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Monitoring the real time growth of a self-assembled monolayer on a polymer electrolyte surface

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Abstract

The growth of a self-assembled monolayer (SAM) at the surface of a polymer electrolyte has been shown to inhibit the formation of the passivating layer that forms when the polymer is in contact with lithium metal. In this work, ac impedance spectroscopy was used to monitor the formation of SAM layers on polyethylene oxide (PEO) polymer electrolyte thin films as a function of time. To monitor SAM growth, thin PEO films were cast onto interdigitated electrodes. The electrodes were subsequently immersed in a saturated SAM solution and the film impedance was measured. SAM molecules with the general formula: $H{-}(CH_2)_{32}{-}(CH_2CH_2O)_y{-}H$ ($y = 2$, 10, 40) were used. Growth occurred due to interactions with the ethylene oxide portion of the SAM molecules with the PEO surface. To visualize SAM growth impedance data at a single frequency sensitive to changes at the solution interface was plotted verses time. At the point of immersion, a sharp increase in impedance was observed. With time, the rate at which the impedance increased slowed and ultimately leveled off presumably indicating the point at which a nearly complete monolayer had formed. SAM growth was verified using attenuated total reflectance infrared spectroscopy (ATR-IR).

Keywords: Polymer electrolyte; Self-assembled monolayer; ac Impedance spectroscopy; Infrared Spectroscopy; Interdigitated microelectrode

1. Introduction

Since their discovery [1], solid polymer electrolytes have garnered considerable attention due to the variety of applications in which they can be used. Since it was first proposed over three decades ago [2] the idea of using polymer electrolytes in batteries, specifically lithium ion polymer batteries, has been a primary driving force in the research and development of these interesting materials. [3–6]

In the most basic form, a lithium polymer battery consists of a solid lithium polymer electrolyte membrane sandwiched between two lithium reversible electrodes. An interesting problem arises when using lithium metal as an electrode material. Over time, a large resistance to ion conduction develops at the interface between the polymer electrolyte and lithium electrode surface. In essence, a nonconducting or passivating layer forms at the electrode/electrolyte interface creating a barrier which results in decreased conductivity [7]. It has been shown that with repeated charge/discharge cycling this interfacial resistance can actually become larger than the resistance of the bulk polymer electrolyte itself [8,9]. This is unfortunate because the use of lithium metal in batteries, specifically as the anode, is highly desirable due to its large electrochemical window and high energy density. These characteristics are important in generating the power needed to operate many of our modern electronic devices. Most recent research in the area of polymer electrolytes for use in batteries has focused on solving the more immediate problem of increasing the bulk conductivity of these materials. Largely unstudied but no less important are issues, such as lithium passivation that exist at the surface or interface of the polymer electrolytes.

One approach to solve the passivation problem is to chemically modify one or both of the mating surfaces [10]. Modification of the lithium surface can be difficult due to its highly reactive nature. Because the polymer electrolyte surface is often nonreactive and is easily accessible working with this surface offers a much simpler approach to surface modification [11–13]. Previous work by Granvalet-Mancini et al. showed that the addition of a self-assembled monolayer (SAM) to the polymer surface altered the interfacial properties of the electrolyte,

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which resulted in a decrease in lithium passivation while maintaining significant ion conduction at the anode [14,15]. Although passivation did ultimately occur, it developed at a much slower rate than in the absence of the SAM layer.

The self-assembly process refers to a molecular monolayer that spontaneously forms on a substrate by adsorption from solution [16]. The molecule typically contains at least one functional group that spontaneously chemisorbs to the surface and a "tail" which self assembles through intermolecular attractions with similar portions of a neighboring molecule. The process results in an ordered molecular layer covering the surface. [17,18] In the lithium passivation work cited above [14,15], *n*-alkyl poly(ethylene oxide) SAMs of varying alky and ethylene oxide chain lengths were used to modify a PEO polymer electrolyte surface. Through IR spectroscopy and atomic force microscopy, they showed that molecules with fewer ethylene oxide groups more readily adsorbed on the surface and were more effective at protecting the lithium metal. Molecules with more ethylene oxide groups showed less adsorption and were less effective. It is reasonable to suspect that the structure of ethylene oxide portion of these molecules plays a critical role in their ability to limit passivation. It has been shown that factors such as solvent effects [19] and substrate head group binding interactions [20] can change the ethylene oxide structure in a SAM thereby decreasing the effectiveness of SAM formation [21–23].

While the above SAM work showed a modified electrolyte surface could provide protection against passivation, it is not yet clear as to what role SAM structure plays. More importantly for battery application, it is not yet understood what role the SAM layer played in ion conduction. It is conceivable that a perfectly formed completely protecting SAM layer might impede ion transfer to the electrode. It is equally conceivable that a SAM poorly formed due to structural defects, while allowing ion transfer, may offer little or no passivation protection. Information on SAM structure, morphology, and monolayer formation is critical to understanding the role the SAM plays in ion conduction and electrode passivation. In this paper, we monitor the real time growth of a self-assembled monolayer on a polymer electrolyte surface using a highly sensitive interdigitated electrode system coupled with ac impedance spectroscopy. The goal of this work is to provide a starting point to better understand how factors such as ion conduction and lithium passivation might be affected by differences in SAM growth and growth conditions.

2. Experimental

2.1. Film preparation

PEO films were made using 900,000 molecular weight poly(ethylene) oxide (Aldrich) and lithium triflate (Aldrich) with a 15:1 ether oxygen to lithium ion ratio. The polymer and salt were dissolved in acetonitrile providing a working solution for the polymer film preparation. Thin films of the PEO polymer electrolyte were created by drop casting the PEO solution onto an interdigitated microsensor electrode (IME) assembly (Abtech Scientific Inc.).

The IME consisted of two interlacing gold electrodes deposited on an insulating glass substrate (Fig. 1 b). Each electrode contained 50 interlacing digit pairs. The individual digit dimensions were 5 mm in width, 5 mm in length, with a gap of 5 mm between each digit. The depth of each digit was approximately 200 nm. Prior to each use, the IME was cleaned by soaking the electrode in acetonitrile for 12 h, followed by a mild etching in an Ar plasma.

The PEO solution viscosity was adjusted so that when cast the resulting solid film completely covered the electrode digits while remaining as thin as possible. Film thickness was estimated using atomic force microscopy (Fig. 1c). Cross section analysis showed that sample thickness varied between approximately 250–500 nm. The PEO coated electrodes were dried at room temperature (18–23 °C) in a desiccator for several days before use.

Semicrystalline waxes (Baker Petrolite) with the general formula:

$H{-}(CH_2)_{32}{-}(CH_2CH_2O)_y{-}H$ were used to create the SAM layer. Saturated SAM solutions were prepared by dissolving excess wax in hexane, followed by vigorous stirring for at least 24 h. All solutions were prepared at room temperature.

2.2. Experimental apparatus

Fig. 1a shows the general apparatus used in the electrochemical growth experiments. To monitor SAM growth, a simple solution cell was constructed using a large diameter test tube and cork. The PEO coated IME was connected with a clip, which was attached to two shielded coaxial cables for electrochemical measurements. The cables ran through two tightly sealed holes in the cork. When fitted in the tube, the cork acted to both suspend the IME assembly in the SAM solution and seal the tube preventing evaporation of the solvent. SAM formation occurred via adsorption from the hexane solution onto the PEO surface. Prior to each run, the dry PEO coated electrode was immersed in pure hexane and monitored for several hours to ensure that solvent effects were not present. After this pre-exposure period, the IME was quickly removed and placed in a cell containing the saturated SAM solution. Electrochemical measurements were taken continuously during the transfer process to ensure the polymer film remained stable and was not negatively affected during the transfer process. The electrochemical measurements continued without pause throughout the course of the SAM growth. The SAM solution was not stirred during the growth period.

SAM growth was monitored by both ac impedance spectroscopy and infrared spectroscopy. Impedance measurements were conducted using a Solatron 1255 gain/phase analyzer with the 1287 electrochemical interface, over the frequency range of 0.1 Hz–10 MHz. During the SAM growth period, data were collected every 30 min for a period of 24–40 h. Infrared absorption experiments were conducted using a Bruker Vector 22 FTIR spectrometer with a single pass horizontal attenuated total reflectance (HATR) attachment (Pike Technologies). In these experiments, several individually PEO coated glass slides were immersed in a SAM solution in similar fashion to the samples in the impedance experiments. The slides were removed from