

New insights into structural and electrochemical properties of anisotropic polymer electrolytes

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Abstract

The inter-relationship between the orthogonal alignment of polymer helices and improvement of lithium-transport properties of polymer electrolytes has been determined by scanning electron microscopy, differential-scanning calorimetry and dielectric spectroscopy. It is suggested that ordering of the polymer electrolyte accompanied by increased conduction properties is achieved by mutual coordination of local dipole moments of the polar CH₂–CH₂–O units during casting under a magnetic field.

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1. Introduction

Since the discovery of ionic conductivity in polyethylene oxide more than two decades ago [1,2], ionically conducting polymers have been the focus of much fundamental and applied research. Such materials have proven to be useful for high-energy-density solid lithium rechargeable batteries and electrochromic devices. Aside from economically important issues, such as application in electric vehicles, portable communication systems and smart windows, ionically conducting polymers feature intriguing properties in terms of basic science as model materials for the investigation of conduction paths in semicrystalline, partially ordered systems. The subject of polymer electrolytes has been extensively covered by review papers and monographs [3–7]. The classical polymer electrolyte consists of organic macromolecules (usually polyether polymer) that are doped with inorganic salts. Poly(ethylene oxide) (PEO) is the most commonly employed polymer in lithium batteries because of the peculiar array in the (–CH₂–CH₂–O–)_n chain providing the ability to

solvate low-lattice-energy lithium salts. The incorporation of salts into the polymer inevitably reduces the freedom of polymer chain motion via binding interactions between the ether oxygens and cations. The anion in this case is dissociated from the cation and does not interact significantly with the chain. Its motion requires free volume between the polymer chains [7]. At high salt concentration, formation of ion pairs and aggregates was detected [3–8]. Ion transport in polymer electrolytes is a complex process that includes long-range ion motion, local motion of polymer segments and inter- and intra-chain ion transport between coordinating sites. The effective ionic conductivity depends mainly on the available coordination sites in the polymer and is influenced by the spacing between sequential coordination sites and by steric effects. In polymer electrolytes, the solvent-site positions appropriate for cation bonding vary with time. Therefore, the conductivity, which is coupled to the micro-Brownian motion of segments of the polymer chains above the glass- or melting-transition temperature, rises significantly with increased flexibility of the chains and rapid relaxation of the host polymer. A rule of thumb for the design of a polymer electrolyte has been to prevent crystallization and to reduce the glass-transition point of the host polymer [3–7].

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However, from the intra-helix location of cations proved by Shriver and Bruce [5], and possible ion motion along the helix suggested by Armand [2], we might reason that enhanced conductivity should come about as a result of permanent conducting pathways for the movement of ions. On this subject, we have recently demonstrated experimentally the preferential ion transport along the aligned helical axis in LiX–PEO polymer electrolytes, where X is an anion, such as iodide, trifluoromethanesulfonate, hexafluoroarsenate, bis(oxalato)borate and trifluoromethanesulfonimide [9–12]. Stretching-induced longitudinal-dc-conductivity enhancement, observed in crystalline LiI–P(EO)_n and Li triflate–P(EO)₂₀ electrolytes, was about 6- to 40-fold and reached 0.1 mS/cm at room temperature, one order of magnitude higher than the best reported value for amorphous polymer electrolytes. The latest publications [13–15] indicate the importance of organizing polymer chains while preserving chain dynamics.

Polymer crystals show very direction-dependent (anisotropic) properties. The configuration of a polymer is defined by the polymerisation method. Typically, solid polymer electrolytes are prepared by casting from solution; this causes preferential planar (XY) orientation of PEO helices and much higher longitudinal than orthogonal conductivity. It should be emphasized, however, that in most practical applications, especially in solid thin-film batteries, the conductivity of PE films in the perpendicular Z direction is crucial. A first approach is then to alter the structure of the polymer electrolyte in such a way as to promote the transition from parallel to perpendicular lamellae of PEO helices and to do so without mechanical means. An important conclusion from our recent study [16] was that casting and drying of LiI-based PEs under an applied magnetic field enhances both intra- and inter-chain ion mobility by about one order of magnitude in the direction perpendicular to the film plane. The magnetic-field effect is even more pronounced in polymer electrolytes with incorporated diamagnetic and ferrimagnetic nano-fillers.

The primary aim of this work has been to obtain an insight into the effect of the length of polymer chain, type of lithium salt and filler on the dielectric relaxation and structural properties of polymer electrolytes cast under magnetic fields of different strengths.

2. Experimental

The electrolytes were prepared from poly(ethylene oxide) (PEO) of 5×10^6 and 10^5 MW (Aldrich) with incorporation of different lithium salts by casting from acetonitrile solution on a teflon tray. All handling of PEs took place under an argon atmosphere in a VAC glove box with water content <10 ppm. LiX:P(EO)_n polymer electrolytes with $n = 3, 6, 7$ and 20 were cast under a homogeneous or gradient magnetic field of 0.1–0.3 T, created by samarium–cobalt permanent magnets in the standard “dipole” arrangement in a home-made device. The gradient magnetic field was produced by

fixing a conically tapered iron shim to one of the magnet poles. 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 nano-size fillers, diamagnetic alumina and ferrimagnetic iron oxide were tested as additives to promote reorientation of the PEs.

Ferrimagnetic particles (MPs) were prepared by treating an aqueous solution of Fe²⁺ and Fe³⁺ (1:2 ratio) with 32% ammonia solution at room temperature [16]. XRD tests showed that the Fe₂O₃ MPs are of about 8 nm size with a lattice parameter of 8.336 Å, close to literature value. The electronic conductivity of the composite PE with 9% Fe₂O₃ (v/v) was negligible (10^{-10} S/cm). Alternatively, 15–30 nm size anti-ferromagnetic Fe₂O₃ hematite was purchased from Nanos-structured and Amorphous Materials, Inc.

Wide-range temperature–frequency (1 MHz to 10 Hz) relaxation tests were performed with a broad-band dielectric spectrometer (Novocontrol BDS 80) with automatic temperature control in the range of –100 to 55 °C and –160 to 100 °C for pure PEO samples and LiI:P(EO)₃ polymer electrolytes, respectively. The measurement accuracy of both the dielectric permittivity and dielectric loss was about 3%. Inserting each of the samples and sealing the sample holder (the diameter of the electrodes was 6 mm) was carried out in a glove box. Three runs were conducted: the first was slow heating of the quenched film; the second was slow cooling and the third was heating of the slow-cooled sample. Measurements were performed in 5 °C steps.

The intra-chain (bulk) and inter-chain (grain-boundary) conductivity of polymer electrolyte and Li/PE interphase resistance (R_{SEI}) was extracted from the Nyquist plots obtained with the use of a computer-interfaced Solartron 1260 frequency-response analyzer over the frequency range 1 MHz to 0.1 Hz. The polymer electrolyte sample of 1.8 cm² area was placed between two lithium electrodes and hermetically sealed in a 2032 coin cell. The accuracy of the calculation of bulk- and grain-boundary resistances (R_{bulk} , R_{gb}) is estimated to be about ±10%.

The lithium ion transference number of polymer electrolytes was determined by a well established steady-state technique introduced by Bruce et al. [17]. The method is based on the analysis of combined dc and ac runs on the symmetrical cell with non-blocking lithium electrodes. The dc measurements of initial (I_0) and the steady-state (I_{ss}) currents were made by polarizing the test cells at voltage bias of 10 mV. The ac impedance measurements were performed before and after applying a bias, to evaluate the value of the interfacial resistance at the beginning and at the end of the test, i.e., R_0 and R_{ss} , respectively. Under these conditions, the lithium ion transference number is given by the following equation:

$$t_{Li^+} = \frac{I_{ss}(\Delta V - I_0 R_0)}{I_0(\Delta V - I_{ss} R_{ss})}$$

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 and composition.

The DSC tests were carried out with TA Instruments module 2010 and System Controller 2100. DSC runs were recorded at a scan rate of 10°min^{-1} up to 350°C . Liquid nitrogen cooling accessory was used for sub-ambient temperature tests.

3. Results and discussion

As can be seen from the plane SEM images of neat PEO and PEs (Fig. 1), the morphology of the films cast under no field and under MF are significantly different. It seems likely that the response of these diamagnetic materials to an external magnetic field occurs by the growth of the grains. The grains, in addition, appear as convex upward domains.

In order to determine whether there are bulk structural changes induced by casting under magnetic field, DSC studies were carried out and some of them are shown in Fig. 2. A weak glass transition is observed at about -60°C for PEO that is in a good agreement with the literature. Fig. 2 also shows that the material melts at about 60°C with a ΔH of 180 J/g . The enthalpy of the PEO melting is scarcely affected by casting under field. The peak, however, is narrower (its FWHM decreases by 6°C), thus indicating the formation of a more ordered structure. Slightly visible splitting of the melting endotherm may indicate the appearance of the second crystalline phase. DSC data for the LiI P(EO)₃ is shown in Fig. 2b. It is clear that there is very little resemblance between the traces for the 1:3 complex and that for the pure polymer. In complexed material the dominant feature is a high-temperature transition at about 310°C , which is attributed to melting of the crystalline LiI:P(EO)₃ phase. In addition, there is a small endothermic event at about 60°C , which is due to trace amounts of pure PEO. The 1:7 LiI:PEO electrolyte exhibits a glass transition at about -4°C with an exothermic recrystallization of the complexed crystalline phase followed by its melting at 68°C . The thermograms of concentrated 1:3 and 1:7 PEs cast under field show two well pronounced endotherms, which denote formation of dual-phase crystalline

compounds. A typical data run for P(EO)₆:LiAsF₆ is shown in Fig. 2d. There is no evidence of the 60°C melting of pure crystalline PEO in the complexed material. Two distinct features with T_{onset} at 124 and 226°C are seen in the DSC trace. The peaks are assigned to the melting of 1:6 and 1:3 PEO:salt complexes, respectively. Application of a magnetic field results in the shift of the first endotherm by about 10°C towards higher temperature; the onset of the second transition does not change. It should be noted that the high-temperature melting occurs vigorously, a fact, which is reflected in the sharp drop of the heat flow. The extremely narrow shape of this peak indicates almost perfectly ordered structure. This is in agreement with large well defined grains seen in the SEM micrographs.

It seems likely that incorporation of 0.1 mol of LiTFSI in the LiAsF₆-based PE does not significantly alter the structure of the solid electrolyte. The effect of the field on the thermal behavior of this sample was similar to that on the lithium imide-free PE.

Figs. 3 and 4 show the Arrhenius plots of the inter- and intra-chain ionic conductivity of concentrated 1:3 lithium iodide-based polymer electrolytes, where the salt is complexed by high (5×10^6) and low (1×10^5) molecular-weight PEOs. The bulk and grain-boundary conductivities (Fig. 4a and b) of short-chain-based PE are higher by a factor of 5–7 than those of the concentrated long-chain PEO film. This may be due to a lesser entanglement of the short host-polymer chains, which, to the first approximation can be related to a lower viscosity. While it is obvious that both conduction processes are influenced by the application of an external gradient magnetic field, the enhancement of the helix-to-helix hopping rate is stronger for the long-chain PEO (Fig. 3b). At 40°C , for example, the σ_{gb} increases by a factor of 14, while σ_{bulk} enhancement induced by magnetic-field casting is only 7-fold. Above 45°C , the effect of field is multiplied. When shorter chains coordinate the lithium, the increases in the inter- and intra-chain cation-motion rates are comparable (factors of 5 and 4, respectively, near ambient temperature). Above 45°C , the positive effect of the field on

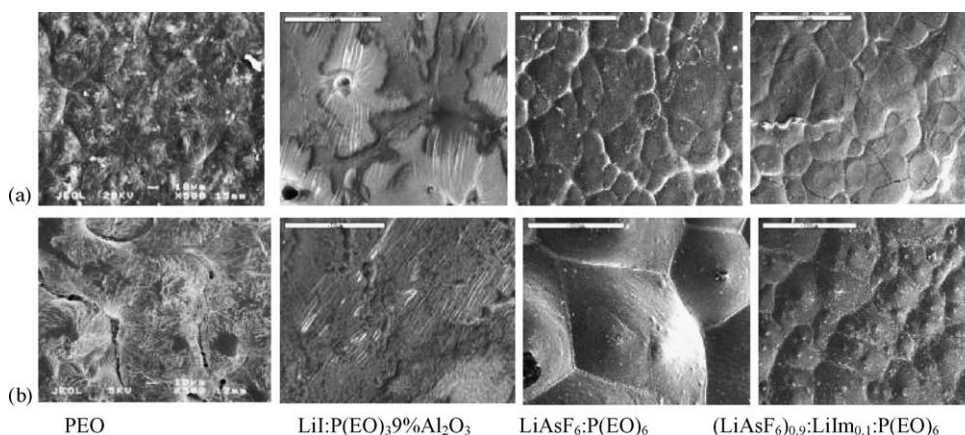


Fig. 1. Planar SEM images of polymer electrolytes: typically cast (a) and cast under a gradient magnetic field (b).

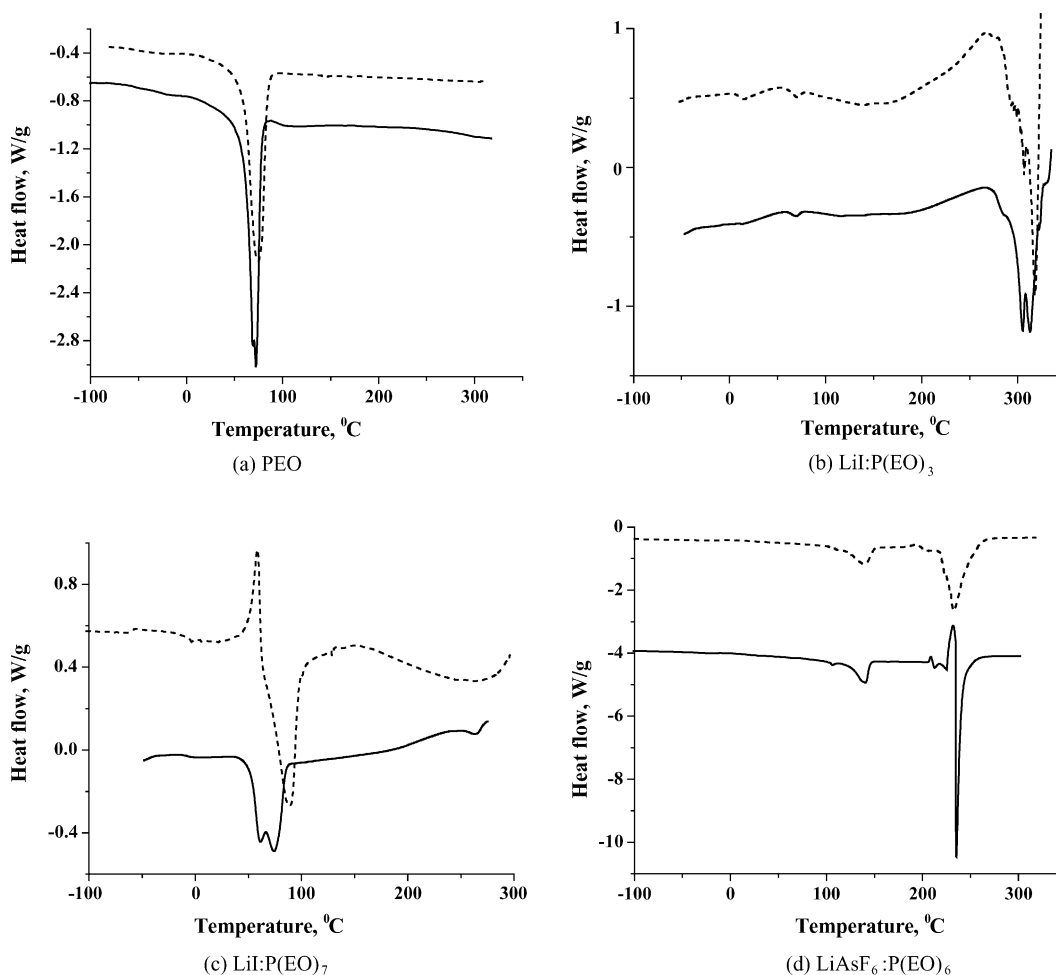


Fig. 2. DSC thermograms of the LiX-P(EO)_n electrolytes: typically cast (short dash) and cast under a GMF (solid).

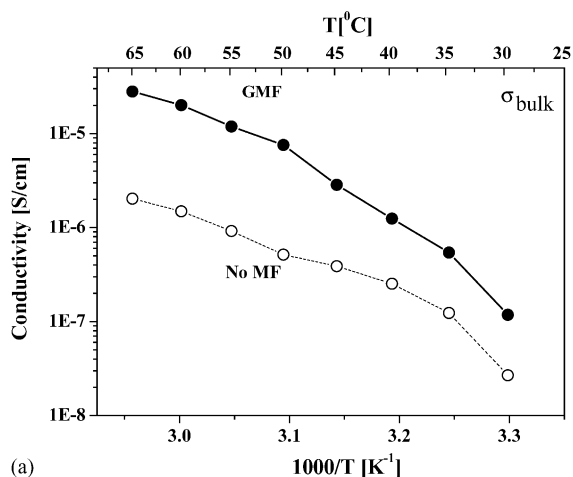
the grain-boundary conductivity of these electrolytes vanishes. Of special interest is the temperature dependence of ion-mobility enhancement induced by the field; this differs significantly for LiI:P(EO)_3 complexes with short- and long-chain polymer hosts (Fig. 5). Whereas the former PE exhibits a monotonic decrease with increasing temperature, the latter shows a sharp increase of σ_{GB} and σ_{bulk} up to 45 °C followed by constant conductivity gain values.

Overall, the effect of the magnetic field is appreciably higher for the PEs with 5×10^6 MW. A similar phenomenon was observed in the case of composite PEs. In our recent work [16], it was found that the magnetic-field effect is extremely strong in concentrated 1:3 composite polymer electrolytes containing 9% diamagnetic alumina. This conclusion was drawn from the observation of a decrease of more than two orders of magnitude in the total impedance of a symmetrical Li/PE cell. When a polymer electrolyte of the same composition was prepared with a shorter-chain PEO the impedance drop caused by a GMF did not exceed one order of magnitude.

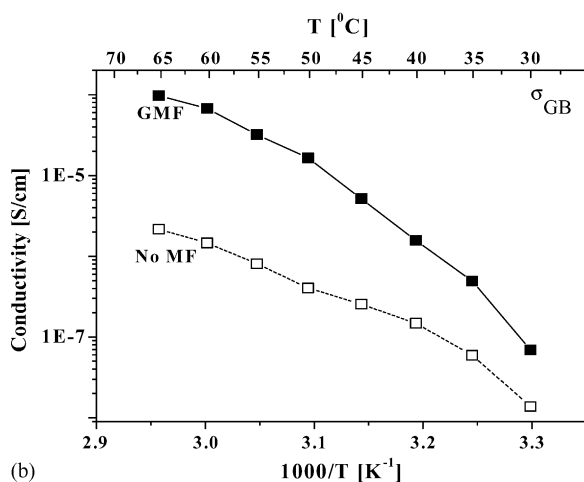
Many highly conducting systems form crystalline 1:6 complexes. Bruce and coworkers [13] showed that in $\text{LiAsF}_6\text{:P(EO)}_6$ complexes (10^3 MW PEO), pairs of PEO

chains fold to form highly aligned cylindrical tunnels within which the Li^+ ions are located and coordinated by the ether oxygens. The anions are located outside these tunnels in the inter-chain space and do not coordinate the cations. The authors also found that the addition of lithium imide salt to the lithium hexafluoroarsenate-based PEs significantly improves ionic conductivity. In our work, $\text{LiAsF}_6\text{:P(EO)}_6$ and mixed $\text{LiTFSI:LiAsF}_6\text{:P(EO)}_6$ with 0.1:0.9 imide to hexafluoroarsenate molar ratio were exposed to a gradient magnetic field during casting. The ion transport properties of these electrolytes are collected in Fig. 6. From the Arrhenius plots (Fig. 6), it is obvious that the addition of LiTFSI has little effect on either intra- or inter-chain ionic conductivity in high-molecular-weight 1:6 PEO complexes obtained by a typical casting process. This is in agreement with the DSC data. The magnetic field has a more profound effect on the conductivity enhancement of mixed-salt electrolytes near ambient temperatures. Here also, the external magnetic field improves the helix-to-helix hopping by one order of magnitude, and the intra-chain cation mobility by a factor of 6.

The necessity of considering the effect of the field strength and its homogeneity, and the fitting of these parameters to the



(a)

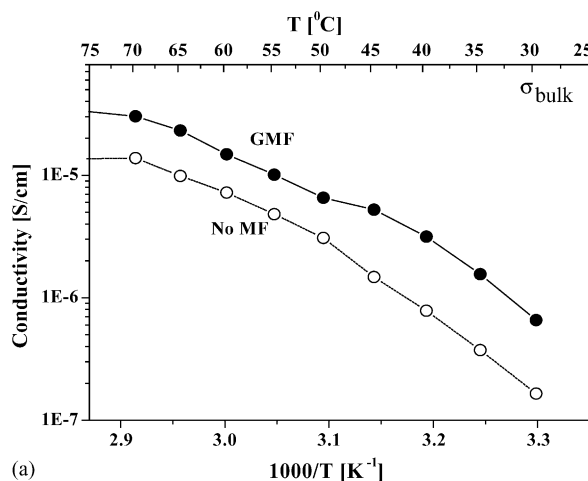


(b)

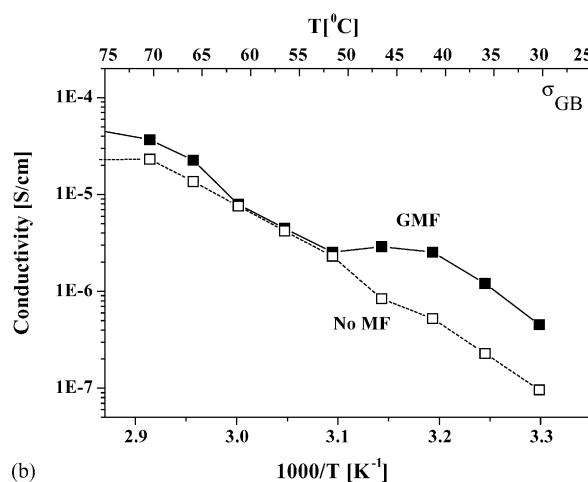
Fig. 3. Arrhenius plots of the intra-chain (a) and inter-chain (b) chain ionic conductivity in LiI-P(EO)₃ polymer electrolytes (PEO = 5 × 10⁶ MW).

electrolyte composition and the size and type of filler, stems from the completely different influence of the field on the conductivity of PEs with paramagnetic and ferrimagnetic fillers. In LiI:P(EO)₃ 9% (v/v) Al₂O₃, the gradient magnetic field applied during casting enhances bulk and grain-boundary ion conduction more strongly than does the homogeneous field.

On the other hand, the composite polymer electrolytes containing 8 nm size γ -iron oxide show similar, or even higher ion-transport properties when subjected to a homogeneous field as compared to a gradient magnetic field (Fig. 7). It should be noted that the influence of both field configurations is greater on the grain-boundary conduction. At 45 °C under the 1.4 kG HMF, σ_{GB} increases 14-fold, while σ_{bulk} —9-fold. Under the 2 kG GMF, factors of 12 and 4.5 for σ_{GB} and σ_{bulk} improvement were measured. The optimization process with the aim of achieving the maximal orthogonal ordering of the helices and of preventing phase separation is under development and will be addressed in a forthcoming publication. The 8 nm ferrimagnetic maghemite ($\chi = 80 \text{ A m}^2/\text{kg}$) was found to be a more effective additive for lithium-ion transport than 30 nm hematite ($\chi = 0.4 \text{ A m}^2/\text{kg}$) (Fig. 8). This is a result



(a)



(b)

Fig. 4. Arrhenius plots of the intra-chain (a) and inter-chain (b) ionic conductivity of LiI-P(EO)₃ polymer electrolytes (PEO = 1 × 10⁵ MW).

of the cumulative effect of a few interconnected parameters: particle size, the structure of the material, its magnetic susceptibility and anisotropy.

Ion transport in dilute polymer electrolytes with EO-to-salt ratio $n \geq 20$ was not found to be appreciably affected by a magnetic field. Diamagnetic alumina is not an effective filler for promoting the orthogonal reorientation of chains in dilute PEs. However, when the magnetic field was applied to LiI:P(EO)₂₀ 9% (v/v) Fe₂O₃ PE, a one-and-a-half order of magnitude σ_{GB} gain was achieved at room temperature [16]. Under these conditions, the improvement in σ_{bulk} was 6-fold.

Inasmuch as crankshaft-like motion associated with short segments of the polymer chain randomly creates suitable coordination sites in solid polymer electrolyte, the hopping rate and conductivity are limited [13]. In disordered systems, therefore, a complicated percolative charge migration is accompanied by larger readjustments of conducting sites, followed by more complicated long-range charge motion. As a result, higher energy barriers limit the profile and the rate of the charge transport. In the MF-ordered PEs, the presence of the permanent coordination sites enabling the hopping of

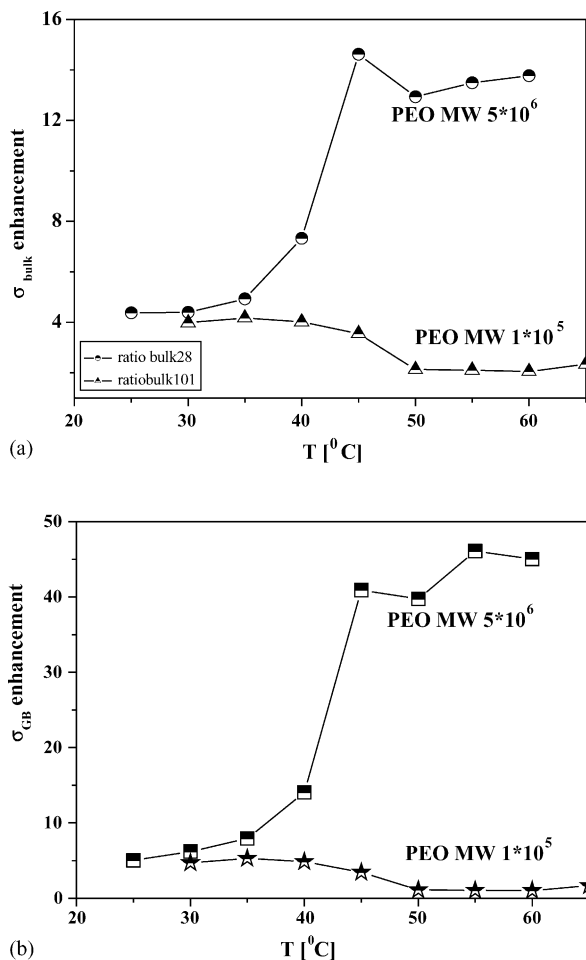


Fig. 5. Bulk (a) and GB (b) conductivity enhancement induced by casting under magnetic field in LiI–P(EO)₃ PEs with high (5×10^6) and low (1×10^5) molecular weight PEO.

cations will not impede the migration rate, as soon as the vibrating ion gains sufficient energy to hop. The preferred orientation of induced dipoles, caused by the magnetic field, should reduce the potential-energy barrier for jumps oriented along the field. As a result, local motions between permanent sites with little perturbations of the chain should require little activation. As anticipated, the apparent activation energy (E_a) of inter-chain conduction is typically higher than E_a of intra-chain conduction for LiI–P(EO)₃ electrolytes; the energy values vary in the range of 100–210 J/mol and 80–120 J/mol, respectively. The addition of alumina lowers by about 20% the absolute values of $E_{a(\text{bulk})}$ and $E_{a(\text{GB})}$ of PEs cast under a gradient field. It is interesting that $E_{a(\text{bulk})}$ of the PEs exposed to a magnetic field decreases more strongly than does $E_{a(\text{GB})}$. Significantly smaller E_a values (by 30%) were measured in the 1:20 composite electrolytes with nano-size iron oxide filler. This points to the possible appearance of an additional interfacial-ion conduction path suggested in [18] or it may be due to improved orthogonal alignment of chains.

It is well established, that in typically cast solid polymer electrolytes the ion transport is dominated by the anions.

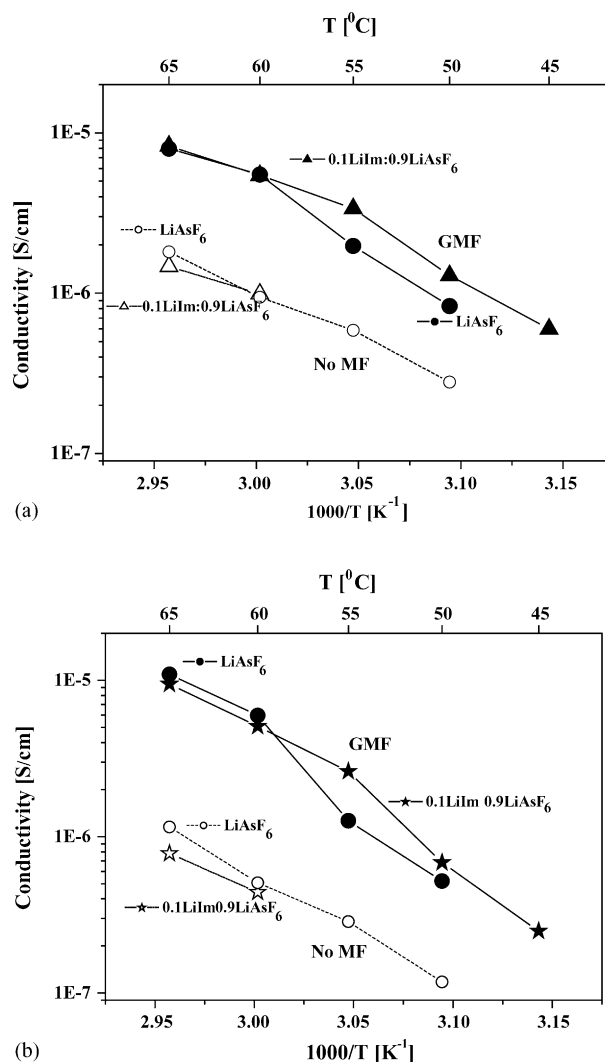


Fig. 6. Arrhenius plots of the intra-chain (a) and inter-chain (b) ionic conductivity of LiAsF₆:P(EO)₆ and (LiTFSI)_{0.1}:(LiAsF₆)_{0.9}:P(EO)₆ polymer electrolytes typically cast (empty symbols) and cast under a GMF (filled symbols).

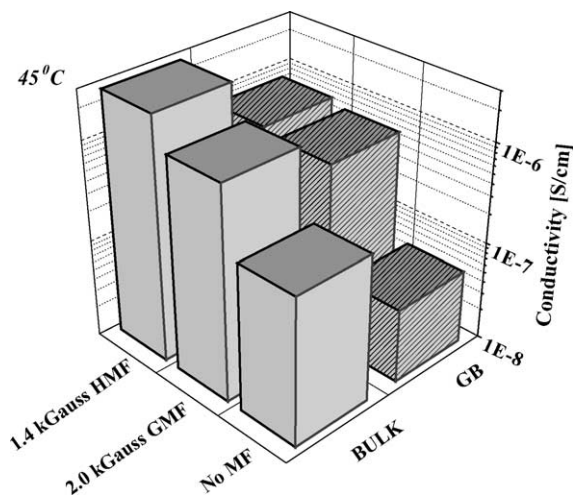


Fig. 7. Influence of magnetic-field strength and its homogeneity on intra- and inter-chain ionic conductivity of LiI–P(EO)₂₀ 9% (v/v) γ -Fe₂O₃ PEs.

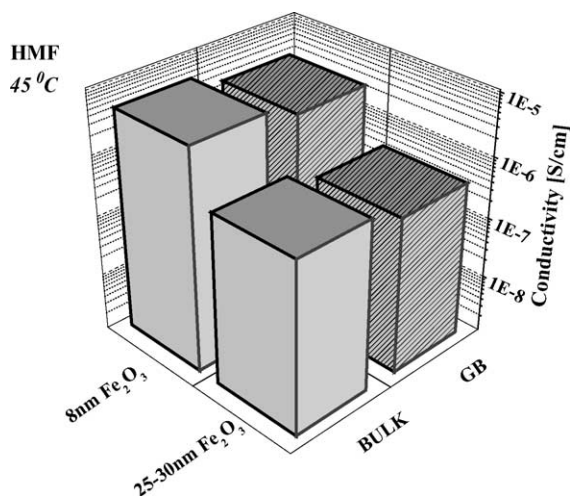


Fig. 8. The effect of type and size of filler on intra- and inter-chain ionic conductivity of LiI-P(EO)₂₀ 9% (v/v) Fe₂O₃.

We have found that casting under a magnetic field increases the cation transference number t_+ almost 2-fold in concentrated CPEs (Table 1). It is suggested that under the MF the PEO chains are forced to adopt conformations that promote the intra-chain cation mobility and preferred cation helix-to-helix hopping.

It is clear that to gain complete understanding of the mechanism of reordering of helices under applied MF will require wide temperature–frequency measurements of dielectric relaxation, magnetic susceptibility, IR, XRD and additional NMR tests. In order to get some insight into the occurring phenomena, a start has been made on dielectric tests of PEO and LiI:P(EO)₃ complexes.

In this study, the real and imaginary components of the complex dielectric permittivity (ϵ^*), namely the permittivity (ϵ') and the dielectric loss (ϵ''), were obtained as a function of temperature and frequency and are shown in Figs. 9–12. Two to three relaxation regions γ , α_a and α_c are usually apparent in PEO [4,19]. The γ -relaxation is ascribed to very small segments of the polymer chain. In our tests, however, the dielectric measurements of pure polymer were conducted above -100°C and therefore only a scarcely visible shoulder of γ -transition has been distinguished. In semicrystalline polymers, the α_a -transition is usually associated with the glass-to-rubber transition of the amorphous phase and reflects

Table 1

Composition	MF	Temperature ($^\circ\text{C}$)	t_+
LiI:P(EO) ₃ :9% Al ₂ O ₃	No	70	0.47
	GMF	70	0.62
LiI:P(EO) ₃ :9% γ -Fe ₂ O ₃ 8 nm	No	30	0.30
	HMF	30	0.58
	No	50	0.20
	HMF	50	0.25
0.67 kG	HMF	50	0.25
1.44 kG	HMF	50	0.49

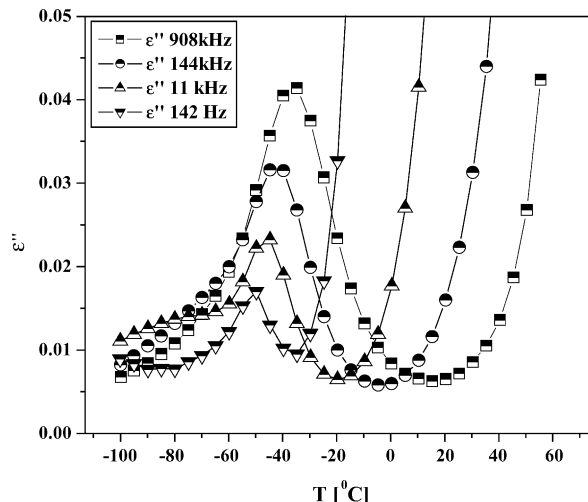


Fig. 9. Plot of the dielectric loss (ϵ'') vs. temperature at different frequency of the typically cast PEO.

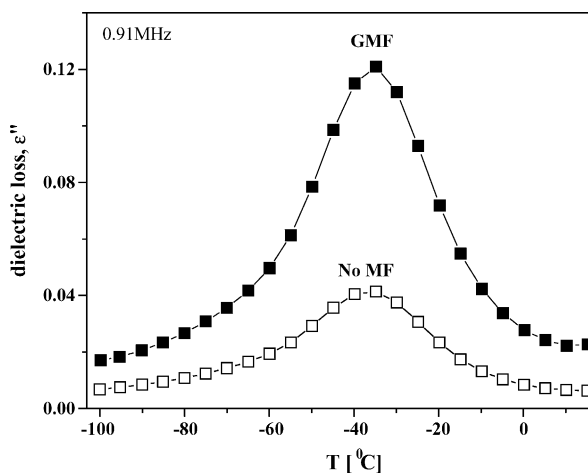


Fig. 10. Plot of the dielectric loss (ϵ'') of the PEO typically cast (no MF) and cast under gradient magnetic field (GMF) vs. temperature at 0.91 MHz.

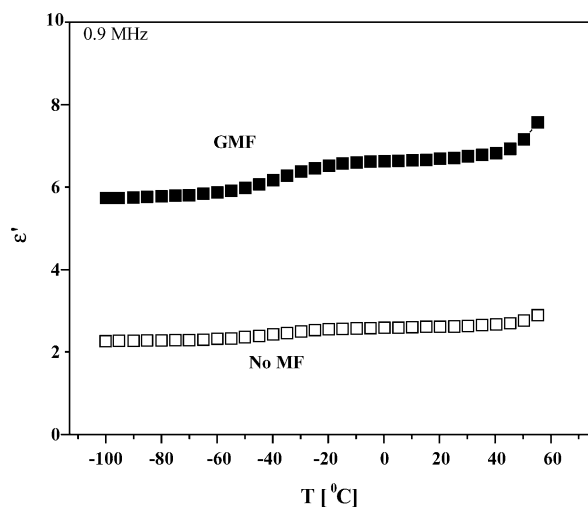


Fig. 11. Plot of the permittivity (ϵ') of high-molecular-weight PEO typically cast (no MF) and cast under gradient magnetic field (GMF).

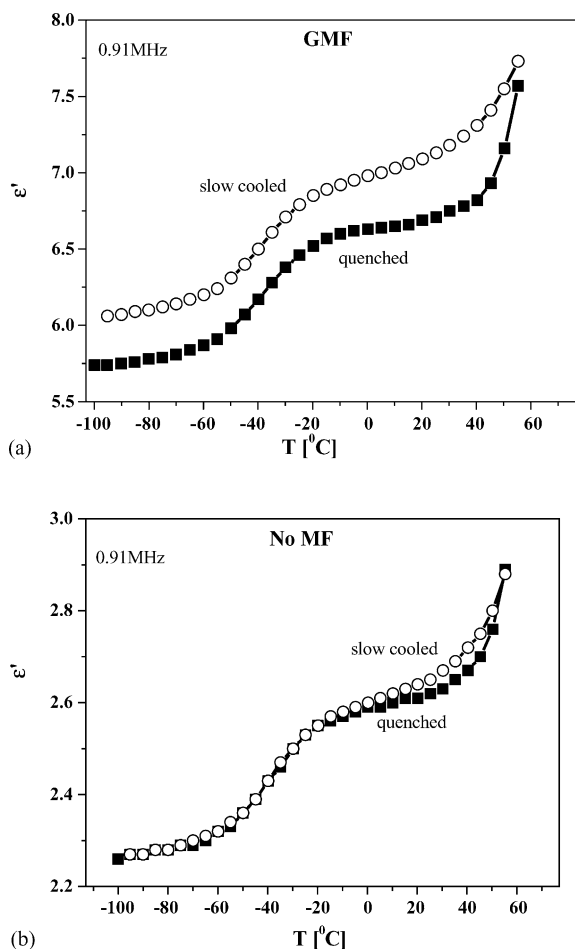


Fig. 12. The effect of quenching and annealing on the dielectric response of high-molecular-weight PEO (a) typically cast (no MF) and (b) cast under gradient magnetic field (GMF).

the cooperative motion of polymer chains. α_c is attributed to the “motion at the surface of the crystallites”, or a “crystal-disordering mechanism” [19,20]. The α_a and α_c dielectric responses merge every so often and are barely distinguishable. We have found that the ε''_{\max} of α -relaxation (Fig. 9) shifts towards higher temperatures with increasing frequency, in agreement with [19] and the position of the main dispersion peak is found to be insensitive to the casting procedure (Fig. 10).

A very large increase in the dielectric loss (Fig. 9), which appears at low frequency, is caused by space charge or electrode-surface effects. This increase is insignificant below T_g .

The real part of the permittivity is an extremely important component affecting the solvation of cations. As can be seen from Fig. 11, the permittivity of high-molecular-weight PEO at room temperature is about 2.6. This implies a very small effect of the solvent on the dissociation of the salt. Fig. 11 compares the permittivity of the two PEO films: typically cast and cast under a gradient magnetic field. The most distinguishing feature of the plots is the significant enhancement of real part of the complex permittivity, which reaches 6.5 at

room temperature for the MF-cast PEO. The strength of the ε'' peak increases as well (Fig. 10). It should be emphasized that at -103°C , where the conductivity process is completely “frozen”, the permittivity of the typically cast PEO is 2.3, while that of MF-cast PEO is 5.7. This indicates, on the one hand, the negligible effect of possible impurities in the PEO on the relaxation response, and on the other hand, the strong influence of the magnetic field on the polarization of the material. The ε'' maximal value was 0.04 and 0.12, for the PEO cast with no field and under GMF, respectively.

The effect of quenching and slow cooling on the dielectric response is best illustrated in Fig. 12. If the memory of the PEO crystal formed during casting under a magnetic field is preserved to a greater degree than that of typically cast polymer, the hysteresis between ε' values of the quenched and annealed samples should be more pronounced. Indeed, comparison of the two samples shows that a rapidly cooled MF-cast sample had lower α -relaxation strength than did the slowly cooled one. For the typically cast PEO there was almost no difference.

The relatively high polarity of PEO is associated with the magnitude of the high dipole moment of a single $\text{CH}_2\text{--CH}_2\text{--O}$ segment of the chain. We believe that during slow evaporation of the solvent at room temperature and under a strong applied magnetic field, the dipole moments of repeating PEO units have enough time to overcome the thermal energy (kT) disrupting their orientation. Assuming significant contribution of the active dipole moments and the correlation between the moments to the dielectric strength of the α -relaxation process in polymer electrolytes, it is suggested that there is mutual parallel orientation of unit dipoles, which do not cancel, but reinforce each other during MF-casting. The permanent dipoles thus created provide enhanced magnetocrystalline anisotropy to the chain and promote the alignment of chains along the field. This is reflected in the permittivity enhancement.

Under a static magnetic field, the alignment occurs so that the axis corresponding to the largest diamagnetic susceptibility becomes parallel to the applied field. The manner in which fibers align depends on the combination of the magnetic axis and the shape axis [21]. Shorter PEO fibers, which possess lower diamagnetic anisotropy, are expected to align to a lesser extent along the field. Indeed, the conductivity enhancement induced by casting under MF of PEs coordinated by low-MW PEO was smaller than that of PEs with high-MW PEO.

The increase in dielectric loss of the PEO cast under magnetic field is very difficult to interpret in any other way except by the growth of lamellar crystals with increased density of defects at their boundaries. Another possible explanation is that parallel orientation of the dipole moments can increase the amplitude of the relaxation process. However, the question of the identification of this relaxation still remains and invites further investigation. It seems likely that under an insufficiently strong applied external field, the shape of the grains can change by the movement of the boundary between

two domains in such a manner that the volume of a domain with higher magnetocrystalline anisotropy increases at the expense of others. The enlargement of grains detected by SEM could be taken as indirect evidence for this assumption.

In PEO–salt complexes, Li^+ cations strongly, but locally, perturb the conformations of pure polymer by lowering the radius of gyration of the PEO chains. This is accompanied by a decrease in the torsional O–C–C–O angle, from 68.4° of the PEO to 47° as found by Frech for the lithium triflate–polyethylene oxide complex [22]. The shape of the helix changes correspondingly from extended in PEO to compressed in polymer electrolytes. All these changes affect the net dipolar response and lead to greater complexity of the relaxation spectra of the LiI:P(EO)_3 PE (Fig. 13). These spectra represent the interplay of several processes including: increase in the number of charge carriers, restriction of segmental motion, formation of ion pairs, cross-linking of the chains via anions. Therefore, the permittivity of the PEs is significantly different from that of the pure polymer (Fig. 14). Casting under a magnetic field increases permittivity even more and ϵ' is almost twice that of the typically cast PE. The permittivity of LiI:P(EO)_3 reaches 7.3 at -103°C and 8.5 at room temperature. While the effect of ion conduction may contribute significantly to the value of ϵ' at room temperature, there is an unambiguous indication of the influence of the applied MF on the rise in the dielectric constant. It is suggested that the 2-fold improvement of real permittivity of the MF-cast PEs favors the dissociation of the salt and by this means enhances the ionic mobility and possibly cation transference number. The impact of the MF on the orthogonal alignment of helices was found to be more effective for concentrated PEs. We attribute this to the formation of more polarizable salt-rich Li–PEO complex domains, sensitive to external magnetic fields. It is believed that both the absolute value of the magnetic susceptibility of the complex and its increased magnetocrystalline anisotropy may assist in the orthogonal orientation of the chains.

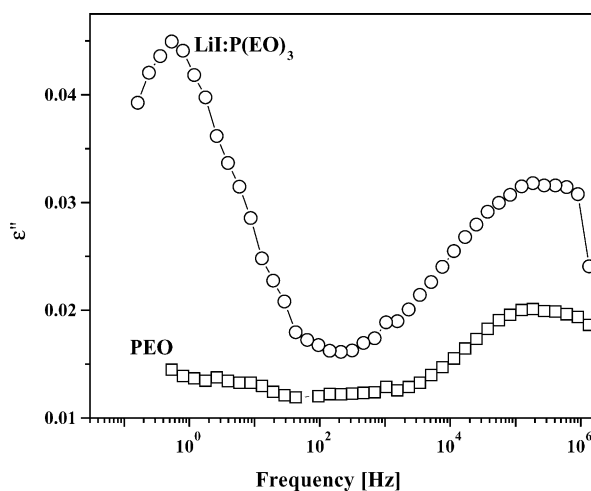


Fig. 13. Relaxation spectra of typically cast PEO and LiI-P(EO)_3 polymer electrolyte.

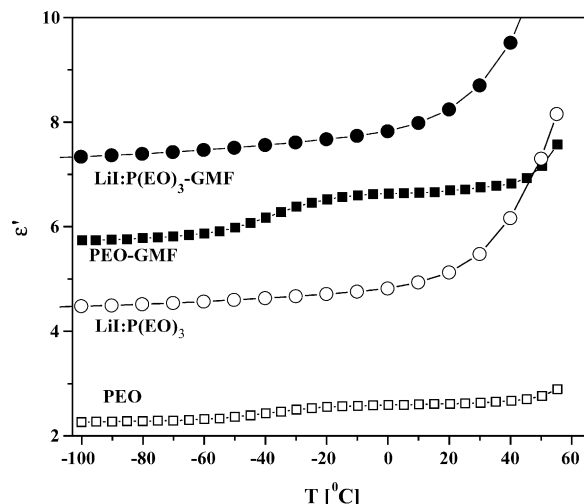


Fig. 14. Plots of the permittivity (ϵ') vs. temperature of PEO and LiI-P(EO)_3 PE typically cast (no MF) and cast under gradient magnetic field (GMF).

In an attempt to explain the enhancement of ionic conduction in MF-oriented PEs by the addition of nano-size fillers, we used the approach suggested by Scanlon et al. [23]. It is assumed that the polarizability of the PEO segments ($\epsilon = 2.5$ at RT) as well as complex domains ($\epsilon = 4.5$) may be locally influenced by the neighboring Al_2O_3 ($\epsilon = 9.8$) or Fe_2O_3 ($\epsilon = 18$) particles. The difference in the relative permittivity of the materials can lead to an inductive effect, in which the PEO polymer chain must compensate locally for the Al_2O_3 dipole moment. This model requires chain rotation and stretching to raise the local dielectric constant of the polymer complex. The low energy of rotation around the C–O bond allows its interaction with the PEO chain and reversal of the dipole orientation when the filler dipole comes into close proximity with the chain. In addition, α -alumina has a small anisotropic diamagnetic susceptibility associated with the lack of symmetry of its hexagonal structure [24]. The magnetocrystalline anisotropy of maghemite is a few orders of magnitude higher. Therefore, the interaction under MF between the PEO–salt complex and fillers is believed to be stronger. It is assumed that, during slow crystallization under applied MF, alumina and maghemite particles, when coming in close contact with the chains, will increase the magnetic dipolar anisotropy of PEO and highly polarizable LiI:P(EO)_3 complex domains. The resultant orthogonal alignment of the PE chains, colinear with the direction of the magnetic field, will initiate the creation of permanent conduction paths, a necessary condition for improved lithium transport.

In our previous studies, the deterioration of Li/PE interfacial resistance (R_{SEI}) was measured in the normal-to-the-plane direction of mechanically stretched polymer electrolyte films. This phenomenon was detected for all conceivable semicrystalline LiI , LiCF_3SO_3 and LiAsF_6 -based PEs. For amorphous lithium bis(oxalato)borate ($\text{LiB}[(\text{OCO})_2]_2$) and trifluoromethanesulfonimide ($\text{LiN}(\text{CF}_3\text{SO}_3)_2$) electrolytes,

however, where insufficient longitudinal orientation of chains was obtained, the negative effect of stretching on the R_{SEI} was less pronounced. As opposed to this observation, casting under a magnetic field is followed by about a one order of magnitude decrease in R_{SEI} . We explain this phenomenon by favorable Li^+ transport via cross-sectional openings of the orthogonally oriented PEO helices, which can be considered as a contributing factor to the rapid formation of a more perfect and stable SEI.

It must be noted, however, that up to now, the conductivity enhancement induced by magnetic-field casting is not enough for practical lithium-battery applications and the need for a true high-molecular-weight all solid-state polymer electrolyte with a conductivity exceeding 0.1 mS/cm at room temperature remains paramount. A promising direction for further research is the reordering of the PEO chains to exploit strong magnetic and electrostatic interactions in order to circumvent these limiting effects.

4. Summary

The low barriers to bond rotation in the PEO backbone allow segmental reorientation of the polymer chain under an applied magnetic field, thus providing permanent conduction paths for ion transport. On the one hand, the intra-chain cation motion via the permanent conduction paths is not limited by the renewal of polymer segmental motion and on the other hand, the ordered helices assist inter-chain hopping.

This is followed by both intra- and inter-chain conductivity enhancement. We believe that this is the alignment of PEO helices that contributes to the conductivity enhancement. As found by the DSC tests the enthalpy of melting transitions does not change significantly when the PEs are cast under magnetic field. This indicates that the content of crystalline phase is not affected by the MF treatment. However, the extremely narrow shape of the melting peaks points to the formation of almost perfectly ordered structure. This is in agreement with large well defined grains seen in the SEM micrographs.

The lithium-transfer number increases from 0.2 to 0.6 in MF-oriented polymer electrolytes. Restriction of ion mobility to the lithium cation by the creation of ordered structures is advantageous for battery applications. The resistance of the solid electrolyte inter-phase decreases by more than one order of magnitude in the lithium cells comprising these MF-oriented polymer electrolytes.

Incorporation of nano-size diamagnetic and paramagnetic fillers to the MF-cast PEs affords us the opportunity to de-

velop solid polymer electrolytes of high mechanical and thermal stability, and improved conductive properties.

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