Block Copolymer Solid Battery Electrolyte with High Li-Ion Transference Number

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The electrochemical properties of a solid polymer electrolyte consisting of a diblock copolymer and lithium bis(oxalato)borate, LiBC4O8 (LiBOB) salt, is reported. The spherical microphase-separated diblock copolymer is composed of a majority poly(ethylene oxide) (PEO) block and a minority random copolymer block of methyl methacrylate (MMA) and lithium salt of methacrylic acid (MAALi), PEO-b-(PMMA-ran-PMAALi). Salt-optimized electrolyte membranes of the diblock copolymer and LiBOB salt exhibited an average lithium-ion transference number (T Li+ ) value of 0.9 at room temperature (21–23°C). The solid-state flexible, translucent polymer electrolyte shows a wide electrochemical stability window and excellent interface properties with the lithium metal electrode. The combination of these properties makes these block copolymer membranes viable electrolyte candidates for flexible lithium-ion batteries.

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The widespread use of high energy density lithium-ion-based batteries has been constrained by the safety concerns of its reactive components. Thus, the need to design, synthesize, and optimize polymer structures for improved energy storage is of critical importance. Also, advances in lithium cathode chemistries have led to the development of batteries that are capable of delivering high discharge potential (>4.5 V),1-3 driving the need for electrolyte materials that are capable of withstanding such high voltage conditions. Unlike traditional liquid electrolytes, solid-state polymer electrolytes possess the high electrochemical stability window required for application in high voltage battery setups. Electrolyte membranes incorporating poly(ethylene oxide) (PEO) with a lithium salt have long been proposed as a viable candidate.4-6 However, such materials have poor room-temperature ionic conductivity due to the semi-crystalline nature of PEO. In addition, PEO-based electrolytes have the intrinsic disadvantage of possessing a low lithium-ion transference number (T Li+ ), exhibiting a value between 0.2 and 0.5.7-10 These polymer–lithium salt systems behave more like an anion transporting medium, resulting in a charge gradient across the medium. This increases the polarization across the polymer film, leading to loss of power drawn from the battery.11-13 Studies done by Doyle et al. showed that better performance is exhibited by polymer materials with T Li+ = 1.0 than those possessing an order of magnitude greater conductivity but a poorer T Li+ value.14 Hence, the interest is to develop a conductive polymer with high ionic conductivity as well as high lithium-ion transference number.15

Numerous electrolytes have been reported that possess single-ion transport properties with lithium-ion transference numbers approaching unity. Single-ion polyelectrolyte systems have been successfully developed where the anion or the counterion is effectively tethered to the polymer matrix.14-16 Further, the use of various anion trappers has been shown to effectively boost the cation transference number.17-20 These approaches, however, sometimes adversely affect the ionic conductivity of the electrolyte. The use of a lithium salt with a bulky counterion remains one of the few viable options available to obtain moderately enhanced transference numbers without significantly sacrificing the ionic mobility of the electrolyte. Here, we explore a polymer–lithium salt matrix containing a bulky anion and a partially charged polymer backbone.

We have previously reported on a diblock copolymer that exhibits nearly 2 orders of magnitude greater ionic conductivity than that shown by traditional PEO homopolymer electrolytes in the absence of ceramic fillers and similar additives.21 The block copolymer microphase separates into spherical domains consisting of a majority PEO block and a minority block of a random copolymer of methyl methacrylate (MMA) and the lithium salt of methacrylic acid (MAALi). Along with salt optimization studies of the diblock copolymer PEO-b-(PMMA-ran-PMAALi) with lithium bis(oxalato)borate, LiBC4O8 (LiBOB) salt, we also carried out thermal studies of the electrolyte material. The presence of the smaller second block and the plasticizing effect of the bulky lithium salt effectively reduced the crystallinity of the solid electrolyte, resulting in its improved ion transporting behavior. In this paper, we discuss the electrochemical properties of the polymer electrolyte and report on its unique transference behavior.

Experimental

The PEO-b-PMMA block copolymer (Mw 3000:500 for PEO:PMMA, polydispersity index of 1.16) was purchased from Polymer Source Inc. LiBOB was obtained from Chemetall GmbH and lithium foil was purchased from Aldrich. The diblock copolymer PEO-b-(PMMA-ran-PMAALi) was synthesized as described in our previous work.21 The electrolyte films with different compositions of the diblock copolymer PEO-b-(PMMA-ran-PMAALi) and the LiBOB salt were solution cast onto Bytac molds inside an Mbraun Labmaster 100 argon glove box. The resultant translucent polymer films (Fig. 1) were dried for several days under an argon atmosphere, followed by at least 48 h of drying under vacuum. The electrochemical properties of the cast electrolyte membranes were tested in CR2032 coin cell enclosures to protect the moisture-sensitive electrolyte materials.

The lithium-ion transference number of the solid electrolyte was measured using Li/polymer/Li coin cells, where electrolyte samples were mounted between two nonblocking lithium metal electrodes. The transference number (T Li+ ) was evaluated by dc potentiostatic measurements in conjunction with ac impedance spectroscopy according to the procedure described by Evans et al.22 Potentiostatic measurements were carried out to determine the initial (I0) and final steady-state (I) currents by applying a dc polarization voltage of 10 mV across the samples. Impedance spectroscopy (frequency range from 1 MHz to 1 Hz) was used to determine the film resistances before (Ri) and after (Rf) the potentiostatic measurements. Transference numbers (T Li+ ) of the electrolyte samples were calculated from the following equation

\[ T_{Li^+} = \frac{I_{f}(\Delta V - I_{R})}{I_{f}(\Delta V - I_{R})} \]  

where \( \Delta V \) is the dc polarization voltage applied across the electrolyte film. A Solartron 1287A/1255B electrochemical testing platform was used to carry out the experiments. The testing parameters were controlled by the associated CorrWare and ZPlot softwares, while...
Figure 1. Electrolyte membrane constructed from the diblock copolymer PEO-b-(PMMA-ran-PMAALi) and the LiBOB salt (picture taken shortly after removal from an argon glove box).

the resulting data were analyzed using CorrView and ZView. All elevated temperature measurements were carried out after equilibrating the coin cells in a Fisher Scientific Isotemp model 281A vacuum oven.

Linear sweep voltammetry was used to determine the electrochemical stability window of the electrolyte material in stainless steel/polymer/Li coin cells, where a 316 stainless steel disk was used as the working electrode while a lithium disk served as the counter electrode. A voltage sweep was carried out on the material between 2.5 and 7 V at a constant scan rate of 1 mV s\(^{-1}\).

Lithium stripping–plating experiments were performed to investigate the interface stability and reversibility behavior of the electrolyte material with the lithium metal electrode. The salt-optimized electrolyte film was mounted between nonblocking lithium electrodes, and a current flux of 0.1 mA/cm\(^2\) was applied on the film with the direction of the current being reversed every hour. Impedance spectroscopy was carried out at various intervals of the galvanostatic cycling.

Results and Discussion

The transference number of an ion is the fraction of the total current that is carried by the respective ion across a given medium. Different ions have dissimilar mobilities and, hence, may carry drastically different portions of the total current. During charge–discharge cycles, the onset of concentration gradients in polymer electrolytes leads to problems such as concentration polarization and results in localized changes of electrolyte properties such as conductivity. The transference number is indicative of the polarity of the material and, thus, the number of cycles the cell can be put through. A large transference number can reduce concentration polarization of electrolytes during charge–discharge steps and, thus, sustain the electrolyte’s power density.\(^{11,13}\)

Under a constant potential bias, if the final steady-state and initial currents are given by \((I_o)\) and \((I_s)\), respectively, then the transference number can be very simply evaluated from \(T_{Li^+} = I_s / I_o\). This holds true for ideal electrolytes under a negligible polarization voltage. In real systems, however, a change in interfacial resistance occurs during potentiostatic studies. We used the methodology suggested by Evans et al.\(^{7}\) to take into account the increase in the electrolyte–electrode interfacial resistance as the potentiostatic current decay is measured. We studied electrolyte samples having the molar composition ethylene oxide (EO):LiBOB = 3:1 and 4:1 based on the salt optimization previously reported.\(^{21}\) Figure 2a shows the impedance profile of two samples before and after the potentiostatic tests. The expected increase in interfacial resistance can be clearly observed between the initial and final impedance responses of the sample with the 4:1 molar composition. The current–time profiles of the same two samples under a constant dc potential bias of 10 mV is shown in Fig. 2b. Using Eq. 1, average transference number values of 0.78 were obtained for the salt-optimized polymer electrolyte materials at room temperature (21–23°C). Table I lists the transference numbers calculated for the two compositions with and without the interfacial resistance correction. At 60°C, average transference number values of 0.75 were obtained for the electrolyte material having the molar composition EO:LiBOB = 4:1.

The large molecular size of the bis(oxalato)borate (BOB\(^+\)) anion was expected to have an effect on the transference number of the lithium ion. However, obtaining such a high transference value in the absence of any anion trap additives was not anticipated. Previous work done by Appetecchi et al. on LiBOB and PEO homopolymer of higher Mw (1 × 105) reported \(T_{Li^+}\) numbers ranging from 0.25 to 0.30 at elevated temperatures (60 and 100°C).\(^{8}\) In view of questions raised about the reliability of dc polarization techniques in nonideal systems, we compared our results with the work reported in Edman et al.\(^{22}\) where electrochemical measurements based on the concentration solution theory was employed to determine the transport behavior. In our system, we suspect the high lithium salt loading to be the determining factor. A similar rise in \(T_{Li^+}\) values with increasing salt concentration \((T_{Li^+} = 0.6 \pm 0.03\) for EO-lithium bis(trifluoromethane sulfone)imide (LiTFSI) = 5:1 at 85°C) was reported and discussed at length in Edman et al.’s study, where solid polymer electrolytes comprising of PEO and

<table>
<thead>
<tr>
<th>Molar composition (EO:LiBOB)</th>
<th>Temperature (°C)</th>
<th>(T_{Li^+} = \frac{I_s}{I_o})</th>
<th>(T_{Li^+} = \frac{I_s}{I_o})</th>
</tr>
</thead>
<tbody>
<tr>
<td>3:1</td>
<td>21–23</td>
<td>0.89 ± 0.07</td>
<td>0.90 ± 0.07</td>
</tr>
<tr>
<td>4:1</td>
<td>21–23</td>
<td>0.83 ± 0.08</td>
<td>0.88 ± 0.05</td>
</tr>
<tr>
<td>3:1</td>
<td>60</td>
<td>0.78 ± 0.11</td>
<td>0.79 ± 0.05</td>
</tr>
<tr>
<td>4:1</td>
<td>60</td>
<td>0.75 ± 0.05</td>
<td>0.78 ± 0.03</td>
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Figure 2. (a) Impedance scans from two electrolyte samples taken before and after potentiostatic measurements at room temperature (21–23°C). (b) Current vs time profile of the polymer films, obtained at room temperature, under a 10 mV dc bias.
LiN(SO$_2$CF$_2$)$_2$, LiTFSI salt, were studied. The increase in transfer number was attributed to the reduction of free volume with rising material density (increasing salt content), resulting in lower anionic mobility. Our diblock copolymer PEO-b-(PMMA-ran-PMAALi) allows for a high salt loading while at the same time forms flexible and translucent films (Fig. 1). Achieving such a high cation (Li$^+$) transference number while avoiding the use of anion trappers and tethered polyanions is of significant interest with regard to the design of future electrolyte matrices.

Considering the high voltage range in which most lithium-based electrode chemistries operate, the electrochemical stability of the electrolyte material and its interfacial interactions with the electrodes have a significant bearing on the long-term performance of the battery. For the energy storage/conversion cells to effectively perform, it is pertinent that the electrolyte materials employed also have a wide electrochemical stability window well beyond the operating potential of the electrodes in the normal Li-ion battery operation temperature range of 20–60°C. Linear sweep voltammetry experiments show that the salt-optimized electrolyte films exhibit an electrochemical stability of 5.0 V at 60°C. For this study, the electrolyte film (molar composition EO:LiBOB = 3:1) was sandwiched between symmetrical lithium electrodes; a current flux of 0.1 mA/cm$^2$ was run through the electrolyte material for an hour before reversing the polarity.

Galvanostatic cycling was performed for 100 cycles. At different cycle intervals, impedance scans were carried out to compare the interfacial resistances evaluated from the dc and ac methods. Typical voltage profiles during the Li plating/stripping cycling are shown in Fig. 4. The overvoltage profile and impedance responses at different cycles (Fig. 5) were used to evaluate the stability of the polymer electrolyte during the lithium plating/stripping cycles. The overvoltage profile (Fig. 5a) of the material shows a voltage increase in the initial cycles (every cycle representing 2 h on the overvoltage–time plot). The subsequent overvoltage trend over the remaining cycles shows good electrolyte material stability to the lithium electrode. To analyze the mechanism for voltage increase, impedance was measured at different cycles, as shown in Fig. 5b. Total resistance values were determined from the impedance responses at low frequency and were compared to those determined from the galvanostatic

Figure 3. Linear sweep voltammetry of electrolyte films made from the diblock copolymer PEO-b-(PMMA-ran-PMAALi) and LiBOB (molar composition EO:LiBOB = 3:1) at (a) room temperature (21–23°C) and (b) 60°C. A scan rate of 1 mV s$^{-1}$ was used with a stainless steel working electrode and a lithium metal counter electrode.

Figure 4. Overvoltage profiles of certain cycles during the Li plating/stripping tests of Li/PEO-b-(PMMA-ran-PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C).

Figure 5. Overvoltage studies of Li/PEO-b-(PMMA-ran-PMAALi) + LiBOB (EO:LiBOB = 3:1)/Li cell at room temperature (21–23°C): (a) Overvoltage vs time profile, (b) impedance responses of the cell obtained at the end of different cycles. The solid lines represent the corresponding data fitting of the impedance scans.
lithium plating/stripping cycling, showing good agreement (Fig. 6a).

The galvanostatic resistance was obtained by dividing the average cycle overvoltage by the current applied. The impedance plots were fitted using an equivalent circuit consisting of a resistance element ($R_i$) in series with two $R/C$ elements (Fig. 6b schematic). $R_E$ represents the conductive resistance of the electrolyte; $R_{\text{SEI}}$ and $R_{\text{CT}}$ represent the high frequency interfacial resistance [formation of a solid electrolyte interface (SEI) passivation layer] and charge-transfer resistance, $C_{\text{SEI}}$ and $C_{\text{dl}}$ are the corresponding interfacial capacitances due to the SEI film and double layer. As shown in Fig. 6b, the ion conductive behavior of the polymer membrane is stable during the Li plating/stripping cycles. LiBOB-based electrolytes have already been shown to exhibit good conduction retention even at elevated temperatures.24-26 The high frequency interfacial resistance ($R_{\text{SEI}}$) does not show much change over the number of cycles and is attributed to the formation of a stable passivation layer. The $R_{\text{CT}}$ shows an initial rise followed by a much lower increment rate. In addition to the profile of the overall interfacial resistance, the individual trends of $R_E$, $R_{\text{SEI}}$, and $R_{\text{CT}}$ validate good electrolyte stability toward the lithium metal.

Conclusions

The tailored solid self-assembled diblock copolymer electrolyte matrix exhibits an exceptionally high lithium-ion transference number of 0.9, compared to a value between 0.2 and 0.5, shown by typical polymer—lithium salt materials. The results reported here demonstrate the effects that the use of higher salt loading, a bulky anion lithium salt, and a partially charged polymer backbone have on the transference number ($T_{\text{Li}^+}$) of the solid-state polymer electrolyte. The electrolyte membrane also has a wide electrochemical stability window and an excellent interfacial stability behavior with the lithium metal electrode. The synergy of these properties makes electrolyte membranes composed of the diblock copolymer PEO-b-(PMMA-ran-PMMAli) and LiBOB salt viable candidates for flexible lithium-ion-based energy conversion/storage devices.

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References