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How Efficient is Li^+ Ion Transport in Solvate Ionic Liquids under Anion-blocking Conditions in a Battery?

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Abstract

An experimental analysis based on very-low-frequency (VLF) impedance spectra and the Onsager reciprocal relations is combined with advanced analysis of dynamic correlations in atomistic molecular dynamics in order to investigate Li^+ transport in solvate ionic liquids (SILs). SILs comprised of an equimolar mixture of a lithium salt with glyme molecules are considered as a promising class of highly concentrated electrolytes for future Li-ion batteries. Both simulations and experiments on a prototypical Li-bistriflimide(TFSI) salt / tetraglyme mixture show that while the ionic conductivity and the Li^+ transport number are quite high, the Li^+ transference number under 'anion-blocking conditions' is extremely low, making these electrolytes rather inefficient for battery applications. The contribution of cation-anion correlation to the total ionic conductivity has been extracted from both studies, revealing a highly positive contribution due to strongly anti-correlated cation-ion motions. Such cation-anion anti-correlations have also been found in standard ionic liquids and are a consequence of the constraint of momentum conservation. The molecular origin of low Li^+ transference number and the influence of anti-correlated motions on Li^+ transport efficiency have been investigated as a function of solvent composition. We demonstrate that Li^+ transference number can be increased either by reducing the residence time between Li^+ and solvent molecules or by adding excessive solvent molecules that are not complexing with Li^+.

Introduction

Since the commercialization of lithium-ion batteries in the early 1990s, the electrolyte composition has remained essentially the same, namely a 1M solution of $LiPF_6$ in an organic carbonate mixture.[1] This type of electrolyte exhibits a high ionic conductivity and a good compatibility with the graphite negative electrode (formation of a stable solid electrolyte interphase). However, there are also severe drawbacks of this electrolyte in battery applications: (i) Due to the volatility of organic carbonates, the electrolyte is flammable, leading to serious safety concerns.[2] (ii) The electrolyte is not stable in direct contact to high-voltage cathode materials, such as $LiNi_{0.5}Mn_{1.5}O_4$, which are tested with the aim of increasing the operation voltage of lithium-ion batteries.[3,4] (iii) The electrolyte is not suitable for lithium-oxygen batteries,[5] which are considered as promising candidates for storing much higher energy densities.

Consequently, there is a strong interest in research on alternative electrolytes. Apart from solid electrolytes, highly concentrated liquid electrolytes have recently attracted a lot of attention. Examples are ionic liquid-based electrolytes,[6,7] water-in-salt electrolytes[8] and solvate ionic liquids (SILs).[9,10] SILs are typically 1:1 ratio mixtures of a lithium salt with solvent molecules forming strong complexes with Li^+ ions, such as triglyme or tetraglyme molecules. In a 1:1 mixture, the majority of glyme molecules is involved in complexation of the Li^+ ions, particularly when the salt anion is weakly coordinating, so that there are only few “free” glyme molecules remaining in electrolyte. This leads to a low vapor pressure and to a broad electrochemical stability window of SILs.[9,10,11] The ionic conductivity σ and the Li^+ ion transport number t_{Li+}^{PFG} are about 10^{-3} S/cm and 0.5, respectively.[10] The transport number $t_{Li+}^{PFG} = D_{Li+}/(D_{Li+} + D_{anion})$ is usually calculated from the tracer diffusion coefficients of the ions obtained from pulsed-field gradient NMR (PFG NMR) measurements. The reported values for σ and t_{Li+}^{PFG} indicate rather good Li^+ ion transport properties in batteries.

However, due to the high ion concentrations in SILs and in other highly concentrated electrolytes, strong ionic interactions lead to complex ion transport mechanisms and to strongly correlated motion of the ions. Kashyap *et al*. showed by means of molecular dynamics simulations that there is a strong difference in the cation-anion dynamic correlations between (solvent + salt) systems and pure ionic systems without solvent molecules.[12] In a (solvent + salt) system with many more solvent molecules than ions, the Coulomb attraction between cations and anions leads to positive dynamic correlations, *i.e*. the neighboring cations and anions move preferentially in the same direction on a time scale related to their association. On the other hand, in ionic liquids, the momentum conservation in the system dictates strongly negative cation-anion correlations, *i.e*. cations and anions move preferentially into opposite directions.[12] These dynamic correlations influence not only the ionic conductivity, but also the Li^+ ion transference number under anion-blocking conditions, t_{Li+}^{abc} in a battery.[13] We note that during stationary battery charging/discharging, only Li^+ ions are transported between the electrodes, and the anions are blocked. For an ideal electrolyte without dynamic ion correlations, the transference number t_{Li+}^{abc} is identical to the transport number t_{Li+}^{PFG}, but dynamic correlations can lead to strong deviations between these quantities.[13]

In this paper, we use a prominent example of an SIL, namely a 1:1 mixture of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) with tetraglyme (G4), see the chemical structure and a snapshot of bulk mixture in Figure 1, to elucidate how in highly concentrated electrolytes with only small fractions of free solvent molecules, the interplay between ion-ion dynamic correlations, characteristic time scale for solvent-cation complexation, and other dynamic correlations influences the Li^+ transference under anion-blocking conditions. To accomplish this task, we combine a novel analysis of two sets of existing experimental data (very-low-frequency impedance measurements on the SIL between Li metal electrodes[13] and concentration-dependent cell potential data[9]) with the results of molecular dynamics (MD) simulations of this SIL using fully atomistic, polarizable force field. We show that the two sets of experimental data yield sufficient information for calculating the three Onsager transport coefficients for the SIL. The obtained Onsager coefficients are in good agreement with the simulation results and demonstrate the important role of negative cation-anion correlations for the Li^+ ion transference number under anion-blocking conditions, t_{Li+}^{abc}. The detailed analysis of MD simulations allows to elucidate the molecular scale mechanisms defining the observed dynamic correlations and the Li^+ transference.

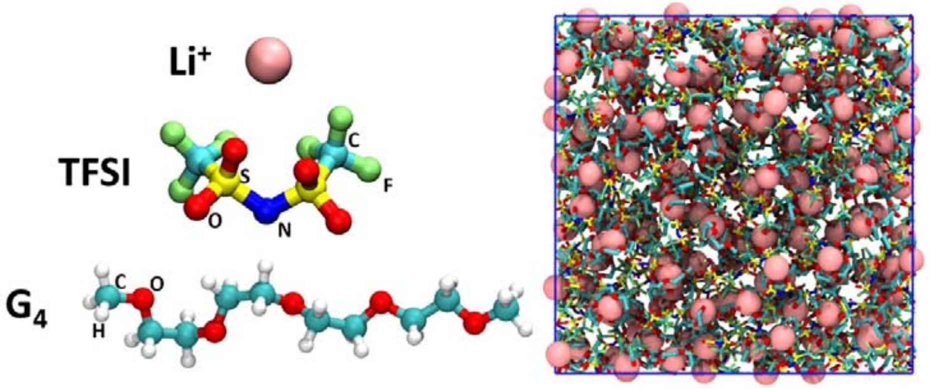

Figure 1. Chemical structure of molecules comprising studied SIL electrolyte (left panel) and a snapshot of the equimolar SIL (right panel).

Methods and Models

Electrochemical impedance measurements. In our recent work, very-low-frequency impedance spectroscopy has been used to study ion transport in the LiTFSI:G4 (1:1) SIL between lithium metal electrodes. From this experiment, we can extract the overall ionic conductivity of $\sigma_{ion} =$ 1.5 mS/cm, the lithium ion transference number under anion blocking conditions $t_{Li+}^{abc} = 0.025$

and the salt diffusion coefficient $D_{salt} = 7 \cdot 10^{-8}$ cm²/s.[13] A schematic illustration of a typical impedance spectrum and a short summary of the data analysis can be found in the SI.

Onsager formalism. As outlined in ref. 13, the Onsager reciprocal relations can be combined with linear response theory in order to describe the relation between the transport properties of a liquid electrolyte under the influence of electrochemical potential gradients and the equilibrium dynamics of the ions. However, as mentioned in ref. 13, the results of very-low-frequency impedance spectroscopy do not yield enough information to obtain quantitative values for the three Onsager transport coefficients of a binary electrolyte. In this work, we present a novel analysis, in which we combine the very-low-frequency impedance data with existing open cell potential of LiTFSI:G4 concentration cells[9] to calculate the three Onsager coefficients and the thermodynamic factor. Furthermore, it is important to note that in ref. 13, we considered only positive directional correlations between cations and anions motion. Here, we consider in addition the possibility of anti-correlated movements of cations and anions, similar to what was found in MD simulations of pure ionic liquids.[12]

In the framework of the Onsager reciprocal relations, the ionic conductivity σ_{ion} can be written as:

$$\sigma_{ion} = \sigma_{++} + \sigma_{--} - 2\sigma_{+-} \tag{3}$$

The Onsager coefficients σ_{++} and σ_{--} can be split into a self part and a distinct part:

$$\sigma_{ion} = \sigma_{+}^{self} + \sigma_{++}^{distinct} + \sigma_{-}^{self} + \sigma_{--}^{distinct} - 2\sigma_{+-} \tag{4}$$

The self-parts are related to the tracer diffusion coefficients of the ions, D_+ and D_-, via the Nernst-Einstein relations:

$$\sigma_{+}^{self} = \frac{c_+ F^2 D_+}{RT} \text{ and } \sigma_{-}^{self} = \frac{c_- F^2 D_-}{RT} \tag{5}$$

The distinct parts $\sigma_{++}^{distinct}$ and $\sigma_{--}^{distinct}$ reflect directional correlations between different cations and between different anions, respectively, while σ_{+-} reflects directional correlations between cations and anions. In an ideal electrolyte without ion interactions, directional correlations do not exist and thus $\sigma_{++}^{distinct} = \sigma_{--}^{distinct} = \sigma_{+-} = 0$. In real electroyltes, preferential movements into the same direction leads to positive values of these transport coefficients, while preferential movements into the opposite direction lead to negative values.

The tracer diffusion coefficients of the ions are usually measured by means of PFG-NMR. In a 1:1 salt:solvent electrolyte containing Li^+ cations and one type of monovalent anion, a Li^+ transport number can be defined as:

$$t_{Li+}^{PFG} = \frac{D_{Li+}}{D_{Li+} + D_-} \tag{6}$$

and as was shown previously,[13] the Li^+ transference number under anion-blocking conditions is given by:

$$t_{Li+}^{abc} = \frac{\beta^2 - 4\alpha + 4\alpha^2}{4(1-\alpha)(\beta-1)} \tag{7}$$

with $\alpha = \sigma_{++}/(\sigma_{++} + \sigma_{--})$ and $\beta = 2\sigma_{+-}/(\sigma_{++} + \sigma_{--})$. While the parameter α tells us whether Li^+ ions ($\alpha > 0.5$) or anions ($\alpha < 0.5$) are more mobile, the β parameter is a measure for the strength of cation-anion dynamic correlations. For an ideal electrolyte, it follows from Eqs. (3)-(7) that $\beta = 0$ and $t_{Li+}^{abc} = \alpha = t_{Li+}^{PFG}$. For real electrolytes, the non-zero values of $\sigma_{++}^{distinct}$, $\sigma_{--}^{distinct}$, and σ_{+-} imply that $t_{Li+}^{abc} \neq t_{Li+}^{PFG}$.

In the following, we assume that the directional correlations between different cations and between different anions are similar, so that $\sigma_{++}^{distinct}$ and $\sigma_{--}^{distinct}$ are either both positive or both negative. In this case, the parameter α should not deviate very strongly from t_{Li+}^{PFG}. Since for LiTFSI:G4 (1:1) it was found that $t_{Li+}^{PFG} = 0.52$, we consider α values in the range from 0.35 to

0.65 and plot in Figure 2 the Li^+ transference number under anion-blocking conditions, t_{Li+}^{abc}, versus the cation-anion correlation parameter β for different values of α. As seen from Figure 2, both strongly positive cation-anion correlations ($\beta \rightarrow +1.0$) and strongly negative correlations ($\beta \rightarrow -1.0$) lead to Li^+ transference numbers $t_{Li+}^{abc} \ll t_{Li+}^{PFG}$. Therefore, the obtained from experiments transference number $t_{Li+}^{abc} = 0.025$ implies that β has to be either in the [-0.89 … -0.95] range or in the [+0.95 … +0.999] range.

In order to decide whether negative or positive β values are physically meaningful, one has to include additional experimental quantities in the analysis. To this end, we use our experimental value for the salt diffusion coefficient of LiTFSI:G4 (1:1), $D_{salt} = 7 \cdot 10^{-8}$ cm²/s, and the literature data for the open cell potential of LiTFSI:G4 concentration cells with transference, $\Delta\varphi(c_{salt})$.[9] As shown in the Appendix A, the Onsager reciprocal relations yield the following expression for the salt diffusion coefficient D_{salt}:

$$D_{salt} = \frac{\sigma_{++}\sigma_{--} - (\sigma_{+-})^2}{\sigma_{++} + \sigma_{--} - 2\sigma_{+-}} \frac{2RT}{F^2 c_{salt}} \frac{\mathrm{dln}(a_\pm)}{\mathrm{dln}(c_{salt})} \tag{8}$$

with $\mathrm{dln}(a_\pm)/\mathrm{dln}(c_{salt})$, denoting the thermodynamic factor. Furthermore, we show in the Appendix B that the relation between the open cell potential $\Delta\varphi$ and the salt concentration c_{salt} is given by:

$$\frac{d\Delta\varphi}{\mathrm{dln}(c_{salt})} = \frac{\sigma_{--} - \sigma_{+-}}{\sigma_{++} + \sigma_{--} - 2\sigma_{+-}} \frac{2RT}{F} \frac{\mathrm{dln}(a_\pm)}{\mathrm{dln}(c_{salt})} \tag{9}$$

The four experimental quantities defined in Eqs. (3), (7), (8), and (9) can be combined to yield the three Onsager coefficients σ_{++}, σ_{--}, and σ_{+-} as well as the thermodynamic factor $\mathrm{dln}(a_\pm)/\mathrm{dln}(c_{salt})$, see Eqs (C1)-(C9) in the Appendix C.

Molecular dynamics simulations. Atomistic molecular dynamics (MD) simulations of bulk SIL electrolytes were conducted using the Atomistic Polarizable Potential for Liquids, Electrolytes and Polymers (APPLE&P) force field, which has been applied in the study of LiTFSI salt in poly(ethylene oxide) (PEO)[14,15] and in ionic liquid systems.[16,17] The transferability of the APPLE&P from LiTFSI/PEO to LiTFSI/glyme systems has been verified in a recent MD study.[18] The 15.0 Å cut-off radius was used for van der Waals interaction and the real part of electrostatic interactions using the Ewald summation.[19] An isotropic polarizability has been assigned to each atomic center and an iterative scheme, minimizing the electrostatic energy of the energy with respect to local electric field, was employed to find distribution of induced dipole moments in the system every time step. A multiple time step integration method was utilized to accelerate the integration, with a 0.5 fs time step for the integration of valence interactions (bends and out-of-plane bending), a 1.5 fs time step for integration short-range (< 8.0 Å) nonbonded interactions and dihedral potentials, and a 3.0 fs time step for integration of remaining nonbonded interactions and reciprocal space of the Ewald summation. The Thole screening parameter of 0.2 has been used to avoid polarizability 'catastrophe'.[20]

Simulations were conducted on systems comprised of 200 glyme molecules and the corresponding amount of LiTFSI ion pairs. Four tetraglyme(G4)-LiTFSI systems with LiTFSI:G4 ratios ranging from 0.25 to 1.0 were investigated in the temperature range 303-373 K, using simulations at 373 K as a primary source for dynamical correlations analysis. In addition, the triglyme(G3) and pentaglyme(G5)-based systems with 1:1 LiTFSI:G_i ratio have been investigated. Also shorter glyme(G1) and diglyme(G2) based systems with 1:2 LiTSFI:G_i ratio and systems comprised of mixture G1 and G2 glymes with LiTFSI:(G1+G2) (1:1) ratio have been studied as well. These systems with shorter glymes, contain the same number of ether oxygen atoms per Li^+ as in G5, G4, and G3-based 1:1 LiTFSI:G_i SILs, but the solvent is comprised of shorter molecules. Initially molecules were randomly placed in a large simulations cell (dimensions around 300 Å) and subsequently subjected to short simulation with shrinking the simulation cell to dimensions approximately corresponding correct density. Then equilibration runs in the NPT ensemble were conducted over 20 ns (or longer) until the fraction of Li^+ coordinated with glymes had stabilized. Production trajectories were ranging from 40-60 ns, depending on temperature and system composition, to allow sufficient sampling of Li^+ local environments, structural correlations, and dynamic properties.

Results and Discussion

LiTFSI:G4 (1:1) structural correlations. First, we briefly summarize structural characteristics in this system. As was demonstrated in previous work[21] and confirmed by our simulations, Li^+ ions are primarily coordinated by oxygens atoms, which are in abundance. The pair correlations functions in the LiTFSI:G4 (1:1) system indicate that each Li^+ on average has about 5.2 oxygen atoms in its first coordination shell (defined as a sphere within 3Å from Li^+ center), 4.3 of which are contributed by glyme molecules and about 0.9 by TFSI anions (see Figures S3-S5 in the SI). The majority of the Li^+ ions are coordinated by a single G4 molecule, *i.e.* G4 molecule effectively wraps around the cation to maximize the interaction of Li^+ with its O_{G4} atoms. Only a small fraction of Li^+ has TFSI-only coordination. Therefore, Li^+ are well dissociated from TFSI anions even at 1:1 composition. If we define "free" glyme molecules as those having only one or no O_{G4} atoms in the first coordination shell of any Li^+, then in the equimolar system we find only 8.5% tetraglyme molecules to be "free".

LiTFSI:G4 (1:1); application of the Onsager formalism in experimental analysis. In Figure 3, we show a plot of $\Delta\varphi$ vs. $\log(c_{salt})$ with the data taken from ref. 9. Since there are only few data points at high salt concentration > 1 M, and the LiTFSI:G4 (1:1) mixture is the electrolyte with the highest salt concentration, the slope $\mathrm{d}\Delta\varphi/\,\mathrm{d}\log(c_{salt})$ for the composition LiTFSI:G4

(1:1) can only be estimated. However, we can argue as follows: When we insert our values for σ_{ion}, t_{Li+}^{abc} and D_{salt} into Eqs. (C5) to (C8) in the appendix C, we have to choose a slope of $\mathrm{d}\Delta\varphi/\,\mathrm{dlog}(c_{salt})$= 2.0 to obtain a β value of -0.92 (mean β value in Figure 2b) or alternatively a slope $\mathrm{d}\Delta\varphi/\,\mathrm{dlog}(c_{salt})$= 0.2 to obtain a β value of +0.975 (mean β value in Figure 2c). Lines with these slopes are shown in Figure 3. Clearly, the black line indicating the slope needed for β = -0.92 matches much better with the experimental data points then the red line indicating the slope needed for β = +0.975. Furthermore, the black line corresponds to a thermodynamic factor $\mathrm{dln}(a_{\pm})/\,\mathrm{dln}(c_{salt})$ = 30, while the red line corresponds to $\mathrm{dln}(a_{\pm})/\,\mathrm{dln}(c_{salt})$ = 0.38. Since it has been shown in the literature that concentrated liquid electrolytes exhibit typically thermodynamic factor $\mathrm{dln}(a_{\pm})/\,\mathrm{dln}(c_{salt}) > 1$,[22] there is strong indication that strongly negative β values around -0.92 are the physically meaningful solution of the Eqs. (C5) - (C8). This implies strongly anti-correlated movements of Li^+ ions and anions. Further support for this will be presented in the next section.

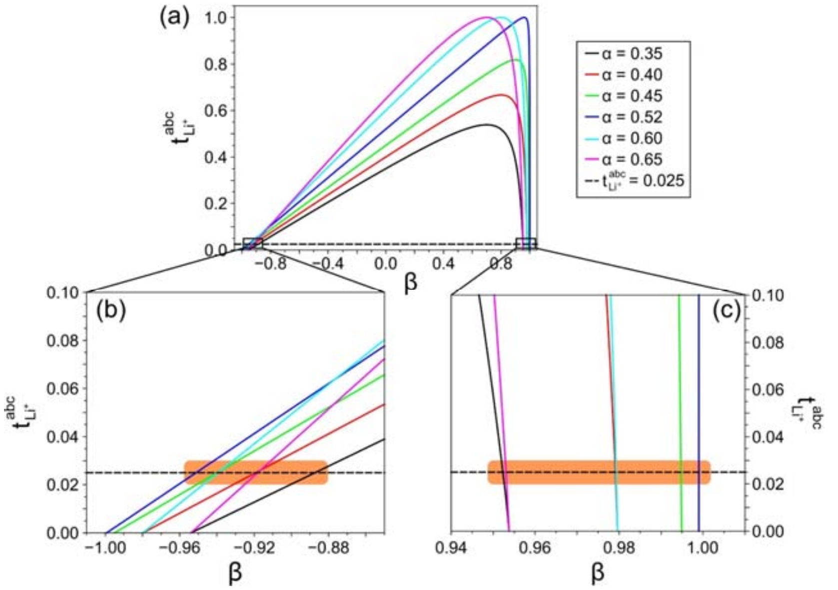

Figure 2 a) Plot of the Li^+ *transference number under anion-blocking conditions,* t_{Li+}^{abc}, *versus the cation-anion correlation parameter β for different α values. The α values indicate whether* *the Li$^+$ ions are more mobile ($\alpha > 0.5$) or the anions are more mobile ($\alpha < 0.5$). b) Zoom into the negative and c) the positive β regime.*

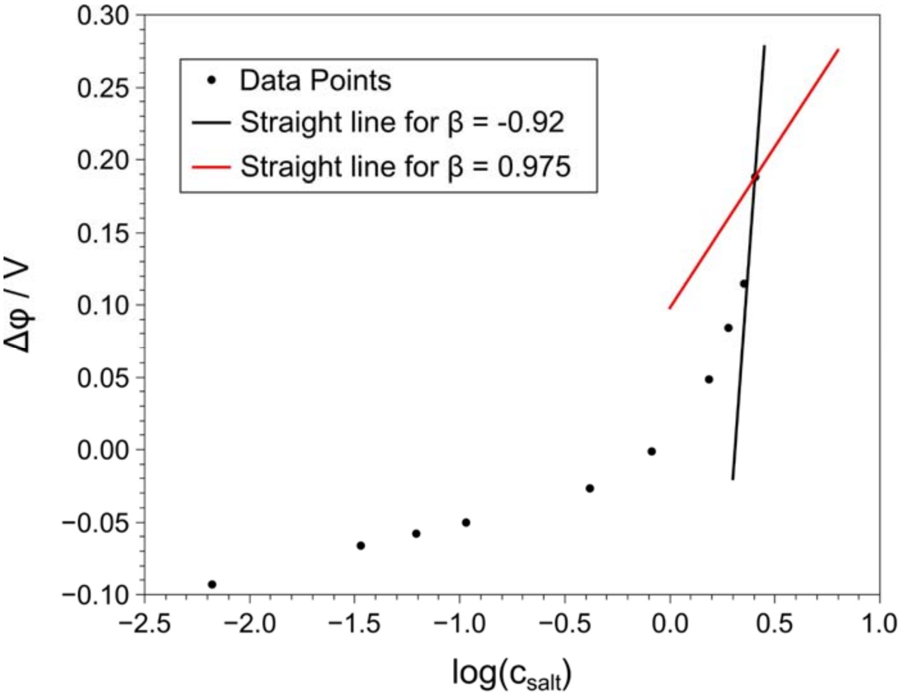

Figure 3. Open cell potential of LiTFSI:G4 concentration cells with transference plotted versus LiTFSI concentration, c_{salt}. The data were taken from ref 9. The meaning of the black and the red line are explained in the text.

LiTFSI:G4 (1:1) dynamic mechanisms. To obtain additional insight into trends obtained from the discussed above experimental analysis, we have analyzed the ion transport mechanisms using MD simulations. Specifically, we focused on the analysis of residence times of O_{G4} and O_{TFSI} atoms in the Li$^+$ first coordination shell. Details of calculations and corresponding residence autocorrelation functions are summarized in the SI. This analysis shows that G4 solvent residence time near Li$^+$ is on the order of 10-100s of ns, while O_{TFSI} is on the order of 10-100s of ps.

In the equimolar system, the diffusion coefficients of all three species are very similar in the entire temperature range investigate (303-373K). Taking into account the very long residence times between Li$^+$ and coordinating G4 molecules, this system can be considered as a classical example of the solvate ionic liquid. Note that diffusivity of Li^+ and TFSI is quite substantial (on the order of D_{Li}=0.072 nm^2/ns, D_{TFSI}=0.065 nm^2/ns at 373 K as obtained from simulations) and while these values are about factor of two lower than experimental values,[18] the resulting transport number $t_{Li+}^{PFG} = 0.52$ is in excellent agreement with experimental data.[13] Therefore, the Li^+ mobility in the electrolyte is quite substantial. However, as discussed above, experimental data indicate that under anion blocking conditions, the effective transference number t_{Li+}^{abc} is very low (~0.025). The advantage of MD simulations is that they allow straightforwardly to define and calculate all contributions (self, distinct, and cross-ion) to the ionic conductivity as defined by Eq.4. Details of equations defining $\sigma_{+}^{self}, \sigma_{++}^{distinct}, \sigma_{-}^{self}, \sigma_{--}^{distinct}$, and σ_{+-} terms are given in the SI. Figure 4 shows the apparent time dependence of these contributions as obtained from MD simulations of the equimolar system. At short time scales (sub-diffusive regime), we see substantial changes in all contributions, but eventually in the long-time limit, all contributions reach steady values that can be related to macroscopic characteristics measured in experiments.

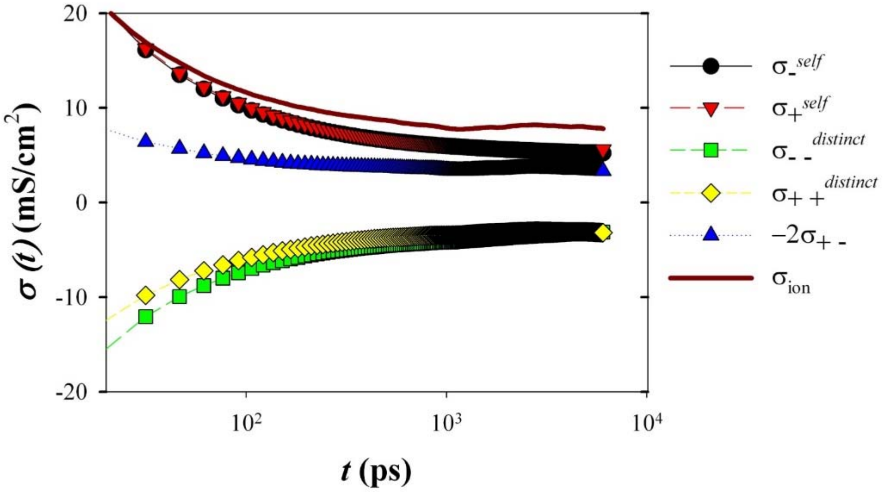

Figure 4. Apparent time dependent contributions to ionic conductivity from various ion-ion correlations as obtained from MD simulations of LiTFSI:G4 (1:1) system at 373K.

The examination of Figure 4 reveals the following trends. As expected, the self-terms provide positive contributions to the total conductivity and are almost equal for Li^+ and TFSI. On the other hand, $\sigma_{++}^{distinct}$ and $\sigma_{--}^{distinct}$ correlations offset the contributions from the self-terms by providing negative contributions with the magnitude of roughly half of the self-terms. This indicates that the motion of distinct ions of the same type are anti-correlated. What is less expected is a strongly *negative* value of σ_{+-} cross correlation, which in combination with the negative sign in Eq.4 leads to large positive contribution to the total conductivity. This positive contribution indicates that there is a strong anti-correlation in the cation-anion motion as well. In conventional electrolytes, where a low amount (on the order of 1M) of Li-salt is partially dissociated in organic solvent, the cation-anion motions are usually positively correlated (resulting in negative contribution to conductivity) reflecting the fact that some ions move as cation-anion (charge neutral) pairs and hence do not contribute to the overall charge transport. This also has been recently demonstrated for IL/solvent mixtures.[23] However, the negative value of σ_{+-} observed in in simulations for the LiTFSI:G4 (1:1) system indicates an opposite effect, *i.e.* the cation and anion motions are anti-correlated.

Often when discussing ion correlations in electrolytes, the ratio of impedance measured conductivity and "ideal" conductivity calculated using the Nernst-Einstein equation based on ion diffusivity, *i.e.* the inverse of Haven ratio $H_R{}^{-1} = \frac{\sigma_{ion}}{\sigma_+^{self} + \sigma_-^{self}}$, is used. A deviation of this ratio from unity indicates contribution from distinct ion-ion correlations, but often it is assumed that this deviation is primarily defined by σ_{+-} correlations and hence can be related to the ion degree of dissociation. If $H_R^{-1} = 1.0$ then there is no cation-anion pairing (*i.e.*, the salt is completely dissociated) and if $H_R^{-1} = 0.0$ then cations and anions move as charge neutral pairs (*i.e.*, fully associated). As we can see from Figure 4, such simplified consideration can be misleading, which is consistent with previous discussion of this issue in ionic liquids and molten salts.[24] First, there are strong contributions from $\sigma_{++}^{distinct}$ and $\sigma_{--}^{distinct}$ correlations. Second, the cation-anion contribution to the ionic conductivity can be positive. Therefore, while H_R^{-1} indeed measures the extent of dynamical correlations between distinct ions, it might have little information on the extent of cation-anion degree of association/pairing related to thermodynamic or structural considerations.

Following the definitions for non-ideality coefficients α and β defined above for anion blocking conditions, our MD simulations yield t_{Li+}^{PFG}= 0.52 and β = -0.87 leading to t_{Li+}^{abc}=0.065 at 373K. While the latter number is somewhat higher than obtained from experiments, the overall trend that $t_{Li+}^{abc} \ll t_{Li+}^{PFG}$ is consistent with experimental analysis. Also, the obtained negative value of β is consistent with the discussion of experimental data (Figure 2 and Figure 3) that concluded that large negative values of β are expected for this system. While there are some differences between simulation and experimental values for β and t_{Li+}^{abc}, which might be due to different temperatures investigated or due to the accuracy of simulations, the overall trends are consistent and simulations confirm that the strong cation-anion anti-correlation is the true characteristic of this SIL.

From a microscopic point of view, the observed trends and contributions to conductivity from various ion-ion correlations can be understood in light of concepts introduced by Kashyap *et al.* upon considering deviations between impedance and NMR conductivities in ionic liquids and electrolytes.[12] They demonstrated that in pure ionic liquids, where only cations and anions are moving, the constrain for conservation of the total momentum in the system must result in anti-correlated cation-anion motion (*i.e.*, providing positive contribution to the total conductivity) as well as anti-correlated contribution from distinct cation-cation and anion-anion correlations (*i.e.,* resulting in the negative contribution to the total conductivity that offsets the positive contribution from cation-anion anti-correlation). In electrolytes with solvent molecules, on the other hand, it is expected that the solvent component can facilitate the momentum exchange in the system, and therefore cation-anion motion can be positively correlated (*i.e.*, providing negative contribution to the total conductivity). However, our simulations demonstrate that LiTFSI:G4 (1:1) SIL, despite a substantial amount of solvent, behaves similar to pure ILs, showing strongly anti-correlated cation-anion motion.

The reason that LiTFSI:G4 (1:1) SIL shows such behavior is the formation of long-lived complexes between G4 molecules and Li^+, therefore effectively eliminating the ability of solvent molecules to efficiently participate in momentum exchange. The residence time of Li^+ with G4 molecules is on the order of hundreds of nanoseconds, a timescale on which these clusters diffuse distances much larger than their size. For example, at 373K on the time scale of Li^+-O_{G4} residence time of 305.4 ns, the average Li^+ mean squared displacement should be around 133.6 nm^2. Hence, on the time scales related to cation and anion diffusion, LiTFSI:G4 (1:1) SIL can be basically considered as IL and hence similar anti-correlated motion is observed between anion and Li-G4 complexes.

Concentration dependence. To further understand the mechanisms and correlations that lead to the low transference numbers and large negative values of β, we have extended our simulations to different compositions in the LiTFSI:G4 system. Specifically, we have investigated 1.0, 0.75, 0.5, and 0.25 LiTFSI:G4 ratios, which correspond to 2.64, 2.20, 1.70 and 0.93M salt concentrations, respectively, at 373K. With the increase of salt dilution, Li^+ continues to be primarily coordinated by G4 molecules, however the fraction of free G4 molecules (not participating in Li^+ coordination) increases from 8.5% at 1.0 to 21.3 %, 44.8% and 70.1% at 0.75, 0.5, and 0.25 compositions, respectively.

Overall, the dynamics of the system becomes significantly faster with increasing dilution. The diffusion coefficients are increasing, and the residence time of O_{G4} atoms in the Li^+ first coordination shell is decreasing substantially. However, the correlation between the Li^+-O_{G4} residence autocorrelation function (ACF) and Li^+ mean squared displacement, shown in Figure 5, does not change much. In order for the ACF to decay, Li^+ should travel basically the same distance independently of composition.

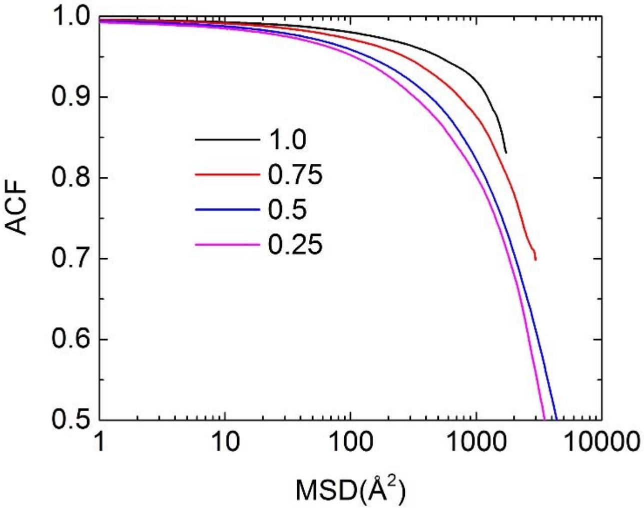

Figure 5 Relationship between Li-O_{G4} relaxation and MSD in LiTFSI:G4 electrolytes at different compositions.

Nevertheless, Figure 6 shows that addition of extra solvent leads to substantial changes in different contributions to the total conductivity as well as the dependence of resulting non-ideality parameters α and β, Li^+ transport t_{Li+}^{PFG} and transference t_{Li+}^{abc} numbers. As we can see from Figure 6a, while the relative (*i.e.,* normalized by the total conductivity) contributions of most terms have a weak concentration dependence, the σ_{+-} contribution to the overall conductivity changes from slightly negative at dilute solutions to highly positive as concentration is approaching the equimolar composition. As a result, the β parameter goes from slightly positive to highly negative value, which in turn leads to a decrease of simulation predicted t_{Li+}^{abc} from ~0.5 in dilute solution to 0.06 in the equimolar mixture. The latter effectively indicates that while there is plenty of ionic mobility at all concentrations and the total conductivity σ_{ion} varies between 8.7 and 13.6 mS/cm, the effective Li^+ transport ($\sigma_{ion} * t_{Li+}^{abc}$) of this electrolyte under anion-blocking conditions in a battery can drop by almost a factor of five (or larger) as the salt concentration increases towards equimolar composition. Such significant drop in Li^+ transference number makes the high concentration tetraglyme-based electrolyte to be rather inefficient. Therefore, while electrolytes with LiTFSI:G4 ratio less than 0.25 show the behavior expected for conventional electrolytes, the effect of diminishing Li^+ transference t_{Li+}^{abc} at high salt concentrations has been previously overlooked.

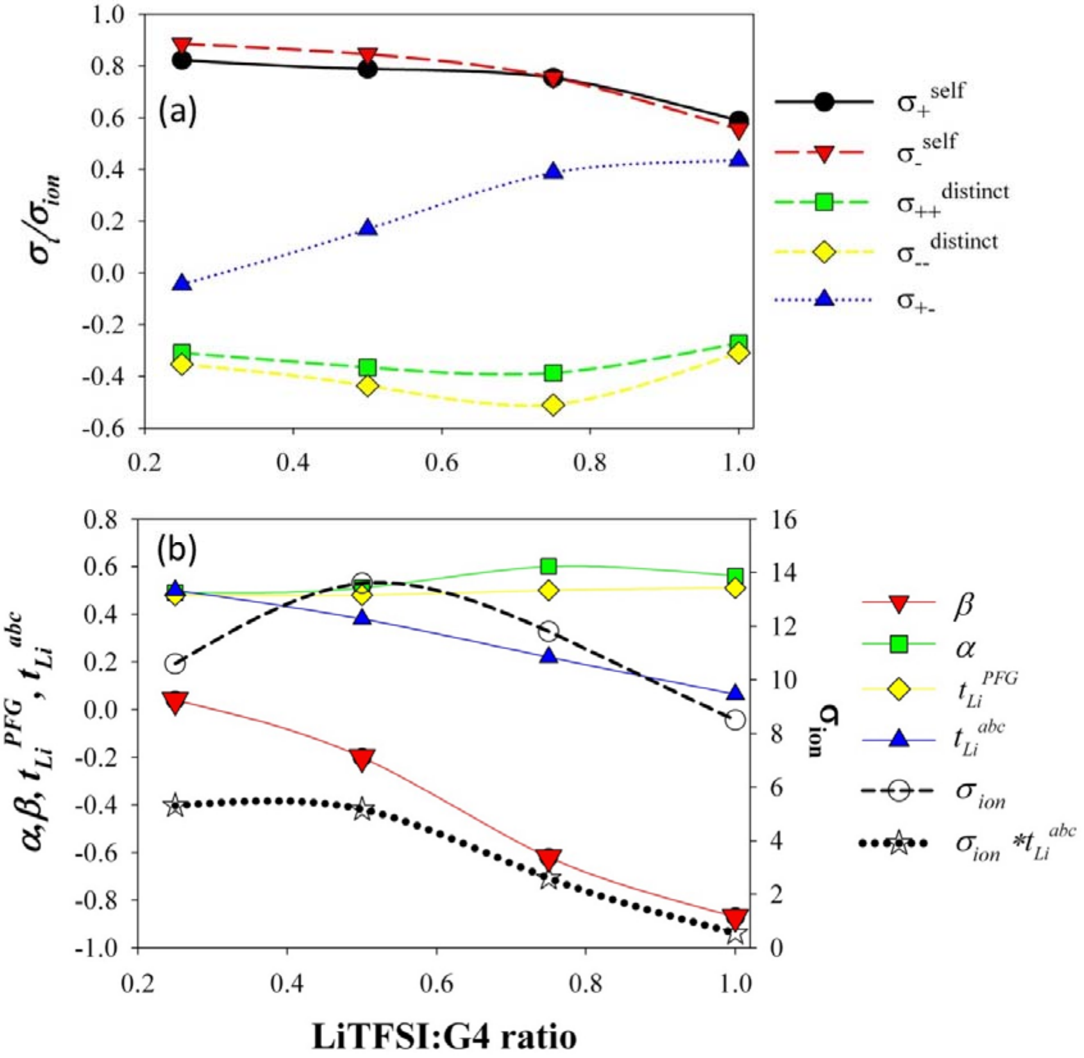

Figure 6. Concentration dependence of (a) normalized (by total conductivity) contributions from different ion-ion correlations, and (b) cation-anion correlation parameters, transport, and transference numbers as well as total conductivity and the product of conductivity and transference number. The data are obtained from MD simulations at 373 K.

Solvent-Li^+ residence time dependence. As we discussed above in the analysis of the LiTFSI:G4 (1:1) system, the long characteristic times for complexation of Li^+ and G4 molecules is one of the key factors that makes this SIL to have dynamic correlations similar to pure ILs and to have low Li^+ transference number under anion blocking conditions. Therefore, it is quite informative to see how the complexation (residence) time of glyme molecules with Li^+ affects the transference number t_{Li+}^{abc}. For this purpose, we have conducted simulations of other glyme-based electrolytes. Specifically we also investigated 1:1 compositions of LiTFSI:G3 and LiTFSI:G5 SILs. In addition, we have investigated electrolytes with smaller glymes (G1 and G2), but kept the same ratio between Li^+ and O_G as in systems containing longer glymes. For example, electrolyte with LiTFSI:G1(1:2) composition has the same Li^+:O_G ratio as in LiTFSI:G3 (1:1) electrolyte, and therefore the Li^+ environment in these two electrolytes can be considered similar, but G1 solvent molecules are only half long compared to G3. Since G1 molecules can only coordinate maximum two O_G with one Li^+, the binding energy (and hence the residence time) between Li^+ and G1 molecules is expected to be lower compared to that between Li^+ and G3 molecules. Similarly, the 1:2 composition of LiTFSI:G2 has the same Li^+:O_G ratio as in LiTFSI:G5 (1:1) electrolyte, while 1:1 ratio of LiTFSI and mixture of G1+G2 is similar to LiTFSI:G4 (1:1) electrolyte . Therefore, by simulating these additional electrolytes and varying the length of coordinating glyme molecules we can analyze systems with various Li-glyme residence times and correlate these residence times with t_{Li+}^{abc} values predicted from simulation. All additional systems were simulated at 373K and resulted in similar low fractions of "free" glyme molecules (*i.e.*, molecules not coordinating any Li^+): 2.5% in LiTFSI:G3 (1:1), 5.8% in LiTFSI:G5 (1:1), 9.2% in LiTFSI:G1 (1:2), 7.6% in LiTFSI:G2 (1:2), and 4.6% in LiTFSI:G1+G2 (1:1).

Note that with changing the molecular weight of glyme solvent we do not only affect the residence time of these molecules with Li^+, but also change electrolyte viscosity and diffusivity of all species in the system. Therefore, we choose the product of the Li^+-O_G residence time and the Li^+ self-diffusion coefficient ($\tau * D_{Li+}$) as effective correlation variable that reflects how far a Li-solvent complex diffuses before it begins to exchange solvent molecules with other complexes. On time scales shorter than τ, these electrolytes can be considered as ILs (*i.e.* demonstrating their

SIL character), where glyme solvents are strongly coupled with coordinating Li^+. On time scales longer than τ, glyme solvents start to exchange between different complexes and hence can facilitate with momentum exchange in the system. Hence if the product $\tau * D_{Li}$ is small, Li-solvent complexes do not diffuse much before they efficiently exchange momentum by exchanging solvent molecules and therefore motion of distinct ions does not have to be strongly coupled to satisfy the momentum conservation. If the product $\tau * D_{Li}$ is large, the diffusive motion of cation and anion are determined in IL-like environment, where solvent molecules do not represent an independent species, but rather can be considered as part of the cation complex. Figure 7 shows simulation predicted t_{Li+}^{abc} and β as a function of $\tau * D_{Li}$ for several glyme-based electrolytes, where the fraction of "free" (not coordinating Li^+) glyme molecules is small (less than 10%) and hence only the residence time of glyme molecules with Li^+ can influence the ion-ion correlations and Li^+ transference number. As we can see there is a clear correlation between these characteristics and $\tau * D_{Li}$. This plot indicates that short-glyme-based electrolytes are much more efficient for Li^+ transference than the longer-glyme-based electrolytes. The same should hold true for other solvents with short residence time in a complex with Li^+ ions. In fact, it has been found experimentally that high-concentration electrolytes based on DME, acetonitrile or ethyl acetate enable a rather fast charging/discharging of electrochemical cells, [26-28] indicating more efficient Li^+ ion transport under anion-blocking conditions than in SILs.

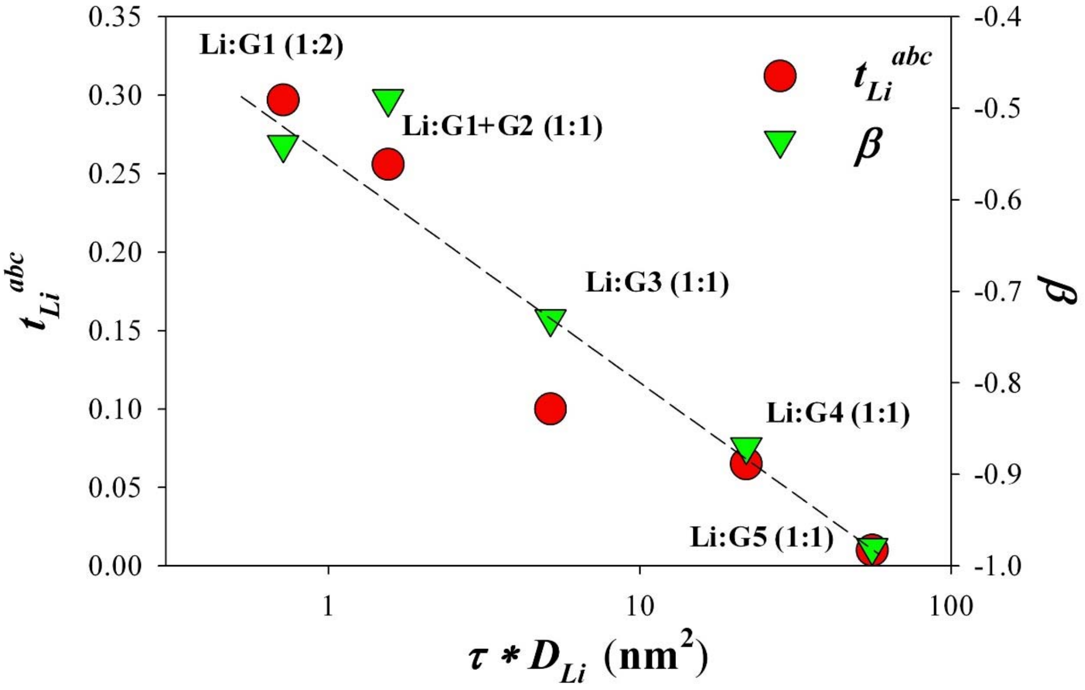

Figure 7. Dependence of the transference number t_{Li+}^{abc} *and of the cation-anion correlation parameter* β *on* Li^+ *displacement over its complexation time with glyme molecules. Data are obtained from simulations of various LiTFSI:glyme systems, where the fraction of free glyme molecules is always less than 10%.*

The importance of the residence time between Li^+ and glyme solvent is further supported by a simulation, where in LiTFSI:G4 (1:1) system we have introduced a harmonic bond between Li^+ and one G4 center oxygen atom, therefore fixing the coordination environment of Li^+ to be only with one glyme molecule during the entire simulation. Forcing Li^+ ions to be bound with the glyme central oxygen allows a compact wrapping of G4 molecules around a Li^+ ion, leading to optimal solvate complexes with minimal cross-interaction between them. This “ideal” SIL structure leads to ~40% larger self-diffusion coefficients of all species (indicating the efficiency of translational motion for solvate complexes), however it also results in $\beta \rightarrow -1.0$ and $t_{Li+}^{abc} \rightarrow 0.0$ indicating that Li^+ transference under anion blocking conditions is very small.

Conclusions.

By combining very-low-frequency impedance spectra of the prototypical solvate ionic liquid LiTFSI:G4 (1:1) between Li metal electrodes with atomistic MD simulations, we demonstrated that the Li^+ transference number of solvate ionic liquids under anion-blocking conditions can be much lower than the Li transport number obtained from PFG-NMR. This effect, which may also be relevant in other highly concentrated electrolytes, diminishes the efficiency of such electrolytes for battery applications. In order to provide sufficient dissociation of the Li salt at high concentrations, solvent molecules need to have a strong binding energy with Li^+ (or with anion) in order to compete with the strong cation-anion binding (*e.g.*, -140.9 kcal/mol for Li-TFSI binding reported from quantum chemistry calculations).[28] In glyme-based SILs with a 1:1 salt:solvent ratio, such a strong interaction between Li^+ and glyme molecules leads to long residence times of solvent molecules near Li^+ ions and results in formation of long-lived complexes. This complexation leads to strong anti-correlated motion of distinct ions in the system, including the cation-anion anti-correlations. While the overall mobility of ions is reasonably high and the Li^+ transport number is close to 0.5, the anti-correlated motion in combination with anion blocking condition results in very low Li^+ transference numbers (0.02-0.06). Such behavior is related to the momentum conservation constraint and inability of glyme molecules complexed with Li^+ to support the momentum exchange between ions. As we demonstrated above and have also illustrated in Figure 8, in order to overcome this detrimental effect for battery applications, one has to modify the electrolyte to improve the momentum exchange in the system and thus to reduce strongly anti-correlated motion of ions. This can be done either by 1) diluting electrolyte with additional solvent molecules that are not complexing with Li^+ ions or 2) decreasing the residence time for solvent molecules near Li^+ cation. The latter can be achieved by switching to shorter glyme molecules, but keeping the Li^+:O_G ration the same. In both approaches, solvent molecules facilitate momentum exchange in the system and therefore the momentum conservation in the system can be accomplished without strong dynamic correlations between ions. This, in turn, leads to increase of Li^+ transference number. So far, this aspect has been overlooked when considering high-salt concentration electrolyte or SILs for battery applications.

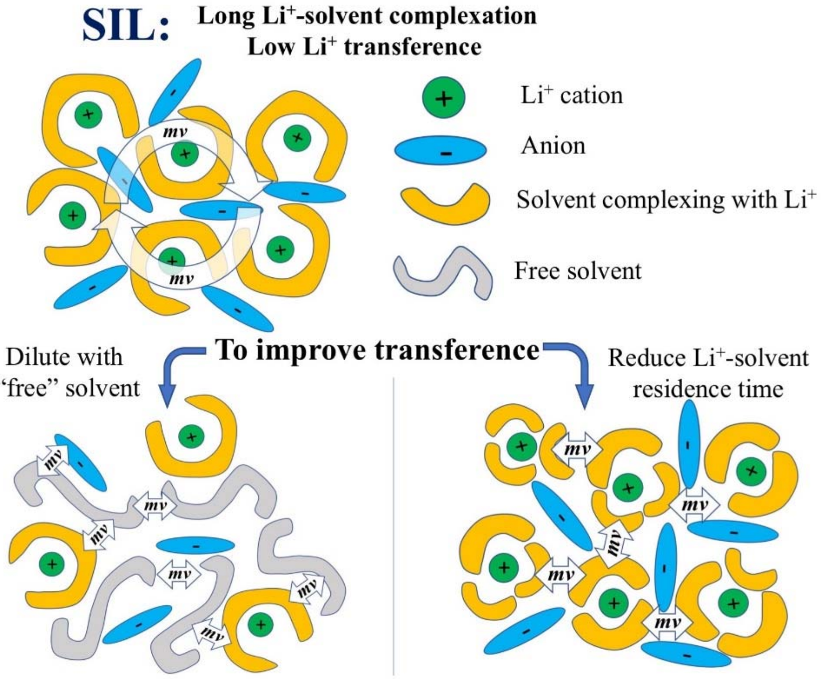

Figure 8. Schematic illustration of SIL with low Li^+ transference number due to momentum conservation constrain and two possible strategies to facilitate the momentum exchange in electrolyte and to increase Li^+ transference.

We note that applicability of an electrolyte in a Li-ion battery is not only related to its ion transport properties, but is also influenced by other physiochemical and electrochemical properties, such as thermal stability, vapor pressure and electrochemical stability window. With regard to these three properties, longer-glyme-based electrolytes (containing G4 and G5 molecules) are superior to short-glyme-based electrolytes (containing G1 molecules). Consequently, Li salt / glyme mixtures containing medium-sized glyme molecules, such as G2 or G3, may be the most promising electrolytes with a good compromise between Li^+ transference under anion-blocking conditions and other physicochemical/electrochemical properties. These electrolytes are located at the border between concentrated electrolyte solutions and solvate ionic liquids.[29]

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Conflicts of interest

There are no conflicts to declare.

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Appendix

A. Derivation of salt diffusion coefficient

In a 1-1 electrolyte with only two types of univalent ions, the Onsager reciprocal relations predict the following expressions for the molar fluxes of cations, J_+, and anions, J_-, and their electrochemical potential gradients, $\mathrm{d}\tilde{\mu}_+/\mathrm{d}x$, and $\mathrm{d}\tilde{\mu}_-/\mathrm{d}x$, respectively:

$$J_+ = -\left(\frac{\sigma_{++}}{F^2}\frac{\mathrm{d}\tilde{\mu}_+}{\mathrm{d}x} + \frac{\sigma_{+-}}{F^2}\frac{\mathrm{d}\tilde{\mu}_-}{\mathrm{d}x}\right) \quad \text{(A1)}$$

$$J_- = -\left(\frac{\sigma_{--}}{F^2}\frac{\mathrm{d}\tilde{\mu}_-}{\mathrm{d}x} + \frac{\sigma_{+-}}{F^2}\frac{\mathrm{d}\tilde{\mu}_+}{\mathrm{d}x}\right) \quad \text{(A2)}$$

Here, σ_{++}, σ_{--}, and σ_{+-} are transport coefficients, while F denotes the Faraday constant. The electrochemical potential gradient of the cations, $\mathrm{d}\tilde{\mu}_+/\mathrm{d}x$, and of the anions, $\mathrm{d}\tilde{\mu}_-/\mathrm{d}x$, respectively, are given by:

$$\frac{\mathrm{d}\tilde{\mu}_i}{\mathrm{d}x} = z_i F\frac{\mathrm{d}\varphi}{\mathrm{d}x} + RT\,\frac{\mathrm{d}\ln(a_i)}{\mathrm{d}x} \quad \text{(A3)}$$

Here, φ is the electrical potential, while a_i and z_i denotes the charge number and the activity of ion type i.

Inserting (A3) into (A1) and (A2) results in:

$$J_+ = -\left(\frac{\sigma_{++}}{F^2}\left[F\frac{\mathrm{d}\varphi}{\mathrm{d}x} + RT\,\frac{\mathrm{d}\ln(a_+)}{\mathrm{d}x}\right] + \frac{\sigma_{+-}}{F^2}\left[-F\frac{\mathrm{d}\varphi}{\mathrm{d}x} + RT\,\frac{\mathrm{d}\ln(a_-)}{\mathrm{d}x}\right]\right) \quad \text{(A4)}$$

$$J_- = -\left(\frac{\sigma_{--}}{F^2}\left[-F\frac{\mathrm{d}\varphi}{\mathrm{d}x} + RT\,\frac{\mathrm{d}\ln(a_-)}{\mathrm{d}x}\right] + \frac{\sigma_{+-}}{F^2}\left[F\frac{\mathrm{d}\varphi}{\mathrm{d}x} + RT\,\frac{\mathrm{d}\ln(a_+)}{\mathrm{d}x}\right]\right) \quad \text{(A5)}$$

Neutral salt diffusion implies that the molar fluxes of cations and anions are identical, i.e. $J_+ = J_- := J$. Furthermore, we replace the ion activities by an average ion activity by $a_\pm = \sqrt{a_+ a_-}$. This leads to:

$$\frac{\mathrm{d}\varphi}{\mathrm{d}x} = \frac{\sigma_{--} - \sigma_{++}}{\sigma_{++} + \sigma_{--} - 2\,\sigma_{+-}}\frac{RT}{F}\frac{\mathrm{d}\ln(a_\pm)}{\mathrm{d}x} \quad \text{(A6)}$$

Inserting (A6) into (A1) then results in:

$$J = -\frac{2\,\sigma_{++}\sigma_{--} - 2\,(\sigma_{+-})^2}{\sigma_{++} + \sigma_{--} - 2\sigma_{+-}}\,\frac{RT}{F^2}\,\frac{\mathrm{d}\ln(a_\pm)}{\mathrm{d}x}$$

$$= -\frac{\sigma_{++}\sigma_{--} - (\sigma_{+-})^2}{\sigma_{++} + \sigma_{--} - 2\sigma_{+-}}\,\frac{2RT}{F^2 c_{salt}}\,\frac{dln(a_\pm)}{dlnc_{salt}}\,\frac{\mathrm{d}c_{salt}}{\mathrm{d}x} \quad \text{(A7)}$$

Here, c_{salt} is the salt concentration in the electrolyte.

Eq. (A7) represents Fick's first law with the salt diffusion coefficient:

$$D_{salt} = \frac{\sigma_{++}\sigma_{--} - (\sigma_{+-})^2}{\sigma_{++} + \sigma_{--} - 2\sigma_{+-}}\,\frac{2RT}{F^2 c_{salt}}\,\frac{\mathrm{d}\ln(a_\pm)}{\mathrm{d}\ln(c_{salt})} \quad \text{(A8)}$$

and with $\mathrm{dln}(a_{\pm})/\mathrm{dln}(c_{salt})$ denoting the thermodynamic factor.

For electrolytes without dynamic ion correlations, we have $\sigma_{+-} = 0$, $\sigma_{++} = (c_{salt}\, F^2 D_+)/RT$, and $\sigma_{--} = (c_{salt}\, F^2 D_-)/RT$, so that we recover the well-known expression for the salt diffusion coefficient of such electrolytes: $D_{salt}^{no\ ion\ corr} = (2D_+D_-)/(D_+ + D_-) \ \cdot \mathrm{dln}(a_{\pm})/\mathrm{dln}(c_{salt})$.

B. Derivation of concentration cell potential with transference

We consider a concentration cell consisting of two half cells with Li metal electrodes in contact to electrolytes with different average ion activities, $a_{\pm}^{(1)}$ and $a_{\pm}^{(2)}$. Between the half cells, ion transference is enabled, e.g. by means of a frit. The Nernst potential difference between the Li metal electrodes and the electrolytes is then given by:

$$\Delta\varphi_{Nernst} = \frac{RT}{F} \cdot \left(\ln(a_{\pm}^{(2)}) - \ln(a_{\pm}^{(1)})\right) = \frac{RT}{F}\,\Delta\ln(a_{\pm}) \qquad \text{(B1)}$$

In equilibrium, only neutral salt diffusion across the frit is possible. Consequently, the diffusion potential across the frit can be deduced from Eq. A(6):

$$\Delta\varphi_{diffusion} = \frac{\sigma_{--} - \sigma_{++}}{\sigma_{++} + \sigma_{--} - 2\,\sigma_{+-}} \frac{RT}{F}\,\Delta\ln(a_{\pm}) \qquad \text{(B2)}$$

Thus, the overall cell potential difference is given by:

$$\Delta\varphi = \Delta\varphi_{Nernst} + \Delta\varphi_{diffusion} = \frac{\sigma_{--} - \sigma_{+-}}{\sigma_{++} + \sigma_{--} - 2\,\sigma_{+-}} \frac{2RT}{F}\,\Delta\ln(a_{\pm}) \qquad \text{(B3)}$$

For small concentration and activity differences, we can write:

$$\frac{\mathrm{d}\Delta\varphi}{\mathrm{dln}(c_{salt})} = \frac{\sigma_{--} - \sigma_{+-}}{\sigma_{++} + \sigma_{--} - 2\,\sigma_{+-}} \frac{2RT}{F} \frac{\mathrm{dln}(a_{\pm})}{\mathrm{dln}(c_{salt})} \qquad \text{(B4)}$$

C. Calculation of Onsager coefficients and thermodynamic factor from experimental quantities

We use the experimentally accessible quantities σ_{ion}, $t_{Li+}^{abc,exp}$, D_{salt}, and $\mathrm{d}\Delta\varphi/\,\mathrm{dln}(c_{salt})$ to define the following four parameters:

$$A_1 \equiv \sigma_{ion} = \sigma_{++} + \sigma_{--} - 2\sigma_{+-} \qquad \text{(C1)}$$

$$A_2 \equiv \sigma_{ion} \cdot t_{Li+}^{abc} = \sigma_{++} - \frac{\sigma_{+-}^2}{\sigma_{--}} \qquad \text{(C2)}$$

$$A_3 \equiv \frac{D_{salt} \cdot \sigma_{ion} \cdot c_{salt} \cdot F^2}{2RT} = (\sigma_{++} \cdot \sigma_{--} - \sigma_{+-}^2) \cdot \frac{\mathrm{dln}(a_{\pm})}{\mathrm{dln}(c_{salt})} \qquad \text{(C3)}$$

$$A_4 \equiv \frac{d\Delta\varphi}{\mathrm{dln}(c_{salt})} \cdot \frac{F}{2RT} \cdot \sigma_{ion} = (\sigma_{--} - \sigma_{+-}) \cdot \frac{\mathrm{dln}(a_{\pm})}{\mathrm{dln}(c_{salt})} \text{(C4)}$$

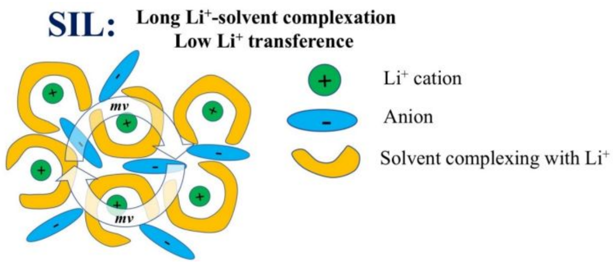
Solving (C1)-(C4) for the three Onsager coefficients and the thermodynamic factor yields:

$$\sigma_{++} = \frac{1}{A_2^2 A_4^2} \cdot (A_1 A_2^2 A_4^2 - 2A_1 A_2 A_3 A_4 + A_1 A_3^2 + 2A_2^2 A_3 A_4 - A_2 A_3^2) \qquad \text{(C5)}$$

$$\sigma_{--} = \frac{A_3^2 \cdot (A_1 - A_2)}{A_2^2 A_4^2} \qquad \text{(C6)}$$

$$\sigma_{+-} = \frac{-A_1 A_2 A_3 A_4 + A_1 A_3^2 + A_2^2 A_3^2 A_4 - A_2 A_3^2}{A_2^2 A_4^2} \qquad \text{(C7)}$$

$$\frac{\mathrm{dln}(a_{\pm})}{\mathrm{dln}(c_{salt})} = -\frac{A_2 A_4^2}{A_3 \cdot (A_2 - A_1)} \qquad \text{(C8)}$$



Anti-correlated motion of cations and anions leads to very low Li^+ transference numbers in solvate ionic liquids.