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Investigation of the inherent electrical potential of PEO electrolyte films

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Abstract

Measurement of the through-plane potential of PEO–lithium triflate electrolyte films has demonstrated that they possess an inherent potential as cast from an acetonitrile solution onto a Teflon substrate. These films have an inherent potential of around 0.2 V and the cast films display a discharge behavior similar to a double layer capacitor system with a small discharge capacitance of 80 nF cm^{-2}. It is postulated that electrochemical properties of the films can be attributed to different salt concentration at the two surfaces. This difference in concentration may result from a matching of the surface-free energy of the Teflon substrate side of the film and the side of the film where evaporation occurs with the lithium triflate species in the polymer. Different spherulite morphologies were also observed for each surface. These morphologies can be assigned to spherulites having much different ion concentrations. Attenuated total reflection (ATR) IR spectroscopy was used to investigate the surface concentrations of free ions, ion pairs and ion multiples of both surfaces of the films. AC impedance spectroscopy of the surfaces of the film was also conducted. These data indicated that there is a difference in the surface concentration of each side. The ability of electrolyte films to exhibit a potential as fabricated may have potential applications as an easily manufactured power source for micro and nanodevices.

Keywords: Double layer capacitor; Inherent potential; Surface concentration; Spherulites

1. Introduction

Recently there has been interest in all solid-state double layer capacitors based upon polymer electrolytes. This interest is due to their potential applications where high power density is desired, such as use in electric vehicles. These capacitor systems also have potential advantages in the ability to take the form of thin films, which can prove especially useful for high-energy power sources, including those for miniaturized devices such as future nanodevices. Poly(ethylene oxide), PEO, made into an electrolyte by complexation with inorganic salts, has been the object of many of these studies [1–8]. The capacitor electrodes in these studies are usually carbon-like in nature, such as activated carbon fiber [1,3,7], carbon black [2], high-density graphite [4–6] and activated carbon [8]. These carbon sources have a high surface area to maximize the interface where charging of the double layer in the PEO electrolyte occurs.

While conducting electrochemical tests on a solvent cast film of PEO electrolyte for battery applications, it was noticed that a film of PEO placed between stainless steel electrodes had an inherent potential or charge. No charging was necessary for the PEO film to exhibit this potential. This is an interesting phenomenon. Questions as to why this potential exists and the power that can be harvested from these as cast films are of interest. This paper is concerned with understanding the occurrence of the inherent potential and its possible relationship to the spherulitic morphology of these films.

2. Experimental

PEO (900,000 molecular weight, Aldrich Chemical) was dissolved in ACS reagent grade acetonitrile (Fisher). $LiSO_3CF_3$, which will be abbreviated LiTf (Aldrich Chemical) was dried at 100 °C in a vacuum oven. It was then added to the PEO solution in the appropriate amount to make an ether oxygen to lithium ion ratio of 15–1. The solution was placed in a Teflon container and the solvent evaporated under a flowing dry nitrogen atmosphere to make the film. This resulted in 60 μm thick

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films of the PEO electrolyte, which were used for all studies. In order to distinguish between the two sides, they will be called the evaporation side, noting the side that comes in contact with the flowing nitrogen where evaporation occurs as the film forms, and the solid substrate side, representing the side that is in contact with the Teflon container during film formation. Films were stored under vacuum or in an argon atmosphere glovebox. All experiments conducted on the films were done within 1 week after preparation. This was done to minimize changes in film crystallinity that can occur after long storage times.

A Keithley model 6430 sub-femtoampere remote source meter was used to measure potentials and to conduct discharge studies. These were conducted using two stainless steel electrodes to make contact on either side of the PEO films. AC impedance spectroscopy data were collected using a Solartron 1260 gain/phase analyzer with a 1296 electrochemical interface over a frequency range from 1 MHz to 1 mHz. Surface AC impedance data were collected by using a two electrode experiment. The two surface electrodes were constructed by cutting a circular stainless steel disk in half. An insulating glass layer, approximately 120 μm thick, was placed between the two halves and glued with an insulating epoxy. Electrical contact was made individually to each of the two semicircular, flat electrodes separated by the insulating glass. In this manner, the stainless steel disk was turned into two semicircular, flat electrodes separated by the insulating glass. Pressing this two electrode configuration on the surface of the polymer electrolyte allowed surface ac impedance data to be collected. All electrochemical tests were conducted in an argon atmosphere glovebox inside a Faraday cage made from aluminum foil. A Digital Instruments Nanoscope IIIa atomic force microscope (AFM) was used to collect images of the PEO electrolyte surface. The sample chamber of the AFM was kept under a dry nitrogen atmosphere as images were collected in order to avoid water absorption.

A Nicolet Avatar E.S.P. FTIR Spectrometer with an attenuated total reflection (ATR) attachment was used to collect ATR FTIR spectra. The ATR cell had a ZnSe crystal cut at 45°. Films were loaded and sealed in the ATR sample cell inside an argon atmosphere glovebox. The sealed cell assured that the films were not exposed to the atmosphere when spectra were collected on the FTIR spectrometer.

3. Results and discussion

While testing a PEO electrolyte film with 15–1 ether oxygen to lithium ion ratio for use as the electrolyte in a $SnO_2/LiCoO_2$ battery system, it was observed that these PEO films exhibited a consistent inherent potential of between 0.15 and 0.2 V. Repeated measurements were made on these films by placing them between two stainless steel electrodes and making measurements using a sub-femtoamp source meter. Fig. 1 shows the discharge of a cast film with a load of 100 pA. Since there are no reactive electrodes in this system, this could be associated with capacitor like behavior. The discharge capacitance, C_{dis}, for the film from its inherent start voltage to complete discharge can be calculated using.

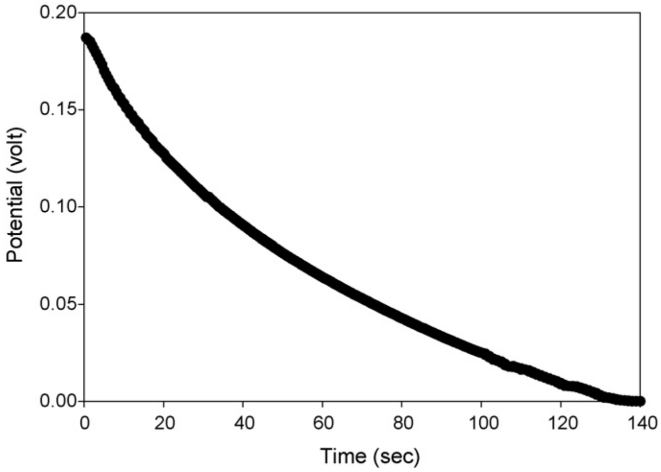

Fig. 1. Discharge capacitance data for a PEO-LiTf film. The discharge load was 100 pA.

$$C_{\mathrm{dis}} = \frac{i\Delta t}{\Delta V} \tag{1}$$

where i is the current load and Δt is the time for the change in voltage ΔV. The data from Fig. 1 give a value of approximately 80 nF cm^{-2}. While capacitance values normalized for the total mass of the capacitor could not be found in the literature for a similar electrolyte system, values normalized for surface area are available for comparison. Hashmi's et al. reports values [7] for a PEO-LiTf-polyethylene glycol double layer capacitor of 0.53 and 22 mF cm^{-2} for graphite and activated carbon cloth electrodes respectively. The inherent capacity for the films studied here is very small, but it is interesting that these solution-cast films can exhibit an inherent voltage with this small discharge capacitance. The question of importance is why these solution-cast films of PEO electrolyte have an inherent potential. Two criteria would seem to be necessary. First, a concentration gradient between the two surfaces that would be considered double layer like in nature must exist. Second, a surface of high area must be available for this double layer concentration gradient to manifest itself. The former of these two criteria will be considered first.

Previous work done by Teeters et al. has shown that the concentration of ions at the surface of a PEO film differed from the bulk [9]. If there is also a difference in concentration between the two surfaces of the film, one could imagine that an inherent concentration gradient between the two surfaces, perhaps a double layer-like system, could naturally be present. It is possible that such a concentration difference between the two surfaces exits because of the difference in free energies that the two surfaces experience as the solvent evaporates during film formation. One surface experiences the Teflon substrate that, relative to the evaporation side, would have a higher free surface energy. This higher free surface energy side, the Teflon side, could be expected to more readily attract many of the forms of the lithium triflate to this surface as the film forms during evaporation. Contrary to the postulation that each surface may have a different concentration, work done by Mattsson et al. [10] and Wenzl et al. [11], on PEO