

Block Copolymer Electrolytic Membranes for All Solid-state Rechargeable Lithium Batteries

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For nearly 20 years, poly(ethylene oxide)-based materials have been researched for use as electrolytes in solid-state rechargeable lithium batteries. Technical obstacles to commercial viability derive from the inability to satisfy simultaneously the electrical and mechanical performance requirements -- high ionic conductivity along with resistance to flow. Here we report the synthesis of poly(lauryl methacrylate)-*b*-poly(oligo(oxyethylene) methacrylate) block copolymer electrolytes in which *both* components have glass-transition temperatures well below room temperature. Microphase separation of the polymer blocks imparts the dimensional stability necessary for thin-film, solid-state battery applications. Electrolytes prepared with these materials display conductivities near 10^{-5} S/cm and are electrochemically stable over a very wide potential window. Cycle testing in prototype batteries demonstrate excellent cyclability and capacity retention.

The lithium solid polymer electrolyte (SPE) battery is arguably the most attractive technology for rechargeable electric power sources, boasting the highest predicted energy density, the fewest environmental, safety and health hazards, low projected materials and processing costs, and greatest freedom in battery configuration. Poly(ethylene oxide) (PEO)-based materials are favored candidates for polymer electrolytes.¹ Although PEO-salt complexes are highly conductive at elevated temperatures ($>10^{-4}$ S cm^{-1} at 70°C), their conductivities drop precipitously at temperatures below the melting point ($T_m = 65^\circ\text{C}$ for PEO). Common strategies to improve conductivity involve modifying the molecular architecture of PEO to suppress crystallization.² While such approaches have resulted in materials whose room-temperature conductivity exceeds 10^{-5} S cm^{-1} , their liquid-like nature typically requires a separator or supporting matrix to allow them to be deployed in a battery configuration. Gel polymer electrolytes combine high ionic conductivity with dimensional stability by infusing a liquid electrolyte into a nonconducting polymer network.^{3,4} However, these systems require suitable packaging of the volatile organics.

Block copolymers offer a novel means to achieve both high ionic conductivity and dimensional stability. These materials consist of two chemically dissimilar polymers covalently bonded end-to-end. At low temperatures or in the absence of solvent, a net repulsion between the polymer blocks induces their local segregation into periodically spaced nanoscale domains. This "microphase separation" event, analogous to crystallization, confers solid-like mechanical properties to the material at macroscopic scales, *even when both polymer blocks are above their respective glass transition temperatures, T_g* .^{5,6} At local scales, however, when $T > T_g$ the mobility

of the polymer chains remains high, even comparable to that in the disordered state.⁷ By choosing an amorphous PEO-based polymer as one block component, continuous ion conducting pathways can be formed in the material upon microphase separation.

For this study, diblock copolymers consisting of a poly(lauryl methacrylate) (PLMA) block ($T_g \sim -40^\circ\text{C}$) and a poly(oligo(oxyethylene) methacrylate) (POEM) block ($T_g \sim -65^\circ\text{C}$) were prepared. POEM employs a PEO side chain with a length of approximately 9 [EO] units, sufficiently low that crystallization does not occur.⁸ The block copolymers were anionically synthesized at -78°C by the sequential addition of lauryl methacrylate (Aldrich) and OEM macromonomer (Polysciences) to a diphenylmethyl potassium initiator in tetrahydrofuran. Upon termination of the reaction with degassed methanol, the copolymer solution was concentrated on a rotary evaporator, precipitated in hexane, and finally centrifuged to isolate the colorless polymer. For comparison purposes, POEM homopolymer was also anionically synthesized following a similar procedure. Molecular weights and compositional characteristics of the polymers are given in Table 1.

Rheological characterization of this system was performed using a Rheometrics ARES rheometer with a parallel plate fixture. The polymer was pressed to a gap width below 1 mm and a stable normal force of approximately 1000 g. The complex shear modulus, $G = G' + iG''$, was then measured as a function of frequency by dynamically shearing the polymer at a fixed strain of 1.5% over the frequency range 0.1 to 250 rad s^{-1} at temperatures from 25°C to 90°C .

Table 1. Molecular weight characteristics of synthesized POEM-based polymers.

	Composition (v:v)	Molecular weight (g/mol)	Polydispersity (M_w/M_n)
PLMA- <i>b</i> -POEM	47:53	64,700	1.1
PLMA- <i>b</i> -POEM	32:68	77,800	1.2
PLMA- <i>b</i> -POEM	23:77	62,900	1.2
POEM	—	100,000	1.3

The rheological behavior of block copolymer varies dramatically depending on whether the material resides in the ordered or disordered state. In the PLMA-*b*-POEM block copolymers, the storage modulus reaches a plateau value at low frequencies while the loss modulus assumes a limiting power law in which $G'' \sim \omega^{0.5}$. This low-frequency scaling behavior is characteristic of a microphase-separated system,⁵ and verifies its solid-like nature. Even after blending with significant amounts (23 wt%) of poly(ethylene glycol) dimethyl ether (PEGDME, Polysciences, $M=430 \text{ g mol}^{-1}$), the low-frequency scaling behavior is preserved, indicating that these short PEO chains stay confined to the POEM domains of the copolymer morphology. The formation of nanoscale domains was further verified by direct imaging with transmission electron microscopy. By contrast, the POEM homopolymer exhibits the low frequency scaling behavior $G'' \sim \omega$, indicative of a polymer in its molten state.

Conductivity measurements were performed on the POEM homopolymer and the PLMA-*b*-POEM block copolymers at fixed salt concentration $[\text{EO}]:\text{Li}^+ = 20:1$. Specimens for

conductivity measurements were initially dried in a vacuum oven at 70°C for 24 hours. LiCF_3SO_3 (lithium triflate) was dried *in vacuo* at 130°C for 24 hours. The materials were then transferred to an inert atmosphere, dissolved in dry THF, and solution cast on a glass die. The polymer/salt complex was then annealed *in vacuo* for 48 hours at 70°C. Under dry nitrogen, the polymer electrolyte was loaded between a pair of blocking electrodes made of type 316 stainless steel, pressed to a thickness of 250 μm , and annealed *in situ* at 70°C for 24 hours. Over the temperature interval spanning -20°C to 90°C electrical conductivity was measured by impedance spectroscopy using a Solartron 1260 Impedance Gain/Phase Analyzer.

Figure 1 illustrates that at room temperature the doped 32:68 PLMA-*b*-POEM block copolymer displays ionic conductivities similar to that of pure POEM. As expected, increasing the POEM content of the copolymer had the effect of increasing conductivity. Significantly higher conductivities were achieved by blending the block copolymer with 23 wt% PEGDME, resulting in σ values exceeding $10^{-5} \text{ S cm}^{-1}$ at room temperature.

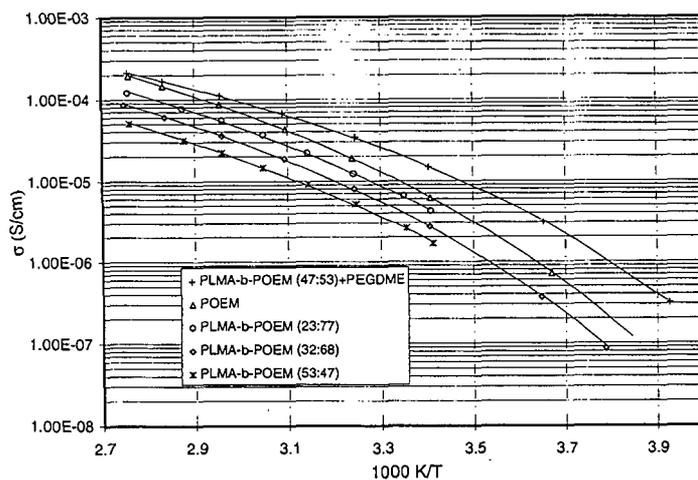


Figure 1. Compositional dependence of conductivity in PLMA-*b*-POEM diblock copolymers doped with LiCF_3SO_3 ([EO]: Li^+ = 20:1).

Cyclic voltammetry was performed on a block copolymer electrolyte (BCE) composed of 87 wt% 32:68 PLMA-*b*-POEM and 23 wt% PEGDME at a salt concentration of [EO]: LiCF_3SO_3 = 20:1 to investigate the range of electrochemical stability of the material. Films were prepared under an inert atmosphere by casting the BCE onto lithium foil from dry THF solution. The resulting films were placed under vacuum at room temperature overnight to remove excess solvent. The BCE was sandwiched between a counter electrode of lithium and a working electrode of aluminum, with a film thickness of approximately 150 μm . A lithium reference electrode was extruded into the cell through the side and positioned near the working electrode. Using a 1286 Solartron Electrochemical Interface, potential was scanned from +2.0 to +5.0 V vs. Li/Li^+ at a sweep rate of 0.5 mV s^{-1} . Current levels below 0.6 $\mu\text{A cm}^{-2}$ were measured between

2.0 and 5.0 V, indicating that the material is electrochemically stable over this voltage interval, which brackets that used in commercial lithium-ion batteries.

The composite cathode of the solid-state battery was prepared by casting a suspension of a mixture of $\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2$ (45 wt%), carbon black (7 wt%), graphite (6 wt%), and BCE (42%) in dry THF solution onto an Al foil heated to 60°C. Evaporation of the THF produced a cathode film ~150 μm in thickness. The resulting cathode film was placed under vacuum for 48 hours at 60°C to remove any moisture present. This material was cut into square electrodes measuring 1 cm on a side. The $\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2$ powder, which serves as the intercalation compound in the cathode, was produced by co-precipitation of hydroxides followed by firing in air at 945°C. Details of oxide synthesis and characterization are published elsewhere¹². The $\text{Li}/\text{BCE}/\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2$ solid state battery was then fabricated by laminating lithium metal, BCE, and the composite cathode film containing $\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2$ together in an argon-filled glove box. Cycle testing was conducted between 2.0 and 4.4 V with a MACCOR Series 4000 Automated Test System at a current density of 0.05 mA cm^{-2} .

Room temperature cycle testing of the $\text{Li}/\text{BCE}/\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2\text{-C-BCE}$ cell is shown in figure 2. Fig. 2(a) shows the first cycle which begins with lithium removal from $\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2$ over the voltage range spanning 3.0 to 4.4 V. A single charging plateau at ~3.6 V is observed, and the initial charging capacity was found to be 136 mAh/g . The first discharge exhibited a capacity of 108 mAh/g and featured the emergence of two voltage steps, one at ~4.0 V and another at ~3.0 V, indicating lithium intercalation at two distinct sites. This behavior is characteristic of the spinel phase $\text{Li}_x\text{Mn}_2\text{O}_4$ for which it is reported that the 3.0 V plateau corresponds to lithium insertion into octahedral sites and the 4.0 V plateau corresponds to lithium

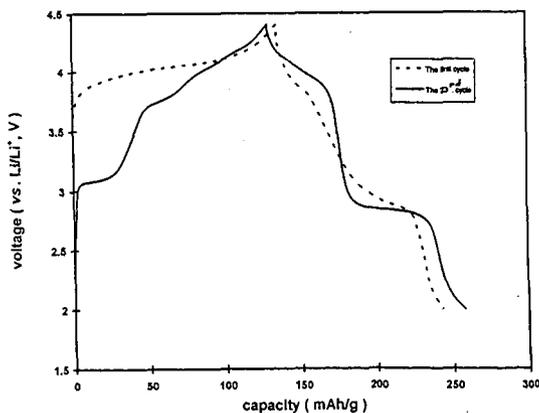


Figure 2. Charge/discharge cycling of the $\text{LiAl}_{0.25}\text{Mn}_{0.75}\text{O}_2/\text{BCE}/\text{Li}$ cell with a current density of 0.05 mA/cm^2 cycled between 2.0 and 4.4 V. (a) first cycle; (b) 23rd cycle.

insertion into tetrahedral sites.¹³ After further cycling, the voltage steps became more distinct as can be seen in Fig. 2(b), which shows the 23rd cycle. After ~12 cycles, the intercalation oxide reached its optimal capacity of ~125 mAh/g . This result indicates that the cell has demonstrated

good cyclability when cycled over both 4.0 V and 3.0 V plateaus. Further discussion of the oxide characteristics is reported in a separate manuscript.¹²

Although several groups had previously investigated PEO-based block copolymers as candidate electrolytes for rechargeable Li batteries,⁹⁻¹¹ the conductivities and temperature window of operation of those materials were not optimized because one block component either crystallized or underwent a glass transition above room temperature. Here we demonstrate that by joining two non-crystallizing polymers with T_g s well below 0°C, a dimensionally stable electrolyte can be prepared with conductivities near that of the POEM homopolymer. We expect that moving to block components with higher room temperature conductivities and/or lower glass transitions should further improve both the ambient temperature performance and temperature window of operation.

Acknowledgments

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