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Stabilization of the polymer electrolyte/lithium metal electrode interface with increased ion conduction using PEO polymer/low molecular weight PE-*b*-PEO diblock copolymer composite bi-layer films

Nassus R. Brown, Tejaswi Makkapati, Dale Teeters *

Department of Chemistry and Biochemistry, The University of Tulsa, 800 S. Tucker Dr., Tulsa, OK 74104, USA

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ABSTRACT

A method of stabilizing the interface of PEO polymer electrolytes with respect to lithium metal, using a composite bi-layered, hybrid film is described. This method utilizes a low molecular weight PE-*b*-PEO diblock copolymer having a general chemical formula of H-$(CH_2)_{32}$-$(O$-$CH_2CH_2)_{10}$-OH that can be positioned at the PEO polymer electrolyte surface. These hybrid films are fabricated by making a thin layer of the PE-*b*-PEO materials by solvent casting and then casting a second layer of standard PEO polymer electrolyte on the PE-*b*-PEO film. This PE-*b*-PEO layer adheres to the polymer electrolyte surface, making a stabilized interface with lithium. This hybrid system not only stabilize the lithium/polymer electrolyte interface but also has the desirable property of increasing ion conduction by almost three orders of magnitude over a standard PEO polymer electrolyte system. The stabilization of the lithium/polymer electrolyte interface and the increase in ionic conduction has been studied by using AC impedance spectroscopy, AFM phase imaging, and attenuated total reflection IR, which allow the mechanism for stabilization and increased ionic conduction to be discussed.

1. Introduction

One of the most challenging components of any type of battery system is the electrode/electrolyte interface. Stabilization, especially at the lithium metal–polymer interface, is critical for this high-capacity battery system to reach its complete technological potential [1]. The formation of a solid electrolyte interphase, SEI, layer is well documented in battery systems [2–9] and stabilizing the lithium metal interface so that destructive reactions are prevented depends on understanding the electrode/electrolyte interface. Solid electrolytes are expected to be more stable when in contact with lithium than liquid and gel electrolytes [10]. However, one of the most studied solid electrolyte systems, the polymer electrolyte systems poly(ethylene oxide), PEO, complexed with lithium salts, can form a passivation layer that can grow over time. This layer can become the largest impedance source in the battery system and can eventually become so impervious to ion movement that the cell cannot function [11,12].

Research has been conducted on the formation of this unstable SEI layer. Croce and Scrosati proposed that the majority of passivation occurs because of water and other impurities in the polymer mixture [13]. However, Bruce and Fauteux [12,14] have shown that other factors such as oxidation reactions and the formation of compounds from other reactions may be more important. Vincent proposed that reactions between the lithium metal, lithium salt, and polymer chains form the SEI layer [15]. Reactions important in this mechanism, including radical formations and chain scissions, have been shown to occur within 15 min of initial contact of PEO electrolyte with lithium metal [16].

Stabilizing the SEI layer in lithium/polymer electrolytes has been attempted by several methods. The addition of inert, ceramic fillers such as Al_2O_3 and TiO_2 or compounds such as $LiAlO_2$ added to PEO electrolyte improved electrochemical compatibility with a lithium metal electrodes [17–19]. Wen et al. demonstrated that a hyperbranched polyester improved interfacial performance [20], while Watanabe used methyl ether chain ends in crosslinked comb PEO electrolytes to reduced charge transfer resistance at the lithium interface [21]. A self-assembled monolayer, SAM, on a polymer electrolyte formed from a low molecular weight polyethylene-*block*-poly(ethylene oxide) diblock copolymer (i.e., PE-*b*-PEO) was found to stabilize the SEI [16,22–25]. The same PE-*b*-PEO wax-like material, when added to a PEO electrolyte in a solution casting process, was found to migrate or “bloom” to the solid surface stabilizing the lithium SEI [26].

This research seeks to reconcile some of the problems associated with solid polymer electrolytes as discussed above by improving the interfacial stability through a method of fabricating a composite bi-layer polymer electrolyte film. These hybrid films are composed of a layer of PEO electrolyte polymer and a layer of PE-*b*-PEO with the PE-*b*-PEO stabilizing the SEI layer formed between lithium and the polymer electrolyte. An interesting phenomenon associated with the low molecular weight diblock copolymer is that it not only stabilizes the SEI layer but

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* Corresponding author. Tel.: +1 918 631 2515.
E-mail address: dale-teeters@utulsa.edu (D. Teeters).

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also increases the ion conduction for the polymer electrolyte film. This enhancement in ion conduction addresses another issue of polymer electrolytes, low ion conduction. The mechanism of stabilization of the SEI and of increased ion conduction will be discussed.

2. Experimental

Two types of polymer electrolyte films were made. A pure PEO electrolyte film was made for use as a standard for comparison to a stabilized system. The stabilized system, a composite bi-layer composed of a standard PEO electrolyte layer and a protective PE-*b*-PEO layer, will be termed a “hybrid” film in this paper.

The standard PEO electrolyte film was fabricated by dissolving 1000,000 MW PEO (Sigma Aldrich) with $LiSO_3CF_3$ (Sigma Aldrich) in acetonitrile. The solution contained the appropriate amounts of polymer and salt to make a polymer film having a 15:1 ether oxygen-to-lithium ion ratio. The solution was placed in a Teflon container, and the solvent was removed by flowing dry nitrogen resulting in a solid polymer electrolyte film.

The creation of what we have termed a hybrid film was a two-step process. The first step involved using a low molecular weight PE-*b*-PEO diblock copolymer having a chemical formula of $H\text{-}(CH_2)_{32}\text{-}(O\text{-}CH_2CH_2)_{10}\text{-}OH$ (Baker Chemical) to make a layer for potential stabilization. An amount of PE-*b*-PEO and $LiSO_3CF_3$ was added to acetonitrile and stirred until some of the PE-*b*-PEO dissolved; however, most of the PE-*b*-PEO suspended in the liquid because of its low solubility. This solution/suspension was poured in a Teflon container, and a stream of nitrogen gas passed over the solution until a dried, solid PE-*b*-PEO/$LiSO_3CF_3$ layer remained. Because of the low molecular weight, this solid is very “waxy” in nature. In the second step, a standard PEO solution was prepared and poured on top of the dry wax film. A flow of nitrogen over the solution evaporated the solvent leaving a standard PEO polymer electrolyte film on top of the original PE-*b*-PEO wax layer. Because of the low solubility of the PE-*b*-PEO, the wax layer remained intact, while the solvent was removed from the standard film solution covering the PE-*b*-PEO solid layer. This resulted in two layers after the final evaporation: the standard PEO electrolyte layer on top of the PE-*b*-PEO layer. However, because of the slight solubility of the PE-*b*-PEO, the two layers had intimate contact with good adhesion. This bi-layer film was 50% PEO and 50% PE-*b*-PEO by weight, and the hybrid films were made so that the ether oxygen-to-lithium ion ratio, for total ether oxygens in the system, was 15:1. The hybrid films used in this study had a total thickness of approximately 100 μm with the PEO layer having a thickness of ~35 μm and the PE-*b*-PEO layer ~65 μm. Even though the PE-*b*-PEO layer had the physical properties of a waxy material, the standard PEO layer gave support to the hybrid film making a film that had excellent physical properties.

AFM data were collected on a Bruker Multimode V AFM, using tapping mode for analyses. AFM phase imaging was particularly useful. In this technique, the interaction forces between the tip and the sample are measured, which provides image contrast caused by differences in surface adhesion and viscoelasticity of different phases contained in the surface. Horizontal attenuated total reflection (HATR)–FTIR spectra were collected on a Nicolet Avatar 360 FTIR ESP fitted with an Avatar multi-bounce HATR contact sampler containing a flat plate with a ZeSe crystal cut at 45°. The average depth of penetration into the surface of the ATR evanescent wave was 1 μm, essentially allowing only the layers of interest to be studied.

All samples were stored and tests conducted in an argon atmosphere glove box. For lithium stability tests, the O_2 and H_2O concentrations in the glove box were adjusted to reach 1000 and 350 ppm, respectively. Since lithium metal is more reactive in these higher levels of O_2 and H_2O, these conditions presented a unique opportunity to take measurements in conditions taxing to the stability of any lithium electrode/electrolyte interface. This technique has been used previously to test the ability of protective layers to control passivation at the lithium/polymer electrolyte interface under demanding conditions [26].

AC impedance data were collected using a Solartron SI 1260 impedance/gain-phase analyzer with a 1296 Dielectric Interface with the frequency being varied from 1.000 MHz to 50 mHz. AC impedance test were conducted by using two test configurations. In one, the film samples were placed between two stainless steel blocking electrodes. In the second test configuration, the polymer film is placed on a stainless steel electrode with a piece of lithium as the second current collector in the test cell. The second stainless steel electrode is placed on top of the lithium metal completing the test configuration. In this manner, one side of the polymer film could be tested against lithium for interfacial stabilization studies.

3. Results and discussion

Work in our laboratory has shown that the presence of crystalline hydrocarbon chains at the surface of a polymer electrolyte can result in stabilization of the lithium/electrolyte interface [16,22–26]. The structure of the hydrocarbon chains present at the surface is very important in interface stabilization and, as such, was investigated by ATR-FTIR spectroscopy. Fig. 1 shows ATR-IR spectra in the 650 to 800 cm^{-1} region for the surface of the PEO standard and the surface of PE-*b*-PEO side of the hybrid films. The appearance of two peaks at approximately 720 and 730 cm^{-1} are indicative of the presence of crystalline hydrocarbon chains of $(CH_2)x$, where x is four or larger [27]. As would be expected, these peaks are not seen in the standard PEO film. The spectral intensities of these two vibrational modes can be related to the amount of crystalline CH_2 at the surface if an internal standard can be used to normalize intensities. This can be done by normalizing intensities of modes in this spectral region to other modes common in all spectra, but not affected by the vibrational dynamics of the 720 to 730 cm^{-1} region. The C–O–C mode at 1100 cm^{-1} (spectral region not shown) was used for normalization purposes. Since the difference in the intensities of C–O–C mode between all the spectra was less than 5%, normalization was not necessary for a relative interpretation of the amount of crystalline CH_2. The high intensities exhibited by the 720 and 730 cm^{-1} modes in the hybrid film represent a significant amount of crystalline CH_2 chains at the surface. The presence of crystalline hydrocarbon chains is important since, as stated previously, crystalline CH_2 chains provide lithium metal/electrolyte stabilization [22–24,26].

To test the ability of the hybrid film to stabilize the lithium/polymer electrolyte interface, ac impedance data were collected for both the standard PEO and the hybrid films when in contact with lithium metal. For these electrochemical stability tests, the O_2 and H_2O concentrations were 1000 and 350 ppm, respectively, in the glove box where test were conducted. The reaction of lithium under these conditions could be determined by observing exposed lithium metal in the glove box. At the start of these tests, lithium metal exposed was very shiny,

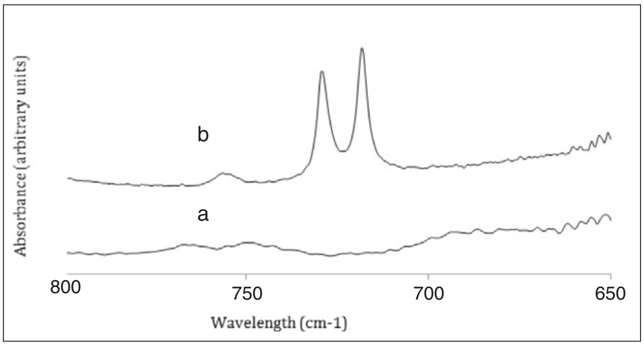

Fig. 1. HATR-IR spectra for (a) the standard PEO film and (b) the hybrid film. Two distinctive peaks found at 730 and 720 cm^{-1} are known to be indicative of crystalline CH_2 chains.