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Block and graft copolymer electrolytes for high-performance, solid-state, lithium batteries

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Abstract

The ideal electrolyte material for a solid-state battery would have the ionic conductivity of a liquid, the mechanical properties of a solid, and the formability of a commodity thermoplastic. If system energy densities >300 Wh/kg are to be achieved, the electrolyte must be light and thin, yet act as a reliable physical separator for the electrodes. In this laboratory it has been shown that this challenge can be met with several classes of microphase-separating polymers, specifically, block and graft copolymers. The attributes and performance limitations of each are described along with the prognosis for their deployment in a solid-state battery.

Keywords: Polymer electrolyte; Solid-state battery; Block copolymer; Graft copolymer

1. Introduction to microphase-separating polymers

Block copolymers consist of two chemically dissimilar polymers covalently bonded end-to-end. Under certain conditions, a net repulsion between the polymer blocks induces their local segregation, or “micro-phase separation”, into periodically spaced nanoscopic domains. Choosing a lithium-salt-solvating polymer as one block component enables continuous ion-conducting pathways to form. The nanoscale morphology confers solid-like mechanical properties to the material even if both polymer blocks reside well above their respective glass transition temperatures, i.e. in the melt regime. When the copolymer consists of two low-T_g, noncrystallizing blocks, films with mechanical properties similar to those of a cross-linked rubber can be obtained without sacrificing the high local chain mobility required for Li^+ conduction. The first such materials synthesized in this laboratory comprised poly(oxy-ethylene)$_9$ methacrylate (POEM), $T_g \cong -60\,^{\circ}C$, which has the capacity to solvate lithium salts, and an alkyl methacrylate such as poly(lauryl methacrylate) (PLMA), $T_g \cong -35\,^{\circ}C$ [1]. Even though both blocks as homopolymers are viscous liquids at room temperature, the resulting block copolymer, POEM-*b*-PLMA, behaves as a rubbery solid.

Fig. 1 gives a schematic representation of how microphase-separation confers solid-like mechanical properties on the block copolymer. Above the order–disorder temperature (ODT) or when dissolved in a solvent the material behaves as a liquid, i.e. the blocks are segmentally mixed. Below the ODT the blocks phase separate but since they are covalently bonded they form so-called microphase domains. The morphology of these domains is determined by the relative sizes of the two blocks. In Fig. 1 the blocks are nearly equal in length and so the resultant morphology is lamellar. The effect of such constrained phase separation is to produce a highly interdigitated structure that behaves as a solid. In parallel, when doped with a lithium salt such as lithium trifluoromethylsulfonate, $LiCF_3SO_3$, also known as lithium triflate, the material becomes an electrolyte capable of conducting lithium ions; hence the term, block copolymer electrolyte (BCE). The lithium ions move from side chain to side chain of the POEM domain which at that length-scale acts as a liquid. Thus, it is by separating the length scales of mechanical behavior and electrical behavior that the same material is able to exhibit solid-like mechanical properties and liquid-like electrical properties.

2. First-generation block copolymer electrolytes

BCEs of the general composition described above were studied and found to possess electrical conductivities at room temperature on the order of $\sim 10^{-6}$ S/cm. These materials were dimensionally stable, i.e. they did not flow, and behaved as elastomers. They were found to be chemically stable in the presence of metallic lithium and electrochemically stable beyond 5 V. Indeed, the only electrochemical activity

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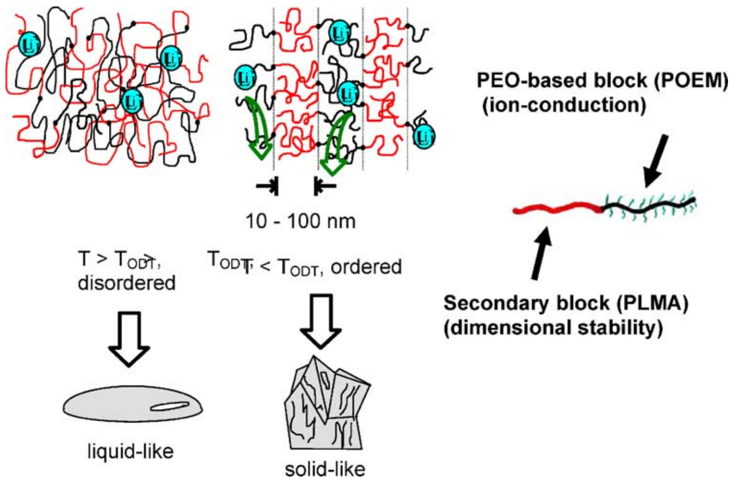

Fig. 1. Schematic illustration of a microphase-separating block copolymer electrolyte (BCE). The hydrophilic PEO-based block solvates the lithium salt. Lithium ions move with liquid-like mobility from side chain to side chain. The hydrophobic secondary block triggers phase separation which in turn confers mechanical stability to the bulk material.

observed was that associated with the decomposition of the dopant lithium salt. The material was easily processed by spin coating from a solution of tetrahydrofuran (THF). Finally, batteries consisting of Li/BCE/$LiMO_2$, where M represents Co or Mn, were charged and discharged at room temperature for hundreds of cycles at rates as high as $C/2$ [1]. One composition incorporating polymethyl methacrylate as the secondary block component showed promise for melt-based processing of electrolyte films [2].

3. Graft copolymer electrolytes (GCEs)

It was also observed in our study of BCEs consisting of POEM-*b*-poly(alkyl methacrylate) that the electrical conductivity varied inversely with the glass transition temperature of the poly(alkyl methacrylate) block component [1]. In an effort to raise the electrical conductivity to even higher values, for the choice of secondary block we turned to poly(dimethyl siloxane) (PDMS) with its T_g of −123 °C, substantially lower than that of any of the alkyl methacrylates in the previous study. To exploit this chemistry we chose to generate a microphase-separating graft copolymer consisting of a backbone of poly(oxy-ethylene)$_9$ methacrylate (POEM) and long side chains of PDMS. POEM-*g*-PDMS with 70 wt.% POEM and doped with lithium triflate proved to be a rubbery solid exhibiting electrical conductivity nearly equivalent to that of POEM homopolymer, a viscous liquid at room temperature.

Termed a graft copolymer electrolyte (GCE), this material was prepared by a facile free-radical synthesis method that is industrially scalable.

Differential scanning calorimetry (DSC) indicated that the material is microphase separated, as two distinct glass transition temperatures were recorded at −136 and −66 °C, which can be associated with PDMS and POEM, respectively. Furthermore, small-angle neutron scattering (SANS) confirmed that the material microphase separates, the domain periodicity measuring ~25 nm, which is consistent with observations of morphology by transmission electron microscopy (TEM). Thermogravimetric analysis (TGA) showed that the material resists thermal decomposition to temperatures exceeding 200 °C. Fig. 2 shows the electrical conductivity of the solid GCE and how nearly it approximates that of the POEM homopolymer which is a liquid on the identical temperature interval.

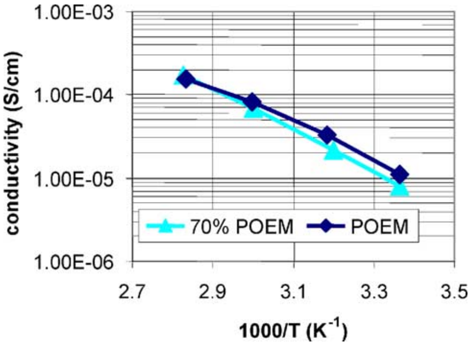

Fig. 2. Temperature dependence of electrical conductivity of POEM-*g*-PDMS (70:30) and POEM homopolymer, each doped with $LiCr_3SO_3$ to a Li:[EO] ratio of 1:20.

Finally, to demonstrate its viability as a battery electrolyte this material was cycle tested at room temperature at rates as high as 2/3 C (200 mA/g cathode) in a cell comprising Li/GCE/VO_x, where VO_x was a film of mixed vanadium oxides (V_2O_3 and V_2O_4) produced by vapor deposition in air of metallic vanadium onto aluminum. After 200 cycles there was no measured loss of capacity [3].

4. Single-ion conducting GCEs

Electrical conductivity is not the only important figure of merit when it comes to assessing the electrical performance

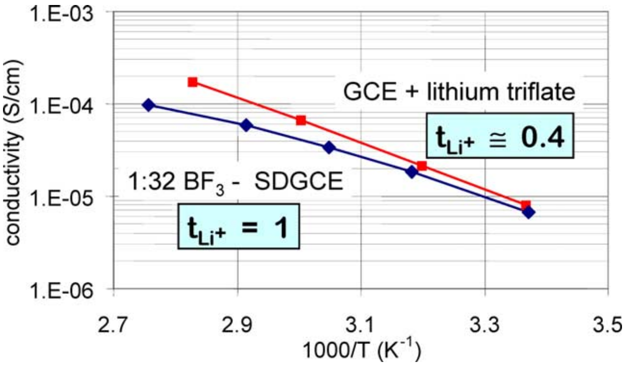

Fig. 3. Temperature dependence of electrical conductivity of salt-doped POEM-*g*-PDMS, "GCE", and the self-doped fluoroborated P(OEM-*r*-LiMA)-*g*-PDMS, "BF_3-SDGCE".

of a battery electrolyte. The lithium ion transference number (t_{Li^+}) is also important, particularly at high drain rates [4]. In an attempt to produce a material that exhibits single-ion Li^+ conduction, the compensating negative charge was introduced in the form of a methacrylate moiety incorporated into the POEM backbone of the POEM-*g*-PDMS graft copolymer [5]. Such a material was termed, self-doped (SD), in contrast to the conventional salt-doped electrolytes we had previously studied. While the value of t_{Li^+} was measured to be unity for resultant poly((oxyethylene)$_9$ methacrylate-*r*-lithium methacrylate)-*g*-poly(dimethyl siloxane) (P(OEM-*r*-LiMA)-*g*-PDMS), this material exhibited unacceptably low electrical conductivity, $\sim 10^{-8}$ S/cm at room temperature. This poor performance was attributed to ion pairing between the dissociated Li^+ and the immobile methacrylate moiety embedded in the POEM backbone. To prevent ion pairing the negative charge was depolarized by the incorporation of BF_3 into the lithium methacrylate moieties [6]. In conjunction with optimization of the Li:[EO] ratio, the result was a 100-fold increase in room-temperature electrical conductivity. As seen in Fig. 3, the fluoroborated material possessed room-temperature electrical conductivity comparable to that of the best performing salt-doped material, the advantage being that the SDGCE exhibited single-ion conduction, i.e. $t_{Li^+} = 1$.

Finally, dc conductivity measurements demonstrated the superiority of the BF_3-SDGCE at high current rates where this material outperformed a bi-ionic salt-doped GCE that exhibited even greater ac conductivity.

5. Towards solid-state, multilayer, thin-film batteries

Meeting the challenge of constructing a solid-state battery that can deliver high current involves not only improving the intrinsic transport properties of the electrode and electrolyte materials, but also reducing the diffusion lengths across the cell. Regarding the latter, there are significant benefits to a multilayer, thin-film geometry: namely, raising the fraction of active material, particularly in the cathode where the addition of binder and conductivity enhancer robs capacity, while simplifying the construction of the battery. Cycle-test data from Li/BCE/VO_x cells consisting of a metallic lithium anode, a solid polymer electrolyte of POEM-*b*-poly(butyl methacrylate) doped with $LiCF_3SO_3$ at [EO]:Li = 20:1, and a fully dense cathode of vanadium oxide provide evidence of the fact that at intermediate drain rates (*C*/2), the performance of the solid-state device is comparable to that of a cell containing the conventional liquid electrolyte [7]. In addition, as current density rises, the observed loss of capacity is comparable for liquid and solid prototype cells, which we take to be indicative of transport limitations in the electrodes or at the electrode–electrolyte interfaces. In other words, there is no performance penalty associated with deployment of the solid polymer electrolyte.

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