Supporting information for:

Molecular Insights into Temperature-Driven Transport Mechanisms in EC-LiTFSI Electrolytes

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S1. Mean square displacement

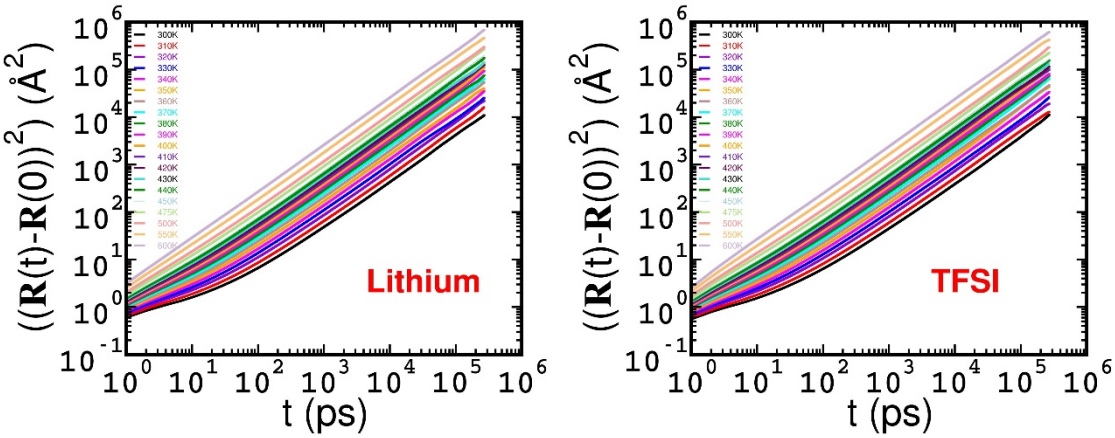


Fig. S1: Mean square displacement of (a) lithium ions and (b) TFSI ions at different temperatures.

S2. Equilibrated density

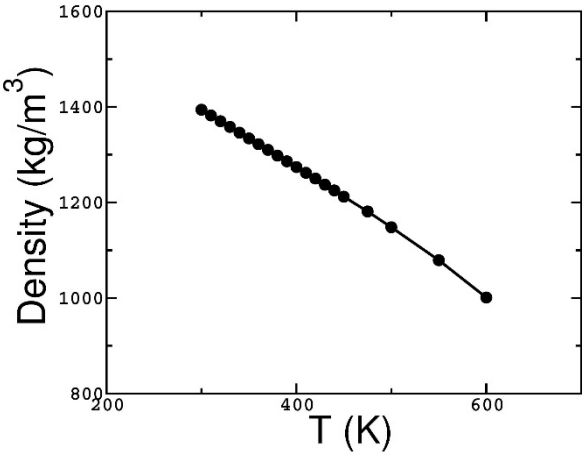
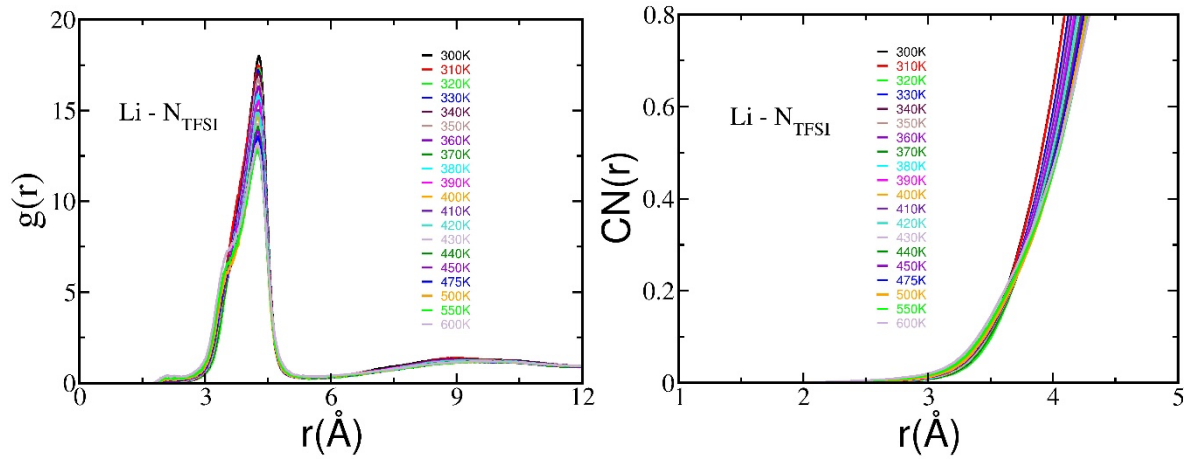


Fig. S2: Equilibrated density of the EC-LiTFSI electrolyte as a function of temperature.

S3. Radial distribution function and coordination number



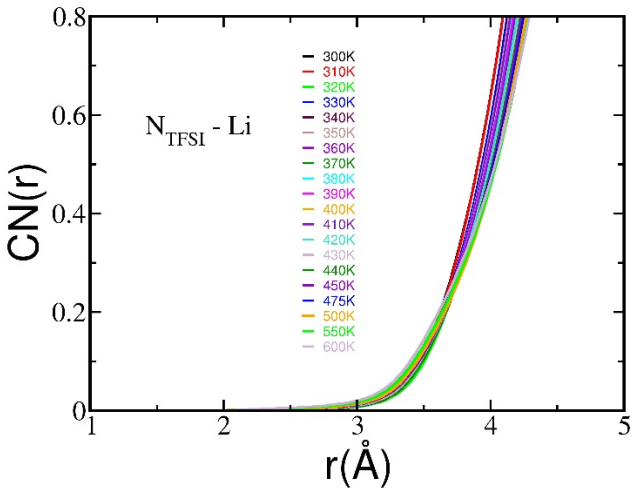


Fig. S3: Radial distribution function representing the (a) lithium-TFSI interactions and the respective coordination numbers: (b) Number of coordinating TFSI ions around lithium ions in the first coordination shell, and the (c) Number of coordinating lithium ions around TFSI ions in the first coordination shell at different temperatures investigated.

S4. Ion-pair correlation function

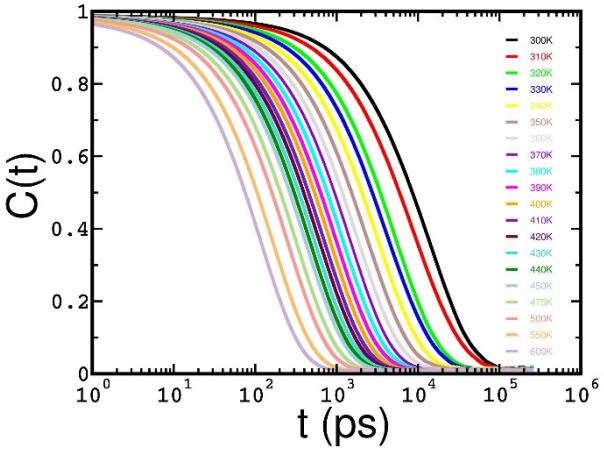


Fig. S4: Ion-pair correlation functions at different temperatures investigated.

S5. Walden's analysis

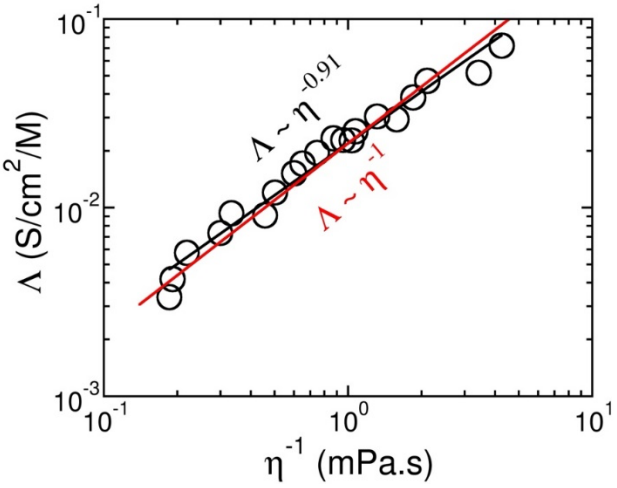


Fig. S5: Relationship between ionic conductivity and viscosity

S6. Einstein and Nernst-Einstein conductivity

The ionic conductivity, including ion–ion correlations, was calculated using the Einstein relation, which evaluates the time derivative of the mean-squared charge displacement of all ions. The expression is given as,

$$\sigma = \lim_{t \to \infty} \frac{e^2}{6tVk_BT} \sum_i \sum_{j>i} \langle z_i z_j \big(\boldsymbol{R}_i(t+t') - \boldsymbol{R}_i(t')\big)\Big(\boldsymbol{R}_j(t+t') - \boldsymbol{R}_j(t')\Big)\rangle,$$

where k_B, e, V, and T are the Boltzmann constant, electronic charge, system volume, and temperature, respectively.

Table S1: Einstein and Nernst-Einstein conductivity values showing consistent increase with temperature for the EC-LiTFSI electrolyte.

T (K)	Einstein Conductivity (S/cm)	NE Conductivity (S/cm)
300	1.65E-03	3.35E-03
320	1.68E-03	5.76E-03
370	5.43E-03	1.52E-02
400	1.25E-02	2.33E-02

S7: System Size Effects on Ionic Diffusion

To assess the influence of the simulation box length on the calculated diffusion coefficients, we performed additional molecular dynamics simulations at four different cubic box lengths, $L = 50$, 60 (original box corresponding to the results shown in the main paper), 70, and 80 Å. For each system, the self-diffusion coefficients of cations (D^+) and anions (D^-) were obtained from the long-time slope of the mean-squared displacement.

Finite size effects in periodic systems arise from hydrodynamic interactions mediated by the simulation box and can be corrected following the Yeh-Hummer formalism (*J. Phys. Chem. B* 2004, **108**, 15873-15879). In this framework, the *true* diffusion coefficient obtained from a finite periodic box (D_L^{PBC}) is related to the infinite-system value (D_{true}) as

$$D_{\mathrm{true}} = D_L^{\mathrm{PBC}} + \frac{2.837\, k_{\mathrm{B}}T}{6\pi\eta L},$$

where k_{B} is the Boltzmann constant, T is the temperature, η is the shear viscosity of the liquid, and L is the box length. This relation predicts a linear dependence of D_L on $1/L$, enabling extrapolation to $1/L \to 0$.

Table S2 summarizes the diffusion coefficients obtained for each box size, and **Fig. S6** shows the corresponding D_L vs $1/L$ plots. Both cations and anions exhibit a weak but monotonic increase in D_L with system size, consistent with hydrodynamic finite size effects. Linear extrapolation yields infinite system diffusion coefficients of $D^+_{\mathrm{true}} = 14.114 \times 10^{-7}$ cm^2/s and $D^-_{\mathrm{true}} = 13.732 \times 10^{-7}$ cm^2/s, respectively for cations and anions. The magnitude of the system size dependence is small compared to the overall variation of diffusion with temperature and composition.

L (nm)	1/L (nm-1)	D_+ (10^{-7} cm²/s)	D_- (10^{-7} cm²/s)
5	0.200	7.09	7.20
6 (original box)	0.167	8.51	7.61
7	0.143	9.16	8.50
8	0.125	9.71	9.90

Table S2. Diffusion coefficients of cations D_+ and anions D_- obtained from molecular dynamics simulations performed at different cubic box lengths L. The corresponding inverse box lengths 1/L are shown for application of the Yeh–Hummer finite size correction.

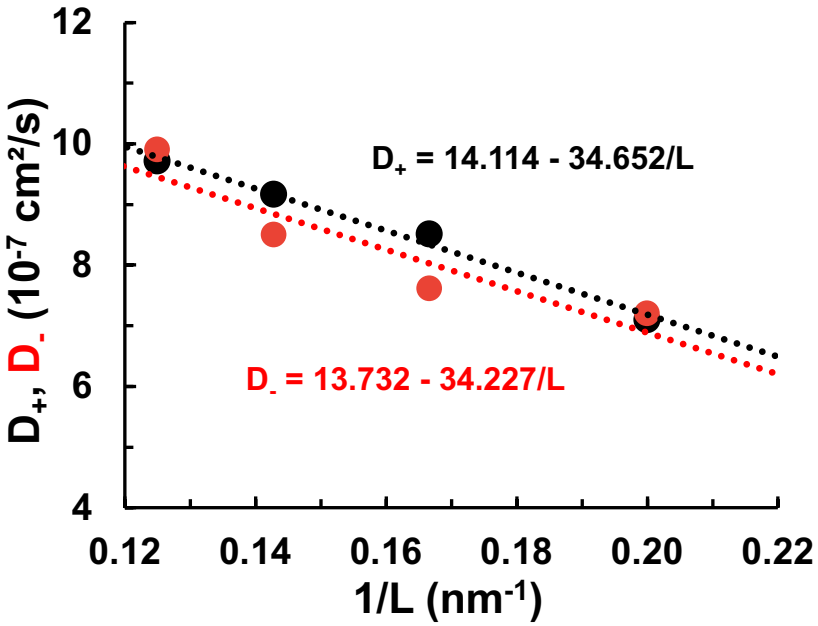


Fig. S6. System-size dependence of the ionic diffusion coefficients. Plots of D versus 1/L for (a) cations (black) and (b) anions (red), along with linear fits, following the Yeh–Hummer finite size correction formalism. The results exhibit a weak but systematic size dependence consistent with hydrodynamic finite size effects.