

A phosphate additive for poly(ethylene oxide)-based gel polymer electrolytes

Robert V. Morford^{a,d}, Daniel T. Welna^d, Clay E. Kellam III^{b,d},
Michael A. Hofmann^{c,d}, Harry R. Allcock^{d,*}

^a Brewer Scientific, Inc., 2401 Brewer Dr., Rollo, MO 65401, USA

^b National Starch and Chemical Co., 10 Finderne Ave., Bridgewater, NJ 08807, USA

^c Dupont Experimental Station, Wilmington, DE 19898, USA

^d Department of Chemistry, The Pennsylvania State University, 104 Chemistry Building, University Park, PA 16802, USA

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Abstract

The influence of an organophosphosphate additive on poly(ethylene oxide) lithium bis(trifluoromethylsulfonyl)imide-based gel polymer electrolytes for secondary lithium battery applications is described. Tris(2-(2-methoxyethoxy)ethyl)phosphate, is compared to the well known gel-battery component, propylene carbonate, through a study of complex impedance analysis, differential scanning calorimetry, and limiting oxygen index combustion analysis. The conductivities of the gels at low concentrations of tris(2-(2-methoxyethoxy)ethyl)phosphate (1.9–4.2 mol%) are higher than those of propylene carbonate-based systems with the same concentration. Despite micro-phase separation at high concentrations of tris(2-(2-methoxyethoxy)ethyl)phosphate (7.0–14.9 mol%), the conductivities remain comparable to systems that use propylene carbonate. The addition of tris(2-(2-methoxyethoxy)ethyl)phosphate to poly(ethylene oxide) gives increased fire retardance, while the addition of propylene carbonate to poly(ethylene oxide) results in increased flammability.

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1. Introduction

The development of high power and high energy density batteries with good performance, safety, and reliability has been an active area of research for the past three decades [1–3]. Advances in electronics, especially portable electronics (i.e. mobile phones, portable computers, etc.), have created a demand for smaller, lighter, yet more powerful energy sources. Since Wright's discovery of poly(ethylene oxide)–metal salt complexes [1], and Armand's subsequent suggestion [2] that solid polymer electrolytes may be useful in lightweight and powerful solid state batteries, numerous reports on their development have been published [4–8]. In particular, lithium batteries have received the most attention, due to the low density and high redox potential of lithium. Several excellent reviews of the literature exist [3,9,10].

Numerous different materials have been examined as the basic components of a lithium battery: anode, electrolyte (metal salt in solid or liquid matrix), and cathode. Many safe and efficient materials have been developed for use as anodes, as well as numerous reversible intercalation cathodes [11–13]. Moreover, a significant amount of research has been focused on the development of materials for the electrolyte layer which transports lithium ions between the anode and the cathode. [9,10] Polar aprotic liquid electrolytes provide good media for the transport of lithium ions [10]. However, organic liquid electrolytes require bulky and sometimes heavy enclosures [14]. Thus, attempts have been made to develop solid polymer electrolytes that allow the use of complex shapes, greater ease of fabrication, reduced weight for containment, lower flammability, and a lower toxicity of the battery components [14]. So far no solid polymer electrolyte is known that efficiently transports lithium ions at commercially viable levels (conductivities $\sim 10^{-3}$ S/cm at 25 °C).

A promising route to circumvent this problem has been to add liquids to polymers to form gel polymer electrolytes (GPEs)

* Corresponding author. Tel.: +1 814 865 3527; fax: +1 814 865 3314.

E-mail address: hra@chem.psu.edu (H.R. Allcock).

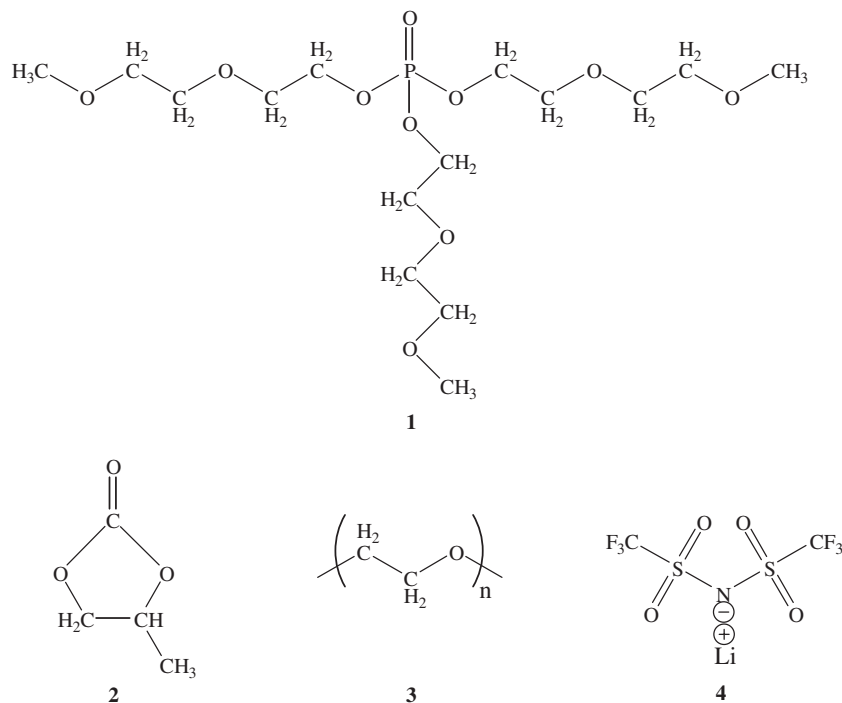


Fig. 1. Components used in GPE fabrication — tris(2-(2-methoxyethoxy)ethyl)phosphate (**1**), propylene carbonate (**2**), poly(ethylene oxide) (PEO) (**3**), and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (**4**).

[14]. This route has produced many free-standing gel materials, with high conductivities. Examples of these systems include poly(ethylene oxide), poly(methyl methacrylate), poly(acrylonitrile), and poly(vinylidene fluoride) plasticized with organic solvents [14–16]. The main disadvantage in the use of organic solvent additives is their volatility and flammability. Although many liquid electrolytes and additives are known, the greatest attention has been focused on liquid carbonates [15–17]. Concern over the flammability and volatility of these compounds prompted us to prepare a new, non-volatile, fire retardant, and conductive phosphate additive initially for use in the gel polymer electrolyte layer of polyphosphazene-based lithium batteries [18,19]. Recently other groups have published work detailing efforts on the development of non-flammable liquid electrolytes [20,21] and polymer electrolyte additives [22].

In our earlier work we identified a new gel polymer electrolyte additive and demonstrated its utility when used in conjunction with polyphosphazene-based polymer electrolytes [18,19]. This compound, tris(2-(2-methoxyethoxy)ethyl)phosphate (**1**), was shown to be essentially non-volatile and significantly less flammable than propylene carbonate (**2**). At low additive concentrations, the phosphate-based gels were amorphous and had higher conductivities than propylene carbonate-based gels. However, at higher loadings of the additives, the phosphate GPEs generated multiple phases, and the conductivities were slightly lower than that of the propylene carbonate-based polyphosphazene gels.

In this study a comparison was made of propylene carbonate and the phosphate as additives in a more widely studied polymer, poly(ethylene oxide) (PEO) (**3**). Two sets of GPEs

were prepared using PEO and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) (**4**), with **1** (**5(a–e)**) and **2** (**6(a–e)**) as the liquid additives (Fig. 1). The GPEs were subsequently analyzed via differential scanning calorimetry, complex impedance and limiting oxygen index analysis. This work described here demonstrates that tris(2-(2-methoxyethoxy)ethyl)phosphate may be a promising replacement for organic carbonates in the more widely used PEO-based gel polymer electrolyte systems.

2. Experimental

2.1. Materials

Phosphorous oxychloride (99%), propylene carbonate (99.7%), tri(ethyl)phosphate (99%), and bis(2-methoxyethyl) ether (99%) were used as received from Aldrich Chemical Company. 2-(2-Methoxyethoxy)ethanol (99%) was obtained from Aldrich and distilled from calcium hydride before use. Triethylamine (99.5%) was obtained from Aldrich and distilled from sodium benzophenone ketyl prior to use. Poly(ethylene oxide) (PEO) (M_w 1,000,000) was obtained from Aldrich and was dried for 2 days at 45 °C under 0.2 mm Hg before use. Tetrahydrofuran (THF) was obtained from EM Science and was distilled from sodium benzophenone ketyl before use. Lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) was donated by the 3M Corporation (HQ-115) and was used as received.

2.2. Equipment

Complex impedance analysis was performed in a constant flow argon glovebox. The gel polymer electrolyte was placed

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