Analysis of diffusion in a solid polymer electrolyte in the context of a phase-separated system

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The salt and ionic diffusion coefficients of the salt $LiN(CF_3SO_2)_2$ (LiTFSI) dissolved in high-molecular-weight poly(ethylene oxide) [PEO] have been measured over a broad concentration range, and the interrelationship of the measured values is demonstrated to be in good agreement with basic electrochemical theory. In the light of recently published structural findings, we propose a biphasic model for the conducting amorphous state, consisting of a stoichiometric $P(EO)_6LiTFSI$ phase dispersed into a salt-containing disordered phase, and analyze the ionic diffusion data within the framework of the Bruggeman-Landauer theory. The agreement between experimental and fitted data is shown to be excellent. We conclude by pointing out and discussing potential weaknesses of our analysis.

Solid polymer electrolytes (SPEs), consisting of an alkaline salt dissolved in a high-molar-mass polymer, are materials with many possible application areas, such as consumer batteries, vehicle propulsion, and recently, light-emitting electrochemical cells [1]. The fundamental knowledge in this field has evolved from the initial discovery of ionic mobility [2], over the report of mobility solely in the amorphous phase [3], to the establishment of a number of distinct stoichiometric crystalline structures [4,5]. However, any conclusive reports regarding the important local structure of the conducting amorphous phase are not available yet, although vibrational spectroscopy [6,7] and neutron diffraction measurements [8] have yielded valuable insight. For instance, it appears as though the local coordination of lithium cations in crystalline complexes is preserved also in the amorphous phase, and that anions do not interact directly with cations in systems that crystallize into an ether-oxygen–to–lithium ratio (n) of 6. The latter group of systems also highlights the direct impact the crystalline structure appears to have on transport properties, since systems that contain an $n=6$ crystalline phase, in general, exhibit significantly higher levels of ionic conductivity (σ) in the amorphous phase than systems containing an $n=3$ crystalline phase [9,10]. In this article we present a complete set of diffusion data for a SPE system that crystallize into an $n=6$ structure, namely, $LiN(CF_3SO_2)_2$ (LiTFSI) dissolved in poly(ethylene oxide) (PEO), and discuss our results in the context of a *phase-separated system also in the amorphous phase*. Diffusion was selected as a suitable probe for such an analysis since it discriminates between various ionic species and subsequently is insensitive to various impurities, which will have a notable effect on, for instance, σ measurements at low salt concentrations.

The PEO-LiTFSI electrolytes were prepared by dissolving preweighed amounts of PEO ($M_n = 5 \times 10^6$ g/mole; Poly-

sciences) and LiTFSI (a gift from the 3M Company) in anhydrous acetonitrile. The solutions were stirred extensively under an inert gas (nitrogen or helium) atmosphere, and thereafter dried under vacuum for a time period of at least 48 h to remove the last traces of the cosolvent. The procedures for pulsed-field-gradient nuclear magnetic resonance (PFG NMR) and restricted diffusion measurements have been described in detail elsewhere [11,12]. All measurements were performed at 85 °C, i.e., slightly above the liquidus line.

In Fig. 1, we present the diffusion coefficients for the lithium cations (D_{Li}), the TFSI anions (D_{TFSI}), and the salt (D_{salt}) in the molar salt concentration (c_{salt}) range of 450–3000 mol/m³. The general trends are that D_{TFSI} is substantially larger than D_{Li} and that D_{salt} is located in between these two values. The latter is expected since an initial quick diffusion of TFSI ions down a concentration gradient, as compared to the motion of lithium ions, will create a minute charge separation, with the negative center being positioned
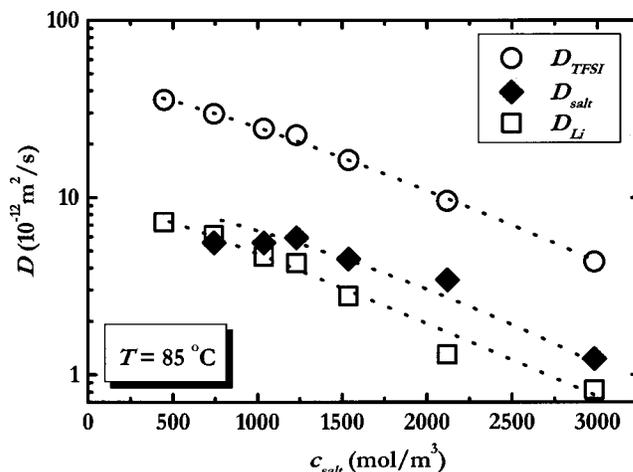
FIG. 1. Diffusion coefficients as a function of molar salt concentration at $T = 85\,°C$ of from top to bottom: TFSI ions, salt, and lithium ions. The dotted lines are a guide to the eye only.

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TABLE I. The mass fraction (M) and the volume fraction (ϕ) of the constituent phases of PEO-LiTFSI electrolytes.

Overall composition	M_{disorder} (below T_m)	$M_{6:1}$	M_{PEO} (below T_m)	$\phi_{6:1}$ (above T_m)	ϕ_{disorder} (above T_m)	n_{disorder} (above T_m)
P(EO)$_8$LiTFSI	0.15	0.74	0.11	0.74	0.26	20
P(EO)$_{12}$LiTFSI	0.15	0.56	0.29	0.56	0.44	40
P(EO)$_{16}$LiTFSI	0.15	0.43	0.42	0.43	0.57	52
P(EO)$_{20}$LiTFSI	0.15	0.35	0.50	0.35	0.65	61
P(EO)$_{30}$LiTFSI	0.15	0.22	0.63	0.22	0.78	74
P(EO)$_{50}$LiTFSI	0.15	0.10	0.75	0.10	0.90	87
P(EO)$_{100}$LiTFSI	0.15	0	0.85	0	1	100

ahead of the average position of the positive lithium ions, and vice versa for the TFSI ions. Such a charge separation will accelerate the slow lithium ions and decelerate the fast TFSI ions, causing both species to move with a constant average drift velocity, $\mathbf{v}_{\text{salt}}$, which is proportional to D_{salt} and the salt concentration gradient, ∇c_{salt}, in accordance with Fick's empirical first law: $c_{\text{salt}}\mathbf{v}_{\text{salt}} = -D_{\text{salt}}\nabla c_{\text{salt}}$. Steady-state diffusion in an electrolytic system is thus fully described by the D_{salt} parameter, both in the dilute and the concentrated regime [13]. An analysis of Fick's law in the context of chemical potentials reveals that a diffusion coefficient, D_i, is directly proportional to the thermodynamic factor $[=1 + d(\ln f_i)/d(\ln c_i)$, where f_i is the activity coefficient] [14]. A strong concentration dependence for D_i, as observed in Fig. 1, is subsequently a signature of a nonideal system. Frequently, this type of nonideal behavior is interpreted in the context of direct ionic interactions, i.e., ionic aggregation reactions, although a changed mobility with salt concentration also can be attributed to ion atmosphere relaxation or connectivity effects.

In the light of recent structural findings for SPEs showing a rather ordered ionic substructure also in the amorphous phase [6,7,8], we have chosen to analyze the concentration-dependent diffusion processes of amorphous PEO-LiTFSI electrolytes in the context of connectivity effects in a phase-separated system. Such an analysis requires knowledge of the salt concentration and volume fraction of the constituent phases. The thoroughly studied phase diagram reveals the formation of a eutectic system, consisting of PEO and $n = 6$ crystallites dispersed in a minority salt-containing disordered region below the solidus line ($T_{\text{solidus}} \approx 40\,°\text{C}$) [15,16,17]. Single crystals of polymers generally take the form of very thin plates or lamellae, with the polymer chain direction transverse to the plane of the lamellae [18]. These crystallites are firmly interconnected by the disordered region, and many polymeric systems, including SPEs [9], form a spherulitic macrostructure. Bruce *et al.* [4,19] have shown that the crystalline structure of the $n = 6$ phase, in a number of SPE systems, is built up of lithium ions located in a row encapsulated by a column formed by two PEO chains. Each lithium ion is coordinated to five out of six possible ether oxygens from the PEO chains with no coordination to the anions, which reside outside the dimensions of the columns in the interchain space. Recent vibrational spectroscopy data [7], in conjunction with an observed generality for both n

$= 3$ [20] and $n = 6$ [19] crystalline SPE structures, yield support for a similar $n = 6$ crystalline structure in the PEO-LiTFSI system.

The n value and mass fraction (M disorder) of the salt-containing disordered phase were accessible through analyses of differential scanning calorimetry (DSC) data [21]. An almost invariable glass transition temperature (T_g) of 37 $\pm 3\,°\text{C}$ for the disordered phase of semicrystalline samples with varying overall salt content ($50 \geq n \geq 8$) was compared with the T_g dependence of high-T heat-quenched samples and revealed the existence of an $n = 9$ disordered phase for all salt concentrations. The ratio of the height of the glass transition event in semicrystalline samples to that of heat-quenched homogenous samples yielded $M_{\text{disorder}} \approx 0.15$. Interestingly, these results for the disordered phase are in good agreement with data obtained from NMR measurements on a PEO-LiCF$_3$SO$_3$ system [3]. Thereafter, it was a straightforward task to calculate the mass fraction of the crystalline $n = 6$ phase ($M_{6:1}$) by equating the overall salt content in the sample with that in the disordered and the crystalline $n = 6$ phases. The mass fraction of the crystalline PEO phase (M_{PEO}) was calculated in a similar manner, and the results are presented in Table I.

To summarize so far, a three-phase system is formed below the solidus line, consisting of PEO and $n = 6$ crystallites interconnected by a disordered $n = 9$ region. However, crystalline SPE phases contain no mobile ions, and the effects of the melting transitions are subsequently of fundamental interest. A recent Raman spectroscopy study performed on this specific system at the crystalline-amorphous phase transition revealed that a large majority of ions exist as single entities, *both* in the crystalline and amorphous state for an overall composition of $n \geq 8$ [7]. Mao, Saboungi, and Price [8] used neutron diffraction data on an amorphous P(EO)$_{7.5}$LiTFSI electrolyte to establish that lithium ions coordinate to on average five ether oxygens belonging to pairs of PEO coils with a considerable degree of extended order. Both these studies strongly indicate that the previously described crystalline $n = 6$ ionic substructure, with lithium ions being shielded from anions by two interlocked PEO chains, is preserved also above the liquidus line. An observation along this line of reasoning was made for a P(EO)$_3$LiCF$_3$SO$_3$ electrolyte, where the sole effect of moving from the crystalline to

the amorphous state was a loss of long range order of the polymeric chains [6]. Thus, it appears as though the ions have a stabilizing effect on the immediate polymeric surrounding, and that for a limited temperature interval above the liquidus line, the local structure of the crystalline $n=6$ phase is preserved. For the crystalline PEO phase, on the other hand, it is well established that T_m directly correlates to a changeover from a highly ordered helical structure to a disordered, random-coil state [22]. With this information at hand, we propose that for a limited temperature interval above the liquidus line a two-phase system prevails, consisting of small but relatively ordered $P(EO)_6LiTFSI$ domains dispersed in a salt-containing disordered phase. The latter is formed via a merger of PEO crystallites and the $n=9$ disordered phase during the melting of PEO. The respective volume fraction (ϕ) of the two phases, and the n value of the disordered phase, were calculated from the mass fraction data of Table I and a density value of 1200 kg/m^3 taken from Ref. [12]. The results are presented in Table I for overall compositions of $8 \leqslant n \leqslant 100$.

The effective diffusion coefficient in a composite, containing periodically spaced spheres with a volume fraction ϕ_s dispersed in a continuous region, was already described by Maxwell in 1873 [23]. However, his classical model does not include the possibility of a variation in concentration of a diffusing species i between the two phases. It is therefore not appropriate for this system, since our model, for instance, predicts that a $P(EO)_{50}LiTFSI$ electrolyte has a 10 times higher concentration of ions in the salt-rich $n=6$ domains than in the surrounding dilute $n=87$ phase. To address this issue we employed an effective-medium model, the Bruggeman-Landauer equation [24,25,26], where the independent variables include the diffusion coefficients of species i in the disordered phase ($D_{\text{disorder},i}$) and the $n=6$ phase ($D_{6:1,i}$), the volume fraction of the disordered phase (ϕ_{disorder}), and the concentrations of the diffusing species in the disordered phase (c_{disorder}) and the $n=6$ phase ($c_{6:1}$):

$$D_{\text{BL},i} = D_{\text{disorder},i}\{(\phi_{\text{disorder}} - \tfrac{1}{2})(1-r) + [(\phi_{\text{disorder}} - \tfrac{1}{2})^2$$
$$\times (1-r)^2 + r]^{1/2}\}. \quad (1)$$

The relative permeability (r) is defined as

$$r = \left(\frac{D_{6:1,i}}{D_{\text{disorder},i}}\right)\left(\frac{c_{6:1}}{c_{\text{disorder}}}\right). \quad (2)$$

The Bruggeman-Landauer equation has been shown to be valid only if $r > 10^{-3}$. This condition is fulfilled for all investigated concentrations, with the direct implication that the $n=6$ domains can be treated as semipermeable obstructions in accordance with the above effective-medium theory [27]. To apply Eq. (1) to our system, we used ϕ_{disorder} as listed in Table I, and the c_{disorder} and $c_{6:1}$ values from Ref. [12]. The $D_{\text{disorder},i}$ values were set equal to the $D_i(n=100)$ values following the prediction of our model that the electrolyte is single phase at this concentration (see Table I). The $D_{6:1,i}$ values are not directly available due to the biphasic nature of concentrated samples, but were selected to $D_{6:1,\text{Li}} = 0.25 \times 10^{-12}$ m^2/s and $D_{6:1,\text{TFSI}} = 1.5 \times 10^{-12}$ m^2/s, respectively,
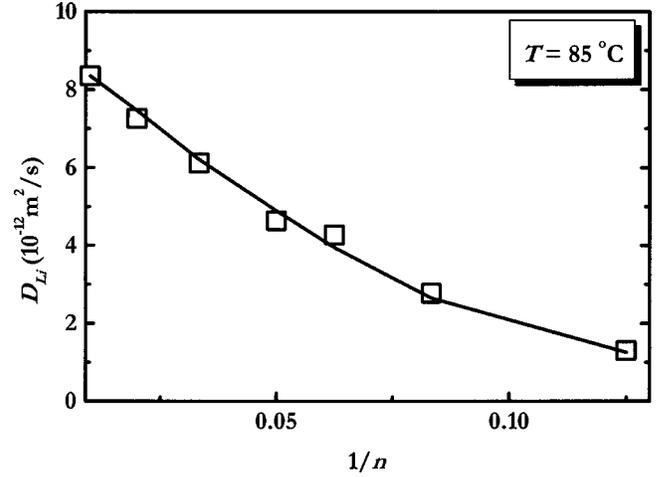
FIG. 2. The diffusion coefficient of lithium ions at $T = 85°C$ as a function of the ratio of lithium ions to PEO oxygens. The solid line represents the fit stemming from applying our biphasic model to Eq. (1).

in order to give the best possible fit of the $D_{\text{BL},i}$ values to the measured values. In Figs. 2 and 3, we present the measured $D_i(i = \text{Li,TFSI})$ values in the form of open symbols, and the $D_{\text{BL},i}$ values in the form of solid lines, as a function of $1/n$ over an extended overall lithium–to–ether-oxygen range ($1/100 \leqslant 1/n \leqslant 1/8$). The agreement between measured and fitted values, obtained with our structural model applied to the Bruggeman-Landauer equation, is excellent.

At this point, it is appropriate to discuss the weaknesses of the above presented analysis. First, the parameter $D_{6:1,i}$ is in principle "free," due to the absence of a single-phase $n = 6$ electrolyte, although an upper limit to its value is given by the measured $D_i(n=8)$ value, when the model predicts the sample to consist of 74% $n = 6$ domains (see Table I). A shift in the $D_{6:1,i}$ values of up to 50% also gives a reasonably good agreement between measured and fitted values. Moreover, it is interesting to note that the selected values yield:
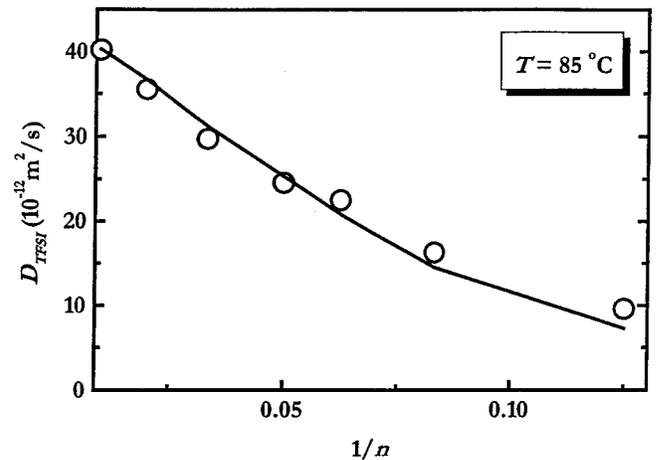
FIG. 3. The diffusion coefficient of TFSI ions at $T = 85°C$ as a function of the ratio of TFSI ions to PEO oxygens. The solid line represents the fit stemming from applying our biphasic model to Eq. (1).

$D_{6:1,\text{Li}}/D_{6:1,\text{TFSI}} \approx D_{\text{disorder,Li}}/D_{\text{disorder,TFSI}}$. An observation that fits in with an absence of ion aggregation in both the disordered and $n=6$ phases, as was recently reported for PEO-LiTFSI electrolytes in this concentration regime [7], and an ion-specific transport process. The latter is relevant since it has been firmly established that Li ions and TFSI ions both require a redistribution of free volume for long-range transport, but that the motion of the former ions also depend on a desolvation-solvation movement of the polymeric chains. The second weakness is related to the fact that only the $n=6$ phase has a concentration of ions that is unaffected by changes in overall composition. This obviously makes the choice of concentration-independent values for $D_{\text{disorder},i}$ to an approximation, although the aforementioned absence of a significant ion aggregation process indicates that such a concentration dependence should be limited. In this context, it was reassuring to find that for dilute samples ($100 \leq n \leq 1000$), where the model predicts a single-phase electrolyte, the D_i values stabilized around the $D_i(n=100)$ values, despite changes in the concentration of ions.

We would like to conclude by emphasizing that the exact quantitative results of the above analysis at this stage are still somewhat crude; the values of the Bruggemann-Landauer equation variables were not directly accessible and we relied on previous DSC results in order to extract these. However, we believe it to be of significant importance, especially in the light of recent structural findings, to demonstrate that the strongly concentration-dependent transport process in the amorphous phase of solid polymer electrolytes can be analyzed in the context of a phase-separated system.

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