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# An electrochemical approach to measuring oxidative stability of solid polymer electrolytes for lithium batteries



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## HIGHLIGHTS

- Voltammetry of solid electrolyte without mass transfer developed.
- Aluminum passivated by polymer electrolyte containing LiTFSI.
- Exchange current density of oxidative degradation determined.
- Polymer electrolyte oxidation sluggish with large thermal activation energy.

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## ABSTRACT

Polymer electrolytes are an interesting class of electrolytes that hold promise for safer, flexible, high-energy batteries. Block copolymer electrolytes that contain polystyrene, poly(ethylene oxide) (PEO) and lithium bis-trifluoromethanesulfonimide salt (LiTFSI) are compatible with lithium metal. However, the compatibility of PEO-based electrolyte with advanced lithium positive electrodes has not been conclusively demonstrated. Therefore, oxidative stability of PEO+LiTFSI and the block copolymer electrolyte with common current collectors and against inert working electrodes have been investigated electrochemically. The solid nature of these polymer electrolytes is a challenge for electrochemical investigations, since most electrochemical experiments have been designed for liquid electrolyte. In order to quantitatively evaluate polymer electrolyte stability, an electrochemical approach especially designed for solid electrolytes is presented. This approach uses a set of linear sweep voltammograms from different, large overpotentials to open circuit voltage, which the authors term variable reverse linear sweep voltammetry. By allowing the cell to relax between each polarization, the first data points of each voltammogram are not mass transfer limited. This yields current versus overpotential data that can be analyzed with a kinetic model, such as the Butler–Volmer model. The block copolymer electrolyte has been found to be quite stable to electrochemical oxidation, up to 5 V at 40 °C. The degradation reaction has been found to be slow with large thermal activation energy.

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## 1. Introduction

Lithium batteries have the highest energy density of any commercially available rechargeable battery (Tarascon and Armand, 2001), and are used in plug-in electric vehicles. However, these commercial batteries have lithium salts dissolved in hazardous flammable organic solvents. Any damage or malfunction in the battery can lead to fires or explosions (Hallinan and Balsara,

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2013). In liquid electrolytes, battery abuse can cause temperatures to rise, and, due to their volatility and reactivity, can lead to dangerous exothermic reactions. These safety concerns can be reduced if a solid-state battery can be produced. Polymers doped with lithium salt have been studied for potential use as an electrolyte for lithium batteries (Hallinan et al., 2013; Soo et al., 1999; Wang et al., 2003). Polymer electrolytes improve safety in several ways. Since these batteries do not leak they are fundamentally safer. In addition, polymer electrolytes are nonvolatile, less reactive, and less flammable.

Poly(ethylene oxide) (PEO), when combined with salt, exhibits a relatively high conductivity compared with other polymer electrolytes. Ionic conductivities as high as  $10^{-3}$  S cm<sup>-1</sup> at elevated

temperature have been observed for PEO+salt mixtures (Lascaud et al., 1994; Panday et al., 2009; Yuan et al., 2013). PEO is studied widely because of its unique ability to solvate many different kinds of salts due to its ether oxygens (Teran et al., 2011). PEO doped with lithium bis-(trifluoromethanesulfonyl)imide salt (LiTFSI) has shown improved ionic conductivities when compared to PEO doped with other salts. This is most likely due to the two strong electron withdrawing groups in the anion causing charge delocalization. This leads to weak lattice energy and facile dissociation (Sylla et al., 1992).

Another characteristic of solid polymer electrolytes relevant to lithium metal batteries is the formation of dendrites. The low shear modulus of PEO allows for dendrites to grow through the electrolyte creating a short circuit in the sample (Rosso et al., 2006). However, it was proposed that if the shear modulus of the solid electrolyte was increased it would prevent dendritic growth (Monroe and Newman, 2005). A block copolymer of glassy polystyrene and PEO (SEO) provides both the mechanical strength and high ionic conductivity necessary to cycle lithium batteries (Hallinan et al., 2013). Previous work demonstrated that conductivities on the order of  $10^{-3}$  (S/cm) are possible at 80 °C with high shear modulus at high molecular weights and an optimal molar salt ratio ( $r$ ) of 0.085 mol of lithium per mole of ethylene oxide repeat unit (Stone et al., 2012).

There is limited information about the electrochemical stability of solid polymer electrolytes. Polymer electrolyte degradation (side-reactions apart from electrochemical reactions of active materials) can happen during charge/discharge cycles. The resulting by-products from such side-reactions can block or consume active sites on the electrode/electrolyte interface, thus leading to decreased energy density and a diminished battery cycle life. Therefore, in order to achieve better performance of lithium polymer batteries, it is of vital importance to gain fundamental knowledge on polymer electrolyte degradation.

A previous study performed by Sylla, Sanchez, and Armand has reported that PEO + LiTFSI complexes have good electrochemical stability over a large potential range when using stainless steel as the working electrode and lithium as the counter and reference electrodes (Sylla et al., 1992). The cyclic voltammogram showed an upturn at approximately 4.5 V. However, the authors called into question impurities on the stainless steel working electrode. In another study from Armand's group, cyclic voltammetry was performed on two electrode cells with either platinum or nickel microdisc working electrodes and lithium metallic foil pressed on stainless steel counter/reference electrodes (Benrabah et al., 1993). A single scan was run on each sample due to the chance of a passivating layer forming from lithium reduction by-products. The samples were stated to have good electrochemical stability, especially towards oxidation, making it suitable for applications in high-energy lithium batteries. However, the upper limit of CV scans was less than 4 V. Thus, the compatibility of PEO + LiTFSI with advanced lithium positive electrodes that operate well above 4 V is still an open question. This work examines anodic stability for PEO + LiTFSI and SEO + LiTFSI electrolytes using working electrodes composed of current collectors commonly employed in lithium batteries (Al and Cu) as well as working electrodes expected to be inert (Au and glassy carbon). The effect of temperature and salt concentration on the oxidative reactions was also examined. The aims were to (1) more thoroughly examine anodic stability of PEO + LiTFSI, (2) evaluate anodic stability of SEO + LiTFSI for the first time, and (3) present a voltammetric method to quantitatively measure electrochemical kinetics in solid electrolytes.

There are several challenges associated with electrochemical studies of solid electrolytes. First, they tend to have much lower conductivity than liquid electrolytes, which means that mass

transport in the electrolyte tends to dominate any electrochemical measurements. Due to limited salt solubility in polymer electrolytes, it is not possible to introduce supporting electrolyte while maintaining a truly solid character. Ionic liquids could be used, but the electrolyte would then be a gel. Methods that are used with liquid electrolytes to minimize mass transport resistance, such as rotating disk electrodes, cannot be used with a solid electrolyte in which convection is not possible. It is also quite challenging to incorporate a reference electrode in a solid polymer electrolyte system. An attempt has been made to do so in this work, but for practical reasons the reference electrode was tens of micrometers from the working electrode (and a similar distance from the counter electrode). Therefore, coupled with mass transport limitations of the polymer electrolyte, no difference was observed between two and three-electrode experiments. Finally, it is challenging to disassemble all-solid, polymer-electrolyte-based cells nondestructively, meaning that analysis of degradation products is more complicated. Polymer electrolyte cells have been disassembled by dissolving away the polymer electrolyte (Hallinan et al., 2013; Stone et al., 2012) but it is unclear how and where the degradation products partition. Limited cycling without thermal annealing prevents adhesion between electrode and electrolyte, but it is unclear what the actual potential will be at an electrode/electrolyte interface with such large surface overpotential (Xu et al., 2014). A clever approach is to incorporate a chemically similar liquid interface between the solid polymer electrolyte and the electrodes (in the form of oligomers) to enable disassembly (Sun et al., 2015). This approach was not used in our work due to the desire to examine high molecular weight, all-solid polymer electrolyte stability. *In situ* spectroelectrochemistry would be an ideal solution, but methods capable of analyzing degradation products have not been developed to date. To address these difficulties we have developed an electrochemical approach to minimize mass transport effects, thereby allowing us to measure equilibrium reactions potentials and degradation kinetics of solid electrolytes.

## 2. Experimental

### 2.1. Materials

Poly(ethylene oxide) was synthesized anionically in benzene from ethylene oxide monomer. N-butyl-Li initiator and phosphazene base catalyst were added to the purified solvent in an argon-filled glove box. The purified monomer was distilled to the solvent initiator mixture and allowed to react at 40 °C for several days. The reaction was terminated with degassed alcohol. The polymer was precipitated three times in excess non-solvent (hexane). All synthesis reagents were obtained from Sigma-Aldrich. Finally the polymer solution was filtered through a micron filter and freeze-dried. The molecular weight of PEO is 143,000 g/mol, determined from gel permeation chromatography in dimethylformamide with 1 M LiBr referenced to polystyrene standards. The polydispersity index (PDI) is about 2. PEO was dried under vacuum at 60 °C overnight. We have found 60 °C the proper compromise between melting PEO crystals (to drive off bound water) and minimizing thermal degradation. The dried PEO was stored in an argon-filled glove box with water and oxygen below 1 ppm.

Anionically synthesized PEO has lower PDI than most commercially available high molecular weight PEO (greater than 100,000 g/mol). Early literature demonstrated extremely poor thermal stability for PEO, perhaps due to peroxide based initiators (Waterman et al., 2002). Based on recent literature, PEO thermal stability is a strong function of the environment (water and oxygen induce degradation at temperatures below 100 °C) and

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