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In-situ study of the influence of crystallization on the ionic conductivity of polymer electrolytes

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Simultaneous impedance measurements and optical observations of polymer electrolytes were conducted in an automated experimental setup, combining an impedance analyser, polarizing microscope with a heating stage and a digital camera. The polymer film was placed between glasses with indium tin oxide conductive layers, forming a transparent cell mounted in a custom-designed holder, which preserved an argon atmosphere. Results of *in-situ* studies for various compositions of poly(ethylene oxide) (PEO) with $LiN(CF_3SO_2)_2$ salt (LiTFSI), as well as pure PEO, are presented. In the investigated systems, crystallization had a strong impact on ionic conductivity. It was found that the initial growth of crystalline structures caused only a small fraction of the total decrease of conductivity. A large decrease in conductivity was observed during the second stage of crystallization, when no significant changes in microscope picture were observed. In pure PEO and the PEO:LiTFSI 6:1 system, a dense crystalline structure developed, resulting in a decrease in conductivity of over two orders of magnitude. In dilute PEO:LiTFSI systems, a "loose" structure was formed, with amorphous areas preserved between crystallites, and conductivity decreased by only a factor of about 6.

Key words: *poly(ethylene oxide); LiTFSI; polymer electrolyte; conductivity; crystallization*

1. Introduction

After early reports that the crystalline phase of PEO-based electrolytes is poorly conductive [1], various efforts have been taken to prevent the polymer electrolyte from crystallizing [2]. A lithium salt with a large and flexible anion, $LiN(CF_3SO_2)_2$ (lithium bis(trifluoromethanesulfone)imide – LiTFSI), was proposed as an inhibitor for crystallization. In the PEO:LiTFSI system, crystalline PEO coexists with the

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amorphous phase for dilute compositions [3], For a range of PEO:LiTFSI compositions between 12:1 and 6:1, a "crystallization gap" region has been reported for low-molecular-weight PEO [3], and very slow crystallization kinetics were observed for a molecular weight of about 10^6 g/mol [4,5]. For higher salt contents, crystalline complexes of PEO and salt are formed with a defined stoichiometry of 6:1, 3:1, and 2:1 EO:Li [3, 4].

The question of the influence of microstructure on ion transport in the electrolyte remains open. It has been evidenced in recent years, that in some systems the crystalline structure can support conductivity [6]. In polymer films with a structure oriented by stretching [7] or by casting in strong magnetic fields [8], much higher conductivities were obtained in the direction of chain ordering than in the perpendicular direction.

Previously, we described the influence of inhomogeneity caused by crystallization on the electrical properties of PEO and PEO with dissolved salts [9]. Polarizing microscope observations of the electrolyte were used as an additional technique, giving information on electrolyte morphology [10, 11]. Recently, simultaneous impedance measurement and microscope observations were introduced for detailed investigation of the influence of crystallization on ion transport [12, 13]. Here, we present an overview of the results obtained for PEO-based electrolytes of different compositions by *in-situ* studies. The discussion is focused on changes in the ionic conductivity of the electrolyte during crystallization.

2. Experimental

PEO:LiTFSI electrolytes were prepared by mixing $LiN(CF_3SO_2)_2$ (Fluka) and PEO (Aldrich, $M_W = 5 \cdot 10^6$ g/mol) in acetonitrile solution. The obtained solution was poured onto a glass dish, and a thin foil was formed after vacuum drying. The samples for *in-situ* measurement were cut from the foil in the form of discs, about 16 mm in diameter.

The polymer sample was placed between two glass plates covered with conductive indium tin oxide (ITO) films, which served as electrodes. The lower glass was glued to the bottom of a copper cylinder, the upper one to a piston made of Nylon®. The piston was centred inside the cylinder by an o-ring and was free to slide along the axis of the cylinder. Spring loading ensured good electrical contact between the sample and ITO electrodes. A screw mechanism limited the distance between the electrodes and maintained the parallel alignment of the plates. The holder was mounted on a custom-designed microscope stage, heated or cooled by Peltier elements. Due to moisture condensation on the glasses, most of the measurements were performed above room temperature.

Impedance measurements were made with a Novocontrol Alpha-N impedance/dielectric analyser from 10^{-2} (or 10^{-1}) to 10^7 Hz using an ac signal of 20 mV rms. Temperature was stabilized prior to the measurement of the impedance spectrum. The

drift in impedance was detected by a special algorithm, comparing impedance values measured at test frequencies at intervals of several minutes [14]. When the value of the root-mean-squared drift exceeded a specified threshold (typically 2% per hour), measurements at constant temperature were repeated, allowing for the automated detection of phase transitions.

For microscope observation, a polarizing microscope Biolar PI (PZO Warszawa, Poland) was used. The pictures were acquired using a digital camera Coolpix 4500 (Nikon). The basic functions of the camera (shutter, zoom) were controlled by a PC serial port and integrated with the measurement software written under LabView (National Instruments).

3. Results and discussion

The conductivity as a function of time during crystallization for the studied systems is depicted in Figure 1. The values of dc conductivity were calculated from the fit of an equivalent circuit to the measured impedance spectra, done with a custom-written program Firdanov [15]. Details regarding the equivalent circuit and fitting procedure have been described elsewhere [9, 13].

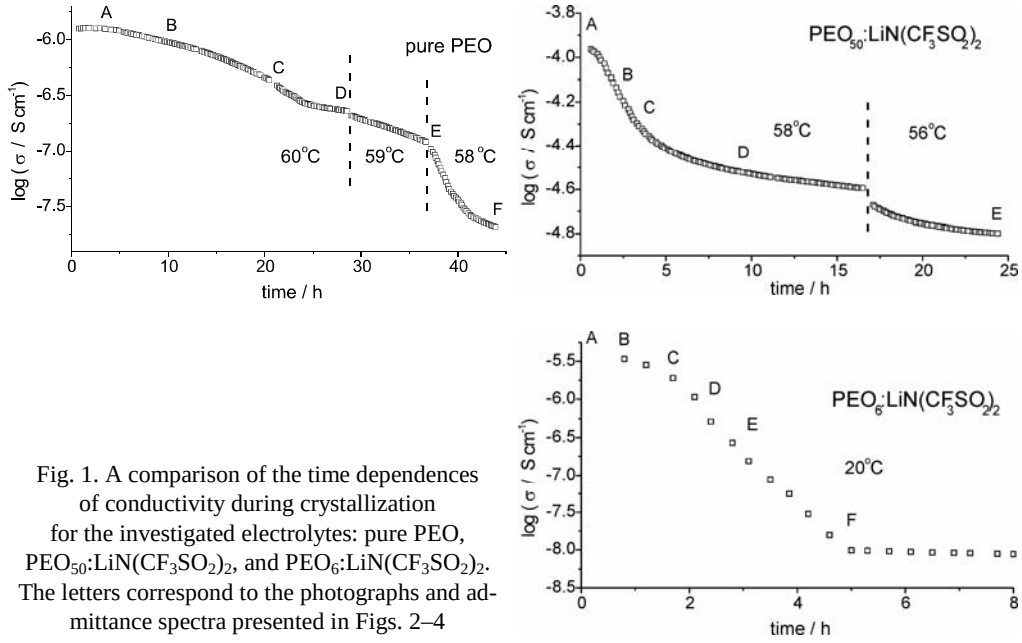

Fig. 1. A comparison of the time dependences of conductivity during crystallization for the investigated electrolytes: pure PEO, PEO_{50}:$LiN(CF_3SO_2)_2$, and PEO_6:$LiN(CF_3SO_2)_2$. The letters correspond to the photographs and admittance spectra presented in Figs. 2–4

3.1. Pure PEO

Prior to the described crystallization process, the PEO sample was fused at 80 ºC and cooled stepwise to 60 ºC. Measurements were performed with a small tempera-

ture step and a strict drift detection criterion in order to obtain stable impedance spectra during crystallization. At 60 ºC, spherulites appeared in the microscope picture.

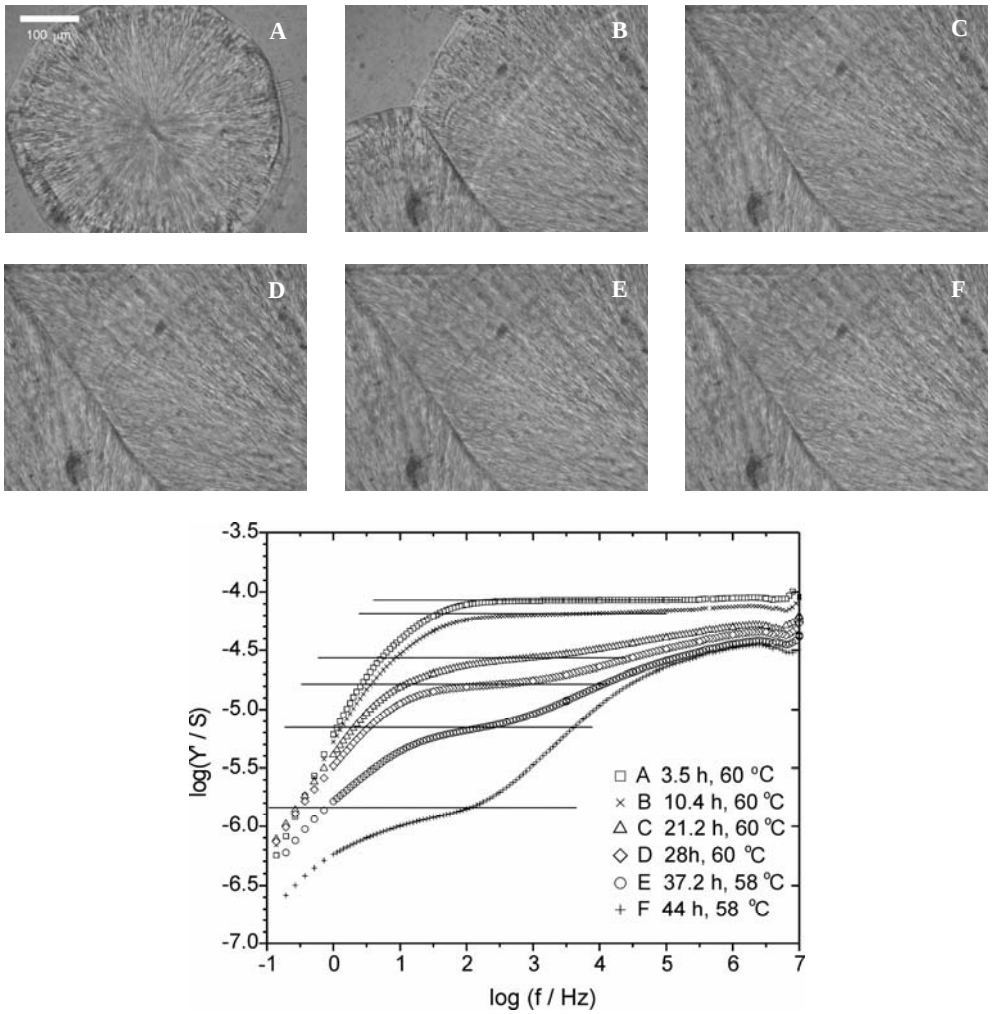

Fig. 2. Polarizing microscope photographs and corresponding spectra of the real part of admittance for pure PEO during crystallization, after cooling to 60 °C. Solid lines mark the dc conductivity estimated by a fit of an equivalent circuit to the data. The time elapsed after cooling to 60 ºC and actual temperature are indicated

Two different stages could be distinguished in the process of PEO crystallization. On cooling to 60 ºC, nucleation followed by a growth of spherulites was observed. The growth of spherulites, which was evident in the microscope pictures, had a relatively small effect on the conductivity, until the crystallites began to constitute a large fraction of the polymer (Fig. 2B). At an early stage of crystallization, when large areas of amorphous phase were still visible around spherulites (Fig. 2A), the plot of log(Y')

versus log(*f*) (Fig. 2, spectrum A) exhibited a single plateau, which extended over four decades of frequency, between 10^2 and 10^6 Hz, and corresponded to the dc conductivity. When the spherulite borders met each other, this single plateau in the log(Y') vs. log(*f*) plot became inclined (Fig. 2, spectrum B) and eventually split into two regions of mild slope divided by a range with a steeper slope around 10^4 Hz (Fig. 2, spectrum C). After about 20 h from the moment of cooling to 60 °C, the entire observation area was filled with spherulites. A decrease of conductivity was still observed. In the second stage of crystallization, upon cooling to 59 °C, and further to 58 °C, no changes in the microscope picture were detected. In contrast, at this stage significant changes in the admittance spectra were observed. These changes are mostly seen in the low frequency region, while only a slight decrease of conductance in the high frequency region may be ascribed to the temperature dependence of conductivity. A constant rate of increase in resistance with time was recorded at 59 °C (Fig. 1). Further cooling to 58 ºC caused an enormous increase in resistance.

To explain the origin of the change in electrical properties, several phenomena should be considered. In the crystallization stage, which occurred after the entire observation area was filled by the spherulites, an additional crystallization process took place within the spherulites, and this process might be responsible for blocking the conductivity pathways. Charge carriers became trapped within the structure, so they no longer could be involved in conductivity or electrode polarization. A second major effect was the hardening of the electrolyte, which could cause deterioration in the electrical contact with the electrodes. A roughening of the surface of the semicrystalline polymer might cause a decrease of the effective contact area. Some areas, like spherulite boundaries, might recess from the electrode when the density of the electrolyte increases.

3.2. PEO_{50}:$LiN(CF_3SO_2)_2$

On cooling the sample from 90 ºC to 57.5 ºC, the nucleation and gradual growth of spherulites were observed in the optical pictures (Fig. 3A–C). High concentration of nucleation centres can be explained by the fact that, despite heating to 90 ºC, the sample was not fully homogeneous. Inhomogeneities probably result from an initial phase separation, or the salt itself acts as a nucleation agent. Due to the high density of nucleation centres, the spherulites impinge on each other relatively early. This process limits the size of spherulites to less than the sample thickness (230 μm). Therefore, a 3-dimensional grain-like structure is formed (Fig. 3D, E). After the impingement of spherulites, the growth slowed down. On photographs taken in regular intervals, only slight changes can be noticed. As one of the possible causes of this phenomenon, an accumulation of non-crystallisable material at the crystallization front was proposed. The salt accumulated at the crystallization front may act as a plasticiser. This would also lead to a higher salt content in the areas between spherulites, which may require heating to higher temperatures than the melting point of PEO in order to homogenize (dissolve) the salt-rich fractions.

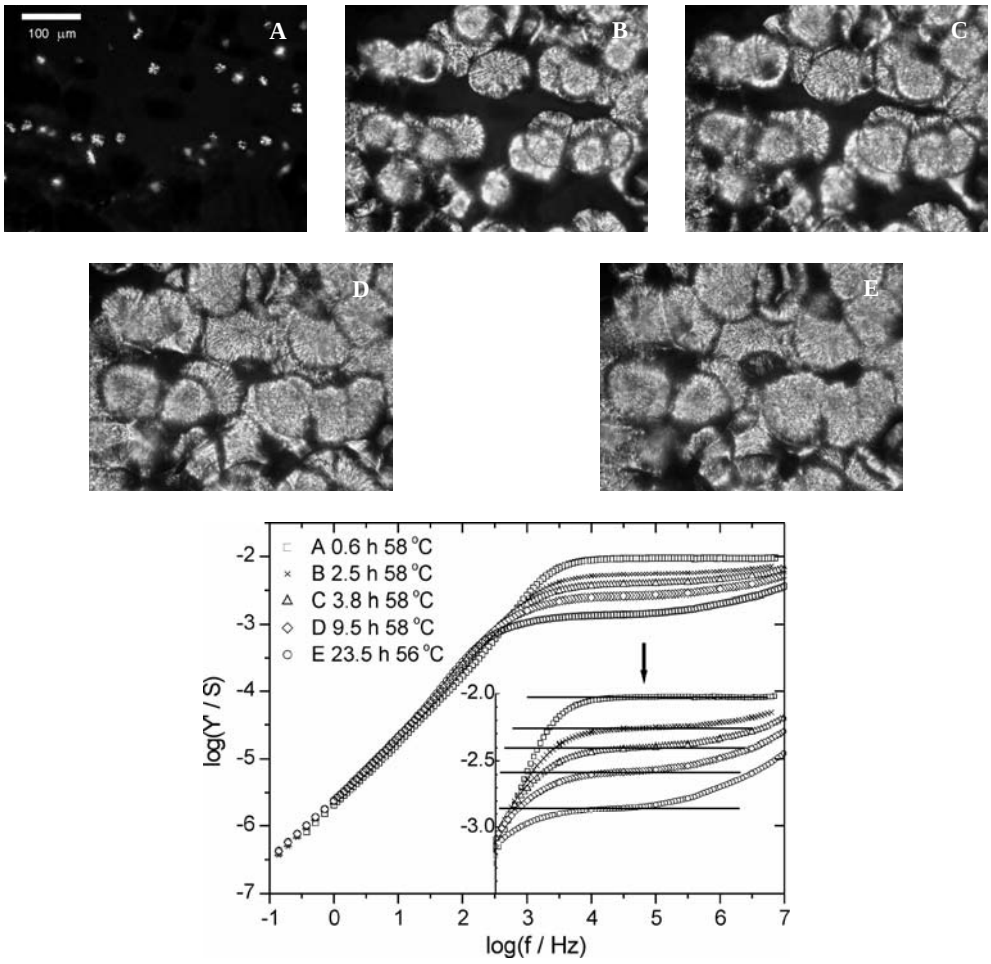

Fig. 3. Polarizing microscope photographs and corresponding spectra of the real part of admittance for PEO_{50}:$LiN(CF_3SO_2)_2$ during crystallization, after cooling to 58 °C. In the insert, the *Y* scale was magnified for clarity. Solid lines mark the dc conductivities obtained from a fit. The time elapsed after cooling to 58 ºC and temperature are indicated

At the early stages of crystallization, changes in the admittance spectra were quite similar to those described for pure PEO. The much higher conductivity values and somewhat different electrode properties, however, caused the characteristic features of the impedance spectrum to shift to higher frequencies. Even during the late stage of crystallization at 58 °C and at 56 °C, no separation of the plateau in the log(*Y'*) versus log(*f*) plot into high and a low frequency regions of mild slope was observed. Following an initial drop with a sigmoidal shape, after about 6 hours from setting the temperature to 58 °C, the conductivity changes slowed down (Fig. 1). A slow decrease of the ionic conductivity was recorded for another 10 hours, until the drift of impedance finally fell below 1% per hour threshold, which was the limit for repeating the meas-

urement. Lowering the temperature to 56 °C caused a further decrease of conductivity with time, which, however, did not affect electrode properties. Despite a grain-like structure developed during crystallization, the PEO:LiTFSI system retained good contact with the electrodes.

3.3. PEO_6:$LiN(CF_3SO_2)_2$

For the investigation of crystallization in isothermal conditions, the $P(EO)_6$:$LiN(CF_3SO_2)_2$ sample was melted at 80 ºC and then fast cooled to 20 ºC (cooling time was about 5 minutes). At this temperature, the measurements were repeated.

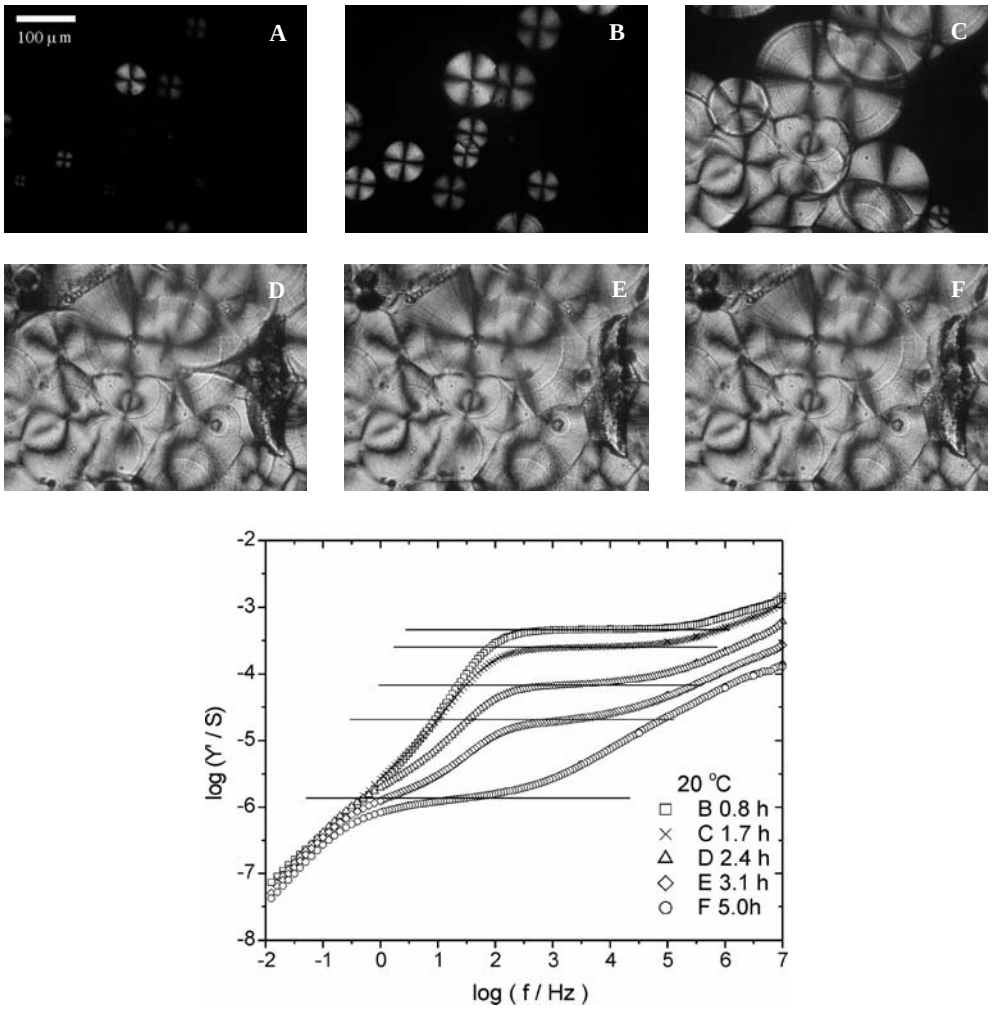

Fig. 4. Polarizing microscope photographs and corresponding spectra of the real part of admittance for PEO_6:$LiN(CF_3SO_2)_2$ during crystallization, after cooling to 20 °C. The time elapsed after cooling to 20 ºC is indicated. Solid lines mark the dc conductivities obtained from a fit

About ten minutes after the temperature of the sample had been stabilized, the first nucleation centres became visible (Fig. 4A). After two hours, the whole observation area was covered with spherulites. The final structure was densely packed, i.e. no black areas corresponding to a free amorphous phase were observed. Large changes were observed in the admittance spectra even after the microscope pictures ceased to exhibit any changes (Fig. 4D–F). The most probable explanation of the continued decrease of conductivity is, like in the case of pure PEO, a densification of the structure (the growth of crystalline structures between existing lamellae) which blocks charge carrier transport through the remaining amorphous phase. In a dense structure, even a small change in the volume fraction of amorphous phase can result in a break in the continuity of the easy conduction path. Another reason for the large drop of conductivity can be an increase in sample stiffness and a loss of contact. This can be related to a transition from spherulites suspended in melt to amorphous regions trapped between dense networks of crystalline lamellae (phase inversion).

4. Conclusions

The results obtained by *in-situ* impedance measurement and optical observations indicate that ionic conductivity of PEO-based electrolytes does not depend directly on the proportions between the amorphous and crystalline phases, but rather on the structure developed during crystallization. Ion transport seems to rely on the existence of amorphous passes between the crystalline structures. In the initial phase of spherulite growth, the changes of impedance were rather small. A significant decrease in conductivity was observed after the borders of spherulites met, and in the subsequent stages of crystallization when changes in the microscope picture were minor. This percolation mechanism of conductivity corresponds well with our earlier results obtained for low-molecular-weight poly(ethylene glycol) [11].

In systems with a developed dense crystalline structure, like pure PEO and the 6:1 PEO:LiTFSI crystalline complex, crystallization strongly affects both bulk and interfacial transport properties. The continuity of the amorphous path through the electrolyte can be broken due to secondary crystallization processes, resulting in a decrease of conductivity. Changes in the electrode part of the impedance spectra may be ascribed to the transition from an amorphous to a solid interface, causing a roughening of the surface and a loss of contact with the electrodes. The cumulative effect of crystallization was a large decrease of conductivity by two orders of magnitude or more.

In dilute systems, like the presented 50:1 EO:Li electrolyte, pure crystalline PEO coexists with an amorphous phase, which seems to have higher salt content than the initial molar ratio. Small areas filled with this phase are seen in the microscope picture, even after long crystallization times. In the grain-like structure, the percolation threshold for ion transport through the remaining amorphous areas can be easily reached. Therefore, the drop in conductivity resulting from crystallization is much smaller.

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