

Supporting Information

Polypropylene carbonate-based electrolytes as model for a different approach towards improved ion transport properties for novel electrolytes

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Transference numbers of Li⁺ in the PEO reference electrolyte

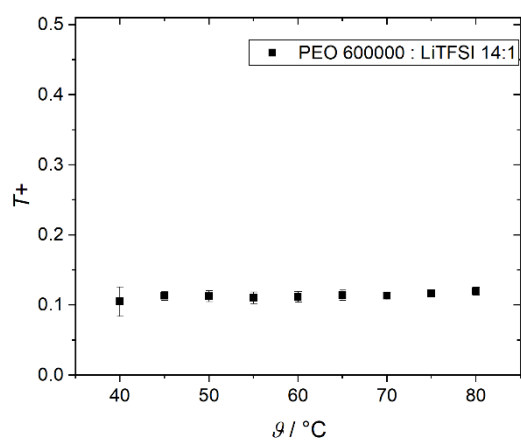


Figure S1 Lithium ion transference numbers of the benchmark reference system PEO-LiTFSI.

Ionic conductivity in the PEO reference electrolyte

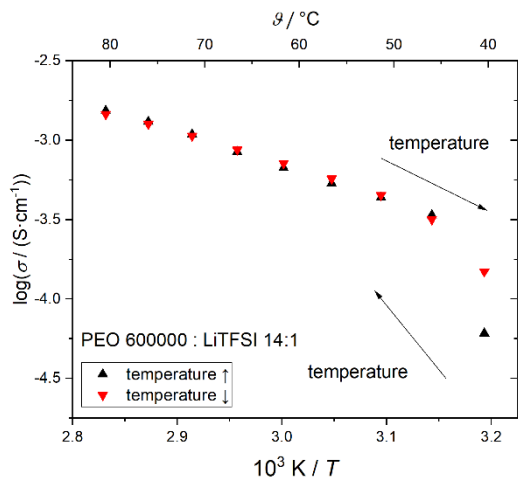


Figure S2 ARRHENIUS-plot of the ionic conductivity of the reference PEO-system.

Ionic conductivity of PPC- and PEC-based electrolytes

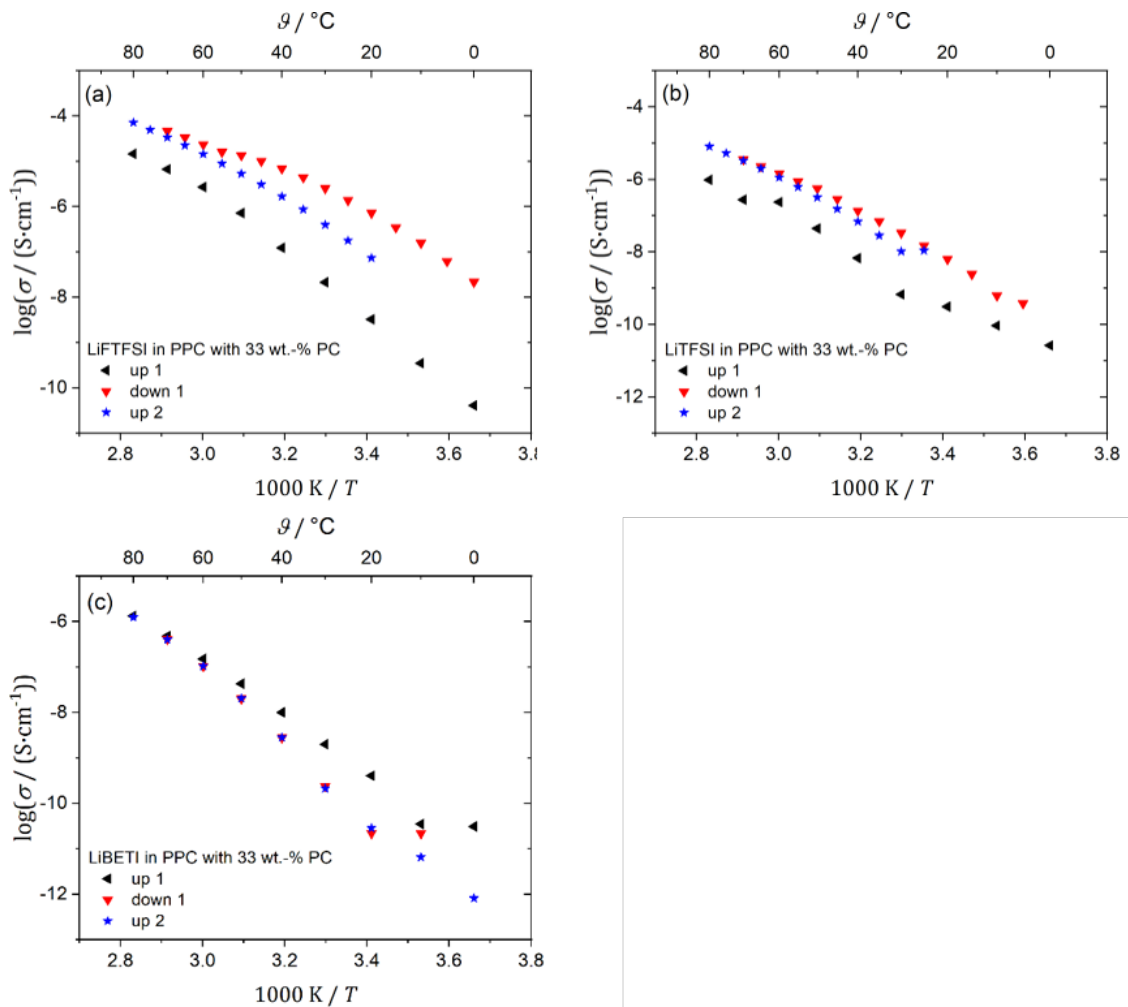


Figure S3 ARRHENIUS-plots of the ionic conductivities of PPC-based gel electrolytes upon repeated heating and cooling. The electrolyte systems (a) PPC-LiTFSI, (b) PPC-LiTFSI and (c) PPC-LiBETI with 33 wt.-% PC, respectively, are shown.

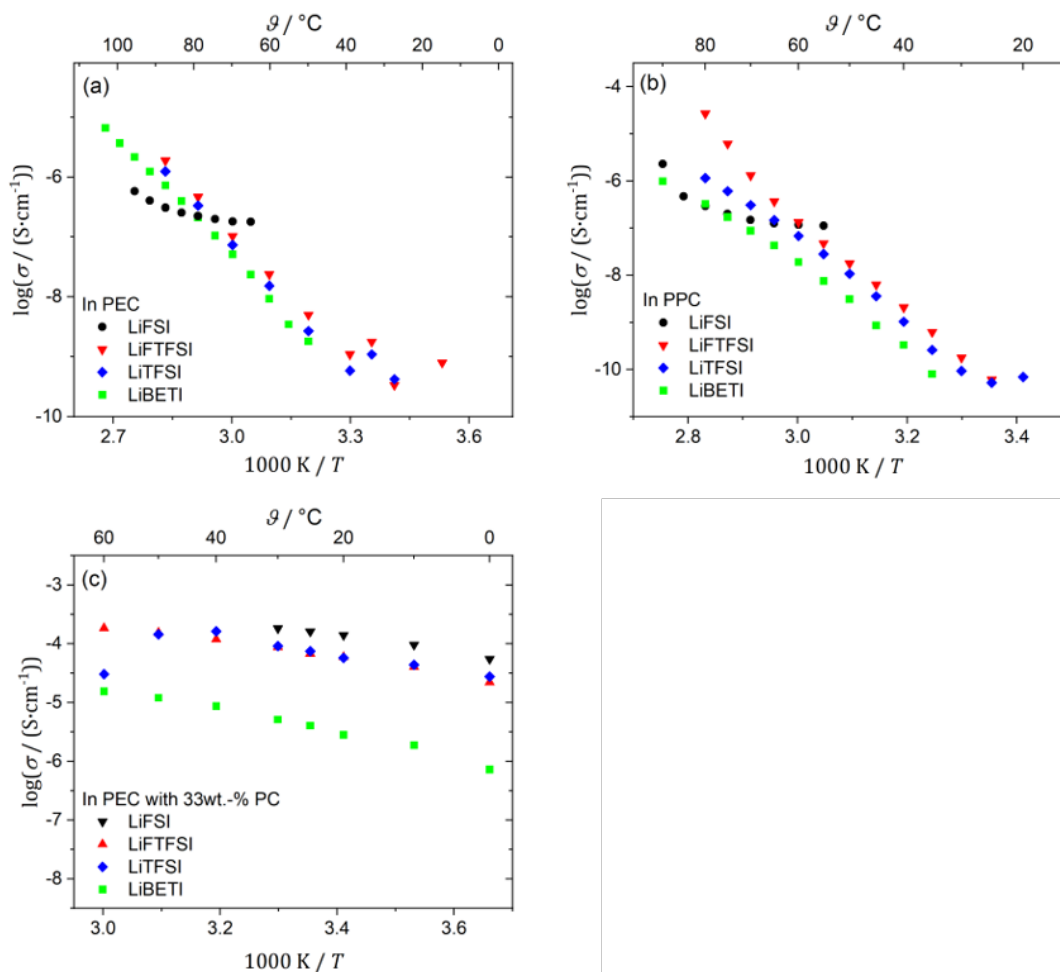


Figure S4 Ionic conductivities for the dry polymer electrolytes based on PEC (a) and PPC (b) and gel polymer electrolytes based on PEC (c). The salt content is $1 \text{ mol}\cdot\text{kg}^{-1}$, respectively.

Transference numbers of Li^+ in PPC-based electrolytes

Table S1: Comparison of transference numbers of Li^+ , ionic conductivity and lithium ion conductivity .

System	$t_{\text{Li}^+}^{[a]}$	T/ °C	$\sigma / \text{S}\cdot\text{cm}^{-1}$ [b]	$\sigma_{\text{Li}^+} / \text{S}\cdot\text{cm}^{-1}$ [c]
PPC LiFSI,	0.37	50	$1.1\cdot 10^{-7}$	$4.2\cdot 10^{-8}$
PPC LiTFSI,	0.48	50	$1.8\cdot 10^{-8}$	$8.6\cdot 10^{-9}$
PPC LiTFSI	0.63	50	$4.0\cdot 10^{-9}$	$2.5\cdot 10^{-9}$
PPC-LiBETI	0.68	50	$3.0\cdot 10^{-9}$	$2.0\cdot 10^{-9}$

[a] Lithium ion transference number determined via the Bruce-Evans method. [b] Ionic conductivity at given temperature derived from EIS-measurement.

[c] Lithium conductivity calculated from transference number measurements and ionic conductivity.

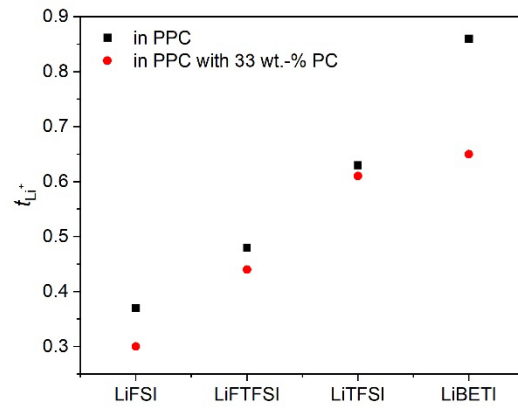


Figure S5: Lithium ion transference numbers of investigated PPC electrolytes at 60 °C. Gel systems are shown in red and dry electrolyte samples are shown in black.

Lithium ion coordination

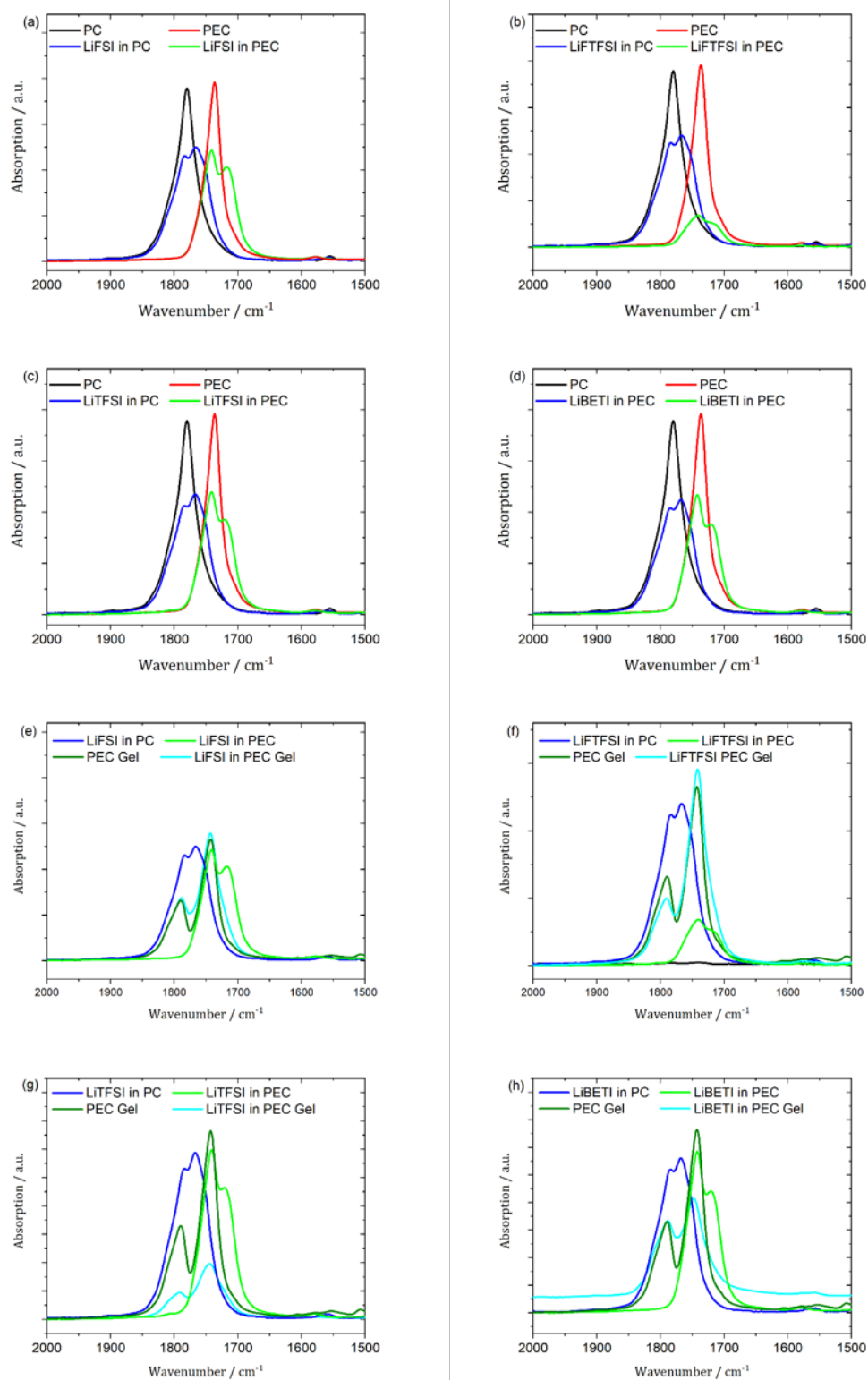


Figure S6: IR – spectra of investigated PEC-based electrolytes. Plotted with pure polymer, salt in solution, gel polymer and salt in polymer, respectively for comparison. Deconvolution was done using Gaussian function.

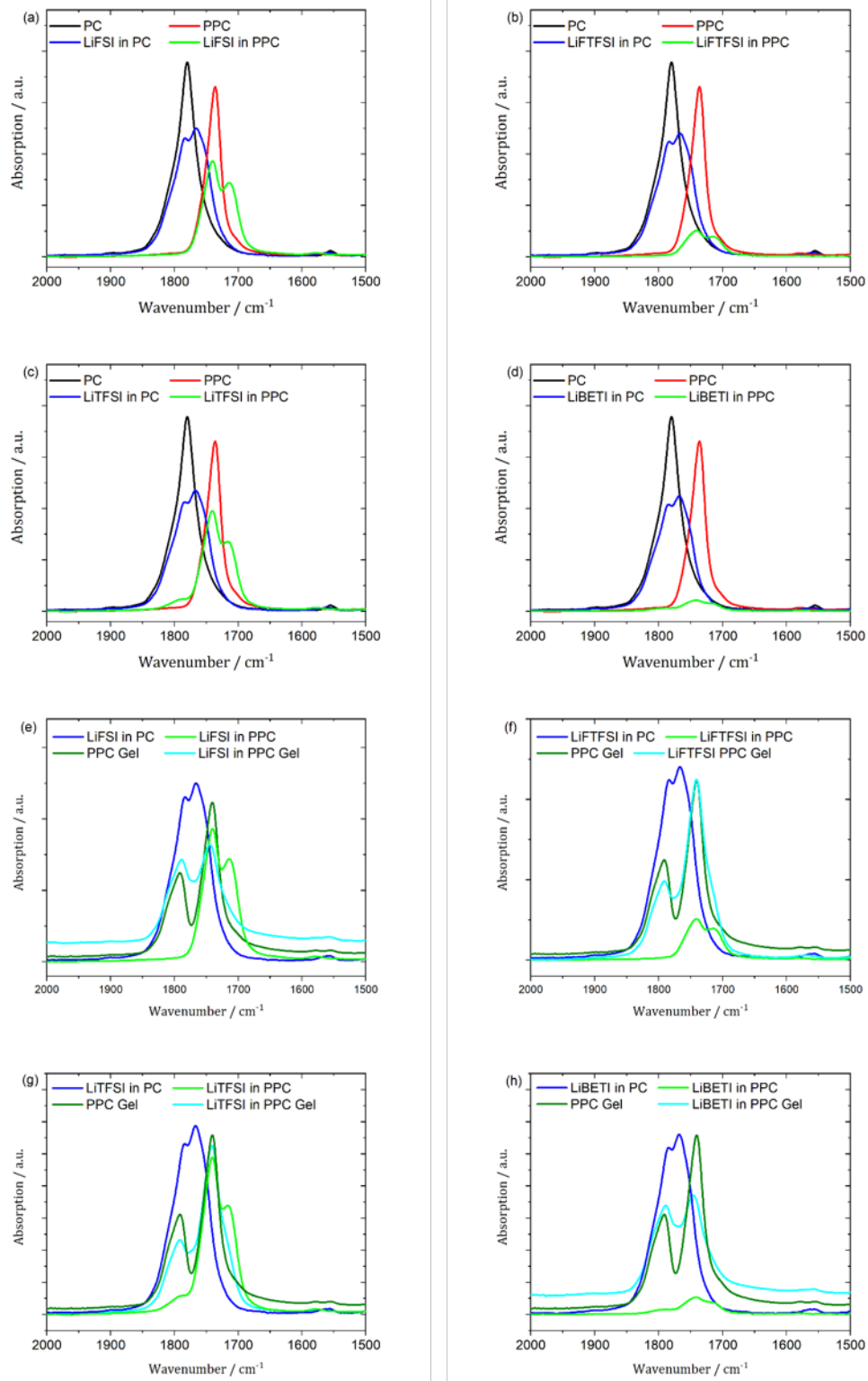


Figure S7: IR – spectra of investigated PPC-based electrolytes. Plotted with pure polymer, salt in solution, gel polymer and salt in polymer, respectively for comparison. Deconvolution was done using Gaussian function.

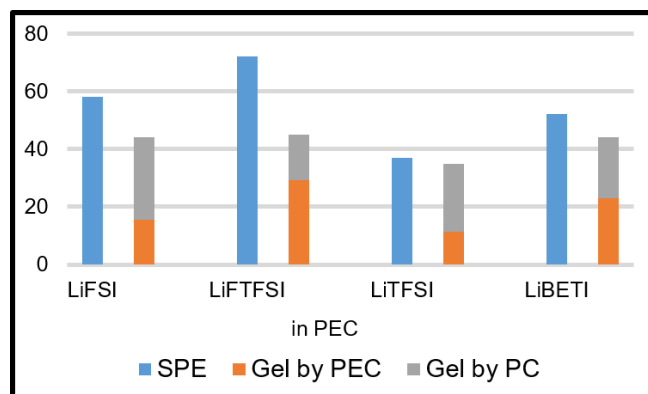


Figure S8 Coordination by the =O - group in PEC - electrolytes determined via IR - spectroscopy. The amount of coordination in the dry polymer electrolytes (SPE) is shown in blue and in orange and grey for the gel electrolytes.

As the PEC polymer electrolyte is exposed to solvent and gelled the coordination of the different salts is reduced significantly. This could be explained by a widening of the structure due to which the conducting salt in between the polymer chains would be coordinated by just one chain. Else, this could be explained by a weakening association because of larger distances or by the solvent taking active part in the transport and coordination of the ions.

Interestingly the overall coordination determined by IR-spectroscopy for the PPC electrolyte increases when going from a dry to a gelled state (see Figure 5). This is unexpected but could be explained by a better aligning of the polymer chains, where the additional CH₃ - group would sterically hinder alignment and coordination in the dry electrolyte but less in the gelled electrolytes. Experimental methods cannot fully reveal the causes of this behaviour

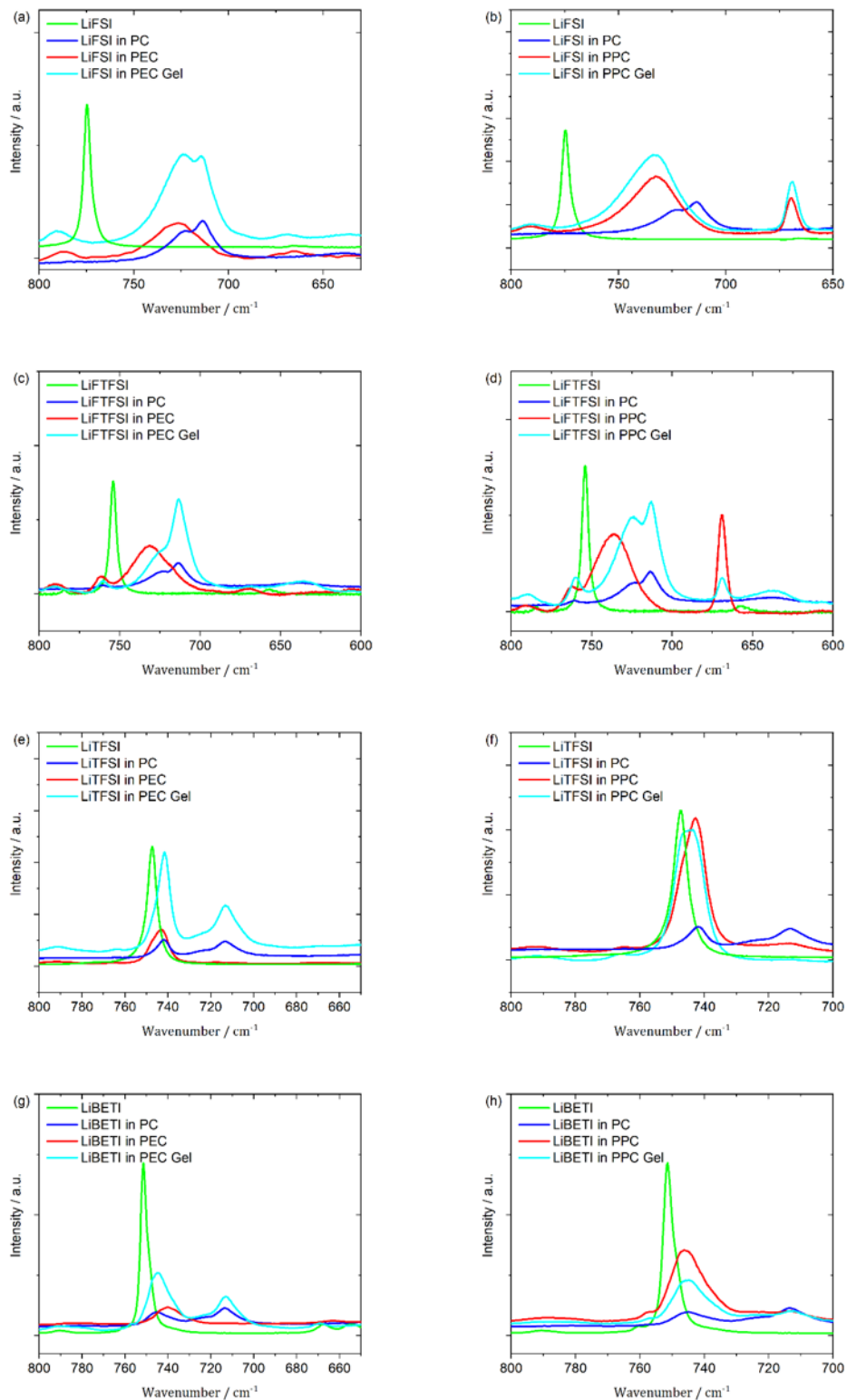


Figure S9: Raman-spectra of the investigated electrolyte systems. Plotted with pure polymer, salt in solution, gel polymer and salt in polymer, respectively, for comparison. Deconvolution was done using Gaussian function

Table S2: Coordination of the conducting salt determined via Raman – spectroscopy. Results for PEC gel electrolytes and dry PPC electrolytes are shown.

System with 33wt-% PC	Agglomerates / %	Solvated / %	System	Agglomerates / %	Solvated / %
PEC LiFSI	1	99	PEC LiFSI	1	99
PEC LiTFSI	8	92	PEC LiTFSI	9	91
PEC LiTFSI	1	99	PEC LiTFSI	17	83
PEC LiBETI	3	97	PEC LiBETI	5	95
PPC LiFSI	1	99	PPC LiFSI	1	99
PPC LiTFSI	6	94	PPC LiTFSI	4	96
PPC LiTFSI	30	70	PPC LiTFSI	18	82
PPC LiBETI	3	97	PPC LiBETI	3	97

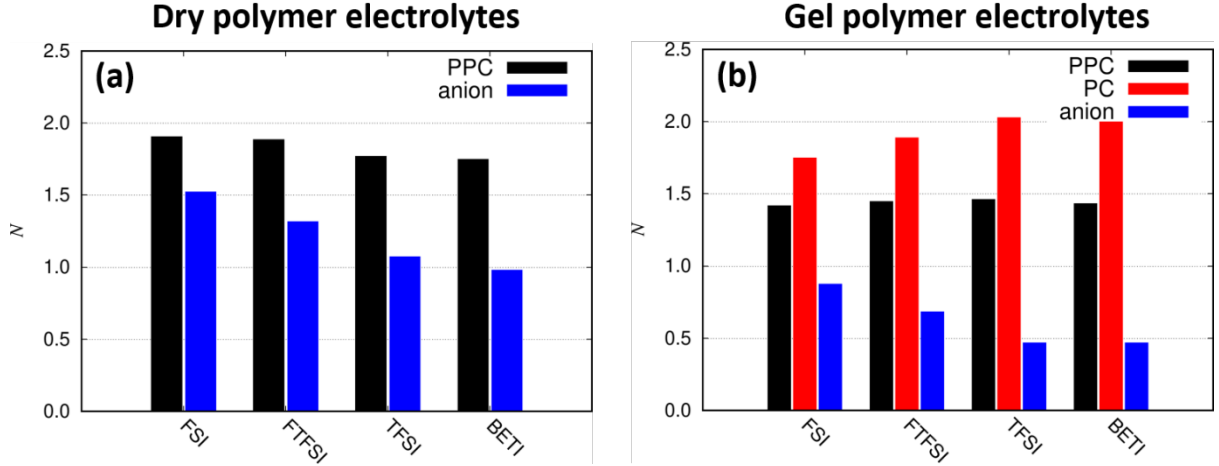


Figure S11. Average coordination numbers N of Li^+ to PPC polymer chains, PC molecules and anions for (a) the dry electrolytes and (b) the gel polymer electrolytes.

Determination of lithium ion coordination lifetimes

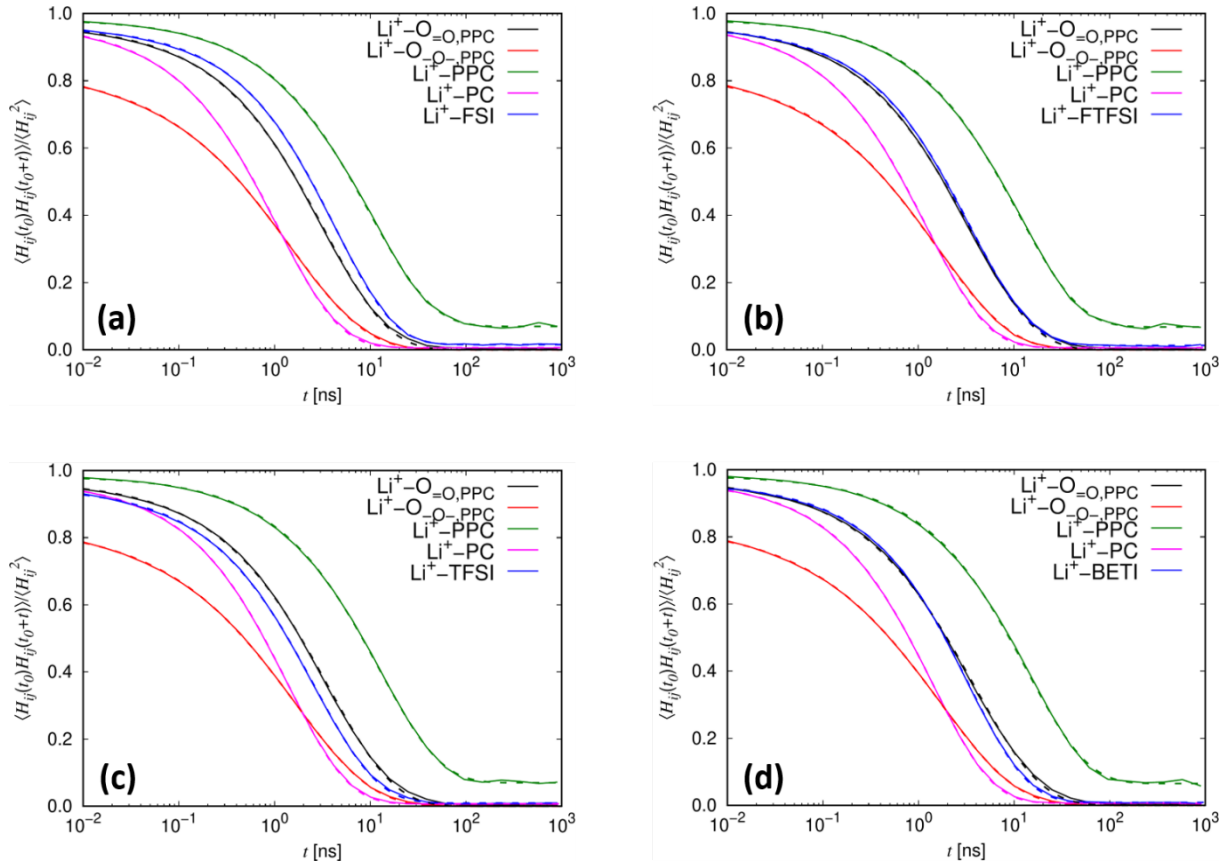


Figure S12. Normalized coordination autocorrelation functions $\langle H_{ij}(t_0)H_{ij}(t_0+t) \rangle / \langle H_{ij}^2 \rangle$ for the gel polymer electrolytes as a function of time. The dashed lines indicate fits by a stretched exponential.

To determine the average coordination lifetimes, we defined the function $H_{ij}(t)$ that is one if ions i and j are coordinated at time t and zero otherwise, and calculated the correlation function $\langle H_{ij}(t_0)H_{ij}(t_0+t) \rangle / \langle H_{ij}^2 \rangle$ [1]. Subsequently, the curves were fitted with a stretched exponential

$$\langle H_{ij}(t_0)H_{ij}(t_0+t) \rangle = \langle H_{ij}^2 \rangle \exp\left(-\left(\frac{t}{\tau}\right)^\beta\right) \quad (1)$$

and the average relaxation times shown in the main text were estimated according to

$$\langle \tau \rangle = \beta^{-1} \Gamma(\beta^{-1}) \tau \quad (2)$$

where Γ is the gamma function.

Ionic diffusivity

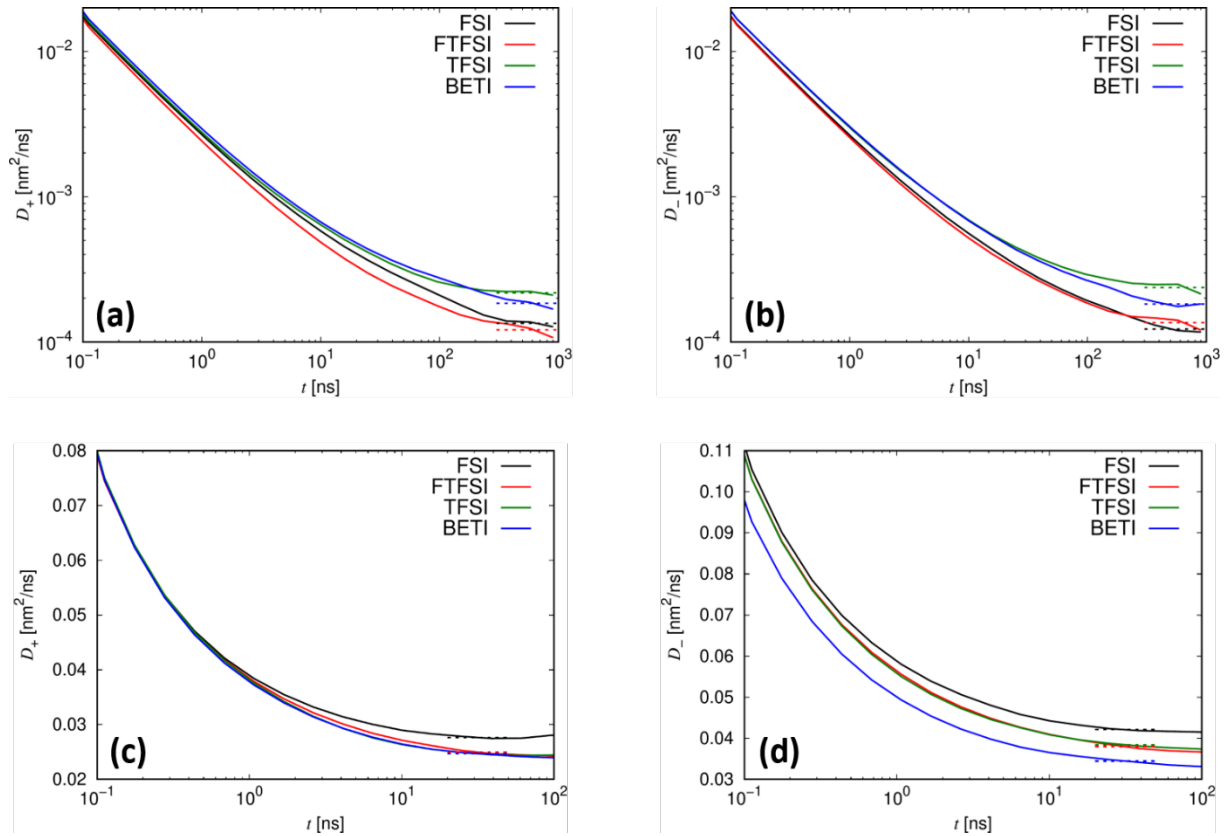


Figure S13. Time-dependent diffusion coefficients $D_i(t) = \langle \Delta R_i^2(t) \rangle / (6t)$ of Li^+ and anions for the different lithium salts. (a) and (b) correspond to the dry electrolytes and (c) and (d) to the gel electrolytes. The thin dash-dotted and dotted lines correspond to the fits, the resulting parameters are shown in Table S3. The fit ranges were $t = 300 \text{ ns} - 1 \mu\text{s}$ for the dry electrolytes and $t = 20 - 50 \text{ ns}$ for the gel polymer electrolytes.

Table S3: Diffusion coefficients of Li^+ and anions as extracted from Figure S4. Note that the fits for the dry electrolytes show rather large statistical uncertainties due to the slow dynamics.

Salt	Dry polymer electrolytes		Gel polymer electrolytes	
	$D_{\text{Li}^+} [\text{nm}^2/\text{ns}]$	$D_{\text{anion}} [\text{nm}^2/\text{ns}]$	$D_{\text{Li}^+} [\text{nm}^2/\text{ns}]$	$D_{\text{anion}} [\text{nm}^2/\text{ns}]$
LiFSI	$1.3 \cdot 10^{-4}$	$1.2 \cdot 10^{-4}$	$2.8 \cdot 10^{-2}$	$4.2 \cdot 10^{-2}$
LiFTFSI	$1.2 \cdot 10^{-4}$	$1.4 \cdot 10^{-4}$	$2.5 \cdot 10^{-2}$	$3.8 \cdot 10^{-2}$
LiTFSI	$2.2 \cdot 10^{-4}$	$2.4 \cdot 10^{-4}$	$2.5 \cdot 10^{-2}$	$3.8 \cdot 10^{-2}$
LiBETI	$1.8 \cdot 10^{-4}$	$1.8 \cdot 10^{-4}$	$2.5 \cdot 10^{-2}$	$3.5 \cdot 10^{-2}$

Ionic conductivity

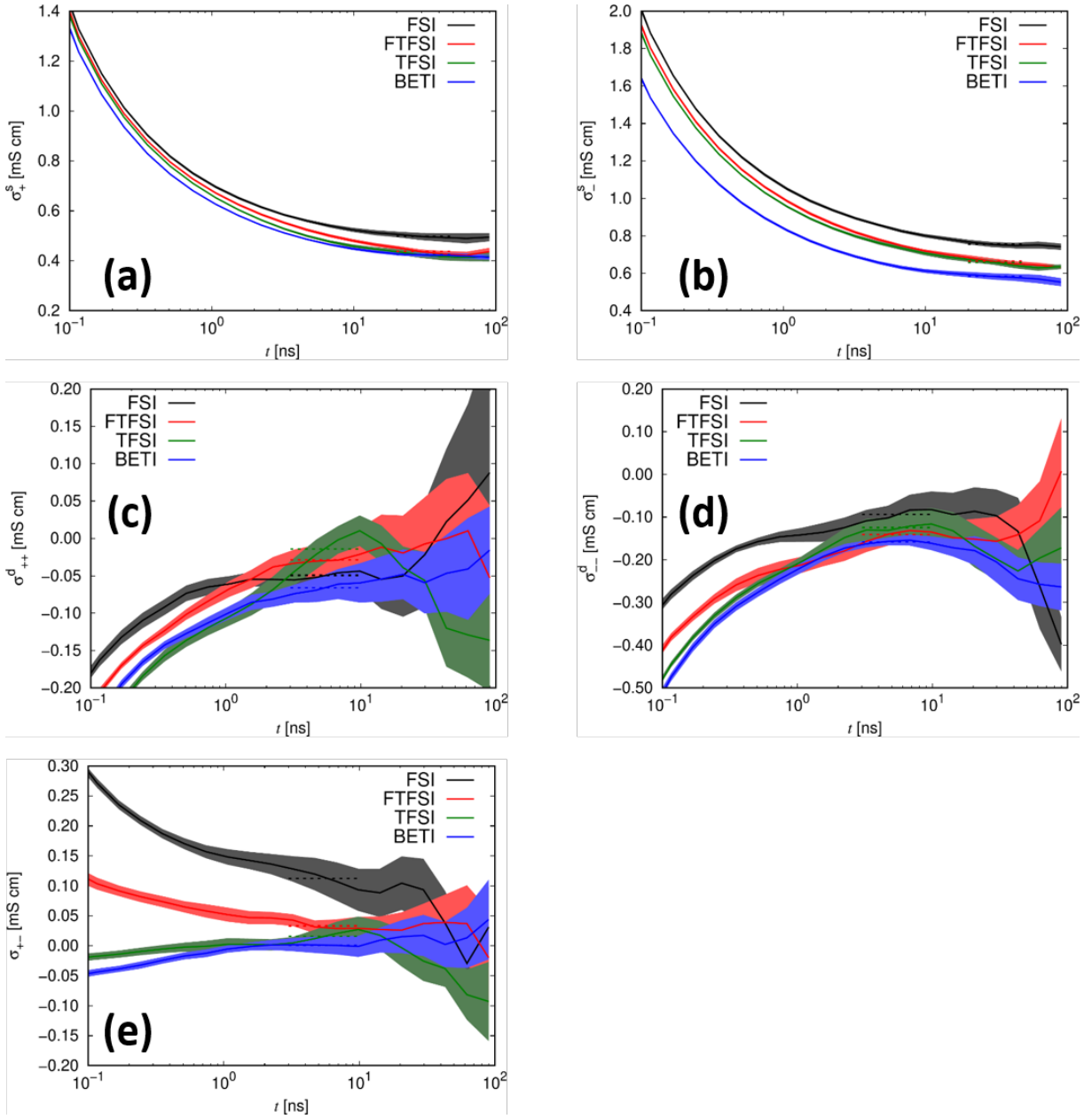


Figure S14. Time-dependent conductivity contributions of cation and anion self-diffusion (σ_+^s and σ_-^s) as well as the cooperative motion of distinct cations (σ_{++}^d), distinct anions (σ_{--}^d) as well as cations and anions (σ_{+-}) for the gel electrolytes. The thin dash-dotted and dotted lines correspond to the fits. The fit ranges were $t = 20 - 50$ ns for σ_+^s and σ_-^s and $t = 3 - 10$ ns for the cross-contributions.

The total conductivity can be calculated from simulation data via ^[2]

$$\sigma = \lim_{t \rightarrow \infty} \frac{e^2}{6Vt k_B T} \sum_{i=1}^N \sum_{j=1}^N z_i z_j \langle \Delta \mathbf{r}_i(t) \Delta \mathbf{r}_j(t) \rangle$$

where e is the elementary charge, V the volume of the simulation box, $k_B T$ the thermal energy, $N = N_+ + N_-$ the total number of cations and anions, z_i the charge number and $\Delta \mathbf{r}_i$ the displacement vector of the i -th ion during time t . The total conductivity can be split into the different contributions discussed in the main text according to the following relations:

$$\sigma_+^s = \lim_{t \rightarrow \infty} \frac{e^2}{6Vtk_B T} \sum_{i=1}^{N_+} \langle \Delta r_i^2(t) \rangle$$

$$\sigma_-^s = \lim_{t \rightarrow \infty} \frac{e^2}{6Vtk_B T} \sum_{i=1}^{N_-} \langle \Delta r_i^2(t) \rangle$$

$$\sigma_{++}^d = \lim_{t \rightarrow \infty} \frac{e^2}{6Vtk_B T} \sum_{i=1}^{N_+} \sum_{j=1}^{N_+} \langle \Delta r_i(t) \Delta r_j(t) \rangle$$

$$\sigma_{--}^d = \lim_{t \rightarrow \infty} \frac{e^2}{6Vtk_B T} \sum_{i=1}^{N_-} \sum_{j=1}^{N_-} \langle \Delta r_i(t) \Delta r_j(t) \rangle$$

$$\sigma_{\pm} = \lim_{t \rightarrow \infty} \frac{e^2}{6Vtk_B T} \sum_{i=1}^{N_+} \sum_{j=1}^{N_-} \langle \Delta r_i(t) \Delta r_j(t) \rangle$$

Simulation snapshots

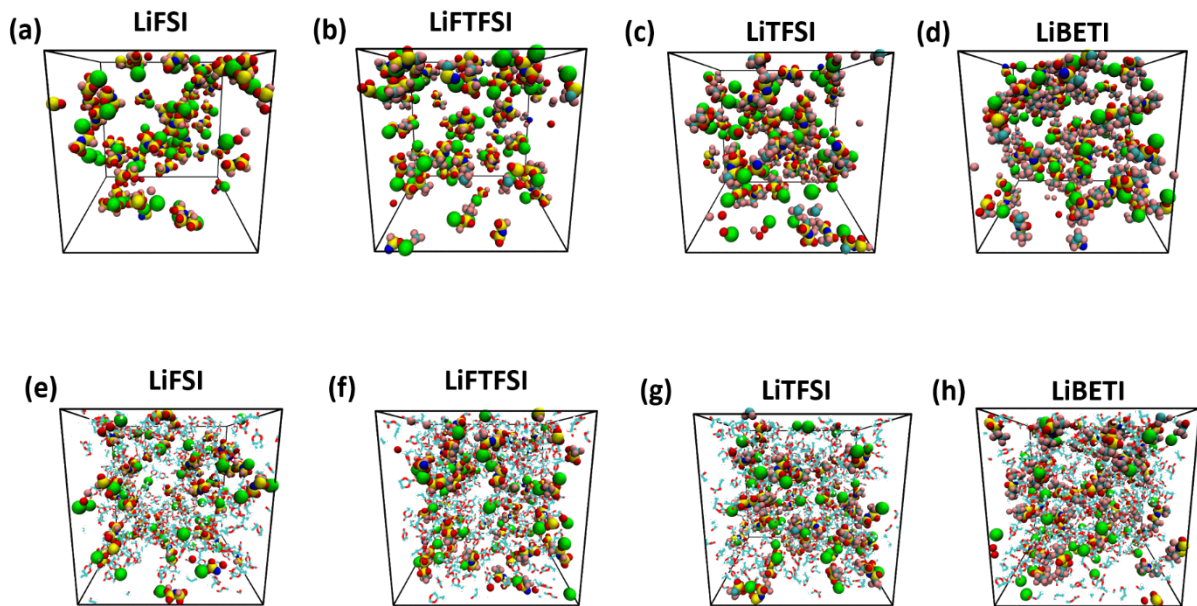


Figure S15. Simulation snapshots of the dry (a-d) and gel polymer electrolytes (e-h). Polymer atoms: invisible, hydrogen: white, lithium: green, carbon: cyan, nitrogen: blue, oxygen: red, fluorine: pink, sulphur: yellow. For the gel electrolytes, PC is shown in line representation.

PFG-NMR

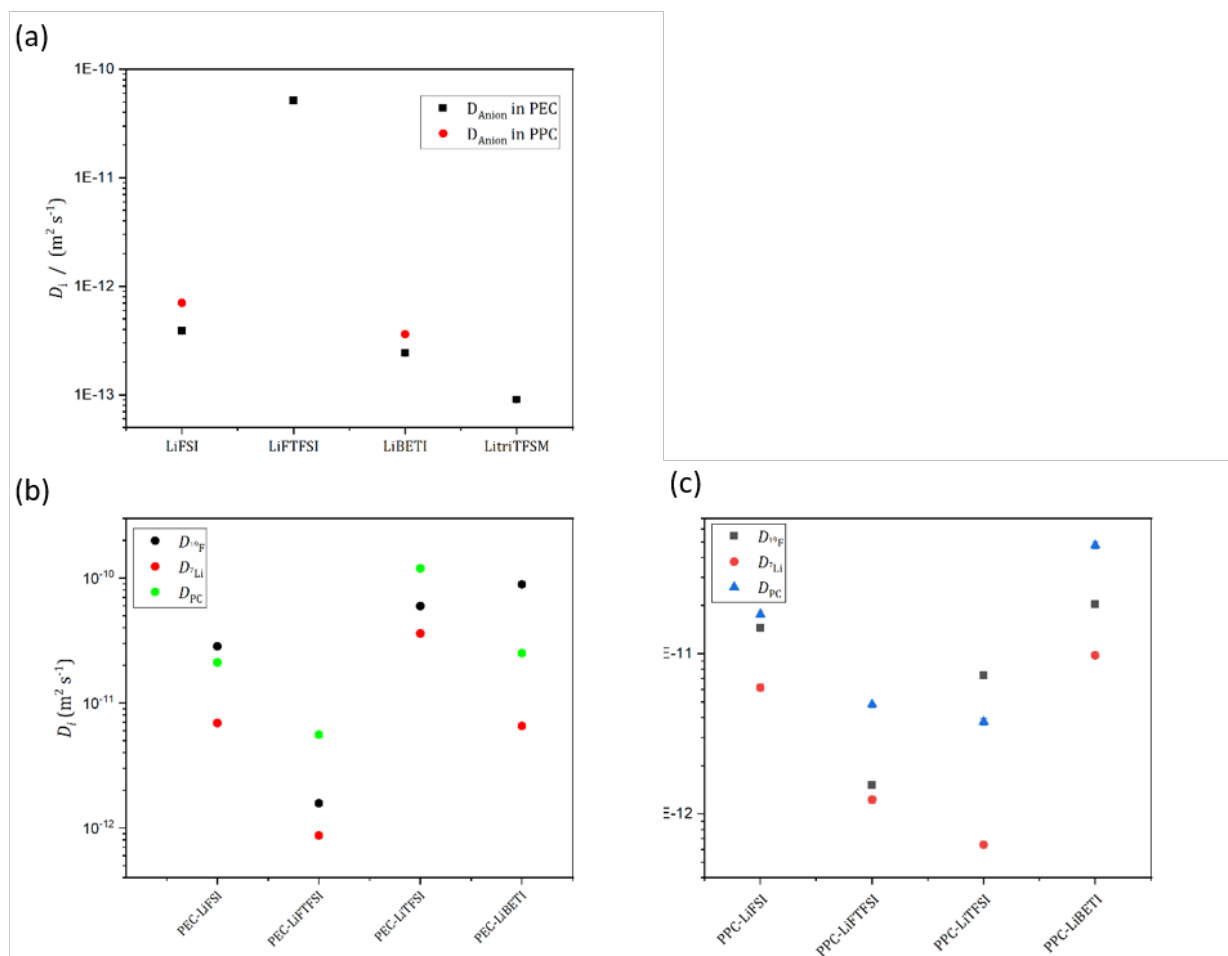


Figure S16: NMR results a) dry b) and c) gel difference between polymer types.

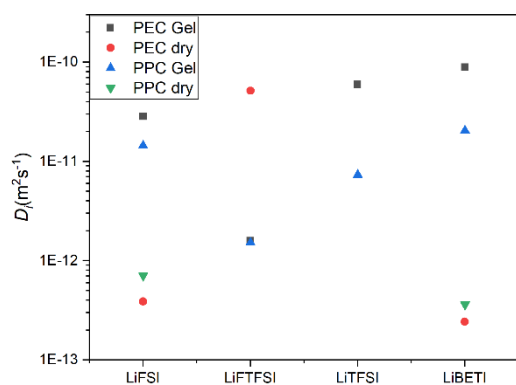


Figure S17: F-Signals in gel and dry polymer electrolytes.

References

- [1] aW. Zhao, F. Leroy, B. Heggen, S. Zahn, B. Kirchner, S. Balasubramanian, F. Müller-Plathe, *J. Am. Chem. Soc.* **2009**, *131*, 15825-15833; bJ. R. Keith, S. Mogurampelly, F. Aldukhi, B. K. Wheatle, V. Ganesan, *Phys. Chem. Chem. Phys.* **2017**, *19*, 29134-29145; cV. Lesch, Z. Li, D. Bedrov, O. Borodin, A. Heuer, *Phys. Chem. Chem. Phys.* **2016**, *18*, 382-392.

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