



New Generation of Ordered Polymer Electrolytes for Lithium Batteries

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In poly(ethylene oxide)-based solid electrolytes, ionic conduction can occur by cations moving inside the helix (along the helix axis) and by anions moving on its envelope. This particular mode of ion transport can be enhanced by alignment of the polymeric structural units. We describe a procedure for orienting the helices in the perpendicular direction, the result of which is a one-order-of-magnitude increase in polymer electrolyte (PE) conductivity and a similar decrease in PE/electrode interphase resistance. This procedure could also be of importance in the orientation of polymers in the nanoscale for various applications.
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Manipulation of large molecules like polymers and the ability to position them in the desired orientation is of great importance in various fields, including thin-film-based devices, microelectromechanical systems, and nanotechnology. Thin-layer technology includes liquid crystal displays (LCDs), sensors, electrochromic displays, advanced high-energy-density batteries, and fuel cells. In these devices, a thin (0.02–0.1 mm) polymer electrolyte (PE) is sandwiched between two electrodes. PE, are generally semicrystalline materials, most commonly derived from the archetypal helical poly(ethylene oxide) (PEO). The common preparation process for the PEO-based PEs is that of casting from solution. This leads to a preferential planar orientation of helices in the parallel-to-the-casting plane, denoted as XY. As a result, the longitudinal conductivity is much higher than that in the perpendicular Z direction. However, in most practical applications, especially in solid thin-film batteries, the conductivity of PE films in the Z direction is crucial. Another factor contributing to high internal resistance (and thus to low power) in lithium-PE batteries is the too-high electrode/PE interphase resistance. To complete the conduction path, ions must at some time jump from helix to helix through the helix “envelope.” This is a slow process that adds yet another resistance to the system. We denote this resistor as R_{inter} or R_{GB} (grain boundaries).

Until now, to get maximum conductivity, the strategy has been to reach the maximum amorphicity of the polymer and the lowest glass-transition temperature (T_g).^{1–3} Molecular-level approaches employed to effectively suppress crystallinity in PEO have included architectural modifications such as branched polyethoxy systems,^{4,5} linear random copolyethers,⁶ and comb copolymers.^{7–9} Despite strenuous efforts over some 20 years involving the preparation of highly amorphous polymer electrolytes with low T_g , the maximum conductivity of such electrolytes remains around 10^{-5} S/cm at room temperature.¹⁰ Theoretical models^{11–13} have been proposed to explain the mechanism responsible for ionic conductivity in these systems, and molecular dynamic (MD) and Monte Carlo (MC) simulations have been carried out for PEO:salt complexes.^{14–18}

Recently, we found a way^{19–24} to increase the ionic conduction of PEs in one direction by a longitudinal alignment of the helices with the use of a stretching procedure. Stretching-induced longitudinal dc-conductivity enhancement, observed in crystalline Li-P(EO)_n and Li triflate-P(EO)₂₀ electrolytes, was about 5- to 40-fold and reached 0.1 mS/cm at room temperature, one order of magnitude higher than the best reported value. Micro- and macrostructural alignment of polymer segments and chains, caused by stretching, was detected by various techniques, including scanning-electron and

atomic-force microscopies (SEM,AFM), IR, and NMR spectroscopies, and X-ray diffraction (XRD). Fourier transform infrared spectrometry (FTIR) tests showed that stretched polymer electrolyte adopts an aligned helical conformation, in which the CH₂ groups all face outward (favoring CH₂ wagging vibrations) and the atoms of oxygen are directed inward, lining the tunnel cavity, and thus favoring cation transport.^{19–25}

Recognition that aligned crystalline PEO chains are energetically more favorable for fast ion transport than are tangled chains^{19–27} prompted our attempts to achieve orientation of the PEO helices perpendicular to the plane of the film, and doing so without mechanical means (*i.e.*, stretching).

In this study we have examined the possibility of producing a rational design of novel polymer materials with extraordinary electrical properties on the basis of structural ordering. The effect of PE casting under a magnetic field and incorporation of diamagnetic and paramagnetic nanosize inorganic fillers is addressed. Suzuki and co-workers demonstrated that due to anisotropic diamagnetic susceptibility highly textured alumina particles can be obtained by application of a strong magnetic field.²⁸ The effect of nanoparticles ordering in magnetic field is even much stronger for iron oxides.²⁹ Although the presence of these fillers complicates the interpretation of the orientation effects, the nanocomposites were included in this study because of the generally high level of interest in these materials, and because of our conjecture that magnetic effects on the particles themselves and the particle surface/polymer interfaces would also yield interesting results.

Experimental

The electrolytes were prepared from PEO (Aldrich, average molar mass 5×10^6) as described elsewhere.²² All handling of PEs took place under an argon atmosphere in a VAC glove box with water content <10 ppm. Li:P(EO)_n polymer electrolytes with $n = 3, 7,$ and 20 were cast under a strong (0.8 T) magnetic field, created by samarium-cobalt permanent magnets in the standard dipole arrangement in a home-made device. Two different field configurations were employed. The first was a relatively homogeneous field with the cast film sandwiched between the magnetic pole pieces. Alternatively, samples were prepared under a highly inhomogeneous field that was produced by fixing a conically tapered iron shim to one of the magnet poles. Samples prepared in the latter manner are referred to as gradient magnetic field (GMF) samples.

The field was continuously applied during the entire stage of solvent evaporation until the final formation of a 100 μm thick film. Two types of nanosize fillers, diamagnetic alumina and ferrimagnetic iron oxide, were tested as additives to promote reorientation of the PE chains. It is clear that the strength of the applied magnetic field must be adapted to the type and concentration of the nanosize filler to avoid phase separation and to obtain the highest degree of

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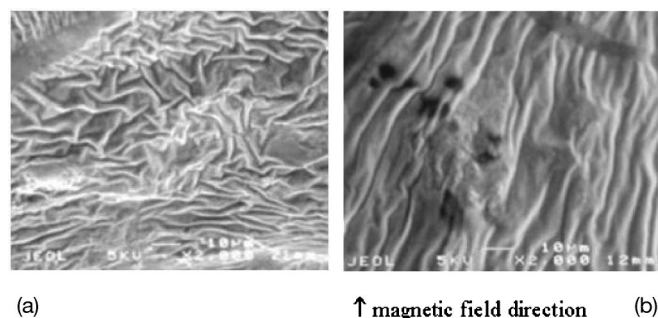


Figure 1. SEM micrographs of the cross section of the LiI (PEO)₃ 9% (v/v) Fe₂O₃ PE (a) typically cast and (b) cast under a magnetic field gradient.

orthogonal orientation of chains. Here we report initial results obtained under nonoptimized conditions.

Ferrimagnetic particles (MPs) were prepared by treating an aqueous solution of Fe²⁺ and Fe³⁺ (1:2 ratio) with 32% ammonia solution at room temperature.³⁰ XRD tests showed that the Fe₂O₃ MPs are of about 8 nm size with a lattice parameter of 8.336 Å, close to literature data. The electronic conductivity of the composite PE with 9% Fe₂O₃ (v/v) was negligible (10⁻¹⁰ S/cm).

The ac conductivity in the perpendicular direction was measured *ex situ* with the use of a computer-interfaced Solartron 1260 frequency-response analyzer over the frequency range 1 MHz to 0.1 Hz.²²⁻²⁴ The polymer electrolyte sample of 1.8 cm² area was placed between two lithium electrodes and hermetically sealed in a 2032 coin cell. A typical complex impedance plot of a symmetrical Li/PE/Li cell is represented by two partially depressed semicircles (where *X* and *Y* axes represent real and imaginary resistances, respectively, plot not shown here). The arc with *f*_{max} around 1 kHz is associated with the resistance of the passivating film [solid electrolyte interphase (SEI)] generated on the lithium electrode in contact with the electrolyte. The introduction of a second time constant in the equivalent circuit (high-frequency arc with *f*_{max} in the range of 0.1 to 1 MHz, and capacitance from 50 to 200 pF/cm²) is attributed to the grain-boundary resistance (*R*_{GB}), which includes contributions of hindered helix-to-helix jump. The bulk ionic conductivity of polymer electrolytes (*σ*_{bulk}) associated with intrachain (or intrahelix) ion mobility is calculated from the high-frequency intercept of this arc with the real-axis (*R*_{bulk}). The accuracy of the calculation of bulk and grain boundary resistances (*R*_{bulk}, *R*_{GB}) is estimated to be about ±10%. Transference-number measurements were carried out according to a procedure described by Appetecchi and co-workers.³¹ A JSM 6300 scanning microscope (JEOL Co.) equipped with a Link elemental analyzer and a silicon detector was used for the study of surface morphology.⁷ Li-NMR measurements were conducted on a Chemagnetics CMX300 spectrometer operating at a ⁷Li resonance frequency of 117.0 MHz. Spectra were acquired by single-pulse excitations of 2 μs duration. Measurements were performed on typically cast PEs and GMF films with the NMR static field both parallel and perpendicular to the gradient (and field) applied during film formation.

Results and Discussion

SEM micrographs of the cross section of the LiI-P(EO)₃ 9% v/v Fe₂O₃ polymer electrolyte are shown in Fig. 1. As was found previously,¹⁹⁻²⁵ there is some planar orientation of helices in as-cast polymer electrolytes. Under the magnetic field gradient (GMF) directed perpendicularly to the plane of the cast film a considerable number of the bundles of helices are aligned in the *Z* direction. The magnetic torques and forces (the latter due to the gradient) that produce the orientation are believed to arise primarily from the diamagnetic susceptibility of the polymer chains. Although the energies associated with reorientation through torques and translation

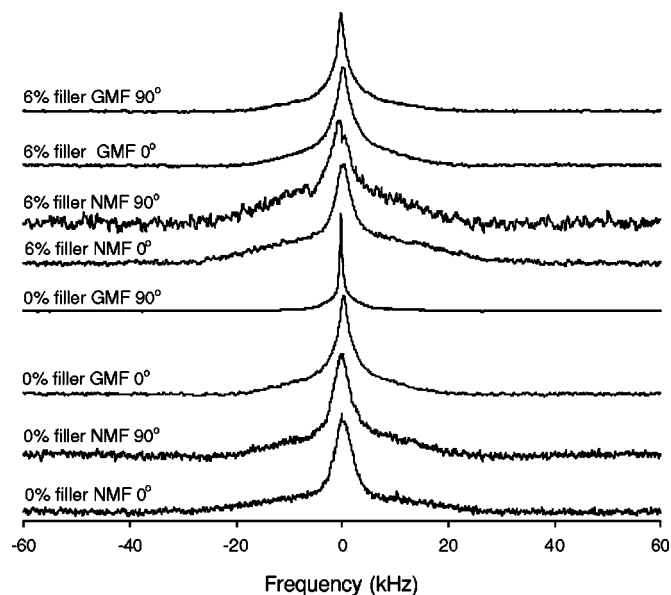


Figure 2. Wide-line ⁷Li NMR spectra of the LiI (PEO)₃ at 22°C.

through forces are expected to be small compared to *kT*, it is plausible that cooperative effects between parallel polymer chains can be sufficient to produce the observed results. Additional forces can also be transmitted from alignment effects on the diamagnetic or paramagnetic filler particles in close contact with the chains. It is expected that nanosize paramagnetic fillers will facilitate the reorientation. The effect of the field strength, gradient, and content of the fillers is under investigation.

Figure 2 shows several wide-line ⁷Li NMR spectra of the LiI:P(EO)₃ complex obtained at 22°C. The samples were either filler-free or contained 6% v/v alumina and were prepared either in a magnetic field gradient or under no field. Spectra are shown for both in-plane and perpendicular-to-plane orientations, with all eight possibilities included in Fig. 2. In most cases, a “rigid” spin-3/2 spectrum is observed, in which both the central and distributed satellite transitions are present, consistent with the behavior of other PEO:Li salt complexes below their crystalline melting points.³² In both filler-free and filler-containing samples, the effect of the GMF results in markedly narrower NMR spectra, suggesting enhanced Li⁺ mobility. The largest anisotropy in the spectra (the difference between the 0 and 90° orientations) is observed for the filler-free materials prepared in GMF. It was expected that orientation effects would produce more highly resolved quadrupole satellite transitions than were observed. The most likely explanation for the satellite distribution in some of the spectra is that there is a corresponding distribution in degree of orientation in the samples prepared in the highly nonuniform magnetic field.

It is well established that ion transport in PEO-based polymer electrolytes is governed by a complex interplay of several processes, of which the two most important are dealt with here. One of them is associated with ion transport along directed molecular structures like the helical chains in PEO. This is denoted as bulk ionic conductivity (*σ*_{bulk}). The other, strongly dependent on the host’s segmental motions, is controlled by ion hopping between such structures and is denoted as grain-boundary conductivity (*σ*_{GB}). Figure 3 shows the Arrhenius plots of the bulk and grain-boundary conductivities of the symmetrical Li cells with concentrated 1:3 LiI:P(EO) PEs. It is obvious that, while both ion-conduction processes are influenced by casting under a magnetic field, the facilitation of interchain hopping by a GMF is more pronounced. At 45°C for instance, the *σ*_{GB} increases by a factor of 14, while *σ*_{bulk} enhancement induced by magnetic-field casting is only sevenfold. Similar behavior is seen for the 1:7 PE, however here the effect of the magnetic field is smaller

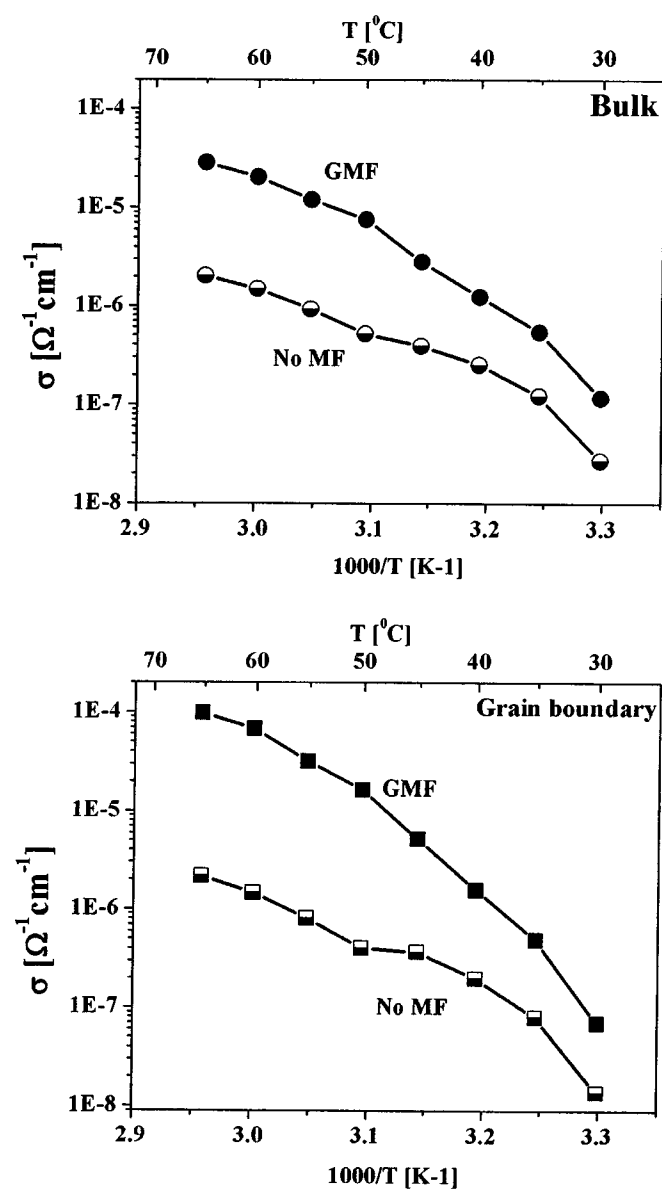


Figure 3. Arrhenius plots of the LiI:P(EO)₃ polymer electrolyte cast without field and under gradient magnetic field.

(factor of 5). The influence of the magnetic field was extremely strong in concentrated 1:3 composite polymer electrolytes containing 9% diamagnetic alumina. This conclusion was drawn from the observation of a decrease by more than two orders of magnitude in the total impedance of a symmetrical Li/PE cell. A gradient magnetic field enhances ion conduction more strongly than does a homogeneous field. The bulk conductivity of composite polymer electrolytes cast under a gradient magnetic field was about one order of magnitude higher than σ_{bulk} of PEs cast under a homogeneous field. Here also the σ_{GB} rises more drastically than does σ_{bulk} . The positive effect of the gradient magnetic field does not disappear on heating of 1:3 and 1:7 concentrated composite PEs up to 65°C. In addition, samples preheated to 95°C and cooled to room temperature, showed the same difference between the total impedance of a Li cell composed of PEs cast under field and those cast under no field. The greatest effect on the enhancement of σ_{GB} at room temperature (factor of 15) was detected when the magnetic field was applied to LiI:P(EO)₂₀ 9% v/v Fe₂O₃ PEs. Under these conditions, the improvement in σ_{bulk} was sixfold. Above 45°C the effect of the mag-

netic field decreased and vanished at a temperature close to T_m of PEO. The addition of nanosize iron oxide to the 1:20 PE cast without field did not significantly affect σ_{bulk} and σ_{GB} . Contrary to typically cast PEs, in all the PEs cast under a strong magnetic field, the σ_{GB} at near ambient temperature was comparable, or even higher than σ_{bulk} . This unambiguously indicates that PE ordering orthogonal to the film plane (see Fig. 1) enhances interchain ion hopping. The apparent activation energy (E_a) of interchain conduction was higher than E_a of intrachain conduction for all the PEs under investigation; the energy values vary in the range of 100-210 J/mol and 80 to 120 J/mol, respectively. This difference increases by about 15-40% when PEs are cast under a magnetic field. In highly concentrated 1:3 polymer electrolytes, the gradient magnetic field increases both $E_{a(\text{bulk})}$ and $E_{a(\text{GB})}$. For 1:7 PEs, however, the reverse effect is observed. The addition of alumina lowers the absolute values of $E_{a(\text{bulk})}$ and $E_{a(\text{GB})}$ of PEs cast under a gradient field by about 20%.

Gadgourova *et al.*²⁶ showed that ion transport in crystalline polymer electrolytes is dominated by the cations, whereas both ions are generally mobile in the amorphous phase. We found that casting under a magnetic field increases the cation transference number t_+ from 0.2 to 0.4 in concentrated PEs and from 0.4 to 0.6 in 1:3 PEs with Al₂O₃. Increase of t_+ in PEs cast under a magnetic field is of great importance to battery applications and can be attributed to preferred cation helix-to-helix hopping.

A noteworthy observation, especially relevant to the subject of lithium-battery power, is the large (about 1-1.5 orders of magnitude) decrease in the Li/PE solid-electrolyte-interphase resistance (R_{SEI}) found for all the PEs cast under a magnetic field. In 1:20 PEs containing paramagnetic particles, the R_{SEI} at room temperature is lower by a factor of 6. The R_{SEI} falls even more markedly (12-fold) following the application of a magnetic field to this electrolyte (Fig. 4). In concentrated PEs the R_{SEI} decreases by a factor of 4 to 7. Above 60°C the effect of the magnetic field on R_{SEI} vanishes. This phenomenon can be explained by the preferential orientation of helices with their cross-sectional ring openings facing the lithium electrode. Li⁺-ion transfer inside the helix through its openings is much faster than that through the "walls," thus contributing to a fall in R_{SEI} .

So far, the conductivity enhancement induced by magnetic-field casting is not enough for practical lithium-battery applications. This is due to only a partial alignment of the helices in the perpendicular direction.

Work is in progress to determine the optimal conditions for obtaining alignment of most of the polymer chains in the desired direction. This way it is expected to get conductivity enhancement of at least a factor of 40 (as was achieved in the stretching tests²²). This will lead to bulk conductivity of over 0.1 mS/cm which is sufficient for lithium batteries and other applications.

Conclusions

The relationship between the alignment of polymer helices and improvement of ion conduction properties of polymer electrolytes has been determined by SEM, NMR spectroscopy, and electrochemical means. Solution casting and drying under applied magnetic field enhances both intra- and interchain ion mobility by about one order of magnitude. The magnetic field effect is even more pronounced in polymer electrolytes with incorporated diamagnetic and ferrimagnetic nanofillers. The lithium transference number increases from 0.2 to 0.6 in MF oriented PEs. The resistance of SEI decreases by more than one order of magnitude in the lithium cells comprising these MF oriented polymer electrolytes. We believe that the ability to create anisotropic shape-persistent, but flexible materials with preferred orientation is promising not only for getting higher power in lithium batteries but for many other nanoscale technological applications.

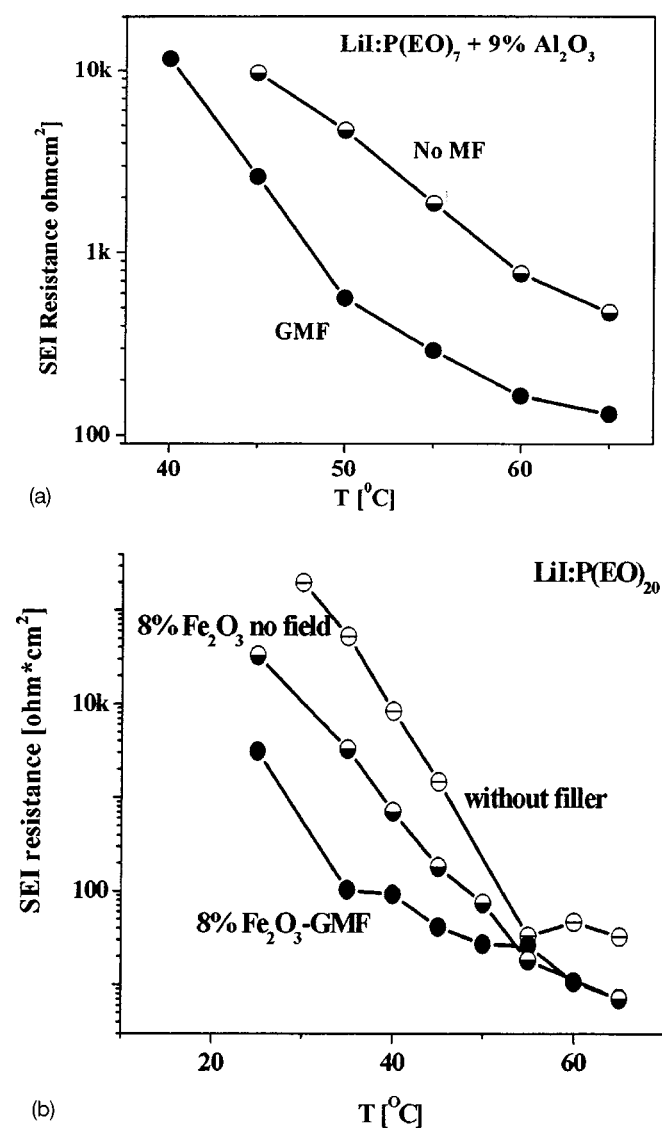


Figure 4. SEI vs. temperature plot of the Li/PE/Li cells with (a) LiI:P(EO)₇ 9% (v/v) Al₂O₃ and (b) LiI:P(EO)₂₀ 9% (v/v) Fe₂O₃ polymer electrolytes.

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