63, (doublet of triplets, JPH = 24.6 Hz,

JHH = 7.8 Hz) 1.04, (m) 0.0 to −0.4; ^{13}C NMR δ (CDCl$_3$) = (s) 71.9, (s) 70.7, (s) 70.4, (s) 63.3, (s) 58.9, (d, JPC = 140.4 Hz) 21.2, (s) 6.9, (s) 3.4]. Synthetic reagents including: LiN(SiMe$_3$)$_2$ (1.0 M in hexanes; Aldrich), EtPCl$_2$ (Strem), NaH (95% in oil; Aldrich), and bromine (Aldrich) were used without further purification. 2-(methoxyethoxy)ethanol was obtained from Aldrich and purified by vacuum distillation. Anhydrous solvents, (diethyl ether, tetrahydrofuran, toluene, and hexanes) were obtained from Aldrich and used as received. Proton, ^{13}C(^{1}H), and ^{31}P(^{1}H) NMR spectra were recorded on a Bruker Ascend Avance III 600 MHz spectrometer using CDCl$_3$ as the NMR solvent to characterize products and intermediates during the synthetic process.

2.2. Electrolyte preparation, characterization and electrochemical evaluation

Eight different electrolyte blends (Table 1) were prepared by mixing different ratios (by volume) of PA-5, with 3:7 ethylene carbonate (EC, Kishida), ethyl methyl carbonate (EMC, Kishida), vinylene carbonate (VC, Sigma Aldrich) and LiPF$_6$ (1.2 M for all electrochemical tests, Kishida). LiPF$_6$ solubility in PA-5 was determined after creating a saturated solution of LiPF$_6$ in neat PA-5 and then analyzing only the liquid portion using inductively coupled plasma-optical emission spectrometry (ICP-OES). Conductivity was determined using a TOA CM-30R conductivity meter. A Cambridge DL-4100 (falling bob) viscometer was used for viscosity measurements. For both viscosity and conductivity, ten measurements were averaged to obtain the values reported. The closed-cup flash point for different blends was measured using a Setaflash 82000-0 equipped with an electric ignition. All electrolyte preparation, as well as the measurement of both conductivity and viscosity was performed in an Ar-filled glovebox with O$_2$ and H$_2$O content below 0.2 ppm. Thermal analysis was obtained using a TA Instruments (NewCastle, DE) model Q200 Differential Scanning Calorimeter (DSC). For data collection, Tzero aluminum hermetic pans were loaded with 2–6 mg of sample and the temperature was cycled between −90 to 250 °C at a rate of 5 °C min^{-1}, under a purge gas (N$_2$) with a flow rate of 50.0 mL min^{-1}.

Electrochemical evaluation using cyclic voltammetry (CV) of the blended electrolytes was performed using 1.0 cm^2 flags of Ni or Al using a PAR 263A potentiostat in a three electrode cell which contained a Li counter and a Li quasi-reference electrode. Voltammetry experiments were either initiated at open circuit progressing in the negative going direction to 0.02 V (vs Li/Li$^+$) at a scan rate of 5 mV s^{-1} (for Ni), or progressed from open circuit to 5.0 V (vs Li/Li$^+$) for the Al flags. Cycling performance was evaluated in coin cells (CR-2032) using a full cell configuration with a Conoco Philips G8 negative electrode, and a Li$_{1+w}$[Ni$_{5.0}$Co$_2$Mn$_3$]$_{1-w}$O$_2$ (NCM-523) positive electrode. Electrodes were formulated and prepared at Argonne National Laboratory (ANL). A Celgard 2500 separator was used for all coin cell investigations. Voltammetry
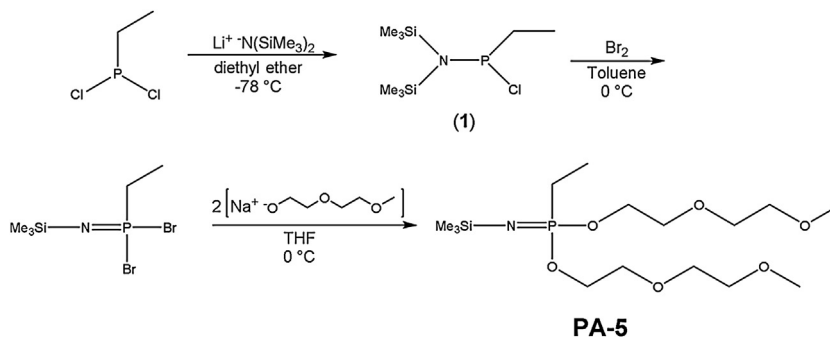

Fig. 1. Synthetic scheme for the production of PA-5 using previously reported techniques.