

# A novel approach for development of improved polymer electrolytes for lithium batteries

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## Abstract

Polymer electrolyte lithium batteries represent the future of safe, high-energy battery systems. Although great strides have been made in the development of new polymer electrolytes and in understanding how these systems function, progress has been evolutionary in its scope. Further advancement of ambient temperature polymer electrolyte batteries will require new approaches that break with tradition. This report deals with new types of liquid polymers that have not been extensively described in the literature. The work presented in this report represents the beginning of the development of new solid polymer electrolytes. These heteroatomic materials combine the better features of several elements to solubilize and transport select lithium salts more efficiently than traditional ethylene oxide-type polymers. Ambient temperature ionic conductivities of  $>1 \times 10^{-3}$  S/cm are common with this class of polymer electrolytes. An overview and rationale of the approach together with reported materials properties are reported.

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## 1. Introduction

The development of a truly solid state high power lithium battery is dependent upon the successful identification of a suitable solid polymer electrolyte. The lithium polymer system is the first solid state battery, which is viewed by many [1] as the future of the rechargeable battery market. At present, the most effective popular lithium battery system is the lithium-ion secondary battery. The electrolytes used in Li-ion batteries are liquid in nature. Aprotic solvents, such as cyclic carbonates, together with a dissolved lithium salts comprise the most popular electrolytes, because they offer good electrochemical performance over a wide temperature range. The trade-off with aprotic solvents is that this wide temperature performance comes at the cost of cell voltage and cathode performance. All aprotic solvents have an electrochemical window of stability. Sulfur-containing solvents such as sulfolane appear to be the most resilient with an electrochemical window of 6.1 V. Organic carbonates such as ethylmethyl carbonate (EM) have narrower electrochemical windows (4.0 V), but offer better ionic conductivity than sulfolane. The optimum electrolyte would be a solid material that offered a wide electrochemical voltage window together with good ionic conductivity.

Work in our laboratory has focused initially on the development of new liquid polymer electrolytes (LPE) that offer the possibility of improved electrochemical performance and thermodynamic stability. Our plans call for eventual synthesis of the solid polymer electrolyte counterpart to these liquid polymer electrolytes. In the work reported here, we have synthesized low MW liquid polymers that feature ethylene oxide groups linked with phosphate groups. The following results describe the relative characteristics of liquid polymer electrolytes prepared using these materials.

There have been a few recent reports of similar work. In particular, Kim and Kim [2] reported the synthesis and preliminary characterization of long chain difunctional polyether phosphates. A room temperature ionic conductivity of  $10^{-4}$  S/cm using  $\text{LiClO}_4$  as the lithium salt in this P,O polymer electrolyte was reported. Later work by Kim and co-workers [3] involved synthesis and more extensive characterization of both di- and trifunctional polyether phosphate polymer electrolytes with high MW. Room temperature ionic conductivities approaching  $10^{-4}$  S/cm were reported. Most recently, Morford et al. [4] reported using a trifunctional low MW polyether phosphate to decrease the flammability of a liquid electrolyte. Morford reported that the polyether phosphate additive improved the conductivity of the liquid electrolyte. Our recent research in this area has sought to identify a liquid polymer electrolyte that could

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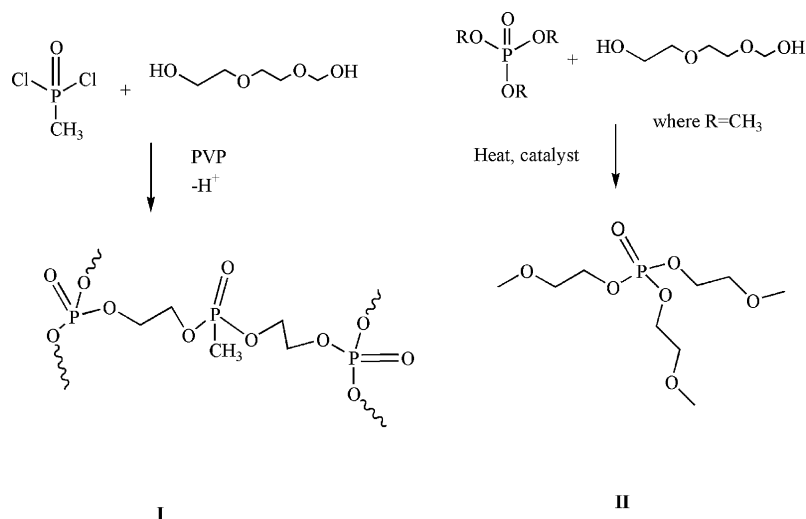


Fig. 1. General synthetic schemes for preparation of the polymers used in the subject liquid polymer electrolytes.

offer superior thermal and electrochemical performance with ambient conductivity comparable to liquid electrolytes. Such a material could be developed into a solid polymer electrolyte or used directly in either a primary, or secondary high voltage Li systems.

## 2. Experimental

Our previous efforts identified P,O polymers as a potentially good candidate for preparation of a liquid polymer electrolyte. These materials are relatively inexpensive to prepare and are based on the use of ethylene oxide moieties as the  $\text{Li}^+$  active site. Our belief is that there is interaction between the P and O in the resulting polymer that enhances the transport of the  $\text{Li}^+$  through the electrolyte matrix. We synthesized a series of materials in which the P:O ratio was varied in an attempt to better understand the stabilizing effect of P on the overall electrolyte. Fig. 1 summarizes the general synthetic scheme used to prepare the subject polymers.

The polymer products resulting from these syntheses were liquids that were vacuum dried at  $50^\circ\text{C}$  before being used to prepare liquid polymer electrolytes.

Using these polymers, several liquid polymer electrolytes were prepared by dissolving  $\text{LiClO}_4$  as the supporting salt in an 8:1 O:Li ( $\sim 1\text{ M}$ ) ratio. The  $\text{LiClO}_4$  was dried under vacuum for 24 h before use. All other chemicals were used as received. Control electrolytes employing ethylmethyl carbonate polyethylene glycol (PEG, 200MW) and ethylene glycol (EG, Aldrich) were prepared with  $1\text{ M}$   $\text{LiClO}_4$  as the supporting electrolyte at  $1\text{ M}$  concentration. All electrochemical characterization experiments were conducted using a Radiometer Model PGZ 301 electrochemical analyzer employing a polypropylene test cell with two stainless steel piston electrodes to house the test electrolytes. Cyclic voltammetry (CV) experiments utilized a  $1\text{ cm}^2$  platinum

foil (Alfa Aesar) as the working electrode, and a  $1\text{ cm}^2$  lithium foil (Alfa) as the counter and reference electrodes. CV experiments were run at  $20\text{ mV/s}$  sweep rate until two reproducible voltammograms were generated for each sample. Electrochemical impedance spectroscopy using stainless steel blocking electrodes and linear polarization experiments were conducted using  $1\text{ cm}^2$  aluminum and copper foils (Alfa) as the working electrode and lithium foil as the counter and reference electrodes. With all of these liquid electrolytes, a nonwoven glass separator (Hollingsworth & Vose Canton, MA) was used as a support. All tests were conducted under dry conditions. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) was conducted on the LPEs using a to determine their thermal characteristics. TA Instruments DSC model Q100 and TGA model Q50 instruments were used for these tests. For qualitative purposes, simple one-cell battery tests and lithium cycling were also conducted using these liquid electrolytes. For the battery tests, a  $1\text{ cm}^2$  lithium metal foil (Alfa Aesar) served as the anode and a  $1\text{ cm}^2$   $\text{LiNiCoO}_2$  electrode (courtesy Yardney Technical Products) served as the cathode.

## 3. Results and discussion

Fig. 2 demonstrates the superior electrochemical stability of our P,O polyether electrolytes.

As shown, the P,O polymer electrolyte containing 100 times more  $\text{LiClO}_4$  results in the generation of is far less current over the entire voltage scan, but particularly at  $+6\text{ V}$  indicating that this electrolyte is far more electrochemically stable than the control electrolyte. As a further indication of the relative stability of our LPE and a further demonstration of its unique chemistry, we compare in Fig. 3 the stability of the same LPE with that of a control composed of the starting material, ethylene glycol, with  $1\text{ M}$   $\text{LiClO}_4$ .

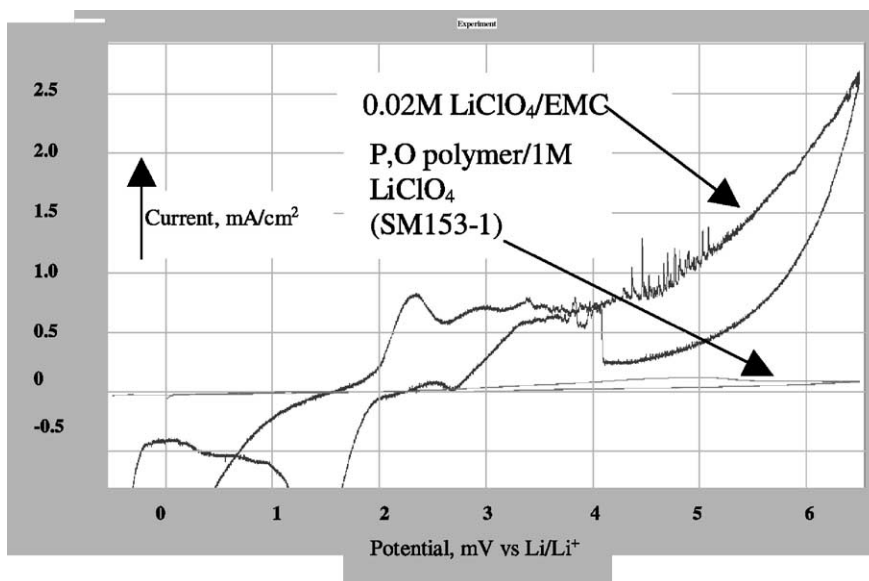


Fig. 2. Comparison of the relative electrochemical stability of the P,O polymer vs. EMC on Pt, sweep rate 20 mV/min.

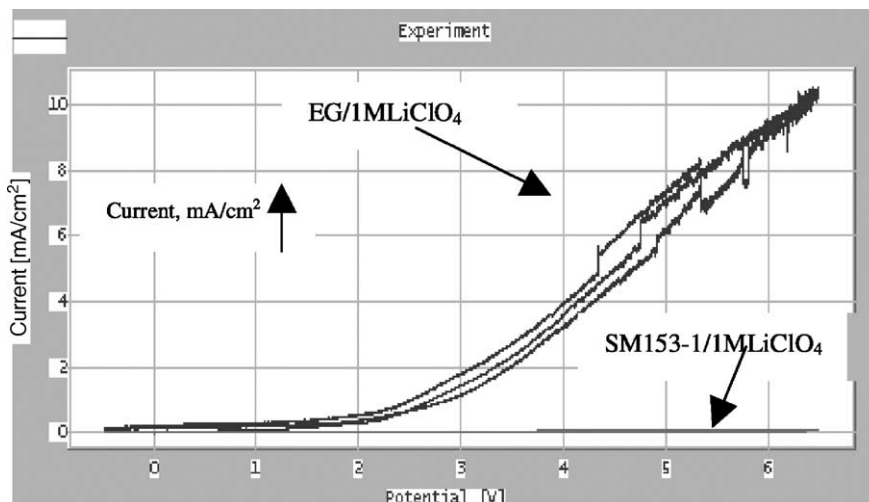


Fig. 3. Comparison of the relative electrochemical stability of EG control vs. P,O LPE.

As can be seen, once again, the P,O LPE generates significantly less current over the entire voltage scan than the control indicating the greater electrochemical stability of the test LPE.

Linear polarization experiments were conducted using aluminum or copper as the working electrode to ascertain the relative corrosivity of our LPEs. Table 1 summarizes these results.

Table 1  
Summary of results

Sample	Salt	Al $i_c$ at 6.5 V vs. L/Li <sup>+</sup> (mA/cm <sup>2</sup> )	Cu $i_c$ at 6.5 V vs. L/Li <sup>+</sup> (mA/cm <sup>2</sup> )	Conductivity $\sigma_T$ (S/cm)
(1) EMC	1 M LiClO <sub>4</sub>	5.10	>100	$1.5 \times 10^{-3}$
(2) EMC	1 M LiIm	2.91	38.0	$1 \times 10^{-2}$
(3) EMC	1 M BETI	2.20	3.2	$1.8 \times 10^{-2}$
(4) SM151-2	1 M LiClO <sub>4</sub>	0.45	1.01	$1.0 \times 10^{-3}$
(5) SM151-2	1 M LiIm	0.70	0.61	$1.3 \times 10^{-3}$
(6) SM151-2	BETI	0.44	0.52	$1.0 \times 10^{-3}$
(7) PEG 200	BETI	0.86	1.3	$7.4 \times 10^{-4}$
(8) TMP	0.5 M LiClO <sub>4</sub>	–	9.9	$4 \times 10^{-3}$

LiIm: bisperfluoromethanesulfonimide, TMP: trimethylphosphate, BETI: bisperfluoroethanesulfonimide.

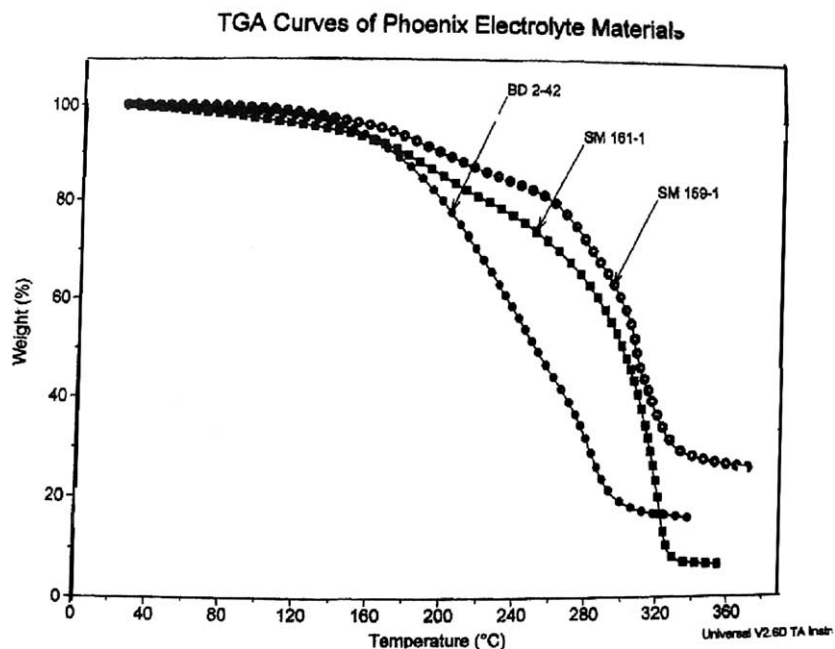


Fig. 4. TGA results for P,O LPEs.

In this table, the results are arranged in descending order of corrosivity (with respect to copper) beginning with the 1 M LiClO<sub>4</sub> in EMC. This electrolyte is very corrosive to both Al and Cu as indicated in columns 3 and 4 in this table. As can be seen, with copper, the corrosion current was >100 mA/cm<sup>2</sup>. From this first sample, electrolytes composed EMC and of lithium bisperfluoromethanesulfonimide (LiIm, 3M Co.) or lithium bisperfluoroethanesulfonimide (BETI, 3M Co.) exhibited significantly less corrosion on both Al and Cu. The BETI electrolyte exhibited the best performance in EMC as has also been found by others [5]. The data beginning with Sample 4 in Table 1, is for a series of electrolytes prepared using a select P,O liquid polymers and three salts. Here again the data are arranged in descending order of corrosivity with respect to copper. As can be seen, with the exception of LiIm on Al result, the P,O polymer electrolyte behaves much as the EMC electrolyte with respect to the type of salt employed. However, the corrosion current generated in the case of the P,O polymer electrolytes was at the very least five times lower than that generated by the EMC electrolytes. This is a clear indication of the far lower corrosivity of the P,O polymer electrolytes. In addition, an electrolyte control prepared using PEG 200 (which was one of the constituents of SM151-2) and BETI was also tested; Sample 7. As can be seen, the corrosion current generated using either Al or Cu was twice that of the comparable SM151-2/BETI electrolyte and with Cu, it was more than twice the current generated with the SM151-2/LiIm electrolyte. These results strongly suggest that the SM151-2 polymer passivates the Al and Cu substrates. The ionic conductivity of the electrolytes was measured from the impedance spectra using the technique described by Scrosati co-workers [6]. As can be seen, the test LPEs

exhibit conductivities approaching that of carbonate liquid electrolytes.

Thermal analysis of our electrolytes was also conducted and the corresponding DSC and TGA results suggest these materials to be potentially useful as electrolytes.

Fig. 4 represents the TGA results for LPEs comparable in composition to the samples previously presented. As can be seen, at least one of these LPEs is quite thermally stable out to 300 °C.

The DSC results for comparable LPEs are presented in Fig. 5.

As can be seen in this figure, the T<sub>g</sub>s for these LPEs are quite low and reflect the composition of the LPE. Sample SM177-1 contained LiClO<sub>4</sub> as the electrolyte salts whereas sample SM175-3 contained LiIm. The lower T<sub>g</sub> for the latter

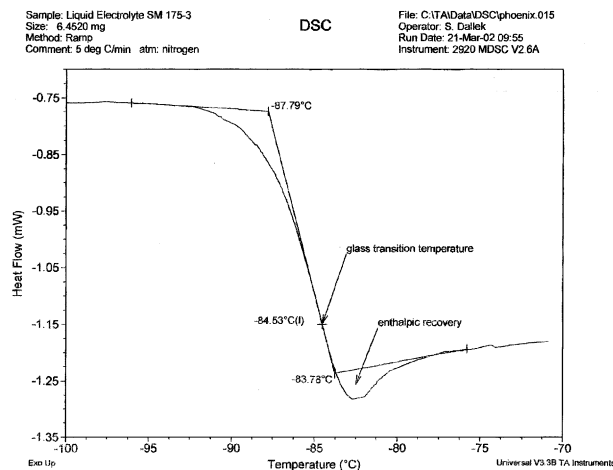


Fig. 5. DSC results for P,O LPEs.

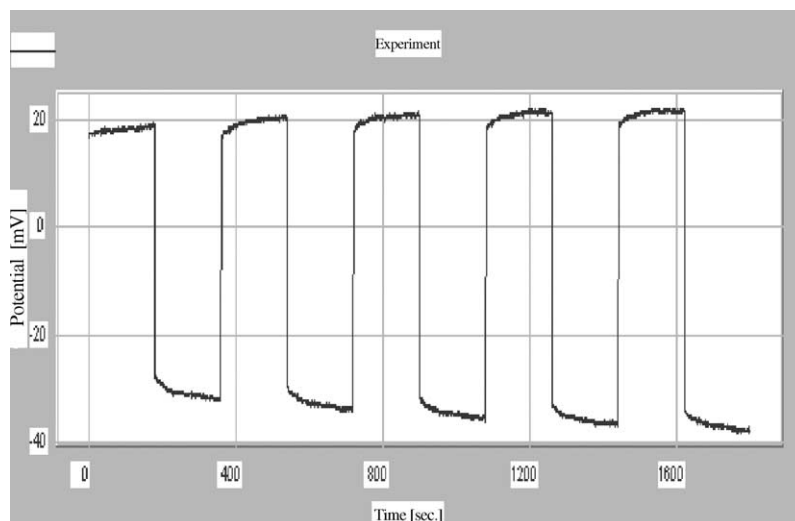


Fig. 6. Lithium Cycling using P,O polymer electrolyte.

sample reflects the effect of using a salt with a lower ionization potential like LiIm.

In addition to these characterization tests, we also conducted some preliminary lithium cycling and battery testing using our liquid polymer electrolytes in simple one-cell samples.

Fig. 6 summarizes the lithium cycling capabilities of our liquid polymer electrolyte. Although these are relatively short cycles, the electrolyte appears to cycle lithium efficiently.

#### 4. Conclusions

The work described here demonstrates that liquid polymer electrolytes can be fabricated using new types of polyether phosphate polymers and select lithium salts. The polymers were synthesized from polyethylene glycols and organophosphates. Electrolytes of these P,O polymers appear to offer thermodynamic stability that is greater than that of the ethylene oxide precursor. These materials also appear to be far less corrosive to aluminum and copper than conventional liquid electrolytes. The glass transition temperature of these new liquid electrolytes is quite low and these materials effectively cycle lithium. If these attractive features can be maintained in higher MW analogs to these polymers,

it could lead the way to a useful solid polymer electrolyte for lithium batteries.

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