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Self-doped block copolymer electrolytes for solid-state, rechargeable lithium batteries

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Abstract

In an attempt to raise the transference number of Li^+ to nearly unity in a solid polymer electrolyte, block copolymer materials have been prepared in which the counterions are tethered to the polymer backbone. This immobilizes the “anion” and, in effect, renders the material a single-ion conductor. For such so-called self-doped block copolymer electrolytes (SDBCEs) Li^+ transference numbers of ~ 0.9 have been measured. In parallel, these materials possess significant ionic conductivity ($\sim 10^{-5} \text{ S cm}^{-1}$ at 35°C). Cyclic voltammetry has shown the SDBCE to be immune to electrochemical breakdown at voltages exceeding 5 V. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

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. In this laboratory, it has been shown that this challenge can be met with a class of polymers known as block copolymers [1]. Block copolymers consist of two chemically dissimilar polymers covalently bonded end-to-end. Under appropriate conditions, a net repulsion between the polymer blocks induces their local segregation, or “microphase separation”, into periodically-spaced nanoscale domains. By choosing a lithium salt-solvating polymer as one block component, continuous ion-conducting pathways can be formed. The nanoscale morphology confers solid-like mechanical properties to the material at macroscopic scales even if both polymer blocks reside well above their respective glass transition temperatures [2–4]. By choosing two low T_g , non-crystallizing blocks, films with mechanical properties similar to those of a crosslinked rubber can be obtained without sacrificing the high local chain mobility required for Li^+ conductivity. Because

microphase separation is thermodynamically reversible with the addition of a common solvent, block copolymers can be readily processed by conventional polymer coating methods.

Proof of this concept has been demonstrated here in our laboratory with the copolymer of poly(oligooxyethylene methacrylate)-*b*-poly(laurel methacrylate) ((POEM)-*b*-(PLMA)) which proved to be mechanically stable but exhibited nearly the same ionic conductivity as the molten POEM homopolymer [1]. With this copolymer serving as both the supporting electrolyte and cathode binder thin-film, solid-state, rechargeable lithium batteries of the type Li/BCE/LiMnO₂ have been constructed. These cells have been multiply cycled at room temperature. Additionally, to demonstrate the utility of the BCE at sub-ambient temperatures, Li/BCE/Al cells have been repeatedly cycled at temperatures as low as -20°C [1]. Although these first-generation BCEs possess properties not previously exhibited by solid polymer electrolytes at room temperature, a number of materials issues still need to be addressed to meet the demanding requirements of a commercially viable solid-state rechargeable battery.

The goal of the present work was to raise the transference number of Li^+ to nearly unity by tailoring molecular architecture. The strategy consisted of attempting to immobilize the counterions by tethering them to the polymer backbone. In this way, Li^+ is introduced not in the form of a soluble salt, e.g. LiCF_3SO_3 , but rather as part of the block copolymer. Thus, in a sense, these systems can be viewed as

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self-doped; accordingly, we have dubbed them self-doped block copolymer electrolytes (SDBCEs).

Preliminary work had identified a class of organic anions with very low charge density that might be suitable for this purpose. Upon copolymer ordering, these attached anions become sequestered within the secondary block nanodomains, while Li^+ ions are localized to the ionically conducting block nanodomains. Binding the counterions should reduce their mobility substantially and result in a dramatic rise in t_{Li^+} , the Li^+ transport number. In principle, it should be possible to raise the value of t_{Li^+} in this manner to 1, thereby making the material effectively a single-ion conductor.

2. Advantages of single-ion conduction

In a battery, single-ion conduction via Li^+ offers performance advantages. First, because in the SDBCE “anion” mobility is severely limited, this prevents salt depletion from occurring in the bulk electrolyte and thereby reduces the attendant undesirable concentration polarization. This should enable the passage of larger currents through the cell.

The SDBCE offers other advantages. For example, a higher value of t_{Li^+} translates into a lower thermal load as a greater fraction of the total cell current is borne by Li^+ ions which participate in faradaic processes at the two electrodes. Furthermore, an increase in t_{Li^+} results in a decrease in the amount of unwanted joule heating of the cell per unit of current, which lessens the chances of thermal runaway. Hence, the SDBCE would enable a safer, more efficient battery capable of operating at higher currents. Moreover, the salts presently used to dope conventional polymer electrolytes are subject to electrochemical breakdown at moderate to high voltages. This limit of electrochemical stability of the salt constrains the accessible voltage range and, consequently, the capacity of lithium polymer batteries. The SDBCE is expected to exhibit improved electrochemical stability and to confer higher energy storage capacity to the battery.

3. Experimental

Block copolymer electrolytes with anions incorporated into the secondary block can be prepared via anionic synthesis methods, e.g. a living synthesis starting with the secondary block, poly(*tert*-butyl methacrylate), or a random acrylate copolymer containing *tert*-butyl methacrylate. The monomer for the ionically conducting block of the copolymer, namely methoxy (poly(ethylene glycol)) methacrylate, is then added to the reactor and allowed to polymerize. Upon completion of the growth of this block the synthesis is terminated with methanol or another appropriate reagent. The *tert*-butyl methacrylate segments in the secondary block can be easily and quantitatively converted into a methacrylic

acid by hydrolysis or *trans*-alcoholysis. Neutralization of this hydrolyzed block copolymer can be accomplished with appropriate metal bases such as lithium methoxide (LiOCH_3).

Following the general polymerization scheme described above, we have prepared a SDBCE structure of poly(lauryl methacrylate-*r*-lithium methacrylate)-*b*-poly(oligooxyethylene methacrylate), P(LMA-*r*-LiMA)-*b*-POEM. The molar ratio of the monomer components was 1:1:1 LMA:LiMA:OEM, giving an effective $[\text{EO}]:[\text{Li}^+]$ ratio of 9:1. Other SDBCE compositions were also prepared as discussed below.

Electrical conductivity measurements were made by impedance spectroscopy using a Solartron 1260 gain/phase analyzer (Solartron Instruments, Beaver Falls, PA) controlled by a personal computer running ZView/ZPlot software (Scribner Associates, Southern Pines, NC). The SDBCE was placed between a pair of blocking electrodes made of 316 stainless steel, pressed to a thickness of 250 μm , and thermostated under continuous argon flow. Impedance measurements were made over the frequency range spanning 10 Hz to 1 MHz.

Li^+ transference number measurements were made in a symmetric cell fitted with faradaically active lithium electrodes (Li/SDBCE/Li). Stepped-potential chronoamperometry was performed with a Solartron 1286 potentiostat (Solartron Instruments, Beaver Falls, PA) controlled by personal computer running Corrware (Scribner Associates, Southern Pines, NC). The voltage step was 55 mV. The same instrumentation was used for electrochemical characterization of the material by cyclic voltammetry which was conducted in a three-electrode cell fitted with a platinum working electrode and lithium reference and counter electrodes. The sweep rate was 0.5 mV s^{-1} .

4. Results and discussion

Fig. 1 compares the electrical properties of SDBCEs that incorporate LiMA at different sites. In the material designated SDB1, LiMA is added to PLMA, i.e. the non-conducting block, while in the material designated SDB3, LiMA is added to POEM, i.e. the conducting block. More information about these materials is reported in Table 1. Comparison of the traces for SDB1 and SDB3 in Fig. 1 shows that, all other things being equal, incorporating LiMA into the non-conducting block produces the material with higher electrical conductivity. Furthermore, as shown previously with conventional, salt-doped materials, the addition of PEGDME raises the absolute conductivity [1].

Transference number measurements on SDB2+PEGDME (23 wt.%) yielded a value of ~ 0.9 — not unity, but considerably greater than the value of 0.4–0.5 measured in salt-doped BCEs. Fig. 2 shows the cyclic voltammogram of SDB2 + PEGDME (23 wt.%) between +2.0 and +6.0 V versus lithium. In contrast to the behavior of salt-doped

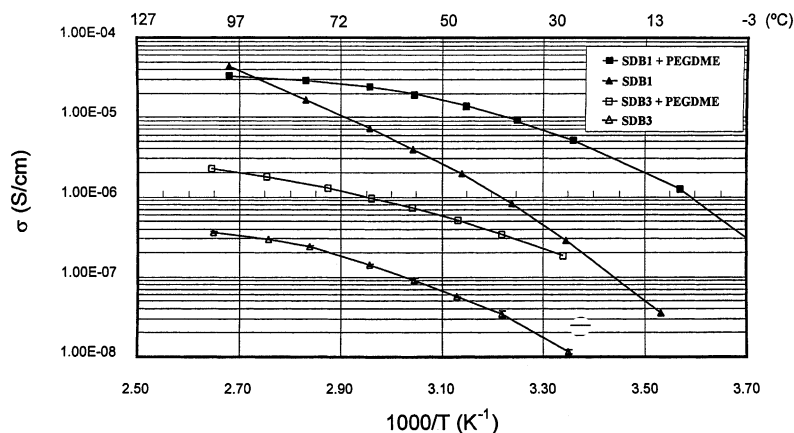


Fig. 1. Comparison of conductivity in P(LMA-*r*-LiMA)-*b*-POEM and P(OEM-*b*-LiMA)-*b*-PLMA electrolytes, respectively, designated as SDB1 and SDB3. Doping ratios of both materials is 9:1 neat and 13:1 with PEGOME added.

Table 1

Lithium ion density and doping ratio of the self-doped electrolyte materials

	Li ⁺ density (normalized)	[EO]:[Li ⁺]
SDB1 (1:1:1)	1.00	9:1
SDB1 (1:1:1) + PEGDME	0.769	13:1
SDB2 (3:1:2)	0.454	18:1
SDB2 (3:1:2) + PEGDME	0.350	27:1

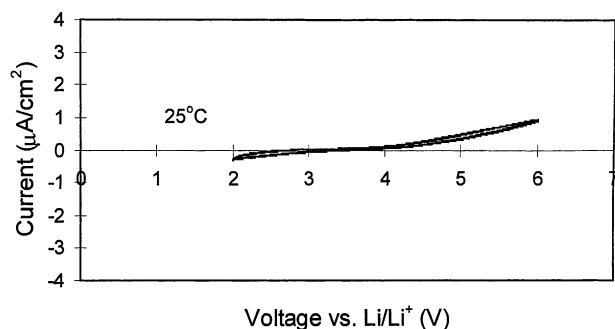


Fig. 2. Cyclic voltammetry on P(LMA-*r*-LiMA)-*b*-POEM(3:1:2) + PEGDME with [EO]:[Li⁺] = 27:1. Lithium counter and reference electrode, platinum working electrode. Sweep rate = 0.5 mV s⁻¹. Two cycles shown.

BCEs, no peak is visible in the vicinity of +4.3 V which means that the useful voltage range of the SDBCE is much greater than that of conventional salt-doped electrolytes. Hence, we see no reason why the SDBCE cannot be subjected to voltages exceeding 5 V.

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