

Short communication

Non-flammable polyphosphonate electrolytes[☆]

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Abstract

This research is directed towards the development of safe, and thermally stable polymeric electrolytes. Advanced electrolytes are described, including thermal test data, which are ionically highly conductive, and non-flammable. These novel multi-heteropolymer electrolytes represent a significant advance in the design of high-performance rechargeable lithium systems that possess superior safety and handling characteristics. Representative results are shown by the figures contained in this text. These DSC/TGA results compare a typical liquid carbonate-based electrolyte system, ethylene carbonate and ethyl methyl carbonate, with novel polyphosphonates as synthesized in this program. These tests were performed with the electrolytes in combination with lithium metal, and the impressive relative thermal stability of the phosphonates is apparent.

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1. Introduction

In spite of the widespread use and deserved promise of lithium batteries, safety issues are still a substantial issue of concern [1–6]. In fact, recalls in January of this year, have involved well over 100,000 cell phone batteries due to overheating accidents [1].

Classically constructed lithium batteries consist of a carbon anode, a metal oxide cathode, and a low viscosity liquid carbonate electrolyte that is very flammable. One approach that is being explored to suppress electrolyte flammability is using phosphate additives, especially trimethyl phosphate (TMP) [2–6]. TMP is a logical choice, since it has seen widespread use as a fire retardant in plastics. Previous work has demonstrated the promise of TMP as a fire suppressant, however, it also has been shown to be unstable to reaction at the anode.

We have undertaken the exploration of novel electrolytes based upon phosphorous chemistry, including P compounds in both the +3 and +5 oxidation states. Some promising thermal results are described herein.

2. Experimental

Polyphosphonates were synthesized in one step, using one of two routes as described previously [7]. Route 1 involved the condensation of an alcohol and the desired chlorophosphorus precursor in the presence of an acid scavenger. Route 2 involved a transesterification under either basic or acidic conditions. Standard workup and characterization procedures were employed with the products, which were obtained in yields of 75–95%.

Samples of different experimental polyphosphonates synthesized at Phoenix, and a standard 50/50 (v/v) ethyl methyl carbonate/ethyl carbonate control were thermally evaluated, all with lithium perfluoromethyl sulfonimide (LiIm) as the ionic salt. For the DSC experimental protocol, lithium metal

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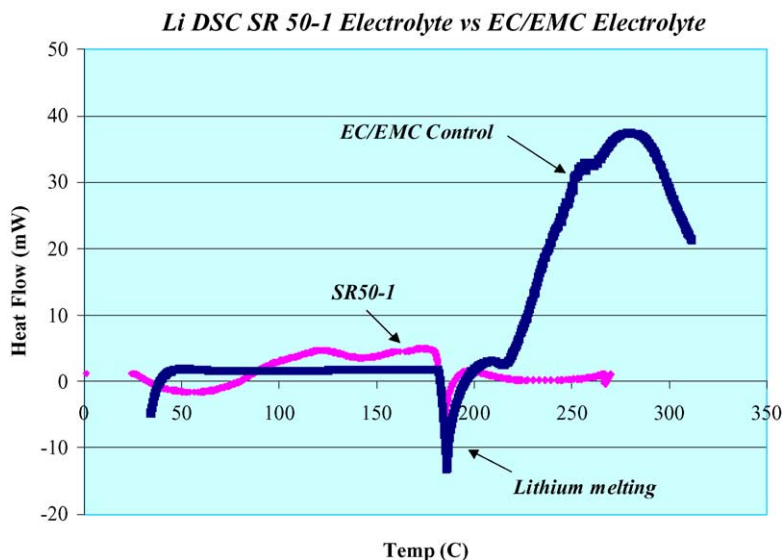


Fig. 1. Differential scanning calorimetry results of experimental polyphosphonate electrolyte SR50-1 vs. a standard ethylene carbonate/ethyl methyl carbonate (EC/EMC) control with 1 M LiIm and in the presence of Li metal.

was combined with the electrolyte and sealed in high pressure capsules in a Dry Room at a dew point of -80°C . Scans were done under N_2 at a scan rate of 10 K min^{-1} on a TA 2920 DSC instrument. TGAs were run under He at a 20 K min^{-1} rate on a TA 951 instrument. Ionic conductivities were obtained, using both RCL and impedance techniques, on all samples and with LiIm as the salt at a 1 M concentration. No other sample additives were present.

3. Results and discussion

Representative syntheses of materials being studied are shown below. These are followed by examples of the thermal

profiles of some candidate electrolytes. These materials have conductivities of $0.6\text{--}1.0 \times 10^{-3}\text{ S cm}^{-1}$ at 22°C .

3.1. The DSC results are very informative

In both the polyphosphonate cases, as well as the control, the electrolytes show relatively flat heat fluxes, suggesting only minimal reaction prior to the lithium melting at 180°C . After the lithium melts a substantial exotherm is observed in control carbonate case indicative of rapid reaction, as is observed in runaway battery reactions that lead to handling and safety issues in state of the art lithium ion systems (Fig. 1). The polyphosphonate curve, however, remains flat, indicating very little reactivity.

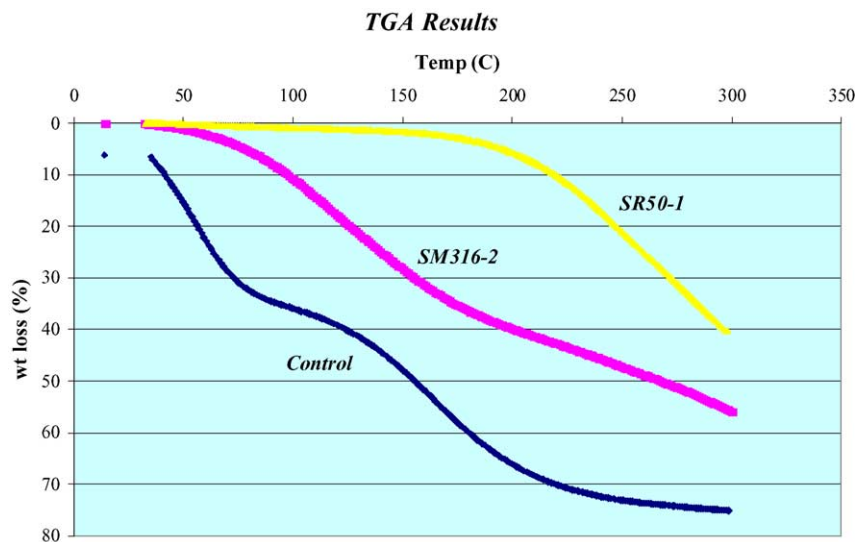
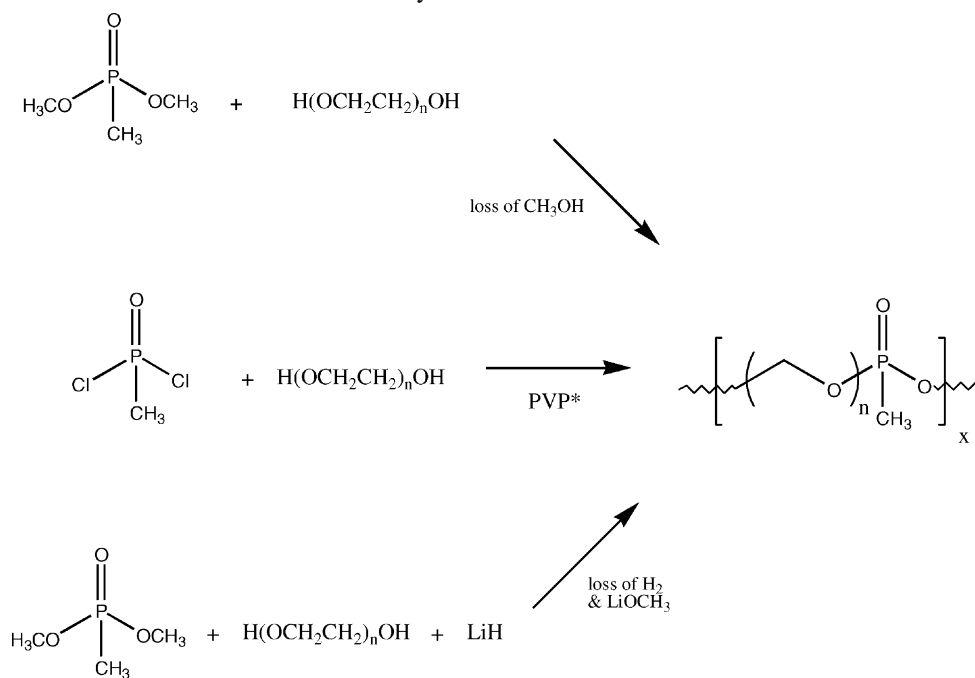


Fig. 2. Thermogravimetric analysis results of experimental polyphosphonate electrolytes SR50-1 and SM316-2 vs. a standard ethylene carbonate/ethyl methyl carbonate (EC/EMC) control with 1 M LiIm and in the presence of Li metal.

The TGA results are shown for these three materials as well (Fig. 2). Here too the polyphosphonates excel compared to the standard carbonate mixture of electrolytes.



* addition of polyvinylpyridine (PVP) results in the removal of HCl as the reaction proceeds

4. Conclusions

The brief set of results given above are representative of a larger set of experimentation that has led us in the formulation of novel phosphorus-based electrolytes that are inherently practical, safe and non-flammable. Lithium batteries comprise many often conflicting requirements. Our ongoing electrolyte research efforts have identified a subset of formulation chemistries that combine high lithium ion conductivities and transference numbers with much safer system chemistries.

Acknowledgements

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