

Conductivity enhancement induced by casting of polymer electrolytes under a magnetic field

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ABSTRACT

We recently presented a procedure for orienting the polyethylene-oxide (PEO) helices in a direction perpendicular to the film plane by casting the polymer electrolytes (PE) under a magnetic field (MF). Here we study the influence of magnetic fields of different strengths and configurations on the structural properties and ionic conductivity of concentrated LiCF_3SO_3 (LiTf) and LiAsF_6 :P(EO) pristine and composite polymer electrolytes containing $\gamma\text{-Fe}_2\text{O}_3$ nanoparticles. Some data of LiI:P(EO) system are shown for comparison. We suggest that the effect of type of salt (LiI, LiTf and LiAsF_6) on the structure–conductivity relationship of the polymer electrolytes cast under magnetic field is closely connected to the crystallinity of the PEO–LiX system. It was found that the higher the content of the crystalline phase and the size of spherulites in the typically cast salt–polymer system, the stronger the influence of the magnetic field on the conductivity enhancement when the electrolyte is cast and dried under MF. Casting of the PE from a high-dielectric-constant solvent results in disentanglement of the PEO chains, which facilitates even more the perpendicular orientation of helices under applied MF. The enhancement of ionic conductivity was appreciably higher in the PEs cast under strong NdFeB magnets than under SmCo. Both bulk (intrachain) and grain-boundary conductivities increase when a MF is applied, but the improvement in the grain-boundary conductivity – associated with ion-hopping between polymer chains – is more pronounced. For LiAsF_6 :(PEO)₃ at 65 °C, the interchain conductivity increased by a factor of 75, while the intrachain conductivity increased by a factor of 11–14. At room temperature, the SEI resistance of these PEs, cast under NdFeB HMF, decreased by a factor of up to 7, as compared to the typically cast polymer electrolytes. The effect of MF on orientation is observed directly down to the molecular level by ⁷Li nuclear magnetic resonance measurements.

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1. Introduction

The possibility of using polymer electrolytes (PE), as the basis of high-energy-density batteries was first recognized by Armand and Wright [1,2] about three decades ago and is still a driving force behind the research performed on these materials. Since 1980, poly(ethylene oxide) (PEO) has been the most intensively studied material for polymer electrolytes. Below its melting point (65 °C), PEO exists as a mixture of crystalline and amorphous phases, composed of partially ordered and entangled helical chains. Until recently, maximizing the ionic conductivity of PEs was achieved

by maximizing the amorphicity of the polymer and lowering its glass-transition temperature (T_g) [3,4]. A variety of attempts to suppress crystallinity in PEO have included modifications of the host polymer, such as synthesis of branched polyethoxy systems [5,6], linear random copolyethers [7], and comb copolymers [8–10]. Despite these strenuous efforts, the maximum conductivity of highly amorphous polymer electrolytes with low T_g remains around 10^{-2} mS cm⁻¹ at room temperature [11].

The preferential ion transport along the aligned helical axis of the polymer in LiX–PEO polymer electrolytes complexed with a wide range of lithium salts, has been experimentally proven [12–14]. Helix-to-helix hopping was found to be the rate-determining step in long-range lithium-ion conduction at temperatures below 65 °C. This is in agreement with the publications of Bruce [15–17], which demonstrated that certain crystalline LiX–PEO complexes can have higher ionic conductivity than their amorphous counterparts of identical composition. Furthermore,

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Table 1
Intensity of magnetic field applied during PE casting and evaporation of solvent.

Type of magnet	Intensity of magnetic field/T	Diameter of magnet/cm	HMF intensity/T		GMF intensity/T	
			Center	Edge	Center	Edge
SmCo	0.82	2.54	0.26	0.12	0.15	0.06
NdFeB	1.22	5.00	0.35	0.12	0.38	0.18

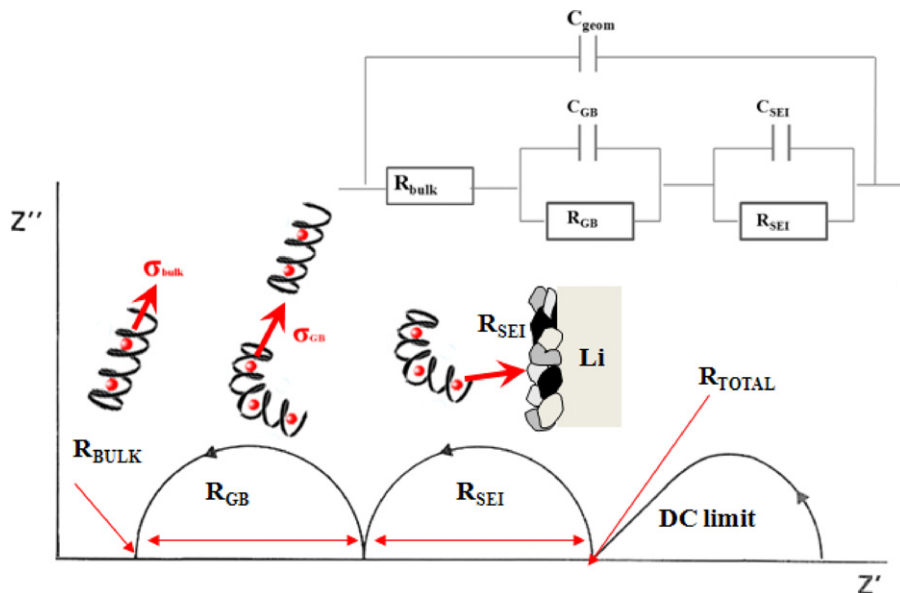


Fig. 1. Schematic presentation of Nyquist plot and equivalent circle used for fitting.

in concentrated PEO-based composite polymer electrolytes (CPE), containing different nanosize inorganic fillers, the crystalline phase was found to be a major contributor to the overall ionic conductivity at temperatures close to the eutectic point [18]. For such CPEs, the interfacial interaction between the filler particles and the polymer–salt complex significantly influences ionic transport, as well [19,20].

The casting of the polymer electrolyte provides mainly parallel-to-the-film-plane helices. This leads to low ionic conductivity in the perpendicular direction, which for most practical applications, especially for high-energy-density all-solid-state batteries, is crucial. Therefore, in order to increase the near-ambient-temperature orthogonal cation mobility (both inside the helical channel and via

helix-to-helix jump), polymer chains should be oriented along the Z-axis.

The recently found solution to the problem of promoting the transition of PEO helices from parallel to perpendicular lamellae crystals, was casting and drying the samples under an applied static magnetic field (MF) [21]. Nanosize particles of magnetic materials improve the vertical alignment of the polymer chains even more. In typically cast (without MF) polymer electrolyte with nanosize ferromagnetic particles, the polymer chains, while mostly parallel to the film plane, are randomly arranged and do not have a net magnetic moment. When the composite polymer electrolyte is cast under a magnetic field, the nanosize ferromagnetic filler particles produce a positive magnetization greater than the force of applied

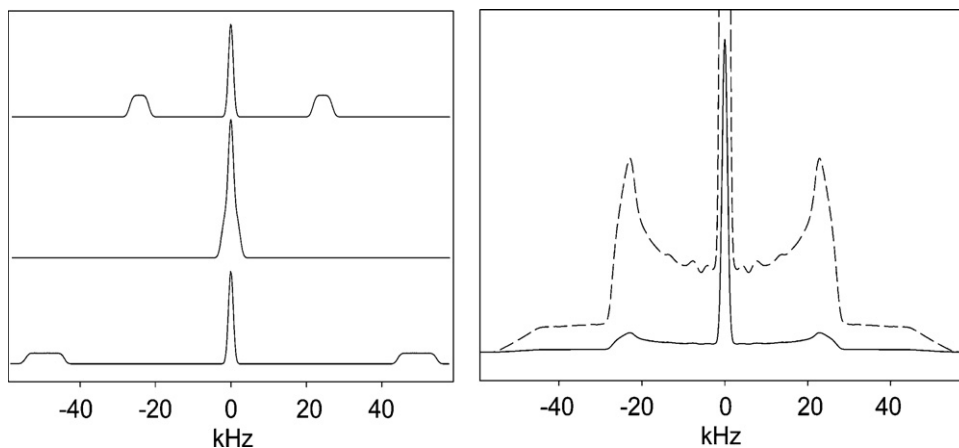


Fig. 2. Simulated spectra of a spin-3/2 nucleus at three different angles between the NMR spectrometer magnetic field and the principal axis of the quadrupole interaction tensor (left). Experimental vs. the simulated "powder pattern" for a randomly oriented polycrystalline sample (right).

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