Electronic Supplementary Information (ESI): Coupled Ion Transport in Concentrated PEO-LiTFSI Polymer Electrolytes

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Table S1: Number of salt molecules and salt concentration of simulated systems

n	$r = $ Li:EO	No of salt molecules	Molar concentration $(\mathrm{mol\,L^{-1}})$
23	0.02	80	0.42
23	0.05	200	0.95
23	0.10	400	1.66
23	0.17	666	2.36
23	0.33	1332	3.51
23	0.50	1998	4.17
100	0.02	80	0.43
100	0.05	200	0.98
100	0.10	400	1.70
100	0.17	666	2.40
100	0.33	1332	3.56
100	0.50	1998	4.23

Finite-size effects

Finite-size effects were evaluated by studying two systems with concentration r = 0.17 and PEO chain length of 100 monomers of double size. The ionic conductivity and ionicity

are lower in the bigger system compared to the normal system size. The Li-ion transport

numbers are similar. The results are summarized in Table S2.

Table S2: Finite-size effects of transport properties in system with concentration r $=$ 0.17 and PEO chain length of n $=$ 100

System size	σ (mS cm^{-1})	σ^{NE} (mS cm^{-1})	t_{Li^+}	$t_{\mathrm{Li}^+}^{\mathrm{NE}}$	Ionicity
Normal size	3.49	2.21	0.52	0.078	1.58
Double size	2.73	2.10	0.52	0.063	1.30

Coordination data

Table S3: Fraction of free Li-ions (not coordinated by anions). Fraction of Li-ions coordinated to number of anions. Fraction of Li-ions coordinated to number of PEO chains

n	$r =$ Li:EO	Free-Li ions	1 anion	2 anions	$\geq$3 anions	0 chains	1 chain	2 chains
23	0.02	0.99	0.01	0	0	0	0.96	0.04
23	0.05	0.99	0.01	0	0	0	0.97	0.03
23	0.10	0.98	0.02	0	0	0	0.98	0.02
23	0.17	0.91	0.09	0	0	0	0.99	0.01
23	0.33	0.25	0.27	0.22	0.26	0.23	0.77	0
23	0.50	0.14	0.17	0.20	0.49	0.44	0.56	0
100	0.02	0.99	0.01	0	0	0	0.96	0.04
100	0.05	0.99	0.01	0	0	0	0.98	0.02
100	0.10	0.98	0.02	0	0	0	0.99	0.01
100	0.17	0.91	0.09	0	0	0	0.99	0.01
100	0.33	0.25	0.24	0.24	0.27	0.22	0.78	0
100	0.50	0.14	0.16	0.21	0.49	0.43	0.57	0

Transport properties at 353 K

Table S4: Transport properties of systems with chain length $n = 100$ at $353\,\mathrm{K}$. Average values from two simulations are provided.

r	L_{++} $(\mathrm{m^2\,s^{-1}})$	L_{--} $(\mathrm{m^2\,s^{-1}})$	L_{+-} $(\mathrm{m^2\,s^{-1}})$	σ $(\mathrm{mS\,cm^{-1}})$	σ^{NE} $(\mathrm{mS\,cm^{-1}})$	$t_{\mathrm{Li^+}}$ (-)	$t_{\mathrm{Li^+}}^{\mathrm{NE}}$ (-)	Ionicity (-)
0.10	1.5×10^{-13}	2.2×10^{-13}	-1.5×10^{-13}	0.25	0.25	0.47	0.38	1.00
0.17	2.5×10^{-13}	2.5×10^{-13}	-2.3×10^{-13}	0.37	0.24	0.51	0.15	1.53
0.33	8.4×10^{-14}	3.0×10^{-14}	-3.6×10^{-14}	0.056	0.029	0.73	0.32	1.95

Glass transition temperature

Table S5: Glass transition temperatures (T_g) of selected polymer electrolyte systems determined from simulations. Average values and standard deviation from three parallels are provided.

n	$r = \mathrm{Li:EO}$	T_g (°C)
23	0.10	-26.6 ± 0.8
23	0.17	-22.0 ± 12.1
23	0.33	-21.1 ± 11.7
100	0.10	-17.7 ± 3.9
100	0.17	-24.0 ± 5.1
100	0.33	-10.2 ± 7.7

Table S6: Cutoff distances used to compute residence times for the different systems

n	$r =$ Li:EO	Li-ether O cutoff (Å)	Li-TFSI N cutoff (Å)
23	0.02	3.68	5.00
23	0.05	3.66	5.00
23	0.10	3.71	5.00
23	0.17	3.71	5.00
23	0.33	3.60	5.42
23	0.50	3.62	5.47
100	0.02	3.66	5.00
100	0.05	3.66	5.00
100	0.10	3.69	5.00
100	0.17	3.71	5.00
100	0.33	3.60	5.42
100	0.50	3.62	5.47
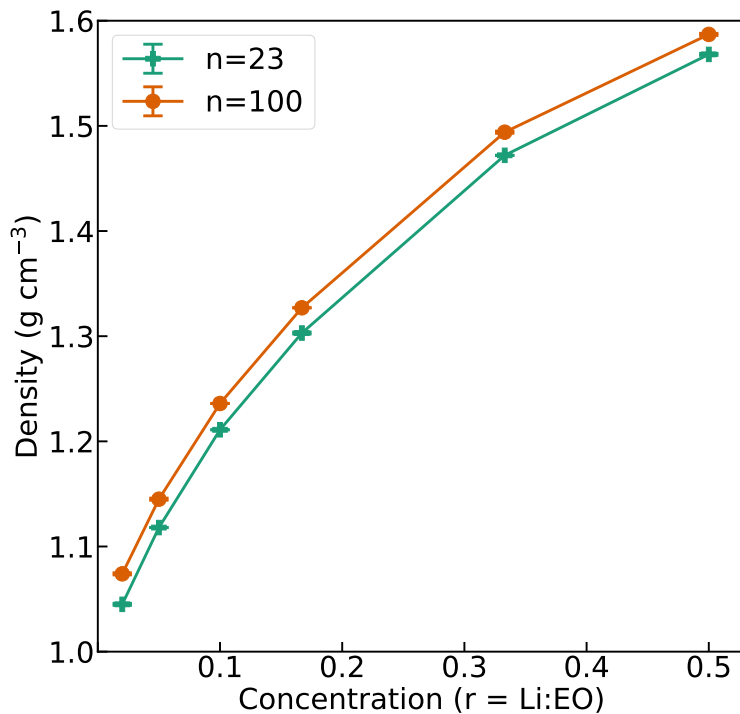
Figure S1: Density of systems as function of salt concentration.
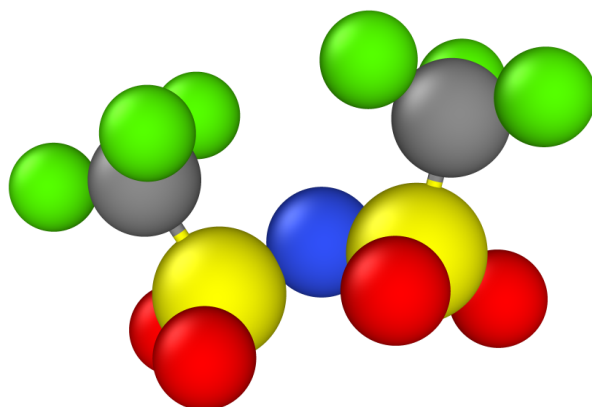
Figure S2: MD snapshot of TFSI anion. Fluorine is green, carbon is grey, sulphur is yellow, oxygen is red, nitrogen is blue.
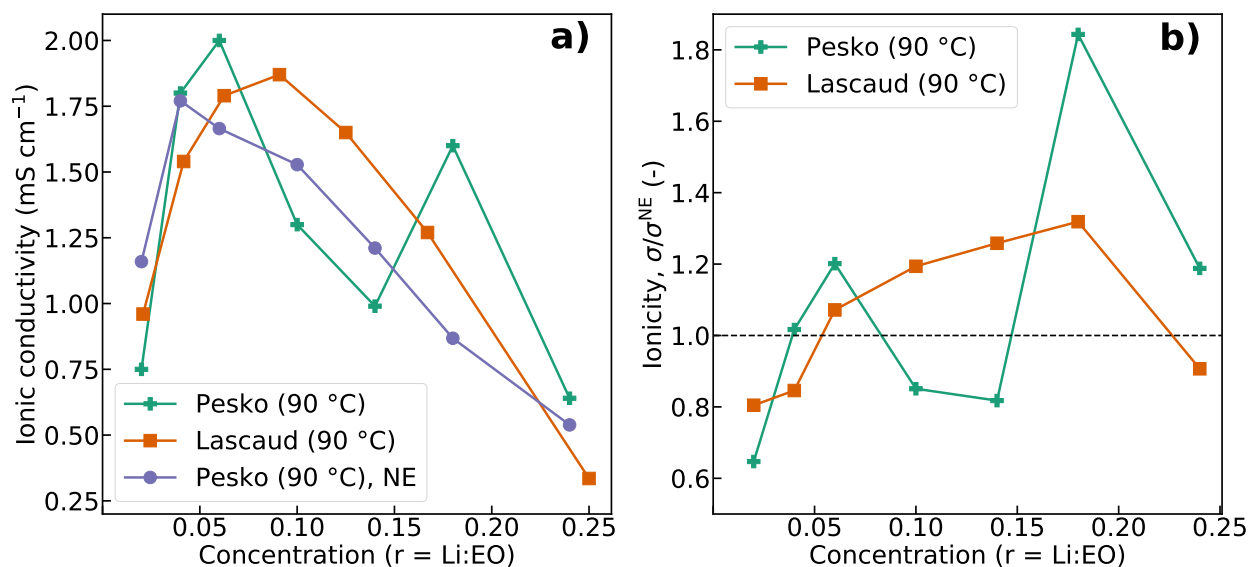

Figure S3: (a) Experimental ionic conductivity and (b) ionicity calculated from the data in (a) as function of salt concentration. The data labelled Pesko (90 °C), NE was calculated using the Nernst-Einstein approximation for ionic conductivity and the self-diffusion coefficients of Li and F species measured by Pesko and Timachova *et al.* using pfg-NMR[1,2]. The other experimental data was measured using electrochemical impedance spectroscopy (EIS)[3,4]. The ionicities in (b) were calculated by dividing the EIS data by the NE data. The ionicity of the Lascaud data was calculated by fitting a polynomial function to the data and dividing by the NE values of the same concentrations.
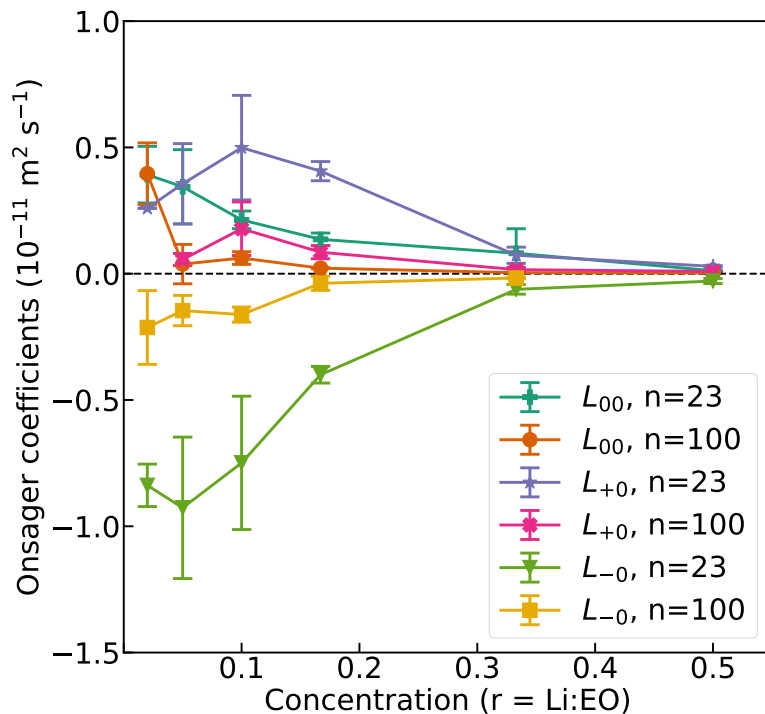
Figure S4: Onsager coefficients involving the solvent (PEO) as a function of salt concentration, denoted as 0 in the plot. These coefficients are dependent on the coefficients presented in the main part. Note that several of the L_{00} values did not reach the diffusive regime.
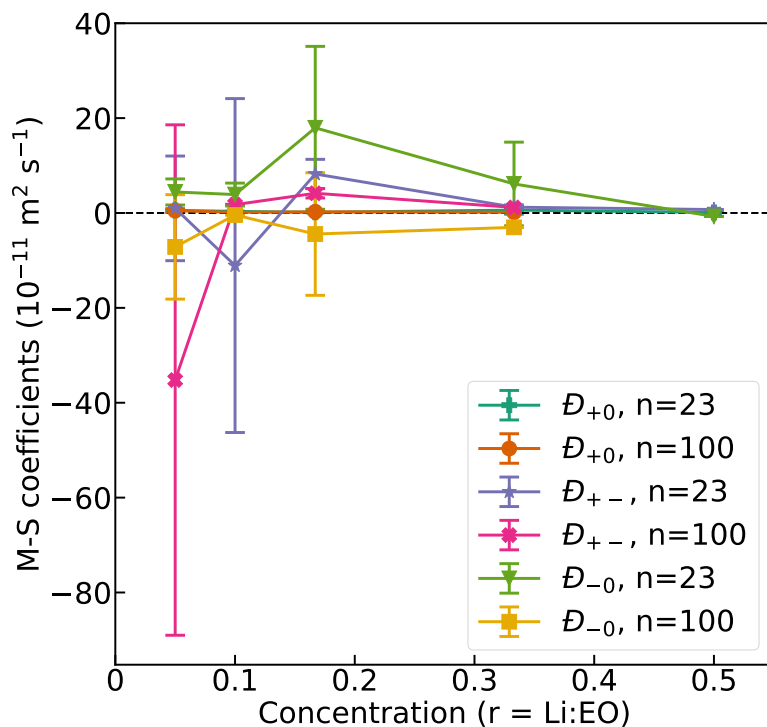

Figure S5: Maxwell-Stefan coefficients as a function of salt concentration. The solvent (PEO) is denoted as 0 in the plot.
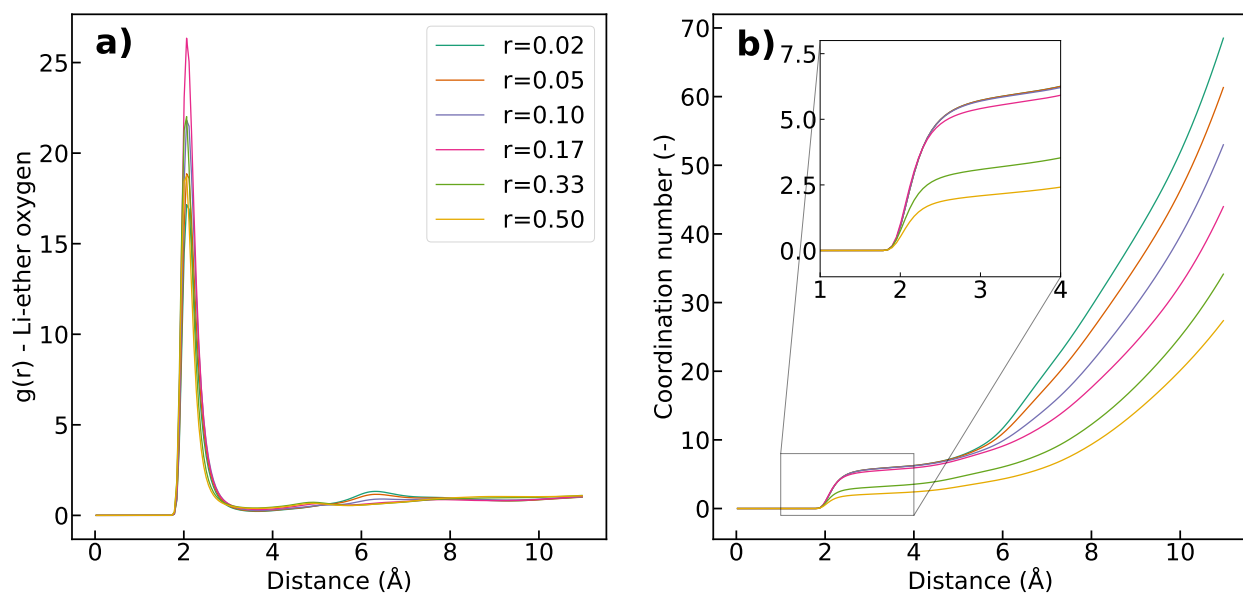
Figure S6: a) Radial distribution functions and b) coordination numbers of Li and ether oxygen for the different salt concentrations with chain length n = 100.
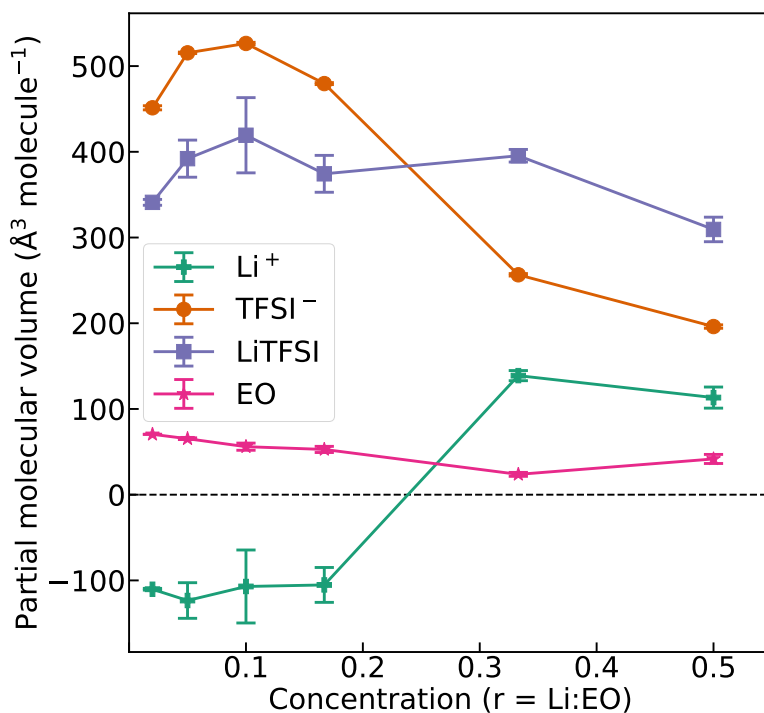

Figure S7: Partial molecular volumes of Li$^+$, TFSI$^-$ and ethylene oxide (EO) for the different salt concentrations with chain length n = 100. The partial molecular volume of LiTFSI is the sum of the volumes of Li$^+$ and TFSI$^-$.
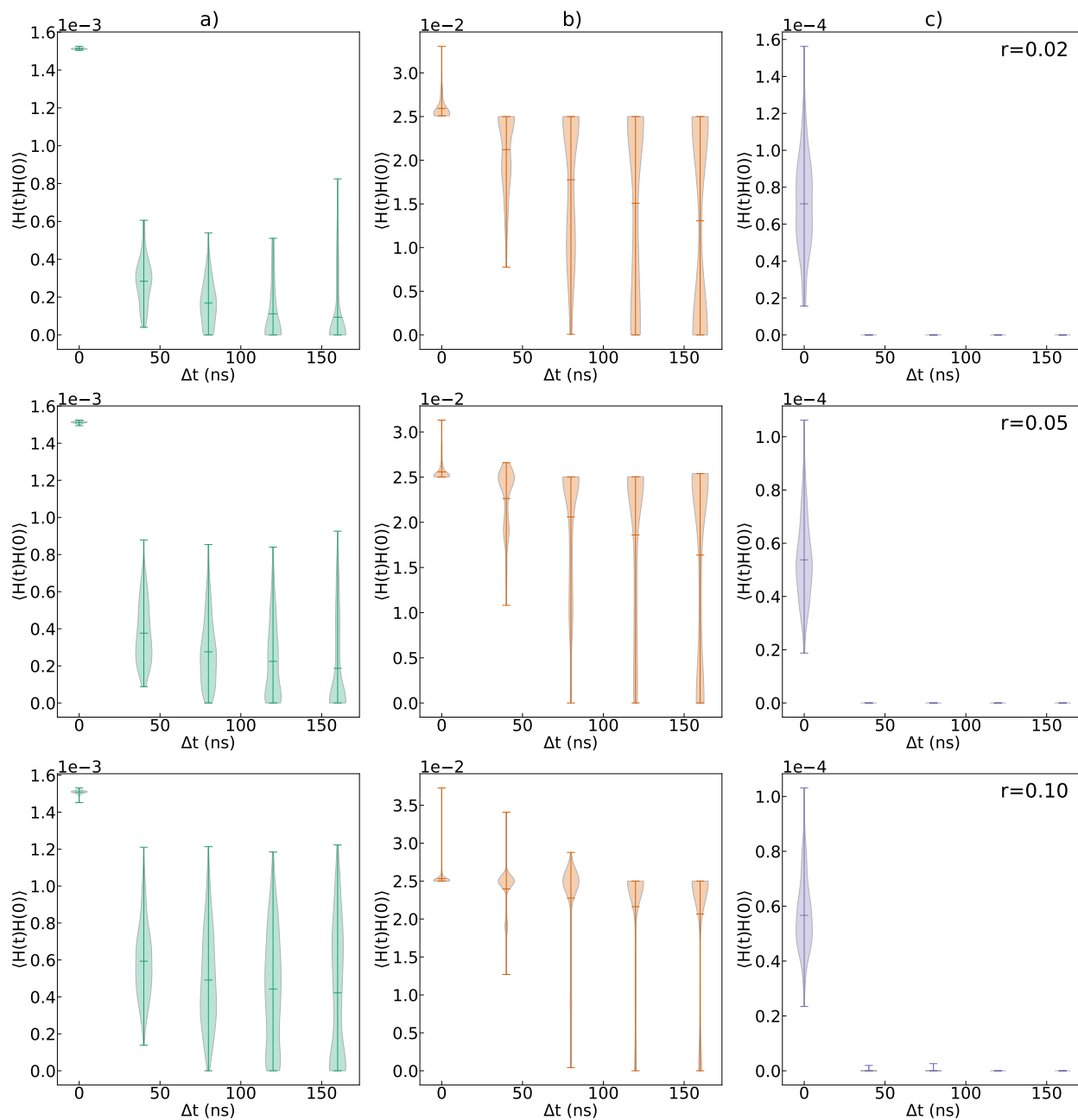
Figure S8: Distribution of the pair lifetime correlation functions at selected time intervals for (a) Li-ether oxygen, (b) Li-PEO chain, and (c) Li-TFSI for the systems with chain length n = 100. Salt concentrations are written in the rightmost plots. Mean and extreme values are marked in the violin plots.
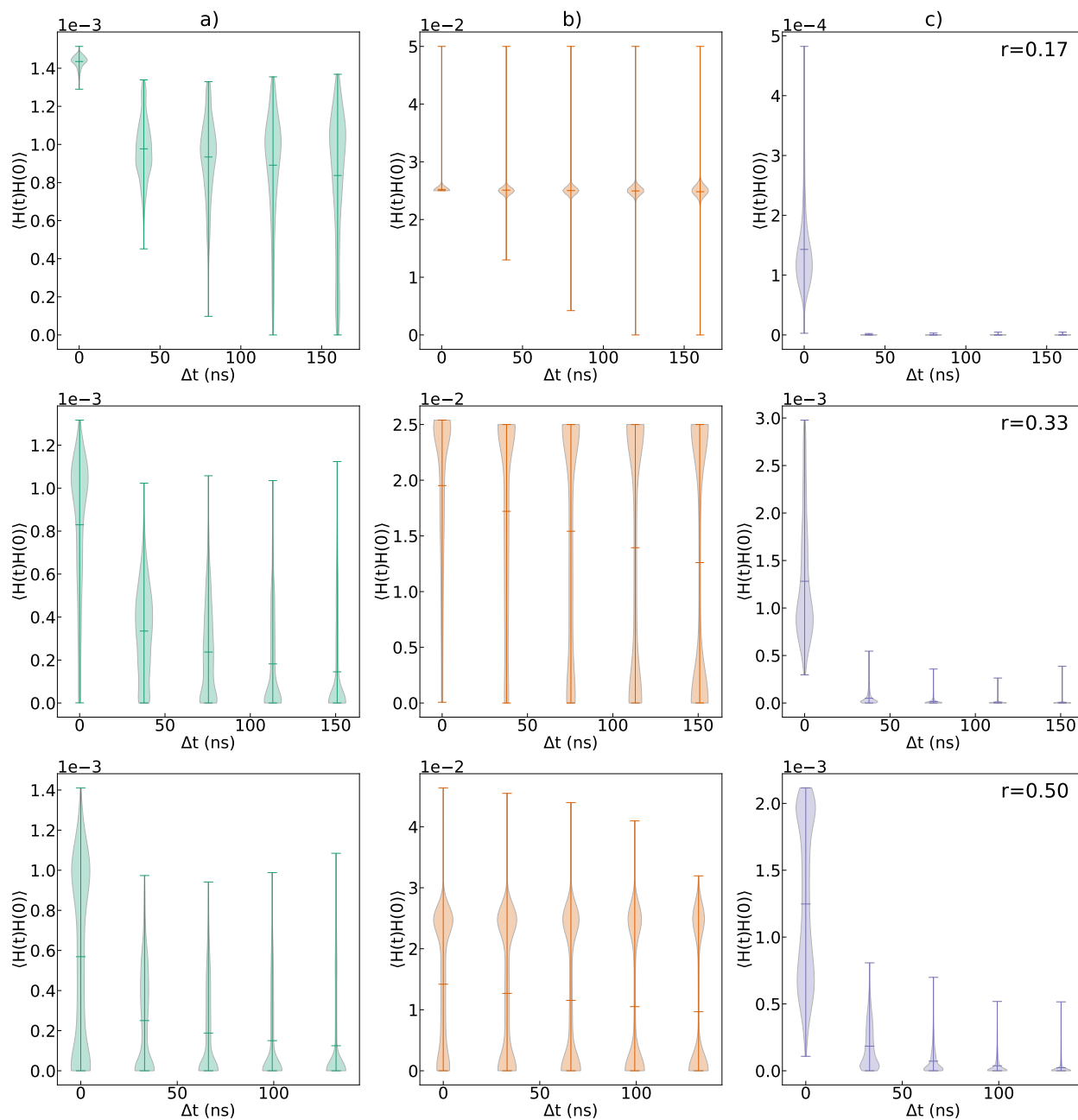
Figure S9: Distribution of the pair lifetime correlation functions at selected time intervals for (a) Li-ether oxygen, (b) Li-PEO chain, and (c) Li-TFSI for the systems with chain length n = 100. Salt concentrations are written in the rightmost plots. Mean and extreme values are marked in the violin plots.

Average number of anions coordinated to Li

The Li displaying strongest and weakest correlation to ether oxygen was determined from the distribution plots of the residence time in Figure S8 and S9. The upper and lower parts of the distributions, corresponding to the Li with stronger and weaker correlations, were determined manually to obtain enough data points.

Table S7: Average number of anions coordinated to Li strongly and weakly correlated to ether oxygen. Upper/lower fractions indicate the part of the distribution used to calculate anion coordination. 0 denotes the minimum and 1 denotes the maximum of the distribution

n	$r =$ Li:EO	Upper fraction	Lower fraction	Average no of anions coordinated
100	0.02	0.6 to 1	-	<0.01
100	0.02	-	0 to 0.1	0.01
100	0.05	0.7 to 1	-	0.01
100	0.05	-	0 to 0.1	0.01
100	0.10	0.8 to 1	-	0.02
100	0.10	-	0 to 0.1	0.02
100	0.17	0.9 to 1	-	0.10
100	0.17	-	0 to 0.2	0.11
100	0.33	0.6 to 1	-	0.91
100	0.33	-	0 to 0.03	2.10
100	0.50	0.6 to 1	-	0.96
100	0.50	-	0 to 0.03	3.05

Examples of the parts of the distributions used to calculate the average anion coordination number are shown in Figure S10. We used the distribution at the longest time interval to calculate the anion coordination above, and mean squared displacement (MSD) and self-diffusion coefficients below.

Table S8: Mean squared displacement (MSD) and estimated self-diffusion coefficients of Li strongly and weakly correlated to ether oxygen in the two most concentrated systems

n	$r =$ Li:EO	Fraction	MSD (Å^2)	Self-diffusion coefficient ($10^{-11}\,\text{m}^2\,\text{s}^{-1}$)
100	0.33	0.6 to 1	135	0.382 (not diffusive)
100	0.33	0 to 0.03	242	0.573 (not diffusive)
100	0.50	0.6 to 1	88	0.142 (not diffusive)
100	0.50	0 to 0.03	213	0.438 (not diffusive)

Table S9: Average number of anions coordinated to Li strongly and weakly correlated to PEO chains. Upper/lower fractions indicate the part of the distribution used to calculate anion coordination. 0 denotes the minimum and 1 denotes the maximum of the distribution

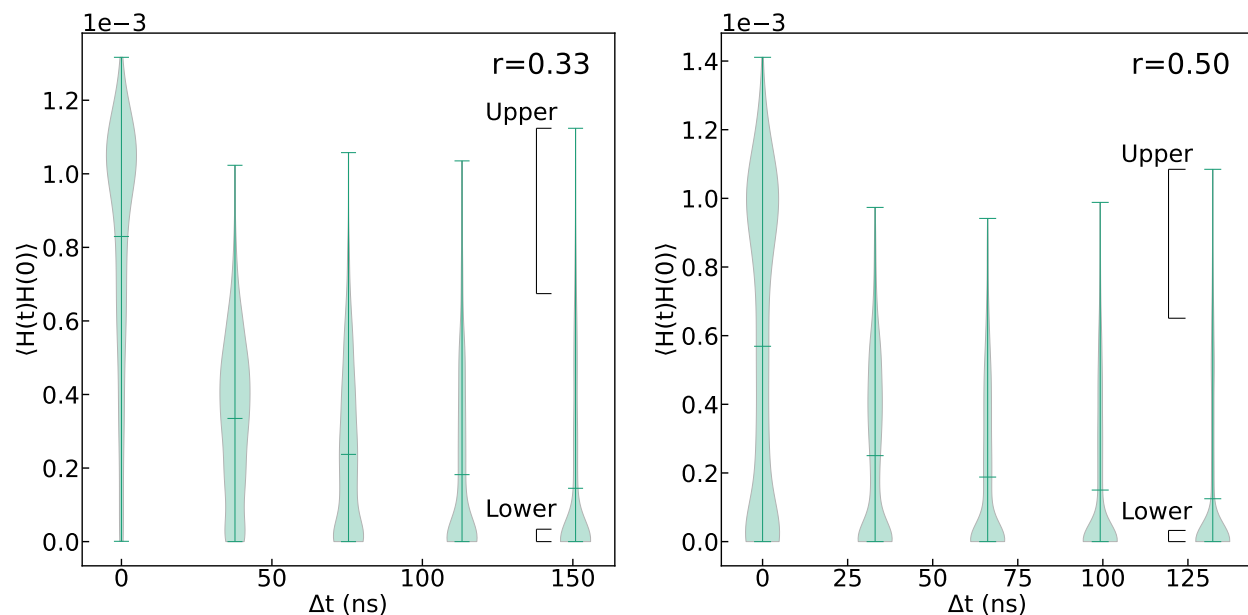| n	$r = $ Li:EO	Upper fraction	Lower fraction	Average no of anions coordinated
100	0.02	0.8 to 1	-	<0.01
100	0.02	-	0 to 0.2	<0.01
100	0.05	0.8 to 1	-	0.01
100	0.05	-	0 to 0.3	0.01
100	0.10	0.8 to 1	-	0.02
100	0.10	-	0 to 0.4	0.02
100	0.17	0.55 to 1	-	<0.01
100	0.17	-	0 to 0.4	0.11
100	0.33	0.7 to 1	-	1.11
100	0.33	-	0 to 0.3	2.35
100	0.50	0.6 to 1	-	1.27
100	0.50	-	0 to 0.3	3.29

Figure S10: Example distribution plots showing the parts used to calculate average anion coordination number. The upper and lower fractions are marked. Salt concentrations are indicated in the plots.
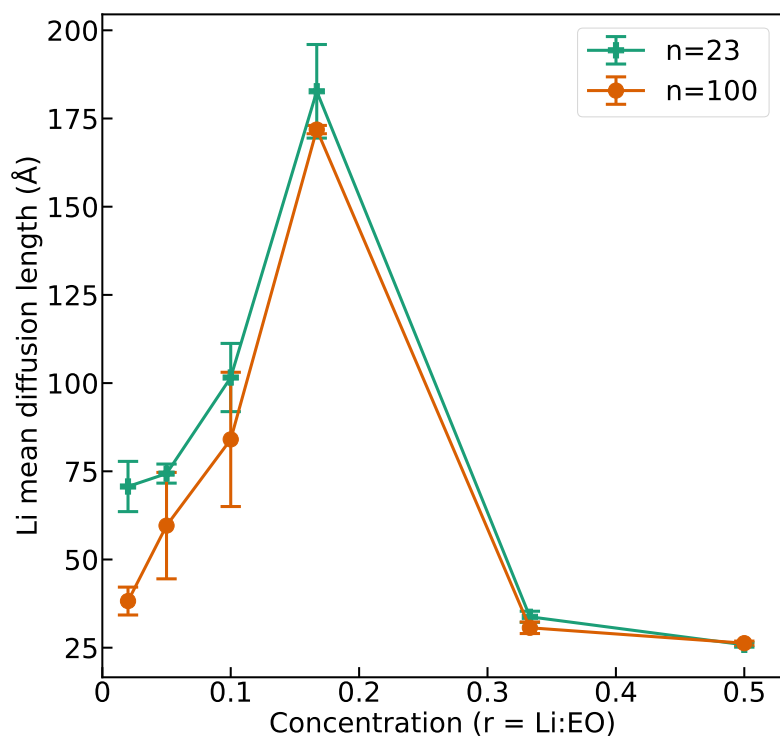
Figure S11: Li mean diffusion length between ether oxygen exchange as a function of PEO chain length and salt concentration.

References

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(2) Timachova, K. Ion Diffusion and Electrochemically Driven Transport in Homogenous and
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(3) Pesko, D. M.; Sawhney, S.; Newman, J.; Balsara, N. P. Comparing Two Electrochemical
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